

## Supporting Information

# Structure and Solution Dynamics of Lithium Methyl Carbonate as a Protective Layer For Lithium Metal

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## **1. Experimental Method**

### **1.1 Material synthesis, electrolyte preparation, and electrochemical test**

Battery grade dimethyl carbonate (DMC), ethylene carbonate (EC), and premixed LP30 electrolyte (1 M LiPF<sub>6</sub> in 1:1 vol ratio EC/DMC) were purchased from BASF. LiI beads (Ultra dry, >99%) was acquired from Alpha Aesar.

The lithium methyl carbonate (LMC) was synthesized via one step reaction by dissolving 2.677 g LiI into either DMC or EC/DMC (1:1 weight ratio). After sitting inside an Ar filled glove box (MTI corporation) for 24 hours, the precipitates were filtered, and then washed by DMC for 3 times. The washed products were dried in the glovebox antechamber under vacuum for 2 hours.

0.1 M, and 0.2 M LiI-EC/DMC electrolytes were prepared by dissolving 0.1338 g, and 0.2677 g LiI into 10g EC/DMC (1:1 weight ratio) inside an Ar filled glove box, respectively.

Li||Cu 2032-type coin cells were used for all the electrochemical studies in this work. Galvanostatic cycling was conducted on an LBT-5V5A battery tester (Arbin instruments). The cycled Cu was recovered by disassembling the coin cell. All the samples were washed by DMC for 3 times and dried in the glovebox antechamber under vacuum.

### **1.2 X-ray diffraction**

The crystal structure of synthesized materials was identified by X-ray diffraction (XRD), acquired using a Bruker D2 advance diffractometer with a Bragg- Brentano  $\theta$ -2 $\theta$  geometry and a Cu K $\alpha$  source ( $\lambda = 1.54 \text{ \AA}$ ). Samples were sealed inside the glovebox by kapton tape, which were scanned from 10° to 50° at a scan rate of 0.05° s<sup>-1</sup>.

### **1.3 Fourier transform infrared spectroscopy**

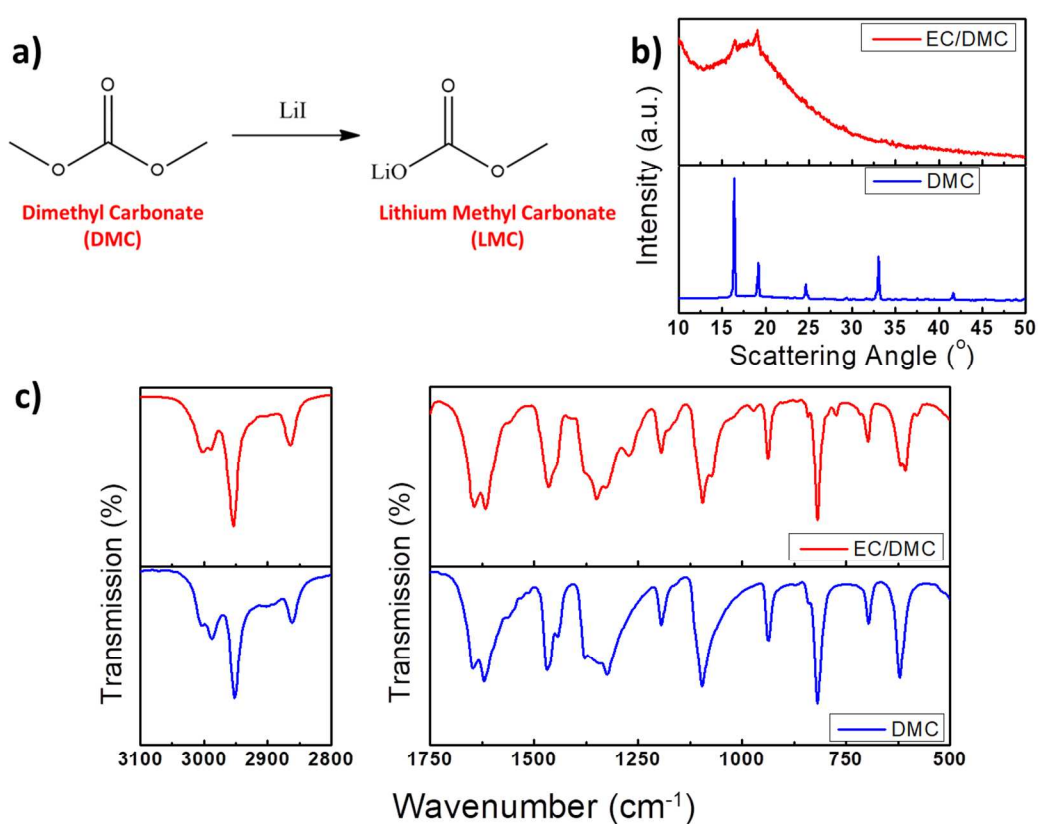
Fourier transform infrared spectra (FTIR) of synthesized materials were conducted using PerkinElmer Spectrometer UATR two (attenuated total reflectance mode, diamond crystal), which were scanned from  $4000\text{ cm}^{-1}$  to  $500\text{ cm}^{-1}$  with a resolution  $1\text{ cm}^{-1}$  and averaged over 4 scans.

