

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

**Carbon-Supported Copper Phthalocyanine (CuPc/C) as a Novel Cathode Catalyst for Polymer Electrolyte
Membrane Fuel Cells --- Effect of Nafion Ionomer as for Alkaline Electrolyte**

Lei Ding^{1,2}, Xianfeng Dai¹, Samir Ibrahim², Yuyu Liu^{2*}, Jinli Qiao^{1*}

¹College of Environmental Science and Engineering, Donghua University,
2999 Ren'min North Road, Shanghai 201620, P. R. China

²Lab of Urban and Regional Environmental Systems, Graduate School of Environmental Studies,
Tohoku University, Aramaki, aza Aoba 6-6-11,
Aoba-ku Sendai 980-8579, Japan

ABSTRACT

Carbon-supported copper phthalocyanine (CuPc/C) nanoclusters, as a novel suitable cathode catalyst in polymer electrolyte membrane fuel cells have been synthesized via a combined solvent-impregnation and milling procedure along with the high temperature treatment. For optimizing the electrocatalytic activity of the catalyst obtained, the electrode with a variety of Nafion ionomer contents in the catalyst layer was screened by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) employing a rotating disk electrode (RDE) technique to investigate the effect of Nafion ionomer as for alkaline electrolyte. For comparative purposes, electrode with various contents of available anion-ionomer was also investigated. The results revealed that the content of Nafion ionomer can affect the ORR activity of the CuPc/C catalyst and an optimal content of Nafion ionomer was around $3.5 \times 10^1 \mu\text{g cm}^{-2}$, which corresponds well with the electrode prepared using available anion-ionomer. Under which, the electrode prepared using Nafion ionomer can produce a comparable performance to that of using available anion-ionomer, giving an on-set potential at 0.1 V with a half-wave potential of -0.03 V. Furthermore, Koutechy-Levich analysis showed that the value of electron transfer number is in a range of 3.40 to 3.74 when electrode with Nafion ionomer contents changing from 2.5×10^1 to $1.6 \times 10^2 \mu\text{g cm}^{-2}$. The membrane electrode assembly (MEA) fabricated with CuPc/C cathode catalyst with a loading of 3.6 mg cm^{-2} and, a Nafion membrane immersed in 3M KOH for 48 hours, reached an initial power density of 3.8 mW cm^{-2} at room temperature.

1. Introduction

It is commonly believed that fuel cells are promising power sources for offering clean and high energy conversion efficiency technology. For obtaining the high catalytic performances, platinum (Pt) supported on carbon black is normally used as the best electrocatalyst for both the anode and the cathode, particular to Nafion[®]-based proton-exchange membrane fuel cells (PEMFCs). However, the widespread commercialization of the fuel cell technology has been hindered so much because of the high cost of Pt and its scarcity. This becomes more serious particular to high loading requirements on the cathode for the oxygen reduction reaction (ORR) due to the sluggish kinetics of Pt (~ 300 mV overpotential loss) [1]. Alternatively, the use of alkaline media in fuel cell applications presents many advantages, both in electrocatalytic activity and in materials stability over acidic media, which can provide more choices for suitable Pt alternatives [2-6].

With respect to non-platinum catalysts, Metal-N₄ macrocycles after heat-treatment, such as Fe- and Co-centered phthalocyanine complexes, are considered to be the most promising non-precious metal catalysts due to their high conjugate structure and relatively good chemical stability [7-10]. Comparatively, little are concerned for other metal centered phthalocyanines, this is because that in strong acidic conditions such as in PEM fuel cells, the catalysts that show high ORR catalytic activity, and at the same time, high stability are strongly desired. However, little progress is achieved because of trade-off relations between these parameters [11,12]. Recent studies indicate that pH could affect the ORR activity of MPcs, which suggests that other metal centered phthalocyanines such as Ni-, Mn- and Cu-centered phthalocyanines, might be more appropriately used in alkaline solutions [13].

As is known to all, electrode preparing is a necessary step in the electrocatalytic activity study of the catalysts for the ORR, particular to the polymer electrolyte membrane fuel cells. Among which, a polymer binder is essential to bind discrete catalyst particles to form a porous catalyst layer that facilitates the transfer of ions, electrons and reactants. In recent years, more and more polymer materials have been used as a binder for preparing MEAs for alkaline membrane fuel cells [14-16]. Bunazawa et al. [17] investigated an anion ionomer solution (labeled as A3) as a binder for alkaline direct methanol fuel cell and, studied the effect of anion ionomer content in the anode and cathode catalyst layers. The results suggested that MEA with 45.4% mass ionomer content shows the highest performance at both anode and cathode electrodes. Zhao et al. [18] used A3 ionomer and polytetrafluoroethylene (PTFE) as the binder in anode catalyst layer for alkaline direct ethanol fuel cells. They found that the PTFE binder yields better performance than does the A3 binder. Unfortunately, up to now, no alkaline binder can completely realize the commercialization like Nafion[®] binder in PEMFC. Hence, it is difficult to choose a suitable binder used for alkaline electrolyte. Generally, in the process of the preparation of the electrode, the thickness of the binder coated on the electrode layer is very thin. Therefore, using Nafion[®] ionomer as the binder may be good choice if it has no significant effect on the O₂ reduction rate.

