



Fabrication and performance of catalyst-coated membranes by layer-by-layer deposition of catalyst onto Nafion for polymer electrolyte membrane fuel cells

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ABSTRACT

In this contribution, four comparative methods are described for the preparation of catalyst coated membranes (CCMs) via using layer-by-layer (LbL) technique. In the first method, LbL composite membrane is immersed into H_2PtCl_6 solution followed by reduction to metallic Pt. Secondly, Pt-C (Hispec 3000) dispersed in the positively charged polyelectrolyte is assembled onto the membrane support. Thirdly, anionic polyelectrolyte with external salt is used for the preparation of CCM. In the fourth method, reductive precipitation of platinum salt loaded on Vulcan XC complexes within LbL multilayer in the presence of Nafion solution takes place. From SEM analysis, it is observed that the polyelectrolytes are deposited onto both sides of the pre-treated Nafion® 117 membrane successfully with Pt loadings of $0.023 \mu\text{g cm}^{-2}$ and $0.15 \mu\text{g cm}^{-2}$ for CCMs prepared according to method 1 reduced in 10 and 30 min, respectively. Single cell performance of MEA-6 based on CCM (PAH/PSS- H_2PtCl_6 -Vulcan XC72-Nafion) prepared according to method 4 displays the best output performance (98 mW cm^{-2}) due to the improved contact between the catalyst layer and the membrane. Furthermore the cell performance of MEA-6 is significantly improved (18%) due to creating new path for fuel and catalyst interaction (three phase boundary) compared to pristine Nafion® 117 based MEA.

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1. Introduction

Without doubt, one of the most studied alternative energy sources is hydrogen energy systems whose most important part is fuel cells. A single proton exchange membrane fuel cell (PEMFC) consists of three types of components: a membrane electrode assembly (MEA), a bipolar (also known as flow-field) plate (BPP) and a seal [1]. Among these components, the key part of a PEM fuel cell is the MEA, where the electrochemical reactions occur and electricity is produced. MEA fabrication methods can be mainly categorized based on the substrate type and the technique used for the catalyst coating process. Nowadays, many techniques have been exploited to fabricate MEAs, in which, the electro-catalyst could be coated either onto a gas diffusion layer (GDL-based MEAs) or directly onto an electrolyte membrane (CCM-based MEAs) [2,3].

The preparation of catalyst coated membrane (CCM) has attracted more attention in the last decade. In CCM technique, the catalyst layers are directly applied to both sides of the electrolyte and it is believed that the MEA prepared by CCM technique yields higher cell performance than the GDL-based MEA due to higher catalyst utilization [4,5] and a better electrolyte/catalyst interface which can effectively reduce the catalyst loading without

sacrificing the cell performance [5–7]. There are several different methods for the preparation of CCMs such as spraying [8–15], painting [16], catalyst decaling [17–20], screen and inkjet printing [21,22].

The sequential electrostatic adsorption of oppositely charged polyelectrolytes by layer-by-layer (LbL) self-assembly was firstly reported by Decher as a promising and efficient method for the preparation of multilayered ultra thin films in a simple way [23]. A major advantage gained from LbL technique is the introduction of a large number of variables that modify the electrolyte or the electrodes depending on the experimental conditions. Other advantages include the use of low cost, non-toxic polyelectrolyte materials, simple fabrication process and miniaturization of the electrochemical components. These features make LbL an attractive technique for fuel-cell assemblies [24]. At the initial, LbL multilayered composite membranes were reported for FC applications [25–29]. Later on, some famous groups have attempted to prepare LbL polyelectrolyte-carbon electrodes (LPCE) for MEAs [24,30–34].

Recently, Farhat and Hammond have reported that the LbL polymer-carbon electrode can be considered as an alternative to conventional graphitic slurry and carbon-cloth-type electrodes. They claimed that LPCEs showed remarkable chemical stability and those made from PDAC [poly(diallyl dimethylammonium chloride)] and PAMPSA [poly(2-acrylamido-2-methyl-1-propane sulfonic acid)]/Hispec 3000 were capable of withstanding strong

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acidic, basic or oxidizing media. In that study, open-circuit potential (OCP) and maximum power density of LbL self-assembled PDAC/PAMPS MEA performing under H_2 /air were found to be almost +0.9 V and 2.0 mW cm^{-2} , respectively [31]. In another study of Hammond's group, Pt was deposited into PANi [poly(aniline)]/PAA[poly(acrylic acid)] and PANi/PAA-co-polyacrylamide films in three different methods and 0.3 mg cm^{-2} metallic Pt loading was achieved [32]. Michel et al. have recently demonstrated that fuel cells with LbL catalyst layers comprised single walled carbon nanotubes (SWCNTs) and carbon fibers (CFs) exhibited peak power densities of 195 mW cm^{-2} and 227 mW cm^{-2} . In that study, Pt utilizations were found to be $408 \text{ mW mg}_{\text{Pt}}^{-1}$ and $580 \text{ mW mg}_{\text{Pt}}^{-1}$, respectively [24] and they used selective heterogeneous nucleation to deposit Pt on the surface of SWCNTs and CFs with Nafion and polyethyleneimine (PEI). In another study of this group, they have synthesized highly active, carbon supported Pt electrocatalysts using a supercritical fluid method and a selective heterogeneous nucleation reaction to disperse Pt onto SWCNT and CF supports. These nanocomposites were then incorporated into catalyst and gas diffusion layers consisting of polyelectrolytes, i.e., Nafion, PANi and PEI using LbL technique. In that study, it was found much higher Pt utilizations, $3198 \text{ mW mg}_{\text{Pt}}^{-1}$ than those of MEAs produced using conventional methods ($\sim 800 \text{ mW mg}_{\text{Pt}}^{-1}$) [33]. Yuan et al. have reported LbL deposition of alternating layers of positively charged PDAC and negatively charged multiwall carbon nanotubes bearing platinum nanoparticles (Pt-CNTs). Based on their results, it was found that PDAC/Pt-CNT multilayer films had unique potential for direct methanol fuel cells (DMFCs) [34]. Although all LbL films prepared in these studies were considered as electrodes for PEM applications, no study has been reported on the preparation of platinum loaded ultra thin membranes by LbL technique. Therefore we want to extend our previous works by describing the preparation of CCMs by an improved fabrication technique (LbL technique) and investigate their cell performances for the first time.

