

Short communication

Study on the electrochemical characteristics of quasi-solid-state electric double layer capacitors assembled with sulfonated poly(ether ether ketone)

Dong-Won Kim^{a,*}, Jang Myoun Ko^a, Wan Ju Kim^a, Jong Huy Kim^b

^a Department of Applied Chemistry, Hanbat National University, San 16-1, Dukmyung-Dong, Yusung-Gu, Daejeon 305-719, Republic of Korea

^b Energy Storage Research Center in Korea Institute of Energy Research, 71-2, Jang-dong, Yusung-Gu, Daejeon 305-343, Republic of Korea

Received 10 August 2005; received in revised form 30 November 2005; accepted 20 December 2005
Available online 15 February 2006

Abstract

Sulfonated poly(ether ether ketone) (S-PEEK) was synthesized by sulfonation of commercial PEEK. The S-PEEK membrane was prepared by casting from organic solution dissolving the polymer, and the polymer electrolyte was obtained by soaking the S-PEEK membrane in water or sulfuric acid solution. The effect of soaking solvent on the liquid uptake and the ionic conductivity of the polymer electrolyte has been investigated. The quasi-solid-state electric double layer capacitors (EDLCs) which consisted of activated carbon electrodes and polymer electrolyte were assembled, and their electrochemical characteristics were studied by cyclic voltammetry and charge–discharge cycle tests.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Electric double layer capacitors; Electrochemical characteristics; Polymer electrolyte; Proton exchange membrane; Sulfonated poly(ether ether ketone)

1. Introduction

Electric double layer capacitors (EDLCs) have recently attracted a considerable attention as promising energy storage devices such as memory back-ups, digital communications, electric vehicles and other devices that require electrical energy at high power levels in relatively short time, because of their high power energy density and long cycle life. A typical EDLC is composed of two activated carbon electrodes and a porous separator filled with liquid electrolyte. The commonly used liquid electrolytes are acids, bases or salts dissolved in organic solvents. However, the use of corrosive liquid electrolytes may cause of dangerous leakage that decreases the safety and the lifetime of EDLCs. In order to reduce the problems associated with the management of corrosive liquid electrolytes, polymer electrolytes have been investigated. They are advantageous over liquid electrolytes on aspect of easy handling and better reliability without electrolyte leakage. Therefore, many efforts

have been attempted to develop solid-state EDLCs using polymer electrolytes [1–5]. Proton exchange membrane (PEM) is a proton conducting polymer material, which can be applied as a polymer electrolyte in EDLCs as well as fuel cells. In the past two decades, the most successful PEM materials were perfluorinated copolymers such as Nafion due to their excellent mechanical properties, chemical stability, and their high proton conductivity in the hydrated state [6–8], but the high cost of the materials was one of the barriers against practical application. An alternative polymer material to be used in solid-state EDLCs or fuel cells is based on sulfonated poly(ether ether ketone)(S-PEEK), as it possesses good thermal stability and mechanical properties, and the proton conductivity can be easily controlled by degree of sulfonation [8–10]. In this work, S-PEEK has been synthesized by sulfonation of commercial PEEK. Polymer membrane was prepared by casting from organic solution dissolving S-PEEK. It offered a more convenient and less expensive process than fabricating perfluorosulfonic acid membrane. Polymer electrolytes were then prepared by immersing the S-PEEK membranes in water or sulfuric acid solution. The effect of soaking solvent on the liquid uptake and the ionic conductivity of the polymer electrolyte has been investigated. The

* Corresponding author. Tel.: +82 42 821 1550; fax: +82 42 822 1562.
E-mail address: dwkim@hanbat.ac.kr (D.-W. Kim).

quasi-solid-state EDLCs with activated carbon as the electrode material and S-PEEK membrane as the polymer electrolyte were prepared, and their electrochemical characteristics were studied.

2. Experimental

2.1. Synthesis and characterization of S-PEEK

PEEK was sulfonated as previously described [10]. PEEK (450G extruded grade, Vitrex[®]) pellets were gradually added into vigorously stirred sulfuric acid (95–98%) in a glass reactor under argon atmosphere. The sulfonation was carried out at room temperature for 96 h. The sulfonated polymer was recovered by precipitating the polymer solution into a large excess of ice-cold water under mechanical agitation. The polymer precipitate was isolated by filtration and washed successively with deionized water until the pH of rinse water was neutral. The obtained S-PEEK was then dried in a vacuum oven at 80 °C for 24 h. ¹H NMR spectra were obtained to determine the degree of sulfonation of S-PEEK in DMSO-*d*₆ solvent on a Bruker-DRX-300 NMR spectrometer with tetramethylsilane (TMS) as an internal standard reference.

