

Platinum-Based Electrocatalysts for Generation of Hydrogen Peroxide in Aqueous Acidic Electrolytes

Rotating Ring-Disk Studies

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The electrocatalytic activity of selenium-, and sulfur-modified polycrystalline Pt electrodes for O_2 reduction in acid media has been examined using rotating ring-disk electrode techniques. The results obtained indicated that, within a rather narrow range of coverages, both Se-, and S-modified Pt surfaces promote O_2 reduction via a two-electron pathway to yield hydrogen peroxide at close to 100% faradaic efficiency over a wide potential region. Also presented in this work is an experimental procedure for Se-modification of high area, unsupported Pt particles based on fluidized packed bed reactor principles. Such a strategy could be readily scaled up opening new prospects for the development of large scale hydrogen peroxide generation in acid media, including electrochemically based, room temperature, Nafion-based oxygen concentrators. (© 2002 The Electrochemical Society. [DOI: 10.1149/1.1525270] All rights reserved.

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The reduction of dioxygen in aqueous electrolytes, including Nafion,1-5 has received extraordinary attention over the past few decades.^{6,7} Much of the research impetus has been driven by the need to improve the performance of gas permeable cathodes for fuel cell applications, including stationary energy generation,⁸ vehicular propulsion,9 and, more recently, portable electronics.10,11 Not surprisingly, most of the emphasis, from a fundamental viewpoint, has focused on the search for electrocatalysts displaying both high activity and selectivity for the four-electron reduction of O₂ to yield water as the product. Yet another electrochemical process that involves O₂ as a reactant is the electrosynthesis of hydrogen peroxide,12-16 an environmentally benign chemical currently being considered for use in diverse technological areas, ranging from the industrial bleaching of paper^{17,18} and wastewater treatment,¹⁹ to oxidation of hazardous chemicals and bioremediation.¹⁷ Although certain types of carbon are effective electrocatalysts for the 2e⁻ reduction of O2 in alkaline media, in terms of potency and high selectivity,⁶ materials displaying equally desirable properties in acid electrolytes are quite rare. Notable exceptions are provided by certain transition metal macrocycles of the phthalocyanine²⁰ and porphyrin types²¹⁻²⁴ and by a few simpler inorganic and organic species, either in solution phase or immobilized on the surface of otherwise inert electrodes by spontaneous adsorption, chemical derivatization, and other means. Unfortunately, many of these molecular electrocatalysts also promote decomposition of hydrogen peroxide²⁵ generating radicals that attack their often delicate structures rendering products devoid of significant activity. Direct generation of H2O2 in acid media is particularly advantageous, as it would meet pH conditions required for Fenton's reagent applications^{26,27} both in chemical synthesis and chemical degradation without further processing. In addition, it could impact markedly the development of lightweight, Nafion-based, roomtemperature electrochemical oxygen concentrators for medical and other applications.²⁸

The approach currently under investigation in our laboratories relies on the use of elemental surface modifiers capable of blocking active sites on Pt responsible for the four-electron reduction of O_2 , while opening pathways for H_2O_2 generation. Based on an initial screening of a large number of atomic species, particularly those capable of undergoing underpotential deposition, sulfur and selenium were selected as the most promising candidates.

This work exploits the well-known virtues of the rotating ring-

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disk electrode (RRDE) technique²⁹ to assess the activity (A) and selectivity (S) of Se- and S-modified polycrystalline Pt surfaces for O₂ reduction to H₂O₂ as a function of coverage and applied potential. The methodologies involved in the preparation and electrochemical characterization of modified Pt electrodes were largely based on the reports of Wieckowski *et al.*^{30,31} for S and Feliu *et al.*³² for Se, and those of Stickney *et al.*³³⁻³⁵ for S- and Se-modified single-crystal Au surfaces. As is shown, faradaic efficiencies for H₂O₂ generation (\hat{f}) approaching 100% can be achieved within a rather narrow range of Se and S coverages.

Experimental

All measurements were performed with a Pt (disk)/Pt (ring) rotating ring-disk electrode (RRDE, Pine Instruments, disk area $= 0.164 \text{ cm}^2$, inner and outer ring diameters, 4.93 and 5.38 mm, respectively, *i.e.*, theoretical collection efficiency N = 0.22), in 0.50 M H₂SO₄ for Se-, or 0.10 M H₃PO₄ (J.T. Baker Ultrex, diluted with ultrapure water, Barnstead) for S-modified Pt surfaces, respectively, at room temperature, using a conventional three-compartment electrochemical cell. Solutions were purged with O₂ for at least 1 h before RRDE data acquisition, and continuously thereafter. A reversible hydrogen electrode (RHE) in the same solution was used as reference, and a platinized Pt foil (see below) as counter electrodes. Prior to dynamic polarization RRDE measurements in O2-saturated solutions, the Pt ring was platinized to prevent rapid contamination with adventitious impurities in the solution. This procedure was performed by cycling the Pt ring in a 2-3% H₂PtCl₆ aqueous solution at 50 mV/s between -0.1 and +1.1 V vs. SCE and then holding at -0.10 V for 3 min. The electrode was then removed from this solution and rinsed thoroughly with ultrapure water before further use. Increases in the actual area of the Pt ring of up to an order of magnitude could be achieved by this methodology.

