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Quasi-solid-state electric double layer capacitors assembled with sulfonated poly(fluorenyl ether nitrile oxynaphthalate) membranes

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ABSTRACT

A series of sulfonated poly(fluorenyl ether nitrile oxynaphthalate) (SPFENO) copolymers with different degrees of sulfonation were synthesized. Their degree of sulfonation was controlled by adjusting the molar ratio of the reactants. The polymer electrolytes prepared with a SPFENO membrane exhibited high ionic conductivities and solution holding capacity, which depended on the degree of sulfonation. The quasi-solid-state electric double layer capacitors (EDLCs) consisted of activated carbon electrodes and polymer electrolytes were assembled, and their electrochemical characteristics were studied by cyclic voltammetry and charge-discharge cycle tests. A SPFENO membrane with proper degree of sulfonation was effective for maintaining high ionic conductivity and keeping good electrode–electrolyte interfacial contact during cycling, which resulted in good cycling performance of the EDLC.

1. Introduction

Electric double layer capacitors (EDLCs) have attracted considerable attention as promising energy storage devices for memory back-ups, digital communications, electric vehicles and energy storage systems that require electrical energy at high power in relatively short time due to their high power energy density and long cycle life [1]. The capacitance of the EDLC arises from the separation of ionic charge at the electric double layer between high specific area carbon electrodes and liquid electrolyte. Commonly used liquid electrolytes are aqueous electrolyte or organic electrolyte. However, the use of corrosive liquid electrolytes may cause leakage that decreases the reliability and lifetime of EDLCs. In order to reduce the problems associated with the management of corrosive liquid electrolytes, various polymer electrolyte systems have been investigated [2–9], which are advantageous compared to liquid electrolytes due to easy handling and better reliability without solvent leakage. They are also flexible and can be easily fabricated as thin and large-area membranes facilitating low internal resistance. One of the most successful polymer electrolyte materials used in EDLCs is perfluorosulfonic acid polymer such as Nafion due to its excellent mechanical properties, chemical stability and high proton conductivity in the hydrated state [10–17]. However, the high cost of the polymer material is a barrier to practical application for solid-state EDLCs. An alternative polymer material for use in EDLCs is based on sulfonated aromatic polymer such as sulfonated poly(ether ether ketone) (SPEEK) [18–23], as it possesses good thermal stability and mechanical properties, and its conductivity can be easily controlled by the degree of sulfonation. Recently, it has been reported that the introduction of nitrile groups into the sulfonated aromatic polymers can improve dimensional stability of the polymer electrolyte film [24,25]. In addition, the introduction of strongly polar nitrile groups promotes the adhesion of polymers to electrode materials via interaction with other polar chemical groups [26].

In this work, we synthesized a novel series of sulfonated poly(fluorenyl ether nitrile oxynaphthalate) (SPFENO) copolymers containing polar nitrile groups. The degree of sulfonation was controlled by adjusting the molar ratio of the reactants. Polymer electrolytes were prepared with the SPFENO membrane and a sulfuric acid solution. The electrochemical characteristics of quasi-solid-state EDLCs assembled with activated carbon electrodes and polymer electrolyte were investigated and compared to those of similar EDLC assembled with an aqueous sulfuric acid solution. More attention was paid to the influence of the degree of sulfonation on the electrochemical performance of EDLCs.

