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Supporting Information

Inhibition of Lithium Dendrites by Forming Rich Polyethylene Oxide-like Species in Solid-Electrolyte-Interphase in a Polysulfide/Carbonate Electrolyte

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EXPERIMENTAL

Materials

Lithium hexafluorophosphate ($LiPF_6$, 99.99% purity), 1,2-dimethoxyethane (DME, 99.5% purity, inhibitor-free), dimethyl carbonate (DMC, 99.9% purity) and ethylene carbonate (EC, 99.9% purity) were obtained from Sigma-Aldrich Corporation. The electrolyte solutions were prepared by dissolving the desired amount of salt into the solvent, and all operations were conducted in a glove box with an Ar atmosphere (< 1 ppm O_2 and < 1 ppm H_2O).

Electrolyte Preparation

Carbonate electrolytes were prepared by dissolving 1 M and 1.1 M $LiPF_6$ in a solution of EC:DMC (1:1 vol.), stirring for 10 h. The 1 M $LiPF_6$ EC:DMC (1:1 vol.) was named as carbonate electrolyte, 1.1 M $LiPF_6$ EC:DMC (1:1 vol.) was used for prepare polysulfide/carbonate electrolyte. Li_2S and S powders with mole ratio = 1:7 are initially added into dimethyl ether (DME) to prepare a Li_2S_8 polysulfide DME solution. The three concentrations (5 mM, 10 mM and 20 mM) of Li_2S_8 polysulfide DME solution were papered by stirring Li_2S and S powders in DME solution for 10 h, until Li_2S and S powers complete dissolution. Then, three concentrations of Li_2S_8 polysulfide DME solution were mixed with 1.1 M $LiPF_6$ EC:DMC with 1:10 volume ratio. Four different concentrations of polysulfide were prepared in the polysulfide/carbonate electrolyte—0 mM, 0.5 mM, 1 mM and 2 mM. All of the electrolytes were further dried with a molecular sieve to reduce the presence of trace water.

Characterization

After the repeated cycling of Li deposition/dissolution, the batteries were held for 48 h and then disassembled for characterization. The Li electrodes were thoroughly washed with anhydrous DME to remove the residual electrolytes and dried in a glove box antechamber under vacuum prior to characterization and analysis. The Li electrodes were transferred into a Sample-Saver storage container filled with purified argon and loaded into the SEM machine in a glove bag purged with purified argon to avoid air contamination. The Li morphology was characterized using a scanning electron microscope (HITACHI SU-4800). XPS profiling data were collected at room temperature with an XPS spectrometer (Thermo Scientific ESCALAB 250Xi). The Li electrodes were also transferred into a Sample-Saver storage container and placed into the XPS machine to avoid air contamination. All spectra were calibrated with the C 1s photoemission peak at 284.8 eV to correct for the charging effect. The Raman spectra were recorded at room temperature using a LabRAM HR Evolution Raman spectrophotometer (HORIBA Scientific). The Raman spectra were excited by a 633 nm laser. The Infrared spectra were recorded at room temperature using a VERTEX 70v Fourier Transform Infrared spectrophotometer (BRUKER).

Electrochemical Measurements

Coin cells of CR2032 type were used to prepare batteries for the morphology and cycling-property study of Li electrodes with different electrolytes. The $LiFePO_4$ (LFP) electrode was prepared by coating an alumina foil with a slurry of LFP, Super P conductive carbon and 1,3-butadiene polymer and sodium carboxymethyl cellulose (90:7:1:2 by weight) in deionized water, evaporating the deionized water solvent and then drying at approximately 120 °C under vacuum overnight. The average capacity of LFP was 1.0 mAh/cm^2. The glove box was filled with purified argon in which the oxygen and moisture contents were each less than 0.5 ppm. The amount of electrolyte added to each coin cell was 150 μL. The Li metal foil (1 mm thick with 99.9% purity) was cut into 15 mm-diameter disks for use as Li electrodes, and the surface passivation layer was removed by a ceramic tip.

