Ag-Pd core–shell electrocatalysts for ethanol oxidation and oxygen reduction reactions in alkaline medium

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Abstract
Ag-Pd core–shell nanoparticles with different thickness of Pd shell are successfully prepared applying polyol methods with 1,2-propanediol as a solvent and reducing agent. A strongly electronic interaction between the sublayer Ag and surface Pd atoms are measured for the Ag-Pd core–shell particles with lower Pd/Ag atom ratios (Pd:Ag $\leq 3:10$), which derives from the near-surface alloying effect. Upon increasing the thickness of Pd shell, the effect of Ag core on surface Pd atoms become weaker, correspondingly the surface Pd atoms present the features closed to pure Pd. All Ag$_{10}$@Pd$_x$/C core–shell catalysts exhibit improved ethanol oxidation reaction (EOR) activities compared to pure Pd/C. Here, the EOR activities of Ag$_{10}$@Pd$_x$/C catalysts decrease when adding the thickness of the Pd shell, in which the Ag$_{10}$@Pd$_{1}$/C with the lowest Pd/Ag ratios (Pd/Ag = 1:10) shows the highest $i_p$ value ten times that of Pd/C. The participation of Ag as a core with low electronegativity and larger lattice constant can increase the electron densities and bring the lattice expansion of surface Pd atoms, due to the electron effect and the geometric effect, which effectively strengthen the bonding energy of reaction species on Pd surface and benefit the OH$^-$ adsorption for EOR, especially in lower Pd/Ag ratios than forming a monolayer Pd. For oxygen reduction reaction (ORR), the Ag$_{10}$@Pd$_x$/C samples also exhibit enhanced activities than pure Pd/C. Differently, there is a volcanic relation between the mass activities and the Pd/Ag atom ratios, where the Ag$_{10}$@Pd$_3$/C with about a monolayer Pd shell exhibits highest ORR activity. The improved ORR activities may be relay on the appropriate OH$^-$ adsorption, the exposed surface Ag atoms and the quick transformation of OH from Pd atoms.

1. Introduction

Small molecule alcohols (e.g. ethanol, methanol, and ethylene glycol) are believed to be promising fuels for fuel cell application [1–3]. Because ethanol is lower toxic, possesses a high energy density of 8.01 kWh kg$^{-1}$ and friendly energy conversion, direct ethanol fuel cells (DEFCs) have attracted great attention, especially in alkaline medium owing to the quick reaction kinetics, less corrosive ability and enabling the use of non-Pt catalysts [4–6]. In alkaline-type DEFCs, Pd-based nano-structured catalysts reported, excepted for Pd metal possessing higher abundance and lower price in contrast with Pt, have shown superior electrocatalytic activities both for electro-oxidation of ethanol [5, 7] and cathodic reduction of oxygen comparative to Pt-based materials [8, 9]. It is widely known that Pd-based catalysts depend strongly on the alloyed elements with Pd, compositions, the particle size, morphology, exposed crystal facets, and so on [4, 6]. Accordingly, optimization of Pd-based alloy (such as alloying Pd with Ni, Co, Cu, Au, and Ag) [10–15] and construction of novel bimetallic and multimetallic Pd-based nano-architectures (such as cubic nanoparticles, nanowires, porous nanostructures, and core–shell nanostructures) [16–20], have been designed to improve the electrocatalytic performances. These reported results established that electronic characteristics of Pd is modified by tailoring the alloyed metals and the morphologies, which optimize the binding energies to the reactive species and intermediates, correspondingly further improving their catalytic activity and stability.
Among the alloying metal elements with Pd, Ag possesses largely different lattice constant (Ag: 4.058 Å vs Pd: 3.888 Å) and electronegativity (Ag: 1.9 vs Pd: 2.2) relative to Pd, then adding Ag into Pd leads to shifting upward of d-band center or increasing of the electron density of Pd [21, 22]. Limited reports show that this tunable electronic structure of Pd sites provides the opportunity for enhancement of chemical adsorption capacity to alcohol precursor, CH₃CO₃ad, intermediates and OH⁻, resulting in the improvement of the ethanol oxidation reaction (EOR) [23–25]. Moreover, the incorporation of Ag can accelerate the reduction desorption of the CO-type intermediates, correspondingly releasing more Pd active sites [26, 27]. For oxygen reduction reaction (ORR), the pure Ag exhibits inferior catalytic activity in alkaline solution, which may be due to its weak binding energy to oxygen compared with Pd according to the computational methods [28]. Precise designing the interaction of Ag and Pd reported that the incorporation not only modulate the structure and electron feature of Pd, also the equally regulate characteristics of Ag, which optimize the oxygen adsorption interaction with surface Ag or Ag-Pd. There is a synergetic effect of the O₂ adsorption on the Pd atoms and rapid disproportionation on alloyed Ag-Pd surface [29]. Thus, the Pd-Ag bimetallic catalysts greatly increase the reaction kinetics for ORR and the electrons number transferred [29, 30]. However, the studies of Pd-Ag alloy nanostructure for ORR are so limited to obtain an efficient conclusion, which requires further insight. Admittedly, Pd is also a precious metal. Arranging Pd atoms as thin shell on Ag core not only greatly reduces Pd content, also can apply the near-face alloying effect to enhance the electrocatalytic activity.

