Sci. Bull. (2015) 60(9):839–849
DOI 10.1007/s11434-015-0763-6

www.scibull.com
www.springer.com/scp

Review

Chemistry

Progress of electrode/electrolyte interfacial investigation of Li-ion batteries via in situ scanning probe microscopy

Xingrui Liu · Dong Wang · Lijun Wan

Received: 18 November 2014 / Accepted: 8 January 2015 / Published online: 12 March 2015

Abstract The electrode/electrolyte interface plays a critical role in the performance of a Li-ion battery. In view of the dynamic and complex nature of the interface, in situ research approaches can provide valuable information of interfacial phenomena during battery operation. In situ scanning probe microscopy (SPM) is a powerful technique used for the interfacial investigation of the Li-ion batteries. The versatile SPM techniques and their various operation modes have been utilized to measure the morphology and other properties of the electrode interface at high resolution. Herein, we discuss the related SPM techniques to study the topography, mechanics and electrochemistry research of electrodes. Recent progresses of in situ SPM research on the electrode/electrolyte interface are summarized. Finally, the outlook of the technique is discussed.

Keywords In situ scanning probe microscopy · Electrode/electrolyte interface · Solid electrolyte interphase · Li-ion battery

1 Introduction

Li-ion batteries (LIBs) are the most popular portable power source in modern life and promises a broad range of application field, such as vehicles, with the development of high energy density, high power density and safe batteries [1, 2]. To achieve such goal, great progress has been made to look for new electrode materials and new battery systems. At the same time, understanding the fundamental electrochemistry at electrode/electrolyte interface of the battery systems has been increasingly acknowledged as an important prerequisite to optimize the battery systems [3]. There are many important interface processes during the operation of batteries, including electrolyte decomposition, the growth of solid electrolyte interphase (SEI) layer and intercalation/deintercalation of Li ions [4]. Obviously, the interface processes directly determine the performance of the batteries. For example, SEI is the irreversible reduction product from the electrolyte and generated on the electrode surface during the initial electrochemical cycles [5]. This delicate interphase plays a crucial role in insuring the reversible behavior of the insertion and extraction of isolated Li ions. At the same time, SEI can sufficiently prevent the penetration of the electrolyte and solvated Li compounds [6, 7]. Therefore, understanding the formation mechanism and properties of SEI is very important for optimizing the surface structure of the electrodes. However, the investigation of the SEI and other interfacial electrochemistry is a challenge task due to their dynamic feature during the electrochemical process.

The development of modern characterization techniques provides great opportunity to study the nature of SEI. The electrode interfaces have been widely investigated in terms of chemical composition, morphology and structure with the assistance of various spectroscopy and electron microscope techniques [8–14]. The emergence of scanning probe microscopy (SPM) techniques has brought new potential in the study of the interface. Representing a big family of probe-based microscopy, such as scanning

X. Liu · D. Wang (✉) · L. Wan
Chinese Academy of Sciences Key Laboratory of Molecular Nanostructure and Nanotechnology, National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China
e-mail: wangd@iccas.ac.cn

X. Liu
University of Chinese Academy of Sciences, Beijing 100049, China

tunneling microscopy (STM) and atomic force microscopy (AFM), SPM has demonstrated its ability of morphological detection at high spatial resolution of nanometer level [15, 16]. Besides, SPM is easy to be implemented under various environments such as liquid and electrochemical environment, which is a great advantage for SPM compared with electron microscopies. Furthermore, characteristics of SPM techniques in real time, real space and high resolution allow them to in situ probe the materials surface at nanoscale. Up to now, the applications of SPM have covered almost all fields of materials science, biology and physics [17–20]. In the case of LIBs, a most attractive utilization of SPM is in situ exploring the evolution of electrode/electrolyte interface during the battery operation process. Since the earliest research of electrochemical STM (EC-STM) study on the morphology of HOPG surface in lithium-ion battery electrolyte in 1995 [21], electrochemical SPM techniques have been successfully applied to reveal the electrode/electrolyte interfacial structure and dynamics in various LIB systems. In addition to topographic observation, in situ SPM techniques have the capability of investigating the mechanics or electrochemistry of the electrode interface for LIBs.

During the past years, SPM has contributed to great progress in understanding the morphology, structure and properties of the interfacial phenomena for LIBs. In this paper, we make effort to review the interfacial investigation of LIBs via in situ SPM techniques. After a brief introduction of in situ SPM techniques, especially those applied to LIBs and sample preparation methods, their applications of studying morphology, mechanics and electrochemical property of selected examples are summarized. In the end, outlook of the perspective of in situ SPM for LIBs is discussed.

2 In situ SPM techniques

The basic equipment and principles of in situ SPM techniques have been published in a series of literature. Here, we briefly list some critical techniques applied to the electrode/electrolyte interfacial research for LIBs [22–25].

2.1 Dynamic topographic and structural analysis

It is common phenomena that the morphological changes occur in the electrodes due to interfacial processes such as SEI growth or lithiation/delithiation of the electrodes. Directly seeing these processes from nanoscale is highly conducive for understanding the mechanism of the electrode/electrolyte interface. A most obvious application of in situ SPM in LIBs is imaging the electrode topography during electrochemical cycling at high resolution. Among various in situ SPM techniques, electrochemical AFM (EC-AFM) is the most powerful tool in the electrode/electrolyte morphological investigation during the discharging and charging process. A valuable feature of EC-AFM is non-destructive imaging of the SEI formation. The SEI is very sensitive to the environment and easy to be mechanically or chemically damaged by ex situ sample preparation and treatment. EC-AFM is very suitable for observing the dynamic morphology of SEI during its formation process. Typically, the AFM unit is placed in an inert gas-filled glove box, which can provide a favorable environment for LIB operation. In order to investigate the interfacial changes during electrochemical cycling, a specially designed electrochemical cell is required. Figure 1 shows the diagram of a typical electrochemical AFM cell with three electrodes. The working electrode is mounted under the cell, and an O-ring is used for avoiding the electrolyte leakage. A ring-shaped counter electrode can effectively increase the area exposed to the electrolyte in the cell and insure stable electrochemical reaction process.

In addition to the dynamic morphological observation, EC-AFM is capable of measuring the structure and thickness of the SEI layer. The AFM tip can serve as a micromachining tool to manipulate the electrode surface locally [26]. “Scraping” is a simple but practical skill to measure the thickness of the thin film [27]. Generally, SEI is soft and easy to be scraped off by tip scanning. Therefore, the thickness of SEI could be easily evaluated by EC-AFM.

2.2 In situ mechanics analysis

In addition to observing the topographic evolution, the working principle and quantitative nature of AFM provide the capability of detecting the interactions between tip and sample [28]. The interaction forces between the tip and sample can be identified by force–distance curve measurement. Useful mechanical properties such as elastic and plastic properties of the sample can be extracted in a quantitative way by analysis of the force curves [29].

The mechanical strength and physical properties of the electrodes and interphase are closely related to their

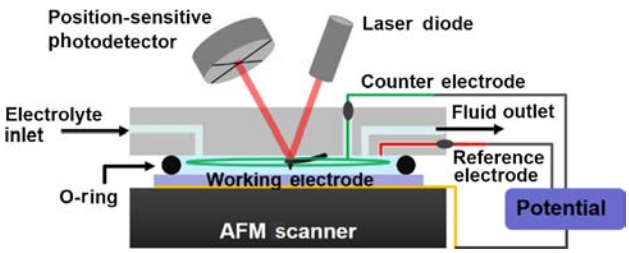

Fig. 1 (Color online) Cross-sectional schematic diagram of an EC-AFM cell