Characteristics of proton exchange membrane fuel cells cold start with silica in cathode catalyst layers

Zhili Miao\textsuperscript{a,b}, Hongmei Yu\textsuperscript{a,*}, Wei Song\textsuperscript{a,b}, Lixing Hao\textsuperscript{a,b}, Zhigang Shao\textsuperscript{a,*}, Qiang Shen\textsuperscript{a,b}, Junbo Hou\textsuperscript{a,b,1}, Baolian Yi\textsuperscript{a}

\textsuperscript{a}Laboratory of Fuel Cells, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, Liaoning 116023, PR China
\textsuperscript{b}Graduate School of the Chinese Academy of Sciences, Beijing 100039, PR China

\textbf{ARTICLE INFO}

Article history:
Received 23 December 2009
Received in revised form 9 March 2010
Accepted 11 March 2010
Available online 18 April 2010

Keywords:
Proton exchange membrane fuel cell
Cold start
Catalyst layer
Nanosized SiO\textsubscript{2}

\textbf{ABSTRACT}

In this study, a novel strategy is reported to improve the cold start performance of proton exchange membrane (PEM) fuel cells at subzero temperatures. Hydrophilic nano-oxide such as SiO\textsubscript{2} is added into the catalyst layer (CL) of the cathode to increase its water storing capacity. To investigate the effect of nanosized SiO\textsubscript{2} addition, the catalyst coated membranes (CCMs) with 5 wt.% and without nanosized SiO\textsubscript{2} are fabricated. Although at normal operation conditions the cell performance with nanosized SiO\textsubscript{2} was not so good as that without SiO\textsubscript{2}, cold start experiments at \textsuperscript{\textdegree}C\textsubscript{0} 8 showed that the former could start and run even at 100 mA cm\textsuperscript{2} for about 25 min and latter failed very shortly. Even at \textsuperscript{\textdegree}C\textsubscript{0} 10, the addition of SiO\textsubscript{2} dramatically increased the running time before the cell voltage dropped to zero. These results further experimentally proved the cold start process was strongly related with the cathode water storage capacity. Also, the performance degradation during 8 cold start cycles was evaluated through polarization curves, cyclic voltammetry (CV) and electrochemical impedance spectra (EIS). Compared with the cell without SiO\textsubscript{2} addition, the cell with 5 wt.% SiO\textsubscript{2} indicated no obvious degradation on cell performance, electrochemical active surface area and charge transfer resistance after experiencing cold start cycles at \textsuperscript{\textdegree}8 C.

© 2010 Professor T. Nejat Veziroglu. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Cold start capacity and survivability are very important to proton exchange membrane fuel cells (PEMFC) for their vehicular applications. It is well-known that the product water changes to ice or frost when the cell encounters subzero environment. When the membrane, local pores and ionomer in the cathode CL are insufficient to retain all the produced water, the open pores will be filled completely with ice, resulting in lack of reactant gases, reducing electrochemical active surface area (ECA) and even shutting down the cell \cite{1,2}.

If the operating temperature of the cell is raised above the freezing point before the cathode CL is filled completely with ice, the cell will be able to start under subzero temperatures successfully without any external aid. Thus, the water-holding capacity of the cathode CL is important to self-cold start of the cell.

In the past several years, the studies of cold start have been focused on the related freeze degradation, the gas purge process and cold start behavior \cite{3–10}. The images of the morphology of fuel cell after cold start process, illustrated the magnitude of damages. Water freezing delaminates the...
catalyst volume changed due to the material destruction or other degradations caused by water phase transition in the CL and the membrane. It was reported that the hydrogen desorption peak of the CL, as observed by the CV tests, would decrease after 10 cold start cycles. There was 5.4% degradation of power density per cold start experiment [7]. It was also reported that the cells could realize startup successfully at subzero temperature with external aids [11]. Also, the single cell was able to startup at -5 °C if it was pre-purged [12,13]. However, there are few reports referring to the successful self-startup from temperature lower than -5 °C.

To improve the water storing capacity of the CL and increase the cell performance at low humidity, hydrophilic materials was reported to be added into the CL. Jung et al. [14] added nanosized SiO2 particles into the CL. Performance of the cells with SiO2 decreased at 100% relative humidity (RH), but increased at 40% and 60% RH. The silica sol (prepared from hydrolysis of TEOS solution) and catalyst inks were mixed and then sprayed on the membrane [15]. When the cell was operated at 120 °C with 24% RH (inlet gases), the cell with 5 wt. % TEOS (relative to Nafion content in the CL) in the cathode CL showed the best performance. When nanosized SiO2 was added into the cathode CL, the hydrophilicity of the cathode CL would increase according to the contact angle measurement [16]. The cell performance was relatively higher at both full and low humidity with the addition of 5 wt.% nanosized SiO2.

