

# The critical potential of the Pb underpotential deposition (UPD) on Pt

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The electrodeposition of a metal ion  $A^{n+}$  on a foreign metal surface B in the sub-monolayer region often takes place at a more positive potential compared to the potential calculated via the Nernst equation. The so called underpotential deposition has been studied by cyclovoltammetry [1] and radiotracer methods [2]. Calculations with a modified Nernst equation basing on physical properties of the deposited and the electrode metal lead to predictions for electrode potentials for the deposition of 50% of  $A^{n+}$  on B ( $E_{50\%}$ -values).  $E_{50\%}$ -values were calculated for the deposition of element 112 to 115 and their homologues Hg, Tl, Pb and Bi on noble metals such as Au, Pt and Pd [3],[4]. According to these predictions it might be possible to perform electrodeposition experiments with element 114. To verify the predictions, more experimental data are necessary. Hevesy and Paneth defined the critical potential  $E_{crit}$  as the potential, at which electrodeposition of a radiotracer on a metal electrode first occurs [5]. Obviously, critical potentials measured in an experiment should be similar to the predicted  $E_{50\%}$  values.

Tab.1 Predicted  $E_{50\%}$  values (vs. Ag/AgCl (3M KCl) electrode) for the deposition of Pb and element 114 on noble metals [3,4]

Electrode	Cu	Pd	Ag	Pt	Au
Ion					
Pb <sup>2+</sup>	-0,52	0,31	-0,47	0,01	-0,40
114 <sup>2+</sup>	1,04	0,66	0,74	1,14	0,64

We carried out deposition experiments with <sup>212</sup>Pb as radiotracer. As electrode metal we chose Pt. <sup>212</sup>Pb was prepared by using a <sup>220</sup>Rn emanating source (<sup>228</sup>Th co-precipitated with Zr-Stearate). The <sup>220</sup>Rn daughter products were collected from the gas phase on a Pt-electrode at a potential of -150V for 24h. <sup>212</sup>Pb was then dissolved with hot 6 N HCl, the solution was evaporated to dryness and dissolved in 0,1 N HCl.

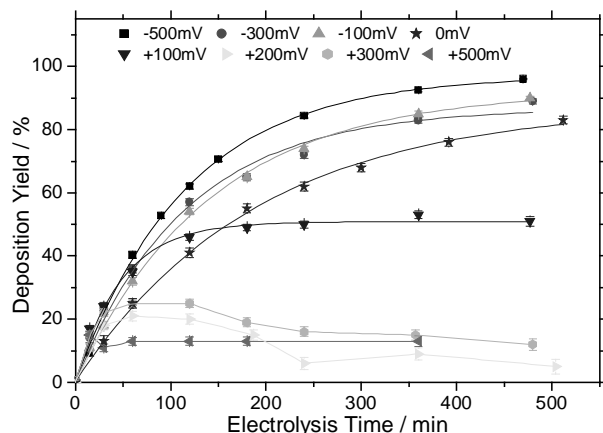


Fig.1 Electrodeposition of <sup>212</sup>Pb on a Pt electrode vs. electrolysis time at different electrode potentials (vs. Ag/AgCl, 3M KCl)

The deposition experiments were performed at constant electrode potentials, see Fig.1, by using a potentiostatic three-

electrode system with a Ag/AgCl (3M KCl) reference electrode, a Pt working electrode and a Pt counter electrode. The area of the working electrode was 2 cm<sup>2</sup>, the total volume of the solution was 20 ml, for agitation a constant nitrogen flow was applied. Prior to the experiment, the working electrode was cleaned at +1400mV for 15 min.

To determine the deposition of <sup>212</sup>Pb vs. the electrodeposition time without disturbing the system, we measured the decrease of the activity in the solution. This experiment was repeated at different electrode potentials. The experimental data were fitted by equation (1).

$$\frac{N_{dep}}{N_{tot}} = \frac{a}{a+b} - \frac{a}{a+b} \cdot e^{-(a+b)t} \quad (1)$$

$N_{dep}$  is the amount of deposited atoms,  $N_{tot}$  is the total amount. The term  $a/(a+b)$  represents the maximum deposition yield for a given electrode potential. The critical potential determined with Joliot's method (Fig. 2) [2] is +190 mV, this is in good accordance with the critical potential of +255 mV for the deposition of Pb on Pt in 1 N HNO<sub>3</sub> measured by Ziv et al. [6]. The predicted  $E_{50\%}$  value (+10 mV) is somewhat lower than the measured  $E_{crit}$ -value, but the difference gets smaller if compared with the potential at which the maximum deposition yield is 50% (approx. +100mV).

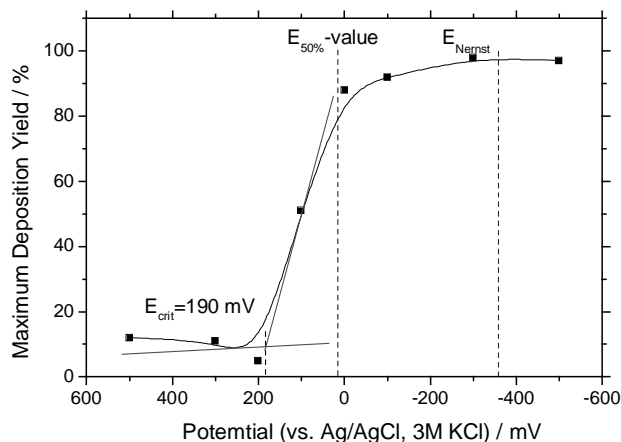


Fig.2 Determination of the critical potential  $E_{crit}$  for the deposition of <sup>212</sup>Pb on Pt in 0,1 N HCl (vs. Ag/AgCl 3M KCl)

The use micro-reference electrodes (0,5-1,5 mm diameter) will allow experiments with small volumes (100μl). This should lead to a drastic decrease in electrodeposition time. Future plans are to develop an automated apparatus for electrodeposition experiments with superheavy elements.

## References

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