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High-loading Pt-alloy catalysts for boosted oxygen reduction reaction performance

Wei Hong¹, Xinran Shen¹, Jian Wang¹, Xin Feng², Wenjing Zhang¹, Jing Li^{1,*}, Zidong Wei^{1,*}¹ School of Chemistry and Chemical Engineering, Chongqing University, Chongqing 400044, China² School of Materials Science and Engineering, Chongqing University, Chongqing 400044, China

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ABSTRACT

To improve performance of membrane electrode assembly (MEA) at large current density region, efficient mass transfer at the cathode is desired, for which a feasible strategy is to lower catalyst layer thickness by constructing high loading Pt-alloy catalysts on carbon. But the high loading may induce unwanted particle aggregation. In this work, H-PtNi/C with 33% (mass) Pt loading on carbon and monodisperse distribution of 3.55 nm PtNi nanoparticles, was prepared by a bimodal-pore route. In electrocatalytic oxygen reduction reaction (ORR), H-PtNi/C displays an activity inferior to the low Pt loading catalyst L-PtNi/C (13.3% (mass)) in the half-cell. While in H₂-O₂ MEA, H-PtNi/C delivers the peak power density of 1.51 W·cm⁻² and the mass transfer limiting current density of 4.4 A·cm⁻², being 21% and 16% higher than those of L-PtNi/C (1.25 W·cm⁻², 3.8 A·cm⁻²) respectively, which can be ascribed to enhanced mass transfer brought by the thinner catalyst layer in the former. In addition, the same method can be used to prepare PtFe alloy catalyst with a high-Pt loading of 36% (mass). This work may lead to a range of catalyst materials for the large current density applications, such as fuel cell vehicles.

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1. Introduction

Polymer electrolyte membrane fuel cells (PEMFCs) are considered as one of the most promising energy conversion technologies due to the low operating temperature, high energy-conversion efficiency and the nice environmental sustainability [1–5]. To reach commercialized application of PEMFCs, low-cost but highly-efficient catalysts for the sluggish oxygen reduction reaction (ORR) is especially important for which ordered intermetallic PtM (*M* = transition metal) alloys represent a typical type of such promising catalysts due to reduced Pt usage and well-improved intrinsic activity and stability [6–11].

Particularly, for PtM nanoparticles loaded on carbon support, Pt loadings on carbon may largely affect the performance of the membrane electrode assembly (MEA) [12,13]. When the absolute Pt loading at the cathode is fixed, a low Pt loading catalyst leads to a thicker catalyst layer which could heavily increase mass transfer resistance and deteriorate the cell performance especially at the high current density region [14]. Simultaneously, the mass transfer limiting current density (*j_d*) can be estimated from the Eq. (1):

$$j_d = nFDc_0/\delta \quad (1)$$

where *n* is mole number, *F* is Faraday's constant, *D* is the effective diffusion coefficient, *c₀* is the bulk (flow channel) reactant concentration, and *δ* is the electrode (diffusion layer) thickness [15]. It means that *j_d* is inversely proportional to *δ*, i.e. the thinner the catalyst layer, the larger the value of *j_d*. Hence, decreasing the catalyst layer thickness by adopting high Pt loading catalyst (Fig. 1) may produce significantly improved single-cell performance.

Presently, typical alloy catalysts have ~20% (mass) Pt loading on carbon support, and when Pt loading is further increased, a real challenge is to remain the monodispersed distribution of PtM nanoparticles at small enough sizes [12]. Normally ordered intermetallic PtM phase is formed along an annealing treatment conducted at 700 °C and even a higher temperature, which frequently induces agglomeration, sintering and size growth of the nanoparticles, leading to loss of specific surface area and the catalytic activity [16–19].

Herein, with PtNi and PtFe as illustration, we demonstrate the synthesis of alloy catalyst with the Pt loading as high as 33%–36% (mass) by using the bimodal-pore strategy (Fig. S1) [1]. The confinement effect of CTAB templated mesopores well prevents the particle growth along the calcination treatment, leading to monodisperse 3.4–3.6 nm intermetallic PtFe/PtNi nanocrystals.

* Corresponding authors.

E-mail addresses: lijing@cqu.edu.cn (J. Li), zdwei@cqu.edu.cn (Z. Wei).

