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In situ AFM studies of SEI formation at a Sn electrode

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ABSTRACT

Early stages of the solid electrolyte interphase (SEI) formation at a tin foil electrode in an ethylene carbonate (EC) based electrolyte were investigated by *in situ* AFM and cyclic voltammetry (CV) at potentials >0.7 V, i.e., above the potential of Sn–Li alloying. We detected and observed initial steps of the surface film formation at ~2.8 V vs. Li/Li$^+$ followed by gradual film morphology changes at potentials $0.7 < U < 2.5$ V. The SEI layer undergoes continuous reformation during the following CV cycles between 0.7 and 2.5 V. The surface film on Sn does not effectively prevent the electrolyte reduction and a large fraction of the reaction products dissolve in the electrolyte. The unstable SEI layer on Sn in EC-based electrolytes may compromise the use of tin-based anodes in Li-ion battery systems unless the interfacial chemistry of the electrode and/or electrolyte is modified.

1. Introduction

Fundamental understanding of processes that occur at the electrode/electrolyte interface during charge and discharge processes is a prerequisite for developing advanced Li-ion battery (LIB) systems with long lifetimes. Interfacial reactions, which include lithium ion insertion/extraction, electrolyte decomposition, and the formation of a solid electrolyte interphase (SEI) layer, determine the irreversible capacity loss, cycle life, and calendar lifetime of LIB systems.

Tin has attracted significant attention as a Li-alloying anode material because it offers a large specific capacity (993 mAh g^{-1} for $Li_{22}Sn_5$) [1] as compared to graphite electrodes (372 mAh g^{-1}). However, a large irreversible capacity loss during early cycles and poor reversible capacity retention are observed, both of which are primarily attributed to large volumetric changes during alloying and dealloying processes, particle decrepitation, and loss of electronic contact [2–4]. These phenomena are mainly responsible for the rapid degradation of Sn-based anodes in LIB systems.

We applied *in situ* atomic force microscopy (AFM) in conjunction with standard electrochemical methods to investigate interfacial processes at the Sn electrode during CV scans at potentials >0.7 V, i.e., above the potential of Sn–Li alloying. Several authors have previously investigated the electrode surface morphology evolution during lithiation and delithiation processes of Sn-based electrodes [2,3,5,6] by using *in situ* AFM. Beaulieu et al. showed some evidence of the SEI layer formation around 1.6 V on Sn thin films [1]. However, the main focus of these studies was to observe and quantify the morphology changes of Sn upon alloying–dealloying with lithium.

Yang et al. studied electrochemical cycling performance of Sn-foil in $LiPF_6$, EC:DMC and suggested that part of the lithium is being consumed irreversibly in the formation of SEI layers. Wagner et al. [7] pointed to a difference in the SEI formation mechanism on graphite and intermetallic anodes. Wachtler et al. [8] showed the effect of electrolyte composition on electrochemical cycling performance of tin-based anodes.

In the work presented herein, we investigated the early stages of SEI layer formation upon polarization at potentials $0.7 < U < 2.8$ V, and surface film reformation during the following CV cycles between 0.7 and 2.5 V. The impact of the electrocatalytic activity of Sn in organic carbonate electrolytes on the electrochemical properties of the Sn anode in Li-ion systems has been evaluated.

2. Experimental

Sn disc electrodes ($d = 1.2$ cm, 0.5 mm thick) were punched from a tin foil (99.998% purity, Sigma Aldrich), and mechanically polished (Silicon carbide paper 2500 and 4000, Struers Inc.) to a surface roughness of ca. 5–10 nm. The electrodes were sonicated in acetone and diethyl carbonate (DEC), dried under a flow of nitrogen, heated at 80 °C under vacuum for a few hours and stored in an Ar-filled glove box.

