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Publisher's version / Version de l'éditeur:

<https://doi.org/10.1016/j.electacta.2009.12.090>

Electrochimica Acta, 55, 2010, pp. 8182-8188, 2010-01-11

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Formic acid electro-oxidation on carbon supported Pd_xPt_{1-x} (0 ≤ x ≤ 1) nanoparticles synthesized via modified polyol method

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ARTICLE INFO

Article history:

Received 29 October 2009

Received in revised form

22 December 2009

Accepted 23 December 2009

Available online 11 January 2010

Keywords:

Bimetallic nanoparticles

PdPt

Formic acid

Direct formic acid fuel cells

Electrocatalyst

ABSTRACT

Carbon supported nanoparticle catalysts of Pd_xPt_{1-x} (0 ≤ x ≤ 1) were synthesized using a modified polyol method and poly(N-vinyl-2-pyrrolidone) (PVP) as a stabilizer. Resulting nanoparticles were characterized by X-ray photoelectron spectroscopy (XPS), cyclic voltammetry (CV) and chronoamperometry (CA) study for formic acid electro-oxidation. Surface composition of the synthesized nanoparticles found from XPS revealed the Pt surface segregation even for the Pd-rich compositions. It is suggested that the surface segregation behavior in PdPt nanoparticles supported on carbon may be influenced, in addition to the difference in Pd and Pt surface energies, by particle size and particle interaction with the support. According to CA, the carbon supported Pd nanoparticles show the highest initial activity towards formic acid electro-oxidation at the potential of 0.3 V (RHE), due to the promotion of the direct dehydrogenation mechanism. However its stability is quite poor resulting in the fast deactivation of the Pd surface. Addition of Pt considerably improves the steady-state activity of Pd in 12 h CA experiment. CA measurements show that the most active catalyst is Pd_{0.5}Pt_{0.5} of 4 nm size, which displays narrow size distribution and Pd to Pt surface atomic ratio of 27–73.

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1. Introduction

Direct formic acid fuel cells (DFAFCs) are convenient power sources for micropower energy devices and offer several advantages if compared to direct methanol fuel cells (DMFCs). Potential advantages are related to the facts that formic acid is a non-explosive liquid, it shows negligible fuel crossover and cathode poisoning, DFAFCs require less water, thus reducing the need to store or recycle water, besides formic acid is a good electrolyte, hence resulting in a lower contact resistance [1–6]. One of the major obstacles for the successful commercialization of DFAFCs is the lack of appropriate catalysts that show high activity for the oxidation of formic acid and stability against poisoning. Palladium is a promising catalyst for the electro-oxidation of formic acid [1–7]. It promotes the oxidation of formic acid via a dehydrogenation mechanism that involves a reactive intermediate such as carboxylic acid [8,9] or a formate species [10], i.e.:

where M denotes metal active sites and X is a reactive intermediate.

According to the dual path mechanism, the less attractive parallel process is the dehydration path involving the formation of adsorbed CO (CO_{ads}) as intermediate species in the oxidation of HCOOH to CO₂:

Pd displays an initial high activity for the oxidation of HCOOH [10–15]. However, its long term performance is poor. Deactivation of Pd activity has been assigned to catalyst surface poisoning by mainly CO, although, other poisoning species such as water, OH, and anions from the electrolyte can also play a role [16–21].

Alloying of Pd with the second metal changes the surface electronic state, resulting in an ensemble effect, which can possibly reduce the catalyst poisoning and increase the activity and lifespan of the catalyst. A number of studies have been carried out recently with the aim to design multi-component Pd catalysts [22–35]. Approaches include the deposition of sub-monolayers of Pd on various supports, such as V, Mo, W and Au [26], Pt and Au single crystals [27–31]. Both Pd–Pt bulk and nano-catalysts [22–35] show high activity and improved stability in DFAFCs. For practical application, the Pd–Pt catalysts have to be prepared as highly dispersed, uniform nanoparticles. Only a few literature reports exist

