Preparation of gas diffusion electrodes using PEG/SiO$_2$ hybrid materials and the effect of their composition on microstructure of the catalyst layer and on fuel cell performance

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Abstract

Gas diffusion electrodes for proton-exchange membrane fuel cells (PEMFC) have been prepared using poly(ethylele glycol) (PEG)/SiO$_2$ hybrid materials. The catalyst layers were composed of carbon-supported Pt catalyst (Pt-CB) and PEG/SiO$_2$ hybrid materials. During the course of the catalyst ink preparation, a proton-conducting hybrid material-coated catalyst was obtained in paste form through sol–gel processes. PEG/SiO$_2$ hybrid materials were incorporated into the catalyst layer by two different approaches. In the first approach, the sol–gel reaction was initiated well before mixing the hybrid materials with catalyst while in the second approach, the gelling reaction was initiated only after mixing of all the constituents. For the optimized composition, the performance of electrodes prepared by the first approach was higher compared to the second approach. The microstructures of the catalyst layers of former electrodes were investigated using mercury porosimetry as a function of composition. It was found that beyond the optimum composition, the cell performance decreased continuously due to excess hybrid materials in the catalyst layer, which blocks the gas diffusion channels. The PEG/SiO$_2$ hybrid material is demonstrated to be a promising electrode material for the PEMFC.
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Keywords: Gas diffusion electrodes; PEMFC; Hybrid materials; Sol–gel process; Catalyst layer; Microstructure

1. Introduction

Fuel cells are considered to be one of the promising alternatives for future electrical energy needs and for a cleaner environment because of their high-energy conversion efficiency and low emission of pollutants [1–3]. Among the several types of fuel cells, the proton-exchange fuel cell (PEMFC) has received a great deal of attention for many years due to some of its specific advantages over others [4]. One of the important areas of research interest in PEMFCs is the development of a low cost membrane for high-temperature operation (>100 °C) with little or no dependence on humidity for hydrogen-based fuel cells (H$_2$/O$_2$FC) and with low methanol permeability for direct methanol fuel cells (DMFC). The main reason for this intense interest is high-cost, restriction of low operation temperature and methanol cross-over problems associated with

presently used plain perfluorosulfonic acid membranes [4–7]. High-temperature operation has several advantages including improvement of electrode kinetics, enhancement of CO tolerance of electrocatalysts and reduction in catalyst loading. Crossover of methanol from anode to cathode will strongly affect the DMFC performance since the presence of methanol at the cathode side not only lowers the fuel efficiency but also polarizes the cathode, and may adversely affect the cathode performance through wetting the hydrophobilized electrode structure and poisoning the catalyst sites for oxygen reduction [8].

Alternatives to commercial Nafion membranes include various modified perfluorinated, partially perfluorinated and non-perfluorinated membranes. In addition to these membranes, attention has been focused on preparation of organic–inorganic hybrid membranes through sol–gel processes [9–12]. In the hybrid membranes, thermal stability is provided by the inorganic backbone, while the organic chains confer the required specific properties such as flexibility and processibility. Recently, a new class of hybrid membranes consisting of SiO$_2$/polymer (polyethylene oxide (PEO); polypropylene oxide (PPO); poly-

tetramethylene oxide (PTMO)) with urethane linking structure has been prepared through sol–gel reactions [13–15]. The hybrid membranes become proton conducting when doped with acidic moieties such as monododecylphosphate (MDP) or 12-phosphotungstic acid (PWA). In recent publications of our group, preparation, characterization and the feasibility of proton-conducting hybrid membranes based on SiO$_2$/PEG (polyethylene glycol) doped with either 4-dodecylbenzene sulfonic acid (DBSA) or PWA as electrolyte in PEMFC has been demonstrated [16–20]. Despite such impressive progress in organic–inorganic hybrid membrane development, realization of their advantages in terms of cell performance is still questionable due to lack of suitable electrodes. Therefore, the main objective of the present study is to prepare gas diffusion electrodes using our hybrid material and carbon supported Pt catalyst intended to be used with homemade hybrid membranes in PEMFC.

The present investigation is necessitated because electrode development must be in parallel with membrane development in order to test the true fuel cell performance of newly prepared membranes. The problem lies in the fact that the conventional Nafion ionomer used in the electrode is not compatible with most of the newly prepared hybrid membranes [21]. Use of dissimilar or incompatible polymers in the membrane and electrode has caused poor adhesion and considerable interfacial resistance at the electrode/membrane interface that play a dominant role in the performance of PEMFC using new membranes. These problems can be solved by making the entire membrane electrode assembly (MEA) using a single material, i.e. by preparing the catalyst paste formulation using a material chemically similar to the new membranes instead of Nafion ionomer. In our recent publication [20], attempts were made to fabricate MEA based on hybrid membranes using Nafion ionomer-based electrodes. However, the cell performance was not satisfactory. Therefore, in this paper attention is focused on preparation of gas diffusion electrodes using our hybrid material and carbon supported Pt catalyst with different compositions. The relationship between the catalyst layers microstructure and cell performance is investigated as a function of catalyst ink compositions.

