

Hydrogel membrane electrolyte for electrochemical capacitors[†]

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Abstract. Polymer electrolytes are known to possess excellent physicochemical properties that are very useful for electrochemical energy systems. The mobility in polymer electrolytes is understood to be mainly due to the segmental motion of polymer chains and the ion transport is generally restricted to the amorphous phase of the polymer. Gel polymer electrolytes (GPE) that are formed using plasticizers and polymers along with ionic salts are known to exhibit liquid-like ionic conductivity while maintaining the dimensional stability of a solid matrix. In the present study, the preparation and characterization of poly(vinyl alcohol)-based hydrogel membranes (PHMEs) as electrolytes for electrochemical capacitors have been reported. Varying HClO₄ dopant concentration leads to different characteristics of the capacitors. The EC comprising PHME doped with 2 M HClO₄ and black pearl carbon (BPC) electrodes has been found to exhibit a maximum specific capacitance value of 97 F g⁻¹, a phase angle value of 78°, and a maximum charge–discharge coulombic efficiency of 88%.

Keywords. Gel polymer electrolyte; hydrogel; supercapacitor; voltammetry; charge-discharge capacitance.

1. Introduction

Electrochemical capacitors (EC) are energy storage devices with high power densities¹ as evident from the Ragone plot given in figure 1. On the basis of the mechanisms involved in the charge-storage process, an EC is classified as an electrical double-layer capacitor (EDLC) or a pseudocapacitor. While energy storage in EDLCs is due to the separation of charges at the electrode-electrolyte interface, the energy storage mechanisms in pseudocapacitors involve fast faradaic reactions such as intercalation, under potential deposition or redox processes occurring at or near an electrode surface at an appropriate potential.²

A variety of electrolytes, both in aqueous and non-aqueous media, in either liquid or solid form have been used to fabricate ECs. Unlike aqueous electrolytes that are stable up to an operating-potential window of ~1.2 V, non-aqueous electrolytes exhibit high operating-potential window of ~4 V and hence high energy density. Polymer-based solid electrolytes (SPEs) that comprise a polymer and an ionic component^{3–5} are quite flexible that can be prepared as thin and high surface area membranes.

Very often, the polymer electrolytes result in good contact at the interface of the electrode and subsequently low equivalent series resistance of the device. Mixing a polymer with an alkali metal salt dissolved in organic solvent results in the formation of a gel-polymer electrolyte (GPE).⁶ GPEs exhibit liquid-like ionic conductivity while maintaining the dimensional stability of a solid system. Various polymers like poly(propylene oxide), poly(ethylene imine), poly(vinyl alcohol),⁷ poly(vinylidene fluo-

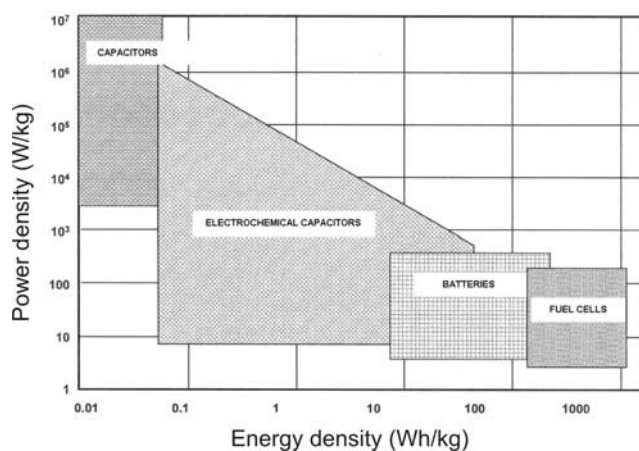


Figure 1. Ragone plot of power density versus energy density for electrochemical energy systems (adapted from ref. 1).

[†]Dedicated to the memory of the late Professor S K Rangarajan

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ride) (PVDF),⁸ etc. have been found to form GPEs with conductivities ranging between 10^{-4} and 10^{-3} S cm⁻¹ under ambient conditions.⁹ The low molecular-weight organic solvents with high dielectric constants that are employed in GPEs are referred to as plasticizers. Solvents, such as ethylene carbonate, propylene carbonate and tetrahydrofuran¹⁰ have been commonly employed as 'plasticizers' in GPEs.^{11,12} These organic solvents are environmentally malignant and hence, replacement of organic solvents with water in GPEs is desirable, which also minimizes the device cost substantially.

