**Nanoporous PdZr surface alloy as highly active non-platinum electrocatalyst
toward oxygen reduction reaction with unique structure stability and
methanol-tolerance**

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Abstract:

Nanoporous (NP) PdZr alloy with controllable bimetallic ratio is successfully fabricated by a simple dealloying method. By leaching out the more reactive Al from PdZrAl precursor alloy, NP-PdZr alloy with smaller ligament size was generated, characterized by the nanoscaled interconnected network skeleton and hollow channels extending in all three dimensions. Upon voltammetric scan in acid solution, the dissolution of surface Zr atoms generates the highly active Pd-Zr surface alloy with a nearly pure Pd surface and Pd-Zr alloy core. The NP-Pd₈₀Zr₂₀ surface alloy exhibits markedly enhanced specific and mass activities as well as higher catalytic stability toward oxygen reduction reaction (ORR) compared with NP-Pd and the state-of-the-art Pt/C catalysts. In addition, the NP-Pd₈₀Zr₂₀ surface alloy shows a better selectivity for ORR than methanol in the 0.1 M HClO₄ and 0.1 M methanol mixed solution. X-ray photoelectron spectroscopy and density functional theory calculations both demonstrate that the weakened Pd-O bond and improved ORR

performances in turn depend on the downshifted d-band center of Pd due to the alloying Pd with Zr (20 at.%). The as-made NP-PdZr alloy holds prospective applications as a cathode electrocatalyst in fuel-cell-related technologies with the advantages of superior overall ORR performances, unique structure stability, and easy preparation.

Keywords: palladium; dealloying; nanoporous; oxygen reduction reaction; electrocatalysis

1. Introduction

The development of highly active electrocatalysts has been an intense research point in the field of proton exchange membrane fuel cells (PEMFCs) [1–4]. It is believed that a major prerequisite for the commercialization of PEMFCs is significantly reducing their fabrication cost. Oxygen reduction reaction (ORR) occurred at the cathode is of practical importance for PEMFCs to achieve the desirable energy output efficiency and utilization lifetime [5–8]. At present, Pt-based alloys have been proven to exhibit the best overall performance for ORR [9–11]. Unfortunately, the high cost and limited abundance of Pt severely hamper its large-scale application as cathode electrocatalysts [12]. Thus, designing and exploring non-Pt electrocatalysts with high catalytic activity and durability are crucial for the industrialization of fuel cells.

Interestingly, Pd shows competitive intrinsic electrocatalytic performance toward the ORR relative to Pt [13,14]. More importantly, Pd is less expensive compared with Pt, which has attracted greatly increasing attention in recent years [15,16]. Moreover, alloying Pd with early-transition-metals, such as Co [17], Fe [18], Cu [19,20], and Ni [21], has been demonstrated to be an effective way to further reduce the cost as well enhance the ORR activity of Pd. By comparison, Zr, one of early-transition-metals, has not yet drawn much attention although the positive alloying effect of Zr on the ORR activity of Pt has been reported by Yoo et al. [22]. Klüner et al. [23] proposed that PdZr alloy may be a good candidate for improving the ORR activity among the Pd series alloys, which can be ascribed to the tiny O₂ dissociation barrier as well smaller reaction energy on PdZr alloy compared with pure Pt(111). Furthermore, it has been proposed

that the combination of an early and a late (Pd or Pt) transition metal elements, such as Pd–Zr system, usually generates a large negative formation enthalpy, thus resulting in the high thermodynamic stability [24]. However, until now there is still a lack of systematic investigations on the preparation of PdZr alloy nanomaterials and their ORR performances.

