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Methanol-tolerant MoN electrocatalyst synthesized through heat treatment of molybdenum tetraphenylporphyrin for four-electron oxygen reduction reaction

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Abstract

A novel non-noble electrocatalyst with an average particle size of approximately 4 nm was prepared by heat-treating carbon-supported molybdenum tetraphenylporphyrin in a flow NH_3 atmosphere. The effects of heating time and temperature on its electrocatalystic properties were investigated. The samples obtained were characterized by X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, and EDX. The results show that the synthesized catalyst has the same composition as that of MoN. This carbon-supported catalyst displays a strong activity towards oxygen reduction reaction (ORR) and a methanol-tolerant property. The catalyzed ORR proceeds by an approximate four-electron reduction pathway from O_2 directly to H_2O.

Keywords: Electrocatalyst; Oxygen reduction; Molybdenum tetraphenylporphyrin and nitride; Direct methanol fuel cells (DMFC)

1. Introduction

Proton exchange membrane fuel cells (PEMFCs), including direct methanol fuel cells (DMFCs), have been recognized as environmentally friendly and highly efficient energy-converting devices. On the path towards PEMFC commercialization, DMFCs seem to be the first possible real products for low-power-demanding applications due to their liquid fuel storage and transportation advantages, when compared to gaseous hydrogen fuel. However, one of the major challenges in DMFC technology is catalysis, including catalyst cost and stability [1,2]. At the current stage of technology, the most practical DMFC catalysts are platinum (Pt)-based catalysts for both anodic methanol oxidation reaction (MOR) and cathodic oxygen reduction reaction (ORR).

There are some drawbacks for Pt-based catalysts in a DMFC in addition to their high cost. For example, when a Pt-based catalyst is used at the cathode, it can also catalyze the chemical oxidation between cathode oxygen and methanol, which has crossed over from the anode to the cathode through the proton exchange membrane. This undesired activity towards methanol oxidation not only depresses the cathode oxygen electrode potential (200–300 mV in a typical DMFC) but also reduces the fuel efficiency. Therefore, the exploration of new DMFC cathode catalysts, which have methanol tolerance, is equally important to anodic MOR catalysts. In this paper, our focus is on the cathode ORR catalysis.

In the effort to explore cost-effective and methanol-tolerant cathode catalysts for DMFCs, non-noble or non-Pt catalysts seem to be the favorites and have been extensively investigated in recent years [3]. These non-Pt materials include transition metal chalcogenides [4], heat-treated macrocycles [5], transition metal oxides [6], and transition metal nitrides [7].

Transition metal nitrides are a new kind of non-noble catalyst which have been explored for fuel cell applications most

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recently. These catalysts, which show a Pt-like behavior for chemisorptions of hydrogen and oxygen, have been investigated as CO-tolerant anode catalysts. Mazza and Trassatti [8] synthesized a TiN compound using a directly nitriding method and found that TiN exhibited an activity towards ORR in alkaline solutions. Zhong's group [7] synthesized a carbon-supported molybdenum nitride catalyst (Mo_2N/C) using a pyrolysis method and explored the possibility of this material as a fuel cell catalyst. In general, the tactic of catalyst synthesis seems to be the key in obtaining active and stable ORR catalysts.

Regarding the synthesis of new catalysts, heat treatment has been recognized as an effective and facile method for catalytic activity improvement [5,9]. Heat treatment of a catalyst can result in a different composition and structure from those of its precursor, and can also affect the fundamental properties of the catalyst and its carbon support, including the loading level of the catalyst on the support, the number of catalytic sites, the acid–base properties of the support, and the distribution of the catalyst particles on the support. A typical example is the heat treatment of macrocyclic metal complexes. When the catalysts are pyrolyzed at a desired high temperature, the molecular structure of the macrocycle is partially or completely destroyed, resulting in a new catalyst which has much better catalyst activity and stability than does the untreated catalyst.

