Applied Surface Science 426 (2017) 217–223

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Operando study of Fe_3O_4 anodes by electrochemical atomic force microscopy

Shuwei Wang[a,1], Weicong Zhang[b,c,1], Yuanning Chen[c,d], Zhengwu Dai[c,d], Chongchong Zhao[a], Deyu Wang[a,*], Cai Shen[a,*]

[a] Ningbo Institute of Materials Technology & Engineering, Chinese Academy of Sciences, 1219 Zhongguan Road, Ningbo, China
[b] Foundation Department, Zhejiang Wanli University, 8 South Qianhu Road, Ningbo, China
[c] Ningbo Baohong Information Technology Co., Ltd., 7 Entrepreneurial Avenue, Ningbo, China
[d] Ningbo Micro Energy Technology Co., Ltd., 7 Entrepreneurial Avenue, Ningbo, China

ARTICLE INFO

Article history:
Received 17 May 2017
Received in revised form 20 July 2017
Accepted 21 July 2017
Available online 24 July 2017

Keywords:
Lithium-ion batteries
Anode
Iron oxide
Solid electrolyte interphase
Atomic force microscopy

ABSTRACT

Present study provided visual evidence of solid electrolyte interphase (SEI) layer formation on Fe_3O_4 anode during charge and discharge using in situ electrochemical atomic force microscopy. AFM images show that SEI layer formed on Fe_3O_4 electrode from fluoroethylene carbonate (FEC)-based electrolyte was more stable and compact than that formed from ethylene carbonate (EC)-based electrolyte. In addition, presence of surface cracks on the electrodes indicated poor formation of an intact SEI layer. This observation was more apparent in the EC-based electrolyte. Lack of an intact SEI layer resulted in decomposition of electrolytes which were reflected by presence of large air bubbles and dendrites on the electrode during CV. Although FEC-based electrolyte improved the performance of Fe_3O_4 anodes in lithium ion batteries, its protective effects were far from perfect. To accelerate the application of Fe_3O_4 or other metal oxide anodes in lithium ion batteries, better electrolytes and sophisticated carbon coating techniques are needed.

1. Introduction

Numerous research efforts have been directed at researching for new electrode materials to develop safe rechargeable lithium ion batteries (LIBs) with high energy density and long cycle life. Transition metal oxide (conversion type anode) is one of the most studied anode materials during the past decades [1–4]. Among them, Fe_3O_4 is regarded as one of the most promising anodes because of its high theoretical capacity (928 mAh g^{-1}), low cost, and environmental benignity [5–12]. Compared to silicon, Fe_3O_4 also has moderate volume change during lithiation/delithiation. By designing nanostructural Fe_3O_4 and constructing Fe_3O_4-based composites, it is possible to shorten the travel distance of the electrons and lithium ions, and to buffer the volume change of Fe_3O_4 during charge/discharge [13–15]. Despite that, Fe_3O_4 anode has not been successfully commercialized to-date due to poor cycling performance. Moreover, Fe_3O_4 anode has surface instability due to the lack of stable solid electrolyte interphase.

Solid electrolyte interphase (SEI), a sacrificial layer reduced from electrolyte solution, enables commercial lithium-ion batteries (LIBs) to operate at a proper potential window range (usually 0–4.2 V, vs. Standard Hydrogen Electrode) in the presence of organic electrolyte [16]. Ideally, SEI layer should be compact, insoluble, and irreversibly adhere to the active surface of electrode in order to prevent further decomposition of the electrolyte. Controlling SEI formation on anode has been considered an important approach for safe and stable battery operation.

