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X-RAY EMISSION DURING ELECTROLYSIS OF LIGHT WATER ON PALLADIUM AND NICKEL THIN FILMS

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ABSTRACT

Electrochemical experiments have been carried out in order to investigate the emission of X-rays during electrochemical hydrogen loading of thin metallic films of Pd and Ni. An estimate of the inventory of the most significant chemical elements in the cells has also been done. The activity was developed within the framework of a cooperative research effort between ENEA and SRI. In order to minimize the background due to environmental contamination, the experimental cells were manufactured using only two materials (pure polyethylene and pure platinum). The thin films were produced by sputtering pure materials on supports made of the same pure polyethylene used for the cells.

1. INTRODUCTION

The theoretical framework proposed by some of the authors [1-3] suggested the possible emission of low energy X-Rays in the metal hydrogen system under electrochemical conditions, created by energetic protons. Calculations using the analysis of the dynamics of hydrogen isotopes in the palladium lattice showed that the coherent behaviour of the Fermi level electrons (plasmons) may create particles up to about 10 keV as showed in Fig.1.

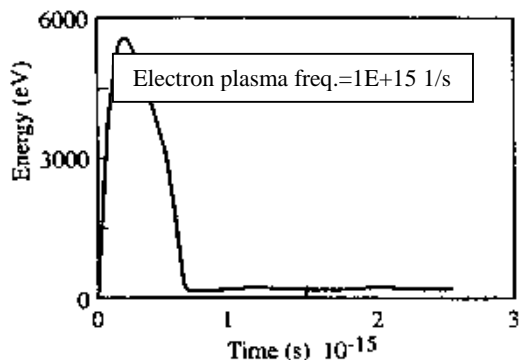


Fig.1 Energy evolution of an energetic hydrogen Isotope confined in Pd lattice (theoretical result).



Fig.2 Detail of the thin film cathode and Pt contact

An experimental strategy was adopted to increase the signal/noise ratio in the X-Ray measurements and to control the chemical species in the experimental cells. The variation of the amount of the monitored species (Fe, Co, Zn, Ag, Cr) was studied by using the accurate mass balance method. The experimental cells were constructed using only two materials (pure polyethylene, and 99.98 % pure Pt). The pure polyethylene was from the Nuclear Activation Analysis (NAA) sample vessels.

2. EXPERIMENTAL APPARATUS AND PROCEDURES

1) Cells

The cell was constructed from a 15 cc polyethylene vessel. Fig.2 shows a detail of the anode-cathode support including the thin film. The anode is a platinum wire wrapped in the shape of a planar spiral. The cathode is a metallic thin film containing Cu and/or Ni or Pd. The cathode contact is made with a "C" shape platinum wire inserted into a polyethylene support. Polyethylene shields prevent the electrolysis between anode and cathode connections.

2) *Thin Films*

The thin film is supported on a plastic disk (pure polyethylene as described above) 12 mm in diameter and 1 mm thick. The films were prepared by sputtering contemporaneously over two identical adjacent plastic support targets, to yield a blank thin film electrode with the same deposition of the working one.

3) *Cleaning Procedure*

- 1) Nitric Acid wash
- 2) 18 Mohm-cm pure water rinse
- 3) Pure ethanol with 20% KOH rinse
- 4) Pure ethanol wash and rinse
- 5) 18 Mohm-cm pure water wash and rinse (several times).

4) *Laboratory Environment*

The film preparation, cleaning process, cell assembly, and all the experiments used for mass balance were performed in a class 100 clean room at the ENEA laboratory using dust-free gloves. The tools used to assemble the cell components were selected to reduce the presence of the elements being measured by NAA, Alloys containing zinc and/or silver were specifically avoided, using CrV Steel, polycarbonate, and carbon steel to construct cell components. Contacts between the cathode, anode, and the power supply terminals were avoided by means of small platinum tubes that were removed before analyses. Tritium measurements of the electrolyte were performed with a Packard 2200 (60% efficiency) beta-detector liquid scintillation counter.