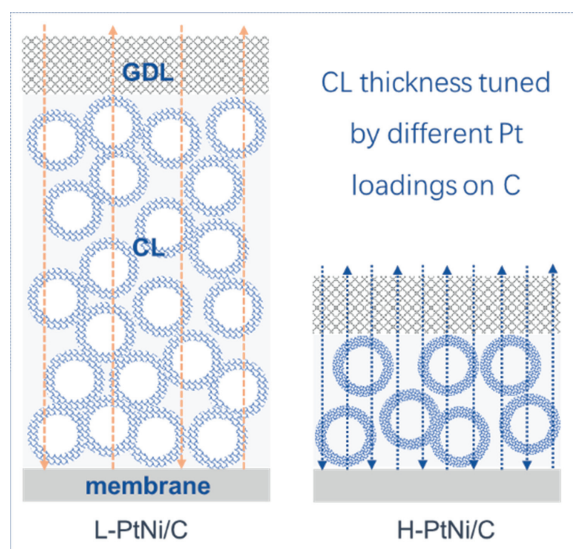


Fig. 1. Schematic illustration of MEA cathodes constructed by catalysts with a high Pt loading (H-PtNi/C) and a low Pt loading (L-PtNi/C) on carbon (GDL = gas diffusion layer; CL = catalyst layer).

And the SiO_2 resultant mesoporous channels together with the hollow structures greatly boost the mass transfer. Interestingly in electrocatalytic ORR, the high Pt loading catalyst, H-PtNi/C, displays an activity inferior to the low Pt loading one, L-PtNi/C, in the half-cell, while delivers a distinctly better performance than the later in a single-cell. Based on this work, a range of high Pt loading catalysts can be prepared which predict a boosted MEA performance and a practical application of fuel cells in the fields such as vehicles.

2. Experimental

2.1. Synthesis of the materials

The synthetic process was illustrated in Scheme S1 (see Supplementary Material). The SiO_2/C was prepared according to the method described in our previous work [1]. In a typical synthesis, 1.2 g CTAB and 0.4 g resorcinol were dissolved in a mixed solvent containing 47 ml deionized water and 13 ml ethanol. Then 0.56 ml formaldehyde and 0.4 ml 28% (mass) ammonia solution were added. Several minutes later, the transparent solution transfers into an emulsion, into which 2 ml TEOS was further introduced. After the emulsion was continuously stirred at 25 °C for 24 h, it was transferred into a 100 ml Teflon-lined autoclave and heated at 80 °C for 24 h. Finally, the collected precipitate was washed and dried, and annealed at 850 °C for 3 h with a heating rate of 1 °C·min⁻¹ under N_2 flow.

To achieve high Pt loading catalyst H-PtNi/C, 0.093 mmol $\text{H}_2\text{-PtCl}_6$ and 0.093 mmol $\text{Ni}(\text{NO}_3)_2$ were dispersed into 50 ml deionized water containing 100 mg SiO_2/C powder, and the obtained mixture was heated to 60 °C and maintained at the same temperature for 12 h. After a subsequent drying treatment, the product was annealed at 800 °C for 4 h under H_2/N_2 (10/90, volume ratio) flow. And after removal of SiO_2 template by a HF etching process, H-PtNi/C product can be finally collected.

The preparation of low Pt loading catalyst L-PtNi/C followed a similar process, except 0.03 mmol H_2PtCl_6 and 0.03 mmol $\text{Ni}(\text{NO}_3)_2$ were used instead. And for high Pt loading catalyst H-PtFe/C, the synthetic process is similar with that for H-PtNi/C, except that $\text{Ni}(\text{NO}_3)_2$ was replaced by $\text{Fe}(\text{NO}_3)_3$.

2.2. Characterizations

X-ray diffraction (XRD) patterns were collected in the range from 20° to 90° on a Rigaku D/Max 2200PC diffractometer using $\text{Cu K}\alpha$ radiation. Transmission electron microscopy (TEM) images were acquired on a Philips Tecnai G2F20 microscope operated at 200 kV. Scanning electron microscope (SEM) images were acquired on a S-4800 HITACHI microscope. Nitrogen sorption isotherms were measured on a Micromeritics Gemini VII 2390 analyzer. X-ray photoelectron spectrometer (XPS) spectra were achieved on a Kratos XSAM800 spectrometer equipped with a monochromatic Al X-ray source (Al KR, 1.4866 keV).

