Supporting Information

Formation Mechanism of the Solid Electrolyte Interphase in Different Ester Electrolytes

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1. Experimental Procedures

Materials: Lithium (Li) metal foils (600 μm) and Cu foils (9 μm) were purchased from China Energy Lithium Co., Ltd and were used as received. Li metal foils were cut into discs with 18 mm diameter and Cu foils were cut into discs with 17 mm diameter. $LiPF_6$, Li bis((trifluoromethyl)sulfonyl)azanide (LiTFSI), diethyl carbonate (DEC) and ethylene carbonate (EC) were all purchased from Suzhou DoDoChem Co., Ltd. Methanol-D (CD_3OH) was purchased from Aldrich Chemical Co., Inc. Parafilm used for sealing was purchased form AS ONE Co., Inc. All materials were kept in a glove box with oxygen and water contents below 1.0 ppm.

Electrolytic cell assembly: The electrolytic cell is manufactured by Huayu Instrument Shanghai Branch. The Cu foil and Li metal foil were connected to a Cu electrode and a platinum electrode respectively. Then, 20 mL electrolyte (1.0 M $LiPF_6$-DEC, EC, EC/DEC (1:1 by vol.)) was added. After that the battery system was sealed with two silicone rings to ensure that the battery is not affected by water and oxygen. All processes were operated in a glove box with oxygen and water contents below 1.0 ppm.

Electrochemical measurements: Assembled electrolytic cells were cycled with a capacity of 3.0 mAh cm^{-2} at 3.0 mA cm^{-2}. The cells were tested using a LAND multichannel battery cycler (Wuhan LAND electronics Co., Ltd.) in 25℃. After 15 cycles, the cells were disassembled to obtain cycled Cu electrode and electrolytes.

Reactions of Li with solvents: A large piece of Li foil (0.8 g) was mixed with various 2 mL solvents (DEC, EC, EC/DEC (1:1 by vol.), fluoroethylene carbonate (FEC), dimethyl carbonate (DMC)) in glass bottles of 20 mL. The assembled glass bottle was sealed with two layers of parafilm. Then the glass bottle was stirred at a rate of 350 r/min and 60℃ on a magnetic heating table (Shanghai Meiyingpu Instrument Co., Ltd) with the help of magnetons. After four days of heating and stirring, the glass bottles were disassembled to obtain the resulted solutions. All processes were operated in a glove box with oxygen and water contents below 1.0 ppm.

Materials Characterizations: 0.5 mL of CD_3OH was added to 1 mL of reacted solutions to remove suspended Li particles thoroughly in the glove box. The treated solutions were enclosed in a centrifuge tube (3 mL) sealed with two layers of parafilm in argon (Ar) to avoid the contact with air during transferring process before characterizations. The ^1H-NMR spectra were acquired on a JNM-ECA600 spectrometer and using CD_3OH as an external reference that has been added. The ^1H MAS spectra were acquired at 81.37 MHz with a recycle delay at 0.5 s. All NMR measurements were conducted at 50℃.

First-principles calculation Details: The first-principles calculations were conducted in Gaussian (G09)[1] program with Becke's three-parameter hybrid method using the Lee-Yang-Parr correlation functional (B3LYP) at 6-31G level.[2] The solvation effect was considered with integral equation formalism variant of the Polarizable Continuum (IEFPCM) model.[3,4] As the interaction between DEC, EC, LEC and LEDC molecules is very weak, the binding energy (E_b) between them is defined as following:

$$E_b = E_{Complex} - E_M - E_N$$

where $E_{Complex}$ is the total energy of SEI-solvent or SEI-SEI complex, E_M is the total energy of former molecule or group, E_N is the total energy of the molecule or group that are going to be added.

2. Supporting Figures

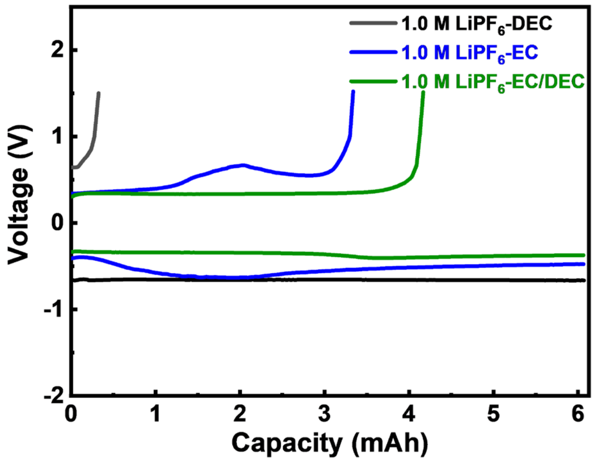

Fig. S1. Electrochemical performance of Li–Cu electrolytic cell with different electrolytes (1.0 M LiPF$_6$-DEC, EC and EC/DEC (1:1 by vol.).

