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Short communication

A high performance polyamide-based proton exchange membrane fabricated via construction of hierarchical proton conductive channels

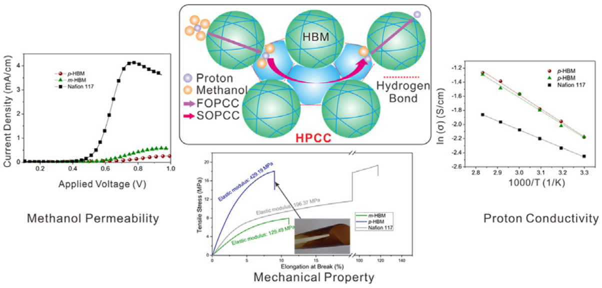
Liying Ma, Weiwei Cai*, Jing Li, Kun Fan, Yao Jiang, Liang Ma, Hansong Cheng**

Sustainable Energy Laboratory, Faculty of Materials Science and Chemistry, China University of Geosciences Wuhan, 388 Lumo RD, Wuhan, 430074, PR China

HIGHLIGHTS

- Propose a novel concept of hierarchical proton conductive channel (HPCC) for PEM.
- Tune HPCC by simply changing the position of two amine groups in the monomers.
- Methanol permeation of the membrane was reduced by ca. 60%.
- Tensile strength was increased by 120%.

GRAPHICAL ABSTRACT



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ABSTRACT

A concept of hierarchical proton conductive channel (HPCC) capable of simultaneously boosting proton conductivity and fuel-permeation resistivity is proposed and the HPCC is optimized to improve the performance of the hyperbranched polyamide proton exchange membrane. The HPCC built *in-situ* in the membrane can be tuned by simply changing two amine groups from the *meta*-position to the *para*-position in the monomers. We demonstrate that the small structural difference between the two monomers may result in remarkable differences in mechanical and electrochemical properties upon polymerization, which enable significantly improved performance of direct methanol fuel cells.

1. Introduction

Development of efficient proton exchange membrane (PEM) fuel cell technologies is paramount for the combat of the rapid consumption of fossil fuels and increasingly pressing greenhouse effect [1]. Unfortunately, the development has been severely hindered by the high expenses of key materials, including precious metal catalysts [2] and PEMs [3,4]. In the past few years, many effective non-noble catalysts have been developed [5–11]. These materials display comparable catalytic performance to the widely used Pt catalysts for the electro-oxidation reaction in anion exchange membrane fuel cells. However, the lack of cost-effective PEM materials has become one of the primary obstacles for commercialization of PEM fuel cells [12,13]. To date, the fully fluorinated Nafion membranes are the dominant PEMs used in

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* Corresponding author.
** Corresponding author.
E-mail addresses: willcai1985@gmail.com (W. Cai), chghs2@gmail.com (H. Cheng).

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most PEM fuel cell devices. However, aside from the high material cost, the relatively low proton conductivity and severe fuel permeation associated with the Nafion membranes prevent the fuel cell devices from being extensively utilized in market place [14]. The performance is particularly problematic when the Nafion membrane is used in a fuel cell fueled with liquid methanol, i.e. direct methanol fuel cell (DMFC), which is recognized to be one of the most promising power supply technologies for portable electronic applications [15,16]. Appropriate construction of proton conductive channels (PCCs) in a PEM is deemed to be the key factor that simultaneously affects proton conduction efficiency, fuel permeation resistivity, and mechanical properties [17]. Numerous studies have been conducted to mimic the structure of Nafion with functionalized side chains hanging on the hydrophobic backbones in order to achieve proper phase-separation [18] in the polymer proton conductors and plenty of low cost non-fluorine polymer ionic conductors [19–23] were designed and synthesized. Unfortunately, it is difficult to significantly raise the ion exchange capacity (IEC) and proton conductivity with this methodology because the sulfonic acid groups are placed only on the chain ends [17]. Based on this consideration, block and graft copolymers were synthesized to construct long-range connected PCCs with a high degree of phase-separation [24]. Fabrication of artificial PCCs with controlled arrays in PEMs is another effective way to improve proton conductive properties [14,17]. However, the cost of the block polymer and artificial PEMs is usually substantial compared to that of the pristine random copolymer PEMs since more sophisticated synthetic steps are required [13,25].

