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Low vanadium ion permeabilities of sulfonated poly(phthalazinone ether ketone)s provide high efficiency and stability for vanadium redox flow batteries

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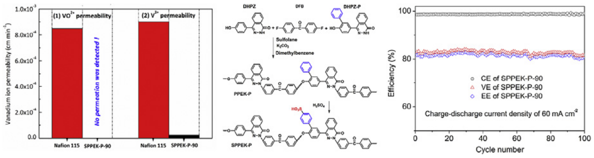
HIGHLIGHTS

- Sulfonated poly(phthalazinone ether ketone)s (SPPEK-P) membranes were prepared.
- SPPEK-P membranes exhibited very low vanadium ions permeability.
- SPPEK-P membranes exhibited good stability and high VRFB cell efficiency.
- SPPEK-P membrane showed stable cell performance over 100 charge-discharge cycles.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of novel sulfonated poly(phthalazinone ether ketone)s containing pendant phenyl moieties (SPPEK-Ps) are synthesized and thoroughly characterized. The chemical structures of the polymers are confirmed by ^1H NMR and FTIR analysis. The physicochemical properties and single cell performance of SPPEK-P membranes are systematically evaluated, revealing that the membranes are thermally, chemically and mechanically stable. The area resistances of SPPEK-P-90 and SPPEK-P-100 are 0.75 Ω cm^2 and 0.34 Ω cm^2, respectively. SPPEK-P membranes are impermeable to the bulky hydrated VO^{2+} ion and exhibited low V^{3+} ion permeability (SPPEK-P-90, 2.53×10^{-5} cm min^{-1}) (Nafion 115 membrane: 9.0×10^{-4} cm min^{-1}). Tests of SPPEK-P-90 in vanadium redox flow batteries (VRFBs) demonstrate a comparable columbic efficiency (CE) and energy efficiency (EE) to that of Nafion 115, where the CE is 98% and the EE is 83% at 60 mA cm^{-2}. Moreover, the SPPEK-P-90 membrane exhibits stable performance in cell over 100 charge-discharge cycles (~450 h).

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1. Introduction

In the development of vanadium redox flow batteries (VRFBs) [1–3], the discovery of suitable ion exchange membranes has attracted much attention [4–7]. The key function of the membrane is to allow proton transport while preventing vanadium ions from migrating between anolyte and catholyte solutions [8]; vanadium ion permeation results in energy loss and decreased performance. Thus, the ideal VRFB membrane should exhibit low permeability of vanadium ions, high proton conductivity, good chemical stability and low cost [9,10].

Among ion exchange membranes, low-cost sulfonated aromatic polymers are regarded as promising VRFB materials [11–13].

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Notably, sulfonated aromatic polymers with rigid backbones have high thermal and mechanical stability [14]. The backbone of sulfonated aromatic polymer is less hydrophobic and the sulfonic acid functional group is less hydrophilic compared to Nafion; this results in less hydrophilic/hydrophobic separation [15,16] which may help prevent the permeation of vanadium ions through the membrane. It has been demonstrated that sulfonated aromatic polymer membranes such as sulfonated poly(arylene thioether) [17], sulfonated poly(arylene ether sulfone) [14], sulfonated poly(fluorenyl ether ketone sulfone)s [18] and sulfonated poly(fluorenyl ether thioether ketone)s [19] exhibited comparable proton conductivity and lower permeability of vanadium ions than Nafion™ membranes while also being lower-cost.

Recently, our research group has reported several kinds of aromatic phthalazinone-containing polymers, such as quaternized poly(phthalazinone ether ketone) [20], quaternized poly(phthalazinone ether sulfone) [21] and quaternized poly(phthalazinone ether ketone ketone) [22], which were used as anion exchange membranes. These polymers with rigid unsymmetrical phthalazinone moieties [23] showed favorable cell performance in VRFB systems.

In the work, a series of novel sulfonated poly(phthalazinone ether ketone)s containing pendant phenyl moieties (SPPEK-Ps) cation exchange membranes were prepared and characterized for all-vanadium redox flow batteries. The sulfonic acid functional groups on the side chains of aromatic polymers increased the aggregation of ionic clusters and resulted in distinct hydrophilic/hydrophobic separation [24,25], improving the proton conduction. To assess their potential as VRFB membranes, the chemical structure, polymer, and membrane properties as well as cell performance were systematically studied.