Hydrogels are 3-dimensional polymeric networks that trap water in the polymer matrices mainly by surface tension and other weak interactions. The water containing GPEs are referred to as hydrogel polymer electrolytes (HPEs). Depending on the nature of the polymer, hydrogels are classified as homopolymeric or copolymeric hydrogels. Hydrogels are further classified as amorphous, semi-crystalline, hydrogen-bonded, supramolecular and hydrocolloidal structures based on the physical nature of the networks.¹³ Poly(vinyl alcohol), discovered in 1924, is one of the most widely investigated polymers¹⁴⁻¹⁶ for hydrogels. It is cheap, non-toxic and chemically stable.¹⁷ The -OH groups of PVA react with -CHO groups of certain aldehydes to form acetal or hemiacetal linkages under acidic conditions.¹⁸ The resultant polymeric entity is water insoluble and gel-like in nature. It can be cast to form thin large surface-area membranes suitable for use as electrolyte-cum-separator in ECs. Hydrogels comprising synthetic polymers, such as PVA, have high structural integrity and good mechanical stability.¹⁹ These hydrogels can also absorb large amount of water in the polymer matrix that helps fine-tuning their ionic conductivity. They, however, possess a fairly high degree of hydrophobicity due to the presence of long carbon-chains with few hydrophilic pendant groups in contrast to hydrogels consisting of natural polymers, such as gelatin.

Lewandowski *et al*²⁰ have reported the performance evaluation of hydrogels based on PEO-KOH-H₂O for ECs. The comparison with 6M KOH as electrolyte for ECs revealed that both the electrolytes behave similar. Potassium poly(acrylate) (PAAK)-based hydrogels such as PAAK-KOH-H₂O and PAAK-KCl-H₂O could be classified as physical hydrogels as no chemical reaction is involved in their formation. Iwakura *et al*,²¹ Nohara *et al*²² and Wada *et al*^{23,24} have reported ECs employing alka-

line cross-linked potassium poly(acrylate) hydrogel, namely PAAK-KOH-H₂O, as the electrolyte and compared their performances with ECs employing 10 M KOH aqueous electrolyte. The performances of the two ECs are reported to be similar. A pseudocapacitor employing a neutral hydrogel, PAAK-KCl-H₂O, as electrolyte and MnO₂·*n*H₂O as the electrode has been reported by Lee *et al*²⁵. The hydrophobic nature of the polymeric component in the hydrogel electrolyte improves the compatibility between the PVDF binder in the electrode matrix and the hydrogel electrolyte, thereby resulting in good penetrability of the latter within the pores of the electrodes. Consequently, the overall cell capacitance increases due to a decrease in the un-wetted electrode area. Wada *et al*²⁶ have reported the performance of aqueous PVA cross-linked with glutaraldehyde as an electrolyte. Blends of polymers such as aldehyde-cross-linked poly(vinyl alcohol)/poly(acrylic acid) (PAA) have been employed by Choudhury *et al*²⁷ to fabricate all solid-state ECs. They have also reported the applications of gelatin hydrogel electrolytes for ECs. A pseudocapacitor based on PVA-H₃PO₄-H₂O hydrogel electrolyte and RuO₂/TiO₂ nanotube composites as electrode has been shown to yield a maximum specific capacitance of ~1263 F g⁻¹.²⁸

The present study reports cross-linked poly(vinyl alcohol) hydrogel membrane electrolytes with varying perchloric acid dopant concentration and their application to electrochemical capacitors.

2. Experimental

2.1 Preparation of acidic PVA hydrogel membrane electrolytes

Acidic PVA hydrogel membrane electrolytes (PHMEs) with varied HClO₄ concentrations were prepared by a solution casting method¹⁸ in which a mixture of an aqueous solution of PVA (M.W. ≈ 1,25,000, SD fine-chem Ltd., India) and an optimized quantity of glutaraldehyde (25% aqueous solution, Merck Ltd., India) was cast on to a glass petri dish and left at ambient conditions of temperature and pressure for about 12 h to allow water to evaporate. After the evaporation of water, perchloric acid (~70%; *d* = 1.67 kg L⁻¹, Merck Ltd., India) of a given concentration was poured on to the petri dish to initiate the cross-linking reaction between PVA and glutaraldehyde. In a typical preparation, ~7.5 mL

