

Supplementary Materials

Additive Stabilization of SEI on Graphite Observed Using Cryo-Electron Microscopy

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Materials and Methods

NCM523||AG Pouch-cell assembly

The 2000 mAh dry pouch NMC532/AG cells were obtained from Capchem Co. Ltd. (a negative/positive capacity ratio (that is, N/P ratio) of 1.05), China to conduct the electrochemical experiments for electrolyte comparison. Before shipping, the pouch cells were vacuum sealed without electrolyte in a dry room. The cells were open and dried in the oven at 85°C under vacuum for 48 h. For each cell, the electrolyte (The

ratio of electrolyte weight to cell capacity (the E/C ratio) was used to quantify the electrolyte amount and was set at 3.0 g Ah^{-1}) was injected afterwards in a glovebox filled with argon.

The baseline electrolyte contains 1.0 mol/L LiPF_6 dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) = 30:70 (volume ratio) (battery grade, Capchem Co. Ltd., China).

The VC/EC-DEC electrolyte contains 1.0 mol/L LiPF_6 dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) = 30:70 (volume ratio) (battery grade, Capchem Co. Ltd., China) with 1% wt VC.

The DTD/EC-DEC electrolyte contains 1.0 mol/L LiPF_6 dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) = 30:70 (volume ratio) (battery grade, Capchem Co. Ltd., China) with 1% wt DTD.

The TPP/EC-DEC electrolyte contains 1.0 mol/L LiPF_6 dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) = 30:70 (volume ratio) (battery grade, Capchem Co. Ltd., China) with 1% wt TPP.

The FEC/EC-DEC electrolyte contains 1.0 mol/L LiPF_6 dissolved in ethylene carbonate (FEC): ethylene carbonate (EC): diethyl carbonate (DEC) = 10:20:70 (volume ratio) (battery grade, Capchem Co. Ltd., China).

After filling the electrolytes, the cells were stand by for 1 h, then pouch cell were sealed and pre-degassing in vacuum. The sealed cells were aged for 48 h /45°C and hot-pressed at 0.8 MPa /60 °C. Before the cycling at large current, all graphite anodes are charged using small current density (0.05C) for three hours at 45°C and then 0.1C for another 3 hours (formation) at 45°C. This process is critical to ensure the activation of the graphite and formation of stable interphase between graphite and electrolyte to enhance its electrochemical performance. And then, the sealed cells were aged for 48 h /45 °C again. The NMC532/AG pouch bag cells was adopted by the constant current/constant voltage (CC/CV) step charge to 4.2 V with 80 mA as the limiting current at 0.2 C, followed by a discharge to 3.0 V using a CC step with the rate of 0.2 C and cycled twice. Afterwards, the NMC532/AG pouch cells were transferred to the Battery Tester (Neware) and conducted the electrochemical cycling at the rate of 1.0 C in the 3.0–4.2 V voltage range and 45 °C. In order to reduce the experimental errors, two NMC532/AG pouch bag cells were tested for all electrolyte systems.

The cathode slurry contains a mixture of 96.5 wt% $\text{LiNi}_{0.5}\text{Co}_{0.3}\text{Mn}_{0.2}\text{O}_2$ (NCM532), 1.5 wt% polyvinylidene fluoride (PVDF), and 2 wt% conductive carbon (Super-P). The anode slurry contained 95.0 wt% graphite, 1.5 wt% carboxymethyl cellulose (CMC), 1.5 wt% Super-P, and 2 wt% styrene butadiene rubber (SBR), respectively. The electrodes were dried in the vacuum condition at 100 °C for 72 h before final assembly. The NCM532/graphite cells were designed to reach a capacity of approximately 2000 mAh and the capacity ratio of cathode : anode is 1 : 1.1.

