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Methanol crossover reduction by Nafion modification via layer-by-layer self-assembly techniques

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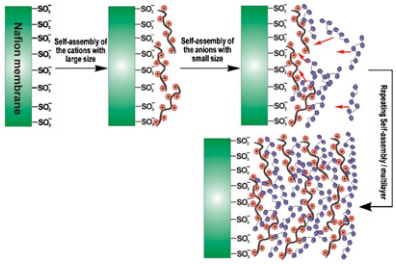
HIGHLIGHTS

- Effect of LbL self-assembly of PEs on permeability and conductivity of Nafion.
- Linear and exponential growth mechanism of self-assembled PE bilayers are observed.
- Exponential growth mechanism is more effective in methanol crossover reduction.

GRAPHICAL ABSTRACT

The exponential growth mechanism of LbL self-assembly of PE bilayers promotes the interdiffusion of PEs, and benefit the methanol crossover reduction of Nafion membrane.



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ABSTRACT

Layer-by-layer (LbL) self-assembly of polyelectrolyte bilayers on the methanol permeability and proton conductivity of Nafion membranes is investigated using polycations PDDA (poly(diallyldimethylammonium chloride)) and PAH (poly(allylamine hydrochloride)) and polyanions PAMP (poly(2-acrylamido-2-methyl-1-propanesulfonic acid)), PAZO (poly(1-(4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido)-1,2-ethanediyl, sodium salt)), PSS (poly(sodium styrene sulfonate)) and PAA (poly(acrylic acid)). The formation of polyelectrolyte multilayers on Nafion membranes is confirmed by AFM and UV–visible spectroscopy. The lowest methanol permeability is observed on the self-assembled PDDA-PAA and PAH-PAA bilayers with the exponential growth process. The observed exponential growth process of polyelectrolyte multilayers with PAA polyanion is most likely related to small monomeric block of PAA, resulting in low steric hindrance and high flexibility and mobility of the ionomers and thus promoting the interdiffusion of PAA during the self-assembly. PDDA polycation shows a much better ability to block methanol crossover in comparison with that of PAH polycation. This study shows the importance of LbL self-assembled multilayer structure on the proton conductivity and methanol crossover properties of modified Nafion membranes for application in direct methanol fuel cells (DMFCs).

1. Introduction

Proton exchange membrane and direct methanol fuel cells (PEMFCs and DMFCs) have been extensively studied as clean and efficient power sources for applications in electric vehicles, residential power sources, and portable electronic devices [1–4]. The state-of-the-art of proton exchange membranes in PEMFCs and DMFCs are perfluorosulfonic acid (PFSA) based membrane, such as Nafion, because of its excellent chemical, mechanical and thermal stability, as well as its relatively high proton conductivity when fully hydrated [5,6]. However, in the case of DMFCs, methanol fuel readily migrates from the anode, through the Nafion membrane,

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to the cathode, reducing the open-circuit potential by as much as 0.15–0.2 V and poisoning the electrocatalysts at the cathode [7]. Methanol crossover seriously retards the commercial viability of DMFCs. Thus, there have been extensive research activities to reduce the methanol permeability of Nafion membranes.

Significant efforts have been made to modify Nafion membranes. One of the approaches is to incorporate hygroscopic metal oxide particles such as SiO_2, ZrO_2, TiO_2 and zirconium phosphate into the hydrophilic domains of the polymer electrolyte membrane or Pd and catalyst layer to enhance the thermal stability, water retention properties and resistance to methanol permeability of the PFSA membranes such as Nafion [8–14]. In the case of silica filler, Nafion/silica composite membranes are usually prepared by re-casting of mixtures of silica and Nafion ionomer, or by tetraethoxysilane (TEOS) hydrolysis sol–gel reaction followed by solution casting or impregnation of membranes with TEOS solution. The Nafion/SiO_2 composite membranes reduce the methanol crossover and improve the water retention properties, but suffer reduced durability. Furthermore, to achieve significant reduction in methanol permeability, the oxide content has to be high (e.g., 20 wt% silica in the case of the Nafion–silica composite [15]. This, in turn, reduces the proton conductivity and the mechanical properties are also seriously affected due to the significant alternation of the membrane microstructure. Addition of heteropoly acids such as phosphotungstic acid ($H_3PW_{12}O_{40}$, PWA) to form Nafion/silica/PWA composite membranes was also reported to be effective to reduce methanol crossover of Nafion membrane and improve the performance of DMFCs [16].

