THE ROLE OF SOLID MECHANICS IN ELECTROMECHANICAL ENERGY SYSTEMS SUCH AS LITHIUM-ION BATTERIES AND FUEL CELLS

Robert M. McMeeking[1,2,3,4]

[1]Mechanical Engineering Department, University of California, Santa Barbara
[2]Materials Department, University of California, Santa Barbara
[3]School of Engineering, University of Aberdeen, Aberdeen, Scotland
[4]INM – Leibniz Institute for New Materials, Campus D2 2, Saarbrücken, Germany

Summary Solid mechanics plays an important role in the functionality and performance of electrochemical energy systems, including lithium ion batteries and fuel cells. As a consequence of Li ions intercalating in battery storage particles, their lattice swells, leading to elastic stress when the concentration of Li ions in the particles is not uniform. Such elastic stresses can damage the particles and degrade the performance of the battery. In solid oxide fuel cells, malfunctions can cause oxidation of the metal electron conductors in the electrodes, causing stress due to transformation strains. These stresses can damage the electrodes and compromise the percolation of the electron and ion conducting networks. Mechanics plays other roles in electrochemical energy systems, and these will be described. A summary of the thermodynamics, transport, and solid mechanics relevant to these electrochemical energy systems will be given, and relevant boundary value problems in mechanics described. Results for stress generation in batteries and solid oxide fuel cells will be summarized.

ELECTROCHEMICAL ENERGY SYSTEMS

In typical current designs of Li ion batteries, the anode consists of graphite or some other form of carbon, in particulate form, embedded in a polymeric binder, with contact among the carbonaceous particles ensuring electrical conductivity. The aggregate is connected to a copper current collector [1]. The cathode has a hierarchical structure with a particulate aggregate of a compound oxide of lithium embedded in a PVDF binder [2]. These particles are joined together by electronically conducting elements to provide current connectivity, usually in the form of carbon coatings on the storage particles. The cathode aggregate is attached to an aluminum current collector. Electrical leads are connected to the two collectors and attach to the load during discharge, and to the power supply during charging. Electrolyte is a Li salt like $LiPF_6$ in an organic solvent, and the separator is a porous polymer, an example being a polyolefin [1].

During discharge, as depicted in Fig. 1, Li^+ ions are extracted from the graphite, and travel from the anode to the cathode through the electrolyte, diffusing through the pores of the separator [1]. In parallel, electrons are released from the anode, and then flow round the electrical load circuit to the cathode collector. The electrons thereafter transfer to the oxide particles. Upon reaching the cathode, the Li^+ ions are inserted into the particles of layered oxide, while the newly arrived electrons engage in an electrochemical reaction that reduces the lithium. The charging cycle is simply the opposite of the discharge phase [1]. Thus, the Li simply shuttle back and forth from one electrode to the other and back during the full service cycle [2].

A major source of damage arises because the storage particles shrink and swell as the Li^+ ions are extracted and inserted. Depending on which particle is used, as much as 100% of the lithium is depleted from the oxide during charging [2,3], leading to significant shrinkage. Upon

very fast charging, the first batch of lithium extracted from the oxide particle will deplete from near its surface, causing a high tensile hoop stress there as the outer layer shrinks. The resulting stress can cause cracks to propagate and damage the material. Thus, comminution of oxide particles can occur during charging [4]. Such damage is observed in electrode material, and is associated with a degradation of performance [5-7].

Solid oxide fuel cells (SOFC) directly transform chemical energy from gasified fuels into electrical energy and heat energy in a highly efficient way. The microstructure of the composite anode and cathode electrodes plays a critical role. Consisting of binary mixtures of electric and ionic conducting particles that form a porous cermet, the electrodes have to allow for the transport of electrons, ions as well as the gaseous reactants and products from and to the electrocatalytically active reaction sites, i.e. a small area close to the interface between electronic and ionic particles at the pore phase known as the three-phase boundary (TPB).

A SOFC's performance is limited by different loss mechanisms. Activation losses occur for the hydrogen oxidation reaction in the anode and the oxygen reduction reaction in the cathode, when electrons are transferred between the respective conduction bands and gas molecular orbitals at the TPB sites. Ohmic losses arise especially for the transport of oxygen ions through the electrolyte from the cathode to the anode reaction sites, but also for the electron transport between the current collectors and the TPB through the percolated electric conducting particle networks. Finally, the diffusive gaseous transport of oxygen through the porous cathode as well as hydrogen and water vapor through the porous anode is governed by concentration losses. These loss mechanisms can directly be correlated to the morphological properties of the microstructure. Activation losses are strongly influenced by the disposable reaction sites, i.e. the amount of TPB in the electrodes, which in turn is linked to the respective electric and ionic conducting particle sizes and volume fractions. Ohmic losses are governed by the effective electric and ionic resistivity of the porous electrode material that depends strongly on the volume fractions and percolation probabilities of the respective particle networks. The pore radii and porosity, also depending on the particle sizes and volume fractions of the porous electrodes, directly affect the gas transport from the fuel channels to the TBP, and consequently the concentration losses. Hence, by optimizing the morphological parameters of the microstructure, i.e. the diameters of the electric and ionic conducting particles, their size ratios and volume fractions, the losses can be controlled and the performance of a SOFC can be further increased.

Problems can arise upon malfunction of the cell, such as a sudden shut down, where O_2 ions can invade the electrode materials and cause oxidation, associated swelling and thus stressing of the electrode aggregate. This can cause cracking and damage. Pore gas pressure can also rise to high levels and lead to delamination within the cell structure.

References

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