Cyclic voltammetry measurements were performed using a Ref 600 potentiostat/galvanostat (Gamry Instruments) in a beaker cell or in an *in situ* AFM cell filled with the 1 M $LiPF_6$, ethylene carbonate and diethyl carbonate (EC:DEC, 1:2 w/w) electrolyte (Novolyte Technologies). The water content of the electrolyte was less than

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2 ppm, as determined by Karl–Fisher titration (Meter-Toledo). All potentials reported in this work are referred to the Li/Li$^+$ reference electrode.

In situ AFM experiments were conducted with Pico SPM (Molecular Imaging) in an Ar-filled environmental chamber. Tin electrodes were placed in the AFM electrochemical cell equipped with Li wire counter and reference electrodes. The cell was filled with the electrolyte and its level was maintained by small additions of DEC from a syringe to compensate for rapid evaporation of DEC. *In situ* AFM imaging was conducted in the constant-force mode, using non-conductive silicon nitride triangular cantilevers (Veeco) or regular silicon tips (Mikromash). Interestingly, the Si tips did not suffer from a possible alteration albeit the Si tip was in mechanical and electronic contact with the Sn electrode. AFM images were obtained at 64 mV intervals during the CV scan at 2 mV s^{-1}.

3. Results and discussion

3.1. Electrochemical behavior

Fig. 1 shows the first cyclic voltammogram of a Sn-foil anode from the open circuit potential (OCP) ~2.8–0.7 V, i.e., still above the potential at which Li alloys with Sn. An irreversible reduction double peak feature appears at 1.45 V and 1.2 V. These peaks are not associated with any oxidation peaks during the reverse scan (deliberately limited to 1.6 V). Interestingly, the peak at 1.45 V remains unchanged whereas the intensity of the reduction peak at 1.2 V nearly quadruples in the second cycle and then diminishes quite significantly in the third cathodic scan.

Galvanostatic charge profiles of a sputtered thin-film tin electrode in 1 M LiPF$_6$ EC/PC 1:1 display an anomalous plateau at 1.6 V [2], and electroplated thin-film Sn electrodes charged in 1 M LiClO$_4$ in propylene carbonate (PC) exhibit a shoulder around 1.2 V [3], which is usually ascribed to electrolyte decomposition or SEI layer formation. Interestingly, galvanostatic polarization of the Sn-foil anode at $i \leqslant -33\ \mu A\ cm^{-2}$ (results not shown here) exhibited an anomalous potential plateau in the range of 1.3–1.6 V, which remained fairly constant for more than 30 h, indicating that the electrolyte reduction processes were never suppressed by surface film formation on the Sn-foil electrode.

When the CV scans were extended to 0.01 V, the CV profile becomes typical for tin or tin-based alloys (Fig. 2). The cathodic peak at 0.65 V is usually attributed to early stages (Li$_x$Sn, $x < 1$) of the Li–Sn alloying process. The intense cathodic current at potentials below 0.38 V corresponds to the formation of highly lithiated phases, i.e., Li$_{4.4}$Sn and Li$_{2.33}$Sn. The anodic scan exhibits two distinct broad maxima at 0.75 and 0.87 V, which correspond to the delithiation of Li$_{4.4}$Sn, Li$_{2.33}$Sn, LiSn, and Li$_{0.4}$Sn phases [1,9].