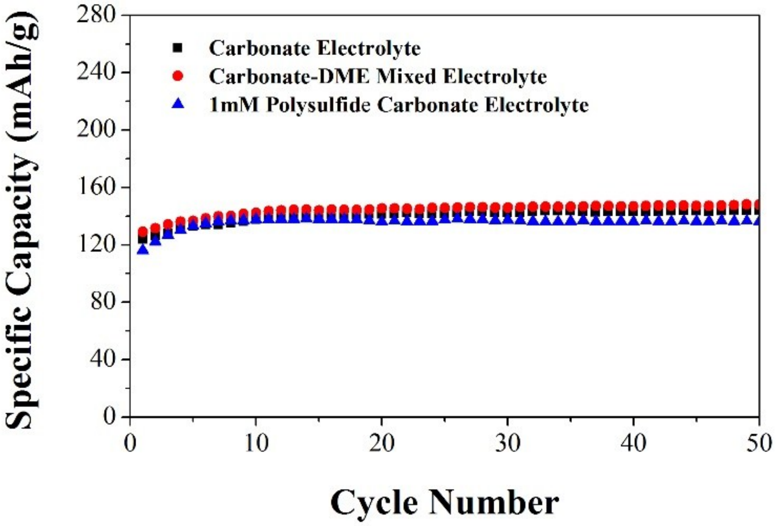

Figure S1. Discharge capacity of LFP | Li batteries using various electrolytes after the 50th cycling at 0.5 mA/cm^2

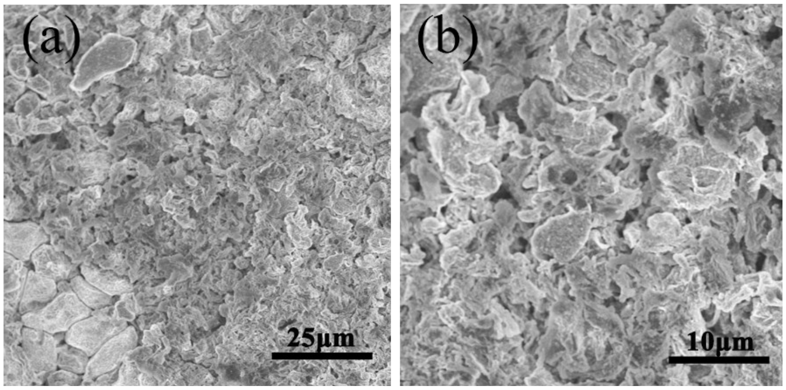

Figure S2. SEM images of the surface morphology of the Li electrodes cycled in carbonate-DME mixed electrolyte after the 50th cycles at 0.5 mA/cm^2 (a) low-magnification top-view SEM image

(b) high-magnification top-view SEM image. The batteries were disassembled at the fully charged state. The amounts of Li deposition were all 1 mAh/cm^2.

The IR results of the commercial PEO and the PEO-like polymers formed on the surface of the Li electrodes after cycling are shown in Fig. S3. The commercial PEO shows IR bands at 1060, 1096 and 1145 cm^{-1}, corresponding to the C-O-C stretching vibration absorption of PEO, Fig. S3(a). The bands at 1344, 1360, 2877 and 2920 cm^{-1} are ascribed to the symmetric and asymmetric CH$_2$-stretching bands of the PEO-like polymer methylene units, respectively.[1] The C-O-C stretching vibration gives a very strong absorption band at 1096 cm^{-1}.

Fig. S3(b) shows the strong bands at 1347, 2850 and 2919 cm^{-1} are ascribed to the symmetric and asymmetric CH$_2$-stretching bands, suggesting that a certain amount of alkyl polymer exist in SEI.[1] The C-O-C stretching vibration absorption band was also observed around 1082 cm^{-1}, confirming that the PEO-like polymer was present in the SEI after cycling in polysulfide/carbonate electrolyte (1 mM), in accordance with the XPS results.