5) *Nuclear Measurements*

The Nuclear Activation Analysis facility of the Nuclear Measurements Laboratory of the Casaccia ENEA Research Center was used for the experiments. The irradiation was performed using the TRIGA 1MW MarkII reactor (neutron flux= $2.6E+12$ 1/cm² s, thermal/fast = 2/1). Irradiation time was 30 hours over five days. Measurements were performed after an appropriate cooling time, using a coaxial Ge(i) ORTEC detector and an ORTEC counting chain. Raw data was treated using ORTEC MAESTRO-II and OMNIGAM software.

Pure standards and standard mixtures of Zn, Ag, Cr, Co and Fe were interspersed with samples among the thirty irradiation positions used. The rotating irradiation facility yielded a beam of homogeneous neutron flux and energy. The proper optimisation of the irradiation beam was confirmed by the high reproducibility of the specific activity of ⁶⁵Zn and ¹¹⁰Ag standards.

X-Ray measurements were performed with an ORTEC planar intrinsic high purity Ge (HPGE) detector. Tritium measurements of the electrolytic solutions have been done with a Packard 2200 (60% efficiency) beta-detector.

3. EXPERIMENTS

Three experimental runs (a, b and c) were carried out. The first run (a) was dedicated to the mass balance of key elements (Fe, Co, Zn, Ag, Cr) using batch NAA measurements coupled with X-Ray detection. The second run (b) was performed to yield isotopic shift analysis and X-Ray detection. The third run (c), still in progress, is being carried out for further measurement of X-Rays, and isotopic shifts.

1) *Blank Cells*

- Blank cell with a dummy cathode (plastic support).
- Blank cell CuNi4a with a Cu/Ni cathode (250/400 Å).

2) *First Run (a)*

- **Cu1a** cell with Cu (450 Å) cathode: mass balance in batch mode.
- **Ni1a** cell with Ni (450 Å) cathode: mass balance in batch mode.
- **CuNi1a** cell: *Ex situ*, post experiment solution and the cathode analysis.

The results were compared with the electrolyte and cathode blanks

- **CuNi2a** and **CuNi3a** cells with Cu/Ni (250/450 Å) cathode: mass balance in batch mode.
- **CuPd1a** cell, with a Cu/Pd (250/450 Å) cathode: mass balance in batch mode.

The electrolyte was dried at 40 C and the cell irradiated. NAA measurements were performed after radioactive cooling.

Increment = Cell Inventory – Blank cell Inventory - Blank Cathode Inventory– Electrolyte Inventory

3) Second Run (b)

Five cells: **Cu1b, Cu2b, Ni1b, Ni2b and CuPd1b.**

After electrolysis, the thin film cathode was removed in a clean room and the spent cathode and blank film were irradiated. NAA measurements were performed after radioactive cooling.

Mass balance in individual mode was determined according to:

Increment = Black Cathode Inventory - Blank Cathode Inventory

4) Third Run (c)

Ni1c, Ni2c, Ni3c, CuPd1c, CuPd2c, CuPd3c.

After electrolysis, these cells and cathodes were be treated as in (b) above.

Cell **CuNi2a** used 10^{-3} M LiSO_4 . All the other cells used 1M Li_2SO_4 electrolyte. Mass balance was performed for Fe, Co, Zn, Ag and Cr. Other elements, including impurities of platinum have been considered as contaminants. The mass balance is calculated as the difference between the amount of each element in the cell after the experiment and sum of the initial amounts of the element in the blank cell, in the metallic films and in the electrolytic solution.

After the electrolysis, each cell is slowly dried at 40 C for several days and then irradiated in a double walled Cartell polyethylene vessel. After “radioactive cooling” platinum is removed from the cell in order to increase the signal/noise (S/N) ratio and the gamma spectrometry measurements were carried out. Table 1 shows the concentration of the elements found in the used materials and in the two blank cells; one without the thin film and one with a Cu/Ni thin film (**CuNi4a**).

The last column of Table 1 reports the extractable substances from the gloves used, as claimed by the manufacturer, after long washing performed with agitation.

However NAA performed on virgin and cleaned polyethylene samples revealed no evidence of significant levels of key elements after handling with gloves.

