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Article

Boosting fuel cell catalysis by surface doping of W on Pd nanocubes

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ABSTRACT

The development of active and durable non-Pt electrocatalysts with well-defined microstructure is of great importance to both fuel cell applications and fundamental understanding. Herein, we report a surface-doping process to prepare well-defined W-doped Pd nanocubes with a tunable atomic percent of W from 0 to 1.5% by using the Pd nanocubes as seeds. The obtained 1.2%W-doped Pd nanocubes/C exhibited greatly enhanced electrocatalytic performance toward oxygen reduction reaction in alkaline media, presenting an enhancement factor of 4.7 in specific activity and 2.5 in mass activity compared to the activity of a commercial Pt/C catalyst. The downshift of the d-band center due to a negative charge transfer from W to Pd intrinsically accounts for such improvement in activity by weakening the adsorption of reaction intermediates. Also, the 1.2%W-doped Pd nanocubes/C showed superior catalytic properties for the ethanol oxidation reaction, showing great potential for serving as a bifunctional electrocatalyst in fuel cells.

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1. Introduction

As the oxygen reduction reaction (ORR) is a rate-determining process in a number of electrochemical energy conversion devices ranging from fuel cells to metal-air batteries, highly active and durable electrocatalysts to accelerate the sluggish kinetics of ORR are the key to improving the performance of these devices [1–3]. Up to now, Pt-based nanocatalysts represent the most effective electrocatalysts toward ORR, and this can be ascribed to their unique electronic structure and excellent chemical stability [4–7]. However, the pro-

hibitive cost and increasing scarcity of Pt has greatly hindered the widespread commercialization of the associated devices. As a result, finding non-Pt electrocatalysts with superior activity toward ORR and durability is technologically important [8–12].

Palladium (Pd), which not only possesses a similar electronic structure and chemical stability to Pt, but also is more abundant than Pt, has thus been regarded as a promising alternative electrocatalyst [13–20]. However, Pd intrinsically binds oxygenated species too strongly, as demonstrated by prior experimental and theoretical studies, leading to difficulty in releasing the adsorbed intermediates and thus insufficient

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catalytic activity toward ORR [21,22]. So far, a few strategies have been exploited to boost the catalytic activity of Pd-based electrocatalysts toward ORR by weakening the binding of adsorbed oxygenated species, e.g., alloying transition metals (Fe, Co, Ni, etc.) with Pd, introducing surface strain, or tuning the microstructure [23–28]. Despite great progress in improving the catalytic properties, the complex structural features of most reported Pd-based electrocatalysts prevent a clear understanding of this enhancement in catalytic activity. It is thus highly desirable to develop improved Pd-based electrocatalysts with well-defined microstructure. Herein, we report a surface-doping process to prepare well-defined W-doped Pd nanocubes with a tunable atomic percent of W from 0 to 1.5% by using Pd nanocubes as seeds. The obtained 1.2%W-doped Pd nanocubes/C displayed substantially improved electrocatalytic performance toward the ORR and the ethanol oxide reaction (EOR) in alkaline media. Based upon the well-defined microstructure, the origin of this enhancement in catalytic activity was further elucidated by analyzing the surface electronic structure.

2. Experimental

2.1. Chemicals

Sodium tetrachloropalladate (II) (Na_2PdCl_4 , 98%), poly(vinyl pyrrolidone) (PVP, $M_w \approx 55000$), potassium bromide (KBr, $\geq 99.0\%$), L-ascorbic acid (AA, $\geq 99.0\%$), palladium (II) acetylacetonate ($\text{Pd}(\text{acac})_2$, 99%), and tungsten hexacarbonyl ($\text{W}(\text{CO})_6$, 97%) were all obtained from Sigma-Aldrich. Ethanol ($\text{C}_2\text{H}_5\text{OH}$) and benzyl alcohol ($\text{C}_7\text{H}_8\text{O}$) were all purchased from Sinopharm Chemical Reagent Co. Ltd (Shanghai, China). All of the chemicals were used without further purification. Ultrapure Millipore water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) was used in all our experiments.

