



# Functionalization of polyvinyl alcohol composite membrane by CoOOH for direct borohydride fuel cells



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## ABSTRACT

A polyvinyl alcohol anion exchange resin composite membrane was functionalized with CoOOH for use in direct borohydride fuel cells (DBFCs) and is detailed in this report. The CoOOH-functionalized membrane has a higher ionic conductivity and a lower borohydride ion permeability than the membrane without CoOOH. The DBFCs with the CoOOH-functionalized membrane achieved better performance, such as a power density peak at  $144 \text{ mW} \cdot \text{cm}^{-2}$  at  $30^\circ \text{C}$ , than did those without CoOOH. Such performance improvement is due to CoOOH functionalization, whereby Co species reduce the crossover of the borohydride ion while maintaining high conductivity for hydroxyl species. With the introduction of the Co species, the conductivity-permeability trade-off dilemma in traditional anion exchange membranes is avoided. Therefore, the functionalization of the membrane helps to elucidate the development of anion exchange membrane fuel cells.

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## 1. Introduction

Direct borohydride fuel cells (DBFCs) are an attractive energy source due to their high electromotive force (1.64 V), large capacity ( $5.67 \text{ Ah} \cdot \text{g}^{-1}$ ), and high rate of energy conversion (91%) [1–4]. DBFCs are suitable for use in alkaline environments, since borohydride is not stable in acidic or even neutral media [5]. Accordingly, an alkaline solution and an anion exchange membrane (AEM) were employed as the electrolytes in the early developmental stages of DBFCs [6–8]. However, AEMs suffered from the borohydride ion crossover problem that reduced cell voltages because of the mixed over-potential resulting from unwanted borohydride oxidation [8–13]. Therefore, it is necessary to develop high hydroxide-conducting polymer electrolytes with strong barriers against borohydride ion movement in DBFCs.

Polyvinyl alcohol (PVA) is an ideal membrane polymer matrix material because of its excellent film-forming properties, good chemical stability, high hydrophilicity and low cost [14–16]. PVA/hydroxyapatite composite membranes have already been used as the electrolyte for DBFCs [17]. Moreover, carbon nanotubes (CNT) added to a PVA membrane achieved a high ionic conductivity of  $0.0805 \text{ S} \cdot \text{cm}^{-1}$ , which is largely attributed to the increased polymer free volume [10].  $\text{Fe}_3\text{O}_4$  nanoparticles grafted on CNT were also added into PVA polymer chains to increase membrane conductivity, since it is well-known that the ionic

conductivity of AEMs can be improved by introducing inorganic materials to the polymer matrix [18,19].

The key function of the membrane is to conduct ions; however, simply increasing the ionic conductivity of the AEMs may also increase borohydride ion crossover. This conductivity-crossover dilemma is avoidable by selectively adjusting the ionic conductivity of AEMs. The objective of this paper is to introduce selective borohydride ion catalytic activity into the membrane without reducing the strong overall conduction.

In our previous work, a series of Co-based catalysts were synthesized and used as the anode in DBFCs [20]. Those Co compounds had good electrocatalytic activity for borohydride oxidation and borohydride hydrolysis [21,22]. In this work,  $\text{CoSO}_4$  was added into the polymer matrix before the casting of membrane. We observed that the DBFCs with the  $\text{CoSO}_4$ -addition membrane exhibited considerably better performances than those without  $\text{CoSO}_4$ -addition. The underlying reason for the improved performance is the suppression of borohydride ion crossover and the increased ionic conductivity induced by the Co species in the membrane.

## 2. Experimental

### 2.1. Preparation of membrane

The CoOOH-functionalized membrane was made from a commercial strong anion exchange resin (AER) (Amberlite IRA-402(OH), hydroxide

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form, Alfa Aesar),  $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$  (Alfa Aesar), and PVA (MW 57000–66000, Alfa Aesar) mixed in a weight ratio of 125:4:250. PVA was dissolved in  $\text{CoSO}_4$  solution and stirred at  $95^\circ\text{C}$  for 2 h to form a gel that was further cooled to  $30^\circ\text{C}$ . The commercial AER powder was then added in order to form the wet composite polymer gel and was then cast on a glass plate. The wet gel dried naturally at room temperature to form a  $\text{CoOOH}$ -functionalized membrane. For comparison, a membrane without  $\text{CoSO}_4$ -addition was similarly prepared. The dried membrane was immersed into a 1 M KOH solution for 24 h before it was used as the electrolyte membrane in DBFCs.