Table 1 Element concentration in the materials and in the blanks

	Electrolyte	Electrolyte	Pt	Glove	Blank	CuNi4a	GloveEx trac.
	1M	1E-3 M	Micro g/g	NAA Analys.	Cell	Blank	
				Micro-g/glov			Micro-g/cm ²
Fe (Micro-gr)	3,200E+00	4,680E+00	8,366E+01	2,350E+02	7,900E-01	8,500E-01	0,013
Co	4,000E-03	5,980E-03	8,960E-02	1,000E+02	1,090E-04	1,280E-03	
Zn	4,300E-01	1,880E-02	3,420E+00	1,000E+04	2,900E-02	9,100E-03	0,14
Ag	1,700E-02	5,200E-03	1,620E+01	1,790E+00	2,800E-03	1,500E-02	
Cr	1,600E-01	2,100E-01	3,100E+01	7,600E+00	7,500E-02	8,200E-02	

Table 2 shows the elemental composition changes calculated for all the cells studied using batch mass balance. Negative changes are due to deposition of elements on to the platinum that was removed before NAA in order to reduce the Pt impurity background.

Table 2 Increment of the elements from mass balance

	1M Electrolyte	Pt	Cu1a	Ni1a	CuNi1a	CuNi2a	CuNi3a	CuPd1a
Elapsed Time (h ^{min})			2 ⁵¹	2 ³⁰	18 ²⁵	1	20 ¹¹	3
Coulomb			1040,4	1029	650	360	2010	780
	μg	μg/g	% Change	% Change	% Change	% Change	% Change	% Change
Fe	3,2	83,7	10,964	-27,314	-56,97	-51,50	157,74	7,276
Co	0,004	0,09	-71,783	-71,606	-33,13	-78,46	-53,78	181,43
Zn	0,43	3,42	185,683	70,613	-0,6910	361,86	8,613	757,71
Ag	0,017	16,2	21,739	2504,78	582,83	258,75	737,74	85,74
Cr	0,16	31	285,283	147,368	-19,958	-49,85	360,42	121,84

The key elemental composition changes might be ascribed to a contamination due to the anodic dissolution of the anode but there is no evidence of anode weight reduction greater than 0,0001g. One may assume that contaminants are present as clusters, primarily close to the surface. In addition the amount of contaminants is not consistent with the current passed through the cells, particularly for Zn and Ag (see. Fig.3 and Fig. 4).

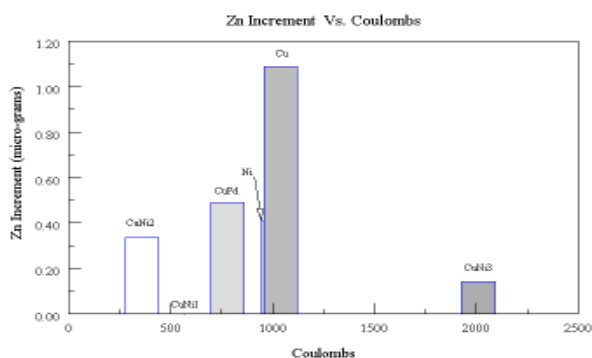


Fig.3 Zn Increment Vs electrolysis charges (run a) (run a)

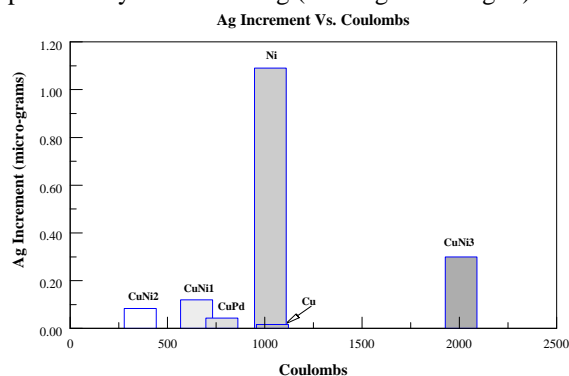


Fig.4 Ag Increment Vs electrolysis charges (run a) (run a)

For the above-mentioned reasons, together with the mounting evidence of non He nuclear ash production, we decided to reconsider the presence of Ag more carefully. The authors developed an isotopic shift analysis in the second series of experiment where five cells (**Cu1b**, **Cu2b**, **Ni1b**, **Ni2b** and **CuPd1b**) experienced with the same cleaning conditions as the first series, but the analyses were performed by comparison between the electrolysed film and the blank one.

