The Electrochemical Oxidation of Aqueous Sulfur Dioxide

I. Experimental Parameter Influences on Electrode Behavior

J. A. O'Brien,^{a,b,*} J. T. Hinkley,^a and S. W. Donne^{b,*,z}

^aCommonwealth Scientific and Industrial Research Organization, Energy Technology, Newcastle, New South Wales 2304, Australia

^bDiscipline of Chemistry, University of Newcastle, Callaghan, New South Wales 2308, Australia

The oxidative behavior of aqueous sulfur dioxide has been assessed on a polycrystalline platinum electrode using cyclic voltammetry with variation in applied experimental parameters. Parameters varied include the acid concentration, reaction temperature, and lower potential limit (E_{low}). Three distinctly different oxidation scenarios were identified. These are defined by E_{low} and, at $E_{\text{low}} < 0.2$ V, acid concentration as well. Observed oxidation scenarios include a limited response (scenario 1), catalytic oxidation (scenario 2), and reaction inhibition (scenario 3). Scenario 1 required an activation energy of $E_A = 83$ kJ mol⁻¹ with a Tafel slope of $b = 114$ mV and transfer coefficient of $\alpha_A = 0.49$. Scenario 2 was found to have a different reaction mechanism to scenario 1 ($\alpha_A = 0.21$), displaying faster reaction kinetics ($b = 74$ mV) and catalytically improved oxidation onset ($E_A = 51$ kJ mol⁻¹). The onset of scenario 2 oxidation was dependent on oxidation kinetics, not thermodynamics, with $dE_{\text{onset}}/dT = -2.132$ mV K⁻¹. The variable response of the electrode is discussed in terms of sulfur species adsorption, including the reductive formation of adsorbed sulfur at potentials less than 0.5 V, and the adsorption of sulfur dioxide with varying adsorption strength.

© 2010 The Electrochemical Society. [DOI: 10.1149/1.3458860] All rights reserved.

Manuscript submitted October 15, 2009; revised manuscript received March 30, 2010. Published July 9, 2010.

Experimental

Equipment.—Potentiostatic and potentiodynamic techniques were carried out using an Autolab potentiostat (model 302N) and advanced procedure editing through Nova 1.4 electrochemical software. The reference electrode was a saturated calomel electrode, and potentials referred to in this paper have been converted to the SHE (also adjusted for temperature).

A Pine Instruments electrode (E4 series) with a platinum disk insert was employed. The electrode cleaning procedure involved soft polishing with a wet Kempad polishing cloth followed by rinsing with acetone and Milli-Q water (> 18.2 MΩ resistivity). For heavy electrode soiling, the electrode was also polished using 0.5 μm alumina particles and sonicated in Milli-Q water for 2 min before final electrochemical cleaning in 1 M H₂SO₄ (repeated CV scans between hydrogen and oxygen evolution).

Solutions.—Acid solutions were made by dilution of 99 wt % H₂SO₄, provided by Scharlau Chemicals, with Milli-Q water. This solution was degassed with N₂ for 10 min before addition of stock Na₂SO₃ solution (1 M). Sulfite solutions were not degassed before addition to solution and some dissolved oxygen may be present as a result. Stock sulfite solutions were prepared using anhydrous Na₂SO₃ (98%), supplied by Ajax Fine Chemicals, and Milli-Q water. CV experiments used a water-jacketed electrochemical cell (100 mL) with the temperature controlled through an external circulation water bath.

Procedures.—Electrode preconditioning procedures involve holding the electrode for 2 min at the specified lower potential limit (E_{low}) followed by five cyclic sweeps (scan rate specified in Fig. 1-3 captions) between E_{low} and 1.4 V vs SHE. Only the final scan is shown. For Tafel slopes, the scan was taken immediately following the last cyclic sweep at 50 mV s⁻¹. The electrode was cleaned (see the Equipment section) with each change in experimental parameter, including between each applied E_{low} value. The active area of the electrode was calculated for a freshly cleaned electrode (cleaning procedure described in the Equipment section) using current function modeling¹⁷ for the completely reversible redox couple Fe(CN)₆^{3-/4-}, yielding a surface roughness of ~ 1.05 .

