NRC Publications Archive Archives des publications du CNRC

Novel method for the estimation of the electroactive Pt area

Bock, C.; MacDougall, Barry

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. / La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.1149/1.1586924>

Journal of the Electrochemical Society, 150, 8, 2003

NRC Publications Record / Notice d'Archives des publications de CNRC:

<https://nrc-publications.canada.ca/eng/view/object/?id=a29059ad-9ba7-4fa7-9f28-7510dab84efa>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=a29059ad-9ba7-4fa7-9f28-7510dab84efa>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Novel Method for the Estimation of the Electroactive Pt Area

C. Bock^{*,z} and B. MacDougall^{*}

National Research Council Canada, Ottawa, Ontario, Canada K1A 0R6

The (COOH)₂ oxidation reaction was studied at potentials below which the oxygen evolution reaction (OER) takes place. Pt was found to catalyze the (COOH)₂ oxidation reaction more strongly than Au, while Ru did not display any activity toward the (COOH)₂ oxidation reaction. Furthermore, under rapid stirring conditions, the (COOH)₂ oxidation reaction using Pt electrodes was shown to be activation controlled. Therefore, the (COOH)₂ oxidation currents can be related to the electroactive Pt area, as shown for a range of polycrystalline, bulk metal Pt, and Pt powder electrodes. The Pt surface area for multicomponent catalyst systems can also be estimated by combining (COOH)₂ oxidation data with the charge needed to oxidize adsorbed CO to CO₂ (CO_{ads} charge), as shown for a range of Pt- and Ru-containing powder electrodes. In fact, the combination of the two methods [(COOH)₂ oxidation current and CO_{ads} charge] can be used as an *in situ* probe to estimate the fraction of Ru in the metallic state in the potential region where CO is adsorbed provided the surface ratio of Pt vs. Ru is known.

© 2003 The Electrochemical Society. [DOI: 10.1149/1.1586924] All rights reserved.

Manuscript submitted December 26, 2002; revised manuscript received February 11, 2003. Available electronically June 23, 2003.

Pt and binary Pt-Ru catalysts have attracted much attention due to their promising use in low-temperature fuel cells.^{1,2} Despite many studies and thorough characterization of these catalysts, the estimation of the true electroactive surface area of these catalysts remains a challenge. Anodic stripping voltammetry of adsorbed CO (CO_{ads}) has been suggested as a possible *in situ* probe for these catalyst systems yielding some information about catalyst composition and surface areas.^{3,4} This method involves the adsorption of CO on the catalyst surface at negative potentials and the oxidation of the CO_{ads} to CO₂ in a subsequent positive potential scan. On Pt surfaces, *ca.* one monolayer of CO is adsorbed at sufficiently negative potentials, thus allowing the conversion of the experimentally obtained CO-to-CO₂ oxidation charge to the electroactive Pt area.³ The CO_{ads} stripping method can be employed to estimate the electroactive Pt area for multicomponent catalyst systems provided that CO does not adsorb on the non-Pt catalyst components. This is typically the case for carbon as well as metal oxides. However, it is known that CO can also adsorb on Au, Hg, and Ru.^{5,6} The case of CO adsorption on surfaces that contain Ru is particularly complicated. Ru oxides, particularly in the presence of Pt,⁵ can be reduced to metallic Ru within and below the potential region where molecular hydrogen is adsorbed/desorbed on Pt, *i.e.*, within the typically used potential range for CO adsorption region. The electrochemistry of Ru is manifold. Ru can be in the metallic state as well as form oxides of various oxidation and hydration states over the potential ranges typically investigated for fuel cell applications.⁷ Clear knowledge of the dependence of the Ru oxidation state and oxide form on potential for Pt-Ru catalyst systems is lacking. Furthermore, it has been proposed that different numbers of CO molecules (in some cases up to two) can adsorb onto a single Ru atom.⁵ It is therefore clear that the use of only CO_{ads} stripping voltammetry for the electroactive Pt area estimation for binary, Ru-containing catalyst systems is very complicated and questionable.

More recently, the use of Cu underpotential deposition (UPD) followed by subsequent oxidative stripping of the UPD Cu has been discussed for the estimation of the electroactive Pt and Ru area.^{8,9} Green and Kucernak have shown that the Cu UPD method can be applied to supported and high-surface area catalyst systems.⁸ The Cu UPD method takes advantage of the fact that Cu is of similar size to Pt and Ru and, hence, one Cu atom per Pt or Ru atom is deposited in the UPD region. It has been shown that one Cu atom is deposited by UPD per metallic Pt and Ru atom using unsupported PtRu alloy powders.⁸ However, the application of the Cu UPD stripping method is limited, as this method requires the exact knowledge of the fraction of Ru present in the metallic state in the Cu UPD region.

In the present work, the currents observed as a result of the electrochemical (COOH)₂ oxidation reaction to CO₂ are related to the electroactive Pt area. The use of this (COOH)₂ oxidation method is probed for a range of unsupported powder catalysts such as Pt, Ru, and two component Pt-Ru systems. First, the faradaic (COOH)₂ oxidation characteristics are discussed using Pt, Ru, and Au electrodes. The (COOH)₂ oxidation reaction is then studied in detail using polycrystalline Pt and Pt powder electrodes distinguishing activation vs. mass-transport reaction rate conditions and testing the accuracy of the (COOH)₂ oxidation method. Pt areas estimated from the (COOH)₂ oxidation method are also compared to the experimentally observed CO_{ads} charges for a range of Pt and Pt-Ru powders. Furthermore, the electrochemistry of the differently prepared Pt-Ru powders is briefly discussed using cyclic voltammetry (CV) characteristics that are normalized for the Pt area estimated using the (COOH)₂ oxidation method.

