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Electrochemical performance of 1-butyl-4-methylpyridinium tetrafluoroborate ionic liquid electrolyte for graphene-based double layer capacitor

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Abstract. Ionic liquids (ILs) have been emerged as the most promising class of electrolytes to achieve high energy density in electrochemical double layer capacitors (EDLCs) due to their unique properties. In this study, 1-butyl-4-methylpyridinium tetrafluoroborate ([BMPy][BF$_4$]) was explored as the electrolyte for graphene based EDLC in presence of co-solvent. Highly viscous [BMPy][BF$_4$] was diluted with two different organic solvents, namely acetonitrile (AN) and propylene carbonate (PC). Different weight ratios of [BMPy][BF$_4$]: organic solvents were investigated and corresponding variation of EDLC's performance was observed. Dynamic viscosity of these IL+solvent mixtures was also measured. Three electrochemical techniques, namely cyclic voltammetry, galvanometric charge discharge, electrochemical impedance spectroscopy were employed to analyse the effectiveness of these electrolyte–electrode systems. Maximum operating voltage 2.2 V was achieved for the four out of six studied systems. For PC based electrolytes, no effect of concentration of PC on operating potential window was observed. However with AN, electrochemical stability decreased with increase in solvent weight percentage. The highest specific energy (49 Wh kg^{-1}) and power (4.13 kW kg^{-1}) were obtained for 3:1 weight ratio of IL to AN. Reverse effect on specific capacitance and internal resistance was noticed for AN and PC based electrolytes.

Keywords. Supercapacitors; operating potential window; electrolyte; capacitance; specific power.

1. Introduction

The ever increasing demand of energy coupled with clean energy has prompted research on energy storage systems. Among the various energy storage devices so far, electro-chemical double layer capacitors (EDLCs) have shown their technical maturity as potential energy storage device [1]. In EDLC, energy is stored through ion adsorption with no chemical reaction forming the double layer of the ions at working electrode/electrolyte interface. EDLCs are confined to a branch of supercapacitors and known for higher cyclic durability and high power density as compared to other energy storage devices, such as batteries and fuel cell. The stored energy density possesses dependency on capacitance of the electrode and operating potential window (OPW) of the electrolyte. Lower electrochemical stability (0.8–1.2 V) of aqueous electrolyte and inflammable and noxious nature of organic electrolyte restricts their application in EDLC [2–5]. Ionic liquids (ILs) with their promising physicochemical properties, e.g., lower

flammability, less heat sensitivity, weakness for chemical changes, wider OPW overcome the drawbacks of aqueous and organic electrolytes [2,6]. A major limitation of IL based electrolytes is relatively high viscosity, which imparts diffusional limitations to ions resulting in an increase in internal resistance (IR) and subsequent decrease in power density. In this regard, dilution of ILs with organic solvents emerges as an alternative approach [3,7]. The most common organic solvent for EDLC is acetonitrile (AN), which is able to enhance ionic conductivity of ILs to a greater extent than propylene carbonate (PC) [8]. However, PC is known for its wider liquid range than AN. In this study, both AN and PC are employed to evaluate the effect of co-solvent on capacitance and OPW.

It is found in literature that the common choice of cations for ILs includes imidazolium and pyrrolidinium with different anions [2,6,9]. The ion pair combination affects both viscosity and electrochemical stability of electrolyte [10]. Literature for ILs, based on pyridinium, sulfonium and ammonium cations, is hard to find regarding EDLC

application. However, literature suggests that ammonium cations offer better cathodic stability than imidazolium ones [11]. Pyridinium ILs are reported to have reasonable ionic conductivity while mixed with organic solvents like PC, AN, ethanol and methanol [12]. Further, tetrafluoroborate (BF_4) anion shows potential in the field of double layer capacitor, in either organic electrolyte or ionic liquids. Therefore, the choice of 1-butyl-4-methylpyridinium (BMPy) cation with BF_4 anion was made in this study.

Butylpyridinium cation with well know anion, namely bis(trifluoromethylsulfonyl) imide (Tf_2N) was studied by Mousavi *et al* [13], where the authors reported nearly 4 V electrochemical stability against glassy carbon electrode. MnO_2-based electrode coupled with 2-methoxypyridinium trifluoroacetate was studied for its energy storage capacity [14]. A series of alkylpyridinium cations were tested with combination of three different acetate anions for RuO_2 electrochemical capacitor and widest OPW of 1.5 V was reported with pseudo capacitive behaviour [15]. [BMPy][Tf_2N] provided stability up to 3 V when used for glassy carbon electrode [16].

