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Electrochemical Study of Methanol Tolerant Oxygen Reduction Reaction Pd_xCo_y/C-

Catalysts from Organometallic Molecular Precursors

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Abstract

In this work, we study the mechanism and kinetics of the oxygen reduction reaction (ORR) over Pd/C, Pd₂Co/C and PdCo₂/C electrocatalysts synthesized by thermal reduction of organometallic $[Pd_3(\mu-3-Ph-pz)_6]$ [Et₄N]₂[Pd₂Co(μ -4-I-3,5-Me_2-pz)₄Cl₄], precursors. such and as $[Et_4N]_2[PdCo_2(\mu-4-I-3,5-Me_2-pz)_4Cl_4]$. The methanol tolerance and formation of peroxide under oxygen reduction reaction conditions were determined using a rotating disk electrode (RDE) and a rotating ring disk electrode (RRDE). The Pd₂Co/C catalysts prepared from [Et₄N]₂[PdCo₂(4-I-3,5-Me₂-pz)₄Cl₄] showed the best ORR activity and higher methanol tolerance, compared with commercial platinum catalysts. The ORR electron transfer number for Pd₂Co/C was 3.7, similar to the Pd/C commercial catalysts. Compared to the commercial catalysts, Pd₂Co/C and PdCo₂/C showed the highest hydrogen peroxide formation (%H₂O₂), 16 and 24\%, respectively. Electrogeneration of hydrogen peroxide has potential application in advanced oxidation processes.

Keywords: PdCo; Oxygen Reduction Reaction; Organometallic Molecular Precursors; Rotating Ring Disk Electrode; H₂O₂

Introduction

Direct methanol fuel cells (DMFC) are promising power sources for portable devices due to their high power density and low operating temperature [1, 2]. However, DMFCs face multiple obstacles that hinder their commercialization. Two of these obstacles are: (1) the crossover of methanol from the anode to the cathode through the membrane and (2) the sluggish kinetics of the oxygen reduction reaction (ORR) at the cathode. Methanol crossover reduces the DMFC efficiency and performance (ca. 200 mV), caused by the mixed potential generated at the cathode [3]. A competition between oxygen reduction and methanol oxidation occurs in Pt electrocatalysts when the methanol crosses over from the anode to the cathode through the membrane [4]. Platinum alloy and non-Pt based catalysts have been studied to reduce the high cost, and improve the ORR activity and methanol tolerance [5-12].

Besides their lower cost, Pd-based electrocatalysts have been widely studied because of their selectivity for ORR in acid media [10, 13-16]. For example, carbon-supported Pd-Co alloy catalysts have shown high methanol tolerance as cathode material in acidic direct methanol fuel cells [4, 17-20]. Moreover, such catalysts have demonstrated good ORR performance [2].

The ORR can proceed by a 4-electron transfer direct mechanism with water as the final product, or an indirect 2-electron transfer mechanism with hydrogen peroxide (H_2O_2) as an intermediate [21, 22]. Equation 1 presents the direct 4e⁻ transfer pathway where oxygen is reduced directly to water.

$$0_2 + 4H^+ + 4e^- \rightarrow 2H_20$$
 [1]

Equations 2 to 4 present the 2e⁻ transfer pathway for oxygen reduction with hydrogen peroxide as an intermediate.

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$$
 [2]
H O + 2H^+ + 2e^- $\rightarrow 2H$ O [3]

$$\Pi_2 O_2 + 2\Pi + 2e \rightarrow 2\Pi_2 O$$
 [3]

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{4}$$

In the 2e⁻ transfer pathway, the peroxide formed is electrochemically further reduced to water, or it disproportionates to water and dioxygen [23]. The peroxide formation causes degradation of the membrane, leading to decrease of cell durability [24, 25]. For ORR, the direct 4e- pathway is desired, but it has been difficult to find catalysts to achieve it. Several theoretical studies of the mechanism and kinetics of ORR in alloy catalysts have been reported [26-28]. Zhang et al. have presented an overview of the proposals put forward towards the improvement of ORR in alloys [29]. The incorporation of Co in Pd electrocatalysts can improve the kinetics and mechanism of ORR.

