

## ***Supporting Information***

### **Understanding the Impacts of Li Stripping Overpotentials at the Counter Electrode by Three-Electrode Coin Cell Measurements**

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## Experimental

### *General Reagents*

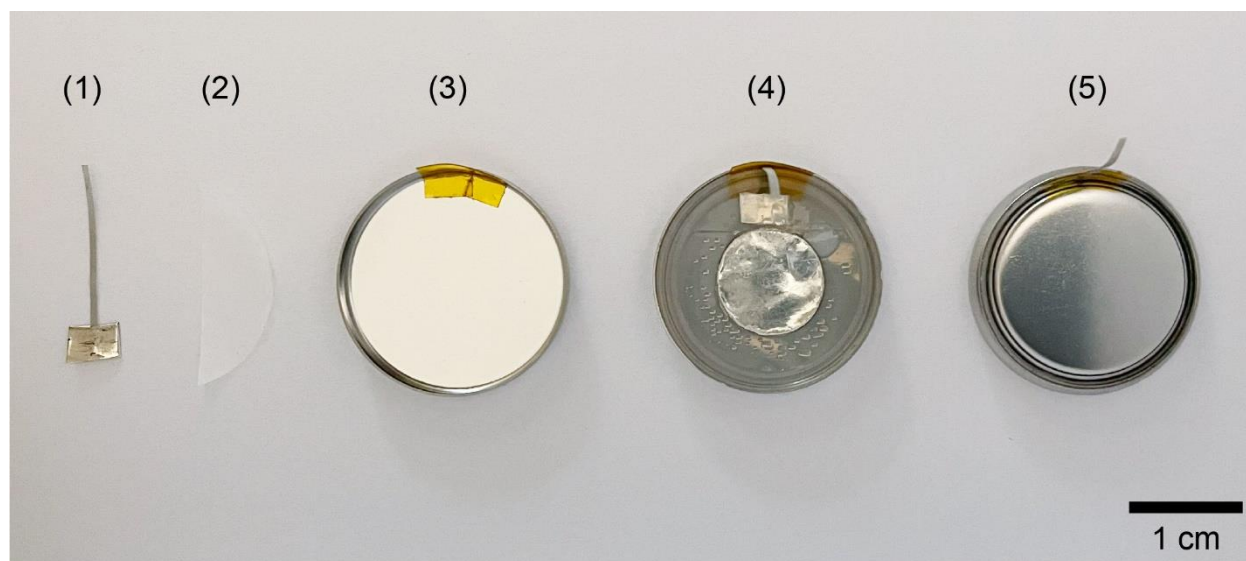
All materials and reagents were obtained from the indicated vendors and used as received, unless otherwise specified. Lithium iron phosphate (LFP) was purchased from MTI Corp., USA. 1-Methyl-2-pyrrolidinone (NMP) was purchased from Sigma-Aldrich (anhydrous 99.5%). Poly(vinylidene fluoride)-co-hexafluoropropylene (PVDF-HFP) (Sigma Aldrich), and super P (TIMCAL Ltd., Switzerland) were dried overnight in a vacuum oven at 60 °C and stored in a desiccator before use. Electrolyte components, EC (ethylene carbonate) (Aldrich, 99+%), DEC (diethyl carbonate) (Aldrich, 99+%), and LiPF<sub>6</sub> (Aldrich, 98+%), and Li metal foil (99.9%, Alfa Aesar) were stored in an argon filled glovebox (Vacuum Atmospheres, USA). The electrolyte solution for this work was 1 M LiPF<sub>6</sub> in EC:DEC=1:1 (v/v) which was prepared in the glovebox. Coin cell components were purchased from Kanematsu KGK Corp., Japan. A polypropylene separator (Celgard 2400) was punched into 19 mm disks and used in the coin cells.

Copper (Cu) foil (Goodfellow, 99.95+%) was immersed in sulfuric acid and washed with running distilled water for a minute followed by rinsing with ethanol. A 1/2-inch diameter punch was used to obtain Cu disks, and the disks were stored in an argon-filled glove box. Before use as an electrode, Li foil was placed in a plastic bag which had been washed with acetone and rolled out with a pasta maker in the glovebox.