Understanding the evolution of SEI layer as well as the structural changes on electrode surface is important for interpreting the performance of conversion type anode. However, up-to-date, the role of SEI layer in performance deterioration of Fe_3O_4 has not been given much attention. In situ scanning probe microscopy (SPM) is a powerful method to investigate morphological changes on the surface of electrode materials during electrochemical process in liquid electrolyte solutions [17–19]. It has the outstanding advantages of being real time, non-invasive and atomic resolution [20–24]. Atomic force microscopy (AFM) technique has been used to study the SEI layer on model system with flat surface such as HOPG [20,21,25–30], silicon anode [31–35], MnO [36,37] and embedded

* Corresponding authors.
E-mail addresses: wangdy@nimte.ac.cn (D. Wang), shencai@nimte.ac.cn (C. Shen).
[1] Equal contribution.

http://dx.doi.org/10.1016/j.apsusc.2017.07.206
0169-4332/

single particle ($LiNi_{0.5}Mn_{1.5}O_4$) electrode [30]. To the best of our knowledge, the structure of SEI layer on Fe_3O_4 anode has not been characterized using direct visualization method.

Present study aimed to investigate the surface structure evolution of SEI layer on Fe_3O_4 formed from EC and FEC-based electrolytes by in-situ AFM. Understanding of the evolution of SEI layer and Fe_3O_4 particles structure will further improve our understanding on how SEI layer of metal oxides affects battery performance.

2. Experimental section

2.1. Preparation of Fe_3O_4 electrode

Fe_3O_4 electrodes were prepared using our previously method [38]. Fe_3O_4 films were deposited directly onto copper electrodes (14 mm in diameter) by applying a constant cathodic current (5 mA) for 600 s. The mixed electrolyte solution of 0.05 M $Fe_2(SO_4)_3$, 1 M NaOH and 0.1 M triethanolamine (TEA) was used for the deposition and kept in an oil bath at 90 °C in air. Copper disk, carbon paper and platinum wire was used as working electrode, counter electrode, and reference electrode, respectively. After deposition, Cu disks were cleaned with water and ethanol, then dried in air. All electrodeposition experiments were performed using an electrochemical workstation (CHI660D, Shanghai Chenhua instrument, Co. Ltd.).

2.2. Battery performance test

Electrochemical measurements were carried out using a 2032-type coin cell system. Weights of the Fe_3O_4 films before and after deposition were determined using analytical balance to the accuracy of 0.01 mg. The average loading of Fe_3O_4 was ~0.8 mg cm^{-2}. 2032-type coin cells were assembled in argon-filled glovebox with oxygen and moisture concentrations below 0.1 ppm. Fe_3O_4 film was used as working electrode and lithium wire was used as counter electrode. Celgard 2400 polypropylene was used as separator. The electrolytes used were comprising of a solution of 1 M lithium hexafluorophosphate ($LiPF_6$) dissolved ether in a mixture of EC/EMC/DMC (1:1:1, volume ratio) or FEC/EMC/DMC (1:1:1, volume ratio). Charge/discharge measurements were carried out galvanostatically at 0.5C over a voltage range of 0.01–2.5 V (vs. Li/Li^+) using a commercial battery test system (LAND model, CT2001A) at room temperature.

2.3. Electrochemical performance and image scanning using EC-AFM

Electrochemical impedance spectroscopy (EIS) spectra were collected with potentiostat/galvanostat 1470E equipped with a frequency response analyzer 1455A from Solartron. In situ AFM (Bruker Icon) experiments were conducted in argon-filled glovebox (MBRAUN, $H_2O \leq 0.1$ ppm, $O_2 \leq 0.1$ ppm) at room temperature. The Li-Fe_3O_4 cell was composed of Fe_3O_4 substrate as working electrode (WE) and Li wire as counter and reference electrodes (CE and RE). Electrolytes used were 1 M $LiPF_6$ dissolved either in a mixture of ethylene carbonate or fluoroethylene carbonate/dimethyl carbonate (EC/DMC or FEC/DMC, volume ratio of 1:1) (Shanshan Corporation). In order to study the SEI layer formation, the Li-Fe_3O_4 cell was studied by cyclic voltammetry (CV) at a scanning rate of 0.5 mV s^{-1} between 3.0 and 0 V. AFM topography was collected simultaneously in ScanAsyst mode using nitride coated silicon probes (tip model: SCANNASYST-FLUID with k = 0.7 N m^{-1}, Bruker Corporation).