In this work we studied Pd_xCo_y/C catalysts derived from the organometallic molecular precursors $[Pd_3(\mu-3-Ph-pz)_{6,}]$, $[Et_4N]_2[Pd_2Co(\mu-4-I-3,5-Me_2-pz)_4Cl_4]$, and $[Et_4N]_2[PdCo_2(\mu-4-I-3,5-Me_2-pz)_4Cl_4]$. The ORR electrocatalytic activity and methanol tolerance of the palladium and palladium-cobalt catalysts synthesized by chemical and thermal reduction of the organometallic precursors was studied. The kinetics and mechanism of the ORR was determined using the rotating ring disk electrode (RRDE) technique. The number of electrons transferred and the amount of peroxide (H₂O₂) formed during ORR was also determined. Electrogeneration of hydrogen peroxide has potential application in advanced oxidation processes [30].

Experimental Section

The synthesis and characterization of the carbon supported electrocatalysts was described in detail elsewhere [31]. Briefly, the chemical reduction (CRht) was carried out by mixing the tailored organometallic precursor such as $[Pd_3(\mu-3-Ph-pz)_6]$ [32-35], $[Et_4N]_2[Pd_2Co(\mu-4-I-3,5-Me_2-pz)_4Cl_4]$, and $[Et_4N]_2[PdCo_2(\mu-4-I-3,5-Me_2-pz)_4Cl_4]$ [36] (See Table 1) with the Vulcan XC-72R in THF solvent under sonication. After uniform dispersion was achieved, excess of reducing agent (NaBH₄) was slowly added dropwise with stirring, the solution was filtered, washed and dried. Then, the resulting solid was heat treated at 600 °C under a N₂ atmosphere. The thermal reduction (TR), of the organometallic complexes, was done by mixing the precursor with Vulcan XC-72R in CH₂Cl₂ under constant stirring followed by sonication until solvent evaporation. The reduction process was performed in a closed tube furnace by increasing the temperature over 620 °C under H₂ atmosphere. The samples were labeled, according to the synthesis method and precursor used as Pd/C (CRht), Pd/C (TR), Pd₂Co/C (TR) and PdCo₂/C (TR). The commercial catalysts on carbon support used were 20% Pd/C (BASF), 20% Pt/C (Alfa Aesar) and 20% PtCo/C (BASF).

The electrochemical measurements were performed using an AutoLab potentiostat (PGSTAT 30) and PINE bipotentiostat (AFCBP1) with a MSRX rotator (PINE Instruments) for the RDE and RRDE experiments, respectively. A three-electrode cell was employed in all experiments with a graphite rod as auxiliary electrode and HglHg₂SO₄ (K₂SO₄, sat.; 0.64 V vs. NHE) as reference electrode. For RDE technique, a glassy carbon electrode (PINE Instruments, E2M) modified with the catalysts ink was employed as working electrode. For RRDE technique, glassy carbon (GC) disk and platinum (Pt) ring from PINE Instruments was used. Working electrodes were polished mechanically in alumina and electrochemically in 0.5 M H₂SO₄. The

catalyst ink was prepared by mixing 1 mg of catalyst, 250 μ L of 2-propanol (Aldrich) and 8 μ L Nafion[®] 5 wt% (Aldrich), followed by sonication for one-half hour. Finally, the GC surface was modified with 8 μ L (RDE) and 10 μ L (RRDE) of the catalysts ink mixture and was allowed to completely dry before the voltammetric experiments were carried out.

The cyclic voltammetry (CV) was carried out in a potential window between -0.65 V and 0.9 V vs. HglHg₂SO₄ in 0.5 M H₂SO₄ at a scan rate of 100 mV/s under argon. A potential window between -0.64 V to 0.66 V and -0.65 V to .076 V vs. HglHg₂SO₄ was used for the Pt electrocatalysts and Pt ring, respectively. ORR activity was determined by linear sweep voltammetry (LSV) at potentials between 0.6 V to -0.5 V vs. HglHg₂SO₄ in oxygen saturated 0.5 M H₂SO₄ solution with a scan rate of 5 mV/s. The study of the electrocatalysts tolerance toward methanol was carried out in 1.0 M MeOH/0.5 M H₂SO₄ solution purged with oxygen for 15 minutes (saturated) at a scan rate of 5 mV/s. The RDE and RRDE measurements were done at rotating speed of 1,600 rpm. Also, a study with varying rotation speed between 500 rpm to 3000 rpm was performed. The ring potential was held constant at 0.56 V vs. HglHg₂SO₄ (ca. 1.2 V vs. RHE) for the peroxide formation detection. The deionized water used for the experiments was previously distilled and pumped through a Nanopure system (Barnstead) to give 18 MΩ-cm resistivity. All electrochemical experiments were carried out at room temperature.

