The Effects of Temperature on the Performance of Electrochemical Double Layer Capacitors.

S.I. Fletcher (University of Strathclyde) — Glasgow, UK — isobel.fletcher@strath.ac.uk
F.B. Sillars, R. Carter, A.J. Cruden, M. Mirzaeian, N.E. Hudson, J. Parkinson, & P.J. Hall (University of Strathclyde)

Introduction.

Electrochemical double layer capacitors (EDLCs) are high power, low energy devices with uses or potential uses in regenerative braking for electric vehicles, uninterruptable power supplies, storage for renewable energy sources and power sources for starter motors. Most of these uses involve exposure to a range of environmental conditions; a typical specification for a battery for an electric vehicle, for example, would be operation from -30 to 65 ^{O}C and preferably -40 to 85 ^{O}C [1]. Specifications for a capacitor would be expected to be similar. Even if a capacitor were not operational under more extreme conditions, a commercially viable capacitor may have to withstand and recover from these conditions.

The Supergen Energy Storage group at Strathclyde University has been developing carbon xerogel electrodes and testing ionic liquid electrolytes for use in electrochemical double layer capacitors (EDLCs). All testing had previously been carried out at 25 ^{O}C and the performance of the EDLCs at other temperatures was unknown. Therefore a test programme was set up to examine the performance of a test cell capacitor at 15, 25 and 40 ^{O}C and also to examine the effect of a short refrigeration at 5 ^{O}C. As a comparison, a commercial 10F capacitor was also tested at 15, 25 and 40 ^{O}C.

Test Cell

i, Electrodes.

The electrodes for the EDLC test cell were manufactured from resourcinol formaldehyde xerogels [2] dried under vacuum, milled, carbonised at 800 ^{O}C, milled and activated with CO_2 at 800 ^{O}C. The xerogel was mixed with 10% carbon black and 10% Kinar binder in acetone and spread on to aluminium foil in a 200µm layer, allowed to dry and cut into 1.3 cm diameter discs.

ii, Electrolyte

Room temperature ionic liquids (RTILs) have attracted considerable interest as electrolytes for EDLCs owing to the increased size of electrochemical window, up to 4.2V for some RTILs [3] compared to 3V for organic electrolytes and 1.23V for aqueous electrolytes. As the energy stored in a capacitor, E, is equal to 1/2 CV^2, where C is capacitance and V is voltage; a small increase in voltage produces a squared increase in energy. The electrolyte used in the EDLC test cell was 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide, chosen for a relatively low viscosity and a large anodic voltage window.

To examine the effects of temperature on the electrolyte viscosity, shear stress was measured [4] at a constant shear rate of 100 s^{-1} for temperatures from 15 to 95 ^{O}C using a TA Instruments AR1000-N Rheolyst rheometer with 0.02 m diameter stainless steel parallel plates set at a gap of 200 µm. Viscosity decreased almost exponentially with increasing temperature, Figure 1.

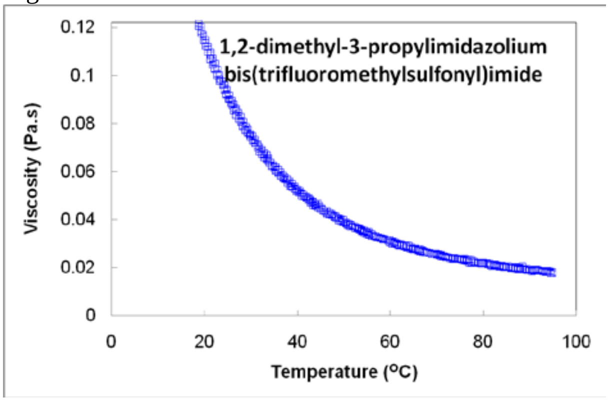

Figure 1: The effect of temperature on electrolyte viscosity.

To examine the effects of temperature on diffusion, self-diffusion coefficients were measured over a range of temperatures by ^{1}H and ^{19}F NMR spectroscopy using a stimulated echo approach and acquired using an AVANCE 400 Bruker NMR spectrometer. The results are shown below in Figure 2.

