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PVA Hydrogel Electrolyte and Porous Polyisoprene Carbon Nanostructure Composite Based Pressure Sensitive Supercapacitor

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Abstract. Narrow operational voltage window can be considered as one of the greatest limitations for aqueous polymer electrolytes. Using freeze-thaw hydrogel preparation method we have synthesized wider potential window electrolytic polyvinyl alcohol (PVA)/Na₂SO₄ and PVA/K₂SO₄ electrolytes. Supercapacitors (SC) have been assembled using novel porous polyisoprene and carbon black composite electrodes. Our SC exhibit pressure sensitive properties therefore this effect is deeper explored here, giving explanation for capacitance increase during pressure application. It is found that up to 2 MPa the capacitance increases due to greater interface between electrode and electrolyte.

1. Introduction

Supercapacitors (SC) are short term energy storage devices which are used to give fast energy boosts when needed. Modern SC are expected to bridge the gap between batteries and conventional capacitors by providing both high power and energy. Flexible solid-state SC have extra advantages like possibility to use them in flexible electronics as well as the absence of liquid electrolyte [1-3]. However, the majority of flexible solid-state SCs can operate in a relatively narrow voltage window therefore limiting the practical use of these devices. Recently it has been stated that wider operational voltage window can be achieved using alkali metal salts as ion sources, e.g. Na₂SO₄ [4, 5].

One of the characteristics determined for SC devices is the ability to sustain stable capacitance during mechanical deformation. We have previously demonstrated that instability of capacitance under mechanical load can be successfully used for pressure sensing [6]. Mechanical load can decrease distance between electrodes, in case of piezoresistive material it can increase or decrease resistance of electrode, change the dielectric permittivity of layer between electrodes or facilitate greater interface between electrode and electrolyte.

Here we present a compressible solid-state SC with an operational voltage window of 4.4 V. PVA/Na₂SO₄ and PVA/K₂SO₄ were chosen to obtain such wide operational window in these poly(vinyl alcohol) cryogel electrolytes. Cryogel electrolytes containing H₃PO₄ and KOH, reported in literature [7-12], were also prepared to establish a comparison with pH neutral salts (Na₂SO₄ and K₂SO₄). Electrochemical characterization gives us information about limitations and energy storage properties of our device. We have investigated how separate parts of the whole supercapacitor device influence



capacitance changes when it is subjected to mechanical load, therefore increasing our knowledge about interaction of SC components under pressure.

2. Results and discussion

Main components contributing to successful solid-state double-layer SC are carbon-based electrodes with current collector and ion conducting electrolyte. For electrodes flexible electro-conductive porous polyisoprene rubber was prepared to allow deformation to take place in our device. As in regard to electrolyte we chose to favour polymer hydrogel electrolyte, specifically cryogels, which are prepared by freeze-thaw method.

2.1. Porous electrode materials

Electro-conductive composite material was created by mixing polyisoprene rubber (PI) solution in chloroform with conductive carbon particles and blowing agent ChKhZ-5 particles dispersed in chloroform. The solvent was evaporated, and composite material was vulcanized under pressure. Main steps of composite material preparation are shown in figure 1.a, where last step shows crosslinked porous rubber samples ready to be used as electrodes. Special care was taken when crosslinking electrode material. First, composite material was molded by pressure in 140 °C temperature for 1.5 minutes. Then this pressure was removed, and crosslinking was continued at higher rate at 160 °C temperature. ChKhZ-5 thermally decomposes at temperature range 150-170 °C so pores are formed simultaneously with crosslinks as sample is not subjected to pressure in this stage.

We started by preparing three different electro-conductive polymer composites – PICB25, PIAC70 and PIGr65. Sample name shows that polyisoprene (PI) has been used as binder and carbon black (CB, PRINTEX-XE2), activated carbon (AC, Sigma Aldrich) and graphene (Gr, CheapTubes) as active electrode material where number shows phr (parts per hundred rubber). Phr values were chosen to be close to maximum content achievable. Electro-conductivity of these materials was measured in temperature range from 12 °C to 58 °C (figure 1.b). It is clearly seen that PICB25 sample shows superior electro-conductivity in comparison to other two materials reaching 7.4 S m⁻¹ conductivity at room temperature (25 °C) while for PIAC70 it is 0.07 S m⁻¹ and 0.03 S m⁻¹ for PIGr65. CB was chosen for further use in samples because it possesses the highest electro-conductivity.

