

Supporting Information for

High energy lithium-oxygen batteries – Transport barriers and thermodynamics

Shyamal K. Das,^a Saomao Xu,^a Abdul-Hamid Emwas,^b Ying Ying Lu,^a Samanvaya Srivastava^a and Lynden A. Archer^{*a}

Experimental details:

Carbon aerogel was synthesized by a hydrothermal method employing resorcinol and formaldehyde as carbon precursors. An aqueous solution of resorcinol, formaldehyde and sodium carbonate was prepared under continuous stirring. The ratios of resorcinol to formaldehyde and to sodium carbonate were kept at 0.185 g ml⁻¹ and 251 respectively calculated on a molar basis. The transparent sol was transferred to a Teflon-lined stainless steel autoclave of capacity 100 ml (70% filling) and heated at 180 °C for 6 h and then cooled to room temperature. The resultant orange color product was recovered by centrifugation and washed with deionized water and freeze dried. The dried product was further calcined at 1000 °C for 4 h in Ar atmosphere at a heating rate of 5 °Cmin⁻¹.

Specific surface area (BET) of carbon aerogel was obtained from nitrogen adsorption-desorption isotherms (Micromeritics ASAP 2020). The morphology was observed by scanning electron microscopy (SEM, LEO 1550 FESEM) and transmission electron microscopy (TEM, FEI Tecnai G2 T12). Raman spectra were taken using a Renishaw In Via Confocal Raman Microscope.

For the working carbon electrode, slurry of the carbon aerogel was prepared with PVdF (Sigma) in a weight ratio of C:PVDf = 90:10 in *N*-methyl-pyrrolidone (NMP). The slurry was cast onto an aluminium mesh current collector and dried in vacuum at 120 °C for 12 h. Typical weight of the electrodes were 2-3 mg. Electrolytes were prepared by mixing ionic liquids (1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide [C₄mpyrr][NTf₂], 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide

[C₄mim][NTf₂], and 1-Butyl-3-methylimidazolium tetrafluoroborate [C₄mim][BF₄]) with battery grade LiN(SO₂CF₃) (LiTFSI). All chemicals were obtained from Sigma Aldrich.

Cyclic voltammetry (CV, CH608 CH Instruments) and galvanostatic charge/discharge cycling (Maccor) were done in 2032 coin-type cells with pure metal Li (Aldrich) as anode, Whatman glass fibre as separator. The air cathode side of the coin cell was drilled with holes for O₂ flow. The assembled Li-O₂ cells were enclosed in custom built leak proof stainless steel containers (Agilent Technologies). All handling was carried out in an Argon filled glove box. The Li-O₂ cell chambers were purged with O₂ gas (Airgas) for 15 minutes and subsequently sealed at required pressures. The cells were equilibrated at open circuit for four hour before starting the experiments. All galvanostatic experiments were performed at constant current density of 70 mAg⁻¹ (normalized to the weight of the carbon) in the voltage range of 2-4.1 V (vs. Li⁺/Li) at required temperatures. Temperature in the range of 25 °C to 150 °C was controlled by placing the Li-O₂ cell containing chambers in convection ovens (MTI corporation). Low temperature measurements were performed at 5 °C using a Thermo Scientific temperature controller (Model: NESLAB RTE7). AC impedance measurements were conducted using a Solartron Frequency Response Analyser (Model 1252) at frequencies ranging from 100 kHz to 100 mHz at 10 mV bias voltage. Ex-situ electronic conductivity of the pristine and discharged electrodes was measured using Cascade Four-Point Probe set up.

For ex-situ SEM, FTIR, electronic conductivity and NMR experiments, the carbon electrodes were harvested after the first discharge/charge cycles and vacuum dried in Ar filled glovebox. Before performing the ex-situ FTIR (Thermo Scientific, NICOLET iZ10), the harvested electrodes were rinsed with acetonitrile. Due to the low vapor pressure of the ionic liquids, however, it was difficult to remove the electrolyte from the harvested carbon cathodes. And, as a result, the vibration spectra signature of the pure ionic liquid electrolytes are always found in the FTIR spectra. High-quality FTIR data could not be obtained at sufficiently low wavenumbers to definitively characterize Li₂O₂ [1]. For NMR experiments, the dried electrodes (without acetonitrile washing) were extracted with D₂O and then the extracted solution was analyzed. The NMR spectra were

obtained using Bruker AVANAC III 700 MHz spectrometers (Bruker BioSpin, Rheinstetten, Germany) equipped with Bruker 5-mm TCI Cryoprobe. All NMR spectra were recorded in D₂O at 298 k using excitation sculpting with gradients water suppression pulse sequence (zgesgp) in the standard Bruker pulse sequence library [2]. The spectra were recorded by collecting 128 free induction decays (FIDs) and digitized into 64 K complex data points over a spectral width of 11600 Hz. The recycle delay time was set to 3 sec and the receiver gain was kept at a constant value of 203. Before Fourier transform, the FID values were multiplied by an exponential function equivalent to a 1 Hz line broadening factor. Bruker Topspin 2.1 software (Bruker BioSpin, Rheinstetten, Germany) was used in all NMR experiments to collect and analyze the data.

References:

1. S. A. Freunberger, Y. Chen, Z. Peng, J. M. Griffin, L. J. Hardwick, F. Barde, P. Novak, and P. G. Bruce, *J. Am. Chem. Soc.* 2011, **133**, 8040
2. T. L. Hwang and A. J. Shaka. *J. Magn. Reson. Series A*, 112 (1995) 275-279.

Supplementary Figures

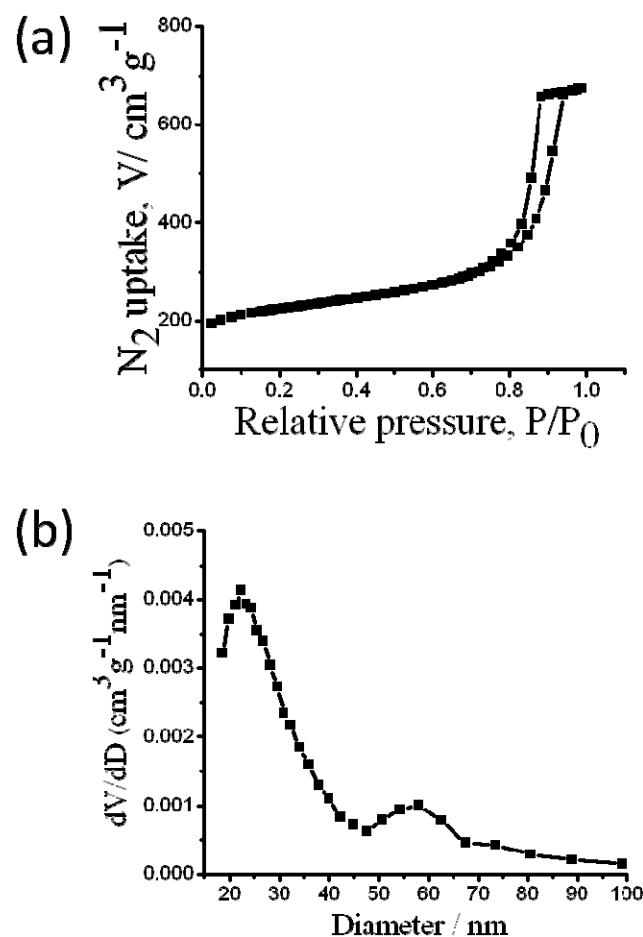


Figure S1. (a) N_2 adsorption/desorption isotherms and (b) pore size distribution of carbon aerogel

