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In situ electrochemical studies of lithium-ion battery cathodes using atomic force microscopy

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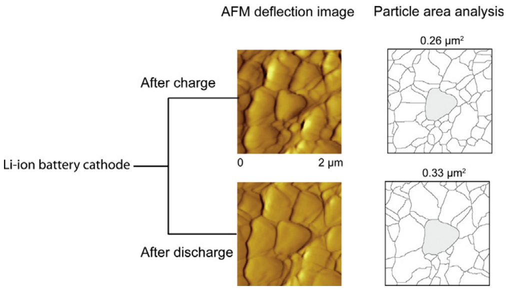
HIGHLIGHTS

- Presented is review of in-situ electrochemical techniques for studying Li-ion battery.
- In-situ AFM allows accurate measurement of morphological changes during cycling.
- Li-wire cell design was chosen for ease of assembly in the glove box.
- During discharge, morphology showed an increase in particle size due to lithiation.
- In-situ AFM electrochemistry is useful for Li-ion battery degradation characterization.

GRAPHICAL ABSTRACT



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ABSTRACT

Lithium-ion (Li-ion) batteries have been implemented for numerous applications, including plug-in hybrid electric vehicles (PHEV) and pure electric vehicles (EV). In an effort to prolong battery life, it is important to understand the mechanisms that cause reduced battery capacity with aging. Past studies have shown that morphological changes occur in aged cathodes. In situ electrochemical studies using atomic force microscopy allow for the direct observation of the morphology of the Li-ion battery cathode, at a nanometer scale resolution, during the cycling of an electrochemical cell. A simple electrochemical cell designed for in situ characterization is introduced. Charge/discharge curves and morphology data obtained during charging and discharging of cells are presented, and relevant mechanisms are discussed.

1. Introduction

Li-ion batteries have long been studied and developed as a power source for portable devices [1]. Since the early 2000s, Li-ion batteries have emerged as an energy storage medium for electric vehicles (EV), hybrid-EV (HEV) and plug in-EV (PHEV) in order to reduce the dependence on non-renewable energy sources. EVs are environmentally friendly because of their lower carbon emissions, and they are more economical to operate than conventional automobiles. Li-ion batteries are used in the automotive industry because of their extended life cycle, and because of their high energy density per unit weight (specific energy) [2,3].

Padhi et al. [4] first introduced lithium iron phosphate ($LiFePO_4$) as a Li-ion battery chemistry for cathode material. The $LiFePO_4$

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cathode has been of interest to researchers because of its coulometric capacity[1] per unit weight ($\approx$170 mAh g^{-1}), high thermal stability, specific energy ($\approx$0.60 Wh g^{-1}), and low toxicity [5–7]. $LiFePO_4$ is a viable option for meeting the requirements set by the United States Advance Battery Consortium (USABC) for the EV [8–10]. Over time, electrochemical properties of Li-ion batteries degrade, which leads to a reduction in storage capacity. Therefore, understanding the underlying mechanisms of the aging phenomenon in Li-ion batteries is of paramount importance in order to extend the life of Li-ion batteries [3,11].

Numerous ex-situ studies have been conducted to study the aging phenomenon in Li-ion batteries. These studies include atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, and other X-ray and neutron techniques [3,11]. These ex-situ studies were conducted by comparing the aged and unaged materials of cathodes and anodes in order to reveal morphological, electrical, and structural changes that occur during cycling. More specifically, studies on the $LiFePO_4$ battery cathode showed that $LiFePO_4$ nanoparticles agglomerate with age. During agglomeration the carbon coating on the particle needed for conductivity might degrade. Agglomeration is believed to result in an increase in surface resistance and a decrease in surface conductivity, which consequently reduces battery capacity [3,12,13]. Nanomechanical characterization experiments have been conducted to observe the effect of increased internal stress during aging [14]. Increases in creep and hardness were found to be associated with the degradation of the polyvinylidene fluoride (PVDF) binder and the formation of a dislocation due to the high internal stress and strain created during lithiation and delithiation. Although ex-situ studies resulted in some understanding of the aging phenomenon, a real time investigation of the battery electrodes during cell operation is only possible through in situ techniques.

In order to conduct in situ electrochemical measurements, custom built electrochemical cells that can operate inside an instrument must be utilized. Each experimental technique has its own set of difficulties associated with its operating conditions. For example, SEM and TEM require the sample to be in a vacuum, while AFM requires an open cell design that allows access to the electrode being investigated. AFM allows for the direct observation of the morphologies of Li-ion based electrodes at high resolution and on a nanometer scale [15–18].

