Supplementary Information

Kosmotropic anion for improving cycling stability of aqueous lithium-ion batteries in salt-in-water electrolytes

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**Method**

**Chemicals**

For electrolyte, LiN(SO2CF3)2 (lithium bis(trifluoromethanesulfonyl) imide, LiTFSI, >99.7%, Kanto), Li2SO4 (99.7% Alfa aesar), LiNO3 (reagent plus, Sigma aldrich), LiCH3COO (98%, Wako), LiClO4, (99.99 %, Sigma aldrich) and LiOH (>98%, Sigma aldrich) were used as received without any purification. For electrodes, LiCoO2 (99.8%), N-methylpyrrolidine (NMP), and H2O2 (30% in H2O) were purchased from Sigma aldrich, and NH4OH was purchased from Fluka (5.0 M).

**Electrode preparation**

LiCoO2 (LCO) powders were mixed with Super P carbon (Timcal) and polyvinyldene fluoride (PVDF, Kynar) binder with 8/1/1 wt%, respectively, using NMP using planetary mixer (Thinky, ARE-310). This slurry was cast on the titanium (Ti) foil (Wellcos, 99.5% thickness (*t*) = 20 μm) or carbon paper (TGP-H-120, Toray) using doctor blade method, followed by drying at 80 oC overnight in the thermal oven (As one, AVO-310NB). Weight of active material was 2.5~5 mg cm-2. The Ti foil was pre-treated using the piranha solution (7/3 v/v of NH4OH/H2O2, respectively) to enhance adhesion.

A Li-excess Mo based cation-disordered rock salt oxide, Li9/7-xNb2/7Mo3/7O2 (LNMO) was prepared according to the previous report.1 The LNMO was cast on carbon paper with 4~8 mg cm-2 of mass loading. This negative electrode was completed by soaking in H2O with stirring for 2 h for extraction of the Li+.

**Electrochemical measurements**

All electrochemical tests were conducted in an argon (Ar)-filled glove box. Half-cell tests were examined through cyclic voltammetry (CV) and galvanostatic cycles. The three-electrode cells were composed of the working electrode (WE) of LCO on the Ti foil (diameter (*d*) = 6 mm), the counter electrode of a platinum (Pt) coil, and the reference electrode of Ag/AgCl (3 M NaCl). All tests were conducted using electrochemical tester (VMP-3, Biologic) in an argon (Ar)-filled glove box (MOTEK). De-gassing process was conducted for all aqueous electrolyte solutions by Ar-gas bubbling.2

Full cells were prepared using the 2032-type coin cells and galvanostatic electrochemical examinations were examined using battery cycler (PNE, PESC05-0.1). The LCO electrode on the carbon paper (*d* = 12 mm) was assembled with the delithiated LNMO (*d* = 14 mm) on the carbon and a piece of GF/C separator (*d* = 19 mm, Whatman®) in an Ar-filled glove box. The weight ratio of active materials for LNMO/LCO was 2 ~ 2.5.

Electrochemical impedance spectroscopy (EIS) tests were conducted with an amplitude of 10 mA and a frequency range of 100 kHz~100 mHz by using an electrochemical tester (VMP-3, Biologic). The EIS for the LCO electrode in the half cell was measured during the galvanostatic test and after holding a programmed potential for 10 min. To measure the electrochemical double-layer capacitance, staircase-potential EIS was conducted for a potential range of 0.3 V ~ –0.3 V vs. Ag/AgCl.3,4 Every potential step of –25 mV was moved, and EIS was measured after holding a programmed potential for 30 min.

**Characterizations**

LCO electrodes were washed with de-gassed distilled (DI) water and dried under vacuum at 60 oC overnight. X-ray diffraction (XRD, Cu K-α, Rigaku) was used to analyze long-range order of crystal structure. Soft X-ray absorption near-edge structure (s-XANES) was measured in the BL11, Synchrotron Radiation (SR) center at Ritsumeikan University. The LCO electrodes were not exposed to air and directly transferred to s-XANES chamber using a hermetic vessel. X-ray photoelectron spectroscopy (XPS, Al K-α, Thermo VG Scientific) was used for surface analysis. All spectra were calibrated to C 1s sp2 hybridization signal at 248.5 eV. Transmission electron microscopy (TEM, FEI Tecnai GE F30 S-Twin (300 kV)) images were attained to observe the surface layer. The OH stretching vibrations of aqueous electrolyte solutions were attained from attenuated total reflection-infrared (ATR-IR) spectroscopy in the range of 400~4000 cm-1 (iS50, diamond window, Thermo Scientific). Confocal Raman spectroscopy (Ramanforce, Nanophoton) was used with a laser of 532 nm wavelength.

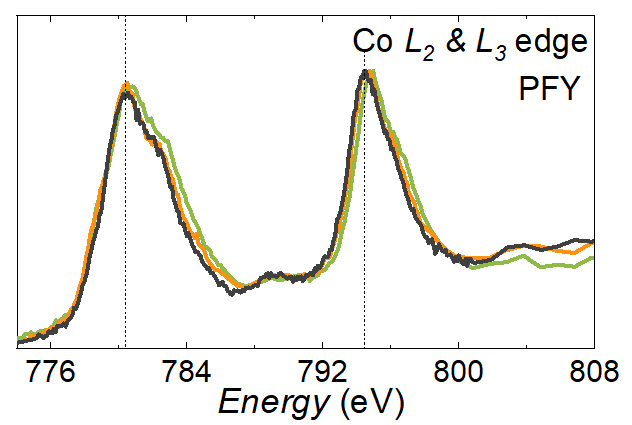
**Mean-field QM/MM Simulations**

Mean-field QM/MM simulations were performed using the DFT-CES (density functional theory in classical Explicit Solvents)5 method. DFT-CES is implemented by combining the Quantum ESPRESSO6 DFT module and Large-scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) molecular dynamics (MD) module.7 Detailed simulation procedure of the DFT-CES can be found from our previous publications5,8-10.

