



Short communication

## A Nafion–silica cathode electrolyte for durable elevated-temperature direct methanol fuel cells

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## ABSTRACT

A novel catalyst layer assisted by a Nafion–silica electrolyte for elevated-temperature direct methanol fuel cells is fabricated through a self-assembly process. The catalyst layer demonstrates good water retention abilities and structural stability during the fuel cell operation. After a dehydration period of 30 min under 25% relative humidity at 100 °C, the proton conductivity of the novel catalyst layer is maintained at  $\sim 0.014 \text{ S cm}^{-1}$ , and the single cell assembled with the novel catalyst layer achieves a maximum power density of  $108 \text{ mW cm}^{-2}$ . Moreover, a stability operation test conducted under 20 ppm CO and a current density of  $100 \text{ mA cm}^{-2}$  demonstrates the structural stability and water retention abilities of the catalyst layer. The cell voltage of a fuel cell featuring the novel catalyst layer decreases from 0.45 to 0.38 V at a slight degradation rate of  $0.6 \text{ mV min}^{-1}$ .

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### 1. Introduction

Direct methanol fuel cells (DMFCs), which use methanol as a liquid fuel, are a promising application that can power future micro- and portable electronic devices because of their high energy density and inherent simplicity of operation [1,2]. However, widespread applications of DMFCs are hindered by technological challenges, such as sluggish methanol oxidation reaction rates on the anode, mixed over-potentials caused by the methanol crossover through the polymer electrolyte membrane, and the poisoning of the catalyst by the crossover methanol or CO intermediate products. It is recognized that the adsorption of CO onto Pt exhibits highly negative value for the standard entropy, indicating that adsorption is strongly favored at low temperatures. Thus, at such conditions, the CO tolerance of Pt-based electrocatalysts are significantly enhanced [3,4]. Conversely, over-potentials at the cathode can be improved at elevated temperatures [5].

The major challenge in operating temperature increases is the enhancement of water retention and thermal stability of membrane electrode assemblies (MEAs) [6]. New research studies are aimed at increasing the water retention of polymer electrolyte membranes for application at highly elevated temperatures or low humidity fuel cells [7–9]. However, increasing fuel cell operating temperatures is still impeded by the low water retention abili-

ties of electrocatalysts. The rapid dehydration of the catalyst layers significantly decrease the reaction kinetics and cell performance.

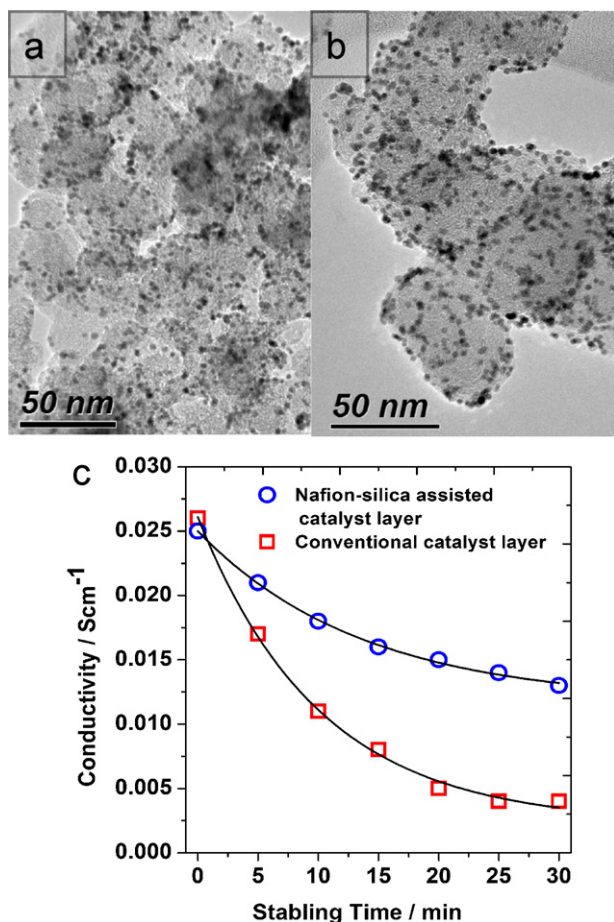
One approach used for such fuel cells is the incorporation of hygroscopic metal oxides, such as  $\text{SiO}_2$  or  $\text{Zr}_3(\text{PO}_4)_4$ , into the catalyst supports and hydrophilic domains of the catalyst layers [10–13], which results in the hydration enhancement of the catalyst layer at low relative humidity (RH) values and proton conduction at elevated temperatures. However, excess hydrophilic particles such as  $\text{SiO}_2$  inhibit proton or electron conduction, resulting in low cell performance or structural instability [13]. Another approach is the introduction of narrow hydrophilic channels in the catalyst layer. Capillary condensation occurs in these channels, reducing the saturation vapor pressure and producing liquid water at low RH [14]. However, this methodology is limited because it also results in electron conductivity decreases and chemical instability of the catalyst supports.