Selenium-modified Pt surfaces were prepared by electrochemical deposition from 1.0 mM SeO₂ in 20 mM H₂SO₄ solutions (J.T. Baker, Ultrex) in a separate three-compartment cell to avoid cross contamination.³⁴ Sulfur-modified Pt surfaces were obtained by placing a small volume of an aqueous Na₂S solution in the concentration range of 0.27-1.0 mM on the Pt disk for a specified period of time followed by thorough rinsing with pure water.³¹ Such electrodes were then immersed in O₂-free 0.10 M H₃PO₄ or 0.50 M H₂SO₄ and the platinized-Pt ring was subsequently cycled at 50 mV/s in the range 0.03-1.49 V *vs*. RHE to oxidize any remaining sulfur or selenium on the surface. Once the ring voltammogram showed features characteristic of clean Pt, the solution was saturated with O₂, and dynamic polarization measurements were then initiated.

The degree of selectivity of Se-, and S-modified Pt surfaces for the $2e^-$ reduction of O_2 to H_2O_2 as a function of coverage and

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Figure 1. Cyclic voltammogram for a Pt disk of a Pt/Pt RRDE in a 1.0 mM SeO_2 in 20 mM H_2SO_4 quiescent solution in the range 0.34 -1.4 V vs. SHE (thin line) at a scan rate v = 5 mV/s. The voltammogram in thick lines was obtained by first scanning in the negative direction from 1.4 down to 0.54 V and then up to 0.74 V vs. SHE under otherwise identical conditions. At this point the scan was interrupted for *ca.* 3 min and then resumed up to +1.4 V vs. SHE.

potential, was determined from the analysis of disk (i_{disk}) and ring (i_{ring}) currents measured with the Pt/Pt RRDE assembly. For all these experiments, the platinized Pt ring was polarized at 1.4 V *vs*. RHE, *i.e.*, positive enough for the oxidation of H₂O₂ generated at the disk to proceed under diffusion-limited conditions.³⁶

Results and Discussion

Se-modified Pt electrodes.-Cyclic voltammetry curves recorded at a scan rate v = 5 mV/s in 1.0 mM SeO₂ in 20 mM H₂SO₄ solutions over the range of 0.34-1.4 V vs. SHE (see thin line, Fig. 1) displayed two sets of peaks, labeled as A, A' (centered at 0.64 and 1.11 V, respectively) and C, C' (centered at 0.44 and 0.83 V, respectively) similar in shape to those reported by Stickney and coworkers for Se deposition on the three low index faces of single-crystal Au.^{33,34} A stripping peak at potentials slightly more negative than C' (denoted as B' by Lister *et al.*) has also been observed for Se on Au, although in this case (see feature centered at 1.07 V), it may have contributions due to Pt oxide formation. Similar experiments in which the scan in the negative direction was reversed at 0.54 V vs. SHE, stopped at 0.74 V vs. SHE (see arrow), and then resumed after ca. 3 min up to 1.4 V, yielded only peak A without any contributions due to B' (see thick solid lines). In an analogy with the assignments of Lister et al.,³⁴ peaks A and A' are ascribed to the surface-limited underpotential deposition (UPD) and stripping of Se, which in this case has also contributions due to Pt oxidation and reduction (see below), whereas C and C' are attributed to the formation and stripping of a second, distinct adsorbed Se phase. Correlations between the shapes and magnitudes of A' and C' were obtained from a series of experiments in which the Pt electrode was scanned at v = 20 mV/s from 1.45 V down to the desired potential, $E_{\rm dep}$, in the region 0.34-0.54 V, held at that value for a certain period of time, τ , in the range 2.5-3.5 min, and then scanned at the same rate up to 1.45 V to oxidize adsorbed Se (see Fig. 2). Cursory inspection of these curves reveals that in the region $E_{dep} < 0.54$ V, and for τ in the range specified, the area under C' increases as the value of E_{dep} becomes more negative, and its peak potential shifts toward more positive values.

Further insight into some of the properties of Se deposits was obtained from measurements in which the potential of the Pt disk



Figure 2. A series of linear potential scans for deposition and stripping of Se on the Pt disk of a Pt/Pt RRDE electrode in a 1.0 mM SeO₂ in 20 mM H₂SO₄ quiescent solution (v = 20 mV/s). The scans in the negative direction were interrupted at various potentials $E_{dep} vs$. SHE in the range 0.34-0.54 V vs. SHE and, after a holding period τ of 2.5 or 3.5 min, resumed in the positive direction. Thin solid line: $E_{dep} = 0.54$ V, $\tau = 3$ min; thick solid line: $E_{dep} = 0.49$ V, $\tau = 3.5$ min; dotted line: $E_{dep} = 0.44$ V, $\tau = 3$ min; dashed line: $E_{dep} = 0.39$ V, $\tau = 3$ min; dot-dash line: $E_{dep} = 0.34$ V, $\tau = 2.5$ min.

