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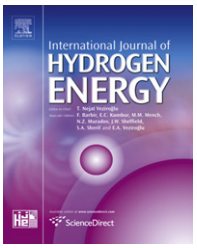

Carbon supported Palladium–Iron nanoparticles with uniform alloy structure as methanol-tolerant electrocatalyst for oxygen reduction reaction

Yu Pan, Fan Zhang, Ke Wu, Zhaoyang Lu, Yu Chen, Yiming Zhou, Yawen Tang*, Tianhong Lu*

Jiangsu Key Laboratory of New Power Batteries, Laboratory of Electrochemistry, School of Chemistry and Materials Science, Nanjing Normal University, 1# Wenyuan Road, Nanjing 210046, PR China

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ABSTRACT

Carbon supported Palladium–Iron bimetallic nanoparticles (Pd–Fe/C) electrocatalyst is synthesized by the direct thermal decomposition method of nontoxic metallic acetate salt. During the preparation of the Pd–Fe/C electrocatalyst, the tedious wash post-treatment of electrocatalyst is effectively avoided due to non-existence of inorganic anion. The physico-chemical properties of the Pd–Fe/C electrocatalyst are characterized by X-ray diffraction analysis (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). These structural analyses reveal that the Pd–Fe/C electrocatalyst possesses the high alloying degree and the small particle size. Electrochemical data indicate that the eletrocatalytic activity of the Pd–Fe/C electrocatalyst for oxygen reduction reaction (ORR) is much higher than that of Pd/C electrocatalyst, which originates from the synergistic effect between Pd atom and Fe atom.

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1. Introduction

Direct methanol fuel cells (DMFC) has been recognized as a feasible power source to replace internal combustion engine for transportation application due to its low emissions of pollutants, high power density, and high energy conversion efficiency [1–11]. Currently, DMFCs have been focused on vehicles, portable devices, and micro fuel cell applications. However, the commercial application of DMFC is still impacted by several problems, including poor kinetics of both the anodic and cathodic reactions and methanol crossover [12–15]. Pt and Pt-based alloys are the most widely used electrocatalysts for the oxygen reduction reaction (ORR) in DMFC. Unfortunately, Pt and Pt-based alloys electrocatalysts have the high electrocatalytic activities to both ORR and methanol oxidation reaction (MOR). Thus, the methanol crossover not only results in the formation of mixed potentials on the cathode electrocatalysts but also lowers the efficiency of the methanol utilization [9]. Consequently, a large number of investigations have been made to develop novel DMFC non-platinum cathode electrocatalysts with the good ORR performance and methanol-tolerant capacity [5].

Up to now, several transition metal compounds, transition metal sulfide, a nd Ru-based alloy and Pd have been proposed as selective electrocatalysts for the ORR in acid medium containing methanol [16–18]. Although these electrocatalysts have high methanol tolerance, their activities

* *Corresponding authors*. Tel.: +86 25 85891651; fax: +86 25 83243286.
E-mail addresses: ndchenyu@yahoo.cn (Y. Chen), tangyawen@njnu.edu.cn (Y. Tang).
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for ORR are significantly lower than that of Pt electrocatalyst. Recent investigations indicate that in-expensive alloying Pd (the price of Pd is 1/4–1/5 as that of Pt) with other metals having smaller atomic size such as Fe, Co and Ni (Pd–M) offer the high catalytic activity for ORR and the high tolerance to methanol oxidation owing to the changes of Pd–Pd bond length, modification of the electron configuration, and/or alteration of the surface species and compositions [13,19–27]. However, Pd–M nanoparticles (NPs) prepared with conventional liquid chemical reduction method usually possesses a structure of the interior Pd-rich and the exterior M-rich (Scheme 1A) because Pd^{II} precursor is easier reduced than M-ion precursor, which is attributed to the fact that the redox potential of Pd^{II}/Pd^{0} couple is much higher than that of $M(ion)/M^{0}$ couple [28]. Obviously, the resultant non-alloyed structure decreases the electrocatalytic activity of Pd–M electrocatalysts for ORR due to the reduction of Pd active sites. In order to obtain Pd–M NPs electrocatalysts with a uniform alloy structure (Scheme 1B), the thermal treatment method is generally used to increase the alloying extent of Pd–M NPs [13,25,29]. Unfortunately, the high temperature heat treatment (>500 °C) unavoidably leads to the increase of particle size, and consequently decreases electrocatalytic activity of Pd–M electrocatalysts for ORR.