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describing the synthesis as well as characterization of bimetallic Pd–Pt nanoparticles for DFAFCs [22,32–34,36]. Pt/Pd nanoparticles have been prepared by the spontaneous deposition of Pd onto carbon supported Pt nanoparticles [34,35]. The resulting catalysts show high activity for formic acid oxidation due to a high tolerance against CO poisoning. Li and Hsing [22] synthesized a large range of carbon supported $\text{Pt}_x\text{Pd}_{1-x}$ ($x=0-1$) nano-catalysts using SB-12 (3-(N,N-dimethyldodecylammonio)propanesulfonate) as the stabilizer. They found that monometallic Pd/C prepared by this method exhibits the best chronoamperometric activity for formic acid oxidation at 0.3 V vs. reversible hydrogen electrode after 30 min. However, they did not report measurements lasting more than 30 min.

In the present study, we prepared carbon supported $\text{Pd}_x\text{Pt}_{1-x}$ ($x=0.67, 0.5, 0.33$) nanoparticle catalysts. A modified polyol method is adapted for this purpose [37], which uses poly(N-vinyl-2-pyrrolidone) (PVP) as a stabilizer for nanoparticles. Recently, we carried out the detailed study on particle size and size distributions of these catalysts by X-ray diffraction (XRD) and transmission electron microscopy (TEM) [38]. In the present work we would like to investigate further the same nanoparticles from the point of view of their surface composition using X-ray photoelectron spectroscopy (XPS) and electrocatalytic performance towards formic acid oxidation.

2. Experimental

2.1. Synthesis of carbon supported nanoparticles

Synthesis method for catalyst preparation is described in detail elsewhere [38]. First, precursor salts and poly(N-vinyl-2-pyrrolidone) (PVP) stabilizer (Av. Mol. Wt. 10,000 g/mol, Sigma) are dissolved in ethylene glycol (anhydrous 99.8% Sigma–Aldrich). The weight of PVP is half that of Pd in the solution. A pH of 11 was maintained during synthesis by addition of NaOH to the solution. The solutions were stirred for 1 h at room temperature. Appropriate amounts of carbon black (Vulcan XC-72, Cabot Corporation) were subsequently added to result in 20 wt.% metal/C loadings and refluxed at 160 °C for 3 h. After cooling to room temperature, the carbon supported catalysts were filtered, washed with an excess of water and then dried for 1 h in air at 80 °C. Precursor salts were PtCl_4 (Alfa Aesar, 99.9% metals basis) and PdCl_2 (Alfa Aesar, 99.9% metals basis).

2.2. XRD measurements

X-ray diffraction powder patterns were collected using a Bruker AXS D8 Advance system θ – θ powder diffractometer, equipped with a Cu tube and a Vantec position-sensitive detector with radial Soller slits to reduce the background at low angles. A divergence slit of 0.2° was used for all experiments to avoid beam-overspill at low angles. The diffractograms were collected between 30° and 100° 2θ with a step of 0.0142° 2θ . Samples were deposited in a flat-surfaced, semi-infinite filled trough machine into a low-background single crystal silicon wafer holder and then gently pressed flat using a glass slide. For all XRD experiments, the sample holder was not rotated during data collection. Experimental intensities were collected with extra care by using very long counts and small angular steps.

2.3. XPS

XPS spectra were obtained using a Kratos Axis Ultra spectrometer equipped with a monochromated Al K α source at 140 W of X-ray energy. The carbon supported catalyst powders were attached to sticky tape for the XPS analyses. For each catalyst, spectra from three independent regions were obtained and the estimated error

was less than $\pm 5\%$. First, a survey spectrum was collected before high-resolution spectra of the C 1s, Pt 4f and Pd 3d core level regions were collected. XPS spectrum of the clean Pt foil, measured at the same conditions as for carbon supported nanoparticles, was used as a standard. Deconvolutions of the XPS spectra were performed using a CasaXPS software program.

2.4. Electrochemistry

All electrochemical measurements were conducted using Parstat 2273 Advanced Electrochemical System (Princeton Applied Research) in conjunction with Electrochemical Power Suite version 2.58 (Advanced Measurement Technology, Inc.) for Windows software program.