Cryo-transfer procedure and material preparation

Under air and room temperature condition, SEI of Artificial graphite (AG) is very reactive and corrodes. Under a TEM electron beam especially, the light Li ion extremely unstable and easy to escape from an ionic crystal or make it amorphous orientation due to the electron beam knock-on damage, radiolysis, charging and heating. This makes it impossible for us to observe. To overcome these challenges, we developed super-low-dose and cryogenic-TEM techniques. First, Pouch Cell of NCM523||AG surface after cycling 200th at 45 °C was opened in an Ar gas glove box, and the cycled AG anode was cleaned with dimethyl carbonate and dried in an 80 °C heating plate. Then, AG particle was put on Cu TEM grid and the sample was quickly smashed into liquid ethane in an Ar gas glove box. Whereafter, to avoid the surface reactions and contaminations of the electrodes in air, the sample was saved, transported and put in an autoloader automatic sampling system of cryogenic-TEM under liquid nitrogen condition. Cryo-HRTEM samples were transferred in cryo-TEM (FEI Krios G3i operated at 300 kV). The microscope was equipped with a Falcon 3 camera (direct electron detection) and maintained their temperature near -192 °C throughout the holder. The cryo-STEM (EELS Mapping) samples were transferred in ETEM (FEI Titan G3 operated at 80 kV) by Fischione MODEL 2550 cryo-holder. The ETEM microscope was equipped with a high-resolution Gatan imaging filter (Gatan Continuum 1069) for EELS mapping. The probe current for EELS maps on the Titan was around 50 pA.

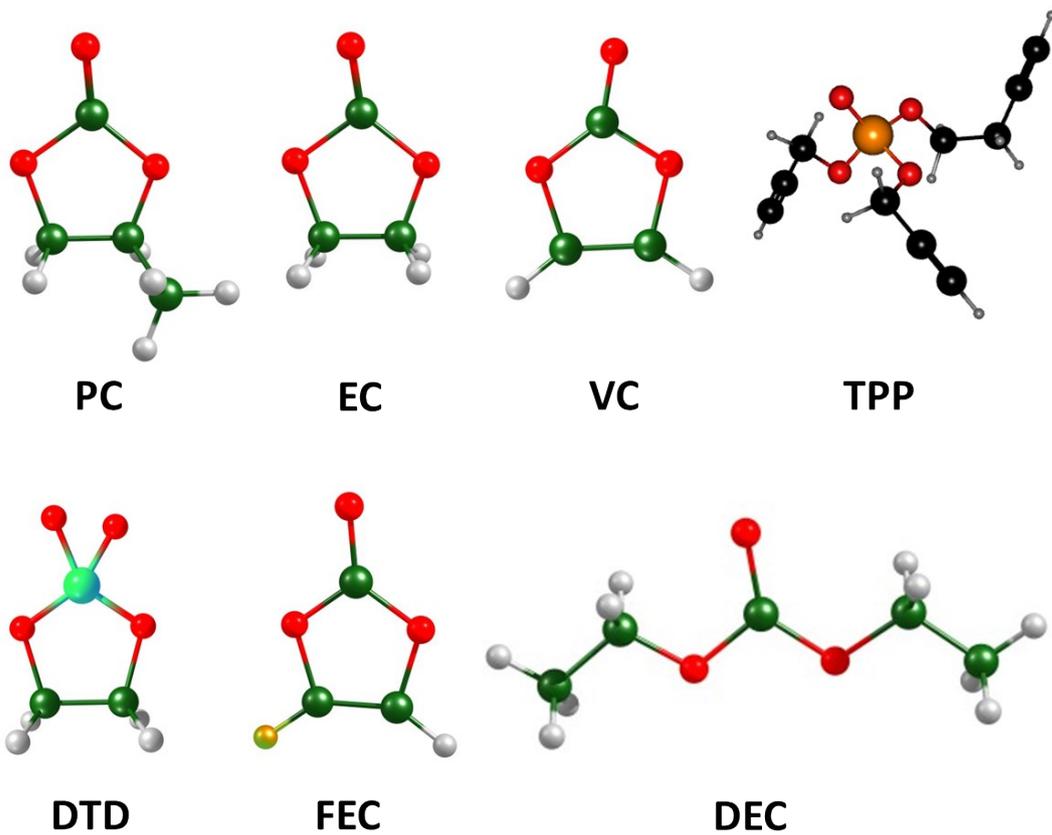


Figure S1. Molecular structure of electrolyte and additives for Graphitic Anode used in this study.