Results of the isotopic ratio of Ag for three cathodes of run (b) are shown in Table 3. A significant change of the Ag isotopic ratio has been found in the cells **Ni1b** and **Ni2b**.

Table 3 Ag isotopic shift

	Ni1b	Ni2b	CuPd1b
¹⁰⁷ Ag (μ g)	<0,019	< 0,034	< 0,026 below detect. limit
¹⁰⁹ Ag (μ g)	0,025	0,06	0,0075
Isotopic Shift %	29,37	47,39	Not estimated

4. X-RAY

X-ray measurements were carried out by placing the bottom of the electrochemical cell in contact with the planar HPGE detector (see Figures 4 and 5). However, despite the meticulous cleaning the



Fig.4 Cell over the detector

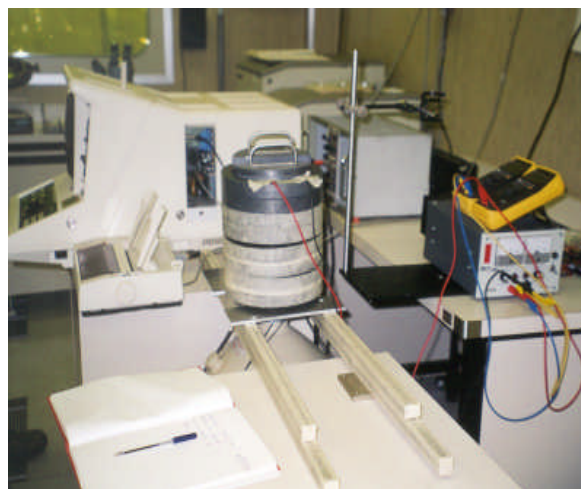


Fig.5 Cell and detector within the lead shield

first set of electrolysed cells, **Cu1a**, **Ni1a**, **CuNi1a**, gave results not distinguishable from the background. The S/N ratio was improved by installing a lead shield (see Fig. 6) around the planar germanium detector and the electrochemical cell. Several blanks have been repeated (without cell, with cell without electrolysis and with Pt-Pt electrolysis) always giving the same result. The introduction of the shield allowed us to detect a small difference between the background and the measurement during the electrolysis using **CuNi2a** and **CuNi3a** cathodes. To increase the signal 2.5 mm of polyethylene and 15 mm of electrolytic solution were eliminated from the bottom of the cell. The electrolysis with palladium was performed again yielding a significant gain in the signal. similar behaviour was observed when measuring cell **CuPd1b** where the signal, despite its the short elect5rolysis time (3 h) was more than twice background (see Fig.6). A small signal is present close to the energy level of the K-alpha transition of Pd. No significant difference between the signal and the blank occurred in the case of cell **Cu2b**, as shown in Fig.7. Similar behaviour was observed in cell **Cu1b**.

