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To cite this version:

Anna A. Łatoszyńska, Pierre-Louis Taberna, Patrice Simon, Wladyslaw Wieczorek. Proton conducting gel polymer electrolytes for supercapacitor applications. Electrochimica Acta, 2017, 242, pp.31-37. 10.1016/j.electacta.2017.04.122 . hal-01599332

HAL Id: hal-01599332

https://hal.science/hal-01599332v1

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To link to this article : DOI: 10.1016/j.electacta.2017.04.122
URL : http://dx.doi.org/10.1016/j.electacta.2017.04.122

To cite this version : Łatoszyńska, Anna A. and Taberna, Pierre-Louis and Simon, Patrice and Wieczorek, *Władysław Proton conducting gel polymer electrolytes for supercapacitor applications*. (2017) Electrochimica Acta, vol. 242. pp. 31-37. ISSN 0013-4686

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Proton conducting Gel Polymer Electrolytes for supercapacitor applications

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Keywords:
proton conduction type mechanism
gel polymer electrolytes
phosphoric acid ester
electrochemical capacitor
wide temperature range,

A B S T R A C T

A non-aqueous, mechanically-stable, proton conducting gel polymer electrolyte has been prepared for Electrochemical Capacitor (supercapacitor) applications. It is based on 2-hydroxymethylmethacrylate monomer mixed with two different solvents (propylene carbonate and N,N-dimethylformamide). It was shown that the capacitive performance changes with the gel electrolyte composition. The proton conduction type mechanism affects ions mobility and transport into the porous carbon electrode. Addition of small amounts of DMF solvent leads to a change in the conduction mechanism from a vehicle- to a Grotthuss-type, and capacitance of 90 F g^{-1} at 20° C was achieved using a 15 wt. % $DPhHPO_4$/P (HEMA)/30 wt. % DMF–70 wt. % PC gel composition. Electrochemical tests were done in a large temperature range (from −40 to 80 °C). The cell delivered a capacitance of 54 F g^{-1} at −40 °C, that is 60% of the value obtained at room temperature, and 90 F g^{-1} at 80 °C within voltage window of 1 V.

1. Introduction

Use of semi-solid – rather than liquid – electrolytes in Electrochemical Capacitors would be of great interest to solve many concerns related to packing, corrosion, self-discharge or leakage currents issues [1]. The key issue is to maintain high ionic conductivity as well as good contact at the electrolyte-electrode interface. This requirement is of particular importance in the case of Electrical Double Layer Capacitors (EDLCs), where high surface area carbons are used as active materials.

Proton conducting systems are very promising as solid ionic conductors because of their superior ionic conductivities [2,3]. They are used as electrolytes or separators in various applications such as photosynthesis [4,5], fuel cells [6–8], sensors [9,10], supercapacitors [11–13] or electrochromic devices [14,15].

Several families of proton conducting-electrolytes have been reported so far, with: i) water-based systems, where water solvent takes part in proton conductivity [2,3,16,17], ii) oxoacids and their salts, where the proton conductivity occurs via self-dissociation [3], iii) blends of organic compounds, containing basic sites with acids, i.e. H_3PO_4 or H_2SO_4 [3,18], iv) xerogels, that are amorphous materials obtained by drying of inorganic gels synthesized by sol-gel method [3,19,20] and v) high-temperature conductors [3,21]. Another class of proton conductors are gel polymer electrolytes (GPE). GPEs consist in a polymer matrix swollen with a solution containing the conducting species dissolved in an appropriate solvent. Various GPEs can be prepared by changing the nature and the ratio of the chemicals, leading to various mechanical and electrical as well as thermal properties [22–27]. Gel electrolytes can be divided into hydrogels and anhydrous systems; hydrogels show the best conductivities, about 10^{-2} Scm^{-1} compared to nonaqueous systems [28,29]. GPEs combine high conductivity with high mechanical stability and can be as well processed into thin films. Accordingly, they are good candidates to be used as electrolytes to assemble semi-solid supercapacitors [11,12,30,31], to solve issues listed above (corrosion, self-discharge or leakage currents, and packing) [11].

Solvents used in protonic GPE must fill several requirements, such as high dielectric constant, low viscosity and large operation temperature range, i.e. low melting and high boiling points. Additionally, they may offer possibility of solvent molecule protonation by a proton donor source [22,32,33]. Two different solvents can be distinguished: protophilic and protophobic. Protophilic solvents lead to a Grotthuss-type proton conductivity

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http://dx.doi.org/10.1016/j.electacta.2017.04.122

mechanism, where the conductivity occurs via protonated and unprotonated solvent molecules. According to their physicochemical properties (high dielectric constant, low viscosity and wide operational temperature range), PC and DMF (or dimethylacetamide, DMA) are appropriate solvents for proton conducting system.

Raducha et al. have synthesized several types of nonaqueous gels plasticized with various polar solvents, such as propylene carbonate (PC), N,N-dimethylformamide (DMF), N-methylpyrrrolidone (NMP) and ethylene glycol [32]. They used phosphoric acid as proton donor source, which is crystalline in anhydrous form. Other polymer matrices were tested, such as various acrylic monomers (methyl methacrylate, glycidyl methactrylate or acrylonitrile) and were synthesized via "in situ" polymerization of monomers. The type of solvent plays a major role in the conduction mechanism. In most of the cases, the polymer matrix is an inert component, except GMA monomer, which used in mentioned example is taking part in proton transport [34,35].

Wieczorek et al. have studied proton conductivity for H_3PO_4 dissolved in various solvents, swollen in a polymer matrix (PVdF) [22]. The highest conductivity at room temperature was obtained for DMF based gels ($3.16.10^{-4}$ S cm^{-1}). A decrease in the conductivity was observed for PVdF-NMP-H_3PO_4 systems ($1.26.10^{-5}$ S cm^{-1}), in agreement with higher viscosity and lower dielectric constant of the NMP. Indeed, the solvent viscosity was found to be the key parameter for achieving high conductivity since it affects charge carriers mobility. Increasing the DMF content (vs. PC) results in increasing the electrolyte conductivity, explained by the different proton transport mechanism in DMF and PC [22].