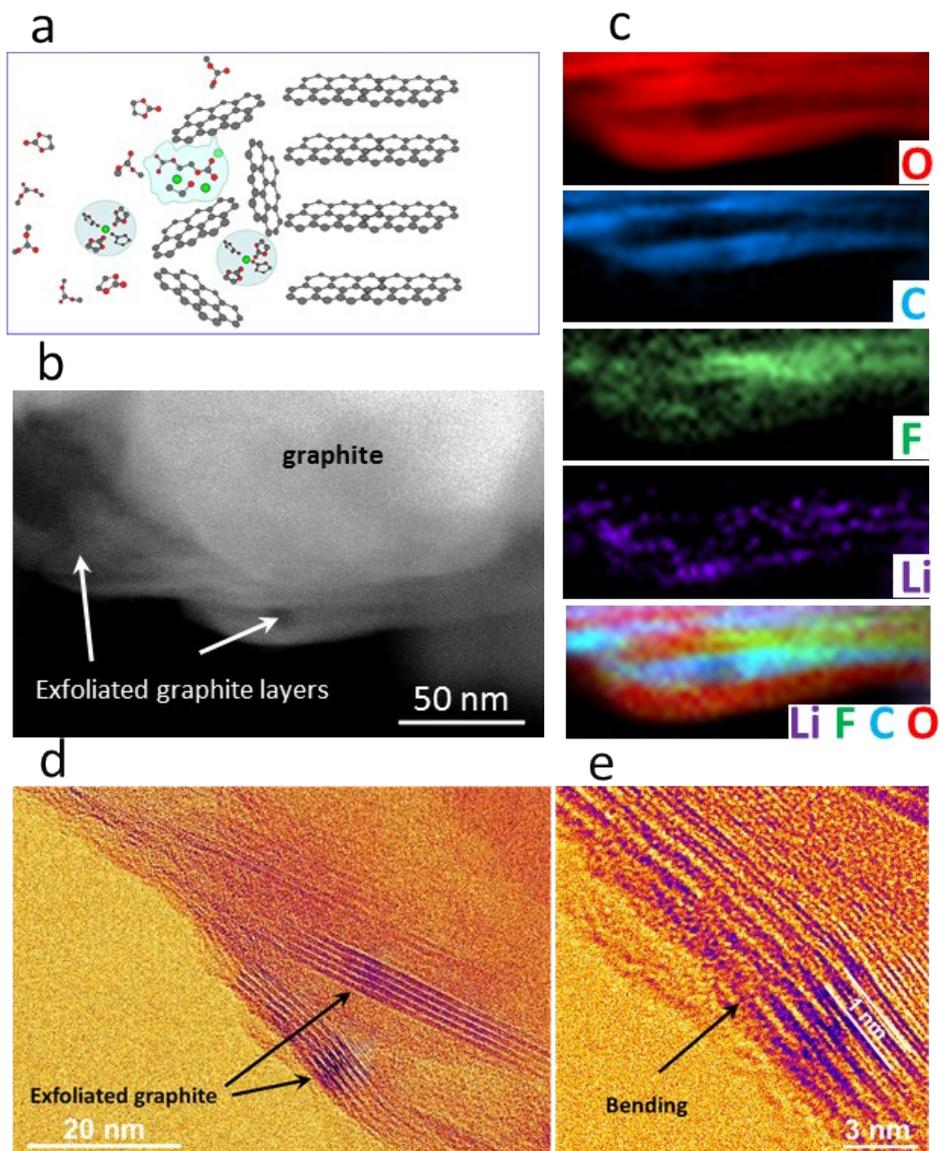


Figure S2. **a.** atomic schematic showing the exfoliation of graphite with PC-DEC electrolyte with 1M LiPF₆; **b** HAADF and **c.** EELS elemental maps; **d-e.** atomic scale HRTEM showing the layer spacing of the exfoliated graphite layers.