of 0.1 g mL^{-1} aqueous solution of PVA was mixed with $\sim 0.15 \text{ mL}$ of 25% aqueous glutaraldehyde solution by stirring for $\sim 2 \text{ h}$ and the solution was cast on a glass petri dish of $\sim 10 \text{ cm}$ diameter. After evaporation of water, 50 mL of HClO_4 solution of a given concentration was added to catalyse the cross-linking reaction between PVA and glutaraldehyde and the mixture was kept at 25°C for the gelation to get completed. The time required for gelation decreased with increasing concentration of HClO_4 . Gelation with HClO_4 concentration of 0.5 M and above took about 10 min to complete whereas gelation with 0.1 M HClO_4 took about 3 days.

2.2 Thermal characterization

PHMEs with varying HClO_4 concentrations were characterized^{29,30} by temperature-modulated differential scanning calorimetry (TM-DSC) in the temperature range between 303 and 373 K using a Metler Toledo DSC 823e differential scanning calorimeter interfaced with TOPEM[®] (Toledo Parametric Evaluation Method) software.³¹

2.3 Electrochemical characterization

Electrochemical characterization of PHMEs with varying HClO_4 concentrations was carried out by following their electrochemical capacitor characteristics. The studies were carried out on all solid-state ECs assembled with various hydrogel electrode assemblies (HEAs). The HEAs comprised optimized PHMEs with varying concentrations of HClO_4 dopants, sandwiched between two carbon papers (Toray TGP-H-090) on which the black pearl carbon (BPC, Cabot corporation, USA) electrode was coated. The carbon used as the electrode possesses a BET surface area of $1500 \text{ m}^2 \text{ g}^{-1}$, micropore area of $720 \text{ m}^2 \text{ g}^{-1}$ and mesopore area of $540 \text{ m}^2 \text{ g}^{-1}$.^{32,33} A slurry was obtained by ultra-sonicating the required amount of BPC with 40% (w/w) Nafion[®] perfluorinated ion-exchange resin (5 wt.% solution, Aldrich Chemical Company, Inc, USA) in isopropyl alcohol. The slurry was then coated on to a pre-weighed Toray carbon paper of 0.28 mm thickness and $\sim 1 \text{ cm}^2$ geometric area. The loading of BPC/Nafion was $\sim 0.1 \text{ mg cm}^{-2}$ per electrode which was kept identical for all the ECs. The HEA was sandwiched between two high-density graphite (HDG) current collectors, each of $\sim 0.2 \text{ cm}$ thickness and $\sim 1 \text{ cm}^2$ geometric area. The HEA in conjunction with HDG

current collectors was wrapped with a teflon tape and fixed inside a teflon holder prior to their performance evaluation studies. A schematic diagram of polymer hydrogel electrolyte-based all solid-state ECs (with a two electrode assembly) employed in the studies is shown in figure 2. Cyclic voltammetry (CV), electrochemical impedance spectroscopy and chrono-potentiometry studies were carried out using an Autolab electrochemical system (Ecochemie BV, The Netherlands). All the electrochemical measurements were conducted at 25°C . The CVs were recorded in the potential range between -0.5 and $+0.5 \text{ V}$ at a scan rate of 5 mV s^{-1} and used for the calculation of specific capacitance. The impedance measurements were carried out in the frequency range between 0.01 Hz and 10 kHz with a perturbation of 5 mV rms . The time constant (τ_0) values were determined from the intersection of plots for normalized imaginary part (Q) and real part (P) of the complex power (S) vs frequency following a procedure reported by Taberna *et al.*³⁴. Discharge capacitance and charge-discharge coulombic efficiency values were obtained from chronopotentiometry recorded at a current density of 0.5 mA cm^{-2} in the potential range between 0 and 1.0 V . Lifecycle tests on the PHME-based ECs were performed under ambient conditions of temperature and pres-

