

High-temperature lithium–polyimide batteries with a solvate complex of lithium bis(trifluoromethanesulfonyl)imide in tetraglyme as electrolyte

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Table of Contents

Experimental section	S2
Figure S1 ^{13}C NMR spectra of the LiTFSI:G4 solvate-ion complexes	S3
Figure S2 NMR high resolution spectra of composition 1. 2D correlation of ^{13}C - ^1H HSQC and ^{13}C - ^1H HMBC and ^{13}C -ig spectrum	S3
Figure S3 SEM images of the initial polyimide powder (a); surface of the composite cathode (b) at a scale of 200 nm	S4
Figure S4 SEM images of the fiberglass separator at a scale of 10 μm (a) and 200 nm (b)	S4
Figure S5 CV of Li//PI cells with electrolytes (a) LiTFSI:G4 (1:1 mol), (b) LiTFSI:G4 (1:2 mol), (c) LiTFSI:G4 (1:4 mol) at a potential scan rate of 2 mV/s	S5
Figure S6 Scheme of the two-electron redox reaction of PI polyimide	S5

Experimental section

To prepare the solutions of solvate ILs, we used the salt $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, purity 99%, commercial product, Sigma Aldrich), and dimethyl ether of tetraethylene glycol (tetraglyme, G4, purity $\geq 99\%$, SigmaAldrich) as a solvent. Electrolytes were prepared in an MBraun argon glove box, the samples were weighed on an analytical balance with an accuracy of 0.0001 g in molar ratios of 1 : 1, 1 : 2, and 1 : 4.

High-resolution spectra of ^1H and ^{13}C were registered using a Bruker Avance III 500MHz NMR-spectrometer. The measurements at frequencies 500 and 126 MHz for ^1H and ^{13}C , respectively, were carried out at the room temperature ($22 \pm 1^\circ\text{C}$). The electrolytes were placed in glass capillaries with a diameter of 2.9 mm and a length of 57 mm in an inert atmosphere box. The capillaries containing the electrolyte were then sealed and placed in standard 5 mm NMR ampoules. The chemical shift scale was calibrated after the DMSO- d_6 signal in a capillary as an external standard (2.50 ppm for ^1H).

Electrolyte conductivity was measured by conductometry using an LCR819 immittance meter (Goodwill Instruments Ltd., Taiwan) at an alternating current of 1 kHz in a Teflon electrochemical cell with flat Pt electrodes. The temperature regime in the range from -35 to 50°C was provided using a TZh-TS-01 cryothermostat (Russia). Before measurement, the samples were kept at each temperature for at least 1 h.

SEM images of the surface morphology of the samples were obtained using a Zeiss LEO SUPRA 25 field-emission scanning electron microscope.

Li-Battery Fabrication

The electrochemical performance of polyimide was evaluated in the CR2032 coin-type lithium batteries. The cathode composition comprising of polyimide (40 wt%), conductive carbon black (40 wt%, Timical Super C65), and PVDF polymer binder (20 wt%, Kynarflex HSV 900, Arkema France) was dispersed in *N*-methylpyrrolidone (NMP, 99%, Aldrich) to obtain $\sim 12\%$ suspension, which was homogenized mechanically (Light Duty Isolab homogenizer). Cathode slurry was applied onto the current collector (20 μm thick graphitized Al-foil, MTI Corp., USA) using tape coating (Gelon Lib. coater). The resulting films were annealed at 150°C , pressed on rollers and dried again for 5 hours at a temperature of 120°C to remove the NMP solvent.

The organic cathode ($d = 1.6$ cm), fiberglass separator (Whatman GF/A Glass microfiber filters, GE Healthcare, Chicago, IL, USA), and lithium anode ($d = 1.6$ cm) were assembled in coin-type lithium batteries using LiTFSI-G2 complexes (0.03 ml) as electrolyte. The cells were assembled inside MBraun argon glove box.

Li-Battery Testing

Cyclic voltammograms in Li//PI cells were recorded on a P-40X potentiostat (Elins, Russia) at a sweep rate of 2 mV s^{-1} .

