

All solid-state redox supercapacitors based on supramolecular 1,5-diaminoanthraquinone oligomeric electrode and polymeric electrolytes

S.A. Hashmi¹, Shunzo Suematsu, Katsuhiko Naoi*

Graduate School of Technology, Tokyo University of Agriculture and Technology, 2-24-16 Naka-Cho, Koganei, Tokyo 184-8588, Japan

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Abstract

Supramolecular conducting oligomeric 1,5-diaminoanthraquinone (DAAQ)-based all solid-state redox supercapacitors have been fabricated with the solid polymer electrolyte, poly vinyl alcohol (PVA)–H₃PO₄ blend and polymeric gel electrolyte poly methyl methacrylate (PMMA)–ethylene carbonate (EC)–propylene carbonate (PC)–tetra ethyl ammonium perchlorate (TEAClO₄) system. The films of gel electrolyte of the optimized composition PMMA (35 wt.%)–EC:PC (1:1 v/v)–1 M TEAClO₄ and polymer electrolyte PVA–H₃PO₄ (50:50 w/w) blend exhibited high ionic conductivity (10^{−4} to 10^{−3} S cm^{−1} at room temperature) with good mechanical strength, suitable for application in electrochemical supercapacitors. The capacitors have been characterized using a.c. impedance spectroscopy, linear sweep voltammetry and prolonged cyclic test. The maximum capacitance value of 3.7–5.4 mF cm^{−2} (equivalent to single electrode capacitance 125–184 F g^{−1} of DAAQ electrode) has been observed for the PMMA–gel electrolyte based capacitor. This corresponds to the energy density 92–135 Wh kg^{−1}. System based on the proton-conducting PVA–H₃PO₄ polymer blend, however has relatively lower capacitance of 1.1–4.0 mF cm^{−2} (equivalent to single electrode capacitance of 36–136 F g^{−1}).

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1. Introduction

In recent years, electrochemical supercapacitors have received a worldwide attention due to their widespread use as alternative and/or complementary power sources in various applications [1–7]. Their high power density and long cycle life make them attractive to be used as rechargeable pulse power source, particularly, in hybrid power design in electrical vehicles [1,2]. In general, the supercapacitors are classified into two categories viz: (a) electrical double layer capacitors (EDLCs) in which large area activated carbons are used as electrode materials [1,2,7–9], and (b) redox supercapacitors. The active oxide materials, e.g. RuO₂·xH₂O [10], NiO_x [11], CoO_x [12] or conducting polymers e.g.

polypyrrole, polythiophene and its derivatives etc. [13–23] are used as active electrodes for redox supercapacitors.

Recently a quinone based supramolecular oligomer 1,5-diamino-anthraquinone (DAAQ) has been introduced by us as a promising electrode material for redox supercapacitor, which exhibits high specific capacity (50–60 Ah kg^{−1}) with aqueous and non-aqueous liquid electrolytes [24,25]. The oligomer is of crystalline nature via π – π stacking. It shows high electrocatalytic activity, electrochemical durability and reproducible redox response over 20,000 cycles with little loss of capacity, about 5% with respect to the initial capacity [26]. Such a high reproducibility is owing to the isotropic lattice expansion and shrinkage of π -stacked supramolecule during repeated ion switching processes.

Most of the reported redox supercapacitors are based on liquid electrolytes [10–20,24–26] which are associated with the well known disadvantages of corrosion, self discharge, bulky design and low energy density, similar as in the case of liquid electrolyte batteries. Major attention has been devoted these days to fabricate solid-state capacitors using solid polymer/gel electrolytes because of their

* Corresponding author.

E-mail address: naoi_lab@cc.tuat.ac.jp (K. Naoi).

