DEPOSITION CONDITION EFFECT OVER MULTILAYERS NANOCOMPOSITE MEMBRANE GROWTH

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Abstract–*This work is dealing with the deposition of self-assembled polyelectrolyte multilayers on Nafion membrane by layer-by-layer (LbL) method, to obtain a proton exchange membrane for direct methanol fuel cell. The formation of self-assembled multilayers film growth was characterized by UV–vis spectroscopy and the proton conductivity was measured using impedance spectroscopy.*

Keywords: *layer-by-layer, polyelectrolytes, UV-Vis spectroscopy, impedance spectroscopy (IS)*

1. INTRODUCTION

Development of thin films with special characteristics has many applications for microfabrication of nano-bio-reactors / devices [1], sensors, drug delivery systems [2] or fuel cells [3]. In the field of direct methanol fuel cells, Nafion membrane is playing a key role as proton exchange, but some deficiencies have been observed, such as falling of proton conductivity at temperatures above 100°C and high methanol permeation, which causes loss of fuel and decreases cathode performance in PEMFCs [4]. These drawbacks can be solved by preparing a Nafion based multilayers thin membrane using electrostatic adsorption of oppositely charged polyelectrolytes layer-by-layer (LbL) self-assembled.

This technique has received much attention during last years being a simple alternative method to obtain nanocomposite thin films in which layers of nanometer thickness are organized in a specific predetermined order. The studies reported in the last years regarding the structural and physical properties of polyelectrolyte multilayers confirmed that layer thickness and molecular organization of adsorbed polymers can be tuned by varying salt concentration, solvent type or pH of the solutions [5]. Also, it was revealed that the structures obtained are not stratified into well-defined layers / multilayers, the polyelectrolyte molecules being interdiffused, the interpenetration increasing with weakness of polyelectrolytes towards a 1:1 ratio of stoichiometric complexes of anionic and cationic pairs [6]. It is the aim of this study to prepare a multilayer methanol blocking film on Nafion membrane using LbL self-assembly of oppositely charged polyelectrolytes. The influences of the deposition conditions, such as concentration and pH of polyelectrolyte solutions over membrane thickness and proton conductivity are analyzed.

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2. EXPERIMENTAL METHODS

2.1. Chemicals

Polysodium(4-styrene sulfonate) (PSS), MW 200.000 g/mol 30% water solution, poly(diallyldiamonium chloride) (PDADMA), MW 200.000-350.000 g/mol 20% water solution, sodium chloride and Nafion 117 membrane, 157 µm in thickness, have been purchased from Sigma-Aldrich, Germany. All aqueous solutions were made with deionized water, further purified with a Milli-Q system (Millipore).

2.2. Layer-by-Layer Self-Assembly on Nafion

Nafion contains both regions - hydrophobic, due to the polyethylene backbone and hydrophilic, given by the sulphonic groups [7], the last of them being responsible for the methanol cross-over when it is used as proton exchange membrane. This is the reason for blocking the hydrophilic areas in order to stop the methanol cross-over through the protonated Nafion membrane. The presence of anionic sulphonic groups on membrane surface, make possible the electrostatic interactions between Nafion and the positively charged PDADMA polyelectrolyte.

The protonation of the Nafion membrane was obtain by treatment for 40 minutes at 80°C in 5 %

H_2O_2, washing in deionised water (DI) and finally, washing in 9 % H_2SO_4, in order to obtain a protonated membrane. Then, the membrane was immersed in each 20 mM (monomole) solution of PDADMA and 20 mM PSS for 10 minutes, at room temperature to deposit the multilayer films on the Nafion membrane. After each dipping step, the membrane was rinsed with deionized water to remove weakly bound polyelectrolyte molecules. The layer-by-layer assembled membrane was finally rinsed with deionized water, followed by protonation in 1 M H_2SO_4 solution and then rinsed again with deionized water.

In order to establish the influence of concentration and ionic strength of polyelectrolytes solutions over film growth two concentrations, 10^{-3} and 2×10^{-2} M, at the same reaction time, 7 minutes, were used. The ionic strength influence was monitored by preparing 2×10^{-2} M solutions of polyelectrolytes using sodium chloride 0.5 M, as solvent. The immersion time was 10 minutes and the obtained membranes were rinsed in deionized water after each deposition step.