One of the factors that influence capacitance of SC is electrode surface area. We added pore forming agent ChKhZ-5 to increase surface area of electrode material. We expected that conductivity of material could decrease after formation of pores and to solve this we increased CB phr to maximum value we could achieve (28) before the material shows decrease of integrity. Porous electrode showed electro-conductivity of 17 S m⁻¹, which is by 11 S m⁻¹ lower than non-porous material (figure 1.c), but it is still a high value for porous rubber composites.

The goal of this research was to prepare pressure sensitive supercapacitors so we tested how the conductivity of electrodes respond to mechanical load. Figure 1.c. demonstrates that for both cases of electrodes (porous and non-porous) small piezoresistive effect was observed – uniaxial pressure causes conductivity to drop. For SC this means that applied mechanical load slows down the propagation of charge to current collectors, because the resistance of electrodes increases. During fast charge-discharge cycles this effect could play a negative role.

By observing the surface of electrode material in figure 1.d we can see that pores are not uniform. Uniformity in this case is strongly dependent on content of filler particles, lower content could yield more uniform pores and higher porosity, but it would mean sacrificing electro-conductive properties.

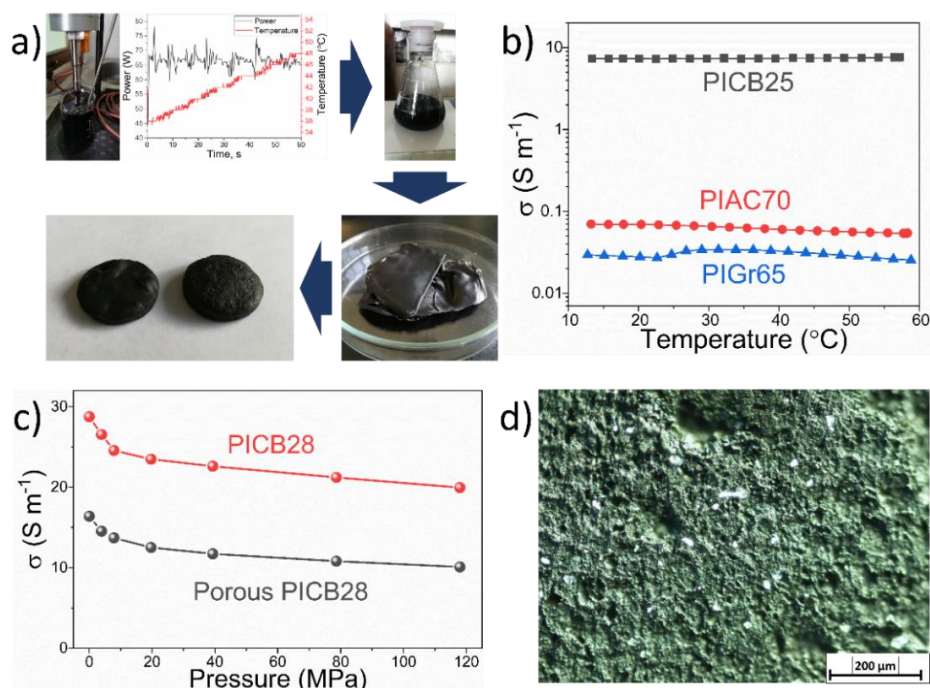


Figure 1. (a) Preparation technology of electro-conductive rubber starting with sonication of carbon particles mixed with CHCl₃, proceeded by mixing with PI/CHCl₃ solution and evaporation of solvent and lastly vulcanization of electrodes. (b) Electro-conductivity measurements of three carbon nanostructure composites. (c) Electro-conductivity of porous and non-porous PICB28 electrodes under various pressure values. (d) Optical microscopy image of porous PICB28 electrode surface, scale 200 μ m.

