Structural, Compositional and Electrochemical Characterization of Pt–Co Oxygen-Reduction Catalysts

S. Axnanda, K. D. Cummins, T. He, D. W. Goodman, and M. P. Soriaga

1. Introduction

It is well known that the H₂–O₂ fuel cell (FC) is an energy source that combines zero pollutant-emission with an elevated chemical-to-electrical energy-conversion efficiency. Advances in the membrane-electrode assembly, in which the electrocatalyst is directly dispersed onto the solid proton-exchange membrane (PEM), have vastly improved the H₂–O₂ PEMFC technology such that, while the cell can be operated at a comparatively low temperature, it is able to generate gravimetric (W kg⁻¹) and volumetric (W cm⁻³) power densities much higher than other types of fuel cells. Unfortunately, the electrocatalysts employed in present-day H₂–O₂ PEMFCs are based on platinum. As a consequence, while bolstered by the fact that Pt is simply the best accessible electrocatalyst, the cell suffers severe commercial handicaps due to exorbitant costs, undesirable contaminant-sensitivity, and deleterious metal dissolution. Economic viability may be realized if the amount of platinum utilized is decreased, but not at the expense of electrocatalytic efficiency.

With respect to catalyst performance, more effort has to be devoted to the oxygen-reduction reaction (ORR), since the difference between the empirical output voltage (ca. 0.9 V) from the thermodynamic value (1.23 V) reflects a voltage efficiency of only about 70%. Recent studies have indicated that, when Pt is alloyed with a less-noble metal such as cobalt, the ORR activity of the alloy is enhanced despite the fact that a smaller amount of Pt is utilized to generate the same power density.

The enhanced electrocatalysis of the ORR afforded by the Pt–Co alloys has been the subject of numerous investigations. Among the explanations suggested for the improved catalysis are: 1) an increase in the 5d-band vacancy in Pt; 2) changes in the interatomic distance and coordination number of Pt; and 3) dioxygen activation at (adjacent) Co sites. A paucity of studies that have examined the influence of the structure and composition of the alloy surface on ORR-catalysis performance remains. It is this context that we have carried out studies on the interfacial and electrochemical properties of Pt–Co alloy thin films. The results from such work are the subject of the present manuscript.
**Experimental Section**

Preparation of the Alloys: The Pt-Co thin films were prepared by metal-vapor deposition in ultra-high vacuum (UHV) as described elsewhere.[16] A doser was constructed from Pt and Co wires tightly wound around a Ta filament. The latter had to be resistively heated at a high current to enable the sublimation of the desired metal onto an ambient-temperature substrate. The thin-film alloys were deposited onto two different high-melting single-crystal materials, Mo(110) and Ru(0001), to explore possible substrate influences.

The calibration of the film-formation (dosage) rate was based upon the “XPS breakpoint” technique[17] in which a plot of photoelectron intensity is obtained as a function of dosage time (Figure 1). Between submonolayer and monolayer coverages, the slope of the plot is a constant. The point at which the slope changes is taken as the time ($t_{ML}$) required to deposit one full monolayer (ML) as well as the start of the formation of the second layer. In the preparation of an n-layer film, the sublimation period was simply equated to ($n \times t_{ML}$). The mixed-metal films thus prepared were annealed at 900 K for 20 min to ensure that Pt and Co had become alloyed. Prior to and subsequent to the electrochemical experiments, interfacial composition was determined by X-ray photoelectron spectroscopy (XPS), low-energy ion scattering spectroscopy (LEISS) or temperature-programmed desorption (TPD); the surface structure was examined by low-energy electron diffraction (LEED).

Comparative experiments were also undertaken with an oriented and metallographically polished bulk Pt$_2$Co(111) single crystal (Princeton Scientific, Princeton, NJ) to ascertain whether or not thin-film effects were operative. The crystal was annealed at 800 K for ten minutes prior to the LEISS measurements.

