



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 1.0M 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.

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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. Tiede 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 index 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 0.01 N NaOH solution using phenolphthalein as the indicator. IEC was calculated by using the following formula:

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

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 polyelectrolyte 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.

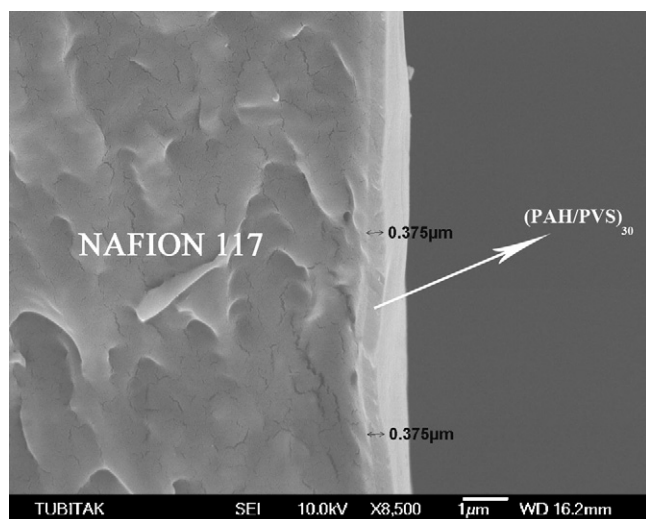


Fig. 1. SEM picture of (PAH/PVS)₃₀ Nafion-composite membrane.

3.1. SEM picture of the multilayered composite membrane

Although the easiest way to follow multilayer build-up is UV–vis spectroscopy [21,35], this technique could not be used because non-presence of UV active groups in PAH/PVS polyelectrolyte system. That is why SEM picture of the multilayered composite LbL membrane prepared from PAH/PVS was taken in order to observe the multilayer formation and it is depicted in Fig. 1. As it is seen from the figure, it was confirmed that the multilayers were formed on both sides of surface modified Nafion membrane homogenously. The thickness of 30 bi-layers of PAH/PVS deposited Nafion-composite membrane is 0.375 μm. In other words, one deposition cycling of PAH/PVS gives a deposited layer roughly in 100 nm thickness. As it is known from the literature, the thicknesses of formed bi-layers mainly depend on the deposition conditions such as pH, concentration of dipping solution, charge density of polyelectrolytes, dipping time and external salt addition [20,21,28].

3.2. Proton conductivity (σ) of the multilayered composite membrane

In the present study, we expected to improve both proton conductivity (σ) and methanol blocking properties simultaneously by using highly charged polyelectrolytes with salt. For this purpose, the influence of monovalent salt (NaCl) addition to the dipping solution on fuel cell performance parameters (proton conductivity, methanol permittivity) of LbL self-assembled composite membrane was systematically studied and the results were listed in Tables 1 and 2 depending on the number of adsorbed bi-layers. The parameters affecting the proton conductivity of the membranes are

Table 2

Comparison of the proton conductivity (σ), methanol permeability (P_M) and membrane selectivity (Φ) values of the LbL self-assembly of composite membranes prepared from PAH/PVS with 1.0M NaCl depending on the number of deposited bi-layers and ion type.

Multilayered composite membrane	Number of deposited bi-layers (n)	σ (mS cm ⁻¹) at 22 ± 1 °C	$P_M \times 10^7$ (cm ² s ⁻¹) ^a	(Φ) ^b (S s cm ⁻³) × 10 ⁻⁴
PAH/PVS with 1M NaCl (Na ⁺ form)	5	7.18	3.27 (45.8%)	2.20
	10	12.42	2.71 (55.1%)	4.58
	20	15.87	–	–
PAH/PVS with 1M NaCl (H ⁺ form)	5	68.84	4.16 (31.1%)	16.55
	10	78.27	3.44 (43.0%)	22.76
	20	92.54	–	–
Nafion® 117	–	37.78	6.04	6.25

^a Percent improvement in methanol barrier properties was given in paranthesis.

^b Membrane selectivity (σ/P_M).

Table 1

Comparison of the proton conductivity (σ) values of (PAH/PVS) _{n} depending on the number of deposited bi-layers.