2.2. Hydrogel electrolytes – preparation and characterization

The hydrogel electrolyte was synthesized using “Freeze-thaw” method (figure 2.a). PVA (Sigma Aldrich, Mw 130000, 99+% hydrolysed) was dissolved in distilled water at 100 °C temperature while being vigorously stirred. After complete dissolution it was cooled to room temperature and when clear, viscous solution was obtained, 20 wt% of 1 M Na₂SO₄, K₂SO₄, KOH or 20 wt% conc. H₃PO₄ was slowly added. This solution was casted in petri dishes and subjected to 3 freeze-thaw cycles in order to prepare white, opaque cryogel as shown in figure 2.a.

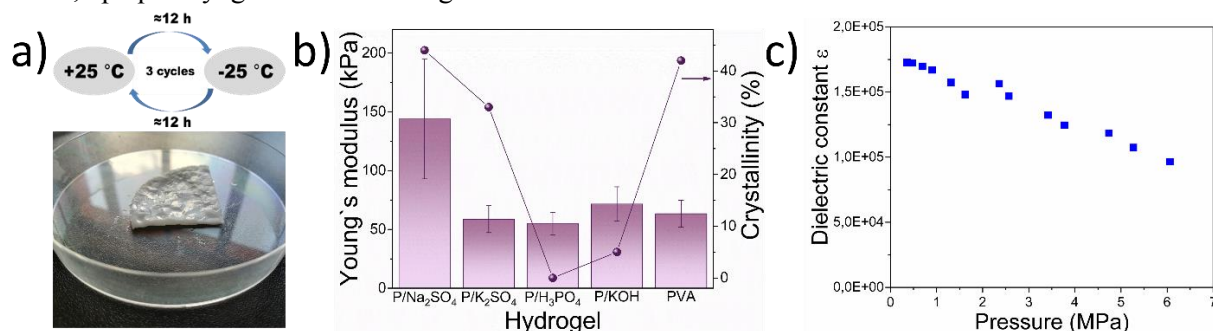


Figure 2. a) Schematic representation of “Freeze-thaw” method and image of the prepared cryogel electrolyte b) Graph showing crystallinity of prepared hydrogels calculated from DSC and corresponding Young’s modulus c) Dielectric permittivity measurements when uniaxial pressure is used on PVA/K₂SO₄ hydrogel with smooth ITO electrodes.

PVA hydrogel without any ion conducting additives was also prepared using “freeze-thaw” method to determine how Na₂SO₄ and K₂SO₄ influence the structure of hydrogel. Differential Scanning

Calorimetry (DSC) of hydrogels show that addition of Na_2SO_4 hasn't made a great influence on the content of crystalline phase and for hydrogels PVA and PVA/ Na_2SO_4 it is respectively 42 % and 44 % as evidenced in figure 2.b. In case of PVA/ K_2SO_4 the crystallinity has slightly decreased and is around 33%. Interestingly, when H_3PO_4 and KOH is used as ion source in hydrogel the crystallinity dramatically decreases (0 % and 5 %) allowing much higher ion mobility in gel electrolyte.

Previously the influence of pressure on electrode conductivity was explored. Here we discuss influence of mechanical load on dielectric permittivity of hydrogel electrolyte. For this purpose, PVA/ K_2SO_4 electrolyte was used. PVA/ Na_2SO_4 showed higher Young's modulus as seen in figure 2.b and could be a better potential candidate for pressure testing, but unfortunately Young's modulus measurements of this hydrogel showed great deviations. Figure 2.c reveals that uniaxial pressure decreases the dielectric permittivity when hydrogel electrolyte is used in combination with smooth ITO electrodes. The changes in the structure of hydrogel caused by pressure reduces the free volume and amorphous phase, hence it decreases the mobility of ions and diminishes their contribution to total dielectric permittivity of hydrogel electrolyte layer.