Experimental

Pt, Ru, and Pt-Ru powder preparation.—A range of Pt, Ru, and Pt-Ru powders were synthesized. The atomic Pt-to-Ru ratio of the starting, *i.e.*, the total bulk powder composition for the Pt-Ru powders was generally maintained constant at 70 to 30 atom %. The following powders were prepared: powder 1, Pt powder formed by the reduction of 3.2 g of H₂PtCl₆·6H₂O (Alfa Aesar) dissolved in 150 mL H₂O with 75 mL of 0.2 M NaBH₄ (Anachemia); powder 2, Ru powder, formed as Pt powder 1, but using 1.6 g RuCl₃ (Alfa Aesar) instead of H₂PtCl₆·6H₂O; powder 3, PtRu alloy formed by the simultaneous reduction of 3.256 g H₂PtCl₆·6H₂O and 0.5603 g RuCl₃ dissolved in 150 mL H₂O with 75 mL 0.2 M NaBH₄. Powder 4, Pt/RuO₂ (thermal) formed by the reduction of 3.256 g H₂PtCl₆·6H₂O dissolved in 150 mL H₂O with 75 mL 0.2 M NaBH₄, after successive washing with H₂O, filtering, and drying in an air oven at 100°C, 0.5603 g of RuCl₃ was distributed (using a mortar) within the Pt powder. This powder mixture was subsequently heated at 500°C under O₂ flow in a tube furnace for 2 h: Powder 5, Pt/RuO₂ (ballmilled), 2.83 g Pt powder (200 mesh, 99.98%, Alfa Aesar) and 0.85 g RuO₂ (electronic grade, Premion, 99.95%, Alfa Aesar) were ballmilled using a Spex 2000 ballmill mixer, as described in detail elsewhere.¹⁰ Powder 6, Pt/Ru, the Pt/RuO₂ (thermal) powder 4 was reduced in a H₂ atmosphere at 100°C for 2 h. After preparation, powders 1-3 were washed thoroughly with H₂O, filtered, and dried in an air oven at 100°C. A PtRu alloy powder of Pt to Ru atom % composition of 54:46 was also prepared in the same manner as powder 3 by the simultaneous reduction of 3.256 g H₂PtCl₆·6H₂O and 0.8591 g RuCl₃. This powder catalyst is referred to as powder 3a.

* Electrochemical Society Active Member.

^z E-mail: christina.bock@nrc.ca

Table I. Summary of catalyst powder characteristics for unused powders.

Powder	Characteristics identified using XRD analyzes ¹⁰	Surface characteristics identified using XPS analyzes ¹⁰
1 (Pt)	Pt powder	Metallic Pt, PtOH
2 (Ru)	Ru powder	Mainly metallic Ru and RuO
3 and 3a (PtRu alloys)	PtRu alloy powders	Metallic Pt, PtOH, Ru and RuO
4 (Pt/RuO ₂ thermal)	Pt and RuO ₂ powder	PtOH, PtO, PtO ₂ , RuO and RuO ₂
5 (Pt/RuO ₂ ball milled)	Pt and RuO ₂ powder	Metallic Pt, PtOH, PtO, RuO and RuO ₂
6 Pt/Ru (H ₂ reduced)	Pt and Ru powder	Metallic Pt, PtOH, metallic Ru, RuO

Working electrode preparation.—The catalyst powders were formed into anodes by sonicating 13 mg of a particular powder in 5 to 20 mL of H₂O for 30 min. Appropriate amounts (1–2 μ L) of the suspension were then pipetted onto and well spread out on 0.2 cm² (geometrical area) glassy carbon disk electrodes (Pine). In some cases, as stated in the appropriate section of the text, catalyst powder suspensions were also pipetted onto *ca.* 0.35 cm² Au foil electrodes [99.9% Au, 0.1 mm thick (Goodfellow)]. The electrodes were dried in air at room temperature and subsequently washed thoroughly with H₂O. The Au foils were firmly attached to Au wire electrodes. The Au electrodes were carefully wrapped with Teflon tape to mask Au not covered with the catalyst powder and to expose a geometrical area of *ca.* 0.12 cm². In some cases, polycrystalline Pt rotating disk electrodes (RDEs) (0.2 cm² geometrical area, Pine) were also used as working electrodes. All (COOH)₂ oxidation studies were carried out using the powder electrodes prepared without the typically used Nafion solution,¹¹ as preliminary studies showed that Nafion slows down the transport of (COOH)₂ to the catalyst sites.

In some cases, as stated in the appropriate section of the text, electrodes were also prepared as described above, however, 13 mg of the powder was dispersed and sonicated in solutions consisting of 300 μ L Nafion 117 solution (5 wt % Nafion dissolved in lower alcohols, Fluka) and 1 mL H₂O. Appropriate amounts (10–50 μ L) were pipetted on Au foil electrodes. The general CV and CO stripping characteristics of a particular powder electrode prepared with and without Nafion were found to be the same.

Cells and electrodes.—Three compartment cells, in which the reference electrode was separated from the working and counter-electrode compartment by a Luggin capillary, were employed for the electrochemical studies. A saturated calomel electrode (SCE) was used as the reference electrode. All potentials reported in this paper are *vs.* the SCE unless otherwise stated. Large surface area Pt gauzes served as counterelectrodes.

Techniques and instrumentation.—Electrochemical experiments were performed using either an EG&G PAR 273 potentiostat or a Solartron SI 1287 electrochemical interface (Solartron Group, Ltd.) both driven by Corrware software program (Scribner, Assoc.). A Pine rotating disc electrode (RDE) Rotator controlled by a MSR speed control system (Pine Instrument Company) was employed for the electrochemical oxidation studies carried out under controlled stirring conditions. A JEOL JSM-5300 scanning microscope, a Kratos Axis X-ray photoelectron spectrometer (XPS) and X-ray diffraction spectrometer (XRD, Scintag 2000) equipped with a Cu K α source were also employed to characterize the catalyst powders.

CO_{ads} stripping voltammetry.—CO was adsorbed onto the Pt-based powder electrodes at –0.1 V by bubbling CO gas (Matheson purity, Matheson gas) through the 0.5 M H₂SO₄ solution for 20 min. Solution CO was subsequently removed by bubbling argon gas (Air Products) for 40 min, holding the potential at –0.1 V. The potential was then cycled at 20 mV s^{–1} between –0.1 V and specific upper limit (*E*+) for two complete oxidation/reduction cycles.

Solutions.—All (COOH)₂ oxidation studies were carried out using 10^{–2} M (COOH)₂ + 0.5 M H₂SO₄ solutions. The solutions

were deoxygenated using high purity argon gas prior to the electrochemical studies. All electrochemical experiments were carried out at room temperature. ACS grade chemicals and high resistivity 18 M Ω water were used. The RuCl₃ powder was dried in air at 135°C prior to its use for the catalyst powder synthesis.