Multilayered composite membrane	Number of deposited bi-layers (n)	σ (mS cm ⁻¹) at 22 ± 1 °C
PAH/PVS	5	61.27
	10	49.58
	20	39.82
Nafion® 117	–	37.78

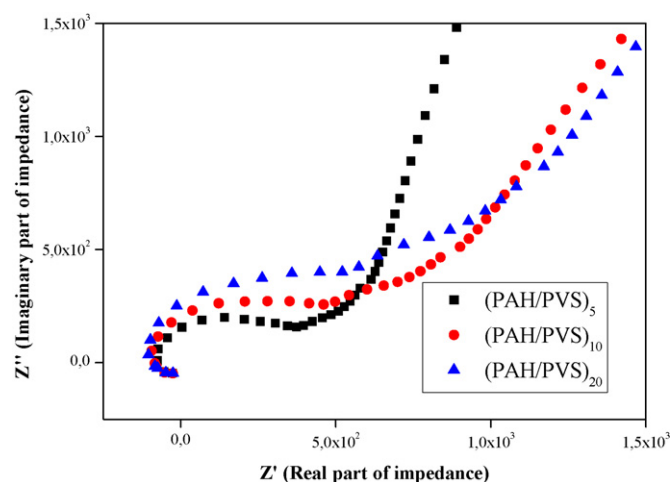


Fig. 2. Nyquist plots of (PAH/PVS) _{n} ($n=5, 10, 20$) without salt.

defined in the following formula.

$$\sigma = nFC_{H^+} \nu_{H^+} \quad (2)$$

where n is an electric charge of carrier protons and equal to 1+, F is Faraday constant ($96,485 \times 10^4$ C mol⁻¹), C_{H^+} is the concentration of the carrier proton and ν_{H^+} is the mobility of carrier proton. Thus the proton conductivity of a membrane mainly is influenced by both of concentration and mobility of the carrier proton. For comparison, the proton conductivity of the pristine Nafion® 117 membrane was calculated in our test system and found to be 37.7 mS cm⁻¹ with two-probe techniques. This result is in good agreement with the reported data in the literature [36].

3.2.1. Influences of charge density (q_c) and salt addition to the dipping solution depending on the deposition number of multilayers

Fig. 2 shows the Nyquist plots of (PAH–PVS) _{n} ($n=5, 10$ and 20) without salt. Also, the calculated proton conductivity values are depicted in Table 1. As it is seen from Table 1, the conductivity values of all LbL self-assembled composite membranes prepared from

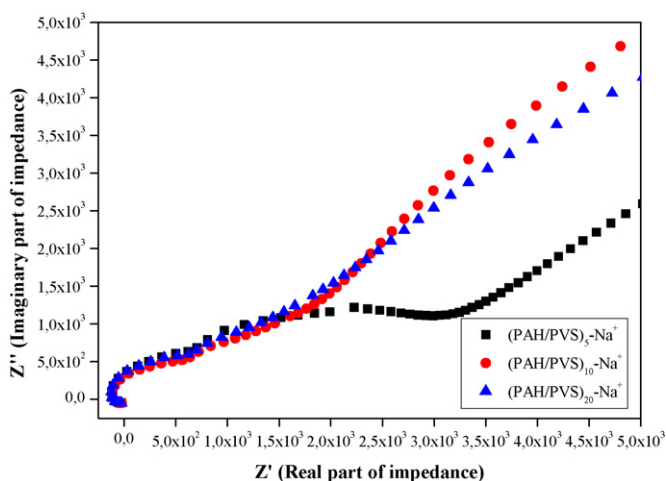


Fig. 3. Nyquist plots of $(\text{PAH/PVS})_n\text{-Na}^+$ ($n = 5, 10, 20$) with 1 M NaCl.