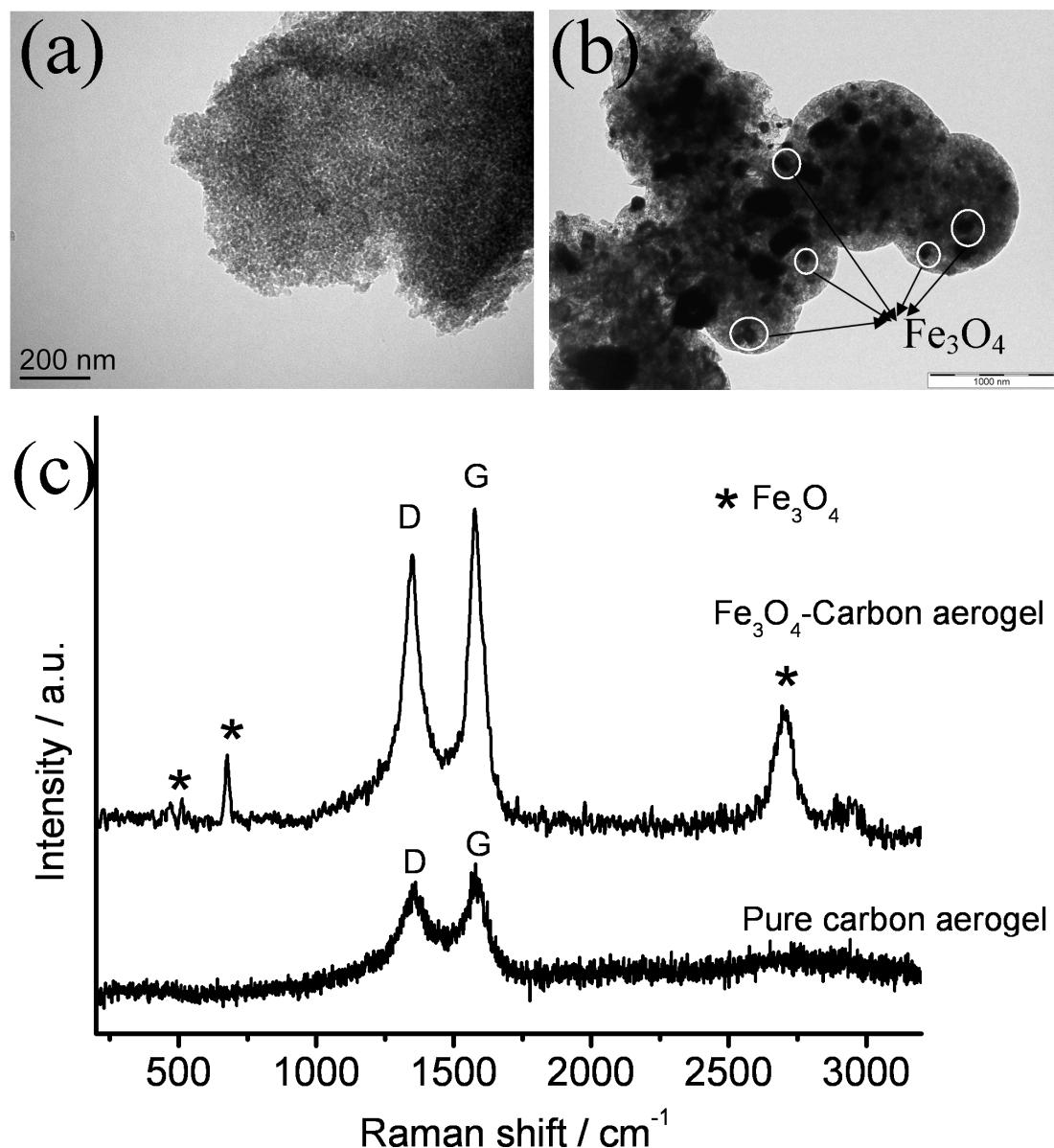


Figure S2. Transmission electron micrographs of (a) pure carbon aerogel and (b) Fe_3O_4 -carbon aerogel; (c) Raman spectra of pure carbon aerogel and Fe_3O_4 -carbon aerogel. * represents the Fe_3O_4 phase [3]. D (1350 cm^{-1}) and G (1580 cm^{-1}) bands can be associated with disordered and ideal graphitic lattice respectively [4].

References:

3. A. Hofmann, S. Thierbach, A. Semisch, A. Hartwig, M. Taupitz, E. Rühl, and C. Graf, *J. Mater. Chem.* 2010, **20**, 7842
4. Z. Yang, J. Shen and L. A. Archer. *J. Mater. Chem.* 2011, **21**, 11092