In DMF-based electrolytes, solvent molecules can be easily protonated from proton donors. In presence of protonated and unprotonated solvent species, the proton conduction takes place by a two-step Grotthuss-type mechanism where protons are exchanged between protonated and unprotonated solvent molecule. This mechanism shows a low activation energy for proton conduction and relatively high ionic conductivity at room temperature ($1.58.10^{-4}$ S cm $^{-1}$) [22].

In systems containing only PC as solvent, PC molecules cannot be easily protonated and the charge transport occurs via polyatomic species of proton donors, so that the proton transport takes place via a vehicle-type mechanism; solvent molecules are not involved in proton transport. This type of mechanism is characterized with high activation energy for conduction and lower room temperature conductivities. The higher viscosity of PC results in a lower ionic charge mobility, which can also be the reason for the lower ionic conductivities measured for GPEs containing only PC as solvent [22].

There is a large variety of choice for gel electrolytes precursors that can be mixed together in various ratios to prepare GPEs. However, besides the ionic conductivity, the reactivity of the different components has also to be taken into account. For instance, in proton conducting GPEs, some monomers can react with proton donors [32]. In the presence of strong acids such as H_2SO_4 or H_3PO_4, the degradation of the C—O bonds in polyethers or polyalcohols used as solvents may occur. Another issue are the solvent-polymer matrix interactions, such as the wettability; for instance MMA or HEMA monomers are not compatible with pure DMF or DMA solution.

In this paper, we have prepared several proton conducting GPEs with various solvent ratios, to be used as electrolytes in supercapacitor applications. The influence of the gel composition on the ionic conductivity, temperature behavior and electrochemical properties has been studied in a large temperature range (−40 to 80 °C). Phosphoric acid ester (diphenyl phosphate) has been chosen as the proton donor source due to its acidic properties (some of phosphoric acid esters are known as stronger acids than orthophosphoric acid itself), which allows reaching ionic conductivity one order of magnitude higher than that of orthophosphoric acid-based electrolytes. This issue was more precisely described in our previous paper [11].

2. Experimental

Unless mentioned, all the chemicals were purchased from Aldrich. Gel polymer electrolyte (GPE) was prepared in a glove-box under Ar atmosphere by mixing propylene carbonate (PC) with 2-hydroxyethyl methacrylate (HEMA), a radical poce:para id="par0075">Unless mentioned, all the chemicals were purchased from Aldrich. Gel polymer electrolyte (GPE) was prepared in a glove-box under Ar atmosphere by mixing propylene carbonate (PC) with 2-hydroxyethyl methacrylate (HEMA), a radical polymerization initiator (benzoyl peroxide, BP) and a cross linking agent (triethylene glycol dimethacrylate, TEGDM). Appropriate amounts of BP (1 wt. %) and TEGDM (5 wt. %) were used with the respect to the polymer content. After stirring for 1 h, the solution was cast as a thin film (∼200 μm) on a glass plate and placed in oven at 60–70 °C for gelation (12 h). The next step was soaking the film with a solution of $DPhHPO_4$ in DMF and left for 1 week. All the prepared electrolytes contained 12.5 wt. % polymer matrix, with various concentrations of $DPhHPO_4$ (from 5 to 40 wt. % of the final GPEs) and various solvent mixture ratio (PC:DMF).

Ionic conductivity was measured using electrochemical impedance spectroscopy technique (EIS) in a temperature range from −40 to 80 °C. Samples were sandwiched between two stainless steel blocking electrodes and placed in a temperature-controlled thermostat. Electrochemical measurements were done using a VMP Multichannel Potentiostat (VMP, Biologic Science Instrument, France), in a frequency range from 10 to 500 kHz.

Differential Scanning Calorimetry (DSC) studies were performed in the −150 to 150 °C temperature range using a DSC Q200 V24.2 Build 107 system equipped with low-temperature measuring head and liquid helium cooling element. Samples were loaded into aluminum pans and stabilized by cooling from the room temperature down to −150 °C. Samples were then heated at 20 °C min^{-1} rate up to 150 °C; an empty pan was used as a reference.

The composite carbon electrodes were prepared by mixing YP80-F activated carbon (Kuraray Chemical Co., LTD) with 5 wt. % poly(vinylidene fluoride – hexafluoropropylene) (PVdF – HFP) binder in acetone. YP-80F is a microporous carbon, with a high specific surface area of 2145 ± 16 m^2 g^{-1}. Ar gas sorption measurements have shown that the carbon structure contains mainly micropores (pore diameter lower than 2 nm), accounting for 87% of the total pore volume and mesopores in the 2 to 7 nm diameter range. 50% of the micropores size is lower than 1 nm [11]. The slurry was casted onto Au disks (thickness, ∼60 μm; surface area, ∼1.29 cm^2), placed in vacuum oven and dried at 120 °C. The carbon mass loadings of the electrodes are given in Table 1. Symmetric cells were assembled using 2-electrode Swagelok® cells [11].

Electrochemical measurements were made at various temperatures (from −40 to 80 °C) using a climatic chamber. Before starting electrochemical measurements, the cells were kept for 4 h

Table 1
Activated carbon mass loading (mg cm^{-2} of electrode).

