

A Model for the Atmospheric Corrosion of Copper

The atmospheric corrosion of copper has been extensively investigated. While the effects of SO_2 are well documented, comparatively little research has been conducted on the synergistic effects of NO_2 or O_3 (species which are frequently present, particularly in experimental accelerated corrosion environments). Researchers from the Swedish Corrosion Institute, Attana AB, and the Royal Institute of Technology in Stockholm recently published work that compares the effects of $\text{NO}_2 + \text{SO}_2$ and $\text{SO}_2 + \text{O}_3$ on the atmospheric corrosion of copper predicted utilizing a combination of the GILDES model and experimental data. The GILDES model expresses the metal/atmospheric interface as five discrete regions – the Gas Interface, the Liquid layer, the Deposition layer, the Electrode layer, and the metal Surface. A set of 86 reactions (and their associated kinetic parameters) taken from the literature was considered in the model, encompassing surface absorption, chemical, and electrochemical interactions. Good agreement between the simulation and experiment was observed for sulfate formation in $\text{SO}_2 + \text{O}_3$. However, poor agreement was observed for the $\text{SO}_2 + \text{NO}_2$ case, where the simulation predicted similar growth kinetics for the first hour, at which point experimentally the growth rate was observed to decrease significantly while the model predicted continued formation. The predicted rates of nitrate formation also differed from experiment, where an experimentally observed induction period was not captured by the model.

From: *J. Electrochem. Soc.*, **152** (5), B178 (2005).

Electrolytic Hydrogen Evolution in DMFCs Induced by Oxygen Interruptions and Its Effect on Cell Performance

The direct methanol fuel cell (DMFC) is a candidate for future power source applications; however, crossover of methanol to the cathode (which is known to induce a large overpotential on the cathode as well as result in fuel underutilization) presents a challenge to widespread use of this type of fuel cell. Researchers from the Hong Kong University of Science and Technology have described another effect of concurrent methanol oxidation and oxygen reduction at the cathode. They reported that the cutoff and startup of oxygen causes the gas diffusion layer under the channel rib to become depleted in oxygen with respect to the channel opening. This nonuniform distribution of oxygen on the cathode following cutoff induces transient gas evolution on the anode. Chromatographic analysis of this evolved gas revealed H_2 and CO_2 as the principal components. The authors

hypothesized that the protons produced in the methanol oxidation reaction are reduced to H_2 in an “electrolytic region” formed under the channel rib. Furthermore, oxygen startup following cutoff induced a temporary increase in fuel cell performance above that found for steady flow under continuous operation. Similar fuel cell performance enhancement was found by inducing electrolytic hydrogen using an external power source.

From: *Electrochem. Solid-State Lett.*, **8** (4), A211 (2005).

Ti-, Al-, and Cu-Doping Induced Gap States in LiFePO_4

Four attributes are necessary for a battery material to reach commercialization: lowest cost, high safety, reasonable performance, and long life. Lithium iron phosphate (LiFePO_4) has attracted significant attention as a cathode material in recent years because of its low cost and good safety attributes. However, the electronic conductivity of the material is extremely poor. A number of attempts have been made to dope this material; however, subsequent studies have led to a controversy as to whether it is even possible for this cathode to be doped. Abbate and co-workers from the Universidade Federal do Parana and the Universidade de Sao Paulo in Brazil used X-ray absorption spectroscopy to study the electronic structure of both pristine and doped LiFePO_4 , with Ti, Al, and Cu as dopants. While the Fe 2p spectra suggest that iron is in the Fe^{2+} state and that the electronic structure is not affected by the presence of the dopant, the O 1s spectra show extra absorption intensity just below the bandgap of LiFePO_4 . The authors interpret this to mean that additional states are induced in the bandgap by doping. This result suggests that it may be possible to alter the bulk electronic structure of LiFePO_4 via the introduction of dopants.

From: *Electrochem. Solid-State Lett.*, **8** (6), A288 (2005).

Nanocrystalline Graphite for Electrochemical Sensing

Over the last few years, there has been increasing interest in carbon-based electrodes for sensing neurological compounds. New materials such as carbon nanotubes and nano- and microcrystalline forms of diamond have been investigated as alternatives to conventional glassy carbon and carbon paste materials. However, the application of these materials is still limited by either slow electron transfer kinetics or the need for surface pretreatment. Based on their preliminary work [*Electrochem. and Solid-State Lett.*, **5**, E32 (2002)], researchers at the University of Louisville, Arizona State University, and Clemson University recently reported

the results of a detailed study on a novel electrode material consisting of nanocrystalline graphite (NCG). This material was synthesized onto platinum wire via microwave plasma chemical vapor deposition. The resulting NCG films gave cyclic voltammetric behavior that was fundamentally different from that seen at other carbon electrode materials, including both glassy carbon and diamond. In particular, it exhibited reversible or quasi-reversible kinetics for several model electron transfer processes. Raman spectroscopy and electron nanodiffraction were used to confirm the presence of nanocrystals of graphite and to support the hypothesis that NCG exhibits electrochemical activity similar to that of edge planes of crystalline graphite. Other attractive features of this NCG material are its ease of synthesis and its stability for extended periods of use. Among other envisioned applications, the NCG material presents an interesting possibility for electroanalytical detection of neurotransmitters *in vivo*.

From: *J. Electrochem. Soc.*, **152** (4), E154 (2005).

Investigation of DMAB Oxidation Mechanism

Dimethylamine borane (DMAB) is a technologically important reducing agent used in the electrodeless deposition of metals, alloys, semiconductors, and insulators. A particularly significant application of DMAB-based electrodeless plating is in microelectronics fabrication, where it is being pursued as a low cost, low temperature replacement for vacuum-based processes for the selective deposition of metals. Nagle and Rohan at the Tyndall National Institute in Ireland recently published the results of an electrochemical study of DMAB oxidation in alkaline solutions. They performed chronoamperometry and cyclic voltammetry experiments at a gold microdisk electrode to investigate the reaction mechanism. They observed that DMAB oxidation occurs in two separate three-electron processes to produce hydrogen gas, water, and $\text{B}(\text{OH})_4^-$ as the reaction products. They comprehensively described the overall oxidation process in terms of a coulomb number that varies between 3 and 6 depending on the chemical conditions. Here, the reaction stoichiometry depends strongly on the ratio of the concentrations of OH^- and DMAB, with hydrogen evolution increasing as this ratio decreases.

From: *Electrochem. Solid-State Lett.*, **8** (5), C77 (2005).

Tech Highlights was prepared by ZENGHE LIU of Abbott Diabetes Care, VENKAT SRINIVASAN of Lawrence Berkeley National Laboratory, and DONALD PILE, DAVID ENOS, and MIKE KELLY of Sandia National Laboratories.