2.4. Characterization

Ex-situ XPS analysis was performed on Kratos Axis Ultra X-ray photoelectron spectrometer using 1253.6 eV Mg Kα X-rays. Samples were removed from the cells and rinsed with dimethyl carbonate (DMC) to remove residual salt and solvent in an argon-filled glovebox. Samples were then transported to XPS facility in sealed bags to avoid contact with air. The analyzed area of electrode was 300 × 700 μm^2. The binding energies were referenced to the hydrocarbon C1s photoelectron peak at 284.8 eV.

3. Result and discussion

Fig. 1 shows the surface structural evolution of Fe_3O_4 electrode during the first lithiation-delithiation cycle in EC-based electrolyte between 3.0 and 0.0 V (vs Li^+/Li) by CV method (OCV is about 2.5 V). XRD has been conducted in our previous work to confirm the crystal structure of Fe_3O_4 [38]. Fig. 1a shows a typical surface structure of Fe_3O_4 electrode for potential between 3.0 to 2.82 V. No obvious changes in the surface structure of Fe_3O_4 electrode can be observed for potential between 3.0 to 1.0 V. When the potential was cycled down to about 0.8 V, very thin SEI layer can be observed (Fig. 1b, indicated by the white arrows). Similar finding can be observed in the first CV curve of Fe_3O_4 electrode cycled in EC based electrolyte at room temperature between 0 and 3.0 V (vs Li^+/Li) at a scan rate of 0.5 mV s^{-1} (Fig. S1). A sudden increase in cathodic peak at around 0.8 V can be ascribed to decomposition of electrolytes and the formation of SEI layer [30]. Decreased reduction potential leads a further growth of the SEI layer (Fig. 1c) and Li insertion. The thick SEI can be found at some area of the particle (indicated by the red arrow in Fig. 1c). Line profiles of Fig. 1 a and c shown the height of SEI layers is ~0–50 nm (indicated in Fig. S2). Fig. 1a' and c' showed after the growth of SEI layer, the Fe_3O_4 particle size changed from 1.62 μm to 1.77 μm. During the reverse scan of potentials, SEI layer formed in EC-based electrolyte was soft and could be modified by AFM tip during imaging. Surface of the SEI layer became smoothened due to repeated scanning by AFM tip (Fig. 1d–h). One should note that during the whole CV process, the volume change (except the cracks) is far less than theoretical predication. This is similar to what have been observed in Si anodes [32,39]. The exact mechanism of this difference is not clear yet.

During discharge process, no obvious Fe_3O_4 particles broken or surface cracks can be observed (Fig. 1a–c). However, obviously particles broken and surface cracks can be observed in the charge process (Fig. 1d–h). Some particles have been broken seriously (indicated by white square area in Fig. 1h). Fe_3O_4 particles showed the volume change as indicated by the arrows, at which the particle size changed from 1.77 μm to 1.87 μm. Also, line profiles of Fig. 1a' and h' shown the height of swelling is ~125 nm (indicated in Fig. S2). Surface cracks (indicated by white arrow in Fig. 1f–h) can be observed during lithium extraction when the potential was cycled back to 3.0 V which continue to increase in sizes until CV completed. Thus, SEI layer formation mainly caused the thickness change while volume change can lead to surface cracks.

Cracking of the SEI layer resulted in exposure of fresh Fe_3O_4 particles to electrolyte; hence, continuous decomposition of electrolyte. Decomposition of electrolyte was also accompanied by formation of large air bubbles (Fig. S3a) and lithium dendrites on the Fe_3O_4 anode (white precipitates in Fig. S3b). Bubble formation is a direct evidence of electrolyte decomposition which is due to poor formation of a proper SEI layer on Fe_3O_4 electrode. Existence of dendrites on the first cycle of charge/discharge is also another indication of poor formation of SEI layer on Fe_3O_4 anode.

Our previous study showed that SEI layer formed on HOPG surface in FEC based electrolyte is denser and harder than that the