Results and Discussion

Effect of E_{low} , acid concentration, and temperature.—The effect of E_{low} on the reaction has been extensively studied in 1 M H₂SO₄⁷ and in this work has been evaluated for several acid con-

* Electrochemical Society Student Member.

** Electrochemical Society Active Member.

^z E-mail: Scott.Donne@newcastle.edu.au

The electrochemical oxidation of aqueous SO₂ in acidic solutions has been extensively studied using a polycrystalline platinum electrode.¹⁻⁶ It has been observed in the literature that the reaction is highly dependent on electrode preconditioning because of reductive formation of surface sulfur species at potentials lower than 0.6 V vs standard hydrogen electrode (SHE).³ These sulfur species have the ability to impact on the catalytic state of the electrode surface over an extensive electrode history (i.e., several repeated cyclic scans), leading to much disagreement and inconsistency in the literature, largely addressed in a recent critical review of work in this field.⁷

This reaction is of great interest with respect to the hybrid sulfur (HyS) cycle, a thermoelectrochemical water splitting cycle for large-scale hydrogen production using either solar or nuclear energy.^{8,9} Within this cycle, dissolved SO₂ is oxidized to H₂SO₄ in the anodic compartment of an acid electrolyzer, whereas hydrogen is evolved at the cathode, that is

High temperatures ($\sim 80^\circ\text{C}$) and acid concentrations (> 6 M) are expected to be required in the acid electrolyzer to allow optimal cycle integration.^{9,10} A tradeoff between these factors and the applied system pressure is required to achieve sufficient SO₂ solubility. Further, acid concentration and temperature both have the ability to affect the expected reversible potential of the electrochemical reaction¹¹ and thus the overall cycle efficiency.

Platinum is presently the preferred catalyst for both reactions in the form of platinized carbon electrodes.^{12,13} Past work has shown declining performance of the anodic reaction on polycrystalline platinum electrodes in solutions of increasing acid concentration¹⁴⁻¹⁶ and an increase in overall performance at high temperatures,^{12,14} although the effect of these variables on the oxidation mechanism has not been investigated in any detail.⁷

In this paper, the oxidation reaction has been investigated in a systematic manner using cyclic voltammetry (CV) in quiescent solutions. Acid concentration, lower potential limit (E_{low}), and temperature have been systematically varied and the CV response assessed.

Figure 1. (Color online) 100 mM SO_2 , 3.5 M H_2SO_4 , and 21°C. Clean electrode held at E_{low} for 2 min followed by repeated cyclic scans to 1.4 V. Forward scan only shown (1 V s^{-1} scan rate) and E_{low} specified in figure.

centrations including 0.1 M (~1 wt %), 1 M (~10 wt %), 3.5 M (~30 wt %), 6.6 M (~50 wt %), and 12.8 M (~80 wt %). The CV response for different E_{low} values has been compared in Fig. 1 for a 3.5 M H_2SO_4 solution.

Electrode response is significantly different for each E_{low} value and three main oxidative peaks can be observed, labeled as peaks I, II, and III in Fig. 1. In the following discussion, the electrode response is referred to in terms of three oxidation scenarios defined by their lower potential limit and qualitative behavior as follows:

1. Limited response for peak I (scenario 1).
2. Substantial catalytic increase in peak I (scenario 2).
3. Inhibition of all oxidative peaks (scenario 3).

A transitional scenario can also be discerned between scenarios 1 and 2, where the growth of peak II can be observed, also accompanied by a slight shift in the oxidation overpotential. Peak III is present to some extent under all oxidation scenarios. These peaks appear in different oxidation regions of the platinum electrode because platinum oxide forms electrochemically at potentials of $E > 0.9 \text{ V}$.¹⁸ Peaks II and III are therefore influenced by the formation of oxides at the electrode surface, whereas peak I occurs before the formation of these species. The influence of platinum oxides on the reaction has been discussed in the literature;⁷ however, the effect is not fully understood.