2.3. Electrochemical characterization.

For electrochemical characterization one side of the crosslinked electrode was painted with silver paint to create current collector. SC was assembled by sandwiching the PVA/ Na_2SO_4 hydrogel electrolyte between two identical electrodes. The operational voltage window was determined using cyclic voltammetry (CV). Results show that widest potential windows can be obtained for PVA hydrogels using Na_2SO_4 and K_2SO_4 (figure 3.a). These same electrolytes show the highest specific capacitance (figure 3.b) which is calculated from CV curves.

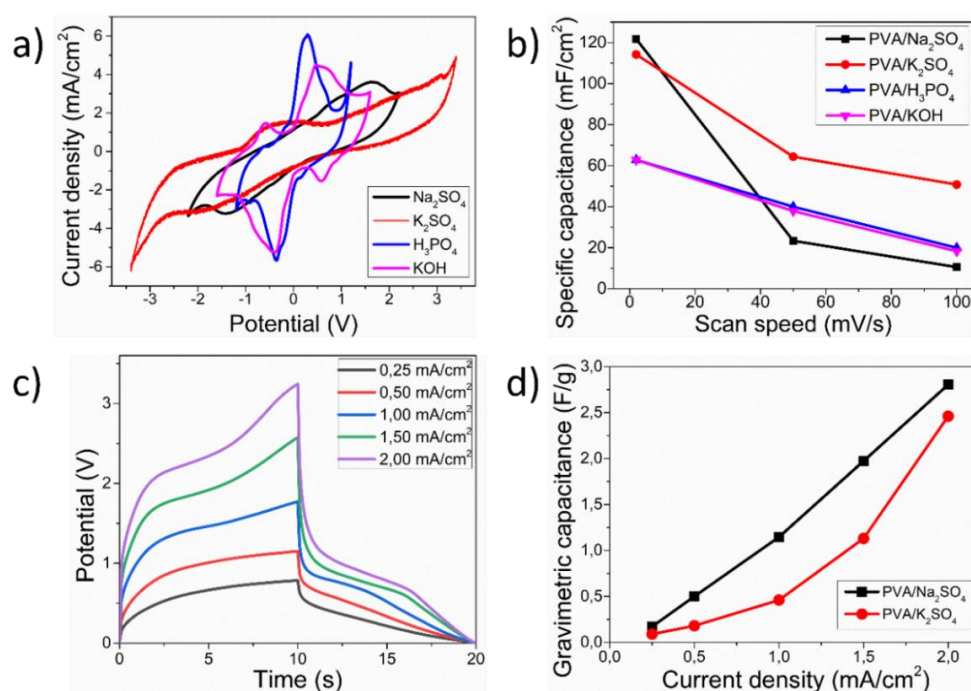


Figure 3. a) CV curves of hydrogel electrolyte SC at 100 mV/s scan speed b) Specific capacitance values obtained from CV measurements c) CP results for SC that is charged for 10 s and discharged for 10 s using various current densities (0.25-2.00 mA/cm^2) d) Gravimetric capacitance values calculated from charge-discharge curves.

Supercapacitors using PVA/ Na_2SO_4 and PVA/ K_2SO_4 were chosen for further testing – for chronopotentiometry (CP) measurements. CP results show that when device is charged using various current densities for 10 s the maximum voltage increase ($V = 3.25$ V) is observed when 2 mA/cm^2 is

used (figure 3.c). The calculated gravimetric capacitance is lower than reported in literature, but it can be explained by the shape of electrodes. To allow compression, they have been prepared relatively thick which needs a higher amount of active electrode material. The highest gravimetric capacitance was obtained for SC using PVA/Na₂SO₄ and it was 2.8 F g⁻¹ (figure 3.d).

2.4. Mechanical load impact on capacitance.

As it was established previously in subsections 2.1. and 2.2., the uniaxial pressure lowers the conductivity of electrode materials, therefore limiting charge distribution rate in electrode material, as well as decreases the dielectric permittivity of hydrogel electrolytes. Lower dielectric permittivity means that mechanical load should have a diminishing impact on capacitance of supercapacitor.

Figure 4.a demonstrates that capacitance of SC increases accordingly to applied pressure. As we have ruled out impact of increased dielectric permittivity and the electrode area doesn't increase, then we must conclude that capacitance increases due to smaller distance between electrodes and increased interfacial contact between electrode and electrolyte when uniaxial pressure is applied.

