

**In-Situ Transmission Electron Microscopy
Observation of Solid Electrolyte Interface Formation
on Si Nanowire Electrode in the Li-ion Battery
Using Liquid Confining Cell**

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Li-ion battery (LIB) is one of the leading candidates for the energy storage systems because of their high gravimetric and volumetric capacity and the high power rates. Recent trend in the LIB technology is to utilize nano-structured electrodes to increase the capacity compared to conventional graphite electrodes. The nano-structured electrodes can accommodate large volume change (~400% for Si) during charge/discharge cycles. This allows the use of Si with theoretical capacity of 4212 mAh/g¹ (an order of magnitude higher than that of conventional graphite electrode) as the anode. Another advantage of using nano-sized electrode is the efficient transport of Li⁺ from the electrolyte to the active material due to the high surface to volume ratio. However, the high irreversible capacity in the thin Si film due to the formation of the solid electrolyte interface (SEI) was reported.^{2,3} On the other hand, properly controlled SEI on the Si thin film prevents the formation of cracks during the charge/discharge cycles decreasing the capacity loss.⁴ Understanding the formation/growth mechanism of the SEI is a key to improve the battery cyclability.

We developed in-situ transmission electron microscopy (TEM) technique to observe the charge/discharge mechanism of the LIB battery electrode in nanometer scale.⁵ However, the method requires the use of an ionic liquid electrolyte with a low vapor pressure due to the high vacuum inside the TEM. In this work, we developed a liquid confining cell to conduct in-situ TEM experiment of the SEI formation using high vapor pressure electrolyte used in the LIBs.

Experimental

Figure 1 shows the schematic illustration of the liquid confining cell. The device consists of the two silicon chips with electron beam transparent silicon nitride membrane windows. W thin film was patterned on the chip as the electrode and SiO₂ was deposited as spacers to secure the space between the two chips to confine the liquid electrolyte. Once the anode and the cathode materials were mounted on each of the chips, the two of the edges were sealed using epoxy glue (Fig. 1B). Si nanowire and LiCoO₂ nano-particles were used as the anode and the cathode, respectively. Then the electrolyte was injected to the device from the non-sealed side inside the argon-filled glove box and the openings were sealed with epoxy glue (Fig. 1C). The electrolyte was inserted by capillary effect when electrolyte was contacted to the opening. The electrolyte used was a 1.0 M LiPF₆ solution in ethylene carbonate (EC)/ethyl methyl carbonate (EMC) (7:3 volume ratio). Figure 2 shows the optical microscopy images of the assembled cell before and after the electrolyte injection. The cell was then mounted on the Nanofactory scanning tunneling microscopy (STM)-TEM holder for the in-situ electrochemical experiment.

Result

Figure 3 shows the temporal evolution of the anode Si nanowire under -3.8 V biasing with respect to the LiCoO₂ cathode. The change in the diameter of the nanowire was observed at the marked region (solid arrow) indicates the electrochemical reaction took place on the nanowire. The high magnification image (Fig. 3C) shows the growth of SEI layers on the surface of the nanowire as indicated by the dashed arrows. The thickness of the layer was ~50 nm which was similar to the value reported in an ex-situ experimental work.⁶

The result demonstrates the liquid confining cell developed in this study is capable of conducting in-situ electrochemical tests inside a TEM and observe the reaction at the electrode surface in nano-meter scale. The device is not only applicable to the LIBs study, but can also be used to observe other applications such as oxidation/reduction reactions in Li-air batteries or fuel cells and corrosions where solid-liquid(gas) interactions play important role.

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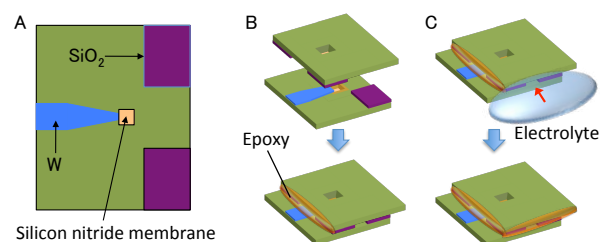


Figure 1. Schematic illustration of the liquid cell.

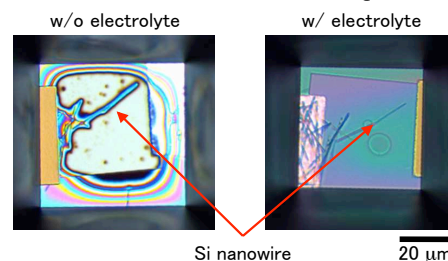


Figure 2. Liquid cell without and with electrolyte.

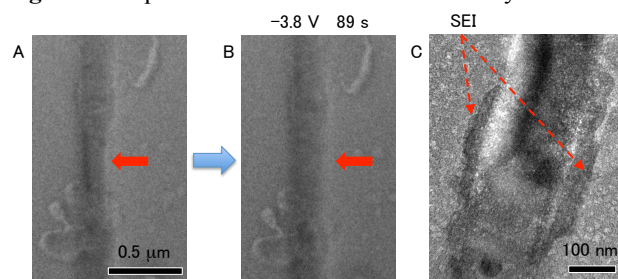


Figure 3. (A,B) Temporal evolution of the Si nanowire under charging. (C) Formation of SEI on the nanowire surface.