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The porous membrane with tunable performance for vanadium flow battery: The effect of charge

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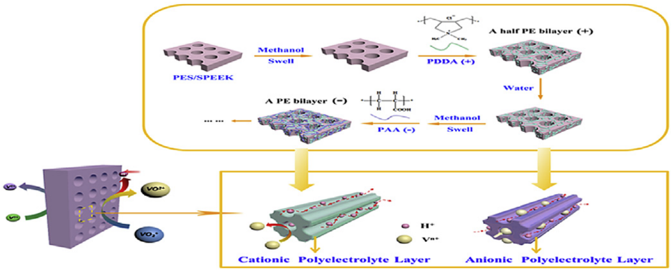
HIGHLIGHTS

- The effect of charges on porous membranes transport behavior in VFB was studied.
- The charge of porous membrane can be tuned via solvent responsive layer-by-layer.
- The positively charged membrane exhibits high selectivity via Donnan exclusion.

GRAPHICAL ABSTRACT



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ABSTRACT

Porous membranes with different charge on the surface and internal pore walls are prepared via the solvent-responsive layer-by-layer (SR-LBL) method. The effect of charge on the transport properties of different ions through the membranes is investigated in detail. The charge property of prepared membranes is tuned by assembling different charged polyelectrolytes (PEs) on the pore walls and the surface of the porous membranes. The results show that in a vanadium flow battery (VFB), the PE layers assembled on the surfaces (including pore walls) are capable to construct excellent ion transport channels to increase proton conductivity and to tune the ion selectivity via Donnan exclusion effect. Compared with the porous membrane with negative charges (7 bilayers), a VFB single cell assembled with a positively charged membrane (7.5 bilayers) yields a higher coulombic efficiency (98%). The water and ion transfer behavior exhibits a similar tendency. In the negative half-cell, the amount of V^{3+} gradually increases as cycles proceed and the amount of V^{2+} stays at a low and stable level. In the positive half-cell, the amount of VO^{2+} decreases; while VO_2^+ is accumulated. The imbalance of vanadium ions at both sides induces the discharge capacity fade.

1. Introduction

Due to increasing concerns on environmental pollution and energy shortage, utilization of renewable energy resources, such as solar and wind power, is becoming an effective means for further sustainable development [1–4]. However, the intermittent and instable nature of renewable sources hinders their further wide

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application. Therefore, large scale energy storage technology is highly needed [5]. Compared with other energy storage technologies, vanadium flow batteries (VFBs), proposed by Maria Skyllas-Kazacos and co-workers in 1984 [6], possess the characteristics of high safety, flexible design, long cycle life and cost effectiveness, and are well-suited for large-scale energy storage [7,8]. In the past several decades, impressive progress has been achieved in VFB technologies for applications like grid management, load leveling and peak shaving backup power [9–11]. As a key part of a VFB, a membrane mainly plays the role of separating the anolyte and catholyte and transferring protons to complete current circuit [12,13]. Currently, the traditionally used commercial membrane is perfluorinated membranes, e.g. Nafion membranes from DuPont, which possesses excellent proton conductivity and chemical stability [14]. However, high cost and low selectivity of a Nafion membrane hinder its further application in a VFB. Non-fluorinated and partially fluorinated membranes, such as poly (fluorenyl ether ketone) (SPFEK) [15], polysulfone (PS) [16], poly (arylene ether ketone) [17], have thus been investigated intensively. However, because of poor chemical stability induced by the ion exchange groups, these membranes cannot really meet the practical requirement [18]. Therefore, our group introduced nanofiltration porous membranes into VFB applications [19]. Different from traditional ions exchange membranes, porous membranes can separate ions with different size mainly by pore size exclusion. Based on this concept, porous membranes with different pore structures have been designed and prepared for VFB applications [20–25]. For example, silica sol-gel [26] and solvent responsive sol-gel methods [27] were employed to modify porous membranes, which effectively increased ion selectivity via pore size regulation.