In view of these facts, in this work, the possibility of constituting new electrocatalysts using carbon-supported

copper phthalocyanine (CuPc) complexes are pursued for the ORR after heat-treatment at high temperatures. We focus on the feasibility by applying Nafion® ionomer as a binder for electrochemical measurements in alkaline solution. Emphasis is made on the effect of Nafion® content on the catalyst layer, whether Nafion® ionomer could affect more or less the ORR activity and how much is the optimal content for catalyst ink preparation. Further more, the preliminary fuel cell test using the conventional hot-pressing MEAs with a Nafion membrane immersed in KOH solution and, carbon supported CuPc as cathode catalyst was also carried out.

2. Experimental

2.1 Materials and catalyst preparation

Copper phthalocyanine was purchased from Sigma Aldrich with 97% purity and used as received. Carbon support (Vulcan XC-72) was purchased from Cobat Corporation. Carbon-supported copper phthalocyanine catalysts were prepared using milling method combined with a heat-treated procedure. Briefly, a mixture of 40 mg CuPc and 60 mg carbon black in 10ml methanol was prepared and carefully milled for about 2 hours in a mortar, then vacuum dried at 40°C for another 1 hour to remove the methanol. The resulting powders were placed in a crystal boat, and pyrolyzed at 800°C for 120 minutes at the rate of 5°C min⁻¹ in a flowing nitrogen atmosphere. The catalyst as-prepared is thus designated as CuPc/C.

2.2 Physical characterization

The crystal-phase X-ray diffraction (XRD) patterns were collected on a Philips PW3830 X-ray diffractometer using Cu- α radiation ($\lambda = 0.15406$ nm). The current was 40 mA and the voltage was 40 KV. The intensity data were collected at 25°C in the 2 θ range from 5° to 90° with a scan rate of 1.20° min⁻¹.

2.3 Electrochemical measurements

Electrochemical evaluation was carried out in a standard three compartment electrochemical cell in 0.1 mol L⁻¹ KOH at room temperature. A pre-cleaned rotating disk electrode (RDE) (Glassy carbon electrode with a diameter of 6.0 mm corresponding to a geometric surface area of 0.283 cm², purchased from Pine Instruments) was used as the working electrode. A Pt wire and a saturated calomel electrode (SCE) were used as the counter and reference electrode, respectively. All measured potentials were converted into the values referring to a standard hydrogen electrode (SHE).

The catalyst ink for RDE measurements was prepared by blending 4 mg of the catalyst and 2 mL of methanol/Nafion® solution which was ultrasonically dispersed for 10 minutes to form a suspension. 10 μ L of this suspension was then pipetted onto the surface of GC electrode and then dried at room temperature. For investigating the effect of Nafion content on the catalyst layer, methanol/Nafion® solution with different scales (70:1, 50:1, 30:1 and 10:1 in mass) were used to form catalyst inks. The Nafion® loadings were 2.5×10^1 , 3.5×10^1 , 5.7×10^1 and 1.6×10^2 μ g cm⁻², respectively.

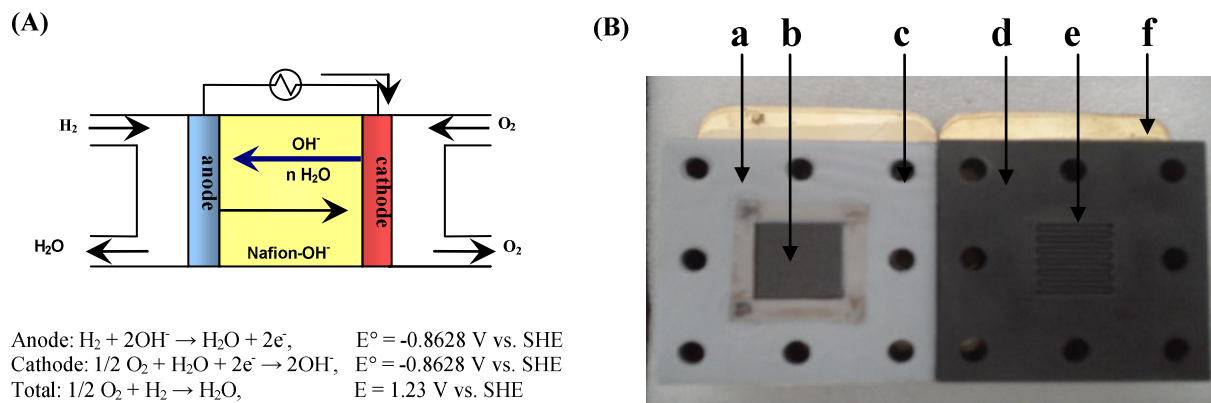
**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

