Examination of Mechanisms for Liquid-Air-Interface Corrosion of Steel in High Level Radioactive Waste Simulants

The tanks used to store nitrate- and nitrite-rich alkaline waste are susceptible to liquid-air-interface (LAI) corrosion. While this attack has been insufficient to perforate tank walls, it does adversely impact the chemistry within the tank. A variety of mechanisms related to local chemistry changes at the LAI have been proposed to explain this phenomenon. However, no conclusive data has been produced to support any of them. In this work, *in situ* Raman spectroscopy, combined with local pH measurements, was employed to probe the concentration of key electrolyte species (e.g., nitrate, nitrite, hydroxyl) at the actual LAI, establishing whether any deviations from the bulk chemistry preceded corrosion initiation. However, both the nitrate and nitrite concentrations (as well as their relative ratio) were found to remain stable prior to corrosion initiation. Similarly, local pH measurements indicated that the pH at the LAI did not deviate from that of the bulk until well after corrosion had been initiated, indicating that local acidification was also not a likely cause of the corrosion attack. The authors conclude that the mechanism of LAI corrosion initiation may be similar to crevice corrosion and that it may be associated with a local pH decrease due to metal ion hydrolysis, but at a length scale below that resolvable by the techniques employed in this study.

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Graphene Oxide Fuel Cell

Graphene oxide (GO), the oxidized form of graphene, is an electronic insulator due to the presence of randomly allocated nonconductive sp^3 carbon in its structure. Following their preliminary report of GO's high proton conductivity (*J. Am. Chem. Soc.* 2013, **135**, 8097), a group of researchers from Kumamoto University in Japan recently described the use of GO as the membrane electrolyte for H_2/O_2 fuel cells. The authors prepared GO suspension by oxidizing graphite powder by the Hummer's method. The suspension was then processed into a paper-like film through filtration. With a thickness of about 10-60 µm, the GO paper exhibited proton conductivities in the range of 10^{-5}-10^{-4} S/cm at low humidity (< 20%) and room temperature. In addition, the GO paper was also shown to be non-permeable to H_2 and O_2. By directly sputtering platinum metal or casting commercial Pt/C catalyst on both sides of the GO paper, simple membrane electrode assemblies (MEAs) were constructed. A non-noble metal oxygen reduction electrode was also prepared on the GO paper. An interesting finding amongst the cell performance results obtained with these MEAs was that the Pt/C electrode on GO showed better performance than that on a 150-µm Nafion membrane.

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Resistive Switching: A Solid-State Electrochemical Phenomenon

In recent years, the memristor, in particular the resistive switcher, has been the subject of many papers. Some descriptions explaining this already known behavior of resistive switching have resulted in misinterpretations of the phenomenon. A scientist at Universität Stuttgart has written a paper to describe the underlying set of electrochemical equilibria of species involved in the processes, and the conditions for the resultant functioning of a resistive switcher. The resistive switcher is based on a mixed ionic-electronic conductor (MIEC) solid electrolyte galvanic cell under load, in which one electrode is under ion-blocking operation mode. Variation in the voltage-induced change in n- and p-type electronic conductivity across the solid electrolyte ultimately gives rise to the observed lagging of resistance behind the voltage change. Because the cause-action relation described is based on idealized conditions, the author discusses additional effects that occur in the behavior of a resistive switcher in practice. Two types of switchers, unipolar and bipolar, are provided with explanations of their differing current-voltage behaviors. To address how this solid-state electrochemistry understanding differs from the explanations prevailing in the literature, the author also provides a critical discussion of those experimental observations and interpretations.

From: ECS J. Solid State Sci. Technol., **2**, P423 (2013).

Electrodeposition of Cu-Ni Alloy Electrodes with Bimodal Porosity

Porous electrodes are widely used in industrial electrochemical systems because they facilitate enhanced mass transport and overall electrochemical reaction rates. Among the numerous applications for porous electrodes are batteries, fuel cells, supercapacitors, and water desalination. Cattarin and coworkers at the Istituto per l'Energetica e le Interfasi in Italy recently reported a preparation method for porous Cu-Ni alloy electrodes that offers advantages over traditional methods such as dealloying or electrodeposition within rigid templates. They demonstrated that electrodeposition of Cu-Ni alloy electrodes at high current densities (3 A/cm^2) from an acidic solution containing copper and nickel sulfate produced alloys with a unique bimodal porosity, due in part to the copious hydrogen evolution that accompanies the alloy deposition. The alloy microstructure consists of pores with dimensions in the tens of microns along with submicron-sized dendrites and other high surface-area features. The authors showed that this porous alloy electrode has excellent performance characteristics for cathodic reduction of nitrate (a common pollutant in water and wastewater streams) with lower overvoltages and dramatically higher peak currents compared to compact electrodes of identical composition. Due to these attributes, along with the relatively low cost of these porous alloys, the authors propose that these electrodes offer great promise in water and wastewater treatment.

From: ECS Electrochem. Lett., **2**, D58 (2013).

Electrochemically Induced p-Type Conductivity in Carbon Nanotubes

The ability to control the conduction characteristics of single wall carbon nanotubes (SWNTs) is crucial for any application in electronics. Recent exciting work has shown that vacuum-annealed n-type SWNTs can transform to p-type when exposed to ambient air. The process can be reversed after annealing, and no underlying mechanism has been proposed that accounts for this marked change in conduction character. However, transfer doping that causes n-type to p-type conduction changes can also be facilitated electrochemically. Researchers at Case Western Reserve University in collaboration with the University of Louisville demonstrated that indeed, electrochemical control of conduction type in SWNTs is possible in humid air. By allowing a surface water film to form on SWNTs, a form of surface transfer doping was made possible by relative shifting of the Fermi level energy according to the Nernst equation. Specifically, the researchers showed that considerable reduction in resistance and a corresponding improvement in Seebeck coefficients could be achieved for a film composed of SWNTs in humid air, as compared to deoxygenated or dry air environments. The authors posited that such effects should be considered when studying SWNTs in humid air and that certain changes in the electrical properties of graphene and multi-walled nanotubes can be explained by this electrochemical phenomenon.

From: ECS Solid State Lett., **2**, M57 (2013).

Tech Highlights was prepared by Zenghe Liu of Google Inc., David Enos and Mike Kelly of Sandia National Laboratories, Colm O'Dwyer of University College Cork, Ireland, and Donald Pile of Nexeon Ltd. Each article highlighted here is available free online. Go to the online version of Tech Highlights, in each issue of Interface, *and click on the article summary to take you to the full-text version of the article.*