Supplementary Information

High Performance Li-ion Sulfur Batteries Enabled by Intercalation Chemistry

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Experimental

Materials. The Graphite based composite electrode (5-10 mg/cm^2) was provided by CAMP Facility at Argonne National Laboratory. For example, the composition and chemistry of the graphite electrode with mass loading of 5 mg/cm^2 is noted in **Table S3**. The Li anode used in the present study is Li chips (99.9%) with dimension of 15.6 mm in diameter and 0.45 mm in thickness. The lithium salts of lithium Bis(trifluoromethanesulphonyl) imide ($LiN(SO_2CF_3)_2$, LiTFSI) and solvents of 1,3-dioxolane (DOL), 1,2-dimethoxyethane (DME) (BASF, USA) were used in the present study. The sulfur cathode used in the present study is based on the integrated Ketjen Black (KB) (Akzo Nobel Corp.) after sulfur loading (IKB).[6] The sulfur/IKB composite (S80/IKB) was prepared by melt-diffusion approach. Certain of sulfur powder (Sigma-Aldrich) (e.g. 80 wt.%) was first mixed with the synthesized IKB by hand mill, then the mixture was transferred to Teflon-lined stainless steel autoclave and heat treated at 155 ^oC for 12 h to improve the sulfur distribution inside the IKB, resulting S80/IKB at last.[6, 30]

Electrolyte preparation. Various types of electrolytes with different concentrations are prepared and used in the present study to evaluate stability of graphite and electrochemical properties of sulfur batteries. Electrolyte was generally prepared by dissolving salts in corresponding solvents by controlling ratios of molar number (salt)/volume (solvent). For example, LiTFSI/DOL electrolytes with molar ratios of 0.5M, 1M, 3M, 5M, 6M, are prepared by dissolving 0.5, 1, 2, 3, 5, and 6 mol of LiTFSI in 1L DOL solvent. The conductivity of the electrolytes was measured by WP 600 Series Meters (Oakton) (**Table S4**).

Electrochemical measurements. The Electrochemical properties of Li/G half-cell, Li/S half-cell and LG/S full-cell were evaluated with CR2325 coin-type cells (Canadian National Research Council). The sulfur composite electrode was composed of S80/IKB composite, carbon conductors, Carboxymethyl cellulose/Styrene Butadiene Rubber (CMC/SBR, 1:2 in weight) water based binder with a weight ratio of 80:10:10. The mass loading of the electrode is around 2 mg cm^{-2} of sulfur. The graphite was lithiated by chemical method, which has already been widely applied in commercial Li-ion batteries for Li compensation. Typically, Li metal foil or powder is pressed directly on top of graphite with several drops of 5M LiTFSI/DOL electrolyte. This method is also scalable simply by stacking many graphite electrodes and Li foils together. For large-area continuously coated graphite anode, this method is also feasible in dry room by using calendar. The coin cells were assembled in a dry and inert MBraun glove box. The electrochemical performance was measured galvanostatically at various C rates on an Arbin BT-2000 battery tester at room temperature. The current density of 1C is 1000 mA g^{-1}.

Characterization. Cycled graphite electrodes were harvested from the Li/G half cells for SEM and TEM characterization. Before the measurements, the electrodes were immersed in DOL solvent for 24 h and then rinsed again with fresh solvent for three times before drying under vacuum. For TEM microanalysis, the graphite electrodes after cycled in various electrolytes were dusted on a lacy carbon TEM grid. Conventional TEM imaging and selective area electron diffraction (SAED) were conducted using Titan 80-300 microscope operated at 300kV. The microscope is equipped with an image Cs corrector for objective lens. A FEI Helios Nanolab dual-beam focused ion beam/scanning electron microscopy (FIB/SEM) microscope was used for SEM imaging and EDS analysis. The operation voltages for SEM imaging and EDS analysis are 5 kV and 20 kV, respectively. The 30 kV Ga^+ ion beam was used for ion milling. To avoid electrode contamination or side reactions with atmospheric moisture and oxygen, the samples were transferred for SEM and TEM analysis in sealed vessels which were filled with Ar gas.