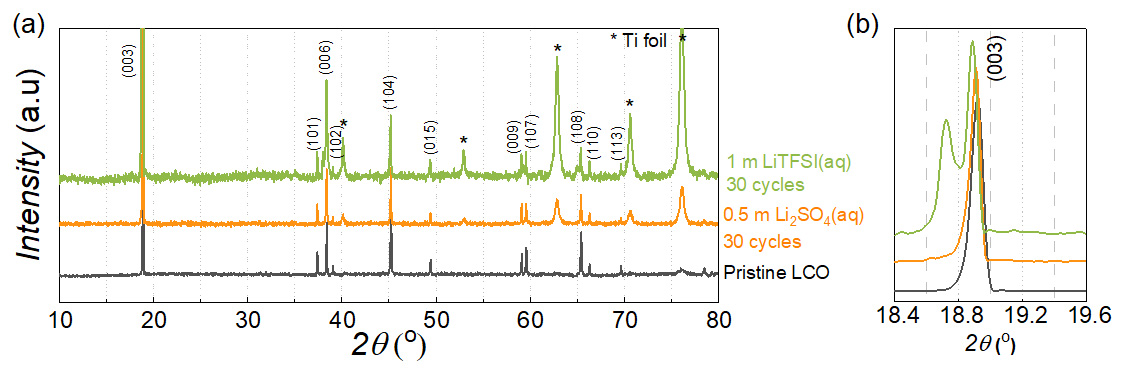
The LCO electrode was modeled as the (003) LiCoO2 surface of Rm space group at a QM level. Half of the outermost CoO2 layer was terminated with hydrogen to block overestimating surface property11, resulting in a stoichiometry of Li0.66CoO2H0.33. Projector-augmented-wave (PAW)12 method was used with the kinetic energy cutoff of 60 Ry and the exchange correlation using the Perdew-Burke-Ernzerhof functional under the generalized gradient approximation (GGA) scheme.13 The strongly localized 3*d* orbital of Co was simulated using GGA+U method with U*eff* value to be 4.91 eV.14 Gaussian smearing was used with a value of 0.02 Ry. The dipole correction along the z-direction was applied to block the unphysical interaction between the images of the cells. The Brillouin zone was sampled by Γￚcentered kpoints of 5Ⅹ5Ⅹ1.

The electrolyte phases of 0.5 m Li2SO4 and 1 m LiTFSI, LiNO3, and LiClO4 were modeled using classical force-fields (FF). 800 numbers of TIP3P15 water molecules were included along with 8 pairs of Li2SO4 or 16 pairs of LiTFSI, LiNO3, and LiClO4 pairs, respectively. Ions were described using the previously developed FFs16-20, and the van der Waals (vdW) parameter of the LCO were described using the universal FF21. Off-diagonal vdW interactions were modeled using the Lorentz-Bertelot mixing rule. We performed canonical ensemble MD simulations at 300 K using the Nosé-Hoover thermostat.22,23

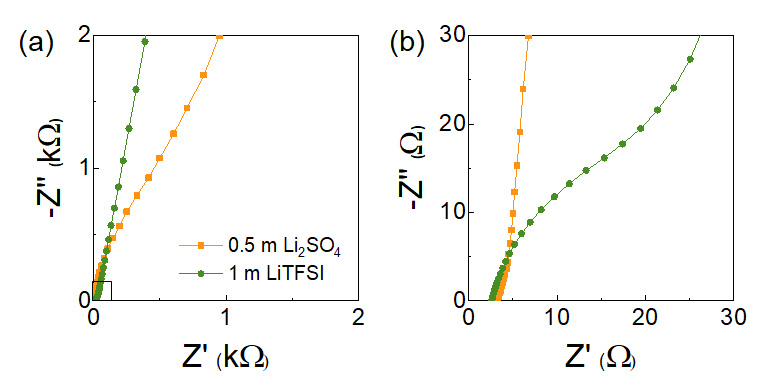
To negatively charge the electrode-electrolyte interface, electrons were inserted to the LCO electrode using DFT, while Li+ were inserted in the electrolyte phase with keeping the total charge of the DFT-CES cell to be zero.



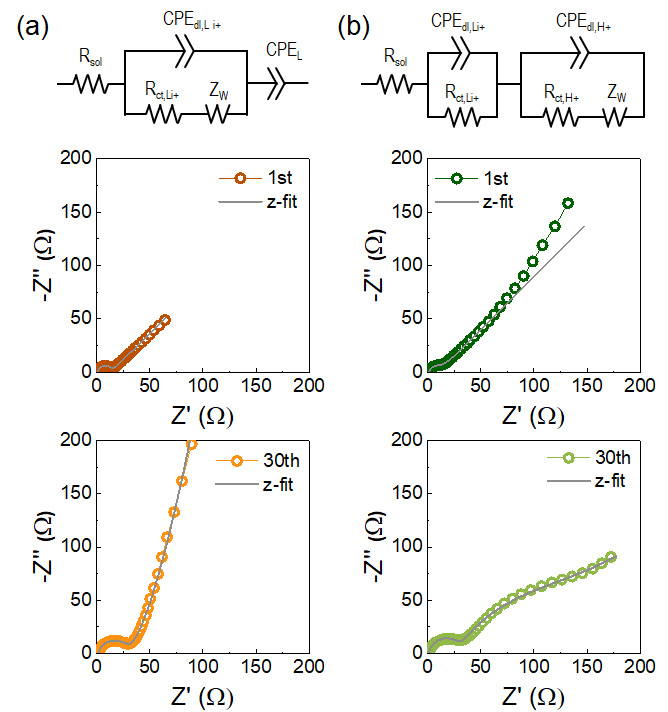
**Figure S1**. XAFS analyses of 30th cycled LCO electrodes with 0.5 m Li2SO4 (orange) and 1 m LiTFSI (green) and pristine LCO (black) in Co *L*-edge PFY mode. Comparing to the spectra for the pristine and the 0.5 m Li2SO4, the main Co3+ peaks with 1 m LiTFSI are shifted to ~0.3 eV for Co *L3* edge and 0.2~0.3 eV for Co *L2* edge.



**Figure S2**. XRD spectra of LCO electrodes. The black, orange, and green spectra are the pristine LCO, the LCO electrode with 0.5 m Li2SO4 after 30th cycle, and the LCO electrode with 1 m LITFSI after 30th cycle, respectively. The asterisk mark indicates Ti foil as the substrate. (b) is the high-magnification curves of (a) at 003 reflection.



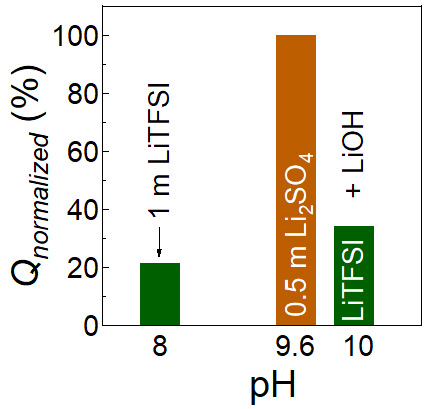
**Figure S3.** Nyquist plots at open circuit potential (OCP) with 0.5 m Li2SO4 (orange, ~0 V) and 1 m LiTFSI (green, ~0.1 V) before galvanostatic cycle. (b) is a high-magnification curves in the square region of (a).