2.2. Synthesis of Pd nanocubes

In a typical synthesis, 8.0 mL of an aqueous solution containing 105 mg of PVP, 60 mg of AA, and 300 mg of KBr were placed in a 20-mL vial and pre-heated to 80°C in an oil bath with magnetic stirring for 10 min. Subsequently, 3.0 mL of an aqueous solution containing 57 mg of Na_2PdCl_4 were quickly injected with a pipette. After the vial had been capped, the reaction was continued for 3 h. Pd nanocubes of roughly 11 nm in size were obtained. The product was collected by centrifugation, washed three times with water, and re-dispersed in 11 mL of benzyl alcohol (1.8 mg mL^{-1}) for further use.

2.3. Synthesis of W-doped Pd nanocubes

In a typical synthesis of 1.2%W-doped Pd nanocubes, 10.0 mL of benzyl alcohol solution containing 3.6 mg of Pd cubic seeds, 5 mg of $\text{Pd}(\text{acac})_2$, and 4.0 mg of $\text{W}(\text{CO})_6$ were placed in a 25-mL three-necked bottle and heated at 180°C under a N_2 atmosphere. The 0.8 and 1.5%W-doped Pd nanocubes were synthesized using the same procedure except for the addition

of 2.0 and 8.0 mg of $\text{W}(\text{CO})_6$, respectively. After the reaction had proceeded for 1 h, the obtained products were collected by washing the sample with ethanol three times. The sample was finally dispersed into ethanol prior to characterization and electrochemical tests.

2.4. Characterization

Transmission electron microscopy (TEM) images were taken using a Hitachi HT7650 microscope operated at 120 kV. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images and energy-dispersive X-ray spectroscopy (EDX) analyses were collected on a JEOL ARM-200F field-emission transmission electron microscope operating at an accelerating voltage of 200 kV using Cu-based TEM grids. X-ray diffraction (XRD) characterization was performed using a Philips X'Pert Pro X-ray diffractometer with a monochromatized Cu K_α radiation source and a wavelength of 0.1542 nm. Compositional analyses were carried out by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Atomscan Advantage, Thermo Jarrell Ash, USA). Surface valence band spectra were collected by high-resolution X-ray photoemission spectroscopy (XPS) on the nanoparticle monolayers. These were recorded on an ESCALAB-250 spectrometer having a monochromatic Al K_α X-ray source ($h\nu = 1486.6 \text{ eV}$), with a spot size of 500 μm .

2.5. Electrochemical measurements

2.5.1. Preparation of working electrodes

Prior to the measurements, the catalyst was prepared by loading the sample on Vulcan XC-72 carbon support with a Pd content of 20 wt%. The catalyst ink was prepared by dispersing as-prepared catalyst in a mixture containing 0.745 mL of deionized water, 0.250 mL of isopropyl alcohol, and 0.005 mL of Nafion (5%). Then 10 μL of the suspension were deposited on the RDE. For the commercial Pt/C and Pd/C catalysts (20 wt% metal loading), the dispersion solution (5 mg mL^{-1}) was prepared and sonicated for 1 h. Four μL of the dispersion were then transferred onto the glassy carbon RDE with a geometric area of 0.196 cm^2 . The total loading amount of Pd or Pt for all measured catalysts was 4 μg for ORR and 2 μg for EOR.

2.5.2. Electrocatalytic measurements

Electrochemical measurements were carried out with a three electrode system on an IM6 electrochemical workstation (Zahner, Germany). A Pt wire and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All potentials were converted to values with reference to reversible hydrogen electrode (RHE). Cyclic voltammograms (CVs) were processed in KOH (0.1 mol L^{-1}) solutions under a flow of N_2 at a sweep rate of 50 mV s^{-1} . The ORR measurements were performed in O_2 -saturated 0.1 M KOH at a rotation rate of 1600 r min^{-1} and a sweep rate of 10 mV s^{-1} . A durability test was performed at room temperature by applying cyclic sweeps between 0.4 and $1.0 V_{\text{RHE}}$ in O_2 -saturated 0.1 mol L^{-1} KOH at a sweep rate of 100 mV s^{-1} . The mass and specific activities were

obtained by normalizing the kinetic current to the loading Pd or Pt mass and real active surface area. The EOR measurements were conducted in an electrolyte solution containing 1.0 mol L⁻¹ KOH and 1.0 mol L⁻¹ ethanol at a scan rate of 50 mV s⁻¹. Chronoamperometric measurements were conducted at 0.75 V_{RHE} in 1.0 mol L⁻¹ KOH and 1.0 mol L⁻¹ ethanol solution and held for 1000 s.