¹ On leave from: Department of Physics, North Eastern Regional Institute of Science and Technology (NERIST), Nirjuli (Itanagar)-791109, Arunachal Pradesh, India. Tel.: +91 360 257734; fax: +91 360 244307; e-mail: sah@nerist.ernet.in.

high ionic conductivity and advantageous mechanical properties including flexibility for proper electrode–electrolyte contact and ability to form thin films of desirable area. The solid-state redox supercapacitors are not widely reported except a few recent studies which include different polymer/gel electrolytes e.g. PMMA–EC–PC–LiClO₄ [23,27], poly ethylene glycol (PEG)–PC–tetra ethyl ammonium tetrafluoroborate (TEABF₄) [28], poly ethylene oxide (PEO)–PEG–LiCF₃SO₃ [21,22], PVA–H₃PO₄ [21,22], PMMA–EC–PC–NaClO₄ [29], etc.

This paper presents the results from the studies on all solid-state redox capacitors fabricated from the supramolecular 1,5-diaminoanthraquinone (DAAQ) oligomeric active electrodes with polymer/gel electrolytes. The polymer electrolyte was based on proton-conducting polymeric system poly vinyl alcohol (PVA)–H₃PO₄ blend and the polymeric gel electrolyte was PMMA–EC–PC–TEAClO₄ system. The performance characteristics of the supercapacitors have been evaluated using a.c. impedance spectroscopy, linear sweep voltammetry and prolonged cyclic tests.

2. Experimental details

The DAAQ oligomer was electrodeposited on carbon paper (Toray International Corp., Japan) potentiostatically at +1.5 V versus Ag/AgCl in a cell containing solution of 10 mM DAAQ monomer +0.5 M tetraethyl ammonium perchlorate (TEAClO₄) + 0.5 M CF₃COOH in propylene carbonate (PC). Details of the preparation technique are published by us elsewhere [24].

Films (200–300 μm thick approximately) of the polymer electrolyte PVA–H₃PO₄ blend (50:50 w/w) were prepared using “Solution-Cast” technique. The preparation procedure of PVA–H₃PO₄ blend was published elsewhere [8]. The gel electrolyte, PMMA–PC–EC–TEAClO₄, was prepared using the following procedure. The appropriate amount of salt, TEAClO₄, was dissolved in to PC:EC mixture (1:1 v/v) by stirring thoroughly. The optimized composition of the liquid mixture was then added with different appropriate amount of polymer matrix, PMMA, to obtain the desired gel electrolytes of different compositions. The PMMA–PC–EC–TEAClO₄ mixture was then kept in oven at 70–80 °C for 10–12 h for gelling followed by slow cooling. The materials [(PVA (Aldrich, MW 124,000–186,000), PMMA (Aldrich, MW 996,000), H₃PO₄ (Kanto Chemical Corp., Japan), EC (Aldrich), PC (Mitsubishi Chemical Corp., Japan) and TEAClO₄ (TCI, Japan)] were used as received.

The electrical conductivity of the PC–EC–TEAClO₄ liquid mixture was measured using conductivity meter (Horiba, Japan, model ES-14). The bulk electrical conductivity of polymer/gel electrolytes was evaluated by impedance spectroscopy. The stainless steel blocking electrodes were used for conductivity measurements.

The capacitor cells were constructed with either the PVA–H₃PO₄ blend or PMMA–PC–EC–TEAClO₄ gel electrolytes sandwiched between two symmetrical DAAQ oligomeric electrodes deposited on carbon sheets. The geometrical surface area of these capacitor cells was kept to about 1.0 cm². The performance of the capacitor cells was characterized using impedance spectroscopy, linear sweep voltammetry and prolonged cyclic tests. The impedance measurements were carried out using a Solartron (1250) Frequency Response Analyser attached with Solartron (1287) Electrochemical Interface. The impedance measurements were performed in the frequency range 60 kHz to 10 mHz at a signal level of 10 mV. The capacitance values were estimated at the frequencies 100 and 10 mHz because the values of the electrochemical capacitance are dominant in low frequency range which are several order larger than the geometrical capacitance. The overall capacitances *C* of the capacitor cells were evaluated using the relation:

$$C = -(\omega Z'')^{-1} \quad (1)$$

where $\omega (=2\pi f)$ is the angular frequency and Z'' the imaginary part of the total complex impedance. The single electrode specific capacitance values were evaluated by multiplying the overall capacitance by a factor of two and divided by the mass of a single active electrode material.