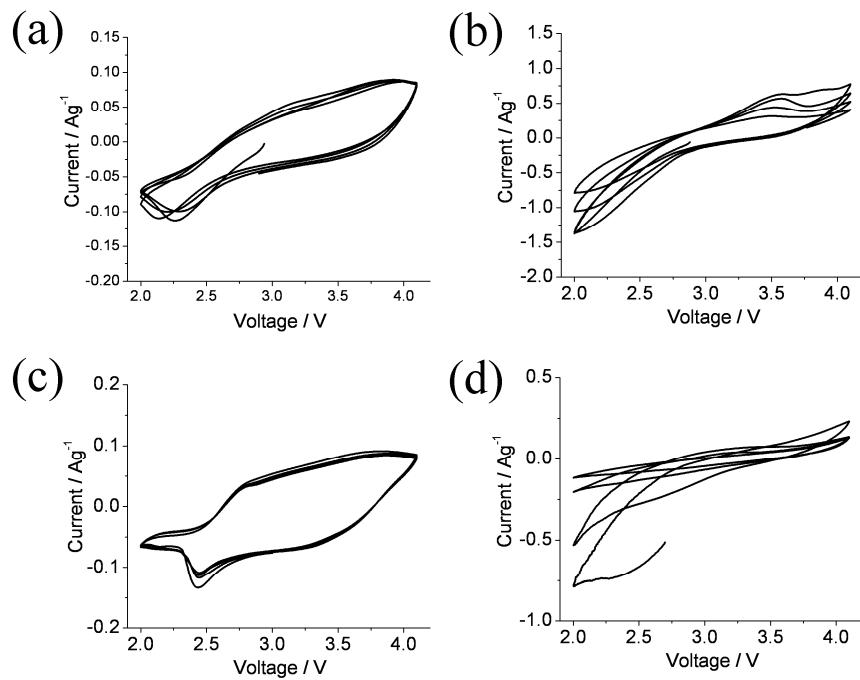


Figure S3. Cyclic voltammetry (CV) curves obtained from the following cells. $[\text{C}_4\text{mim}][\text{BF}_4]$ ionic liquid cells at (a) 25 °C and (b) 150 °C. $[\text{C}_4\text{mim}][\text{NTf}_2]$ ionic liquid cells at (c) 25 °C and (d) 150 °C. The scan rate is 0.2 mVs⁻¹. Voltage range is 2 V to 4.1 V.

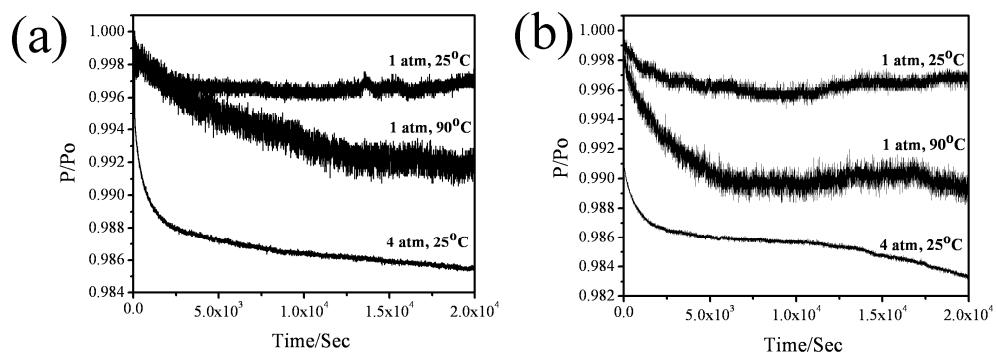


Figure S4. Variation of relative pressure (P/P_0) with time for O_2 absorption in (a) $[C_4mim][NTf_2]$ and (b) $[C_4mim][BF_4]$ ionic liquids at various thermodynamic conditions.

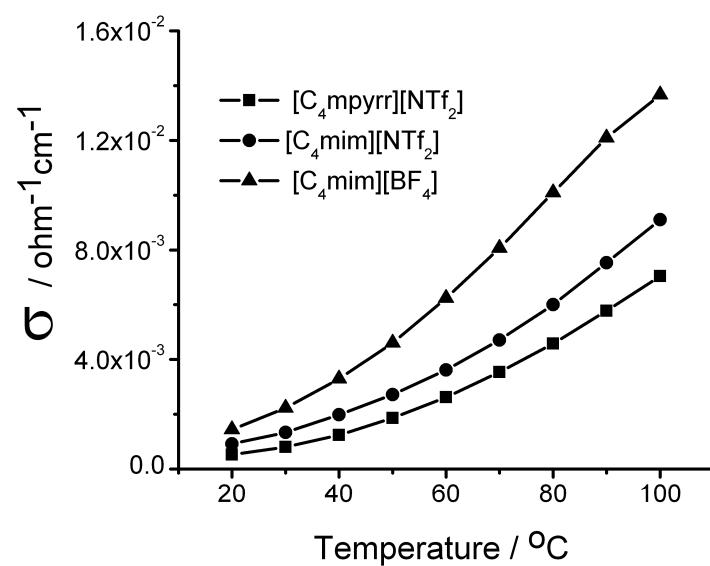


Figure S5. Variation of Li^{+} -ion conductivity with temperature for all ionic liquid electrolytes.

