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ARTICLE INFO

ABSTRACT

The need of new electrolytes with wide electrochemical window, good stability and conductivity has promoted novel ionic liquids (ILs) as new solutions for supercapacitors. In this work, four hydrophobic room temperature ionic liquids based on organic superbase-derived cations and Trifluoromethanesulfonimide (TFSI) anion were synthetized. The structures of the novel ILs were analyzed, characterized and their performance as a supercapacitor electrolyte was evaluated. The ILs have high decomposition temperatures of up to 490 °C and electrochemical window up to 4.8 V. It was found that there was an optimal chemical structure providing the best stability and operational potential window coupled with moderate conductivity. The IL with the shortest alkyl chain structure provided the highest conductivity but suffered from instability. The performance of the ILs with longer alkyl chains was hindered by lower conductivities and, in the case of the largest chemical structures, also by reduced cyclic stabilities in open air. However, the ionic liquid with moderate alkyl chain length was found to be stable even in open air providing decent conductivity, which can be utilized in future research to develop other hydrophobic ionic liquids suitable as supercapacitor electrolytes.

1. Introduction

Energy storage devices convert available electrical energy into (electro)chemical energy in batteries and supercapacitors to store that for later utilization. A number of different devices and technologies associated with energy applications exist and are commercialized today; however, there is significant room for improvement. The characteristics of the chemical reactions determine the performance of the energy storage device. In batteries, energy conversion takes place in the electrodes via redox chemical reactions, which results in low power densities, whereas supercapacitors have superior power densities due to the fast electrostatic surface interactions. Supercapacitors with high power properties and long cycle life have therefore been long envisioned to supplement and even replace batteries in many electrochemical energy storage application fields. Ionic liquid (IL) research in supercapacitors has grown interest over the past years due to their intrinsic properties compared to traditional organic electrolytes which have several serious disadvantages such as relatively low conductivity, volatility and

flammability of the solvents, toxicity and high environmental impact leading to serious safety concerns and high costs [1,2]. Aqueous electrolytes on the other hand are known to have extremely good conductivity, work safety and non-flammable nature. However, the overall energy storage performance is limited by the maximum potential window of water electrolysis. In carbon-based supercapacitors there are numerous carbon nanomaterial based research reports where the material performance have long been assessed using IL electrolytes alongside with organic electrolytes and aqueous electrolytes [3–9].

Ionic liquids are known to be a large family of synthetic ionic compounds that usually have low melting point, negligible volatility and large potential windows. Typical disadvantage of ILs is high viscosity leading to poor ionic conductivity at room temperature and below, thus limiting their applicability as electrolytes in supercapacitors and, overall, ILs still haven't reached the power performance of organic electrolytes [2,10]. There is, however, still plenty of room to advance and potential to come up with totally new concepts to improve the ILs electrolytic performances in supercapacitor. Because ILs are applied

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non-solvated, they provide charged species at the electrolyte/electrode interface, eliminating a need for electroactive species to diffuse.

As the features of ionic liquids are influenced by both cation and anion structures, choosing the right one is obviously important [11,12]. It has been discovered that the choice of anion has the greatest impact on the characteristics of ILs, especially water miscibility, which is crucial in electrochemical applications. The electrochemical window (EW) of ILs is more significant than specific capacitance since the energy retained by a supercapacitor is related to the square of the operating voltage. Due to water electrolysis, water content is the primary factor determining the electrochemical window of an ionic liquids, narrowing both the cathodic and the anodic potential limits [13–16].

Despite the fact that electrochemical window limitations reflect the electrochemical stability of the ILs, it is challenging to compare different cation and anion combinations because of lack of data on ILs with common ions and undefined IL purities as well as differences in analytical methodologies, conditions and used electrodes [17]. However, some general conclusions can be drawn. For example, halide anions have clearly shown their ability to produce hydrophilic ILs that are miscible with water in any amount, whereas hydrophobic anions are exemplified by BF_4, PF_6, and TFSI. But even though BF_4 and PF_6 are said to exhibit high electrochemical stability, their questionable hydrolytic stability and anticipated emissions of hydrofluoric acid and other compounds prevent their use in IL chemistry from becoming more widespread [18]. Additionally, it was observed that the EWs for TFSI-based ILs with equivalent cations were wider than those for BF_4-based ILs. [19, 20].