PAH/PVS free salt were higher than that of pristine Nafion®117. This improvement can be explained by the increase in the number of carrier proton. One can also see from Table 1 that the proton conductivities of $(\text{PAH-PVS})_5$ and $(\text{PAH-PVS})_{20}$ were 61.3 and 39.8 mS cm^{-1} , respectively. This reduction in proton conductivity with the number adsorbed bi-layers may be explained by the formation of thicker bi-layers which can limit the mobility of carrier proton. Interestingly, proton conductivity value of PAH/PVS system was nearly 2 times higher than obtained from PAH/PSS system due to the high charge density of PVS. The charge density (q_c) is expressed in terms of the number of ion pairs per number of carbon atoms in the repeating unit of the complex formed by the polycation and polyanion. While q_c of the PAH/PVS system is 0.2, this value for PAH/PSS system is only 0.09. Thus the preparation of composite membranes with highly charged polyelectrolytes caused an improvement in the number of carrier proton which will promote proton conduction along the membrane [37]. As it is known from the literature, the charge density of the polyelectrolytes depends not only on the molecular structure but also on the degree of ionization of the polar groups. The ionization strongly depends on the pH of the aqueous polyelectrolyte solution as it is shown in our recent work and the literature [28,34].

In order to explore the variation in proton conductivity as a function of salt addition to the polyelectrolyte solution, the build-up of multilayers was examined by the presence of salt. For this purpose, it is especially preferred for more concentrated salt addition (1 M) in order to obtain composite membranes with higher proton conductivity and membrane selectivity values. The Nyquist plots of multilayered composite membrane in Na^+ form were depicted in Fig. 3 and the calculated conductivity values were listed in Table 2. As it is seen from Table 2, the proton conductivity of Na^+ form in multilayered composite membrane was lower than that of pristine Nafion®117. This reduction in conductivity is attributed to the low mobility of the inverted Na form by ion exchange reaction. For confirmation, we calculated the IEC values of the both pristine Nafion and five/ten bi-layers deposited of PAH/PVS composite membranes in Na^+ form and found that IEC values were sharply decreased from 0.87 to 0.08 and 0.07 mequiv. g^{-1} , respectively. Thus IEC results confirmed our explanation of salt concentration effect. Another explanation may be the lower water uptake in the case of Na^+ form of multilayered composite membranes which may suppress the mobility of charge carrier species and limit the proton conductivity. As it is known from the literature, the mobility of the cation is affected by the water content or the volume fraction

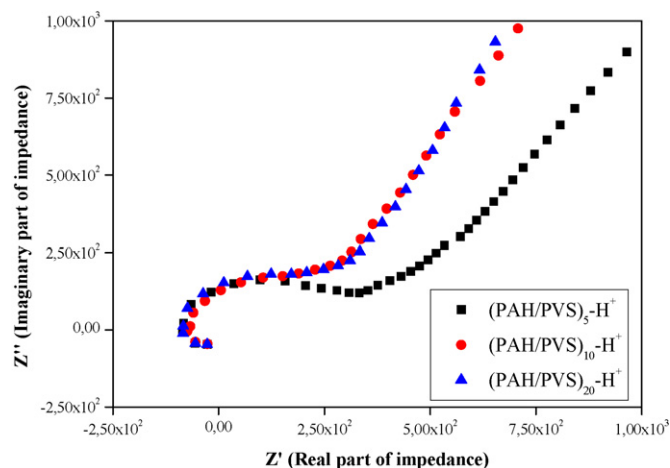


Fig. 4. Nyquist plots of $(\text{PAH/PVS})_n\text{-H}^+$ ($n = 5, 10, 20$) with 1 M NaCl.

of water in the membrane [30]. The cationic conductivity in the composite membrane is determined by two major factors that are the amount of residing water in the ionic channel and the interaction between cations and sulfonic acid groups. Furthermore, with an increase in the number of adsorbed bi-layers, the proton conductivity of the composite membranes was slightly increased and reached to 15.9 mS cm^{-1} for $(\text{PAH/PVS})_{20}\text{-Na}^+$ with 1.0 M salt. The reason might be that the larger thickness prevents the oppositely charged polyelectrolyte chains from complete interpenetration and neutralization of their charges. In that case more excess charges are present in the membrane, which may effectively conduct the protons along the membrane.

