



Short communication

## The effects of temperature on the performance of electrochemical double layer capacitors

S.I. Fletcher<sup>a,\*</sup>, F.B. Sillars<sup>a</sup>, R.C. Carter<sup>b</sup>, A.J. Cruden<sup>b</sup>, M. Mirzaeian<sup>a</sup>, N.E. Hudson<sup>c</sup>, J.A. Parkinson<sup>c</sup>, P.J. Hall<sup>a</sup>

<sup>a</sup> Department of Chemical & Process Engineering, University of Strathclyde, Montrose St., Glasgow, G1 1XJ, UK

<sup>b</sup> Department of Electronic & Electrical Engineering, University of Strathclyde, 204 George St., Glasgow, G1 1XW, UK

<sup>c</sup> Department of Pure & Applied Chemistry, University of Strathclyde, 295 Cathedral St., Glasgow, G1 1XL, UK

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### ABSTRACT

An electrochemical double layer capacitor test cell containing activated carbon xerogel electrodes and ionic liquid electrolyte was tested at 15, 25 and 40 °C to examine the effect of temperature on electrolyte resistance ( $R_S$ ) and equivalent series resistance (ESR) measured using impedance spectroscopy and capacitance using charge/discharge cycling. A commercial 10F capacitor was used as a comparison. Viscosity, ionic self-diffusion coefficients and differential scanning calorimetry measurements were used to provide an insight into the behaviour of the 1,2-dimethyl-3-propylimidazolium electrolyte. Both  $R_S$  and ESR decreased with increasing temperature for both capacitors. Increasing the temperature also increased the capacitance for both the test cell and the commercial capacitor but proportionally more for the test cell. An increase in temperature decreased the ionic liquid electrolyte viscosity and increased the self-diffusion coefficients of both the anion and the cation indicating an increase in dissociation and increase in ionic mobility.

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### 1. 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  $65$  °C and preferably  $-40$  to  $85$  °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 °C and the performance of the EDLCs at other temperatures was unknown. Furthermore, there is a paucity of published data on the effects of temperature on the performance of this type of EDLC.

Yuyama et al. [2] tested 1 M propylene carbonate solutions of 14 ammonium salts, nine of them room temperature ionic liq-

uids (RTILs), as electrolytes in palm shell derived, activated carbon EDLCs. Test cells were galvanostatically charged at 0.2 A to 3.0 V and charged to remain at 3.0 V for 30 min, then galvanostatically discharged at a current of between 0.2 and 5 A to 0 V. The internal or equivalent series resistance (ESR) of the cells was measured at 1 kHz at 25 and  $-30$  °C. Thermal stability was assessed as a lifetime test by continuous charging at 3.0 V at 70 °C with regular cooling to 25 °C to measure the ESR as opposed to measuring the ESR at 70 °C. For the 14 electrolytes, the ESRs at  $-30$  °C were between 6 and 30 times the ESRs at 25 °C. This was attributed, at least in part, to an increase in viscosity with decreasing temperature decreasing the mobility of the ionic species present. It should be emphasised that these results are for 1 M solutions and not pure ionic liquids. The 70 °C tests were primarily to accelerate deterioration at an elevated temperature to compare electrolytes, as opposed to assessing cell performance at 70 °C.

An earlier paper by the same group [3] tested three electrolytes, one organic and two RTILs, in phenol resin charcoal based electrode EDLCs at temperatures from 25 to 150 °C. Capacitors were galvanostatically charged at 1.50 mA from 0 to 2.5 V, charged to maintain 2.5 V for 30 min before being galvanostatically discharged at 15 mA to 0 V. This was repeated for all electrolytes at temperatures of 25–70 °C and up to 150 °C for one of the RTILs. The organic electrolyte EDLC showed a slight decrease in capacitance with increasing temperature. The 1-ethyl-3-methylimidazolium tetrafluoroborate electrolyte EDLC capacitance increased slightly

\* Corresponding author. Tel.: +44 141 548 2075; fax: +44 141 548 2539.

E-mail address: [isobel.fletcher@strath.ac.uk](mailto:isobel.fletcher@strath.ac.uk) (S.I. Fletcher).

before decreasing with temperature but could not be charged to the full 2.5 V at 70 °C owing to decomposition of the electrolyte. The second RTIL, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate, EDLC showed a decrease in capacitance from 40 to 150 °C.