The electrochemical characteristics of the cells were evaluated using a BTS-5V10mA battery analyzer (Neware Technology Ltd., China) cycling at different current values in the range of 1.0–3.5 V. The Li/PI cells were tested at room temperature without prior development, and at 100°C the cells were pre-cycled for 20 cycles and then allowed to reach a steady state.

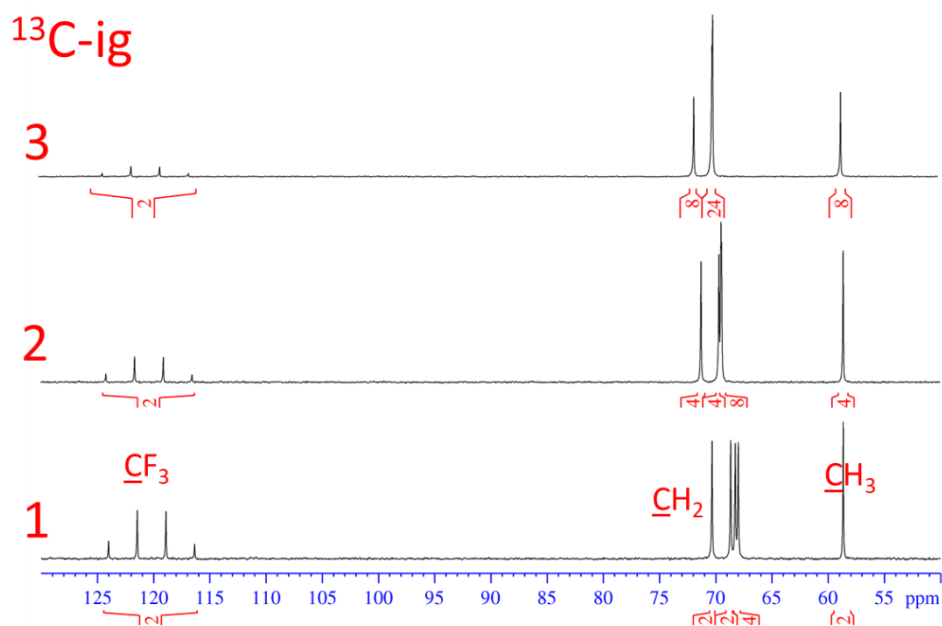


Figure S1 ^{13}C NMR spectra of the LiTFSI:G4 solvate-ion complexes of composition 1, 2 and 3 (1 – LiTFSI:G4 (1:1 mol.); 2 – LiTFSI:G4 (1:2 mol.); 3 – LiTFSI:G4 (1:4 mol.))

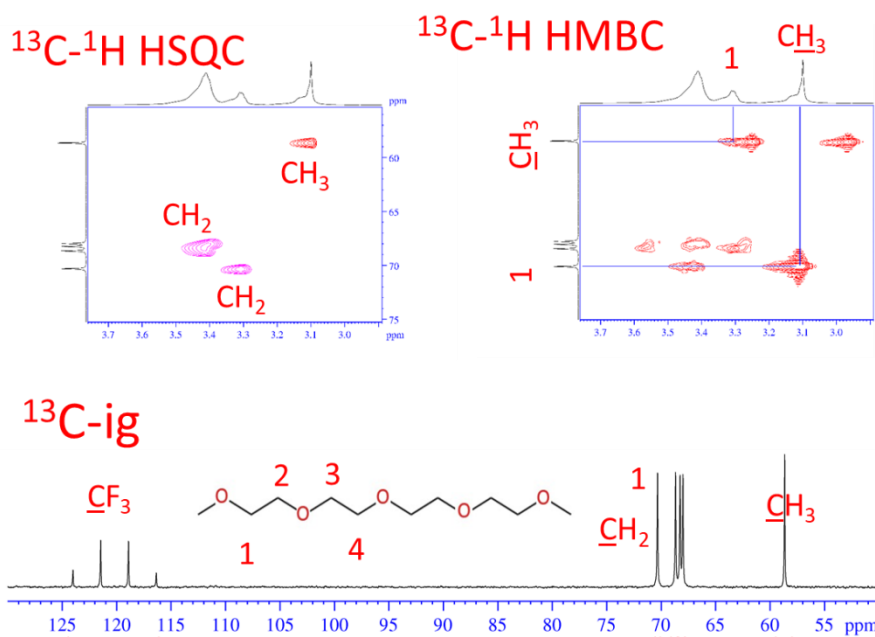
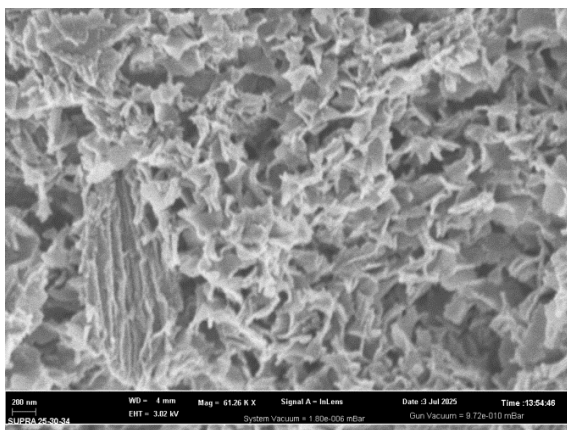
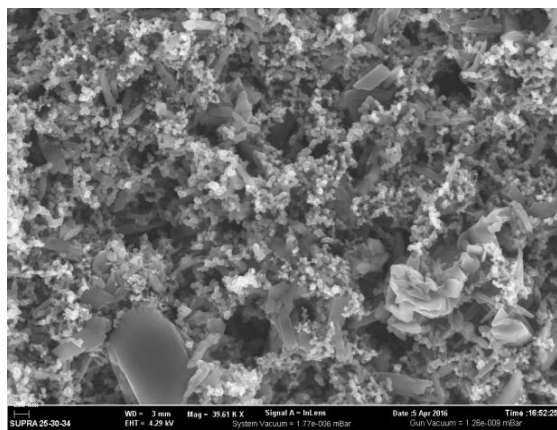


