Electrodeposition of Polonium and Interaction between the Deposited Polonium and Based-Electrode Materials

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The electrodeposition of far less than monolayer of ^{210}Po on various metal or carbon electrodes was investigated. A special attention was paied on the penetration of Po deposited at the surface into the bulk of electrode materials, M_{el}. The extent of the penetration (D) was estimated meausring the energy of α particle emitted from deposited ^{210}Po by means of α-ray spectrometry and taking the stopping power of M_{el} for ^{4}He into account. The deposited Po easily penetrate into such metals as Pb, Tl and Te, but hardly into such M_{el} as stainless steel, glassy carbon or metals of Pt, Ta, Co, Ni, Nb, Mo and W. The extent, D. also depends on the deposition potential.

INTRODUCTION

The electrodeposition process of a metal on a metal electrode, M_{el}, can be categorized into following four steps[1]; (1) the mass transfer of the metal ion in solution to the surface of M_{el}, (2) the discharge of the ion producing the metal atom, M^0, (3) the crystallization of M^0 on the surface of M_{el} and (4) the penetration of M^0 deep into M_{el} from the surface due to the diffusion of M^0, the dissolution of M^0 in M_{el} and/or the formation of metallic compounds between M^0 and M_{el}.

Step (4) is considered to be important not only in the elucidation of the electrode process but also in the estimation of the stability of the deposited layer and in the improvement of the sensitivity to analyze trace metal ions in solutions by the anodic stripping voltammetry[2,3]. Studies on step (4), however, are very few compared with those on the other steps, (1) to (3), and such detailed investigations as on the extent or the rate of the penetration have not been available.

In the present work, ^{210}Po is electrodeposited on various M_{el} from an extremely dilute aqueous solution and the penetration of discharged Po into M_{el} is measured by means of the α-ray spectrometry taking the stopping power of M_{el} for α particle into account[4]. ^{210}Po decays emitting α-ray of 5.3 MeV and produces stable ^{206}Pb (half-life; 138.38 dyas).

II. EXPERIMENTAL

Chemicals

The carrier-free ^{210}Po stock solution (Product of AMERSHAM Co. Ltd., Lon-

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don) was about $1 \text{ mCi} \cdot \text{ml}^{-1}$ in Po and 0.5 M in HNO_3. The Po solution was used within 2 months after preparation. Other reagents used were of reagent grade.

Electrode materials

Metal plates (0.1 cm t) of Ag, Al, Au, Pd, Pt (more than 99.99% purities), Bi, Cd, Co, Cu, In, Mo, Nb, Ni, Pb, Ta, Sb, Sn, Te, W, Zn (more than 99.9% purities) and stainless steel (SUS 304), and a glassy carbon plate (0.2 cm t, Tokai Carbon, GC-20) were employed as electrode materials, M_{el}, after polishnig by means of emery paper (No. 1200) to mirror like surfaces or electropolishing (in case of Pb)[2] followed by washing with ethanol and then water under ultrasonic treatments[3]. The electrode surface area was 0.2 cm².

Apparatus

^{210}Po was deposited on various M_{el} by the electrolysis using a potentiostat (Hokuto Denko Co., Type HA-211) with the aid of a calomel (sat. KCl) reference electrode (denoted as SCE) and a platinum wire counter electrode.

The α-ray spectra were measured by a silicon surface-barrier detector (Seikiko-gyo Lab., Type SVC-9) and a multichannel analyzer (ORTEC, Model 6240B).

Electrolyses were carried out at $25 \pm 1°C$ and α-ray spectra were measured at room temperature.

III. RESULTS AND DISCUSSION

Electrodeposition of ^{210}Po

After electrolysis for 30 min at a definite potential in 10 ml of stationary solution which was 10^{-11} M in ^{210}Po and 0.5 M in HNO_3, the amount of Po electrodeposited (Q_{dep}) on an electrode was determined by the α-counting. Electrode materials which do not dissolve even at fairly positive potentials were selected for this study.

