



Hydrocarbon membranes with high selectivity and enhanced stability for vanadium redox flow battery applications: Comparative study with sulfonated poly(ether sulfone)s and sulfonated poly(thioether ether sulfone)s



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ABSTRACT

A series of sulfonated poly(ether sulfone) copolymers (SPES-Xs) with varying degrees of sulfonation were prepared and investigated as ion-exchange membranes for vanadium redox flow battery (VRFB) applications. Sulfonated poly(thioether ether sulfone) copolymers (SPTES-Xs) were initially synthesized via polycondensation, and the SPES-Xs were then obtained by oxidation of the corresponding SPTES-Xs. The SPES-X membranes showed reduced vanadium-ion permeability, low area resistance, and, thereby, much superior selectivity compared with the parent SPTES-X membranes and a Nafion115 membrane. In single-cell VRFB performance tests, a SPES-50 membrane with an ion-exchange capacity of 1.80 meq/g exhibited a higher coulombic efficiency (>99%) and energy efficiency (76–89%) than the Nafion115 membrane over a wide range of current densities from 40 to 100 mA/cm² and a significantly larger capacity retention (>62%) during 200 charge-discharge cycles. The SPES-X materials, in which every benzene ring is deactivated by the presence of electron-withdrawing sulfone linkages, showed much better chemical stability during *ex situ* and *in situ* tests than the SPTES-X materials, which contain an electron-donating thioether linkage in their repeat unit.

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1. Introduction

All-vanadium redox flow batteries (VRFBs) have received increased attention in recent years as a possible solution for large-scale energy storage systems due to their advantageous properties, such as high efficiency, long cycle life, design flexibility, and safety [1–3]. VRFBs are mainly composed of positive and negative electrolytes, electrodes, and separators. Ion-exchange membranes (IEMs) commonly serve as separators to separate the two electrolytes in VRFBs, allowing proton transfer to complete the circuit. Almost all existing commercial VRFBs use perfluorosulfonic acid (PFSA) polymer membranes, e.g. Nafion membranes, which exhibit

excellent proton conductivity and outstanding electrochemical stability. Nevertheless, the extremely high cost of Nafion membranes (they are the most expensive component in a VRFB stack, accounting for ~40% of the stack cost [4,5]) is the main obstacle to their industrial application in VRFBs. Moreover, Nafion membranes are highly permeable to vanadium species, leading to undesired vanadium-ion transport across the membranes during charge-discharge cycling [6]. The large vanadium-ion crossover through the Nafion membranes results in decreased coulombic efficiency (CE) and an imbalance of the electrolyte, which leads to capacity loss [7,8]. Therefore, developing alternative IEMs that are inexpensive and highly selective is necessary for the wide commercialization of the VRFB technology.

In recent years, a variety of sulfonated hydrocarbon membranes have been investigated as replacements for PFSA membranes, including sulfonated poly(arylene ketone)s [9–11], sulfonated polyimides [12,13], sulfonated poly(arylene sulfone)s [14,15], and sulfonated poly(phenylene)s [16,17]. Generally, sulfonated

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hydrocarbon membranes are cheaper and exhibit reduced vanadium-ion permeability compared with Nafion membranes. Therefore, some VRFBs assembled with hydrocarbon membranes have exhibited comparable or higher efficiencies and larger capacity retention capabilities than those using Nafion membranes.

Nevertheless, the poor chemical stability of hydrocarbon membranes when exposed to the VRFB electrolytes remains a critical issue [18–21]. Hydrocarbon membranes normally suffer from physical and/or chemical degradation under VRFB operating conditions, which lowers the long-term reliability of batteries utilizing these membranes. For example, a study on sulfonated Radel (S-Radel) by Kim et al. showed that this polymer exhibits better selectivity than Nafion117 and comparable energy efficiency; however, it can only withstand a few cycles before physically degrading [18]. Although there are a very limited number of studies on the degradation mechanisms of hydrocarbon membranes, it is clear that the strongly oxidizing vanadium (V) ions are responsible for the degradation of these membranes [19]. Hickner et al. proposed a degradation mechanism for S-Radel, where the vanadium (V) oxygen species first attacks the polymer by incorporating hydroxyl groups into the polymer backbone and then oxidizes them into quinone groups [20]. According to this mechanism, the authors suggested that reducing the electron density on the aromatic backbone might lower the risk of hydrocarbon-membrane degradation. Later, the same research group applied a synthetic strategy to incorporate partially fluorinated moieties into the polymer backbone to enhance the chemical stability of sulfonated poly(arylene ether). They concluded that the electron-withdrawing power of fluorine shields the aromatic backbone, rendering the fluorinated aromatic polymers more stable as expected [21]. In contrast, Zhang et al. proposed a different mechanism for the degradation of a sulfonated poly(ether ether ketone) (SPEEK) membrane in a VRFB medium [22]. Under strong acidic conditions, the ethereal oxygen atoms in SPEEK can be easily protonated and become strong electron-withdrawing groups. The protonated ether groups, together with the strong electron-withdrawing sulfonic acid group, then induce a strongly electrophilic carbon center on the benzene ring, which leads to further attack from the lone pair of electrons on the vanadium oxygen species. Based on this mechanism, they suggested that the chemical stability of the membrane could be improved through introducing electron-donating groups to the aromatic backbone, which will reduce the reactivity of the electrophilic carbon center on the benzene ring.

