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High activity of a Pt decorated Ni/C nanocatalyst for hydrogen oxidation

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ABSTRACT

The Pt decorated Ni/C nanocatalysts were prepared for hydrogen oxidation reaction (HOR) in fuel cell. By regulating the contents of Pt and Ni in the catalyst, both the composition and the structure affected the electrochemical catalytic characteristics of the Pt-Ni/C catalysts. When the Pt mass content was 3.1% percent and that of Ni was 13.9% percent, the Pt-Ni/C-3 catalyst exhibited a larger electrochemically active surface area and a higher exchange current density toward HOR than those of pure supported platinum sample. Our study demonstrates a feasible approach for designing the more efficient catalysts with lower content of noble metal for HOR in fuel cell.

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1. Introduction

Over the last several decades, many researchers actively searched for new, environmentally friendly energy sources due to the rapid increase of energy demand and the depletion of fossil fuel reserves [1–9]. Fuel cells have been considered as a class of the most promising power sources with high energy density and high efficiency [1,10–14]. The alkaline fuel cell (AFC) was one of the earliest developed space power cells for the Apollo space program of the National Aeronautics and Space Administration from the USA in the 1960s [15]. Also, combating the rapid rise in atmospheric CO₂ to avoid its disastrous impacts on the Earth and satisfying the ever-increasing demand for energy are both top global priorities [16,17]. Recently, Xie et al. [18] reported a CO₂-mineralization fuel cell (CMFC). In this system, CO₂ and industrial alkaline wastes were used as feed stock, and industrially valuable NaHCO₃ was pro-

duced concomitantly during the generation of electricity. Fig. 1 contains a schematic diagram of the AFC and the CMFC.

The anodic reaction of both the AFC and the CMFC entails the hydrogen oxidation reaction (HOR). However, the most commonly utilized catalyst, Pt is both expensive and scarce. Therefore, it is critical to either find an efficient yet cheap catalyst that does include Pt or to utilize less content Pt catalysts and more efficiently by reducing the the size or changing the support [19–21]. In the all kinds of exploration for catalyst, the study of nanostructured catalyst for electrocatalysis is one of the most efficient strategies. Zhang and his co-workers [22] reviewed the recent progress of nanostructured materials in electrochemical energy conversion and storage. Li et al. [23] showed a ultrafine jagged platinum nanowires that enhanced ORR activity. Liao and his co-workers [24] studied the alloying effect of Ir- based alloy nanocrystals with different metal species on the catalysis of HOR. The galvanic replacement reaction

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Fig. 1. The schematic illustrations. (a) alkaline fuel cell (AFC); (b) CO₂-mineralization fuel cell system.

is a powerful strategy for synthesizing Pt-M bimetallic catalysts with reduced sizes and different particle structures. Zhang and his co-workers [25] showed the formation of Pt/Ag nanoboxes using a galvanic replacement reaction and subsequently exhibited the catalyst's high surface area and excellent catalytic activity for the methanol oxidation reaction. Alia, et al. [26] reported that Pt-coated Cu nanowires were high activity for the HOR in base.

In this study, we attempted to synthesize nano-sized Pt-Ni/C catalysts in two steps, namely, the impregnation-reduction process and the galvanic replacement reaction. The catalysts were characterized by transmission electron microscope (TEM), X-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM) and X-ray diffraction (XRD). The electrocatalytic performance of these nanocatalysts for HOR was investigated by voltammetry and Tafel slope measurements. The results show that the Pt-Ni/C catalyst synthesized by the galvanic replacement reaction has a higher electrocatalytic activity toward the HOR than that of the Pt/C catalyst purchased from Johnson Matthey company.

2. Experimental

2.1. Catalyst preparation

One gram of Vulcan carbon XC-72 was immersed into an aqueous solution of Ni(NO₂)₂ (0.7784 g of Ni(NO₃) in 40 ml DI water) under stirring. The mixture solution was evaporated to dryness slowly using a water bath (70 °C) under stirring after the ultrasonic treatment for 2 h. The impregnated Ni/C was dried at 110 °C overnight and calcined in N₂ at 350 °C for 4 h and in H₂ at 350 °C for 2 h. The Ni loading on the surface of XC-72 carbon was controlled to be 20 wt%.