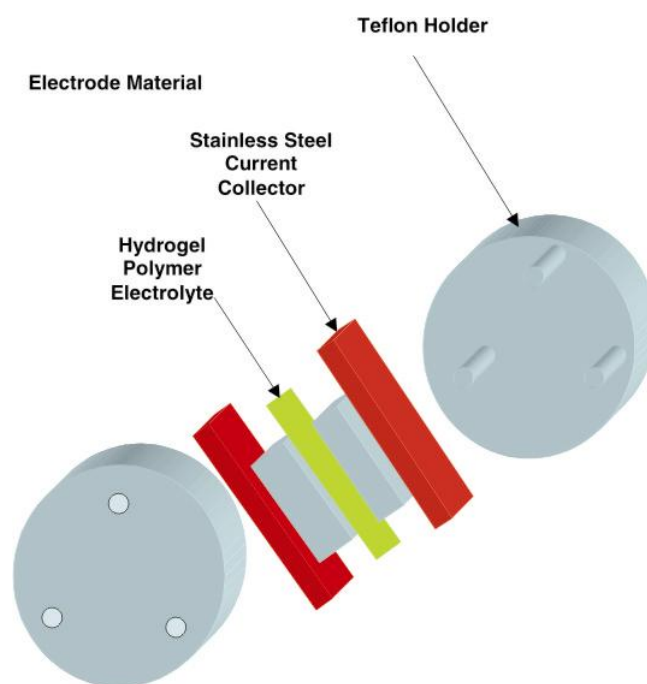


Figure 2. Schematic diagram of polymer hydrogel membrane electrolyte-based all solid-state EC employed in this study.

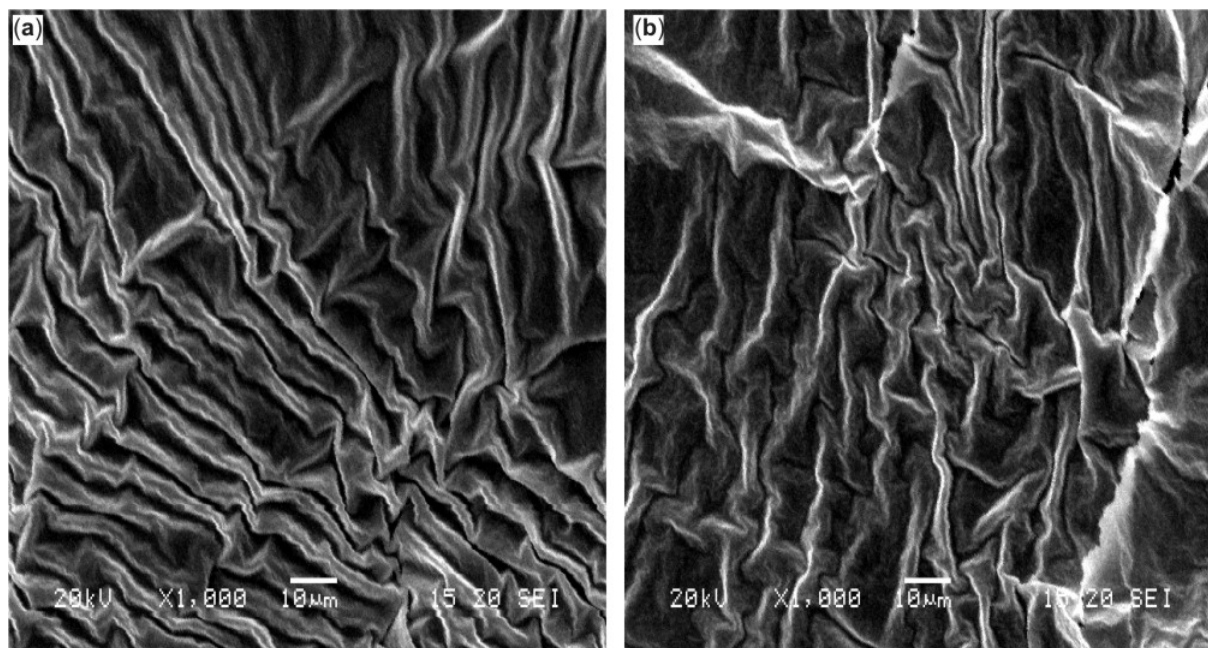


Figure 3. Scanning electron micrographs of a typical acidic PVA hydrogel membrane electrolyte prepared with 1.0 M HClO_4 : (a) planar-view and (b) cross-sectional view.

sure and under 100% relative humidity, in a closed chamber.

3. Results and discussion

The PHMEs employed in the present study are ~ 0.5 mm thick, transparent, colourless, and mechanically stable with abundant amount of water absorbed in the polymer hydrogel matrix. The planar and cross-sectional scanning electron micrographs of a typical PHME prepared with 1.0 M HClO_4 are shown in figure 3a and b, respectively. Both the PHMEs show morphologies with several folds of $\sim 5 \mu\text{m}$ thickness. The stability of the PHMEs decreases with increase in the concentration of HClO_4 . The room temperature ionic conductivity of the membrane is found to be of the order of mS/cm and is due to the presence of HClO_4 .