The geometrical area of the glassy carbon (GC) electrode was 0.196 cm². The RRDE have surface areas of 0.2475 cm² for the GC disk and 0.1866 cm² for the Pt ring. The electroactive surface area (ESA) was determined by measuring the charge of the Pd oxide reduction region, from the CV in 0.5 M H₂SO₄, divided by the theoretical charge for a palladium oxide monolayer reduction (424 μ C/cm²) [37-39]. For platinum, ESA was determined by measuring the charge of the Pt hydrogen adsorption/desorption region, from the cyclic

voltammetry in 0.5 M H₂SO₄, divided by the theoretical charge of 210 μ C/cm² [40-42]. All currents were normalized to the ESA of the electrode. The mass activity (MA) was determined by dividing the current by the catalyst mass (mg_M, where M is Pd or Pt).

The number of electrons transferred per oxygen (*n*) and the molar fraction of peroxide formation $(x_{H_2O_2})$ were calculated using the following equations [43, 44]:

$$n = \frac{4i_D}{i_D + (i_R/N)}$$
^[5]

$$x_{H_2O_2} = \frac{2i_R/N}{i_D + (i_R/N)}$$
[6]

where i_D is the disk current, i_R is the ring current and *N* is the collection efficiency of the RRDE. The collection efficiency (*N*) of 37% was provided by the manufacturer of the ring-disk electrode [8]. The currents (i_D and i_R) at 0.06 V vs. HglHg₂SO₄ (ca. 0.7 V vs. RHE) corresponding to typical fuel cell operating potential was used for determination of number of electrons transferred and peroxide formation.

The morphology of the Pd₂Co and PdCo₂ nanoparticles was determined by electron microscopy techniques. A Carl Zeiss LEO-922 TEM microscope with Scanning TEM (STEM) capabilities was used to obtain transmission electron microscopy images of the carbon-supported nanoparticles. Also, a FEI Tecnai F20 with acceleration voltage of 200kV was used. The FEI T12 Spirit TEM STEM with accelerating voltage of 120 kV was used to obtain the scanning transmission electron microscopy images. High resolution scanning electron microscopy (SEM) images and energy-dispersive X-ray fluorescence spectroscopy (EDS) mapping was performed in a FEG Hitachi S-5500 ultra high resolution electron microscope at 30 kV.

Results and Discussions

The morphology and composition of the Pd-based catalytic nanoparticles supported on carbon was reported previously [31]. Figure 1 shows the cyclic voltammograms for Pd/C, Pd₂Co/C and PdCo₂/C electrocatalysts in 0.5 M H₂SO₄. From the voltammograms, the hydrogen adsorption/desorption peaks was observed for the Pd/C (CRht) and Pd/C (TR) catalysts (see Figure 1a). However, the hydrogen adsorption/desorption peaks were not defined for Pd₂Co/C (TR) and PdCo₂/C (TR) (see Figure 1b and 1c). The voltammetry for the Pd₂Co/C (CRht) and PdCo₂/C (CRht) catalysts are not presented, because previous studies showed incomplete reduction of their precursors [31]. X. Li et al. have explained that Co incorporation within the Pd-Co catalysts prevents the dissolution of hydrogen into Pd [45]. L. Zhang et al. proposed that the differences in CV might be due to the formation of Pd-Co alloy [46]. Table 2 presents the electrochemical surface area (ESA) obtained from the CV. The Pd/C (CRht) has larger ESA than Pd/C (TR) catalysts, attributed to the smaller particle size. The Pd₂Co/C (TR) and PdCo₂/C (TR) have practically the same ESA, probably because the % of metal in the PdCo₂/C (TR) is greater than Pd₂Co/C (TR) [21].

