Electrochemical Sensing of Biomarkers and Drugs Using Functional Nanomaterials

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C-reactive protein (CRP) is a common biomarker of cardiovascular disease, which is one of the leading causes of premature death worldwide. The determination of CRP from human serum is thus important for the diagnosis of the cardiovascular disease. In this talk, we report on the development of an electrochemical immunosensor for the detection of CRP antigens, where the CRP antibodies were immobilized on graphene oxide-based nanomaterials. The immobilization of CRP antibodies was characterized by the in-situ polarization modulation infrared reflection absorption spectroscopy. Various electrochemical methods such as cyclic voltammetry, square wave voltammetry, and electrochemical impedance spectroscopy were employed to assess the performance of the prepared electrochemical immunosensor, showing high selectivity and sensitivity for the efficient detection of the CRP. In addition, the development of advanced nanomaterial-based electrochemical sensors and biosensors for the detection of pharmaceutical compounds has garnered immense attention due to their advantages, such as high sensitivity and selectivity, real-time monitoring, and ease of use. Strategies for the design of high-performance electrochemical sensors and biosensors tailored toward specific pharmaceuticals will be discussed.

The Investigation of Local Electrochemical Reactivity of Copper Cold Spray Coatings

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In line with international best practices, the Nuclear Waste Management Organization's (NWMO) plan for the long-term disposal of used nuclear fuel is to use an engineered and natural multi-barrier system contained within a deep geological repository. One immediate barrier involves applying a corrosion-resistant copper coating that is approximately 3 mm thick onto carbon steel containers, which will act as the host of the used fuel bundles. Two main techniques have been considered for the application of copper coatings: electrodeposition (ED) and cold spray (CS). Although thorough research has been performed to understand the corrosion properties of such copper materials, [1, 2] the specimens are typically prepared to a smooth surface finish prior to in-lab testing. Yet, the microstructural features of the CS coating, such as pores and oxides, are unevenly distributed throughout its depth, which may affect the homogeneity of the coating's corrosion properties. The primary objectives of this study are to investigate the impact of coating thickness and redox mediators on the corrosion behaviour of copper coatings. To address this issue, this work employs macro- and microelectrochemical measurements, as well as complementary surface analysis techniques, including X-ray micro-computed tomography, scanning electron microscopy, and energy-dispersive X-ray spectroscopy. The objective is not only to investigate any possible significant differences in the electrochemical behaviour of the CS copper coating at different depths but also to correlate its response to the material's microstructure and damage morphologies at such depths.

In addition, this research seeks to enhance corrosion studies on metal coatings by employing scanning electrochemical microscopy (SECM) imaging in feedback mode to link electrochemical activity with inhomogeneities on the CS Cu coating surfaces. SECM is commonly used to assess the local electrochemical reactivity of corroding surfaces. One significant criticism of using SECM in corrosion research is the need for a redox mediator, which could react with the metal. [3] The findings from this study are anticipated to improve the understanding of the feedback mode in corrosion investigations and contribute to the future development of SECM as a more quantitative tool for in situ analysis of corroding systems.

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Coupling Liquid-Fed Electrochemical CO_2 Reduction with Glycerol Oxidation in a Zero-Gap Membrane Electrode Assembly Electrolyzer

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Abstract

Using reactive carbon solutions as liquid feedstocks for electrochemical carbon dioxide reduction (eCO_2R) offers a promising route to circumvent the energy-intensive steps of CO_2 purification, compression, and transportation in carbon capture and conversion. Despite advancements in liquid-fed electrolyzers that enhance selectivity and activity at the cathode, the effect of substituting the conventional oxygen evolution reaction (OER) with alternative anodic reactions has yet to be elucidated. In this work, we couple liquid-fed eCO_2R with the glycerol oxidation reaction (GOR) as the dominant anodic process and compare the resulting selectivity and activity to those obtained when OER serves as the anodic reaction under identical electrolyzer configurations. We demonstrate that the peak selectivity of our copper nanoparticle catalyst toward multi-carbon products shifts from 150 to 300 mA cm^{-2} while maintaining comparable Faradaic efficiency, upon replacing OER with GOR as the dominant anodic reaction. We further show that the total amount of cathodic and anodic multi-carbon products generated from eCO_2R paired with GOR is about an order of magnitude greater than that obtained from eCO_2R coupled with OER at the same cell voltage, indicating that an increased amount of valuable products can be produced using the eCO_2R–GOR system with the same energy input. Overall, by evaluating the productivity,

the stability and the energy efficiency, we show that GOR is arguably a more promising anodic reaction to pair with eCO_2R than OER.

Keywords: Liquid-fed CO_2 electrolyzer, glycerol oxidation reaction, multi-carbon products

Optimizing LPBF-Produced Austenitic ODS Steels: The Influence of HIP and Heat Treatment

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Materials used in nuclear reactors must withstand extreme service conditions, including high temperatures and intense neutron irradiation. Oxide dispersion-strengthened (ODS) steels are among the most promising candidates for such applications due to their superior high-temperature strength and irradiation resistance. Traditionally, ODS steels are produced via powder metallurgy followed by sintering. However, recent advances in additive manufacturing have sparked growing interest in fabricating ODS steels by laser powder bed fusion (LPBF).

In this study, 316L austenitic stainless steel with the addition of 1 wt.% Y_2O_3 (particle size 1–2 µm) was manufactured using LPBF (AconityMini system) and subsequently post-processed by hot isostatic pressing (HIP) and heat treatment, Figure 1. To evaluate the effect of HIP and heat treatment on the material's properties, both mechanical and corrosion tests were conducted. Electrochemical tests included open circuit potential and cyclic potentiodynamic polarization measurements in chloride containing solution, while mechanical evaluation was made based on uniaxial tensile testing.

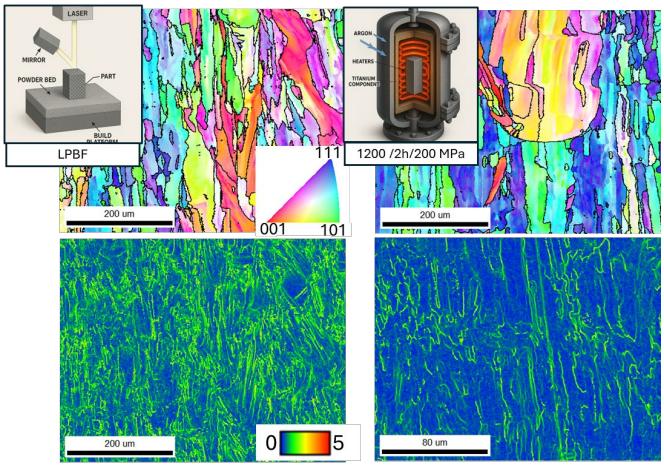

Fig.1 LPBF and HIP microstructures

The results before and after HIP treatment were systematically compared, providing insight into the influence of HIP on the microstructure, mechanical performance, and corrosion behavior of LPBF-produced 316L ODS steels. It was stated that microstructural changes induced by HIP increase elongation but reduce corrosion resistance. On the other hand, heat treatment, depending on the conditions, enhances the ability to repassivate.

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In-Situ Electrochemical Analysis of Atmospheric Copper Corrosion under Gamma Radiation

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Canada's plan for the safe and long-term management of high-level waste is to store it in used nuclear fuel containers (UFC) that will be placed in a suitable deep geological repository (DGR).[1] Copper is the proposed exterior container corrosion barrier material by Canada's Nuclear Waste Management Organization (NWMO).[2–4] The assured reliability of the copper coatings under gamma radiation is necessary as it will take the used fuel hundreds of years to decay to background levels. As the UFCs cool and water droplets condense on their surfaces, gamma radiation can influence corrosion by producing oxidizing radiolysis species (H_2O_2, HNO_3, HOCl) that may accelerate the copper's corrosion rate.