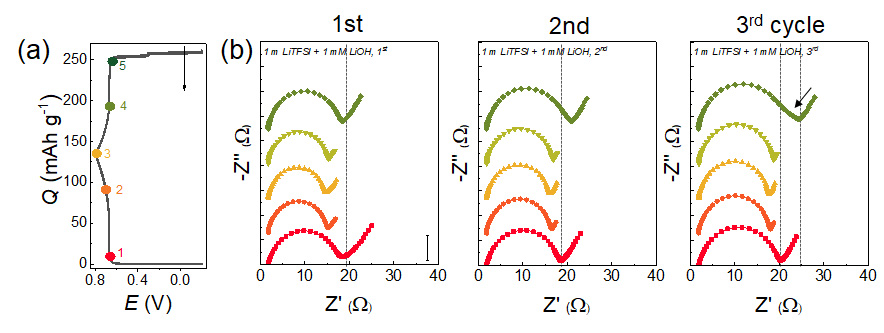
**Figure S4.** Equivalent circuits (top) and Nyquist plots of LCO half-cells with (a) 0.5 m Li2SO4 (orange), and (b) 1 m LiTFSI (green) after 1st cycle (middle) and 30 cycles (bottom). Unlike **Figure 2** where EIS was measured at different charging and discharging states for initial 3 cycles, EIS in **Figure S4** was measured after continuous 30 cycles, followed by rest for 30 min. The solid lines are the fitting curves using corresponding equivalent circuits.24,25 Rsol, Rct,Li+, Rct,H+, and Zw indicate the resistance of bulk electrolyte solution resistance, the charge-transfer (ct) resistance for Li+ intercalation/extraction, the ct for H+ (de)intercalation, and the Warburg impedance, respectively. The CPEdl,Li+, CPEdl,H+, CPEL indicate the constant phase elements (CPE) of double-layer capacitances for Li+ and H+ (de)intercalation, and limited capacitance at the electrode surface, respectively. The Rct,H+ term was enlarged with 1 m LiTFSI after 30 cycle in contrast to negligible Rct,H+ with 0.5 m Li2SO4.

**Table S1.** Summary of Rsol, Rct,Li+, and Rct,H+ values acquired from EIS fitting based on the equivalent circuits in **Figure S4**.

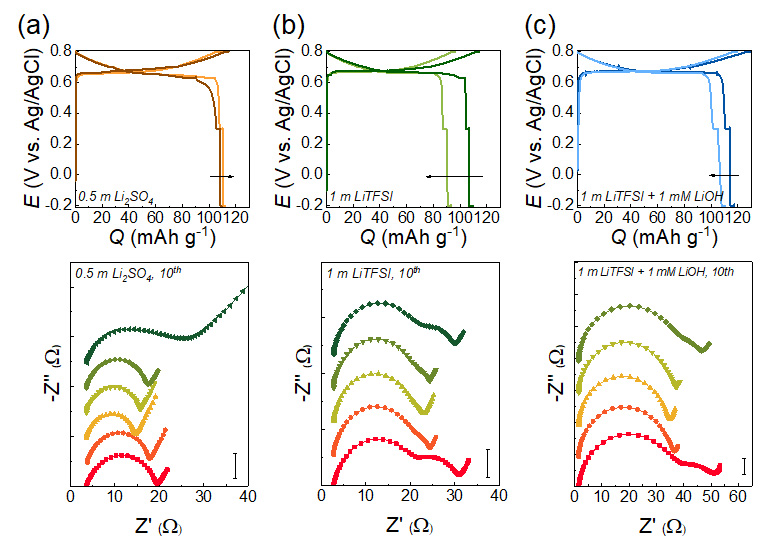
|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | 0.5 m Li2SO4 | | 1 m LiTFSI | |
| Unit: Ω | 1st cycle | 30th cycle | 1st cycle | 30th cycle |
| **Rsol** | 1.09 | 1.75 | 1.38 | 1.33 |
| **Rct,Li+** | 1.75 | 27.8 | 1.28 | 27.6 |
| **Rct,H+** | - | - | 11.2 | 147.3 |



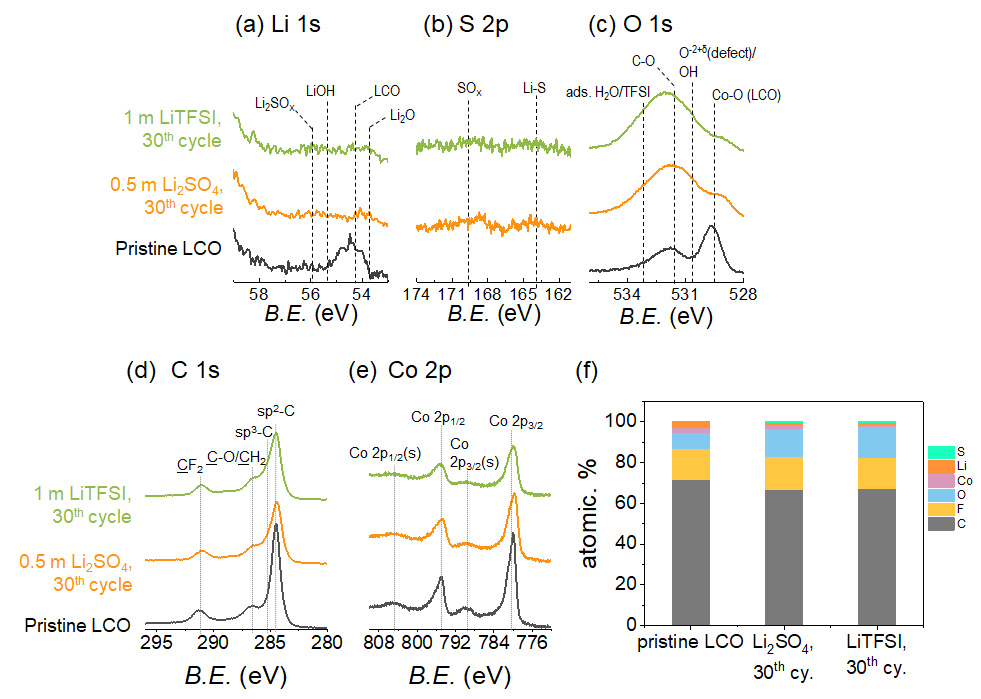
**Figure S5.** Correlation between pH of electrolyte solution and normalized capacity (*Qnormalized*) at 30th cycle. 1 m LiTFSI showing pH ~8 (green) provided 21.4% of *Qnormalized* for LCO. 0.5 m Li2SO4 having pH ~9.6 (brown) showed ~100% of *Qnormalized* for LCO. pH ~10 of 1 m LiTFSI made by adjusting LiOH showed 34.2% of *Qnormalized*. Obviously, the capacity is not entirely determined from pH.



