



Short communication

Effect of Nafion aggregation in the anode catalytic layer on the performance of a direct formic acid fuel cell

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ABSTRACT

The effect of Nafion ionomer aggregation within the anode catalytic layer for a direct formic acid fuel cell (DFAFC) has been investigated. By simple heat treatment, the aggregation states of Nafion ionomers in aqueous solution can be tuned. Nafion agglomerate sizes in the solution decrease and aggregate size distribution becomes narrow with the increase in heat-treatment temperature. At a heat-treatment temperature of ca. 80 °C, nearly monodispersed Nafion ionomers corresponding to an aggregate size of ca. 25 nm in the solution are observed. The use of small Nafion ionomer agglomerates in the Nafion solution for anode catalytic layer significantly improves the performance of the passive DFAFCs. Impedance analysis indicates that the increased performance of the passive DFAFC with the anode using Nafion solution pretreated at elevated temperatures could be attributed to the decrease in charge-transfer resistance of the anode reaction. The decrease in Nafion aggregation within the catalyst ink leads to an increase in Nafion ionomer utilization within the catalyst layer and an improvement in catalyst utilization; thus enabling us to decrease Nafion loading within the anode catalytic layer but with slight improvement in DFAFC's performance.

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1. Introduction

Direct formic acid fuel cell (DFAFC) shows fascinating prospects for micro-power generation [1,2]. The use of formic acid as a fuel has several advantages in comparison to the use of methanol because formic acid is nontoxic and has two orders of magnitude lower crossover flux through a Nafion membrane than methanol, thus allowing the use of highly concentrated fuel solution in a DFAFC [3]. However, there are several technological issues that have to be addressed before its practical applications. These challenges include sluggish kinetics of both anode and cathode reactions, excessive fuel and water permeability through the polymer electrolyte membrane and very limited lifetime [4,5]. Many efforts have been devoted to develop novel Pd based nanosized catalysts for formic acid oxidation [6–8]. Only a few studies focused on the improvement in DFAFC's performance [1,2].

For proton exchange membrane fuel cells including DMFC and DFAFC, the membrane electrode assembly (MEA) is a key component of a DFAFC. As a part of the MEA, catalyst layer (CL) plays a key role in determining the MEA's performance. Nafion ionomers used both as a proton conductor and as a binder within the CL facil-

itate the extension of the three-dimensional reaction zone and an increase in catalyst utilization [9,10]. Too low Nafion loading will lead to a poor contact between the electrolyte and catalyst particles and thereby a poor cell performance. Very high Nafion content would cause a decrease in cell performance due to blocking of the catalyst sites, blocking of the electrode pores, reduction of gas permeability and increase in mass transfer resistance. Efforts to this end have involved the optimization of Nafion loading within the CL and the development of novel preparation methods for the MEAs [10–12].

It is known that each catalyst particle (as an effective reactive site) at least connects with one Nafion ionomer as a proton conductor and with one catalyst support particle or catalyst particle itself as an electron conductor to ensure a high catalyst utilization and a better cell performance. However, Nafion ionomers in the solutions and within the CL generally exist as aggregated states, thus leading to an insufficient Nafion and catalyst utilization. In the meantime, the large Nafion aggregates within the CLs would also block the electrode pores, thus decreasing mass transport. Aiming to improve the triple-phase region of catalytic layer and catalyst utilization, several reports have focused on novel methodologies for the development of the MEAs [13–15]. For example, by controlling the temperature of diffusive layer during the CL fabrication, the PEMFC's performance could be enhanced due to the increased pore volume of the CL, particu-

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larly in the secondary pore of the catalyst layer [13]. Recently, Wang et al. first found that the Nafion aggregation particles can be significantly suppressed by the addition of NaOH into Nafion solution, thus leading to a small agglomerate size distribution within the catalyst ink and to an increased DMFC's performance [14].

In this communication, we report a novel and simple strategy for preparation of the MEA for the DFAFCs. By simply heat treatment at various temperatures, the Nafion aggregation states could be easily decreased, enabling us to evaluate the effect of Nafion aggregation within the CL on the cell performance.

2. Experimental

2.1. Measurement of Nafion aggregation in Nafion solution

As-received Nafion ionomer solution (Nafion 5 wt% in water and alcohol, Aldrich) diluted with four times ultrapure water and heat-treated at different temperatures for 1 h, and then mixed ultrasonically at room temperature for a period of time.

