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Article

Enhanced oxygen reduction reaction performance over Pd catalysts by oxygen-surface-modified SiC

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ABSTRACT

Obtaining a detailed understanding of the surface modification of supports is crucial; however, it is a challenging task for the development and large-scale fabrication of supported electrocatalysts that can be used as alternatives to Pt-based catalysts for the oxygen reduction reaction (ORR). In this study, commercial silicon carbide (SiC) was modified through surface oxidization (O-SiC) to support the use of Pd nanoparticles (Pd NPs) as electrocatalysts for ORR. The obtained Pd/O-SiC catalysts exhibited better ORR activity, stronger durability, and higher resistance to methanol poisoning than that exhibited by commercial Pt/C. The role of the support in enhancing the ORR performance, especially the oxidization of SiC surfaces, was discussed in detail based on the experimental characterizations and density functional theory calculations. The underlying mechanism of the superior ORR performance of Pd/O-SiC catalysts was attributed to the charge transfer from SiC_xO_y to Pd NPs on the surfaces of SiC and the strong metal-support interactions (SMSIs) between Pd and SiC_xO_y. The charge transfer enhanced the ORR activity by inducing electron-rich Pd, increased the adsorption of the key intermediate OOH, and decreased the Gibbs free energy of the critical ORR step. Furthermore, SMSIs enhanced the ORR stability of the Pd/O-SiC catalyst. This study provided a facile route for designing and developing highly active Pd-based ORR electrocatalysts.

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1. Introduction

Fuel cells have attracted significant research interest as clean energy technology owing to their high efficiency and low emissions [1–4]. Pt/C is used as a cathodic oxygen reduction reaction (ORR) catalyst in state-of-the-art fuel cells [1,5–7]. However, the high cost, limited Pt reserves, and low stability of commercial Pt/C hinder their widespread use in fuel cells [8,9]. Thus, new strategies are needed to develop Pt-free ORR catalysts. The electron structure and chemical properties of Pd are

similar to those of Pt; however, Pd reserves are 50 times higher than Pt reserves [10]. Moreover, Pd has an excellent resistance against methanol and carbon monoxide poisoning [11]. These characteristics make Pd a promising alternative to Pt in ORR catalysts. However, the ORR activity of commercial Pd/C catalysts is lower than that of the commercial Pt/C. Therefore, several research have focused on improving the activity of Pd-based ORR catalysts.

Enhancing the ORR activity of Pd-based catalysts has two aspects. One aspect involves the alloying of Pd with transition

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metals, such as Co [12,13], Fe [13,14], Au [8,15], Cu [8,15,16], Ni [1,17,18], Mo [19], and W [20]. However, bimetallic or polymetallic electrocatalysts often suffer from undesirable performance owing to the limited interaction between different components [1]. The other aspect is to load Pd on various supports [21–24] that are not based on carbon. Carbon corrosion experienced by carbon supports during fuel cell operation under harsh conditions leads to the migration and agglomeration of catalyst particles, induces the loss of catalytic activity, and decreases the durability of cells [4,25,26]. Some alternative support materials enhance the stability of catalysts. Our previous work [22] showed that after loading Pd NPs on TiO₂ modified with oxygen vacancies (TiO₂-V_O), strong metal–support interactions (SMSIs) between Pd NPs and TiO₂-V_O occurred and changed the electronic structure of Pd NPs [27]. The electron-rich Pd obtained through electron transfer from the support to Pd NPs exhibits excellent ORR activity. However, the complex TiO₂-V_O preparation and weak charge transfer from TiO₂-V_O to Pd NPs limit the widespread application of Pd/TiO₂-V_O catalysts. Therefore, it is necessary to develop strong electron-donating supports by applying a simple fabrication method to tune the electronic structure of Pd and further improve the ORR performance.

