

Impurity Measurements by Instrumental Neutron Activation Analysis on Palladium, Nickel and Copper Thin Films

A. Rosada¹, E. Santoro², F. Sarto³, V. Violante³, P. Avino⁴

¹*FIM, R.C. Casaccia, ENEA, Rome, Italy*

²*FPM, R.C. Casaccia, ENEA, Rome, Italy*

³*FPM, R.C. Frascati, ENEA, Rome, Italy*

⁴*DIPIA, ISPESL, Rome, Italy*

E-mail: emilio.santoro@enea.it

Abstract. Nowadays, the main cold fusion experiments are performed during electrolysis processes onto palladium, nickel and copper thin films. In studies devoted to verify the nuclei formation during these tests, a specific research activity has been developed at ENEA Research Centers: different experiments were set up for verifying and testing the data present in literature. Each step of the procedure has been analyzed and deeply investigated: the materials such as electrolysis equipments, electrolytic solutions, electrodes, etc. were preliminarily analyzed by Instrumental Neutron Activation Analysis (INAA) for identifying and reducing all the pollution sources.

Successively, different experiments were performed using films of palladium, nickel and copper as electrodes. At the end of each test, all the materials and the electrolytic solutions used and the blank as well, were analyzed by INAA for checking and measuring the presence of nuclei originating from nuclear transmutations.

1. Introduction

Some abnormal electrochemical facts have long been known to the scientific community, not related to the chemical phenomena occurring during the electrolysis: unexpected excess of heat and X-ray emission. The possibility of obtaining more heat than that generated by electrochemical reactions, was shown by Fleischmann and Pons in 1989 [1]. After, Jones [2] considered the possibility of cold fusion reaction p/D taking place in the lattice of a metal at temperature slightly above ambient temperature, cold compared to peak thermonuclear fusion temperatures (10^8 K) [3].

While there are clear evidences [4-7] on excess heat not justified through electrochemical reactions, there is less clearness, but still high uncertainty about the other related phenomena such as neutron production [3,8], ⁴He production [5,7,9], tritium production [10-12], nuclear ash formation [13-16].

Because these possibilities are just random, sporadic, of low intensity and not related to each other, it should be considered the X-ray emission and the production of new species from nuclear transmutation reactions occurring during the experiments. Our attention is addressed to this second task for understanding what may actually happen in condensed matter.

Some authors [13,14] stated that after electrolysis experiments on mono- or multi-layered thin films of Pd and Ni, performed using both light and heavy water and various electrolytes (e.g., Na₂CO₃ or LiOH), new atomic species may be observed in condensed matter. According to these authors, some of the observed species are present at low levels and cannot be regarded as impurities, but real nuclear transmutation products. Some other authors reported the observations of new atomic species hypothesizing their production by nuclear transmutations in condensed matter during electrolysis experiments on mono- and multi-layered thin-films [16].

The main critical point of this approach is the contamination levels of the single components used during the electrolysis process. For these reason we set up some experiments analyzing the electrodes with relative blanks and the electrolytic solutions with relative standards by the Instrumental Neutron Activation Analysis (INAA). Preliminarily, some candidate materials have been undergone to INAA, discarding those without minimum impurities content; after, the blanks (i.e., electrodes and electrolytes) and the electrodes and operated electrolytes exhausted, were analyzed.

From the analytical point of view, the INAA was chosen because it is a non destructive analytical method (i.e., all samples can be stored and analyzed again) and highly sensitive (very low limit of detection, LOD, high sensitivity and high precision) (table 1), is a bulk method (INAA is an analytical technique that allows to analyze the entire mass of the sample) [17], permits the determination in the same sample up to 50-60 elements with no chemical sample manipulations (no errors due to excess contamination, positive artifacts, or down due to loss of material, negative artifacts).

Table 1. Nuclear data (radioisotope, cross section, half-life, peak energy and limit of detection) of the elements investigated in this study (a: calculated according to ref. 18; h: hour; m: minute, d: day; y: year).

