

## Supporting Information

# Effect of Electrolyte Additive on Cycling Performance of Li Metal and Kinetic Mechanism Analysis

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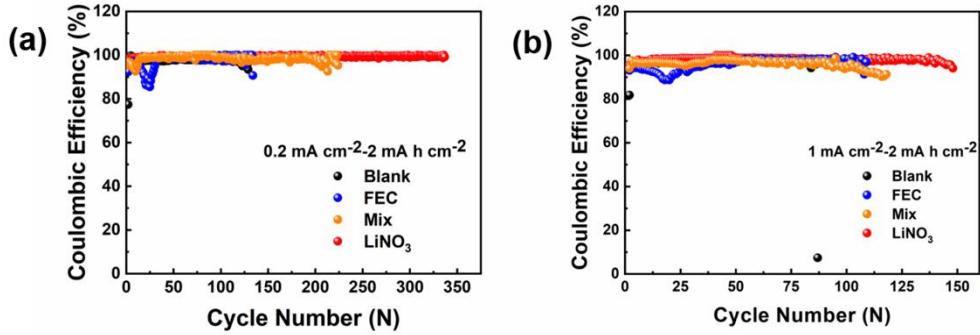
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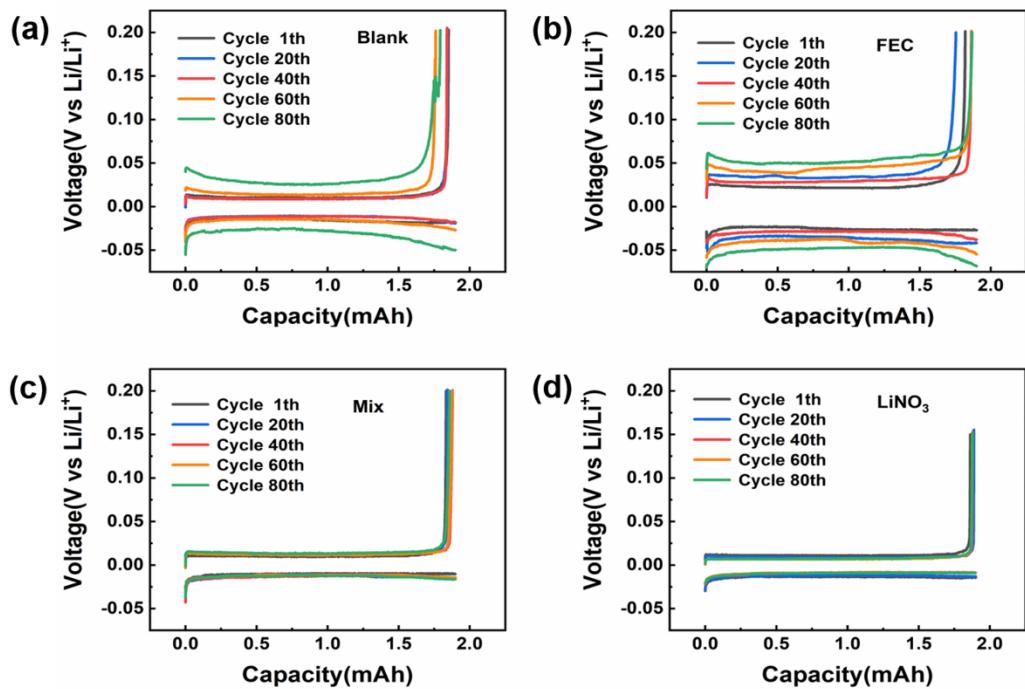
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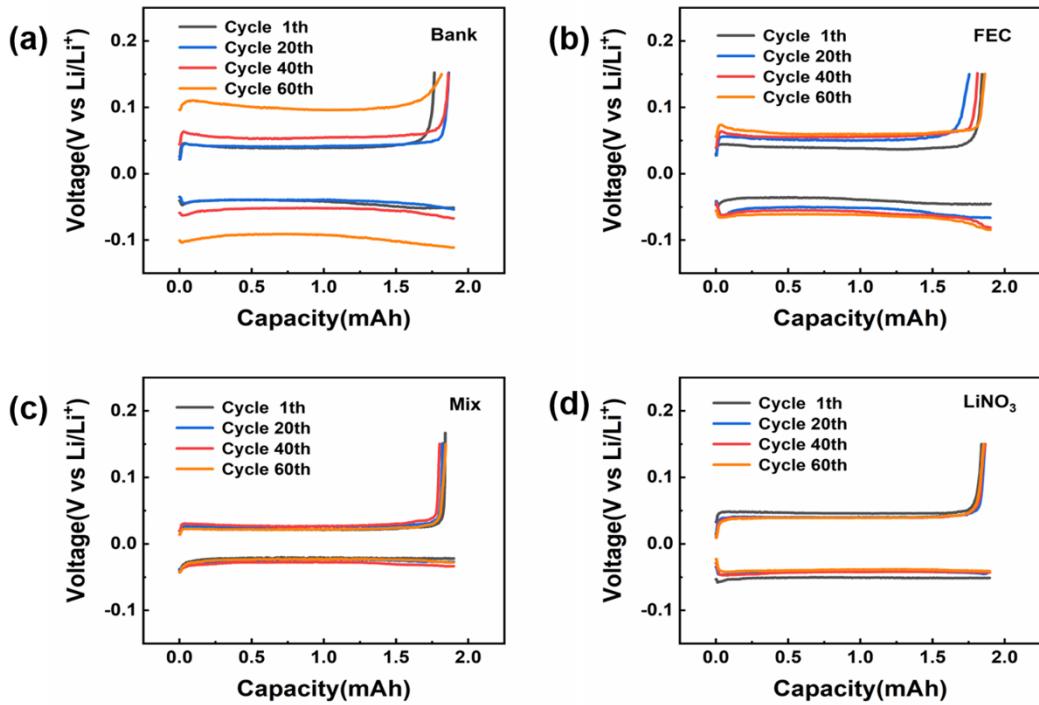
## Supplementary Figures