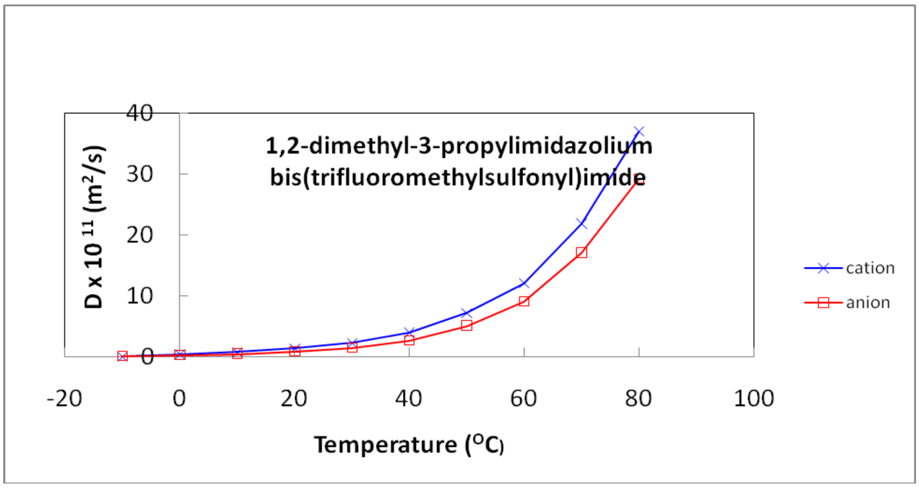

Figure 2: Effect of temperature on the electrolyte ionic self diffusion coefficient, D.

As increasing temperature increases the degree of dissociation in a RTIL decreasing the viscosity, Figure 1 and increasing the self diffusion coefficient, Figure 2.; it was expected that the ionic conductivity of the electrolyte would increase at higher temperatures improving the performance of a capacitor.

Most RTILs do not degrade at temperatures below ~ 400 ^{O}C, 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide is reported to have a degradation temperature of 457 ^{O}C [5] therefore higher ambient temperatures are unlikely to cause problems and may well be beneficial. Many RTILs, however, have melting temperatures above the coolest ambient conditions likely to be experienced by the motor compartment of an electric vehicle.

The melting temperature and other phase changes in [dmpim][TFSI] were measured using differential scanning calorimetry for temperatures from 130 to -150 ^{O}C [4], Figure 3.

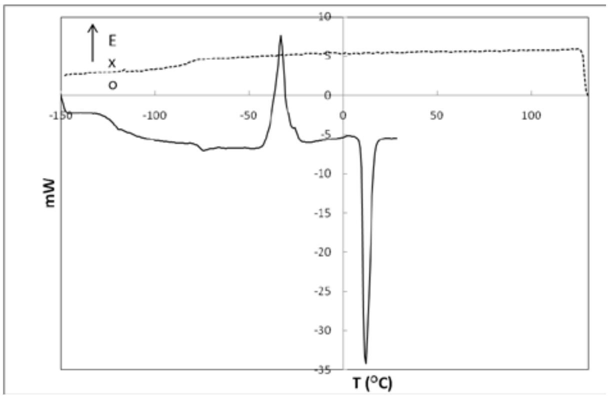

Figure 3. DSC trace for 1,2,-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide. Dashed lines cooling, solid lines heating.

RTILs exhibit a variety of phase transition behaviour and on cooling many have the ability to form supercooled liquids up to 200 ^{O}C below the melting temperature [6,7,8,9]; some form crystals, others merely undergo a glass transition. [dmpim][TFSI] underwent a glass transition when cooled, sometimes cold crystallised when heated then melted to form a liquid at 8 ^{O}C. Owing to this ability to supercool, [dmpim][TFSI] should remain liquid below the melting temperature for a length of time dependent on the temperature and possibly also the rate of cooling.

<u>Test Procedure</u>
The test cell was constructed as shown in Figure 4. The separator lies directly on top of the right hand electrode. Endplates were constructed from stainless steel and the main body from PTFE.