2. Experimental

2.1 *Materials*

[BMPy][BF_4] [purity >97% (T)] and PC (anhydrous 99.7%, mp −55°C and bp 240°C) were purchased from Sigma Aldrich. AN with purity >99.9% (mp −48°C and bp 81°C) was purchased from Spectrochem Pvt. Ltd. India. Working electrode (Reduced Graphene Oxide, RGO) was collected from VSSC, Thiruvananthapuram. The IL was vacuum dried for 24 h at 80°C prior to experimental measurements.

The water content of [BMPy][BF_4] was measured employing Karl Fischer Titration (KFT) method (Metrohm 787 KF Titrino). Karl Fischer reagent (526 KFR) was collected from Thermo Fisher Scientific India Pvt. Ltd. The measurement was repeated thrice. The observed water content of the IL was 0.37 wt%.

2.2 *Determination of viscosity*

The IL was kept in a vacuum oven at 80°C for 24 h so that volatile impurities could escape. Firstly 3.5 M (~ 25 wt% of AN), 2 M (~ 50 wt% of AN) and 1 M (~ 75 wt% of AN) solutions of IL in AN were prepared by mixing them well using a SPINIX vortex shaker. Thereafter PC based solutions were also prepared using same weight percentages of solvent. The solutions are labelled as solvent_I, solvent_II and solvent_III in order of increasing weight percentage of solvent. Dynamic viscosity of the electrolyte samples was determined by using interfacial rheometer (Make: Anton-Paar Model: Physica MCR301).

2.3 *Electrochemical measurements*

Electrolyte solutions were prepared as discussed in the last section. All the experiments were carried out using a three-electrode configuration at 25°C. RGO, spiral platinum wire and Ag/Ag$^+$ [17] were used as working, counter and reference electrode, respectively. Cyclic voltammetry (CV) was performed to determine the operating voltage window (OPW) of the electrolyte at different scan rates. The expression, used for calculation of specific capacitance (*C*), is given below [18].

$$C = \frac{1}{2vm(V_f - V_i)} \int_{V_i}^{V_f} I(V)dV \tag{1}$$

where *m* indicates the electrode's working mass, *v* represents the scan rate, $V_f - V_i$ defines the OPW and $I(V)$ is the potential dependent current. Further, galvanometric charge–discharge (GCD) was performed to confirm the OPW obtained from CV. Cell capacitance was also measured using equation (2) [18] and further equivalent series resistance (ESR) was also calculated.

$$C = \frac{I}{dV/dt} \tag{2}$$

where *I* is the current per active mass of working electrode (A g^{-1}) and *dV/dt* represents the discharge voltage profile's slope in the linear region. Finally, EIS study was executed from 100000 to 0.01 Hz at potential of 0.0 V *vs*. open circuit potential for the best solvent concentration.

3. Results and discussion

3.1 *Viscosity of the electrolyte solutions*

Figure 1 summarizes the viscosity of the electrolyte solutions studied in this work, as well as viscosity of pure IL at 25°C. Viscosity of pure [BMPy][BF_4] observed in this work shows close match with literature [19] and it is much higher than its solution in organic solvents. Reduction in viscosity is more for AN than PC, which signifies higher ability of AN to enhance the diffusional behaviour of the ions. The higher viscosity of PC (2.53 cp) [20] than AN (0.37 cp) [21] affects the viscosity of respective solutions. The molecules of non-viscous organic solvent AN can easily break the ionic interaction between the ion pairs the IL and result in comparatively low viscous electrolyte solutions. Moreover, addition of both the organic solvents lowers the interaction energy between the ions that decreases the viscosity of IL significantly.