It is known that electrocatalytic reactions are an integrated display correlated with the electrocatalysts' architecture as well as surface activity [25]. Consequently, it is essential to optimize the ORR performances of Pd–Zr alloy electrocatalysts by engineering their morphology with simple and scaled preparation route. At present, great efforts have been devoted to developing ORR nanocatalysts with various morphologies, such as nanowires [26], nanotubes [27], and “core–shell” nanoparticles [28] etc. These nanocatalysts are usually synthesized by chemical reduction methods. For instance, the “core–shell” nanostructured electrocatalysts are usually obtained by synthesizing the “core” supports and followed by the coating of the other material [28–30]. The preparation process is relatively complicated, and usually involves the assistance with organic solvents as the surfactants or stabilizing agents. It is noted that nanoporous structures made by dealloying method represent a desired class of multifunctional catalytic nanoarchitectures for electrocatalytic reactions. The interconnected nanoscaled skeletons and unblocked voids embedded in the network skeleton facilitate the electron conductivity and mass transport during electrocatalysis [31,32]. Dealloying method has been recognized as an effective and versatile strategy for the controlled preparation of nanoporous alloy materials [33–35]. By comparison with chemical reduction method,

dealloying method has high reproducibility with no organic agents involved, which is especially appropriate for large-scale synthesis and easy to achieve the composition control. In current work, we focus on alloying Pd with Zr to explore the effects of Zr in PdZr alloy on the catalytic activities of Pd toward ORR. Meanwhile, combining with special nanoporous architecture is of important significance to further improve its mass activity and structure stability. Herein, we successfully fabricated nanoporous PdZr (NP-PdZr) alloy with a predetermined alloy composition by a simple room-temperature dealloying method. Upon voltammetric treatment in acid solution, the dissolution of surface Zr atoms from Pd-Zr alloy generates the highly active surface alloy electrocatalysts with a nearly pure Pd surface and Pd-Zr alloy core. Recent fundamental studies on single crystal surfaces have suggested that the specific activity could be promoted by nearly an order of magnitude on the fine tuned near surface configuration comprised of a nearly pure metal surface and alloy sub-surface, which usually termed as a surface alloy [36–38]. Compared with commercial Pt/C and NP-Pd catalysts, the as-made NP-PdZr surface alloy displayed dramatically improved structure stability besides superior ORR specific activities. In addition, NP-PdZr surface alloy also shows a unique methanol tolerance with almost no activity loss in the presence of 0.1 M methanol.

2. Experimental section

Pd₁₆Zr₄Al₈₀ ternary alloy foils and Pd₂₀Al₈₀ (at.%) binary alloy foils were made by melting the corresponding pure metals Pd, Zr, and Al (99.99%) in an arc-furnace, respectively, and followed by melt-spinning under the protection of Ar atmosphere

similar to our previous studies [39]. All agents were obtained in analytical grade from Shanghai Sinopharm Chemical Reagent Ltd. Co of China. All nanoporous metals were fabricated by **etching** the corresponding alloy foils in 0.5 M NaOH solution for 48 h at room temperature. The prepared samples were cleaned with ultra-pure water (18.2 MΩ) before drying at room temperature in air. The John–Matthey Pt/C (20 wt.%) catalysts were provided by Alfa Aesar.

Powder X-ray diffraction (XRD) data were collected using a Bruker D8 advanced X-ray diffractometer with Cu Kα radiation ($\lambda=1.5418 \text{ \AA}$) **with a stepwise technique (2θ steps of 0.01, collection time equal to 4 s·step⁻¹). The semiquantitative phase analysis was carried out by using the Rietveld method with the MAUD program [40]. JEOL JSM–6700F field emission scanning electron microscope (SEM) with an Oxford INCA X-sight energy dispersive X-ray spectrometer were used for the microstructure and chemical compositions characterization. Transmission electron microscopy (TEM) images were taken on a JEM–2100 high-resolution transmission electron microscope (200 kV). X-ray photoelectron spectroscopy (XPS) spectra were obtained on an ESCALab250 X-ray photoelectron spectrometer, using monochromatized Mg Kα X-ray as the excitation source. Binding energies were calibrated using the C 1s peak (284.6 eV) as the reference line. **The surface area and pore size distribution were measured with a Quadrasorb SI–MP (Quantachrome Instruments) using the Brunauer–Emmett–Teller (BET) method.****