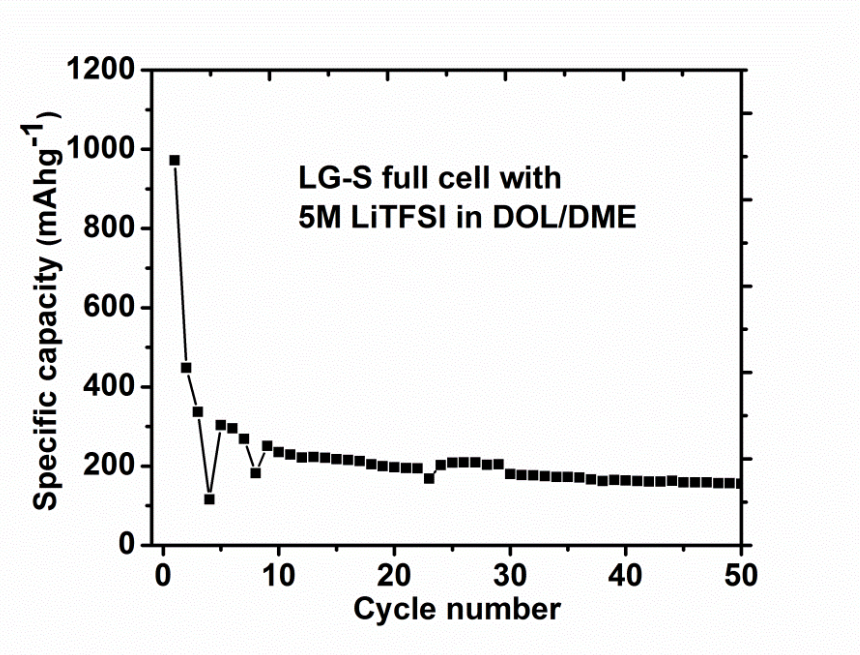

Fig. S1. Cycling performance of LG/S full cell in 5M LiTFSI/DOL/DME (1:1 v:v) electrolyte at 0.1C between 1.0 and 3.0 V.

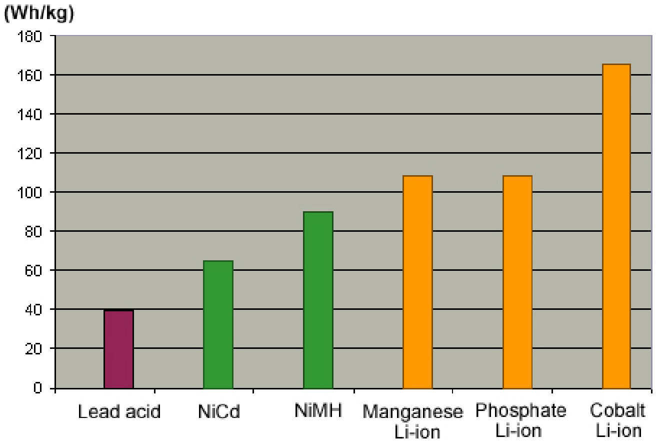

Fig. S2. Energy densities of common battery chemistries. (Data source: http://batteryuniversity.com/learn/article/the_high_power_lithium_ion)

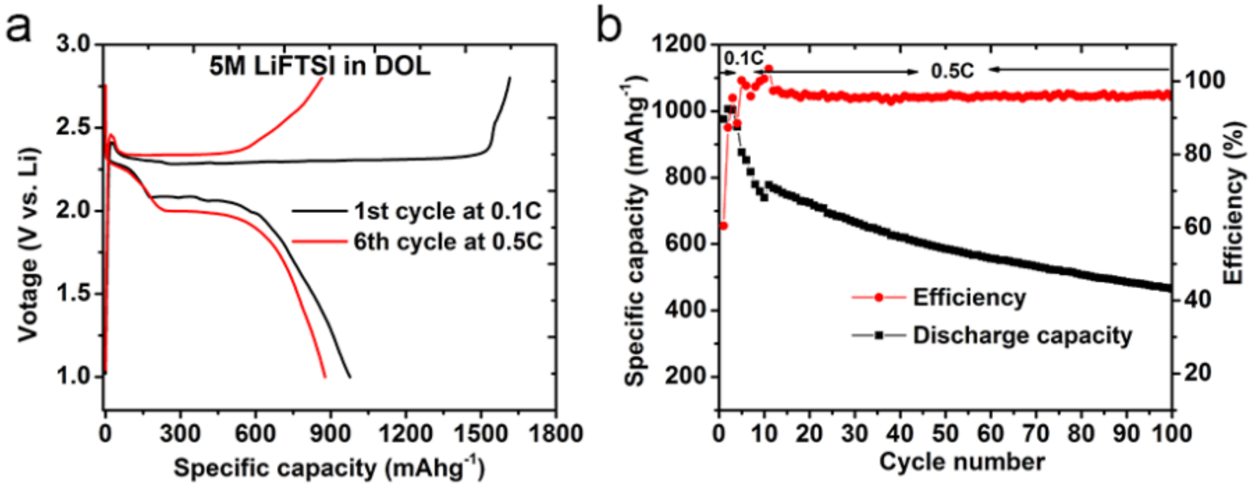

Fig. S3. (**a**) Charge/discharge curves of Li-S cell in 5M LiTFSI/DOL electrolyte at 0.1 and 0.5 C within voltage range of 1.0-3.0 V, and (**b**) corresponding cycling performance and Coulombic efficiency. Lithium metal was used as the anode in these tests and sulfur loading of cathode is above 2 mg cm^{-2}.

