Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels.

Supporting Information

Solventless Thermal Crosslinked Flexible Polymer Protective Layer for Highly Stable Lithium Metal Batteries.

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Experimental section

Materials

Poly (ethylene glycol) dimethacrylate (M_n 550, Sigma-Aldrich) was used as polymer film of protective layer. And tert-Butyl pivalate (Sigma-Aldrich) was employed as initiator of radical polymerization. Lithium (MTI Korea) was used as working, reference and counter electrode. The separator of polyethylene (20 µm) and electrolyte of 1 M $LiPF_6$ in EC (ethylene carbonate)/DEC (diethyl carbonate) (50/50 by volume, 50 mL) were obtained from Asahi Kasei Chemicals Corporation and PANAX ETEC Co. Ltd, respectively. $LiFePO_4$ (Hanwa Chemicals), PVdF (arkema) and Super P (MTI korea) were employed as cathode material.

Preparation of PEGDMA protective layer

0.01 g of tert-Butyl pivalate was added into 1 g of poly (ethylene glycol) dimethacrylate. This solution was stirring at room temperature and dropped onto lithium metal surface. This droplet coated with the bar coater to make a film on the lithium metal surface. After casting process, polymerization of Poly (ethylene glycol) dimethacrylate was obtained for 1 minute with 100 ℃ on hot plate. Manufacturing processes of PEGDMA protective layer were performed in an argon-filled glove box.

Preparation of $LiFePO_4$ electrode

The cathode materials were prepared by mixing the $LiFePO_4$, super P and poly-(vinylidene fluoride) in a weight ratio of 8:1:1 in N-methyl pyrrolidone to ensure homogeneity. This slurry was coated on an Aluminum foil (18 um) and dried under the convection oven at 120 °C for 2 h and the vacuum oven at 120 °C for 12 h. Then the electrode foil was cut with 16 mm in diameter. The loading density of this electrode is 1.8 mg cm^{-2}.

Electrochemical measurements

Coin cells (CR2032) were assembled to evaluate stability of Li metal surface after galvanostatic charge and discharge. All processes were carried out in an argon-filled glove box. In symmetrical cell test, Li metal is working electrode. Also, Li metal is counter and reference electrode. PE separator and 1M $LiPF_6$ in EC/DEC were used as separator and electrolyte, respectively. Cell tests were conducted with a current density of 1, 5 mA cm^{-2}. The charge and discharge time are 1 hour each. After cycle test is completed, the cell is opened with a scissor in a glove box, then washed with a few drops of diethyl carbonate (DEC) to measure SEM and XPS. To evaluate the rate capability, LFP/Li test was investigated. First cycle was performed with 0.1 C. Then, this cell was cycled in different C rates such as 0.2 C, 0.5 C, 1.0 C, 2.0 C, and 5.0 C respectively. Finally, 0.2c was performed to estimate the capacity recovery rate.

Table S1. Absorption peaks table of ATR FT-IR of c-PEGDMA.

Functional group	**Peaks [cm^{-1}]**
C-O stretching of ethylene oxide	1242~1250
C-H bending of alkane	1421~1454
C=C stretching of alkene	1636~1639
C=O stretching of conjugated aldehyde	1716~1724
C-H stretching of aldehyde	2867~2869
C-H stretching of alkane	2939~2945

(1) Socrates G. Infrared Characteristic Group Frequencies: Tables and Charts, 3rd Edition, Wiley & Sons: New York, 2004.

(2) Kiefer, J.; Fries, J.; Leipertz, A. Appl. Spectrosc. 2007, 61, 1306.