The essential features of the optimal IL electrolyte include a wide electrochemical window, low volatility, outstanding thermostability, low viscosity and superior ionic conductivity. In practice it is not straightforward to find all of these properties in a particular ionic liquid. The majority of common ILs are based on dialkylimidazolium cations, which contain an electrochemically active hydrogen in the C2 position of the imidazole ring, which can make them unsuitable for electrochemical operations [21]. Nevertheless, organic superbases with extremely reactive imine nitrogen in the heterocyclic ring, like 1,8-diazabicyclo [5.4.0]undec-7-ene (DBU), can be easily quaternized in high yields to form stable cationic structures which can be easily separated from unreacted materials. There are several different alkylated superbase-derived ionic liquids with TFSI anion that have already been studied, and their physicochemical characteristics, such as thermal behavior, density, viscosity, and electrochemical properties were defined [21–25]. They were shown to have ionic conductivities between 3.2 and 3.5 mS cm^{-1} and EW ranges between 4.3 and 4.6 V, which are broader than that of the typical 1,3-dialkylimidazolium ionic liquids, making them preferable candidates for electrochemical devices.

In this work, four different ILs were synthesized, prompted by the need to produce ILs with enough stability and electrolytic qualities to suit the use of supercapacitors. Organic alkylated DBU superbase-derived ILs with different alkyl chain lengths in the cation structure in conjunction with TFSI anion were prepared. The thermal and electrochemical properties as well as the structures and purities of the synthetized ILs were investigated. The performance and the long-term stability in open air of the synthesized ILs in supercapacitors were then evaluated and compared to a commercial IL.

2. Materials and methods

2.1. Materials

Commercial 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide [Pyr14][TFSI] (Sigma-Aldrich 40963) was used as the reference ionic liquid as obtained. Other ionic liquids were synthesized with use of 1,7-diazabicyclo[5.4.0]undec-7-ene (DBU) supplied by TCI chemicals. Prior to use, the superbase was dried in absolute vacuum and stored with molecular sieves. All the other chemicals such as

bromoethane, 1-Iodobutane, 1-chlorohexane, chloromethyl ethyl ether, bis(trifluoromethanesulfonyl)imide (TFSI) and all the solvents were of analytical purity, acquired from Alfa Aeser and Sigma Aldrich were used as obtained.

2.2. Ionic liquids preparation

Diazabicycloundecene ionic liquids were synthesized according to the brief procedure [26]. The quaternization reaction was carried out in a round bottom flask reactor. 0.1 mol of 1,8-diazabicyclo(5.4.0)undec-7-ene (DBU) was dissolved in cyclohexane and placed in the reactor to which 0.15 mol of halide was slowly added while cooling the slurry in ice bath. The reaction mixture was left to react for 24 h while magnetically stirred at room temperature. After the reaction, solid salt precipitated at the bottom of the vessel while the supernatant cyclohexane layer was decanted. The remaining halogen salt was washed with 200 ml of diethyl ether and vacuum dried at 80 °C. The resulting material was collected and further processed in following step [21,27]. Upon the anion metathesis reaction 0.01 mmol of obtained quaternized DBU salt was reacted with equimolar amount of bis(trifluoromethanesulfonyl) imide lithium salt in 20 ml of deionized water in a round bottom glass reactor supplied with a magnetic stirrer. The mixture was then left to react for 8 h at room temperature forming a separate hydrophobic organic phase. Consequently, the product was then extracted with excess of dichloromethane and dried overnight with $MgSO_4$ desiccant following by concentration under reduced pressure at 90 °C for 12 h to obtain the very pure ionic liquid.

2.3. Characterization

Structures of all synthesized ionic liquids were confirmed with ^{1}H and ^{13}C NMR analyzes made in d-chloroform at room temperature on a 500 MHz Bruker Avance-III HD spectrometer supplied with Bruker SmartProbeTM. The content of carbon, hydrogen, nitrogen and sulfur were detected with CHNS Thermo Fisher Scientific FLASH 2000 analyzer. Water impurities in ionic liquids were followed with a Metrohm 851 Titrando automatic coulometric Karl Fischer (KF) titrator connected to an 860 KF Thermoprep oven. All analyzes were performed at 110 °C in a dry N_2 gas atmosphere with a flow rate of 90 ml min^{-1}. The thermal stabilities of the samples were analyzed by TA Discovery SDT 650 in temperature range of 25–700 °C using heating rate of 10 °C min^{-1}.

