



## Introducing catalyst in alkaline membrane for improved performance direct borohydride fuel cells



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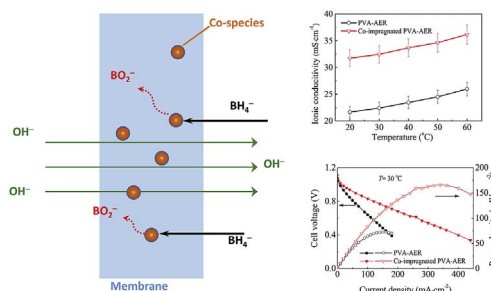
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### HIGHLIGHTS

- Catalyst was introduced in composite alkaline membrane uses as electrolyte for DBFC.
- Addition of catalyst increased ionic conductivity of membrane.
- Addition of catalyst reduced fuel cross-over and electrode polarization.
- DBFC using that membrane achieved OCV 1.11 V and  $P_{\max} = 166 \text{ mW cm}^{-2}$  at 30 °C.
- Idea of adding catalyst in membrane may apply in other electrochemical devices.

### GRAPHICAL ABSTRACT



### ARTICLE INFO

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### ABSTRACT

A catalytic material is introduced into the polymer matrix to prepare a novel polymeric alkaline electrolyte membrane (AEM) which simultaneously increases ionic conductivity, reduces the fuel cross-over. In this work, the hydroxide anion exchange membrane is mainly composed of poly(vinylalcohol) and alkaline exchange resin.  $\text{CoCl}_2$  is added into the poly(vinylalcohol) and alkaline exchange resin gel before casting the membrane to introduce catalytic materials.  $\text{CoCl}_2$  is converted into  $\text{CoOOH}$  after the reaction with  $\text{KOH}$  solution. The crystallinity of the polymer matrix decreases and the ionic conductivity of the composite membrane is notably improved by the introduction of Co-species. A direct borohydride fuel cell using the composite membrane exhibits an open circuit voltage of 1.11 V at 30 °C, which is notably higher than that of cells using other AEMs. The cell using the composite membrane achieves a maximum power density of  $283 \text{ mW cm}^{-2}$  at 60 °C while the cell using the membrane without Co-species only reaches  $117 \text{ mW cm}^{-2}$  at the same conditions. The outstanding performance of the cell using the composite membrane benefits from impregnation of the catalytic Co-species in the membrane, which not only increases the ionic conductivity but also reduces electrode polarization thus improves the fuel cell performance. This work provides a new approach to develop high-performance fuel cells through adding catalysts in the electrolyte membrane.

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## 1. Introduction

The ever-increasing demand on powering portable devices has generated a worldwide effort towards the development of high-energy-density power sources [1]. Polymer electrolyte membrane fuel cells (PEMFCs) have attracted increasing interest as promising power sources for portable and transportation applications because of their high energy densities, low operating temperatures and ease of transportation and storage [2–4]. As a key component, PEMFCs including direct borohydride fuel cells (DBFCs) use an electrolyte membrane (a proton or hydroxide conducting polymer membrane) to separate the anode from the cathode as well as to conduct reactants such as proton ( $H^+$  cations) for acidic fuel cells or hydroxide ion ( $OH^-$  anions) for alkaline fuel cells. Currently used electrolyte membrane was mainly fluoropolymer based materials such as Nafion, developed by DuPont. Although the Teflon-like molecular backbones give those materials excellent long-term stability in both oxidative and reductive environments, the fuel cells using Nafion membrane suffered from using expensive precious cathode catalyst and some technological problems [1,3,5].

On the other hand, alkaline polymer electrolyte membranes (AEMs), in which the charge carriers are  $OH^-$  ions rather than protons, have been considered as an attractive electrolyte membrane regarding the fast fuel cell reaction kinetics and application of non-precious metal catalysts [3,6–8]. However, there are still some challenges with AEMs. The ionic conductivity of AEMs is lower than that of Nafion membrane. The cells using AEMs suffer from fuel cross-over from anode to cathode and insufficient stability as well as carbonation [3]. To overcome these challenges, tremendous effort should be put into improving the ionic conductivity and stability and reducing the fuel cross-over.

It is well known that mixing some inorganic materials into a polymer matrix will change the mechanical, thermal and chemical properties [9]. Using a solution casting method, Li et al. prepared quaternized poly(arylene ether sulfone)/nano  $ZrO_2$  composites with high hydroxide ion conductivities over  $41.4 \text{ mS}\cdot\text{cm}^{-1}$  at  $80^\circ\text{C}$  [10]. Recently, Liu et al. grafted  $Fe_3O_4$  nanoparticles on carbon nanotubes (CNTs) and then added them into Nafion or poly(vinyl alcohol) (PVA) matrix to prepare hybrid membrane. The direct methanol fuel cell using the hybrid membrane exhibited higher proton conductivity, lower methanol permeability, and higher peak power density than the pristine Nafion or PVA membranes [10,11]. Further studies indicate that the addition of inorganic fillers into a polymer matrix facilitates a reduction in the glass transition temperature and the crystallinity of the polymer. Therefore, the amorphous phases of the polymer matrix as well as the ionic conductivity, are increased.

