PdPb bimetallic nanowires as electrocatalysts for enhanced ethanol electrooxidation

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ABSTRACT Less-expensive but efficient electrocatalysts are essential to accelerate the commercialization of fuel cells. Herein, ultrathin PdPb nanowires (PdPb NWs) with a diameter of around 3.5 nm were prepared by using a one-step hydrothermal method. The introduction of Pb in Pd-based bimetallic nanostructures produced high differences in the morphology from Pd nanoparticles (NPs) to various PdPb NWs. All the as-prepared PdPb NWs exhibited better electrocatalytic activity and durability than Pd NPs due to the synergistic effect. Especially, Pd₆₅Pb₃₅ possessed the highest current density of about 3460 mA mg_{Pd}^{−1} for the ethanol electrooxidation which was around 6.3 times higher than commercial Pd/C. The high-performance of Pd₆₅Pb₃₅ is attributed to the defect-rich and stable nanowire structure with optimized surface atomic arrangement, as evidenced by high resolution transmission electron microscopy measurements and long-time treatment in an acidic media. The differences in the morphologies and electrocatalytic activities of PdPb NWs with varied Pb contents have also been discussed and analyzed.

Keywords: PdPb nanowires, electronic structure, lattice defects, electrocatalysis, ethanol electrooxidation

INTRODUCTION

Direct ethanol fuel cells (DEFCs) have attracted widespread concern due to their high energy density, conversion efficiency, low cost and safety for storage [1,2]. Palladium (Pd) is a commonly used and promising anode catalyst for DEFCs [3–6]. However, the limited reserves, high price, sluggish reaction kinetics and poor tolerance to poisoning intermediates of Pb hinder its commercialization.

Compared with pure Pd, Pd-based bimetallic alloy catalysts can be a good choice, which can reduce the cost

and improve the electrocatalytic activity due to their synergistic effect between the two elements [7,8]. Hence, great efforts have been devoted to the syntheses of Pd-based bimetallic nanostructures, for example, Pd/Cu [9,10], Pd/Ag [11–13], Pd/Pb [14], Pd/Sn [15,16]. Especially, Pb has drawn increasing attention due to its stronger promoting effects on ethanol oxidation reaction (EOR), resulting in the geometric effect, the electronic effect as well as the bifunctional mechanism [17]. Additionally, high durability of the electrocatalyst is also a significant factor for its practical application [18,19]. Previous literatures demonstrated that the poisoning intermediates (such as carbonaceous residues) adsorbed on the catalyst surface would seriously reduce its catalytic activity [20]. Recent advances reveal that alloying Pd with Pb shows excellent tolerance to poisoning intermediates during the EOR by weakening the bond energy of Pd–CO or promoting the reaction more thoroughly.

Apart from the bifunctional mechanism, the morphology and structure of the materials also have a great influence on the performance [21–33]. Recently, some high-efficiency Pd-based nanostructures have been designed and fabricated like nanoflowers [13,25], nanocubes [26], nanosheets [27] and NWs [6,28,29]. Among them, one-dimensional (1D) nanostructures have attracted tremendous attention due to their unique properties such as large specific surface area, superior electron transport and high flexibility [20,30]. Besides, rich lattice defects in 1D NWs generated during their growth process can provide more active sites to improve the catalytic performance [15,20,29]. Therefore, if the superiorities of morphology and composition can be integrated to Pd-based bimetallic catalysts, it would greatly promote the development of DEFCs.

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Herein, we demonstrate a facile and efficient chemical co-reduction route to obtain 1D PdPb bimetallic nanowires (PdPb NWs). The composition and morphology of PdPb NWs could be easily controlled, and their tortuous structure has uniform diameter and high aspect ratios, which can maximize the utilization of Pd atoms. Experimental data shows that PdPb NWs possess large electrochemically active surface areas and exhibit greatly enhanced electrocatalytic activities toward ethanol electrooxidation compared with Pd nanoparticles (NPs) and commercial Pd/C. In addition, we found that the control experiments show that the introduction of Pb is the key factor to successfully form the NW structure.