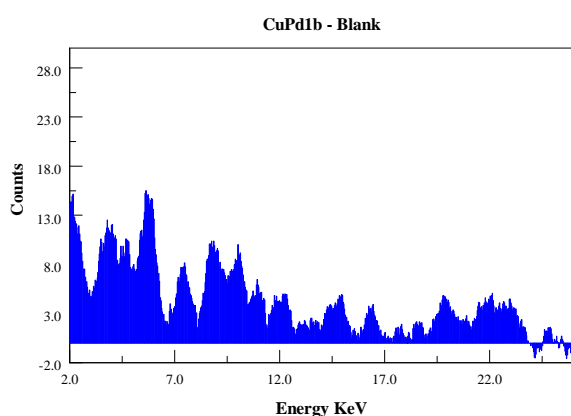


Fig.6 Cu/Pd after the background was subtracted

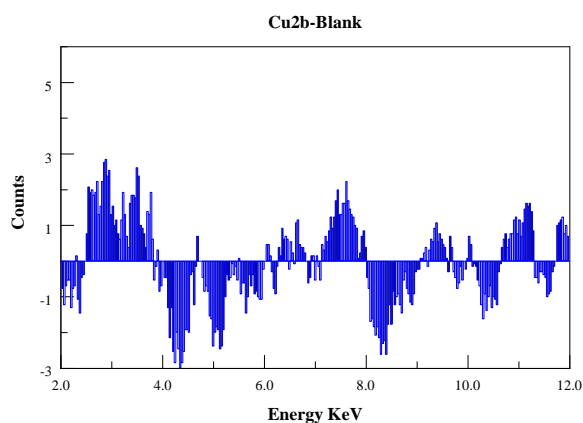


Fig. 7 Cu2b after the background was subtracted

A clear but low intensity signal was also seen with cell **Ni1b**, while a weak signal was detected from cell **Ni2b** (see Fig. 8 and 9). These cells have been analysed for the Ag isotopic shift.

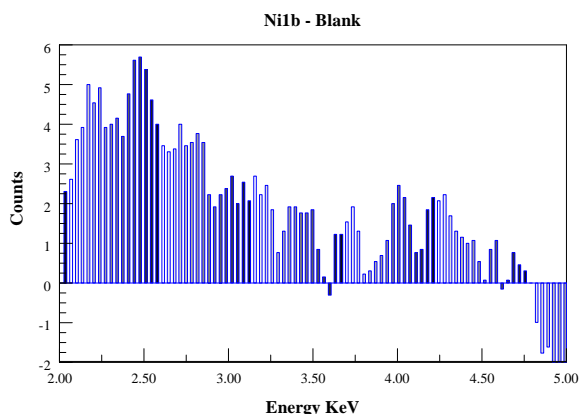


Fig.8 Ni1b after the background was subtracted

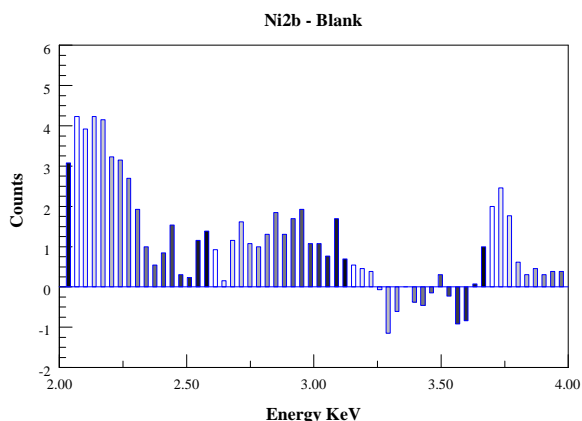


Fig.9 Ni2b after the background was subtracted

No evidence of X-Ray emission was obtained from cell **Ni1c** (see Fig.10) so that a new experiment was carried out by adding 10% of D₂O to the electrolyte of the **Ni2c** cell. Fig.11 show the difference between the signal and the blank measured with a non-operating cell containing 100% of D₂O electrolyte (1M Li₂SO₄). A clear signal is observed above background.