GPE type	*Electrode coating (mg cm^{-2})*
90 wt. % PC–10 wt. % DMF	3.6
80 wt. % PC–20 wt. % DMF.	3.4
70 wt. % PC–30 wt. % DMF	4.1
60 wt. % PC–40 wt. % DMF	4.4

until the desired temperature was reached, which was found to ensure that the cell temperature was the same temperature as that of the chamber. Electrochemical impedance spectroscopy measurements of 2-electrode supercapacitor cells were made between 100 kHz and 1 mHz. Cycling voltammetry (CV) experiments were performed at scan rates of 1, 5 and 10 mV s^{-1} and constant current charge/discharge tests (GCPL) were carried at 0.075 A g^{-1}. The gravimetric capacitance C_{am} of active material (in F g^{-1}) was estimated from the cell capacitance C_{cell} according to Eq. (1):

$$C = 2x\frac{C_{cell}}{m_{ac}} \quad (1)$$

where C is the electrode capacitance (F g^{-1} of carbon), C_{cell} is the cell capacitance (F), and m_{ac} the weight of activated carbon at one electrode [11].

3. Results and Discussion

2-hydroxyethyl methacrylate (HEMA) monomer was selected as the polymer matrix, as already proposed in previous work [11,32,36]. HEMA-based polymer gel electrolytes are transparent and freestanding membranes that show high flexibility and good mechanical stability. The elastic properties depend on the solvent content [22,37] and the main role of polymer matrix is to ensure good mechanical properties [32]. All the prepared electrolytes contain 12.5 wt. % of HEMA.

Ionic conductivity in gel is achieved in the solvent phase, by protonation of solvent molecules by the proton dopant [3,22,38]. The selected methacrylic monomer is compatible with propylene carbonate and the gel synthesis is possible by simple radical polymerization. However, when PC is only used as solvent, the solvent molecules cannot be easily protonated and the formation of charge carriers in PC occurs mostly via the self-dissociation of proton donor, leading to low conductivity values. The addition of a protophilic solvent such as DMF, contributes to proton conduction by a Grotthus-type mechanism, which is proton transport via an exchange of protons between protonated and unprotonated solvent molecules.

Unfortunately, the preparation of gels based only on DMF and PHEMA polymer matrix is impossible since HEMA is not compatible with DMF. Enrichment of methacrylic based matrix with DMF is possible by combining PC and DMF solvents, by soaking DMF into PC based gel. The maximum of DMF content that can be added to HEMA-based gels is 40 wt. % in solvent phase; beyond this value, a phase separation occurs. Fig. 1 shows the ionic conductivity of GPE containing 15 wt. % of diphenyl phosphate, with PC:DMF ratios ranging from 9:1 to 6:4. The possibility of the protonation of solvent molecules by the proton dopant in the system being very important. The lowest conductivity value was obtain at 20 °C for the DMF-free GPE ($1.6.10^{-4}$ S cm^{-1}); it further increases up to $5.3.10^{-4}$ S cm^{-1} for 30 wt. % DMF content. Below 0 °C, highest values were reached for the 10 wt. % DMF composition. For temperatures beyond 0 °C, the highest conductivity were obtained for 30 wt. % of DMF. The protophilic solvent (DMF) itself contribute to proton conduction by a Grotthus-type mechanism (proton transport via an exchange of protons between protonated and unprotonated solvent molecules).

Electrolyte thermal stability was assessed by Differential Scanning Calorimetry (DSC). Table 2 shows DSC data obtained for gel polymer electrolytes PHEMA-$DPhHPO_4$-PC-DMF gels containing various PC-DMF ratio. The only phase transition occurring in the −150 to 150 °C temperature range (Fig. 2) is the glass temperature transition of the samples. A slight decrease of T_g is observed when adding 10 wt. % of DMF compared to DMF-free electrolyte, in agreement with previous results; this is ascribed to the change of the solvent composition [39]. The lowest value of T_g was obtained for the sample containing 10 wt. % of DMF; further increase in DMF concentration results in strengthening of the system (assumed to be linked with improved interactions between the solvent and the polymer matrix), thus leading to a decrease of T_g.

Based on results, the (PC:DMF) ratio was fixed at (70:30). The decrease of the activation energy E_a (see Table 2) of DMF-containing GPE suggests that proton conduction is mainly achieved

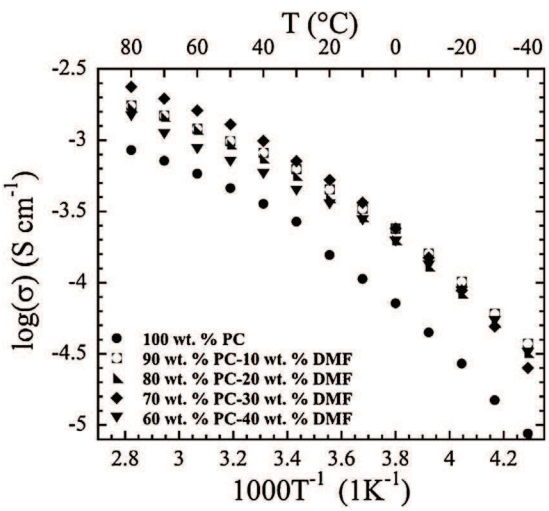

Fig. 1. Ionic conductivity as a function of inverse temperature for PHEMA-$DPhHPO_4$-PC-DMF system, where ester concentration was 15 wt. % and various PC-DMF ratio.

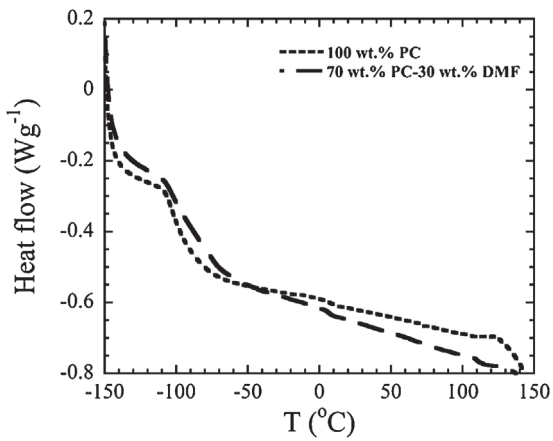

Fig. 2. DSC plots for PHEMA based electrolyte (where 12.5 wt. % is polymer matrix and15 wt. % of diphenyl phosphate)prepared with various PC − DMF solvent ratio.