Here, we report a novel catalyst layer assisted by a Nafion–silica electrolyte for elevated-temperature DMFCs. The preparation procedure and properties of the catalyst layer are studied in detail. Results show that the catalyst layer possesses excellent water retention abilities, elevated-temperature performance, and structural stability.

### 2. Experimental

Nafion ionomers (EW = 1000, 5 wt.% Nafion) were transferred to an ethylene glycol solution (EG) by distilling a mixing solution of 100 mL Nafion and 100 mL EG solution. The solution was

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**Fig. 1.** TEM image of (a) the Pt/C catalyst assisted with silica–Nafion electrolyte, and (b) Pt/C catalyst prepared from the same route. (c) Proton conductivity degradation of the catalyst layer assisted with silica–Nafion electrolyte, and the conventional catalyst layer.

evaporated at 180 °C. One gram of tetraethoxysilane (TEOS) was dissolved in 80 mL of the Nafion/EG mixture and stirred for 2 h to form a silica–Nafion–EG electrolyte. The final SiO<sub>2</sub> content in the composite silica–Nafion was about 5 wt.%.

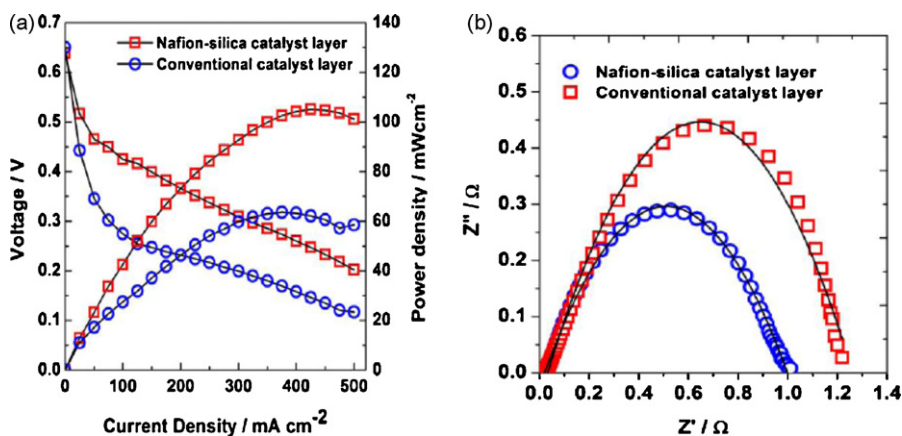
The Pt/C electrocatalyst assisted by the silica–Nafion electrolyte was prepared by a pulse-microwave-assisted polyol route [15]. Chloroplatinic acid, with a Pt content of 0.15 g, was added to the silica–Nafion–EG solution by ultrasonic treatment for 30 min, followed by the addition of 0.35 g carbon black ( $S_{\text{BET}} \sim 240 \text{ m}^2 \text{ g}^{-1}$ ) into

