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Posibility of using 1-alkoxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides as Electrolytes for Electrochemical Capacitors

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1-alkoxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides have been successfully synthesized in high yields by the reaction of chlorides or bromides with lithium bis(trifluoromethylsulfonyl)imides. All ionic liquids (ILs) obtained were heavier than water and their densities ranged from 1.28 to 1.50 $g \cdot mL^{-1}$. They were thermally stable and all showed 50% thermal decomposition at around 450˚C. Electrochemical characterization of obtained ILs was also performed in order to assess the possibility of using synthesized ILs as electrolytes for electrochemical capacitors. The conductivity of these new compounds and capacitance properties over a wide range of temperatures were performed. A good correlation of the physical properties of ILs with capacitance values was observed.

Keywords: Ionic liquids, synthesis of ionic liquids, electrolyte, electrochemical capacitor

1. INTRODUCTION

Synthesized ionic liquids (ILs) have been developing since the early 1990s. These compounds of unique, inherent properties have found a lot of applications in various branches of the industry. In electrochemistry, they have turned out to be very useful as electrolytes. Their most valuable features are that they are nonflammable, nonvolatile, chemically and thermally stable and have a wide electrochemical potential window. Especially the possibilities to operate in the wide range of potential (up to 6V, average 3.5 - 4.5V) without the decomposition of electrolytes distinguish these substances from organic (up to 2.7V) and aqueous electrolytes (up to 1.23V) 1,2. Nevertheless, the ILs are characterized by low conductivity and high viscosity, which makes it hard to moisten microporous carbon material.. These cause a decrease of their effectiveness as electrolytes in electrochemical double layer capacitors (EDLC) 34.

On the other hand, the ionic liquids technology offers the possibility of designing new compounds with expected features. It was noted that both anions and cations are affected on the inherent properties of ionic liquids as conductivity, thermal stability and others. The anions: bis(trifluoromethylsulfonyl)imide ($TFSI^-$) and tetrafluoroborate (BF_4^-) found the wider application in electrochemistry. The first of them guarantees the high temperature safety and durability of electrochemical devices 4. The most common cations are imidazolium and pyrrolidinium cations, not only in the electrochemical branch. While the former typically display the highest conductivities, the latter feature the widest electrochemical window, even exceeding 5V 25.

In addition, the governments and industry put emphasis on the ecological solution, also in the production of electrochemical devices, such as capacitors, fuel cells. The capacitors based on the electrode of activated carbon and ionic liquids as electrolyte are an eco-friendly innovation. In the majority of previous works the ionic liquids were mixed with the organic solvents (for example: polycarbonate PC, acetonitrile ACN) for increasing their conductivity 2,3. These still used the toxic, flammable substances and it is not the best way. The objective was to synthesize solvent-free ionic liquids electrolytes with good electrochemical properties. In the literature we can also find another kind of application of ionic liquids as electrolytes in supercapacitors. They can be based on the polymer electrolytes for all-solid-state supercapacitors, and offer promising perspectives for further development of capacitors 6-8. Moreover, studies are conducted ino the addition of organo-redox shuttle as hydroquinone to ionic liquids electrolytes to improve the capacitance by psedocapacitance reaction 9.

In our studies we tested the ionic liquids with pyridinium cations with alkyloxomethyl substituents and $TFSI^-$ anion as an electrolyte. The group of ILs whose structure based on pyridine ring has not been widely studied for capacitor applications. Mayrand-Provencher et al. applied the ionic liquids based on pyrilidium for capacitors with film RuO_2 electrodes. The mono-substituted pyridinium cations were used. They found this class of ionic liquid very promising in the case of their low viscosity (from 2.77 to 87.9 cP) along with conductivities ranging from 1.10 to 11.25 mS/cm 10. They also showed that the length of the alkyl chain has an influence on the properties of ILs. Moreover, the influence that the length of alkyloxomethyl substituent of pyridine ring has on the electrochemical properties was also researched. Furthermore, Sato et al. showed that ionic liquids with a methoxyethyl group incorporated into the aliphatic quaternary ammonium cations, such as *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium exhibit satisfying properties as electrolytes in EDLC. In this design of ionic liquids $TFSI^-$ and BF_4^- were also chosen as anions 5.

Ionic liquids based on 4-(dimethylamine)pyridine are reported in scientific publications. 1-Alkoxymethyl-4-(dimethylamine)pyridinium acesulfamates have been successfully tested as components of potential wood preservatives 11. 1-Butyl-4-(dimethylamine)pyridinium di(cyano)amide 12, 4-(dimethylamine)-1-methylpyridinium carbonate and methylcarbonate 13 as well as 4-(dimethylamine)-1-hexylpyridinium methanesulfonate 14 are patented as novel base stable ionic liquids and therefore used as solvents in chemical reactions, especially base catalysed chemical reactions and reactions comprising the use of strong bases. 1-alkyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides were synthesized of homologues C_1, C_2, C_4 and C_6 15 -21.

