In-situ Observation of Zn Electrodeposition with Environmental TEM

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Zinc-air battery is one of the most promising next-generation high-capacity batteries. Some problems, however, should be solved for practical use, e.g., dendrite formation in case of charge. In order to overcome these problems, it is important to reveal mechanisms of reaction, degradation and so on. Environmental transmission electron microscopy (ETEM) can provide dynamic and direct observations of reactions in batteries at very high spatial resolution. In this study, a special ETEM specimen holder enabling to pack liquid electrolyte between two thin membranes and to apply voltage for electrochemical reaction has been adopted. Here, we report ETEM observations of electrochemical deposition and dissolution of zinc metal as preliminary experiments toward in-situ observations of the zinc-air battery reactions.

Figures 1 show TEM images obtained in-situ during the Zn electrodeposition procedure in zinc sulfate solution (0.1 ML) with Titan ETEM (300kV), corresponding to 1.0, 2.0, 4.0 and 6.0 seconds after applying voltage. In these images, nucleation of Zn small crystals is clearly seen as indicated by the arrows, and they had grown to the dendrites having up to 1 μm in length. In addition to the dendrite formation, layered deposition also occurred on the surface of the Pt electrode, as shown in the upper-right image, and the thickness had reached to about 200 nm. By applying inverse voltage, electrodissolution of the deposited Zn had been observed. It is then found that Zn dendrites are generated from same sites on the electrode during electrochemical reaction cycles. Figures 2(a) and (b) show nucleation of the Zn dendrite at 1st and 4th cycles, respectively. Here, it can be confirmed that the nucleation sites are same in both images, as indicated by the arrows. This means that there are sites where Zn is preferentially deposited on the electrode. This is probably caused by the crystallinity of the electrode surface, and if so, it is possible to develop the technique for suppressing the dendrite formation by revealing relationship between the surface structures and the deposition nucleation.

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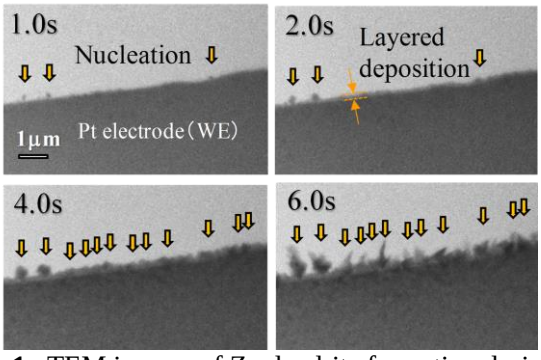

Fig. 1. TEM images of Zn dendrite formation during electro -chemical reaction in liquid electrolyte.

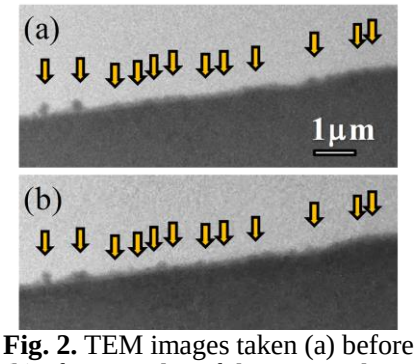

Fig. 2. TEM images taken (a) before and (b) after 4 cycles of depositio / disssolution.