Table 2
Conductivity, activation energy and T_g values obtained from DSC measurements, for proton conducting gels based on PHEMA, containing different solvents ratio and 15 wt. % diphenyl phosphate.

Proton Donor	Solvent	σ (S cm^{-1}) at 20 °C	E_a (kJ mol^{-1}) (20–80 °C)	T_g (°C)
$DPhHPO_4$ (15 wt. %)	100 wt. % PC	1.6×10^{-4}	23.4	−103.2
	90 wt. % PC–0 wt. % DMF	4.5×10^{-4}	16.1	−107.5
	80 wt. % PC–20 wt. % DMF	3.9×10^{-4}	17.9	−105.5
	70 wt. % PC–30 wt. % DMF	5.3×10^{-4}	16.7	−102.3
	60 wt. % PC–40 wt. % DMF	3.6×10^{-4}	18.0	−87.0

by a Grotthuss-type mechanism, moving to a vehicle-type mechanism for DMF-free electrolytes.

Fig. 3 shows the change of the ionic conductivity versus the reverse of the temperature plots for a PHEMA-$DPhHPO_4$-PC-DMF system containing (70:30) PC:DMF wt. % ratio, for various $DPhHPO_4$ contents. Two temperature regions can be identified on the plot: above ∼−10 °C, the conductivity increases with increasing amount of $DPhHPO_4$; below∼−10 °C, the conductivity decreases with increasing $DPhHPO_4$ concentrations.

Differential Scanning Calorimetry measurements of gel samples containing various proton donor content shows similar trends as previously observed (see Table 3). Only one phase transition was observed [11], associated with the glass temperature transition (T_g) which increases with the acid concentration. Increasing the diphenyl phosphate concentration resulted in mechanical strengthening of the gel (associated with improved interactions between solvent and polymer matrix); as a result, increased T_g values were found. The calculated activation energy values (see Table 3) fall in the range of 15.6–21.6 kJ mol^{-1} and increase. The lower E_a values suggests a Grotthuss-type conductivity mechanism at low ester concentrations (5 and 15 wt. %), moving to a vehicle-type mechanism at higher ester concentration (30 and 40 wt. %) [32].

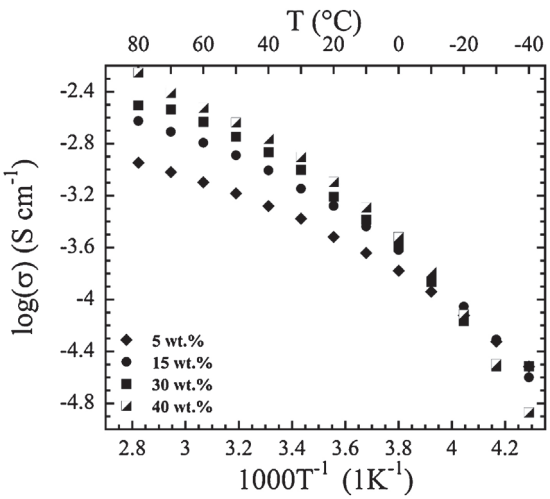

Fig. 3. Ionic conductivity as a function of the irreverse temperature for PHEMA-$DPhHPO_4$-PC-DMF system, where 30 wt. % in solvent phase is DMF.

3.1. Electrochemical Characterizations

2-electrode Swagelok® cells were assembled with gel electrolyte acting as well as separator. GPEs based on PHEMA polymer matrix doped with 15 wt. % of diphenyl phosphate were used. Various PC-DMF solvent ratios were studied. The activated carbon weight loading is given in Table 1. Fig. 4a shows the Cyclic Voltammogramms (CVs) of 2-electrode cells assembled with carbon electrodes (see experimental section) using DMF-free GPE (15 wt. % $DPhHPO_4$/PHEMA/PC). The CVs show a resistive behavior, associated with the low conductivity of the electrolyte. When pure PC (DMF–free) is used as solvent phase, proton transport occurs via polyatomic species of proton donor which are trapped in polymer network. The charge carriers mobility in the electrolyte is low, resulting in high resistance.

When small amount of DMF (10 wt. % in solvent mixture) is added to the GPE, the rectangular-shaped CV signatures evidence a typical capacitive (see Fig. 4a). This can be attributed first to the change in the proton conducting mechanism from vehicle- to Grotthuss-type previously mentioned, that increases the electrolyte conductivity. Additionally, the decrease in the viscosity of the solvent phase following DMF addition may lead to a swelling of the GPE electrolyte, thus improving the surface contact area between the highly porous carbon and the GPE [11]. Room temperature measurements have shown that a concentration of 10 wt. % of DMF was enough to reach decent capacitive of about 80 F g^{-1} (Table 4). The capacitance does not change dratisticly with increasing DMF contents.

Fig. 4b shows the capacitance change versus scan rate, calculated from CV experiments. Highest capacitance was obtained at 1 mV s^{-1} (80 F g^{-1}) and appears to be independent from the DMF content at low potential scan rate. However, increasing the DMF content in the electrolyte improves the capacity retention behavior

Table 3
Conductivity, activation energy and T_g values obtained from DSC measurements for proton conducting gels based on PHEMA, different proton donor content and PC-DMF ratio 7:3.

