TECH HIGHLIGHTS

Parameter Sensitivity Analysis of Pit Initiation at Single Sulfide Inclusions in Stainless Steel

Recently, there have been numerous studies utilizing mathematical modeling to study the process of pit initiation. A model previously defined by Webb and Alkire (*J. Electrochem. Soc.,* **149**, B286, 2002) which hypothesized that pit initiation occurs by depassivation of the stainless steel due to an accumulation of thiosulfate ions above a critical concentration in the presence of chloride, and that the rate of inclusion dissolution is catalyzed by chloride, was solved using a finite difference method by Kamrunnahar *et al.* at the University of Illinois. Parameters in the simulation included diffusion coefficients for 20 species, chemical/electrochemical rate constants, and equilibrium constants. A sensitivity analysis was performed to assess which of the aforementioned parameters are significant in defining/impacting the pit initiation process at a sulfide inclusion in stainless steel. The analysis demonstrated that the Tafel slope of the electrochemical rate of sulfide dissolution had a large, nonlinear effect on the process and was the most significant variable. The electrochemical rate constant for sulfide dissolution also had a substantial impact on the calculated electrochemical potential, local pH, and chromium ion concentrations. The analysis further demonstrated that the model outputs were insensitive to changes in the other input parameters.

From: J. Electrochem. Soc., **151** *(2), B90 (2004)*

Finite Difference Digital Simulation of Electrogenerated Chemiluminescence

A fascinating aspect of radical-ion chemistry is the production of chemiluminescent species via homogeneous electron transfer reactions in organic electrolytes. Extensive research has been conducted in this area for over thirty years, and electrogenerated chemiluminescence (ECL), wherein the excited state species are produced electrochemically, is now the basis for certain deoxyribonucleic acid (DNA) instrumental analysis methods and for various immunoassays. Researchers at the University of North Carolina recently described the use of a commercially available digital simulation code (DigiSim, from Bioanalytical Systems, Inc.) to model complex ECL reaction mechanisms. The authors (including S. W. Feldberg, author of the seminal papers on digital simulation) modeled not only the voltammetric response (as is typically done with digital simulation) but also the photonic output. They accomplished this by including an "artificial electron transfer" step involving the photon as a counting device to allow accurate tracking of radiation-producing reactions. Both radiative and nonradiative pathways for decay of the excited state species were included in the complex mechanistic schemes considered in the paper, and good agreement between simulated and experimental results for cyclic voltammetry and ECL of 9,10-diphenylanthracene was obtained.

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Electrochemical Porosity

Porous electrodes are finding widespread applications in state-of-the-art energy technologies such as batteries, fuel cells, and supercapacitors. Understanding the microstructure of porous electrodes is essential for advancing the performance of these devices. Although various techniques are available to analyze the microstructure of porous materials, they are typically *ex situ* with respect to electrochemistry. As a result, it has been extremely difficult to correlate the microstructure of porous electrodes with their electrochemical behavior. Recently, an *in situ* technique was described by researchers at the Pohang University of Science and Technology in South Korea, the Institut National de la Recherche Scientifique, Energie, Materiaux, et Telecommunications in Canada, and the Battery Research Institute of LG Chem Limited in South Korea. Termed electrochemical porosimetry by the authors, the new methodology is based on a model that correlates electrochemical impedance data with microstructural information. Pore length and pore size distribution can be obtained by fitting the model to experimental impedance data for a porous electrode. This geometric information was validated for microporous, mesoporous, and macroporous samples. The authors anticipate utility of the technique as a nondestructive probe not only in the investigation of electrochemical devices, but in other technological areas as well.

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Li Conductivity in Li_xMPO_4 (M = Mn, Fe, Co, Ni) Olivine Materials

Olivine-based materials, specifically lithium-iron phosphate (Li_xFePO_4), have received a great deal of attention for use as cathodes in lithium-ion cells due to their low cost, superior safety attributes, and other characteristics. Unfortunately, the material suffers from poor rate capabilities generally attributed to its low conductivity. The scientific literature has limited information on the relative importance of ionic *vs.* electronic conductivity in these materials. Morgan and co-workers from Computational Modeling Consultants and the Massachusetts Institute of Technology recently reported first-principles calculations that estimate the intrinsic ionic diffusivity in olivine materials, which is determined by the activation energy for Li hopping and is the ionic diffusivity assuming a high concentration of highly mobile electrons. Using the generalized gradient approximation to density functional theory, the authors suggest that Li diffuses through one-dimensional (1D) channels with little crossover between channels. In addition, they calculate diffusion coefficients on the order of 10^{-9} cm^2/s, comparable to values estimated in lithium cobalt oxide, suggesting that Li diffusion is rapid in olivine-based materials. Therefore, the authors conclude that the rate capability in these materials is most likely from electron conductivity limitations. However, the predominant 1D diffusion means that the material would be susceptible to defect blocking, which in turn can result in reduced rate capabilities.

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An Interface-Free-Energy Approach to Semiconductor Electrode Chemistry

Studying the surface chemistry of electrodes under electrochemical conditions is critically important to understanding adsorption, corrosion, deposition, and other important processes. As the hypothesis for a recent publication, Chazalviel *et al.* at CNRS-Ecole Polytechnique in France discuss how the solid/liquid interface free energy is expected to govern the wetting behavior of immersed electrode surfaces, and how careful measurements of the contact angle as a function of electrode potential may be used as a sensitive, practical tool for monitoring surface chemistry changes. They describe the principles and implementation of a novel gravimetric method for measurement of advancing and receding solid/liquid contact angles and present results for Si electrodes in HF and for Ge electrodes in H_2SO_4 and $HClO_4$. The results are in excellent agreement with previous studies, including *in situ* infrared spectroscopy investigations of these semiconductor surfaces. As one example, silicon hydrophilicity (in the electropolishing regime) and hydrophobicity (at cathodic potentials where the surface is known to be covered with covalently attached hydrogen) were clearly observable in the gravimetric contact angle measurements.

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