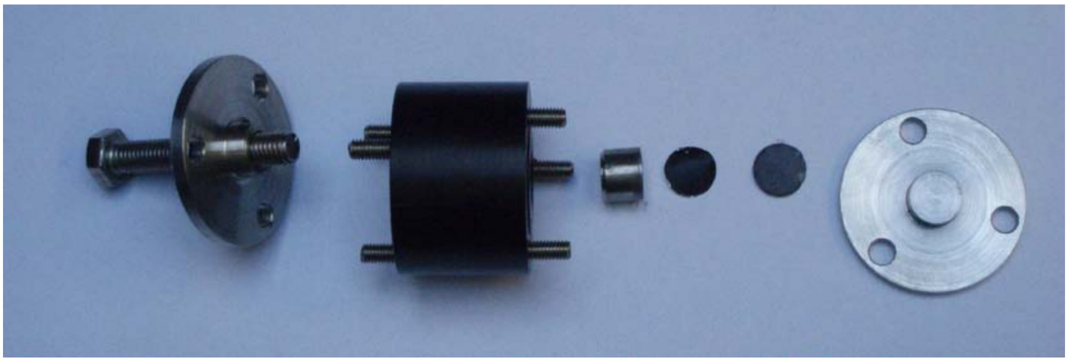

Figure 4: Test Cell.

A commercial 10F capacitor with carbon aerogel electrodes and an organic electrolyte consisting of a quaternary ammonium salt dissolved in propylene carbonate, was used as a comparison.

The test cell was connected to a Solartron 1470E frequency response analyser and impedance spectroscopy carried out at 0.1, 1.35 and 2.6 V at an amplitude of 10 mV and frequencies of between 1 MHz and 10 mHz. MultiStat Explorer software was used to curve fit the semicircle from the first part of the Nyquist plots to estimate the equivalent series resistance (ESR) of the electrodes and electrolyte.

The cell was then galvanically charged and discharged twenty times from 0 to 2.6 V at charge/discharge currents of 0.002, 0.004, 0.008 and 0.016 A and the results used to calculate the capacitance of the cell at each current.

Impedance spectroscopy was carried out for the 10 F capacitor at 0.1, 1.1 and 2.2 V, again at frequencies from 1 MHz to 10 mHz. The 10 F capacitor was galvanically charged and discharged twenty times between 0 and 2.3 V at currents of 0.032, 0.064 and 0.128 A.

Both the test cell and 10 F capacitor were tested inside a Friocell temperature control chamber at 15, 25 and 40 ^{O}C. A test cell was then tested at 25 ^{O}C, cooled to 5 ^{O}C at a rate of 0.5 ^{O}C/min, held at 5 ^{O}C for one hour, reheated to 25 ^{O}C at a rate of 1.5 ^{O}C/min and re-tested.