In this study, it is aimed to prepare a new type of LbL self-assembled CCMs with enhanced fuel cell performance using PAH [poly(allylamine hydrochloride)], PSS [poly(styrene sulfonic acid)] and PAMPSA. For this purpose, four different methods of platinum incorporation into LbL film were followed: (i) reductive precipitation of platinum salt complexed within the LbL film, (ii) polyelectrolyte colloidal platinum followed by LbL adsorption, (iii) reductive precipitation of platinum salt impregnated into complex layer of PAH/PSS by dipping of LbL composite film in platinum salt solution and (iv) reductive precipitation of platinum salt loaded on Vulcan XC complexed within LbL multilayer in the presence of Nafion solution. Inspired by the Hammond's reports [31,32], all methods have been modified to prepare ultra low amount of platinum containing LbL multilayered composite membrane with enhanced cell performance compared to pristine Nafion[®]117. The methods used here offer simplicity of LbL technique over conventional techniques such as sputtering, molecular imprinting and spraying methods which need special and expensive equipments for the preparation of CCM. Performance tests of MEAs obtained from CCMs were performed and the performance results were discussed in terms of Pt loading methods and compared with pristine Nafion[®]117.

2. Experimental

2.1. Chemicals

Polyelectrolytes, poly(allylamine hydrochloride) (PAH) (Mw: 15,000), PSS (Mw: 70,000) and poly(2-acrylamido-2-methyl-1-propane sulfonic acid) (PAMPSA) (Mw: 2,000,000), were supplied

from Aldrich and used as received. Hydrogen hexachloroplatinate and sodium salts of borohydride were obtained from Aldrich and used without further purification. Hispec 3000 (platinum, nominally 20% on carbon black) from E-TEK Company was used as catalyst. Vulcan XC72R (Cabot, bulk density of 6 lb ft^{-3}) was used as catalyst support material. Commercial gas diffusion electrodes ($0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$) were purchased from E-TEK Company. Nafion[®]117 commercial membrane was received from Ion Power Company, Inc. ($175 \mu\text{m}$) with a nominal equivalent weight of $1100 \text{ g equiv.}^{-1}$ while Nafion[®]117 solution (5%) was purchased from Quitech. Ultra pure hydrogen and air were supplied from commercial suppliers. Sulfuric acid (95–98%) and hydrogen peroxide (35%) were obtained from Riedel de Haen and used as received. Milli-Q ultra-pure water was used in all deposition experiments (Millipore $18.2 \text{ M}\Omega$ at 25°C). Prior to deposition, Nafion membrane was treated according to our previous study [25].

2.2. Techniques

Field Emission Scanning Electron Microscopy (FE-SEM) was used to observe multilayer formation on membrane support. Also, thicknesses of all LbL multilayers and the dispersion of platinum within LbL multilayer prepared from PAH/PAMPSA were found from SEM analysis. The sample broken after cooling in liquid nitrogen was sputtered with gold and measured by a FEI instrument at an operation voltage of 5 kV. Furthermore, the formation of LbL self-assembled PAH/PSS multilayers on Nafion membranes was monitored by using Perkin Elmer Lambda 35 series UV-vis spectroscopy with integrating sphere as a function of the number of deposited layers. ICP-MS (Inductive Coupling Plasma-Mass Spectroscopy) analysis was performed to determine catalyst loading within the LbL film by using Thermo Elemental X-series ICP-MS. Multilayer deposition of polyelectrolytes on the membrane surface was automatically controlled by KSV dipping machine with a rate of 50 mm min^{-1} in all experiments.

2.3. Preparation of catalyst coated membranes (CCMs)

In four different methods applied here, LbL deposition technique was used to form CCMs with ultra low platinum loading. Firstly, the solutions of PAH and PSS in a concentration of 0.01 mol L^{-1} and PAMPSA in a concentration of 3 wt% were prepared in Milli-Q water. pH of the polyelectrolyte solutions was adjusted to 1.8 by adding aqueous HCl. The preparation of ultrathin polyelectrolyte multilayered films has started with the immersion of, e.g., a negatively charged substrate in an aqueous solution of cationic polyelectrolyte so that a thin layer of this compound was adsorbed and the surface charge of the substrate reverted. Subsequent dipping of this substrate into a solution of an anionic electrolyte again led to adsorption of a thin layer and the surface charge was rendered negative again. Multiple repetitions of the adsorption steps yielded to a multilayer film with alternating positive and negative excess charges.