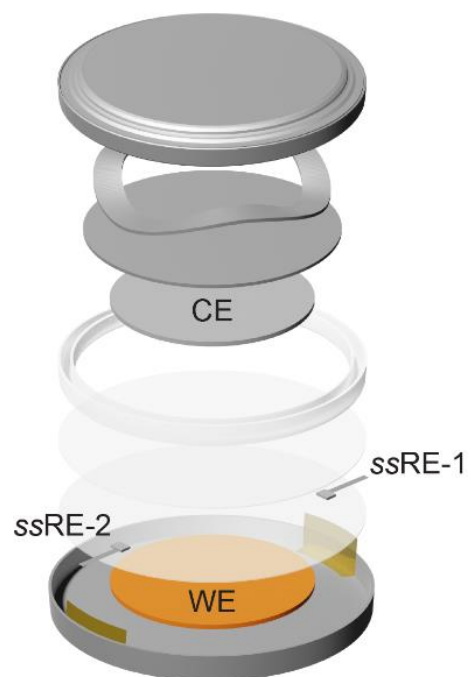
Refined Li (*rLi*) was prepared by melting Li in mineral oil. Mineral oil containing Li was heated to 200 °C with stirring in a fume hood. When Li started to melt, isopropanol (IPA) was added dropwise to dissolve lithium oxides and promote agglomeration of the *rLi*.<sup>1</sup> After cooling *rLi* to room temperature, the Li agglomerate was transferred into the glovebox. The *rLi* chunks were washed with hexane to remove mineral oil and cut with a ceramic knife to remove the oxide layer. Fresh Li was placed in a clean zip bag and rolled into a foil using the pasta maker.

### *Electrochemical Measurements*

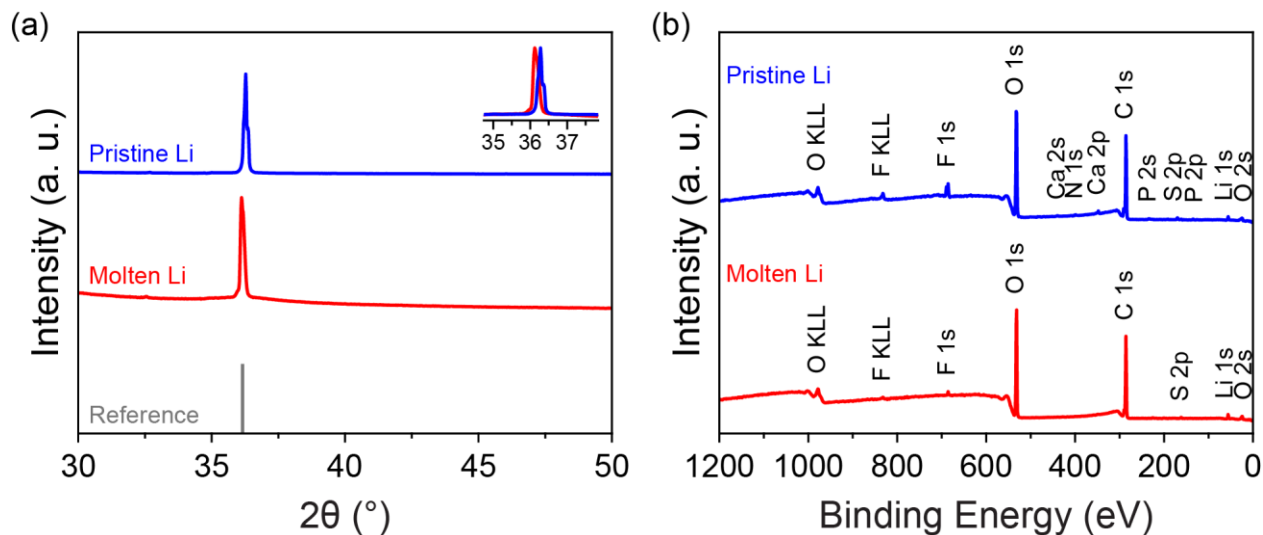
All LFP||Li cells were pre-cycled 20 times at 0.5 C prior to any further analyses via galvanostatic cycling in the three-electrode configuration with a cut-off voltage of 2.5 V – 4.0 V (*vs.* Li<sup>+</sup>/Li) using a BT2000 (Arbin Instruments, USA) unless otherwise stated. Galvanostatic intermittent titration technique (GITT) was performed following 10 charge/discharge cycles at 0.5 C. The analysis employed a 30-minute, 0.1 C current pulse, followed by a three-hour relaxation period. The same cell was tested in the two- and three-electrode configurations and the obtained diffusion coefficients were compared. Potentiostatic electrochemical impedance spectroscopy (PEIS) was performed on precycled cells using a 5-mV amplitude and a frequency range from 400 kHz to 50 mHz. Cyclic voltammetry measurements were performed on precycled cells. The resulting profiles were corrected for *iR* drop, with the resistance corresponding to the resistance between the WE and CE/RE or WE and *ss*RE for two-electrode and three-electrode cell measurements, respectively. The same cell was tested in the two- and three-electrode configurations and the results compared.