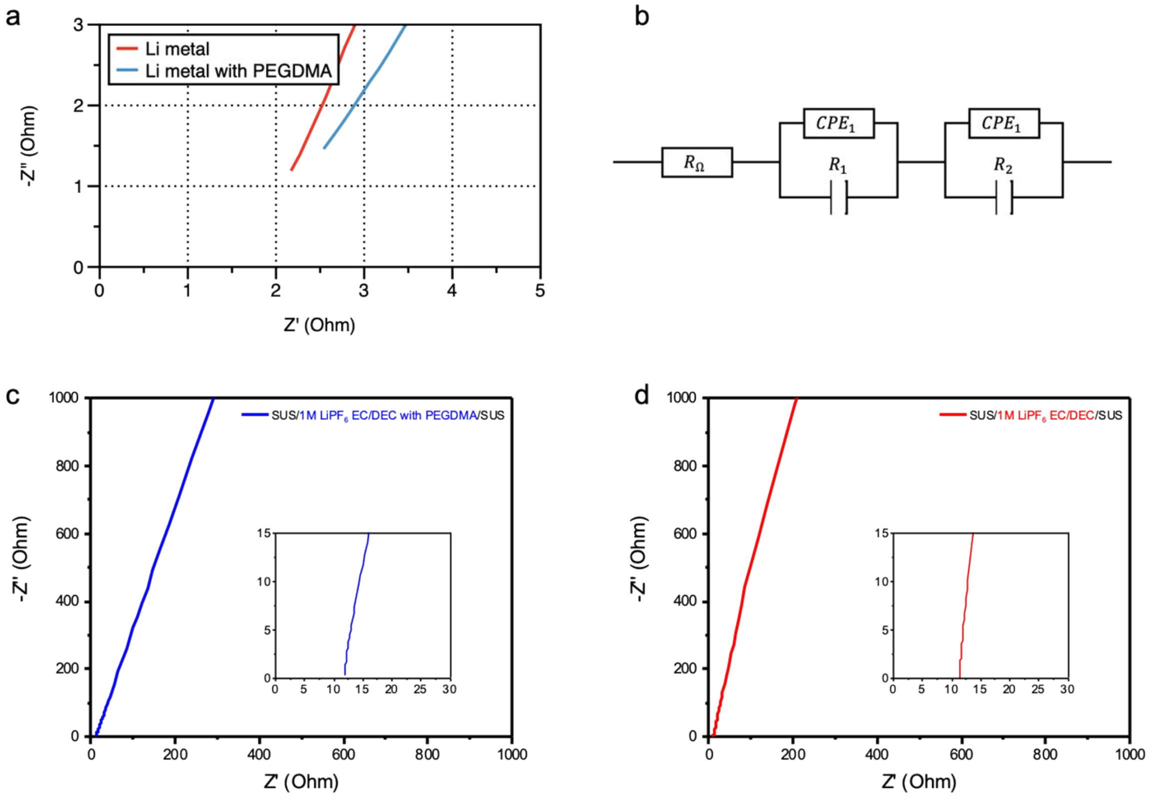
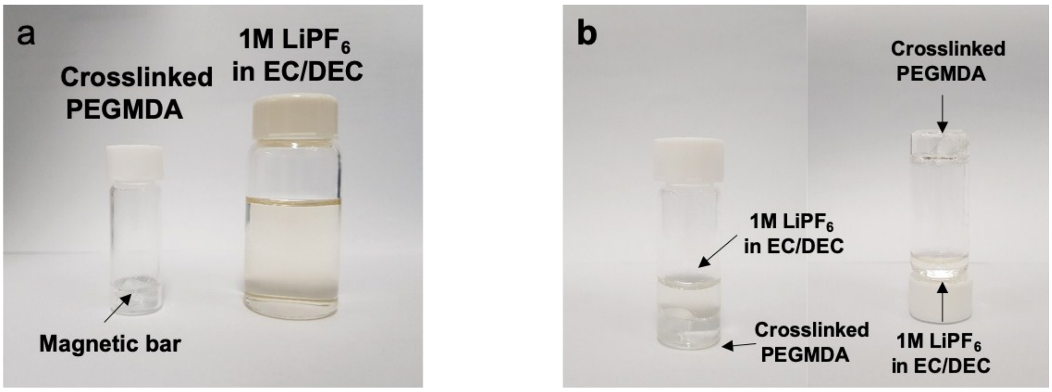


Fig. S1 (a) Nyquist plot of Li metal (red) and Li metal with PEGDMA (blue), (b) Equilibrium circuit of Li symmetrical cell, (c) Nyquist plot of 1M $LiPF_6$ in EC/DEC with PEGDMA using stainless steel (SUS), (d) Nyquist plot of 1M $LiPF_6$ in EC/DEC using stainless steel



After 7 days

Fig. S2 (a) Images of crosslinked PEGDMA and 1M LiPF$_6$ in EC/DEC (b) Images of mixed with crosslinked PEGDMA and 1M LiPF$_6$ in EC/DEC after 7 days

