

Electrolyte Reaction with the Surface of High Voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ Cathodes for Lithium-Ion Batteries

Lithium nickel manganese spinel [$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ (LNMS)] is a cathode material being developed to operate at high voltages and to provide efficient cycling to nearly 5.0 V vs. Li. Researchers at University of Rhode Island collaborating with Lithion, Inc. found that Li coin cells using LNMS and ethylene carbonate (EC)/diethyl carbonate (DEC)/dimethyl carbonate (DMC) electrolyte 1:1:1 (v/v/v) stored at low voltages (4.0–4.5 V) result in low concentration of electrolyte decomposition products on the cathode surface, whereas high concentrations of poly(ethylenecarbonate) (PEC) exist on cathode surfaces of Li coin cells that were stored at high voltages (4.7–5.3 V). The coin cells stored at low voltage also show low residual current, whereas those stored at the higher voltage range show increased residual current which corresponds to electrolyte oxidation on the surface of the electrode at high potential. Surface analysis on the disassembled LNMS/Li cells reveals the presence of decomposition products such as Li_2CO_3 , metal oxide, Li alkoxides, and poly(ethylenecarbonate). The researchers show that PEC forms at potentials above 4.7 V. Surface analysis of EC-free cells supports the hypothesis that EC is the source of PEC, the main component of the cathode SEI and that the films are caused by oxidative polymerization of EC.

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Direct Ammonia Alkaline Anion-Exchange Membrane Fuel Cells

Few choices are available when selecting a fuel for low temperature fuel cells. With high hydrogen content (liquid ammonia stores more hydrogen than liquid hydrogen for a given volume), low cost and global availability, as well as well established industrial infrastructures, ammonia is an attractive fuel candidate. However, it is not compatible with the conventional proton exchange membrane fuel cells unless a cracking reactor is on-board to obtain the stored hydrogen. Researchers from the Heriot-Watt University of the United Kingdom recently demonstrated the use of ammonia directly as a fuel for alkaline anion-exchange membrane fuel cells operating at room temperature. The membranes used were prepared by blending poly(vinyl alcohol) with different anion-exchange polymers. The catalysts used were non-noble-metal based, including a MnO_2 -carbon co-precipitate for the cathode and Cr-decorated Ni nano-particles for the anode. Aqueous ammonia solution and ammonia gas were used as fuels and wet oxygen/air was the oxidant. Compared with hydrogen used as fuels in these same cells, the ammonia fuels exhibited similar or slightly better performance in terms of power density and

open circuit voltage. Further optimization is under way to improve the early stage performance of these direct ammonia fuel cells.

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Effect of Morphology and Hydrogen Evolution on Porosity of Electroplated Gold

Electrodeposited cobalt-hardened gold is a critical material for connector applications due to its combination of low electrical contact resistance, high corrosion resistance, and high wear resistance. As gold is a high cost material, it is desirable to reduce the deposit thickness as much as possible. Unfortunately, porosity of the gold deposit limits the degree to which this can be accomplished, as pores extending to the underlying substrate material substantially reduce the corrosion resistance of the deposit. The porosity of gold deposits for a cobalt-hardened gold deposited from a cyanide bath was evaluated as a function of plating technique (*i.e.*, DC or pulse plating), current efficiency, and deposit morphology. Pores tended to be located at the boundaries of features (*e.g.*, grains) in the microstructure and were often round in shape, suggesting they are the result of hydrogen bubbles produced during the plating process, increasing in number as the rate of hydrogen production increased. An approximately linear relationship was found between the deposition current efficiency (*i.e.*, portion of the current which goes to deposition vs. hydrogen production) and deposit porosity. For a given current efficiency, pulse plating resulted in a lower porosity than DC plating, with the key requirements to achieve a low porosity deposit being a fine grain structure, a smooth surface, and a relatively high current efficiency.

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Scanning Electrochemical Microscopy Approach Curves for Ring Microelectrodes

Electrochemical techniques can be combined with other analytical probes and sensors, sometimes resulting in a microring electrode geometry. One example is a ring electrode on the distal end of a pipet. As stationary electrodes on a flat substrate, ring electrodes have been extensively characterized. However, in the case of the scanning electrochemical microscopy (SECM) technique, whereby a microelectrode is rastered or advanced toward a substrate under investigation, the theory of approach curves using microring electrodes is less developed. Researchers at the Université du Québec à Montréal report analytical approximations for approach curves for a ring micropipet electrode in both positive and negative feedback modes. The authors began by modeling the microring electrode with an air-filled void in the micropipet. They extended the study to include the case that solution, say for injection purposes at a channel

or pump in a biological cell, fills the void to a height above the microring opening. The effect this height, the internal glass radius dimension, and the time scale have on the current was characterized. The authors recommend making the internal glass radius dimension small to decrease the effect of the solution height on the measurement, because practically, measured currents are not influenced by a solution height greater than a critical minimum height—which decreases with decreasing microring size.

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Measurement of Photoelectrolysis Reaction Rates by Microscopic Imaging of Evolved Gas Bubbles

The use of solar energy to produce hydrogen fuel *via* the electrolytic splitting of water in a semiconductor photoelectrochemical cell has been widely studied because of its potential positive impact on the global energy situation. However, significant challenges remain in the further maturation of this technology, including the need for improved stability of semiconductor electrodes against corrosion and improved understanding of charge transfer sites and mechanisms. Leenheer and Atwater at the California Institute of Technology have reported a novel experimental approach to measuring the water-splitting photoelectrolysis reaction rate by microscopic imaging of evolved oxygen bubbles. They illuminated n-type SrTiO_3 with above-bandgap radiation in oxygen-saturated 1.6 M KOH, and imaged gas product evolution at the surface using an optical microscope equipped with a 10X objective. Although SrTiO_3 is not suitable for solar applications, it was ideal for development of this new experimental technique because it does not corrode, thereby allowing direct comparison of reaction rate measurements by different methods. The authors demonstrated excellent quantitative agreement between reaction rates determined from photocurrent measurements (Faraday's law) and gas bubble size measurements (ideal gas law). They envision further refinements of this technique to allow comparisons of the effects of heterogeneous catalysts or electrode morphology changes.

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