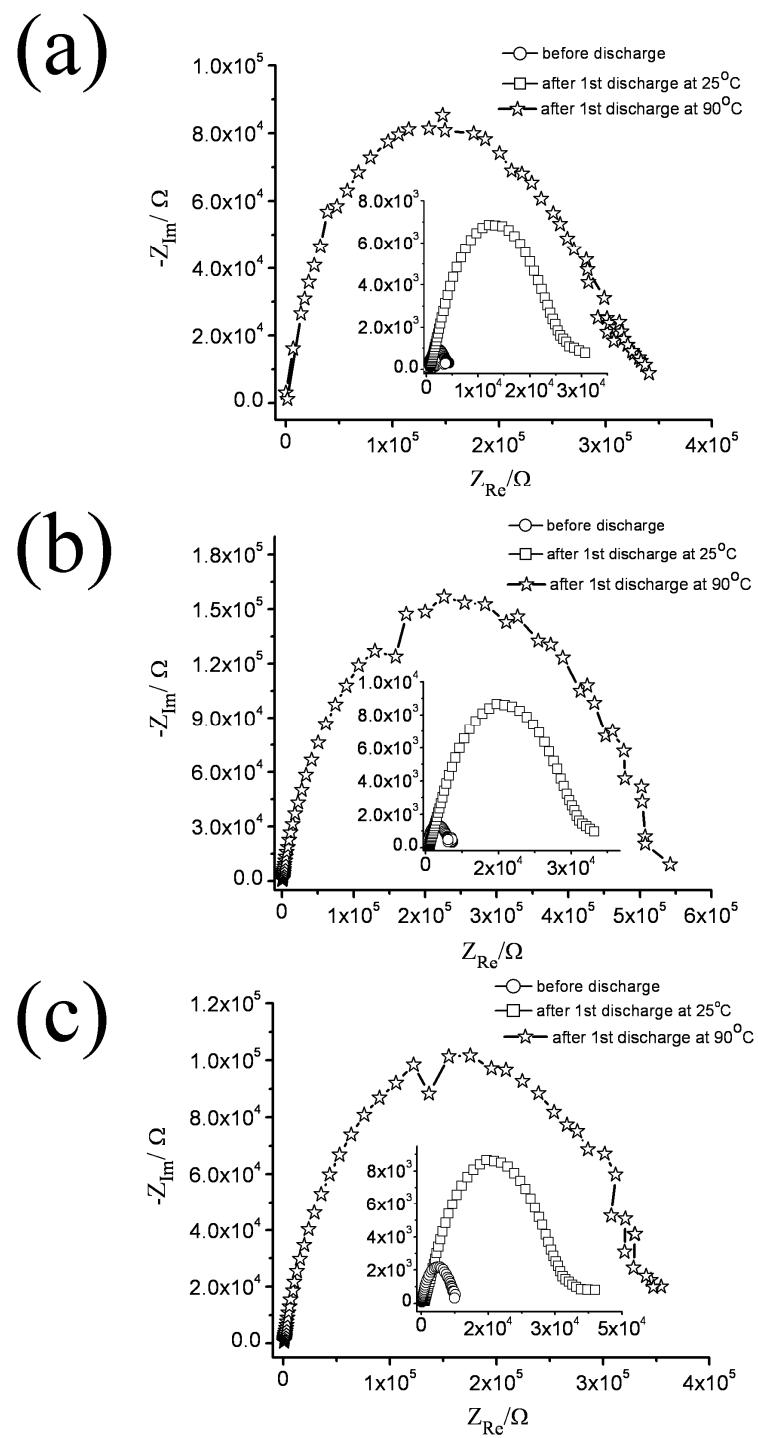


Figure S6. AC impedance spectra (Nyquist plot) for (a) $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$, (b) $[\text{C}_4\text{mim}][\text{NTf}_2]$ and (c) $[\text{C}_4\text{mim}][\text{BF}_4]$ ionic liquid cells before discharging (open circuit potential) and after 1st discharge cycle at 25 °C and 90 °C. Inset shows the data for before discharging and after 1st discharge cycle at 25 °C.

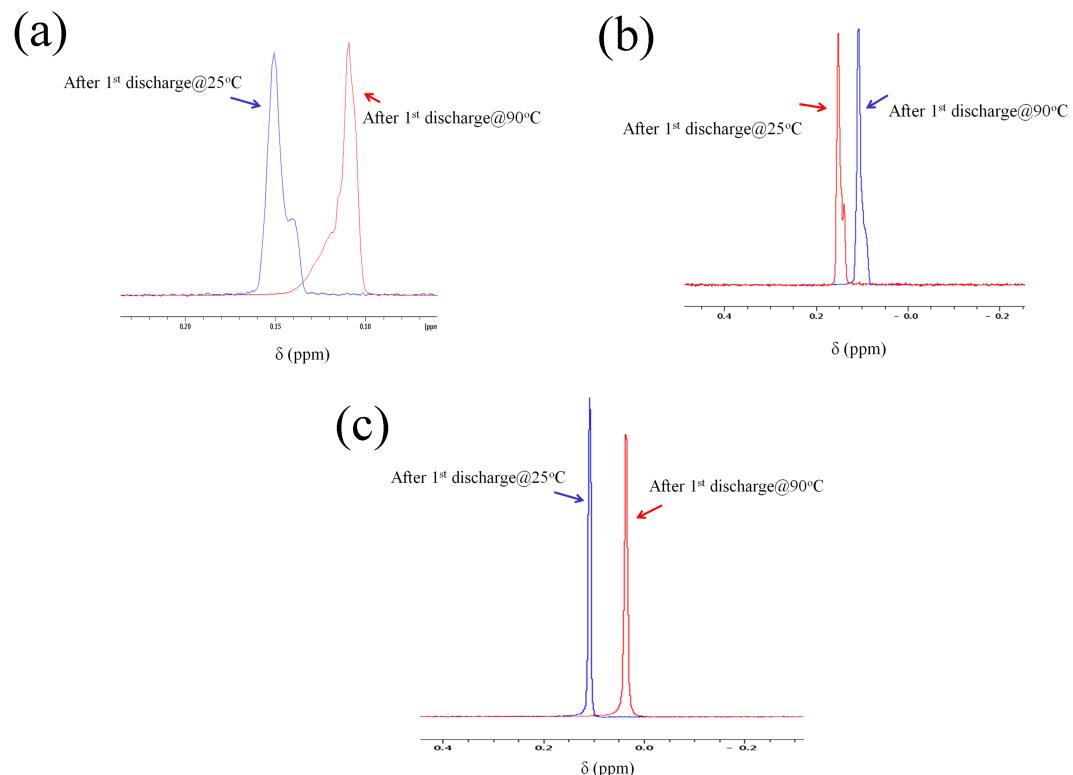


Figure S7. ${}^7\text{Li}$ NMR spectra of the solution obtained by washing the composite electrodes with D_2O after cycling in (a) $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$, (b) $[\text{C}_4\text{mim}][\text{NTf}_2]$ and (c) $[\text{C}_4\text{mim}][\text{BF}_4]$ ionic liquid cells at 25 °C and 90 °C.