There are many studies regarding the copper corrosion behaviour, such as the humid air radiolysis model (HARM) and groundwater radiolysis model (GWRM) to predict the long-term integrity of copper coated UFCs. [4,5] However, there remains a gap between these models and direct experimental validation. While research had characterized copper corrosion in bulk solutions, there are no studies providing in-situ electrochemical measurements of corrosion within a droplet under gamma radiation.[4,6] This work bridges the gap by introducing a novel experimental approach that integrates droplet electrochemistry with ionizing irradiation. This approach directly quantifies real-time copper corrosion rates under aerated, humid repository-like conditions. The findings will provide foundational electrochemical data to assess the long-term integrity of copper UFCs and serve as an essential benchmark for the validation and refinement of existing radiolysis models.

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In-Situ Electrochemical Analysis of Atmospheric Copper Corrosion under Gamma Radiation

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Investigating the Colloidal Stability of 50 nm Gold Nanoparticles via DLS for Electrochemical Applications

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As a precious metal, gold is highly resistant to corrosion and oxidation under certain conditions. However, for the nano-sized gold, due to its large specific surface area and higher surface energy, its chemical and electrochemical reactivity increases compared to bulk gold. In the electrochemical systems, interactions between gold nanoparticles (AuNP) and ions, ligands, or solvent molecules can lead to aggregation, ligand adsorption, or surface transformations. Employing Dynamic Light Scattering (DLS), a non-destructive optical technique that measures fluctuations in scattered light to determine the hydrodynamic diameter and size distribution of particles. We have utilized DLS technology to study the intermolecular forces and stability of AuNPs that are crucial for electrochemistry.

In this work, we will present DLS measurements performed on 50 nm AuNPs dispersed in different electrolytes at different temperatures. We measured the time evolution of hydrodynamic size, polydispersity index, and absolute intensity to evaluate the stability of AuNPs in the electrolytes and provide guidelines for designing electrolyte media that preserve AuNPs dispersion over the timescales of electrochemical experiments. Additionally, we will outline the possibilities of integrating these stabilized nanoparticles into corrosion or sensing tests to predict the dispersion behaviour of AuNPs under potential bias.

In Situ Monitoring of Hypochlorite Decay Under Radiation Using Differential Pulse Voltammetry

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Understanding how concentrations of corrosive species evolve under radiation is essential for assessing the long-term performance of materials in nuclear environments. In this study, differential pulse voltammetry (DPV) was employed to monitor the concentration of hypochlorite (OCl^-), a reactive oxidant formed during the radiolysis of chloride-containing electrolytes under γ-radiation. Calibration curves established under non-irradiated conditions enabled *in situ* quantification of OCl^-, with concentrations independently validated using UV–vis spectroscopy. Simulations modeled the results of the DPV data, which revealed that in early stages Cl^- is the prevailing species in the system and contributes more than radiolytically produced species to the decay of OCl^- under radiation. The results of the modeling showed that in the early stages of γ-radiation exposure, hypochlorite decay was steady, which was in agreement with the DPV measurements conducted. As the exposure time increased, the $[H_2O_2]$ increased and became significant in reacting with OCl^- in the system. The model indicated that radiolytically generated chlorine-centered intermediates, enabled by the presence of Cl^-, contributed to OCl^- decomposition under irradiation, with the overall decay proceeding more slowly than predicted by existing kinetic parameters. Although DPV is a well-established electroanalytical method, its integration directly within a γ-radiation field represents a methodological advance. Here, we demonstrate the capability of *in situ* electrochemical detection of radiolytic oxidants using DPV under active irradiation. By coupling radiation chemistry with electrochemical sensing, this radiation electrochemical approach provides a framework for real-time monitoring of reactive species in irradiated conditions and offers a valuable tool for evaluating the chemical environment driving material degradation in nuclear waste management contexts.

Cu as a lone dopant in a titanium suboxide fuel cell catalyst support

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This work involves the bottom-up sol-gel synthesis of a Cu-doped Ti_4O_7 support material (TOC), which shows great potential as an alternative to the conventional carbon support in Pt/C catalysts.[1] Here, we demonstrate the advantages of the metal oxide support regarding long-term stability and activity, where Pt/C typically degrades rapidly due to various Pt agglomeration and dissolution mechanisms, in addition to carbon corrosion.[2] The TOC support shows a mesoporous nanostructure with high electronic conductivity, while also demonstrating strong metal support interactions with Pt nanoparticles for enhanced oxygen reduction (ORR) activity and stability compared to the commercial Pt/C.

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Corrosion Behaviour of Natural Copper as an Analogue for Manufactured Copper in Neutral Chloride Solutions.

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The international best practice for the safe management of used nuclear fuel is disposal in a deep geologic repository (DGR) using a multi-barrier system, with the sealed waste container being one of the critical barriers. In Canada, Sweden and Finland, the corrosion barrier will be Cu, chosen for its thermodynamic stability under the anoxic conditions expected in a DGR for most of the time. To demonstrate that containers will provide long-term containment, performance assessment models must be developed, based on short-term data generated under simulated DGR conditions in laboratories and underground laboratories. Natural analogues (long-lived geological Cu deposits) can be used to validate these models, provided their in-laboratory corrosion performance can be shown to be similar to that of manufactured Cu materials.

In this study, the composition, microstructure and electrochemical/corrosion performance of one billion-year-old natural metallic Cu specimens from various mines in the Keweenaw Peninsula region of Michigan (USA) have been investigated, using electrochemical and surface analytical techniques.

Cu specimens from the various mines exhibit slight differences in corrosion rates in deaerated (dissolved oxygen concentrations in the μM range) neutral chloride solutions. Non-uniform corrosion with porous and non-protective copper(I) oxide deposition was observed on one mine specimen. These differences appear to be attributable to variations in material composition and microstructure. Compared with manufactured Cu (wrought, electrodeposited, and cold-sprayed Cu), natural Cu specimens exhibit a similar corrosion rate, except for the Cu sample from Adventure mine. Analyses are underway to investigate the factors controlling the various surface morphological and compositional features and their influence on corrosion.

Surface Structure Dependence of the Hydrogen Evolution Reaction at Nickel Electrodes

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Monocrystalline nickel electrodes (abbreviated as Ni(hkl)) are prepared using the controlled atmosphere flame fusion (CAFF) technique developed in our laboratory and are used to study the hydrogen evolution reaction (HER) in 0.10 M aqueous NaOH solution. The main objective of this research is to determine whether the surface arrangement of atoms of the Ni(hkl) electrodes affects the mechanism and kinetics of the HER. Because the shape of cyclic voltammetry (CV) of metallic electrode materials depends on the surface arrangements of atoms (with all other experimental conditions being the same), the quality of the Ni(hkl) electrodes is verified by conducting CV measurements, which confirm that the Ni(hkl) electrodes are of high quality and their surfaces atomically ordered. The mechanism and kinetics of the HER at the Ni(hkl) electrodes are analyzed by conducting linear sweep voltammetry (LSV) measurements at a very low potential scan rate (s = 0.10 mV s-1) to ensure steady-state conditions. Then, the LSV transients are used to prepare Tafel polarization plots, from which the Tafel slope (b) and exchange current density (j_o) values are determined. These Tafel plots show two distinct linear regions, for which the values of b and j_o are calculated; they are found to depend on the surface geometry of the Ni(hkl) electrodes. Tafel plots for the HER occurring at polycrystalline Ni materials (bulk Ni and Ni foam) reveal only one linear region. Thus, the electrochemical behavior of the Ni(hkl) electrodes is entirely different. The values of j_o are converted to the turnover number (*TON*) of H_2 molecules being produced per surface atom per unit of time. An analysis of the values of j_o and *TON* shows that the Ni(111) and Ni(110) electrodes reveal comparable electrocatalytic activities towards the HER, and about twice higher than that of the Ni(100) electrode. Finally, CV measurements are performed to examine the state of the Ni(hkl) electrodes after the LSV measurements, thus after the electrolytic H_2(g) generation. The CV transients are different than those obtained prior to the HER and point the possible development of a nickel hydride (NiH_x) in the near-surface region of the Ni(hkl) electrodes. The values of j_o and *TON* for the Ni(hkl) electrodes suggest that nanomaterials used as cathodes in the industrial scale HER should possess a significantly high percentage of Ni(111) and Ni(110) facets.

