A Kinetic Study of the Electrochemical Oxidation of Alberta Coal Slurries

George Thomas,*† S. Whitcombe, M. D. Farebrother, and V. I. Birss*
Department of Chemistry, The University of Calgary, Calgary, Alberta, Canada, T2N 1N4

ABSTRACT

The kinetics of the Fe\(^{3+}\)-mediated electrochemical oxidation of four types of Alberta coals in acidic slurries have been investigated. A critical examination of the previously reported mechanisms and kinetic treatments for the electrochemical oxidation of coal slurries is provided. In this work, a new approach was developed to analyze and to determine the rate constant of the electrochemical oxidation of coal, shown here to be an irreversible process. Two second-order rate constants, \(k_c\) and \(k_{c,2}\), representing the initial (0 to ca. 6h) and subsequent (ca. 6 to 24h) stages of electrochemical oxidation, respectively, were obtained from this approach. A correlation between these rate constants and the fixed carbon content (rank) was observed for the coals studied.

The demonstrated feasibility of the electrochemical conversion of coal in acidic slurries, first published by Coughlin and Farooque (1-4), has spawned further interest in this new process. It has been shown by numerous subsequent workers (5-11) that Fe\(^{3+}\) released from the coal into these acidic slurries is implicated in the oxidation of coal (reaction [1]) and the Fe\(^{3+}\) generated by this reaction is re-oxidized at the anode (reaction [2])

\[
\text{Fe}^{3+} + \text{Coal} + \text{nH}_{2}\text{O} \rightarrow \text{Fe}^{4+} + [\text{PCoal} + q\text{CO} + r\text{CO} + \text{other products}] + \text{sH}^+ \quad [1]
\]

\[
\text{Fe}^{3+} \rightarrow \text{Fe}^{2+} + e^- \quad [2]
\]

Here, \(k_c\) and \(k_{c,2}\) are the rate constant for reaction [1] and the mass-transfer rate constant (Fe\(^{3+}\) to the electrode), respectively. Various other research groups (5-14) have carried out numerous analyses of the kinetics of coal oxidation, and of the gaseous products (1-5, 7, 8, 10, 16, 17). Also, numerous analyses of the kinetics of the electrochemical coal oxidation reaction have been made (7-11, 18-20), although no common agreement regarding the best model of the rate of diffusion of Fe\(^{3+}\) to the coal particle surface and to carry out the data interpretation (to determine the mechanism of electrochemical oxidation of coal) has been reached.

Background

Dhooge et al. (7, 8) were the first to attempt to analyze the kinetics and mechanism of slurry oxidation by assuming a pseudo-first order reaction (w.r.t. Fe\(^{3+}\)), and obtained a rate constant of 2.6 × 10^{-5} s^{-1} at 20°C for the electrochemical oxidation of sub-bituminous San Juan coal. This determination of the rate constant of the oxidation of coal may not be valid, since steady-state current conditions are not generally observed (5, 11, 15, 18) at any time of electrolysis, unless the concentration of the coal is very large excess to that of Fe\(^{3+}\), as was the case in Ref. (7 and 8).

Anthony and Linge (9) found that the rate of coal oxidation was independent of the Fe\(^{3+}\)/Fe\(^{2+}\) concentration and proportional to \(t^{-1/2}\), indicating a mass transport controlled reaction. Although they did not provide any values for the rate constants obtained from their results, it was concluded that the rate of oxidation depends solely on the concentration of active sites on the coal particle surfaces, that different sites on the coal surface may react at different rates, and that numerous reactions (with different rate constants) could be observed at once.

In the kinetic treatment presented by Kreysa et al. (11), reversible second-order reaction kinetics (first order in Fe\(^{4+}\) and coal) were assumed. However, their method of data analysis to obtain the coal reaction rate as a function of time led to a maximum rate at ca. 80 min of reaction [Fig. 7 of Ref. (11)]. The consequence of the presence of this maximum is that the reverse rate constant for reaction [1], obtained by a curve fitting method, was not, greater than the forward rate constant. However, this is unreasonable as this would suggest that oxidized coal exposed to a Fe\(^{3+}\)/1M H\(_2\)SO\(_4\) solution would oxidize Fe\(^{3+}\) at open-circuit potential (OCP) conditions. In fact, it is known (7, 8, 11) that under OCP conditions, coal is oxidized by Fe\(^{3+}\) in 1M H\(_2\)SO\(_4\), as in reaction [1].

