High Performance Ag Rich Pd-Ag Bimetallic Electrocatalyst for Ethylene Glycol Oxidation in Alkaline Media

Xue-Li Xing, Ya-Fei Zhao, Hong Li, Chiao-Tzu Wang, Qiao-Xia Li, and Wen-Bin Cai

1 Shanghai Key Laboratory of Materials Protection and Advanced Materials in Electric Power, College of Environmental and Chemical Engineering, Shanghai University of Electric Power, Shanghai 200090, People’s Republic of China
2 Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Collaborative Innovation Center of Chemistry for Energy Materials, Department of Chemistry, Fudan University, Shanghai 200433, People’s Republic of China

Efficient electrocatalysts at decreasing cost for ethylene glycol (EG) oxidation reaction are highly demanded for generating electricity out of direct EG fuel cells and producing hydrogen from EG electroreforming cells. In this work, carbon-supported Pd-Ag bimetallic catalysts (PdAgxC) with varying atomic ratios (x: y = 2: 1, 1: 1, 1: 2, 1: 3 and 1: 4) are synthesized by adding a Pd(II) precursor solution in a preformed Ag colloid in the presence of ascorbic acid followed by mixing with carbon black, and then are screened for EG electrooxidation in alkaline media. ICP-AES, TEM, XRD and XPS are used to characterize the obtained PdAgxC catalysts. The resulting PdAg3 nanoparticles exhibit similarly mean sizes of ca. 9.5 nm and an essentially alloy structure with a Pd surface enrichment rather than a typical Ag core-Pd shell structure. Electrocatalytic evaluation reveals that the as-synthesized PdAgxC catalysts display a “volcano” profile in terms of the Pd mass activity with increasing y: x value, and the PdAg3/C yields the most enhanced and durable activity among all the catalysts examined. Both electronic and bifunctional effects may account for this enhancement based on the existing guideline for bimetallic catalysts.

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Among various alcohols fed for low temperature fuel cells, ethylene glycol (EG) receives increasing interest, owing to its low toxicity and permeability, high boiling point (473 K), high theoretical energy density (7.56 kJ mol⁻¹ L⁻¹) as well as renewability from biomass-based resources. EG could also be used as a promising sacrificial molecule for EGOR in alkaline media to substitute Pt. Nevertheless, EGOR remains unclear, calling for a comprehensive investigation into the surface reactivity toward targeted reactions. In addition to the electronic effect, the bifunctional effect in the bimetallic Pd catalysts may also affect the surface reactivity. Therefore, synthesizing and screening bimetallic Pd catalysts provides an effective way to enhance the activity and stability of Pd toward many electrocatalytic reactions.
nanoparticles as seeds followed by unique restructuring of Ag and Pd. Attention was paid in the synthesis to avoid the use of highly removed surfactants. The resulting Pd$_{x}$Ag$_y$/C catalysts show essentially an alloy nature with surface Pd enrichment, the x : y dependency on electrocatalytic activity and stability for EGOR was examined carefully, revealing that the Pd$_{1}$Ag$_{3}$/C catalyst was the best one for the desired reaction.

**Experimental**

**Reagents.**—PdCl$_2$ (A.R.), Pd(NO$_3$)$_2$·2H$_2$O (A.R.) and Vulcan XC-72 carbon black were obtained from Aldrich and Cabot, respectively, NaBH$_4$ (A.R., purity ≥ 99.8%), NaCl(A.R., purity ≥ 99.8%) and AgNO$_3$ (A.R., purity ≥ 99.8%) were purchased from Sinopharm Chemical Reagent Company. All the aqueous solutions were prepared with 18.2 MΩ cm Milli-Q water (Millipore, USA). 0.01 M Na$_2$PdCl$_4$ solution was prepared by dissolving 0.001 mol of PdCl$_2$ and 0.002 mol of NaCl in 100 mL of H$_2$O.

