Surface Composition of Pd Cathodes

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Abstract

Results will be presented for the surface analyses of cathodes before and after electrolysis using X-ray Photoelectron Spectroscopy (XPS). Composition as a function of depth was obtained by employing argon ion sputtering to gradually erode away the surface. Although most of the emphasis will be on Naval Research Laboratory (NRL) Pd (i.e., Johnson Matthey high purity sponge processed into rod and plate at NRL), data will also be presented from other Pd sources and from reported excess heat-producing cathodes provided by SRI International and NAWC, Naval Air Warfare Center at China Lake, CA. XPS results will be compared with bulk sample cathode and anode analyses obtained by Glow Discharge Mass Spectroscopy (GDMS) and with electrolyte solution analyses obtained by Inductively Coupled Plasma (ICP) Spectroscopy.

Introduction

Impurities on the cathode surface are expected to exert an influence on the ability of cathodes to attain D(H)/Pd ratios near unity and to retain this high loading for the time required to obtain excess heat. For example, Pd (and Pt) are the most efficient electrocatalysts for promoting reduction of D_2O and H_2O to form D_2 and H_2. The presence of other impurities would reduce the rate of this reaction (depending on the impurity, this could amount to many orders of magnitude). In addition, the ability to promote the dissociation of D_2 to form an adsorbed deuterium atom (D) and, subsequently absorbed D, could be reduced by the presence of surface and bulk impurities. The presence of Pt, a common contaminant found in Pd, could also be deleterious to obtaining high loadings since Pt is also an excellent recombination catalyst for the reaction: $D_{ads} + D_{ads} = D_2$. Since absorbed D is known to occupy interstitial positions within the Pd lattice, impurities, especially those of the lighter elements, can block these positions. For example, C atoms can penetrate into the Pd lattice if exposed to C-containing gases at moderate temperatures[1] (as might occur during processing). Interstitial solid solutions up to PdC_{015} can form which can totally block the formation of β-PdH which develops at H/Pd = 0.65 and is a precursor phase to the attainment of high loading. B, which also enters the Pd lattice interstitially, is known to totally block β-Pd-H formation at a concentration of 16 atomic%[2]. Blockage of H atom ingress by the presence of high concentrations of C and B in the Pd lattice could also be caused by the formation of carbides and borides of Pd. B, at concentrations less than 10 at.% where borides do not form as indicated by the Pd-B binary phase diagram, will promote H absorption due to the expansion of the Pd lattice caused by the presence of B[3]. Thus, smaller amounts of interstitial impurities could actually exert a positive influence on the attainment of high loadings.

Experimental

The XPS spectra were recorded with a Surface Science Laboratories Model SSX-301 system utilizing a monochromatic A1 Kα source. Survey scans from 0 to 1000 eV binding energy were recorded at a 100 eV pass energy. Sputtering was accomplished with a Perkin Elmer differentially pumped ion gun utilizing 3 kV argon ion beam at 20 mA emission current and a 3x3 raster. Base pressure of the main chamber and fast entry chamber was $1x10^{-9}$ torr and $1x10^{-7}$ torr, respectively. In order to preserve the vacuum in the main chamber on occasion it was necessary to pump on the sample in the fast entry chamber overnight to remove the remaining absorbed D or H. A description of each sample examined can be found in the text and figure captions. A complete description of sample processing and electrochemical history can be obtained from the authors.

Results and Discussion

XPS of Unused Cathodes

A survey spectrum of a Johnson-Matthey 99.9% purity wire as received is shown in Figure 1A. Even though the Pd 3d doublet is clearly visible the surface is composed mostly of carbon and oxygen due to the large difference in peak area sensitivity factors ($Pd3d_{5/2}$=9.48, C1s=1.00, O1s=2.93). Si, Cl and Mg are also present but to a much lesser extent than C and O. This is a representative spectrum for all cathode materials examined which included NRL Pd and Pd-B rod, Engelhardt #3 and Johnson-Matthey 'special batch' rods from SRI, Goodfellow 99.95% and 99.99+% wire, and Johnson-Matthey 99.9% and 99.997% wire. In all cases the principal contaminants were always C and O and the Pd 3d doublet was always visible. The Cls peak was in all cases anywhere from approximately ½ to double the height of the Pd 3d doublet. This puts the contamination level of all surfaces easily in excess of 50 at.%. Other minor contaminants found included S and Na. On the surface most of the elements as determined from their binding energy were in the oxidized state except for C which appeared to be graphitic (B.E.=284.0eV). Sample preparation such as vacuum annealing and acid etching in aqua regia did not appear to significantly alter the surface composition. These data illustrate the ability of the Pd surface to become significantly contaminated upon exposure to air and water.

