

Advanced porous polybenzimidazole membranes for vanadium redox batteries synthesized via a supercritical phase-inversion method

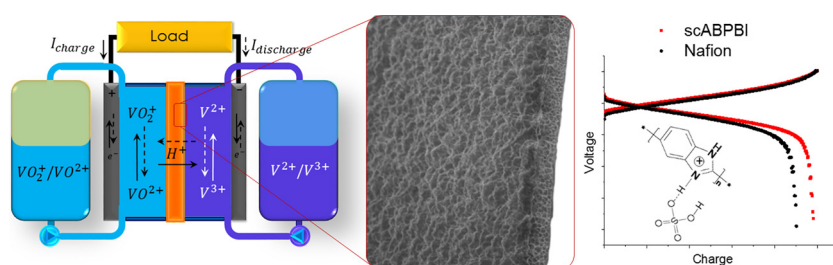
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GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Vanadium redox flow battery
Polybenzimidazole
Membrane
Supercritical carbon dioxide

ABSTRACT

Porous poly(2,5-benzimidazole) membranes for vanadium redox battery applications were prepared using supercritical CO₂ assisted phase inversion method. Membrane morphology, electrolyte uptake, proton and vanadyl ion transport properties as well as membrane performance in single cells of VRBs are studied. Highly selective ABPBI membranes with fibrous structure and improved ion transport properties are obtained. Significant improvement in proton conductivity is observed (values up to 27 mS cm⁻¹ are achieved), while VO₂⁺ permeability is preserved at a low level (4.1 × 10⁻⁸ cm² min⁻¹). Single VRB cells with the modified ABPBI membranes demonstrate improved coulombic efficiency without significant deterioration of the voltage efficiency as compared to Nafion membranes. As a result, the energy efficiency of single VRB cells with the new membranes is significantly improved in a low current density region (20–40 mA cm⁻²) as compared to Nafion 115 based cells (up to 14% improvement).

1. Introduction

The transition from fossil fuel based energy generation schemes to renewable-based generation systems such as solar and wind energy requires the development of efficient energy storage that would maintain the balance between energy consumption and production rates. Vanadium redox flow batteries (VRB) are considered to be promising stationary electrochemical energy storage devices suitable for such purposes [1] due to the relatively high efficiency, independent power

and energy scaling and low maintenance costs [2,3].

In VRBs energy is stored in two separate tanks filled with aqueous electrolytes, catholyte and anolyte, containing cations of vanadium in different oxidation states: V(V) and V(II) in a fully charged state, respectively. During battery operation, the electrolytes are pumped through cells containing a cathode and an anode where the electrochemical reactions take place. During discharge process V(V) is reduced to V(IV) at the cathode and V(II) is oxidized to V(III) at the anode, while in reverse the reactions proceed in the opposite direction during the