3.2 *Solvation effect on OPW*

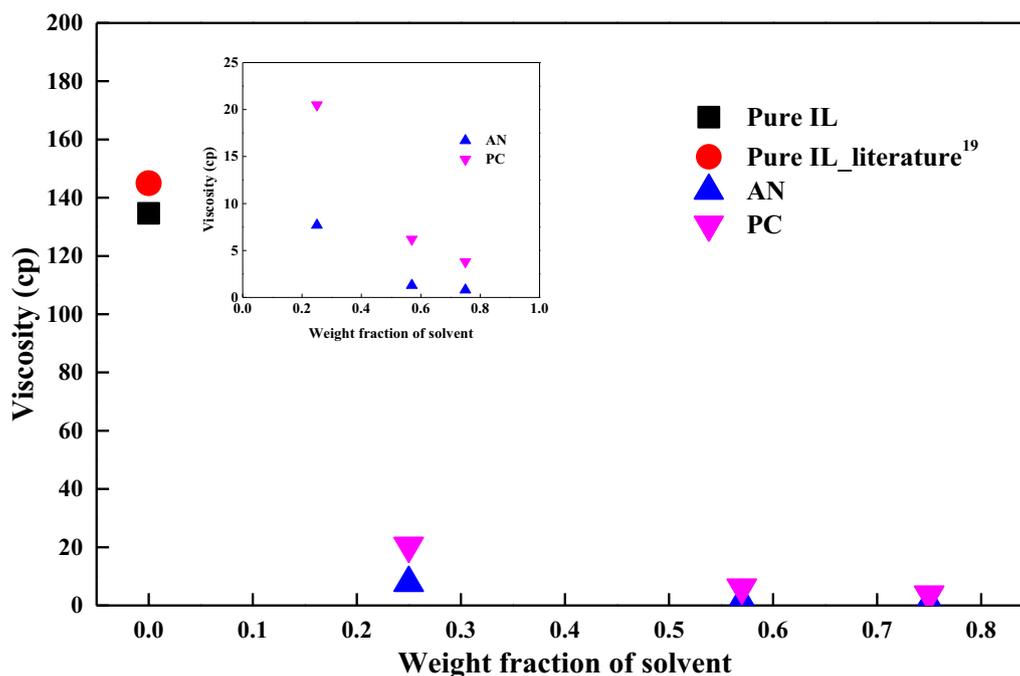The OPW is commonly controlled by the electrolyte's cathodic and anodic stability limit, within which the

Figure 1. Effect of co-solvent on dynamic viscosity of the IL.

electrolyte does not undergo reduction or oxidation. The electrochemical window is reported relative to the potentials of a reference, which is Ag/Ag$^+$ in this study. The maximum OPW of RGO based EDLC was determined using CV and GCD techniques by measuring the cathodic and anodic stability limits of different mixtures of [BMPy][BF$_4$] in AN (figure 2) and PC (figure 3). Results from CV and GCD techniques confirm reproducibility of OPW data. For AN-based electrolytes, widest OPW (2.2 V) was obtained for 25% AN in IL, i.e., AN_I, whereas for other two compositions the measured electrochemical stability is limited to only 1.7 V. However, OPW of 2.2 V was obtained with all concentrations of PC. The higher concentration of PC does not shrink the OPW of the electrolyte solution unlike AN. Previous work done by the authors also confirmed that increased wt% of AN narrowed the OPW of imidazolium ILs [22] (figure 4). A potential difference of 2.2 V applied to AN_II electrolyte solution leads to the tendency of appearance of peaks at both the ends indicating evolution of gas [23] when compared to PC_II solution (figure 5). Studies on tetraethylammonium tetrafluoroborate (TEABF$_4$) salt as a solution of equal concentration in AN and PC also showed that TEABF$_4$/PC system had OPW wider by 0.5 V than TEABF$_4$/AN [6]. Moreover, wider temperature range of PC than AN as mentioned in section 2.1 leads to better thermal stability of PC based electrolytes.

The observed electrochemical stability of [BMPy][BF$_4$] is found to be lower than imidazolium and pyrrolidinium based ILs [3,13,24] which specifies higher resistance of imidazolium and pyrrolidinium cations to oxidative and

reductive conditions [25]. Literature reported that IL electrolytes are electrochemically stable up to 5–6 V with Pt or glassy carbon electrode, whereas for supercapacitors it is limited to 3.5–4 V [26]. Figure 4 represents a comparison of OPW of the electrolyte solutions, studied in this work, with 1-alkyl-3-methylimidazolium (AMIM) Tf$_2$N ILs, substituted by ethyl ([EMIM][Tf$_2$N]), propyl ([PMIM][Tf$_2$N]) and butyl ([BMIM][Tf$_2$N]) groups [22], at similar AN concentration with RGO electrode.