Although the heat-treatment effect on these metal macrocycle properties has been well-documented, a full understanding of the mechanism of the catalyst reaction during the heat-treatment process and the resulting improvement in catalytic activity has not yet been achieved. In particular, there is no general agreement on the composition and structure of the resulting catalyst. Therefore, the characterization and identification of the active catalyst composition and structure formed after the heat treatment of metal macrocycle seem to be critical to our understanding of the improved ORR catalytic activity.

The objective of this work is to explore new, cost-effective oxygen reduction catalysts for DMFC made by heat-treating molybdenum tetraphenylporphyrin supported on carbon. In this synthesis process, a heat-treatment procedure in an NH_3 environment at different temperatures (from 600 to 1000 °C) was explored. The obtained catalyst was then characterized physically through sophisticated instrument methods. The results show that this catalyst has a composition of MoN/C. The electrocatalytic activity of the MoN/C catalyst towards ORR was investigated by means of cyclic voltammetry (CV) and rotating disc electrode (RDE). The measurements show that this catalyst has a comparatively strong electrocatalytic ORR activity and a strong methanol-tolerant property.

2. Experiment

2.1. Catalyst preparation

Analytic-grade molybdenum tetraphenylporphyrin was supplied by Beijing Reagent Corp. and was used as received. Carbon black (XC-72) was purchased from Cabot Corp. and was used as received. In a typical catalyst synthesis, carbon black was added into a tetrahydro furan solution containing 0.0176 M molybdenum tetraphenylporphyrin at room temperature. After ultrasonic agitation for 30 min, the mixture was then evaporated at 60 °C and dried in air at 80 °C overnight. The obtained powder was transferred to an NH_3 flushed quartz reactor inside a tubular resistance furnace. The sample was then heated at different temperatures ranging from 600 to 1000 °C for different times to obtain the final catalyst powder.

2.2. Physical and surface characterization

Powder X-ray diffraction (XRD) data were collected on a Bruker D8 Discover X-ray diffractometer using Cu Kα radiation between 10 and 90° with a step size of 0.02°. High-resolution transmission electron microscopy (TEM) images and dispersive X-ray spectroscopy (EDS) analysis were collected on a JEOL JEM-2010 transmission electron microscope. Surface analysis of the catalyst was performed by X-ray photoelectron spectroscopy (XPS).

2.3. Electrochemical test

CV and RDE measurements were conducted using a three-electrode electrochemical cell in a 0.5 M H_2SO_4 solution for ORR at ambient temperature. The working electrode was a thin layer of Nafion-bonded catalyst cast on a rotating disk electrode. A standard hydrogen electrode and Pt plate were used as the reference and the auxiliary electrode, respectively. Electrochemical measurements were performed using an EG&G Model 273A potentiostat/galvanostat controlled by M270 software.

3. Results and discussion

3.1. XRD analyses

XRD is normally useful in determining the presence of an inorganic phase in the catalyst particles. Fig. 1 shows the XRD patterns of the catalyst power obtained after heat-treating MoTPP/C at 700 °C in flow NH_3 atmosphere for different times

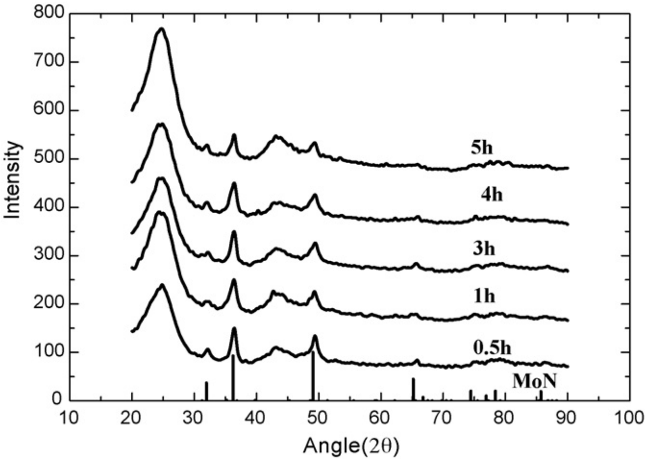


Fig. 1. XRD patterns of the catalyst synthesized by heating MoTPP/C in a NH_3 atmosphere at 700 °C for different time periods.