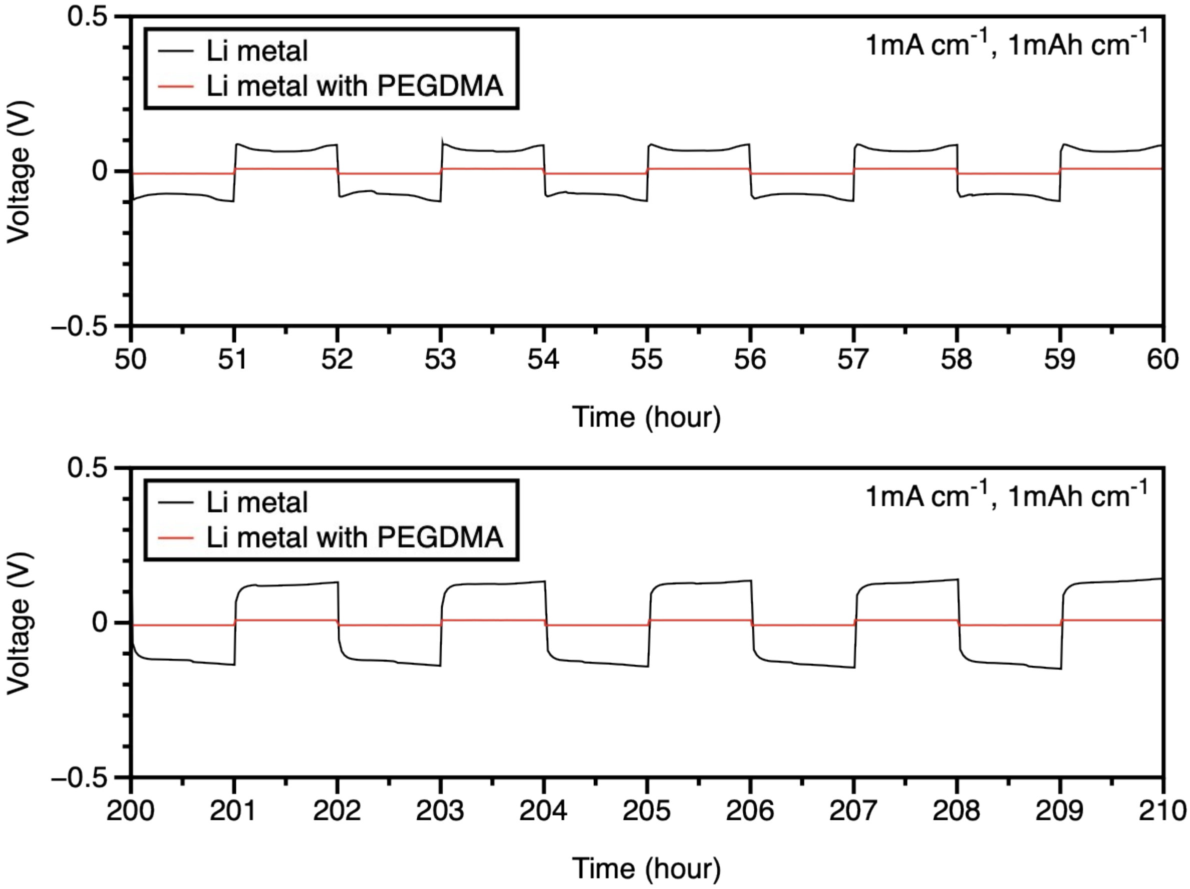


Fig. S3 The voltage profile of symmetrical cell tests with the bare Li metal (black) and Li metal with PEGDMA (red) at 50~60 h (upper) and 200~210 h (lower) with 1mA cm^{-2}

