

ARTICLE

Determination of the Real Surface Area of Palladium Electrode

Lan-lan Fang, Qian Tao, Ming-fang Li, Ling-wen Liao, Dong Chen, Yan-xia Chen*

Hefei National Laboratory for Physical Sciences at Microscale, Department of Chemical Physics, University of Science and Technology of China, Hefei 230026, China

(Dated: Received on March 1, 2010; Accepted on April 16, 2010)

Four methods, including voltammetric measurement of double layer capacitance, surface oxides reduction, under potential deposition of Cu and carbon monoxide (CO) stripping have been applied to evaluate the real surface area of a polycrystalline Pd (pc-Pd) electrode. The results reveal that the second and third methods lead to consistent results with deviations below 5%. And from the determined double layer capacitance and CO stripping charge, it is deduced that the double layer capacity unit area is $23.1 \pm 0.4 \mu\text{F}/\text{cm}^2$ and the saturated CO adlayer should be ca. 0.66 ML in order to ensure that the real surface area as determined is consistent with the other two techniques. The applicability as well as the attentions when applying these techniques for the determination of the real surface area of pc-Pd electrodes have been discussed.

Key words: Polycrystalline Pd electrode, Real surface area, Double layer capacitance, Oxygen adsorption, Under potential deposition, CO stripping

I. INTRODUCTION

Palladium is one of the most important materials due to its unique catalytic activities toward various reactions of technological significance. For example, Palladium is one of the most active catalysts (or catalyst component) for the treatment of automotive exhausts (especially NO reduction) [1–6], for oxygen reduction in low temperature fuel cells [7–11] and for the conversion of contaminants (such as trichloroethylene and tetrachloroethylene in groundwater) into benign end products *etc.* [12]. Besides, palladium has the ability to absorb more than 800 times of its own volume of hydrogen at room temperature and atmospheric pressure, underlining its important applications in a hydrogen economy in the near future [13, 14].

In order to evaluate the electrocatalytic activity of Pd based electrocatalysts and improve the catalytic performance, knowledge of the real surface area of such electrodes is extremely important, because it is required to calculate the specific activity of a given electrochemical process. Adsorption of probe molecules (such as O or CO *etc.*) [15–19] or metal atoms under potential metal deposition (upd) such as Cu, Ag, Sn, and Tl, which are known to undergo upd on Pd without forming a surface or bulk alloy [20–31]) and double layer capacitance measurements have been frequently used for such purpose [32–37]. However, each method has special limitations or even based on certain assumption which

may not always fulfilled in real cases [33]. In most previous studies, usually only one method is exploited to estimate the real surface area, and the errors for such estimation are always not given. In order to figure out the best way for evaluating the real surface area of Pd electrode and get the information on the errors associated with each method, we have carried out systematic analysis of real surface area of pc-Pd electrode by the four methods mentioned above, including voltammetric measurement of double layer capacitance, surface oxides (PdO) reduction, under potential deposition of Cu and carbon monoxide (CO) stripping have been applied to evaluate the real surface area of a polycrystalline Pd (pc-Pd) electrode. The values determined from different approaches are carefully compared, the applicability and limitations associated with different approaches will be discussed.

II. EXPERIMENTS

Pd sheet (99.99%, 20 mm×30 mm×0.2 mm, Tianjin Aida Metal Corp. China) was used as working electrode (WE), the geometric area of the WE exposed to electrolyte was ca. 1 cm². It was mechanically polished with diamond pastes and alumina powders with diameter from 3 μm to 0.25 μm successively, and then cleaned ultrasonically with Milli-Q water. A dual thin layer flow-cell (cell volume of 15 μL) with Pt foils and a reversible hydrogen electrode (RHE) as counter and reference electrodes were used [38]. All the potentials in this study are given with respect to RHE. Electrode potential was controlled by a potentiostat (CHI400a, Shanghai Chenchua, China). All the experiments were

* Author to whom correspondence should be addressed. E-mail: yachen@ustc.edu.cn

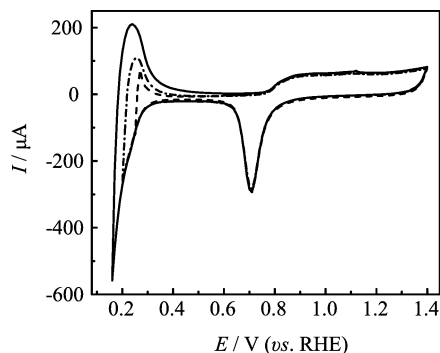


FIG. 1 Cyclic voltammograms of Pd electrode in 0.5 mol/L H_2SO_4 solution with different lower potential limits. E_1 , 0.25 V (dashed line), 0.2 V (dotted line), and 0.15 V (solid line), scan rate: 50 mV/s.

carried out at room temperature.