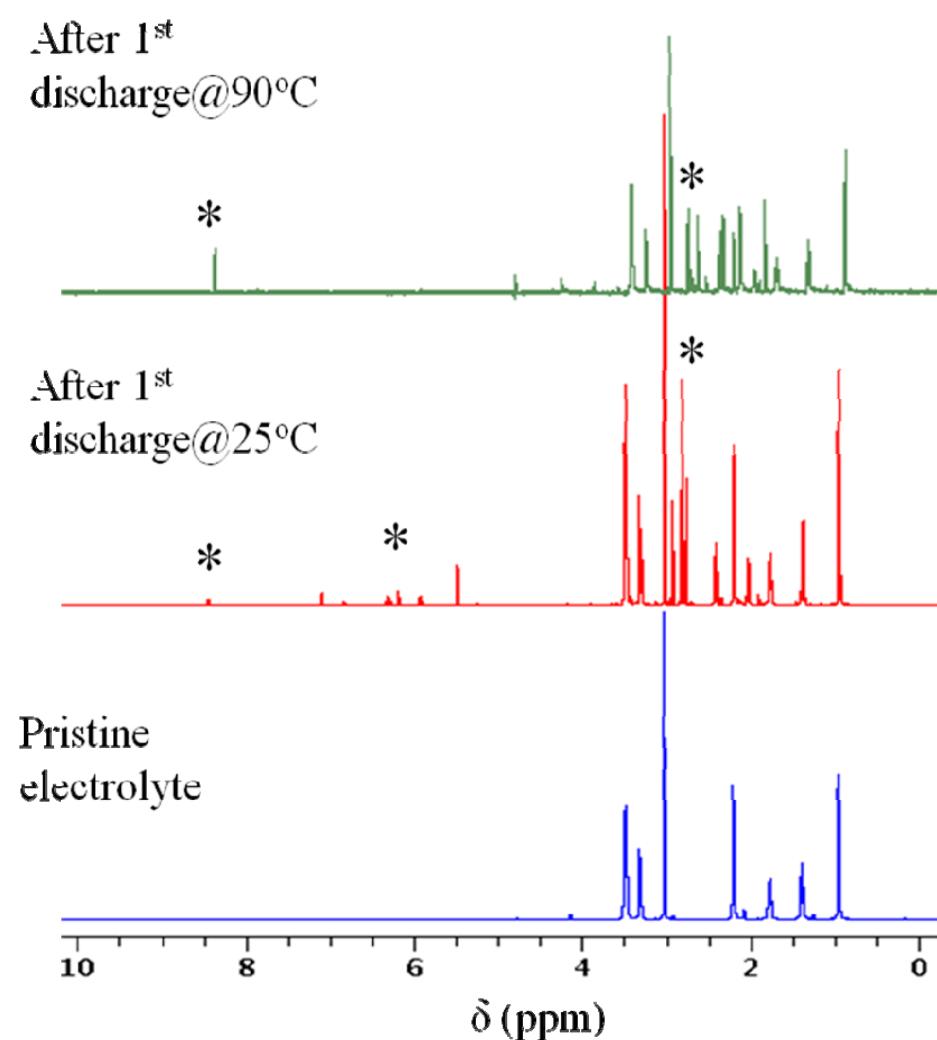


Figure S8. ^1H NMR spectra of the solution obtained by washing the composite electrode with D_2O after cycling in $[\text{C}_4\text{mpyrr}][\text{NTf}_2]$ ionic liquid cell at 25 °C and 90 °C. The * symbol denotes the region of additional NMR peaks.

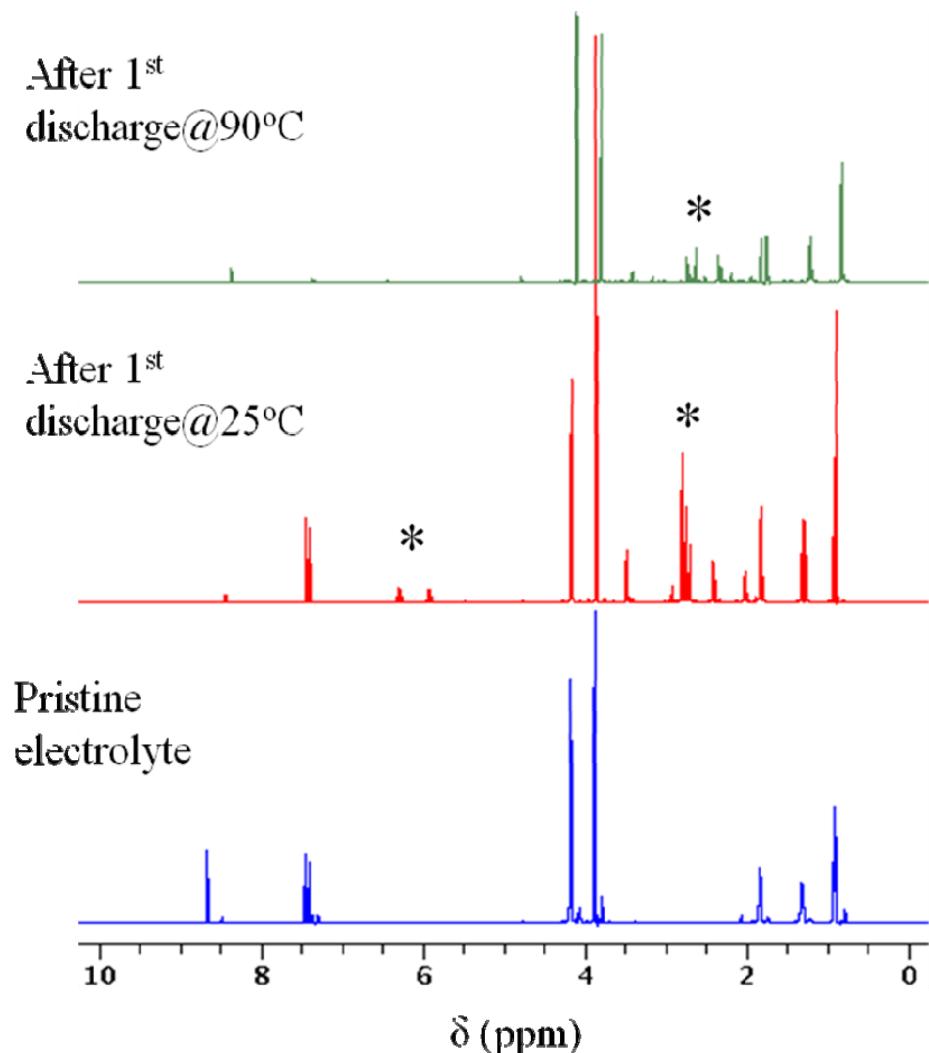


Figure S9. ^1H NMR spectra of solution extracted by washing the composite electrode with D_2O after cycling in $[\text{C}_4\text{mim}][\text{NTf}_2]$ ionic liquid cell at 25 °C and 90 °C. The * symbol denotes a region of additional NMR peaks.

