Impact of different synthesis methods on the electrocatalytic activity and stability of Pd-Fe/C nanoparticles for oxygen reduction reaction in fuel Cells

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Abstract: The rational synthesis of active, durable and low cost catalysts has of particular interest for fuel cell applications. The structural properties of fuel cell catalysts can be modulated by different synthesis methods, which significantly influence the oxygen reduction reaction at the cathode. In this study, we describe the effect of microwave and impregnation reduction methods on the electrocatalytic property and stability of carbon supported palladium-iron nanoparticles (Pd_3Fe/C) for oxygen reduction reaction in proton exchange membrane fuel cells. The physical and electrochemical properties of the nanoparticles have been characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), cyclic voltammetry (CV) and Rotating Disc Electrode (RDE) techniques. The XRD results revealed that the impregnation reduction method provides better degree of alloying between Pd and Fe relative to microwave assisted polyol reduction method. The nanoparticles prepared by impregnation reduction method exhibit superior ORR mass activity and improved stability compared to those prepared by microwave polyol method. This is attributed to higher degree of alloying, compressive lattice strain and well defined crystal structure resulting from appropriate thermal treatments during preparation.

1. Introduction

The oxygen reduction reaction in fuel cells is a structure and surface sensitive reaction that depends on the properties of catalysts including particle size, morphology, crystal structure, degree of alloying and lattice parameters [1,2]. These parameters are often optimized during synthesis steps and strongly dependent on the preparation methods employed [3]. Therefore, the choice of an appropriate preparation method is a stringent requirement to investigate fuel cell catalysts with enhanced catalytic activity and improved stability. Pd-Fe/C alloy catalysts has been studied for ORR in both proton exchange membrane fuel cells and direct methanol fuel cells [4,5] and their activity towards ORR is significantly influenced by different synthesis methods. For example, the Pd_3Fe/C nanoparticles synthesized by thermal treatments of a mixture of Pd/C (E-TEK) and $FeCl_3$ solution exhibits higher performance towards ORR than those prepared by decomposing a mixture of $PdCl_2$ and $FeCl_3$ salts on carbon particles [4]. However, the origin of this discrepancy in activity of the same alloy catalysts with respect to the synthesis methods is not well documented. Therefore, establishing the origin of the

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impact of different synthesis methods on the electrocatalytic activity and stability of Pd_3Fe/C catalysts has of great significance for investigating similar catalysts with better ORR activity.

In this report, the impact of microwave polyol and impregnation reduction methods on the electrocatalytic activity and stability of Pd_3Fe/C nanoparticles has been explained. The results obtained indicate enhanced ORR activity and improved stability of Pd_3Fe/C nanoparticles prepared by impregnation reduction method that could be associated with the higher degree of alloying and smaller interatomic distance.

2. Experimental

Carbon supported Pd-Fe alloy nanoparticles with a Pd:Fe molar ratio of 3:1 and total metal loading of 20 wt% were prepared by impregnation and microwave polyol reduction methods [6,7]. Appropriate amounts of $PdCl_2$ and $FeCl_3 \cdot 6H_2O$ precursors on Vulcan XC-72R carbon were mixed under ultrasonication with subsequent thermal treatment in a microwave and tube furnace to obtain the desired catalysts. Pd/C (20 wt% Pd loading) catalyst was also prepared using microwave polyol method under similar conditions for reference. The electrochemical measurements were carried out in 0.1 M $HClO_4$ solution by depositing a thin film of the catalyst ink on a glassy carbon working electrode (5 mm diameter).

3. Results and Discussion

Fig.1a and b shows the XRD patterns and enlarged (220) peaks of the catalysts prepared by microwave polyol method (denoted as Pd/C-MWP and Pd_3Fe/C-MWP) and impregnation reduction method (denoted as Pd_3Fe/C-400IMP and Pd_3Fe/C-600IMP, which are annealed at 400 and 600 ^oC, respectively). All the patterns show single phase face centered cubic (fcc) crystal structure and the diffraction peaks of the alloy catalysts shift to higher angles relative to the reference pure Pd/C, indicating lattice contraction due to the incorporation of smaller Fe atoms into Pd lattice [8].

