

Short communication

## Effect of Nafion<sup>®</sup> ionomer aggregation on the structure of the cathode catalyst layer of a DMFC

Suli Wang<sup>a,b</sup>, Gongquan Sun<sup>a,\*</sup>, Zhimou Wu<sup>a,b</sup>, Qin Xin<sup>a</sup>

<sup>a</sup> Direct Alcohol Fuel Cell Laboratory, Dalian Institute of Chemical Physics, Chinese Academy of Science, 457 Zhongshan Road, Dalian 116023, China

<sup>b</sup> Graduate School of the Chinese Academy of Sciences, Beijing 100039, China

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### Abstract

The effect of Nafion<sup>®</sup> ionomer aggregation in solution on the structure of the cathode catalyst layer of a direct methanol fuel cell (DMFC) was investigated by dynamic light scattering (DLS), laser particle sizer, electron probe microanalysis (EPMA) and scanning electron microscopy (SEM). The results showed that large aggregation particles were suppressed by the addition of NaOH to aqueous solutions of Nafion<sup>®</sup>, which led to a smaller agglomerate particle size distribution in the catalyst ink. The cathode catalyst layer made from the catalyst ink with NaOH addition showed a more uniform distribution of sulfur and Pt elements, a higher electrochemical active surface area (48% increase) and achieved a better performance in the DMFC than one made from the catalyst ink without NaOH addition.

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**Keywords:** Direct methanol fuel cell; Nafion<sup>®</sup> solution; Aggregation behavior; Membrane electrode assembly

### 1. Introduction

The direct methanol fuel cell (DMFC) is a potential power source for electronic devices and portable applications due to its high energy density, low pollution and convenient refueling. The membrane electrode assembly (MEA) is the heart of DMFC, in which the electrochemical reactions take place at the three-phase boundary zone consisting of catalyst, reactants and electrolyte [1]. The performance of an MEA for the DMFC is greatly affected by the formation of a polymer electrolyte network and the uniformity of the polymer electrolyte on catalyst particles in the catalyst layer [2].

Much effort has been dedicated to maximizing the catalyst/electrolyte interface, in order to extend the three-phase reaction zone. Initial electrodes for polymer electrolyte membrane fuel cells (PEMFC) were developed from PTFE bonded electrodes for the phosphoric acid fuel cell (PAFC). Although a perfluorosulfonated ionomer (PFSI) membrane was used as an electrolyte for the PEMFC, the membrane did not penetrate

deeply into the electrodes as a liquid electrolyte did. As a consequence, the catalyst utilization was low and thus high catalyst loading was needed [3]. As a consequence, the PFSI solution dissolved in an alcoholic solvent was impregnated in the catalyst layers to increase the contact area between Pt particles and PFSI. Thereby, the Pt loading decreased as the Pt utilization increased [4–6]. An innovative catalyst layer was prepared on the membrane from an ink with a Nafion<sup>®</sup> ionomer instead of PTFE by direct casting or a decal process. The protonic conductivity both inside the catalyst layer and across the interface between the catalyst layer and the Nafion<sup>®</sup> membrane was increased and the three-phase reaction zone was significantly improved [7–9]. Uchida et al. proposed a new method to prepare the electrode, which focused on a colloidal form of the PFSI [10–12]. The continuous network of Nafion<sup>®</sup> ionomers throughout the catalytic layer was increased. However, Arico et al.'s studies showed that the main obstacles to maximizing the contact area between the catalyst and electrolyte were the significant difference in the size of carbon particles and Nafion<sup>®</sup> micelles, as well as the tendency for the latter to aggregate [13].

In this study, the effect of Nafion<sup>®</sup> ionomer aggregation behavior on the structure of the cathode catalyst layer for a DMFC was investigated. NaOH was used to suppress the

\* Corresponding author.

E-mail address: [gqsun@dicp.ac.cn](mailto:gqsun@dicp.ac.cn) (G. Sun).

aggregation of Nafion<sup>®</sup> ionomer in diluted aqueous solution. Dynamic light scattering (DLS) and a laser particle sizer were used to identify the particle size both in the Nafion<sup>®</sup> solution and in the catalyst ink. The structure of cathode catalyst layer was characterized by scanning electron microscopy (SEM), N<sub>2</sub> adsorption and electron probe microanalysis (EPMA). The performance of the electrode was investigated through electrochemical analysis and a single cell evaluation.