The four different methods used for platinum incorporation into LbL film are described as follows:

Method 1. Reductive precipitation of the platinum salt inside the LbL film: Initially, PAH/PSS LbL self-assembled thin film was deposited on Nafion[®]117 according to procedure reported by our recent articles [25,35]. Subsequently, these membranes were soaked in a $10 \text{ mM } H_2PtCl_6$ solution for 10 min or 30 min. The dosing process was followed by rinsing the LbL composite membrane in pure water (pH 2.5). $PtCl_6^{2-}$ salt was then reduced to platinum black clusters by soaking the composite membrane into 2.0 mM NaBH_4 solution adjusted to pH 4 for 10 or 30 min. Finally LbL self-assembled CCMs including Pt were immersed into 1 N HCl to convert them into proton form. The number of deposited layers of

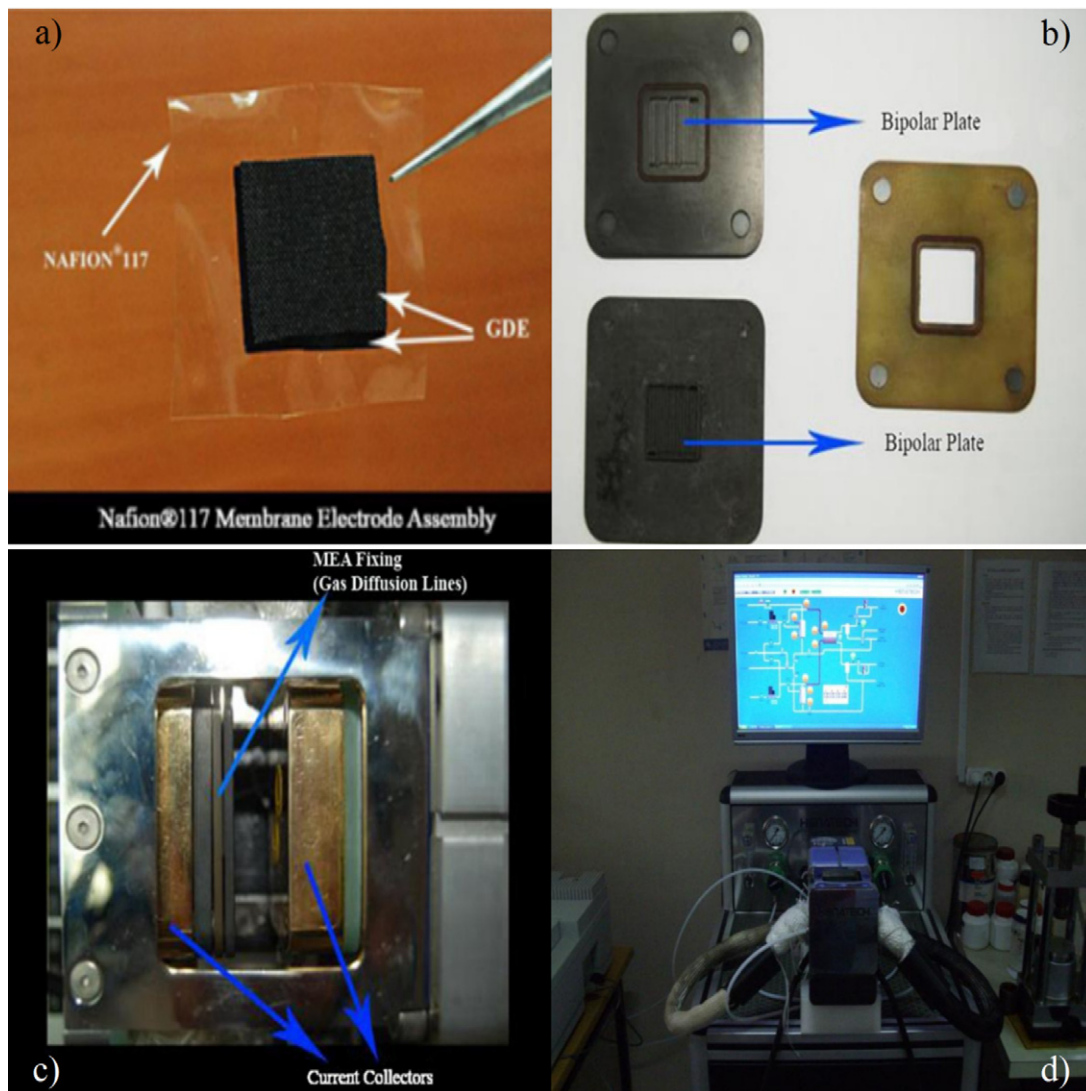


Fig. 1. The pictures of (a) Nafion®117 based MEA, (b) bipolar plates, (c) MEA fixture system and (d) PEM test station.

PAH/PSS was changed to control the catalyst loading on the Nafion surface.