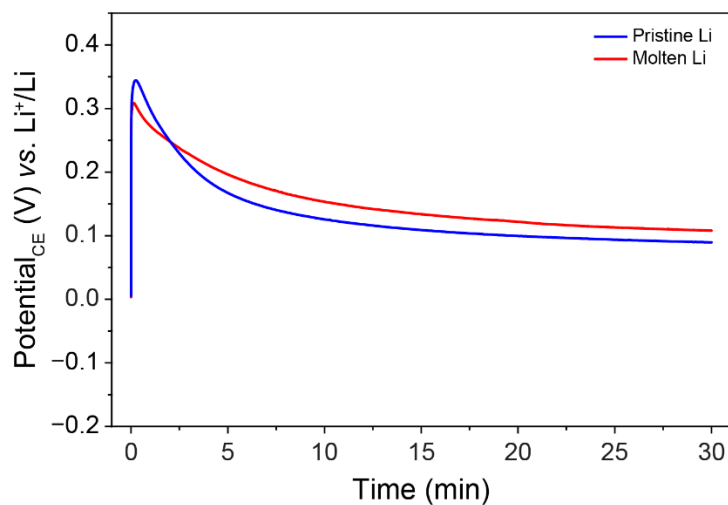
**Figure S1.** Photograph of modified cell components involved in each step of cell assembly. The assembly is described from left to right. (1) The *ssRE* made by embedding a stainless-steel strip in Li metal. (2) A partial Celgard separator to be placed on top of the *ssRE* to prevent electrical contact between the *ssRE* and CE. (3) A modified coin cell base where Kapton tape has been placed on the bottom/edge of the cell to prevent electrical contact between the *ssRE* and WE. (4) Partial assembly of the modified cell. First Li is placed in the base of the cell, followed by electrolyte and a full Celgard disk separator (19 mm diameter). The *ssRE* is then placed in the cell with the stainless-steel strip folded at a 90 ° angle such that it extends up and out of the cell. The *ssRE* is placed such that the stainless-steel strip contacts the Kapton tape and not the metal edge of the cell. The partial Celgard separator is then placed on top of the *ssRE*, followed by the cell gasket. (5) The finished cell assembly. The CE, spacer, spring, and cell cap are subsequently placed in/on the cell to finish cell assembly as normal. The stainless-steel mesh strip which extended from the cell was pressed down flat onto the cell cap before the cell was sealed to prevent it from breaking off in the press. No additional insulation was needed in this work between the stainless-steel mesh and the cell cap, as both the CE and RE were Li. In a case where the CE and RE are different materials, an additional insulating layer such as Kapton tape should be placed on the cell cap, under the stainless strip to prevent a short. The sealed cell was sufficiently airtight to allow for cycling measurements to be conducted for a month following cell assembly. If necessary (such as in the case of using a thicker or more porous stainless-steel mesh), epoxy could be applied around the extended strip to achieve a better seal.



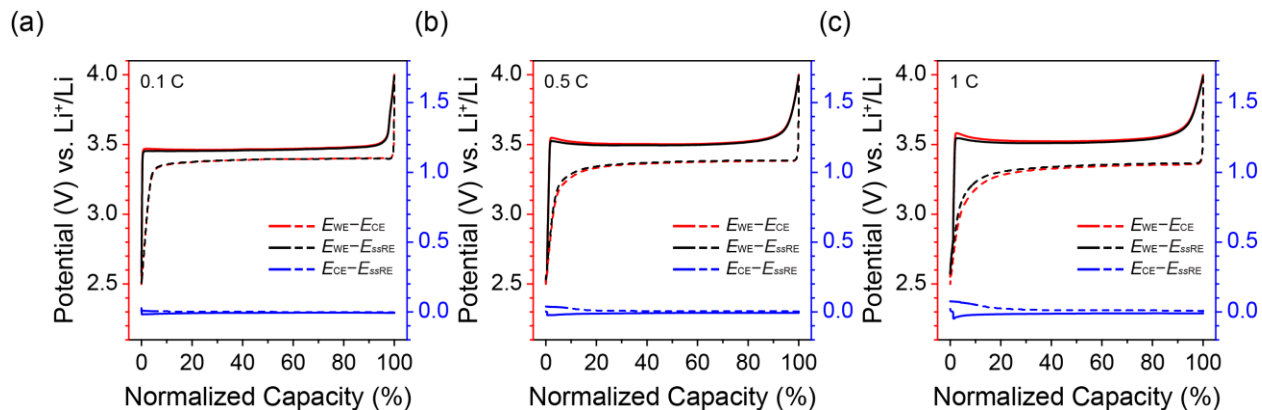
**Figure S2.** Schematic diagram of the four-electrode coin cell design.