was first scanned in 1.0 mM SeO₂ in 20 mM H₂SO₄ solutions in the negative direction at v = 20 mV/s, subsequently reversed at 0.54 V, and finally stopped and held at $E_{dep} = 0.73$ V vs. SHE for ca. 3 min. The electrode was removed from the solution under potential control, washed thoroughly with ultrapure water, and then reimmersed in a deaerated, Se-free 0.50 M H₂SO₄ solution in a different cell without potential control. No evidence for hydrogen adsorption was found for such Se-modified electrodes cycled between 0.08 and 0.73 V (see curve a, in panel A, Fig. 3) consistent with the blocking of active sites on the Pt surface. Moreover, a subsequent scan in the positive direction up to 1.43 V (see dotted line in panel A, Fig. 3) yielded a well-defined peak A' over virtually the same region where Pt oxidation occurs on the bare metal in Se-free 0.50 M H₂SO₄, *i.e.*, 0.9-1.4 V (see thin solid line in Fig. 3), in agreement with the results shown in Fig. 1.

The coverage of Se, θ_{Se} , was determined by subtracting the charge obtained by integrating the stripping curve up to 1.45 V (see dotted lines, Fig. 3) from +0.73 to 1.45 V and 1.45 to 1.35 V during the reverse scan, from the voltammetric curve for the same Pt electrode over the same potential range in a solution devoid of Se, *i.e.*, ca. 0.144 mC for the Pt electrode used for these experiments (see thin solid line, Fig. 3). The oxide corrected Se-stripping charge in this case yielded a value of 0.161 mC. If it is assumed that UPD Se is present as a zero valent species and its oxidation up to 1.45 V vs. SHE is not kinetically hindered, standard redox potentials would predict for the oxidation of the UPD layer (in the potential range in question) to proceed via a 6e⁻ process. On this basis, the extra charge under the linear scan (dotted lines) in Fig. 3 would be consistent with the stripping of *ca.* 1.7×10^{14} atoms. The actual area of Pt estimated from the charge associated with hydrogen adsorption/ desorption in Se-free solutions (see thin solid line, panel A, Fig. 3), *i.e.*, 220 μ C/cm², is about 0.230 cm² (roughness factor *ca.* 1.4); hence, the number of Se atoms per Pt atom on the surface would correspond to a Se coverage, θ_{Se} , of about one-half a monolayer. This value is in excellent agreement with that reported by Huang et al.33 for Se on Au(100) for experiments in which the scan was



Figure 3. Panel A, cyclic voltammograms of a bare Pt disk of a Pt/Pt RRDE in the range 0.03-1.43 V vs. SHE (thin solid line) and of the same electrode modified by preadsorbed Se (see text for details) in the range 0.08-0.73 V vs. SHE (curve a, thick solid line) in 0.50 M H₂SO₄, v = 20 mV/s. Also shown in this panel is a linear scan in the range 0.73 to 1.43 V for a Semodified Pt disk surface recorded immediately after holding at 0.73 V under otherwise identical conditions (see dotted line). Panel B, stripping curves for the Se-modified Pt disk in panel A as a function of E_{dep} ($\tau = 3$ min, see inset in this panel) under otherwise identical conditions as those specified in panel A. Panel C, plot of selenium coverage, θ_{Se} vs. E_{dep} .

reversed between peaks A and C, for which the onset of Au oxide formation occurs at more positive potentials compared to Pt.

A series of experiments involving this same basic protocol were then performed to determine θ_{se} as a function of E_{dep} in the potential region about peak A. Once immersed into the Se-free solution, the Se-modified electrode was scanned in the negative direction to assess blockage of hydrogen adsorption, and then scanned in the positive direction up to 1.45 V. The results obtained for various E_{dep} values (see insert, panel B, Fig. 3), including a plot of $\theta_{se} vs. E_{dep}$, based on coulometric analyses of these data are shown in panels B and C, in Fig. 3, respectively. In earlier studies,³² problems were encountered for determining θ_{Se} on Pt(110) and Pt(100), the two low index surfaces which would more closely resemble Pt(poly), because the potentials required for full electro-oxidative desorption of Se are too high to avoid compromising the single-crystalline character of their surfaces. This behavior is unlike that observed by the same authors for Se on Pt(111), which displays a sharply defined surface bound, 4e⁻ redox process, thereby allowing reliable coulometric determination of θ_{Se} .