the 10 mL silica–Nafion mixture. The pH of the mixed suspension was adjusted to 10 by 1.0 mol L<sup>-1</sup> NaOH/EG solution. After dispersion with high-speed stirring and ultrasonication for 30 min, the Pt ions in the suspension were reduced to Pt<sup>0</sup> by three intermittent microwave-heating cycles with pulses every 5 s. After reduction, the pH of the suspension was adjusted to 2 by HCl to promote the adsorption of Pt nanoparticles onto the carbon support. The mixture was denoted as Pt/C catalyst assisted with silica–Nafion electrolyte.

Suspension of catalyst ink was made from the Pt/C catalyst assisted with silica–Nafion electrolyte mixed with iso-propanol (weight ratio of 1:10) stirred in an ultrasonic bath continuously at ambient temperature for 30 min. The catalyst ink was then screen-printed onto the GDL (TGP-060) to form the cathode catalyst layer of the DMFC. The Pt loading of cathode catalyst layer was controlled at 0.4 mg cm<sup>-2</sup>. A conventional Pt/C cathode was also prepared by a similar route without silica nanoparticles, the Pt loading was also 0.4 mg cm<sup>-2</sup>. The anode catalyst layer was prepared with 60 wt.% Pt–Ru/C catalyst (Pt:Ru = 1:1 molar ratio, Johnson Matthey). For the preparation, Pt–Ru/C catalyst, Nafion solution (Nafion net weight to Pt–Ru/C catalyst was 1:3) and iso-propanol was vigorously stirred, and screen-printed onto the GDL (TGP-060) to form the anode catalyst layer. The Pt loading on the anode was 0.8 mg cm<sup>-2</sup>. Then Nafion 115 membrane and catalyst-coated GDL were bonded together by hot pressing under 10 MPa at 125 °C for 90 s to form the membrane electrode assembly of the DMFC.

The water retention of the catalyst layer was measured by balancing the catalyst layer in 100% RH at 100 °C atmosphere for 4 h, and then dehydrating in 25% RH at 100 °C. The proton conductivity of the catalyst was measured using an impedance analyzer (CHI660 electrochemical station) as described in previous research [16,17]. The ends of the samples were covered with Nafion films. The membrane (4 cm × 2 cm) was sandwiched between two Pt sheets (2 cm × 2 cm). One Pt sheet was used as the working electrode and the other as the reference and counter electrode. Electrochemical impedance spectra (EIS) were obtained in the frequency range of 10 Hz to 100 kHz and a signal amplitude of 10 mV.

The electrochemical performance of a single DMFC was measured by a CHI660 electrochemical station with 2 M methanol as the fuel and oxygen with 20 ppm CO as the oxidant at 100 °C. The methanol and oxygen flow rates were 20 mL min<sup>-1</sup> and 200 sccm, respectively. The humidity of the air was kept at 25% RH. The stability of the catalyst layer was measured at 100 mA cm<sup>-2</sup> and 100 °C. The single cells were assembled with either a silica–Nafion or conventional cathode, Nafion 115 electrolyte membranes, and a Pt–Ru anode. Electrochemical impedance spectroscopy (EIS) of the single cells was performed using the cathode as the working electrode and a dynamic hydrogen electrode (DHE) as the counter and reference



**Fig. 2.** (a) Polarization performance and (b) impedance spectra of single cells using catalyst layer assisted with silica–Nafion electrolyte, as well as the conventional catalyst layer.

electrodes, at a cell voltage of 0.5 V and an amplitude of 5 mV over a frequency range from 10 mHz to 10 kHz.

