

Research Article

Electrooxidation of Hydrogen on Ni-Organic Metal Complex Catalysts in Acidic Media for PEMFCs

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Novel organic metal complexes with N_2O_2 coordination structure which showed high hydrogen oxidation reaction were synthesized. The catalytic activity was found to strongly depend on the heat-treatment temperature and the structural properties.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) are considered to be one of the most promising future energy powers. Despite many efforts have been devoted to the development of PEMFCs, problems which need to be solved in terms of efficiency, power density, stability, and reliability still remain [1, 2].

It is well known that platinum (Pt) supported on carbon black is normally used as the most active electrocatalyst for oxygen reduction and hydrogen oxidation reactions in PEMFCs due to its high catalytic activity and excellent chemical stability [3, 4].

Nevertheless, the widespread commercialization of fuel cell technology has been greatly hindered because platinum is expensive, and its estimated amount is too small to supply a huge number of fuel cell vehicles. Also, the current state of art for achieving active materials is far from sufficient due to the low utilization efficiency of Pt. It becomes more serious when high loadings are required on the cathode due to the sluggish kinetics of Pt [2, 5–9]. These difficulties have created enormous interests in the search for less expensive, more efficient electrocatalysts as well as less loading of catalyst during the past decades. With respect to identifying alternative electrocatalysts, better substitutes such as Pt-free catalysts have been sought for more than a decade. Several promising candidates have been proposed in the past, such as oxides [10, 11], carbides [12, 13], Pd- [14–17] and

Ru-based binary catalysts [18–23], macrocycles (porphyrin or phthalocyanine), and nonprecious metal catalysts [24–27].

Though it is important to learn oxygen reduction reaction (ORR) properties of the catalysts, little is concerned for the materials that could replace platinum as the anode catalyst in PEMFCs since the requirements for good resistance to both CO and acid are difficult to meet for normal alloy catalysts.

Most recently, the tungsten carbide has been regarded as a promising candidate to replace Pt/C catalyst because it has the same behavior and anticorrosion properties as the platinum catalyst. But it shows very low activity toward the hydrogen oxidation reaction (HOR) [28]. Except for tungsten carbide and Ir-based binary alloys [23], N-ligand organic complexes of simple molecules containing transition metal center would be the better choices over alloy or oxide catalysts in view of their cost and structural potentiality [14].

In this work, the possibility of constituting new electrocatalyst was pursued for HOR using N-ligand organic complexes containing transition metal center of Ni (II). The design of novel Pt-free catalyst could not only decrease the cost of catalyst for fuel cell, but also has the structure potentiality by changing the organic structure.

The physical-chemical properties of the catalysts were studied by transmission electron microscope (TEM), cyclic voltammetry (CV), and linear sweep voltammetry (LSV) to provide more insight into the hydrogen oxidation of

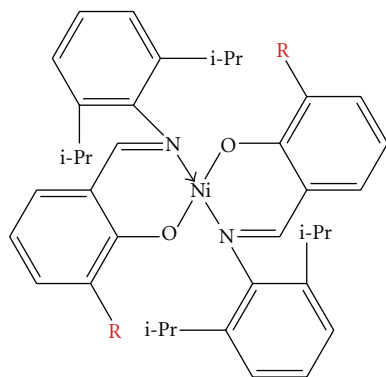


FIGURE 1: Chemical structure of organic metal complexes tested (R = H, CH₃, and i-Pr, resp.).

Ni(bmdiph)/C catalyst. The results of characterizations and also their implications to the exploration of the nanoparticles as fuel cell catalysts were discussed. Emphasis was placed on the heat-treated temperature for the hydrogen oxidation catalytic activity of Ni(bmdiph)/C. Effects of the structural aspects of substituent on the metal complexes were also investigated.

2. Experimental Details

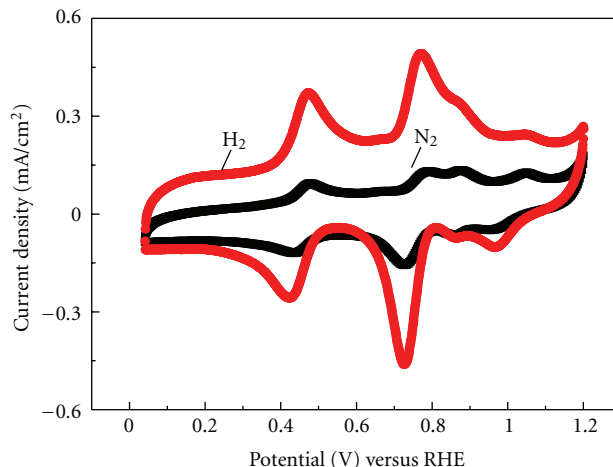
2.1. Catalyst Preparation and Characterization. Catalyst was prepared by depositing each organic metal complex, Ni(diph), Ni(bmdiph), and Ni(bidiph), respectively, with Vulcan XC-72 carbon black (Cabot Corporation, $S_{\text{BET}} = 236.8 \text{ m}^2/\text{g}$) in ethanol in a mortar, and drying in vacuum at 40°C for 1 h. Then it was processed by thermal treatment in an N₂ atmosphere from 273–673 K for 2 h in a furnace with a heating rate of 20°C min⁻¹, which was optimized for achieving effective catalysts.

