

## Materials Science inc. Nanomaterials &amp; Polymers

# Modular Platform for Synthesis of Poly(Ionic Liquid) Electrolytes for Electrochemical Applications in Supercapacitors

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Pyrrolidinium based poly(ionic liquids) (PIL) are successfully obtained and characterized. Special attention is paid to the detailed characterization of the polymer products to determine their molecular-mass characteristics and to establish the composition-property relationship when selecting polymer electrolytes suitable for electrochemical tests. Characterization is performed using: chromatographic methods-combined gel permeation chromatography (GPC) with triple detection-refractometry, UV and laser light scattering; spectroscopy methods-Fourier transform infrared (FTIR), proton (1H) NMR spectro-

scopy; thermogravimetric analysis (TGA) and TGA/gas chromatography (GC)/mass selective detection (MSD). Supercapacitors based on commercial activated carbon, with electrolyte containing PIL dissolved in dimethylformamide (DMF) have been developed and preliminary charge/discharge galvanostatic tests in a two-electrode supercapacitor cell as well as an assessment of electrodes material and its stability in the polymeric ionic electrolyte were conducted. The PIL supercapacitor demonstrates stable capacitance characteristics and is promising for further studies in this direction.

## Introduction

Supercapacitors (SC) are electrochemical energy storage devices that store and release energy by reversible adsorption and desorption of ions at the interfaces between electrode materials and electrolytes. Due to its large energy capacity and long lifetime, as well supply with relatively short time, supercapacitors breakthrough in many applications, such as electric vehicles, portable electronic devices, and power sources for memory backup.<sup>[1]</sup>

Over the last few years, the scientific efforts have mainly focused on the development of composite electrode structures based on carbon, metal oxide and conductive polymer in the supercapacitors.<sup>[1-3]</sup> The achieving these good electrochemical performances are only possible with the correct choice of the electrolyte type. A large variety of electrolytes have been developed and reported in the literature to date. Aqueous electrolytes, organic electrolytes, ionic liquids electrolytes, redox-type electrolytes and solid or semi-solid electrolytes have been explored during the past several decades.<sup>[4-8]</sup> There has been no perfect electrolyte developed, meeting all the requirements. Each electrolyte has its own advantages and disadvantages.

Polymer electrolytes (PE), a type of solid electrolyte, are promising for supercapacitors. Through changing the chemistry of the PE, their ionic conductivity and stability can be readily tuned.<sup>[9]</sup> For supercapacitors, many PE have been developed that conduct protons (H<sup>+</sup>),<sup>[7,10]</sup> lithium (Li<sup>+</sup>) ions,<sup>[11,12]</sup> hydroxides (OH<sup>-</sup>),<sup>[13]</sup> or ionic species from ionic liquids (IL).<sup>[14,15]</sup> Selection of the electrolyte chemistry depends on its material compatibility with the electrodes and current collectors, as well as its suitability for the application. PE can either be pressed between electrodes as free-standing films or applied directly on the electrodes from their precursor solutions during cell assembly.<sup>[16,17]</sup> The latter method provides the much-desired internal contact between the electrode and the electrolyte, minimizing interfacial resistance, and maximizing capacitance of the device in the solid state.<sup>[9]</sup> The properties and physical attributes of the PE are highly dependent on the salt to polymer ratio. For example, with salt-in-PE, the polymer acts as a matrix, where the ionic conductor is dispersed. The polymer swelling, morphology (crystalline vs. amorphous), and uptake of the electrolyte determine its ionic conductivity. With polymer-in-salt electrolytes, the polymer acts mainly as a binder to create a network of conducting sites and provides secondary support for ionic transport. The degree of hydration in these electrolytes affects the number of available ions and the dominant conduction mechanism. Furthermore, these PE are highly sensitive to mechanical stresses and environmental fluctuations. To address these issues, additives such as inorganic fillers, plasticizers, or cross-linking agents have been explored.<sup>[18]</sup> On the other hand, it is known that the properties and physical attributes of the polymers in solid state and in solution depend to the greatest extent on their molecular mass characteristics. Commercially available poly(diallyldimethyl

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ammonium) chloride (pDADMAC) widely used for preparation of corresponding poly(diallyldimethyl ammonium) bis(trifluoromethanesulfonyl) imide used as polymeric ionic liquids (PIL) is of high molecular weight (300–500 000 Da) and polydispersity index. To the best of our knowledge, the influence of molecular weight of polymer as matrix in PIL on the electrochemical characteristics of a supercapacitor system based on them has not been studied so far.