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Effects of α-irradiation on the oxidation of electrodeposited UO_2 films using in-situ RBS

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Nuclear energy serves as a reliable, environmentally friendly, and cost-efficient source of power, standing as the second-largest global contributor to low-emission electricity generation, following hydropower sources. However, the continuous operation of nuclear power plants brings the critical responsibility of managing the long-term storage and disposal of spent nuclear fuel. To address this challenge, Canada is planning to build a deep geological repository (DGR) system, which will be constructed at a depth of approximately 500 to 800 metres in the region of Wabigoon Lake Ojibway Nation and the Township of Ignace, Ontario. The DGR relies on corrosion-resistant used fuel containers (UFCs) and other barriers, and it is anticipated to provide safe and long-term containment of radioactive waste. However, it remains essential to consider the unlikely possibility of UFC failure, which could allow groundwater to encounter the fuel. The majority of radionuclides in the spent fuel are embedded within the fuel matrix, and the rate at which the fuel dissolves when exposed to groundwater will influence how quickly these radionuclides might be released into the surrounding environment. The containers are expected to maintain their integrity for a long duration, with any potential breaches anticipated to occur only after the β- and γ-radiation levels have significantly decayed, making α-radiation the predominant radiation source affecting the fuel surface and thus a key area of focus. The α-radiation may cause cumulative damage to the fuel matrix while it is stored in the containers and possibly create soluble U^{VI} compounds. Given that U^{VI} solubility is several orders of magnitude higher than that of U^{V} and U^{IV}, this could substantially accelerate the dissolution of the fuel. Consequently, it is very important to thoroughly investigate the direct interactions between high-energy α-particles and the UO_2-based nuclear fuels, as these interactions may significantly influence the dissolution rate and the release of radionuclides.

This research employs an innovative methodology to explore the impact of α-particles on UO_2-based fuels through in-situ α-irradiation experiments. This approach enables a detailed examination of the fuel's surface oxidation state by having a thin-layer configuration subjected to α-irradiation. The method utilizes electrodeposited UO_2 thin film specimens and the Western Tandetron accelerator's Rutherford backscattering beamline to deliver high-energy, high-flux α-particles. To develop high-quality UO_2 thin films, the electrodeposition parameters were optimized by conducting thorough characterizations of the films deposited on copper substrates. Characterization techniques, including scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and Raman spectroscopy, helped evaluate key properties such as the surface morphology, elemental composition, crystalline phase, and structural integrity of the electrodeposited UO_2 thin films. The findings indicated that employing potentials around -1 V (vs. saturated calomel electrode (SCE)) and current densities around -5 mA/cm^2 during electrodeposition was most effective, resulting in stable films with minimal cracking, enhanced adhesion to the substrate, and improved crystallinity following an annealing process. In the next step, UO_2 thin films were carefully grown onto copper-coated silicon nitride (SiN) windows using the optimized electrodeposition parameters. These samples were then integrated into a specially designed in-situ cell (Fig. 1) to conduct α-irradiation experiments. Investigations of the effects of high-energy α-particles via in-situ α-irradiation experiments are currently underway. The surface oxidation states of UO_2 films after α-irradiation will be explored, and the effects of α-irradiation on the dissolution rate, surface morphology, and phase structure of the UO_2 samples will be studied.

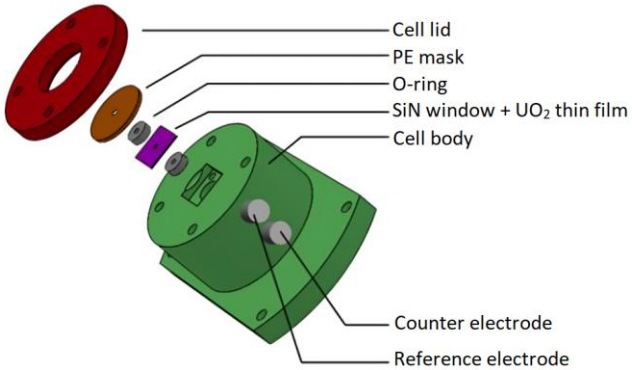

Fig 1. Schematic illustrations of the in-situ cell for α-irradiation experiments

INVESTIGATING THE CORROSION OF COLD-SPRAYED COPPER EMBEDDED IN BENTONITE WITH DIFFERENT DENSITIES UNDER SEAWATER

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Abstract

The safe disposal of used nuclear fuel involves using a multi-barrier system called a deep geological repository [1]. In Canada's program, copper-coated used fuel containers will be encased in boxes of highly compacted bentonite clay and stored 500 m underground in crystalline rock [1]. The remaining space within the repository will be filled with gap-fill bentonite material. The bentonite must be sufficiently dense to prevent microbial growth and inhibit microbially influenced corrosion. This study examined copper corrosion in bentonite at dry densities of 1250, 1450, and 1600 kg/m³, using specialized vessels called "ocean modules" deployed at 2300 m depth at the Endeavour node of Ocean Networks Canada's NEPTUNE observatory in the Pacific Ocean. After two years in the saline, microbially active environment, scanning electron microscopy analysis revealed varying corrosion morphologies depending on the density of the gapfill bentonite in which the copper was embedded. Focussed-ion beam cross-sectioning confirmed higher film thickness on the specimens extracted from low-density bentonite. X-ray photoelectron spectroscopy analysis identified corrosion products including Cu_2O, Cu_2S, $CuSO_4$, and $Cu(OH)_2$ at the lowest density.

The effects of chloride and sulphate on the growth of sulphide films on copper in anoxic sulphide solutions

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Abstract

The structure and properties of copper sulphide films on copper have been studied in anoxic sulphide solutions containing either chloride or sulphate anions as anticipated in Swedish and Canadian groundwaters. The growth of films was investigated using cyclic voltammetry, corrosion potential and electrochemical impedance spectroscopy measurements, and the surface and cross-sectional morphologies of the films were characterized using scanning electron microscopy and focused ion beam sectioning.

Under conditions of controlled electrochemical potential, the properties of the sulphide film formed were dependent on both the sulphide concentration and the concentration of chloride or sulphate. These ions change the ionic strength of the solution and have different adsorption abilities. At low ionic strengths, film growth was partially or completely controlled by ion migration within the pores in the film. At higher ionic strength, provided that the sulphide concentration was not too high, the film became more porous, with the growth rate controlled by the interfacial reaction of sulphide at

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the base of the pores in the film. Under the latter conditions, the film growth rate decreased as the chloride or sulphate concentrations were increased. This can be attributed to the strong co-adsorption of sulphide with either sulphate or chloride anions with sulphate suppressing the rate more than chloride, possibly due to the well characterized co-adsorption of sulphate and coordinated water.

Under naturally corroding conditions, both chloride and sulphate exerted a significant influence on film properties. When the chloride concentration was low, the film was coherent and compact, and grew according to a logarithmic law, demonstrating the corrosion process was mainly controlled by Cu^{+} transport through the film. When the chloride concentration was increased (to ≥ 0.5 M) the film became more porous, but its growth rate decreased. This was attributed to the displacement of sulphide from the Cu surface by chloride. At extremely high chloride concentrations (i.e., 5.0 M), the film grew two-dimensionally, with growth supported by transport of Cu^{I} complexes and clusters but partially blocked by the accumulation of particulate deposits within the pores.

Sulphate was also observed to have a concentration-dependent influence on film structure. At low concentrations (i.e., 0.1 M), the influence was minor, but as the concentration was increased, the film became more porous as observed with increasing chloride concentration. These results indicate that the important feature influencing the properties of the film is the ionic strength of the solution, with the corrosion rate controlled by the ability of the anion to interfere with the interfacial reaction of sulphide with the exposed Cu surface. Sulphate appears to have a bigger influence than chloride in suppressing the film growth rate.