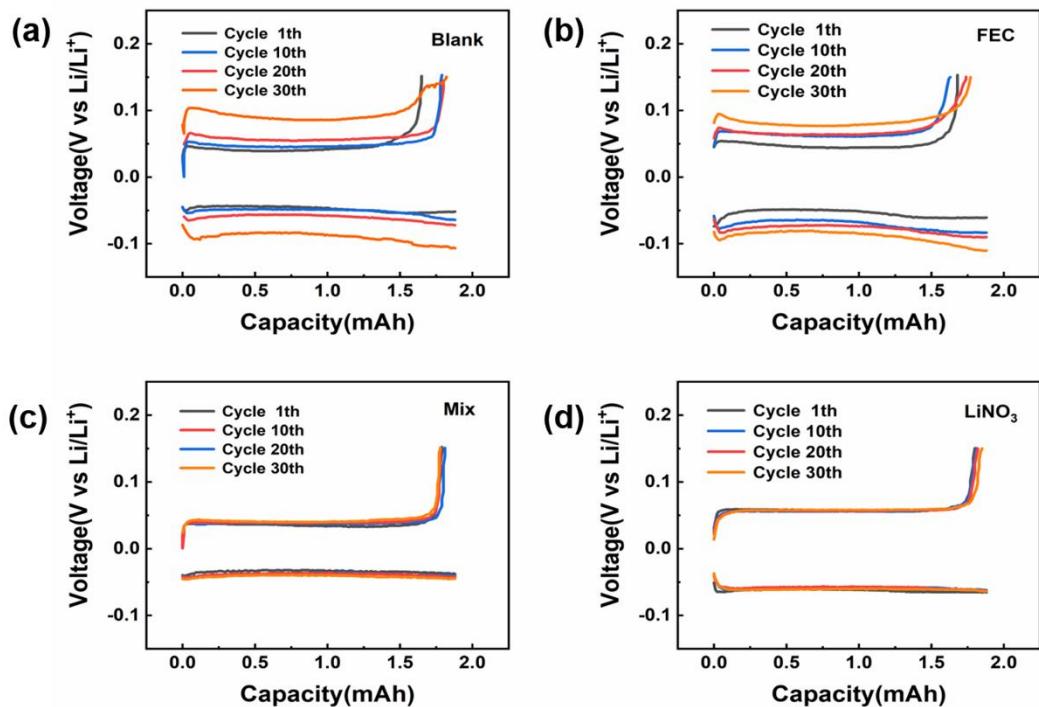
**Figure S1.** Cycling performance of the Li | Cu cells with four electrolytes at various current densities: (a)  $0.2 \text{ mA cm}^{-2}$ , (b)  $1 \text{ mA cm}^{-2}$  for a capacity of  $2 \text{ mA h cm}^{-2}$ .