Xu et al. [4] tested an EDLC with an activated carbon fibre based electrode and RTIL electrolyte. The capacitor was galvanostatically charged and discharged from 0 to 2 V at seven current densities for temperatures of 25, 40 and 60 °C. The IR drop, the sharp decrease in voltage at the start of the discharge, decreased with increasing temperature. The specific capacitance increased from 160 F g<sup>-1</sup> at 25 °C to 181 F g<sup>-1</sup> at 60 °C and increases in capacitance with increasing temperature were observed at all current densities. This was attributed mainly to the increased mobility of ions at higher temperatures.

None of these authors used the same or even a similar RTIL electrolyte, to the one used in this work nor were carbon xerogel electrodes used, although this is less likely to be of importance. Therefore a test programme was set up to examine the performance of a test cell capacitor at 15, 25 and 40 °C. As a comparison, a commercial 10F aerogel capacitor was also tested over the same range of temperatures.

## 2. Experimental

### 2.1. Electrodes

The electrodes for the EDLC test cell were manufactured from resorcinol formaldehyde xerogels [5] dried under vacuum, milled, carbonised at 800 °C, milled and activated with CO<sub>2</sub> at 800 °C. The xerogel was mixed with 10% carbon black and 10% Kynar binder in acetone and spread on to aluminium foil in a 200 μm layer, allowed to dry and cut into 1.3 cm diameter discs.

### 2.2. Electrolyte physical properties

Room temperature ionic liquids (RTILs) have attracted considerable interest as electrolytes for EDLCs owing to the increased size of electrochemical window, up to 4.2 V anodic for some RTILs [6] compared to 3 V for organic electrolytes and 1.23 V 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 the combination of a relatively low viscosity, a reasonably high ionic conductivity for an RTIL and a large anodic voltage window. A large number of alternative ionic liquids were considered but were rejected on the grounds of a higher viscosity, a smaller anodic window than obtainable with organic electrolytes or in the case of tetraborofluorates and hexafluorophosphates, the ability to react to produce fluorine or hydrofluoric acid [6–12]. A higher viscosity will reduce the mobility of ions in the electrolyte and production of fluorine or hydrofluoric acid presents safety issues and corrosion problems for the materials of construction of the capacitor. Both 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide and 1-methyl-3-ethylimidazolium bis(trifluoromethylsulfonyl)imide have been patented by Covalent Associates Inc., Corvallis, USA but the former RTIL cation is claimed to have a slightly wider anodic voltage window before breakdown occurs [13].

To examine the effects of temperature on the electrolyte viscosity, shear stress was measured [7] at a constant shear rate of 100 s<sup>-1</sup> for temperatures from 15 to 95 °C using a TA Instruments AR1000-N Rheolyst rheometer with 0.02 m diameter stainless steel

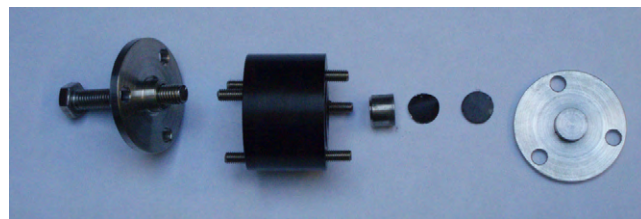


Fig. 1. Test cell.

parallel plates set at a gap of 200 μm. The viscosity was determined as shear stress/shear rate.

To examine the effects of temperature on diffusion, self-diffusion coefficients of the 1,2-dimethyl-3-propylimidazolium cations and bis(trifluoromethylsulfonyl)imide anions contained in the electrolyte were measured over a range of temperatures by <sup>1</sup>H and <sup>19</sup>F NMR spectroscopy using a stimulated echo approach and acquired using an AVANCE 400 Bruker NMR spectrometer. Owing to the relatively high viscosity of the ionic liquid, a Shigemi tube was used to reduce the formation of convection currents during measurements.

Most RTILs do not degrade at temperatures below ~400 °C, 1,2-dimethyl-3-propylimidazolium bis(trifluoromethylsulfonyl)imide is reported to have a degradation temperature of 457 °C [8] well above the temperature range used in these tests.

