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Short communication

All-solid supercapacitor based on polyaniline and sulfonated poly(ether ether ketone)

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Abstract

An all-solid supercapacitor has been fabricated using polyaniline (Pani) and sulfonated poly(ether ether ketone) (SPEEK). A composite electrode is made from chemically-synthesized Pani, SPEEK, electronically conducting carbon black and polytetrafluoroethylene (PTFE). SPEEK acts as both separator and electrolyte. The unit cell consists of two electrodes made from a p dopable Pani composite electrode separated by a SPEEK membrane with a thickness of 50 μm. As the electrodes of the capacitor are made from same p dopable Pani material, the cell is a type I (p–p) capacitor. The cell characteristics are studied using cyclic voltammetry, charging–discharging, and impedance analysis. The unit cell capacitance is 0.6 F, which corresponds to 27 F per g of the active polymer material.

Keywords: Supercapacitor; Polyaniline; Sulfonated poly(ether ether ketone); Solid electrolyte

1. Introduction

Supercapacitors are promising devices for delivering high power density. Digital communications, electric vehicles and other devices that require electrical energy at high power levels in relatively short pulses have prompted considerable research on supercapacitors [1–3]. The electrode materials used for the capacitors are normally carbon with a high surface area, noble metal oxides and conducting polymers [4,5]. Conducting polymers have attracted use for electrochemical capacitors because of a combination of high charge density compared with carbon and a low cost compared with metal oxides [6,7]. In carbons with high surface area, energy storage arises due to charge separation of electronic and ionic charges at the interface between the electrode material and the electrolyte solution. Hence, so-called 'electric double-layer' capacitors are produced. In conducting polymers and in metal oxides, fast faradic charge transfer takes place at the electrode material and so-called 'redox' or 'pseudocapacitance' is produced [1,8,9].

Various liquid electrolytes, both aqueous as well as organic solutions, are used for capacitor assembly. The potential window range for aqueous systems is around 1.23 V. It can be extended, however, by judicious choice of the supporting electrolyte and/or a solvent [10–24]. In recent years, solid electrolytes have been investigated for supercapacitors [25–30]. Solid electrolytes are advantageous over liquid electrolytes in respect of easy handling and reliability without electrolyte leakage. Development of non-aqueous systems is gaining momentum due to the higher energy density of the systems. Recently, a supercapacitor based on Nafion, a proton-conducting polymer membrane, has been hybridized with a direct methanol fuel cell [31]. There are many ionomers/polyelectrolytes which can perform similarly when used as all-solid supercapacitors. Sulfonated poly(ether ether ketone) (SPEEK) has been used as proton-conducting polymer membrane in a fuel cell [32]. It is expected that SPEEK can also act as potential material for an all-solid capacitor. Moreover, the concentration of the sulfonic acid group can be varied in SPEEK.

In this preliminary study, an all-solid capacitor with polyaniline as the electrode material and SPEEK as the solid electrolyte has been prepared. The properties of the electrode material have been studied by incorporating the capacitor in a unit cell assembly. Charging and discharging of the unit cell are also discussed.

2. Experimental

2.1. Materials

Poly(ether ether ketone) (PEEK) powder, Victrex, Grade 450P, was obtained from the UK, and sulfuric acid,

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dimethlyacetamide (DMAC) and NH_4OH from Qualigens (India). Teflon suspension was supplied by Hindustan Fluoro Carbon Corp (India). All the materials were used as received without further purification. Conducting carbon powder was (Vulcan XC-72) received from the Cabot Corporation and conducting carbon paper from Toray, Japan.

2.2. Preparation of SPEEK

The PEEK powder was dissolved in concentrated H_2SO_4 for 1 h at 25 °C. After that, the solution was heated to 55 °C and stirred for 1.5 h. The resulting SPEEK solution was then precipitated in a ice/water mixture under stirring. The solution was then filtered and product washed thoroughly with distilled water to remove residual sulfuric acid. The solid product was dried in oven at 55 °C to constant weight. The SPEEK was characterized for its ion-exchange capacity in order to determine the equivalent weight.

2.3. Preparation of SPEEK membrane separator

The SPEEK was dissolved in DMAC to make a 15% solution. The solution was poured on a glass plate and homogenously spread by means of a doctor blade. The film was dried in a dust-free atmosphere at room temperature for 60 h. Further drying was performed in an air oven at 120 °C for 24 h. The film thickness was maintained at around $50 \pm 5\,\mu m$.

2.4. Purification of conducting carbon black

Conducting carbon black was purified by soxhletting with water for more than 24 h. The resulting powder was dried at 80 °C to constant weight and stored. The powder was used in the preparation of electrodes.