Table 1
Changes in the binding energy of Mo before and after heat treatment at different temperatures

Heat-treatment temperature	Untreated MoTTP/C	600 °C	700 °C	750 °C
Mo^{6+} 3d5/2	236.07412	236.03588	235.89764	235.99055
Mo^{5+} 3d5/2	234.68602	234.13359	234.07087	233.89179
Mo^{4+} 3d5/2	232.96555	232.82067	232.74803	132.41965

as marked at each spectrum. For comparison, the spectrum and the peak locations and relative intensities for MoN are also plotted in Fig. 1. The peak locations and relative intensities for MoN are cited from the JCPDS database. It can be seen that the diffraction peaks for the synthesized catalyst, which can be attributed to the hexagonal MoN phase ($2\theta = 31.937, 36.239, 49.066, 65.186$) and carbon black Vulcan XC-72R ($2\theta = 25, 43$) are the same as those for the baseline MoN data, suggesting that the catalyst obtained in this paper is MoN with negligible impurities. This result is different from those reported in the literature [10], where the products were MoN with Mo_2N by nitriding of molybdenum. There is also no visible change in the phase structure with the changing heating time, indicating that heat-treatment time has no significant effect on the phase structure of MoN at 700 °C.

In order to determine the particle size of the catalyst powder, the peak (0 1 4) of MoN was analyzed in detail. Using the Deby–Sherrer relation and taking the resolution of the instrument into account, the average particle size obtained on the support is about 4 nm.

The mechanism of metal nitride formation has been proposed to be the occurrence of a metal cluster during the metal macrocycles pyrolysis. In our case, with the presence of NH_3, the following reaction may occur and may provide the source of active nitrogen for the MoN formation at high temperatures:

$$2NH_3 = 3H_2 + 2[N] \tag{1}$$

The active nitrogen atom formed in reaction (1) could react with the Mo metal cluster to form a MoN phase.

Fig. 2 shows the temperature dependency of the XRD patterns for the catalyst synthesized by heating MoTPP/C in an NH_3 atmosphere for 3 h. There are no significant differences in the peak location of the MoN when the temperature is changed, indicating that temperature has no significant effect on the composition of MoN formed from 600 to 1000 °C. However, there is an exception at 1000 °C. The XRD spectrum at 1000 °C is different from those at lower temperatures (600–900 °C). This spectrum has narrower and more intensive peaks, and the peak for the carbon support has disappeared. This could be because the carbon support was removed by hydrogen reduction reaction with carbon at such a high temperature.

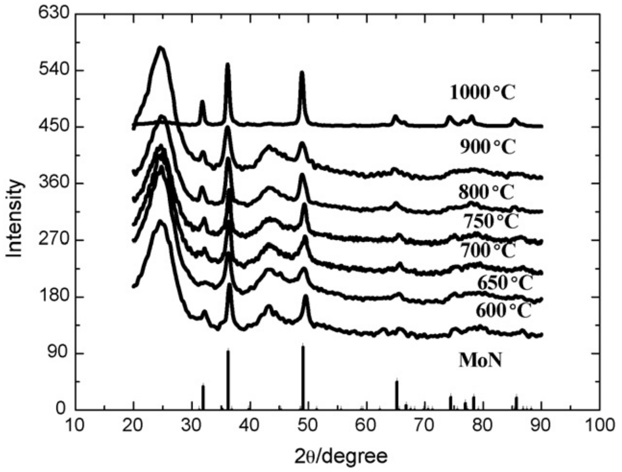


Fig. 2. XRD patterns of the catalyst synthesized by heating MoTPP/C in a NH_3 atmosphere for 3 h at different temperatures.

