

### New Stable High Voltage Electrolyte Solvent

Due to the anodic instability of existing electrolyte solvents used in commercial lithium ion and lithium metal-based batteries, overcharge of these cells results in oxidative cleavage of the solvent's bonds and the formation of gaseous products that can lead to a reduced cycle life and even to cell rupture. However, some cell overcharge is required in order to obtain cell balance within a battery pack, which is needed for pack safety and long life. Researchers at Arizona State University have synthesized an ethyl methyl sulfone (EMSF) solvent that, when combined with various lithium salts, has shown anodic stabilities of up to 5.8 V vs  $\text{Li}^+/\text{Li}$ . The electrolytes were analyzed using both cyclic and linear sweep voltammetry, utilizing lithium foil counter and reference electrodes coupled with either platinum, activated charcoal or  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  as a working electrode. Although EMSF has a melting point of 36.5° C, it spontaneously liquifies with lithium salts to form solutions that are thermally stable between 0° C and about 220° C. Solutions of 1M lithium salt/EMSF were also found to have very good conductivities that ranged between  $10^{-2}$  and  $10^{-3}$  S/cm at 25° C. The authors envision that this solvent may enable the use of more exotic cathode materials offering lithium cell voltages greater than 5 V. Currently, other non-cyclic sulfones are being investigated and their performance in lithium ion cells evaluated.

*From: J. Electrochem. Soc., 144, L70 (1997).*

### Tribochemical Polishing

Chemical mechanical polishing (CMP) is widely used in the semiconductor industry to planarize surfaces. CMP methods rely on a combination of mechanical abrasion and surface chemistry to achieve smooth surfaces. State-of-the-art finishing of ceramic pieces also relies on the use of abrasives. However, using abrasives with ceramics and other brittle materials can lead to microcracks, scratches, asperities, or holes from missing grains, which can act as stress concentrators. Hah and Fischer at the Stevens Institute of Technology in New Jersey have introduced a new polishing technique called tribochemical polishing. They have demonstrated the technique by polishing flat planes in silicon nitride ball bearings using a rigid polishing pad without added abrasives. For silicon nitride, the technique relies on friction to stimulate the chemical dissolution of the silicon nitride in water to form soluble silica and ammonia. The authors investigated several solution chemistries and process conditions, and found an optimum polishing pressure range. If the pressure is too high, mechanical wear occurs, but if it is too low, hydroplaning occurs, and the reaction stops. Under one set of conditions, the authors report a surface roughness of only 0.5 nm, as measured by atomic force microscopy.

*From: J. Electrochem. Soc., 145, 1708 (1998).*

### Oxidation Studies of Silicon Oxynitride Ceramics

Polycrystalline silicon oxynitride ( $\text{Si}_2\text{N}_2\text{O}$ ) has attracted attention for advanced high temperature structural applications due to its excellent chemical, refractory, and thermomechanical properties. However, silicon-based ceramics are known to be thermodynamically unstable when exposed to an oxidizing environment. Oxidation leads to degradation that can significantly limit the performance and long-term stability of  $\text{Si}_2\text{N}_2\text{O}$  components. Manassis and Du of the Stevens Institute of Technology, New Jersey, and Larker of the Lulea University of Technology, Sweden, have investigated the oxidation kinetics of high purity polycrystalline  $\text{Si}_2\text{N}_2\text{O}$  ceramics under carefully controlled oxidation conditions. Hot isostatically pressing

equal molar amounts of high purity  $\text{Si}_3\text{N}_4$  and  $\text{SiO}_2$  without sintering additives produced the  $\text{Si}_2\text{N}_2\text{O}$  ceramics used. The authors indicate that the oxidation kinetics of high purity  $\text{Si}_2\text{N}_2\text{O}$  follow a parabolic rate law in dry  $\text{O}_2$ , and  $\text{O}_2$ -Ar and  $\text{O}_2$ - $\text{N}_2$  gas at partial pressures of 0.1 to 1 and 5 atm, respectively, in the temperature range 1000 to 1300° C. This parabolic behavior indicates molecular oxygen diffusion is the rate-limiting step during the oxidation of  $\text{Si}_2\text{N}_2\text{O}$ , whereas outward diffusion of nitrogen does not affect the oxidation process. Additionally, the higher activation energy value for the oxidation of  $\text{Si}_2\text{N}_2\text{O}$  compared to Si, in this temperature range, may indicate some structural characteristics of the oxide grown on  $\text{Si}_2\text{N}_2\text{O}$  and Si in terms of density and/or intrinsic stress.

*From: J. Electrochem. Soc., 145, 1398 (1998).*

### Surface Imaging Technique

James, Garfias-Mesias, Moyer, and Smyrl at the University of Minnesota described a method for simultaneous scanning electrochemical and topographic imaging of a sample surface. The method employs shear-force feedback to maintain the relative positioning of the probe with respect to the sample. In this way, the investigators state that large electrochemical currents can be observed due to the close proximity of the sample surface and probe. Another feature of this approach is that the feedback control for maintaining relative distances works well in the liquid environment of an electrochemical cell, and is stated to be stable for hours. Potential applications for this technique are diverse, and may include corrosion processes, structure activity relationships of catalytic systems, and reactivity of heterogeneous surfaces.

*From: J. Electrochem. Soc., 145, L64 (1998).*

### In Situ Measurements of the Electrochemical Dissolution of Gold

Gold is a metal known for its excellent chemical inertness, which has led to its use in a variety of technological applications. For example, gold is used as an electrode and interconnect material for microcircuits and microsensors, and it is routinely deposited by a combination of common photolithographic, evaporation, and/or electroplating processes. Gold is also widely used as a working electrode in fundamental electrochemical studies and electroanalytical techniques. In many of these applications, a fundamental understanding of the electrochemical inertness of gold (i.e., its stability in corrosive liquids at anodic bias potentials) is critical. Researchers at Hokkaido University in Japan have reported the results of an in situ electrochemical quartz crystal microbalance (EQCM) study of gold dissolution in perchloric acid solutions containing small amounts of chloride ion. They carefully determined the voltammetric and potentiostatic behavior of a Au (111)-oriented electrode surface over a wide anodic potential range. Simultaneously, the mass changes associated with the prevailing interfacial processes, which were ascribed to chloride ion adsorption, water molecule adsorption, gold dissolution, oxide formation, and oxide reduction, were recorded. Among the key findings of this research was that gold dissolves exclusively via a three-electron oxidation process in the anodic potential region studied. The authors found no evidence for a one-electron oxidation process under these experimental conditions.

*From: J. Electrochem. Soc., 145, 1614 (1998).*

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