The morphology of catalyst particles was observed by TEM analyses with a JEM 2010 EX microscope, at 200 kV.

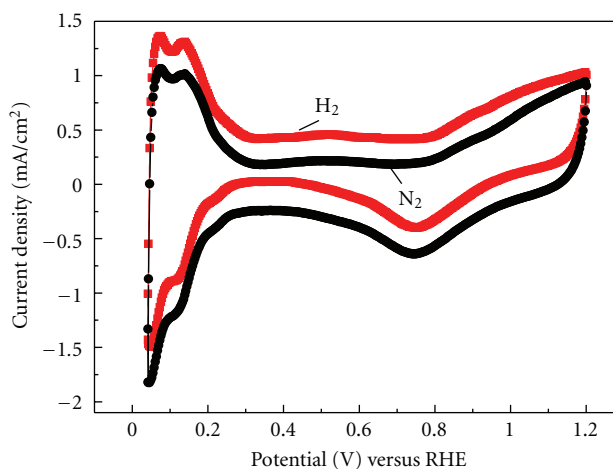
Figure 1 showed the chemical structure of organic metal complexes, where R was H, CH₃, and i-Pr groups, respectively.

2.2. Electrochemical Testing. The electrocatalytic activities of the catalysts for the hydrogen oxidation were identified using a rotating disk electrode (RDE) by CV and LSV techniques. Two milligrams of Ni(bmdiph)/Vulcan XC-72 catalyst was suspended into 1 mL of methanol/Nafion solution (50:1 wt%) to prepare the catalyst ink. Then 10 μL of the ink was transferred to a clean glassy carbon (GC) disk electrode (6 mm diam.). The amount of overall loadings of the mixed catalyst on the apparent electrode area of the GC disk (0.283 cm²) was $7.1 \times 10^{-5} \text{ g cm}^{-2}$. Therefore, the current density reported here was all using the geometric area of the carbon electrode. For comparison, 40% Pt/C (Johnson Matthey, JM) was measured at the same procedures.

The electrochemical HOR activity of catalyst was tested in a glass cell consisting of a three-electrode system in 0.5 M H₂SO₄ at 25°C, which was saturated with pure nitrogen in



(a)



(b)

FIGURE 2: CV curves of a GC electrode coated with (a) Ni(bmdiph)/C (without heating) and (b) 40% Pt/C (JM company), recorded in a 0.5 M H₂SO₄ (the solution was bubbled with (a) pure N₂ and (b) H₂, at a scan rate of 50 mV/s).

order to expel oxygen in the solution. The saturated calomel was used as the reference electrode, and a platinum wire was used as the counter electrode. All potential in this work was referred to reversible hydrogen electrode (RHE). The measurements were carried out by using a rotating disk electrode (RDE, Pine 5908 Triangle Drive Raleigh, NC21617) by CV at 50 mV s⁻¹ and LSV at 5 mV s⁻¹, to determine the current density at room temperature in the N₂ and H₂ streams. Each electrolyte had been saturated with hydrogen for 30 min until the experimental system was stable before each HOR electrochemical measurement.

3. Results and Discussion

3.1. Activity of 40% Ni(bmdiph)/C towards HOR. Figure 2 compared the CV curves of the GC electrode coated with Ni(bmdiph)/C (without heat curing) and 40% Pt/C (JM company), respectively, in the H₂- and N₂-saturated 0.5 M H₂SO₄ solutions.

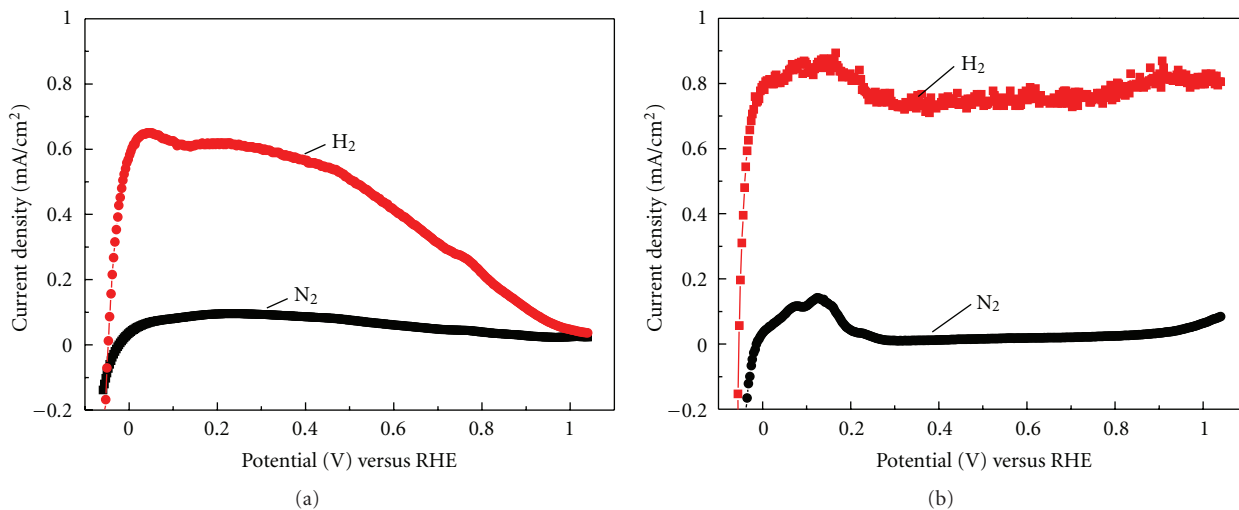


FIGURE 3: The LSV curves of Ni(bmdiph)/C (home-made, without heat curing) and 40% Pt/C (JM company) at rotation rate of 300 rpm in H₂-saturated or N₂-saturated 0.5 M H₂SO₄ solution at room temperature.