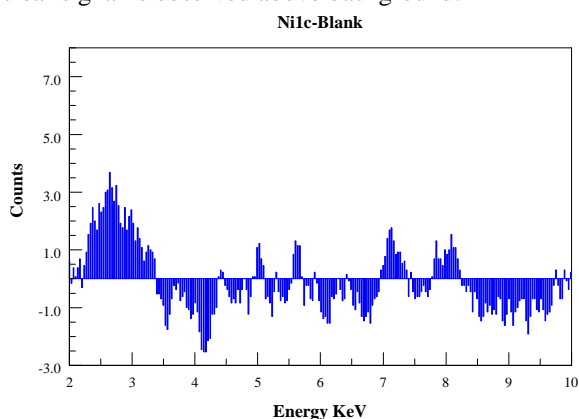


Fig.10 Ni1c after the background was subtracted

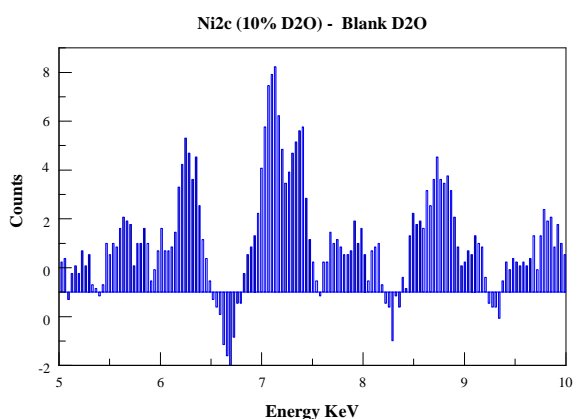


Fig.11 Ni2 after the background was subtracted

This result prompted us to repeat the experiment, as cell **Ni3c**, with pure D₂O electrolyte. No particular evidence of a signal above background was obtained in this case, as shown in Fig.12. We attempted to reproduce the successful experiments from the first and second runs using CuPd thin film cathodes. Although no signals above background were detected from cell **CuPd1c**, a signal clearly above the background was obtained from cell **CuPd2c**, particularly in the low energy range (see Fig.13). this low energy X-ray is similar to what would be expected from Pd K- α emission.

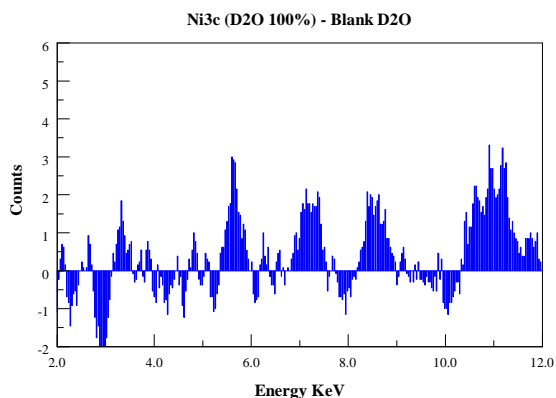


Fig.12 Ni3c after the background was subtracted

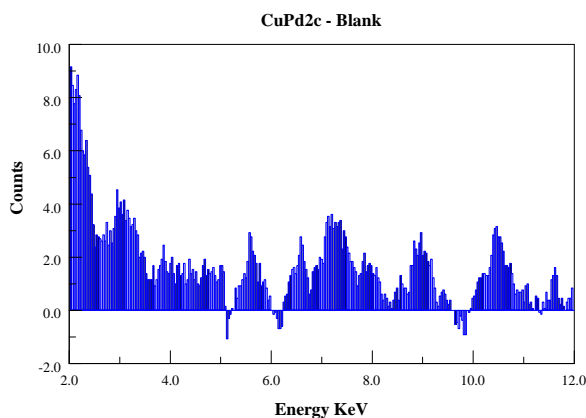


Fig.13 CuPd2c after the background was subtracted

5. TRITIUM MEASUREMENTS

Tritium measurements have been done in the electrolytes before and after the electrolysis for all the experienced cells. In all cases the measurements gave the same values of the background. Only the Ni1a cell electrolyte, after the electrolysis gave a significant increasing of the tritium level: 46 Bq (1.5 nCi) for 10 cc of electrolyte. This value is roughly 10 times the background. Since we have been working with high purity water (18 M ohm-cm) and pure substances, a possible explanation is a reaction between proton and lithium-7 (or deuteron and Lithium-6) occurring within the double-layer.

6. CONCLUSIONS

The X-Ray results seem to be in agreement with the proposed theoretical picture of energetic particles (i.e. hydrogen isotopes in ionic state) in condensed matter, producing nuclear interactions. The measurements reveal a reasonably reproducible effect, especially in the palladium hydrogen system. Qualitative mass balances and isotopic shift measurements seem to show that nuclear processes different from $D+D \rightarrow {}^4\text{He}+\text{heat}$ occur in condensed matter at or near the interfaces where coherent electronic phenomena like plasmon-polariton interactions take place. The authors consider these results to be preliminary and useful to plan further studies in this interesting research field.

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