The aim of this work is to demonstrate both the physicochemical and electrochemical properties of ionic liquids based on alkoxomethyl derivatives of 4-(dimethylamine)pyridinium and $TFSI^-$ anion and their potential application as electrolytes in EDLC.

2. EXPERIMENTAL METHODS

2.1. Preparation of 1-alkoxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides

A saturated aqueous solution of $LiN(SO_2CF_3)_2$ was added to a stoichiometric amount of a saturated hot aqueous solution of 1-alkoxymethyl-4-(dimethylamine)pyridinium chlorides prepared according to the published method 2223. The mixture was stirred at room temperature for 2h, which ensured a heterogeneous mixture. After the phases were separated, the aqueous phase was decanted and the obtained salt was washed with water until chloride ions were no longer detected using $AgNO_3$. The prepared salt was dried for 10 h at 80ºC in vacuum (20 mmHg).

^{1}H NMR spectra were recorded on a Varian XL 300 spectrometer at 300 MHz with tetramethylsilane as the standard; ^{13}C NMR spectra were recorded on the same instrument at 75 MHz. A Metter Toledo DA 110M scale was used for the mass/density measurements, while a micro Ostwald viscometer was used for viscosity measurements. Melting points were determined by Mettler Toledo DSC Instruments model cooled with an intracooler. Thermal decomposition temperatures were measured in the dynamic heating regime using a TGA (Mettler Toledo Star^e TGA/DSC1 unit (Leicester, UK)) under nitrogen. NMR data of selected ILs are shown below.

*1-methyloxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imide (**IL1**)*

^{1}H NMR ($CDCl_3$) 3.27 (s, 6H), 3.36 (s, 3H), 5.33 (s, 2H), 6.89 (dd, J = 4.0, 2H), 8.06 (dd, J = 4.0, 2H), ^{13}CNMR 40.2, 56.9, 87.2, 107.7, 113.3, 117.6, 121.8, 126.1, 140.6, 157.1,

*1-ethyloxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imide (**IL2**)*

^{1}H NMR ($CDCl_3$) 1.21 (t, J = 7.0, 3H), 3.27 (s, 6H), 3.56 (t, J = 5.6, 2H), 5.37 (s, 2H), 6.87 (dd, J = 4.0, 2H), 8.07 (dd, J = 4.0, 2H), ^{13}CNMR 14.5, 40.3, 65.8, 85.9, 107.8, 113.4, 117.6, 121.9, 126.2, 141.2, 157.1,

*1-propyloxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imide (**IL3**)*

^{1}H NMR ($CDCl_3$) 0.89 (t, J = 7.4, 3H), 1.59 (sec, J = 10.1, 2H), 3.28 (s, 6H), 3.44 (t, J = 6.6, 2H), 5.38 (s, 2H), 6.89 (dd, J = 3.6, 2H), 8.07 (dd, J = 3.7, 2H), ^{13}CNMR 10.1, 22.3, 40.3, 71.7, 86.1, 107.8, 113.4, 117.6, 121.9, 126.1, 140.5, 157.1,

*1-butyloxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imide (**IL4**)*

^{1}H NMR ($CDCl_3$) 0.89 (t, J = 7.3, 3H), 1.54 (m, 2H),1.34 (m, 2H), 3.28 (s, 6H), 3.48 (t, J = 6.6, 2H), 5.38 (s, 2H), 6.89 (dd, J = 4.0, 2H), 8.07 (dd, J = 4.0, 2H),^{13}CNMR 13.5, 18.8, 31.0, 40.3, 69.9, 86.1, 107.8, 113.4, 117.6, 121.9, 126.2, 140.5, 157.1,

*1-pentyloxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imide (**IL5**)*

^{1}H NMR (CDCl$_3$) 0.87 (t, *J* = 9.9, 3H), 1.57 (q, *J* = 6.9, 2H),1.27 (m, 4H), 3.28 (s, 6H), 3.47 (t, *J* = 6.5, 2H), 5.38 (s, 2H), 6.89 (dd, *J* = 3.9, 2H), 8.07 (dd, *J* = 4.0, 2H),^{13}CNMR 13.7, 22.1, 27.7, 28.6, 40.3, 70.2, 86.1, 107.8, 113.3, 117.6, 121.6, 126.1, 140.5, 157.1,

*1-octyloxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imide (**IL8**)*

^{1}H NMR (CDCl$_3$) 0.87 (t, *J* = 6.7, 3H), 1.28 (m, 10H), 1.56 (t, *J* = 7.1, 2H), 3.28 (s, 6H), 3.47 (t, *J* = 6.5, 2H), 5.37 (s, 2H), 6.89 (dd, *J* = 6.0, 2H), 8.07 (dd, *J* = 5.8, 2H), ^{13}CNMR 14.0, 14.1, 22.5, 25.7, 29.02, 29.09, 31.6, 40.3, 70.3, 86.2, 107.8, 113.3, 117.6, 121.7, 126.1, 140.5, 157.1.

