

Li/Polymer Electrolyte/Water Stable Lithium-Conducting Glass Ceramics Composite for Lithium-Air Secondary Batteries with an Aqueous Electrolyte

Next generation electric vehicles will require higher energy density storage. Lithium-air technology is a promising technology that approaches the energy density of gasoline-air. Cycle life for this battery chemistry has been limited for several reasons, including the reactivity of the lithium metal with the electrolyte. To address this challenge, researchers from Mie University and Colorado School of Mines have incorporated a protective polymer electrolyte interlayer, $\text{PEO}_{18}\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, with a lithium-conducting glass ceramic, $\text{Li}_{1-x-y}\text{Ti}_{2-x}\text{Al}_x\text{Si}_{3-y}\text{O}_{12}$ (LTAP) for stability against lithium metal. The ionic conductivity of the layered electrolyte reached $5 \times 10^{-4} \text{ S/cm}$ at 60°C and $1 \times 10^{-3} \text{ S/cm}$ at 80°C due to the local relaxation and segmental motion of the PEO chains above 55°C . The suitability of the polymer electrolyte layer was demonstrated with a symmetrical lithium cell at 60°C showing no change in its $800 \Omega \text{ cm}^2$ cell resistance. Initial electrochemical results demonstrate the charge and discharge capability at current densities up to 0.25 mA/cm^2 at 60°C . This multi-layered electrolyte provides a stable lithium reducing environment and a barrier to water. This layered electrolyte approach is potentially applicable to lithium-air, lithium-water, and nonaqueous lithium chemistries with trace water content.

From: *J. Electrochem. Soc.*, **155**, A965 (2008).

Thermal Stability of Pore Sealing Using Parylene N

The semiconductor industry's continuous drive to smaller devices places high demands on fabrication materials and processes. Key performance parameters such as resistance-capacitance (RC) delay, and parasitic capacitance can be improved with the use of low- k dielectrics such as porous oxides. However, these porous materials are susceptible to penetration by precursor molecules and other process chemicals that can degrade performance. Researchers at Rensselaer Polytechnic Institute, the University at Albany, and Freescale Semiconductor, Inc. recently reported the results of a study into the thermal stability of a pore sealing material, Parylene N. They used Rutherford backscattering spectroscopy (RBS) to demonstrate that a 1 nm Parylene N coating deposited using the Gorham method completely seals a porous methyl silsesquioxane (MSQ) against penetration of Co deposited by chemical vapor deposition (CVD). Further, high temperature (400°C) annealing of the Parylene N in an Ar-H_2 forming gas does not affect the pore sealing properties of the film. Electrical tests of capacitors with a Parylene N-sealed MSQ dielectric also showed that the coating remains conformal and pinhole free after 400°C

heat treatment. Since multilevel integrated circuit (IC) fabrication requires numerous temperature cycles at temperatures up to 400°C , these and other results showed that Parylene N is an effective pore sealant for low- k dielectrics and that it is suitable for integration into back end of line (BEOL) processes in IC fabrication.

From: *J. Electrochem. Soc.*, **155**, H819 (2008).

Colorimetric Determination of Lithium Content in Electrodes of Lithium-Ion Batteries

Determination of lithium content in different parts of lithium-ion batteries with good spatial resolution is crucial for the postmortem analyses of cycled batteries. Several analytical techniques, including X-ray diffraction, *in situ* Raman spectroscopy, transmission electron microscopy and electrochemical coulometry, have been used to determine the amount of active lithium in graphite anodes, each of them featuring specific advantages and drawbacks. As a continuing effort in this area, a new fast and low-cost method was recently reported by researchers at the Paul Scherrer Institut of Switzerland. This technique is based on the phenomenon that graphites, as well as other intercalation materials used in lithium-ion batteries, change their color upon electrochemical insertion of lithium ions. In their study, *in situ* colorimetry was developed as a straightforward technical method to measure the local state of charge of lithium-ion battery electrodes. A laboratory cell with a glass window was built for *in situ* characterization of intercalation materials. Calibration curves of red, green, and blue color values vs. state of charge were acquired and used for mapping of lithium distribution in battery electrodes. The lithium distribution in anodes of aged lithium-ion batteries was found to be highly heterogeneous.

From: *J. Electrochem. Soc.*, **155**, A862 (2008).

Investigating Thin Li-Halide Cathodic Interlayers for Improved Electron Injection

Electron injection into the electroluminescent polymer layer is an important rate-limiting step in the operation of polymer light-emitting diodes (PLEDs). Since these semiconducting polymers are better hole transporters than electron transporters, enhanced electron injection is important for achieving balanced current components in the device. Previous research had demonstrated improved device efficiency by inserting a thin compound interlayer, such as an alkali metal fluoride, between the Al cathode and the electroluminescent polymer. Researchers from The Ohio State University investigated the effects of using various Li-halide salts instead of various fluorides. Current density-voltage (J - V) and luminescence-voltage (L - V) measurements and electroluminescence (EL) emission spectra were taken of PLEDs based on poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylenevinylene] (MEH-

PPV). The results showed improvement in the operating performance of devices employing thin ($\sim 5 \text{ nm}$) Li-halide cathodic interlayers as the halide was changed to higher atomic number. A lower turn-on voltage was also observed for these devices compared to one not using a cathodic interlayer. Compared to a device employing a Li metal interlayer, the device with the LiBr interlayer slightly exceeded in luminance and approached closely in the other metrics.

From: *Electrochem. Solid-State Lett.*, **11**, J76 (2008).

PEG, PPG, and Their Triblock Copolymers as Suppressors in Copper Electroplating

Copper electrodeposition from an acidic plating bath is the current method for on-chip production of interconnects for microelectronics. In order to accomplish the superconformal filling necessary to achieve the geometries required by such applications, a series of plating bath additives are utilized. These additives include a promoter, a suppressor, an accelerator, and a leveler. The role of the suppressor is to increase the overpotential required for copper ion reduction by a surface interaction with the promoter. Most studies reported in the literature have explored the effectiveness of polyethylene glycol (PEG) alone. In this study, a series of suppressors including polypropylene glycol (PPG), along with triblock copolymers of PEG and PPG terminated either with ethylene oxide terminal blocks (EPE) or propylene oxide terminal blocks (PEP), were compared to PEG alone. The extent of suppression of copper reduction varied over a range of 50mV, with PPG being the most effective, and PEG the least. Significant differences were observed in both the suppressor adsorption and desorption processes. In the case of the latter, the molecular weight of each chemistry played a major role. The authors conclude that the variations observed in the aforementioned two processes may play a large role in the effectiveness of a particular chemistry as a suppressor. While planar deposits were able to be achieved utilizing each of the chemistries explored in this study, the lowest surface roughness was achieved with EPE by a wide margin.

From: *J. Electrochem. Soc.*, **155**, D632 (2008).

Tech Highlights was prepared by Zenghe Liu of Abbott Diabetes Care, Aron Newman of Physical Sciences, Inc., David Enos and Mike Kelly of Sandia National Laboratories, and Donald Pile. 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.