In-situ characterization of strain in lithium battery working electrodes

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HIGHLIGHTS

- We investigate relationship between electrode capacity and mechanical deformation.
- *In-situ* monitoring of the working electrode surface is performed.
- Digital image correlation is used to quantify electrode strains.
- The effect of constraint due to substrate stiffness is examined.

ARTICLE INFO

ABSTRACT

During lithiation and detlithiation, substantial volumetric changes occur within the electrode materials used for rechargeable lithium batteries. The magnitude of these deformations is inherently linked to the electrical capacity of the battery electrical capacity, which tends to degrade with repeated cycling. In this work, the relationship between electrical discharge capacity and mechanical deformation state is examined using *in-situ* imaging of the working electrode surface within a custom CR2032 coin cell lithium battery. Digital image correlation is used to quantify electrode strains throughout the discharge–charge process. The effect of constraint due to substrate stiffness is investigated for two film materials: traditional graphite and a carbon nanotube based composite. Results for all cases show that as discharge capacity decreases with repeated cycling, increasing residual electrode strains are observed. The thin, compliant foil substrates allowed over double the bi-axial strain state to be induced within electrodes, compared to that found for the thick copper disk substrates under the same electrical cycling conditions.

1. Introduction

The rapid upsurge in mobile consumer electronics device usage has in large part fueled the current substantial demand for high performance rechargeable lithium ion batteries. Due to their outstanding capacity-to-weight ratios, low charge loss rates, and minimal hysteresis effects, lithium ion batteries have become the dominant power storage choice for applications across multiple industrial and consumer sectors. Future advances in lithium ion battery performance will likely come from new material developments and optimization of the coupled chemical, electrical, and mechanical interactions that take place within these rechargeable power storage units. Selection of the anode material is one of the key considerations affecting lithium ion battery capacity and performance degradation, as these issues are intrinsically related to break-down mechanisms occurring at the material microstructure level.

Graphite has served as the standard anode choice for the first generations of mass produced lithium ion batteries, primarily due to its cost effectiveness. Some of the major limitations of graphite include its relatively low specific capacity (only 372 mAh g^{-1}) [1], and substantial irreversible capacity losses during the initial discharge–charge cycles [2–5]. A major source of irreversible capacity loss is the formation of a solid electrolyte interface (SEI) film on the anode surface, the prevalence of which is directly related to the Brunauer–Emmett–Teller (BET) surface area and anode material density [3–8].

Alternative materials to carbon-based anodes offer enticing theoretical specific capacities, including silicon (4200 mAh g^{-1}), tin (994 mAh g^{-1}), magnesium (3350 mAh g^{-1}), Li$_4$Ti$_5$O$_{12}$ (mAh g^{-1}) and others [9]. The downside to higher specific capacity materials is the generally larger volumetric change induced during lithiation/

delithiation cycles. Such deformations can induce damage modes that can drastically shorten the overall battery service lifetime such as delamination from the current collector or cracking within the anode material [10–17].

One coping mechanism is to use nanoscale-sized particulate forms of these materials in composite anodes. The large volumetric expansions are focused within the nanoscale structures, which are surrounded by binder materials that are typically more compliant. The reduced constraint conditions can help to limit mechanical damage within the intercalated material. Zhang et al., demonstrated that nanowires made with carbon, aluminum or copper coatings significantly reduced radial expansion and tensile stresses, in addition to improving electronic conduction [18]. Numerous examples of this general strategy have been reported, including use of nanostructured forms of silicon [19,20]. However, silicon-based nanoscale particulate (nanowires, nanospheres, etc.) have been shown susceptible to intercalation cracking over a range of dimensional feature sizes [21–23] due to the extremely large volume changes and stress gradients within individual structures caused by lithiation fronts.

The use of nanoscale carbon-based particulate for anodes has also been explored, with highly encouraging results. In particular, carbon nanotubes (CNTs) have been widely used for lithium ion battery electrodes, with recent studies showing that CNT-based anodes can provide high electrical capacity, while reducing anode pulverization due to cycling dramatically [24]. Additionally, aligned carbon nanotube anodes have demonstrated limited capacity degradation after upwards of 50 discharge–charge cycles [25]. The effects of different carbon nanostructure morphologies (single wall, double wall, and multi-wall carbon nanotube configurations) have also been investigated [26], showing the influence of surface area on SEI film growth and capacity degradation. Hybrid combinations of these materials have also been attempted [27] using carbon nanotube infused silicon composite films as anodes.