Most of the contamination observed in Fig. 1A is found to reside in approximately the top 10Å as illustrated in the survey shown in Fig. 1B obtained after a 10s argon ion sputter (sputter rate 1Å/s for SiO_2). Most of the original C and O have been removed and the Pd peaks now dominate the spectrum. An additional 20s sputter produces a further reduction in contaminant levels (see Figure 1C) although the effect is not as dramatic as that observed with the initial 10s sputter. Figures 1B and C also indicate the presence of Pt in this sample. This agrees with the GDMS results for this material which showed the presence of 1100 ppm Pt impurities. In the samples sputtered for longer than 30s, all the impurities were removed except for C (and Pt for 99.9% purity Pd). C would persist to the deepest levels indicating that it either was a bulk contaminant or that it diffused from the surface to the bulk during processing.

XPS of Used, Non-heat Producing Cathodes

The data for NRL-processed Pd cathodes is divided into two groups based on the XPS results. The first group comprises the thickest overlayers containing large concentrations of both Cu and Pt relative to Pd. The Cu and Pt can either be near the surface or buried under a silicate-containing overlayer. All of these samples were electrolyzed for approximately 1000 hrs. The second set of samples all contained thinner overlayers than the first with very little Cu. A high Pt concentration, however, was found on all of these samples. These samples were all electrolyzed for 500 hrs. or less and they received a large number (6) of cathodic-anodic current reversals.

