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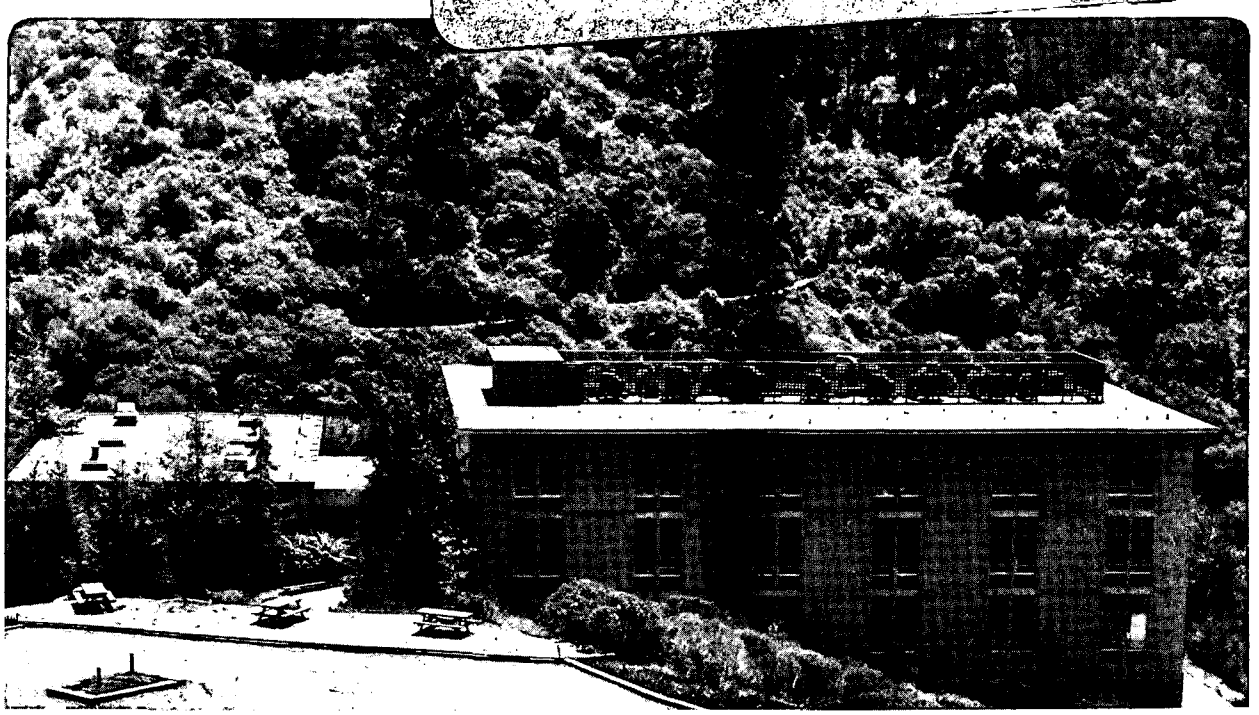

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THE STRUCTURE AND ACTIVITY OF Pt-Co ALLOYS AS OXYGEN REDUCTION ELECTROCATALYSTS

Bruce C. Beard and Philip N. Ross, Jr.

Materials and Molecular Research Division
Lawrence Berkeley Laboratory
University of California
Berkeley, CA 94720

ABSTRACT

Carbon supported Pt-Co (3:1 atom ratio) catalysts were prepared in both acid and alkaline aqueous media, followed by heat treatments to promote alloy formation. Both preparations began with a commercial 10% Pt on carbon catalyst with Pt particle sizes of 15-30 Å. Significantly greater alloying was observed in the acid media prepared catalyst. X-ray diffraction studies of the acid prepared catalyst demonstrated lattice parameters tending away from Pt (3.927 Å) and toward that for Pt_3Co (3.831 Å), greatly increased particle sizes, and significant ordering evidenced by the presence of superlattice reflections. In all cases, the base media prepared catalysts were alloyed to a lesser extent, were of moderately increased particle size and gave no indication of alloy ordering. Activity testing under phosphoric acid fuel cell conditions demonstrated that the most highly alloyed catalysts had the greatest activity. Loss of cobalt in the phosphoric acid environment was the lowest in catalysts which were the most alloyed.

INTRODUCTION

We report here the study of platinum-cobalt alloys as an alternative air cathode catalyst for phosphoric acid fuel cell (PAFC) applications. Platinum has long been used for oxygen reduction catalysis owing to its superior activity among pure metals. Platinum possesses the best oxygen adsorption character for oxygen reduction by not forming a surface oxide in a potential region of practical utility in fuel cell cathodes. Nonetheless, we have suggested [1] that platinum still adsorbs oxygen too strongly for optimal oxygen reduction activity, and that adsorption behavior somewhere between platinum and gold might provide improved oxygen reduction rates. Alloys of platinum therefore have been studied and some have been found to display superior performance over pure platinum [2-5].