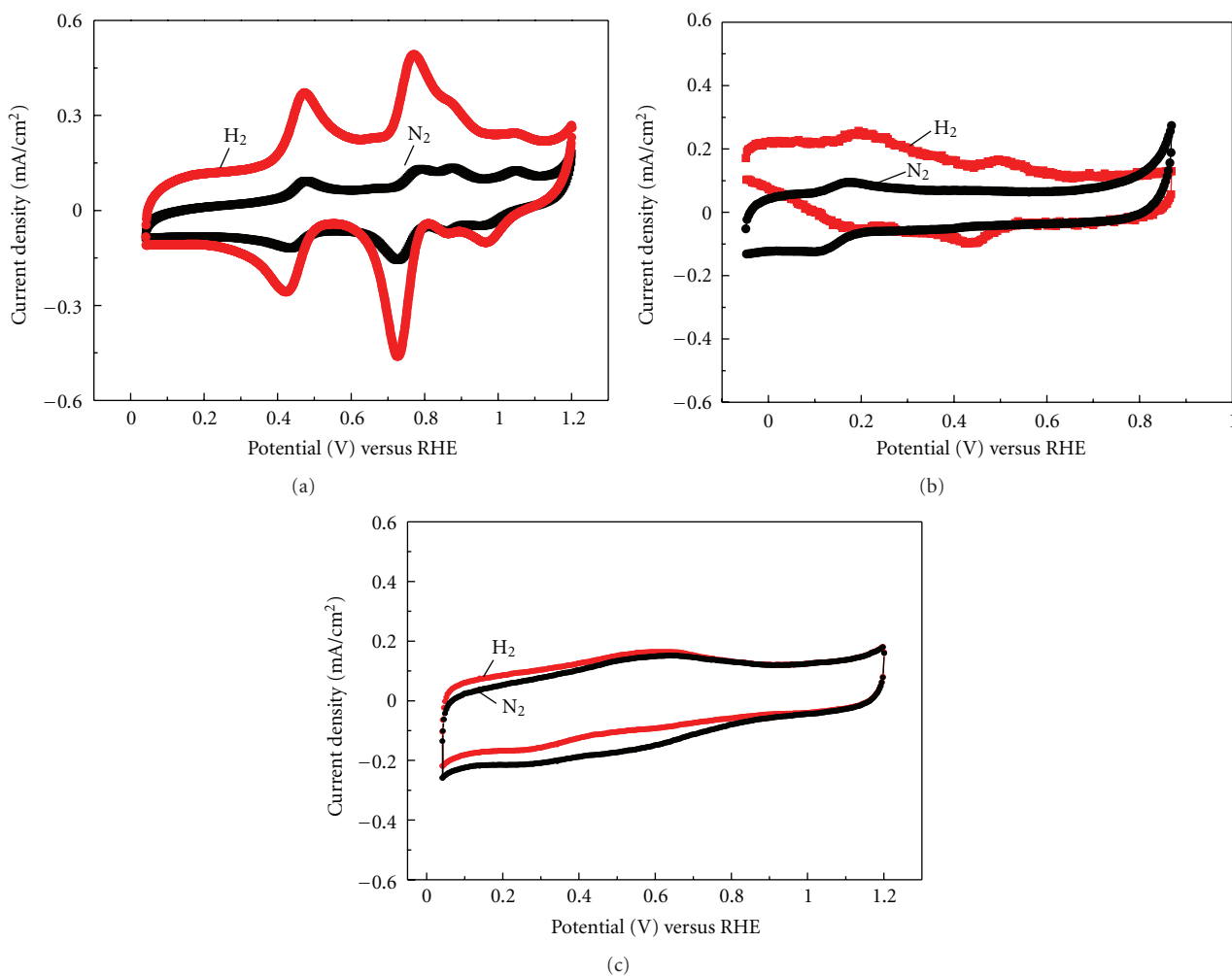


FIGURE 4: CV curves of Ni(bmdiph)/C calcined at different heat-treated temperatures, in 0.5 M H₂SO₄ solution at the scan rate of 50 mV/s. From the top to the bottom, (a), without heat curing, (b), 200°C, and (c), 400°C.