EXPERIMENTAL SECTION

Materials and reagents

Palladium chloride (PdCl_2), lead nitrate ($\text{Pb}(\text{NO}_3)_2$), sodium chloride (NaCl), formic acid, polyvinylpyrrolidone (PVP) (molar weight = 58,000) and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd. All the chemicals used in this study were analytical grade and used without further purification. Doubly distilled water was used in the experiments, except ultrapure water (18.2 M Ω cm) for electrochemical measurements.

Synthesis of PdPb NWs

In a typical synthesis, PdCl_2 (30 mg), NaCl (25 mg), PVP (108 mg) and a certain amount of $\text{Pb}(\text{NO}_3)_2$ were dissolved in 20 mL of doubly distilled water, followed by 2 h vigorous stirring. Then, 3 mL formic acid (88 wt%) was added in the above solution and kept stirring for 5 min. After that, the resulting yellow solution was transferred into a Teflon-lined stainless-steel autoclave and kept in an oven at 150°C for 10 h. After cooling down to room temperature, the products were collected by centrifugation and washed with distilled water and ethanol for several times, and then PdPb NWs were obtained after drying at 60°C for 24 h. The amounts of $\text{Pb}(\text{NO}_3)_2$ in the synthetic solutions were 0, 5, 10, 15 and 20 mg and the corresponding PdPb products were named as Pd NPs, $\text{Pd}_{80}\text{Pb}_{20}$, $\text{Pd}_{65}\text{Pb}_{35}$, $\text{Pd}_{55}\text{Pb}_{45}$ and $\text{Pd}_{50}\text{Pb}_{50}$, respectively.

Characterization

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were measured with a JEOL JEM-2100 plus at an accelerating voltage of 200 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray (EDX) elemental mapping were carried out with a

JEM-F200 transmission electron microscope. The X-ray diffraction (XRD) patterns were investigated on a Rigaku Ultima IV X-ray diffractometer (XRD, Cu K α radiation λ = 0.15418 nm). X-ray photoemission spectroscopy (XPS) was recorded with an ESCALab220i-XL electron spectrometer. Inductively coupled plasma-optical emission spectrometry (ICP-OES) was conducted using an Optima 8000 instrument.

Electrochemical measurements

All the electrochemical measurements were performed in the CHI760E electrochemical station with a typical three-electrode cell at room temperature. A platinum foil was used as the counter electrode and a saturated calomel electrode (SCE) in acid solution or an Hg/HgO electrode in alkaline media as the reference electrode. PdPb NWs modified glass carbon electrodes (GCEs) with a diameter of 3 mm were employed as the working electrodes. The working electrodes were prepared by dropping 10 μL well-dispersed catalyst ink (1.0 mg sample in 1 mL ultrapure water) on the surface of bare GCEs. The working electrode was activated in 0.5 mol L $^{-1}$ H_2SO_4 solution with 50 mV s $^{-1}$ scan rate at room temperature and then performed in an aqueous solution of 1 mol L $^{-1}$ KOH containing 1 mol L $^{-1}$ $\text{C}_2\text{H}_5\text{OH}$ to investigate the electrooxidation of ethanol at a scan rate of 50 mV s $^{-1}$.

RESULTS AND DISCUSSION

The morphologies and structures of all the samples were investigated by TEM and HRTEM. The $\text{Pd}_{65}\text{Pb}_{35}$ and $\text{Pd}_{55}\text{Pb}_{45}$ were selected and characterized by HAADF-STEM. The HAADF-STEM (Fig. 1a) and TEM (Fig. 1b) images of $\text{Pd}_{65}\text{Pb}_{35}$ show that the as-prepared NWs are uniform and tortuous with a large aspect ratio. The NWs are about 3.5 ± 0.4 nm in width and hundreds of nanometers in length. However, the morphologies and structures of $\text{Pd}_{80}\text{Pb}_{20}$, $\text{Pd}_{55}\text{Pb}_{45}$ and $\text{Pd}_{50}\text{Pb}_{50}$ are different (Fig. S1). The Pd contents of the PdPb bimetallic samples were determined by ICP-OES to be 80.8, 64.5, 54.9 and 48.9 wt% for $\text{Pd}_{80}\text{Pb}_{20}$, $\text{Pd}_{65}\text{Pb}_{35}$, $\text{Pd}_{55}\text{Pb}_{45}$ and $\text{Pd}_{50}\text{Pb}_{50}$, respectively.