In this work, cold start capacity of cells with and without nanosized SiO2 (5 wt.% relative to the whole cathode CL) in the cathode CL were comparatively investigated. The different operating conditions such as the temperatures and the start current densities were performed on the two cells. The effect of cold start on the cell performance was also studied by analyzing the polarization curves, CV and EIS during 8 cold start cycles at the start current density of 50 mA cm⁻².

2. Experimental

2.1. Preparation of MEAs and assembly of single cell

Two MEAs were prepared, which were a standard MEA and a SiO2-doped MEA, respectively. To prepare the standard MEA, the catalyst ink was firstly formed by mixing 40 wt.% Pt/C (Johnson Matthey Inc.), 5 wt.% Nafion solution (DuPont) and isopropyl alcohol. The catalyst ink was then sprayed onto a PTFE substrate and finally transferred onto a Nafion® 212 membrane to form a CCM. To prepare the SiO2-doped MEA, additional 5 wt.% nanosized SiO2 (based on the whole cathode CL) was added into the cathode catalyst ink. Both of the anode and the cathode were the same platinum loading of 0.4 mg cm⁻². The fabricated CCMs were pressed with wet-proofed Toray carbon paper to form the MEAs. The effective area of the MEA was 4 cm².

2.2. Cold start process

First, the cells which experienced pre-conditioning, performance test and electrochemical measurements, were purged by RH 20% gas until the RH of outflow gas reached 30% (both the anode and the cathode). Second, reactant gases were fed at a rate of 30 ml min⁻¹ for about 1 min to ensure an open circuit voltage above 1.0 V. Then, the cell was started up at 50 mA cm⁻² with 30 ml min⁻¹ flow rate for both H2 and O2 [12], after the cell was kept at the temperature between -8 °C and -10 °C for 1.5 h in a climate chamber. After the startup procedure, the cell was taken out of the climate chamber and characterized with cell performance and electrochemical measurement tests. Finally, the cell was purged and put into the climate chamber again for the next cold start cycle. Each cell repeated the cold start process eight times.

2.3. Cell performance test and electrochemical measurement

After the cold start process, the cell was operated at 50 mA cm⁻² for 30 min. The operating temperature was 60 °C. Then, the characterization of the cell performance was conducted with gas flow rates of 100/30 mL min⁻¹ of O2/H2 at atmospheric pressure, respectively, which was recorded by a KFM 2030 impedance meter (Kikusui, Japan). After the performance measurement, in-situ EIS was also measured by this impedance meter. The perturbation amplitude for the sinusoidal signal was 150 mV (peak to peak) over a frequency range of 10 kHz–0.5 Hz.

A cyclic voltammetry test was applied to measure the ECA of the cathode electrode using a BI-STAT 2 channel Potentiostat (USA, Princeton). The humidified hydrogen and ultra pure nitrogen gas were fed to the anode and the cathode with flow rates of 30 and 50 mL min⁻¹, respectively. The CV measurement was carried out between 0 and 1.0 V with a sweep rate of 50 mV s⁻¹.

3. Results and discussion

3.1. Cell performance

Initial cell performance of the two cells is shown in Fig. 1. The performance of the cell with 5 wt.% nanosized SiO2 in the cathode CL was lower than that of the cell without SiO2 in the whole current density region. It might be attributed to the isolative characteristic of the nanosized SiO2 or due to the high humidity of the reactive gas. This result is very consistent with the previous work [14].

The two cells started up from -8 °C at 50 mA cm⁻² and the variations of voltages during the startup are shown in Fig. 2. The voltage of the cell with 5 wt.% SiO2 was lower than the one without SiO2 during the initial period, which accords well with the cell performance shown in Fig. 1. After 15 min operation, the voltage of the cell without SiO2 fell off. On the contrary, the cell with 5 wt.% nanosized SiO2 was operating continually for more than 2 h. The cold start performance of the PEMFC was measured by the time a cell could operate before it was shutdown by ice filling in the cathode CL [17]. Due to hydrophilicity of the nanosized SiO2, the cathode CL of the cell with 5 wt.% nanosized SiO2 could retain more product water than the one without SiO2. If the time during which the cell could operate is used to judge the cold start performance of PEMFC,
compared with the cell without SiO₂, the cold start capability of the cell with 5 wt.% nano SiO₂ was better.