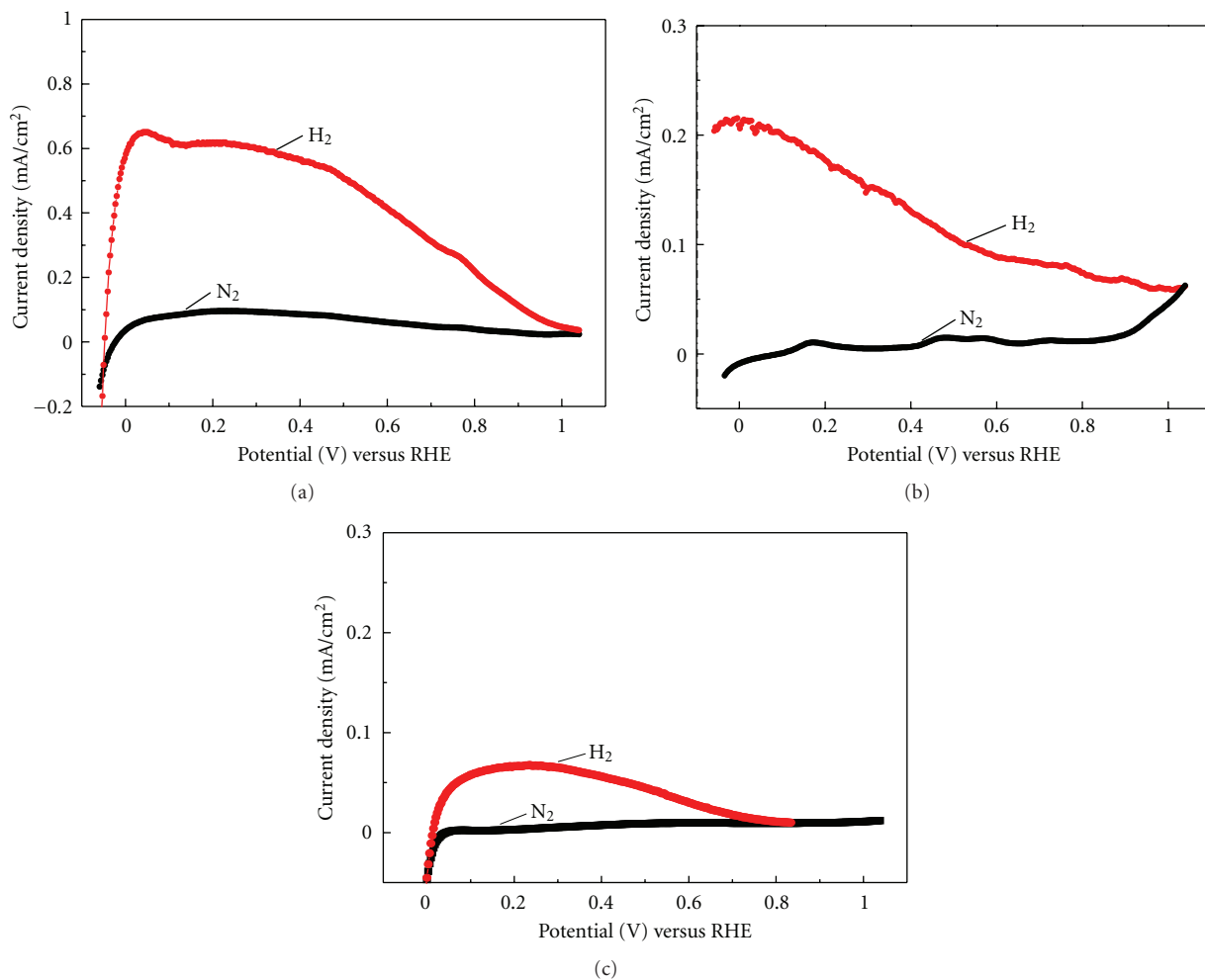


FIGURE 5: The LSV curves of Ni(bmdiph)/C prepared at different heat-treated temperatures at rotation rate of 300 rpm in H₂-saturated or N₂-saturated 0.5 M H₂SO₄ solution at room temperature, from the top to the bottom, (a), without heat curing, (b), 200°C, and (c), 400°C.

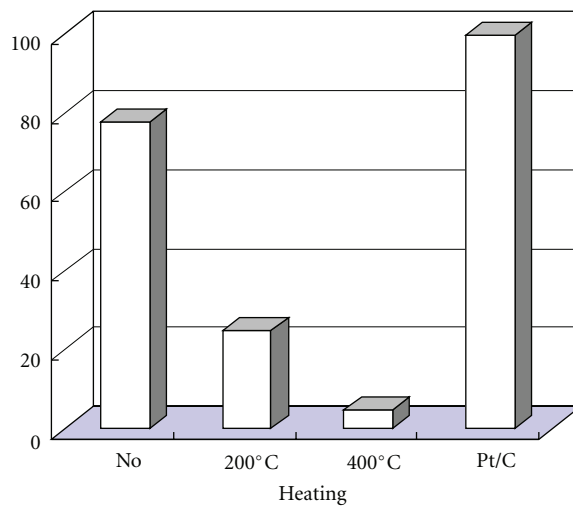


FIGURE 6: Relative current ratio of Ni(bmdiph)/C to Pt/C catalyst.