In the present work, a modular platform for the synthesis of pyrrolidinium based polymers for application as PIL in supercapacitor systems is proposed. The polymer is obtained applying a multi-step procedure. Initially, a diallyl amine hydrochloride monomer was synthesized, followed by its polymerization and subsequent functionalization. Preliminary charge/discharge galvanostatic tests in a two-electrode supercapacitor cell as well as an assessment of electrodes material and its stability in the polymeric ionic electrolyte were conducted.

## Results and Discussion

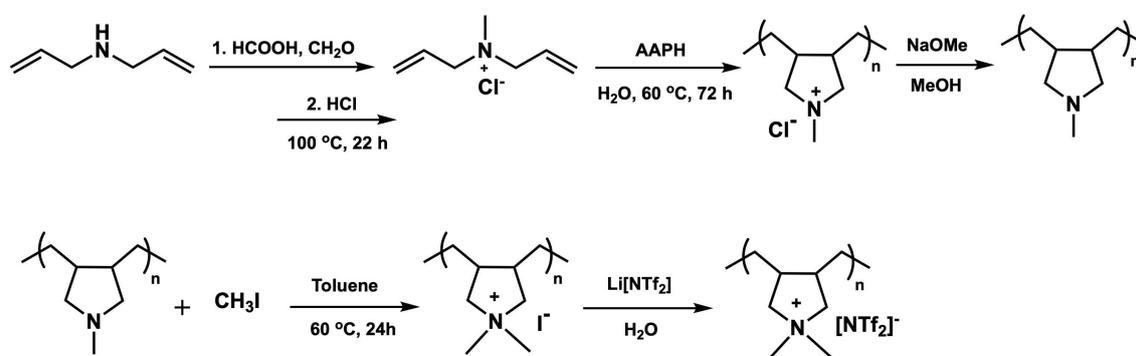
Preparation of targeted polymer electrolyte ionic liquids was reached by the reaction of anion exchange with suitable salts. In general, two main strategies have been used for the synthesis of PILs: the first one consists of direct polymerization of IL monomers bearing different counter-anions<sup>[19–22]</sup> and the second one relies on chemical modification of existing polymers by anion exchange reaction.<sup>[23–25]</sup> Both synthetic routes have been already applied for the preparation of various pyrrolidinium-based PIL.<sup>[26,27]</sup>

In the present work, we synthesized pyrrolidinium-based PILs by applying the anion exchange method to a poly(diallyl methyl ammonium iodide). The synthetic pathway for the preparation of PIL is presented on Scheme 1. The synthesis involved four main steps. In the first step, a modified Eschweiler-Clarke reaction was applied for the synthesis of diallyl methyl amine hydrochloride monomer using the already described conditions.<sup>[27]</sup> In the second step poly(diallyl methyl amine) (PDAMA) was obtained by ring-closing free radical polymerization of the prepared monomer. The successful polymerization was confirmed by <sup>1</sup>H-NMR analyses (see Supporting Information). All the signals characteristic for

pyrrolidinium backbone are present in the <sup>1</sup>H-NMR spectrum. In the next step the tertiary amine groups of PDAMA were quaternized in toluene with methyl iodide as quaternizing agent. The quaternization was quantitative (100%) as calculated from the product's <sup>1</sup>H-NMR spectrum. In the last step the iodine anion was replaced by the fluorinated [NTf<sub>2</sub>]<sup>-</sup> anion applying a direct anion exchange. During the reaction the initially water-soluble polymer precipitated completely in water due to the hydrophobic character of the formed ionic liquid.