3.2.2. Influences of ion form in multilayered composite membranes depending on the deposition number of multilayers

The effect of ion type in the PAH/PVS multilayered composite membrane on the proton conductivity was investigated by inverting the LbL composite membrane from Na^+ form to H^+ form. Fig. 4 shows the Nyquist plots of $(\text{PAH-PVS})_n\text{-H}^+$ ($n = 5, 10, 20$) with 1.0 M NaCl. The proton conductivity values of the composite membrane in H^+ form were 6–10 times larger than those of Na^+ form. This large increase in proton conductivity value is mainly attributed to higher mobility of the H^+ form than that of Na^+ form. This result is well agreed with the Okada's study [29]. In this study, they reported that the mobility of H^+ form was 6–9 times larger than that of other alkali cations. Also, another explanation may be that Na^+ are less hydrophilic than H^+ and cause a lower amount of water absorption as compared with H^+ . This would result in the smaller volume of hydrophilic domains inside the membrane which will cause lower ionic mobility. Okada et al. have reported some important reports on the transport mechanism of perfluoro-sulfonated membranes with H^+ form, alkali metal cation and binary cation systems. Proton conductivity values of H^+ form composite membrane were provided by two transport mechanisms, i.e., Grotthuss and vehicle mechanisms like reported earlier by Okada et al. [31]. Our results are in good agreement with the transport data given in the literature [31,38,39]. Contrarily PAH/PVS free salt system, the proton conductivity of all composite membranes in H^+ form have exhibited an increase with the number of deposited layers.

Consequently, it can be concluded that the proton conductivity of the LbL Nafion-composite membrane in H^+ form prepared from polyelectrolytes with salt was significantly improved and reached to a value which is nearly 3 times higher than pristine Nafion®117.

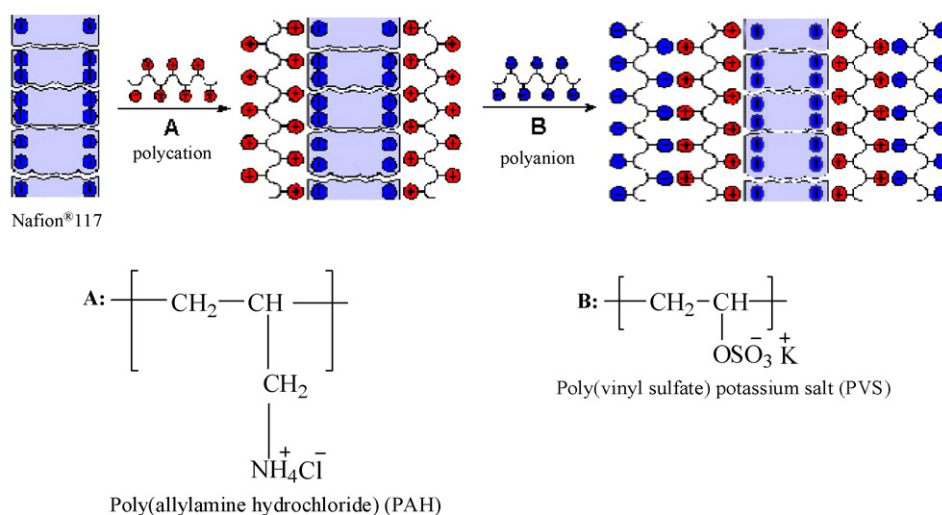


Fig. 5. An idealized scheme of multilayer formation upon alternating Layer-by-Layer assembly of PAH and PVS on Nafion membrane which inhibits methanol cross-over and the chemical structures of the polyelectrolytes used.

3.3. Methanol permeation (P_M) across multilayered composite membranes

Highly methanol permeation (P_M) through the proton conducting polymer membrane is a very important problem to be solved for DMFC applications. In Nafion based membranes, methanol diffusion rate and the proton conductivity are in a trade-off relationship with each other, i.e., the membrane having higher proton conductivity shows higher alcohol cross-over. As we know from the literature, generally, alcohols penetrate into the hydrophilic regions in the membranes, which suggest the formation of ionic cluster regions consisting of alcohols, protons, and sulfonic acid groups. Since alcohols and proton both transport through the ionic cluster regions, the expansion of the diffusion space by swelling results in their faster diffusion. Because alcohols move in the expanded space by the vehicle mechanism, the membrane swelling is another important factor for the fast diffusion. The other parameter affecting the methanol permittivity through the membrane is the channel structure of ionic cluster regions and/or the interaction with sulfonic acid groups. Thus, the channel structure of the ionic cluster regions prevents fast alcohol diffusion in the membranes [27,32]. In another study, it is reported that the cationic form of the Nafion membrane strongly influences on the methanol and water permeability values. The water and methanol permeability values of the Nafion membranes decrease in the cation form which has higher atomic number [40].

