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12th International Symposium on EIS

— 聚焦科技前沿 · 汇流百家之言 · 共谋发展未来 —

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Preface

It is our great pleasure that the 12th International Symposium on Electrochemical Impedance Spectroscopy is able to be held in Beijing, on site, from July 2 to 7, 2023. It is the first time in China after more than thirty years since the birth of the symposium in 1989 in France. This symposium was scheduled to be held in 2022. However, it had to be postponed, due to the outbreak of Covid-19. To be honest, it was a difficult decision to postpone the EIS2022 in the height of Covid-19, as this is a symposium occurring every three years and there has never been one postponement in the previous 11 symposia ever since its inception. Yet considering the true spirit of a symposium in the Greek era, which literally means to drink together while discussing literature and philosophy, we decided not to yield to the temptation of utilizing the convenience of online, ex situ meeting, but to fulfill our duty of providing a cozy environment for face-to-face meeting, networking, sharing and discussing, which has to be onsite, in situ. During these time, we were under tremendous pressure regarding the uncertainty of when the pandemic will stop or at least subside, so that the international travel can resume. In the end, our patience and prayer paid off in that we are able to welcome friends and practitioners of EIS from the world to meet here in Beijing.

In EIS2023, advances in the theory and applications in EIS in various fields will be presented by about 300 participants from 21 countries and regions. The focus is on the corrosion and energy storage & conversion. 15 plenary lectures are invited. The Session in the memory of Prof. Chunan Cao was organized, a poster session has been scheduled. Four tutorials are arranged. And as a new attempt to attract and train graduate students in this rather niche meeting, the three-minute-thesis (3MT) competition has been introduced.

We are deeply grateful to the International Scientific Committee for t heir advices and to the Local Organizing Committee for their efforts in making this postponed symposium possible.

On behalf of the scientific committee and the local organizers, we warmly welcome all the participants and wish you a pleasant stay and a successful meeting.

雍兴跃

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Beijing University of Chemical Technology

张剑波

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Contents

Plenary Presentation

On the constant phase element determination from EIS and cyclic voltammetry experiments

Divino Salvador RAMÍREZ RICO,[1] Samantha Michelle GATEMAN,[2] Oumaïma GHARBI,[1]
Mirelle TURMINE,[1] and Vincent VIVIER[1,*]
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Several techniques can be used to experimentally determine the interfacial capacitance of an electrode, which is a crucial parameter. For an ideally polarizable electrode, the electrochemical interface consists of a capacitive-like behavior accounting for the electrical double layer (EDL) as well as the possible presence of a thin oxide film that may form at the electrode's surface. Discussions about the determination of the capacitance depending on the method used have been already reported in the literature.[1-3] For instance, cyclic voltammetry is a routine electrochemical technique used for the determination of electric properties of super capacitors or energy storage devices. Typically, the capacitive charge is determined through the variation of sweep rate in a more or less constant (non-faradaic) current domain and is often used to estimate the performances of these electrode. Similarly, electrochemical impedance spectroscopy (EIS) can also be used as a useful technique for the determination of interfacial processes, including the capacitive behavior of the interface. In practice, the measured capacitance depends on the frequency, and to account for such a behavior, a constant phase element (CPE) is often assumed/used during analysis of EIS instead of a pure capacitor.[4] This makes it difficult to analyze the experimental data and to compare results from one publication to the other.

In this presentation, we will review how capacitance measurements obtained by cyclic voltammetry and EIS can be performed and can differ significantly even though they aim to measure the same physical quantity. Special attention will be paid to the analysis of results obtained with these two techniques on various high-surface area carbon electrodes. This discussion will be complemented by a theoretical approach based on interfacial modeling.

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Impedance techniques used in the elaboration of reaction models: a critical discussion.

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The application of the electrochemical impedance technique in the study of reaction mechanisms began in the 1970s with research carried out at the Paris VI laboratory directed by I.Epelboin (1). It was emphasized that reaction mechanisms should be studied at different pH, anion concentrations, and system polarization (2-4). In the early 1980s, commercial devices began to be developed and the use of the impedance technique grew significantly in the literature. Later, variants of the local use of this technique began to emerge, a fact that allowed small-scale information about the reaction processes that were taking place in the system (5-6). Variants of impedance measurements have also been developed (7-8).

Despite the immense advance achieved and briefly reported above, impedance today, except in rare cases, is practically limited to its use in open circuit potential (corrosion potential) where a single measurement is performed and an equivalent circuit is proposed to adjust this measurement. The parameters of this circuit, although not always present, are interpreted physically and an attempt is made to correlate with any electrochemical processes that are occurring in the corrosion potential. The impedance variation with physical-chemical parameters (pH, concentration) or potential (anodic and cathodic polarization) is practically forgotten in most studies. However, it is an elementary fact and common knowledge that corrosion is a complex process, involving at least one anodic, cathodic reaction and, eventually, mass transport in the solution or surface of the material. Trying to understand this phenomenon by restricting the impedance measurements to a single potential, where all these processes occur simultaneously, is a difficult task and, not infrequently, a speculative task. In this lecture, we will bring this discussion in a critical way, presenting results with examples of broad studies that allowed shedding light on practical corrosion processes coupling classical measures of polarization, electrochemical and electrohydrodynamic impedances.

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The EIS of active and coated corrosion systems

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In memory of Prof. Cao who significantly advanced the EIS theory in corrosion science, this presentation first reviews the EIS model that Cao developed for steadily corroding electrodes. The presentation then shows the application of this methodology in interpreting the EIS behaviour and understanding the active dissolution of Mg and its alloys. This method can also be used in a film-covered electrode, such as anodized Mg. Compared with the EIS analysis based on the electrochemical state parameters as proposed by Cao, an equivalent circuit is much commonly setup in practice to simulate the processes involved in corrosion if the corresponding electrochemical steps can be clearly defined. For example, the EIS spectra of porous concrete and those of steel under organic coatings can be predicted simply by using an equivalent circuit. Therefore, with the aid of a special equivalent circuit, a single line coil electrode may be employed as a electrochemical sensor to detect the corrosivity of a corrosion system even without using a reference electrode or a counter electrode. This idea is theoretically deduced and experimental verified. Cao’s EIS model and the equivalent-circuit method may lead to slightly different understandings of detailed electrochemical processes, which is briefly discussed in the presentation as well.

Embedded Impedance Spectroscopy: The Challenge of high performance at limited resources

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Impedance spectroscopy has established itself as a measurement method for characterization, instrumentation, and sensing. Laboratory devices offer outstanding possibilities for measuring the complex impedance over a wide frequency range enabling accurate measurement but are not always practical and affordable for field applications. Dedicated embedded systems implementations are therefore essential to transfer the method more broadly into field applications. Embedded impedance spectroscopy systems do not have to realize the universality of use and thus the highest accuracy like laboratory devices. They only have to meet the measurement and frequency range requirements that are necessary for the intended application. However, they can quickly reach their hardware and software limitations in doing so. In addition, special requirements for field sensors must be met, such as fast measurement, high efficiency in the generation of the excitation signal, AC signal analysis, and in all further signal processing for information extraction, which must be robust and automatic.

For these reasons, in designing embedded solutions impedance spectroscopy, several critical aspects should be fundamentally addressed such as the suitability of measurement procedures, methodologies for reducing measurement time and realizing fast and robust measurement, and critical implementation issues of measurement procedures and methods for information extraction of the targeted information. The plenary talk will address these topics and highlight the design aspects of this method for several field applications, such as battery diagnosis, bioimpedance spectroscopy in wearables, and physical and chemical sensors.

Temperature Dependent EIS Investigation of Batteries with Metallic Lithium Anode

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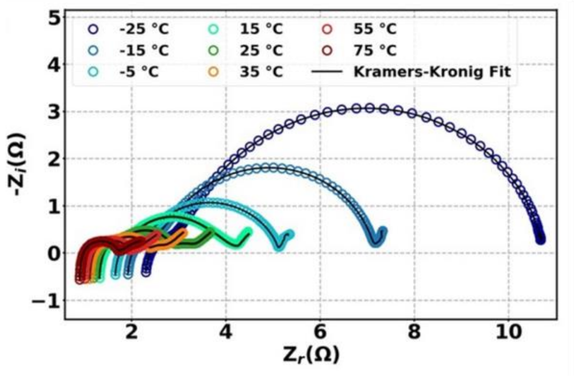
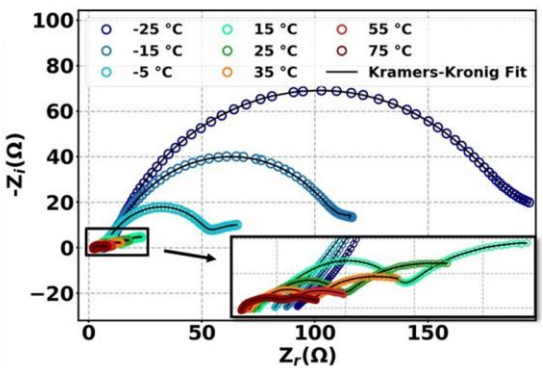
Metallic lithium anodes are invaluable in increasing the energy and power densities of batteries. Though they are yet to be commercialized for rechargeable batteries, primary batteries employing them have been on the market for decades.

Employing commercially available primary batteries, we have investigated the kinetics of various electrochemical processes occurring on the metallic lithium electrode via temperature dependent EIS measurements. The cells we will be reporting have the well-known lithium thionyl chloride and lithium manganese oxide chemistries. Though widely different in electrolyte and cathode, both chemistries employ a metallic lithium anode.

Through investigations of the temperature dependence of the parallel resistances of the semicircle representing the solid electrolyte interface(SEI) and the charge transfer of lithium oxidation, activation energies for the lithium ion transport across the SEI and the anodic reaction for the batteries have been measured. Further, the processes have been observed to be temperature independent above a certain threshold indicating a transition to a non-thermally activated process.

We will be presenting our findings along with a future outlook of both temperature-dependent EIS and metallic lithium anodes.


Lithium Thionyl Chloride


Lithium Manganese Oxide

Electrochemical deposition and characterization of hydroxyapatite–based composite coatings on titanium for biomedical applications

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Bone implant materials are increasingly attracting attention in the biomaterials field. Among them, hydroxyapatite (HAP) has stood out as a prospective biomaterial due to excellent osseointegration ability, owing to its similarity with natural bone. However, due to the lack of adhesive and antibacterial properties, it is usually combined with polymers and antibacterial agents. Natural polymer chitosan (CS) was proven as an effective component of HAP-based composites, improving the adhesion and serving as a drug carrier. Inclusion of antibiotics into composite biomaterials has gained a lot of attention, as it is thus possible to achieve the desirable antibacterial activity. Gentamicin (Gent) was shown to be one of the most effective antibiotics in treating bone infections.

Composite antibacterial HAP/CS/Gent coating was obtained on titanium substrate using electrophoretic deposition at constant voltage of 5 V. The bioactivity of deposited coating, i.e. the growth of new HAP phase on the HAP/CS/Gent coating surface during exposure to simulated body fluid (SBF) at 37°C, has been proved by electrochemical impedance spectroscopy and potentiodynamic sweep. The corrosion current density values obtained from polarization measurements exhibited a decreasing trend over the time of immersion in SBF. Similarly, the EIS measurements showed an increased impedance of HAP/CS/Gent coating, along with decreased coating capacitance and double layer capacitance, indicating the formation of a new biomimetic HAP layer on the coating surface. These results, along with XRD and FT-IR, proved the strong potential for biomimetic mineralization of HAP/CS/Gent coating. Biological assays (test in suspension and agar diffusion method) indicated strong antibacterial activity against *Staphylococcus aureus* and *Escherichia coli*, while MTT and DET cytotoxicity tests pointed to non-toxic effect against MRC-5 (human origin fibroblasts) and L929 (mice origin fibroblast) cell lines. The coating ability to induce and promote osseointegration was confirmed also by alkaline phosphatase activity (ALP) assay, suggesting that HAP/CS/Gent coating is an excellent candidate for bone tissue engineering.[1,2]

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Potential-dependent impedance shapes of electrochemical interfaces

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Electrochemical impedance spectroscopy (EIS) has been widely used to characterize electrochemical interfaces. EIS plots of electrochemical interfaces often have the same shape but varying sizes at different potentials. In such cases, EIS data can be fitted using a same equivalent circuit model, and potential dependency of model parameters is then subject to further analysis. In this talk, I will present two examples where such a practice is problematic because EIS shapes change with varying potentials.

The first example considers an electrolyte thin film, be it solid or liquid, in contact with an ideally polarizable electrode. An exact analytical solution to the EIS of this system is obtained only when the electrode is at the potential of zero charge (pzc) and initial distributions within the electrolyte solution are strictly uniform.[1] Otherwise, we have to resort to numerical solutions. We found that EIS shapes change with shifting the electrode potential, as shown in Figure (a). Between the high-frequency semicircle and the low-frequency vertical line, a tilted line develops in mediate frequency range when the electrode potential deviates from the pzc. The characteristic frequency of this tilted line is related to the thickness of the electrolyte thin film.

The second example brings into play Faradaic reactions, Figure (b). Specifically, we consider the deposition reaction of a monovalent metal cation. Near the equilibrium potential of this deposition reaction, EIS plots are composed of a high-frequency semicircle ascribed to the double-layer capacitance and charge transfer resistance in parallel, and a low-frequency ‘semicircle’, known as the finite-length Warburg impedance. Strikingly, with further increasing the overpotential, we observe an inductive loop in the low frequency range. This low-frequency inductive loop represents an impedance fingerprint of the coupling effects between Faradaic reactions and double-layer charging process.

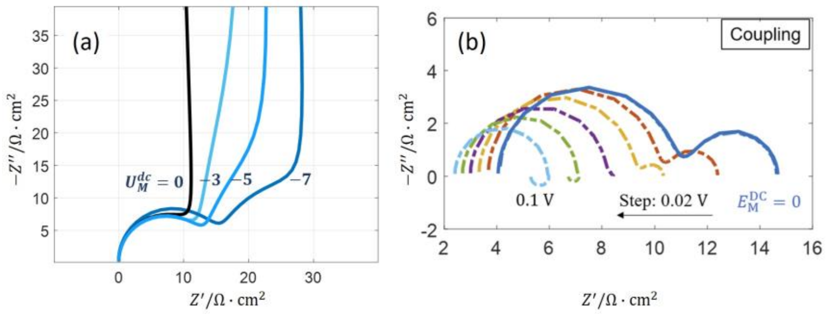

Figure (a) EIS of an ideally polarizable electrode at different electrode potentials (unit: k_BT/e_0). (b) EIS plot of a metal-solution interface with metal deposition reaction at different electrode potentials.

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New in-situ and operando capabilities of Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) for electrochemical system identification

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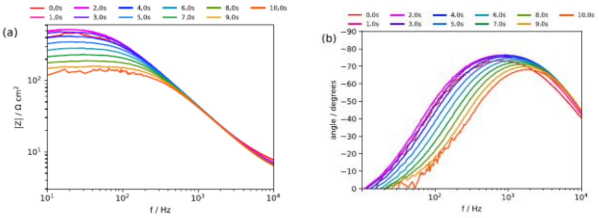
In many electrochemical systems, the components undergo modifications during operation. In that case, regular electrochemical impedance measurements are no longer valid to monitor the changing process parameters as the required stationarity is not guaranteed. To overcome this restriction, we have developed Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) [1,2]. It is a multisine technique that only excites certain frequencies and each excited frequency is applied continuously, providing continuous information on the system. The time evolution of the process is then accessible through the analysis of the response to the multisine at the non-excited frequencies, which allows to extract the time-varying impedance.

Besides stationarity, EIS also requires the system to behave linearly. Yet, many processes are inherently nonlinear. More recently [3,4], we also developed a technique to detect and quantify nonlinear distortions, and to estimate the so-called Best Linear Time-Varying Approximation (BLTVA) of nonlinear time-varying systems. As a result, measurements not neatly satisfying the linearity assumption can still be processed and interpreted.

The technique is successfully applied and will be illustrated for several in-situ and operando studies of inherently non-stationary and/or nonlinear systems: corrosion, water uptake in coatings, electrorefining of Cu, AC electrograining (see figure 1 as illustration) and anodizing of Al, conversion coatings on Zn, and Li-ion batteries.

Figure 1: Time-varying impedance data, (a) amplitude and (b) phase angle, after electrograining of Al [2].



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Electrochemical noise spectroscopy: technique and applications

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Electrochemical noise spectroscopy technique consists in measuring fluctuations of current, potential of the working electrode and also fluctuations of the electrolyte resistance between the reference electrode and the working electrode (screening effects). On the contrary to global techniques such as electrochemical impedance spectroscopy or cyclic voltammetry in which the measures are averaged in time and over the electrode surface, electrochemical noise technique can be used to detect and analyze in real time elementary events occurring at or near the working electrode surface. This technique has been successfully applied to characterize pitting corrosion [1], to determine the size and departure rate of bubbles on a gas-evolving electrode [2], to characterize the composition of oil-brine mixtures in a flow-loop cell [3], or to characterize flowing particle at millimeter scale [4] as well as micrometric scale in a microfluidic channel [5].

However, some attention should be taken while using this technique since valid electrochemical noise measurements are obtained only with adequate equipment. In addition very few commercial instruments currently allow correct noise measurement that is mainly due to the lack of anti-aliasing filters [6,7].

In this presentation, we will discuss some theoretical and experimental bases providing the minimum knowledge in order to achieve valid electrochemical noise measurements. Some examples of application will be presented to illustrate different concepts.

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3D Impedance Analyses on Fractal Pore Structures in Localized Corrosion on Copper

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It is well known that impedance spectrum of simple cylinder porous electrode describes straight-line of 45 degree slope in the high frequency range on Nyquist plane [1]. We reported an impedance method to analyze the branched (fractal) porous electrode with transmission line model (TLM) [2, 3]. In the case of electrode with fractal pores, the slope of straight-line decreases depending on the fractal dimension [3].

A time-invariance is required in the reaction for precise measurement of impedance spectrum. The time-invariance of the electrode means no variation of electrode reaction rate during the measurement of the impedance spectrum. If the electrode reaction rate changes during the measurement time of impedance spectrum, the low frequency components of impedance may contain significant errors due to the time variation. Stoynov *et al.* [4] proposed the method to compensate the deviation of low frequency impedance for non-stationary electrode by using 3–dimensional (3D) Nyquist plot, whose axes are real, imaginary parts and time. We [5] applied this method “3D EIS” to the investigation of anodic dissolution mechanisms of metal. In addition, we [6-9] developed a 3D EIS to determine electrochemical impedance by the galvanostatic control with small amplitude of AC current input. This method “g-EIS” enables us the simultaneous measurement of potential-time curve and successive impedance spectra.

The branched pitting corrosion often occurs on copper tubes used in heat-exchanger units in air-conditioners and leads to leakage of heat-exchanger fluid for several months. [10, 11] The morphology is characterized by the fractal structure in which pits of several ten micro-m diameter are formed on copper surface and smaller pores are developed on the pit walls randomly. In this lecture, I present the application of above-mentioned EIS methods to the investigation of initiation and growth of branched pores in localized corrosion on copper.

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Corrosion Electrochemistry, Surface Film Properties and Scratching Repassivation in High Temperature Pressurised Water for Nuclear Power Plant

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It was generally recognized that the nucleation and propagation of localized corrosion was strongly related to the properties of the oxide film formed on the metal surface. A considerable number of investigations have been devoted to the identification of the oxide film. However, the oxide film formed in high temperature water is difficult to be characterized. The objective of this work was to investigate the electrochemical behavior and the oxide film properties of various materials in high temperature pressurized water for nuclear power plant, to understand the corrosion mechanisms, to improve the corrosion properties of the materials and to insure the lifetime of equipment in nuclear power plant.

The effects of dissolved oxygen and hydrogen, pH of solution, surface finishing of material, and even Zn injection into the solution on the electrochemical behavior and the oxide film properties of various materials in high temperature pressurized water by means of *in-situ* potentiodynamic polarization measurements, electrochemical impedance spectra (EIS), Mott–Schottky plots, *in-situ* scratching repassivation kinetics, *ex-situ* X-ray photoelectron spectroscopy, scanning electron microscopy, transmission electron microscopy and Grazing incidence X-ray diffraction in Synchrotron Radiation Facility analysis. The related growth mechanisms of the oxide films were also discussed.

There exist different mechanisms from lower temperature to high temperature and the Arrhenius equation does not work. The change in water chemistry from pure to primary water was found to vary the film structure from duplex to triple layer, and lead to change in the morphology of NiO on the surface. The increased pH and solution conductivity of primary water also accelerate the dissolution of Cr species and enhance the electrochemical corrosion. The Ni-rich and Cr depleted inner layer formed under both water chemistries is porous and not protective. The scratching repassivation results confirm the applicability of the slip-dissolution model for explaining stress corrosion cracking by means of electrochemical measurement. Compared with other methods of evaluating stress corrosion cracking susceptibility of engineering materials, studying the repassivation kinetics by rapid scratch technique is more economical and time-efficient evaluation method for nuclear materials in high temperature pressurized water.

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Insight into battery processes using a combination of systematic impedance measurements and physics based transmission line modeling

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Modern battery electrodes contain an enormous number of active particles (up to 10^{14} per 1 cm^2 of metallic substrate) and at least 3 or 4 other phases (binders, coatings, conductive additive, electrolyte) that provide its proper functioning. The mass and charge transport in such a system is inherently complex. By contrast, measured impedance spectra of battery electrodes contain a relatively small amount of distinct features (typically one or two arcs and a diffusion-related line). This disparity makes a proper analysis of battery processes using impedance spectroscopy (and indeed any other electrochemical technique) difficult or at least ambiguous. To partly overcome this inherent problem we have recently proposed various approaches, all of which rely on a suitable combination of systematic experiments and appropriate modeling tools. For example, in experiments one can systematically vary the essential electrode parameters such as thickness, porosity, electrolyte concentration, amount of additives, calendaring conditions etc. and observe how those variations affect the impedance response. In addition, one can also use different types of cells (half cells, symmetric cells, full cells, 3-electrode cells). Often it is beneficial to also employ various non-electrochemical (either in- or ex-situ) techniques to get as much information as possible about the studied battery system. After collecting a large amount of experimental data, one needs appropriate modeling tools to extract the information about the ongoing battery processes. We have recently shown that physics-based transmission line modeling is a good compromise which can provide accurate information about all relevant physical parameters (diffusion coefficients, transport numbers, conductivities, exchange current density, contact resistances etc.) while still being computationally inexpensive (5 - 10 seconds per spectrum). We will demonstrate the above experiment-based-modeling approach on several battery electrodes and cells of practical interest.

Integrated Scanning Electrochemical Probes for Imaging Surface inhomogeneities and Localized Corrosion of Metals

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Various electrochemical inhomogeneities always exist at the interface of metal/solution, and play an important and often controlling role in localized corrosion of metals in given environment. They may become a vital influence in many electrochemical process, such as batteries, electrodeposition, electrolyte and electrocatalysis as well. The traditional research techniques of electrochemistry involving potential, current density or ac impedance measurements over bulk specimens can only provide its average and whole information. It is necessary to develop in situ imaging techniques for further characterizing electrochemical and environmental inhomogeneities at the interface of metal/solution for the localized corrosion system. In this work, various electrochemical scanning tunneling microscope (ECSTM) integrated scanning electrochemical probes have been developed for in situ imaging corrosion potential, current density, local ac impedance, local chloride ion and pH. Higher spatial resolution, precise measurement and local information of morphology-propertiy have been achieved based on such probes integration. The mechanism and kinetic behavior of localized corrosion of metals can be further understood by using these novel electrochemical probes appropriately.

Analyzing Impedance Spectra with the Probabilistic Distribution of Relaxation Times

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Electrochemical impedance spectroscopy (EIS) is a widely used technique for studying electrochemical systems, but its data interpretation using physical models or equivalent circuit models can be challenging due to their problem-specific nature and lack of physical meaning, respectively. In this context, the distribution of relaxation times (DRT) has emerged as a complementary approach, but recovering DRT from EIS data is an ill-posed inverse problem. To address this, we propose formulating the DRT problem in a Bayesian statistical framework, which offers inherent flexibility in incorporating prior knowledge about the DRT.

Two prior models are proposed: one using regularization penalty coefficients as multivariate random vectors to achieve timescale-dependent regularization for better DRT recovery, and another using weights of fitting residuals as random vectors to detect anomalies in EIS data and improve robustness against experimental noise. This approach is extended to the context of Gaussian processes, where Bayesian statistics can be used to determine hyperparameters univocally.

In addition, this presentation shows a novel deconvolution method based on deep neural networks (DNNs) that allows for the analysis of multidimensional EIS spectra and their dependence on experimental conditions. The deep-DRT method developed in this article does not require regularization or specific spacing on state variables, making it an appealing approach to examine complex EIS spectra and open a new research direction in the area of EIS analysis and DRT deconvolution.

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Conductive covalent organic polymers for electrocatalytic energy conversion applications

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Abstract

Covalent organic polymers (COPs), amorphous porous network materials synthesized through irreversible chemical bonding, have garnered significant attention in electrocatalytic energy conversion, including fuel cells, electrolytic water systems, and CO_2 electrolysis cells (Fig.1). COPs not only inherit the advantages of tunable porosity, modifiable backbone and atomically precise structure, and large specific surface area to accommodate abundant reaction sites, etc., but their irreversible kinetics also make them hydrothermal stability, acid and alkali resistance as well as ordered over short distances, allowing atomically metric control of molecular components, while maintaining random orientation and disordered porosity. Here, we have described the key factors that influence the electrocatalytic activity of COPs, including intrinsic conductivity, activity, and mass transfer, along with an overview of recent developments in COPs. In addition, we discuss possible future research directions for improving continuous performance, including controlled construction of high-performance active centers for higher current density at high voltage conditions, new processing technologies for membrane electrode assembly to avoid uneven distribution and incomplete exposure of active centers, further exploration of the electrocatalytic mechanism of COPs, and multi-factor analysis tools to track multiple influencing factors across different scales. Such strategies are expected to improve the intrinsic electrocatalytic activity of COPs, overcome challenges in stability, mass transfer, and apparent activity, and promote further research and development of COPs as electrocatalysts.

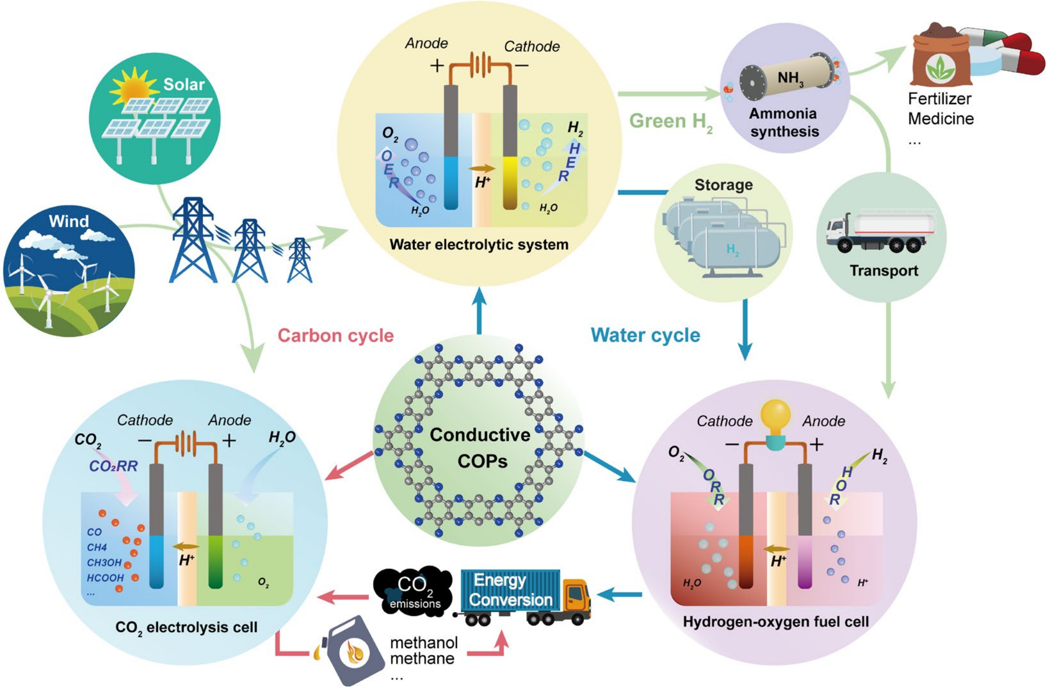

Fig. 1 Schematic diagram of the clean energy use cycle via conductive COPs.

In the Memory of Academician Cao Chunan

Design rules of equivalent circuit of corroded electrode based on mixed potential theory and its fitting example

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Electrochemical corrosion process occurs at the contact interface between metal electrode material and electrolyte solution, which includes at least one anode reaction and one cathode reaction at the same time. It is a steady state in which all cathode reactions and all anode reactions are coupled according to the rule of electric neutrality. In recent years, electrochemical impedance spectroscopy (EIS) has been developed into a common method to measure the corrosion rate of materials and judge the electrode process by designing equivalent circuit fitting. However, in the selection and design of equivalent circuit, only the error of numerical fitting is considered, and the corresponding relationship between the component parameters in equivalent circuit and the specific electrode process is basically ignored. According to the mixed potential theory of electrochemical corrosion, the electromotive force of corroded battery is equal to the difference between the equilibrium potential of anode reaction and cathode reaction. In the process of electrochemical corrosion, the electromotive force of the corroded battery can be divided into three terms, namely, the solution IR_{sol} drop, the anode overpotential η_a and the cathode overpotential η_c. Therefore, this study proposes that the solution resistance, anode impedance and cathode impedance should be in series in the equivalent circuit design. If the corroded anode reaction or cathode reaction contains multiple anode processes or cathode processes respectively, they are in parallel connection in their respective parts of the equivalent circuit, and the algebraic sum of the total currents in the parallel parts of the cathode or anode is zero. In addition, this paper introduces some research cases handled according to this rule.

Corrosion induced hydrogen permeation and environment sensitive fracture of AISI 4135 steel in marine tidal zone

海洋潮差区 AISI 4135 钢腐蚀诱发氢渗透和环境敏感断裂

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High-strength steels are increasingly used in marine engineering; however, they suffer from potential risks of corrosion induced hydrogen permeation, and therefore environment sensitive fracture. In this study, the corrosion induced hydrogen permeation and environment sensitive fracture behaviours of AISI 4135 steel in the marine tidal zone were investigated using electrochemical and slow strain rate test techniques respectively based on field exposure.

The study shows that the degree of pitting corrosion has a positive relationship with out of water /in water time ratio for the AISI 4135 steel samples placed in the tidal zone. A higher out of water /in water time ratio is conducive to pitting corrosion. The average depths of pits for the samples exposed at the HTL, MTL, and LTL were 212.75 ± 21.21 μm, 147.89 ± 9.04 μm and 121.73 ± 18.1 μm, respectively.

A higher out of water /in water time ratio is conducive to hydrogen permeation. The hydrogen contents in the AISI 4135 steel samples exposed at the HTL, MTL, and LTL were 5.60×10^{-2} wt ppm, 1.72×10^{-2} wt ppm, and 2.33×10^{-2} wt ppm, respectively.

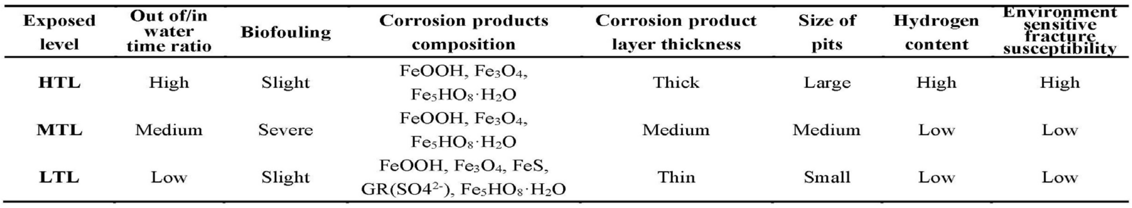
The lower hydrogen content at the MTL compared with that at LTL is considered to be partially the shielding effect of fouling on corrosion. The hydrogen permeation behavior of the AISI 4135 steel in marine tidal zone is not only directly related to the corrosion of steel, including the corrosion rate and the CPL, but also directly or indirectly affected by environmental factors, especially SRBs and macro-fouling organisms.

The AISI 4135 steel sample exposed at the HTL exhibited higher environment sensitive fracture susceptibilities and correspondingly larger elongation loss (I_δ) and reduction-in-area loss (I_ψ) values of 28.2% and 26.0%, respectively. In comparison, the steel samples exposed at the MTL and LTL had lower environment sensitive fracture susceptibilities and correspondingly smaller I_δ values of 6.0% and 3.2%, and I_ψ values of 2.2% and 2.7%, respectively.

The higher environment sensitive fracture susceptibility of the steel sample exposed at the HTL is combinedly determined by localised AD and HE. Under tensile stress, surface cracks were preferentially initiated in the corrosion pits, triggering brittle shear fracture of the sample placed at the HTL. However, the cup-and-cone fracture of the tensile samples exposed at the MTL or LTL is mainly governed by MVC and slightly impacted by HE.

The main characteristics of corrosion, hydrogen permeation and environment sensitive fracture sensitivities of the tested steel in marine tidal zone are summarised in Table 1.

Table 1 Characteristics of corrosion, hydrogen permeation and environment sensitive fracture sensitivities of AISI 4135 steel in marine tidal zone



Exposed level	Out of/in water time ratio	Biofouling	Corrosion products composition	Corrosion product layer thickness	Size of pits	Hydrogen content	Environment sensitive fracture susceptibility
HTL	High	Slight	FeOOH, Fe_3O_4, $Fe_5HO_8\cdot H_2O$	Thick	Large	High	High
MTL	Medium	Severe	FeOOH, Fe_3O_4, $Fe_5HO_8\cdot H_2O$	Medium	Medium	Low	Low
LTL	Low	Slight	FeOOH, Fe_3O_4, FeS, GR($SO4^{2-}$), $Fe_5HO_8\cdot H_2O$	Thin	Small	Low	Low

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Effect of Coupling Interaction on Local Corrosion Kinetics of Pure Iron under a Saline Droplet

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Different positions of the metal interface covered by the salt droplets show significant differences in corrosion behavior. In addition to the local parameters of the droplet morphology, corrosion products and chemical species, the distribution of the anode and cathode regions under the droplet is also affected by the coupling of the interface electrode. In this paper, the comparison between uncoupling and coupling states, and the influence of coupling on the corrosion behavior of metal under droplets were studied using concentric three-electrode array. In the coupled state, some electrode units undergo anodic polarization and the corrosion potential shifts positively, while other electrode units undergo cathodic polarization and negatively shift the corrosion potential, and their corrosion kinetic parameters also affect each other. If the anode is in the center, the anode charge transfer resistance of the anode unit decreases, the cathode charge transfer resistance increases, and the oxygen diffusion resistance increases; if it is at the edge of the droplet, the cathode and anode charge transfer resistance and oxygen diffusion resistance are both will decrease because the anodic polarization shifts the three-phase boundary at this location. If cathodic polarization occurs, the cathode charge transfer resistance decreases, the anode charge resistance increases, and the oxygen diffusion resistance increases significantly, which may be due to the change in its interfacial properties in the coupled state, which increases the difficulty of oxygen diffusion.

Keywords: Atmospheric corrosion, Corrosion kinetics, Coupling interaction, Polarization

The application of EIS in the long-term and active corrosion protection of multifunctional coatings

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Coating is an efficient technology for marine engineering equipment corrosion protection. Unfortunately, as defect sites, micropores and microcracks are often attacked by corrosive media (such as Cl, O_2, and H_2O) during long-term service, which unavoidably poses localized blistering and poor adhesion and eventually deteriorates the protective performances of coating, especially in harsh marine environments. Multifunctional composite materials are prepared and introduced into coatings to reduce their initial microdefects, improve barrier properties, and endow active corrosion protection[1].

The corrosion inhibition performance of cerium and imidazole derivatives for metal has been confirmed in various environments. Some works also studied the influence of cerium and imidazole derivatives on the structure and properties of the coating [2]. However, some deficiencies, such as complicated synthesis methods, insufficient long-term and active corrosion protection effects, still need to be addressed. Herein, to solve the above problems, we design and synthesize two multifunctional composite materials named GO-CN/CON-U and PDA-GO-CeO_2. Afterward, two intelligent composite coatings with passive/active protection and mechanics reinforcement are obtained.

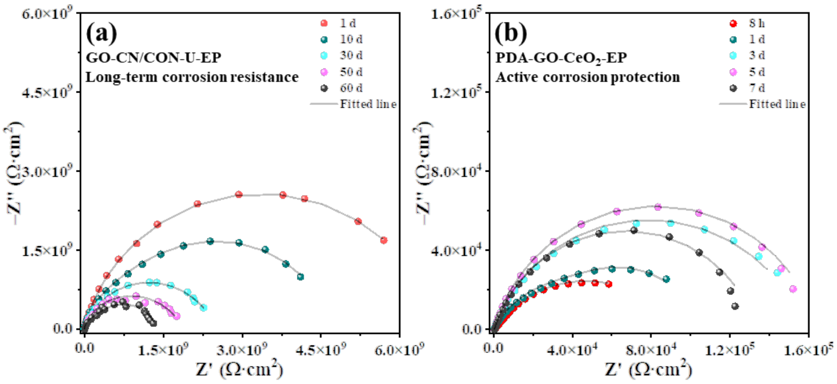

Fig. 1 (a) The long-term corrosion resistance of GO-CN/CON-U-EP coating and (b) active corrosion protection of PDA-GO-CeO_2 coating with an artificial scratch for Q235 steel in 3.5 wt.% NaCl solution at different immersion times.

Electrochemical Impedance Spectroscopy (EIS), as an in-situ and nondestructive technique, was applied to understand the long-term corrosion resistance of GO-CN/CON-U-EP coating and active corrosion protection of PDA-GO-CeO_2 coating [3]. As shown in **Fig. 1a**, thanks to the crosslinking density and strength of coating being improved by the interaction between GO-CN/CON-U and epoxy resin, the impedance value still exceeds 10^9 $\Omega{\cdot}cm^2$ after immersion in 3.5 wt.% NaCl solution for 60 day. The impedance value (**Fig. 1b**) of PDA-GO-CeO_2 coating exhibits a trend of initially increasing and then stabilizing before decreasing for steel during 7 day, demonstrating its active corrosion protection. Undoubtedly, EIS is essential for evaluating the long-term and active protection of the coating.

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Research and application of an in-situ detection probe for metal artefacts based on electrochemical impedance technology

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Ancient metal heritage has been buried for thousands of years in different environment and suffered from varying degrees of corrosion. The original metal surfaces generated a rust layer with markedly different physicochemical properties and a complex rust composition, which seriously affected the stable preservation of cultural heritage. To extend the life of metal artefacts, the conservation should generally carry out cleaning, desalination, corrosion inhibition, reinforcement, sealing and daily monitoring to enhance the corrosion resistance. The electrochemical impedance technique has been justifiably introduced into the monitoring and material condition assessment of metallic artefacts based on the requirements of the specific concept of conservation.

To avoid damaging the integrity and original authenticity of cultural heritage, the construction of a reasonable electrochemical detection probe, to achieve in-situ and non-destructive monitoring of metallic artefacts, is a hot research topic in the international academic community. In this presentation, a pen-type probe was designed to effectively ensure stable residence of the electrolyte on the rough surface of the artefacts with a defined testing area and stable electrochemical data through the electrode layout within the probe, the shape following, and the reduction of the junction potential. The study has also compared the impedance data tested by the probe and the solution system, analysing the corrosion behaviour and equivalent circuit of the impedance spectrum and describing the mechanisms of the continued rusting of cultural heritage. The probe can be applied to rusted metal artefacts by in-situ detection with stable and reproducible data. It has a broad application prospect in the field of metal heritage conservation and monitoring.

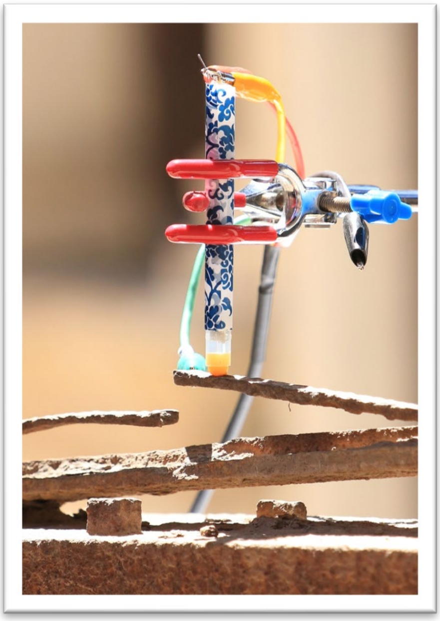

Figure 1 In-situ detection probe being in working progress

Non-stationary electrochemical characteristics of stress corrosion cracking and its application

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Stress corrosion cracking (SCC) is one of the major threats to the operational safety of many industrial load-bearing equipment or materials in petroleum, petrochemical, chemical, or nuclear power industries. SCC mechanism has been widely emphasized by the industry and is the basis of stress corrosion diagnosis, assessment and protection. Authors of this report have conducted an in-depth study on the electrochemical mechanism of stress corrosion and its applications for decades. It is concluded that stress corrosion cracking of steels is an interactive process of fracture and electrochemical reactions, and its two-dimensional characteristics of cracking and expansion determine that SCC has non-stationary electrochemical properties. The fresh metal surface continuously exposed by crack expansion and the non-stationary electrochemical process caused by dislocation outcrop movement are the two main non-stationary electrochemical processes in the SCC process, which have a decisive influence on the SCC and its mechanism. Due to the above two mechanisms, SCC in aqueous phase media is generally characterized as controlled by a mixture of anodic dissolution and hydrogen embrittlement mechanisms (AD+HE). Based on the above understanding, a quantitative theoretical model for SCC sensitivity and life prediction is proposed, and various SCC monitoring and detection techniques as well as composition design methods for SCC-resistant steels are established and have been applied in a large number of engineering applications.

Key words: Stress corrosion cracking, Non stationary electrochemistry, Prediction model, SCC-resistant steel

Electrochemical Impedance sensor for early failure monitoring of coatings in offshore wind power station

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In this work, we developed a kind of coating degradation monitoring website composed of miniature impedance sensor, data logger and transmit network for field diagnosis of early failure of marine coatings based on microelectronics and electrochemical impedance spectroscopy (EIS). The aging process of polyurethane-based coatings in salt spray test chamber was also studied by using the impedance sensor. Several critical indexes related to EIS, such as phase angle, breakpoint frequency, specific capacitance, and impedance modulus were proposed to evaluate the severity of coating degradation. The results indicated that the impedance sensor could accurately monitor degradation process of coatings by sensing the coating capacitance.

Through experimental running of the coating degradation monitoring unit installed in an offshore wind power station, it is found that the single and two-electrode coating capacitance sensors exhibited higher sensitivity to the aging process of organic coatings than the conventional three-electrode sensor. Online corrosion monitoring on key parts or components can provide support for the safety and preventive maintenance of steel jackets and piles of offshore wind power tower. It is expected that the on-site coating network will contribute substantially to the real-time detection of coating failure and preventive maintenance .

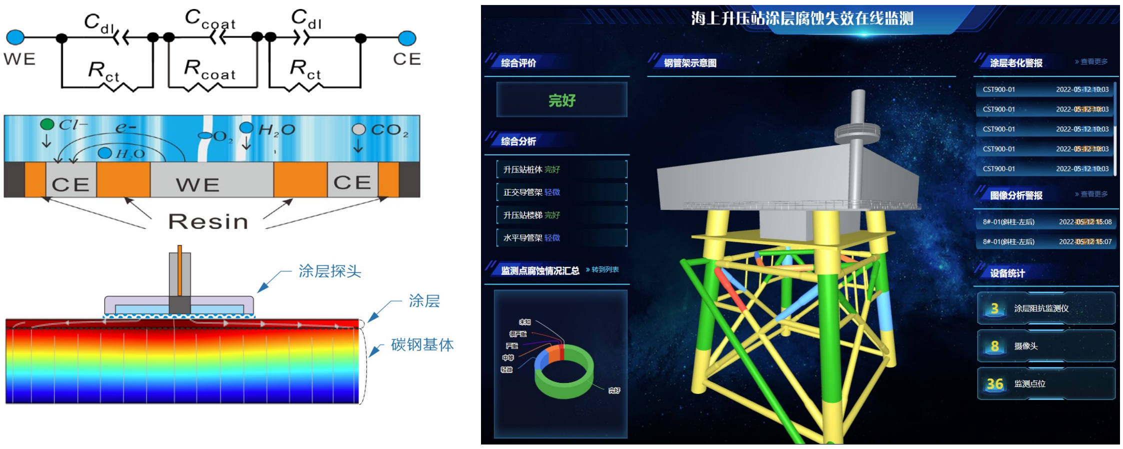

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Figure 1. schematic of field coating ageing monitoring based on impedance(a), and 3D visual presentation of coating status based on capacitance sensor on an offshore wind power station(b).

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Study of corrosion of high-strength steel in 3.5% NaCl solution under hydrostatic pressure using electrochemical impedance spectroscopy

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In the deep-sea environment, the failure of the alloys results from the multiple physicochemical factors, which is more complicated than the compared to the offshore environment. Some studies reported the ionic transport near the electrode, which shows that ions take on vibrational energy from charged surfaces, and ions close to the metal surface vibrate around the Helmholtz plane [1-3]. In this work, EIS was used to study the electrochemical corrosion behaviour of Ni-Cr-Mo-V steel which is equipped by hydrostatic pressure and tensile stress. The EIS results suggest that the steel behaves as a porous electrode. In this condition, Tribollet et al. [4] provide an electrical model where a distributed impedance in space as a transmission line in the conducting pores, as shown in Fig. 1, and tensile stress and hydrostatic pressure accelerate the rate of electrochemical reactions. Meanwhile, the polarization cures also confirm these results; in the region of low overpotential is small, but with the increase of potential, the Tafel slope *b*a decreases gradually from 72 mV to 36 mV. The slope of 36 mV is similar to the anodic Tafel slope of the planar iron electrode in an acidic solution containing chloride ions. It is mainly due to the rapid thinning of the effective reaction region with the increase of polarization, making the porous surface close to the planar electrode. Accordingly, the kinetic formula of the anodic dissolution reaction for the alloy with porous surface under hydrostatic pressure and stress could be expressed, and the change in the surface stress/energy of the solid will also be reflected in the structure of the solid/liquid interface. We try to extend the compression effect of hydrostatic pressure on the electric double layer to tensile stress and pressure-stress action on the double layer so as to study the acceleration of electrochemical rate or corrosion rate in the coupled environment.