Efforts were also made in our studies to establish whether θ_{se} measured in Se-containing solutions, under otherwise identical conditions, differed from the values determined by the method described above for E_{dep} values in the region in which the activity and



Figure 4. Plots of i_{disk} (upper panel), i_{ring} (middle panel), and $|i_{ring}/i_{disk}|$ (lower panel) *vs*. E_{disk} for a bare (curves a) and Se-modified Pt disk of a Pt/Pt RRDE electrode (curves b-f) in O₂-saturated 0.50 M H₂SO₄ at ω = 400 rpm for θ_{Se} = 0.15 (curves b), 0.25 (curves c), 0.34 (curves d), 0.51 (curves e), 1.24 (curves f). (See inset Fig. 3 and also text for details).

selectivity of the Se-modified surfaces were found to be optimum (*ca.* $1/2 = \theta_{Se}$, see below). As evidenced by the data collected (not shown), the differences in θ_{Se} observed in independent experiments were about 3% and thus regarded as negligible. This is an important observation as it indicates that the emersion/washing/immersion procedure, at least for the most active Se-modified surfaces, does not lead to changes in θ_{Se} , providing a useful strategy for preparing Se-modified Pt in high area form, as would be required for technical applications. It is also essential to note that the onset of O₂ reduction occurs at potentials negative to the onset of Se-stripping (see below), allowing the electrocatalytic properties of such surfaces for this reaction to be examined as a function of θ_{Se} in the absence of Se in solution.

Rotating disk-ring electrode dynamic polarization curves for O_2 reduction.—Correlations between θ_{Se} and electrocatalytic activity for O_2 reduction were obtained using five E_{dep} values (see inset, Fig. 3) at a single rotation rate, $\omega = 400$ rpm. In each case, E_{dep} was set by scanning the electrode in a 1.0 mM SeO₂ in 20 mM H₂SO₄ in a separate cell to potentials in the negative direction at 20 mV/s to the desired value and holding for 3 min. Immediately thereafter, the Se-modified Pt electrode was removed from the solution under potential control, rinsed thoroughly with pure water, and immersed in the O₂-saturated (more than 30 min purging) Se-free 0.50 M H₂SO₄ without potential control.

Plots of $i_{\rm disk}$, $i_{\rm ring}$, and $|i_{\rm ring}/i_{\rm disk}|$ vs. $E_{\rm disk}$ for five different values of $E_{\rm dep}$ (or equivalently $\theta_{\rm Se}$), and $\tau = 3$ min (see curves b-f, Fig. 4 and inset in Fig. 3), including those obtained with bare Pt (curve a), are shown in Fig. 4. For $\theta_{\rm Se} = 1.25$, for which the stripping curve shows a quite prominent peak B', the electrode displayed virtually no activity, *i.e.*, $i_{\rm disk} = i_{\rm ring} = 0$. This behavior was unlike



Figure 5. Plots of i_{lim} (solid circles, left ordinate) and $2i_{\text{ring}}/N$ (open circles, right ordinate) vs. θ_{Se} based on the data shown in Fig. 4 at ω = 400 rpm (see caption for details). The collection efficiency based on the geometry of the RRDE assembly is 0.22.

that found in the range $0.15 < \theta_{se} < 0.50$, *i.e.*, $0.54 \le E_{dep} \le 0.69$, for which the limiting currents for O₂-reduction, i_{lim} , measured at 0.18 V vs. SHE (see left ordinate, Fig. 5), as well as the amount of H₂O₂ generated at the disk, as judged by the magnitude of i_{ring} (see right ordinate, Fig. 5), were quite significant. In fact, for $\theta_{se} = 1/2$ ($E_{dep} = 0.54$ V), $|i_{ring}/i_{disk}|$ ca. 0.21 and $i_{lim}(\theta_{se} = 0) = 2i_{lim}(\theta_{se} = 0.5)$, which are consistent with the quantitative reduction of O₂ to yield H₂O₂ as the only product (note that for bare Pt, i_{ring} is negligible). Prompted by its unique performance, the overall electrocatalytic characteristics of ($\theta_{se} = 0.5$)Pt surfaces were examined in more detail.

Plots of i_{disk} (upper panel), i_{ring} (middle panel), and $|i_{\text{ring}}/i_{\text{disk}}|$ (lower panel) *vs*. E_{disk} for Pt/($\theta_{\text{Se}} = 0.5$)Pt RRDE in O₂-saturated 0.50 M H₂SO₄ at $\omega = 400$ (curve a), 900 (b), 1600 (c), and 2500 rpm (d) are shown in Fig. 6. As indicated, $|i_{\text{ring}}/i_{\text{disk}}|$ for 0.07 $< E_{\text{disk}}$

< 0.6 V, is *ca.* 0.21 for all ω , affording strong evidence that O₂ reduction over this voltage range proceeds predominantly via a 2e⁻ pathway to yield H₂O₂. Additional support for this view was obtained from the linear character of the Levich plot, $i_{\rm lim} vs. \omega^{1/2}$, for which the slope was -0.167 mA cm⁻² s^{1/2}, *i.e.*, about half that obtained for O₂ reduction on bare (Se-free) Pt, (a 4e⁻-process) for which the experimental slope was -0.356 mA cm⁻² s^{1/2} (see Fig. 7).

