Membrane electrode assemblies based on sol–gel hybrid membranes — A preliminary investigation on fabrication aspects

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Abstract

This paper reports the preliminary results on fabrication of membrane electrode assemblies (MEA) for proton exchange membrane fuel cells (PEMFC) based on sol–gel hybrid membranes. In order to identify a suitable method, various fabrication strategies were investigated. For this purpose, hybrid membranes made from alkoxysilane-endcapped poly(ethylene glycol) (PEG) precursor consisting of monophenyl trimethoxysilane (MPh) as silica phase modifier and 4-dodecylbenzene sulfonic acid (DBSA) as proton source (PEG/SiO$_2$/DBSA); and MPh and 12-phosphotungstic acid (PWA) (PEG/SiO$_2$/PWA) are used as model compounds. For the better interface of MEA, impregnation solutions of similar chemical nature with hybrid membranes were examined. Polarization curves are exclusively used to evaluate the quality of MEA. A maximum current density of 80 mA cm^{-2}, obtained with hot-pressed MEA, is the highest performance among the five different preparation methods. Good contact between the hybrid membrane as an electrolyte and the catalyst coated carbon cloth as electrodes in the MEA is achieved by coating electrodes as well as membrane with precursor sol. The flexibility of sol–gel hybrid membranes shows scope for further improvement in performance compared to hybrid membranes from solution-blending. The implications of each preparation methods are analyzed.
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Keywords: Sol–gel hybrid membranes; Membrane electrode assembly; Interface; Polarization curves

1. Introduction

For last few years, proton conducting hybrid membranes prepared through sol–gel process have actively been considered as one of the promising candidates for both hydrogen/oxygen fuel cells (H$_2$/O$_2$FC) and direct methanol fuel cells (DMFC) due to their attractive properties [1–9]. A major motivation for this intense interest on hybrid membranes is high cost, limitation in cell operation temperature, and methanol cross-over of plain perfluorosulfonic acid membranes [10–12]. The hybrid composites are considered as biphasic materials, where the organic and inorganic phases are mixed at the nanometer to sub-micrometer scales. The flexibility in sol–gel synthetic approach offers the poten-

tial for molecular engineering of composition and properties of a diverse range of materials. The presence of organic phase makes the hybrid materials more flexible while their thermal stability has greatly been enhanced by inorganic part. Recently, a new class of hybrid membranes consisting of SiO$_2$/polymer (polyethylene oxide (PEO); polypropylene oxide (PPO); polytetramethylene oxide (PTMO)) with urethane linking structure through sol–gel reactions has been reported [1–3,5]. The hybrid membranes become proton conductive when doped with acidic moieties such as monododecylphosphate (MDP) [1,2] or 12-phosphotungstic acid (PWA) [2–4]. In our recent publications, preparation, characterization and microstructure of proton conducting hybrid membranes based on SiO$_2$/PEG (polyethylene glycol) doped with either 4-dodecylbenzene sulfonic acid (DBSA) or PWA have been investigated [7–9,13]. In this paper, we attempted to prepare membrane electrode assemblies (MEA) by various procedures using these sol–gel hybrid membranes.

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The MEA is often stated to be the heart of the PEMFC because its performance essentially depends on the quality of MEA. The conversion efficiency of MEA depends on many factors including type and thickness of both membrane and gas-diffusion material, nature of binder used in the electrodes, the binder to catalyst ratio and finally the method used for MEA preparation. Most of the work carried out in the literature on MEA fabrication is mainly based on per-fluorinated membranes such as Nafion. One of the important advances made in electrode preparation is introduction of Nafion as binder in the catalyst layer as a replacement of Teflon. Reduction of catalyst loading was made possible through extension of three-dimensional zone in the electrode by use of supported catalyst rather than pure Pt black and by impregnation of electrode with proton conductor [14,15]. Catalyst utilization was also improved by directly coating the catalyst layer on membrane or by decal process which resulted in an enhanced connectivity between electrolyte and catalyst [16–18]. Over the years, MEA fabrication procedures fine-tuned for Nafion and the optimal hot-pressing conditions are reported [19] to minimize the activation and ohmic over-potentials. A brief overview on interfacial aspects of the PEMFC has been presented elsewhere [20].

Later for other new membranes, the fabrication procedures optimized for Nafion were extended with minor modifications but satisfactory MEA could not be obtained in most cases. The main reason for the inferior performance of these MEA is partial or complete delamination of electrodes from membrane [21–25]. The problem lies in the fact that the solubilized Nafion used as binder in these electrodes is not compatible with many of the other polymers which leads to higher ohmic resistance at the interface as a consequence, cell performance decreased drastically. In order to reduce this phenomenon, electrode design has been modified and the Nafion solution used for impregnating the electrode was replaced with polymer dispersion compatible with membrane [26–28] and improvement in cell performance was observed [27]. However, membranes commercially available today are generally not available in a dissolved form nor can they be dissolved and recast. Recently, this problem could overcome for sol–gel hybrid membranes by simply replacing the Nafion with precursor sol [6,29].

