Thick zinc electrodeposition on copper substrate for cyclotron production of ⁶⁴Cu

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Abstract. Zinc-68 electrodeposition on a copper substrate was investigated for the production of ⁶⁴Cu radionuclide. The electrodeposition experiments were carried out by acid plating baths. Operating parameters such as pH, temperature, and current density are also optimized. The current efficiency was measured at different current densities. The optimum conditions of the zinc electrodeposition were as follows: 6.2 g·l⁻¹ zinc, pH = 3, dc current density of ca. 85.54 mA·cm⁻² at 30°C with 98% current efficiency. SEM photomicrographs demonstrated fine-grained structure of the deposit obtained from the optimum bath.

Key words: zinc electrodeposition • zinc-68 target • Cu-64 • production • cyclotron isotope

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Introduction

The copper-64 physical-decay parameters ($t_{1/2} = 12.7$ h, $E_{\beta^+} = 0.66$ MeV, $E_{\beta^-} = 0.58$ MeV, $I_{\beta^+} = 17.8\%$, $I_{\beta^-} = 38.4\%$, $I_{EC} = 43.8\%$ [2, 11]) show some potential for endoradiotherapy applications in addition to its usefulness as a PET radiotracer [1]. It could become an effective radiotherapy agent for cancer treatment. Copper-64 is widely labeled as DTPA-peptide, DOTA-peptide or monoclonal antibody in colon cancer studies. Copper-64 labeled antibodies have shown promising results as radioimmunotherapy (RIT) agents [2]. Research has also shown that ⁶⁴Cu-PTSM is a potential tumor blood-flow quantification agent and hypoxia [9].

To produce ⁶⁴Cu several nuclear processes were considered; ⁶⁴Ni(p,n)⁶⁴Cu and ⁶⁸Zn(p, α n)⁶⁴Cu reactions were found to be most suitable [13, 14], partly because they could be used at a medium to low-energy cyclotrons. The Agricultural, Medical, Industrial Research School employs a Cyclone-30 (IBA, Belgium). Consequently, targetry for the second reaction was considered in this work. Solid targets of these accelerators are made up of pure copper backing on which target materials, such as zinc, are electrodeposited.

The electrodeposition of zinc is carried out by alkaline, acid and androgynous baths. Zinc alkaline baths consist of two types: cyanide or non-cyanide baths. The cyanide baths have high throwing power and assure excellent deposits. Temperature is a very important parameter of the baths. Correct control of the bath temperature can lead to 100% current efficiency; however, the use of cyanide baths has been limited because of their pollution.

Non-cyanide alkaline baths are used more than the other zinc electrodeposition baths. The amount of zinc in the bath is important as it affects the current efficiency which is usually 60-80%.

Zinc can be plated from several types of acid solutions, primarily based on either zinc sulfate or zinc chloride. Chloride baths have higher throwing power than sulfate acidic baths [5]. Hence chloride acid bath was chosen for this work.

Zinc chloride acid baths usually consist of zinc chloride, sodium chloride and ammonium chloride or potassium chloride. Addition of sodium or potassium acetate increases the conductivity [8].

Experimental

Material

Electrolysis solution was prepared from 40 g of NH₄Cl, 5.8 g of 68 ZnCl₂, in 450 ml of deionized water. Between the electrodes 1 A dc-current was used. Before plating zinc and to make certain about a good adhesion, a copper plate was cleaned with a sandpaper (1000 grade) followed by rinsing the copper plate with deionized water.