To design Pd-Ag bimetallic catalysts with a core–shell structure, a feasible synthetic method is needed to manipulate the microstructure. Polyols are convenient to produce the core–shell nanostructure through continuous reduction for the easy-reducible noble metal, such as Pd, Ag, etc, in which choosing a reduction temperature is important to deposit a Pd shell in the presence of Ag cores avoiding Pd nucleation in homogeneous polyol solution [31–33]. Otherwise, their same crystalline structure and similar electronic structure can facilitate the formation of Ag@Pd core–shell structure and high alloying degree [34]. So, uniform Ag₈₁₀@Pd₄ nanoparticles on XC-72 (Ag₈₁₀@Pd₄/C) were prepared through a continuous reduction process using polyol methods, in which the surficial composition are adjusted by changing the Pd/Ag atom ratios. Transmission electron microscope (TEM (HRTEM)), x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS) and element mapping were applied to measure the physical characteristics of the prepared Ag₈₁₀@Pd₄/C catalysts. And, the electrocatalytic activities for EOR and ORR are evaluated in alkaline solution.

2. Experimental section

2.1. Material preparation and physical characterization

A polyol method was applied to prepare the Ag₈₁₀@Pd₄ core–shell nanoparticles through a continuous reduction procedure by using 1,2-propanediol as a reducing agent [35]. Firstly, NaOH (0.6 g) was dissolved in 1,2-propanediol (15 ml) under a temperature of 110 °C and this alkaline solution was cooled to room temperature. Oleic acid (0.4233 g) and a uniform suspension of XC-72 (0.0867 g) dispersed in 1,2-propanediol (10 ml) were then mixed with the above alkaline solution and this mixture was maintained at 20 °C under N₂ atmosphere and stirring. At this temperature 1,2-propanediol solution (10 ml) containing AgNO₃ (0.0196 g) was slowly dropped into the mixture solution, which reaction was continued with stirring for 30 min to prompt the deposition of Ag completely. After the formation of Ag/C (Ag/XC-72 mass ratio: 0.193), the colloid solution was heated to 60 °C. Next, a calculated volume of H₂PdCl₄ resolved in 1,2-propanediol solution (25 mM L⁻¹) was added drop by drop into the reaction flask. After the reacting solution was held at 60 °C for 2 h under stirring at N₂ atmosphere, the black colloid was centrifuged, washed several times with ethanol and dried in a vacuum oven overnight at 30 °C. The Ag@Pd particles with different Pt/Ni atom ratios (1:10–7:10) were synthesized. Meantime, Pd/C and Ag/C catalysts were synthesized for comparison.

A JEOL JEM-2100FFEF microscope operated at 200 kV is used to perform the TEM (HR-TEM). The size distribution were collected by measuring ca. 200 particles randomly in the TEM images. EDS elemental analysis for a single nanoparticle were conducted on an FEI Titan Themis G2 60 using scanning transmission electron microscope (STEM) on operation of 300 kV (αmax = ~100 mrad). An x-ray diffractometer (Bruker D8 Advance) was used to carry out Power XRD test at 4° min⁻¹ using Cu Kα. A Kratos Ltd. XSAM-800 spectrometer was utilized to conduct XPS measurement with a Cu Kα radiation to characterize the chemical states and species. And, the software XPSPEAK41 was used to fit the XPS data.