**Catalyst synthesis.**—The nominal metal loading for all catalysts was 20 wt%. All the Pd$_{x}$Ag$_y$/C bimetallic catalysts were prepared by using the seeded-growth method, in which an Ag colloidal solution was synthesized and then mixed with a PdCl$_4^{2-}$ solution, followed by addition of ascorbic acid, and finally loaded on carbon black. Specifically, the procedures for preparing the most promising (Ag/C)Pd$_{1}$Ag$_{3}$/C catalyst is briefly described as follows: 130 mg of sodium citrate and 17.7 mg of AgNO$_3$ were mixed in 50 mL of H$_2$O. The mixture was ultrasonicated for 20 min to disperse carbon powder. Then, 15 mL of a freshly prepared ice-cold 0.1 M NaBH$_4$ aqueous solution was added dropwise into the above solution through a constant-flow pump at 0.5 mL min$^{-1}$, followed by mixing with 3.5 mL of 0.01 M Na$_2$PdCl$_4$. Then 5 mL of freshly prepared 0.1 M ascorbic acid aqueous solution was then added dropwise to the solution through a constant-flow pump at 0.5 mL min$^{-1}$. Such a mixture was vigorously stirred for 1 h, and then 45 mg of Vulcan XC-72 carbon pretreated with HNO$_3$ was added to the solution. The powder in the solution was stirred continuously at 30°C for 48 h, then filtered and rinsed with ultrapure Milli-Q water repeatedly. The Pd$_{1}$Ag$_{3}$/C catalyst was finally vacuum-dried at 50°C overnight. For preparing the other Pd$_{x}$Ag$_y$/C bimetallic catalysts, all the other procedures are largely same except the amounts of the Pd(II) and Ag(I) precursors and carbon black were adjusted according to the atomic Pd/Ag ratio.

For the synthesis of the Ag/C, Ag colloidal nanoparticles was directly loaded on carbon black support without adding Pd(II) precursor and ascorbic acid in the Ag colloidal solution. The Pd/C was prepared by using the coreduction of Pd(NO$_3$)$_2$ and AgNO$_3$ with NaBH$_4$ as the reducing agent. Briefly, 3.15 mL of 50 mM Na$_2$PdCl$_4$, 250 mg of sodium citrate and 67 mg of Vulcan XC-72 carbon were mixed in 50 mL of H$_2$O. The mixture was ultrasonicated for 20 min to disperse carbon powder. Then, 15 mL of a freshly prepared ice-cold 0.1 M NaBH$_4$ aqueous solution was added dropwise into the aqueous mixture under vigorous stirring through a constant-flow pump at 0.5 mL min$^{-1}$ in an ice-water bath. The suspension was kept stirring for 3 h in the ice-water bath and another 12 h at 30°C. After that, the powder in the solution was filtered and rinsed with ultrapure Milli-Q water repeatedly, and vacuum-dried at 70°C for overnight.

For comparison, another Pd$_{1}$Ag$_{3}$/C (20 wt%) catalyst was also prepared by using the coreduction of Pd(NO$_3$)$_2$ and AgNO$_3$ with NaBH$_4$ as the reducing agent, according to the report of Reference 39 (noted as Pd$_{1}$Ag$_{3}$/C-NaBH$_4$).

**Materials characterization.**—The compositions of as-synthesized catalysts were determined on inductively coupled plasma-atOMIC emission spectrometry (ICP-AES, Hitachi P-4010). The structures of these catalysts were examined by X-ray diffraction (XRD, D8 Advance X-ray Diffractometer) with the Cu Kα radiation at the 2θ angle from 30° to 90°. The morphology and size distribution of the catalysts were characterized by transmission electron microscopy (TEM, JEOL JEM-2010 microscope). The binding energies of core level electrons of Pd and Ag were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI-5000C ECSA) with the Mg Kα radiation (1253.6 eV), and the C 1s peak at 284.6 eV was used as the reference for calibration.

**Electrochemical measurements.**—The working electrode was a glassy carbon electrode (GCE, 3 mm in diameter) coated with a catalyst layer. The catalyst ink was prepared by mixing 1 ml of ethanol and 120 µl of 5 wt% Nafion solution and 2 mg of catalyst and sonating for 20 min, and 5.6 µL of this ink was transferred onto a freshly polished GCE and dried naturally to form a catalyst layer. A platinum foil and a saturated calomel electrode (SCE) served as counter and reference electrodes, respectively. The electrochemical measurements were run with a CHI 660B electrochemistry workstation.

