

Trace Elements Added to Palladium by Electrolysis in Heavy Water

TP-108743

Effective October 22, 2009, this report has been made publicly available in accordance with Section 734.3(b)(3) and published in accordance with Section 734.7 of the U.S. Export Administration Regulations. As a result of this publication, this report is subject to only copyright protection and does not require any license agreement from EPRI. This notice supersedes the export control restrictions and any proprietary licensed material notices embedded in the document prior to publication.



Trace Elements Added to Palladium by Electrolysis in Heavy Water

TP-108743

Technical Progress, November 1999

EPRI Project Manager

A. Machiels
T.O. Passell

DISCLAIMER OF WARRANTIES AND LIMITATION OF LIABILITIES

THIS DOCUMENT WAS PREPARED BY THE ORGANIZATION(S) NAMED BELOW AS AN ACCOUNT OF WORK SPONSORED OR COSPONSORED BY THE ELECTRIC POWER RESEARCH INSTITUTE, INC. (EPRI). NEITHER EPRI, ANY MEMBER OF EPRI, ANY COSPONSOR, THE ORGANIZATION(S) BELOW, NOR ANY PERSON ACTING ON BEHALF OF ANY OF THEM:

(A) MAKES ANY WARRANTY OR REPRESENTATION WHATSOEVER, EXPRESS OR IMPLIED, (I) WITH RESPECT TO THE USE OF ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT, INCLUDING MERCHANTABILITY AND FITNESS FOR A PARTICULAR PURPOSE, OR (II) THAT SUCH USE DOES NOT INFRINGE ON OR INTERFERE WITH PRIVATELY OWNED RIGHTS, INCLUDING ANY PARTY'S INTELLECTUAL PROPERTY, OR (III) THAT THIS DOCUMENT IS SUITABLE TO ANY PARTICULAR USER'S CIRCUMSTANCE; OR

(B) ASSUMES RESPONSIBILITY FOR ANY DAMAGES OR OTHER LIABILITY WHATSOEVER (INCLUDING ANY CONSEQUENTIAL DAMAGES, EVEN IF EPRI OR ANY EPRI REPRESENTATIVE HAS BEEN ADVISED OF THE POSSIBILITY OF SUCH DAMAGES) RESULTING FROM YOUR SELECTION OR USE OF THIS DOCUMENT OR ANY INFORMATION, APPARATUS, METHOD, PROCESS, OR SIMILAR ITEM DISCLOSED IN THIS DOCUMENT.

ORGANIZATION(S) THAT PREPARED THIS DOCUMENT

University of Texas, Austin

ORDERING INFORMATION

Requests for copies of this report should be directed to the EPRI Distribution Center, 207 Coggins Drive, P.O. Box 23205, Pleasant Hill, CA 94523, (800) 313-3774.

Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. POWERING PROGRESS is a service mark of the Electric Power Research Institute, Inc.

Copyright © 1999 Electric Power Research Institute, Inc. All rights reserved.

CITATIONS

This document was prepared by

University of Texas, Austin
Department of Chemistry
Austin, TX 78712

Principal Investigators

B.F. Bush

J.J. Lagowski

This document describes research sponsored by EPRI.

The publication is a corporate document that should be cited in the literature in the following manner:

Trace Elements Added to Palladium by Electrolysis in Heavy Water, EPRI, Palo Alto, CA: 1999. TP-108743.

REPORT SUMMARY

EPRI sponsored an experimental program to investigate the trace element changes brought about in palladium after extensive electrolysis in heavy water electrolytes. Of particular interest were cathodes which had experienced episodes of excess heat production beyond all electrical and other inputs. This report details the careful analysis of a particular cathode by neutron activation (NAA) as compared with the identical simultaneous analysis of virgin palladium material from which the cathode was fabricated.

Background

Palladium (Pd) cathodes electrochemically charged with deuterium (D) have exhibited episodes of excess heat beyond all inputs. To confirm or refute the suspicion of a possible nuclear reaction producing the excess heat, trace element changes were measured in a cathode with a history of excess heat production relative to the amounts present in virgin material from the same palladium production batch.

Objectives

To measure by an unequivocal method, namely (NAA), low levels of elements added to a palladium cathode during a lengthy electrolysis in 0.1 to 1.0 molar lithium deuterioxide during which excess heat production had been observed.