Millipore Milli Q water, sulfuric acid (GR, from Sinopharm), CuSO_4 (AR, from Sinopharm) were used to prepare the solutions. Supporting electrolyte used in all measurements in this study was 0.5 mol/L H_2SO_4 and constantly purged by N_2 (99.999%, Nanjing Special Gas Corp.). During the experiments, the electrode potential was controlled by designed program and the electrolyte solution was flowed continuously through the cell with a flow rate of 2 ML/min. Before the measurement, continuous potential cycles in the potential region from 0.2 V to 1.4 V at a scan rate of 0.05 V/s in 0.5 mol/L H_2SO_4 were carried out to clean Pd electrode surfaces until the standard cyclic voltammogram (CV) was obtained (Fig.1).

III. RESULTS AND DISCUSSION

A. Double layer capacitance measured by voltammetry

A representative set of CVs for pc-Pd electrode recorded in 0.5 mol/L H_2SO_4 solutions in the potential range from lower potential limit E_1 ($E_1=0.25, 0.20$, or 0.16 V) to 1.4 V is given in Fig.1. From the CVs it is seen that Pd electro-oxidation commences at 0.75 V, while in the negative-going scan the oxides reduction starts at 0.8 V and with a peak at potential of 0.7 V. The cathodic current observed at $E < 0.35$ V is attributed to H adsorption and absorption processes occur concurrently. All these phenomena agree well with the literature report [17, 27, 39, 40]. Furthermore, it is seen that the magnitude of the corresponding H oxidation current in the subsequent positive-going scan after reversed at E_1 changes significantly with the E_1 . The lower the E_1 , the higher is the H oxidation current and the higher is the upper potential where H oxidation current is still observed, which may extend into the double layer region. The latter may most probably originate from the oxidation of absorbed H atoms in the bulk of

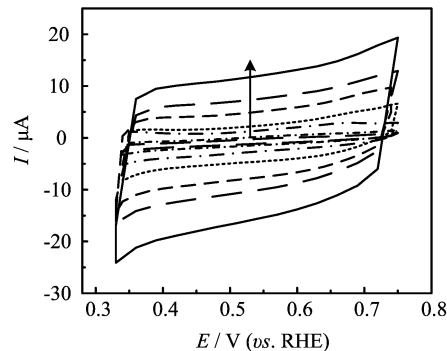


FIG. 2 A typical set of cyclic voltammograms of Pd electrode recorded in 0.5 mol/L H_2SO_4 in the potential region from 0.35 to 0.75 V. Scan rate: 10, 20, 50, 100, 200, 300, and 500 mV/s (arrow direction).

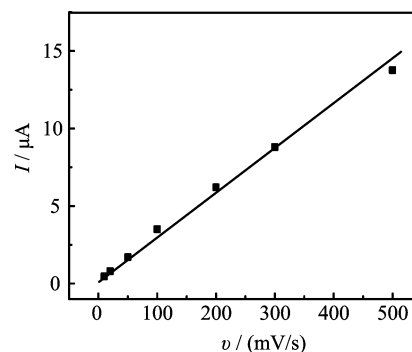


FIG. 3 Dependence of the double layer charging current as a function of scan rate, the current under examination is recorded at 0.55 V.

Pd electrode formed in the previous potential scan at $E < 0.2$ V, which diffused to the surface slowly at the potentials where H oxidation takes place [27].