Pd NPs with the size of about 5 ± 2 nm were obtained without $\text{Pb}(\text{NO}_3)_2$ (Fig. S1a, e and i) and various morphologies were generated with the increasing content of Pb. If the content of Pb (Pb^{2+} in precursors) increased to twice stoichiometry of the $\text{Pd}_{65}\text{Pb}_{35}$, NW disappeared and the interconnected large particles formed. In addition, the $\text{Pd}_{55}\text{Pb}_{45}$ is net-work structured, as shown in Figs S1c, g and S2a. Obviously, Pb is the key factor to form the NW structure possibly due to the co-deposition feature of

Figure 1 Morphology and structure characterization of $\text{Pd}_{65}\text{Pb}_{35}$ NWs. (a) HAADF-STEM image, (b) TEM image and the corresponding SAED pattern, (c) HRTEM image and (d) HAADF-STEM elemental mappings of $\text{Pd}_{65}\text{Pb}_{35}$ NWs.

bimetallic nanostructure. In Fig. 1c, the lattice spacing of the $\text{Pd}_{65}\text{Pb}_{35}$ is ~ 2.33 Å corresponding to (111) lattice plane while that of the Pd NPs is 2.25 Å [34]. Further analysis reveals that all the as-prepared PdPb NWs have different lattice expansion of about 2.31, 2.39 and 2.43 Å for $\text{Pd}_{80}\text{Pb}_{20}$, $\text{Pd}_{55}\text{Pb}_{45}$ and $\text{Pd}_{50}\text{Pb}_{50}$, respectively (Fig. S1j–l). The small lattice expansion of the PdPb NWs should be attributed to the alloying action of Pd with Pb, whose lattice spacing is about 2.85 Å for the (111) plane. Moreover, the HRTEM image (Fig. 1b) reveals a large number of convex/concave area, stacking faults and kinks in $\text{Pd}_{65}\text{Pb}_{35}$ providing abundant lattice defects. This ultrafine NW structure not only facilitates the utilization of the Pd in the electrocatalysis but also improve the conduction of electrons in the catalytic process, thus accelerating the reaction kinetics [30].

The selected area electron diffraction (SAED) pattern of $\text{Pd}_{65}\text{Pb}_{35}$ (insert in Fig. 1b) exhibits continuous diffraction rings indicating a polycrystalline structure of $\text{Pd}_{65}\text{Pb}_{35}$ with a high crystalline nature [35,36]. The $\text{Pd}_{80}\text{Pb}_{20}$, $\text{Pd}_{55}\text{Pb}_{45}$ and $\text{Pd}_{50}\text{Pb}_{50}$ show similar results, as shown in the insert of Fig. S1b–d. The diffraction spots of Pd NPs SAED pattern is relatively blurred, due to the

small particle size (insert in Fig. S1a). The STEM-EDS elemental mapping was conducted to investigate the distribution of Pd and Pb in the bimetallic alloy. As shown in Fig. 1d, the mapping of $\text{Pd}_{65}\text{Pb}_{35}$ illustrates that both Pd and Pb distribute homogeneously through the whole NWs, confirming the alloyed feature of $\text{Pd}_{65}\text{Pb}_{35}$. The elemental mapping of $\text{Pd}_{55}\text{Pb}_{45}$ (Fig. S2b) shows a stronger signal of Pb indicating that there are more Pb atoms in $\text{Pd}_{55}\text{Pb}_{45}$ than $\text{Pd}_{65}\text{Pb}_{35}$.