Moreover, it is thought that increasing the number of ion-exchange groups in the polymer accelerates the degradation of sulfonated hydrocarbon membranes [23,24]. Fujimoto et al. investigated sulfonated Diels Alder poly(phenylene)s with different ion-exchange capacities (IECs), and found that the oxidative stability of the polymers decreased with increasing IEC [16]. However, very recent studies on the application of polyoxadiazole-based and polybenzimidazole-based membranes in VRFBs have demonstrated that hydrocarbon membranes not containing conventional ion-exchange groups also display some degradation in the harsh VRFB medium [25–29]. Consequently, despite the publication of some reports attempting to clarify the degradation mechanism of hydrocarbon membranes, the understanding of their poor chemical stability is still very limited, which is probably due to the complicated medium of VRFBs (strongly acidic, oxidizing, and high electric potential).

In this work, we aimed to understand more about the degradation of hydrocarbon membranes and develop sulfonated hydrocarbon membranes with enhanced stability for VRFB applications through conducting comparative study with sulfonated poly(ether sulfone) copolymers (SPES-Xs) and sulfonated poly(thioether ether sulfone) copolymers (SPTES-Xs). SPES-Xs were chosen because

every benzene ring in their polymer backbone is adjacent to a strongly electron-withdrawing sulfone linkage group. Meanwhile, SPTES-Xs possess a thioether linkage in their repeat unit that has an electron-donating nature. Although there have been a few reports focusing on some polymer blend membranes using SPES copolymers for VRFB applications [30,31], we believe more detailed study on the structure-property relationship of this kind of polymers is required, especially in terms of oxidative stability and VRFB performance. In particular, a comparative study between SPTES-Xs and SPES-Xs can be helpful to investigate the structural effect on the stability because their only difference in structure is whether all benzene rings are deactivated by electron withdrawing linkage groups or not. Since SPES-Xs are directly prepared from the corresponding SPTES-Xs, we can assume no difference in other structural parameters, such as degree of sulfonation and degree of polymerization between them.

In the synthesis, SPTES-Xs were first prepared through polycondensation of sulfonated and non-sulfonated difluoride monomers, and the SPES-Xs were then obtained through oxidation of the SPTES-Xs, which converted the SPTES-Xs thioether linkages to sulfone linkages. Solvent-cast SPTES-X and SPES-X membranes with IECs ranging from 1.68 to 2.14 meq/g were fully characterized in terms of their various physical and electrochemical properties, including swelling ratio, area resistance, and vanadium-ion permeability. In particular, the effect of the electron-withdrawing sulfone groups on the oxidative stability of the SPES-X membranes was carefully analyzed by comparing their *ex situ* and *in situ* stability with those of the SPTES-Xs membranes containing the electron-donating thioether groups. In single-cell VRFB performance tests, a SPES-50 membrane with an IEC of 1.80 meq/g exhibited a higher energy efficiency (EE) (75%) and CE (>98%) than the corresponding cell with a Nafion115 membrane, and a significantly larger capacity retention (>93%) during 200 charge-discharge cycles.

2. Experimental

2.1. Materials

4,4'-Thiodiphenol (TDP) was obtained from Sigma-Aldrich and dried at 80 °C prior to use. 4,4'-Difluorodiphenyl sulfone (DFDPS) was provided by Richem and recrystallized with ethanol. Disodium 3,3'-disulfonated-4,4'-difluorodiphenylsulfone (SDFDPS) was prepared from DFDPS according to the literature method [32] and purified by recrystallization with ethanol/H₂O and then dried under vacuum at 120 °C prior to use. Anhydrous potassium carbonate (K₂CO₃) was purchased from Sigma-Aldrich and dried under vacuum at 80 °C. N,N'-Dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), vanadium pentoxide (V₂O₅, ≥98%), and toluene were obtained from Sigma-Aldrich. Acetic acid (glacial, 99.5%), sulfuric acid (97%), and 30% hydrogen peroxide (H₂O₂) were provided by Samchun, Merck, and Junsei, respectively. 2-Propanol (IPA) was obtained from Samchun and used without further purification. Nafion 115 was acidified in a 1.5 M H₂SO₄ aqueous solution at room temperature for 24 h, and then washed with distilled water and dried on a vacuum plate for 1 h.

2.2. Synthesis of sulfonated poly(thioether ether sulfone) copolymers (SPTES-Xs)

Sulfonated poly(thioether ether sulfone) copolymers (SPTES-Xs; X denotes the molar feed ratio of SDFDPS relative to the total difluoride-monomer content) were prepared via direct copolymerization of SDFDPS and DFDPS with TDP (Fig. 1). The typical procedure for preparing SPTES-50 is as follows. A 100 ml four-neck

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