S-modified Pt electrodes.-Shown in Fig. 8 are dynamic polarization curves obtained in O₂-saturated 0.10 M purified H₃PO₄ solutions at a scan rate of 10 mV/s and $\omega = 900$ rpm for a Pt disk (of a Pt-Pt RRDE), which had been previously exposed to a solution 0.27 mM Na₂S for 3 min (curve a) and for 20 s (curve c). Curve b in that figure was recorded under the same conditions for an electrode prepared by the same procedure using, instead, a 1.0 mM Na₂S solution for 20 s. Corresponding i_{disk} and i_{ring} data recorded with a S-free Pt-Pt RRDE at the same rotation rate (not shown in this figure) yielded, as before, large i_{disk} with i_{ring} about two orders of magnitude lower. These data indicate that the O₂-reduction activity is rather low for large sulfide exposure (curve a); as the exposure is reduced however, both i_{disk} and i_{ring} increase (curve c), signaling significant H2O2 generation at the disk. In fact, increasing the concentration of sulfide, while keeping the time of exposure constant (20 s), decreased i_{disk} , but increased i_{ring} (curve b), *i.e.*, the selectivity (S) of the S-modified Pt electrode was greatly enhanced.



Figure 6. Plots of i_{disk} (upper panel), i_{ring} (middle panel), and $|i_{ring}/i_{disk}|$ (lower panel) *vs*. E_{disk} for a Pt ($\theta_{Se} = 0.5$)/Pt RRDE electrode in O₂-saturated 0.50 M H₂SO₄ at $\omega = 400$ (curve a), 900 (curve b), 1600 (curve c), and 2500 (curve d) rpm. $E_{ring} = 1.38$ V *vs*. SHE.

This phenomenon was explored in more detail by performing measurements in which sulfur was gradually removed from a S-modified Pt disk (19 μ L of 1.0 mM Na₂S solution for 5.5 min) by scanning the potential in stages to potentials sufficiently positive for sulfur to undergo partial oxidation to solution phase sulfate at v = 10 mV/s. Prior to sulfide exposure, the Pt disk was cleaned by electrochemical cycling in O₂-free 0.10 M H₃PO₄. Following S adsorption, the platinized Pt ring was cycled in O₂-free 0.10 M



Figure 7. Plots of $i_{\rm lim}$ vs. $\omega^{1/2}$ for a bare Pt disk (curve a) and a Pt ($\theta_{\rm Se} = 0.5$) disk (curve b) of a Pt/Pt RRDE in 0.50 M H₂SO₄ solutions (see text for other conditions).



Figure 8. Dynamic polarization curves for O₂ reduction in O₂-saturated purified 0.10 M H₃PO₄ solutions for a S-modified Pt disk electrode of a Pt/Pt RRDE prepared by exposure to an aqueous solution 0.27 mM Na₂S for 3 min (curve a) for 20 s (curve c) followed by rinsing with ultrapure water. Curve b was obtained via the same procedure, except that the Pt disk electrode was placed in contact with a 1.0 mM Na₂S solution for 20 s ($\omega = 900$ rpm, $\upsilon = 10$ mV/s, $E_{ring} = 1.3$ V vs. SHE).

 H_3PO_4 at 50 mV/s in the range -0.07 to 1.4 V vs. SHE to oxidize any sulfur that may have adsorbed on the surface. Once the ring voltammogram showed features characteristic of clean Pt, the solution was saturated with O2. After collecting RRDE data for the freshly prepared S-modified Pt disk surface at $\omega = 900$, the electrode was cycled in the same solution once in the range R= 0.10-0.70 V at 10 mV/s, and a new set of polarization curves recorded under otherwise identical conditions. This procedure was followed for a total of 18 cycles with R = 0.10-0.70 (cycles 2-4); R = 0.10-0.90 (cycles 5-8); R = 0.10-1.00 (cycles 9 and 10), and R = 0.10-1.10 V (cycles 11-18). Shown in Fig. 9 are plots of i_{disk} , $i_{\rm ring}$, and $|i_{\rm ring}/i_{\rm disk}|$ vs. $E_{\rm disk}$ for the first, seventh, and 18th cycles. Data of this type collected for the entire series of cycles was then used to create plots of i_{lim} ($E_{\text{disk}} = +0.10 \text{ V}$), i_{ring} ($E_{\text{ring}} = 1.3 \text{ V}$), and $|i_{\rm ring}/i_{\rm disk}|$ vs. number of cycles, a parameter that correlates at least qualitatively with a monotonic decrease in sulfur coverage, θ_{s} . This does not represent a serious limitation, as the conclusions made from the analysis of the data do not rely on a quantitative knowledge of θ_{s} . As shown in Fig. 10, the overall activity of Pt is low for large $\theta_{\rm S}$, increases to reach a plateau up to about cycle 10 and finally increases even further as the sulfur is oxidatively removed from the surface. The amount of H₂O₂ produced, on the other hand, is small for high θ_{s} , reaches two plateaus, and finally decreases after the 14th cycle. Particularly interesting, however, is the fact that, despite variations in i_{disk} and i_{ring} , $|i_{\text{ring}}/i_{\text{disk}}|$ (see, lower panel, Fig. 10) is very high, ca. 0.25, and independent of θ_{s} up to cycle ten, decreasing monotonically thereafter. It becomes evident from these data,



