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TITLE Combined Electrochemical/Surface Science Investigations of Pt/Cr Alloy Electrodes

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COMBINED ELECTROCHEMICAL/SURFACE SCIENCE INVESTIGATIONS
OF Pt/Cr ALLOY ELECTRODES

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Chromium addition improves the performance of carbon-supported Pt electrodes for oxygen reduction in phosphoric acid fuel cells. To clarify the role of chromium and its chemical nature at the electrode surface, we have performed a combined electrochemical/surface science investigation of a series of bulk $Pt_xCr_{(1-x)}$ alloys ($0 \leq x \leq 1$). In this paper we report the surface characterization of the starting electrodes by XPS, electrochemical results from cyclic voltammetry in 85% phosphoric acid, and post-electrochemical surface characterization. For Cr contents less than 40%, the electrodes were quite stable up to +1.6 V vs DHE. The surface Cr was largely oxidized to Cr^{+3} for surfaces at open circuit and those exposed at potentials < +1.4 V. For intermediate Cr levels, Cr was leached from the surface region by +1.5 V, leaving a porous Pt electrode with increased electrochemical hydrogen adsorption capacity. For $Pt_{0.2}Cr_{0.8}$, treatments at +1.4 V and above led to the appearance of Pt^{4+} and Cr^{6+} species, apparently stabilized in a porous phosphate overlayer up to 50 Å thick. The Pt electrochemical hydrogen adsorption capacity was simultaneously increased by a factor of 15.

I. INTRODUCTION

Altering the surface chemical properties of a noble metal by alloying with another transition metal has been an active area of research for both electro-chemists [1] and surface scientists [2]. Specifically, supported PtCr alloys have drawn considerable interest [3] as electrocatalysts possessing superior performance to pure Pt for oxygen reduction in the phosphoric acid fuel cell. Among the several explanations for the reported [3] enhanced electrocatalytic activity of PtCr alloys for O_2 reduction are a decrease in the bulk lattice constant [4], the presence of a reactive species not found on pure Pt, and simply increased Pt surface area. Thus, this system is interesting from both a fundamental and practical point of view. In this work we present preliminary results correlating electrochemical properties of bulk PtCr alloys with their surface composition as revealed by electron spectroscopies. A full presenta-tion of these results including similar studies made in H_2SO_4 appear elsewhere [5].

II. EXPERIMENTAL

The PtCr alloys were made by arc melting a mixture of the pure elements (5N pure) in an Ar atmosphere. Samples were spark cut, polished on one side with diamond polish to a mirror finish, and ultrasonically cleaned. For poten-tiostatic control, a Pt wire was spot welded to the back of the electrode, which was soaked in concentrated H_2SO_4 to remove any Cu left from spot welding. Electrochemical cycling was performed in a 30-mℓ Kel-F cell. The reference was a dynamic hydrogen electrode, ~+0.040 V vs RHE [6]. All potentials are quoted with respect to DHE.

Electronic grade 85% H_3PO_4 was treated with H_2O_2 to remove oxidizable impurities [7]. Prior to electrochemical measurements the solution was degassed with ultra-high purity argon. Usually 50 cycles were made between +0.04 V and the desired upper limit and the potential brought to +0.40 V (double layer region) before removing from potentiostatic control. The electrode was immediately removed from solution and washed with pure water in an ultrasonic cleaner. The samples were then ultrasonically cleaned in absolute ethanol, and placed in the vacuum chamber for analysis.

X-ray photoelectron spectroscopy (XPS) was performed in a Leybold-Hereaus apparatus described previously [8], using a Mg-Kα X-ray source. Spectra were collected at 100 eV pass energy, referenced to a Ag $3d_{5/2}$ peak at 367.91 eV binding energy (B.E.) for pure Ag, with a full width at half maximum (FWHM) of 1.67 eV. All spectra were referenced to the Fermi level of the sample. Sputter cleaning was achieved with a 3 kV Ar^+ ion beam.

