

Cathodic Current Delivery Capacity and Stability of Crevice Corrosion under Atmospheric Environments

Under atmospheric conditions, a thin electrolyte layer may form on a metal surface above a particular relative humidity. The relative humidity at which point this layer may form, as well as the composition of the electrolyte layer itself once it has formed, is a direct function of the composition and quantity of deliquescent salts present on the metal surface as well as the temperature. Once a sufficient electrolyte layer exists, stable crevice corrosion may be supported, provided a cathode of sufficient current-delivering capacity can exist outside of the crevice mouth. More specifically, the stability of a propagating crevice corrosion site requires that the anode dissolve at a sufficiently high rate to maintain the critical chemistry within the crevice, while a wetted surrounding area provides sufficient cathodic current to drive that anodic dissolution rate. In this paper, the authors present an analytical method developed to predict the maximum cathodic current available from a metal surface coated with a thin-layer electrolyte given only a limited number of readily quantified input parameters. These analytical calculations of the maximum cathode current were coupled to an extension of the pit stability product, which predicts the total anodic current required to maintain a propagating crevice of known geometry/active area. This coupling allows an analysis of the potential for stable crevice corrosion under atmospheric conditions where a thin-electrolyte layer is formed, and thus quantification of compatibility requirements between anode and cathode for a given set of exposure conditions.

From: *J. Electrochem. Soc.*, **155**, C360 (2008)

Electrochemical Impedance Spectroscopy of Electrochemically Self-Assembled Lithium-Iodine Batteries

The *in situ* fabrication of self-formed/ assembled batteries makes them well suited for integration into autonomous microelectromechanical systems. A group at Rutgers University characterized the formation of self-assembled lithium-iodine secondary cells using *in situ* EIS and Raman spectroscopy. The cells were formed by the electrochemical dissociation of a LiI-based composite material into a polyiodide at the positive electrode and lithium at the negative electrode. Residual LiI-based material acts as an electrolyte between the two electrode regions. The Nyquist plots of formed cells contained three depressed semicircles. The semicircle diameter magnitudes were attributed to resistive processes. After conducting a series of experiments on unformed cells utilizing different current collector materials, the authors credited the highest frequency resistive process to cationic conductivity in the LiI-based material and the middle-frequency resistive process to an SEI (solid-electrolyte interphase) layer that

forms at the lithium electrode interface. By analyzing the EIS spectra of individual electrodes in formed three-electrode cells, the lowest frequency, and rate-limiting, process was attributed to a combination of electronic, cationic, and anionic transport in the positive electrode material. *In situ* Raman spectroscopy showed that the positive electrode consisted of the polyiodides I_3^- and I_5^- and that the ratio of I_5^- to I_3^- increased during cell formation.

From: *J. Electrochem. Soc.*, **155**, A590 (2008)

Electroanalytical Studies of Antibody-Bound Glucose Oxidase

Development of new methodologies and materials for the immobilization of biological molecules is an exciting and important research area in bioanalytical, environmental, and biomedical applications. For electrochemical biosensors, enzymes are typically immobilized in inorganic, sol-gel, or polymeric matrices. Recently, researchers from the National University of Singapore investigated the feasibility of using immunoglobulin (IgG) as an immobilization matrix for glucose oxidase (GO). The effects of binding GO to IgG on its enzymatic activity and kinetics were studied using cyclic voltammetry and scanning electrochemical microscopy. These studies indicated a comparatively small reduction in the enzyme-mediator reaction rate when the GO enzyme was bound to IgG, compared to other immobilization methods. The turnover numbers for IgG-bound GO adsorbed on gold and glass substrates were 475-740 and 103-354 s^{-1} , respectively, using ferrocenemethanol as the mediator. The suitability of the IgG-based immobilization method to entrap GO on the electrode surface was demonstrated in an amperometric glucose biosensor fabricated using physically adsorbed IgG-bound GO immunocomplex on a gold electrode. The same approach is potentially applicable in other enzyme-based biosensors.

From: *J. Electrochem. Soc.*, **155**, F177 (2008)

Silica-filled Nonwoven Separator for Lithium-Ion Batteries in High-Power Applications

An increasing number of high-power applications, such as power tools and hybrid and battery electric vehicles, are using lithium-ion batteries. Higher rate applications demand lower internal resistance and, consequently, greater porosity of the separator separating the electrodes within the cell. Microporous polyolefin membranes, commonly used in low-power, high-energy density applications, perform poorly under high-rate conditions and suffer low thermal stability. To address this challenge, a group of Japanese researchers fabricated and tested a composite membrane comprised of silica nanoparticles filling the relatively large pores of a nonwoven separator. The authors sought the desirable properties of increased wettability and thermal stability of the

ceramic particles without the drawback of inflexibility of a ceramic separator. Simultaneously, the ceramic particles filling the pores of the nonwoven separator diminish the risk of a short circuit arising from growth of lithium dendrites. Their new composite separator, when compared with the silica-free nonwoven and microporous membranes, exhibited better wettability, higher maximum power, and better thermal stability at 150°C. However, only those composite separators that had a Gurley value – a measure of smaller pore size and greater pore structure complexity – greater than 200 s 100 cm⁻³ were successful at maintaining a low irreversible capacity loss comparable to that of the microporous polyolefin membrane (Gurley value ~725 s 100 cm⁻³).

From: *J. Electrochem. Soc.*, **155**, A699 (2008)

Electrothermal Bonding of Carbon Nanotubes to Glass

Mats of vertically aligned carbon nanotubes (CNTs) have generated substantial interest due to their superior thermal and electronic transport characteristics. Incorporation of these materials into devices must consider the underlying issues of the adhesion of the CNTs onto substrates within the device architectures. Given the low cost, the breadth of applications, and the abundant science to be explored in soda-lime, borosilicate, and other glasses joined with CNTs, sufficient motivation exists to explore novel approaches to adhere CNT mats to the substrates. Researchers from the School of Mechanical Engineering and the Birck Nanotechnology Center of Purdue University have developed a new approach to the electrothermal adhesion of CNT mats to glass substrates by controlling alkali ion migration and absorption through the glass-CNTs heterostructure. Depending on the type of glass employed, the flow of Na⁺ or K⁺ ions, facilitated by a heightened thermal environment (~200°C), and the subsequent transfer of charges at the glass interface led to an enhanced bond between the nanotubes and the glass. The authors confirmed the increased alkali content along the CNT surface via X-ray photoelectron spectroscopy. The strength of the glass-CNTs bond compared favorably against short-range van der Waals forces and may be enhanced by optimizing the dimensions of the CNTs and by preloading the mats during the bonding process.

From: *J. Electrochem. Soc.*, **155**, K161 (2008)

Tech Highlights was prepared by Zenghe Liu of Abbott Diabetes Care, David Enos of Sandia National Laboratories, Donald Pile and Craig Walker of Valence Technology, Inc., and James Dickerson of Vanderbilt University.