The Pt-Ni/C catalysts were synthesized by the partial galvanic displacement of Ni/C. Pt-Ni/C-1: An ethanol solution with Ni/C dispersion (0.3378 g Ni/C in 300 ml methanol) was added to a 500-ml three-necked, round-bottomed flask. Following 30 min of flowing Ar under an ultrasonic treatment, the flask was heated in an oil bath at 100 °C for 5 min. Next, a chloroplatinic acid solution (18.6 mg of chloroplatinic acid in 50 ml of water) was injected dropwise into the reaction mixture over a 15-min period. The reaction mixture was continually stirred and heat-

ed at 100 °C for 3 h, and was centrifuged then washed using ethanol and DI water 5 times. Finally, the obtained catalyst was dried at 60 °C in a vacuum oven for 6 h.

Pt-Ni/C-2, Pt-Ni/C-3, Pt-Ni/C-4, Pt-Ni/C-5: The synthetic approach was similar to that used to produce Pt-Ni/C-1, except for the mass of chloroplatinic acid. The masses of chloroplatinic were 28.7, 39.2, 61.4, 85.7 mg, respectively, and Pt theoretical loading mass were 3%, 4%, 6%, and 8%, respectively.

2.2. Characterization

XRD patterns were taken on a Bruker D8 Discover (40 kV and 30 mA) and collected in the 2θ range of 10° to 80° over 20 min. Inductively coupled plasma mass spectrometry (ICP-MS) experiments were conducted with a Thermo Scientific iCAP Q spectrometer. Catalyst compositions were determined by examining five concentrations calibrated to a blank and three standards. Each measurement was run three times with a standard deviation of less than 2% and an elemental dwell time of 0.15 s. Compositions were calculated on the basis of the Pt to Ni ratio, assuming that these metals accounted for the total catalyst mass. XPS was performed on an XSAM800 instrument using Al K α radiation at a power of 150 W (30 mA, 8 kV). TEM images were taken with a PhillipsCM300 microscope at 300 kV. The structure, particle distribution and surface composition of catalyst was examined by the scanning electron microscope (SEM, SPA400, 5 kV) equipped with energy dispersion spectrometer (EDS, 20 kV).

2.3. Electrochemical measurements

The electrocatalytic performance of our solid Pt-Ni/C catalysts was compared to a commercial Pt catalyst (20 wt% Pt/C sample, purchased from Johnson Matthey). Rotating disk electrode (RDE) experiments were performed in a three-electrode glass cell equipped with a glassy carbon working electrode ($A = 0.0314 \text{ cm}^2$), a Pt wire counter electrode, and a mercury/mercurous oxide reference electrode. The working electrode was coated with Pt/C, Pt-Ni/C-1, Pt-Ni/C-2, Pt-Ni/C-3, Pt-Ni/C-4, and Pt-Ni/C-5, with depositions corresponding to a Pt loading of 10 $\mu\text{g-Pt}/\text{cm}^2_{\text{disk}}$. Cyclic voltammetry (CV) tests were conducted at room temperature in an N₂-saturated KOH

solution (0.1 mol/L). These electrocatalysts were analyzed with steady state voltammograms taken between -0.955 and 0.1 V (vs. a mercury/mercurous oxide reference electrode, {MMO}) at 50 mV/s. The Tafel curves were obtained at room temperature in an H_2 -saturated KOH solution (0.1 mol/L). These electrocatalysts were analyzed with steady state voltammograms taken between -1.1 and -0.7 V (vs. a mercury/mercurous oxide reference electrode {MMO}) at 10 mV/s and 1600 r/min.

3. Results and discussion

3.1. Element analysis results

The amounts of Pt and Ni in the catalyst were determined by ICP-MS. The results (Table 1) indicate that the true values of Pt and Ni are both less than the theoretical values. The main reason is that inevitably the surface of the Ni/C was partly oxidized before the reaction. The NiO on the Ni/C was dissolved in the solution when the galvanic displacement reaction proceeded as $NiO + 2H^+ \rightarrow Ni^{2+} + H_2O$. Because of the inevitable oxidation, the metals mass amounts were slightly below 20%.