Figure 9. Plots of $i_{\rm disk}$, $i_{\rm ring}$, and $|i_{\rm ring}/i_{\rm disk}|$ vs. $E_{\rm disk}$ for the first, 7th, and 18th oxidative cycles for a S-modified Pt disk surface of a Pt/Pt RRDE prepared by placing 19 μ L of a 1.0 mM Na₂S solution for 51/2 min followed by rinsing with ultrapure water ($\omega = 900$ rpm). $\upsilon = 10$ mV/s. The dotted line in the right panel was collected during the scan in the negative direction.

that despite the changes in the activity (\mathcal{A}) of S-modified Pt due to changes in θ_S , the surface, within a certain range of θ_S , displays very high selectivity (\mathcal{S}) toward H₂O₂ generation. Also noteworthy is the fact that cycle ten coincides with the onsets for the increase in both i_{disk} and i_{ring} and an overall decrease in $|i_{ring}/i_{disk}|$. Based on these results, four electrocatalytic regions (I-IV in Fig. 10), can be



Figure 10. Plots of i_{lim} ($E_{\text{disk}} = +0.10 \text{ V } vs$. SHE), i_{ring} , and $|i_{\text{ring}}/i_{\text{disk}}|$ data extracted from the complete series of 18 oxidation cycles for a S-modified Pt disk electrode (see caption Fig. 9 for details).



Figure 11. Plots of $i_{\rm disk}$, $i_{\rm ring}$, and $|i_{\rm ring}/i_{\rm disk}| vs$. time recorded for a Se-modified Pt disk electrode of a Pt (platinized)/Pt RRDE polarized at $E_{\rm disk} = 0.13$ V and $E_{\rm ring} = 1.38$ V vs. SHE in O₂-saturated 0.50 M H₂SO₄ at $\omega = 200$ (curve a), 400 (curve b), and 900 rpm (curve c).

defined as region I (cycles 1-3), where \mathcal{A} for peroxide generation increases steadily to reach in region II (cycles 4-8) a maximum both in \mathcal{A} and \mathcal{S} . Based on the rather large and constant $|i_{ring}/i_{disk}|$, the faradaic efficiency for this process in both these regions appears close to 100%. As the cycling is continued, *i.e.*, region III (cycles 11-14), the amount of H₂O₂ produced increases but at lower faradaic efficiency f and finally region IV represents a gradual activation of the Pt surface for 4e⁻ reduction, *i.e.*, lower \mathcal{S} for H₂O₂ generation.

Transient experiments .-- Insight into the stability of Se- and S-modified Pt as electrocatalytic surfaces for the reduction of O2 was obtained from measurements in which i_{disk} and i_{ring} for the Pt/Pt RRDE were monitored as a function of time in O2-saturated acid electrolytes at various rotation rates. Plots of i_{lim} ($E_{\text{disk}} = 0.13 \text{ V}$), $i_{\rm ring}~(E_{\rm ring} = 1.38 \text{ V})$ and $|i_{\rm ring}/i_{\rm disk}|$ as a function of time for Semodified Pt ($\theta_{Se} = 0.5$) in 0.50 M H₂SO₄ solutions recorded at $\omega = 200$ (curve a), 400 (curve b), and 900 rpm (curve c) are shown in Fig. 11. These curves are characterized by an initial period in which both \mathcal{A} and \mathcal{S} for the Se-modified Pt disk electrode are high, followed by a region in which \mathcal{A} decreases, but \mathcal{S} remains virtually unaffected. At longer times, both i_{disk} and i_{ring}/i_{disk} fell to very low values signaling significant deactivation. In the case of $\omega = 400$ rpm (curve b) polarization of the disk and ring was discontinued at about ca. 100 min for ca. 48 min keeping the electrode rotating, and then resumed under the same initial conditions. As shown in Fig. 12, the activity of the disk electrode was to a large extent restored, although the time to deactivation was shortened considerably. Based



Figure 12. Plots of i_{lim} ($E_{\text{disk}} = +0.13$ V), i_{ring} ($E_{\text{ring}} = 1.38$ V), and $|i_{\text{ring}}/i_{\text{disk}}|$ as a function of time for a Se-modified Pt ($\theta_{\text{Se}} = 0.5$) disk of a Pt/Pt RRDE in 0.50 M H₂SO₄ solutions at $\omega = 400$ rpm. Polarization of the disk and ring was discontinued for *ca.* 48 min keeping the electrode rotating and then resumed under the same initial conditions.

on the results shown in Fig. 11 and 12, this deactivation does not seem to be caused by Se desorption, but rather to adsorption of a solution-phase impurity that desorbs under open-circuit conditions. In fact, assuming a diffusion coefficient of 5×10^{-6} cm²/s and also that adsorption occurs under pure diffusion control, the onset to deactivation (*ca.* one monolayer) would correspond to the contaminant being present at a concentration of *ca.* 10^{-8} M.

Much faster deactivation was found in the case of S-modified Pt electrodes as illustrated by transient data of the same type as that shown in Fig. 13 acquired between cycles 6 and 7 (see Fig. 10) at $E_{\rm disk} = +0.10$ V. Despite the gradual loss in activity, (see Fig. 13) $|i_{\rm ring}/i_{\rm disk}|$ remained virtually unchanged, *i.e.*, electrode deactivation does not lead to losses in specificity, as was found for Se-modified Pt electrodes. Rather unambiguous evidence for an impurity, and not sulfur desorption, as being responsible for deactivitation was found upon cycling the deactivated electrode (cycle 8) into the oxide formation region, a procedure that restored fully the activity and selective of the surface (see Fig. 10).