2.2. Electrochemical experiment

All electrochemical investigations were performed by using pure ILs (1-alkyloxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides) without any additional solvent. The electrochemical impedance spectroscopy was used for conductivity measurements. For capacitance measurements, NORIT® carbon after chemical activation (KOH), with a specific surface area of 2070 m^2/g was used. Cycling voltammetry, galvanostatic and electrochemical impedance spectroscopy experiments were performed with a two electrode Swagelok system to estimate capacitance values expressed in F/g per one electrode. All electrochemical measurements were performed by using VMP/3 (BIOLOGIC, France).

3. RESULTS AND DISCUSSION

1-alkoxymethyl-4-(dimethylamine)pyridinium chlorides were prepared in very good yields by the nucleophilic attack of 4-(dimethylamine)pyridine on chloromethyl alkyl ethers according to the S$_N$1 mechanism. The obtained halides were used as synthetic precursors for ILs. The metathesis reactions were conducted in aqueous solutions using the LiN(SO$_2$CF$_3$)$_2$, and gave high yields (90÷97%). The product salts are listed in Table 1. Almost all of the prepared salts were liquid at room temperature (RTILs).

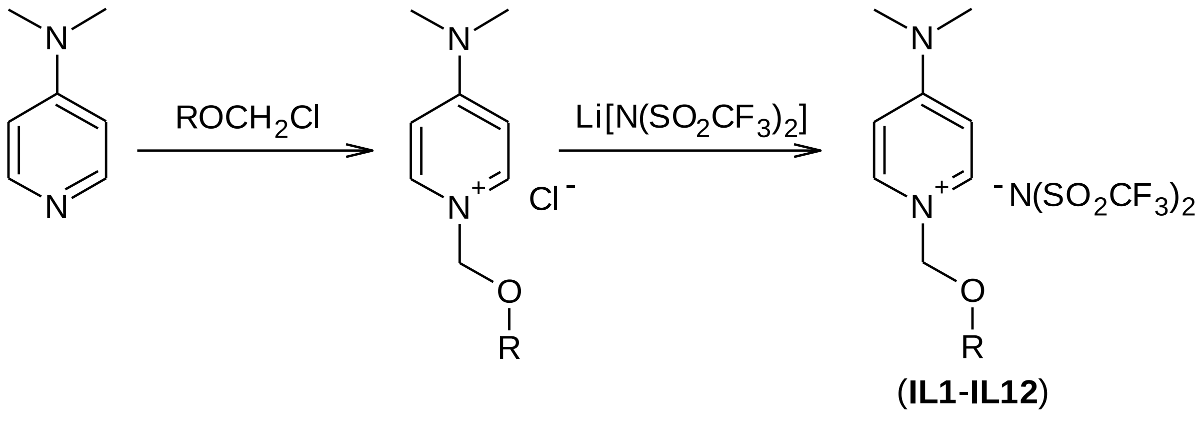

Figure 1. Preparation of 1-alkoxymethyl-4-(dimethylamine)pyridinium salts

All of the salts were found to be stable in air, and in common organic solvents such as $CHCl_3$, ethyl acetate, and ethanol. The RTILs showed high solubility in alcohols, DMSO, ethyl acetate, and $CHCl_3$, but were visually immiscible with hexane and water.

Some physical properties of the new RTILs were studied. All of the RTILs were found to be denser than water. Density values at 20ºC are presented in table 1. The densities ranged from 1.28 to 1.50 g·mL^{-1}. As is typical of RTILs with a range of alkyl chain lengths, increasing chain length means a decrease in density. Viscosity data at 20ºC are also presented in Table 1. The viscosity/chain length relationship showed the inverse trend to the density/chain length relationship: thus, viscosity increased with increasing alkyl chain length of the cation. The densities slightly increased for the compound contained oxygen atom.

Table 1. The physicochemical properties of the prepared 1-alkyl- and 1-alkoxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides

Salt	R	Yield [%]	M.P[a] [ºC]	Density[b] [g·mL^{-1}]	Viscosity[c] [mPa·s]
IL1	CH_3OCH_2	91	liquid	1.50	89.5
IL2	$C_2H_5OCH_2$	92	liquid	1.46	99.3
IL3	$C_3H_7OCH_2$	94	liquid	1.42	98.6
IL4	$C_4H_9OCH_2$	93	liquid	1.39	97.5
IL5	$C_5H_{11}OCH_2$	95	liquid	1.37	106.7
IL6	$C_6H_{13}OCH_2$	94	liquid	1.34	123.8
IL7	$C_7H_{15}OCH_2$	96	liquid	1.32	138.2
IL8	$C_8H_{17}OCH_2$	95	liquid	1.30	151.3
IL9	$C_9H_{19}OCH_2$	93	liquid	1.28	164.6
IL10	$C_{10}H_{21}OCH_2$	97	28-30	-	-
IL11	$C_{11}H_{23}OCH_2$	93	33-37	-	-
IL12	$C_{12}H_{25}OCH_2$	91	41-44	-	-

[a] Melting points determined by visual observation using a Büchi Melting point B-540.
[b] Density determined by density meter (DDM 2911 - Rudolph Research Analytical) at 20°C.
[c] Viscosity determined using a rheometer (Rheotec RC30-CPS) with coneshaped geometry (C50-2) at 20°C.