The XRD patterns of Pt/C, Ni/C, Pt-Ni/C-1, Pt-Ni/C-2, Pt-Ni/C-3, Pt-Ni/C-4 and Pt-Ni/C-5 were illustrated in Fig. 2. The broad diffraction peak at approximately 24° is due to the hexagonal structure of Vulcan carbon XC-72. According to JCPDS. 04-0802, the three main diffraction peaks of Pt/C(JM) are assigned to Pt(111) (39.7°) Pt(200) (46.3°) and Pt(220) (67.8°). Analogously, the Ni/C also shows three main diffraction peaks at 44.3° , 51.7° and 76.2° , which are assigned to the Ni (111), Ni (200) and Ni (220) planes. In the case of Pt-Ni/C catalysts, as Pt content increases and Ni content decreases, the diffraction peaks of Pt (111) become more evident, while these of Ni gradually become smaller. The XRD pattern of Pt-Ni/C-1 shows three apparent diffraction peaks of Ni and almost no diffraction peaks of Pt. In contrast, Pt-Ni/C-5 has both noticeable diffraction peaks of Pt and Ni. It is worth noting that the diffraction peaks of both Pt and Ni are not shifted in the XRD patterns of Pt-Ni/C.

The phenomenon is different from many papers regarding the PtNi alloy catalyst. Hu et al. [27] and Luo et al. [28] showed that due to Ni, the diffraction peaks of Pt had slightly higher 2θ values in PtNi catalysts prepared by similar a synthetic method. Zhang et al. [29] and Hu et al. [30] also showed that the diffraction peaks of Pt had slightly higher 2θ values in PtNi catalysts prepared by entirely different synthetic methods. However, the Pt-Ni/C catalysts contain the characteristic peaks of the Pt (fcc) structure, and the lattice of Pt shows no change. Unlike the

Fig. 2. The XRD patterns of Pt/C (1), Ni/C (2), Pt-Ni/C-1 (3), Pt-Ni/C-2 (4), Pt-Ni/C-3 (5), Pt-Ni/C-4 (6), and Pt-Ni/C-5 (7).

other PtNi alloy, the catalysts of Pt-Ni/C retain the characteristic of Ni nano-particles and Pt nano-particles completely.

3.2. Electrochemical performances

Electrochemical measurements were utilized to determine the electrochemically active surface area (ECSA) and HOR activities. The ECSA values of the Pt-based catalysts were determined from CV curves in a KOH electrolyte (0.1 mol/L) by the charge associated with hydrogen desorption, assuming a Coulombic charge of $210 \mu C/cm^2$ (Fig. 3).

In the potential region from 0 to 0.4 V, we observe the typical hydrogen adsorption and desorption peaks [31]. In the series of Pt-Ni/C catalysts, there are no evident hydrogen desorption peaks when the amount of Pt is small, only a relatively large double layer. As the Pt amount in the Pt-Ni/C catalyst increases, the hydrogen desorption peaks become larger. When the content of Pt is 3.1% , the ECSA is $66.90 m^2/g$, which is 1.24 times larger than that of Pt/C ($54.12 m^2/g$). However, as the content of Pt continues to rise, the hydrogen desorption peaks and the ECSAs decrease.

The catalysts were evaluated for HOR during anodic linear polarization scans at 900 r/min and 10 mV/s in a hydrogen saturated 0.1 mol/L KOH electrolyte. Tafel plots were obtained by correcting the HOR branch of the activity data by subtracting the diffusion overpotential and determining the kinetically limited HOR currents. The corrected kinetic currents collected at 900 r/min were fit with a linear function to determine the Tafel slope from the high current density region prior to the onset of the mass-transport limit. Additionally, both the HOR and HER branches of the corrected kinetic currents for the catalyst were fit using the Butler-Volmer equation [32] with $a = 0.5$. The Tafel slope (Fig. 4) indicate that the change trend of the exchange current density is similar to the ECSA. The Pt-Ni/C-3 presents the biggest exchange current density, which is 1.6 times as high as that of Pt/C(JM).

