

Supporting Information

Reversible Cycling of Graphite Electrode in Propylene Carbonate Electrolyte Enabled by Ethyl Isothiocyanate

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Supplementary Note 1

The direct verification of reversible Li^+ ion intercalation into and de-intercalation out of the graphite electrode in the 2% EITC-PC electrolyte was executed by an *in-situ* Raman study. **Figure S1** presents the variation of Raman spectra of graphite electrode during the charge-discharge process. Upon charge, the major peak of the pristine graphite at 1580 cm^{-1} is initially stationary but then broadened and shifted toward higher frequencies after the voltage reaches below 0.2 V , which corresponds to the formation of dilute stage 1 and its conversion to stage 4 of graphite electrode. Once the voltage passes 0.11 V , two new peaks at 1575 cm^{-1} and 1602 cm^{-1} appear and increase at the expense of the original peak, which is correlated with the consecutively phase transitions stage 4-stage 3 and stage 3-stage 2L. After the voltage is decreased to 0.07 V and lower, the peak at 1602 cm^{-1} gradually diminishes, which indicates the phase transitions from stage 2L to stage 2. Finally, all original peaks were entirely missing and a new broad line appeared around 1500 cm^{-1} after the voltage drops below 0.039 V , which reflects the final phase transition from stage 2 to stage 1 of graphite. During the discharge process, the above evolution of peak intensity and position were retrospectively observed. This result provides compelling evidence for the reversibility of graphite in EITC-PC electrolyte.

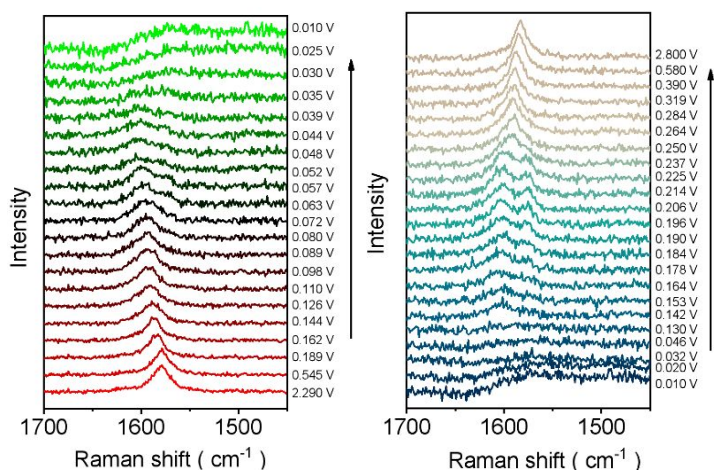


Figure S1. *In-situ* Raman spectra of a graphite electrode during charge (left) and discharge (right) in 2% EITC-PC electrolyte.

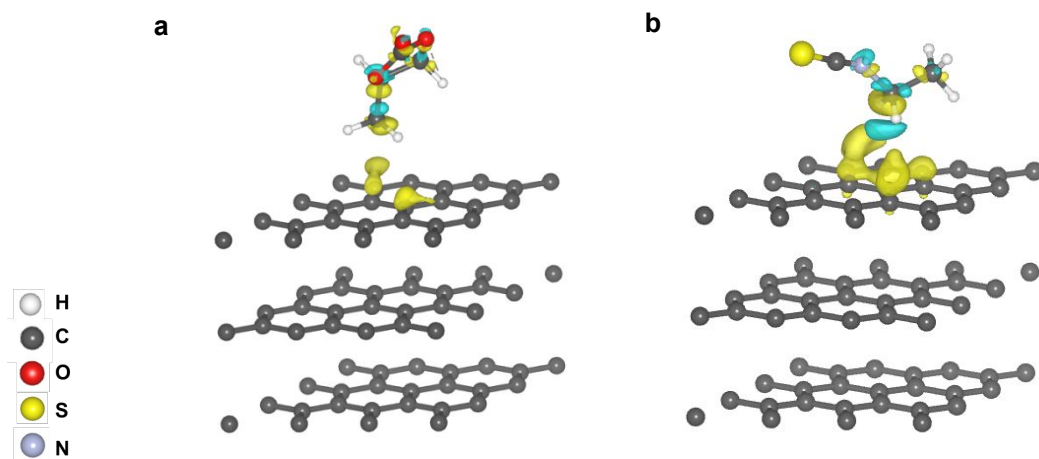


Figure S2. The charge density difference in the optimized adsorption geometry of (a) PC and (b) EITC on graphite surface. The yellow and blue isosurfaces represent charge accumulation and charge depletion in space, respectively. The isosurface level is 0.0002 au.

Supplementary Note 2

Figure S3 displays the ^{19}F ssNMR measurements performed on graphite electrode retrieved from the Li-graphite cells charged in STD-PC and 5% EITC-PC electrolytes. In these two electrolytes, the F-containing species in the SEI are formed from the decomposition of LiPF_6 . LiF (~ 204 ppm) and PO_2F_2^- (~ 80 ppm) species are detected in both SEIs. Relatively, the LiF signal is much more pronounced in the 5% EITC-PC electrolyte, consistent with the XPS results.