In this paper, results on preparation of membrane electrode assemblies based on sol–gel hybrid membranes are reported.

2. Experimental

2.1. Membranes

In the present study, two hybrid membranes, which are prepared in our previous studies from alkoxysilane-endcapped poly(ethylene glycol) precursor via sol–gel processes [7,13], utilized to fabricate MEA. They are: (i) DBSA-doped PEG/SiO$_2$ membrane consisting of 80 wt.% MPh and 20 wt.% DBSA (MPh80DBSA20) [7] and (ii) PWA-doped

PEG/SiO$_2$ membrane composed of 20 parts per 100 of rubber (phr) MPh and 120 phr PWA (MPh20PWA120) [13]. The sol–gel hybrid membranes were washed thoroughly before MEA fabrication. For comparison, Nafion115 and another hybrid membrane composed of 20 wt.% poly(vinyl alcohol) (PVA) and 80 wt.% PWA, prepared by solution-blending [30], were also studied. The reasons for using Nafion115 and PVA/PWA membranes, as reference materials, are due to the fact that Nafion is the most commonly used proton exchange membrane material and PVA/PWA possesses relatively high selectivity [30], i.e. proton conductivity to methanol permeability ratio. Pretreated Nafion115 and PVA/PWA membranes were stored in deionised water until use.

2.2. Measurement of proton conductivity and methanol permeability of membranes

Proton conductivity of membranes was obtained from the AC impedance measurements using two electrodes configuration. The resistance value associated with the membrane conductivity was determined from the high frequency intercept of the impedance with the real axis. The conductivity was calculated using the equation [7,8]

$$\sigma = \frac{L}{RA} \tag{1}$$

where σ, L, R, and A denote the membrane conductivity, thickness of the membrane, the measured resistance on the membrane, and the cross-sectional area of the membrane perpendicular to current flow, respectively.

Methanol permeability of membranes was determined using a home-made side-by-side glass diffusion cell. The membrane was clamped between well-stirred donor (A) and receptor (B) compartments with a membrane cross-sectional area of 3.19 cm^2 exposed to the solutions in both compartments. The receptor compartment ($V_B = 80$ ml) was initially filled with water, while the donor compartment ($V_A = 80$ ml) was charged with a methanol solution (3 wt.%). The diffusion cell was kept in a thermostat at 35 °C. The concentration difference between the two compartments leads to a flux of methanol across the membrane. The concentration of methanol in the receptor compartment was measured using gas chromatography (GC) (Shimadzu GC14) at regular intervals. Methanol permeability was determined from the slope of the plot of methanol concentration in the receptor compartment versus time as described elsewhere [7,8].

2.3. Electrode preparation

Carbon cloth 'A' (E-TEK Inc.) with a thickness of 350 μm and 15 wt.% Teflon was used as support to prepare homemade electrodes. The diffusion layer was prepared from carbon black (Vulcan XC72) with 10 wt.% Teflon as binder for cathode and 10 wt.% Nafion as binder for anode. The carbon loading was maintained at 2 mg cm^{-2}. Carbon-supported Pt catalyst bound with Nafion was used to prepare cata-

lyst layer of cathode and anode of H_2/O_2FC and also for cathode of DMFC. Carbon-supported Pt–Ru with Nafion binder was used as anode catalyst of DMFC. Note that in an isolated experiment, precursor sol was used as binder to prepare catalyst ink. In all cases, the catalyst loading was $3\,mg\,cm^{-2}$. Some experiments, in H_2/O_2FC, were carried out using E-TEK electrodes with $0.4\,mg\,cm^{-2}$ Pt loading and $0.6\,mg\,cm^{-2}$ Nafion impregnation. In order to improve both the contact area between catalyst in the electrode and membrane; and bonding between electrodes and membrane, three different impregnation solutions (the solution/dispersion used to impregnate the catalyst layer) were investigated for home-made electrodes. They are: (i) 5% Nafion solution, (ii) 5% DBSA solution and (iii) precursor sol (prepared for the MPh80DBSA20 hybrid membrane casting).

2.4. Fabrication of membrane electrode assembly

The following five different strategies were adopted to fabricate membrane electrode assemblies using hybrid membranes.

2.4.1. Mechanical pressing
Electrodes are just placed on both sides of membrane in FC test fixture and assembled. Here, the interface was not optimized.

2.4.2. Hot-pressing
Electrodes are placed on both sides of membrane and pressed in a hot-press at $45\,^{\circ}C$ under $10\,kg\,cm^{-2}$ pressures for 3 min.

2.4.3. Decal transfer
Catalyst layer coated glass fiber reinforced Teflon sheets were cold pressed on membrane to transfer the catalyst layer onto membrane. Then diffusion layer coated carbon cloth either mechanically pressed or hot-pressed on this membrane.

2.4.4. Catalyst coated membrane (CCM) method
Here, catalyst layer was directly coated on membrane and diffusion layer coated carbon cloth either mechanically pressed or hot-pressed on this membrane.