Linear sweep voltammetry (LSV) in acid solution saturated with oxygen at rotation speed of 1,600 rpm was used to determine the catalysts' activity toward oxygen reduction reaction (ORR) and their methanol tolerance. Figure 2 shows linear sweep voltammograms of the (a) Pd/C, (b) Pd₂Co/C and (c) PdCo₂/C catalysts without and with 1 M MeOH in 0.5 M H₂SO₄. Figure 2a shows that Pd/C (CRht) has less ORR activity than the Pd/C (TR) catalyst. Table 2 summarizes the cathodic current density and mass activity for the oxygen reduction reaction at 0.1 V vs. HglHg₂SO₄ in 0.5 M H₂SO₄ solution for the carbon supported catalytic nanoparticles using RDE techniques. The Pd/C (TR) has a somewhat higher current density than Pd₂Co/C (TR). Nevertheless, Pd₂Co/C (TR) has higher mass activity than Pd/C (TR).

Table 3 presents the results for the ORR onset potentials at specific current density and mass activity for the Pd/C, Pd₂Co/C and PdCo₂/C catalysts with and without methanol, using the RDE technique. The Pd/C (TR) has a positive onset potential of 28 mV when compared with Pd/C (CRht) at a current density of -20 μ A/cm². This result was unexpected, because the Pd/C (CRht) has the smallest particle size and largest superficial area and should thus have greater ORR catalytic activity. The oxygen reduction reaction in Pd₂Co/C (TR) has a positive onset potential of 30 mV when compared with PdCo₂/C (TR) at a current density of -20 μ A/cm². In term of mass activity, the Pd₂Co/C (TR) had a positive shift of the ORR onset potential of 26 mV when compared with PdCo₂/C (TR). The Pd₂Co/C (TR) catalyst has a similar ORR onset potential when compared with Pd/C (TR) catalysts. These results confirm that the incorporation of the non-noble metal (cobalt) into the catalyst does not affect the electrocatalytic activity towards ORR and might even be improving it.

The methanol tolerance of the Pd catalysts was determined. The Pd₂Co/C (TR) and PdCo₂/C (TR) have higher current densities and mass activity in the presence of methanol (see Figures 2b and 2c). For all Pd catalysts, slightly positive shifts in the ORR onset potentials in presence of methanol were observed. Tarasevich et al. has explained that methanol increases the solubility of oxygen, which may be the reason for this increased activity [47]. These results confirm the activity toward ORR with high methanol tolerance of the Pd-based carbon supported catalysts.

The voltammetric measurements of the commercial carbon-supported catalysts were carried out to compare their ORR activity and MeOH tolerance with those of our catalysts. The Pt/C catalyst has the higher electrochemical surface area (see Table 2). LSV in presence of methanol was carried out to determine the selectivity of the catalysts for oxygen reduction. Figure 3 shows the oxygen reduction electrocatalytic activity without and with methanol for Pd/C, Pt/C and

PtCo/C commercial catalysts. In the LSV, can be observed the well-defined kinetics, mixed and diffusion regions of commercial Pt/C and PtCo/C electrocatalysts. The ORR activity trend is PtCo/C > Pt/C > Pd/C. The presence of cobalt in the Pt catalyst improves the ORR electrocatalytic activity. The Pd/C commercial catalyst has overpotential of 67 mV and 128 mV than Pt/C and PtCo/C commercial catalysts, respectively (see Figure 3).

The PtCo/C commercial catalyst presents the higher mass activity towards the oxygen reduction reaction in acid solution. In presence of MeOH, the observed ORR electrocatalytic activity was from best to worst: Pd/C >> Pt/C >>> PtCo/C; the latter two catalysts have poor electrocatalytic activity towards ORR in presence of methanol. In the Pt/C catalyst, with MeOH, the methanol oxidation and oxygen reduction reaction occur simultaneously, causing a mixed potential [3]. It is well known that Pt carbon-supported catalysts have better ORR activity and worse MeOH tolerance than Pd carbon-supported catalysts [48, 49]. The incorporation of cobalt in the platinum catalyst improves the methanol tolerance, but was not selective to ORR, as shown Figure 3. The advantage of the Pd catalysts is its selectivity to oxygen reduction reaction in acid media.