Initially, cyclic voltammograms (CVs) were carried out by scanning the disk potential from -0.3 to 0.6 V to measure the surface behavior of the catalyst in N₂-saturated 0.1 M KOH solution. For ORR measurements, the solution was then bubbled by pure O₂ to form an O₂-saturated in 0.1 M KOH solution. A CV was recorded in O₂-saturated electrolyte with the scan rate of 50 mV s⁻¹. For more quantitative measurements of ORR activity, linear sweep voltammetry (LSV) was conducted on the catalyst-coated RDE in the potential range between -0.7 and 0.2V in O₂-saturated 0.1 M KOH solution at desired rotating rates. In order to ensure a steady state in each point of the curve, a slow sweeping rate of 5 mV s⁻¹ was applied.

2.4 Single cell tests

The cell configuration: H₂ | Pt/C | Nafion-OH⁻ | CuPc/C | O₂, was used in a single cell of PEMFC. The fabrication of MEAs was prepared by following steps: (i) The standard anode ink was prepared by mixing 40% Pt/C (Johnson Matthey) with a solution of 5 wt% Nafion[®] (DuPont) and isopropanol, and then sonicated for 4 h, where the ratio of Pt/C catalyst to Nafion[®] was 3:1. the catalyst ink was sprayed onto carbon papers (Toray TGP-H-090) to deposit a catalyst layer with a Pt loading of 0.5 mg (Pt) cm⁻². (ii) For cathode with non-platinum catalyst, the catalyst inks were prepared by mixing 40% CuPc/C with a solution of 5 wt% Nafion[®] and isopropanol, and then sonicated for 4 h, where the ratio of CuPc/C catalyst to Nafion[®] was also 3:1. Similar to the anode fabrication, the catalyst ink was sprayed onto carbon papers to deposit a catalyst layer with a CuPc loading of 3.6 mg cm⁻². (iii) Nafion-OH⁻ membrane was prepared using a Nafion[®] membrane with a size of 4 × 4 cm immersed in 3 M KOH for 48 hours. The Nafion solution was also used for the corresponding binders for both of the anode and the cathode. The Nafion[®]-OH⁻ membrane was sandwiched with two same pieces of carbon papers coated with catalyst and binder, and then were hot-pressed at a pressure of 10 MPa at 75 °C for 3 min.

Scheme 1 shows the working mechanism of polymer electrolyte membrane fuel cell. The MEAs with an active area of 4 cm² was inserted into a fuel cell hardware which consisted of graphite block with machined serpentine flow channel and copper current collector (Scheme 1 (B)). Pure hydrogen and oxygen were supplied to enter the anode and cathode channels at a flux of 100 and 60 ml min⁻¹, respectively, through a humidifier maintained at 25°C under ambient pressure. Polarization curves were obtained using a fuel cell evaluation system (GE/FC1-100).



Scheme 1. (A) working mechanism of polymer electrolyte membrane fuel cell;
 (B) photograph of polymer electrolyte membrane fuel cell showing silicon sheets (a), MEA (b),
 screw hole (c), graphite block (d), gas channel and (e) and current collector (f).

3. Results and discussion

3.1 physical characterization

Figure 1 shows the XRD patterns of the CuPc/C catalysts synthesized at different heat-treatment temperatures. The first large broad peak located at about $2\theta = 25^\circ$ was observed for all the XRD patterns, which is attributed to the diffraction of carbon. From Figure 1, it can be seen that CuPc/C without heat-treatment showed some quite strong diffraction peaks due to the crystalline nature of CuPc. However, these peaks disappeared after heat-treatment at 600°C . For catalyst sample heat-treated at 800°C , two new small diffraction peaks centered at 43.3° and 50.4° were clearly observed, indicating that part of the CuPc on the carbon support may have decomposed, forming the new $\text{Cu-N}_x\text{-C}$ compositions. According to literature [19-21], these two diffraction peaks may correspond to the characteristic diffraction peaks of metallic Cu. When catalyst sample was further heat-treated at 900°C , the shape of these peaks becomes strong and narrow, indicating the growth of metallic Cu cluster particles after decomposition of the CuPc structure. Since the porosity of the catalyst may be blocked by metallic Cu which are not active for the ORR, the heat-treatment temperature for CuPc/C synthesis should not be higher than 800°C in order to obtain the high electrocatalytic activity. Thus, for a more detailed analysis of the effect of Nafion[®] ionomer, the CuPc/C heat-treated at 800°C was chosen for further study.

