SHORT COMMUNICATION

A 5 W liquid-feed solid-polymer-electrolyte direct methanol fuel cell stack with stainless steel

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1. Introduction

The use of stainless steel as replacement for graphite in polymer-electrolyte-membrane fuel cells (PEMFCs) has been reported [1], with little difference in performance and corrosion of stainless steel even after prolonged testing of the PEMFC stacks. Therefore, for stationary applications where stack weight is not as critical as for transportation, the ruggedness of stainless steel, as well as its low-cost relative to graphite, make it an attractive material for practical use. To our knowledge, similar studies on solid polymer electrolyte direct methanol fuel cell (SPE-DMFC) stacks with stainless steel flow-distributors are lacking in the literature. As a part of our ongoing research [2, 3] on direct methanol fuel cells, this communication reports the performance of a 5 W liquid-feed stainless steel SPE-DMFC.

2. Experimental details

The preparation and characterization of the catalysts both for the anode and cathode have been described elsewhere [2, 3–6]. A brief description of the preparation of these catalysts is given below.

2.1. Preparation of $Na_6Pt(SO_3)_4$ and $Na_6Ru(SO_3)_4$ precursors

$Na_6Pt(SO_3)_4$ and $Na_6Ru(SO_3)_4$ were used as precursors for catalyst preparation. $Na_6Pt(SO_3)_4$ was prepared by dissolving 1 g of H_2PtCl_6 in 100 ml of distilled water and the pH of solution was adjusted to 7 by adding $NaHSO_3$. The solution was then gently warmed until it became colorless. The pH of the solution was raised to 6 by adding Na_2CO_3 when a white precipitate of $Na_6Pt(SO_3)_4$ was obtained; this was filtered, washed copiously with distilled water to remove chloride ions, and dried in an air oven at 80 °C for 2 h. $Na_6Ru(SO_3)_4$ was prepared by dissolving 207 mg of anhydrous $RuCl_3$ in 50 ml of 0.1 N HCl. The pH of the solution was adjusted to 7 by adding Na_2CO_3. Then the pH of the solution was lowered to 3 by adding $NaHSO_3$. After heating the solution at 80 °C for 30 min, the pH of the solution was raised to 6 by adding Na_2CO_3 where a greyish-blue precipitate of $Na_6Ru(SO_3)_4$ was obtained, which was filtered, washed copiously with distilled water and dried in an air oven at 80 °C for 2 h.

2.2. Preparation of Pt/C for the cathode

The required amount of Ketjen Black (EC) 600-TD (Akzo Chemie) carbon (80 mg) was suspended in distilled water and agitated in an ultrasonic water bath at 80 °C to form carbon slurry. 400 mg of $Na_6Pt(SO_3)_4$ was dissolved in 50 ml of 0.5 M H_2SO_4 and diluted to 150 ml with distilled water. This solution was added drop by drop to the carbon slurry with constant stirring at 80 °C. 50 ml of H_2O_2 (30%) was slowly added to it with temperature maintained at 80 °C, which resulted in vigorous gas evolution, and the slurry was further stirred for 1 h. Platinized-carbon substrate was obtained by reducing with 1 wt.% formic acid solution which was washed copiously with hot distilled water, filtered and dried in an air oven at 80 °C for 2 h.

2.3. Preparation of Pt-Ru/C for the anode

The required amount of Ketjen Black carbon (33 mg) was suspended in water (50 ml) and agitated in an ultrasonic bath to form a thick carbon slurry. 653 mg of $Na_6Pt(SO_3)_4$ was dissolved in 50 ml of 0.5 M H_2SO_4 and diluted to 750 ml with distilled water. The pH of the solution was adjusted to 5 by adding 10 wt.% NaOH solution. 100 ml of H_2O_2 (30%) was added to it drop by drop with constant stirring. The pH of the solution was adjusted to 5. To this solution, 560 mg of $Na_6Ru(SO_3)_4$ dissolved in 150 ml of 0.5 M H_2SO_4 was added drop by drop. The pH of the solution was again adjusted to 5 after the gas evolution ceased. The carbon slurry was now slowly added to it under constant stirring. Hydrogen gas was bubbled through this admixture for 1 h, and the suspension was allowed to settle; afterwards, it was washed copiously with hot distilled water and dried in an air oven at 80 °C for 2 h.