2.4.5. Clamping of precursor sol-impregnated electrodes
Catalyst layer of electrodes and both sides of hybrid membrane were coated with precursor sol. Then electrode are placed on both sides of membrane and clamped between two heavy plates. Finally, the whole unit was kept in an oven at $60\,^{\circ}C$ for gelling.

During hot-pressing and clamping, positioning frames made from glass fiber reinforced Teflon sheets were used to avoid displacement of electrodes.

2.5. Single cell tests

The fabricated MEA was assembled in test cell and performance was evaluated. The polarization measurements were carried out using MACCOR Model 2200 fuel cell test station. The gases are allowed to pass through stainless steel humidifiers before entering into fuel cell inlets and the flow rates were controlled by mass flow controllers. The 2 M methanol was fed by a small pump (FMI 'Q' pump) with a flow rate of $3\,ml\,min^{-1}$. For comparison, experiments were also carried out with MEA fabricated from Nafion115 under similar experimental conditions.

3. Results and discussion

3.1. Analysis of sol–gel hybrid membranes properties for PEMFC applications

In order to exploit the advantages, such as low cost and easy preparation, of sol–gel hybrid membranes for fuel cells applications, their properties which are closely related to both H_2/O_2FC and DMFC, are analyzed and compared with reference materials. The proton conductivity, methanol permeability and selectivity (the ratio of proton conductivity to methanol permeability, ϕ) of sol–gel hybrid membranes are given in Table 1 along with Nafion115 and PVA20PWA80. At room temperature, the conductivity of MPh80DBSA20 hybrid membranes is about three times lower than that of Nafion115 reference membrane while two times higher than MPh20PWA120. Meanwhile, the conductivity of PVA20PWA80 is about one order lower than that of MPh80DBSA20. These results clearly indicate that among the two sol–gel hybrid membranes, MPh80DBSA20 seems to be the ideal choice as model compound to be used in MEA fabrication studies for H_2/O_2FC. Therefore, MPh80DBSA20 membrane was used extensively.

For the successful operation of DMFC, the membrane should be capable of both an efficient proton conductor as well as good methanol barrier. Therefore, while evaluating new membranes for DMFC application, one has to consider both proton conductivity and methanol permeability. It can be seen from Table 1 that compared to Nafion115; sol–gel hybrid membranes show strong resistance to methanol per-

Table 1
Comparison of properties of hybrid membranes and Nafion115

Membrane	Proton conductivity $(S\,cm^{-1})$	Methanol permeability $(cm^2\,s^{-1})$	Selectivity, ϕ $(\times 10^3\,S\,cm^{-3}\,s)$[a]
MPh80DBSA20	4.07×10^{-3}	2.0×10^{-8}	187.29
MPh20PWA120	2.09×10^{-3}	9.63×10^{-8}	21.7
Nafion115	0.012	1.8×10^{-6}	6.86
PVA20PWA80	4.62×10^{-4}	8.31×10^{-10}	555.35

[a] Ratio of proton conductivity to methanol permeability.

meation. The methanol permeability of MPh80DBSA20 and MPh20PWA120 are nearly 90 and 19 times, respectively, lower compared to Nafion115. Another important parameter which commonly used in evaluation of different membranes for DMFC is selectivity (ϕ) [31] because it combines both proton conductivity and methanol permeability. Comparison of ϕ values of sol–gel hybrid membranes and Nafion115 in Table 1, shows that MPh80DBSA20 has highest value of 187.29×10^3 S cm^{-3} s followed by MPh20PWA120 of 21.7×10^3 S cm^{-3} s. Although MPh80DBSA20 has lower conductivity than Nafion115, it could attain high ϕ value mainly because of tremendous reduction in its methanol permeability. It is obvious that a significant reduction in methanol cross-over could be possible if MPh80DBSA20 is used. Interestingly, the other reference material, PVA20PWA80, exhibit highest ϕ value due to its lowest methanol permeability. Therefore, it is quite nature to expect highest performance from this material in DMFC among these four membranes under similar experimental conditions and in fact it did so as we will be seen in Section 3.2.5.

