Tech Highlights

Corrosion Resistance of Copper-Coated Contacts

Atmospheric corrosion of noble metal coated electrical contacts in sulfur containing environments generally manifests itself as sulfidation of the underlying copper through defects in the noble metal layer. The practical impact of this corrosion is an increase in the resistance of electrical contacts that are made to such surfaces and a subsequent reduction of device reliability. Evaluation of such materials is typically done *via* exposure to mixed flowing gas environments designed to simulate and accelerate relevant degradation modes. Unfortunately, these environments themselves are generally less severe than actual exposure conditions in locations such as Central and Latin America, Asia, and parts of the Middle East. In this work, copper which had been coated with a 2.45 µm layer of nickel beneath an 0.12 µm layer of gold was exposed to a gas stream containing 4 ppm H₂S at 90% RH and 40°C. This highly aggressive environment accurately simulates behavior in the aforementioned geographic regions. Degradation of the gold plated copper resulted in the formation of corrosion product blooms originating from defects in the gold and nickel layers which, after formation, migrated along the surface of the gold layer forming a halo of corrosion product surrounding the original bloom. Cross sectional analysis of corrosion sites revealed a layered structure with copper sulfide on the surface covering a nickel sulfide layer. Beneath this corrosion product, corrosion of the copper was observed to be undercutting the protective gold layer, which the authors postulate may eventually lead to flaking of that layer.

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Room-Temperature Carbonate Fuel Cell

Kohl and coworkers at the Georgia Institute of Technology recently demonstrated the feasibility of a room-temperature carbonate fuel cell system. With modified anion exchange membranes to transport carbonate, the cells were operated with hydrogen, 1 M methanol, and pure methanol fuels using dry O₂ and CO₂ as the cathode gases. CO, was produced at the anode, and O₂ and CO₂ were necessary at the cathode for operation, indicating that carbonate was the conducting ion. The cell offers carbon monoxide tolerance as well as the potential to use non-precious metal catalysts (e.g., nickel), especially at the air cathode. Another significant advantage of the carbonate cycle is that when methanol is used as the fuel at the anode, water is not necessary to oxidize methanol (as in PEM cells). Thus, the anode does not consume water and it may not need to be carried with the fuel, which would significantly increase the energy density of the system.

In an effort to improve the system performance, work is underway to improve the carbonate membrane, its sensitivity to high pH values, and the interface between the electrodes and membranes.

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Local Ion Environment of Soggy Sand Electrolytes

Soggy sand electrolytes (SSEs) are typically composed of fine acidic oxide particles dispersed in a nonaqueous salt solution. This new type of soft matter electrolyte possesses enhanced ionic conductivity arising from preferential adsorption of one ion type on the surface of the particles, thereby establishing a high concentration of compensating ions in the space charge region at the liquid-particle interface. To further corroborate the mechanism, the authors used X-ray absorption spectroscopy (XAS) to investigate the location of ions in the composite system. RbBr (0.01 M) in ethylene carbonate-dimethyl carbonate and LiBr (0.1 M) in tetrahydrofuran liquid electrolytes with varying volume percents of silica particles served as prototype SSEs. The X-ray absorption near edge structure (XANES) data of the RbBr system revealed sharpening peaks in the Br K-edge with increasing silica content, suggesting local order of Br-ions along the oxide surface. Data fitting of extended X-ray absorption fine structure (EXAFS) data in the LiBr system was best accomplished having the Br-ion coordinated to the OH group of silica. The EXAFS data led the researchers to conclude that the Br-ion is largely adsorbed to the silica surface leading to dissociation of the Li-Br ion pair. Consequently, excess Li-ion concentration forms a space charge region near the oxide particle.

From: Electrochem. Solid-State Lett., 9, A564 (2006)

Scanning Kelvin Probe Force Microscopy for Surface Analysis of Aluminum Alloys

Muster and Hughes discuss the advantages and limitations to applying Scanning Kelvin Probe Force Microscopy (SKFPM) to understanding the contributions to potential differences on the surface of a copper-bearing aluminum alloy (AA2024). When mapping carefully prepared samples, SKFPM is able to provide estimates of potential differences between the matrix phase and various intermetallic particles. In particular, SKFPM was shown to predict relative potentials for S-phase and Al-Cu-Fe-Mn that were in agreement with literature data for electrochemically determined potentials. The authors demonstrated, however, that care must be taken in interpreting the SKFPM results as the contact potential difference (CPD) is a combination of surface potential

and potential losses across interfaces, oxide layers, and contaminant layers (e.g., carbonaceous films). For example, an aluminum oxide was shown to contribute approximately 10 mV of potential drop per nm of oxide film: as the oxide film approaches 250 nm, SKPFM measurements tend to yield a homogeneous potential even for heterogeneous samples (i.e., containing secondary phases). Additional artifacts were shown to emerge when scanning over corrosion pits. If the scan rate is too high or the pit too deep, the SKFPM technique shows a potential increase where one may not actually exist. The authors conclude that SKFPM is a valuable technique but that samples should always be analyzed with complementary techniques such as SEM, XPS, and AES.

From: J. Electrochem. Soc., 153, B474 (2006)

In Situ Monitoring of Hydrogen Storage Alloy Negative Electrode during Charging

Hydrogen storage alloys used in nickelmetal hydride cells are thought to crack during cycling due to the strain resulting from the insertion of the hydrogen into the alloy lattice during charge. While the cracking has been confirmed by ex situ studies, no in situ technique has been used to understand and characterize the cracking phenomenon. In a first of its kind, Inoue and coworkers from the Osaka Prefecture University show the use of acoustic emission (AE) to detect the elastic waves generated during the cracking of MmNi_{3.6}Mn_{0.4}Al_{0.3}Co_{0.7} alloy particles. The technique involves monitoring the duration of the AE signal (expressed as a waveform) and the distribution of frequencies (expressed as a power spectra) while simultaneously performing electrochemistry. As the AE signal is also sensitive to the hydrogen evolution side reaction, the authors first characterize the nature of the signal when evolving hydrogen on a Cu electrode. By comparing this spectra to that on the alloy particle, the authors show that the signature of particle cracking can be discerned from that for the hydrogen evolution. Ex situ SEM analysis is used to confirm the cracking of the alloy. Based on the analysis of the AE signal, the authors suggest that alloy cracking occurs intensely during the first charge and is completed within the first half of charging process. On the other hand, hydrogen evolution is seen to occur continuously.

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