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2.4. Membrane-electrode assembly

Both the anode and cathode consisted of a backing layer, a gas-diffusion layer and a reaction layer. The Teflonized carbon paper (Kureha) of 0.3 mm thickness was employed as the backing layer in these electrodes. To prepare the gas-diffusion layer, Ketjen Black carbon was suspended in water and agitated in an ultrasonic bath. To this, 10 wt.% of Teflon (Fluon-GP2) suspension was added with continuous agitation. The required amount of cyclohexane was then added to it drop by drop. The resultant slurry was spread on to the Teflonized carbon paper and dried in an air oven at 80 °C for 2 h. To prepare the reaction layer, the required amount of Pt/C (cathode) or Pt-Ru/C (anode) was mixed with 10 wt.% of Teflonized carbon obtained by mixing activated carbon with 10 wt.% of Teflon suspension followed by heating in air oven at 350 °C for 30 min. This mixture was suspended in water and agitated in an ultrasonic water bath, and a 15 wt.% of Nafion solution (Aldrich) was added to it with continuous stirring. The paste thus obtained was spread on to the gas-diffusion layer of the electrode, and cold pressed at $75 \, \text{kg cm}^{-2}$ for 5 min. The Pt content in both the cathode and anode was maintained at about $5 \, \text{mg cm}^{-2}$. A thin layer of Nafion® solution was spread on to the surface of each electrode. The membrane electrode assembly (MEA) was obtained by pressing the cathode and anode on either side of a pre-treated Nafion-117 proton exchange membrane by compaction under a pressure of $50 \, \text{kg cm}^{-2}$ at 125 °C for 3 min. The MEA thus obtained was about a millimeter in thickness.

2.5. Fuel cell stack assembly

A liquid-feed SPE-DMFC stack was assembled with the two membrane electrode assemblies in series. The anode and cathode of the MEA were contacted on their rear with gas/fluid-distributing plates machined from stainless steel in which channels had been formed. The channels were machined to achieve minimum mass-polarization in the SPE-DMFC. The ridges between the channels made electrical contact with the backs of the electrodes to conduct the current to the external circuit. The channels supplied the fuel (methanol) to the anode and oxidant (oxygen) to the cathode. Electrical heaters were placed behind each of the steel blocks in order to heat the cell to the desired operational temperature. The methanol solution was pumped to the anode chamber through a peristaltic pump and the unreacted methanol solution was collected back in the reservoir. Pressurized oxygen gas at a defined pressure (1–4 bar) was introduced into the cathode chamber. The stainless steel blocks were also provided with connectors for electrical contacts and tiny holes to accommodate the thermocouples. Galvanostatic-polarization data on the
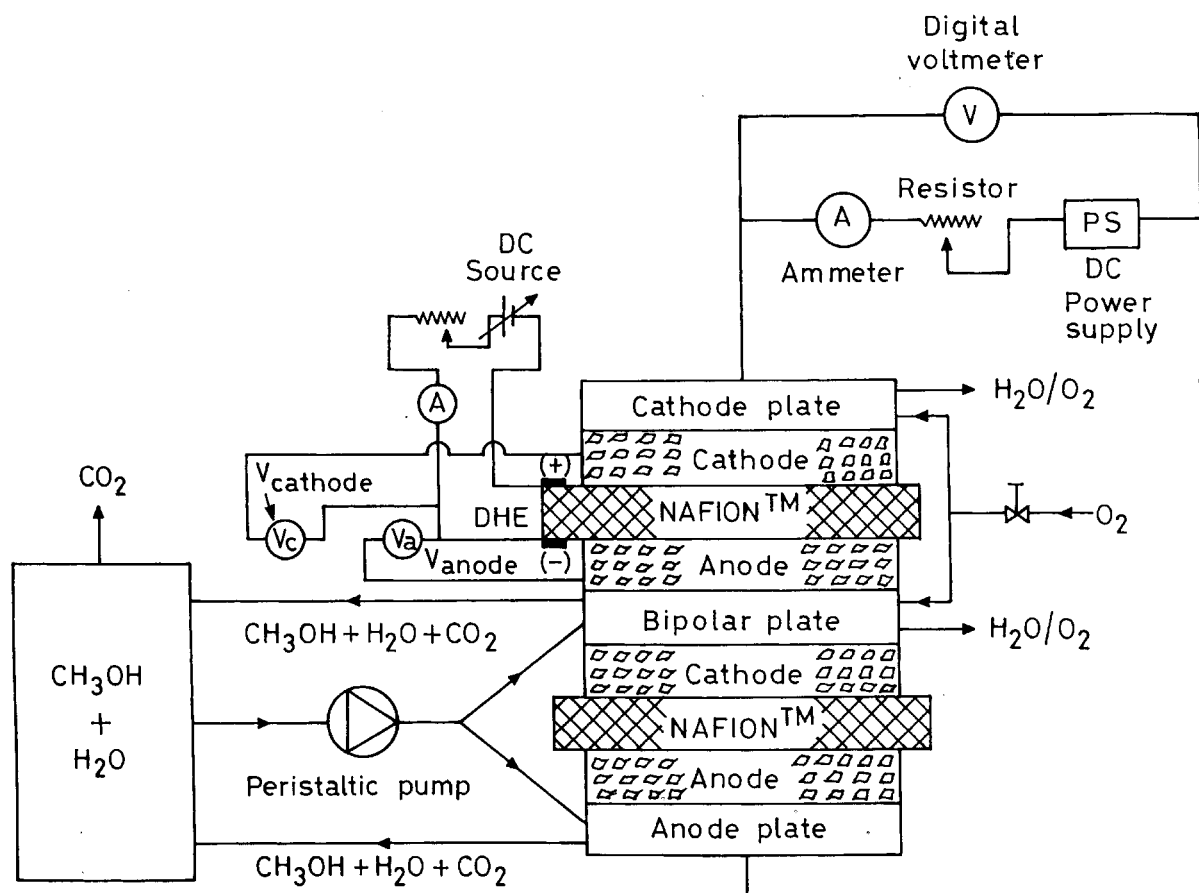