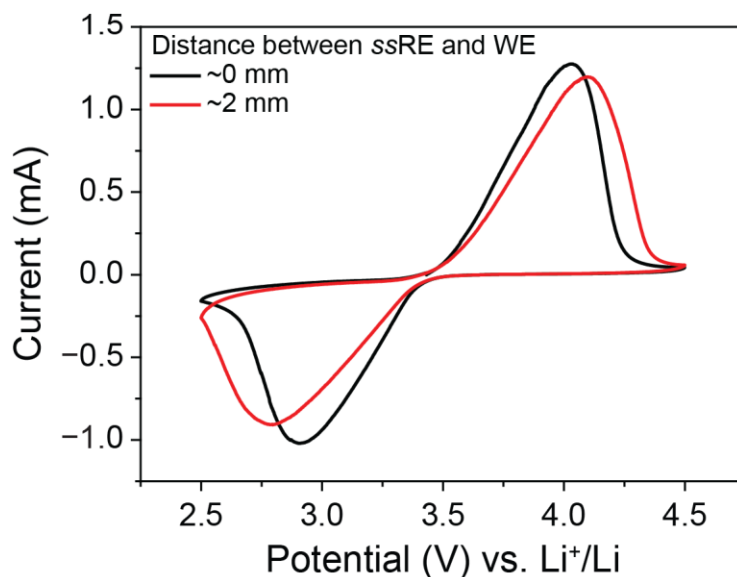
**Figure S3.** (a) X-ray diffraction (XRD) patterns of the pristine lithium and the molten lithium compared to the reference lithium pattern and (b) X-ray photoelectron spectra of the two lithium samples.



**Figure S4.** Potential profiles of the CE vs. the ssRE where the WE and CE were pristine lithium (blue) or molten lithium (red) in a Li||Li cell. The cell was cycled in the three-electrode coin cell configuration at a current density of  $\pm 1 \text{ mA cm}^{-2}$ .

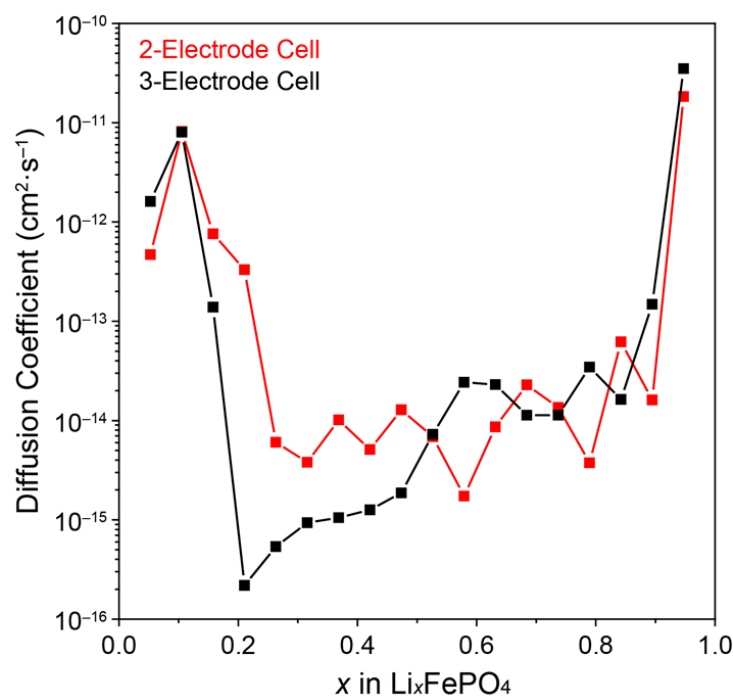


**Figure S5.** Normalized charge/discharge curves from galvanostatic charge/discharge experiments with LFP||Li cells where the mass loading is less than those in Figure 4a-c ( $0.8 \text{ mg cm}^{-2}$  vs.  $3.1 \text{ mg cm}^{-2}$  for cells in Figure 4a – c). The current densities are (a) 0.1 C, (b) 0.5 C, and (c) 1 C with the black trace representing the potential of the WE vs. ssRE and the red trace representing the potential of the WE vs. CE/RE. The change in the potential of the CE during the measurement is shown in blue. In all electrode traces, the solid line represents the charging cycle, and the dotted line shows the discharge cycle.