2.4.1. Electrochemical cell and electrolyte solutions

Experiments were carried out in a Pyrex three-compartment electrochemical cell. During the experiments, H_2 gas (99.997% Linde Canada Limited) was bubbled through the Pt/Pt-black reference electrode compartment. High-purity Ar gas (99.998% Linde Canada Limited) was passed through the working electrode compartment. The large surface area gauze Pt counter electrode was contained in a separate compartment. All potentials were measured with respect to a RHE immersed in the supporting electrolyte solution (0.1 M or 0.5 M H_2SO_4) in a separate compartment provided with a Luggin capillary.

The H_2SO_4 and $\text{HCOOH} + \text{H}_2\text{SO}_4$ solutions were prepared from ACS certified grades of sulfuric acid (98%), formic acid (88%) (Fisher Scientific Canada) and nanopure water (18 M Ω cm).

2.4.2. Working electrode

A glassy carbon disc electrode (GCDE) (0.196 cm² geometrical surface area, Pine Research Instrumentation Company) was used as a working electrode. The catalyst powders were formed into electrodes by sonicating 13 mg of the carbon supported catalyst powders in 1 mL of H_2O and 300 μL of the Nafion solution for 15 min, forming a catalyst ink. Subsequently 2.5 μL of catalyst ink was applied to a glassy carbon disc. The catalyst layer was then dried in air at 80 °C for 30 min. All electrochemical experiments were carried out at room temperature.

2.4.3. Cyclic voltammetry and chronoamperometry

Cyclic voltammetry (CV) experiments were conducted at 10 mV s^{−1} in 0.5 M H_2SO_4 starting from the open circuit potential for 5 cycles between the potential limits of 0–1.1 V. CVs in 0.1 M $\text{HCOOH} + 0.1$ M H_2SO_4 solutions were recorded starting from the open circuit potential for 10 cycles between 0 and 1.1 V potential limit at 10 mV s^{−1}. Here we report the 10th cycle. For chronoamperometric measurements the potential was first held at 0.1 V for 300 s, then stepped to 0.3 V for 12 h. Ar gas was bubbled through the electrolyte solution before and during the 12 h experiments.

3. Results and discussion

3.1. XRD

Detailed XRD investigation of the carbon supported $\text{Pd}_x\text{Pt}_{1-x}$ electrocatalysts is reported in Ref. [38] along with the TEM results. Here we summarize the main findings, which are helpful in the discussions of $\text{Pd}_x\text{Pt}_{1-x}$ electrocatalytic activities for formic acid oxidation. Recently, we demonstrated [39] that for Pt and Pt–Ru clusters smaller than 5 nm, Scherrer's formula is not adequate for the simultaneous interpretation of the nanoparticle sizes and composition from their diffraction patterns. The theoretically and computationally developed approach is based on Debye's exact formula for scattering by randomly oriented molecules [40]. This

Fig. 1. Slow scan XRD pattern of the carbon supported $\text{Pt}_{0.5}\text{Pd}_{0.5}$ electrocatalyst.

approach considers the nanocrystal to be a molecule and does not involve approximations other than the widespread assumption that atomic scattering factors are spherically symmetrical. The Debye's formula is given by:

$$|F(R)|^2 = \sum_{m=1}^N \sum_{n=1}^N f_m(R) f_n(R) \frac{\sin(2\pi R d_{mn})}{2\pi R d_{mn}} \quad (5)$$

where F is the scattering amplitude, R is the reciprocal vector, N is the number of atoms in the crystallite, $f_m(R)$ is the scattering factor of atom m , and d_{mn} is the distance between atoms m and n . The formula allows calculation of powder pattern profiles of nanoparticles with high precision.