Keywords: Copper; Sulphide; Corrosion; Nuclear waste disposal

Highly Active and Stable TONC and PtNi/TONC as Bifunctional ORR/OER Electrocatalysts

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The development of durable and bifunctional oxygen reduction and oxygen evolution electrocatalysts remains critical for advancing next-generation energy conversion and storage devices such as fuel cells and rechargeable metal–air batteries.[1] We prepared a novel bifunctional PtNi/TONC electrocatalyst by a bottom-up sol-gel approach, where the TONC support consists of a Ti_4O_7 core doped with Ni and Cu. The resulting support and catalyst were characterized in alkaline media and both showed excellent ORR and OER activity, achieving a ORR half-wave potential of 0.84 V_{RHE} and 0.88 V_{RHE} in addition to an OER overpotential of 360 mV. Furthermore, these samples showed incredible stability with no signs of degradation after 48 hours of galvanostatic hold at 10 mA/cm^2, instead a major enhancement was observed in OER performance throughout the stress test. We attributed the excellent properties of the TONC and PtNi/TONC catalysts to the nature of the Ni and Pt active sites, where in-depth XPS analysis revealed the unique surface composition of these materials.

This study demonstrated that integrating doped conductive titanium suboxides with well-dispersed bimetallic nanoparticles offers a versatile platform for designing high-performance bifunctional electrocatalysts.

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The Corrosion Behaviour of Copper Exposed to Simulated and Natural Groundwater Solutions Under Anoxic Conditions

The chemistry of groundwaters can have a significant effect on corrosion processes. Therefore, it is important to understand why and how natural and simulated groundwaters affect the corrosion processes of materials used underground, to avoid costly or possibly dangerous corrosion-induced structural failures. This presentation will discuss the results of the electrochemical measurements and surface analyses employed to investigate the effects of simulated groundwater and the fluids from drilled boreholes on the corrosion of cold sprayed (CS) and wrought (SKB) copper. This work contributes to the knowledge base required to build confidence in Canada's plan for safe, long-term storage of used nuclear fuel. This plan involves encapsulating used nuclear fuel in containers made from copper-coated steel, packed in bentonite clay buffer, and buried at least 500 m underground in a deep geologic repository (DGR).

Methods have been successfully developed to make a synthetic groundwater designated CR-10[1] that simulates the groundwaters present within Canadian crystalline rock. Both the CR-10 and natural groundwaters contain primarily calcium, sodium, and chloride solutes. The results from corrosion potential measurements and potentiodynamic polarization (PDP) experiments in CR-10, drilled borehole fluids and 0.17 M NaCl solutions have shown no significant difference between the corrosion behaviour of CS and SKB copper specimen in CR-10 and 0.17 M NaCl solutions under anoxic conditions. However, corrosion potential measurements obtained in the borehole water solution were more positive than those recorded in the CR-10 and 0.17 M NaCl solutions. Electrochemical impedance spectroscopy (EIS) and linear polarization resistance (LPR) measurements were conducted in both solutions and the results showed higher resistance values for CS and SKB copper exposed to natural and CR-10 solutions, and lower resistance values for samples in 0.17 M NaCl solutions. X-ray photoelectron spectroscopy (XPS) was also performed on each sample after the experiments. Analyses of the copper LMM auger peak showed that both types of copper had a small amount of only Cu_2O on the surface after a 24 hour period of exposure to 0.17 M NaCl solution and natural and synthetic groundwaters.

The resistance values obtained from EIS and LPR measurements suggest that under anoxic conditions, CR-10 and borehole water solutions are less corrosive to CS and SKB copper than 0.17 M NaCl solutions. By studying copper corrosion in the more complex groundwater solutions and comparing the results to those of experiments done in simpler solutions, we aim to understand how the species present in Canadian groundwaters in contact with crystalline rock affect copper corrosion processes.

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ECS Canadian Section Fall Meeting 2025, Western University (London, ON), October 20, 2025

Investigating the Stress Corrosion Cracking of Copper Exposed to Nitrite Solutions

Yoel Emun, Kevin Daub, Jason D. Giallonardo, Mehran Behazin, Suraj Persaud

Canada's long-term strategy for the safe disposal of used nuclear fuel involves the construction of a deep geological repository (DGR). Central to this strategy is the encapsulation of fuel bundles within carbon steel containers coated with copper. For this container, copper serves as a corrosion-resistant barrier, although oxidant availability is very limited within the DGR. However, through radiolysis processes, it is possible that oxidizing species such as nitrite (NO_2^-) as a by –product of humid radiolysis may be present at early stages of the DGR lifetime.

Nitrites are of concern due to their established ability to induce stress corrosion cracking (SCC) in copper under sufficient tensile stress. However, prior research has demonstrated that the nitrite concentrations anticipated within a DGR are significantly lower than the reported 0.3 M [NO_2^-] threshold for SCC initiation. Nevertheless, a comprehensive understanding of the underlying SCC mechanisms and the identification of early-stage degradation processes (i.e., crack precursors) remain critical.

To address these knowledge gaps, this study employs an electrochemical approach to evaluate the influence of nitrite concentration on the SCC susceptibility of copper. Potentiodynamic polarization testing was conducted on copper specimens in 0.1 M, 0.5 M, and 1.0 M KNO_2 solutions to assess the concentration-dependent electrochemical behavior. Results revealed that while Cu in 0.1 M KNO_2 solutions exhibited active behaviour, Cu in 0.5 M KNO_2 and 1.0 M KNO_2 solutions exhibited two distinct active-passive transitions. Given that SCC is often preceded by the formation of the passive condition, Cu U-bend samples were subjected to potentiostatic holds at each transition potential to identify the most critical potential region for crack initiation and propagation. Characterization of corrosion mechanisms and possible SCC was supported with long-term U-bend exposure experiments in similar solutions of interest.

To simulate the environment in which formation of nitrite is possible (i.e. humid air), the temperature of 65 °C was chosen as a temperature of interest, as the DGR may still contain oxygen. Both electrochemical testing and long-term U-bend exposures were conducted at 65 °C to evaluate the influence of increased oxidation kinetics on SCC susceptibility.

Post-exposure characterization included scanning electron microscopy (SEM) with electron backscatter diffraction (EBSD) as well as X-ray diffraction (XRD).

Towards Small Modular Reactor Deployment: Localized Degradation Study of Stainless Steel 316-L with Scanning Electrochemical Cell Microscopy

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Small modular reactors (SMRs) have recently emerged as cost-effective, scalable, and environmentally friendly energy solutions in Canada.[1] However, one of the main challenges in the SMR deployment is the knowledge gap in their material behaviour. Stainless steel 316-L (SS 316-L) has been proposed as the material for SMR water cooling systems. As a passivating alloy with microstructural features such as inclusions and grain boundaries, SS 316-L could be vulnerable to localized degradation which needs to be studied under ambient and in-service SMR conditions.[2,3]

Scanning electrochemical cell microscopy (SECCM) is a high-throughput, high-resolution technique that could be used to correlate localized corrosive behaviour to the material's microstructure. While SECCM is frequently used to study actively corroding materials, the technique's application on passivating systems has been limited due to several issues including droplet instability and higher currents required for analysis.[4,5] In this work, experimental and data analysis considerations for SECCM on the passivating SS 316-L under ambient conditions will be discussed. Electrolyte choice, footprint diameter analysis and the found correlation between the alloy's microstructure and electrochemistry will be presented.

Having established the robust methodology for analyzing the localized corrosion in passivating systems such as SS 316-L in ambient conditions, our future steps would be to study this system under in-service SMR environment such as high temperature, and irradiation. We believe that understanding the localized degradation behaviour of the industrial alloys is a first step in ensuring the safe, long-term nuclear energy supply in Canada.

