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Ionic liquid electrolyte for supercapacitor with high temperature compatibility

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Abstract. This work describes the electrochemical investigation of two ionic liquids (ILs), 1-ethyl-3-methylimidazolium acetate (EMIM Ac) and 1-butyl-3-methylimidazolium chloride (BMIM Cl), as electrolytes in supercapacitors (SC). A comprehensive study on high temperature (HT) endurance that is required for system integration in microelectronics has also been carried out. It has been found that EMIM Ac containing SC performs better than a BMIM Cl containing SC, and HT treatment improves the capacitive performance.

1. Introduction

Supercapacitors are getting tremendous attention in recent years as they can fill the gap between traditional capacitors and batteries with their high power capability, decent energy density and remarkable lifetime [1]. Owing to their unique performance characteristics, SCs are often integrated in microelectronics systems [2]. Many concurrent encapsulation and packaging techniques for printed circuit board (PCB) electronics, such as reflow soldering [3], are high temperature (HT) processes, which require the SC to withstand elevated temperature (more than 100 °C) for a certain period of time [2]. The HT exposure specifically requires an electrolyte that is compatible with harsh temperature and pressure. Aqueous and organic electrolytes are unsuitable for HT exposure due to the presence of water or high vapor pressure [4]. In contrast, Ionic liquids (ILs), also known as room temperature (RT) molten salts are an appropriate option as an electrolyte because of their high thermal stability [5]. Moreover, they possess valuable intrinsic properties such as low vapor pressure, non-flammability, high electrochemical stability and wide voltage range [5].

In this work, we have evaluated two different ILs, 1-ethyl-3-methylimidazolium acetate (EMIM Ac) and 1-butyl-3-methylimidazolium chloride (BMIM Cl), as potential electrolytes for SCs that can withstand the HT required for microelectronics encapsulation. SC devices were fabricated by using activated carbon (AC) electrodes, EMIM Ac or BMIM Cl electrolyte and glass fiber (GF) separators. In order to mimic the packaging and encapsulation requirements, fabricated devices were exposed to HT and compared in terms of their electrochemical performance.

2. Experimental

2.1. Electrode preparation

For electrode preparation, initially AC powder and carbon black were mixed and finely ground in a quartz mortar. Afterwards the mixture was added to a beaker containing acetone and

polytetrafluoroethylene (PTFE) binder (in the form of 60 wt.% dispersion in H_2O suspension). The weight ratio of the AC powder, carbon black and PTFE was 80:10:10. The mixture in acetone was kept in a sonicator for 30 min and then transferred to a 75 °C water bath. After the solvent (acetone) evaporation, an obtained dough was processed into a freestanding thin film by a rolling press machine. Then, the film was dried in vacuum for 24 h at 80 °C. Pellets with 10 mm diameter were punched out from the dried film and used as electrodes. A single electrode was approximately 3 mg in mass, 100 µm in thickness, and 10 mm in diameter.

2.2. SC device assembly and high temperature exposure

A symmetrical two electrode SC device was prepared by sandwiching two AC electrodes with a separator/electrolyte in between and assembled in a Swagelok® cell. In total, four devices were assembled, three with EMIM Ac electrolyte and one with BMIM Cl electrolyte. Two devices containing EMIM Ac and BMIM Cl electrolytes were compared without any HT treatment. The other two devices containing EMIM Ac were subjected to HT treatment at 190 °C for 2 h and at 120 °C for 6 h. HT treatment was provided by placing the cells into DZF-6020 oven.

2.3. Electrochemical measurement

All the devices were kept 'as is' for 24 h before measurement in order to give enough time for the electrolyte ions to penetrate into the electrodes. The following electrochemical measurements were conducted on a Gamry Reference 3000 AE potentiostat to evaluate the electrochemical performance of the devices: cyclic voltammetry (CV), galvanostatic charge discharge (GCD), cyclic charge/discharge (CCD) and electrochemical impedance spectroscopy (EIS). Capacitance was calculated from both CV and GCD measurements according to the following equations:

$$C_s = \frac{4}{m\Delta V v_s}\int_{V_1}^{V_2} I(V)dV \qquad \text{(F/g)} \qquad (1)$$

$$C_s = \frac{4 \times I_d \times \Delta t}{m \times \Delta V} \qquad \text{(F/g)} \qquad (2)$$

where C_s is the specific capacitance of a single electrode, $I(V)$ is the current response, V_1 and V_2 are lower and upper potential limits, respectively, ΔV is the working voltage range excluding IR drop, v_s is the scan rate, I_d is the discharge current, Δt is the discharge time and m is the total mass of both electrodes.