Results and Discussion

Characteristics of the catalyst powders.—In parallel work, XRD and XPS spectroscopy were used for the characterization of the catalysts powders used here and the results are summarized in Table I. The raw XRD and XPS data are shown and discussed in detail elsewhere.¹⁰ The XPS studies showed that both the Pt and Ru salt precursors are reduced to mainly metallic Pt and Ru for the case of powders 1 and 2, respectively. Furthermore, the XRD data showed the Pt-Ru based powders 3 and 3a to consist of PtRu alloys, while powders 4 and 6 exist of mixed phases of nonalloyed Pt and Ru components. The Ru was found to consist in different oxide forms, namely RuO and RuO₂ (no metallic Ru), for powders 4 and 5 and Ru in the mainly metallic state and lower oxide forms namely RuO (no RuO₂) for powders 3, 4, and 6.

(COOH)₂ oxidation characteristics. CV studies.—Figure 1 shows typical CV characteristics recorded at 20 mV s^{–1} in 10^{–2} M (COOH)₂ + 0.5 M H₂SO₄ solutions using Pt and Ru powder electrodes and a Au foil electrode. The Pt and Ru powders were supported using Au foil electrodes, as described in the Experimental section. Steady-state CV characteristics were generally obtained within less than five to seven complete oxidation/reduction cycles for all (COOH)₂ oxidation studies reported in this work. For the Pt powder and Au foil electrodes, a (COOH)₂ oxidation current is observed, while the Ru powder electrode appears not to have any activity for the (COOH)₂ oxidation reaction within the potential

Figure 1. Typical CVs for Au foil, Pt and Ru powder electrodes recorded at 20 mV s^{–1} in quiescent 10^{–2} M (COOH)₂ + 0.5 M H₂SO₄ solutions.

range studied here. The exact amount of the mainly metallic (see Table I) Ru powder deposited onto the Au support electrode was not estimated, but a Ru powder layer was clearly visible, indicating the presence of a sufficient amount of Ru. Furthermore, as observed for the Ru powder electrode, the glassy carbon (GC) RDE was also found not to display activity for the $(\text{COOH})_2$ oxidation reaction, thus justifying the use of this electrode as support for the Pt and Pt-Ru powders. The $(\text{COOH})_2$ oxidation reaction is seen to take place at more negative potentials (*ca.* 80 mV estimated roughly by extrapolation as shown in Fig. 1) for the Pt powder than for the Au electrode. This result suggests that Pt catalyzes the $(\text{COOH})_2$ oxidation reaction more strongly than Au and much more effectively than Ru. The fact that the $(\text{COOH})_2$ oxidation reaction takes place at more negative potentials on Pt than on Au and not at all on Ru suggests that the $(\text{COOH})_2$ oxidation currents observed for Pt-containing electrodes are directly related to the Pt area, particularly for electrodes exposing no or little Au to the electrolyte solution. The reduction peak seen in the CV in Fig. 2 is due to the reduction of Pt oxide formed during the positive cycle.

The electrochemical $(\text{COOH})_2$ oxidation reaction that takes place at potentials below the OER using polycrystalline Pt electrodes has been studied previously.¹² It has been shown that in acidic solutions $(\text{COOH})_2$ is oxidized to CO_2 according to the following net reaction¹²

Johnson *et al.*¹² suggested three possible, detailed reaction pathways for the oxidation reaction of $(\text{COOH})_2$ using Pt electrodes. All three reaction pathways involve adsorptive interaction of the oxalic acid with the Pt surface (according to a Temkin isotherm) thus emphasizing the importance of the electrode state/nature on the $(\text{COOH})_2$ oxidation reaction. It should also be noted that the electrochemical $(\text{COOH})_2$ oxidation reaction is fundamentally different from the CH_3OH and CO oxidation reaction. In the case of $(\text{COOH})_2$ the rate-determining step is the breaking of the carbon-carbon bond and the $(\text{COOH})_2$ molecule itself has a sufficient number of oxygen atoms to be electrochemically converted to CO_2 . Therefore, additional oxygen, supplied from, *e.g.*, adsorbed OH species, is not needed for the $(\text{COOH})_2$ oxidation reaction, as is the case for the CH_3OH and CO oxidation reaction to CO_2 .

RDE $(\text{COOH})_2$ oxidation studies using thin-layer Pt powder electrodes.—Previously conducted outswep rate studies and limiting current calculations using unstirred solutions showed that the electrochemical $(\text{COOH})_2$ oxidation reaction observed using Pt catalyst electrodes takes place under mass-transport controlled conditions.¹³ However, the $(\text{COOH})_2$ oxidation reaction needs to take place under activation-controlled conditions in order to relate the $(\text{COOH})_2$ oxidation current to the real Pt area. Hence, in this work, the $(\text{COOH})_2$ electrolyte solutions were rapidly stirred employing a rotating disk electrode arrangement to ensure that the $(\text{COOH})_2$ oxidation reaction takes place under activation-controlled conditions. Furthermore, the powder electrodes were prepared as thin layers of small total surface areas to allow all Pt catalyst sites to be involved in the activation-controlled $(\text{COOH})_2$ oxidation reaction, as discussed in the following sections. The total Pt surface area was generally less than 0.2 cm^2 for studies involving positive potentials, and hence high anodic currents, while a higher total surface area could be employed for studies carried out at lower potentials. In all cases, the experimentally observed currents were compared to the theoretical limiting current to ensure that the studied $(\text{COOH})_2$ oxidation reactions took place under activation controlled conditions.