The physicochemical properties of the selected bis(trifluoromethylsulfonyl)imides are presented in Table 2. They were thermally stable and all showed 50% thermal decomposition at around 450˚C. Thermal decompositions of 1-alkoxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides were conducted in two stages. The first one began at approximately 300˚C and consisted in eliminating alkoxymethyl substituent from moiety (Fig 2). The evidence is percentage values of weight loss that increases together with the number of carbon atoms in the substituent and that correspond to the percentage of mass of the substituent in the molecular mass of moiety. Pure chloromethylalkyl ethers are also thermally unstable and decompose to formaldehyde and alkyl chloride at the temperature of about 200˚C. In the case of differential scanning calorimetry analysis (DSC) the five liquid salts exhibited glass transition temperatures at range -67÷-70˚C. They fulfill the requirement of United States Advanced Battery Consortium (USABC) and the Department of Energy (DOE) according to the thermal stability of energy storage systems.

Table 2. The physicochemical properties of the selected synthesized salts

Salt	T_g[a]	T_c[b]	T_m[c]	T_{onset}[d]	T_{onset}[e]
IL3	-67	-	-	308	462
IL7	-70,3	-22	5,1	298	455
IL8	-69,1	-18,8	7,4	304	449
IL11	-	-3,9	34,3	300	452

[a] Glass transition temp determined by DSC.

[b] Crystalization temp determined by DSC

[c] Melting point on heating determined by DSC.

[d] Decomposition temp determined from onset to 5 wt % mass loss.

[e] Decomposition temp determined from onset to 50 wt % mass loss.