2.3. Electrochemical measurements

The three-electrode system tests were conducted in 0.1 mol·L⁻¹ HClO_4 solution with a graphite rod as counter electrode, the Ag/AgCl (3.0 mol·L⁻¹ KCl) electrode as reference electrode and the glassy carbon rotating disk (0.196 cm²) loaded with our catalysts as working electrode. All potentials in this work were converted to a reversible hydrogen electrode (RHE) scale. The uniform catalyst ink was prepared by ultrasonication-assisted mixing of catalyst powder, ethanol and Nafion solution for 60 min, which was then loaded onto the glassy carbon electrode and dried at room temperature. The final Pt loading for all catalysts was fixed at 17.8 $\mu\text{g}\cdot\text{cm}^{-2}$.

Prior to electrochemical measurements, all working electrodes were pretreated by cycling the potentials between 0.05 V and 1.2 V at 50 mV·s⁻¹ in N_2 -saturated electrolyte for electrochemical cleaning (typically 60 cycles). Electrochemical active surface area (ECSA) was calculated by CO stripping method. Oxygen reduction reaction (ORR) measurements were performed in O_2 -saturated electrolyte under a rotating speed of 1600 r·min⁻¹ at a scan rate of 10 mV·s⁻¹. The ORR data was collected after ohmic iR drop compensation. The accelerated durability test (ADT) was conducted in O_2 -saturated 0.1 mol·L⁻¹ HClO_4 solution at room temperature by cycling the potentials between 0.6 and 1.1 V for 10,000 CV cycles at a sweep rate of 50 mV·s⁻¹.

The ECSA of Pt was calculated according to Eq. (2):

$$\text{ECSA} = Q_{\text{CO}} / (0.42 \times [\text{Pt}]) \quad (2)$$

where Q_{CO} (mC) is the charge estimated from the integrated area of the CO dissolved peak. 0.42 mC·cm⁻² is the adsorption charge of monolayer CO on Pt, and $[\text{Pt}]$ is the loading of Pt on the glass carbon electrode. The specific kinetic current densities (j_k) can be calculated from Eq. (3):

$$j_k = \frac{j_d j}{j_d - j} \quad (3)$$

where j , j_k and j_d represent the measured current density (at 0.9 V), kinetic current density (at 0.9 V) and the diffusion limiting current density, respectively.

2.4. MEA preparation and testing

The prepared PtNi catalysts and commercial Pt/C (Pt loading = 20% (mass), mean diameter <3.5 nm, carbon support: Vulcan XC-72R) were measured in a MEA. The catalyst was dispersed into a dispersion containing isopropanol and 5% (mass) Nafion ionomer (type D520, made by DuPont), with Nafion content in the catalyst layer set at 35% (mass). The as-prepared catalyst ink was then applied to the surface of 5 cm² gas diffusion layer (thickness = 0.21 mm, type HCP120, made by HeSen) and dried. The membrane used was Nafion 211 (thickness = 25.4 μm , made by DuPont). The cell temperature was kept at 80 °C, the back pressure was kept

at 200 kPa, and the gas flow rate for both H_2 and O_2 was $250\text{ ml}\cdot\text{min}^{-1}$.

3. Results and Discussion

The microstructures of the materials were firstly investigated. All the SiO_2/C , H-PtNi/C and L-PtNi/C products show monodispersed spherical morphology with the particle sizes from 210 to 239 nm (Fig. S2(a)–(b)). TEM images (Fig. 2(a)–(b) and (e)–(f)) indicate the hollow structures of H-PtNi/C and L-PtNi/C with the shell thickness of 35 nm and void size of 128–160 nm. Simultaneously, 3.40–3.55 nm PtNi nanoparticles are well dispersed in the shells of H-PtNi/C and L-PtNi/C, while with a distinctly higher dispersion density in the former. In the HRTEM images (Fig. 2(d) and (h)), the interplanar distance of 0.218 nm can be well ascribed to (1 1 1) plane of PtNi. The HAADF-STEM image and the corresponding elemental mappings (Fig. 2(i)–(l)) clearly demonstrate the homogeneous distribution of element Pt and Ni in H-PtNi/C. The inductively coupled plasma-mass spectrometry (ICP-MS) analysis gives that the Pt loading is 33.0% (mass) in H-PtNi/C, being 2.48 times that of L-PtNi/C (13.3% (mass)). Meanwhile, for H-PtNi/ SiO_2/C sample, the atomic Pt/Ni ratio is 54/47 which after HF etching, changes into 58/42 in H-PtNi/C. Similarly, the Ni content slightly decreases from Pt/Ni ratio of 48/52 before etching to 54/46 after etching in L-PtNi/C. This observation indicates that although certain Ni loss during HF etching treatment, the main alloy phase is well remained.

