

Enhanced Performance of the Solid Alkaline Fuel Cell Using PVA-KOH Membrane

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Poly(vinyl alcohol) (PVA) is a polyhydroxy polymer, which is very common in practical applications because of its easy preparation and biodegradability. In this work, the alkaline solid polymer electrolyte membrane, based on potassium hydroxide doped PVA, was proposed for the fuel cell applications, aiming at a new cost-effective, easy preparing and chemical stable alkaline anion exchange membrane using physical cross-linking procedure. The membrane electrode assemblies (MEAs) using KOH doped PVA as membranes, were prepared with commercial platinum catalyst. We have investigated the performance of the solid alkaline fuel cell (SAFC) and results are presented to show current-voltage characteristics.

Keywords: Poly(vinyl alcohol), physical cross-linking, solid alkaline fuel cell, MEA performance

1. INTRODUCTION

To overcome the drawbacks of the PEM fuel cells, a concept of using solid alkaline anion exchange membranes (SAAEMs) evoked great interest [1]. Alkaline fuel cells (AFCs) are the cheapest of fuel cells to manufacture.

One of the advantages of the AFCs is the faster kinetics of oxygen reduction reactions in an alkaline media, which allows the use of non-precious metal electrocatalysts such as silver catalysts and perovskite-type oxides [2]. The catalyst required for the electrodes can be any of a number of different chemicals that are inexpensive compared to those required for other types of fuel cells. In addition, the water management is improved due to the electro-osmotic drag transporting water away from the cathode and the so-called alcohol 'crossover' problem is also highly reduced because of the opposite movement of the hydroxide ion to the movement of proton in acidic membrane [3].

Alkaline fuel cells were first developed in the 1930s by F. T. Bacon, thus they pre-date PEM fuel cells and represent one of the oldest fuel cell types. Early alkaline fuel cells operated with H₂ as the fuel at a temperature between 50 °C and 200 °C and employed a liquid electrolyte (*e.g.* an aqueous solution of KOH) [1]. NASA used such fuel cells in the 1960s to power Apollo space missions [4]. The technology, however, has suffered from problems arising from the use of liquid (aqueous) electrolytes; in particular the inevitable shunt currents and poisoning by carbon dioxide which leads to the formation of carbonate precipitates in the liquid electrolyte. The strongly alkaline electrolytes absorb even the smallest amount of CO₂, which in turn eventually reduces the conductivity of the electrolyte. Consequently pure hydrogen (rather than an impure hydrogen stream containing CO) and highly purified oxygen (rather than air) must be used as the fuel and oxidant feeds. The use of such high purity oxygen, in particular, increases significantly the cost of generating electricity with a liquid electrolyte alkaline fuel cell. Today, researchers have moved to polymeric anion exchange membranes as the hydroxide transport medium in an alkaline fuel cell [5].

The quaternized polymers based on alkaline anion exchange membranes have been proposed as electrolytes in alkaline fuel cells such as polysiloxane, poly(oxyethylene) methacrylates, polysulfone, cardo poly(ether sulfone), poly(phthalazinon ether sulfone ketone), poly(ether imide) and radiation-grafted PVDF and FEP. However, the quaternized polymers are unstable in alkaline medium at temperatures above 60 °C [5 - 9].

PVA is a polyhydroxy polymer, which is very common in practical applications because of its easy preparation and biodegradability [10]. It has been selected as polymer matrix in view of its film-forming capacities, hydrophilic properties and high density of reactive chemical functions favorable for cross-linking by irradiation, chemical or thermal treatments [11 - 13]. It is reported that PVA gels prepared by freeze-thaw technique resulted in higher mechanical strength in comparison with cross-linking of PVA by chemical or irradiative methods [14]. One of the major challenges with the development of SAAEMs is the availability of suitable ionic conductivity with high chemical stability under fuel cell operating conditions.