Figure S2 NMR high resolution spectra of composition 1 – LiTFSI:G4 (1:1 mol.).

2D correlation of ^{13}C - ^1H HSQC and ^{13}C - ^1H HMBC and ^{13}C -ig spectrum

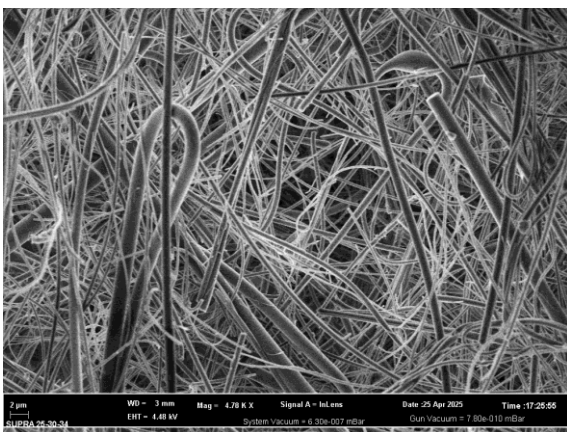


(a)

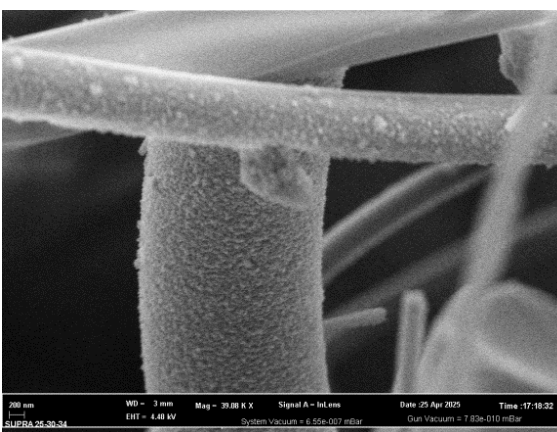


(b)

Figure S3 SEM images of the initial polyimide powder (a); surface of the composite cathode (b) at a scale of 200 nm



(a)



(b)

Figure S4 SEM images of the fiberglass separator at a scale of 10 μm (a) and 200 nm (b)