<u>Results</u>

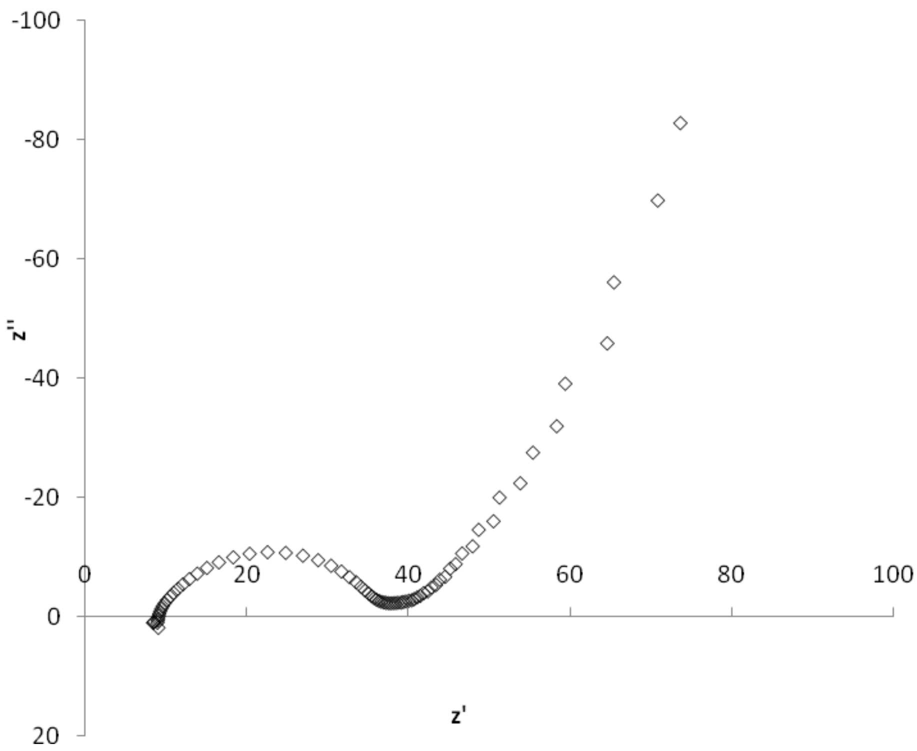

Figure 5: Nyquist plot for test cell impedance at 2.6 V and 25 ^{O}C.

Table 1: The effect of temperature on ESR for the test cell.

	15 ^{O}C	25 ^{O}C	40 ^{O}C	Before refrigeration	After refrigeration
Voltage (V)	Resistance (Ohms)	Resistance (Ohms)	Resistance (Ohms)	Resistance (Ohms)	Resistance (Ohms)
0.1	2.54	3.03	0.76	1.63	1.85
1.35	2.19	2.70	1.62	1.72	1.85
2.6	2.19	2.29	4.20	1.70	1.82

Table 1 and Figure 5 show the effect of temperature on ESR for the test cell. All impedance measurements both for the test cell and the commercial capacitor, produced Nyquist plots similar to Figure 5. An increase in temperature from 15 to 40 ^{O}C had little or no effect on the ESR. Similarly, refrigeration at 5 ^{O}C for one hour may have slightly increased the ESR but not by a significant amount.

Table 2: The effect of temperature on ESR for the 10F commercial capacitor.

	15 ^{O}C	25 ^{O}C	40 ^{O}C
Voltage (V)	Resistance (Ohms)	Resistance (Ohms)	Resistance (Ohms)
0.1	0.034	0.042	0.037
1.1	0.040	0.039	0.034
2.2	0.040	0.033	0.028

Table 2 shows the effect of temperature on the ESR of the commercial capacitor. ESR showed a slight decrease with increasing temperature for the two higher voltages. As these values were obtained from curve fitting, the uncertainty of this method of measuring ESR is likely to be greater than the differences between ESRs.

Table 3: Effect of temperature on capacitance of test cell.

	15 ^{O}C	25 ^{O}C	40 ^{O}C	Before refrig.	After refrig.
mA	F/g	F/g	F/g	F/g	F/g
0.002	45.11	50.55	56.88	20.91	21.65
0.004	39.85	44.62	53.51	19.8	20.06
0.008	34.25	37.1	52.17	18.52	18.46
0.016	27.6	27.23	47.97	16.69	16.4

Increasing the temperature increased the capacitance of the test cell at all currents, Table 3. Refrigeration for 1 hour at 5 ^{O}C however had no effect on capacitance (note the test cell used for the refrigeration experiment was not the same cell used for the earlier 15, 25 and 40 ^{O}C tests).

Table 4: Effect of temperature on capacitance of commercial capacitor.

	15 ^{O}C	25 ^{O}C	40 ^{O}C
mA	F	F	F
0.032	6.8	7.03	7.11
0.064	6.73	6.96	7.03
0.128	6.61	6.85	6.91

Increasing the temperature increased the capacitance of the commercial capacitor at all currents but proportionally not by as much as for the test cell, Table 4. Capacitance could not be calculated per gram for the commercial capacitor as the weight of electrode material was unknown.

Conclusions.

No significant effect of temperature on ESR was observed for either the test cell or the commercial 10 F capacitor. Increasing the temperature, however, did increase the capacitance for both capacitors, with the test cell capacitance proportionally increasing more than the commercial cell capacitance.

Refrigeration for one hour at 5 ^{O}C did not affect either the capacitance or the ESR of the test cell. Further tests will be carried out subjecting the test cell to progressively longer periods of refrigeration. Further testing will also measure the breakdown voltage at 15, 25 and 40 ^{O}C.

Acknowledgement

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