Method 2. Carbon–polyelectrolyte colloidal dispersion: Fuel cell grade carbon-black with 20% Pt loading (Hispec 3000) colloidal dispersion was prepared by stirring and sonicating 0.1 g dry powder in 100 ml of anionic polyelectrolyte. PAMPSA was especially chosen for this method owing to its high viscosity. The stability of Hispec/PAMPSA system was reported to be moderate according to Hammond's report [31]. After the preparation of colloidal dispersion, LbL self-assembly of PAH/PAMPSA–Hispec 3000 colloidal system was carried out by alternate dipping of the pre-treated Nafion membrane into positively and negatively charged polyelectrolytes.

Method 3. Addition of H_2PtCl_6 as an external salt into PSS solution: In this method, H_2PtCl_6 was firstly dissolved in PSS and this solution was then coated on a pre-treated Nafion membrane with alternate immersion of cationic (PAH) polyelectrolyte. Finally $PtCl_6^{2-}$ inside the multilayers was reduced to platinum black clusters by soaking the composite membrane into 2.0 mM $NaBH_4$ solution for 30 min as explained in method 1.

Method 4. Addition of H_2PtCl_6 as an external salt into PSS solution in the presence of C powder and Nafion solution: Apart from method 3, Nafion solution and carbon powder (Vulcan XC72) were added

into PSS solution. Then the similar procedure was applied according to method 3.

The MEAs prepared in this study are given in Table 1 depending on the experimental procedure for the preparation of CCMs and platinum loading conditions.

2.4. MEA preparation and cell performance tests

For the preparation of MEAs, 4 cm × 4 cm CCMs prepared by LbL technique and 2.5 cm × 2.5 cm commercial gas diffusion electrodes (GDEs) were assembled by hot pressing. All MEAs prepared in this study were pressed under the same conditions (145 °C, 500 psi, 5 min, then at 60 °C, 250 psi for half an hour). According to our pre-experiments about hot pressing conditions, it was found that this temperature and pressure were enough to get good adhesion of GDEs to CCMs. MEA was then compressed between two bipolar plates by using automatic fuel cell test fixture system with 5 bar. Concerning the cell performance test, 100 ml min⁻¹ hydrogen was fed into anode side and 300 ml min⁻¹ dry air was fed into cathode side. As it is known from literature, the best performance values were obtained if MEA was working under 100% humidity [36–39]. The cell temperature was set to 75 °C and the lines between humidification tanks and cell were heated up to

Table 1

MEA codes depending on CCM types prepared in different Pt loading conditions and LbL multilayer thicknesses.

MEA code	Method for CCM	Cationic polyelectrolyte	Anionic polyelectrolyte	Number of deposited bilayer	Pt agent	Reductive precipitation time (min)	Multilayer thickness (μm)
MEA-1	1	PAH	PSS	20	H_2PtCl_6	10	0.75
MEA-2	1	PAH	PSS	100	H_2PtCl_6	10	1.15
MEA-3	1	PAH	PSS	100	H_2PtCl_6	30	1.2
MEA-4	2	PAH	PAMPSA	20	Hispec 3000	–	0.17
MEA-5	3	PAH	PSS	100	H_2PtCl_6	30	1.26
MEA-6	4	PAH	PSS	20	H_2PtCl_6	30	0.8

temperature higher than 75°C to prevent possible water condensation. Before the performance test, the heater and humidification lines were purged with nitrogen and MEAs were conditioned for 6 h under reactant and oxidant feeding at 100% humidified condition and 75°C . The polarization curves were then obtained by scanning at 2.5 mV s^{-1} from OCV value to 0.1 V of fuel cell performance tests which were repeated several times to obtain accurate performance results. The pictures of Nafion[®] 117 based MEA, MEA fixture system, bipolar plates and PEM test station are shown in Fig. 1.

3. Results and discussion

3.1. Characterization of multilayer formation

SEM picture of the CCM prepared from PAH/PAMPSA–Hispec 3000 by LbL technique was taken in order to observe the multilayer formation and it is depicted in Fig. 2.

As it is seen from Fig. 2, the polyelectrolytes were deposited onto both sides of the pre-treated Nafion[®] 117 membrane successfully.

