

Chloride Ion Interaction with Oxide-Covered Aluminum Leading to Pitting Corrosion

Corrosion would be a much more common phenomenon were it not for the passive oxide film that forms on and protects the underlying metal. Instead, localized (crevice, pitting) corrosion commonly occurs through non-homogenous environments and through the action of aggressive anions such as the chloride ion. The authors of this review article recognized that many proposed mechanisms of Cl^- interacting with the passive film, particularly those of aluminum, have been described, but no consensus has been reached by the research community. These authors embarked on summarizing what is known about the Cl^- interactions with passive films on Al, and a couple of Al alloys. After quickly addressing the fact that Cl^- is adsorbed by the positively charged surface of passive films typically having a potential of zero charge \sim pH 9, the authors present experimental evidence for Cl^- being incorporated into the passive film, being present below, as well as above the pitting potential. The authors assert that the body of evidence shows that Cl^- incorporation occurs via ion migration and leads to reaction at the oxide/metal interface. These reviewers add their interpretation of the data and present McCafferty's stepwise model as the best explanation consistent with all experimental data.

From: *J. Electrochem. Soc.*, **161**, C421 (2014).

Modeling Volume Change due to Intercalation into Porous Electrodes

Lithium-ion batteries are electrochemical devices whose performance is influenced by transport processes, electrochemical phenomena, mechanical stresses, and structural deformations. Many mathematical models already describe the electrochemical performance of these devices. Some models go further and account for changes in porosity of the composite electrode. Other models focus on the coupled volume expansion and resulting stresses arising from the (de)lithiation process. Researchers from the University of South Carolina, in their article published in the JES Focus Issue on Mathematical Modeling of Electrochemical Systems at Multiple Scales, considered both of these factors in developing a model that accounts for stresses that build up in a porous electrode due to active material volume change. For their calculations, the authors assumed a 100% volume change in the active material component of the electrode coating. The cell casing presented the bounds on the expanding electrode, ranging from rigid, non-compliant to flexible, compliant casing. As expected, the volume change for the more rigid casing is accommodated by the porosity and consequently leads to increased ionic resistance. For the compliant casing,

the volume change in the active material translates more into dimensional change. The authors present their model results as a function of state of charge. Their equations can be incorporated into porous electrode theory for a more complete battery model and better understanding of battery performance and failure mechanisms.

From: *J. Electrochem. Soc.*, **161**, E3297 (2014).

InZnSnO-Based Electronic Devices for Flat Panel Display Applications

Thin film transistor (TFT) advances will play a key role in the system-on-panel (SoP) concept for driver, sensor, memory and other devices in compact displays. In flat panel display technology, TFTs with better pixel transmittance and low-power, reliable switching capabilities, are needed for SoP systems and circuitry. Higher mobility materials should offer enhanced transparency, electrical response and stability, and ease in processing. Advances in amorphous oxide materials offer the possibility of integrating resistive random access memory (RRAM) devices for non-volatile memory applications, and display panel integration in TFT form. In their report as part of the JSS Focus Issue on Oxide Thin Film Transistors, researchers at the National Chiao Tung University in Taiwan have demonstrated a versatile amorphous InZnSnO (a-IZTO) oxide semiconductor in TFT and RRAM technologies for SoP applications. When fabricated as a TFT device, the a-IZTO thin film exhibited a high field effect mobility of $39.6 \text{ cm}^2/\text{V}\cdot\text{s}$ with enhanced electrical stability. The a-IZTO film also retained $>80\%$ transmittance in the visible frequency range. As a RRAM device, excellent resistive switching characteristics were observed over several hundred cycles. A conceptual memory array architecture is postulated with each node comprising the a-IZTO TFT connected to one RRAM cell structure (1T1R). These high mobility oxide films are promising materials for low-cost technologies for integration into system-on-panel applications.

From: *ECS J. Solid State Sci. Technol.*, **3**, Q3054 (2014).

Superconformal Filling of Through Vias

Through vias are useful in creating 3D integrated circuits and packages because they enable the fabrication of vertical interconnections through the substrate (typically silicon, sometimes glass). Here, electroplating processes can be used to fill the via with a conductive material such as copper. Researchers at The State University of New York at Binghamton recently reported the results of a study on the use of plating inhibitors (chloride ion and tetranitroblue tetrazolium chloride, TNBT) to the superconformal filling of narrow ($50 \mu\text{m}$), high aspect ratio ($\text{AR}=6$) through-glass vias. The plating

solution was 0.88 M CuSO_4 containing 40 ppm Cl^- and 40 ppm TNBT. By optimal choice of other critical plating parameters (current density, time), the authors showed that via filling can be precisely controlled so it proceeds by the so-called "butterfly" plating mechanism, whereby the copper plating bridges across the diameter in the middle of the via. This effectively produces two blind vias that then fill very nicely as the plating process proceeds. Establishment of a concentration gradient of the Cl^- and TNBT inhibitors leads to a substantially higher electrodeposition rate in the middle of the via compared to rates at the flat surface or at the via openings; therefore, there is only minimal copper deposition produced on the surface during the via fill, which is desirable.

From: *ECS Electrochem. Lett.*, **3**, D30 (2014).

Nanoparticle-Carbon Nanofiber Composites for Pt-Free Dye-Sensitized Solar Cells

Over the past few decades, dye-sensitized solar cells (DSSCs) have been actively studied given their promise of reasonable efficiency, fabrication costs, and environmental friendliness. One route to making DSSCs more economical is decreasing or eliminating the amount of Pt used in the counter electrode. Researchers in Korea investigated the use of a TiO_2 nanoparticle-carbon nanofiber (CNF) composite as an alternative catalyst at the counter electrode. Three composites containing different amounts of nitrogen-doped TiO_2 were synthesized using electrospinning. Complete DSSCs were fabricated, characterized, and tested for their performance. The highest weight percent sample ($13.8 \text{ wt}\%$) investigated gave the highest values for the metrics of photocurrent density ($15.65 \text{ mA}/\text{cm}^2$), fill factor (60.5%), and power-conversion efficiency (6.31%). Each of these values comparably matched or slightly exceeded those for the Pt counter electrode sample. The authors speculated that the combination of high surface roughness of the TiO_2 particles on the CNFs and the decreased charge transfer resistance stemming from the highly catalytic TiN phases resulted in enhanced reduction of I_3^- at the counter electrode. This work demonstrated a cheaper DSSC, with improved performance, using a TiO_2 -CNF composite.

From: *ECS Solid State Lett.*, **3**, M33 (2014).

Tech Highlights was prepared by Mike Kelly of Sandia National Laboratories, Colm O'Dwyer of University College Cork, Ireland, and Donald Pile of Nexeon Limited. Each article highlighted here is available free online. Go to the online version of Tech Highlights, in each issue of Interface, and click on the article summary to take you to the full-text version of the article.