The effect of Nafion membrane thickness on performance of all tungsten-cobalt heteropoly acid redox flow battery

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HIGHLIGHTS

- Effect of PEM thickness on the performance of all $H_6[CoW_{12}O_{40}]$ RFB was investigated.
- The effect of Nafion membrane thickness on CE and VE of the RFB was opposite.
- The RFB with N211 exhibited high power density of $0.56\,W\,cm^{-2}$ at $0.6\,A\cdot cm^{-2}$.
- The RFB with N211 showed high CE, EE and capacity retention during 100 cycle test.

GRAPHICAL ABSTRACT
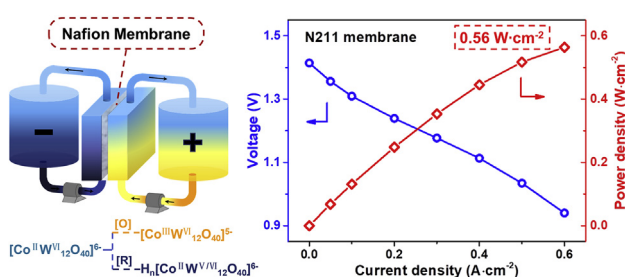
ABSTRACT

Recently, we have reported a new all tungsto-cobalt heteropoly acid redox flow battery (all $H_6[CoW_{12}O_{40}]$ RFB) with high coulombic efficiency. Because of the relatively large ion size and high negative charge, the tungsto-cobalt heteropoly acid anion is difficult to cross Nafion membrane, which makes it possible to employ thinner Nafion membrane in all $H_6[CoW_{12}O_{40}]$ RFB. In this study, three types of Nafion membranes with different thickness, namely, N212 (50 μm), N211 (25 μm), and N-17 (home-made, 17 μm) are used as polymer electrolyte to investigate its effects on the performance of all $H_6[CoW_{12}O_{40}]$ RFB. The ion permeability increases while the area specific resistanceas decreases as reducing the membrane thickness. As a result, the RFB with N211 membrane exhibits best comprehensive performance, which exhibites the energy efficiency of 88.6% at current density of $0.10\,A\,cm^{-2}$ and the power density of $0.56\,W\,cm^{-2}$ at $0.60\,A\,cm^{-2}$. Moreover, the battery delivers impressive cycling performance of 100 cycles with an average coulombic efficiency of 99.4%, energy efficiency of 80.0%, and capacity retention of 99.98% per cycle at current density of $0.20\,A\,cm^{-2}$.

1. Introduction

Redox flow batteries (RFBs) are considered as the most promising large-scale devices for storage and conversion owing to their flexible and scalable energy capacity benefited from uncoupled power and energy devices [1,2]. This unique architecture permits the RFBs to solve the mismatch between the intermittent supply of these renewable resources and variable demand [1–5]. However, most of the traditional RFBs, such as all-vanadium RFB [6–8], ferrum-chromium RFB [2,9] and ferrum-vanadium RFB [10–12], suffer from serious ion permeation through ion-exchange membranes (IEMs) and low kinetics constants of active species, which resulting in high self-discharge rate, low coulombic efficiency (CE), low energy efficiency (EE) and low power density [8].

