

Electrochemical in-situ Raman Spectroscopic Studies at the Lithium ion Active Material Particle Surface during the Charge-Discharge Processes

Tadashi Awatani, Ritsuko Kitano, Hideto Imai,
Jiping Ye, Takashi Matsumoto

NISSAN ARC Ltd, 1 Natsushima-cho, Yokosuka,
Kanagawa, Japan 237-0061

1. Introduction

In development of a highly efficient lithium ion battery for commercial use, it is of the upmost importance to directly understand the electrochemical behavior at the surface of the commercially-practical active particle, where the Li^+ ion transfer actually takes place. The electrochemical behavior of the anode active material particle during the charging and discharging processes was studied by Raman spectroscopy [1] using an original in-situ electrochemical spectroscopic cell that allowed one to study the surface state at the active particle of interest.

2. Method

The graphite anode electrode was prepared by mixing of pyrolytic carbon coated graphite with PVDF binder. A half cell was prepared with the lithium metal counter electrode and electrolyte solution using 1 M LiPF_6 EC/DEC (7:3). All electrochemical Raman spectral measurements were measured under confocal alignment. High resolution Raman mapping measurements were carried out under 532 nm excitation, while, progressive spectra in the charge and discharge potential processes were obtained during a potential sweep rate of 10 mV/min and measured under 633 nm excitation.

3. Results and Discussion

Figure 1(a) shows the composite Raman mapping image showing the compositional distribution of anode active particles taken at charged state (held at constant voltage of 50 mV). The individual composition map was constructed via multivariable analysis to represent individual intercalation state LiC_6 , LiC_{12} and organic deposit distribution. The intercalation state was differentiated by using the G-peak positional shift [2] as shown in the G-peak center map in Figure 1(b). Li^+ ion intercalation state map showed that even at high “charged” state, the anode active material that participated as active (LiC_6) and inactive (C_6) particles were clearly resolved.

The detailed Raman spectral change with charging and discharging process at the anode particle circled within Figure 1 is shown in Figure 2. The series of in-situ electrochemical Raman spectra was obtained during the charging (1750 mV~50 mV) and discharging cycle (50~1200 mV) at the graphite anode active material particle. During the charging stage, region (a) in Figure 1, the G-peak positioned at 1580 cm^{-1} (Raman active graphite structure mode, $E_{2g}(2)$ mode) initially broaden and a new peak positioned at higher wavenumber of 1600 cm^{-1} appeared with increasing level of Li^+ ion insertion [2]. The G-peak during the charged state (50 mV) shown in region (b), vanished at high Li^+ ion intercalation due to increased expansion of the graphite interlayer.

Additionally, an interesting unknown spectral feature was observed at low wavenumbers, shown in region (c), where peak positioned at 152 cm^{-1} was observed. This peak showed a reversible behavior that increased in intensity with increasing Li^+ ion insertion

contents into the graphite interlayer and decreased accordingly with the discharging process. Comparative analysis of this spectral feature with the simultaneously obtained current (charge) data showed the peak was observed at only highly-charged state was consistent to Li metal deposition at the graphite anode particle surface [3].

Further details of the in-situ electrochemical Raman spectroscopic and mapping results will be presented during the talk.

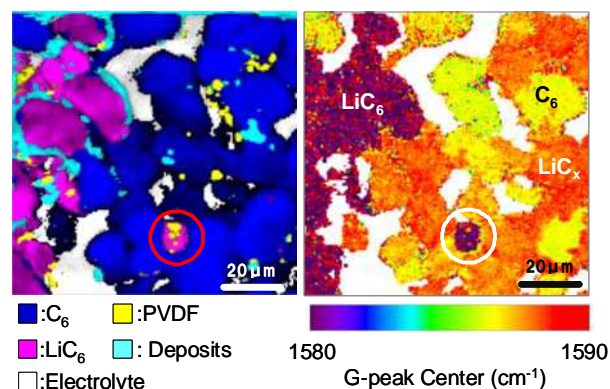


Figure 1. EC-in-situ Raman mapping result showing the (a) compositional map of anode active material particles (b) G-peak center map showing the Li^+ ion intercalation state distribution.

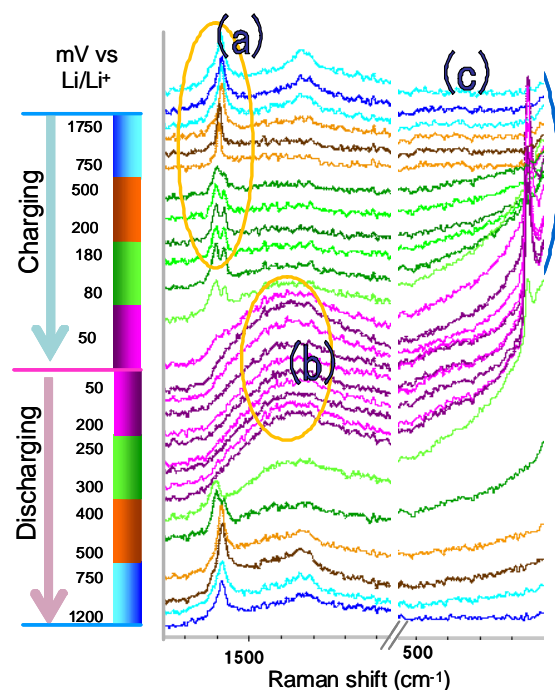


Figure 2 EC-in-situ Raman series spectra during charging and discharging processes at the graphite anode active material particle surface.

Reference

- [1]. R. Baddour-Hadjean and J.P Pereira-Ramos, Chem. Rev. 2010, 110, 1278–1319.
- [2]. L.J. Hardwick, H. Buqa, P. Novák, Solid State Ionics 177 (2006) 2801-2806.
- [3]. T. Awatani, et al. in preparation.