Supporting Information

Enabling Solid-state Li Metal Batteries by In-situ forming Ionogel Interlayers

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As shown in Fig. S1, the ionic conductivities of the LATP pellet and the ionogel are determined to be 1.75 mS cm^{-1} and 1.43 mS cm^{-1} at 60 ℃ respectively.

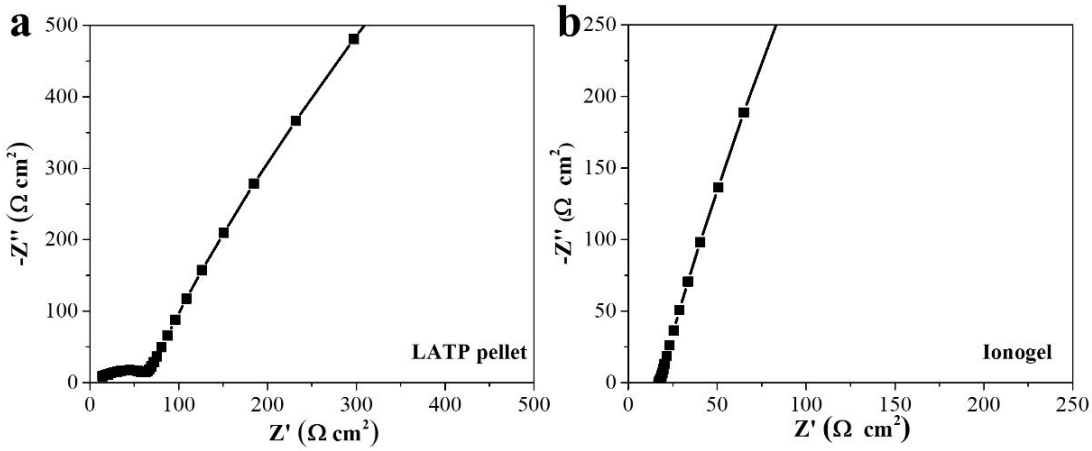

Fig. S1. The electrochemical impedance spectra of (a) the LATP pellet, and (b) the ionogel at 60 ℃.

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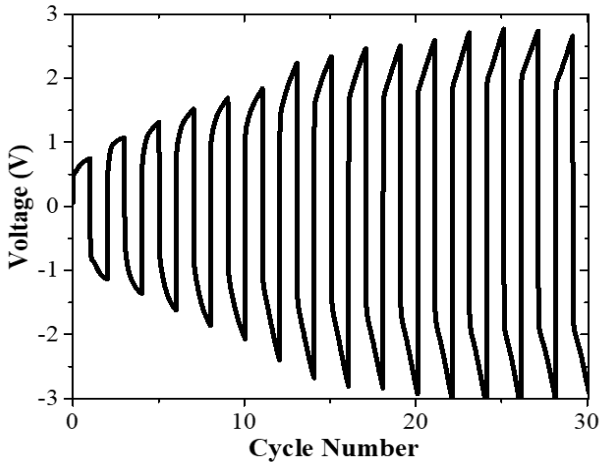

Fig. S2. The cycling performance of the Li/Li symmetric cell with the bare LATP pellet.

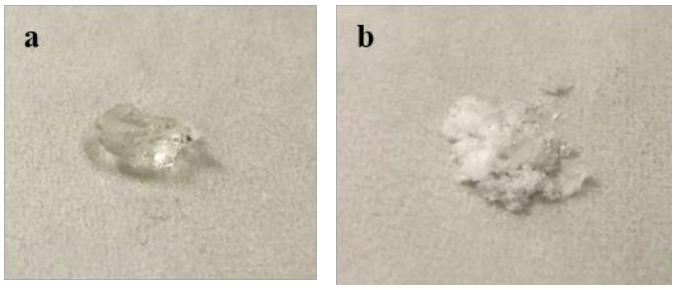

Fig. S3. Digital images of ionogel (a) and polymerized PEGDA polymer (b). The ionogel exhibits the elastic jelly-like texture, while PEGDA shows a brittle glass-like texture.