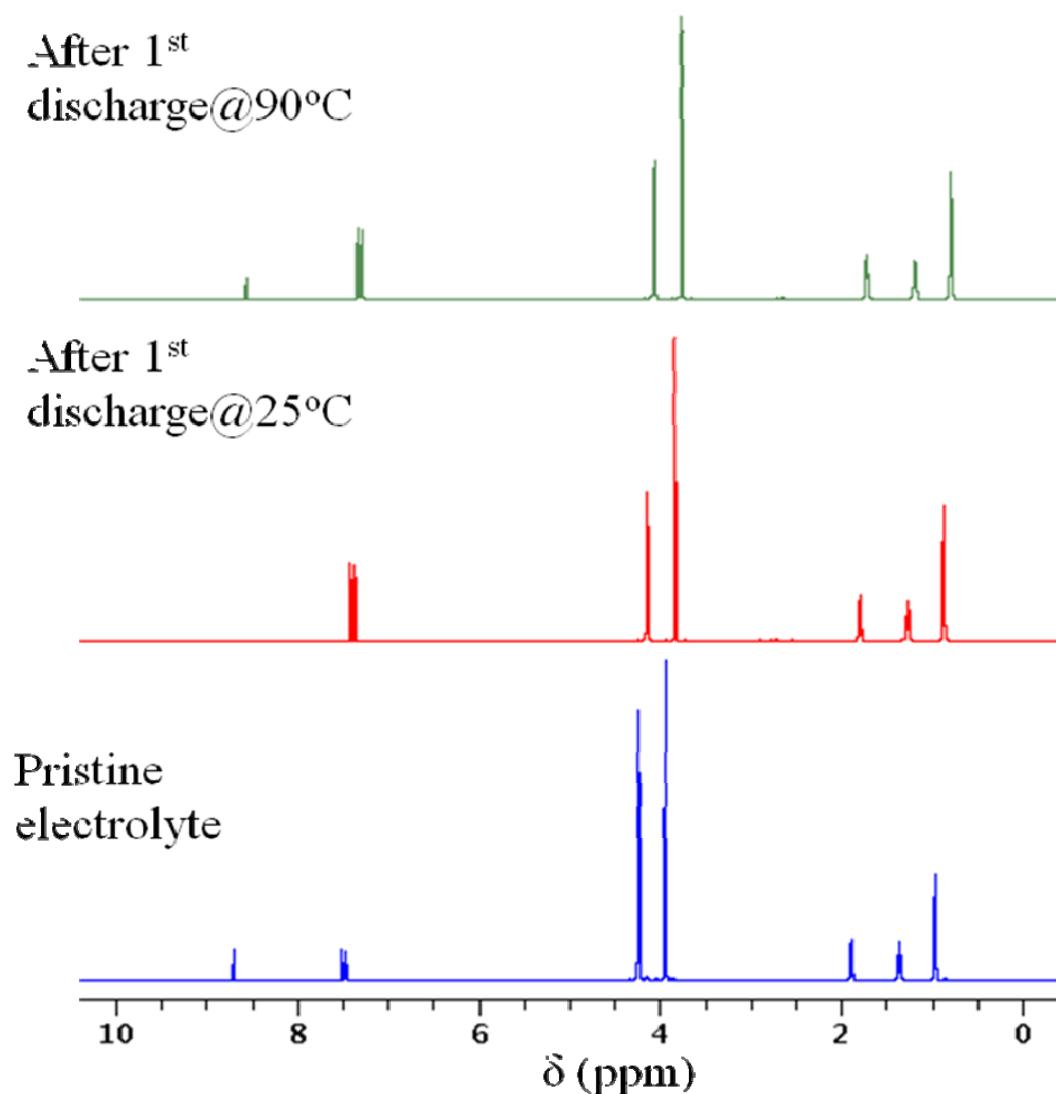


Figure S10. ^1H NMR spectra of solution extracted by washing the composite electrode with D_2O after cycling in $[\text{C}_4\text{mim}][\text{BF}_4]$ ionic liquid cell at 25 °C and 90 °C.

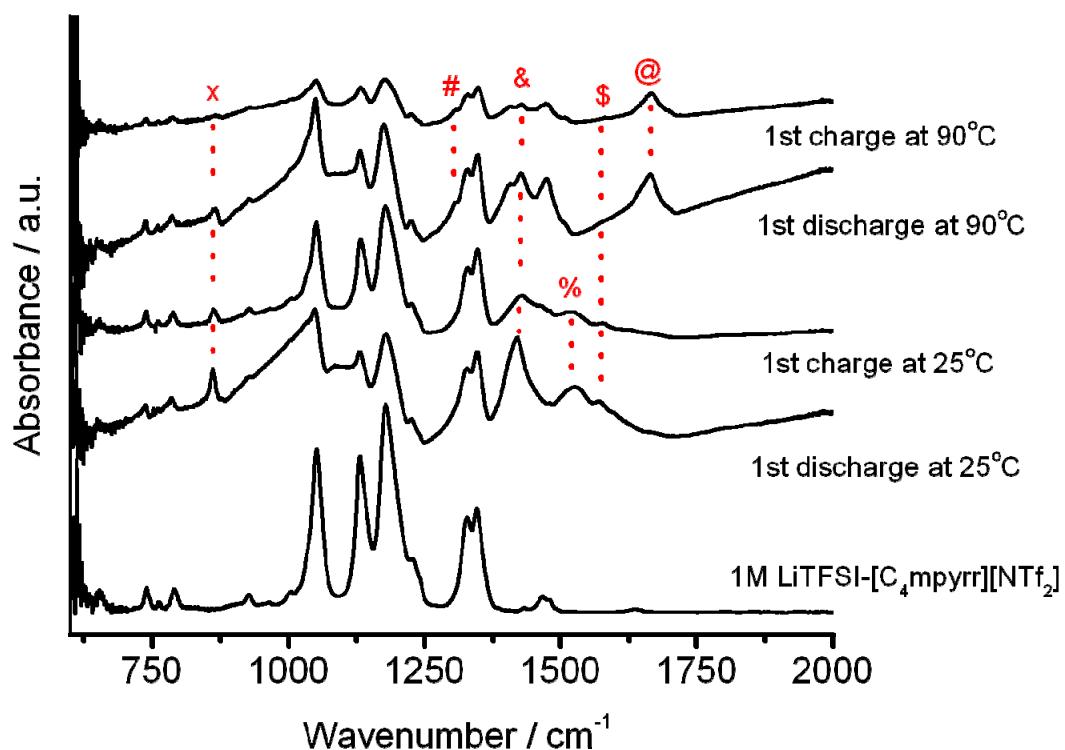


Figure S11. FTIR spectra of the carbon cathodes extracted from [C₄mpyrr][NTf₂] ionic liquid cells at various conditions as mentioned in the figure text. The various symbols, x, #, &, \$, %, @, are used to denote what appears to be additional FTIR peaks as a result of various cell discharge products.