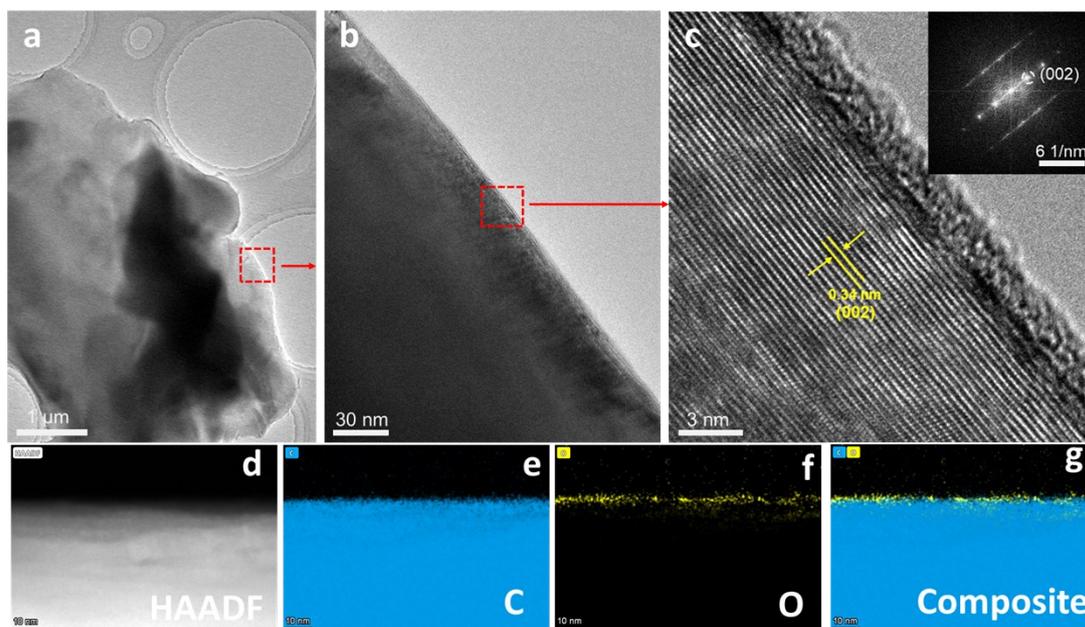


Figure S3. Cryo-TEM analysis of the fresh graphite. **a-b.** large-scale TEM image showing the clean surface of fresh graphite; **c.** HRTEM and FFT showing the lattice of the graphite with ~ 1.5 nm oxidized amorphous layer; **d-g.** HAADF STEM image and C, O, and composite map showing the graphite surface.