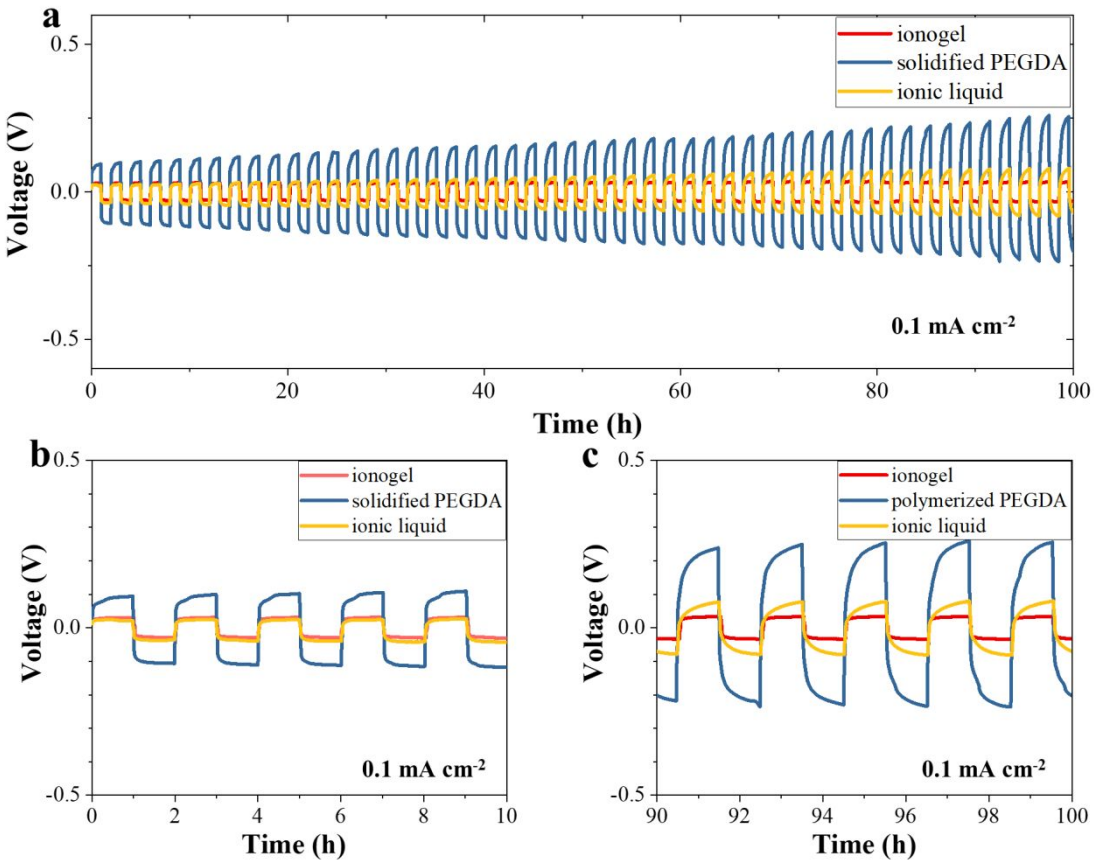

Fig. S4. (a) The long-term cycling of Li/Li symmetrical cells with the ionogel, solidified PEGDA and ionic liquid interlayers. (b, c) Charge-discharge curves of Li/Li symmetric cells at first and last 10 hours at 0.1 mA cm^{-2}.