2.2. Membrane preparation and liquid uptake

Dried S-PEEK was dissolved at a concentration of 20 wt.% in *N,N*-dimethylacetamide (DMAc). The resulting viscous polymer solution was cast with a doctor blade onto a glass plate, and left to allow the solvent to evaporate slowly at room temperature for 12 h, then finally dried in a vacuum oven at 60 °C for 24 h. The thickness of the dried membranes was in the range of 60–80 μm. The dried membranes were transferred into a glove box, weighed and immersed in deionized water or 0.25 M H₂SO₄ solution overnight. The liquid on the surface of wetted membrane was removed using tissue paper before reweighing. Liquid uptake was calculated as follows:

$$\text{uptake (\%)} = (W_w - W_d) / W_w \times 100$$

where W_w and W_d were the weights of the wet and dried membrane, respectively. The wetted S-PEEK membrane was sandwiched between two stainless steel (SS) electrodes for conductivity measurements. The ac impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over the frequency range 10 Hz–100 kHz. The ionic conductivity (σ) was calculated from the impedance data, using the relation $\sigma = t/RA$, where t and A were the thickness and area of the polymer electrolyte film, respectively, and R was the bulk

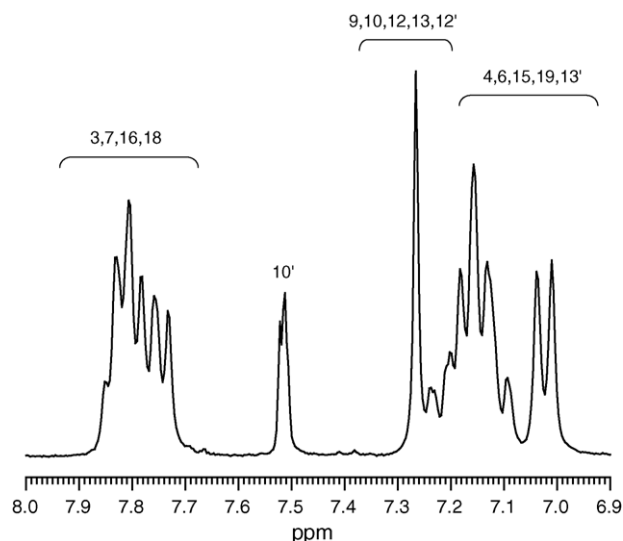


Fig. 1. ¹H NMR spectrum of S-PEEK in DMSO-*d*₆.

resistance derived from the intersect on a complex impedance plane with the real axis.

2.3. Cell assembly and electrical measurements

To make the electrodes for EDLC, 85 wt.% activated carbon powder (MSC 30), 10 wt.% super-P carbon and 5 wt.% S-PEEK were mixed in deionized water to form a homogeneous paste, which was then coated on a titanium foil. Water soluble S-PEEK with high degree of sulfonation was used as a binder. Activated carbon powder has a specific surface area of 3000 m² g⁻¹. The electrode was roll-pressed to enhance particulate contact and adhesion to current collector. The thickness of electrodes ranged from 35 to 45 μm after roll-pressing, and their active area was 4 cm². EDLC was assembled by sandwiching the polymer electrolyte between two electrodes. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. Cyclic voltammetry (CV) measurements were carried out in the potential range of 0–0.9 V. The scanning rates for CV were 2, 5, 10, 20, 50 mV s⁻¹. The charge and discharge cycling tests of EDLCs were conducted over a voltage range of 0–0.9 V with Toyo battery test equipment (TOSCAT-3000U).

3. Results and discussion

¹H NMR spectrum of S-PEEK in DMSO-*d*₆ is shown in Fig. 1. ¹H NMR analysis of S-PEEK obtained from the sulfonation reaction was reported in details previously [10,11]. It will be only briefly recalled here that the hydrogen 10' (Fig. 2) is

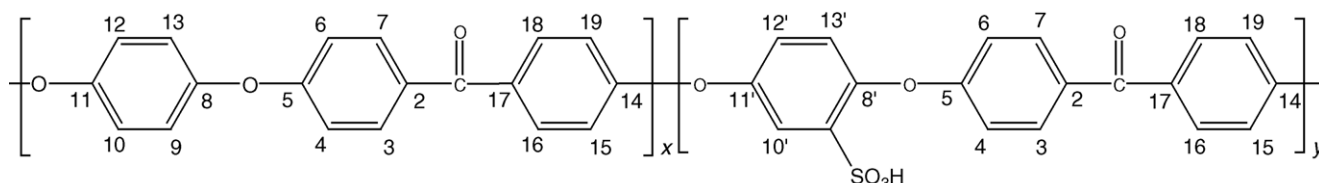


Fig. 2. Chemical structure of the sulfonated poly(ether ether ketone). Degree of sulfonation can be calculated by $y/(x+y)$.