3.2. XPS analyses

In order to study the change in Mo binding energy before and after the heat treatment, XPS spectra were collected at different temperatures, as shown in Fig. 3. After a conventional curve fitting for peak separation, the binding energies for three different Mo species were obtained; these are summarized in Table 1 together with those of untreated MoTTP/C for comparison. Since the oxidation states are consistent with results reported for bulk MoN [11], one can assume that these Mo species should belong to a nitride phase. In Fig. 3, the spectra of two possible states of j values ($j = 5/2$ and 3/2, respectively), observed between 224 and 241 eV, should arise from the spin–orbit coupling of the Mo3d subshell. After the sample was heat-treated at 700 °C, the doublet peaks of Mo3d(5/2) shifted from the values of 236.0 eV, 234.6 eV, and 232.9 eV to the values of 235.8 eV, 234.0 eV, and 232.7 eV, respectively. The changes in the binding energy of Mo3d(5/2) for Mo^{4+}, Mo^{5+}, and Mo^{6+} species before and after heat treatment are 0.2 eV, 0.6 eV, and 0.17 eV, respectively.

Fig. 4 shows the XPS spectra of the Mo3p and N1s levels for MoN at different temperatures. It can be seen that the N1s peaks overlap severely with the Mo3p3/2 peaks at all temperatures. Curve fitting shows that the binding energy of N1s in nitrogen atoms shifts from a higher energy level to a lower one after it engages in a nitride. The binding energy of N1s at 700 °C is the largest among the different temperatures.

Normally, Mo and its oxides are not catalytically active towards ORR. In the case of heat-treated MoTPP, after the formation of Mo nitride, the interaction between Mo and N in the nitride could change the profile of binding and adsorption/desorption energies of O_2, resulting in a favorable situation for electron transfer of oxygen reduction [12].

3.3. TEM and EDX characterization

In order to further confirm the formation of a MoN phase after the heat treatment of MoTPP/C, TEM and EDX images

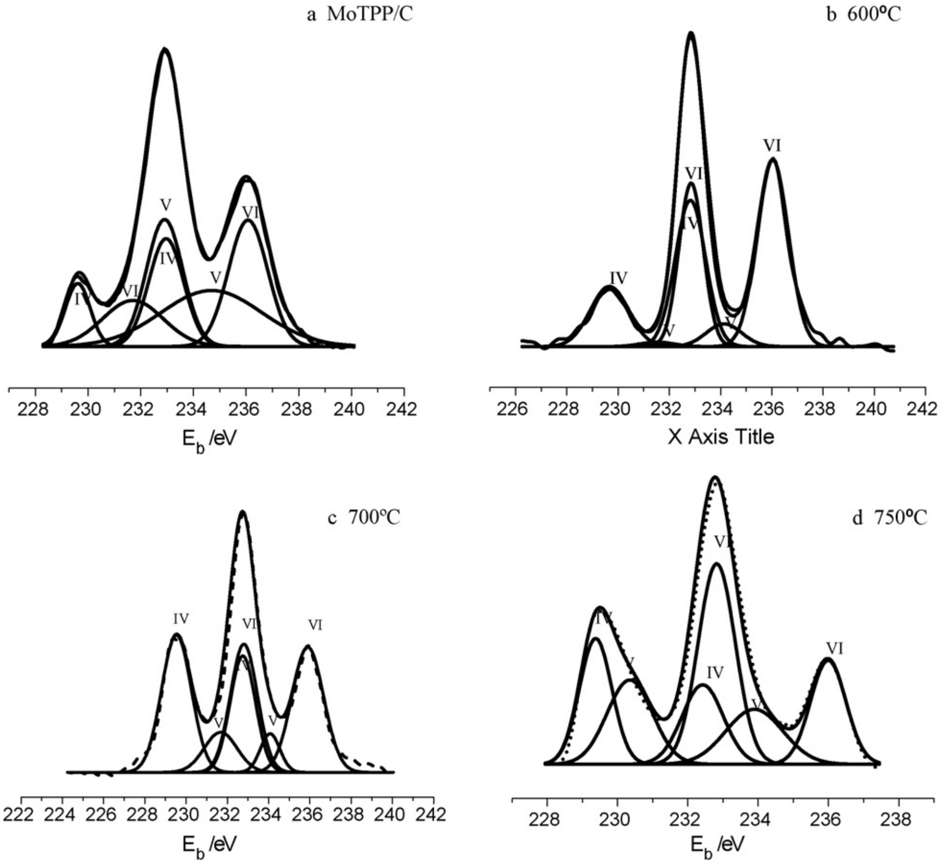


Fig. 3. XPS spectra of Mo3d at different temperatures.