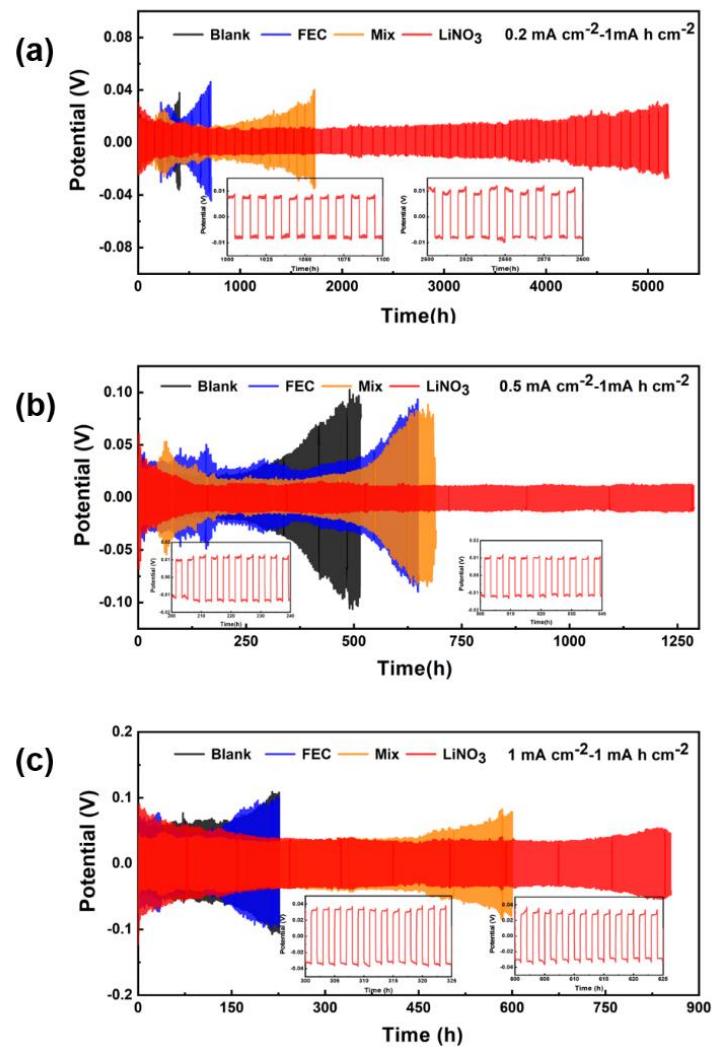
**Figure S2.** Voltage profiles for the Li | Cu cell cycled in four electrolytes at  $0.5 \text{ mA cm}^{-2}$  for a capacity of  $2 \text{ mA h cm}^{-2}$ : (a) Blank electrolyte; (b) FEC electrolyte; (c) Mix electrolyte; (d) LiNO<sub>3</sub> electrolyte.



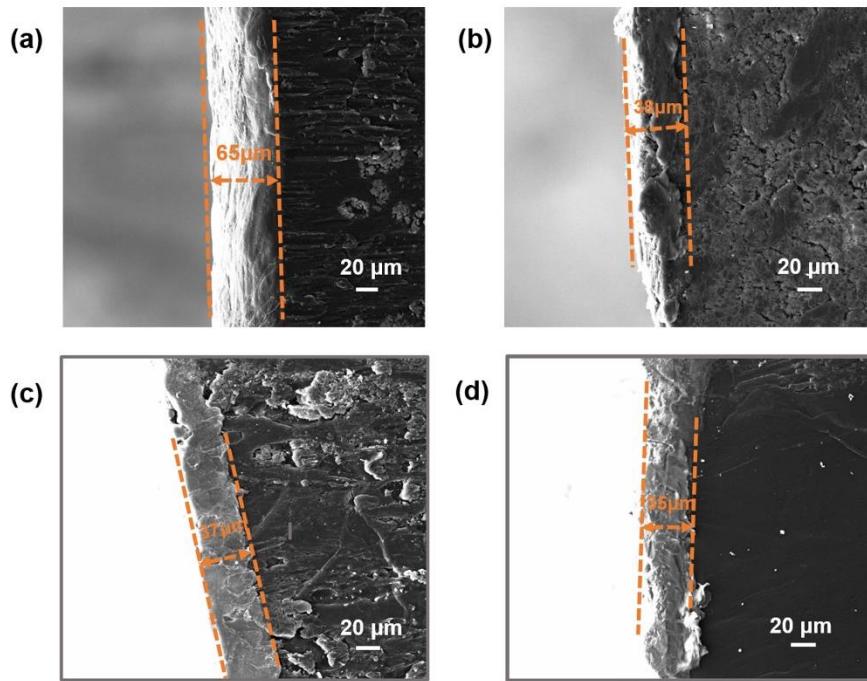
**Figure S3.** Voltage profiles for the Li | Cu cell cycled in four electrolytes at  $2 \text{ mA cm}^{-2}$  for a capacity of  $2 \text{ mAh cm}^{-2}$ : (a) Blank electrolyte; (b) FEC electrolyte; (c) Mix electrolyte; (d)  $\text{LiNO}_3$  electrolyte.