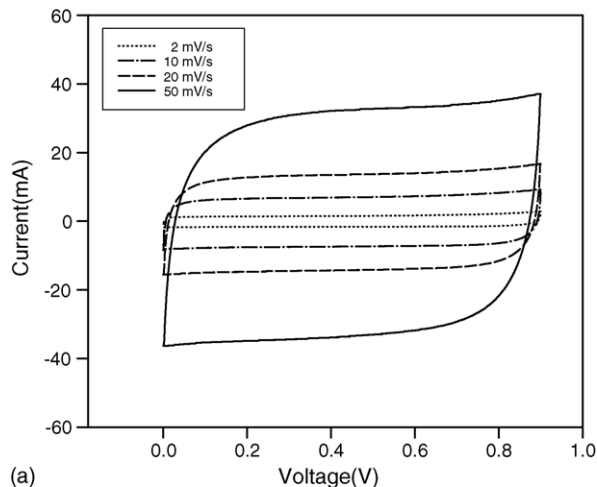
Table 1
Liquid uptake and room temperature ionic conductivity of S-PEEK membranes soaked by different solutions

Soaking solution	Thickness (μm)	Uptake (%)	Ionic conductivity (S cm^{-1})
H_2O	80	43.8	2.0×10^{-3}
0.25 M H_2SO_4	80	45.2	4.2×10^{-3}

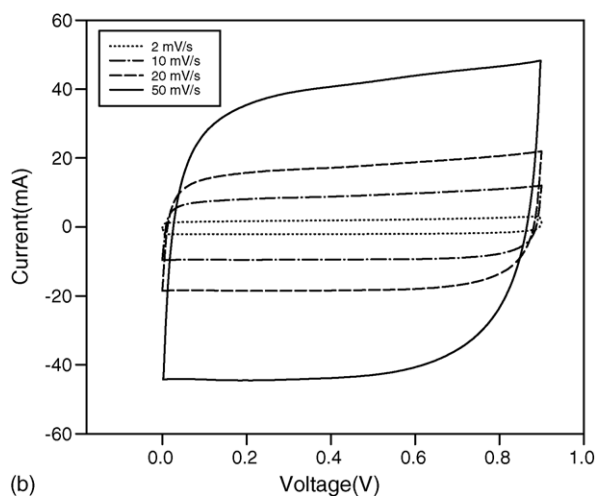
significantly down-field shifted in the presence of a sulfonic acid group. It can be observed from Fig. 1 that the 10' proton shows a distinct signal at $\sigma = 7.52$ ppm. The peak area for 10' proton was used for estimation of the $-\text{SO}_3\text{H}$ group concentration or degree of sulfonation in the S-PEEK. The degree of sulfonation calculated from the peak area ratio between 10' proton and all the other aromatic protons was 0.67. The liquid uptake and the ionic conductivity after soaking of the S-PEEK membrane in water or 0.25 M H_2SO_4 solution are given in Table 1. Soaking solutions are well encapsulated in the S-PEEK membrane due to their high affinity for S-PEEK, which gives no solvent exudation from the polymer electrolyte film (i.e., wetted S-PEEK membrane) upon long storage. The amount of sulfuric acid solution absorbed is slightly greater than that of water absorbed by the S-PEEK membrane. This result is due to the fact that the S-PEEK membrane has higher affinity for sulfuric acid, because the S-PEEK membrane has a sulfonic acid group in the side chain. The polymer electrolyte prepared with H_2SO_4 solution also exhibits a higher ionic conductivity than that prepared with water. The higher value of ionic conductivity for the S-PEEK membrane soaked by H_2SO_4 can be attributed to the high concentration of ions in the sulfuric acid solution itself. The ionic conductivity of 0.25 M H_2SO_4 used in soaking the S-PEEK membrane is $8.7 \times 10^{-2} \text{ S cm}^{-1}$.