Figure 2 shows a plot for $(\text{COOH})_2$ oxidation current, $i_{\text{p,a}}$, extracted from raw *i*-*E* curves at 1.1 V as a function of the square root of the rotation rate ($\omega^{1/2}$) using the polycrystalline (0.2 cm^2 , geometrical area) Pt RDE. (The *i*-*E* curves were recorded at 20 mV s^{-1} .) It is seen that at sufficiently high rotation rates [≥ 2000

Figure 2. $i_{\text{p,a}}$ ($\diamond$) and i_{lim} ($\triangle$) dependence for the $(\text{COOH})_2$ and $\text{Fe}(\text{CN})_6^{4-}$ oxidation reaction, respectively, on $\omega^{1/2}$ using a 0.2 cm^2 (geometrical area) Pt RDE. 10^{-2} M $(\text{COOH})_2$ in $0.5 \text{ M H}_2\text{SO}_4$ ($\diamond$) and $5 \text{ mM K}_4\text{Fe}(\text{CN})_6$ in 1 M KCl ($\triangle$) solutions were used. The solid lines represent the best fit to the experimental data.

rotations per minute (rpm)], the $i_{\text{p,a}}$ values are independent of the rotation rate. The $i_{\text{p,a}}$ values measured at higher rpm (≥ 2000 rpm) were found to vary by $\pm 2 \cdot 10^{-4} \text{ A cm}^{-2}$, thus accounting for the scatter in the experimental $i_{\text{p,a}}$ data. At lower (≤ 1000) rpm, a decrease of the $i_{\text{p,a}}$ value with decreasing $\omega^{1/2}$ is observed, indicating that elements of mass-transport control are present at these lower rotation speeds. The result indicates that by operating at rotation rates larger than 2000 rpm, it is possible to study the $(\text{COOH})_2$ oxidation reaction under activation-controlled conditions.

It is well known that the mass-transport limited current (i_L) is proportional to $\omega^{1/2}$, according to the Levich equation,¹⁴ as follows

$$i_L = B\omega^{1/2} = 0.20nFAD^{2/3}\nu^{-1/6}\omega^{1/2}c^0 \quad [2]$$

In Eq. 2, n is the number of electrons [2 in the case of the $(\text{COOH})_2$ oxidation reaction studied here], F is Faraday's constant, A the surface area, D the diffusion coefficient ($5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$), ν the kinematic viscosity ($0.01 \text{ cm}^2 \text{ s}^{-1}$), ω the rotation rate in rpm, and c^0 the concentration (in this case: $10^{-5} \text{ mol cm}^{-3}$). B is the slope of a plot of i_L vs. $\omega^{1/2}$ and is defined as shown in Eq. 2. Therefore, for a 0.2 cm^2 electrode, a theoretical slope of $4.8 \cdot 10^{-5} \text{ A rpm}^{-1/2}$ is calculated using this relationship, and a D value of $5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. This value is of the same order of magnitude as the experimentally obtained slope value of $3 \cdot 10^{-5} \text{ A rpm}^{-1/2}$ for the $(\text{COOH})_2$ oxidation data observed at lower (≤ 1000) rpm, although only two data points are used in this experiment. The i_L dependence for the $\text{Fe}(\text{CN})_6^{4-}$ oxidation reaction ($\triangle$) on $\omega^{1/2}$ is also shown in Fig. 2. An experimental slope of $1.2 \cdot 10^{-5} \text{ A rpm}^{-1/2}$ is found for this one-electron reaction using $5 \text{ mM K}_4\text{Fe}(\text{CN})_6$ in 1 M KCl solution. The experimental slope for the Fe oxidation reaction is very close to the theoretical slope of $1.4 \cdot 10^{-5} \text{ A rpm}^{-1/2}$, calculated using a D value of $6.5 \cdot 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.¹⁶

Figure 3 shows a typical *i*-*E* curve recorded at 20 mV s^{-1} in a $10^{-2} \text{ M} (\text{COOH})_2 + 0.5 \text{ M H}_2\text{SO}_4$ solution using a polycrystalline (0.2 cm^2 , geometrical area) Pt RDE rotated at 2000 and 5000 rpm. It is seen that the *i*-*V* curves are qualitatively and quantitatively essentially the same (within an experimental current density variation of $\pm 2 \cdot 10^{-4} \text{ A cm}^{-2}$ estimated at the peak maximum), *i.e.*, independent of the rotation rate, as typically observed for a faradaic

Figure 3. Typical CVs recorded at 20 mV s^{-1} in $10^{-2} \text{ M (COOH)}_2 + 0.5 \text{ M H}_2\text{SO}_4$ solution using a polycrystalline (0.2 cm^2 , geometrical area) Pt RDE at 2000 and 5000 rpm. The 7th steady-state cycles are shown.

reaction that is activation-controlled. Consistent with this view of an activation controlled mechanism, the experimentally observed peak currents are also smaller than the i_L currents predicted for this oxidation reaction, as a i_L value of $2.2 \cdot 10^{-3} \text{ A}$ is predicted by Eq. 2 for 2000 rpm and a 0.2 cm^2 electrode. Additional support for an activation as opposed to a mass-transport controlled reaction was given from sweep rate studies. i - E curves recorded for the same electrode and conditions, but employing different sweep (10 - 30 mV s^{-1}) yielded the same i - V curves. However, the shape of the experimentally observed i - V curves (Fig. 3) is different than typically observed for a classical activation-controlled reaction. For a classical electron transfer reaction taking place under activation-controlled conditions, an increase in current with increasing potential in an exponential manner is predicted¹⁵ unlike the decrease in current, and hence current maximum, observed here for the $(\text{COOH})_2$ oxidation reaction. Nevertheless, for the $(\text{COOH})_2$ oxidation reaction studied here a current maximum (and not a limiting current) at *ca.* 1.1 V (vs. SCE) is observed. This experimentally observed current maximum and decrease in the $(\text{COOH})_2$ oxidation current is believed to be related to a continuous passivation of the Pt surface taking place with increasing potentials.¹⁷ In previous work, it has been reported that a steady decrease in $(\text{COOH})_2$ oxidation current takes place at potentials more positive than 1.3 V vs. reversible hydrogen electrode, (*i.e.*, *ca.* 1.05 V vs. SCE) due to passivation of the Pt surface.¹⁷ This passivation is believed to be linked to the formation of higher Pt oxide films. Consistent with this view, it has also been observed, that a preformed, thick Pt oxide film displays little or no activity to oxidize $(\text{COOH})_2$ in the more positive potential region where O_2 is evolved.¹⁸

It is noteworthy that rotation rates of at least 3000 rpm were used for the $(\text{COOH})_2$ oxidation experiments carried out in the subsequent parts of this work. The influence of the rotation rate was also tested in each $(\text{COOH})_2$ oxidation experiments to ensure that the reaction takes place under activation-controlled conditions.

