



## Short communication

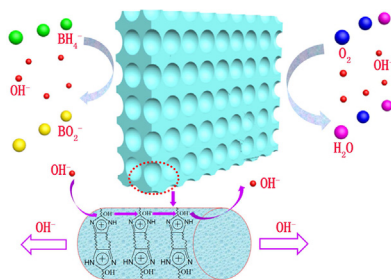
# Porous polybenzimidazole membranes with excellent chemical stability and ion conductivity for direct borohydride fuel cells

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## HIGHLIGHTS

- Porous membranes based on polybenzimidazole (PBI) are firstly introduced in DBFC application.
- The prepared porous membranes were proved to be exceptionally stable in alkaline solutions.
- The porous membranes can effectively separate  $\text{BH}_4^-$ , while transport  $\text{OH}^-$  under DBFC operating condition.
- PBI porous membranes show very good prospective usages in DBFC.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Porous membranes based on polybenzimidazole (PBI) are firstly introduced in direct borohydride fuel cell application (DBFC). Membranes with different thicknesses and porosity are successfully fabricated via water vapor phase inversion process. The prepared membranes show excellent ion conductivity and chemical stability under DBFC operating condition. Compare with Nafion 115, the prepared membranes show higher ion conductivity, as a result, much higher peak power density. No weight loss is observed after immersing the prepared membranes in a 3 M NaOH solution for 30 days, indicating the excellent chemical stability of porous PBI membranes. And the DBFC cells assembled with prepared membranes could discharge at  $200 \text{ mA cm}^{-2}$  for more than 250 h without voltage decay, which is the longest time reported by far. This work provides a totally new idea for fabricating versatile DBFC membranes.

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## 1. Introduction

Direct borohydride fuel cell (DBFC), which was fueled with alkaline borohydride solutions was firstly demonstrated by Amendola et al., in 1999 [1]. It has been regarded as an attractive energy source for portable and mobile applications due to its features like high volumetric energy density, high theoretical open circuit voltage, ambient operating temperature and so forth [2]. At

the same time, the DBFC can successfully avoid CO catalyst poisoning on the anode. In addition, the thermal management and internal processing of system are greatly simplified by using liquid as reactants at ambient temperature.

As a key component of a DBFC, a membrane serves as a physical separator to prevent the cross mix of liquid fuel or  $\text{BH}_4^-$ , while still transport  $\text{OH}^-$  or other ions to complete the circuit [3]. A DBFC is normally in the alkaline medium due to the fact that borohydride is not stable in neutral and acidic medium. Thus a membrane in a DBFC should carry the characteristics of high selectivity on  $\text{BH}_4^-$ , high conductivity and high chemical stability under alkaline condition. The currently used perfluorosulfonic acid membranes

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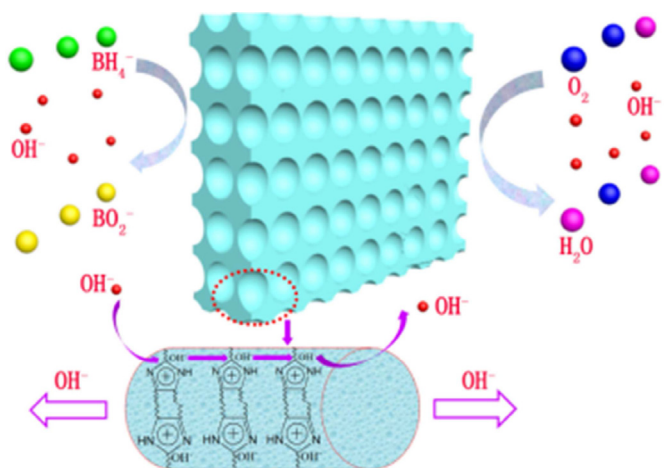
(Nafion) suffer from extremely high cost and borohydride decomposition induced by  $\text{Na}^+$  migration. Anion exchange membranes can effectively suppress the  $\text{Na}^+$  migration, however, their low chemical stability under alkaline medium limited their further application [4].