3. Results and discussion

3.1. Morphology and microstructure

Typically, the W-doped Pd nanocubes were synthesized via a two-step seed-mediated growth approach. In the first step, Pd nanocubic seeds with an average diameter of 11.0 nm [Fig. S1] were prepared using a protocol developed by Jin et al. [29]. The surface doping of W was then implemented by the addition of W(CO)₆, together with Pd(acac)₂, into a suspension of the pre-formed Pd nanocubic seeds in benzyl alcohol at 180 °C for 1 h [Fig. 1(a), see Supporting Information for details]. The XRD pattern of the sample [Fig. S2] obtained using the standard

procedure corresponds well to face-centered cubic (fcc) Pd. A representative TEM image of the sample [Fig. 1(b)] clearly shows the well-preserved cubic shape of the product after the doping process. The average size of these nanocubes was determined to be 13.0 nm by counting more than 100 particles [Fig. S3], implying the formation of a 1-nm-thick overgrowth layer along each side of the cube. The HAADF-STEM image recorded from an individual nanocube [Fig. 1(c)] exhibits well-defined fringes corresponding to the {200} plane of fcc Pd. The compositional distribution was detected by EDX. As shown in Fig. 1(d), the EDS line-scanning profile definitely indicates that the W element is located mainly at the external surface of the cubes, suggesting the successful formation of W-doped Pd nanocubes. We further estimate that the depth of the doping layer is ca. 5 atomic layers according to the thickness of the overgrowth layer and the distribution profile of the W. The atomic percent of W in the nanocubes was determined to be 1.2%, by ICP-AES (hereafter we denote the sample as 1.2%W-doped Pd nanocubes for convenience). XPS analysis [Fig. 1(e)] also confirms the presence of Pd and W in the obtained nanocubes. As shown in Fig. 1(e), the peaks at 341.1 and

Fig. 1. (a) Schematic illustration of the formation process of W-doped Pd nanocubes. (b) TEM image of W-doped Pd nanocubes. (c) HAADF-STEM image of an individual W-doped Pd nanocube. (d) EDX line-scanning profile of an individual W-doped Pd nanocube. (e) Pd and W XPS spectra recorded from the W-doped Pd nanocubes.

335.9 eV can be assigned to metallic Pd $3d_{3/2}$ and Pd $3d_{5/2}$ peaks, respectively [30]. W is present in both the oxidized state and the metallic state, with peaks at 37.8 and 35.7 eV ascribed to $W^{5+} 4f_{5/2}$ and $W^{5+} 4f_{7/2}$, and 34.4 and 32.2 eV ascribed to metallic W $4f_{5/2}$ and W $4f_{7/2}$, respectively [31]. The peak at 41.5 eV is assigned to the WO_x loss feature, which is in good agreement with previous studies [32].

For comparison, W-doped Pd nanocubes with different doping concentrations were synthesized by simply varying the amount of $W(CO)_6$ precursor. When 2.0 and 8.0 mg of $W(CO)_6$ were added, the W concentrations were 0.8 and 1.5 at%, respectively. TEM images (Fig. S4(a) and (b)) further demonstrate the formation of W-doped Pd nanocubes. Importantly, size distribution histograms (Fig. S4(c) and (d)), obtained by counting more than 100 particles for each sample, clearly show similar average sizes for W-doped Pd nanocubes with different concentrations of W. The doping of W was also confirmed by W 4f XPS spectra (Fig. S4(e) and (f)). The WO_x loss feature was not found for the 0.8%W-doped Pd nanocubes, which may be related to the low W content. Notably, the Pd XPS $3d_{3/2}$ peak position shifted to a lower binding energy with an increase in W content, which can be attributed to a negative charge transfer from W to Pd. Such W-doped Pd nanocubes with similar sizes thus make them an ideal platform to investigate the effects of doping.