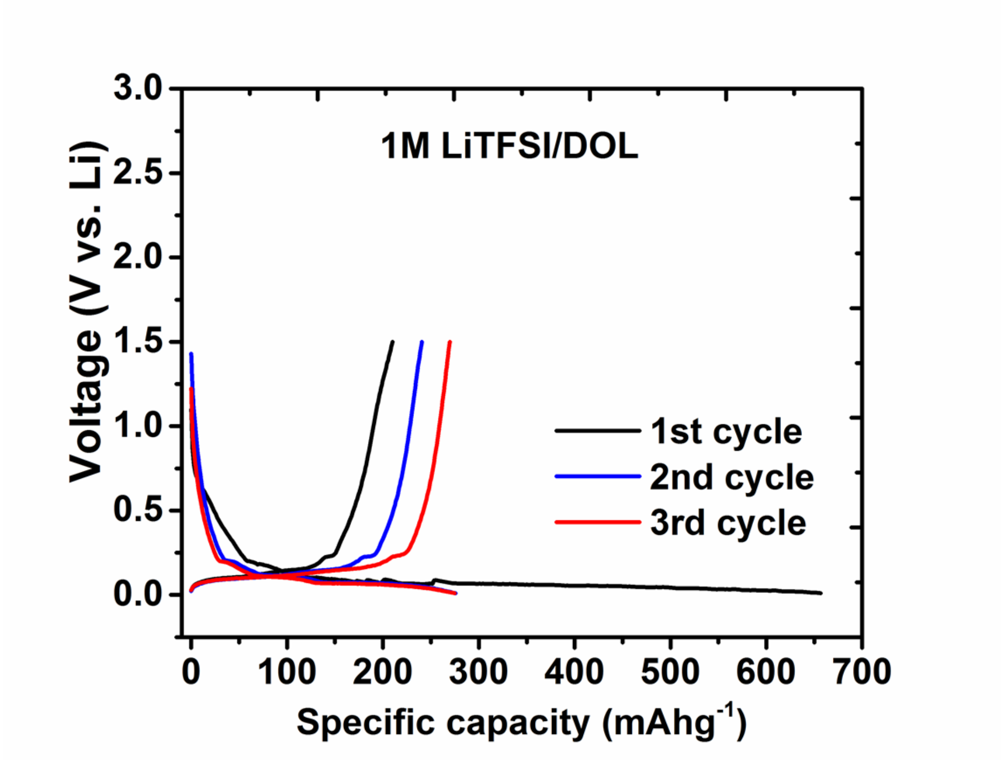

Fig. S4. Charge/discharge curves of Li/G half cell with 1M LiTFSI/DOL electrolyte at 0.1C rate.

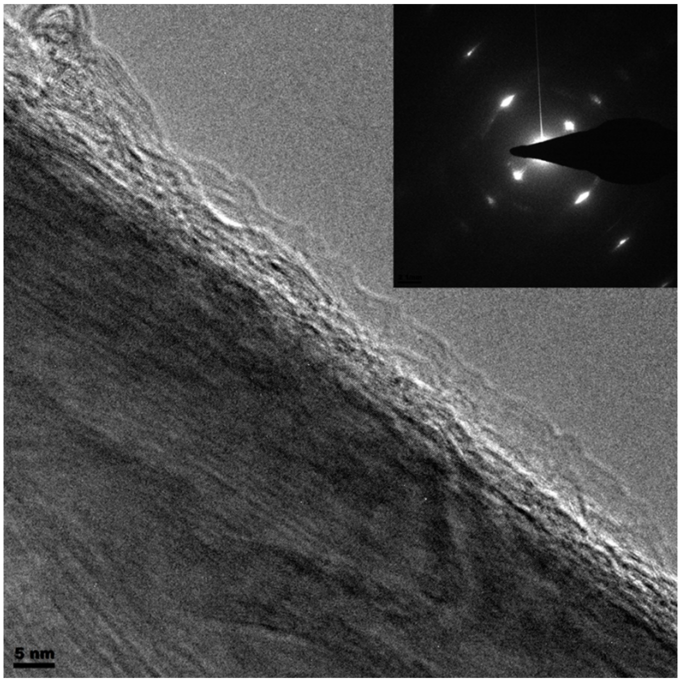

Fig. S5. TEM image and corresponding SAED of graphite after 5 CV cycles in 1M $LiPF_6$/EC/EMC electrolyte at 0.05 mV/s (0.01-2.0 V).