For most of the electrolytes, conventionally the cathodic limit is set by the reduction potential of cation and the anodic limit is bounded by the oxidation potential of anion. However, reported literature states that this convention may not be true always [13,27,28] and anodic stability can be limited by oxidation of cation. The observed OPW in our study is narrower than reported imidazolium ILs with BF$_4$ anion [2,29]. Moreover, the observed OPW of [BMIM][BF$_4$] (figure 4), investigated with the same working electrode by the authors [30], is also wider than [BMPy][BF$_4$]. This happened due to the lower anodic limit. This predicts that pyridinium cation has probably suffered from oxidation earlier than BF$_4$ anion, since wider electrochemical stability of BF$_4$ was reported from computational studies [31]. Electrochemical stability of 1.2 V was obtained by Ruiz and co-workers [14] for 2-methoxypyridinium trifluoroacetate and MnO$_2$ based electrode. Apart from type of the electrolytes, electrochemical stability also depends on the impurity of the electrolyte solution, trace of water present and type of electrode material [11].
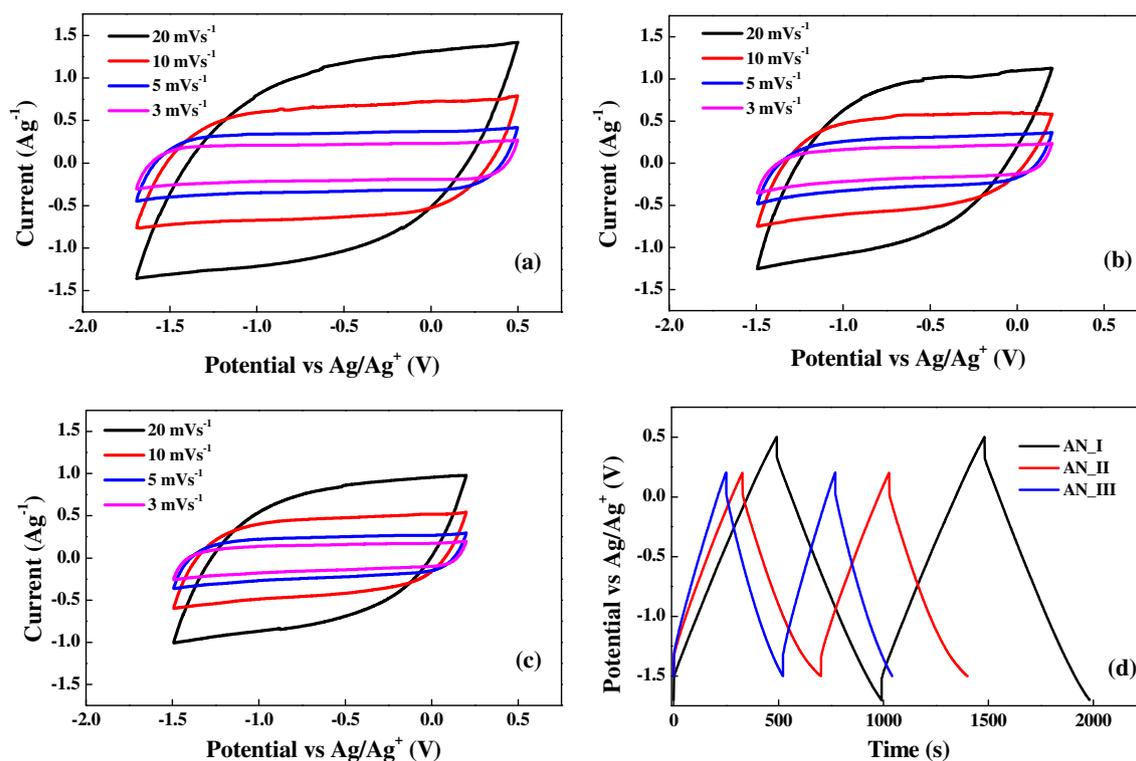
Figure 2. CV plots of [BMPy][BF$_4$] in (**a**) AN_I, (**b**) AN_II, (**c**) AN_III solutions and (**d**) GCD cycles for the three AN based solutions at 0.3 A g^{-1}.