3.2. Electrocatalytic activity

The electrocatalytic ORR properties of W-doped Pd nanocubes were then evaluated using the rotating disk electrode (RDE) method. Prior to the measurement, the catalyst was prepared by loading the sample on a Vulcan XC-72 carbon support. For comparison, the ORR properties of Pd nanocubes/C, commercial Pt/C, and Pd/C (20 wt% Pd or Pt nanoparticles with an average size of ~ 3 nm on Vulcan XC-72 carbon) were also measured. Fig. S5 shows CVs of different catalysts conducted at room temperature in a N_2 -saturated 0.1 mol L^{-1} KOH solution with a sweep rate of 50 $mV s^{-1}$ in the potential range 0.16–1.26 V versus RHE (V_{RHE}). As hydrogen can penetrate into the Pd lattice, the electrochemical surface active area (ECSA) of Pd-based catalysts was calculated based on the charge of the reduction of PdO at around 0.72 V_{RHE} with correction for the double-layer, assuming 0.405 $mC cm^{-1}$ for the reduction of a monolayer of PdO on the catalyst surface [33]. For commercial Pt/C, the ECSA was estimated based on the charge associated with the desorption of hydrogen. The specific ECSAs were determined to be 40.5, 48.5, 25.7, 23.7, 21.1 and 20.6 $m^2 g^{-1}_{Pd/Pt}$ for commercial Pt/C, Pd/C, Pd nanocubes/C, 0.8%W-doped Pd nanocubes/C, 1.2%W-doped Pd nanocubes/C, and 1.5%W-doped Pd nanocubes/C, respectively. Of note, the potential of the $Pd(OH)_2$ reduction peak follows the

Fig. 2. (a) Corresponding positive-going ORR polarization curves recorded in an O_2 -saturated 0.1 mol L^{-1} KOH solution with a sweep rate of 10 $mV s^{-1}$ and a rotation rate of 1600 $r min^{-1}$. (b, c) Specific and mass ORR activities given as kinetic current densities normalized to the ECSAs and metal masses of the catalysts, respectively. (d) Comparison of durability between commercial Pt/C and 1.2%W-doped Pd nanocubes. The comparison is based on the mass activity at 0.9 V_{RHE} . The color scheme in (a) applies to all other graphs.

trend $\text{Pd/C} < \text{Pd nanocubes/C} < 1.5\% \text{ W-doped Pd cubes/C}$, indicating weak adsorption on W-doped Pd nanocubes [15]. To compare the catalytic activities of these catalysts toward ORR, positive going ORR polarization curves were recorded at room temperature in an O_2 -saturated 0.1 mol L^{-1} KOH solution, as shown in Fig. 2(a). The specific and mass activities of these catalysts were then derived by normalizing the kinetic current densities, which were obtained according to the Koutecky-Levich equation, against the ECSA and Pd or Pt mass, respectively. As shown in Fig. 2(b) and (c), the 1.2%W-doped Pd nanocubes exhibit the highest specific and mass activities among these catalysts. At $0.9 \text{ V}_{\text{RHE}}$, the specific activity of 1.2%W-doped Pd nanocubes/C was 1.18 mA cm^{-2} , which was 4.7, 6.6, 2.7, 1.6 and 1.4 times higher than that of commercial Pt/C (0.25 mA cm^{-2}), commercial Pd/C (0.18 mA cm^{-2}), Pd nanocubes/C (0.43 mA cm^{-2}), 0.8%W-doped Pd nanocubes/C (0.72 mA cm^{-2}), and 1.5%W-doped Pd nanocubes/C (0.87 mA cm^{-2}), respectively. It should be noted that the specific activity of the 1.2%W-doped Pd nanocubes/C catalyst surpassed most reported Pd-based catalysts for alkaline ORR [34–40]. The mass activity of these catalysts also showed the same trend as the specific activity. At $0.9 \text{ V}_{\text{RHE}}$, the 1.2%W-doped Pd nanocubes/C exhibited a mass activity of $0.25 \text{ A mg}^{-1}_{\text{Pd}}$, 2.5 times greater than that of commercial Pt/C ($0.10 \text{ A mg}^{-1}_{\text{Pt}}$).

We further investigated the long-term durability of the 1.2%W-doped Pd nanocubes/C through an accelerated durability test (ADT) at room temperature, and benchmarked it with commercial Pt/C catalyst. As shown in Fig. 2(d), the 1.2%W-doped Pd nanocubes still maintained a mass activity of $0.21 \text{ A mg}^{-1}_{\text{Pd}}$ after 10,000 cycles in O_2 -saturated conditions, showing a decrease of 14.8% with respect to the initial activity. By contrast, Pt/C lost 40.0% of its initial mass activity. Generally, the durability of catalytic properties is highly dependent on structural stability. We then checked the morphologies of these catalysts before and after 10,000 electrochemical cycles by TEM (Fig. S6). Unlike the serious aggregation found for the commercial Pt/C catalyst, the morphology of the 1.2%W-doped Pd nanocubes showed negligible change, suggesting superior

durability for 1.2%W-doped Pd nanocubes/C catalyst.