Previously reported studies [28–30] have demonstrated that SiO₂ supplies electrons to Pd that generates electronegative Pd when Pd is loaded onto SiO₂. Our previous work [21] showed that SiO₂ enhanced the ORR activity in an alkaline solution; however, the ORR stability was poor. Compared with SiO₂, SiC has an electron-donating activity similar to that of metal NPs [31] and higher chemical and electrochemical durability [32–36]. Thus, SiC has attracted considerable attention as a catalyst support in fuel cells in recent years [32,33,37,38]. The interaction between metals and SiC was weak [36,39]; therefore, SiC with specific morphologies [40] or with modified surfaces (oxidization [39,41,42] or Ti coating [38]) were synthesized to anchor metal NPs and to enhance physical or chemical interactions. However, the preparation of these SiC-based supports was either complex or costly. Surface oxidization of SiC during preparation, preservation, or application under aerobic conditions was inevitable [33]. The above analysis indicates that SiC with oxygenic groups on their surfaces generated under mild conditions are promising supports for Pd-based ORR catalysts owing to their facile and large-scale preparation and strong interaction with metals. To the best of our knowledge, the effect of oxygenic groups, which are present on SiC surfaces, on the ORR performance has not been investigated yet. Hence, a detailed investigation on the effects of these oxygenic groups on ORR is essential for understanding, designing, and developing SiC-supported catalysts with excellent ORR performance.

In this study, Pd NPs were loaded onto O-SiC using a simple deposition precipitation method. The ORR performance of the Pd/O-SiC catalysts in a solution (0.1 mol/L KOH) was superior than that of the commercial Pt/C. By combining experiments with density functional theory (DFT) calculations, the underlying mechanism for achieving excellent ORR activity of Pd/O-SiC was revealed. The excellent ORR activity of Pd/O-SiC was ascribed to the charge transfer from O-SiC to Pd NPs. The SMSIs

between the Pd NPs and O-SiC improved the stability of the catalysts.

2. Experimental section

2.1. Materials

SiC (99.9%, 40 nm), PdCl₂ (>99%), KOH (analytical purity), and NaBH₄ (analytical purity) were purchased from Sigma-Aldrich. Commercial Pt/C (20 wt% Pt) and Pd/C (10 wt% Pd) were obtained from Alfa Aesar. The reagents were used without further purification.

2.2. Preparation of Pd/O-SiC catalysts

Pd/O-SiC was synthesized using a modified deposition precipitation method [21]. First, SiC (40 mg) and PdCl₂ (a calculated mass) powders were dispersed in 10 mL of deionized water in a round-bottomed flask via ultrasonication for 30 min. Subsequently, a KOH solution (1 mol/L) was added dropwise to the PdCl₂-SiC solution until pH reached 10. Then, NaBH₄ was added as a reductant and the mixture was magnetically stirred for 1 h. Finally, the product was obtained after filtering, washing, and drying overnight in a vacuum oven at 60 °C. The obtained products with different Pd loadings were labeled in accordance with X-ray photoelectron spectroscopy (XPS) results (Table S2) as 1.0 wt% Pd/O-SiC, 1.8 wt% Pd/O-SiC, and 2.5 wt% Pd/O-SiC. Unless stated otherwise, Pd/O-SiC indicates the 2.5 wt% Pd/O-SiC catalyst.

2.3. Material characterization

Sample morphologies were observed using transmission electron microscopy (TEM, Tecnai G2F30S-Twin) at 300 keV. High-angle annular dark-field scanning TEM and energy-dispersive X-ray (EDX) spectroscopy analyses were conducted with a FEI Titan G2 80-200 ChemiSTEM. The powder X-ray diffraction (XRD) patterns of the samples were obtained using an X-ray diffractometer (Xpert-Pro) with Cu K_α radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV. XPS data were recorded on an X-ray photoelectron spectrometer (Thermo Scientific ESCALAB250Xi) equipped with an Al K_α X-ray radiation source.