For the evaluation of the cold start experiments, the total product water is calculated according to the following equation [6].

\[
m_{H_2O} = \frac{M_{H_2O}}{2F} \int I \, dt
\]  

(1)

Where \(m_{H_2O}\) is the total product water, \(M_{H_2O}\) the molecular weight of water and \(I\) the cell current. For the cell without SiO₂, the total product water was 4.2 mg cm\(^{-2}\) during the startup process.

To further illustrate the effect of current density on the cold start process, the cold start experiment results are compared in Fig. 3. In Fig. 3a, the cell without SiO₂ shut down within 1 min at the current densities of 100 and 200 mA cm\(^{-2}\), and only lasted for 15 min at 50 mA cm\(^{-2}\). However, the cell with 5 wt.% nanosized SiO₂ was able to startup from 50 mA cm\(^{-2}\) and ran throughout the investigated time (Fig. 3b). Furthermore, the cell with 5 wt.% nanosized SiO₂ was able to operate longer than the one without SiO₂ at 100 mA cm\(^{-2}\).

In the case of low current density, the reaction current distributed uniformly throughout the pores in CL, and the water retaining capacity of CL could be fully utilized. However, in the case of high current density, the reaction current was not distributed uniformly. Water was produced more quickly and less time was available for the product water to transfer to the membrane. Consequently, the ice formation was more severe in the cathode CL at higher current densities. Higher amount of product water could form an ice sheet at the electrode interface before water retaining capacity of the cathode CL was fully utilized [9].

Fig. 4 gives the performance for the two cells during 8 cold start cycles. The cold start tests were operated at –8 °C and at 50 mA cm\(^{-2}\) with 30 ml min\(^{-1}\) flow rate for both H\(_2\) and O\(_2\). Fig. 4a shows that there is a small performance loss of the cell without SiO₂. The voltage difference between the 2nd cold start cycle and the 1st cold start cycle was more than 0.04 V at 1 A cm\(^{-2}\). However, no performance loss was observed in the whole investigated current density range from the 2nd cold start cycle to the fourth cold start cycle. There was a visible
voltage loss at high current density for the 5th cold start cycle. The cell could not operate at more than 600 mA cm\(^{-2}\) after the 5th cold start cycle. This situation had been observed previously [4], and it was most likely related with the water blocking effect. Since this cell could not startup successfully during the cold start, the product water formed ice to hinder the access of the reactant gas to the reaction site. As a result, both the reversible and irreversible performance lost contributes to such phenomenon [18].

Fig. 4(b) indicates that there is no visible performance loss for the cell with 5 wt.% nanosized SiO\(_2\) within the 8 cold start cycles. The cell could startup from \(-10\) °C at 50 mA cm\(^{-2}\) successfully. Due to the addition of nanosized SiO\(_2\), the water capacity of the cathode CL increased. The ice did not fill all the pores of the cathode CL, and then the oxygen reduction reaction could proceed during the cold start process. Therefore, the cell performance did not have an obvious performance loss with the cold start.

When the cells were operated under \(-10\) °C at 50 mA cm\(^{-2}\), two characteristics in the voltage curves can be seen in Fig. 5. First, they were almost the same at the initial performance measurements at low current density. Second, the cold start operation of the cell with 5 wt.% nanosized SiO\(_2\) lasted longer. This was mainly attributed to the hydrophilic SiO\(_2\) addition into the cathode CL. The CL was able to retain more product water, and thus the cell shutdown was delayed. Since ice formation of the cell with SiO\(_2\) is reduced, SiO\(_2\) could help the ionomer water absorption. This opens more time for the water in the ionomer of the cathode CL to diffuse into the membrane [19,20]. According to Eq. (1), the total product water was 2.51 and 1.78 mg cm\(^{-2}\), for the cell with 5 wt.% and without nanosized SiO\(_2\) in the cathode CL, respectively.