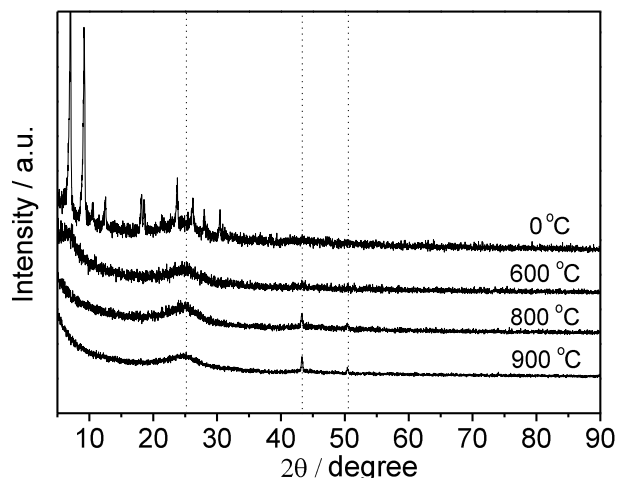


Figure 1. X-ray diffraction spectra of the CuPc/C catalysts before and after heat-treatment at 600, 800 and 900°C, respectively.

3.2 Electrochemical activity of CuPc/C catalyst towards ORR

Figure 2 shows CVs for the ORR on the CuPc/C electrode prepared with different Nafion[®] ionomer contents in the catalyst layer, measured in O₂-saturated 0.1 M KOH solution (where the CuPc/C catalyst loading on GC electrode was fixed of 140 μg cm⁻²). It can be seen that CVs of CuPc/C electrode prepared with Nafion[®] contents of 2.5×10^1 and 3.5×10^1 μg cm⁻² show the same oxygen reduction peak position (-0.06 V), but the latter gives 25% higher current density than the former. When Nafion[®] contents were increased to 5.7×10^1 and 1.6×10^2 μg cm⁻², the oxygen reduction peaks were at -0.1 and -0.12 V, respectively. Both are lower than that of CuPc/C electrode prepared with Nafion[®] contents of 2.5×10^1 and 3.5×10^1 μg cm⁻². Also, the peak current densities of CuPc/C electrode prepared with Nafion[®] contents of 5.7×10^1 and 1.6×10^2 μg cm⁻² are both smaller than the values observed for CuPc/C catalyst with 3.5×10^1 μg cm⁻² Nafion[®] content. The above results indicate that the optimal Nafion[®] ionomer content in the catalyst layer should be around 3.5×10^1 μg cm⁻².

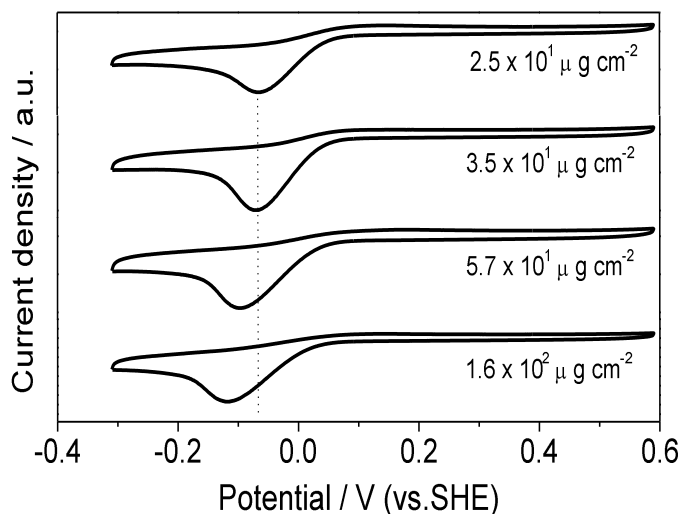


Figure 2. The cyclic voltammogram curves recorded in O₂-saturated 0.1 M KOH solution for the CuPc/C electrode coated with different Nafion[®] ionomer contents. Scan rate: 50 mV s⁻¹.

For further clarifying the effect of Nafion[®] ionomer content on the ORR activity, LSV was conducted on CuPc/C electrodes with different Nafion[®] contents in an O₂-saturated 0.1 M KOH solution (Figure 3). For a better comparison, the LSV curves of CuPc/C electrode prepared with available anion-ionomer are also depicted in the same figure. According to rotating disk theory, the overall measured current density (i) of the oxygen reduction at each electrode potential (E), shown in Figure 3, can be expressed as being dependent on the kinetic current density (i_k) and the diffusion-limited current density (i_d). The relationship between these current densities can be expressed by the following equation [22].

$$i_k = \frac{ij_d}{j + j_d} \quad (1)$$

Several important kinetic parameters for ORR on CuPc/C electrodes prepared with Nafion[®] ionomer and available anion-ionomer are summarized in Table 1. It can be seen that for CuPc/C electrode prepared with different contents of Nafion[®] ionomer, the onset potentials increase with decreasing Nafion[®] loading. Comparatively, for CuPc/C electrode prepared with different contents of available anion-ionomer, the onset potentials have no significant change with decreasing available anion-ionomer loading, and all are little higher than those of prepared with Nafion[®] ionom-

