

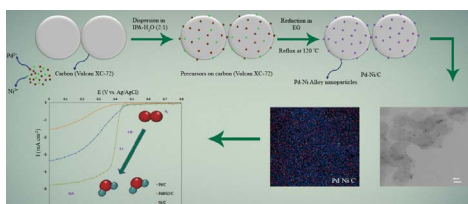


Research paper

Preparation of bimetallic alloyed palladium-nickel electro-catalysts supported on carbon with superior catalytic performance towards oxygen reduction reaction

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GRAPHICAL ABSTRACT



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ABSTRACT

Bimetallic alloyed palladium-nickel electro-catalysts supported on carbon (Vulcan XC-72) with various Pd to Ni atomic ratios have been successfully synthesized by an impregnation technique for the oxygen reduction reaction (ORR). The electro-catalysts are structurally characterized by XRD, FESEM-EDX, ICP-OES, TEM, and XPS. The EDX and mapping images confirm that Pd and Ni elements have been uniformly dispersed in the Pd₈Ni₂/C. TEM images illustrate that the metallic nanoparticles have been considerably distributed on the substrate with low agglomeration. Cyclic voltammetry (CV), rotating disk electrode (RDE), and chronoamperometry (CA) are applied to specify the electrochemical properties of the Pd-Ni alloys. It is demonstrated that the Pd₈Ni₂/C exhibits higher ORR activity and methanol tolerance in comparison with the Pd/C. Significantly, the Pd₈Ni₂/C shows higher durability than the Pd/C, this is attributed to a lower loss of electrochemical active surface area in the accelerated durability test (ADT). The Koutecky-Levich analysis suggests that the Pd₈Ni₂/C proceed the ORR through a 4e⁻ process. The enhanced activities are connected with the synergistic effects and alloyed structures of the Pd-Ni samples. Finally, excellent performances in higher power density and stability are achieved when Pd₈Ni₂/C is utilized as the novel cathode catalyst for passive direct methanol fuel cells (DMFCs).

1. Introduction

Within the last few years, fuel cell technology has been increasingly considered as an alternative energy source to the progressive concern with the fast declination of fossil fuels. Proton exchange membrane fuel cells (PEMFCs) are able to turn chemical energy into electrical energy, so many researchers have studied them for their

quick start-up, high energy efficiency, high power density, no loss of electrolyte, as well as low emissions [1,2]. Direct methanol fuel cells (DMFCs) have also been widely considered for promising clean energy devices. In comparison to PEMFCs, DMFCs are more beneficial because their methanol liquid fuel is safe to be stored and transported and can be directly used without any reforming process [2–6]. However, DMFCs faced two crucial hurdles, methanol crossover and

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Nomenclature			
A	Electrode surface area	IPA	Isopropyl alcohol
ADT	Accelerated durability test	k	Electron transfer rate constant
B ₂₀	Width of the peak at half-height	m	Loadings of catalyst
C	Concentration of the reactant	MEA	Membrane electrode assembly
d	Average crystallite size	n	Number of electrons
D _b	Diffusion coefficient	OCV	Open circuit voltage
D _b ^{1/2} c _b	Permeability	RDS	Rate determining step
ECSA	Electrochemical active surface area	S	Catalyst surface area
EG	Ethylene glycol	t	Time
F	Faraday constant	α	Transfer coefficient
GC	Glassy carbon	η	Overpotential
GDL	Gas diffusion layer	θ	Angle at the maximum of the peak
I	Current density	λ	Wavelength of the x-ray
I _K	Kinetic current density	ν	Kinematic viscosity
I _D	Diffusion-limited current density	ρ	Density
		ω	Electrode rotation rate

relatively low ORR rates [1,7,8].

Due to the alcohol permeation through the polymeric membrane (alcohol crossover phenomenon), the ORR rate is slow in DMFCs [9,10]. Despite numerous attempts to solve the problem, methanol unexpectedly reacts at the cathodic side, so methanol crossover decreases the potential and performance in DMFCs. Moreover, the strong O=O bond is the cause of much more sluggish ORR kinetics at the cathode. Using platinum in the cathode is an effective method to solve this problem, owing to its remarkable stability and activity. The high price and the limited accessibility of platinum are considered major constraints of DMFC commercialization [4,9,11–13]. Due to these issues, several steps have been taken to develop platinum-based catalysts in low platinum loading or non-platinum materials because of their lower cost, higher reaction rate, and stability [11,14–18].