A similar response to applied E_{low} can also be seen for solutions of different acid concentrations. However, the oxidation scenario observed for each E_{low} value is also defined to some extent by acid concentration for $E_{\text{low}} < 0.2 \text{ V}$. A comparison of the CV behavior at specified E_{low} values and acid concentrations of 1, 3.5, and 6.6 M are shown in Fig. 2. Results in 0.1 and 12.8 M H_2SO_4 have been omitted from Fig. 2 as they exhibit substantially different behavior. In 0.1 M H_2SO_4 , the electrode response is not as dependent on E_{low} , whereas the response in 12.8 M is severely inhibited for all E_{low} values.

Several observations can be made from Fig. 2. First, by increasing acid concentration, the current density of the oxidation reaction is effectively diminished. Second, a change in the oxidation scenario for each acid concentration is observed at $E_{\text{low}} = 0.1 \text{ V}$, with the

Figure 2. (Color online) 100 mM SO_2 and 21°C (acid concentration specified in figure). Clean electrode held at E_{low} for 2 min followed by repeated cyclic scans to 1.4 V. Forward scan only shown (1 V s^{-1} scan rate) and E_{low} specified in figure.

oxidation in 6.6 M H_2SO_4 becoming suddenly inhibited. This difference in the oxidation scenario for applied acid concentrations was proposed from the analysis of published literature⁷ and is clearly shown here. Finally, the detailed modeling of Gorensek et al.¹¹ predicts that the reversible potential of the reaction increases in solutions of increasing acid activity; however, Fig. 2 shows that the onset potential for the oxidation does not, in fact, vary greatly with significant changes in acid concentration. This is also in opposition to the experimental results of C3lon-Mercado and Hobbs,¹² who found that the open-circuit potential of a platinized carbon electrode in SO_2 saturated H_2SO_4 did, in fact, increase with increasing acid concentration, changing by 0.05 V between 3.5 and 6.6 M H_2SO_4 . Figure 2 shows that a change of this magnitude is not observed in the present study. There are several possible reasons for this difference, including possible differences in the behavior of particulate Pt used¹² compared to the polycrystalline surface used in this work. The difference may also be a result of the different electrochemical procedures used. C3lon-Mercado and Hobbs used a negative scan, starting at high electrode potential scanning backward. Hysteresis of the reaction is well known² and the influence of surface oxides likely had an impact on these results. Unfortunately, the reason for this difference cannot be clearly seen as CV results were shown only in the form of Tafel plots¹² and, thus, onset and peak potentials are difficult to discern.

To investigate the effect of temperature on the oxidative behavior of the reaction, two E_{low} values were tested in 1 M H_2SO_4 : 0.4 V (scenario 1) and 0.2 V (scenario 2), as shown in Fig. 3. At $E_{\text{low}} = 0.4 \text{ V}$, peak II can be seen to emerge as the temperature increased, along with a decrease in onset and peak potentials at higher

Figure 3. (Color online) 100 mM SO₂ and 1 M H₂SO₄ (temperature specified in figure). Clean electrode held at E_{low} for 2 min followed by repeated cyclic scans to 1.4 V. Forward scan only shown (50 mV s⁻¹ scan rate) and E_{low} specified in figure.

temperatures. For $E_{\text{low}} = 0.2$ V, the shape of the voltammogram does not change, but the onset and peak potentials are shifted to lower potentials with increasing temperature. This is in opposition to thermodynamic predictions, i.e., $dE^0/dT = +0.784$ mV K⁻¹,¹⁹ whereas $dE_{\text{onset}}/dT = -2.132$ mV K⁻¹ for $E_{\text{low}} = 0.2$ V. This observation strongly suggests that the reaction under these conditions is not limited by thermodynamics but is, in fact, kinetically limited.

