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Self-assembly of highly charged polyelectrolyte complexes with superior proton conductivity and methanol barrier properties for fuel cells

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ABSTRACT

The paper is concerned with the formation of Layer-by-Layer (LbL) self-assembly of highly charged polyvinyl sulfate potassium salt (PVS) and polyallylamine hydrochloride (PAH) on Nafion membrane to obtain the multilayered composite membranes with both high proton conductivity and methanol blocking properties. Also, the influences of the salt addition to the polyelectrolyte solutions on membrane selectivity (proton conductivity/methanol permeability) are discussed in terms of controlled layer thickness and charge density.

The deposition of the self-assembly of PAH/PVS is confirmed by SEM analysis and it is observed that the polyelectrolyte layers growth on each side of Nafion membrane regularly. $(PAH/PVS)_{10}$–Na^+ and $(PAH/PVS)_{10}$–H^+ with 1.0 M NaCl provide 55.1 and 43.0% reduction in lower methanol permittivity in comparison to pristine Nafion, respectively, while the proton conductivities are 12.4 and 78.3 mS cm^{-1}. Promisingly, it is found that the membrane selectivity values (Φ) of all multilayered composite membranes in H^+ form are much higher than those of Na^+ form and perfluorosulfonated ionomers reported in the literature. These encouraging results indicate that composite membranes having both superior proton conductivity and improved methanol barrier properties can be prepared from highly charged polyelectrolytes including salt for fuel cell applications.

1. Introduction

Direct methanol fuel cells (DMFC) are expected to become important power sources for transport and portable applications due to their high energy density and simplified design [1–3]. The commercialization of DMFC and micro-DMFC is limited by the high cost of the platinum catalyst and methanol cross-over across polymer based membrane [4,5]. The major limitation of the commercially available perfluorosulfonated membranes is that for direct methanol fuel cells they exhibit significant methanol cross-over from anode to cathode which causes a mixed potential and reduces the electrical performance. Therefore, to reach high performance membranes, methanol permeability should be reduced. In this respect, some approaches, such as use of diluted methanol and operation at low temperatures, were studied and reported a significant decrease in DMFC performance [6,7]. Another approach to suppress methanol cross-over is the modification of fluorinated and non-fluorinated membranes (PBI, sPEEK etc.) through the addition of inorganic components. This approach can dramatically reduce the methanol cross-over with slightly sacrificing the proton conductivity. For this purpose, there is very intensive research activity in the modification of Nafion based composite membranes such as Nafion–silica [8–10], Nafion–zirconium phosphate [11], Nafion–cesium ions [12] and Nafion–polymer composites. Recently conductive polymers, polyaniline (PANi), polypyrrole (PPy) and polybenzimidazole (PBI) were introduced into Nafion to limit the methanol permeability [13–16]. In an alternative approach for blocking methanol permeation effectively, various multilayered composite membrane structures were investigated. In these studies, polyvinyl alcohol (PVA) and polyether ether ketone (PEEK) were used as thin barrier films on Nafion [17,18] and it was reported that the methanol permittivity value dramatically decreased due to the formation of thick barrier film on Nafion membrane with sacrificing the proton conductivity.

Layer-by-Layer (LbL) method consists of alternate dipping of the membrane support in oppositely charged polycation and polyanion electrolyte solutions, as reported by Decher and other groups [19–21]. The versatility, simplicity and flexibility of the build-up process are the main advantages of this deposition technique for the surface modification. Tieke and co-workers have reported many works on LbL assembled composite membranes showing high selective ion permeation and separation factor [22–25].

Up to now, the use of LbL method for the preparation of multilayered composite membrane was studied scarcely. Recently, Farhat

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and Hammond have reported that the deposition of a polyelectrolyte multilayer membrane on a porous support using the LbL technique and they offered LbL technique as an alternative method to fabricate a membrane-electrode assembly [26]. In another study, Jiang et al. have reported that poly(diallyldimethylammonium chloride) (PDDA)/poly(styrene sulfonic acid) (PSS) was deposited on Nafion 1135 membrane by LbL and observed that the methanol cross-over current density significantly decreased with an increase in the number of deposited layer [27]. In our recent study, we optimized the LbL deposition conditions for polyallylamine hydrochloride (PAH)/PSS system in order to achieve both high proton conductivity and methanol blocking properties simultaneously [28]. On the other hand, transport mechanism of alcohol and proton through Nafion-like perfluorosulfonated ionomer depending on the ion type and equivalent weight of membranes was discussed by Okada et al. in detail [29–32]. So far, the influences of external salt addition to polyelectrolyte dipping solution and use of highly charged polyelectrolyte, PVS, on fuel cell performance have not been reported.

In the present study, it is aimed to demonstrate the influences of use of highly charged polyelectrolytes and salt addition to polyelectrolyte solution on proton conductivity and methanol permeability of the LbL self-assembled Nafion-composite membrane. The relation of the thermal, conductive and methanol permeation properties was analyzed with the thickness, charge density and charge type of deposited polyelectrolyte bi-layers.