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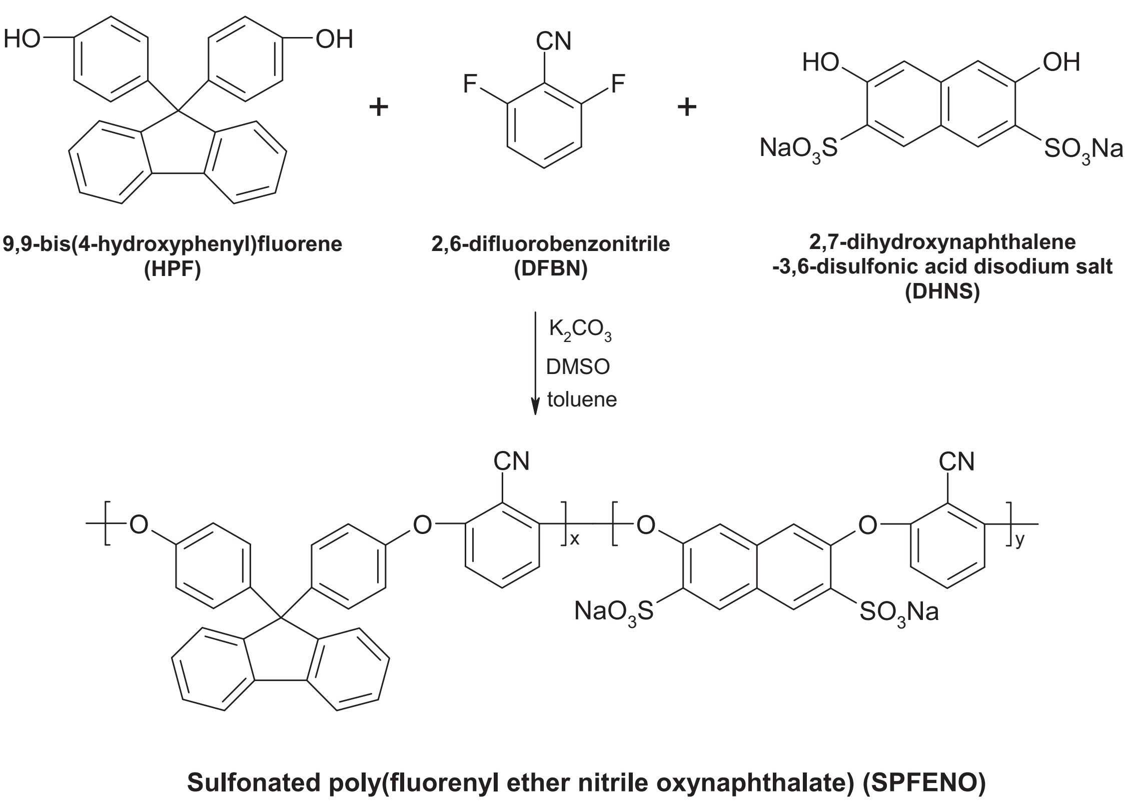

Fig. 1. Reaction scheme for the synthesis of SPFENO copolymers.

2. Experimental

2.1. Synthesis and characterization of SPFENO

9,9-Bis(4-hydroxyphenyl)fluorene (HPF) was purchased from TCI (Tokyo Chemical Industry, Japan) and recrystallized before use. 2,6-Difluorobenzonitrile (DFBN) and 2,7-dihydroxynaphthalene-3,6-disulfonic acid disodium salt (DHNS) were purchased from TCI and used without further purification. Dimethyl sulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), toluene and anhydrous potassium carbonate were purchased from Sigma–Aldrich and used as received. The SPFENO copolymers were synthesized by the nucleophilic substitution polycondensation reaction (Fig. 1), as described previously in detail [27]. After reaction and purification, the fibrous polymer was collected as a product. The resulting polymer was denoted "SPFENO-*N*," where *N* refers to the molar ratio of DHNS to diol monomers. ^{1}H NMR spectra were obtained to determine the degree of sulfonation of SPFENO in DMSO-d_6 solvent on a VARIAN (Mercury 300) NMR spectrometer with tetramethylsilane (TMS) as an internal standard reference.

2.2. Preparation of the membrane and polymer electrolyte

The sulfonated SPFENO copolymer in sodium salt was dissolved in NMP (10%, w/v). The solution was cast with a doctor blade onto a glass plate and dried at 50 °C for 24 h. The membrane was peeled from the glass plate by immersion in de-ionized water. The acid form of the SPFENO membrane was obtained by boiling the sodium form of the membrane in 0.5 N H_2SO_4 for 2 h, followed by washing with boiling water to remove excess H_2SO_4 from the acidified membrane. Finally, a transparent, yellowish membrane was obtained. The thickness of the dried membranes was 60–80 μm. The mechanical properties of the acidified membranes were measured with a universal test machine (AGS-J, Shimadzu) using the ASTM D882 method. Each membrane was strained at a speed of 1 mm min^{-1}. For liquid uptake measurements, the dried membrane was weighed and immersed in 0.5 M H_2SO_4 solution. The liquid on the surface of the wet membrane was removed using tissue paper before reweighing. Uptake was calculated as follows:

$$\text{uptake}\,(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100, \tag{1}$$

where W_{dry} and W_{wet} are the weight of the dried and wet membranes, respectively. The uptake of each sample was measured at least five times to ensure data reproducibility. Ion exchange capacity (IEC) of the membrane was determined by titration, as previously described [27]. For conductivity measurements, the polymer electrolyte prepared by soaking the SPFENO membrane in 0.5 M H_2SO_4 solution was sandwiched between two stainless steel (SS) electrodes. AC impedance measurements were performed using an impedance analyzer (CH Instruments, Model 604A) over a frequency range of 10 Hz–100 kHz. The ionic conductivity (σ) of the polymer electrolyte in the transverse direction (across the membrane) was calculated from the impedance data, using the relation $\sigma = t/(RA)$, where t and A are the thickness and area of the polymer electrolyte film, respectively, and R is the bulk resistance estimated from the intersection on a complex impedance plane with the real axis.

2.3. Cell assembly and electrical measurements

To make the electrodes for the EDLC, 85 wt.% activated carbon powder (MSC-30, Kansai Coke) and 10 wt.% super-P carbon was mixed with carboxy methyl cellulose (CMC) (3 wt.%) and styrene-butadiene rubber (SBR) (2 wt.%) as a binder in aqueous medium. The activated carbon powder has a specific surface area of 3000 m^2 g^{-1}. The resultant slurry was cast on a titanium foil using a doctor blade. The electrode was air dried overnight and then dried under vacuum at 40 °C for 24 h. The electrode was roll-pressed to enhance particulate contact and adhesion to the current collector. The thickness of the electrodes ranged from 30 to 40 μm after roll-pressing, and their active mass loading was about 5 mg cm^{-2}. The EDLC was assembled by sandwiching the polymer electrolyte between two carbon electrodes. Before assembling the EDLC, the polymer electrolyte was prepared by pre-impregnating the SPFENO membrane with 0.5 M H_2SO_4 solution. The cell was then enclosed in a metallized plastic bag and vacuum-sealed. A similar type cell was also assembled using a 0.5 M H_2SO_4 aqueous solution with a paper separator (thickness: 40 μm, Nippon Kodoshi Co.) for comparison. Cyclic voltammetry (CV) measurements were performed in the potential range of 0–0.9 V. The scanning rates for CV were 5, 10, 20 and 50 mV s^{-1}. The charge and discharge cycling tests of the EDLCs were conducted over a voltage range of 0–0.9 V with battery test equipment (PNE Solution, PEBC50.2) at room temperature.

3. Results and discussion

The degree of sulfonation for SPFENO copolymers was determined by analyzing their ^{1}H NMR spectra, as reported earlier [27]. In this study, the degree of sulfonation was defined as the ratio of the sulfonated unit to the total repeat unit of SPFENO (i.e., y in Fig. 1). The degree of sulfonation for the SPFENO copolymers synthesized is summarized in Table 1. The calculated degree of sulfonation values were very close to the expected values based on the molar ratio of reactants. The tensile strength of the polymer membranes prepared with SPFENO copolymers is given Table 1. The SPFENO membrane exhibited good tensile strength, which was higher than that of sulfonated poly(arylene ether ketone) (SPAEK) with same IEC value [28] and comparable to those of sulfonated poly(fulorenyl ether ketone) (SPFEK) [29]. The nitrile groups on aromatic rings of SPFENO have much stronger polarity and basicity compared with ketone links in SPAEK and SPFEK, which enhances inter-/intramolecular interactions in SPFENO copolymers, consequently giving high mechanical strength.