In this work, a review of various in situ electrochemical cells used during Li-ion battery investigations is presented. Reasons for selecting AFM techniques are given. Different electrochemical cell designs used for in situ AFM experiments are described. Then a two-electrode electrochemical cell design is proposed, and the results of in situ AFM electrochemical studies on a $LiFePO_4$ battery cathode are presented.

2. Review of in situ electrochemical cells

Various in situ techniques have been applied to the study of Li-ion batteries, including optical, electron, AFM, neutron and X-ray techniques. Table 1 presents a summary of design requirements and comments on different electrochemical cells for each experimental technique. Schematics of cell designs are shown in Fig. 1(a)–(c). The following is a more detailed discussion of each technique and the in situ electrochemical cells utilized.

2.1. Optical

Optical methods include Raman microscopy and optical microscopy, which require a top cover that allows light to pass through, as shown in Fig. 1(a).

The Raman microscope technique is desirable for studying the structural and chemical composition of a sample. A Raman microscope is extremely useful for studying carbonaceous material, and it is useful for studying lithium intercalation through the carbon coating of cathodes [19]. Li^+ extraction and insertion has been observed on $LiNi_{0.8}$ $Co_{0.15}Al_{0.05}O_2$ cathodes [20]. The electrochemical cell used in this experiment was designed with a glass top cover to allow monochrome light to pass through. Panitz et al. [19] had a similar electrochemical cell design. They reported that when the thickness of the electrolyte layer was reduced from 0.5 mm to 0.2 mm, it resulted in an improved optical efficiency.

Though the optical in situ technique can only be utilized to probe morphological changes on the surface of the cathode, it does provide resolution on a micron scale [21]. An electrochemical cell utilized for the in situ optical microscopy technique is given in Fig. 1(a). Harris et al. [22] used the color change of graphite as an indicator of the extent of lithiation in order to obtain spatial profiles of Li intercalation. Quartz upper glass was used, however it was stated that lithium degrades the quartz material and a sapphire glass would yield better results.

2.2. Electron

The electron microscope can observe morphological changes on the nanometer scale. It requires an electrochemical cell with a transparent window to an electron beam. The experiments are conducted in a high vacuum and require electrolytes that are compatible, such as ionic liquids and solid electrolytes.

In situ TEM has been limited by the requirement of having ultra-thin samples ($\sim$100 nm thickness) and a focused ion beam (FIB). TEM provides morphological, structural and compositional information using the techniques of imaging, diffraction and spectroscopy respectively [23]. Brazier et al. [24] were the first to conduct an ex-situ TEM observation of a solid state Li-ion battery. The first significant in situ electrochemical cell design was created by Liu and Huang [25] (also see Liu et al. [26]), which used ionic liquid electrolytes (ILEs). These electrolytes were shown to perform better in a high vacuum because of their ultra-low vapor pressure. Unocic et al. [27] created an in situ electrochemical cell that used a MEMS-based biasing microchip platform to seal the highly volatile electrolyte between two transparent electron SiN_x membranes. In order to improve spatial resolution, an energy-filtered transmission electron microscope (EFTEM) (to minimize chromatic aberrations) was used, followed by an electron energy loss spectroscope (EELS) to determine chemical changes.

In situ SEM studies were first performed by Orsini et al. [28]. Their electrochemical cell design did not allow for the cycling of the cell inside the SEM, thus the cycling was done outside of the SEM. After cycling, the cell was cooled down to −20 °C to pause the electrolyte degradation process, and then it was transferred to the SEM in an air-tight container. Raimann et al. [29] designed an electrochemical cell to have the least amount of evaporation of the electrolyte as possible by moderating the size of the exposed working electrode (pinhole diameter), the amount of electrolyte used, and the vacuum level inside of the SEM. However, this method reduced the resolution due to the scattering of electrons in the gas atmosphere that was created as the electrolyte evaporated. The problem faced when using conventional liquid electrolytes was eliminated [21] by using ionic liquids, which are very stable even in ultra-high vacuums because of their very low vapor pressure.

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[1] The total Amp-hours available when the battery is discharged at a certain discharge current from 100% state-of-charge to the cut-off voltage. Capacity is calculated by multiplying the discharge current by the discharge time.