Tafel slopes and activation energy.—The effect of temperature on the reaction can also be analyzed quantitatively in terms of Tafel plots; these results are then applied to the Arrhenius equation to find the activation energy of the reaction at each E_{low} . The method and equations are taken from Bard and Faulkner.²⁰

Tafel slopes have been determined from data at a scan rate of 5 mV s⁻¹. The linear scan, starting at E_{low} and finishing at 1.4 V vs SHE, was then converted to a Tafel plot by plotting the reaction overpotential ($\eta = E_{\text{SHE}} - E^0$) vs the log of the current density. The overpotential has been calculated as per the procedure described by O'Brien et al.,⁷ dependent on the reaction temperature (~ 0.1 V). The resulting positive slope b has been taken as the Tafel slope, which is equal to $(1 - \alpha_A)F/(2.3RT)$ with an intercept $\log i_0$.²⁰ Here, α_A is the overall anodic transfer coefficient, i_0 is the exchange

Figure 4. Arrhenius plot for 100 mM SO₂ in 1 M H₂SO₄ at $E_{\text{low}} = 0.4$ and 0.2 V as indicated.

current density (A cm⁻²), and other variables retain their usual meanings. i_0 can then be converted to k^0 , the standard heterogeneous rate constant (cm s⁻¹), via the equation

$$i_0 = F A k^0 c_{\text{SO}_2} \quad [3]$$

Using this k^0 value, an Arrhenius plot can be constructed according to

$$\ln k^0 = \ln(M) - \frac{E_A}{RT} \quad [4]$$

where E_A is the activation energy of the reaction (J mol⁻¹) and M is a constant known generally as the frequency factor.²⁰ Results for reaction at $E_{\text{low}} = 0.4$ and 0.2 V are shown in Fig. 4, and calculated variables are listed in Table I. This analysis shows that the activation energy of the reaction is directly affected by E_{low} , as is the reaction mechanism, indicated by the difference in observed Tafel slopes/transfer coefficient. The observed Tafel slopes found here for each scenario also agree with those found in past investigations. O'Brien et al.⁷ qualitatively separated the Tafel slopes of the two oxidation scenarios observed in the literature; the values observed here are consistent with the range described.

Sulfur coverage and effects.—It is possible that all effects observed from variation in E_{low} , acid concentration, and reaction temperature are, in fact, a result of their effects on the reductive formation of sulfur at the electrode surface, which can occur at potentials of less than ~ 0.45 V²¹ according to the reaction

The effect of E_{low} , acid concentration, and temperature on the reductive charge passed at a clean electrode while holding at E_{low} for 2 min before CV is shown in Fig. 5.

The reductive charge for a monolayer of sulfur can be calculated for the 4 electron reduction of SO₂, assuming the adsorption of either 1 atom of sulfur per available atom of platinum (one-site adsorption, S:Pt = 1:1), or 1 atom of sulfur per 2 available atoms of platinum (two-site adsorption, S:Pt = 1:2). For a polycrystalline platinum surface, the number of surface atoms has been estimated as 1.3×10^{15} atoms cm⁻²,¹⁸ resulting in an estimate of

Table I. Transfer coefficient, Tafel slope, and activation energy.

E_{low}	α_A	Tafel slope	E_A
0.4 V	0.49	114 mV	83 kJ mol ⁻¹
0.2 V	0.21	74 mV	51 kJ mol ⁻¹

Figure 5. (Color online) Reductive charge passed on a clean electrode for a period of $t = 2$ min, E_{low} value indicated. (a) 100 mM SO_2 , 3.5 M H_2SO_4 , 21°C, log scale y-axis; (b) 100 mM SO_2 , 21°C; and (c) 100 mM SO_2 , 1 M H_2SO_4 . Dashed lines indicate the calculated charge for (a-c) sulfur layer formation up to monolayer and (a) bilayer coverages for both one- and two-site adsorptions.