Figure 2 is a series of survey spectra taken from the surface and various depths of an NRL Pd plate electrode. The following elements are found at the surface: Si, O, C, Cu, Nb, Pt, Zn, Na, Mg and Ca. The Zn, Mg, Ca and Na appear to be ubiquitous in small quantities to nearly all the samples examined by XPS. Several examples of much higher Ca concentrations also have been found. ICP analysis of the D_2O and the LiOD electrolyte before and after electrolysis show the presence of Na and Ca (before electrolysis: 0.00-0.07 ppm Ca, 0.01-0.30 ppm Na; after electrolysis: 0.00-0.18 ppm Ca, 0.16-2.53 ppm Na). No Zn or Mg above 0.01 ppm, however, was observed in any solution making their source uncertain. Nb is found on all samples in which a Pt-clad Nb mesh was used as the anode. Nb is exposed to the electrolyte at all points where the material has been cut and at spot welds where damage to the Pt film can occur. The Cu (its potential source will be discussed later) is found to be in the +2 oxidation state as is indicated by the two sets of 3p doublets occurring between 930 and 970 eV. Due to their small area sensitivity factors, the major components of this surface are O, Si and C. Besides Cu (which has a sensitivity factor similar to that of Pd and Pt), the oxygen is also associated with both C, as evidenced by the small shoulder on the high binding energy side of the Cls peak, and Si. The binding energy of the Si peaks is indicative of the presence of a silicate-type species. The bulk of the C detected on the surface is merely the so-called 'adventitious' carbon contamination found on all air-exposed surfaces. No Pd is evident on the surface. In fact, Pd is not detected until after approximately 150s of sputtering and even then the Pd $3p_{3/2}$ peak is only a small shoulder on the Pt $3d_{3/2}$ peak. The Pd peak