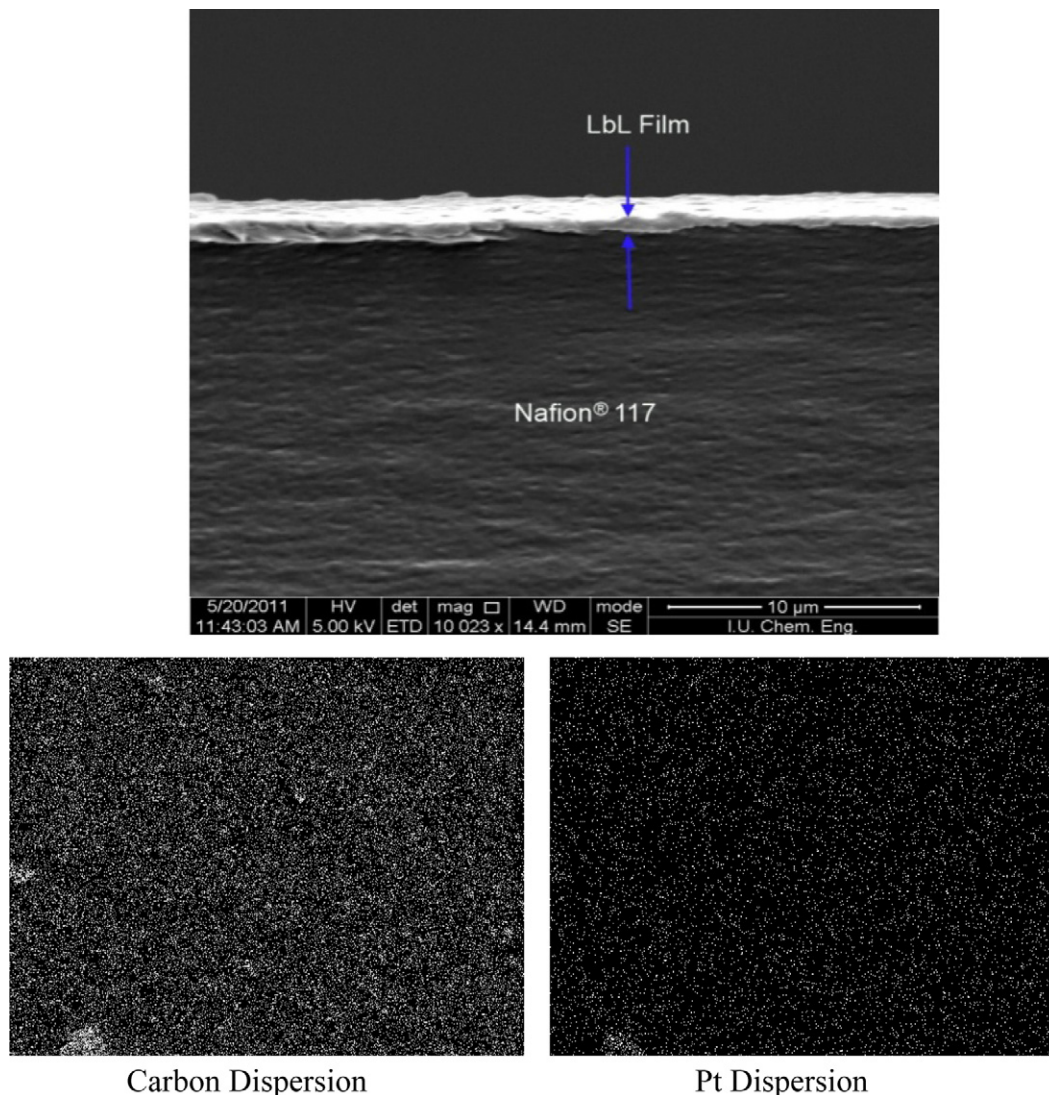


Fig. 2. Cross-sectional SEM picture of 20 bilayer of self-assembled PAH/PAMPSA–Hispec 3000 and Pt/C dispersion by SEM-EDAX.

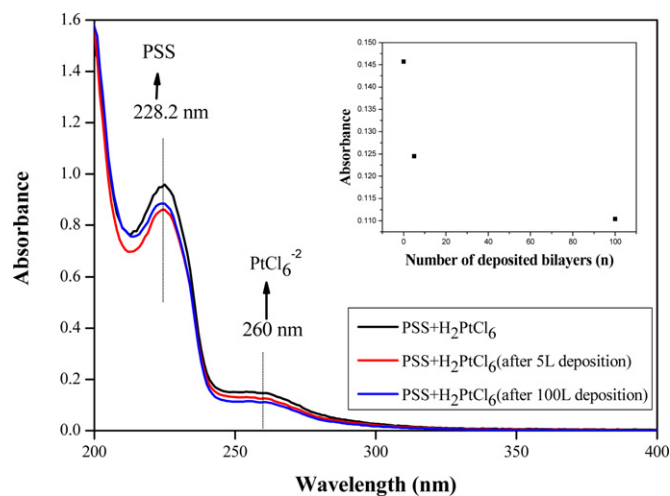


Fig. 3. UV-vis absorption spectra of PSS+H₂PtCl₆ solution (10⁻² monomole, pH=1.8) after 5 and 100 bilayer deposition.

The thickness of 20 bilayer of PAH/PAMPSA–Hispec 3000 deposited CCM was found to be in the range of 160–170 nm (roughly thickness of a bilayer is 8 nm). Also it is observed that Hispec 3000 was homogeneously dispersed on the membrane surface (inset of Fig. 2–SEM EDAX).

In addition, UV–vis spectroscopy was used to examine the platinum loading into LbL multilayer prepared from PAH/PSS + H₂PtCl₆ on membrane support and the UV spectra are given in Fig. 3. As an example, UV spectroscopy of H₂PtCl₆ containing PSS solution used for the formation of PAH/PSS + H₂PtCl₆ layers according to method 3 was followed. As it is known from literature, the sodium salt of PSS and PtCl₆²⁻ anion have characteristic peaks at 228 nm and at 260 nm, respectively. As one can see from Fig. 2 that the peak attributed to PtCl₆²⁻ (260 nm) was decreased with the number of deposited layers. In other words, the platinum loading into the multilayer increased with the number of deposited bilayer. However, this increase in platinum loading in LbL film does not grow (inset of Fig. 3) linearly. This result showed that the trapped catalyst inside the multilayer film does not depend on the number of deposited layers regularly.