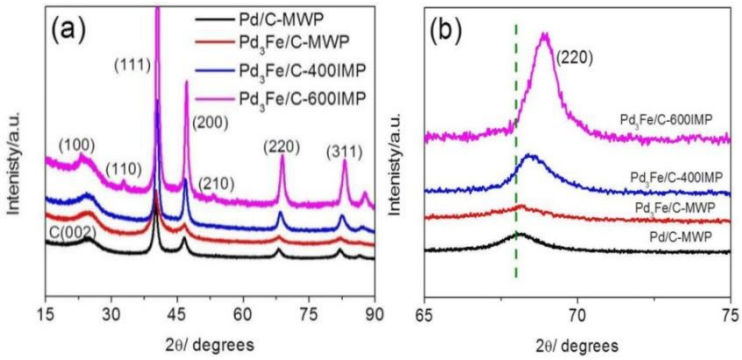

Figure 1. XRD patterns (a) and enlarged (220) peaks (b) of the as prepared catalysts using impregnation and microwave polyol reduction methods.

The lattice dimensions of the as prepared catalysts are listed in Table 1 that demonstrate the smaller lattice parameters of the samples prepared by impregnation reduction method than those prepared by microwave polyol reduction method. This might be attributed to the increase degree of alloying and lattice contraction caused by the incorporation of more Fe atoms into the Pd fcc structure, which is also revealed by the shift in the diffraction peaks of Pd_3Fe/C-400IMP and Pd_3Fe/C-600IMP catalysts to higher angles compared with that of Pd_3Fe/C-MWP catalyst [1,9]. The additional

diffraction peaks observed for the Pd_3Fe/C-600IMP catalyst at about 23° and 33° are assigned to (100) and (110) superlattice peaks, respectively, suggesting long range ordering of Pd and Fe atoms in the alloy due to the further thermal treatment [6,10]. The average crystallite size of the Pd-Fe alloys is smaller than that of pure Pd/C catalyst (Table 1) due to the lattice contraction and less aggregation of Pd on alloying with Fe [8].

Table 1: Structural and electrochemical analyses results of the as prepared catalysts

Sample	crystallite size/ nm	Lattice parameter/ nm	$E_{1/2}$ (mV)	Mass Activity (mA mg^{-1} Pd) at 0.80 V
Pd/C-MWP	8.4	0.38925	722	15.2
Pd_3Fe/C-MWP	6.2	0.38792	737	30.5
Pd_3Fe/C-400IMP	6.9	0.38764	745	35.5
Pd_3Fe/C-600IMP	7.5	0.38527	767	104.2

The TEM images and particle size distribution histograms of the as prepared catalysts are presented in Fig.2a-d. It is clearly observed that the nanoparticles are uniformly distributed on the carbon support in all the catalysts (insets of Fig.2a-d). The average particle size of Pd/C, Pd_3Fe/C-MWP, Pd_3Fe/C-400IMP and Pd_3Fe/C-600IMP catalysts, obtained from more than 100 nanoparticles in their corresponding TEM images, is 7.2 nm ± 1.8 nm, 5.2 nm ± 1.4 nm, 6.2 nm ± 1.6 nm and 7.1 nm ± 1.4 nm, respectively, which agrees well with the XRD results. The Pd-Fe alloy nanoparticles prepared by impregnation reduction method exhibit a slight increase in the average particle size relative to that prepared by microwave polyol reduction method due to the higher thermal treatment applied during synthesis. However, the smaller standard deviation for Pd_3Fe/C-600IMP suggests better dispersion of the nanoparticles on the carbon support.