The particle dispersion of the Nafion ionomer solution was measured by dynamic light scattering (DLS) Nano-ZS90 System (Malvern Instruments Ltd, UK) at 90° with an equilibration time of 4 min at room temperature.

2.2. MEA preparation

The membrane pretreatment procedures involved boiling the membrane in 5 vol.% H₂O₂ solution, washing with ultrapure water, boiling in dilute H₂SO₄ and washing with water for 2 h in turn. The pretreated membranes were kept in water prior to the fabrication of MEAs.

A slurry which consisted of Vulcan XC-72 carbon and PTFE (20 wt%) was coated onto the carbon paper (TGPH060, 20 wt% PTFE, Toray) to form the cathode diffusion layer. The XC-72 carbon loading was ca. 2 mg cm⁻².

The anode and cathode catalysts used in this work were Pd black (Sigma–Aldrich) and 60% Pt/C (HiSpec9001, Johnson Matthey), respectively. An appropriate amount of Nafion solution (5 wt%, Aldrich) was firstly dispersed into a mixture of isopropanol and water with a volume ratio of 1:1 and then pre-heated at different temperatures for 1 h. Then, such a mixture was cooled down to room temperature. Subsequently, the anode catalyst was added to this mixture to ultrasonically form the catalytic ink. The catalyst ink was then sprayed on the diffusion layer. The metal loading was 4.0 ± 0.1 mg cm⁻² for both cathode and anode. The Nafion ionomer loadings are 15, 10 and 7 wt% for the anode and 20 wt% for the cathode, respectively. The MEAs were prepared by hot-pressing both anode and cathode on both sides of a pre-treated Nafion212 membrane (H⁺, DuPont) at 130 °C and 6 MPa for 3 min.

2.3. Single cell test

The MEA performance was evaluated in a single cell with an active cross-sectional area of 4 cm². The MEA was sandwiched between two Au–Pt-deposited titanium plates with open areas of ca. 33% for anode and cathode, respectively. The polarization curves of the passive DFAFCs under air-breathing mode at a temperature of ca. 25 ± 1 °C were obtained on an Arbin FCT testing system (Arbin Instrument Inc., USA) by using 10 M HCOOH solution. For each discharging current point along the polarization curve, a period of 2 min waiting time was used to obtain the stable voltage. The discharging curves at a constant current density of 40 mA cm⁻² were obtained for the passive DFAFCs fueled with 6.0 ml of 10 M HCOOH solution.

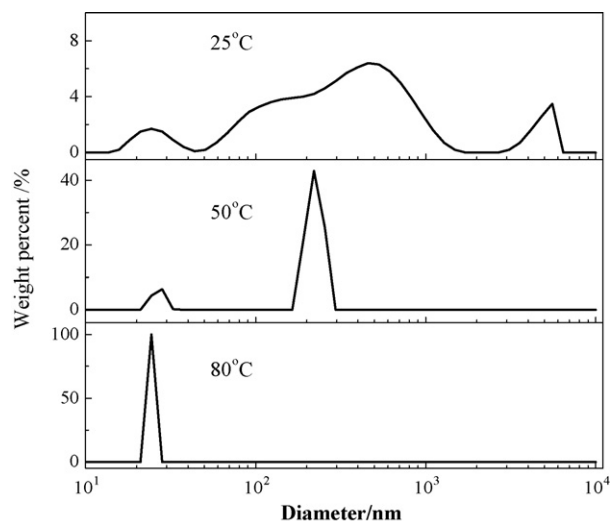


Fig. 1. Particle size distributions of dilute Nafion solution after heat treatment at different temperatures.

2.4. Electrochemical characterizations

Electrochemical impedance spectra (EIS) were recorded using Solartron SI1287 Potentiostat and Solartron 1255B Frequency Response Analyzer. All anode impedance spectra recorded were measured between anode and DHE at the cathode, and the over-potential of the DHE is negligible according to the previous work. Impedance spectra were obtained at a frequency range between 100 kHz and 0.01 Hz, and the amplitude of the sinusoidal voltage signal is 10 mV. The resultant impedance spectra were analyzed based on electrical circuit element model. The values of the model elements were determined by fitting the experimental data with Z-view software.

For all the electrochemical measurements, the cells were placed in a thermostated container at a temperature of ca. 25 ± 1 °C.