2. Experimental

2.1. Preparation of PEG/SiO$_2$ hybrid sol for catalyst ink preparation

Alkoxysilane-endcapped PEG precursor, required for the preparation of hybrid sol, was synthesized according to our previous publication [16]. The chemical structure of hybrid precursor is shown in Fig. 1. The silica phase of this precursor was further modified with monophenyl trimethoxysilane (MPh) to improve mechanical properties. 4-Dodecylbenzene sulfonic acid (DBSA) was incorporated into the hybrid network in order to impart proton-conducting property. The chemical structure of MPh and DBSA are also shown in Fig. 1. In the hybrid sol, the total weight of (MPh + PEG precursor) was kept at 2 g, in which MPh contributes 80 wt% and the remaining 20 wt% by hybrid precursor. While, the DBSA content was maintained at 20% by weight with respect to the total weight of (MPh + PEG precur-
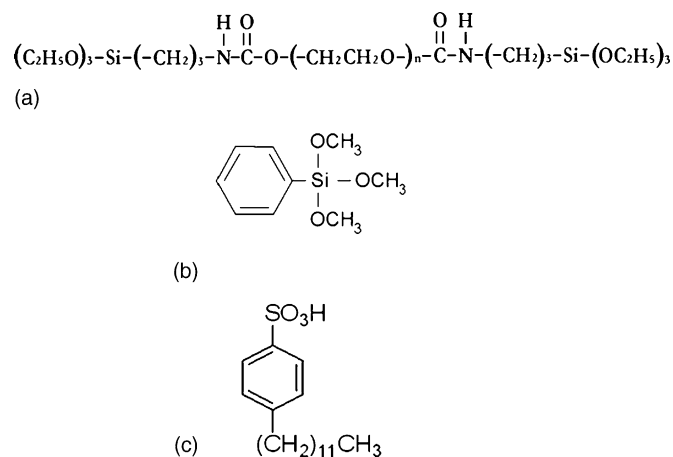

Fig. 1. The chemical structure of PEG/SiO$_2$ hybrid constituents: (a) alkoxysilane-endcapped PEG precursor, (b) monophenyl trimethoxysilane (MPh) and (c) 4-dodecylbenzene sulfonic acid (DBSA).

sor). Hereafter, the hybrid sol is named by MPh80DBSA20. The procedure for the preparation of hybrid sol is given in Fig. 2. The amount of MPh (wt%) and DBSA (wt%) present in the hybrid sol were determined as follows:

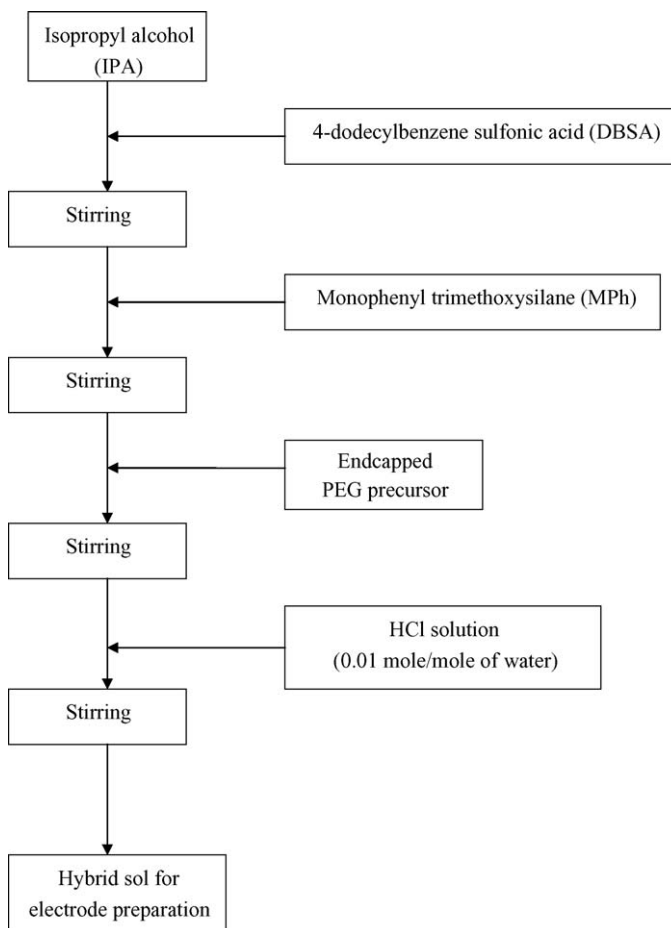$$MPh\,(wt\%) = \frac{MPh\,(weight)}{[PEG\,(weight) + MPh\,(weight)]} \times 100$$

Fig. 2. Flow chart for the preparation of MPh80DBSA20 hybrid sol.

$$DBSA\,(wt\%) = \frac{DBSA\,(weight)}{[PEG\,(weight) + MPh\,(weight)]} \times 100$$

2.2. Preparation of electrodes and single cell test

The gas diffusion layer was formed over wet-proofed E-TEK carbon cloth of 350 μm in thickness. The diffusion ink was prepared by mixing the carbon black, Teflon, IPA and water in an ultrasonication bath until uniform paste was obtained. The paste was uniformly coated over the carbon cloth by brushing. The cloth was dried in air at 120 °C for 1 h followed by thermal treatment at 280 °C for 30 min and finally sintered in air at 340 °C for 30 min.