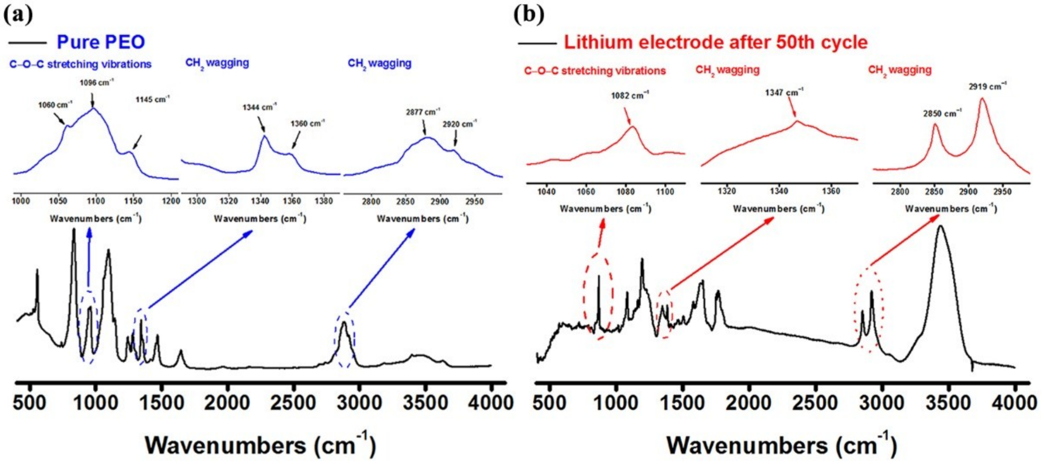

Figure S3. Infrared spectra of (a) pure commercial PEO film and (b) Li anode after 50 cycles in polysulfide/carbonate electrolyte (1 mM).

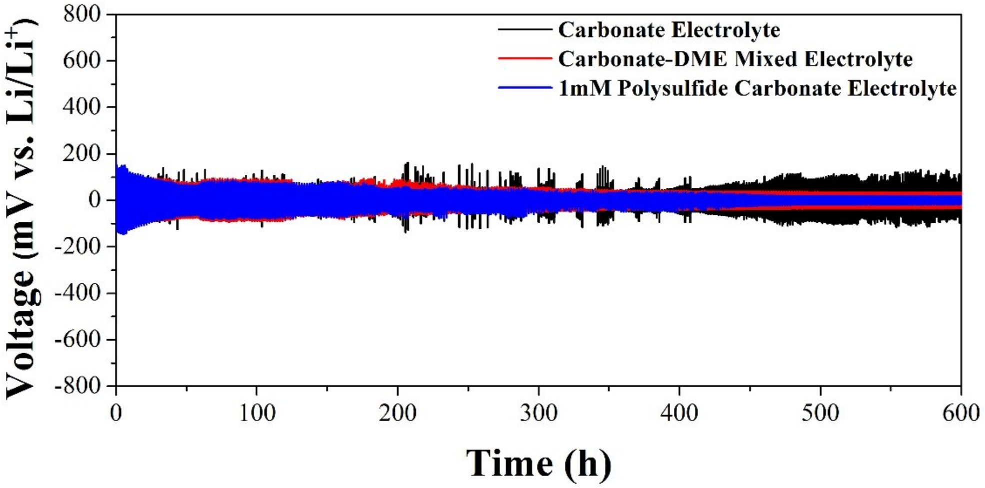

Figure S4. Voltage profiles for Li plating–striping as a function of time in symmetric cells using carbonate electrolyte (black), carbonate-DME mixed electrolyte (red) and 1 mM polysulfide/carbonate electrolyte (blue) with current density of 1 mA/cm^2 for 1 mAh/cm^2.

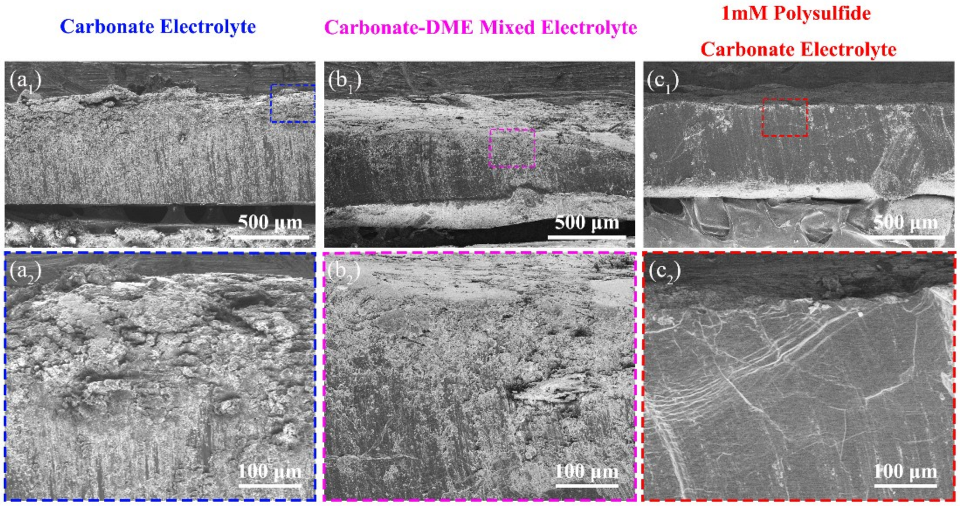

Figure S5. Side-view SEM images of Li electrode at 1 mA/cm^2 after the 300th cycling in (a$_{1-2}$) carbonate electrolyte, (b$_{1-2}$) carbonate-DME mixed electrolyte and (c$_{1-2}$) 1 mM polysulfide/carbonate electrolyte. The amount of Li deposition is 1 mAh / cm^2.