Fig. 1 shows an XRD powder diffraction pattern of the carbon supported $\text{Pd}_{0.5}\text{Pt}_{0.5}$ catalysts. Both Pd and Pt have face-centered cubic structure with similar lattice parameters. As we point out in Ref. [38], carbon Vulcan XC-72 has pronounced reflections near 25° and 45° 2θ , which overlap with the main Pt peaks (111) and (200) located at around 40° and 46° 2θ , respectively. Therefore, analysis of XRD patterns was carried out at the fcc (220) peak around 68° 2θ that sits at relatively uniform background and does not interfere with the peak of interest. Fig. 2 summarizes the (220) reflections of all nanoparticles prepared in the present work. Pd-rich nanoparticles show narrower peaks if compared to the Pt-rich composition suggesting that larger particles are formed in the former case. Another interesting feature on the XRD patterns (Fig. 2) is that Pd and $\text{Pd}_{0.67}\text{Pt}_{0.33}$ show a narrow peak top and a wide peak base. This peak shape indicates the broad range of particle sizes, since the larger particles contribute to the peak top and the small particles are seen in the peak base. Table 1 summarizes the results of the XRD analysis and TEM [38]. As seen from Table 1, for $\text{Pd}_{0.5}\text{Pt}_{0.5}$ and $\text{Pd}_{0.33}\text{Pt}_{0.67}$ catalysts, the measured $2\theta_{\text{max}}$ values (68.02° and 68.10° , respectively) are both larger than expected values for bulk Pt (67.53°) and Pt nanoparticles ($<67.53^\circ$). This represents direct experimental evidence that alloy nanoparticles are

Fig. 2. Slow scan XRD patterns of the carbon supported $\text{Pd}_x\text{Pt}_{1-x}$ nanoparticles over the (220) reflection: (a) Pd, (b) $\text{Pd}_{0.67}\text{Pt}_{0.33}$, (c) $\text{Pd}_{0.5}\text{Pt}_{0.5}$, (d) $\text{Pd}_{0.33}\text{Pt}_{0.67}$, and (e) Pt.

formed for these two compositions. For $\text{Pd}_{0.67}\text{Pt}_{0.33}$, the $2\theta_{\text{max}}$ value (68.11°) is only slightly smaller than that for bulk Pd (68.19°) and an odd peak shape (Fig. 2 pattern b) is observed. It is therefore not clear whether a mixture of monometallic Pd and Pt particles or an alloy phase is formed in this case.

We can conclude that Pd-rich preparations have larger particle size with a broad range of crystallite sizes, while Pt-rich preparations have more homogeneous size distributions, with dominant sizes around 3–4 nm suggesting that Pt facilitates the formation of the electrocatalysts with smaller particle size.

3.2. XPS

Fig. 3a and b shows the example of the experimental and deconvoluted XPS spectra for the Pt 4f and Pd 3d core regions of the carbon supported $\text{Pd}_{0.5}\text{Pt}_{0.5}$ and $\text{Pd}_{0.67}\text{Pt}_{0.33}$ catalysts, respectively. The results of the deconvoluted spectra for all synthesized $\text{Pd}_x\text{Pt}_{1-x}$ catalysts are summarized in Table 2. The position of the C 1s peak (284.4 eV) was used to correct for possible charging effects. The XPS spectra of Pt 4f (Fig. 3a and c) and Pd 3d (Fig. 3b and d) region are found to be composed of two pairs of doublets. It is seen in Table 2 that both Pd and Pt are present in the metallic and oxidized forms. Surface oxidation of Pd and Pt is expected, as these catalysts are exposed to air. The observed peak positions for metallic Pt $4f_{7/2}$ and Pt $4f_{5/2}$ are located at ~ 71.4 and $\sim 74.9\text{ eV}$. The binding energy difference ($\Delta E_{\text{BE}} = 3.6\text{ eV}$) between these two maxima is that expected from Pt $4f_{7/2}$ and Pt $4f_{5/2}$ core level peaks. These peaks are shifted to higher binding energy compared to the Pt 4f XPS signal of 70.9 eV for the sputter cleaned Pt foil measured at the same conditions as spectra for $\text{Pd}_x\text{Pt}_{1-x}$ [41–43]. This shift might be indicative of a contribution from metal–support interaction of nanoparticles with support as was demonstrated by Hall et al. for

Table 1

Summary of experimental XRD and TEM results for carbon supported $\text{Pd}_x\text{Pt}_{1-x}$ nanoparticles [38].