The linear sweep voltammetry was carried out at different scan rates between a floating potential of –0.8 and 0.8 V using a BAS-100 computer controlled potentiostat. The capacitance values from this technique were evaluated using the relation

$$C = \frac{i}{s} \quad (2)$$

where ‘*i*’ is the current and ‘*s*’ the scan rate.

3. Results and discussion

3.1. Characteristics of electrolytes

The composition of the PMMA–PC–EC–TEAClO₄ based gel electrolytes was optimized to get high ionically conducting and mechanically stable material. In this process, the composition of EC–PC–TEAClO₄ liquid mixture was first optimized by measuring the electrical conductivity. The EC:PC mixture of the ratio 1:1 v/v was taken. The optimum composition of liquid electrolyte mixture for gel preparation was taken to be EC:PC (1:1 v/v) added with 1 M TEAClO₄. Different weight percent (10–40 wt.%) of PMMA was then added to the liquid mixture to obtain the gel electrolyte films. The electrical conductivity of the gel films was measured as a function of the PMMA content. A slight decrease in conductivity has been observed on increasing the polymer content in the electrolyte system. It may be noted that the decrease in conductivity has been observed in terms of multiples, not in order. It is established that in the salt–solvent–polymer

composition, PMMA acts as an inert network, which entrap the liquid electrolyte to form gel system [30,31]. The ionic conductivity in the gel electrolytes is basically due to liquid electrolytes entrapped in the PMMA like polymer networks.

Further, it has also been observed that for the lower content of PMMA, only a portion of liquid electrolyte is utilized in the gel formation. Rest of the liquid remains phase separated and the solid gel electrolytes appears floating into it. Beyond the 35 wt.% addition of PMMA, almost all the liquid electrolyte becomes utilized in the gel formation. A composition of the gel electrolyte comprising of 1 M TEAClO₄ in EC:PC (1:1 v/v) with higher content (35 wt.%) of PMMA has been chosen for the present studies as it offers mechanically stable free standing film with acceptable electrical conductivity of the order of 10⁻³ S cm⁻¹.

The proton-conducting polymer electrolyte PVA–H₃PO₄ blend was previously reported by Petty-Weeks and Polak [32] and by Hashmi et al. [8]. A weight ratio of 50:50 of PVA:H₃PO₄ was chosen for the present study. The polymer electrolyte PVA–H₃PO₄ blend and the gel electrolyte, PMMA–PC–EC–TEAClO₄ system, show the electrical conductivity of the order of 10⁻⁴ to 10⁻³ S cm⁻¹ at room temperature (25 °C). This order of conductivity of the polymer/gel electrolytes is acceptable values as it offers low resistance (of the order of 100 Ω cm²) when the electrolytes are used in the form of thin films.

The electrochemical stability i.e. working voltage range of the electrolytes is another important parameter, from their application point of view in electrochemical devices (e.g. batteries, supercapacitors, etc.), which is necessary to be evaluated. The working voltage range of aqueous based proton-conducting electrolytes (such as PVA–H₃PO₄ blend in the present case) has already been established to be limited to 1.2 V. The working voltage range of PMMA–EC–PC–TEAClO₄ gel electrolyte was checked by cyclic voltammetry using stainless steel electrodes. Fig. 1

shows the cyclic voltammogram observed with stainless steel electrodes and PMMA–gel electrolytes, which shows the electrochemical stability of gel electrolytes in the range from –2.5 to 2.5 V. Therefore, the cut-off voltage of the capacitor based on the PMMA–gel (under present study) is limited to 2.5 V.