Power density and energy density of a device were calculated from GCD measurements based on the following equations:

$$C = \frac{C_s}{4} \qquad \text{(F/g)} \qquad (3)$$

$$E = \frac{C\Delta V^2}{2 \times 3.6} \qquad \text{(Wh/kg)} \qquad (4)$$

$$P = \frac{E \times 3600}{t} \qquad \text{(W/kg)} \qquad (5)$$

where C is the specific capacitance of the device, ΔV is the voltage range excluding IR drop, E is the energy density of the device and P is the power density of the device.

3. Results and discussions

3.1. Performance comparison of non-treated device

Figure 1 presents the CVs of EMIM Ac and BMIM Cl containing SCs at different scan rates. At a fast scan rate of 200 mV/s, EMIM Ac containing cell exhibits a fairly symmetric and semi rectangular CV curve (Figure 1a). The deviation from an ideal rectangular shape (a characteristic of electrochemical

double layer mechanism, i.e. EDL behavior) is due to the high resistive nature of ILs. However, the performance improves at a slow scan rate. The specific capacitance of EMIM Ac containing SC at 5 mV/s is calculated to be of 82 F/g which is almost 2.5 times more than specific capacitance at 200 mV/s.

For the BMIM Cl containing SC, the CV curve (Figure 1b) at a fast scan rate of 200 mV/s is less rectangular and rather asymmetric. This suggests a presence of very high resistance in the device, which might originate from the higher viscosity of BMIM Cl compared to the viscosity of EMIM Ac electrolyte. Also, at slow scan rates, there is a noticeable deformation in the end of charging and in the beginning of discharging cycles. A plausible explanation for the deformation can be the higher reactivity (corrosiveness) of Cl^- anion in BMIM Cl compared to Ac^- anion in EMIM Ac [6, 7], which facilitates faradic reactions. The specific capacitance is calculated to be 75 F/g at the slowest scan rate, while it decreases to 31 F/g at a high scan rate of 200 mV/s.

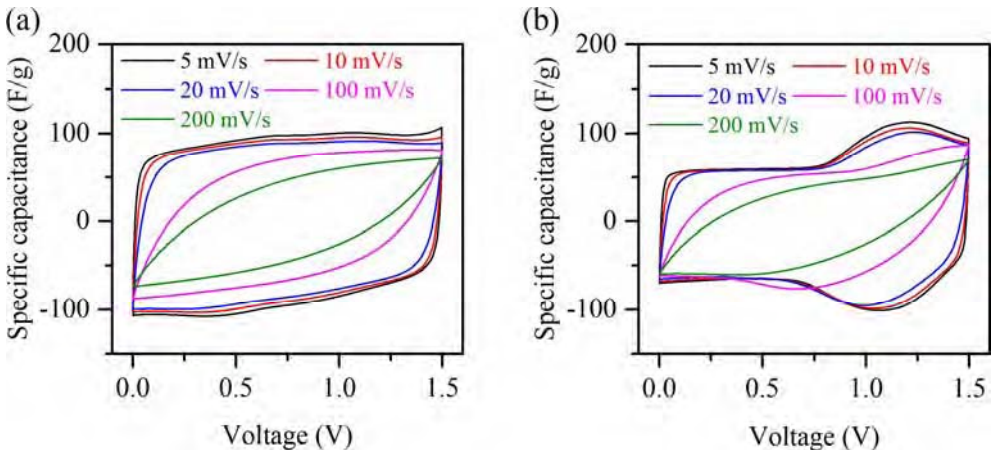

Figure 1. CVs of SC containing EMIM Ac (a), BMIM Cl (b). The total mass of electrodes for EMIM Ac and BMIM Cl containing SC are 5.57 and 6.26 mg, respectively.