2.2. Electrochemical measurements

Electrochemical performances were studied on a CHI760A potentiostat using a typical three-electrode configuration. A glassy carbon (GC, geometric area: 0.196 cm², Pine) electrode coated with the prepared catalysts, a Pt foil and a saturated calomel electrode were applied as the working electrode, the counter
electrode and the reference electrode, respectively. Catalyst (5 mg) was dispersed into Naion/isopropyl alcohol solution (1 ml, 0.05 wt%) by ultrasonic for 30 min to form an ink, and the catalyst ink (20 µl) was then pipetted onto GC surface and dried at room temperature. All potentials in this work are quoted relative to the reversible hydrogen electrode (RHE). Cyclic voltammogram (CV) measurement was applied to study the behaviors in blank 0.1 M KOH and the activities for EOR in the mixture solution containing 0.1 M KOH + 1.0 M C₆H₅OH at 50 mV s⁻¹ under Ar-saturated atmosphere. The ORR activity was measured in 0.1 M KOH solution under O₂-saturated atmosphere at 5 mV s⁻¹ by an electrode rotation rate of 1600 rpm. The ORR kinetic current (I_k) was calculated using the Koutecky–Levich equation (I_k = I × I_L/(I_L−I)), where I_L and I are the limiting diffusion current and the measured current at each potential, respectively. The all electrochemical tests were conducted at 27 ± 1 °C.

3. Results and discussion

3.1. Physical characterization

The fabrication of Agₓ/Pdᵧ nanoparticles in this paper applies the commonly used polyol process with 1,2-propanediol both as a solvent and the reductant. Here, a low reduction temperature of 20 °C was applied to deposit Ag core particles because of a relative high electrode potential of Ag⁺/Ag, and 60 °C is chosen to deposit a Pd shell in the presence of Ag cores avoiding Pd nucleation quickly in homogeneous polyol solution. The TEM images of the Agₓ/Pdᵧ/C samples with Pd/Ag atom ratios of 1:10, 3:10, 5:10 and 7:10 (figures 1(a)–(d)) and the corresponding size-distribution histograms (insets) present that the Agₓ/Pdᵧ particles with an average size of 8–10 nm are uniformly dispersed on XC-72 supports. The representative HRTEM images of the Agₓ/Pdᵧ/C exhibit lattice fringes with a spacing of 0.236–0.239 nm at the core and 0.226–0.230/0.199–0.201 nm at the shell, corresponding to (111) plane of Ag and (111)/(200) planes of Pd, respectively, which reveal the formation of a core–shell nanostructure (figures 1(e) and (f)). Furthermore, the lattice fringes of Pd shell in Agₓ/Pdᵧ particles with a (111) spacing of 0.226–0.230 nm measured are slightly larger than the spacing of Pd (111) plane (~0.224 nm) in the Pd/C samples, indicating a lattice expansion of surface Pd coated on the Ag core (Pd: 0.128 nm, Ag: 0.134 nm) [27]. Thus Pd lattice expansion originates from Ag-Pd core–shell structure of Pd atoms coated on the Ag core with a larger atom radius. STEM-EDS elemental mapping analysis in the mixed Pd-Ag image exhibits the Pd atoms were abundantly distributed on surface of the Ag-Pd nanoparticles, forming a Pd-rich shell coated on Ag cores (figure 1(g)). The line-scanning analysis of Agₓ/Pdᵧ nanoparticles also demonstrates that Ag atoms are mainly dispersed in the core and the Pd elements are dispersed uniformly across the whole sphere. These results of the element scanning measurements confirm that the Ag-Pd core–shell nanostructure was successfully prepared.

