

## Improved Electrochemical Performance of $\text{Li}_2\text{MnSiO}_4/\text{C}$ Composite Synthesized by Combustion Technique

Researchers are interested in silicates as polyanionic cathode materials for Li-ion batteries because of their high theoretical capacities. A group in India reports that nanocrystalline  $\text{Li}_2\text{MnSiO}_4$ , synthesized from a combustion technique using citric acid as a chelating agent, can exhibit electrochemical discharge capacity of 164 mAh/g with a current density of 0.01 mA/cm<sup>2</sup> when mixed with 20% acetylene black.  $\text{Li}_2\text{FeSiO}_4$ , another silicate analog, had been found earlier to have a reversible capacity of only 130 mAh/g. The authors used scanning electron microscopy (SEM) to show that heating the as-synthesized  $\text{Li}_2\text{MnSiO}_4$  in the presence of acetylene black has an effect on the microstructure. The additional carbon present in the matrix acts as a buffer preventing grain growth and the formation of large, hard agglomerates during heat-treatment. The authors compared 10 and 20% loadings of conductive carbon and observed the effect on particles under SEM and on electrical properties employing electrochemical impedance spectroscopy. The 20% loading resulted in a higher reversible capacity than the 10% loading. The addition of acetylene black prevents impedance growth in the cell during cycling. The results from cyclic voltammetry and discharge profiles indicate two redox couples at 2.9/3.6 and 4.3/4.5 V vs. Li which suggest a two-stage Li insertion mechanism.

From: *J. Electrochem. Soc.*, **156**, A677 (2009).

## Pyruvate/Air Enzymatic Biofuel Cell Capable of Complete Oxidation

A biofuel cell employs biocatalysts, such as enzymes, to convert the chemical energy in a biofuel into electrical energy. Most enzymatic biofuel cells contain bioanodes with single enzymes to partially oxidize biofuels. The partial oxidation is a much less efficient energy utilization process compared with the complete oxidation of biofuels achieved in living cells. Progress in maximizing the energy density of pyruvate, a biofuel produced from the metabolism of glucose and complex carbohydrates, was recently reported by researchers at the Saint Louis University. The authors developed carbon bioanodes incorporating a number of enzymes involved in the Krebs cycle which is responsible for metabolism of complex fuels in mitochondria. Combining such an anode employing five enzymes with a regular platinum oxygen cathode resulted in a cell that reached a current density of 3.92±0.48 mA/cm<sup>2</sup> and a power density of 0.93±0.09 mW/cm<sup>2</sup>, corresponding to a 5.9-fold increase in current density and a 4.6-fold increase in power density

compared with pyruvate/air organelle-based biofuel cells previously reported in the literature. Complete pyruvate oxidation was confirmed by <sup>13</sup>C NMR monitoring of the fuel solution in this cell.

From: *Electrochem. Solid-State Lett.*, **12**, F26 (2009).

## Characterization of the Corrosion Products of Crevice Corroded Alloy 22

In an effort to gain insight into the processes that control the localized corrosion of Alloy 22 (a Ni-Cr-Mo-W alloy), the nature of the corrosion products formed via active crevice corrosion were explored. Crevice corrosion was driven electrochemically in 100°C, 4 M NaCl utilizing a PTFE-wrapped, ceramic crevice former. The electrochemical behavior included the four stages characteristic of crevice corrosion – initiation, propagation, stifling, and arrest. Loose, black corrosion products were found in regions where active crevice corrosion had taken place. Dark green precipitates were found outside of the creviced region, and in addition, the bulk solution turned green in color. In regions where active dissolution took place, then repassivated, the passive oxide films were similar in nature to passive films observed on bulk Alloy 22 surfaces. Regions where significant dissolution took place exhibited a nickel-enriched, chromium-depleted near-surface region. The corrosion products within the crevice were depleted in nickel, chromium, and iron, but enriched in molybdenum and tungsten. Corrosion products present outside of the crevice on uncorroded regions of the Alloy 22 surface contained high chromium to nickel and molybdenum to nickel ratios relative to the bulk alloy composition. Significant nickel was also measured in the test solution, either as Ni<sup>2+</sup> or a nickel chloride complex.

From: *J. Electrochem. Soc.*, **156**, C313 (2009).

## Electroless Copper Deposition for All-Copper Flip-Chip Connections

State-of-the-art packaging of integrated circuits typically uses solder balls to make electrical connections to the substrate. Although this has been very successful in meeting the demands of today's high-performance electronic modules, solder does have disadvantages in flip-chip packaging applications, including those related to formation of brittle copper-iron intermetallics, low electromigration resistance, and difficulty in underfill processing for ball grid arrays as the pitch size progressively shrinks (from 130 μm today to 90 μm in 2020). Researchers at the School of Chemical and Biomolecular Engineering at the Georgia Institute of Technology recently reported dramatic improvements in an all-copper chip-to-substrate connection fabrication process.

They used an acceleration-suppression approach to electroless copper plating that allowed them to accelerate the flip-chip plating process, but not to an extent that moved the process out of the desired kinetically controlled region. They accelerated the transport of reactants and products in the spatially restricted regions by plating at elevated temperatures between 45-70°C, but simultaneously suppressed the overall deposition reaction rate by addition of poly(ethylene glycol) (PEG), which has the added benefit of producing void-free copper deposits. The inclusion of PEG in the electroless copper bath also allowed a significant time reduction (from 19 hours to 3 hours) in this copper pillar bonding process.

From: *J. Electrochem. Soc.*, **156**, D226 (2009).

## LiMnPO<sub>4</sub> as an Advanced Cathode Material for Rechargeable Lithium Batteries

In the pursuit of advanced batteries for electric vehicles (EVs), cell designers need to address the trade-off between higher energy density and safety. Researchers at Bar-Ilan University and High Power Lithium have synthesized and tested carbon-coated LiMnPO<sub>4</sub> nanoparticles that can serve as a safe electrode material with a competitive energy density. The authors performed a detailed structural and surface analysis, including X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and differential scanning calorimetry (DSC), which provides complementary information to the electrochemical testing. This olivine-based structure compares to LiFePO<sub>4</sub> with a 0.6-0.7 V greater operational voltage and equivalent capacity. DSC results show that delithiated LiMnPO<sub>4</sub> evolves less heat in the presence of electrolyte than LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA). Electrochemical testing of C-LiMnPO<sub>4</sub> with a 20 wt% carbon content results in a practical capacity of 140 mAh g<sup>-1</sup>. The C-LiMnPO<sub>4</sub>, with a relatively high 68 m<sup>2</sup>/g surface area, has limited reactivity with the organic carbonate-based electrolyte with the ability to cycle hundreds of times at 60°C. This electrode material is a promising improvement to LiFePO<sub>4</sub> by providing a higher energy density while still providing for safe operation.

From: *J. Electrochem. Soc.*, **156**, A541 (2009).

Tech Highlights was prepared by Zenghe Liu of Abbott Diabetes Care, Aron Newman of Physical Sciences, Inc., Arnold Stux of Rochester Institute of Technology, 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.