

Degradation mechanism of LiCoO₂ in aqueous lithium-ion batteries

Hyunjeong Oh^a, Moony Na^a, Keisuke Yamanaka^b, Toshiaki Ohta^{*,b}, Hye Ryung Byon^{*,a}
^a *Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST) and
Advanced Battery Center, NanoCentury, KAIST Institute, 291 Daehak-ro, Yuseong-gu,
Daejeon 34141, Republic of Korea*

^b *Synchrotron Radiation Center, Ritsumeikan University, Kusatsu, Shiga, 528-8577, Japan*

E-mail: ohj2010@kaist.ac.kr, hrbyon@kaist.ac.kr

Since the accidents that nonaqueous lithium-ion batteries catch fire have been often reported, aqueous electrolyte solution-based rechargeable lithium batteries (ARLB) have been highlighted. However, the conventional positive electrodes of lithium transition-metal oxide such as LiCoO₂(LCO) and LiNi_{1/3}Mn_{1/3}Co_{1/3}O₂(NMC) have suffered from poor cyclability in aqueous electrolyte solution. The layered two-dimensional structure of LiCoO₂(LCO) shows notably poor stability at low pH, which may be attributed to surface degradation of LCO from water [1] or H⁺ intercalation [2]. The fundamental understanding of degradation process of such positive electrodes is still superficial.

Here we shed light on irreversibility of LCO electrode during charge and discharge process using various X-ray measurement techniques. Three different LCO electrodes, examined via cyclic voltammetry or galvanostat in aqueous solution (with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI), pH = ~6.8), basic solution (with LiTFSI and LiOH, pH = ~9) and nonaqueous electrolyte solution (with LiTFSI and 1:2:1 volume ratio of EC: DMC: DEC), were compared. The LCO electrodes in nonaqueous and basic aqueous solution show the formation of cathode-electrolyte interphase (CEI), and the resulting stable capacity retention for initial 5 cycles. However, severe oxygen evolution reaction (OER) occurs in basic solution as the working potential range is narrow in the aqueous solution and LCO acts as the OER catalyst [3], thereby the basic solution is expected to degrade the cell performance rapidly. The LCO with neutral aqueous electrolyte solution exhibits capacity fading during cycling, despite negligible OER. The X-ray photoelectron spectroscopy (XPS) and X-ray absorption near-edge structure (XANES) spectra reveal insignificant presence of CEI and short-range distortion of oxygen for both surface and bulk LCO, while trivial change is observed in long-range order acquired from X-ray diffraction (XRD). It is therefore believed to H⁺ intercalation instead of Li⁺ to distort local oxygen of LCO in the absence of CEI. We also suggest development of surface protection layer of LCO in ARLB to improve cycling performance, which will be discussed in the presentation.

References:

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