Non-reactive plating vessels were hollow Perspex cylinders (diameter 6 cm, height 20 cm) fitted with an axial Pt anode wire mounted at the bottom by means of a tube-end fitting with perforated septum. Four symmetrical windows (22.36 or 11.69 cm²) on the vertical side wall allow positioning up to four copper cathodes (targets backing). Each slot is sealed by an O-ring fittedwindow. The slot geometrical shape determines the actual target electrodeposition area. Windows liquid-tight sealing is realized by stainless steel mechanical pestles mounted on a PVC ring surrounding plating vessel and by pressing the copper backing against O-ring seal. An external PVC ring is fitted with four supporting pins to hold a motor-stirrer combination in position. The stirrer is a hollow perforated POM cylinder mounted on the axis of a dc motor and surrounding the platinum anode. The stirrer rotation speed is set at 600 rpm. Its rotating direction is reversed after each 8 s improving deposit homogeneity. To keep the desired temperature at a preset level, a heater (a series of six isolated $1 \Omega/1$ W resistors), through which an appropriate dccurrent is forced (1.1 A – 40°C up to 1.8 A – 60°C) is circularly mounted at the bottom of the vessel. An insulated sensor, introduced through the stirrer supportplate, monitors the plating bath bulk temperature. As electrolysis to depletion requires long-time (up to 24 h) plating, evaporation of plating solution occurs. To maintain a constant liquid volume, 450 ml, a conductivity glass/graphite sensor monitors the solution level and actuates a peristaltic pump at the required rate, supplying distilled water to compensate evaporation losses. The home-made electronic rack-mounted includes a motor/stirrer control, an adjustable dc voltage generator card and four V/I converters coupled to current boosters.

Enriched zinc-68 is expensive, so natural zinc chloride (99.99% purity) and ammonium chloride was purchased from Fluka Chemical Company to carry out initial experiment. The freshly prepared solution of zinc chloride was introduced into a plating vessel. This refined procedure is a result of several repeated experiments with different acidity of the bath, different temperature and electroplating currents.

All the electrodeposited Zn target layers were examined for morphology by a scanning electron microscopy (SEM) technique (using a Jeol model JSM 6400 at an accelerating voltage of 20 kV).

The thermal shock tests involved heating of the target up to 300°C (the temperature that the zinc layer can experience during a high current irradiation) for 1 h followed by submersion of the hot target in cold water (15°C). The thermal shock test is a measure of the incorporation of plating bath compounds into the zinc crystal lattice and/or of their presence in the carrier/zinc layer interface. In both cases irradiation will cause a loss of target material, peeling off, and a decrease of the copper-64 yield.

Methods

In order to optimize the Zn electrodepositing, the experimental conditions were investigated as follows:

Calculations of required deposit thickness

To take full benefit of excitation function and to avoid the formation of radionuclidic impurities, the proton entrance energy should be 35 MeV [4, 7]. The physical thickness of the zinc layer is chosen in such a way that for a given beam/target angle geometry the particle exit energy should be 20 MeV. According to SRIM code (the stopping and range of ions in matter); the thickness has to be 1640 μ m for 90° geometry [15]. To minimize the thickness of the zinc layer, 6° geometry is preferred, in which case a 164 μ m layer is recommended.

Zinc targets are prepared by constant current electrolysis of the metal from acid plating solutions.

Pretreatment of Cu-backing

Zinc is a relatively noble metal; copper, being less noble than zinc, forms immersion deposits on the surface. This tends to happen even when the base metal enters a zinc solution hot and fresh, that is, with a voltage already applied. The inevitable result of this phenomenon is poor adhesion of subsequent deposits. To minimize this effect, it was concluded that if the plating was carried out very rapidly, a good adhesion would be obtained on all electroplated targets.

Embrittlement of metals has been recognized for many years but, as two authors have pointed out, some other defects in electrodeposits, such as blistering, cracking, gas pits, peeling off and poor adhesion, may also be related to hydrogen evolution in ways not yet identified. Plating on a dietary or greasy surface inevitably leads to blistering or peeling off. Cathodic cleaning in either acid or alkaline solutions provides large quantities of hydrogen for absorption [6]. In all experiments, the substrate surface was cleaned with a sandpaper (1000 grade) and immersed in a nitric acid bath of 2 M. Then, the surface was washed with water and its oil contaminators were removed by a mixture of alkali cleaning powders. Finally, the surface was washed with acetone.