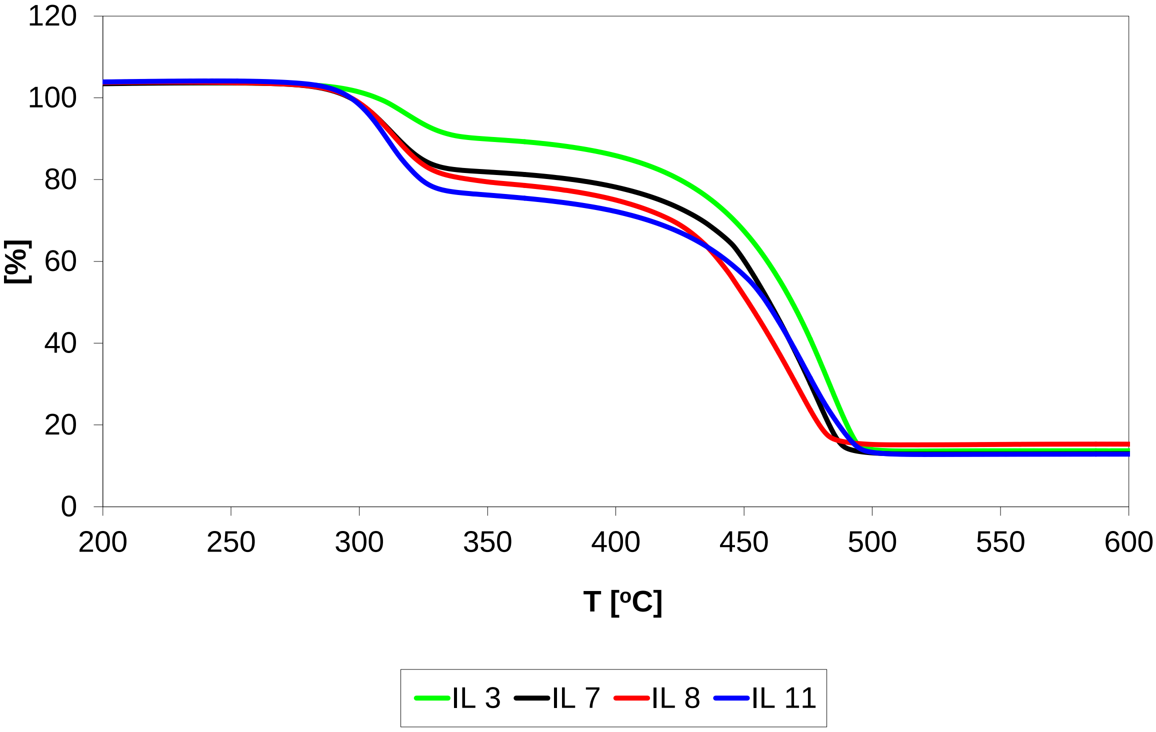

Figure 2. Thermal decomposition of obtained compounds

The electrochemical capacitors should operate in a wide range of temperatures because they are exposed to various environmental conditions. For this reason, the conductivity in the different temperature was examined for each 12 ionic liquids. Three of them which demonstrated the highest values were chosen as the electrolytes in the ELDC. The electrode systems based on the prepared alkoxymethyl derivatives of pyridinium cation were tested in the range of temperature from 25ºC to about 75ºC. It was shown (Fig. 2) that synthesized ILs are stable up to 330º C and have only 25% of decomposition up to 450ºC. It was proved that this kind of electrolytes will be thermally stable in high temperatures.

Moreover, the conductivity is one of the most important features of substances when the potential application as the electrolyte in the capacitors is tested. The most frequent values of conductivity for ILs are found in the range of 0.1-14 mS/cm under normal conditions and 20-30 mS/cm under 60-80ºC 5. Tested derivatives of pyridinium showed conductivity typical of ILs electrolyte, which was shown in Fig.3. Both the anion and cation of the ILs have a significant influence on this parameter. According the literature, the IL with anion TFSI$^-$ showed the relatively high conductivity compared to ILs based other anions used in the electrochemical applications 5. In this study, only cations have an influence on change of conductivity. It is reduced with the increase of the alkyl chain length in the alkoxymethyl substitution of pyridinium ring. A rapid rise of conductivity with temperature for a few ionic liquids is presented in Fig.3. Conductivity values estimated by using impedance spectroscopy in the range from 20 to 75°C have increased significantly with increasing temperatures. It was obvious that higher temperatures decreased the viscosity of the ILs. The similar tendency was showed by Flecher et al. for imidazolium electrolytes 5.

A lower length of ILs chain has a significant influence on value of capacity EDCL, as shown in Fig. 4. The highest capacitance obtained in the room temperature (25ºC) is for IL1 (112 F/g). Increasing capacitance is dependent on the value of conductivity. Charge propagation is another main parameter to take into consideration in electrochemical capacitor applications. The best potentiodynamic curve (Fig.4) was obtained for IL1.

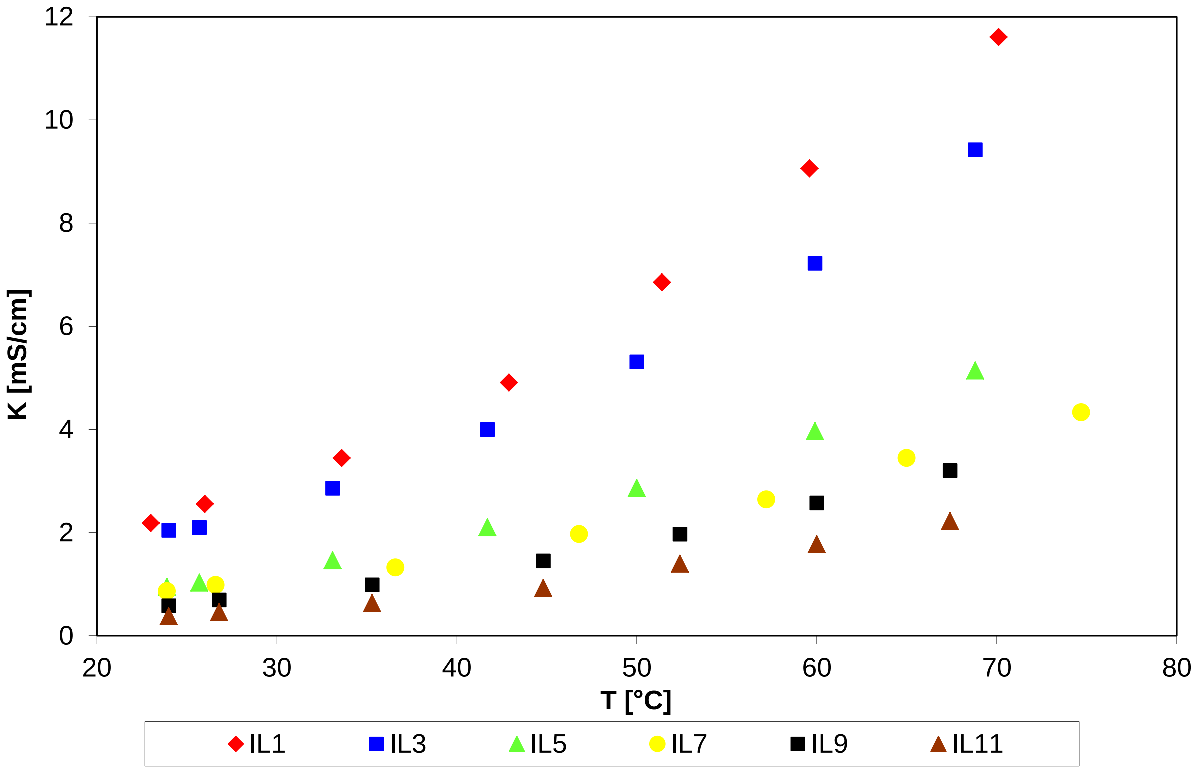

Figure 3. Conductivity versus temperature for 1-alkyloxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides

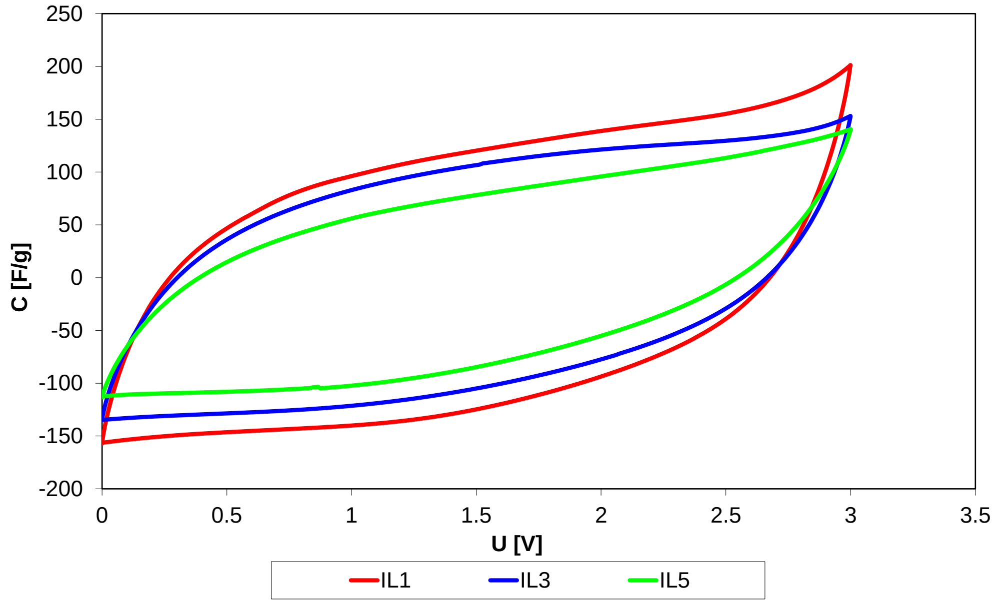

Figure 4. Voltammetry characteristics (5 mV/s at 25°C) for the activated carbon in three different electrolytes: **IL1** – 112 F/g, **IL3** – 95 F/g, **IL.5** – 77 F/g

The electrochemical impedance measurements were conducted in three different temperatures: 25ºC, 35ºC, 45ºC. The relationship of capacitance versus frequency shows that IL1, characterized by the best electrochemical properties, supplies unsatisfactory capacitance at frequencies higher than 100 mHz (Fig.5). With increasing frequency, the capacitance values decrease dramatically. The Nyquist curves are similar to systems working in organic electrolytes with an acetonitrile solvent.

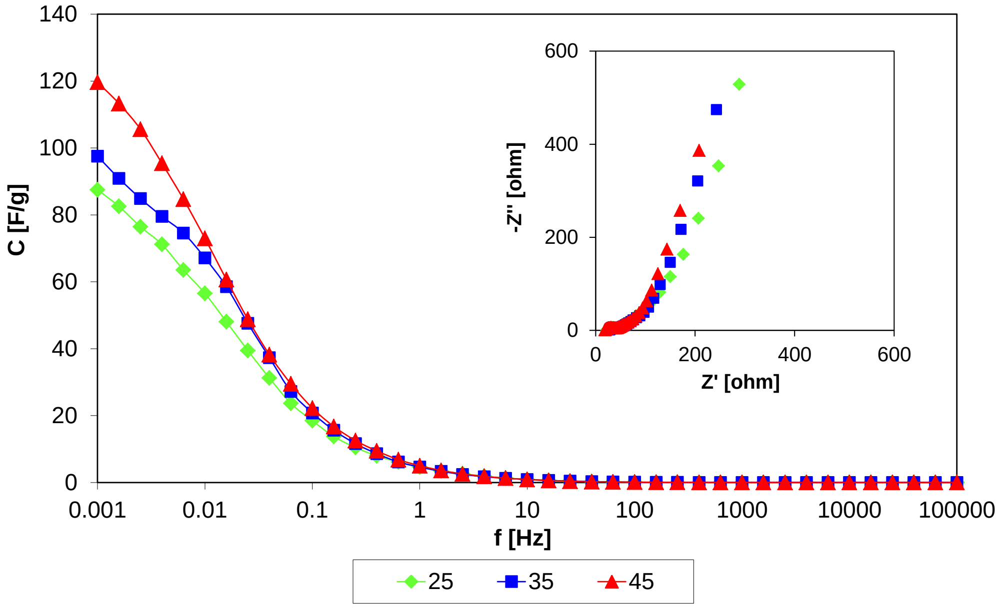

Figure 5. Capacitance versus frequency and Nyquist plots for supercapacitors built from active carbon and **IL1** as electrolyte at different temperatures.