In this article, the alkaline solid polymer electrolyte membrane based on alkaline doped poly(vinyl alcohol) (PVA–KOH) was proposed aiming at a new cost-effective, easier preparing and chemical stable SAAEM using physical cross-linking procedure for the fuel cell applications. Compared to other cross-linking procedures, physical method is the simplest and cheapest way of obtaining PVA-KOH solid alkaline membrane suitable for fuel cell applications as suggested by experiments presented in this paper. The membrane electrode assemblies (MEAs) using KOH doped PVA as membranes, were prepared with commercial platinum catalyst. We have investigated the performance of the solid alkaline fuel cell (SAFC) and results are presented to show current-voltage characteristics.

2. EXPERIMENTAL

2.1. Membranes preparation

Membranes based on poly(vinyl alcohol) were prepared from 5 wt% of PVA (Mw ~195000, Aldrich, Germany) water solution by freezing/thawing process. This process involves physical cross-

linking of polymer chains and was carried out in glass molds (20 cm x 20 cm) separated by rubber gaskets of various size to obtain PVA membranes of three different thicknesses. PVA solution was poured into the glass mold and left in freezer at -18 °C for 18 h. After that period PVA solution was thawed at room temperature for 6 h. The cycle of freezing and thawing was repeated four times. Prepared PVA gels were taken out from molds, dried to constant mass and left in 6 M KOH solution for 24 hours, before MEA preparation.

2.2. Membrane and electrode assembling

The anodes and cathodes were made by loading 0.2 mg cm⁻² of 40 wt% Pt/C (AlfaAesar) on carbon paper (PT75, AvCarb), as support electrode, and subsequently anode and cathode were cold pressed with PVA-KOH membrane between them, to obtain three different MEAs, with an active area of 8 cm².

2.3. Measurements and characterization

Specimens of 1 cm diameter are immersed in 6 M KOH solution and uptake of KOH, Q , was calculated as:

$$Q = 100 \times m_{\text{KOH}}/m_d = 100 \times (m_e - m_d)/m_d \quad (1)$$

where m_{KOH} is the weight of absorbed KOH solution after 24 h, m_e is the weight of polymer specimen soaked in KOH for 24 h, and m_d is the weight of the dry specimen. For each membrane sample obtained Q is the average value of three measurements.

The ionic conductivity of the formed membranes was measured by an AC impedance technique using an electrochemical impedance analyzer Gamry 750, where the AC frequency was scanned from 100 kHz to 0.1 Hz at a voltage amplitude of 10 mV. Fully hydrated membranes were sandwiched in a Teflon conductivity cell equipped with stainless steel electrodes having area of 4 cm². Ionic conductivity, σ (S cm⁻¹), was calculated according to the following equation:

$$\sigma = d/RA \quad (2)$$

where d is the thickness of the membrane between two potential sensing stainless steel plates, R is the membrane resistance, and A is the membrane surface.

The cross section of H₂|Pt/C|PVA–KOH|Pt/C|O₂ MEAs was examined with a scanning electron microscope (SEM, JEOL JSM-5800). The samples were coated with a thin layer of Pd-Au alloy and the structure was imaged at an acceleration voltage of 5 kV.

The SAFC configuration MEAs: H₂|Pt/C|PVA–KOH|Pt/C|O₂, were used in a single-cell power-voltage measurements. The MEA was inserted into fuel cell hardware Heliocentris. Assembled fuel cell was fed with oxygen (cathode) and hydrogen (anode) gas stream at flow rate of 0.3 l/min and 0.6

l/min, respectively. Current – voltage curves were collected using electronic load station HephastMini150.

Electrochemical impedance spectra (EIS) were recorded in a pseudo-potentiostatic regime, in two electrode arrangement using Gamry G-750 Potentiostat/Galvanostat. All impedance spectra were recorded from 0.1 Hz to 100 kHz. In order to investigate the home made fuel cells characteristics, ac spectra were obtained at open circuit voltage (OCV) and fuel cell operating current of 0.5 A.