Recently polymers carrying heterocyclic rings have been reported for alkaline fuel cells applications. The basicity in a conjugated structure enables the use of this kind of polymers like polyoxadiazoles (POD), polybenzoxazole, polybenzimidazole (PBI), polypyridine in fuel cells, since they are able to transport protons or  $\text{OH}^-$  after doping with acid or base [5,6]. In a DBFC, POD membranes have been investigated and showed very good stability [7]. Unlike the typical anion exchange membranes, the conductivity of these heterocyclic polymer membranes is mainly determined by doped alkaline solutions [8,9]. In this case, the conductivity is normally limited by their swelling in electrolytes. Porous membranes have received wide attention for battery application recently due to their attractive features like high chemical stability, high conductivity and low cost [10,11]. The main function of porous membranes is to separate fuels from protons or other ions, for DBFC, a porous membrane can be employed to separate  $\text{BH}_4^-$ , while still transport  $\text{OH}^-$ . A Porous membrane could provide more free volumes to adsorb alkaline solutions to ensure its  $\text{OH}^-$  conductivity, therefore, overcome the limitation of heterocyclic membranes. To ensure the ion selectivity of porous membranes, the pores should be disconnected and the pore walls could provide multi-barriers for  $\text{BH}_4^-$ . To realize this idea, PBI was selected as matrix, membranes with highly symmetric sponge-like pores were firstly fabricated and investigated for DBFC application. In this design, all pores (sponge cells) are disconnected to ensure their high selectivity on  $\text{BH}_4^-$ , while, each free volume (pore) is filled with alkaline solution when soaked them in the DBFC electrolyte to provide membrane with high conductivity (Scheme 1). The physical and electrochemical properties of the prepared membranes were investigated in detail.

## 2. Experimental

### 2.1. Polymer synthesis

PBI polymers were prepared via aromatic nucleophilic substitution condensation of DCDPE and DABZ, as reported elsewhere (Scheme 2) [12]. The mixture of phosphorus pentoxide and MSA was used as solvent, the temperature was kept at 140 °C.



**Scheme 1.** Principle of designed membranes for DBFC application.

### 2.2. Membrane preparation

PBI membranes with highly symmetric sponge structures were prepared via water vapor induced phase inversion method [13]. The as-prepared polymer was dissolved in DMAC to form a 15 wt% solution. After degassing, the solutions were cast on a glass plate and quickly transferred to a box with constant temperature (50 °C) and relative humidity (100%) under normal atmospheric pressure. After 10 min, the membranes were peeled off and immersed in water.

### 2.3. Measurement

FT-IR was recorded on a BRUKE TENSOR 27.  $^1\text{H}$  NMR was determined by BRUKER DRX400 with dimethyl sulfoxide as solvent and tetramethylsilane as internal standard.

The area resistance of membranes was detected following the method in literature [7]. A conductivity cell was separated into two compartments by a membrane, each part was filled with a 3 M NaOH solution. The effective area of the cell ( $S$ ) was 1  $\text{cm}^2$ . Electric resistances were measured by electrochemical impedance spectroscopy over a frequency range from 100 kHz to 100 Hz at room temperature. The resistance of the cell with ( $r_1$ ) and without a membrane ( $r_2$ ) was detected. The area resistance  $r$  was calculated by the following equation (1):

$$r = (r_1 - r_2)S \quad (1)$$

Where  $S$  represents the area of the tested membranes.

The permeability measurement was conducted on a diffusion cell at ambient temperature as reported elsewhere [14]. The diffusion cell was separated by a membrane, where the left cell was filled with 1 M  $\text{NaBH}_4$  and the right cell was filled with deionized water. At certain time intervals, the concentration of  $\text{BH}_4^-$  in the left cell was determined via the voltammetric method [7]. A three-electrode cell, which consists of a gold working electrode, a graphite counter electrode and a mercury/mercury oxide reference electrode, was used for the test. The permeability ( $P$ ) of  $\text{BH}_4^-$  was calculated via the method described elsewhere [15].

The permeability of  $\text{OH}^-$  through a membrane was determined with a diffusion cell as described above. The right cell was filled with 70 ml 3 M NaOH aqueous solution and the left one was filled with 70 ml deionized water and the concentration of  $\text{OH}^-$  was characterized by Mettler Toledo pH meter. The permeability was calculated by Fick law [10].

The membrane porosity was detected via the following procedure. The prepared membranes with size of 3 × 3 cm were immersed in deionized water to be fully saturated. The saturated membranes were weighed after quickly wiping up the surface water with tissue paper. Then the samples were dried in vacuum oven at 85 °C for 48 h and weighed. The membrane porosity is calculated by Eq. (2):

$$\varepsilon = \frac{(m_{\text{wet}} - m_{\text{dry}})/\rho}{s \times d} \times 100\% \quad (2)$$

where  $\varepsilon$  is the porosity of the membrane,  $m_{\text{wet}}$  and  $m_{\text{dry}}$  are the mass of wet membrane and dry membrane respectively,  $\rho$  is water density,  $s$  is membrane area,  $d$  is membrane thickness.

The alkaline stability of prepared membranes was investigated by immersing a 9  $\text{cm}^2$  membrane in a 3 M NaOH solution at 40 °C, where the weight of membranes was detected at different time intervals.

The DBFC single cell assembly and cell performance evaluation were followed the literature' report [7]. Pt/C was used as electro

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