

Graphite Anode Stabilization in Propylene Carbonate by Lithium Bis(oxalate)borate

Ethylene carbonate (EC) is an indispensable electrolyte solvent in many state-of-the-art lithium-ion battery applications due to its high dielectric constant, low viscosity, and ability to effectively protect against graphite anode exfoliation. However, its high eutectic temperature in electrolyte systems prevents its use in many low temperature applications. Significant efforts have thus been made to replace EC with a structurally similar but much lower melting counterpart, propylene carbonate (PC), for use at low temperatures. Since PC-based electrolytes severely exfoliate the graphene structure, researchers have examined a number of approaches to stabilize graphite anodes, including coating the graphite with amorphous carbon or adding other molecular components to the PC-LiPF₆ electrolyte. As part of a continuing program (see: *Electrochem. Solid-State Lett.*, **4**, E1 (2001); **5**, A26 (2002)) aimed at exploring the utility of lithium bis(oxalate)borate, a novel electrolyte salt, researchers at the U.S. Army Research Laboratory in Maryland recently discovered that it can effectively stabilize graphite materials in PC-rich or even neat PC solutions. Further, it supports reversible lithium ion intercalation/deintercalation, a property that has never been observed for any salt known to the lithium-ion industry. The authors state that this finding, in combination with other proven merits of this salt, offers unprecedented flexibility for the efforts of reformulating lithium-ion battery electrolytes.

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Langmuir-Blodgett Films Incorporating a Viologen Derivative and Tetracyanoquinodimethane

The electrochemical properties of redox molecules immobilized on electrode surfaces have been widely studied for applications in molecular electronics, bioelectronics, electrocatalysis, mediated electron transfer, and electroanalysis. Researchers at Ciudad Universitaria in Zaragoza, Spain used ultraviolet-visible spectroscopy, infrared spectroscopy, and cyclic voltammetry to examine a Langmuir-Blodgett (LB) film containing a viologen dication (1,1'-dioctadecyl-4,4'-bipyridinium) and tetracyanoquinodimethane anion radical. The presence of the large organic anion prevents the incorporation of water and dissolved oxygen into the LB films, thereby yielding a cathodic/anodic surface coverage ratio near unity. The films show very reversible electrochemical processes and a shift toward negative redox potentials for the viologen. This shift is attributed to steric hindrance resulting from the presence of the large TCNQ anion radical between the electrode surface and the viologen. The authors did not observe a splitting of the first viologen voltammetric reduction peak for well-ordered monolayers; however, above the collapse pressure of 34 mN/m, aggregation of the viologen moieties results in peak splitting.

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Water Electrolysis in a Centrifugal Field

Water electrolysis is an attractive process for the small-scale production of high purity oxygen and hydrogen. Inefficiencies in commercial electrolysis cells arise from high overpotentials at the anode and cathode and from large ohmic drops due to gas bubbles in the electrolyte and blanketing the electrode surface. Cheng, et al. at the University of Newcastle upon Tyne in the United Kingdom recently reported the intensification of water electrolysis in centrifugal fields. Using a simple electrolysis cell, they studied the current-voltage characteristics for various acceleration rates, temperatures, and electrolyte concentrations. At 80°C, a cell voltage reduc-

tion of 700 mV (compared to stationary conditions) was achieved at a current density of 3 kA/m² for a centrifugal acceleration of 190 G. The authors determined that centrifugal force enhances mass transport within the cell and removes gas bubbles from the electrodes, membranes, and electrolytes, thereby decreasing cell voltage. The energy required to power the centrifuge is significantly smaller than the energy savings from the reduced cell voltage, thereby making this process attractive.

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Molecular Layer Electrodeposition of Semiconductors

Compound semiconductor films are commonly synthesized by molecular beam epitaxy, chemical vapor deposition, or vapor phase epitaxy in the fabrication of optoelectronic devices. To date, stringent material quality requirements have excluded electrodeposition for synthesis of semiconductor compounds for this application. In a recent report, Shalini Menezes of InterPhases Research in California described a novel electrochemical deposition scheme for preparing molecular layer structures of semiconductor materials. The successive electrodeposition of monolayers of the compound was performed from a single electrolyte containing all of the constituent elements. Menezes showed that controlling the kinetics of the competing reactions by careful regulation of temperature, electrolyte composition, deposition potential, solution volume, and anodic dissolution potential is critical to producing a film of the desired stoichiometry. The author demonstrated the versatility and unique features of this method, known as molecular layer electrodeposition (MLE), by growing CuInSe₂ films that are commercially important in solar cell applications.

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Inhibition of Corrosion-Related Reduction Processes via Chromium Monolayer Formation

Chromate conversion coatings (CCCs) are extensively used on aluminum alloys primarily because of their excellent corrosion resistance. CCCs are applied with a solution containing Cr(VI), a known carcinogen, so there is great interest in developing safe and effective alternatives. An improved understanding of the corrosion-resistant properties of chromium will enable better design of replacement technologies. Clark and McCreery at The Ohio State University recently reported a study of the relationship between the reactions of Cr(VI) and the cathodic inhibition of the oxygen reduction reaction (ORR) under field conditions commonly encountered by aluminum alloys. They used copper electrodes as models of Cu-containing intermetallic compounds and redistributed Cu. In addition, Cr(VI) reduction to Cr(III), known to be an integral reaction in the formation process of CCCs, was examined on Pt and glassy carbon electrodes to permit a wider potential range than is possible with Cu. Hydrodynamic voltammetry, potential step, and cyclic voltammetry experiments revealed that the mechanism of inhibition involves reduction and irreversible adsorption of Cr(III) that blocks adsorption sites, thereby preventing oxygen chemisorption. Formation of this Cr(III) film inhibits the ORR over the entire potential range relevant to Al2024-T3 corrosion.

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