III. RESULTS

III.1. Characterization of Polished PtCr Alloys

To ascertain whether the surface of the alloys is representative of the bulk, XPS spectra of Pt(4f) and Cr(2p) regions were recorded for each alloy as well as for pure Pt and Cr. Figure 1 shows spectra for polished samples that have been briefly (<5 min) sputtered clean with Ar^+ ions to remove surface contamination. Spectra for unsputtered samples were also recorded; peak intensities were decreased due to surface contamination (C,O) and significant amounts of Cr oxide were observed in the Cr(2p) XPS region. From the areas (I) under the Pt and Cr peaks the atomic ratios of Cr/Pt could be obtained for both unsputtered and clean alloys:

$$Cr/Pt = S(I_{Cr}/I_{Pt}) \quad , \tag{1}$$

where S is the scaling ratio chosen to best fit this data. It's value agrees
within 25% of the value predicted from the bulk XPS signals (I°) for clean,
pure Pt and Cr:

$$S = (I^\circ_{Pt}/I^\circ_{Cr}) \times (\rho^\circ_{Cr}/\rho^\circ_{Pt}) \quad , \tag{2}$$

where ρ° is the bulk atomic density of the pure element. The results are shown
in Fig. 2. The surface composition in both sputtered and unsputtered samples
corresponds well with the bulk. Thus, neither Pt nor Cr surface segregates in
these alloys even under air oxidation at room temperature [9], and there is no
evidence of significant selective sputtering of either element.

An interesting consequence of alloying is the smooth increase in Pt(4f)
binding energy as the Cr content increases (Fig. 2), explained below on the
basis of final state effects. The Cr(2p) B.E. sharply decreases from the lean-
est Cr alloy, $Pt_{0.9}Cr_{0.1}$. As could be seen in Fig. 1, this alloy showed a very
broad Cr(2p) peak which included signal from oxidized Cr (Cr_2O_3 at 576.4 eV)
even after 10 min sputtering in vacuum. We feel this is due to minor oxygen
impurities even at significant depths in this alloy (probably present at grain
boundaries).

III.2. Electrochemical Results: Cyclic Voltammetry

Our electrochemical results are presented elsewhere in detail [5]. In
summary, for all the alloys, repeated cycling up to +1.4 V in 85% phosphoric
acid led to no dramatic changes in peak shapes or areas in cyclic voltammetry,
except such as would be expected from the usual surface cleanup. For alloys

with Cr content <50%, this was also true up to +1.6 V. However, marked in-
creases in the Pt-related voltammetric peak areas resulted from cycling the
$Pt_{0.5}Cr_{0.5}$ and $Pt_{0.2}Cr_{0.8}$ alloys to $\geq$+1.5 V. The amount of this increase grew
with the cycling voltage, the number of cycles, and with Cr content. After 50
cycles to +1.6 V, the $Pt_{0.2}Cr_{0.8}$ alloy showed Pt-related features for hydrogen
adsorption which were 15 times larger than those expected for a smooth surface
of this composition. The lineshapes, however, were very similar to those
obtained pure Pt voltammetry. The use of these hydrogen adsorption peaks to
assess surface area of Pt electrodes has been described [10]. We interpret
this increase in voltammetric charge as due to a large increase in Pt surface
area, related to significant structural changes in the surface of the alloy as
discussed below. More specific details of the voltammetric peak shapes are de-
scribed elsewhere [5].

III.3. Surface Characterization of the Electrochemically Treated Alloys

In order to assess the effect of electrochemical treatment of these
alloys, it was necessary to examine the effect on surface composition of both
the electrolyte solution and the atmosphere to which the alloys were exposed.
In Fig. 3 selected Cr(2p) XPS spectra are presented for $Pt_{0.5}Cr_{0.5}$ subjected to
a variety of treatments. Surface Cr is easily air oxidized, as evident from
the large peak at 576.4 eV characteristic of Cr^{3+} [11], consistent with previ-
ous observations [12]. Immersing the alloy in H_3PO_4 for 52 min without any
potentiostatic control (i.e., at open circuit) also produces significant Cr^{3+}.
The Cr signal has diminished due to the presence of P and O in the surface (as
seen by XPS) which we interpret as incorporated phosphate species. Thus, it is

clear that Cr^{3+} is present on the surface of the alloy before any electro-chemical measurements even begin. On the other hand, the Pt(4f) B.E. remains unchanged from its metallic state [13]. This result was found for all alloys and pure metals.

