SUPPORTING INFORMATION

A) Coupled techniques complementary information

GC conditions

Helium was used as the GC carrier gas and maintained at a constant flow rate of 1.3 mL min^{-1}. To achieve good chromatographic peaks resolution, the programmable temperature gradient was optimized from 40 to 250 °C as follows:

Gas: the capillary column was ramped from the initial temperature of 40 °C, held for 6 min, increased at 10 °C min^{-1} up to 90 °C, increased at 5 °C min^{-1} up to 190 °C, held for 5 min, increased at 10 °C min^{-1} up to 250 °C where it was held for 10 min. The total duration of GC analysis was 52 min.

Liquid: the capillary column was ramped from the initial temperature of 40 °C, held for 5 min, increased at 10 °C min^{-1} up to 250 °C where it was held for 10 min. The total duration of GC analysis was 36 min.

The transfer line was maintained at 250 °C. The ion source was set at 200 °C.

FTIR conditions

Transfer line temperature and light-pipe temperature were kept constant at 200 °C during the analysis. Real time spectra were recorded by addition of 16 scans, with a spectral resolution of 4 cm^{-1} and 32 background scans. The scan range was from 4000 to 650 cm^{-1}.

MS conditions

Tuning of the mass spectrometer was done automatically using the ions resulting from perfluorotributylamine ionization. The mass spectrometer was operated with a filament current of 250 μA and electron energy of 70 eV in the electron ionization (EI) mode. The mass range was 10-300 u and data acquisition and processing were performed with Xcalibur 2.0.7 software.

B) Electrochemical cell assembling and lithiation procedures

Electrochemical cell assembling procedure

The negative active material is composed of 90 wt. % of SFG6 graphite (TIMCAL - particle size of 6.5 μm (d90) and BET surface area of 17 m^2 g^{-1}) and 10 wt% Super P carbon black. The electrolyte composition was 1 M $LiPF_6$ in ethylene carbonate (EC) and dimethyl

carbonate (DMC) (50/50, w/w) from commercial sources known as LP30® (Merck). The Swagelok-type half-cells were assembled in an argon-filled glove-box using 10-15 mg composite powder as working electrode, an electrolyte-impregnated Whatman GF/D borosilicate glass fibre separator and a lithium metal foil.

Lithiation procedure

Once assembled, the cells were subjected to a C/20 galvanostatic discharge (forming LiC_6) at 20 °C. The cells were cut off at 0.01 V vs. Li^o/Li^+.

C) Lithiated graphite sample preparation for GC/FTIR/MS analysis

After disassembling the electrochemical cell inside the argon-filled gloves box, the EC/DMC (1/1 w/w) – $LiPF_6$ 1M electrolyte-soaked lithiated graphite was introduced into a DSC aluminum crucible. After being sealed, the loaded can was pierced then immediately placed into a laboratory-designed stainless steel cell. This cell was introduced in a furnace heated from room temperature to 200 °C at 10 °C min^{-1} then maintained at this temperature for 3h. Then, 0.7 mL of the evolved gases was taken with a syringe equipped with a valve and injected to the GC injector.

D) Commercial cell opening and electrolyte sample preparation for liquid GC/MS analysis

The cell opening was performed in an argon-filled glove box (with < 1 ppm H_2O, and < 1 ppm O_2). Care was taken to avoid short-circuits that could induce extra degradation; the tabs were isolated with dielectric tape avoiding contact with the glove-box metallic parts; ceramic cutters and plastic tweezers were used for manipulation. As the cell was “swollen”, the casing edges were cut carefully, not to short-circuit the electrodes. Once the casing was opened, the internal contacts between the current collectors and the tabs were cut. Successively, the anode/separator/cathode assembly was unrolled carefully, the electrodes were removed and a separator sample of approximately 9 cm^2 was introduced in 1 mL of dried acetonitrile (H_2O < 0.001%). After dilution (1:100) and filtration, 0.1 µL of the solution was injected into the GC.