This laboratory has investigated a variety of platinum-transition metal alloys as potential PAFC cathodes, [6]. The principle concept invoked in all of these previous studies was the alteration of the electron distribution of the platinum through its bonding with the base metal. Group IV and V transition metals alloyed with platinum are characterized by highly exothermic free energies of formation. The bonding in these systems has been described by the Engle-Brewer valence-bond model in which electron density from the base

metal is transferred into the d-band of the platinum [7]. Since a new electron configuration results with electron density increased in the d-band of Pt, altered catalytic activity might be expected.

In a previous study [8], we reported that the Pt_3Ti alloy demonstrated an initial catalytic activity equivalent to that of pure platinum despite particle sizes five times greater. The practical problem with Pt_3Ti is the high reactivity of the titanium. Titanium is oxidized at the surface of the alloy followed by dissolution in the aggressive acid electrolyte. Dealloying of the catalyst was rapid, causing the activity to revert back to that of the pure Pt of comparable particle size [8].

The present study of Pt-Co alloys followed a working hypothesis that the more noble nature of cobalt might retard the dealloying process while yet sufficiently altering the surface catalytic behavior of the platinum to obtain increased oxygen reduction activity. The composition and structure of supported Pt-Co alloys were characterized by the same multi-technique approach we used in the previous study [8] of Pt-Ti alloys. Appropriate background information on these techniques is given in that report and references therein. Supported Pt-Co alloys were tested under fuel cell conditions for catalytic activity and for Co stability, i.e. depletion.

PREPARATION

All catalysts were prepared starting from commercially available carbon supported Pt catalyst obtained from the Prototech Company (Newton Highlands, MA). The Pt loading of the material used was 10% by weight with a narrow particle size distribution of from 15-30 Å.

The catalysts designated as Series A were prepared as follows. 0.016 g of $Co(OH)_2$ was dissolved in a 50 ml volume of a 1:1 water:methanol mixture. Dropwise addition of dilute HCl brought the solution pH to 2. One gram of the Pt on carbon catalyst was slowly added into this solution while aggitated in an ultrasonic mixer. Mixing was continued until dryness.

A series of catalysts designated as Series B was prepared by the addition of 0.05 g of $Co(NO_3)_2{*}6H_2O$ to a 50 ml volume of a 1:1 water:methanol mixture. Following complete dissolution of the salt, NH_4OH was added to the solution to a final pH of 11. One gram of the Pt on carbon catalyst was slowly added into this solution while aggitated in an ultrasonic mixer. Mixing was continued until dryness.

In each case cobalt was added to the platinum on carbon catalyst to obtain a 3:1 platinum to cobalt ratio. From the amount of cobalt added in the preparation, the cobalt loading was ~1 wt%. Three heat treatments were performed on each catalyst. The heat treatment duration was 2 hours at

temperatures of 700, 900, 1200°C. All heat treatments were performed under inert gas atmosphere and the catalysts remained under inert gas following the heat treatments until they cooled to room temperature. The 700 and 900°C heat treatments were done in a Pt boat while the 1200°C was done in a graphite crucible.

INSTRUMENTATION

X-ray diffraction (XRD) analysis of the supported catalysts was performed using Cu K_{α} radiation in Siemens D-500 diffractometer. Powder specimens were held in a 2.5 cm x 2.5 cm x 1 mm trough cut into the surface of a lucite block. Powders were pressed into the trough with a glass slide to obtain an even, smooth distrubition of the powder.

X-ray fluorescence (XRF) spectra were collected with a Tracor X-ray Spectrace 4020. An Intel 8086 microprocessor controls data acquisition and analysis. A Rhodium x-ray source and a Si(Li) detector are used for excitation and collection of the fluorescence data.

X-ray photoelectron spectroscopy (XPS) was performed in a Physical Electronics 548 Auger/ESCA system. The spectrometer uses a Mg K_{α} (1253.6 eV) x-ray source and a double-pass cylindrical mirror analyzer. The system is ion pumped with a base pressure following bake-out of 4 * 10-8 Pa. Samples were

introduced into the analysis chamber by a rapid introduction probe. The binding energy scale linearity was checked by using the separation between the Cu (2p) and (3p) photoelectron lines. Absolute binding energy was referenced to 83.8 eV for the Au (4f, 7/2) photoelectron peak. For analysis the catalyst specimens were mixed with Teflon powder (10 wt%) as a binder and then pressed into a 5mm hole drilled through a 2 cm * 1 cm * 1 mm aluminum holder. The aluminum holder was then mounted onto the probe tip. The data collection and analysis system used for XPS have been described elsewhere [9].

Extended x-ray absorption fine structure (EXAFS) experiments were performed on the new beamline VI at SSRL. The experiments were performed with beam conditions of 3 GeV and 60 mA. The powders were mounted on a porous graphite fiber substrate using Teflon as a binder. The EXAFS specimen holder and fluorescence detector were obtained from F.W. Lytle [10]. Fluorescence detection was chosen owing to the superior S/N capability in highly dispersed systems [11]. Data evaluation was performed using software provided by Sandstrom [12].