From the base CV shown in Fig.1 with $E_1 > 0.25$ V, it is safe to assume that in the potential region from 0.35 V to 0.75 V, double layer charge is the only process taking place at Pd electrode. In order to use the capacitance measurements to determine the real surface area of Pd electrode, CVs in the potential region from 0.35 V to 0.75 V are recorded at different sweep rates from 10 mV/s to 500 mV/s (Fig.2). Under such conditions, the double layer capacitance (C_d) can be expressed as below:

$$C_d = \frac{dQ}{dE} = I \frac{dt}{dE} = I \left(\frac{dE}{dt} \right)^{-1} \quad (1)$$

where Q is the charge associated with the anodic oxidation, I is current measured at various scan rate, dE/dt is the potential scan rate. From the data shown in Fig.2, the current at 0.55 V is plotted as a function of potential scan rate and shown in Fig.3. The slope of the linear plot in Fig.3 gives the value of C_d of the Pd electrode under examination, which is found to be 54 μF .

According to Ref.[37], a capacity (C_s) of $44.5 \mu\text{F}/\text{cm}^2$ was estimated for the smooth Pd electrode in H_2SO_4 in the same potential range. Thus the real surface area of the Pd electrode used in this study is estimated to be ca. 0.61 cm^2 . As mentioned above, the geometric area of the WE exposed to electrolyte was ca. 1 cm^2 , so it is considered that the value $44.5 \mu\text{F}/\text{cm}^2$ is incorrect from the determined surface area in the following methods, it is deduced that the double layer capacity unit area is $23.1 \pm 0.4 \mu\text{F}/\text{cm}^2$ (it should be noticed that this capacity value contains both the contribution for the pure double layer charging as well as pseudo capacity due to sulfate adsorption/desorption).

B. Charge of a full monolayer of PdO

In order to use this method (the Charge for the formation of a full monolayer of PdO) to figure out the real surface area of a Pd electrode, firstly, we find out the upper potential limit at which oxygen is chemisorbed in a monoatomic layer with a one-to-one correspondence with the surface Pd atoms [15–17]. Under such condition, the charge associated with the formation or reduction of the chemisorbed oxygen layer is

$$Q_o = 2eN_A\Gamma_oA \quad (2)$$

where N_A is Avogadro constant, and Γ_o is the surface concentration of atomic oxygen, which is equal to the density of Pd atom at the surface N_{Pd} . From the value of N_{Pd} per unit surface area, the reference charge q_o^s is calculated, which is ca. $420 \mu\text{C}/\text{cm}^2$ for the case with Pd [15, 17].

Figure 4 shows a selected set of CVs of Pd electrode recorded in $0.5 \text{ mol/L H}_2\text{SO}_4$ with different upper potential limit for 1.1 V to 1.7 V. And the integrated charge for the reduction of oxygen covered Pd electrode (after double layer correction) are plotted as a function of the upper potential limit, which is given in Fig.4(b). According to Ref.[17], the coordinates at the point where the straight line changes its slope correspond to the formation of a complete PdO monolayer. At higher potentials a further oxidation occurs on the surface, which leads to the formation of Pd oxides with higher valence state (a change from two to more than two electrons per Pd atom or thick Pd oxide layers can be formed). The value of the charge associated with the inflexion point in Fig.4(b) is $Q_o \approx 500 \mu\text{C}$, which corresponds to a real surface area of 1.19 cm^2 (Q_o/q_o^s).

C. Charge for the stripping of saturated Cu or CO adlayer

When using Cu_{upd} method to determine the real surface area of a rough metal electrode, typically three steps are involved: (i) The charge associated with the anodic oxidation of the Cu_{upd} (Q_{Cu}) associated with underpotential deposition of a saturated Cu adlayer at

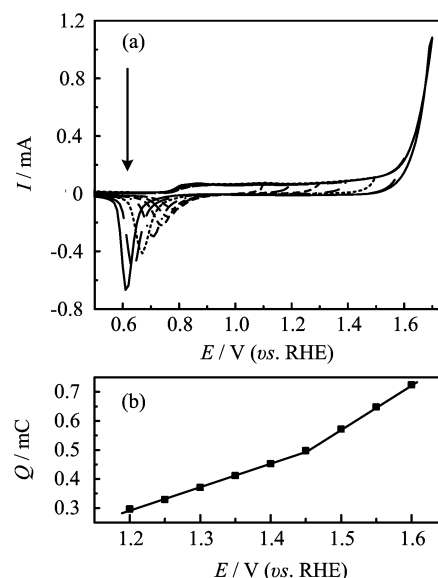


FIG. 4 (a) Series of cyclic voltammograms of Pd electrode in $0.5 \text{ mol/L H}_2\text{SO}_4$ with different higher potential limit E_h for 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, and 1.7 V (arrow direction), scan rate: 50 mV/s . (b) The integrated charge for the reduction of oxygen covered Pd electrode (after double layer correction) as a function of the upper potential limit.