All electrochemical measurements were performed using a PINE AFCBP1 electrochemical workstation. A conventional three electrode cell was employed in all

experiments with Pt foil as a counter electrode and mercury sulfate electrode as the reference electrode. The ORR activity was taken on MSR rotation ring–disk electrode (RDE, Phychemi Company Limited) in 0.1 M HClO₄ solution saturated with oxygen at a scan rate of 10 mV s⁻¹. All potentials in this work are provided with respect to the reversible hydrogen electrode (RHE). The NP–Pd₈₀Zr₂₀ and NP–Pd catalyst were dispersed in a mixed solution of 1.0 mg of catalyst sample, 1.5 mg of carbon powder, 800 μL of ethanol, and 200 μL of Nafion (0.5 wt.%), and the mixture was ultrasonicated for one hour to obtain a well–dispersed suspension. Pt/C catalyst ink (about 1 mg mL⁻¹) was also prepared following the same procedure as described above except for further addition of carbon powder. Appropriate catalyst inks were dropped onto a pre–polished rotating disk electrode (5 mm in diameter). After drying, the catalyst film modified glassy carbon rotating disk electrode was obtained. The loading of Pt for the Pt/C catalyst was 15.7 μg cm⁻², and the loadings of Pd for NP–Pd₈₀Zr₂₀ and NP–Pd was determined to be 12.5 and 17.2 μg cm⁻², respectively. Prior to electrochemical measurements, the electrolytes were first purged with high–purity N₂ for 30 min except for the ORR measurements. The electrochemical active surface areas (ECSAs) of the Pd–based catalysts were determined by measuring the charge of the Pd oxide reduction region, from the cyclic voltammetry in N₂–purged 0.1 M HClO₄ solution in the range of 0 to 1.35 V at the scan rate of 50 mV s⁻¹, divided by the theoretical charge for a palladium oxide monolayer reduction (420 μC cm⁻²) [41]. The ECSA of Pt was evaluated by integrating the charge correlated with H desorption in N₂–purged 0.1 M HClO₄ solution at the scan rate of 50 mV s⁻¹, in which the theoretical charge for a

desorption of a hydrogen monolayer is $210 \mu\text{C cm}^{-2}$ Pt with the double layer corrected [42]. The ECSAs of NP-Pd₈₀Zr₂₀, NP-Pd, and Pt/C were measured to be 68, 77, and 73 m² g⁻¹ by using the methods stated above.

All density functional theory (DFT) simulations were performed with VASP program [43], using the gradient-corrected PBE exchange-correlation functional [44]. The electronic wave functions were expanded in a plane wave basis set with an energy cutoff of 400 eV. For all the cases, we employed a four-layer slab model with the forth layer fixed. Repeated slabs were separated by more than 10 Å to avoid artificial interactions between each other. The Pd₁₃Zr₃ (111) surface was modeled as a periodically repeated 2×2 -unit cell in three dimensions with sixteen atoms per cell and four layers of atoms to model the case of the used electrocatalyst. The Pd₁₃Zr₃ (111) surface was modeled as a pure Pd outermost monolayer with 75% Pd in the second layer and below. The geometries were optimized until the forces on all the unconstrained atoms were less than 0.02 eV Å⁻¹. The Brillouin zone integration was done on a regular $5 \times 5 \times 1$ Monkhorst-Pack k-points grid [45]. The density of state calculations were evaluated at the same level except with a $13 \times 13 \times 1$ Monkhorst-Pack k-points mesh. On all the surfaces considered in this study, face centered cubic hollow site is the most favorable oxygen atom adsorption site. The oxygen adsorption energy (ΔE_{O}) is calculated as $\Delta E_{\text{O}} = E(\text{slab}) + E(\text{O}) - E(\text{ads/M})$, in which $E(\text{slab})$ and $E(\text{O})$ are the energies of the clean slab and isolate oxygen atom in vacuum, respectively, while $E(\text{ads/M})$ is the energy of the adsorbate-M adsorption system.