The crystal structures and compositions of the as-prepared samples were investigated by XRD and XPS measurements. XRD patterns (Fig. 2a) of the samples demonstrate the successful formation of PdPb bimetallic nanostructures. For Pd NPs, the diffraction peaks at 39.9° , 46.5° , 67.9° and 82.1° match well with the standard face-centered cubic (fcc) Pd (JCPDS PDF No. 46-1043). While for PdPb NWs, these characteristic diffraction peaks have a slightly negative shift compared with the pure fcc-Pd. Moreover, the more content of Pb, the more negative shift of the diffraction peaks. These phenomena indicate the gradual increase of cell size with the continuous increase of Pb content in the PdPb bimetallic nanostructures [10,37]. The elaborate variation of inner

Figure 2 (a) XRD patterns of Pd NPs, Pd₈₀Pb₂₀, Pd₆₅Pb₃₅, Pd₅₅Pb₄₅ and Pd₅₀Pb₅₀, (b) XPS spectra of the Pd 3d region (Pd 3d_{5/2} and Pd 3d_{3/2}) and (c) Pb 4f region (Pb 4f_{7/2} and Pb 4f_{5/2}) of Pd₆₅Pb₃₅ NWs and (d) Pd 3d XPS spectra of Pd NPs, Pd₈₀Pb₂₀, Pd₆₅Pb₃₅, Pd₅₅Pb₄₅ and Pd₅₀Pb₅₀.

structure of the bimetallic nanostructures can also be reflected by the XPS results [38]. The high-resolution XPS spectrum of Pd in the Pd₆₅Pb₃₅ (Fig. 2b) exhibits two main peaks at binding energies (BE) of 334.96 and 340.26 eV, corresponding to the Pd 3d_{5/2} and Pd 3d_{3/2} of metallic Pd, respectively. Pd⁰ and Pd²⁺ are coexistence but the zerovalent state is predominant in the catalyst according to the Pd 3d peak. The slight Pd²⁺ is attributed to the formation of Pd–O_{ads} and the surface PdO, which are in good agreement with that of the reported Pd and Pd-based catalysts [8,39,40].

Moreover, another two peaks (Fig. 2c) located at 136.52 and 141.51 eV for Pd₆₅Pb₃₅ are attributed to the Pb 4f_{7/2} and 4f_{5/2}, respectively, and Pb is mainly in zerovalent state in the catalysts as well. Compared with the standard binding energy (BE) value of Pd NPs, a slightly negative shift of the Pd 3d BE of PdPb NWs is observed and Pd₆₅Pb₃₅ displays the most significant shift as shown in Fig. 2d. The BE shift demonstrates the formation of PdPb alloy which might be due to the electronic interactions between Pd and Pb. Electron transfer would occur between Pb and Pd due to the difference in the electronegativities of the two elements, leading to the decrease of

the d-band center and weakening the toxic intermediates adsorption onto the surface of the catalyst, then improving the catalytic performance of ethanol electro-oxidation [41].

In order to uncover the formation mechanism of the PdPb NWs, the intermediate products yielded at different reaction times from the synthesis system of Pd₆₅Pb₃₅ NWs were investigated by TEM and XRD (Fig. 3 and Figs S3, S4). A large number of NPs were obtained with a diameter of 5 ± 0.7 nm at $t = 15$ min (Fig. 3a) and the corresponding XRD pattern (Fig. S3) showed that the NPs were mainly composed of Pd atoms. At the same time, some NPs started to accumulate and connect with each other (marked by the red line in Fig. 3a) which was suggested to be the initial state of NWs. After 30 min, more and more short wavy nanorods formed, as shown in Fig. 3b. In addition, the XRD data reveals that a large amount of Pb²⁺ ions are reduced which may be the key factor in promoting the formation of PdPb NWs. As the reaction further proceeded, the short nanorods continued to grow, while most of NPs disappeared (Fig. 3c). When the reaction was extended to 3 h, the distinct NW structure of PdPb alloy formed (Fig. 3d). After further 3 h

Figure 3 TEM images of the intermediates from the synthetic system for $\text{Pd}_{65}\text{Pb}_{35}$ with different reaction times: (a) 15 min, (b) 30 min, (c) 60 min and (d) 3 h. The scale bars are 20 nm. (e) Schematic illustration of the formation mechanism of $\text{Pd}_{65}\text{Pb}_{35}$ NWs.

reaction process, the ultrafine NWs with a large aspect ratio were successfully fabricated (Fig. S4). Their morphology did not significantly change when the reaction time was extended to 10 h (Fig. 1b). It is worth noting that the composition of the intermediate products almost unchanged after 6 h reaction according to the analyses of XRD data in Fig. S3. The stable structure of $\text{Pd}_{65}\text{Pb}_{35}$ is beneficial to its catalytic performance. The schematic illustration of the growth mechanism of the PdPb NWs is shown in Fig. 3e.