The cyclic voltammetry (CV) was run on a GCE-supported catalyst layer in a N$_2$-saturated 1 M NaOH solution at 50 mV s$^{-1}$ within the potential range from −1.0 V to 0.1 V. The electrochemical surface area (ECSA) was calculated by integrating the charge associated with the peak area of CO desorption region through anodic CO stripping experiment, first by bubbling CO (∼99.9% purity) for 20 min, and then purging the dissolved CO by bubbling N$_2$ for 40 min while holding the potential at −0.9 V. At last, cyclic voltammogram for the CO stripping was recorded from −1.0 V to 0.1 V at 50 mV s$^{-1}$. The corresponding ECSA of a catalyst was evaluated by using Equation 1:

$$ECSA = Q / (m \times \alpha \times Q_{co}) \tag{1}$$

in which $Q$ is the electro-oxidation charge of the CO ad-layer, $m$ is the total mass of Pd loaded on GCE, and $Q_{co}$ is approximately 0.42 mC cm$^{-2}$ for the oxidation of a monolayer of CO on smooth Pd surface.

Cyclic voltammograms of EGOR on different catalysts were measured in 1 M ethylene glycol + 1 M NaOH solution between −1.0 V and 0.1 V at 50 mV s$^{-1}$ while chronoamperometric curves were recorded in the same solution at −0.3 V for 3600 s. All electrochemical measurements were run at 18 ± 1°C.

**Results and Discussion**

**TEM and HRTEM.**—The metal weight percentages and the Pd:Ag atomic ratios for the as-synthesized Pd-based catalysts are close to the desired values within measurement errors according to the ICP-AES assay, as listed in Table I. Figs. 1a–1f are TEM images for Pd$_{x}$Ag$_{y}$/C 18.3 3.72 106.60 Pd$_{1}$Ag$_{3}$/C 18.7 2.82 101.62 Pd$_{1}$Ag$_{2}$/C 18.0 1.81 86.59 Pd$_{1}$Ag$_{4}$/C 18.3 3.72 106.60 Pd/C 19.2 — 62.06 Pd$_{1}$Ag$_{4}$/C 18.6 0.52 58.08 Pd$_{1}$Ag$_{2}$/C 17.1 1.00 72.72 Pd$_{1}$Ag$_{3}$/C 18.0 1.81 86.59 Pd$_{1}$Ag$_{1}$/C 18.3 3.72 106.60 of the Pd$_{x}$Ag$_{y}$/C catalysts. The EDS mapping patterns for Pd$_{x}$Ag$_{y}$/C in Figs. 1g–1j in a larger scale suggest that Pd and Ag elements are distributed rather uniformly from particle to particle.

The structure and composition of an arbitrarily selected metallic nanoparticle from the Pd$_{1}$Ag$_{3}$/C catalyst were further characterized by HRTEM as well as EDS elemental analysis. The HRTEM image of the Pd$_{1}$Ag$_{3}$/C nanoparticle showing in Fig. 2a reveals a d-spacing of 2.28 Å for two adjacent lattice fringes, corresponding to that of

| Catalysts | ICP-AES | CO stripping |
|-----------|---------|--------------|
| Pd$_{1}$Ag$_{3}$/C | 18.6 | 0.52 | 58.08 |
| Pd$_{1}$Ag$_{2}$/C | 17.1 | 1.00 | 72.72 |
| Pd$_{1}$Ag$_{3}$/C | 18.0 | 1.81 | 86.59 |
| Pd$_{1}$Ag$_{4}$/C | 18.3 | 3.72 | 106.60 |
| Pd/C | 19.2 | — | 62.06 |