3. RESULTS AND DISCUSSIONS

3.1. KOH uptake and ionic conductivity of alkaline PVA

The alkaline PVA membranes were obtained using procedure given in Section 2. The membrane samples with different thickness appeared transparent and homogeneous with mechanical flexibility. Results of the ionic conductivity measurements using AC impedance are given below in Table 1. The intercept with the Z' (Re Z) axis was taken as the bulk resistance, R , of the polymer electrolyte membrane. The A is surface and d membrane thickness.

Table 1. Ionic conductivity and KOH uptake of the alkaline PVA membranes measured at 25°C

Membrane sample	Q (%)	m_{KOH} (mg)	d (cm)	$R \times A$ ($\Omega \text{ cm}^2$)	Σ (S cm^{-1})
PVA1	107	11.2	0,0047	0,570	0,0083
PVA2	111	28.9	0,0082	0,893	0,0092
PVA3	106	41.7	0,0110	0,901	0,0122

The values for KOH uptake, Q , and the weight of KOH solution imbibed by polymer specimens of 1 cm diameter are summarized in Table 1. The values for Q are quite similar for all samples since there is no difference in preparation procedure. What differs is the amount of imbibed KOH solution as a consequence of various thicknesses of membranes. As expected, higher ionic conductivity is obtained for the samples with higher KOH content. It can be seen that the ionic conductivity measured at 25 °C reached a maximum value of $1.2 \times 10^{-2} \text{ S cm}^{-1}$ for the thickest PVA doped with 6 M KOH solution. This is two order of magnitude higher ionic conductivity than obtained by directly mixing a viscous PVA solution with concentrated KOH aqueous solution as reported elsewhere [5]. This result suggests that some of KOH molecules are taken into the polymer by water molecules. The chemical interaction, such as dipole–dipole interaction including hydrogen bonding and induction forces, may take place between C–O and OH groups on PVA and KOH during alkali doping, which is helpful for the ionic conductivity of PVA. Some authors report that the ionic conductivity decreases with additional doping of KOH concentration in solution, for example, when KOH concentration in solution is higher than 6 M [5]. It seems that more OH^- could not be taken into

the polymer at high KOH doping solution due to the weak ionic mobility (caused by formed ion-pairs or increased viscosity), thus a decrease in ionic conductivity.

3.2. Single-cell performance test

Investigations of the $\text{H}_2|\text{Pt}/\text{C}|\text{PVA}-\text{KOH}|\text{Pt}/\text{C}|\text{O}_2$ FC were comprised of the current–voltage characterizations. This characterization is the basic method for evaluation of the fuel cell performance.

The performance of MEA, measured in terms of the current generated in the external circuit, depends on the overall outcome of a series of successive steps: mass transport and surface reaction at the anode, proton conduction in the membrane, surface reaction with charge transfer and mass transport in the cathode compartment.

The Fig. 1a shows I – V characteristics of the AFCs using KOH doped PVA as SAAEM. It can be seen that the peak power of 0.35 W was achieved for the $\text{H}_2|\text{Pt}/\text{C}|\text{PVA2}-\text{KOH}|\text{Pt}/\text{C}|\text{O}_2$ FC, at cell voltage of almost 0.5 V, with a peak current of 0.8 A at room temperature. The open circuit potential of all SAFCs was found to be around 0.98 V.

It can be seen that even with low catalyst loading (0.2 mg cm^{-2} both on the anode and on the cathode) SAFCs containing PVA1 and PVA2 membranes exhibited very good performance. It is also evident that MEA assembled using the PVA2-KOH membrane showed best performance in spite of slightly lower ionic conductivity. This result proved how important is to optimize the thickness of membrane among the other parameters which influence performances of MEA. In many articles preparation of MEA and subsequent testing in an AFC station are not presented, which are unavoidable steps for overall prediction of usefulness of selected membrane in an SAFC.