In electrochemically cycling the $Pt_{0.5}Cr_{0.5}$ alloy between +0.040 and +1.0 V, the extent of surface oxidation of Cr does not change, although some loss of Cr is already observed (Fig. 3). Upon cycling up to +1.4 V, the Cr(2p) intensity characteristic of the Cr^{3+} state diminishes strongly so that very little oxidized Cr remains in the surface region (Fig. 3) and the Pt/Cr atomic ratio is increased to 2.6 times the bulk value. We conclude that the oxidized Cr is leached from the electrode and transferred to solution. In the case of H_2SO_4, this was confirmed by chemical analysis of the solution [5]. Appar-ently, the remaining Cr is shielded from oxidation by solution or by ai with a surrounding snell of Pt atoms. This loss of Cr is even more dramatic when the electrode is cycled to +1.6 V, giving a Pt/Cr atomic ratio of 7.2 from XPS intensities (compared to its bulk value of 1.0). The $Pt_{0.2}Cr_{0.8}$ alloy behaves differently and will be discussed below. The two lower Cr content alloys also show a loss of Cr^{3+} XPS signal when cycled to +1.6 V, but enough Cr° is left (protected by the Pt matrix) that the Pt/Cr ratio never exceeds 8 times the bulk value.

The depth of the chemically affected region is estimated by the (cali-brated) sputtering time required to bring the Pt/Cr XPS ratio back to its bulk value. By this criterion, the $Pt_{0.5}Cr_{0.5}$ alloy is depleted of Cr to only 80 Å when cycled to +1.6 V in H_3PO_4, compared to a 210 Å affected layer for $Pt_{0.2}Cr_{0.8}$. Results in H_2SO_4 show that Cr depletion depths calculated this way agree with those calculated from the amount of Cr found in solution [5].

The behavior of $Pt_{0.2}Cr_{0.8}$ when cycled to high positive potentials is unique among these alloys. In general it is observed [5] that the oxidation state of Pt does not change greatly with electrochemical treatment. At most, in samples cycled to high positive potentials, the Pt(4f) B.E. falls a few tenths of an eV, consistent with the loss of Cr and the corresponding shift in the metallic Pt level as per Figs. 1 and 2. However, when $Pt_{0.2}Cr_{0.8}$ is cycled to +1.6 V, a new Pt(4f) signal appears at 74.6 eV B.E., characteristic of Pt^{4+}, as shown in Fig. 4 [13,14]. The appearance of such highly oxidized Pt was unique to this alloy for cycling to +1.6 V. Thus, it appears that the high chromium content in some way catalyzes the formation of Pt^{4+}. Note that Pt^{4+} has also appeared when a pure Pt electrode was held at +2.0 V vs SHE or higher in 1N H_2SO_4 [14]. In that case, careful analysis indicated that Pt^{4+} was present as an hydroxide, $Pt(OH)_4$ [14]. We have no reason to change this interpretation for the Pt/Cr alloys, but only to point out that Pt^{4+} appears at much lower voltages here.

To compare directly with these experiments, the $Pt_{0.2}Cr_{0.8}$ alloy was treated using the same procedure, i.e., the alloy was first cycled 5 times to the upper voltage limit, then held there for 15 min, and removed from solution at that voltage under potentiostatic control. (The sample was then washed as usual.) The only difference here is in our solution, 85% H_3PO_4 instead of 1N H_2SO_4. The results are shown in Fig. 4. Already at +1.4 V, the Pt^{4+} peak has appeared, and it predominates by +1.6 V. Since increasing pH will only destabilize the oxidized states of Pt [15], we can conclude that alloying with 80% Cr decreases the potential for generation of Pt^{4+} surface species by about 0.6 V.

In addition to this interesting property of the $Pt_{0.2}Cr_{0.8}$ alloy, there was no significant decrease in the Cr/Pt XPS ratio upon electrochemical treatments up to +1.6 V in H_3PO_4; although, absolute signal intensity did decrease (Fig. 4). Moreover, for treatments to +1.6 V, which led to the massive appearance of Pt^{4+} species, the entire metal-like Cr(2p) intensity had been converted to a peak at 577.5 eV B.E. (Fig. 4). This value exceeds that for Cr_2O_3 (576.6 eV), and is closer to that expected for CrO_3 (578.1 eV) [11]. The appearance of a Cr^{6+} species may be correlated with the large onset of anodic current at >+1.5 eV in the cyclic voltammetry of this alloy [5]. A similar onset for pure Cr has been shown to be due to the breakdown of the transpassive Cr^{3+} oxide layer and the massive appearance of Cr^{6+} ions in solution [11]. The $Pt_{0.2}Cr_{0.8}$ electrode and electrolyte solution also showed a distinct yellowish tint, characteristic again of a Cr^{6+} species. Nevertheless, the surface Cr/Pt ratio indicates no selective loss of Cr from the surface region, and is associated with the presence of Cr^{6+} and Pt^{4+} species. Such behavior was not observed in sulfuric acid solutions.