For the purposes of stability and activity testing the catalyst were fabricated into electrodes of the type described by Kunz and Gruver [13]. These electrodes were immersed in oxygen saturated electrolyte, and subjected to a slow (2 mV/s) potential sweep from 0.9 to 0.6 V (versus reversible hydrogen electron in same electrolyte, RHE). The potential was held at

0.6 V (RHE) for 48 hours, a return sweep to 0.9 V was then collected. The electrochemical experiment was performed by an EG&G 273 potentiostat. X-ray flourescence, analysis was performed on the electrodes before and after the electrochemical testing.

RESULTS

1. X-ray Diffraction

X-ray diffraction analysis was used to characterize the structure and approximate size of the supported metal crystallites. Table I lists the XRD results. Lattice parameter values were based upon the 2-theta position of the (311) diffraction line, and the particle size estimates were based upon peak broadening of the (111) line relative to a bulk Pt foil. The lattice parameter of the FCC unit cell of pure platinum is 3.927 Å, while the alloy Pt_3Co, still FCC, has a contracted lattice parameter of 3.831 Å.

In Series B the as-prepared specimen has a lattice parameter value indicative of pure Pt. The particle size of the as-prepared specimen was below the limit of determination (≈25 Å), suggesting that the immersion in the basic media had no effect on the original Pt particle distribution. No additional diffraction lines were observed in the diffraction pattern of the as-prepared specimen suggesting

that the deposited cobalt phase was amorphous. No clear trend in lattice parameter change due to heat treatment temperature appeared. Particle sizes increased as expected with increasing heat treatment temperature. In no case was there any evidence of superlattice diffractions. Diffraction lines from the 1200°C specimen were, however, strongly asymetric to the high two-theta side. An estimation of the second peak position from high resolution scans of both the (111) and (311) diffraction peaks, gave lattice parameter values of 3.843 and 3.849 Å, respectively. This result indicates the presence of a second phase which has a lattice parameter close to that for the Pt_3Co alloy. This two-phase alloy formed only after a large increase in the particle size. A reasonable explanation would be that at higher temperature Pt and Co are more mobile, leading to increased particle agglomeration and metal alloying.

In Series A the as-prepared catalyst was altered slightly from the original condition of the Prototech catalyst. Most notable was the appreciably larger particle size of this specimen compared to that from the as-prepared Series B catalyst. It seems that the acidic solution used in the Series A preparation affects the high surface area Pt particles, possibly by a dissolution/deposition process since, according to Pourbaix [14], Pt is slightly soluble in chloride at pH 2. Lattice parameter values changed significantly following the 700°C heat treatment, with subsequent heatings yielding very

small changes in the lattice parameter. Particle size values for Series A at each heat treatment were found to be larger than the corresponding catalyst in Series B. Final particle size of the Series A 1200°C specimen (120 Å) was about four times greater than the original Pt catalyst. Much to our surprise faint evidence of superlattice diffractions were observed from the 700°C Series A catalyst. At 1200°C the superlattice diffractions were clearly evident (Fig. 1). The 900°C sample was anomolous, displaying two-phase alloy behavior without observable superlattice lines. Based upon a visual fitting, the higher two-theta (311) peak indicates a lattice parameter of 3.832 Å, close to that for the ordered phase Pt_3Co, but without superlattice reflections. Despite the evidence for ordering in the 1200°C catalyst, the lattice parameter is 0.033 Å larger than the anticipated value for Pt_3Co.

2. X-ray Photoelectron Spectroscopy

XPS reference data of the Pt(4f) and Co(2p) photoelectron levels were collected from a bulk polycrystalline Pt_3Co specimen. Following a mild sputter the Pt(4f, 7/2) peak appeared at 71.15 eV while the Co(2p, 3/2)was at 778.0 eV. The platinum was shifted 0.25 eV up from the metallic binding energy while the cobalt appeared where expected for metallic cobalt. Spectra from the Series A as-prepared specimen

indicated Co to be present as a Co(II) hydroxide, while the platinum (4f, 7/2) was observed at high binding energy (71.5 eV) due to chemisorbed oxygen on the surface of the highly dispersed particles. Heat treatment of Series A catalyst to 1200°C shifted the platinum to 71.2 eV. The cobalt spectra in heat-treated catalysts were extremely difficult to collect due to the very small signal levels. The cobalt concentration was low for XPS analysis and heating caused much of the cobalt to diffuse into the support or into the platinum, lowering the effective surface concentration even more. The noisy Co(2p) spectra obtained indicated a Co(2p) binding energy above that expected for the metal, although the strong satellite structure of Co(II) did not appear to be present. Even employing long-counting times (>1 hr.) we could not obtain spectra of sufficently high quality to make a determination of the valence state(s) of Co in the heat-treated catalysts.