-0.84 mC cm^{-2} for monolayer coverage and -1.64 mC cm^{-2} for bilayer coverage assuming one-site adsorption. The calculated values for charge should be halved to determine the expected charge for two-site adsorption (indicated in Fig. 5). The charge passed is indicative only of the sulfur coverage for the CV responses in Fig. 1-3 because during CV sweeps, sulfur oxidation and SO_2 reduction may take place, leading to some variation in sulfur coverage. The number of sulfur atoms adsorbed per atom of platinum is contentious, as is the exact oxidation state of the adsorbed sulfur, as discussed in a recent paper.⁷

Figure 5a shows that as the E_{low} value is decreased, a small increase in the reductive charge occurs until a slightly higher increase at 0.1 V and a dramatic increase at 0 V (note log scale in Fig. 5a). The increase at 0 V coincides with an inhibited response of the electrode at this E_{low} , supporting literature observations that the formation of multilayers of sulfur are detrimental to the reaction,²² most likely as a result of the insulating properties of sulfur at this high coverage. The literature also suggests that the best catalytic behavior is attained with a bilayer sulfur coverage.²² This coverage is attained for one-site adsorption, as indicated in Fig. 5a, for $E_{low} = 0.3 \text{ V}$ without the expected catalytic increase ($E_{low} = 0.4 \text{ V}$ for two-site adsorption). This is possibly the result of a change in the expected sulfur coverage at the electrode surface following electrode cycling and subsequent removal of some surface sulfur species and the difficulty of estimating the exact surface coverage of sulfur. Best results are, in fact, observed for $E_{low} = 0.2 \text{ V}$ (Fig. 2), where a coverage greater than the bilayer is observed.

If the reductive charge is compared as a function of applied acid concentrations at each E_{low} value (Fig. 5b), the reductive charge is only moderately affected by acid concentration until 0.1 V, where a substantial increase can be observed with increasing acid concentration. The significantly different voltammograms observed at this potential for each acid concentration can then be linked to variation in the formation of sulfur layers, most likely a result of the increasing reversible potential for sulfur formation in solutions of increasing acidity.

Finally, even though the appearance of peak II occurs when increasing the temperature for $E_{low} = 0.4 \text{ V}$ (Fig. 3), the reductive charge increases only slightly (Fig. 5c), suggesting that the emergence of peak II is not related to the reductive formation of sulfur layers in this case. For $E_{low} = 0.2 \text{ V}$, sulfur formation increases with temperature. Improved performance at higher temperatures could then be linked to increased sulfur formation as long as the amount of sulfur does not exceed the multilayer coverage observed for an inhibited scenario. However, the improvement is most likely due to kinetic improvement at higher temperatures, as discussed below.

Catalytic behavior and reaction mechanism.— Three main peaks have been observed in Fig. 1-3, identified as peaks I, II, and III in Fig. 1. The origin of these electrochemical peaks may involve a

combination of effects such as oxidation on different surface sites, oxidation by multiple steps, change in oxidation mechanism due to the presence of surface oxides, and involvement of various adsorbed sulfur species. The adsorption of electroactive species is likely to be crucially important as aqueous SO_2 has been observed to be strongly chemisorbed to the platinum electrode surface over a wide potential range.^{7,23-25} This strong adsorption has been proposed to be inhibiting to electrochemical oxidation, possibly as a result of lateral dipole repulsions of adsorbed molecules and steric effects.²² It is therefore possible that the catalytic effect of the adsorbed sulfur is to prevent, or at least modify, adsorption of SO_2 .