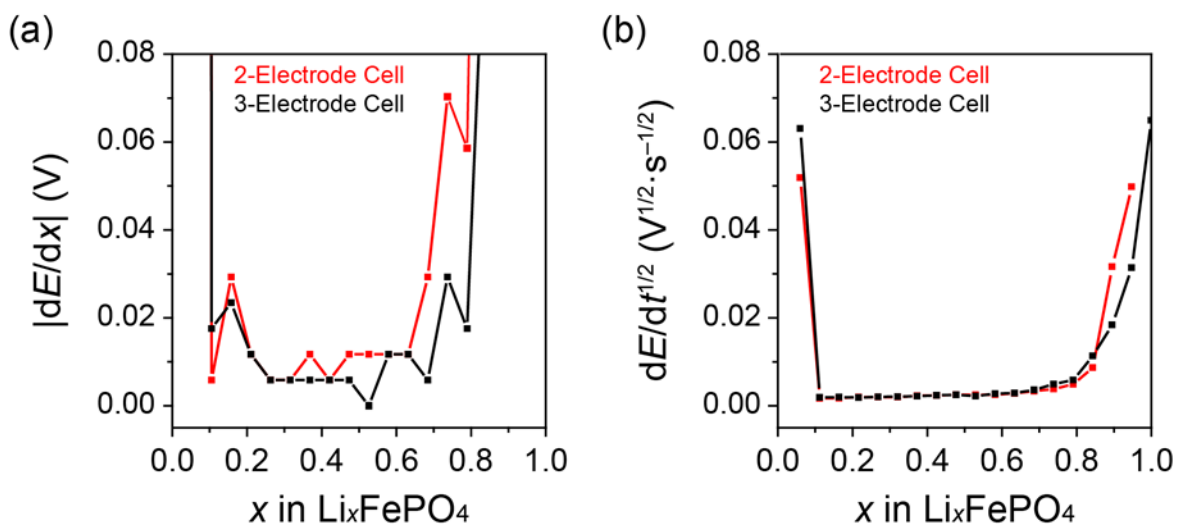


**Figure S6.** CVs of LFP||Li cells run in the three-electrode configuration at  $1 \text{ mV s}^{-1}$  with the ssRE placed at  $\sim 0 \text{ mm}$  from the edge of the WE (black) and  $\sim 2 \text{ mm}$  from the edge of the WE to the ssRE (red) with a mass loading of  $\sim 1.8 \text{ mg cm}^{-2}$ . Note, neither voltammogram was corrected for  $iR$  drop to demonstrate its effect on the voltammetric response.