Figure 4 shows a comparison between our Pd-based and the commercial catalysts in ORR activity and methanol tolerance shows that the former have higher current density (Fig. 4a). The ORR onset potential decreases in the following order: $PtCo/C > Pt/C > Pd_2Co/C$ (TR) $\geq Pd/C$ (TR) $\geq Pd/C$ (TR) $\geq Pd/C > Pd/C > PdCo_2/C$ (TR) at -2 mA/mg_M. As discussed above, the Pt catalysts have better ORR activity and poor MeOH tolerance. The better ORR activity of Pt/C catalyst compared with Pd/C and Pd-Co/C catalysts has also been reported by others [4, 46, 47]. On the other hand, Pd-based carbon-supported catalysts have a high tolerance towards methanol. Also, a slight positive shift of the onset potential for our catalysts in presence of methanol is noted (see Figure 4). This

comparison shows that Pd_2Co/C (TR) is the best among the Pd catalysts studied here, in agreement with literature reports [4]. The incorporation of cobalt to palladium catalysts improves the electrocatalytic oxygen reduction activity without affecting the methanol tolerance.

Figure 5 shows the ORR activity for the Pd₂Co/C (TR) catalysts upon variation of rotation speed from 500 rpm to 3000 rpm. Similar voltammetry was observed for the Pd/C (CRht), Pd/C (TR) and PdCo₂/C (TR) catalysts (not shown). In the voltammograms, the kinetic regions are the same with changes in the rotation speeds. The mixed kinetic-diffusion and diffusion-controlled regions show an increase of current densities with increasing rotation speeds. The ORR voltammograms are highly affected by the rotation speed of the electrode, as higher rotation speed facilitates the mass transport of oxygen to the electrode surface [50]. Similar results were observed for the commercial catalysts (not shown). The ORR mechanism can be inferred from the Koutechy-Levich plot ($1/i vs. 1/\omega^{1/2}$), according the following equation [42]:

$$\frac{1}{i} = \frac{1}{i_K} + \frac{1}{i_L} = \frac{1}{i_K} + \frac{1}{0.62n\text{FAD}^{2/3}\text{C}\nu^{-1/6}\omega^{1/2}}$$
[7]

where $i_{\rm K}$ is the kinetic current density, $i_{\rm L}$ the mass transport limiting current, *n* the number of electrons (e⁻) transferred in the reaction, F Faraday's constant, A the electrode area, D the diffusion coefficient, C the concentration of oxygen in the solution, *v* the kinematic viscosity and ω is the rotation speed. Figure 6 shows the nearly straight line Koutechy-Levich (K-L) plots for our (a) Pd/C (CRht) and Pd/C (TR), (b) Pd₂Co/C (TR) and PdCo₂/C (TR) catalysts, and (c) Pd/C, Pt/C and PtCo/C commercial catalysts, indicating a first-order oxygen reduction reaction [4]. The results reveal that the ORR principally follows a 4e- transfer pathway, with lesser contributions by 4e- and 2e- pathways with peroxide as intermediate. The RRDE data presented below corroborate the conclusions derived from the K-L plots.

Rotating ring disk electrode technique was applied to the study of the ORR kinetics and to distinguish between the $4e^-$ and $2e^-$ transfer mechanisms at carbon supported palladium and palladium-cobalt nanocatalysts by determining the amount of peroxide formed. In the RRDE experiment, the potential of ring was held at 0.56 V vs. HglHg₂SO₄, where the oxidation of the H₂O₂ formed on the disk electrode during ORR is limited by diffusion [51].