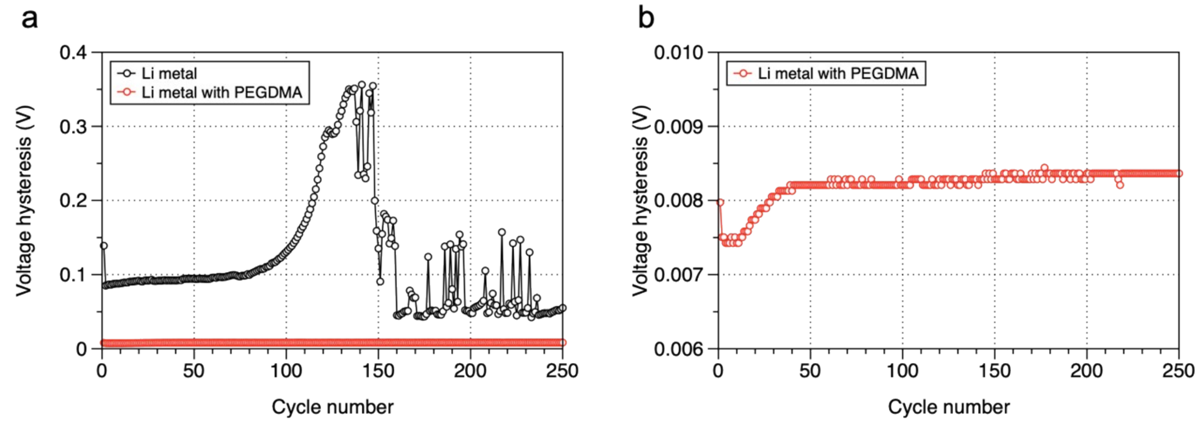


Fig. S4 (a) The voltage hysteresis of Li metal (black) and Li metal with PEGDMA (red) at 1mA cm^{-2} (b) The voltage hysteresis of Li metal with PEGDMA at 1mA cm^{-2}