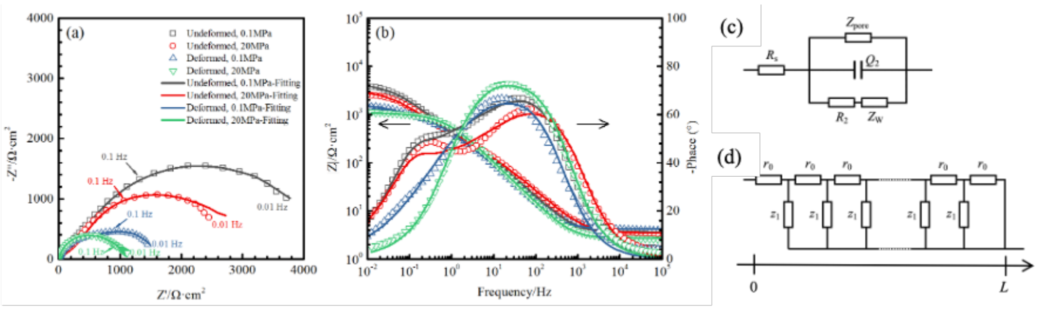

Fig. 1 EIS measurements of the Ni-Cr-Mo-V steel. (a) Nyquist plots, (b) Bode plots under 0.1 MPa without U-bend, 20 MPa without U-bend deformation, 0.1 MPa with U-bend deformation, and 20 MPa with U-bend deformation, respectively, (c) the equivalent circuit for the EIS, and (d) the impedance of Z_{pore} that is through the micropores fitted by transmission line method.

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The Effect of Rich Silicon particles on the Corrosion Behavior of Multilayer Aluminum Alloy Composite Plates in NaCl solution

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Aluminum alloy is one of the commonly used metal materials in marine engineering, but the mechanical properties of a single aluminum alloy are often difficult to meet the requirements of large-scale marine equipment. The composite of several aluminum alloy sheets is a potential method to improve their mechanical properties. However, the improvement of mechanical properties may also lead to a decrease in corrosion resistance. Although extensive research has been conducted on the manufacturing process of composite materials, there are few reports on their corrosion behavior. Due to the electrochemical properties of corrosion, various electrochemical methods such as electrochemical impedance spectroscopy (EIS), polarization curves, and electrochemical noise can be used to detect the corrosion mechanism. However, research on the corrosion behavior of aluminum alloy composite plates is limited.

This article investigates the corrosion resistance of multi-layer aluminum alloy composite plates through polarization curves, electrochemical impedance spectroscopy, and corrosion morphology analysis. The influence of matrix orientation on corrosion mechanism was discussed.

The corrosion resistance of Al composite materials in the plane direction is higher than that in the cross-sectional direction, which is manifested by the lower anode current density in the polarization curve.

There are many silicon rich particles in the outer layer of Al composite materials, with the silicon rich particles serving as the cathode and the surrounding Al matrix serving as the anode. Due to corrosion, grooves are formed around silicon rich particles.

The measured EIS data shows that there are basically two capacitor semicircles in the figure, and the radius of the capacitor semicircle is related to the corrosion rate, while a larger radius means a higher charge transfer resistance. Use different electrochemical equivalent circuits to fit EIS data. The fitting results of EIS are consistent with the polarization data.

Acknowledgments:

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Study on the rapid detection method for coating performance based on phase angles with three methods of correlation analysis

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The failure process and electrochemical behavior of ten organic anti-corrosion and weather resistance coatings on steel and Al alloy substrates in different accelerated corrosion environments were studied by electrochemical impedance spectroscopy (EIS) method. Because the variation of the phase angles in middle frequency can reflect the protective property of the coatings effectively, three important correlation analysis methods, including Pearson correlation coefficient, Cosine Similarity and Euclidean distance methods were applied to deeply analyze the EIS data of the ten coating systems (totally 60 samples) with the help of computer programming to determine the phase angle and its corresponding frequency which possesses the highest correlation with the low-frequency impedance modulus ($|Z|_{0.01\mathrm{Hz}}$). Firstly, the Pearson correlation coefficient (r) was used to analyze the EIS data of all the coating samples and the results showed that the top eight frequencies at which the phase angles have the strongest correlation ($r \geqslant 0.90$) with $|Z|_{0.01\mathrm{Hz}}$ is in the range of 0.85 Hz to 41.75 Hz. Based on this result, then Cosine Similarity and Euclidean distance methods were used to analyze the correlation furtherly. Combined with the weight sum analysis (*wsum*) and the average coefficient of association (*average*), it was obtained that for the studied ten coating systems and environments combination, at around 4.52 Hz frequency the phase angle variation has the strongest correlation with the impedance $|Z|_{0.01\mathrm{Hz}}$. Thus, the phase angle at middle frequency range around 4.52 Hz can be applied to quickly detect and evaluate the protective performance of organic coatings on the site.

Keywords: Solvent-free epoxy coating; Low alloy steel; Protective performance; EIS; lifetime prediction

In-situ preparation of triazole polymerization films on copper surface via SI-ATRP method and their performance against copper corrosion

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Abstract: As one of the most advanced macromolecular in-situ film forming technologies, the living polymerization provides an effective method for in-situ fabricating functional films on material surface. In this paper, the triazole film of polymerized (1-tosyl-1H-1,2,3-triazol-4-yl) methyl acrylate (P-TTMA) is in-situ prepared on copper surface via surface-initiated atom transfer radical polymerization (SI-ATRP) method. The P-TTMA film with different degree of polymerization (DP) is obtained by regulating the polymerization time of SI-ATRP reaction. The preparation of P-TTMA film is confirmed via various characterization. The DP value of P-TTMA film shows an S-shaped variation as the polymerization time increasing. The electrochemical test is performed to evaluate the anticorrosion performance of different P-TTMA films for copper. The relationship between the polymerization behavior of P-TTMA and its corrosion inhibition efficiency is further investigated. The result demonstrates that the P-TTMA films exhibit good anticorrosion performance for Cu in 3.5wt.% NaCl solution. The P-TTMA obtained by 48h polymerization time, with the DP value of 105, exhibits the stable and good protection performance. The anticorrosion performance of P-TTMA film can be optimized via regulating the SI-ATRP reaction. This paper provides a new idea for preparing inhibition film with a certain degree of polymerization and protection performance on metal surface. It is expected to be widely applied in the sophisticated field of material protection.

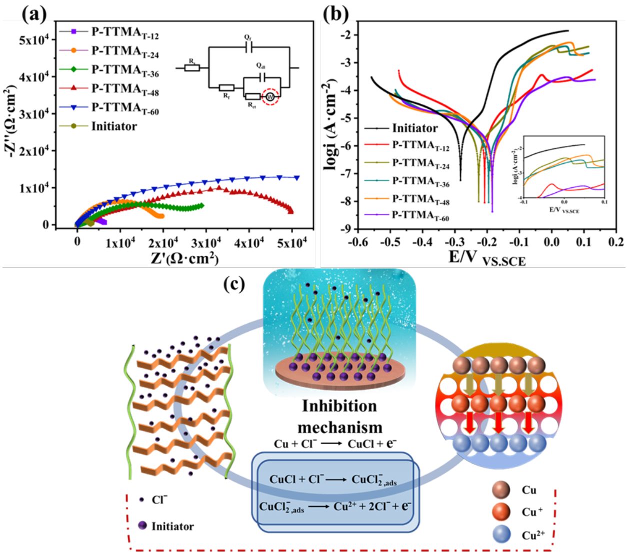

Fig. 1. Nyquist plot (a) and polarization curve (b) of copper electrodes with different P-TTMA film after 1h immersion in 3.5 wt.% NaCl solution; Schematic diagram of the corrosion inhibition mechanism of P-TTMA for copper (c).

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The physical significance and universality of electrochemical active energy in metal electrodeposition

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Abstract:
Metal electroplating process contains many procedures including at least the directed migration and dissociation of complex metal ions, the discharge of the dissociated metal ions, the transfer of the discharged metal atoms along the substrate surface and the lattice incorporation of the atoms (adatoms) to the periphery of a growing nucleus, and all of them result in the so-called electrochemical noise of different frequency (*f*). Consequently, the *f*-depended noise energy can be theoretically adopted to distinguish different procedures, and even to distinguish the nucleation and growth procedures (although the nucleation and growth of the deposit crystallites always proceed sequentially and even concurrently during metal electroplating process). Among these procedures, the involved electrochemical reactions (such as the breaking of the old bonds and the formation of the new bonds) cause the energy transfer between the electrode system and the environment. Part of the energy is consumed as heat, and the other part (in the form of 'work') results in the change of the electrode surface state (such as the formation of metal deposits) expressing as the variation of the electrode potential (E). In fact, E itself is just a measure of energy in essence in the fields of physics and electrochemistry.

In physics, energy is traditionally divided into two parts, namely the kinetic energy and the static energy, and both of them can be transformed to each other. In electrochemical noise theory, the acquired E is also divided into two parts, namely the dc-shift and the electrochemical noise superimposed on dc-drift (EN), and both of them can also be transformed to each other. Moreover, it is widely accepted that EN is related to the electrochemical reaction rate. However, the physical significance of (the absolute) EN energy (E^a) is scarcely reported, especially, the physical significance of the EN energy consumed only in the involved electrochemical reactions (defined as the electrochemical active energy E^{D}) is not investigated.

In this report, a new method is firstly proposed for the selection of reasonable EN sampling frequency. Secondly, the common action mechanism of main electroplating factors on E^{D} being affecting the charge transfer rate is discovered, and the physical significance of E^{D} is made certain being a new index to characterize the difficulty level of the formation of the initial deposit monolayer. Thirdly, it is ascertained that, in the re-plotted energy distribution plot (obtained from the fast wavelet analysis of EN using db4 wavelets), the energy deposited in the crystal D_J of higher (such as D_8) and lower J value reflect the information about the nucleation and growth of the initial deposit monolayer, respectively. Lastly, the physical significance and universality of E^{D} in metal electrodeposition are confirmed theoretically and experimentally.

Wear & Corrosion

Tribocorrosion behaviors of three nickel-based superalloys in sodium chloride solution

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The tribocorrosion behaviors of three nickel-based superalloys (Incoloy 800, Incoloy 825, and Inconel 625) in 3.5 wt% NaCl are studied under the cathodic, natural-corrosive, and anodic polarization states. XPS depth profiling confirms that the tribofilm compositions not only strongly depended on the alloy compositions but also significantly affected by the polarization potentials. With the potential increases from − 0.80 to +0.25 V, the decreased COF originates from the increasing content of Cr oxides in the tribofilm. The compound Ni/Fe oxides were worn away from Inconel 625 while Fe oxides contribute the main mass loss of Incoloy 800 and 825. The tribofilm with more Fe oxides (Incoloy 800 and 825) delivers a lower COF value but larger wear volume.

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Xian-Zong Wang, Yuhui Jiang, Yanfei Wang, Chengping Ye, Cheng-Feng Du, Probing the tribocorrosion behaviors of three nickel-based superalloys in sodium chloride solution, ***Tribology International*** 172 (2022) 107581. https://doi.org/10.1016/j.triboint.2022.107581

Alkene Catalyzed wear and corrosion on black phosphorus for nanopatterning

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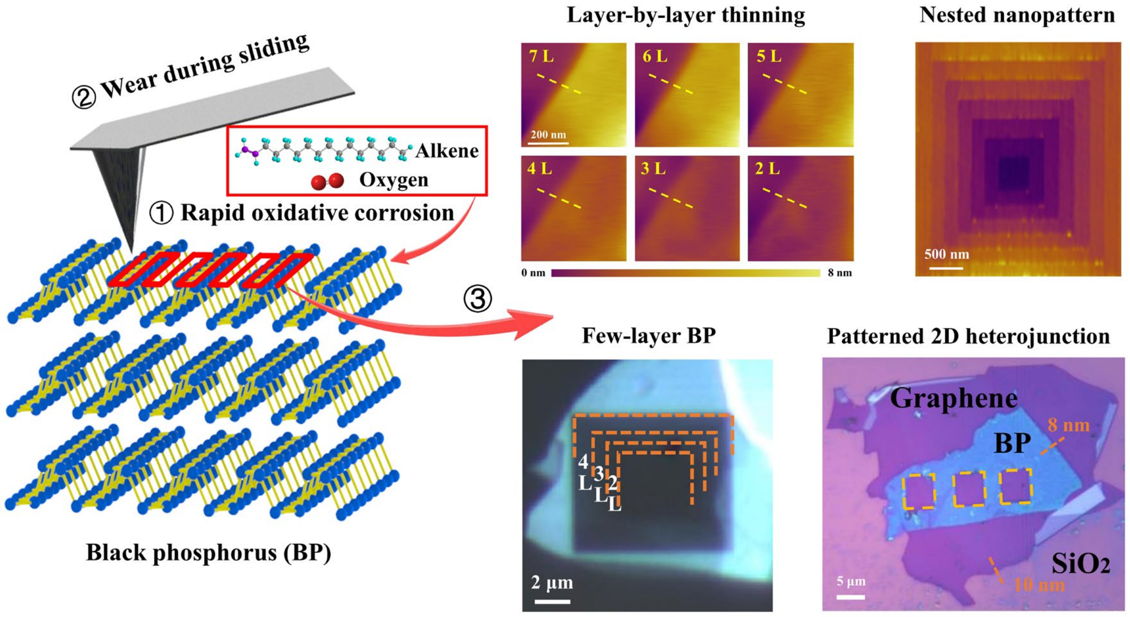
Black phosphorus (BP) exhibits a great potential in the applications for electronic and optoelectronic devices, whose performance depends on the thickness of BP nanoflake. Unfortunately, the efficient generation of the well-defined BP nanoflake with desirable thickness remains challenging. Here, the method involving alkene catalyzed wear and corrosion of BP was proposed to fabricated nanopatterned BP by layer-by-layer thinning. The enhanced electron affinity of oxygen with the assistance of carbon-carbon double bond in the alkene can accelerate the oxidative corrosion of BP. After rapid oxidation, the superficial phosphorus oxide can be readily removed by the mechanical effect during the sharp AFM probe sliding against the phosphorus oxide, resulting in significant wear of BP. By adjusting the number of sliding, the layer-by-layer thinning of BP can be achieved, allowing fabricating nanopatterned BP, BP nanoflake with arbitrary thickness and nanopatterned 2D heterojunction. This nanopatterning technology can be further used to fabricate the BP field-effect transistor with enhanced capability for current modulation, showing great potential applications for designing the high-performance nanodevices.



Hydro-abrasive erosion behaviors of HVOF sprayed carbide-based cermet coatings in simulated seawater slurries

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Abstract – This paper aims at the hydro-abrasive erosion (HAE) behaviors in simulated seawater slurries under different flow velocities (FVs) and sand concentrations (SCs) of high-velocity oxygen-fuel (HVOF) sprayed carbide-based cermet coatings. The WC-Ni coating possessed worse anticorrosion property and superior HAE resistance regardless of FV and SC, and its HAE resistance was less affected by FV (80.6%) as well as SC (59.4%) in contrast with the Cr_3C_2-NiCr coating (141.4% and 103.8%) by taking the increment of VLR as the evaluation criteria. Higher FV and SC both contributed to the HAE degradation of the coatings, while FV had a greater effect on their HAE resistances than SC. The HAE failure mechanisms of both coatings under different FVs and SCs were also explained.

Electrochemical characterization of copper corrosive wear mechanism in chemical mechanical polishing

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Copper has been widely used as the interconnect material in microchips owing to its superior electrical properties and cost-effectiveness [1]. Chemical mechanical polishing (CMP) is utilized in the dual damascene technology to achieve local and global planarization of the surface for fabricating copper interconnects [2]. In essence, copper CMP can be considered a dynamic corrosive wear process, where copper is first corroded through the synergistic effect of oxidation and complexation, and then the weakened copper surface film is worn by abrasive particles [2]. To provide a guide for optimizing the CMP process, we investigated the copper corrosive wear mechanism in CMP with several electrochemical techniques, including open-circuit potential, potentiodynamic polarization, cyclic polarization, and chronoamperometry. It is revealed that the copper removal mechanism in CMP can be corrosion-enhanced wear dominant [3, 4]. Based on this, we assessed composite corrosion inhibitors in copper CMP to control corrosion and corrosive wear, improving the surface quality. It is found that composite corrosion inhibitors can be roughly classified into two groups. In the first group, the components show a synergistic effect, such as 1,2,4-triazole and polyamine [5], 1,2,4-triazole and polyacrylic acid. In the second group, the components show a competitive effect, such as 1,2,4-triazole and 5-methyl-benzotriazole. The underlying mechanism was preliminarily studied with electrochemical characterization. It is recommended to use the first group to obtain a more substantial corrosion inhibition effect.

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Role of protein in fretting-crevice corrosion of CoCrMo alloy used for artificial implants

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Joint replacement is an effective solution to osteoarthritis. However, there is fretting-crevice corrosion in the fixed position of artificial joint, which leads to joint loosening and metal ion release. CoCrMo alloy, as an artificial joint material, has excellent corrosion resistance and wear resistance. Therefore, the crevice corrosion and fretting corrosion of CoCrMo alloy in simulated bio environment were studied, and the effect of protein on fretting-crevice corrosion was explored. The results show that during crevice corrosion, the proteins in the solution accumulate at the crevice mouth, which changes the solution environment inside the crevice.In addition, in the solution environment inside the crevice, the protein also has a significant effect on the fretting corrosion of CoCrMo alloy.

Tribo-corrosion investigation during the chemical mechanical polishing (CMP) process of integrated circuit

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Chemical mechanical polishing (CMP) is the key process to achieve both the local and global surface planarization of of integrated circuit (IC) and other precise instruments. To obtain an ultra-smooth surface and efficient material removal of materials (Cu, Ru, Co, et al.), the "chemical-mechanical interaction" effect plays the key role during the polishing process. In this case, the tribo-corrosion investigation during the metal CMP process draws attentions in the fundemental research. Tribo-corrosion setup is the most commonly used method (shown in Fig. 1a), in which the metals are immersed in electrolyte and are subject to external mechanical abrasion. Two outcomes could be meausred: 1) the changes of the electrochemical signal during mechanical abrasion; 2) the changes of wear traces under exteral applied voltage. It should be noted that this traditional tribo-corrosion setup could only be used to investigate the tribo-corrosion behavior qualitatively, and the abrasion condition is far away from the real polishing condition. We built a CMP-electrochemical apparatus to combine the real CMP machine with the potentiostat (Fig. 1b). This apparatus could measure the electrochemical signals during the real polishing process, which could reflect the tribo-corrosion behaviros of metals during CMP. It was found that different metals (Cu, Ru) show distinct tribo-corrosion behavors during CMP. We also demonstrate how this kind of research plays the guiding role in the CMP process optimization.

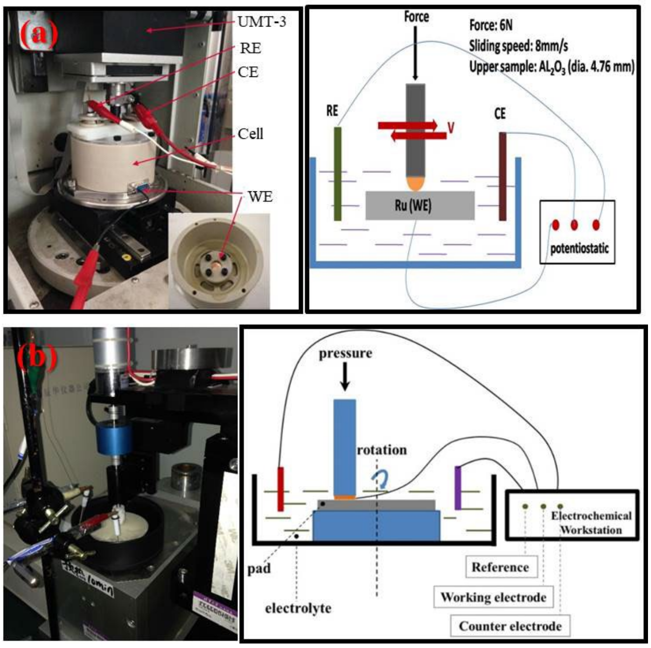

Figure 1 (a) Traditinal tribo-corrosion setup; (b) CMP-electrochemcial setup

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Significant role of repassivation in the critical flow velocity phenomenon of erosion-corrosion of passive materials

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Erosion-corrosion is the main cause for the premature failure of various flow handling components, such as pipelines, pumps, valves, impellers, hydroturbines and so on, in many industries, due to the well-known interaction between mechanical erosion and electrochemical corrosion resulting from the relative motion between a corrosive fluid and a material surface. Therefore, inhibiting or controlling erosion-corrosion damage is of great significance for the safe service of flow handling components. Generally, there exists a critical flow velocity (CFV) phenomenon for erosion-corrosion of passive materials, in which erosion-corrosion is severe only when the flow velocity exceeds a threshold value. Therefore, the CFV can be used as an effective parameter evaluating erosion-corrosion resistance, with higher CFV corresponding to higher erosion-corrosion resistance. This study clarifies that the electrochemical repassivation process, occurring subsequent to the depassivation of passive films caused by erosion, plays a significant role in the CFV phenomenon for erosion-corrosion of passive materials, based on which a CFV prediction model is established. Firstly, the effect of pitting on the CFV of stainless steel is investigated and it is found that the occurrence of pitting can decrease CFV drastically. It implies that the CFV phenomenon could be affected by repassivation, since repassivation is a significant process dominating pitting corrosion. Then, we design colour-labelling and ion-labelling experiments to study the depassivation behavior of passive films formed on titanium and prove that the root cause of CFV phenomenon can be attributed to the competition between erosion-induced depassivation and the subsequent electrochemical repassivation of passive films. At the flow velocity where depassivation and repassivation rates are equal to each other, the critical condition is reached. On this basis, we further design a single particle impingement set-up to simulate the depassivation-repassivation unit damage process in erosion-corrosion of passive materials. And then, a simple, reliable and universal method for obtaining repassivation time is proposed by unifying and simplifying the repassivation current–time functions for common film growth models, and is verified by using the experimental data obtained from single particle impingement tests. By employing the aforementioned method, the effect of depassivation on repassivation under erosion-corrosion conditions is studied. The results show that the repassivation rate increases with the depassivation degree. Based on all the findings above, a theoretical CFV prediction model is established, in which the CFV is confirmed to be dependent of repassivation rate. Such the model can predict the CFV for erosion-corrosion of passive materials.

Localized corrosion of AA5083 in a simulated dynamic seawater/air interface studied by EIS and advanced characterization

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Localized corrosion of the aluminium alloy AA5083-H111 in a simulated dynamic seawater/air interfacial zone and a full seawater immersion zone was investigated with electrochemical impedance spectroscopy and electrochemical noise. Al-Fe/Ti intermetallic particles (IMPs) on localized corrosion were examined with focused ion beam, transmission electron microscopy and energy dispersive x-ray spectroscopy. As compared with the full immersion zone, the interfacial zone showed higher oxide film resistance and charge transfer resistance, which was attributed to the high oxygen flux in that zone. Localized corrosion arose from IMPs that posessed an Al-Fe phase and a Ti enriched phase.

The effect of wetting time on localized corrosion in a dynamic seawater/air interface zone was also investigated. Longer wetting time resulted in a more serious localized corrosion degree and thus led to an uneven and incomplete corrosion products film. This was attributed to the presence of a thin electrolyte layer upon the alloy, restricting the effective repassivation of the corrosion pits.

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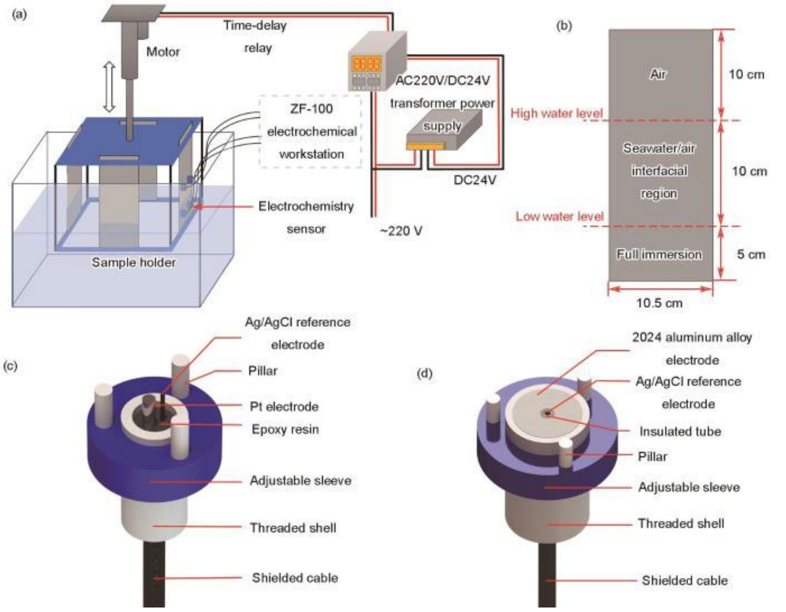

Fig.1 A self-built dynamic seawater/air corrosion measurement platform (a) overview of the corrosion platform; (b) 2024 aluminum sample which is divided into three regions: atmosphere region, seawater/air interfacial region, and full immersion region; (c) detail of the corrosion electrochemical sensor used in the EIS measurement; (d) detail of the corrosion electrochemical sensor used in the electrochemical noise measurement

Dahai Xia, associate professor from Tianjin University, his main research interest is corrosion electrochemistry. Currently, he serves as deputy editor of Anti-Corrosion Methods and Materials, Associate editor of Corrosion Communications, editorial board member of Chinese Journal of Corrosion and Protection.

The research progress on adsorption-desorption of corrosion inhibitor under the pipe flow condition

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The injection of inhibitor is one of the most useful strategies to mitigate the corrosion of surface pipelines and downhole strings used in oil and gas field or some other new energies such as geothermal energy. Under such field conditions, the adsorption-film-type inhibitor is the most common and effective one and its inhibition performance is determined by the capabilities of adsorption and desorption. Therefore, it is highly significant to study the adsorption-desorption of corrosion inhibitor under field conditions such as the pipe flow condition.

Here we focus on the research progress on adsorption-desorption of corrosion inhibitor under pipe flow condition and give a short review. Three aspects have been payed attention to:

1) Can the inhibitor molecule be removed in the single phase flow?

2) Can the inhibitor molecule be removed in the liquid-solid flow?

3) How to increase the inhibition efficiency of the inhibitor under the pipe flow condition?

We combined and analysed the work from the authors across the whole world including ourselves, our co-authors and other scientists, and then tried to answer the three questions as mentioned above. We hope this presentation can help the design and development of highly effective corrosion inhibitor used in multi-phase flow condition, and mitigate the loss of metal and alloys. Ultimately, prolong the service life of materials and reduce the carbon emission.

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Study on wear and corrosion resistance of Ti3alc2/resin-based composite coating by high-energy ball milling process

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The ternary layered ceramic Ti3AlC2 material has both metal and ceramic properties, namely, good electrical and thermal conductivity, relatively low friction coefficient, and good corrosion resistance, making it have broad application prospects in chemical corrosion resistant environments and as functional materials. In this paper, the method of high-energy ball milling was used to refine the Ti3AlC2 grains and improve their dispersibility in epoxy resin. An organic coating was prepared by spraying. The phase composition and surface morphology of the sample before and after corrosion were measured using XRD and SEM, respectively. The electrochemical and tribological properties of the sample were tested using an electrochemical workstation and a ball and disk tester, thereby exploring its wear and corrosion mechanism.

Key words: Ti3AlC2; High energy ball milling; Corrosion; Wear mechanism

Measurements & Analysis and Sensors

Determination of Corrosion Rate with Electrochemical Harmonic Measurement and Analysis

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The nonlinear nature between the current and voltage in the electrochemical reaction provides the foundation of electrochemical harmonic technique, which is a relatively novel technique in the field of corrosion compared with traditional Linear Polarization Resistance (LPR), electrochemical impedance spectroscopy (EIS) and electrochemical noise technique. The promises, applications and challenges of electrochemical harmonic technique is reviewed and discussed. One of the applications for the corrosion rate of carbon steel in HCl solution is studied with electrochemical harmonic measurement and analysis (HA). The corrosion rate with HA is consistent with that measured by LPR and EIS. The set up and mechanism of electrochemical harmonic measurement and analysis is introduced from the theory and application in the present research.

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Impedance Spectroscopy: Quo Vadis?

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The application of impedance spectroscopy is increasing, as are the problems and issues in the technique. The trouble is suggested to originate from the modeling using constant phase elements (CPEs) for the additive impedance arcs,[1] widely applied across disciplines. It has been shown that the additive Havriliak-Negami type dielectric relaxations with characteristic frequency exponents, temperature-independent, and the time constants thermally activated as for the conduction mechanisms can explain the temperature and frequency dependence of non-trivial impedance responses of solid electrolytes. The approach supports the current constriction mechanism rather than the space charge theory for the blocking grain boundaries for many polycrystalline solid electrolytes. It also comprises a full complex capacitance description of universal dielectric relaxation (UDR) known in the AC conductivity spectroscopy for long, for the pseudo dielectric originating from the mobile charge carriers.[2–5] Clearly differently activated 'huge grain boundary impedance' is suggested to be explained by the mixed conduction. Materials studied for conductors of various ionic carriers or for the dielectric (and insulating) properties exhibit similar features. Prohibitingly painstaking model exploration and parameter determination is now greatly assisted by Python coding[6,] and the demonstration to finally persuade the community is hoped to be soon available.

Transmission line models (TLM) are essential for the Nernst-Planck mechanism for ambipolar diffusion by ions and electrons in ionic crystals,[7] mentioned above as mixed conduction, and by cations and anions in electrolytes. TLM also describes the porous electrodes or percolating networks in general.[8–10] Electrochemical systems like batteries, fuel cells, electrolyzers, etc. are concerned. Affliction by CPEs in the physics-based TLM appears to be resolved by the special interfacial CPE with the exponent ½.[9,10] Frequency dispersion with exponents ½ appears to be widely applicable, as the interfacial polarization is likely distributed in space and time by diffusion of the species, and the fractal nature of the percolative network. Different physics described by the same equivalent circuit models (ECM) should not be confused. When the heterogeneity is to be combined with the diffusion in the homogeneous medium, numerical simulation, rather than analytical expressions, may be needed. Parameterization by the circuit elements is nonetheless useful and hence recommended.

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Significance of impedance measurements in skin phantom with 2, 3 and 4 electrodes configuration. Measurements and simulations

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Abstract: The need for a true non-invasive method to estimate the glucose levels in patient's blood has driven the search for new ways of getting this estimation [1]. One of these proposed methods is based on the principles of EIS, referred to in this domain as bioimpedance [2]. Results from different authors have evidenced the existence of a correlation between the glucose level in the blood and the electrical properties of the patient's skin, as determined by impedance measurements [3]. However, these results have also shown that optimization of the measurements is necessary to obtain more accurate and reliable estimations. To achieve this goal, deeper studies considering the effect of factors like electrodes configuration and geometry, among others, are needed. In this work, we present the exploration of these effects considering both simulation and experimental measurements for 2, 3, and 4 electrodes configuration, by using a skin phantom to eliminate the biological variations that could interfere with the measurements. This skin phantom is produced by a protein gel whose electrical properties are modulated by adding a different amount of NaCl. The first results show that rectangular electrodes for all three configurations lead to less dispersive measurements and that in the case of 4 electrodes configuration, it is possible to detect individual layer contributions for a multilayer system, provided that the resistance of each layer is different enough. This opens the possibility of deconvolution of the contribution of each layer in real skin and, thus, the assessment of the best parameter to correlate with the glucose level in patients' blood.

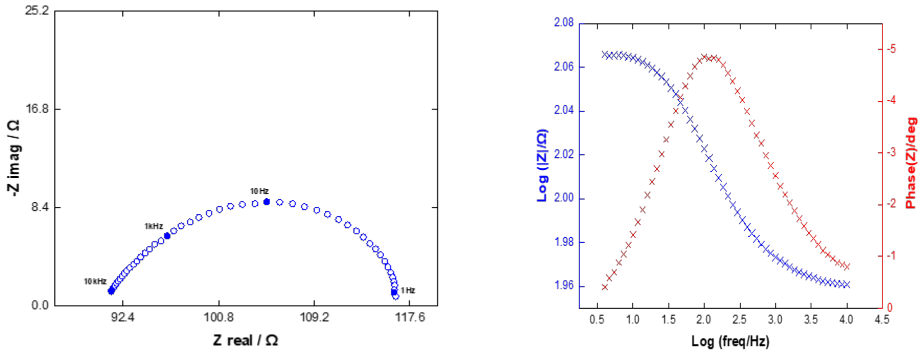

Fig1. Experimental impedance plots (Nyquist and Bode) for rectangular 4-electrodes configuration

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Investigating the diffusion of water and ions in organic coatings using coupled ORP-EIS and in situ ATR-FTIR in Kretschmann geometry

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Organic coatings are used for protection of metallic substrates from corrosive environments. One of the main governing protection mechanisms of organic coatings is slowing down the transport of species such as water, oxygen, and ions. Arrival of these species at the buried interface can induce a loss of adhesion and the initiation of corrosion. Understanding the transport mechanism of these penetrants as the major reason of coating failure is of a great importance to design a durable, high-performance coating. Ion and water uptake happen in conjunction, although water uptake precedes the ion uptake.

In this work, the diffusion of water and ions in organic coatings is studied using odd random phase electrochemical impedance (ORP-EIS). Polyethylene glycol diacrylate-based UV-cured coatings are used as a case study. Studying the resistivity distribution over the thickness of the coating through Voigt element modelling [1], two layers are identified with different resistivity distributions. These layers are correlated with the ion diffusion of the coating, as described by the two-layer model identified by Nguyen et al. [2]. In the outer layer, the penetration of ions introduces a decrease in the coating resistivity, whereas in the inner layer the resistivity remains relatively constant, only decreasing slightly due to ingress of water. Using this electrical equivalent circuit to fit the EIS results, the water uptake and penetration depth of the ions can be identified [3].

While the model is identifying the ion diffusion, a complementary technique is needed for a better understanding of the dynamics of the system. Therefore, in a next step, the accuracy of the model is tested using an integrated spectro-electrochemical technique, coupling the ORP-EIS measurements with ATR-FTIR in Kretschmann geometry [4], which is measured simultaneously and covers the same time domain. This combination is used to obtain a better understanding of the water and ion uptake, while providing molecular scale data on local chemistry changes at the coating/metal buried interface. Three different coating thicknesses are considered, from 100 µm to 200 µm. The measurements are performed using an electrolyte containing infrared active ions (SCN^-), which can be detected at the interface when they have penetrated through the coating. Results show that the ions are arriving at the interface at the same time as calculated using the two-layer model, providing a validation for the model accuracy.

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Machine learning to predict electrochemical impedance spectra (EIS): Can EIS be replaced by constant current techniques?

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Electrochemical impedance spectra (EIS) have been widely used to diagnose the battery state of health (SOH), because the battery SOH is influenced by resistance-induced overvoltage (polarizations), i.e., ohmic (R_Ω), activation (charge transfer; R_{ct}), and concentration polarization (mass transport; R_{mt})[1]. However, the implementation of onboard EIS measurement is hindered, due to the high cost of the measurement equipment, test results subject to SOC, and time-demanding measurements. Here, we predicted impedance spectrum by battery charging voltage curve based on electrochemical mechanistic analysis and machine learning.

As reported, both EIS and charging curves can be used to predict battery SOH[2]. This indicates that the DC charging curve can also demonstrate the dynamic behaviors inside a battery (e.g., charge transfer and mass transfer). Besides, in constant current charging process, it has been found that the voltage change in the first few milliseconds corresponds to R_Ω, and the voltage change of first several seconds corresponds to R_{ct}, and the voltage change of first 100 seconds corresponds to R_{ct}[1]. It further confirms that both the EIS and constant current technique can express same electrochemical information.

Battery charging curves as input were used to predict EIS, as shown in **Fig. 1**. The experimental results show that the proper partial voltage range has high accuracy for EIS prediction. The predicted errors for impedance spectrum are less than 1.9 mΩ. This provides a new perspective and means for EIS interpretation.

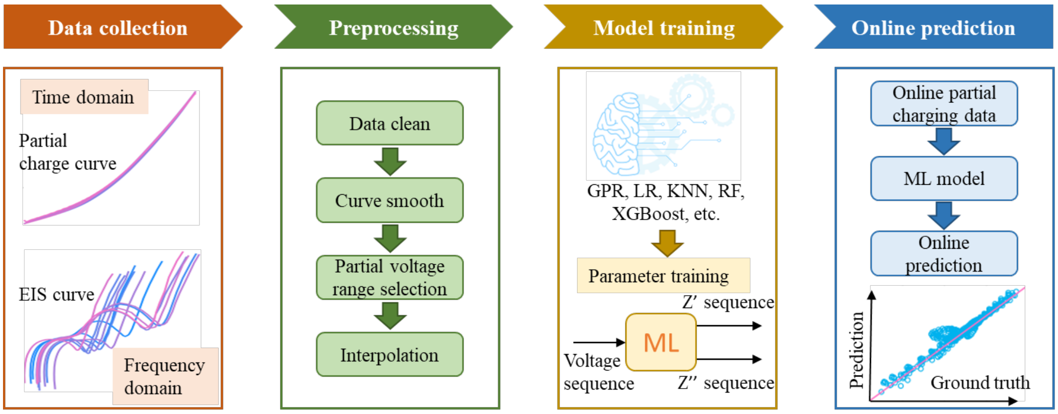

Fig. 1 Charging voltage curve were used to predict electrochemical impedance spectra.

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Investigation of the Unstable Phenomenon of Electrochemical Impedance Spectroscopy Measurements for Pt Electrode in a Rotating Disk Electrode

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Abstract: The instability of Pt electrode during EIS measurement was investigated in RDE. Our results show that this unstable phenomenon is mainly reflected on charge transfer resistance (R_{ct}). The range of R_{ct} change exhibits a strong dependence on the applied potential. During the repeated EIS tests at above 0.8 V, R_{ct} continuously increase as the testing time, while the double-layer capacitance of Pt electrode reduces, implying the formation of Pt-oxides on the electrode interface. Furthermore, the stability becomes worse at higher potential. After repeated experiment for eight times at 0.9 V, R_{ct} increases to 3.5 times higher of the initial value.

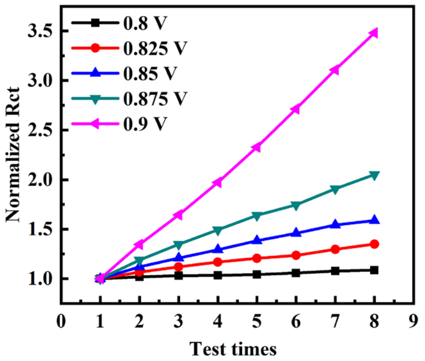

Figure 1. Normalized Rct as a function of test times at different potentials in 0.1M $HClO_4$ on RDE.

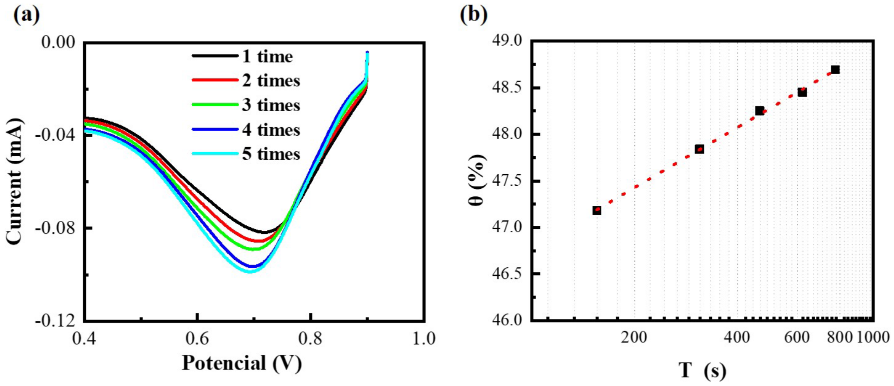

Figure 2. (a) CV curves after EIS experiments and (b) plots of Pt-oxide coverage as a function of time at 0.9 V in 0.1M $HClO_4$ on RDE

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Nanoplasmonic Material Based Photoelectronic Biosensing for Personalized Immune Monitoring

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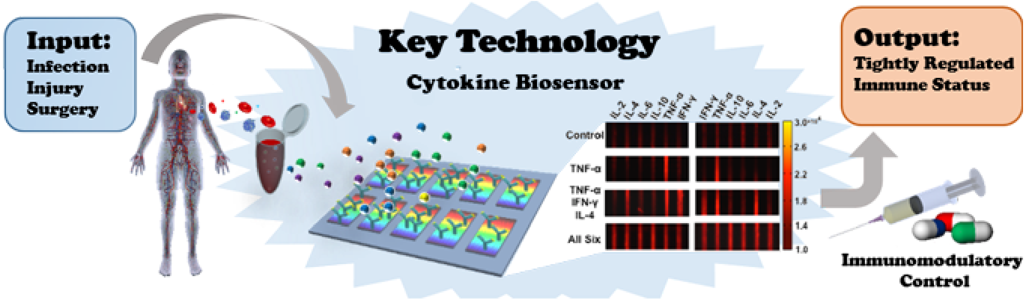

Abstract: The framework of precision medicine envisions a world in which diseases are diagnosed not simply on the basis of a patient’s symptoms but on accumulated data that reveals the fundamental mechanistic bases of human diseases. This raises an emerging demand for transformative tools/biosensors that can measure the biochemical and biological markers to understand the dynamical response of the patient status in a rapid and accurate manner. Cytokines, key biomolecules serving as intercellular mediators, are instrumental in regulating various immune response functions. Rapid and accurate quantification of these immune fingerprints has become crucial for effective treatment of immune-related diseases, especially in point-of-care situations that demand immediate treatment decisions informed by a precise assessment of the patient's immune status. Derived from the emerging clinical demands, we recognize the urgent need for advanced cytokine immunoassays. Such immunoassays necessitate enhanced sensor performance characterized by high sensitivity, throughput, and multiplexing capability, combined with a swift turnaround time and low system complexity. Here, we introduce several novel plasmonic nanomaterial-based optofluidic biosensors integrated with photoelectronic biosensing for comprehensive immune functional analysis, from whole blood down to the single-cell level. The multi-scale research both experimentally and theoretically will bridge the gap in fundamental understanding of immune system and enhance the applicability, diagnosis, and prediction power for immune diseases. The developed platforms would ultimately gear the biologists and clinicians with capability to real-time monitor the immune status of patients, a transformative achievement that has immense potential towards safe, effective, and personalized immune therapy.

Proton conductivity measurement of electrospun nanofiber with self-bonding and pre-conditioning

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Polymer electrolyte fuel cell (PEFC), as an efficient hydrogen energy conversion device, has been developed for decades. Catalyst layer (CL), where the oxygen reduction reaction occurs, predominantly determines the performance of PEFC. Since 1889, the mass activity of catalyst layer has been improved for more than three orders of magnitudes, thanks to the invention of PFSA ionomer and highly dispersed catalyst on nano-sized carbon support. In recent years, introducing order into CL is bringing the CL performance to a higher level. The CLs with state-of-the-art performance feature nanofiber structures. One type of is ionomer nanofibers deposited with Pt/C catalyst on the surface, and another type is composite nanofiber containing ionomer, Pt/C catalyst, and binding polymer. Their superior performance may come from the ordered mass transport network and the size effect of nanofiber conductivity. To further improve the CL performance, the structure-property-performance relationship of ionomer nanofibers or composite nanofibers needs to be clarified.

In this work, we designed a setup to measure the proton conductivity of a single ionomer or composite nanofiber. We developed a self-bonding method to fix the nanofiber on the micro-electrode and a pre-conditioning method to remove the carrier polymer in the nanofibers. Electrochemical impedance spectroscopy (EIS) was used to extract the proton conduction resistance. Four-probe method was adopted to eliminate the electrical contact resistance and interfacial effect. We prepared nanofibers with different size, polymer type, polymer content, and ionomer type by controlling the ink recipe and electrospinning parameters. The measurement results show that the proton conductivity of nanofiber is one order of magnitude higher than bulk properties and increases with decreasing nanofiber radius. This is attributed to the oriented ionic morphology along the nanofiber. The proton conductivity of nanofibers decreases with increasing carrier polymer content and improves after removing carrier polymer by pre-conditioning. These characterization work can provide guidance to the design and optimization of catalyst layer with electrospun ionomer or composite nanofibers.

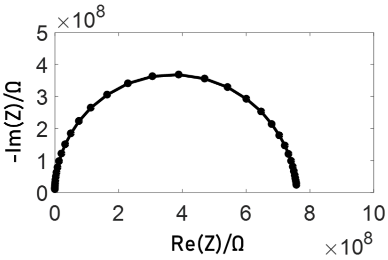

Figure 1. The typical EIS of ionomer nanofiber.

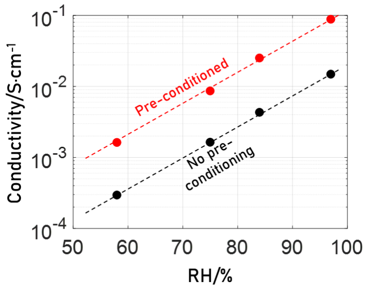

Figure 2. The effect of pre-conditioning on the proton conductivity of ionomer nanofiber.

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Data-driven optimization model customization for atmospheric corrosion on low-alloy steel

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Mathematical models are widely used across various fields [1], including corrosion prediction [2], due to their effectiveness and speed. However, the quality of the data set plays a critical role in determining the performance of the model. Traditional corrosion data collection methods are time-consuming and expensive, and the lack of data continuity further limits the effectiveness of mathematical models for corrosion assessment. Furthermore, the rust layer has a significant impact on the corrosion resistance of structural and weathered steels [3], yet there are only a few studies on the effect of rust layer evolution on corrosion kinetics.

This study utilized a state-of-the-art sensor to gather a big-data set of corrosion on low-alloy steel under six distinct meteorological conditions. Through modeling and calculations, we discovered that the effectiveness of the rust layer is a dynamic process that can be influenced by changes in weather, resulting in unpredictable levels of protection. We determined that prolonged periods of moisture have the most detrimental impact, while higher temperatures have a positive effect. To enhance the accuracy of corrosion assessment, We digitized and incorporated this dynamic process into the model that demonstrates promising results, and emphasized the significance of considering rust layer evolution in corrosion modeling.