Quantifying the mechanical deformations associated with lithiation/delithiation is critical for optimal battery performance and lifetime design, but direct measurement of electrode mechanical deformations that accompany electrical cycling of lithium ion battery systems is challenging. Nearly all other previous studies attempting to measure *in-situ* electrode deformations have employed optically-based methods for observing the electrode inside a custom battery arrangement. Sethuraman et al., [28,29] analyzed a silicon thin film system by using a laser optical detection method to determine *in situ* stress and mechanical property changes during discharging/charging. *In-situ* mechanical stress evaluation for Ni–Sn alloy anodes was performed by Chen et al., [11] using another laser measurement technique. In a similar way, Qi and Harris [30] used a custom battery fixture to observe deformation and cracking of a graphite electrode. In that study, the graphite deformation was determined using digital image correlation (DIC). Other uses of DIC includes a recent study by E.M.C. Jones et al., [31] in which lithium ion battery composite electrodes were investigated.

One important issue not addressed by many of these previous works is the role of the mechanical constraint on the anode material, specifically the current collecting substrate. In this work, the effect of substrate stiffness is investigated with respect to the residual strain development and capacity degradation that accompany electrical cycling of lithium ion batteries. Two battery electrode materials are studied, a traditional graphite system and a carbon nanotube-based variation. In both cases, a custom coin cell configuration is used to facilitate *in-situ* strain measurements optically by the digital image correlation method. Both the first-cycle and repeated cycling strain effects are explored.

2. Experimental

2.1. Materials and sample preparation

Lithium batteries were fabricated based on a modification of the standard CR2032 coin cell configuration. The custom variation of this battery cell enables optical imaging of the working electrode throughout the process of battery cycling. Graphite-based thick films (10 μm) deposited on copper substrates were used as the working electrode within the custom coin cell batteries. To investigate the effects of substrate constraint, two types of copper substrates were tested, 16 μm thick copper foils and 635 μm copper disks. While thick copper current collectors may be cost prohibitive for some commercial applications, the 635 μm copper disks used in this work allowed for direct testing of substrate stiffness influence in a controlled manner by varying only one parameter. In practice, the stiffness of a substrate may be controlled in a variety of other, more cost-effective manners to obtain optimal battery performance. In addition, the effects of using conductive carbon nanotubes (CNTs) as graphite replacement were studied.

Graphite electrodes were prepared by mixing 80 wt% graphite powder, 10 wt% carbon black, and 10 wt% polyvinylidene fluoride (PVDF) binders in N-Methyl-2-pyrrolidone (NMP) solvent. The well-mixed slurry was deposited over the copper substrate, and a film casting doctor blade apparatus was used to skim the wet electrode to a thickness of 10 microns. The electrodes and substrates were then immediately put into a laboratory oven at 115 °C for 15 min.

Specimens containing the conductive CNTs as a graphite replacement were prepared in a similar manner. The CNTs used in this study were purchased in bulk commercially (Cheaptubes.com) and had diameters in a range of 60–80 nm and lengths in the range of 10–15 μm. The 80 wt% CNTs were first combined with 10 wt% carbon black and blended in an industrial mixer a period of 12 h. Next, 10 wt% PVDF binder and NMP solvents were injected into the mixture, which was then blended for an additional 12 h. The slurry was then cast onto the copper substrates, skimmed to the proper thickness, and finally oven cured at 115 °C for 15 min.

To allow optical access to the working electrode, a 6.35 mm diameter through-hole was first placed through the center of the coin cell cover cap using a mechanical punch. A 12 mm diameter round, 0.15 mm thick glass cover slip (Ted Pella) was bonded to the top surface of the cell cap by applying CRL 349 ultraviolet adhesive (Loctite Impruv), followed by a 2 min UV exposure cure. This top cover was found to be sufficient to seal the coin cell, but necessitated a custom fixture during crimping to prevent damage to the glass window.

The custom CR2032 coin cell was assembled in an Argon filled glove box. All parts, including cell cap, gasket, spring (Hohsen), and glass fiber separator (Advantec) were put into a 80 °C heated chamber (Buchi glass oven B585) and connected to a vacuum pump for 8 h to completely remove water moisture and evaporated solvent prior to assembly. For all coin cell configurations, a pure lithium metal disk (Sigma Aldrich) was used as the counter electrode. Additional through-holes, approximately 6 mm in diameter, were created in both the lithium metal disk and the separator while housed under the assembly glove box using a gasket punch.

An electrolyte consisting of 1 M LiPF6-EC:DMC (1:2 by volume) was used throughout this work, with ca. 0.5 mL volume used for each cell. After stacking the layers and adding the electrolyte, a hand-operated crimping tool (Hohsen) was used to close and seal the coin cell batteries. A schematic showing the individual coin cell layers and an actual completed coin cell after assembly are shown in Fig. 1.