One further feature that can be correlated with the appearance of Pt^{4+} and Cr^{6+} species after cycling to +1.6 V is the simultaneous growth in XPS intensity for phosphorus and oxygen transitions. Using tabulated XPS sensitivity factors [13a], we calculate a stoichiometry of $\sim PO_{4.8}$ from the P/O XPS ratio. This is in reasonable agreement with that of a phosphate species, PO_4^{3-}. We feel that the reason Cr does not appear by XPS to be selectively lost from the surface of these alloys upon cycling is that it is somehow complexed by this phosphate species and an equilibrium is established between solution and surface Cr species. Furthermore, this phosphate seems to form a porous film on the surface, since the Pt and Cr XPS features are severely attenuated by its

presence. The extent of attenuation for the $Pt_{0.2}Cr_{0.8}$ alloy after +1.6 V cycling would indicate a layer ~50 Å thick. Note that this film is not rinsed off by ultrasonic cleaning in water, which indicates something more than a residue from the solution. In addition, the film is electrochemically permeable, as evidenced by the large Pt-related peaks in the cyclic voltammetry. It is Pt metal, not Pt^{4+} that gives the peaks observed; therefore, the electrochemistry samples an area below the region accessed by XPS, which sees only Pt^{4+}.

IV. DISCUSSION

The smooth increase in Pt(4f) B.E. with increasing Cr content for the clean alloys is somewhat hard to understand. The relative electropositivity of Cr would predict charge transfer to the Pt, which would cause an opposite shift in the initial state for the photoemission process. The shift can, however, be understood on the basis of final state effects. Shirley et al. [16] have addressed the differences in core level binding energies across the transition metal series for the bulk metal minus that of the free gaseous atom. These trends are understandable in terms of a final state effect, where the additional neighbors in the solid state help to screen the final state core hole. The greater the polarizability of the metal, the greater this difference. Thus Pt shows a very large difference. Chromium shows an anomalously small difference due to the unusual stability of the d^5 configuration. Thus adding Cr to Pt will reduce the extent of final state screening and lead to an increase in the Pt core level B.E.; and vice versa. These trends are seen in Figs. 1 and

2, and point to the importance of final state effects in understanding core-level spectra of alloys. For the 10%-Cr alloy, significant oxidation of the Cr is maintained even in the sputtered sample, giving an anomalously large $Cr(2p_{3/2})$ B.E.

An interesting point of our results is the fact that high Cr levels seem to catalyze the oxidation of Pt to Pt^{4+}. The appearance of Cr^{6+} is undoubtedly important since it is easily obtained at $>+1.4$ V [12], and is known to oxidize Pt to Pt^{4+} oxide (PtO_2 or $Pt(OH)_4$) [17]. Since bulk Pt is not oxidized electrochemically to Pt^{4+} until $+2.0$ V [14], the catalytic action of Cr (or Cr^{6+}) may be due to its proximity to Pt atoms which have few Pt neighbors in the alloy structure. Due to the relative ease of oxidation of both dispersed Pt and Cr, and the possibility for oxygen sharing by Pt and Cr, such Pt is likely to be more easily oxidized than bulk Pt. A role of the phosphate may be to complex Cr^{6+} oxides and make them less soluble in the concentrated phosphoric acid solutions thus holding them at the surface to oxidize or capture Pt. These complexed ions are ionic conductors, as the H_3PO_4 itself is; this allows electrochemical access to fresh electrode beneath the layer. Below the region sampled by XPS, there must be increased Pt° surface area, as evidenced by the increase in cyclic voltammetric peaks. This increase in exposed Pt° atoms may be due to the general lattice breakup caused by Cr oxidation.

The increase in Pt surface area may be the main explanation for the role of Cr in supported electrocatalysts for the oxygen reduction reaction in fuel cells. Indeed, studies on the O_2 reduction kinetics made on these same alloys indicated no increase in activity per surface Pt atom for any of the alloys compared to pure Pt [18]. The O_2 reduction reaction is usually run at $+0.9$ V,

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far below the potentials where the massive Pt area increase occurred in our one hour experiments. However, fuel cell electrodes contain very finely divided metal which may be thermodynamically easier to oxidize than bulk metal (this is implied in the oxidation of Pt in $Pt_{0.2}Cr_{0.8}$), and over thousands of hours the same increase in Pt surface area may be observed at lower potentials. As for more fundamental explanations, we point out that the surface chromium always appears to be largely oxidized. Thus, the system can hardly be described in terms of the bulk properties of the alloys, as has been attempted in the past [4]. It is more reasonable to consider the influence of Cr_2O_3 on the Pt, rather than that of metallic chromium.