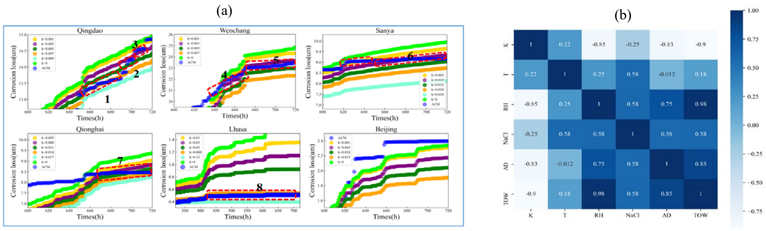

Fig.1 Results of the dynamic evolution of the rust layer calculated by parametric scanning and numerical calculation

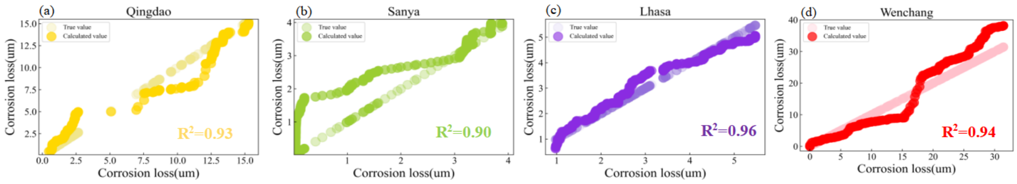

Fig.2 Comparison of predicted and true values after the model incorporates the dynamic effect of the rust layer

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Mahalanobis-Taguchi Method Based Anomaly Detection for Lithium-Ion Battery Module

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In recent years, fire accidents of electronic devices equipped with lithium-ion batteries (LIBs) have become a problem. These fire accidents are sometimes triggered by a single defective battery cell, but it is difficult to completely remove the defective cell by the inspection at the time of manufacturing. This is because some defective cells only have fast degradation speed, so the degree of anomalies is too small to detect immediately after the manufacturing. In order to reduce the risk caused by such gradually increasing anomaly, we have been focusing on anomaly detection technologies for battery chargers and battery management systems (BMSs) because they can continue to watch the change of the battery cells over using time. In this study, we developed an anomaly detection technology using Mahalanobis-Taguchi (MT) method and succeeded in detecting a defective cell in a series battery module with high sensitivity.

Five new LIB cells US18650FTC1 (LFP/Gr, made by Murata Manufacturing Co., Ltd.) were prepared. One cell was stored in the environment of 85 °C for 25 days to make it defective. New cells 1~4 and the defective cell 5 were connected in series and charged by a potentio/galvanostat (BioLogic SP-240). The voltage change of each cell were measured by a data logger (Yokogawa DL950) (Fig. 1a), and from the voltage transition curves of each cell after the charging, impedance parameters R_1, R_2 and R_3, which have the characteristics of the bulk, the charge transfer, and the diffusion resistances, were calculated, respectively. For each cell n, degree of anomalies was calculated using MT method in seven cases, assuming that all the other cells except the cell n are normal: when only R_1 was used, only R_2 was used, only R_3 was used, R_1 and R_2 were used, R_2 and R_3 were used, R_3 and R_1 were used, and all three were used. Based on the dispersion of R_1, R_2 and R_3, the 95% threshold of the degree of anomalies was calculated.

The result of the degree of anomalies is shown in Fig. 1b. The degree of anomalies of the cells 1~4, which are the normal cells, did not show the abnormal value in any case. On the other hand, the degree of anomalies of the cell 5 showed the abnormal value in four cases: when only R_2 was used (▲), R_1 and R_2 were used (○), R_2 and R_3 were used (△), and all three were used (×). Since each case includes R_2, it is considered that the charge transfer resistance especially contributed to the sensitivity in this case.

This anomaly detection method is easy to install into chargers and BMSs. We think that the use of this technology can improve the safety of electronic devices with LIBs.

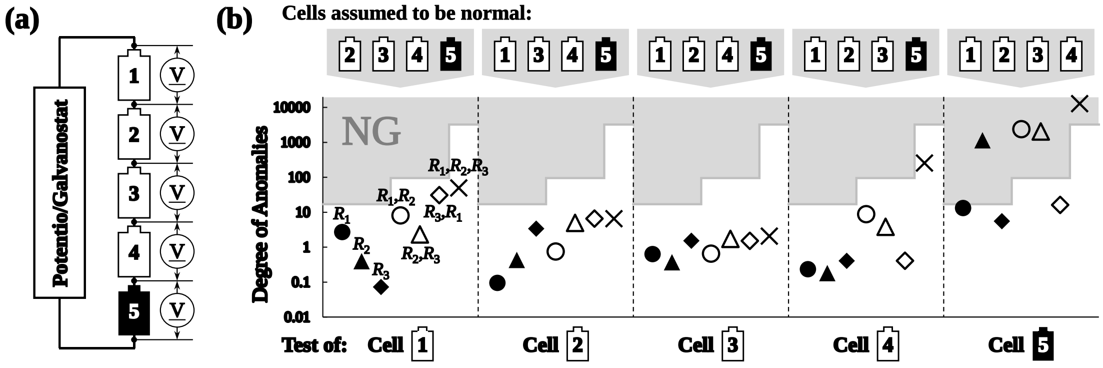

Fig. 1. Schematic diagram of the experiment (a) and the result of the MT method (b).

Acknowledgements:

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A Comparative Study of Frequency Response Analysis Methods for PEM Fuel Cell Diagnostics

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The PEM fuel cell is a promising key player in the transition to a sustainable energy system and economy. The large-scale commercialization of PEM fuel cell calls for fast responsive diagnostic and characterisation tools to assess performance, identify performance-limiting bottlenecks and predict imminent failure during operation. Electrochemical impedance spectroscopy (EIS) applies a harmonic perturbation to one electric signal, voltage or current, while measuring the response of the other. EIS has been widely accepted and applied in the PEM fuel cell community, due to its ability to separate multiple electrochemical processes within the cell. However, EIS comes short when the time constants for different electrochemical processes, e.g. oxygen transport and faradic reaction, are too close to each other.

Apart from the electric variables used in EIS, the oxygen concentration plays a crucial role in ORR. Oxygen concentration can be probed by pressure perturbation, giving rise to the idea of electrochemical pressure impedance spectroscopy (EPIS). Several groups [1-4] have measured EPIS via perturbing the cathode outlet pressure of the PEM fuel cell. Schiffer et al. [5] reported a numerical model for EPIS, with good agreements with experiments lower than 0.4 A/cm^2. However, the pressure variation applied to the cathode outlet propagates into the channel and the connected pipes and the humidifier, which leads to a dependence of the measured transfer relation on these auxiliary devices, introducing complexity to the analysis.

To avoid the effect exerted by the pressure variation, electrochemical concentration impedance spectroscopy (ECIS) has been measured and analysed by Sorrentino et al. [6-8] via applying oxygen concentration oscillations at the inlet. Alternatively, Sun et al. [9] introduced the electrochemical concentration admittance spectroscopy (ECAS) as depicted in Fig. 1, which perturbs the voltage and measures the oxygen concentration variation at the cathode outlet, and thus can be measured simultaneously with EIS. Here, we present a comparative study of EPIS, ECIS and ECAS via a physical model-based analysis. The parameter sensitivities of these methods will be compared. The potential usage and limitations of EPIS, ECIS and ECAS will be discussed.

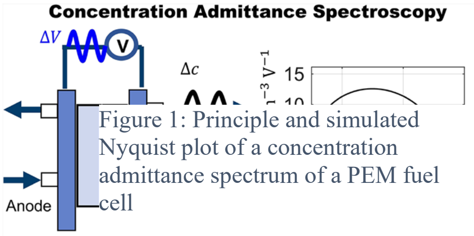

Figure 1: Principle and simulated Nyquist plot of a concentration admittance spectrum of a PEM fuel cell

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The Relationship between Microstructure and Electrochemical Impedance of Ag/AgCl Electrode for Chloride Detection

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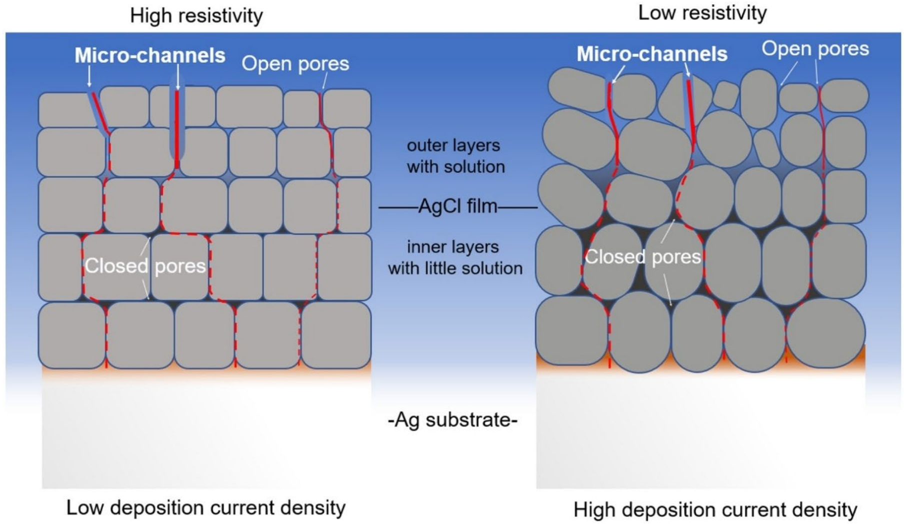
The electrochemical behaviour of Ag/AgCl electrode for chloride detection is closely related to the microstructure of AgCl film on the electrode surface. In this study, the surface properties and electrochemical behaviour of Ag/AgCl electrode prepared with different current density were investigated. With a higher current density, the distance for ions diffusion through the boundaries of AgCl grains was reduced, due to the relaxation oscillation and formation of more spherical AgCl grains and porous AgCl film. As a result, both the electrical resistivity of AgCl film and R_{ct} of Ag/AgCl electrode decreased.



Graphical abstract

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Impact of cavitation erosion intensity on the electrochemical impedance spectroscopy of 7050AA aluminium alloy in NaCl solution

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Aluminium alloy is a preferred material for ship propellers due to its high specific strength. In this work, we studied the impact of cavitation erosion intensity on the electrochemical impedance spectroscopy of 7050AA aluminium alloy in NaCl solution. The EIS consists of high frequency loop, mid frequency loop and low frequency inductance loop. The two capacitance loops are analysed with the measurement model. For the cavitation time of 0.5 ~ 4h, in function of the immersion time we have $Z(t) = k(t)*Z_N$, with the immersion time, only the active area is changing. The possible reaction mechanism on aluminium alloy is discussed by the process model.

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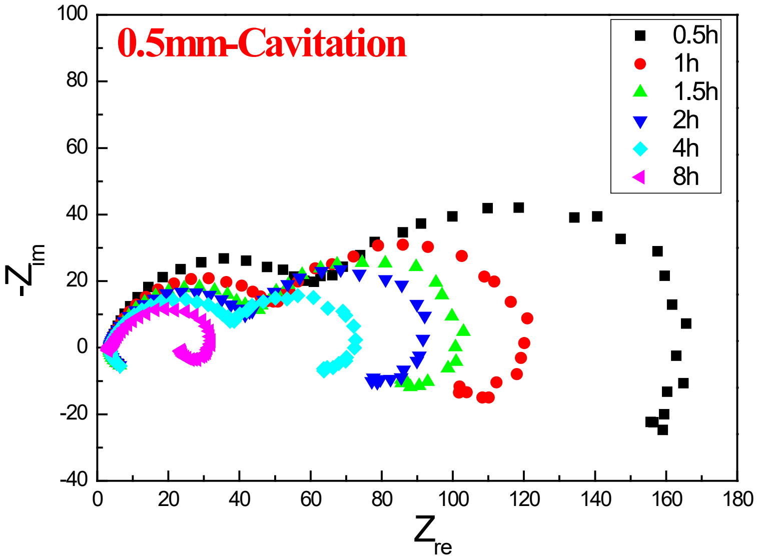

Fig. 1 EIS of 7075AA during cavitation erosion process (the distance between the ultrasonic horn tip and the aluminium alloy is 0.5mm)

Electrochemical measurements in small droplet of electrolyte: example of the use of ionic liquids

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Reducing the surface area of working electrodes for microelectrochemical measurements is crucial for microanalysis and to better understand the role of interface texture on electrochemical response, allowing rapid screening of materials of different compositions. We recently shown that this technique can be used for performing local impedance spectroscopy measurements[1] as well as being advantageously combined with the wettability characterization of the interface.[2] When the solvent used is an aqueous solvent, we are limited for the duration of the experiment, by the progressive evaporation of the drop. An interesting approach consists in using ionic liquids, in order to get rid of this problem. These solvents which are nowadays widely used for electrochemistry applications can in particular be used in corrosion science as inhibitors.

In this presentation, we will show how to carry out local surface modifications by working in a droplet of ionic liquid in order to study the corrosion inhibition of a metal by different electrochemical techniques, especially electrochemical impedance spectroscopy, and then to characterize the protective film and/or the corrosion products by several surface analysis techniques (SEM, XPS, Raman spectroscopy). In the end, working in a small volume drop (0.4 µL and less) will allow to multiply the number of experiments on a large dimension electrode in order to have also a statistical approach of the metal reactivity according to its texture. In a second step, the local reactivity of the protected material with respect to an aggressive environment such as chloride-containing solutions will be investigated by EIS coupled to contact angle measurements.

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Operando EIS and its application to Li-ion batteries

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Electrochemical impedance spectroscopy (EIS) is a powerful non-invasive tool for characterising electrochemical systems. However, EIS is limited by the constraints of linearity and stationarity, while many electrochemical systems inherently behave in a nonlinear and nonstationary way. Regarding linearity, the voltage over the electrodes is a nonlinear function of the current through the electrodes. Linearity is achieved by applying a small amplitude zero-mean current excitation around an operating point, such that the nonlinear function is quasi linear in this range. It is also clear that the impedance of electrochemical systems is time-varying. Take for instance Li-ion batteries: the impedances of fully charged and fully discharged cells are different, the same for pristine and aged cells, or cells kept at room temperature and in freezing environments. Accordingly, the impedance of electrochemical systems can only be measured at operating points (fixed temperature and SoC in the case of Li-ion batteries), which is limiting. How can we measure a battery’s impedance while it is charging or discharging (and hence the SoC is changing during the measurement)? Or how can we measure the impedance of an electrochemical system while the temperature is changing?

To overcome the aforementioned limitations, we have developed operando EIS. This technique reveals information on the impedance from measurements not satisfying linearity and stationarity [1,2]. It allows to measure the impedance of electrochemical systems along a time-varying trajectory, for instance, while charging or discharging Li-ion batteries [3,4]. For this purpose, a nonzero-mean odd random phase multisine current excitation is used, and the time-varying impedance along the trajectory is estimated from the spectrum of the voltage response. This estimation is done in the setting of the best linear time-varying approximation (BLTVA) [1], allowing the data to be nonlinear. Moreover, nonlinear distortions in the measurements are detected and quantified, the noise level is estimated, uncertainty bounds are enclosed on the time-varying impedance, and low frequencies can be attained using a numerical drift signal removal technique [2].

In this research, the operando EIS technique is detailed and applied to monitor the impedance of commercial LG M50 Li-ion batteries while charging and discharging. Moreover, we demonstrate that the battery’s impedance while charging, discharging, and resting are different from each other [3].

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Acrylate-based self-healing elastomer coating enhanced by photothermal MXene composites with anti-corrosion property

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Background: The self-healing phenomenon is a widely existing biological mechanism in nature. Applying this feature to artificial materials can effectively improve some properties of the materials. Anti-corrosion coatings with self-healing properties have better practicality and longer service life than traditional ones, which is significant for metal corrosion protection. Self-healing coatings are divided into two categories: intrinsic self-healing coatings based on physical or chemical interactions, including non-covalent interactions such as van der Waals forces [1], and extrinsic self-healing coatings. The efficiency of energy dissipation and reorganization in the actual self-healing process of the coating decreases with increasing times of repairs. Various studies have shown that providing a photothermal effect is a feasible method to improve the stability of cyclic self-healing. **Methods**: We introduced MXene composite $Ti_3C_2@Cu_2O$ as a photothermal filler to achieve the photothermal effect through non-radiative relaxation of electron-hole pairs, by which the stable cyclic self-healing performance was achieved. Benzyl methacrylate (BMA) and butyl acrylate (BA) were selected to introduce a non-covalent interaction (van der Waals force) provided by ester and alkyl chains as the driving force for self-healing, and the copolymer material PBMA-BA was obtained by 365 nm UV-initiated radical polymerization. The impedance modulus of the coating before and after the damage was tested by electrochemical impedance spectroscopy (EIS). **Results**: We performed tensile tests on the elastomers, of which Young's modulus is up to 48 MPa, indicating impressive strength and toughness. The photothermal filler can rise to 90°C under 808 NIR light irradiation, which can greatly promote molecular chain movement in the coating. Impedance tests showed that the low-frequency impedance modulus ($|Z|_{0.01\ \mathrm{Hz}}$) of the coating before and after the scratch was above $10^7\ \Omega\ \mathrm{cm}^2$, proving that the coating has excellent self-healing corrosion protection properties. **Conclusion**: The acrylate-based elastomer coating we synthesized with excellent anti-corrosion properties and efficient self-healing properties by introducing non-covalent interactions, providing an idea for the design of photothermal self-healing elastomer coating materials.

Keywords: Self-healing elastomer coating; Corrosion protection; Photothermal effect; Acrylate-based copolymer; Electrochemical impedance Spectroscopy

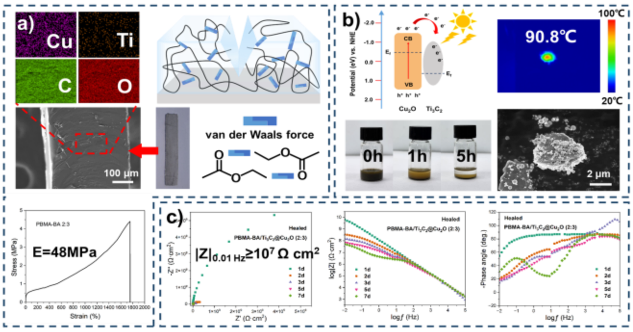

Fig. a) SEM images, self-healing mechanism, and stress-strain curve of PBMA-BA elastomer; b) photothermal mechanism, maximum temperature, stability in elastomer solution, and SEM image of the filler; c) EIS plots of the healed coating system after being damaged at the initial immersion stage.

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The Measurement Model Regression Program

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Interpretation of impedance spectra requires in principle an evaluation of the error structure and a process model that accounts for the proposed reactions and physics. The measurement model was developed in our group in the 1990s as a tool to extract the stochastic part of the impedance measurement from repeated measurements and to assess the consistency of the measured impedance with the Kramers-Kronig relations.[1-3] Our measurement model approach has been difficult to explain, in no small part because our original measurement model program, written in a combination of FORTAN and Matlab® programming languages, was not generally available. We were reluctant to share the code because each new version of Matlab® broke the Matlab® part of the program, and a part of the FORTRAN code was not ours to share.

A new version of the measurement model has been written in the Python language and is available under the open-source license GNU GPL Version 3, which allows free use for scientific purposes but limits commercial use.[4] The new code was written from the ground up in Python, although some portions of the backend libraries, such as numpy, use C. Unlike many Python-based impedance regression programs, the measurement model program provides a graphical-user-interface that facilitates navigation through the different stages of the measurement model analysis. This program also allows regression of arbitrary functions to impedance data. Rather than employ electrical circuit components such as resistors and capacitors, this part of the program is equation-based. The formula is input as Python code and may make use of imported Python packages. The equation-based approach enables regression of a broad range of models.

The objective of this tutorial is to introduce the measurement model program and suggest ways in which it can be employed for interpretation of impedance spectroscopy data. Our goal is that, by providing the tools needed for a more sophisticated analysis of impedance data, we will allow students to take full advantage of the information that can be extracted from electrochemical impedance spectroscopy measurements.

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Determination of dielectric properties of mimicking biological tissues by electrochemical impedance spectroscopy

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Tissue-mimicking materials are widely developed and used as substitutes in many medical branches, including surgical procedures, medical imaging, machine calibration, training, and simulations. Usually, these materials are fabricated either by chemical synthesis or additive manufacturing (3D printing), to mimic the mechanical, optical or, as in the present work, electrical properties of the targeted tissues.

The aim of this work is to fabricate a biomaterial that mimics, as closely as possible, the dielectric properties of bone in the context of spinal surgery, where low-frequency electrical stimulation is performed to verify the correct placement of titanium pedicle screws around the nerve structure [1].

To obtain a tissue mimicking the bone of the spine, different mixtures of hydrogels containing chitosan and hydroxyapatite (HAp) were prepared by varying the concentrations and/or the pH of the hydrogels. Electrochemical impedance spectroscopy measurements have been performed within these hydrogels to determine their electrical properties from 1 Hz to 1 MHz. An example of result is shown in Fig.1, where both the conductivity and the relative permittivity of four hydrogels are compared to those of cancellous bone [2].

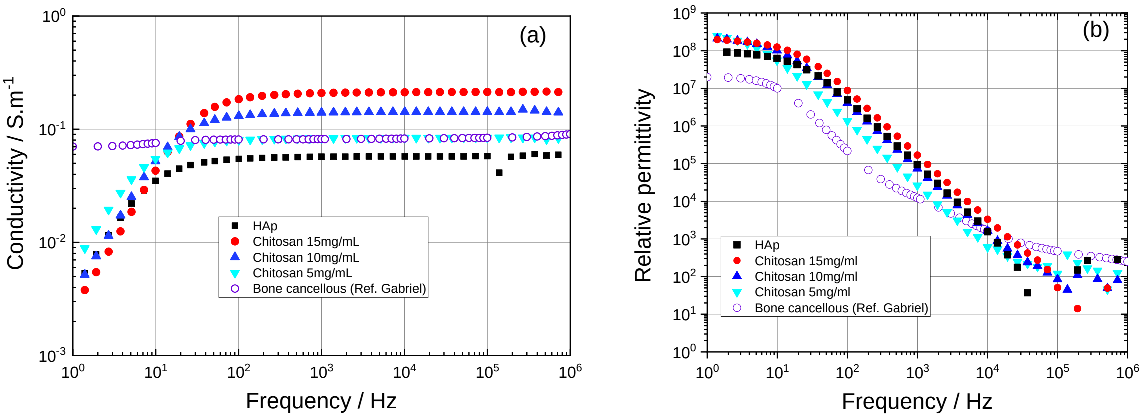

Fig. 1: Electrical properties of different mimicking biological tissues compared to that of bone cancellous measured by Gabriel et al. (a) conductivity and (b) relative permittivity

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Frequency response of Gibbs free energy and enthalpy changes of electrochemical systems analyzed as thermometric transfer functions.

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Poster

When a charge transfer reaction occurs in the electrode interphase, heat is generated as a byproduct. This heat is the sum of reversible effects as the electrochemical molar Peltier heat, Π, and irreversible effects like overpotential and the Joule effect. These effects have been calculated by measuring temperature changes, ΔT^*, in the electrode/electrolyte interface using either calorimetric or electrochemical techniques involving direct current [1].

Recently, Sánchez-Amaya et al. [2] adapted the thermometric methods to census the modulated variation of interfacial temperature, $VIT(\omega)$, when a sinusoidal current, in a range of frequencies ω, flows at the interphase. $VIT(\omega)$ measurement can be seen as a transfer function defined as $\Delta T^*(\omega)/\Delta E(\omega)$, where $\Delta E(\omega)$ is a sinusoidal polarization perturbation. Besides, the authors found a correlation between Electrochemical Impedance Spectroscopy, $EIS(\omega)$, and $VIT(\omega)$ which allowed calculate $\Pi(\omega)$ and entropy changes, $\Delta S(\omega)$, as thermometric transfer functions.

This work resumes the Sánchez-Amaya proposal and presents a theoretical-experimental strategy to calculate for the first time two new thermometric transfer functions: Gibbs free energy, $\Delta G(\omega)$, and enthalpy changes, $\Delta H(\omega)$ using previously reported transfer function: $VIT(\omega)$, $\Pi(\omega)$ and $\Delta S(\omega)$. As results, Nyquist diagrams of $\Delta G(\omega)$ and $\Delta H(\omega)$ (Figure 1) are computed with earlier experimental data of ferrocyanide/ferricyanide electrochemical system [2] and a brief interpretation is given.

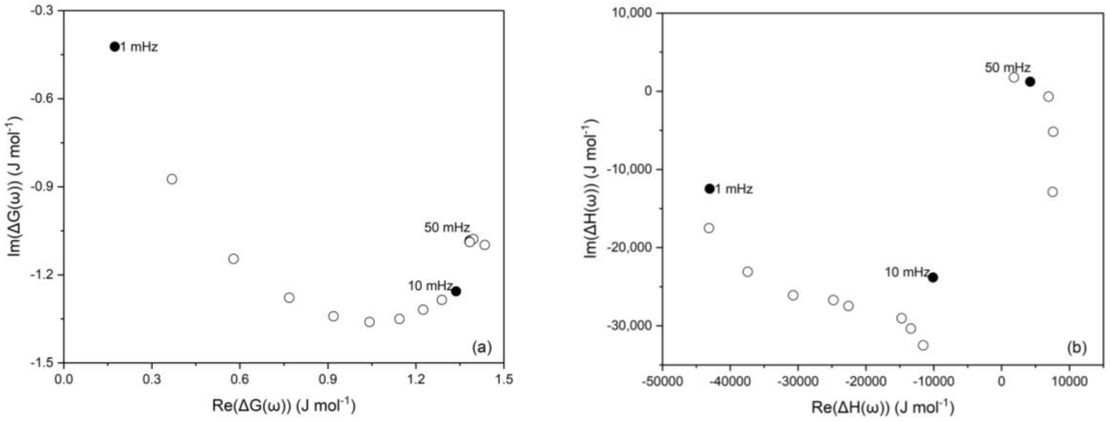

Fig. 1 Nyquist diagrams of 0.1 M $Fe(CN)_6^{3-}$/ 0.1 M $Fe(CN)_6^{4-}$ system. (a) $\Delta G(\omega)$, (b) $\Delta H(\omega)$.

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Uncertainty estimation on bioimpedance measurements

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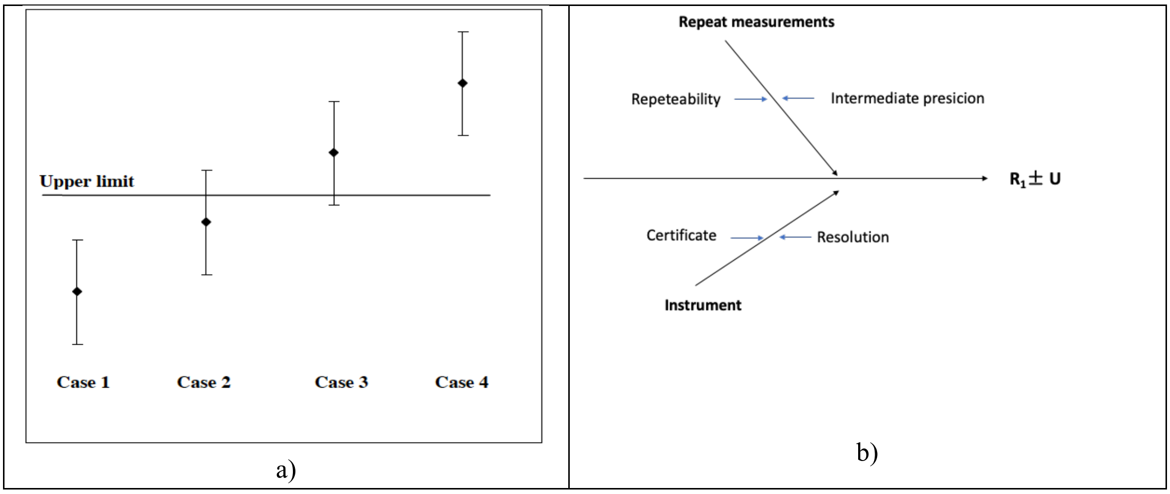
Uncertainty (U) estimation of any measurement is important because offer an idea about accuracy measurement results. There are few international guides about the topic [1], and even, national standards in some countries, like in México [2]. For some measurements, like water and health, to report U of the measurements is very common, however, in some other fields, like in electrochemistry, it is rarely reported.

Regarding impedance technique, its use is wide, from corrosion to bioimpedance measurements. Independently of the procedure, resistance, capacitance and inductance values can be obtained from the spectra, and decisions are taken considering this values. In figure 1a, it is possible to see the importance of the uncertainty value that is pair with a reference value (mean ± U), which can be obtained from the spectra. This value can help us to decide to accept or to reject results and make decisions.

To estimate U, an Ishikawa diagram is usually used, which considerate the mainly sources of uncertainty. In figure 1b, it is possible to see an exercise of uncertainty estimation in bioimpedance measurements, when a resistance is calculated. Only two uncertainty sources are shown, considering that a protocol has been followed and several conditions have been controlled.



a)

b)

Figure 1.- Importance of uncertainty results a), and uncertainty sources in bioimpedance measurements b).

Information shown in figure 1 is discussed with the intention that electrochemical researchers think about uncertainty of their measurements, mainly when bioimpedance or impedance is used, and metrology impact be taking into account in this field.

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Classification of the Galvanlic Corrosion States for Multi-Metals Jointed Pipelines Based on Adaboost Algorithm

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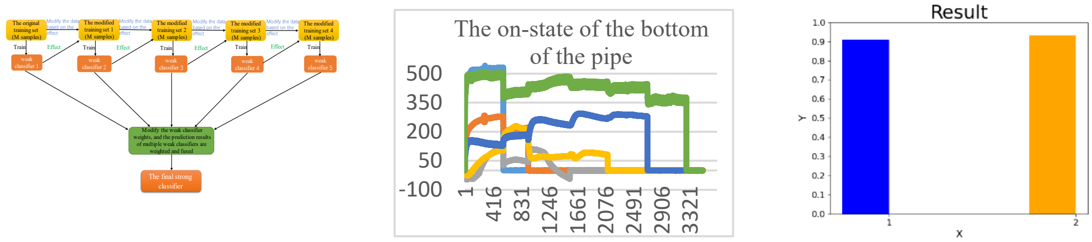
The interconnection of various metal pipes in the marine piping system of ships leads to galvanic corrosion, and makes the corrosion condition difficult to be monitored. This paper aimed to simulate a marine piping system with multi-metals jointed parts together, to monitor the potential difference, and to establish a mathematical model using machine learning methods to detect galvanic corrosion failures in seawater pipes. Therefore, the Adaboost machine learning algorithm was chosen to complete the fault detection task. This algorithm has advantages such as high accuracy, fast computation, and no overfitting issues, predicting its suitability for this type of fault detection.

Firstly, a simulated experiment was conducted on a marine piping system to measure the potentials at six differently coupled points. Secondly, artificial faults were introduced by simulating pipe circulation blockage and insulation failure in dissimilar metal pipes. Thus, two sets of different fault conditions can be simulated. Finally, a subset of actual measured potential data was selected as a test dataset to evaluate the accuracy of the model. The model's output regarding the fault types was compared to the actual fault types, and the accuracy was calculated. It was indicated that the model achieved an above 0.9 classification accuracy. This model could be used to classify the fault detection.



(a) (b) (c)

Fig.1 (a) The flowchart of the Adaboost algorithm (b) The potential difference data of six measurement points under the pipe's bottom conducting state (c) Illustration of test set results

Table.1 Classification results of a subset of test data for fault detection

potential difference 1	Potential difference 2	Potential difference 3	Potential difference 4	Potential difference 5	Potential difference 6	Actual values	Predicted values
497	218	-41	-19	154	495	1	1
520	250	-32	20	151	499	1	1
532	279	122	103	135	488	1	1
0	0	-28	72	236	484	1	1
378	320	137	-85	390	344	2	2
384	265	152	-80	414	352	2	2
0	300	195	-12	374	501	2	2
0	0	192	25	414	412	2	2

An electrochemical sensor based on Au@Ag NPs/MnO_2 NFs for H_2O_2 detection

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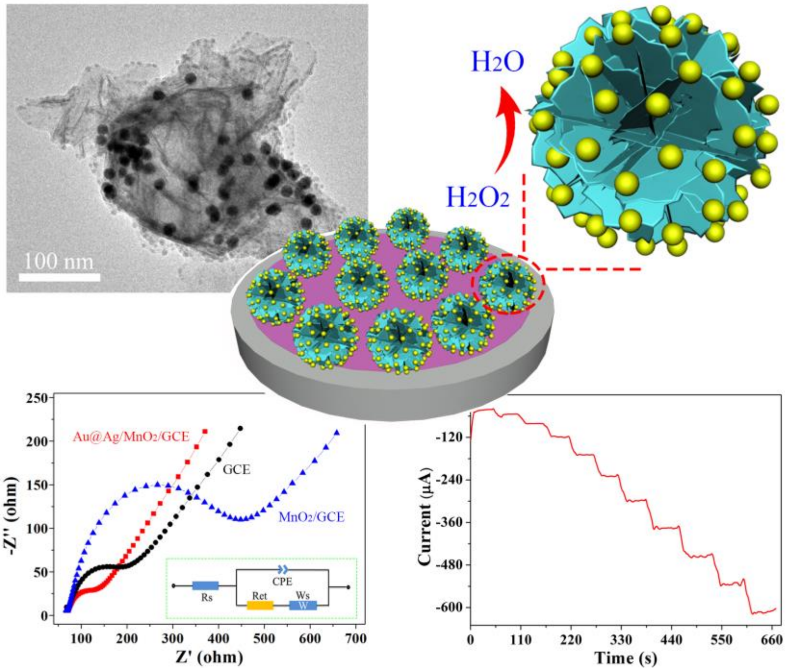
Hydrogen peroxide (H_2O_2) is a significant byproduct of enzymatic reactions in human blood, which potentially causes cardiovascular, cancer, and Alzheimer. Designing a sensitive H_2O_2 sensor is required for our health. We prepared gold and silver core-shell nanoparticles loaded on manganese dioxide nano-flowers (Au@Ag NPs/MnO_2 NFs), and used them to fabricate an electrochemical sensor for H_2O_2 detection. Due to valence catalysis of manganese and the vacant d orbitals of noble metal, Au@Ag NPs and MnO_2 NFs possess good catalytic activity for H_2O_2. Additionally, MnO_2 NFs can hinder the agglomeration of Au@Ag NPs, and Au@Ag NPs enhance the conductivity of MnO_2 NFs. Based on the above advantages, Au@Ag NPs/MnO_2 NFs show excellent catalytic activity for H_2O_2. And the catalytic activity was researched by colour reaction of tetramethylbenzidine. Under optimal conditions, the developed electrochemical sensor has a good linear relationship between 1 and 10 mM for H_2O_2. It has acceptable selectivity and stability and is expected to be used in practical detection.



Schematic diagram, The TEM of Au@Ag NPs/MnO_2 NFs, The EIS, The i-t of the sensor.

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Analysis of electrochemical impedance spectrum response characteristics of SOFC at low current density

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Solid oxide fuel cell (SOFC) has the highest theoretical energy density among several fuel cells and is considered to be widely used in distributed power stations. However, due to the high thermal stress and the agglomeration of nickel and carbon deposition of anode catalyst caused by hydrocarbon fuel, its operating life is one of the biggest issues to promote widespread diffusion of SOFC [1]. As a method to diagnose the degradation mechanism of SOFC, electrochemical impedance spectroscopy (EIS) has been widely used [2]. However, in the past EIS studies at open-circuit voltage (OCV) and low current density, impedance analysis is not clear. Impedance in the frequency range of 0.1 Hz to 10 Hz was regarded as gas transmission impedance in some research work, and the gas transport impedance accounts for the largest proportion in OCV and low current density [3][4]. Based on the EIS test, this paper analyzes the physical process of SOFC in the electrode at OCV and low current density to obtain the characteristic frequencies corresponding to various impedance components, and then discusses the changes of gas adsorption/desorption impedance, charge transfer impedance and gas transfer impedance.

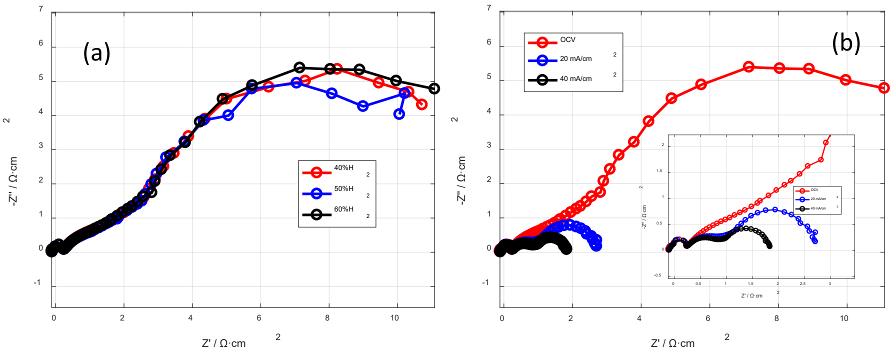

Figure 1 Electrochemical impedance spectroscopy of SOFC at 750 °C: (a).Different hydrogen concentration (40%,50%,60%); (b). Different load current (OCV,20 mA/cm^2, 40 mA/cm^2)

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An electrochemical sensor for trypsinogen 2 detection

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Acute pancreatitis has been reported to be associated with overexpression of trypsinogen 2 caused by gene mutations. Based on earlier studies, a rapid detection method of Trypsinogen 2 in the early diagnosis of acute pancreatitis was established. After a series of modifications on bare electrodes, electrochemical impedance spectroscopy was measured to analyse the modification effect. Electron transfer resistance on the electrode surface varies greatly due to layer-by-layer modification on the screen-printed carbon electrodes (SPCE). After depositing gold nanoparticles on bare working electrode (WE) of SPCE, the electron transfer resistance (R_{et}) decreases. As predicted, the R_{et} increases with each modification step, indicating the successful modification of each reaction on the WE. This strategy may be continuously developed into a novel, rapid, and non-invasive detection method.

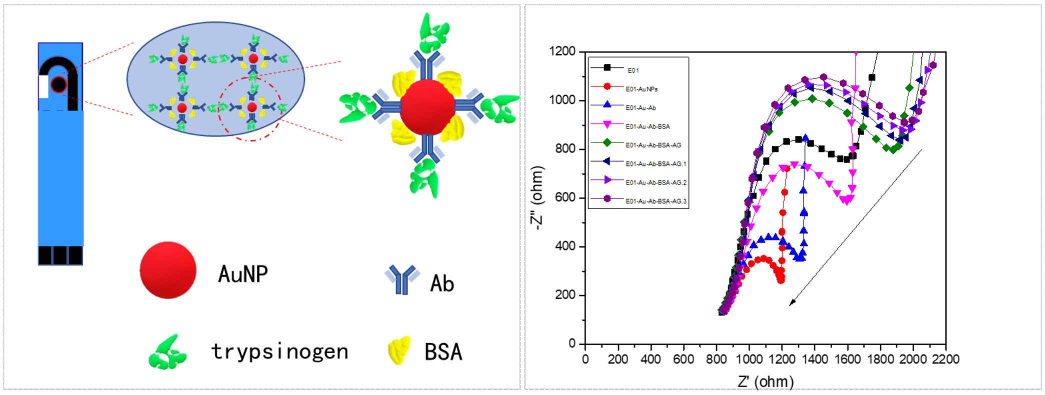

Figure 1. Scheme of preparation of protein detection sensor and electrochemical impedance response after modification of each layer. Bovine serum albumin (BSA) blocked the blank sites on the surface of gold nanoparticles to prevent nonspecific adsorption.

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Metallic Corrosion

The effect of Cl^- and applied potential for corrosion resistance on CrMnFeCoNi high entropy alloys by electrochemical measurements in sulfuric acid solutions

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High entropy alloys (HEAs) are consisted of five or more elements in equimolar or near-equimolar ratios. The HEAs exhibit a simple solid–solution structure, and promise properties such as high strength and ductility, improved fatigue resistance, fracture toughness, and thermal stability. In this work, we focused on the Cantor alloy, which is a five component, equimolar CrMnFeCoNi alloy. Considerable research has already been devoted to the study corrosion resistance of alloys in sulfuric acid[1] or in NaCl solutions[2]. Indeed, study of the corrosion resistance of alloys in mixture of sulfuric acid and chloride ions solutions is really interesting as previously discussed in the literature[3], and also, it's necessary for application of high entropy alloys.

In this work, we studied corrosion resistance of Cantor alloy in 0.5 M H_2SO_4 with different Cl^- concentrations by electrochemical impedance spectroscopy (EIS) (Fig.1), potentiodynamic polarization and potentiostatic polarization. A specific attention has been paid to characterize the passive film properties as a function of the chloride concentration and potential. In addition, we also investigated the reaction mechanism at different applied potentials on Cantor alloy in 0.5 M H_2SO_4 with and without Cl^- ions in solution.

From the analysis of EIS results, we can determine the static capacitance, which are nearly constant with Cl^- concentrations (except 10 and 50 mM). From polarization curve, we observed that the current density sharply increases when Cl^- concentration is higher than 250 mM. The result can be compared to the work of Lee et al.[3] Additionally, we can envision a reaction mechanism accounting for the different shapes of the EIS responses measured at different applied potentials.

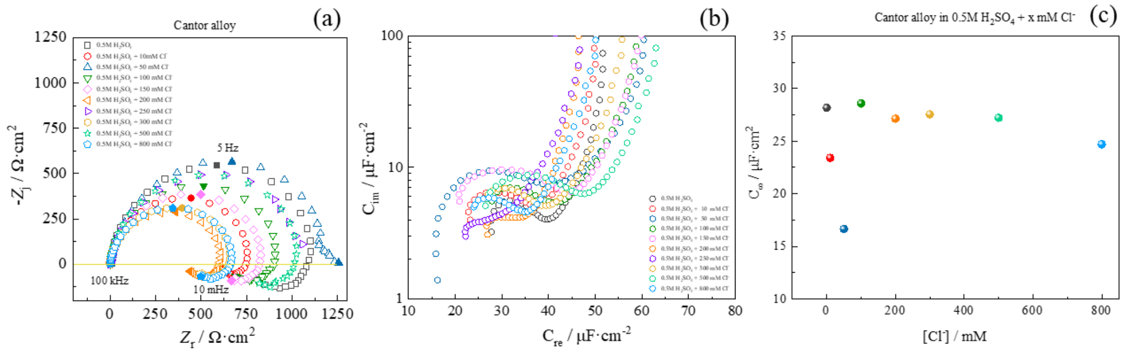

Fig. 1. (a): Nyquist plot of Cantor alloy in 0.5 M H_2SO_4 with different Cl^- concentrations,
(b): cole-cole representation of the complex capacitance,
(b): Variation of the infinite capacitance calculated from (b) as a function of Cl^- concentration.

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Study on the metal/salt hydrate interfaces under solid-liquid transitions of phase change material based on EIS and EN methods

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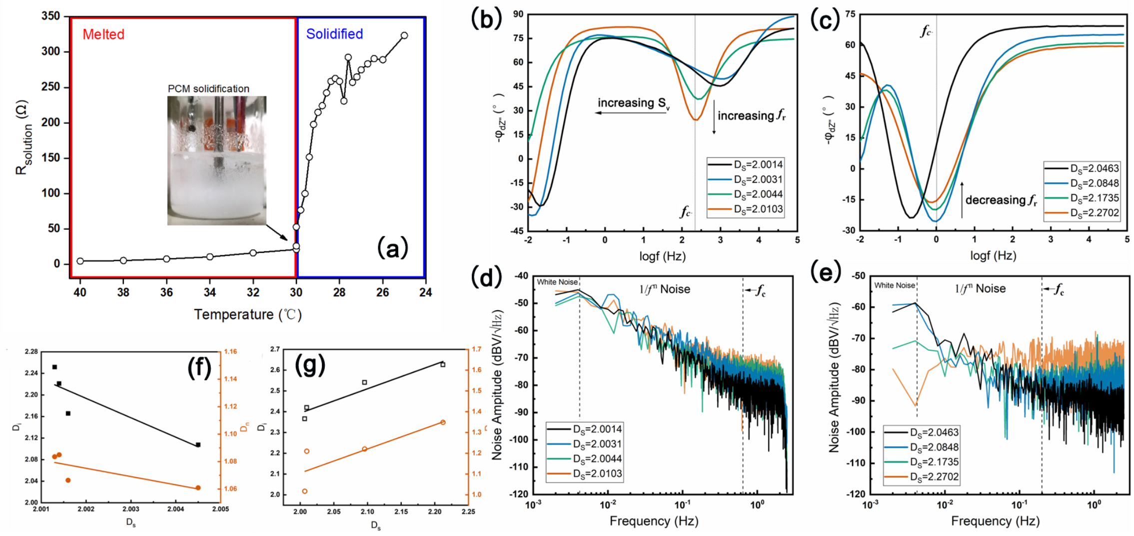
Abstract: The corrosion of salt hydrate phase change material (PCM) on the capsuled metal containers has become a main threat in long-term usages. Traditional corrosion investigate methods, such as weight loss and morphology analysis cannot provide detailed information on the pitting process of corroded surface. Moreover, the electrochemical methods applied on the PCM electrolyte/electrode interfaces were limited due to the nucleation of molten phase change materials triggered by electric field between the electrodes. In this work, the in-situ electrochemical impedance spectroscopy (EIS) and electrochemical noise (EN) method were applied on the corrosion behavior study of aluminium alloys in solid/molten state $Na_2HPO_4{\cdot}12H_2O$ PCMs. Discussions had been focused on electrochemical characteristics on the metal/salt hydrate interfaces during phase transitions of the electrolyte. Meanwhile, the numerical relationship between EIS and EN results was discussed based on fractal dimensions, which further drew connections to the fractal geometry of the corroded surface

The EIS spectra in Fig. b and c showed that the influence of pitting on the metal/electrolyte interfaces were different in solid and molten state PCMs. The time constant dispersion occurred at the oxide film in solid state PCM and at the electrode surface in molten state PCM. When immersion time elapsed, the breakdown of the passivation state resulted in the transformation of CPE behavior from middle frequency to low frequency domain. Also, the results of the ohmic resistance (R_s) measurements (Fig. a) indicated that in the early stage of PCM corrosion, the huge R_s difference between solid and molten state PCM also contributed to the diversity of the EIS spectra. EN results (Fig. d and e) showed that there was a typical pitting noise signal in solid state PCM during the 240hrs immersion, while in molten state PCM, the noise signal showed a transition from pitting corrosion to uniform corrosion after 96hrs. The breakdown-repassivation process was found in the potential noise of solid state PCM but vanished in molten state PCM due to the serious corrosion in melted alkaline media. Meanwhile, the fractal dimension of EIS and EIS methods in Fig. f and g had shown a good linear relationship, which meant the two methods had commonality in the characterization of pitting behaviors.



(a) Ohmic resistance (R_s) of the PCM electrolytes; (b) and (c) EIS results; (d) and (e) EN results; (f) and (g) Fractal dimensions based on EIS and EN methods

Effect of barnacle adhesion on the corrosion and hydrogen permeation behavior of high-strength steel in marine environment

藤壶附着对海洋环境高强度钢腐蚀行为和氢渗透行为的影响规律

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Barnacle (model organism of macrofouling [1]) adhesion can change the corrosion behavior and hydrogen permeation behavior of high-strength steel in service in marine environment. In this study, a field exposure experiment was set up in Jiaozhou Bay, Qingdao. The effect of barnacle adhesion on the corrosion behavior of steel was analyzed by electrochemical impedance spectroscopy (EIS) measurement, and the effect of barnacle adhesion on the cathodic protection of steel was analyzed by constant potential/constant current polarization measurement. The hydrogen permeation behavior of steel was monitored by electrochemical method, and the hydrogen permeation sensor was fabricated.

