Evidence has been obtained in our laboratories\(^1\) that the differential reflectance of polycrystalline Pt, Pt(poly), electrodes in aqueous perchloric acid solutions up to potentials where only a single form of oxide is believed to form can be represented in terms of additive contributions due to the unoxidized or bare, and oxidized sites, expressed for each case in terms of the product of their corresponding potential dependent coverage, \(\theta_i(E)\), where \(i = \text{bare or oxidized}\), and a linear function of the applied potential, \(E\). More recently,\(^2\) this model was applied to the analysis of data collected on quasi perfect Pt(111) microfacets formed by melting and cooling the tip of Pt microwires, and found to account quantitatively for the optical response associated with the adsorption of hydrogen, hydroxyl, and bisulfate in acidic electrolytes.

This brief communication seeks to extend this strategy to the oxidation of Pt(poly) surfaces in 0.1 M HClO\(_4\) over a potential range wide enough to include the higher oxidation state Pt oxide.\(^3\) As will be shown, analyses of the data acquired made it possible to construct plots of the coverage of the unoxidized and the two forms of Pt oxide as a function of \(E\).

### Experimental

All experiments were performed at room temperature (ca. 290 K) in Ar (PP300, 99.998%, Airgas)-purged aqueous 0.1 M HClO\(_4\) (70%, Ultrapure, EMD) solutions in ultrapure water (18.3 Ω cm, EASY-pure UV system, Barnstead). The instrumentation and techniques employed were the same as those specified in detail elsewhere,\(^4,5\) including a low-power red laser (Coherent Inc. Red Eagle 635-10, \(\lambda = 635\) nm, 10 mW) aimed at normal incidence toward the center of the disk of a rotating ring disk electrode, RRDE, assembly, (Area = 0.164 cm\(^2\), Pine Instruments, Model AFE7R8PTPT). Potential control of the RRDE was achieved with a bipotentiostat (AFRDES, Pine Instruments) and data were collected with an acquisition card (NI, USB-6009) connected to a personal computer. After the electrode and cell were properly aligned, a set of cyclic voltammograms was recorded to ensure surface cleanliness. The specific protocol developed for the acquisition of optical data is shown in Panel A, Scheme 1. As indicated therein, a series of potential scans were performed in the positive direction from 0.05 to 1.4 V at a rate \(\nu = 10\) mV/s, followed by scans in the opposite direction at \(\nu = 100\) mV/s. About 15 to 20 acquisitions were required for the optical signal collected during the scans in the positive direction to achieve acceptable signal to noise ratios. Immediately thereafter, a series of linear potential scans were performed at \(\nu = 10\) mV/s between 0.05 V and values in the range 0.8 \(\leq E \leq 1.4\) V in increments of 50 mV followed by scans at \(\nu = 100\) mV/s down to 0.05 V (see Panel B, Scheme 1). Once the sequence was completed, a few additional scans of this type involving selected upper potential values were collected yielding virtually identical results as those obtained during the initial series. All coulometric analyses were based on scans recorded toward negative potentials.

### Theoretical Formalism

The optical method employed in the analysis herein presented assumes that the potential dependent differential reflectance, \(-\Delta R/R\), can be expressed as the sum of individual terms associated with each of the three surface sites involved, i.e. bare, or bearing adsorbed water, and two forms of Pt oxide.\(^3,6-8\) denoted hereafter as Ox1 and Ox2. The corresponding coverages of these species, i.e. \(\theta_{\text{bare}}, \theta_{\text{ox1}}\) and \(\theta_{\text{ox2}}\), are obtained by solving the following system of equations:

\[
\theta_{\text{bare}} + \theta_{\text{ox1}} + \theta_{\text{ox2}} = 1 \tag{1}
\]

\[
\theta_{\text{ox1}} + 2\theta_{\text{ox2}} = Q_0/Q_H \tag{2}
\]

\[
-\Delta R/R = A(E) \times \theta_{\text{bare}} + B(E) \times \theta_{\text{ox1}} + C(E) \times \theta_{\text{ox2}} \tag{3}
\]