## 2. Experimental

### 2.1. Measurement of Nafion<sup>®</sup> aggregation in Nafion<sup>®</sup> solution and catalyst ink

Acid-form Nafion<sup>®</sup> 1100 (SE-5142, DuPont) was purchased from DuPont as a 5 wt.% solution, containing a mixture of water, methanol, propanol and an unspecified mixed ether.

The Nafion<sup>®</sup> solutions S-1 and S-2 were prepared from as-received Nafion<sup>®</sup> solution diluted with deionizer water and NaOH aqueous solution to ca. 5 mg mL<sup>-1</sup>, respectively. The concentration of NaOH in the S-2 was ca. 0.05 M.

To prepare the cathode catalyst ink, Pt black catalyst (HISPEC<sup>TM</sup> 1000 from Johnson Matthey Corp.) was mixed with the above Nafion<sup>®</sup> solutions S-1 and S-2; the resulting mixtures were agitated in an ultrasonic bath to form homogeneous inks, which were denoted as I-1 and I-2, respectively. The anode catalyst ink was prepared with a PtRu black catalyst (HISPEC<sup>TM</sup> 6000 from Johnson Matthey Corp.) and Nafion<sup>®</sup> solution S-1 in the same way.

The particle size distribution of Nafion<sup>®</sup> ionomer in S-1 and S-2 was measured with a Coulter<sup>®</sup> particle analyzer (N4 plus) and that in catalyst ink was obtained by a laser particle sizer (BT-9300) at 20 °C.

### 2.2. Preparation of membrane electrode assemblies

To prepare a catalyst coated membrane (CCM), a piece of Na<sup>+</sup> formed Nafion<sup>®</sup> 115 membrane was held on a vacuum table at 60 °C, then the cathode catalyst ink was applied to one side of the membrane by hand painting. The anode ink was sprayed onto the other side of the membrane. The resulting Pt loading was 6.3 mg cm<sup>-2</sup> and the Nafion<sup>®</sup> content was 10 wt.% in the cathode catalyst layer; the Pt-Ru loading was 4.5 ± 0.2 mg cm<sup>-2</sup> and the Nafion<sup>®</sup> content was 15 wt.% in the anode catalyst layer.

The CCM was re-protonated to the H<sup>+</sup> form in 0.5 M sulfuric acid at 80 °C for at least one hour, followed by rinsing with deionized water. The CCMs prepared with I-1 and I-2 catalyst inks were denoted as CCM-1 and CCM-2, respectively.

Finally, the anode and cathode diffusion backings with a dimension of 2 cm × 2 cm were placed on the corresponding side of the CCM to form the MEAs.

### 2.3. Characterization of cathode catalyst layer

The surface morphologies of the cathode catalyst layers were examined with a JEOL JSM-5600LV SEM.

The distribution of fluorine, sulfur and platinum was investigated by electron probe microanalyzer (EPMA-1600).

The BET surface area of the cathode catalyst layer was obtained on an ASAP 2000 system (Micromeritics).

### 2.4. Electrochemical measurements

In situ cyclic voltammetry (CV) of the cathode catalyst layers at 60 °C was performed using an EG&G PAR 273 potentiostat at a scan rate of 20 mV s<sup>-1</sup> as described by Thomas et al. [14].

### 2.5. Single cell test

MEA performance was tested in a single cell. The MEA was fitted between two stainless steel plates with a punctual flow bed. The polarization curves were obtained using a Fuel Cell Test System (Arbin Instrument Corp.) under the operation conditions of 60 °C, 1 M methanol solution with a flow rate of 1 mL min<sup>-1</sup> and dry oxygen at 2 atm.

Anode polarizations were measured by EG&G PAR 273A potentiationstat/galvanostat at 60 °C. The anode compartment was supplied with 1 M methanol aqueous solution serving as the working electrode at 60 °C. The cathode was fed with 50 mL min<sup>-1</sup> humidified H<sub>2</sub> acting as the counter electrode and dynamic hydrogen electrode (DHE) [15]. The resistance of methanol/H<sub>2</sub> cell was measured by electrochemical impedance spectroscopy (EIS). IR corrected cathode polarizations were obtained by summing IR corrected anode polarizations with IR corrected cell performance.