EIS results of steel indicated that the steel with barnacle adhesion had higher corrosion products layer resistance (Rr) and charge transfer resistance (Rct), i.e., barnacle adhesion can slow down the corrosion rate of steel. The monitoring results of the hydrogen permeation current density of high-strength steel under nature corrosion state indicated that barnacle adhesion can reduce the hydrogen permeation current density by slowing down the hydrolysis rate of corrosion products (Fig. 1).

The results of constant potential/constant current polarization measurements indicated that barnacle adhesion can make the cathodic protection current density of high-strength steel decrease, cathodic protection potential negative shift. However, macrofouling adhesion can promote the formation of localized corrosion, and barnacle metabolites can also promote hydrogen penetration, accordingly, barnacle adhesion increased the hydrogen permeation current density on the steel surface (Fig. 1).

Owing to the corrosion of high-strength steel, it is mostly under cathodic protection state in actual engineering. Meanwhile, barnacle can promote the corrosion and hydrogen permeation process of steel under cathodic protection state. Accordingly, barnacle adhesion is potentially dangerous to the service safety of steel structures in marine environment.

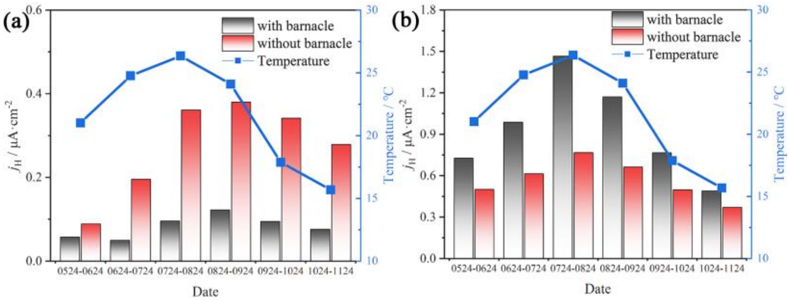

Fig.1 Variation of average hydrogen permeation current density of steel with time during 6 months of field exposure experiment, (a): nature corrosion state; (b) cathodic protection state

Acknowledgements

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Effects of dissolved oxygen and hydrostatic pressure on the corrosion behavior of mooring chain steel in simulated deep-sea environments

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With the consumption of oil and natural gas resources on land, the exploitation of Marine resources is increasing. In Chain, 23% of oil resources and 30% of natural gas resources are in the ocean, and up to 70% of oil and gas resources are in the deep sea. At present, offshore engineering has tended to mature, and deep-sea engineering is in the initial stage. There is small amount of information on the properties deterioration of marine engineering materials in complex deep-sea environments, such as high hydrostatic pressure and low dissolved oxygen, which is very unfavorable to the safety and development of deep-sea engineering.

In this paper, effects of dissolved oxygen and hydrostatic pressure on the corrosion form of mooring chain steel in simulated deep-sea environments were investigated. To elucidate the corrosion evolution process and mechanical properties deterioration of mooring chain steel in simulated deep-sea environments, potentiodynamic polarization tests, CLSM and SEM analysis of corrosion morphology, SSRT after immersion were conducted.

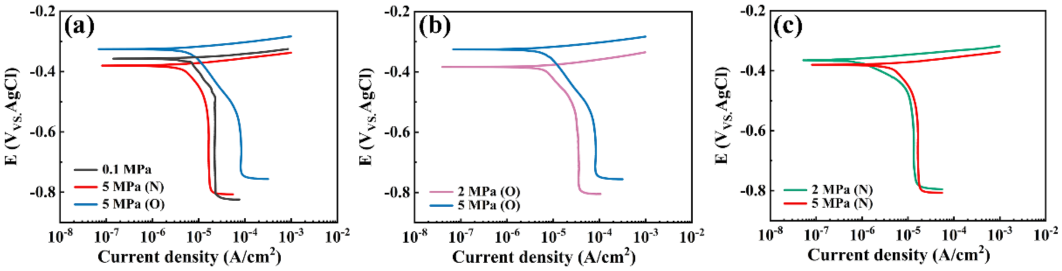

Fig.1 Potentiodynamic polarization curves of mooring chain steel under different dissolved oxygen content and hydrostatic pressure (a) different oxygen content, (b) different hydrostatic pressure with enough oxygen, (c) different hydrostatic pressure with limited oxygen.

According to potentiodynamic polarization (Fig.1), the dissolved oxygen content is a major factor affecting the corrosion behavior of mooring chain steel. The hydrostatic pressure also affects the corrosion behavior of mooring chain steel, accelerating corrosion process.

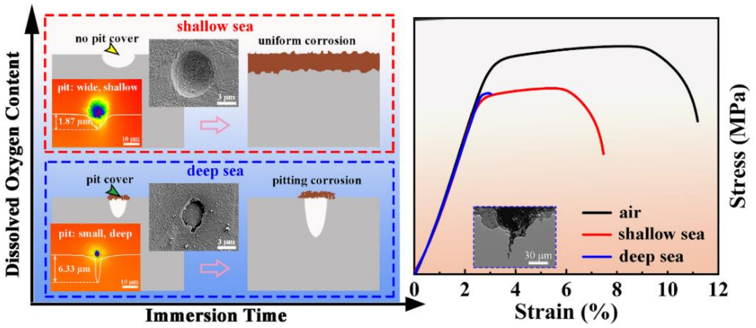

Fig.2 The corrosion evolution process of mooring chain steel in shallow sea and deep sea environments and stress-strain curves after immersion for 200 days in both environments.

Compared with uniform corrosion of mooring chain steel in shallow sea with sufficient oxygen, low dissolved oxygen leads to the corrosion dominated by pitting with pit covers. The severe pitting is the main factor and causes remarkable ductility loss of the steel after long-term immersion in simulated deep-sea environments.

A brief summary of the operando ORP-EIS study regarding the consumption of copper electroplating additives

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Electrodeposition additives are key components to enhance the electrochemical deposition of metals, either in pure plating applications or during the electrorefining (ER) of metals. Many different additives, either organic or inorganic, are applied in industry, depending on the type of process. This work focusses on thiourea and chloride as common additives used for copper ER. This electrochemical industrial process consumes an impure copper anode and produces a pure (99.995 %) copper cathode, while the anode impurities remain in the electrolyte. Additives assist the electroreduction process to produce smooth copper deposits, which is essential to avoid short circuits and the formation of unwanted cathode morphologies that can entrap impurities.

Electroplating additives can be consumed during the process [1,2] and the consumption of these additives affects the plating process and the plating results [2]. Therefore, in operando monitoring of the additive activity is of great importance for the plating industry. Thiourea is a crucial but complex additive in copper ER. It is known to degenerate into formamidine disulfide (FDS) and both thiourea as FDS can undergo interactions with either copper ions in the solution or the cathode surface. Yet, time dependent additive studies and fundamental knowledge of the effect of aged electrolyte on the cathodic part of the ER process are scarce.

In this research, operando Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) [3,4] is applied to investigate the electrochemical effect of the additives and by-products on the ER of copper [5,6]. The ORP-EIS is performed in operando by adding a direct current to the multisine ORP-EIS input signal [7]. The advantages of the ORP-EIS, including detecting non-linearity and non-stationarity in experiments, are demonstrated in the past by the SURF research group [7]. We highlight the importance of non-stationarities and non-linearities in operando plating experiments [5,6]. Moreover, the operando ORP-EIS technique reveals information regarding the time dependent mechanisms involving the cathode process: diffusion, adsorption, catalysis, inhibition, to name few.

A brief overview is given of the experimental approach, the problems encountered and how these problems were solved to allow the use of operando ORP-EIS to extract information of additive activity. The additive behaviour on the copper plating system as a function of time is also discussed.

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Insight into physical interpretation of electrochemical impedance spectra of Mg

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The Electrochemical Impedance Spectroscopy (EIS) has been widely applied to study the corrosion behavior and mechanism of different bare and coated metals, due to its low disturbance to the tested sample, high sensitivity for electrochemical reaction detection, and capability for diffusion-limited reactions identification. EIS has been actively used to reveal the corrosion mechanism of Mg and its alloys as well. However, the analysis and interpretation of EIS results for Mg are controversial. Assignment of the observed time constants to the specific processes at electrode electrolyte interface is still debated. Despite wide application of EIS on Mg, diverse equivalent circuits are used by different researchers to fit similar impedance spectra. The ambiguous interpretations of the origin of time constants that appear in different frequency ranges may cause the misleading explanations for Mg corrosion behavior. Hence, it is essential to reveal the physical interpretations of each time constant in impedance spectra of Mg-based materials for a better understanding of respective corrosion mechanisms.

In this work, we thoroughly discussed the physical interpretations of time constants in Mg impedance spectra, which are revealing for the investigating the corrosion behavior of Mg and its alloys. Conventional EIS measurements [3] and Tribo-EIS measurements [4] were performed to investigate the evolution of high frequency (HF) and middle frequency (MF) capacitive loops in impedance spectra of pure Mg under different surface states. The assignment of the HF time constant is confirmed through investigation of the oxide/hydroxide films formed at Mg surface in NaCl solution with different initial pH values. The detailed characterization of the interface using TEM confirms the assignment of the HF time constant to the barrier properties of the MgO-based surface film. Moreover, Tribo-EIS measurements were performed on pure Mg in NaCl solution to identify the origin of the HF and MF time constants of Mg. The influence of abrasion introduced by tribometer on impedance spectra was investigated on Mg with different exposed surface areas. The resistances associated to the two time constants on the abraded surface were deduced from the fitted results, verifying that the HF time constant originates from the barrier properties of the MgO-based surface film and the MF time constant stems from the charge transfer process. Additionally, the non-stationarity of EIS measurement on several Mg-based materials in number of electrolytes was studied. The results indicate that the impedance spectra of Mg-based materials in aqueous electrolytes is influenced by the internal non-stationarity of Mg-electrolyte system and the external non-stationarity induced by EIS measurement. Accordingly, the origin of inductive behavior of Mg-based materials is discussed.

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Electrochemical Impedance Spectroscopy Evaluation on the Corrosion of GCr15 Bearing Steel Coated with Rust Preventive Oil Film

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Abstract: The corrosion of bearings usually occurs during their transportation and storage processes due to electrochemical interactions between bearings and the surrounding atmosphere, and rust preventive oil as an insulating layer isolating bearings from ambient atmosphere is often applied before they are delivered. In this work, the corrosion of GCr15 bearing steel electrode, coated with rust preventive oil film (ZYS Bearing Research Institute Co., Ltd.), in NaCl electrolyte has been investigated. For electrochemical measurements, the three-electrode system was used with the rust preventive oil coated GCr15 bearing steel sample as working electrode, Pt foil as counter electrode, and saturated calomel electrode (SCE) as reference electrode. Fig. 1 schematically shows the setup for open circuit potential (OCP) and electrochemical impedance spectroscopy (EIS). The OCP was initially carried out to obtain a stabilized electrochemical system for subsequent EIS measurement. Considering the lower density of rust preventive oil than that of NaCl electrolyte, the working electrode is vertically placed with plane working surface oriented downward, and thus it allows examining and characterizing the corrosion of GCr15 bearing steel electrode under the covering of a thin rust preventive oil film. Besides, the frequency range for EIS measurement is from 100 kHz to 10 mHz using a small AC amplitude of 5 mV for the excitation of electrochemical activity of the system steel/coated oil film/electrolyte, and Gamry Reference 600 electrochemical workstation was employed.

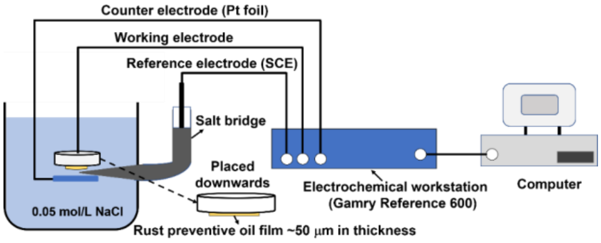

Fig. 1 Setup in illustrating the employed electrochemical measurements.

The obtained EIS impedance diagram can be separated into three regions that represent independent relaxation phenomena [1-2]. The prominent high frequency region (10 MHz–10 Hz) represents capacitance C_{oil} and resistance R_{oil} caused by the rust preventive oil film. The C_{oil} has been interpreted as the capacitance of the electric capacitor consisting of rust preventive oil film and the inside penetrated NaCl electrolyte, and the R_{oil} has been interpreted as the rust preventive oil film resistance due to the NaCl electrolyte penetration. The medium frequency region (10 Hz–100 mHz) represents pseudo capacitance CPE_{ads} and resistance R_{ads}, caused by the adsorption layer of corrosion inhibitor molecules to GCr15 bearing steel electrode surface. During the low frequency region (100–10 mHz), R_{ct} is regarded as the charge transfer resistance for the electrochemical reactions and in this case has a meaning of corrosion resistance, and CPE_{dl} is the non-ideal double layer capacitance at the interface of rust preventive oil film and GCr15 bearing steel electrode surface. Besides, the Warburg element R_{w} represents the diffusion resistance to mass transport of all the involved ions in the electrochemical system.

The analyses find that the EIS characterization is powerful in obtaining information about the metal/coated oil film/electrolyte system properties, such as penetration of electrolyte through the rust preventive oil film, reactivity of the interface, adsorption of inhibitor molecules, and barrier properties to corrosion electrolyte. Besides, adsorption mechanism of the inhibitor molecules has been discussed.

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EIS comparative study and critical EEC analysis of the native oxide layer of additively manufactured and wrought 316L stainless steel

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Metal additive manufacturing (MAM), a process by which complex multifunctional metal parts are produced in a layer-by-layer fashion, is characterized by highly localized melting and rapid solidification, which promotes the formation of a very fine microstructure with unique directional growth features. Numerous studies have demonstrated that the unique microstructure generated during MAM has a significant influence on the corrosion performance of these materials. However, the results are somewhat inconclusive, contradicting each other in some cases.

Some researchers have suggested that the higher corrosion resistance exhibited by additively manufactured (AM) 316L stainless steel (SS) compared to the wrought material is the result of better barrier properties of the native oxide film. Nevertheless, they all concluded that the thickness and the composition of the oxide film on AM 316L specimens are very similar to that of the oxide on wrought material. Therefore, a more detailed and in-depth characterization of the native oxide layer formed on AM and wrought 316L SS could definitely contribute to the overall understanding of the corrosion behavior of these materials.

In this work, a comparative EIS study of the native oxide layer of AM and wrought 316L SS was conducted. A careful examination of the data was carried out in order to properly identify the appropriate model to fit the EIS response. From the parameters calculated by fitting the EIS data and a complementary XPS analysis, the electrical and dielectric characteristics of the passive oxide layers of the specimens were obtained. Clear differences were noticed between the two materials, contributing to the overall understanding of the corrosion performance of the materials analyzed.

A planar and cross-sectional study of the electrochemical and localized corrosion behavior of a quad-layer Al alloy composite in chloride-containing environment

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Abstract:

The electrochemical corrosion behavior of a quad-layer Al alloy composite (4045/7072/3003/4045) with a thickness of 1.2 mm was investigated in 3.5 wt. % NaCl solution. Electrochemical impedance spectroscopy (EIS), potentiodynamic polarization and scanning electron microscopy (SEM) were used to study the corrosion behavior of the Al alloy composite from its planar surfaces (Plane A and Plane B) and its cross-sectional plane (RD direction). The EIS results showed that the corrosion resistance of both Plane A and Plane B decreased with the increasing of immersion time, and the corrosion resistance of Plane A was slighter greater than that of Plane B. SEM results showed that the corrosion in Plane A was pitting while uniform corrosion occurred in Plane B. It can be seen from the EBSD results that the textures in Plane A and Plane B were in different types, resulting their differences in corrosion initiation. The corrosion in the cross-sectional direction was galvanic corrosion, including the micro-galvanic corrosion between the second phase and the Al matrix, and the galvanic couples of different layers the Al alloys.

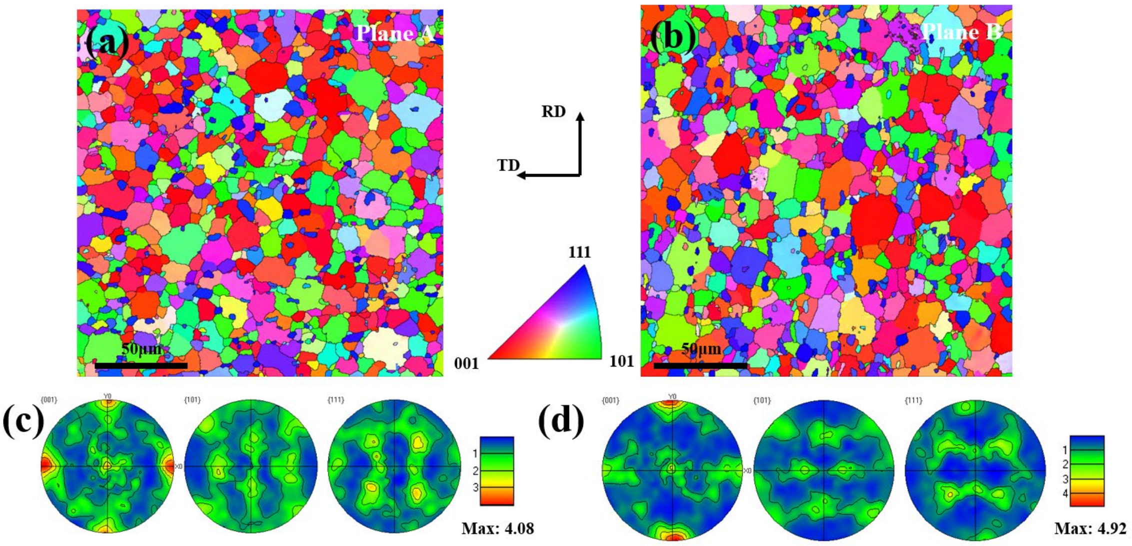

Fig. 1. Inverse pole figure maps (IPFs) and pole figures (PFs) of the Plane A (a, c) and Plane B (b, d).

Co-based metal organic framework sensitized TiO_2 nanorods arrays for enhanced photocathodic protection of 316L stainless steel

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Marine metal corrosion protection is getting more attention as marine engineering advances. Although 316L stainless steel (316L SS) has an excellent resistance to corrosion and is utilized in offshore applications, it is vulnerable to pitting corrosion over time. The development of photogenerated cathodic protection technology offers the possibility of protecting metallic marine equipment. The one-dimensional TiO_2 nanorods suffer from poor light absorption efficiency and carrier compounding despite having high electron transport characteristics. The stability of Co-based layered double hydroxides (LDH), which have a lamellar structure and are useful in photocatalytic water oxidation and supercapacitor materials, still needs to be improved. Metal-organic frame material (MOF) is a crystalline porous material formed by the self-assembly of metal center and organic ligand through coordination bond, which has the advantages of high porosity, low density and large specific surface area. Co-based MOF in particular has excellent thermal stability, chemical stability, and light absorption capacity. This study was motivated by this and used the hydrothermal approach to manufacture TiO_2 nanorods, electrodeposit Co-based LDH material onto the nanorods, and then alter the surface Co-LDH to Co-MOF by ligand exchange. TiO_2 nanorods and Co-MOF/TiO_2 photoanodes were characterised morphologically and the corrosion resistance of 316L SS coupled composite photoanodes was investigated electrochemically in a simulated marine corrosive environment.

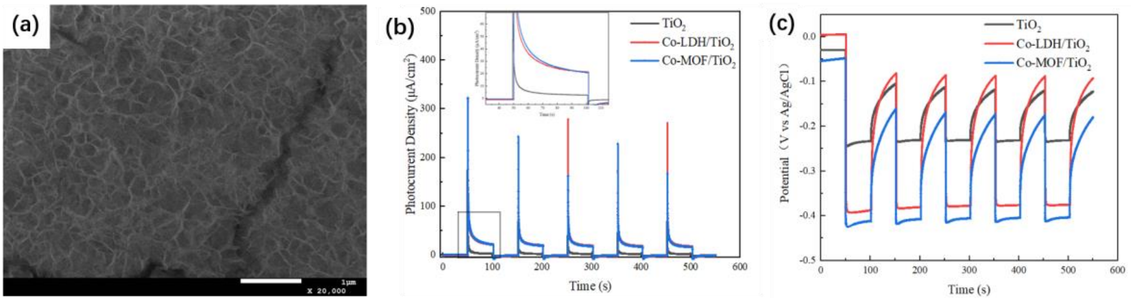

Fig.1 (a) SEM image of Co-MOF/TiO_2; Electrochemical performance test about of pure TiO_2, Co-LDH /TiO_2 and Co-MOF/TiO_2 composites in the intermittent illumination condition (b) Photocurrent density curve (c) OCP curve.

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Study on corrosion mechanism and low cycle fatigue behaviour of Q345R steel influenced by Thiobacillus ferrooxidans

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As one of the important corrosion types, microbial corrosion has been studied by many scholars in the aspects of corrosion loss, corrosion damage, environmental pollution, and stress corrosion damage caused by microbial corrosion, but there is a lack of research on the acceleration of pre-corrosion fatigue behavior and corrosion mechanism of metal materials by simulating microbial corrosion environment. This paper aims at the corrosion problem of *T. ferrooxidans* in the mining environment. Q345R steel is used as the matrix material for the pre-corrosion fatigue test. Using scanning electron microscope (SEM), electrochemical test, and other microscopic characterization methods to analyze the mechanism of *T. ferrooxidans* promoting material corrosion and its influence on corrosion fatigue failure. The results of the study show that the life activity of *T. ferrooxidans* intensifies the corrosion of carbon steel ferrite, the corrosion damage accumulates along the ferrite grain boundaries, and as the corrosive medium digs more profound, the ferrite grains peel off, the material takes on a ferrite deficient gully-like corrosion appearance, and the stress concentration of corrosion pits are the cause of multiple cracking sources. According to the low cycle fatigue data, the corrosion effect of *T. ferrooxidans* did not change the material's cyclic hardening and Masing properties. Still, it did reduce the cyclic hardening rate of the material, with a relative reduction in fatigue life of 27.1% to 53.3% at four sets of strain amplitudes. The predicted results based on the Manson-Coffin equation show that the corrosion effect of *T. ferrooxidans* significantly affects the plastic strain life. Therefore, fitting the fatigue toughness model based on the plastic strain energy density, a relative reduction of 55.4% in the fatigue toughness index was obtained for the *T. ferrooxidans* system.

Atomic understanding microstructure of copper-aluminum alloys with improved chemical stability

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Copper alloys are composed of copper as the matrix and adding one or several other elements. Copper alloys have been widely used in the marine industry due to their excellent seawater corrosion resistance and resistance to marine biological fouling. Aluminum bronze alloy is one of the most resistant alloys in copper alloys for flow corrosion, but its flow corrosion resistance still cannot meet the requirements of new marine alloy materials at this stage. At present, the relevant research mainly focuses on the composition, properties, processing technology and application of aluminum bronzes, but the microstructure of aluminum bronze alloys and the microalloying and corrosion properties are relatively lacking. Therefore, studying the intrinsic relationship between the microstructure and corrosion properties of aluminum-bronze alloys, exploring their corrosion kinetic mechanisms, and establishing a model of the relationship between flow corrosion rate and seawater flow rate have certain practical significance, which can provide a theoretical basis for the development of new marine alloy materials. In this paper, the single-phase copper-aluminum alloy structure with certain thermodynamic stability is theoretically designed with aluminum-bronze alloy as the main research object, and the relationship between microstructure and microalloying and corrosion properties is studied and discussed.

Following are the important features concerning the results reported herein.

1) The microstructure of aluminum bronze is mainly controlled by aluminum content, as a result, when the aluminum content is less than 8wt.%, the microstructure at room temperature is a face-centered cubic single-phase solid solution. Based on this, the CuAl(111)(Cu:Al=15:1, atomic ratio) slab models with a face-centered cubic (FCC) structure are firstly obtained after a bulk optimization.
2) Al atoms can be enriched to a certain extent in the surface and subsurface layers of copper-aluminum alloys. Based on the substitution mechanism of alloys, the formation energy is used to prove the formation trend of these alloy structures. The alloy has the lowest formation energy in the surface and subsurface segregation Al, indicating that the alloy structure of the guest metal Al in the surface and subsurface segregation has certain thermodynamic stability.
3) The stability of the alloy was studied by calculation. Copper atom vacancy formation energy is a feasible indicator for predicting the stability of copper-based alloys, because larger vacancy formation energy indicates stronger intermetallic bonding and less release tendency. In this case, the value of vacancy formation energy on the surface of pure Cu (111) is calculated as 1.08 eV. In comparison, the vacancy formation energy (1.10 eV) of the surface layer of CuAl alloy is higher than that of the vacancy formation energy on the surface of pure Cu (111) (1.08 eV), in addition, copper vacancies are formed at different positions on the surface of CuAl-Al$_{seg.}$ alloy As a comparison, the vacancy formation energy (1.16 eV) of the surface of CuAl-Al$_{seg.}$ alloy is higher than that of CuAl (1.10 eV), therefore, CuAl-Al$_{seg.}$ has better structural stability.
4) The model structures used in this calculation are the thermodynamically stable CuAl-Al$_{seg.}$ structure. The d-partial density of states (d-PDOS) of the surface layer Cu atoms in various samples. As observed, the recorded d-band center of CuAl-Al$_{seg.}$ is -3.70 eV, which is more negative than -2.37eV of Cu and -2.66 eV of CuAl. The negatively shifted d-band center contributes to the weakening of corrosive media adsorption on the alloy surface.

This work was supported by the National Natural Science Foundation of China (grant No. 22278016).

Microstructure construction and insight into chemical stability for Cu-Ni alloys with controllable composition at atomic level

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Our country has a vast ocean area and rich resources. The development of marine engineering construction and related engineering technology is the key to the utilization of marine space and resources, and the construction of marine engineering. Copper and copper alloys are widely used in the marine material industry as important materials for seawater piping systems. The copper-nickel alloys with a Ni content of 10% is usually called white copper alloys like B10. Its main components are Cu and Ni, and it also contains other alloying elements such as Fe and Mn. Copper-nickel alloys have excellent corrosion resistance with excellent mechanical and physical properties. However, with the increasingly importance of Cu-Ni alloy in marine engineering, more attention is payed to its corrosion resistance. Many researchers have resorted to optimizing composition and applying protective layers in order to solve corrosion problems. In this paper, the corrosion problem of Cu-Ni alloys is analyzed on a theoretical level by modelling the alloy and using MS software through DFT calculations. A model of a Cu-Ni alloy with Ni enrichment in the sub-surface layer or even in the third layer on the basis of Cu-skin is obtained. Through analysis, this structure is conducive to the thermodynamic stability of the copper-nickel alloy and the improvement of corrosion resistance. In this way it is possible to better analyses how vacancies are formed on the surface of the alloy and how copper and nickel migrate across the vacancies on the surface. At the same time, the model provides a certain reference for further analysis of the corrosion of copper-nickel alloys in seawater.

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This work was supported by the National Natural Science Foundation of China (grant No. 22278016).

Failure analysis of a heat exchanger tube of 70/30 cupronickel

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This paper presents a failure analysis performed to investigate the leakage of heat exchanger tubes made of 70/30 cupronickel. The cooling heat exchanger was in service in a marine environment with seawater flowing in the tubes. Some tubes showed leak failure after one year of service. Visual examination, chemical analysis, tensile strength measurements, microscopic examinations and energy dispersive spectroscopic analyses were conducted to determine the root cause of the failure. Visual investigation revealed the inner wall of the heat exchanger underwent severe pitting corrosion. A comprehensive failure analysis of the heat exchanger revealed the denickelification process on the internal side of the damaged tubes. Intergranular corrosion was observed to initiate under the areas of denickelification which finally led to pinhole leakage.

Keywords： 70/30cupronickel, Seawater, Intergranular corrosion, Failure analysis, Heat-exchanger failures

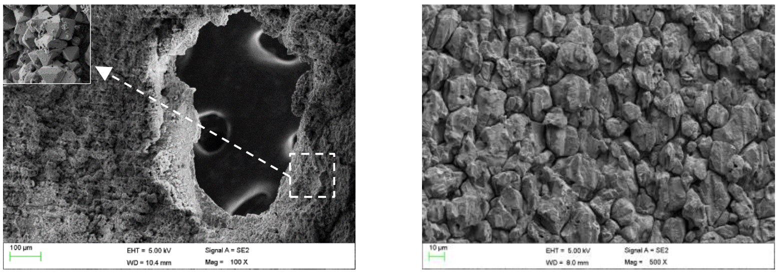

Figure 8 SEM micrographs at the failed region

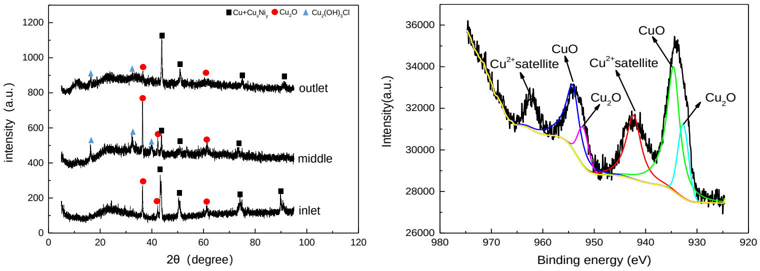

Figure 13 The XRD pattern and XPS of the corrosion product power scraped form the surface

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Study on the Mechanism of 7075 Aluminum Alloy Corrosion by Penicillium funiculosum

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Aviation fuel, which is rich in hydrocarbons, can be an easy breeding environment for microorganisms, resulting in possible corrosion failure of structural materials in fuel systems. In this paper, 7075 aluminum alloy used for aircraft fuel tanks was used as the matrix material, and Penicillium, a common species in jet fuel, was used as the experimental microorganism strain. The corrosion behavior of this aluminum alloy in the presence of *Penicillium funiculosum* was investigated using the corrosion weight loss method, electrochemical tests, scanning electron microscopy, and inductively coupled plasma optical emission spectrometry. The research results show that *Penicillium funiculosum* secretes a large amount of organic acids during the reproduction process, thereby reducing the pH of the culture medium. The acidic corrosive medium environment accelerates the damage to the oxide film on the surface of aluminum alloy. In addition, the exposed second-phase precipitation particles in the aluminum alloy matrix function as an anode in an acidic medium, resulting in the formation and dissolution of aluminum cations under the release of electrons, which process will promote the corrosion of aluminum alloy and cause the observed intergranular pitting morphology. At the same time, the occurrence of the hydrogen evolution reaction consumes proton and electrons in the medium and aggravates the local corrosion of aluminum alloy.

Effect of electron shuttle riboflavin on Escherichia coli corrosion of X80 pipeline steel

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Endogenous electron shuttling riboflavin (RF) is used as a carrier to investigate its effect on the corrosion of Escherichia coli (E.coli) in X80 pipeline steel by cyclic voltammetry (CV), corrosion weight loss, electrochemical testing, scanning electron microscopy (SEM), energy spectrum analysis (EDS) and diffraction of x-rays (XRD) analysis. The CV results showed that the E.coli bacterium and its metabolites did not exhibit electro-active. The redox peak appeared in the system after adding 10ppm RF, indicating that E.coli can use RF for extracellular electron transfer. The corrosion weight loss rate showed that the corrosion rate of X80 pipeline steel of E.coli + 10ppm RF system was about twice that of E.coli system. XRD test results showed that RF did not change the corrosion pathway of E.coli but only affected the corrosion process of E.coli. Electrochemical tests showed that the corrosion current density of the E.coli + 10ppm RF system was about twice that of the E.coli system. Therefore, RF as an electron shuttle can accelerate the corrosion of X80 pipeline steel by E.coli.

Keywords: X80 pipeline steel; Escherichia coli; Riboflavin; Electron shuttle

Effect of Thiobacillus ferrooxidans on the corrosion behavior and low cycle fatigue performance of Q345R steel

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As one of the types of corrosion, microbial induced corrosion has been studied by many scholars in terms of corrosion loss, corrosion damage, environmental pollution, stress corrosion damage, etc. However, there is a lack of simulating microbial induced corrosion environment to accelerate the pre-corrosion fatigue behavior and corrosion mechanism of metal materials. In this paper, to address the corrosion problem of Thiobacillus ferrooxidans (*T. ferrooxidans*) in the mining environment, pre-corrosion fatigue tests were conducted with Q345R steel, and microscopic characterization such as scanning electron microscopy (SEM) and electrochemical testing were used to analyze the mechanism of *T. ferrooxidans* promoting material corrosion and the effect on the corrosion fatigue failure mechanism. The results show that the life activity of *T. ferrooxidans* aggravates the corrosion of carbon steel ferrite, the corrosion damage accumulates along the ferrite grain boundaries, and with the deep digging of corrosive media leads to the stripping of ferrite grains and thus the material shows a gully-like corrosion morphology with ferrite loss, and the deep corrosion pits are the cause of the emergence of multiple cracking sources. The low-week fatigue data show that the corrosion effect of *T. ferrooxidans* does not change the cyclic hardening properties and Masing properties of the material, but it decreases the cyclic hardening rate of the material, and the fatigue life is relatively reduced by 27.1% to 53.3% under four groups of strain amplitudes. The predicted results based on the Manson-Coffin equation show that the corrosion effect of *T. ferrooxidans* has a significant effect on the plastic strain life. Therefore, the fatigue toughness index of *T. ferrooxidans* group was obtained to be relatively reduced by 55.4% based on the plastic strain energy density fitted to the fatigue toughness model.

Keywords: Q345R steel; Thiobacillus ferrooxidans; Corrosion mechanism; Low cycle fatigue

Investigation of Local Corrosion Behavior and Mechanism for TA2/HAl77-2/316L SS Coupling System under Seawater Liquid Film
人工海水液膜下 TA2/HAl77-2/316L SS 耦合体系局部腐蚀行为研究

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Behavior and mechanism of local corrosion for TA2/HAl77-2/316L SS coupling system under seawater liquid film was investigated using microarray electrode technology and EIS technology. The effect of Cl^- concentration, liquid film thickness, and temperature of artificial seawater for corrosion were discussed in detail. Local corrosion parameters, such as the maximum potential difference (ΔE_{max}), the maximum anode current density ($I_{a,\,max}$), the local corrosion intensity factor (LCII), and cathode to anode area ratio (Sc/Sa) were extracted to characterize the local corrosion degree of microarray electrodes quantitatively. The results showed that HAl77-2 and most of the 316L SS electrode wires in the microarray electrodes were performed as anodes, while the TA2 and the rest of 316L SS electrode wires were performed as cathodes. When the concentration of Cl^- increased from 1.9 *wt.*% to 4.3 *wt.*%, the anode potential shifted negatively and the anode current tended to increase. The anode current was maximum when the concentration of Cl^- was 3.1 *wt.*%. Anodic corrosion potential shifted negatively, and coupling current increased with the liquid film thickness increasing. The corrosion potential of cathode 316L SS was not significantly affected by the thickness of the liquid film. The cathode corrosion potential shifted negatively firstly and then positively. The corrosion potential of TA2 was the most negative when the liquid film thickness was 400um, and the electric coupling current was the largest.

Key words: EIS; liquid film; galvanic system; corrosive pitting

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NIR-induced corrosion regulation strategy for biodegradable Mg alloy

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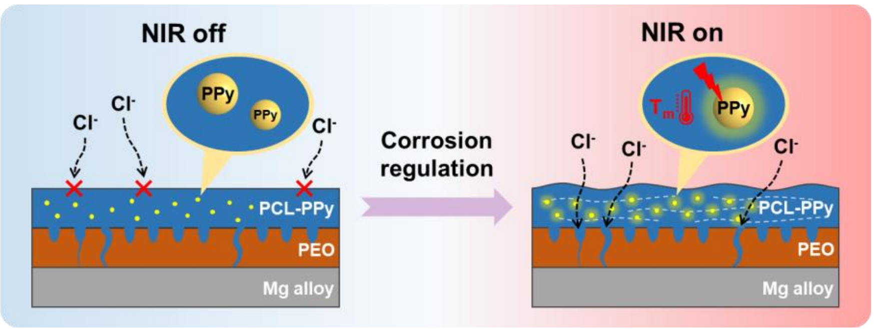
At present, biodegradable Mg-based implants used in clinical practice have shown high reliability and corrosion resistance, which is hardly degradaded in service for more than ten months [1-3]. However, an overlong degradation period of Mg-based implants increases the risk of infection and the frequency of follow-up for patients. Therefore, controlling the degradation rate of Mg-based implants is an urgent challenge for their clinical application. Herein, we prepare a novel protection system composed of a plasma electrolytic oxidation layer and a polypyrrole-loaded polycaprolactone composite coating on an Mg alloy. During NIR irradiation, the polymer coating integrates binary roles including the NIR response of polypyrrole to achieve the designed temperature, and the transition of polycaprolactone from a rubbery state to a viscous state upon heating. The electrochemical results showed that the system exhibits satisfactory corrosion resistance in simulated body fluid with ~9.2×10^{-13} A/cm^2 of the corrosion current density (i_{corr}) and ~3.3×10^{9} Ω/cm^2 of the electrochemical impedance at 0.01 Hz ($|Z|_{0.01\ \mathrm{Hz}}$). After NIR irradiation for 1 hour, both i_{corr} and $|Z|_{0.01\ \mathrm{Hz}}$ decreased rapidly by 4 orders of magnitude. It was further confirmed by tracking the change of the wettability during the state transition of the coating that the electrolyte rapidly infiltrated into the substrate through the increased molecular chain distance to accelerate its degradation. Hence, this work provides a new strategy for regulating the corrosion rate of Mg-based implants.

Keywords: Near infrared (NIR) light; Corrosion regulation; State transition; Biodegradable Mg alloy



Scheme 1. Schematic of NIR-induced corrosion regulation strategy for Mg alloy.

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Local corrosion behavior of X80 steel welded joints under micro-turbulence induced by welding reinforcement height

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Corrosion failure accidents owing to flow erosion and pipeline corrosion frequently occur during transportation(1-3). The welding reinforcement height (WRH) can induce locally micro-turbulent flow field, which aggravates local corrosion of welded joints(4). In this study, a high wall shear stress (WSS) experimental setup was established to conduct the online electrochemical corrosion test. The influences of WRH sizes on local corrosion of welded joints were studied at different flow rates. The electrochemical signals of the local corrosion of X80 welded joints at different flow rates were monitored in real time using electrochemical impedance spectroscopy (EIS). In addition, the corrosion products composition and properties were analyzed. The results show that the micro-turbulent flow fields induced by the WRHs can enhance ion mass transfer near the welded joints. The corrosion products on the WRH surface also present different microscopic morphologies at different flow rates. In strong flow fields, the locally enhanced WSS can peel off the dense corrosion product partially, leading to the electrochemical distribution of large cathode and small anode, which accelerates the occurrence and development process of the local corrosion of welded joints. This study can potentially provide scientific guidelines for the corrosion protection of long-distance oil and gas pipelines.

Keywords: Welding reinforcement height; Micro-turbulence; Corrosion product; Ion mass transfer

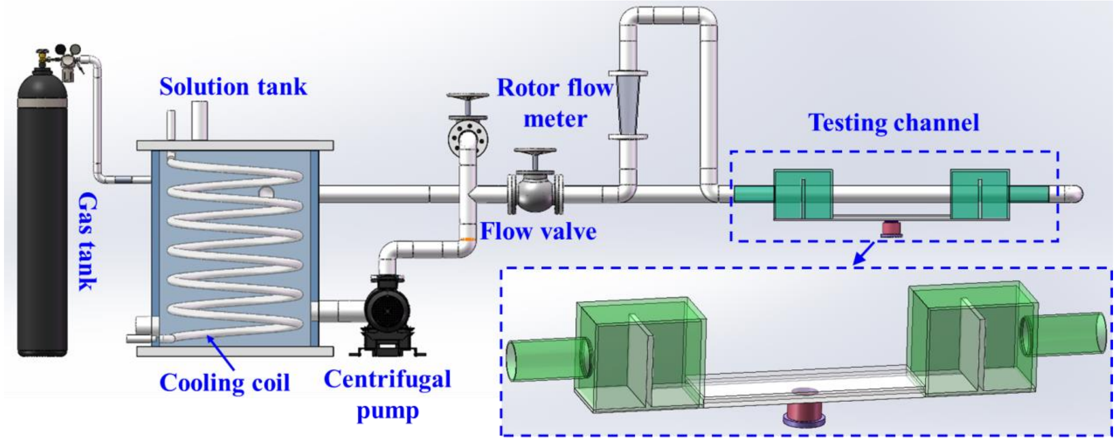

Fig. 1 Single-phase flow-accelerated corrosion loop system

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Effect of Cu^{2+} and Hg^{2+} on the corrosion behavior and mechanism of Al-2 %Zn coatings in 3.5 % NaCl solution

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Aluminum alloys that are widely used in heat exchange systems are severely degraded in the form of localized corrosion and general corrosion in acidic, alkaline and humid chloride ion-containing environments [1]. Meanwhile, a certain amount of Cu^{2+} and Hg^{2+}, polluting heavy metal ions, in offshore seawater can also have complex effect on the corrosion process of aluminum alloys [2] causing reduction of service life. Hence, various Al-Zn coatings have been widely applied as a surface treatment strategy due to their flexible preparation methods and excellent corrosion protection in corrosive media [3]. Therefore, it is essential to explore the corrosion process of aluminum coatings in seawater containing Cu^{2+} and Hg^{2+}. However, previous related studies are mostly focused on pure aluminum or polished aluminum alloys [4] rather than alloy coatings. There have been few reports on the effect of Cu^{2+} and Hg^{2+} in seawater on the corrosion behavior and mechanism of Al-Zn coatings.

Here, this paper focused on investigating the corrosion behavior and mechanism of the Al-2 %Zn coating in 3.5 wt.% NaCl solutions containing Cu^{2+} and Hg^{2+}. The reduction of Cu^{2+} and Hg^{2+} occurs as part of the cathodic reaction during the corrosion process. In the presence of metal ions, the characteristics of the impedance spectrum are changed from the inductive semicircles to two capacitive semicircles with the extension of the immersion time. Combined with the results of X-ray photoelectron spectroscopy (XPS), mixed potential value and scanning electron microscopy (SEM) and energy dispersion spectroscopy (EDS), the authors gained a deeper understanding of the influence of Cu^{2+} and Hg^{2+} on the corrosion mechanism of Al-2 %Zn coatings. The results show that the corrosion process is inhibited at low concentrations of metal ions and promoted at high concentrations. Although the critical concentrations of the two metal ions are different, the reason for the above effects is due to the competitive relationship between the reduction of Cu^{2+}/Hg^{2+} and O_2 in the cathodic reaction, which in turn causes differences in corrosion behavior.

Acknowledgements

This work was supported by Ministry of Science and Technology of the People's Republic of China, Grant numbers: 2022YFB3705801.

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Application of electrical impedance spectroscopy in cathodic protection studies

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The effectiveness of cathodic protection is closely related to appropriate establishment of cathodic protection criterion, where the lower limit potential of cathodic protection is mainly determined by the hydrogen evolution reaction (HER) process [1]. Thus, it is of interest to investigate the mechanism of hydrogen evolution reaction under cathodic protection conditions. Usually, the HERs are mainly coupled by Volmer-electrochemical discharge reaction with Tafel chemical recombination reaction or Heyrovsky electrochemical desorption reaction. However, the rate-determining step under different HER route varies depending on experimental conditions, which may lead to the same Tafel slope of cathodic polarization curves corresponding to different HER mechanisms [2]. Therefore, it is not rigorous enough to infer its mechanism for HER process only from the slope of the polarization curve, and even wrong conclusions may be obtained.

Here, the authors consider the fact that HER proceeds in a Volmer-Tafel route at a positive cathodic protection potential, when the factors affecting the interfacial current are, in addition to the cathodic polarization potential, the coverage of adsorbed hydrogen atoms on the electrode surface, and thus the impedance spectrum generally exhibits a double time constant characteristic. At sufficiently negative potentials, the electrode surface would be saturated with adsorbed hydrogen atoms, i.e., the surface coverage is close to "1" and no longer varies with potential. Therefore, as HER proceeds in the Volmer-Heyrovsky route, the impedance will exhibit a clear single time constant [3-5].

Based on above understanding, the authors investigated the nature of HER affected by common environmental factors, such as temperature and stress, through impedance spectroscopy at different cathodic protection potentials, in order to gain a deeper understanding of HER process and the hydrogen embrittlement （HE） of X80 steel. The results show that the threshold potential for the transition of HER mechanism is around -950 mV (vs. SCE) under all experimental conditions. The tensile stress or temperature have less influence on the value of that critical potential, but increase the activity of HER on the surface of X80 steel to a larger extent, and X80 steel shows high hydrogen embrittlement sensitivity due to accelerated HER beyond that threshold potential value.

Acknowledgements

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Research on the Correlation between ICG and Tensile Properties of Alloy 625

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Alloy 625 has excellent comprehensive properties and is widely used in environments that require high-temperature performance, such as aerospace and steam pipelines. However, there are harmful precipitates such as Laves phases in alloy 625 which have been exposed to high temperatures for a long time. These micron-sized precipitates will have adverse effects on both the mechanical properties and corrosion resistance of alloy 625. In this paper, SEM and TEM were applied to investigate the influence of different aging treatment temperatures on the evolution of precipitates in alloy 625. Deep learning combined with image pro plus software was applied to calculate the distribution and volume fraction of Laves phases in alloy 625. Finally, the double-loop electrochemical reactivation (DL-EPR) and Electrochemical Impedance Spectroscopy (EIS) were applied to investigate the correlation between the tensile properties and intergranular corrosion properties of alloy 625.

The results show that: as the aging temperature (873-993K) increases, the elongation of 625 alloy first rapidly decreases and then slightly increases. This trend of change is attributed to the growth of Laves phase at grain boundaries and the precipitation of γ" phase. In addition, with only a small amount of SEM images for training, the deep network architecture U^2-net can quickly and accurately calculate the Laves phase size and volume fraction in alloy 625. The DL-EPR results indicate that with the increase of Ra, the elongation first increases and then decreases, indicating a good correlation between high Ra value and low elongation for aged alloy 625. The EIS results are consistent with the DL-EPR results, and samples with higher Ra values even exhibit two time constants, indicating local corrosion on the surface of the sample.

