



# In-situ investigation of solid-electrolyte interphase formation on the anode of Li-ion batteries with Atomic Force Microscopy



Lixin Wang<sup>a</sup>, Da Deng<sup>a</sup>, Leonid C. Lev<sup>b</sup>, Simon Ng<sup>a,\*</sup>

<sup>a</sup>Department of Chemical Engineering and Materials Science, Wayne State University, USA

<sup>b</sup>Manufacturing Systems Research Lab, Warren Technical Center, General Motors Company, USA

## HIGHLIGHTS

- In-situ AFM is used to study SEI formation on the surface of graphite Li-ion electrode.
- It is observed that SEI is composed of a top particle layer and a bottom insertion layer.
- A top particle layer and a second layer underneath the top layer were observed in SEI.
- A dynamic competition mechanism between two layers of SEI is proposed.

## ARTICLE INFO

### Article history:

Received 6 March 2014

Received in revised form

22 April 2014

Accepted 22 April 2014

Available online 30 April 2014

### Keywords:

In-situ AFM

HOPG

Graphite

SEI

Lithium ion batteries

## ABSTRACT

Solid-electrolyte interphase (SEI) formation at highly ordered pyrolytic graphite (HOPG) surface has been studied with in-situ AFM. The morphology and thickness of both the top particle layer of the SEI and the bottom layer of the SEI that was caused by lithium insertion were investigated. The formation mechanism of the SEI was proposed accordingly. Ex-situ FESEM and EDS were also used to analyze the composition of the electrode after cycling to confirm the proposed mechanism.

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

In-situ Atomic Force Microscopy (AFM), as a powerful tool for investigating surface morphology, has found its way into the study of solid-electrolyte interphase (SEI) in Li-ion batteries in recent years. Several groups have reported their results on the SEI evolution on Sn electrode [1], silicon electrode [2,3], and carbon based materials studied by in-situ AFM [4–10]. Mechanisms have also been proposed to explain the phenomenon at the SEI during charge–discharge processes. For example, Inaba et al. observed that the basal surface of HOPG raises 1 nm at a discharge voltage of 1.1 V. They believe this hill-like raise is caused by the co-intercalation of solvated lithium ion due to the conductivity of the tested area [4]. The mechanism of the SEI formation is therefore proposed as two steps: firstly, the insertion of the solvated lithium

ion into the basal plane; secondly, the direct decomposition of solvent to form a blister layer which prevents further solvent co-intercalation. The formation of the surface film on graphite composite electrodes was observed by Jeong et al. in an EC/DEC based electrolyte [7]. Instead of swelling at the basal plane, they observed the curling of the graphite flake edges at a discharge voltage below 1.4 V. Significant morphology changes were observed after the voltages steps reduction due to the large amount of precipitations on the surface.

These studies [1–10] show the effectiveness of in-situ AFM to study SEI, and the role of SEI formation during charging and discharging Li-ion batteries. However, the effect of solvent decomposition products on lithium ion insertion, the thickness changes, and the compositions of the SEI during the cycling have not been fully elucidated. A better understanding of the formation and evolution of SEI during charge and discharge will provide valuable data to determine the role of SEI in the failure mechanism of Li-ion batteries. In addition, it might provide some insight on how to

\* Corresponding author. Tel.: +1 313 577 3805; fax: +1 313 577 8171.

E-mail address: [sng@wayne.edu](mailto:sng@wayne.edu) (S. Ng).

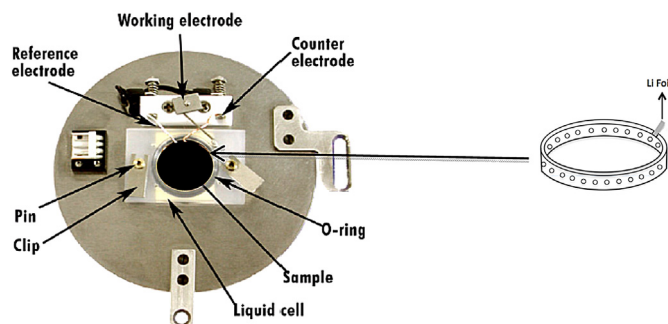


Fig. 1. Photo of liquid cell with electrochemistry setup.

optimize the SEI layer in a dynamic balance state, before it eventually becomes a complete insulator. Thus, storage and operating conditions can be controlled and optimized to extend battery life and improve performance.

In this report, a step-by-step evolution of both the solvent decomposition layer and the intercalation of solvated lithium ions, as well as the interactions between the two at different discharge voltages in the first charge–discharge cycle, are investigated. The thickness of the SEI is measured by scratching away both layers. A possible dynamic competition mechanism of the SEI formation has been proposed based on the experimental results. A HOPG plate is chosen as the electrode for the mechanism study due to the uniformity of its surface, more accurate thickness, easier operation of AFM probes on its smooth and renewable surface. A graphite composite electrode, which is more close to commercial Li-ion electrode, was studied followed by the studies of the HOPG surface. Very similar phenomenon has been found in the graphite composite electrode as well. The in-situ tested graphite composite samples are then characterized using ex-situ SEM and EDS to confirm the morphology and composition of the SEI layers.