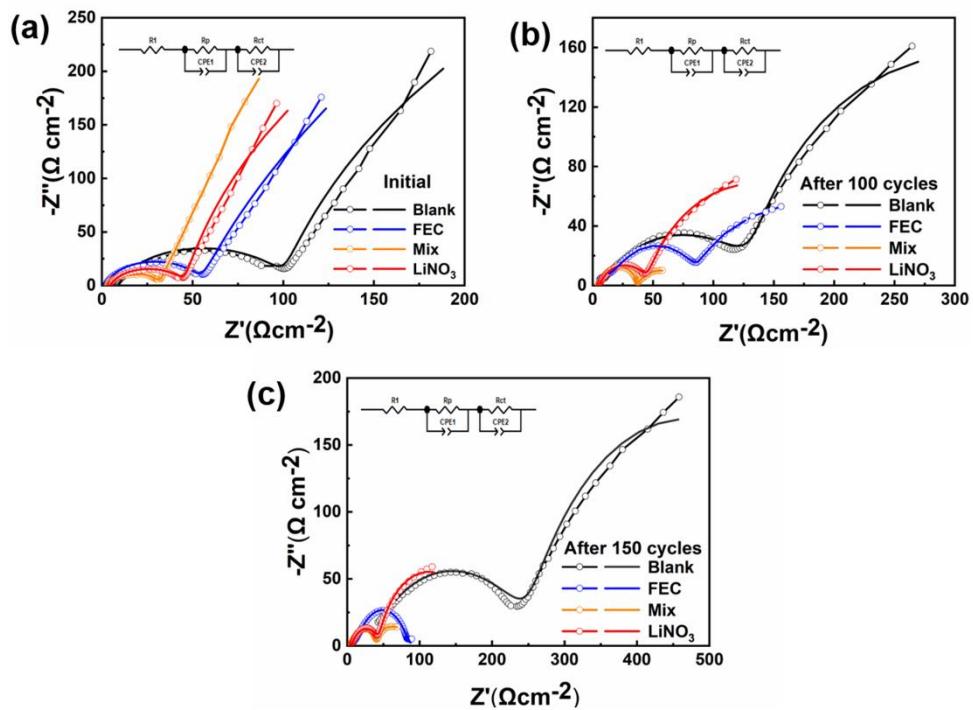
**Figure S4.** Voltage profiles for the Li | Cu cell cycled in four electrolytes at  $5 \text{ mA cm}^{-2}$  for a capacity of  $2 \text{ mAh cm}^{-2}$ : (a) Blank electrolyte; (b) FEC electrolyte; (c) Mix electrolyte; (d)  $\text{LiNO}_3$  electrolyte.



