Electro-plating and stripping of lead dendrites observed by operando scanning electron microscopy with an electrochemical cell

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In electrochemistry, a nanoscale viewpoint to the reactions at the interface between an electrode and an electrolyte is indispensable. At the initial stage of electroplating, nanoscale islands seem to randomly form on a substrate and afterward grow up into a thin layer. As the energy storage devices such as a lithium-ion battery or a fuel cell, nanoscale dendrite structures or solid electrolyte interface layer (SEI) formation would dominate the performance of devices. Several groups conducted both visualizing and measuring the reaction of the interface of electrode-electrolyte through in-situ transmission electron microscopy (TEM). Historically, Ross et al. of IBM firstly achieved such observation[1], and subsequently White et al. visualized and analyzed lead dendrites in aqueous solution in-situ TEM[2]. Oshima et al. developed a new type of an electrochemical cell for TEM observation, which was more conventional than the previous one and observed thin copper (Cu) coating processes[3]. Sacci et al. utilized the electrochemical cell for in-situ TEM to analyze the lithium dendrite nucleation and SEI formation at the edge of a gold working electrode during electrodeposition[4]. In most of the previous works using in-situ TEM, the current density of TEM electron beam was high for high resolution TEM images, which causes bubbling of H_2 formation in the liquid electrolyte due to electron beam irradiation. Practically, the current density should be reduced to avoid it, resulted in lower magnifications of the TEM. Thus, we conducted operando scanning electron microscopy (SEM) observation, since the current density of SEM is relatively lower than that of TEM. In addition, the sample preparation for SEM is easier than of that of TEM. As concerned with industrial applications, nanomaterials such as nanoparticles or nanowires with around 100 nm in size have been synthesized mainly by electrochemical methods. The spatial resolution of SEM can be high enough to investigate the electrochemical reactions for nanomaterials. The electrochemical cells for operando SEM have been commercially available, but they have some disadvantage for laboratory research in regard to high cost, experimental limitation and so on.

We developed a conventional electrochemical cell for scanning electron microscopy (SEM) (in-lens FE-SEM (S-5200, Hitachi)) to observe the processes of electro-plating and stripping simultaneously with measuring the cyclic voltammetry using two electrode terminals. Lead dendrites on an Au electrode in a 1.5 M $Pb(NO_3)_2$ solution in the cell were grown and decomposed during a cyclic of voltammogram. The operando SEM observation revealed that initially Pb islands formed, followed by dendritic growth. The substrate shape dependence of the process will be discussed.

References:

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[2] E. R. White et al., ACS Nano. 6 (2012) 6308.

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[4] R. L. Sacci et al., Chem. Commun. 50 (2014) 2104.