Conversion of $(\text{COOH})_2$ oxidation currents to Pt surface area.—The following relationship between the oxidation current (i_a) and potential, E , applies for an activation-controlled oxidation reaction at sufficiently high overpotentials¹⁵

$$i_a = nFAk_0c(\text{COOH})_2 \exp^{\alpha_a nF/RT(E-E^0)} \quad [3]$$

Table II. $(\text{COOH})_2$ oxidation currents and R_{APt} factors for a range of Pt electrodes.

	$i_{p,a}(\text{COOH})_2^a$ (A)	A_{Pt}^b (cm^2)	$R_{\text{APt}} (= i_{p,a}/A_{\text{Pt}}^b)$ (A cm^{-2})
Pt RDEs	$1.65 \pm 0.2 \cdot 10^{-3}$	0.16 ± 0.01	$1 \pm 0.05 \cdot 10^{-2}$
1st Pt powder	$1.02 \pm 0.1 \cdot 10^{-3}$	0.104 ± 0.005	$0.98 \pm 0.05 \cdot 10^{-2}$
2nd Pt powder	$1.8 \pm 0.2 \cdot 10^{-4}$	0.018 ± 0.0001	$1 \pm 0.05 \cdot 10^{-2}$
3rd Pt powder	$1.65 \pm 0.1 \cdot 10^{-3}$	0.173 ± 0.009	$0.95 \pm 0.05 \cdot 10^{-2}$
4th Pt powder	$7.9 \pm 0.8 \cdot 10^{-4}$	0.073 ± 0.004	$1.09 \pm 0.05 \cdot 10^{-2}$

^a Steady-state $i_{p,a}$ values extracted at 1.1 V vs. SCE from raw i - V curves recorded at larger than 3000 rpm and 20 mV s^{-1} in $10^{-2} \text{ M (COOH)}_2 + 0.5 \text{ M H}_2\text{SO}_4$ solutions. Experiments were carried out at different rpm confirming that the $i_{p,a}$ value is independent of the rotation rate.

^b Pt surface area (A_{Pt}) estimated from CO_{ads} stripping voltammetry using a charge-to-area conversion factor of $420 \mu\text{C cm}^{-2}$.³

In Eq. 3, n is the number of electrons (*i.e.*, two for the $(\text{COOH})_2$ to CO_2 oxidation reaction), F is Faraday's constant, k_0 is the standard heterogeneous rate constant for the $(\text{COOH})_2$ oxidation reaction, α_a is the transfer coefficient, R is the gas constant, T is the temperature, and E^0 is the standard potential. Equation 3 shows that the activation-controlled oxidation current, i_a , is proportional to the electrode area (A), and hence, this equation can be used to relate the ratio of the experimentally observed i_a values to the real Pt area, A_{Pt} . This ratio, R_{APt} , is defined as follows

$$R_{\text{APt}} = \frac{i_a}{A_{\text{Pt}}} = nFk_0c(\text{COOH})_2 \exp^{\alpha_a nF/RT(E-E^0)} \quad [4]$$

Equation 4 predicts the R_{APt} ratio to be constant for a particular $(\text{COOH})_2$ concentration and potential, even if the Pt electrodes have different areas. This is shown in Table II, which summarizes the experimentally observed $i_{p,a}$ and A_{Pt} values for Pt RDE and Pt powder electrodes (*i.e.*, all electrodes contain only Pt and no Ru). The ratio of the $i_{p,a}$ to A_{Pt} values, *i.e.*, the value of the R_{APt} factor at 1.1 V , is also given in Table II. The A_{Pt} values were estimated from the CO_{ads} charge using a charge-to-area conversion factor of $420 \mu\text{C cm}^{-2}$.³ Average R_{APt} values of $1 (\pm 0.05) \cdot 10^{-2} \text{ A cm}^{-2}$ are found for the Pt powder and polycrystalline Pt electrodes tested. The R_{APt} ratios are essentially the same for the Pt powders and the Pt RDEs indicating that the $(\text{COOH})_2$ oxidation reaction is not influenced by the particle size of the Pt powders studied here.

The relationship of Pt area and CO_{ads} charge. The conversion factor (f_{APt}).—We introduce a conversion factor, f_{APt} , that relates the electroactive Pt area to the experimentally obtained CO_{ads} stripping charge, as follows

$$A_{\text{Pt}} = \frac{Q_{\text{CO}_{\text{ads}}}}{420 \mu\text{C cm}^{-2}} f_{\text{APt}} \quad [5]$$

In this work, the f_{APt} factor is taken as unity for Pt (Ru-free) electrodes. However, it should be noted that only close to one monolayer of CO (*ca.* 80 - 90%)³ is adsorbed on Pt surfaces, and hence, Pt areas estimated using the CO_{ads} stripping charge, *i.e.*, Eq. 5 and an f_{APt} factor of unity, are somewhat lower than the true Pt areas. Despite this fact, a f_{APt} factor of unity is used here, as this error is eliminated in the Pt area estimation using the $(\text{COOH})_2$ method introduced in this work.

As discussed above, the f_{APt} factor for the Pt electrodes is expected to be unity, while the f_{APt} value for Pt-Ru electrodes is likely to be less than unity and expected to be influenced by the electrode composition. Metallic Ru contributes to the CO_{ads} charge, however,

it is inactive toward the $(\text{COOH})_2$ oxidation reaction (as shown above), thus reducing the value of the f_{APt} conversion factor. With increasing surface fraction of metallic Ru vs. Pt, the contribution of the Ru sites to the CO_{ads} charge increases, and hence the f_{APt} value is predicted to decrease. In fact, the value of the f_{APt} factor for a particular catalyst yields the fraction of the CO_{ads} molecules that adsorb onto Pt sites, and vice versa, the value of $1-f_{\text{APt}}$ yielding the fraction of CO_{ads} molecules on the other catalyst components (*i.e.*, Ru in the present study). It is clear that the f_{APt} value needs to be estimated for each individual powder. The f_{APt} value for Pt-Ru powders can be obtained from the experimentally determined Pt area values estimated from $(\text{COOH})_2$ oxidation experiments, *e.g.*, using the R_{APt} value of $1.00 \pm 0.05 \cdot 10^{-2} \text{ A cm}^{-2}$ estimated at $i_{\text{p,a}}$, *i.e.*, 1.1 V for $10^{-2} \text{ M } (\text{COOH})_2$ in $0.5 \text{ M H}_2\text{SO}_4$ solutions, and combining Eq. 4 and 5 as follows

$$f_{\text{APt}} = \frac{\frac{i_a}{R_{\text{APt}}}}{\frac{Q_{\text{CO}_{\text{ads}}}}{420 \mu\text{C cm}^{-2}}} = \frac{A_{\text{Pt}}}{\frac{Q_{\text{CO}_{\text{ads}}}}{420 \mu\text{C cm}^{-2}}} \quad [6]$$