3. RESULTS AND DISCUSSIONS

Both UV-Vis spectroscopy (Hitachi High Technologies U-0080D spectrophotometer) and impedance spectroscopy (PARSTAT 2273, Princeton Applied Research) have been used to monitor the growth of the self-assembled multilayers of polyelectrolytes on Nafion membrane and the proton conductivity of the resulting membrane.

3.1. UV-Vis measurements

The UV-Vis spectra of protonated Nafion and Nafion with 2, 4, 6, 8, 10 and 12 bilayers of PDADMA/PSS deposited from 10^{-3} M aq. sol. are presented in figure 1. PSS has a characteristic UV absorbance at 228 nm [8], due to the sulphonic group and the cationic polyelectrolyte, PDADMA, is transparent in UV domain, so the absorbance is related only to the PSS. This graphs show that the absorbance at 228 nm is not so well marked out, but if it is ploted the absorbance dependence (*A)* over deposited bilayers (*n)*, at this wavelength, it can be observed, indeed an increasing, which is not in proportional with *n*, as it is revealed in the inset graph (*S* represents the slope, giving by the liniar fitting).

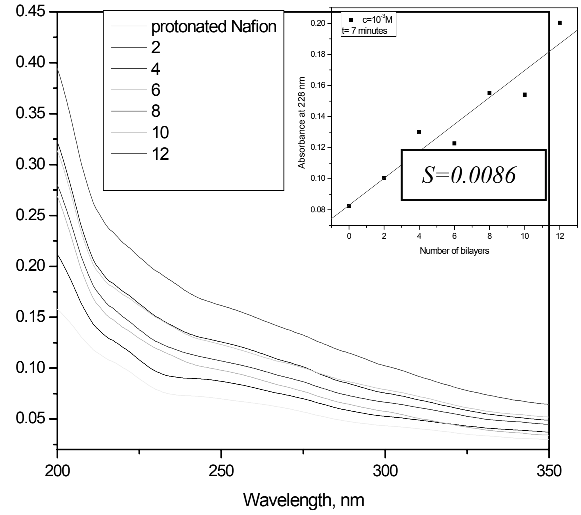

Fig. 1. UV–Vis absorption spectra of self-assembled multilayer membranes composed of 2–12 bi-layers of PDADMA/PSS, at the concentration of 10^{-3}M.

By increasing the both polyelectrolyte concentrations to 2×10^{-2} M, at the same deposition time, the UV-Vis absorption results obtained for protonated Nafion with self-assembled bilayers are shown in figure 2.

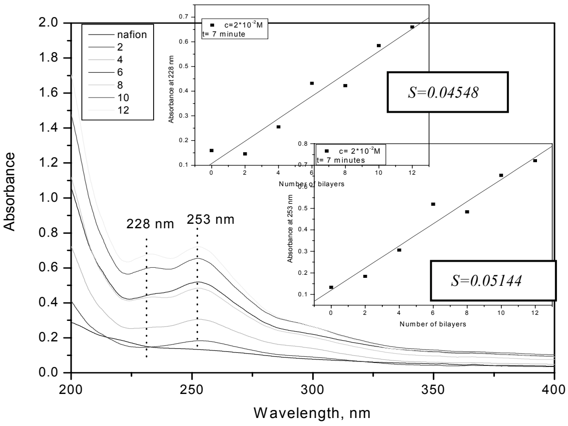

Fig. 2. UV–Vis absorption spectra of self-assembled multilayer membranes composed of 2–12 bi-layers of PDADMA/PSS, at the concentration of 2×10^{-2} M.

Very small values of the absorbance at 228 nm are evident, but a generally increasing with the deposited bilayers is also present. A supplementary absorbance band at 253 nm, more pronounced, which is missing in the case of Nafion, is observed. This band is related to the aromatic ring from PSS. Comparing the slopes of the linear fitt of the intensity peak absorbance at 228 nm values' graphs, for concentrations, 10^{-3} and 2×10^{-2} M, it can be observed that the second one is at least 5 times higher. This analysis indicates that the multilayer films deposited on Nafion were thicker for more concentrated polyelectrolytes solutions [9], consequence of the stronger electrostatic interactions when concentrated polyelectrolytes solutions are used.