The wide range of a potential window is the most characteristic of ionic liquid electrolytes. The operating range from 0V to 3V was chosen for capacitors based on alkyloxymethyl derivatives of pyridinium. The capacitor with similar electrolytes as N-methoxymethyl-N-methylpyrrolidium also operated in the approximate range 25. It is higher than the range for the aqueous electrolyte (1.23V) and for the organic solvent (2.7V). Due to this fact, energy (which is dependent on voltage squared – formula 1) and power of devices could be enhanced several times.

$$E = \frac{1}{2}CU^2 \qquad 1$$

Fig. 6 presents galvanostaic charge/discharge for two different ILs. The highest value of capacitance is reached for ILs with a smaller length of the chain. The charge/discharge galvanostatic profile was typical of the capacitor with quite a high internal resistance, which is connected with low conductivity of the ILs.

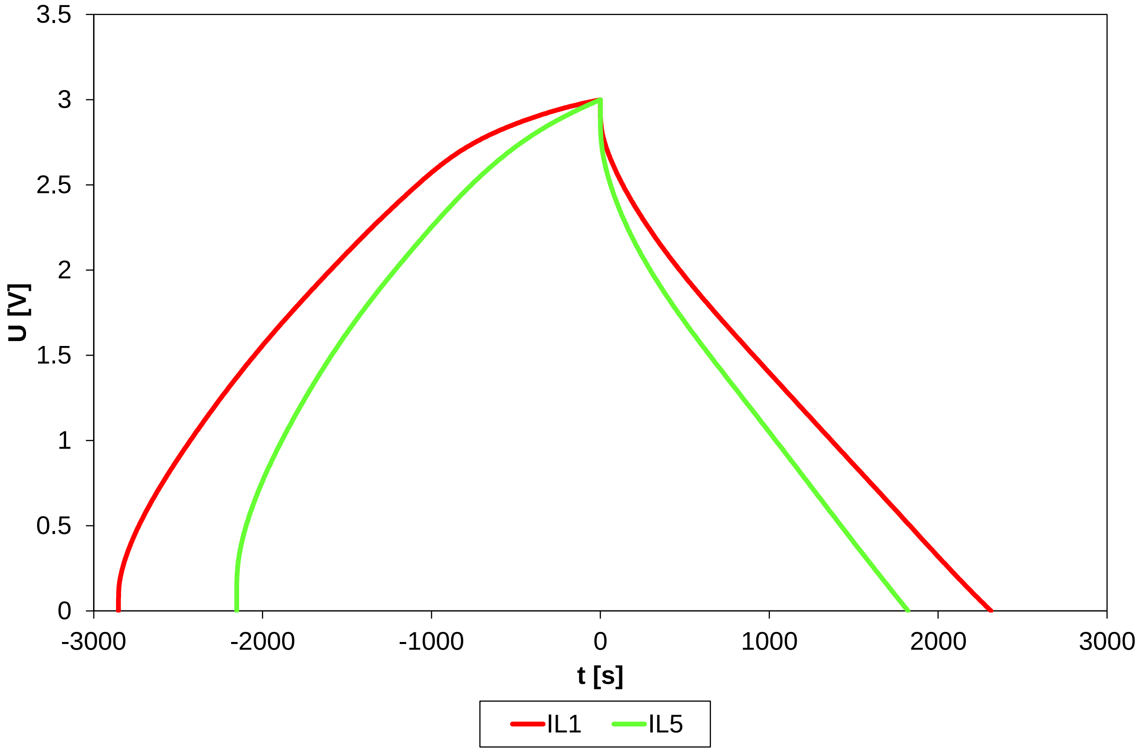

Figure 6. Galvanostatic charge/discharge (100 mA/g at 25°C) for supercapacitors built from active carbon (**IL1** – 157 F/g, **IL5** – 125 F/g)

Obviously, the highest energy of 42.7 Wh/kg (without ohmic drop) has been found for the sample with IL1. It is 12 times higher than for material with similar capacitance working in water medium 3.5 Wh/kg (U = 0.8 V), 9 times higher than psedocapacitance materials working in water medium 4.7 Wh/kg [26] and twice higher than for material working in organic medium ca. 20 Wh/kg [27].