In order to study the effect of dopant concentration on the degree of cross-linking, PHMEs with varying HClO_4 concentrations have been analysed by DSC techniques. The basic principle of TMDSC is to overlay the isothermal or ramped temperature with a time series of stochastic temperature pulses of different durations.³¹ The DSC data for a typical PHME prepared with 1.0 M HClO_4 are shown in figure 4. The glass transition temperature (T_g) values for PHMEs doped with 0.1, 1.0 and 2 M HClO_4 are

found to be 369, 347 and 347 K, respectively. A decrease in T_g value is observed with increasing HClO_4 concentration. This is attributed to the plasticizing effect due to the formation ion-clusters and reveals an increase in segmental mobility in the PHMEs.³⁵

The CVs for ECs employing BPC electrodes and PHMEs with 0.1, 0.5, 1.0, 1.5 and 2.0 M HClO_4 are shown in figure 5(i) (a–e), respectively. The specific capacitance values determined using equation at 0 V bias, increases from 13.4 to 95.6 F g^{-1} as the concentration of HClO_4 in the PHME is increased from 0.1 to 2.0 M. The average specific capacitance, calculated using the charge associated with the voltammograms, increases from 12.8 to 91.2 F g^{-1} in the same concentration range of HClO_4 . The increase in capacitance with increasing dopant concentration may be explained on the basis of an increased ionic conductivity of the membrane and subsequently an increased accessibility of BPC surface by dopant ions during cycling of voltage. The low concentration of ions present in 0.1 M PHME may not be sufficient to access all the active sites of BPC electrodes that possess high surface area. With increasing dopant concentration, there will be a corresponding increase in the number of ions available to complete the electric-double layer formation at the electrode/electrolyte interface, leading to better utiliza-

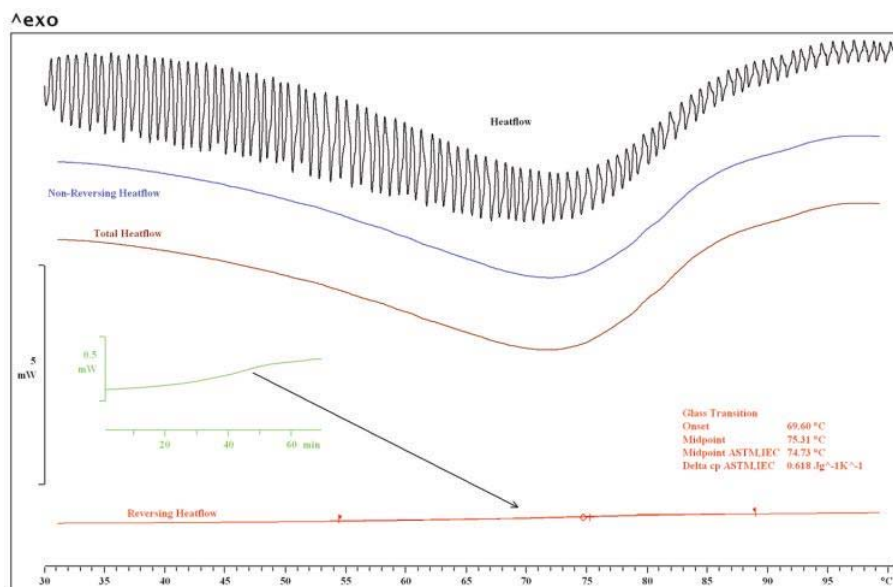


Figure 4. DSC data for a typical PVA hydrogel membrane electrolyte prepared with 1.0 M HClO₄.

tion of BPC electrode. The enhanced utilization of electrode material in the ECs employing PHMEs doped with high concentrations of HClO₄ might be responsible for enhanced capacitance.