Fig. 1. Schematic diagram of the 5 W liquid-feed SPE-DMFC stack with dynamic hydrogen reference electrode for single electrode potential measurements.

activated SPE-DMFC were obtained with 2 M methanol at 70 °C and 90 °C under oxygen pressure of 1–4 bar.

A 5 W fuel cell stack was assembled by connecting two monopolar plates and a bipolar plate in series with each plate having an active area of $25 \, \text{cm}^2$. A dynamic hydrogen reference electrode (DHE) was also assembled by coupling two palladium-gold grids (5 mm × 5 mm) on to the Nafion membrane. A small dc voltage was imposed between these electrodes. The negative electrode, which generates hydrogen, was used as reference. This reference electrode was calibrated against a bubbling standard hydrogen electrode. The current through the DHE was adjusted to give a potential diference of ∼1 mV. A schematic diagram of the fuel cell stack is shown in Fig. 1. The dimensions of the channels for the anode were 50 mm × 2 mm × 2 mm with 0.5 mm ridge thickness between the two channels. Each channel was provided with an inlet and an outlet for liquid flow. The dimensions of the channel for the cathode were 50 mm × 2 mm × 1 mm and the ridge thickness between the two channels was 1 mm.

3. Results and Discussion

The polarization data for the SPE-DMFC stack at 70 °C and 90 °C along with the polarization data for one of the cells and its constituent electrodes at 4 bar oxygen pressure are shown in Figs. 2 and 3, respectively. A comparison of the stack performance at these temperatures as oxygen pressure is varied from 1 to 4 bar is presented in the insets to Figs. 2 and 3. It is clearly seen that the performance of the stack improves with increase in oxygen pressure and temperature. However, the single electrode polarization data presented in Figs. 2 and 3 show a decrease in the anodic overpotential for methanol electrooxidation while an increase in cathodic overpotential is observed for the electroreduction of oxygen with increase in temperature from 70 °C to 90 °C. The

Fig. 3. The performance of the 5 W liquid-feed SPE-DMFC stack with 2 M methanol and 4 bar oxygen pressure at 90 °C: (a) anode performance, (b) cathode performance, (c) single cell performance, and (d) stack performance. The inset shows the effect of varying oxygen pressure from 1 bar to 4 bar. Maximum power-density: $0.2 \, \text{W} \, \text{cm}^{-2}$.

increase in overpotential at the cathode with increase in temperature may be attributed to methanol crossover from the anode across the Nafion-117 membrane.

