Introduction

Restoration of electrical interfaces has potential to increase the reliability and safety of microelectronic devices and high performance energy storage devices. In microelectronics, mechanical or thermal damage can lead to a loss of conductance across a damaged pathway and performance degradation or failure of the circuit. In Li-ion batteries, continued cycling of silicon anodes results in cracking or pulverization of the particles, and ultimately destruction of the conductive network. Here, we consider an approach to increase cycle lifetimes and reliability through restoration of conductance in composite electrodes via the use of microencapsulated components that form a conductive network when released.

A typical battery is composed of several electrochemical cells that are connected in series and/or in parallel to provide the required voltage and capacity, respectively. Each cell (Fig. 1) consists of a positive (cathode) and a negative electrode (anode) separated by an electrolyte solution containing dissociated salts, which enable ion transfer between the two electrodes [1].

The electrodes in Li-ion batteries have a complex microstructure. Micro- or nano- particles of active material are mixed with conductive carbon and a polymeric binder and then made into a porous composite. When the electrodes are connected, Li diffuses into (insertion) and out of (deinsertion) the active particles, causing significant expansion or contraction. For Li-ion batteries, cracking, deterioration, and electrochemical pulverization occur during the massive volume changes associated with the intercalation and deintercalation of Li+ ions during charge and discharge, respectively. As this damage accumulates, there is significant degradation of the efficiency and eventually failure of the battery. New anode designs currently focus on accommodating the volume change through changes in the material architecture, e.g. via incorporation of Si nanoparticles and nanowires. Here, we consider an alternate approach to increase cycle lifetimes and reliability through restoration of anode conductivity.

Recent investigations have demonstrated the ability to restore electrical conductivity of thin metal films through the use of microencapsulated components that form a conductive network when released [2,3]. Successful translation of this microencapsulated approach to the extreme environment of a Li-ion battery anode presents significant challenges. In this paper, we report on the encapsulation of several types of conductive particles and the integration of these capsules into commercially available anode materials. We develop a unique half-cell to observe and measure the deformation during lithiation and assess our ability to restore conductivity in a battery. We anticipate that our healing strategy will increase the lifetime and reliability of advanced batteries.

Microencapsulation of Conductive Particles

In this study, robust microcapsules were prepared with high loading (up to 20 w/v %) carbon black present in liquid core (Fig. 2a). Increased hydrophobicity of the nanoparticles was achieved through the functionalization of oxidized carbon...
black with octadecylamine. Fig. 2b contains an SEM image of functionalized carbon black (FCB) filled microcapsules. The potential for conductance restoration of electrodes was first evaluated by crushing FCB microcapsules on an electrode line cracks introduced by a fiber removal method, with a maximum recovery of 100% of original conductance. FCB filled microcapsules demonstrated significant particle release (Fig. 2c) compared to unfunctionalized carbon black. The performance was also compared with microencapsulated graphene and carbon nanotubes.

The microcapsules have been successfully incorporated in a composite anode. Crack damage in the electrode causes the capsules to rupture and release their content. In situ recovery of electrode materials is currently in progress. A variety of liquid cores, polymer shells, conductive particles, and polymer binders are under investigation. We identify promising encapsulated systems based on the ability to survive anode fabrication and coin cell assembly.

3. Crack Observation and Strain Measurement during Lithiation

In order to design and assess our self-healing concepts, we need to observe deformation and quantify the strain levels that induce cracking in anodes materials. We have designed and fabricated a custom battery cell hat enables imaging of the anode during insertion and extraction of Li. The cell is fully sealed with a quartz window for optical access. In future experiments, we plan to quantify the anode strain using a digital image correlation technique and use the cell to establish the feasibility of our healing concept.

Fig. 1. Schematic of a Li Ion Battery

Fig. 2. (a) Schematic of microencapsulated conductive particles, (b) SEM of encapsulated functionalized carbon black, and (c) release of carbon black from ruptured capsule.

References