3.2. Studies on fabrication of MEA based on sol–gel hybrid membranes

3.2.1. Effect of fabrication method

Presently, there is no specific method available to fabricate MEA using sol–gel hybrid membranes. The general procedures for MEA preparation, which were optimized for the perfluorinated ionomers, were still used although the constituents and properties of these two membranes are different. Thus, in order to obtain a reasonable performance as expected from the properties, it will be necessary to develop an optimized procedure for MEA preparation. In this section, different strategies were adopted to prepare MEA in an attempt to identify a suitable MEA fabrication method for sol–gel hybrid membranes. Fig. 1(a) shows the potential versus current density characteristics of MEAs fabricated by different methods using MPh80DBSA20 hybrid membrane in H$_2$/O$_2$ mode at ambient conditions. The MEA fabricated by hot-pressing shows highest current density of 80 mA cm^{-2} at 85 mV followed by mechanically pressed MEA with 37 mA cm^{-2} at 47 mV. The maximum current densities of MEAs prepared by clamping of precursor sol-impregnated electrodes and CCM were about 3.5 and 5.7 times, respectively, lower than that of hot-pressed MEA. Due to poor performance, the polarization curve of decal transfer MEA is not shown here. The lower current density of mechanically pressed MEA compared to hot-pressed is not a surprise because in the former case, interface is not optimized. The higher current density of hot-pressed MEA is attributed to the result of improved contact between membrane and electrodes [15] although the hot-pressing conditions are milder. The surprising observation is that of lower performance of MEA obtained by clamping of sol-impregnated electrodes. Here, we anticipated higher performance due to chemical similarity
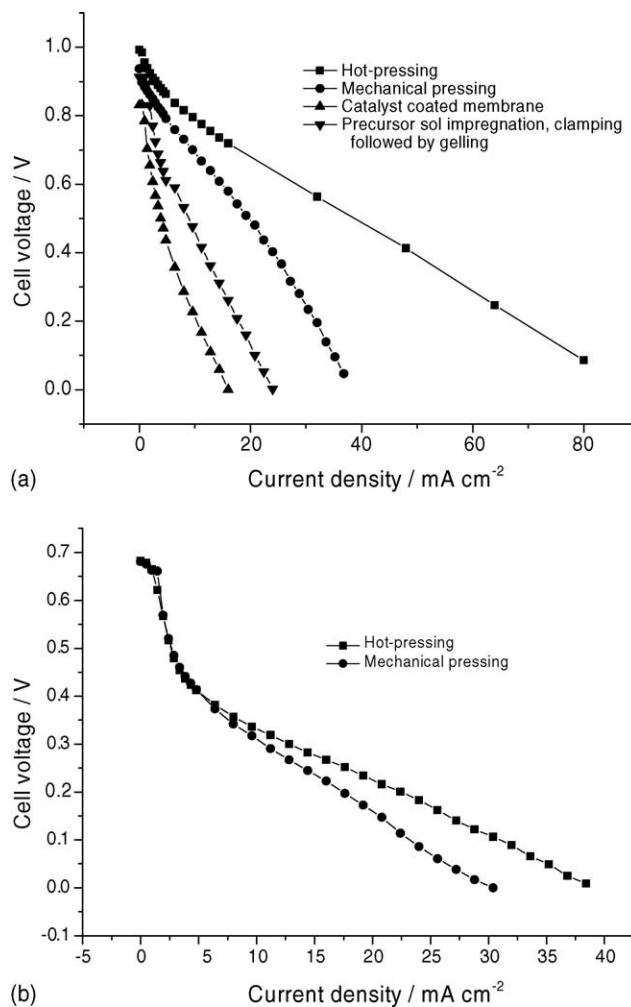

Fig. 1. (a) Effect of MEA fabrication procedure on polarization curves of H$_2$/O$_2$FC. Membrane: MPh80DBSA20; conditions: fuel cell temperature (T_{FC}) = H$_2$ humidification temperature (T_{H_2}) = O$_2$ humidification temperature (T_{O_2}) = RT; flow rate: H$_2$ = O$_2$ = 100 ml min^{-1}. (b) Effect of MEA fabrication procedure on polarization curves of DMFC. Membrane: MPh80DBSA20; conditions: T_{FC} = T_{O_2} = RT; O$_2$ flow rate = 100 ml min^{-1} and 2 M methanol was supplied to anode at a flow rate of 3 ml min^{-1}.

between impregnation solution (precursor sol) and membrane, and the improved adhesion of electrode and membrane. The latter behavior is generally expected to lead an extension of three-phase bounders [15,32]. The poor performance of CCM and decal transfer MEAs is mainly due to unsatisfied bonding between membrane and catalyst layer and incomplete transfer catalyst layer (CL), respectively. In the former case, adhesion between CL and hybrid membrane can be improved if precursor sol is used to prepare CL. Similar observations were made in the DMFC also, as shown in Fig. 1(b). The maximum current density of mechanically pressed MEA is decreased to 30 mA cm^{-2} compared to 38 mA cm^{-2} of hot-pressed MEA. Presently, the single cell tests in DMFC were restricted to only these two fabrication methods.

3.2.2. Effect of impregnation solution

It was claimed in the few reports available on fuel cell tests with sol–gel hybrid membranes [5,6,9] that higher performance is possible if the Nafion ionomer used for making proton path in the electrode is replaced with precursor sol itself. However, no detailed study is available to the best of our knowledge. Therefore, it will be highly rewarding to probe this aspect in detail to develop a novel MEA fabrication method for sol–gel hybrid membranes with appreciable performance and lifetime. In order to investigate the effect of impregnation solution, three different solutions were examined (see Section 2.4). Among the three impregnation solutions, precursor sol is used to cast the hybrid membrane and the DBSA is doped into the sol–gel matrix as proton source in DBSA-doped PEG/SiO$_2$ hybrid membranes. Thus, these two have chemical similarity with MPh80DBSA20. Therefore, better adhesion between electrode and membrane, and appreciable performance with long-term interfacial stability can be expected from precursor sol impregnation of gas-diffusion electrodes.