Element	Product nuclide	Cross Section [19] (barn)	Half life		γ -Ray used (keV)	LOD ^a (ng)
Ag	¹⁰⁸ Ag	35	2.41	m	632.9	0.1
Ag	^{110m} Ag	37.2	250.4	d	657.7	
Al	²⁸ Al	0.232	2.246	m	1778.8	30
As	⁷⁶ As	4.3	26.3	h	559.2	0.001
Au	¹⁹⁸ Au	98.8	2.70	d	411.8	6×10 ⁻⁵
Br	⁸⁰ Br	8.5	17.4	m	617.0	0.002
Br	⁸² Br	2.69	1.47	d	776.5	
Cl	³⁸ Cl	0.428	37.2	m	1642.4	2
Co	⁶⁰ Co	37.2	5.272	y	1332.5	0.06
Cr	⁵¹ Cr	15.9	27.7	d	320.0	0.1
Cu	⁶⁴ Cu	4.5	12.74	h	1345.8	
Cu	⁶⁶ Cu	2.17	5.1	m	1039.0	0.4
Eu	¹⁵² Eu	5900	12.7	y	1408.0	2
Fe	⁵⁹ Fe	1.15	45.1	d	1099.2	20
Ga	⁷² Ga	4.71	14.1	h	834.0	0.002
Hf	¹⁸¹ Hf	12.6	42.4	d	482.2	0.02
Mg	²⁷ Mg	0.038	9.45	m	1014.4	20
Mn	⁵⁶ Mn	13.3	2.58	h	846.6	8×10 ⁻⁵
Mo	⁹⁹ Mo	0.45	2.75	d	141.0	0.03
Na	²⁴ Na	0.53	15.02	h	1368.6	0.004
Ni	⁵⁸ Co	0.113	70.78	d	810.7	6
Pd	¹⁰⁹ Pd	12	13.46	h	88.1	
Pd	^{109m} Pd	0.2	4.69	m	188.9	
Sb	¹²² Sb	6.25	2.70	d	564.0	0.001
Se	⁷⁵ Se	51.8	120.4	d	264.6	0.1
Sm	¹⁵³ Sm	206	1.948	d	103.1	5
Ta	¹⁸² Ta	21	115	d	1221.3	0.01
V	⁵² V	4.88	3.75	m	1434.2	0.9
W	¹⁸⁷ W	37.8	24.0	h	685.7	0.001
Zn	⁶⁵ Zn	0.78	243.8	d	1115.5	0.1

In this study we analyzed the following elements: Ag, Al, As, Au, Br, Cl, Co, Cr, Cu, Eu, Fe, Ga, Hf, Mg, Mn, Mo, Na, Ni, Pd, Sb, Se, Sm, Ta, V, W, Zn.

2. Experimental Part

2.1 Electrolysis process

2.1.1 Apparatus and Conditions. The experimental cell (Fig. 1), 15 mL polyethylene vessels, have been constructed using pure polyethylene (PET) (Kartell S.p.A., Milan, Italy) containers at very low impurity levels. The anode is a Pt wire (99.98% pure Pt) wrapped in the shape of a planar spiral. The cathode is a metallic thin film containing Cu, or Ni, or Pd, deposited onto a polyethylene disk (12 mm diameter and 1 mm thickness) made of the same ultrapure material of the cell; after the etching treatment of the supports the films were prepared by sputtering contemporaneously over two adjacent polyethylene targets to obtain a blank film electrode with the same deposition of the working one. The cathode contact is made with a "C" shape platinum wire inserted into a polyethylene support to prevent the electrolysis between anode and cathode connections. The electrolysis conditions were: time 1-5 hours, solution LiSO₄ 10⁻⁴, 10⁻³ and 1M, current 5-190 mA and voltage: 3-7 V.

Before the process, all the equipments were cleaned. The cleaning procedure is the following: washing

with $18 \text{ M}\Omega \times \text{cm}^{-1}$ ultrapure distilled deionized water; washing with HNO_3 65% (Merck Specpure, Darmstadt, Germany) for 1 minute; rinsing with $18 \text{ M}\Omega \times \text{cm}^{-1}$ ultrapure distilled deionized water; rinsing with KOH 20% in ethanol (ultrapure reagent) (Carlo Erba, Milan, Italy); rinsing with ethanol (ultrapure reagent) (Carlo Erba); rinsing several times with $18 \text{ M}\Omega \times \text{cm}^{-1}$ ultrapure distilled deionized water; drying at room temperature. The Pt wire is cleaned by acetone and ethylene in a previous supplementary step. The handling occurs with acrylic gloves. The film preparation, cleaning procedure, cell assembly and all the experiments were performed in a class 100 clean room using dust-free gloves. The tools used to assemble the cell components has been selected to avoid the presence of contaminants.