The electrochemical windows were determined with cyclic voltammetry using Gamry Reference 620 Potentiostat (Glassy carbon working electrode, silver/silver-chloride reference electrode and platinum counter electrode). Cyclic voltammograms were recorded for three cycles in the potential range −5.0 V to +5.0 V with a scan rate of 0.1 V/s in sample solutions of ionic liquids dissolved in acetonitrile. The sample solutions were first deaerated with N_2 after which the N_2 gas outlet was kept above the solution during the measurement. The conductivity measurements were performed with electrochemical impedance spectroscopy (EIS) measurements with 10 mV potential in frequency range of 1 MHz to 1 Hz, using Princeton Applied Research VersaSTAT 3 potentiostat connected to the measurement cell. Conductivity of the ILs was calculated by dividing the cell constant with the resistance, where the resistance was determined by the intercept of Z''=0 in Nyquist plot. The cell constant was calibrated multiplier of the specific cell conductivity of 0.1 M and 1 M KCl solutions at 20 °C (κ = 11.615 * 10^{-3} S cm^{-1} and 99.17 10^{-3} S cm^{-1}, respectively) obtained from literature [28].

2.4. Supercapacitor measurements

Carboxyl functionalized single wall carbon nanotubes (SWCNT-COOH) from Sigma Aldrich (652490) were used as the electrode material. The CNTs were mixed in isopropyl alcohol (IPA) in 3 g/L ratio and sonicated for 30 min. The CNT suspension was then vacuum filtered on

hydrophilic PVDF filter membrane (Durapore Millipore GVWP4700) in ~2 mg/cm² CNT mass ratio. After 24 h of drying in air, the CNT film easily detached from the membrane and was then subsequently cut into 1 × 1 cm pieces of freestanding SWCNT-COOH films.

Two-electrode cell consisting of two SWCNT-COOH films, a separator filter paper (Whatman 1, cat. no. 1001-047) and current collector plates of Inconel 600 superalloy (Goodfellow) was assembled. (Supporting information, Fig. S1 a). The setup was held together with alligator clips. Before assembly, the CNT electrodes (Supporting information, Fig. S1 b and c) and separator were wetted with ionic liquid electrolyte. The electrochemical performances of the assembled supercapacitor devices were evaluated with Princeton Applied Research VersaSTAT 3 potentiostat. The measurements were done in N₂ atmosphere (in Aldrich AtmosBag, Sigma-Aldrich Z530212) and in open air. The temperature related measurements were done using a hot plate where the temperature was measured with a K-type thermocouple.

3. Results and discussion

3.1. Ionic liquid study and optimization

For the purpose of this study, four ionic liquids [DBU-C2][TFSI], [DBU-C4][TFSI], [DBU-C6][TFSI] and [DBU-C1-O-C2][TFSI] were prepared and studied along with one commercially available [Pyr14] [TFSI] IL, as shown in Fig. 1a) and b), respectively. [Pyr14][TFSI] was used as a reference IL due to its good conductivity and stability [29,30] and having the same TFSI anion as the synthesized DBU-cation based ILs. All synthesized materials were analyzed by NMR, elemental analysis and Karl-Fisher titration to confirm their structure and purity (see Supporting information).

Study of thermal stability of synthesized ILs (Fig. 1c) showed that the materials were stable up to the range of temperatures 362 to 490 °C. [Pyr14][TFSI] has been reported to be stable up to 452 °C [29] which is slightly lower than the highest decomposition temperature here. Alkylated ionic liquids had a temperature stability as high as 490 °C while the ether modified IL showed drastic decline in thermal stability and were stable up to 362 °C (Fig. S2, SI). More precisely, the ether modified IL displayed two prominent drops in thermal stability at 362 °C and at 480 °C. Lower temperature is most probably associated with the decomposition of the ethoxy group and higher with the decomposition of the appended DBU.