3. Results and discussion

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It is well known that selective dissolution of more reactive element from an alloy frequently generates a porous structure with nanosized ligaments and pores [46,47]. Considering that Al is amphoteric and more reactive, and thus can be easily dissolved in a common alkaline solution under free corrosion without any loss of Zr and Pd, we chose ternary PdZrAl as the source alloy. Generally, it is believed that the ternary route is more preferable for generating a nanoporous structure with higher porosity and better composition control. If taken alloy-fabrication cost into consideration, Al is more abundant with a relatively low price in the designed ternary PdZrAl alloy. The composition of the PdZrAl source alloy was first identified by X-ray energy-dispersive spectroscopy (EDS). As illustrated in Fig. S1a, the composition of the ternary alloy is around Pd₁₆Zr₄Al₈₀ (at.%), which is consistent with our initial feeding ratio during alloy melting. The bimetallic ratio between Pd and Zr in the dealloyed sample was further confirmed by EDS (around 80:20), which in turn indicates an excellent control of the resulting nanoalloy compositions by means of the dealloying strategy. As shown in EDS spectra, a most majority of Al atoms were removed to a lower level. It should be mentioned that the surface reactivity of the as-made electrocatalyst will not be influenced by the little residual Al atoms which were usually trapped inside the nanoporous ligaments.

The microstructure of the resulted sample was characterized by electron microscope. By selectively etching Al from PdZrAl alloy in 0.5 M NaOH solution, an open bicontinuous nanosponge structure was successfully fabricated as shown in Fig. 1a. From high-magnification SEM image (Fig. 1b), it can be clearly found that the resulted

1 nanostructure is composed of the interconnected nanosized ligaments with the main size
2 distributed around 7 nm. TEM was further employed to characterize the detailed
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4 microstructure. The sharp contrast between the inner bright region and interconnected
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6 dark backbone in Fig. 1c further confirms the formation of a bicontinuous network
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8 nanostructure with the interconnected channels running through the framework. The
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10 typical high-resolution TEM (HRTEM) image (Fig. 1d) further verifies the nanoporous
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12 structure of PdZr alloy. It is clearly observed that the highly ordered lattice fringes were
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14 clearly resolved along several ligaments with the lattice space measured to be ~0.221
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16 nm, corresponding to the (111) plane spacing for PdZr alloy. The surface area and pore
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18 size distribution of the NP-Pd₈₀Zr₂₀ alloy were measured by using the BET method. As
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20 shown in Fig. S2, the pore size of NP-Pd₈₀Zr₂₀ mainly distributes in the range of 8 to 18
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22 nm with the surface area measured to be ~47.9 m² g⁻¹.
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33 To gain more insights into the structure formation, XRD measurement was conducted
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35 to characterize the crystal structure of the PdZrAl precursor alloy and resulted sample.
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37 The diffraction peaks of PdZrAl precursor alloy displayed in Fig. 2 can be assigned to a
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39 PdAl₆-type crystal structure by detailed comparison. However, the peak position and
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41 relative intensity of these diffraction peaks are slightly different from the standard
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43 PdAl₆ diffraction pattern, which may arise from the different alloy compositions as well
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45 the rapid solidification processing during alloy melting. In addition, no diffraction peaks
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47 correlated with individual pure metals or their oxides were observed in the Fig. 2,
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49 indicating the preferential formation of the PdZrAl alloy. Upon selective leaching of Al
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51 from the ternary alloy, it is observed that the diffraction peaks of the PdZrAl precursor
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disappeared, and only a set of three diffraction peaks emerge at 40.4, 45.4, and 68.0 (2 θ), which show slight shifts to more positive positions relative to pure Pd. These peaks can be indexed to the (111), (200), and (220) planes of face-centered cubic (fcc) PdZr alloy in a Fm-3m space group, indicating that Zr atoms uniformly distributed into the fcc structure of Pd. The available XRD data were further simulated by the Rietveld method. Fig. S3 shows the Rietveld simulation of the XRD pattern for NP-Pd₈₀Zr₂₀ alloy, which further indicates that the Pd₈₀Zr₂₀ is mainly composed of Pd-like fcc single-phase PdZr alloy structure. The cell parameter of Pd₈₀Zr₂₀ alloy is calculated to be 3.8754 Å (Table S1), which is slightly smaller than the value of pure Pd (3.8908 Å), indicating a contraction of the lattice parameters of Pd. The contraction of the lattice parameter of Pd is due to the replacement of a fraction of Pd atoms by smaller Zr atoms, which is commonly observed in other reports upon combining with other transition metals [28,48–50]. These results suggest that palladium metal, which is characterized by the Fm-3m space group [51], easily forms alloy with Zr. It is noted that no diffraction peaks associated with individual Pd and Zr atoms or their oxides were observed in XRD spectra, providing a strong evidence for the formation of a homogenous single-phase PdZr alloy. As the dissolution of Al takes place, the remained Pd and Zr atoms will undergo a reconstruction process to form the bicontinuous nanoporous PdZr alloy architecture. On the basis of the above analysis, it can be concluded that the combination of etching process and alloy melting is a simple and effective method for the preparation of NP-PdZr alloy and especially suitable for the controlled production of bimetallic catalysts.