3.2. Characteristics of capacitors

Different model capacitor cells were constructed using the two types of electrolytes and electrodeposited DAAQ oligomeric electrode namely, (a) DAAQ|PVA–H₃PO₄|DAAQ and (b) DAAQ|PMMA–EC–PC–TEAClO₄|DAAQ. The typical impedance spectra of different capacitor cells are shown in Fig. 2. It should be noted that the pure capacitor shows the impedance behaviour, which is a straight line parallel to the imaginary axis. The DAAQ oligomer electrodes show capacitive behaviour with both the polymer electrolyte, PVA–H₃PO₄, and PMMA–gel electrolyte. The impedance response for both the capacitor cells shows a small semicircle in the higher frequency range followed by the steep rising portion at the lower frequency range. A typical high frequency semicircle is shown in Fig. 2B as inset. The higher frequency semicircular spur reflects the bulk properties of the electrolytes and the charge transfer process at electrode–electrolyte interfaces, whereas the steep rising behaviour in the lower frequency range indicates the capacitive nature of the cells. The equivalent circuit of such impedance response can be represented by a modified Randles circuit, as shown in Fig. 2C [15]. The semicircle, which is observed to be slightly suppressed, is attributed to the parallel combination of double layer capacitance, C_{dl}, and charge-transfer resistance, R_{ct}, in series with a Warburg impedance/constant phase element (cpe). The detailed impedance analysis is required, but it could not be done due to non-availability of the suitable analytical techniques/software with us.

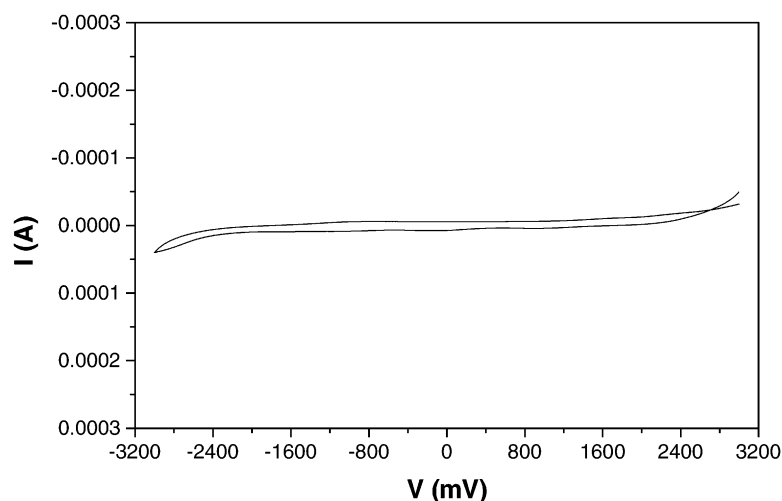


Fig. 1. Cyclic voltammogram of PMMA–EC–PC–TEAClO₄ gel electrolyte with stainless steel electrodes at room temperature (25 °C) recorded at the scan rate 10 mV s⁻¹.