Catalyst	Average size from XRD ^a (nm)	Average size from TEM (nm)	$2\theta_{\text{max}}$ of (220) nanoparticles ($^\circ$)	$2\theta_{\text{max}}$ of (220) bulk metals ($^\circ$)
Pd/C	10.0	12.0 ± 3.0	68.11	68.19
$\text{Pd}_{0.67}\text{Pt}_{0.33}/\text{C}$	7.0	8.5 ± 4.0	68.10	
$\text{Pd}_{0.5}\text{Pt}_{0.5}/\text{C}$	4.0	4.7 ± 0.5	68.02	
$\text{Pd}_{0.33}\text{Pt}_{0.67}/\text{C}$	3.8	–	67.85	
Pt/C	3.5	3.5 ± 0.5	67.04	67.53

^a From (220) fcc peak using Debye's formula (5) [40].

Fig. 3. XPS spectra for the Pt 4f (a + c) and Ru 3d (b + d) core level region of carbon supported $\text{Pd}_x\text{Pt}_{1-x}$ nanoparticles. The C 1s peak position (284.4 eV) was used to correct for possible charging effects. Fig. 4a and b shows the spectra for the carbon supported $\text{Pd}_{0.5}\text{Pt}_{0.5}$, while Fig. 4c and d shows the spectra for the $\text{Pd}_{0.67}\text{Pt}_{0.33}$ (c + d) nanoparticles. $\circ$ represents the experimental data, the grey and black lines represent the deconvoluted peaks and the sum of the deconvoluted peaks, respectively.

Pt/C system [44] and by Shukla et al. for Pt–Ru/C and Pt–Sn/C catalysts [45]. Small cluster size effect can also contribute to the binding energy shift, as was reported earlier [46]. Deconvolution of the Pd 3d region suggests the catalysts to consist of Pd metal and PdO. The core level binding energies of $\text{Pd}_{5/2}$ level for Pd metal and PdO are close to those reported in the literature value of 335.1 and 336.6 eV [41].

The surface energies of Pt and Pd are $\gamma_{\text{Pt}} = 2.203 \text{ J cm}^{-2}$ and $\gamma_{\text{Pd}} = 2.05 \text{ J cm}^{-2}$ [47], respectively. From the thermodynamic point of view, one would expect Pd to be a “surface-active” component since it features a relatively low surface energy. It is well known that the most “surface-active” component is the component with the lowest surface energy, which would minimize the energy of the system. This is not the case here as $\text{Pd}_x\text{Pt}_{1-x}$ catalysts synthesized in ethylene glycol have excess of Pt at the surface (Table 2). Surface segregation behavior in PdPt nanoparticles supported on carbon might be influenced not only by the difference in Pd and Pt surface energies, but also by the particle size, interaction of nanoparticles with the carbon support and synthesis procedure. Ramirez Caballero and Balbuena [48] have studied the effect of the nanocluster size on the surface segregation of Pd–Pt of 2 and 4 nm size using classical molecular dynamic (MD) simulations. They found that at concentrations of Pd below a certain threshold, Pt segregates to the surface. They demonstrated that the threshold concentration strongly depends on the size, being approximately 50% for the 2 nm nanoparticles and around 60% for the 4 nm. It can be hypothesized that larger PdPt clusters would further increase the concentration threshold and lead to a Pt enriched surface for high Pd concentration. According to this hypothesis, $\text{Pd}_x\text{Pt}_{1-x}$ nanoparticles synthesized in the present work would

show Pt excess at the surface as for Pt-rich, as well as for Pd-rich compositions.