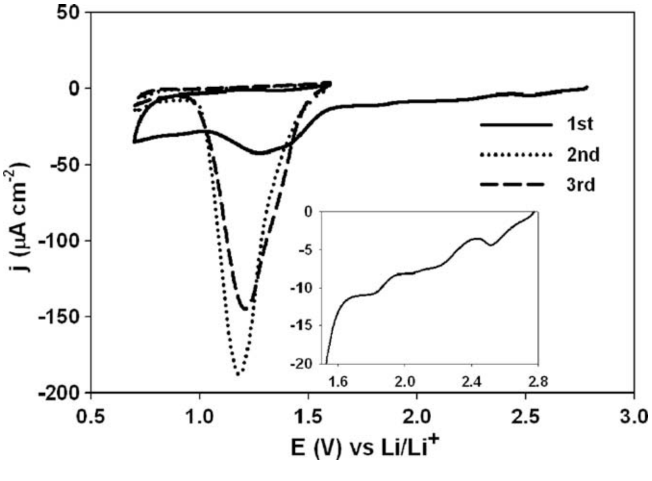

Fig. 1. Cyclic voltammogram of a Sn-foil electrode in 1 M LiPF$_6$, EC:DEC (1:2 w/w) from the OCP ~2.7 V to 0.7 V and the following cycles between 0.7 V and 1.6 V (scan rate: 1 mV s^{-1}). The inset shows the early stages of the first half-cycle.

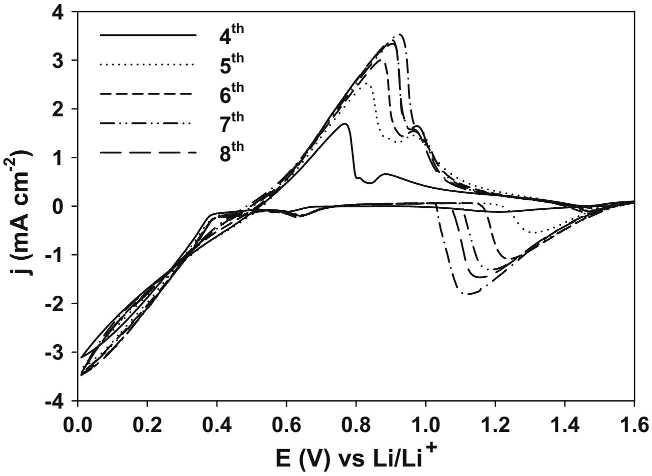

Fig. 2. Cyclic voltammograms of a Sn-foil anode in 1 M LiPF$_6$, EC:DEC (1:2 w/w) between 1.6 and 0.01 V (scan rate: 1 mV s^{-1}).

The previously observed irreversible cathodic peaks at ca. 1.45 and 1.2 V appear in the cathodic and anodic scans, respectively. During the following scans, the intensity of the reduction peaks at 1.45 and 1.2 V increases significantly with a gradual shift of the peaks position toward lower potentials. Such a trend was already reported for electrodeposited Sn thin-film electrodes in 1 M LiPF$_6$, EC:DEC (1:1 w/w) [10] and 1 M LiClO$_4$, PC [3], and was attributed to significant changes in the electrode surface morphology upon alloying/dealloying processes [1,3,10]. The observed steady increase of the cathodic peak intensity is associated with Sn surface particle decrepitation, which results from large volumetric changes of Sn crystallites upon lithiation–delithiation with Li. This effect is responsible for gradual increase of the electrode active surface area, continuous regeneration of a fresh tin surface, and SEI reformation [4].

3.2. In situ AFM characterisation of Sn surface phenomena

To monitor the interfacial phenomena the surface of the Sn-foil anode was imaged continuously with an *in situ* AFM probe while scanning the potential from the OCP to 0.7 V. Figs. 3 and 4 show the first and the following two CV scans and the corresponding AFM images, respectively.

The AFM images recorded during the initial CV scan (Fig. 3) exhibit two distinct phases of surface film formation: (i) from OCP at 2.7 V to 2 V, and (ii) at potentials $2.5 \leqslant U \leqslant 0.7$, which correspond to the electrolyte reduction peaks observed at the CV plot. Note that the contaminant particle visible at the two initial AFM images was originally used as a reference but eventually it was dragged away by the AFM tip during the subsequent AFM scans.

The AFM images recorded at 2.7 V show no evidence of any spontaneous surface film formation. However, formation of some surface features can be observed at the Sn electrode at potentials as high as 2.5 V, which most likely correspond to a cathodic peak on the CV. The peak at 2.5 V, but of somewhat smaller intensity, is also visible in the inset of Fig. 1. It tends to vanish during the second cycle, and its intensity varies strongly from one experiment to another. This peak could originate from reactions with oxygen