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Electrochemical Insights into Nitrate-Enhanced Biofilm-Mediated Corrosion of Mild Steel by *Bacillus licheniformis*

Abstract

Microbiologically influenced corrosion (MIC) contributes significantly to global material loss, yet the mechanistic role of anaerobic microbial activity in accelerating corrosion remains poorly understood. This study explores how nitrate-reducing *Bacillus licheniformis* influences mild steel corrosion in LB medium through extracellular electron transfer (EET) processes. Corrosion behavior was continuously monitored over 14 days using cyclic electrochemical techniques, including open circuit potential (OCP), linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS), combined with weight-loss analyses to quantify material degradation. The presence of nitrate significantly enhanced metal loss, which coincided with biofilm maturation and development on the steel surface. Electrochemical measurements corroborated these observations, revealing a progressive decline in polarization resistance in bacterial system in the presence of nitrate, whereas sterile controls maintained relatively high resistance throughout the experiment. These findings suggest that nitrate respiration facilitates electron uptake from steel surfaces, accelerating biofilm-mediated corrosion. By integrating continuous electrochemical monitoring with weight-loss assessments, this study provides a detailed mechanistic link between nitrate respiration, biofilm formation, and MIC progression, offering valuable insights for understanding anaerobic corrosion pathways and informing potential mitigation strategies.

Keywords: MIC, nitrate-reducing bacteria, anaerobic respiration, EET, biofilms, mild steel.

Electrochemical Insights into Nitrate-Enhanced Biofilm-Mediated Corrosion of Mild Steel by *Bacillus licheniformis*

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Abstract

Microbiologically influenced corrosion (MIC) contributes significantly to global material loss, yet the mechanistic role of anaerobic microbial activity in accelerating corrosion remains poorly understood. This study explores how nitrate-reducing *Bacillus licheniformis* influences mild steel corrosion in LB medium through extracellular electron transfer (EET) processes. Corrosion behavior was continuously monitored over 14 days using cyclic electrochemical techniques, including open circuit potential (OCP), linear polarization resistance (LPR), and electrochemical impedance spectroscopy (EIS), combined with weight-loss analyses to quantify material degradation. The presence of nitrate significantly enhanced metal loss, which coincided with biofilm maturation and development on the steel surface.

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Keywords: MIC, nitrate-reducing bacteria, anaerobic respiration, EET, biofilms, mild steel.

Influence of HIP Treatment on the Microstructure and Tribocorrosion Behaviour of Co28Cr6Mo Produced by LPBF

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Metallic biomaterials are widely used in orthopedic, spinal, and dental applications. Among all the metallic biomaterials, CoCrMo alloys demonstrate suitable mechanical properties, high wear resistance, and low corrosion rates, making them a suitable choice for withstanding friction and wear during service. Traditionally, these implant materials are manufactured using casting and forging methods. However, nowadays, additive manufacturing processes, such as laser powder bed fusion (LPBF), have replaced traditional techniques in producing hip, knee, and spinal implants. This manufacturing method can address challenges like mismatched implant design, non-physiological load-bearing, and inadequate osteointegration. Furthermore, LPBF CoCrMo alloys demonstrate better corrosion resistance compared to other manufacturing methods, such as casting. However, LPBF can have some main disadvantages, such as porosities, residual stresses, and defects. Hot isostatic pressing (HIP) can create a homogeneous and dense microstructure by applying high temperature and pressure. Additionally, it can be an effective method for achieving the desired strength, ductility, and wear resistance. The corrosion properties of CoCrMo alloys are highly dependent on their microstructure. Therefore, adjusting the microstructure through heat treatments, such as HIP, can benefit LPBF CoCrMo alloys in terms of strength and corrosion resistance, which are key factors influencing their tribocorrosion characteristics. This study investigates the correlation between the microstructure and the tribocorrosion behaviour of LPBF Co28Cr6Mo, focusing on how HIP post-manufacturing heat treatment affects the alloy's electrochemical and tribological properties. By considering the outcomes of this research, further modifications to the microstructure and, consequently, tribocorrosion properties can be expected, thereby enhancing their potential for biomedical applications.

Cathodic Corrosion of Au(111) in the Ionic Liquid [MPPip][TFSI] and the Influence of the Residual Water Content: an *in situ* STM Study

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Cathodic corrosion describes the reductive dissolution of noble metals at potentials negative of 0 V vs. NHE.[1] Hydrogen adsorbed on the electrode, high pH values, and the presence of stabilizing cations facilitate this process.[1] Due to these requirements, the presence of water appears to be a necessary condition for observing cathodic corrosion.[2] Nevertheless, this phenomenon can also be observed in some non-aqueous electrolytes.[3] Ionic liquids (ILs) are particularly suitable for studying the initial stages of cathodic corrosion, as they have significantly broader electrochemical stability windows than water.[4,5]

In this study, the initial stages of cathodic corrosion of a Au(111) surface in the IL *N*-methyl-*N*-propylpiperidinium bis(trifluoromethane)sulfonimide ([MPPip[]TFSI]) with different amounts of residual water were studied by *in situ* scanning tunnelling microscopy (STM). It could be shown that corrosion started at the so-called ‘elbows’ of the herringbone reconstruction. With increasing water content, the number of pits on the surface increased.

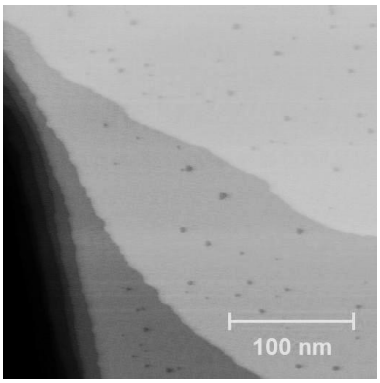

Figure 1: Pits formed by cathodic corrosion of the Au(111) surface in [MPPip][TFSI] at -1.4 V vs. Zn/Zn[TFSI]$_2$ and a water content of 20 ppm.

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Scanning Gel Electrochemical Microscopy Advances Towards Biological Applications

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Scanning Gel Electrochemical Microscopy (SGECM) employs microelectrodes that contain a flexible gel at the electrode-surface interface.[1] In the literature, this technique has been applied to hydrophobic substrates.[2–5] However, challenge arises when probing hydrophilic surfaces, as gel electrodes become unstable under such conditions, which limits their application to biological systems severely. This presentation reports the development of strategies to improve gel stability when probing hydrophilic substrates. To this end, the shape of the gel electrode was controlled by optimizing key parameters, including the RG of the microelectrode, gel solution pH, and deposition potential. Stability of the gel when probing hydrophilic substrate was achieved by unifying the solvent composition of the gel electrode and substrate. For the first time, SGECM was successfully conducted on agar substrates, where ferrocenemethanol embedded within the agar gel was detected by SGECM as it diffuses through the gel electrode to the electrode tip. These findings highlight the potential of SGECM for potential future biological applications, particularly in studying biofilms. Biofilms are important target with hydrophilic surface where gel probes could be used for tracking molecular transport through gel-to-gel interactions.

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Corrosion behaviour of oxidized uranium carbide and metallic uranium

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The strategy for nuclear waste disposal focuses on isolating spent fuel within a deep geological repository (DGR). CANDU fuel pellets (UO_2) are an optimal waste form due to their low solubility under the anticipated neutral anoxic conditions. However, during the early development stages of nuclear power, metallic uranium and uranium carbide fuels were utilized in research studies. Due to their high reactivity in water, air, and hydrogen, these legacy materials present a disposal challenge, with conversion to the stable oxide form as one possible risk-mitigation strategy. Research on the corrosion of UO_2 and SIMFUELs (simulated used fuels) concentrated on the influence of H_2O_2 and dissolved H_2, the key reactive water radiolysis products under container failure scenarios.