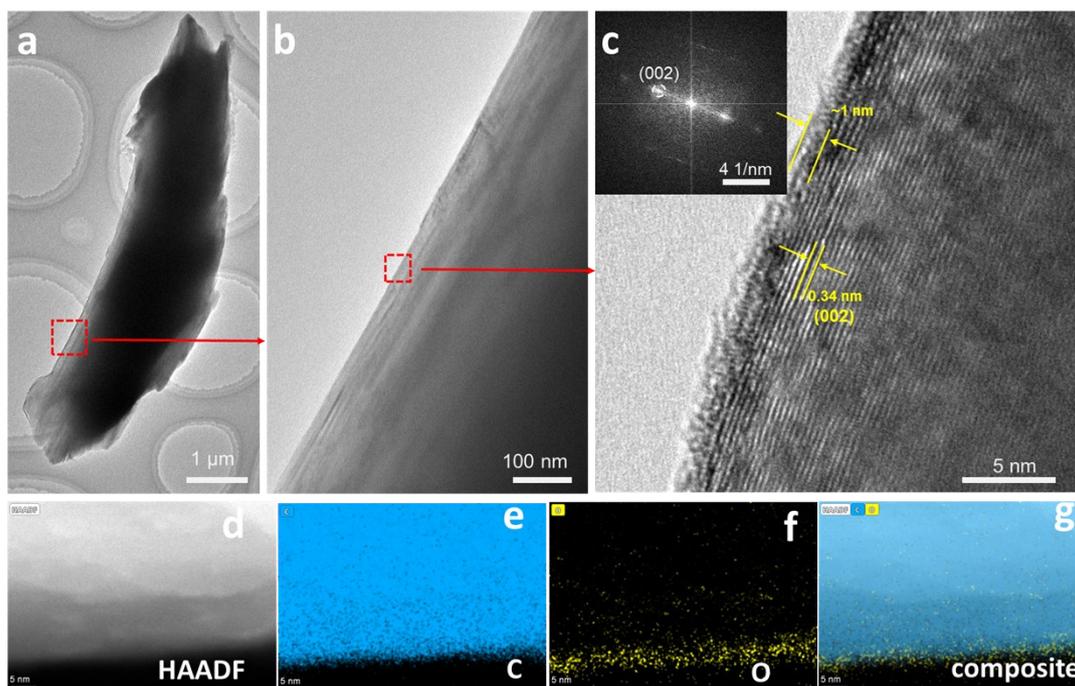


Figure S4. Cryo-TEM analysis of the graphite soaked in the EC:DEC electrolyte for 24 hours. **a-b.** large-scale TEM image showing the clean surface of graphite; **c.** HRTEM and FFT showing the lattice of the graphite with ~1nm oxidized amorphous layer; **d-g.** HAADF STEM image and C, O, and composite map showing the graphite surface.