RTILs exhibit a variety of phase transition behaviour and on cooling many have the ability to form supercooled liquids up to 200 °C below the melting temperature [9,10,14,15]; some form crystals, others merely undergo a glass transition. The melting temperature and other phase changes in [dmpim][TFSI] were measured using a nitrogen flushed Mettler Toledo DSC 30 differential scanning calorimeter at a scan rate of 10 C min<sup>-1</sup> for temperatures from –150 to 130 °C [7].

### 2.3. Test cell

The test cell was constructed as shown in Fig. 1. The separator lies directly on top of the right hand electrode. Endplates were constructed from stainless steel and the main body from PTFE. The test cell was assembled inside an argon flushed drybox, the top was screwed on to the PTFE body, the first electrode loaded, the separator added together with enough electrolyte to saturate the separator, the second electrode was put in place and the bottom plate loosely screwed together. The test cell was then placed under vacuum in the drybox port for 5 min before being returned to the main part of the drybox, fully tightened and sealed with parafilm.

### 2.4. Commercial capacitor

A commercial 2.5 V 10 F PowerStor B Series capacitor with carbon aerogel electrodes and an organic electrolyte consisting of a quaternary ammonium salt dissolved in propylene carbonate was used as a comparison to the laboratory made EDLC test cell.

### 2.5. Test procedure

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 and 10 MHz. MultiStat Data Explorer software (Solartron Analytical, AMETEK Measurement Technology, Farnborough, UK) was used to curve fit the semicircle from the first part of the Nyquist plot to estimate the equivalent series resistance (ESR) of the electrodes and electrolyte.

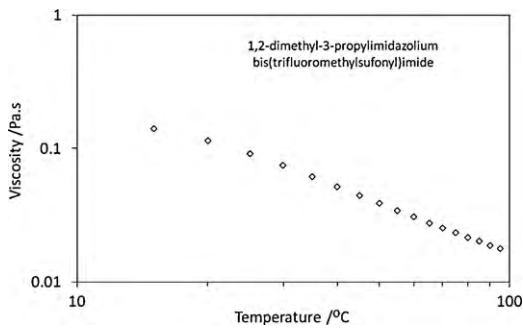


Fig. 2. The effect of temperature on electrolyte viscosity.

The cell was then galvanostatically charged and discharged 20 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 were 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 an amplitude of 10 mV and frequencies from 1 to 10 MHz. The 10 F capacitor was galvanostatically charged and discharged 20 times between 0 and 2.3 V at currents of 0.032, 0.064 and 0.128 A. Higher currents were necessary owing to the larger capacitance of the commercial EDLC.

Both the test cell and 10 F capacitor were tested inside a Fricell temperature control chamber at 15, 25 and 40 ± 0.1 °C.

### 3. Results

#### 3.1. Electrolyte properties

Previously reported work [4] showed the electrolyte to be Newtonian, i.e. independent of shear rate between 10 and 1000 s<sup>-1</sup>. The viscosity of the electrolyte decreased almost as a power law with increasing temperature, Fig. 2.

The self-diffusion coefficients of both the 1,2-dimethyl-3-propylimidazolium cation and the bis(trifluoromethylsulfonyl) imide anion increased indicating an increased amount of dissociation with increasing temperature, Fig. 3.

#### 3.2. Differential scanning calorimetry

Fig. 4 shows the differential scanning calorimetry (DSC) trace for the electrolyte for temperatures between -150 and 130 °C. [dmpim][TFSI] underwent a glass transition when cooled, sometimes cold crystallised when heated, then melted to form a liquid at 8 °C. The lowest temperature used for

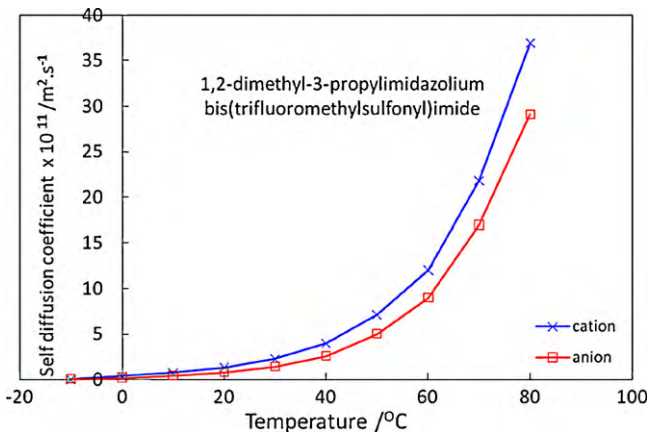


Fig. 3. Effect of temperature on the electrolyte ionic self-diffusion coefficient.

