Understanding the interfacial reactions of LiCoO₂ positive electrodes in aqueous lithium-

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Figure S1. XAS spectra of LCO (black), and reference powders of Co_3O_4 (red) and $Co(OH)_2$ (blue) at (a) Co *L* edge and (b) O *K* edge. Bottom to top graphs are taken with PFY, TEY and PEY modes, respectively. In Co L_3 edge spectra, the white line of LCO at 780.3 eV and Co(OH)₂ at 778.4 eV indicate Co^{III} and Co^{II} signal, respectively.



Figure S2. XRD patterns of pristine LCO (black), 5 cycled LCO with 1 m LiTFSI in EC/DMC/DEC (red) and 5 cycled LCO with 1 m LiTFSI(aq) at pH 8 (blue). (a) Wide angle range and (b) High magnification graphs at the 003 reflections.



Figure S3. XPS surface analysis of pristine LCO (black), 5 cycled LCO with 1 m LiTFSI in EC/DMC/DEC (red), 5 and 10 cycled LCO with 1 m LiTFSI(aq) (blue and pale blue, respectively). (a) C 1s, (b) O 1s, (c) Li 1s, (d) Co 2p, (e) F 1s, and (f) S 2p binding energy (BE) region. (g) Atomic % of all elements. The red letters indicate chemical species observed only with non-aqueous electrolyte solution. Atomic % of F, S, O, and Li is also increased with non-aqueous medium.



Figure S4. ICP-OES analysis of dissolved Li and Co in pure water and acidic solution (1 mM

H2SO4) after OCP for 1 h.



Figure S5. XRD patterns of LCO as prepared (black), after holding at OCP for 1 h, after anodic LCV by 0.8 V, and 1.1 V at a scan rate of 0.2 mV s⁻¹ from bottom to top graphs. The blue and brown graphs are LCO with aqueous 1 m LiTFSI solution at pH 8 and pH 3, respectively. The asterisk mark indicates XRD of carbon paper as the substrate.



Figure S6. Cyclic voltammograms (CVs) of LCO electrodes cycled at (a) pH 8, (b) pH 3 solution containing 1 m LiTFSI at a scan rate of 1 mV s⁻¹. All redox signals disappear from the 2nd cycle with acidic solutions.



Figure S7. Galvanostatic voltage profiles of LCO at pH ~11 of 1 m LiTFSI(aq) at 0.2 C. The long charging plateau at ~0.8 V vs. Hg/HgO arises from the oxygen evolution reaction (OER)



Figure S8. XPS of LCO electrodes as prepared (black), 5 cycled at pH 8 (blue). and 5 cycled at pH 11 with LiTFSI(aq) in O 1s BE region. At pH 11, the Co-O lattice signal at 529.7 eV is retained.



Figure S9. XAS spectra of LCO before and after galvanostatic cycles with LiTFSI(aq) at pH 8 (blue) and pH 11 (yellow) and pH ~8 (blue). (a–b) Co L_3 edge spectra with (a) PFY and (b) PEY mode. (c–d) O *K* edge spectra with (c) PFY and (d) PEY mode. CC and DC indicate charge and discharge, respectively.



Figure S10. Nyquist plots of LCO electrodes in half cells with 1 m LiTFSI(aq) at (a) pH 8 and (b) pH 11, analyzed by using electrochemical impedance spectroscopy (EIS). Galvanostatic cycled were performance for 3 cycles, and EIS was measured at OCP and -0.2 V after each cycle with a frequency range of 100 kHz ~0.1 Hz. (c) Equivalent circuit for fitting to Nyquist plots. R_{sol} , R_{ct} , and Z_w indicate the resistance of bulk electrolyte solution resistance, the charge-transfer (ct) resistance, and the Warburg impedance, respectively. The CPE_{dl}, CPE_L indicate the constant phase elements (CPE) of double-layer capacitances and limited capacitance at the electrode surface, respectively. The R_{ct} values are summarized in **Table S1**.

	Charge-transfer resistance (R_{ct} , Ω)	
-	pH 8	pH 11
OCP	9.3	9.8
1 st cy.	11.9	12.1
2 nd cy.	12.6	16.0
3 rd cy.	13.4	29.4

Table S1. Summary of R_{ct} acquired from EIS analysis (Figure S10).



Figure S11. The effect of LiBOB on LCO cells. 1 mM LiBOB (~pH 4, light brown) was added to 1 m LiTFSI(aq) and compared with 1 mM H_2SO_4 (~pH 3, brown). (a) Anodic LSVs at a scan rate 0.25 mV s⁻¹. (b–c) XRD patterns of (b) 003 reflections and (c) wide angle at different potential. The asterisk mark indicates carbon paper as the substrate. (d–e) XAS spectra in (d) O *K* edge and (e) Co *L3* edge regions, after holding at OCP for 1 h. Bottom to top spectra are PFY, TEY, and PEY modes.



Figure S12. Characteristics of polydopamine (PDA) coating layer on LCO. (a) TEM image of LCO surface with PDA layer. Inset is the molecular unit of PDA. (b) Galvanostatic voltage profile with 1 m LiTFSI (aq) at pH 8 for 5 cycles. A current rate was 0.2 C. (c) Capacity retention of LCO/PDA (cyan) compared to bare LCO (black). (d) Water droplets contacting to pristine LCO (left) and LCO/PDA surfaces (right).



Figure S13. TEM images of LCO surfaces treated with (a-b) 1 wt% and (c) 0.25 wt% LiTHion solution. The amorphous-film thickness is 5 nm and 3~4 nm for 1 wt% and 0.25 wt% LiTHion coating, respectively.



Figure S14. XPS spectra of as-prepared LCO (black), as-prepared LCO/LiTHion (dark green), and 30 cycled LCO/LiTHion electrode (pale green) at 0.5 C with 1 m LiTFSI(aq) at pH 8. (a) C 1st, (b) O 1s, (c) Li 1s, (d) F 1s, and (e) S 2p BE regions. The pale green letters indicate chemical species of LiTHion.



Figure S15. XAS spectra of as-prepared LCO at OCP (black), 30 cycled bare LCO (gray), asprepared LCO/LiTHion at OCP (dark green), and 30 cycled LCO/LiTHion (pale green) with 1 m LiTFSI(aq) at pH 8. (a) Co L_3 edge and (b) O *K* edge spectra with PFY (bottom) and PEY (top) mode.