Keywords: Alloy 625, Aging heat treatment, DL-EPR, Elongation, U^2-net, EIS

Acknowledgments:

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Electrochemical characteristics of the additive manufacturing AlSi10Mg alloy in a 3.5 wt.% NaCl solution

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Much attention has been paid to the additive manufacturing(AM) technology, due to its significant advantages in manufacturing parts with complex structures [1]. However, multi-scale defects generate inevitably in the process of additive manufacturing[2], leading to the inhomogeneity of the electrochemical properties for additive manufacturing alloys. Thus, corrosion microcells will be formed on their surfaces once additive manufacturing parts are exposed to service environments. Finally, additive manufacturing parts will be subjected to serious corrosion in their service environments.

In this paper, the electrochemical characteristics of the additive manufacturing AlSi10Mg alloy in a 3.5% NaCl solution were studied by electrochemical impedance spectroscopy (EIS) in conjunction with X-ray Computed Tomography. Firstly, the micro-defects in the additive manufacturing AlSi10Mg alloy were qualitatively identified using X-ray Computed Tomography (Fig.1). Some micro-defects with different sizes and shapes were observed from Fig 1 and these defects were mainly micro-pores. About 50% of micro-pores had the size range of 0.4-1.2μm and the maximum pore diameter was 7.6 μm. Fig.2 showed that the EIS spectra of the AM AlSi10Mg alloy was characterized by a depressed capacitance loop with two time constants within 7 hours. After that, its EIS spectra started to have two capacitance loops, and the magnitude of the modulus decreased with the elapsed time. After the EIS spectra were fitted using an equivalent circuit, it was found that the R_{ct} and CPE parameter of the Q_{dl} also decreased with the elapsed time, indicating that the surface oxide film was destroyed and the corrosion reaction at the interface of oxide film/substrate was accelerated which led to local corrosion eventually.

Keywords: additive manufacturing; micro-defects; electrochemical characteristics; corrosion; AlSi10Mg;

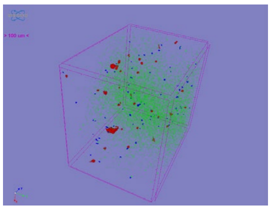

Fig.1 3D morphology of pore defects.

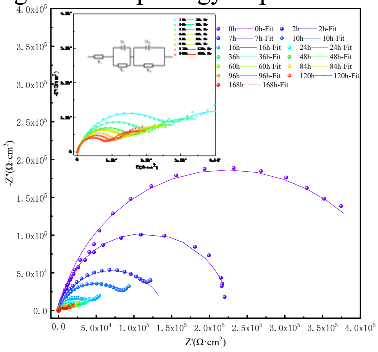

Fig.2 EIS spectra of additive manufacturing AlSi10Mg in 3.5% NaCl solution at different immersion times.

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Study on Cathodic Polarization Behaviors of High Strength Stainless Steel

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To study the polarization behavior of high strength stainless steel at different cathodic polarization potentials and to determine the reasonable cathodic protection potential range of high strength stainless steel. The corrosion products on the surface of the samples were observed and analyzed by cathodic polarization combined with scanning electron microscope and energy dispersive spectrometer. The effect of cathodic polarization potential on the cathodic product film on the surface of the high strength stainless steel and the cathodic protection effect of the high strength stainless steel in seawater were studied. When the cathode polarization potential was negative to -0.9V, hydrogen evolution occurred on the surface of the sample. Electrochemical impedance spectroscopy test and fitting results show that when the polarization potential is -0.7V, the charge transfer resistance of electrode reaction is the maximum, and the corrosion is completely suppressed. It was found that the polarization current density decreased first and then increased with the negative shift of potential. EDS analysis of the surface products showed that the density of calcium and magnesium deposited layer increased first and then decreased. The reasonable protection potential of the high strength stainless steel in seawater environment is -0.5V ~ -1.0V.

Key Words: Ocean engineering; High strength stainless steel; Cathode polarization; Electrochemical behavior

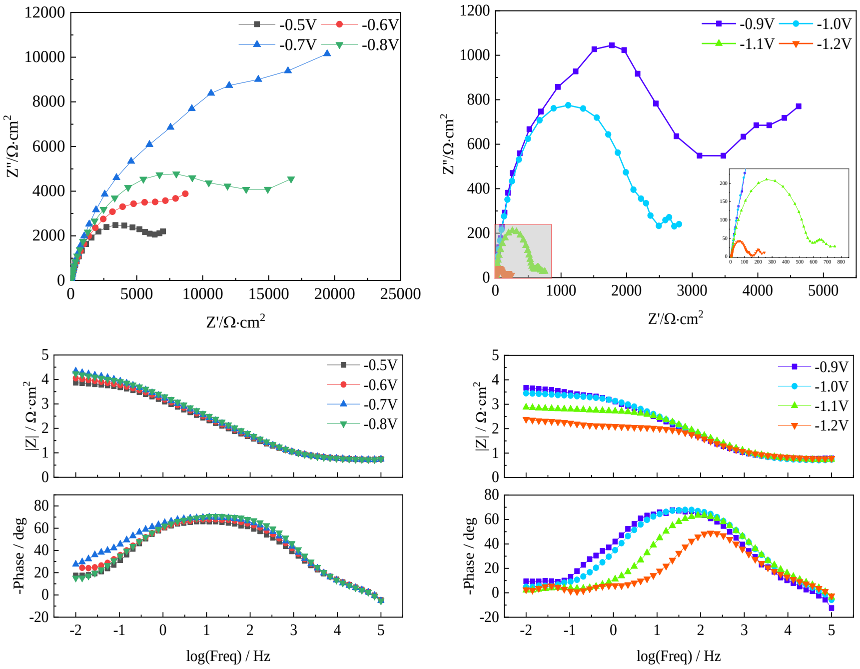

FIGURE 1 Nyquist (a),(b) and Bode (c),(d) plots of the high strength stainless steel at different cathodic polarization potentialsin natural seawater solution.

Study on the electrochemical corrosion process of as-cast nickel-aluminum bronze under cavitation

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Nickel-aluminum bronze alloys are widely used in ship propellers because of its good corrosion resistant performances and mechanical properties. In general, propellers made of nickel aluminum bronze were subjected to cavitation corrosion, due to the synergistic effect between cavitation mechanics and electrochemical corrosion. In this paper, the electrochemical process of as-cast nickel-aluminum bronze under cavitation was studied.

The EIS spectra of nickel aluminum bronze in a 3.5% NaCl solution under cavitation were shown in Fig.1. The Nyquist plots was composed of a capacitive loop in a high frequency region and an inductive loop in a low frequency region, showing that EIS spectra had two time constants. With increasing cavitation time, the impedance modulus at a low frequency decreased gradually, indicating that the heavy cavitation corrosion occurred to nickel aluminum bronze in a 3.5% NaCl solution under cavitation. When the electrodes made of nickel aluminum bronze in a 3.5% NaCl solution were polarized, its EIS spectra under cavitation were shown in Fig.2. If the electrode was cathodically polarized, its EIS spectra under cavitation was composed of two capacitive loops with two time constants. When it was anodically polarized, its EIS spectra under cavitation was a capacitive loop with one time constant. The impedance modulus at a low frequency under cathodic polarization was much larger than that under anodic polarization, indicating that cathodic polarization resulted in decreasing electrochemical corrosion, Finally, cavitation erosion was retarded, due to that synergistic effects were decreased.

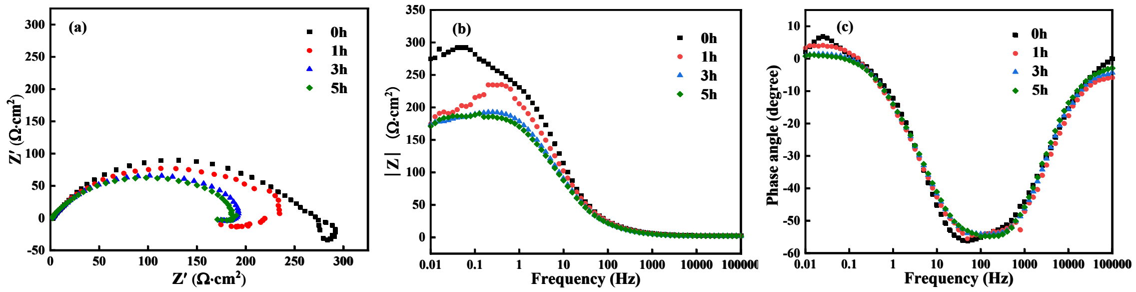

Fig.1 EIS spectra of nickel aluminum bronze in a 3.5% NaCl solution under cavitation (a, Nyquist plot; b-c, Bode plots)

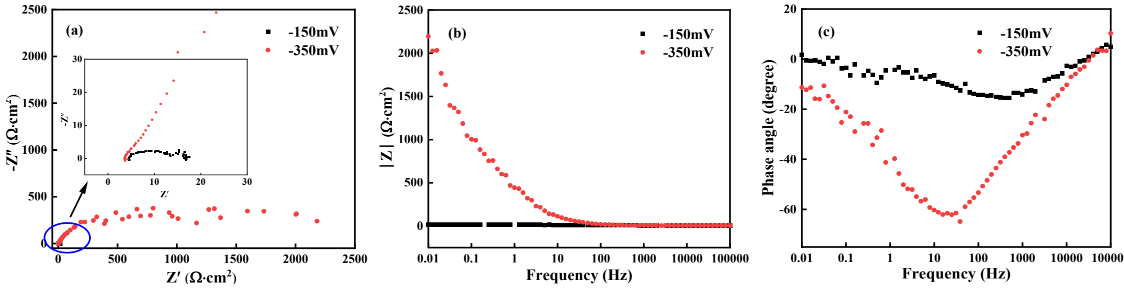

Fig.2 EIS spectra of nickel aluminum bronze in a 3.5% NaCl solution under cavitation when it was cathodically and anodically polarized (a, Nyquist plot; b-c, Bode plots)

Inhibitors

The Electrochemical behavior of Amorphous Alloy - From Corrosion to Electrocatalysis

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Metallic glasses (MGs) are one type of metastable metal materials, which can be obtained by super-quick solidification and other methods. When melts are solidified, the atoms are too late to arrange and crystallize in an orderly manner, and the obtained solid alloy is a long-range disordered structure. The disordered structure and metastable state provide unusual structural properties. For example, high catalytic activity is due to the surface with more unsaturated centers and higher surface energy. MGs have good physical properties of soft magnetic property, strength, and wear resistance. So it is used in industrial manufacturing, power electronics, and aerospace as structural parts and functional materials. It also has excellent chemical properties of acid and alkali resistance, anti-corrosion, and biological and industrial degradability. In petrochemicals, medical devices, green energy, MGs have been widely used as a protective coating, biocompatible material, and catalysts.

This presentation will present series MGs in forms of bulk and coating, about their corrosion resistance in acidic solution and electrochemical mechanism in passivation. Based the design of chemical composition of Pd-based MGs, we developed a high entropy MGs shows great properties both in corrosion resistance and electrocatalysis.

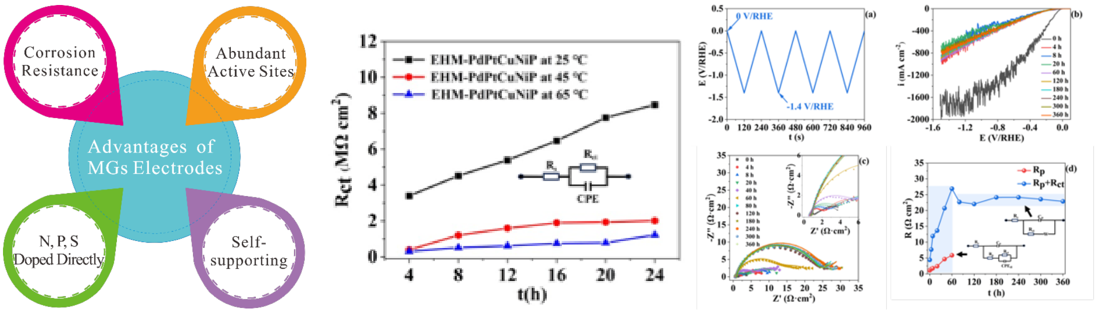

Fig. 1 The Advantages of MGs Electrodes, the corrosion resistance of PdPtCuNiP MGs, and the electrocatalysis property in HER under fluctuated potential (from left to right).

Self-healing performance of ethyl-cellulose based supramolecular gel coating highly loaded with different carbon chain length imidazoline inhibitors in NaCl corrosion medium

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Surface coating is the most effective corrosion protection method, which could isolate the metal substrate and the corrosive medium. In this research, the anti-corrosion performance and self-healing ability of an ethyl-cellulose based supramolecular gel coating were improved through pre-loading high concentration (up to 25 wt.%) imidazoline inhibitor. The imidazoline inhibitors with different carbon chain were used to enhance the anti-corrosion performance and introduce self-healing property to the supramolecular gel coating. And the inhibitor molecular became an important part of the gel coating via the supramolecular effect. The inhibitor dissolved in the dispersion phase of gel coating could enhance the barrier effect of coating. For the coating with 25 wt.% imidazoline inhibitor, the impedance at low frequency of coating remains above 10^9 Ω cm^2. In addition, the inhibitor in the gel coating could pre-adsorb on the steel to form an adsorption film to enhance the anti-corrosion performance of the coating. For the scratched coating, the inhibitor released form coating scratches could form an adsorption film and stop the corrosion reactions of steel. The impedance of scratched area coating with inhibitor is above 10^5 Ω cm^2, which is one order larger than that of coating without inhibitor. The scanning kelvin probe (SKP) results revealed the self-healing distance of gel coating with inhibitor in NSS test is about 0.5 – 0.7 mm. The carbon chain length of inhibitor could affect the barrier effect of intact coating and the self-healing performance of the scratched coating, and the anti-corrosion mechanism of this new kind of self-healing coating are shown in Figure 1.

Keywords: upramolecular gel coating, imidazoline inhibitor, carbon chain length, self-healing.

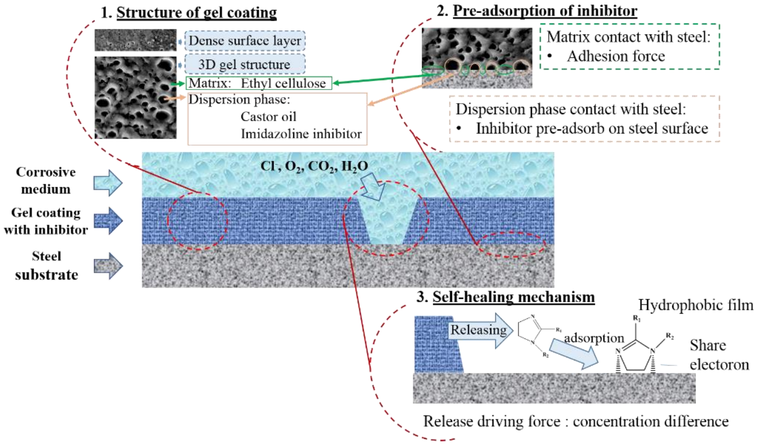

Figure 2. The anti-corrosion mechanism of gel coating with imidazoline inhibitor.

Effect of Tween 85 and calcium malate as hybrid additives on the performance of alkaline aluminum-air batteries

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This paper reports the corrosion inhibition effects of tween 85 (T-85) and calcium gluconate (CM) as additives in 4 M NaOH for aluminum-air battery. The hydrogen evolution experiments, the electrochemical measurements, the SEM morphological characterization, the infrared spectroscopy, and the related molecular dynamics calculations are used to investigate the performance of the additives. This study implies that all additives can inhibit corrosion of aluminum alloys. Antagonistic effects are observed at low concentrations of the hybrid system compared to the single T-85. The anodes have the lower self-corrosion rate of hydrogen evolution and the higher utilization efficiency in presence of the hybrid additives of 30mg/L T-85+1mg/L CM.

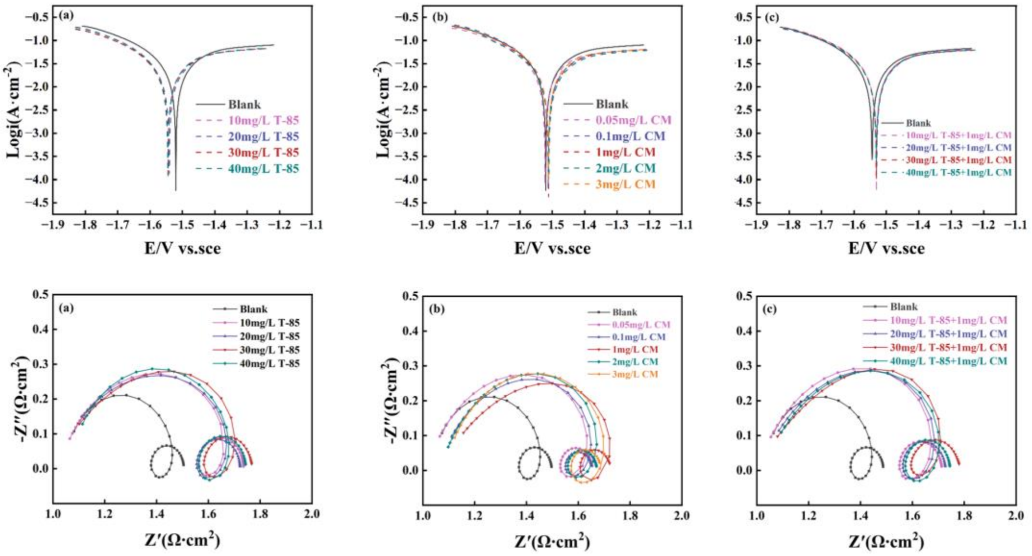

Fig. 1. Polarization and impedance curves of AA5052 aluminum alloy electrode in 4M NaOH solution with different additive concentrations: (a) T-85; (b) CM; (c) T-85+CM; (d) T-85; (e) CM; (f) T-85+CM

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*Corresponding author: Daquan Zhang (1968-), male, PhD, professor, the research fields are the anti-corrosion of metal and the environmental protection in electric power industry.

Fund project: National Natural Science Foundation of China (Project No. 52071198, 21776172)

Keywords: Aluminum-air battery; Self-corrosion; Corrosion inhibitors; Tween 85; Calcium malate

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Corrosion Inhibition of [EMIM]SCN for Copper in 3.5% NaCl Solution

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An imidazolium-based ionic liquid, 1-ethyl-3-methylimidazole thiocyanate ([EMIM]SCN), was investigated to inhibit the corrosion of copper in 3.5% NaCl solution through electrochemical technology, weight loss experiment and surface analysis. The polarization curves showed that the addition of [EMIM] SCN significantly shifted the corrosion potential negatively, meanwhile, the current density of the cathodic polarization curves were significantly reduced. However, when its concentration was 0.004 M and above, [EMIM] SCN also inhibited the anodic reaction of copper in 3.5% NaCl solution, but the inhibition effect on the anode obviously decreased with the increase of temperature. The electrochemical impedance spectrum (EIS) demonstrated that the impedance of copper electrode in 3.5% NaCl solution increased with the concentration of [EMIM]SCN, indicating that the protective film formed by [EMIM]SCN on the copper surface inhibited the corrosion of copper in 3.5% NaCl solution. The results of potentiostatic polarization curve and weight-loss experiment proved that [EMIM]SCN was an effective corrosion inhibitor for copper in 3.5% NaCl solution. XPS analysis results confirmed that [EMIM]SCN formed a stable protective film on the surface of copper. The protective film was composed of CuSCN precipitation and imidazolium cation adsorption film, which synergistically inhibit the corrosion of copper in 3.5% NaCl solution.

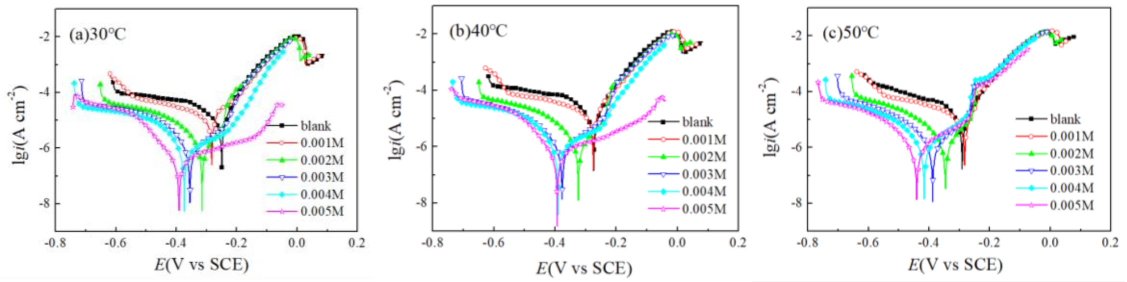

Fig.1 Polarization curves of copper in 3.5% NaCl with different concentrations of [EMIM]SCN.

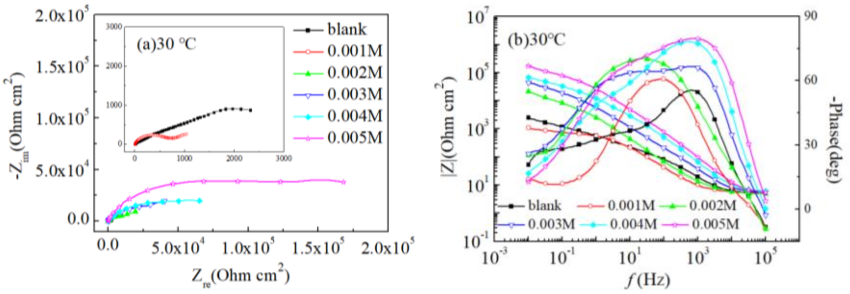

Fig.2 EIS of copper in 3.5% NaCl solution with different concentration of [EMIM]SCN.

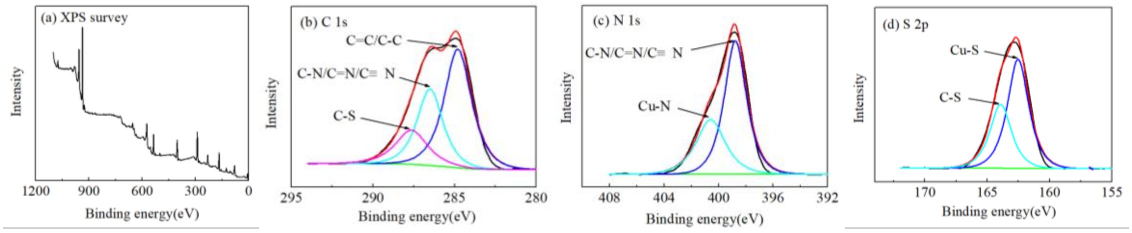

Fig.3 Fitting diagrams of Langmuir adsorption isotherm and Arrhenius equation

Benzothiazole derivatives-based supramolecular assemblies as efficient corrosion inhibitors for copper in artificial seawater: Formation, interfacial release and protective mechanisms

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Host-guest assemblies for β-cyclodextrin (β-CD) loaded with 2-mercaptobenzothiazole (MBT) or 2-aminobenzothiazole (ABT) were constructed to distinguish their anticorrosive mechanisms for copper in aqueous phase. Their protective efficacies were assessed by weight-loss, electrochemical, surface and solution analyses for copper in the artificial seawater. Achievements proposed that MBT and ABT were stably incorporated in β-CD with distinct thermodynamic traits, which earned the optimal inhibition efficiencies of 95.6 % and 89.2 % at 0.5 g/L dosage following cathodic-dominated mixed-type inhibition mechanism. Coupling theoretical simulations, varied guest release mechanisms and different bonding strengths of Cu-S and Cu-N accounted for the differentiated inhibition behaviors.

Ce post-treatment on the corrosion resistance of aa2024-t3 anodized in TSA and sealed with hybrid coatings

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Cr-based anodizing and surface treatments are the benchmark for protection of Al alloys in aircrafts. Despite self-healing properties and good corrosion resistance, chromate compounds are toxic for health and the environment; therefore, following other industrial sectors, the use of these chemicals for surface treatment will soon be prohibited in the aerospace industry. Anodizing in tartaric-sulfuric acid (TSA) is a promising environment compliant alternative, which is already being used at industrial level. However, the corrosion resistance of the anodized layer alone is not sufficient to guarantee the required safety levels for an aircraft and more complex systems should be employed. In this study, the corrosion resistance of AA2024-T3 specimens anodized in TSA and subsequently post-treated in a Ce-H2O2 solution and sealed by a hybrid sol–gel coating (3-glycidoxypropyltrimethoxysilane and tetraethoxysilane) was investigated by means of global (EIS) and local (LEIS) electrochemical impedance spectroscopy. EIS experiments demonstrated that the Ce post-treatment enhanced the performance of the sol-gel protection system; moreover, long-term corrosion protection was achieved for hydrolysis solution aged for up to six months. On the other hand, LEIS revealed self-healing ability for the Ce post-treated samples. The morphology of the sealed anodic films, their thicknesses and the Ce distribution were evaluated by field emission scanning electron microscopy (FE-SEM). The relatively long shelf life of the hydrolysis solution is a good prospect for industrial use of the proposed treatment.

Keywords: anodizing, TSA, hybrid sol-gel aging, EIS

Tailoring corrosion and discharge performance of Mg anode by corrosion inhibitor

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Abstract

The effect of various amounts of 5-sulfosalicylic acid (SSA) on the corrosion and discharge property of pure magnesium (Mg) is studied systematically. It was found that SSA plays a vital role in regulating the dissolution kinetics of the substrate and re-deposition rate of discharge product at the metal/electrolyte interface. Low concentration of SSA can be used as corrosion inhibitor for active Mg surface as it chelates with impurity element (Fe^{3+}), while high concentration of SSA increases dissolution rate of Mg since large amount of SSA also acts as complexing agent for the dissolved Mg^{2+}. In terms of discharge performance, addition of 0.1 M SSA improves the utilization efficiency and lowers the discharge potential in the meanwhile under different current densities. The anode demonstrates low and stable discharge potential (-1.83 V) for 10 hours at 2.5 mA cm^{-2} in SSA containing electrolyte. Localized corrosion of the substrate has been significantly facilitated during discharge test. “Thorn-like effect” has been observed for the first time for Mg with addition of complexing agent.

Water-Soluble AIE Molecule As a Fluorescence Indicator And Novel Corrosion Inhibitor For N80 Steel

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Aggregation induced luminescence (AIE) materials exhibit broad application prospects in the fields of food, biology, environmental detection and other fields due to their unique luminescent properties. There are few reports on their application in the field of metal corrosion protection. In this work, a new corrosion inhibitor was synthesised and applied as a high-efficient corrosion inhibitor for N80 steel in 15% HCl solution. The corrosion inhibition efficiency was evaluated using weight loss method and electrochemical measurements. The adsorption behaviour of inhibitor molecule and corrosion mechanism were further studied using in-situ electrochemical tests and liquid atomic force microscopy (AFM) monitoring, complemented with some surface characterizations. Results indicated that the corrosion inhibition capability of TBTPY-Py increased with the rising concentration, and the optimal corrosion inhibition efficiency reached 96.98% at 50 mg/L. TBTPY-Py successfully adsorbs on the metal surface and can form a dense hydrophobic protective layer. In addition, a fluorescence microscope was used to real-time monitor the AIE effect during the adsorption and film formation process of corrosion inhibitor molecules on the metal surface. With the extension of TBTPY-Py molecular adsorption time, the AIE effect on the metal surface was significantly enhanced, while the corrosion rate of the metal decreased, proving that the formation of corrosion inhibitor adsorption film effectively inhibited the corrosion process of the metal.

Exploration of Imidazol-4-Methylimine Thiourea as Effective Corrosion Inhibitor for Mild Steel in Hydrochloric Medium: Experimental and Theoretical Studies

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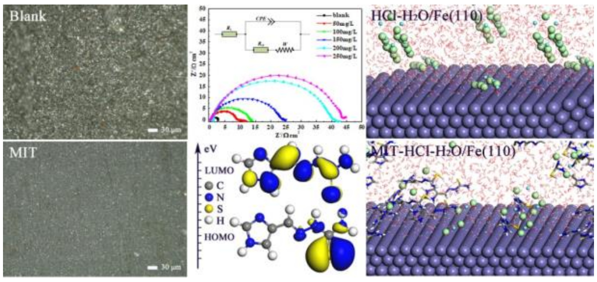
Mild steel is widely used in industrial and agricultural production [1,2]. However, in some industrial applications, HCl is frequently used in industrial cleaning processes for the MS equipment, where it can attack the metals and initiate corrosion [3,4]. This corrosion trends to degrade the performance of mild steel, causing huge economic loss or even accidents, thereby shortening the service life of MS. The addition of corrosion inhibitors is considered as a straightforward and effective way to address this problem [5,7]. In this work, a Schiff base compound of imidazol-4-methylimine thiourea (MIT) has been successfully synthesized *via* a nucleophilic addition reaction between imidazole-4-carbaldehyde and thiosemicarbazide, and then explored as an effective corrosion inhibitor for mild steel in HCl medium. The chemical structure of the MIT molecule was confirmed by FT-IR, NMR and EI-MS. The inhibition performance of MIT was evaluated by gravimetric measurements, electrochemical tests, and surface analyses. The results indicated that the optimal concentration of MIT was 200 mg/L in 1.0 M HCl solution at 298 K, with an inhibition efficiency of 93.7%. The adsorption of MIT molecules on mild steel was demonstrated to be an exothermic process according to the Langmuir adsorption isotherm, belonging to a mixed adsorption mechanism of physical and chemical adsorption (ΔG°_{ads}=-31.87 kJ mol^{-1}, 298 K), which effectively retards the MS corrosion process by blocking both anodic and cathodic reactions. Furthermore, theoretical calculations based on density functional theory and molecular dynamics simulations indicate that the corrosion inhibition mechanism of MIT molecules is mainly attributed to two effective ways, involving shielding effect of the MIT-adsorption film with multiple anchors and decrease of aggressive ions.



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Coatings & Films

Self-lubricating polymeric materials with self-healing functions

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This work aims to design and develop a strong and flexible intelligent polymer material with ultra-low friction, endow it with self-healing function through bionic method, extend the service life of polymer lubricating materials, and improve reliability and safety. The intellectualization of non-elastomer materials was realized by microcapsule oil storage and non-covalent bond reversible reforming, which endowed the rigid polymer with the function of spontaneous interfacial lubrication and crack repair under external stimulation. In terms of self-lubricating function, the influence of parameters such as lubricating medium type, microcapsule size and surface characteristics, contact load and sliding speed on interface contact behavior was systematically explored, and the coupling relationship between microstructure mechanics and lubrication performance of self-lubricating materials was analyzed; In terms of self-healing function, the factors affecting the self-healing efficiency of materials were studied, and the optimal repair conditions were proposed based on the economy of the repair process. The regulatory effects of polymerization temperature and U2-diol content on the mechanical properties of materials were discussed. Finally, the friction, repair and mechanical behaviors of the bi-functional polymer materials were explored by combining the self-lubrication and self-healing functions. The application potential of this functional polymer material in engineering practice was verified by bearing performance tests.

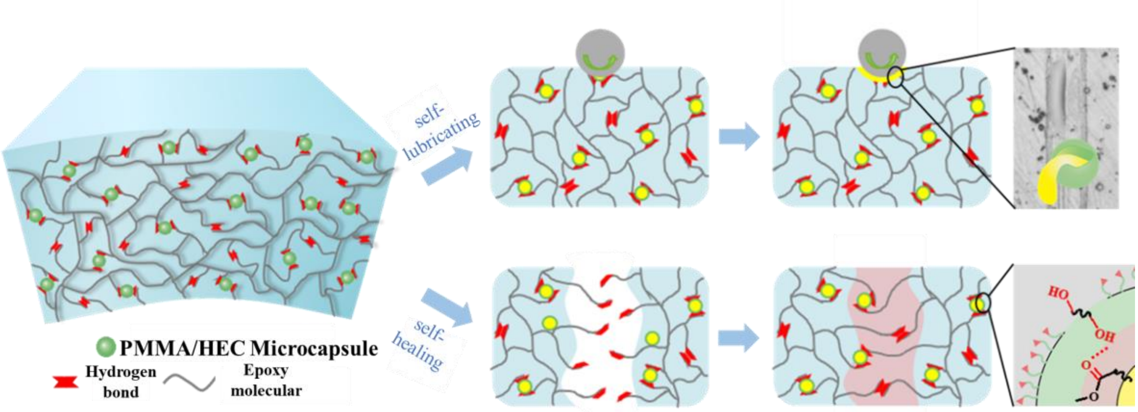

Fig. 1 Schematic diagram of lubrication and repair mechanism of bifunctional polymer materials

Investigation of self-healing coatings via macro/microscale electrochemistry

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Self-healing coatings can autonomously repair the coating defects by intrinsic and/or extrinsic strategies to recover the corrosion protection effects. The self-healing properties of coatings are generally investigated using macro/microscale morphological observation, macroscale electrochemical measurements such as open-circuit potential (OCP) test and electrochemical impedance spectroscopy (EIS), and microscale electrochemical measurements such as scanning electrochemical microscopy (SECM), scanning Kelvin probe microscopy (SKP), and localized electrochemical impedance spectroscopy (LEIS). Macro/microscale electrochemistry offers quantified data about the self-healing performance of coatings, which is of great significance in the research field of smart coatings.

In this work, different kinds of micro/nanocapsules containing corrosion inhibitors (such as benzotriazole, 2-mercaptobenzothiazole, carbon dots, and phenanthroline) and/or healing agents (including polycaprolactone and ethylene vinyl acetate) are prepared. These capsules are loaded into epoxy coatings to achieve the self-healing effect. EIS is used to reflect the influence of micro/nanocapsules on the corrosion protection and self-healing properties of coatings. Generally, the magnitude of the low frequency impedance modulus ($|Z|_{0.01\mathrm{Hz}}$) is an important semi-quantitative parameter to evaluate the corrosion protection performance of coatings. In addition, the phase angles plots and the number of time constants can also reflect the corrosion activity of different coatings. To further validate the self-healing performance of coatings, SECM is employed to study the local corrosion activity by detecting the variation of Fe^{2+} oxidation current distribution and oxygen reduction current distribution around the coating scratches during immersion in corrosive media. The coating with outstanding self-healing property confirms its great potential in smart coating design and intelligent corrosion control.

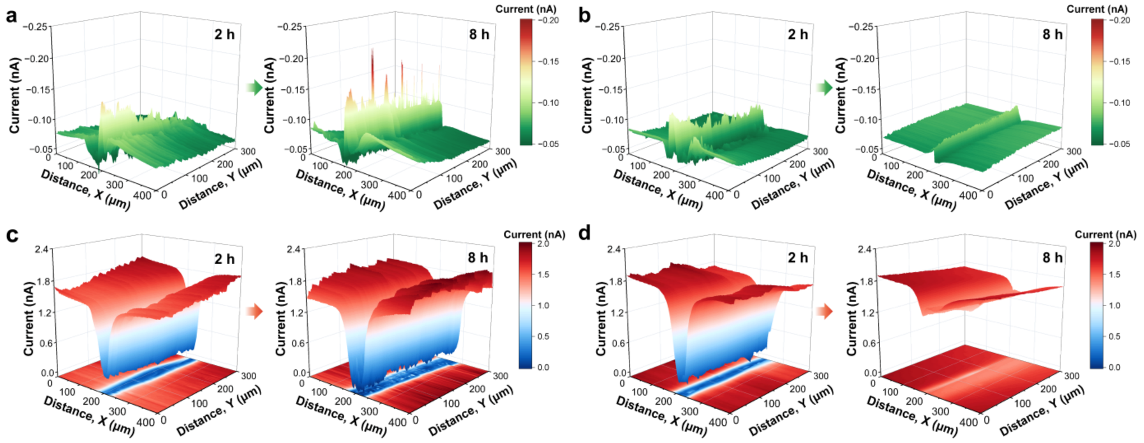

Fig. SECM mapping of the scratched (a) blank epoxy coating and (b) composite coating after immersion in 3.5 wt.% NaCl solution for 2 h and 8 h at probe tip potential +0.60 V vs. Ag/AgCl reference electrode; SECM mapping of the scratched (c) blank epoxy coating and (d) composite coating after immersion in 3.5 wt.% NaCl solution for 2 h and 8 h at probe tip potential -0.75 V vs. Ag/AgCl reference electrode.

Damaged mechanism of organic coating caused by the synergistic effect between alternating load and corrosion

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Generally, organic coatings are subjected to the synergistic effects induced by multi-factors in their service environments, resulting in their failures with multi-modes. To explore the damaged mechanism of the coated aluminum alloy, in this work, the failures of the organic coating protecting system for an aluminum alloy were studied by the combination of accelerated tests and electrochemical impedance spectroscopy (EIS). Firstly, the coating impedance index (CI) was defined as Eq. (1). The equation calculation formula of the synergistic effect (ΔCI) was proposed as Eq. (2) to study the synergistic effect.

$$CI = \lg\frac{R_{c0}}{R_{ci}} + \lg\frac{C_{c0}}{C_{ci}} + \lg\frac{C_{dl0}}{C_{dli}} + \lg\frac{R_{ct0}}{R_{cti}} \quad (1)$$

$$CI_{C,M} = CI_C + CI_M + \Delta CI \quad (2)$$

Where αc0, Qc0, and αci, Q_{ci} were the CPE parameters of EIS spectra for the organic coatings before and after tests, Rc0 and R_{ci} were their coating resistance. α_{dl0}, Q_{dl0}, and αdli, Q_{dli} were the CPE parameters of the interface at the coating/substrates before and after tests. R_{ct0} and R_{cti} were the charge-transfer resistance of the interface at the coating/substrates before and after tests. In addition, the parameter $CI_{C,\ M}$, CI_C, CI_M, and ΔCI were coating impendence index under the interaction of mechanical and corrosion, only corrosion, only mechanical actions, and their synergistic effect, respectively.

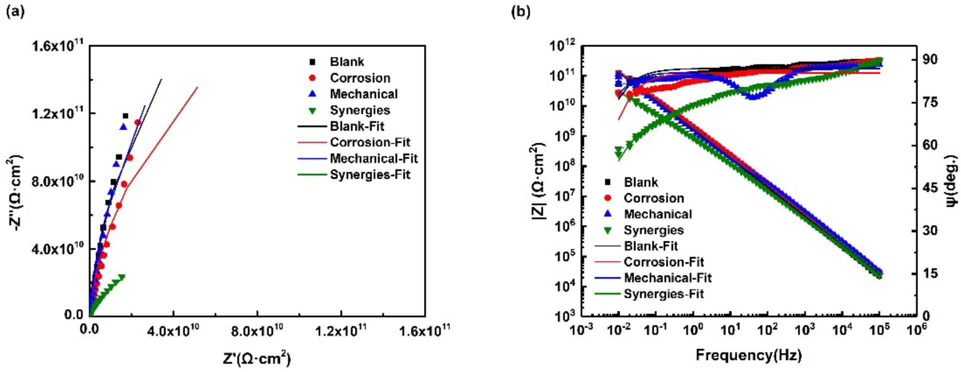

Fig. 1 EIS spectra of the organic coatings under different conditions.

Secondly, the EIS spectra of the organic coatings under different conditions were tested and the results were shown in Fig. 1. The electrochemical parameters were obtained by fitting EIS spectra in accordance with equivalent electric circuits. The values of $CI_{C,\ M}$, CI_C, CI_M, and ΔCI were calculated with Eq. (1) and (2). The results showed that the values of $CI_{C,\ M}$, CI_C, CI_M, and ΔCI were 2.6879, 0.1934, 0.4585, and 2.0360, respectively. The values of CI_C/CI_M are 0.3988 << 1, indicating that mechanical action plays a key role in the failure process of organic coating. In addition, the value of ΔCI was over 1, showing that the interaction between corrosion and mechanics accelerated the failure of the organic coating under alternating loads. It was concluded that the synergistic effect between corrosion and mechanical effect was very stronger and that it can accelerate the damage of organic coatings although the corrosion effect was relatively lower than the mechanical effect in the failure of organic coating.

Keywords: Organic coating, Alternating load, Corrosion, Synergistic effect, EIS, Accelerated tests

This research was supported by the National Natural Science Foundation of China (52171062)

Application of ORP-EIS coupled with ATR-FTIR in Kretschmann geometry as an integrated spectro-electrochemical technique to investigate the separate transport of water and ions in organic coated metals

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Electrochemical impedance spectroscopy is a highly utilized technique to investigate the anti-corrosive performance of organic coatings. One of the main governing protection mechanisms of organic coatings, is slowing down the transport of corrosive species such as water, oxygen, and ions. Understanding the transport mechanism of these penetrants as the major reason of coatings failure is of a great importance to design a durable, high-performance coating. Although EIS can provide valuable data on the electrochemical state of the system, the necessity of application of other complementary techniques for a better understanding of the dynamics of the system has been extensively proven in literature [1]. In this work, Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) as an established method to gain reliable experimental data is coupled with ATR-FTIR in Kretschmann geometry. This integrated spectro-electrochemical technique is contributing to a better understanding of the separate transport of water and ions in a polyethylene glycol diacrylate-based coating while providing molecular scale data on local chemistry changes at the coating/metal buried interface [1-3]. ORP-EIS data are modelled with an Electrochemical Equivalent Circuit (EEC) model, containing a Young impedance for representing the resistivity distribution inside the coating due to the penetration of ions [2]. The output of this integrated experiment pointed out faster kinetics of water uptake than ion diffusion, and initiation of corrosion before formation of a new time-constant in ORP-EIS data, detected by ATR-FTIR measurements.

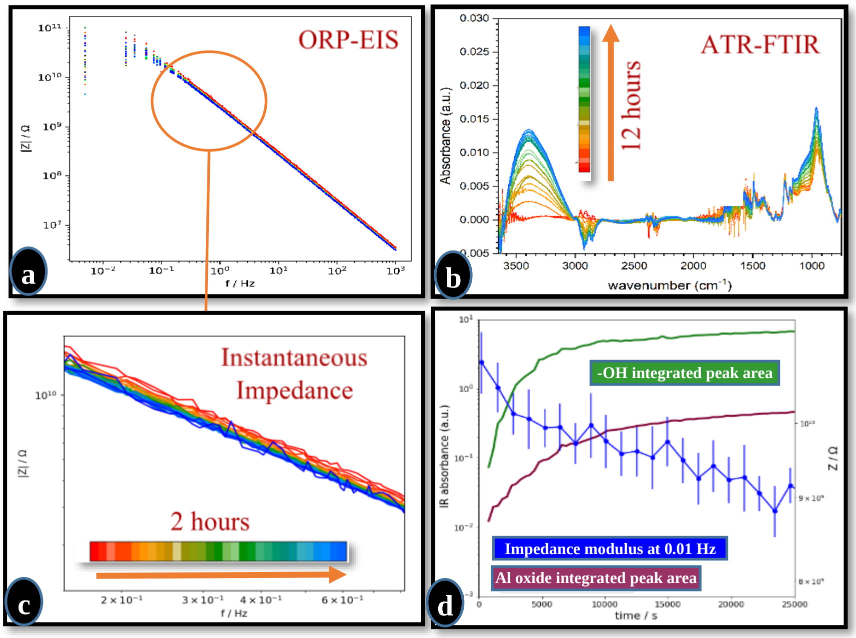

***Figure*:**

a) *ORP-EIS bode modulus plot of an exposed sample.*

b) *ATR-FTIR data of a coated crystal exposed sample.*

c) *Instantaneous impedance calculation over the first 2 hours in presence of non-stationarities.*

d) *Correlation between ATR-FTIR and ORP-EIS data, showing increase in water content and aluminium hydroxide contribution while the impedance at low frequency (0.01 Hz) is decreasing.*

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The relationship between growth mechanism of product film and in situ electrochemical behaviour of N80 steel in CO_2 corrosion at different conditions

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In petroleum and natural gas exploitation, CO_2 plays an important role in the corrosion of pipelines and related facilities. It is generally believed that ferrous carbonate ($FeCO_3$) formed at carbon steel surface in a CO_2 environment would alleviate the corrosion attack by impeding the diffusion of corrosive media. However, the presence of scaling ions in solution results in complex product film, which increased the uncertainty of corrosion, making CO_2 corrosion more complicated. Although many studies had been focused on the complicated product film and its influence on corrosion, uncertainties still exist. For example, many issues like the in situ electrochemical behaviour at high temperature and pressure, the influence of scaling ions, like Ca^{2+} and Mg^{2+}, on the structure of corrosion product film, the growth process of $FeCO_3$ at different exposure time, the 3D microstructure of the product film and its relation to corrosion behaviour, and so on.

The present work focused on the growth behaviour of CO_2 corrosion product and the relationship among corrosion rates, electrochemical behaviour and the microstructure of the product film in different conditions, including immersion time, temperature and the presence of different concentrations of Ca^{2+}. At condition of 120℃, 2 MP CO_2 and 3.5% NaCl, the exposure time had remarkable influence on the corrosion rate, electrochemical behaviour and microstructure of the product film. With increase of exposure time, corrosion rates decreased notably. The diameter of capacitive arcs increased, indicating the rising of protectiveness of the product film. SEM images showed that, with the increase of exposure, the $FeCO_3$ crystal turned from regular rhombus shape to stratified structure, which can be ascribed to the dissolution and recrystallization on the formed crystal. Detail analysis from XRD and XPS revealed the product film growth process. Additionally, synchrotron irradiation 3D μ-CT was applied to analysis the 3D structure of the product film. It showed that the porosity of the corrosion product films decreased with the increase of exposure time, which was in good agreement with corrosion rate and electrochemical results.

Consequently, the influence of Ca^{2+} on the growth mechanism of CO_2 corrosion products was also investigated by weight loss, in situ electrochemical measurements and analysis of corrosion products. With the increase of Ca^{2+} concentration in solution, the crystallinity of product film, $Fe_xCa_{1-x}CO_3$, weakened and gradually turned to amorphous structure, which provided less protectiveness and elevated the corrosion rate. The high concentration of Ca^{2+} resulted in the “unstable” growth of $Fe_xCa_{1-x}CO_3$. At 10000 mg L^{-1} Ca^{2+}, complicated $Fe_xCa_{1-x}CO_3$ structures with different Ca content formed. The linear relation between Ca^{2+} concentration in solution and molar fraction of Ca in the film was also proposed.

Additionally, investigation was carried out regarding the scale formation behaviour of N80 steel in CO_2 environment at different temperatures and immersion time by in-situ electrochemical and surface analysis techniques. It showed that the temperature and immersion time had significant influence on electrochemical behaviour, which was due to the different scales formed on N80 steel surface. The scales formed at 60℃ and 90℃ were mainly corrosion products. At 120℃ and 150℃, the scale consists is $CaCO_3$. The formation of $CaCO_3$ inhibits the corrosion and the formation of $FeCO_3$. $CaCO_3$, formed in 150℃, is aragonite, which provides better protection to substrate for its compact structure.