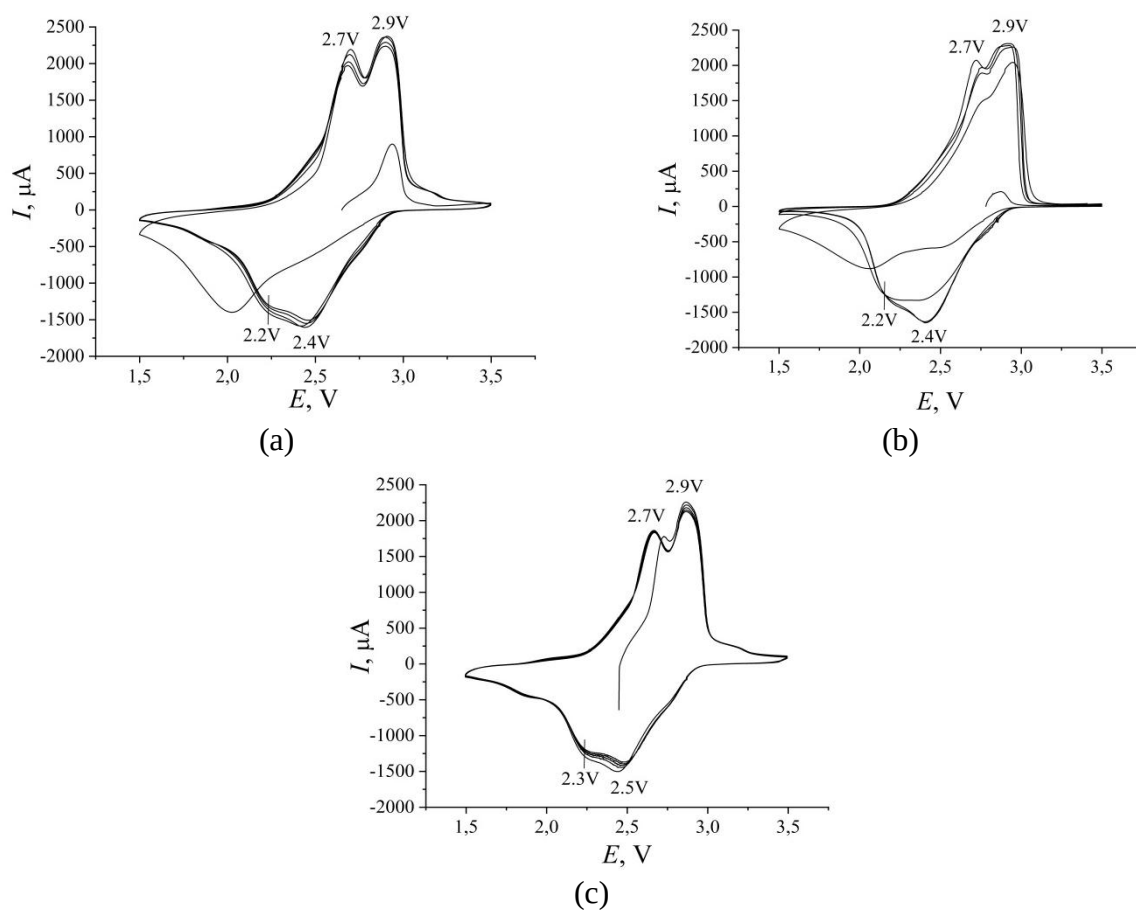


Figure S5 CV of Li//PI cells with electrolytes (a) LiTFSI:G4 (1:1 mol), (b) LiTFSI:G4 (1:2 mol), (c) LiTFSI:G4 (1:4 mol) at a potential scan rate of 2 mV/s

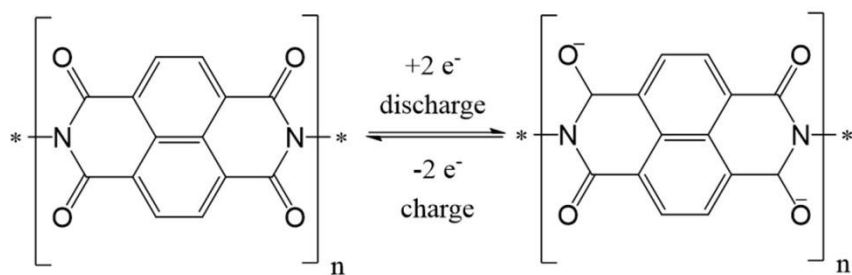


Figure S6 Scheme of the two-electron redox reaction of PI polyimide