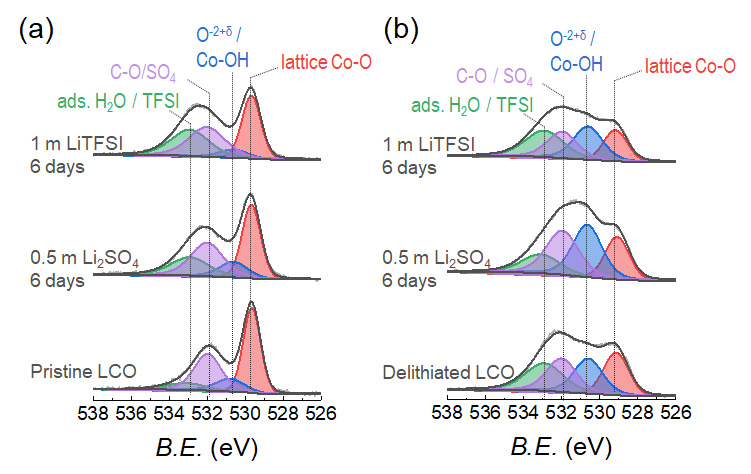
**Figure S6.** Galvanostatic profiles and corresponding EIS analysis of LCO cells for 3 cycles with 1 m LiTFSI at pH of 10, prepared by addition of 1 mM LiOH. (a) Galvanostatic profiles for consecutive 3 cycles. The arrows indicate galvanostatic profiles from the 1st to the 3rd cycle. (b) Nyquist plots after potential holding for 10 min for charging process at the potential 1 (red, 0.66 V), 2, (orange, 0.7 V), and 3 (yellow, 0.8 V), and subsequent discharging process at 4 (light green, 0.7 V), and 5 (green, 0.66 V) in (a). The panels in (b) correspond from the 1st (left) to the 3rd cycle (right). The y-axis scales indicate 5 .



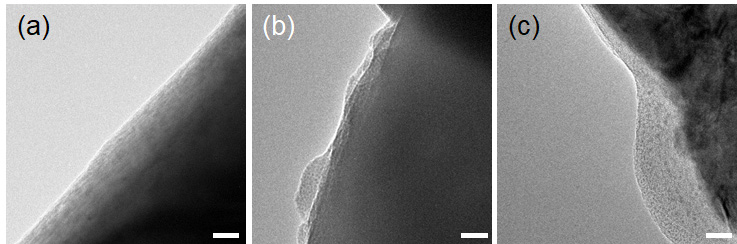
**Figure S7.** Comparative galvanostatic profiles (top panels) and corresponding EIS (bottom panels) of LCO cells for the 10th cycle. Electrolyte solutions are (a) 0.5 m Li2SO4, (b) pH ~8 of 1 m LiTFSI, and (c) pH ~10 of 1 m LiTFSI. The arrows in the galvanostatic profiles indicate from 1st and 10th cycles. Nyquist plots were acquired after potential holding for 10 min for charging process at the potential of 0.66 V (red), 0.7 V (orange), and 0.8 V (yellow), and subsequent discharging process at 0.7 V (light green), 0.66 V (green), 0.7 V), and 0.63 V (dark green, Li2SO4 only). The y-axis scales indicate 5 .



**Figure S8**. XPS results of pristine LCO (black), 30th cycled LCO with 0.5 m Li2SO4 (orange), and 1 m LiTFSI (green). (a) Li 1s, (b) S 2p, (c) O 1s, (d) C 1s, (e) Co 2p, and (f) atomic % of C, F, O, Co, Li, and S. The Co-O lattice of the LCO (529.7 eV), oxide defect/hydroxide peak (530.8 eV), C-O (531.8eV) arising from carbonaceous particles appeared after 30 cycles.26,27 The intense peaks of sp2-C (284.5 eV), sp3-C (285.2 eV), and C-O (286.6 eV) emerged from the Super P carbon, while CH2 (286.7 eV) and CF2 signal (291 eV) arose from the PVdF binder in the C 1s BE region.28-31 In the Co 2p BE region, Co 2p3/2 (780 eV), Co 2p1/2 (795 eV) and their satellite (s) peaks (790 eV and 805 eV, respectively) arising from Co3+ appeared for all samples. It is noted the satellite signal of Co2+ (786 eV) is not visible, indicating the absence of Co2+ on the LCO surface after cycling.28-31



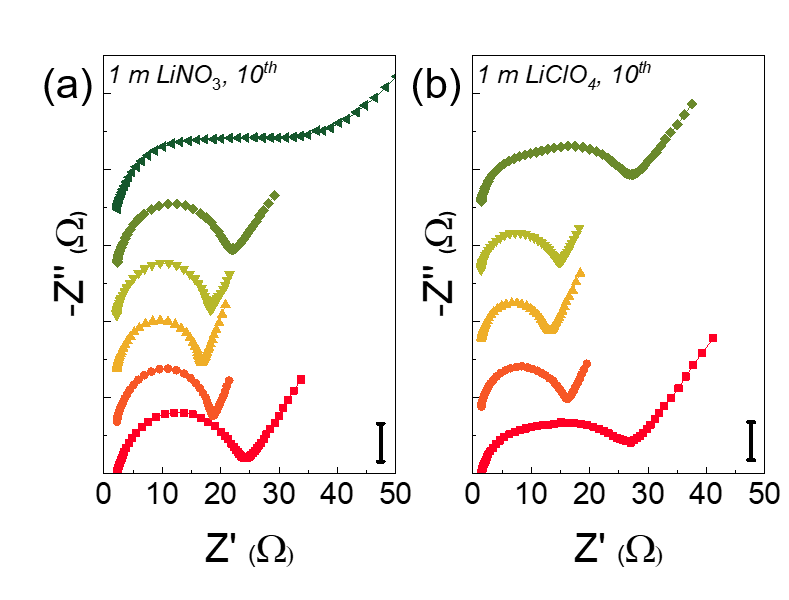
**Figure S9.** XPS O 1s BE regions of (a) pristine LCO and (b) as-prepared delithiated LCO electrodes in the bottom panel. These samples were immersed in 0.5 m Li2SO4 (middle) and 1 m LiTFSI for 6 days (top panel). The delithiation of LCO was carried out with 0.5 m Li2SO4 at 0.8 V, and a current rate of 0.5C. It appears to the enhanced O-2+δ and Co-OH signals and the relatively reduced lattice Co-O only after the delithiation.