This study focuses on the characterization and corrosion behaviour of oxides formed by uranium carbide oxidation using different procedures. The oxides were characterized using surface analytical techniques, and the influence of H_2O_2 and H_2 on their corrosion was studied electrochemically in aqueous chloride/bicarbonate solutions. The morphology and composition of specimens varied with the conditioning procedure. The corrosion potential increased on the addition of H_2O_2 but was insensitive to H_2 (Ar/H_2 (95%/5%)) sparging for $0.1\ \mu M < [H_2O_2] < 5\ \mu M$, indicating fuel oxidation despite the presence of H_2. However, for a H_2O_2 concentration of 0.1 μM, the corrosion potential was limited to –250 mV (vs SCE) when H_2 was present, indicating the suppression of fuel oxidation by H_2 at low $[H_2O_2]$, consistent with previous results reported for CANDU fuels and SIMFUELs.

Atmospheric Corrosion of Hydrothermally-Oxidized Copper in Contact with Bentonite

Na Wang[1], Jian Chen[1], Xuejie Li[1], Elham Salehi Alaei[1], Mohammad Sabeti[1], Mehran Behazin[2], Dmitrij Zagidulin[1], David W. Shoesmith[1], James J. Noël[1 3]

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Canada's plan for the long-term disposal of used nuclear fuel involves sealing it in copper-coated steel containers (UFCs) surrounded by highly compacted bentonite (HCB) blocks and burying it in a deep geological repository (DGR). In a DGR, radioactive decay generates heat, creating warm conditions that desiccate parts of the bentonite, resulting in shrinkage. This will create gaps between the bentonite and copper, leaving some bentonite residue on the copper surface. During the early stage of a repository, the UFC surface is exposed to humid air, which could lead to accelerated non-uniform corrosion. This study examines the impact of various bentonite forms, including BR (bentonite residue), BS (bentonite slurry), and HCB, on the corrosion of hydrothermally oxidized copper.

The analysis of corrosion products after the exposure revealed that CuO was the dominant phase across all samples, with minor quantities of Cu_2O and $Cu(OH)_2$ also present. Over the five-month exposure period, a compositional evolution was observed, characterized by an increase in Cu_2O and $Cu(OH)_2$ and a concomitant decrease in CuO. The surface morphology was largely stable, though crystal growth emerged on the Control and BR-covered samples. In contrast, HCB-covered copper exhibited minimal crystal growth, nearly identical to the hydrothermally pre-oxidized copper before corrosion. After the removal of corrosion products, most samples displayed a generally rough surface with polishing lines still partially visible, and some exhibited corrosion pits approximately 2–3 μm in depth. Quantitatively, the corrosion rate and penetration depth decreased over time for all types of samples, with the HCB-covered samples consistently demonstrating the lowest corrosion rate and penetration depth.

Investigation of Corrosion Behaviour of Al-Si Alloy Using Scanning Electrochemical Cell Microscopy

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Abstract

Corrosion significantly impacts industries worldwide, with annual costs in Canada alone reaching $63 billion. Aluminum-silicon (Al-Si) alloys have emerged as promising corrosion-resistant materials for various applications in the automotive sector due to their excellent corrosion resistance, lightweight properties, and high thermal conductivity.[1-2] However, the heterogeneous nature of their microstructure leads to localized corrosion behaviour that cannot be fully captured by traditional macroscale electrochemical techniques.[3] While these conventional methods provide valuable insights into overall corrosion resistance, they fail to describe corrosion activity at the nanoscale and microscale, where microstructural variations significantly influence corrosion initiation and propagation mechanisms.

This study employs scanning electrochemical cell microscopy (SECCM) to investigate the microstructural influences on the localized corrosion behaviour of Al-Si alloys in 0.5 M NaCl solution. SECCM is a high-resolution scanning probe technique that extracts localized corrosion parameters at specific measurement points. By conducting electrochemical tests within a nanoscale or microscale droplet, corrosion processes can be analyzed with precision at these length scales. By correlating electrochemical activity with specific microstructural features observed using field-emission scanning electron microscopy (FE-SEM) and energy-dispersive X-ray spectroscopy (EDX), variations in silicon or aluminum concentration, pitting mechanisms, and surface film formation can be analyzed and identified. SECCM results demonstrated that areas with a higher aluminum concentration exhibited increased corrosion rates, indicating that aluminum is more susceptible to corrosion compared to the silicon component of the alloy. EDX analysis and electrochemical results revealed trace elements, which may contribute to overall corrosion rates. This potential influence will be explored in future work. This research aims to enhance the understanding of the corrosion processes of Al-Si alloys at the nanoscale. The insights gained will contribute to the development of more corrosion-resistant Al-Si alloys, ultimately improving their longevity and performance in real-world automotive applications.

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Understanding Corrosion Mechanisms in Materials for Spent Fuel Storage and Disposal

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ABSTRACT

Spent nuclear fuel, after being withdrawn from reactor, undergoes wet storage, dry storage, reprocessing, and finally deep geological disposal. Corrosion is a critical factor leading to failure of storage and disposal facilities. In wet storage, spent fuel is stored in a borated water environment, where water absorbs decay heat generated by the fuel and provides radiation shielding. Neutron absorber panels are critical components in spent fuel pools, as they absorb neutrons to maintain a subcritical state. Corrosion of these panels can degrade their neutron absorption efficiency. This report presents an analysis of the corrosion behavior of B_4C/Al neutron absorber materials in borated water environment. After reprocessing, spent nuclear fuel is converted into nuclear waste, and deep geological disposal is currently the most reliable method for permanent disposal of such waste. A dual-walled container design, featuring a carbon steel inner vessel and a copper outer layer, is a promising configuration used for encapsulating nuclear waste. The influence of hydrogen permeation, bentonite buffer material, galvanic corrosion on integrity of dual-walled container are evaluated using electrochemical methods accompanied by surface analysis techniques.

Investigating Localized Corrosion of Copper Coatings using Scanning Electrochemical Cell Microscopy

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Corrosion poses a persistent challenge to the structural integrity and durability of materials essential to human civilization. Accurate quantification of corrosion rates is critical for understanding degradation mechanisms and improving material durability. However, most conventional electrochemical techniques rely on applying external polarization to the working electrode, which can alter surface chemistry and distort the true corrosion behaviour.[1]

To overcome this limitation, we are developing a novel methodology to determine localized corrosion rates in situ without applying external polarization. The approach utilizes Scanning electrochemical cell microscopy (SECCM), a high-resolution scanning probe microscopy technique that enables local measurements of corrosion properties by enclosing the electrochemical cell within a droplet formed at the tip of a nano- or micropipette.[3] SECCM enables time-dependent monitoring of open-circuit potential variations at the microscale, allowing us to assess the natural electrochemical response of the material under near-equilibrium conditions.

Copper thin films are used as a model system due to their widespread application as corrosion-protective coatings.[4] By integrating SECCM with complementary microscopy methods, it will enable precise quantification of material loss over time in situ. This approach provides a powerful framework for evaluating true corrosion kinetics of thin-film coatings and offers new insights into designing durable, corrosion-resistant materials for long-term applications.

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Towards Understanding the Corrosion Mechanism of Copper-Coated Used Fuel Containers in Nitric Acid

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Corrosion poses a persistent challenge to the structural integrity and durability of materials essential to human civilization. Metals are primarily polycrystalline, and different microstructural features present at the submicron to micron scale add complexity to their overall corrosion behaviour.[1] A detailed mechanistic understanding of corrosion under environmental conditions is crucial for developing effective material fabrication strategies, enabling the design of materials with enhanced long-term corrosion resistance.