The first of these equations accounts for the fact that the sites on the surface are either unoxidized, or bare, or are oxidized forming at low potentials, Ox1, which then transforms into a higher oxidized species, Ox2, as the potential is driven toward more positive values. As has been proposed in the literature,\(^3,6-8\) the formation of Ox2 involves the transfer of twice the number of electrons as compared to that required to produce Ox1. The latter is made explicit in Eq. 2, where \(Q_0\) is the charge associated with Pt oxidation and \(Q_H\) that determined from hydrogen adsorption assuming one electron per surface site, which provides a measure of the total number of Pt sites exposed to the electrolyte. Lastly, Eq. 3 relates the normalized differential reflectance, \(-\Delta R/R = -(R(E_{\text{ox2}})-R(E_{\text{ox1}}))/R(E_{\text{refl}})\), where \(R(E_{\text{refl}})\) and \(R(E_{\text{ox2}})\) are proportional to the intensity of the light reflected off the electrode surface recorded at a reference potential, \(E_{\text{refl}}\), set at 0.05 V in this case, and at any arbitrary sampling potential, \(E_{\text{sam}}\), to the sum of contributions associated with each type of site, i.e. represented by the product of \(\theta_i(E)\) and an empirical linear function unique to each type of site that accounts for changes in the optical signal induced by the applied potential, i.e., \(A(E), B(E)\) and \(C(E)\).

ECS Electrochemistry Letters, 4 (9) H46-H49 (2015)
Scheme 1. Potential-time protocol involved in the acquisition of optical (Panel A) and electrochemical data (Panel B). The blue and black segments represent linear potential scans at rates of $\nu = 10$ mV/s, and $\nu = 100$ mV/s, respectively. The analysis of the optical data was performed by averaging over the response of slow scans. Only a few full scans are shown as examples.

Results and Discussion

Shown in Fig. 1 (see solid circles, left ordinate) is a plot of $-\Delta R/R$ vs potential, $E$, for Pt(poly) in 0.1 M HClO$_4$ recorded at a scan rate $\nu = 10$ mV/s over the range $0.05 \leq E \leq 1.4$ V averaged over 18 scans (See Experimental section). Also displayed in this figure (blue line, right ordinate) is a single linear scan voltammogram acquired simultaneously.

Correlations between the charge associated with the formation of the oxides, $Q_O$, and $E$ were obtained from coulometric analyses of the voltammetric scans recorded toward negative potentials, as reported by Novak and Conway,$^{11}$ at a scan rate $\nu = 100$ mV/s. A series of such curves are displayed in Fig. 2, where the dashed blue line was used as the background for the current integration. Data acquired in two completely independent experiments involving the same Pt electrode are displayed in the form of $Q_O/Q_H$ vs $E$ in Fig. 3 (see solid and empty circles).

The potential dependent functions associated with each of the sites were determined following the same type of analysis as that described in a previous communication.$^{2}$ Specifically, $A(E)$ (bare sites) was obtained from a linear fit to the $\Delta R/R$ data in the double layer region,

Fig. 1. Plot of $-\Delta R/R$ vs $E$ for the Pt disk of a Pt/Pt RRDE in quiescent, Ar-purged 0.1 M HClO$_4$ solution recorded while the potential was being scanned toward positive values at a scan rate, $\nu = 10$ mV/s (blue curve, right ordinate). The open circles represent data obtained in an identical independent experiment. See text for details.

Fig. 2. Linear scan voltammogram for the Pt disk of the Pt/Pt RRDE in 0.1 M HClO$_4$ solution recorded at $\nu = 100$ mV/s. The blue dotted line was used as the background for the coulometric analysis.