Special attention is paid to the detailed characterization of the polymer products to determine their molecular-mass characteristics. Characterization is performed using: chromatographic methods-combined size exclusion chromatography (SEC) with triple detection-refractometry, UV and laser light scattering and proton (<sup>1</sup>H) nuclear magnetic resonance (NMR) spectroscopy. Thermal stability of PIL product is tested by means of TGA to establish the composition-property relationship when selecting polymer electrolytes suitable for electrochemical tests. The chemical nature of the copolymers was confirmed by NMR and FTIR spectroscopy. The <sup>1</sup>H-NMR spectra of PIL confirmed the chemical structure of the polymer backbone. Moreover, the FTIR spectra present the strong bands at 1348, 1177, 1133 and 1051 cm<sup>-1</sup> corresponding to the NTF<sub>2</sub><sup>-</sup> anion and absorption bands at 1473 cm<sup>-1</sup> and between 3100 and 2880 cm<sup>-1</sup> attributed to –CH<sub>3</sub> bending vibrations and –CH<sub>2</sub> stretching vibrations respectively, originating from the polymer backbone.

The chromatogram taken by SEC analysis (see Figure S1 in the Supporting Information) shows that polymer product with a relatively narrow monomodal molecular weight distribution (PDI = 2.04) is obtained. The existence of a shoulder at the side of the higher elution time was attributed to the non-“living” mechanism of the reaction typical for the selected polymerization technique. Since it is known that the ionic conductivity decreases with increasing content of the polymer and/or its molecular weight, respectively, the authors aimed to obtain a PIL polymer product with a lower molecular weight compared to the widely used so far commercial product of M<sub>w</sub> in the range of 300 000–500 000 Da. Moreover, lowering the polymer molecular mass lowers the viscosity of the PIL solution and improves the electrochemical performance of the supercapacitor cell. Absolute number (M<sub>n</sub>) of 15 000 Da and weight (M<sub>w</sub>) of



Scheme 1. Synthesis of PIL.

30 500 Da molecular masses, which are of an order of magnitude lower than previously used were calculated using coupled concentration and operating at 658 nm wavelength MALLS detectors and applying the Zimm formalism model.

TGA was employed to study the thermal stability of precursor PDAMA polymer and PIL polymer as well as to evaluate the effect of the anion type (iodine and fluorinated [NTF<sub>2</sub>], resp.) on the thermal stability of the quaternized polymer products. Traditionally, the weight loss due to the product decomposition during TGA analysis was plotted as a function of temperature and presented in Figure 1.

The examined precursor polymer as well as its quaternized products exhibit thermal stability beyond 360 °C. The polymer PDAMA precursor starts to decompose over 450 °C, significantly higher than that reported for the same conventionally used polymer, but of an order of magnitude higher molecular weight 400 000–500 000.<sup>[16]</sup> Polymer quaternization decreases thermal stability to about 320 °C for product with iodine anion but the anion exchange reaction with fluorinated [NTF<sub>2</sub>] anion leads to an increase of the thermal stability above 400 °C. The latter proves the already observed strong dependence of thermal stability on the anion type.<sup>[17]</sup> It is important that the obtained final polymer products do not show weight loss at low temperatures which is evidence for their non-hygroscopic nature thus making such polymeric materials suitable for electrochemical applications since it is well known that the presence of water worsens their performance.

Combined TGA/GC/MSD analysis can provide reliable data about the components inherent in the structure during heating. In our study, by the use of coupled TGA/GC/MSD equipment, in accordance with the transitions observed in the TGA curve of mass loss, the collection of mixture of degrading components was done at a certain temperature (at about 20% of mass loss) which was then fractionated by GC. The chromatograms of TFSI–Li, PDAMA and PIL are presented in Figure 2.

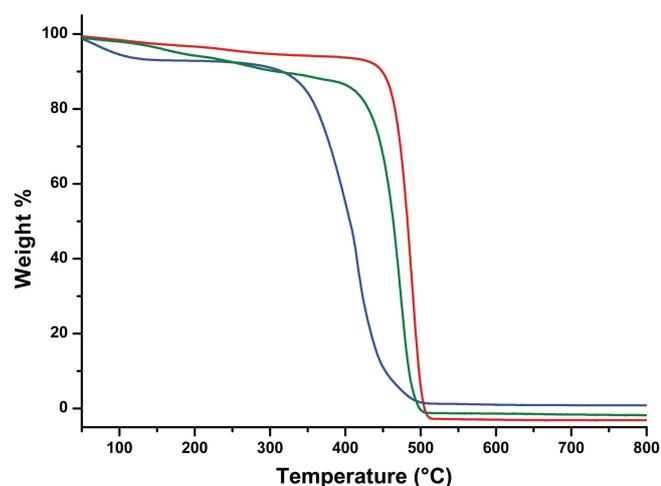


Figure 1. TGA mass loss curves of PDAMA (red line), quaternized with iodine (blue line) and with fluorinated [NTF<sub>2</sub>] (green line) anions polymer.