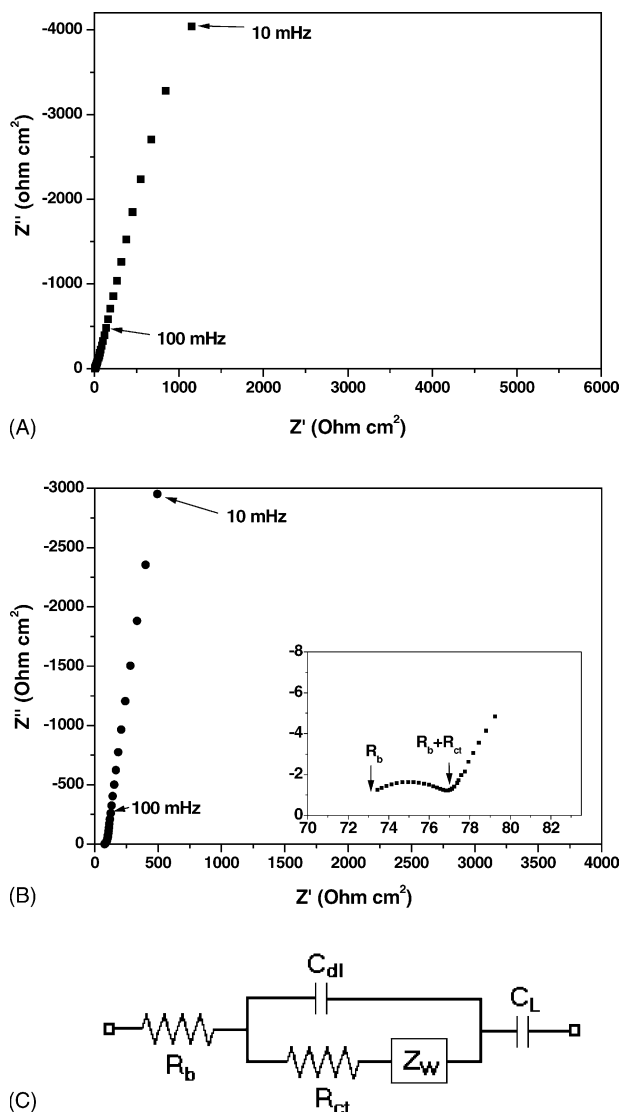


Fig. 2. Typical impedance plots of the capacitor cells: (A) DAAQ|PVA–H₃PO₄|DAAQ, and (B) DAAQ|PMMA–EC–PC–TEABF₄|DAAQ. Part (C) shows the modified Randles circuit, representing an equivalent circuit for capacitor cells (R_b is the bulk resistance; R_{ct} the charge-transfer resistance; C_{dl} the double layer capacitance; Z_w the Warburg impedance and C_L is limiting capacitance).

The values of bulk resistance R_b and charge-transfer resistance R_{ct} could be easily evaluated from the intercepts on the real axis of the complex impedance response. These parameters along with the total resistance R and the capacitance values (evaluated from Eq. (1)) at frequencies 100 and 10 mHz are summarized in Table 1. A comparison indicates that the

cell comprising DAAQ electrode with the gel electrolyte the impedance response is more close to the ideal capacitive characteristics as compared to the cell with PVA–H₃PO₄ blend (Fig. 2). The DAAQ oligomeric electrode shows the relatively larger capacitance value of 3–6 mF cm⁻² (equivalent to the single electrode capacitance of 125–184 F g⁻¹ of DAAQ electrode) with gel electrolyte as compared to that with the polymer electrolyte, PVA–H₃PO₄ blend. The predominant reasons for relatively lower value of the capacitance of PVA–H₃PO₄ based capacitors are the possible charge loss due the larger charge-transfer resistance, R_{ct} , values and relatively poor contact at the electrode–electrolyte interfaces. The incorporation of highly flexible and conducting gel electrolytes can make a vast improvement in such interfacial properties leading to the high capacitance values.

Further, the value of single electrode double layer capacitance of the system comprising of activated carbon fabrics (ACF) electrode and PVA–H₃PO₄ electrolyte was reported to be 70–90 F g⁻¹ of carbon [8]. The double layer capacitance of the capacitor was recently observed to be 123 F g⁻¹ of carbon with the gel electrolyte (PMMA–EC–PC–TEABF₄) and activated carbon electrode [9]. The redox supercapacitors based on conventional conducting polymers such as polypyrrole, polythiophene etc. with similar electrolytes also show the single electrode specific capacitance values in the range of 50–100 F g⁻¹ of electroactive electrode materials [21–23]. This comparison indicates that the DAAQ is a prominent electrode material for all solid-state redox supercapacitors. The corresponding energy density for the DAAQ/gel electrolyte based capacitors has been found to be 92–135 Wh kg⁻¹ (evaluated for a maximum potential window of 2.3 V for DAAQ oligomeric electrode).