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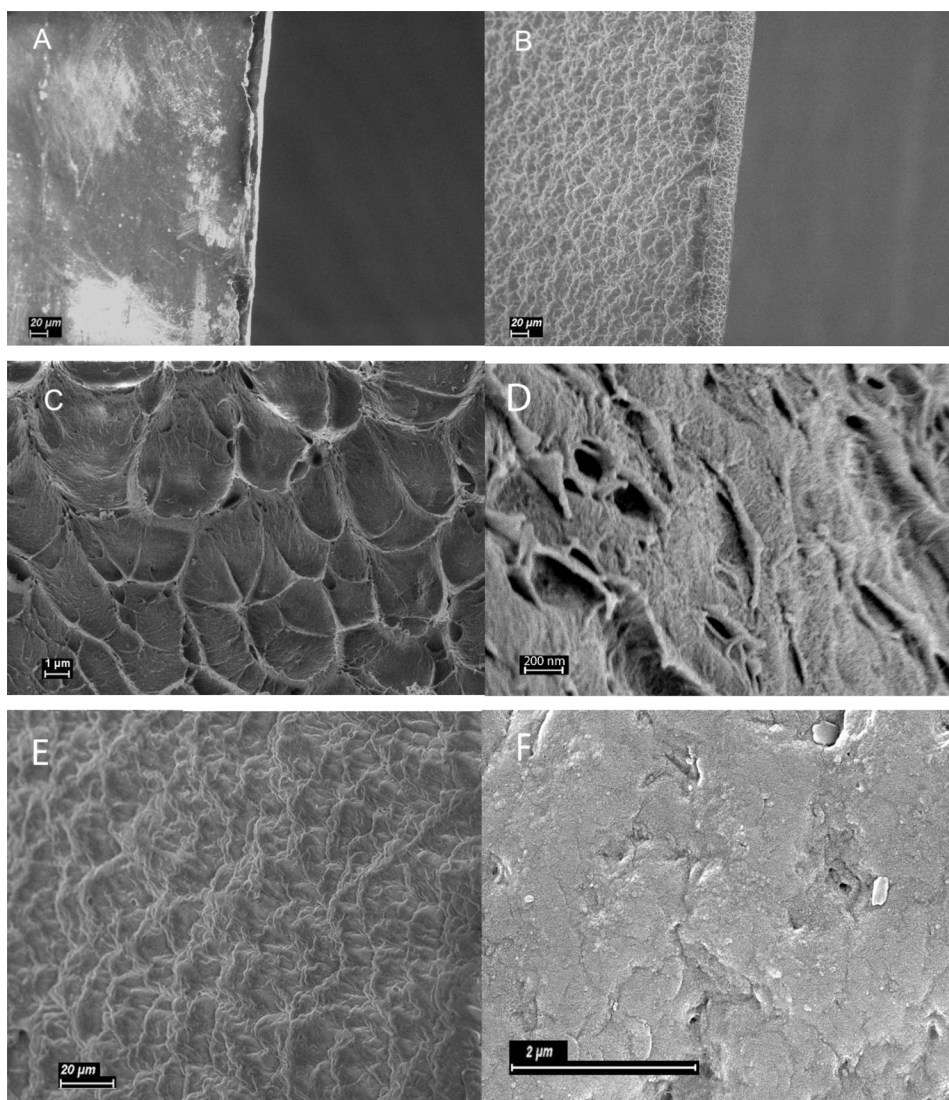


Fig. 1. SEM micrographs of the pristine ABPBI membrane (A), and scABPBI (B) cross-section of the scABPBI (C) cross-section of the scABPBI coated with sputtered Pt film at higher magnification (D) and images of scABPBI surface at higher magnification (E,F).

Table 1

The specific volume increase of scABPBI relative to dense ABPBI membranes (V/V_d) due to the presence of non-flooded pores determined by hydrostatic weighing in hexane, isopropanol and water.

Liquid	Surface tension, mN m^{-1}	V/V_d
Hexane	18	1.05
Isopropanol	23	1.06
Water	72	1.08

charge process.

The key component of the VRB is an ion exchange membrane (IEM) that separates the electrodes, prevents cross-mixing of the soluble redox-active V(II) (anolyte) and V(V) (catholyte) species and provides ionic transport of counter ions (H^+) to complete the electrochemical circuit. An ideal membrane should be impermeable to vanadium cations, have high proton or anion conductivity, high chemical stability to oxidation and reduction by the electrolytes. The most commonly used membrane material for VRBs is sulfonated perfluorocarbon polymer Nafion [4] and its different modifications [5,6]. Though Nafion demonstrates good chemical stability and high proton conductivity, its high permeability to vanadium cations [7] and extremely high cost

(more than 15% of the total cost of the battery system [1]) stimulates the research for alternative IEM materials.

Since liquid electrolytes based on sulfuric acid solutions are used in VRBs, there is no need in choosing membranes with intrinsic ionic conductivity like Nafion. An alternative approach is to use porous membranes of cheaper polymers, which swell in aqueous acidic solutions. It has been shown recently that polybenzimidazoles (PBIs) are promising membrane materials for VRBs [1,4]. They are less expensive than fluorinated membranes and they are almost impermeable to vanadium cations due to the polycationic nature of protonated PBI chains swollen in acidic electrolyte [4]. The main disadvantage of such membranes is rather low proton conductivity as compared to Nafion. One way to improve the conductivity is to make the polymer structure porous. Porous polymer membranes are usually prepared by a wet phase inversion process [8,9]. An alternative way to obtain the porous structure is to induce phase separation using a supercritical fluid, for example CO_2 (scCO_2), as a non-solvent for the polymer [10–15]. This method has several advantages as compared to the wet phase inversion method:

- after decompression the prepared membrane is easily obtained without any extra post-treatment required;
- CO_2 is a green solvent, which can be easily recovered after being

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