The XRD patterns of the Agₓ/Pdᵧ/C samples and the corresponding magnified XRD peaks of (111) plane are showed in figure 2, where the diffraction responses of pure Pd/C and Ag/C are also given. The XRD responses of pure Pd/C and Ag/C give characteristic diffraction peaks of FCC crystalline structure, in which the characteristic peaks at 2θ values of 39.80°, 46.30°, 68.20° and 82.12°, and at 20 values of 38.12°, 44.30°, 64.45° and 77.41° are indexed to the (111), (200), (220) and (311) planes of FCC Pd and Ag, respectively (figure 2(a)). All prepared Agₓ/Pdᵧ/C catalysts in the XRD patterns exhibit a single peak at given crystalline planes with 2θ values closed to those of Ag/C. Such as, upon increasing the Pd/Ag atom ratios from 1:10 to 7:10, the (111) planes of Agₓ/Pdᵧ/C catalysts exhibit 2θ values of 38.14°, 38.16°, 38.18°, 38.20°, 38.40°, 38.50° and 38.60°, gradually slightly shifting to higher scanning angles without separate nucleation of Pd. These XRD results suggest that Pd forms a thin shell on Ag cores rather than aggregating to individual particles. Notably, the positive shifting of 2θ values mean that a few Pd atoms are alloyed with Ag core or prompt the lattice contraction of Ag core, which, in turn, bringing out the increasing surface Pd-Pd atomic spacing evidenced by TEM analysis.

The XPS measurement is applied to evaluate the surface chemical states. The Pd XPS patterns of the prepared Agₓ/Pdᵧ/C catalysts exhibit that the Pd 3d spectra are fitted to two pairs of doublet between 332 eV and 347 eV (figure 3(a)), meaning that the composition of surface Pd contains the Pd⁰ and Pd²⁺ species. The binding energies for XPS of pure Pd/C and Ag/C are given for comparison in table 1. The Pd³⁺ XPS signal is fitted to 335.79, 335.83, 335.85 and 335.89 eV for the Agₓ/Pdᵧ/C catalysts with Pd/Ag atom ratios of 1:10, 3:10, 5:10 and 7:10, respectively (table 1). In comparison with Pd³⁺ XPS peak of 335.87 eV for the pure Pd/C catalyst, the Pd 3d binding energy of the Agₓ/Pdᵧ/C with the highest Pd/Ag ratio of 7:10 is in accordance with the value of Pd/C, and with decreasing the thickness of Pd shell, the binding energies demonstrate a gradually negative shift, more deviating from that of pure Pd/C. As well known, the alloying of Ag and Pd with different electro-negativity (Pd: 2.2, Ag: 1.93) evidently increases the electro density of surface Pd atoms, resulting in the negative deviation of the Pd 3d binding energies. But, the geometric effect deriving from their different lattice constant brings the lattice variation of surface Pd and Ag core, which results in the shift of d-band center. Here, in the Ag-Pd core–shell nanostructure, the surface Pd
atoms are alloyed with the sublayer Ag identified by XRD. For the Ag$_{10}$@Pd$_x$/C with lower Pd/Ag atom ratios (Pd:Ag ≤ 3:10) not higher than that forming a monolayer Pd shell, there is a strongly electronic interaction between the sublayer Ag and surface Pd atoms deriving from this near-surface alloying effect. Upon increasing the thickness of Pd shell, surface Pd atoms present the feature closed to pure Pd because of weak electronic interaction of Ag core and surface Pd atoms. The XPS spectra of Ag 3d are deconvoluted into characteristic peaks of Ag$_{0.3d5/2}$ and Ag$_{0.3d3/2}$, confirming the metallic Ag$^0$ as the main species (figure 3(b)). The Ag core coated with lower Pd amount than forming a Pd monolayer have the similar binding energies with Ag/C. As increasing the Pd amount, the Ag core is compressed by the surface Pd atoms through...
Table 1. The binding energies of Pd and Ag species for the Ag@Pd/C catalysts.