the metal electrode is measured by voltammetry. (ii) The charge density for the formation of a full monolayer Cu (q_{Cu}^s) at the smooth metal electrode may either be calculated based on a chosen model, *e.g.*, polycrystalline surfaces are commonly taken as an average of the faces of the three base low-index faces. In the present study, we use the experimentally determined according to Ref.[30], where $q_{\text{Cu}}^s \approx 407 \mu\text{C}/\text{cm}^2$. (iii) The real surface area of the sample is given by

$$A = \frac{Q_{\text{Cu}}}{q_{\text{Cu}}^s} \quad (3)$$

One representative CV for Cu_{upd} and the subsequent oxidation of the Cu layer at the Pd electrode recorded in $0.5 \text{ mol/L H}_2\text{SO}_4 + 1 \text{ mmol/L CuSO}_4$ is given in Fig.5. The two peaks at 0.36 and 0.48 V together with a broad shoulder at 0.55 V in the positive-going scan are attributed to oxidation of Cu at (100+110), 111, and (100+110) face respectively [30]. During the negative-going scan, the cathodic peaks for Cu deposition are found to be negatively shifted for 30 mV, which can be explained by the fact that in solution containing 1 mmol/L CuSO_4 , the slow mass transport of Cu^{2+} to the electrode surface may cause concentration overpotential for the Cu_{upd} process. Since the current for Cu_{upd} and H deposition or absorption may superimpose at $E < 0.3 \text{ V}$ (Fig.5), it is not sure whether a saturated Cu adlayer is formed or not.

In order to figure out the lower potential limit where a saturated adlayer of Cu is formed at a Pd electrode,

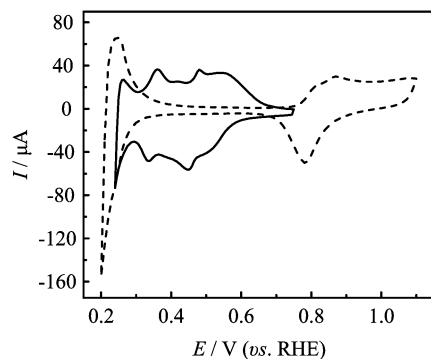


FIG. 5 Cyclic voltammograms of Pd electrode in 0.5 mol/L $\text{H}_2\text{SO}_4 + 1 \text{ mmol/L CuSO}_4$ (solid line), scan rate: 20 mV/s. For comparison, the blank CV for Pd in 0.5 mol/L H_2SO_4 (dashed line) is also shown.

one more experiment is done as following after the deposition of the Cu layer by scanning the potential from 0.75 V to various E_1 , the electrode potential was held at E_1 , and the electrolyte is switched back to Cu free supporting electrolyte and the cell and tubes are carefully washed to ensure that any residual Cu^{2+} in the cell is removed. After that Cu stripping is measured by firstly scanning negatively from E_1 to 0.2 V then scanning positively to 0.75 V in Cu^{2+} free supporting electrolyte. One representative set of I - E curves for Cu stripping in 0.5 mol/L H_2SO_4 with different lower E_1 from 0.34 V to 0.28 V are given in Fig.6(a). From Fig.6(a) it is clearly seen that if E_1 for Cu deposition is higher than 0.3 V, there is still significant current for H adsorption and oxidation when the potential scans down to 0.2 V. In contrast, when $E_1 \leq 0.3 \text{ V}$, cathodic current for H adsorption or absorption drops sharply, and the corresponding peak for H oxidation peak at 0.25 V in the positive-going scan also disappears, indicating that the surface is fully saturated with Cu.