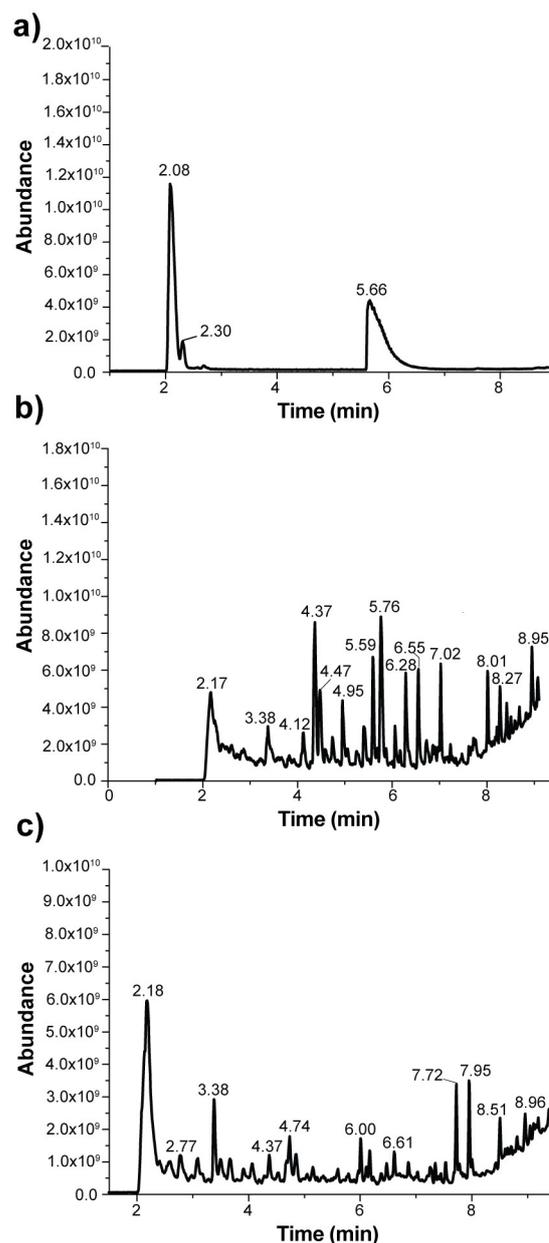


Figure 2. GC chromatograms of TFSI–Li (a), PDAMA (b) and PIL (c).

Finally, the mass of decomposed components was determined by MSD and identified by comparison with the data collected in the NIST MS spectral library. The decomposed species of highest probability formed after process of heating of TFSI–Li salt, synthesized PDAMA polymer and final PIL obtained after quaternization and anion exchanging taken by MSD are listed in Table 1.

Careful consideration of the data presented in Table 1 confirms the existence of characteristic components derived in the process of decomposition of corresponding compounds–TFSI–Li salt, PDAMA and PIL. For example, similar species observed in the chromatogram of the polymeric ionic liquid

Table 1. Primary decomposition products of TFSI-Li, PDAMA and PIL.