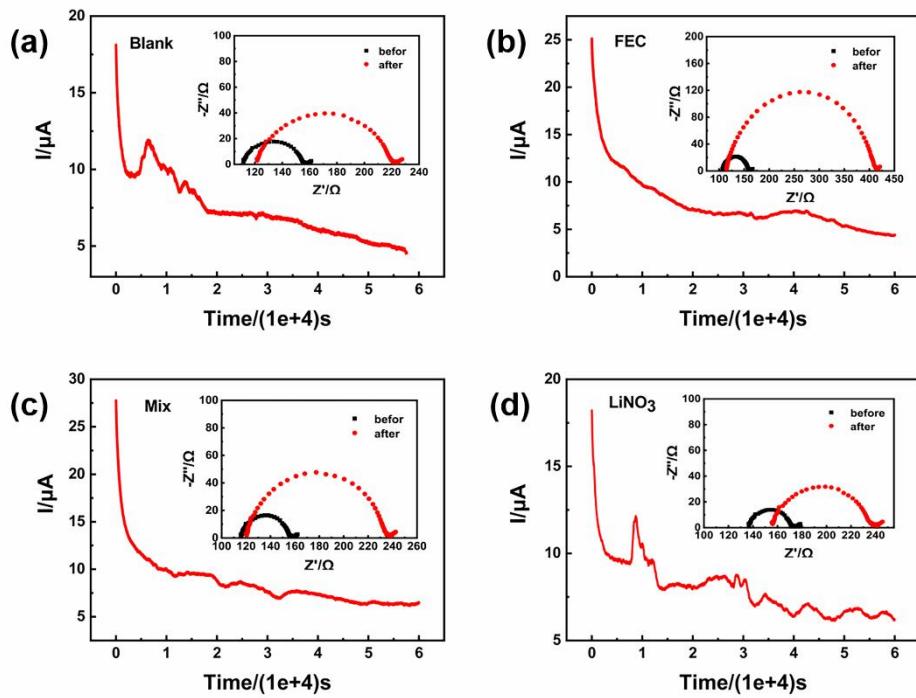
**Figure S5.** Cycling performance of the symmetric Li | Li cells with four electrolytes at various current densities, the insets are expanded views from the plot of LiNO<sub>3</sub>: (a) 0.2 mA cm<sup>-2</sup>, (b) 0.5 mA cm<sup>-2</sup>, (c) 1 mA cm<sup>-2</sup> and for a specific capacity of 1 mAh cm<sup>-2</sup>.



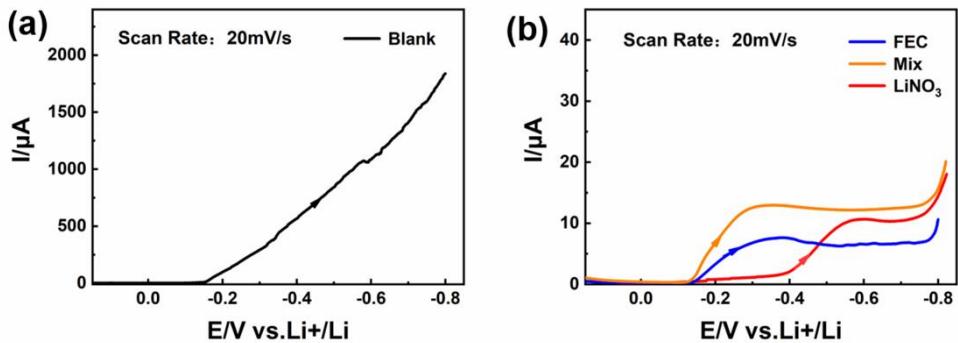
**Figure S6.** SEM images of the Cu foil electrodes at Li deposition state after 100 cycles of galvanostatic stripping/plating at  $1 \text{ mA cm}^{-2}$  for a capacity of  $0.5 \text{ mAh cm}^{-2}$  with four electrolytes: cross-sectional images of the Li metal anode with (a) the Blank sample, (b) FEC sample, (c) Mix sample, and (d) the  $\text{LiNO}_3$  sample.