It should be noted that any $(\text{COOH})_2$ oxidation current can be used for the Pt area estimation carried out in such a manner provided that the R_{APt} factor is estimated for the corresponding potential. Using additional $(\text{COOH})_2$ oxidation current data and R_{APt} values found and estimated for a range of potentials, clearly increases the accuracy of the method. Furthermore, it is possible to estimate the $(\text{COOH})_2$ oxidation currents at potentials less positive than 1.1 V. This is particularly important for catalysts that may corrode at such positive potentials, as is often observed for catalysts containing Ru. In this work, CO_{ads} stripping voltamograms were also recorded before and after $(\text{COOH})_2$ oxidation studies were carried out for a particular catalyst. A decrease in CO_{ads} charge would indicate a loss of catalyst due to either catalyst detachment from the support and/or partial dissolution of the catalyst, while changes in the shape of the CO_{ads} stripping peak (typically a shift of the oxidation wave to more positive potentials) likely indicates the preferential dissolution of Ru from the catalyst system. In this work, it was found that all Pt powders 1, the Pt/RuO₂ (thermal) powder 4, Pt/Ru (H₂ reduced) powder 5, and the PtRuO₂ (ballmilled) powder 6 electrodes did not dissolve or detach from the glassy carbon support, as a result of the $(\text{COOH})_2$ oxidation studies carried out involving potentials as high as 1.2 V. However, it was necessary to restrict the potential range of the other PtRu alloy electrodes powders 3 and 3a, to potentials less negative than 0.8 V to avoid changes in the catalyst area as well as dissolution of the Ru component.

It is noteworthy that the shapes of the experimentally observed current density J - V curves for the individual Pt and Pt-Ru powders were found to be essentially the same for all powders investigated in this work. This is shown in Fig. 4 for Pt powder 1 and Pt/RuO₂ (thermal) powder 4 electrodes. The experimentally observed currents were normalized using the CO_{ads} charges and f_{APt} factors of unity and 0.55 for the Pt powder 1 and the Pt/RuO₂ (thermal) powder 4, respectively. Figure 5 shows J - V curves for Pt powder 1 and PtRu alloy powder 3 electrodes for the limited potential range of up to 0.8 V. The current scales were normalized using a f_{APt} factor of unity and 0.7 for the Pt powder 1 and the PtRu alloy powder 3, respectively. The limited E range was selected to avoid preferential dissolution of Ru from the catalyst surface, as discussed above. It is seen that the shape of the J - V curves for the Pt and the PtRu alloy powders are essentially the same within the E range of *ca.* 0.75 to 0.8 V, *i.e.*, within the E range used in this work to estimate the f_{APt} factors for the PtRu alloy powder electrodes. The meaning of the value of these f_{APt} factors is discussed in more detail in the following paragraph.

Figure 4. Typical J - V curves for Pt powder 1 (thick line) and Pt/RuO₂ (thermal) powder 4 (thin line) electrodes recorded at 8000 rpm and 20 mV s^{-1} in $10^{-2} \text{ M } (\text{COOH})_2 + 0.5 \text{ M H}_2\text{SO}_4$ solutions. The currents were normalized using the experimentally observed CO_{ads} charge and a f_{APt} factor of unity and 0.55 for the Pt powder and Pt/RuO₂ (thermal) powder 4 electrodes, respectively.

These f_{APt} factors listed in Table III can be used to calculate the Pt area from the experimentally observed CO_{ads} charge for any electrode made up of the corresponding Pt-based catalyst and using Eq. 5. Furthermore, the value of the f_{APt} factor indicates the fraction of CO that is adsorbed on Pt sites, and hence this factor also yields information about the fraction of CO adsorbed on the Ru sites of the catalysts studied here. This is clearly seen for the PtRu alloy catalyst powders 3 and 3a. The f_{APt} factor of 0.7 found for the PtRu powder 3 suggests that 70% of the adsorbed CO molecules adsorb on Pt

Figure 5. Typical J - V curves for Pt powder 1 (thick line) and PtRu alloy (Pt:Ru atomic ratio of 0.7:0.3) powder 3 (thin lines) electrodes recorded at 8000 rpm and 20 mV s^{-1} in $10^{-2} \text{ M } (\text{COOH})_2 + 0.5 \text{ M H}_2\text{SO}_4$ solutions. The currents were normalized using the experimentally observed CO_{ads} charge and a f_{APt} factor of unity and 0.7 for the Pt powder and PtRu alloy powder 3 electrodes, respectively. The J - V curve for the Pt powder electrodes is the average of experimental data collected for three individual Pt powder electrodes, while the actual raw data for three individual PtRu alloy electrodes are shown in Fig. 6.

Table III. f_{APt} values and XPS data for a range of Pt and Pt-Ru powder electrodes.

Pt-based powder type	f_{APt}^a	Pt (atom % ^b)
Pt (1)	1 ± 0.05	1
PtRu alloy (3)	0.7 ± 0.05	0.7
PtRu alloy (3a)	0.54 ± 0.03	0.55
PtRuO ₂ (thermal) (4)	0.55 ± 0.03	0.36
PtRu (H ₂ reduced) (5)	0.45 ± 0.02	0.44
PtRuO ₂ (ballmilled) (6)	0.5 ± 0.03	0.54

^a The f_{APt} factors are estimated from (COOH)₂ oxidation studies and CO_{ads} stripping voltammetry, as described in the text.