In order to incorporate hybrid material into catalyst layer, two approaches were adopted. In the first approach, the hybrid material was prepared in the form of hybrid sol then mixed with catalyst to prepare proton-conducting hybrid material-coated catalyst. The weight mixing ratios of hybrid sol/catalyst were 0.1125–5. Here, the sol–gel reaction was initiated prior to mixing the hybrid material with catalyst and the catalyst ink formed by stirring (see Fig. 3). Five electrodes with different weight ratios of hybrid sol/catalyst = 0.1125, 0.225, 1, 3 and 5 were prepared. In the second approach, constituents of the hybrid end product were first mixed with catalyst in a sequence (followed to prepare hybrid sol) and then sol–gel reaction initiated. The
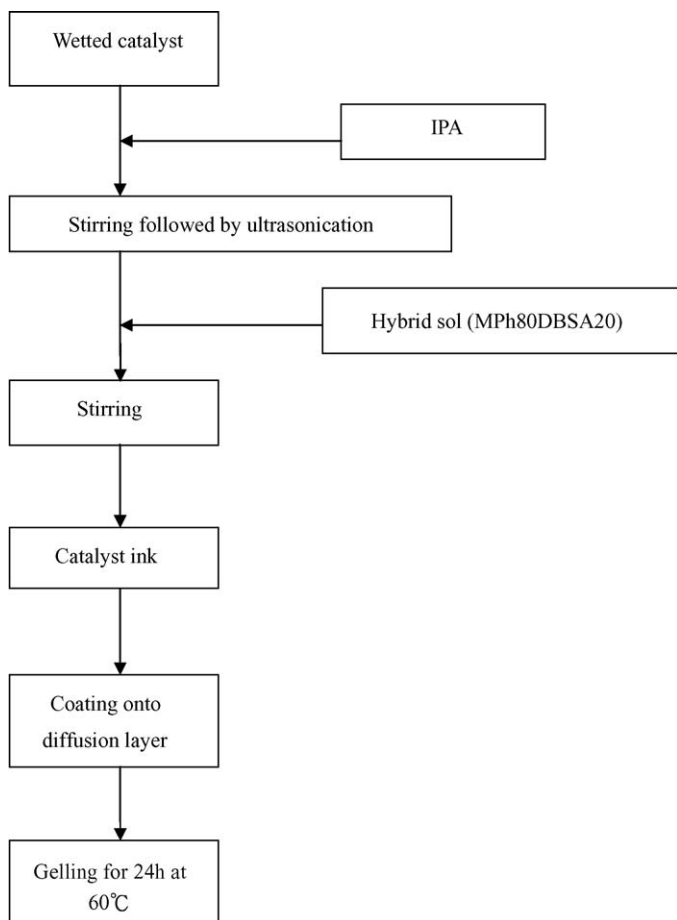

Fig. 3. Flow chart for the preparation of catalyst layer by hybrid sol addition approach.
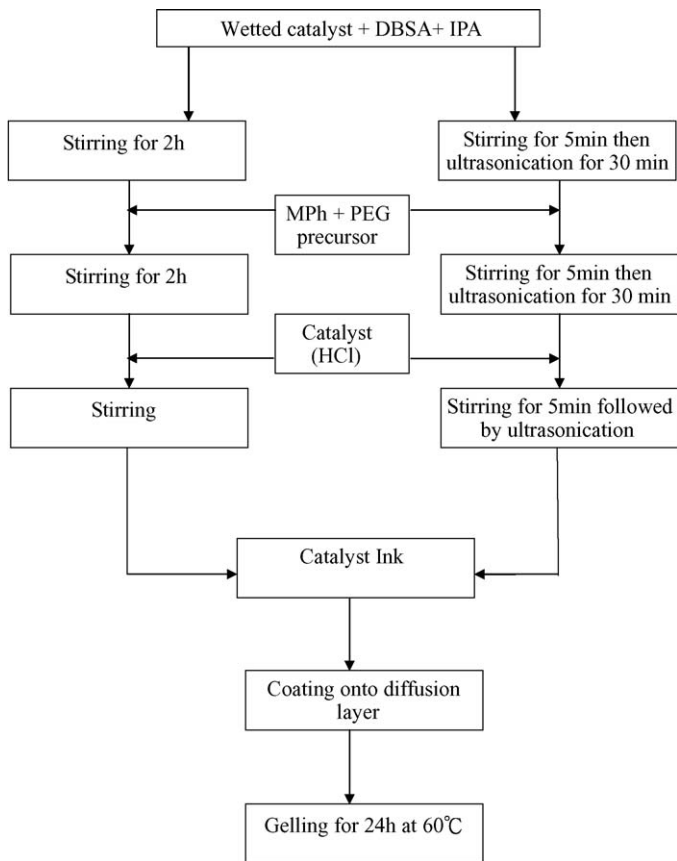

Fig. 4. Flow chart for the preparation of catalyst layer by sequential addition of hybrid constituents.

catalyst ink was formed by either stirring or ultrasonication as shown in Fig. 4. Four electrodes with different weight ratios of DBSA/catalyst = 0.5, 1, 2.125 and 3 were prepared while the weight ratio of (MPh + PEG precursor)/catalyst was kept at 0.55. The amount of Pt catalyst loading was kept at 3 mg cm^{-2} in both approaches.

