## Abstract

Understanding of the dendritic structure growth and stripping mechanism during electrochemical reactions is of great importance to improve the functionality of electrochemical technique devices. Thus, a lot of devoted works had been conducted to uncover the mechanisms qualitatively and quantitatively through combination of typical electrochemical measurements using macro scale electrodes. As an imaging technique during electrochemical reactions, electron microscopies with high resolution meet the desire for both the local structure of electrode and the dendrite formation at nanometer level characterization. For most of the previous works, transmission electron microscopy (TEM) was utilized for in-situ real time observation of metallic crystallization inside the liquid specimen. There have been difficulties like damages due to electron beam irradiation at thigh electric current densities and preparation of liquid specimen with thicknesses of thinner than 100 nm, which is the limitation of transmission of electrons in TEM, and so on. As for the 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 the thickness of the specimen.

We developed a conventional in-situ electrochemical cell with two electrode terminals for SEM to observe the processes of electro-plating and stripping simultaneously with measuring the cyclic voltammetry. The cell was sized to fit into the small space of the custom-made specimen holder for Hitachi S-5200 Fe-SEM with several current feedthroughs, each of which was connected to a coaxial cable. The front plane of 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 liquid electrolyte at the center of the insulator plate. The insulator had a circular depressed seat for a silicon nitrite TEM grid. Two Au wires inserted into Kapton tubes were connected to the two coaxial cables respectively and inserted through the wire-holes of cell body and insulator; only the Au wires were set to the concentric hole and connected to two vapor-deposited Au electrodes on the one side of the TEM grid. There were two concentric circular seats for O-rings on a cell cover; one was smaller than the silicon nitrate grid and the other one was larger than that. Care was taken so as not for electrolyte to leak to the vacuum environment during SEM experiments. When the applied potential was varied, electrochemical reactions occurred at the end of the vapor-deposited electrode and were observed through a small thin silicon nitrite membrane window of TEM grid with a thickness of 50 nm, through which the SEM electron beam was able to pass.

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 that the electro-deposition and stripping of Pb on a nanoscale, which were consistent with the cyclic voltammogram curves. From the SEM observation, we distinguish the growth modes of Pd deposits, exhibiting the particulate band structures and dendrite strucutres, 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. This study demonstrated the potential of in-situ high-resolution SEM combined with the electrochemical cell.



**Key words: electrochemical cell, scanning electron microscopy, cyclic voltammetry, electro-plating and stripping**