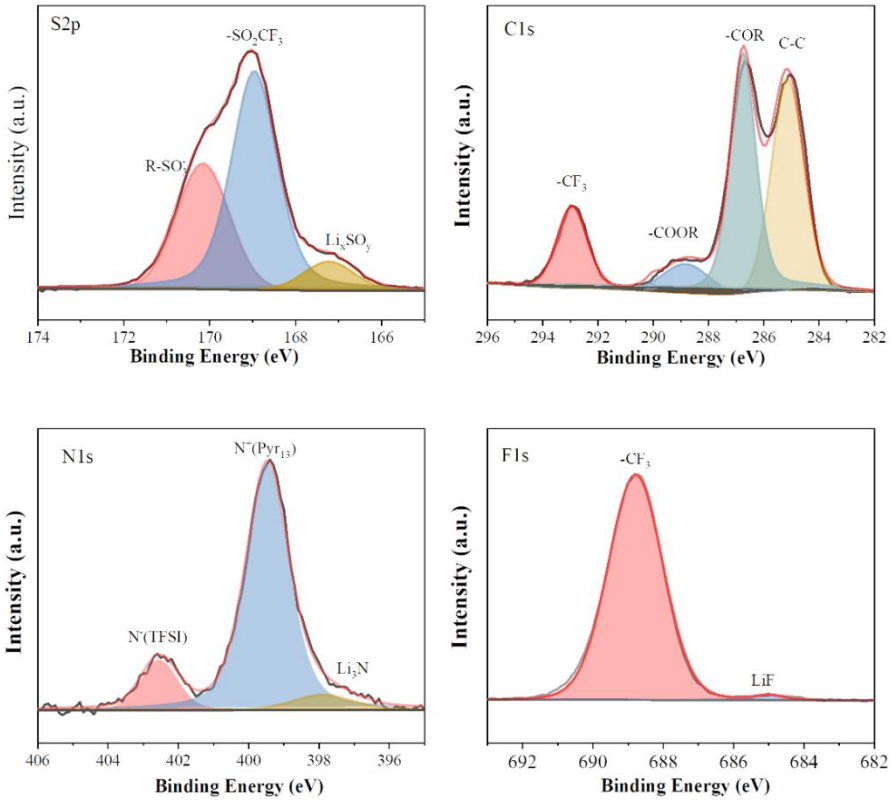

Fig. S5. XPS results of Li metal surface protected by the ionogel interlayer after cycling, indicating the formation of stable SEI layers on the anode surface.[1,2]

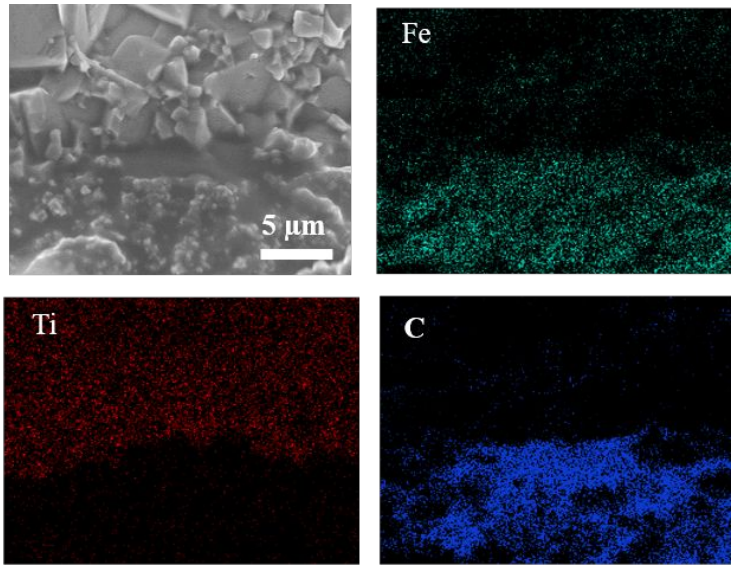

Fig. S6. SEM image and the energy dispersive X-ray (EDX) mapping of the SSE/cathode interface. The ionogel well infiltrates into the porous $LiFePO_4$ electrode and fill the gaps at the SSE/cathode interface.

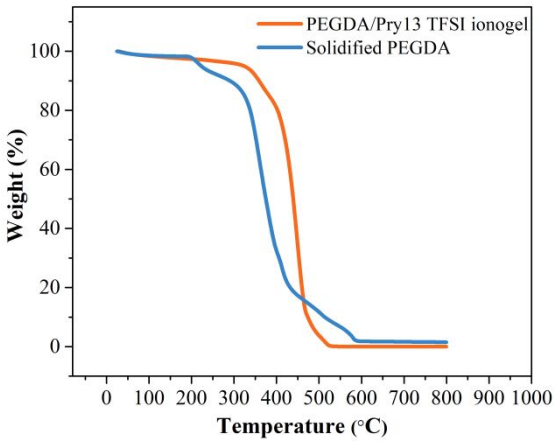

Fig. S7. The TGA results of the PEGDA/Pyr_{13}TFSI ionogel and solidified PEGDAThe thermal stability of the ionogel is much better than that of the PEGDA.