Conclusions and Future Prospects

The results obtained in this work have provided ample evidence that the amount of adsorbed sulfur or selenium can have a profound effect on the overall electrocatalytic activity and selectivity of polycrystalline Pt for the reduction of dioxygen in acid electrolytes. Although actual coverages of the surface modifiers could only be reliably determined for Se, analysis of results obtained with the RRDE



Figure 13. Plots of i_{disk} , i_{ring} , and $|i_{\text{ring}}/i_{\text{disk}}|$ as a function of time following polarization of the S-modified Pt disk electrode at +0.10 V vs. SHE between cycles 6 and 7 (see text for details). ω : 900 rpm.

for both types of modified Pt surfaces indicated that dioxygen can be reduced to hydrogen peroxide at nearly 100% faradaic efficiency over a wide potential range provided the coverage of Se or S are set within a rather narrow range. Unlike S, for which the coverage can be changed by anodic stripping, although in an as yet noncontrollable fashion, θ_{Se} can be readily adjusted by polarizing the Pt electrode at the desired value within the UPD region to yield the highest activity and selectivity. Furthermore, subsequent emersion and



Figure 14. Schematic diagram of a fluidized-type minireactor for Se modification of high area Pt. W.E (working electrode), R.E. (reference electrode), and C.E. (counter electrode).



Figure 15. Charge vs. potential of a Pt foil (11 cm² cross-sectional area) in 20 mM H₂SO₄ obtained with the minireactor in Fig. 14, while the main compartment was purged with Ar (open circles). The data in solid circles was obtained in an otherwise identical experiment, except that 0.4 mg Pt black was added to the solution (filled circles).

washing and subsequent immersion in either deareated or O_2 -saturated acidic solutions devoid of Se do not seem to affect the actual surface coverage. On this basis, it would seem possible to prepare Se-modified high area Pt surfaces of that specified θ_{Se} using fluidized packed-bed-reactor-type techniques. Promising results were obtained with a minireactor shown schematically in Fig. 14, which consists of two chambers separated by a Nafion tube. The outside or working electrode compartment houses a large Pt foil or cathode current collector mounted along the inner walls of a Teflon nipple. Prior to the actual experiments, the Nafion tube was filled with high area Pt using two Pt wires inserted one from the bottom and one from the top, which serve as current collectors for the anode. The bottom of the cell is then closed, and the main chamber filled with an acid solution through the top of the cell. A Teflon tube pressed to fit into an orifice drilled into the wall of the nipple was



Figure 16. Plot of charge vs. time for a Pt foil recorded upon stepping the potential from *ca.* 0.84 down to 0.54 V vs. SHE in a 1 mM SeO₂ + 20 mM H₂SO₄, (dotted line) using the minireactor in Fig. 14. The curve (solid lines) was obtained in an otherwise identical experiment except that the 0.40 mg Pt black was added to the same solution before application of the potential step (see text for details).

used to connect the main reactor chamber to an external compartment that houses the reference electrode. During operation, the solution in the main reactor chamber which contains the high area Pt is agitated continuously by bubbling Ar gas.

For these preliminary experiments, the reactor was filled first with a 20 mM H_2SO_4 solution and a cyclic voltammogram recorded after deaeration yielded features characteristic of clean Pt (not shown). The potential of the Pt foil was then stepped from +0.74 V vs. SHE (platinum-oxide-free) to the desired potential E_{dep} and held at that value while recording the current for *ca.* 80 s, a time sufficient for the current to reach steady state. Immediately thereafter, the electrode was stepped back to +0.74 V for a few minutes and then stepped to a new E_{dep} value. Shown in Fig. 15 (open circles) are plots of the charge obtained from integration of the steady-state background current as a function of potential. Once the entire series was completed, 0.40 mg Pt black was added into the cell and the same type of experiments repeated yielding the results shown in solid circles in the same figure.

The solution was then replaced by deaerated 1 mM $SeO_2 + 20$ mM H_2SO_4 solution and the potential stepped from + 0.84 to + 0.54 V vs. SHE while monitoring the current (see dotted line in Fig. 16). Immediately thereafter, 0.40 mg Pt black (Alfa) was added and the potential stepped from +0.84 to +0.54 V vs. SHE yielding the charge vs. time curve shown in Fig. 16 (solid line). As indicated, the charge difference between the Pt black and the foil is larger in the presence compared to the absence of Se in solution, and therefore consistent with the adsorption of Se on the Pt black surface. Unfortunately, the amounts of Se-modified Pt that could be prepared with this minireactor were found to be too small to carry out meaningful electrocatalytic experiments. However, high activities and selectivities for the reduction of dioxygen to hydrogen peroxide in acid electrolytes were observed recently in our laboratory for high area Pt particles embedded on the surface of a glassy carbon rotating disk electrode modified by Se in situ,³⁷ providing clear evidence that the effects observed for massive Pt can indeed be reproduced for the technically more relevant Pt blacks.