3.3 *Determination of specific capacitance*

The shape of the CV curves (figures 2a–c and 3a–c) does not show any sign of redox peaks confirming that resultant capacitance is purely double layered in nature. Specific capacitances for all the six systems were calculated by equations (1 and 2) (figure 6). Reverse trends of specific capacitance can be observed for AN and PC. From CV, linear decrease in charge storage capacity is found for AN series of electrolytes; however, GCD gives equal specific capacitance for AN_I and AN_II. This is because of the difference in time scales of these two techniques. Results obtained reveals the dependency of specific capacitance on co-solvent concentration. The trend obtained for [BMPy][BF$_4$] solutions in AN is different from [AMIM] [Tf$_2$N] ILs [22]. Addition of 25% of AN to [BMPy][BF$_4$] is capable of resulting the highest value of specific capacitance despite its higher viscosity (figure 1) than other two AN-based solutions. However, nearly 56% AN was needed to obtain the maximum specific capacitance for [AMIM][Tf$_2$N] ILs [22]. Hence, effect of organic solvent on specific capacitance varies with the type of IL. In current work, addition of more AN weakens the ionic nature of the electrolyte by lowering concentration of ionic species and hence specific capacitance reduces for AN_III. On the contrary, 25% of PC shows the lowest performance regarding specific capacitance. Moreover, with increase in amount of PC linear increase in specific capacitance can be

observed from both CV and GCD, which elucidates higher ionic conductivity with larger amount of PC. Literature suggested that ionic conductivity of 0.65 M TEABF$_4$/AN solution is more than thrice of that for 0.65 M TEABF$_4$/PC [6]. This supports our findings for [BMPy][BF$_4$] with AN and PC. Even though PC_III solution offers the highest charge storage capacity among all three PC concentrations, it is not higher than AN_I and AN_II.

3.4 *Analysis of ESR from GCD*

The IR decrease in GCD is resulted as a combined effect of charge transfer resistance and bulk resistance of electrolyte [32], is by definition known as the IR or the ESR. ESR was computed using equation (3) [33] and plotted in figure 7.

$$\mathrm{ESR} = \frac{\Delta V}{\Delta I} \tag{3}$$

where ΔV depicts the difference in potential at the origin of discharge and ΔI is mathematically written as $|I_{\mathrm{charging}}| + |I_{\mathrm{discharging}}|$.