Table 1

The ICP results for the catalysts.

Catalyst	Pt mass ^a (%)	Ni mass ^b (%)	Pt mass ^b (%)	Total metal mass ^b (%)
Pt-Ni/C-1	2	16.62	1.70	18.32
Pt-Ni/C-2	3	15.37	2.43	17.80
Pt-Ni/C-3	4	13.90	3.10	17.00
Pt-Ni/C-4	6	12.90	5.59	18.49
Pt-Ni/C-5	8	10.75	7.28	18.01

^a Theoretical value; ^b Experimental value.

Fig. 3. CV curves of Pt/C vs Pt-Ni/C-1 (a), Pt-Ni/C-2 (b), Pt-Ni/C-3 (c), Pt-Ni/C-4 (d), Pt-Ni/C-5 (e) at 50 mV/s in an argon saturated 0.1 mol/L KOH electrolyte. (f) The ECSA of different Pt-Ni/C catalysts and Pt/C.

3.3. TEM images and structural properties

To further confirm the relationship of the structure property and the electrochemical performance, the Ni/C and Pt-Ni/C-3 samples were analyzed by TEM, XPS and EDS tests.

The morphology and size of Pt-Ni/C-3 were characterized

by SEM, TEM and HRTEM techniques. From Fig. 5(a), Pt nanoparticles were well-dispersed on the carbon. The nanoparticles were considered to be spherical while the particle diameter was among 4 to 9 nm (Fig. 5(b)). The TEM image from Fig. 5(a) reveals the distinct morphology that the replacement of Ni atoms by Pt atoms is partial and marginal. The HRTEM image of the nanocatalyst shows two dominant formations of the

Fig. 4. HOR/HER kinetic activities of Pt/C vs Pt-Ni/C-1 (a), Pt-Ni/C-2 (b), Pt-Ni/C-3 (c), Pt-Ni/C-4 (d), Pt-Ni/C-5 (e) at 900 r/min and 1 mV/s in a hydrogen saturated 0.1 mol/L KOH electrolyte. (f) HOR mass exchange current densities of Pt-Ni/C catalysts and Pt/C. Exchange current values were derived from Butler-Volmer fitting of HOR/HER data in the low overpotential region (−0.05 to +0.05 V vs RHE).

Fig. 5. (a) TEM image of Pt-Ni/C-3; (b) nanoparticle diameter distribution of Pt-Ni/C-3; (c) HRTEM image of Pt-Ni/C-3.

face-centered cubic (fcc) (1 1 1) lattice image with the lattice fringe of 0.223 and 0.19 nm (Fig. 5(c)). In contrast with the d -spacing values calculated from XRD (Table 2), the d -spacing values of Pt in the Pt-Ni/C-3 sample from the HRTEM image is in accord with XRD result but slightly smaller than that of the (1 1 1) plane of Pt/C (0.230 nm). The d -spacing values of Ni in the Pt-Ni/C-3 sample from the HRTEM image agree with the values of Ni in the Pt-Ni/C-3 and Ni/C samples calculated from XRD. These results suggest the replacement of Ni atoms by Pt atoms again, which further promotes the formation of Pt-Ni/C.

The survey scan, along with the Ni 2*p* and the Pt 4*f* XPS spectra of Pt-Ni/C-3, is given in Fig. 6. Based on curve fitting with a mixed Gaussian-Lorentzian line shape as in Fig. 6(a), Ni appears to exist in various states. It can be deduced that the surface Ni species in Pt-Ni/C-3 is mainly composed of NiO (854.8, 861.8, and 873.2 eV), Ni(OH)₂ (856.5 and 880.3 eV) [33,34]. There is no Ni(0) on the surface in Pt-Ni/C-3, but only the Ni oxidized species do not appear in the XRD curves (Fig. 2), since the amount of oxidized species is too small comparatively

to be observed by XRD. It is shown in Fig. 6(b) that the 4*f* core-level spectrum consists of two peaks for metallic Pt at 71.6 (Pt 4*f*_{7/2}) and 74.8 eV (Pt 4*f*_{5/2}) [35]. In agreement with the XPS analysis, it can be concluded that the Pt particles are exposed on the surface of Ni particles and carbon dedetected by EDS but the Ni oxidized species on the surface of carbon (Table 3).