3. Results and discussion

3.1. The aggregation behavior of Nafion ionomer in Nafion solution

Generally, as-received Nafion ionomer solution exhibits very broad agglomerate size distributions. Fig. 1 shows the DLS agglomerate size distributions of dilute Nafion solution heat-treated at 25, 50 and 80 °C, respectively. For the solution heat-treated at 25 °C, there are very broad peaks ranging from ca. 25.4 to 4582.0 nm. As reported, the peaks of less than 100 nm are commonly designated as the particle size distribution of Nafion single molecular chains [15]. The large peaks of higher than 100 nm are due to the existence of aggregations of Nafion ionomers [15–17]. Thus, for the dilute Nafion solution pre-heated at 25 °C, most of Nafion ionomers existed as aggregated states in the solution and only ca. 7.1 wt% of Nafion ionomers as single molecular chains [15]. When the Nafion solution was heat-treated at 50 °C, there are two peaks located at 26.7 and 223.1 nm, respectively. About 11.0 wt% of Nafion ionomers existed as single molecular chains. Clearly, the very large Nafion ionomer aggregates broke up to form small aggregates and single molecular chains upon heating. Furthermore, when the Nafion solution was heat-treated at ca. 80 °C, there is only one peak centered at 24.4 nm, indicating that nearly all Nafion ionomers existed as single molecular chains. We assessed that the Nafion ionomer size of single molecular chains is ca. 25 nm in dilute Nafion solution. Obviously, the large aggregation ionomers are depressed to

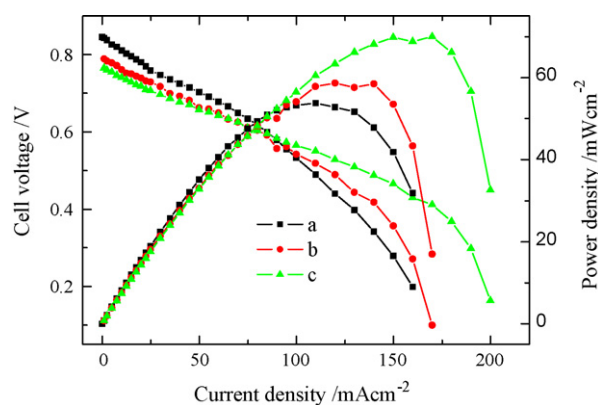


Fig. 2. Polarization curves of three passive DFAFCs with the anode catalyst ink pre-heated at 25 °C (a), 50 °C (b) and 80 °C (c) with a Nafion loading of 15 wt%.

the small ones at elevated temperatures. Clearly, the Nafion aggregation states in the solution can be easily changed by simple heat treatment [17,18]. In this case, it is convenient for us to evaluate the effect of Nafion aggregation behavior within the CL on the cell performance.

3.2. Performance comparison of the passive DFAFCs

Fig. 2 is a performance comparison of the passive DFAFCs with anode catalytic layer made with Nafion solution pre-heated at three different temperatures. It is clear that the open circuit voltage of the passive DFAFC decreases with the increase in heat-treatment temperatures for the Nafion solution. When the Nafion solution for the anode catalyst ink was pre-heated at 25 °C, the maximal power density of a passive DFAFC is only 53.7 mW cm⁻². When the Nafion solution was pre-heated at 50 °C, a maximal power density of ca. 58.6 mW cm⁻² was obtained. However, when the Nafion solution was pre-heated at 80 °C, a maximal power density of ca. 69.9 mW cm⁻² was obtained, clearly indicating that the power density of the passive DFAFC can be improved significantly by pre-heating the Nafion solution for the preparation of anode catalyst ink. Obviously, the use of small Nafion ionomer agglomerates in Nafion solution for the anode catalytic layer significantly improves the performance of the passive DFAFCs, probably suggesting that a better contact between Nafion ionomer and catalyst particle was obtained when the Nafion solution was pre-heated at elevated temperatures. Additional SEM analysis indicates that the agglomerates on the anodes made from the catalytic ink heat-treated at elevated temperatures exhibit a compact and uniform distribution, indicating that the catalyst particles connected well with small ionomers to form small aggregation state. Additional energy dispersive X-ray (EDX) analysis also shows that more Pd content was distributed on the surface of the anode when the catalytic ink was pre-heated at elevated temperature, suggesting that the use of small Nafion ionomer agglomerate results in a good distribution and high utilization of the Pd catalyst particles and thereby a better DFAFC's performance.