Surface Characterization: Surface characterization was carried out in a UHV chamber ($5 \times 10^{-10}$ Torr base pressure) equipped with LEISS, XPS, TPD, and LEED. The sample, mounted to two copper holders, could be heated to 1500 K resistively, and to 2400 K by an electron beam. The sample could be cooled to 90 K via a liquid-nitrogen reservoir connected to the copper holders. The sample temperature was monitored with a 5% Re/W-26% Re/W (C-type) thermocouple spot-welded at the rear of the substrate.

The LEISS measurements made use of a 1 keV He$^+$-ion beam, at currents no higher than 10 nA, incident at a 45° angle relative to the surface normal. These conditions were chosen to ensure that the amount of surface atoms sputtered would be negligible; to further preclude surface damage, only one LEISS spectrum was collected for each sample. For the XPS work, an Al K$_{\alpha}$ source was employed at a 45° angle of incidence. The photoelectrons were collected and analyzed by a concentric hemispherical analyzer.

Electrochemistry: For the electrochemical experiments, the sample was transferred through a differentially pumped sliding seal to an ante-chamber that was held at a total pressure of two atmospheres with ultrahigh purity gases (N$_2$ for inert-atmosphere work or O$_2$ for fuel-cell operations); the differentially pumped seals maintained UHV conditions in the main chamber. The apparatus used in this experiment is shown in Figure 2.

![Figure 1](image1.png) **Figure 1.** The “XPS breakpoint” metal-doser calibration method. The point at which the slope changes (the “break point”) signals the completion of one ML and the onset of the second ML. The data shown are for the Pt and Co dosers and a Mo(110) substrate. The intensity ratios were based upon one ML and the onset of the second ML. The data shown are for the Pt and Co dosers and a Mo(110) substrate. The intensity ratios were based upon one ML and the onset of the second ML.

![Figure 2](image2.png) **Figure 2.** A schematic representation of an integrated LEED–TPD–XPS–LEISS–EC apparatus.

Open-circuit, potentiostatic and potentiodynamic electrochemical experiments were conducted with an EG&G PARC Model 273 voltamnograph controlled by manufacturer-encoded software. A three-electrode system was employed with a Pt wire as the auxiliary electrode and a custom-built Ag/AgCl (0.1 M Cl$^-$) electrode, calibrated against a standard hydrogen electrode (SHE), as reference. Unless otherwise indicated, cyclic voltammetry (CV) was performed at a potential-scan rate of 1 mV s$^{-1}$. All solutions were prepared from Milli-Q water (18 MΩ resistivity) and ultra-high purity reagents; electrolytic solutions contained 0.1 M H$_2$SO$_4$.

The open-circuit potential (OCP) exhibited by the subject alloys is a direct measure of the electrocatalyst voltage efficiency: the closer the observed value is to the thermodynamic voltage (1.23 V), the greater the tendency towards enhanced ORR electrocatalysis. There are, of course, other performance metrics of fuel-cell efficiency. However, such measures are themselves fundamentally dependent upon the voltage efficiency; in other words, there would be little value in the evaluation of, for example, the power efficiency, if the voltage efficiency were unacceptably low.

2. Results and Discussion

2.1. LEISS

Figure 3 shows LEISS spectra of a Mo(110) substrate onto which a 10 ML film was prepared from a 1:4 Pt-to-Co co-depo-
sition ratio. In Figure 3a, 2 ML of Pt were initially deposited, followed by 8 ML of Co. In Figure 3b, the reverse deposition sequence was used in which 8 ML of Co were deposited first.