3.2. Electrochemical active surface area

The ECAs of the cells with no SiO\(_2\) and 5 wt.% nanosized SiO\(_2\) in the cathode CL were also investigated. The CV curves are shown in Fig. 6 and the calculated ECA results are shown in Fig. 7. The ECA reflected the active surface area of the cathode CL and could be calculated on the base of the hydrogen desorption peak area (HDA) [21]. A HDA decrease of the cell with no SiO\(_2\) is observed in Fig. 6(a). This result is consistent with the previously reported results [22]. The decreased cell performance was also observed. However, there was no significant performance decrease of the cell with 5 wt.% nanosized SiO\(_2\) in the cathode CL with the cold start cycles, indicated in Fig. 6(b). Furthermore, the ECA’s of the cell with 5 wt.% nanosized SiO\(_2\) did not change, as shown in Fig. 7, while for the one with no SiO\(_2\), the ECA was quite different — it decreased from 39.8 g \(^{-1}\) m\(^2\) to 25.2 g \(^{-1}\) m\(^2\) after the first cold start. This indicates that the number of catalytically active sites decreased. After the 8th cold start, the ECA of the cell with no SiO\(_2\) was 18.0 g \(^{-1}\) m\(^2\).

3.3. Electrochemical impedance spectra

Fig. 8 shows the effect of the cold start cycles with the start current density of 100 mA cm\(^{-2}\) on the EIS responses for the cells with 5 wt.% and without nanosized SiO\(_2\). Generally, the anodic polarization is very small and could be neglected. EIS spectra of H\(_2\)/O\(_2\) PEMFC are practically determined by the cathode [23]. The impedance spectrum includes a highest frequency intercept with the real axis denoting the sum of
interfacial contact and material bulk resistance ($R_1$), a higher frequency arc reflecting the combination of a charge transfer resistance ($R_{ct}$), a double layer capacitance ($C_{dl}$) and a lower frequency arc correlated with the mass transport process. The double layer capacitance is considered to be a constant phase element.

The values of $R_1$ did not increase with the cold start cycles in Fig. 8. This indicates that the sum of membrane resistance and the contact resistance between the membrane, electrodes and bipolar plates remained constant. At 100 mA cm$^{-2}$, the $R_{ct}$ of the cell without SiO$_2$ changed from 0.47 $\Omega$ cm$^2$ to 0.77 $\Omega$ cm$^2$ after seven cycles in Fig. 8(a). The increase rate was 43.66 m$\Omega$ cm$^2$ per cycle, which was consistent with the cell performance results. With the cold start cycle, the cell with hydrophilic CCM showed an obvious increase trend in the polarization resistance[7]. The cell without SiO$_2$ was not able to startup from $-8$ °C at 50 mA cm$^{-2}$ because of the ice in the pores of the cathode CL. The pore volume expansion was caused by ice formation. Once the ice had melted, a thin water film would form and block the pores in the cathode CL, and so oxygen diffusion would be blocked by the thin water film, which would induce a decay in the cell performance. Also, the increase of $R_{ct}$ ascribed to the catalyst specific surface area decrease should be considered.

In addition, $R_{ct}$ of the cell with 5 wt.% nanosized SiO$_2$ fluctuated less than the one without SiO$_2$ in Fig. 8(b). The increase rate was 8.1 m$\Omega$ cm$^2$ per cycle. The charge transfer process related to the oxygen reduction reaction was influenced by the proton transport and oxygen infiltration to the catalyst sites. Due to the hydrophilicity of nanosized SiO$_2$, the cell was able to startup from $-8$ °C at 50 mA cm$^{-2}$ for 8 cycles with no visible performance decrease. The performance was
not influenced by the ice formation. Thus, the charge transfer resistance changes of the cell with 5 wt.% nanosized SiO$_2$ were not obvious with the number of the cold start cycles.

4. Conclusion

The hydrophilic nano SiO$_2$ was added in the cathode catalyst layer and its effect on the cold start behavior was investigated as well as the related degradation by comparative study at different current densities and temperatures. The addition of SiO$_2$ made the cell capable of starting and running even at 100 mA cm$^{-2}$ from $-8 \degree C$ for about 25 min while the cell without the SiO$_2$ failed very shortly after the cold start. Even at $-10 \degree C$ the cold start performance was dramatically improved for the cell with SiO$_2$. Furthermore, although the catalyst layer with SiO$_2$ could hold more water than that without SiO$_2$, there was no evident performance loss, cell resistance increase and ECA decay observed for the cell with nano SiO$_2$ during the 8 cold start cycles.

Acknowledgments

This work was financially supported by the National High Technology Research and Development Program of China (863 Program, No. 2007AA05Z123) and the National Natural Science Foundations of China (No. 20636060, No. 20876154).

REFERENCES