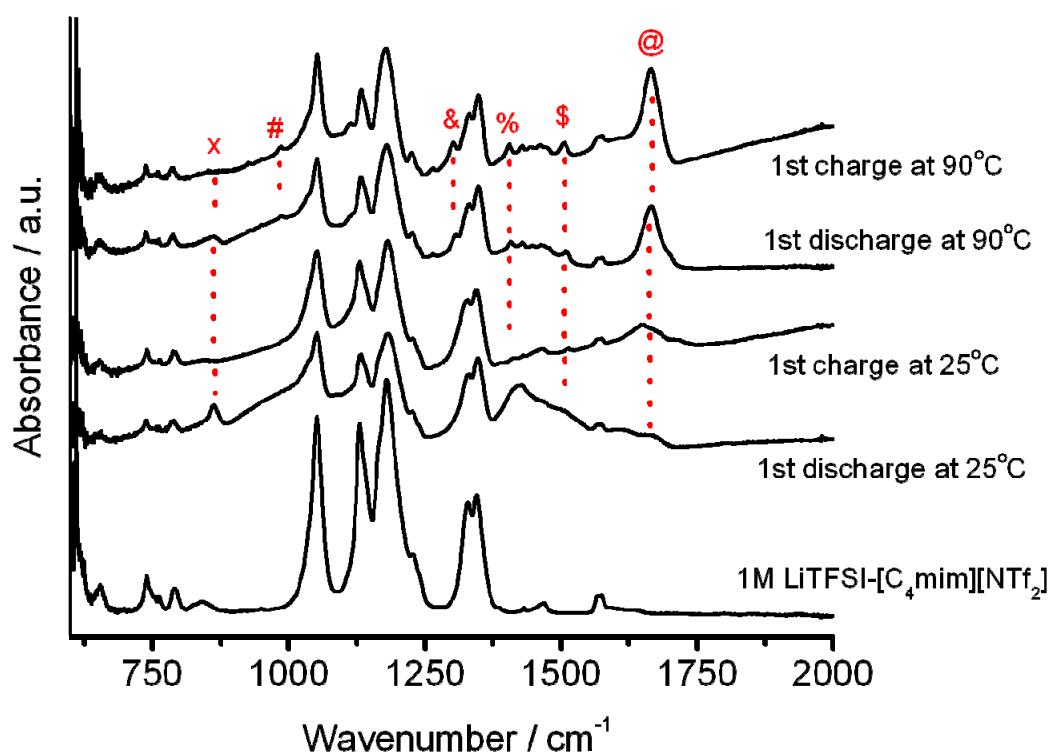


Figure S12. FTIR spectra of the carbon cathodes extracted from [C₄mim][NTf₂] ionic liquid cells at various conditions as mentioned in the figure text. The various symbols, x, #, &, \$, %, @ denote the additional FTIR peaks as a result of various discharge products.

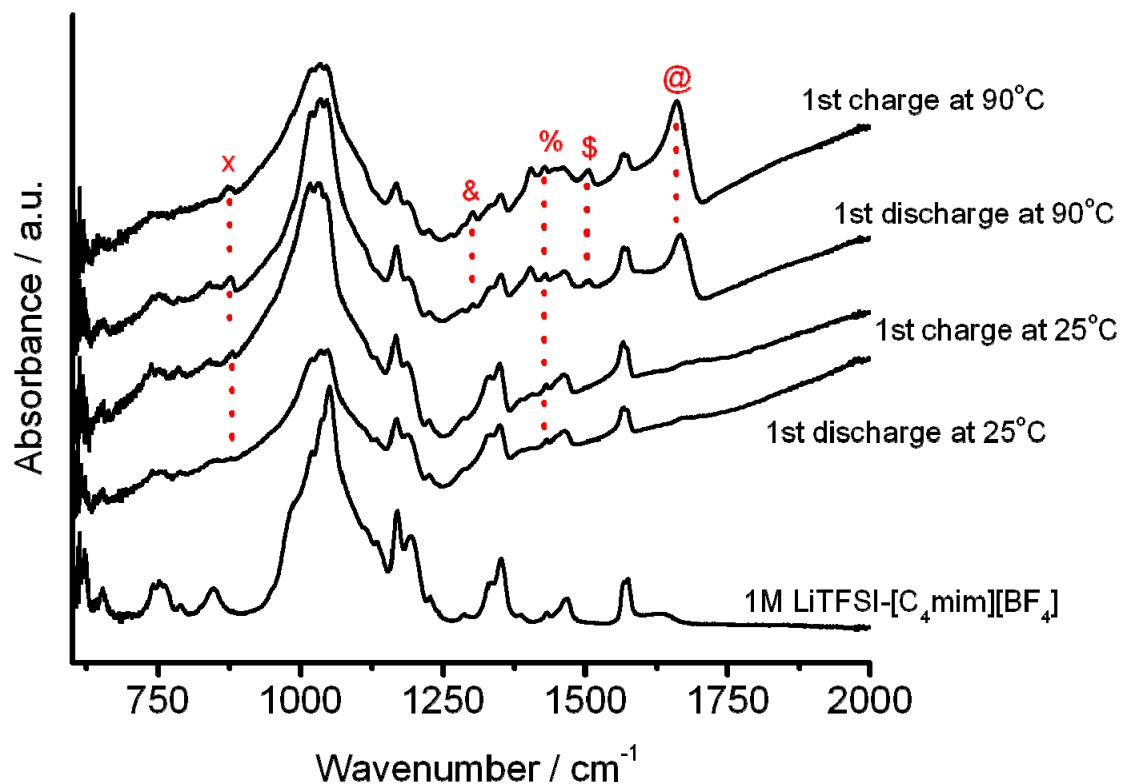


Figure S13. FTIR spectra of the carbon cathodes extracted from [C₄mim][BF₄] ionic liquid cells at various conditions as mentioned in the figure text. The various symbols, x, &, \$, %, @ denote the additional FTIR peaks as a result of various discharge products.