Influence of current density

Zinc enhancement in the bath causes reduction of deposit adhesion at low current density, and insufficient zinc cause a burn-up of the deposit at high current density. So, variety of the optimum of the current density is completely relative to zinc percent in the bath.

According to some publications [3, 10] concerning concentrations of zinc salt, a bath with 89 g·l⁻¹ NH₄Cl, 12.9 g·l⁻¹ ⁶⁸ZnCl₂ was prepared. Low cathode efficiency was observed at low temperature, high pH and high metal content [6]. Use of a very low current density leads to a rather poor quality of the deposit, whereas a very high current density reduces the overvoltage of hydrogen, decreases the quality of the deposit and the current efficiency [12]. Hence, an optimal range of current density and bath acidity was investigated.

Influence of pH

Adjusting the bath acidity is important for the effect of bath efficiency and coating physical properties. A large reduction of acidity causes hydrogen reduction and simultaneously sediment of the basis salts on the cathode. Moreover, increasing the bath acidity reduces electroplating current efficiency. After preparing of the zinc bath for studying effects of solution acidity on electroplating quality, the acidity was changed from 2 to 5.5.

Influence of temperature

Increasing the temperature of the solution increases the mobility of the ions and reduces the viscosity of the solvent. As a result, it reduces concentration polarization and thus enhances the quality of the deposit (fewer tendencies to dendrite formation) and the current efficiency [12]. Influence of temperature on the deposit quality was considered at 30°C and 40°C.

Target quality control

To estimate the quality of the electroplated zinc targets some criteria had to be taken into account such as homogeneity, morphology, visual appearance of the zinc layer and thermal shock test. The thermal shock tests involved the heating of the target up to 300° C for 1 h followed by submersion of the hot target in cold water (15°C).

The homogeneity of the zinc layer is important as it may seriously affect the production rate of copper-64. This was determined by measuring the thickness of several parts of the layer by a micrometer and calculation of standard deviation of the data.

The electrodeposited Zn target layers were examined for morphology by a scanning electron microscopy (SEM) technique.

Table 1. Influence of current density, $89 \text{ g} \cdot \text{l}^{-1} \text{ NH}_4 \text{Cl}$, $12.9 \text{ g} \cdot \text{l}^{-1} \text{ ZnCl}_2$ solutions, 24°C , pH = 7, t = 20 min

I (mA·cm ^{−2})	t_0^* (µm)	t_{c}^{**} (µm)	Current efficiency (%)
2.99	1.12	1.12	67.82
5.13	2.15	2.15	75.75
6.84	2.92	2.92	77.02
8.55	3.88	2.88	81.80
10.26	4.74	4.74	83.36
17.10	7.65	4.02	42.42
34.21	16.71	0.41	2.36

* t_0 – mean thickness of the deposit in micrometers.

** t_c – mean thickness of the deposit in micrometers after CIF cleaning.

Results

The current efficiency was determined at different current densities using dc current at pH of 7 at room temperature. Results of these experiments indicate that higher current efficiency is obtained with increasing current density. Maximum thickness of the obtained deposits was about 5 μ m in these experiments (Table 1).

The deposits were weighed immediately after plating, and then they were cleaned with a print-board eraser to remove the weak-adhering grains from deposit surfaces. The deposits were re-weighed; comparing the weight before and after cleaning. High differences between them were observed. Therefore, further experiments were carried out at pH of 2, 3 and 5.5 (Figs. 1b, 1c, 1d). Fig. 1a relates to pH 7.

In the next experiments, the quality of deposit was improved and the difference of deposit thickness before and after cleaning was decreased.

The acquired data from further electroplating experiments showed that decreasing of deposit thickness after cleaning is negligible at pH 3 (Fig. 1c) as compared with pH 2 and 5.5 (Figs. 1b, 1d), furthermore the quality of the deposits was more suitable at pH 3. Therefore, an optimum dc current density of 85.54 mA·cm⁻² at pH 3 should be applied to achieve a suitable deposit and best current efficiency (Tables 2–4).

