

***In Situ* Studies of the Effect of CO₂ on the NaCl-Induced Atmospheric Corrosion of Copper**

Atmospheric corrosion of copper is frequently initiated by air-borne salt particles deposited on the metal surface. At elevated humidity levels the salt particle deliquesces and a droplet of concentrated salt solution results. Corrosion of the underlying copper then takes place. Due to the increased availability of oxygen at the perimeter of the droplet, cathodic activity is elevated in this region, forming a galvanic couple with the anodic region that exists beneath the bulk of the droplet. The increased cathodic activity at the edge of the droplet results in locally alkaline conditions which in turn lowers the solution/oxide surface tension, resulting in the formation and growth of a thin solution layer from the perimeter of the droplet. The distance over which this layer spreads is dictated by the aforementioned liquid-oxide surface tension. Under normal atmospheric conditions (350 ppm CO₂), CO₂ is absorbed into this thin alkaline layer, resulting in carbonate formation and a commensurate reduction in the pH. The reduced pH increases the solution-oxide surface tension thereby hindering further expansion of the thin solution layer. However, at low CO₂ levels (below 5 ppm), acidification due to carbonate formation does not occur, and the thin solution layer (and the local cathode beneath it) continues to increase in size, driving corrosion beneath the droplet.

From: *J. Electrochem. Soc.*, **152** (9), B342 (2005).

Hydrogen Mapping across Crevices

Crevice corrosion is a localized corrosion process that occurs as a result of the occluded cell that forms under a crevice on the metal surface. Inside the crevice, the reduction of protons to atomic hydrogen leads both to hydrogen absorption and to molecular hydrogen generation. Absorbed hydrogen can diffuse in the metal and lead to hydrogen embrittlement. Researchers at the National Institute for Materials Science in Japan employed the silver decoration technique on the back side of a 0.5 mm thick iron sample to map the distribution of hydrogen permeation caused by the formation of a 600 μm crevice on the front surface of the sample. In the silver decoration technique, silver crystals form where hydrogen atoms permeate the sample and reduce silver ions from the exclusive solution containing a silver salt. The researchers verified that silver was only reduced by atomic hydrogen and not by a galvanic reaction with the passivated iron substrate. Scanning electron micrographs revealed a variation in the amount of silver deposits in the intermediate region between the passive region near the mouth opening and

the crevice bottom where hydrogen evolution occurred, with the greatest area coverage occurring at 12 mm into the 25 mm deep crevice. Metal thinning in the active region was determined not to be the major contributor to the greater accumulation of silver in the intermediate region.

From: *Electrochem. Solid-State Lett.*, **8** (9), B30 (2005).

Synthesis of Li⁺ Ion Conductive Block Copolymer Electrolyte with Microphase Separation Structure

Solid-state lithium batteries have attracted a great deal of attention in recent years because of the inherent safety advantages of systems that do not contain liquids. Typical solid polymer electrolytes [e.g., polyethylene oxide - (PEO)] tend to have lower transport properties compared to liquid electrolytes, but have much stronger mechanical properties. The desirable mechanical characteristics have been a driving force for the interest in the use of PEO in Li-metal batteries. However, as the mechanical strength increases, the ionic conductivity decreases because both transport and mechanical properties are related to the segmental motion in the polymer. Therefore, it has traditionally been impossible to realize polymers with good mechanical stability that also exhibit reasonable ionic conductivity. Niitani and co-workers in Japan have demonstrated a novel method of achieving both of these characteristics by decoupling the two properties via the use of block copolymers. The authors synthesized a PEO/polystyrene (PSt) block copolymer with microphase separation and characterized its performance in a lithium-metal/LiCoO₂ cell. The PEO phase allows for fast ion conduction and the PSt phase provides good mechanical strength, and the resulting polymer was observed to have a conductivity of 10⁻⁴ S/cm at room temperature. Cells made with the polymer exhibit capacities of 100 mAh/g with reasonable rate capability at 30°C.

From: *Electrochem. Solid-State Lett.*, **8** (8), A385 (2005).

Novel Composite Coatings for Heat Sink Applications

The design of heat sinks to handle the increasingly high thermal output of advanced integrated circuits is becoming ever more important. In fact, the lack of suitable heat sinks has been a limiting factor in the implementation of high performance processors in certain applications. An ideal heat sink material combines a high heat absorption capacity with good thermal conductivity to deal with both thermal spikes and sustained thermal loads. Researchers at the Katholieke Universiteit Leuven in Belgium have

reported the development of a novel composite coating for these applications. They added microencapsulated paraffin particles to a plating electrolyte and produced electroplated copper coatings that included as much as 35 vol % of the microcapsules. The paraffin phase change material (PCM) in the microcapsules absorbs energy when it melts. During this phase change, the temperature of the paraffin remains constant, thereby providing the coating with good thermal spike absorption characteristics. Combined with the high thermal conductivity (400 W/m K) of copper, the authors propose that coatings of this type will find utility as a thermal interface material in heat sink applications. The thermal and microstructural properties of these composite films were characterized by differential scanning calorimetry and scanning electron microscopy. Optimal coatings produced by the researchers to date have a heat absorption capacity of 10.9 J/g.

From: *J. Electrochem. Soc.*, **152** (7), C457 (2005).

Electrochemical Impedance Biosensor for Glucose

Accurate blood glucose monitoring is critical in controlling diabetes mellitus and minimizing diabetic complications. Based on either optical or electrochemical principles, a glucose sensor generally relies on indirect detection of the products of glucose oxidation in the presence of a glucose specific redox enzyme. Researchers at Clarkson University in New York recently reported a reagentless electrochemical impedance glucose sensor that employs the D-glucose/galactose receptor protein from *E. coli* for direct glucose detection. The biological platform for this sensor is a Au surface to which the protein is immobilized through formation of a Au-S bond to a genetically engineered cysteine residue at the N-terminus. The impedance signal detects the extensive ligand-induced domain motion within the protein upon glucose binding. The sensor glucose response is linear near the equilibrium dissociation constant (~0.2 μM) of this protein, which is much lower than the physiological glucose level. Further, this sensing approach demonstrates the general applicability of electrochemical impedance spectroscopy in conjunction with periplasmic binding proteins as a method for detecting small molecules.

From: *Electrochem. Solid-State Lett.*, **8** (8), H61 (2005).

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