| Catalyst       | Pd\(^0\)_3d\(5/2\) | Pd\(^0\)_3d\(3/2\) | Pd\(^{2+}\)_3d\(5/2\) | Pd\(^{2+}\)_3d\(3/2\) | Ag\(^0\)_3d\(5/2\) | Ag\(^0\)_3d\(3/2\) |
|----------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------|
| Ag\(_{10}\)@Pd\(_3\)/C | 335.75              | 341.06              | 338.40              | 343.70              | 368.60              | 374.60              |
| Ag\(_{10}\)@Pd\(_3\)/C | 335.83              | 341.14              | 338.40              | 343.70              | 368.54              | 374.54              |
| Ag\(_{10}\)@Pd\(_5\)/C | 335.85              | 341.16              | 338.40              | 343.70              | 368.52              | 374.52              |
| Ag\(_{10}\)@Pd\(_7\)/C | 335.89              | 341.20              | 338.40              | 343.70              | 368.50              | 374.50              |
| Pd/C Ag         | 335.87              | 341.17              | 338.40              | 343.70              | –                   | –                   |
| Ag/C            | –                   | –                   | –                   | –                   | 368.64              | 374.64              |

Figure 3. XPS spectra of Pd 3d and Ag 3d for Ag\(_{10}\)@Pd\(_x\)/C, Ag\(_{10}\)@Pd\(_3\)/C, Ag\(_{10}\)@Pd\(_5\)/C and Ag\(_{10}\)@Pd\(_7\)/C catalysts.

geometric effect, where the binding energies for Ag\(_{10}\)@Pd\(_x\)/C more deviate from that of pure Ag/C. This variation of electronic interaction through changing the thickness of Pd shell on Ag core can lead to different electrocatalytic performance of surface Pd.

3.2. Cyclic voltammetric measurement

Figure 4 presents CVs of the Ag\(_{10}\)@Pd\(_x\)/C samples and the correspondingly enlarged voltammetric peaks related to the reduction desorption of the adsorbed oxygenated species. All Ag–Pd core–shell catalysts exhibit the similar CV characteristics of two reduction peaks at ca. +0.982 V and +0.600 V vs RHE on the negative CV scans, corresponding to the desorption of the adsorbed oxygenated species on the Ag and Pd atoms, respectively. The electrochemically active areas of unit Pd (ECSA) are calculated using the equation (ECSA = Q/\(m_{pd}C\)) according to desorption peak area of the oxygenated adsorbates, in which Q and C refer to total adsorbed oxygen charge and the charge density of monolayer adsorption of O atoms, respectively [27]. The calculated ESCA are 72.33, 59.14, 46.58, 43.00, 42.20, 37.77 and 39.21 m\(^2\)/g\(_{pd}\) for Ag\(_{10}\)@Pd\(_x\)/C samples with increasing Pd/Ag atom ratios from 1:10 to 7:10, respectively (table 2). All Ag\(_{10}\)@Pd\(_x\)/C samples exhibit enlarged ECSA compared with Pd/C (28.12 m\(^2\)/g\(_{pd}\)) and ECSA values decrease along with increasing the Pd/Ag atom ratios tending to that of pure Pd/C (figure 4(b) and table 2), suggesting that Ag core increase the Pd active sites and this enhancement depended on the thickness of Pd shell with an stronger effect.
Table 2. The $E_0$ and ECSA of the $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ catalysts.

| Catalyst            | $m_{\text{Pd}}$ (ug) | $Q_{\text{O}^*}$ (mC) | ECSA (cm$^2$) | ECSA/$m_{\text{Pd}}$ (m$^2$ g$^{-1}$) | $E_0$  |
|---------------------|-----------------------|------------------------|---------------|--------------------------------------|-------|
| $\text{Ag}_{10}\text{@Pd}_1\text{/C}$ | 1.58 | 0.0480 | 1.1429 | 72.33 | 0.6096 |
| $\text{Ag}_{10}\text{@Pd}_2\text{/C}$ | 3.10 | 0.0770 | 1.8333 | 59.14 | 0.6072 |
| $\text{Ag}_{10}\text{@Pd}_3\text{/C}$ | 4.57 | 0.0894 | 2.1286 | 46.58 | 0.5987 |
| $\text{Ag}_{10}\text{@Pd}_4\text{/C}$ | 5.99 | 0.1082 | 2.5762 | 43.00 | 0.6001 |
| $\text{Ag}_{10}\text{@Pd}_5\text{/C}$ | 7.38 | 0.1308 | 3.1143 | 42.20 | 0.5987 |
| $\text{Ag}_{10}\text{@Pd}_6\text{/C}$ | 8.70 | 0.1380 | 3.2857 | 37.77 | 0.5927 |
| $\text{Ag}_{10}\text{@Pd}_7\text{/C}$ | 9.896 | 0.1630 | 3.8810 | 39.21 | 0.5927 |
| Pd/C                | 20       | 0.2362 | 5.6238 | 28.12 | 0.5006 |