In order to develop a deeper understanding of the improved specific activity of the W-doped Pd nanocubes toward ORR, we experimentally analyzed the variation of electronic structures for the W-doped Pd nanocubes by surface valence-band photoemission spectra using high-resolution XPS. As shown in Fig. 3, the positions of d-band centers (with regard to Fermi level) for W-doped Pd nanocubes monotonously shifts downwards from -2.49 to -3.08 eV as the W content increases from 0 to 1.5%, consistent with the positive shift trend for the reduction potential of $\text{Pd}(\text{OH})_2$. The downshifting of d-band centers with increasing W content can be ascribed to the accumulated negative charge density of the Pd atoms due to a negative charge transfer from W to Pd [41,42]. In principle, the downshift of d-band centers can pull more of the antibonding states below the Fermi level, which in turn weakens the adsorption of reaction intermediates [43–45]. As such, it can be concluded that the downshifting of d-band centers arising from the doping of W is an intrinsic cause for the improved specific activity of 1.2%W-doped Pd nanocubes toward ORR given that the Pd binds oxygenated species too strongly [46,47]. It is noted that the catalytic activity of W-doped Pd nanocubes shows a volcano-like variation when further increasing the content of W to 1.5%, which can be rationalized based on the Sabatier principle [48].

Finally, we evaluated the electrocatalytic performance of the 1.2%W-doped Pd nanocubes/C toward the EOR in alkaline medium, a half reaction at the anode of direct ethanol fuel cells (DEFCs). As shown in Fig. 4(a), the catalytic activities of the catalysts were characterized by CV in a mixture of 1.0 mol L^{-1} KOH and 1.0 M ethanol aqueous solution. The 1.2%W-doped Pd nanocubes/C showed the highest forward peak current density of $6.6 \text{ A mg}^{-1}_{\text{Pd}}$, which was 2.2 and 5.1 times higher than those for Pd nanocubes/C ($3.0 \text{ A mg}^{-1}_{\text{Pd}}$) and commercial Pd/C ($1.3 \text{ A mg}^{-1}_{\text{Pd}}$), respectively. Such greatly enhanced catalytic activity of 1.2%W-doped Pd nanocubes/C can be attributed to surface doping with W, which downshifts the d-band center of the catalyst and thus facilitates the efficient release of free Pd active

Fig. 3. Surface valence band photoemission spectra of pure Pd nanocubes and Pd nanocubes with different amounts of W doping. The d-band centers are marked with white lines.

Fig. 4. (a) CVs of 1.2%W-doped Pd nanocubes/C, Pd nanocubes/C and commercial Pd/C in 1.0 mol L⁻¹ KOH + 1.0 mol L⁻¹ ethanol solution. (b) Chronoamperometric measurements of 1.2%W-doped Pd nanocubes/C and commercial Pd/C. The color scheme in (a) applies to both graphs.

sites by weakening the adsorption of carbonyl species. Chronoamperometry (CA) was employed to evaluate the stability of these catalysts. As shown in Fig. 4(b), initial rapid decreases in current density were observed for both 1.2%W-doped Pd nanocubes/C and Pd/C catalysts, which could be ascribed to the accumulation of strongly adsorbed reaction intermediates on the surface active sites. Importantly, the 1.2%W-doped Pd nanocubes/C showed much greater durability with respect to commercial Pd/C catalyst after a 1000-s durability test. Taken together, we have demonstrated 1.2%W-doped Pd nanocubes as an excellent catalyst for catalyzing both ORR and EOR in DEFCs with both superb catalytic activity and durability.