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

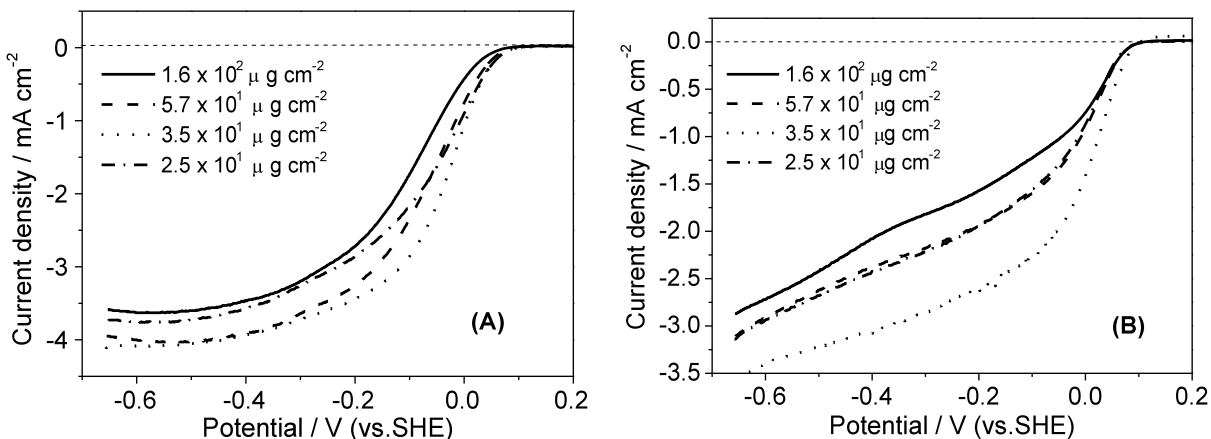


Figure 3. Polarization curves for the ORR on the CuPc/C catalysts, measured in O₂-saturated 0.1 M KOH at room temperature. (A) Nafion[®] solution for the catalyst ink preparation; (B) anion-ionomer for catalyst preparation. Scan rate: 50 mV s⁻¹. Electrode rotation rate: 1500 rpm.

Table 1. Comparison of several kinetic parameters for ORR on CuPc/C electrode prepared with different contents of Nafion[®] ionomer and available anion-ionomer (potential versus SHE)

| Binder loading (μg cm ⁻²) | | Onset Potential (V) ^a | Δ <i>E</i> _{1/2} (V) ^a | <i>i</i> _k at 0.05 V (mA cm ⁻²) ^a | Potential (V) at 0.1 mA cm ⁻² ^a |
|--|-----------------------------|--|---|--|--|
| 1.6 × 10 ² | Nafion [®] ionomer | 0.08 | -0.105 | 1.40 | 0.045 |
| | anion-ionomer | 0.11 | - | 0.32 | 0.074 |
| 5.7 × 10 ¹ | Nafion [®] ionomer | 0.09 | -0.06 | 3.90 | 0.061 |
| | anion-ionomer | 0.11 | 0.00 | 0.33 | 0.073 |
| 3.5 × 10 ¹ | Nafion [®] ionomer | 0.10 | -0.03 | 4.50 | 0.066 |
| | anion-ionomer | 0.11 | 0.02 | 0.65 | 0.085 |
| 2.5 × 10 ¹ | Nafion [®] ionomer | 0.10 | -0.06 | 2.90 | 0.068 |
| | anion-ionomer | 0.11 | 0.00 | 0.29 | 0.070 |

a) rpm 1500

er. Similarly, the half wave potential shows the positive shift from -0.06 to -0.03 V for Nafion[®] content changing from 2.5×10^1 to 3.5×10^1 μg cm⁻², but starts to fall with further increasing the content of Nafion[®] ionomer (Figure 3A). These observations indicate that the content of Nafion[®] ionomer can affect the ORR activity of the CuPc/C catalyst and, the optimal content of Nafion[®] ionomer is about 3.5×10^1 μg cm⁻². It should be mentioned that the optimal content of available anion-ionomer in CuPc/C electrode is also about 3.5×10^1 μg cm⁻², which leads to a highest half wave potential. However, all of catalysts prepared here have no well-defined diffusion-limiting current plateau (Figure 3B), suggesting that the distribution of active sites on these catalysts is less uniform and oxygen diffusion rate is slower in the available anion-ionomer layer.

