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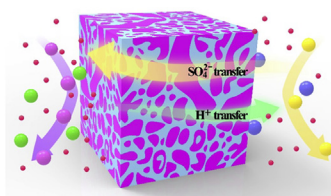
# Polyvinylpyrrolidone-based semi-interpenetrating polymer networks as highly selective and chemically stable membranes for all vanadium redox flow batteries

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## HIGHLIGHTS

- Polyvinylpyrrolidone-based semi-interpenetrating polymer networks were designed.
- The PVP-based SIPNs were employed in vanadium redox flow batteries (VRFBs).
- The CEs of VRFBs reached almost 100% at a current density from 40 to 100 mA cm<sup>-2</sup>.
- The EEs of VRFBs were more than 3% higher than those of VRFBs with Nafion 212.
- The good chemical stability was proved by an immersion test and a cycling test.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Vanadium redox flow batteries (VRFBs) with their high flexibility in configuration and operation, as well as long cycle life are competent for the requirement of future energy storage systems. Nevertheless, due to the application of perfluorinated membranes, VRFBs are plagued by not only the severe migration issue of vanadium ions, but also their high cost. Herein, we fabricate semi-interpenetrating polymer networks (SIPNs), consisting of cross-linked polyvinylpyrrolidone (PVP) and polysulfone (PSF), as alternative membranes for VRFBs. It is demonstrated that the PVP-based SIPNs exhibit extremely low vanadium permeabilities, which contribute to the well-established hydrophilic/hydrophobic microstructures and the Donnan exclusion effect. As a result, the coulombic efficiencies of VRFBs with PVP-based SIPNs reach almost 100% at 40 mA cm<sup>-2</sup> to 100 mA cm<sup>-2</sup>; the energy efficiencies are more than 3% higher than those of VRFBs with Nafion 212. More importantly, the PVP-based SIPNs exhibit a superior chemical stability, as demonstrated both by an *ex situ* immersion test and continuously cycling test. Hence, all the characterizations and performance tests reported here suggest that PVP-based SIPNs are a promising alternative membrane for redox flow batteries to achieve superior cell performance and excellent cycling stability at the fraction of the cost of perfluorinated membranes.

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## 1. Introduction

Due to the gradual depletion of fossil fuels, the development of renewable energies, such as solar and wind energy, has been vitalized with some promising progress that has been achieved in the last decades [1–4]. Their inherent intermittence characteristics, however, make renewable energies unreliable power sources for mature electrical power infrastructures. The electrochemical storage technologies, which can efficiently convert the electricity generated from the renewable energies into chemicals and reversibly release the electricity according to demand, are therefore particularly indispensable to level the fluctuation of power generation and enable the intermittent renewable energies to be integrated into the electrical grid [5,6]. Redox flow batteries (RFBs) have gained increasing attention as one of competent electrochemical storage technologies over the past few decades and some significant improvements have been made in not only the development of novel redox couples but also in the optimization of operation conditions [7–9].

Among these RFBs, vanadium redox flow batteries (VRFBs) invented by Skyllas-Kazacos in the 1980s, which employ the same vanadium element in four different chemical states, have been widely investigated due to their significant merits [2,10–12]. Specifically, the inherent issue of crossover contamination can be minimized with the application of the same vanadium element and the electrolyte can be readily regenerated during the course of routine maintenance procedures [13]. Moreover, the electrochemical kinetics of redox couples (V(II)/V(III) in the negative half-cell and V(IV)/V(V) in the positive half-cell) are sufficiently high and reversible, which can guarantee high efficiency and excellent electrochemical reversibility for practical applications [14,15]. Furthermore, the vanadium redox couples possess a suitable potential, which can potentially reduce the gassing side reactions and withstand deep charge and discharge process [2,16].