Figure 4. (a) CVs of the prepared catalysts and (b) magnified CV peaks for the reduction desorption of the adsorbed oxygenated species in 0.1 M KOH at 50 mV s$^{-1}$ under Ar-saturated atmosphere and 27 °C.

between Ag core and surface Pd when Pd/Ag atom ratios are lower than forming a monolayer Pd. Furthermore, the desorption potentials of the adsorbed oxygenated species ($E_0$) of all $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ samples exhibit higher potentials in comparison with Pd/C (0.5006 V), and the $E_0$ shift to higher potential with decreasing the thickness of Pd shell. Such as, the $E_0$ values for $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ samples are 0.6096, 0.6072, 0.5987, 0.5987, 0.5927, and 0.5927 V with adding Pd/Ag atom ratios from 1:10 to 7:10 (table 2). The shift of $E_0$ signifies that oxygenated adsorbates are easier to desorb from $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ samples with the lower coating of Pd shell, predicting higher ORR activities.

3.3. EOR activity measurements

The electrocatalytic properties towards EOR of Pd/C, Ag/C and $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ are investigated by CV test (figure 5(a)), where the EOR currents of unit Pd for all $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ catalysts are calculated with respect to Pd metal mass on electrode (figure 5(b)). All $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ samples exhibit higher peak current ($i_p$) in contrast with Pd/C catalyst, implying that the Ag core can enhance EOR activity of surface Pd. The relationship between $i_p$ values of $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ and the Pd/Ag ratios is plotted in figure 5(c), where the $i_p$ values decrease along with the thickness of Pd shell, confirming that the enhancement of Ag core on surface Pd atoms for EOR is dependent on the thickness of Pd shell. Obviously, when the Pd/Ag ratios ($\leq$3) are lower than forming a monolayer Pd on Ag core, the EOR activities in $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ samples are improved remarkably, in which the $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ catalyst with the lowest Pd/Ag ratios (Pd/Ag = 1:10) shows the highest $i_p$ value (2.3870 A/mgPd) ten times of that of Pd/C (0.2153 A/mgPd) (figure 5(c)). And, the decreasing rate of $i_p$ for the $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ samples slows down along with the Pd/Ag ratios, also relying on the degree of Pd coating on Ag core. Moreover, the $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ samples with the lower Pd/Ag atom ratios exhibit the lower onset potential, the more negative $E_p$ (figure 5(c)). Otherwise, as revealed in figure 5(d), the impedance arc diameter of $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ with different Pd/Ag atom ratios are similar and less relative to that of Pd/C. Tafel curves were obtained by plotting the variation of $E$ as a function of the logarithmic value of $I$ at the beginning of rising part of their forward CV curves. Tafel slopes of EOR were calculated to compare the kinetic properties of Ag-Pd core–shell catalyst (figure 5(e)) [35], where Ag-Pd core–shell nanostructures show lower Tafel slopes than pure Pd/C, implying the better catalytic activity. Thus EOR results show that $\text{Ag}_{10}\text{@Pd}_x\text{/C}$ core–shell structures possess an enhanced EOR activity than pure Pd/C and their EOR activities are dependent on the thickness of Pd shell. The Chronoamperometric analysis (i)–(t) on representative $\text{Ag}_{10}\text{@Pd}_3\text{/C}$ and Pd/C was used to investigate catalytic stability (figure 5(f)). From the $i$–$t$ curves, current density reduction for pure Pd/C is faster than that of $\text{Ag}_{10}\text{@Pd}_3\text{/C}$ both in the beginning time prior achieving...
Figure 5. CVs (a), and forward cycles of unit Pd (b) of the prepared Ag_{10}\text{@}Pd\text{}/C and Pd/C measured in 0.1 M KOH + 1.0 M C_{2}H_{5}OH under Ar-saturated atmosphere at 50 mV s\textsuperscript{−1} and 27 °C; (c) the plot of \(I_{p}\) and \(E_{p}\) related Ag\textsubscript{10}\text{@}Pd\text{}/C with different Pd/Ag ratios; (d) the impedance curves of the representative catalysts; (e) Tafel plots derived from the rising part of forward CV curves; (f) chronoamperometric curves of prepared Pd/C and Ag\textsubscript{10}\text{@}Pd\text{}/C at 0.709 V (vs RHE).