2.5. Electrode preparation

Pani was synthesized chemically following the method of MacDiarmid et al. [33]. De-doping of Pani was performed by stirring in 0.5 M NH_4OH for 5 h. The powder was filtered, washed thoroughly with water, and dried at 80 °C under vacuum to constant weight. The Pani powder was mixed with purified conducting carbon powder, a Teflon suspension (10% suspension in ammonia solution), and a SPEEK solution (10% solution in DMAC). The composition is given in Table 1. The ingredients were mixed thoroughly to yield a paste, which was then applied to carbon paper by a rolling method. After fabrication, the electrode was dried for over 48 h at 80 °C.

Table 1
Composition of capacitor electrode

Component	Composition (wt.%)
Pani	40
Carbon powder	38
PTFE	2
SPEEK	20

2.6. Unit cell fabrication

The structure of all-solid capacitor using SPEEK and Pani is shown in Fig. 1. Two pieces each 2.5 cm × 2.5 cm were cut from the large electrode for fabrication of a unit cell. The electrodes and a SPEEK membrane of similar size were hot pressed for 30 s at 180 °C. This minimized the ohmic resistance and established a good contact between the electrode and the SPEEK membrane. In the assembly shown in Fig. 1, SPEEK acts as both a separator and a solid electrolyte. The carbon paper serves as a current-collector.

2.7. Characterization

Cyclic voltammetry (CV) and impedance analysis of the supercapacitor were performed using an AUTOLAB from Eco Chemie. The charging and discharging characteristics of the supercapacitor were also studied with the same equipment. The scanning rate for CV was 5, 10 and 25 $mV\,s^{-1}$ and the impedance analysis was conducted at open-cell potential in range 1 MHz to 0.01 Hz.

3. Results and discussion

The configuration of the capacitor is shown in Fig. 1. The Pani concentration in the electrode is 40 wt.% whereas that of SPEEK is 20 wt.%. The equivalent weight of the SPEEK was 595 g. The fabricated unit cell was studied for electrochemical characterization. The results were confirmed by repeating the experiment with other cells of the same size and composition. Cyclic voltammograms for the capacitor at the

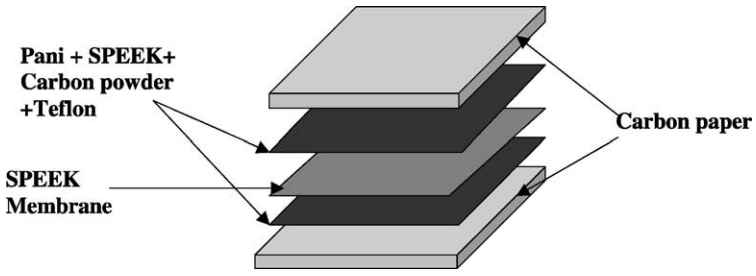

Fig. 1. Construction of unit cell assembly of all-solid supercapacitor.

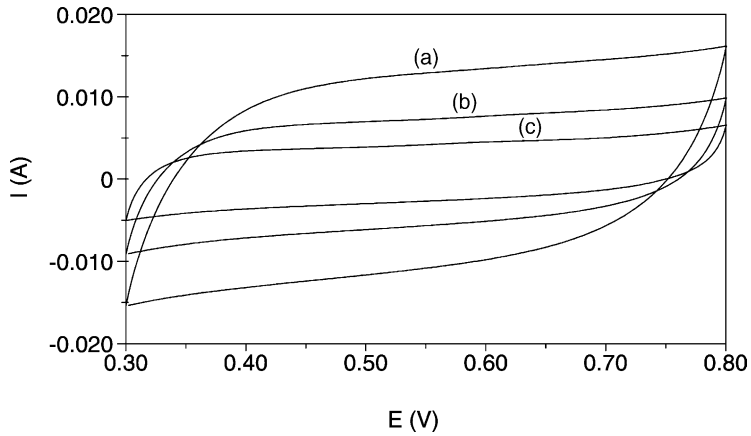

Fig. 2. Cyclic voltammogram of all-solid supercapacitor based on SPEEK: (a) 25, (b) 10, and (c) 5 mV s^{-1}.