2.4. Electrochemical measurements

The ORR catalyst performance tests were conducted using a ring-disk electrode (RDE) connected to a CHI760D electrochemical analyzer (CH Instruments) in O₂-saturated 0.1 M KOH electrolyte media at room temperature. The standard three-electrode system consisted of a glassy carbon electrode (GC, 4.0 mm in diameter) with the catalyst as the working electrode, Pt wire as the counter electrode, and Ag/AgCl (KCl, 3 M) as the reference electrode. All potentials vs. the Ag/AgCl electrode were calibrated against the reversible hydrogen electrode (RHE) using the following equation: $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 \text{ V} + 0.059 \times \text{pH}$. To prepare the working electrode, 4.0 mg of catalyst and 1.6 mg of Vulcan XC-72R car-

bon (Cabot Corporation, a conducting reagent) were first added to a mixture containing 100 μL of Nafion (5 wt%) solution and 900 μL of absolute ethanol. Then, the mixture was ultrasonicated for 30 min to obtain the catalyst ink. Finally, 5 μL of homogeneous black ink was uniformly dropped on the GC electrode and dried at room temperature. The working electrode for electrochemical tests was thus obtained.

Cyclic voltammograms (CV) curves of the catalysts were recorded over the potential range of 0–1.2 V (vs. RHE) at room temperature using a O_2 -saturated 0.1 M KOH solution at a scan rate of 100 mV s^{-1} . Linear sweep voltammetry (LSV) measurements were conducted in the same range as the CV tests with a sweep rate of 20 mV s^{-1} and at different rotation rates (400, 625, 900, 1225, 1600, and 2025 rpm). Electrochemical impedance spectroscopy (EIS) analyses were performed at frequencies from 10^6 Hz to 1 Hz with an amplitude of 5 mV. The tolerance of the catalysts to methanol was evaluated through current (i)-time (t) chronoamperometry at 0.5 V_{RHE} with the addition of 2 mL methanol to KOH electrolyte. The stability of ORR catalysts was also measured through i - t chronoamperometry at 0.5 V_{RHE} without the presence of methanol.

Rotating RDE (RRDE) voltammogram measurements were performed using the same procedures as those used for RDE. Hydrogen peroxide yield (HO_2^- %) and electron-transfer number (n) were calculated using the following equations [43]:

$$n = 4I_d / (I_d + I_r/N), \quad (1)$$

$$\text{HO}_2^- \% = 200 \times \frac{I_r/N}{I_d + I_r/N}, \quad (2)$$

where I_d is the disk current, I_r is the ring current, and N represents the H_2O_2 collection coefficient (0.39) at the Pt ring.

2.5. Computational methods

DFT calculations were conducted using the Vienna *ab initio* simulation package [22], and projector augmented wave potentials were applied [44–46]. XRD and XPS results suggested that the SiC support was β -SiC with an exposed (111) crystal plane and surface oxygen coverage of approximately 20%. Thus, β -SiC (111) with and without 20% surface oxygen coverage were used as the SiC and O-SiC models, respectively. The graphene model was used to represent the carbon materials, and the Pd_4 cluster was used to represent the Pd NPs. The β -SiC (111) surface was modeled using periodic slabs of two bilayers with the bottom bilayer fixed. The (4×4) SiC (111) surface unit cell was set with lattice constants ($a = 12.39 \text{ \AA}$, $b = 12.39 \text{ \AA}$, and $c = 23.22 \text{ \AA}$). The Pd_4 cluster was loaded on various support models with optimized structures. Brillouin zone integration was conducted with a $4 \times 4 \times 1$ k -point, and the convergence criteria of the force and energy were 10 $\text{meV \AA}^{-1}$ and 0.01 meV, respectively.

3. Results and discussion

Schematic of the preparation of Pd/O-SiC catalysts is shown in Scheme 1.