The voltage profiles of 3rd cycle of Li | Cu electrolytic cells in different electrolytes show after the same capacity of lithium plating (6.07 mAh), there is almost no stripping of lithium in 1.0 M LiPF$_6$-DEC (0.35 mAh), yet there is a certain amount of lithium stripping in 1.0 M LiPF$_6$-EC and EC/DEC (1:1 by vol.) (3.33 mAh, 4.17 mAh respectively).

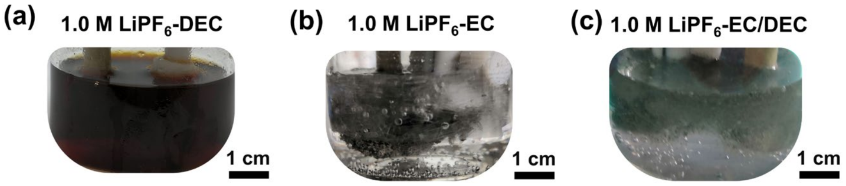

Fig. S2. Optical image of electrolytic cells after cycles with various electrolytes: (a) 1.0 M LiPF$_6$-DEC, (b) 1.0 M LiPF$_6$-EC, (c) 1.0 M LiPF$_6$-EC/DEC (1:1 by vol.).

In 1.0 M LiPF$_6$-DEC, large amounts of reaction products change the color of electrolyte, while the electrolytes of 1.0 M LiPF$_6$-EC and 1.0 M LiPF$_6$-EC/DEC (1:1 by vol.) remain clear after cycles.

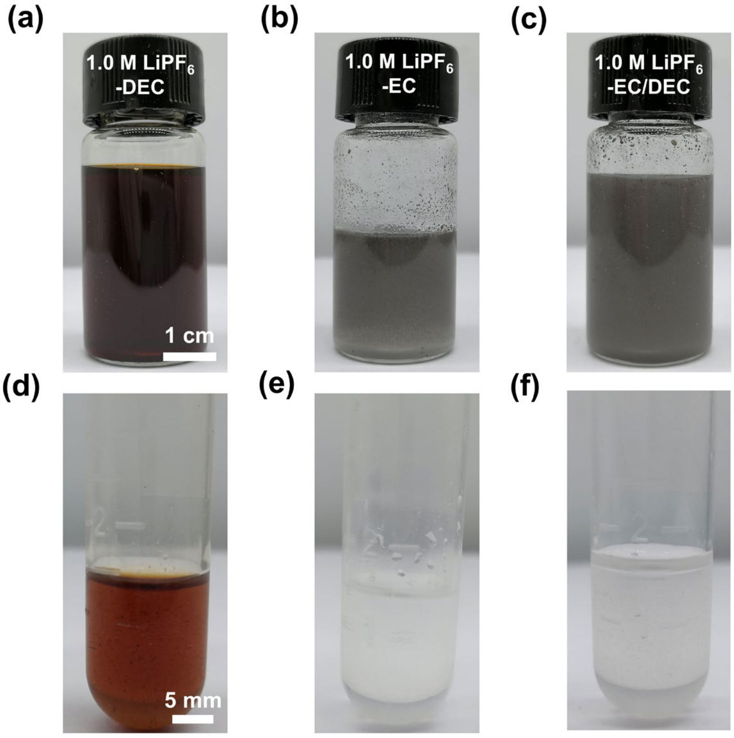

Fig. S3. Optical images of solutions obtained from the cycled electrolytic cells with various electrolytes (a) 1.0 M $LiPF_6$-DEC, (b) 1.0 M $LiPF_6$-EC, (c) 1.0 M $LiPF_6$-EC/DEC (1:1 by vol.) and after adding 0.5 mL CD_3OH (d) 1.0 M $LiPF_6$-DEC, (e) 1.0 M $LiPF_6$-EC, (f) 1.0 M $LiPF_6$-EC/DEC (1:1 by vol.).

After consuming the lithium in the solutions by adding CD_3OH, the solution with 1.0 M $LiPF_6$-DEC remains brown, indicating the massive existence of the reaction products in the solution. However, the solutions in (e, f) are slightly turbid, revealing that the amounts of reaction products in the solution are very small.