4. CONCLUSIONS

It was demonstrated that the 1-alkoxymethyl-4-(dimethylamine)pyridinium bis(trifluoromethylsulfonyl)imides has good physicochemical properties for application as electrolytes in the supercapacitor based on the carbon material. These compounds are characterized by the high thermal stability (up to 400ºC) and conductivity typical of ionic liquids. Moreover, the conductivity and viscosity increase as the temperature, which has an influence on the capacitance. The highest value of capacitance (157 Fg^{-1}) and energy 12 times higher than for water medium was obtained for electrochemical capacitor based on the IL1. A good correlation of the physical properties of ILs with capacitance values was observed. Increasing capacitance is dependent on the value of conductivity which is strictly connected with the length of the chain. The lower length of the chain ILs, the higher value of conductivity and capacitance.

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References

1. H. Ohno, Electrochemical Aspects of Ionic Liquids, John Wiley & Sons, New Jersey, (2005).
2. C. Arbizzania, M. Biso, D. Cericola, M. Lazzari, F. Soavi, M. Mastragostino, *J. Power Sources*, 185 (2008) 1575.
3. W.-J. Cho, C.-G. Yeom, B. C. Kim, K.M. Kim, J.M. Ko, K.H. Yu, *Electrochim. Acta*, 89 (2013) 807.
4. S.I. Fletcher, F.B. Sillars, R.C. Carter, A.J. Cruden, M. Mirzaeian, N.E. Hudson, J.A. Parkinson, P.J. Hall, *J. Power Sources*, 195 (2010) 1484.
5. T. Sato, G. Masuda, K. Takagi, *Electrochim. Acta*, 49 (2004) 3603.
6. C.-W. Liew, S. Ramesh, A. K. Arof, *Int. J. Hydrogen Energ.*, 39 (2014) 2953.
7. S. Sathyamoorthi, V. Suryanarayanan, D. Velayutham, *J. Power Sources*, 274 (2015) 1135.
8. M.-J. Shi, S.-Z. Kou, B.-S. Shen, J.-W. Lang, Z. Yang, X.-B. Yan, *Chinese Chem. Lett.*, 25 (2014) 859.
9. J. P. C. Trigueiro, R. L. Lavall, G. G. Silva, *J. Power Sources*, 256 (2014) 264.
10. L. Mayrand-Provencher, S. Lin, D. Lazzerini, D. Rochefort, *J. Power Sources*, 195 (2010) 5114.
11. M. Stasiewicz, A. Fojutowski, A. Kropacz, J. Pernak, *Holzforschung*, 62 (2008) 309.
12. M. Muldoon, J.F. Brennecke, E.J. Maginn, E.F.V. Scriven, C.H. McAteer, R. Murugan, Aminopyridinium ionic liquids, US 7687513 B1 20100330, (2010).
13. K. Fukunaga, A. Nishida, Y. Mine, S. Fukuda, K. Kashiwagi Process for preparation of fatty acid alkil esters and catalysts for production of fatty acid alkil esters, WO 2009133846 A1 20091105, (2009).
14. M.J. Earle, U. Frohlich, S. Huq, S. Katdare, R.M. Lukasik, E. Bogel, N.V. Plechkova, K.R. Seddon, Preparation of quaternary ammonium compounds as base stable ionic liquids, WO 2006072785 A2 20060713, (2006).
15. A. Diedrichs, J. Gmehling, *Fluid Phase Equilibr.*, 244 (2006) 68.
16. J.O. Valderrama, A. Toro, R.E. Rojas, *J. Chem. Thermodyn.*, 43 (2011) 1068.
17. P. Luis, A. Garea, A. Irabien, *J. Mol. Liq.*, 152 (2010) 28.
18. S. Stolte, M. Matzke, J. Arning, A. Böschen, W.-R. Pitner, U. Welz-Biermann, B. Jastorffa, J. Rankea, *Green Chem.*, 9 (2007) 1170.

19. J.M. Crosthwaite, M.J. Muldoon, J.K. Dixon, J.L. Anderson, J.F. Brennecke, *J. Chem. Thermodyn.*, 37 (2005) 559.
20. A. Chapeaux, L.D. Simoni, M.A. Stadtherr, J.F. Brennecke, *J. Chem. Eng. Data*, 52 (2007) 2462.
21. B.R. Mellein, S.N.V.K. Aki, R.L. Ladewski, J.F. Brennecke, *J. Phys. Chem. B*, 111 (2007) 131.
22. J. Pernak, L. Michalak, J. Krysiński, *Pharmazie,* 49 (1994) 532.
23. J. Pernak, L. Michalak, *Heterocycles,* 37 (1994) 311.
24. J. Ranke, A. Othman, P. Fan, A. Müller, *Int. J. Mol. Sci.*, 10 (2009) 1271.
25. K. Yuyama, G.Masuda, H.Yoshida, T. Sato, *J. Power Sources*, 162 (2006) 1401.
26. K. Lota, G. Lota, A. Sierczynska, I. Acznik, *Synthetic Met.*, 203 (2015) 44.
27. E. Frackowiak, G. Lota, J. Machnikowski, C. Vix-Guterl, F. Béguin, , *Electrochim. Acta*, 51 (2006) 2209.