There are five notable features in Figure 3a: 1) Below 600 K, no Pt peak \( \frac{E}{E_0} \approx 0.98 \) is observable. This suggests that 8 ML of Co completely covers the 2 ML of Pt. 2) At 700 K, a Pt peak emerges. At this temperature, the Pt underlayer and the Co overlayer have started to intermix. 3) Between 800 and 1000 K, the ratio of the Pt and Co peak \( \frac{E}{E_0} \approx 0.83 \) areas is invariant, which provides evidence for the formation of a stable fixed-composition alloy. 4) At \( T < 1000 \) K, no Mo substrate peak \( \frac{E}{E_0} \approx 0.89 \) is found. This signifies that the alterations in the Co and Pt signal intensities at lower temperatures are due to alloy formation and not to thermal desorption of Co and/or Pt. 5) At temperatures greater than 1000 K, the peak intensities for both Co and Pt decrease while a barely discernible peak for Mo emerges—thermal desorption of both Pt and Co is indicated.

In Figure 3b, three aspects are noteworthy: 1) Below 600 K, a Co peak is present. This signifies that a 2 ML Pt overlayer is not sufficient to completely mask the Co underlayer. 2) Between 800 and 1000 K, the peak–intensity ratios are identical to those in Figure 3a. This documents the fact that, irrespective of the order of metal deposition, alloy formation takes place at the same temperature range. 3) Above 1000 K, the LEISS spectra are identical to those in Figure 3a. The implication is that the temperature-induced desorption of both Pt and Co atoms has transpired to expose the Mo substrate.

Additional 10 ML films of different Pt:Co co-deposition stoichiometric ratios (1:9, 2.5:7.5, 5:5, 7.5:2.5, 8.8:1.2, and 9.5:0.5) were investigated. The results, in terms of LEISS spectra, are summarized in Figure 4. In each case, a stable alloy was formed at the outermost layer when the deposits were annealed at 1000 K. Qualitatively, it can easily be ascertained from the relative peak heights that the mixed-metal composition at the top layer is vastly different from that in the bulk. At this point, it should be mentioned that LEISS results essentially identical to those shown in Figure 3 and 4 were obtained when a Ru(0001) substrate \( \frac{E}{E_0} \approx 0.91 \) was used in lieu of Mo(110).

It may be noted from the data in Figure 4 that the Pt:Co peak–intensity ratios are not precisely constant but exhibit a slight dependence on the stoichiometry of the bulk co-deposit. However, it is of greater significance to recognize that, while the dosage ratios are conspicuously dissimilar, the variations in the selvedge–layer composition are not as disparate. This fact becomes quite clear when the peak intensities are converted to surface concentrations,\(^{20}\) and the stoichiometric fraction of Pt (or Co) at the alloy surface is plotted as a function of the relative amount of Pt (or Co) in the bulk. Such a plot, which represents the surface phase diagram of the outermost layer of the alloy, is shown in Figure 5 for films prepared on two different substrates, Mo(110) and Ru(0001).

It is important to immediately realize the absence of a substrate effect since the surface phase diagram at Mo(110) is identical to that at Ru(0001). It should likewise be promptly
noted that there is a preferential enrichment (segregation) of Pt at the surface regardless of the initial bulk concentration. This is not unexpected since Pt has a lower surface-free energy than Co. It also ought to be emphasized that: 1) the surface phase diagram is independent of the order or sequence of metal deposition, 2) the near-convergence between the surface and bulk compositions occurs only when the bulk composition is almost entirely Co or is predominantly Pt, and 3) the discrepancy is most dramatic when the fraction of Co in the bulk is higher than 90%.

Perhaps the most significant trend in Figure 5 is that, for films in which the Co bulk composition is between 30% to 70%, the interfacial fraction of Pt is almost a constant value not far removed from 75%. In other words, the thermodynamically favored composition at the outermost layer is a 3:1 Pt-to-Co ratio; that is, Pt₃Co.

