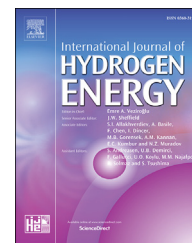




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# Stable and effective proton exchange membrane formation via cross-linking the polymeric proton donor and proton acceptor in a layer-by-layer structure

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## ARTICLE INFO

### Article history:

Received 6 November 2017

Received in revised form

9 January 2018

Accepted 15 February 2018

Available online 7 March 2018

### Keywords:

Layer by layer

Cross-link

Polymer electrolyte membrane fuel cell

Proton donor

Proton acceptor

## ABSTRACT

Systematic arrangement of the proton donor and acceptor as a layer-by-layer (LbL) structure is one of the simplest surface modification methods to improve the proton conductivity of a proton exchange membrane. In general, LbL assembly occurs via physical or chemical interaction between each deposited layer. Here, the stabilization of the proton donor and acceptor polymers by cross-linking those two layers together was applied as a concept. The challenge was the molecular design of the proton donor and acceptor polymer species to each have compatible cross-linkable functional groups as well as proton transfer species in the molecules. Poly(acrylic acid) decorated with different amounts of thiol groups (PAA-M) was synthesized, while benzimidazole decorated branching polyethyleneimine was functionalized with maleimide groups (BIm-PEI-MI). The cross-linkable proton donor and acceptor were alternately LbL deposited on a sulfonated poly(ether ether ketone) (SPEEK) surface. The LbL membrane with an optimum crosslink level showed a proton conductivity of up to 2 orders of magnitude higher than that of the pure SPEEK membrane even at a temperature as high as 170 °C.

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## Introduction

Proton exchange membrane fuel cells (PEMFCs) are well known as a promising alternative green energy generator due to their high energy efficiency [1], zero emission, silent operation, high power density and flexible operating range [2]. However, once the fuel cell system operates the generated heat accumulates causing partial dehumidification, which then leads to a reduced proton conductivity and lower fuel cell

performance. Conventional PEMFCs with a Nafion<sup>®</sup> membrane are limited to use at a low operation temperature (<80 °C). However, high-temperature operation of a fuel cell system would benefit from the kinetically enhanced proton conductivity and catalyst tolerance to carbon monoxide of up to 3–5% by volume, leading to more flexibility in the purity of the hydrogen gas (H<sub>2</sub>) fed that can be used, so, for example, the H<sub>2</sub> from the petroleum cracking process can be used with less purification steps [1]. As the result, there have been many attempts to develop a PEM with a high temperature durability.

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<https://doi.org/10.1016/j.ijhydene.2018.02.092>

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For example, a Krytox-silica-Nafion<sup>®</sup> composite membrane was found to increase the water retention and maintained the proton conductivity at 80–130 °C without humidification [3].

Heat tolerant proton conductive N-heterocyclic molecules, where proton transfer can be processed through their intermolecular hydrogen bond (H-bond) network [4], have been used as additives for anhydrous PEM [5]. For example, synthesis of a Nafion-benzimidazole (BI) blend as a PEM gave a high thermal stability and high proton conductivity of  $8.64 \times 10^{-3}$  S/cm at 200 °C [6]. A high molecular weight polybenzimidazole (PBI) grafted with BI pendant groups showed a high proton conductivity of 0.15 S/cm at 180 °C with a phosphoric acid doping level of 13.1 [7].

The way that N-heterocycles can act as a proton acceptor provides the improvement in acid loading and proton transfer in terms of proton donor-acceptor cooperation [7]. The synthesis of a BI tethered poly(acrylic acid) (PAA) polymer to form a proton donor (carboxylic acid unit) and acceptor (BI unit) copolymer [8] improved the proton conductivity by around 2 orders of magnitude compared to that for PAA.

Layer-by-layer (LbL) assembly is one of the most practical modification methods to assemble layers of any molecules on any surfaces as long as they have electrostatic interaction at the interfaces. The LbL film preparation can be performed under many driving forces, such as van der Waals forces, hydrophobic interactions, coordination-bonds, H-bonds, covalent bonds, biospecific interactions and host-guest interaction [9].