The polarization curves of different impregnation solutions are presented in Fig. 2. Nafion-impregnated electrodes show superior characteristic over the entire current density range. DBSA-impregnated electrodes also gave the same current density but at about 100 mV lower cell potential. With precursor sol, two approaches were adopted. In the first method, electrodes were impregnated with precursor sol, and allowed in an oven for 24 h for gelling then hot-pressed with membrane. In the second approach, MEA is constructed by clamping the sol-impregnated electrodes as already discussed in the previous section. Generally, the performance of sol-impregnated MEAs are poor, particularly with that of hot-pressed. When Nafion is replaced with precursor sol as impregnation solution, the performance deteriorates probably due to mass transport problems by retarding the access of reactant to the active catalyst sites, i.e. some of the catalyst
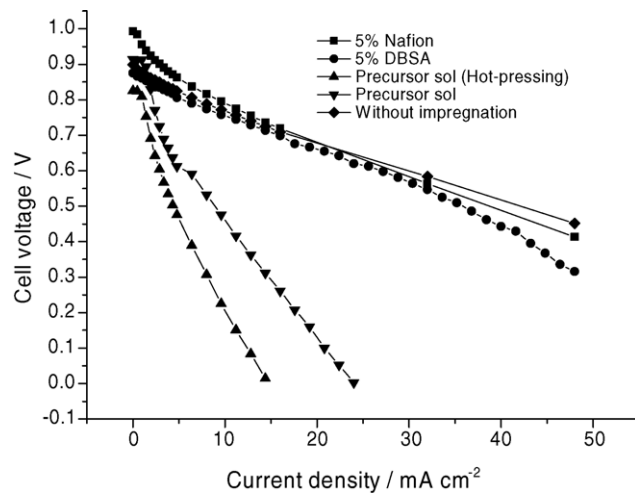
sites covered with thick layer of precursor sol can introduce mass transport problems for the fuel cells reactions. Thus, the effective area available for fuel cells reactions can be smaller than the actual loading. Therefore, to realize the benefit of precursor sol impregnation, the parameters such as amount and viscosity of precursor sol, and gelling conditions have to be optimized. Presently, work is under progress in this direction.

Surprisingly, the MEA fabricated by hot-pressing using electrodes without any impregnation gave highest performance. A maximum current density of 48 mA cm^{-2} was observed at 452 mV. This clearly shows that in the present case (i.e. with MPh80DBSA20 hybrid membrane) impregnation of electrodes with impregnation solution does not always lead to higher current density but may resulted in lower performance if the procedure is not optimized as observed with precursor sol. On the other hand, hot-pressing yielded high performance irrespective of impregnation solution as shown in Fig. 3. Generally, the bonding between electrodes and membrane improves during hot-pressing and if the electrodes are impregnated with impregnation solution then a plastic flow of impregnation solution occurs in the membrane and electrode under pressure and temperature. Optimum conditions are essential to attain higher current density from hot-pressed MEA. In the present case, the impregnation of electrodes does not yield any positive effect in contrary to the earlier observation with Nafion membrane [15,32] primarily due to mild hot-pressing conditions used in the case of DBSA and Nafion impregnation solutions and lack of optimization conditions with precursor sol-impregnated electrodes.

Apart from performance, one can noticed differences in open circuit voltages (OCV) among different MEA of H$_2$/O$_2$FC. For MPh80DBSA20 hybrid membrane, the OCV values varied from 825 to 997 mV. The lower OCV of similar hybrid membrane was attributed to permeation of gas through membrane [6,29]. In our case, all the polarization curves were
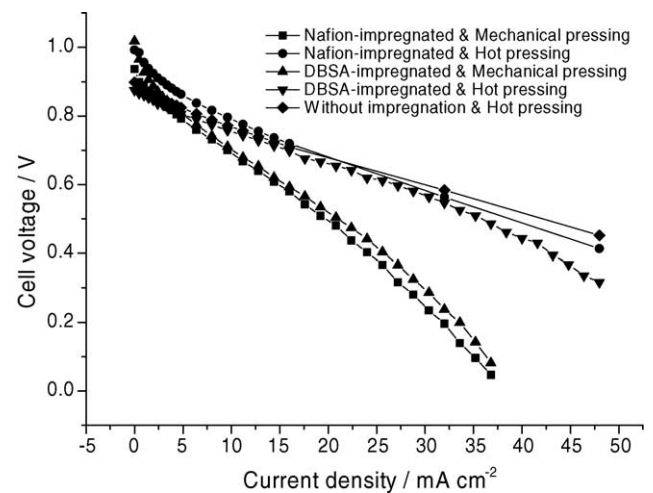

Fig. 2. Effect of impregnation solution on polarization curves of H$_2$/O$_2$FC. Membrane: MPh80DBSA20; conditions: $T_{FC} = T_{H_2} = T_{O_2} = $ RT; flow rate: H$_2$ = O$_2$ = 100 ml min^{-1}.