To explore the effects of Nafion ionomer aggregation within the anode catalytic layer for the DFAFCs, EIS of the MEAs in the DFAFCs were analyzed. Fig. 3A shows the anode impedance spectra together with fitted curves based on an equivalent circuit model as shown in Fig. 3B. The marked points are the experimental data, while the solid lines are the fitted curves. In this model, the constant phase elements (CPEs) are used to replace ideal capacitors, which are commonly found in conventional equivalent circuit models, to account for the non-uniform structure of the related electrode section [19,20]. The physical meanings of each element employed in the equivalent circuit model are as follows:

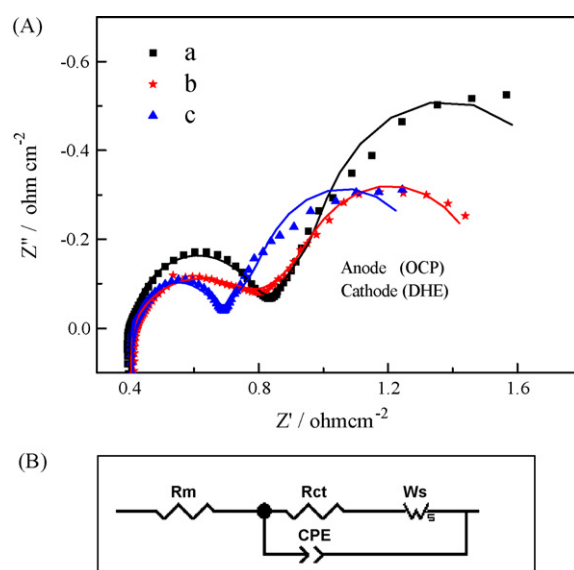


Fig. 3. EIS curves (A) and equivalent circuit (B) of the passive DFAFCs' anodes (vs. DHE) with the anode catalyst ink pre-heated at 25 °C (a), 50 °C (b) and 80 °C (c) with a Nafion loading of 15 wt%.

- (1) R_m denotes the ohmic resistance.
- (2) The capacitive CPE describes the capacitive behavior of the real anode with the roughness of the Pd black catalyst layer and non-uniform catalyst distribution, where R_{ct} and W_s represent the charge-transfer resistance of anode reaction and finite-length Warburg impedance, respectively. The conventional double-layer capacitance is replaced by a constant phase element (CPE) because the capacitance caused by the double-layer charging is distributed along the length of the pores in the porous electrode.

The good agreement between experimental and simulated data shown in Fig. 3A reveals the model validity as shown in Fig. 3B. The fitted parameters are provided in Table 1. From the interception with real axis at high-frequency region, the ohmic resistances of three passive DFAFCs are nearly the same, which are reasonable because the same anode catalyst and Nafion membrane were used in this work. Main differences in EIS spectra can be distinguished in the middle-frequency arcs, which are ascribed to the charge-transfer resistances of the anode reaction. Obviously, the heat treatment of Nafion solution for the preparation of anode catalyst ink leads to a decrease in charge-transfer resistance of the DFAFC, probably indicative of a better contact between catalyst particle and Nafion ionomer and thereby high catalyst and Nafion utilizations. The decrease in Nafion aggregation states after heat treatment implies that the Nafion loading within the CL could be decreased. Further XPS studies indicate that the heat treatment of the catalytic ink leads to a better dispersion of Pd nanoparticles and Nafion aggregates in the solution and to a strong interaction between

Table 1

Fitted parameters for the CPE-based equivalent circuit model for the anodes of the passive DFAFCs.

Heat-treated temperature for the Nafion solution (°C)	25	50	80
R_m (Ohm cm ²)	0.3988	0.3996	0.408
R_{ct} (Ohm cm ²)	0.412	0.4088	0.268
W_s-R (Ohm cm ²)	0.976	0.719	0.668
W_s-T (F cm ⁻²)	6.0525	4.24	5.48
W_s-P	0.571	0.515	0.536
CPE- T (F cm ⁻²)	0.04	0.12	0.052
CPE- P	0.842	0.613	0.818