Proton Donor	Conc. (wt. %)	σ (S cm^{-1}) at 20 °C	E_a (kJ mol^{-1}) (20–80 °C)	T_g (°C)
$DPhHPO_4$	5	3.0×10^{-4}	15.6	−109.1
	15	5.3×10^{-4}	16.6	−102.3
	30	6.2×10^{-4}	20.4	−80.3
	40	8.0×10^{-4}	21.6	−63.3

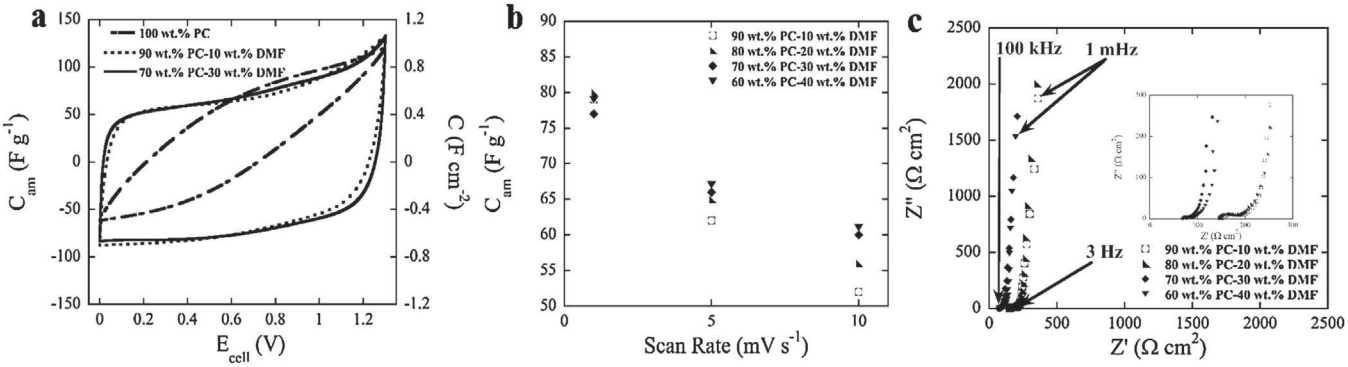

Fig. 4. a) Cyclic voltammograms of a symmetrical supercapacitor with GPE doped with phosphoric acid ester (15 wt. % $DPhHPO_4$/PHEMA/solvent). CV was recorded at room temperature at a scan rate of 1 mV s^{-1}. b) Capacitance change with the potential scan rate and with various scan rates at room temperature. C) Nyquist plots 2-electrode supercapacitor cells.

Table 4
Equivalent series resistance (ESR), specific capacitance value per gram of average mass (C_{am}) for the symmetrical supercapacitors obtained at different temperature, tested in 15 wt. % $DPhHPO_4$/PHEMA/PC-DMF with various PC/DMF contents GPEs.

T (°C)	Cut-off potential (ΔE in V)	90 wt. % PC–10 wt. % DMF		80 wt. % PC–20 wt. % DMF		70 wt. % PC–30 wt. % DMF		60 wt. % PC–40 wt. % DMF	
		ESR (Ωcm^2)	C_{am} ($F g^{-1}$) at 74 mA g^{-1}	ESR (Ωcm^2)	C_{am} ($F g^{-1}$) at 74 mA g^{-1}	ESR (Ωcm^2)	C_{am} ($F g^{-1}$) at 74 mA g^{-1}	ESR (Ωcm^2)	C_{am} ($F g^{-1}$) at 74 mA g^{-1}
−40	0–1.3	1870	43	2350	45	800	54	850	57
−20	0–1.3	720	57	850	60	255	62	365	63
RT	0–1.3	190	76	180	70	82	94	90	84
40	0–1.2	110	80	110	80	37	86	46	85
60	0–1.1	80	81	75	82	25	90	32	86
80	0–1.0	54	80	50	84	19	89	24	85

at high rates; this can be attributed to the improved conductivity of the gel electrolyte and the associated decrease in the viscosity.

The improvement of the electrochemical properties of the electrolyte with the DMF content is clearly observed in Fig. 4c that shows the impedance spectroscopy measurements at room temperature (20 °C). The vertical increase of the imaginary part at low frequency confirms the capacitive nature of the electrochemical storage for all cells. The equivalent series resistance (ESR) calculated from the high frequency value at null imaginary part, decreases for increased DMF content (see Table 4). Considering that all the GPE samples have the same thickness (200 μm), these results are in good agreement with the change of the ionic conductivity. The observed decrease in capacitance at −40 °C originates from the reduced ion mobility at such low temperature; however 54% and 70% of the initial room temperature capacitance were still measured at −40 °C for 10 and 30 wt. % DMF content, respectively; this highlights the capability of our proton conducting gel electrolytes for operating at low temperature.