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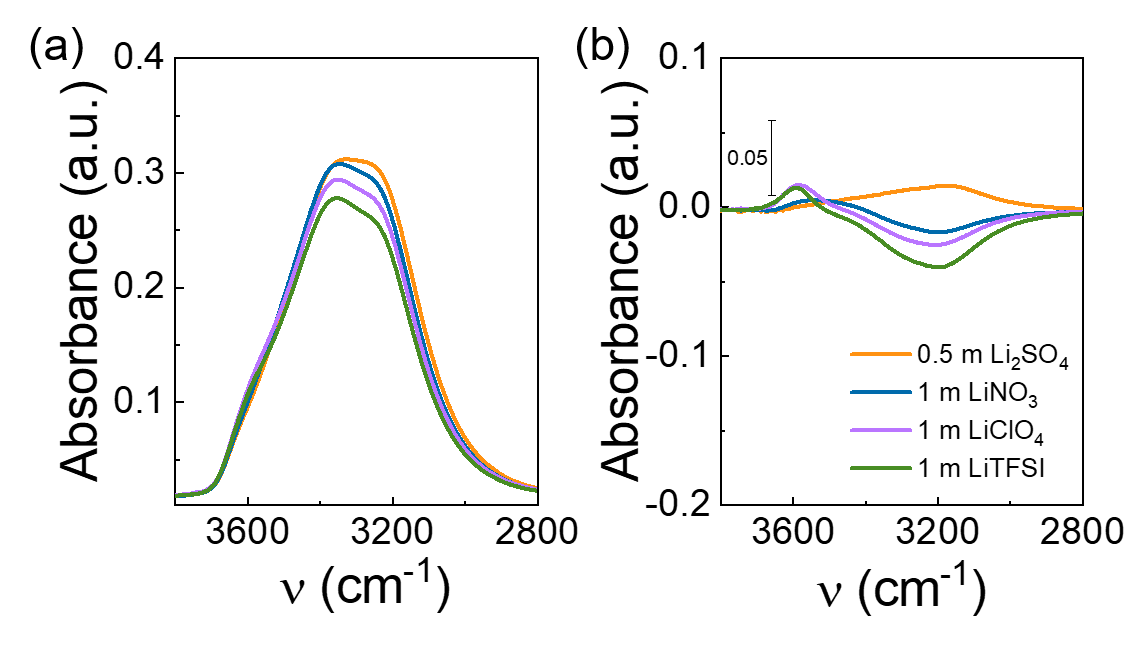
**Figure S10.** TEM images of (a) pristine LCO surface, and (b-c) 30th cycled LCO surfaces with (b) 0.5 m Li2SO4 and (c) 1 m LiTFSI. All scale bars indicate 20 nm.

**Table S2.** Measured molar (mol L-1) concentrations.

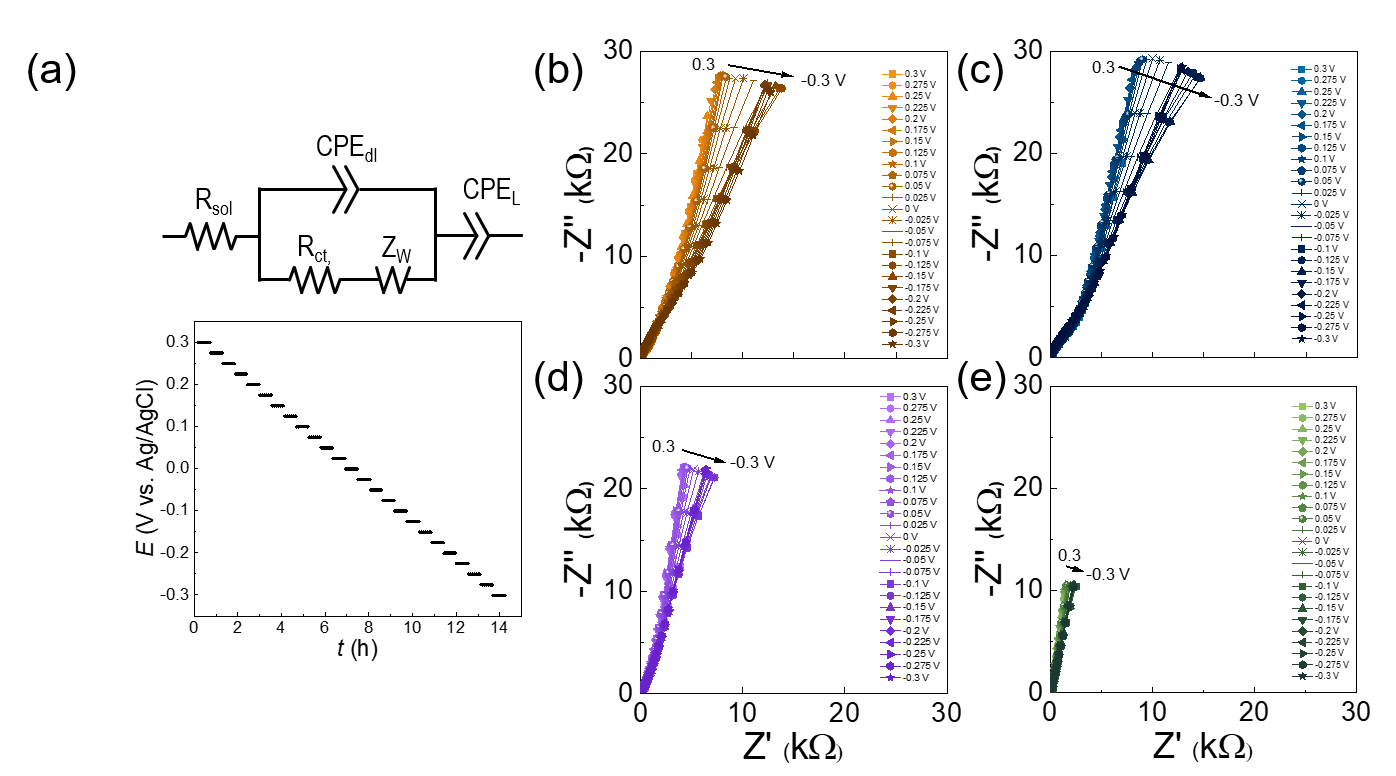
|  |  |  |
| --- | --- | --- |
|  | m (mol kg-1) | M (mol L-1) |
| Li2SO4 | 0.5 | 0.49 |
| LiNO3 | 1 | 0.98 |
| LiClO4 | 1 | 0.95 |
| LiTFSI | 1 | 0.88 |