It is expected that blocking the hydrophilic ionic domains, which are primarily associated with $-\text{SO}_3^-$ clusters on the Nafion membrane surface, and closing of the channels of Nafion membrane would effectively suppress methanol cross-over. Therefore, we tried to plug these pores and block the hydrophilic domains by the formation of thicker multilayered films on the surface of treated Nafion for limiting the methanol permeability in this study. The proposed mechanism is depicted in Fig. 5 which shows the plugging of special channels of Nafion membrane by the formation of bi-layers in different thickness.

Methanol permeation was measured using a home-made U-shaped two chamber apparatus described in detail previously in Section 2.2 [28]. Prior to testing, each membrane, whose area was 2 cm^2 , was soaked in ultra pure water for 1 h at room temperature. The methanol concentration in ultra pure water compartment was significantly increased and then reached a plateau over 30 h. Therefore all methanol permeation tests were carried out during this time.

3.3.1. Influences of salt addition to the dipping solution depending on the deposition number of multilayers

The permeation rates (P) of methanol through the composite membranes consisting of different number of bi-layers of PAH/PVS with NaCl are given in Table 2. In our experimental system, methanol permeation rate was found to be $6.04 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ for Nafion[®]117 at 22°C , which compares well with those of 4.8×10^{-6} and $5.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ measured at 60 and 70°C , respectively [24]. It is seen that Na^+ form of the LbL self-assembled membranes have exhibited significant lower methanol permeation values than that of pristine Nafion due to the formation of multilayered films. (PAH/PVS)₅- Na^+ and (PAH/PVS)₁₀- Na^+ containing 1.0 M NaCl on Nafion enabled methanol permeability of the membrane to decrease by 45.9% ($3.27 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$) and 55.1% ($2.71 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$), respectively. The methanol permeation rates of the composite membranes with salt dramatically decreased with the number of adsorbed bi-layers. The main reason for this significant reduction in the methanol permeability is the larger thickness of the individual polyelectrolyte layers which provides closing the pores more effectively. Another explanation may be lower hydrophilicity of Na^+ form of composite membrane which causes a significant reduction in water and methanol transport. We also compared the methanol permeability value of the LbL composite membrane depending on the salt presence and we found that (PAH/PVS)₅- Na^+ with 1.0M NaCl exhibited nearly 2 times higher methanol barrier properties than that of the membrane prepared by the polyelectrolyte solutions without salt [28].

3.3.2. Influences of charge density (q_c) and ion form in multilayered composite membranes depending on the deposition number of multilayers

To observe the effect of ion form in multilayered composite membrane, methanol permeation tests of the composite membranes in proton form were carried out and the results compiled in Table 2. The methanol blocking properties of (PAH/PVS)₅- H^+ and (PAH/PVS)₁₀- H^+ with 1 M NaCl were improved by 31.1 and 43.0% compared to Nafion[®]117, respectively. Interestingly, it is expected that the methanol permittivity is inversely proportional to q_c . Thus the methanol permittivity is high when highly charged polyelectrolyte was used instead of weak polyanion. However, it is found that the methanol blocking properties were significantly improved with the number of adsorbed bi-layers prepared from highly charged polyelectrolytes. This can be explained by the formation of thicker

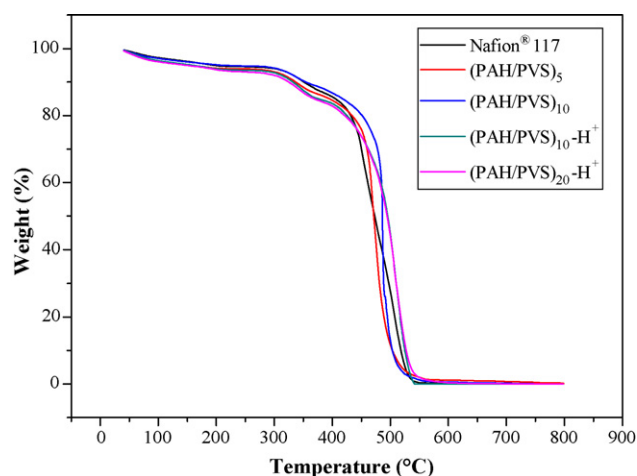


Fig. 6. TGA curves of (PAH/PVS) $_n$ ($n=5, 10$) and (PAH/PVS) $_n$ -H $^+$ ($n=10, 20$) with 1.0M NaCl depending on the number of deposited bi-layers.

multilayers which can plug the pores of the Nafion more effectively than that of less thicker membrane.