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FIGURE CAPTIONS

1. Pt(4f) and Cr(2p) regions of the XPS spectra for polished and sputter cleaned alloys: A) pure Pt; B) $Pt_{0.9}Cr_{0.1}$;
    c) $Pt_{0.65}Cr_{0.35}$; D) $Pt_{0.5}Cr_{0.5}$; E) $Pt_{0.2}Cr_{0.8}$; F) pure Cr.

2. a) Cr/Pt atomic ratios obtained from XPS peak intensities for the alloys and pure elements.
    b) Binding energies for $Pt(4f_{7/2})$ and $Cr(2p_{3/2})$ on sputtered clean alloys and pure elements, from data in Fig. 1.

3. XPS spectra of $Pt_{0.5}Cr_{0.5}$ Cr(2p) region after sputter cleaning, air oxidation, exposure to H_3PO_4 solution, and electrochemical cycling. Peak positions for Cr metal (574.1 eV) and Cr_2O_3 (576.4 eV) are indicated by arrows. [11].

4. XPS spectra of Pt(4f) and Cr(2p) regions for $Pt_{0.2}Cr_{0.8}$ electrochemically treated in 85% H_3PO_4. The sample cycled to +1.6 V 50 times was removed at +0.40 V; the samples held at +1.4 V and +1.6 V were removed under potentiostatic control at those potentials while being rinsed with fresh H_3PO_4.
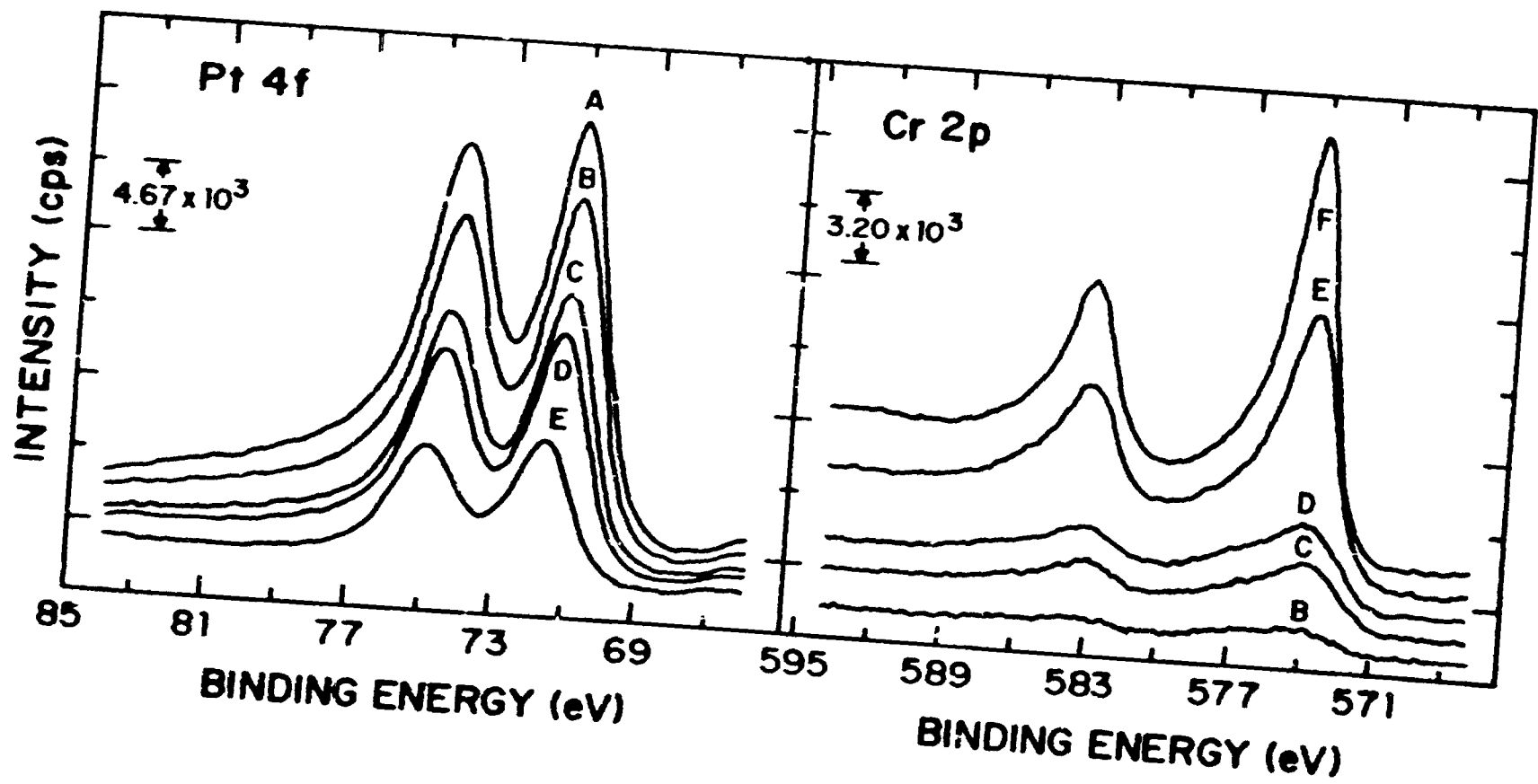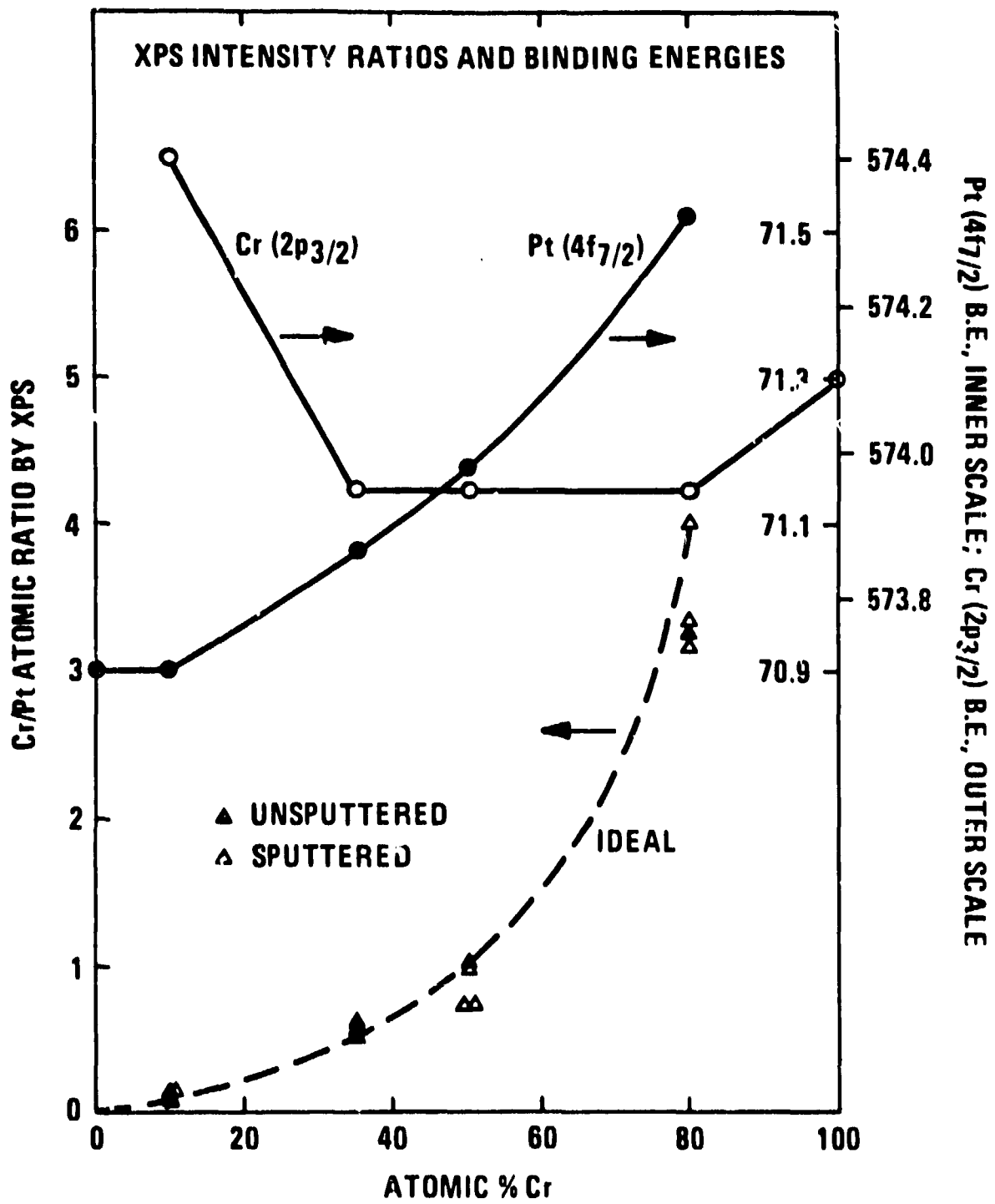
Fig. 1