Approach

The project team performed neutron activation analyses (NAA) of a small diametral slice of a 2 mm diameter Pd rod cathode and a similar slice of the virgin rod from which the cathode had been originally fabricated. All elements susceptible to NAA at a flux of $1E12$ n/cm²-sec under irradiations of 10 minutes and 3 hours were detected and reported. Since NAA is isotope specific, any changes in the isotopic ratios within palladium were also accessible by this method.

Results

Increases in the elements cobalt (Co) (>4X), chromium (>5.4X), cesium (Cs) (>2X), europium (Eu) (1.3X), iron (Fe) (56X), and zinc (Zn) (12X) were noted relative to the virgin material. The conventional explanation for such increases is the cathodic deposition of electrolyte impurities on the cathode surface. The samples were slices through the diameter of the cathode rods and hence the surface layer was minimized relative to the bulk. However, the sample analyzed had some 0.033 cm² of surface area, less than 5% of the total surface area exposed to the electrolyte. The ratio of Pd-108 relative to Pd-110 in both samples was also measured. Pd-108 was depleted in the active sample relative the virgin material by an apparent 28% with the one sigma error limits extending from 7% to 49%.

EPRI Perspective

The cathode sample along with the virgin material were volunteered by S. Pons of IMRA. However, the precise amounts of excess heat produced by this cathode have not yet been made available. Hence it is not yet possible to relate these elemental changes to a specific quantity of excess heat. The isotopic ratios of the added elements should be those of the elements found naturally. If some new nuclear process produced them, the isotopic ratios for those elements with more than one isotope (Cr, Eu, Fe, and Zn) should be altered from those found naturally. The only heat producing nuclear reaction capable of producing Cr, Co, Fe, and Zn is the fission of palladium isotopes. If the apparent depletion in Pd-108 is confirmed, this may indicate that the lighter isotopes of Pd are more susceptible to fission than the heavier ones. Clearly this one experiment is not definitive, only suggestive. NAA could be used to find whether or not the Zn-64/Zn-68 ratio of the added Zn is significantly different from natural. It is also interesting to note that NAA measurements on other cathodes have also shown significant zinc increases. Since the zinc in at least one of those cases, cathode C-2 from work at SRI International, was mostly at the surface, it was assumed at the time that it was there by conventional cathodic deposition from electrolyte impurity zinc. However it is plausible that nuclear processes producing zinc also favors the surface. Again, the proof of a nuclear source for the increased zinc (and possibly other multi-isotope elements), will be resolved by NAA that shows the isotopic abundance ratios to be significantly different from those found naturally. Related EPRI reports include TR-104195, TR-104188, TR-108474, and Volume 1 and 2 of TR-107843.

ABSTRACT

Palladium samples taken from the center section of a 2-mm diameter cylindrical heat-producing cathode and similar material from the original stock palladium rod adjacent to that used for the cathode have been analyzed by neutron activation analysis for trace element impurity differences. The focus was on all elements for which NAA is appropriate and sensitive. Although it is known that electrolysis deposits impurity metals on cathodic surfaces from the electrolyte (lithium deuterioxide in this case), this occurs only at the external surface of the rod. The samples were cut diametrically to minimize the surface relative to the bulk or interior portion of the cathode. Large increases in iron and zinc of a factor of 56 and 12 respectively were observed in the active cathode relative to the virgin material. Smaller but significant increases were observed for chromium, cobalt, and cesium. In addition, the Pd-110/Pd-108 ratios were determined. Preliminarily, it appears that Pd-108 was depleted in the active cathode relative to Pd-110 as compared with that ratio in the virgin material. Possible sources of these changes in addition to the conventional explanations are discussed.

CONTENTS

| | |
|-----------------------|----------|
| 1. INTRODUCTION | page 1-1 |
| 2. RESULTS | page 2-1 |
| 3. DISCUSSION..... | page 3-1 |
| 4. CONCLUSION..... | page 4-1 |

1 INTRODUCTION

In the search for possible products of nuclear reactions to account for the excess heat observed in highly deuterated palladium cathodes in electrochemical cells, it was natural to consider activation analysis by thermal neutrons (NAA). This method has a high sensitivity for a wide range of elements at the levels of parts per billion (ppb) and up. It is blind to such elements as helium, but it has sensitivity for a broad range of elements and even isotopes within elements having more than one isotope. Hence as a means of surveying the possibilities in a generally unambiguous way without destroying the samples for the application of other possible analytical methods, it became the method of choice.