Electrochemical characteristics of ionic liquids, such as electrochemical window, conductivity and water content are presented in Table 1. It is known that altering the alkylated cation chain of IL may change its characteristics, and that IL hydrophobicity increases with lengthening alkyl chains, producing wider EW [31,32]. However, the dominant impact on electrochemical stability comes from the anion

variation. In this work, it was found that for the case of relatively narrow range of alkyl chains, from C2 to C6, the length does not visibly affect the stability of the cation as much, resulting in electrochemical window range of 4.7–4.8 V which is in the same range of common commercial and lately reported novel based ILs with TFSI-anion (Table S1, SI). It has to be noted that these values are also are higher than in other kinds of ILs, such as imidazolium, sulfonium and guanidinium based ones [33]. It can be stated that even though there are some differences in water impurities in ILs this does not affect the electrochemical stability, which is almost constant. This is aligned with the claim that in case of clearly hydrophobic ILs the water impurities have minor influence on the overall characteristics [24]. Present water impurities are in the scope of commercial ILs (for [Pyr14][TFSI] ≤ 400 ppm) and, therefore, are considered acceptable. It is also important to note that the CVs of the screened EWs show some minor peaks, bumps, or plateaus as visible in Fig. S3. These could be a consequence of a minor increase in currents brought on by processes like double layer charging [34] or presence of impurities, which is relatively common for the ILs [16].

The conductivity appears to have a clear trend where the ILs with longer alkyl chains have lower conductivities. Previous reports have suggested that the relationship between the molar conductivities of the ILs and their self-diffusion might explain this tendency [21,35,36]. Nevertheless, this could also be explained by increased Van der Waals interaction and hydrogen bonding between anion and cation alkyl chains. Higher number of hydrogen atoms in the longer chains results in stronger interactions and thus lowered mobility of charged species [37]. Similarly, in literature examples of ILs incorporating the imidazolium [11] and pyrazolium cation [33] extending the cation alkyl chains resulted in increased viscosities. Furthermore, the ether bond in the alkyl chain in [DBU-C1-O-C2][TFSI] did not bring any significant improvement to the ILs conductivity and stability. Though research in this area is encouraging, as ether modification has been shown to reduce viscosity and improve conductivity of ILs [38].

3.2. Supercapacitor performance evaluation

The supercapacitor structure was set up in classical stacked assembly as described in the experimental section. The capacitance performance of the synthesized ionic liquids in comparison to commercial [Pyr14] [TFSI] IL was first assessed with cyclic voltammetry in 2.5 V potential window. The synthesized [DBU-C2][TFSI] IL was found to be unstable and solidified after few cycles in 2.5 V voltage window. A clear redox peak can be seen at ~2 V during the first cycle when using slower scanning speeds as well as the subsequent capacitance drop in following cycles (Supporting information Fig. S4 a) ending in solidification in a few minutes. Therefore, [DBU-C2][TFSI] was determined to be unsuitable as supercapacitor electrolyte in our experiments as synthetized. The
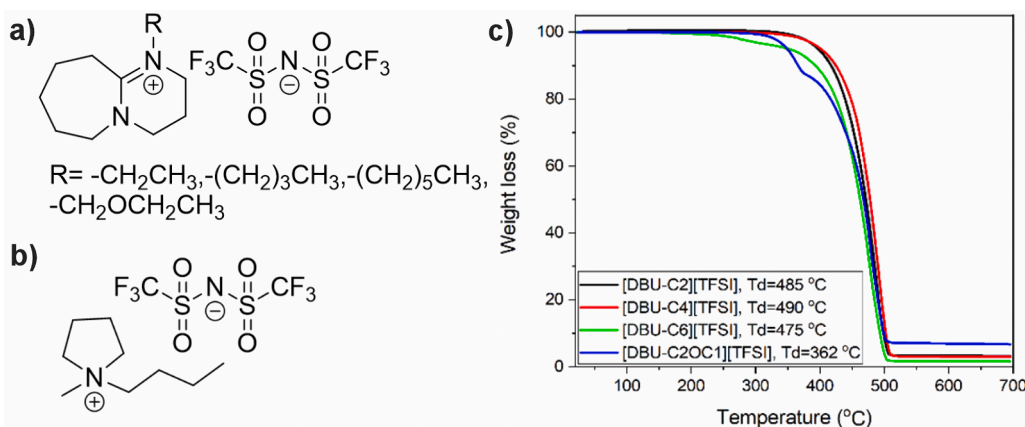
Fig. 1. (a) Structure of the synthesized [DBU-C2][TFSI], [DBU-C4][TFSI], [DBU-C6][TFSI], [DBU-C1-O-C2][TFSI] ionic liquids and (b) commercial [Pyr14][TFSI] ionic liquid. (c) Thermal gravimetric analysis curves for the synthesized ionic liquids.