a stable status and the passage time, which means that the Ag-Pd core–shell structure of appropriate Pd coating have higher durability.

It is well known that there is the geometric effect and ligand effect of the metal core substrate on the coated metal shell in core–shell nanostructure, which originate from the combination of different metal elements with distinct electronegativity and atomic radius. For Ag-Pd core–shell samples, when the Pd/Ag ratios (\(<\leqslant 3\)) are lower than forming a monolayer Pd on Ag core, there is a strong effect of sublayer Ag core on the surface Pd atoms because of the near-surface Pd-Ag alloying. Continuously increasing the Pd/Ag ratios, this interaction of Ag core on the surface Pd atoms become weaker due to an increased distance. Such interaction increases the electron density of Pd atoms testified by the XPS results with the lower binding energies of Pd 3d in Ag\textsubscript{10}\text{@}Pd\text{}/C structure compared to pure Pd/C, cause the lattice expansion of surface Pd observed from the HETEM and XRD tests, and prompt to expose more active sites calculated from the ECSA. The higher electron density of Pd effectively strengthen the bonding energy of reaction species, especially for the Ag\textsubscript{10}\text{@}Pd\text{}/C particles of lower Pd/Ag atom ratios with near-surface alloying effect, and correspondingly accelerate the reaction kinetics of the EOR. Otherwise, the enhancement effect for EOR of Ag\textsubscript{10}\text{@}Pd\text{}/C samples maybe due to the geometric effect: the Pd atoms (\(d = 0.138 \text{ nm}\)) are arranged on Ag core (\(d = 0.145 \text{ nm}\)), where the \(d\)-band center of Pd shifts up deriving from the larger lattice constants of Ag core. In alkaline media, the step of adsorbed OH\textsuperscript{−} species reacting with the adsorbed CH\textsubscript{3}COO\textsubscript{ads} generating
CH$_3$COO$^-$ are regarded as the rate-determining step. The shifting upwards of the $d$-band center facilitates the OH$^-$ adsorption and further enhance EOR activity.

3.4. ORR activity measurements

Figure 6(a) gives the ORR steady-state polarization curves. Pure Ag/C sample shows much lower ORR activity with an more negative half-wave potential than Pd/C in the polarization curves (figure 6(a)). The mass activities for ORR of unit Pd in figure 6(b) were obtained by normalizing the $I_k$ by the Pd loading on the working electrode. The specific area activities in figure 6(c) of Pd were obtained by normalizing $I_k$ by the ECSA of Pd. The corresponding activity comparison under given potentials are presented (figures 6(b) and (c)), respectively. All Ag$_{10}$@Pd$_x$/C core–shell catalysts show higher ORR mass activities and specific area activities than the pure Pd/C, and their ORR activities also mainly depended on the thickness of the Pd shell. The mass activities and the specific area activities both exhibit a ‘volcano’ type of dependence on the Pd/Ag atom ratios, where the Ag$_{10}$@Pd$_3$/C sample with the Pd amount forming about a monolayer Pd shell demonstrates the highest activity for ORR, superior to the Pd/C by ca. 3–4 times for the mass activity and about 9–10 times for the specific area activity at 0.86 V vs RHE.