Fig. 3. Impregnation solution vs. fabrication method on polarization curves of H$_2$/O$_2$FC. Membrane: MPh80DBSA20; conditions: $T_{FC} = T_{H_2} = T_{O_2} = $ RT; flow rate: H$_2$ = O$_2$ = 100 ml min^{-1}.
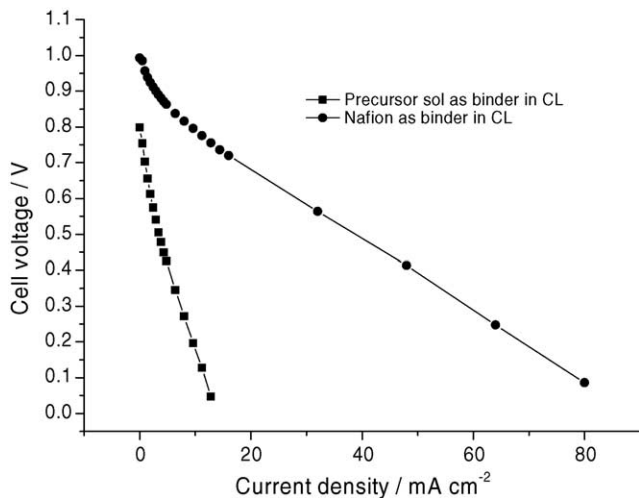
Fig. 4. Effect of catalyst layer binder on polarization curves of H_2/O_2FC. Membrane: MPh80DBSA20; conditions: $T_{FC} = T_{H_2} = T_{O_2} = RT$; flow rate: $H_2 = O_2 = 100\,ml\,min^{-1}$.

Fig. 5. Variation in current density of DMFC with operation time. Membrane: MPh80DBSA20; conditions: $T_{FC} = T_{O_2} = RT$; O_2 flow rate $= 100\,ml\,min^{-1}$ and 2 M methanol was supplied to anode at a flow rate of $3\,ml\,min^{-1}$.

recorded under identical experiments conditions using identical membrane, therefore, the differences obviously arose from factors other than membrane properties, such as composition and microstructure of catalyst layer. These factors ultimately determine the efficiency of catalyst layer in the half cell reactions involved, thus decide the OCV of fuel cell. The observed results in OCV also manifested that its value depended on nature of impregnation solution used; and with a particular impregnation solution, the OCV was highly influenced by MEA fabrication methods. Detailed work is under progress to address how these factors influence the OCV.

3.2.3. Precursor sol as binder in catalyst ink

In a further attempt to improve the interface, the usual binder in catalyst ink, Nafion, was replaced with precursor sol and i–V characteristics of these two binders are compared in Fig. 4. The maximum current density of precursor sol-based MEA is about 6 times lower than that of Nafion-based MEA. It clearly indicates the requirement of optimization of experimental conditions to realize benefit of precursor sol as catalyst ink binder. We believe that direct coating of catalyst layer, made with precursor sol as binder, onto hybrid membrane will yield strong bonding between CL and membrane and in future this will be one of the ways to improve the performance of MEA based on hybrid membrane.

3.2.4. Stability of interface

For a successful application of PEMFC, not only the performance but also the lifetime of the MEA is also essential. Generally, it is observed in the literature that the main cause for the failure of new membranes in PEMFC is not the membrane breakdown but because of delamination of electrodes from membrane, i.e. poor stability of interface. The stability of the interface is highly influenced by the compatibility between membrane and impregnation solution. In
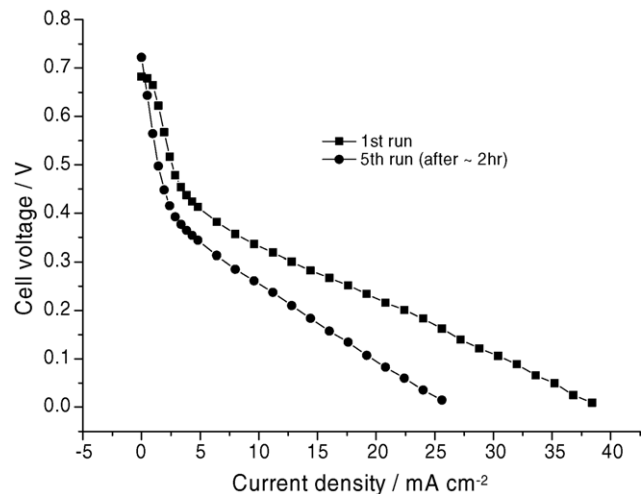
many instances, MEAs fabricated with non-Nafion membrane end up with poor membrane electrode interface due to different chemical nature of commonly used impregnation solution (mostly, Nafion solution) and the newly developed membranes [24,25]. To overcome this problem, same chemical nature impregnation solutions were used in some reports [6,27–29]. In order to see this effect in hybrid membranes, the polarization curves are recorded with Nafion-impregnated MEAs at regular intervals for H_2/O_2FC as well as DMFC. In H_2/O_2 mode, we could observe a stable performance for at least one week during repeated shut down and start. But in the case of DMFC, performance deterioration is obvious within few hrs of operation as shown in Fig. 5. The maximum current density of $38\,mA\,cm^{-2}$ is decreased to $26\,mA\,cm^{-2}$ after 4 cycles (within 2 h of experiment) and the process is irreversible. The performance deteriorates rapidly in DMFC compared to H_2/O_2FC because in the former case the MEA is always in contact with liquid. The presence of aqueous methanol on anode side makes the delamination process very easily and results in failure of MEA. Although it takes time, Nafion-impregnated electrode based MEA eventually led to poor interfacial stability in H_2/O_2FC also. Our experiences from the present work suggest that fabrication of MEA by clamping the precursor sol-impregnated electrodes can avoid the delamination problems.

