

Improving Si-Based Electrode Cyclability by Decreasing Particle Volume Percentage

Increased energy density is one performance improvement sought in the maturation of Li-ion batteries. Negative-electrodes based on silicon have a larger theoretical gravimetric capacity than electrodes based on carbon. However, Si-based electrodes exhibit poor cyclability compared to carbon electrodes, which are used in commercial cells. The large volume change (~270% expansion upon lithiation) of the active material is believed to be the source of this poor cycling performance. Researchers from Amiens and Bordeaux, France, have investigated increasing the practical gravimetric capacity of Li-ion cells recognizing that a large capacity necessarily leads to a large change in volume. They developed an approach to design the Si-based negative electrode according to the largest volume condition when the Si particles are in the lithiated state. Their theoretical model, extendable to other electrode systems, uses geometric considerations of the packing of the particles of active material in the mixture of binder and conductive additive. Experiments on an electrode containing 33 wt% Si (100 nm powder) + 33 wt% carboxymethyl cellulose binder + 33 wt% carbon-black Sp showed capacity retention stable at ~2000 mAh/g of Si (compared to 3579 mAh/g theoretical). After accounting for the low loading of Si, the reversible capacity of ~667 mAh/g is significantly better than (~twice) that found in commercial carbon-based electrodes.

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Investigation of Low-Temperature Impedance Increase of Lithium-Ion Cells

Lithium-ion batteries have been replacing older battery chemistries in numerous applications ranging from consumer electronics to power tools, and possibly in hybrid-electric-vehicles in the near future. The push to use lithium-based cells is primarily due to their superior energy and power compared to other chemistries. However, this advantage is lost when operating the battery at temperatures below 0°C where a significant increase in the impedance of the cell has been observed. Numerous reasons have been given for the increased impedance with no clear understanding on the exact cause of this problem. Abraham and colleagues from the Argonne National Laboratory in Illinois have performed studies on well characterized electrodes to shed light into the impedance increase. The authors use a $\text{Li}_{4/3}\text{Ti}_{5/3}\text{O}_4$ anode in order to prevent the formation of the solid electrolyte interphase (SEI) and binder and carbon-free cathodes fabricated by sol-gel spin coating. Using this system, the authors argue that the low-temperature limitation is connected with the kinetics of the electrochemical lithiation/delithiation reaction with little contribution from the binder, or from ohmic/diffusional effects. Interestingly, the activation energy of the process was seen to be relatively independent of the active material. The authors suggest

that the impedance can be decreased by increasing the electrochemical area and/or by changing the electrolyte composition.

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Electrochemical Process for Micropattern Transfer Without Photolithography

Researchers at the Newcastle University in the United Kingdom recently reported a maskless electrochemical microfabrication method to realize micropattern transfer without resorting to photolithography. In this method, a substrate, which is the anode, is placed in an electrochemical reactor in close proximity to a tool carrying the micropattern, which is the cathode. Although the anode is etched over its entire surface, it etches at a higher rate on the areas opposing exposed regions of the cathode, hence, reproducing a pattern on the anode. The process exploits the transition from active to passive electro-dissolution to form etched patterns on a metal. By using copper as the substrate, it was found that sinusoidal shapes were transferred when etching proceeded under active dissolution, such as in acidified electrolytes and at low etching currents. Rectangular features were transferred when active etching was followed by an oxide film formation, such as in acid-free electrolytes and at higher dissolution currents. The maximum etch depth was attained during active etching, and the depth was actually reduced during passive etching when a rectangular shape was produced. As a rule of thumb, the ratio of the feature size to the electrode gap should be about 1:3 to obtain pattern transfer.

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The Interaction Between Alloyed Molybdenum and Dissolved Bromide in the Pitting Corrosion of Stainless Steels

Molybdenum is known to impart increased localized corrosion resistance to stainless steels. This beneficial effect is reduced significantly in bromide solutions as compared to chloride solutions. Previous researchers have concluded that the beneficial effect of Mo is the result of the formation of a polymolybdate network at the metal/solution interface, and that bromine in some manner interferes with the formation of that network. In this paper, artificial pit electrodes (*i.e.*, pencil electrode) constructed from a Mo free stainless steel (304SS) and a Mo containing stainless steel (316SS) were evaluated in chloride and bromide solutions, and the kinetics of the pit propagation process explored. In bromide solutions, these experiments illustrated that as the limiting current density of the artificial pit electrode approached values comparable to an actively propagating pit, the pitting potentials of 304SS and 316SS converged. In other words, the presence of Mo in the 316SS did not impart an increased resistance to pit propagation in bromide containing solutions. Based upon the kinetic data obtained from artificial pit electrodes, it was concluded that while the effective Tafel coefficient of 316SS is greater than that of 304SS in chloride

solutions, it is lower in bromide solutions, leading to the aforementioned convergence in bromide solutions at large current densities. Furthermore, the rapidity of the pit propagation kinetics suggest that the impact of molybdenum on localized corrosion resistance is unlikely to be due to the formation of a polymolybdate network, but rather the result of a direct complexation of some form which is in turn more rapid for bromide than chloride.

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Characteristics for Intermetallic Phases Common to Aluminum Alloys as a Function of Solution pH

This work by Birbilis and Buchheit of The Ohio State University is an excellent example of the insight that can be gained into the corrosion behavior of an alloy by examining the response of the component phases and drawing comparisons to the response of the bulk material. Using a microcell to perform electrochemical experiments, the authors characterized the open circuit potential, passive current behavior, pitting potential and cathodic response of secondary phases prominent in 7xxx series alloys. Examination of these parameters as a function of electrolyte pH revealed both how the particles may influence the local environment and, in turn, how the exposure environment influences the fate of the individual particles. By performing open circuit exposures on a bulk alloy in acidic, neutral, and alkaline electrolytes the authors generated data that convincingly demonstrate how the microstructure and environment combine to determine the final damage state. Interestingly, the nature of the attack changes from what the authors describe as stochastic at acidic pH, to deterministic (strongly linked to the presence of individual phases) at neutral pH and finally to a general rapid dissolution at alkaline pH. The ability to reconcile the behavior of the alloy with the behavior of the secondary phases is successful due to consideration of not only the thermodynamics of the system (*e.g.*, comparison of the open circuit potentials and relative nobility of the phases) but also due to consideration of the system kinetics (*e.g.*, cathodic current density and passive current density as a function of pH). This work emphasizes the point that the corrosion behavior of component phases in heterogeneous materials may depend strongly on the test environment and extending the results from one environment to another may result in erroneous predictions of alloy behavior.

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Tech Highlights was prepared by Donald Pile of Valence Technology, Inc., Zenghe Liu of Abbott Diabetes Care, Venkat Srinivasan of Lawrence Berkeley National Laboratory, and David Enos and Doug Wall of Sandia National Laboratories.