### **1.4 Cryo-TEM**

Micrographs were recorded on a field emission gun (FEG) JEM-2100F Cryo TEM, equipped with a OneView camera and operated at 200 keV. The Li metal was directly deposited in a lacey carbon grid at  $0.5\text{ mA/cm}^2$  for 20mins. The TEM samples were loaded onto the cooling holder in a home-made glovebox and transferred to TEM system with continuously Ar flowing. The images were taken at a magnification of 500 kx when the temperature of samples reached about 100 K. All the processes avoid any exposure to air and liquid  $\text{N}_2$ , minimizing the potential damage to Li metal.

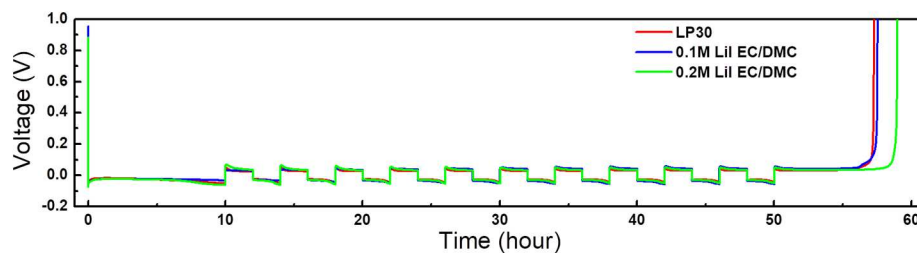
### **1.5 Scanning electron microscopy**

Focused ion beam (FIB) etching technique was used to get the cross-section image of the deposited Li metal film. Gallium was used as the source of sputtering ions at an acceleration voltage of 30 kV. 5 nA current was first applied to etch a large triangle void and then 0.3 nA was used to clean the cross-section surface to remove the damage. The sample was adhered to a double-sided carbon tape and placed on a specimen holder. The prepared sample was sealed in a laminate plastic bag inside the glovebox for transferring to the SEM. The approximate time of sample exposed to air (from a sealed environment to the SEM stage) was less than 3 s.