In Fig. 3(a), H-PtNi/C and L-PtNi/C show similar XRD patterns and the four diffraction peaks located at 2θ of 40.9° , 48.2° , 70.8° and 85.5° , are well-indexed to the (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes of faced-centered cubic (fcc) Pt. Besides, the peaks are slightly shifted to higher angles in comparison to those of Pt/C, suggesting that the smaller Ni atoms alloyed into fcc Pt structure induce a concomitant lattice contraction. XPS analysis was conducted to evaluate the electronic properties of Pt and Ni elements in the catalysts. The survey spectra (Fig. S3(a)) indicate existence of

Pt and Ni species in H-PtNi/C and L-PtNi/C. High resolution Pt XPS spectra (Fig. 3(b)) display two pairs of doublet peaks, assigned to oxidized Pt^{2+} and metallic Pt^0 respectively, with the later at a distinctly larger percentage [20–23]. In addition, Pt binding energies of H-PtNi/C and L-PtNi/C are 0.3 eV more positive than those of Pt/C, implying certain electron transfer due to introduction of Ni [24–27]. Fig S3 exhibits that the atomic Pt/Ni ratio by XPS measurement is 44/56 for L-PtNi/C and 52/48 for H-PtNi/C. Compared to the corresponding ratios of 54/46 and 58/42 measured by ICP which represent the bulk composition, it can be deduced that L-PtNi/C surface owns a higher content of Ni and a lower content of Pt than that of H-PtNi/C. It implies the better dispersion of Pt species at the surface region of L-PtNi/C.

The porosities of the materials were characterized by N_2 adsorption method. H-PtNi/C and L-PtNi/C show typical type-IV isotherms with rapid increase in the low (<0.03) and high P/P_0 (>0.97) region, indicating existence of copious micropores and macropores (Fig. 3(c)). Simultaneously, the slow adsorption increase and the distinct hysteresis loop in the middle P/P_0 region (0.5–0.95) exhibit existence of mesopores in the materials. The pore size distribution curves suggest that 2–9 nm mesopores are included in H-PtNi/C and L-PtNi/C, and their BET specific surface areas reach 464.4 and $636.4\text{ m}^2\cdot\text{g}^{-1}$, respectively. By normalizing the surface area to the mass of the carbon support, the estimated BET surface area is 693 and $734\text{ m}^2\cdot\text{g}^{-1}$ for the carbon phase in H-PtNi/C and L-PtNi/C respectively, clarifying that the two alloy materials indeed have similar porous characteristics.

The above results indicate that apart from different Pt loadings, H-PtNi/C and L-PtNi/C own similar morphology, microstructure, surface electronic structure and porosity characteristics. Such well-designed structures allow direct correlation of Pt loadings with the electrocatalytic performances. Firstly, the two catalysts were evaluated in a three-electrode testing system (Fig. 4(b)). Under same Pt loadings on the working electrodes, H-PtNi/C ($E_{\text{onset}} = 1.037\text{ V}$, $E_{1/2} = 0.929\text{ V}$) and L-PtNi/C ($E_{\text{onset}} = 1.037\text{ V}$, $E_{1/2} = 0.934\text{ V}$) display quite similar onset and half-wave potentials,