The relation between Q_{dep} and applied potentials thus obtained is plotted in Fig. 1. The diffusion-controlled limiting Q_{dep} attained at sufficiently negative potentials is far less than the amount for mono-layer deposition (*ca.* $0.2 \text{ }\mu\text{g} \cdot \text{cm}^{-2}$). Therefore, the contribution of the interaction among Po atoms themselves at the surface of the electrode can be neglected in the electrodeposition and the penetration processes of Po.

Defining the half-deposition potential, $E_{1/2}^{dep}$, as the potential where Q_{dep} is a half of the limiting Q_{dep} after the half-wave potential in the ordinary voltammetry, $E_{1/2}^{dep}$ for the deposition of Po are $+0.63$, $+0.51$, $+0.44$ and $+0.06$ V vs SCE at Pt, Au, Ta and GC electrodes, respectively.

Since the bonding energy between discharged Po(0) and carbon is extremely small and, hence, the deposition of Po on GC requires the crystallization overpotential to form the Po(0)-Po(0) bonding, $E_{1/2}^{dep}$ at GC lies at more negative potential than the formal potential for Po(0)/Po(II) couple, ca. $+0.40$ V vs SCE[5].

At metal electrodes (M_{el}), $E_{1/2}^{dep}$s are at more positive than the formal potential because of bonding between Po(0) and M_{el} (Underpotential deposition). Generally,

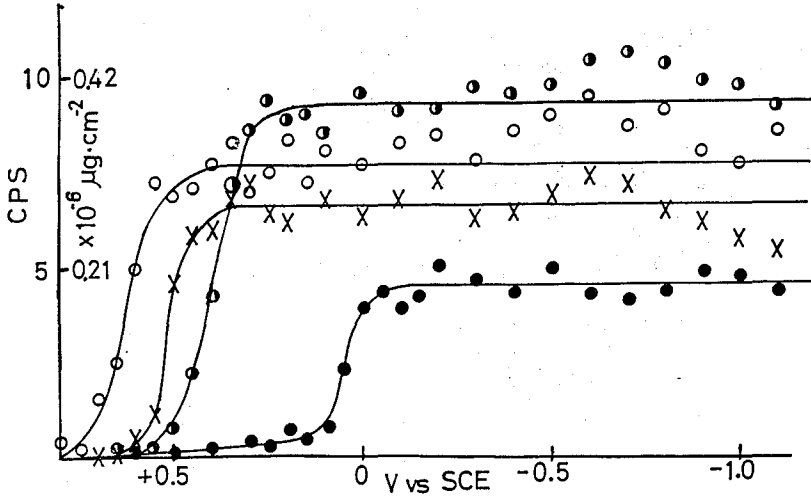Fig. 1. Relation between electrode potential and amount of Po deposited.
Electrolysis for 30 min in a solution of 0.08 $\mu C \cdot ml^{-1}$ (8.4×10^{-11} M) ^{210}Po and 0.5 M
HNO$_3$. Electrode materials; 1: Pt, 2: Ta, 3: Au, 4: GC.

the extent of the underpotential, U_p, is correlated to the difference of work func-
tion, $\varPhi$, of the depositing metal, M^0, and that of M_{el} by eqn. (1)[6,7],

$$U_p = (1/2e) \{\varPhi(M^0) - \varPhi(M_{el})\} \qquad (1)$$

where e is the elementary charge.

   Although the critical evaluation of U_p for the deposition of Po based on eqn (1)
is difficult at the moment because of the uncertainty in $\varPhi$ of Po reported, the order
of $E_{1/2}^{dep}$ at Pt, Au and Ta electrodes is essentially the same as that of $\varPhi$ for these metals
($\varPhi$: 5.40, 5.0 and 4.15 eV for Pt, Au and Ta, respectively[7,8]).

   Distinguishable discrepancy was not observed in $E_{1/2}^{dep}$ when the concentration
of Po in the electrolytic solution was changed from 10^{-11} to 10^{-9} M.