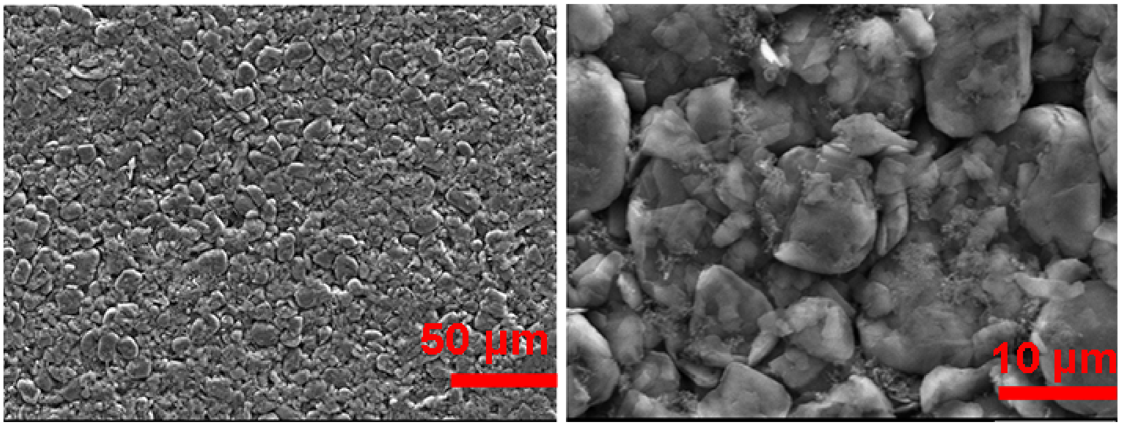

Fig. S6. SEM images of pristine graphite electrode at different magnification.

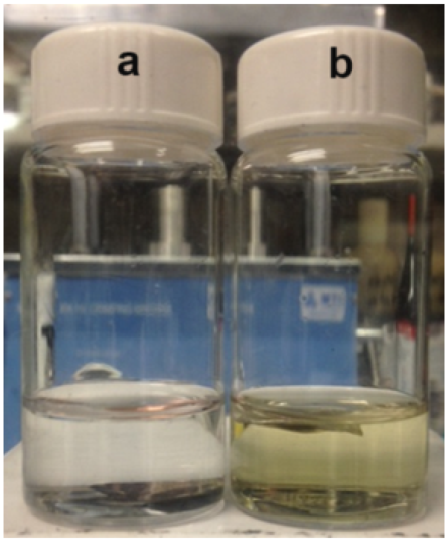

Fig. S7. Digital photograph of the DOL/DME solvent containing (**a**) graphite electrode harvested from LG-S full-cell after 100 cycles and (**b**) Li metal electrode harvested from Li-S hal-cell after 100 cycles.

Table S1. Cell design of Li-ion sulfur pouch cell with capacity of 3Ah.

Pouch cell parameters						
Width (mm)	Length (mm)	Layers	Cell weight (g)	Cell capacity (mAh)	Voltage	Energy density (Wh/kg)
41.5	75	10	24.76	3009	2.1	255

Cell design information				
Electrode			**Quantity**	**Weight(g)**
Anode	Capacity (mAh/g)	360.0	10 (double- layer coating)	9.32
	Loading	95.5%		
	Length (mm)	68.5		
	Width (mm)	37.50		
	Area Weight (mg/cm^2)	18.14		
	Area capacity (mAh/cm^2)	6.24		
Cu foil	Thickness (mm)	0.008	10	1.87
Anode tab	/	/	1	0.13
Cathode	Capacity (mAh/g)	1000.7	10 (double- layer coating)	4.7
	Loading	64.0%		
	Length (mm)	67.0		
	Width (mm)	36.00		
	Area Weight (mg/cm^2)	9.74		
	Area capacity (mAh/cm^2)	6.24		
Al foil	Thickness (mm)	0.012	11	0.86
Cathode tab	/	/	1	0.04
Packing foil	Thickness (µm)	86	1	0.97
Electrolyte	/	/		6.32
Separator	Thickness (µm)	11		0.54
Sealant	/	/	1	0.01

Table S2. Price comparison of traditional cathode materials and sulfur (Source: https://www.eiseverywhere.com)

Materials	Unit price($/kg)
$LiCoO_2$	28
$Li(Ni_{0.33}Mn_{0.33}Co_{0.33})O_2$	25
$Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$	27
$LiMn_2O_4$	19
$LiFePO_4$	24
Sulfur	0.17

Table S3. Composition and physical parameters of the graphite electrode (graphite electrode with mass loading of 5 mg/cm^2 as an example).

Composition (wt %)				**Porosity (%)**	**Thickness (μm)**		
CGP-A12	Timcal C45 carbon	Oxialic acid	PVDF		Cu foil	Coating	Total
89.8	4	0.17	6	38.8	10	43	53

Table S4. Ionic conductivity of DOL based electrolyte solutions with various concentrations of LiTFSI.

LiTFSI/solvent (mol/L)	**Ionic conducity ($mScm^{-1}$)**
0.5	0.63
1	1.87
2	3.91
3	4.43
5	3.35
6	2.44