Ionic conductivities and uptake of the SPFENO membranes when soaked in a 0.5 M H_2SO_4 solution are shown in Fig. 2. It is seen that the solution uptake increased with increasing degree of sulfonation. The naphthalane sulfonic acid groups in the SPFENO chain are much more hydrophilic than fluorenyl groups, resulting in enhanced solution absorption with increasing the degree of sulfonation. Soaking solution was well encapsulated in the polymer membrane. As seen in Fig. 2, ionic conductivities also increased with the degree of sulfonation of the SPFENO copolymer. Since the number of available sulfonic acid groups in the polymer membrane and free ions in the absorbed H_2SO_4 solution increased with the degree of sulfonation, the ionic conductivities increased with the degree of sulfonation. Accordingly, the polymer electrolyte prepared with SPFENO-50 exhibited the highest ionic conductivity. The ionic conductivities of SPFENO-based polymer electrolytes are not as high as other hydrocarbon-based sulfonate polymer systems proposed as proton exchange membranes (PEMs) in fuel cells [25–32]. This may be arising from different method for conductivity measurements. Conductivities of fully hydrated PEMs used in fuel cells were usually measured by four probe method, which may give higher ionic conductivity values than our systems that measured using a symmetrical two-electrode cell configuration, because the contact resistance could be minimized in the first method. The conductivity values measured with the same polymer electrolyte by two different methods showed slight differences; in particular those obtained by two-electrode cell configuration were underestimated. It should be noted that the conductivity values of SPFENO-based polymer electrolytes were higher than those of other proton conducting polymer electrolytes for solid-state EDLCs [33,34].

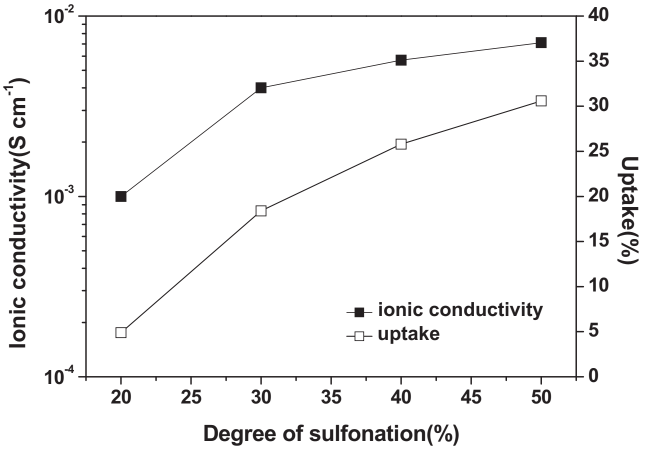

Fig. 2. Ionic conductivities and uptake of electrolyte solution in SPFENO-based polymer membranes, as a function of the degree of sulfonation.

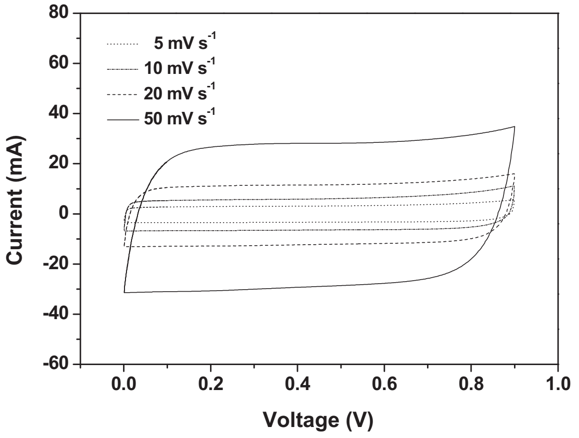

Fig. 3. Cyclic voltammograms of the EDLC assembled with polymer electrolyte based on the SPFENO-40 membrane.

Cyclic voltammograms for the EDLC assembled with polymer electrolyte based on SPFENO-40 are presented in Fig. 3, which were obtained at different scan rates. The shape of the cyclic voltammogram was approximately rectangular and there were no peaks due to redox reactions, which suggest that the charge and discharge reversibly occurred at the electric double layer. The current value increased with increasing scan rate, which is generally expected for an EDLC. The rectangular shape of the cyclic voltammogram was well maintained, even at a scan rate as high as 50 mV s^{-1}.