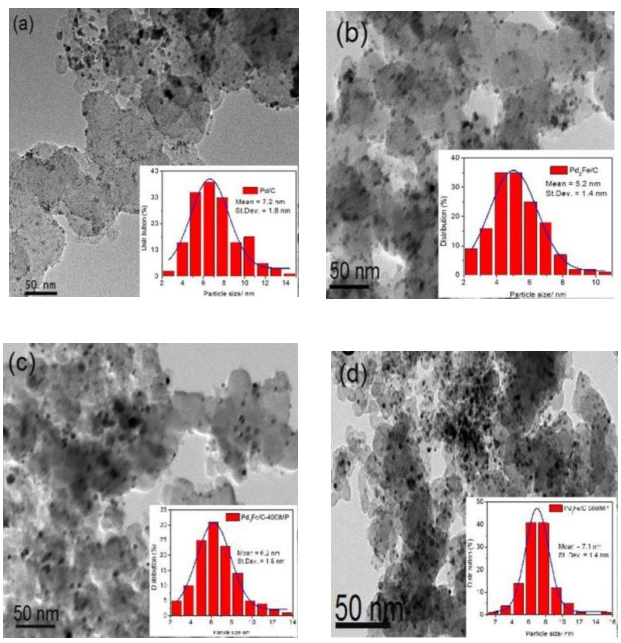

Figure 2. TEM images of (a) Pd/C-MWP, (b) Pd_3Fe/C-MWP, (c) Pd_3Fe/C-400IMP and (d) Pd_3Fe/C-600IMP catalysts. Insets: The corresponding particle size distribution histograms.

Fig.3a displays the ORR polarization curves for Pd/C-MWP, Pd_3Fe/C-MWP, Pd_3Fe/C-400IMP and Pd_3Fe/C-600IMP catalysts in O_2 saturated 0.1 M $HClO_4$ solution obtained from the RDE

measurement at scan rate of 5 mV s^{-1} and speed of 1600 rpm. The Pd_3Fe/C-400IMP and Pd_3Fe/C-600IMP catalysts exhibit a higher positive shift in half wave potential ($E_{1/2}$) than that of Pd_3Fe/C-MWP catalyst (Table 1), indicating enhanced ORR activity on their surfaces. The mass activity is obtained by normalizing the kinetic current density to Pd loading and Pd_3Fe/C-400IMP and Pd_3Fe/C-600IMP catalysts show remarkably higher activity than that of Pd_3Fe/C-MWP catalyst (Fig.3b). Furthermore, the mass activity of Pd_3Fe/C-600IMP catalyst is 3.4 times higher than that of Pd_3Fe/C-MWP catalyst at 0.8 V. This activity enhancement would probably be due to the well-defined crystal structure that leads to optimal compressive lattice strain and higher degree of alloying [10].

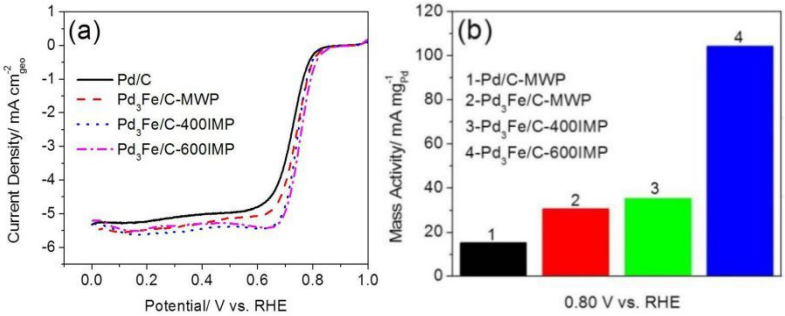

Figure 3. (a) ORR polarization curves of the as prepared catalysts in O_2 saturated 0.1 M $HClO_4$ solution at a sweep rate of 5 mV s^{-1} and rotation rate of 1600 rpm and (b) Kinetic current densities of the as prepared catalysts normalized to loading of Pd at 0.80 V.