A number of cathodes have been observed to produce excess heat in long runs of electrolysis. It was felt that any new elements produced by nuclear reactions should have been increased from the normal impurity levels by measurable amounts if the excess heat observed was high enough per unit mass of palladium. For example, 10 parts per million (ppm) of an element of atomic weight 60 for which the heat production by some nuclear process amounts to 10 million electron volts (Mev) per atom, requires 0.16 megajoules per gram of palladium. The cathodes commonly used weigh from 1 to 10 grams. Taking a 1-gram cathode as an example, the 10 ppm increase in the impurity element of atomic mass 60 requires that the excess power episodes observed with the cathode integrated over the time of the episodes must have totaled 160 kilojoules.

S. Pons of IMRA volunteered a cathode that had experienced such episodes of excess heat well above the required levels of several hundred kilojoules. It was this cathode and its virgin counterpart that were analyzed in this study. Because it is known that impurities in the lithium deuterioxide electrolytes are readily deposited on cathode surfaces, the samples analyzed were slices through the diameter of the cylindrical cathode. Thus less than 5% of the total cathode surface was contained within the roughly 20-milligram samples.

2 RESULTS

The experimental results are shown in Table 2-1. Sample 1 was a 22.1 milligram slice of the active cathode and sample 2 was a 29.3-milligram sample taken from the virgin material from which the cathode had been originally fabricated. The samples were irradiated in the research reactor of the University of Texas at a flux of about $1E12$ neutrons/cm²-sec for 10 minutes and 3 hours respectively. The induced radioactivity was quantitatively determined by gamma ray spectroscopy using a germanium crystal detector cooled to 77K.

Table 2-1 Trace Elements in Electrolyzed and Virgin Pd

| ELEMENT | | ELECTROLYZED Pd | VIRGIN Pd | RATIO |
|----------|------|-----------------|-----------|-------|
| Cerium | (Ce) | <5 ppm | <5 ppm | NA |
| Cobalt | (Co) | 2 ppm | <0.5 ppm | >4 |
| Chromium | (Cr) | 27 ppm | < 5 ppm | >5.4 |
| Cesium | (Cs) | 14 ppm | <7 ppm | >2 |
| Europium | (Eu) | 0.04 ppm | 0.03 ppm | 1.3 |
| Iron | (Fe) | 13870 ppm | 247 ppm | 56 |
| Hafnium | (Hf) | <0.5 ppm | <0.4 ppm | NA |
| Rubidium | (Rb) | <20 ppm | <20 ppm | NA |
| Selenium | (Se) | < 3 ppm | <3 ppm | NA |
| Zinc | (Zn) | 60 ppm | 5 ppm | 12 |

In addition, gamma rays from Pd-109 and Pd-111 were observed in order to check the ratio of Pd-108 to Pd-110 in the two samples. For identically irradiated samples the ratio of Electrolyzed / Virgin for Pd-109 (from Pd-108 neutron, gamma reaction) was 0.72 plus or minus 0.21. A similar ratio for Pd-111 (from Pd-110 neutron, gamma reaction) was 1.10 plus or minus 0.04. This implies an apparent depletion in the electrolyzed sample of the Pd-108 relative to Pd-110 of between 7 and 49% (one sigma limits).

If we take the 7 % number as the value, this implies a loss of $2.3E18$ atoms of Pd-108. At 10 Mev per atom lost, this amounts to 3.6 megajoules for the sample and extrapolating to the total cathode assuming homogeneity gives 163 megajoules of excess heat. Of course total homogeneity is not likely in the electrochemical cell. The total excess heat generated by this cathode has not been made available to us as yet. To get 163 megajoules of excess heat would require an episode with an excess power of 10 watts for 4527 hours or about 0.5 years. The conclusion we must draw is that homogeneity is unlikely for excess heat episodes or that our measurement of Pd-108 depletion is in error. However it should be noted that Roulette, Roulette, and Pons²⁻¹ report one cell giving a total net excess heat of 294 megajoules and another yielding 102 megajoules.

²⁻¹ Roulette, T., Roulette, J., and Pons, S. "Results of Icarus 9 Experiments Run at IMRA Europe", Proceedings of the Sixth International Conference on Cold Fusion - Progress in New Hydrogen Energy, Volume 1, pages 85-92, published by The Institute of Applied Energy, Tokyo, Japan, October 1996.

3 DISCUSSION

This is only a single experiment that bears repeating on other samples of palladium. However if we take it at face value and further assume that the fraction of the total cathode surface area has limited our sensitivity to the conventional surface deposits of electrolyte impurities, then we must explain how such increases could have been caused by nuclear reactions.