Kawakami et al. (19) is also based on the assumption of competitive adsorption of Fe\(^{3+}\) and Fe\(^{2+}\) on the coal surface. If this assumption is correct, a loss of Fe\(^{2+}\) from the slurry due to adsorption on the coal surface should be observed. It will be shown in our work that this is not the case. It is also noteworthy that the rate constants reported by Kawakami et al. (19) also incorporate the rate constant of the oxidation of pyrite which leaches into the slurry during the electrolysis.

In a mathematical treatment of the electrochemical oxidation of different ranks of Alberta coals in acidic slurries, Lalvani (20) has assumed that the rate of oxidation is limited by the rate of diffusion of the oxidant (Fe\(^{3+}\)) to the coal particle surface and is therefore determined by the thickness of the diffusion layer around the coal particles. Such a model is difficult to visualize when considering the porous, irregular nature of the coal particles. Lalvani's treatment (20) predicts an observed constant current with time of electrolysis, which has never been reported in the literature (1-5, 7-11, 13, 15, 16).

We have been studying the electrochemical oxidation of different ranks of Alberta coals in acidic slurries (15-17, 21). Because of the inadequacies of the previously reported kinetic methods discussed above, we have developed a modified approach to analyze the kinetics of electrochemical oxidation of coal by Fe\(^{3+}\), in acidic slurries. The coal oxidation reaction can be visualized as a reaction between surface active sites such as hydroxyl, phenolic, carboxylic, acyl, etc. groups and Fe\(^{3+}\) as suggested in the literature (1-4, 6, 8-10, 12, 13). The slow step in the overall process is presumed to be the interaction of these two reactants during the electron transfer process, similar to the model proposed by Kreysa et al. (11), and hence a second-order reaction is assumed. The overall kinetic treatment is most simi-
lar to that of Kreyesa et al. (11), except that we have assumed an irreversible reaction. Finally, the rate constants for the $\text{Fe}^{3+}$-mediated oxidation of four different Alberta coals are determined, and our attempts to correlate these with the coal properties are discussed in this paper.

### The Kinetic Model

The electrochemical oxidation of coal mediated by $\text{Fe}^{3+}$ in acidic slurries is usually carried out under potentiostatic conditions at an applied potential of 1.0 V vs. RHE (5, 7, 8, 11, 13, 15-17, 19, 20). Under these conditions, the current as reaction [2] proceeds is measured as a function of electrolysis time. The current contains information about the total concentration of $\text{Fe}^{3+}$ ($C_{\text{Fe}}$) in the slurry as well as its rate of consumption at the electrode, ($dC_{\text{Fe}}/dt)_{\text{coal}}$, as in Eq. [3] and [4]

$$I_t = nFAC_k(C_{\text{Fe}})$$

$$I_t = -nFV \frac{dC_{\text{Fe}}}{dt}$$

where $I_t$ is the measured current for reaction [2], $A$ is the area of the electrode, $V$ is the volume of the slurry, $F$ is the Faraday constant, and $n = 1$ for the $\text{Fe}^{2+}$ redox couple. In Eq. [4], the subscript $e$ indicates that this change in $C_{\text{Fe}}$ is brought about solely by the electrochemical oxidation of $\text{Fe}^{3+}$ at the electrode, and the negative sign is consistent with the decrease in the $\text{Fe}^{3+}$ concentration at potentials at which oxidation ($\rightarrow$) currents are tracked.