Many novel electrolytes with relatively large ion size and/or negative charge, such as Br^-/Br_3^- [13], I^-/I_3^- [3], organic anion pairs [13–19], ionic polymer, and metal complexes [15,16,19–21] have been developed to reduce the permeability of energy storage ions in state-of-
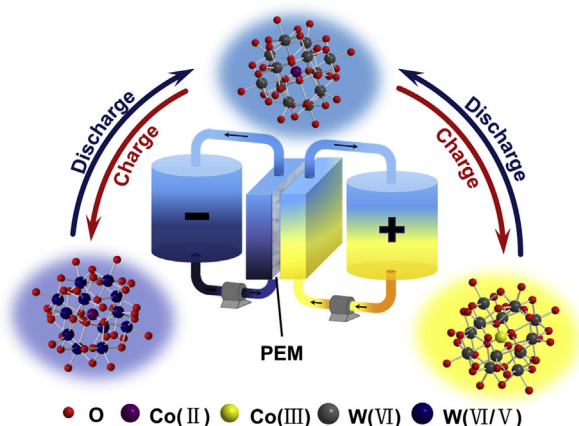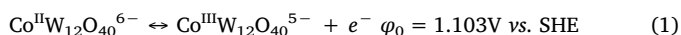
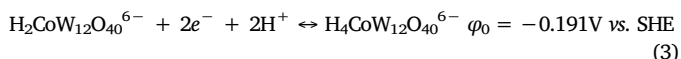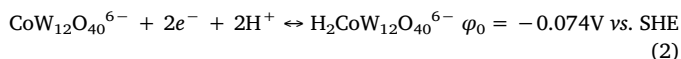**Scheme 1.** The working principle of an all $H_6[CoW_{12}O_{40}]$ RFBs. The $[CoW_{12}O_{40}]^{n-}$ is drawn in ball-and-stick notation. (Charging: Negetive electrode: $W^{VI} \rightarrow W^{VI/V}$, Positive electrode: $Co^{II} \rightarrow Co^{III}$, H^+ transfers from positive electrode to negetive electrode; Discharge: Negetive electrode: $W^{VI/V} \rightarrow W^{VI}$, Negetive electrode: $Co^{III} \rightarrow Co^{II}$, H^+ transfers from negetive electrode to positive electrode.).

Fig. 1. Energy density versus max power density of selected RFB systems. Viologens (violet): [14–16]. Flavins (yellow): [17,18]. Anthraquinones (magenta): [13,19]. Polyoxometalates (navy): [26,27]. Typical all-vanadium redox flow battery (black) [7,24].]. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the-art ion exchange membrane (i.e., Nafion). Moreover, some of them achieve amazing power density above 0.6 W cm^{-2} [19,22,23], which is significantly higher relative to the typical all-vanadium electrolyte (< 0.15 W cm^{-2}) [7,24]. Recently, we have also demonstrated an aqueous redox flow battery with a tungsten-cobalt heteropoly acid ($H_6[CoW_{12}O_{40}]$) as the electrolyte for both the anode and cathode [25]. The working principle of all $H_6[CoW_{12}O_{40}]$ RFBs is shown in Scheme 1. In aqueous solution, $H_6[CoW_{12}O_{40}]$ molecule dissociates to H^+ and $[CoW_{12}O_{40}]^{6-}$ as a strong acid. During the battery charging and discharging process, the cobalt atom in $[CoW_{12}O_{40}]^{6-}$ is oxidized or reduced reversibly at the positive electrode, whereas tungsten atoms are reduced or oxidized at the negative electrode. H^+ moves through the IEM as the charge carrier. The electrochemical reactions of the RFB are as follows:

At positive electrode:

$$Co^{II}W_{12}O_{40}^{6-} \leftrightarrow Co^{III}W_{12}O_{40}^{5-} + e^- \quad \varphi_0 = 1.103V \text{ vs. SHE} \quad (1)$$

At negative electrode:

$$CoW_{12}O_{40}^{6-} + 2e^- + 2H^+ \leftrightarrow H_2CoW_{12}O_{40}^{6-} \quad \varphi_0 = -0.074V \text{ vs. SHE} \quad (2)$$

$$H_2CoW_{12}O_{40}^{6-} + 2e^- + 2H^+ \leftrightarrow H_4CoW_{12}O_{40}^{6-} \quad \varphi_0 = -0.191V \text{ vs. SHE} \quad (3)$$

$[CoW_{12}O_{40}]^{6-}$ anion has relatively large size and high negative charge, making it difficult to cross the Nafion membrane, while H^+ can transfer readily. Therefore, the battery overcomes the problems of cross contamination and ion permeation through proton exchange membranes (*eg.* Nafion). Meanwhile, the slight permeation and fast kinetic [25] makes it possible to employ thinner membrane to reduce the internal resistance of the battery and release the restricted power outputs [7,19]. However, excessively thin membrane would cause serious permeation of the electrolyte, leading to the failure of RFBs. Thus, choosing a membrane with both low area resistance and slightly permeation is necessary.