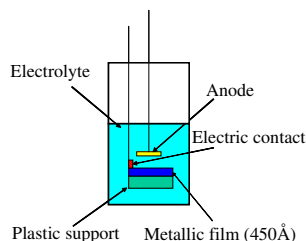


Fig. 1 - Electrolytic cell

2.1.2 Electrolysis Experiments. Two series of experiments were performed [20]: 1) mono layer, double layer (Cu/Ni) and multi layer thin-films (Cu/Ni/Pd/Ni/Pd) electrodes (450, 250/450, and 250/450/450/450/450 Å thicknesses, respectively) either electrolyzing Li_2SO_4 10^{-4} and 1M solutions (ultrapure compounds dissolved in $18 \text{ M}\Omega \times \text{cm}^{-1}$ ultrapure distilled deionized water); 2) mono and double layer electrodes (Cu; Ni; Cu/Ni and Cu/Pd) and Li_2SO_4 10^{-3} and 1 M.

2.2 INAA analysis

2.2.1 Sample and Standard Preparation. After electrolysis the thin-film cathodes were removed in a clean room: the spent cathodes and relative blanks, put directly into the irradiation vessels, were irradiated and analyzed; 1 or 2 mL of spent solutions and relative blanks were put into the irradiation vessel, gently dried in stove at 40°C , and then irradiated. All the other samples (PET supports, Pt wire, lab gloves and lab papers) were undergone to the same treatment. The standards were prepared starting from calibrated solutions $1000 \mu\text{g mL}^{-1}$ of each pure element (Carlo Erba). Known quantities of each solution were exactly dosed by mean of a micropipette (Eppendorf) into the irradiation vessel, gently dried in stove at 40°C , and irradiated.

2.2.2 Irradiation. The samples are undergone to two different neutron irradiations: 1) in the pneumatic channel position (Rabbit) of the TRIGA MARK II reactor at the R.C. ENEA-Casaccia for 1 minute at neutron flux of $1.25 \times 10^{13} \text{ n}\times\text{cm}^{-2}\times\text{s}^{-1}$ (fluence $7.5 \times 10^{14} \text{ n}\times\text{cm}^{-2}$); 2) in the rotating rack (Lazy Susan) of the TRIGA MARK II reactor for 30 hours at neutron flux of $2.6 \times 10^{12} \text{ n}\times\text{cm}^{-2}\times\text{sec}^{-1}$ (fluence $2.8 \times 10^{17} \text{ n}\times\text{cm}^{-2}$). The rack is maintained in constant rotation to make consistent and uniform flow and energy spectrum of neutrons incident.

2.2.3 Measurements. The γ measurements were carried out by mean of a counting system constituted by a HPGe detector (EG&G Ortec, Oak Ridge, TN, USA) (resolution 1.70 keV at 1332.50 keV, relative efficiency 23%, peak to Compton ratio 58:3), an ORTEC 672 amplifier and a multichannel buffer ORTEC 918A connected to 8k channel analyzer through data acquiring system ADCAM MAESTRO II. The energy and efficiency calibrations were performed by ^{137}Cs - ^{60}Co (furnished by Laboratorio Metrologia delle Radiazioni Ionizzanti, ENEA-Casaccia) and ^{152}Eu (furnished by Centre Energie Atomique, France) sources, respectively.

3. Results and Discussion

3.1 Preliminary tests on electrodes, solutions and equipment

Preliminary some tests are performed on materials used in the experiments: in particular, we analyzed blank electrodes, electrolytic solutions, PET support, Pt wire, lab gloves and lab paper.

Table 2 shows the element levels, expressed as Bq, in blanks (mono-, double- and multi-layer electrodes and Li₂SO₄ 1 M electrolyte).

Table 2. Activities of some elements determined in blank electrodes (Bq) and electrolytic solution (Bq mL⁻¹) after Rabbit irradiation.