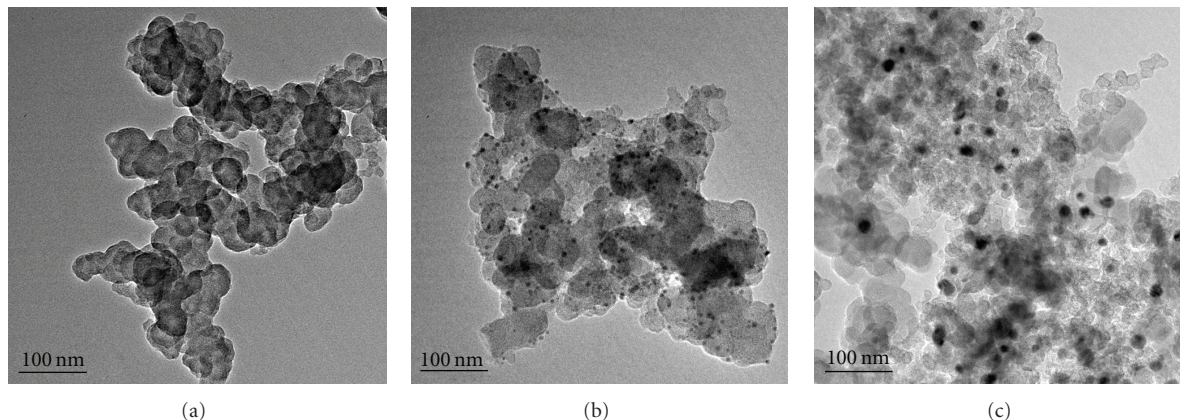


FIGURE 7: TEM images of the catalyst calcined at different temperatures, (a), without heat curing, (b), calcined at 200°C, and (c), calcined at 400°C.

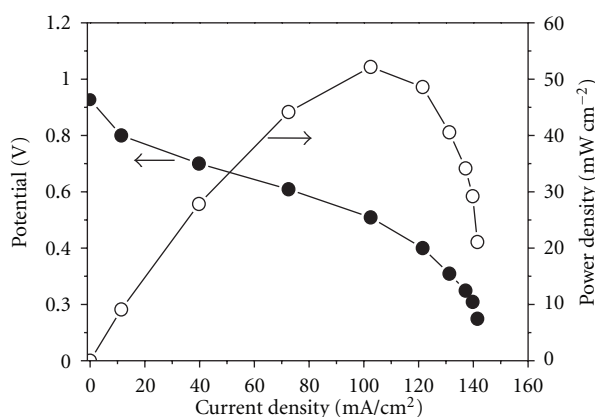


FIGURE 8: Cell voltage as a function of current density for single PEM fuel cells using Pt/C catalyst as cathodes and Ni(bmdiph)/C as anode, ●—Potential ○—Power density.

In Figure 2(a), it was noticed that in the positive scanning in N₂ atmosphere, the current started to rise around 0.4 V versus RHE, and two reversible oxidation peaks were observed at about 0.45 and 0.8 V for the unheated sample, which were assigned to the Ni^{2+/3+} and Ni^{1+/2+} redox couples of the Ni(bmdiph)/C.

The oxidation peaks of Ni species in H₂ atmosphere, which were assigned to the Ni^{2+/3+} and Ni^{1+/2+} redox couples of the Ni(bmdiph)/C catalyst at about 0.45 and 0.8 V, increased obviously comparing with that in the N₂ atmosphere. It indicated that the unheated Ni(bmdiph)/C had very good electrochemical activity towards hydrogen oxidation. Furthermore, the appearance of two redox couples suggested that Ni(bmdiph)/C might provide two different active sites for HOR, which will be discussed in the following section. Comparing CV curves of Ni(bmdiph)/C with Pt/C catalyst (Figure 2(b)), it was found, however, that the current density produced by the hydrogen oxidation of Ni(bmdiph)/C was still lower than that of Pt/C. It meant that the activity of Ni(bmdiph)/C towards HOR was still lower than that of Pt/C catalyst.

Figure 3 displayed the LSV curves of Ni(bmdiph)/C (home-made, without heat curing) and 40% Pt/C (JM company) at rotation rate of 300 r.p.m in H₂-saturated or N₂-saturated 0.5 M H₂SO₄ solution at room temperature. In Figure 3(a), a big difference between current densities which were, respectively, under H₂ and N₂ atmospheres was observed. Hydrogen desorption peaks were observed at the voltage between 0 and 0.4 V, which could be attributed to the charge exchange during electroadsorption of H atom on the catalyst. A wide peak of current density of the hydrogen oxidation reaction can be observed, and its value reached to 0.65 mA/cm², which indicated a very high activity of Ni(bmdiph)/C towards HOR. In Figure 3(b), the peak of current density of hydrogen oxidation reached to 0.9 mA/cm² for Pt/C catalyst at the voltage range of 0 and 0.2 V. Comparing with the hydrogen oxidation activity of Ni(bmdiph)/C (Figure 3(a)), though the peak of the current density of Pt/C catalyst was higher than that of Ni(bmdiph)/C catalyst, the range of current density of HOR peak of Ni(bmdiph)/C was wider than that of Pt/C. From the figures of LSV, it was found that the area of the desorption peaks of Ni(bmdiph)/C, which is at the range of 0~0.4 V, was close to that of Pt/C catalyst (at the range of 0~0.2 V). The high electrochemical surface area and low cost were main advantages of Ni(bmdiph)/C catalyst, and thus it had the potential to replace the application of Pt/C catalyst in PEFMC for hydrogen oxidation.