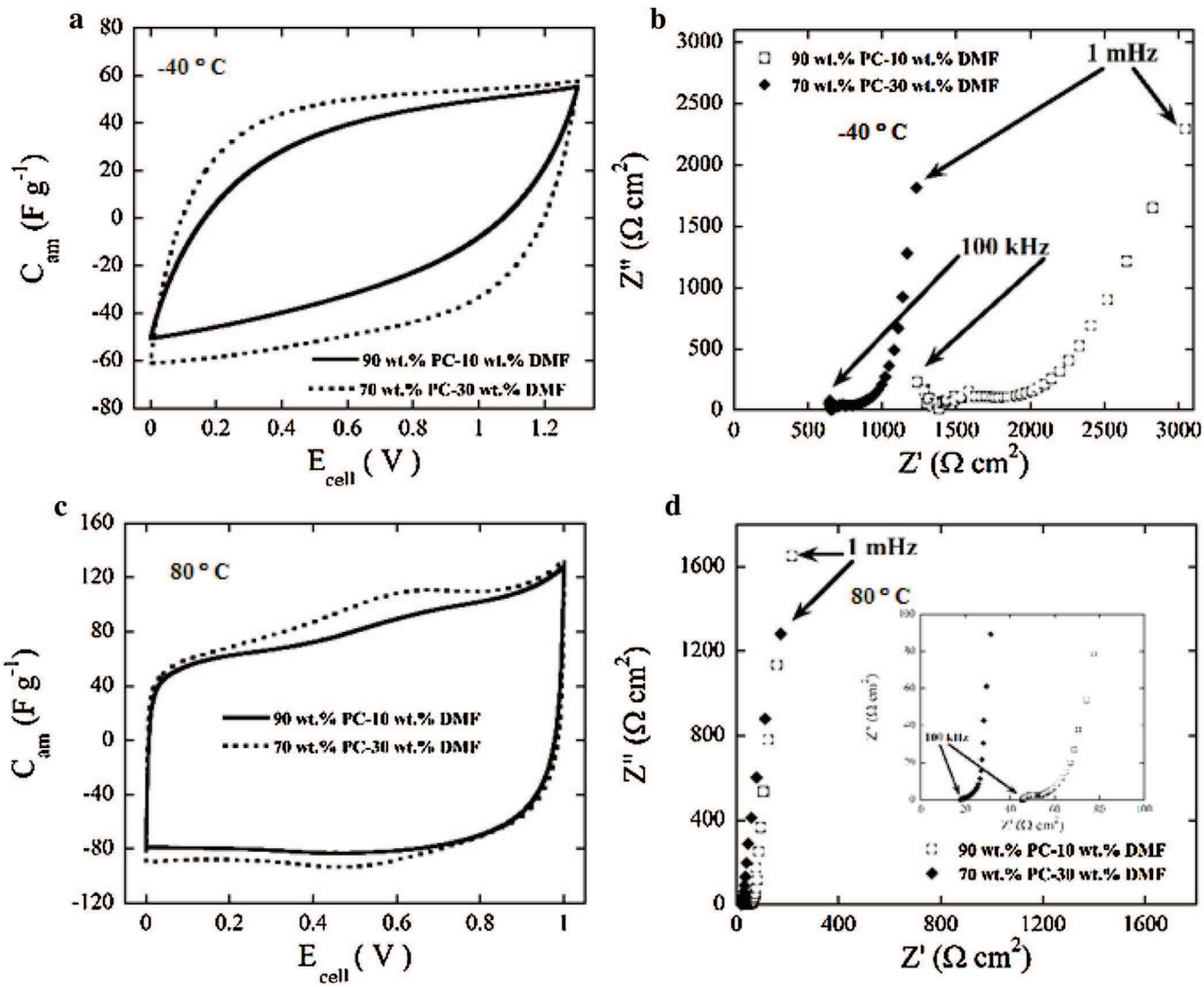

Fig. 5. Electrochemical characterization of symmetrical supercapacitor with polymer gel electrolyte (15 wt. % $DPhHPO_4$/PHEMA/DMF-PC different ratio): CVs collected at 1 mV s^{-1} (a) and corresponding a Nyquist plots (b) collected at −40 °C. CVs collected at 1 mV s^{-1} (c) and corresponding a Nyquist plots (d) collected at 80 °C.

The temperature change also affects the voltage window. At higher temperatures (80 °C, see Fig. 5c), the maximum voltage is 1.0 V, while at room temperature (20 °C) it reaches 1.3 V. The voltage window is higher than for previously analyzed cells with phosphoric acid (1.0 V) or for aqueous proton conducting GPE. Fig. 5 shows the electrochemical characterization of the cell assembled with GPE containing 10 and 30 wt. % of DMF. Fig. 5a shows comparison of voltammograms at scan rate 1 mV s^{-1} and 5b the corresponding the Nyquist plots at −40 °C. Although the ESR were found to be high (1870 Ω cm^2 and 797 Ω cm^2 for 10 and 30 wt. % of DMF, respectively), the Nyquist plots signature at −40 °C is still capacitive. The electrochemical signature is mainly controlled by ohmic drops (see Fig. 5a); however, it is capacitive as can be seen from the rectangular shape of the CVs.

Fig. 5c and d show the CVs and Nyquist plots of the same supercapacitors cells cycled at 80 °C at 1 mV s^{-1}. The Nyquist plots shows a clear decrease of the series resistance reaching 54 Ω cm^2 (DMF 10 wt. %) and 19 Ω cm^2 (DMF 30 wt. %); as well as a capacitance increase thanks to improved electrolyte conductivity. However, the temperature increase decreases the maximum voltage window from 1.3 V (20 °C) down to 1.0 V at 80 °C, in agreement with increased electrochemical reactions kinetic for proton reduction and solvent oxidation [36].

Fig. 6 summarizes the capacitance change with temperature calculated from previous cyclic voltammetry experiments. As expected, a capacitance decrease is observed with decreasing the temperature, associated with the lower ionic conductivity of the GPEs. Only the cells assembled with GPEs containing 30 and 40 wt. % of DMF were able to reach capacitance higher than 50 F g^{-1} within a maximum voltage window of 1.3 V (see Table 4).

3.2. Long-term cycling tests

To control the capacitance value stability of carbon based capacitors with proton conducting GPE with different PC-DMF ratio, long term galvanostatic charge/discharge experiments were performed in the potential between 0 and 1.3 V. Fig. 7 shows the change of the capacitance with the cycle number, measured during charge/discharge tests at a constant current of 74 mA g^{-1}.

The long term cycling tests were performed up to 1000 cycles for four solvents ratios. The electrolyte with 30 wt. % of DMF and 70 wt. % of PC according to our results gave the higher capacity and

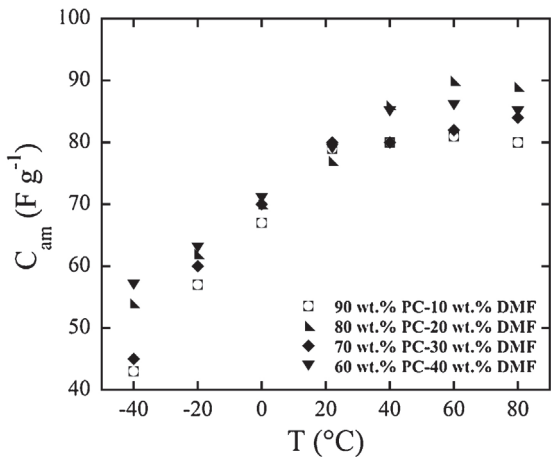

Fig. 6. Capacitance change with the temperature for the 2-electrode supercapacitor cells assembled with GPE electrolytes containing various PC:DMF ratios. Capacitance were calculated from cyclic voltammetry experiments.