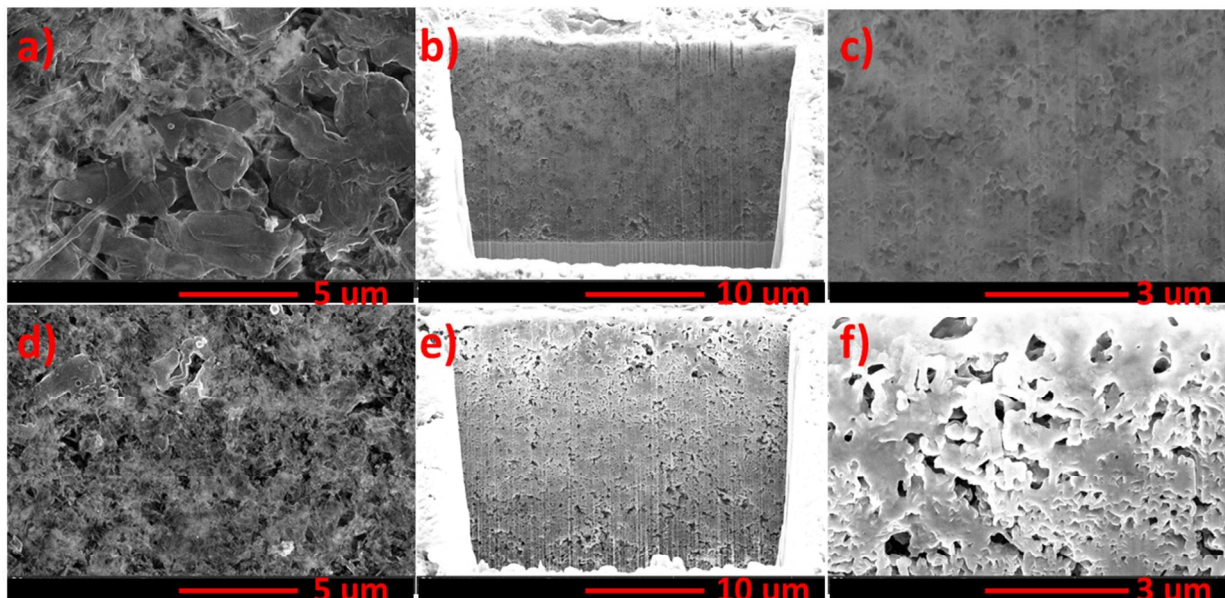


**Figure S1.** a) The reaction schematic of DMC and LiI; b) XRD and c) ATIR spectra of precipitates from LiI-DMC and LiI-EC/DMC.

The peaks at  $3002\text{ cm}^{-1}$ ,  $2988\text{ cm}^{-1}$ ,  $2952\text{ cm}^{-1}$ , and  $2862\text{ cm}^{-1}$  are assigned to the C-H stretch of  $\text{CH}_3$ . There are  $\text{CO}_2$  stretch features at  $1646\text{ cm}^{-1}$ ,  $1620\text{ cm}^{-1}$ ,  $1378\text{ cm}^{-1}$ ,  $1349\text{ cm}^{-1}$ , and  $1324\text{ cm}^{-1}$ . The C-H bend peaks are  $1468\text{ cm}^{-1}$ , and  $1442\text{ cm}^{-1}$ . The C-O stretch signatures are observed at  $1194\text{ cm}^{-1}$ ,  $1095\text{ cm}^{-1}$ ,  $1074\text{ cm}^{-1}$ , and  $936\text{ cm}^{-1}$ . A few peaks at  $818\text{ cm}^{-1}$ ,  $696\text{ cm}^{-1}$ , and  $620\text{ cm}^{-1}$  come from the  $\text{CO}_2$  bend modes. Those peak assignments are consistent with previous studies on the LMC structure.<sup>1-4</sup>



**Figure S2.** The comparison of Li||Cu cell voltage profiles cycled in LP30, 0.1 M LiI-EC/DMC, and 0.2 M LiI-EC/DMC electrolytes at  $0.5 \text{ mA cm}^{-2}$ . Prior to the test, a condition cycle was carried out on all the cells, in this step a Li film was first deposited onto the Cu foil at  $0.5 \text{ mA cm}^{-2}$  for 10 hours, and then fully stripped to 1 V. Another Li film ( $5 \text{ mAh cm}^{-2}$ ) was deposited again, only  $1 \text{ mAh cm}^{-2}$  capacity of Li film was stripped and plated for 10 cycles. Finally, the Li film was fully stripped to 1 V. The current density during this test was  $0.5 \text{ mA cm}^{-2}$ .



**Figure S3.** SEM images of plated Li on LMC coated Cu foil after 15 repeating plating and stripping, at  $0.5 \text{ mA/cm}^2$ , for  $1 \text{ mAh/cm}^2$ . a) is the top view and b), c) are the cross section view of LMC coated Cu cycled in LMC saturated LP30; d) is the top view and e), f) are the cross section view of LMC coated Cu cycled in LP30.

## REFERENCES

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