The morphologies of O-SiC and Pd/O-SiC were observed with TEM, as shown in Figs. 1 and S1. Pd NPs with a mean di-

Scheme 1. Synthesis of Pd/O-SiC.

ameter of 5.2 nm were well dispersed over the O-SiC support, and no apparent agglomeration of Pd NPs was observed in the TEM image of Pd/O-SiC (Fig. 1(a)). As shown in Fig. 1(b), the lattice fringes of the Pd NPs clearly exhibited a lateral spacing of 0.225 nm, which matched well with those exhibited by the Pd (111) crystal planes. The chemical composition and elemental dispersion of Pd/O-SiC were determined using EDX mapping analysis (Figs. 1(c)–(h)). The results indicated that four well-distributed elements (Si, C, O, and Pd) were present in the Pd/O-SiC catalyst. The distribution of O was consistent with that of Si and C and was caused by the uniform oxidation of the SiC surface.

The XRD patterns of O-SiC and Pd/O-SiC with various Pd loadings are shown in Fig. 2(a). The peaks at 35.7° , 60.0° , and 72.0° in the XRD pattern of O-SiC were assigned to the SiC (111), (220), and (311) lattice planes (JCPDS, 01-1119), respectively. A small shoulder observed for the SiC support at 33.6° was related to the characteristic stacking faults in β -SiC [35]. When the Pd NPs were supported on O-SiC, the peaks of O-SiC remained unchanged most likely because of the excellent physical and chemical stabilities of SiC [47]. No Pd peaks were observed in the XPS pattern of 1.0 wt% Pd/O-SiC because of the high dispersion of the Pd NPs and low Pd loading [31]. Two peaks at 40.1° and 46.7° that appeared at 1.8 wt% Pd loading corresponded to Pd (111) and Pd (200) facets, respectively, and their intensity increased with an increase in the Pd content. The presence of Pd (111) in 2.5 wt% Pd/O-SiC further confirmed the TEM result (Fig. 1(b)). The absence of characteristic SiO_2 diffraction peaks in the XRD patterns of the O-SiC support and Pd/O-SiC catalysts (Fig. 2(a)) was ascribed to the amorphous SiO_2 film that was only formed on the SiC surfaces at room temperature [39] and the low SiO_2 content of the monolithic substrate.

Fig. 1. TEM characterization of the Pd/O-SiC catalyst. (a) TEM image (inset: Pd particle size in the Pd/O-SiC catalyst); (b) HRTEM image; (c) EDX pattern; (d–h) EDS elemental mapping images of Si, C, O, and Pd in Pd/O-SiC.

Fig. 2. XRD and XPS characterizations of catalysts. (a) XRD patterns; (b) Pd 3d; (c) Si 2p; (d) C 1s XPS high-resolution spectra of O-SiC and Pd/O-SiC with various Pd loadings.

XPS data were collected to investigate the interaction between the Pd NPs and the O-SiC support. The chemical states of Pd, Si, and C in Pd/O-SiC were detected, as shown in Figs. 2(b)–(d). The Pd 3d peaks of the Pd/O-SiC and Pd/C catalysts are shown in Fig. 2(b). The peaks of Pd/C at 336.07 and 341.24 eV were assigned to metallic Pd, whereas the other two peaks at 337.99 and 343.15 eV were attributed to PdO [21] originating from the partial reoxidation of metallic Pd by O₂ or H₂O when the catalyst was exposed to air [48]. The comparison of Pd 3d spectra with the Pd/C catalyst revealed that the peaks of metallic Pd and PdO in Pd/O-SiC significantly shifted to a lower binding energy, and the shift became increasingly noticeable with an increase in the Pd loading. These results clearly indicated that O-SiC donated more electrons to Pd than C, and the charge transfer from the O-SiC support to the Pd surface affected the electronic structures of the Pd NPs [49]. In the Si 2p spectra of the O-SiC support (Fig. 2(c)), the two peaks at 100.8 and 101.8 eV were assigned to Si-C and Si-O [35], respectively. Si-O was formed because of the surface oxidation of SiC; this interpretation was consistent with the TEM results (Fig. 1). The ratio of Si-O to Si-C decreased after Pd was loaded onto O-SiC (Fig. 2(c)). This reduction corresponded to the instability of SiO₂ in the KOH solution. The gradual shift of the Si 2p peak position to a higher binding energy (up to 0.2 eV) with an increase in the Pd loading was ascribed to the lower electronegativity of Si than that of Pd, Si, C, and O elements and agreed well with the previously reported results [50]. Fig. 2(d) shows the C 1s spectra of O-SiC and Pd/O-SiC. The two peaks at 282.7 and 283.5 eV of O-SiC corresponded to SiC and SiC_xO_y [50], respectively, and the intensity of the SiC_xO_y peaks increased after Pd deposition (Table S1). SiC_xO_y originate from the surface oxidation of the SiC support, as mentioned previously. SiC was further oxidized when Pd NPs were loaded on O-SiC in alkaline solution. The further oxidation of SiC in alkaline solution was

