

**In situ scanning electron microscopy observation of ion distribution variation
at the electrode-electrolyte interface in an electrochemical cell**

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Many works have been conducted to qualitatively and quantitatively study the mechanism through the combination of macroscopic electrochemical measurements. As an imaging technique in electrochemistry, high-resolution electron microscopy meets the desire to observe the local structure of the electrode and the dendrite formation on a nanoscale. For example, high-resolution transmission electron microscopy (TEM) was used for in-situ real-time observation of metallic crystallization inside liquid samples. However, there are problems such as damages due to electron beam irradiation at high electric current densities and difficulties in preparation of liquid samples with thicknesses less than 100 nm for TEM. Meanwhile, in-situ pseudo-real-time scanning electron microscopy (SEM) observation is more practical than TEM observation, because of relatively low current density and no particular requirement for sample preparation. We developed a conventional in-situ electrochemical cell with two electrode terminals for SEM to observe the processes of electro-plating and stripping for simultaneous measurement of the cyclic voltammetry [1]. The cell was sized to fit into the small space of a custom-made sample holder for in-lens high-resolution field-emission SEM (Hitachi, S-5200) with several current feedthroughs, each of which was connected to a coaxial cable. The cell body possessed a drain on the side of an insulator plate with two holes for the cables, as well as a vessel for a liquid electrolyte at the center of the insulator plate. The insulator had a circular depressed seat for a silicon nitride (SiN) TEM grid. Two Au wires inserted into Kapton tubes were connected to the two coaxial cables, and inserted through the wire holes of the cell body and insulator; only the Au wires were connected to two Au electrodes vapor-deposited on one side of the TEM grid. There were two concentric circular seats for O-rings on a cell cover; one was smaller than the SiN grid and the other one was larger than that. Care was taken so as not for the electrolyte to leak into the vacuum environment during SEM experiments. When the applied electric potential was varied, electrochemical reactions occurred at the end of the vapor-deposited electrode and were observed through the small thin SiN membrane window of the grid with a thickness of 50 nm.

Using the instrument, we observed in-situ consecutive SEM images of electro-deposition and stripping of Pb on the Au electrode through the SiN membrane window while measuring the cyclic voltammogram. The SEM images clearly showed the electro-deposition and stripping of Pb on a nanoscale, in accordance with the cyclic voltammogram curves. From the SEM observation, we distinguished the growth modes of Pb deposits, exhibiting the particulate band structures and dendrite structures, depending on the roughness of the electrode. The brightness of SEM images in the electrolyte region changed in the course of the cyclic voltammetry, which implied the change of Pb concentration of the electrolyte near the electrode. Furthermore, we developed a three-terminal electrochemical cell for the SEM to precisely control the electric potential of the electrode, one of which is used as a reference electrode. Therein, a fine-smoothed Au wire is used as a working electrode; the results will be presented.

Reference: [1] G. He, Y. Oshima, and M. Tomitori, JJAP 60 (2021) 035509.