Although traditional macroscale electrochemical measurements provide a material's surface-averaged corrosion rate, they cannot detect corrosion mechanisms at the localized level.[2] Therefore, there is a need for localized techniques to have a better mechanistic understanding at the submicron to micron scale. Scanning electrochemical cell microscopy (SECCM) is a high-resolution scanning probe microscopy technique that enables local measurements of corrosion properties by enclosing the electrochemical cell within a droplet formed at the tip of a nano- or micropipette.[3] Using SECCM with other colocalized microscopy techniques provides insights into how specific microstructural features influence and/or dictate corrosion behaviour at a localized scale by statistically analyzing corrosion rates at each point of measurement using retraction curve methodology.[4]

Our research is relevant to the nuclear waste management field, as copper-coated containers for storing spent nuclear fuel must remain intact for long periods within deep geological repositories.[5] Given that the Mark II design features a 3mm copper coating, the margin for localized corrosion is limited, making it a particularly critical concern. This necessitates a detailed understanding of localized corrosion at the microscale. Therefore, this study aims to investigate the influence of the microstructural features of copper coatings on the material's surface-averaged response using SECCM. Particularly during the emplacement of copper-coated containers, radiolysis-induced nitric acid will condense on the copper surface, necessitating an investigation of the corrosion mechanism on these coatings. Using SECCM, we will probe whether enhanced dissolution at certain grains stems from faster kinetics of certain crystal orientations or galvanic interactions between adjacent grains. The insights derived from this research will contribute to a more robust understanding of the long-term durability of copper containers under repository conditions, thus supporting the safety and sustainability of nuclear waste storage.

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Towards Understanding the Corrosion Mechanism of Copper-Coated Used Fuel Containers in Nitric Acid

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Challenges in Quantitative SECM for Corrosion Studies of Ferrous Materials: The Role of Redox Mediator–Substrate Interactions

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Abstract: A key challenge in using scanning electrochemical microscopy (SECM) in feedback mode for corrosion studies is decoupling the redox mediator's (RM) influence from the intrinsic reactivity of the substrate. In this work, we combine macro- and micro-electrochemical experiments with finite element modelling to investigate how two widely used RMs, ferrocenemethanol (FcMeOH) and hexaammineruthenium (III) chloride ($Ru(NH_3)_6^{3+}$), affect the corrosion behavior and SECM response of iron and stainless steel (SS-316L). The apparent rate constants extracted from SECM measurements highlighted a clear dependence on substrate passivation. SECM measurements over iron revealed that the applied potential required to induce FcMeOH oxidation caused ultramicroelectrode fouling via iron oxide deposition, thereby compromising measurement reliability. In contrast, $Ru(NH_3)_6^{3+}$ underwent reduction at the active Fe surface, leading to local mediator depletion and a feedback response characterized by a steeper current decay than typically observed over passive surfaces. On SS-316L, negative feedback was observed with both mediators, reflecting the presence of a stable passive film. This study identifies key pitfalls in SECM corrosion analysis and demonstrates how RM–substrate interactions can affect interpretation. These findings offer practical guidance for improving the quantitative reliability of SECM in probing localized corrosion processes of ferrous alloys.

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Localized Electrochemical Impedance Spectroscopy with Scanning Electrochemical Cell Microscopy (SECCM-LEIS)

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Combining electrochemical impedance spectroscopy (EIS) with scanning electrochemical cell microscopy (SECCM) enables high-resolution, localized interrogation of interfacial electrochemical properties. However, the unique geometry of the SECCM probe, particularly the capillary, can introduce artifacts that compromise the fidelity of impedance measurements. In this work, we systematically examine how capillary size, electrode spacing, and tapering influence the measured EIS response. Using a two-electrode configuration with Ag/AgCl wires, we isolate resistive and inductive contributions arising from the internal solution path and capillary walls. Equivalent-circuit modeling reveals that the inductive loops commonly observed at high frequencies originate from ion dynamics near the glass interface and are magnified as the capillary diameter decreases.

Despite these effects, SECCM-LEIS remains robust for metallic systems, where interfacial impedance dominates at low frequencies. Our results highlight that capillary-induced impedance components become increasingly significant at high frequencies, in some cases overshadowing the true interfacial response, whereas at lower frequencies their contribution is minor compared to that of the droplet–substrate interface. This distinction is critical when investigating conductive or corroding metallic substrates. By carefully characterizing and accounting for these capillary-derived impedance elements, SECCM-LEIS can be applied with confidence for high-resolution electrochemical studies.

Overall, these findings clarify the origin and magnitude of non-ideal impedance features in SECCM measurements and offer a framework for improving both the design of SECCM probes and the interpretation of localized EIS data in complex interfacial systems.

Investigating Corrosion of Oxide-covered Copper in an Aqueous Thiosulfate Solution for Nuclear Waste Containment Applications

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The internationally accepted approach for the permanent disposal of high-level nuclear waste is burying it in a deep geological repository (DGR) with several barriers to ensure safe and long-term isolation. In Canada, the used nuclear fuel will be loaded into steel containers, called used fuel containers (UFCs), coated with copper as the corrosion-resistant material.

Initially, upon emplacement of the UFCs, the condition in a DGR will be oxidizing, due to the presence of trapped oxygen. This will lead to the formation of various copper oxides, e.g., Cu_2O, CuO, and $Cu(OH)_2$ on the container surface, but after oxygen depletion, the DGR environment is expected to be anoxic. During this long-term anoxic phase, the dominant cause of container degradation will be reaction with bisulfide produced by sulfate-reducing bacteria (SRB) remote from the UFCs. On the other hand, bisulfide produced by SRB may undergo oxidation by reacting with residual oxidants during the transition from oxidizing to anoxic or, during the anoxic period, with oxidants created by water radiolysis induced by radioactive decay. These processes will result in the formation of a mixture of oxy-sulfur species such as sulfate (SO_4^{2-}), sulfite (SO_3^{2-}), and thiosulfate ($S_2O_3^{2-}$), among which thiosulfate is known as an aggressive corrosion agent.

This study aims to investigate the interaction of thiosulfate with oxide-covered copper to probe the behaviour expected during the transition between oxic and anoxic conditions in a DGR. Therefore, a dual-layer copper oxide film consisting of a base layer of Cu_2O and some Cu(II) compounds such as CuO and $Cu(OH)_2$ on top of it was formed electrochemically on wrought copper in a strongly alkaline solution. The oxide was then exposed to an aqueous solution containing thiosulfate ions with a concentration of 1×10^{-3} M, and a range of electrochemical and surface analysis techniques were utilized to determine what products formed on the copper surface. Comparing the electrochemical behaviour and surface properties of the oxide film before and after exposure to thiosulfate showed changes in the structure of the oxide film which can be attributed to the influence of thiosulfate ions on the oxide film. After a 24-hour period of exposure to thiosulfate solution, the presence of Cu_2O was confirmed as the dominant phase while no CuO was observed anymore, and some Cu_2S was detected by Raman spectroscopy. SEM images also showed slight damage in most areas of the oxide film due to immersion in the thiosulfate solution as the sharp and uniform crystals were transformed to flattened and amorphous crystals. Further investigations are underway to elucidate the mechanism of conversion of copper oxides to Cu_2S after exposure to thiosulfate ions.

Electrochemical Surface-Enhanced Raman Spectroscopy (EC-SERS) as a platform for biomolecule detection using modified Screen-Printed Eelctrodes

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Abstract

Electrochemical surface-enhanced Raman spectroscopy (EC-SERS) is an analytical technique that combines the molecular fingerprinting ability of Surface-enhanced Raman spectroscopy (SERS) with the sensitivity of electrochemical control. This dual capability makes it a promising approach for non-invasive diagnostics in biofluids such as tear fluid. In this work, we explore the potential of EC-SERS as a detection platform using screen-printed electrodes modified with metallic nanostructures such as silver nanoparticles (AgNPs) or gold nanorods (AuNRs), to detect biomolecules of clinical relevance such as Uric Acid, Nicotinic Acid and l-Lactate. By modulating the potential at the electrode surface, differences in analyte response and spectral features were investigated. Results reveal characteristic Raman bands of the analytes that were only visible upon electrochemical modulation, signifying the potential of EC-SERS as a technique for clinical diagnosis.

