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Novel sulfonated polyimide/zwitterionic polymer-functionalized graphene oxide hybrid membranes for vanadium redox flow battery

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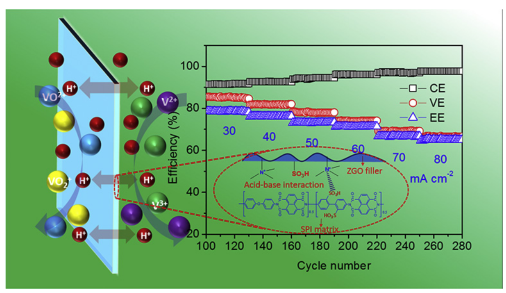
HIGHLIGHTS

- Zwitterionic polymer-functionalized graphene oxide (ZGO) was prepared.
- Interfacial interaction of hybrid membrane was well regulated via ZGO fillers.
- Low vanadium ion permeability and high proton conductivity realized.
- SPI/ZGO membranes kept excellent stability over 280 times charge−discharge tests.

GRAPHICAL ABSTRACT



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ABSTRACT

Hybrid membranes (SPI/ZGO) composed of sulfonated polyimide (SPI) and zwitterionic polymer-functionalized graphene oxide (ZGO) are fabricated via a solution-casting method for vanadium redox flow battery (VRB). Successful preparation of ZGO fillers and SPI/ZGO hybrid membranes are demonstrated by FT-IR, XPS and SEM, indicating that ZGO fillers is homogeneously dispersed into SPI matrix. Through controlling the interfacial interaction between SPI matrix and ZGO fillers, the physicochemical properties, *e.g.*, vanadium ion barrier and proton transport pathway, of hybrid membranes are tuned via the zwitterionic acid-base interaction in the hybrid membrane, showing a high ion selectivity and good stability with the incorporated ZGO fillers. SPI/ZGO-4 hybrid membrane proves a higher cell efficiencies (CE: 92−98%, EE: 65−79%) than commercial Nafion 117 membrane (CE: 89−94%, EE: 59−70%) for VRB application at 30−80 mA cm^{-2}. The assembled VRB with SPI/ZGO-4 membrane presents a stable cycling charge−discharge performance over 280 times, which demonstrates its excellent chemical stability under the strong acidic and oxidizing conditions. SPI/ZGO hybrid membranes show a brilliant perspective for VRB application.

1. Introduction

Since reported by Skyllas-Kazacos et al. in 1985, vanadium redox flow battery (VRB) has been extensively explored in light of its high energy efficiency, deep discharge capability and flexible operation [1−4]. Ion exchange membrane (IEM), a separator for electrolyte, is a key component in VRB system, which controls the large-scale commercialization of VRB [5−9]. The ideal IEM for VRB is expected to possess high proton conductivity, low vanadium ion permeability and good chemical stability.

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Although Nafion, a commercial ion exchange membrane, has been the preferred membrane for VRB due to its high proton conductivity and good chemical stability, the high vanadium ion permeability and extremely high cost still remain a concern for its practical application in VRB [10–14]. Recently, developing non-fluorinated membranes has been paid on sulfonated aromatic polymers, such as sulfonated poly(ether ether ketone) (SPEEK) [6,15], sulfonated poly(sulfone) (SPSF) [5,16], sulfonated poly(phthalazinone ether ketone) (SPPEK) [17–19] and sulfonated polyimide (SPI) [20–24], and they have been proved to be an alternative for VRB application. Their rigid structure and less connected ionic channels of aromatic polymers may effectively prevent vanadium ion crossover, and then improve the columbic efficiency of VRB cell; however, the conflict between high proton conductivity and low vanadium ion permeability is still difficult to overcome [25]. Tuning the interfacial interaction of hybrid membranes through the incorporated functional fillers into polymer matrix is proved to be a successful method to break the trade-off hurdle between proton conductivity and vanadium ion permeability. For example, inorganic particles like TiO_2, AlOOH, tungstophosphoric acid (ATP), mesoporous silica, ZrO_2 and graphene-based nanofillers have been introduced into polymer matrix to reduce vanadium ion permeability and improve stability depending upon the hydrogen bonding network formed in the interfacial zone [15,18,20,21,26–30]. Undesirably, the above interfacial state in hybrid membranes hinders vanadium ion and proton transporting process at the same time. Through the simple incorporation of inorganic fillers, a desirable vanadium ion permeability can be realized; however, a compromising proton conductivity is followed. At present, by adjusting the acid-base interfacial interaction in the interfacial zone of hybrid membranes, an alternative choice to restrict vanadium ion crossover and improve the stability of membranes is utilized in VRB system. Li et al. prepared a polymer acid-base blend membrane (SPEEK/PAN) for VRB application, showing a low vanadium ion permeability and swelling ratio. VRB with this acid-base blend membrane exhibited a columbic efficiency (CE) of 96% and an energy efficiency (EE) of 83.5% at 80 mA cm^{-2} current density, and kept a stable performance after 150 times cycling tests [31]. Besides, Liu et al. also developed an acid-base blend membrane (SPEEK/PEI) used for VRB, and obtained a good cell performance [32]. In our previous work, acid-base hybrid membranes composed of SPI and NH_2-rGO were successfully fabricated, proving a low vanadium ion permeability and high proton conductivity simultaneously. The exhibited low vanadium ion permeability and high proton conductivity was ascribed to the constructed proton transport pathway by acid-base interaction in the interfacial zone of membrane [23]. Actually, zwitterionic polymers containing both anionic and cationic groups proved a good VRB cell performance due to the Donna exclusion effect and proton donator of zwitterionic groups [33]. Thus, incorporating the zwitterionic polymer functionalized graphene oxide into SPI matrix was developed to obtain a promising membrane for VRB system with both low vanadium ion permeability and high proton conductivity, especially for the dual coordination influence of zwitterionic polymers and graphene oxide.