Penetration of discharged polonium, Po(0), into electrode metals

   The penetration of Po(0) discharged at the surface of M_{el} into M_{el} was inves-
tigated by measuring the α-ray spectra of deposited ^{210}Po.

   If the deposited Po penetrate deep into M_{el}, the energy of α-ray is lowered by
the stopping power of M_{el}. Hence, the extent of the penetration (D, μm) can be
determined from the energy shift of α-ray using "^{4}He projected ranges (R_p, μm)"
given as eqn (2) by Zieglar[4].

$$R_p(E) = \exp(A_1 + A_2 EE + A_3 EE^2 + A_4 EE^3 + A_5 EE^4 + A_6 EE^5) \qquad (2)$$

$$D = R_p(E_0) - R_p(E_i) \qquad (3)$$

In eqn (2), E, EE and A$_i$s are the energy of α particle in keV, ln E and constants
given for individual metal, respectively. E_0 and E_i are the energy of α particle
emitted from ^{210}Po deposited at the surface of M_{el} and that penetrated to a definite
distance from the surface (*cf*. Fig. 2). Equation (2) is valid for α particle of E
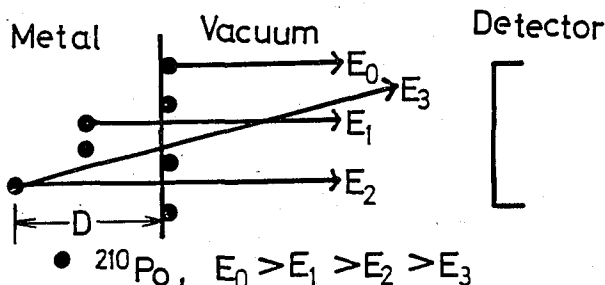
(51)

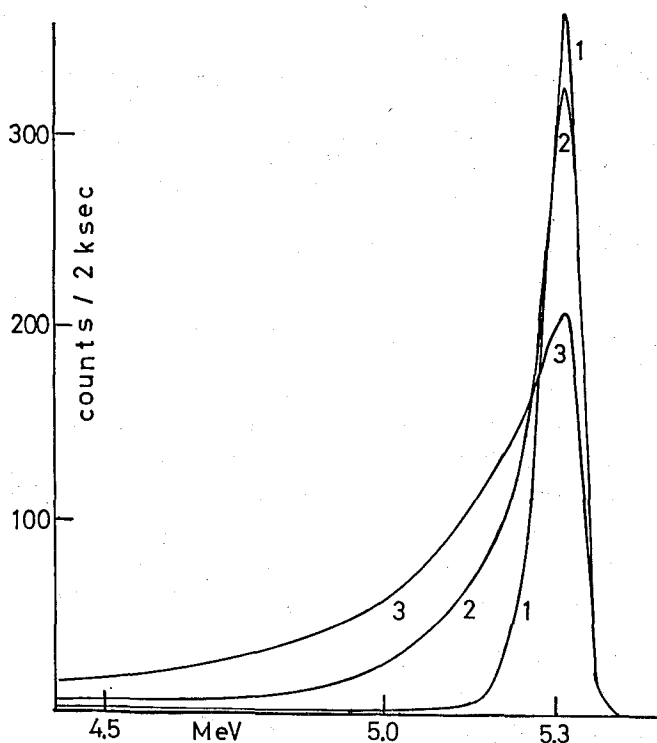Fig. 2. Energy of α particles emitted from ^{210}Po at the surface and penetrated in a metal electrode.

Fig. 3. α-ray spectra of electrodeposited ^{210}Po.
Deposited at -1.0 V vs SCE for 3 hrs in a solution of 0.016 $\mu Ci \cdot ml^{-1}$ (1.68×10^{-11} M) in ^{210}Po and 0.5 M in HNO_3. Electrode materials; 1: Pt, 2: Bi, 3: Pb. Amount of ^{210}Po deposited on Pt, Bi, and Pb were 0.60×10^{-6}, 1.2×0^{-6} and 1.3×10^{-6} $\mu g \cdot cm^{-2}$, respectively.

between 1 keV and 10 MeV.