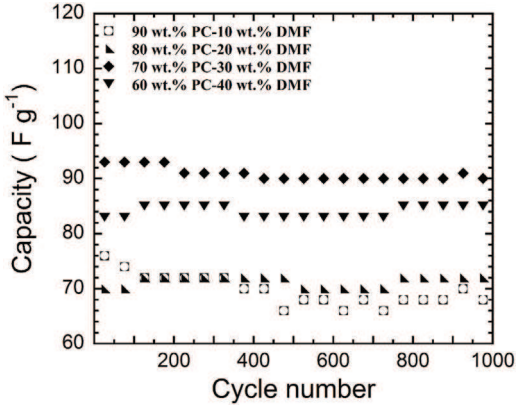

Fig. 7. Long term cycling test of capacitor cells with GPE.

the highest capacity retention after 1000 cycles (an initial capacitance of 94 F g^{-1} and a capacity retention of 96%). The reason of it is the highest ionic conductivity of this sample (see Fig. 1) compare to other samples with different DMF content.

4. Conclusion

This work focused on the preparation of proton conducting gel polymer electrolytes (GPE) for applications in supercapacitors. It was shown that the capacitive performance changes with the gel electrolyte composition. Firstly, the solvent type, mostly through the different proton conducting mechanism, affects the electrochemical performance of the carbon. The vehicle type mechanism for proton conduction in PC based GPE, which does not involve solvent molecules in transport, strongly affects ions mobility and transport into the porous carbon electrode. Addition of small amounts of DMF solvent leads to a change of conduction mechanism from a vehicle- to a Grotthuss-type mechanism, where proton transport is achieved via solvent phase. DMF addition allows improved porous carbon structure accessibility to the ions and appearance of double layer effect.

Supercapacitor cells were assembled with different gel compositions and tested at various temperatures (from −40 to 80 °C). It was shown that the best properties were obtained for EDLC using a gel electrolyte containing 15 wt. % $DPhHPO_4$/P (HEMA)/30 wt. % DMF–70 wt. % PC. The capacitance was about 90 F g^{-1} (at 20 °C), within a maximum voltage window of 1.3 V. The use of organic solvents (PC, DMF) allowed increasing the temperature range from −40 °C up to 80 °C. At −40 °C, the capacitance reached 54 F g^{-1}, that is 60% of the value obtained at room temperature (90 F g^{-1}). At higher temperatures (80 °C), the capacitance was 90 F g^{-1} with an operation voltage window of 1 V. The results obtained in this work confirm that GPEs are interesting candidates for replacing liquid electrolytes in supercapacitors devices for specific applications.

Acknowledgments

This work was supported within the frame of the MPD/2010/4 Project belonging to the MPD Program of Foundation for Polish Science (co-financed by the European Union, Regional Development Fund).

We would like to thank to PhD Grażyna Zofia Żukowska for her help in this work.