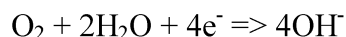


Sociedad Mexicana del Hidrógeno A.C.
Mexican Hydrogen Society

CICY
Yucatan Center for
Scientific Research



When Nafion[®] ionomer is used as a binder, the proton exchange Nafion[®] ionomer would be converted into the potassium exchange Nafion[®] ionomer when the coated electrode was measured in KOH solution. For ORR in alkaline solution, the reaction can be written as:



The cation-exchange membrane with fully impregnated by K⁺ ion in KOH solution should have a blocking effect for fast OH⁻ removal. For these reasons, the onset potentials and half wave potentials of CuPc/C electrode prepared with Nafion[®] ionomer are lower to some extent than those of CuPc/C electrode prepared with available anion-ionomer. However, the kinetic current densities, i_k at 0.05V for the ORR on the CuPc/C electrodes coated with Nafion[®] ionomer are all much higher than those with available anion-ionomer (Table 1). At the same time, at a defined current density of 0.1 mA cm⁻², the overpotentials of the CuPc/C electrode prepared with Nafion[®] ionomer are all lower than 0.068 V, while, when coated with available anion-ionomer, the overpotentials of the CuPc/C electrodes are all higher than 0.07 V. Hence, it is reasonable to conclude that CuPc/C still shows very good catalytic activity for the ORR by applying Nafion[®] ionomer as a binder.

3.3 Rotating disk electrode studies of O₂ reduction

The kinetics of the ORR on GC electrodes coated with different content of Nafion[®] ionomer were measured at different electrode rotating rates using RDE technique. Figure 4 shows typical RDE curves at various rotation rates for the ORR on carbon-supported CuPc electrodes coated with Nafion[®] loading of $3.5 \times 10^1 \mu\text{g cm}^{-2}$ in O₂-saturated 0.1 M KOH. It can be seen that the ORR limiting currents for CuPc/C catalyst prominently increased with the rotating rate, along with the onset potential for the ORR unchanged on the same catalyst. The number of electrons tr-

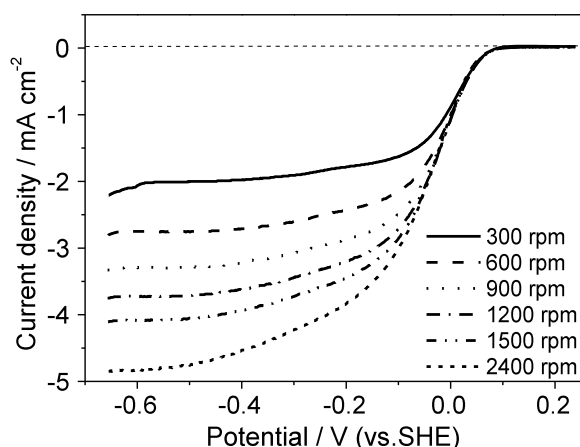


Figure 4. RDE polarization curves at different rotation rates for oxygen reduction on CuPc/C electrode prepared with Nafion[®] ionomer content of $3.5 \times 10^1 \mu\text{g cm}^{-2}$ in 0.1 M KOH solution. Scan rate: 5 mV s⁻¹.

ansferred per O₂ molecule (n) was calculated from the Koutecky-Levich (K-L) equation [23]:

$$\frac{1}{j} = \frac{1}{j_k} + \frac{1}{j_f} + \frac{1}{j_d} = \frac{1}{j_k} + \frac{1}{j_f} + \frac{1}{0.62nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6}\omega^{1/2}} \quad (2)$$

Where j is the measured current density at -0.6 V, j_k is the activation controlled current density, j_f is the effect of Nafion® ionomer inside the catalyst layer on the measured current density, which may be negotiable if the equivalent Nafion® ionomer thickness is much small ($j_f \rightarrow \infty$), j_d is the O₂ diffusion limiting current density, n is the number of electrons transferred per oxygen molecule, F is Faraday constant, C_{O_2} is the concentration of dissolved oxygen in the solution, D_{O_2} is the diffusion coefficient of O₂ in the solution, ν is the kinetic viscosity, and ω is the electrode rotating rate in rpm. The plot of $\frac{1}{j}$ vs. $\omega^{-1/2}$ according to Equation (2) can give a slope of

$(0.62nFC_{O_2}D_{O_2}^{2/3}\nu^{-1/6})^{-1}$, from which the electron transfer number (n) can be estimated if other parameters are known. Figure 5 shows the Koutecky-Levich plots for the ORR at the potential of -0.6 V on the CuPc/C electrode