In a recent study [26], we demonstrated that a hyperbranched polyamide PEM is capable of effectively minimizing the fuel permeation and improving the proton conduction. The PEM was shown to outperform a Nafion 117 membrane by at least 15 times for resisting methanol permeation with 100% higher proton conductivity. A DMFC device fabricated with the PEM displays excellent performance with a nearly neat methanol solution. In this paper, we propose a novel concept of hierarchical PCCs (HPCCs). In these HPCCs, the high sulfonic acid contents make the proton conduction *via* the PCCs within the macromolecules, referred to as the first-order PCC (FOPCC), much more efficient than the process in conventional linear polymer conductors due to the well-connected proton channels arising from the high IEC value (>2 mmol/g) and the uniform 3D matrix topology (Scheme 1a). In addition, the connections among the macromolecules, referred to as the secondary-order PCC (SOPCC), through the abundant hydrogen bonds formed by the end –COOH groups and the active water molecules hydrogen-bonded with the surface –COOH species are capable of effectively promoting proton conduction, as illustrated in Scheme 1a. The excellent cooperativity between FOPCC and SOPCC not only makes the proton conduction more efficient but also effectively raises the fuel permeation resistance and enforces the mechanical strength of the membranes. The concept of HPCCs can be used for optimization of PEM membrane performance.

Here, we show that the HPCCs in the hyperbranched polyamide PEMs can be tuned by judiciously selecting the positions of two $-NH_2$ groups in the diaminobenzenesulfonic acid (DSA) monomers for synthesis of the hyperbranched macromolecules (HBMs) as schematically illustrated in Scheme 1b–c. It was demonstrated that simply changing the two $-NH_2$ groups from the *meta*-position to the *para*-position in the monomers can result in remarkable differences in mechanical and electrochemical properties of macromolecules. Upon appropriate HPCC optimization, methanol permeation through the *p*-HBM PEM synthesized from *p*-DSA (*para* substituted DSA, 2,5-diaminobenzenesulfonic acid) was reduced by ca. 60% compared to the value through the *m*-HBM PEM synthesized from *m*-DSA (*meta* substituted DSA, 2,4-diaminobenzenesulfonic acid). The tensile strength of *p*-HBM was increased by 120% from the value of *m*-HBM. The performance of the DMFC with the *p*-HBM membrane at the high methanol concentration of 20 M was improved by 12% compared to the case with the *m*-HBM membrane as a result of the HPCC optimization.

2. Experimental

2.1. Materials

Monomers, trimesic acid (TA), *p*-DSA and *m*-DSA, and catalyst (triphenylphosphite, TPP) for polymerization were purchased from Sigma Aldrich and used as received. Lithium chloride (LiCl) purchased from Sigma Aldrich was dried at 100 °C in vacuum oven for 24 h before use. N-methyl-2-pyrrolidone (NMP) was distilled from P_2O_5, and pyridine (Py) was distilled from KOH before use. Nafion 117 membrane with a dry thickness of 0.177 mm was purchased from Dupont Co. (USA).

2.2. Polymerization

Following the synthetic routes shown in Scheme 1b–c, TA (2m mmol), DSA (*p*-DSA, *m*-DSA or *o*-DSA, 2n mmol, m:m = 1.05:1), LiCl (0.32 g), TPP (1 mL), NMP (4 mL) and Py (3 mL) were added into a 100 mL two-necked round-bottom flask, and the reaction was maintained at 100 °C for 2 h with stirring under an argon atmosphere. Upon completion, the products were washed with methanol and ultrapure water several times and dried at 80 °C under a reduced pressure for 24 h.

Membrane preparation and characterizations of the synthesized materials/PEMs are described in details in Supporting Information.

3. Results and discussion

The HPCC was designed to simultaneously achieve high proton conductivity, low fuel permeability and strong mechanical stability for the HBM membranes. To this end, optimization of the HPCCs *via* careful design of monomer structures is of essential importance. To demonstrate the concept, *p*-DSA, *m*-DSA and *o*-DSA (*ortho* substituted DSA, 3,4-diaminobenzenesulfonic acid) were selected as the monomers for the synthesis of HBMs with the HPCCs constructed *in-situ*. We note that the activity of *o*-DSA in the polymerization was found to be too low to obtain a hyperbranched macromolecule due to the strong steric hindrance between the two neighboring $-NH_2$ groups in *o*-DSA. Successful polymerization of the *m*-HBM and *p*-HBM polymers with COOH end-capped groups synthesized from the specific ratio of precursor monomers with excessive TA was verified by the ^1H NMR and FT-IR data (Fig. S1).

The formation of the connected network among the HBM molecules is a consequence of extensive hydrogen bonds formed between the –COOH groups of the HBM molecules during the membrane preparation. The interaction between the functional groups gives rise to one of the strongest hydrogen bonds [27–29].

Owing to the different positions of the two active $-NH_2$ groups in the DSA monomers, the polymerization processes undergo different growth pathways to yield two HBM macromolecules (Fig. 1a). The *p*-HBM macromolecules tend to grow uniformly in all directions since the two $-NH_2$ groups, which react with the –COOH groups in the TA monomers, are well-separated in *p*-DSA and topologically advantageous to enable linkages with their reactive counterparts. In contrast, the two asymmetric $-NH_2$ groups in m-DSA lead to much less uniform growth of the m-HBM macromolecules. Therefore, the *p*-HBM polymers can form more spherical-like macromolecular structure, which facilitates more tight