Fig. S8 shows the cycling performance of the symmetric cell with ionogel interlayers at increasing current densities, starting from 0.05 mA cm^{-2} with an increasing step of 0.05 mA cm^{-2}. The cell followed an ohmic current–voltage behavior up to 0.65 mA cm^{-2}. After that the overpotential showed a sudden increase and fluctuations, which can be ascribed to the occurrence of side reactions at the interface and the formation of fractures of the LATP pellet. Thus, the 0.65 mA cm^{-2} is identified as the critical current density for the ionogel-modified LATP solid electrolyte.[3]

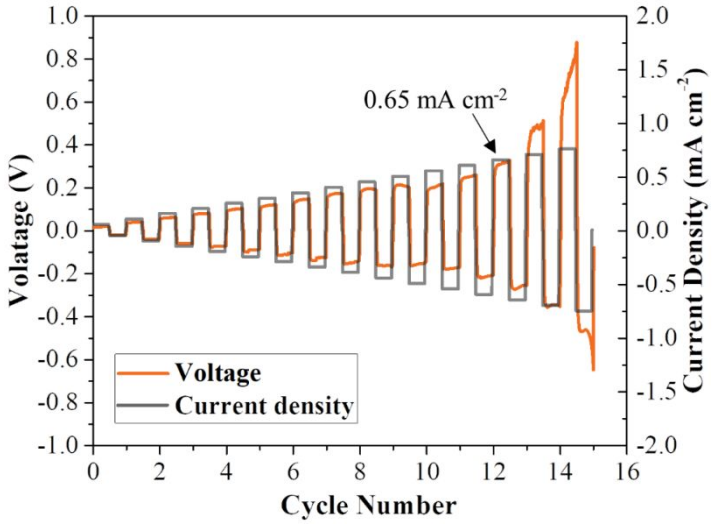

Fig. S8. Li plating/stripping graph for the Li/ionogel/LATP/ionogel/Li symmetric cell at increasing current densities.

As shown in Fig. S9, the Li/Li symmetric cell with ionogel interlayers stably ran for over 100 hours at room temperature.

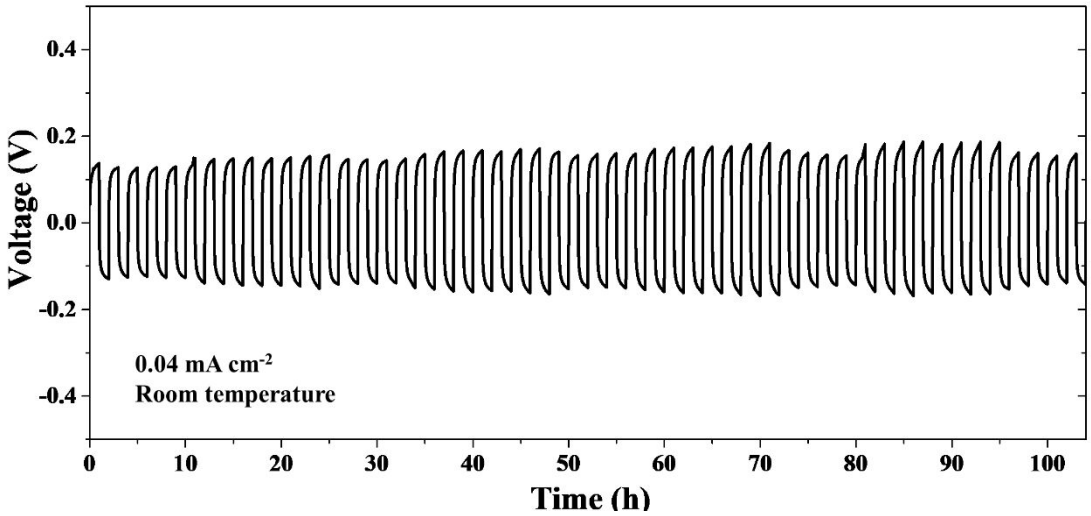

Fig. S9. Cycling test of the Li/Li symmetric cell with ionogel interlayers at room temperature.