Nafion® 115 was utilized as proton-conducting membrane in order to simplify the evaluation procedure for the new hybrid electrolyte to be applied in catalyst layer. The electrodes were just placed on both sides of membrane (i.e. no special treatment such as hot-pressing the electrodes and membrane was given to optimize the interface of electrode/membrane) in the fuel cell fixture and assembled. The polarization measurements were carried out using MACCOR Model 2200 fuel cell test station. The gases were allowed to pass through stainless steel humidifiers before entering into fuel cell inlets. For comparison, Nafion® ionomer-based electrodes were also prepared using optimized procedure and evaluated under similar experimental conditions. Note that all the polarization curves reported in this paper are not corrected for iR drop.

2.3. Measurement of pore size distribution and specific pore volume

The microstructure characteristics of the catalyst layer were investigated using the mercury intrusion porosimetry technique. The pore size distribution and specific pore volume in the catalyst

layer were calculated from an intrusion curve obtained using a mercury intrusion pore sizer (Auto Pore IV 9500, Shimadzu). Four different samples with different weight ratios of hybrid sol/catalyst = 0, 0.225, 3 and 5 were analyzed for this purpose.

3. Results and discussion

3.1. PEG/SiO₂ hybrid as electrode material for PEMFC

As mentioned in the introduction, electrode development must parallel with membrane development in order to test the true fuel cell performance of newly prepared membranes, because use of dissimilar polymer electrolytes in the membrane and electrode causes both poor adhesion at the membrane/electrode interface, and lower performance. The PEG/SiO₂ hybrid materials, which were used previously to prepare hybrid membranes [16], are used as a model compound for electrode preparation due to the fact that one of the membranes, MPh80DBSA20, was successfully tested in a PEMFC [20]. For example, the performance of our hybrid membrane was higher than that of PWA-doped polytetramethylene oxide (PTMO)/SiO₂ hybrid membrane [22] even when the former was operated at room temperature (RT) compared to evaluation of the latter at 80 °C. Another important aspect that has to be taken into consideration is the viscosity of the hybrid formulation used. It is well known that during sol–gel process, the viscosity of the hybrid formulation rises rapidly when the condensation polymerization commences after the hydrolysis of metal oxide [9]. Hence, the hybrid composition and experimental conditions are to be carefully optimized so that the viscosity of the catalyst paste relating to the sol–gel process is well controlled in order to obtain reproducible microstructure of catalyst layers. By adopting suitable catalyst ink preparation procedure, an appropriate viscosity could be maintained for the catalyst paste till completion of coating. Therefore, MPh80DBSA20 seems to be the ideal choice for the preliminary investigation.

3.2. Different approaches to incorporate PEG/SiO₂ hybrid as electrode material

As described in Section 2, two approaches were adopted to incorporate the PEG/SiO₂ hybrid as electrode material. For which, the composition of hybrid/catalyst weight ratios were optimized as follows.

3.2.1. Optimization of hybrid sol to catalyst weight ratio

Fig. 5 shows steady-state current–voltage curves of electrodes prepared with various contents of hybrid sol in the catalyst layer. The cell performance increases with increasing hybrid sol/catalyst weight ratio from 0.1125 to 0.225. Further increase in hybrid content does not contribute any improvement. In fact, the performance decreased as hybrid content increased. Thus, it can be concluded that the optimum composition of hybrid sol/catalyst is 0.225. The excess hybrid seems to deteriorate the gas diffusion as evidenced by the appearance of diffusion tails at higher current densities. To confirm our supposition that lower performance at higher content of hybrid arose due
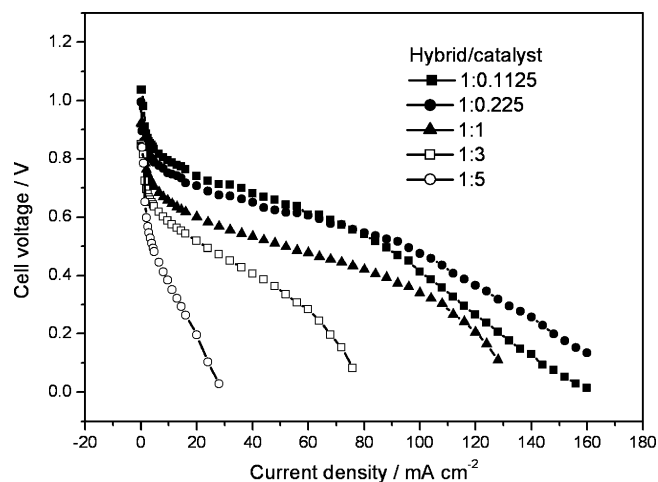

Fig. 5. Dependence of cell performance on PEG/SiO₂ hybrid content (*based on MPh80DBSA20 hybrid sol to catalyst weight ratio*) in the catalyst layers. Catalyst layers were prepared by hybrid sol addition approach. Fuel cell temperature (T_{FC}) = H₂ humidification temperature (T_{H_2}) = O₂ humidification temperature (T_{O_2}) = RT.

to mass-transport problem, characterization of these electrodes was carried out in terms of microstructure of catalyst layers, and the results are discussed in Section 3.4.