Table 1
Summary of electrochemical windows and conductivities of the synthesized ionic liquids.

Ionic liquid	Anodic limit potential (V)	Cathodic limit potential (V)	Electrochemical window (V)	Conductivity (mS/cm)	Water content (ppm)
[DBU-C2] [TFSI]	2.7	−2.0	4.7	1.398	348
[DBU-C4] [TFSI]	2.5	−2.2	4.7	0.979	673
[DBU-C6] [TFSI]	2.6	−2.2	4.8	0.704	890
[DBU-C1-O-C2] [TFSI]	2.4	−2.4	4.8	1.001	685

exact mechanism for this strong redox reaction is unknown but is likely due to some impurities within the IL reacting under applied electric voltage resulting in elevated melting temperature of the IL. As the melting point of [DBU-C2][TFSI] is close to room temperature [21] even a small change in the liquid mixture can result in solidification in room temperature. Regardless, the close to room temperature melting point even in completely pure IL would significantly limit the applicability of the IL in supercapacitor applications. To manipulate the ILs melting point, one approach is to increase the chain length in the alkylated ILs. The increase of the alkyl chain length often results in less effective ion packing and a lower melting point in cations with carbon chains longer than three carbons. Indeed, on the example of quaternary ammonium ionic liquids it was proven that increasing the asymmetry of cation through attachment of hetero alkyl chain leads to lowering of the ILs melting point [39–41]. However, the longer alkyl chain also reduces the mobility of the ions resulting in reduced conductivity.

In cyclic voltammetry measurements (Fig. 2a) the commercial [Pyr14][TFSI] provided the highest specific device capacitance of 11.3 F/g with 10 m/s scan speed while the [CBU-C4][TFSI], [CBU-C6][TFSI] and [DBU-C1-O-C2][TFSI] provided capacitances of 9.7 F/g, 5.8 F/g and 7.4 F/g respectively. Using higher scan rates, the capacitance dropped significantly with all ILs. This was due to high series and charge-transfer resistances at room temperature ($R_s \approx 110~\Omega$, $R_{ct} \approx 80~\Omega$ for [DBU-C4] [TFSI], $R_s \approx 180~\Omega$, $R_{ct} \approx 130~\Omega$ for [DBU-C6] [TFSI] and $R_s \approx 120~\Omega$, $R_{ct} \approx 90~\Omega$ for [DBU-C1-O-C2][TFSI] (Supporting information Figure S4 b) caused by the relatively high viscosity of the synthesized ionic liquids whereas the commercial [Pyr14][TFSI] provided comparable lower resistances ($R_s \approx 40~\Omega$, $R_{ct} \approx 50~\Omega$). Because of their high molecular weight, ionic liquids are known to have high viscosities [42], which in turn

limits their conductivity [43] and thus the performance as supercapacitor electrolyte. This behavior can also be seen here as in elevated temperatures the resistances of the assembled supercapacitors dropped drastically resulting in ~200 % to ~800% improvements in capacitances. The ILs also demonstrated excellent temperature stability up to 120 °C (Fig. 2c and d) when using moderate 100 mV/s scan rate. The increased temperature decreases the viscosity of the ionic liquids, resulting in increased ion mobility and conductivity [21]. To determine the stability of the ionic liquids in open air, a series of experiments were performed out of the glovebox. It was found that all tested ionic liquids performed similarly in open air as in N_2 atmosphere (Fig. 2e and f). This affirmed the hydrophobic characteristic of the TFSI anion in the tested ILs resulting in excellent stability in open air atmosphere.