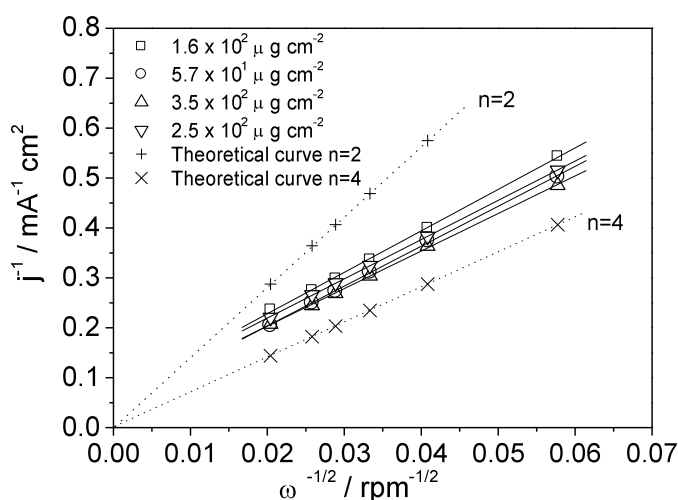


Figure 5. Koutecky-Levich plots for the ORR on CuPc/C electrode coated with different contents of Nafion® ionomer at -0.6 V vs. SHE

prepared with different contents of Nafion® ionomer derived from the data in Figure 4. The plots for the two-electron and four-electron transfer processes of the ORR are also shown in Figure 5. It can be seen clearly that the K-L slopes of CuPc/C electrode coated with different contents of Nafion® ionomer are all close to that of four-electron transfer reaction. Based on these slopes, we can calculate the electron transfer number and found that it changes with increasing the content of Nafion® ionomer: 3.40 for $1.6 \times 10^2 \mu\text{g cm}^{-2}$, 3.52 for $5.7 \times 10^1 \mu\text{g cm}^{-2}$, 3.74 for $3.5 \times 10^1 \mu\text{g cm}^{-2}$ and 3.58 for $2.5 \times 10^1 \mu\text{g cm}^{-2}$. These results indicate that content of Nafion® ionomer can affect not only the ORR activity of the CuPc/C catalyst but also the ORR electron transfer number. At a lower Nafion® loading ($2.5 \times$

10^1 and $3.5 \times 10^1 \mu\text{g cm}^{-2}$), the value of electron transfer number is bigger than that at a high Nafion[®] loading (5.7×10^1 and $1.6 \times 10^2 \mu\text{g cm}^{-2}$), which is attributed to difference of Nafion[®] thicknesses in the catalyst layer.

3.3 Single-cell performance

Finally, to further study the effect of Nafion[®] ionomer as for alkaline electrolyte, electrical test in a real H₂/O₂ single-cell was performed based on a Nafion[®] membrane rinsed with 3 M KOH for about 48 hours. Figure 6 shows the fuel cell polarization curve and power density profile obtained using pure O₂ as the oxidants and pure H₂ as the fuel at room temperature, a humidifier maintained at 25°C under ambient pressure. As shown in Figure 6, the open-circuit voltage around 0.75 V can be observed, which is lower than 1.0 V found for fuel cells with Co- and Fe-centered phthalocyanines as cathode catalysts [24]. The maximum power density at ambient temperature of Nafion[®]-OH⁻ membranes reached 3.8 mW cm⁻². Although the power density is still very low in comparison with reported in the literature [24], this initial value indicates the promising application of Nafion[®]-OH⁻ membranes and Copper phthalocyanines for alkaline fuel cell. Considering the initial value in this paper, future work has then to be focused on the optimization of the experimental conditions in order to further improve the fuel cell performance.

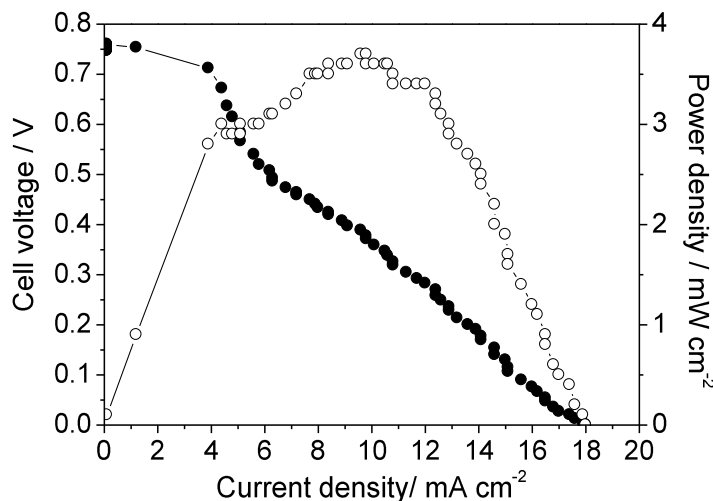


Figure 6. PEMFC performance of MEAs with CuPc/C based cathodes using Nafion[®]-OH⁻ membrane

4. Conclusions

This paper is focused attention on the Nafion[®] binder for electrocatalytic measurements and single-cell tests for an alkaline fuel cell. Electrochemical techniques such as CV, LSV and RDE were used to investigate the effect of the Nafion[®] ionomer content in the CuPc/C-based catalyst layer on the ORR. The results indicate that the electrocatalytic activity varies with the Nafion[®] loading and, the best performance is obtained from the CuPc/C electrode coated with $3.5 \times 10^1 \mu\text{g cm}^{-2}$, which is in a well agreement with the one studied using available anion-ionomer. An onset potential of 0.1 V and a half wave potential of -0.03 V are achieved in alkaline electrolyte. Besides the ORR kinetic rate, the ORR electro transfer number was also increased from 3.40 to 3.74 with decreased the content of Nafion[®].