The value of capacitance of the cell comprising of liquid electrolyte with DAAQ electrode is expected to be quite larger as compared to that the polymer/gel electrolyte based capacitors. This difference is possibly due to inaccessibility of the solid polymer/gel electrolytes to form proper interfacial contact throughout the volume of the active electrode materials. Further, a larger fluctuation in the values of capacitance and charge-transfer resistance, R_{ct} , has been observed for PVA–H₃PO₄ based capacitors as compared to the gel-based capacitors. This is possibly owing to the fact that the proton-conducting PVA–H₃PO₄ polymer electrolyte is relatively more sensitive to the ambient temperature and humidity conditions. A detailed study on the temperature and humidity dependence of the electrical properties of PVA–H₃PO₄ polymer electrolyte based electrical dou-

Table 1
Electrical parameters of different capacitor cells from impedance analysis

Capacitor cells	R_b (Ω cm ²)	R_{ct} (Ω cm ²)	R (Ω cm ²)		C			
			100 mHz	10 mHz	100 mHz	10 mHz		
DAAQ PVA–H ₃ PO ₄ DAAQ	7.0–15.0	1.0–45.0	160–750	1150–2750	0.6–2.7 mF cm ⁻²	20–92 F g ⁻¹	1.1–4.0 mF cm ⁻²	36–136 F g ⁻¹
DAAQ PMMA–gel DAAQ	42.0–78.0	4.0–10.0	130–140	490–850	3.2–4.9 mF cm ⁻²	109–166 F g ⁻¹	3.7–5.4 mF cm ⁻²	125–184 F g ⁻¹