In addition to SEM and UV analyses, ICP-MS analysis of platinum containing self-assembled membrane prepared according to method 1 in different reduction times (10 and 30 min) was performed to determine the amount of catalyst trapped inside LbL multilayer. Our results showed that the amounts of metallic platinum within LbL film reduced with NaBH₄ were found to be 0.023 μg cm⁻² and 0.15 μg cm⁻², respectively. As it is seen from ICP-MS results, the catalyst loading was very low by LbL deposition technique but it can be understandable when it is considered that the total thicknesses of coated bilayer were at the range of 0.17–1.26 μm. In other words, it can be emphasized that Pt loading can be improved by the formation of thicker multilayer.

One can also see from Table 1 that the thicknesses of CCMs varied in the range of 0.17–1.26 μm. The thickness of MEA-1 (0.75 μm) was lower than that of MEA-2 (1.15 μm) although the same polyelectrolyte couples and platinum agent were used in the experiments. This difference can be attributed to the number of deposited bilayer. However, it can be again emphasized that the platinum loading did not increase linearly with number of deposited layers as it is mentioned above. Furthermore, if the thickness of MEA-3 was considered, it can be concluded that reductive precipitation time of platinum salt did not significantly affect the multilayer thickness and the thickness values stayed nearly the same. When highly viscous PAMPSA and Hispec 3000 (20%

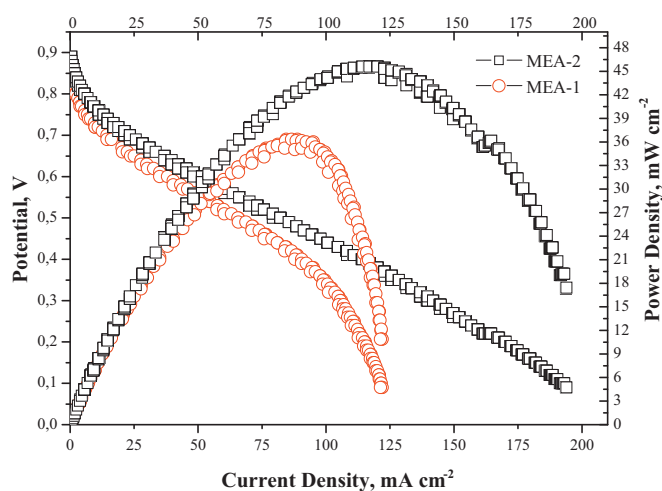


Fig. 4. Polarization and power density curves of MEA-1 and MEA-2 (hydrogen: 100 ml min⁻¹, air: 300 ml min⁻¹, humidity: 100%, cell temperature: 75 °C).

Pt/C) were used, interestingly the multilayers in lowest thickness were observed. The thickness of MEA-6, Vulcan XC (carbon powder) and platinum salt (H₂PtCl₆), was found to be 0.80 μm. This result showed that the multilayers can be formed thicker if platinum salt can be added into the dipping solution as an external salt as explained in literature [35].

3.2. Single cell performances of CCMs

20 and 100 bilayer of PAH/PSS LbL composite membrane was loaded with platinum by reductive precipitation of the platinum salt, H₂PtCl₆, inside the LbL film using NaBH₄ as the reductant. As it is known from literature, this approach of using free charged groups to complex and reduced metal salts has been demonstrated to be successful for the introduction of a number of metals within multilayered composite films [32]. In this method, 20 and 100 bilayer composite membrane was immersed into the platinum salt solution for at least 10 min to give the PtCl₆²⁻ salt enough time to permeate and complex with the ion pair site inside the LbL film. PAH/PSS LbL multilayer allows the singly charged BH₄⁻(aq) ions to permeate much more rapidly inside the LbL before the doubly charged PtCl₆²⁻ ions can start to leach out. This effect allows the reduction of most of the PtCl₆²⁻ salt to platinum black [32].

Figs. 4 and 5 illustrate a series of polarization and power density curves for MEAs prepared according to method 1 at 75 °C on 100% relative humidity. As one can see from Fig. 4, the peak power densities of MEA-1 and MEA-2 increased with increment of deposited bilayer from 20 to 100 and were found to be 37 and 45 mW cm⁻², respectively. This result may be attributed to the more amount of Pt loading with the number of deposited PSS and this leads to lower activation losses resulting in slight increment in power density. For comparison, LbL composite membrane was immersed into reductive agent for 30 min to observe the effect of reduction time. It is found from Fig. 5 that the reductive precipitation time for the preparation of CCM according to method 1 has significant effect on the peak power density. The power density of MEA-3 is found to be almost 2 times higher than that of MEA-2. This result can be attributed to the more amount of Pt loading with the reductive precipitation time leading to lower activation losses. ICP-MS results of MEA-2 and MEA-3 prepared according to method 1 confirmed this explanation. Further Pt utilizations of MEA-2 and MEA-3 were determined and found to be 90.0 mW mg_{Pt}⁻¹ and 179.9 mW mg_{Pt}⁻¹, respectively. If the cell performance of MEA-2 and MEA-3 was compared, it can be briefly stated that there is no linear relation between platinum loading and peak power

