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ScienceDirect
Journal of Power Sources 163 (2006) 300–303
JOURNAL OF POWER SOURCES
www.elsevier.com/locate/jpowsour

Short communication

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

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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.

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

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doi:10.1016/j.jpowsour.2005.12.059

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. ^{1}H 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 H_2SO_4 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 resistance derived from the intersect on a complex impedance plane with the real axis.

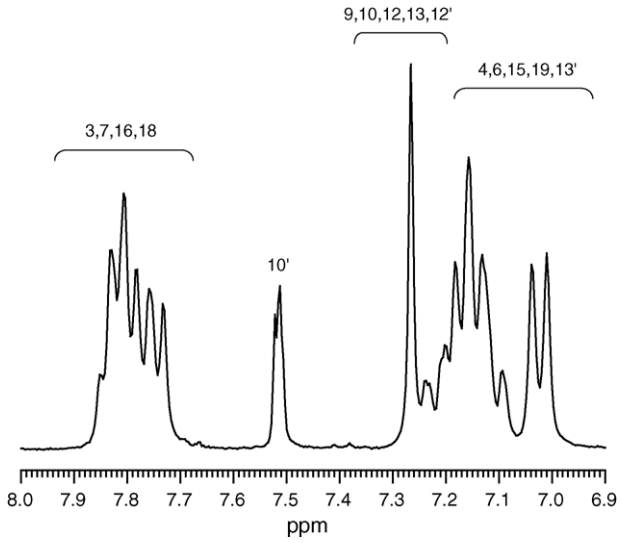

Fig. 1. ^{1}H NMR spectrum of S-PEEK in DMSO-d_6.

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 $m^2\,g^{-1}$. 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 cm^2. 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

^{1}H NMR spectrum of S-PEEK in DMSO-d_6 is shown in Fig. 1. ^{1}H 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

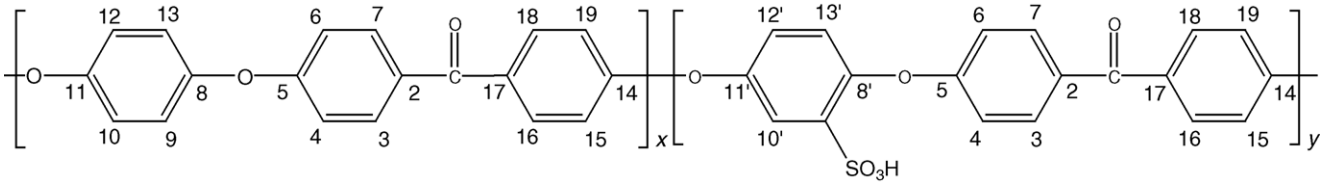

Fig. 2. Chemical structure of the sulfonated poly(ether ether ketone). Degree of sulfonation can be calculated by $y/(x+y)$.