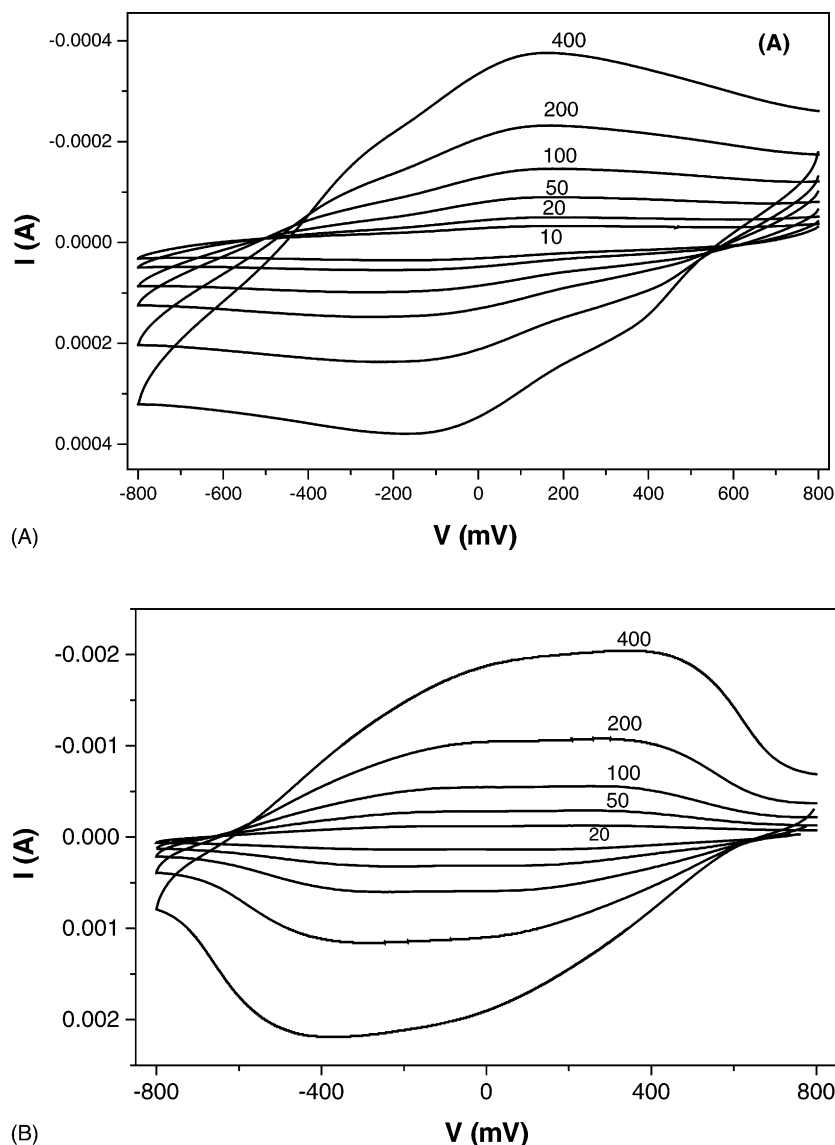


Fig. 3. Cyclic voltammograms of the capacitor cells: (A) DAAQ|PVA–H₃PO₄|DAAQ, and (B) DAAQ|PMMA–EC–PC–TEAClO₄|DAAQ at different scan rates. The scan rates (mV s⁻¹) are marked in the figures.

ble layer capacitors has already been carried out by Hashmi et al. [8].

Fig. 3 represents the cyclic voltammograms of the two capacitor cells at the different voltage scan rates. The response for each capacitor cell has been observed to be dependent on the scan rate which is expected for a capacitor cell [33]. At the lower scan rates, both the capacitor cells show the voltammogram close to a square shape, which is the characteristic of a capacitor. Particularly, the gel electrolyte based cell shows the almost square shaped voltammogram even for the higher scan rates (200–400 mV s⁻¹) although some deviation/tilt in the shape cannot be ruled out (Fig. 3B). In addition, some reversible peaks overlapping to the regular square shape of voltammogram have also been observed, predominantly appearing particularly in the case of aqueous PVA–H₃PO₄ polymer electrolyte based capacitor

cell (Fig. 3A). This feature is owing to the electrochemical reversible hydroquinone to quinone (HQ \rightleftharpoons Q) reaction [25] when DAAQ oligomer is in association with the aqueous proton-conducting PVA–H₃PO₄ like polymer electrolyte.

The values of the capacitance have been evaluated from cyclic voltammetry (using Eq. (2)) which have been found to be in good agreement with the values evaluated from the impedance measurements (discussed above). The scan rate dependence of the capacitance of both the capacitor cells is shown in Fig. 4. A comparison indicates that the capacitor cell DAAQ|gel electrolyte|DAAQ shows almost a constant value of capacitance after a slight initial decrease. A relatively larger decrease in capacitance values with respect to scan rate has been observed for DAAQ|PVA–H₃PO₄|DAAQ cell. This indicates a better electrode–electrolyte contact along with the smooth and fast switching behaviour in

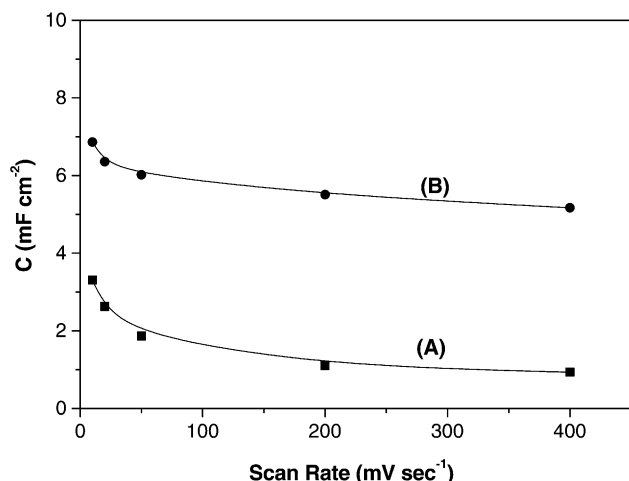


Fig. 4. Variation of the capacitance of the capacitor cells: (A) DAAQ|PVA-H₃PO₄|DAAQ, and (B) DAAQ|PMMA-EC-PC-TEAClO₄|DAAQ as a function of scan rates.

gel electrolyte based capacitor cells as compared to the PVA-H₃PO₄ based system.