## 3. Results and discussion

### 3.1. The aggregation behavior of Nafion<sup>®</sup> ionomer in Nafion<sup>®</sup> solution and catalyst ink

DLS measurements were made in order to determine the particle dispersion of the Nafion<sup>®</sup> ionomer in the S-1 and S-2 solutions. The results are shown in Fig. 1. Two main peaks of the particle size distributions were observed in the above mentioned solutions. The small one (<100 nm) corresponded to the particle size distribution of Nafion<sup>®</sup> single molecular chains. The appearance of the large one (>100 nm) suggested the existence of aggregations of Nafion<sup>®</sup> molecules [16]. Most of Nafion<sup>®</sup> ionomer aggregated seriously in S-1 and only ca. 22% Nafion<sup>®</sup> ionomer existed as single molecular chains (Fig. 1a), while more than 75% of Nafion<sup>®</sup> ionomer was in single molecular chains in S-2 (Fig. 1b).

It was reported that two aggregation processes of Nafion<sup>®</sup> molecules occurred in the alcohol/water mixture [17]. Nafion<sup>®</sup> molecule aggregated through its hydrophobic backbone to form rod-like primary aggregations, with the ionic side chains surrounding around the surface of the rod-like structures. These primary aggregation particles aggregated again through the hydrophilic ionic side chains to form secondary aggregations. Comparing Fig. 1a with b, it was found that the presence of NaOH in the solution decreased the size of the aggregations. Similar results have also been reported that large aggregations

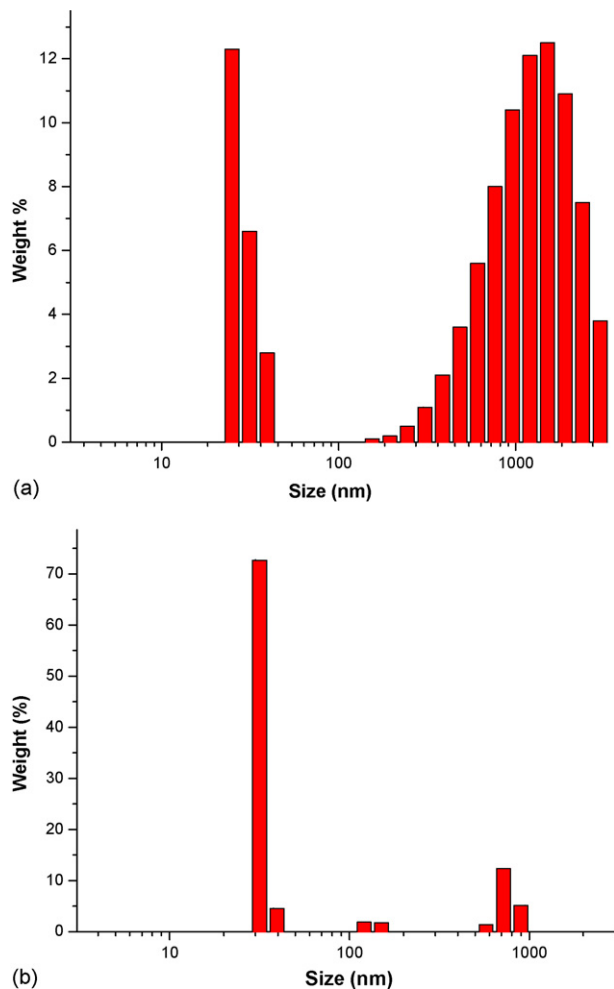


Fig. 1. Particle size distributions of  $5 \text{ mg mL}^{-1}$  Nafion<sup>®</sup> solutions: (a) as-received Nafion<sup>®</sup> solution diluted with water (S-1) and (b) as-received Nafion<sup>®</sup> solution diluted with aqueous NaOH (S-2).

were suppressed by the addition of LiCl or NaCl [16,18]. It is believed that these large aggregations were formed via electrostatic interactions, which might originate from the attraction between nonionic ion pairs and could be suppressed in an environment of high ionic strength [18]. Therefore, it is suggested that the large particles shown in Fig. 1a were the results of intermolecular ionic aggregations, which were dissociated by the addition of 0.5 M NaOH into the Nafion<sup>®</sup> solution to shield the  $-\text{SO}_3\text{H}$  ionic interactions. As a result, about 75% of the Nafion<sup>®</sup> particles were centered around 30–40 nm in S-2. While those particles distributed in the region of 500–1000 nm were the results of primary aggregations.