3.2.5. Comparison of different hybrid membranes

Finally, the performance of our model sol–gel hybrid membranes is compared with similar sol–gel hybrid membranes reported in the literature and the reference materials Nafion115 and PVA20PWA80. Fig. 6 shows such a comparison in H_2/O_2 mode with MEAs made from E-TEK electrodes. Among sol–gel hybrid membranes, even at room temperature, the performance of DBSA-doped
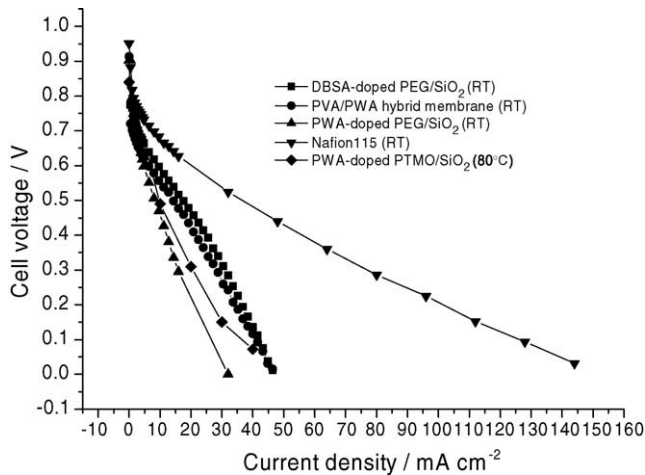
Fig. 6. Comparison of i–V characteristics of different membranes in H_2/O_2 mode. E-TEK electrodes were used. Except PWA-doped PTMO/SiO$_2$ hybrid membrane [5], all other membranes were evaluated at room temperature.

PEG/SiO$_2$ (MPh80DBSA20) membrane is higher than that of PWA-doped polytetramethylene oxide (PTMO)/SiO$_2$ (PTMO/PWA) at 80 °C. But the maximum current density of PWA-doped PEG/SiO$_2$ (MPh20PWA120) is lower than both MPh80DBSA20 and PTMO/PWA. Because of its higher proton conductivity, the maximum current density obtained with Nafion115 is higher than others. The current density of PVA/PWA is similar to MPh80DBSA20. Similar comparison can be found for DMFC in Fig. 7. The performance of sol–gel hybrid membrane MPh80DBSA20 is slightly lower compared to PVA/PWA which has highest selectivity amongst membranes studied. However, the current density of another sol–gel hybrid membrane, MPh20DPWA120, is not appreciable. All the membranes have higher OCP value compared to Nafion115 mainly due to their higher selectivity. The advantages of sol–gel hybrid membranes over PVA/PWA are that:
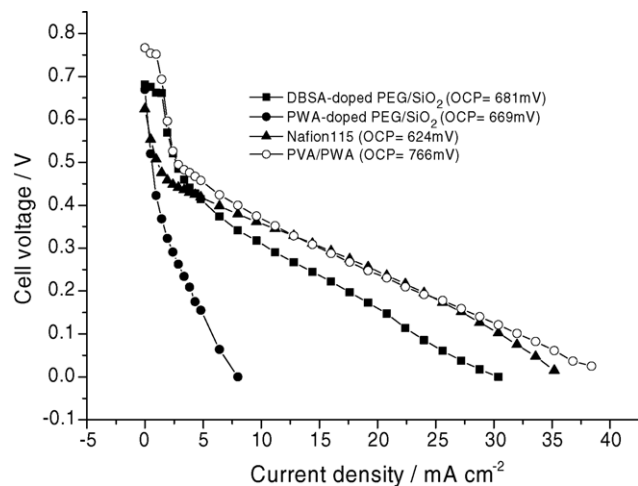

Fig. 7. Comparison of i–V characteristics of different membranes in DMFC mode. Conditions: $T_{FC} = T_{O_2} = $ RT; O_2 flow rate $= 100\,ml\,min^{-1}$ and 2 M methanol was supplied to anode at a flow rate of $3\,ml\,min^{-1}$.

(i) sol–gel membranes have higher conductivity in spite of lower doping density of acid moieties; (ii) flexible compared to brittle nature of PVA/PWA which often resulted in failure of MEA; (iii) it is very difficult to maintain balance between membrane properties, and flexibility of PVA/PWA compared to sol–gel membranes; (iv) above all, there is scope for sol–gel membranes for improvement of both performance and interfacial stability when optimized sol-penetrated electrodes used in MEA preparation but no such scope for PVA/PWA membranes. Because at low PWA content, their conductivity and methanol permeability is not promising, and the material suffers seriously from shrinking problem while at higher PWA content membrane is too brittle.

