

In situ atomic force microscopy analysis of morphology and particle size changes in Lithium Iron Phosphate cathode during discharge



Dervis Emre Demirocak, Bharat Bhushan*

Nanoprobe Laboratory for Bio- & Nanotechnology and Biomimetics, The Ohio State University, 201 W. 19th Avenue, Columbus, OH 43210, United States

ARTICLE INFO

Article history:

Received 12 January 2014

Accepted 25 February 2014

Available online 5 March 2014

Keywords:

In situ electrochemical cell

Li-ion battery

Atomic force microscopy

Aging

Rate capability

LiFePO₄

ABSTRACT

Li-ion batteries offer great promise for future plug-in hybrid electric vehicles (PHEVs) and pure electric vehicles (EVs). One of the challenges is to improve the cycle life of Li-ion batteries which requires detailed understanding of the aging phenomenon. In situ techniques are especially valuable to understand aging since it allows monitoring the physical and chemical changes in real time. In this study, in situ atomic force microscopy (AFM) is utilized to study the changes in morphology and particle size of LiFePO₄ cathode during discharge. The guidelines for in situ AFM cell design for accurate and reliable measurements based on different designs are presented. The effect of working electrode to counter electrode surface area ratio on cycling data of an in situ cell is also discussed. Analysis of the surface area change in LiFePO₄ particles when the cell was cycled between 100% and 70% state of charge is presented. Among four particles analyzed, surface area increase of particles during Li intercalation of LiFePO₄ spanned from 1.8% to 14.3% indicating the inhomogeneous nature of the cathode surface.

© 2014 Elsevier Inc. All rights reserved.

1. Introduction

Energy storage technologies are becoming increasingly important as the worldwide shift to the renewable energy technologies accelerates [14,36]. Environmental pollution, global warming due to excessive fossil fuel consumption and the depletion of fossil fuels in mid future are the main driving mechanisms behind this paradigm shift. Development of energy storage technologies is especially critical for mobile applications where proposed energy storage technology should perform on a par with fossil fuels for widespread market penetration at an affordable cost. Most prominent energy storage technologies that are under continuous development for mobile applications as of today are batteries, supercapacitors and hydrogen storage [30,37]. Among these, batteries such as nickel metal hydride (NiMH) and Li-ion are the most mature technology and already utilized in commercial plug-in hybrid electric vehicles (PHEVs), Toyota Prius – NiMH, and pure electric vehicles (EVs), Tesla Model S – Li-ion [24].

Li-ion batteries are considered for future EV applications due to their superior gravimetric and volumetric energy density [37,26]. Among many others, LiFePO₄ chemistry is one of strongest candidates due to its high energy density, longer cycle life, thermal stability, rate capability and safety [28,39]. Further improvements

in energy density, cycle life, cost and safety are highly desirable for widespread market penetration of Li-ion batteries. To improve the cycle life of Li-ion batteries and to develop improved materials for Li-ion batteries aging phenomenon should be understood completely. In 2000s, various in situ and ex situ techniques were developed to understand the aging characteristics of Li-ion batteries. In situ techniques are especially valuable since they allow real time investigation of the interfacial and bulk phenomena while cycling the cell. Among different in situ techniques such as transmission electron microscopy [18], Raman [20], X-ray [32], neutron [31] and spectroscopic ellipsometry [19], atomic force microscopy (AFM) is particularly useful to study morphological and surface changes as well as solid electrolyte interphase (SEI) formation in Li-ion batteries [1,13,26]. AFM allows nanoscale imaging of virtually any material. In addition, AFM can be utilized to measure the mechanical and electrical properties of the materials by operating at different modes [8,9]. Beyond contact and phase/tapping mode imaging, electrochemical strain microscopy, force spectroscopy, current sensing AFM, Kelvin probe microscopy, scanning spreading resistance microscopy have been utilized to study Li-ion batteries [27,5,6,25,40].

Anode of a Li-ion battery forms SEI layer at low potentials (i.e., <1.5 V) due to limited electrochemical stability of the nonaqueous alkyl carbonate based electrolytes commonly used in Li-ion batteries (i.e., ethylene carbonate, propylene carbonate, dimethyl carbonate) [4]. Therefore, SEI layer formation as well as

* Corresponding author.

E-mail address: Bhushan.2@osu.edu (B. Bhushan).

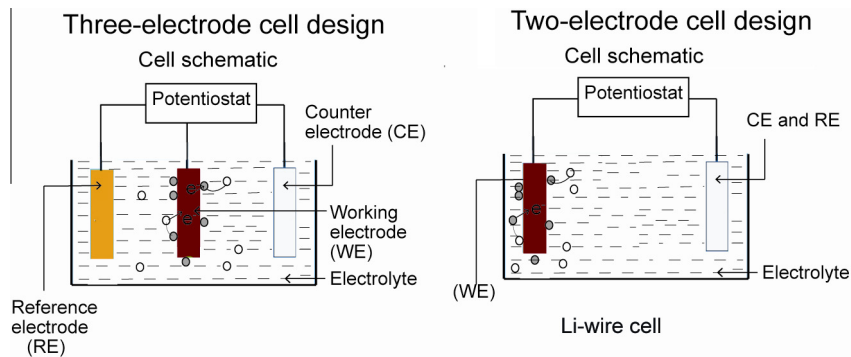


Fig. 1. Two and three electrode cell designs [29].

morphological and structural changes during Li de-/intercalation process (i.e., Sn anode expands 400% by volume upon Li intercalation) in anode materials have been studied by in situ AFM extensively [2,3,7,12,21,15]. On the other hand, in situ AFM studies on cathode materials are rather scarce [11,29]. This is partly because alkyl electrolytes are more stable at higher potentials (i.e., up to 4.5 V) [4]. Therefore, SEI formation is less pronounced on the cathode surface, but not totally eliminated (i.e., 1–2 nm in thickness) [22]. Apart from SEI formation, morphological and particle size changes in cathode are still important to understand the aging phenomenon which is the focus of this work.