3.2. Effect of Heat-Treated Temperature of Ni(bmdiph)/C towards HOR. Figure 4 showed the CV curves of Ni(bmdiph)/C calcined at different heat-treated temperatures, in 0.5 M H₂SO₄ solution at the scan rate of 50 mV/s. The cyclic voltammogram of all catalysts reached a steady state soon after the cyclic voltammetry started. However, the shapes of the cyclic voltammogram were based on the heat-treatment conditions. It was observed that the current density of Ni(bmdiph)/C was affected obviously by heat treatment temperatures. There were two oxidation peaks of the Ni(bmdiph)/C without heat treatment in H₂ atmosphere, which were assigned to the Ni^{2+/3+} and Ni^{1+/2+} redox couples,

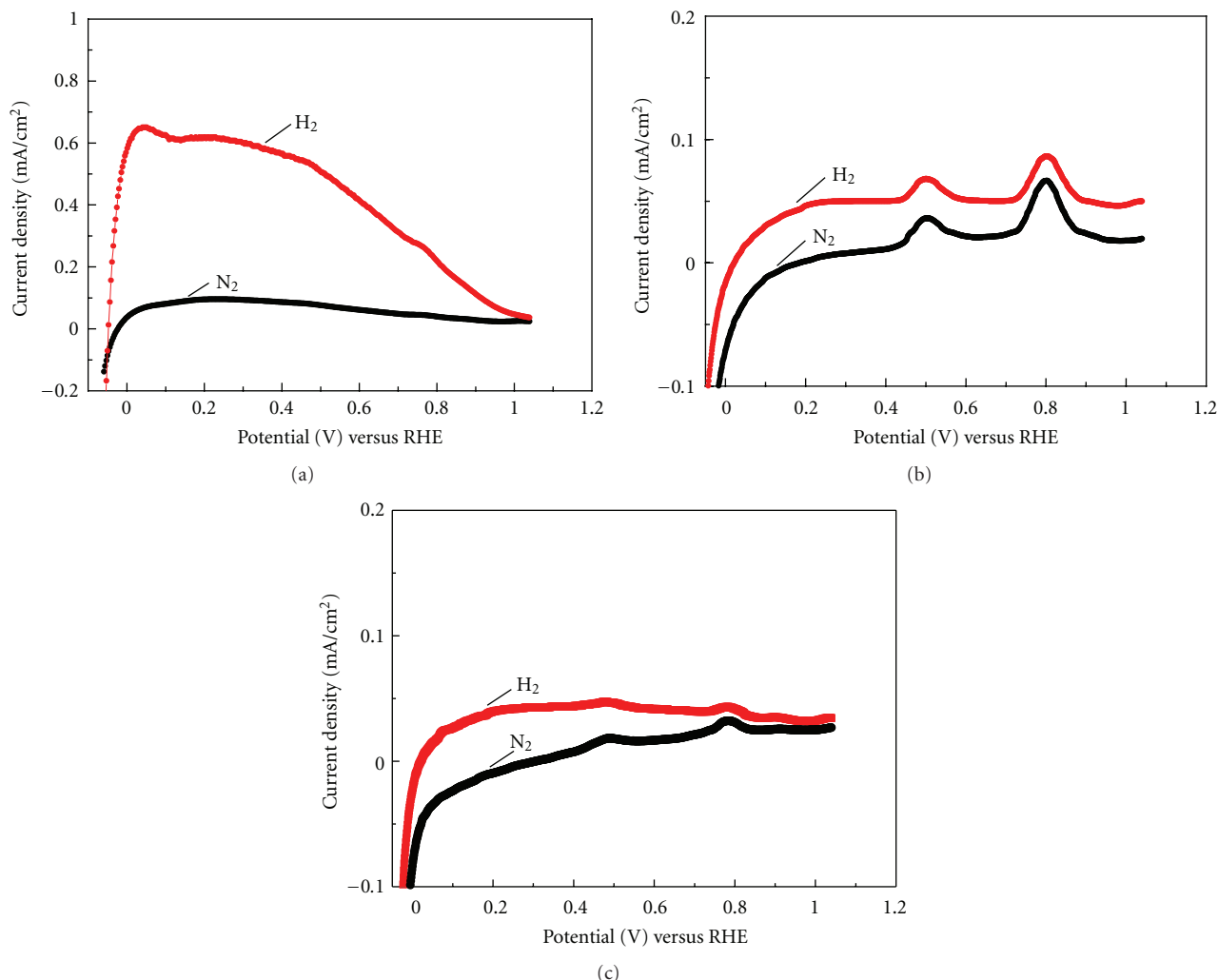


FIGURE 9: CV curves of Ni-organic metal complex with different substituent, in 0.5 M H₂SO₄ solution at the scan rate of 50 mV/s. From the top to the bottom, the substituent was changed from CH₃- to H- and to i-Pr-.

respectively, at 0.45 and 0.8 V versus RHE. After heat treatment at 200°C, the peak of current density around 0.8 V almost disappeared, and the peak at 0.45 V versus RHE drastically decreased. After heat treatment at 400°C, both current density peaks at 0.45 V and 0.8 V versus RHE diminished.

It was clear that the higher the heat-treated temperature was, the lower the peak of the current density was. The unheated Ni(bmdiph)/C showed good electrochemical HOR activity, and the hydrogen oxidation peak around 0.5 V was much higher comparing with that of Ni(bmdiph)/C heat-treated at 400°C. It was clear that the activity of Ni(bmdiph)/C towards HOR decreased due to increasing heat treatment temperature.