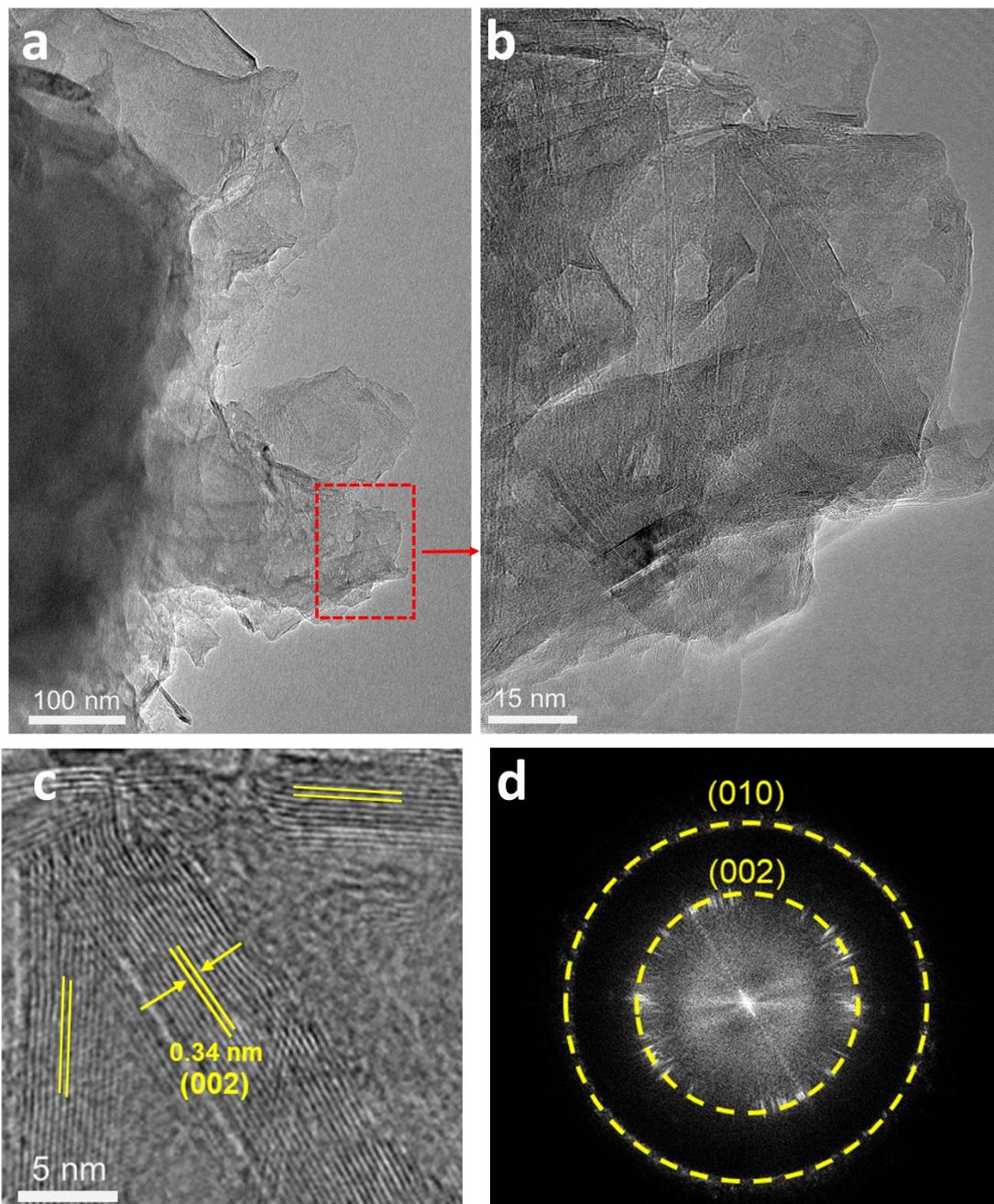


Figure S5. Cryo-TEM analysis of the graphite after 200 cycles in baseline electrolyte solution containing 1.0 mol/L LiPF_6 dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) with 30:70 volume ratio at 45°C without formation process. **a.** large-scale cryo-TEM image showing the exfoliated surface of graphite; **b.** cryo-TEM showing the interconnected network of the exfoliated graphite; **c.** HRTEM and **d.** FFT showing the lattice of the exfoliated graphite layers.