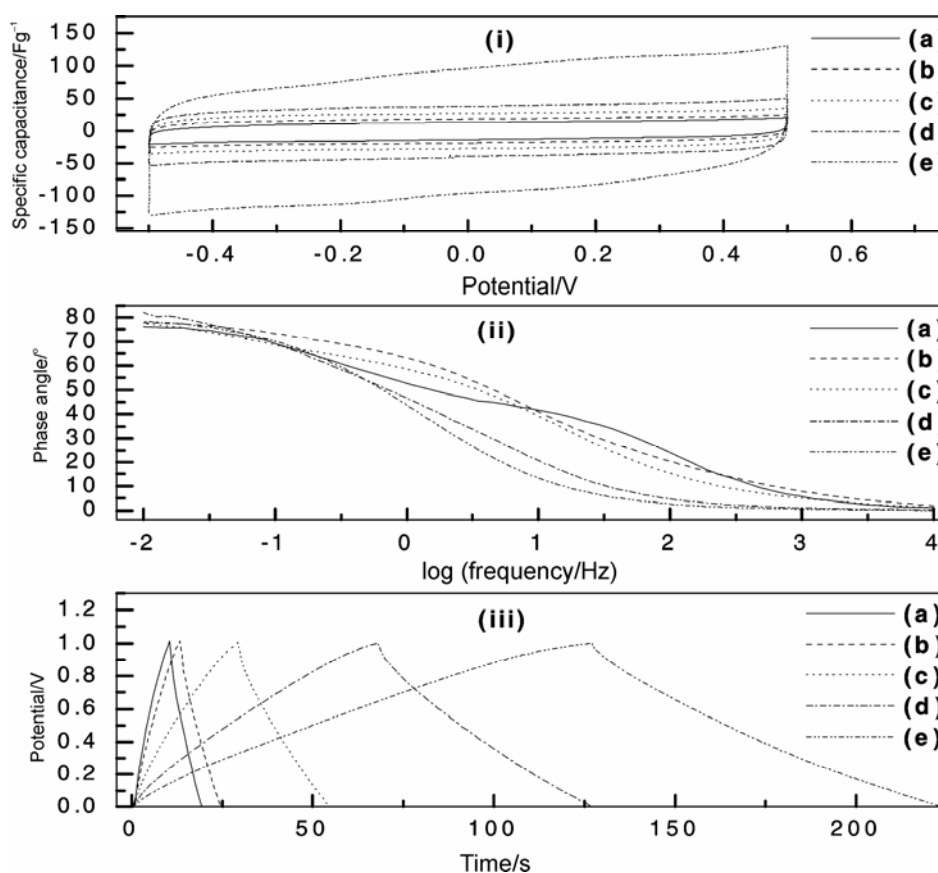
The electrochemical impedance data in Bode form for the ECs employing PHMEs containing 0.1, 0.5, 1.0, 1.5 and 2.0 M HClO₄ are shown in figure 5(ii) (a–e), respectively. The phase angle of the ECs at 1 Hz increases from 76 to 82° as the concentration of HClO₄ in the PHME is increased from 0.1 to 1.5 M. There is a slight decrease in the phase angle when the dopant concentration is further increased from 1.5 M to 2.0 M. The increase in phase angle with increasing dopant concentration suggests an improvement in the capacitive behaviour of the ECs, though the increase is small. Further, the data suggest that the electrode-electrolyte interface behaves like a pure capacitor even at low concentration of the dopant and consequently small number of ionic species present in the electrolyte. The chronopotentiometric data for the aforesaid ECs with PHMEs containing 0.1, 0.5, 1.0, 1.5 and 2.0 M HClO₄ are shown in figure 5 (iii) (a–e), respectively. With increasing HClO₄ concentration in the PHME, an increase in both charge and discharge times is observed. The unequal time-scales associated with the first few cycles of the charge and discharge processes reveal that the charging and discharging processes have different kinetics of formation of the double layer in the initial stages and this need to be

probed further. It should be emphasized that the voltammograms are nearly rectangular revealing no pseudofaradaic reaction in the mechanism of capacitive action. Hence, the observed differences are mainly due to the double layer formation. The discharge capacitance increases from 8.7 to 96.8 F g⁻¹ as the concentration of HClO₄ in the PHME is increased from 0.1 to 2.0 M. The coulombic efficiency increases from 85 to 87% as the concentration of HClO₄ in the PHME increases from 0.1 to 1.5 M. The increase in efficiency is only marginal. With further increase in the concentration of HClO₄ in the PHME to 2.0 M, the charge-discharge efficiency decreases to 76% and this is in parallel with the observation on phase angle as a function of dopant concentration. The results pertaining to the electrochemical studies are summarized in table 1.