## 2. Experiment

The experiments were performed in a liquid cell from Agilent technology with an insert to fix Li-strip in place as shown in Fig. 1 [11]. A  $1.5 \times 1.5 \text{ cm}^{-2}$  square HOPG (ZYH grade, Momentive) was mounted at the bottom of the liquid cell. A lithium metal strip ( $0.2 \times 5 \text{ cm}$ , 99.9% pure, 0.75 mm thick, Alfa Aesar) was placed

inside the insert around the wall of the liquid cell as the reference and counter electrode. The lithium strip contacted with the electrolyte through the round holes on the insert. 1.0 M  $\text{LiPF}_6$  ethylene carbonate/dimethyl carbonate solution (1:1 volume ratio) was placed in the liquid cell sealed with an O-ring and a PTFE liquid cell frame. The liquid cell frame was pinned to the stainless steel sample holder by two pins to ensure the tightness. The AFM scanner was placed at the center of the liquid cell. The electrodes were then connected to the build-in electrochemical testing of the AFM system from the connector. The voltage range of 0.02–3.0 V was used in the electrochemical test with a  $0.5 \text{ mV s}^{-1}$  charge–discharge rate. All the operations were done inside a glove box filled with dry Ar gas to prevent oxidation and moisture contamination of the electrode materials and the electrolyte.

The graphite composite electrode was rinsed with EC/DMC (1:1) solution thoroughly and completely dried inside the glove box. Field emission scanning microscopy (FESEM) and energy dispersive X-ray spectrometer (JSM-7600F at 15 kV) were used to characterize the morphology and composition of the dry sample.

## 3. Results and discussion

### 3.1. Electrochemical testing

The electrochemical test is performed on the HOPG sample in the liquid cell described above. As shown in the cyclic voltammogram curve, redox current was observed when the discharge voltage is around 2.5 V. A redox peak at 0.95 V was observed in the first discharge process at the scan rate of  $0.5 \text{ mV s}^{-1}$ , indicating the occurring of a redox reaction. However, the peak disappeared after the eighth cycle, which indicates that the reactions responsible for the 0.95  $V_{\text{Li}}$  peak are not reversible (Fig. 2).

### 3.2. SEI morphology evolution during the first charge–discharge cycle on the surface of HOPG

The morphology change of the HOPG surface was observed by AFM synchronously. Since the AFM probe and the cyclic voltammetry were performed at the same time, one AFM image shows a range of charging as indicated in Fig. 3. As shown in Fig. 3 a and b, there is slight topographical change on the HOPG surface between the discharge voltage of 3.0–1.65 V. Particles of about 100 nm at the interphase of the electrode/electrolyte start to form at a discharging

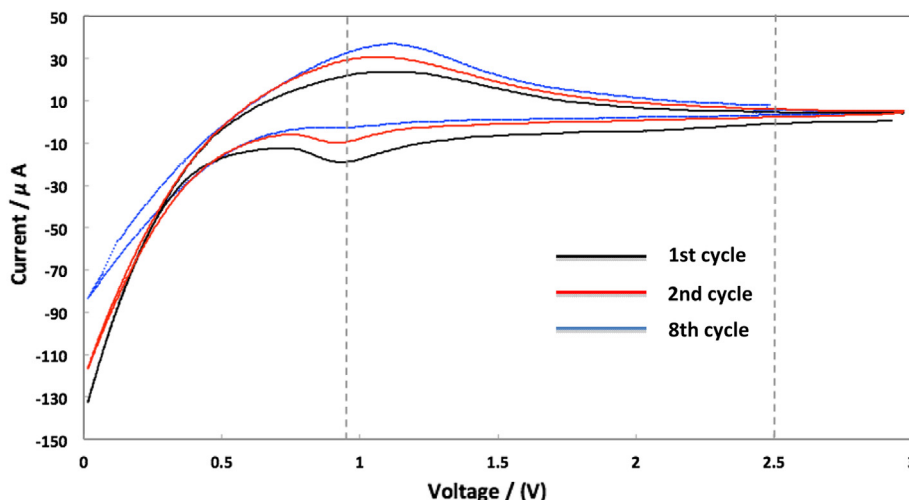


Fig. 2. Cyclic voltammogram of the graphite electrode with a scan rate of  $0.5 \text{ mV s}^{-1}$ .

Download English Version:

<https://daneshyari.com/en/article/1284056>

Download Persian Version:

<https://daneshyari.com/article/1284056>

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