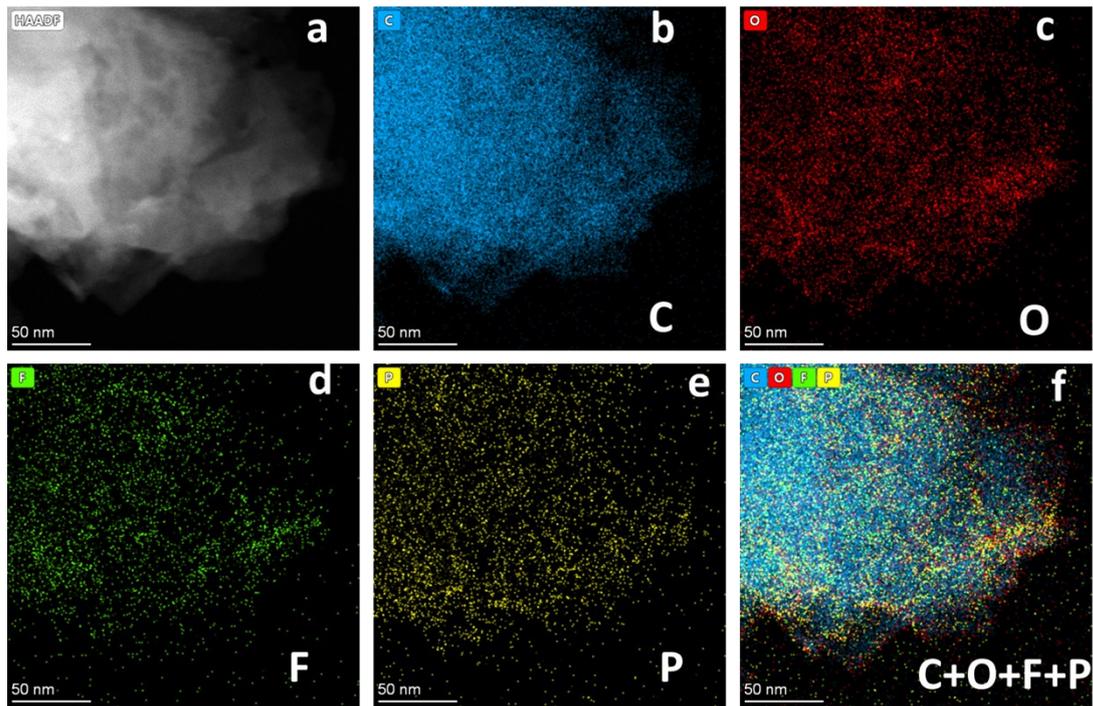


Figure S6. Cryo-TEM analysis of the graphite after 200 cycles in baseline electrolyte solution containing 1.0 mol/L LiPF_6 dissolved in ethylene carbonate (EC): diethyl carbonate (DEC) with 30:70 volume ratio at 45°C without formation process. **a.** cryo-HAADF STEM image showing the exfoliated interconnected graphite layers; **b.** C map; **c.** O map; **d.** F map; **e.** P map; **f.** composite map obtained using EDS.

In addition, we studied the graphite surface using cryo-TEM and EDS cycled without formation after 200 charge-discharge cycles at the rate of 1.0 C in the 3.0–4.2 V voltage range and 45°C . As clearly shown by Figure S5&S6, exfoliation of graphite is much worse than the ones with proper formation process.

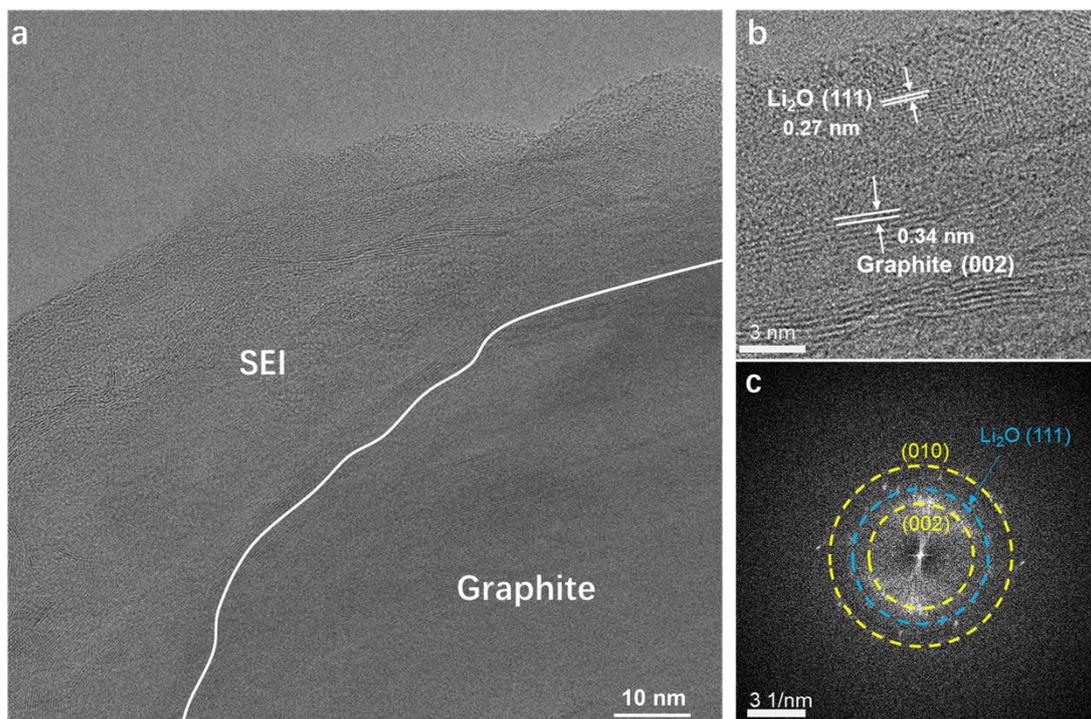


Figure S7. cryo-TEM analysis showing the minor amount of graphite exfoliation using the formation process of 2 cycles between 3.0 and 4.2 V at a rate of C/100 at room temperature. (a) low-magnification image showing the SEI on graphite; (b) HRTEM showing the Li_2O lattices and exfoliated graphite layer lattice; (c) FFT of panel a showing the detected (111) crystal planes of Li_2O , and (010)&(002) crystal planes of graphite layers.