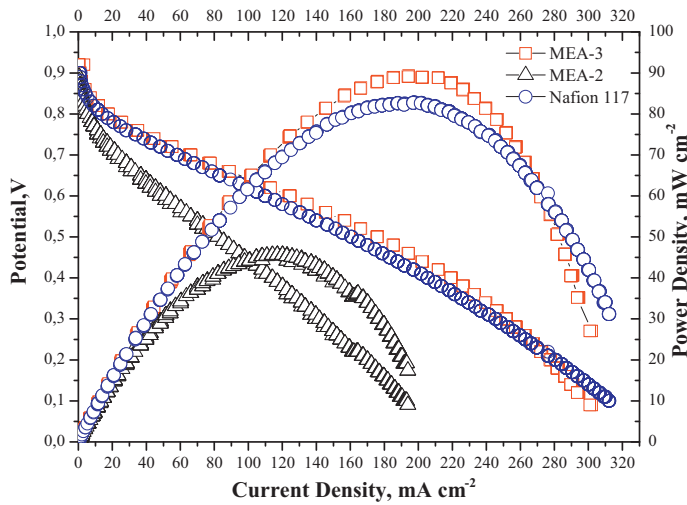


Fig. 5. Polarization and power density curves of MEA-2, MEA-3, Nafion® 117 (hydrogen: 100 ml min⁻¹, air: 300 ml min⁻¹, humidity: 100%, cell temperature: 75 °C).

density. This situation may be explained by the distribution of catalyst converting hydrogen to proton form. Another important parameter probably is the electrochemical active surface area of samples. Again, it can be observed from Fig. 5 that ohmic losses are significantly reduced while activation losses slightly dropped. This observed phenomenon in ohmic losses may be corresponded to the reductive agent which may expand the multilayer coated on the membrane and protons transport to the membrane faster.

Comparing CCMs prepared according to method 1 with pristine Nafion® 117, it can be emphasized that the maximum power density of Nafion based MEA is higher than that of MEA-1 and MEA-2. In our opinion, this can be explained that the multilayer on the each side of Nafion® 117 can block the transport of hydrogen onto catalyst layer. Also, the trapped catalyst amount can be considered insufficient for creating new path for fuel and catalyst interaction (three phase boundary). In the case of MEA-3, the polarization curves and maximum power density values are similar to those of pristine Nafion® 117 based MEA.

On the other hand, the mass transport polarizations of all CCMs were found to be higher than those of pristine Nafion® 117 based MEA. This behavior can be attributed to the formation of multilayers which restrict the diffusion of gaseous or product form at the cathode side, on both sides of membrane support. Also, more hydrophilic nature of LbL films may improve their water retention capability at high current density area and this may lead to more resistance to diffusion of gas (hydrogen) to the catalyst inside LbL film. Similar results were observed for MEA-1, MEA-3 and MEA-6.

In the second method, highly viscous PAMPSA was used as an anionic polyelectrolyte to obtain carbon–polyelectrolyte colloidal dispersion. In this method, Hispec 3000 (20% Pt/C) was dispersed in PAMPSA by using ultrasound and the obtained cell performance result is shown in Fig. 6. The peak power density of MEA-4 was found to be 36 mW cm⁻², which was more than 2 times lower than that of pristine Nafion® 117 based MEA. The possible reason of this poor result may be the high viscosity of PAMPSA creating dense LbL multilayer without porosity. So, this situation may not allow transportation of reactant gases to three phase boundary region. The other possibility is continuous desorption of the colloidal particles from the film surface into the PAMPSA solution during assembly. The similar result was reported by Hammond and Farhat [32].

Thirdly, H₂PtCl₆ was added into PSS and this solution was then coated on a pre-treated Nafion with alternate immersion of cationic

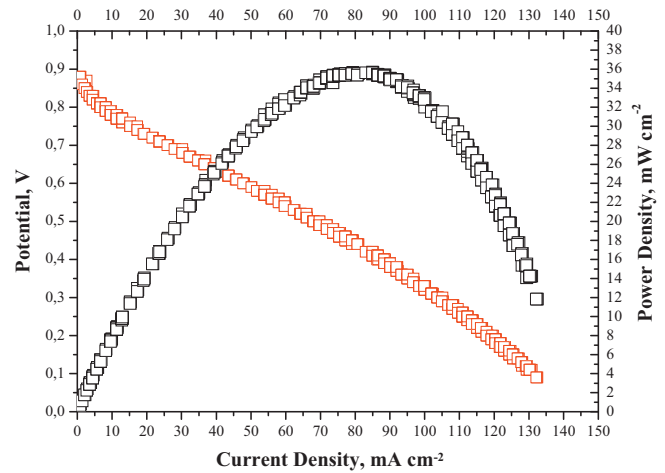


Fig. 6. Polarization and power density curves of MEA-4 (hydrogen: 100 ml min⁻¹, air: 300 ml min⁻¹, humidity: 100%, cell temperature: 75 °C).

(PAH) polyelectrolyte. Subsequently PtCl₆²⁻ within the multilayers was reduced to platinum black clusters by the presence of reductive agent. The polarization and power density curves of MEA-5 are plotted in Fig. 7. MEA-5 prepared according to method 3 exhibited the lowest power density among the other MEAs. This result can be attributed to the weakness of interfacial compatibility between catalyst layers and membrane. May be the another explanation is that H₂PtCl₆ can act as a salt for PAH/PSS system and this can lead to a thicker multilayer formation on the membrane support yielding a significant reduction in proton conductivity along the composite membrane. Similar results were reported in one of our previous works and literature [35,40].