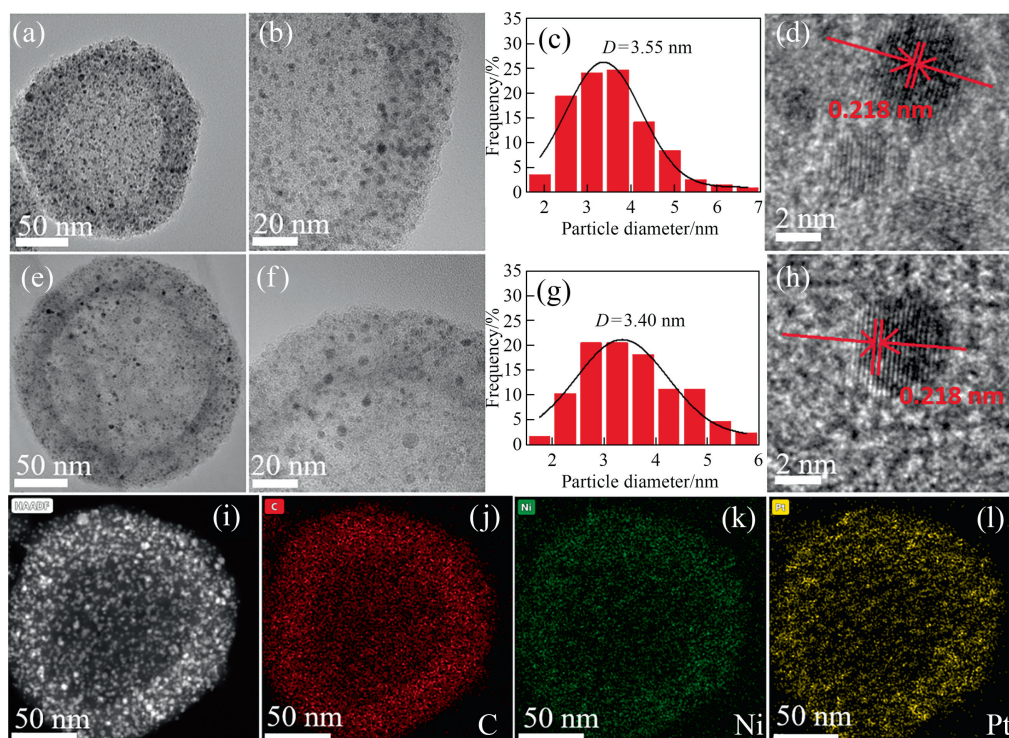


Fig. 2. TEM images of (a), (b) H-PtNi/C and (e), (f) L-PtNi/C. The size distribution plots of PtNi nanoparticles in (c) H-PtNi/C and (g) L-PtNi/C. HRTEM images of (d) H-PtNi/C and (h) L-PtNi/C. (i) HAADF-STEM image and (j)–(l) elemental mappings of H-PtNi/C.