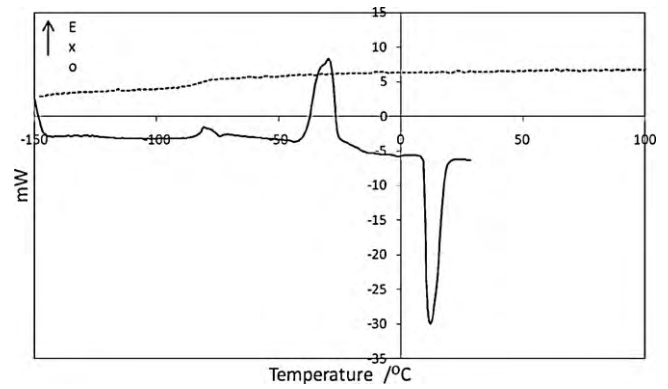


Fig. 4. DSC trace for 1,2-methyl-3-propylimidazolium bis(trifluoromethylsulfonyl) imide. Dashed lines cooling and solid lines heating.

capacitor testing was 15 °C, well above the melting temperature.

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

#### 3.3. Impedance spectroscopy

A typical Nyquist plot of  $z''$  versus  $z'$  is shown in Fig. 5, in this instance for the test cell at 2.6 V for 15, 25 and 40 °C. Fig. 6 shows a Nyquist plot for the test cell at 25 °C and 0.1, 1.35 and 2.6 V, all voltages measured versus open circuit. All impedance measurements both for the test cell and the commercial capacitor at all three temperatures and voltages, produced Nyquist plots similar to Figs. 5 and 6.

The high frequency semi-circle from each Nyquist plot was used to estimate the electrolyte resistance,  $R_s$  from the high frequency intercept, the interparticle resistance,  $R_i$  from the difference between the low frequency and high frequency intercepts and the equivalent series resistance (ESR) from the value of  $z'$  at 1 kHz; given in Tables 1 and 2. For the test cell, at all voltages,  $R_s$  decreased as temperature increased,  $R_i$  increased slightly with an increase in temperature from 15 to 25 °C then decreased with a decrease in

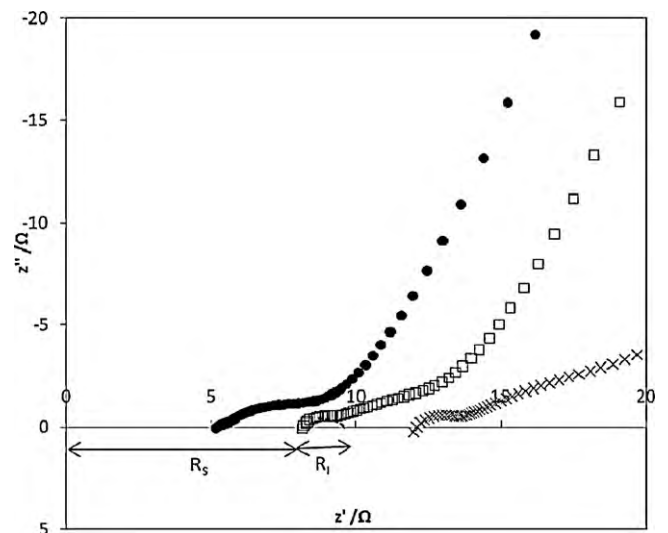


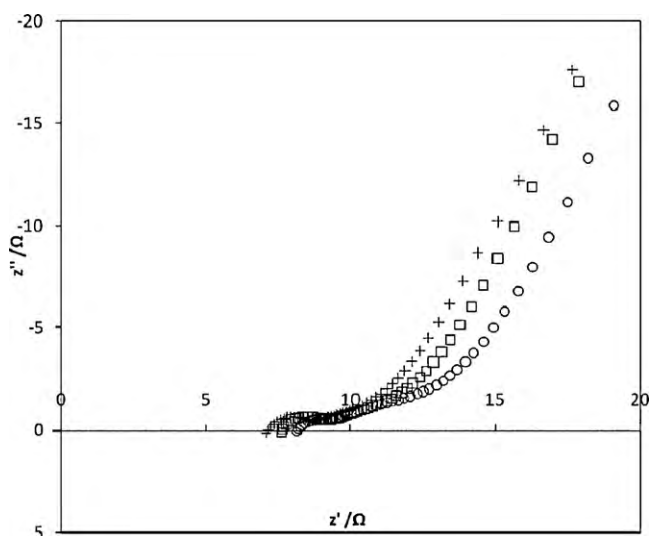
Fig. 5. Nyquist plot for test cell impedance at 2.6 V for ×, 15 °C; □, 25 °C; ●, 40 °C showing  $R_s$  and  $R_i$  for 25 °C.