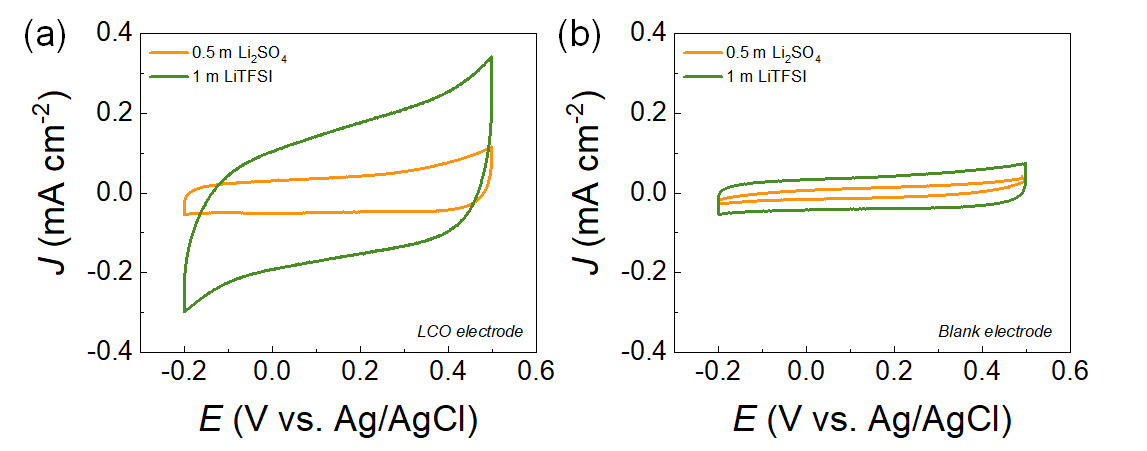
**Figure S11.** EIS of LCO cells for the 10th cycle during galvanostatic cycle. Electrolyte solutions are (a) 1 m LiNO3 (b) 1 m LiClO4. Nyquist plots were acquired after potential holding for 10 min for charging process at the potential of 0.66 V (red), 0.7 V (orange), and 0.8 V (yellow), and subsequent discharging process at 0.7 V (light green), 0.66 V (green), 0.7 V), and 0.63 V (dark green, LiNO3 only). The y-axis scales indicate 5 .



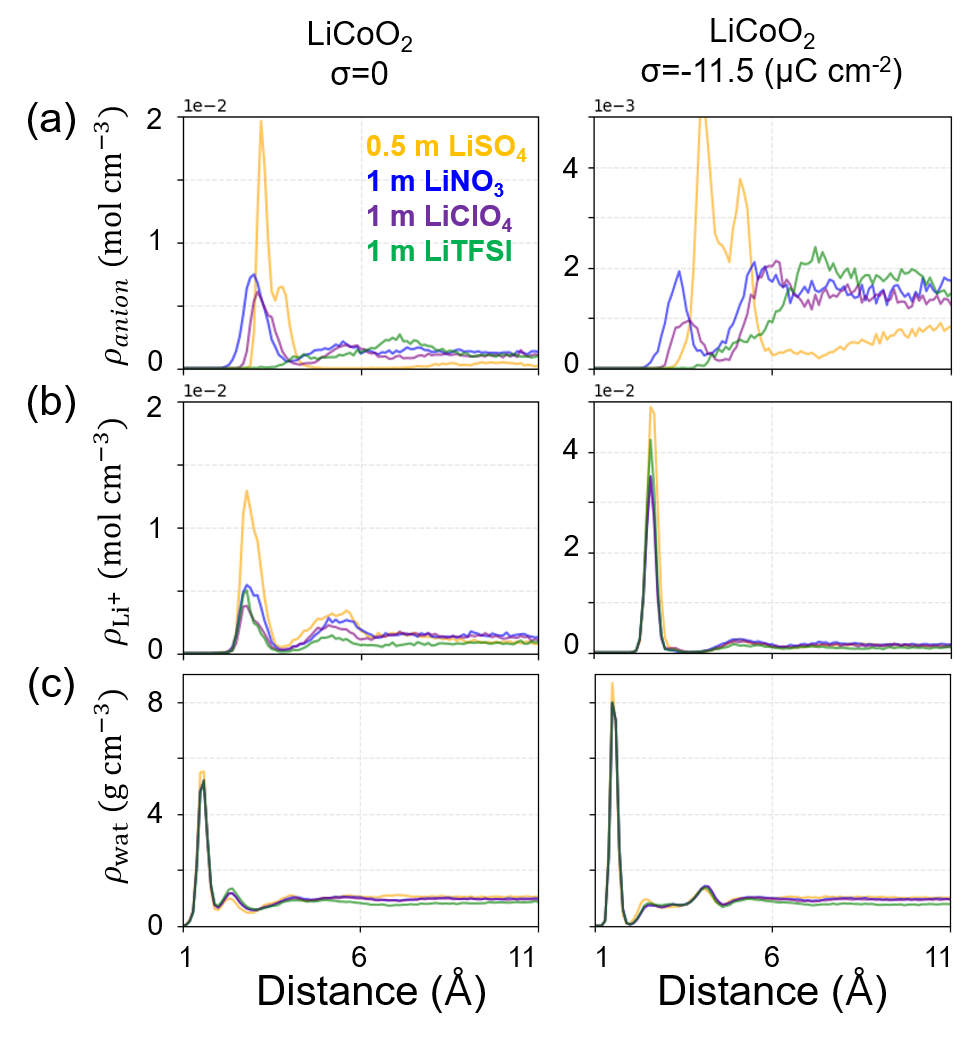
**Figure S12.** Comparative ATR-IR spectra of 0.5 m Li2SO4 (orange), 1 m LiNO3 (blue), 1 m LiClO4 (purple), and 1 m LiTFSI (green). (a) ATR-IR spectra at O-H stretching region. (b) Corresponding differential O-H vibration signals from pure water.