The stability and capacitance retention performance of the ionic liquids were then assessed with increasing potential windows (Fig. 3a). Of the synthesized ILs, the [DBU-C4][TFSI] exhibited stabile potential window up to 3.4 V with 85 % retention followed with recovery to 98 % after 12 h rest period. However, in higher potential windows, the performance starts to drop quicker without recovery. With [DBU-C4][TFSI] this recovery behavior was seen after each period of 100 cycles in all tested potential windows whereas the capacitance performance with [DBU-C6][TFSI] and [DBU-C1-O-C2][TFSI] ionic liquids steadily dropped to ~60 % after 100 cycles with subsequent 3.0 V, 3.2 V and 3.4 V potentials without recovery. One possible reason for this could be that some redox reactions are occurring within [DBU-C6][TFSI] and [DBU-C1-O-C2][TFSI] in over 3 V potentials that are not easily detectable from the CV-curves. The byproducts of these reactions are likely then to foul the electrode surface leading to smaller active surface area in subsequent charging cycles. The assembled supercapacitor with commercial
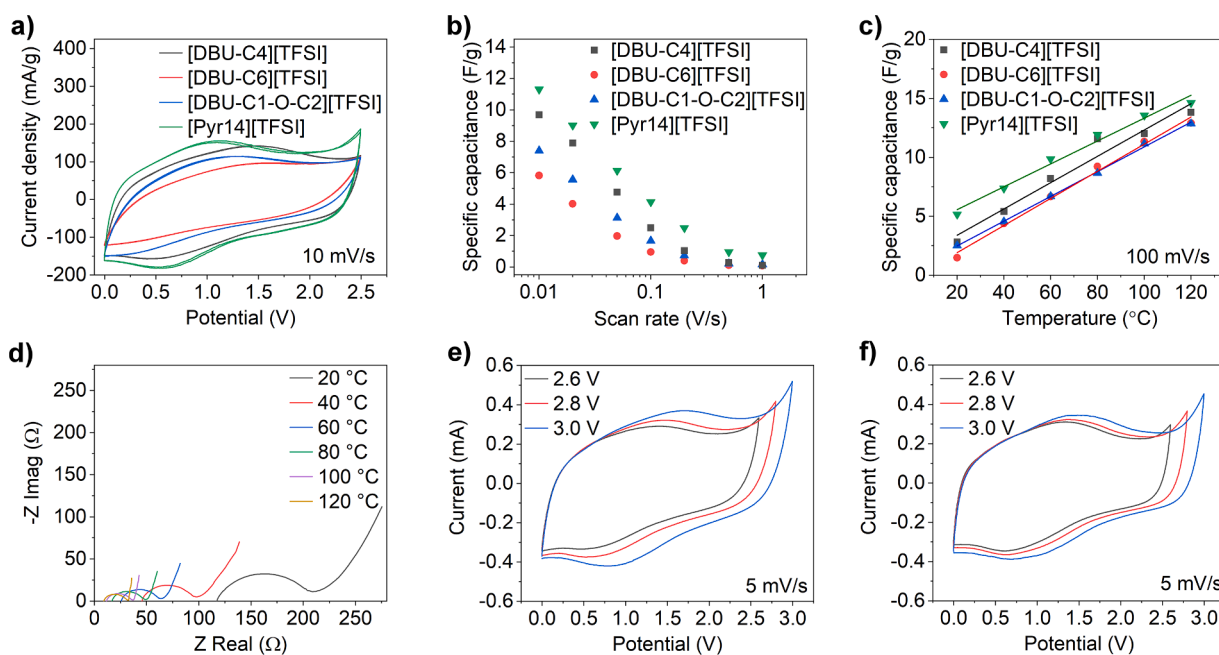
Fig. 2. (a) Cyclic voltammetry curves of the assembled supercapacitors with different ionic liquid electrolytes using 10 mV/s scan rate. (b) Calculated specific capacitances with different scan rates in cyclic voltammetry, (c) Calculated specific capacitances at different temperatures measured with cyclic voltammetry with 100 mV/s scan rate. (d) Nyquist diagrams of EIS measurement of supercapacitor assembly with [DBU-C1-O-C2][TFSI] electrolyte at different.
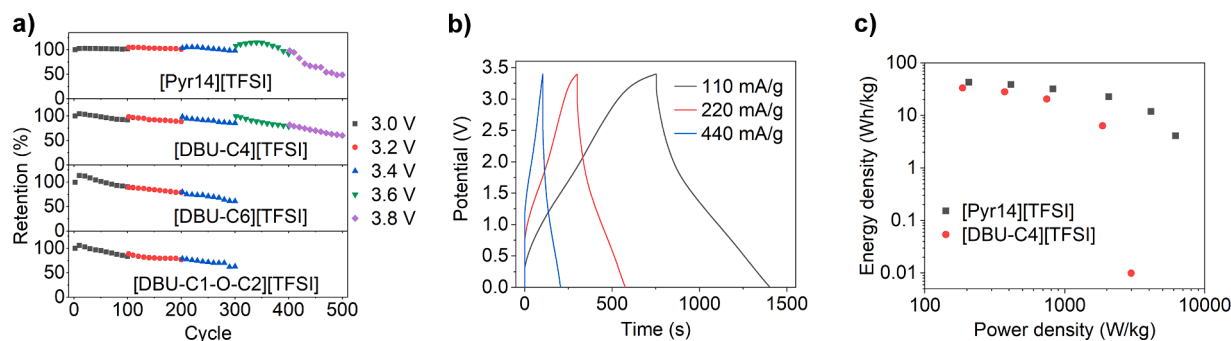
Fig. 3. a) Cyclic potential window evaluation, b) Charge-discharge curves of supercapacitor with [DBU-C4][TFSI], c) Ragone plot of [DBU-C4][TFSI] and commercial [Pyr14][TFSI] ionic liquids.