2. Experimental

2.1. Materials

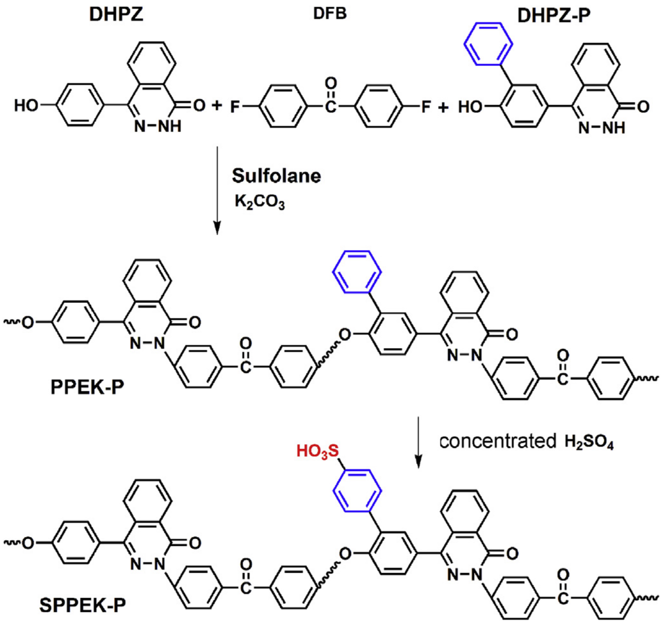
4-(4-hydroxyphenyl)-2,3-phthalazin-1-ketone (DHPZ, purity>99.5%) and 4-(3-phenyl-4-hydroxyphenyl)-2,3-phthalazin-1-ketone (DHPZ-P, purity>99.5%) were supplied by Dalian Polymer New Material Company (China); 4,4-difluorobenzophenone (DFB, purity>99.5%) was purchased from Yanji Chemical Company (China); Xylene (purity>99%), anhydrous potassium carbonate (purity>99%) and concentrated sulfuric acid (95–98%) were purchased from Bodi Chemical Company (China); Sulfolane (purity≥99.5%) was purchased from Liaoyang Guanghua Chemical Co., LTD and purified by distillation; Vanadyl sulfate ($VOSO_4$, purity>98%) was purchased from Shanghai Lvyuan Fine Chemical Plant. Other chemicals were analytical grade, obtained from commercial source.

2.2. Synthesis of SPPEK-Ps

As shown in Scheme 1, the synthesis of the SPPEK-P-*x* polymer involved two steps: the synthesis of the PPEK-P polymer and the subsequent sulfonation to yield SPPEK-P-*x*.

2.2.1. Synthesis of PPEK-P-x polymer

PPEK-P polymers were synthesized by direct nucleophilic polycondensation from DHPZ, DHPZ-P and DFB. The polymers are referred to as PPEK-P-*x*, where *x* is the molar fraction of DHPZ-P in the total feed of DHPZ-P and DHPZ, with the molar fraction of DFB equal to the sum of DHPZ-P and DHPZ. For example, in the synthesis of PPEK-P-70, DHPZ-P (0.7 mmol), DHPZ (0.3 mmol), DFB (1 mmol), and K_2CO_3 (1.2 mmol) were fed into a reaction vessel equipped with a mechanical stirrer, a water cooled condenser and nitrogen purge inlet and outlet. Sulfolane was the solvent and xylene was the water-carrying agent in the reaction. The mixture was first stirred under N_2 at 160 °C for 2 h to remove the water and xylene and then polymerized at 200 °C for at least 20 h. During the polymerization, an appropriate amount of sulfolane was regularly added in the vessel to continue the reaction. When the polymerization finished, the reaction product was quickly poured into hot water and boiled to remove impurities including inorganic salts. Finally, the polymer PPEK-P-70 was obtained after drying the product in vacuum at 100 °C for 12 h.



Scheme 1. Synthesis of SPPEK-Ps.

2.2.2. Preparation of SPPEK-P-x polymer

SPPEK-P polymers were prepared by sulfonation reactions of PPEK-Ps. Concentrated sulfuric acid was used as the solvent and sulfonating agent. The PPEK-P-*x* and concentrated sulfuric acid were mixed together with a mass ratio of 5% and then reacted at 30 °C for 7 h. The sulfonated product was subsequently precipitated in cold water and washed repeatedly to neutral with deionized water. The final product was dried under vacuum at 80 °C for 12 h.

2.3. Preparation of SPPEK-P membranes

SPPEK-P membranes were prepared by a solution casting method [24]. 1.0 g SPPEK-P-*x* powder was dissolved in 10 mL NMP to form a homogeneous solution. The solution was cast onto a clean, smooth glass plate at 80 °C using a casting knife, for at least 12 h to evaporate the solvent. The thickness of the wet membrane could be controlled mainly by adjusting the space between the casting knife and the glass plate, as well the spread speed, when the concentration of the solution was invariable. The coated glass plate was then submerged into deionized water to delaminate the ~50 μm thick membrane.

2.4. Characterization of polymer

^{1}H NMR (Varian INOVA 400 M) and FTIR spectra (Nicolet AVATAR 330) were used to determine the chemical structures of PPEK-Ps and SPPEK-Ps. In the ^{1}H NMR measurements, deuterated chloroform was used as the solvent for PPEK-Ps and deuterated

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