



In situ electron microscopy and X-ray photoelectron spectroscopy for high capacity anodes in next-generation ionic liquid-based Li batteries

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ABSTRACT

Based on electron microscope techniques developed for ionic liquids (ILs), which have both high stability under vacuum and an antistatic nature, specially-designed Li battery cells with all components contained in actual Li batteries were fabricated for *in situ* electron microscope observation. Various interesting anode behaviors in the Li battery were observed. For example, Si thin flake active material can store Li(I) electrochemically, causing the morphology to change into a ribbon-like or isotropic expanded structure. Surprisingly any damage to the Si material was not recognized by nanoscale imaging because of the thin layer structure that can release internal stress spontaneously during lithiation. In addition, the Li metal deposition process was directly observed and a similar approach can be applied to *in situ* X-ray photoelectron spectroscopic analysis.

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1. Introduction

Currently, Li-ion batteries (LIBs) are widely used in many industrial products including laptops, smartphones, and electric vehicles. They support our comfortable modern life everywhere. However, further improvements in LIB devices are required because of technological advances that require shorter charging times and higher capacities. To meet these requirements, many interesting approaches have been proposed [1–3]. One proposal is the use of high capacity anodes using ionic liquid (IL) electrolytes [4–14]. ILs are liquid salts that contain only cationic and anionic species and can maintain a liquid state below 373 K. They are classified in the same family as molten salts with eutectic points greater than 373 K. The desirable features of ILs, e.g., negligible vapor pressure, flame resistance, wide electrochemical window, and relatively high ionic conductivity, are similar to those of molten

salts, except for the handling temperature [15–17]. These features are controllable by designing ionic structures in the ILs, and some IL electrolytes for next-generation batteries have been produced by the same approach [15,16,18–23]. Another advantage of using IL electrolytes is that *in situ* and *operando* analytical techniques, which require vacuum conditions, can be conducted along with the electrochemical measurements, because the IL electrolyte has a negligible vapor pressure.

Investigating the battery reactions by *in situ* and *operando* analytical techniques provides a rare opportunity for obtaining in-depth information on time-resolved changes [24–29]. Several scanning electron microscopy (SEM) techniques have been developed for the *in situ* observation of battery reactions in next-generation high capacity LIBs using specially made cells with the IL electrolytes [30,31]. Morphology variations in Si active materials for high-capacity anodes [32] and several Si composite anodes [33,34] have been observed by an *in situ* SEM technique at the micrometer scale. Lithiation/delithiation of the Si materials has been investigated using an *in situ* backscattered electron (BSE) imaging [32]. In this study, we applied the same concept to *in situ* field emission-scanning electron microscopy (FE-SEM) and *in situ* X-ray photoelectron spectroscopy (XPS). This was performed to

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obtain more detailed information on the nanoscale morphology changes occurring at the interface between the high capacity anodes and electrolytes. In addition, the surface morphology of polyimide-binder Si microparticle anodes was also examined by a novel *in situ* SEM observation cell.

2. Experimental

In situ FE-SEM observation and *in situ* XPS analysis of the binder-free anodes were performed using full cells with mesh-type anodes, LiCoO₂ cathode (3.0 mAh cm⁻², Piotrek Co., Ltd. (Japan)), and glass microfiber filter separator (GF/A, Whatman (UK)). Binder-free handmade Si anodes were prepared using an electrophoretic deposition (EPD) method [32]. The solution used for the binder-free Si anode preparation was dry acetone containing 1.0 g L⁻¹ of Si active materials, 0.4 g L⁻¹ of acetylene black (Strem Chemicals (USA)), and 1.0 g L⁻¹ citric acid monohydrate (Wako (Japan)). The Si active material used was Si thin flakes (Si LeafPowder[®], thickness: 100 nm, lateral size: 4–5 μm, Oike & Co., Ltd. (Japan)). Acetylene black was added as a conduction supporting agent for the Si anodes. A platinum plate was used as the cathode and a copper mesh was served as the anode. The electrodes were separated by 2 cm in the solution and the voltage difference between the two electrodes was set to 100 V and the EPD duration was 15–120 s. For the Li metal deposition/stripping experiment, a Cu mesh anode was used. The electrolytes were 1-ethyl-3-methylimidazolium bis(fluoromethylsulfonyl)amide ([C₂mim][FSA], Kanto Chemical Co., Inc. (Japan)) IL with 0.9 M lithium bis(fluoromethylsulfonyl)amide (Li[FSA], Nippon Shokubai Co., Ltd. (Japan)), 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide ([C₂mim][TfSA], Kanto Chemical Co., Inc. (Japan)) IL with 0.9 M Li[FSA], or lithium bis(trifluoromethanesulfonyl)amide (Li[TfSA], Morita Chemical Industries Co., Ltd. (Japan))–tetraglyme solvate ionic liquid in a 1:1 molar ratio. All Li batteries for *in situ* experiments were assembled in an argon-filled glove box (VAC, OMNI-LAB, H₂O, O₂ < 1 ppm) and immediately placed on a sample stage in the SEM

or XPS system.