[Pyr14][TFSI] IL still had retained 98 % of its original capacitance up to potential window of 3.4 V giving much more stable retention performance without the need of recovery period. Interestingly, after the GCD measurements with 3.4 V window, the positive current collector plate showed signs of corrosion with [Pyr14][TFSI] ionic liquid, whereas the plates were still clear after the measurements cycles with [DBU-C4] [TFSI] (Fig. S5, supporting information) indicating that [DBU-C4] [TFSI] had better stability at 3.4 V potential window. This is in agreement with the previously reported results where [Pyr14][TFSI] has been shown to have good cyclability up to ~3.5 V potential range using activated carbon electrodes in a full cell setup [44,45].

The performance of [DBU-C4][TFSI] supercapacitor was further assessed with galvanostatic charge–discharge measurements in 3.4 V potential range (Fig. 3b) and compared to the commercial [Pyr14] [TFSI]. With very low current density (110 mA/g) the specific device capacitance reached 21 F/g whereas with moderately higher current density (440 mA/g) the respective capacitance was 13 F/g which is close to the value measured with CV at the lowest scan rate used. With higher current densities the voltage drop caused by the resistances is clearly visible limiting the power performance of [DBU-C4][TFSI] compared to the commercial [Pyr14][TFSI]. However, the highest energy density values were relatively close to each other (33 Wh/kg and 43 Wh/kg respectively) with respective maximum power densities achieved being 3.0 kW/kg and 6.2 kW/kg (Fig. 3c). Overall, when evaluating the performance of the synthetized ionic liquids in a full cell supercapacitor, [DBU-C4][TFSI] gave the best performance and stability providing slightly poorer performance numbers than the commercial IL. The performance was mainly limited by higher resistivities which affected the performance especially in high power densities at room temperature.

4. Conclusions

In this work, four different DBU superbase-derived ILs with TFSI anion were synthesized and characterized and their performance was evaluated as supercapacitor electrolyte. [DBU-C2][TFSI] had the shortest alkyl chain in the cation structure and thus exhibited the highest conductivity but was found to be electrochemically unsuitable at room temperature due to the close to room temperature melting point. ILs with longer alkyl chains had a slightly wider electrochemical window (4.7 vs 4.8 V) but suffered from reduced conductivity. [DBU-C4][TFSI] exhibited excellent long term electrochemical stability even in open air environment, with up to 3.4 V potential window in full cell setup and had the best overall performance of the synthesized ILs providing device energy densities close to commercial [Pyr14][TFSI] IL using SWCNT-COOH electrodes (33 Wh/kg and 43 Wh/kg respectively). Performance of the ILs with larger cation chemical structures were found to be less electrochemically stable in cyclic testing in open air and was also hindered by the lower conductivity in case of the largest alkyl chains. It was observed that there was an optimal structure for DBU-based ionic liquid for room temperature supercapacitor application which can be

utilized in future research upon development of hydrophobic ionic liquids as supercapacitor electrolytes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The measurement data and the data for the figures in this research is available at data repository Zenodo: DOI: https://doi.org/10.5281/zenodo.10091264.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.electacta.2023.143659.

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