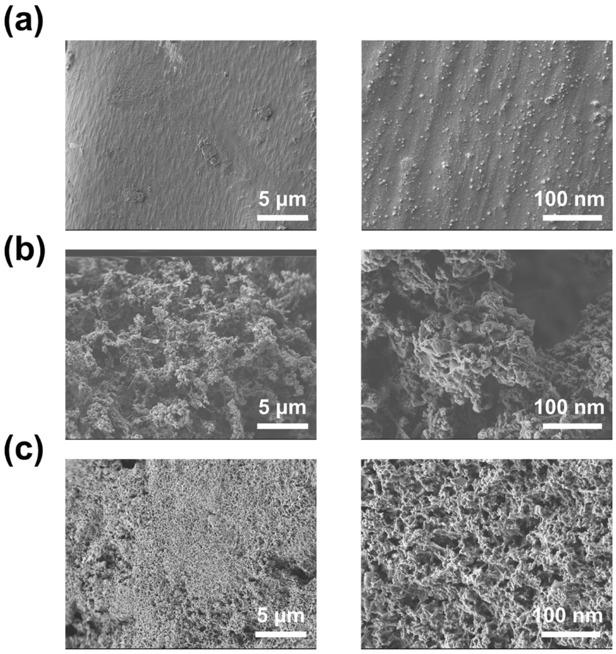

Fig. S4. SEM images of Cu foil after cycles with various electrolytes: (a) 1.0 M $LiPF_6$-DEC, (b) 1.0 M $LiPF_6$-EC, (c) 1.0 M $LiPF_6$-EC/DEC (1:1 by vol.).

In 1.0 M $LiPF_6$-DEC, no obvious Li deposit is found upon Cu foil, while similar Li deposits are observed in 1.0 M $LiPF_6$-EC or EC/DEC electrolyte.

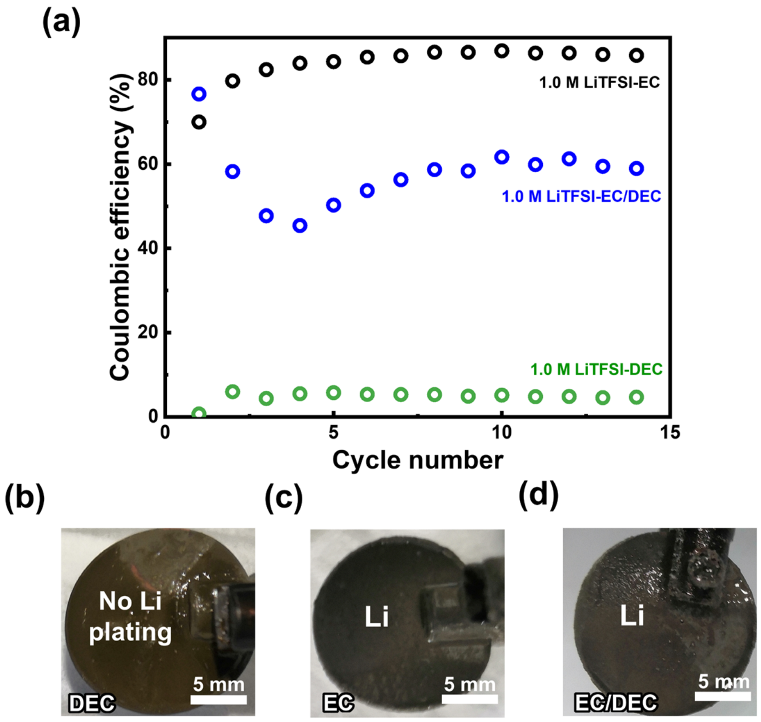

Fig. S5. Electrochemical performance of Li-Cu electrolytic cell with different electrolytes (1.0 M LiTFSI-DEC, EC and EC/DEC (1:1 by vol.). (a) Coulombic efficiency in different electrolytes. Plated Li morphology in various electrolytes: (b) 1.0 M LiTFSI-DEC, (c) 1.0 M LiTFSI-EC, (d) 1.0 M LiTFSI-EC/DEC (1:1 by vol).

Due to the continuous reactions between Li and DEC, there is no Li residue on Cu foil for (b), while large amounts of Li remain on Cu foil due to the self-limiting reactions between Li and EC.