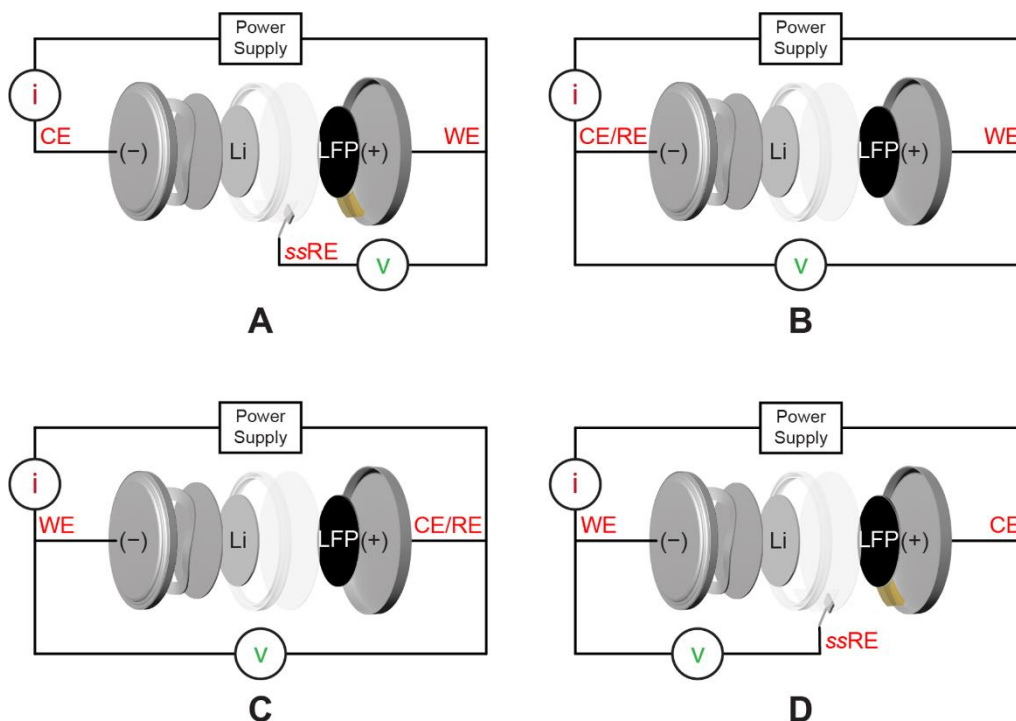




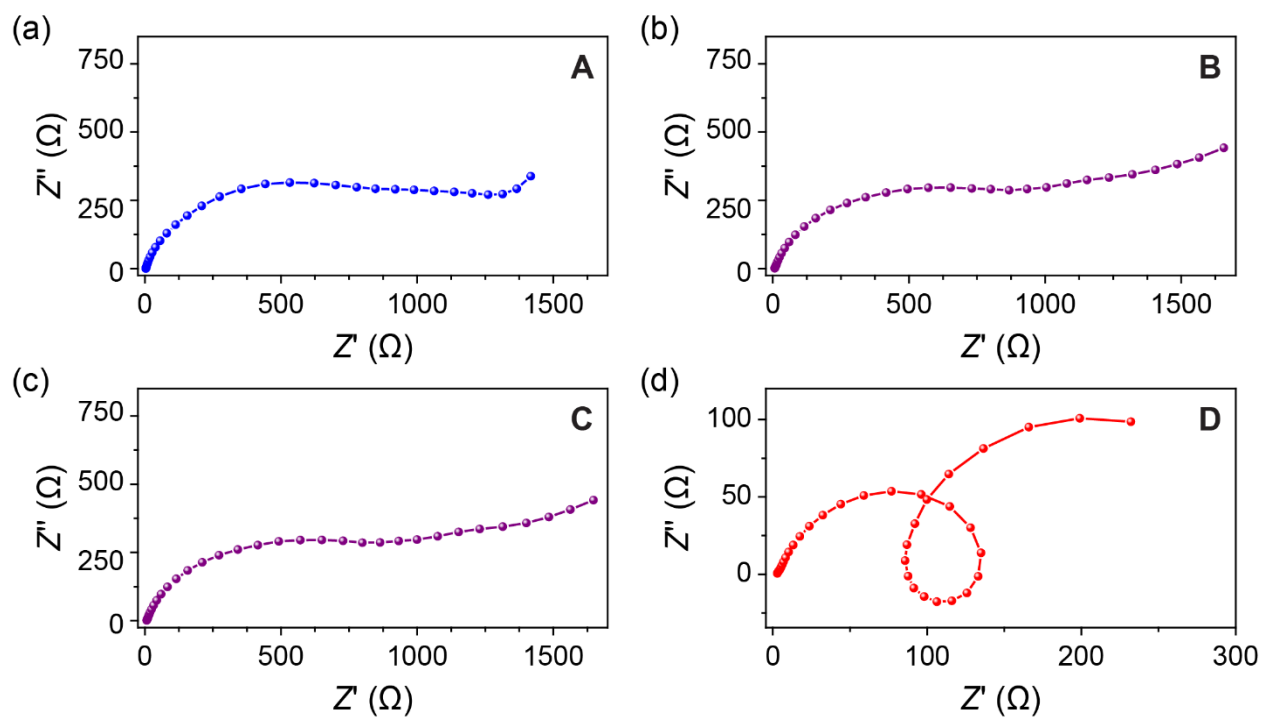
**Figure S7.** Diffusion coefficients determined from the charging process of LFP||Li cells by GITT analysis. The red points represent the two-electrode configuration and the black points represent the three-electrode configuration.