confirmed by analyzing the O content (Table S2). The formation of SiC_xO_y was beneficial for anchoring Pd and enhancing the stability of Pd NPs [32].

XPS analysis indicated that C and O-SiC supports have different effects on the electronic structures of the Pd NPs. These effects were further explored using DFT calculations (Fig. 3). The Bader charge and charge density difference analysis of Pd₄ supported on O-SiC and C indicated opposite charge transfer directions in Pd₄/O-SiC and Pd₄/C. The Bader charge analysis showed that the total electron transfer from O-SiC and C to Pd₄ was −0.22 and 0.21 e (Figs. 3(c)–(d)), respectively, further proving the XPS results (Fig. 2(b)). The binding energy of Pd₄ on O-SiC was considerably higher than that on C (−9.92 eV vs. −1.08 eV) (Figs. 3(c)–(d)), and the induced SMSIs were beneficial for improving the stability of the catalyst [51].

The ORR performance of Pd/O-SiC was compared with that of the commercial Pt/C, Pd/C, and O-SiC. Fig. 4(a) shows the CV curves of these catalysts. The O-SiC support exhibited poor ORR

Fig. 3. Electronic structures of Pd/O-SiC and Pd/C. Charge density difference, binding energies, and Bader charge of Pd₄ supported on O-SiC (a,c) and graphene (b,d). The blue and yellow areas in Fig. 3(a)–(b) represent negative and positive charges, respectively.

activity with an onset potential of 0.72 V_{RHE} . When Pd NPs were loaded onto the O-SiC support, the onset potential of the Pd/O-SiC catalyst exhibited a positive shift because of the good ORR activity of the Pd noble metal [4,52]. Compared with commercial Pd/C, Pd/O-SiC displayed a higher positive onset and half-wave potentials, which indicated that the support played a critical role in enhancing the ORR activity. Moreover, the onset and half-wave potentials of Pd/O-SiC improved even further than those of the commercial Pt/C. The results indicated that the ORR activity of Pd/O-SiC was better than that of the commercial Pt/C because of the electron-rich Pd induced by the charge transfer from O-SiC to Pd NPs [21,22]. The LSV responses of the catalysts are shown in Fig. 4(b), and they were used to confirm the ORR activity. Pd/O-SiC exhibited onset and half-wave potentials of 0.97 and 0.86 V_{RHE} , respectively. The values indicated that Pd/O-SiC outperformed the commercial Pt/C, and they were superior to those of O-SiC (0.72 and 0.61 V_{RHE}) and the commercial Pd/C (0.95 and 0.78 V_{RHE}). The ORR activity of Pd/O-SiC was also significantly better than those of many previously reported Pd-based catalysts in alkaline electrolytes (Table S3).