To analysis the change of the catalysts after and before the electrochemical test, we also performed the XPS measurement for the catalyst after the 5000 times CV test. In the Fig. 6(a) and (c), we almost can't see any difference in the XPS spectrum of Ni. But there is a weak peak at 72.7 eV in the Fig. 6(d), but it does not appear in the Fig. 6(b). This is the oxidation peak of Pt, but the area is very small. It indicated that the very little Pt on the surface of catalyst had been oxidized. However the ratio of Pt oxidized species is so small that is hardly any influence.

3.4. Comprehensive analysis and discussion

The similar trend between the ECSAs and the exchange cur-

Fig. 6. The XPS spectra of Ni 2*p* (a), Pt 4*f* (b) in Pt-Ni/C-3 before the electrochemical test and Ni 2*p* (c), Pt 4*f* (d) in Pt-Ni/C-3 after the electrochemical test.

Table 2

D-spacing values and the lattice parameter of Pt/C, Ni/C and Pt-Ni/C-3.

Sample	2 θ for Pt (111) (°)	d-spacing ^a (nm)	Lattice parameter ^b (nm)	2 θ for Ni (111) (°)	d-spacing ^a (nm)	Lattice parameter ^b (nm)
Pt/C	39.134	0.230	0.39837	—	—	—
Ni/C	—	—	—	44.351	0.20408	0.3533
Pt-Ni/C-3	40.341	0.22339	0.4051	44.380	0.20338	0.3523

^a Calculated using Bragg's equation: $2d \sin \theta = n \lambda$.^b Calculated using the equation $d_{hkl} = a / \sqrt{h^2 + k^2 + l^2}$ for the face centered-cubic crystal system ($\lambda = 1.5406$).**Table 3**

EDS analysis of the surface in Pt-Ni/C-3.

Element	wt%	Atom%
C K	25.29	70.46
Ni K	41.96	23.92
Pt M	32.75	5.62

rent density suggests that the structure of Pt-Ni/C and the contents of Pt and Ni are the primary cause.

Due to the galvanic displacement reaction, the Pt particles are well-decorated on the Ni particles. When the amount of Pt is small and Ni is the major ingredient, the Ni acts as the main attachment site for H₂. The j_0 of HOR reaction on the face of Ni is approximately 10^{-3} – 10^{-6} A/cm² in the base, which is 1–2 orders of magnitude less than the diffusion limiting current of the H₂ solubility. Thus, the catalytic effect on the HOR is poor. The Ni will generate Ni(OH)₂ because of its frangibility toward oxidation, and the potential of the reaction is only more positive by 0.11 V than the equilibrium potential of H₂. Therefore, the Ni will disturb the H₂ oxidation reaction, since the HOR occurs at and near the equilibrium potential. The Pt-Ni/C-1 catalyst with 1.7 wt% Pt has a low catalytic activity. However, with the increase of Pt content, up to the point where the Ni particles are almost wrapped by Pt, the oxidation of H₂ reaches a maximum. Moreover, when the content of Pt is too larger, the cover layer of Pt will be thick, and the effective Pt will decrease, diminishing the catalytic effect.

4. Conclusions

Five Pt-Ni bimetallic catalysts with a lower content of Pt for HOR were successfully synthesized by a new method of the impregnation-reduction at 1st step and galvanic replacement approach at 2nd step. The obtained nanocatalysts have a homogeneous decorated topology, and are highly dispersed. The successful introduction Pt on a Ni-based catalyst with high performance reduces the cost of the catalyst. The series of Pt-Ni/C catalysts and commercial Pt/C sample have been compared for HOR in base solution. Pt-Ni/C samples showed potentially superior to the commercial Pt/C sample in terms of activity area and mass exchange current densities by 1.24 and 1.6 times, respectively. The higher electrocatalytic activities of Pt-Ni/C catalysts are most likely due to the unique decorated structure together with the synergistic role of Pt and Ni in the catalyst. Therefore, the low Pt content electrocatalyst Pt-Ni/C

has a lower cost and the higher catalytic activity toward the hydrogen oxidation reaction, as a new improved platinum catalyst, which has great potential for application in CMFCs and AFCs.