Recently, it was reported that methanol permeability can be effectively reduced by the use of a new proton conducting membrane [7]. Efforts are also being made to develop methanol tolerant oxygen reduction catalysts [8–10]. It is believed that by making use of improved engineering and stainless steel flow-distributors, it is possible to circumvent the deleterious effect of methanol/oxygen crossover across the bipolar plates in SPE-DMFC stacks.

As seen from Fig. 4, the DMFC stack can deliver 5 W power at the load current-density of $300 \, \text{mA} \, \text{cm}^{-2}$ at 90 °C. The endurance test data for the stack at 50 and $100 \, \text{mA} \, \text{cm}^{-2}$ of load currents over a duration of 8 h at 70 °C and 90 °C are given in Fig. 5. In the inset to this figure, the endurance data for the stack at 90 °C under a load current-density of $100 \, \text{mA} \, \text{cm}^{-2}$, and of one of the cells along with its constituent electrodes, are given. From these data, it
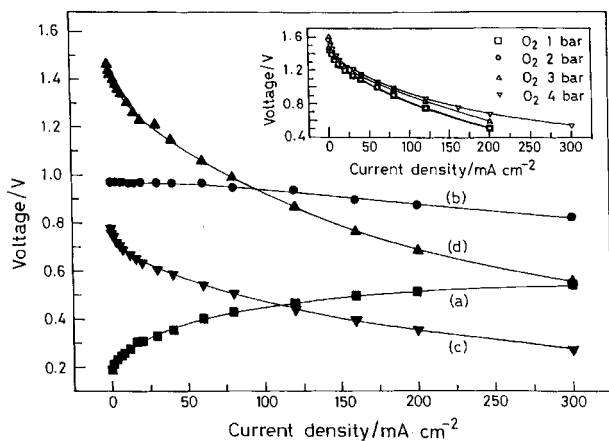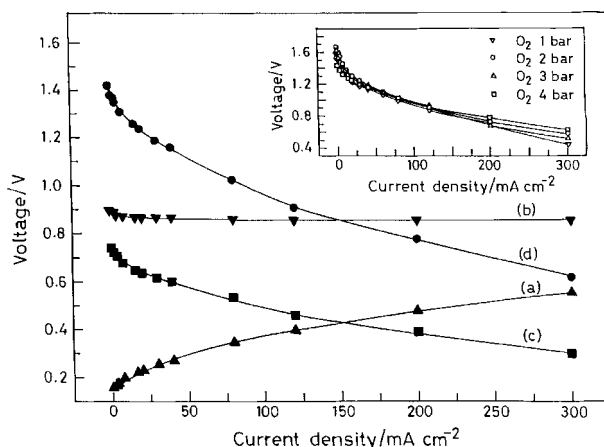

Fig. 2. Performance of the 5 W liquid-feed SPE-DMFC stack with 2 M methanol and 4 bar oxygen at 70 °C: (a) anode performance, (b) cathode performance, (c) single cell performance, and (d) stack performance. The inset shows the effect of varying the pressure from 1 bar to 4 bar.
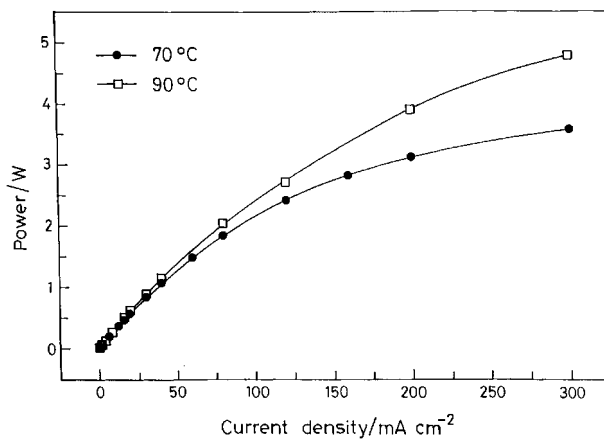