different scan rates are presented in Fig. 2. Both electrodes were made from same polymer and it represents a Type I class of capacitor. Good capacitor performance is obtained and this suggests that SPEEK can be used as a solid polymer electrolyte. The shape of the voltammogram is close to a rectangular one. The scanning was performed in the voltage range of 0.3 to 0.8 V. Similar behavior has been reported for gel and Nafion membrane electrolytes [31]. The capacitance calculated from the voltammogram gives approximately 0.6 F, which corresponds, to 27 F per g of active polymer material. The charging and discharging curve of the Pani–SPEEK supercapacitor at room temperature when it charged to 1 V at 20 mA is shown in Fig. 3. The capacitor shows typical charging–discharging performance. The charging and discharging capacitance can be calculated using the following equation [27]:

$$C = \frac{It}{\Delta V} \quad (1)$$

where C, I, t and ΔV are the capacitance, charging/discharge current, charge/discharge time and potential difference, respectively. The capacitance estimated from the curves is approximately 0.625 F and this corresponds to a specific capacitance of 28 F per g, which is close to the value calculated by cyclic voltammetry. The low value can be attributed to the low concentration of sulfonic acid groups in the electrode matrix.

The capacitance and the internal resistance are of great importance for capacitor performance. The impedance spectrum for the unit cell is shown in Fig. 4. The spectrum

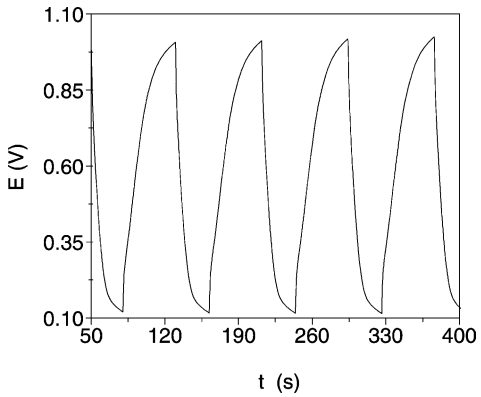

Fig. 3. Charging and discharging curves of all-solid supercapacitor based on SPEEK.

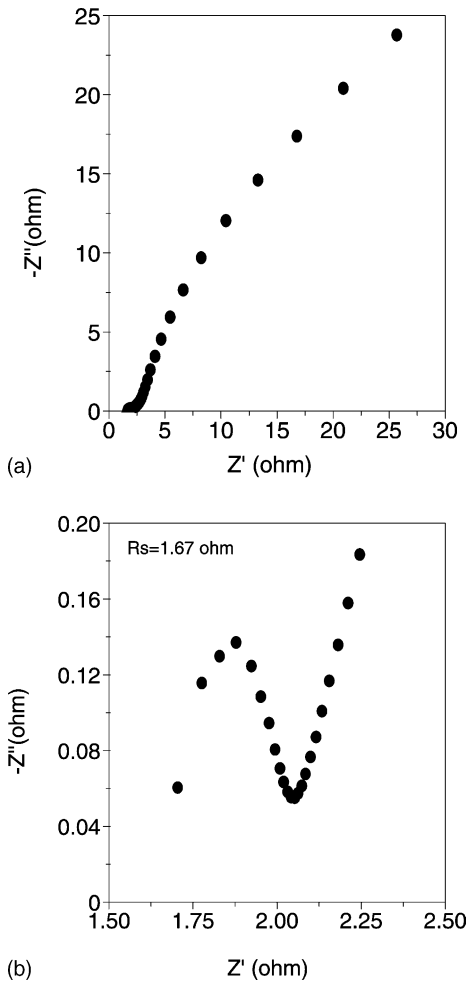

Fig. 4. Impedance spectrum of all-solid supercapacitor using SPEEK.

displays a small semicircle at high frequency followed by a transition to linearity at low frequency. At high frequency, it represents a diffusion process and at low frequency it represents capacitive behavior [30]. The impedance value for the capacitor can be determined from the spectrum. The intersection of the semicircle with the real axis gives the resistance value R and from the spectrum it is estimated to be about 1.67 Ω (Fig. 4b). The low value can be attributed to a low ohmic resistance between the electrode and the separator|electrolyte. The time constant RC is approximately 1 s. This parameter determines the rate at which the supercapacitor can be charge and discharged, and hence limits the power of the capacitor.

4. Conclusions

Pani has been synthesized chemically and PEEK was sulfonated using sulfuric acid. An all-solid supercapacitor with Pani and sulphonated PEEK has been fabricated. SPEEK was used both as an electrolyte and a separator membrane. The performance of the supercapacitor has been studied by means of cyclic voltammetry, charge–discharge testing and impedance analysis. The capacitance measured from cyclic voltammetry is 27 F per g of active polymer material. Charge and discharge curves show a similar capacitance value. The study has demonstrated that a SPEEK-based electrolyte may be a promising material for supercapacitors. Detailed studies for optimization of the various parameters for making more efficient capacitors are in process.

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