The suitable concentration of reducing agent is crucial to the synthesis of nanomaterials, which can affect the reducing rate of the metal ions and then produce high influence on the morphology of obtained materials [34]. In this study, adjusted concentrations of formic acid (2 and 4 mL) were introduced as reducing agent to prepare the PdPb NWs (PdPb-Fa_2 and PdPb-Fa_4). The TEM images in Fig. S5 show that no obvious difference in the morphology but a smaller aspect ratio compared with the $\text{Pd}_{65}\text{Pb}_{35}$. The diffraction peaks of XRD patterns (Fig. S6) of the samples are located in the same value of 2θ indicating that PdPb-Fa_2 and PdPb-Fa_4 have similar crystal structure.

The electrochemical performance of the as-prepared catalysts for ethanol oxidation was investigated by a series of electrochemical measurements. Fig. 4a shows the cyclic voltammetry (CV) curves of PdPb bimetallic NWs and Pd NPs modified GCEs in $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$ solution at a scan rate of 50 mV s^{-1} . The peaks at -0.23 – 0.1 V (vs. SCE) were attributed to the hydrogen adsorption/desorption at the surface of catalysts and the reduction peak of the produced Pd oxide at around 0.4 V (vs. SCE) [10,42]. It is obvious that the reduction peaks of Pd oxide of PdPb alloy exhibit a little negative shift compared with the Pd NPs and the $\text{Pd}_{65}\text{Pb}_{35}$ has the largest shift among all the samples, suggesting that the surface of bimetallic alloys become more active and the surface atoms of $\text{Pd}_{65}\text{Pb}_{35}$ give the strongest interaction with the oxygen adsorbate [43,44].

The electrochemically active surface area (ECSA), an important parameter for electrocatalysts, was estimated by reduction region of Pd oxide based on the formula $\text{ECSA} = Q/(0.424 \times \text{Pd}_m)$, where Q stands for the corresponding electrical quantity of the integral of the peak from the reduction of Pd (II) oxide [15]. The calculated ECSAs are about 58, 62, 51, 36 and $32 \text{ m}^2 \text{ g}^{-1}$ for Pd NPs, $\text{Pd}_{80}\text{Pb}_{20}$, $\text{Pd}_{65}\text{Pb}_{35}$, $\text{Pd}_{55}\text{Pb}_{45}$ and $\text{Pd}_{50}\text{Pb}_{50}$, respectively. Furthermore, PdPb NWs (PdPb-Fa_2 and PdPb-Fa_4) obtained from the variation of reductant (formic acid) only has a relative smaller reduction region of Pd oxide than $\text{Pd}_{65}\text{Pb}_{35}$ (Fig. S7a), indicating a slight decrease in the ECSAs compared with that of $\text{Pd}_{65}\text{Pb}_{35}$. To evaluate the electrocatalytic performance of the PdPb NWs, the electrocatalytic behavior of ethanol was investigated in alkaline medium. The mass activity of the catalyst is usually used to evaluate the catalytic performance. In Fig. 4b, two well-defined anodic peaks can be observed in the process of electrooxidation of ethanol. The strong peak in the forward scan is attributed to the direct oxidation of ethanol which is usually used to characterize the electrocatalytic performance of the sample [20]. $\text{Pd}_{65}\text{Pb}_{35}$ exhibits the highest catalytic current density (mass activity) of $3460 \text{ mA mg}_{\text{Pd}}^{-1}$, which is about 6.3 times higher than the commercial Pd/C, while 1684, 2928, 2294 and $2046 \text{ mA mg}_{\text{Pd}}^{-1}$ for Pd NPs, $\text{Pd}_{80}\text{Pb}_{20}$, $\text{Pd}_{55}\text{Pb}_{45}$ and $\text{Pd}_{50}\text{Pb}_{50}$, respectively. PdPb- Fa_2 and PdPb- Fa_4 exhibit excellent electrocatalytic performances for EOR similar to $\text{Pd}_{65}\text{Pb}_{35}$ as shown in Fig. S7b. Another peak, observed during the reverse scan, implies the removal of the incompletely oxidized carbonaceous residues produced in the forward scan [20,45] and the ratio of I_f (current density of forward scan) to I_b (current density of backward scan) could be used to evaluate the catalyst tolerance