XPS was further performed to examine the electron structure of the NP-Pd₈₀Zr₂₀ sample. As shown in Fig. 3a, the core-level Pd 3d spectra of NP-Pd₈₀Zr₂₀ alloy display a doublet with the binding energies located at 335.5 and 340.7 eV for Pd 3d_{5/2} and Pd 3d_{3/2}, respectively, showing a shift to higher binding energy upon alloying with Zr compared with the 335.1 eV for pure Pd 3d_{5/2} [52]. The upshift of the binding energy for Pd in NP-Pd₈₀Zr₂₀ alloy could be ascribed to the changes in the electron density around Pd due to the formation of PdZr alloy as demonstrated by XRD as well the lower electronegativity of Zr. The upshift also suggests that the density of states at the Fermi level decrease (or an increase of the d-vacancy) by filling the Pd d-band, i.e., the electron transfer from Zr to Pd. Another weak doublet signal around 336.8 and 342.1 eV can be assigned to the Pd 3d_{5/2} and Pd 3d_{3/2} electrons of PdO [53,54]. Fig. 3b presents the XPS spectra for the Zr 3d core level region, in which the peak around 180.5 eV can be ascribed to metallic zirconium, whereas the peaks around 182.3 and 184.7 eV can be assigned to the formation of Zr oxides [55]. The existence of Zr oxides can be ascribed to the surface oxidation of the sample during dealloying and drying.

As mentioned above, NP-Pd₈₀Zr₂₀ alloy has the nanosized interconnected backbone, which favors the electron conductivity and mass transport during electrocatalysis [56]. In addition, the interconnected voids running through the network skeleton are beneficial for molecular mobilization along the channels. Recently, Erlebacher et al. [57] also demonstrated that incorporating with ionic liquids to improve the dissolution of oxygen in electrolyte is a powerful way to improve the catalytic activity of nanoporous architecture. Such an integral architecture provides a desired multifunctional platform

for electrocatalysis applications. Motivated by these results, we carried out a series of studies on the ORR electrocatalytic activities of NP-Pd₈₀Zr₂₀ alloy.

Fig. 4a presents the relatively stable cyclic voltammetric (CV) curve of NP-Pd₈₀Zr₂₀ alloy in 0.1 M HClO₄ solution at room temperature. Intriguingly, there is no evident oxidation signal emerged associated with Zr, further indicating the formation of uniform PdZr alloy as illustrated in XRD. The CV curve of PdZr alloy is consistent with the typical CV feature of pure Pd, revealing the formation of a surface alloy structure with Pd enriched surface and PdZr alloy core upon voltammetric scan in acid solution. Fig. 4b illustrates the ORR polarization curves of NP-Pd₈₀Zr₂₀, NP-Pd, and commercial Pt/C catalysts obtained at a rotation speed of 1600 rpm. Clearly, there are two distinguishable potential features emerged with a well-defined diffusion-limited currents region below 0.7 V followed by a mixed kinetic/diffusion-controlled region between 0.7–1.0 V [58,59]. In an attempt to assess their intrinsic ORR activities, the specific kinetic activities of all catalysts were calculated based on ECSAs. From Fig. 4c, NP-Pd₈₀Zr₂₀ surface alloy exhibits much higher specific kinetic activity than those of NP-Pd and Pt/C catalysts over a potential from 0.84 to 0.92 V. Fig. 4d further shows the specific and mass activities for all catalysts at 0.90 V. Evidently, NP-Pd₈₀Zr₂₀ alloy shows the highest specific activity with the value of ~ 0.25 mA cm⁻² at 0.9 V, which is 3.8 times of NP-Pd, and also higher than that of Pt/C catalysts (0.15 mA cm⁻²). Additionally, NP-Pd₈₀Zr₂₀ alloy also exhibits superior mass activity among all catalysts. If taken the noble metal mass into account solely, NP-Pd₈₀Zr₂₀ alloy exhibits a higher mass activity (0.17 A mg⁻¹), which is about 3.4 times higher than that of NP-Pd (0.05 A