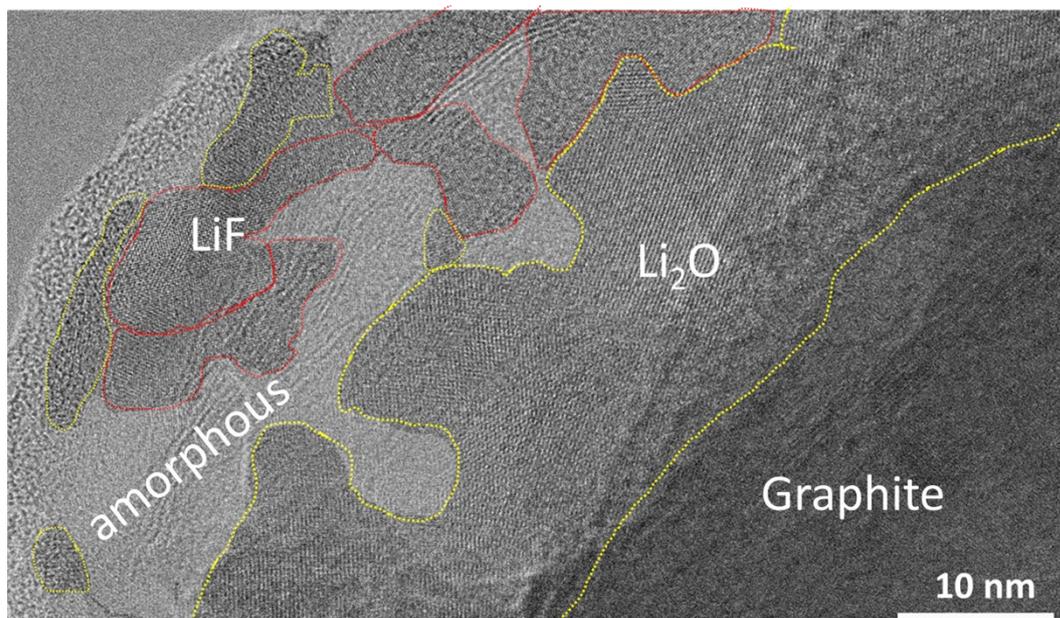


Figure S8. Cryo-TEM analysis of the Li₂O-rich region in the SEI on graphite using FEC additive.

Table 2 Battery performance comparison with previous literatures

No.	T(°C)	Rate	Pouch cell	Electrolyte	Cycle #	Capacity Retention
Ref.2	45 °C	0.5C/0.5C	LiNi _{0.6} Co _{0.6} Mn _{0.6} O ₂ /graphite	1M LiPF ₆ , EC:DEC= 3:7	200	79.1%
Ref.3	60 °C	0.5C/0.5C	LiNi _{0.8} Co _{0.15} Al _{0.05} O ₂ /graphite	1M LiPF ₆ , EC:DEC= 3:7	140	35%
Ref.4	45 °C	1.0C/1.0C	LiNi _{0.5} Co _{0.3} Mn _{0.2} O ₂ /graphite	1M LiPF ₆ , EC:DEC= 3:7	150	35%
Ref.5	RT	0.5C/1.0C	LiNi _{0.8} Co _{0.1} Mn _{0.1} O ₂ /graphite	1M LiPF ₆ , EC:DMC= 1:1	100	40%
Ref.6	45 °C	1C/1C	LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂ /graphite	1M LiPF ₆ , EC- DEC	200	55%
Ref.7	45 °C	0.33C/0.3 3C	NCM422/graphite	1M LiPF ₆ , EC:DEC= 3:7 with 2%VC	200	74%
Our work	45 °C	1.0C/1.0C	LiNi_{0.5}Co_{0.3}Mn_{0.2}O₂/graphite	1M LiPF₆, EC:DEC= 3:7	200	50%

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