Figure 4 (a) CV curves of the PdPb NWs and Pd NPs modified GCEs in 0.5 mol L⁻¹ H₂SO₄ solutions at a scan rate of 50 mV s⁻¹. CV curves of the PdPb NWs and Pd NPs modified GCEs in 1 mol L⁻¹ KOH + 1 mol L⁻¹ C₂H₅OH normalized by the mass of Pd (b) and surface area (c). Scan rate: 50 mV s⁻¹. (d) Mass activities and I_f/I_b ratios of the PdPb NWs as well as Pd NPs.

towards the CO poisoning [26,46]. As depicted in Fig. 4d, Pd₆₅Pb₃₅ has the I_f/I_b ratio at 1.75, higher than those of Pd NPs (0.99), Pd₈₀Pb₂₀ (1.34), Pd₅₅Pb₄₅ (1.47) and Pd₅₀Pb₅₀ (1.40), indicating Pd₆₅Pb₃₅ possesses the excellent anti-poisoning property among all the samples. Moreover, the higher I_f/I_b values of PdPb NWs than that of Pd NPs imply that the addition of Pb in the catalyst changes the electronic structure of palladium and then reduces the adsorption energy of CO-like species [47], promoting the electrocatalytic performance.

It should be mentioned that Pd₆₅Pb₃₅ and Pd NPs have the similar ECSA but their electrocatalytic performances are different. For a better understanding of the catalytic performance, the electrocatalytic current densities normalized to the ECSAs are shown in Fig. 4c. Pd NPs show the lowest value of 2.90 mA cm⁻² while PdPb NWs can reach a higher value (4.70, 6.75, 6.37 and 6.39 for Pd₈₀Pb₂₀, Pd₆₅Pb₃₅, Pd₅₅Pb₄₅ and Pd₅₀Pb₅₀, respectively). This phenomenon reveals that the synergies between Pd and Pb show positive influence on the performance. Careful analyses reveal that there are many convex/concave regions and kinks observed on the Pd₆₅Pb₃₅ NWs from the HRTEM images (Fig. 1c). When a large Pb atom occupies the original Pd lattice position, the lattice

parameter expands, generating compressive strain, the d-band center decreases, and the adsorption capacity for the reaction intermediates declines [48]. Thus, the complex structure contains a large number of lattice defects which can further improve the electrocatalytic performance towards EOR [49].

Apart from the catalytic current density, Pd₆₅Pb₃₅ also exhibits the visible enhancement in the kinetics of EOR according to the most negative shift of the onset potential among all the samples [29] (Fig. 5a). Fig. 5b shows the CV curves of Pd₆₅Pb₃₅ at various scan rates. The forward scan peak current densities are enhanced with the increasing sweeping rate. With a detail analysis, there is a linear relationship between the forward scan peak current density and the square root of the sweep rate ($V^{1/2}$) (Fig. 5c), suggesting that the kinetics of the EOR on Pd₆₅Pb₃₅ follows a diffusion-controlled process [13,25]. After the CV test of 600 cycles, the morphology of the catalyst is still similar to the original Pd₆₅Pb₃₅ but with slight differences in the diameter of NWs and more networks formed, as shown in Fig. S8.

The durability of the samples toward EOR was investigated by the chronoamperometry technique at -0.1 V as shown in Fig. 5d and Fig. S7c. The polarization

Figure 5 (a) The comparison of onset potentials on various PdPb NWs and Pd NPs for EOR. (b) CV curves of the Pd₆₅Pb₃₅ modified GCE at different scan rates. (c) Corresponding plot of forward peak current *versus* the square root of the scan rate. (d) Chronoamperometric curves of the PdPb NWs and Pd NPs modified GCEs at -0.1 V.