Electrochemical Surface-Enhanced Raman Spectroscopy (EC-SERS) as a platform for biomolecule detection using modified Screen-Printed Eelctrodes

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Corrosion Behaviour of an Iron Thermal Spray Coating for an Internal Combustion Engine

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Abstract

Over recent decades, the automotive industry has worked tirelessly to improve fuel efficiency in response to increasing environmental concerns and regulations. A significant portion of this effort has focused on substituting iron-based components with lightweight alloys. As a result, it has become the industry practice to fabricate large components, once made of iron-based materials, out of aluminum, magnesium, or other lightweight alternatives. While aluminum offers attractive weight reduction, it may not meet the strength, wear, or hardness properties necessitated in applications where contact is made between moving components, e.g., between an engine bore and a piston ring. Here, a wear-resistant iron-based insert or coating is generally applied to achieve the necessary physical properties. However, corrosion within a combustion engine is a complex and dynamic system owing to the inherent variabilities of fuel composition and quality, operating temperatures, and general driving behaviour. After engine operation, during cool-down, the opportunity for water vapours to deliquesce onto internal surfaces becomes a concern in the corrosion process known as ‘cold corrosion’.

During cold corrosion, several solution variables have the potential to accelerate the corrosion of iron-based coatings. To better understand the corrosion behaviour, a combination of electrochemical corrosion tests and surface analytical techniques were combined to study the corrosion behaviour of thermal spray coatings with solution parameters such as pH, F^-, and Cl^- (etc.). The role of coating microstructure was also studied in the context of thermal spray coatings. Data will be presented from a combination of results from field service parts and laboratory-based testing.

Electric Double Layer Formation in Charged Droplets and Confined Geometries

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The electric double layer (EDL) formed by ions in solution surrounding a charged surface is a fundamental concept in electrochemistry that has been studied for over a century through analytical theory and modeling. In this work, we explore the formation of the electric double layer in charged droplets—a phenomenon that has not been previously reported [1,2]. In such droplets, the surface becomes polarized due to interactions with the surrounding air as well as the net charge carried by the system. As expected, an excess of cations versus anions results in distinct solvent polarization at the droplet surface. Interestingly, anions give rise to an EDL structure that deviates from the conventional model. We also examine the solvation behavior of cations and anions, including ion pairing. Furthermore, the study is extended to investigate solutions confined between two parallel charged surfaces.

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Measuring Hydrogen in Repository Relevant Metals Using Commercial Hydrogen Sensors

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Nuclear waste management organizations around the world share the same goal – the safe disposal of nuclear waste. As such, it is critical to understand the corrosion behaviour of all metallic components, including those which comprise low-, intermediate- and high-level waste packages, in the anticipated deep geological repository (DGR) conditions. When there is oxygen present upon sealing of the DGR, it is rapidly consumed. It is this anoxic environment that determines the long-term corrosion behaviour of the metals. Corrosion under these conditions, irrespective of the metal in question, results in the evolution of hydrogen gas. Once evolved, the hydrogen has the potential to be absorbed by the metallic materials. Hydrogen adsorption has the potential to affect the mechanical properties of the canister materials and therefore this process must be understood.

Traditionally the detection of small amounts of hydrogen in a metal sample requires costly analytical instrumentation such as mass spectrometers and thermal conductivity detectors. An economical alternative of interest is a commercially-available hydrogen sensor used in conjunction with a tube furnace, mass flow controllers and pressure transducers, to quantify hydrogen outgassing from a material as it is heated. Being able to measure evolved hydrogen as a function of ramp rate and temperature allows for the quantification of hydrogen as well as the potential discernment between various types of traps within the metal.

Thermal desorption experiments were performed on electrodeposited copper using ramp rates from 3 to 30°C/min to a maximum temperature of 1000°C. Fitting of peaks to the data with analysis using the Kissinger equation resulted in the calculation of net activation energies. This simple process suggests that for the material studied, up to a third of the reversibly trapped hydrogen was located at the grain boundaries which may impact mechanical properties under low strain rates.

Electrochemical Conversion of Substituted Phenol Derivatives

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Phenolic compounds have applications in biotechnology and agriculture industries and may redeploy into the environment as waste. Traditionally, the conversion of phenolic pollutants is achievable using harsh chemical treatments. However, the selective conversion of phenolics into new functional molecules can also be achieved *via* milder, greener and more sustainable avenues such as electrosynthesis [1]. The electro-oxidation of phenolic compounds generates a variety of products, including quinones, polymers and new carbon-carbon bond formation, further resulting in new value-added chemicals of industrial interest. Herein, the electrochemical conversion of 2,6-di-tert-butylphenol (DTBP), 2,6-diphenylphenol (DPP), and 5-chloro-2-(2,4-dichlorophenoxy)phenol (triclosan) were compared to a traditional chemical oxidation process [2,3]. All compounds underwent conversion during cyclic voltammetry (CV) or after addition of an oxidizing agent and resulted in significant colour changes. The product formation was monitored by UV-Vis spectroscopy and further characterized by X-ray single crystal diffraction (SC-XRD) and gas chromatography-mass spectrometry (GC-MS). Uniquely, the carbon-carbon bond dimerization was observed. Overall, the data suggest that the product yield and the selectivity of electrosynthesis were dependent on the parameters used, and that electrosynthesis may allow for reaction selectivity, which is not achievable by chemical means.

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Molecular LOGICS of Li Metal Battery: From Interface to Interphase

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Conventional electrochemistry centers on well-defined charge-transfer processes at idealized, “clean” solid–liquid interfaces. In contrast, next-generation energy systems—such as high-energy-density lithium-metal batteries (LMBs)—present a far more complex interfacial landscape, where the formation of a solid–electrolyte interphase (SEI) fundamentally reshapes electron–ion interactions. Although essential for enabling LMBs, the molecular formation mechanisms, evolving structure, and spatial heterogeneity of the SEI remain incompletely understood.

In this talk, I will present our recent efforts to decode the molecular principles governing SEI functionality. By combining electrochemical analysis, non-washing X-ray photoelectron spectroscopy (XPS), and synchrotron-based X-ray absorption spectroscopy (XAS), we elucidate how decomposition pathways and microscale heterogeneities dictate SEI composition and performance. Our findings reveal that not all decomposition products remain in the SEI—many persist dissolved—highlighting the critical role of semi-soluble, anion-derived species (e.g., LiF) in forming robust, porous, electrolyte-trapping interphases.

Furthermore, we reinterpret the classical electric double layer (EDL) within nanoconfined SEI environments, uncovering key interfacial properties that govern the reversibility of lithium plating and stripping. By retro-engineering the EDL at the molecular scale, we establish essential design principles to optimize the next-generation LMBs. These insights bridge molecular interfacial chemistry with macroscopic battery performance, providing a rational framework for electrolyte and interface engineering toward durable, high-efficiency energy storage systems.

Particle-particle interface corrosion of cold sprayed copper in nitric acid solutions

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Cold spray (CS) has been considered one of the two techniques for applying Cu as the corrosion-resistant layer on the Canadian-designed used (nuclear) fuel container (UFC). The resulting CS Cu must maintain its integrity in its lifetime, contemplated to be more than 10^6 y, in a deep geological repository (DGR), where the UFCs will be emplaced. Therefore, it's important for the corrosion of CS Cu to be investigated and evaluated under the various conditions corresponding to different periods in the DGR. Previous work reported the possible production of HNO_3 droplets on the UFC due to the radiolysis of humid air during the early stages of the DRG[1]. Thus, work is being carried out in HNO_3 bulk solutions with higher-than-anticipated concentrations as an accelerated approach to study the corrosion of CS Cu.

In preliminary work, CS Cu exhibited particle-particle interface (PPI) corrosion, but the mechanism was not elucidated[2]. In this study, we show that the PPI corrosion is initiated by the oxide inclusions at the PPI and sustained by the confined geometry left behind. Given the importance of the oxygen inclusions, the effect of the oxygen content in CS Cu on the PPI corrosion is also investigated. It has been discovered that PPI corrosion propagates faster for CS Cu with higher oxygen content.

Moreover, strategies are developed to mitigate the PPI corrosion. Microstructural engineering of the oxide inclusions by employing a higher annealing temperature leads to the consolidation of the oxide inclusions, thereby reducing the corrosion penetration depth. Besides, Cl^- is found to be an effective inhibitor for PPI corrosion. PPI corrosion is completely blocked even when [Cl^-] is as low as 1 mM.

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