**Table 1**  
The effect of temperature on  $R_S$ ,  $R_I$  and ESR for the test cell.

Voltage (V)	15 °C			25 °C			40 °C		
	$R_S$ ( $\Omega$ )	$R_I$ ( $\Omega$ )	ESR ( $\Omega$ )	$R_S$ ( $\Omega$ )	$R_I$ ( $\Omega$ )	ESR ( $\Omega$ )	$R_S$ ( $\Omega$ )	$R_I$ ( $\Omega$ )	ESR ( $\Omega$ )
0.1	12.1	2.41	14.7	7.37	2.98	10.6	5.27	0.67	5.96
1.35	12.2	2.23	14.5	7.40	2.70	10.3	5.13	0.57	5.63
2.6	12.4	1.86	14.4	7.63	2.39	10.2	5.13	0.68	5.80

**Table 2**  
The effect of temperature on  $R_S$ ,  $R_I$  and ESR for the 10F commercial capacitor.

Voltage (V)	15 °C			25 °C			40 °C		
	$R_S$ ( $\Omega$ )	$R_I$ ( $\Omega$ )	ESR ( $\Omega$ )	$R_S$ ( $\Omega$ )	$R_I$ ( $\Omega$ )	ESR ( $\Omega$ )	$R_S$ ( $\Omega$ )	$R_I$ ( $\Omega$ )	ESR ( $\Omega$ )
0.1	0.043	0.048	0.073	0.041	0.041	0.068	0.039	0.036	0.064
1.1	0.043	0.049	0.073	0.041	0.038	0.067	0.039	0.034	0.063
2.2	0.044	0.039	0.069	0.041	0.032	0.064	0.040	0.028	0.060



**Fig. 6.** Nyquist plot for test cell impedance at 25 °C for +, 0.1 V; □, 1.35 V; ○, 2.6 V.

temperature from 25 to 40 °C and ESR followed the same trend as  $R_S$ , decreasing with increasing temperature. For the commercial capacitor all resistances were one to three orders of magnitude smaller than for the test cell. This can be attributed to the use of an organic electrolyte as opposed to a RTIL and improved electrical contacts within the commercial device.  $R_S$ ,  $R_I$  and ESR all decreased slightly with increasing temperature. Proportionally, the changes in resistances with temperature were much smaller for the commercial capacitor than for the test cell. These results are in agreement with the effects of temperature on ESR reported by Yuyama et al. [2] for an organic electrolyte.

### 3.4. Galvanostatic charge/discharge

Increasing the temperature increased the capacitance of the test cell at all currents with the exception of 0.016 mA and 25 °C where the capacitance was slightly lower than at 15 °C, Table 3. This is

**Table 3**  
Effect of temperature on the capacitance of the test cell.

mA	15 °C, F g <sup>-1</sup>	25 °C, F g <sup>-1</sup>	Change <sup>a</sup> , %	40 °C, F g <sup>-1</sup>	Change <sup>a</sup> , %
0.002	45.11	50.55	12.1	56.88	26.1
0.004	39.85	44.62	12.0	53.51	34.3
0.008	34.25	37.1	8.3	52.17	52.3
0.016	27.6	27.23	-1.3	47.97	73.8

<sup>a</sup> Expressed as a percentage of 15 °C value.