However, with such Cu stripping CVs and the blank CV recorded in the 2nd cycle it is not possible to determine the charge associated with the oxidation of the Cu layer (Fig.6(a)), since current associated with the oxidation of a certain amount of H in the potential region from 0.25 V to 0.35 V are included in the I - E curves of Cu stripping, which is superimposed with the capacitive current due to double layer charging. To overcome this drawback, we had done one more experiments, by directly scanning the electrode potential from E_1 to 0.8 V, the CVs are given in Fig.6(b). From which the charge associated with deposition of a monolayer of Cu can be determined according to the following equation:

$$A = \frac{Q_{\text{Cu}} - Q_{\text{dl}}}{q_{\text{Cu}}^s} \quad (4)$$

where Q_{dl} is the background charge spent in the same potential range in the absence of Cu_{upd} layer. The Cu stripping charge of a saturated Cu adlayer formed at

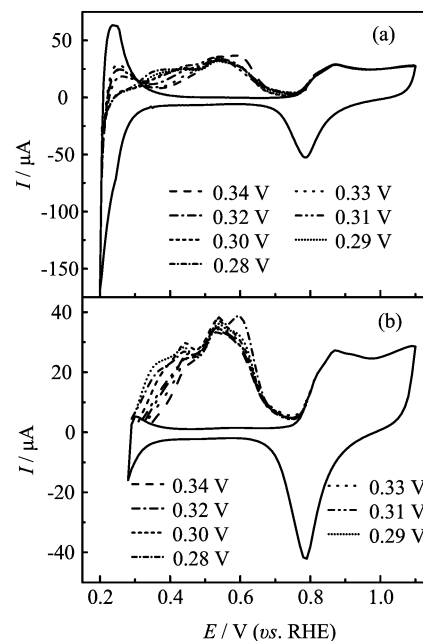


FIG. 6 Cyclic voltammograms of Cu stripping at Pd electrode in 0.5 mol/L H_2SO_4 after removing the Cu^{2+} in the cell. (a) the electrode potential firstly negatively scanned to 0.2 V and (b) the electrode potential was directly reversed at E_1 for Cu deposition. The Cu layer was deposited by scanning in 0.5 mol/L $\text{H}_2\text{SO}_4 + 1 \text{ mmol/L CuSO}_4$ from 0.75 V to various of E_1 (as shown in the figure). Scan rate: 20 mV/s.

0.28 V is ca. 0.47 mC, which corresponds to a real surface area of 1.15 cm^2 for the Pd electrode examined. This value is slightly smaller (5%) than what is determined by the measurement of the charge for PdO formation, which is probably due to the fact that q_{Cu}^s for the examined pc-Pd electrode may be slightly higher than its actual case.

The principle for using stripping charge of saturated CO adlayer to estimate the Pd electrode area is quite similar to that for Cu stripping. One representative CV for the stripping of a saturated CO adlayer predeposited at 0.35 V at Pd electrode in 0.5 mol/L H_2SO_4 is given in Fig.7. It is seen that at Pd electrode, CO_{ad} oxidation takes place at 0.75 V, with a peak at 0.91 V and a long tail extending to 1.25 V. The net faradic charge for the oxidation of a saturated CO adlayer ($Q_{\text{net}}^{\text{CO oxidation}}$) is determined by the following equation [42]:

$$Q_{\text{net}}^{\text{CO oxidation}} = Q_{\text{total}}^{\text{CO stripping}} - Q_{\text{o}}^{\text{Pd}} + Q_{\text{initial}}^{\text{CO adsorption}} \quad (5)$$

where $Q_{\text{total}}^{\text{CO stripping}}$ is the charge density obtained by integration of the CO stripping voltammogram between 0.35 and 1.3 V, $Q_{\text{ox}}^{\text{Pd}}$ is the charge density obtained by integration of the voltammogram of the CO-free surface between the same potential limits, and $Q_{\text{initial}}^{\text{CO adsorption}}$ is the charge density displaced at 0.35 V by the potentiostatic adsorption of CO. The latter is derived from the