Cyclic voltammograms for EDLCs assembled with polymer electrolyte based on S-PEEK are presented in Fig. 3, which are obtained at different scan rates. The shape of the cyclic voltammogram is close to a rectangular one and there are no peaks due to redox reactions, which suggest that charge and discharge reversibly occur at the electric double layer. Similar CV results have been previously reported in the supercapacitor assembled with Nafion membrane [4,12]. The currents are higher in the EDLC assembled with S-PEEK soaked by H_2SO_4 , which means the higher capacitance of the cell. It is due to the higher concentration of ion species to be adsorbed and desorbed in electric double layer of the EDLC. The currents are very stable and unchanged through cycling in both the EDLCs, regardless of the type of soaking solvent, which indicates excellent reversibility of the electrochemical reaction. The charge and discharge curves of EDLC assembled with S-PEEK soaked by H_2SO_4 are given in Fig. 4, which are obtained at a constant current density of 2 mA cm^{-2} . Almost linear charge and discharge curves were observed, which corresponds to those of the ideal EDLC. These curves are also in good agreement with those from the cyclic voltammograms shown in Fig. 3. The specific discharge capacitance in the curves can be calculated using the following equation:

$$C = (it)/(\Delta V W_c)$$



(a)



(b)

Fig. 3. Cyclic voltammograms of the EDLCs assembled with polymer electrolyte based on S-PEEK membrane soaked by different solution. (a) H_2O and (b) 0.25 M H_2SO_4 .

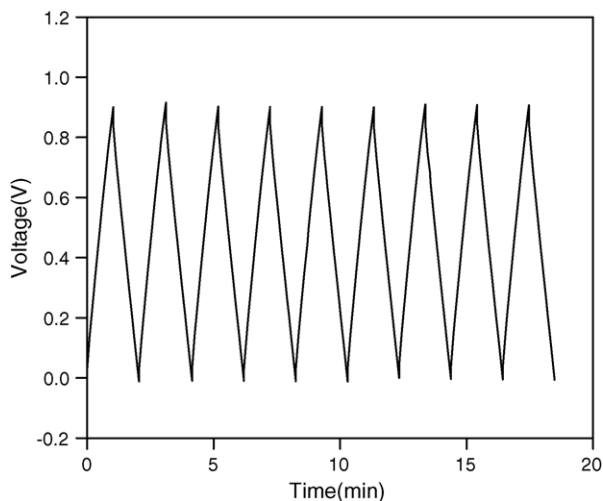


Fig. 4. Charge and discharge curves of EDLC at a current density of 2 mA cm^{-2} (101th–109th cycles). The polymer electrolyte was prepared by soaking the S-PEEK membrane in 0.25 M H_2SO_4 solution.

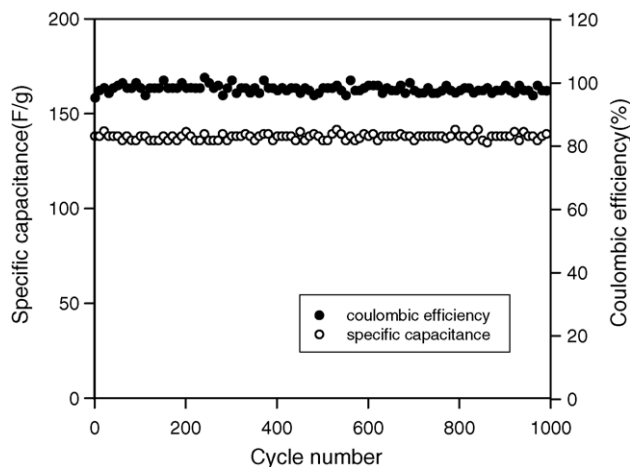


Fig. 5. Specific discharge capacitance and coulombic efficiency as a function of cycle number for the EDLC assembled with polymer electrolyte, which are obtained at a current density of 2 mA cm^{-2} .

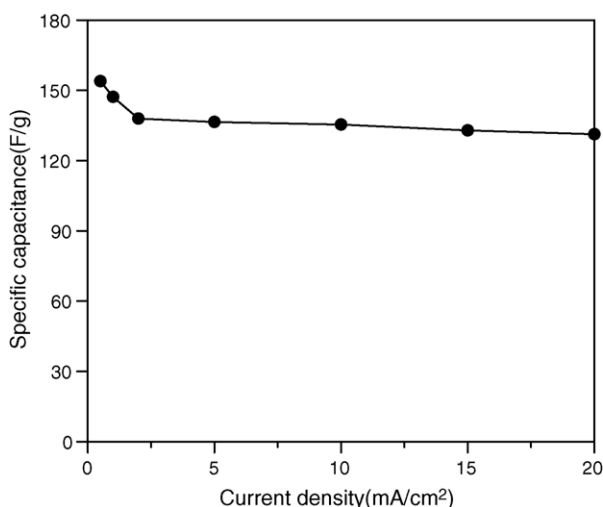


Fig. 6. Specific capacitance as a function of current density for the EDLC assembled with polymer electrolyte.