In the fourth method, H₂PtCl₆ was firstly mixed with Vulcan XC and this mixture and Nafion solution were subsequently dispersed into PSS solution by means of an ultrasonic stirrer. Fig. 8 shows the polarization and power density curves of MEA-6. Promisingly, the highest power density was found to be 98 mW cm⁻² among all MEAs outlined in Table 1. Furthermore the cell performance of MEA-6 is significantly improved (18%) compared to pristine Nafion® 117 based MEA (85 mW cm⁻²) due to the improved contact between the catalyst layer and the membrane. This significant increase in power density can be attributed to the existence of both Vulcan XC increasing the porosity of gas diffusion area in LbL structure and Nafion solution leading to a larger and more effective three phase boundary (TPB) regions. Another possibility of

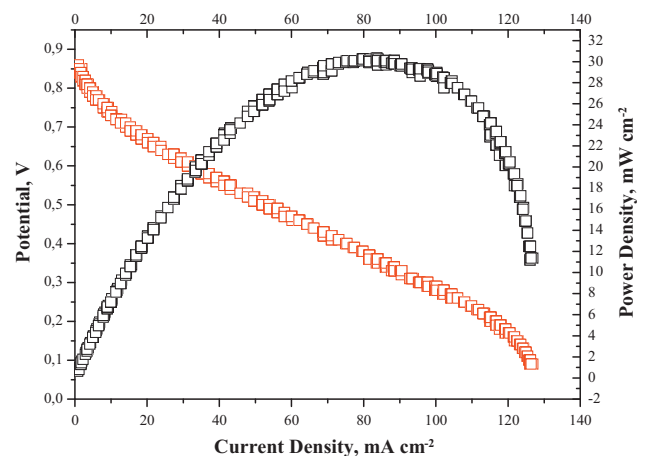


Fig. 7. Polarization and power density curves of MEA-5 (hydrogen: 100 ml min⁻¹, air: 300 ml min⁻¹, humidity: 100%, cell temperature: 75 °C).

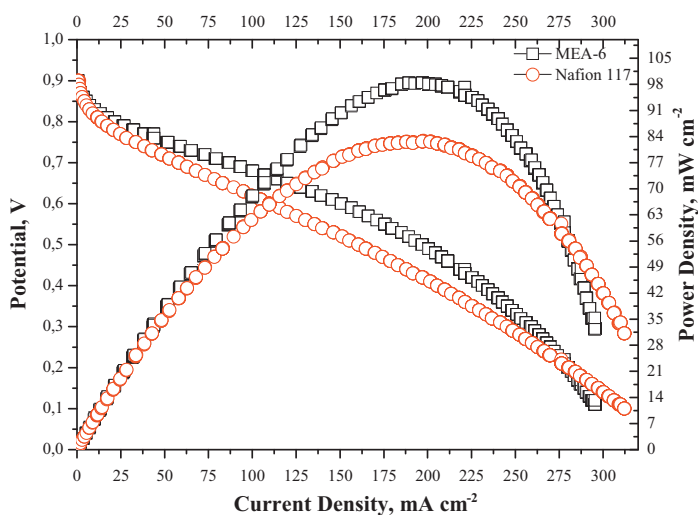


Fig. 8. Polarization and power density curves of MEA-6 and MEA of pristine Nafion® 117 (hydrogen: 100 ml min⁻¹, air: 300 ml min⁻¹, humidity: 100%, cell temperature: 75 °C).

observed highest peak power performance for MEA-6 is the addition of carbon which improves the electronic conductivity between platinum particles, which is as important as the membrane ionic conductivity, and a better gas distribution.

4. Conclusion

In this study, an alternative method is offered for the preparation of catalyst coated membrane (CCM) via using layer-by-layer (LbL) technique. CCMs are prepared according to four different methods and the multilayer formation is then confirmed by SEM and UV-vis analysis. From SEM analysis, it is observed that the polyelectrolytes are deposited onto both sides of the pre-treated Nafion® 117 membrane successfully. Pt loadings of CCMs prepared according to method 1 reduced in 10 and 30 min are found to be 0.023 μg cm⁻² and 0.15 μg cm⁻², respectively. This very low catalyst loading can be understandable when it is considered that the total thickness of coated bilayer is in the range of 0.17–1.26 μm. Further Pt utilizations of MEA-2 and MEA-3 were determined and found to be 90.0 mW mg_{Pt}⁻¹ and 179.9 mW mg_{Pt}⁻¹, respectively.

The fuel cell performance of 100 bilayer of PAH/PSS–H₂PtCl₆ deposited on Nafion membrane prepared according to method 1 is found to be higher than those of MEAs (90 mW cm⁻²) due to the more amount of Pt loading. If Pt loading is carried out according to methods 2 and 3, the ohmic polarization curves show that the ionic resistivity drastically increases due to incompatibility between catalyst layer and electrolyte (see Figs. 6 and 7). MEA-6 (PAH/PSS–H₂PtCl–Vulcan XC72–Nafion) prepared according to method 4 displays the best output performance (98 mW cm⁻²) due to the improved contact between the catalyst layer and the membrane. Another possibility is the addition of carbon which improves the electronic conductivity between platinum particles and provides a better gas distribution. Compared to pristine Nafion® 117 based MEA, the cell performance of MEA-6 is significantly improved (18%). In other words, this interesting and promising result exhibits that ultra low platinum loading within LbL multilayer causes a

drastic enhancement in cell performance due to creation of new path for fuel and catalyst interaction (three phase boundary).

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