Under typical experimental conditions, when reactions [1] and [2] occur simultaneously, the overall flux of $\text{Fe}^{2+}$ at time, $t$, is the measured current, $I_t$, ($dC_{\text{Fe}}/dt)_{\text{coal}}$, in the coal slurry depends both on the rate of $\text{Fe}^{2+}$ oxidation (consumption of $\text{Fe}^{2+}$ at the anode, ($dC_{\text{Fe}}/dt)_{\text{coal,a}}$, and the rate of electrochemical oxidation of $\text{Fe}^{3+}$ (consumption of $\text{Fe}^{2+}$) at the cathode, ($dC_{\text{Fe}}/dt)_{\text{coal,c}}$, and can be expressed as

$$I_t = \frac{dC_{\text{Fe}}}{dt}_{\text{Total}} = \frac{dC_{\text{Fe}}}{dt}_{\text{coal,a}} + \frac{dC_{\text{Fe}}}{dt}_{\text{coal,c}}$$

The rate of generation of $\text{Fe}^{2+}$ is determined by the rate of the reverse reaction [1], while $\text{Fe}^{2+}$ is consumed at different rates at the electrode, depending on its concentration and $k_c$. Differentiating Eq. [3] w.r.t. time and rearranging, we obtain

$$\frac{dC_{\text{Fe}}}{dt}_{\text{coal,c}} = \frac{1}{nFAk_c} \frac{dl}{dt}$$

for the overall flux in the concentration of $\text{Fe}^{3+}$. From Eq. [4], we obtain the rate of consumption of $\text{Fe}^{2+}$ at the electrode at 1.0 V under potentiostatic conditions

$$\frac{dC_{\text{Fe}}}{dt}_{\text{coal,a}} = \frac{-1}{nFV} I_t$$


$$\frac{dC_{\text{Fe}}}{dt}_{\text{coal}} = \frac{1}{nFAk_c} \frac{dl}{dt} + \frac{1}{nFV} I_t$$

Equation [8] is a global equation which can describe any electrocatalytic process similar to that represented by reactions [1] and [2]. In this particular case, it can be used to calculate the rate of oxidation of coal by $\text{Fe}^{2+}$, as suggested by Kreyesa et al. (11).

Assuming second-order kinetics, the rate of oxidation of coal (reaction [1]) can also be expressed as

$$\frac{dC_{\text{coal}}}{dt} = k_c C_{\text{coal}} C_{\text{Fe}}$$

where $C_{\text{coal}}$ is the total concentration of $\text{Fe}^{3+}$ in the slurry. The concentration of coal at time, $t$, $C_{\text{coal,t}}$, is very difficult to estimate due to the heterogeneous and variable nature of coal surfaces. $C_{\text{coal}}$ can be expressed as follows

$$C_{\text{coal,t}} = C_{\text{coal,o}} - C_{\text{coal,t}}$$

where $C_{\text{coal,o}}$ represents the initial concentration of active sites before the commencement of electrochemical oxidation, while $C_{\text{coal,t}}$ represents the concentration of sites which have reacted from $t = 0$ to $t$. The charge, $Q_t$, passed after time, $t$, of electrolysis is directly related to $C_{\text{coal,t}}$. However, $Q_t$ also contains the charge equivalent to the $\text{Fe}^{3+}$ concentration present in the slurry at time, $t$, i.e., $nF(C_{\text{Fe}} - C_{\text{coal,t}})$. Therefore

$$Q_t = nFV(C_{\text{Fe,o}} - C_{\text{coal,t}}) + zFV(C_{\text{coal,t}})$$

The value of $z$ (the number of electrons involved in the complete oxidation of each active site on the coal surface) is difficult to estimate. Depending on the oxidation state of the carbon atom in the reacting functional group of the active site, $z$ can vary from 1 to 8. Kreyesa et al. (11) have used a value of 2 for $z$ as per the mechanism of coal oxidation suggested in their paper. However, the exact value of $z$ is unknown, and hence we have assumed $z = 1$ for ease of calculation.

