Battery analysis using *in situ* synchrotron, neutron and NMR methods

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Introduction

In situ analysis enables us to observe dynamic behavior occurring in an operating battery without touching its components and so actual processes associated with charging/discharging can be elucidated. The main difficulty in *in situ* analysis has been low time resolutions, namely, it often takes so long time to measure one spectrum/pattern that the status changes during the measurement are unacceptably large. Recently the measuring probes have been much improved and we can observe the phenomena at practical charging/discharging rates. In this study, three *in situ* techniques developed in the RISING project of NEDO, namely synchrotron X-ray, neutron and nuclear magnetic resonance (NMR) methods, are shown and their application to lithium battery analysis using their measurement characteristics are demonstrated.

Experimental method

Synchrotron X-ray experiments were performed at Spring-8 and Ritsumeikan SR center, Japan. Neutron experiments were employed in J-PARC, Japan. NMR spectra were measured using a spectrometer at a magnetic field of 14.1 T with a wide-bore static probe.

Results and discussion

Synchrotron X-ray based methods shows the greatest time resolution (ca. 1 s) for measuring an X-ray absorption spectrum or an X-ray diffraction pattern. The space resolution of 1-100 μm is also available.

For $LiFePO_4$ electrodes, we tracked the phase transition behavior under 1C rate charging conditions [1] and figured out that there are various intermediate states between the LFP (discharged) and FP (charged) phases that have not been clarified with *ex situ* analysis. The smaller the particle size was, the greater the intermediate states changes until it reached to the thermodynamically stable FP phase. At much higher rate of 10C, we found a new metastable crystalline phase “LixFP” [2]. This result shows that such a metastable phase can be a kinetically favorable intermediate when a strong motive force (large polarization) exists in the system.

We examined $LiNi_{0.5}Mn_{1.5}O_4$ as another example. It has been known that there are two phase transitions in its charging processes, namely $LiNi_{0.5}Mn_{1.5}O_4$ (Li1) to $Li_{0.5}Ni_{0.5}Mn_{1.5}O_4$ (Li0.5) and Li0.5 to $Ni_{0.5}Mn_{1.5}O_4$ (Li0). With the *in situ* measurement, it turned out that the Li0.5 phase is clearly observed during charging and is obscure during discharging, showing the thermodynamically reversible but kinetically asymmetric behavior. Using potential step experiments and kinetic analysis, this phenomenon is ascribed to the slow phase transition between Li0.5 and Li0, compared to that between Li1 and Li0.5. The high time resolution was effective in data acquisition during the potential step experiments.

For the analysis of reaction distribution in the electrode, we persuade both the time and space resolutions [3]. In the case of $LiFePO_4$ electrodes, there was great reaction inhomogeneity inside the electrode, due to the non-relaxing nature of the two-phase coexistence reaction. These analytical results are useful for fabricating electrodes with high rate capability and designing charge-discharge protocols with low electrode degradation.

Phenomena at the interface were also elucidated for an $LiCoO_2$ electrode with *in situ* surface sensitive X-ray absorption method [4]. It is shown that the surface cobalt species is reduced with the strong reducing power of the organic solvents and this causes the irreversible behavior at the surface. The effect of coating on the stability of the surface species was also clarified with this method [5].

Neutron is a powerful probe for battery analysis as it has even better permeability than synchrotron X-ray and clearly detects light elements such as lithium and oxygen. Nevertheless, so far there has been limited application to the battery analysis mainly due to its low time resolution. Thanks to the J-PARC facilities offering strong power to the neutron beamlines, we can now employ *in situ* measurements with a small cylindrical cell. In our experiments we clearly and simultaneously observed neutron diffraction peaks corresponding to the graphite and layered oxide as respectively negative and positive electrode materials.

NMR as a probe for lithium battery analysis is particularly useful to detect environmental changes around lithium with high sensitivity. As it is unfortunately difficult to apply magic-angle spinning techniques to the *in situ* analysis, obtaining meaningful spectra with paramagnetic materials remains challenging. We here examined *in situ* NMR analysis of a cell containing an $LiCoO_2$ positive electrode [6]. The ^7Li signal changes were tracked during charging and discharging and the signal intensity was semi-quantitatively evaluated. The behavior can be mainly correlated with the crystal structure changes, nevertheless, information characteristics to the NMR method such as small lithium deficiency in the lithium cobaltate (and hence subtle irreversibility) was also obtained. In addition, signals from the lithium species in the negative electrode and the electrolyte were simultaneously detected and analyzed.

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