Electrochemical investigation of titanium alloy corrosion triggered by electroactive *Desulfovibrio ferrophilus* biofilm in simulated seawater containing exogenous electronic shuttle

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Titanium alloys are widely used in marine engineering due to their excellent overall mechanical properties and corrosion resistance [1]. Excellent biocompatibility of titanium alloy contributes to microbiologically influenced corrosion (MIC) triggered by adhering biofilms [2]. In this work, A series of electrochemical methods, in particular electrochemical impedance spectroscopy (EIS), were used to investigate the MIC behaviour of titanium alloys induced by electroactive *Desulfovibrio ferrophilus* biofilm. The addition of the electron shuttle significantly reduced the impedance and R_{ct} values of the titanium alloy and decreased the phase angle in the low frequency region (Fig. 1a, b, c, d), indicating that the electron shuttle accelerated the destruction of the protective layer of the titanium alloy surface in the *D. ferrophilus* environment and decreased the energy barrier for the bacteria to obtain electrons. The Hilbert-Huang transforms revealed the formation of corrosion pits (Fig. 2). Potentiodynamic polarization curves measurements proved that riboflavin-shuttle increased the anodic dissolution rate

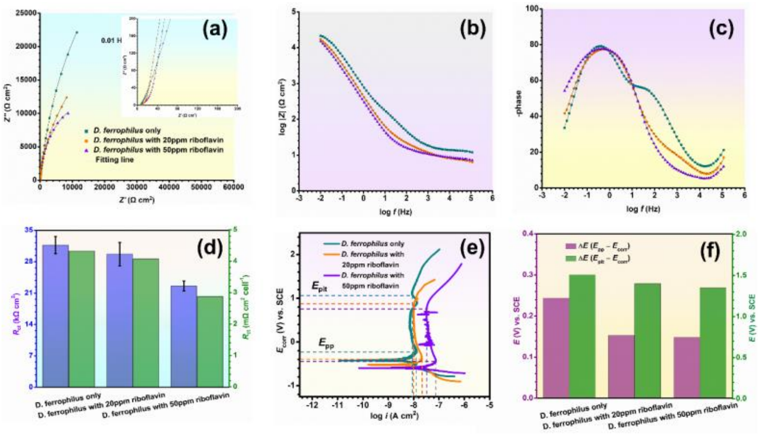

Fig. 1. EIS plots (a, b, c), Rct values (d), Tafel curves (e) and Δ*E* values (f) of TC4 samples in different broths.

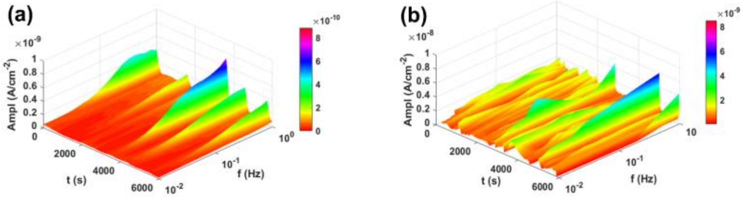

Fig. 2. Hilbert-Huang spectra on day 14: SRB without (a) and with 50 ppm riboflavin (b).

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Degradation of a solvent-free general epoxy coating in three simulated environments and its lifetime prediction

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Abstract: The failure process of an environmentally friendly solvent-free epoxy coating in 3.5% NaCl solution, neutral salt spray and alternating hot and cold temperature immersion environments was investigated by using electrochemical impedance spectroscopy (EIS), open circuit potential (OCP) and adhesion test methods. The failure mechanism of the coating in three accelerated corrosion environments was investigated by equivalent electrical circuit fitting combined with Fourier transform infrared spectroscopy (FTIR) and Scanning electron microscopy (SEM-EDS). The protective performance, failure criteria and life prediction methods of the solvent-free epoxy coating on 9440 low alloy steel were discussed. The results indicated that the deterioration of the coating in 3.5% NaCl immersion and salt spray is mainly a physical process, while in the alternating hot and cold temperature immersion it is also accompanied with change in chemical structure. A reference criterion of failure for the solvent-free epoxy coating on 9440 steel is suggested to about $1\times10^7\ \Omega\ \mathrm{cm}^2$, because corrosion products were observed on the surface of steel substrate under electron microscopy before the blisters occurring on the coating by naked eyes. The empirical linear relationship between low-frequency impedance modulus ($\ln(|Z|_t - |Z|_m)$) and time is available in predicting the service lifetime of the solvent-free general epoxy coating, in which the determination of the failure criterion is a key influencing factor. The prediction result obtained by using $1\times10^7\ \Omega\ \mathrm{cm}^2$ of low-frequency impedance as the criterion at failure is closest to the actual results. The empirical formula was improved by replacing the impedance $|Z|_t$ to the phase angle at 15 kHz ($\varphi_{15\ \mathrm{kHz}}$). It was found that the phase angle ($\varphi_{15\ \mathrm{kHz}}$) dropping to 70 ° can be used to be a failure threshold for the epoxy coating lifetime prediction.

Keywords: Solvent-free epoxy coating; Low alloy steel; Protective performance; EIS; lifetime prediction

Operando ORP-EIS for in situ monitoring of metal surface treatment processes

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Electrochemical Impedance Spectroscopy (EIS) is employed to study the electrochemical processes that satisfy the causality, linearity and stationarity requirements [1]. These requirements hinder the application of the conventional EIS to investigate ongoing electrochemical processes including anodizing and conversion treatments. However, in situ monitoring the oxide film formation can provide an opportunity to better control the properties of the oxide layer. Hence, in situ monitoring of the surface treatment processes is of prime importance.

The Odd Random Phase Electrochemical Impedance Spectroscopy (ORP-EIS) technique, developed in our research group, can measure the time-resolved impedance of non-stationary systems [2]. This methodology was recently extended to quantify nonlinear distortions and obtain Best Linear Time Varying Approximation (BLTVA) of nonlinear time-varying processes like the corrosion process [3]. In the current research, the operando ORP-EIS technique is applied for in situ monitoring of the anodizing of aluminum (Al) [1] and the conversion treatment of zinc. For the anodizing process, according to figure1, the capacitive time constant can correspond to the barrier properties of the oxide layer and enables us to follow the growth of the barrier oxide layer. Moreover, the inductive time constant may be an indication of the surface charge accumulation [4]. On the other hand, this technique makes it possible to monitor the conversion treatment of zinc and the role of organic and inorganic additives on the barrier properties of the conversion layer in situ in the bath. Therefore, the operando ORP-EIS plays a key role to study and better control the surface treatment processes.

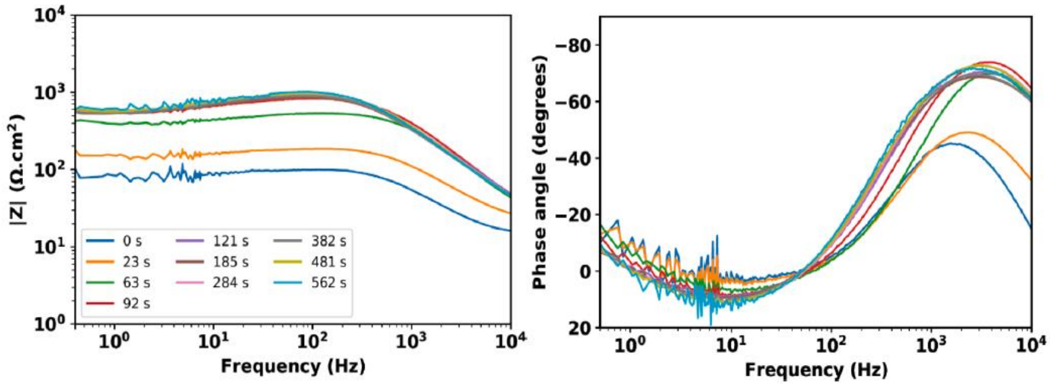

Figure1: Bode plot during the anodizing of AA2024 in the 0.1 M H_2SO_4 solution at room temperature. The anodizing DC potential 20 V (1 min sweep at a rate of 20 V/min and 9 min plateau at 20 V).

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A bifunctional epoxy coating doped by cerium (III)-8-hydroxyquinoline: early self-reporting and stimuli-responsive inhibition on corrosion of Al substrate

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Recently, anti-corrosion coatings with auto-inhibition and self-reporting on their premature flaws are becoming more and more attractive. In this work, we engineered a cerium nitrate/8-hydroxyquinoline (Ce-HQ) hybrid pigment to endow epoxy coatings with corrosion self-inhibiting and fluorescent self-reporting performances via molecule design. The Ce-HQ pigments were synthesized by physical mixture and then dispersed into the commercial epoxy coating. Once the epoxy coating gets degraded, the underneath aluminum alloy matrix may corrode to produce Al^{3+} ions, which can compete with Ce^{3+} ions in Ce-HQ complex, and then chelate with dissociative 8-HQ to form fluorescent Al-HQ complex, due to the higher bonding strength of Al^{3+} with 8-HQ than Ce^{3+} ions. Thus, not only the responsive releasing of Ce^{3+} ions and 8-HQ can inhibit the underlying Al alloy, but the newly formed Al-HQ complex could indicate the location and severity of coating flaws through fluorescent emission under UV light. Electrochemical impedance evidenced that the composite epoxy coating containing 1% mass Ce-HQ presents high corrosion resistance even after 504 h of salt spray test, showing 90% corrosion refraining efficiency. This work may enlighten an approach to developing self-healing and self-diagnosis coating for premature corroded Al alloy beneath coatings via reactive release and fluorescent visualization.

Keywords: Epoxy coating; 8-hydroxyquinoline; Corrosion inhibitor; Fluorescent visualization; Coating defect.

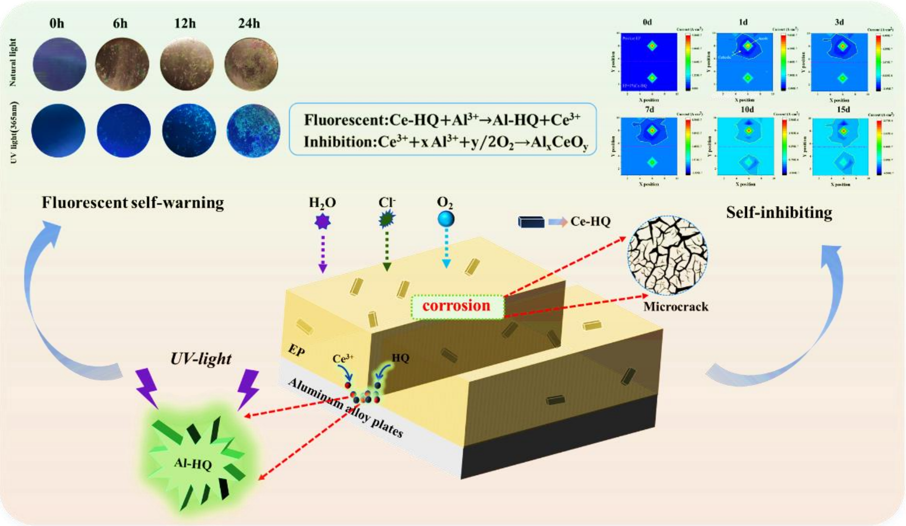

Fig.1 Schematic illustration of corrosion inhibition and fluorescence self-warning mechanism on coating defects on Al substrate.

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An EIS study of corrosion resistance and antibacterial activities of a new composite coating on AZ91 magnesium alloy surface

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Magnesium alloys have considerable potential as gastrointestinal stapler due to their favorable mechanical properties, biocompatibility and degradable properties [1]. In this study, we prepared chitosan-stearic acid-Ag nanoparticles/micro-arc oxidation (CS-SA-Ag NPs/MAO) coatings on the surface of AZ91 magnesium alloy and investigated their corrosion resistance in simulated intestinal fluid (SIF) inoculated with intestinal sulfate-reducing bacteria (SRB) [2]. The antimicrobial properties, biocompatibility, and mechanical bonding properties of the composite coatings were also investigated [3]. The experimental results indicated that the hydrophobic copolymer CS-SA formed by SA grafting on CS through amination reaction closely covered the surface of MAO, and the static contact angle of the composite coating reached 135.7 ± 2.1°. After 21 days of immersion in SIF, SRB proliferated on the surface of AZ91 magnesium alloy, resulting in dense corrosion pits, while the composite coating showed excellent corrosion resistance and bacterial inhibition with almost no SRB adherence and growth. The stabilized impedance modulus, the positive shift of E_{corr} and the decrease of i_{corr} also demonstrated the superb corrosion resistance of the composite coating. Fibroepithelial cells grew well during contact incubation on the coating surface, and the micron scratch test results showed that the bond strength of the coating increased slightly after immersion, meeting the required biomechanical compatibility of the implanted material.

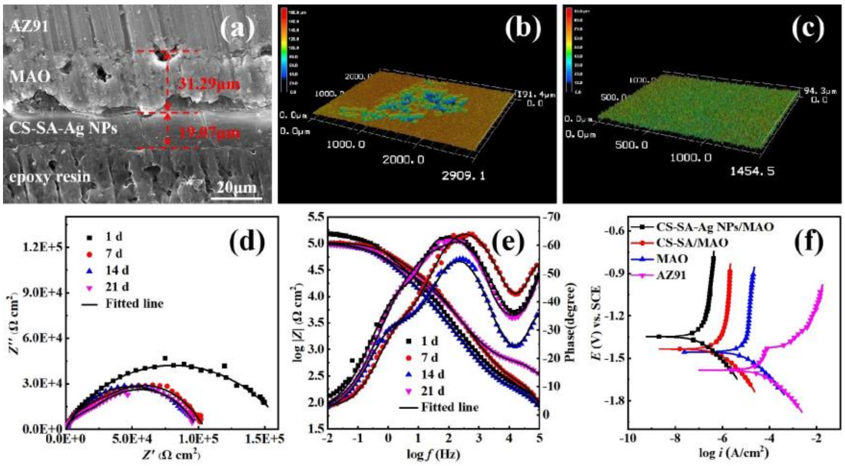

Fig. 1. Cross-sectional view (a); 3D morphologies of (b) AZ91 substrate; (c) the composite coating; Nyquist and Bode plots of EIS (d, e); Potentiodynamic polarization curves (f).

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The surface chemical reconstruction of Cu-Al alloys: Improving their service performance in harsh environment

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Copper alloy has become one of the main forces of marine materials in service due to its excellent seawater corrosion resistance, marine biofouling resistance, comprehensive mechanical properties and processing properties. However, due to the harshness of the marine corrosive environment, corrosion failure of copper alloy parts often occurs during service, resulting in higher maintenance costs of marine equipment, and even threatening the safety of equipment. The corrosion resistance of copper alloy is closely related to its microstructure. It is an important way to improve its corrosion resistance by adjusting the microstructure through appropriate processes, and it is also a hot research topic in the field of materials. First of all, it is necessary to clarify the relationship between the microstructure characteristics and corrosion behavior of copper alloy. However, there is a lack of relevant research in this field, and there are many contradictions and disputes. Therefore, it is of great theoretical significance and practical value to study the relationship between microstructure and corrosion behavior of typical marine copper alloys. However, because it is difficult to synthesize CuAl alloy with precise composition and controllable structure at the atomic level based on the experimental route, there are few reports in recent years. As a result, the corrosion resistance mechanism of CuAl alloy is still unclear. In order to understand the above alloys from the atomic point of view, the theoretical design and structural characterization of CuAl alloy were carried out by using DFT calculation through simple and accurate control of its composition and lattice structure.During the construction of the Cu-Al alloys, the CuAl (111) (Cu:Al =14:1, atomic ratio, the same below) slab models with a face-centered cubic (FCC) structure are firstly obtained after abulk optimization.Following are the important features concerning the results reported herein.

1) The segregation of Al atom exists in the surface and sub-surface layer of Cu-Al binary alloy. When Al segregates 11 atoms on the surface layer, the lowest formation energy(ΔE_f) of the alloy is -8.90eV, and the structure is the most stable. While Al segregates 10 atoms in the sub-layer, the lowest ΔE_f of the alloy is -7.13eV. Comparing the ΔE_f of the two structures above, it is concluded that the binary alloy Cu-Al is the most stable structure when the surface segregation has 11 Al atoms. The segregation of Al in sublayer is calculated on the basis of CuAl-b11, and the lowest ΔE_f of five Al atoms in sublayer is -10.92eV.
2) The cohesive energy(ΔE_c) of Cu is 277.55eV, while the ΔE_c of CuAl-b11 and CuAl-b11-y5 are 240.51eV and 243.68eV, which are close to the ΔE_c of pure copper,which show that CuAl-b11 and CuAl-b11-y5 have thermodynamic stable structure. Additionally, CuAl-b11 and CuAl-b11-y5 have the lowest ΔE_c in the corresponding binary alloys, which indicates that they have thermodynamic stability.
3) According to the comparison of activation energy barrier(ΔE_a) between CuAl-b11 and CuAl-b11-y5, CuAl-b11-y5 has a lower ΔE_a of 3.98eV than CuAl-b11, indicating that CuAl-b11-y5 alloy has a more stable thermodynamic structure than CuAl-b11 alloy.
4) The value of vacancy formation(ΔE_{vac}) energy of pure Cu (111) surface is calculated as 1.27 eV. In contrast, the ΔE_{vac} of CuAl-b11-y5 (1.51eV) is higher than that of CuAl-b11 (1.48eV),which shows that the segregation of Al atoms in the sublayer helps to improve the stability of *structure.
5) The center of d band(ε_d) recorded by CuAl-b11 is -3.40eV, which is more negative than that of pure Cu (- 2.42eV). In contrast, the ε_d of CuAl-b11-y5 is -2.46eV, which is slightly negative than that of pure Cu. The negative shift of the ε_d helps to weaken the adsorption of oxygen on the alloy surface, inhibit the occurrence of oxidation reaction, and make the alloy more corrosion resistant. Similarly, the ε_p of Al atoms in CuAl-b11 and CuAl-b11-y5 are - 2.31eV and - 2.46eV, which are more negative than that of CuAl (-1.42eV).

This work was supported by the National Natural Science Foundation of China (grant No. 22278016).

具有坚固超疏水性的多功能耐用无氟防腐涂层的设计与实现

Design and realization of versatile durable fluorine-free anti-corrosive coating with robust superhydrophobicity

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Bio-inspired superhydrophobic coatings are of increasing interest in marine corrosion protection due to superior barrier and shielding effects. Herein, a robust durability, self-cleaning and anticorrosion superhydrophobic coating based on epoxy resin matrix has been successfully fabricated by spraying technology without using any fluorine materials. The prepared coating possessed excellent superhydrophobicity and is applicable to a variety of substrates, which was ascribed to the effect of low-surface energy material kaolin modified by titanate coupling agent. SEM and LSCM observed that the coating has the morphology feature of "hills and mountains", which can store air to reduce solid-liquid contact. The prepared coating had greater impedance modulus and charge transfer resistance by EIS test, and displayed outstanding durability in salt spray environment compared with epoxy coating. In addition, the abrasion, standard cross-cut tape and self-cleaning tests indicated that the superhydrophobic coatings had robust mechanical stability and excellent resistance to contaminants, which lays the foundation for the application of superhydrophobic coating in practical environment.

Features of electrochemical impedance spectroscopy during the failure of conductive coatings

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Conductive coatings first appeared in the twentieth century. In the past ten years, conductive coatings have been applied in various military and civil industries such as electronics, electrical appliances, aviation, chemical industry and printing. However, there are two problems in the practical application of conductive coatings: one is that the conductive property of coatings is too low, the other is that the potential difference between coatings and metal substrate is too large.

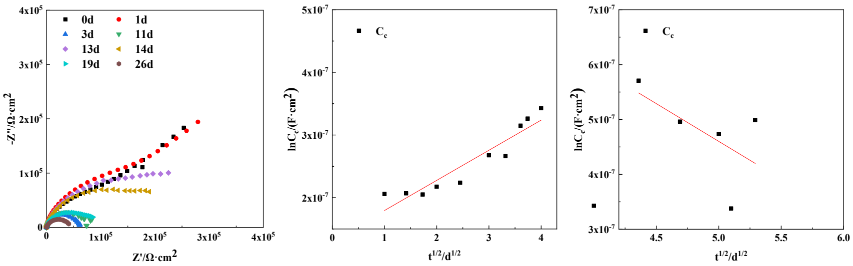
In this paper, based on the principle of galvanic corrosion, galvanized graphite conductive filler is prepared, which can reduce the potential difference and greatly improve the conductivity of the coatings. Secondly, the electrochemical behavior between galvanized graphite coatings and aluminum alloy substrate was analyzed by electrochemical method and the corrosion failure process of coating system was studied deeply. The main conclusions are as follows:

(1) After chemical galvanizing, the galvanic corrosion tendency between coating and aluminum alloy decreases but the corrosion degree increases;

(2) The failure process of zinc coated graphite coating can be divided into two stages according to the characteristics of electrochemical impedance spectrum. Accordingly, the transmission behavior of corrosive medium in the coating can be divided into Fick diffusion and non-Fick diffusion.

(3) In the process of coating failure, the micropore resistance and interfacial charge transfer resistance of the coating increase first and then decrease, which indicates that the corrosion resistance of the coating increases first and then decreases.

Keywords: conductive coatings, corrosion failure, electrochemical characteristics



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Global and local electrochemical behaviors of the in-situ conversion coating of Mg alloy based on EIS and SVET

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Mg and its alloys are widely used in communication, aerospace, lightweight engineering and other fields, due to its unique physical and chemical properties [1]. However, Mg and its alloys have active chemical properties, and it is easy to be corroded and worn in the practical services. Therefore, huge economic losses occurred and potential security risks existed [2]. In this work, a self-assembly composite coating was constructed on the surface of the Mg alloy by chemical conversion and silanization treatment, and the global and local electrochemical behaviours of the composite coating were studied by EIS and SVET.

The EIS results showed that the impedance modulus at low frequency ($|Z|_{0.01}$) of Mg alloy with the composite coating was much higher than that of the Mg alloy, and it increased at first, and then decreased with time, showing that this composite coating can protect Mg alloys from corrosion. After immersed for 40 hrs, an inductive loop in low frequency region was observed, indicating that this coating was subjected to pitting damage. SVET results were showed in Fig.2. In the early immersion stage, the distribution of the surface current density for this coating was fluctuant state, showing that the surface of this coating was a dynamic equilibrium sate, due to the existence of pores in the coating. With the increasing time, the surface current density of this coating became more uniform, further indicating that this coating has a better anti-corrosion performance. However, the pitting was obviously observed based on the SVET results after 40 hrs. This was consisted with the global EIS results.

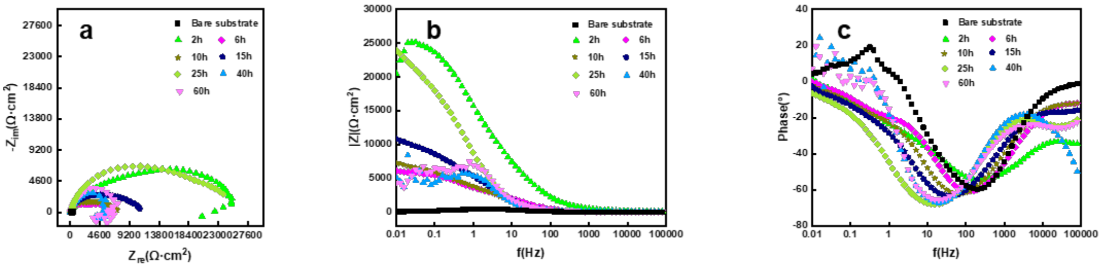

Fig.1 EIS spectra of composite coating with and without this coating in a 0.5% NaCl solution (a: Nyquist plot; b-c: Bode plots)

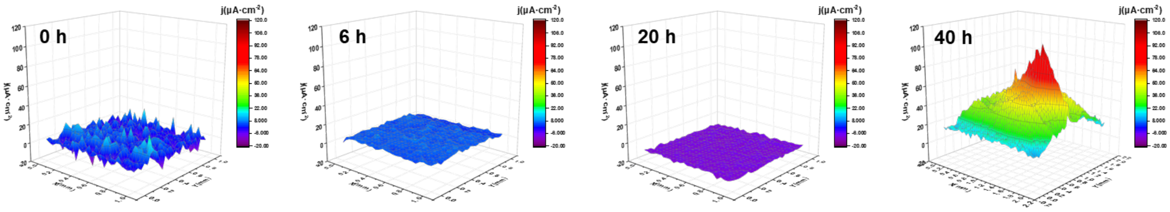

Fig.2 Current density distributions of the specimens with this coating

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Preparation and Electrochemical Corrosion Behavior of Graphene-Al_2O_3 Mixed Coating on Carbon Steel Substrate

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In the research of metal corrosion protection, the exploration of conductive anti-corrosion coatings is of great significance for practical engineering applications with dual requirements for conductivity and corrosion protection[1], such as the corrosion protection of grounding grids in the power systems[2]. As a revolutionary material with excellent physical properties[3], graphene is increasingly playing an important role in the research of non-metallic coatings in the field of metal corrosion protection[4]. In this work, an electrodeposition method of stable graphene-Al_2O_3 composite coating on Q235 carbon steel substrate was investigated, and the microstructure, electrical conductivity and electrochemical properties of the composite coating were characterized and analyzed. The results of electrostatic / dynamic potential polarization curve measurements and electrochemical impedance spectrum analysis show that the composite coating not only has good corrosion inhibition characteristics, but also has good electrical conductivity characteristics. In addition, the inhibition mechanism of the graphene-Al_2O_3 coating on corrosion behavior of carbon steel is also discussed in the 3.5% NaCl solution (See Fig. 1), which can be provides a technical reference for engineering application of the combination of electrical conductivity and anticorrosion function.

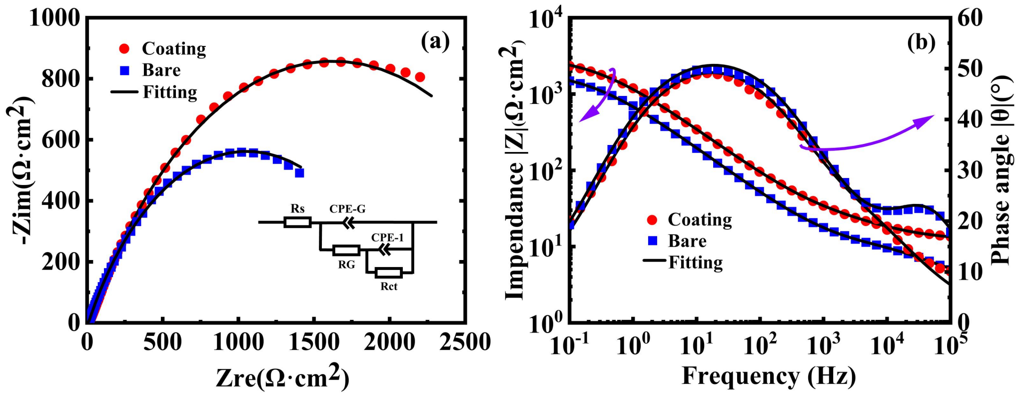

Fig. 1 (a) Nyquist and (b) Bode plots of the bare and coated Q235 steels in the 3.5% NaCl solution.

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Study on the corrosion resistance of highly conductive composite coatings

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High conductive coating has been widely used in electronics, aviation and other fields. However, good electrical conductivity makes this type of coating very susceptible to corrosion damage during its services. Therefore, it is of great practical significance to obtain a high conductive coating with a good corrosion resistant performance.

In this paper, a variety of conductive fillers were used to prepare high conductive coatings. The effect of the addition of corrosion inhibitors on the corrosion resistance of the high conductive coating was studied by electrochemical technology. Experimental results showed that:

Fristly, when 70 wt.% silver-coated copper filler was added to this coating, the square resistance of the coating was 0.081 Ω/□, but its salt spray resistance was poor.

Secondly, the polarization results showed that the corrosion inhibition rate was up to 99.0% after the corrosion inhibitors [m(benzotriazole):m (2-mercaptobenzothiazole sodium):m (ethanolamine phosphate) =$A_3B_1C_3$] was added, and the optimal concentration of the corrosion inhibitor was 12000 ppm.

Thridly, EIS spectra showed that the arc radius of the capacitance-reactance increases significantly, and the phase Angle in the bode diagram is also significantly closer to -90°. The impedance modulus at the low-frequency of the coating increased from 526.6 $\Omega \cdot cm^2$ to 3104 $\Omega \cdot cm^2$ after the corrosion inhibitor added into the conductive coating. However, although its corrosion resistance was significantly improved, but the conductivity of the coating decreased, and its square resistance increased to 0.133Ω /□.

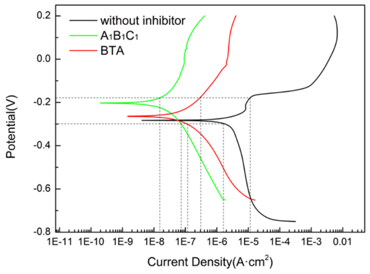

Fig.1 Potentiodynamic polarization curves of red copper and silver under different inhibitor ratio

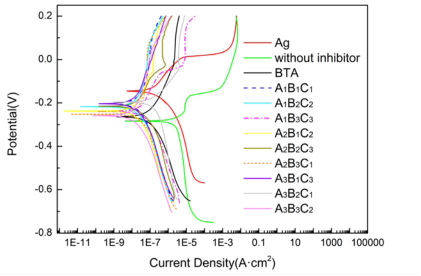

Fig.2 Potentiodynamic polarization curves of red copper in different inhibitor environments

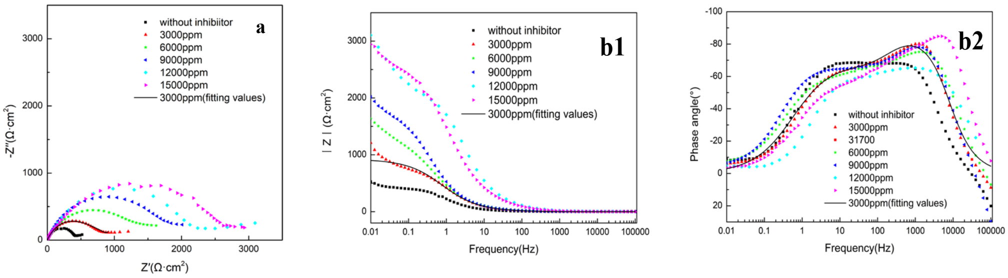

Fig.3 EIS spectra of the conductive coating containing Ag/Cu powders and mixed inhibitors
（a: Nyquist plots; b1-b2: Bode plots）

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Effects of Tensile Stress on the Corrosion Electrochemical Behaviors of Coated 2024-T3 Al-Alloys*

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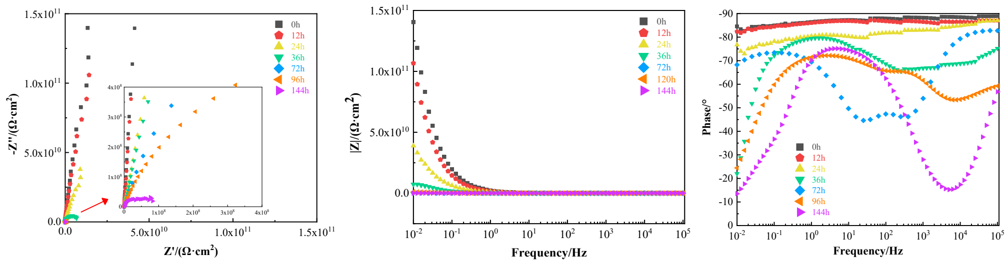
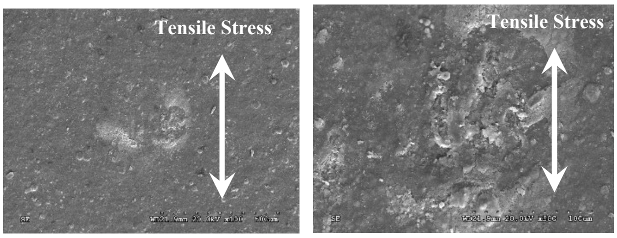
Al-alloys are commonly used in many industry fields, such as aerospace, supercomputing, shipbuilding due to the good specific strength and formability. Organic coatings are usually used for protecting Al-alloys from corrosion. However, the failure of coated structures is often accelerated when they are subjected to the tensile stress. Finally, the mechanical properties of coated structures decrease because of the occurrence of local corrosion to the metallic structures. Therefore, the effects of tensile stress on the corrosion electrochemical behaviors of the coated 2024-T3 Al-alloy were significantly studied.

In this article, the electrochemical behaviors were studied by accelerated tests in conjunction with electrochemical impedance spectroscopy(EIS). The EIS spectra of the coated Al-alloy electrodes in a 3.5% NaCl solution during they were loaded with constant tensile stress were shown in Fig.1. It was found from **Fig.1** that the Nyquist plot was a large capacitive loop with one time constant at the early stage. With time elapsed, EIS spectra became a depressed capacitive loops with two time constants, indicating that there were obvious effects of tensile stress on the corrosion electrochemical behaviors of the coated 2024-T3 Al-alloy in a 3.5% NaCl solution. After the coated 2024-T3 Al-alloy was immersed in a 3.5% NaCl solution under the constant loads for 144 hrs, the surface of the coated Al-alloy became rougher and some rust spots were observed, showing that tensile stress induced the forming and growing of some new micro-defects, and at the same time, the original micro-defects in organic coatings grew with time. In this case, these micro-defects gradually became the transportation channels of corrosive media in organic coatings. Finally, the failure of organic coatings was accelerated due to the synergistic effects.



Nyquist Bode(a) Bode(b)

Fig.1 EIS spectra of the coated Al-alloy electrodes in a 3.5% NaCl solution under constant loads



(a) Rust Spots (b) Enlarged View

Fig.2 Surface morphology of the coated Al-alloy after it was immersed in a 3.5% NaCl solution under constant loads for 144 hrs

Keywords: Aluminum Alloy, Organic Coating, Coating Failure, Tensile stress, Accelerated Tests, EIS
*This project was funded by National Natural Science Foundation of China (52171062)

Application of EIS on antifouling coatings

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Abstract: EIS has proven to be an effective method for evaluating the protective performance and studying the failure mechanism of coatings and has been widely used in the field of anticorrosion coatings, but little research on application to antifouling coatings. In this study, the failure behavior of self-polishing antifouling coatings in freshwater, seawater, and alternating freshwater/seawater environments was investigated by using EIS in combination with adhesion testing and morphological characterization. It was shown that self-polishing antifouling coatings fail first in alternating freshwater/seawater environments, followed by freshwater and finally seawater.

The failure of self-polishing antifouling coatings in alternating freshwater/seawater environments can be divided into three stages: rapid penetration of the medium, reaction at the coating/metal interface and spalling of the coating. EIS of the antifouling coating at different stages is shown in Figure 1 and exhibits different characteristics in three failure stages. The permeability of freshwater is better than seawater and its main role in the first stage. Corrosiveness of seawater is stronger than freshwater and dominates in the second stage. The alternation of freshwater and seawater leads to a significant decrease in the adhesion of the coating to the metal interface, which eventually leads to the failure of the coating. This study proves that EIS can be used to study antifouling coatings in depth as well, providing a new method for performance testing and life prediction of antifouling coatings.

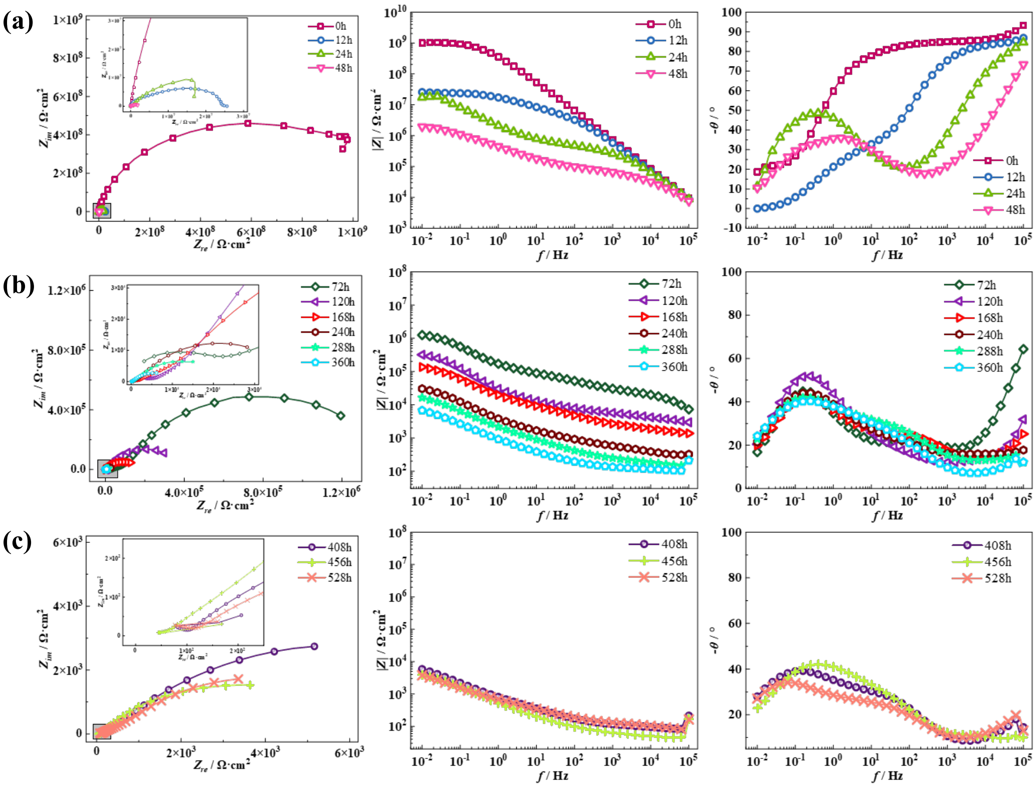

Figure1. EIS characteristics of failure process for self-polishing antifouling coating:
(a) Stage I, (b) Stage II, (c) Stage III

Battery

Scientific basis of energy storage technology for iron-chromium redox flow batteries

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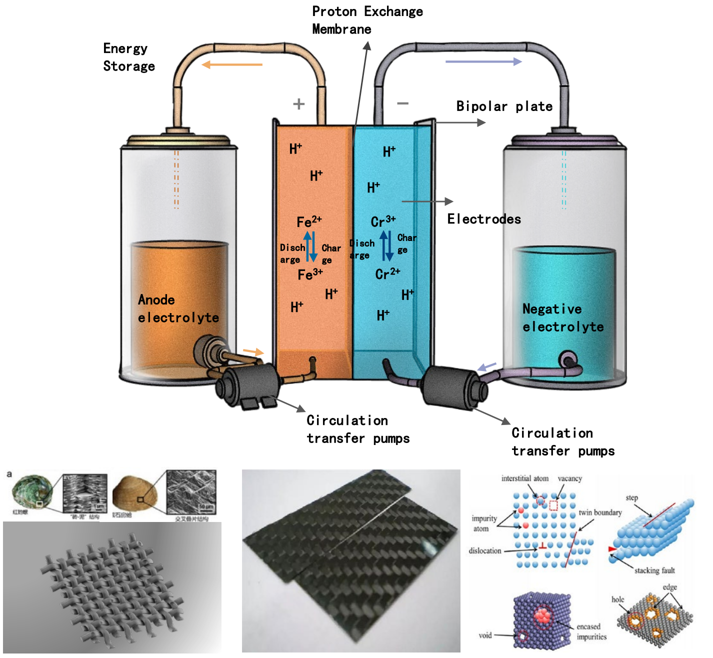
The iron-chrome flow battery technology shows the advantages of low cost, long life, intrinsic safety, and wide temperature operation. It is a large-scale grid-level energy storage technology. However, there are still problems, such as low current density, difficult control of hydrogen evolution side reactions, and easy attenuation of cycle energy density at this stage, which affect the commercial-scale applications. Quan Xu research group revealed the key regulatory factors of electrode density enhancement and inhibitions, took the lead in preparing three-dimensional biomimetic woven carbon cloth to significantly reduce the electric resistance of electrodes, whilst improved the surface-active sites of electrodes by introducing surface functional groups and modifying defect sites. It is the first to propose graphite bipolar plate open flow channel and wetting modification design, which considerably reduces the concentration polarization and suppress the side reaction of hydrogen evolution. A series of achievements have been applied to the construction of small-scale and pilot-scale tests and 100 kW/400 kWh demonstration project. The system has achieved the direct current side energy efficiency of 80.1%, current density of 140 mA/cm^2, and completed the technical appraisal.



3D bionic braided carbon cloth electrode

Bionic carbon fossil graphitization process

Electrode surface defect design improves the deposition efficiency of Bi and In catalysts

Figure 1. Construction of surface defects and heteroatom doping of 3D biomimetic woven carbon cloth

In-situ measurement of multi-physics field and voltage loss distribution in proton exchange membrane fuel cells

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The reaction state in proton exchange membrane (PEM) fuel cells is affected by the multi-physics fields, including the temperature, relative humidity, and gas supply, which are difficult to observe. Especially when the active area is large, there is a significant uneven distribution in the reaction, resulting in decreasing performance of fuel cells. However, existing methods can not effectively obtain the complex multiple operating states simultaneously, which bring about difficulties in understanding the uneven voltage loss in the fuel cells. Hence, a novel method is developed to obtain the distribution of temperature, humidity, current density, and high frequency resistance based on printed circuit board technology. Various kinds of voltage losses in each area of fuel cells can be decoupled using the measured date of the multi-physics fields. Using this method, effects of operating conditions on the multi-physics fields and voltage losses in fuel cells can be analyzed. In addition, the changes inside the fuel cell are also investigated during the dynamic loading process. The results show that the flow field configuration, operation conditions, and dynamic loadings affect the distributions of reaction states in the fuel cell. This method is helpful to observe the internal multi-physics fields, and understand the influence mechanism of operating conditions and dynamic loadings on the performance of fuel cells.

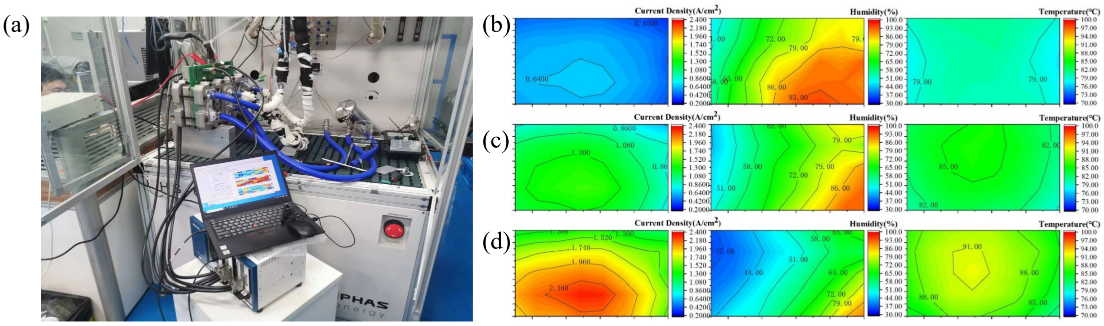

Figure 1. (a) Experimental setup, and measured distributions of current density, humidity and temperature at the current densities of (b) 0.6A/cm^2, (c) 1.2A/cm^2, (d)1.8A/cm^2

A Theoretical Study on the Mechanical Effect on Impedance Response of Lithium Ion Batteries: from Single Particle to Porous Electrode

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The crystal lattice of the material of lithium ion battery changes with the stoichiometric change of Li$^+$, which leads to the structural variation and induces stress of the particles and the electrodes. The induced stress could lead to particle fracture, electrode delamination and eventually the severe capacity decrease during cycling. To alleviate severe stress-induced degradation in cell life, understanding the mechanical effect on the electrochemical processes inside the battery, is critical. In the previous study, the theoretical study on the mechanical effect is focused in the time domain,[1-4] while the mechanical effect on the electrochemical processes in the frequency domain is seldom discussed before.

In this study, we derived the impedance model in the particle and electrode scales to study the mechanical effect on the electrochemical impedance, as shown in Figure 1. In the particle scale, the coupling of the Li$^+$ intercalation /de-intercalation reaction at the particle surface and the surface stress is considered. A characteristic semicircle in low frequency range, which is due to the stress effect, is found. The visualizability of the stress-induced semicircle in the experiments is found to be related to the characteristic frequency of the Li+ diffusion. Through simplifying the model expression under three different limiting cases, two dimensionless number are defined to evaluate the stress effect. In the electrode scale, the mechanical interaction of the particles is considered and the modified impedance model is derived using theoretical framework for the impedance response of porous electrode.[5] The impedance response of the electrode is found to be influenced by the effective mechanical properties and the connection between current collector and electrode. Finally, the impedance models for the single particle and porous electrode are verified using the single particle experiments and coin cell respectively.

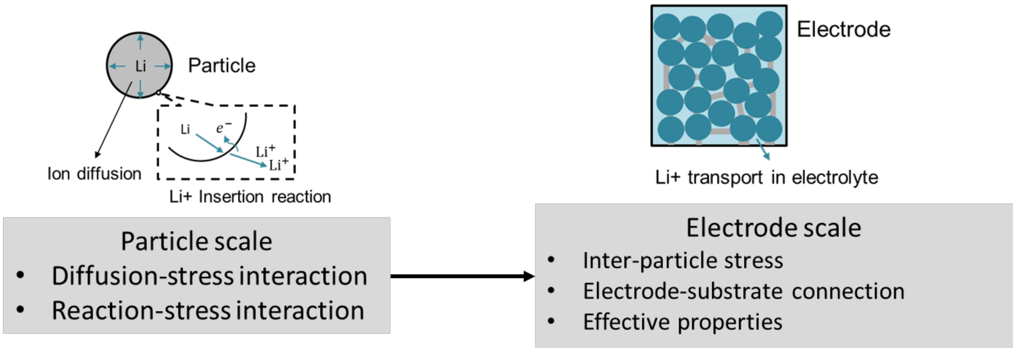

Figure 1. Framework of this study

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Study on Discharge Reaction of Polysulfide-Insoluble Lithium-Sulfur Battery with Faradic Impedance Measurement

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Lithium-Sulfur battery (LiSB) has attracted attention as a new generation secondary battery. However, one of the major problems is dissolution of discharge products of lithium polysulfides (Li_2Sn: n = 1, 2, 4, 6 and 8) that cause the self-discharge. Recently, super-concentrated electrolyte solution (SCES), which consists of only two or three times as much solvent as lithium salt, has been attracting attention as a LiSB electrolyte due to its low solubility of the polysulfides. Watanabe and Dokko et al. [1] proposed polysulfides insoluble LiSB using a sulfolane (SL)-based SCES. On the other hand, the discharge reaction paths of the LiSB are currently unclear due to the strong dependence on the electrolyte solution. In this contribution, we carried out *in situ* electrochemical impedance spectroscopic measurement (EIS) [2,3] to obtain further insight into the reaction paths during discharge.