3.2.2. Optimization of hybrid content based on DBSA to catalyst weight ratio

The steady-state polarization curves of electrodes prepared according to a stoichiometric calculation of hybrid contents based on controlling DBSA contents in the catalyst layer are shown in Fig. 6. As in the previous case, the catalyst loading was kept at 3 mg cm⁻². The cell performance increases marginally with increasing DBSA/Pt ratio from 0.5 to 1. The performance decreases with further increase. However, in the present case, there is no diffusion tails in the polarization curves. The optimum composition of DBSA/Pt is found to be 1. The excess DBSA may cause hindrance to gas diffusion and/or affect the
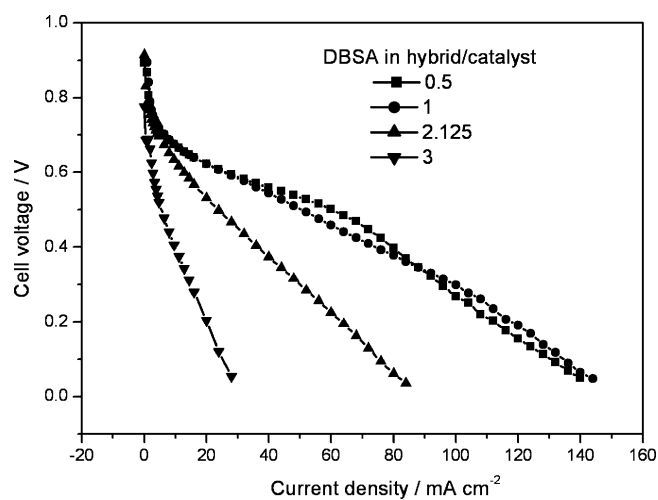

Fig. 6. Dependence of cell performance on PEG/SiO₂ hybrid content (*based on DBSA to catalyst weight ratio*) in the catalyst layers. Catalyst layers were prepared by sequential addition of hybrid constituents. $T_{FC} = T_{H_2} = T_{O_2}$ = RT.
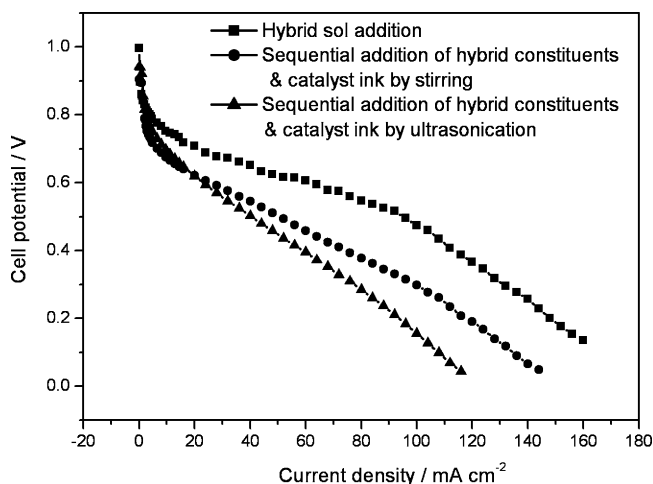
Fig. 7. Comparison of cell performance of PEG/SiO$_2$ hybrid-based electrodes, in which the hybrid was incorporated into catalyst layers by different approaches.

proton transport network of the electrode resulting in lower performance.

3.3. Identification of suitable approach to incorporate hybrid material into catalyst layer

Fig. 7 shows comparison of fuel cell performances, in which optimized amount of PEG/SiO$_2$ hybrid material was incorporated into catalyst layers of electrodes by different approaches as discussed earlier. The catalyst loading is kept constant at 3 mg cm^{-2}. Under identical experimental conditions, the performance of the cell with catalyst layer prepared by direct addition of hybrid sol is relatively higher compared to other two with their catalyst layers prepared by sequential addition approach. It unambiguously shows that electrode performance depends on the structure of the electrode and this, in turn, depends on the fabrication techniques when the same materials are used. Further investigation to ascertain the exact reasons for this behavior will be taken up in future. Since direct addition of hybrid sol appears to be more suitable route to incorporate PEG/SiO$_2$ hybrid materials into the catalyst layers, further characterization studies were carried out on these electrodes using mercury intrusion porosimetry to establish the relationship between microstructure of catalyst layer and polarization properties.