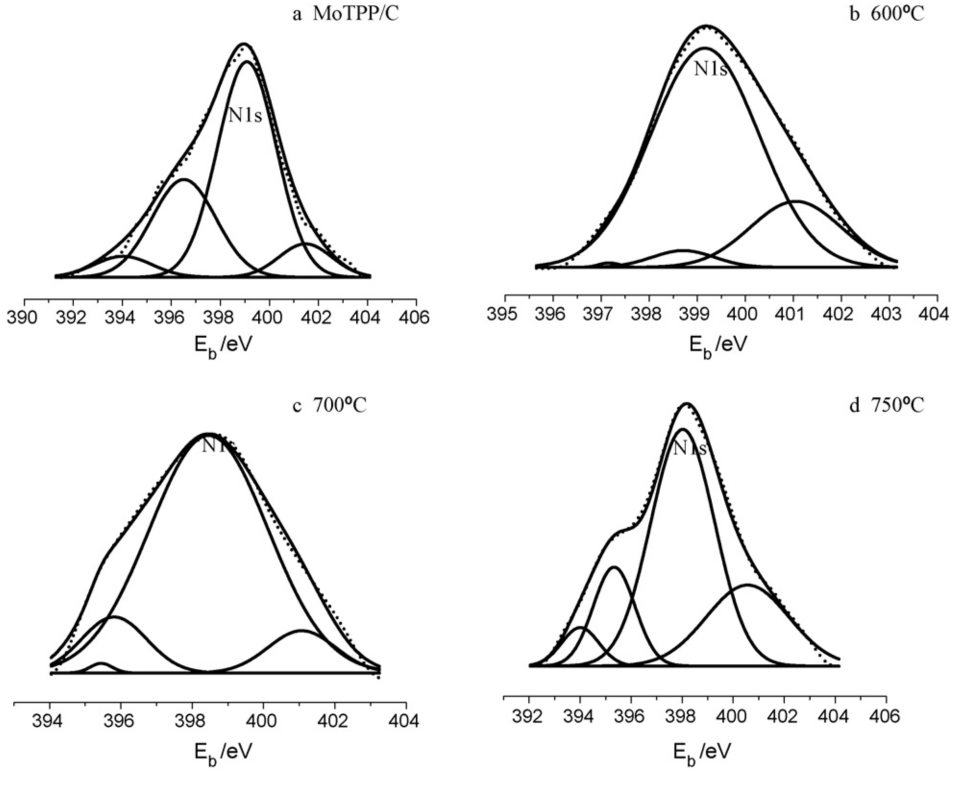
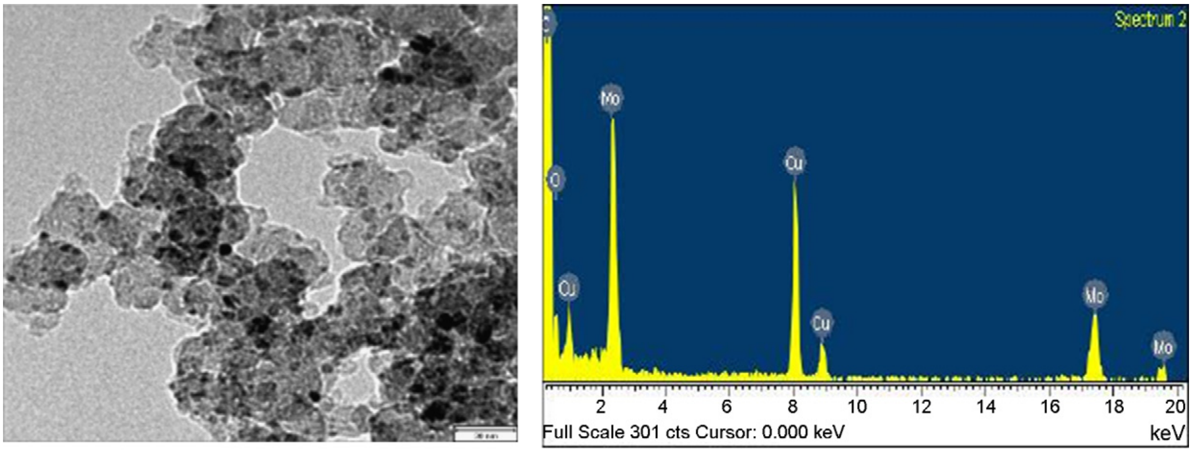


Fig. 4. XPS spectra of Mo3p and N1s levels at different temperatures.