Figure 3 realizes α-ray spectra of ^{210}Po obtained by the following procedure; ^{210}Po was electrodeposited on various M_{el} at -1.0 V vs SCE for 3 hrs in a solution which is 0.016 $\mu Ci \cdot ml^{-1}$ (1.68×10^{-11} M) in ^{210}Po and 0.5 M in HNO_3, and the M_{el} with deposited Po was washed with water and then aceton. After drying the M_{el} was set in a vacuum chamber and the α-ray spectrum was measured by a surface

barrier type detector. The deposition potential, -1.0 V, is negative enough for the deposition of Po and, at this potential, the dissolution of all M_{el} invsetigated does not take place even in acidic media.

The penetration of Po into Pt is considered to be negligible since the spectrum exhibited a sharp peak at around 5.3 MeV which is the energy of α-ray from ^{210}Po itself. The obvious tailing toward lower energy range was observed in the spectrum when M_{el} was Pb or Bi indicating the serious penetration of ^{210}Po into these M_{el}.

In Fig. 4, α-ray spectra in Fig. 3 are replotted as functions of the logarithm of counts vs energy. In the followings we will discuss the extent of the penetration (D) employing the energy (E_D) at which the extrapolation of the straight part in the logarithmic plot (indicated by broken lines in Fig. 4) merges in the back ground under the assumption that E_D is the energy of α particle emitted from ^{210}Po which penetrated into the deepest part in M_{el}. Substituting thus obtained E_D into eqns (2) and (3), D is estimated as 0.46, 3.0 or 5.1 μm for Pt, Bi and Pb, respectively. In this connection, when M_{el} on which Po had been deposited were stood for 3 days at room temperature in air, the increase of D was not observed.

Following to the procedure mentioned above, D for various M_{el} other than Pt, Bi and Pb were examined. Although the results were not so reproducible, roughly speaking, D were more than 3 μm when M_{el} were Te and Tl, 1 to 3 μm when Cd, In, Sn and Sb, and less than 1 μm when Al, Co, Ni, Cu, Zn, Nb, Mo, Pd, Ag, W, GC and stainless steel (SUS 304).

These results suggest that D is strongly related to melting pionts and/or hardness of metals which are controlled by lattice energies of metals. Po may penetrate
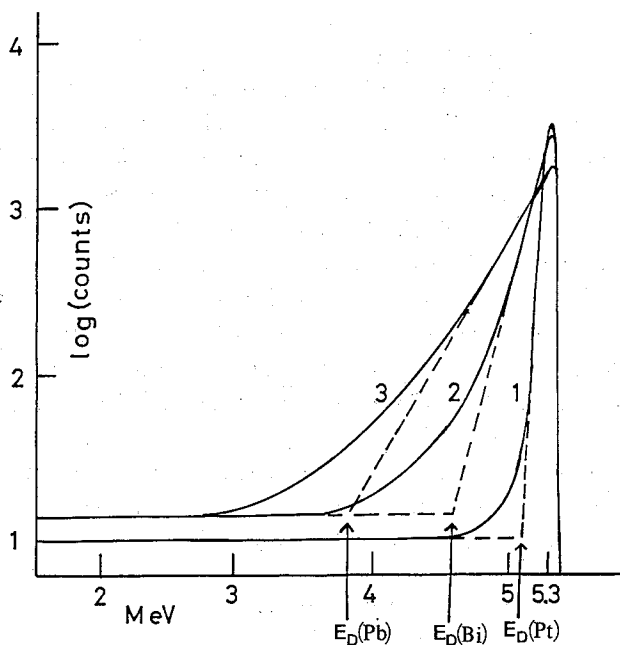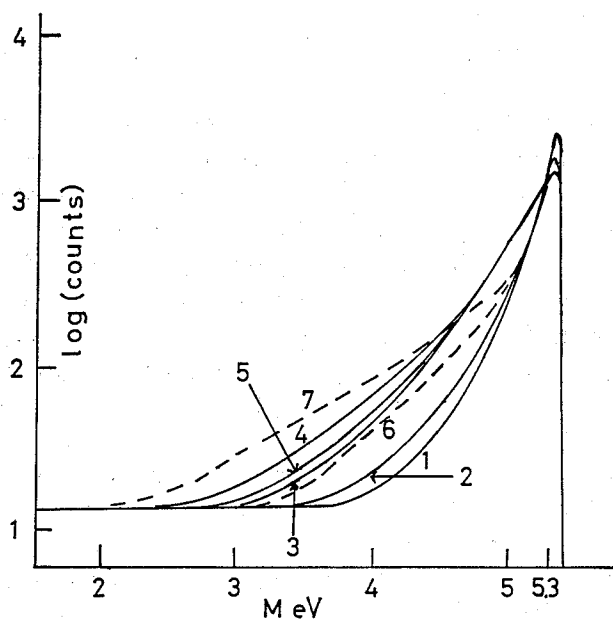