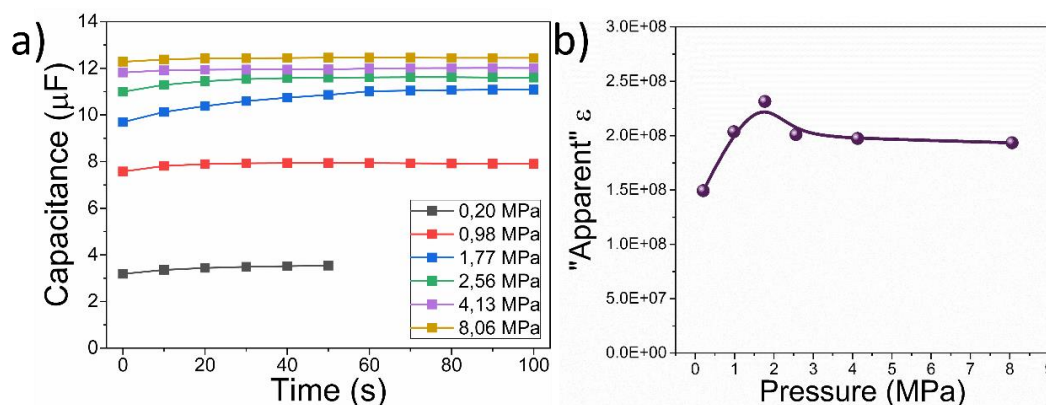


Figure 4. a) Impact of pressure on capacitance of SC using porous PICB28 and PVA/K₂SO₄ b) “Apparent” dielectric permittivity of SC device depending on the applied pressure.

To determine whether this capacitance increase is mainly due to closer distance between electrodes or better interface between electrode and electrolyte we calculated the “apparent” dielectric permittivity. Term “apparent” dielectric permittivity was used because it was calculated using the dimensions of device as the area of electrode. But in reality the rough and porous surface area of the specific electrode should be taken into account when dielectric permittivity is calculated. Therefore, the calculated dielectric permittivity is much higher (by 3 orders) than the one obtained from measurements that used ITO electrodes (figure 4.b) which is smooth and for which dimensions of device can indeed be used as the electrode area. The most interesting about this is the increase of permittivity when pressure up to 2 MPa is applied. “Apparent” permittivity slightly increases but as we have determined previously with measurements using ITO electrodes it should decrease. Hence, we can conclude that better interfacial contact is created when pressure up to 2 MPa is applied, which causes higher capacitance. When pressure is higher than 2 MPa capacitance increase can be mainly attributed to decrease of distance between electrodes because dielectric permittivity doesn't change as evidenced in figure 4. b.

3. Devices and methods

Electro-conductivity of electrode was measured with Agilent 34970A data acquisition/switch unit. Scanning electron spectroscopy images were obtained with Phenom Pro desktop SEM. Electrochemical measurements: cyclic voltammetry (CV) and chronopotentiometry (CP) were conducted with VoltLab PGZ301 potentiostat at room temperature (22 °C) using Swagelok type cell. Dielectric properties and capacitance for mechanical load dependent experiments were measured with Agilent E4980A LCR meter while mechanical load was provided by universal material testing machine Zwick/Roell Z2.5.

4. Conclusions

Use of cryogel electrolyte containing K and Na sulphates allows wider potential window of assembled devices, resulting in devices better suitable for integration in circuits. Applied uniaxial pressure decreases the conductivity of electrode material limiting charge distribution in electrode material when pressure is applied, which is not favourable for pressure sensors. Dielectric constant of electrolyte decreases under mechanical load, therefore, pressure should have a diminishing effect on capacitance. As can be seen from results effect is opposite – pressure increases the capacitance. We have concluded that weaker pressure (up to 2 MPa) increases capacitance mainly due to improvement of interfacial conditions. When pressure is higher than 2 MPa capacitance increases mainly due to smaller distance between electrodes.

Acknowledgements

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