3. Extended X-Ray Absorption Fine Structure (EXAFS)

Cobalt K-edge EXAFS spectra were collected for all of the Series B catalysts. The data reduction methods and the procedure for interpreting EXAFS spectra were the same as those we described previously [8] for Ti K-edge spectra from Pt-Ti alloys. Figure 2 shows the radial distribution functions for the Series B catalysts, derived from the Fourier transform of $k^3 * \chi(k)$. Figure 3 shows the radial distribution functions

for standard reference materials that serve as candidate materials for the chemical state and structure of the cobalt in the catalyst. The characteristic coordination shells are labelled in the figure from the known crystallographic structure of the standard compounds. Comparison of the radial distribution functions from the catalyst with those of the standard compounds may be used to "fingerprint" the chemical state of the Co in the catalyst as a function of heat-treatment. The as-prepared catalyst had only one strong peak in the radial distribution function at a length characteristic of a Co-O bond (it is not possible to identify the type of oxide from this alone as the first neighbor O bond lengths are not very different). The absence of a Co-Co scattering feature at greater scattering distance suggests the Co is possibly atomically dispersed. After heating to 700°C a second feature at ~2.6 A scattering distance appears which is attributed to Co-Co scattering. Upon heating to 900°C the Co-Co feature becomes dominent, and the radial distribution function compares very favorably with reference data of Co_3O_4. There is no major feature following the 900°C heat treatment which may be assigned to an interaction between platinum and cobalt. This does not eliminate the possibility, however, that some finite amount of alloying may have occurred. In the EXAFS spectra from the as-prepared, 700°C and 900°C specimens, the edge energy was 7712 eV. After the 1200°C heat-treatment, the

edge changed to 7708 eV and the radial distribution function changed dramatically. Two peaks appeared at 2.25 Å and 4.99 Å. These correspond to the first and second Co-Pt bond distances in the Pt_3Co alloy. The shift in the edge energy is indicative of a change in the chemical state of the cobalt. Cobalt-Cobalt scattering will be weak compared to that from Co-Pt due to the much larger scattering cross-section of Pt. The broad peak at 2.25 Å has structure on the left and right side which is due to the presence of remaining oxide.

4. Activity Measurement as PAFC Cathode

Activity measurements were collected from the as-prepared and 1200°C specimens from both series. For the Series A as-prepared specimen very little difference was observed in the electrochemistry before and after the 48 hour holding period at 0.6 V. The standard potential, measured at 100 mA and corrected for IR drop (between the Luggin capillary and the electrode surface) was ~725 mV (vs. RHE). The 1200°C Series A catalyst had no change in activity following the holding period, during which the average potential of this electrode was ~750 mV. The series B 1200°C specimen also displayed stable performance over the delay period at ~735 mV, while the as-prepared sample showed anomolous behavior apparently due to a physical breakdown of the electrode.

5. X-ray Fluorescence

X-ray fluorescence data were collected before and after the activity testing of the as-prepared and 1200°C specimen from each series, Table II. Comparison of the before-test ratio values to that from a bulk Pt/Co alloy, (approximate composition 21 at% cobalt) indicates that in all cases less than a 3:1 Pt:Co stoichiometric amount of cobalt was present in the catalyst. Both the as-prepared catalysts had lower cobalt to platinum ratios than the 1200°C catalyst despite the fact that the former were the precursors to the latter. Secondary excitation of the cobalt atoms by the fluorescence of neighboring platinum atoms in the larger alloy particles is believed to account for this observation. Indeed this could account for the apparent low concentrations of cobalt compared to the bulk alloy standard, since secondary fluorescence would be dependent upon the degree of alloying. The loss results indicated a significant effect of alloying. Both the as-prepared (not heat-treated) catalysts lost in excess of 80% of the cobalt present, whereas the 1200°C catalyst lost <30%, with the Series A 1200°C sample losing only 15%.

6. X-ray Diffraction Analysis of Tested Catalysts

The four electrochemically tested catalysts were also examined by x-ray diffraction (Table III). Quite surprisingly, in each case two phase behavior was observed, characterized by

the splitting of the (311) reflection (Fig. 2). The least intense of the (311) peaks appeared at higher angle (two-theta degrees). The lattice parameter from this weaker peak was in each case very close to that of Pt_3Co, (3.831 Å). Each as-prepared (not heat-treated) catalyst also illustrated a greater than two-fold increase in particle size. For the 1200°C Series A catalyst no evidence remained of superlattice lines which were observed prior to the electrochemical testing. Particle size of the heat treated catalysts also increased following electrochemical testing.

DISCUSSION

In both preparations the cobalt is deposited from solution, and the most probable form of the resulting cobalt phase is an hydroxide. The EXAFS data from the as-prepared catalyst show only Co-O interactions, indicative of a highly dispersed cobalt-oxygen moeity. XPS of an as-prepared catalyst shows the Co(2p, 3/2) peak at 781.1 eV with strong satellite structure characteristic of reference XPS data of Co(II) hydroxide [15]. Platinum particles in the as-prepared materials should be unchanged from their original form, but in Series A the particles show about a 50% increase in size relative to the starting material. Pourbaix [14] indicates the possibility of finite Pt dissolution in acidic chloride

solutions at a pH of 2. With the high surface areas involved, much of the Pt could be dissolved, then re-deposited upon drying. Particle sizes are consistantly larger in Series A relative to Series B possibly due to the initial re-distribution and resulting co-precipitation of Pt with the cobalt. Alloying was also much more rapid in Series A as a result of increased platinum-cobalt contact prior to the heat treatments. In Series B, particle sizes remained small until the 1200°C heat treatment, a temperature at which Pt diffusion resulting in particle size growth is known to occur [16]. Only following the 1200°C heat treatment in Series B is there indication of alloy formation (as the second phase observed in XRD). Series A on the other hand demonstrates a lower lattice parameter and weak superlattice reflections after a 700°C heat treatment. The physical characteristics of the two series of catalysts therefore depend strongly upon the solution chemistry under which they were prepared. The acid chloride media is apparently responsible for increased alloying and particle size due to the initial co-precipitation of some of the platinum with the cobalt, while Series B behaves similarly to material prepared by physical mixing of cobalt oxide with the Pt on carbon catalyst. A similar example is given in our previous work with Pt-Ti alloys [8].