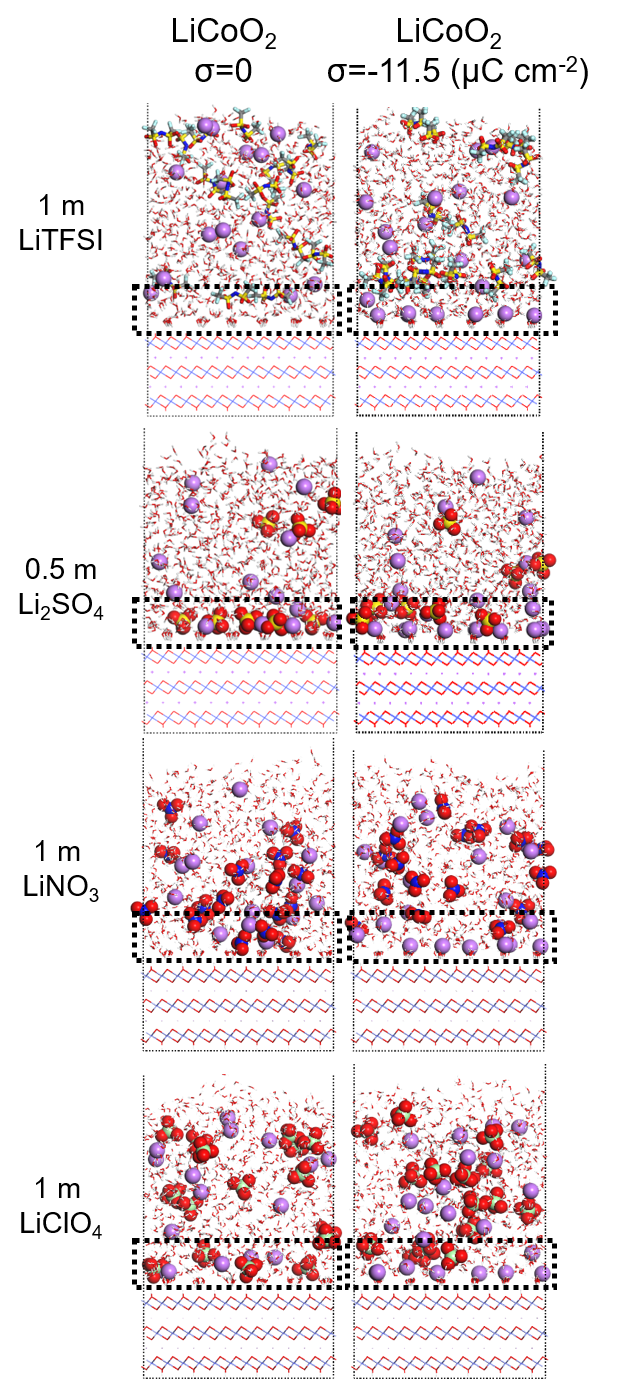
**Figure S13.** Nyquist plots and Bode plots of the LCO electrode and equivalent circuit with various electrolyte solutions. The staircase-potential EIS was conducted for every potential step of –25 mV and following 30 min rest in a potential range of 0.3 V ~ –0.3 V vs. Ag/AgCl. (a) An equivalent circuit model and representative staircase-potential curve. (b-f) Nyquest plots with (b) 0.5 m Li2SO4, (c) 1 m LiNO3, (d) 1 m LiClO4, and (e) 1 m LiTFSI.

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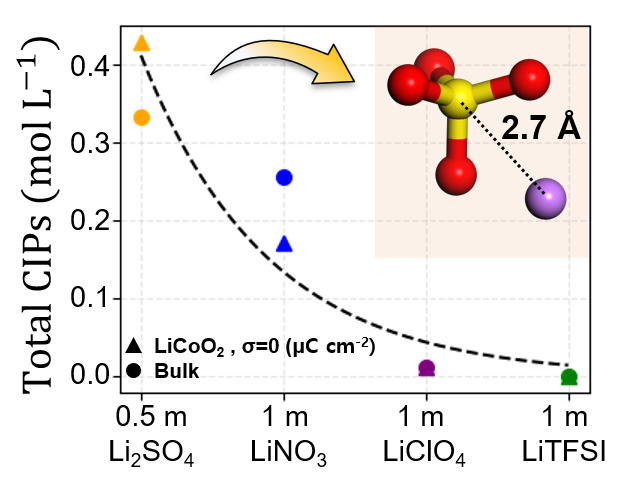
**Figure S14.** CV curves of LCO electrodes in the non-faradaic potential region (–0.2 ~ 0.5 V) at a scan rate of 50 mV s-1. (a) CV profiles of the LCO electrode, and (b) CV curves of the blank electrode (LCO-free carbon + binder electrode). The orange and green curves indicate 0.5 m Li2SO4 and 1 m LiTFSI, respectively. These results indicate superior adsorption property of TFSI– on both the LCO and the additive carbon in the EDL range relative to that of SO42–.



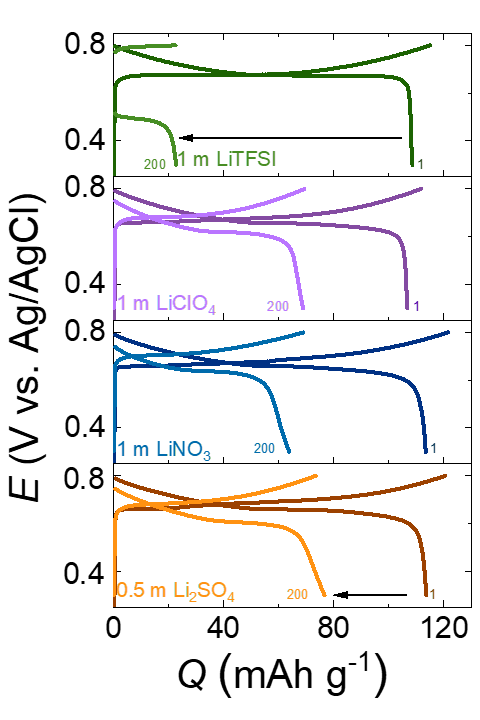
**Figure S15.** Local concentrations of (a) anion (), (b) Li+ (), and (c) density of water () along the surface normal direction. The distance is referred to the top-most atoms of the electrode. Left panels are the uncharged LiCoO2, and the right panels are for the cathodically (negatively) charged LiCoO2 by *σ* = -11.5 *μ*C cm-2.



**Figure S16.** Representative double-layer structures for different double-layer charging states (*σ*) with varying salts, which are obtained from mean-field QM/MM simulations. Color codes are; purple for Li+, red for O, yellow for S, grey for C, and cyan for F, blue for N, and light green for Cl. Ionic species are displayed using spheres while water and LCO are displayed using sticks. The regions for analyzing ion quantities or free water density are shown with a dashed line.