CHM-VG-8069

Fig. 2.

Cr (2p) REGION OF $Pt_{0.5} Cr_{0.5}$

Cr METAL

Cr_2O_3

SPUTTERED CLEAN

4.67×10^2

AIR, 2 MIN.

SOL'N, 52 MIN.

+1.0 V

+1.4 V

+1.6 V

INTENSITY (cps)

591   586   581   576   571   566
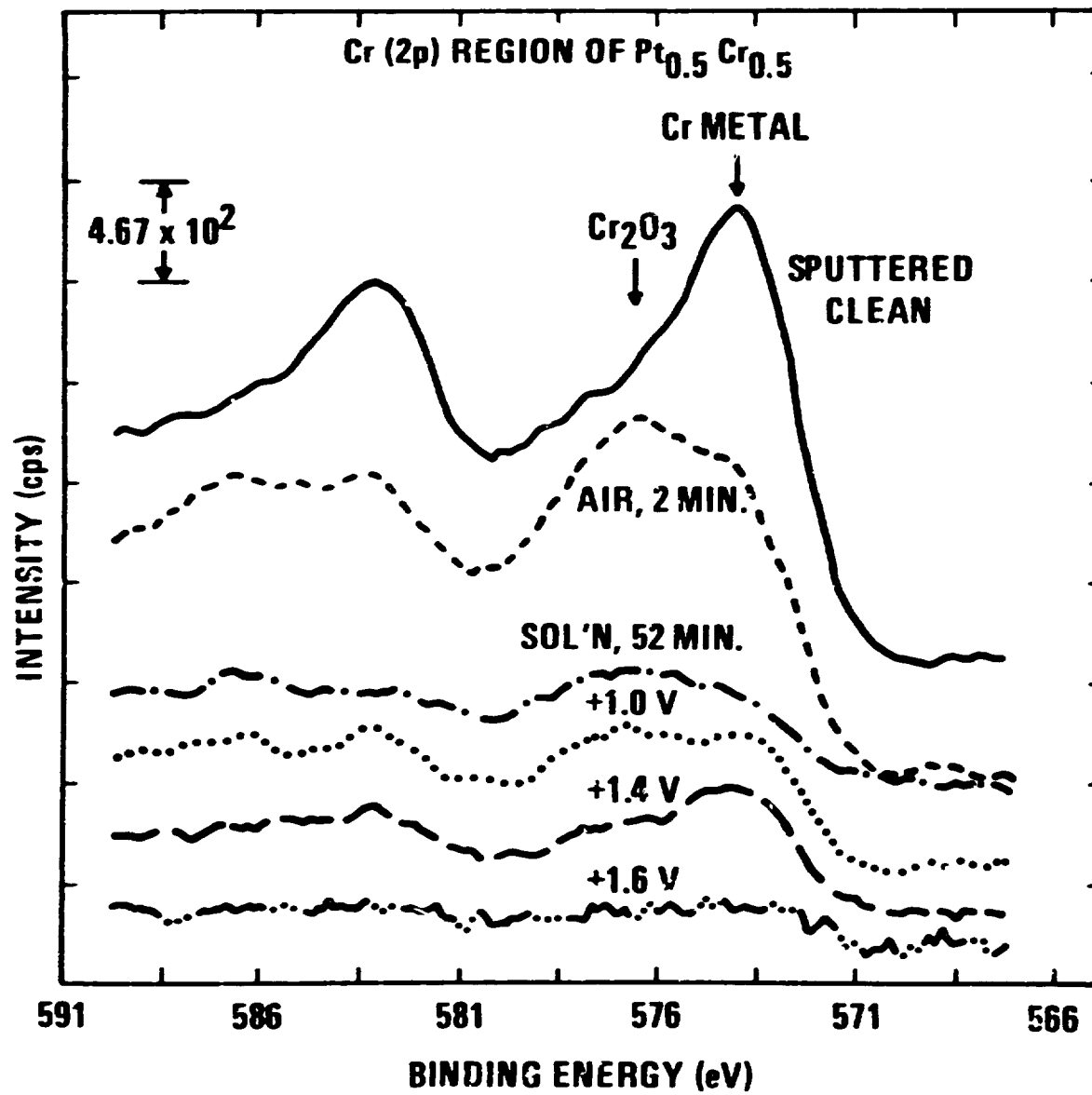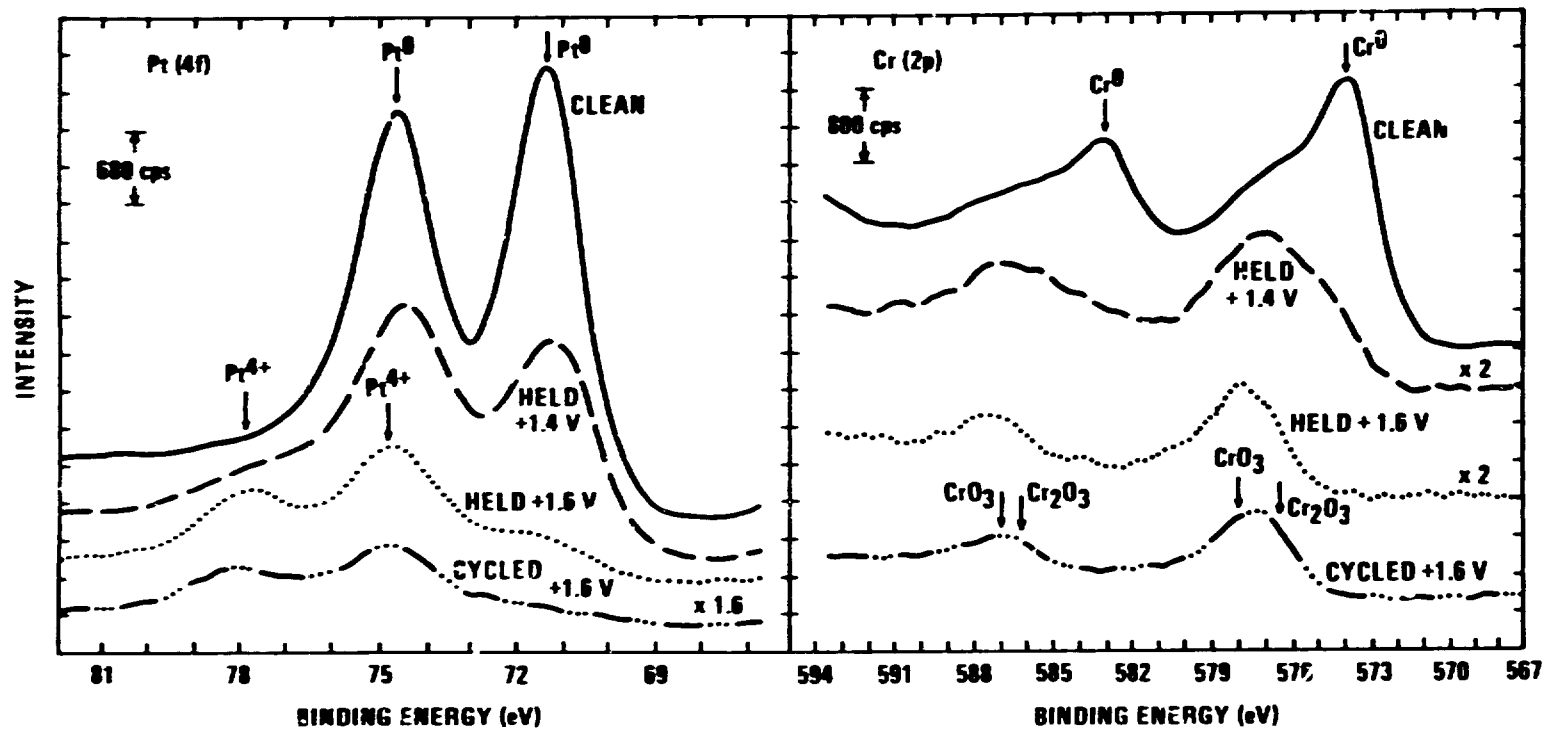
BINDING ENERGY (eV)

Fig. 3

Fig. 4

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