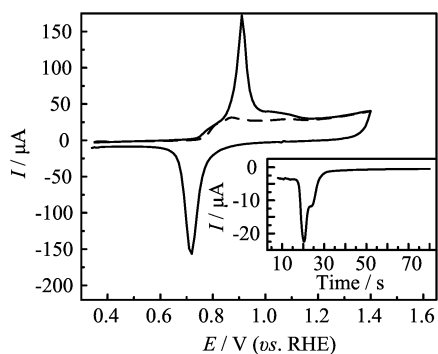


FIG. 7 Cyclic voltammograms of CO stripping at Pd electrode in 0.5 mol/L H_2SO_4 after dosing a saturated CO adlayer at 0.35 V and removing the residue CO in the cell (solid line), scan rate: 20 mV/s. The base CV after stripping off of CO is also shown for reference (dotted line). Inset: $I-t$ curve recorded during CO adsorption onto Pd electrode when holding the electrode potential at 0.35 V.

$I-t$ curve recorded upon CO adsorption at 0.35 V (inset in Fig.7). From such data, $Q_{\text{net}}^{\text{CO oxidation}}$ is estimated to be ca. 0.33 mC for the Pd electrode.

In order to use the CO stripping charge to determine the real surface area of the pc-Pd electrode, the coverage of saturated CO adlayer must be known. However, well accepted value of the coverage of saturated CO adlayer on pc-Pd electrode is not available so far. A series of studies from Weaver's group on CO adsorption at three base single crystalline Pd electrode revealed that in electrochemical environment, the saturated coverage of CO_{ad} at these electrodes are 0.75 ML at Pd(111) [43], 0.8 ML at Pd(100) [44], and 1.0 ML at Pd(110) electrodes [45], respectively. Supposing that pc-Pd composed of three base faces with equal contribution and the CO population at different base planes are not distorted by the edges neighboring to other planes, a saturated CO adlayer of 0.85 ML is expected. Taking that oxidizing a full monolayer of CO consumes 420 $\mu\text{C}/\text{cm}^2$ of charge [47] and the coverage of a saturated CO adlayer is 0.85 ML, the real surface area of Pd electrode is estimated to be 0.93 cm^2 from the measured CO stripping charge. This value is ca. 21% smaller than the average real surface area (1.18 cm^2) determined from measurements of PdO reduction as well as Cu stripping.

On the other hand, the geometric area of the WE is ca. 1 cm^2 . Considering the fact that it is impossible that the pc-Pd electrode prepared with the method described in this study has a roughness factor below 1.0. Hence we think the deviation must come from the fact that the saturated CO coverage at such Pd electrode is much smaller than what have been reported in previous studies [41–45]. If we take the averaged real surface area determined by the other two methods as described above as the standard, the saturated CO_{ad} coverage is estimated to be 0.66 ML. This value is quite close to

TABLE I Real surface area of pc-Pd electrode determined by four different methods (C^{s} is 44.5 $\mu\text{F}/\text{cm}^2$ [37] and 23.1 \pm 0.4 $\mu\text{F}/\text{cm}^2$ of this work).

	$q^{\text{s}}/\mu\text{L}$	$Q/\mu\text{C}$	S/cm^2
Double			1.18
PdO	420 [15, 17]	499	1.19
Cu_{upd}	407 [30]	468	1.15
CO	420 [47]	330	1.18

that (0.68 ML to 0.63 ML) for CO adsorbed at pc-Pt electrodes [42, 46]. Taking into account the facts the bulk structures and lattice constants of Pd and Pt are very close to each other, and CO prefers bridge-bonded configuration at Pd electrodes (one molecule occupies more sites than linear-bonded configuration), we think this number is more reliable than those with the coverage of CO $\theta_{\text{CO}} \geq 0.75$ ML, which have been reported in earlier studies [43–45]. This also demonstrates that carefully determination of the real surface area is very critical for further analysis of adsorbate coverage as well as the kinetics of electrocatalytic reactions.