where i , t , ΔV , W_c are the discharge current, discharge time, potential difference and the weight of activated carbon in the electrode. The specific capacitance estimated from the curves is 138.4 F g^{-1} . Fig. 5 shows the specific capacitance and the coulombic efficiency as a function of cycle number. The coulombic efficiency was calculated from the ratio of the discharge capacitance to the charge capacitance. With repeated cycling, the discharge capacitance hardly decreased, which shows a convincing evidence of the good cycle life of an EDLC employing the S-PEEK membrane. This result suggests that the polymer electrolyte prepared with S-PEEK membrane is stable under charge–discharge cycles and keeping good interfacial contact with the activated carbon electrodes. The coulombic efficiency was maintained to be higher than 98% after a few initial cycles. The high rate capability of EDLC was evaluated. Fig. 6 represents the specific capacitance of EDLC obtained at different current densities, ranging from 0.5 to 20 mA cm^{-2} .

The capacitance decreases slightly with increasing current density. At a current density of 20 mA cm^{-2} , the cell gave a specific capacitance of 131 F g^{-1} , which corresponds to 95% of the capacitance obtained at 2 mA cm^{-2} . Good performance at a high current rate may be ascribed to efficient ionic conduction in the polymer electrolyte and favorable interfacial contacts between activated carbon electrodes and polymer electrolyte in the EDLC.

4. Conclusions

S-PEEK has been synthesized by sulfonation of commercial PEEK, and its degree of sulfonation was calculated to be 67%. The polymer electrolyte was prepared by soaking a S-PEEK membrane in water or sulfuric acid solution. Soaking solutions are well encapsulated in the polymer electrolyte film due to their high affinity for S-PEEK, which gives no solvent exudation from the film. The polymer electrolyte has an ionic conductivity of $4.3 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature and is a free-standing film sufficient to prepare the thin solid electrolyte for EDLC. EDLC assembled with S-PEEK soaked by H_2SO_4 exhibited higher specific capacitance than that of EDLC assembled with S-PEEK soaked by water. Quasi-solid-state EDLCs which consisted of carbon electrodes and polymer electrolyte based on S-PEEK membrane exhibited excellent cycle life and high rate capacitance. With further efforts to improve the cell performance, the polymer electrolyte prepared with S-PEEK membrane is believed to be a potential candidate as an electrolyte material for solid-state EDLCs.

Acknowledgement

This work was supported by the Core Technology Development Program of the Ministry of Commerce, Industry and Energy (MOCIE).

References

- [1] Y. Matsuda, M. Morita, M. Ishikawa, M. Ihara, J. Electrochem. Soc. 140 (1993) 109.
- [2] T. Osaka, X. Liu, M. Nojima, T. Momma, J. Electrochem. Soc. 146 (1999) 1724.
- [3] A. Lewandowski, M. Zajder, E. Frackowiak, F. Beguin, Electrochim. Acta 46 (2001) 2777.
- [4] P. Staiti, M. Minutoli, F. Lufrano, Electrochim. Acta 47 (2002) 2795.
- [5] P. Sivaraman, V.R. Hande, V.S. Mishra, Ch. Srinivasa Rao, A.B. Samui, J. Power Sources 124 (2003) 351.
- [6] A. Eisenberg, H.L. Yeager, Perfluorinated Ionomer Membranes, ACS Symposium Series 180, American Chemical Society, Washington, DC, 1982.
- [7] S.R. Samms, S. Wasmus, R.F. Savinell, J. Electrochem. Soc. 143 (1996) 1498.
- [8] F. Lufrano, P. Staiti, M. Minutoli, J. Power Sources 124 (2003) 314.
- [9] B. Yang, A. Manthiram, Electrochem. Solid-State Lett. 6 (2003) A229.
- [10] P. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, J. Membr. Sci. 229 (2004) 95.
- [11] S.M.J. Zaidi, S.D. Mikhailenko, G.P. Robertson, M.D. Guiver, S. Kaliaguine, J. Membr. Sci. 173 (2000) 17.
- [12] K.W. Park, H.J. Ahn, Y.E. Sung, J. Power Sources 109 (2002) 500.