To investigate the surface morphology of the polyimide-binder Si microparticle anode, CR2032-type coin cells were used with a hole (ϕ 5 mm) in the bottom case, LiCoO₂ cathode, and separator at the center (Fig. 1). The polyimide-binder Si anodes were prepared in a dry room in accordance with previous reports [35,36].

We converted SEM (S-3400N, Hitachi (Japan)), FE-SEM (SU5000, Hitachi (Japan)), and XPS systems (AXIS Ultra DLD, Kratos (UK)) into *in situ* set-ups by attaching feed-through terminals to examine the electrochemical anode reaction. All electrochemical experiments were controlled with a potentiostat/galvanostat (VersaSTAT 4, Princeton Applied Research (USA)). *Ex situ* SEM images were obtained after rinsing the specimens with battery-grade dimethyl carbonate (Wako (Japan)) in an argon-filled glove box.

3. Results and discussion

3.1. *In situ* FE-SEM observation of the binder-free Si thin flake electrode

It is well-known that the Si thin flake composite anode shows many desirable properties [37]. Recently the *in situ* observation of a binder-free Si thin flake anode was achieved using a common SEM set-up, not a field-emission type [32]. The expansion and shrinkage of Si thin flakes were observed during charge and discharge processes, respectively, functioning as the anode active material for next-generation LIBs. Interestingly, two types of morphology variations were detected. The first was a flat-plate type expansion/shrinkage and the other was a ribbon-type change. No serious damage to the Si thin flakes was observed as a result of the morphological changes. However, this finding was based on SEM observation at the micrometer scale, implying that high-resolution SEM images are required for further investigation.

Fig. 2 shows the high-resolution FE-SEM and BSE images of a binder-free Si thin flake electrode before and after charging. Before charging, original flat plate-like Si thin flakes and acetylene black

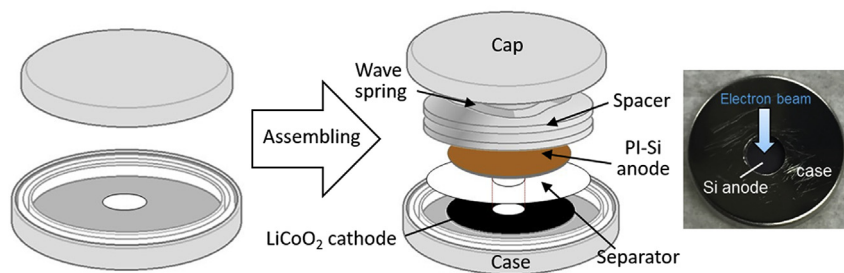


Fig. 1. Schematic drawing and photograph of the novel coin-type cell for *in situ* SEM observation of the polyimide-binder Si anode.

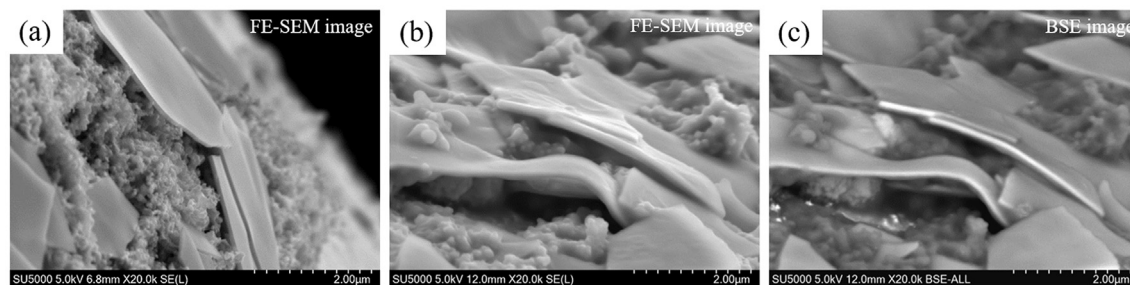


Fig. 2. *In situ* (a, b) FE-SEM and (c) BSE images of the binder-free Si thin flake electrode (a) before and (b, c) after charging. The electrolyte used was a 0.9 M Li[FSA]-[C₂mim][FSA] IL. The charge process was conducted at 0.5C. The cut off voltage for charge process was -3.88 V vs. LiCoO₂.

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