References

[1] R.J. Latham, S.E. Rowlands, W.S. Schlindwein, Supercapacitors using polymer electrolytes based on poly(urethane), Solid State Ionics 147 (2002) 243–248.
[2] K.D. Kreuer, On the development of proton conducting materials for technological applications, Solid State Ionics 97 (1997) 1–15.
[3] K.D. Kreuer, Proton conductivity: Materials and applications, Chemistry of Materials 8 (1996) 610–641.
[4] R. Brimblecombe, A. Koo, G.C. Dismukes, G.F. Swiegers, L. Spiccia, Solar Driven Water Oxidation by a Bioinspired Manganese Molecular Catalyst, Journal of the American Chemical Society 132 (2010) 2892-.
[5] J.H. Kim, M. Lee, C.B. Park, Polydopamine as a Biomimetic Electron Gate for Artificial Photosynthesis, Angewandte Chemie-International Edition 53 (2014) 6364–6368.
[6] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, Alternative polymer systems for proton exchange membranes (PEMs), Chemical Reviews 104 (2004) 4587–4611.
[7] K.D. Kreuer, On the development of proton conducting polymer membranes for hydrogen and methanol fuel cells, Journal of Membrane Science 185 (2001) 29–39.
[8] S.J. Peighambardoust, S. Rowshanzamir, M. Amjadi, Review of the proton exchange membranes for fuel cell applications, International Journal of Hydrogen Energy 35 (2010) 9349–9384.
[9] C. Schwandt, D.J. Fray, The titanium/hydrogen system as the solid-state reference in high-temperature proton conductor-based hydrogen sensors, Journal of Applied Electrochemistry 36 (2006) 557–565.
[10] N. Fukatsu, N. Kurita, K. Koide, T. Ohashi, Hydrogen sensor for molten metals usable up to 1500 K, Solid State Ionics 113 (1998) 219–227.
[11] A.A. Latoszynska, G.Z. Zukowska, I.A. Rutkowska, P.-L. Taberna, P. Simon, P.J. Kulesza, W. Wieczorek, Non-aqueous gel polymer electrolyte with phosphoric acid ester and its application for quasi solid-state supercapacitors, Journal of Power Sources 274 (2015) 1147–1154.
[12] H. Gao, K. Lian, Advanced proton conducting membrane for ultra-high rate solid flexible electrochemical capacitors, Journal of Materials Chemistry 22 (2012) 21272–21278.
[13] M. Skunik, M. Chojak, L.A. Rutkowska, P.J. Kulesza, Improved capacitance characteristics during electrochemical charging of carbon nanotubes modified with polyoxometallate monolayers, Electrochimica Acta 53 (2008) 3862–3869.
[14] K.C. Ho, T.G. Rukavina, C.B. Greenberg, TUNGSTEN-OXIDE PRUSSIAN BLUE ELECTROCHROMIC SYSTEM BASED ON A PROTON-CONDUCTING POLYMER ELECTROLYTE, Journal of the Electrochemical Society 141 (1994) 2061–2067.
[15] Z. Florjanczyk, W. Bzducha, M. Kedzierski, Proton conducting gels for electrochemical devices, Macromol. Symp. 152 (2000) 223–241.
[16] I.V. Kozhevnikov, Catalysis by heteropoly acids and multicomponent polyoxometalates in liquid-phase reactions, Chemical Reviews 98 (1998) 171–198.
[17] M.T. Pope, Heteropoly and Isopolyoxometalates, (1983) Berlin.
[18] F.M. Gray, Solid Polymer Electrolytes, VCH Publisher, New York, 1991.
[19] O. Lev, Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich, S. Sampath, Sol-gel materials in electrochemistry, Chemistry of Materials 9 (1997) 2354–2375.
[20] U.L. Stangar, N. Groselj, B. Orel, P. Colomban, Structure of and interactions between P/SiWA keggin nanocrystals dispersed in an organically modified electrolyte membrane, Chemistry of Materials 12 (2000) 3745–3753.
[21] T. Norby, Solid-state protonic conductors: principles, properties, progress and prospects, Solid State Ionics 125 (1999) 1–11.
[22] W. Wieczorek, G. Zukowska, R. Borkowska, S.H. Chung, S. Greenbaum, A basic investigation of anhydrous proton conducting gel electrolytes, Electrochimica Acta 46 (2001) 1427–1438.
[23] G. Zukowska, J.R. Stevens, K.R. Jeffrey, Anhydrous gel electrolytes doped with silicotungstic acid, Electrochimica Acta 48 (2003) 2157–2164.
[24] G. Zukowska, J. Williams, J.R. Stevens, K.R. Jeffrey, A. Lewera, P.J. Kulesza, The application of acrylic monomers with acidic groups to the synthesis of proton-conducting polymer gels, Solid State Ionics 167 (2004) 123–130.
[25] E. Zygadlo-Monikowska, Z. Florjanczyk, E. Wielgus-Barry, E. Hildebrand, Proton conducting gel polyelectrolytes based on 2-acrylamido-2-methyl-1-propanesulfonic acid (AMPSA) copolymers. Part II. Hydrogels, Journal of Power Sources 159 (2006) 392–398.
[26] G. Zukowska, N. Chojnacka, W. Wieczorek, Effect of gel composition on the conductivity of proton-conducting gel polymeric electrolytes doped with H3PO4, Chemistry of Materials 12 (2000) 3578–3582.
[27] G.Z. Zukowska, V.J. Robertson, M.L. Marcinek, K.R. Jeffrey, J.R. Stevens, Structure of proton-conducting anhydrous gel electrolytes based on poly (glycidyl methacrylate), Journal of Physical Chemistry B 107 (2003) 5797–5805.
[28] W. Wieczorek, J.R. Stevens, Proton transport in polyacrylamide based hydrogels doped with H3PO4 or H2SO4, Polymer 38 (1997) 2057–2065.
[29] P. Pissis, A. Kyritsis, V.V. Shilov, Molecular mobility and protonic conductivity in polymers: hydrogels and ionomers, Solid State Ionics 125 (1999) 203–212.
[30] K. Lian, H. Gao, Advances in solid polymer electrochemical capacitors for high rate applications, Conference on Energy Harvesting and Storage – Materials, Devices, and Applications II, Orlando, FL, 2011.
[31] M. Schroeder, P. Isken, M. Winter, S. Passerini, A. Lex-Balducci, A. Balducci, An Investigation on the Use of a Methacrylate-Based Gel Polymer Electrolyte in High Power Devices, Journal of the Electrochemical Society 160 (2013) A1753–A1758.
[32] D. Raducha, W. Wieczorek, Z. Florjanczyk, J.R. Stevens, Nonaqueous H3PO4-doped gel electrolytes, Journal of Physical Chemistry 100 (1996) 20126–20133.
[33] J.R. Stevens, W. Wieczorek, D. Raducha, K.R. Jeffrey, Proton conducting gel H3PO4 electrolytes, Solid State Ionics 97 (1997) 347–358.
[34] K. Jeffrey, W. Wieczorek, D. Raducha, J. Stevens, Dynamics of the hydrogen and phosphate ions in proton conducting gel D3PO4 electrolytes: A H-2 and P-31 nuclear magnetic resonance study, Journal of Chemical Physics 110 (1999) 7474–7482.
[35] A.M. Grillone, S. Panero, B.A. Retamal, B. Scrosati, Proton polymeric gel electrolyte membranes based on polymethylmethacrylate, Journal of the Electrochemical Society 146 (1999) 27–31.
[36] J. Reiter, J. Velicka, M. Mika, Proton-conducting polymer electrolytes based on methacrylates, Electrochimica Acta 53 (2008) 7769–7774.
[37] H. Nithya, S. Selvasekarapandian, P.C. Selvin, D.A. Kumar, J. Kawamura, Effect of propylene carbonate and dimethylformamide on ionic conductivity of P(ECH-EO) based polymer electrolyte, Electrochimica Acta 66 (2012) 110–120.
[38] J.C. Lassegues, Proton Conductors: Solid, Membranes and Gel – Materials and Devices, Cambridge University Press, Cambridge, 1992.
[39] G. Zukowska, W. Wieczorek, M. Kedzierski, Z. Florjanczyk, Nonaqueous gel electrolytes doped with phosphoric acid esters, Solid State Ionics 144 (2001) 163–173.