mg⁻¹), and 1.5 times higher than that of Pt/C (0.11 A mg⁻¹). In current work, the measured activities of the commercial Pt/C catalyst are analogous to those reported in other literature [60]. These results indicate that apart for the special nanoporous architecture, the alloying effect of Zr also contributes to the increased ORR activity of Pd, which was consistent with Klüner et al.' suggestion. Fig. S4 presents the corresponding Tafel plots for all catalysts by using the Koutecky–Levich method. For NP–Pd₈₀Zr₂₀, the slope is estimated to be 81 mV dec⁻¹ in the potential range from 0.92 to 1.0 V, whereas the Tafel slopes for NP–Pd and Pt/C catalysts are 73 and 78 mV dec⁻¹, respectively. The different Tafel slopes for ORR catalysts can be attributed to the different adsorption states of oxygenated species, particularly for OH adsorption on the catalyst surface, which is responsible for the “lower” Tafel slope at high potentials in HClO₄ solution [61]. Markovic et al. [62] demonstrated that the adsorbed OH on the Pt surface not only blocks the Pt surface sites but also significantly affects the kinetics of O₂ reduction and the Tafel slope by altering the adsorption energy of the O₂ reduction intermediates. It is considered that the lower amounts of OH adsorbed on the NP–Pd₈₀Zr₂₀ surface leads to the higher Tafel slope relative to the Pt/C catalyst, which favors the reaction kinetics of O₂ reduction. DFT analysis further demonstrated this point as discussed below.

Besides the required high activities, the excellent stability also plays another decisive role for the commercialization of the PEMFCs [63]. Herein, the continuous CV scans were conducted to determine the stability of all the catalysts for the ORR as shown in Fig. 5. For Pt/C catalyst, after 5, 000 potential cycles the half–wave potential showed a

22 mV degradation with about 19% loss of ECSAs relative to the initial value (Fig. 5e and f). Intriguingly, NP-Pd₈₀Zr₂₀ alloy (Fig. 5a and b) showed a less degradation in the half-wave potential (17 mV) and ECSAs (~14%) than Pt/C catalyst despite Pd is more reactive than Pt in acid media. As for the poor stability of Pt/C catalyst, the aggregation of the Pt nanoparticles induced by the high specific surface energy of Pt nanoparticles [64] and the corrosion of carbon support are often observed in the electrochemical system [65]. Either CO₂ or CO formed due to carbon corrosion during long term scan in acid solution usually makes Pt nanoparticles fall off the carbon support with the relatively larger loss of ECSAs for Pt/C catalyst [65]. In addition, the presence of oxygen-containing species formed on carbon surface not only decreases the conductivity of Pt/C catalysts but also weakens the interaction between the carbon support and Pt nanoparticles, resulting in an accelerated sintering of Pt nanoparticles [66]. During long term scanning the interaction between the Pt nanoparticles and the carbon support leads to the more severe loss of ECSAs and catalytic activity over Pt/C catalyst, where Pt catalyzes the oxidation of carbon and the oxidation of carbon accelerates the sintering of Pt particles [66,67]. With regard to the NP-Pd catalyst, an evident decline in ORR activities occurred with a decrease of 24% in the ECSAs and a degradation of 25 mV in half-wave potential (Fig. 5c and d). In addition, the mass activities of all catalysts after 5, 000 CV cycles were further given in Fig. S5. It is interesting to find that after 5, 000 cycles the mass activity of the NP-Pd₈₀Zr₂₀ (0.13 A mg⁻¹) catalyst still remained 76% relative to the initial activity. By comparison, Pt/C and NP-Pd catalysts underwent larger loss of the mass activities with 68 and 60%