IV. CONCLUSION

Four different methods have been exploited to determine the real surface area of a pc-Pd electrode and the real surface area determined are summarized in Table I. The surface area determined from oxygen adsorption is large than the method with Cu_{upd} (ca. 5%). the double layer capacitance per unit area is 23.1 \pm 0.4 $\mu\text{F}/\text{cm}^2$. On the other hand, CO stripping method depends critically on the value of saturated CO_{ad} coverage. Our results reveal that the saturation coverage of CO at pc-Pd with CO dosed 0.35 V is ca. 0.66 ML, which is much smaller than 0.75 ML as reported earlier. These results reveals that all these four methods can be used for the determination of the real surface area of smooth pc-Pd electrodes. However, when using such methods, still great attentions needs to be paid.

As for the method by the determination of double-layer capacitance through the measurements of double-layer charging current, one needs to pay attention to the fact that the double-layer capacitance of the Pd electrode changes with the electrolytes used for the measurements (values varying from a few to several tenth of $\mu\text{F}/\text{cm}^2$ are reported) as well as with electrode potential. Thus the application of this approach requires knowledge of the potential range to which the double-layer capacitance refers.

When using the approach of determining the charge of formation and reduction of PdO, an arbitrary value of 420 $\mu\text{C}/\text{cm}^2$ is assumed for the reduction of 1 ML of PdO, if the distribution of the base faces at the surface changes, this value will change correspondingly. Furthermore, in order to apply this method, one needs to

know precisely the potential range that corresponds to the formation of 1 ML of PdO in a CV transient.

As for the approach using the charge density associated with the under potential deposition of Cu, the lower potential limit where exactly one monolayer of Cu is deposited need to be carefully measured experimentally. One should pay attention to the fact that at pc-Pd electrode, the surface distribution of Cu_{upd} is unknown, and the surface stoichiometry of the adsorbed layer has been found to dependent on the metal nature and crystallize size, *i.e.*, the usual assumption of Cu:Pd=1:1 may not always be valid.

V. ACKNOWLEDGMENTS

This work was supported by the one Hundred Talents' Program of the Chinese Academy of Science, the National Natural Science Foundation of China (No.20773116), and 973 program from the Ministry of Science and Technology of China (No.2010CB923302).