Whereas the data in Figures 3–5 provide evidence for the preferential surface segregation of Pt, they also show that such process was not sufficient to generate a platinum-only overlay or “skin”. Invariably, Co was found to co-exist with Pt and Pt₃Co was the most favored composition. This observation is of considerable significance since it contradicts results from a previous study which indicated that, when a bulk polycrystalline Pt₃Co alloy was subjected to high temperatures, a Pt skin was created.† The discrepancy between the two studies is not presently understood. However, it is clear that the rationale cannot be due to substrate influences since the surface phase diagrams for the alloy films on Mo(110) and Ru(0001) are identical. It likewise cannot be attributed to thin-film effects because, as illustrated in Figure 6, the LEISS spectrum for a bulk Pt₃Co single crystal shows a prominent Co peak. The latter would not have been observed were Co not present on the surface.

Figure 6. LEISS spectrum of a bulk Pt₃Co(111) single crystal annealed at 800 K for 10 min. Experimental conditions as in Figure 3.

It may be pointed out that, if catalytic dioxygen activation were to transpire at (adjacent) Co sites,[15,22,23] the presence of Co at the outermost layer would have to be a precondition; that is, for such a mechanism to be possible, the existence of a Pt skin at the interface needs to be ruled out.

2.2. LEED

The presence (or absence) of long-range two-dimensional order of the Pt–Co alloys can be ascertained from the LEED patterns such as those displayed in Figure 7. The fact that distinct LEED spots are observed indicates that the alloy interface is crystalline and well-ordered. Figure 7a shows a LEED pattern that, because of additional (albeit dim and diffuse) spots is non-hexagonal; that is, non-Pt(111)-like. Such a pattern is typical for when the Pt:Co atom-percentage ratio is close to 3:1. Under these conditions, the outermost layer appears to be compositionally homogeneous (Pt₃Co) and structurally single-crystalline. Figure 7b represents a LEED pattern for alloys that contained greater than 75 atom-percentage of Pt. The spot pattern is now distinctly hexagonal, reminiscent of a pure Pt(111) surface. At such high Pt surface concentrations, the outermost layer is most likely heterogeneous, populated by comparatively wide Pt(111) terraces interspersed with small domains of single-crystalline Pt₃Co.

2.3. XPS

When Pt is alloyed with Fe-group metals, the 5d-band vacancy in Pt is increased because of the higher 5d-band vacancy in the less-noble metals. It has thus been postulated that any enhancement in the activity of Pt-M alloys (where M is an Fe-group metal) can be rationalized in terms of an increase in the 5d-band vacancy in Pt.[21] Supposedly, this facilitates the initial charge transfer from the 2π molecular orbital of O₂ to the 5d band of Pt which, in turn, leads to an increase in the Pt-to-O₂ 2π* back-donation. As a consequence, the O=O bond is easily weakened and activated (broken). Since a measure of the extent of 5d-band vacancy in alloyed Pt can be obtained from the (positive) shift in the core-level binding energies, 4f₁/₂ binding-energy shifts were measured for alloys of four different Pt:Co stoichiometric ratios and the results are shown in Figure 8. It can be seen that the 4f₁/₂ binding energy of Pt is shifted upward by 0.3 eV when the bulk Pt:Co ratio is 3:1. When the amount of Co was increased to PtCo₅, the E₀ shift was elevated by 0.9 eV; the same value measured at still higher Co fractions. Since, as shown below, the Pt₃Co alloy yielded
the highest voltage efficiency, a shift of 0.3 eV in $E_B$ is evidently the optimum value. Presumably, too high a 5d-band vacancy serves to strengthen the Pt/C0 bond that then leads to a retardation of the O$_2$-reduction reaction rate.[21]

2.4. Electrochemistry

Figure 9 shows a plot of the open-circuit potential as a function of the alloy-surface composition in O$_2$-saturated 0.1 m H$_2$SO$_4$ solution. The highest voltage, 0.86 V, was obtained for the alloy with a composition corresponding to Pt$_3$Co. This value is 0.68 V greater than that of pure Co and 0.22 V greater than that of pure Pt, yet it is considerably lower than the ideal potential of 1.23 V. In a control experiment, in which the acid solution was thoroughly deaerated with N$_2$, an OCP of ca. 0.5 V was obtained for all alloy compositions. An OCP of 0.86 V corresponds to a voltage efficiency of 70%. Also shown is the single data point for the bulk Pt$_3$Co single crystal. The measured OCP is exactly the same as that for the Pt$_3$Co thin film and serves to further buttress the contention that the ten-layer alloy film behaves just like the bulk material.