3.4. Influence of PEG/SiO$_2$ hybrid sol content on catalyst layer microstructure

Fig. 8 shows the integration curves of pore volumes per unit weight of CB-Pt versus pore diameter (d) for selected samples. It can be seen that the cumulative pore volume decreases with increasing PEG/SiO$_2$ hybrid content in the catalyst layer. Two different types of micropores are observed for all the electrodes with a critical boundary around 0.1 μm. The pores with a diameter below 0.1 μm are termed as primary pores while pores having diameter above 0.1 μm are termed as secondary pores. Watanabe and co-workers have done extensive work on the microstructure of catalyst layers [23–27], and reported [23]
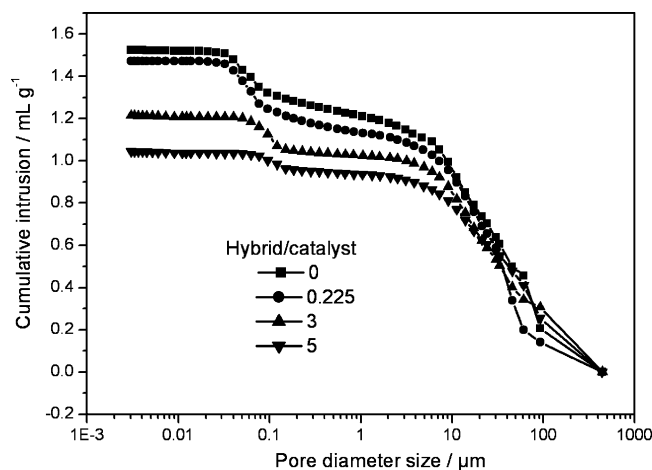

Fig. 8. Integration curves of pore volume per unit weight of Pt-CB as a function of pore diameter.

that the primary and secondary pores are corresponding to space within Pt-CB agglomerates and space between agglomerates, respectively. The boundary size between primary pore diameter (d_{Prim}) and secondary pore diameter (d_{Sec}) of samples with different compositions was determined from the second derivative of pore volume data in Fig. 8. The boundary between d_{Prim} and d_{Sec} increases with increasing hybrid content as shown in Fig. 9.

The relationships between the specific pore volumes and hybrid content are shown in Fig. 10. Incorporation of PEG/SiO$_2$ hybrid material into catalyst layers leads to continuous decrease of secondary pore volume (V_{Sec}). Addition of optimum amount of hybrid to catalyst ratio at 0.225 decreases the value of V_{Sec} suddenly from that without hybrid, and then decreases linear with further increase in hybrid content. Although the primary volume (V_{Prim}) decreased with hybrid content, the V_{Prim} values of samples with PEG/SiO$_2$ hybrid are higher than that without hybrid. In other words, V_{Prim} increased initially by the incorporation of optimum hybrid, and then decreased with further increase in hybrid content. These observations indicate that PEG/SiO$_2$ hybrid material penetrates into both pores but pref-
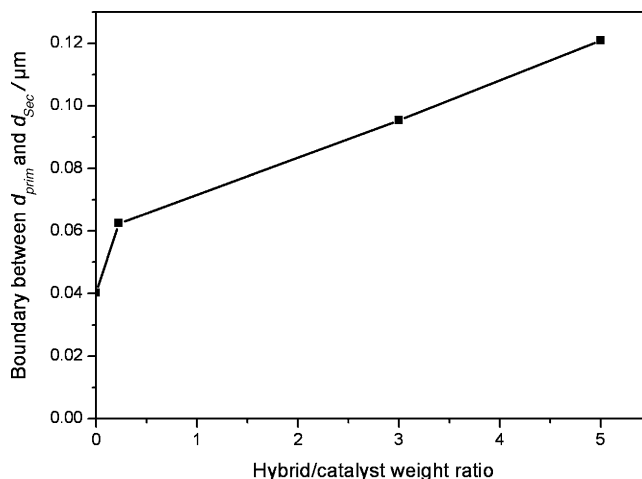

Fig. 9. Change in the boundary between primary and secondary pore diameters as a function of PEG/SiO$_2$ hybrid content.
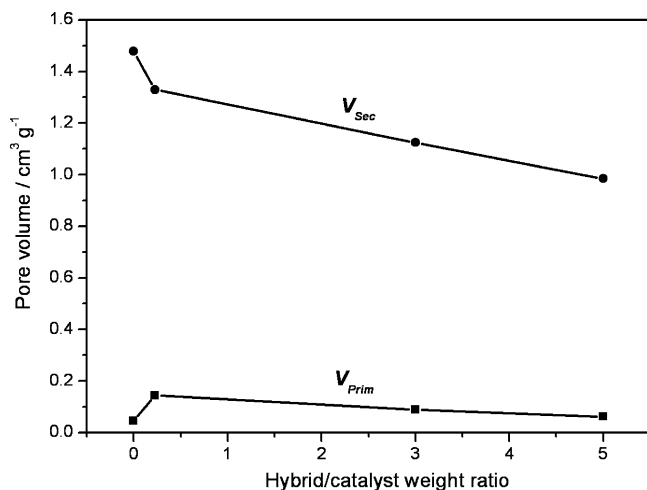
Fig. 10. Effect of PEG/SiO$_2$ hybrid content in the catalyst layers on primary and secondary pore volumes.