^b Atomic fraction of Pt (atomic Pt concentration divided by the total atomic concentration of Pt and Ru) obtained from XPS data, as discussed in detail elsewhere.¹⁰ The atomic fraction of Pt data indicated in the third column for the powders 4, 5, and 6 are thought to be lower than the actual values due to possible inhomogeneities of the Pt and Ru phase within the catalyst particles that could complicate the XPS analyses. Relative errors in the atom % Pt values are ca. 2%.¹⁰

sites, while 30% are adsorbed on other sites, *i.e.*, Ru. Similarly, the f_{APt} factor of 0.54 estimated for the PtRu alloy powder 3a suggests that 54% of the adsorbed CO molecules are adsorbed on Pt sites, while 46% are adsorbed on Ru sites. This, and the fact that the surface atomic fraction of Pt to Ru for these two PtRu alloy powders 3 and 3a is 0.3:0.7 and 0.54:0.46, respectively, suggests that one CO molecule adsorbs per Pt as well as Ru site. These results further suggest that the Ru sites are likely present in their metallic state at the potential of -0.1 V where CO is adsorbed, as CO adsorption onto the oxide covered Ru surface is generally not observed.

The f_{APt} factors for the PtRuO₂ (thermal) powder 4, PtRu (H₂ reduced) powder 5, and PtRuO₂ ballmilled powder 6 are less than unity indicating that CO also adsorbs onto Ru sites. In fact, 45% (powder 4), 55% (powder 5), and 50% (powder 6) of the CO_{ads} molecules adsorb onto Ru sites, thus further suggesting that a significant fraction of the Ru sites of these powders are in the reduced Ru metal state.

Current-normalized background CVs (in 0.5 M H₂SO₄) for different powders.—In this section, current-normalized CV characteristics for the Pt and Pt/Ru powders are discussed. The CVs were recorded in 0.5 M H₂SO₄ and the currents were normalized for the Pt area using the f_{APt} factors shown in Table III. The powder electrodes were prepared by sonicating 13 mg of the powder in 1 mL H₂O and 0.3 mL Nafion solution, as discussed in the Experimental section. Figures 6a and b show the normalized CV characteristics for the Pt and Pt-Ru powder electrodes recorded at 10 mV s⁻¹, *i.e.*, at a sweep rate sufficiently low to allow time for all catalyst sites to be electrochemically converted. Figures 6a and b show that the characteristic CV shape for polycrystalline Pt is observed for the Pt powder electrode, while for all Pt/Ru powders a redox reaction ascribed to the oxidation/reduction of the Ru sites is observed within the potential of ca. 0.05 V and an arbitrarily selected upper cycling limit of 0.55 V. This indicates that all Pt-Ru powders studied in this work contain Ru sites that display oxidation/reduction behavior within a similar potential range, in fact, within a potential range of interest for practical fuel cell applications. The shape and magnitude of the normalized currents are different for the individual powders. The latter is not unexpected, as in fact, the Ru surface concentration (*i.e.*, the amount of Ru on the surface per Pt surface area) is different for all powders studied here, as shown in Table III. It is also noteworthy that, between 0.05 and 0.5 V, the shape of the CV curve for the Pt/Ru (H₂-reduced) powder 5 is essentially the same as that found for bare Ru metal cycled under the same experimental conditions,⁷ indicating that the Ru component of this particular powder behaves like bare Ru metal.

Figure 6. Typical background CVs for Pt and Pt-Ru powder electrodes in 0.5 M H₂SO₄. The potential was cycled at 10 mV s⁻¹ between -0.22 and 1.1 V for the Pt powder electrode, while an upper cycling limit of 0.55 V was employed for the Pt-Ru powder electrodes. The current scale is normalized for the Pt area calculated using the f_{APt} factors listed in Table III. (a) shows the CVs for Pt powder (no. 1), PtRu alloy (no. 3), and PtRuO₂ (thermal) (powder no. 4) electrodes, while (b) shows the same for Pt powder (no. 1), Pt/Ru (H₂ reduced) (no. 5) and PtRuO₂ (ballmilled) (powder no. 6) electrodes.

The charge observed between 0.05 and 0.55 V was calculated for the Pt-Ru powders. For this calculation, the current observed for the Pt powder electrode was used as the baseline and subtracted from the monitored currents. Table IV shows the oxidation charges normalized for the Pt area [$Q_{\text{O}(\text{APt})}$] obtained in this manner for different Pt-Ru powder electrodes. It should be noted that the normalized charge value for the Pt/Ru (H₂ reduced) powder electrode is very close to the value observed in previous work,⁷ thus further supporting the Pt surface-area estimation introduced in this work. The number of electrons per Pt and Ru atom [$e_{\text{Pt}(\text{atom})}$ and $e_{\text{Ru}(\text{atom})}$, respectively] are also shown in Table IV. The numbers of electrons per Pt and Ru were calculated as shown in Eq. 7 and 8, respectively

Table IV. Pt and Ru area normalized oxidation charge values for different Pt/Ru powder electrodes.

	$Q_{\text{ox/Apt}}^a$ (C cm^{-2})	$e_{\text{Pt(surface-atom)}}^-$ ^b	$e_{\text{Ru(surface-atom)}}^-$ ^c
PtRu alloy (3)	$1 \cdot 10^{-4}$	0.4	0.9
PtRuO ₂ (thermal) (4)	$2.6 \cdot 10^{-4}$	1	1.2
PtRu (H ₂ reduced) (5)	$5.3 \cdot 10^{-4}$	1.9	1.5
PtRuO ₂ (ballmilled) (6)	$2.8 \cdot 10^{-4}$	1.1	1.1

^a Experimentally observed oxidation charge per Pt area ($Q_{\text{ox/Apt}}$), calculated as described in the text.

^b Number of electrons per Pt atom ($e_{\text{Pt(surface-atom)}}^-$), calculated using Eq. 7.