Table 1
Characterization of the SPFENO-based membranes.

Copolymer	DFBN (mmol)	HPF (mmol)	DHNS (mmol)	Degree of sulfonation from ^{1}H NMR	Tensile strength (MPa)	IEC measured (mequiv g^{-1})
SPFENO-20	10	8	2	0.21	59.1	0.90
SPFENO-30	10	7	3	0.31	48.9	1.30
SPFENO-40	10	6	4	0.40	33.0	1.64
SPFENO-50	10	5	5	0.51	19.8	2.17

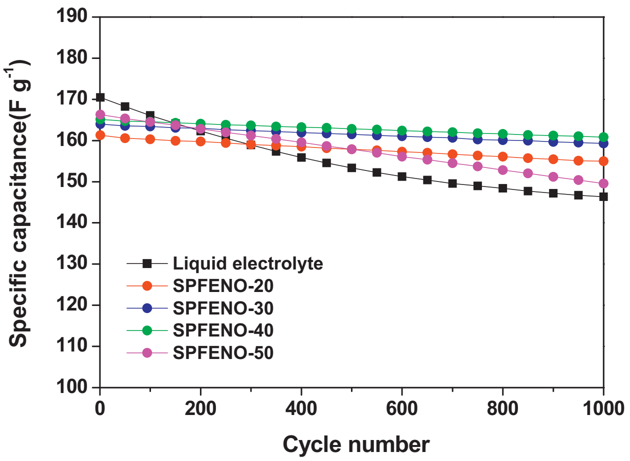

Fig. 4. Specific discharge capacitance as a function of cycle number at a current density of 5 mA cm^{-2} for the EDLCs assembled with SPFENO membranes with different degrees of sulfonation.

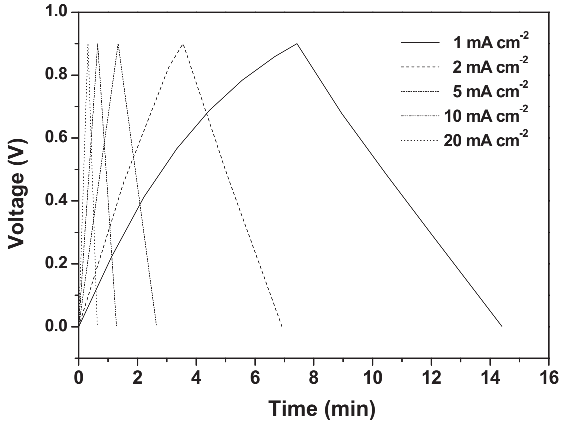

Fig. 5. Charge and discharge curves of the EDLC prepared with the SPFENO-40 membrane, which were obtained at different current rates.

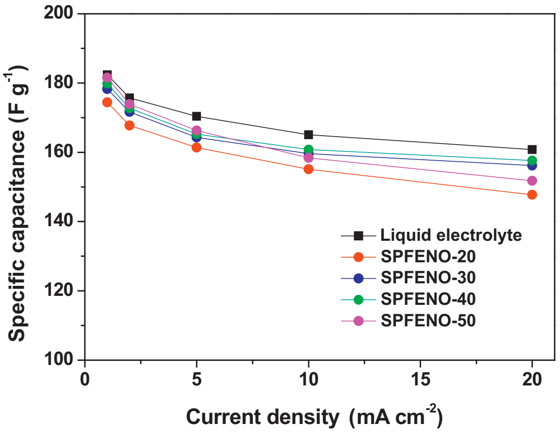

Fig. 6. Specific capacitance as a function of current density for the EDLCs assembled with SPFENO membranes with different degrees of sulfonation.