retained, respectively. These results give strong evidence that it is the perfect combination of alloying effect with Zr atoms and the special nanoporous architecture that contributes to improving the structure stability of NP-Pd₈₀Zr₂₀. The macroscopic interconnected nanoscaled skeleton and the compressed Pd skin in NP-Pd₈₀Zr₂₀ surface alloy, formed during the CV scans, not only result in the enhanced resistance of Pd to dissolution but also suppress the structure coarsening because of the strain effect [59].

Given that methanol permeation to the cathode will dramatically degrade the fuel cell's power efficiency, the methanol tolerance for ORR catalysts presents a significant challenge in direct methanol fuel cells (DMFCs) [68]. Consequently, the high methanol tolerance for an ORR catalyst is vital for its application in DMFCs. The ORR polarization curves of NP-Pd₈₀Zr₂₀ catalyst in the presence of 0.1 M methanol was further provided in Fig. 6. It can be clearly observed that the ORR current on the NP-Pd₈₀Zr₂₀ catalyst undergoes a little decay in the potential range from 0.6 to 0.85 V in the presence of 0.1 M methanol, which may originate from the formation of the oxidized Pd surface during the methanol oxidation. However, there was almost no currents decay when the potentials higher than 0.85 V in the presence of 0.1 M methanol. Taking these results into consideration demonstrates that NP-Pd₈₀Zr₂₀ surface alloy possesses a high methanol tolerance in the 0.1 M HClO₄ and 0.1 M methanol mixed solution. With regard to Pd, there is almost no catalytic activity for methanol electrooxidation in acidic media [69]. As expected, NP-Pd₈₀Zr₂₀ surface alloy has a better selectivity for ORR than methanol, which renders NP-Pd₈₀Zr₂₀ alloy attractive as a promising ORR electrocatalyst in DMFCs.

DFT calculations enable us to directly correlate the enhanced ORR performances of NP-Pd₈₀Zr₂₀ alloy with the changes of Pd electronic structure. Pd₁₃Zr₃ (111) slabs with pure Pd surface were employed in order to be close to the experimental case. Fig. 7 shows that the ΔE_O of the Pd₁₃Zr₃ (111) (-3.79 eV) corresponding to the most stable fcc hollow site is markedly lower than that of pure Pd (111) (-4.33 eV). Interestingly, upon incorporating with Zr the ΔE_O of the Pd₁₃Zr₃ (111) slab was substantially reduced relative to that of the Pt (111) slab (-4.24 eV). It is believed that strong adsorption of O atoms on Pd usually results in the formation of the oxidized unreactive Pd surface, where the ORR rate is seriously delayed by the removal of oxygenated species [25]. Thus, it is considered that the decreased ΔE_O of PdZr is favorable for achieving an optimum balance between the adsorption energies of oxygenated species and their surface coverage, eventually leading to more active sites for O₂ adsorption and activation. Additionally, the d-band center of Pd in PdZr is calculated to be -2.53 eV, which is similar to that of Pt (-2.72 eV), but an obvious negative shift occurs relative to pure Pd (-1.95 eV). The downshift of the d-band center of Pd relative to the Fermi level means the decrease of an electron back-donation from the Pd 4d orbital to the 2p* orbital of O, consequently weakening the O-Pd bonding [25,70,71], which is consistent with the above XPS observations as well as previous report [23]. The downshift of the Pd d-band center and the decreased ΔE_O on Pd are proposed to be the possible origination for the higher ORR activity of NP-PdZr alloy than Pt/C and NP-Pd catalysts. Therefore, it is conclusive that alloying Pd with Zr could effectively tune the ORR reaction kinetics by appropriately modifying the electron structure of Pd, resulting

in superior ORR activity of Pd.