^c Number of electrons per Ru atom ($e_{\text{Ru(surface-atom)}}^-$), calculated using Eq. 8.

$$e_{\text{Pt(atom)}}^- = \frac{Q_{\text{O(Apt)}} A_{\text{Pt(atom)}}}{Q_{e^-}} \quad [7]$$

$$e_{\text{Ru(atom)}}^- = \frac{Q_{e_{\text{Pt(atom)}}^-} f_{\text{APt}}}{1 - f_{\text{APt}}} \quad [8]$$

In Eq. 7, the area of a Pt atom ($A_{\text{Pt(atom)}}$) is taken as $6.1 \cdot 10^{-16} \text{ cm}^2$ ¹⁹ and the charge of an electron (Q_{e^-}) as $1.6 \cdot 10^{-19} \text{ C}$.²⁰ Of particular interest is the comparison of the values of the number of electrons per Ru atom for the different Pt-Ru powders. The data shown in Table IV suggest that almost one electron per Ru atom is passed within the potential range investigated here (*i.e.*, up to 0.55 V) for the PtRu alloy powder 3, while a larger number of electrons is suggested to be involved for the other three powders. For powders 4 and 6 (*i.e.*, the two powders containing the RuO and RuO₂ phase) the number of electrons per Ru atom are very similar, namely 1.2 and 1.1, respectively. This is possibly consistent with the fact that the Ru phases of these two powders are essentially the same.¹⁰ These results suggest that the normalized-CV approach obtained using the f_{APt} factors can yield useful information about the Ru electrochemistry of Pt-Ru electrocatalysts, which is likely relevant to the development and understanding of fuel cell catalyst systems. It should be noted that influences of double-layer charging have not been accounted for in the above calculation of the number of electrons per Pt and Ru atom.

Conclusions

It has been shown that the activation-controlled (COOH)₂ oxidation current can be related to the electroactive Pt area for Pt-based catalysts. The combination of the CO_{ads} stripping voltammetry and the activation-controlled (COOH)₂ current was applied to estimate the Pt surface area for a range of Pt-Ru powder electrodes. It was also found that the combination of these two methods can yield *in situ* information about the fraction of CO molecules that adsorb on Pt vs. the ad-metal (*i.e.*, Ru in this work) catalyst sites. For the case of PtRu alloy electrodes, it was found that one mole of CO adsorbs per Pt as well as Ru sites at -0.1 V , *i.e.*, the potential used for CO

adsorption in this work. Furthermore, valuable information about the electrochemistry of the Ru component of Pt-Ru catalysts can be gained from background CV characteristics that are normalized using the Pt area estimated using the (COOH)₂ oxidation method.

However, care must be taken to apply this method for the estimation of the electroactive Pt area and possible extraction of the fraction of CO molecules that adsorb on the individual catalyst sites. The catalysts must be stable within the potential range used to measure the (COOH)₂ oxidation current. Furthermore, a thin layer of catalyst particles must be applied to the electronically conductive support, and the (COOH)₂ oxidation reaction must be carried out under controlled and rapid stirring conditions. It is also noteworthy that activation-controlled currents are more susceptible to impurities and electrode poisoning effects than mass-transport limited currents. This is due to the fact that for mass-transport controlled conditions, the electrode area collapses to the geometrical area, while the real electroactive area determines the activation-controlled currents.

Acknowledgments

The authors thank P. L'Abbe (National Research Council Canada) for making the electrochemical cells used in this work and G. Pleizier (National Research Council Canada) for the XPS analyses. Helpful discussions with Dr. E. Gileadi (Tel-Aviv University, Israel) are also greatly appreciated.

The National Research Council Canada assisted in meeting the publication costs of this article.

References

1. J. O'M. Bockris and H. Wroblowa, *J. Electroanal. Chem.*, **7**, 428 (1964).
2. M. Watanabe and S. Motoo, *J. Electroanal. Chem.*, **60**, 267 (1975).
3. H. Gasteiger, N. Markovic, P. N. Ross, and E. Cairns, *J. Electrochem. Soc.*, **141**, 1795 (1994).
4. H. N. Dinh, X. Ren, F. H. Garzon, P. Zelenay, and S. Gottesfeld, *J. Electroanal. Chem.*, **491**, 222 (2000).
5. K. Kinoshita and P. N. Ross, *J. Electroanal. Chem.*, **78**, 313 (1977).
6. K. A. Friedrich, F. Henglein, U. Stimming, and W. Unkauf, *Electrochim. Acta*, **45**, 3283 (2000).
7. S. Hadzi-Jordanov, H. Angerstein-Kozlowska, and B. E. Conway, *J. Electroanal. Chem.*, **60**, 359 (1975).
8. C. L. Green and A. Kucernak, *J. Phys. Chem. B*, **106**, 1036 (2002).
9. S. A. S. Machado, A. A. Tanaka, and E. R. Gonzalez, *Electrochim. Acta*, **36**, 1325 (1991).
10. C. Bock, M.-A. Blackely, and B. MacDougall, In preparation.
11. T. J. Schmidt, H. A. Gasteiger, and R. J. Behm, *J. Electrochem. Soc.*, **146**, 1296 (1999).
12. J. W. Johnson, H. Wroblowa, and J. O'M. Bockris, *Electrochim. Acta*, **9**, 639 (1964).
13. C. Bock, A. Smith, and B. MacDougall, *Electrochim. Acta*, **48**, 57 (2002).
14. E. Gileadi, *Electrode Kinetics for Chemists, Chemical Engineers, and Material Scientists*, VCH Publishers, Inc., New York (1993).
15. A. J. Bard and L. R. Faulkner, *Electrochemical Methods, Fundamentals and Applications*, John Wiley & Sons, Inc., New York (1980).
16. L. Lipp and D. Pletcher, *Electrochim. Acta*, **42**, 1091 (1997).
17. J. Giner, *Electrochim. Acta*, **4**, 42 (1961).
18. C. Bock, A. Smith, and B. MacDougall, in *Energy and Electrochemical Processes for a Cleaner Environment*, C. Comninellis, M. Dogle, and J. Winnick, Editors, PV 2001-23, p. 23, The Electrochemical Society Proceeding Series, Pennington, NJ (2001).
19. T. D. Jarvi and E. M. Stuve, in *Electrocatalysis*, J. Lipkowitz and P. R. Ross, Editors, Wiley-VCH, Inc. New York (1998).
20. *Handbook of Chemistry and Physics*, 71st ed., D. R. Lide, Editor, CRC Press, Inc., Boston, MA (1990-1991).