Equation [11] can be rearranged as

$$C_{\text{coal,t}} = \frac{Q_t}{zFV} - \frac{1}{z} (C_{\text{Fe,o}} - C_{\text{Fe,t}})$$

Substituting Eq. [12] into Eq. [10]

$$C_{\text{coal,t}} = C_{\text{coal,o}} - \frac{Q_t}{zFV} + \frac{1}{z} (C_{\text{Fe,o}} - C_{\text{Fe,t}})$$


$$\frac{dC_{\text{Fe}}}{dt}_{\text{coal,t}} = \frac{k_c}{k_F A} \left[ C_{\text{coal,o}} - \frac{Q_t}{zFV} + \frac{1}{z} (C_{\text{Fe,o}} - C_{\text{Fe,t}}) \right]$$

As $(C_{\text{Fe,o}} - C_{\text{Fe,t}}) = C_{\text{coal,o}} - 1/k_F A (I_t - I_o)$, and substituting it into Eq. [14], leads to Eq. [15]

$$\frac{dC_{\text{Fe}}}{dt}_{\text{coal,t}} = k_c \left[ \frac{Q_t}{zFV} - \frac{1}{zFk_c A} (I_t - I_o) \right]$$

Equating [8] and [15] and rearranging, leads to Eq. [16]

$$\frac{1}{(I_o - I_t)} \left[ \left( \frac{dl}{dt} \right) + \frac{Ak_c}{V} I_t \right] = k_c \left[ \frac{Q_t}{zFV} - \frac{1}{zFk_c A} (I_t - I_o) \right]$$

Equation [16] permits the determination of the rate constant, $k_c$, of the coal oxidation reaction. A plot of $1/(I_o - I_t)$ vs. $[dl/dt] + Ak_c/V I_t$ vs. $[Q_t - VAk_c/I_t] - I_o$ should give straight line plots with a slope of $k_c/zFV$. Equation [16] also allows the calculation of the initial concentration of active coal sites, $C_{\text{coal,o}}$, from the $y$ intercept of the plots.

### Experimental

The experimental methodology is briefly described in this section. A more detailed account has been presented elsewhere (15, 16).

**Electrochemical.—** The electrochemical experiments were carried out utilizing standard three-electrode circuitry, with a PAR 175 universal programmer and a PAR 273 potentiostat interfaced to an Apple IIe microcomputer. The long-time electrolysis data were collected and processed with the use of the PAR 323 corrosion software. A HP 7045B X-Y recorder was used to record all other electrochemical data.

The electrolysis experiments were carried out at 90°C in a three-compartment cell (Fig. 1). A high purity platinum foil (Aldrich Chemical Company, 99.999%, 7 cm$^2$) was used as the working electrode (WE), the anode during electrolysis, while a larger area Pt gauze electrode and a reversible hydrogen electrode (RHE) were used as the counter (CE) and reference (RE) electrodes, respectively. The coal
slurry containing known amounts of added FeSO₄ was stirred at a reproducible rate during each experiment using a large Teflon-coated stir bar driven by a magnetic stirrer. The coal samples were obtained from the department of Coal and Hydrocarbon Processing of the Alberta Research Council, Edmonton, Alberta, Canada. The origin (sample type), geological formation, rank, and particle size of these coal samples are given in Table 1.

In these experiments, Fe³⁺ was generated continuously at the electrode at 1.0V vs. RHE. The I/t data were collected over a period of 24h or more and the charge passed during the duration of the experiment was determined by integrating the area under the I/t plots. The I/t response for each experiment was analyzed by computer to obtain the rate constants from Eq. [16].

The mass-transfer rate constant, kₘ, was estimated from the limiting anodic current (Iₘₐₓ) obtained from the electrolysis of a fresh coal slurry containing a known amount of added FeSO₄. (Eq. [17])

\[ I_{\text{lim}} = nF A k_m C_{R}^* \]  

where \( C_{R}^* \) is the initial bulk concentration of Fe²⁺ in the slurry.