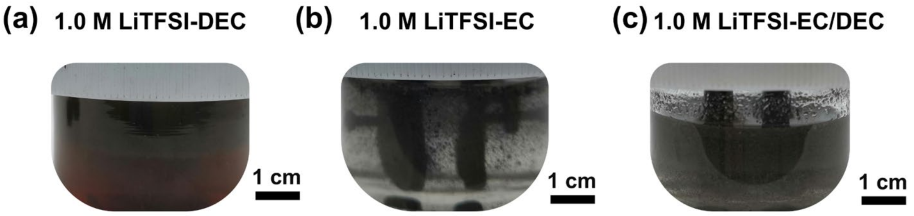

Fig. S6. Optical images of electrolytic cells after cycles with various electrolytes: (a) 1.0 M LiTFSI-DEC, (b) 1.0 M LiTFSI-EC, (c) 1.0 M LiTFSI-EC/DEC (1:1 by vol.).

In 1.0 M LiTFSI-DEC, large amounts of reaction products change the color of electrolyte, while the electrolytes of 1.0 M LiTFSI-EC and 1.0 M LiTFSI-EC/DEC (1:1 by vol.) remain clear after cycles.

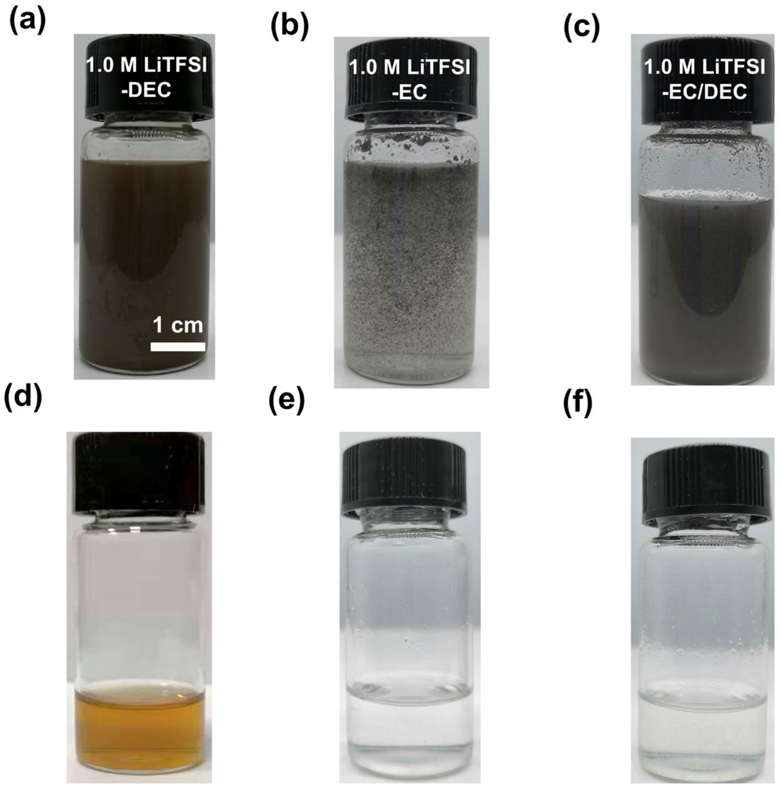

Fig. S7. Optical images of solutions in electrolytic cells after cycles with various electrolytes (a) 1.0 M LiTFSI-DEC, (b) 1.0 M LiTFSI-EC, (c) 1.0 M LiTFSI-EC/DEC (1:1 by vol.) and after adding 0.5 mL CD_3OH (d) 1.0 M LiTFSI-DEC, (e) 1.0 M LiTFSI-EC, (f) 1.0 M LiTFSI-EC/DEC (1:1 by vol.).

After consuming the lithium in the solutions by adding CD_3OH, the solution with 1.0 M LiTFSI-DEC remains brown, indicating the massive existence of the reaction products in the solution. The same Tyndall Effect of the solution is also detected. However, the solutions in (e, f) are slightly turbid, revealing that the amounts of reaction products in the solution are very small.

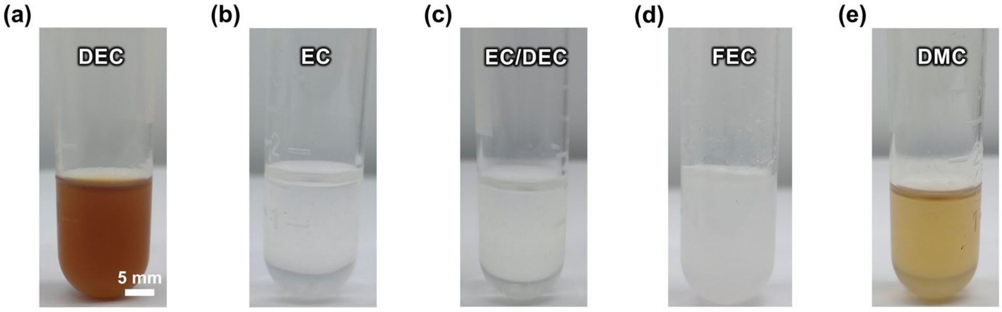

Fig. S8. Optical images of various solutions adding 0.5 mL CD_3OH of different solvents reacted with Li after stirring at 60℃ for 4 days (a) DEC, (b) EC, (c) EC/DEC (1:1 by vol.) (d) FEC, (e) DMC.