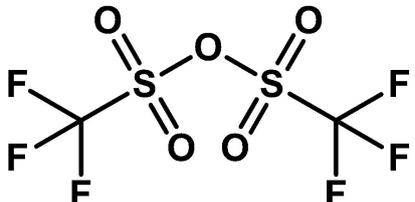
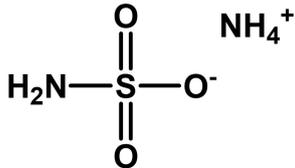
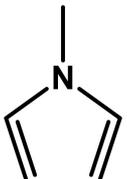
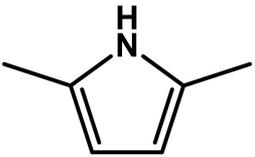
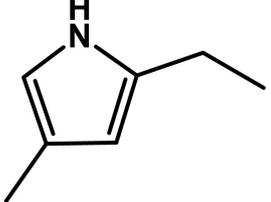
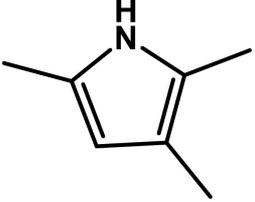
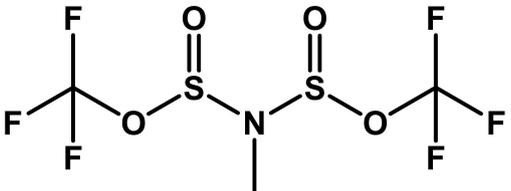
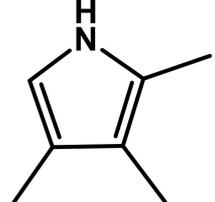
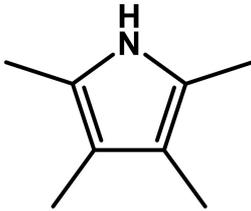
Sample	Degrading component Retention time, min	Probability, %	Name	Formula
TFSI-Li	2.09	40	Trifluoromethanesulfonic anhydride	
	5.60	72	Ammonium sulfamate	$\text{NH}_4^+$ 
PDAMA	3.38	78	1-Methyl-1H-pyrrole	
	4.37	66	2,5-Dimethyl-1H-pyrrole	
	5.59	72	2-Ethyl-4-methyl-1-H-pyrrole	
	5.76	50	2,3,5-Trimethyl-1H-pyrrole	
PIL	3.38	97	Bis(trifluoromethyl)methylimido disulfurous acid	
	6.00	45	2,3,4-Trimethyl-1H-pyrrole	

Table 1. continued				
Sample	Degrading component		Name	Formula
	Retention time, min	Probability, %		
	7.72–7.95	79	2,3,4,5-Tetramethyl-1H-pyrrole	

with masses corresponding to pyrrole derivatives are also found in the chromatogram of the precursor PDAMA polymer.

At the same time, the presence of bis(trifluoromethyl) methylimido disulfurous acid among the degradation components of PIL indicates the presence of TFSI. Thus, the predicted chemical structure of the PIL polymer proposed by NMR and FTIR spectroscopy analyses was confirmed by MSD results which proved the existence of components in degradation products corresponding to species characteristic for pyrrolidinium backbone of the PDAMA prepolymer as well as component corresponding to the  $\text{NTf}_2$  anion derived from TFSI–Li salt which is an indication for successfully conducted anion exchange reaction. Detailed reports from the performed TGA/GC/MSD experiments with analysis of the obtained mass spectra for the individual components are presented in Figure S2 in the Supporting Information.

The resulting polymer is used as an electrolyte in supercapacitor cells. Its low molecular mass implies high ionic conductivity, which plays a dominant role in determining the electrochemical performance of these systems.<sup>[28]</sup> Preliminary electrochemical tests were applied with the system consisting of AC-electrodes and various amounts of PIL dissolved in DMF. In order to go insight into electrochemical performance of polymer electrolyte, in Figure 3 are shown the dependencies of the discharge capacitance as a function of current load and cycle number.

The symmetrical supercapacitor, in electrolyte containing 10–35 wt.% PIL in DMF and voltage window 0,1–2,0 V demonstrates a stable discharge capacitance of charge-discharge process, in the whole range of current loads. The comparison reveals also that the capacitance on SC in electrolyte containing 35% PIL is with slightly worse performance, especially at lower current load, but this system is the most stable by long term test.