Figure 5 displayed the LSV curves of Ni(bmdiph)/C prepared at different heat treatment temperatures at rotation rate of 300 r.p.m in H₂-saturated or N₂-saturated 0.5 M H₂SO₄ solution at room temperature. The hydrogen oxidation peaks appeared around 50 mV. The current density peak decreased with increasing of temperature, which followed the same sequences of the CV curves. After treatment at

400°C, the peak of current density decreased obviously to 0.05 mA/cm², which further confirmed that Ni(bmdiph)/C without heating-curing had the highest activity toward hydrogen oxidation.

Figure 6 compared the relative current ratio of Ni(bmdiph)/C catalysts (calcined at different temperatures) with Pt/C catalyst (40%, JM company) at the voltage of 50 mV versus RHE. From the curves of LSV (Figure 5), it was found that the hydrogen oxidation activity of Ni(bmdiph)/C without heat curing was about 78% of that of Pt/C. We could also found that Ni(bmdiph)/C treated at 400°C exhibited the poorest electrochemical activity towards hydrogen oxidation among those catalysts. Its electrochemical activity was only 10% of that of Pt/C catalyst. It was clear that the heat treatment of catalyst played important roles in the catalytic activity towards hydrogen oxidation as most metal complexes undergo thermal degradation above 200°C [29]. Therefore, it was very likely that the very catalytic activity after high-temperature treatment was due to the degradation of the metal complex.

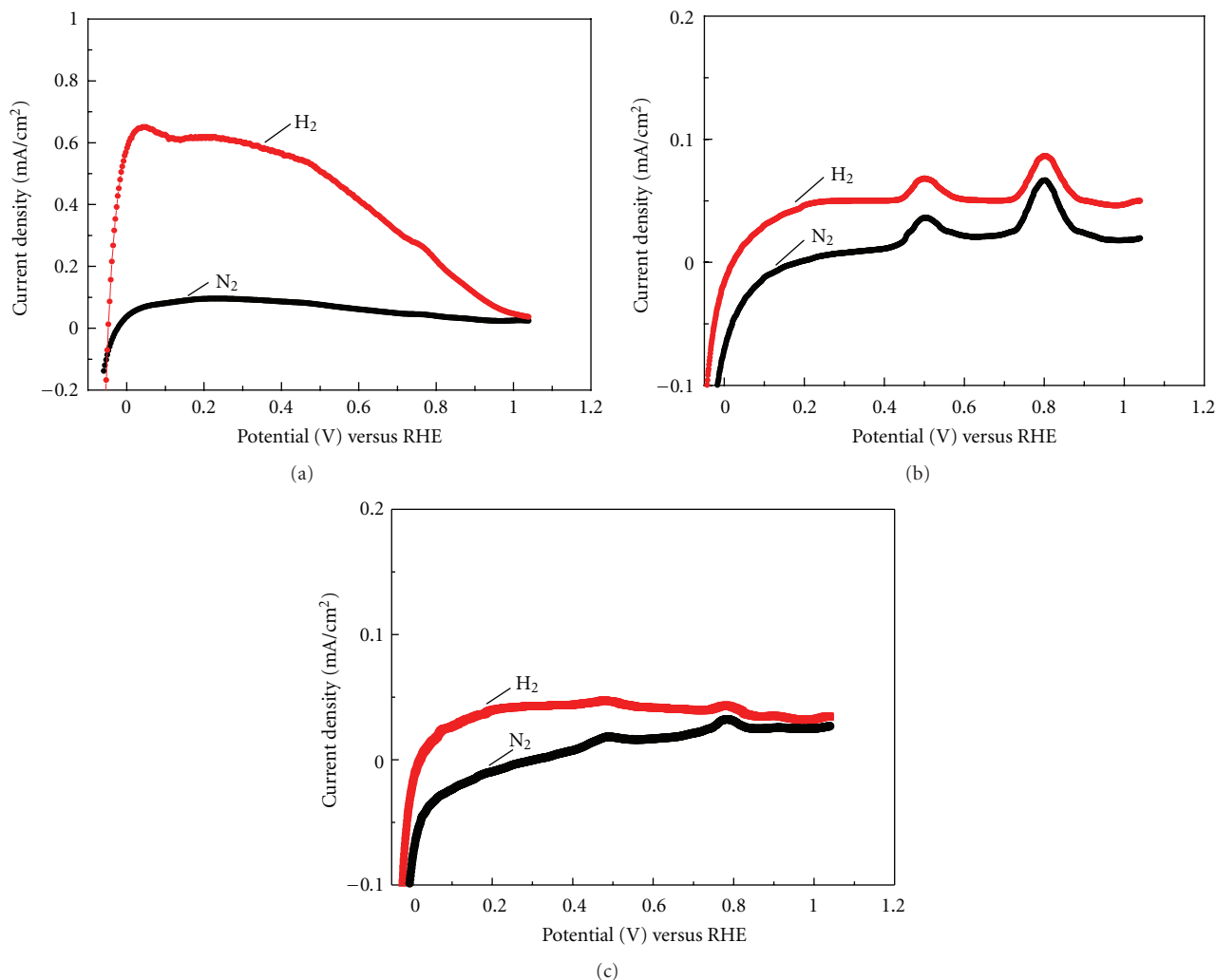


FIGURE 10: LSV curves of Ni-organic metal complex with different substituent, in 0.5 M H_2SO_4 solution at the scan rate of 50 mV/s. From the top to the bottom, the substituent was changed from CH_3 - to H- and to i-Pr-.