does not become easily discernible until somewhere between 360 and 600 seconds of sputter time. As sputtering proceeds both Cu and Pt, which were just observable on the surface, increase as the quantity of silicate species slowly decreases. The Cu and Pt reach a maximum after about 600s of sputter time and then decrease as the amount of Pd increases. After 1500s both Cu and Pt are still present which indicates that a relatively thick overlayer has grown on this electrode.
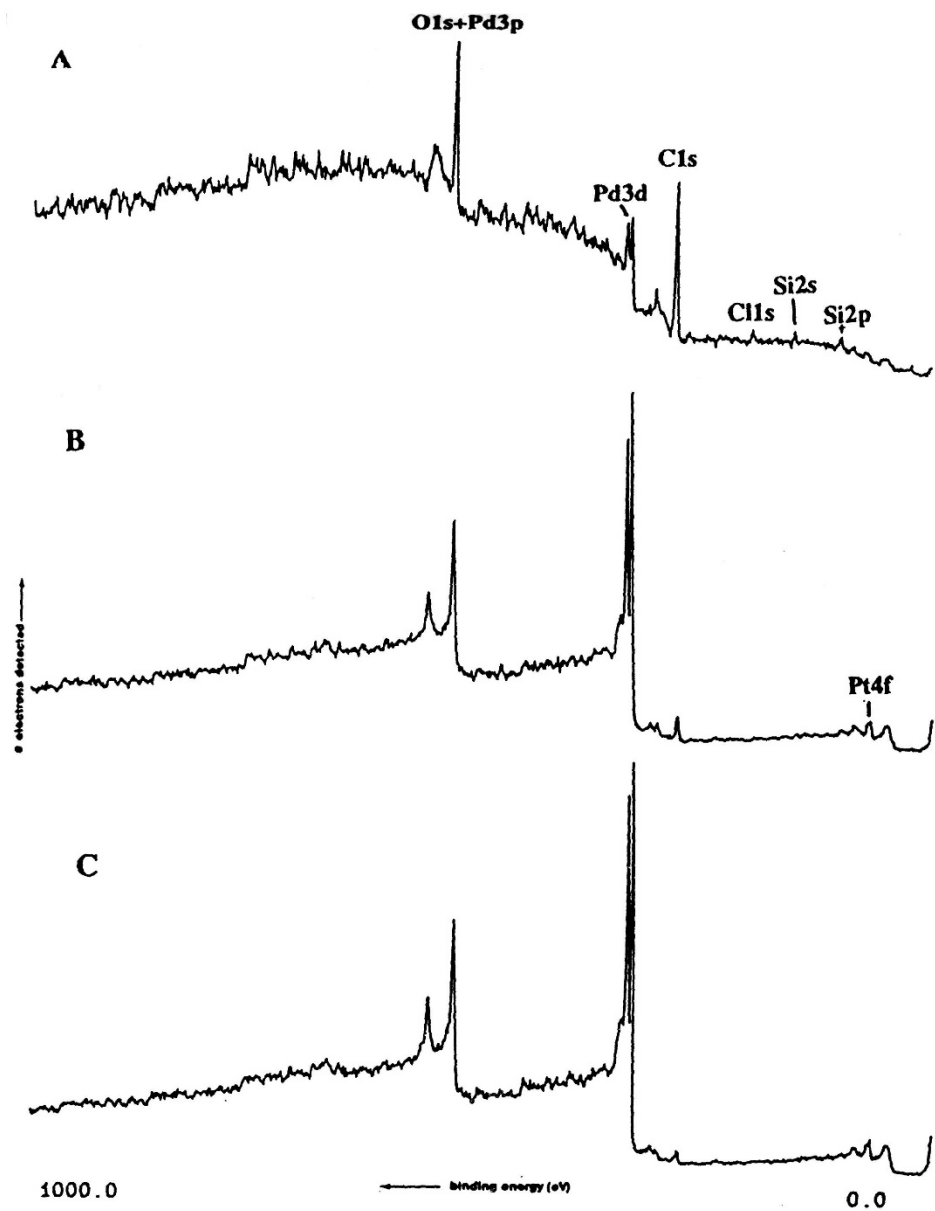
Figure 1. XPS survey spectra obtained from a 1-mm diameter Johnson Matthey 99.9% purity palladium wire (#010280, Lot K11C06). A: Surface, B: After 10-sec. sputter, see: After 30s sputter. Scans from 0 eV (right) to 1000 eV (left) binding energy.
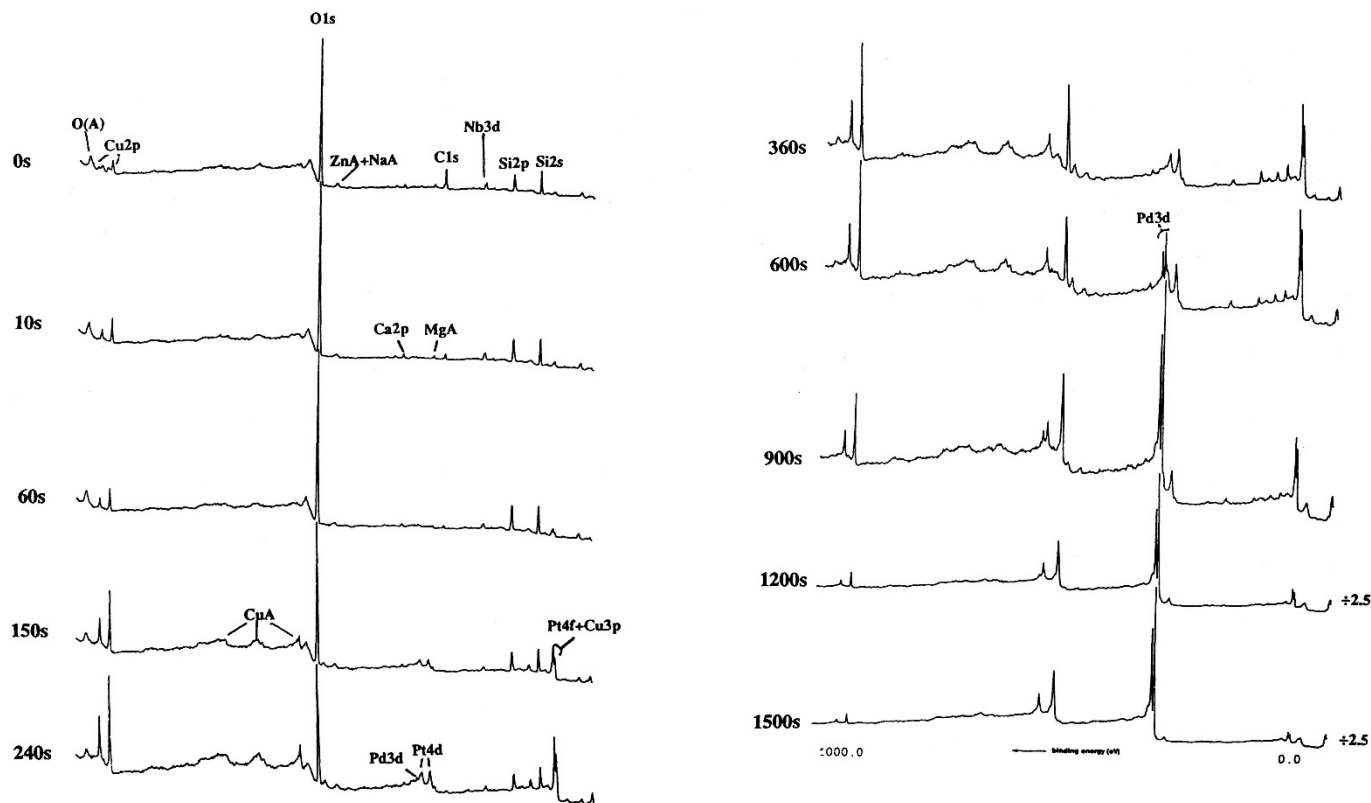
Figure 2. Series of XPS survey spectra obtained at various total sputter times from a large grain (600μm), 99.99% purity Pd plate cathode, 3.5x0.7x0.07cm thick, etched in aqua regia after spot-welding of Pt resistance wires using Pd/Pd-Ag welding tips, Pt-clad Nb mesh anode, pyrex cell, 0.1 M LiOD (Li from Johnson Matthey, D_2O from Ontario Hydro), 980 hrs. total electrolysis time, highest current density=370 mA/cm^2. Scans from 0 eV (right) to 1000 eV (left) binding energy.
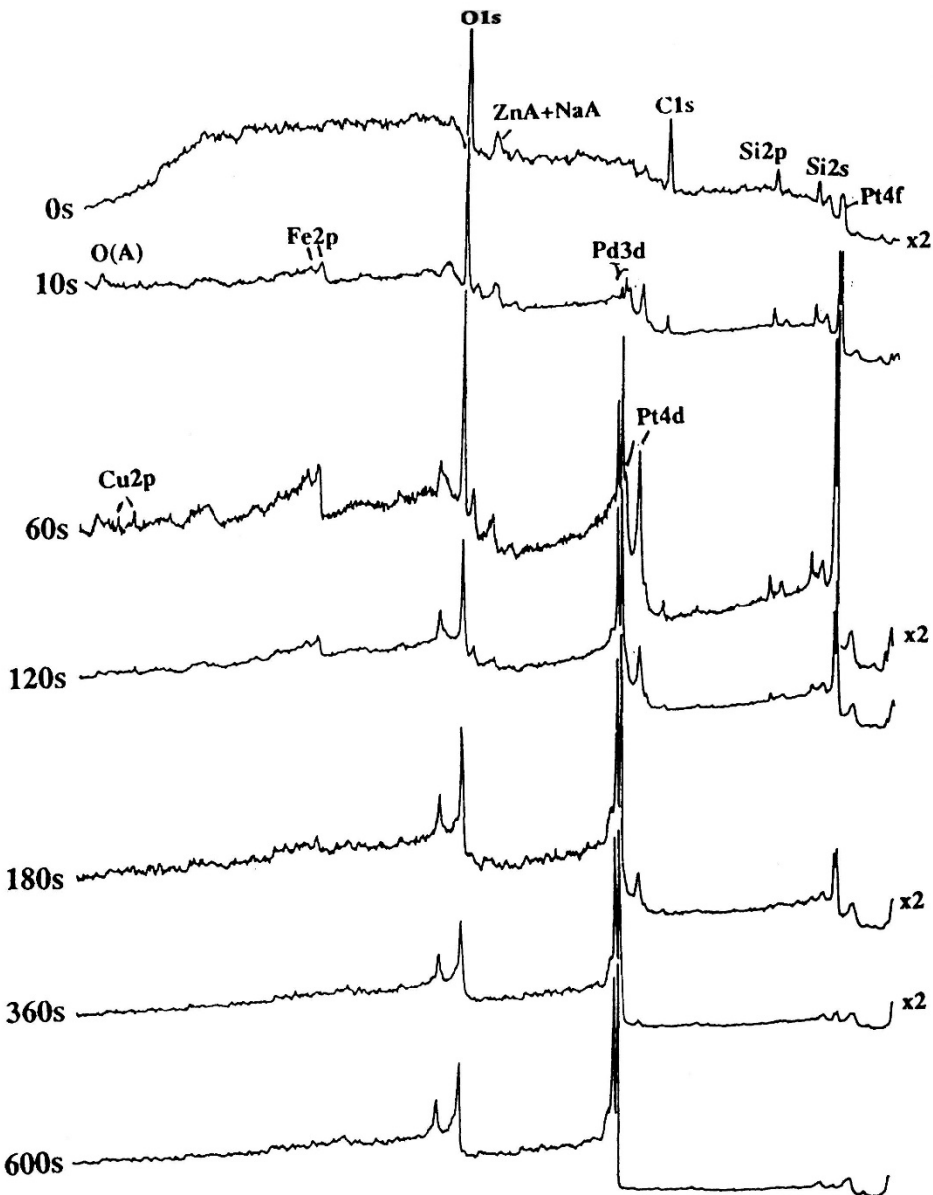
Figure 3. Series of XPS survey spectra obtained at various total sputter times from a large grain (600μm), 99.99% purity Pd rod cathode, 3.5 cm long by 0.4 cm in diameter, etched in aqua regia after Pt resistance wires attached by spot-welding with Pd/Pd-Ag electrodes, Pt mesh anode, pyrex cell, isoperibol calorimeter, 0.1 M LiOD (Li from Johnson Matthey, D_2O from Ontario Hydro), 460 hrs. total electrolysis time, highest current density=455 mA/cm^2. Scans from 0 eV (right) to 1000 eV (left) binding energy.