The a.c. response of the electrochemical capacitors has been studied by following the complex capacitance and complex power vs frequency. Complex power normalized real part, $|P|/|S|$ and imaginary part, $|Q|/|S|$ vs frequency have been proposed³⁴ as a complementary representation of the impedance response for the electrochemical capacitors, $Z'' = f(Z')$. Using these plots, it is possible to evaluate the time constant (τ_0) of an electrochemical capacitor. The time constant corresponds to the value of 45° for the phase angle. It represents a transition for the electrochemical capacitor between a resistive behaviour for frequency higher than $1/\tau_0$ and a

Table 1. Electrochemical data for the ECs employing BPC electrodes and PHMEs with varying HClO₄ concentration.

HClO ₄ concentration (M)	Electrochemical data obtained from				
	CV at 0 V	CV by integrating total enclosed area	Bode plot at 1 Hz	Chronopotentiometry at 0.5 mA cm ⁻²	
	Specific capacitance (F g ⁻¹)	Average specific capacitance (F g ⁻¹)	Phase angle (°)	Specific capacitance (F g ⁻¹)	Charge- discharge efficiency (%)
0.1	13	13	76	8	86
0.5	19	18	77	11	86
1.0	27	27	77	25	87
1.5	39	39	82	59	88
2.0	96	91	78	97	77

**Figure 5.** Electrochemical data for ECs employing PHMEs containing (a) 0.1, (b) 0.5, (c) 1.0, (d) 1.5 and (e) 2.0 M HClO₄ dopant, derived from (i) cyclic voltammetry, (ii) electrochemical impedance spectroscopy, and (iii) galvanostatic chronopotentiometry.

capacitive behaviour for frequency lower than $1/\tau_0$. The value of time constant for an electrochemical capacitor is inversely proportional to its power. The variation in time constant values for the ECs employing BPC electrodes and acidic pristine PHMEs doped with varying concentrations of HClO₄ are shown in figure 6(i). Plots of normalized

reactive power $|Q|/|S|$ and active power $|P|/|S|$ vs frequency are shown for a dopant concentration of 1 M, in figure 6(ii). The time constant values are found to be ~100, 110, 100 and 130 ms for the ECs employing PHMEs doped with 0.5, 1.0, 1.5 and 2.0 M HClO₄. The time constant values are found to be almost identical for all the capacitors examined

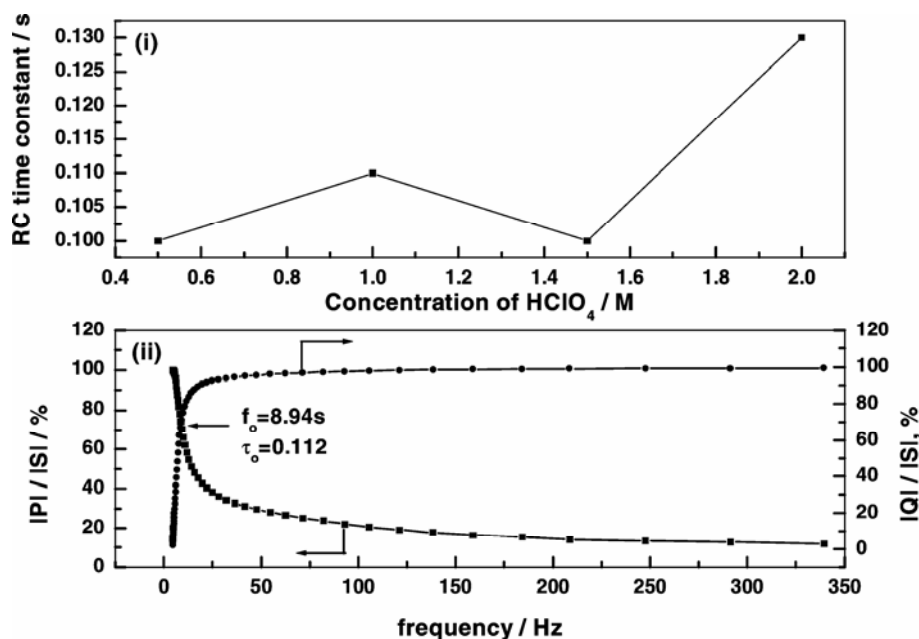


Figure 6. (i) Plot of time constant vs HClO₄ concentration and (ii) plots of normalized reactive power and active power vs frequency for the ECs using acidic pristine PHME (dopant concentration, 1 M).