Element	Mono Cu	Mono Ni	Mono Pd	Double Cu/Ni	Multi Cu/Ni/Pd/Ni/Pd	Li ₂ SO ₄ 1 M
Ag	<5840	<1500	<2200	<2790	<1660	<114
Al	<62	209±1	468±8	2223±12	558±14	3954±50
As	<41	<2	<5	<13	<12	<123
Au	<13	2±1	<3	<5	<3	
Br	<391	<29	145±30	404±111	<133	8920±662
Cl	<32	<30	111±16	168±18	78±15	<81
Cu	298000±2490	2330±105	<166	259140±1308	163560±1742	
Mg	<89	<21	<26	<51	<39	<252
Mn	56±17	66±4	109±5	118±8	143±10	<94
Na	<8	<3	<4	<3	<7	1217±80
Ni	46±16	322±8	<13	318±26	698±36	
Pd	1093±348	7±1	27869±178	337±6	43933±421	
V	<19	<13	205±7	609±10	130±13	<520

It can be noted that typical environmental contaminants such as Al, Br, Cl and Na, are at levels around or below the Minimum Detectable Activity (MDA). The electrodes are clean: the only interesting issue regards a significant activity of Cu and Pd and of Ni and Pd in mono-layer Ni and Cu electrodes, respectively. This is most likely due to a memory effect despite an accurate cleaning of the sputtering system. For the electrolyte, the only relevant fact concerns the activities of Al, Br and Na: the levels depend on the impurities composition of the lithium sulfate.

Table 3 shows the levels of the elements investigated in materials used in the experiments such as PET support, Pt wire, laboratory gloves, laboratory paper and the two solutions (Li₂SO₄, 10⁻³M and 1M).

Table 3. Activities of some elements determined in PET support after etching, lab gloves, lab paper (Bq), Pt wire (Bq g⁻¹) and electrolytic solution (Bq mL⁻¹) after Lazy Susan irradiation.

Element	PET support	Lab gloves	Lab paper	Pt wire	Li ₂ SO ₄ 10 ⁻³ M	Li ₂ SO ₄ 1M
Ag	6.19±0.12	<238	<0.75	1986±46	<0.05	<0.2
Co	0.27±0.07	52±21	18.1±0.6	<33	0.26±0.03	<0.2
Cr	9.43±0.35	<4430	115±6	<15000	4.8±0.2	<10
Eu	<0.08	<224	<1.6	<503	<0.05	<1.6
Fe	<0.35	<500	7.8±1.6	<229	0.79±0.07	<0.7
Hf	4.42±0.05	<407	37±1	<239	<0.11	<0.7
Ir	0.16±0.03	<239	<1.1	3020100±18138	<0.05	<0.4
Ni	<0.13	<410	<2	<44	<0.07	<0.4
Sb	<0.06	<185	46±1	<553	0.16±0.03	1.7±0.2
Se	<0.1	<213	<2	<249	<0.07	1.1±0.4
Ta	0.59±0.11	<374	629±8	1510±61	0.64±0.10	0.98±0.29
Zn	1.14±0.11	3919700±47784	820±12	148±52	0.59±0.10	1.76±0.29

The main considerations regard the levels of Zn in lab gloves, Ta and Zn in lab paper and Ag, Ir, Ta and Zn in Pt wire. The highest level of Zn in laboratory gloves is due to the ZnO or ZnSO₄ present inside the gloves as lubricant. This level should be not significant for our experience because, being inside the gloves, Zn can not be transported in the experiment. Maybe, other contamination source of Cr, Hf and Zn is the mould during the etching process. Finally, the values of such elements can justify a possible contamination from Pt wire.

Table 4 shows the results of the elements investigated after the first series of experiments using Li₂SO₄ as electrolytic solution on mono- (Cu, Pd and Ni), double- (Cu/Ni) and multi-layers, obtained subtracting the blank level. Among elements the Au levels are due to a contamination from the platinum anode because of the erosion occurring during the electrolysis process. Other considerations can be applied to Zn, and Mo, W, Cr which belong to the same chemical group and have the same chemical behavior. Further, they participate both to the preparation of the thin-film during the etching process and during the deposition of the thin-film. For these reasons, they can derive from a contamination occurring before the experiments. The most interesting result is the V level: in the various electrodes V amount is reproducible and ranges between 204 and 228 ng except for the mono Pd-layer (25 ng). Finally, levels of other elements are around or below MDA (e.g. As) and index of minimum contamination (e.g. Na)

Table 4. Activities (Bq) of some elements determined in spent electrodes and V amount (ng) after the first series of experiments. The second column reports the irradiation position (IP): R as Rabbit and LS as Lazy Susan. n.d.: not determined.