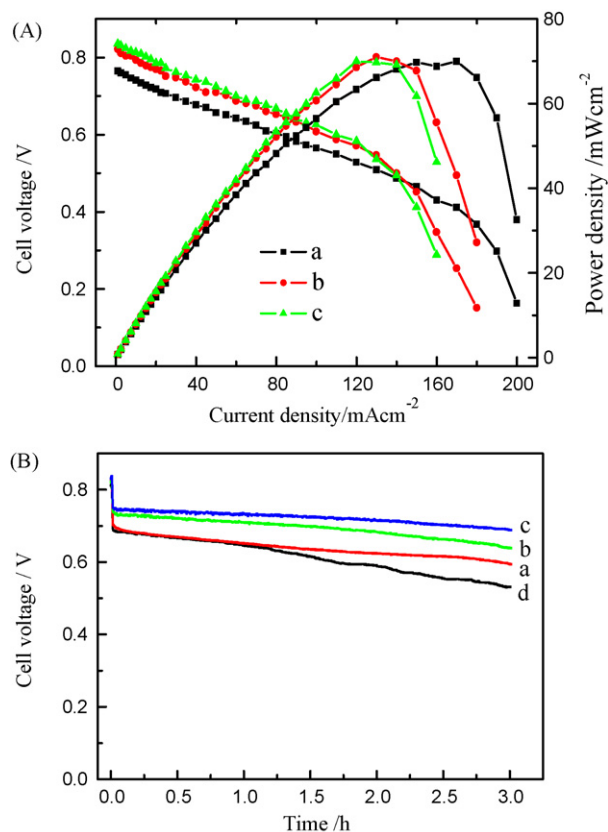


Fig. 4. Polarization curves (A) and discharging curves (B) of the passive DFAFCs with the anode catalyst ink using Nafion solution pre-heated at 80 °C with a Nafion loading of 15 wt% (a), 10 wt% (b) and 7 wt% (c) as well as pre-heated at 25 °C with a Nafion loading of 15 wt% (d).

Pd nanoparticles and Nafion ionomers, which could explain the decreased charge-transfer resistance and thereby increased performance of the passive DFAFCs.

Fig. 4A demonstrates the polarization curves of three passive DFAFCs with different Nafion loadings within the anode catalytic layer made with Nafion solution pre-heated at 80 °C. The maximal power densities of three passive DFAFCs are quite similar when the Nafion solution for the anode catalyst ink was pre-heated at 80 °C, clearly indicating that the pre-heated temperature for Nafion solution plays an important role in determining the performance of the passive DFAFCs and that the heat treatment leads to a decrease in Nafion agglomerate size, thereby to a better contact between catalyst particle and Nafion ionomer even at a very low Nafion loading. Thus, the Nafion loading within the anode CL could be significantly decreased due to an improved Nafion utilization.

Fig. 4B shows the galvanostatic curves of three passive DFAFCs with the anode catalyst ink pre-heated at 80 °C and with different Nafion loadings at a given current density of 40 mAcm⁻². For a comparison, the galvanostatic curve of the passive DFAFC with the anode catalyst ink pre-heated at 25 °C and with a Nafion loading of 15 wt% is also given in the figure. It can be seen that the discharge voltage of the passive DFAFCs continuously decays with time, probably due to the water flooding at cathode side, to the possible change in fuel concentration during the testing and to the poisoning effect of anode catalysts [3,5]. However, three passive

DFAFCs with the catalyst ink from the Nafion solution pre-heated at 80 °C exhibited the enhanced performance. The best performance was found for a passive DFAFC with a Nafion loading of 7 wt% within the catalyst ink using Nafion solution pre-heated at 80 °C. Obviously, the decrease in Nafion ionomer aggregates in the solution is beneficial to the increase in both Nafion and catalyst utilizations and to the decrease in Nafion loading within the catalytic layer.

4. Conclusions

In summary, we have found that the Nafion aggregate sizes in the solution decrease and that the agglomerate particle size distribution becomes narrow with the increase in heat-treatment temperature until nearly monodispersed Nafion ionomers were obtained at ca. 80 °C. The use of small Nafion ionomer agglomerates in the solution for the anode catalytic layer significantly improved the performance of the passive DFAFCs. Such increased performance of the DFAFCs could be due to an effective contact between catalyst particle and Nafion ionomer, which leads to a high Nafion and catalyst utilization. In our laboratory, the effect of Nafion ionomer aggregation within the catalytic layers on fuel cell performance has been extended into the direct methanol fuel cells, the similar conclusions were also obtained.

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