At the end, the feeble Zn of the deposit was easily removed by simple rubbing of the surface layer with a print-board eraser. The feeble zinc was not observed in the optimum conditions of the electrodeposition. Neither crater formation nor peeling off was observed during the thermal shock treatment.

Table 2. Influence of current density, $89 \text{ g} \cdot l^{-1} \text{ NH}_4 \text{Cl}$, $12.9 \text{ g} \cdot l^{-1} \text{ ZnCl}_2$ solutions, 24°C , pH = 5.5, t = 20 min

I (mA·cm ⁻²)	t_0^* (µm)	t_{c}^{**} (µm)	Current efficiency (%)
2.99	0.64	0.64	38.36
5.13	2.20	2.20	77.44
6.84	3.23	3.23	85.22
8.55	4.63	4.63	97.72
10.26	5.21	5.21	91.54
11.97	6.34	6.34	95.63
17.10	7.36	7.36	77.65
34.21	19.85	0.06	5.99

 t_0 – mean thickness of the deposit in micrometers.

** t_c – mean thickness of the deposit in micrometers after CIF cleaning.



Fig. 1. The thickness of a zinc deposit on the Cu backing vs. current from 89 g·l⁻¹ NH₄Cl, 12.9 g·l⁻¹ ZnCl₂ solutions, 24°C, time = 20 min; a - pH = 7; b - pH = 5.5; c - pH = 3; d - pH = 2; e - pH = 3, 30°C; f - pH = 3, 40°C. t_0 = mean thickness of the deposit in micrometers, t_c = mean thickness of the deposit in micrometers after CIF cleaning.

The maximum current efficiency was 94.40% at a current density of 2.99-85.54 mA·cm⁻² at room tem-

Table 3. Influence of current density, $89 \text{ g} \cdot \text{I}^{-1} \text{ NH}_4 \text{Cl}$, $12.9 \text{ g} \cdot \text{I}^{-1} \text{ ZnCl}_2$ solutions, 24°C , pH = 3, t = 20 min

Ι	t_0^{*}	t_{C}^{**}	Current efficiency
$(mA \cdot cm^{-2})$	(µm)	(µm)	(%)
2.99	0.41	0.41	25.25
5.13	2.68	2.68	70.70
6.84	3.60	3.60	76.01
8.55	5.16	5.16	90.69
10.26	5.71	5.71	86.03
11.97	6.99	6.99	73.73
17.10	14.36	14.36	75.69
34.21	26.87	26.87	94.40
51.32	26.70	26.70	94.30
68.43	42.84	40.28	83.50
85.54	43.67	40.31	92.04

* t_0 – mean thickness of the deposit in micrometers.

** t_c – mean thickness of the deposit in micrometers after CIF cleaning.

perature and 98.20% at 30°C in the same electroplating time (Table 5).

In all experiments that were carried out at 30°C the difference of the deposit thickness before and after

Table 4. Influence of current density, $89 \text{ g} \cdot \text{I}^{-1} \text{ NH}_4 \text{Cl}$, $12.9 \text{ g} \cdot \text{I}^{-1} \text{ ZnCl}_2$ solutions, 24°C , pH = 2, t = 20 min

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	I (mA·cm⁻²)	t_0^* (µm)	t_{c}^{**} (µm)	Current efficiency (%)
	2.99	0.59	0.59	36.07
	5.13	1.61	1.61	56.81
	6.84	2.26	2.26	59.65
	8.55	3.28	3.28	69.19
	10.26	3.46	3.46	60.81
	11.97	4.90	4.90	73.77
	17.10	5.82	5.82	61.36
	34.21	31.80	31.80	72.79
	85.54	28.80	28.80	60.68

* t_0 – mean thickness of the deposit in micrometers.

