Characterization of Partial Entropy Change of Electrode Reaction of $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$

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The partial entropy change ($d\Delta S$) of electrochemical reaction is one of the main causes of heat generation during charge and discharge for lithium-ion battery (LIB). Thermal simulation is important for LIB to ensure safety, and without information of $d\Delta S$, we cannot estimate variation of temperature of LIB accurately. In addition, $d\Delta S$ is a thermodynamic parameter which relates to potential of electrochemical reaction. Since lithium exchange occurs between anode and cathode in LIB and mean value of lithium ion concentration in electrolyte is kept constant, $d\Delta S$ reflects variation of crystal and electronic structures as well as lithium composition of active materials in each electrode. There are some previous works to evaluate $d\Delta S$ of reaction for commercially available LIBs[1], and half-cells[2] of electrode materials combined with lithium metal anode, where $d\Delta S$ has been caracterised from temperature dependency of open circuit voltage (OCV). In this study, $d\Delta S$ of reaction of $Li_xNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ (NMC) which is one of major cathode materials currently used in LIBs has been measured by the same method, and dependencies on not only lithium conposition x but also temperature have been discussed.

Figure 1 shows the measured values of $d\Delta S$ of lithium intercalation reaction for NMC (*vs.* Li/Li^+). At the room temperature, maximum is shown at $x = 0.7$ and around. Temperature dependency is small in the higher temperature for all composition range. On the contrary, in the lower temperature, large temperature dependency is found in the composition range of $x > 0.8$. However, crystal phase transition of NMC has not been clearly observed for this composition and temperature ranges by *ex-situ* XRD analysis. Since OCV has continued to decrease long time even in constant tempetature condition at lower temperature, relaxation process of lithium distribution may cause this variation of $d\Delta S$.

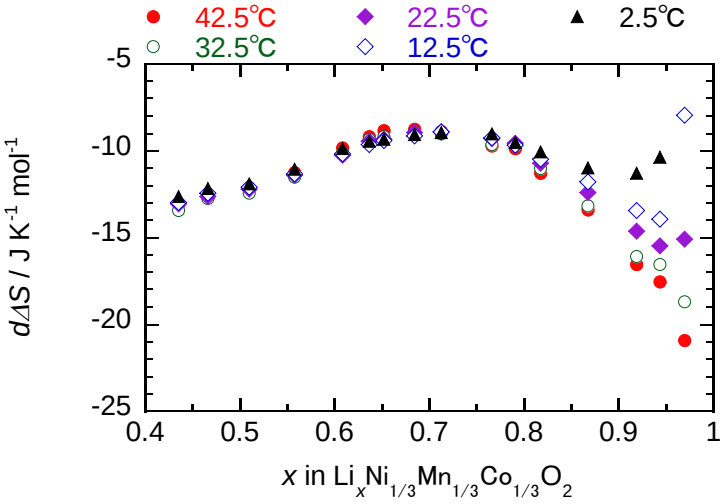

Fig. 1. The partial entropy change, $d\Delta S$, of intercalation reaction of NMC *vs.* Li/Li^+ at several temperatures.

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References:

[1] K.Takano, Y. Saito, K. Nozaki, K. Kato, A. Negishi, T. Kato, J. Appl. Electrochem. 32 (2002) 251-258.
[2] Y. F. Reynier, R. Yazami, B. Fultz, J. Electrochem. Soc. 151 (2004) A422-A426.