- [1] L. F. de Mello, F. B. Noronha, and M. Schmal, *J. Catal.* **220**, 358 (2003).
- [2] G. L. Chiarello, D. Ferri, J. D. Grunwaldt, L. Forni, and A. Baiker, *J. Catal.* **252**, 137 (2007).
- [3] G. Denuault, C. Milhano, and D. Pletcher, *Phys. Chem. Chem. Phys.* **7**, 3545 (2005).
- [4] J. C. Chen, F. Y. Chang, and M. Y. Wey, *Catal. Commun.* **9**, 1106 (2008).
- [5] J. Cortes, E. Valencia, G. Aguila, E. Orellana, and P. Araya, *Catal. Lett.* **126**, 63 (2008).
- [6] K. T. D. Roseno, M. A. S. Baldanza, D. V. Cesar, and M. Schmal, *Catal. Lett.* **129**, 85 (2009).
- [7] J. L. Fernandez, V. Raghuvver, A. Manthiram, and A. J. Bard, *J. Am. Chem. Soc.* **127**, 13100 (2005).
- [8] J. L. Fernandez, D. A. Walsh, and A. J. Bard, *J. Am. Chem. Soc.* **127**, 357 (2005).
- [9] M. H. Shao, K. Sasaki, and R. R. Adzic, *J. Am. Chem. Soc.* **128**, 3526 (2006).
- [10] M. H. Shao, T. Huang, P. Liu, J. Zhang, K. Sasaki, M. B. Vukmirovic, and R. R. Adzic, *Langmuir* **22**, 10409 (2006).
- [11] O. Savadogo, K. Lee, K. Oishi, S. Mitsushima, N. Kamiya, and K. I. Ota, *Electrochem. Commun.* **6**, 105 (2004).
- [12] W. Sriwatanapongse, M. Reinhard, and C. A. Klug, *Langmuir* **22**, 4158 (2006).
- [13] A. Mandelis and C. Christofides, *J. Appl. Phys.* **70**, 4496 (1991).
- [14] E. C. Walter, F. Favier, and R. M. Penner, *Anal. Chem.* **74**, 1546 (2002).
- [15] D. A. J. Rand and R. J. Woods, *J. Electroanal. Chem.* **31**, 29 (1970).
- [16] M. W. Breiter, *J. Electroanal. Chem.* **81**, 275 (1977).
- [17] A. N. Correia, L. H. Mascaro, S. A. S. Machado, and L. A. Avaca, *Electrochim. Acta* **42**, 493 (1997).
- [18] A. Czerwinski, *J. Electroanal. Chem.* **379**, 487 (1994).
- [19] G. Maruszczak and A. Czerwinski, *Anal. Lett.* **28**, 2547 (1995).
- [20] R. R. Adzic, M. D. Spasojevic, and A. R. Despic, *J. Electroanal. Chem.* **92**, 31 (1978).
- [21] F. Ficcoglu and F. Kadirgan, *J. Electroanal. Chem.* **346**, 187 (1993).
- [22] S. H. Cadle, *Anal. Chem.* **46**, 587 (1974).
- [23] J. Okada, J. Inukai, and K. Itaya, *Phys. Chem. Chem. Phys.* **3**, 3297 (2001).
- [24] S. Szabo, *J. Electroanal. Chem.* **77**, 193 (1977).
- [25] T. Chierchie and C. Mayer, *Electrochim. Acta* **33**, 341 (1988).
- [26] O. A. Petrii, S. Y. Vasina, and I. G. Homchenko, *Elektrokhimiya* **13**, 1162 (1977).
- [27] P. M. Rigano and C. C. Mayer, *T. Electrochem. Acta* **35**, 1189 (1990).
- [28] E. A. Koliadko, S. Lu, and B. I. Podlovchenko, *Elektrokhimiya* **28**, 385 (1992).
- [29] I. Bakos and S. Szabo, *Electrochim. Acta* **46**, 2507 (2001).
- [30] A. Cuesta, L. A. Kibler, and D. M. Kolb, *J. Electroanal. Chem.* **466**, 165 (1999).
- [31] Y. M. Maksimov, A. S. Lapa, and B. I. Podlovchenko, *Elektrokhimiya* **25**, 712 (1989).
- [32] K. Kusmierczyk, M. Lukaszewski, Z. Rogulski, H. Siwek, J. Kotowski, and A. Czerwinski, *Pol. J. Chem.* **76**, 607 (2002).
- [33] S. Trasatti and O. A. Petrii, *Pure Appl. Chem.* **63**, 711 (1991).
- [34] P. Waszczuk, P. Zelenay, and J. Sobkowski, *Electrochim. Acta* **40**, 1717 (1995).
- [35] S. Smolinski, P. Zelenay, and J. Sobkowski, *J. Electroanal. Chem.* **442**, 41 (1998).
- [36] S. Smolinski and J. Sobkowski, *J. Electroanal. Chem.* **463**, 1 (1999).
- [37] M. Lukaszewski and A. Czerwinski, *Electrochim. Acta* **48**, 2435 (2003).
- [38] Y. X. Chen, M. Heinen, Z. Jusys, and R. Behm, *Angew. Chem. Int. Ed.* **45**, 981 (2006).
- [39] T. Chierchie, C. Mayer, and W. J. Lorenz, *J. Electroanal. Chem.* **135**, 211 (1982).
- [40] J. Horkans, *J. Electroanal. Chem.* **209**, 371 (1986).
- [41] H. Unterhalt, G. Rupprechter, and H. J. Freund, *J. Phys. Chem. B* **106**, 356 (2002).
- [42] A. Cuesta, A. Couto, A. Rincon, M. C. Perez, A. Lopeze-Cudero, and C. Gutierrez, *J. Electroanal. Chem.* **586**, 184 (2006).
- [43] S. Z. Zou, R. Gomez, and M. J. Weaver, *J. Electroanal. Chem.* **474**, 155 (1999).
- [44] S. Z. Zou, R. Gomez, and M. J. Weaver, *Langmuir* **15**, 2931 (1999).
- [45] S. Z. Zou, R. Gomez, and M. J. Weaver, *Surf. Sci.* **399**, 270 (1998).
- [46] R. Gomez, J. M. Feliu, A. Aldaz, and M. J. Weaver, *Surf. Sci.* **410**, 48 (1998).
- [47] T. Vidakovic, M. Christov, and K. Sundmacher, *Electrochim. Acta* **52**, 5606 (2007).