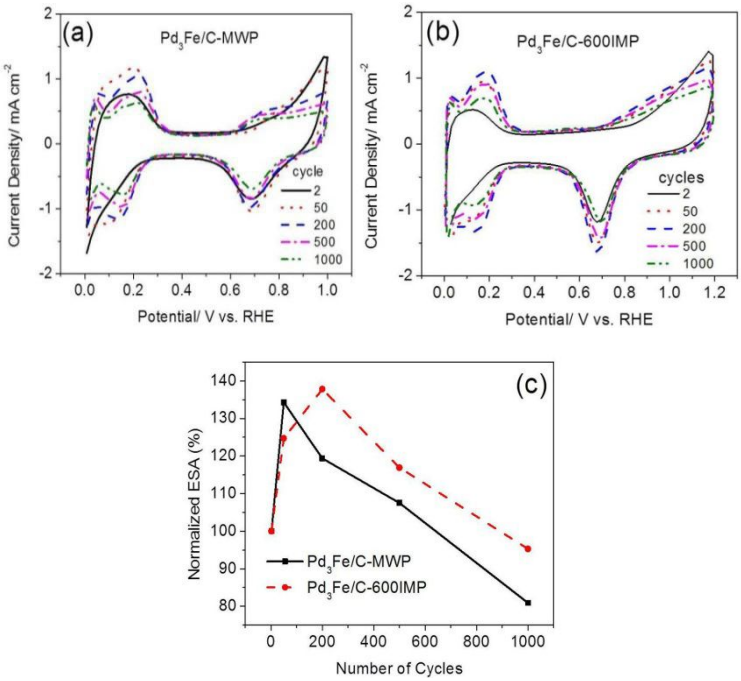

Figure 4. Cyclic voltammetry curves of (a) Pd_3Fe/C-MWP and (b) Pd_3Fe/C-600IMP in N_2 saturated 0.1 M $HClO_4$ solution at a scan rate of 50 mV s^{-1} for various numbers of potential cycles, and (c) normalized ESA as a function of cycle number for Pd_3Fe/C-MWP and Pd_3Fe/C-600IMP catalysts.

Fig.4a and b presents the cyclic voltammetry curves of Pd_3Fe/C-MWP and Pd_3Fe/C-600IMP catalysts collected in N_2 saturated 0.1 M $HClO_4$ solution after various potential cycles at scan rate of 50 mV s^{-1} and Fig.3c shows the corresponding loss in electrochemical surface area (ESA) with potential cycling. The ESA was calculated by integrating the charge corresponding to reduction of surface Pd oxide using the standard charge density of 420 μC cm^{-2} [1]. It can be clearly observed that the ESA of Pd_3Fe/C-600IMP catalyst decays at a lower rate than that of Pd_3Fe/C-MWP catalyst with increasing potential cycles. This illustrates that the Pd_3Fe/C-600IMP catalyst is more stable than that of Pd_3Fe/C-MWP catalyst, which could be attributed to the higher degree of alloy homogeneity and formation of well-defined crystal structure obtained after appropriate thermal treatment during preparation. It has been reported that the less durability of $Pd_{80}Ni_{20}$ for long term operation is due to the incomplete alloying of Pd and Ni during preparation [11]. Therefore, the Pd-Fe/C alloy nanoparticles with higher degree of alloying between Pd and Fe exhibit better durability.

4. Conclusion

Carbon supported Pd-Fe alloy nanoparticles prepared by impregnation reduction method showed higher degree of alloying and smaller lattice parameters than those prepared by microwave polyol reduction method due to the incorporation of more Fe atoms into the Pd structure. The higher degree of alloying and the lattice contraction leads to further enhancement of the catalytic activity towards ORR in fuel cells. The study demonstrates that the impregnation reduction method provides Pd-Fe/C alloy nanoparticles with better alloy homogeneity and smaller interatomic distance suitable for enhancing the oxygen reduction reaction. In addition, stability of the Pd-Fe/C catalysts have been improved by increasing the degree of alloying and distribution of the alloying atoms in the crystal structure through further annealing at optimized temperature under reductive atmosphere.

Acknowledgments

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