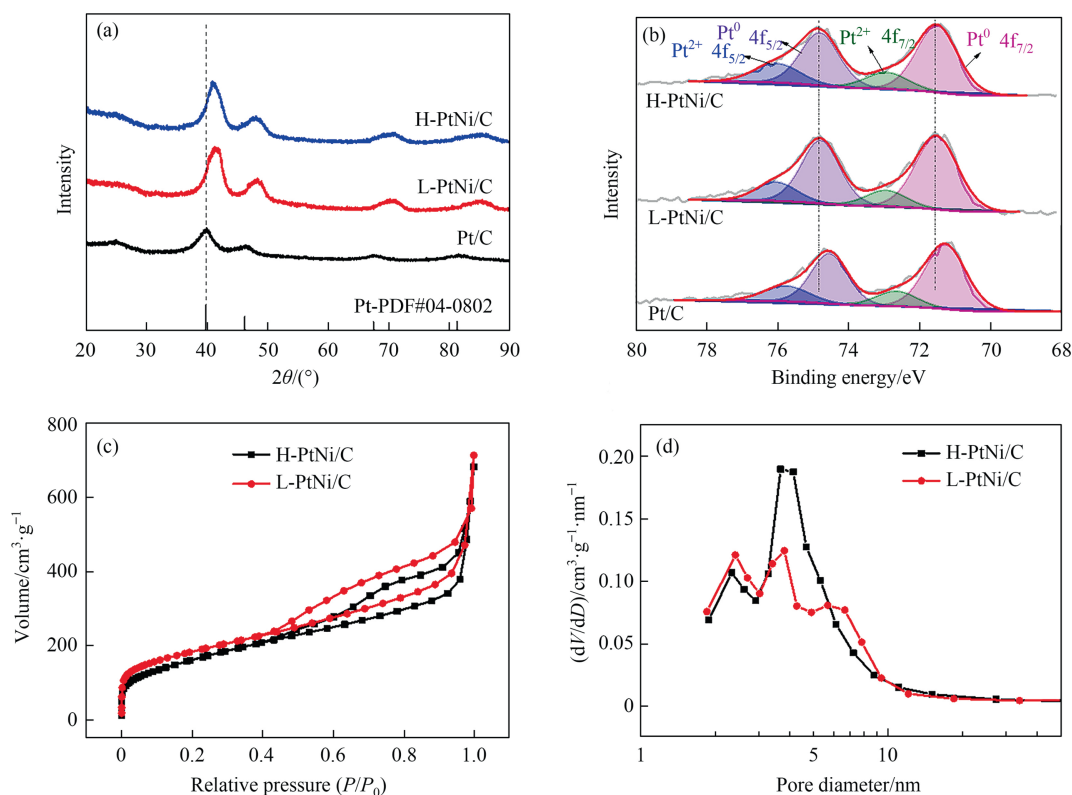


Fig. 3. Physical characterizations of the samples: (a) XRD patterns, (b) Pt 4f high-resolution XPS spectra, (c) N_2 adsorption/desorption isotherms and (d) pore size distribution plots.

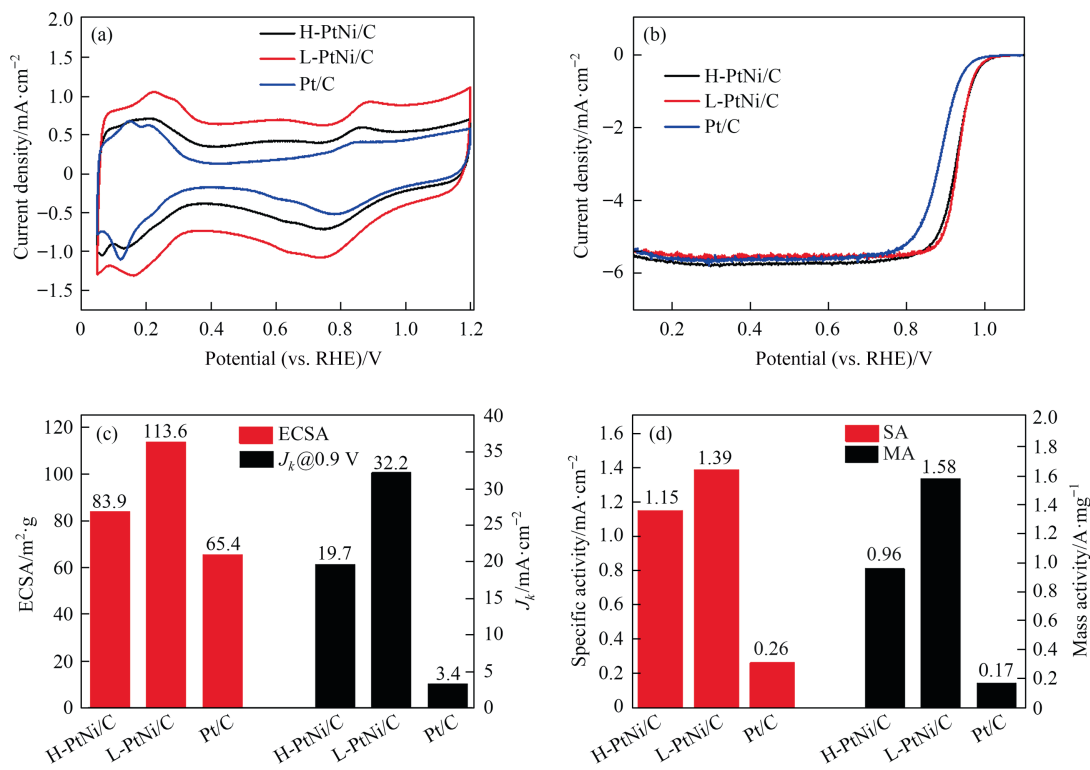


Fig. 4. Electrochemical tests conducted in $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ solutions. (a) CV curves recorded in N_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ solutions at a scan rate of $50 \text{ mV} \cdot \text{s}^{-1}$; (b) ORR polarization curves recorded in O_2 -saturated $0.1 \text{ mol} \cdot \text{L}^{-1} \text{ HClO}_4$ solutions at a sweep rate of $10 \text{ mV} \cdot \text{s}^{-1}$ and a rotation rate of $1600 \text{ r} \cdot \text{min}^{-1}$; (c) The ECSA and J_k ; (d) Specific activity and mass activity estimated at 0.9 V versus reversible hydrogen electrode (RHE).