Figure 2a and Figure 2b demonstrate the GCD curves of EMIM Ac and BMIM Cl containing SCs. Voltage loss, also known as IR drop, is noticeable even at a low current density of 0.5 A/g for both devices due to slow kinetic properties of ILs at RT. The typical triangular shape of EMIM Ac containing SC (Figure 2a) at all current densities represents almost perfect EDL behavior. Non-linear charge and discharge curves of BMIM Cl containing SC clearly indicates the presence of faradaic reactions, which is in agreement with the CV results.

Figure 2c represents the CCD curve of both devices. Interestingly, capacitance gradually increases to 104% at 5000th cycle for EMIM Ac containing SC. This unusual increase of capacitance may has been caused by the continuous wetting of electrode pellets by the electrolyte. Also repetitive charge/discharge might have opened up more pores of AC electrodes. In a sharp contrast, capacitance decreased dramatically over the measurement on BMIM Cl containing SC and retained only 86% at 3500th cycle. The inferior stability of BMIM Cl compared to EMIM Ac should be originated from the stronger chemical reactivity of Cl^- anions compared to Ac^- anions, which increases with cycling. Acetate-based ILs are less toxic and corrosive compared to halogen-containing ILs [6, 7].

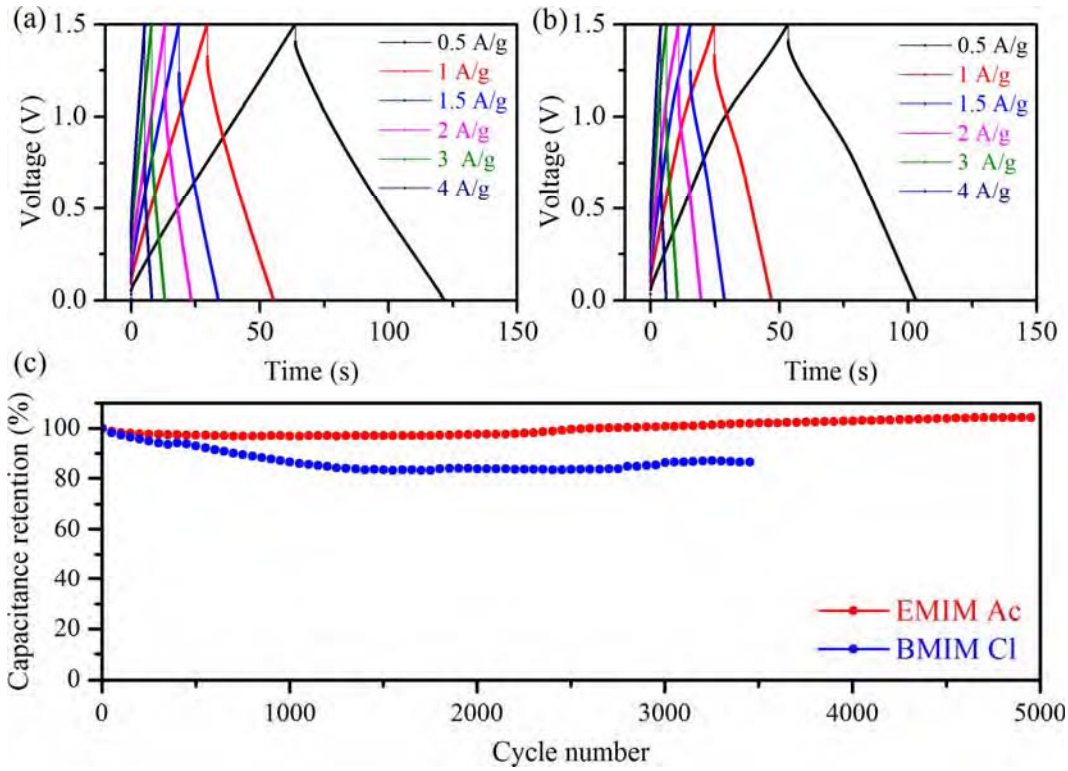

Figure 2. GCD curves at selected current densities of EMIM Ac (a), BMIM Cl (b) containing SC, and CCD measurement at 3 A/g (c).

