

High Temperature Supercapacitors using Water-in-Salt Electrolytes: stability above 100 °C

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Experimental Setup

Electrode Preparation and Cell Assembly

The electrodes were composed of commercial activated carbon (YEC-8B), which was purchased from Fuzhou Yihuan Carbon Co., commercial graphene nanoplatelets (C750) were supplied by XG Sciences, conductive carbon black ("Super P") was purchased from TIMCAL and the Poly(vinylidene fluoride) (761 PVDF) was provided by Kynar. Electrodes were fabricated via slurry casting using the following method:

- 761 PVDF was dissolved and homogenised in N-methyl-2-pyrrolidone (NMP), purchased from Sigma-Aldrich, for 5 minutes to give a 5% weight ratio in the final suspension.
- The corresponding percentage of Super P (5 %) or C750 (15, 25 or 95 %) was slowly added to the binder solution whilst stirring.
- The corresponding percentage of YEC-8B carbon (90, 80, 70 or 0 %) was added slowly whilst the binder solution was stirred.
- Once all the slurry components had been added to the solution was left to stir for 2 hours

The coatings were applied to carbon-coated aluminium foil, provided by Toyol Carbo, using a doctor blade at thicknesses between 100 and 150 µm. The coatings were then dried in an oven at 80 °C for 12 hours. The electrodes for coin cells were cut into discs, with a 15 mm diameter.

The electrolytes used were 21 molal (m) lithium bis(trifluoromethyl-sulphonyl)imide (LiTFSI) dissolved in deionised water and 21 m LiTFSI + 7 m trifluoromethanesulphonyl (LiTFO) dissolved in deionised water. The salts for each electrolyte were purchased from Sigma-Aldrich and had a purity of 99%.

Two electrode CR2032 coin cells were assembled in air at room temperature each using two pieces of cellulose separator (Nippon Kodashi) and either the 21 m LiTFSI or 21 m LiTFSI + 7 m LiTFO electrolyte. The coin cells were made with symmetric ($m^+/m^-=1$) or asymmetric ($m^+/m^-=1.3$) electrode masses, where the superscript denotes the polarity of the relevant electrode.

Electrochemical Measurements

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and galvanostatic charge-discharge (GCD) measurements were performed using a PGSTAT302N potentiostat (Metrohm Autolab) at various temperatures (20 °C to 120 °C). Galvanostatic cycling measurements were performed at 1 A g⁻¹ using a 32 channel Basytec Cell Test System. All electrochemical measurements were performed on mass symmetric or asymmetric CR2032 coin cells, where a minimum of 4 coin cells were measured.

The capacitance of the devices was calculated from the GCD profiles using the following equation:

$$C_s = \frac{4I}{m_B \frac{dV}{dt}}$$

where C_s is the gravimetric capacitance, I is the applied current, m_B is the mass of both electrodes within the cell and $\frac{dV}{dt}$ is the gradient of the linear region in the discharge profile.

High temperature electrochemical measurements were performed using an in-house designed temperature chamber. Before any electrochemical measurements were taken the coin cells were heated up and held at the desired temperature (40-120 °C) for 30 minutes. The temperature of the coin cell was monitored during testing at elevated temperatures using a Voltcraft AT-200 Digital Multimeter with a K-type Thermocouple placed on the surface of the coin cell, see Figure S1.

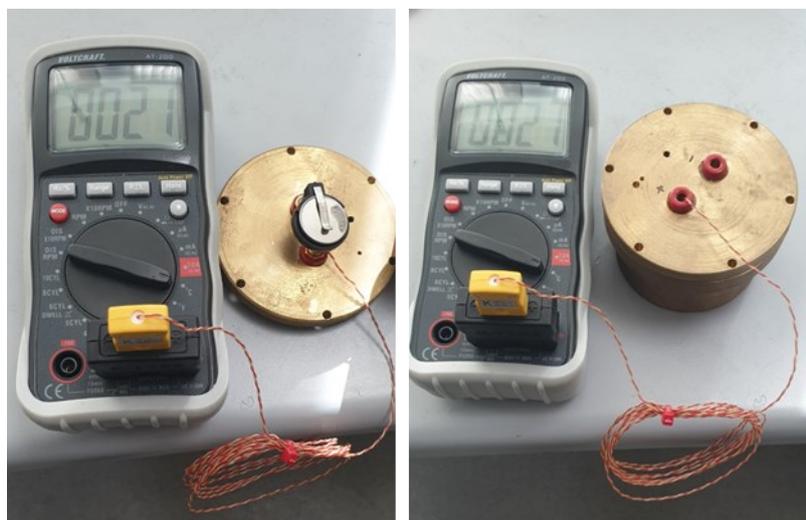


Figure S1. Photographic image of the high temperature cell

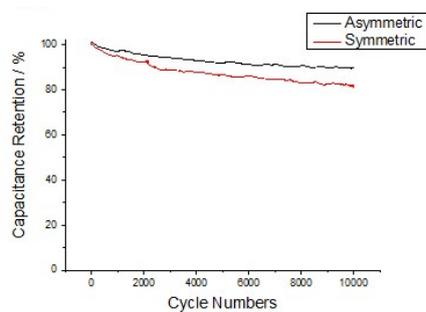


Figure S2. Capacitance retention vs. cycle number for mass symmetric and asymmetric 25 % graphene containing supercapacitors at a current density of 1 A g⁻¹.