The EDLC assembled with SPFENO-based polymer electrolyte was subjected to charge and discharge cycling in a voltage range of 0–0.9 V at a constant current density of 5 mA cm^{-2}. Fig. 4 shows the specific capacitance of EDLCs assembled with SPFENO membranes with different degrees of sulfonation as a function of the cycle number. For comparison, the cycling result of the cell assembled with liquid electrolyte (0.5 M sulfuric acid solution) is also given in the figure. It can be seen that the cycling performances of the EDLCs are dependent on the degree of sulfonation of the SPFENO membrane. The initial capacitance of the EDLC increased with increasing degree of sulfonation of the SPFENO membrane. The cell assembled with the SPFENO-50 membrane exhibited the highest initial capacitance of 166.3 F g^{-1}. The high value can be attributed to the high concentration of mobile ions at the interface between the electrode and electrolyte because the SPFENO-50 membrane had the highest uptake of sulfuric acid among the membranes considered. On the basis of the results in the previous literature, the specific capacitance values are fairly high as compared to those (~130 F g^{-1}) of solid-state EDLCs with Nafion membranes [17,35,36]. An exact comparison between our results and those of previous works is not easy because the specific capacitance is significantly dependent on the specific surface area of an activated carbon powder [37,38]. It is plausible that high specific capacitance in this work may be partly attributed to the high specific surface area (3000 m^2 g^{-1}) of the activated carbon. With respect to cycle life, the degree of sulfonation also affected the capacitance retention of the cell. SPFENO-20 may be less effective for preventing the leakage of the sulfuric acid due to the low solution retention of the membrane, thus decreasing the ionic conductivity and also degrading the interfacial contacts between the polymer electrolyte and carbon electrodes. The large capacitance decline of the EDLC assembled with SPFENO-50 was ascribed to the gradual loss in mechanical strength of the membrane during cell operation. During a prolonged cycle, a dimensional change in the membrane may occur due to large swelling behavior in its highly hydrated form, leading to gradual deterioration of the interfacial contact between the electrolyte and electrodes. Accordingly, the cell assembled with the SPFENO-40 membrane exhibited the most stable cycling behavior, which suggests the polymer electrolyte based on SPFENO-40 maintained a high ionic conductivity and good interfacial contacts with the activated carbon electrodes during cycling. In fact, the polymer electrolyte was hardly separated from the carbon electrodes after the repeated cycling, which may be due to the adhesive properties of polymer electrolyte. A gradual decrease in capacitance of the cell assembled with a liquid electrolyte may be related to solvent exudation from the cell. The discharge capacitance of the EDLC with SPFENO-40 was 97% of the initial value after 1000 cycles, while it was 86% in the case of the EDLC with liquid electrolyte.

Rate capabilities of the EDLCs assembled with SPFENO membranes were evaluated. The typical charge and discharge curves of the EDLC prepared with SPFENO-40 at different current rates are shown in Fig. 5. Even at a high current density of 20 mA cm^{-2}, linear charge and discharge curves were observed. Fig. 6 represents the specific capacitance of the EDLCs assembled with SPFENO membranes with different degrees of sulfonation, which were obtained at different current densities. For all EDLC systems, the capacitance of the cell decreased with increasing current density, irrespective of the type of membrane. As shown in the figure, the cell with the SPFENO-40 membrane had the highest capacitance at a high current rate. At a current density of 20 mA cm^{-2}, the cell delivered a specific capacitance of 158 F g^{-1}, which is comparable to that of a cell with liquid electrolyte. The above results suggest that SPFENO-40 effectively achieves a high solution-holding capacity and maintains high ionic conductivity and good interfacial contact with the activated carbon electrodes, which result in good cycling performance.

4. Conclusions

A novel series of sulfonated poly(fluorenyl ether nitrile oxynaphthalate) copolymers with varying degrees of sulfonation were synthesized by nucleophilic substitution polycondensation. The

SPFENO membrane impregnated with sulfuric acid was used as a polymer electrolyte for EDLC application. Sulfuric acid was well encapsulated in the polymer membrane due to its high affinity for SPFENO. The SPFENO membrane with a degree of sulfonation of 40 was effective for achieving high performance of the quasi-solid-state EDLC. The fact that the polymer electrolyte had high ionic conductivity and good interfacial contact with the carbon electrodes was responsible for the favorable electrochemical characteristics, which were comparable to those of EDLCs assembled with an aqueous H_2SO_4 solution.

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