Fig. 3. Plots of $Q_O/Q_H$ vs $E$ based on the data in Fig. 2 (scattered circles). The open and solid circles represent two independent set of measurements.
i.e. $0.5 \leq E \leq 0.7$ V, and then used to calculate $B(E)$ from Eq. 3, by assuming $\text{Ox2}$ in the range $0.5 \leq E < 1.0$ V, is negligible, i.e.

$$B(E) = \frac{-\Delta R/R_{\text{bare}}^0 - A(E) \times \theta_{\text{bare}}}{\theta_{\text{Ox1}}}$$

[4]

In this equation $\Delta R/R_{\text{bare}}^0$ represents the optical data in that potential domain, $\theta_{\text{Ox1}} = Q_{\text{Ox1}}/Q_{\text{H}}$ is the coverage of $\text{Ox1}$ derived from the coulometric analysis using linear interpolation (see solid lines in Fig. 3) for values other than those obtained experimentally (scattered symbols in that same figure) and $\theta_{\text{bare}} = 1 - \theta_{\text{Ox1}}$. Lastly, an analogous strategy was employed to find $C(E)$ over the potential range $1.35 \leq E \leq 1.4$ V, where $\theta_{\text{bare}}$ in Eq. 3 can be assumed to be negligibly small,

$$C(E) = \frac{-\Delta R/R_{\text{bare}}^0 - B(E) \times \theta_{\text{Ox2}}}{\theta_{\text{Ox1}}}$$

[5]

where $\theta_{\text{Ox1}}$ and $\theta_{\text{Ox2}}$ can be obtained from Eqs. 1 and 2 above using the experimental coulometric data.

Explicit expressions for the best linear fits for $A(E)$, $B(E)$ and $C(E)$ functions are given in the left column in Table I which are then used to generate values of the coverages as a function of potential by rearranging Eqs. 1–3, namely

$$\theta_{\text{Ox1}} = \frac{-\Delta R/R_{\text{bare}}^0 + A(E) \times (Q_{\text{Ox1}}/Q_{\text{H}}) - 1 - B(E) \times Q_{\text{Ox1}}/Q_{\text{H}}}{A(E) - 2B(E) + C(E)}$$

[6]

$$\theta_{\text{Ox2}} = 1 - \theta_{\text{bare}} - \theta_{\text{Ox1}}$$

[7]

$$\theta_{\text{bare}} = \theta_{\text{Ox2}} - Q_{\text{Ox1}}/Q_{\text{H}} + 1$$

[8]

where, $-\Delta R/R_{\text{bare}}^0$ represents the optical data over the entire potential range of interest. The resulting $\theta_{\text{bare}}(E)$ and $\theta_{\text{Ox1}}(E)$ were then fitted with analytic functions (not shown here), which together with $\theta_{\text{Ox1}}(E) = 1 - \theta_{\text{bare}}(E) - \theta_{\text{Ox2}}(E)$ were used in Eq. 3 to generate new linear empirical functions (see right column in Table I). The solid lines in Fig. 4 represent the best fits to the experimental $-\Delta R/R$ vs $E$ data based on these analytical functions. The new set of empirical linear functions were then introduced in Eqs. 6–8 to yield a new set of $\theta_{\text{bare}}$ (black), $\theta_{\text{Ox1}}$ (red) and $\theta_{\text{Ox2}}$ (blue), shown as scattered solid points in Fig. 5. A subsequent refinement (not presented here) produced very similar results and the overall iterative process was not pursued further. Also displayed in this figure in open circles are the results of a completely independent experiment performed with the same electrode after polishing, which yielded virtually identical outcomes.

The dependence of the coverage of $\text{Ox1}$ on the applied potential over the potential range negative to the onset of $\text{Ox2}$ formation, $E < \text{ca. 1.1 V vs RHE}$, is in agreement with that reported earlier by Shi et al. using optical means. Similar results were more recently published by Wakisaka et al. based on the analysis of the $\text{O1s}$ X-ray photoelectron spectroscopy (XPS) spectra of electrodes emersed under potential control without exposure to the ambient atmosphere. Although the Pt 4f$_{5/2}$ XPS spectrum in their work was consistent with the presence of $\text{PiO}$ for $E > 1.1$ V, no quantitative analysis of its dependence on potential was pursued.

In conclusion, the primitive optical model introduced in earlier publications can account quantitatively for the potential dependence of the two forms of oxide on Pt(poly) electrodes in perchloric acid solutions. Efforts are underway to explore whether this model is sufficiently general to be applicable to other metal electrodes, such as Au, including single crystal surfaces, the results of which will be reported in due course.
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