Comprehensive comparison of performance metrics is summarized in Table 1. Based on the results, it can be concluded that the EMIM Ac containing SC demonstrates superior EDL behavior compared to BMIM Cl containing SC. This can be due to the better compatibility of EMIM Ac electrolyte with AC electrode. Also IL with shorter alkyl chain usually has lower viscosity compared to IL with longer alkyl chain [8]. In general, viscosity is inversely proportional to ionic conductivity, therefore, EMIM Ac with the shorter ethyl chain possesses comparatively higher conductivity than BMIM Cl with the longer butyl chain, which results in better capacitive behavior for the EMIM AC containing SC. Cyclic stability measurements clearly indicate that the EMIM Ac containing SC holds greater stability as an electrolyte compared to BMIM Cl.

3.2 Non-treated vs heat-treated device

Considering the possible requirements on packaging and encapsulation of a SC device in electronics systems, electrochemical measurements after HT treatment were carried out and results are presented in this section. Based on the results of the non-treated devices, only EMIM Ac containing SCs were selected and subjected to heat treatment. After HT treatment, devices were cooled down to RT before starting electrochemical measurements. The differences between treated devices and a non-treated device are observed in order to investigate the thermal influence on the electrochemical performance.

Figure 3a presents CV curves of HT treated and non-treated devices containing EMIM Ac electrolyte. The curves not only maintain standard rectangular shape but also become wider with HT treatment. This phenomenon indicates improved charge accumulation on the electrode/electrolyte interface during the heat treatment. The calculated specific capacitances of the SCs without and with treatment at 120 °C for 6 h and 190 °C for 2 h are 73, 79 and 81 F/g, respectively. Figure 3b demonstrates the GCD curves of the same devices. It can be seen that the duration of charge and discharge time increases with HT treatment. Also, the IR drop reduces significantly suggesting improved kinetics of the electrolyte ions. The calculated specific capacitance of the corresponding three SCs are 71, 78 and 77 F/g. The slightly

different values of the specific capacitance calculated from CV and GCD measurements are expected as the applied currents in both techniques were different. Overall, the results clearly indicate that HT treatment improves the capacitive performance. This is mostly due to an accelerated electrolyte ion penetration into an electrode material as a consequence of HT exposure.

