X-ray Diffraction Measurements below Ambient Temperature on Over-stoichiometric $LiCoO_2$

Kazuhiko Mukai

Toyota Central Research & Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan

In spite of extensive studies on lithium-ion battery (LIB) materials, lithium cobalt oxide $LiCoO_2$ still keeps a dominant-position in positive electrode material for commercial LIB. As a function of lithium content, i.e. as x in Li_xCoO_2 decreases from 1, stoichiometric $LiCoO_2$ (ST-LCO) which is prepared with Li/Co ~ 1 exhibits a structural phase transition between rhombohedral (*R*-3*m*) and monoclinic (*C*2/*m*) phases at x ~ 0.5 [1], while over-stoichiometric $LiCoO_2$ (OST-LCO) which is synthesized with Li/Co > ~ 1.05 maintains the rhombohedral (*R*-3*m*) phase at x ~ 0.5 [2]. This is clearly understood by the change in charge and discharge curves around 4.1 V (see Fig. 1). According to our X-ray diffraction (XRD) measurements on ST-LCO, the x = 0.53 sample shows two structural phase transitions at ~ 330 (= T_{s1}) and 140 K (= T_{s2}). To elucidate the structural change of LCO, we have performed XRD measurements for the OST-LCO sample in the temperature (T) range between 300 and 100 K at the synchrotron radiation facility, SPring-8, Japan.

Figure 2 shows the XRD patterns for the OST-LCO sample with x = 0.51 at (a) 300 and (b) 200 K. The XRD pattern at 300 K is assigned as the rhombohedral (*R*-3*m*) phase as reported previously [2], whereas that at 200 K is assigned as monoclinic (*C*2/*m*) phase. This indicates the structural phase transition (= T_{s1}) between the rhombohedral (*R*-3*m*) and monoclinic (*C*2/*m*) phases as in the case for ST-LCO. Based on the T dependence of lattice parameter β_M as shown in Fig. 3, the OST-LCO sample is found to exhibit another structural phase transition around 170 K (= T_{s2}). That is, as T decreases from 200 K, β_M decreases with decreasing T down to 170 K, and then gradually increases with further decreasing T. This suggests that the crystal structure for the OST-LCO sample changes into the rhombohedral (*R*-3*m*) symmetry again below 170 K.

Acknowledgements

The XRD experiment was performed at the SPring-8 with the approval of the Japan Synchrotron Radiation Institute (Proposal No.2011A1854). The author appreciates Mr. Y. Kishida, Dr. H. Nozaki, and Mr. K. Dohmae for help with the XRD measurements. This work was partially supported by Grant-in-Aid for Scientific Research (C), 25410207, MEXT, Japan.

References

[1] T. Ohzuku and A. Ueda, J. Electrochem. Soc., **141** (1994) 2972.
[2] S. Levasseur et al., Chem. Mater. **15** (2003) 348.
[3] K. Mukai et al., J. Power Sources, **192** (2009) 684.

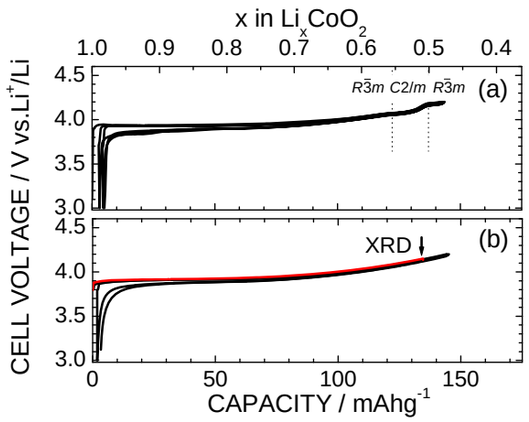

Fig. 1. Charge and discharge curves of (a) ST-LCO/Li and (b) OST-LCO/Li cells operated with a current density of 0.17 mA·cm^{-2} at 298 K. The Li/Co ratio for staring material is 1.02 for ST-LCO and 1.05 for OST-LCO. The arrow in (b) indicates the Li composition (x = 0.51) for the low-T XRD measurements.

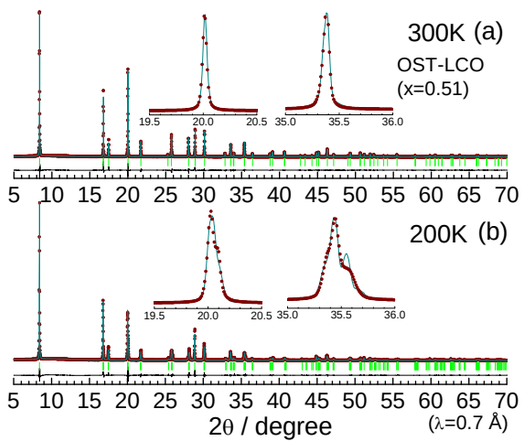

Fig. 2. Rietveld analyses for the OST-LCO sample with x = 0.51 at (a) 300 and (b) 200 K. The XRD patterns at 300 and 200 K are assigned as rhombohedral (*R*-3*m*) phase and monoclinic (*C*2/*m*) phase, respectively.

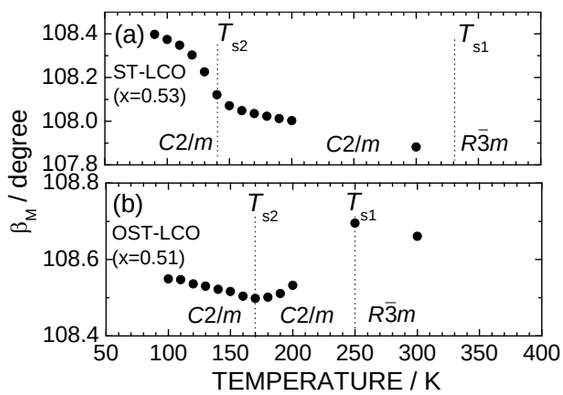

Fig. 3. Temperature dependence of lattice parameter β_M for the (a) ST-LCO sample with x = 0.53 and (b) OST-LCO sample with x = 0.51.