From the above results, we can deduce that the large aggregations in Nafion<sup>®</sup> solution are mainly caused by intermolecular ionic aggregations. These secondary ionic aggregations can be dissociated by adding NaOH to the Nafion<sup>®</sup> solution.

Particle size distributions of catalyst ink, I-1 and I-2, are shown in Fig. 2. It is clearly seen that the catalyst and Nafion<sup>®</sup> ionomer dispersed in the aqueous solution formed bigger agglomerates than those dispersed in the aqueous solution with NaOH addition. The particle size distribution was mainly in the

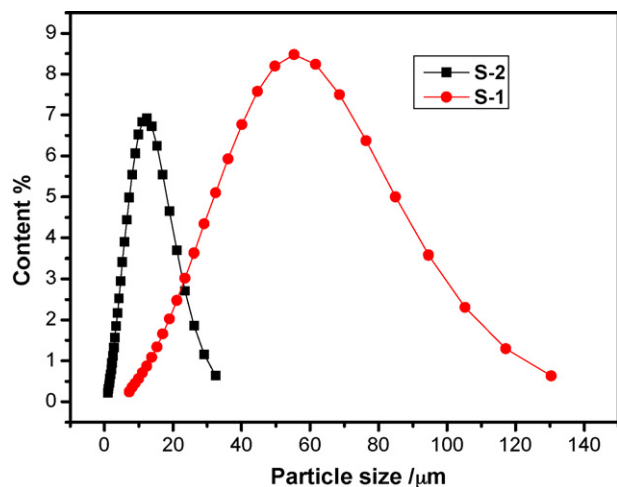


Fig. 2. Particle size distribution in catalyst ink prepared with different Nafion<sup>®</sup> solution (S-1 and S-2).

region of 7–160  $\mu\text{m}$  and 1–40  $\mu\text{m}$  for I-1 and I-2, respectively. Obviously, the aggregation behavior of the Nafion<sup>®</sup> ionomer in solution affected the agglomeration size of the Nafion<sup>®</sup> ionomer and catalyst in the catalyst ink. The smaller particle size of Nafion<sup>®</sup> ionomer in solution resulted in smaller agglomeration