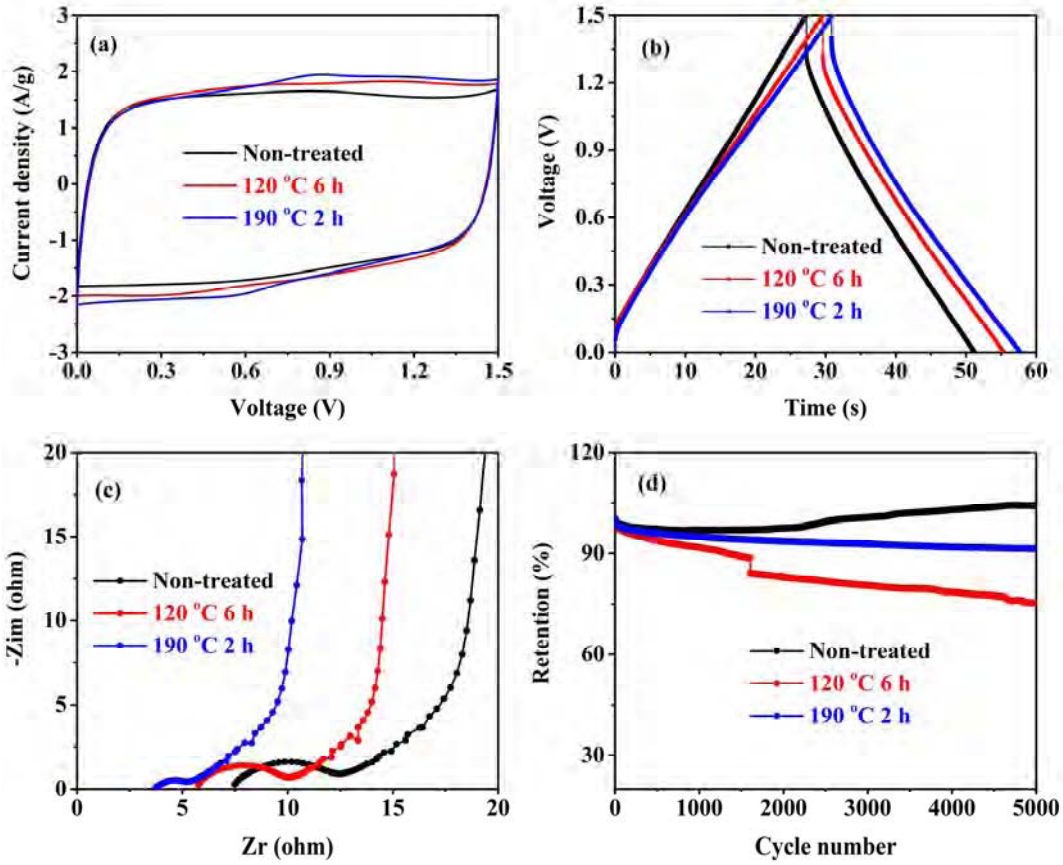

Figure 3. Comparison of electrochemical performance of EMIM Ac containing SC with and without temperature treatment: CVs at 20 mV/s (a), GCD plots at 1 A/g (b), Nyquist plots (c), CCD at 3 A/g (d). The total mass of electrodes for non-treated, 120 °C and 190 °C treated cells are 5.57, 5.55 and 7.61 mg, respectively.

Figure 3c represents Nyquist plots instigated from EIS measurements. The initial intercept of a plot in the *x*-axis at high frequency region represents bulk electrolyte resistance. It can be clearly seen that the resistance decreases with the heat treatment. The equivalent series resistance (ESR) is obtained from the semicircle in the mid-high frequency region and it is also decreased and shifted to the left. Calculated ESR values are 12.68, 10.33 and 5.39 ohms for non-treated, treated at 120 °C and treated at 190 °C cells, respectively.

Figure 3d compares the cycling stability of the non-treated and treated devices. The capacitance retention of 120 °C treated cell is not up to the mark as it shows a 23% loss in the end of 5000 cycles. The 190 °C treated cell exhibits better capacitance retention than the 120 °C treated one, retaining 94% of the initial capacitance. When treated at lower temperature (120 °C), the cell was exposed for longer duration (6 h) than treated at 190 °C (2 h). Therefore, it is likely that duration might have played more crucial role than temperature itself. As it mentioned before, unlike the treated cells, the non-treated cell exhibits increased capacitance over the cycling period.

Table 1 Electrochemical properties of SCs containing different electrolytes [a]

Type	Electrolyte	Specific capacitance (F/g)	Energy density (Wh/kg)	Power density (W/kg)	Capacitance retention (%)
Non-treated	EMIM Ac	82	4.52	680	104
	BMIM Cl	75	4.11	665	86
Heat treated	EMIM Ac/120	90	4.74	663	77
	EMIM Ac/190	93	5.27	703	94

[a] *Specific capacitance is calculated from CV at 5 mV/s, energy density and power density are calculated from GCD at 1 A/g, and capacitance retention is relative to first cycle value at 3 A/g from CCD measurement.*

4. Conclusion and future work

A thorough electrochemical investigation of EMIM Ac and BMIM Cl ILs as potential electrolytes for SCs has been carried out. EMIM Ac outperforms BMIM Cl by means of capacitance and cyclic stability. Moreover, HT treatment (at 190 °C for 2 h) of SC containing EMIM AC not only retained the capacitive behavior but also improved the performance, which assures the feasibility of integrating the SC in microelectronics that requires elevated temperature treatment. Compared to higher temperature, longer duration of HT treatment is more detrimental to cycling stability. As a future work, more detailed investigation should be focused on understanding the influence of heating duration on cyclic stability. Lastly, in depth electrochemical investigation of EMIM AC electrolyte containing SC operating at different elevated temperatures and finding the temperature limit should be beneficial as well.

Acknowledgements

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