The transition elements Cr, Co, Fe, and Zn are possible fission products of Pd, for which the energy available from the mass change of about 20 Mev per fission or 10 Mev per fission product atom assuming binary fission. This is the only nuclear process we have imagined capable of producing these elements from elements in the cell. The Cs increase observed may be from the 0.1 Molar LiOD electrolyte, it being an alkali element similar to lithium.

If fission to stable elements in the transition metal region around iron is occurring, then it is likely that the isotopic distribution of such elements will be different from those found in nature. The obvious next step in this work will be to determine, where possible, the isotopic abundance ratio of at least 2 isotopes within those elements with more than one. After looking at the possibilities available to NAA, zinc and chromium appear to be the most likely candidates. In the Zn case, the Zn-64/Zn-68 ratio would be sought and in the Cr case, the Cr-50/Cr-54 ratio would be sought for comparison with those in nature.

4 CONCLUSION

These measurements are so far only suggestive of possible nuclear reactions occurring in highly deuterated palladium. Similar work with heat-producing palladium sampled from those exposed only to deuterium gas would be far more free of the problem of cathodic deposition for palladium exposed cathodically for long periods to imperfectly pure electrolytes. Some suggestive early results from gas loaded palladium was given by Mo, Cai, Wang, Wang, and Li⁴⁻¹. They found alterations in the Zn-64/Zn-68 ratios from gas-exposed samples relative to the same ratios in natural zinc. The most severe alteration showed an enhancement of the Zn-64 to Zn-68 ratio by 34% relative to the ratio for natural zinc. Their unexposed palladium showed no zinc present. Gas-exposed palladium is likely to be reacting at its surface and hence the products of such reactions should be concentrated at the surface. Experiments should be performed which separately measure surface material and material well below the surface.

⁴⁻¹ Mo, D.W., Cai, Q.S., Wang, L.M., Wang, S.Z., and Li, X.Z., "The Evidence of Nuclear Transmutation Phenomena in Pd-H System Using NAA", Proceedings of the Seventh International Conference on Cold Fusion, page 259-263, April 19-24, 1998, Vancouver, B.C., Canada, Published by ENECO, University of Utah Research Park, 391-B Chipeta Way, Salt Lake City Utah 84108

About EPRI

EPRI creates science and technology solutions for the global energy and energy services industry. U.S. electric utilities established the Electric Power Research Institute in 1973 as a nonprofit research consortium for the benefit of utility members, their customers, and society. Now known simply as EPRI, the company provides a wide range of innovative products and services to more than 1000 energy-related organizations in 40 countries. EPRI's multidisciplinary team of scientists and engineers draws on a worldwide network of technical and business expertise to help solve today's toughest energy and environmental problems.

EPRI. Electrify the World

WARNING: This Document contains information classified under U.S. Export control regulations as restricted from export outside the United States. You are under an obligation to ensure that you have a legal right to obtain access to this information and to ensure that you obtain an export license prior to any re-export of this information. Special restrictions apply to access by anyone that is not a United States citizen or a Permanent United States resident. For further information regarding your obligations, please see the information contained below in the section entitled "Export Control Restrictions."

Export Control Restrictions

Access to and use of EPRI Intellectual Property is granted with the specific understanding and requirement that responsibility for ensuring full compliance with all applicable U.S. and foreign export laws and regulations is being undertaken by you and your company. This includes an obligation to ensure that any individual receiving access hereunder who is not a U.S. citizen or permanent U.S. resident is permitted access under applicable U.S. and foreign export laws and regulations. In the event you are uncertain whether you or your company may lawfully obtain access to this EPRI Intellectual Property, you acknowledge that it is your obligation to consult with your company's legal counsel to determine whether this access is lawful. Although EPRI may make available on a case by case basis an informal assessment of the applicable U.S. export classification for specific EPRI Intellectual Property, you and your company acknowledge that this assessment is solely for informational purposes and not for reliance purposes. You and your company acknowledge that it is still the obligation of you and your company to make your own assessment of the applicable U.S. export classification and ensure compliance accordingly. You and your company understand and acknowledge your obligations to make a prompt report to EPRI and the appropriate authorities regarding any access to or use of EPRI Intellectual Property hereunder that may be in violation of applicable U.S. or foreign export laws or regulations.

© 1999 Electric Power Research Institute (EPRI), Inc. All rights reserved. Electric Power Research Institute and EPRI are registered service marks of the Electric Power Research Institute, Inc. EPRI. ELECTRIFY THE WORLD is a service mark of the Electric Power Research Institute, Inc.

TP-108743