Development of in-situ Raman technique for Li ion battery

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Introduction
In recent years, Lithium ion batteries have attracted much attention as a power source for vehicles. However, the higher capacity and power are required for the future automotive application. In order to achieve the higher reaction efficiency, it is crucial to understand interfacial reactions between electrode and electrolyte. A few studies have been reported regarding to the reaction using in-situ Raman. They focused on the changes of crystal structure and surface of electrodes during charge-discharge reaction [1, 2]. In this study, we developed in-situ Raman technique to understand the Li ion behavior at the interface.

Experimental
The excitation wavelength of Raman were 532, 1064 nm. A specially designed electrochemical cell equipped with optical window was constructed to perform in-situ Raman. LiNi0.5Mn1.5O4 (LNCM) as a positive electrode and graphite carbon as a negative were used in this study. Ethylene carbonate (EC) / ethyl-methyl carbonate (EMC) / dimethyl carbonate (DMC) with LiPF6 was employed as an electrolyte (Electrode configuration is shown in Fig. 1).

Figure 2 shows Raman spectra at ex-situ measured with 532, 1064 nm laser respectively. Lines around 600-1000 cm⁻¹ are assigned to electrolyte, i.e. EC and EMC, and 1300-1600 cm⁻¹ are graphite [3, 4]. Only with 1064 nm, both information of electrode and electrolyte could be detected, due to the difference of penetration depth. Figure 3 shows variation of in-situ Raman result under potentiostatic condition measured with 1064 nm. On Raman spectra there is no effect of fluorescence generated in the decomposition of LiPF6 with 532 nm. Fluorescence caused a measurement problem in the previous study [5]. Raman spectra suggest that an electrolyte state, Li ion solvated/un-solvated, changes during charge reaction.

**Results and discussion**

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**References**