



# Novel sulfonated poly(ether ether ketone)/oxidized g-C<sub>3</sub>N<sub>4</sub> composite membrane for vanadium redox flow battery applications



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## ABSTRACT

A novel oxidized g-C<sub>3</sub>N<sub>4</sub> (OCN)-modified Sulfonated poly(ether ether ketone) (SPEEK) composite membrane were fabricated via a solution-casting method. The physicochemical properties of composite membranes with different oxidized-C<sub>3</sub>N<sub>4</sub> content were characterized, including water uptake, swelling ratio, ion exchange capacity, proton conductivity, vanadium ion permeability and ion selectivity. It was found that when the content of OCN incorporated into SPEEK matrix was 1%, this composite membrane showed a low vanadium ion permeability ( $9.09 \times 10^{-7} \text{ cm}^2 \text{ min}^{-1}$ ) and high ion selectivity ( $6.60 \times 10^4 \text{ S min cm}^{-3}$ ). The vanadium redox flow battery (VRB) assembled with this membrane at  $60 \text{ mA cm}^{-2}$  exhibited a higher coulombic efficiency (98%) than Nafion 117 membrane (95%). Moreover, in cycling tests VRB assembled with this composite membrane showed a more stable cycle performance compared with that of Nafion 117 membrane. Thus, the OCN-modified SPEEK composite membrane has a potential application for VRB system.

## 1. Introduction

In recent years, the crisis of energy has accelerated the development of solar and wind energy. All-vanadium redox flow battery (VRB), as an important energy storage system, has been greatly explored, because of its renewability and sustainability. The VRB firstly proposed by M. Skyllas-Kazacos [1], has attracted considerable attention due to its fast response time, long cycle life and deep-discharge capability. It has been considered as a promising storage energy technology [2–4].

In the VRB cell, as a key component, the proton exchange membrane (PEM) not only separated positive and negative electrolytes, but also formed ionic conduction channels to complete the circuit during charge and discharge process. An ideal IEM for the VRB application should have high ionic conductivity, low permeability of vanadium ions, good stability and low cost [5]. Currently, Nafion 117 membrane produced by DuPont Company was the most commonly used in VRB. Although the Nafion 117 membrane showed good chemical stability and high proton conductivity, the high vanadium ion permeability and cost have limited its wide application [6–9].

To address the issue, sulfonated aromatic polymer membranes, such as sulfonated poly(ether ether ketone) (SPEEK) [10,11], sulfonated poly(fluorenyl ether ketone) (SPFEK) [12–14], sulfonated polyimide (SPI) [15,16], and sulfonated polysulfone (SPSF) [17,18] have been widely

investigated as candidates for VRB application. Among these membranes, SPEEK was paid more attention for its lower cost and lower vanadium ion permeability compared with Nafion 117 membrane. The properties of SPEEK membrane were mainly dependent on its degree of sulfonation (DS) [19]. SPEEK membrane with high DS has high proton conductivity which was desired for VRB, but it led to poor stability and high vanadium ion permeability which greatly limited its further application in VRB [20]. Thus, some effective ways were to incorporate nano-sized inorganic filler materials into SPEEK matrix such as SiO<sub>2</sub>, TiO<sub>2</sub> and Graphene oxide [21,22], which could improve comprehensive properties of SPEEK matrix.

Graphitic carbon nitride(g-C<sub>3</sub>N<sub>4</sub>)-modified SPEEK membrane has been reported and showed high proton conductivity and low methanol crossover in proton exchange membrane fuel cells [23]. The OCN exhibited a similar stacked 2D structure as graphene oxide. It was expected that abundant functional groups, high surface area and intrinsic stability of oxidized g-C<sub>3</sub>N<sub>4</sub> could contribute to improvement of performance of PEM, because of the two-dimensional OCN nanosheets could effectively hinder transport of vanadium ions. The hydrophilic surface oxygen-containing functional groups of OCN networks were prone to form hydrogen bonds with polymer chains, which was favorable for the formation of the hydrophobic/hydrophilic separation structure in the resultant composite membranes [24]. In

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addition, according to Grotthuss mechanism, the carboxyl groups at the defects could form proton hopping sites, which was helpful to improve proton conductivity [25]. Herein, in this paper novel OCN-modified SPEEK membranes were prepared and used in the VRB system. The swelling ratio, water uptake, proton conductivity, vanadium ions permeability and thermal properties of the hybrid membrane were investigated. The VRB single cell performance with the composite membranes was discussed in detail.

## 2. Experimental

### 2.1. Material

Poly(ether ether ketone) (PEEK) (Vitrex, PEEK 450PF) was dried under vacuum at 100 °C for 24 h. Nafion 117 membrane was purchased from DuPont company, Nafion 117 membrane was soaked in H<sub>2</sub>O<sub>2</sub> solution (5 V%) and heated in water bath at 80 °C for 1 h, next then Nafion 117 membrane was immersed in 0.5 mol/L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution (98 wt%) and heated in water bath at 80 °C for 1 h. Finally, the membrane was stored in deionized water for further use. All the other analytical reagents, including Thiourea N, N-Dimethylacetamide (DMAC), HNO<sub>3</sub> (65 wt%), NaCl, NaOH, VOSO<sub>4</sub> and MgSO<sub>4</sub>·7H<sub>2</sub>O were provided by local chemical suppliers and used without further purification.