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Graphical Abstract

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The Pt decorated Ni/C nanocatalysts prepared by the partial galvanic displacement exhibited a better catalytic activity for H_2 oxidation reaction than that of commercial Pt/C catalyst.

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在氢气氧化反应中具有高催化活性的Pt修饰的Ni/C纳米催化剂

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摘要: 随着能源需求的进一步增多和化石能源的大幅度减少, 新型环境友好型能源成为近十年许多科研工作者的着力点。其中, 燃料电池作为一种高效率、高能量密度、环境友好型能源引起了人们的关注。氢氧燃料电池研究最早、应用最早, 具有得天独厚的优势。此外, 由于近些年 CO_2 的大量排放, 造成了严重的温室效应, 其处理也是一个严峻的课题。谢和平课题

组提出的CO₂矿化发电,不仅可以处理CO₂,也可以作为新型能源应用,前景广阔。而不论是氢氧燃料电池还是CO₂矿化电池,其阳极反应均为氢气氧化反应(HOR)。Pt作为目前仍无法取代的HOR反应催化剂,不仅全球储量有限且价格昂贵,所以,寻找一种价格低廉催化性能好的催化剂成为这些新能源进一步应用的重要课题之一。对此人们进行了大量探索,主要包括尝试不同的载体、改变金属颗粒尺寸形貌等。其中,伽伐尼置换法对于制备纳米核壳结构催化剂以及降低金属颗粒尺寸、增加比表面积均有很大帮助。基于此,本文采用浸渍法和伽伐尼置换法制备了用Pt修饰Ni/C的纳米催化剂,使得纳米级活性金属均匀分散在载体上,加之双金属效应,相对于纯Pt/C催化剂,催化能力提高。

浸渍法制得Ni/C前驱体,再将其置于纯乙醇中,用H₂PtCl₆作为Pt源置换部分Ni,得到Pt修饰的Ni/C催化剂。XRD射线衍射测试结果表明,一般的PtNi合金由于晶格相互影响,只会出现Pt的偏移衍射峰,而该催化剂均出现明显的PtNi两种元素的衍射峰,PtNi晶格互相没有影响。循环伏安法测试结果表明,在Pt-Ni/C系列催化剂中,Pt和Ni含量不同,其电化学活性面积(ECSA)各不相同。在金属总含量一致的前提下,随着Pt含量的增加,催化剂ECSA先增加后减小,最大值为66.90 m²/g,是市售Pt/C (54.12 m²/g)的1.24倍。Tafel测试HOR/HER反应交换电流密度的结果与ECSA结果一致,而Pt-Ni/C催化剂的交换电流密度最高可达485.45 A/g,是市售Pt/C (301.91 A/g)的1.6倍。对性能较好的Pt-Ni/C催化剂进行了表征,X射线光电子能谱结果发现,该催化剂载体上只有少部分Ni的氧化物裸露在表面,大部分为Pt。而透射电镜结果表明,该催化剂纳米级活性金属颗粒尺寸一致,且均匀地分散在载体表面。

综合催化剂表征和电化学性能测试结果可知,使用伽伐尼置换法得到的Pt修饰的Ni/C催化剂分散均匀、颗粒尺寸小,且由于Pt作为主要催化活性金属分散于催化剂表面,而Ni作为辅助金属并不直接参与HOR反应,使得该催化剂具有较高的电化学活性。在Pt含量较少时,由于有很多Ni在催化剂表面,且催化层厚度较大,故催化活性一般。随着Pt含量的增加和Ni含量的减少,当催化剂表面只有很少Ni及相关化合物时,由于Pt比表面积大,故活性最高。当Pt含量继续增加时,Pt在Ni表面厚度增加,很多Pt被包裹,故催化活性再次降低。

关键词: 铂催化剂; 伽伐尼置换法; 碳负载的Ni催化剂; 氢气氧化反应; 电化学活性面积

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