

Anisotropy of Electronic and Ionic Transport in LiFePO₄ Single Crystals

The lithium iron phosphate (LiFePO₄) cathode has attracted a lot of attention, especially with its recent introduction as a cathode in power tool batteries. Over the last decade, this material has been transformed from a low-rate cathode to one able to sustain power densities that rival competing Li-ion technologies. However, the exact nature of conduction in this material is still controversial with debate on which species (electron or Li-ion) is limiting, and with no clear knowledge on the anisotropy of transport within the crystal. Amin and coworkers from the Max Planck Institute in Germany clarify some of these issues by measuring electronic and ionic conductivities and chemical diffusion of Li in single crystals *via* the use of blocking electrodes. The authors grow single crystals in different crystallographic orientations and measure the conductivity using both AC and DC techniques. The authors conclude that in LiFePO₄, the electronic conductivity is higher than the ionic conductivity and, therefore, the binary diffusion coefficient is limited by the Li-ion mobility. More interestingly, in variance with first-principle models for this chemistry, the results suggest that the Li transport occurs in two-dimensions, as opposed to only in one-dimension, as previously thought. Based on these results, the authors conclude that grain arrangement that results in transport along [100] direction should be avoided to ensure good performance.

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Stretched Recast Nafion for Direct Methanol Fuel Cells

One drawback of using Nafion in a direct methanol fuel cell (DMFC) is its high methanol permeability, which leads to cathode depolarization and a loss in power output. Research efforts to overcome this problem include investigations on numerous replacement materials for Nafion in a DMFC, as well as on modified Nafion to improve its methanol barrier property. However, in all of these studies, a drop in the proton conductivity of the membrane was observed when its methanol permeability was reduced. In their recent report, researchers at Case Western Reserve University devised a method to fabricate uniaxially stretched recast Nafion membranes with a morphology that (i) is stable and does not change after exposure to hot methanol/water mixtures and (ii) restricts methanol permeation but does not lower proton conductivity. Membrane electrode assemblies with the stretched recast Nafion membranes (draw ratio of 4) performed much better than Nafion 117 and nonstretched recast Nafion in a DMFC. With a 1.0 M methanol feed, the power density at 0.4 V with stretched recast

Nafion was 38% higher than that with Nafion 117. At 80°C, the difference between stretched recast Nafion and Nafion 117 was even more pronounced. The maximum power density nearly doubled and the power output at 0.4 V was 2.3 times greater with a stretched recast membrane.

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Effect of Electrolyte Composition on Li⁺ Solvation and Transport Through the Solid Electrolyte Interface

For more than a decade, lithium-ion battery technology has experienced widespread commercial use, despite limitations in service temperature and safety issues. Since the electrolyte serves an important function in cell operation, researchers at the U.S. Army Research Laboratory have focused on the factors that affect electrolyte performance. Correlations between electrolyte composition and activation energies of Li⁺ transport at the electrode surface are introduced in this first of several planned reports. Electrochemical impedance spectroscopy measurements were taken at selected temperatures for calculating activation energies for the Li⁺ desolvation and film diffusion (through the solid electrolyte interface - SEI) processes. The activation energy for the so-called charge transfer process (or desolvation) strongly depended on solvent composition according to the ratio of cyclic (ethylene carbonate - EC) and linear (dimethyl carbonate - DMC) carbonates in the electrolyte. A gradual transition occurs between lower (<60 kJ mol⁻¹) and higher (~70 kJ mol⁻¹) activation energies in DMC-rich and EC-rich solvents, respectively. The transitional composition regime of 20-40% EC content, which has been adopted for use in batteries based on empirical results, can be now be understood as a compromise between forming a protective SEI layer and maintaining a low energy barrier for Li⁺ transport across the interface.

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Microelectrochemical Study of Alloy C22 in Chloride Solutions below the Critical Pitting Temperature

The critical pitting temperature (CPT) for a metal represents the temperature below which stable pitting does not occur at any applied potential less positive than that required to drive transpassive dissolution. The CPT is typically evaluated in concentrated chloride solutions, and has been demonstrated to be insensitive to the actual chloride concentration in the range of 0.01 to 5M. Experiments performed by a number of researchers at temperatures below the CPT have found that while stable pit formation is not observed, anodic transients indicative of metastable pitting events are observed for a number of stainless steel and titanium alloys known

to be highly resistant to localized attack in such environments. In this work, Alloy C22, a highly corrosion resistant Ni-Cr-Mo alloy, was potentiostatically polarized below the onset of transpassive dissolution in 0.5M HCl and 5M LiCl solutions at temperatures below the CPT. These experiments revealed numerous small anodic transients consistent with those observed by other researchers for stainless steel and titanium alloys, which have been attributed to metastable pitting events. As post-test examination was unable to reveal any physical signs of metastable pitting, the transients were reported as "localized passivity breakdown events." These results demonstrate that the high localized corrosion resistance of Alloy C22 arises primarily from its resistance to pit propagation, rather than from any exceptional stability of its passive film.

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Synthesis and Characterization of Composite Coatings for Thermal Actuation

Phase change materials (PCMs) such as paraffin and hydrated salts are principally known for their high heat capacity during phase transformation. The phase change is also frequently accompanied by a volume change that is detrimental to use of these materials in heat storage applications because it can lead to unwanted thermal stresses. However, a large volume change over a small temperature range can be used in thermal actuation applications. Researchers at Katholieke Universiteit Leuven in Belgium reported the synthesis and thermal expansion properties of copper coatings containing paraffin as the PCM. Microencapsulated paraffin was added to a copper sulfate electroplating bath, and Cu/paraffin composite films were electrodeposited at room temperature to produce nominal film thicknesses of about 100 μm. The authors characterized the films by scanning electron microscopy, differential scanning calorimetry, and vertical dilatometry. Coatings with a 40% microcapsule loading and a heat capacity of 12 kJ kg⁻¹ during phase transformation were obtained. The thermal expansion of the composite showed a sharp increase in a small temperature range above the melting point, an ideal property for a thermal actuator, and the authors explained their results in terms of a thermoelastoplastic model. Unfortunately, this nonlinear behavior disappeared during subsequent heating cycles due to plastic deformation of the copper matrix.

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