### 2.2. Preparation of OCN

The pristine g-C<sub>3</sub>N<sub>4</sub> was prepared by directly heating Thiourea at 550 °C for 3 h in air with a ramp rate of ≈ 5 °C min<sup>-1</sup>. The obtained bulk g-C<sub>3</sub>N<sub>4</sub> was milled into powder. Firstly, 1 g of bulk g-C<sub>3</sub>N<sub>4</sub> was treated in the mixture of concentrated sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) (20 ml) and nitric acid (HNO<sub>3</sub>) (40 ml) overnight at room temperature [26]. The mixture was diluted with deionized water (1 L) and washed for several times. Second, 100 mg of bulk oxidized-C<sub>3</sub>N<sub>4</sub> was dispersed in 100 ml water, and then ultrasound for 6 h. The initial formed suspension was centrifuged at 5000 rpm to remove the residual unexfoliated nanoparticles.

### 2.3. Nanocomposite membrane preparation

5 g PEEK were added to H<sub>2</sub>SO<sub>4</sub> (98 wt%, 100 ml) with stirring at 45 °C for 4 h, then the polymer solution was slowly poured into excess ice-cold water with continuous agitation to terminate the sulfonation reaction. After washed with water until the pH reached neutrality, the SPEEK was dried at 100 °C for 12 h under vacuum environment. The DS of SPEEK was 51% determined by titration method.

The composite membrane was prepared using the conventional solution casting method. In details: firstly, 1 g SPEEK was dissolved in 7 ml DMAC, and then certain amount of OCN was dispersed in 3 ml DMAC under sonication for 2.5 h to form a stable suspension. Next, the suspension was transferred into polymer solution. The mixture was sonicated and stirred for 12 h, respectively. Finally, the solution was cast onto a stainless steel plate and dried at 80 °C for 10 h, then dried at 100 °C for 8 h. after cooling to room temperature. The membrane was peeled off from the plate and then soaked in 1 mol L<sup>-1</sup> H<sub>2</sub>SO<sub>4</sub> solution for 24 h. and the membrane was immersed into deionized water for 24 h to remove the excess acid. Next, the membrane was stored in deionized water for further use. The composite membrane was designated as S/OCN-X, where X represented the weight percentage of the OCN nanosheets relative to SPEEK matrix. Pure SPEEK membrane was prepared and treated under the same procedure. Nafion 117 membrane had a better low vanadium permeability than other Nafion membranes [27]. Thus, Nafion 117 membrane was chosen as benchmark and pretreated according to the literature [6].

## 2.4. Characterization

### 2.4.1. The structure of oxidized-C<sub>3</sub>N<sub>4</sub> nanosheets

The chemical structure of the OCN nanosheets was determined using X-ray diffraction (XRD). Fourier transform infrared spectra (FT-IR) was conducted with FT-IR spectrometer (model Magna560; Nicolet, Madison, WI). The spectral range was 450–4000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> min<sup>-1</sup>.

### 2.4.2. The morphology of membrane

The morphology of cross-sections of membrane was observed by a Hitachi S-4800 (Japan) scanning electron microscope (SEM). To view the membrane cross-sections, the samples were prepared by fracturing the membranes in liquid nitrogen and then coated with gold.

### 2.4.3. Water uptake and swelling ratio

The Weight and length of hydrated membranes were measured immediately after the surface water was wiped off. Then, the wet membrane was dried under vacuum at 100 °C for 24 h. The dry membrane was measured quickly. The water uptake and swelling ratio of the membrane were calculated according to the following equations:

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

$$\text{Swelling ratio(\%)} = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{wet}}} \times 100\% \quad (2)$$

where  $W_{\text{wet}}$  and  $W_{\text{dry}}$  were the mass of wet and dry membranes, respectively.  $L_{\text{wet}}$  and  $L_{\text{dry}}$  were the length of wet and dry membrane, respectively.

### 2.4.4. Ion exchange capacity (IEC) and proton conductivity

IEC was calculated by the traditional titration technique. a small sample was fully immersed in 50 ml 1 mol L<sup>-1</sup> NaCl solution for 24 h. The resultant solution was titrated with 0.01 mol L<sup>-1</sup> NaOH, using phenolphthalein as indicator. Then the membrane was dried and weighed. The IEC was calculated by the following equation:

$$\text{IEC}(\text{mmol g}^{-1}) = \frac{C_{\text{NaOH}} \times V_{\text{NaOH}}}{W_{\text{dry}}} \quad (3)$$

where  $V_{\text{NaOH}}$  was the volume of consumed NaOH solution and  $C_{\text{NaOH}}$  was the concentration of NaOH solution.

The proton conductivity of the sample membrane was measured by electrochemical impedance spectroscopy (EIS) using a Solartron (1287 + 1260) electrochemical station (USA, AMETEK, Inc.). The proton conductivity of sample membrane was calculated by following equation:

$$\sigma(\text{Scm}^{-1}) = \frac{L}{A \times R} \quad (4)$$

where A and L were the effective area and thickness of sample membrane, R was the sample membrane resistance.

### 2.4.5. Permeability of VO<sup>2+</sup> and ion selectivity

The membrane (active area was 3.14 cm<sup>2</sup>) was exposed to 1 M VOSO<sub>4</sub> in 2 M H<sub>2</sub>SO<sub>4</sub> solution in right reservoir and to 1 M MgSO<sub>4</sub> in 2 M H<sub>2</sub>SO<sub>4</sub> solution in left reservoir, and the volume of each solution was 28 ml [28]. The two solutions were continuously magnetically stirred to avoid concentration polarization. 3 ml Sample from the MgSO<sub>4</sub> reservoir was taken out and measured by a UV-vis spectrometer (TU-1900, Beijing Purkinje General Instrument Co., Ltd., China) at regular time intervals. The VO<sup>2+</sup> permeability of membrane was calculated by following equation [29]:

$$V_R \frac{dC_R(t)}{dt} = A \frac{P}{L} [C_L - C_R(t)] \quad (5)$$

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