Figure 7 presents the RRDE voltammograms of our Pd/C (CRht), Pd/C (TR), Pd₂Co/C (TR) and $PdCo_2/C$ (TR) catalysts for the oxygen reduction reaction and the peroxide formation. It is observed that above +0.1 V the reaction is kinetically controlled, but diffusion controlled below -0.1 V. In the -0.1 to +0.1 V range, the ORR is controlled by a mix of kinetic and diffusion process. Figure 8 shows the oxygen reduction reaction and the peroxide formation for the Pd/C, Pt/C and PtCo/C commercial catalysts at rotation speed of 1,600 rpm. The ring current is not significant above 0.1 V and starts to increase from the mixed region to the diffusion process region. The calculated percentage of peroxide formation (%H₂O₂) and number of electrons transferred (n) during the oxygen reduction are listed in the Table 4. Because the formation of peroxide is dependent of the potential, the values were calculated at a typical fuel cell operating potential of 0.70 V vs. RHE. The ring currents are negligible with respect to disk current for the Pt/C commercial, PtCo/C commercial and our Pd/C (TR) electrocatalysts. The negligible peroxide formation (<10%) indicates a four-electron process with water as principal product [10]. The number of electrons transferred in the oxygen reduction reaction is 3.9 for the Pt/C, PtCo/C and Pd/C (TR). For the Pd/C commercial, Pd/C (CRht) and Pd₂Co/C (TR), similar formation of peroxide was found, indicating a mix of 4e⁻ and 2e⁻ transfer pathways. The value of *n* is the same for the Pd/C commercial and Pd₂Co/C (TR) catalyst (n = 3.7). Typically, the overall n < 4, because of the oxygen reduction mixed pathways (2e⁻ and 4e⁻). Adzic and co-

workers calculated the number of electrons involved in the ORR to be approximately 3.9 for a Pd_2Co/C alloy electrocatalyst [10]. The higher H_2O_2 formation was found in the $PdCo_2/C$ (TR) catalysts with a value of 24%. RRDE voltammograms in presence of MeOH of the Pd/C and Pd-Co/C bimetallic catalysts are similar to those obtained in the absence of methanol (not shown). The oxygen reduction by 4e⁻ transfer pathway is the principal one for all catalysts studied here, although 2e⁻ transfer pathways are present.

Electron Microscopy of Pd2Co/C Catalyst

STEM image and elemental maps line scan of Pd₂Co/C and PdCo₂/C catalysts particle was done. The X-ray fluorescence emission line scan shows that the nanoparticle is composed of the elements palladium and cobalt (see Figure 9). The nanoparticle is bimetallic and not an oxide of the metals. Figure 10 and 11 show FE-SEM and X-ray fluorescence mapping images for the Pd (red), Co (cyan) and C (green) elements for the Pd₂Co/C (TR) and PdCo₂/C catalysts, respectively. In the X-ray fluorescence mapping image, it can be observed the carbon signals from the support (Vulcan) throughout the image and the Pd and Co signals at only one area. The bimetallic particle was formed like a palladium core and cobalt shell. The literature explains that homogeneous alloys on the surface of a metal with high negative fee energy for oxide formation (Co) and metal with high standard reduction potential (Pd) can increase the ORR catalytic activity [19, 52].

Conclusions

The RDE technique was used successfully to study the ORR activity and MeOH tolerance of the Pd-based carbon supported electrocatalysts. The most positive onset potential was determined for the Pd_2Co/C (TR) electrocatalyst, which exhibits the highest mass activity

compared to the other Pd-based catalysts. A positive onset potential shift was found for the Pdbased/C catalyst in presence of MeOH. The palladium catalysts have better methanol tolerance than Pt catalysts. The Pd-Co/C bimetallic catalysts are selective to the oxygen reduction reaction. The percentage of H₂O₂ formation for the Pd-based catalyst was between 7% and 24%. The oxygen reduction by 4e⁻ transfer pathway with water as product was the principal pathway for all catalysts, although 2e⁻ transfer pathway with peroxide as intermediate also occurred, but to a lesser extent. The number of electrons transferred in the oxygen reduction reaction was found for the Pd₂Co/C (TR) electrocatalyst to be 3.7. From the RRDE measurements, our Pd₂Co/C catalyst was found to have the same kinetics and mechanism as the Pd/C commercial catalysts. The Pd₂Co/C can be an excellent cathode electrocatalyst for direct methanol fuel cells. Compared to the commercial catalysts, Pd₂Co/C and PdCo₂/C showed the highest hydrogen peroxide formation (%H₂O₂), 16 and 24%, respectively. Electrogeneration of hydrogen peroxide has potential application in advanced oxidation processes.