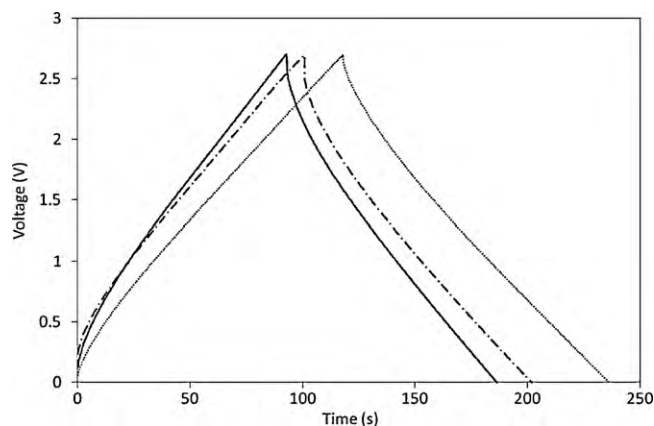
**Table 4**  
Effect of temperature on the capacitance of the commercial capacitor.

mA	15 °C, F	25 °C, F	Change <sup>a</sup> , %	40 °C, F	Change <sup>a</sup> , %
0.032	6.8	7.03	3.4	7.11	4.6
0.064	6.73	6.96	3.4	7.03	4.5
0.128	6.61	6.85	3.6	6.91	4.5

<sup>a</sup> Expressed as a percentage of 15 °C value.

in agreement with the results reported by Xu et al. [4] for a RTIL electrolyte EDLC. Increasing the temperature also increased the capacitance of the commercial capacitor at all currents but proportionally by much less than the test cell, Table 4. Capacitance could not be calculated per gram for the commercial capacitor as the weight of electrode material was unknown; however it is the *relative* increase or decrease of capacitance that is important here. A scaled up version of this test cell, exhibiting increased sensitivity of performance to changes in temperature compared to existing devices, could potentially prevent commercialisation. Change in capacitance is expressed as a percentage of the capacitance measured for the same current at 15 °C.

Charge/discharge curves are shown in Figs. 7 and 8 for the test cell and commercial capacitor respectively. Both capacitors charged and discharged more slowly with increasing temperature although this effect was more noticeable for the test cell than for the commercial capacitor.



**Fig. 7.** Charge/discharge curves for the test cell; 0.02 A; —, 15 °C; - - -, 25 °C; ···, 40 °C.

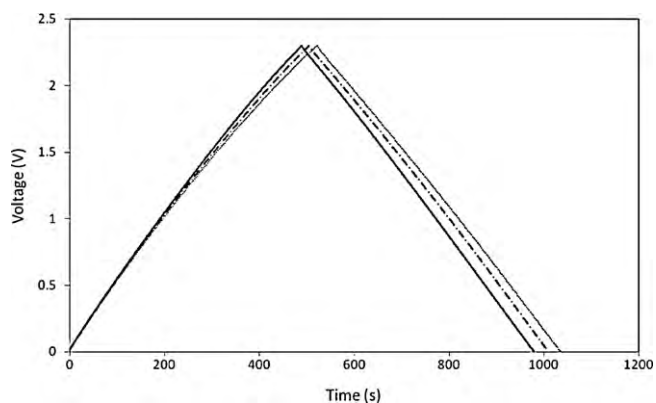


Fig. 8. Charge/discharge curves for the commercial 10 F capacitor; 0.032 A; —, 15 °C; - - -, 25 °C; . . . , 40 °C.

#### 4. Conclusions

The NMR self-diffusion and viscosity measurements suggest an increasing amount of dissociation in the ionic liquid electrolyte with increasing temperature, decreasing the viscosity and increasing the ionic mobility.

Both electrolyte resistance,  $R_S$ , and equivalent series resistance, ESR, for the test cell decreased with increasing temperature and increasing ionic mobility. For the commercial capacitor with an organic electrolyte,  $R_S$ ,  $R_I$  and ESR all decreased with increasing temperature but proportionally less than in the RTIL electrolyte test cell.

Increasing the temperature also increased the capacitance for both capacitors, with the test cell capacitance proportionally increasing more than the commercial cell capacitance. This effect may have to be taken into consideration for some applications, were the test cell to be scaled up to a commercial device operating over a wide range of temperatures. The increased voltage window and hence energy storage ability of RTIL electrolyte EDLCs could, for

some applications, be partially negated by increased sensitivity to temperature and reduction of capacitance at lower temperatures compared to organic electrolyte EDLCs.

Further tests will be carried out subjecting the test cell to progressively longer periods of refrigeration at 5 °C. Further testing will also measure the breakdown voltage of the electrolyte at 15, 25 and 40 °C.

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