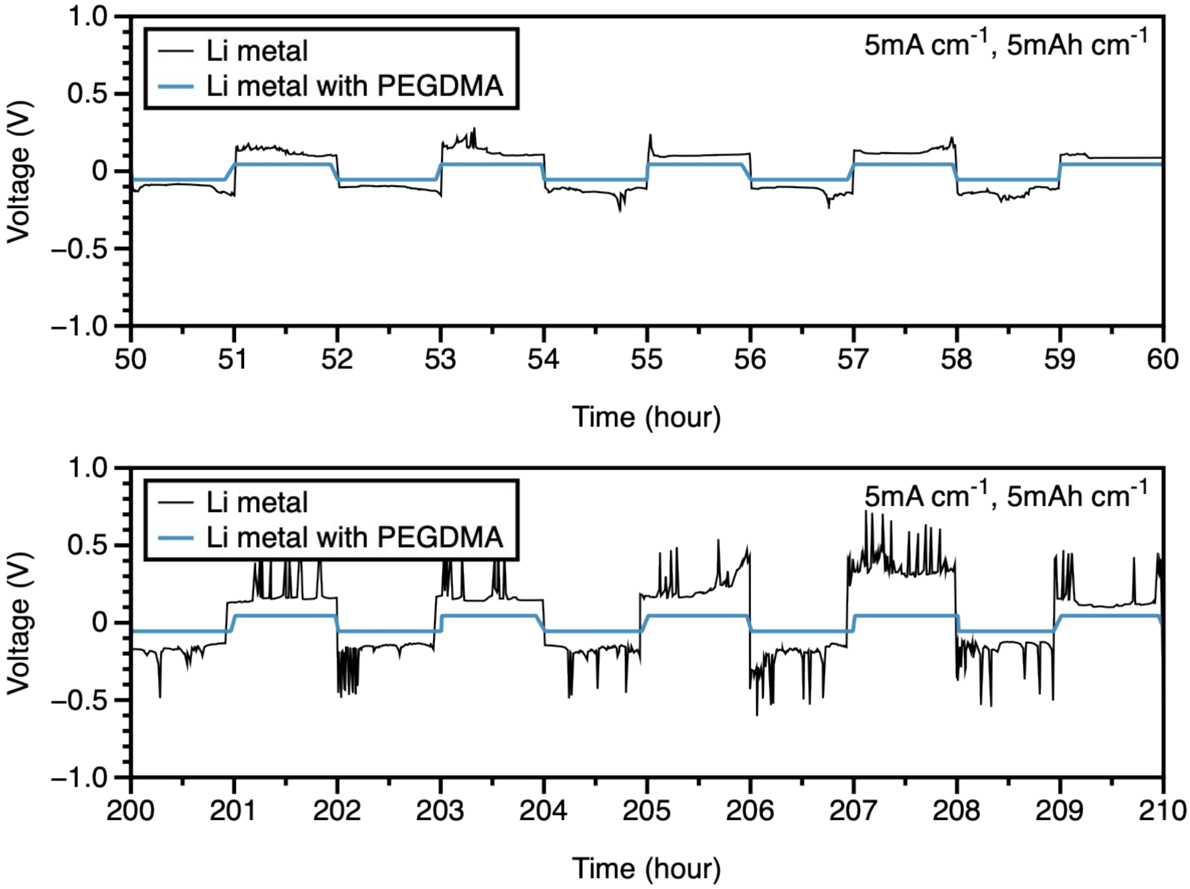


Fig. S5 The voltage profile of symmetrical cell tests with the bare Li metal (black) and Li metal with PEGDMA (blue) at 50~60 h (upper) and 200~210 h (lower) with 5mA cm^{-2}

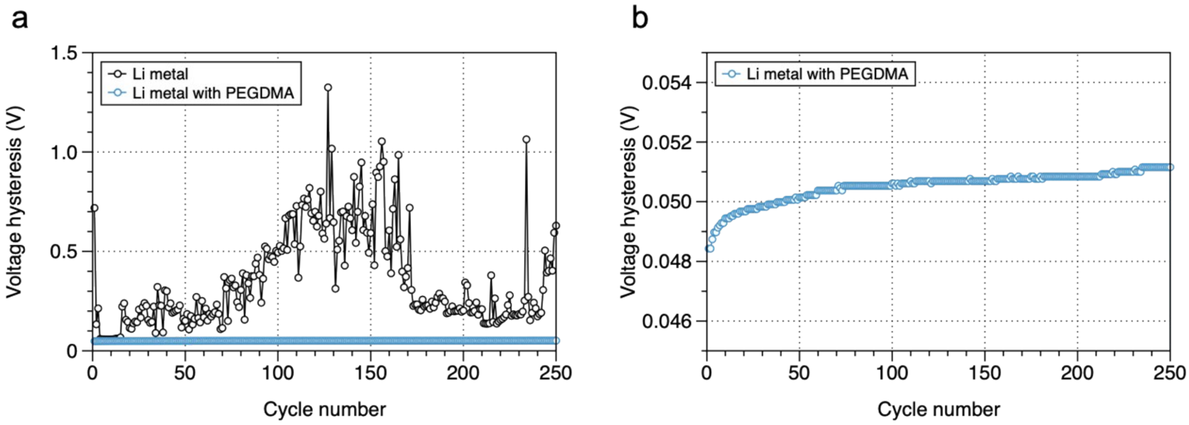


Fig. S6 (a) The voltage hysteresis of Li metal (black) and Li metal with PEGDMA (blue) at 5mA cm^{-2} (b) The voltage hysteresis of Li metal with PEGDMA at 5mA cm^{-2}

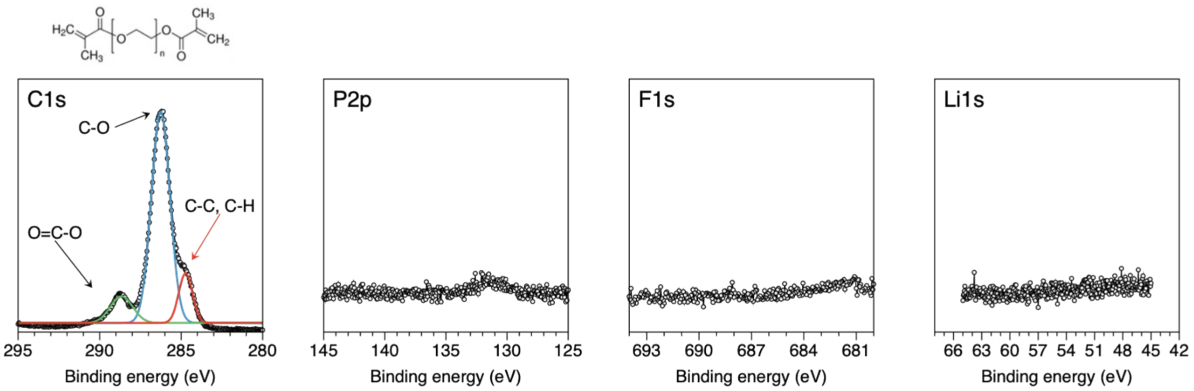


Fig. S7 C1s, P2p, F1s, and Li1s XPS core spectra of Li metal with PEGDMA without cycle.