For complete insight of how successful this system is, and importance of these results, Fig. 1b, shows current-voltage characteristics of the PEMFC obtained using the same Heliocentris hardware. The MEA in the PEMFC was made from commercial components 40 wt% Pt/C (AlfaAesar) and Nafion 115 membrane with an active area of 8 cm^2 . MEA was assembled by hot pressing the anode, membrane, and cathode together. Nafion 115 membrane was treated in 3% $\text{H}_2\text{O}_2(\text{aq})$, and then in 1 M $\text{H}_2\text{SO}_4(\text{aq})$ for 1 h at $80 \text{ }^\circ\text{C}$, followed by a careful washing step with double distilled water.

Platinum loading was the same as for $\text{H}_2|\text{Pt}/\text{C}|\text{PVA}-\text{KOH}|\text{Pt}/\text{C}|\text{O}_2$ FC, 0.2 mg cm^{-2} both on the anode and on the cathode. These experiments do not address design issues, such as influence of the various designs of current collector plates, gas channels and operating parameters such as pressures and temperatures, on fuel cell efficiency. That is the reason why the presented powers for both systems $\text{H}_2|\text{Pt}/\text{C}|\text{PVA}-\text{KOH}|\text{Pt}/\text{C}|\text{O}_2$ FC and $\text{H}_2|\text{Pt}/\text{C}|115 \text{ Nafion}|\text{Pt}/\text{C}|\text{O}_2$ are not as high as they might be if these parameters were optimized. However, comparison of two MEAs clearly shows excellent performance of the solid alkaline PVA membrane cross-linked by physical means. The power obtained with $\text{H}_2|\text{Pt}/\text{C}|\text{PVA2}-\text{KOH}|\text{Pt}/\text{C}|\text{O}_2$ FC is higher than $\text{H}_2|\text{Pt}/\text{C}|115 \text{ Nafion}|\text{Pt}/\text{C}|\text{O}_2$ FC. This result was not reported in the literature and could be very important for further investigations and analysis.