Even though impressive progress has been recently achieved in VFB technologies, some challenges still exist. Especially the transport behavior of different ions through a porous membrane has not yet been fully investigated in a VFB. Essentially, ion transport across a porous membrane is closely related to the unique features of nanoscale ion transport channels, e.g. the geometry and surface charge characteristics [12,28,29]. When channel dimensions are in the order of the Debye length, the surface characteristic of the channels plays a significant role in the ionic transport behavior [30]. Different surface charge on pore wall and surface will greatly affect ion transport through the membranes, owing to the different electrostatic interactions between ions in the electrolytes and the charged species on the pore wall and membrane surface. To fabricate porous membranes with tunable charge characteristics will thus be highly beneficial to investigating ion transport mechanism. Layer-by-layer (LBL) self-assembly technology is an effective way to fabricate thin film via electrostatic interaction between oppositely charged species on the surface of substrates [31]. In the membrane field, LBL could create composite membranes with controlled properties of thin top layer, e.g. thickness and charge. Recently, a solvent-responsive layer-by-layer (SR-LBL) method was proposed to establish ion transport channels within porous membranes [19]. The polyelectrolyte (PE) layers were successfully assembled on the pore wall and membrane surface by tuning the “open or close” state of the pore structure. Therefore, it could well tune the charge characteristics of the pore wall and membrane surface via assembling different charged PEs.

In this work, PES-based porous membranes with different charges on the internal pore walls and membrane surface were prepared by the SR-LBL method. The charge on the pore wall and membrane surface was adjusted via assembly of PEs with different charge. The effect of surface charge of membranes on VFB performance, especially transfer behavior, was investigated (Scheme 1). Poly (diallyldimethylammonium chloride) (PDDA) and poly (acrylic acid) (PAA) are selected as cationic and anionic PE, respectively. The positively charged membranes were prepared by leaving PDDA as the last layer, while the negative charged membranes were prepared by deposing the last layer of PAA. The influence of surface charge on the membrane performance like cell performance, ions transfer, etc. will be investigated in detail.

2. Experimental section

2.1. The preparation of charged membrane with multilayer PEs

The porous substrate membranes are prepared via water immersion phase inversion technique. Sulfonated poly (ether ether ketone) (SPEEK) is synthesized by direct sulfonation of poly (ether ether ketone) (PEEK) (Changchun Jilin University Special Plastic Engineering Research) with concentrated sulfuric acid (Jinzhou Gucheng Chemical Reagent Co., Ltd.) at 70°C for 2 h [21]. The coating solution was prepared from 35 wt% total concentration of poly (ether sulfone) (PES, Changchun Jilin University Special Plastic Engineering Research) and prepared SPEEK in N,*N*-dimethylacetamide (DMAC, Tianjin Damao Chemical Reagent Factory). The weight ratio of SPEEK in the polymer was kept at 20%. The solution was cast onto a clean glass plate at room temperature with less than 40% relative humidity. The glass plate was then immersed into water to form a PES/SPEEK composed porous membrane. The thickness of the prepared membranes is 130±3 μm. Nafion 115 membranes are treated based on our previously reported work [32]: Nafion 115 membrane is treated in a 3 wt% H_2O_2 solution at 80°C for 60 min, then boiled in deionized water at 80°C for 30 min and immersed in a 1 M H_2SO_4 solution at 80°C for 30 min. The treated Nafion 115 membrane is rinsed and stored in deionized water before use.

The porous membranes with PEs layers of different charge were prepared as reported in our previous paper [21]: firstly, a substrate membrane was immersed in methanol (Beijing Chemical Works) for 10 min to open the pores; then the swelling membrane was immersed into 2 wt% PDDA (M_w = 200000–350000 g mol^{-1}, Aladdin Chemistry Co. Ltd.) for 10 min. After assembling the cationic PE, the prepared membrane was fully rinsed with excess deionized water to wash redundant PEs. A similar process was used for adsorption of 2 wt% PAA (M_w = 3000 g mol^{-1}, Aladdin Chemistry Co. Ltd.). The above procedure is repeated to prepare charged membranes with different PEs layers. A bilayer is defined as double PE layers composed of one PDDA layer and one PAA layer. The charge is tuned via assembly of PEs with different charge on the surface and the internal pore walls. The porous membrane with positive charge was prepared via assembling PDDA on the toplayer. The PAA was used to tune surface charged property as negative surface charge. For example, “3.5 bilayers” represents that 3.5 bilayers of PDDA/PAA are assembled on membrane surface or 3 bilayers of PDDA/PAA and a single layer of PDDA are introduced on the support membrane, which means that “3.5 bilayers” exhibits positive charge. Similarly, the membranes with 5.5 and 7.5 bilayers exhibit positively charged property, while, the membranes with 7 bilayers possess negatively charged property.

2.2. Characteristics of prepared membranes

The surface and cross-section morphologies of the prepared membranes were characterized by field emission scanning electron microscopy (FE-SEM, QUANTA 200FEG). The cross-section of samples was obtained by breaking them in liquid nitrogen. Gold coating is needed for all the samples before measurement. The chemical structure of the composite membranes was confirmed by attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR, NICOLET iS50, Thermofisher Co. Ltd.). Each spectrum was