The cyclic stability is also one of the important parameters for evaluating the supercapacitor performance and is assessed by conducting 2500 charge/discharge cycles at a current density of  $60 \text{ mA g}^{-1}$  and 4500 cycles at  $120 \text{ mA g}^{-1}$  (Figure 3b). The specific capacitance of SC with 10 wt.% PIL falls down upon the charge/discharge cycles. After 5000 cycles at  $120 \text{ mA g}^{-1}$ , the capacitance retention rate of the SC with 10 wt.% PIL is only 55%, while the SC with 35 wt.% PIL exhibits an excellent cycle stability and its capacitance

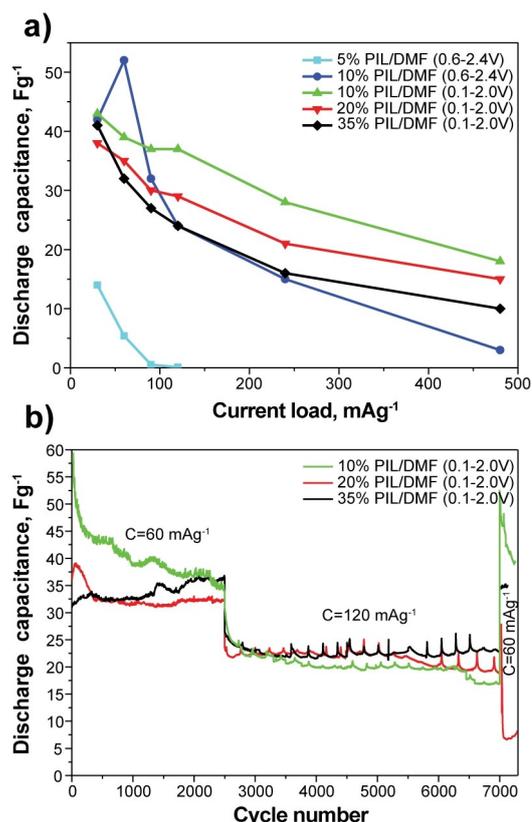


Figure 3. Discharge capacitance of symmetric supercapacitors with YP-50F in PIL/DMF electrolyte as a function of the current load (a) and of the cycle number (b).

retention in the final 5000 cycles is 87%, which is a good result compared to the literature data for such systems.<sup>[29–32]</sup> This supercapacitor displays not only high stability of the discharge capacitance for more than 7000 cycles but also a high effectiveness of charge-discharge process (Table 2). The reason for the result can be explained by the change in the electrode/electrolyte interface, which is essential in controlling the storage and delivery of charge.<sup>[32]</sup> The presence of a larger amount of polymer (more than three-fold increase—from 10 to 35%) leads to increased viscosity of the electrolyte and takes longer for it to penetrate into the smaller pores of the

**Table 2.** Effectiveness of charge-discharge process.

Cycle/% PIL in DMF	1000 at 60 mA $g^{-1}$	2000 at 60 mA $g^{-1}$	3000 at 120 mA $g^{-1}$	5000 at 120 mA $g^{-1}$	7000 at 120 mA $g^{-1}$
10% PIL	92.36	92.19	96.65	96.34	96.30
20% PIL	92.91	93.40	97.12	97.47	97.84
35% PIL	95.35	98.62	98.00	98.49	98.35

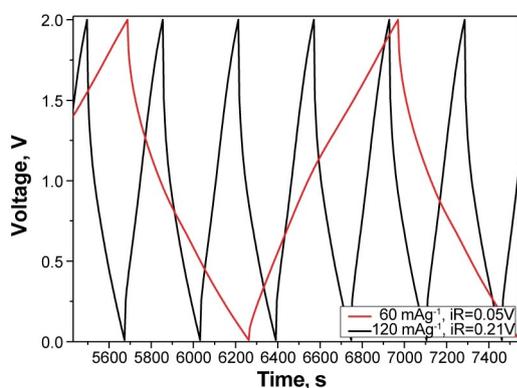
electrodes. The ionic conductivity of the electrolyte at different PIL content also plays a significant role for the effect obtained.

The charge/discharge curves of SC with 35 wt.% PIL measured at 60 mA $g^{-1}$  and 120 mA $g^{-1}$  are shown in Figure 4 and the values obtained correspond fully to the SC capacitance. It can be seen that the electrodes have stable electrochemical properties in the electrolyte and the capacitor voltage varies nearly linearly with time with a good columbic effect (98% at 60 mA $g^{-1}$ ) during both charging and discharging, which indicates a good capacitive behavior.