Fig. 11. Change in Tafel slope as a function of PEG/SiO$_2$ hybrid content/catalyst weight ratio.

erentially filled into secondary pores as in the case of Nafion ionomer [28] and borosiloxane (BSO) ionomer [24]. Also, it appears that PEG/SiO$_2$ hybrid material, formed through sol–gel reaction, functions as primary pore forming agent as well. This discrepancy arises from the use of an electrolyte sol with which an extensive, in-situ gelling reaction takes place and affects the microstructure in catalyst agglomerate. Here, we confined our discussion only to explain why the performance decreases and diffusion tails appear with increasing hybrid sol weight ratio beyond the optimum level.

Now, it is quite obvious from pore size analysis that PEG/SiO$_2$ hybrid found to exist mainly in the secondary pores (gas diffusion channels). This seems to be the main reason for the appearance of diffusion tails at higher current densities and lower performance when the hybrid content in the catalyst layer exceeds the optimum level. Our conclusion is also supported from the fact that the Tafel slope of oxygen reduction reaction at optimum hybrid content is relatively near (if not equal) to the theoretical value, i.e., 70 mV dec^{-1} [26,27] compared to other compositions as shown in Fig. 11. Thus, at optimum composition, supply of both protons and reactants to the catalyst sites was relatively higher so that cell could reach higher performance and no diffusion tails at higher current density. Beyond this optimum composition, gas supply was hindered with increasing hybrid content since it mostly occupies the gas supplying channels. Therefore, cell performance decreases progressively with hybrid content. Besides blocking the gas supplying channels, the excess hybrid additionally contributed to the mass-transport problem by increasing the catalyst layer thickness.

3.5. Evaluation of the feasibility of using PEG/SiO$_2$ hybrid as electrode material

In order to evaluate the feasibility of using PEG/SiO$_2$ hybrid as electrode material, preliminary investigations were carried out with hybrid-based electrodes. For this purpose, performances of hybrid-based electrodes are compared with conventional elec-
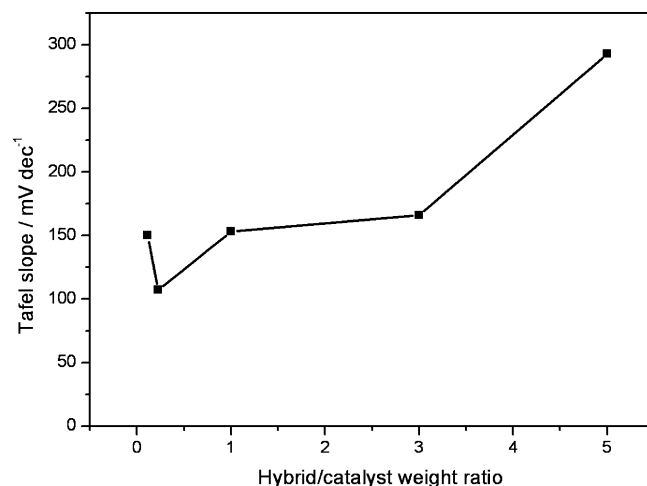
trodes based on Nafion ionomer, and performance stability test also carried out.

Fig. 12 shows a comparison of cell performances, in which PEG/SiO$_2$ hybrid and the Nafion ionomer (as reference) were employed in the catalyst layers as electrode materials. It can be seen that the performance of PEG/SiO$_2$ hybrid-based electrodes is lower than that of Nafion ionomer-based electrodes. It is clear that PEG/SiO$_2$ hybrid sol composition has to be optimized, i.e. other than MPh80DBSA20 composition has to be applied for catalyst ink preparation to obtain comfortable current density for practical applications.

Continuous discharge test was conducted on one of the Nafion 115 membrane/hybrid-based electrodes assemblies to investigate the stability of the PEG/SiO$_2$ hybrid materials under fuel cells operational conditions. During such continuous operation, a constant current density of 20 mA cm^{-2} was drawn from the cell, and the cell potential recorded at regular intervals. A typical cell performance is shown in Fig. 13. The cell showed nearly a constant voltage during continuous operation over a longer
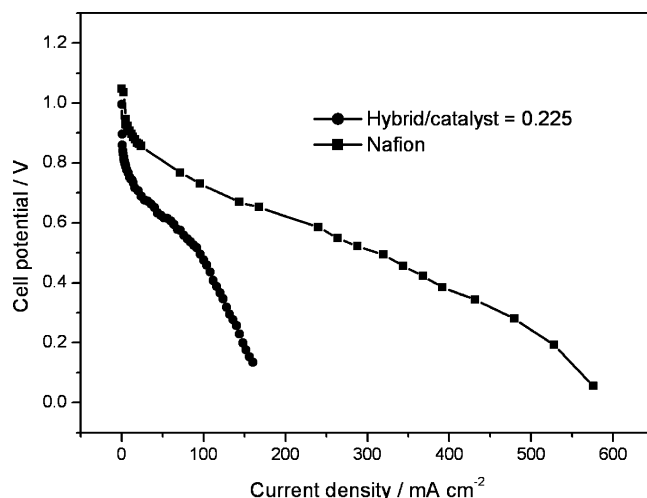