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a (111) plane of an face-centered-cubic (fcc) structured crystal, this value is slightly larger than that for Pd(111), or 2.24 Å, but smaller than that for Ag(111), or 2.36 Å. At a first glance, our preparation procedures might lead to a distinct Ag core-Pd shell structure, however, this may not be true. On one hand, due to different equilibrium redox potentials, i.e., $\psi^{0}_{\text{Ag}^{+}/\text{Ag}}$ (0.79 V vs SHE) and $\psi^{0}_{\text{Pd}^{2+}/\text{Pd}}$ (0.95 V vs SHE), galvanic displacement reaction occurred to some extent when Ag seeds met with Pd(II) species, in which Ag$^{+}$ ions diffused outwards and Pd atoms deposited inwards. As ascorbic acid was dropwise added, both the resulting Ag$^{+}$ ions and the remaining Pd(II) species were co-reduced gradually. This, together with the inter-diffusion of two metals, helps to mix Ag and Pd atoms, to form an alloy structure with surface Pd enriched. On the other hand, the mismatch of lattice constants between Pd (3.89 Å) and Ag (4.09 Å) is as high as 5.14%, resulting in the non-coherent interface with a large density of defects, which may further prevented Pd conformal overgrowth on the
The galvanic displacement and the lattice mismatch may also lead to reconstruction and formation of smaller Pd-Ag bimetallic nanoparticles.\(^27\) The evidence of an alloy structure can be found later in the XRD characterization, as neither isolated Ag nor Pd phase can be clearly identified. In fact, Figs. 2b–2d indicate that the Pd and Ag elements had almost consistent mapping across the nanoparticle, a repplot of the Pd/Ag elemental signal ratio in Fig. 2f along the arrow direction in Fig. 2e further suggests relative higher Pd concentration in the outer layers of the Pd\(_1\)Ag\(_3\) alloy nanoparticles. In other words, the Pd\(_1\)Ag\(_3\) nanoparticles assume an alloy structure with surface Pd enrichment, in agreement with the following XPS analysis.

**XRD characterization.** —The XRD patterns for Pd/C and Pd\(_x\)Ag\(_y\)/C catalysts are shown in Fig. 3, where the four features correspond to the fcc Pd crystalline structure. Sharp and intense XRD peaks for the Ag/C suggest larger Ag nanoparticles. In fact, the formation of Ag colloidal particles with a mean size of ca. 20 nm was found using the similar synthetic procedures.\(^28\,30\) The relative broader peaks with Pd\(_x\)Ag\(_y\)/C are consistent with smaller particle sizes, or ca. 9.5 nm, suggesting the formation of the Pd-Ag nanoalloy from Ag colloidal seeds is probably accompanied with restricted aggregation or geometric restructuring of Ag nanoparticles. If it were a typical Ag-core@Pd-shell structure, one would expect rather significant XRD features for the monometallic Ag core, especially for Ag-rich bimetallic catalysts. As mentioned in the above, the preferred alloy structure formation may arise from significant lattice mismatch between Ag and Pd and in-out inter-diffusion. The characteristic diffraction peaks of the Pd\(_x\)Ag\(_y\)/C catalysts shift toward smaller angles from those of Pd/C with increasing y: x value, owing to a larger Ag lattice constant.\(^29\,30\) Additionally, as arrowhead-marked in Fig. 3, for the Pd\(_1\)Ag\(_2\)/C, Pd\(_1\)Ag\(_3\)/C, Pd\(_1\)Ag\(_4\)/C and Ag/C catalysts a weaker shoulder peak around ca. 36\(^\circ\) possibly due to Ag\(_2\)O resulted from the aerial oxidation of exposed surface Ag atoms.\(^37\)

**XPS analysis.** —X-ray photoelectron spectroscopy (XPS) was further conducted to determine the surface composition and the oxidation state of the two metals of the Pd/C, Pd\(_x\)Ag\(_y\)/C and Pd\(_x\)Ag\(_y\)/C catalysts (Fig. 4). Shown in Fig. 4a, the binding energy of Pd 3d\(_{5/2}\) electrons is positively shifted by 0.35 eV for Pd\(_1\)Ag\(_3\)/C as compared to that for Pd/C. In contrast, Fig. 4b shows that the binding energy of Ag 3d\(_{5/2}\) electrons is negatively shifted by 0.50 eV as compared to that for monometallic Ag. Apart from Ag(0) species, Ag(I) also accounts for a significant composition of the surface layers determined by ex situ XPS, in line with the above XRD result. The shifts of core-level binding energies for Ag(0) and Pd(0), consistent with the result reported by Lam et al.,\(^44\) indicate a partial electron transfer between these two metals. Furthermore, based on the XPS peak areas and corresponding calibration factors, the Pd: Ag molar ratio estimated is ca. 2: 1 for the outer layers of the Pd\(_1\)Ag\(_3\) nanoparticles, significantly higher than the bulk average value (ca. 1: 2.8) as determined by ICP-AES. This, together with the above STEM EDS line scan elemental analysis result, confirms a surface Pd-enriched nanoalloy structure.