In our previous study, we demonstrated that YP-50F have a basic character, but also contain acidic functional groups such as phenolic, carbonyl and carboxyl groups.<sup>[33]</sup> In turn, carbonyl groups contribute to the pseudocapacitance reactions through their interaction with basic electrolytes,<sup>[34,35]</sup> which is reflected on their character. Not least the obtained polymers have significantly lower molar masses than those known so far in the literature, which is a prerequisite for higher conductivity and improvement of the electrochemical performance of the supercapacitor cell.

The observed values for voltage drop during the discharge process are low and correspond well to the values of discharge capacitance and effectiveness of charge-discharge process. In the voltage window studied the electrolyte is stable (Figure 3b and Table 2).

This is confirmed by the conducted long-term tests over 7 000 cycles (capacitance retention over 85%, Figure 3b) and by the stable electrochemical properties in the electrolyte (galva-



**Figure 4.** Galvanostatic charge-discharge curves of symmetric supercapacitors with YP-50F in 35% PIL electrolyte at current rate of 60 mA $g^{-1}$  and 120 mA $g^{-1}$ .

nostatic charge-discharge curves in Figure 4). Therefore, the electrolyte analysis at different stages is not necessary.

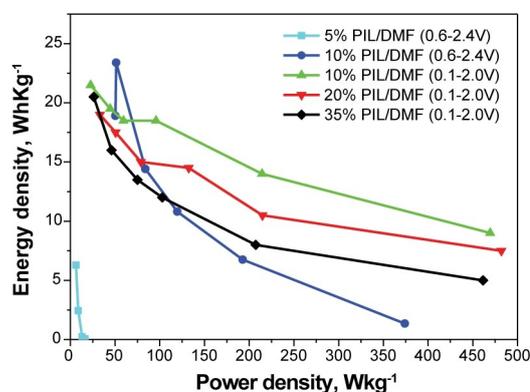
The relationship between energy density and power density of the PIL SCs is indicated in Ragone plots (Figure 5).

The SC with 10% PIL in voltage range 0.6–2.4 V possesses maximum energy density of 23.4 Wh $kg^{-1}$  at a power density of 51.4 W $kg^{-1}$ , which drops sharply with increasing of the power density. At power density 120 W $kg^{-1}$  the same SC working in different voltage windows (0.1–2.0 V) shows energy density of 18.5 Wh $kg^{-1}$  and the SC with 35% PIL–12.0 Wh $kg^{-1}$ . These values of energy density are comparable and, in some cases, higher than those obtained for symmetric SCs with a polymer electrolyte from other authors.<sup>[36–39]</sup> The high energy density of SC with 10% PIL can be mainly attributed to the wide working voltage window and the chemical composition of the surface functional groups of the YP-50F.

## Conclusion

A multistep synthetic strategy is applied for synthesis of novel pyrrolidinium-containing polymers and their turning into polymeric ionic electrolyte with high conductivity suitable for impregnation of composite electrodes or as additives in PIL electrolytes. The obtained polymers have 10 times lower molecular masses than those known so far in the literature, which is a prerequisite for higher conductivity and improvement of the electrochemical performance of the supercapacitor cell. It is also shown that the pore size distribution and chemical surface properties of the carbon materials contribute greatly to electrochemical performance of supercapacitors.

The developed symmetrical supercapacitor in electrolyte containing 10–35 wt.% PIL in DMF demonstrates a stable discharge capacitance. In the presence of 35% PIL the highest stability for more than 7000 cycles (capacitance retention 87%) and a high effectiveness of charge-discharge process (over 98%) is observed. These results can serve as a guide for further improvement of the supercapacitor capacitance by optimizing the composition of the PIL electrolyte, as well by creating a hybrid device.



**Figure 5.** Ragone plot of symmetric supercapacitors with YP-50F in PIL/DMF electrolyte.

## Supporting Information Summary

The supporting information provides details for materials used, experimental procedures for PIL synthesis, physico-chemical and electrochemical characterization techniques, electrode preparation and supercapacitor assembling, SEC chromatograms and reports from the performed TGA/GC/MSD experiments.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** Electrochemistry · Polymer electrolyte · Polymerization · Pyrrolidinium based polymers · Supercapacitor systems

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