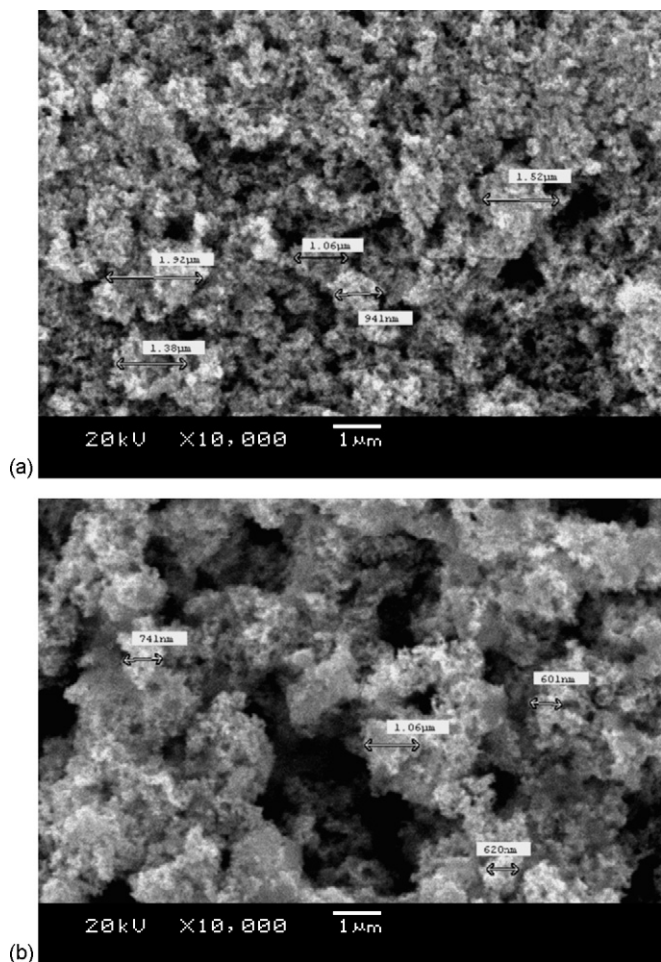


Fig. 3. SEM images of cathode catalyst layer prepared by using: (a) S-1 and (b) S-2 Nafion<sup>®</sup> solutions.

Table 1  
BET surface area and ESA of catalyst layers prepared with S-1 and S-2 Nafion® solutions

Sample	Pt black	S-1	S-2
BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	29.69	7.00	13.86
ESA ( $\text{m}^2 \text{g}^{-1}$ )	–	9.43	13.94

in catalyst ink. It also indicated that the dispersion of catalyst particles in I-2 was better than that in I-1.

### 3.2. Effect of the aggregation behavior of Nafion® ionomer in Nafion® solutions on the structure of cathode catalyst layer

The size of the agglomerate was reflected in the structure of the cathode catalyst layer through the drying process after applying catalyst ink onto the membrane. SEM images of the catalyst layers surface are presented in Fig. 3. Many agglomerates existed on the surface of electrode. Bigger pores which can reach several micrometers existed among the agglomerations on the catalyst layer made from I-2 than from I-1. However, the agglomerations on the electrode made from S-1 were combined well with the ionomer to form large porous flakes. As a result, most of the pores observed by SEM were less than  $1 \mu\text{m}$ . The different morphologies of the catalyst layers might be due to the different aggregation size of Nafion® ionomers in S-1 and S-2, which further led to the different agglomeration sizes in the catalyst ink.

Table 1 showed the BET surface area of Pt black and catalyst layers prepared from S-1 and S-2 Nafion® solutions. The BET surface area of Pt black powder was  $29.70 \text{ m}^2 \text{ g}^{-1}$ , which was in agreement with the reference provided by JM Corporation, whereas that of the catalyst layers prepared with S-1 and S-2 were 7.00 and  $13.86 \text{ m}^2 \text{ g}^{-1}$ , respectively. The smaller BET surface of the catalyst layer made from I-1 could be attributed to the poor dispersion of Pt particles in S-1. DLS studies showed that most of Nafion® ionomer in S-1 aggregated to form large aggregations, which led to poor contact between the catalyst and the aggregations. The poor dispersion of Pt particles in S-1 shown by the laser particle sizer results indicated that many Pt particles might form agglomerations and be embodied by the Nafion® aggregations. This resulted in a smaller BET surface area. Whereas, better dispersion of Pt particles in S-2 made smaller Nafion® ionomer and Pt particles in good contact with each other, thus a larger BET surface area was obtained.

It is possible to image the surface structure of the catalyst layer and to determine the local element distribution by EPMA. The distributions of fluorine and sulfur indicate how the Nafion® ionomer distribute the catalyst layer, whereas the distribution of platinum gives the location of the catalyst particles. Fig. 4 showed the EPMA mapping for the elements S and Pt in the catalyst layers made from I-1 and I-2. It can be seen that the distributions of Pt and S were more even on the catalyst layer made from I-2 than from I-1. This was attributed to the better dispersion of Pt in S-2, as demonstrated in the above laser particle sizer results. The more uniform distributions of Pt and S in catalyst layer made from I-2 could indicate that a larger electrochemical active surface area (ESA) would be obtained.