High ionic conductivity is the most important property of an electrolyte. However, simple improvement of ionic conductivity of the AEMs is hard to solve the cross-over problem. It may be interesting to see what will happen if catalytic inorganic materials were added into the polymer matrix.

It has been reported that anion exchange resin (AER) and PVA composite membrane can be used as an electrolyte for alkaline fuel cells [12,13]. However, the conductivity of PVA-AER composite membrane was not reported. In this work,  $CoCl_2$  was introduced into the PVA-based membrane, and the membrane was used as an electrolyte in the DBFC.  $CoCl_2$  was further converted into  $CoOOH$  after the reaction with KOH solution. It is interesting to find that the DBFC using that membrane exhibits much better performance than the DBFC using Nafion N117 membrane. The key reason is attributed to the combination of improved ionic conductivity and reduced cross-over of the electrolyte membrane. A new strategy for the design of high-performance membrane for fuel cell applications is proposed.

## 2. Experimental

### 2.1. Preparation of alkaline membrane

The composite alkaline membrane was prepared from a commercial strong AER (Amberlite IRA-402(OH), hydroxide form, Alfa Aesar) and PVA (MW 57000–66000, Alfa Aesar) at a weight ratio of 1:2. PVA was dissolved in de-ionized water and stirred at  $95^\circ\text{C}$  for 2 h to form a gel. After the gel was cooled down to room temperature, the commercial AER powder was mixed with PVA gel to form the wet composite polymer gel. The wet composite polymer gel was cast on a glass plate, and the thickness of the wet gel on the plate was controlled at about 1 mm. The wet gel dried naturally at room temperature to form a PVA-AER blend membrane.

The  $CoCl_2$ -added composite alkaline membrane (Co-impregnated PVA-AER) was made by adding  $CoCl_2\cdot 6H_2O$  into the PVA gel at a weight ratio of 2:125 before mixing with AER. The nominal percent of the  $CoCl_2$  impregnated into the membrane was 0.4 wt% and 1.0 wt%. The following processes were similar to those of PVA-AER membrane. The thickness of the dried PVA-AER and Co-impregnated PVA-AER membrane was about 200  $\mu\text{m}$ . The schematic diagram for the preparation of the membranes was shown in Fig. S1. All the dried membranes were immersed in 1 M KOH solution up to 24 h. Then the membranes were washed several times with de-ionized water and stored in the de-ionized water before use.

### 2.2. Microstructure characterization

The crystal structure of the synthesized membranes was identified by X-ray diffractometer (XRD, Philips X'PERT-PRO) with  $Cu K\alpha$  radiation. The microstructure of the membranes was investigated by scanning electron microscopy (SEM, Hitachi SU70). The composition was tested by an energy dispersive spectrometer (EDS) equipped in a SEM (Hitachi S3400) operated at 15 kV. The X-ray absorption near edge structure (XANES) measurements were performed on BL14W in Shanghai Synchrotron Radiation Facility (SSRF). The electron beam energy of the storage ring at SSRF was 3.5 GeV, and the maximum stored current was about 210 mA. All measurements for XANES were performed in fluorescent mode, and a dwell time of 2 s was used to collect the fluorescent signals for each energy point. The fluorescent signals induced by the injected X-ray were recorded by the fluorescent detector. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Fisher Scientific, Escalab 250Xi. The thermal stability of the prepared membrane was analyzed using a differential scanning calorimetry and thermogravimetric analyzer (DSC-TGA, SDT Q600, TA Instrument, USA). Measurements were carried out by heating from room temperature to  $700^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}\cdot\text{min}^{-1}$  with about 10 mg sample under  $N_2$  atmosphere with a  $N_2$  flow rate of  $20 \text{ mL}\cdot\text{min}^{-1}$ . The water uptake of the dried membrane was  $\sim 15\%$  based on the TGA results.

### 2.3. Physicochemical characteristics

To get the alkaline uptake (AU) and swelling degree (SD), both the weight and the dimension of dry membranes (denoted as  $m_{\text{dry}}$  and  $L_{\text{dry}}$ ) were measured before immersed in 1 M KOH solution at  $30^\circ\text{C}$  for 48 h. Then the membrane was washed with deionized water several times to remove residual KOH and wiped dry with lens paper. The wet mass  $m_{\text{wet}}$  and the dimension  $L_{\text{wet}}$  of the membranes were measured. The AU and the SD were calculated by:

$$AU(\%) = \frac{m_{\text{wet}} - m_{\text{dry}}}{m_{\text{dry}}} \times 100 \quad (1)$$

$$SD(\%) = \frac{L_{\text{wet}} - L_{\text{dry}}}{L_{\text{dry}}} \times 100 \quad (2)$$

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