### Results and Discussion

**Long-time electrolysis experiments.—**The electrochemical oxidation of pretreated (15, 16) Alberta coals was typically carried out at a potential of 1.0V vs. RHE in a H₂SO₄ slurry containing known amounts of added FeSO₄. The rate of oxidation of the coal in the slurry could be established from the analysis of the current vs. time (I/t) response. A typical set of I/t data collected from an experiment in which 6g of Vesta (200 mesh) coal was oxidized in 120 ml of 1M H₂SO₄ containing 15 mM of FeSO₄ at 90°C at 1.0V vs. RHE is plotted in Fig. 2 (curve (a)). As seen in the figure, the current decreases fairly rapidly at short times but then decreases more slowly at longer times. This decay of the current with time, as compared to the theoretical response when the coal completely regenerates Fe²⁺ by reaction [1] [Fig. 2, curve (b)] has been reported previously in the literature and has been attributed to the build-up of oxidized organic functionalities at the coal surface with time of electrolysis (1-5, 7-13). It is important to note that in all of our experiments, the current decreases continuously with time, although slowly at long times of oxidation [Fig. 2, curve (a)]. A steady-state I/t response, as suggested by Lalvani (20) and Dhoooge et al. (7, 8), has never been observed.

Various experiments were designed to test the concept of reversibility of reaction [1], as was proposed by Kreysa et al. (11). In one experiment, the electrochemical oxidation of coal was carried out for ca. 24h and then the cell was kept at OCP conditions for ca. 64h. The Fe³⁺ concentration was then measured using voltammetric methods. If any appreciable degree of reversibility had been present, the solution should have contained some Fe³⁺ ion. The absence of Fe³⁺ in the slurry, as shown in Fig. 3 after ca. 64h at open-circuit conditions, clearly demonstrates the negligible rate of the reverse reaction. The addition of Fe³⁺ solu-

### Table I. Origin, rank, and particle sizes of Alberta coals

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Geological formation</th>
<th>ASTM rank</th>
<th>Particle size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mesh</td>
<td>µm</td>
</tr>
<tr>
<td>Luscar-Sterco</td>
<td>Mynheer/Valdor</td>
<td>hvB C</td>
<td>&gt;200 &lt;65</td>
</tr>
<tr>
<td>Luscar-Sterco</td>
<td>Mynheer/Valdor</td>
<td>hvB C</td>
<td>48-64 250-350</td>
</tr>
<tr>
<td>Highvale</td>
<td>Paskapoo</td>
<td>Sb B</td>
<td>&gt;200 &lt;65</td>
</tr>
<tr>
<td>Highvale</td>
<td>Paskapoo</td>
<td>Sb B</td>
<td>48-64 250-350</td>
</tr>
<tr>
<td>Antelope-Bow City</td>
<td>Oldman</td>
<td>Sb B</td>
<td>&gt;200 &lt;65</td>
</tr>
<tr>
<td>Antelope-Bow City</td>
<td>Oldman</td>
<td>Sb B</td>
<td>48-64 250-350</td>
</tr>
<tr>
<td>Vesta (Central Battle River)</td>
<td>Horseshoe/Canyon</td>
<td>Sb C</td>
<td>&gt;200 &lt;65</td>
</tr>
<tr>
<td>Vesta (Central Battle River)</td>
<td>Horseshoe/Canyon</td>
<td>Sb C</td>
<td>48-64 250-350</td>
</tr>
</tbody>
</table>

* Samples collected from Alberta Plains Coal Region.
* Sb = Sub-bituminous. hvB = high volatile bituminous.

---

Fig. 1. Schematic diagram of the electrochemical cell

![Fig. 1. Schematic diagram of the electrochemical cell](image)

**Fig. 2.** I/t response obtained at 90°C and 1.0V in 1M H₂SO₄ with (a) 6g of Vesta coal (200 mesh) + 15 mM FeSO₄; (b) the theoretical response when Fe²⁺ is regenerated at 100% efficiency by another species such as coal.

**Fig. 3.** Schematic voltammograms for the oxidation of 15 mM Fe²⁺ in 1M H₂SO₄ at 90°C in presence of coal: (a) before the start of electrolysis; (b) after 24h of electrolysis at 1.0V vs. RHE (coal oxidation); (c) 64h at open-circuit potential conditions after the electrolysis.
tion to the coal slurry at any stage in the electrochemical oxidation was found to raise the current instantaneously, as shown in Fig. 4, indicating the dependence of the reaction rate on the concentration of Fe$^{3+}$. The rate constants of the Fe$^{3+}$-mediated oxidation of Alberta coals have been determined from the observed I/t response using Eq. [16]. Typical plots of I/(t - I) vs. I for two particle sizes of Highvale coal are shown in Fig. 5. It can be seen that two slopes (i.e., two rate constants, \(k_{c,1}\) and \(k_{c,2}\), respectively) are obtained from this treatment, probably indicating that the mechanism of coal oxidation changes with time of oxidation (15, 16). These rate constants are presented in Table II for two particle sizes for each of the four Alberta coals, along with selected properties of coal. It should be noted that these rate constants were found to be independent of the coal:Fe ratios.