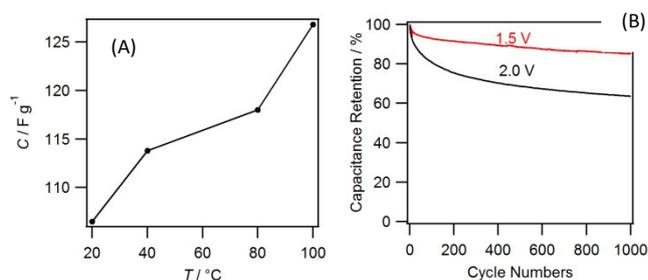


Figure S3. **A)** The capacitance vs. temperature for the 25 % graphene, 70 % AC and 5 % PVDF coin cell measured at 0.2 A g^{-1} . **B)** Capacitance retention vs. cycle number for the mass balanced 25 % graphene coin cell at $100 \text{ }^{\circ}\text{C}$ using 1.5 V or 2 V as the upper limit. The electrolyte used was 21 m LiTFSI in water.

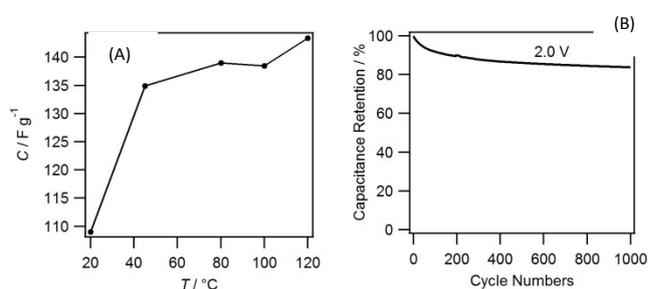


Figure S4. **(A)** The capacitance vs. temperature for the 25 % graphene, 70 % AC and 5 % PVDF coin cell measured at 0.2 A g^{-1} . **B)** Capacitance retention vs. cycle number for the mass balanced 25 % graphene coin cell at $110 \text{ }^{\circ}\text{C}$ using 2 V as the upper limit. The electrolyte used was 21m LiTFSI + 7m LiTFO in water.

Post High Temperature Testing

The performance of the coin cells at room temperature, after undergoing high temperature measurements, was evaluated. Figure S5 shows the rate and cycling performance of the two electrolytes after being tested at elevated temperatures.

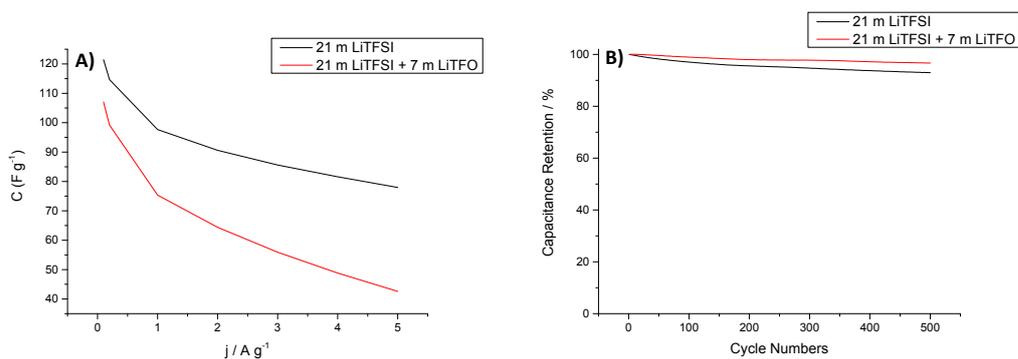


Figure S5: **A)** Plot showing the capacitance vs. current density. **B)** Plot showing the capacitance retention vs. cycle number for the 25 % graphene, 70 % AC and 5 % PVDF coin cells using both the 21 m LiTFSI and 21 m LiTFSI + 7 m LiTFO electrolytes. These capacitance and cycling measurements were obtained at $20 \text{ }^{\circ}\text{C}$ after testing the cells at the highest possible temperatures for each electrolyte, $100 \text{ }^{\circ}\text{C}$ for 21 m LiTFSI electrolyte and $120 \text{ }^{\circ}\text{C}$ for the 21 m LiTFSI + 7 m LiTFO.

It can be seen from Figure S5 that the rate and cycling performance of the cells after high temperature testing is unaffected. The return to normal performance after heating indicates the suitability of both the 21 m LiTFSI and 21 m LiTFSI + 7 m LiTFO electrolytes for high temperature applications.