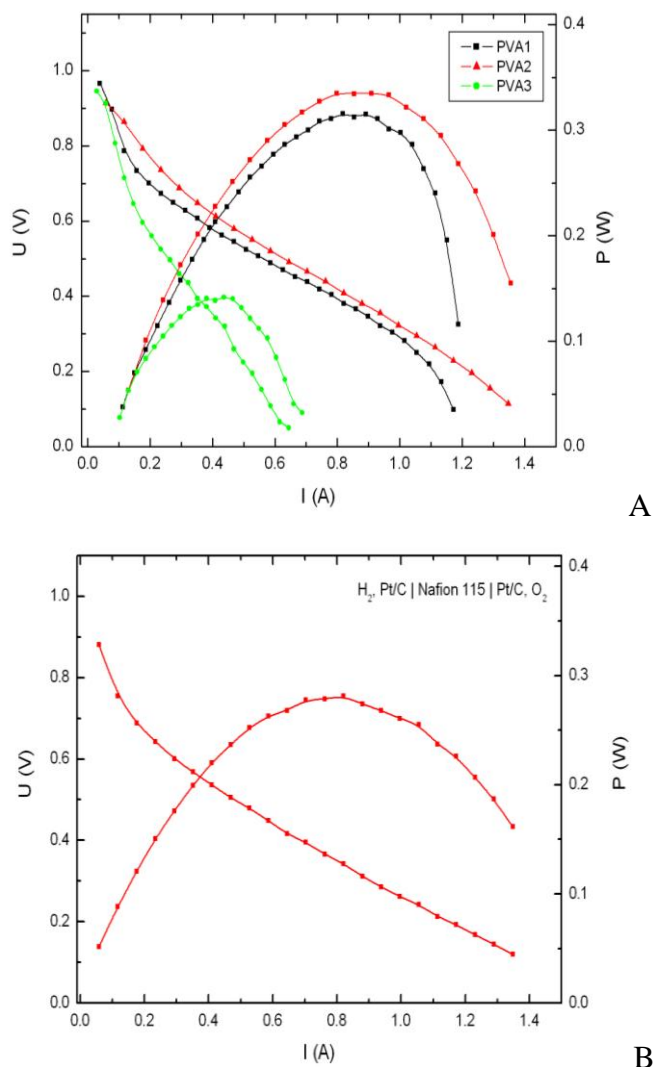


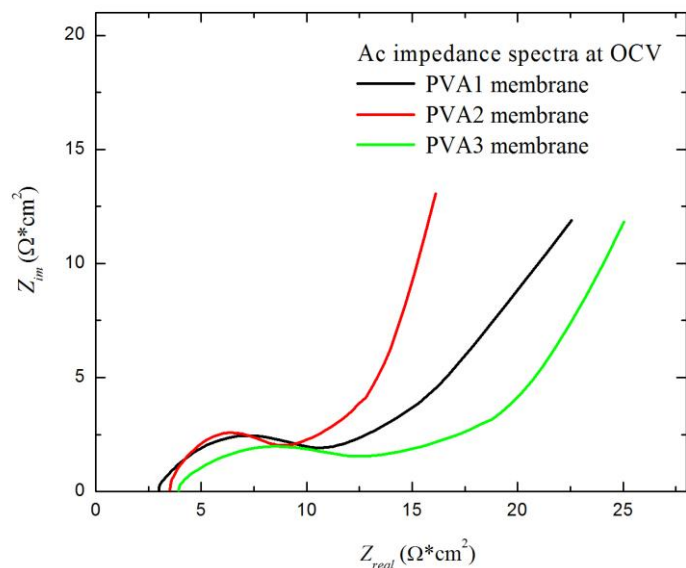
Figure 1. *I*–*V* characteristics: a) the solid alkaline $H_2|Pt/C|PVA\text{--}KOH|Pt/C|O_2$ fuel cell using KOH doped physically cross-linked PVA as membrane; b) PEM, $H_2|Pt/C|Nafion 115|Pt/C|O_2$. Catalyst loading 0.2 mg cm^{-2} of Pt on each electrode.

3.3. EIS spectra

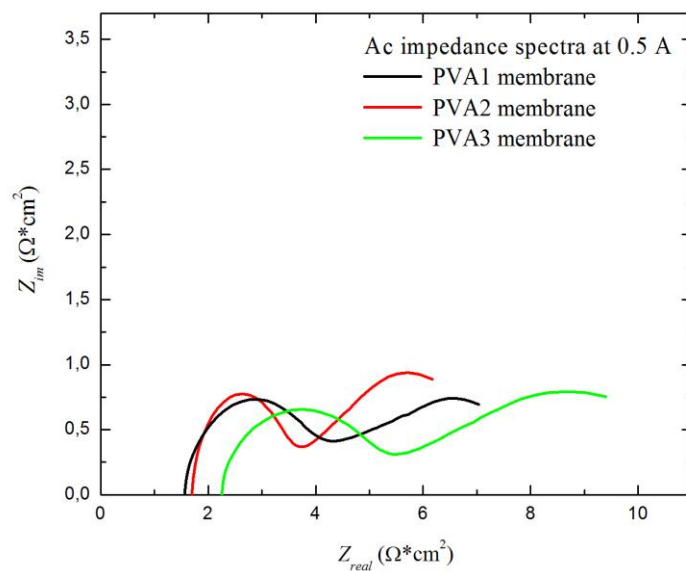
The EIS analysis of the fuel cell consists of gathering information on the surface reactions at the electrodes and through the membrane. The simplest behavior of the impedance spectrum for the SAFC contains two or three merged impedance arcs in the Nyquist plot. The high-frequency intercept of the single impedance arc on the real axis represents the total ohmic resistance of the cell, which can be expressed as the sum of the contributions from contact resistances between components and ohmic resistances of the cell components such as the membrane, catalyst layer, gas diffusion layer, and current collector plates [15]. The cathode kinetic behavior is represented with the impedance at low frequencies while the anode kinetic behavior is represented with high frequencies loop. The diameter

of the kinetic loop is a measure of the charge transfer resistance of the hydrogen oxidation reaction (HOR) or the oxygen reduction reaction (ORR).