Peak I has been identified in the literature as an irreversible two electron oxidation,⁴ which is also diffusion limited,^{1,4,5} and has been proposed to occur on an electrode surface covered with a bilayer of sulfur.²² We can speculate that, if sulfur formation indeed weakens the adsorption of SO_2 , the mechanism of peak I is the straight, irreversible oxidation of either dissolved or weakly adsorbed SO_2 over an electrode covered with several sulfur layers. Oxidation is possibly facilitated by a fast charge transfer via S-S bridging, as proposed by Matveeva and Kasatkin.²⁶ In this case, the activation barrier is most likely a result of the dielectric constant of sulfur, overcome by increasing temperature. Although the formation of sulfur is observed to increase with temperature at this E_{low} value, it is possible that this sulfur formation has little direct effect on the oxidation reaction, i.e., once a certain coverage is passed, the increased sulfur at the electrode surface does not affect the oxidation reaction until higher coverages (scenario 3). For this mechanism, the increase in oxidative overpotential and current density is purely a kinetic effect.

Peak II has been shown here to emerge both with decreasing E_{low} and with increasing temperature. The growth of peak II with decreasing E_{low} has been linked to sulfur formation, whereas its emergence with temperature has not (Fig. 5c). The two variables may therefore exert the same phenomena, i.e., decrease in the adsorption strength of SO_2 by sulfur formation or increased temperature. The kinetics of this oxidation reaction are more sluggish than for peak I and exhibit a different oxidation mechanism (Table I), possibly due to a more limited charge transfer in the absence of S-S bridging and a mechanism involving a more strongly adsorbed reactant. Peak II also occurs in the region where platinum oxides form, though it has been observed that the formation of sulfur leads to a suppression of oxide formation.⁷ Peak III is most certainly influenced by surface oxide species although, as it is difficult to separate this peak from peak II due to overlap, mechanistic information about this peak is difficult to even speculate on.

Sulfate adsorption may also impact the oxidation mechanism. Using the radiotracer method, it was observed by Szklarczyk et al.²⁵ in solutions of 0.5 M H_2SO_4 that the product of SO_2 oxidation is not desorbed from the electrode; adsorbed sulfate has also been identi-

fied following oxidation using surface enhanced Raman spectroscopy.²⁷ This may explain the limitation of the oxidation reaction in acids of increasing concentration because the sulfate product would be more difficult to remove from the electrode surface in acids of high concentration as a result of the concentration gradient. The reaction would then become limited by the diffusion of the adsorbed product species back into the solution, leading to a decrease in oxidation current. The decreasing response in solutions of increasing acid concentration has been observed several times in the past; however, it was invariably attributed to the decreasing activity of the electroactive ion, aqueous SO₂, in more concentrated solutions.¹⁴⁻¹⁶

Conclusions

The oxidation of aqueous SO₂ on a bulk platinum surface is strongly dependent on electrode preconditioning and the H₂SO₄ electrolyte concentration. A significantly different oxidation behavior can be observed under certain electrode preconditioning conditions, oxidation scenarios also observed to be sensitive to the acid concentration at $E_{\text{low}} < 0.2$ V. The majority of this behavior can be explained by the reductive formation of adsorbed sulfur at potentials below 0.5 V. Sulfur apparently alters the strong adsorption of aqueous SO₂ to the unmodified platinum electrode surface. As the potential is swept to an increasingly cathodic lower potential limit, sulfur coverage is expected to increase, causing first a catalytic response before an almost complete inhibition of the electrode at high sulfur coverages.

Oxidation scenarios involving an electrode partially and completely covered in sulfur show evidence of proceeding through different reaction mechanisms, with oxidation on an electrode where platinum sites are completely covered with sulfur performing the best kinetically. The onset of oxidation for best performance has further been identified as being controlled, not by reaction thermodynamics, but by oxidation kinetics, with an activation energy of 53 kJ/mol. To reduce the reaction overpotential further and improve the cycle efficiency of the HyS cycle, this activation barrier must be either overcome or removed. The origin of this activation barrier cannot be identified using purely CV techniques, and more advanced electrochemical techniques are required. Inhibited oxidation in acids of increasing concentration is a further barrier to the progression of the acid electrolyzer as it limits the achievable current density. It is

proposed here that this limitation is due to the strong adsorption of the sulfate product. If this adsorption can be avoided, higher current densities may be achieved.