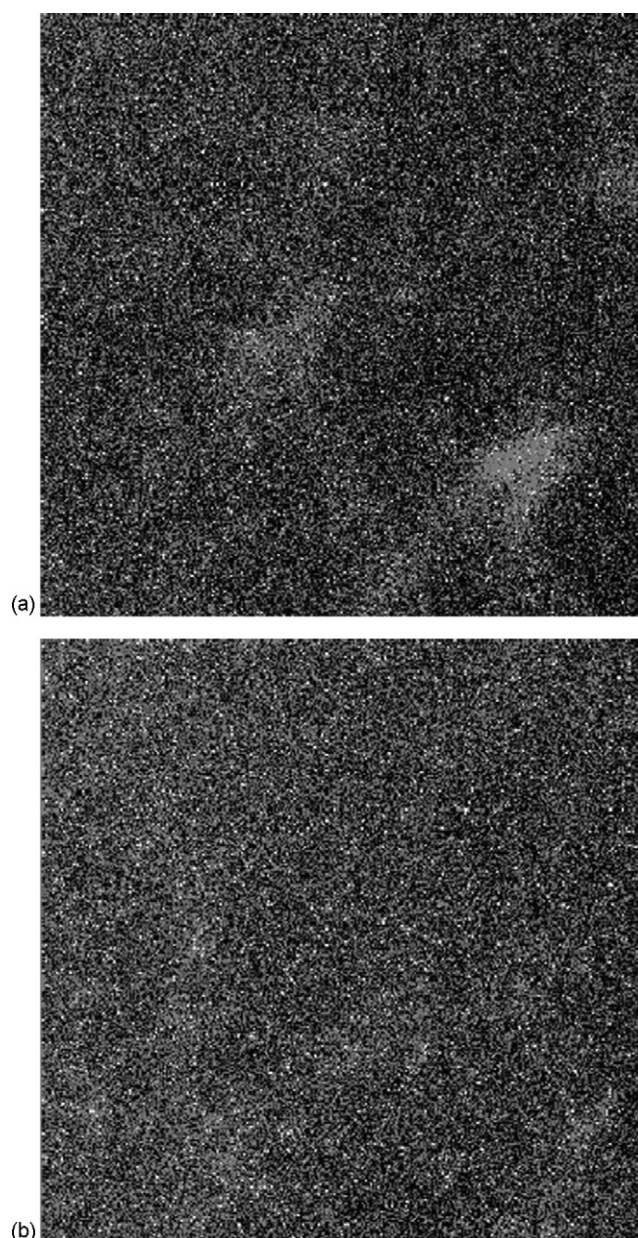


Fig. 4. EPMA face scanning analysis of catalyst layer prepared with: (a) S-1 and (b) S-2 Nafion® solutions. Scanning size:  $60 \mu\text{m} \times 60 \mu\text{m}$ . White: S element and black: Pt element.

Therefore, the aggregation behavior of the Nafion® ionomer in dilute solutions affects not only the size of the agglomerates in the catalyst ink, but also the morphology, the BET surface area and the element distribution of the catalyst layer. From the above results, it can be concluded that the contact area between the Nafion® ionomer and the catalyst is increased in a catalyst layer made from S-2 compared with that made from S-1.

### 3.3. Effect of the aggregation behavior of Nafion® ionomer in Nafion® solution on ESA of cathode electrode and the performance of DMFC

Cyclic voltammetry was used to probe the combined protonic/electronic access to the Pt sites in the cathode catalyst layer.

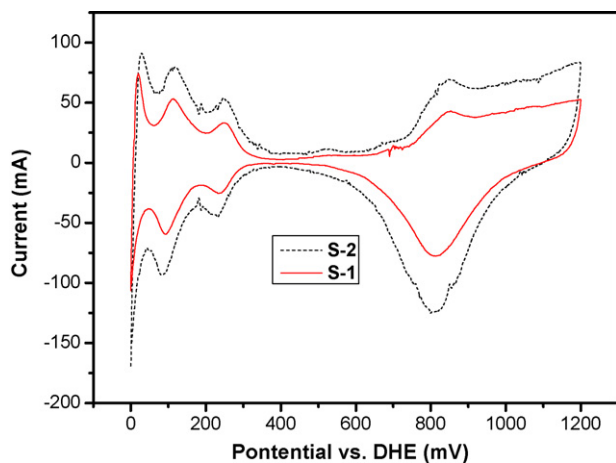


Fig. 5. Cyclic voltammograms curves of cathode prepared with different Nafion<sup>®</sup> solution.