In the case of increasing the ionic strength of the polyelectrolytes solutions, the obtained UV-Vis spectra for protonated Nafion and the deposited multilayers are presented in figure 3:

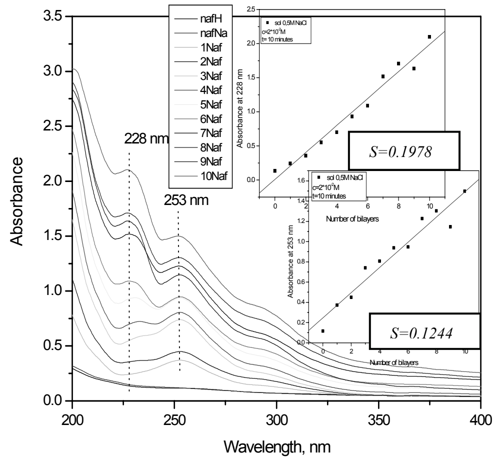

Fig. 3. UV–Vis absorption spectra of self-assembled multilayer membranes composed of 2–10 bi-layers of PDADMA/PSS, at the concentration of 2×10^{-2} M in the presence of NaCl.

This figure reveals that the absorbances at 228 and 253 nm are much higher in the case of adding NaCl, then using aq. sol. of polyelectrolytes. This is explained by reducing the electrostatic repulsions between the charges of polyelectrolytes chains; the charges are screened by the counterions of the added salt and the chains will have a coiled conformation [10], so there are obtained thicker films.

3.2. Proton Conductivity

In order to evaluate the effect of PDADMA/PSS multilayer formation on proton conductivity of the polyelectrolyte-Nafion composite membrane, the proton conductivities were measured at 25ºC, in transversal configuration, in which, the multilayers nanocomposite membrane is sandwiched between the two platinum flat electrodes (schematic presented in figure 4).

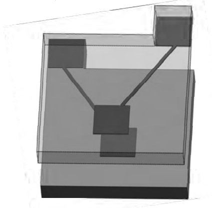

Fig. 4. Schematic representation of conductivity measurement system.

In this case, the proton conductivity is given by the equation 1:

$$\sigma_{trans} = \frac{l}{R_{m-trans} \cdot A} \approx \frac{0,02}{R_{m-trans}} (S \cdot cm^{-1}) \qquad (1)$$

where l is the distance between the electrodes (~ 200 µm), A – section area (1 cm^2) and $R_{m\text{-}trans}$ – membrane resistance. The membrane resistance have been extracted from the impedance plot assuming a simplified equivalent circuit, $\mathbf{R_{m\text{-}trans}(QR)}$, $R_{m\text{-}trans}$ – membrane resistance; Q – constant phase element characteristic to the capacity of double layer at the interface eletrodes/membrane, R – resistance of the charge transfer at interface.

The impedance spectroscopy measurements were taken in the range of 1Hz–100 kHz, applying an AC of 10mV at open circuit potential (OCP). Figure 5 shows the Nyquist (a) and Bode (b) plots of self-assembled multilayers membranes composed of 2-13 bilayers of polyelectrolytes at the concentration of 2×10^{-2} M and the same deposition time, 7 minutes.