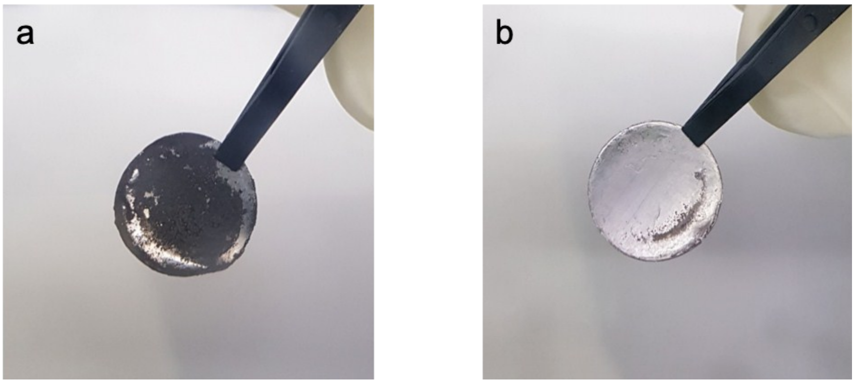


Fig. S8 (a) Surface image of Li metal sample after 100 cycles, (b) Surface image of Li metal with PEGDMA sample after 100 cycles.

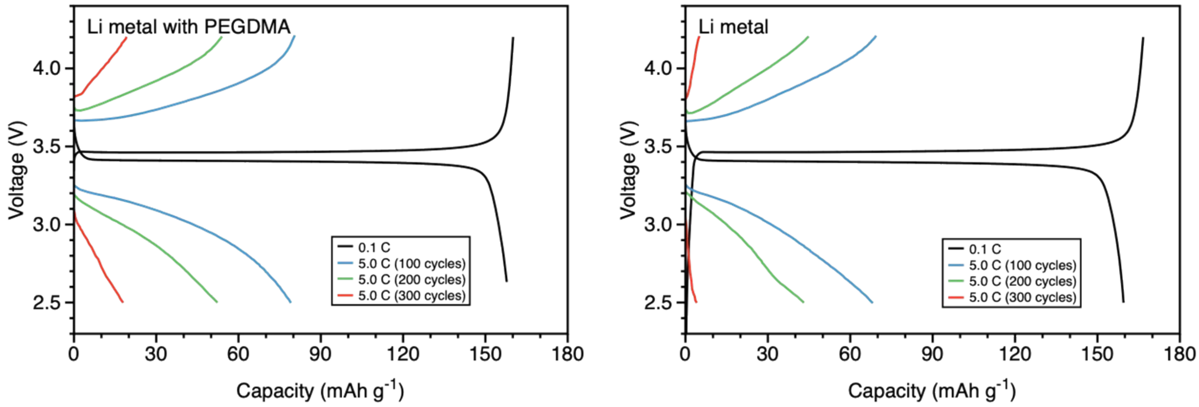


Fig. S9 Charge/discharge profile of $LiFePO_4$ sample with bare Li metal (a) and Li metal applied PEGDMA (b) at 0.1 C and 1.0 C after 100, 200, and 300 cycles.

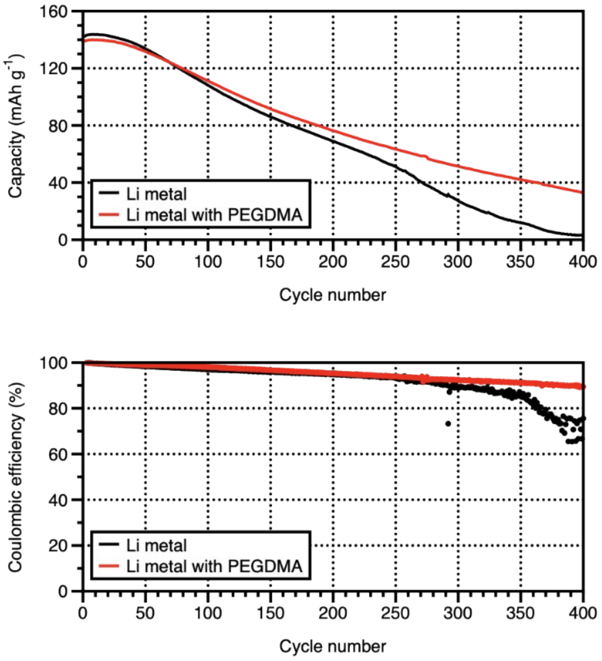


Fig. S10 The graph of cycle capacity (upper) and Coulombic efficiency (lower) at 1.0 C.

