## **Supporting Information**

## Constructing a Stable Lithium Metal-Gel Electrolyte Interface for Quasi-Solid-State Lithium Batteries

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## **Experimental Section**

*Synthesis*: 0.5 g PEO (molecular weight of ~100,000) was firstly dispersed in 10 g tetraethylene glycol dimethyl ether (TEGDME) and the suspension was stirred at 25 °C for 2 h. Photoinitiator (2-hydroxy-2-methyl-1-phenyl-1-propanon) was added into monomer (ethoxylated trimethylolpropane triacrylate) with a mass ratio 1 %. Subsequently, 0.06 g LiNO<sub>3</sub>, 0.65 g lithium bis(trifluoromethane)sul-fonimide (LiTFSI), 0.2 g SiO<sub>2</sub> powder and 3 mL PEO suspension were added into 1 mL monomer solution and the mixture was heated at 50 °C for 4 h. dpn-GE was obtained by polymerizing the precursor solution with 365 nm ultraviolet light for 10 min.

*Characterizations*: Thermogravimetric analyses (TG/DTA Netzsch) were performed from 30 to 800 °C at a heating rate of 5 °C min<sup>-1</sup> under nitrogen atmosphere. X-ray diffraction (XRD) analyses were carried out with Rigaku D/max-2500 operated with Cu K $\alpha$  radiation ( $\lambda$ =1.5405 Å) at 40 kV and 200 mA. The ex-situ images of Li deposit were observed on a field emission scanning electron microscope (SEM, JEOL 6701F). X-ray photoelectron spectroscopy (XPS) was performed on ESCALab 250 Xi (Thermo Scientific) with 200 W monochromatized Al K $\alpha$  radiation. *In situ* optical microscopy study (OLS-4000 OLYMPUS) were performed in a home-built electrochemical cell with a transparent window, where Li symmetric cells with different electrolytes were assembled and the process of Li deposition/dissolution was captured in real time.

*Electrochemical measurements*: The ionic conductivity and activation energy of dpn-GE was investigated by electrochemical impedance spectroscopy (EIS) over a frequency range from 0.1 to 100000 Hz with a temperature range from 20 to 80 °C. To calculate the transference number, the cell assembled with two Li foils was tested by chronoamperometry and EIS. Asymmetric cells were assembled with stainless steel electrode, Li foil and dpn-GE. The plating/stripping stability and voltage window were evaluated with asymmetric cells by cyclic voltammetry and linear sweep voltammetry, respectively.

To evaluate the plating/stripping efficiency with dpn-GE, coin cells assembled with Li foils, Cu electrodes and dpn-GE was tested with a deposition capacity of 1 mA h cm<sup>-2</sup> under a current density of 0.5 mA cm<sup>-2</sup>. The Coulombic efficiency was calculated based on the ratio of charge and discharge capacity to evaluate the reversibility of the plating/stripping process. Galvanostatic charge/discharge tests were performed with Li symmetric cells at current densities of 0.2 and 0.5 mA cm<sup>-2</sup>.

For full cells, LiFePO<sub>4</sub> (LFP) and Se/C cathodes were prepared by mixing active materials, super P and polyvinylidene difluoride (the mass ratio is 8:1:1) on carbon-coated aluminum foils. Thin Li foils with a thickness of 50  $\mu$ m were employed as anodes. dpn-GE and liquid electrolyte (1M LiTFSI dissolved in DOL/DME) were applied as electrolytes. The full cell tests were performed at room temperature. All assemblies were performed in a glove box filled with argon.



Figure S1. Combustion tests with different electrolytes.



Figure S2. XRD patterns of PEO, polyacrylate and dpn-GE. The inset shows the optical image of dpn-GE membrane.



Figure S3. Arrhenius plot of the dpn-GE at different temperatures ranging from 20 to 80 °C.



**Figure S4.** (a) Cyclic voltammetry and (b) linear sweep voltammetry of dpn-GE at a scan rate of 0.1 mV s<sup>-1</sup>.



**Figure S5.** Optical images of Li metal anodes before (a) and after plating 2 (b), 3 (c) and 4 (d) mA h cm<sup>-2</sup> of Li with LE (1 M LiTFSI dissolved in DOL/DME).



**Figure S6.** Cycling profile of Li symmetric cell with dpn-GE at a current density of 0.2 mA  $cm^{-2}$ .



Figure S7. (a) Rate and (b) cycling performance (0.5C) of Li|LFP full cell with dpn-GE.



**Figure S8.** Cycling performance of Li-Se full cells with different electrolytes at (a) 0.2C and (b) 0.5C. (c) Galvanostatic charge/discharge profiles of Li-Se full cell with dpn-GE at different rates.

Video S1. Direct observation of interfacial evolution on the electrode-gel electrolyte interface.