## 2.2. Membrane characterization

Energy dispersive spectrometer (EDS) tests were carried out on a scanning electron microscope (Hitachi S3400) equipped with an EDS (EDAX Phoenix). The X-ray diffractometer (XRD) and X-ray absorption near edge structure (XANES) measurements were performed on a BL15U at the Shanghai Synchrotron Radiation Facility. The ionic conductivity of the membrane was measured by a two-probe AC-impedance method under a fully humidified atmosphere. The membrane resistance was measured from 1 Hz to 10 kHz at a voltage of 5 mV. The ionic conductivity ( $\sigma$ ) was calculated as follows [16]:

$$\sigma = \frac{t}{R_{\text{mem}} \times A}, \quad (1)$$

where  $t$  was the membrane thickness,  $R_{\text{mem}}$  was the membrane resistance and  $A$  was the electrode area.

The borohydride ion permeability was tested in a side-by-side diffusion cell at  $25^\circ\text{C}$ . Both sides were first filled with a solution of 50 mL 0.1 M NaOH, and then extra 0.1 M  $\text{NaBH}_4$  was added to only one side. The extent of borohydride ion transport through the membrane was determined by sampling solution from the receiving compartment in time intervals for concentration measurement using the spectrophotometric method proposed by Werner et al. [23]. The permeability was calculated from the slope of the concentration, which is a function of the elapsed

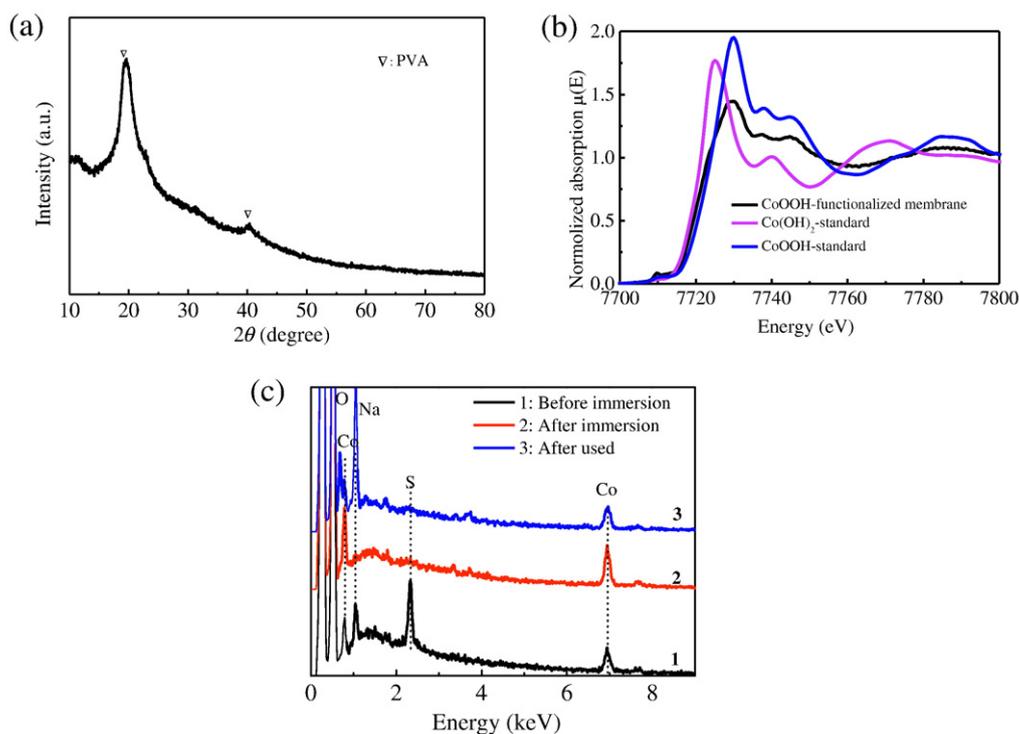
time, the receiving compartment volume, the membrane thickness, the effective membrane area, and the initial borohydride concentration in the source compartment [10].

