

Depth Profiling of Solid Electrolyte Interphase in Li-Ion Battery Electrodes with Glow Discharge Optical Emission Spectroscopy

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Cell capacity deterioration especially on long duration use and at high temperature is a serious problem in Li-ion battery (LIB). It is well known that solid electrolyte interphase (SEI) formed in the graphite electrode is closely related to cell performance. There are numerous studies on characterization of SEI with XPS, FT-IR, and NMR, which give us qualitative information of SEI components. In general, side reactions such as SEI formation inhomogeneously occur, so that quantitative analysis as well as the in-plane and in-depth distribution of SEI components should be also important in order to elucidate the cell deterioration mechanism.

Radio frequency glow discharge optical emission spectroscopy (rf-GD-OES) is an in-depth elemental analysis technique using Ar ion sputtering. It enables us to profile LIB electrode in depth direction with 1 nm-100 μm scale. In previous works, GD-OES was applied to positive and negative electrodes with various states of charge.^{1,2} Depth profiles from their surface to current collector were successfully collected. Lithium concentrations at various depths were correlated with results of ICP-MS analysis. Low sputtering rate and redeposition in graphite electrodes were main obstacles for practical application of GD-OES to deteriorated electrode, because it was difficult to obtain reliable intensities from samples within a suitable measurement time.³ In this study, SEI in capacity-faded graphite electrodes was studied by GD-OES depth profiling. In order to improve the reliability of GD-OES measurement, the reactive sputtering with small amount of hydrogen was studied.⁴ Separately, SEI layer deposited on the electrode surface was analyzed in detail by a low sputtering rate with a low duty cycle of pulse.

Commercially available Al-laminated type cell samples were composed of LiM_2O_4 -based positive electrode and graphite negative electrode.⁵ A cycle test for 300 or 600 cycles under 2.5-4.0 V cut-off voltages and C/2 current rate at 25 or 45 $^\circ\text{C}$, or a storage test for 46 or 85 days at 45 $^\circ\text{C}$ was operated for them. After these tests, the cells were disassembled and the negative electrode samples were rinsed with dimethyl carbonate in an argon-filled glove box. Then the samples were measured with rf-GD-OES (GDA750: Rigaku/Spectrums). The measuring spot size was 4 mm in diameter. In the high-rate measurement for the whole electrode layer, a discharge gas of Ar-1% H_2 was used. In the detailed surface measurement for SEI layer deposited on the electrode, the duty cycle of pulse was reduced to 10%. Ne discharge gas was used for its high sensitivity in detecting F. Measured elements and the emission lines were H (121.57 nm), Li (610.41nm), C (156.14nm), O (130.22nm), F (685.60nm), P (177.50nm), Mn (403.45 nm), and Cu (327.49 nm).

Figure 1 shows a GD-OES depth profile of the graphite electrode layer for 45 $^\circ\text{C}$ -600 cycle cell (72.9%, the lowest capacity retention among the tests). The sputtering time was about 5000 s for 50-60 μm thickness

by use of Ar-1% H_2 , which was much faster than 16000 s in the case of conventional pure Ar. The contents of Li, P, and Mn are high in the surface region and decrease toward Cu current collector; it indicates inhomogeneous distributions of them in-depth of the electrode. Li and P could be attributed to SEI component. Mn would be attributed to the species which were dissolved from the positive electrode during the cycling or storage, migrated and precipitated on the negative electrode. The Li content increased with degradation degree of the samples, and its depth profile showed a gradual decline, suggesting that SEI film in the inner layer increased with the cell degradation.

Figure 2 shows the detailed surface profile of the graphite electrode for 45 $^\circ\text{C}$ -300 cycle cell (72.9 % capacity retention). The peaks in 0-40 nm indicate the SEI layer deposited onto the electrode surface. The amount of Li in the graphite electrode was smaller at 45 $^\circ\text{C}$ cycle than those at 25 $^\circ\text{C}$ cycle and storage. This result did not correspond to the degradation degree.

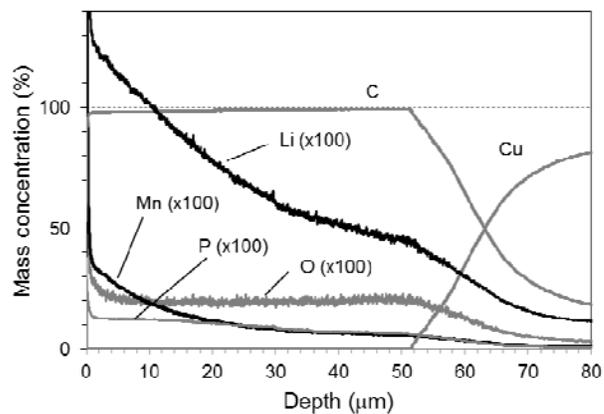


Fig. 1 GD-OES depth profile for a degraded graphite electrode (45 $^\circ\text{C}$ -600 cycles, 72.9 % capacity retention).

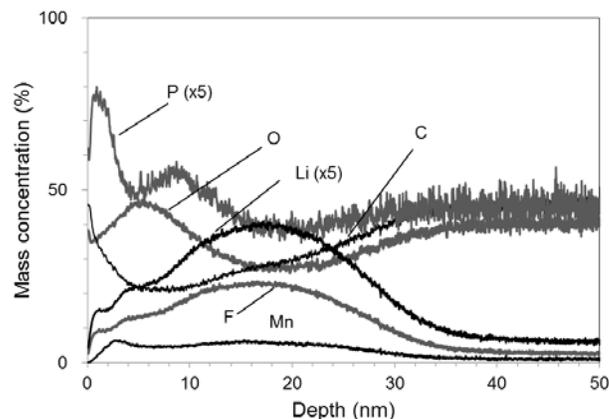


Fig. 2 Detailed surface profile for a degraded graphite electrode (45 $^\circ\text{C}$ -300 cycles, 81.3 % capacity retention). The depth value was corrected by a new electrode before test as a reference.

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