Normally, for a metal of different valences (like in metal oxides), the gain (or loss) of partial electron would cause a decrease (or increase) of binding energies of its core level electrons in XPS spectrum. However, this may not apply in the case of bimetallic alloys. In fact, M. Watanabe et al.\(^44\) explained in details that for Pt-Ru or Pt-Co alloy a positive shift of Pt core level binding energy should otherwise indicate the partial electron transfer to Pt from a less noble Ru or Co. Along this line, a positive shift of Pd 3d\(_{5/2}\) core level on Pd-Ag/C in our XPS measurement may be caused by the partial electron transfer from Ag to Pd atoms. This electron transfer direction is consistent with their electronegativities (EN) in Pauling scale, i.e., EN (Pd) = 2.20 eV, EN (Ag) = 1.93 eV, as well as work functions (WF), i.e., WF (Pd) = 5.2 eV, WF (Ag) = 4.26 eV. Similarly, electron transfer from Ag to Pd for Ag core@Pd shell was confirmed by Tsang et al. by using surface probe infrared spectroscopy.\(^46\) Also notably reported is that the direction of the core-level shift is commensurate with that of the valence band shift.\(^44\) Accordingly, the XPS result suggests the d-band center of Pd in the as-synthesized Pd\(_x\)Ag\(_y\)/C or Pd\(_x\)Ag\(_y\)/C is downshifted and that of Ag upshifted. This suggestion is to some
The Pd/C and PdxAg/C catalysts produced a typical voltammetric glassy carbon electrode respectively coated with different catalysts. Fig. 5b presents the apparent current densities observed on the same facilitates the comparison of Pd-mass activities of different catalysts. The sum of Pd and Ag mass loadings is same for the electrochemical measurement, Fig. 5a electrode areas (Fig. 5b), respectively. Since the electrocatalytic EGOR were examined by cyclic voltammetry. Fig. 6a shows the typical Pd-mass normalized CVs for the PdxAg/C catalysts in 1 M NaOH solution containing 1 M EG at 50 mV s\(^{-1}\) and Fig. 6b the corresponding mass and specific activities, using the peak currents in the positive-going potential (forward) scan to evaluate the activities while the electrochemical surface area (ECSA) of each catalyst was obtained by anodic CO stripping measurement and listed in Table I. It can be seen that Pd1Ag3/C exhibited both the highest Pd-mass activity and specific activity, i.e., 7.93 A mg\(^{-1}\) Pd and 7.82 mA cm\(^{-2}\), which are 5.54 and 3.15 times higher than those of Pd/C, i.e., 1.43 A mg\(^{-1}\) Pd and 2.31 mA cm\(^{-2}\), respectively. In addition, the onset oxidation potential on the Pd1Ag3/C is \(-0.69\) V, that is, the modified electronic properties of Pd and Ag favor the electrocatalytic EGOR.

Electrocatalytic properties of PdxAg/C catalysts.—Shown in Fig. 5 are the cyclic voltammograms (CVs) for the PdxAg/C and Pd/C catalysts in a N\(_2\)-saturated 1 M NaOH solution, with currents being normalized to the Pd masses loaded (Fig. 5a) and the geometric electrode area (b), respectively. Since the sum of Pd and Ag mass loadings is same for the electrochemical measurement, Fig. 5a facilitates the comparison of Pd-mass activities of different catalysts. Fig. 5b presents the apparent current densities observed on the same glassy carbon electrode respectively coated with different catalysts. The Pd/C and PdAg/C catalysts produced a typical voltammetric profile in the alkaline media with corresponding cathodic peaks appearing at ca. \(-0.4\) V being attributable to the reduction of PdO to Pd. The PdO to Pd peak areas in Fig. 5b reflected the exposed surface Pd sites of the tested catalyst layers of a given total metal mass. Specifically, the Pd/C catalyst layer yields the largest surface active area, consistent with its higher Pd loading and much smaller Pd particle sizes. Also it was noted that the Pd1Ag3/C catalysts did not exhibit significant H adsorption/desorption peaks, especially for the Ag-rich ones, again in accordance with the modified electronic property of Pd. It was mentioned that the decreased H diffusivity in Pd-Ag bimetallic alloys may also minimize the H adsorption/desorption feature.