## 2.3. Fuel cell test

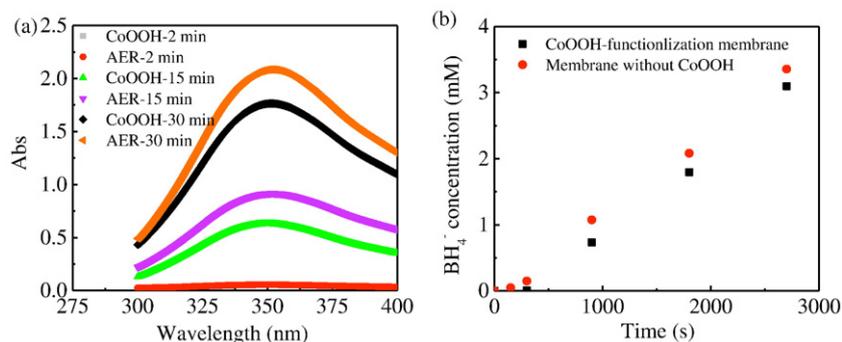
Cell performances were evaluated using a PFX-2011 battery tester (Kikusui Electronics Corp.) with a humidified  $\text{O}_2$  flow rate of  $50 \text{ mL} \cdot \text{min}^{-1}$  under 0.2 MPa at  $30^\circ\text{C}$ . The cell configuration had a working area of  $6 \text{ cm}^2$ , and details regarded the test system can be found in our previous work [20]. Polypyrrole-modified carbon-supported cobalt hydroxide ( $\text{Co}(\text{OH})_2$ -PPy-BP) was used as catalyst at a loading of 5 and  $3 \text{ mg} \cdot \text{cm}^{-2}$  for both the anode and cathode. An alkaline  $\text{NaBH}_4$  solution containing  $\text{NaBH}_4$  (5 wt%) and NaOH (10 wt%) was used as fuel with a flow rate of  $10 \text{ mL} \cdot \text{min}^{-1}$ .

## 3. Results and discussion

The XRD result of the membrane with  $\text{CoSO}_4$ -addition is shown in Fig. 1(a). Two peaks are observed approximately 20 and 40 degrees, which were reported as resulting from the polymer matrix [24]. No peaks are observed related to the Co compounds, and this result indicates that adding  $\text{CoSO}_4$  does not produce a crystalline phase. The XANES spectrum of the membrane with  $\text{CoSO}_4$ -addition, together with the spectra of standard  $\text{Co}(\text{OH})_2$  and  $\text{CoOOH}$  samples, is shown in Fig. 1(b). The absorption energy and position for the membrane with  $\text{CoSO}_4$ -addition are similar to that with standard  $\text{CoOOH}$ , and this result shows that the valence of the Co ion in the membrane with  $\text{CoSO}_4$ -addition is +3. The composition of the membrane with  $\text{CoSO}_4$ -addition was tested by EDS, the results of which are shown in Fig. 1(c). S and Co are identified at 2.34 keV and 6.97 keV, respectively, in the membrane before it was immersed into KOH solution and verify that  $\text{CoSO}_4$  was incorporated into the polymer. However, only Co is detected after the membrane was immersed into KOH solution. The disappearance of S indicates that the  $\text{SO}_4^{2-}$  anion might be replaced by  $\text{OH}^-$  to form  $\text{Co}(\text{OH})_2$  or even  $\text{CoOOH}$ . Due to the strong alkaline characteristics



**Fig. 1.** (a) XRD spectrum (b) XANES spectrum of Co element of the  $\text{CoOOH}$ -functionalized membrane, the XANES spectra of standard  $\text{Co}(\text{OH})_2$  and  $\text{CoOOH}$  samples are also given in (b), (c) EDS spectra of the  $\text{CoOOH}$ -functionalized membrane (1-before KOH immersion, 2-after KOH immersion, 3-after used in DBFC).



**Fig. 2.** (a) The absorption curves of the solution in the receiving compartment separated by the membrane with and without  $\text{CoSO}_4$ -addition at time interval. (b) The borohydride ion concentration dependent on the elapsed time.

of AER and KOH, firstly  $\text{CoSO}_4$  reacts with the  $\text{OH}^-$  to produce the  $\text{Co}(\text{OH})_2$ . Then the formed  $\text{Co}(\text{OH})_2$  is further oxidized into  $\text{CoOOH}$  with the help of  $\text{O}_2$  in air and the alkaline environment, which was commonly observed in previous work [25,26]. The  $\text{Co}(\text{OH})_2 \rightarrow \text{CoOOH}$  oxidation reaction in KOH was reported to occur through a two-step mechanism process [26]. The aforementioned XANES results support the existence of  $\text{CoOOH}$ . Elemental Co is still detected in the membrane after it is used as electrolyte in DBFCs, thereby demonstrating the high stability of the Co species in the membrane.