Table II shows the sequence of the electrochemical activity of the coals is parallel to their fixed carbon (FC) content, as demonstrated in Fig. 6. In this figure, the electrochemically measured rate constant is plotted vs. the FC content of the coal. As seen in the figure, a reasonable correlation can be drawn between the rate constant of a coal obtained from mediated electrochemical oxidation and its FC content. However, a detailed study of the activity of coals of a wide range of ranks towards electrochemical oxidation is necessary in order to make a firm conclusion about the correlation.

It should be noted that a considerable degree of deviation from straight-line behavior was observed in all experiments in the short-time range (0-1h) of electrolysis. This may be related to the presence of a wide variety of functional groups on the coal particle surfaces at early times of oxidation. More precise experiments are being carried out in our laboratory to determine the rate constants in the initial stages of coal oxidation. The results of this work will be presented in a future publication.

The concentration of active sites on the initially exposed surfaces of the coal particles can be estimated from the y-intercepts of the plots of the type shown in Fig. 5. The initial concentration of the sites of 6g of Highvale (200 mesh) coal (corresponding to \(k_{c,1}\) and \(k_{c,2}\), estimated from the respective y-intercepts of \(k_{c,1}\) and \(k_{c,2}\), was found to be ca. 0.24M. This concentration, on conversion to charge, yields a maximum obtainable charge, \(Q_c\), predicted by Eq. [16]. Also a substantial activity still remains after 65h of electrolysis. These results indicate that after prolonged electrolysis, the simplistic view of coal oxidation proposed above may need modification. It is likely that as the coal surface becomes more oxidized with time, \(C_{coal}(t)\) begins to increase as sites beneath the surface become accessible to oxidation by Fe$^{3+}$, i.e., the coal surface area increases with time. It is also possible that as the oxidation reaction proceeds, the coal particles crack and new oxidizable sites are exposed to solution, thereby also increasing \(C_{coal}(t)\) with time. Both of these processes would be highly desirable and would make the coal more active to electrochemical oxidation than anticipated, perhaps even resulting in the eventual total oxidation of the coal particles.

**Conclusions**

The various mechanisms and kinetic treatments previously reported in the literature for the electrochemical oxidation of coal mediated by Fe$^{3+}$ have been critically examined and found to be inadequate. A new approach to the analysis of the I/t data and the determination of the relevant kinetic parameters for the electrochemical oxidation of coal has been developed. This method was then used to determine the kinetics of the electrochemical oxidation of four types of Alberta coals. Two rate constants, \(k_{c,1}\) and \(k_{c,2}\),

### Table II. Electrochemical rate constants for the oxidation of Alberta coals by Fe$^{3+}$ (and related data) at 90°C

<table>
<thead>
<tr>
<th>Coal type (origin)</th>
<th>Rate constants $^a$ (1/mol·s) $\times 10^3$</th>
<th>Fixed carbon $^b$ (%)</th>
<th>Volatile matter $^b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal Valley</td>
<td>19.0 (12.0)</td>
<td>61.6</td>
<td>33.4</td>
</tr>
<tr>
<td>Highvale</td>
<td>11.0 (8.0)</td>
<td>58.6</td>
<td>41.4</td>
</tr>
<tr>
<td>Bow City</td>
<td>15.0 (12.0)</td>
<td>59.3</td>
<td>40.7</td>
</tr>
<tr>
<td>Vesta</td>
<td>12.0 (8.0)</td>
<td>60.5</td>
<td>41.2</td>
</tr>
</tbody>
</table>

$^a$ Values without parentheses are for 200 mesh; those in parentheses are for 60 mesh.