An example of a surface containing a thin overlayer after electrolysis is shown in Fig. 3. The surface contains silicate along with C and Pt. No Cu or Pd is observable in the first survey spectrum. After removal of much of the surface C contamination with a 10s sputter etch Pd is observed along with a significant increase in Si, O and Pt. Further sputtering removes the silicate with a concomitant increase in Pd. After 180s the Si has all been removed but Pt is still present. The Pt 4f signal decreases until after 600s where it is just barely discernible above the noise. Compared to the final spectrum shown in Figure 2 obtained at 2.5 times the total sputter time for this sample, it is easy to observe that the film on this electrode is much thinner. In addition, Cu never becomes a significant component of these types of films.

Film thickness appears to correlate with total electrolysis time. In addition, composition with respect to Cu is very different between the two different types of electrodes. Interestingly, there also appears to be a correlation with the maximum D/Pd obtainable. The thinner, non-Cu-containing overlayers reached loadings of D/Pd = 0.7 while the thicker, Cu-containing overlayers were found on samples with D/Pd = 0.9[4]. This indicates that the development of these Cu-rich layers at long electrolysis times may, in fact, have been beneficial to obtaining high loadings by acting as a blocking agent to D egress from the Pd lattice. The quest for low levels of excess heat with more sensitive calorimeters than used in our studies might have proven very interesting with these samples.