Tafel slopes of ORR were obtained by plotting current densities against potential in kinetic transport controlled region (figure 6(d)), which confirm that the Ag-Pd core–shell samples have fast kinetic with the similar Tafel slope values in comparison with Pd/C even at lower Pd coating. Various rotation rates on Ag$_{10}$@Pd$_3$/C were used to record the corresponding polarization curves to examine the ORR kinetics of the Ag-Pd core–shell structure (figure 6(e)). The transferred electron number ($n$) values during oxygen reduction are calculated as 3.78–3.87 according the Koutecky–Levich (K-L) equation [16], which suggest that Ag$_{10}$@Pd$_x$/C core–shell catalysts catalyze O$_2$ via 4e$^-$ to directly form H$_2$O mainly. Further, the $i-t$ curves are plotted to evaluate the stability in ORR atmosphere (figure 6(f)), in which the Ag$_{10}@$Pd$_3$/C catalysts exhibit slower decay, confirming the better durability of the Ag-Pd core–shell nanostructure.

It is well known that the reduction potentials of the oxygenated adsorbates ($E_0$) are usually used to evaluate the ORR activities, where there is a volcaonic relationship between the specific area activities and $E_0$. Usually, the higher $E_0$ mean easier desorption of the oxygenated intermediates, which indicate better ORR electrochemical properties. As indicated in figure 5(c), the Ag$_{10}@$Pd$_x$/C catalysts exhibit larger electrochemical activity surface areas and more positive stripping potential than Pd/C, which suggesting that Ag participation can increase the active sites and the corresponding site activity. Based on Hammer and Norskov’s calculation, Pd alloyed with Ag element of larger atom radius can make the up-shift of $d$-band center, which enhance the chemisorption of oxygenated adsorbates and correspondingly do not facilitated ORR reaction. But, the addition of the electron density for Pd originating from their different electro-negativity brings the down-shift of $d$-band center. Additionally, since the ORR activity is affected by O$_2$ and hydroxyl species, the surface Ag-Pd alloy maybe enhance hydroxyl species on Ag or Ag-Pd alloy, then lower the OH$^-$ adsorption on Pd or transfer the OH$^-$ from the Pd atoms, which can quickly release more active Pd sites [29]. Thus, the enhancement for the ORR of Ag$_{10}@$Pd$_x$/C catalysts may be due to the increased ECSA per unit mass Pd, the low adsorption/desorption energy of the oxygenated adsorbates measured in the CV measurements and the formation of Ag-OH. Meantime, the Ag$_{10}@$Pd$_x$/C catalysts with lower Pd/Ag...
ratios can expose more Ag atoms on surface and present a strong effect of Ag core on surface Pd atoms. Although Ag has an improvement on the catalytic activity for ORR of Pd, the Ag-Pd core–shell nanoparticles still require further insight.

4. Conclusion

Ag10@Pdx/C with a different thickness of Pd shells are synthesized by applying polyol methods with 1,2-propanediol as solvent and reducing agent. The HRTEM, STEM-EDS elemental mapping analysis and XRD measurements confirm the formation of Ag@Pd core–shell nanostructure. The Ag10@Pdx/C catalysts with lower Pd/Ag atom ratios (Pd:Ag ≤ 3:10) exhibit a strongly electronic interaction between the sublayer Ag and surface Pd atoms deriving from this near-surface alloying effect. Upon increasing the thickness of Pd shell, surface Pd atoms present the feature closed to pure Pd because of weak interaction of Ag core on surface Pd atoms. The Ag10@Pdx/C core–shell structure exhibit an improved EOR activity in comparison with pure Pd/C and a dependence of the activities on the thickness of Pd shell, in which the Ag10@Pdx/C catalyst with the lowest 1:10 Pd Ag−1 ratio shows the highest ip value ten times of that of Pd/C. The enhancement for EOR of Ag10@Pdx/C catalysts maybe due to the electron effect: Higher electron density effectually enhancing the bonding energy of reaction species on Pd surface, and the geometric effect: The shifting upwards of the d-band center of Pd arising from the larger lattice constants of Ag benefiting the OH− adsorption. The Ag10@Pdx/C samples also exhibit enhanced activities towards ORR than pure Pd/C.

Differently, there is a volcanic relation between the ORR mass activities and the Pd/Ag atom ratios, where the Ag10@Pdx/C sample with the Pd/Ag atoms ratio (Pd:Ag = 3:10) forming about a monolayer Pd shell exhibits the optimized mass activities for ORR. The addition of Ag can optimize the OH− adsorption, expose surface Ag atoms and transform OH from Pd atoms quickly.

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