Element	IP	Mono Cu	Mono Ni	Mono Pd	Double Cu/Ni	Multi Cu/Ni/Pd/Ni/Pd
Activities						
Ag	R	<4150	n.d.	n.d.	<3750	<3430
Ag	LS	n.d.	42±1	<0.5	<0.6	<0.6
Al	R	446±8	<137	<39	<167	<145
As	R	<27	<5.2	<2.4	<16	<8.8
Au	R	<9	38±4	<3.4	15±7	16±7
Au	LS	n.d.	8490±33	1423±8	592±3	1481±11
Br	R	<200	<98	<70	390±138	<156
Br	LS	n.d.	66±1	<8	27.3±0.6	<8
Cl	R	<7	<28	<34	<29	<35
Co	LS	n.d.	2.5±0.5	<0.4	<0.6	2.3±0.4
Cr	LS	n.d.	129±4	<7.4	64±3	<11
Fe	LS	n.d.	<1.3	<1.2	4.5±0.4	<1.6
Mg	R	<57	<37	<16	<55	<49
Mn	R	94±13	99±7	<13	113±11	29±10
Mo	LS	n.d.	9.3±0.5	<0.8	1.4±0.2	32.4±0.4
Na	R	<9	18±7	<6	<12	<10
Sb	LS	n.d.	34±1	5.7±0.4	8.4±0.6	21.2±0.9
V	R	12766±81	12733±81	1507±29	13795±102	17424±425
W	LS	n.d.	578±2	<42	<50	112±3
Zn	LS	n.d.	82±2	71±1	11.8±1.4	92±4
Amount						
V		212	210	25	228	204

Table 5 shows the levels of the elements investigated in this study during the second series of experiments. For Cu/Ni double layers we are set up two different tests. Although it is already considered the subtraction of the blank, there are measurable levels of Ag, Cr, Fe, Se, Ta and Zn. This may be due to minimal presence of contaminants (detectable only by INAA). These contaminants are deposited on the cathode during the electrolysis process: even if they are measurable, this is really an apparent enrichment and, according to us, this is not due to transmutation phenomena in condensed matter. Furthermore, the levels of some elements, expressed as ng, show that ultra-trace levels of contamination should always be considered.

Table 5. Activities (Bq) and amount (ng) of some elements determined in spent electrodes after the second series of experiments (Lazy Susan irradiation position).

Element	Mono Cu	Mono Ni	Double Cu/Ni	Double Cu/Ni	Double Cu/Pd
Activities					
Ag	3.6±0.3	144±2	8.89±0.24	39.1±0.63	6.03±0.30
Co	<0.37	<0.39	<0.50	1.33±0.39	8.9±0.3
Cr	598±3	341±2	69±2	733±3	475±3
Eu	1.85±0.83	<1.07	<0.81	<1.46	<1.24
Hf	<0.94	<1.2	<1.1	<1.3	<1.2
Ir	76±6	451±3	156±1	407±3	154±1
Ni	<1.2	<1.34	<1.67	<1.70	2.08±0.20
Sb	<0.82	<0.82	<0.73	<1.04	<1.34
Se	5.88±0.32	4.15±0.32	<0.59	2.36±0.33	<0.88
Ta	9.75±0.44	6.46±0.48	<2.1	6.75±0.61	21.3±1.3
Amount					
Ag	27±2	1083±28	67±2	294±8	45±3
Co	<0.66	<0.70	<0.89	2.4±0.7	15.9±0.6
Cr	1020±9	582±3	117±3	1250±9	810±7
Fe	3410±160	2500±180	3060±270	3990±270	4790±25
Zn	1509±78	825±3	354±24	567±33	920±50

4. Conclusion

INAA was useful to investigate the possible formation of new species attributable to the transmutation phenomena. For this purpose we studied each system component and, after the experiments, the electrodes and electrolytes. Resuming the results it can be evidenced: a) the Ag, Au, Ir, Ta and Zn levels are due to contamination problem from platinum anode (mainly because of the erosion occurring during the electrolysis process); b) the presence of Cr, Hf, Mo, W and Zn can be attributed to mould during the etching process and to their participation to the thin-film preparation; c) the contamination of Ag, Co, Cr, Fe and Zn at very low levels (detectable only by INAA) can be attributed to cathode deposition during electrolysis. Actually, this is an “apparent” enrichment and not due to transmutation phenomena in the condensed matter

The only anomaly which is difficult to give some explanations regards the V levels (ranging between 25-280 ng) found in the first experiment. The proportionality with the applied current and the evidence on all kind substrates is pointing in the direction of an eventual contamination.

Finally, our consideration regards the future researches: a good strategy is to use suitable markers (e.g. radiotracers).

5. Reference

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