Despite their significant merits, the commercialization of VRFBs has been hampered by the relatively high cost, which is partially induced by the expensive perfluorinated membranes. Based on the cost analysis made by department of energy of USA, the separator cost covered the major component of total system costs (44% for 0.25 MWh and 27% for 4 MWh) [7,17]. The fabrication of novel membranes with the high chemical stability, low vanadium permeability, desired ionic conductivity and low cost is one of the critical research objectives for the VRFB research community [12,18]. In most reported works, the sulfonated polymer, either by direct copolymerization of sulfonated monomers or post-sulfonation of existing polymers, have been widely researched for VRFBs [19–23]. Meanwhile, anion exchange membranes (AEMs) have been gradually applied in VRFBs due to the Donnan exclusion effect that can largely reduce the transmembrane diffusion of vanadium ions [24,25]. However, the chemical stability of functional groups, including the pyridinium groups and quaternary ammonium groups, is the critical issue for AEMs in the harsh acid environment [26–29]. We also noticed that nanofiltration (NF) membranes have also been vitalized in the VRFBs recently [30–32]. The nanopores in NF membranes are utilized to transport the ions with small hydrated ionic sizes while blocking the vanadium ions with relatively larger ionic sizes. Despite the significantly lower cost of NF membranes, the pore sizes need to be carefully tailored and this is highly dependent on the fabrication procedure and/or the ratio between the inorganic additive and the organic polymer [32,33].

In this work, we fabricated a new category of membrane, namely semi-interpenetrating polymer networks (SIPNs), and applied them in VRFBs. In fact, SIPNs have been widely developed as proton exchange membranes [34] and anion exchange

membranes [35,36] for the fuel cell membrane application since SIPNs possess a series of unique properties as well as the versatile of polymer candidates. However, there is no report on the application of SIPNs in VRFBs except the recent work reported by Wu et al. [37]. Herein, we selected polysulfone (PSF) and polyvinylpyrrolidone (PVP) as the hydrophobic polymer and hydrophilic polymer respectively to form SIPNs, as illustrated in Fig. 1. After the dissolution of the two polymers in a solvent to form a miscible solution, the polymer backbones become entangled with each other and form a well-established hydrophilic/hydrophobic microstructure after the evaporation of the solvent and the photo-induced cross-linked process. Different from NF membranes, the nanopores formed in the hydrophobic backbones are filled with the cross-linked hydrophilic polymer, which will hinder the crossover of vanadium ions, thereby largely reducing the permeability of vanadium ions. Meanwhile, hydrogen bonding networks between the interpenetrated hydrophilic and hydrophobic component will be established, guaranteeing the chemical stability of SIPNs in the harsh environment. More importantly, the pyrrolidone segments in PVP can be protonized by the sulfuric acid. This protonation process endows the hydrophilic domains being positively charged, which largely reduce the vanadium ion permeability due to the Donnan exclusion effect between the protonated pyrrolidone segments and vanadium ions. In this situation, VRFBs assembled with PVP-based SIPNs exhibit superior cell performance and excellent cycling stability. These results testify that PVP-based SIPNs are the promising candidates for the industrial application in redox flow batteries.

## 2. Experimental

### 2.1. Materials

Polyvinylpyrrolidone (PVP, MW = 360,000), dimethylformamide (DMF) and 4, 4'-Diazido-2, 2'-stilbenedisulfonic acid disodium salt tetrahydrate (DAS, ≥99.0%) were purchased from Sigma-Aldrich. Sulfuric acid (95 wt%) and magnesium sulfate heptahydrate (≥99.5%) were purchased from VWR. Polysulfone (Udel-P3500) was donated by Solvay Advanced Polymers, LLC. Vanadyl sulfate (VOSO<sub>4</sub>·xH<sub>2</sub>O (≥99%)) was purchased from Shenyang Haizhongtian Fine Chemical Factory. All the chemicals were used as received without any further purification.

### 2.2. Preparation of SIPNs

The SIPNs were prepared by a photo-induced cross-linked process, as reported elsewhere [38]. Generally, a predetermined weight of PSF and PVP was completely dissolved in DMF to form a homogenous solution (5 wt%). The polymer solution was subsequently cast upon a clean glass plate using a micrometer adjustable film applicator. The plate was then introduced inside a forced convection oven. To completely evaporate the solvents, the oven temperature was dwelled at 120 °C for 12 h and subsequently cooled down room temperature. The membranes with a rough thickness of 50 μm were then peeled off from the glass plate. After the membranes were submerged into aqueous DAS solution (5 wt %) for 2 h, the membranes were removed from the solution, washed with methanol solution, dried in a vacuum oven at 40 °C for 1 h. Finally, the membranes were irradiated for 30 min with an ultraviolet lamp. The as-prepared membranes were denoted as SIPNs-x, in which x was presented the PVP content in the membrane.

### 2.3. Material structure characterizations

A field emission scanning electron microscope (FESEM, JEOL 7100) was used to determine the morphology of the membrane

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