The sequential adsorption of oppositely charged polyelectrolytes (PEs) by layer-by-layer (LbL) self-assembly is an efficient method for obtaining multilayer thin films with unique properties and with high control over layer thickness in nanoscale [17–22]. In this method, two oppositely charged PEs dissolved in aqueous solution are alternatively deposited on a support surface by means of electrostatic interactions. After each dipping cycle, the surface charge is reversed, which enables deposition of a subsequent layer. The process leads to the formation of a final multilayer structure that is stabilized primarily by strong electrostatic forces. We showed previously that Nafion membrane modified using LbL self-assembly of PEs is an effective methanol-blocking multilayer thin film [23]. A DMFC using a Nafion membrane self-assembled with four poly(diallyldimethylammonium chloride) (PDDA, polycation) and poly(sodium styrene sulfonate) (PSS, polyanion) bilayers, displayed a 42% increase in the power density. Xiang et al. employed purple membrane (PM) as a methanol-blocking agent on Nafion (R) membranes using layer-by-layer (LbL) self-assembled PDDA/PM multilayer films [24]. With five PDDA/PM bilayers, either double-sided or single-sided modification, methanol permeability was reduced by 73.4–64.7% in comparison with unmodified Nafion 212. The results demonstrated the promising potential of PM as effective methanol blocking species in direct methanol fuel cells. In addition to polyelectrolytes, heteropolyacids such as PWA and metallic nanopartilces such as Pd and Pt can also be self-assembled to Nafion membranes with reduced methanol permeability and enhanced performance of the surface modified Nafion membranes [25–28].

The proton conductivity of the LbL self-assembled multilayers is shown to be related to the molecular structure of the layer. Yilmaztürk et al. showed that the proton conductivity of self-assembled poly(allylamine hydrochloride)/poly(vinyl sulfate) (PAH/PVS) with 5 bilayers, $(PAH/PVS)_5$ was nearly twice higher than that obtained on (PAH/poly(sodium styrene sulfonate) $(PSS)_5$ due to the higher charge density of PAH/PVS as compared to that of PAH/PSS [29]. However, although LbL self-assembly of PE multilayer on Nafion membranes has been shown to be effective to enhance the performance of DMFCs, little is known about the effect of the PE multilayer

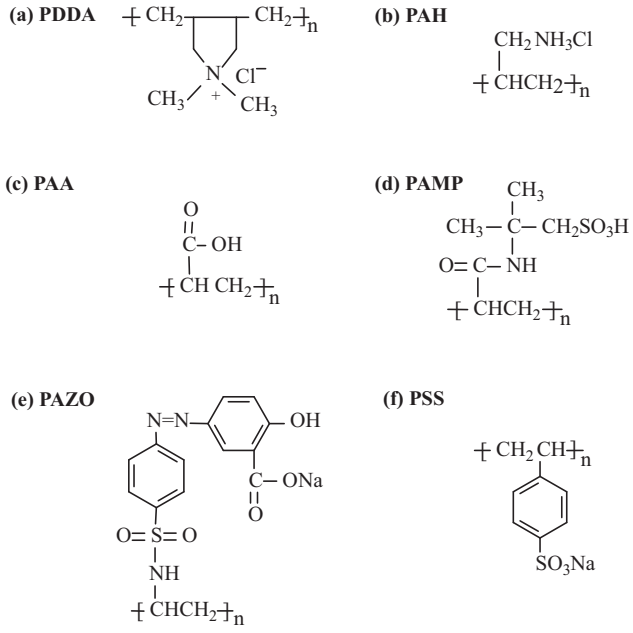

Fig. 1. Molecular structure of polyelectrolytes (PEs) used.

structure on the permeability properties of Nafion membranes. In this work, we used the commercially available polycations PDDA and PAH and polyanions PAMP (poly(2-acrylamido-2-methyl-1-propanesulfonic acid)), PAZO (poly(1-(4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido)-1,2-ethanediyl, sodium salt)), PSS and PAA (poly(Acrylic acid)) (Fig. 1). PAZO is a comblike polymer with very large monomeric block while PAA consists of a linear ethylene main chain and much smaller side group. We show that the growth mechanism of the LbL multilayer PE structures on the Nafion membranes is related to the structure of the polyanions and this in turns strongly affects the methanol permeability and proton conductivity of self-assembled Nafion membranes. The results show a close correlation between the nature of the bilayer PE thin films and the methanol permeability of Nafion membranes.

2. Experimental

2.1. Materials

Poly(diallyldimethylammonium chloride) (PDDA, 35 wt% in water, average $M_w < 100{,}000$), poly(allylamine hydrochloride) (PAH, average $M_w \sim 70{,}000$), poly(Acrylic acid) (PAA, average $M_w \sim 450{,}000$), poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMP, 15 wt% in H_2O, average $M_w \sim 2{,}000{,}000$), poly(sodium styrene sulfonate) (PSS, 30 wt% in H_2O, average $M_w \sim 70{,}000$), and poly(1-(4-(3-carboxy-4-hydroxyphenylazo) benzene sulfonamido)-1,2-ethanediyl, sodium salt) (PAZO, average $M_w \approx 65{,}000$–$100{,}000$) were obtained from Aldrich–Sigma and used without further treatment. Nafion membrane (112, 50 μm) were obtained from DuPont, which was treated according to the standard procedure of 30 min in a 5 wt% H_2O_2 solution at 80 °C, 30 min in Milli-Q water at 80 °C, and 30 min in an 8 wt% H_2SO_4 solution at 80 °C. After each treatment, the membrane was rinsed in Milli-Q water three times to remove traces of H_2O_2 and H_2SO_4. The membrane was stored in Milli-Q water before use. Sulfuric acid (95–97%), hydrogen peroxide (30%), and methanol were obtained from Fluka. Milli-Q water (Millipore, 18.2 MΩ cm at 25 °C) was used in the experiments.