



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

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ARTICLE INFO

Article history:

Received 14 May 2011

Received in revised form 19 August 2011

Accepted 18 September 2011

Available online 1 October 2011

Keywords:

Degree of sulfonation

Electric double layer capacitor

Polymer electrolyte

Proton exchange membrane

Sulfonated aromatic polymer

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.

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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 poly-

mer 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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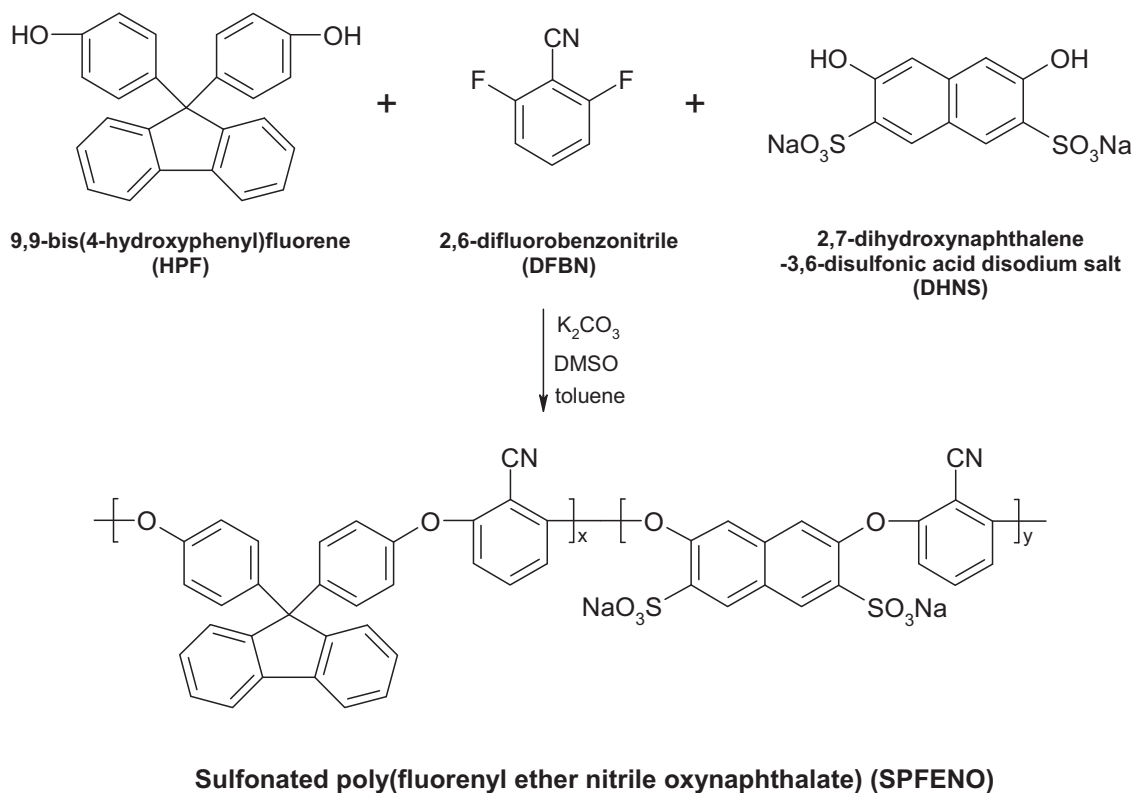


Fig. 1. Reaction scheme for the synthesis of SPFENO copolymers.

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. ¹H 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 H₂SO₄ for 2 h, followed by washing with boiling water to remove excess H₂SO₄ 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 H₂SO₄ solution. The liquid on the surface of the wet membrane was removed using tissue paper before reweighing. Uptake was calculated as follows:

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

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 H₂SO₄ 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 m² 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

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