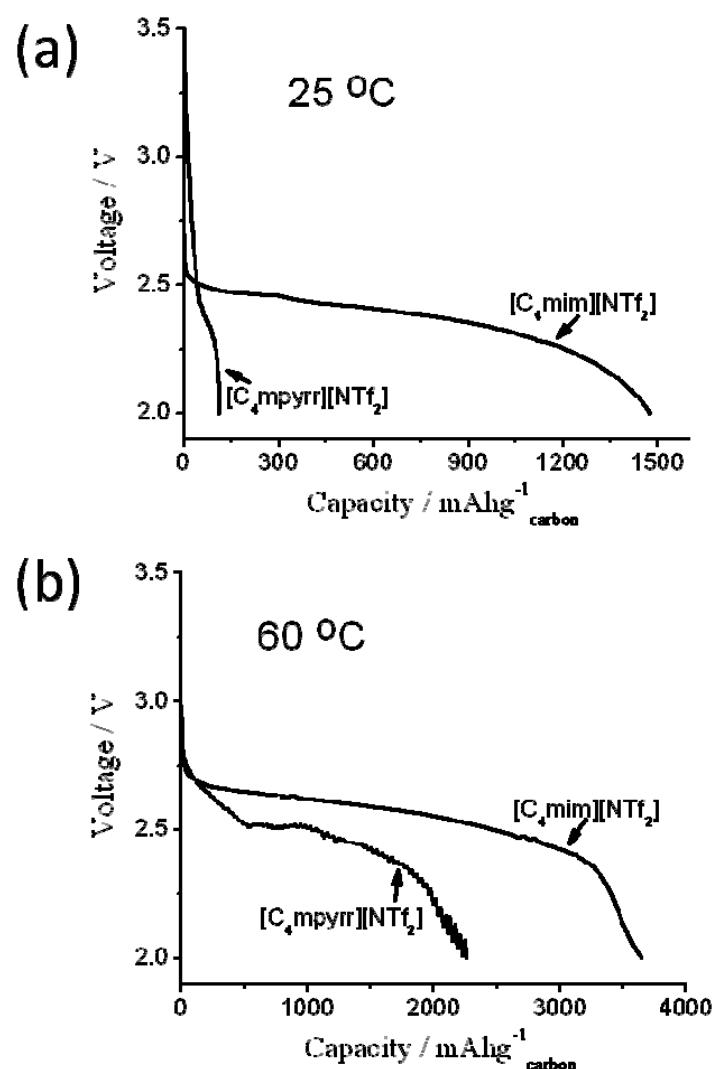


Figure S14. Comparison of galvanostatic discharge curves obtained from $[\text{C}_4\text{mpyrr}]\text{[NTf}_2]$ and $[\text{C}_4\text{mim}]\text{[NTf}_2]$ ionic liquid cells at a current density of 70 mA g^{-1} at 25°C and 60°C .

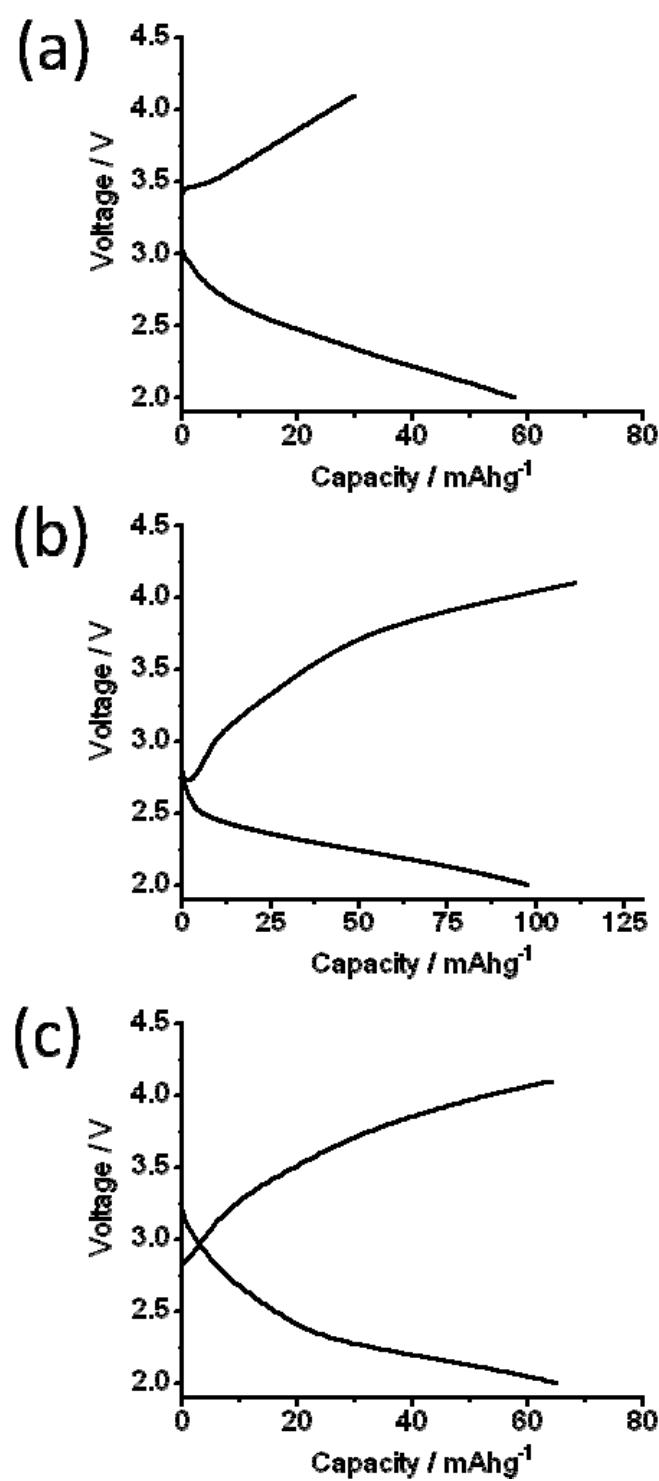


Figure S15. Galvanostatic discharge/charge curves obtained from (a) [C₄mpyrr][NTf₂], (b) [C₄mim][NTf₂] and (c) [C₄mim][BF₄] ionic liquid cells at a current density of 70 mA g⁻¹ at 5 °C at 1 atm O₂ pressure.

Supporting Table S1. Henry's Law Constants of O₂ absorption in Ionic Liquids

| Ionic liquid | Henry's constant, H _{O₂} (bar) | | |
|--|--|--------------|--------------|
| | 1 atm, 25 °C | 1 atm, 90 °C | 4 atm, 25 °C |
| [C ₄ mptyrr][NTf ₂] | 798 | 609 | 377 |
| [C ₄ mim][NTf ₂] | 1357 | 650 | 227 |
| [C ₄ mim][BF ₄] | 2371 | 1187 | 562 |

Supporting Table S2. Diffusion coefficient of O₂ in Ionic Liquids

| Ionic liquid | Diffusion coefficient, D _{O₂} (x 10 ⁻¹⁰ m ² s ⁻¹) | | | | |
|--|---|-------|-------|-------|--------|
| | 25 °C | 45 °C | 60 °C | 90 °C | 150 °C |
| [C ₄ mptyrr][NTf ₂] | 5.49 | 9.36 | 14.22 | 27 | 79 |
| [C ₄ mim][NTf ₂] | 8.76 | 15.88 | 22.10 | 42 | 116 |
| [C ₄ mim][BF ₄] | 1.79 | 3.29 | 5.90 | 12.8 | 47 |

Supporting Table S3. Electronic conductivity of the pristine and discharged carbon cathodes obtained from 25 °C and 90 °C operated ionic liquid Li-O₂ cells.

| Ionic liquid | Electronic conductivity (S cm ⁻¹) | | |
|---|---|--------------------------|---------------------------|
| | 25 °C | 90 °C | Pristine carbon electrode |
| [C ₄ mppyr][NTf ₂] | (4-7) x 10 ⁻³ | (2-4) x 10 ⁻⁴ | |
| [C ₄ mim][NTf ₂] | (2-5) x 10 ⁻³ | (2-4) x 10 ⁻⁴ | (2-7) x 10 ⁻¹ |
| [C ₄ mim][BF ₄] | (2-5) x 10 ⁻³ | (2-4) x 10 ⁻⁴ | |