To overcome the effect of reduction potential of precursor on the structure of Pd–M NPs and the effect of high temperature heat treatment on the particle size of Pd–M NPs, a low temperature thermal decomposition method of organometallic precursor (≤300 °C) has been used to synthesize Pd–M NPs with the high alloying degree [20]. In the thermal decomposition method, carbonyl–metal cluster complex is generally used as reaction precursor [20]. However, the difficulty in synthesis of carbonyl–metal cluster complex and the high toxicity of carbonyl–metal cluster complex impede strictly its wide application. In this work, nontoxic palladium acetate and iron acetate precursors are used to prepare carbon supported Pd–Fe NPs (Pd–Fe/C) electrocatalyst with high alloying degree by direct thermal decomposition method.

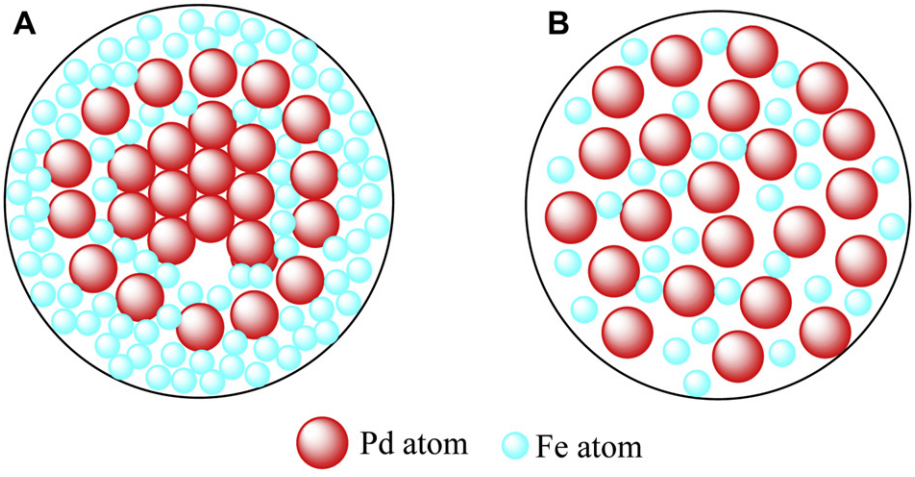
2. Experimental section

2.1. Preparation of electrocatalysts

All chemical reagents were analytical grade. Acetic acid (CH_3COOH), Palladium acetate ($Pd(CH_3COO)_2$) and ferrous acetate ($Fe(CH_3COO)_2$) were obtained from Shanghai Chemical Regent Ltd. Vulcan XC-72 carbon was obtained from Cabot Company. Carbon supported Pd–Fe nanoparticles (Pd–Fe/C) electrocatalyst with 20 wt.% Pd and 10 wt.% Fe were prepared as follows: 52 mg Vulcan XC-72 carbon, 31.6 mg $Pd(CH_3COO)_2$, 24.5 mg $Fe(CH_3COO)_2$, and 26 mL pure acetic acid were mixed ultrasonically. Then, acetic acid in obtained suspension was removed by heat treatment for 3 h at 100 °C. Subsequently, the resultant blank powder was heat-treated under the mixed gas of nitrogen and hydrogen with a volume ratio 9:1 for 1 h at 300 °C. After sample was cooled to room temperature, the Pd–Fe/C electrocatalyst was obtained (note: the obtained Pd–Fe/C electrocatalyst need not any post-treatment about wash and drying.). For comparison, the 20 wt.% Pd/C electrocatalyst with 3 nm particle size was also prepared according to our previous reported method [30].

2.2. Characterization of electrocatalysts

The decomposition temperature of $Pd(CH_3COO)_2$ and $Fe(CH_3COO)_2$ were determined using Diamond thermogravimetric-differential (TG–DTA) thermal analysis instrument under an N_2 atmosphere. X-ray diffraction (XRD) measurements were performed with Model D/max–rC diffractometer using Cu Kα radiation ($\lambda = 0.15406$ nm) operating at 45 kV and 100 mA. High resolution transmission electron microscopy (HRTEM) was carried out using a JEOL-4000Ex microscope operating at 200 kV with the nominal resolution. The composition of the electrocatalyst was determined by energy dispersive spectrometer (EDS) with vantage digital acquisition engine. X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Thermo VG Scientific ESCALAB 250 spectrometer with



Scheme 1 – Pd–M NPs with (A) a structure of the interior Pd-rich and the exterior M-rich and (B) a structure of a uniform alloyed atom, respectively.

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