CRACK FORMATION AND AUTONOMIC RESTORATION OF CONDUCTIVITY IN BATTERY ANODES

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1 Introduction

A variety of complex damage mechanisms in Li-ion batteries can lead to a significant loss of conductivity and eventual system failure. 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 [2]. 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 [3,4]. 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.

2 Microencapsulation of Conductive Particles

A schematic of a two-capsule strategy to heal crack damage and restore conductivity in an electrode is shown in Fig. 1. Conductive particles such as graphite flake or carbon black are encapsulated in a soluble binder. A suitable solvent is then encapsulated in a polymeric shell wall. Crack damage in the electrode causes the solvent capsules to rupture and dissolve the binder of the microspheres containing particles. The crack is re-filled with conductive particles, the damage is repaired, and conductivity restored.

Microcapsules are prepared by the encapsulation of solvent via the formation of a cross-linked polymer shell by in situ emulsion polymerization. Soluble

microspheres are fabricated by a solvent evaporation method. Both the microcapsules and microspheres have been successfully incorporated in a Si particle/cellulose binder anode as shown in Fig. 3. A variety of liquid cores, polymer shells, conductive particles, and polymer binders are investigated. 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 (Fig. 4) that 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 [2] and use the cell to establish the feasibility of our healing concept.

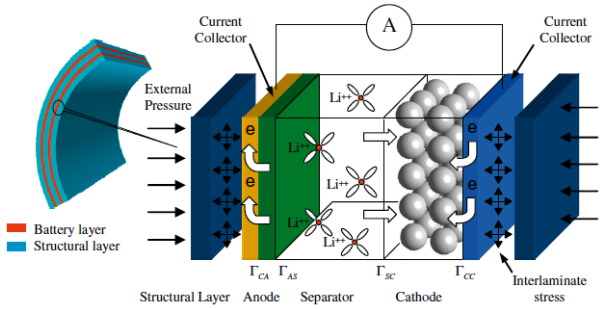

Fig.1. Schematic of a Li Ion Battery

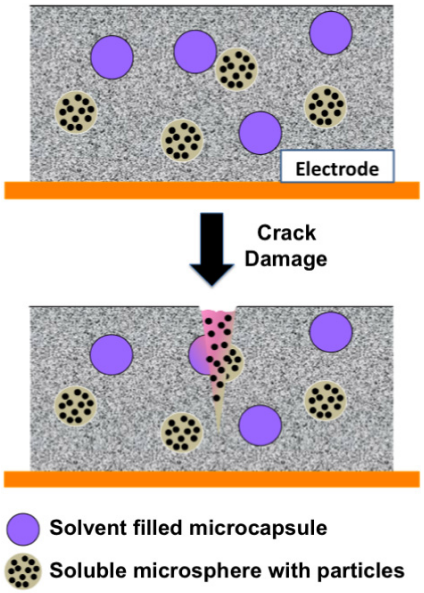

Fig. 2. Self-healing concept for battery anodes.

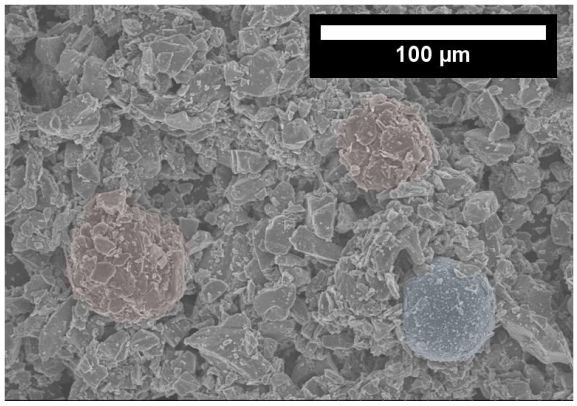

Fig. 3. PMMA/graphite soluble spheres (red) and EPA filled capsules (blue) in a Si/CMC anode.

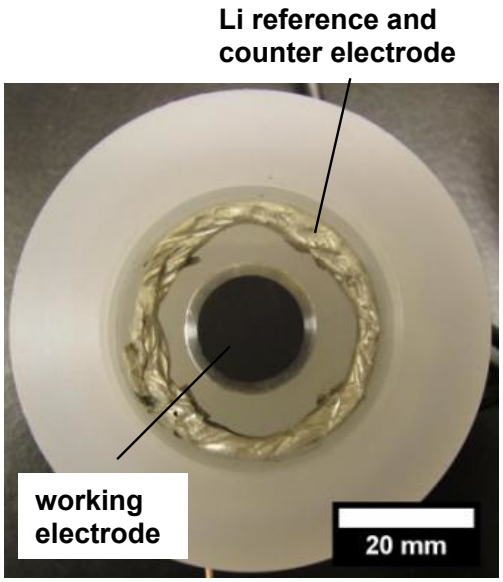

Fig. 4. Half-cell for observation and measurement of anode strain during lithiation.

References

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