The transferred electron number (n) of ORR was obtained using the K-L equation and RRDE experiment was conducted to understand the mechanism of the ORR process in more detail (Figs. 4(c)–(d)). As shown in Fig. 4(c), the RDE curves of Pd/O-SiC obtained at various rotation rates (400–2500 rpm) were analyzed using the K-L equation [22]. The n value was approximately 4.0 above the range of 0.50 V_{RHE} to 0.65 V_{RHE} , indicating a 4e transfer mechanism [53]. RRDE experiment was further conducted (Fig. 4(d)) to identify the ORR mechanism, as

indicated before. The H_2O_2 yield was close to 0, and the n value per O_2 molecule was approximately 4.0 in the potential range of 0–0.8 V_{RHE} . These results were in accordance with those obtained using the K-L equation, which indicated that H_2O_2 formation was negligible and O_2 was directly reduced to H_2O on the Pd/O-SiC catalyst [54].

The ORR kinetics of the catalysts were explored using the Tafel slopes calculated for the polarization curves at 1600 rpm (Fig. 4(e)). The Tafel slope (83 $mV\ dec^{-1}$) of Pd/O-SiC was much lower than those of O-SiC (147 $mV\ dec^{-1}$) and the commercial Pd/C (115 $mV\ dec^{-1}$) and was comparable to that of the commercial Pt/C (80 $mV\ dec^{-1}$). The low Tafel slope indicated the fast ORR kinetics of Pd/O-SiC in alkaline electrolytes [55]. EIS characterization was also performed to further illustrate the charge transfer properties of the catalysts. The Nyquist plots obtained with EIS clearly showed that Pd/O-SiC presented a lower real axis intercept and smaller high-frequency semicircles than Pd/C and O-SiC (Fig. S2). These results indicated the lower electron-transfer impedance of Pd/O-SiC and further confirmed that Pd/O-SiC improved the electron transfer between the Pd/O-SiC interface and electrolyte [56,57].

The methanol oxidation tolerance of Pd/O-SiC and Pt/C is shown in the inset of Fig. 4(f). When methanol was introduced into the KOH electrolyte, no clear change in the current density of Pd/O-SiC was observed, whereas the Pt/C catalyst exhibited a significant current drop. These results suggested that Pd/O-SiC possessed strong resistance against the methanol crossover effect [58]. The stability of the catalysts was also evaluated through $i-t$ chronoamperometry experiments (Fig. 4(f)). Pd/O-SiC achieved a high current retention of 96.5%,

Fig. 4. Electrochemical analysis of catalysts. (a) CV results for Pd/O-SiC, O-SiC, Pd/C, and Pt/C catalysts in O_2 -saturated 0.1 M KOH solution obtained with a scan rate of 100 $mV\ s^{-1}$. (b) ORR polarization curves of different catalysts acquired at 1600 rpm. The potential scan rate was 20 $mV\ s^{-1}$. (c) Rotation-rate-dependent voltammograms of Pd/O-SiC in 0.1 M KOH solution at 400–2500 rpm. The inset shows the K-L plots of the Pd/O-SiC catalyst. (d) RRDE measurements (1600 rpm) of Pd/O-SiC (inset: Electron-transfer numbers and peroxide percentage of the Pd/O-SiC electrode). (e) Tafel plots of Pd/O-SiC, O-SiC, Pd/C, and Pt/C catalysts. (f) Chronoamperometric responses for ORR at Pd/O-SiC and Pt/C electrodes. The inset shows the comparison of the methanol oxidation tolerance of Pd/O-SiC and Pt/C at 0.50 V_{RHE} .

whereas Pt/C displayed a considerable current loss of 34.9%. An accelerated durability test was also conducted to assess the stability of the Pd/O-SiC catalyst. Fig. S3 shows negative shift of only 10 mV in half-wave potential after 3000 cycles. These results demonstrated that Pd/O-SiC possessed better stability than the commercial Pt/C [59]. The outstanding durability of Pd/O-SiC might be related to the SMSIs between Pd and SiC_xO_y.