3.3. Electrochemistry

3.3.1. Cyclic voltammetry

Fig. 4 shows cyclic voltammograms (CVs) of the carbon supported $\text{Pd}_x\text{Pt}_{1-x}$ electrocatalysts in 0.5 M H_2SO_4 in the potential range of 0–1.1 V at 10 mV s^{-1} . The hydrogen adsorption/desorption region provides the information about the active surface area of the catalyst. Cyclic voltammograms suggest that the resulting catalysts have a high active surface area, which is influenced by the particle size and the presence of agglomerates. The smallest voltammetric charges are found for carbon supported Pd and $\text{Pd}_{0.67}\text{Pt}_{0.33}$ electrocatalysts, which display the largest particle size. Pt-rich composition of $\text{Pd}_{0.5}\text{Pt}_{0.5}$ and $\text{Pd}_{0.33}\text{Pt}_{0.67}$ shows the higher voltammetric charges than Pt catalyst, indicating the appearance of additional active sites in the bimetallic systems. Therefore, using poly(N-vinyl-2-pyrrolidone) (PVP) for nanoparticle stabilization appears not to affect the active sites availability, whilst the presence of agglomerates does, and a lower voltammetric charge was found for the larger Pd and $\text{Pd}_{0.67}\text{Pt}_{0.33}$ catalysts.

All synthesized nanoparticles have been tested for formic acid electro-oxidation. Fig. 5 shows the forward and reverse scans of CVs obtained for carbon supported Pd and Pt (a) and $\text{Pd}_{0.67}\text{Pt}_{0.33}$, $\text{Pd}_{0.5}\text{Pt}_{0.5}$, $\text{Pd}_{0.33}\text{Pt}_{0.67}$ (b) in 0.1 M $\text{HCOOH} + 0.1 \text{ M H}_2\text{SO}_4$ solution at 10 mV s^{-1} . No clear inhibition of HCOOH oxidation can be observed on Pd (Fig. 5a). Onset potential is much lower on Pd nanoparticles compared to Pt and current maximum occurs at 0.3 V. As carbon monoxide poisoning is not seen on the Pd/C

Table 2 Summary of the deconvoluted XPS data for carbon supported Pd_xPt_{1-x} catalysts.

Catalyst	Species	Binding energy (eV)	FWHM (eV)	Assignment	A ₁ /A ₂ ^a	at.% per species	at.% Pd:Pt ratio
Pd	Pd 3d _{5/2}	335.3	1.0	Pd metal	1.14	16.6	100
	Pd 3d _{5/2}	336.6	2.4	PdO	1.48	39.1	
	Pd 3d _{3/2}	340.5	1.0	Pd metal		16.1	
	Pd 3d _{3/2}	342.1	2.4	PdO		26.3	
Pd _{0.67} Pt _{0.33}	Pd 3d _{5/2}	335.5	1.0	Pd metal	1.26	18.8	43.2:56.8
	Pd 3d _{5/2}	336.6	2.5	PdO	1.51	39.9	
	Pd 3d _{3/2}	340.8	1.0	Pd metal		14.9	
	Pd 3d _{3/2}	342.0	2.5	PdO		26.4	
	Pt 4f _{7/2}	71.4	1.1	Pt metal	0.91	12.2	
	Pt 4f _{7/2}	72.0	2.1	PtO	1.32	41.7	
	Pt 4f _{5/2}	74.6	1.1	Pt metal		14.4	
	Pt 4f _{5/2}	75.4	2.1	PtO		31.6	
Pd _{0.5} Pt _{0.5}	Pd 3d _{5/2}	335.4	1.0	Pd metal	1.28	20.7	26.7:73.3
	Pd 3d _{5/2}	336.5	2.4	PdO	1.40	35.1	
	Pd 3d _{3/2}	340.7	0.9	Pd metal		16.8	
	Pd 3d _{3/2}	341.6	2.4	PdO		28.3	
	Pt 4f _{7/2}	71.4	1.1	Pt metal	0.95	16.4	
	Pt 4f _{7/2}	72.1	2.0	PtO	1.29	28.3	
	Pt 4f _{5/2}	74.6	1.1	Pt metal		18.6	
	Pt 4f _{5/2}	75.6	2.0	PtO		36.7	
Pd _{0.33} Pt _{0.67}	Pd 3d _{5/2}	332.4	1.5	Pd metal	1.13	23.1	18.3:81.7
	Pd 3d _{5/2}	335.6	2.5	PdO	1.36	32.9	
	Pd 3d _{3/2}	340.9	1.5	Pd metal		20.6	
	Pd 3d _{3/2}	339.6	2.5	PdO		23.4	
	Pt 4f _{7/2}	71.3	1.4	Pt metal	0.89	22.8	
	Pt 4f _{7/2}	72.2	2.1	PtO	1.41	31.1	
	Pt 4f _{5/2}	74.8	1.4	Pt metal		25.0	
	Pt 4f _{5/2}	75.9	2.2	PtO		20.8	
Pt	Pt 4f _{7/2}	71.5	1.2	Pt metal	1.11	17.8	0
	Pt 4f _{7/2}	72.3	2.3	PtO	1.20	34.2	
	Pt 4f _{5/2}	74.8	1.3	Pt metal		19.6	
	Pt 4f _{5/2}	75.7	2.3	PtO		28.5	