Alluded to in the above discussion are the sources of some of the impurities. Si most certainly comes from the etching of the Pyrex[R] or quartz container by the concentrated LiOD or LiOH. ICP analysis of the used solutions indicated that Si was present anywhere from approximately 30 to 80 ppm in the experiments where Pyrex[R] containers were used while around 10-20 ppm were found for experiments conducted in quartz holders. The source of Pt, found on every electrode examined with XPS, was likely from oxidation of the Pt anode at high current density. ICP analysis, however, showed less than 0.1 ppm Pt in all solutions. Another possible source was the Pd itself since most Pd used contained above 30 ppm Pt. Only one very high purity Pd sample containing a very small Pt level was examined: Johnson-Matthey 1mm diameter wire, 99.997% purity, where Pt by GDMS=1.9 ppm[5]. XPS indicated that very little Pt was present on this electrode.

A similar argument applies to the Cu except that, unlike Pt, there is no single solid source of Cu exposed in the cell. Sources of Cu include: D_2O, Li used to make LiOD from the D_2O, spot welds where Cu-containing tips are used, the Pt anode, the Pd cathode, Pyrex[R] or quartz and the Teflon[R] used for the cell top and to shield the electrical connections. The Pyrex[R], quartz and Teflon[R] seem unlikely candidates to supply such large amounts of a metallic impurity. The spot welds are unlikely as Cu was found on several cathodes where the welding tips were made of Pd and Pd-Ag alloy rather than Cu. Also, the cathodes were always acid etched after spot welding was completed. The Li was reported to have 20 ppm of Cu but so little is used to make up the 0.1M concentration that there is not enough present to supply such large amounts of Cu assuming the surface of the cathodes are uniformally covered. The Li was also reported to contain 90 ppm of Na and 78 ppm of Ca; these could have been the source of those impurities often found in small quantities on the cathode surface. The D_2O was not the source as believed in an earlier study[4]. Extremely pure D_2O was provided by Ontario Hydro in which the Cu

concentration was less than 0.005 ppm; our ICP analysis indicated that there was less than 0.01 ppm in both the D_2O (Ontario Hydro and Cambridge Isotope) and the 0.1M LiOD. The Pt anode could be the source but GDMS analysis of one anode indicated that only 0.25 ppm Cu was present. A Pt anode was examined by XPS after an experiment and no Cu was observed on its surface. The final source is the Pd cathode itself. The NRL Pd material was found to contain 24 to 27 ppm Cu which was likely obtained from arc melting of the sponge which was conducted on a Cu hearth. Calculations indicate, assuming surface segregation of the bulk Cu, that this is enough Cu assuming uniform distribution in the bulk (verified by depth measurement made with GDMS) to provide concentrations found in the surface films observed on used cathodes. Two cathodes which produced high Cu were reground and polished on a lathe. High Cu was found again re-observed on both cathodes after electrolysis. In addition, a higher than usual Ca level found on one of the cathodes was repeated after repolishing and electrolysis. One of the 'high Cu' cathodes was examined by GDMS as a function of depth. Cu was found at a concentration of nearly 80 ppm throughout the entire sample suggesting that initially this NRL sample had a larger than average Cu content. Cu was also found on an NRL Pd rod electrode tested at SRI in a degree of loading experiment. Cu was found on a 99.9% purity 1mm Johnson-Matthey wire which contained 24 ppm Cu by GDMS. Little Cu was found on two NRL samples run at China Lake. A number of different chemicals, however, were added to the electrolyte in an attempt to increase D uptake. These may have had an influence on Cu mobility. One anomaly, however, does exist and this is the large Cu concentration found on a 99.997% purity Johnson-Matthey wire cathode. GDMS indicated that this material contained only 0.11 ppm Cu. Electrical connections to this cathode were made, however, with Cu spot welding tips. Even though these cathodes were acid etched after spot welding, perhaps some Cu remained behind.