4. Conclusions

In conclusion, we have demonstrated a surface-doping process to prepare well-defined W-doped Pd nanocubes with a tunable atomic percent of W from 0 to 1.5% by using the Pd nanocubes as seeds. Compared with commercial Pt/C catalyst, the 1.2%W-doped Pd nanocubes/C shows 4.7 and 2.5-fold enhancement in specific activity and mass activity, respectively. Moreover, even after 10,000 cycles of accelerated durability test in O₂-saturated conditions, the 1.2%W-doped Pd nanocubes/C catalyst presents a drop of 14.8% in mass activity, compared to a large drop of 40.0% for commercial Pt/C. In catalyzing EOR, the 1.2%W-doped Pd nanocubes/C catalyst exhibits a peak current density of 6.6 A mg⁻¹_{Pd}, which is 5.1 and 2.2 times higher than for commercial Pd/C and Pd nanocubes/C, respectively. The 1.2%W-doped Pd nanocube catalyst also displays a superior catalytic stability toward EOR compared to commercial Pd/C. The improved catalytic activity of the W-doped Pd nanocubes/C catalyst can be ascribed to the optimized d-band center based on analysis of the electronic structure, which effectively regulates the adsorption of reaction intermediates on the surface of the catalyst. We believe that our work not only provides a promising bifunctional electrocatalyst for fuel cells but also offers a general strategy for the design of optimized well-defined heterogeneous catalysts by a surface-doping process.

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Graphical Abstract

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Boosting fuel cell catalysis by surface doping of W on Pd nanocubes

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W-doped Pd nanocubes were synthesized by a surface-doping process using Pd nanocubes as seeds. The W-doped Pd nanocubes showed substantially improved fuel cell catalysis, including the alkaline oxygen reduction reaction and the ethanol oxidation reaction, which can be attributed to a downshift of the d-band center of the catalyst due to negative charge transfer from W to Pd.

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通过表面钨掺杂大幅提升钯纳米立方体的燃料电池催化性能

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摘要: 发展兼具高活性和高稳定性的规整非铂电化学催化剂无论对于燃料电池的推广应用还是基础研究都具有重要意义。我们将钯纳米立方体(Pd nanocubes)作为晶种, 使用表面掺杂的手段制备了一种表面结构规整的钨掺杂钯纳米立方体(W-doped Pd nanocubes)。通过改变合成过程中所加入羧基钨前驱体的量以调控表面钨的原子比例, 继而获得了钨原子比例分别为0%, 0.8%, 1.2%, 1.5%的纳米立方体。所制W-doped Pd nanocubes/C催化剂在碱性条件下的氧还原反应中表现出优异性能, 其中1.2%W-doped Pd nanocubes/C催化剂性能最佳, 在0.9 V_{RHE}时比活性达1.18 mA cm⁻², 质量活性达0.25 A mg⁻¹_{Pd}, 分别是商业Pt/C催化剂的4.7倍和2.5倍。研究表明, 随着钨的掺杂量从0%增至1.5%, 钨掺杂钯纳米立方体的d带中心从-2.49 eV逐渐降至-3.08 eV。同时, 光电子能谱结果表明, 随着钨掺杂量的增加, 钯的3d峰位向低能逐渐偏移, 说明了钨掺杂导致了电荷由钨转向钯。而d带中心的下移能够将更多的反键态拉下费米能级, 继而导致反应中间体的吸附减弱。因此, 由钨到钯的电荷转移导致的d带中心的下移, 继而引起的反应中间体对催化剂的吸附作用变弱是氧还原催化活性增强的原因。而过高的W掺杂(1.5%)导致活性的降低也可以用Sabatier规则解释。在循环测试10000圈之后, 1.2%W-doped Pd nanocubes/C催化剂的质量活性仅仅减少了14.8%, 而商业Pt/C催化剂减少了40%, 可见其具有极佳的稳定性。而且循环测试之后的透射电镜表征显示, 相比于团聚严重的商业Pt/C催化剂, 1.2%W-doped Pd nanocubes/C催化剂仍然分散良好, 其形貌也几乎没有发生变化。此外, 该催化剂对乙醇氧化反应也表现出优异的性能。在1.0 mol L⁻¹氢氧化钾和1.0 mol L⁻¹乙醇混合溶液中, 测试峰电流达6.6 A mg⁻¹_{Pd}, 是Pd nanocubes/C催化剂的2.2倍, 商业Pd/C催化剂的5.1倍。这同样得益于适量钨掺杂所导致的催化剂d带中心下移引起的含碳中间体吸附的削弱。经过1000 s的稳定性测试, 1.2%W-doped Pd nanocubes/C同样表现出高于商业Pd/C催化剂的稳定性。优异的氧还原和乙醇氧化性能表明所制1.2%W-doped Pd nanocubes/C是一种极具潜力的双功能燃料电池催化剂。

关键词: 钯基金属催化剂; 表面掺杂; 氧还原; 乙醇氧化; d带中心

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