For AN based electrolyte, lower IR decrease was observed as compared to PC (figures 2d and 3d) confirming higher IR with PC (figure 7). The IR values for IL+AN solutions as predicted by GCD reside in the range of 10–20 Ω. Variation of ESR with AN concentration is insignificant even though the
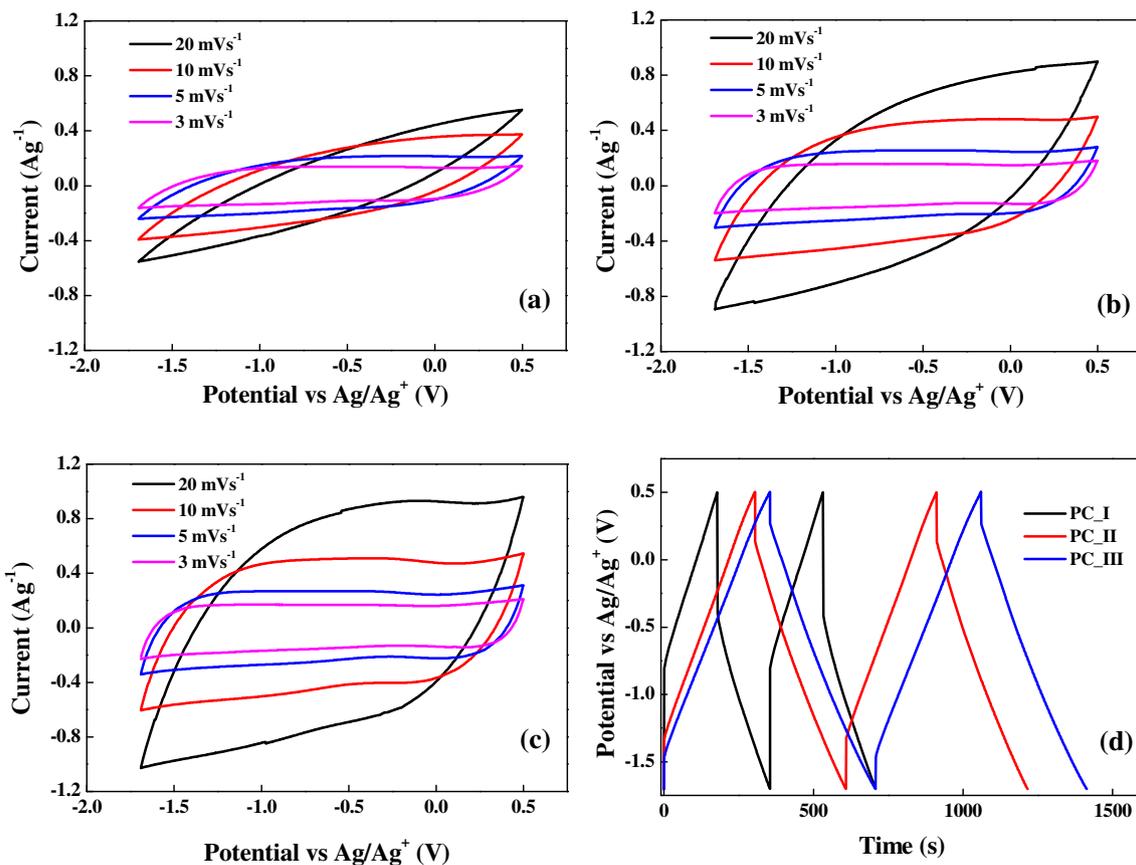
Figure 3. CV plots of [BMPy][BF$_4$] in (**a**) PC_I, (**b**) PC_II, (**c**) PC_III solutions and (**d**) GCD cycles for the three PC based solutions at 0.3 A g^{-1}.
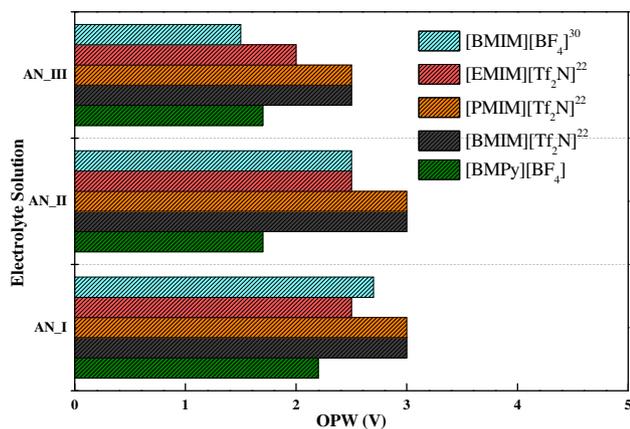

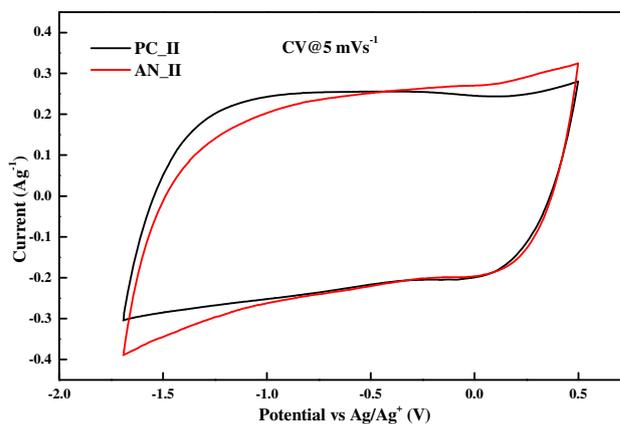**Figure 4.** Comparison of OPW with imidazolium IL based systems with same working electrode.

Figure 5. Comparison of electrochemical stability of AN and PC based IL solutions.

highest can be observed for AN_III. However, PC solutions show reduction in ESR with increase in solvent concentration. PC_I electrolyte solution offers the highest IR among all, resulting in the lowest current density (figure 3a) and specific capacitance (figure 6). Such a high value of ESR is not favourable for the durability of the EDLC. The high viscosity ($\sim$20 cp) of this solution eventually reflects in the resistance to