**Figure S17.** Number of contact ion pairs (CIPs). SO42--Li+ CIP structure is shown in the inset.



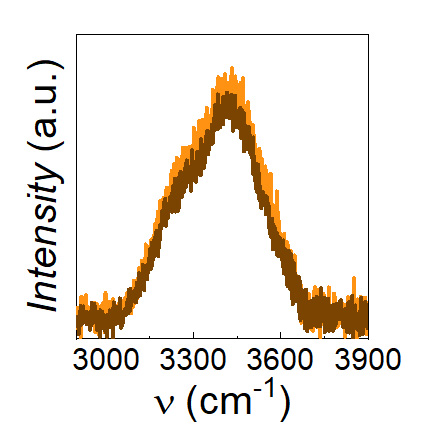
**Figure S18.** Galvanostatic cycling performances at 1st and 200th cycles with various electrolyte solutions, 0.5 m Li2SO4, 1 m LiNO3, 1 m LiClO4, and 1 m LiTFSI (from bottom to top). The current rates were 0.5 C, and the potential ranges were 0.3 ~ 0.8 V vs. Ag/AgCl. Comparative capacity retention and Coulombic efficiency (CE) for 200 cycles.



**Figure S19.** Comparative capacity retention and Coulombic efficiency (CE) for 200 cycles at 0.5C.

**Table S3.** Capacity retention ratios (a) after 100 cycles in the potential range of -0.2 ~ 0.8 V (**Figure 2b**), (b) after 100 cycles and (c) after 200 cycles in the potential range of 0.3 ~ 0.8 V (**Figures S18-19**).

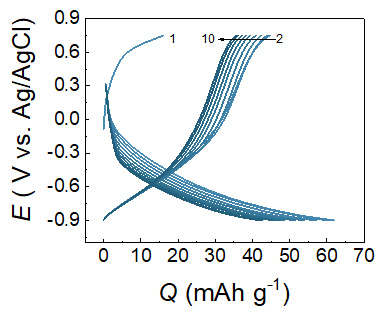
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| --- | --- | --- | --- |
|  | Capacity retention (*Qnormalized* %) | | |
|  | -0.2 ~ 0.8 V | 0.3 ~ 0.8 V | |
|  | 100 cycles | 100 cycles | 200 cycles |
| 0.5 m Li2SO4 | 72.5 | 85.4 | 67.4 |
| 1 m LiNO3 | 33.0 | 82.8 | 56.1 |
| 1 m LiClO4 | 13.3 | 85.4 | 64.6 |
| 1 m LiTFSI |  | 71.0 | 20.7 |

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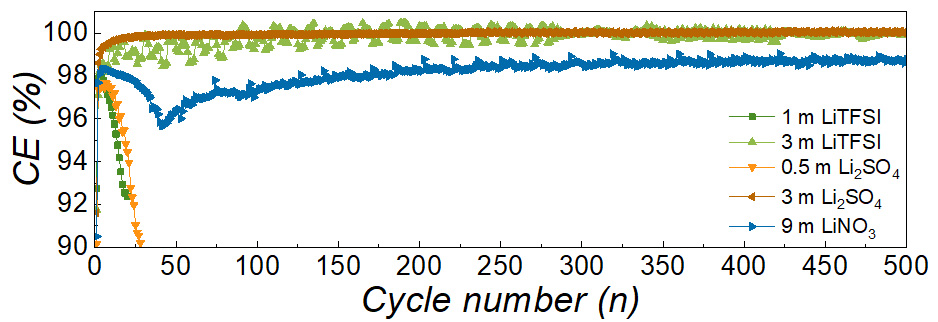
**Figure S20.** Raman spectra of 0.5 m (light orange) and 3 m (dark brown) Li2SO4 at (O-H stretching region. The negligible vibration change indicates no appearance of the water-in-salt characteristics by 3 m.



**Figure S21.** ATR-IR spectra from 0.1 m to 3 m Li2SO4 at (a) IR-inactive symmetric stretching band ((SO42-)) at ~981 cm-1 and (b) IR-active anti-symmetric stretching band ((SO42-)) at ~1101 cm-1. With increasing concentration, the (SO42-) signal is apparent, and (SO42-) shifts to low wavenumber, which are in good agreement with the previous report.32 Emerging (SO42-) is understood to the symmetry decrease of the SO42- stretch by forming the ion pairs. A marginal band splitting of the (SO42-) suggests the formation of the solvent-separated ion pairs (SIP).

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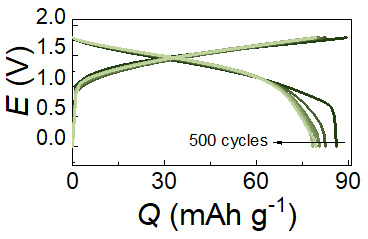
**Figure S22.** Galvanostatic profiles of Li9/7-xNb2/7Mo3/7O2 (LNMO) for 10 cycles with 1 m LiTFSI. The current rates were 0.5C, and the potential ranges were -0.9 ~ 0.75 V vs. Ag/AgCl.

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**Figure S23.** Coulombic efficiency (CE) of full cells consisting of (+)LiCoO2 and (–)Li9/7-xNb2/7Mo3/7O2 electrodes with 1 m LiTFSI (green), 3 m LiTFSI (light green), 0.5 m Li2SO4 (orange), 3 m Li2SO4 (brown), and 9 m LiNO3 (blue) electrolyte solution. Among the various electrolyte solutions, 3 m Li2SO4 only maintained stable CE close to 100% of CE 500 cycles.

**Table S4.** Summary of CE of full cells at 20th, 50th, and 500th cycles (**Figure S23**).

|  |  |  |  |
| --- | --- | --- | --- |
|  | CE (%) | | |
|  | 20th cycle | 50th cycle | 500th cycle |
| 0.5 m Li2SO4 | 94.44 | 98.46 |  |
| 1 m LiTFSI | 92.38 | 96.77 |  |
| 3 m Li2SO4 | 99.80 | 99.92 | 100.09 |
| 3 m LiTFSI | 98.90 | 99.27 | 99.92 |
| 9 m LiNO3 | 97.97 | 96.38 | 98.79 |



**Figure S24.** Voltage profiles of a full cell with 21 m LiTFSI for 500 cycles. The negative electrode was LNMO, and the current rate was 0.5C. Capacity retention was estimated to ~92%.

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