The exact reduction reaction involved in the transformation of cobalt hydroxide to the alloy is not known,

however, it can be represented by the following:

$$Co(OH)_2 + 2\ H_2 + 3\ Pt \rightarrow Pt_3Co + 2\ H_2O$$

Sufficient H_2 is present in the carbon support to act as the reducing agent. The free energy of the reaction above is negative at room temperature if we use the reported free energy of mixing of Pt_3Co of -2.5 kcal/mol [17]. The water: hydrogen ratio must be maintained below ~7.5:1 to assure the formation of the alloy phase, which is easily accomplished with a flow of dry hydrogen. Heat treatments therefore aid in the formation of the alloy by increasing the mobility of the platinum on the carbon support. Once in contact with the cobalt hydroxide, conversion to the alloy is thermodynamically favorable.

The observed XPS binding energies for platinum in all cases showed a shift of 0.25 eV above the expected value for metallic platinum. The cobalt in the bulk alloy demonstrated a metallic binding energy, while the spectra from the supported materials were too noisy to determine the chemical state for cobalt. The question as to whether electronic changes accompany alloying is still not answered as it is difficult to analyze the shift observed in the platinum in the absence of a determination of the chemical shifts for cobalt.

Ordering of the Pt-Co alloy occurred following heat

treatment at 700°C and 1200°C in Series A as indicated by the superlattice reflections observed from both samples. As mentioned above, the superlattice reflection intensity (due to an orderly replacement of Pt atoms at the fcc corners with Co atoms) should be 10% of the fundamental reflections assuming complete ordering [18]. At less than complete ordering the intensity of superlattice reflections decreases as the square of the decrease of ordering. Based on tabulated lattice parameter values for various Pt/Co alloy compositions [19] the compositions of the Series A 900°C and 1200°C catalysts were 80 $\pm$ 2 at% platinum. From the Pt-Co phase diagram, 80 at% Pt is just within the boundary for an ordered Pt_3Co phase, which exists in a narrow composition range centered at 75 at% Pt [20]. The presence of superlattice reflections in our catalyst samples at 80 $\pm$ 2 at% Pt are, therefore, reasonably consistent with the bulk alloy phase diagram and reflects the thermodynamic favorability of the ordered state in this alloy system.

The XRD analyses summarized in Table 1 showed that for Series A catalyst the evolution for the ordered alloy phase at 1200°C passed through a two-phase region at 900°C. In the two-phase state, one of these phases appears to be of the same composition as the ordered alloy but is disordered. Because x-ray diffraction is a volume-averaging technique, and because ordered phase diffract more strongly than disordered phases,

XRD analysis weights larger crystallites and ordered phases more heavily than smaller crystallites and disordered phases. It is possible, then that even the 1200°C sample is two-phase as well with some amount of disordered alloy second phase present but masked by stronger diffracted intensity from the ordered phase. This would account for the anomalous lattice parameter if we presume the disordered alloy phase is of lower Co content. Two-phase character would be consistent with the post-test XRD analyses, which indicated two-phases formed in the 1200°C sample <u>after</u> fuel cell testing. In each of the four tested catalysts, one phase had a lattice parameter close to ($\pm$ 0.1%) that for Pt_3Co, with the second phase being closer to pure Pt. It is known from the XRF results that a sizable fraction of the cobalt initially present was lost during fuel cell testing. From the known solubility of cobalt oxides in strong acids [14], loss of any unalloyed cobalt would be expected, but the XRD results suggest some cobalt was lost from the alloy phase(s) as well. The majority of cobalt remaining in the catalyst was as an alloy with a nominal composition of 75 at% (from the lattice parameter), suggesting that this alloy may have sufficient stability in PAFC cathodes to be of practical interest. The disappearance of superlattice lines suggests, however, that sufficient cobalt was lost from the ordered phase to drop the composition below the ordered phase boundary.

There does indeed appear to be a correlation between the structure and activity of the Pt-Co alloy. The highest electrocatalyst activity was observed from the catalyst which displayed the greatest alloy formation prior to the testing. The particle size of this catalyst was ca. four times greater than the pre-cursor Pt on carbon catalyst. Therefore, on an active surface area basis the Pt-Co alloy displays an activity at least four times greater than the pure platinum. Also, this same catalyst sustained the lowest cobalt depletion due to the aggressive phosphoric acid electrolyte. The loss of cobalt reported above was based on total cobalt observed, which may not represent the loss of cobalt from the alloy, as the XRF technique does not differentiate between alloyed and non-alloyed cobalt. Therefore, the cobalt which was lost could have come from non-alloyed cobalt remaining from the preparation, while the cobalt as alloy was stable to dissolution. The data did display the trend of greatest cobalt loss in samples alloyed to the least extent.