Fig. 4. The power output of the 5 W liquid-feed SPE-DMFC stack at 70 °C and 90 °C as the function of load current density.
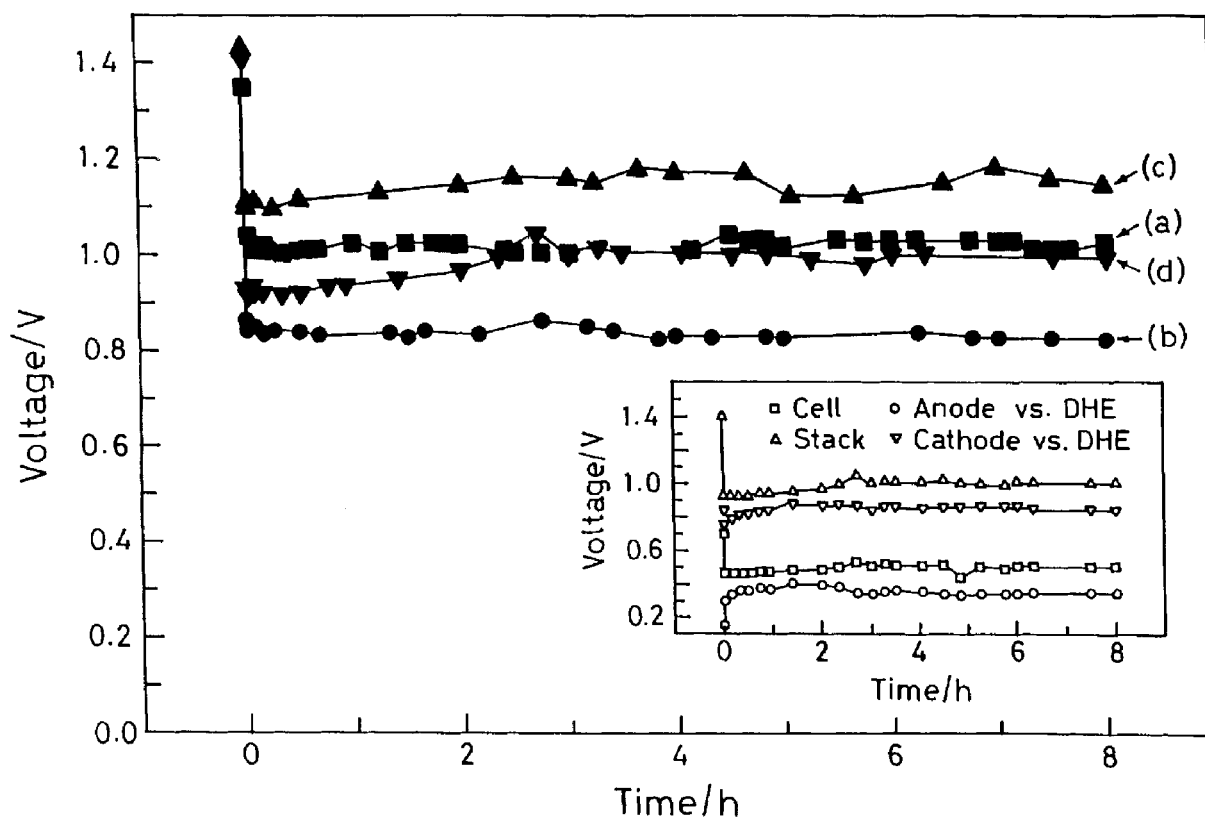
Fig. 5. Endurance test data for the 5 W liquid-feed SPE-DMFC stack: (a) 50 mA cm^{-2} at 70 °C, (b) 100 mA cm^{-2} at 70 °C, (c) 50 mA cm^{-2} at 90 °C and (d) 100 mA cm^{-2} at 90 °C. The inset shows the endurance test data for the stack at 90 °C under load current density of 100 mA cm^{-2} along with one of its cells and its constituent electrodes. Methanol flow-rate: 1 ml min^{-1}; oxygen flow-rate: 60 ml min^{-1}.

is seen that both the stack and the cell show little deterioration in performance.

4. Conclusions

This study suggests that the performance of a liquid-feed SPE-DMFC stack with stainless steel flow-distributors is comparable to one fabricated with graphite. The SPE-DMFC stacks with stainless steel, besides being rugged, are cost effective compared to graphite.

Acknowledgements

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