charge transfer by limiting the ion diffusion. Reduction of viscosity, 50% (AN_I, $\sim$10 cp) can lower the ESR by 60 ohms (Ω). Both AN_III and PC_III possess close value of ESR, which is also reflected in charge storage capacity. AN_I and AN_II depict nearly equivalent specific capacitance and ESR (figures 6 and 7) from GCD. However, owing to better OPW of AN_I, it is more favourable for higher energy storage.
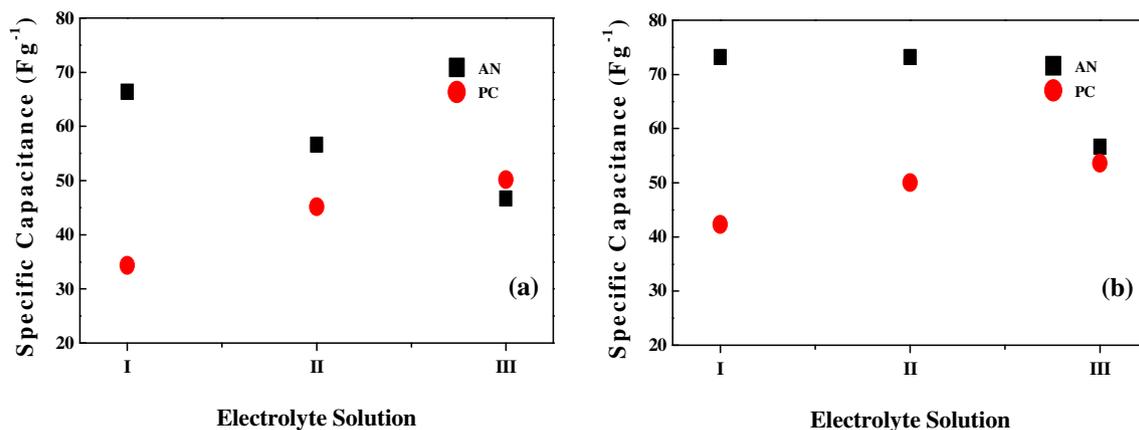
Figure 6. Specific capacitance (**a**) from CV at 3 mV s^{-1} and (**b**) GCD at 0.3 A g^{-1}.
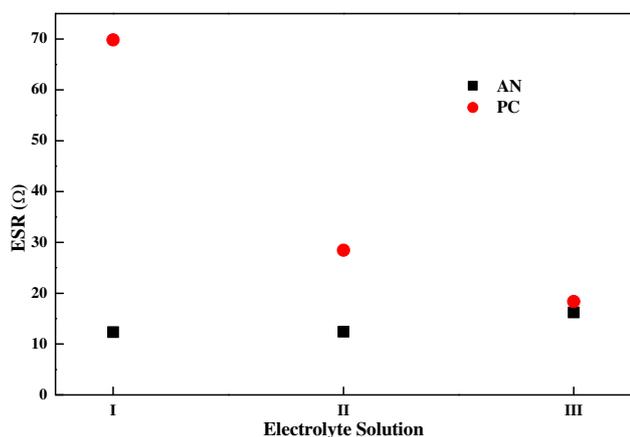

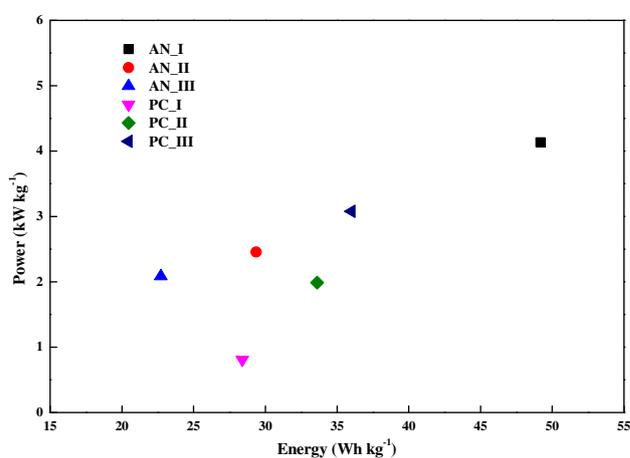**Figure 7.** Equivalent series resistance from GCD at 0.3 A g^{-1}.

Figure 8. Power *vs.* energy plot.