The cyclic voltammogram of pure Pt in deaerated 0.1 m H$_2$SO$_4$ shows that the onset of surface oxide (or hydroxide) formation takes place at 0.68 V, although the amount formed at this potential is minuscule compared to that when the potential is at 1.23 V. This means that, even at saturation concentrations, O$_2$ gas is unable to oxidize a pure Pt surface to an extent that the OCP would be driven up to 1.23 V. The effect of Co is clearly the facilitation of O$_2$ activation. It is further surmised that the oxygen atoms formed on the Co sites irreversibly “spill over” to the Pt sites. The amount of Pt surface oxide is then increased, accompanied by a boost in the OCP.[22] The present work points to Pt$_3$Co as the optimal selvedge-layer concentration for such a synergistic process.[23]

Cyclic voltammograms for alloys of other Pt–Co concentrations were also collected in deaerated and O$_2$-saturated 0.1 m H$_2$SO$_4$. A single-cycle set of CVs for the Pt$_3$Co cathode is shown in Figure 10. The voltammograms were initiated from the OCP and the potential was initially scanned in the negative direction down to the hydrogen-evolution region. The morphologies of the current–potential curves are not too different from those of pure Pt. In a deaerated solution, there is an appreciably wide double-layer potential “window” between the hydrogen-evolution and oxygen-evolution regions. In O$_2$-saturated solution, a massive cathodic wave due to dioxygen reduction appears at potentials immediately below the OCP. The high cathodic current persists even after the potential sweep is reversed in the positive direction. The fact that these voltammetric results are similar to those for pure Pt is not unexpected since two-thirds of the surface is made up of Pt.

An important issue that needs to be addressed concerns the nature (structure and composition) of the alloy interface after an external electrochemical treatment or under fuel-cell conditions. This question can be adequately answered by the appli-
cation of LEISS and/or other surface-sensitive analytical techniques after the alloy electrode is emersed (removed under potential control) from solution. Illustrative results from such type of experiments are shown in Figure 11. Figures 11a,b, respectively, depict LEISS and XPS data of Pt–Co alloys before and after cyclic voltammetry between 0.0 V to 1.4 V. Significant reductions in the coverage of Co, as indicated by the decrease in LEISS and XPS intensities, are obvious. However, when the upper potential limit was decreased from 1.4 V to 1.0 V, the amount of Co corroded is not as considerable (Figures 11c,d).

To simulate fuel-cell reaction conditions, the Pt3Co alloy was immersed in O2-saturated 0.1 m H2SO4 at open circuit and under potential control; the surface composition of Co was then measured at pre-determined time intervals over a period of one hour. The results are represented by the corrosion (dissolution) profile in Figure 12; surface concentrations were obtained from the LEISS data. It can be seen in this figure that: 1) regardless of the applied voltage, there is an immediate drop from 20% to 18% in the absolute Co concentration; 2) irrespective of the external potential, the surface concentration of Co becomes independent of time after the initial rapid decrease; 3) at \( E_{\text{Applied}} \leq E_{\text{OCP}} \), the Co surface concentration quickly converges to a constant value of approximately 18%; 4) at potentials more positive than OCP, the initial decline in surface concentration is much more precipitous (from 20% to 11%), but the amount of Co retained is unchanged even after prolonged reaction times.