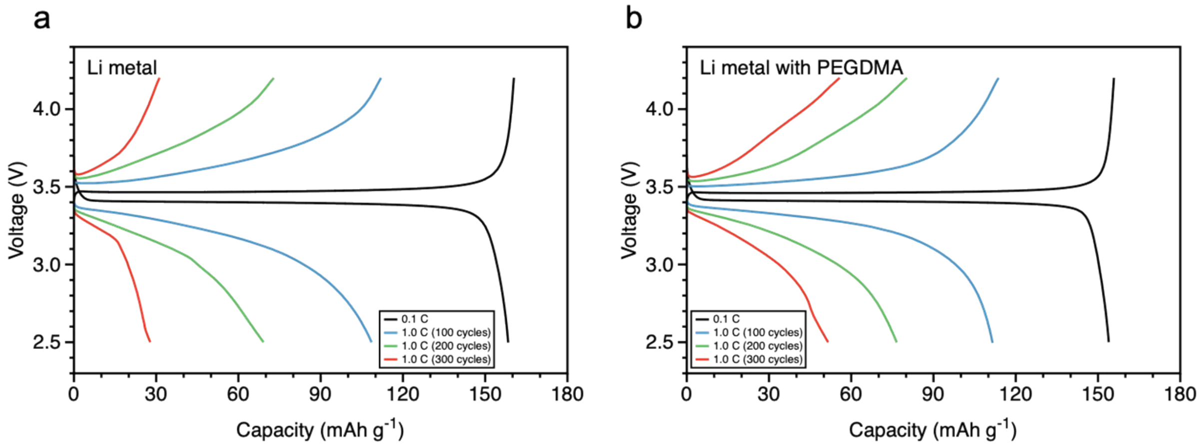


Fig. S11 Charge/discharge profile of LiFePO$_4$ sample with bare Li metal (a) and Li metal applied PEGDMA (b) at 0.1 C and 5.0 C after 100, 200, and 300 cycles.

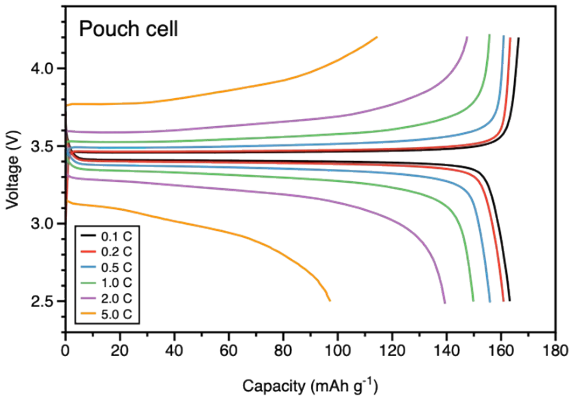


Fig. S12 Charge/discharge profile of $LiFePO_4$ pouch sample with bare Li metal with PEGDMA

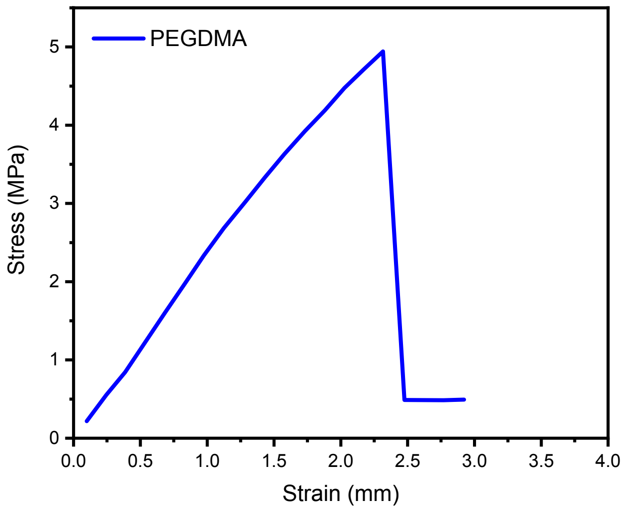


Fig. S13 The mechanical property of c-PEGDMA film