2. Experimental

2.1. Materials

Polyallylamine hydrochloride (PAH) (Mw: 15,000) and polyvinylsulfate potassium salt (PVS) (Mw: 170,000) were supplied from Aldrich and used as received. Nafion®117 commercial membrane was received from Aldrich Company (175 μm) with a nominal equivalent weight of 1100 g equiv.$^{-1}$. Sulfuric acid (95–98%), hydrogen peroxide (35%) and methanol (99.7% purity) were obtained from Riedel de Haen, NaCl was supplied from Fluka. Mili-Q ultrapure water was used in all deposition experiments and AC measurements (Milipore 18.2 MΩ at 25 °C). Prior to deposition, Nafion membrane was treated according to the procedure reported previously [28]. For the preparation of self-assembled multilayered composite membranes, the dipping method reported by Tieke et al. was used [15] and described in our recent paper [28].

2.2. Characterization

The formation of the LbL self-assembled multilayers on membrane surface prepared from PAH/PVS was confirmed by Scanning Electron Microscopy (SEM). In SEM analysis, dried composite membrane was manually fractured after cooling in liquid nitrogen. The sample was sputtered with gold and palladium mixture in 10 nm thickness and measured by a JEOL/JSM-6335F instrument at an operation voltage of 5 kV. Proton conductivity (σ) of the LbL self-assembled composite membranes was measured by two-probe AC method using a Solartron 1260 Frequency Response Analyzer (FRA) and Solartron 1296 Dielectric Interface. The membrane was cut in 2 cm × 2.5 cm dimensions and impedance measurements were performed in water at 22 ± 1 °C. The test system used was described in our recent paper [33]. Methanol permeation measurements of the LbL composite membranes were carried out at 22 ± 1 °C by using a U-shaped home-made apparatus which consists of two different compartments filled with 20 mL of ultrapure Mili-Q water and 10 M methanol solution. The concentration of methanol diffused through the composite membrane was detected by using a Zeissler refractive indexer and the methanol permeation rate was calculated as explained in our recent study and literature [28]. TG measurements of the samples were carried out with a Seiko EXSTAR 6000-TGA/DTA 6300 model instrument. TG curves were recorded of the multilayered composite membranes in acid form $(PAH/PVS)_n$–H^+ and in sodium form $(PAH/PVS)_n$–Na^+ at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere in the temperature range of 40–800 °C.

Ion exchange capacity (IEC) values of Na^+ and H^+ form of self-assembled composite membranes were determined by titration method [33]. A sample membrane in proton form was soaked in saturated NaCl solution for 48 h at room temperature to exchange H^+ with Na^+. Then, H^+ released into the solution was titrated with a 0.01N NaOH solution using phenolphthalein as the indicator. IEC was calculated by using the following formula:

$$\text{IEC} = \frac{VM}{m_{\text{dry}}} \qquad (1)$$

where IEC is the ion exchange capacity expressed in mequiv. g^{-1}; V is the added titrant volume at the equivalent point expressed in mL, M is the molar concentration of the titrant and m_{dry} is the dry mass of the sample expressed in g.

2.3. Preparation of Na^+ and H^+ form of multilayered composite membranes

Firstly, PAH and PVS were dissolved in Mili-Q water in a concentration of 10^{-1} and 10^{-2} moles L^{-1}, respectively. The pH of the polyelectrolyte solutions was adjusted to 1.8 by adding aqueous HCl. The solutions of PAH and PVS contained NaCl in concentration of 1 moles L^{-1} was prepared to observe the salt effect. The preparation of ultra thin polyelectrolyte films starts with the immersion of, e.g., a positively charged substrate in an aqueous solution of an anionic polyelectrolyte so that a thin layer of this compound is adsorbed and the surface charge of the substrate reverted. Subsequent dipping of this substrate into a solution of a cationic electrolyte again leads to adsorption of a thin layer and the surface charge is rendered positive again. Multiple repetition of the adsorption steps leads to a multilayer film with alternating positive and negative excess charges. Finally all prepared LbL composite membranes in Na^+ form were inverted into H^+ form by immersing into 1 N HCl for 1 h. The adsorption steps were repeated up to 10 times for methanol permeation measurements and from 5 to 20 times for AC conductivity tests. Five bi-layers deposited PAH/PVS Nafion-composite membranes in Na^+ and H^+ form were donated as $(PAH/PVS)_5$–Na^+ and $(PAH/PVS)_5$–H^+, respectively. For comparison, Nafion®117 (EW = 1100) was also tested as a reference membrane.

3. Results and discussion

The structure of the multilayer films is strongly based on the deposition conditions such as concentration of adsorbing species, adsorption time, concentration and type of added salt, and temperature. The most frequently used control parameters are the ionic strength and pH of the solution [21,34]. In our recent study, we optimized the deposition conditions of PAH/PSS system and we found that the polyelectrolyte concentration and pH as 10^{-1} moles L^{-1} and 1.8, respectively [28]. In principle, we tried to control the deposited layer thickness and charge density by using both highly charged polyelectrolyte and salt addition to the dipping solution. During the deposition experiments and test measurements of all prepared Nafion-composite membranes, no physical change was observed. Even when 20 bi-layers of PAH/PVS was deposited on the membrane support, the obtained composite membrane was clear and highly mechanically stable as well as pristine Nafion.