



Surface-layer formation by reductive decomposition of LiPF_6 at relatively high potentials on negative electrodes in lithium ion batteries and its suppression



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HIGHLIGHTS

- Surface layer on negative electrodes was investigated for LiPF_6/EC –DMC electrolyte.
- In-situ X-ray reflectivity analyses etc revealed a surface layer (other than SEI).
- The layer was formed by a reductive decomposition of LiPF_6 around 2.6 V vs Li.
- Such an inactive surface layer influences the battery performance.
- How to circumvent the formation of the passivate layer was discussed.

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ABSTRACT

In using a LiPF_6 /ethylene carbonate–dimethyl carbonate electrolyte for lithium ion batteries (LIBs), a certain reductive reaction is known to occur at a relatively high potential (ca. 2.6 V vs. Li^+/Li) on Sn electrode, but its details are still unknown. By means of in-situ X-ray reflectometry, X-ray photoelectron spectroscopy, scanning electron microscopy observations and electrochemical measurements (by using mainly Sn electrode, and additionally Pt, graphite electrodes), we have found out that this reduction eventually forms an inactive passivation-layer consisting mainly of insulative LiF ascribed to the reductive decomposition of LiPF_6 , which significantly affects the battery cyclability. In contrast, a solid-electrolyte interphase (SEI) is formed by the reductive reaction of the solvent at ca. 1.5 V vs. Li^+/Li , which is lower than the reduction potential of LiPF_6 . However, we have found that the formation of SEI preempts that of the passivation layer when holding the electrode at a potential lower than 1.5 V vs. Li^+/Li . Consequently, the cyclability is improved by suppressing the formation of the inactive passivation layer. Such a pretreatment would be quite effective on improvement of the battery cyclability, especially for a relatively noble electrode whose oxidation potential is between 1.5 V and 2.6 V vs. Li^+/Li .

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1. Introduction

The surface layer, formed on a negative electrode by the reductive decomposition of an electrolyte in Li ion batteries (LIBs), passivates the electrode surface and prevents a further decomposition of the electrolyte on the surface. The surface layer having a good Li ion conductivity in addition to a sufficient electrical isolation [1,2] is often called “solid-electrolyte interphase (SEI)”. The

properties of the surface layer dominate the various battery performances, e.g. the irreversible capacity, power and the degradation of the battery. Although there have been many works on those formed by the reduction reaction of the solvent [3–6], few studies have been reported on the influences on battery properties of a surface layer formed due to the decomposition of a solute. However, through an atomic force microscope observation, Lucas et al. [7] reported a certain small change on a surface of a Sn negative electrode at ca. 2.6 V vs. Li^+/Li during cyclic voltammetry (CV) scan. It is expected that the surface morphologic change at the high potential can be ascribed to the reductive decomposition of the solute, because the potential of 2.6 V is higher than the reduction

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potential of the solvent, ca. 1.5 V vs. Li^+/Li , at which the SEI is formed by the reductive reaction of the EC–DEC/DMC solvent (EC: ethylene carbonate, DEC: diethyl carbonate, DMC: dimethyl carbonate). However, the details of the reductive reaction at the relatively high potential has not been understood yet to date.

It is thus worthwhile to investigate a mechanism and influences on the battery properties of the reductive reaction around 2.6 V vs Li^+/Li . In the present work, by using a two-electrode cell composed of a Sn electrode, a Li electrode, and a LiPF_6/EC –DMC electrolyte, we have found out that a considerably thick surface layer formed due to the reduction reaction at about/below 2.6 V in a two-electrode-CV profile. As demonstrated in the pioneering works, [8–10] the in-situ X-ray reflectivity (XRR) measurement is a quite suitable for analyzing characteristics of thin surface layers. Then, in combination with the in-situ XRR measurement, scanning electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and conventional electrochemical measurements, here we have evaluated the properties (such as density, thickness, composition, etc.) of the surface layers formed on the electrode. Based on the results, we discuss a plausible formation mechanism of the surface layer on the electrode. In addition, LiClO_4 was also tested as a solute instead of LiPF_6 to check whether or not the surface layer is formed without F ion species in the electrolyte. Furthermore, we have examined whether the similar surface layer is formed on Pt and graphite electrodes, instead of Sn. Finally, we mention the degradation behaviors in battery cycle tests by comparing two kinds of electrodes with the different surface layers formed by holding the electrodes at 2.0 V and 1.2 V, being higher and lower than the SEI formation voltage.

2. Experimental

2.1. Electrode preparation and battery construction

Flat and smooth Sn electrode samples for in-situ XRR measurements were prepared on a Si wafer by DC-magnetron sputtering at room temperature. For the XRR analyses, the sputtering time and the power were set at 300 s and 50 W, respectively. For the battery tests, a relatively thick Sn electrodes were prepared on Cu foils by sputtering for 900 s with 50 W. Pt plates mechanically polished with an emery paper were used for electrodes, and pyrolytic graphite plates (Panasonic) were used for graphite electrodes.