The adsorption of the key intermediate and the Gibbs free energy of the ORR pathway were investigated (Fig. 5) to reveal the underlying mechanism that improves the ORR performance of Pd/O-SiC than that of the commercial Pd/C. Figs. 5(a) and (b) show the stability structures of the OOH intermediate adsorbed on Pd₄/O-SiC and Pd₄/C. The adsorption energy of OOH on Pd₄/O-SiC (−2.13 eV) was higher than that on Pd₄/C (−1.71 eV). The Gibbs free energy diagrams of the ORR of Pd₄/O-SiC and Pd₄/C are shown in Fig. 5(c). At the equilibrium potential (1.23 V_{RHE}), the formation of OOH* was an endergonic process, and the Gibbs free energies of OOH* formation on Pd₄/O-SiC and Pd₄/C were 0.12 and 0.53 eV, respectively, indicating that OOH* was easier to generate and more stable on Pd₄/O-SiC than on Pd₄/C. The reaction steps from OOH* to O* on Pd₄/O-SiC and Pd₄/C were exergonic and facile to complete, and the Gibbs free energy of the step from O* to OH* on Pd₄/O-SiC was equal to that on Pd₄/C. Hence, OOH* was the key ORR intermediate, and the better ORR performance of Pd₄/O-SiC compared to Pd₄/C was related to the reduced Gibbs free energy.

To entirely avoid the surface oxidation of SiC during preparation, preservation, or application under aerobic conditions is difficult. Therefore, Pd/O-SiC and Pd/SiC were compared using DFT calculations (Fig. 6) to further understand the role of oxidized SiC surface in enhancing the ORR performance of Pd NPs. The adsorption energy of the Pd₄ cluster on SiC was higher than that on O-SiC (−12.05 eV vs. −9.92 eV), and the electron transfer from SiC to the Pd₄ cluster was more significant than that from O-SiC (−1.54 e vs. −0.22 e) (Figs. 3(a), 3(c), and 6(a)–(b)). The reduction in charge transfer from O-SiC to the Pd₄ cluster was ascribed to the strong electronegativity of oxygen. However, the adsorption energy of OOH* on Pd₄/O-SiC

Fig. 5. Optimized structures and binding energies of OOH adsorbed on Pd₄/O-SiC (a) and Pd₄/C (b); (c) Gibbs free energy diagrams of ORR over Pd₄/O-SiC and Pd₄/C.

Fig. 6. DFT calculations of Pd₄/SiC. (a) Bader charge and binding energies of Pd₄ supported on SiC; (b) Charge density difference of Pd₄/SiC. Blue and yellow areas represent negative and positive charges, respectively; (c) Optimized structures and binding energies of OOH adsorbed on Pd₄/SiC; (d) Gibbs free energy diagrams of ORR over Pd₄/SiC and Pd₄/O-SiC.

(−2.13 eV) was higher than that on Pd₄/SiC (−1.39 eV), and the Gibbs free energy of OOH* formation on Pd₄/O-SiC (0.12 eV) decreased on Pd₄/SiC (0.86 eV) (Fig. 6(c)–(d)). The increased adsorption energy of the key intermediate OOH* and the decreased Gibbs free energy of the crucial ORR step induced by the SiC surface oxidation enhanced the ORR performance [22].

4. Conclusions

Commercial SiC with SiC_xO_y on its surface was used to support Pd NPs through a simple deposition precipitation method. Compared with commercial Pt/C, the prepared Pd/O-SiC catalyst had a better ORR activity with a positive shift of 10 mV in the half-wave potential, superior stability with a lower current drop (3.5% vs. 34.9%) after 10 h, and stronger resistance against methanol poisoning in 0.1 mol/L KOH electrolyte. The surface oxidation of SiC played a vital role in enhancing the ORR performance of the Pd NPs. Charge transfer from O-SiC to Pd resulted in electron-rich Pd. The electronegative Pd increased the adsorption of the key intermediate OOH and decreased the Gibbs free energy of the key ORR step, thereby enhancing the ORR performance. This work provided an efficient strategy for the design and large-scale preparation of excellent Pd-based ORR electrocatalysts.

Electronic supporting information

Supporting information is available in the online version of this article.