(TEM) (EDX)

Fig. 5. TEM micrograph and EDX pattern for the catalyst formed by heat treatment of MoTTP/C at 700 °C.

were recorded separately, as shown in Fig. 5. The TEM micrograph of MoN/C formed by heat-treating MoTTP/C at 700 °C clearly shows that the molybdenum nitride phase with a particle diameter of 4–5 nm is well dispersed on the carbon and did not segregate into domains. The EDX pattern shows molybdenum is present, but the carbon peak is so high that the nitron peak is restrained.

3.4. Electrochemical measurements of the catalysts towards ORR

Fig. 6 shows the cyclic voltammograms of the glassy carbon (GC) electrode coated with MoTTP/C and heat-treated MoN/C in the O_2- and N_2-saturated solutions. The electrode modified by MoTPP/C has no catalytic activity towards ORR. However, after heat treatment, the resulting MoN/C catalyst displays strong catalytic activity. The ORR onset potentials are about 0.58 V (vs. NHE), which is higher than that of the Mo_2N catalyst [7].

In order to optimize the heat-treatment temperature and investigate the kinetics of the ORR catalyzed by the MoN/C catalyst, RDE measurements were carried out. The MoN/C catalyst for the sample treated at 700 °C exhibits a relatively large limiting diffusion current. Fig. 7(a) shows the ORR curves at different rotating rates from 400 to 3000 rad/mits. Typically, the reaction appears to be under a combined kinetic-diffusion control; the electrode rotation has an effect on the reaction rate at very high overpotentials for the ORR.

The Koutecky–Levich equation for O_2 reduction was used to determine the electron transfer number of the catalyzed ORR. The plots of the reciprocal of current density versus the reciprocal square root of rotating rate, shown in Fig. 7(b), can give a slope of $0.62nFAD\mathrm{o}_2{}^{2/3}\ \nu^{-1/6}C_\mathrm{O}$, where F is the Faraday constant, n is the number of electrons transferred per molecule of O_2, A is the geometric area of the disk electrode, $D\mathrm{o}_2$ and C_O are the diffusion coefficient and the concentration of dissolved oxygen in 0.5 M H_2SO_4, respectively, ν is the kinematic viscosity

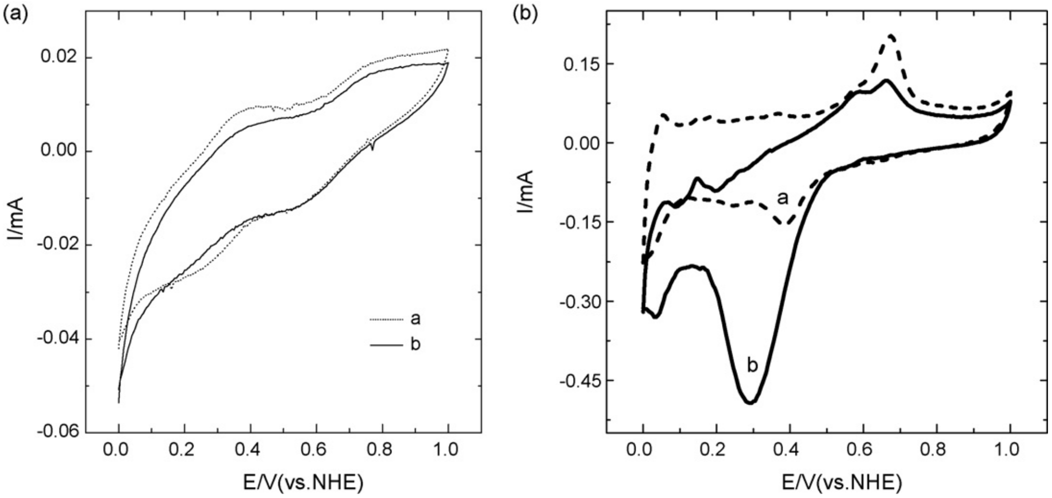


Fig. 6. Cyclic voltammograms of a GC electrode coated with (a) MoTTP and (b) heat-treated MoTTP/C at 700 °C, recorded in a 0.5 M H_2SO_4 (the solution was bubbled with (a) pure N_2 and (b) O_2).

