Development of in situ Transmission Electron Microscopy of the Anode Reaction in a Lithium-Ion Battery

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Graphite has been used for many years as the anode material in lithium ion batteries. However, there is a strong demand for improved energy density per weight or volume. As an alternative material to graphite, Sn and Si are being considered. However, in these materials, large volume changes due to the phase transformation that occurs during charge and discharge cause rapid degradation of the electrode. Microstructural analysis during the degradation process using a transmission electron microscope (TEM) is a powerful method. To observe the cell reaction with a liquid phase in a TEM, the use of ionic liquids as electrolytes is effective. In particular, agar-based ionic liquid [1] is excellent due to the stability under electron irradiation. In this study, we have developed a sample preparation method for observing the anode reaction of a lithium ion battery using the agar-based ionic liquid in a TEM. Also, in the aid of in-situ TEM observation of the anode reaction of the lithium ion battery, we have developed partially lithium charged gelatin coated Sn nanoparticles which is stable in an oxidative environment. The microstructure of lithiated Sn particles has been analyzed by TEM.

Gold needles several microns in size were prepared by dispersing diamond powders on a cross-section of gold wire and then irradiating Ar ions perpendicularly to the surface. Samples were coated with a thin film of agar-based ionic liquid with a thickness of 10 nm. The thin film of agar-based ionic liquid (1-butyl-3-methylimidazoliumchloride) in which 15 mol% of lithium salt (LiCl) had been dissolved was prepared by sonicating the agar-based ionic liquid in distilled water. Electric properties of the agar-based ionic liquid were measured using a TEM-STM holder in a JEOL JEM 3100F microscope. We have prepared a green compact of gelatin-coated Sn nanoparticles as an electrode and then lithium was charged in the particles by applying an electric current in an ionic liquid (P14TFSI) in which 20 mass% of lithium salt (LiTFSI) had been dissolved. The microstructure of the particles was analyzed before and after charging with JEOL JEM-2010F microscope.

Figure 1 shows the TEM image of the gold needles with few microns in length and a few hundred nanometers in thickness which are coated with agar-based ionic liquid film on the surface of the specimen. In the left lower side of Fig. 1, a suspended thin film of agar-based ionic liquid film is observed in between the gold needles. In the right upper side of Fig. 1, Pt coated W nano-probe of the STM holder is observed. By bringing the probe into contact with the agar-based ionic liquid film, we have obtained a current-voltage curve which shows ±3V of potential window. Figure 2 (a) shows a TEM image of lithium charged gelatin-coated Sn particles and Figure 2 (b) shows the electron diffraction pattern obtained from the white circle in Fig. 2 (a). As shown in Fig. 2 (a), the gelatin film is still retained coating on the surface, however, the electron diffraction pattern in Fig. 2 (b) indicates the particle are lithiated to be Li_7Sn_2. The result reveals that lithium ions can pass through the gelatin film without any damage which will promise the gelatin coated particles can work as an anode electrode of the lithium ion battery.

We have established method for observing the electrode reaction simultaneously measuring the electric properties. Further, we have showed gelatin-coated Sn nanoparticles as a candidate anode material of the lithium ion battery. We believe by combining these results, in-situ TEM observation of the lithiation process of gelatin-coated Sn nanoparticles will be given.

References

[1] C. Takahashi, T. Shirai, M. Fuji, Solid State Ionics 241 (2013) 53-61.

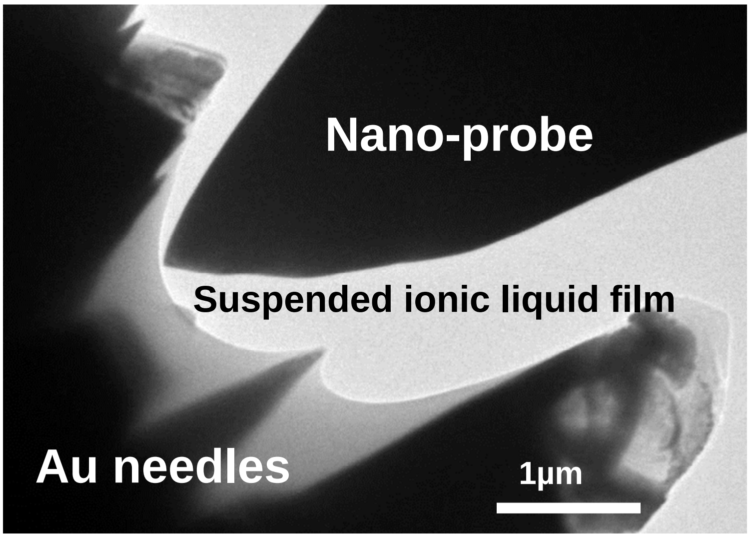

FIG. 1. An agar-based ionic liquid film suspended between gold needles

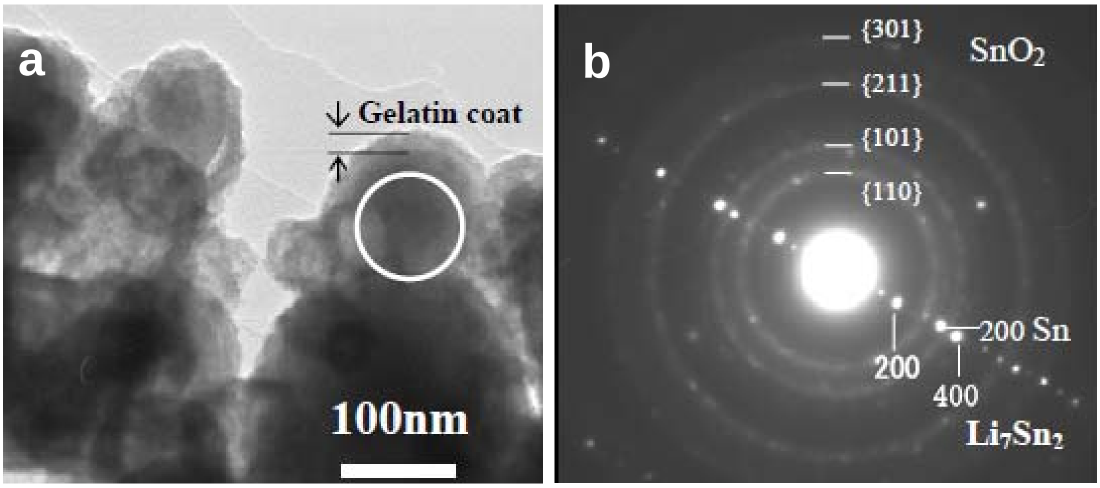

FIG. 2 (a) TEM image of lithium charged gelatin-coated Sn particles. The gelatin coating is retained after lithiation. (b) The electron diffraction pattern obtained from the white circle in (a). Li_7Sn_2 phase is indexed as well as Sn and SnO_2.