In order to overcome the limitations in PEMs, there are a number of studies related to LbL assembly. For example, Nafion<sup>®</sup> membranes with LbL of polyelectrolytes, including poly(diallyldimethylammonium chloride) and poly(allylamine hydrochloride) as the polycations and PAA, poly(2-acrylamido-2-methyl-1-propanesulfonic acid), poly(1-(4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido)-1,2-ethanediyl sodium salt) and poly(sodium styrene sulfonate) as the polyanions have been developed. The LbL Nafion<sup>®</sup> membranes have a lower methanol permeability [10]. Nafion<sup>®</sup> composite membranes with LbL of chitosan and silicotungstic acid had a 47% lower methanol permeability and a higher membrane selectivity, but a 22% lower proton conductivity than the pure Nafion<sup>®</sup> membrane [11]. Recently, we succeeded in preparing a LbL membrane by simple surface deposition with PAA as the proton donor and BI decorated branched polyethylenimine (BIm-PEI) as the proton acceptor [12].

Cross-linking reactions in LbL deposition are mainly for stabilizing the deposited nanolayer films [13,14]. In case of LbL deposition, a fast cross-linking process with the lowest number of purification steps is preferable. Maleimide thiolene click chemistry, a general alkyne-azide cycloaddition, is known as one of the most reactive reactions since it proceeds via nucleophilic addition without requiring a catalyst and so has the advantage of not only a fast reaction rate but also no catalyst removal step [15,16].

The packing structure and molecular mobility of proton conductive species affect the proton transfer efficiency [17–19]. Herein, we propose our concept of a novel cross-linked-LbL membrane of mercapto group decorated PAA (PAA-M) as the proton donor and maleimide group functionalized BIm-PEI (BIm-PEI-MI) as the proton acceptor on a

sulfonated poly(ether ether ketone) (SPEEK) surface. The rationale was that by introducing cross-linking into the interlayer structure, the tightened layers of those proton transfer species might help create a more efficient proton transfer pathway and improve the overall proton transfer efficiency of the PEM.

## Experiment

### Materials

The PEEK powder was a gift from JJ-Degussa Chemicals (Thailand) Ltd. 2-(Chloromethyl)benzimidazole (MBz), branched polyethylenimine (bPEI;  $M_w$  25,000 g mol<sup>-1</sup>), PAA ( $M_w$  450,000), deuterated dimethyl sulfoxide (DMSO-d<sub>6</sub>), 2-mercaptoethanol and 3-maleimidopropionic acid (MI) were purchased from Aldrich Co., Germany. Potassium hydroxide and DMSO were bought from Acros Co. Germany. All chemicals were used as-received except for bPEI, which was dried under vacuum at 80 °C for 15 h before use.

### Synthesis and preparation of the SPEEK membrane

Dry PEEK (2 g) was dissolved in 200 mL concentrated (98% w/v) sulfuric acid and left with stirring at room temperature for 8 h, before being precipitated in ice-cooled deionized water (DW). The white precipitate was harvested, washed thoroughly with DW for neutralization and then dried at 80 °C for 24 h and kept in a dry place. The SPEEK membrane was formed by solvent casting, where SPEEK was dissolved in DMSO to 5% (w/v) and then cast in a 3 × 3 × 0.5 cm glass mold at 80 °C for 24 h.

### Synthesis and preparation of the BIm-PEI-MI

The modification of bPEI with BIm was performed as reported previously [19]. In brief, KOH (0.36 g, 6.4 mmol) was added to 10 mL of 20% (w/v) bPEI (46.5 mmol) in DMSO and held at 90 °C for 30 min. Thereafter, 20 mL of 5.35% (w/v) MBz (6.4 mmol, or 0.2 equivalent of the primary and secondary amine contents in bPEI) in DMSO was added drop-wise to the bPEI solution and the reaction was allowed to proceed overnight under a nitrogen (N<sub>2</sub>) atmosphere. The solution obtained was neutralized by 1 M HCl and dialyzed against DW several times before freeze-drying to obtain the BIm-PEI. Next, 2 g of the BIm-PEI product was dissolved in 50 mL DMSO and adjusted to pH 4 by 1 M HCl. The BIm-PEI solution was stirred under a N<sub>2</sub> atmosphere at room temperature for 4 h before adding MI (6.7 mg, 0.04 mmol or 0.02 equivalent of BIm group in BIm-PEI), and coupled by the addition of 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (15.0 mg, 0.08 mmol) followed by N-hydroxysulfosuccinimide (9.0 mg, 0.08 mmol) in 10 mL DW for 15 h at 4–25 °C beforehand. The reaction was performed overnight under a N<sub>2</sub> atmosphere and room temperature before dialyzing against DW several times and freeze-drying to obtain the BIm-PEI-MI-2. The same method was performed to synthesize BIm-PEI-MI-x, where x is the amount of substituted MI groups compared to 100 BIm units, and was 2, 5, 10, and 20 mmol (or 0.02, 0.05, 0.10 and 0.20 equivalents of BIm group in BIm-PEI), respectively.

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