CONCLUSIONS

The formation of the Pt_3Co ordered alloy crystallites was observed in catalysts prepared by impregnation of a Pt/carbon catalyst with cobalt from both acidic and basic media. The acidic media was found to be superior to the basic media in

terms of alloy formationdue to the partial dissolution and redeposition of some of the Pt during the cobalt impregnation, i.e. resulting in Pt-Co co-deposition. Achieving physical contact between the cobalt phase and the Pt particles appears to limit the extent of alloying in these preparation procedures. Alloyed catalyst showed a higher activity than those which were predominantly pure Pt, with the catalyst having the greatest extent (as the fraction of Pt present) of alloying having the highest air cathode activity, on the order of four times greater than pure Pt. The stability of this alloy catalyst was also encouraging based on 48 hour test results. Further work is needed to identify the mechanism of catalytic by cobalt in PAFC cathodes.

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FIGURE CAPTIONS

Fig. 1. X-ray diffraction scan of Series A 1200°C specimen. Arrows indicate the position of the superlattice reflections.

Fig. 2. Cobalt K-edge EXAFS radial distribution plots from the Series B catalysts, demonstrating the conversion from Co-O species to Pt/Co alloy.

Fig. 3. Co K-edge EXAFS radial distribution plots for selected reference cobalt compounds.

Fig. 4. (311) X-ray diffraction line from the Series B 1200°C catalyst before and after electrochemical testing. Dashed line indicates expected peak location for pure platinum.