### 3. Results and discussions

Fig. 1a displays the TEM image of the Pt/C catalyst assisted with a silica–Nafion electrolyte. For comparison, the Pt/C catalyst prepared from the same route without silica is presented in Fig. 1b. The results show that both samples have narrowly distributed Pt nanoparticles with an average particle size of 2–3 nm dispersed on the carbon support. Due to the low contrast, the silica particles cannot be clearly observed from the TEM image. However, EDAX showed that the S and Si elements were uniformly associated in the Pt/C catalyst assisted with the silica–Nafion electrolyte. This indicates that the silica–Nafion electrolyte is maintained in the catalyst powders. The uniform dispersal of the silica–Nafion electrolyte was most likely due to the self-assembly of the silica precursor and the Nafion electrolyte. Acidifying the TEOS solution significantly increases the proton adsorption reaction of SiOH, resulting in the formation of positively charged  $\text{SiOH}_2^+$  [18]. In the presence of Nafion ionomers, self-assembly occurs between the silica with positively charged surface groups and Nafion with negatively charged sulfonated ( $\text{SO}_3^-$ ) end groups by electrostatic forces. The Nafion assembled on the silica surface reverses the surface charge, stabilizing the silica nanoparticles and preventing grain growth. The Nafion electrolyte which covers the silica structure also makes the composite highly conductive to protons, and is more stable than the physically mixed Nafion/silica composite.

The water retention of the Pt/C catalyst layer assisted with the silica–Nafion electrolyte was measured in situ by a proton conductivity test after dehydration for various periods of time. For comparison, a conventional Pt/C catalyst layer prepared from the Pt/C catalyst and Nafion ionomers was also measured under the same conditions. The results in Fig. 1b demonstrate the water retention ability of the catalyst layer under high temperature and low humidity conditions. After drying in 25% RH at 100 °C for 30 min, the proton conductivity of the Pt/C catalyst layer assisted with the silica–Nafion electrolyte was maintained at  $\sim 0.014 \text{ S cm}^{-1}$ , with a total loss of about 40% compared to the original state. However, the proton conductivity of the conventional catalyst layer decreased rapidly under the same conditions. After 30 min of operation, the proton conductivity was reduced to  $\sim 0.003 \text{ S cm}^{-1}$ , about 1/8 that of the original state. The superiority of the novel catalyst layer may be attributed to its uniform dispersal and the Nafion-covered silica configuration in the catalyst nanocomposite. The closely packed Nafion electrolyte silica nanoparticles effectively deliver water molecules to the proton conductive channels and prevent the electrolyte from dehydration.

Fig. 2a shows the polarization performance, while Fig. 2b shows the impedance curves of single cells using the catalyst layer assisted with the silica–Nafion electrolyte and Nafion 115 membranes under 25% RH at 100 °C. The cell assembled with the conventional catalyst layer and Nafion 115 membranes was tested under the same conditions. The EIS spectra the single cells were analyzed using the cathode as the working electrode and the dynamic hydrogen electrode (DHE) as the counter and reference electrodes at a cell voltage of 0.5 V. The performance of the cell assembled with the conventional catalyst layer decreased sharply in the low current density region, suggesting the rapid dehydration of the cell at elevated temperatures and low humidity conditions. The performance recovered slightly with the increase in current, most likely due to the water produced in the cell. For the cell using the catalyst layer assisted with the silica–Nafion electrolyte, the initial voltage drop was much slower, indicating its improved water retention abilities. The maximum power density of the cell using the catalyst