Fig. 4. As Fig. 3, but logarithmic plots.

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Fig. 5. Effect of deposition potential on α-ray spectra of ^{210}Po deposited
on Pb.
Electrodeposition for 3 hrs in a solution of 0.016 μCi·ml^{-1}
(1.68×10^{-11} M) in ^{210}Po and 0.5 M in HNO$_3$. Deposition
potential; 1: -0.60, 2: -0.75, 3: -1.00, 4: -1.50, 5: -1.75
V vs SCE. Curves 6 and 7; as curve 1, but electrolyzed for
12 hrs at -0.75 and -1.50 V, respectively, in 0.5 M HNO$_3$
without Po after deposition at -0.60 V.

easily in metals of which lattice energies are small.

The relation between the extent of penetration and the electrode potential for
the electrodeposition of Po was also studied using Pb as M_{el}. Curves 1 to 5 in Fig.
5 are the results obtained by the same procedure as that for Curve 3 in Fig. 4 but
variing the electrodeposition potential to a potential between -0.6 and -1.75 V
vs SCE where the dissolution of Pb does not occur. Po penetrated deeper with the
deposition potential more negative in the range -0.6 to -1.5 V. When Pb elec-
trode on which Po had been deposited at -0.6 V under the same condition as for
Curve 1 was further electrolyzed for 12 hrs at -0.75 or -1.50 V in 0.5 M HNO$_3$
solution in the absence of Po, the penetration proceeded depending on the electroly-
sis potential as demonstrated in Curve 6 or 7. Employing Bi as M_{el} instead of Pb,
similar phenomena were observed.

The effect of electrodeposition or electrolysis potential on the penetration of Po
indicates that the energy level of free electron in M_{el} plays very important roll in the
mobility of such discharged atoms as Po(0) in M_{el}.

REFERENCES

(1) S. H. Cadle and S. Brukenstein; *Anal. Chem.*, **44**, 1993 (1972).
(2) Z. Yoshida; *Bull. Chem. Soc. Jpn.* **54**, 562 (1981).

(3) Z. Yoshida and S. Kihara; *J. Electroanal. Chem.*, **172**, 39 (1985).

(4) J. F. Ziegler; *"Helium, Stopping Powers and Ranges in All Elemental Matter"*, Pergamon Press, New York, Vol. 4 (1977).

(5) W. M. Latimer; *"Oxidation Potentials"*, Prentice-Hall, New York, 2nd Ed., p 88 (1952).

(6) D. M. Kolb, M. Przasnyski and H. Gerisher; *J. Electroanal. Chem.*, **54**, 25 (1974).

(7) S. Trasatti; *"Adv. Electrochem. and Electrochem. Eng."*, John-Wiley & Sons, New York, Vol. 10, p213 (1977).

(8) S. Trasatti; *J. Electroanal. Chem.*, **33**, 351 (1971).