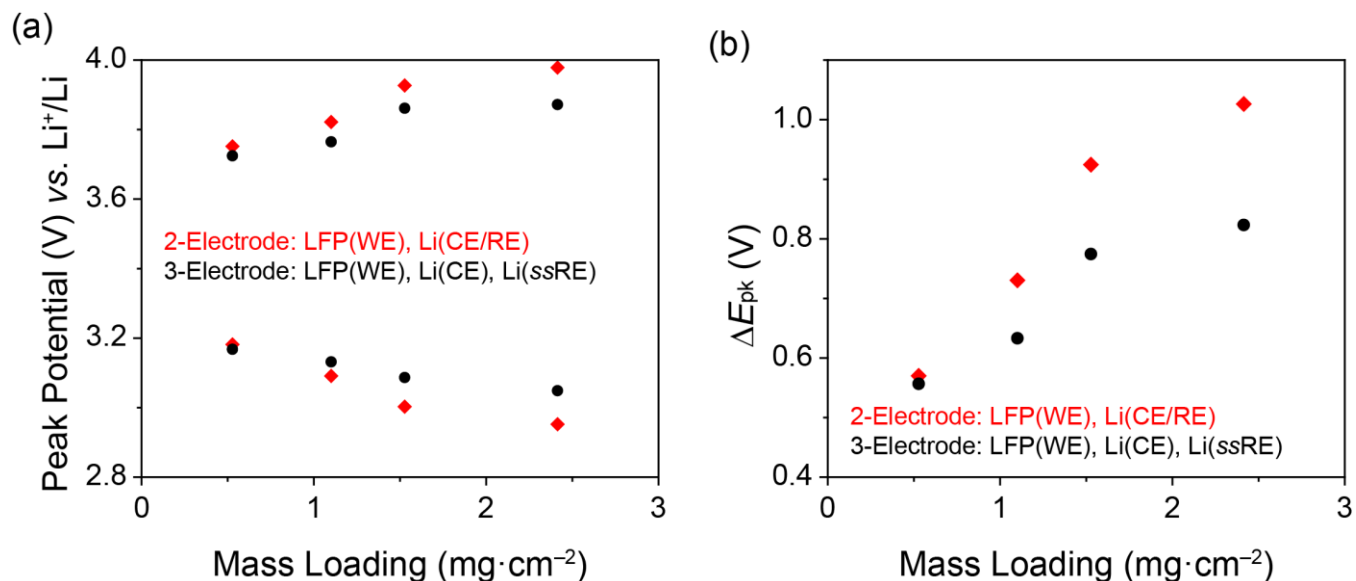
**Figure S8.** (a) Values of  $|dE/dx|$  and (b)  $dE/dt^{1/2}$  with  $x$  in  $\text{Li}_x\text{FePO}_4$  during discharge of LFP||Li half-cells in GITT experiments. The red points represent the two-electrode configuration, and the black points represent the three-electrode configuration.



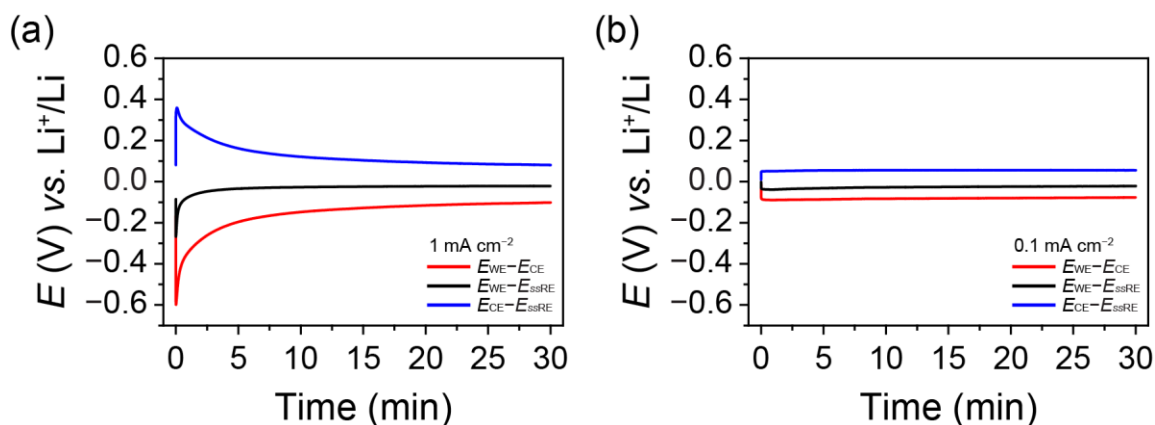
**Figure S9.** Schematic of cell configurations used for potentiostatic electrochemical impedance spectroscopy: **A** LFP (WE) Li (CE) ssRE (RE), **B** LFP (WE) Li (CE/RE), **C** Li (WE) LFP (CE/RE), and **D** ssRE (WE) Li (CE) LFP (RE).