The electrocatalytic activities of the PdxAg/C catalysts toward EGOR were examined by cyclic voltammetry. Fig. 6a shows the typical Pd-mass normalized CVs for the PdxAg/C catalysts in 1 M NaOH solution containing 1 M EG at 50 mV s\(^{-1}\) and Fig. 6b the corresponding mass and specific activities, using the peak currents in the positive-going potential (forward) scan to evaluate the activities while the electrochemical surface area (ECSA) of each catalyst was obtained by anodic CO stripping measurement and listed in Table I. It can be seen that Pd1Ag3/C exhibited both the highest Pd-mass activity and specific activity, i.e., 7.93 A mg\(^{-1}\) Pd and 7.82 mA cm\(^{-2}\), which are 5.54 and 3.15 times higher than those of Pd/C, i.e., 1.43 A mg\(^{-1}\) Pd and 2.31 mA cm\(^{-2}\), respectively. In addition, the onset oxidation potential on the Pd1Ag3/C is \(-0.69\) V, that is, the most negative one among those detected for all the tested catalysts. Additionally, the ratio between the peak current in the forward scan (I\(_f\)) and that in the backward scan (I\(_b\)) has been often used to roughly indicate the tolerance of a catalyst surface to poisoning species: the higher the ratio, the higher tolerance. As Table II shows, the I\(_f\)/I\(_b\) ratio for a Pd1Ag3/C catalyst was higher than that for Pd/C, and the ratio for the Pd1Ag3/C is among the highest, indicating its potentially good

| Catalysts     | E_{onset} (V) | I\(_f\) (A mg\(^{-1}\) Pd) | I\(_b\) (A mg\(^{-1}\) Pd) | I\(_f\)/I\(_b\) |
|--------------|--------------|-----------------|-----------------|----------------|
| Pd/C         | -0.53        | 1.43            | 1.24            | 1.15           |
| Pd1Ag1/C     | -0.60        | 2.91            | 1.64            | 1.77           |
| Pd1Ag2/C     | -0.61        | 3.71            | 1.97            | 1.88           |
| Pd1Ag3/C     | -0.65        | 6.69            | 3.18            | 2.10           |
| Pd1Ag4/C     | -0.69        | 7.93            | 2.52            | 3.16           |
| Pd1Ag5/C     | -0.67        | 6.28            | 1.91            | 3.29           |

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*Figure 5.* CVs for the Pd\(_x\)Ag\(_y\)/C and Pd/C in 1.0 M NaOH solution at 50 mV s\(^{-1}\) with currents normalized to Pd masses loaded (a) and the geometric electrode area (b), respectively. The inset in (b) shows the CV for Ag/C in otherwise same conditions with the axial labels omitted.

*Figure 6.* Pd-mass normalized CVs for Pd-based catalysts in 1 M NaOH solution containing 1 M EG at 50 mV s\(^{-1}\). The inset shows the CV for the Ag/C in otherwise same conditions (a). The calculated mass and specific activities based on the peak currents in the positive-going potential scan (b).
anti-poisoning property toward EGOR. Further durability verification of the catalysts toward EGOR at constant potential will be compared using chronoamperometry curves (vide infra). The parameters in Table II demonstrate a “volcano-like” dependence of electrocatalytic activity on bimetallic composition x:y, and the Pd$_x$Ag$_y$/C catalyst exhibits the most durable oxidation current.