EIS spectra of operating SAFC using as prepared PVA membranes are presented at Fig. 2.



A



B

Figure 2. Ac impedance spectra of the solid alkaline H₂|Pt/C|PVA–KOH|Pt/C|O₂ fuel cells using PVA1, PVA2 and PVA3 membrane at: a) OCV and b) operating current of 0.5 A.

The AC impedance spectra of the SAFC consist of two pronounced arcs, belonging to the anode impedance at higher frequencies, and the cathode at lower frequencies, since the electrode reactions take place in the alkaline media. The anode and the cathode charge transfer arcs decrease with increasing current density (decreasing voltage), as expected. However, it can be seen that the cathode charge transfer arc decreases more rapidly with increasing polarization. On the other hand,

water formed on the anode side is partially blocking the Pt active sites, thus the decrease of the impedance response is relatively lower.

These results are in good accordance with the measured performance of the SAFCs using these membranes. It is obvious that the impedance spectra of the SAFCs using PVA1 and PVA2 membrane are similar, in terms of electrolyte resistance and charge transfer resistances, which explains similar polarization curves. The SAFC utilizing PVA3 membrane exhibits higher ohmic resistances, as well as charge transfer resistances, which limits the performance of the SAFC.

3.4. SEM characterization

SEM photographs for the cross-sectional views of solid alkaline membranes PVA–KOH and $H_2|Pt/C|PVA-KOH|Pt/C|O_2$ MEAs are shown in Fig. 3. Prior to the experiment, the samples were freeze-fractured in the liquid nitrogen.