Figure 6 (a) CV curves of the Pd₆₅Pb₃₅ modified GCE in 1 mol L⁻¹ KOH + 1 mol L⁻¹ C₂H₅OH; (b) mass activities and ratios of I_f/I_b after scanning different cycles in 0.5 mol L⁻¹ H₂SO₄.

currents of all the samples exhibit a rapid decay in the initial 10 s, which is probably attributed to the formation of the poisonous intermediate species during the EOR process in alkaline media [50]. After running for 1000 s, Pd₆₅Pb₃₅ remains at the highest current density of 1497 mA mg_{Pd}⁻¹ among all the samples. In addition, the PdPb NWs show better durability than the Pd NPs according to the electrochemical test data, indicating that the addition of Pb can improve the durability of the alloy. This matches well with the results of the I_f/I_b ratio.

In order to further confirm the relationship of electrocatalytic performance and structure for the Pd₆₅Pb₃₅, CV curves for EOR of Pd₆₅Pb₃₅ after sweeping different cycles in 0.5 mol L⁻¹ H₂SO₄ solution are shown in Fig. 6a. The forward peak current density shows a slight increase in the initial cycles due to the removal of impurities, like PVP molecules adsorbed on the surface of the Pd₆₅Pb₃₅ during the synthesis process, exposing more active sites [10]. The higher value of I_f/I_b (Fig. 6b) also indicates that Pd₆₅Pb₃₅ possesses good anti-poisoning property. Then,

the peak current declines significantly with the extension of the cycle number. The current density after 6 cycles reduced by 25.5% compared with that after 2 cycles, because the continuous CV treatment leads to the slight change of bimetallic structure of Pd₆₅Pb₃₅. The change in the arrangement of PdPb NWs reduces their anti-poisoning property, confirmed by the decreased value of I_p/I_b .

In addition, the CV curves of Pd₆₅Pb₃₅ soaked in 0.5 mol L⁻¹ H₂SO₄ for different times were used to analyze the structure stability of the catalyst. As shown in Fig. S9a, the forward peak current maintains at about 1950 mA mg⁻¹ even for the soaking time of 4 h. The same electrochemical test was conducted with Pd₅₀Pb₅₀, the highest Pb content among all samples, and the electrocatalytic performance exhibited a high difference at different times of acid-treatment (Fig. S9b). The results reveal that the surface of Pd₆₅Pb₃₅ has a reasonable atomic arrangement which can enhance the electrocatalytic performance and structural stability.

CONCLUSION

In summary, we demonstrated a facile strategy for preparing PdPb NWs with a large aspect ratio by using formic acid as a reducing agent. The electronic structure of Pd in PdPb NWs was optimized and adjusted by changing the introduced amount of Pb relative to Pd NPs. The introduction of Pb in PdPb nanostructures not only affected the morphology and structure but also improved the electrocatalytic activity of the catalyst for EOR due to the synergistic effect. All the as-prepared PdPb NWs showed higher current density and better durability than Pd NPs and commercial Pd/C. The highest catalytic current of 3640 mA mg_{pd}⁻¹ was observed for Pd₆₅Pb₃₅ NWs due to its unique structural features. These results are helpful to design and prepare efficient, less expensive and stable Pd-based bimetallic or trimetallic nanostructured electrocatalysts for fuel cells.

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PdPb双金属纳米线作为增强乙醇电氧化的电催化剂

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摘要 价格低廉且高效的电催化剂是加速燃料电池商业化的关键. 本文采用一步水热法制备出直径约3.5 nm的超细PdPb纳米线. 在钯基双金属纳米结构中引入铅后, 不同组成的PdPb纳米线与钯纳米颗粒的形貌差异较大. XRD、TEM、XPS和电化学表征结果证实, 由于双金属间的协同效应, PdPb纳米线的电催化活性和耐久性均优于钯纳米颗粒. 其中, Pd₆₅Pb₃₅的乙醇电氧化电流密度最高, 可达3460 mA mg_{Pd}⁻¹, 约为商业Pd/C的6.3倍. HRTEM测试和经酸性介质长期处理后的表征结果显示, Pd₆₅Pb₃₅表面原子的优化排列和丰富的缺陷使其表现出高性能. 此外, 本文讨论和分析了不同铅含量的PdPb纳米线之间形貌和电催化活性的差异.