After consuming the lithium in the solutions by adding CD_3OH, the solution with DEC (a) and DMC (e) remains brown, indicating the massive existence of the reaction products in the solution. However, the solutions in (b, c, d) are slightly turbid, revealing the amounts of reaction products.

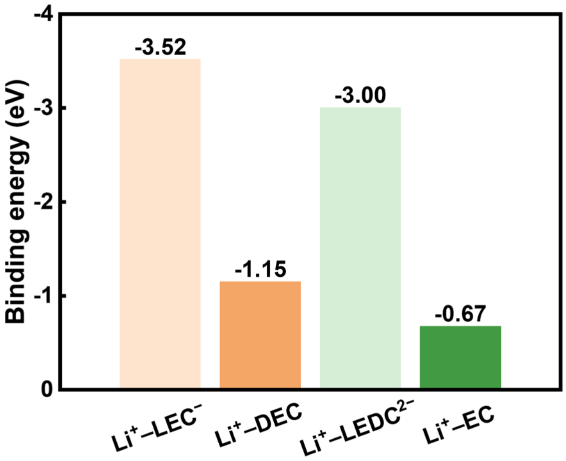

Fig. S9. Contrast of binding energy between Li^+ and anions (LEC^- and $LEDC^{2-}$) or solvents (DEC and EC).

The binding energies between Li^+ cations and LEC^- or $LEDC^{2-}$ anions are significantly higher (–3.25 eV and –3.20 eV respectively) than those between Li^+ cations and DEC or EC solvents (–1.15 eV and –0.67 eV respectively). As a result, Li^+ in LEC and LEDC are difficult to dissociate, then LEC and LEDC are likely to exist in electrolyte by the form of molecules.

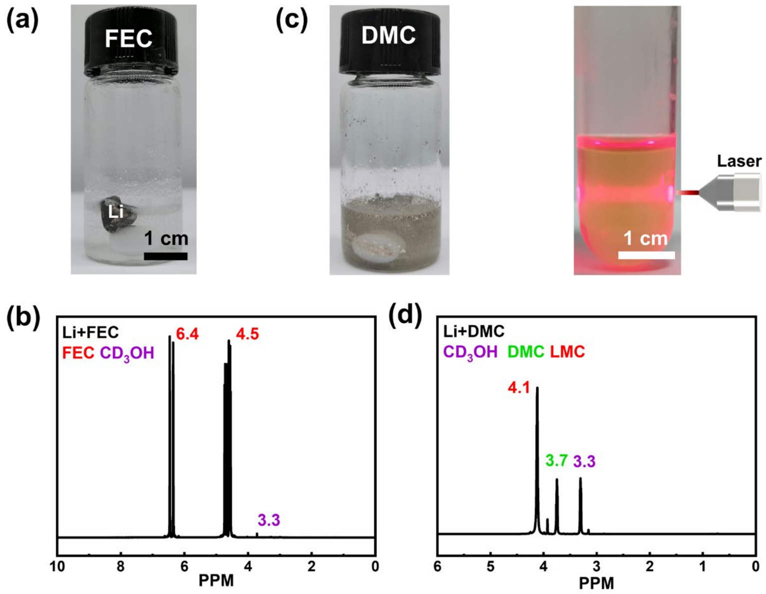

Fig. S10. Reactions between Li and different solvents.

Optical images of the solutions of Li with different solvents: (a) FEC, (c) DMC after stirring at 60℃ for 4 days. The Tyndall Effect of the solution with DMC after adding CD_3OH (right panel of (c)) indicates the reaction products of Li and DMC is the colloid and well distributed in the solvents, maintaining stable for 14 days. Corresponding ^{1}H-NMR of the reaction products of Li and (b) FEC, (d) DMC after stirring at 60℃ for 4 days. The LMC reaction products of Li and DMC can be detected in the solution, while the LEDC, LiF reaction products of Li and FEC cannot be detected in the solution, indicating the reaction between Li and DMC is not self-limited and the reaction between Li and FEC is self-limited.

3. References

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(3) E. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.,* 1997, **107**, 3032-3041.

(4) S. Miertuš, E. Scrocco, J. Tomasi, *Chem. Phys.,* 1981, **55**, 117-129.