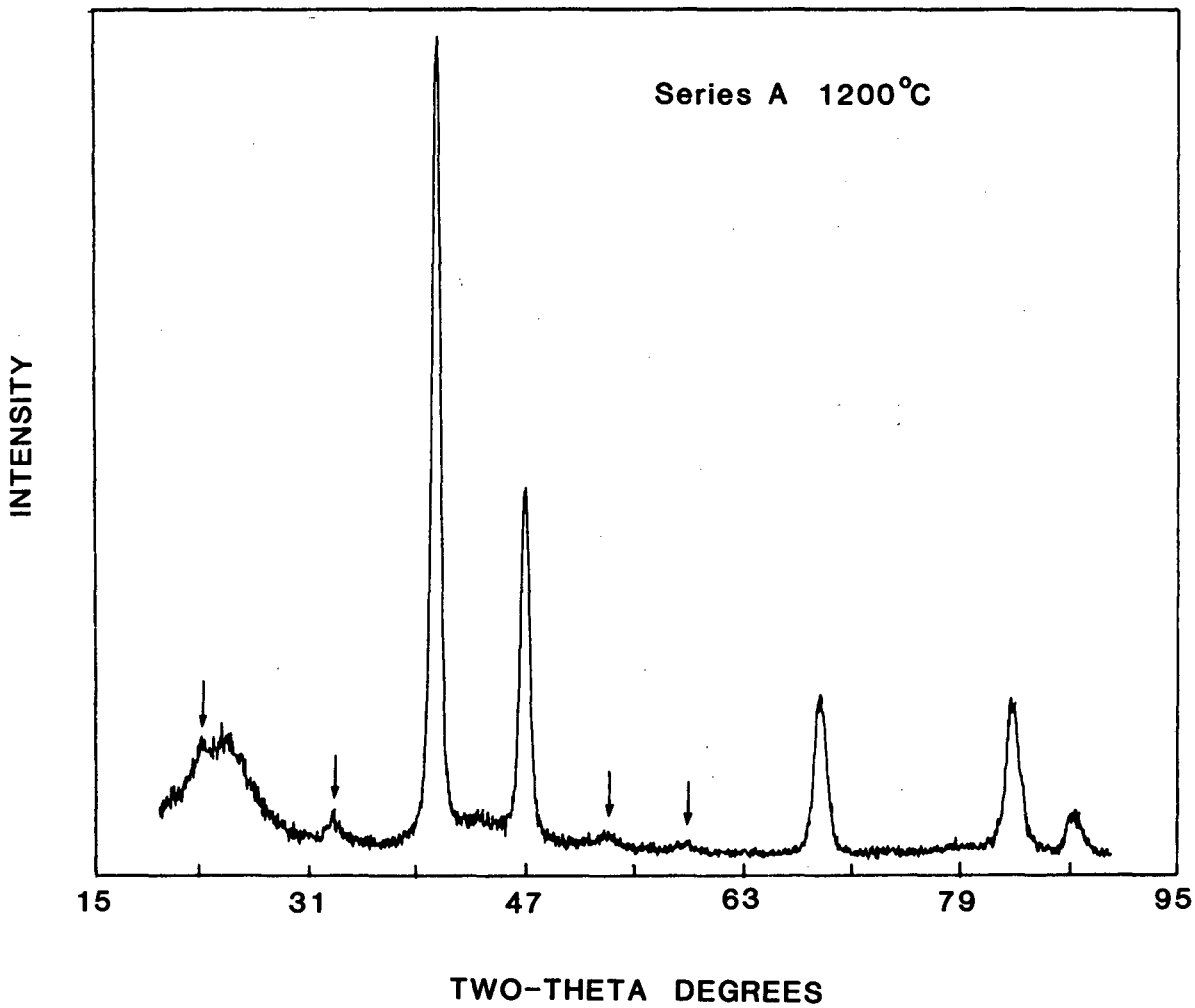

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Fig. 1

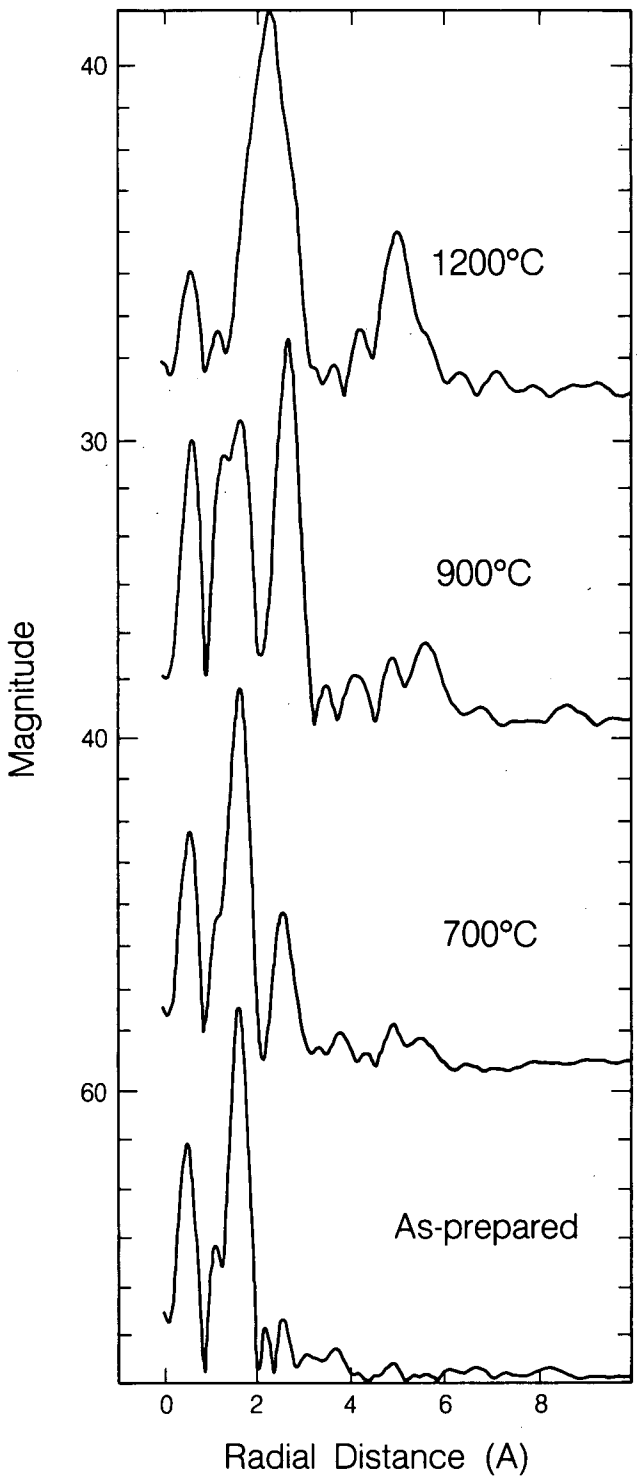

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Fig. 2

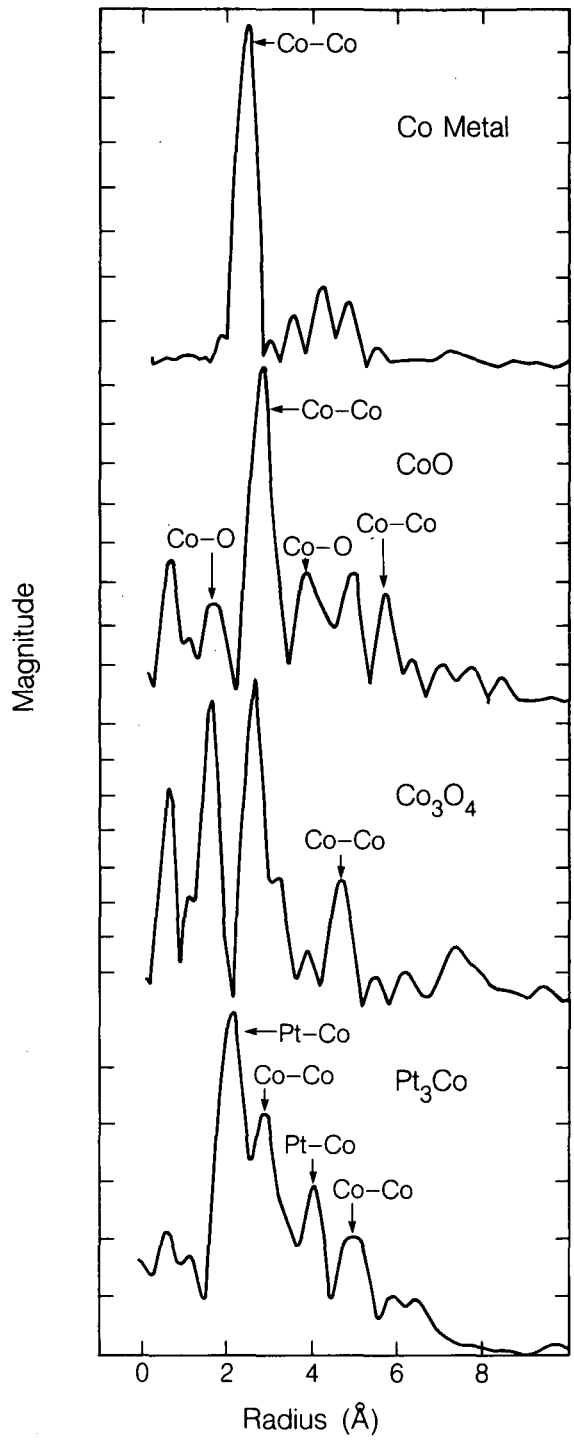