3.5 *Determination of energy and power density*

The conclusive rating of an EDLC is the energy and power densities in order to compare the performance with batteries and fuel cells. Calculation of these two parameters were done using following relations [9], where the OPW and specific capacitance are depicted by *V* and *C*, respectively, ESR denotes the equivalent series resistance and *m* represents the mass of the working electrode.

$$E = \frac{1}{2}CV^2 \tag{4}$$

$$P = \frac{V^2}{4\text{ESR} \times m} \tag{5}$$

AN_I electrolyte solution performs the best by delivering the highest specific energy and power following PC_III (figure 8). The energy and power for AN_I is almost double of the other two AN solutions due to its wider OPW, higher specific capacitance and lower ESR. Despite of having lower ESR than PC_III, AN_II and AN_III results in lower specific power due to their narrower OPW. Higher ESR of PC_I leads to the least specific power. Moreover, the

change in specific power with solvent concentration shows agreement with the ESR data. The observed specific energy values are greater than aqueous KOH [2] systems even though they are significantly lesser than the same obtained for [AMIM][Tf$_2$N] ILs in our earlier work [22]. However, AN_I offers much higher energy density than pure [BMPy][Tf$_2$N] (21 Wh kg^{-1}) with activated carbon electrode [34].

Additionally, reduction in viscosity and enhancement in ionic conductivity of ILs at higher temperature is achievable [35,36], which enhance power density. Therefore, ILs can be used in pure form at elevated temperature. Furthermore, the drawbacks of higher viscosity of room temperature ILs and narrower electrochemical stability of IL + organic solvents can be vanquished by developing novel eutectic mixtures based on IL [37].

3.6 *Electrochemical impedance study*

The results obtained so far elucidate that AN_I and PC_III are the best electrolyte solutions than other two of their
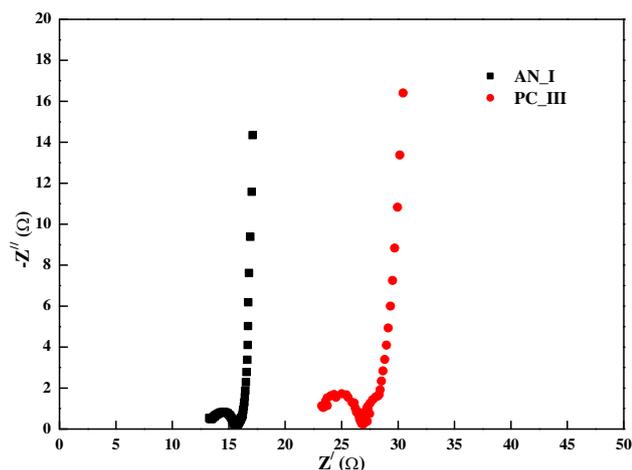
Figure 9. Nyquist plot for the best solutions with AN and PC.

respective categories. Therefore, only these two systems were opted for impedance experiments as mentioned in section 3.3. The Nyquist plot (figure 9) reflects the resistive and capacitive nature of the system in three parts. The first part is the insertion of the plot on the *x*-axis, which corresponds the solution resistance (R_s) and the semicircle whose diameter gives the charge transfer resistance (R_{ct}). This part is the consequence for the ESR study as discussed already. The charge transfer resistance can be classified as the ionic and electronic resistances [38]. Figure 9 clearly depicts higher R_s and R_{ct} for PC_III than AN_I, which is also proved from reported ESR study (figure 7). The next part shows the Warburg impedance (Z_w) represented by the 45° line. This part is more prominent for PC_III than AN_I, indicating lager diffusional resistances. The last part possesses a nearly vertical end at lower frequencies due to pure capacitive nature. For both the electrolytes, capacitive behaviour of EDLC is confirmed by the steep increase in vertical line of Nyquist plot in the low frequency region. Thus, ions at the lower frequency range easily access the surface area of the working electrode. This leads to a higher contribution of specific capacitance. The vertical tail for AN_I is more noteworthy than PC_III resulting in improved specific capacitance.

4. Conclusions

[BMPy][BF$_4$] IL resulted in narrower OPW than commonly used imidazolium ILs. Addition of organic solvents lowered the viscosity of the IL significantly, weakening the ionic interaction. Both the solvents behaved differently in regard to electrochemical characterization. With the increase in AN wt% in the IL electrolyte, both OPW and specific capacitance decreases with a slight increase in ESR. On the contrary, addition of more amount of PC did not affect the OPW and confirmed large reduction in ESR; hence, enhancement in specific capacitance was obtained.

Impedance studies for AN_I and PC_III revealed good capacitive nature of these electrolyte systems. AN_I has come up as the best electrolyte solution by delivering the highest specific capacitance, energy and power densities. However, PC has wider liquid range than AN and hence can serve for a larger temperature range.

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