Assuming  $210 \mu\text{C cm}^{-2}$  for the electro-oxidation of a monolayer of adsorbed hydrogen atoms on a Pt surface, the charge associated with this electrooxidation process was used to calculate the ESA of the Pt catalyst [19]. The cyclic voltammetry curves are shown in Fig. 5. The calculated ESA is summarized in Table 1. The ESA of CCM-1 and CCM-2 were  $9.43$  and  $13.94 \text{ m}^2 \text{ g}^{-1}$ , respectively. This strongly implied that the electrode prepared from the S-2 Nafion<sup>®</sup> solution made more Pt sites accessible to protons/electrons, and thus more active sites for electrochemical reaction were obtained. The higher ESA of CCM-2 was attributed to the better contact between the Nafion<sup>®</sup> ionomer and the catalyst in I-2, which resulted in an extended catalyst/ionomer interface. This result is in good agreement with the EPMA results. While for a catalyst layer made from I-1, the BET surface area was lower than ESA, which might be due to the different test environment for N<sub>2</sub> adsorption and cyclic voltammetry. The Nafion<sup>®</sup> ionomer in the catalyst layer expanded during the cyclic voltammetry test. It was reported [20] that the pore volume of the catalyst layer boiled in  $0.5 \text{ M H}_2\text{SO}_4$  increased at least 20 times more than the unboiled one. In

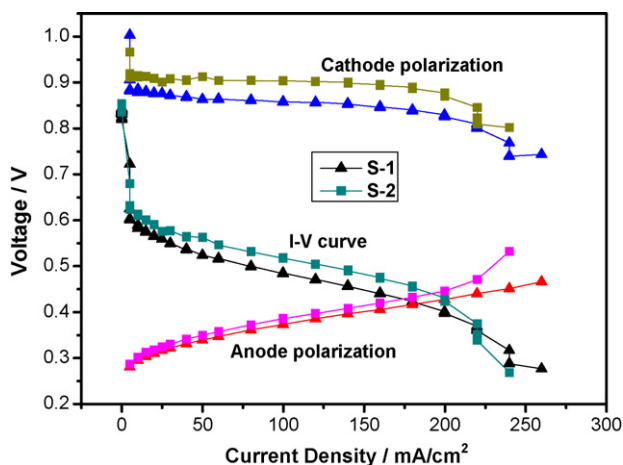


Fig. 6. Performance of MEAs with cathode prepared with different Nafion<sup>®</sup> solution. Operation conditions:  $60^\circ\text{C}$ ,  $2 \text{ atm O}_2$ ,  $100 \text{ sccm}$ ;  $1 \text{ M methanol}$ ,  $1 \text{ mL min}^{-1}$ .

this case, the total surface area of the catalyst layer might quite different from the BET surface area obtained under a certain vacuum before N<sub>2</sub> adsorption.

IR-corrected cathode polarization curves as shown in Fig. 6 were used to evaluate the effect of the Nafion<sup>®</sup> aggregation behavior on the cathode performance. It could be distinguished that the cathode prepared with I-2, exhibited a higher cathode performance compared with that prepared with I-1. This might result from the aggregation behavior of Nafion<sup>®</sup> in the NaOH based ink, which led to a better contact between the Nafion<sup>®</sup> ionomer and the catalyst particles in the catalyst layer and a more uniform distribution of sulfur and Pt elements in the catalyst layer, representing a higher utilization of the catalyst.

#### 4. Conclusion

The large aggregation particles in a Nafion<sup>®</sup> aqueous solution were significantly suppressed by the addition of NaOH to the solutions, which was attributed to the dissociation of intermolecular ionic aggregations. Compared with the Nafion<sup>®</sup> solution without NaOH addition, a better dispersion of catalyst and Nafion<sup>®</sup> ionomer in the catalyst ink were obtained with this NaOH added Nafion<sup>®</sup> solution. As a result, the distribution of sulfur and Pt elements were more uniform in the catalyst layer. The electrode prepared with NaOH added Nafion<sup>®</sup> solution achieved a higher ESA and better performance for a DMFC, than did the one prepared with Nafion<sup>®</sup> aqueous solution without NaOH addition.

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