** t_c – mean thickness of the deposit in micrometers after CIF cleaning.

Table 5. Influence of current density, $89 \text{ g} \cdot \text{I}^{-1} \text{ NH}_4 \text{Cl}$, $12.9 \text{ g} \cdot \text{I}^{-1} \text{ ZnCl}_2$ solutions, 30°C , pH = 3, t = 20 min

I (mA·cm⁻²)	t_0^* (µm)	t_{C}^{**} (µm)	Current efficiency (%)
2.99	1.45	1.45	87.30
6.84	3.34	3.34	85.86
8.55	4.30	4.30	90.66
10.26	5.25	5.25	93.01
11.97	6.30	6.30	94.88
17.10	9.30	9.30	96.97
34.21	18.66	18.66	98.30
51.32	27.99	27.99	98.25
85.54	46.60	46.60	98.20

* t_0 – mean thickness of the deposit in micrometers.

** t_c – mean thickness of the deposit in micrometers after CIF cleaning.



Table 6. Influence of current density, $89 \text{ g} \cdot \text{l}^{-1} \text{ NH}_4 \text{Cl}$, $12.9 \text{ g} \cdot \text{l}^{-1} \text{ ZnCl}_2$ solutions, 40°C , pH = 3, t = 20 min

I (mA·cm ⁻²)	t_0^* (µm)	t_{c}^{**} (µm)	Current efficiency (%)
2.99	1.34	1.34	81.16
8.55	3.85	3.85	80.05
10.26	4.80	4.80	84.42
11.97	5.30	5.30	79.73
17.10	7.90	7.90	83.21
34.21	16.12	16.12	84.72
51.32	24.00	24.00	72.68
85.54	40.20	40.20	84.72
85.54	39.80	39.80	83.89

* t_0 – mean thickness of the deposit in micrometers.

** t_c – mean thickness of the deposit in micrometers after CIF cleaning.



Fig. 2. SEM of a zinc deposit on the Cu backing grown at a current density of $85.54 \text{ mA} \cdot \text{cm}^{-2} 89 \text{ g} \cdot \text{l}^{-1} \text{ NH}_4 \text{Cl}$, $12.9 \text{ g} \cdot \text{l}^{-1} \text{ ZnCl}_2$ solutions, time = 20 min, pH = 3; a – 30°C, 45.9 µm thickness, b – 40°C, 39.8 µm thickness.

cleaning was very low (Fig. 1e). The repeat of these experiments at 40°C and the same time showed that the current efficiency decrease (Table 6), but the deposit thickness is difference between before and after cleaning (Fig. 1f).

The evaluation of quality of the layers was achieved by comparison of the SEMs in terms of size and form of the Zn nuclei and the extent to which they overlapped each other. The smaller, more spherical and more overlapping nuclei were considered to be a good plating quality.

SEM photomicrograph showed that granulometry of electroplated targets with a current density of 85.54 mA·cm⁻² at 30°C had good adhesion between deposit and backing. Moreover, the deposit had a small granulometry, but at 40°C it was not as good as that at 30°C (Figs. 2a, 2b).

Conclusion

⁶⁴Cu can be produced by electroplated zinc on copper backing using zinc chloride/ammonium chloride solution. The electrodeposition experiments were continued for depletion of ⁶⁸Zn ($\eta > 98\%$) with 164 µm and an optimum amount of zinc-68 (6.2 g·l⁻¹) in the bath. The layer thickness is no longer time-controlled, but is governed by the amount of Zn present in the plating bath. As the electrodepositions satisfy thermal shock test, beam current irradiation of higher than 200 µA can be applied. The electrodeposition of ⁶⁸Zn using chloride baths gives quite acceptable quality for the irradiation purposes.

To produce no-carrier-added ⁶⁴Cu, ⁶⁸Zn can be electroplated on gold-coated copper backing or on nickel-coated copper backing.

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