^a Area of 4f_{7/2} peak divided by area of 4f_{5/2} peak for Pt and area of 3d_{5/2} divided by area of 3d_{3/2} for Pd.

electrocatalysts, this process is presumably very slow. Current in the reverse scan is smaller, indicating partial Pd surface oxidation and/or poisoning, which are consistent with previous studies on Pd [11,12,14,15,21,22]. For the Pt catalyst (Fig. 5a), the current is low until 0.3 V, since the surface is almost completely poisoned by adsorbed carbon monoxide CO_{ads}. At 0.3 V, the anodic current

increases due to CO_{ads} oxidation as seen in the peak around 0.55 V, together with oxidation of formic acid on sites that were previously blocked by CO_{ads} and reaches a maximum near 0.9 V. The high overpotential observed at Pt nanoparticles is likely due to formic acid oxidation through the dehydration pathway (2)–(4) [8,9]. At higher potentials, formic acid oxidation is deactivated as a result of Pt surface oxidation. In the negative scan, the surface remains inactive, until partial reduction of the irreversibly formed Pt surface oxides takes place, and further current increase is due to the formic acid oxidation on the “CO_{ads} free” surface with a maximum current at 0.6 V. From this point, adsorbed CO is formed again and blocks formic acid oxidation at the Pt surface.

For the Pd_xPt_{1-x} bimetallic electrocatalysts (Fig. 5b), the cyclic voltammograms show features similar to CV on Pt. Current is lower in the forward scan and high in the negative going scan, where a current increase and a broad current peak due to formic acid oxidation on the CO_{ads} and oxide free surface is observed. Onset potential on these catalysts is lower if compared to Pt indicating that formic acid oxidation is facilitated on the Pd-containing catalysts. However as can be seen from the CVs the prevailing mechanism is dehydration pathway (2)–(4), occurring through the formation of CO_{ads}. This is in agreement with the XPS finding about the Pt segregation on the catalysts surface. Since Pd atoms are also present on the surface, it is likely that both pathways (1) and (2)–(4) take place at the bimetallic surface, nevertheless the former process is slower.

3.3.2. Chronoamperometry

Chronoamperometric curves for formic acid electro-oxidation on Pd_xPt_{1-x} catalysts are shown in Fig. 6. Fig. 6a presents current densities per atomic weight of Pd and Fig. 6b per atomic weight of Pt in the electrocatalyst layer, which was deposited

Fig. 4. Cyclic voltammograms of the carbon supported Pd_xPt_{1-x} nanoparticles in 0.5 M H₂SO₄ at 10 mVs⁻¹: (a) Pd_{0.33}Pt_{0.67}, (b) Pd_{0.5}Pt_{0.5}, (c) Pt, (d) Pd_{0.67}Pt_{0.33}, and (e) Pd. Current densities are given per total metal loading: m_{Pd} + m_{Pt} in the catalyst layer.