In this study, first, in situ AFM cell design guidelines are presented to improve the accuracy and repeatability of the measurements as well as to facilitate the assembly process in a glove box environment. The effect of working electrode (WE) to counter electrode (CE) surface area ratio is discussed based on in situ AFM cell cycling data. A selected in situ cell design is used to study morphological and particle size changes in LiFePO_4 cathode. Since the morphological changes are particularly important to understand the aging phenomenon, surface area change in LiFePO_4 particles was analyzed during discharge by motif analysis (i.e., how particles shapes evolve during discharging). Surface area analysis of four different particles during discharge from 100% to 70% state of charge (SOC) is presented and the underlying reasons for the different surface area change in LiFePO_4 particles are discussed.

2. Experimental details

2.1. Extraction of LiFePO_4 cathode

LiFePO_4 cathode was extracted from the commercial cell ANR26650 with 2.5 Ah nominal capacity (A123 Systems, Inc, Waltham, MA). Extraction procedure was explained in detail in our previous work [29]. In brief, cap of the commercial cell was cut by a tube cutter after discharging at 1 C rate, and jelly roll was removed from the stainless steel casing in air. Then, cathode and anode sheets were separated carefully. LiFePO_4 cathode was coated on both sides of an aluminum current collector. One side of the LiFePO_4 cathode coating was removed by applying 1-methyl 2-pyrrolidinone (Sigma Aldrich, St. Louis, MO) using Q-tips. Finally, one sided cathode sheets were punched by using a circular die-punch set to prepare samples for in situ experiments.

2.2. Electrochemical measurements and half cell details

All in situ AFM cycling data presented in this work was collected using the two electrode Li-foil cell (see Section 3.1). The diameters of LiFePO_4 cathode (WE) was 25.4 mm (1 in), whereas inner and outer diameters of hollow Li foil disk (CE) were 22.2 mm (0.875 in) and 25.4 mm (1 in), respectively. Li-foil cell

was cycled in constant current (CC) and constant voltage (CV) modes. The nonaqueous electrolyte was 1:1 ethylene carbonate (EC)/dimethyl carbonate (DMC) with 1 M lithium hexafluorophosphate (LiPF_6) salt (Novolyte technologies, Zachary, LA). Gamry Reference 600 (Gamry Instruments, Warminster, PA) potentiostat was used to collect all charge and discharge curves at different C rates. C rate is the rate of charge or discharge of a cell relative to its maximum capacity. For instance, 1 C rate will charge a cell from 0% to 100% state of charge (SOC) in 1 h. SOC is defined as the current battery capacity as a percentage of its maximum capacity [26].

Li-wire and Li-foil cell (see Section 3.1) were manufactured using Teflon[®] and glass filled Teflon[®], respectively. Glass filled Teflon[®] was used for Li-foil cell to improve the rigidity of the small cell parts. Coin cell parts (see Section 3.1), CR 2032 meshed casing, spacer and spring, were made of 304 stainless steel and available from MTI Corporation, Richmond, CA.

2.3. AFM details

An Agilent 5500 AFM (Agilent Technologies, Chandler, AZ) placed in a custom built glove box with an argon atmosphere was used to collect all AFM images which were taken in contact mode using a gold coated silicon probe (Budget Sensor ContGD) with a force constant of 0.2 N m^{-1} and a resonant frequency of 13 kHz [29]. An AFM scan speed of 1 Hz or slower was used to obtain an image with a 512×512 resolution. AFM images were then post-processed using Gwyddion software, and particles sizes were analyzed by Pico Image software.

3. Results and discussion

In the following sections, first, in situ AFM cell design guidelines along with the three different cell designs are presented. Then, based on the selected in situ cell design, effect of the working electrode to counter electrode surface area ratio is discussed. Finally, AFM images of the LiFePO_4 cathode that are collected during discharge are given and the morphological and particle size changes in LiFePO_4 cathode are discussed.

3.1. In situ AFM cell design guidelines

In situ AFM cell design has a significant effect in AFM experiments. Various in situ cell designs are given in the literature [10,11,32], but their rate capability, electrolyte evaporation rate, accuracy and repeatability are seldom reported. Moreover, ease of assembly process of an in situ cell is usually neglected. In the following section, cell design guidelines are presented in detail.

The main challenges and objectives in designing an in situ AFM cell can be summarized as follows: (1) The opening in the middle of the cell, required to accommodate the AFM probe, causes

Download English Version:

<https://daneshyari.com/en/article/607284>

Download Persian Version:

<https://daneshyari.com/article/607284>

[Daneshyari.com](https://daneshyari.com)