

## Microelectrode Study of the Commercial Process for Adiponitrile Production

Adiponitrile is produced in large quantities (billions of pounds each year) as a precursor to hexamethylenediamine, a monomer used in the production of nylon-6,6. Since 1965, the cathodic hydrodimerization of acrylonitrile has been a major route for the commercial production of adiponitrile. The importance of the production cost of adiponitrile on the economics of the nylon industry has led to considerable research activity. Researchers at BASF and the University of Southampton in England have reported the results of an investigation of the cathodic processes that occur in technologies that use undivided, bipolar cells containing a stack of closely spaced steel plates. In the cells of interest here, lead electroplated onto the steel serves as the cathode. The researchers studied the importance of several side reactions, including reduction of Fe(III), Fe(II), Pb(II), oxygen, and water, on the overall efficiency of the process. They also studied the influence of various electrolyte additives (quaternary ammonium cation, EDTA, and triethanolamine). Lead microelectrodes were used in the study, resulting in mass transfer coefficients that were similar to those for a parallel-plate reactor with pumped electrolyte flow. Among other key findings, the authors concluded that for a process carried out in conditions where the reduction of acrylonitrile is mass-transport controlled, only 3% of the charge is lost to various cathodic side reactions.

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## Simultaneous Quartz Crystal Microbalance and Ring-Disk Measurements

Neither electrochemical experiments nor weight loss experiments alone can unambiguously elucidate metal dissolution mechanisms when both electrochemical and chemical dissolution processes are active. Simultaneously performing weight loss measurements and electrochemical experiments can overcome this problem. Previous efforts to combine quartz crystal microbalance (QCM) weight loss measurements and electrochemical experiments using a rotating ring-disk electrode (RRDE) failed because of stray capacitance introduced by the rotating electrode. Researchers at CNRS, Physique des Liquides et Electrochimie, Université Pierre et Marie Curie in France, recently demonstrated good results with a stationary impinging jet ring-disk electrode experiment where the working electrode is also a component of a QCM. In their approach, the hydrodynamics are very similar to that of the rotating ring-disk electrode. Gabrielli, Keddam, Minouflet-Laurent, and Perrot demonstrated the utility of the device during an investigation of the dissolution of copper in sodium chloride/sodium bicarbonate solutions. This device allowed them to uncover a relevant feature of the mechanism of copper dissolution, namely that a purely chemical step, the adsorption of chloride ion onto the copper, precedes the electrochemical dissolution step.

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## Carbon/Carbon-Composite Bipolar Plate for Proton Exchange Membrane Fuel Cells

Proton exchange membrane fuel cells (PEMFC) have been the focus of interest in vehicular applications of fuel cells because of their rapid start-up feature. Current challenges for this technology include reducing the cost and weight of the cell stack. To achieve this goal, one of the key components requiring improvement is the high-density graphite bipolar plate, for which both material and machining costs are currently prohibitive. Researchers at Oak Ridge National Laboratory have reported a new type of bipolar plate material for PEMFC, a carbon/carbon-composite, which they fabricated by slurry molding a chopped-

fiber preform followed by sealing with chemically vapor-infiltrated carbon. The fabrication route is promising for overcoming the cost barrier because it lends itself to continuous processes and economies of scale. In addition, the resulting component is hermetic, has exceptionally high electronic conductivity (200-300 S/cm), has a low density (0.96 g/cm<sup>3</sup>), and exhibits high biaxial flexure strength (175 ± 26 MPa). Cell testing of a single-sided plate indicated high efficiency and very low cell resistance, and corrosion testing indicated only minimal corrosion occurs in fuel cell environments.

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## Changes in the Electronic Structure of Chemically Deintercalated LiCoO<sub>2</sub>

Engineering the behavior of electrode materials presupposes an understanding of the prevailing electrochemical processes. In the case of LiCoO<sub>2</sub>, one of the oxides used as an active material in the cathodes of lithium-ion rechargeable batteries, it was generally assumed that it is the metal center undergoing oxidation and reduction during charge and discharge of the battery. However, researchers at the Universidade de Sao Paulo and the Universidade Federal De Parana in Brazil have provided some initial experimental evidence suggesting that this view is not correct. Using the cobalt 2p X-ray absorption spectra of chemically prepared Li<sub>x</sub>CoO<sub>2</sub>, Montoro, Abbate, and Rosolen determined that the cobalt is initially in the low-spin trivalent state in the fully lithiated compound, and that it remains so throughout deintercalation to stoichiometries as low as Li<sub>0.46</sub>CoO<sub>2</sub>. The oxygen 1s spectra, on the other hand, exhibits significant changes in the electronic structure over this range of lithium content, suggesting that it is the oxygen undergoing oxidation/reduction.

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## Niobium Electrodeposition in Molten Fluoride Media

The electrodeposition of refractory metals (e.g., Ta, Nb, Hf, Zr, and W) from molten alkali fluorides can be used to prepare coatings to protect metals against corrosion or high-temperature oxidation in specialized applications. Smooth, coherent coatings of niobium can be obtained by dc processes only at low current densities, with correspondingly low deposition rates. This is attributable to limitations resulting from mass transfer control of the electrode process. Researchers at the Université Paul Sabatier and at Ecole Nationale Supérieure de Chimie de Toulouse in France demonstrated that pulsed electrodeposition of niobium from a eutectic mixture of lithium fluoride and sodium fluoride at 780° C produces coatings with texture, morphology, and crystallographic properties that are comparable to those produced by dc electrodeposition, but at increased deposition rates. They further showed that optimization of key deposition parameters (niobium ion concentration, pulse current density, pulse on-time, and pulse off-time) results in smooth, continuous coatings that can be deposited with faradaic efficiencies as high as 98%.

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