**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

ionomer from 1.6×10^2 to $3.5 \times 10^1 \mu\text{g cm}^{-2}$. An initial power density of 3.8 mW cm^{-2} was obtained with a Nafion[®] membrane rinsed with 3 M KOH for about 48 hours. As discussed in this paper, it is expected that an improved ORR activity could be achieved when changing the Nafion[®] ionomer to an anion ionomer. However, at the present, the anion ionomer is not so common used as Nafion[®] ionomer and, it's difficult to get. Our work demonstrated that in the process of alkaline fuel cell study, it's reasonable by applying Nafion[®] ionomer as substitute for anion ionomer considering that CuPc/C catalyst still shows promising catalytic activity for the ORR when Nafion ionomer is used as a binder.

5. Acknowledgements

We give our thanks to the financial support from the National Natural Science Foundation of China (21173039), Specialized Research Fund for the Doctoral Program of Higher Education, SRFD (20110075110001), Environmental Protection Engineering Center for Pollution Treatment and Control in Textile Industry, China (20110927) and the Shanghai Leading Academic Discipline Project (B604) Fund.

6. References

- [1] H. R. Colón-Mercado and B. N. Popov, J. Power Sources, 155, 253 (2006).
- [2] C. J. Song, L. Zhang and J. J. Zhang, J. Electroanal. Chem., 293, 587 (2006).
- [3] L. Xu, J. L. Qiao, L. DING, L. Y. HO, L. L. Liu and H. J. Wang, Acta Phys Chin Sin, 2251, 27 (2011).
- [4] K. Gong, F. Du, Z. Xia, M. Durstock and L. Dai, Science, 323, 760 (2009).
- [5] J. H. Kim, A. Ishihara, S. Mitsushima, N. Kamiya and K. I. Ota, Electrochim. Acta, 52, 2492 (2007).
- [6] K. Lee, A. Ishihara, S. Mitsushima, N. Kamiya and K. I. Ota, Electrochim. Acta, 49, 3479 (2004).
- [7] M. Lefevre and J. P. Dodelet, Electrochim. Acta, 48, 2749 (2003).
- [8] R. Baker, D. P. Willkinson and J. Zhang, Electrochim. Acta, 53, 6906 (2008).
- [9] R. Cheng, H. Li, D. Chu and G. Wang, J. Phys. Chem. C, 113, 20689 (2009).
- [10] Y. Nabae, S. Moriya, K. Matsubayashi, S. M. Lyth, M. Malon, L. Wu, N. M. Islam, Y. Koshigoe, S. Kuroki, M. Kakimoto, S. Miyata and J. I. Ozaki, Carbon, 48, 2613 (2010).
- [11] Y. Lu and R. G. Reddy, Electrochim. Acta, 52, 2562 (2007).
- [12] J. Ozaki, S. Tanifuji, N. Kimura, A. Furuichi, and A. Oya, Carbon Japan, 44, 1298 (2006).
- [13] N. Sehloho, and T. Nyokong, J. Electroanal. Chem. South africa, 595, 161 (2006).
- [14] E. H. Yu and K. Scott, J. Power Sources, 137, 248 (2004).
- [15] C. Coutanceau, L. Demarconnay, C. Lamy and J. M. Léger, J. Power Sources, 156, 14 (2006).
- [16] K. Scott, E. Yu, G. Vlachogiannopoulos, M. Shivare and N. Duteanu, J. Power Sources, 175, 452 (2008).
- [17] H. Bunazawa and Y. Yamazaki, J. Power Sources, 182, 48 (2008).
- [18] Y. S. Li, T. S. Zhao and Z. X. Liang, J. Power Sources, 190, 223 (2009).



**9th International Symposium on New Materials and Nano-Materials for
Electrochemical Systems
XII International Congress of the Mexican Hydrogen Society
Merida, Mexico, 2012**

- [19] H. Zhu, X. Li and F. Wang, Int J Hydrogen Energy, 36, 9151 (2011).
- [20] A. Sakar and A. Manthiram, J. Phys. Chem. C, 114, 4725 (2010).
- [21] R. Wang, H. Li, H. Feng, H. Wang and Z. Lei, J. Power Sources, 195, 1099 (2010).
- [22] C. V. Rao and B. Viswanathan, J. Phys. Chem. C, 111, 16538 (2007).
- [23] A. J. Bard and L. R. Faulkner, Electrochemical Methods, Fundamentals and Applications, 2nd ed., John Wiley & Sons, Inc., N. Y., (2000).
- [24] I. Kruusenberg, L. Matisen, Q. Shah, A. M. Kannan and K. Tammeveski, Int J Hydrogen Energy, 37, 4406 (2012).