Fig. 5 shows the variation of the capacitance for each capacitor cell, evaluated from CV (using Eq. (2)) as a function of voltammetric cycles between -800 and 800 mV at the scan rate of 100 mV s⁻¹. For the initial few cycles, a sharp decrease in the capacitance values has been observed predominantly for the capacitor cell with the gel electrolyte (Fig. 5B). This initial decrease in capacitance is possibly attributed to the charge consumption in some possible irreversible faradic reaction(s) associated with loosely bound surface groups at the electrode-electrolyte interfaces. In contrast, the proton-conducting PVA-H₃PO₄ based cell shows a slight increase in capacitance value for the initial few cycles. As per the physical observation, it had been noted that the PVA-H₃PO₄ film is relatively tough as compared to the PMMA based gel electrolyte (of the composition under

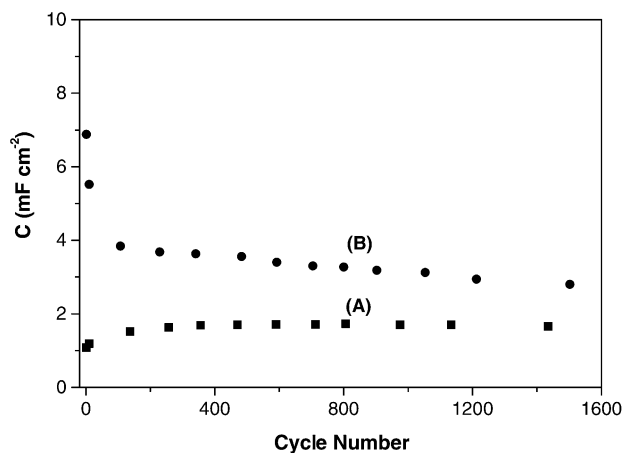


Fig. 5. Capacitance of the two capacitor cells: (A) DAAQ|PVA-H₃PO₄|DAAQ, and (B) DAAQ|PMMA-EC-PC-TEAClO₄|DAAQ as a function of voltammetric cycles at the scan rate 100 mV s⁻¹.

the present study) which is more soft, spongy and flexible. The gel electrolyte would offer relatively better formation of interfacial contact with electrodes as compared to the PVA-H₃PO₄ polymer electrolyte film. The initial slight increase in the capacitance value for the DAAQ/PVA-H₃PO₄ capacitor is possibly attributed to the proper formation of interfaces for initial few cycles. After initial decrease/increase of the capacitance value for both the capacitor cells, reasonably stable values have been observed for more than 1400–1500 cycles (Fig. 5).

4. Conclusion

All solid-state redox supercapacitors based on supramolecular conducting oligomeric 1,5-diaminoanthraquinone electrode with the solid polymer electrolyte (PVA)-H₃PO₄ blend and polymeric gel electrolyte (PMMA)-EC-PC-tetra ethyl ammonium perchlorate have been fabricated and characterized. The optimized composition of polymer/gel electrolytes, showing room temperature conductivity of the order of 10⁻⁴ to 10⁻³ S cm⁻¹ and good mechanical strength, were observed to be suitable electrolytes for their application in redox capacitors. The capacitors based on gel electrolyte give highest capacitance of approximately 3.7–5.4 mF cm⁻² (equivalent to single electrode capacitance 125–184 F g⁻¹ of DAAQ electrode). An energy density of about 92–135 Wh kg⁻¹ has been evaluated for a maximum potential window of 2.3 V for DAAQ oligomeric electrode. A relatively lower capacitance values of approximately 1.1–4.0 mF cm⁻² (equivalent to single electrode capacitance of 36–136 F g⁻¹ of DAAQ) have been observed for the proton-conducting PVA-H₃PO₄ polymer blend based capacitors. For both the capacitor cells based on PVA-H₃PO₄ polymer blend and PMMA-gel electrolyte, a reasonably stable values have been observed for more than 1400–1500 voltammetric cycles after some initial decrease or increase of the capacitance values.

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