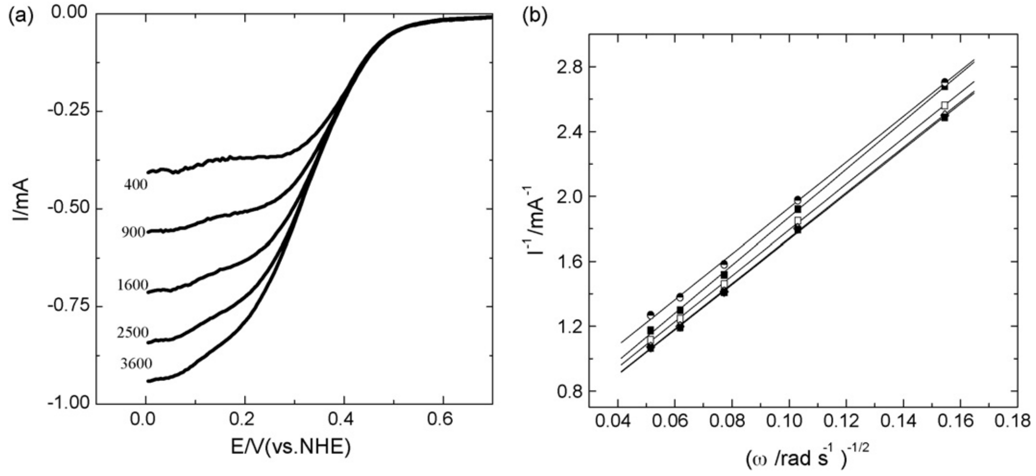


Fig. 7. (a) Polarization curves for ORR at a GC electrode coated by MoN/C catalyst (obtained with 700 °C heat treatment) at different rotation rates in 0.5 M H_2SO_4 solution saturated by O_2; (b) Levich–Koutecky plots, data from (a) (lines from bottom to up: 0.04 V, 0.045 V, 0.1 V, 0.145 V, 0.2 V, respectively).

value (0.0095 $cm^2\ s^{-1}$). The electron transfer number obtained based on the measured slope value was 3.8, which is close to 4. This result suggests that the catalyzed ORR by MoN/C is a four-electron process from O_2 to water.

3.5. *Methanol-tolerant property of synthesized MoN/C catalyst*

Fig. 8 shows typical cyclic voltammograms recorded on a GC electrode coated with a synthesized MoN/C catalyst in 0.5 M H_2SO_4 solution and 0.5 M H_2SO_4 + 5.0 M CH_3OH. The cathodic waves starting from 0.58 V (vs. NHE) are the catalyzed ORR responses. When 5.0 M methanol was added to the solution, the magnitude of the cyclic voltammogram wave was almost unchanged, with methanol present even after several potential–current cycles. This result clearly indicates that the MoN/C catalyst has a strong electrochemical resistance to methanol oxidation. As mentioned in the introduction, it is highly desirable to use a cathode catalyst that has no catalytic activity towards methanol oxidation. It is believed that this MoN/C could eliminate the negative effect of the methanol crossover when used as a cathode catalyst for DMFCs. Unfortunately, due to the fact that the onset potential is somewhat low, it may be feasible to use such a catalyst only in a low current density range. More work is underway towards optimizing the catalytic activity with a focus on increasing the onset potential.