As discussed in the above section, the electron transfer occurs from Ag to Pd. It is known that the C-C bond cleavage for ethanol or ethylene glycol is favored on Pt or Pd electrode at negative potentials. Along this line, electron-enriched Pd surface may also favor the C-C bond cleavage during EGOR. Moreover, the downshift of Pd d-band center in the as-synthesized Pd$_x$Ag$_y$/C catalyst may weaken the adsorption of possible poisoning intermediates such as CO and HO-CH$_x$ on Pd sites from the C-C bond cleavage, in favor of leaving more Pd active sites. On the other hand, although Ag is largely inactive for EGOR as seen in the inset of Fig. 6a, the moderate d-band upshift of Ag favors the adsorption of OH$_{ad}$, or the enhancement of the oxophilicity of Ag. In other words, Ag provides more OH$_{ad}$ at lower potentials to promote the EGOR process including the removal of the poisoning species on adjacent Pd sites, given that OH$_{ad}$ is the essential reactant pair. Synergically, the Pd$_x$Ag$_y$/C catalysts demonstrated significantly upgraded electrocatalytic activities, featuring with a negative shifted onset oxidation potential and an increased oxidation peak current. Nevertheless, too high Ag content may reduce significantly the active Pd sites on the surface, which may account for the start of decrease in electrocatalytic activity when the Pd: Ag atomic ratio changes from 1:3 to 1:4. In this regard, the role of Ag in Pd-Ag alloy catalyst toward EGOR is similar to that of Ru in Pt-Ru alloy catalyst toward methanol oxidation reaction, in which both electronic effect and bifunctional effect synergically account for.

To highlight the advantage of the present seeded-growth synthesis, carbon supported Pd$_x$Ag$_y$ catalyst was also prepared by the traditional NaBH$_4$ co-reduction method and tested for EGOR in otherwise same conditions. The TEM image in Fig. 7a shows that serious agglomeration of metallic nanoparticles existed in the Pd$_x$Ag$_y$/NaBH$_4$ catalyst, and Fig. 7b indicates the corresponding CV peak current toward EGOR on Pd$_x$Ag$_y$/C-NaBH$_4$ is only 3.92 A mg$^{-1}$. Much lower than that on Pd$_x$Ag$_y$/C, and the peak potential of the former is also more positive than that of the latter.

In order to further evaluate the durable electrocatalytic activity of the Pd$_x$Ag$_y$/C catalysts toward EGOR in the same solution, the chronoa omniperometry was applied at −0.3 V for 3600 s. Fig. 8 indicates that Pd$_x$Ag$_y$/C kept the highest oxidation current during the whole process, for example, at 3600 s the mass-activity was 2.79 A mg$^{-1}$ for this catalyst, that is 3.3, 2.6, 1.3, 3.6 and 8 times as high as that observed on Pd$_x$Ag$_y$/C, Pd$_x$Ag$_y$/C, Pd$_x$Ag$_y$/C, Pd$_x$Ag$_y$/C and Pd/C, respectively. Notably, the Pd$_x$Ag$_y$/C catalyst deactivated to a larger extent than expected from the above CV measurement. Based on all the above characterizations and measurements, we can conclude that the as-synthesized Pd$_x$Ag$_y$/C is the optimal bimetallic catalysts under examined for EGOR in alkaline media.

Conclusions

Carbon supported Pd$_x$Ag$_y$ bimetallic catalysts with varying compositions have been synthesized through seed-growth method using Ag colloid as seeds, resulting in Pd$_x$Ag$_y$ nanoparticle sizes of ca. 9.5 nm with an essentially alloy structure with surface Pd enrichment, as characterized by variety of methods. Electrocatalytic evaluation reveals that the as-synthesized Pd$_x$Ag$_y$/C catalysts display a “volcano-like” relationship for the Pd-mass activity as a function of bimetallic composition, and the Pd$_x$Ag$_y$/C catalyst yields the most enhanced and durable EGOR oxidation current among all the catalysts examined. The slightly downshifted d-band center of Pd and the bifunctional effect of more oxophilic Ag may account for this enhancement based on the existing guideline for bimetallic catalysts. The present work provides a unique synthetic tactic for obtaining carbon supported Pd-Ag bimetallic nanoalloy catalysts with potential application in efficient electrooxidation of ethylene glycol, thus promoting the development of the direct alkaline ethylene glycol fuel cell as well as the hydrogen production electrolyzer based on electroreforming of ethylene glycol.

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