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Fig. 3

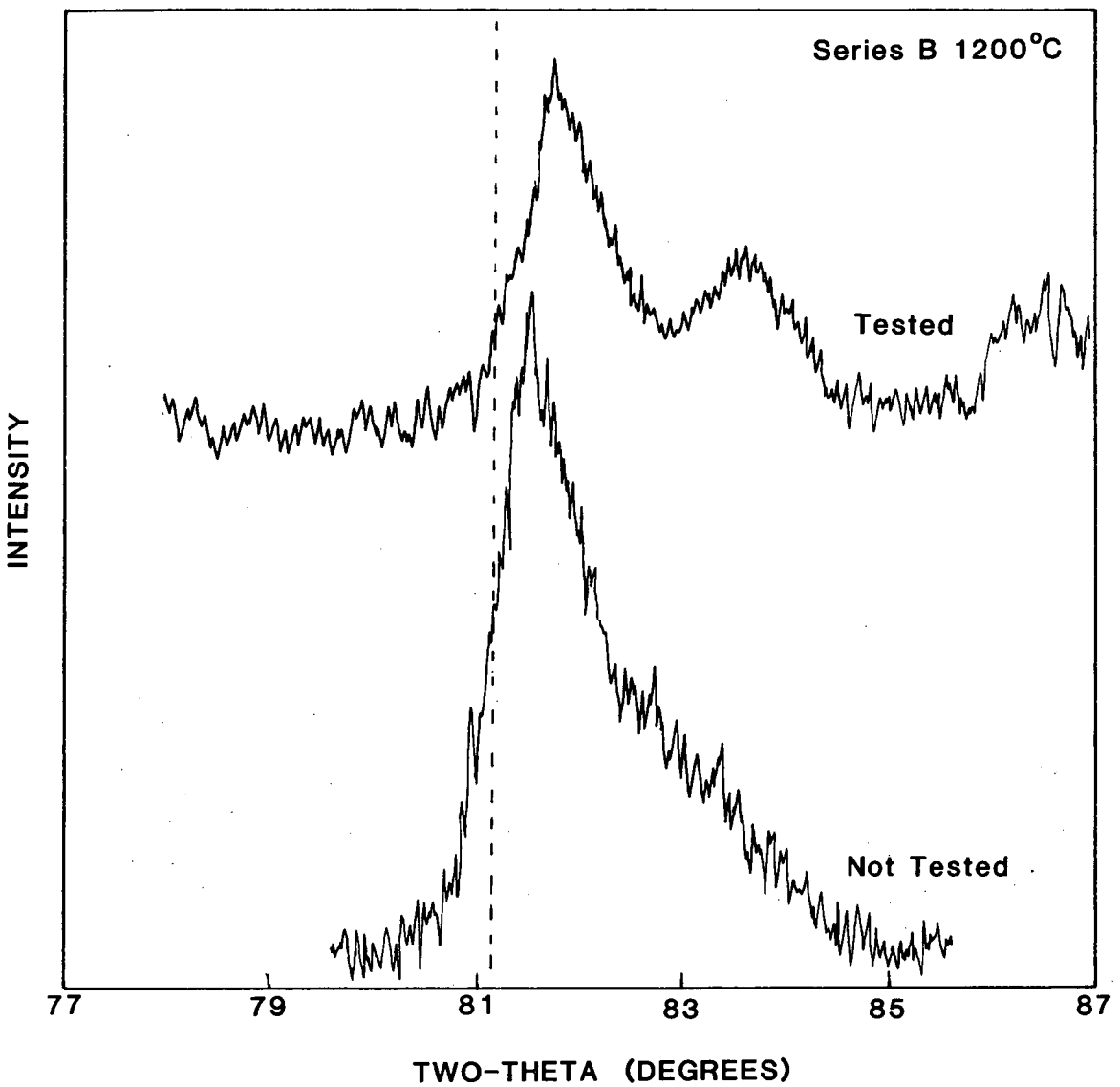

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Fig. 4

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