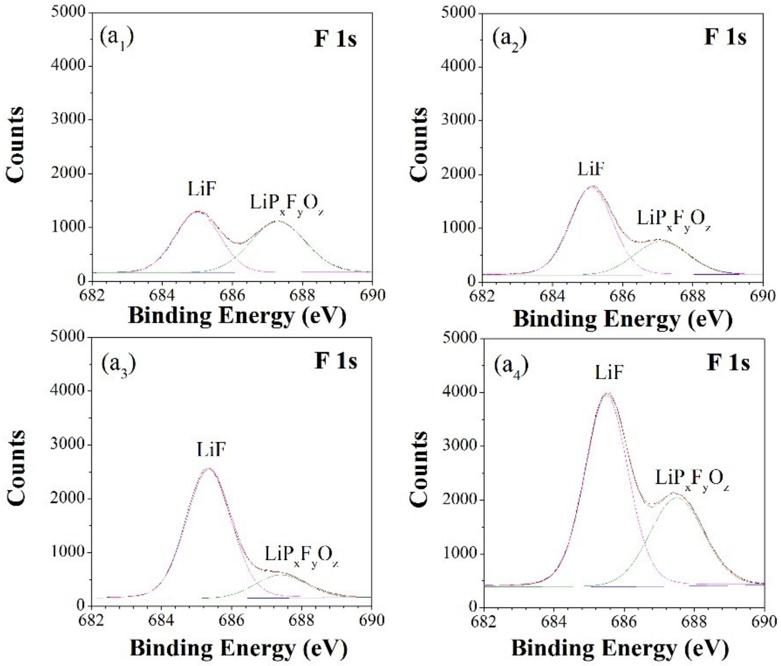

Figure S6. XPS analysis of F element on the surface of Li electrode cycled in polysulfide/carbonate electrolyte (1 mM) at 0.5 mA/cm^2. (a_1) after the 1st cycle, (a_2) after the 10th cycle, (a_3) after the 25th cycle and (a_4) after the 50th cycle.

Fig. S7 shows the Raman spectra of carbonate-DME without polysulfide, with 1 mM polysulfide carbonate electrolyte and 1 mM polysulfide carbonate electrolyte after cycling. Compared with the electrolyte without polysulfide (with 10% DME solvent), four additional characteristic peaks at around 280, 472, 711 and 791 cm^{-1} were observed for the electrolyte with 1 mM polysulfide, which are associated with polysulfide ions.[2] After cycling, these four additional characteristic peaks did not show significant changes, suggesting the polysulfide were not consumed during cycling.

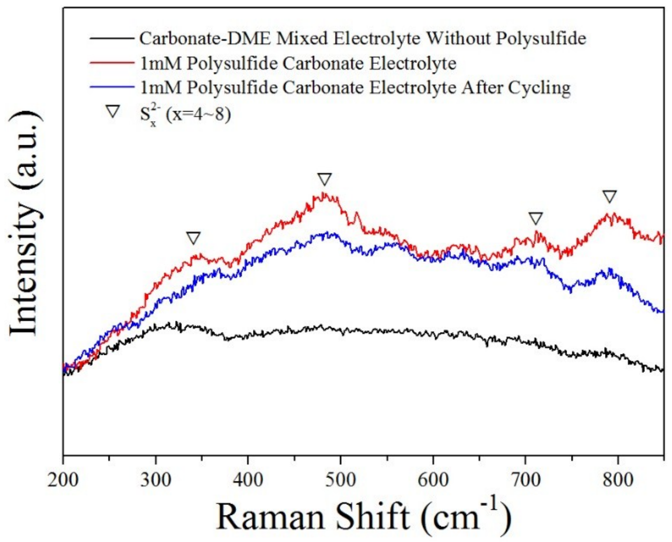

Figure S7. The Raman spectrum of carbonate-DME without polysulfide, 1 mM polysulfide carbonate electrolyte and 1 mM polysulfide carbonate electrolyte after cycling.

REFERENCES

[1] P. Harder, M. Grunze, and R. Dahint , G. M. Whitesides, P. E. Laibinis, J. Phys. Chem. B., 1998, **102**, 426-436.

[2] J. T. Yeon, J. Y. Jang, J. G. Han, J. Cho, K. T. Lee and N. S. Choi, *J. Electrochem. Soc.*, 2012, **159**, A1308-A1314.