A two-electrode-cell consisting of the above electrodes as a “positive” electrode, a lithium metal sheet (Honjo Metal) as a “negative” electrode and an electrolyte with 1 M LiPF_6 or 1 M LiClO_4 (EC/DMC = 1/2 in volume, Kishida Chemical) were sealed in a laminated aluminum cell in an Ar-gas-filled glove box, where both moisture and oxygen content were less than 2 ppm. Water contents in the electrolytes were measured to be less than 80 ppm by Karl Fischer titrations (KEM, MKC-610). A cell/applied voltage set for the two-electrode-cell is, of course, not exactly equal to the value based on a Li reference electrode. However, since the current densities used in the present electrochemical measurements were small, so that the polarization of Li electrode is considered to be negligibly small, and we use the cell voltage in a unit of “V (vs. Li)”.

2.2. Electrochemical tests and in-situ XRR measurement

A cyclic voltammetry (CV) test and a battery cycle test were performed by a potentiostat/galvanostat (Biologic, VMP3), where the positive electrode was defined as a working electrode (WE) and the Li negative electrode was a counter/reference electrode (CE/RE); the two-electrode-CV scan was carried out from the initial OCV to 0.01 V at a sweep rate of 0.1 mV s^{-1} . In the battery charge/

discharge cycle test, the current was set at a rate of 1C (0.07 mA cm^{-2}) for the Sn electrode, and the cut off voltages were set at 1.2 V and 0.01 V for charge and discharge, respectively. The Sn electrodes for the battery tests were prepared by holding them at 2.0 and 1.2 V for 5 h before the tests to compare the effects of the surface layers formed at these two potentials on the battery cyclability.

Parallel and monochromatic Mo $K\alpha$ radiation was obtained for XRR measurements by using the rotating anode X-ray generator, RINT-2500 (RIGAKU), with a Ge(111) single crystal incident monochromator. In-situ XRR profiles for the working electrode were obtained by decreasing the cell voltage from the initial open circuit voltage (OCV = 2.80 V) with a potentiostat/galvanostat (Biologic, SP200); to obtain each XRR profile, the positive electrode was kept for 30 min at each voltage, where each step was 25 mV, corresponding to the average scan rate of 0.014 mV s^{-1} .

2.3. SEM observation and XPS analyses

Images of surface and cross section of the electrodes were observed by a field-emission scanning electron microscopy (JEOL JSM-6500F). For the FE-SEM observation, two kinds of discharged (lithiated) Sn electrodes were prepared by holding the electrodes at 2.55 V and 1.2 V for 12 h in the LiPF_6 electrolyte, respectively. The electrode samples were taken out from the cell, washed by the solvent (EC/DMC = 1/2 in v/v) and then by DMC in the glove box, dried for 1 h in vacuum, and transported to the SEM in an Ar gas atmosphere.

Chemical bondings of the surface layer formed on the Sn electrode were investigated by X-ray photoemission spectroscopy (XPS, JEOL JPS-9010TRX) with Mg $K\alpha$ radiation (1254 eV), and those of the bulk (or near the Sn bulk) were also evaluated from the profiles after etching by Ar-ion sputtering at 300 eV. The electrode samples for the XPS analyses were prepared in the same procedure as those for the SEM observations; the typical samples were prepared by holding at 2.0 V and 1.2 V for 12 h in the same electrolyte. The energy calibration was done with Si 2p (99.7 eV) coming from the Si wafer.

3. Results

Fig. 1 shows the CV profile obtained for the Sn electrode. The profiles below 0.77 V show the typical CV for the formation of Sn–Li compounds. [3,11,12] In the higher voltage region, three cathodic peaks are observed at 1.40, 1.70, and 2.55 V in the first cycle. The peaks at 1.40 and 1.70 V (“b”, surrounded by a solid line square) are

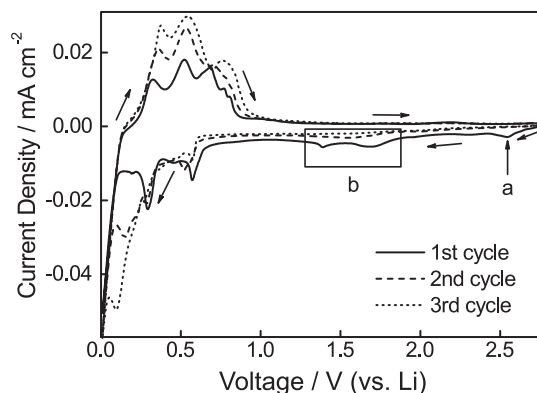


Fig. 1. Cyclic voltammogram of the Sn electrode between 0.01 and 2.80 V at a sweep rate of 0.1 mV s^{-1} in a mixed EC/DMC solvent with 1 M LiPF_6 solute. Arrows indicate the direction of the sweep.

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