Based on the above the experimental observations, NP-PdZr surface alloy not only shows markedly enhanced overall ORR performance but also displays a better selectivity for ORR than methanol. It is suggested that the changes of Pd electronic structure is responsible for the enhanced the ORR performances. The specific structure integrity also plays a significant role for the improved ORR performances of NP-PdZr alloy in terms of easy transport of electrons and adsorbed reaction medium. Additionally, the stained surface of PdZr alloy caused by the formation of NP-PdZr surface alloy also contributes to alleviating the dissolution and redeposition of Pd.

4. Conclusions

In summary, nanoporous PdZr surface alloy with controllable bimetallic ratio has been successfully synthesized by a simple dealloying method. Electrochemical tests have revealed that the as-made NP-Pd₈₀Zr₂₀ surface alloy not only displays superior specific and mass activities toward ORR but also possesses higher structure stability compared with NP-Pd and commercial Pt/C catalysts. In addition, the NP-Pd₈₀Zr₂₀ also shows a unique methanol tolerance with almost no activity loss in the presence of 0.1 M methanol. The improved overall ORR performances of NP-Pd₈₀Zr₂₀ alloy could be ascribed to its specific structure integrity and continuity as well as the suitable changes of Pd electronic structure induced by alloying with Zr. Hence, the as-made NP-Pd₈₀Zr₂₀ surface alloy holds great practical potential in clean energy and environmental science fields with the obvious advantages of excellent ORR performances and facile preparation without involving complicated processes and assistance of organic reagents.

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Figure Captions:

Fig. 1. SEM (a and b), TEM (c), and HRTEM (d) images of the resulted sample by etching the PdZrAl alloy in 0.5 M NaOH solution for 48h at room temperature.

Fig. 2. XRD patterns of PdZrAl and the dealloyed sample. The standard patterns of Pd (JCPDS 65–2867), Zr (JCPDS 65–3366), PdAl₆ (JCPDS 42–1286), and Al (JCPDS 65–2869) are also attached for clear comparison.

Fig. 3. XPS data of Pd 3d (a) and Zr 3d (b) core levels for the NP–Pd₈₀Zr₂₀ alloy.

Fig. 4. (a) CV curve of NP–Pd₈₀Zr₂₀ alloy in 0.1 M N₂–purged HClO₄ solution. Scan rate: 50 mV s^{–1}. (b) Polarization curves for the ORR on NP–Pd₈₀Zr₂₀, NP–Pd, and Pt/C catalysts in the O₂–saturated 0.1 M HClO₄ solution at room temperature at 1600 rpm, Scan rate: 10 mV s^{–1}. (c) Specific kinetic current densities for all catalysts at different potentials. (d) Specific kinetic and mass kinetic current densities at room temperature for all catalysts at 0.9 V.

Fig. 5. CV curves (scan rate: 50 mV s^{–1}) and ORR polarization curves (scan rate: 10 mV s^{–1}) for NP–Pd₈₀Zr₂₀ (a and b), NP–Pd (c and d), and Pt/C (e and f) catalysts before and after 5, 000 potential cycles in 0.1 M oxygen–containing HClO₄ solution from 0.6 to 1.0 V vs RHE with the scan rate at 50 mV s^{–1}.

Fig. 6. ORR polarization curves of NP–Pd₈₀Zr₂₀ alloy in 0.1 M O₂–saturated HClO₄ solution without and with 0.1 M methanol at 1600 rpm, respectively. Scan rate: 10 mV s^{–1}.

Fig. 7. (a) The most stable adsorbed schematic model of O atoms adsorbed on Pd₁₃Zr₃ (111), Pd (111), and Pt (111) slabs. (b) The corresponding d band center and

ΔE_O .

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Fig. 1

Fig. 2

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Fig. 5

Fig. 6

Fig. 7

b

	Pd ₁₃ Zr ₃ (111)	Pd(111)	Pt(111)
d band center	-2.53eV	-1.95eV	-2.72eV
ΔE_o on fcc hollow site	-3.79eV/fcc	-4.33ev/fcc	-4.24ev/fcc

Figure Captions:

Fig. 1. SEM (a and b), TEM (c), and HRTEM (d) images of the resulted sample by etching the PdZrAl alloy in 0.5 M NaOH solution for 48h at room temperature.

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