In this study, we investigated three types of Nafion membranes, namely, N212, N211, and home-made N-17 in all tungsto-cobalt heteropoly acid RFBs. The thicknesses of the three membranes N212, N211, and home-made N17 are 50, 25, and 17 μm, respectively. The ion permeability increases while the area specific resistances decreases as reducing the membrane thickness. N211 membrane exhibited both low area resistance and slight permeation. The corresponding battery
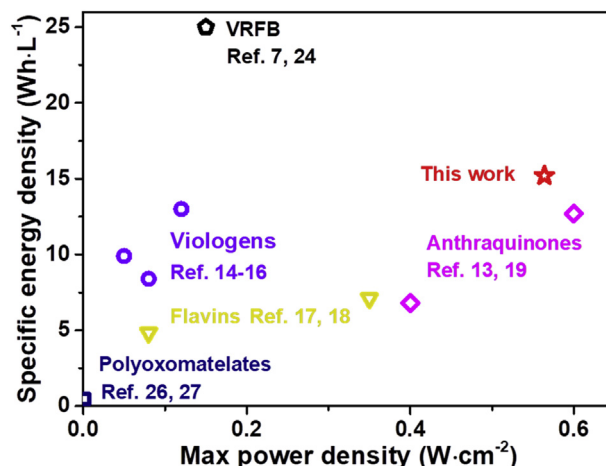
exhibited the EE of 88.6% at 0.10 A cm^{-2}, while the power density reached 0.56 W cm^{-2}, along with the high energy density (15.2 Wh·L^{-1}), the comprehensive output performance of all tungsto-cobalt heteropoly acid RFB stands out from the recently reported new types of aqueous RFBs (Fig. 1). Furthermore, the RFB delivered an impressive cycling performance of 100 cycles with an average CE, an EE, and a capacity retention of 99.4%, 80.0%, and 99.98% per cycle at 0.20 A cm^{-2}, respectively.

2. Materials and methods

2.1. Synthesis and characterization details of $H_6[CoW_{12}O_{40}]$

The synthesis of $H_6[CoW_{12}O_{40}]$ was carried out by the method invented by Baker in 1956 and 1966 [28,29]. $H_6[CoW_{12}O_{40}]$ electrolyte (0.8 mol L^{-1}) was prepared by evaporation of its solution, while the concentration of electrolytes was determined using a Cintra10e UV spectrometer (GBC, AUS) in the wavelength range 400–800 nm. The maximum absorption peak was observed at 624 nm. All the reagents used in the synthesis were purchased from Beijing Chemical Factory, China and used without further purification.

2.2. Membranes preparation

The home-made N-17 membrane was synthesized by ethanol solution with 20 wt% Nafion (Dupont, USA). The solution was first diluted to 1 wt%, and 10 mL diluted solution was cast to a mold of 6 cm × 6 cm at 60 °C for 12 h and then heated up to 110 °C for 1 h. N212 and N211 were procured from Dupont, USA, and all the membranes were pretreated with deionized water at 80 °C for 0.5 h and stored in deionized water.

2.3. Ion permeability

Ion permeability was determined by measuring the diffusion of $[CoW_{12}O_{40}]^{6-}$ in a device with two symmetric reservoirs, divided by N212, N211, or N-17 membrane. 0.2 mol L^{-1} $H_6[CoW_{12}O_{40}]$ was sealed in the left reservoir, and equal amounts of glucose-saturated solution with 0.6 mol L^{-1} H_2SO_4 was sealed in the right reservoir to balance the osmotic pressure. Samples of the solution from the right reservoir were taken out at a regular time intervals and used to measure the concentration of $[CoW_{12}O_{40}]^{6-}$ by UV–vis spectroscopy.