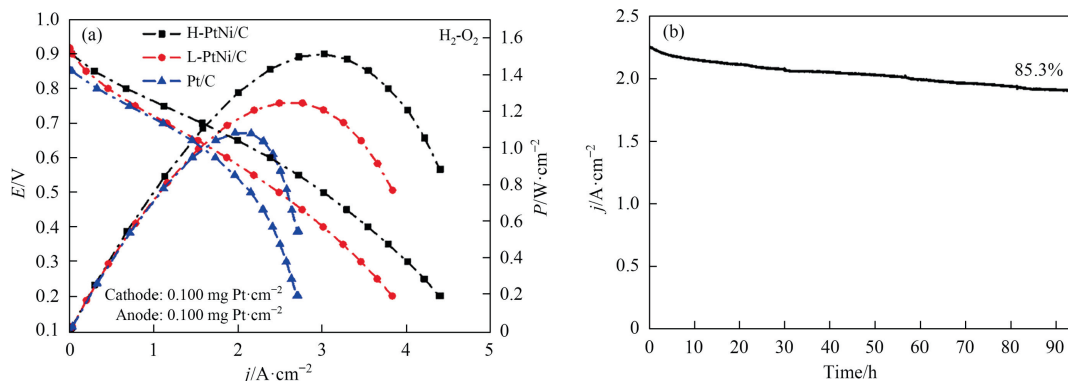


Fig. 5. (a) Polarization curves and power densities of H₂-O₂ fuel cells with H-PtNi/C, L-PtNi/C and Pt/C, as the cathodes with 0.100 mg Pt·cm⁻² loading; 60% PtRu/C was used as anode with 0.100 mg Pt·cm⁻² loading. $P_{H_2} = P_{O_2} = 200$ kPa@100% relative humidity. (b) H₂-O₂ fuel cell lifetimes tested at 0.6 V for 95 h with H-PtNi/C as the cathode.

which are distinctly better than those of commercial Pt/C ($E_{onset} = 1.007$ V, $E_{1/2} = 0.889$ V). Furthermore, the electrochemical surface areas (ECSA, Fig. 4(c)) estimated from CO stripping curves (Fig. S4) are 83.9, 113.6 and 65.4 m²·(g Pt)⁻¹ for H-PtNi/C, L-PtNi/C and Pt/C, respectively, of which the value of L-PtNi/C is 35.4% higher than that of H-PtNi/C. The specific activity (SA) calculated by normalizing current density at 0.9 V against ECSA is 1.39 mA·cm⁻² for L-PtNi/C, which is 1.2 and 5.3 times higher than those of H-PtNi/C (1.15 mA·cm⁻²) and commercial Pt/C (0.26 mA·cm⁻²), respectively (Fig. 4(d)). Also, the mass activity (MA) of L-PtNi/C catalyst reaches 1.58 A·mg⁻¹ @0.9 V, being significantly higher than those of H-PtNi/C (0.96 A·mg⁻¹) and Pt/C (0.17 A·mg⁻¹). These results clearly demonstrate that both PtNi catalysts own distinctly better electrocatalytic performance in comparison with Pt/C. Simultaneously, L-PtNi/C gives better ORR catalytic activity than H-PtNi/C in a three-electrode testing system. This can be ascribed to the different surface Pt/Ni ratios of the two catalysts. As displayed in Fig. S3, surface Ni content of the H-PtNi/C catalyst is lower than that of L-PtNi/C, indicating that the Pt shell of H-PtNi/C is thickened and the Pt utilization is reduced, which then decreases the ECSA of the catalyst [28,29].