3.4. Thermogravimetric analyses (TGA) of the multilayered composite membranes

Commercially available perfluorinated membranes have a limited range of working temperature for fuel cell applications. In order to investigate the influence of multilayer formation and charge type in multilayered composite membrane on thermal stability, TG analyses of the membranes in H $^+$ and Na $^+$ form were carried out and TG curves are depicted in Fig. 6 depending on the number of deposited bi-layers. The detailed TGA results are also given in Table 3.

Fig. 6 shows TG curves of (PAH-PVS) $_n$ -H $^+$ ($n=10, 20$) with 1 M NaCl and (PAH-PVS) $_n$ ($n=5, 10$) without salt comparatively. The TG traces of the multilayered composite membrane in H $^+$ and Na $^+$ (not shown) exhibited different profiles. Decomposition of the prepared composite membrane in proton form has occurred mainly in three steps related to a water loss (i), side chain group (-SO $_3$ H) decomposition (ii) and backbone decomposition (iii), respectively, while composite membrane in Na $^+$ form has degraded in one step. The first degradation step of Nafion $^{\text{®}}$ 117 membrane has started at 293.5 °C and 10% weight loss occurred at 346.6 °C. Subsequently, the degradation of perfluorosulfonated backbone has completed at 542.9 °C. Similar curves were obtained by Surowiec and Bogoczek in the investigation of Nafion $^{\text{®}}$ 117 acid form [41]. The composite membranes prepared from polyions free salt have exhibited nearly the same TG patterns compared to pristine Nafion. The thermal degradation of (PAH/PVS) $_n$ -Na $^+$ occurred in only one stage and the onset temperature was roughly 150 °C higher than that observed

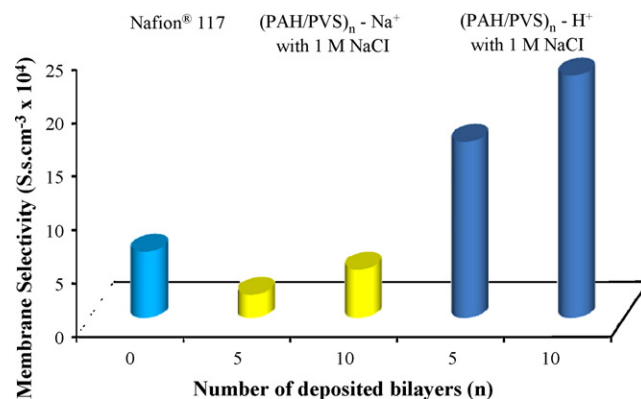


Fig. 7. Comparative membrane selectivity (Φ) values of the multilayered composite membranes depending on the number of deposited bi-layers and ion type.

for (PAH/PVS) $_n$ -H $^+$. This is attributed to the formation of sodium salt of PVS by ion exchange reaction. As it is known from the literature, the water content of the membranes decreases progressively with increasing counter charge density and indicating that (PAH/PVS) $_n$ -Na $^+$ presents lower water loss due to their large ionic radii [42,43]. On the other hand, the thermal behavior of PAH/PVS deposited Nafion-composite membrane in acid form is similar to pristine Nafion $^{\text{®}}$ 117 due to the fully inversion of ions from Na $^+$ to H $^+$ form. As a consequence, it can be concluded that the thermal properties of the LbL self-assembled composite membrane depend on the water content, cation size and ion type in multilayered structure.