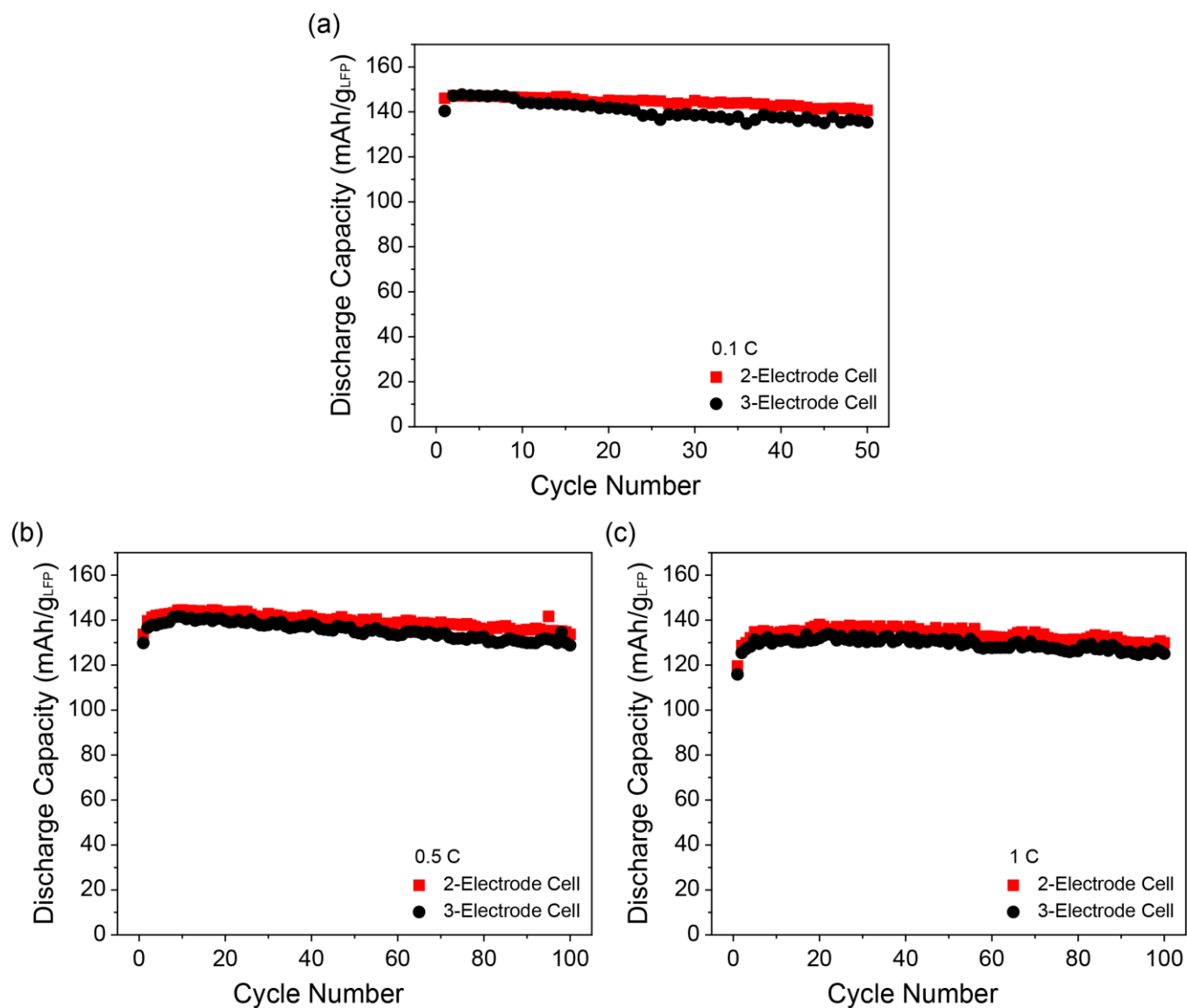
**Figure S10.** Nyquist plots corresponding to the cell configurations in Figure S9, where the Nyquist plot in (a) corresponds to **A**, (b) corresponds to **B**, (c) corresponds to **C**, and (d) corresponds to **D**.



**Figure S11.** LFP||Li cells run in the two-electrode (red) and three-electrode (black) configuration for cyclic voltammetry measurements at  $1 \text{ mV s}^{-1}$  and their corresponding (a) peak potentials with mass loading of LFP and (b)  $\Delta E_{\text{pk}}$  values in V with mass loading of LFP.



**Figure S12.** Comparison of potential profiles of the WE vs. ssRE (black), CE vs. ssRE (blue), and WE vs. CE (red) with different current densities in a Li||Li cell. The cell was tested in the three-electrode coin cell configuration at a current density of (a)  $-1 \text{ mA cm}^{-2}$  and (b)  $-0.1 \text{ mA cm}^{-2}$ .



**Figure S13.** LFP||Li cells run in the two-electrode (red) and three-electrode (black) configuration for galvanostatic charge/discharge cycling at (a) 0.1 C, (b) 0.5 C and (c) 1 C.

## References

1. Furukawa, T.; Hirakawa, Y.; Kondo, H.; Kanemura, T., Dissolution Behavior of Lithium Compounds in Ethanol. *Nucl. Mater. Energy* **2016**, 9, 286-291.