Acknowledgments

J.O'B. acknowledges the CSIRO for funding and the provision of a research internship.

University of Newcastle assisted in meeting the publication costs of this article.

References

1. A. J. Appleby and B. Pichon, *J. Electroanal. Chem.*, **95**, 59 (1979).
2. C. Quijada, A. Rodes, J. L. Vázquez, J. M. Pérez, and A. Aldaz, *J. Electroanal. Chem.*, **394**, 217 (1995).
3. C. Quijada, A. Rodes, J. L. Vázquez, J. M. Pérez, and A. Aldaz, *J. Electroanal. Chem.*, **398**, 105 (1995).
4. E. T. Seo and D. T. Sawyer, *Electrochim. Acta*, **10**, 239 (1965).
5. R. M. Spotnitz, J. A. Colucci, and S. H. Langer, *Electrochim. Acta*, **28**, 1053 (1983).
6. M. R. Tarasevich, *Sov. Electrochem.*, **22**, 1469 (1987).
7. J. A. O'Brien, J. T. Hinkley, S. W. Donne, and S.-E. Lindquist, *Electrochim. Acta*, **55**, 573 (2010).
8. L. E. Brecher, S. Spewock, and C. J. Warde, *Int. J. Hydrogen Energy*, **2**, 7 (1977).
9. M. B. Gorenssek and W. A. Summers, *Int. J. Hydrogen Energy*, **34**, 4097 (2009).
10. Y. H. Jeong and M. S. Kazimi, *Nucl. Technol.*, **159**, 147 (2007).
11. M. B. Gorenssek, J. A. Staser, T. G. Stanford, and J. W. Weidner, *Int. J. Hydrogen Energy*, **34**, 6089 (2009).
12. H. R. Colón-Mercado and D. T. Hobbs, *Electrochem. Commun.*, **9**, 2649 (2007).
13. S. K. Lee, C. H. Kim, W. C. Cho, K. S. Kang, C. S. Park, and K. K. Bae, *Int. J. Hydrogen Energy*, **34**, 4701 (2009).
14. A. J. Appleby and B. Pinchon, *Int. J. Hydrogen Energy*, **5**, 253 (1980).
15. P. W. T. Lu and R. L. Ammon, *Int. J. Hydrogen Energy*, **7**, 563 (1982).
16. B. D. Struck, R. Junginger, D. Boltersdorf, and J. Gehrmann, *Int. J. Hydrogen Energy*, **5**, 487 (1980).
17. R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).
18. A. J. Bard, *Electroanalytical Chemistry: A Series of Advances*, Marcel Dekker, New York (1976).
19. S. Bratsch, *J. Phys. Chem. Ref. Data*, **18**, 1 (1989).
20. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, John Wiley & Sons, New York (2001).
21. *Standard Potentials in Aqueous Solutions*, A. J. Bard, R. Parsons, and J. Jordon, Editors, International Union of Pure and Applied Chemistry, New York (1985).
22. C. Quijada, J. L. Vázquez, and A. Aldaz, *J. Electroanal. Chem.*, **414**, 229 (1996).
23. A. Q. Contractor and H. Lal, *J. Electroanal. Chem. Interfacial Electrochem.*, **93**, 99 (1978).
24. I. R. Moraes, M. Weber, and F. C. Nart, *Electrochim. Acta*, **42**, 617 (1997).
25. M. Szklarczyk, A. Czerwinski, and J. Sobkowski, *J. Electroanal. Chem.*, **132**, 263 (1982).
26. E. S. Matveeva and E. V. Kasatkin, *Sov. Electrochem.*, **19**, 801 (1984).
27. T. Wilke, X. Gao, G. Takoudis, and M. Weaver, *J. Catal.*, **130**, 62 (1991).