The anodic oxidation of the alloy surface that comes about at potentials above the OCP (Figure 10) accounts for the comparatively larger decrease in the Co concentration at \( E_{\text{Applied}} > E_{\text{OCP}} \). This is because the oxidized surface of Co is not impervious to dissolution in highly acidic media. The fact that slightly more than half of the initial Co concentration is retained on the surface suggests that an appreciable quantity of Co is rendered relatively inert towards anodic dissolution when alloyed to Pt.

The combination of LEISS, XPS and TPD was used to establish the source of the dissolved Co; that is, whether the atoms that are oxidatively desorbed into the solution phase emanate only from the topmost layer or also originate from the sub-surface. Figure 13 shows Co XPS data after the Pt3Co thin film was subjected to ten-minute constant-voltage exposures at different potentials. When the applied potential was kept between 0.6 V and 1.1 V, the post-EC spectra show constant peak inten-

![Figure 11. LEISS and XPS of Pt–Co (1:4 bulk ratio) taken before and after CV scans at two different potential ranges: a) and b) 0.4–1.4 V range; c) and d) 0.0–1.0 V range. Significant Co dissolution occurs at the higher applied voltage.](image)

![Figure 12. The dissolution profile of Pt3Co in terms of the amount of Co that remains at the outermost layer as a function of applied potential and time. The surface concentrations were obtained from the LEISS measurements.](image)

![Figure 13. Co XPS spectra before and after 10-minute immersion of the alloy film in O2-saturated 0.1 m H2SO4 at pre-selected potentials.](image)
sities. However, when the potential was increased to 1.23 V, both the LEISS (Figure 11) and XPS (Figure 13) data show a considerable decrease in the Co peak intensity. The loss of Co from the selvedge layer is indicated by the LEISS results. Since XPS peaks also bear information on at least two sub-surface layers, the lowered Co XPS peak intensity is suggestive of cobalt dissolution also from the sub-surface region.

The above corrosion scenario is supported by TPD experiments. Figure 14 shows TPD spectra for unalloyed (Figure 14a) and Pt-alloyed (Figure 14b) Co thin films. The decrease in the intensities of the post-EC TPD peaks is simply too drastic to be rationalized only in terms of Co corrosion from the topmost layer; a dissolution mechanism that includes atoms from the near-surface (or even bulk) regions is patently warranted.

3. Conclusions
Pt–Co thin-film electrocatalysts have been characterized using LEISS, XPS, LEED, TPD and EC. For comparative purposes, LEISS and EC were also carried out on a bulk Pt3Co(111) single crystal. The extensive experimental work resulted in the establishment of the surface phase diagram of the alloy film marked by a substantial divergence between the composition at the interface and that in the interior. When a dual-layer deposit of Pt and Co was annealed at high temperatures, alloy formation transpired in which the outermost layer became single-crystaline and enriched in Pt. The preferential surface segregation of Pt, however, was not sufficient to generate a platinum-only overlayer or “skin”. Invariably, Co was found to co-exist with Pt, independent of the substrate [Mo(110) or Ru(0001)] employed and Pt3Co was the most favored composition. The same result, the absence of a Pt skin, was likewise indicated at the post-thermally-annealed surface of the bulk Pt3Co(111) monocrystal.

For alloy-film surfaces more enriched in Pt than Pt3Co, the topmost layer was constituted primarily, but not exclusively, of Pt(111) domains. The proclivities of the alloys towards enhanced catalysis of the oxygen-reduction reaction were assessed in terms of their voltage efficiencies, as manifested by the open-circuit potential (OCP) in O2-saturated sulfuric acid electrolyte. The Pt3Co surface, whether from the thin film or the bulk single crystal, exhibited the highest OCP, a significant improvement over pure Pt but still appreciably lower than the thermodynamic limit. The degradation of the Pt3Co thin-film surface was predominantly due to Co corrosion. A minimal amount was spontaneously dissolved upon simple immersion in solution; slightly higher dissolution occurred at potentials above the OCP. The fraction that was not immediately corroded proved to be stable even after prolonged periods at potentials more positive than the OCP.

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