3.3. Characterization of Ni(bmdiph)/C Catalyst. Figure 7 showed the TEM images of Ni(bmdiph)/C catalyst calcined at different temperatures. It was found that Ni(bmdiph)/C without heat treatment uniformly dispersed on the surface of carbon support and the particles of Ni were close to spherical shapes with a mean particle size of 4 nm. But after heat treatment, respectively, from 200°C to 400°C, it was clearly seen that the particle size of catalyst obviously grew up, respectively, about 8 nm and 10 nm, and also the aggregation of catalysts happened. It was clear the high-temperature treatment would lead to the easy aggregation of the catalyst particles. The sample without heat treatment is evidently smaller than the one after heat treatment.

High temperature could change the surface texture of active species and thus affect the catalytic activity toward hydrogen oxidation. Ni(bmdiph)/C catalyst without heat treatment had small particle size (at 4 nm), which was significantly smaller than the one calcined at higher temperature. This might be one of the reasons for the decreased performance of single fuel cell after heat treatment. The high-temperature

treatment made the particle size of catalyst increase, and thus the active surface area of catalyst declined. That might be the reason for the increasing overpotential of the electrochemical reaction and thus the declining performance for hydrogen oxidation.

3.4. Single-Cell Performance. In order to investigate the catalytic performance of Ni(bmdiph)/C catalyst, member electrode assembly (MEA) based on the Ni(bmdiph)/C catalyst was prepared, and single cell testing was carried out.

Figure 8 showed the cell voltage as a function of current density for single PEM fuel cells using Pt/C catalyst as cathode and Ni(bmdiph)/C as anode under a H_2/O_2 condition. MEA was fabricated with the Pt/C catalyst in the cathode side at a loading of 0.5 mg cm^{-2} and Ni(bmdiph)/C at anode side at a loading of 0.5 mg cm^{-2} . One can see that the open-circuit potential was around 0.94 V. The active area of the fuel cell was 4 cm^2 . It achieved a power density of 52 mW cm^{-2} at 0.5 V. Comparing with other reported organic metal complex catalysts, even though Ni(bmdiph)/C was almost at

the same open-circuit voltage (OCV) values as that of Pt/C, the performance of single cell still needs further improvement. Through the optimization of the synthesis of organic complex and the MEA manufacture processes, the performance of Ni(bmdiph)/C will be improved. As the scarcity and the cost of Pt, completely or partly replacement of Pt by organic complex would be highly considered.

3.5. Effect of the Substituent for Ni-Organic Metal Complex Catalysts towards HOR. In order to investigate the structure effect on the organic metal complexes in more detail, substituent was changed from R = CH₃ to R = H and R = i-Pr, which was corresponding to Ni(bmdiph), Ni(diph)/C, and Ni(bidiph)/C. Figures 9 and 10 were the CV and LSV curves of Ni-organic metal complex with different substituent. It was found that Ni(bmdiph) was much active towards HOR than that of Ni(diph)/C and Ni(bidiph)/C. The catalytic activity for hydrogen oxidation was in the order of Ni(bmdiph)/C \gg Ni(diph)/C > Ni(bidiph)/C. Although electron withdrawing effect of i-Pr group was larger than that of -CH₃ and -H, effect of steric hindrance of i-Pr group was larger than that of CH₃- and H-groups. It might be the main reason for the decreased activity of Ni(bidiph). Though the details of the hydrogen oxidation of organic complex were not yet clear and further investigation was needed, these facts suggested that the structure of the organic complex appeared to be a crucial factor for the HOR activity. Above results can be interpreted as a first indication that Ni(bmdiph)/C catalyst may be a very promising candidate for usage as the anode catalyst in H₂/O₂ PEMFCs. More detailed work on stability characterization and further improvement is going on to investigate the mechanism of the catalytic activity of Ni-complex oxides.

4. Conclusions

A novel nonnoble Ni-complexes (Ni-N₂O₂)/C electrocatalysts have been successfully prepared in a flow N₂ atmosphere. The carbon-supported catalyst displayed a strong activity towards HOR. The effects of heating temperature and substituent groups on its electrocatalytic properties were investigated. It was found that the activity of Ni(bmdiph)/C toward HOR was influenced obviously by heat treatment conditions and followed the order of without heat curing >200°C >400°C. Ni(bmdiph)/C without heat curing was only about 22% inferior to that of a commercial 40% Pt/C (JM company). Substituent groups played important roles in the hydrogen oxidation activity for Ni-organic metal complex catalysts. The substitution of H-group by CH₃-group made Ni(bmdiph)/C exhibit the highest activity, while the steric hindrance of i-Pr-group might cause the decrease of electrochemical activity of Ni(bidiph)/C. The samples obtained were characterized by TEM. TEM results showed that the synthesized Ni(bmdiph)/C without heat curing had excellent dispersion of Ni particles on the carbon support while high-temperature treatment would lead to the easy aggregation of Ni particles.

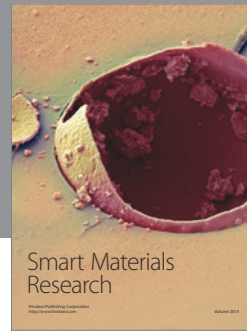
Acknowledgments

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