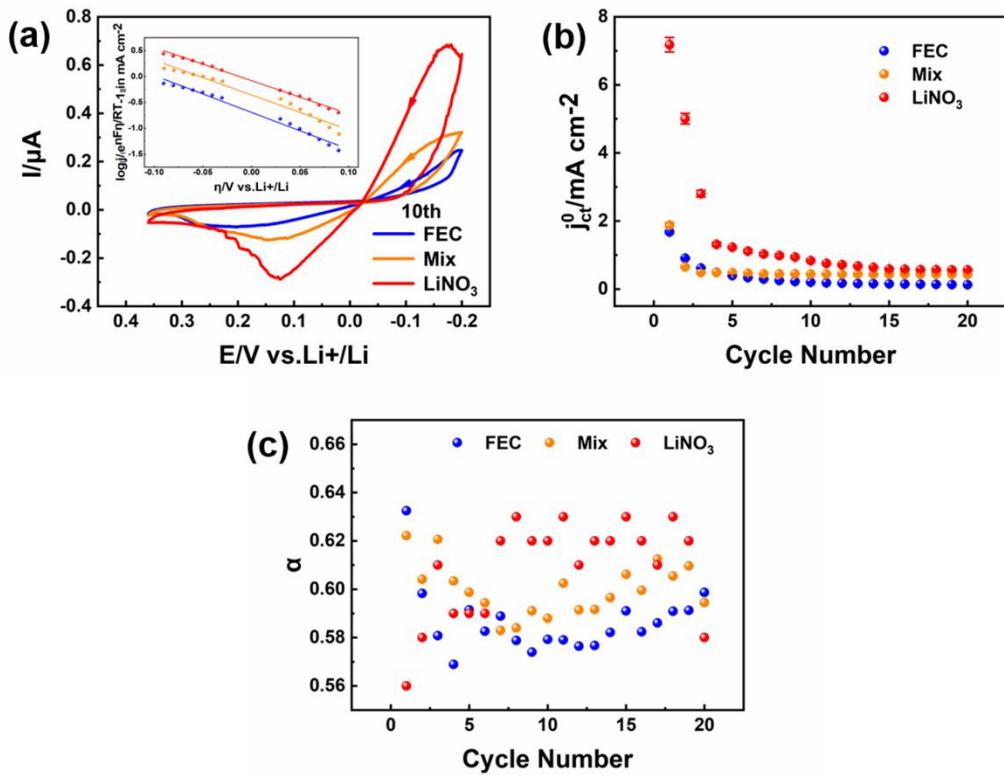
**Figure S7.** Nyquist plots of  $\text{Li} \mid \text{Cu}$  cells using four electrolytes, at open circuit voltage; the inset is the fitting circuit, and the line-symbol is the fitting curve. The impedance was measured (a) initial, (b) after the 100th cycle, and (c) after the 150th cycle, at a current density of  $1 \text{ mA cm}^{-2}$  and the plating/stripping capacity of  $0.5 \text{ mAh cm}^{-2}$ .



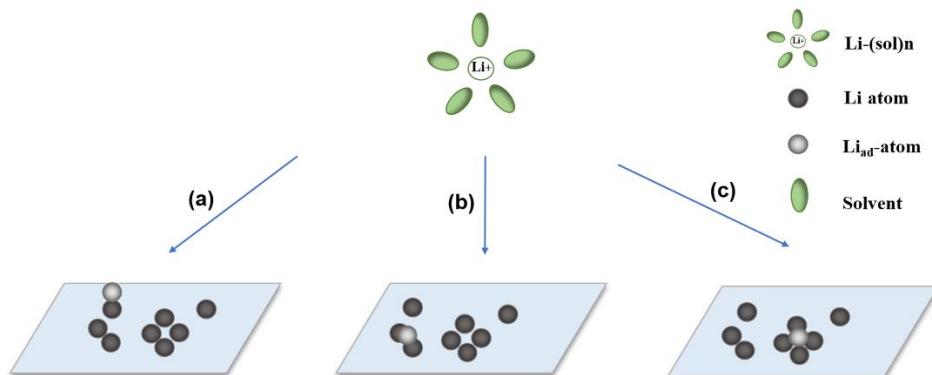
**Figure S8.** Chronoamperometry and AC impedance spectra (from 1 Hz to 100 kHz) of Li | Li cells with four electrolytes,  $\Delta V = 0.003$  V: (a) Blank electrolyte; (b) FEC electrolyte; (c) Mix electrolyte; (d)  $\text{LiNO}_3$  electrolyte.