As shown in Fig. S10, the SSLMB with ionogel interlayers was capable to deliver a specific capacity of 125.7 mAh g^{-1} at 0.2 C and 117.8 mAh g^{-1} at 0.3 C at room temperature, and no obvious decay was detected after 80 cycles.

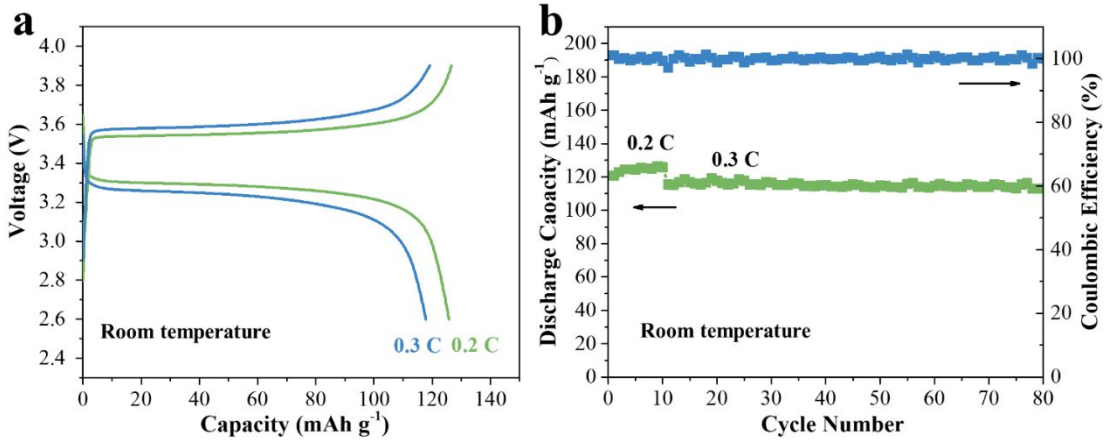

Fig. S10. Electrochemical characterizations of the Li/ionogel/LATP/ionogel/LFP full battery at room temperature. (a) Voltage profiles of 0.2 C and 0.3 C. (b) The cycling performance.

A full battery with a high LFP loading of 12 mg cm^{-2} (purchased form Shenzhen Kejing Technology Co.) has been assembled and evaluated, as shown in Fig. S11. Under the current density of 0.1 mA cm^{-2}, the SSLMB delivered a high areal capacity of 1.8 Ah cm^{-2} and a specific capacity of 146.5 mAh g^{-1}, and the capacity retained 129.6 mAh g^{-1} after 10 cycles.

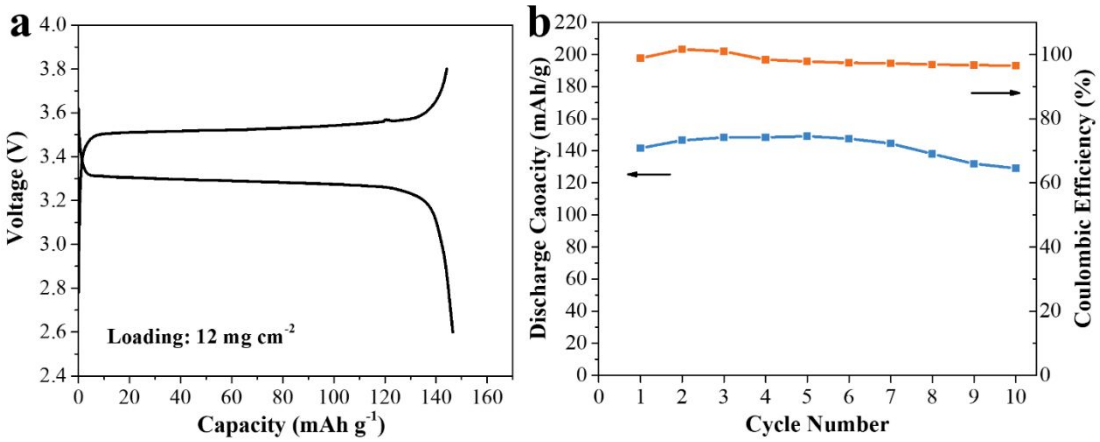

Fig. S11. Electrochemical characterizations of SSLMBs using high-loading LFP cathode (12 mg cm^{-2}, 2.04 Ah cm^{-2}) under the current density of 0.1 mA cm^{-2} at 60 ℃. (a) The voltage profile of the 2^{th} cycle. (b) The cycling performance.