The ionic conductivity is measured at  $30^\circ\text{C}$  for both the membranes with and without  $\text{CoSO}_4$ -addition. The results show that similar to many previous reports, the ionic conductivity is significantly increased from  $22.4 \pm 1.8$  to  $32 \pm 2.1 \text{ mS}\cdot\text{cm}^{-1}$  with the addition of  $\text{CoSO}_4$  [18,19]. The absorption curves of the solution in the receiving compartment at time intervals are shown in Fig. 2(a). As shown in Fig. 2(a), the curves reach a peak in the vicinity of 350 nm, and the maximum values vary with the time. The maximum absorbance is used to calculate the borohydride ion concentration with the help of calibration curves. The borohydride ion concentration as a function of time is shown in Fig. 2(b). The slopes of the permeated borohydride ion concentration against elapsed time for the membranes with and without  $\text{CoSO}_4$ -addition are  $1.28$  and  $1.31 \mu\text{M}\cdot\text{s}^{-1}$ , respectively. The measured thicknesses of the membranes with and without  $\text{CoSO}_4$ -addition are  $260 \pm 5$  and  $272 \pm 5 \mu\text{m}$ , respectively. The permeabilities of both membranes are calculated to be  $2.77 \pm 0.21 \times 10^{-6}$  and  $2.97 \pm 0.30 \times 10^{-6} \text{ cm}^2\cdot\text{s}^{-1}$ , respectively. High borohydride ion permeability and high ionic conductivity usually coexist in an AEM, since borohydride ions typically behave similarly to hydroxyl. This behaviour is the conductivity-permeability trade-off dilemma in AEMs. However, compared to a membrane without  $\text{CoSO}_4$ -addition, a  $\text{CoOOH}$ -functionalized membrane can simultaneously achieve lower permeability and higher conductivity because the introduced Co species are effective catalysts for borohydride hydrolysis. Some borohydride ions are hydrolysed when permeating the

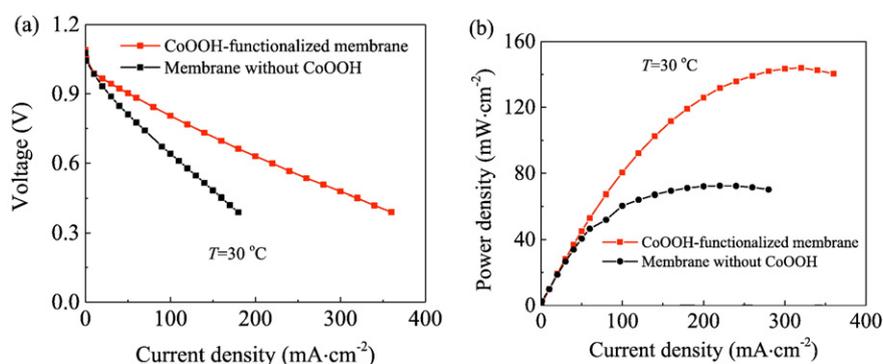
membrane, while hydroxyl ions can transport quickly. Consequently, the amount of the borohydride ions arriving at the receiving compartment decreases for the  $\text{CoOOH}$ -functionalized membrane.

The cell performances of the DBFCs using the membranes with and without  $\text{CoSO}_4$ -addition are measured at  $30^\circ\text{C}$  under the same test conditions for comparison (Fig. 3). The open circuit voltages of the DBFCs using the membranes with and without  $\text{CoSO}_4$ -addition are  $1.09 \text{ V}$  and  $1.06 \text{ V}$ , respectively. As the discharging current density increases, the voltages of the test cells decrease gradually. The voltage rate of decrease in the cell using the membrane without  $\text{CoSO}_4$ -addition is higher than that with  $\text{CoSO}_4$ -addition. The maximum power densities obtained in the test cells using the membranes with and without  $\text{CoSO}_4$ -addition are  $144$  and  $72 \text{ mW}\cdot\text{cm}^{-2}$ , respectively. It was reported that the maximum power density of DBFCs using NaOH-doped PVA and NaOH-doped PVA/CNT membranes were  $96$  and  $91 \text{ mW}\cdot\text{cm}^{-2}$  under similar test conditions [10].

The DBFCs using the  $\text{CoOOH}$ -functionalized membrane clearly perform better than those using the membrane without  $\text{CoOOH}$ . Such improvement is attributed to the introduction of  $\text{CoOOH}$  into the polymer membrane to reduce the crossover of borohydride, because Co ions catalyse borohydride effectively. The ionic conductivity of the membrane is improved by adding inorganic material ( $\text{CoSO}_4$ ) in the PVA matrix, as well. The high ionic conductivity and low permeability of the  $\text{CoOOH}$ -functionalized membrane significantly improve the cell performance.

#### 4. Conclusions

In this study, a  $\text{CoOOH}$ -functionalized membrane was prepared and used as an electrolyte membrane for DBFCs. The DBFCs using the  $\text{CoOOH}$ -functionalized membrane exhibited considerably better performances than those using the membrane without  $\text{CoOOH}$ . The  $\text{CoOOH}$ -functionalized membrane has a hybrid structure and has several



**Fig. 3.** Comparison of cell performances for the DBFCs using the  $\text{CoOOH}$ -functionalized membrane and the membrane without  $\text{CoOOH}$  (a) the relationship of voltage with discharge current density and (b) the relationship of power density with the discharge current density at  $30^\circ\text{C}$ .

functional improvements over the non-functionalized membrane's properties. A novel approach to design a high-performance AEM for DBFCs is demonstrated in this study.

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