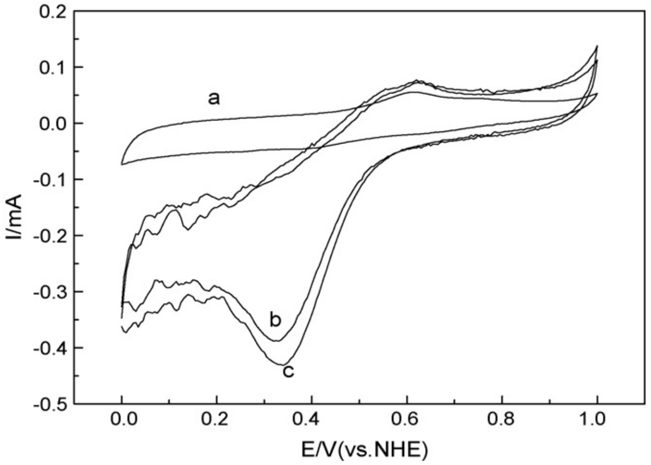


Fig. 8. Cyclic voltammograms of a GC electrode coated with MoN/C catalyst (obtained with 700 °C heat treatment) in (a) 0.5 M H_2SO_4 solution saturated by N_2, (b) 0.5 M H_2SO_4 solution saturated by O_2, and (c) 0.5 M H_2SO_4 + 5.0 M methanol solution saturated by O_2. Potential scan rate: 20 mV s^{-1}.

3.6. *Stability test*

To examine the long-term stability of the synthesized MoN/C electrocatalyst, chronoamperometry tests were conducted at 0.40 V versus NHE in a solution containing 0.5 M sulfuric acid. At such an electrode potential, a current density of 0.15 mA cm^{-2} was obtained. After more than 10 h of testing at this potential, no significant current decay could be observed. This preliminary result shows that the nanoparticles MoN/C electrocatalyst has long-term stability, which is valuable for practical performance. More detailed work on stability characterization and further improvement is going on.

4. Conclusion

Heat treatment of MoTTP/C in a flow NH_3 atmosphere can generate an ORR electrocatalyst with an average particle size of approximately 4 nm. The effects of heating time and temperature on the catalyst composition were investigated. The results show that the heating time has almost no effect on the synthesized catalyst. The catalyst was characterized by XRD, XPS, TEM, and EDX; the results show that this catalyst can be attributed to the hexagonal MoN phase. With respect to the ORR activity, this catalyst was also examined in an acidic solution containing saturated oxygen by CV and RDE methods. The measurements indicate that this catalyst has strong ORR activity, proceeding via an approximate four-electron pathway, through which the molecular oxygen is directly reduced to H_2O.

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References

[1] L.T. Weng, P. Bertrand, G. Lalande, Appl. Surf. Sci. 84 (1) (1995) 9–211.
[2] P. Gouerec, M. Savy, Electrochim. Acta 44 (1999) 2653–2661.
[3] L. Zhang, J. Zhang, D. Wilkinson, H. Wang, J. Power Sources 156 (2006) 171–182.
[4] K. Lee, L. Zhang, J. Zhang, J. Power Sources 165 (2007) 108–113.
[5] C.W.B. Bezerra, L. Zhang, H. Liu, K. Lee, A.L.B. Marques, E.P. Marques, H. Wang, J. Zhang, J. Power Sources 173 (2007) 891–908.
[6] J.-H. Kim, A. Ishihara, S. Mitsushima, N. Kamiya, K.-I. Ota, Electrochim. Acta 52 (2007) 2492–2497.
[7] H. Zhong, H. Zhang, G. Liu, Y. Liang, J. Hu, B. Yi, Electrochem. Comm. 8 (2006) 707–712.
[8] F. Mazza, S. Trassatti, J. Electrochem. Soc. 110 (1963) 847.
[9] F. Jaouen, M. Lefèvre, J. Dodelet, M. Cai, J. Phys. Chem. B 110 (2006) 5553.
[10] Y. Nishi, S. Tokunaga, S. Moriya, J. Mater. Sci. Lett. 6 (1987) 1450–1452.
[11] T. Bécue, J.-M. Manoli, C. Potvin, G. Djéga-Mariadassou, J. Phys. Chem. B 101 (1997) 6429.
[12] Z. Shi, J. Zhang, Z. Liu, H. Wang, D.P. Wilkinson, Electrochim. Acta 51 (2006) 1905.