Then the two alloy materials were measured in membrane electrode assembly (MEA) at the cathodic Pt loading of 0.100 mg·cm⁻² under H₂-O₂ flow. As displayed in Fig. 5(a), the current density at 0.6 V reaches 2.37 A·cm⁻² for H-PtNi/C, being 1.26 and 1.38 times those of L-PtNi/C (1.88 A·cm⁻²) and Pt/C (1.72 A·cm⁻²), respectively. Also, H-PtNi/C delivers a peak power density of 1.51 W·cm⁻², which also greatly outperforms those of L-PtNi/C (1.25 A·cm⁻²) and Pt/C (1.08 A·cm⁻²), respectively. More importantly, it is observed that Pt/C demonstrates rapid voltage decrease at the region of high current density (>2 A·cm⁻²), implying certain flooding in the MEA, while the two alloy catalysts deliver rather stable output in this region. The mass transfer limiting current density of H-PtNi/C (4.4 A·cm⁻²) is 1.16 and 1.63 times higher than those of L-PtNi/C (3.8 A·cm⁻²) and Pt/C (2.7 A·cm⁻²), indicating the efficient mass transfer in the H-PtNi/C electrode. Besides, after 95 h of continuous operation at 0.6 V, the single-cell assembled with H-PtNi/C catalyst decays only 14.7%, meaning a nice durability.

The observation that in electrocatalytic ORR, H-PtNi/C displays an activity inferior to L-PtNi/C in the half-cell, while delivers a distinctly better performance than the later in a single-cell, is especially interesting for which the possible reasons may include:

- (1) In the three-electrode system, the effect of mass transfer can be ignored considering the ultralow Pt loading and the continuous rotation of working electrode. While the relatively larger ECSA of L-PtNi/C leads to the higher utilization efficiency of Pt species, making it perform better than H-PtNi/C;

- (2) In MEA which owns a significantly higher loading of catalyst, mass transfer is widely recognized to be crucial to the cell performance and the mass transfer limiting current density (j_d) can be estimated by the Eq. (1). It shows that j_d is inversely proportional to δ , i.e. the thinner the catalyst layer, the larger the value of j_d . In our work, when the absolute Pt loading at the cathode is fixed, the thickness of the catalyst layer assembled by L-PtNi/C (Pt = 13.3% (mass)) should be ~4 times that of H-PtNi/C (Pt = 33% (mass)) theoretically. And our measured thickness (Fig. S5) of 45.0 μ m and 10.4 μ m for L-PtNi/C and H-PtNi/C, respectively, matches well with the theoretical ones. Thus ultra-thin electrode brought by the high Pt-loading H-PtNi/C supplies highly efficient mass transfer and inhibits flooding, facilitating the stable long-term operation of MEA, particularly in the region of high current density.

The reported method is further extended to preparation of high Pt loading H-PtFe/C materials. In Fig. S6, the sample demonstrates the same hollow sphere morphology with uniform dispersion of 3.4 nm PtFe alloy nanoparticles in the carbon shells. The HAADF-STEM image and the corresponding elemental mappings display dense alloy particle decoration and consistent distribution of elemental Pt and Fe. ICP-MS measurement gives the Pt loading of 36.0% (mass), and XRD pattern indicates the intermetallic L1₀-PtFe phase contained. In electrocatalytic ORR (Fig. S7), H-PtFe/C gives the half-wave potential of 0.931 V and mass activity of 1.03 A·mg⁻¹ at 0.9 V in the three-electrode system. While the MEA assembled with H-PtFe/C at the cathode reaches a peak power density of 1.78 W·cm⁻² and a current density of 2.55 A·cm⁻² at 0.6 V under the cathodic Pt loading of 0.100 mg·cm⁻², representing a promising high Pt loading catalyst.

4. Conclusions

In summary, H-PtNi/C catalyst with average PtNi particle size of 3.55 nm and Pt loading as high as 33% (mass) was successfully prepared by a bimodal-pore strategy. In electrocatalytic ORR, H-PtNi/C displays an activity inferior to L-PtNi/C in the half-cell. While in H₂-O₂ fuel cell, the peak power density and limiting current density of H-PtNi/C reaches 1.51 W·cm⁻² and 4.4 A·cm⁻² under cathodic loading of 0.100 mg·Pt·cm⁻², being 21% and 16% higher than the corresponding values of 1.25 W·cm⁻² and 3.8 A·cm⁻² generated by L-PtNi/C (13.3% (mass)), respectively. It can be ascribed to the ~4 times thinner catalyst layer in the former and thus significantly improved mass transfer efficiency. In addition, the same method exhibits nice universality by which PtFe alloy catalyst with a

high-Pt loading of 36% (mass) can also be prepared. In principle, this work can be extended to preparation of a range of catalytic materials with high loadings of active sites for use in various fields.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary Material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.vaccine.2019.08.065>.

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