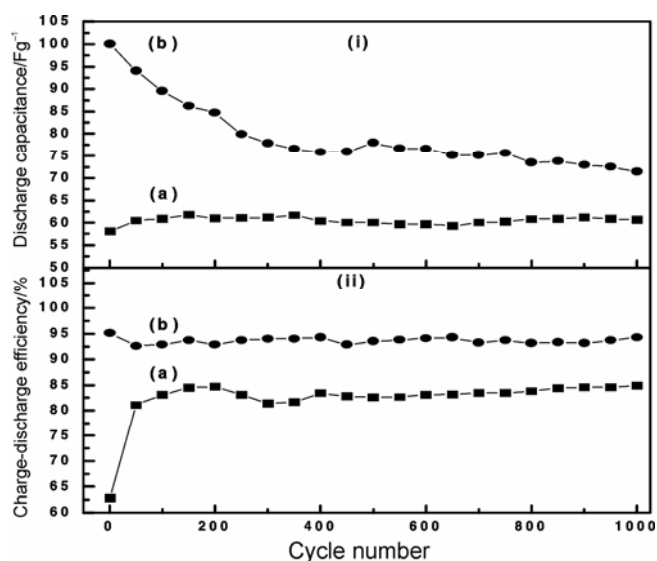


Figure 7. Plots of (i) discharge capacitance and (ii) coulombic efficiency as a function of charge-discharge cycle number for the ECs employing acidic PHMEs doped with (a) 1 M and (b) 2 M HClO₄.

and this could be due to the facile transport of protons in the gel electrolyte media.

The cycle life data for the ECs employing PHMEs doped with 1 and 2 M HClO₄ are given in figure 7. The discharge capacitance and charge-discharge coulombic efficiency values are evaluated from the chronopotentiometric data. The graphs (a) and (b) in figure 7(i) depict the variation in discharge capacitance with cycle number for the ECs employing

PHMEs doped with 1 and 2 M HClO₄, respectively. The EC with 1 M HClO₄-doped PHME has a lower discharge capacitance than that of the EC with 2 M HClO₄-doped PHME. The 1 M HClO₄-doped PHME-based EC has a stable discharge capacitance of ~61 F g⁻¹ for 1000 charge-discharge cycles. The initial discharge capacitance for the 2 M HClO₄-doped EC is ~100 F g⁻¹, which decreases rapidly and attains a stable value of ~70 F g⁻¹ after 400 charge-discharge cycles. The difference in the behaviour of 2 M HClO₄ dopant as compared to other concentrations manifest in all the electrochemical data. The EC assembled with 1 M HClO₄-doped PHME has lower charge-discharge efficiency as compared to the EC assembled with 2 M HClO₄-doped PHME. The charge-discharge efficiency for the EC employing 1 M HClO₄-doped PHME is ~63% for the first charge-discharge cycle, which gradually increases to ~85% for the 150th cycle and then subsequently stabilizes at ~83% for the rest of the cycles. The charge-discharge efficiency for the EC employing PHME containing 2 M HClO₄ is stable at ~94% for 1000 cycles.

The present studies using PVA-based hydrogels throw many unanswered questions based on the dopant concentration in the gel. The formation of double layer at the electrode/electrolyte interface is bound to get affected by the porosity of the surface. In other words, the diffusion of ions in to the micropores and mesopores of the carbon used in the pre-

sent study is expected to play a major role in the formation kinetics of the double layer. Further studies are required to decipher these aspects.

4. Conclusions

Acidic PHMEs with varying concentrations of HClO₄ dopants are prepared by solution-casting method and characterized by physical, thermal as well as electrochemical techniques. The PHMEs show planar morphologies with ~5 μm-sized folding features. The T_g values of the gels decrease with increasing HClO₄ concentration. The average specific capacitance value increases from 12.8 to 91.2 F g⁻¹ as the concentration of HClO₄ in the PHMEs is increased from 0.1 to 2.0 M. The τ_0 values are almost identical for variously doped PHME-based ECs. The doped PHME-based ECs exhibit almost stable capacitive performances for 1000 charge–discharge cycles. The present study reveals that other hydrogel based on, for example, bile acids and various supramolecules will be of interest in electrochemical capacitors.

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