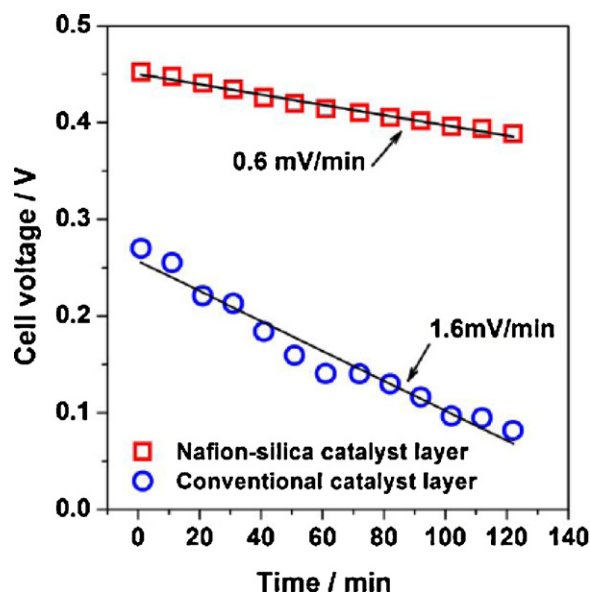


Fig. 3. Polarization stability of the single cells using catalyst layer assisted with silica–Nafion electrolyte, as well as the conventional catalyst layer.

layer assisted with the silica–Nafion electrolyte was  $108 \text{ mW cm}^{-2}$ , while that for the cell using the conventional catalyst layer was  $62 \text{ mW cm}^{-2}$ .

The high performance of the cells using the catalyst layer assisted with the silica–Nafion electrolyte was also supported by the impedance responses of the cells, as shown in Fig. 2b (impedance responses are characterized by a single arc). However, the size of the impedance arc for the reaction on the cell using the catalyst layer assisted with the silica–Nafion electrolyte was significantly smaller than that of the cell with using the conventional catalyst layer. The  $R_{ct}$  for the former was  $1.02 \Omega$ , significantly smaller than the  $1.24 \Omega$  obtained for the latter.

Fig. 3 shows the performance stability of the fuel cell using the catalyst layer assisted with the silica–Nafion electrolyte, as well as that using the conventional catalyst layer, at  $100 \text{ mA cm}^{-2}$ . To demonstrate the CO-resistance of the catalyst layer under elevated temperatures, 20 ppm CO was added to the oxidant stream. As shown in Fig. 3, the cell voltage of the fuel cell assembled with the conventional catalyst layer decreased significantly from the initial value of 0.27 V to a final value of 0.08 V after 120 min with a degradation rate of  $1.6 \text{ mV min}^{-1}$ . The sharp decrease of the performance can be attributed to the dehydration of the electrolyte and the CO poisoning of the catalyst. Humidity changes introduce a large amount of stress to the electrolyte membranes and films, leading to electrolyte dehydration. Thus, long-term dehydration destroys the electrolyte film in the catalyst layer, further decreasing the proton transportation pathway and proton conductivity of the electrolyte. The cell voltage for the fuel cell using the catalyst layer assisted with the silica–Nafion electrolyte decreased from 0.45 to 0.38 V with a degradation rate of  $0.6 \text{ mV min}^{-1}$ . The results demonstrate the structural stability and water retention ability of the catalyst layer assisted with the silica–Nafion electrolyte.

### 4. Conclusions

A novel catalyst layer assisted with a Nafion–silica electrolyte for elevated-temperature DMFCs is reported in this communication. After a dehydration period of 30 min under 25% RH at 100 °C, the proton conductivity of the novel catalyst layer was maintained at  $\sim 0.014 \text{ S cm}^{-1}$ , higher than that of the conventional catalyst

layer, which was  $\sim 0.003 \text{ S cm}^{-1}$ . At 25% RH and  $100^\circ\text{C}$ , the single cell assembled with the novel catalyst layer achieved a maximum power density of  $108 \text{ mW cm}^{-2}$ , higher than that of the cell using the conventional catalyst layer, which was  $62 \text{ mW cm}^{-2}$ . The high performance of the cells using catalyst layer assisted with the silica–Nafion electrolyte may be attributed to the water retention of the catalyst layer and the low  $R_{\text{ct}}$  of the cell reaction. During the stability operation test under 20 ppm CO and a current density of  $100 \text{ mA cm}^{-2}$ , the cell voltage for the fuel cell using the catalyst layer assisted with the silica–Nafion electrolyte decreased from 0.45 to 0.38 V at a slight degradation rate of  $0.6 \text{ mV min}^{-1}$ . This demonstrates the structural stability and water retention ability of the catalyst layer.

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