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References

 H. Y. Liu and F. C. Anson, J. Electroanal. Chem. Interfacial Electrochem., 158, 181 (1983).

- C. R. Martin, L. D. Whiteley, D. R. Lawson, and M. N. Szentirmay, *Polym. Prepr.* (Am. Chem. Soc. Div. Polym. Chem.), 29, 442 (1988).
- A. K. Shukla, P. Stevens, A. Hamnett, and J. B. Goodenough, J. Appl. Electrochem., 19, 383 (1989).
- F. A. Uribe, T. E. Springer, and S. Gottesfeld, J. Electrochem. Soc., 139, 765 (1992).
- S. Gottesfeld, I. D. Raistrick, and S. Srinivasan, J. Electrochem. Soc., 134, 1455 (1987).
- Kinetics and Mechanisms of Electrode Processes Vol. 7, M. R. Tarasevich, A. Sadkowski, and E. B. Yeager, Editors Plenum Press, New York (1983).
- R. Adzic, in *Electrocatalysis*, J. Lipkoswki and P. N. Ross, Editors, p. 197, Wiley-VCH, Inc., New York (1998).
- 8. A. J. Dickman, AMD (Am. Soc. Mech. Eng.), 40, 337 (2000).
- 9. A. J. Appleby, Sci. Am., 281, 74 (1999).
- 10. C. K. Dyer, Sci. Am., 281, 88 (1999).
- S. R. Narayanan, T. I. Valdez, and F. Clara, in *Direct Methanol Fuel Cells*, S. R. Narayanan, S. Gottesfeld, and T. Zawodzinski, Editors, PV 2001-4, p. 254, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
- 12. P. C. Foller and R. T. Bombard, J. Appl. Electrochem., 25, 613 (1995).
- 13. P. Piela and P. K. Wrona, J. Phys. Chem. B, 105, 1494 (2001).
- 14. A. Alvarez-Gallegos and D. Pletcher, Electrochim. Acta, 44, 853 (1998).
- 15. K. B. Lee, M. B. Gu, and S.-H. Moon, Eng. Life Sci., 1, 237 (2001).
- 16. P. Tatapudi and J. M. Fenton, J. Electrochem. Soc., 140, L55 (1993).
- 17. R. P. Sethi, B. K. Rao, and D. Srinivas, Chem. Ind. Dig., 14, 95 (2001).
- 18. F. P. Komarov, Bum. Prom., , 11 (1969).
- 19. M. Ficek and M. Ficek, Chemik, 47, 9 (1994).
- 20. J. Zagal, P. Bindra, and E. Yeager, J. Electrochem. Soc., 127, 1506 (1980).
- N. Kobayashi, T. Matsue, M. Fujihira, and T. Osa, J. Electroanal. Chem. Interfacial Electrochem., 103, 427 (1979).
- A. Bettelheim, R. J. H. Chan, and T. Kuwana, J. Electroanal. Chem. Interfacial Electrochem., 99, 391 (1979).
- A. Bettelheim, R. J. H. Chan, and T. Kuwana, J. Electroanal. Chem. Interfacial Electrochem., 110, 93 (1980).
- P. A. Forshey, T. Kuwana, N. Kobayashi, and T. Osa, in *Advances in Chemistry Series*, K. M. Kadish, Editor, Vol. 201, ACS, Washington, DC, (1982).
- 25. F. Beck, J. Appl. Electrochem., 7, 239 (1977).
- 26. T. Harrington and D. Pletcher, J. Electrochem. Soc., 146, 2983 (1999).
- 27. K. Fukatsu, S. Kokot, and D. P. Schweinsberg, Text. Res. J., 69, 769 (1999).
- 28. D. A. Scherson, Patent (2002), In press.
- A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd ed., Wiley, New York (2001).
- Y. E. Sung, W. Chrzanowski, A. Zolfaghari, G. Jerkiewicz, and A. Wieckowski, J. Am. Chem. Soc., 119, 194 (1997).
- Y.-E. Sung, W. Chrzanowski, A. Wieckowski, A. Zolfaghari, S. Blais, and G. Jerkiewicz, *Electrochim. Acta*, 44, 1019 (1998).
- 32. J. M. Feliu, R. Gomez, M. J. Llorca, and A. Aldaz, Surf. Sci., 289, 152 (1993).
- 33. B. M. Huang, T. E. Lister, and J. L. Stickney, Surf. Sci., 392, 27 (1997).
- 34. T. E. Lister and J. L. Stickney, J. Phys. Chem., 100, 19568 (1996).
- B. W. Gregory, M. L. Norton, and J. L. Stickney, J. Electroanal. Chem. Interfacial Electrochem., 293, 85 (1990).
- 36. S. L. Gojkovic, S. Gupta, and R. F. Savinell, Electrochim. Acta, 45, 889 (1999).
- 37. Y. Mo, S. Sarangapani, A. Le, and D. A. Scherson, In press.