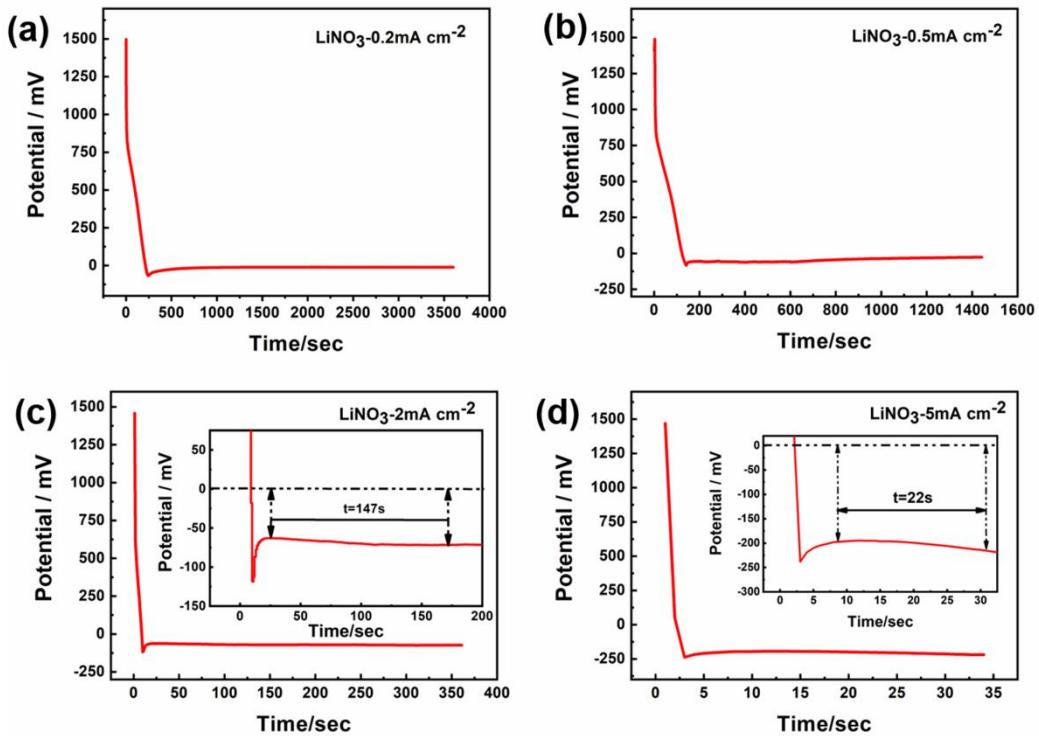
**Figure S9.** Steady-state polarization curve of  $\text{Li}^+/\text{Li}$  couple in four electrolytes, arrows indicate scan direction: scan rate: (a)  $20 \text{ mV s}^{-1}$  for Blank electrolyte; (b)  $20 \text{ mV s}^{-1}$  for FEC, Mix,  $\text{LiNO}_3$  electrolytes.



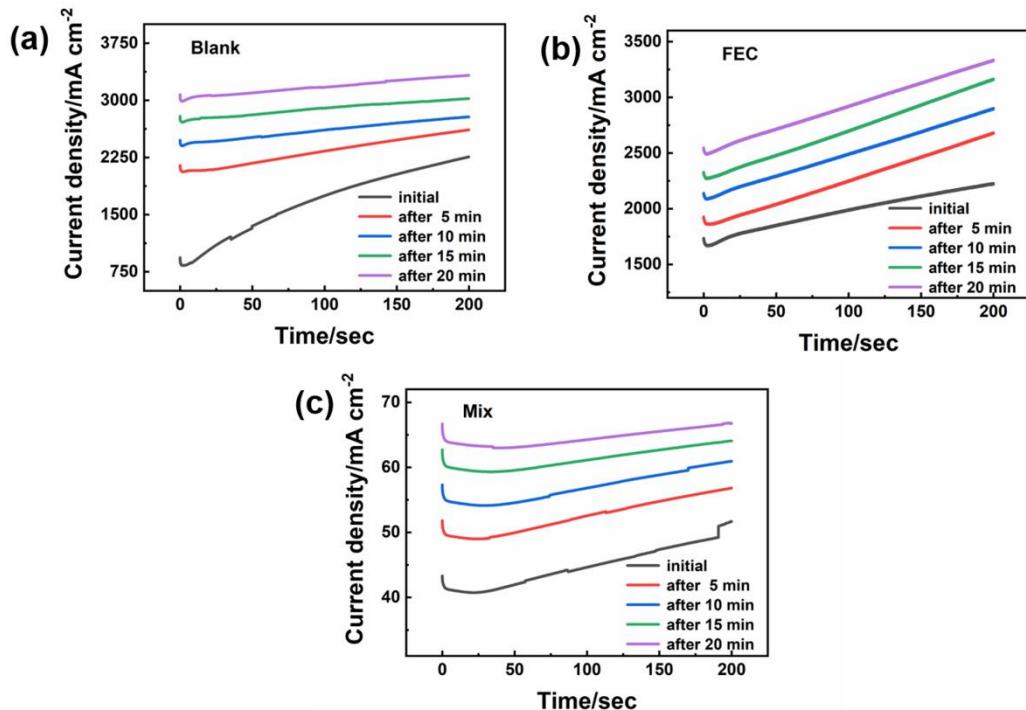
**Figure S10.** (a) Cyclic voltammetry for the Ni microelectrode of the 10th cycle in four electrolytes; the scanning rate is  $20 \text{ mV s}^{-1}$ , the arrows indicate scan direction, and the inset is the Allen–Hickling plot of Li plating/stripping. (b) Trend of exchange current density,  $j_{ct0}$ , during 20 cycles. (c) trend of transfer coefficient  $\alpha$  during 20 cycles.