Among different non-platinum cathode electro-catalysts, palladium nanoparticles have been extensively considered for their excellent ORR performance as well as high resistance to the crossover of methanol in DMFCs [19–21]. A Pd face-centered cubic (fcc) structure has the same significant properties of atomic size and electronic configuration as those of Pt. Besides, it is reasonably priced and enormously abundant in comparison to Pt [22–25]. However, the stability of Pd in oxidative, acidic, and high temperature conditions is lower than Pt, and the ORR activities of Pd are not as much as Pt [9,26,27]. It is recommended that alloying other transition elements, like Cu, Fe, Co, and Zr with Pd drastically affects the increase of activity [28–31]. The superior electrocatalytic activity of bimetallic alloys is commonly clarified by two factors [32–35]: the structural effect which is referred to a synergetic fashion in bimetallic electro-catalysts compared to each metal alone, and the electronic effect which is concerned with changing the electronic properties of the second element.

Because of its low cost, nontoxic properties, and great resources, nickel has been intensely scrutinized as an alternative to be alloyed with Pd [36]. Theoretically, density functional theory (DFT) calculations of bimetallic alloys indicate that Ni doping of Pd can be directed to weaken the Pd-O bond resulting from a considerable downshifting of the Pd d-band center [37]. Pd and Ni are devoted to one column of the periodic table, these elements create a solid solution which is similar to the composition of an fcc crystal structure [38]. Thus, it is essential to study how Pd-based alloy electro-catalysts affect the ORR. Recently, Xu et al. applied the one-step mild dealloying method to synthesize a homogenous Pd-Ni catalyst which showed superior ORR activity with higher specific and mass activities compared to Pt/C [39]. Li et al. achieved carbon-supported Pd-Ni catalysts through a chemical

reduction method. In alkaline conditions, these catalysts revealed higher ORR activity and lower onset potential as compared to Pd/C [38]. Despite the mentioned studies, it is still necessary to analyze the influence of Ni alloying with Pd.

In this work, bimetallic alloyed palladium-nickel catalysts supported on carbon Vulcan with different Pd to Ni atomic ratios (Pd-Ni/C) were prepared using the impregnation process towards the ORR electrocatalysis. For more comparison, a similar method was also taken to prepare Pd/C and Ni/C electro-catalysts without adding Ni and Pd precursors, respectively. The as-prepared Pd-Ni alloys were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy coupled with energy dispersive X-ray (FESEM-EDX), inductively coupled plasma optical emission spectroscopy (ICP-OES), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS). Cyclic voltammetry (CV), rotating disk electrode (RDE), and chronoamperometry (CA) were employed to examine the electrochemical properties of each electro-catalyst and the outcomes are discussed in detail. In case the potential was repeatedly cycled, accelerated durability test was used to study the durability of the samples. This research also considered how continuous cycling affects the ORR performance and morphology of catalysts through CV and TEM. Finally, the role of Pd/C and Pd₈Ni₂/C as the cathode electro-catalysts was examined in a passive DMFC. The outcomes revealed that Pd₈Ni₂/C is a suitable material with superior stability and catalytic activity for passive DMFC applications.

Up to now, for the first time we have scrutinized Pd-Ni alloy role with the optimal Pd to Ni atomic ratio in order to apply it as an effective cathode catalyst in actual passive DMFCs. Particularly, other earlier researches were restricted to the three-electrode half-cell condition. Besides, no report has ever been issued on the effect of Ni on Pd in the cathode of actual passive DMFCs.

2. Experimental section

2.1. Materials

Nickel (II) chloride hexahydrate (NiCl₂·6H₂O), Palladium (II) nitrate dihydrate (Pd(NO₃)₂·2H₂O), Sulfuric acid (H₂SO₄), Methanol (CH₃OH), Ethylene Glycol (EG), Sodium hydroxide (NaOH) and Isopropyl alcohol (IPA) were all purchased from Merck. To support the synthesized samples, carbon Vulcan XC-72 (from Cabot Corp.) was used as the substrate. Nafion solution 5% (from Sigma-Aldrich) was employed to generate the ink. N₂ (99.5%), O₂ (99.2%), and Ar (99.9%) were

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