Journal of Membrane Science 343 (2009) 137–146

Contents lists available at ScienceDirect

Journal of Membrane Science

journal homepage: www.elsevier.com/locate/memsci

A novel approach for highly proton conductive electrolyte membranes with improved methanol barrier properties: Layer-by-Layer assembly of salt containing polyelectrolytes

Serpil Yılmaztürk, Hüseyin Deligöz*, Mesut Yılmazoğlu, Hakan Damyan, Faruk Öksüzömer, S. Naci Koç, Ali Durmuş, M. Ali Gürkaynak

Istanbul University, Engineering Faculty, Chemical Engineering Department, 34320 Avcilar-Istanbul, Turkey

ARTICLE INFO

Article history:
Received 3 June 2009
Received in revised form 9 July 2009
Accepted 10 July 2009
Available online 21 July 2009

Keywords:
Layer-by-Layer (LbL)
Membrane
Self-assembly
Direct methanol fuel cell
Proton conductivity

ABSTRACT

A series of highly proton conductive electrolyte membranes with improved methanol barrier properties are prepared from polyallylamine hydrochloride (PAH) and polystyrene sulfonic acid (PSS) including salt by Layer-by-Layer (LbL) method. The effects of added salt type (NaCl, $MgCl_2$) and salt concentration (1.0 M, 0.1 M) on proton conductivity (σ) and methanol barrier properties of the LbL self-assembled composite membranes are discussed in terms of controlled layer thickness and charge density. Furthermore, the influences of ion type in the multilayered composite membranes are studied in conjunction with physicochemical and thermal properties.

The deposition of the self-assembly of PAH/PSS film on Nafion is followed by UV–Vis spectroscopy and it is observed that the polyelectrolyte layers growth on both sides of Nafion membrane regularly. $(PAH/PSS)_5–Na^+$ and $(PAH/PSS)_5–H^+$ with 1.0 M NaCl exhibits 49.6 and 27.8% reduction in lower methanol permittivity in comparison with the pristine Nafion® 117, respectively, while the proton conductivities are 12.97 and 74.69 mS cm^{-1}. Promisingly, it is found that the membrane selectivity values (Φ) of all multilayered membranes in H^+ form are much higher than that of salt form (Na^+ and Mg^{2+}) and perfluorosulfonated ionomers reported in the literature. Also, we find out that the use of polyelectrolytes with high charge density causes a further improvement in proton conductivity and methanol barrier properties simultaneously. These encouraging results indicate that upon a suitable choice of LbL deposition conditions, composite membranes exhibiting both high proton conductivity and improved methanol barrier properties can be tailored for fuel cells.

1. Introduction

Direct methanol fuel cells (DMFCs) 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 problem [4,5]. The major limitation of the commercially available perfluorosulfonated membranes is that for direct methanol fuel cells they exhibit significant cross-over of methanol from anode to cathode which causes a mixed potential and reduces the electrical performance. Methanol cross-over decreases the performance of DMFCs in three main ways: (i) poisoning of the cathode catalyst, (ii) fuel efficiency reduction and (iii) electrode potential reduction due to methanol oxidation at the cathode. Some passive approaches to methanol cross-over reduction, such as the use of diluted methanol and operation at low temperatures, negatively affect DMFC performance [6,7]. An active approach to the 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. Therefore 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 a thin barrier films on Nafion and

---

* Corresponding author. Tel.: +90 212 473 7070/17758; fax: +90 212 473 71 80.
E-mail addresses: hdeligoz@istanbul.edu.tr, hdeligoz1972@yahoo.com
(H. Deligöz).

0376-7388/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.memsci.2009.07.019

it was reported that the methanol blocking properties was significantly improved due to the formation of thick barrier film on Nafion membrane with sacrificing the proton conductivity [17,18].

There are some methods for deposition of ultrathin/thin films on a substrate such as spin coating, self-assembling Layer-by-Layer (LbL), sputtering, evaporation and Langmuir–Blodgett [19]. Among them, the latter three have to be performed by quite sophisticated and expensive equipments, while the other methods are simple and cheaper. 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 [20]. LbL self-assembled multilayers are novel materials studied extensively in recent years due to their numerous potential applications, versatility and simplicity [21]. Tieke and co-workers have reported many works on LbL self-assembled composite membranes showing high selective ion permeation and separation factor [22–25]. The alternate adsorption of cationic and anionic polyelectrolytes proceeds under complex formation of the polyelectrolytes according to following equation:

$$P^+X^- + P^-M^+ \leftrightarrow P^+P^- + M^+X^-$$

In which P^+ and P^- stand for polymer-bound, positively and negatively charged groups, respectively and M^+ and X^- are, respectively, the small metal and halogen counter ions. Since each polymer chain contains a large number of charged groups, a physically cross-linked network structure is formed in which PP ion pairs represent the cross-linking sites.

Up to now, the use of LbL method for the preparation of multilayered composite membrane for fuel cell applications was studied scarcely. Farhat and Hammond have recently reported that the deposition of a polyelectrolyte multilayer membrane on a porous support using the LbL technique which they offered 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 technique and observed that 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 polyallyamine 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 perflourosulfonated ionomer depending on the ion type and equivalent weight of membranes was discussed by Okada et al. in detail [29–32]. Finally they concluded that the proton transport in acid and salt form of Nafion was governed by Grotthuss and vehicle mechanism, respectively [32].

As far as we know, no study is available about the influences of external salt addition to dipping solution and ion types in the multilayered membranes on fuel cell performance. In the present study, it is aimed to demonstrate the effect of salt addition to the polyelectrolyte solution and ion types on proton conductivity and methanol permeability of the LbL self-assembled Nafion-composite membranes. 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. Moreover, we investigated the use of highly charged polyvinylsulfate potassium salt (PVS) as anionic polyelectrolyte instead of PSS to observe the charge density effect.

2. Experimental

2.1. Chemicals

Polyallylamine hydrochloride (PAH) (Mw 15,000), polystyrene sulfonic acid sodium salt (PSS) (Mw 70,000) and polyvinylsulfate potassium salt (PVS) (Mw: 170,000) were supplied from Aldrich and used as received. Nafion®117 membrane was purchased from Aldrich Company (thickness of 175 μm). Concentrated sulfuric acid (95–98%), hydrogen peroxide (35%) and methanol (99.7% purity) were obtained from Riedel de Haen. NaCl and $MgCl_2{\cdot}6H_2O$ were supplied from Fluka and used as received. 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].

2.2. Characterization

The formation of LbL self-assembled multilayers on the membrane surface prepared from polyelectrolytes including salt was monitored by using a PerkinElmer Lambda 35 series UV–vis spectroscopy with an integrating sphere accessory as a function of the number of deposited bi-layers. 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 [28,33]. 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 $(PAH/PSS)_n$–H^+ and in sodium form $(PAH/PSS)_n$–Na^+ at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere in the temperature range of 40–800 °C. Dried composite membranes were manually fractured after cooling in liquid nitrogen. Cross-section of the samples were 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.

Ion exchange capacity values (IEC) 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 0.01 N NaOH solution using phenolphthalein as the indicator. IEC was calculated by using the following formula:

$$\mathrm{IEC} = \frac{VM}{m_{\mathrm{dry}}} \quad (1)$$

where, IEC is the ion exchange capacity expressed in meq 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 PSS were dissolved in Mili-Q water in a concentration of 10^{-1} moles $L^{-1}$and PVS in a concentration of