Acknowledgments

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FIGURES



Figure 1. Cyclic voltammograms of (a) Pd/C (CRht) and Pd/C (TR), (b) Pd₂Co/C (TR) and (c) PdCo₂/C (TR) catalysts in 0.5 M H₂SO₄ at a scan rate of 100 mV/s.



Figure 2. Rotating disk electrode (RDE) linear sweep voltammograms for (a) Pd/C, (b) Pd₂Co/C and (c) PdCo₂/C catalysts without (solid line) and with 1 M MeOH in 0.5 M H₂SO₄ (dashed line) purged with oxygen for 15 min before each experiment, scan rate of 5 mV/s and rotation speed of 1,600 rpm.







Figure 4. Rotating disk electrode (RDE) linear sweep voltammetry for (a) oxygen reduction reaction activity and (b) methanol tolerance for Pt/C (solid line), PtCo/C (dashed line), Pd/C (dotted line) commercial and our Pd/C (dash-dotted line), Pd₂Co/C (dash-dot-dotted line) and PdCo₂/C (short dashed line) catalysts. Scan rate of 5 mV/s and a rotation speed of 1,600 rpm.



Figure 5. Rotating disk electrode (RDE) linear sweep voltammetry of the Pd_2Co/C catalyst in 0.5 M H_2SO_4 saturated with oxygen at varying rotation speeds and scan rate of 5 mV/s.

MA

R



Figure 6. Koutechy-Levich plots of the RDE study of ORR in 0.5 M H_2SO_4 of the (a) Pd/C (CRht) and Pd (TR), (b) Pd₂Co/C (TR) and PdCo₂/C (TR), and (c) commercial Pd/C, Pt/C and PtCo/C catalysts.



Figure 7. Rotating ring disk electrode (RRDE) voltammograms of the (upper) disk (i_D) and (lower) ring (i_R) currents for Pd/C (CRht) (solid line), Pd/C (TR) (dashed line), Pd₂Co/C (TR) (dash-dotted line) and PdCo₂/C (TR) (dash-dot-dotted line) catalysts in 0.5 M H₂SO₄ saturated with oxygen at scan rate of 5 mV/s and speed rotation of 1,600 rpm. The ring potential was held at 0.56 V vs. HglHg₂SO₄ (ca. 1.2 V vs. RHE) for the peroxide formation detection.



Figure 8. Rotating ring disk electrode (RRDE) voltammograms for the commercial Pd/C (solid line), Pt/C (dashed line) and PtCo/C (dash-dotted line) catalysts in 0.5 M H_2SO_4 saturated with oxygen at scan rate of 5mV/s and speed rotation of 1,600 rpm; (upper) i_R and (lower) i_D are disk and ring measured currents. The ring potential was held at 0.56 V vs. HglHg₂SO₄ (ca. 1.2 V vs. RHE) for the peroxide formation detection.



Figure 9. STEM images and elemental line scan in particle after thermal reduction process of Pd_2Co precursor on carbon Vulcan.

MAN



Figure 10. Scanning electron microscopy image and energy dispersive X-ray analysis (SEM-EDS) elemental mapping showing the Pd, Co, and C X-ray fluorescence maps for the Pd₂Co/C catalysts.



Figure 11. High resolution SEM with energy dispersive X-ray analysis (SEM/EDS) elemental mapping images for the Pd, Co, and C elements in the PdCo₂/C catalyst material.

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TABLES



Note: *From Ref. 33-36. Copyright © 2004, American Chemical Society. **From Ref. 37. Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Table 2. The cathodic current density and mass activity for the oxygen reduction reaction at 0.100 V vs. $Hg|Hg_2SO_4$ in 0.5 M H_2SO_4 . Electrochemical charge and calculated electrochemical surface area for the catalytic nanoparticles using rotating disk electrode techniques.