Fig. 5. Cyclic voltammograms of carbon supported Pt and Pd (a); and Pd_xPt_{1-x} nanoparticles (b): A, Pd_{0.33}Pt_{0.67}; B, Pd_{0.5}Pt_{0.5}; C, Pd_{0.67}Pt_{0.33} in 0.1 M HCOOH + 0.1 M H₂SO₄, 10 mV s⁻¹. The current densities are given with respect to (a) metal loading of either Pd or Pt for currents obtained on Pd or Pt nanoparticles, respectively; and (b) Pd loading only.

on the glassy carbon electrode. To ensure complete steady-state behavior, the chronoamperometric experiments were allowed to run for 12 h at 0.3 V vs. RHE. Initial catalytic activity of all carbon supported catalysts decreases considerably, indicating surface poisoning and/or surface oxidation. Pt nanoparticles show the lowest activity towards formic acid oxidation (Fig. 6b). Initial activity of Pd is very high but then decreases abruptly without reaching a steady-state even after 12 h. Decrease in Pd activity is related to the formation of poisonous intermediates and/or dissolution of Pd in acidic solution. Addition of Pt to Pd lowers the initial activity of the catalysts compared to the pure Pd. However, the presence of Pt stabilizes the overall performance of the catalyst and shows its beneficiary effect. Moreover, Pd_{0.5}Pt_{0.5} catalyst has inferior initial current density, if compared to Pd. However after 12 h, the current density of Pd_{0.5}Pt_{0.5} is almost one order of magnitude higher (14.5 mA mg⁻¹ of Pd) than for Pd (1.5 mA mg⁻¹ of Pd), with the steady-state attained after 2 h at the Pd_{0.5}Pt_{0.5} surface. The inferior activity of Pd_{0.33}Pt_{0.67} catalyst is probably related to the low surface concentration of Pd atoms (18 at.%) found from XPS measurements (Table 2), while lower activity of Pd_{0.67}Pt_{0.33} might be due to the larger particle size and particle agglomera-

Fig. 6. Chronoamperograms of the carbon supported Pd_xPt_{1-x} nanoparticles (as indicated in figure) in 0.1 M HCOOH + 0.1 M H₂SO₄ at 0.3 V. Currents are normalized per (a) Pd metal loading in atomic weight; and (b) Pt metal loading in atomic weight.

tion found from TEM and XRD measurements. Catalytic activity per Pd loading for formic acid oxidation after 12 h increases as follows: Pd < Pd_{0.67}Pt_{0.33} < Pd_{0.33}Pt_{0.67} < Pd_{0.5}Pt_{0.5}. Therefore, Pt plays an important role in stabilizing not only average particle size as found from XRD measurements but also Pd surface against poisoning and/or dissolution. After analyzing the electrochemical data, it can be concluded that the presence of a small amount of the Pt sites on the surface leads to the stabilization of the Pd activity towards formic acid oxidation; at the same time increasing Pt content leads to the decrease of the catalyst activity. The latter is likely due to the contribution from the dehydration mechanism observed on Pt.

4. Conclusions

In the present work we synthesized Pd_xPt_{1-x} ($0 \leq x \leq 1$) nanoparticles using a modified polyol method with poly(N-vinyl-2-pyrrolidone) (PVP) stabilizing agent and tested them for the formic acid electro-oxidation. Pd-rich compositions have larger particle size and broader distribution of particle sizes if compared to monometallic Pt and Pt-rich nanoparticles. From XPS data we found that in bimetallic PdPt nanoparticles Pt tends to segregate on the surface and excess of Pt was found even for Pd_{0.67}Pt_{0.33} composition. Particle size and size distribution might influence the Pt surface enrichment, which in turn, has an effect on the electro-

catalytic activity of $\text{Pd}_x\text{Pt}_{1-x}$. Monometallic Pd shows high initial current densities for formic acid electro-oxidation due to the promotion of the direct dehydrogenation pathway on Pd sites however, in 12 h operation its activity decreases without reaching a steady-state. Chronoamperometric measurements conducted for 12 h demonstrated that $\text{Pd}_{0.5}\text{Pt}_{0.5}$ catalyst has the best catalytic performance towards formic acid oxidation per metal loading. Present work highlights the beneficiary effect of the Pt, in the stabilization of both particle size and catalytic activity of the bimetallic $\text{Pd}_x\text{Pt}_{1-x}$ nanoparticle catalysts towards formic acid oxidation.

Acknowledgements

Authors would like to thank Sander Mommers for XPS measurements and Centre for Catalysis Research and Innovation (CCRI) at the University of Ottawa.

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