Fig. 12. Comparison of cell performances, in which PEG/SiO$_2$ hybrid and the Nafion ionomer were employed in the catalyst layers as electrode materials.
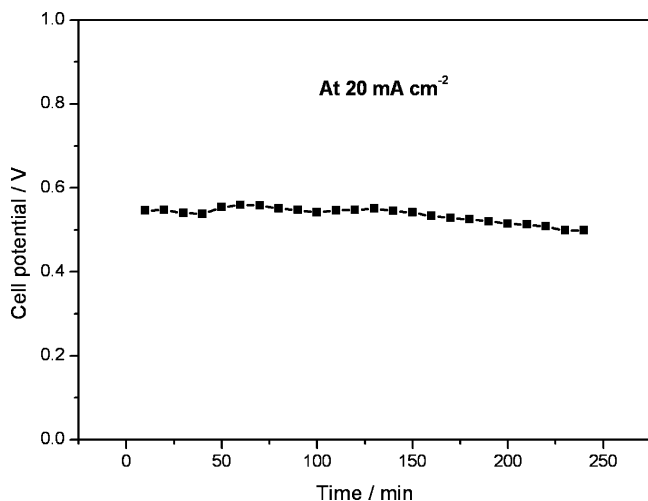
Fig. 13. Performance stability of PEG/SiO$_2$ hybrid-based electrodes under continuous current drawing of 20 mA cm^{-2} at RT.

period of time. Although the current density is somewhat lower for practical applications, nearly constant cell potential during continuous operation test indicates that no degradation of new hybrid material occurs under given experimental conditions. The polarization curves of the cell before and after continuous discharge tests also showed (not shown here) similar performance. These results, although far from being an optimized system, demonstrate the feasibility of using PEG/SiO$_2$ hybrid materials as future electrode material for PEMFC.

3.6. Scope for future direction of the work

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 electrode fabrication procedures are not in phase with membrane development, except very recent contribution by Watanabe et al. [25–27]. In the past, some research groups have reported polarization curves [22,29,30], but mostly using the MEA prepared by general procedures optimized for Nafion which resulted in poor performance and capable of running only few hours.

The present work is started based on our earlier findings [20] that: (i) to make use of sol–gel hybrid membranes in PEMFC, it is necessary to use hybrid sol-impregnated electrodes in order to avoid the MEA delamination; (ii) reasonable cell performance and long term operation is possible only when hybrid materials are used as one of the catalyst layer components using optimized electrode fabrication procedure. In this preliminary investigation, it is demonstrated that PEG/SiO$_2$ hybrid can be used as electrode material by replacing Nafion ionomer. In the second part, it is aimed to achieve the higher and steady cell performance with PEG/SiO$_2$ hybrid membrane/hybrid material-based electrode assemblies compared to that of hybrid membrane/Nafion ionomer-based electrode assemblies reported in ref. [20] and improve the durability of MEA.

For the sake of simplification and also to minimize any additional influencing parameters such as MEA fabrication procedure, Nafion 115 was utilized as polymer electrolyte membrane, and no special treatment was given to optimize the interface of electrode/membrane during evaluation of PEG/SiO$_2$ hybrid electrolyte as catalyst layer material. Now, work is under progress to meet the requirements of this concern, viz. use of hybrid membrane and optimization of interface to solve delamination problem. Some improvements were made in terms of steady performance for long period if the catalyst layer containing optimized amount of PEG/SiO$_2$ hybrid electrode material was coated directly onto hybrid membrane. The results of detailed study on this aspect will be published in our future article.

4. Conclusions

As an electrode material, PEG/SiO$_2$ hybrid could be successfully incorporated into the catalyst layer of a PEMFC gas diffusion electrodes through a new approach, namely hybrid sol addition. The optimum composition for this approach was found to be 0.225 in hybrid sol/catalyst weight ratio. Pore size analysis on the microstructures of catalyst layers revealed that PEG/SiO$_2$ hybrid material penetrates into both primary and secondary pores but preferentially filled into the latter which acted as gas supplying channels. At optimum composition, supply of both proton and reactants to the catalyst site appears to be relatively high so that the cell could reach higher performance. Beyond that, the excess hybrid materials block the gas diffusion channels leading to appearance of diffusion tails at higher current densities. A continuous discharge test demonstrated the stability of the PEG/SiO$_2$ hybrid material under fuel cell experimental conditions. Although the performance of electrodes with our hybrid material was lower than that of Nafion ionomer-based electrodes, and we believe that this may be improved by fine-tuning the hybrid sol composition. Thus, in future, higher performance will be achieved with hybrid membrane/hybrid-based electrodes assemblies compared to hybrid membrane/Nafion ionomer-based electrodes assemblies under stringent experimental conditions.

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