

A Solid-State, Rechargeable, Long Cycle Life Lithium-Air Battery

A LiO₂ battery in theory has the highest energy density among known electrochemical power sources—as much as five to ten times that of the commercially available lithium ion batteries. However, technical challenges such as low energy efficiency and poor rechargeability, as well as safety concerns, remain as obstacles to the development of a practical rechargeable LiO₂ cell since it was first demonstrated about 12 years ago. Researchers from the University of Dayton Research Institute, Air Force Research Laboratory, and E-KEM Sciences recently reported significant progress. The authors built a totally solid-state, rechargeable, LiO₂ cell using a Li metal anode and a carbon glass-ceramic composite air cathode. A highly Li-ion conductive solid electrolyte membrane was fabricated from glass- and polymer-ceramic materials. This mostly inorganic solid-state electrolyte isolated the reactive lithium metal from moisture and atmospheric gases and prevented dendritic shorts. The cell exhibited excellent thermal stability and rechargeability in the 30-105°C temperature range. Compared to only a few charge/discharge cycles as reported previously for similar cells, this cell underwent 40 charge/discharge cycles and showed reversible charge/discharge voltage profiles with low polarizations. The measured energy density reached 750 Wh/kg, about 2-3 times that as previously reported.

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Lithium Tetrafluoro Oxalato Phosphate as Electrolyte Additive for Lithium Ion Cells

The solid electrolyte interface (SEI) layer is an important driver in determining the performance of lithium ion batteries. This relatively thin layer is formed on the graphite anode on the 1st charge via the reduction of the electrolyte and provides a means of isolating the electrode from the electrolyte and prevents further solvent reduction. However, it is well known that formation of a stable, low-impedance SEI can be difficult and is aided by the use of small amount of electrolyte additives. Qin and coworkers at Argonne National Laboratory in Illinois report on the use of lithium tetrafluoro oxalato phosphate as a promising additive to extend the life of lithium ion cells. This compound has previously been studied as a salt, but was known to cause a large impedance rise, while showing better cycling performance. Qin and coworkers propose to use small amounts of the compound to take advantage of the beneficial effects without causing higher impedance. The authors report that using 1-3% of the additive results in an increase in the initial impedance of the cell (by 33 to 100%), but that after 200 cycles the impedance growth was

suppressed. Aging studies on half-cells suggest that the additive is effective in significantly increasing the capacity retention at 55°C.

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Fabrication and Testing of CIGS Nanowire Arrays for Applications in Solar Cells

Copper indium gallium (di)selenide (CIGS) materials are being extensively studied for their applications in thin-film photovoltaic cells. CIGS films can be manufactured by a number of methods, including vacuum-based co-evaporation of copper, indium, gallium, and selenium. Researchers at the Università di Palermo in Italy recently reported their study into electrodeposition of CIGS nanowires as a possible lower-cost approach to producing materials for photovoltaic cells and modules. They used anodized alumina as a template into which they electrodeposited CIGS in a single-step electrochemical process. Dissolution of the template resulted in CIGS nanowires, which were characterized by scanning electron microscopy and x-ray diffraction. The nanowires are amorphous materials of stoichiometry Cu_{0.203}In_{0.153}Ga_{0.131}Se_{0.513} when deposited at -0.9 V vs. NHE from a solution with a Ga/(Cu+In+Se) molar ratio of 2.4. Photoelectrochemical measurements showed that the CIGS nanowires are photoactive with an optical band gap of approximately 1.55 eV. The nanowires exhibit p-type conductivity, in contrast to results reported by other research groups, indicating that electrodeposition parameters strongly influence semiconducting properties. Further work in this area is underway, as is a study of the effect of post-electrodeposition heat treatment on the composition and crystallinity of CIGS nanowires.

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Kinetics of the Lithium Ion Charge Transfer Reaction at the SiO Electrode

Users of portable devices are demanding ever-increasing energy density out of lithium ion batteries. Recently, researchers have investigated silicon as an anode active material because of its high specific charge capacity. Unfortunately, the large volume changes associated with the Si-Li alloying reaction negatively affect the mechanical stability and cycle life of the electrode. Research has shown that SiO, an alloy of amorphous Si domains and amorphous SiO₂ domains, exhibits small volume change while maintaining a relatively high specific charge capacity. Scientists from Kyoto University investigated the charge transfer kinetics of SiO in several electrolytes using electrochemical impedance spectroscopy (EIS). They identified the Nyquist plot features associated

with the interfacial charge transfer reaction by comparing the Nyquist plots from various voltages. Then, the researchers performed EIS on SiO in four different electrolytes over a range of temperature and fit the charge transfer conductivities to an Arrhenius model to determine the interfacial lithium ion transfer activation energy for SiO in each electrolyte. The activation energies for the SiO electrode were lower than those for graphitic electrodes, and the activation energies did not change with electrolyte—suggesting that the charge transfer kinetics were not significantly influenced by lithium ion desolvation.

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Computational Modeling of Bounding Conditions for Pit Size on Stainless Steel in Atmospheric Environments

Long term field exposures have demonstrated that the maximum pit depth for materials undergoing localized corrosion tends to plateau with time. This apparent maximum pit depth which is achieved can be the result of (i) limitations in the total anodic current that can be generated within the pit, (ii) limitations in the total cathodic current which can be supplied by the cathode, or (iii) the magnitude of the solution resistance, and thus the ohmic potential drop, between the propagating pit and the cathode supporting it. Under atmospheric exposure conditions, the electrolyte is present as a thin layer, and thus even small currents can lead to substantial ohmic losses between the pit (anode) and the cathode. In this paper, the authors construct a model through which the anodic current requirement for stable pit propagation, the capacity of the cathodic region surrounding and supporting the pit, and the electrical properties of the electrolyte film were combined to predict the maximum pit size that could form for a particular material under a given set of environmental conditions. The model was then used to predict the maximum size of a hemispherical pit in type 304 and type 316 stainless steels after exposure to atmospheric conditions. The results from the calculations agreed well with several sets of exposure data for near-seacoast exposures on three continents for exposure times out to 26 years.

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