A positive electrode slurry was obtained by mixing a sulfur S8, a Ketjen black (KB, EC600JD, Lion Corporation) and a carboxymethyl cellulose (CMC2200, Daicel) at a weight ratio of 60 : 30 : 10. The Slurry was spread on an Al foil to obtain a KB-S composite electrode. A negative electrode and a separator were used a lithium metal foil (Honjo Metal) and a glass separator (GA-55, Advantec), respectively. The SL-based SCES was prepared by mixing LiTFSA, SL and hydrofluoroether as the molar ratio of 1 : 2 : 2. The LiSB was assembled using three-electrode typed cell in an Ar-filled glove box. *In situ* EIS measurements were conducted at 0.05C-rate using an electrochemical measurement system (SP-150e, BioLogic). The DC current was superimposed with a small AC current adjusted so that the response voltage amplitude did not exceed 5 mV. The measurements were carried out in the frequency range from 500 kHz to 10 mHz. The measurement was carried out at 303 and 315.5 K.

Figure 1 shows the instantaneous impedance spectra of KB-S composite electrode at DOD = 5 and 20 % measured at 303 and 315.5 K. At 303K, the impedance spectrum at DOD = 5 % exhibits three capacitive semicircles and an inductive loop. At a DOD = 20 %, a capacitive semicircle, that does not converge on the real axis, is observed in the low frequency range (< 1 Hz). At DOD = 5%, the diameter of semicircle at 2.95 kHz decreases as measurement temperature increases, however, the inductive loop at low frequency range is still observed. At DOD = 20 %, the capacitive semicircle at 64.6 mHz decreases with increasing measurement temperature, and a new capacitive semicircle at 17.4 Hz is observed. The impedance spectra at 64.6 mHz is the Faradic impedance related to changes in the electrode state, suggesting that multi-step reactions occur in each DOD for the Li-S battery using SL based SCES.

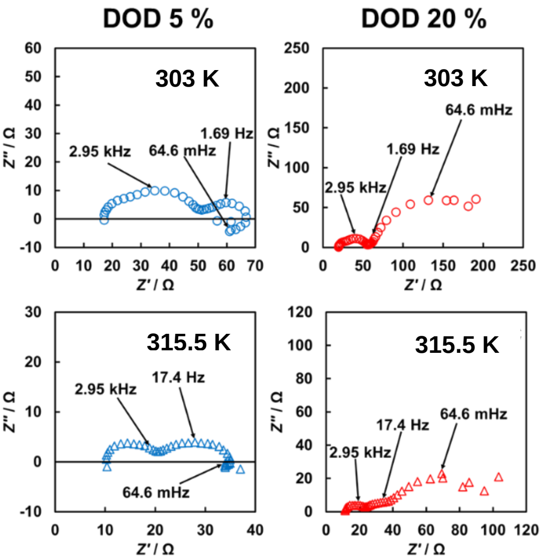

Fig.1 Impedance spectra of SKB cathode at 303 K (upper) and 315.5 K (bottom). (DOD = 5 and 20 %)

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A systematic Study on the impedance response of All-solid-state Thin-film Lithium Battery

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With the advantages of ultra-thin thickness, high volumetric energy density, long cycling life and excellent safety performance, all-solid-state thin-film lithium batteries have a promising prospect in portable and micro devices[1-3]. Compared with the porous structure of the electrodes in conventional lithium-ion batteries, all-solid-state thin-film lithium batteries owns a much simpler structure, in which the electrode and solid-state electrolyte are stacked in layer through vaporizing and atomic or molecular depositing different materials on the substrate. This stacked structure spatially separated different composites in layers, which reduces the difficulty in interpreting EIS data compared with the porous electrode in conventional lithium-ion batteries. Making use of this simple structure, the electrochemical processes at different domain and phases can be more effectively detected using electrochemical methods such as EIS. However, according to our knowledge, the previous researches focused on the optimization of material and its processing methods. Characterizing it using electrochemical methods and interpreting its data is inadequately discussed before.

In this study, an all-solid-state thin-film lithium battery with crystallization $LiCoO_2$, amorphous lithium phosphorous oxynitride (LiPON) and lithium metal thin films has been respectively fabricated via RF magnetron sputtering under mixed gases of argon and oxygen($95\%Ar$-$5\%O_2$), RF magnetron sputtering under pure nitrogen and high vacuum evaporation. The battery with the size of 20mm×20mm surface area between the cathode and solid-state electrolyte and approximately 2μm thickness of each thin films was tested in cell cycling. Derived from the CC-CV charging process at 0.02 mA, the capacity of the cells is approximately 0.2mAh. The discharge capacity at a high rate is below 75% of the one at 0.1 C, which obviously shows a poor rate performance. To further study the rate performance of battery, the Electrochemical impedance spectroscopy (EIS) of the battery was measured at every 10% SOC from 0 SOC to 100% SOC to allocate the contribution of different electrochemical processes in the overall impedance of the battery. Based on the EIS data measured at different SOCs, a physical-based impedance model, which considers the Li+ transport and dielectric effect in the electrolyte, electrochemical reactions at the interfaces and Li+ diffusion in the cathode material is derived and is applied to interpret the EIS data. The kinetic properties of the cathode and solid electrolyte is obtained through the impedance model through fitting the impedance model to the experimental. This work shows that all-solid-state thin film lithium batteries can be used as a ‘reduced-order’ model battery for the composite solid-state lithium batteries and conventional LIBs and helps in mechanism study of these batteries.

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Determining the fast-charging boundary and achieving lithium plating early warning with EIS for safe lithium-ion batteries

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The development of extremely fast charging (XFC) is an important key technology for battery energy storage [1].

Our research team started with the development of fast charging electrolytes and lithium evolution detection, systematically studied the charge transfer kinetics under the interaction of ternary positive electrode and carbon negative electrode, and analysed the positive and negative electrode dynamic properties of high specific energy ternary soft pack batteries through electrochemical impedance spectroscopy (EIS). At the same time, a weakly solvated electrolyte (WSE) was introduced to promote charge transfer at the graphite carbon material/electrolyte interface by reducing the de-solvation energy barrier. The final developed electrolyte can achieve fast charging capacity (80% charge in 10 minutes) of soft pack batteries at high surface density (2.6 mAh/cm^2) without causing lithium evolution, and its performance indicators are comparable to the most advanced level reported in the world. Based on the understanding of the negative electrode/electrolyte interface in lithium-ion batteries [2, 3], it is pointed out that there is a close correlation between electrochemical active surface area (ECSA) and double layer (EDL) capacitance. A in-situ real-time lithium analysis detection method that can be applied to batteries is proposed, which can non-destructive and quantitative detect lithium. By using the three-electrode technology to first decouple the impedance evolution of the negative electrode surface during lithium insertion and lithium precipitation, based on equivalent circuit analysis, it was found that the EDL capacitance on the graphite negative electrode surface increased during the occurrence and growth of lithium precipitation, which can be used as a quantitative indicator for lithium precipitation [4]. Based on the above findings, a lithium evolution detection technology using dynamic electrochemical impedance spectroscopy (DCM) is proposed to overcome the three-electrode limitation, achieving real-time in-situ monitoring and dynamic warning of lithium evolution on the negative electrode surface under working conditions.

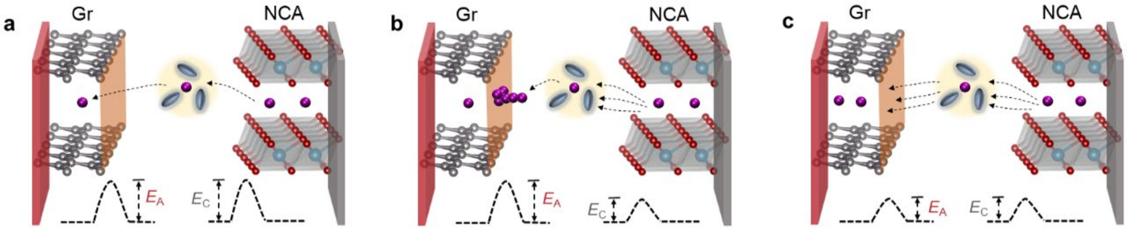

Figure 1. Schematic diagram of fast charging of lithium battery by balancing the positive and negative energy transition state

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Operando Electrochemical Impedance Spectroscopy for Monitoring Lithium-ion Batteries during Fast Charging

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Electrochemical impedance spectroscopy (EIS) is a powerful technique for characterization of lithium-ion batteries (LIBs). It has extensively been used in laboratory research, but not yet in industrial applications, e.g., electrical vehicles (EVs). This is because the latter needs measurements of EIS during operation and achieving valid EIS measurements in dynamic conditions has been a long-lasting challenge. In this work, NMC622/graphite batteries are characterized by the recently developed operando odd random phase EIS (ORP-EIS) under a practical (> 1C) charging condition (Fig.(a))[1]. The validity of the EIS data concerning the linearity and the stationarity is quantitatively assessed based on the robust theoretical framework of ORP-EIS [2][3]. As shown in Fig.(b), the measured impedance data reveals the evolution of charge-transfer phenomena along changes of state-of-charge (SoC), which is consistent to the observation we have made in a stationary EIS study [4]. Equivalent electric circuit model and graphical analysis methods are applied to monitor the SoC of the batteries under various charging conditions including different temperatures, C-rates, and state-of-health (SoH). As indicated in Fig.(c), the charge transfer resistance R_{ct} shows a characteristic parabola-like feature, and it varies consistently according to the charging conditions. This work demonstrates that operando ORP-EIS is a robust technique for monitoring LIBs while conducting a fast charging under various practical conditions and could provide unique physical insights for battery management systems on top of conventional current/voltage-based monitoring methods.

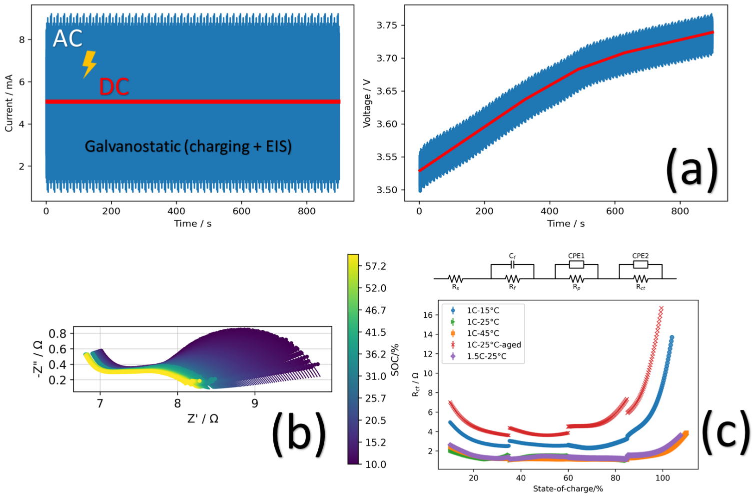

***Figure**: (a) Input and output integrated AC/DC signal of galvanostatic operando ORP-EIS.*
(b) Nyquist plot of an operando ORP-EIS on NMC622/graphite batteries.
(c) Equivalent electrical circuit model and extracted charge transfer resistance R_{ct} under various charging conditions.

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基于参比电极的磷酸铁锂电池低温电化学阻抗谱研究

Study on Low-Temperature Electrochemical Impedance Spectroscopy of $LiFePO_4$ Batteries Based on Reference Electrode

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The capacity and power of lithium iron phosphate ($LiFePO_4$) batteries are significantly declined at temperatures below 0°C. To further explore the impact of cathode and anode on the $LiFePO_4$ batteries when the temperature goes down, this paper proposes a method for testing and studying the electrochemical impedance spectra (EIS) of cathode and anode of batteries based on a reference electrode. A three-electrode battery with a reference electrode implanted is used to test the battery impedance at different temperatures and different states of charge on the cathode, anode, and the full cell separately. The impedance spectrum analysis indicates that the ohmic internal resistance, solid electrolyte interface impedance, and charge transfer impedance increase with the decrease of the cell temperature. However, the diffusion impedance gradually disappears at low temperatures in the test frequency range. Furthermore, by assembling cathode and anode symmetric button cells, the change of diffusion impedance at low temperatures is tested to analyze its effect on the cell's performance. Finally, the full frequency analysis of battery impedance at low temperatures is realized. The experimental data suggests that the cathode charge transfer impedance is highly related to temperature, while the anode is diffusion impedance. These findings should be valuable for the low-temperature performance improvement of $LiFePO_4$ batteries and the optimization of the structure of cathode and anode materials.

Keywords: $LiFePO_4$ battery; Reference electrode; Symmetrical cell; Low-temperature electrochemical impedance spectroscopy

Superlattice-Stabilized WSe_2 Cathode for Rechargeable Aluminum Batteries

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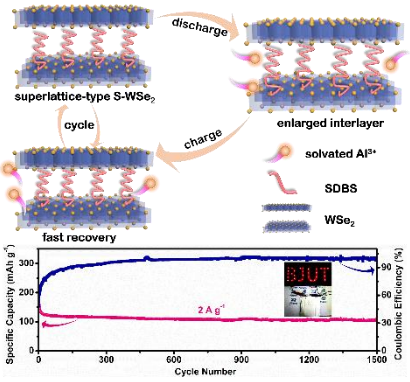
Rechargeable aluminum batteries (RABs), with abundant aluminum reserves, low cost, and high safety, give them outstanding advantages in the post-lithium batteries era. However, the high charge density (364 C mm^{-3}) and large binding energy of three-electron-charge aluminum ions (Al^{3+}) de-intercalation usually lead to irreversible structural deterioration and decayed battery performance. Herein, to mitigate these inherent defects from Al^{3+}, we proposed an unexplored family of superlattice-type tungsten selenide-sodium dodecylbenzene sulfonate (SDBS) (S-WSe_2) cathode in RABs with a stably crystal structure, expanded interlayer, and enhanced Al-ion diffusion kinetic process. Benefiting from the unique advantage of superlattice-type structure, the anionic surfactant SDBS in S-WSe_2 can effectively tune the interlayer spacing of WSe_2 with released crystal strain from high-charge-density Al^{3+}, and achieve impressively long-term cycle stability (110 mAh g^{-1} over 1,500 cycles at 2.0 A g^{-1}). Meanwhile, the optimized S-WSe_2 cathode with intrinsic negative attraction of SDBS significantly accelerates the Al^{3+} diffusion process with one of best rate-performance (165 mAh g^{-1} at 2.0 A g^{-1}) in RABs. Our findings pave a new direction towards durable and high-performance electrode materials for RABs.



Research on Carbonation Behavior of Bipolar Membrane Fuel Cell

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As a prospective membrane electrode design strategy, Bipolar Membrane Fuel Cells (BPMFCs) achieve different working pH values on each side of the cathode and anode catalytic layers, with high-efficiency kinetics for HOR and ORR reactions, and non-precious metal catalysts loadable onto the cathodic alkaline side, by constructing a bipolar interface composed of a PEM/AEM composite. The unique design structure of BPMFCs can theoretically avoid the significant performance degradation caused by anode overpotential loss after carbonation reaction in traditional Alkaline Membrane Fuel Cells (AEMFCs).

In our work, it was found that the performance of BPMFC under CO_2 intake conditions only declined by 5%, and the overpotential loss was much lower than that of alkaline batteries. In order to explore the reason, we used the DRT analysis method to split the impedance spectra of BPMFC at different time domains and studied the extent of restriction on mass transfer, cathodic ORR, and anodic HOR of the battery. In fuel cell research, the EIS-DRT method can show the extent of limitation of the battery on mass transfer, cathodic ORR, and anodic HOR as characteristic peak area under different time domains. The results of DRT analysis showed that carbonation only slightly affected the cathodic ORR reaction of the battery and did not result in HOR restriction. In subsequent research, BPMFC was switched to pure oxygen discharge after complete carbonation, and the CO_2 concentration emitted from the anode and cathode was analyzed, studying the "self-cleaning" process of BPMFC and its corresponding changes in battery voltage during discharge. The dynamic ion balance mode of BPMFC during discharge was determined, and the understanding of the electrode-polymer electrolyte interface was further deepened.

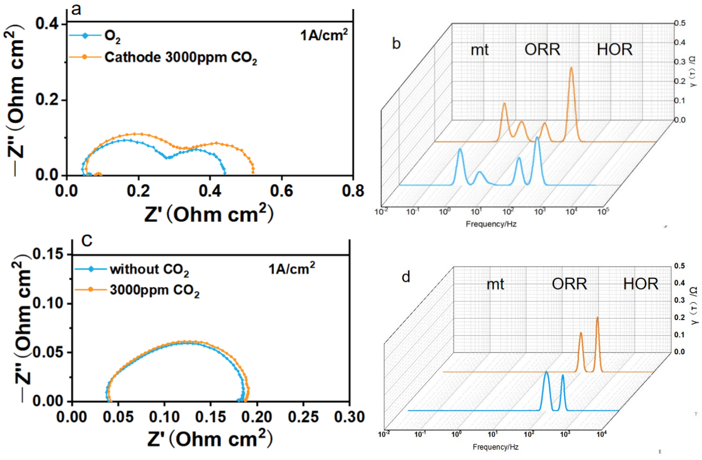

Fig.1 DRT results of electrochemical impedance spectroscopy and Nyquist plot transformation of AEMFC(a,b) and BPMFC(c,d).

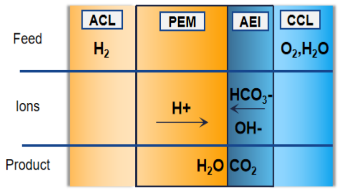

Fig.2 Schematic diagram of ionic dynamic balance during BPMFC operation.

Research progress of CuS as cathode materials for rechargeable magnesium batteries

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CuS has high theoretical specific capacity and good conductivity, which is considered as one of the most potential cathode materials for rechargeable magnesium batteries. However, its low cycle stability and rate performance limit its development. Firstly, the basic structure of CuS and its charging and discharging mechanism as magnesium ion cathode material are introduced, and then the common preparation methods of CuS and their advantages and disadvantages are summarized, including solid phase method, hydrothermal method, solvothermal method, microwave synthesis method and one-pot method. Then, the research progress of its modification is introduced, including material nanocrystallization, material combination, anion substitution and cation doping. On this basis, the future research direction and development trend of CuS are prospected. Future research on CuS will mainly focus on the following three aspects: (1) Develop appropriate preparation methods to synthesize CuS with special morphology and nanostructure, such as nanorods, nanoflakes, nanoribbons, hollow nanocubes; (2) The future modification research can start with the combination of several methods to develop nanocomposites with special morphology or anionic replacement materials, which is expected to further improve the electrochemical performance of CuS; (3) The mechanism study of electrochemical performance modification of CuS materials is limited and needs further study.

Unexpected Effects in Galvanostatic EIS of Randles' Cells: Initial Transients and Harmonics Generated

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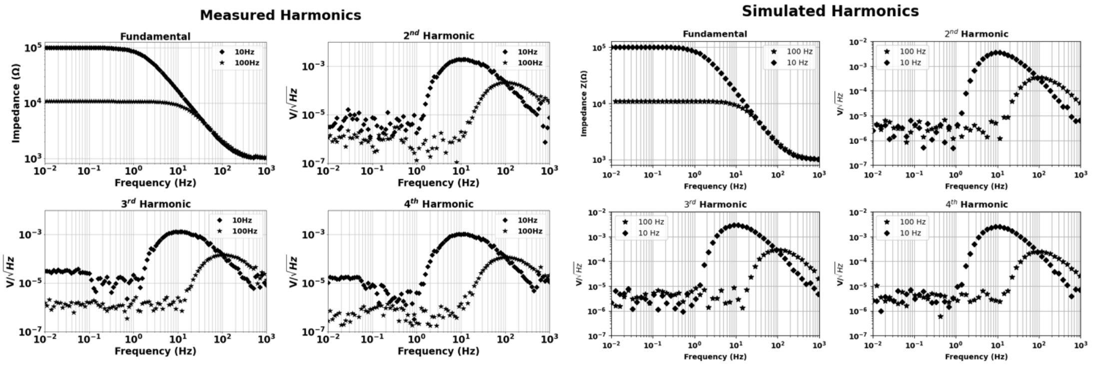
Non-linear response in Electrochemical Impedance Spectroscopy (EIS) has recently been a point of interest since it provides valuable information about physical and electrochemical properties of the investigated cell. This non-linear response can be explained via kinetic and transport arguments, however proper controls must be employed to rule out experimental artifacts[1]. One potential artifact is the start-up (initial) transient.

In this study, we have built several equivalent simplified Randles cells, both physically and virtually, and measured their higher order harmonics. The nonlinear response in these systems were unexpectedly non-monotonous which required investigation. These investigations were done via measurements and simulations.

The simulations were done according to Kirchoff's law, summarizing the current distribution among a resistance and a capacitor. The results perfectly overlapped in terms of signal shapes, amplitudes and frequencies, which shows that the response signal and harmonics solely depend on the modelled parameters. When a small amount of noise added to the simulated signal, the graph looked completely identical to the measurement result.

We investigated algorithms to clean up the effect and compared results with the strategies of major equipment manufacturers. We will be presenting measurement and simulation details as well as discuss methods for proper nonlinear higher harmonic measurements.



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Development of an Odd Random Phase Electrochemical Impedance Spectroscopy Sensor for Battery Management Systems

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Lithium ion batteries (LIB) are used in many applications for energy storage, for example in electric vehicles. A lot of research is performed with the aim of developing more environmentally friendly and safer batteries with better performance and longer life. One way of improving performance and lifetime of a battery is by creating sensors that are capable of monitoring the state of a battery cell stack in real time. These sensors can detect the start of degradation and failure mechanisms before a loss of performance occurs. This information can be used as an input for a battery management system (BMS) that can make decisions on the best operating and charging conditions for each individual battery in the cell stack.

Odd Random Phase multisine Electrochemical Impedance Spectroscopy (ORP-EIS) has proven to be a powerful technique to characterise LIB, with capability of identifying the state of health (SoH) and state of charge (SoC) based on the impedance response of the charge transfer reaction of the cathode and the solid electrolyte interphase [1]. Furthermore, it provides information on the stochastic noise levels, non-stationarity and non-linearity of the system, which identifies the accuracy and validity of the results. In this work, an ORP-EIS sensor is designed to operate with an advanced BMS for the *in situ* identification of the SoH and SoC of a battery cell stack. It is capable of application of the ORP-EIS signal, data acquisition and data processing through an embedded processor. The battery cells under study are commercially available and use NMC and graphite as positive and negative electrode, respectively. Their internal impedance is very low (mΩ range), and therefore the signals are easily distorted by external influences, which provides an additional challenge for accurate readings.

[1] X. Zhu et al., Electrochimica Acta 287 (2018) 10-20

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Electroactive Sites for Oxygen Electroreduction Over Heteroatom Doped Carbon Interpenetrating Networks in Acid Electrolyte

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With the advent of the hydrogen society, the fuel cell has attracted wide attention. The Fe-N-C catalyst has received wide attention because of its low price and high activity, and it may be used as an alternative platinum group metal (PGM) catalyst to solve the limitations caused by the slow oxygen reduction reaction (ORR) process in proton exchange membrane fuel cell (PEMFC). However, the catalytic activity of the Fe-N-C catalyst still has a certain gap compared with commercial Pt/C. Here, we provide a way to increase the catalytic activity of Fe-N-C catalysts by increasing high-efficiency active sites. We synthesized a self-supporting interpenetrating network catalyst (CNT@CNP) derived from ZIF-8 and polyaniline（PANI) double carbon sources. The CNT@CNP provides abundant at-interface FeN_4 active sites, which effectively improves its activity. The DFT calculation results also prove that the FeN_4 at the zigzag edges plays a very important role in the ORR catalysis process. Moreover, the DFT calculation results show that the two oxygen-containing groups, epoxy, and ketone, can promote the ORR activity of FeN_4. Our results provide an innovative idea for solving how to improve the activity of FeN_4 structure in the ORR 4-electron process in acidic systems.

1) The simultaneous use of two carbon sources, polyaniline（PANI) and ZIF8, can synthesize a self-supporting interpenetrating network structure with efficient active sites.
2) By means of DFT calculations, it is proved that the catalytic activity of the active site at the interface position is higher, especially at the zigzag and armchair edge positions.
3) The experimental results show that the type and ratio of oxygen tube energy groups have an impact on the catalytic activity of ORR, and DFT calculations have been used to prove that some oxygen functional groups, such as ketone and epoxy groups, can improve the catalytic activity.

Jagged carbon nanotubes from polyaniline: Strain-driven high-performance for Zn-air battery

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Metal-air batteries and alkaline exchange membrane fuel cells (AEMFCs) have been considered as promising clean energy alternatives to solve the current worldwide energy crisis and environmental pollution, because of their high efficiency, environment-friendly and continuable development. However, the major obstacle for the applications of these new energy systems is that the oxygen reduction reaction (ORR) is sluggish in kinetics. At present, great efforts have been devoted to the development of non-precious metal-based catalysts like metal-free carbons with rich resources, low costs, and high efficiency. However, the specific activity of the current carbon-based catalysts has not yet met the requirements of commercial application. So, the authors propose that the designing of unique morphology, abundant defect, and inherent strain is a promising strategy for high performance of metal-free carbons, based on the editability in composition and morphology of carbons. Different from common pyrolytic carbons, we provide a smart strategy for well-defined jagged carbon nanotubes (JCNTs) derived from polyaniline, through controllable $ZnCl_2$-assisted carbonization and NH_3-activation. The strained JCNTs exhibit outstanding ORR activity and electrochemical stability in alkaline solution, which exceed the-state-of-art Pt/C and recently reported most carbon-based catalysts. These metrics show that the strain design sheds a light for developing high-performance nanocarbons as next-generation catalysts for batteries and fuel cells. Following are the important features concerning the results reported herein.

1) Polyaniline, with inherent twisted molecular chains in which the phenyl ring and amino groups are alternately connected non-linearly, is an ideal precursor to fabricated jagged carbon nanotubes (JCNTs) via facile $ZnCl_2$-assisted carbonization and then NH_3-activation.
2) The obtained JCNTs preserve the twisted structure of polyaniline in nature and feature abundant zigzag or armchair structures composed of carbon and nitrogen atoms, resulting in a high lattice strain level.
3) There exists a strain-dependent ORR activity of the JCNTs, exceeding state-of-the-art Pt/C in alkaline medium, with the half-wave potential reaching 0.88V (vs RHE). A Zn-air battery equipped with the catalyst as cathode exhibits a power density of up to 142 mW cm^{-2} and long-term charge-discharge cycle stability.
4) The designing of the strained JCNTs may shed a light on developing high-performance carbon-based materials as next-generation catalysts for batteries and fuel cells.

Reference: C. Jin, H. Deng, J. Zhang, Y. Hao, J. Liu. * Jagged carbon nanotubes from polyaniline: Strain-driven high-performance for Zn-air battery. Chem. Eng. J., 2022, 434, 134617.

Study on Effect of I/C and ionomer distribution on the performance of Electrospinning Catalyst Layer by EIS

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Abstract

Proton exchange membrane fuel cell (PEMFC), as an efficient energy conversion device with no emissions, has been developed and applied in many areas for decades. Catalyst layer (CL), where the oxygen reduction reaction occurs, is the key component and affects the performance of PEMFC greatly. The electrospinning CL, which consists of composite nanofibers, shows better performance than the conventional CL[1]. The nanofiber-network structure can bring an efficient proton conduction pathway even with less ionomer content. The large porosity and multi-model pore size distribution benefit gas transport and reduce the mass transport resistance. However, the optimal ionomer content and ionomer distribution are still not clear. There are few studies about the influence of the ionomer content and distribution on the performance of electrospinning CL. In this work, we prepared electrospinning CLs with different I/C ratios by adjusting the ionomer content in the ink, and different ionomer distributions by alternate electrospinning ionomer nanofibers and composite fibers (consisting of Pt/C catalyst, ionomer and carrier polymer). Then we investigated the effect of I/C ratio and ionomer distributions on the Charge transfer resistance, proton conduction resistance and gas transport impedance (Rmt) with the help of electrochemical impedance spectroscopy (EIS). The results show with the decreasing of I/C ratio, the activation overpotential decreases, the mass transport overpotential and Rmt first decrease and then increase; the CL with an I/C ratio at 0.8 has higher ECSA and lower ionomer coverage. Alternate electrospinning CL and composite CL show better performance than the conventional one at the same I/C ratio.

Keywords: PEMFC, electrospun CL, ionomer, EIS

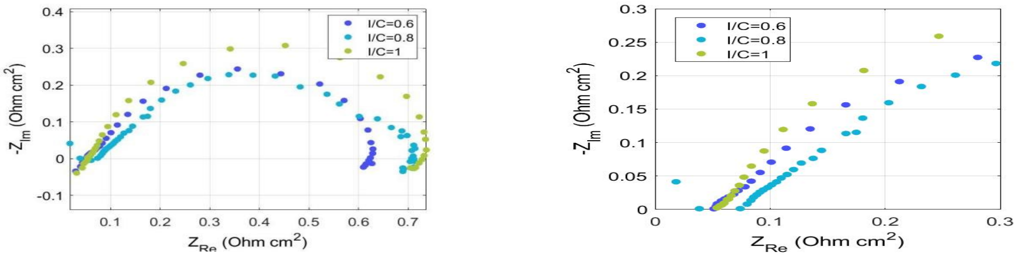

Figure 1 H-N EIS of different ionomer contents at 0.1 V

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In-situ investigation of the dynamic loadings for proton exchange membrane fuel cell with a large active area: considering the in-plane heterogeneity

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The distribution of the internal state of large-area proton exchange membrane fuel cell (PEMFC) is uneven and hard to be observed during operation. Operating conditions such as temperature, relative humidity and stoichiometric ratio all have an effect on the internal state of the cell and ultimately affect its output performance. In this study, an online monitoring system that can simultaneously monitor temperature, humidity, current density and high frequency resistance (HFR) distribution of the cell is designed to explore the influence mechanisms of the changes of operation conditions. The test of HFR distribution is realized by monitoring the local voltage and current of each area while applying alternating current with an electronic load. Flow flied structure is machined on the current density monitoring plate so that it can be used as a polar plate to directly contact with the membrane electrode assembly (MEA) to collect the most real signal. A commercial 320cm^2 10-cell stack is used in the experiments. Results show that the distribution trend of electric density and HFR at steady state is counterintuitive. The current density in the middle area is larger even though the HFR in this area is higher. Besides, the increase of temperature and air stoichiometric ratio help to improve the uniformity of current density, while the increase of air inlet humidity shows the opposite. The effects of air inlet humidity and air stoichiometric ratio on the humidity and HFR distributions are mainly concentrated in the air-inlet area. It is found that a medium air inlet humidity (60%) is enough to create a state of high humidity in each area. Further increase of humidity aggravates the flooding instead, leading to the decline of output performance. Under the condition of low air inlet humidity, a proper increase of air stoichiometric ratio does not cause a significant increase in HFR. However, an excessive air stoichiometric ratio eventually leads to a decline in cell performance because of the reduction of the humidity in the air-inlet area which increases the HFR. This study is helpful to understand the influence mechanism of operating conditions on the internal state and performance of PEMFC, which helps to better formulate the strategy of operating condition management.

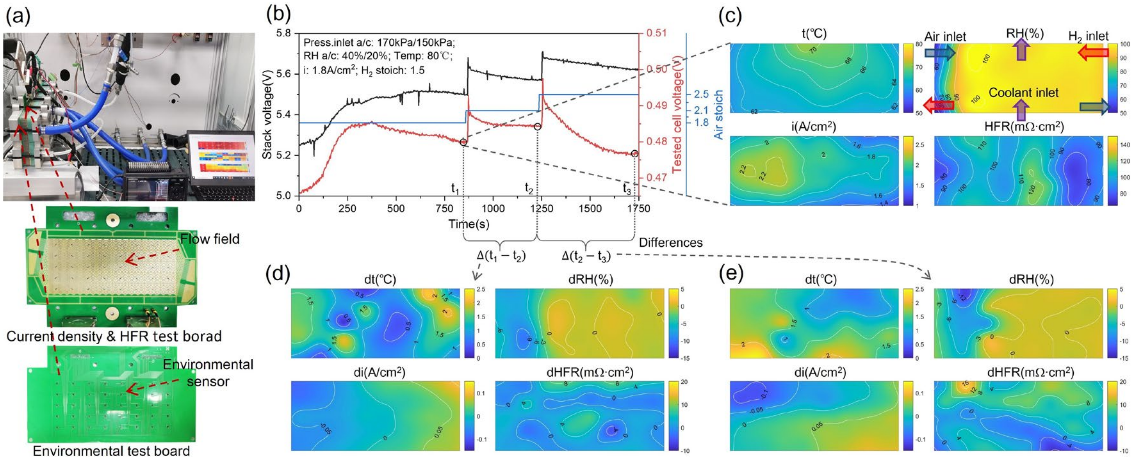

Figure 1. The experimental setup and the test boards (a), voltage output with the change of air stoichiometric ratio (b), internal state distributions when air stoichiometric ratio is 1.8 (c), and their changes when air stoichiometric ratio increases from 1.8 to 2.1 (d), and from 2.1 to 2.5 (e).

Electrochemical Impedance spectroscopy for accessible carbon

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The advent of accessible carbon materials has led to a new breakthrough in fuel cell performance enhancement.

Accessible carbon has larger pore size volume and higher porosity comparing with traditional carbon material. It is important to test the performance of accessible carbon and characterize the structure of accessible carbon for the development and characterization of its performance. The use of electrochemical impedance spectroscopy is an effective way to characterize the properties of accessible carbon. The uniqueness of the accessible carbon structure makes the proton conductivity an important factor in the performance of fuel cells.

Electrochemical impedance spectroscopy is used to characterize accessible carbon materials and to investigate the effect of humidity on the performance of accessible carbon. The results of the electrochemical impedance spectroscopy tests provide an in-depth understanding of the accessible carbon structure.

Analysis of degradation mechanism in unitized regenerative fuel cell based on the EIS method

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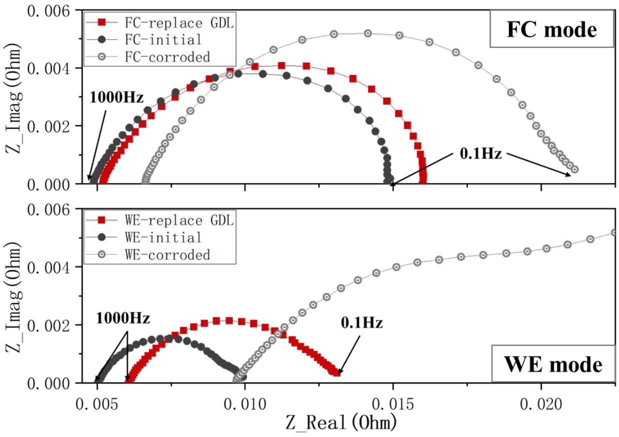
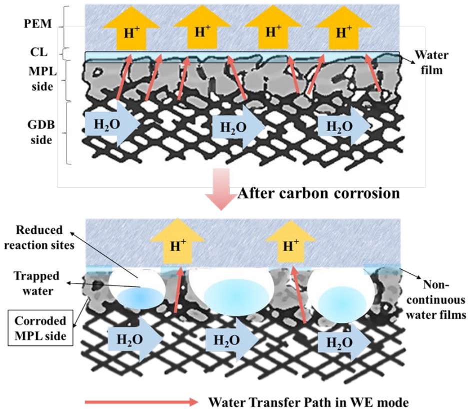
Abstract: Unitized regenerative fuel cell (URFC) is an independent electrochemical device, which can function either in fuel cell (FC) mode or water electrolysis (WE) mode, shall be considered as an optimum hydrogen conversion system due to its high specific energy density and renewable. The degradation of Unitized Regenerative Fuel Cell (URFC) performance is a key issue hindering its further development. However, to date, the scientific community has devoted little attention to the mechanisms of URFC degradation, especially under cyclic reversal conditions.

In this study, an EIS experimental measurement protocol for URFC degradation was established and two durability tests were carried out through the cyclic experiment and comparative experiment. The round-trip efficiency (RTE) of the cell exhibits a high degree of degradation accompanied by a significant increase in ohmic and mass transfer impedance.

The EIS experimental results confirm that the degradation occurs mainly in the water electrolysis (WE) mode, and accelerates with increasing electrolytic voltage. Carbon corrosion on the MPL side of the GDL is found to be the main cause of the degradation of the URFC, with over 31% of the area corroded. Eventually, the performance of the degradation cell was re-improved by replacement with new GDLs. The RTE of the cell has recovered to over 43% and the increase in ohmic and mass transfer impedance has been suppressed.

This research reveals that the corrosion of the GDL does not directly cause an increase in electronic resistance but rather destroys the microporous structure between the CCM and the GDL which in turn leads to a reduction in the water transport capacity of the interface. This not only leads to a reduction in the effective reaction site at the interface, but more importantly, causes an increased resistance to interfacial water transport and a decrease in hydration of the proton exchange membrane (PEM), leading to a distinct increase in the CCM proton conduction resistance. Our perspectives are also confirmed by subsequent verification experiments of GDL replacement. Ultimately, an intrinsic mechanism between the URFC performance degradation and carbon corrosion is established





(a) EIS comparison of cell after GDL replacement in FC mode and WE mode **(b)** Mechanisms of degradation due to carbon corrosion

An investigation of surface prelithiated SiO_x anode materials and its interfacial properties to electrochemical performance

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SiO_x (x=0-2) is the next generation anode material for lithium-ion battery owing to its high capacity (> 1000 mAh/g) and low cost. However, volume expansion, extreme high initial irreversible reaction, and fast cycle fading cause SiO_x not easy to adopt to a higher amount in a commercial anode electrode composition. Currently, the occupation of SiO_x is only 5-30 wt% in a composite with graphite. There are several methods for improving those problems aforementioned such as electrolyte additive, material morphology design, and prelithaited process.

To overcome the crack from initial volume expansion as well as lithium-ion loss from solid electrolyte interphase (SEI) formation, prelithiated manufacturing is a welcome process. According to our study, the prelithaited SiO_x is able to provide nearly 92% initial columbic efficiency (CE), which is much higher than that without prelithiation (only 60-70% CE). Normally, there are three methods in adopting prelithiated SiO_x such as material electrochemical preformation, directly coating lithium powder on material, and electroplating lithium metal on Cu foil. However, those methods need additional processes for material preparation in advance. Furthermore, high cost and moisture highly sensitive are still the keys in inhibiting mass production to commercial products.

Herein, we provide a new methodology to overcome high cost and moisture highly sensitive issues as well as deliver high ionic conductance for high-rate performance. Several lithiated organic monomers are developed, which is used to cover on SiO_x surface. With the lithiated organic coverage, surface prelithatied SiO_x is able to provide outstanding cycle and rate performance. The lithium-ion compensation from lithiated organic coverage clearly demonstrates an important assistance from surface to bulk in electrochemical cycling. Fig. 1 shows the Nyquist plot of SiO_x after the first and 100 cycles. Fig. 1a demonstrates the prelithatied layer slightly decreases the interfacial impedance after the first cycle. Fig. 1b shows the this prelithatied layer significantly promotes the ionic transfer at interface which contributes to the battery performance.

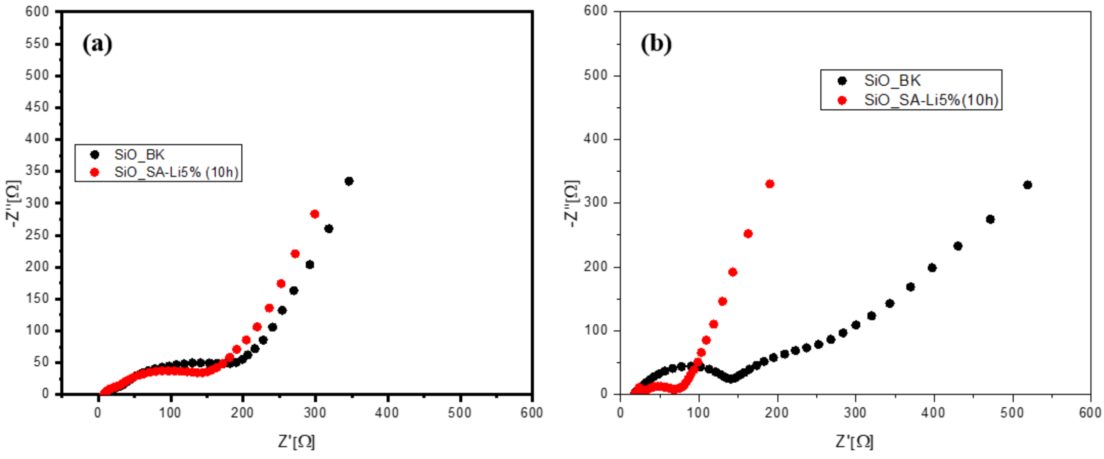

Figure 1 The Nyquist plot SiO_x electrodes at (a) the 1st and (b) the 100th cycles.

Electrochemical performance of an internal methanol reformer with a $CsH_5(PO_4)_2$-Doped Polybenzimidazole Membrane

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Methanol has a lower reforming temperature (200–300 °C), compared to other hydrocarbon fuels. By using a methanol steam reformer, methanol can be converted into a hydrogen-rich gas that may be utilized in fuel cells. But the working temperature between convetional HT-PEMFC (140–180 °C) and methanol steam reformer is mismatching.

Recently, our team prepared a molten proton conductor electrolyte membrane, which was prepared by doping the PBI membrane into molten $CsH_5(PO_4)_2$. Although molten proton conductor-doped PBI membranes have high proton conductivity (10^{-2} S cm^{-1} at 220 °C) and good mechanical properties, the correspondingly prepared membrane electrode assembly (MEA) does not exhibit the expected Electrochemical performance.

The main impediment to the performance of fuel cells is considered to be due to the poor interfacial contact between the catalyst layer (CL) of the gas diffusion electrode (GDE) and the molten proton conductor electrolyte membrane. This is because the molten phosphate only weakly penetrates into the CL, which means it is difficult to build a proton transmission channel from the membrane to the CL. **Figure 1(a)** shows Schematic diagram of MEA after treating with PA. The active area in the CL depends on its electrolyte content and a low active area in the CL could reduce the performance of the MEA. **Figure 1(b)** shows the Nyquist plots of MEAs treated with different amounts of PA. For example, 10PA-PBI/Cs MEA means that the amount of PA is 10 mg cm^{-2}. Based on the molten proton conductor electrolyte membrane, by coating PA on the CL of the GDE, a proton transport channel can be established between the CL and electrolyte membrane to greatly improve their interfacial contact, thereby greatly improving the performance of the MEA.

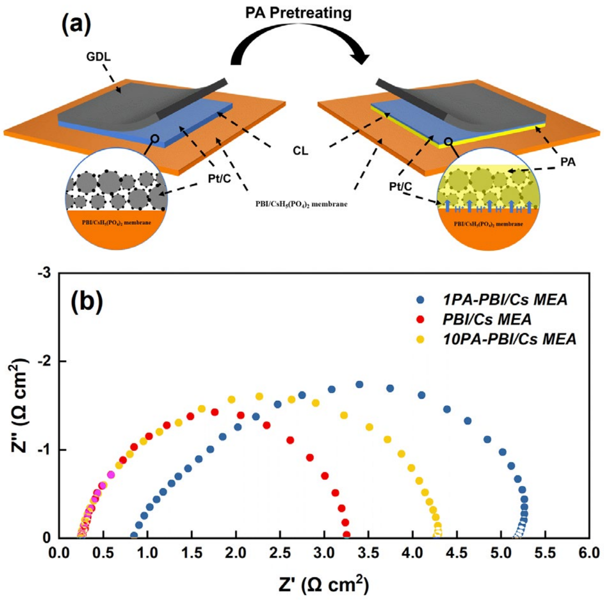

Figure 1 (a) Schematic diagram of PBI/Cs MEA before and after pretreating the GDE with PA. (c) Nyquist plots of MEAs treated with PA under 160 °C and at constant output current density of 20 mA cm^{-2}.

Catalyst coated membrane method to fabrication membrane electrode assembly for high temperature proton exchange membrane

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High temperature proton exchange membrane fuel cells (HT-PEMFC) have recently gained attraction due to the superiority caused by operating temperature elevated (140~200°C)[1]. The membrane electrode assembly (MEA) is one of the most vital components of fuel cell and plays a key role in cell performance. The fabrication of MEA can be divided into catalyst coated membrane (CCM) and catalyst coated substrate (CCS) methods according to different locations of catalyst attachment.

Compared to CCS method, CCM method provides closer contact between catalyst layer and membrane to form better three-phase boundaries, resulting in a relatively high output power density of cells. Moreover, CCM method can increase the rate of catalyst utilization. However, the mainstream approach to prepare MEA for HT-PEMFC is still CCS method because of the high swelling rate and low mechanical strength of phosphoric acid (PA) doped PBI membrane[2]. But Li et al[3] has found that PBI membrane treated with $CsH_5(PO_4)_2$ had lower swelling rate of 25%, higher tensile strength and provided a surface conducive to catalyst adhesion.

The recent work aimed to fabrication the CCM-based MEA for HT-PEMFC by using the characteristics of the PBI membrane treated with $CsH_5(PO_4)_2$ different from the PA doping PBI membrane[4]. Figure 1(a) illustrates the surface morphology image of CCM-based MEA. It was evident that no cracks appear in the surface of catalyst layer, and the catalyst distribution was relatively uniform. Figure 1(b) shows the comparison of power density and polarization curves of CCM-based MEA and CCS-based MEA. It has found that the power density of CCM-based MEA based on $CsH_5(PO_4)_2$-doped membrane was the highest, while the CCS-MEA based on the same membrane was much lower, and the CCS-MEA based on the PA-doped membrane was also lower, implying that the new CCM method enhanced the HT-PEMFC performance by contrast with CCS method. The better cell performance of CCM-based MEA was attributed to the good interface contact between membrane and catalyst layer, leading to the interfacial resistance decreased.

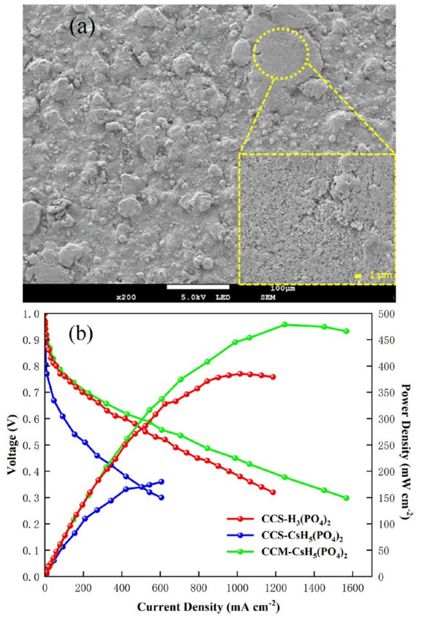

Figure 1. (a) Morphology of CCM-based MEA surface. (b) polarization curves of CCM-based MEA and CCS-based MEA.