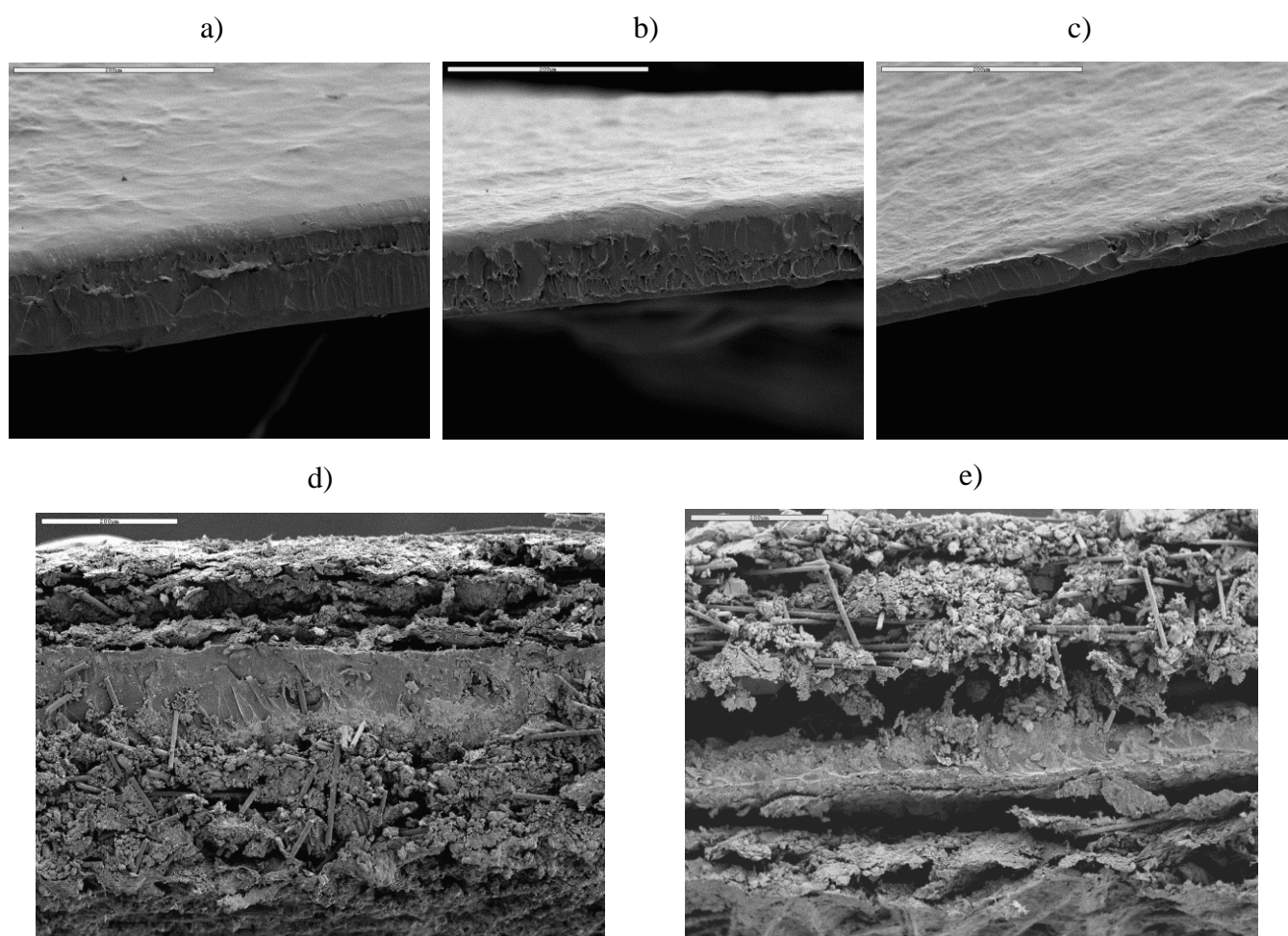


Figure 3. SEM micro-photographs for the cross-sectional views of solid alkaline membranes PVA–KOH: a) PVA3 - 0.0110 cm, b) PVA2 – 0.0082 cm and c) PVA1 – 0.0047. Magnification 250 ×; the cross-sectional views of $H_2|Pt/C|PVA-KOH|Pt/C|O_2$ MEAs: d) PVA2 membrane and e) PVA1 membrane. Magnification 150 ×.

SEM observations of the sections of a membrane showed that the structure is very compact and membranes are homogeneous and dense material without any degradation or holes or phase separation phenomena. Also, there were neither gaps nor cracks between the particles and polymer matrix, which proves the excellent chemical stability due to the cross-linkage in PVA matrix.

4. CONCLUSIONS

In this work, the solid alkaline polymer electrolyte membrane based on alkaline doped poly(vinyl alcohol) (PVA–KOH) was proposed for the fuel cell application aiming at a new cost-effective, easy preparing and chemical stable SAAEM using physical cross-linking procedure.

Ionic conductivity of membranes was measured at 25 °C and reached a maximum value of $1.2 \times 10^{-2} \text{ S cm}^{-1}$ for the thickest PVA doped with 6 M KOH solution. The SEM results demonstrated a dense structure of PVA–KOH membranes. The membrane electrode assemblies using KOH doped PVA as membranes, were investigated for the peak power. Results showed excellent current-voltage characteristics. Comparison of $\text{H}_2|\text{Pt}/\text{C}|\text{PVA-KOH}|\text{Pt}/\text{C}|\text{O}_2$ FC and $\text{H}_2|\text{Pt}/\text{C}|\text{Nafion 115}|\text{Pt}/\text{C}|\text{O}_2$ FC MEAs, using same fuel cell hardware and under same operating conditions clearly shows excellent performance of the solid alkaline PVA membrane cross-linked by physical means. This result was not reported in the literature and could be very important for further investigations and analysis on solid alkaline fuel cells.

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