$^b$ Dry ash free, measured for the pretreated coal samples.

Fig. 4. I/t response obtained for 6g of Vesta (60 mesh) + 15 mM FeSO$_4$ at 90°C: (a) from regular electrolysis; (b) when the concentration of Fe$^{3+}$ in the slurry was increased at t = 1500 min by the addition of ferric sulfate solution.

Fig. 5. Second-order kinetics plots for the oxidation of 12g of Highvale coal at 1.0 V vs. RHE and 90°C in 1M H$_2$SO$_4$: (a) 200 mesh; (b) 60 mesh.

Fig. 6. Electrochemical coal oxidation rate constant ($k_c$) as a function of fixed carbon content of the coal.
Electrocatalysis of Anodic Oxygen-Transfer Reactions
Ultrathin Films of Lead Oxide on Solid Electrodes

Hsiangpin Chang* and Dennis C. Johnson**

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, Iowa 50011

ABSTRACT

Ultrathin films (ca. <0.5 μm) of lead oxide, concluded to be PbO2, were generated on the surfaces of Au, Pt, Ti, and GC electrodes during rapid voltammetric dissolution of thick films (> ca. 10-100 μm) of β-PbO2 deposited from acidic solutions containing Pb2+. These PbO2 films were stable at potential values > ca. 0.5V negative of the peak potential for cathodic stripping of bulk PbO2. Ultrathin films of PbO2 were produced, in turn, by anodization of the PbO films in Pb2+ solutions. Results are emphasized here for the voltammetric and microscopic characterization of these thin films at Au electrodes. The formation of the stable PbO film during cathodic dissolution of thick PbO2 films is concluded to be the result of a deficiency of H+ in the interfacial region between the substrate and the porous thick oxide films. Ultrathin PbO films were oxidized to ultrathin PbO2 films during a positive potential scan and were determined to be electrocatalytically active for oxidation of dimethylsulfoxide (DMSO) at E > 1.5V vs. SCE when Bi3+ was present in the test solutions.

The electrocatalysis of anodic oxygen transfer reactions at pure and doped PbO2-film electrodes has been the subject of much recent study in our laboratory (1-10). The apparent heterogeneous rate constants for anodic oxidation of numerous inorganic and organic compounds which require the transfer of oxygen from H2O to the oxidation species remained on the surface of a Au electrode after the induction period (1). Research described here was predicated on the basis of a presumed requirement for the surface stabilization of adsorbed hydroxyl radicals (OH•ads) at catalytic sites generated by the various procedures for surface modification. Significant increases in rate constants have been observed at Bi(V)-doped PbO2-film electrodes for oxidation of Mn2+ to MnO2 (-1.5), phenol to benzoquinone (1), and other compounds. The oxidation of CN- to CNO- was observed to be electrocatalyzed at Fe(III)-doped PbO2 (6, 7) and the oxidation of toluene to benzyl alcohol was electrocatalyzed at a Cl- doped PbO2-film electrode in acidic sulfate media (8). The activity of Bi(V)-doped PbO2 electrodes was also obtained for pure PbO2-film electrodes when Bi3+ was added to the test solution (9). Activation of these electrodes has been concluded to occur when Bi3+ is anodically adsorbed as Bi(V) (9, 10). The activity persisted when the electrode was transferred to a Bi3+-free solution, provided the potential was not allowed to shift sufficiently negative to permit cathodic desorption of Bi(V) (i.e., < ca. 1.5V vs. SCE in 0.1M HClO4).

A major concern for the large-scale application of pure or doped PbO2-film electrodes is the possible entry of Pb2+ into the environment as the result of chemical or electrochemical dissolution of the oxide films into the product mixture. This could be especially serious for continuous electrolysis in flowing streams where extremely large volumes of product solution can be involved. Recently, we reported evidence that a small quantity of a Pb2+-containing species remained on the surface of an Au electrode after the anode deposition and subsequent cathodic stripping of Pb2+. Ultrathin PbO2 film electrodes were obtained for pure PbO2-film electrodes with the result of a significant decrease in the induction period (1). Research described here was predi-