In this work, zwitterionic polymer functionalized graphene oxide (ZGO) was introduced into SPI matrix to fabricate the SPI/ZGO hybrid membranes for VRB. The physicochemical properties including water uptake, swelling ratio, vanadium ion permeability and proton conductivity were investigated. Furthermore, the cell performance and operating stability of VRB with SPI/ZGO hybrid membranes were also evaluated in detail. The effect of zwitterionic acid-base groups on the VRB cell performance was deeply investigated and their perspectives were also discussed.

2. Experimental

2.1. Materials

Natural graphite powders (NGP) (325 mesh) are kindly provided by Qingdao Laixi Graphite Co., Ltd. 4, 4′-Oxydianiline (ODA) and 1, 4, 5, 8-Naphthalenetetracarboxylic dianhydride (NTDA) are purchased from Sinopharm Chemical Reagent Co., Ltd.. 2, 2'-benzidinedisulfonic acid (BDSA), 4-vinylbenzyl chloride (VBC) and sodium 4-vinylbenzenesulfonate (NaSS) are provided by J&K Scientific Ltd, and used as received. Concentrated H_2SO_4 (98%), $KMnO_4$, $NaNO_3$, H_2O_2 (30%), HCl (37%), ceric ammonium nitrate (CAN), N,N-dimethylformamide (DMF), m-cresol, triethylamine, trimethylamine (TMA) and benzoic acid are provided by Tianjin Guangfu fine Chemical Research Institute and used as received. Nafion 117 membrane is purchased from DuPont (Beijing, China).

2.2. Preparation of GO and ZGO

Graphite oxide is prepared from natural graphite powder (325 mesh) through a modified Hummers method, as reported in our previous work [34].

ZGO is prepared via a polymerization procedure similar to the method reported in the literature [35]. Typically, 100 mg GO powder is re-dispersed into 100 mL deionic water by ultrasonication followed by adding 1 g VBC and 1 g NaSS (dispersed in 10 mL deionic water). And then, 1 g CAN in 1 mol L^{-1} HNO_3 is dropped into the mixture. The polymerization process is conducted at 80 °C for 24 h under N_2. After cooling to room temperature, this product is isolated by centrifugation and washed with deionic water and DMF for 5 times to remove the unreacted monomers. Afterwards, the product is quaternized using TMA, and then acidified by 1 mol L^{-1} HCl. The obtained ZGO is dried at 60 °C for 12 h in vacuum oven. The detailed preparation process of ZGO and AGO is presented in Fig. 1.

2.3. Preparation of SPI/ZGO hybrid membranes

SPI with a 50% sulfonation degree is synthesized according to the study of Genies et al. [36]. SPI/ZGO hybrid membranes are prepared by a solution-casting method. First, the predetermined weight of ZGO is dispersed in m-cresol by ultrasonication for 30 min, and then SPI is dropped and stirred at 60 °C for 12 h. The homogenous solution is cast on a clean glass plate, which is firstly

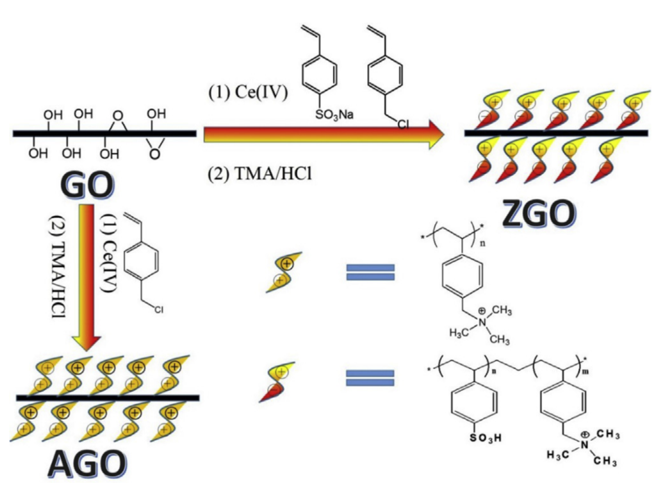

Fig. 1. Preparation process of ZGO and AGO.