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Preparation of Membrane Electrode Assemblies by Directly Coating Electrolyte Dispersion onto Catalytic Layer

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Proton exchange membrane fuel cells (PEMFCs) are considered an important energy source for portable and transportation applications that require clean and efficient electricity. This technology has been proven to provide sufficient output power and durability, but slow manufacturing speed and high manufacturing costs remain important obstacles. Membrane electrode assemblies (MEAs) are the core components of PEMFCs, which directly determines their performance and cost.[1]

Concerning the structure and preparation method of MEA directly determineing its power output and preparation speed, a novel and simple method for manufacturing MEA has been proposed. In this method, the dispersed electrolyte was deposited on the surface of the catalytic layer (CL) and the dried electrolyte membrane layers on the CLs were stacked facing each other.[2] This approach could eliminate the prefabrication process of the proton exchange membrane (PEM), increase the PEM/CLs interface connection and improve the water management capability at high current density and low humidity.

Recently, we have studied the relationship between different deposition methods of electrolyte dispersion and the properties of MEAs. Due to the higher ohmic resistance caused by the rough membrane layer surface generated in the spraying method and the higher charge transfer resistance caused by the excessive penetration of electrolyte dispersion into CL in the blade-coating method, the combining of spraying and blade-coating methods (spraying first, blade coating later) was preferred for the electrolyte dispersion deposition. The MEA prepared by spraying first and then blade-coating had excellent cell performance. This is because the cracks on the surface of GDE could be covered by the ionomer sublayer prepared by spraying, preventing excessive electrolyte dispersion from entering the CL during the scraping process. The subsequent scraping process could make the membrane layer smoother and reduce the PEM/PEM interface resistance.[3]

Furthermore, we combined ePTFE reinforcement with an appropriate electrolyte dispersion deposition method to fabricate a reinforced MEA-DMD-R (Figure 1a).[4] Compared with the catalyst-coated membrane type MEA (0.88 W cm^{-2}) base on the Gore-select membrane, the MEA-DMD and MEA-DMD-R has higher performance (1.07 and 1 W cm^{-2}) (Figure 1b). The mechanical durability of MEA-DMD-R was significantly improved under the limitation and supporting effect of ePTFE reinforcement and GDE on the deformation of PEM.

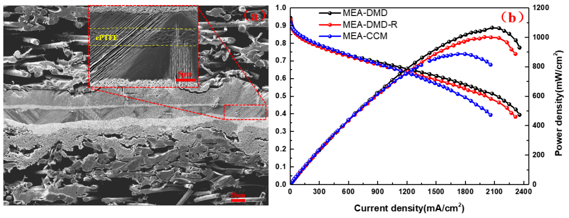

Figure 1. (a) the cross-sectional morphologies of MEA-DMD-R. (b) Polarization curves for various MEAs (H_2/air, 80 °C).

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Comparison of different methods for cross section preparation of ePTFE reinforced perfluorosulfonic acid membranes

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Proton exchange membrane (PEM) is the heart of a proton exchange membrane fuel cell (PEMFC), and its functional integrity and durability profoundly impact the performance and lifespan of the PEMFCs [1]. Due to the superior proton conductivity and physical/chemical stability, the perfluorosulfonic acid (PFSA) membranes are widely used, such as Nafion® and Aquivion® series membranes [1]. However, pristine/free-standing PFSA membranes possess high sweeling rate, which results in their severe mechanical degradation, especially under cycle humidity conditions [1]. Intercalating a layer of expanded polytetrafluoroethylene (ePTFE) reinforcement skeleton into the membrane is an efficient method to restrain the swelling of PFSA membranes, which has been applied to produce commercial reinforced PFSA membranes, such as Gore® and Nafion XL® membranes [1]. During the development of ePTFE reinforced PFSA membranes (ePTFE-RM), their cross-sectional morphologies are usually examined by the scanning electron microscope (SEM), which is a key characterization to analyse the internal structures of the ePTFE-RM. From the cross-sectional morphologies, we can determine the thicknesses of the membrane and ePTFE skeleton layer. Furthermore, the interface combination state between the PFSA ionomer and ePTFE skeleton and the ionomer filling rate in porous ePTFE skeleton can also be examined. These results are critical information guiding the development of advanced ePTFE-RM [2, 3].

At present, there are mainly three kinds of methods to prepare the cross sections of the ePTFE-RM, including liquid-nitrogen brittle failure, ultrathin sectioning, and ion beam cutting. However, relative research comparing these three methods is scarce. In this study, we compare the morphologies of the cross sections of the home-made ePTFE-RM based on these three methods. The cross section prepared by the liquid-nitrogen brittle failure method exhibits a concave-convex morphology (Figure 1a). The cross section of the membrane bulk seems to have been damaged due to the tensile stress. Obviously, this method may cause interference in morphology characterization. In contrast, the ultrathin sectioning method can provide a relatively flat membrane cross section (Figure 1b). However, the ePTFE/PFSA layer seems to be crimped due to the blade cutting. Hence, this method can hardly provide a perfect cross section. Relatively speaking, the ion beam cutting method can fabricate a very flat and neat cross section (Figure 1c). The cross-sectional morphology of the ePTFE/PFSA layer is clearly observed without damage. Evidently, the ion beam cutting method is the best cross section preparation method for the cross-sectional SEM characterization of ePTFE-RM.

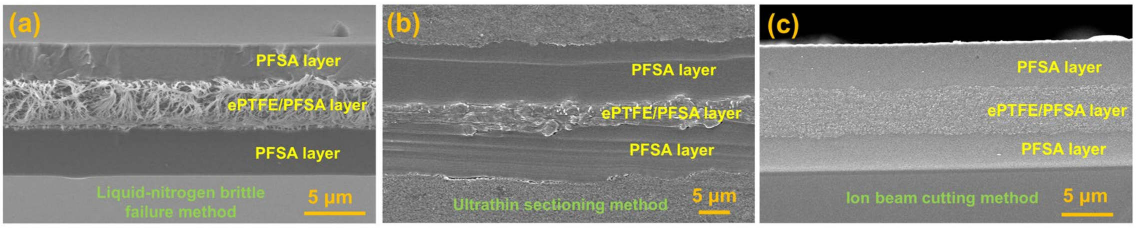

Figure 1. Cross-sectional morphologies of the home-made ePTFE-RM based on the different cross section preparation methods (liquid-nitrogen brittle failure, ultrathin sectioning, and ion beam cutting, respectively).

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EIS Investigation of Vitzrocell C and D Size Li/$SOCl_2$ and Li/$SOCl_2$/SO_2Cl_2 Mixture Batteries

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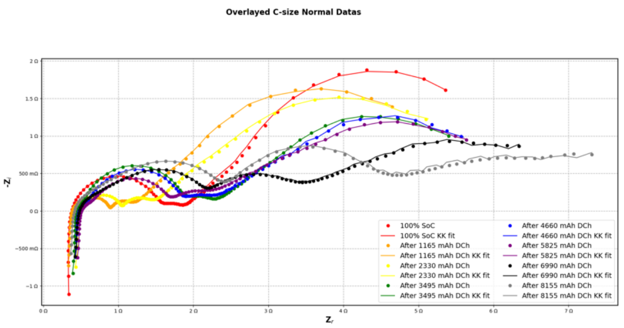
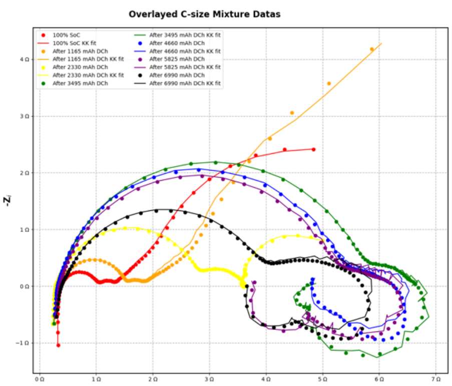
In this work, we have investigated electrochemical impedance spectroscopy (EIS) of Vitzrocell C and D size bobbin type batteries with different chemical compositions. First, EIS of 100% Li/$SOCl_2$ battery of C and D size were measured at various states of charge throughout the battery capacity. Then, equivalent circuit models were fit to various frequency regions for understanding electrochemical characteristics. Further, a mixture chemistry that consists of metallic Li anode and 85% $SOCl_2$ combined with 15% SO_2Cl_2 was investigated in the same manner with D and C size batteries. The results compared with the regular Li/$SOCl_2$ battery and our previously measured various commercial Li/$SOCl_2$ batteries[1,2].

In addition, temperature was varied to study the kinetics of various parameters obtained from impedance spectroscopy at a broad range starting from -25°C to 65°C. Arrhenius plots were generated from resistance values, showing that electrochemical properties of these cells are highly temperature and geometry dependent.

Lastly, baseline subtraction has been a popular method that has been applied to EIS measurements in recent years. We have investigated a custom-made subtraction algorithm alongside with Gamry Instruments©' Framework algorithm, applied to mixture batteries' EIS measurements. Moreover, nonlinear harmonic analysis of all battery types was investigated with and without baseline subtraction option to differentiate the effect.

We will be presenting the temperature dependent measurement results along with the studies of nonlinearity and baseline subtraction.





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Degradation Detection of Li-ion Batteries by Impedance Parameters Determined from Charge Curve

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Li-ion batteries (LIBs) are expected to be a major power sources for electric vehicles and airplanes because of its high energy density and light weight. The inspection and monitoring of the conditions of LIBs are strongly required for the safety use. An electrochemical impedance spectroscopy (EIS) is powerful tool to investigate electrochemical properties of LIBs because the EIS gives the information regarding inner structure and interfacial reactions in batteries without the destruction. Our laboratory in Tokyo University of Science developed two methods to determine the electrochemical impedance of LIBs by the galvanostatic control, i. e., 3D EIS during the measurement of charge/discharge curves [1-4], and short time impedance determination with a wavelet transformation (WT) [5-7]. These methods enable us the simultaneous measurement of charge/discharge curves and impedance spectra of LIBs. For example, the DC and AC signals to measure impedance spectra are charge/discharge current and small amplitude of sinusoidal current, respectively, in the case of 3D EIS [1-4].

In this presentation, we report a method to determine impedance parameters from the charge curves of LIBs without imposing exiting signals like sinusoidal waves. The voltage relaxation after CC and CV charges includes three times constants related to electrolyte resistance, charge transfer at electrolyte/electrode interface, and diffusion of lithium-ions. The impedance parameters determined from voltage relaxation are changed with the degradation ratio of LIBs. In addition, we present a highly sensitive method to detect degradation of LIBs, on the basis of the impedance parameters determined from charge curve. An anomaly analysis of LIBs was carried out with Mahalanobis-Taguchi method. The Mahalanobis distances calculated from the plural impedance parameters allows highly sensitive detection for a few percent of degradation of LIBs.

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Effect of Water on Local Transport Resistance in Catalyst Layer of PEMFC

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Abstract

Resistance of oxygen transport through ionomer to platinum surface R_{ion} in catalyst layer (CL) limits the performance of proton exchange membrane fuel cell (PEMFC), especially for that with low platinum loading. Measuring the limiting current density under dilute oxygen atmosphere is a common method to characterize the local transport resistance R_{local}, which is usually viewed equal to R_{ion} since the water produced during the measurement is very small. However, it's usually assumed that all Pt is covered by ionomer or the ORR reaction only occurs on the Pt covered by ionomer, which contradicts with some existing experimental results [1][2]. Such a contradiction makes the physical meaning of R_{local} ambiguous. In this work, we revisit the evolution process of Pt/ionomer interface and Pt/water interface with potential change, measure the change of ECSA and CL transport resistance with relative humidity (RH) of CL with different ionomer coverage. The result shows that with the increase of RH, the water combines with ionomer firstly and then forms liquid water film on the surface of Platinum, leading to different change slope of ECSA and CL transport resistance. This result indicates two aspects of water on R_{local}, one is that with higher water content, the intrinsic resistance of ionomer decreases, another is that under high humidity, water as a proton source covers more Pt surface area and makes it electrochemically active, leading to smaller R_{local}. For the Pt area covered by water, the proton conduction may be the limiting factor instead of gas transport, and electrochemical impedance spectroscopy (EIS) under H2/N2 atmosphere is performed to measure the proton conductivity under different RH to distinguish the limitation.

Keywords: PEMFC, catalyst layer, local transport resistance, water, EIS

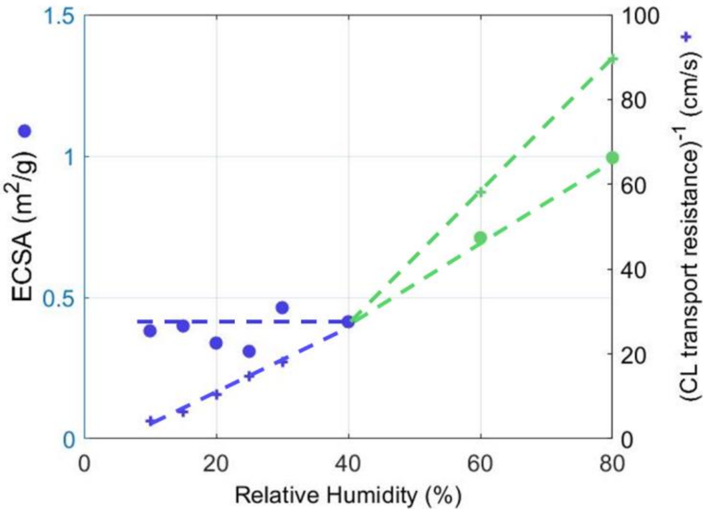

Figure 1 The change of ECSA (•) and the reciprocal of CL transport resistance (+) with RH

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Electro-catalysis

Effects and EIS Analysis of Pure Water Electrolysis with Overlapping Cathode/Anode EDLs

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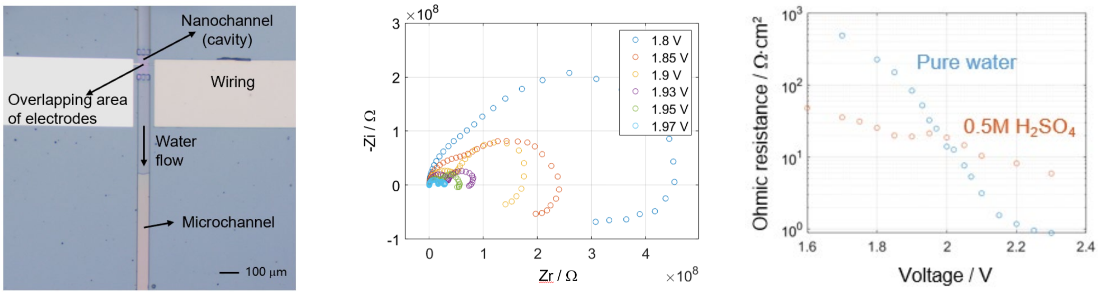
In the renewable future, electricity prices will be significantly reduced, while the capacity factor of water electrolysis devices will also drop due to energy fluctuations. Thus, electrolyzers are required to juggle both high energy efficiency and low material costs. However, the existing technologies have difficulties to fulfill the requirement, as those with high efficiency inevitably utilize precious metal catalysts or solid electrolytes.

We identify the potential to maintain both high efficiency and low material costs for WE when electric double layers (EDLs) at the cathode and anode are brought into deep overlap. The strong electric field within the overlapping EDLs accelerates the migration of ions, thus both improving voltage efficiency and allowing the absence of membranes or added electrolytes. The only relevant paper[1] substantiated that pure water can be electrolyzed continuously and efficiently. However, they did not recognize the side effect of the overlapping EDLs. The H2 and O2 generated within the nanogap can easily diffuse to the opposite electrode and trigger side reactions, which reduce the current efficiency and also interfere with the main effect of pure water electrolysis.

To obtain the performance of the main effect of the pure water electrolysis, we eliminate the crossover of H_2 and O_2 using the flow of electrolyte. Nanofluidic reactors are developed, as shown in Fig.1(a), which drive pure water through the nano-cavity between the electrodes. The EIS of the pure water electrolysis demonstrate the shape of two conductance semicircles and one inductance semicircle, as shown in Fig.1(b), which represent ohmic polarization, activation polarization and surface adsorption, representatively. Moreover, the ohmic resistance of the pure water, extracted from the EIS, shows a higher sensitivity with the strength of the electric field than that of the acid, as shown in Fig.1(c), indicating the significance of water dissociation reaction of pure water electrolysis.



(a) (b) (c)

Fig. 1. (a) Microscope picture of the nanofluidic reactor; (b) EIS of pure water electrolysis with the electrode distance of 100 nm; (c) comparison of the ohmic resistance of the water electrolysis between pure water and acid

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Pioneering Performances of RuIr Nanoalloys towards Efficient Acidic Water Splitting

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Water electrolysis has been deemed as the feasible and sustainable technology to provide hydrogen with the growing utilization of abundant renewable sources, which could significantly mitigate the environmental pollution and world energy supply. In contrast to the traditional alkaline water electrolysis, acidic water electrolysis technology has been regarded as an enabling strategy for energy conversion by merit of higher energy efficiency, more compact design, greater gas purity. However, large-scale deployment of acidic water electrolysis has been restricted by the lack of an efficient and durable electrocatalyst for OER, because most metals dissolve in the working potential region according to Pourbaix diagrams. Herein, we employ a simple and scalable one-pot pyrolysis approach to synthesize ultrafine RuIr binary alloy nanocrystalline catalysts with dendritic morphology at the micro level by thermal reduction of polyols. A large number of co-coherent and semi-coherent phenomena and lattice distortion result in a large number of grain boundaries between grains. These grain boundaries make the RuIr alloy catalyst form an open structure on the micro level, increase the exposed active sites on the surface, the RuIr alloy exhibits prominent catalytic activity. The rising valence state of surface Ir atoms leads to the formation of high valence Ir^{4+} ions, which produces the “Ir-protective skeleton” to prevent the further dissolution of Ru atoms, ensuring the long-term stability of the OER catalyst. Specifically, the optimized RuIr alloy offer the excellent electrocatalytic OER activity and robust stability, featuring low overpotential of 192 mV at a current density of 10 mA cm^{-2} in 0.5 M H_2SO_4 and no detectable activity decay under operation has been observed for 30 h. These metrics show that alloying to cause surface chemical reconstruction may be a valuable guide to develop affordable high-performance catalysts for large-scale water splitting.

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Towards Ultra-high Resolution and Localized EIS for Advanced Energy Research

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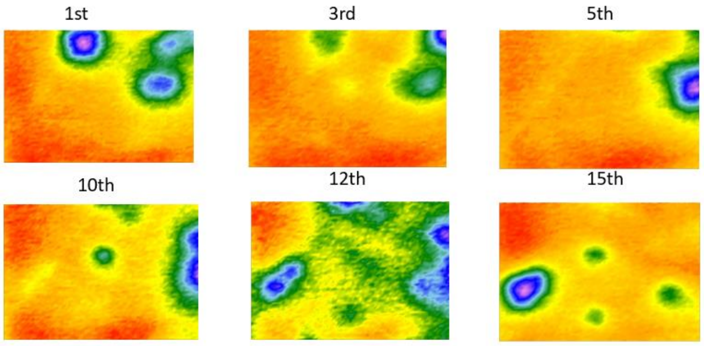
Recently, according to advanced battery quickly developed, such as high capacity, solid state battery and fuel cell etc. For these advance energy devices, higher capacity lower impedance, and ionic conductivity is very important for metal solid state battery, and catalyst active site evaluation is also vital for fuel cell research.

Conventional electrochemical impedance spectroscopy capability cannot meet these extreme requirements. Bulk electrochemical data that represents a surface-averaged response to the initial excitation. This averaging may conceal microscopic reaction mechanisms. Localized electrochemical impedance spectroscopy (LEIS) can help to overcome this limitation and to improve the understanding of reaction kinetics and mechanisms.



Time resolved images

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Platinum composite titanium-based substrate for electrocatalysis

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Carbon neutralization becomes a hotspot in today's energy area. Hydrogen energy is clean and efficient, which makes it a more ideal energy source compared with traditional fossil fuel. The noble-metal like Pt is the most efficient electrocatalyst. Since its high cost made it difficult to commercialize. Finding an ideal carrier to maximize the coefficient of utilization of Pt. Herein we present multiple scenarios of our works.

We took Ti sheet as substrate. Anodization was performed. The transition metal Ni was chosen to form a bimetallic catalyst with Pt acts as main active sites by electrodeposition. the nickel can prevent the Pt from being poisoned by carbon monoxide. Furthermore, the strong interaction between TiO_2 and Pt can hinder the catalyst agglomeration, which will improve the stability of Pt during long cyclic performance. The PtNi/TNTs/Ti composite electrode owns a high ECSA of 505 cm^2 mg^{-1} and a high mass activity of 780 mA cm^{-2}.

For the self-supporting electrocatalyst for HER. We took the Ti-mesh as substrate for anodization. The platinum nano-clusters were loaded by atom layer deposition on the TiO_2 NTs. The Pt_x/TiO_2 NTs@3D-Ti significantly improves the hydrogen evolution ability of platinum and improve the mass activity of Pt. The electrocatalyst exhibit a low Tafel slope of 37.7 mV dec^{-1} and low overpotential of 53 mV at 10 mA cm^{-2}.

And for other Ti-based catalyst. We took MXene, a newly synthesized 2D material in recent decades, as carrier. The ultrathin $Ti_3C_2T_x$ MXene was prepared by a simple two step etching procedure, which showed a high specific surface area. The sample showed a high double layer capacity of 64.98 mF·cm^{-2}, which is 14 times as large as that of HF prepared MXene, indicating a larger electrochemically active surface area. With Pt loading, the sample delivered better HER performance than Pt/C in the LSV test (~51mV at 10 mA·cm^{-2}). This work provides an effective route for the preparation of ultrathin MXene sheets leading to superior HER performance.

Analysis of Proton Transport in Electrospun Catalyst Layer

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Abstract

Electrospun catalyst layer (E-spun CL) exhibits superior performance and durability compared with the conventional coated CL.[1,2] These enhancements are attributed to two aspects, one is the homogeneous distribution of catalyst and ionomer, enlarging the area of ionomer-Platinum interface and increasing electrochemical surface area (ECSA) of CL, and another is the superior conductivity of ionomer nanofiber with the diameters of hundreds of nanometers[3], which is about an order of magnitude higher than the proton conductivity of bulk ionomers, further increase the conductivity and accessibility of proton in CL. Such excellent proton accessibility and conductivity of E-spun CL makes it possible to reduce ionomer content to enhance gas transport while keeping good proton transport. To verify this idea, we fabricated E-spun CL with different ionomer/carbon ratio (I/C) from 0.6 to 1 and characterized their proton transport resistance and gas transport resistance through electrochemical impedance spectroscopy (EIS) and limiting current density methods, respectively. The results indicated the best I/C of E-spun CL is smaller than 0.6, which is smaller than the coated CL, and the smaller ionomer content makes E-spun CL has smaller gas transport resistance and better performance, as shown in Fig.1.

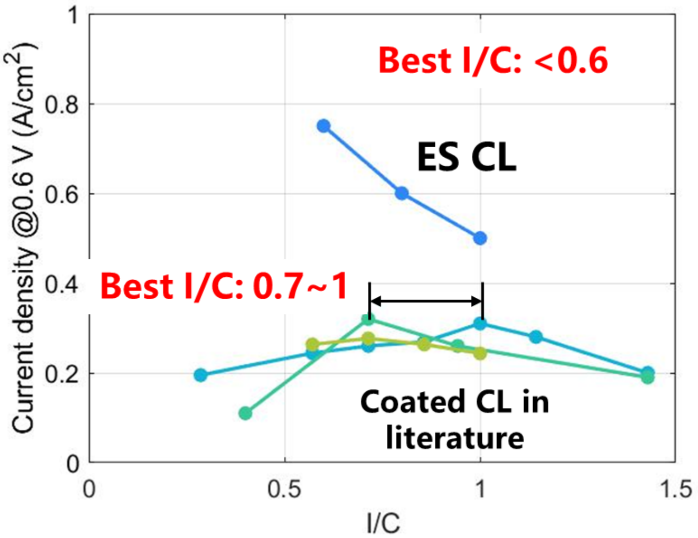

Fig.1 Effect of I/C on the performance of E-spun CL and coated CL.

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Insight into the Origin of Pseudo Peaks Decoded by DRT/ DDC for EIS

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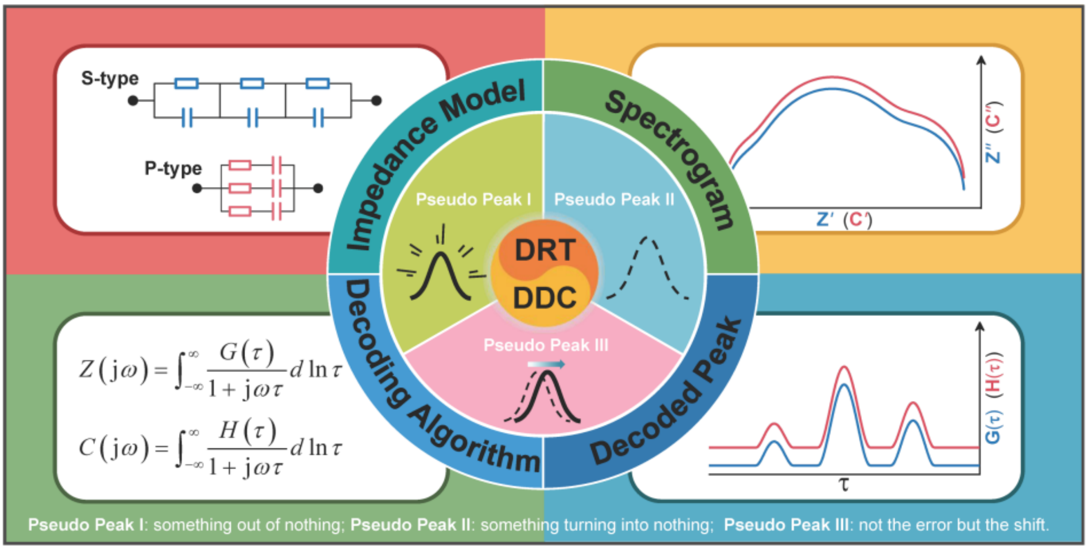
Electrochemical impedance spectroscopy (EIS) is a powerful diagnosis tool. However, it is still a challenge to separate the overlapped physicochemical processes. Both distribution of relaxation times (DRT) and distribution of differential capacity (DDC) can be used to solve above question. But, it is still an open question how to identify pseudo peaks decoded by the DRT/DDC method. In this work, a new insight into the origin of pseudo peaks are presented from the viewpoint of the symmetry of the DRT/DDC method, in term of the impedance model, the spectrogram, the decoding algorithm, and the decoded peak. First, pseudo peaks are identified into three sorts, i.e. the one is decoded at a given frequency but really does not exist; the one really exists at a given frequency but is not decoded; the one is decoded but its real position shifts. Secondly, the decoded peaks by the DRT/DDC method are quantitatively evaluated with respect to the penalty factor, the peak intensity, and the impedance model. Thirdly, the solution to pseudo peaks decoded by the DRT/DDC method is validated based on the simulated impedance spectra from integer to fractional-order models. Finally, insight into the origin of pseudo peaks decoded by the DRT/DDC method are concluded and the future work is proposed. The results obtained in this work might improve the reliability of the DRT/DDC method for EIS diagnosis.



Pseudo Peak I: something out of nothing; **Pseudo Peak II**: something turning into nothing; **Pseudo Peak III**: not the error but the shift.

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Pyrolysis-free COP-based Electrocatalysts Applied in Energy Devices

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The acute increase in the concentration of carbon dioxide (CO_2) in the atmosphere has intensified the urgent need for clean and sustainable energy technologies to achieve carbon neutralization as soon as possible1. Proton exchange membrane fuel cells (PEMFC) and zinc-air batteries (ZABs) devices are typical clean energy conversion devices, whereas their sluggish oxygen reduction reaction (ORR) at the cathode requires highly efficient electrocatalysts to ensure the progress of the reaction. In recent years, transition metal-nitrogen-carbon (M-N-C) electrocatalysts have shown great promise and application potential in ORR, but such catalysts usually require high-temperature pyrolysis above 700 °C for synthesis. Its components and structures tend to be complicated, and the active center is not clearly understood, which brings great challenges to the study of catalytic mechanism and restricts the further performance improvement and scale-up preparation of catalysts. Based on the challenges and requirements of M-N-C electrocatalysts in the current research, we utilize pyrolysis-free covalent organic polymer (COP) materials to solve many challenges and problems of pyrolysis-free M-N-C catalysts.

1. We designed a series of fully closed π-conjugated COP materials, which contained well-defined FeN_4 configurations whereas discrepant delocalized conjugated carbon matrix in the molecular structure. We systematically explore the structure-activity relationship between the carbon coordination environment and ORR catalytic activity and thereby improving the catalytic activity of FeN_4 site sites.

2. New strategy for F-closed edge and $3dz^2$-orbital adjustment strategy for the electronic configurations of pyrolysis-free COP catalytic materials was proposed, and the developed pyrolysis-free COP catalyst was directly assembled into fuel cell, in which its peak power was improved by an order of magnitude.

3. An electron donor-acceptor regulation strategy was proposed to guide the preparation of solution-processable COP catalysts; based on the solution processability of COP, combined with NiFeLDH, a bifunctional oxygen electrocatalyst with ultra-high performance was prepared at the kilogram level.

Fig. 1 structure logic diagram

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Solid-phase Thermal Migration Synthesis of Fe-N-C Catalyst Toward High Efficiency Oxygen Reduction in both Alkaline and Acidic Media

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Recently, in order to solve the problems of energy crisis and environmental pollution, the efficient and clean energy conversion devices are needed to be developed, such as fuel cells and metal-air batteries. But the sluggish in kinetics of the cathode oxygen reduction reaction (ORR) is the key step to limit the widely application of these energy supply systems, which depends on the development of high efficiency catalyst for ORR. Because of its strong catalytic ability, platinum (Pt) is widely used in the electrocatalysis of ORR, but its high prices, rare reserves on the earth and low stability hinder the large-scale commercial application of platinum-containing electrodes. To address this issue, a lot of works have been done to find alternative electrode catalytic materials with low cost, sufficient reserves and high stability in various electrolytes. However, it is still a grand challenge to develop a nonprecious-metal electrocatalyst for oxygen reduction reaction (ORR) with both high activity and excellent stability to replace the Pt-based catalysts. Herein, we propose a solid-phase thermal migration method to synthesize FeNCNTs catalysts. The half-wave potential of FeNCNTs is 30mV superior to commercial Pt/C in alkaline medium, while it is only 100mV less than commercial Pt/C in acidic media. Impressively, the FeNCNTs-based zinc-air battery exhibits a outstanding power density higher than the one assembled by commercial Pt/C. Combining experimental results and density functional theory (DFT) calculations, we further reveal that the origin of high-ORR activity of FeNCNTs is from the Fe-pyridinic-N4 species at the end of zigzag type carbon nanotubes, because such molecular structure is the key, leading to the active site increase in an order of magnitude which successfully clarifies the bottleneck puzzle of why a small amount of iron in the FeNCNTs can exhibit extremely superior ORR activity.

1) Polyaniline contains a large amount of N element, in which benzene rings and amino groups are alternately connected in a non-linear manner, which is an ideal precursor for the preparation of porous N-doped carbon nanotubes (NCNTs) by carbonization followed by NH3 activation.
2) The Fe-doped NCNTs retained the basic structure of NCNTs and formed Fe-N sites with higher ORR catalytic activity. The special electronic structure of Fe-NC resulted in the higher catalytic activity of FeNCTs (with 0.87 V The half-wave potential is higher than 0.84V of commercial Pt/C).
3) The design of FeNCNTs may facilitate the development of high-performance nonprecious-metal materials as next-generation fuel cell catalysts.
4) Through DFT calculation, the origin of the high activity of FeNCNTs was explored and its ORR reaction process was revealed.

A method for structure design and performance prediction of W/Sn-doped PtCu-based ternary alloy catalysts for oxygen reduction

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Platinum is the most viable catalytic material for the oxygen reduction reaction (ORR), a process key to the operation of proton exchange membrane fuel cells (PEMFCs). However, the scarcity of this element in the earth crust and its ever-increasing price have made it a challenging task to commercialize PEMFCs as a zero-emission technology for future transportation. In this regard, how to reduce the material cost while retaining the catalytic performance has been an active subject of research over several decades. Pt-based alloy nanocrystals have shown great success in oxygen reduction electrocatalysis owing to their unique surface and electronic structures. In order to further balance stability and performance of catalysts, we need to add the third component to the binary alloy to obtain the ternary alloy. However, there are still many problems in the actual synthesis process of ternary alloys. In detail, the relative contents of the three components, variety of elements used, the synthesis conditions, all of them can probably affect the performance of the catalysts, which are often very time-consuming and laborious in actual synthesis exploration. For the above purpose, we have took W/Sn-doped PtCu-based ternary alloys as example and developed a calculation method to predict the structure, stability, synthesis conditions and activity of ternary alloy catalysts quickly. Following are the main contents and results of this method

1) All calculations are performed based on density functional theory (DFT), using the Dmol^3 code with the spin-unrestricted method. Five kinds of energy, the analysis of d-band centre, the work function and the free energy diagrams of oxygen reduction are carried out respectively.
2) We use the formation energy to predict the microstructural trend of the ternary alloy, and use the activation energy barrier to provide guidance for the synthesis conditions. At the same time, the comprehensive analysis of energy and geometry structure can help us predict the trend of catalyst stability improvement. At last, through the analysis of d-band centre, compressive strain, and free energy diagrams of the alloys, We explore the sources of ORR activity in W/Sn-doped PtCu-based ternary alloys and make corresponding predictions.

The plasmon-mediated photoelectrochemical water-oxidation studied by a combination of electrochemical impedance spectroscopy and surface-enhanced Raman spectroscopy on an ultramicroelectrode

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Plasmon-mediated chemical reaction (PMCR) is promising in storing solar energy in chemicals, because it utilizes visible light which is with the largest proportion of the solar energy on the earth. However, it remains desired to improve the efficiency of PMCR by (photo-)electrocatalysis, because the energy of hot-carriers excited by visible light is not high. In this context, to obtain thorough understanding for rationally improving electrocatalyst, we developed a novel combination method of electrochemical impedance spectroscopy (EIS) and in-situ electrochemical surface-enhanced Raman spectroscopy (SERS). By EIS, the hot-carriers-transfer can be quantified. By SERS, the fingerprints of surface species at the intermediate stages can be revealed. To well correlate EIS and SERS, an ultramicroelectrode was employed as a working electrode, where the laser spot well overlapped the surface area of an ultramicroelectrode.[1] In this way, the PMCR, EIS and SERS on an ultramicroelectrode were excited and measured simultaneously in one measurement.

By using this combination method of EIS and SERS, we investigated the plasmon-mediated photoelectrochemical water-oxidation which is usually a bottleneck in applications. In this system, a Au-nanoparticles-covered-Au ultramicroelectrode was used, where the surface plasmons of Au nanoparticles were excited. We found negative shift of the onset potential of water-oxidation, increase in photocurrent density, decrease in electron-transfer resistance and fingerprints of surface hydroxide intermediates, which were well correlated in one measurement. The correlated EIS and SERS gave a straightforward insight of the kinetics of plasmon-mediated photoelectrochemical water-oxidation regarding hot-carriers, surface species and reaction rate. We explored the pH-, laser-wavelength and laser-power-density-dependences, which will be reported in this presentation.

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一步法制备二氧化钛纳米管锚定铂基催化剂用于甲醇氧化反应

One-step synthesis of PtM anchored on TiO_2 nanotube arrays for methanol oxidation

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Exploring highly efficient, CO-tolerant and stability catalyst, such as Pt-based bimetallic catalyst for methanol oxidation reaction (MOR) is pressingly demanded towards commercialization of direct methanol fuel cells (DMFCs). A series of PtM bimetallic particles modified Titanium dioxide nanotube (TNT) had been synthesized by one-step electrochemical synthesis as anode catalysts for methanol oxidation reaction. The obtained PtM/TNTs/Ti electrode exhibits a large electrochemical active area. Bimetallic catalyst electrode demonstrated high electrocatalytic activity, which enhanced MOR and electrode durability significantly. According to further structure analysis, the improvement in catalytic activity was attributed to lattice compression when transition metal atoms entered the Pt lattice. And density functional theory (DFT) calculations indicated that the remarkably enhanced catalytic performance on PtNi through lattice compression arising from the enhanced OH adsorption. An insight into growth mechanism is also proposed according to the first-principle calculations. It appears promising that this simple, low energy, and low-cost method could be used to prepare a hybrid integrated electrode for use in energy and environmental applications. The obtained electrode is expected as the candidate electrode to output high power density in DMFCs.

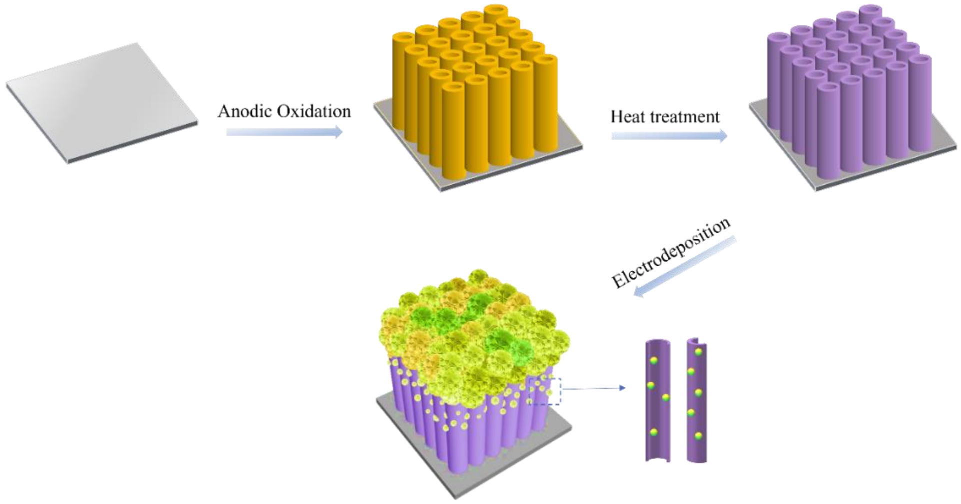

Figure 1. Schematic diagram of the fabrication of PtM/TNTs/Ti electrode[1].

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通过铂元素结合具有高电化学活性面积的超薄 Ti3C2Tx MXene 提高析氢性能

Ultrathin $Ti_3C_2T_x$ MXene sheets with high electrochemically active area anchored Pt boosting hydrogen evolution

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Carbon neutralization becomes a hotspot in today's energy area. Hydrogen energy is clean and efficient, which makes it a more ideal energy source compared with traditional fossil fuel. MXene, a new kind of transition metal carbides firstly found in 2011, owning its unique 2D layered structure made by carbon atomic layer sand transition metal atomic layers has shown its application in many fields like batteries and supercapacitors. Due to its 2D structure, it can provide many active sites for HER. The nonuniformly morphology and restacking effect of the 2D MXene sheets still hinder its activity in catalyst and further restrict its practical use in HER. To reduce platinum usage, ultrathin MXene sheets with little restacking effect were prepared. The ultrathin MXene was prepared by a simple two step etching procedure, which showed a high specific surface area, low charge transfer resistance. The sample showed a high double layer capacity of 64.98 mF·cm^{-2}, which is 14 times as large as that of ordinary HF prepared MXene, indicating a larger electrochemically active surface area. It showed a much better HER performance of ~190mV at 10mA·cm^{-2}. The better performance attributes to 0.4wt% Pt loaded. The sample exhibited a better HER performance of ~75mV at 10mA·cm^{-2} and a Tafel slope of 61.7mV·dec^{-1} close to 40wt% commercial Pt/C. The sample performed better than Pt/C in a 3h chronopotentiometry test and hardly changed in ECSA after the cyclic experiment. With more Pt loading, the sample delivered better HER performance than Pt/C in the LSV test (~51mV at 10 mA·cm^{-2}). This work provides an effective route for the preparation of ultrathin MXene sheets with a larger electrochemically active area and more active sites for Pt loading, leading to superior HER performance.

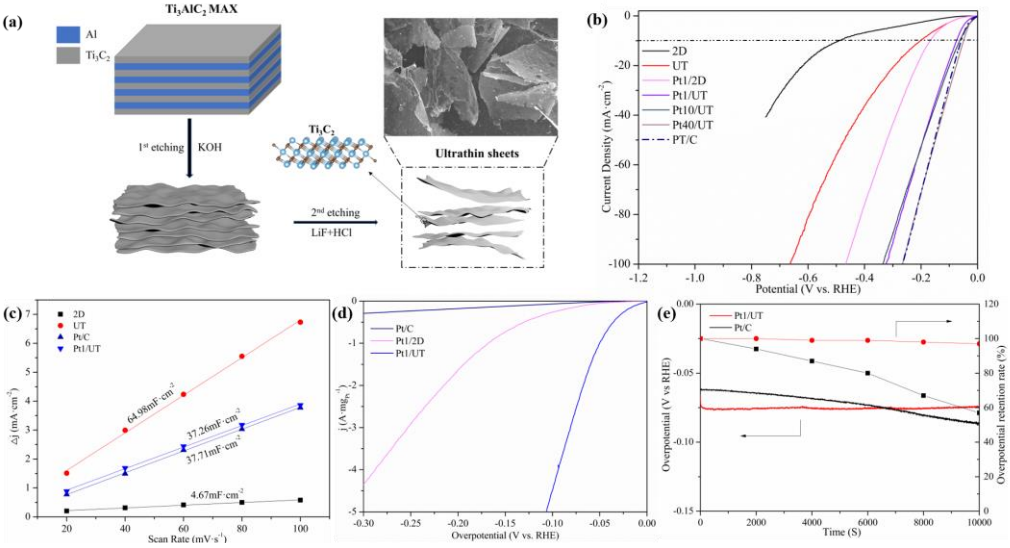

Fig1. (a) Schematic diagram of synthesis and morphology of ultrathin MXene sheets. (b) linear scan voltammetry curves of different samples. (c) electrochemical active area of traditional MXene sheets (2D), ultrathin MXene sheets (UT), Pt/C and ultrathin MXene sheets anchoring 1wt.% platinum (Pt1/UT). (d) mass activity of Pt/C 1wt.% platinum anchored with 2D and UT. (e) 3h Chronopotentiometry test and overpotential retention rate of Pt1/UT and Pt/C

Electrochemical Impedance Diagnosis of the Hydrogen Electrode Reactions in Alkaline

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The alkaline polymer electrolyte fuel cells (APEFCs) have achieved significant development in recent years, but the development of the anodic non-noble catalysts still faces serious challenges. As the basis for material researching, exploring the mechanism of the hydrogen electrode reaction (HER/HOR) has crucial scientific value. Currently, the mainstream view considers that the hydrogen evolution reaction (HER) and the hydrogen oxidation reaction (HOR) exhibit a good symmetry on Pt under alkaline conditions, and the hydrogen electrode reaction follows a Tafel-Volmer mechanism with Volmer as the rate-determining step. However, due to the extremely low solubility of hydrogen, the traditional rotating disk electrode (RDE) testing method is affected by the diffusion limited current, so the kinetic research can only be carried out around the finite polarization region near the hydrogen equilibrium potential.

In order to expand the potential window of the hydrogen electrode reaction research, a three-electrode testing method based on a waterproof gas diffusion electrode (GDE) was established in this work, and the kinetic information of the hydrogen electrode reaction which is far away from the equilibrium potential can be obtained. At the same time, electrochemical impedance spectroscopy (EIS) provides more information of reaction and interface structure beyond the polarization curve. From the impedance diagnosis results within ±200 mV potential range, it was found that with the increasing degree of deviation from the hydrogen equilibrium potential, the asymmetry between HER and HOR on Pt under alkaline conditions is shown. In other words, the impedance behavior of HER and HOR have different potential dependencies, which can hardly be discovered from the I-V curve. This study has deepened the understanding of the hydrogen electrode reaction mechanism on Pt in alkaline.

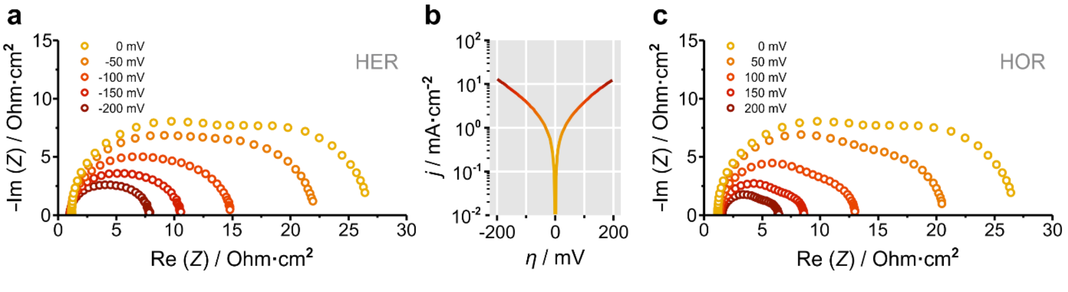

Fig. 1 The Nyquist plots of the AC impedance data in (**a**) negative polarization and (**c**) positive polarization. (**b**) The I-V curve on a sputtering Pt GDE in 0.1 M KOH at 5 mV/s.

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Evolution of components and electrochemical response characteristics of hydrogen-charged copper surface

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The application of a Cu coating to provide enhanced container lifetimes, is under consideration in many countries, since Cu is anticipated to have a very low corrosion rate under deep geological repository conditions. However, there are few studies concerning the influence of hydrogen permeation on the integrity and corrosion performance of Cu coatings. In this work, hydrogen permeation and corrosion behaviour of Cu coated carbon steel under simulated nuclear waste disposal conditions of the Beishan area have been investigated. The steady-state hydrogen permeation current through carbon steel (Q235) was found to be significantly decreased by a Cu coating with a thickness of several micrometers and the calculated diffusion coefficient of carbon steel with Cu coating was similar to the reported diffusion coefficient for pure Cu. Based on the morphology characterization by SEM and FIB-SEM, chemical component analysis by XRD and XPS of the hydrogen-charged surface, copper hydride (CuH) was proposed to formed during the hydrogen charging process with its subsequent decomposition leading to the formation of porous and partially protective layer composed of CuOH and Cu_2O when exposed to simulated groundwater. Due to the presence of the film layer formed during hydrogen charging and immersion, at least two ill-defined responses in the EIS Bode phase spectrum. An equivalent circuit with two-time constants $[R_s(Q_f(R_f(Q_{dl}R_{ct})))]$ is appropriate to fit the EIS spectra. Constant phase elements (Q), calculated according to the equation $Q=1/[Y_0(j\omega)^n]$. For the hydrogen-charged Cu coating surface, both R_f and R_{ct} increase with immersion time. This is likely caused by the formation of a CuOH&Cu_2O complex film resulting from CuH decomposition, which appears to confer an improved corrosion resistance (the increased R_{ct}) of the Cu surface. Capacitive dispersion can be caused by many factors, e.g., surface reactivity, inhomogeneity, roughness and fractal geometry, etc. The low values of n, in the case of the hydrogen charged surface, were to be expected given the rough and porous nature of the surface films and the variation in composition with depth of the film on the hydrogen charged surface indicated by the XPS spectra.

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