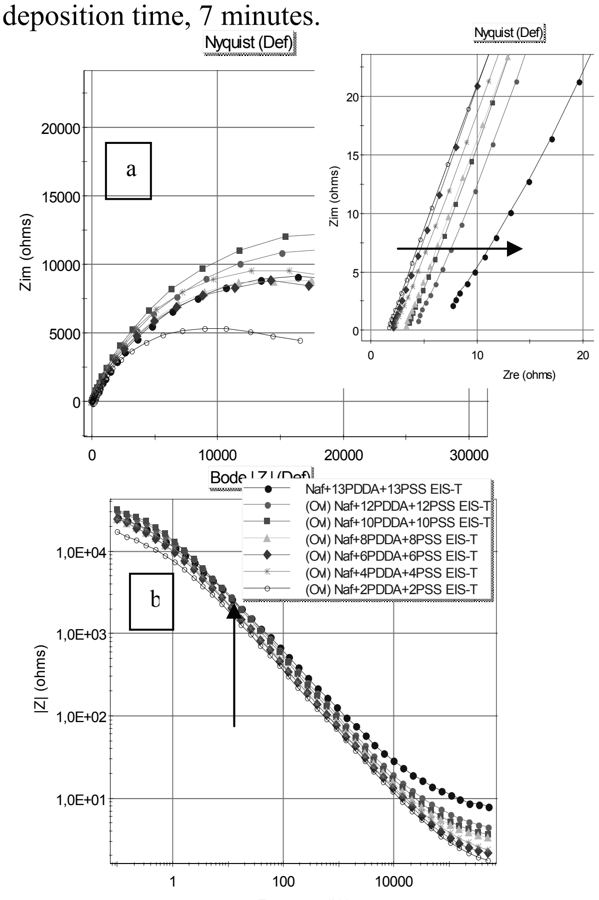

Fig. 5. Nyquist (a) and Bode (b) plots of self-assembled multilayer membranes composed of 2–13 bi-layers of PDADMA/PSS, at the concentration of 2×10^{-2} M and 7 minutes, deposition time

The Nyquist diagram shows an increasing of the membrane resistivity with bilayers number, starting with the fourth bilayer, supported also by the Bode diagram. The calculated multilayer membrane conductivities are in the range of $1.19\times10^{-2} - 0.34\times10^{-2}$ S cm^{-1}, decreasing with the bilayers number, as it is depicted in figure 6:

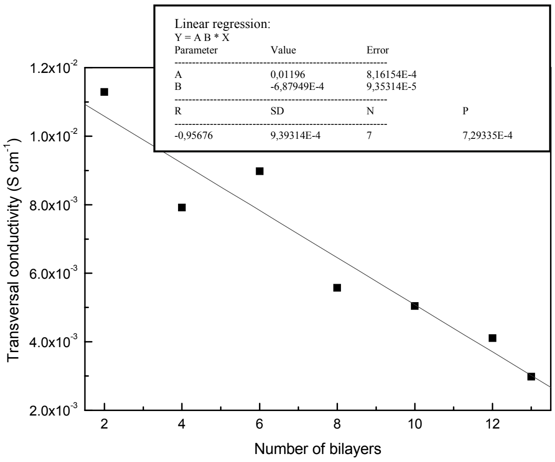

Fig. 6. Transverse conductivities variation as a function of number of deposited bilayers

It can be observed that the values can be linear fitted, a more pronounced decreasing being observed after the sixth bilayer. The obtained conductivities are in good agreement with the present studies [11]: the increasing of the concentration give rise to higher conductivites for the multilayer membranes, as in table 1:

Table 1. Proton conductivity changes of the composite membranes

Multilayers membrane/ experimental conditions	Number of bilayers	Proton conductivity at 25°C (S cm^{-1})
$(PDADMA/PSS)_n$ aq solutions, c = 10^{-3}M	2	$1{,}28\times10^{-2}$
	6	$1{,}05\times10^{-2}$
	10	$0{,}58\times10^{-2}$
$(PDADMA/PSS)_n$ aq solutions, c = 2×10^{-2}M	2	$1{,}19\times10^{-2}$
	6	$0{,}95\times10^{-2}$
	10	$0{,}45\times10^{-2}$
$(PDADMA/PSS)_n$ c= 2×10^{-2}M, NaCl 0,5 M	2	$1{,}31\times10^{-2}$
	6	$1{,}09\times10^{-2}$
	10	$0{,}83\times10^{-2}$

4. CONCLUSIONS

The multilayer structures on Nafion membrane were fabricated by LbL self-assembly of PDADMA and PSS, the influence of concentration and ionic strength of polyelectrolytes solution over the membranes thickness and proton conductivity being monitored. It has been observed that the usage of more concentrated solutions leads to more significant increasing of the membrane thickness. The same observation is made in the case of increasing ionic strength, also.

Regarding proton conductivity of the self-assembled composite membranes, there is a decreasing given by the multilayers films grown on Nafion membrane, from 1.31×10^{-2} S cm^{-1} to 0.34×10^{-2} S cm^{-1}, when 13 bilayers were deposited. For envisaged application, it is appropiate a number of 6-8 bilayers to be assembled, depending on solution concentration and ionic strength.

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