Surface segregation of various elements during H or D absorption has been observed previously. Surface enrichment of ppm bulk contaminants Ag and Rh has been detected with Pd electrolysis in both H- and D-based acid electrolytes[7]. The room temperature segregation of La has been observed in the hydride battery material $LaNi_5$[8]. Running the electrode through charge-discharge cycles causes the La to diffuse to the surface where it is oxidized by the KOH electrolyte. The $La(OH)_3$ blocks H ingress and reduces the efficiency of the battery. Normally La mobility in the $LaNi_5$ lattice is practically zero at room temperature. The authors believe that the enhanced La mobility is caused by the severe distortion at the boundaries of the hydrogen-rich and hydrogen-poor regions which arise during charging and discharging. The severe lattice defects occurring over relatively large areas cause short circuit diffusion paths for the La atoms. The same type of mechanism could account for the enriched Cu and Pt surface layers found on used Pd cathodes.

XPS of Heat-Producing Cathodes

Two sources of heat-producing cathodes, NAWC at China Lake and SRI International, provided samples for XPS analysis. Only analysis of the SRI cathode will be described here. The SRI Pd cathode examined was sample number P15, a Pd rod made from Engelhard #1 material which was SRI's most successful heat-producing material. This sample was annealed and electrolyzed in 1991. Details of the P15 experiment have been published[9]. From ICPMS data provided by SRI, the Engelhard #1 Pd is of 99.9% purity containing 140 ppm Pt and 13 ppm Cu plus significant levels of many other impurities. Heat-producing electrodes from China Lake[10] examined by XPS include: Johnson-Matthey high purity wires electrolyzed in two different calorimeters, NRL Pd rod and NRL Pd-B alloy rods.

Shown in Figure 4 are a series of survey spectra taken of the surface of the SRI P15 cathode and after various sputter times. The surface is a mixture composed of carbon- and oxygen-containing species of which silicate is the most prevalent. Small amounts of Pt, S, Zn, Na and N are also seen. No Pd is present on the surface. After a 10s-sputter some silicate is removed which results in a small increase in the C1s signal and a large increase in the Pt4f doublet. After 30s the Si is nearly all removed, the C begins to decrease, and the Pt and Pd continue to increase. Cu is also visible now. After 60s the metallic impurities, Cu and Pt, reach their maximum while C continues to decrease slowly and Pd increases. Further sputtering continues to uncover the Pd while the other impurities decrease. After 900s total sputter time, only Pt and C impurities are still visible. These are contaminants which are likely part of the bulk. As evidenced by the peak binding energies, the carbon always appeared to be mostly in the graphitic state while the Pt, even on the surface, was in the metallic state. The profile does not look all that different from that obtained for relatively thin overlayer samples tested at NRL and depicted in Figure 3. The P15 electrode was loaded to a maximum D/Pd of 0.99 and it produced anywhere from 5 to 10% excess power over the total input power. These amounts were just below the sensitivity of the NRL isoperibol calorimeters. This fact makes trying to draw conclusions based on the XPS results as to what impurities are necessary on the surface to obtain high loadings and excess power very difficult. Also, at the end of SRI's experiments, they normally switch the potential on the cathode so that an anodic current is flowing in order to de-load the sample before removal from the cell. This could oxidatively remove certain species from the overlayer that normally would have been present.

Several observations can be made concerning excess heat-producing electrodes. All contain layers on part or all of the electrode which are relatively thin in the sense that Pd is either observed on the surface or very early in the sputter profile and the peaks due to Pd rise rapidly with continued sputtering. Pt is always visible on the surface of these electrodes. The electrodes, with the exception of the high purity Johnson-Matthey used at China Lake (2.2 ppm Pt by GDMS), generally have a large Pt impurity concentration in the bulk. Pt and Pd are in the metallic state when found on the surface. A silicate layer is observed on the surface but this can be sputtered away fairly rapidly. There is usually a graphitic component to the carbon which appears to extend, along with the Pt, into the bulk. Copper is a small impurity as are Zn, Na, Ca and Mg. Many of these observations can also be made for the cathode materials run at NRL. Since, however, the excess heat observed in the analyzed samples generally did not exceed 10% of the input power and the sensitivity of the NRL calorimeters was in the range of 10% and above, using the XPS data for NRL-run samples as representative of non-excess heat producing electrodes may not be correct. As a final note, many of the impurities found in the surface layers are also present in the bulk of the cathode at the ppm level. Certainly the source of all the impurities found on the surface is not the bulk: however, as discussed above there is data to suggest that loading and de-loading H-storage materials can greatly increase the room temperature diffusion rates of bulk elements.

