



## Research Paper

## Proton conducting Gel Polymer Electrolytes for supercapacitor applications



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## ABSTRACT

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  $90 \text{ F g}^{-1}$  at  $20^\circ \text{ C}$  was achieved using a 15 wt. % DPH<sub>4</sub>P<sub>4</sub>/P (HEMA)/30 wt. % DMF–70 wt. % PC gel composition. Electrochemical tests were done in a large temperature range (from  $-40$  to  $80^\circ \text{ C}$ ). The cell delivered a capacitance of  $54 \text{ F g}^{-1}$  at  $-40^\circ \text{ C}$ , that is 60% of the value obtained at room temperature, and  $90 \text{ F g}^{-1}$  at  $80^\circ \text{ C}$  within voltage window of 1 V.

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## 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.  $\text{H}_3\text{PO}_4$  or  $\text{H}_2\text{SO}_4$  [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  $10^{-2} \text{ Scm}^{-1}$  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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mechanism, where the conductivity occurs via protonated and unprotonated solvent molecules. According to their physico-chemical 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-methylpyrrolidone (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 methacrylate 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 ( $3.16 \cdot 10^{-4} S cm^{-1}$ ). A decrease in the conductivity was observed for PVdF-NMP- $H_3PO_4$  systems ( $1.26 \cdot 10^{-5} S cm^{-1}$ ), 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 ( $1.58 \cdot 10^{-4} S cm^{-1}$ ) [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 super-capacitor 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 ( $\sim 200 \mu m$ ) 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<sub>4</sub> in DMF and left for 1 week. All the prepared electrolytes contained 12.5 wt. % polymer matrix, with various concentrations of DPhHPO<sub>4</sub> (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<sup>–1</sup> 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  $2145 \pm 16 m^2 g^{-1}$ . 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,  $\sim 60 \mu m$ ; surface area,  $\sim 1.29 cm^2$ ), 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<sup>®</sup> 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

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