3.5. Membrane selectivity of the multilayered composite membranes

Fig. 7 shows the membrane selectivity (Φ) of multilayered composite membranes comparatively. The selectivity factor (Φ) is defined as the ratio of proton conductivity to methanol permeability and used as an indicator of the suitability of a given membrane for DMFC application [44]. All the prepared Nafion-composite membranes in H $^+$ form had 3–4 times higher membrane selectivity than that of Nafion $^{\text{®}}$ 117 (6.25×10^4 S s cm $^{-3}$). The membrane selectivity of (PAH/PVS) $_{10}$ -H $^+$ with 1.0M NaCl system was improved and reached to nearly 22.8×10^4 S s cm $^{-3}$. Lower selectivity for Na $^+$ form of composite membrane is attributed to its low proton conductivity which is almost 2 times lower than pristine Nafion. Evaluated membrane selectivity results obtained in the present study are higher than those reported in the literature [13,14]. Another promising result is that the membrane selectivity of LbL multilayered composite membrane prepared from PAH/PVS was higher than that of PAH/PSS system due to high charge density of PVS. Conclusively, we expect that the membrane selectivity

Table 3

TGA results of (PAH/PVS) $_n$, (PAH/PVS) $_n$ -Na $^+$ and (PAH/PVS) $_n$ -H $^+$ with 1.0M NaCl depending on the number of deposited bi-layers and ion type.

Multilayered composite membrane	Number of deposited bi-layers (n)	T_i (°C)	T_{10} (°C)	T_{50} (°C)	T_f (°C)
(PAH/PVS) $_n$	5	291.9	334.3	469.7	559.9
	10	299.6	352.7	485.4	551.7
(PAH/PVS) $_n$ -Na $^+$ with 1 M NaCl	5	423.9	469.0	487.0	540.0
	10	436.2	468.0	489.2	542.3
	20	448.6	467.2	507.0	544.4
(PAH/PVS) $_n$ -H $^+$ with 1 M NaCl	10	302.3	328.8	493.3	554.4
	20	298.8	322.7	492.5	558.9
Nafion $^{\text{®}}$ 117	-	293.5	346.6	471.3	542.9

[T_i] refers to initial temperature where degradation of sulfonic acid groups in the membrane has occurred; [T_{10}] refers to temperature where 10% of weight loss has occurred; [T_{50}] refers to temperature where 50% of weight loss has occurred; [T_f] refers to temperature where degradation of the samples has completed.

can be further improved by choosing anionic and cationic polyelectrolytes consisting of high charge density and salt with increasing dipping cycles.

4. Conclusion

In this study, we reported a novel approach for the preparation of Nafion-composite membranes with improved proton conductivity and methanol barrier properties by LbL technique. To explore the variation in proton conductivity and methanol permeability in function of physicochemical parameters, the build-up of multilayers was examined by using highly charged polyelectrolyte (PVS) and salt addition to the dipping solution. Three main results are found in the present study; first, the proton conductivity and methanol permeation rates of the LbL self-assembled composite membrane strongly depend on the thickness of coated bi-layers and type of charge carriers in the individual electrolyte layers which can be varied by salt addition to dipping solution and ion type in the multilayers. The proton conductivity values of (PAH/PVS)₁₀-Na⁺ and (PAH/PVS)₁₀-H⁺ with 1.0 M NaCl were 12.4 and 78.3 mS cm⁻¹, respectively, while the methanol barrier properties of the corresponding composite membranes were 55.1 and 43.0%. Second, highest improvement in both proton conductivity and methanol barrier properties can be achieved for the membranes obtained from polyelectrolytes with salt and subsequently inverted into H⁺ form. Membrane selectivity (Φ) value of (PAH/PVS)₁₀-H⁺ was 22.8×10^4 S s cm⁻³ which is nearly 4 times higher than that of pristine Nafion[®] 117. Third, both proton conductivity and methanol blocking properties of the Nafion-composite membranes were improved by using polyelectrolytes with high charge density instead of weakly charged ones. Furthermore, the TG results indicated that the thermal stability of Nafion membranes was not sacrificed with the multilayer formation on the surface.

Our encouraging results indicated that a new type of advanced polymer electrolyte membrane with superior proton conductivity and improved methanol barrier properties can be prepared by LbL self-assembly technique in which salt added highly charged polyelectrolytes were used as a dipping solution. In our next study, the influences of the use of both polyions with high charge density such as PVA and PEI and solely number of deposited bi-layers on membrane selectivity and fuel cell performance will be studied in detail.

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