### 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. LiNi<sub>x</sub>Co<sub>y</sub>Mn<sub>z</sub>O<sub>2</sub> (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 LiPF<sub>6</sub> was employed as an electrolyte (Electrode configuration is shown in Fig. 1).



#### **Results and discussion**

Figure 2 shows Raman spectra at *ex-situ* measured with 532, 1064 nm laser respectively. Lines around 600-1000 cm<sup>-1</sup> are assigned to electrolyte, i.e. EC and EMC, and 1300-1600 cm<sup>-1</sup> 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  $\text{LiPF}_6$  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.







Fig. 3 Variation of *in-situ* Raman spectra at various potentials vs. Li/Li<sup>+</sup>

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