| Nanocatalysts | Current density (A/cm ²)* | Mass activity (A/mg _M)* | Surface area (cm ²) [#] |
|---------------------------|---------------------------------------|--|---|
| Pd/C (CRht) | -7.03 x10 ⁻⁶ | -7.79 x10 ⁻⁴ | 0.726 |
| Pd/C (TR) | -3.34 x10 ⁻⁵ | $-1.23 \text{ x} 10^{-3}$ | 0.216 |
| Pd ₂ Co/C (TR) | -3.29 x10 ⁻⁵ | $-1.35 \text{ x}10^{-3}$ | 0.116 |
| PdCo ₂ /C (TR) | -1.45 x10 ⁻⁵ | -5.20 x10 ⁻⁴ | 0.119 |
| Pd/C commercial | -7.36 x10 ⁻⁶ | -9.58 x10 ⁻⁴ | 0.994 |
| Pt/C commercial | -9.38 x10 ⁻⁵ | $-4.70 \text{ x} 10^{-2}$ | 2.965 |
| PtCo/C commercial | -5.19 x10 ⁻⁴ | $-7.05 \text{ x}10^{-2}$ | 0.516 |

Note: *Cathodic current density and mass activity for oxygen reduction reaction at 0.100 V vs. HglHg₂SO₄. For oxygen reduction reaction (ORR) activity, the solution was purged with oxygen for 15 min at 10 mL/min before each experiment. [#]Electrochemical surface areas were calculated from the electrochemical Pd surface oxide reduction charge and the conversion factor of 424 µC cm²; and for Pt from the hydrogen desorption charge and the conversion factor of 210 µC cm².

Table 3. Oxygen reduction reaction onset potentials at specific current, current density and mass activity for our Pd/C, Pd_2Co/C , $PdCo_2/C$ and the commercial Pd/C, Pt/C and PtCo/C catalysts with and without methanol using RDE techniques.

| | at -0. | 20 μA/cm ² | at -2 | mA/mg _M |
|---------------------------|-----------------------|-----------------------|-----------------------|--------------------|
| Nanocatalysts | E (V) | E (V) w/MeOH | E (V) | E (V) w/MeOH |
| Pd/C (CRht) | 0.080 | 0.084 | 0.085 | 0.090 |
| Pd/C (TR) | 0.108 | 0.113 | 0.096 | 0.102 |
| Pd ₂ Co/C (TR) | 0.110 | 0.118 | 0.096 | 0.104 |
| PdCo ₂ /C (TR) | 0.087 | 0.098 | 0.070 | 0.082 |
| Pd/C commercial | 0.083 | 0.082 | 0.091 | 0.089 |
| Pt/C commercial | 0.150 | - | 0.214 | - |
| PtCo/C commercial | 0.211 | - | 0.233 | - |

Note: All potentials are vs. HgIHg₂SO₄. Current densities were determined using the electrochemical surface area. Mass activities were determined for our catalysts using the weight of Pd metal from ICP analysis and for commercial catalysts the % metal provided by the supplier.

Table 4. Determination of the hydrogen peroxide formation $(\%H_2O_2)$ and number of electrons (*n*) for the oxygen reduction reaction using RRDE techniques.

| Dd/C (CDht) | % Π 2 U 2 | n |
|-------------------|-------------------------|-----|
| Pu/C (CKIII) | 11 | 3.8 |
| Pd/C (TR) | 7 | 3.9 |
| Pd_2Co/C (TR) | 16 | 3.7 |
| $PdCo_2/C$ (TR) | 24 | 3.5 |
| Pd/C commercial | 14 | 3.7 |
| Pt/C commercial | 5 | 3.9 |
| PtCo/C commercial | 4 | 3.9 |
| | | |
| CHR . | | |

Highlights

- Oxygen reduction reaction (ORR) catalyst of the type Pd/C, Pd₂Co/C and PdCo₂/C were successfully synthesized by thermal reduction of organometallic precursors, such as [Pd₃(μ-3-Ph-pz)₆], [Et₄N]₂[Pd₂Co(μ-4-I-3,5-Me₂-pz)₄Cl₄], and [Et₄N]₂[PdCo₂(μ-4-I-3,5-Me₂-pz)₄Cl₄].
- 2. The methanol tolerance and formation of hydrogen peroxide under oxygen reduction reaction conditions were demonstrated.
- 3. Compared to the commercial catalysts, Pd₂Co/C and PdCo₂/C showed the highest hydrogen peroxide formation (%H₂O₂), 16 and 24%, respectively. Electrogeneration of hydrogen peroxide has potential application in advanced oxidation processes.