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Graphical Abstract

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Enhanced oxygen reduction reaction performance over Pd catalysts by oxygen-surface-modified SiC

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Charge transfer from SiC_xO_y on the surface of SiC to Pd NPs enhanced the ORR activity by inducing electron-rich Pd.

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部分氧化碳化硅提高钯催化氧还原反应性能

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摘要: 燃料电池具有能量转换效率高的优点, 是能量转换与储存的高效器件之一。目前, 燃料电池阴极氧还原反应(ORR)动力学缓慢, 并且催化ORR大量使用铂碳(Pt/C)催化剂, 由于Pt储量少, 价格高, 载体碳材料易发生碳蚀导致催化剂稳定性降低, 限制了其进一步商业化应用。钯(Pd)与Pt为同族元素, 具有相似的结构和化学性质, 其储量是Pt的50倍, 同时, Pd具有良好的抗甲醇毒性和抗一氧化碳毒性, 因此, 被视为燃料电池中阴极Pt催化剂的潜在替代品。但商用Pd/C催化剂的ORR活性较Pt/C差, 因此, 大量的研究工作集中在提高Pd基ORR催化剂的活性方面: 将Pd与具有3d轨道的金属形成合金或将Pd负载到不同的载体上。通过选择合适的载体影响Pd的电子结构, 从而提高催化剂活性和稳定性, 是一种较简单的、有利于规模化生产Pd基ORR催化剂的方法。

碳化硅(SiC)具有良好的电化学稳定性、热稳定性、机械强度和较强的供电子能力, 可被用作ORR的金属催化剂载体。然而, 由于金属与SiC作用较弱, 需要制备特殊形貌的SiC或将SiC表面改性; 通常, 这些SiC基载体的制备过程复杂并且成本高。而在有氧条件下制备、保存或使用SiC时, 其表面不可避免地被氧化, 这种在温和条件下生成的表面具有含氧官能团的SiC, 由于制备过程简便, 可以大规模生产, 且与金属有强的相互作用, 是一种很有前景的ORR的Pd基催化剂载体。对于用于替代Pt基催化剂的负载型Pd基ORR催化剂的开发和大规模制造来说, 对载体表面改性的深入了解是一个重要并且具有挑战性的课题。目前尚未发现关于SiC表面的含氧基团对ORR性能影响的报道。因此, 详细考察SiC载体上含氧基团在ORR中的作用对于理解、设计和开发具有优异ORR性能的SiC负载催化剂至关重要。

本文采用沉积沉淀法在表面部分氧化的碳化硅(O-SiC)均匀负载了平均直径为5.2 nm的Pd纳米颗粒。与20 wt%商业Pt/C相比, 制备的2.5 wt%Pd/O-SiC催化剂显示出较好的ORR活性(半波电位正向移动10 mV), 较好的稳定性(10 h后, 电流密度损失3.5% vs. 34.9%), 和较高的抗甲醇毒性。结构表征及密度泛函理论(DFT)计算结果表明, 与Pd/C相比, Pd/O-SiC具有优异的ORR性能主要是由于O-SiC载体对Pd纳米颗粒具有电子调控作用, 使Pd带负电。富电子Pd增强了ORR关键中间体OOH的吸附, 降低了反应的吉布斯自由能, 从而提高了ORR活性。另外, O-SiC载体对Pd纳米颗粒具有大的结合能和较好的SiC稳定性, 增强了Pd/O-SiC催化剂的抗甲醇毒性及稳定性。DFT计算结果表明, SiC表面部分氧化后, 仍保持对Pd的较高结合能, 同时大幅增强了催化剂对中间体的吸附, 降低了ORR关键电化学步骤吉布斯自由能, 从而提高了氧还原性能。因此, 本工作明确了SiC表面氧化的作用, 同时提供了一种简易大规模制备高效负载型铂基替代ORR催化剂的策略。

关键词: 碳化硅; 表面氧化; 氧还原反应; 密度泛函理论; 电荷转移; 富电钯

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