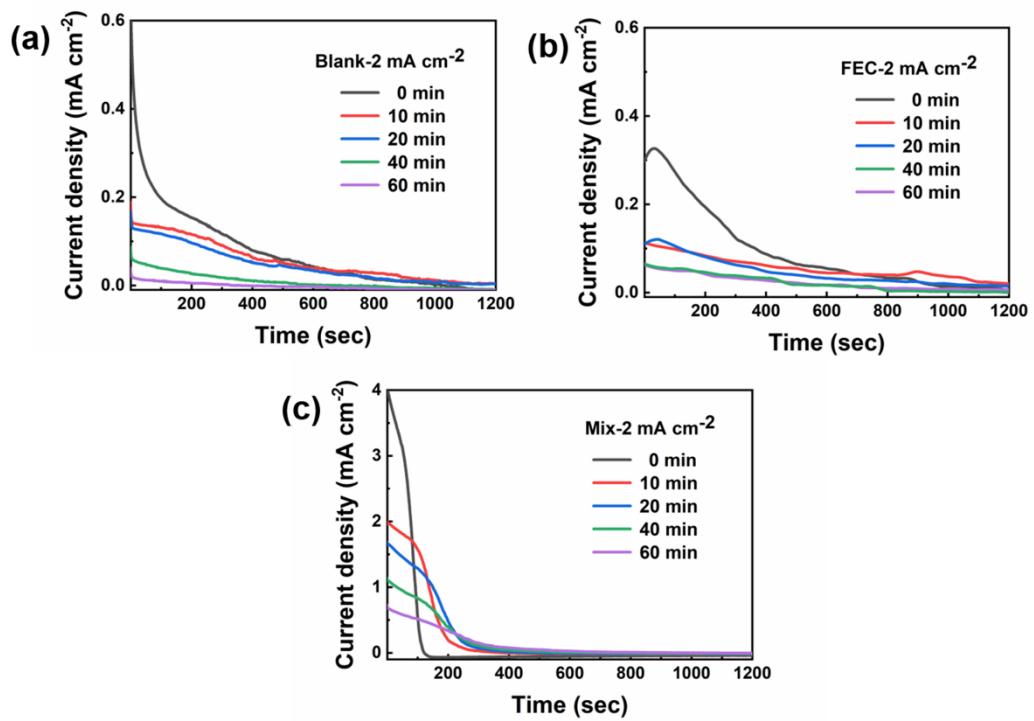
**Figure S11.** Schematic diagram of differences of the micro discharge path of solvated Li ion, micro chemical environment and number of metal lithium bonds of the newly formed adsorbed lithium atoms. (a) one Li-Li bond. (b) two Li-Li bonds. (c) four Li-Li bonds.



**Figure S12.** E-t response profiles of Li plating on Ni microelectrode in  $\text{LiNO}_3$  electrolytes at various current densities: (a)  $0.2\text{ mA cm}^{-2}$ , (b)  $0.5\text{ mA cm}^{-2}$ , (c)  $2\text{ mA cm}^{-2}$ , (d)  $5\text{ mA cm}^{-2}$  for a capacity of  $0.2\text{ mAh cm}^{-2}$ .



**Figure S13.** Potentiostatic current transient for Li crystallization on the Ni microelectrode (the initial potential is  $-140\text{ mV}$ ) in (a) Blank electrolyte; (b) FEC electrolyte; (c) Mix electrolyte.



**Figure S14.** (a) J-t transients for the dissolution of Li from the Ni microelectrode following electrodeposition and various periods on open circuit in (a) Blank sample; (b) FEC sample; (c) Mix sample.