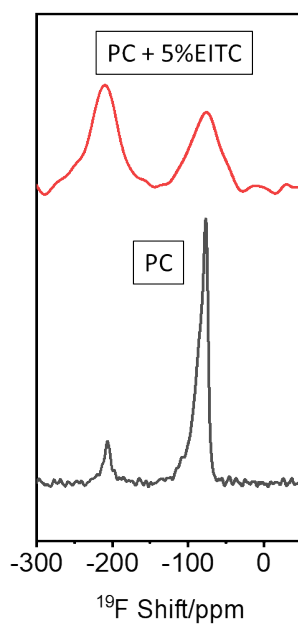


Figure S3. ^{19}F ssNMR spectra collected on graphite electrodes charged in (black) STD-PC and (red) 5% EITC-PC electrolytes.

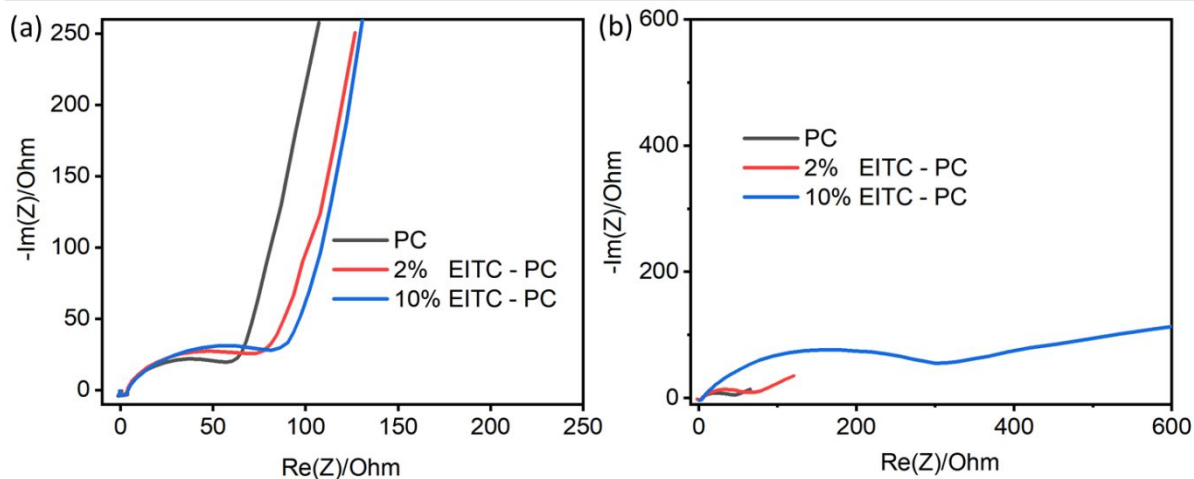


Figure S4. Impedance spectra of Li-graphite half cells with different electrolytes. (a) OCV condition; (b) after 2 cycles at C/10, the PC group was charged at C/10 for 40 hours because of the infinite plateau at 0.8 V vs. Li^+/Li .

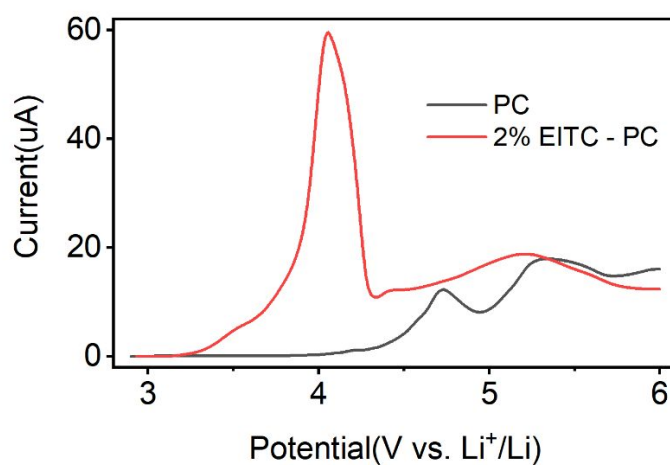


Figure S5. LSV test results of the PC-electrolyte and the 2% EITC-PC electrolyte.

Table S1.

The table compiles the works with the standard 1.0 M electrolyte concentration and the concentrations of the additives are less than 10 wt%. The table excludes the co-solvent studies (PC~ 50 wt%) and does not include the additive studies that only show cyclic voltammetric data.

#	Publications	Name of Additive	Performance
1	Journal of The Electrochemical Society 146 (1999) 470	Ethylene sulfite	1 st cycle, 429 mAh g ⁻¹ at 0.05 C, no cycling data.
2	Journal of Power Sources 119–121 (2003) 368	Acrylonitrile	2 nd cycle, 350 mAh g ⁻¹ , 3 th cycle to 325 mAh g ⁻¹ at 0.05C.
3	Electrochemistry Communications 6 (2004) 126	Vinyl ethylene carbonate	no cycling data, first cycle coulombic efficiency 85%, average coulombic efficiency around 98% for 30 cycles.
4	Journal of Power Sources 158 (2006) 578	2-Cyanofuran	2 nd cycle, 350 mAh g ⁻¹ , 15 th cycle 330 mAh g ⁻¹ at 0.16C
5	Energy Environmental Science 2 (2009) 1102	Vinyl ethylene sulfite	2 nd cycle 310 mAh g ⁻¹ , 35 th cycle 300 mAh g ⁻¹ at 0.01C
6	Electrochemistry Communications 40 (2014) 80	Methyl vinyl sulfone, Ethyl vinyl sulfone	1 st cycle coulombic efficiency, <70%
7	This work	Ethyl isothiocyanate	1 st cycle coulombic efficiency 84%, second cycle capacity 360 mAh g ⁻¹ , 40 th cycle capacity 345 mAh g ⁻¹ , average coulombic efficiency 99.3%