3.3. Problems encountered in the present study and future directions for improvement

Throughout this investigation, emphasis is given mostly on fabrication aspects of MEA rather than their performance. During MEA fabrication, we followed the sequence by which the fabrication procedures are presented in Section 2.4 one by one due to the following reasons. Keeping the difficulties in handling some of hybrid membranes in mind, mechanical pressing method was selected as the first step to screen the suitability of membrane for PEMFC because it does not involve any extreme conditions such as high temperature, pressure, etc. It is worthy to mention that in many instances our attempts to fabricate MEA using DBSA as well as PWA-doped PEG/SiO$_2$ hybrid membranes (other than MPh80DBSA20 and MPh20PWA120) failed mainly due to their unsatisfactory mechanical properties. Even with this milder conditions, MPh20PWA120 membrane develops crakes between at the edge of carbon cloth and glass fiber reinforced Teflon gasket, which placed between exposed area of membrane and graphite plates to prevent reactant leakage. Therefore, most of the studies were carried out with MPh80DBSA20 membrane and only a few experiments with MPh20PWA120. In the second step, Nafion-impregnated electrodes were placed on both sides of MPh80DBSA20 and hot-pressed at 45 °C under $10\,kg\,cm^{-2}$ pressures for 3 min with the view that this will lead to bonding between electrodes and membrane. Hot-pressing temperature was selected on the basis of our earlier findings that the glass transition temperature (T_g) of MPh80DBSA20 was near 52 °C [7]. Our attempts to increase the hot-pressing temperature very close to T_g of MPh80DBSA20 failed because high content of inorganic phase coupled with high degree of cross-linking led to membrane destruction. It is obvious from Fig. 1 that even under the milder hot-pressing condition, current density of H_2/O_2FC increases appreciably. In addition to this, the bonding between electrodes and membrane lasted for a considerable period with dismantling and assembling of MEA from fuel cell test fixture. However, the electrodes delaminated from the membrane slowly with time. The delamination phenomena of hot-pressed MEAs were commonly ascribed to the incompatibility between Nafion ionomer used in electrodes

and membranes, as in the present study. In our case, apart from this incompatibility, mild conditions of hot-pressing also partly responsible for the delamination. In the third step, catalyst layer was directly transferred onto membrane by decal method [16] instead of coating on carbon cloth. However, the complete transfer of catalyst layer was not possible due to mild conditions which in turn led to poor performance. In order to have good contact between CL and electrolyte, catalyst ink was directly coated on hybrid membrane and the performance was found to be not satisfied due to poor bonding between Nafion ionomer in the catalyst ink and hybrid membranes. Thus, it was felt that, in order to obtain optimized interface for better performance and long lifetime of MEA, a fabrication method involving precursor sol as a component of interface is essential. Based on this background, we have developed a new novel method which involves impregnation of precursor sol on both sides of membrane and catalyst layer of electrodes then electrode are placed on both sides of membrane and clamped between two heavy plates and allowed for gelling. Presently, the performance of this new method is not higher than that of hot-pressed MEA but the bonding between electrode and membrane is very strong. Therefore, work is under progress to optimize the conditions such as amount of precursor sol and gelling conditions.

Most of the previous works on sol–gel hybrid membranes have been mainly addressed on preparation and characterization aspects. On the other hand, until recently, the developments of electrode and optimized MEA preparation procedures are not in phase with membrane development. Some research groups have reported polarization curves [4–6], but mostly using the MEA prepared by general procedures optimized for Nafion which resulted in poor performance and capable of running only few hours. In order to make use of sol–gel hybrid membranes as future proton exchange membrane in H_2/O_2FC as well as DMFC, it is necessary to develop the proper procedures for MEA preparation using optimized electrodes probably precursor sol as one of the components in the interface.

4. Conclusions

The present study was carried out as a preliminary stage in which various options were explored to fabricate membrane electrode assemblies based on newly synthesized sol–gel hybrid membranes. By the virtue of its simple assembling procedures, mechanical pressing strategy can be used to screen the suitability of new membranes for PEMFC applications without laborious fabrication procedures. Preliminary investigations suggest that hot-pressing is the promising approach to achieve higher performance. The performance of decal transfer and catalyst coated membranes MEAs, prepared from Nafion solution as catalyst ink binder, is not satisfied because of poor bonding between catalyst layer and membrane. The interfacial stability is improved tremendously in MEA prepared from precursor sol-coated electrodes and membrane.

However, experimental conditions have to be optimized to attain better performance. Sol–gel hybrid membranes have good balance between properties and flexibility compared to PVA/PWA hybrid membranes prepared by solution-blending method. The present study points that in order to make use of sol–gel hybrid membranes as proton exchange membranes in both H_2/O_2FC and DMFC, it is necessary to fine-tune the precursor sol impregnation and gelling conditions and/or develop new procedures for MEA preparation using optimized electrodes with precursor sol as one of the interfacial components.

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