Conclusions

1. Prolonged electrolysis at high current density in basic solution results in the formation of a relatively thick layer on the cathode (>1000Å) composed of a varied elemental composition with very little or no Pd identifiable on the surface. 20 different elements have been

identified from XPS analysis of over 30 different electrode surfaces. Cationic, anionic and organic species in the electrolyte have been detected as part of these surface overlayers. The anodes, however, remain relatively film-free.

2. The source of some of the elements found in the cathode overlayer may be bulk diffusion of impurities such as Pt and Cu caused by the severe lattice distortion produced by absorption of large quantities of D or H.

3. Longer electrolysis times (~1000 hrs.) produced thicker films on NRL Pd cathodes compared to shorter times (<500 hrs.).   In addition, the thicker films contained larger quantities of both Cu and Pt relative to Pd and in general higher loadings were obtained with these films present. This suggests that thicker films may help block the egress of D from the Pd lattice.

4. Thinner films where Pd was present at or near the surface were found on excess heat producing electrodes obtained from SRI and NAWC (exceptions are where large quantities of certain species were added to the electrolyte to prolong or initiate excess heat formation). Very little copper was found in these films but appreciable amounts of Pt were present. Thin films with low Cu content may be necessary for excess heat measurement.
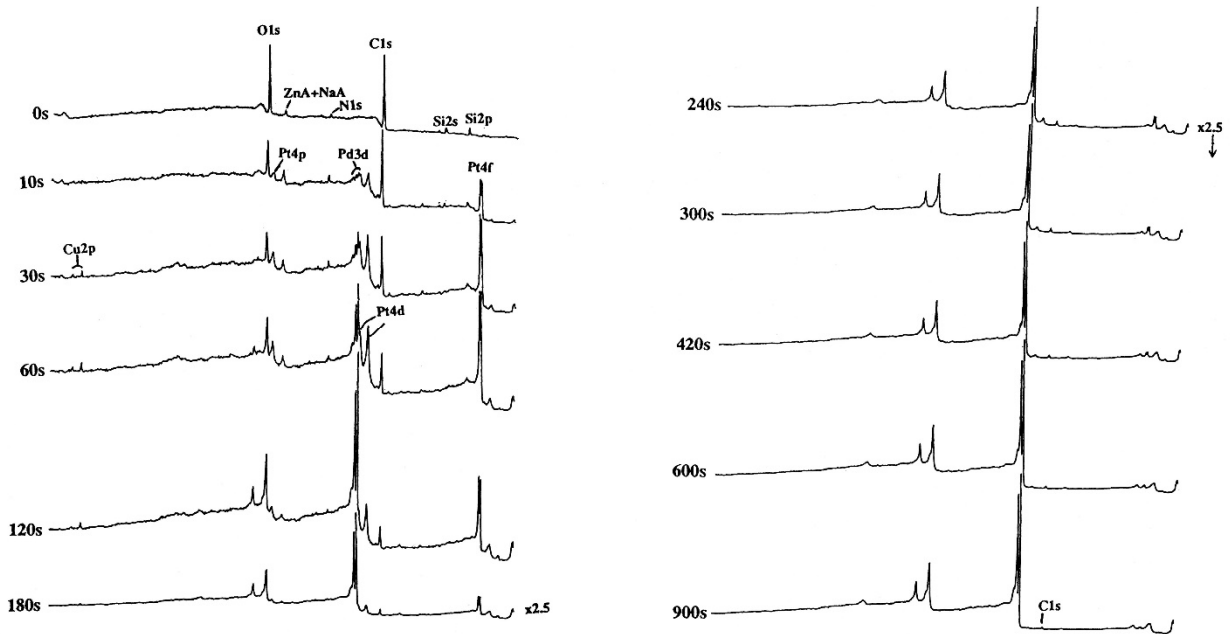

Figure 4. Series of XPS survey spectra obtained at various total sputter times from an SRI excess heat producing Pd rod cathode (#P15, Engelhardt #1 Pd). Scans from 0 eV (right) to 1000 eV (left) binding energy.

Acknowledgment

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