As shown in the CV test in Fig. S12a, the ionogel interlayer exhibits an electrochemical window up to 4V and is stable with the Li metal.[4] The Li/Li symmetric cell was assembled to further evaluate the stability of the ionogel against the Li metal. As shown in Fig. S12b, the ionogel remained stable with the Li metal anode after cycling for 200 hours.

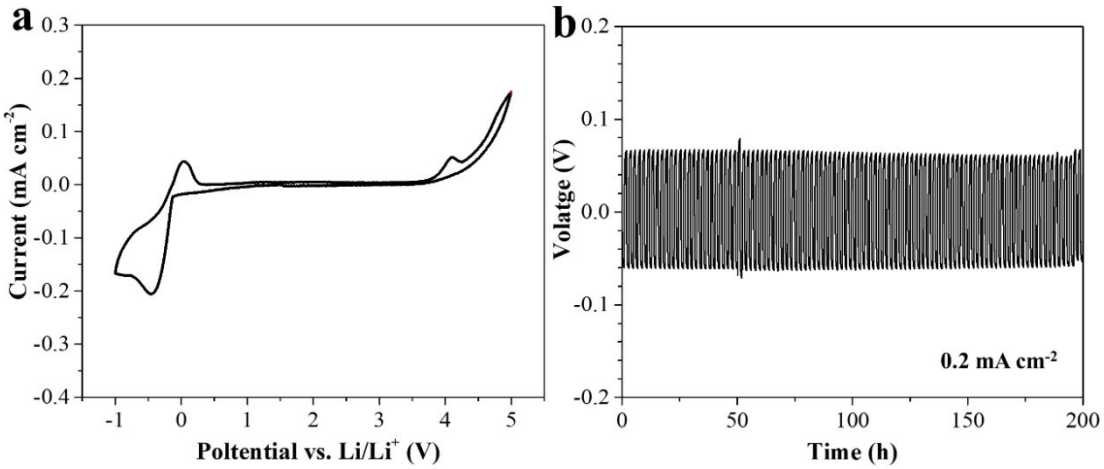

Fig. S12. (a) The cyclic voltammetry (CV) of the ionogel with Li metal as counter electrode at room temperature. (b) The cycling performance of the Li/ionogel/Li symmetric cell at 60 ℃.

References

(1) Zheng, B.; Zhu, J.; Wang, H.; Feng, M.; Umeshbabu, E.; Li, Y.; Wu, Q.-H.; Yang, Y. Stabilizing Li10SnP2S12/Li Interface via an in Situ Formed Solid Electrolyte Interphase Layer. ACS Appl. Mater. Interfaces 2018, 10 (30), 25473–25482.

(2) Ma, Q.; Zeng, X.; Yue, J.; Yin, Y.; Zuo, T.; Liang, J.; Deng, Q.; Wu, X.; Guo, Y. Viscoelastic and Nonflammable Interface Design–Enabled Dendrite-Free and Safe Solid Lithium Metal Batteries. Adv. Energy Mater. 2019, 9 (13), 1803854.

(3) Tippens, J.; Miers, J. C.; Afshar, A.; Lewis, J. A.; Cortes, F. J. Q.; Qiao, H.; Marchese, T. S.; Di Leo, C. V.; Saldana, C.; McDowell, M. T., Visualizing Chemomechanical Degradation of a Solid-State Battery Electrolyte. *ACS Energy Letters* **2019,** *4* (6), 1475-1483.

(4) Lu, Z.; Yu, J.; Wu, J.; Effat, M. B.; Kwok, S. C.; Lyu, Y.; Yuen, M. M.; Ciucci, F., Enabling room-temperature solid-state lithium-metal batteries with fluoroethylene carbonate-modified plastic crystal interlayers. *Energy Storage Mater.* **2018**, *18*, 311-319.