A Preliminary Electrochemical Study of Plutonium in Carbonate Solutions on Hanging Mercury Drop Electrode

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The production of UO_2' by electrochemical reduction and precipitation from carbonate solutions is a newly developed method[1] and could, probably, be used for the reprocessing of reactor fuels. In this context the electrochemistry of plutonium in carbonate solutions is of particular interest. The scope of the present work was to investigate the general electrochemical behaviour of the plutonium carbonato complexes on the mercury electrode. Out of a multitude of papers covering plutonium chemistry, none deals with this specific problem.

The formal redox potential of Pu (IV)/Pu (III) couple is very positive (about + 0.98 V[2] *vs.* N. H. E. in 1 *M* $HClO_4$), thus the electrochemical investigation on mercury electrodes necessitates the use of strong complexing media exhibiting large differences in stability between the oxidized and the reduced complex forms.

EXPERIMENTAL

A stock solution of plutonium-239 in 4 *M* HNO_3 was prepared after Ryan and Wheelwright[3]. In such a solution plutonium is predominantly in the + 4 oxidation state.

Samples were prepared by adding a concentrated stock solution of Pu (IV) into carbonate solution. A hanging mercury drop electrode (HMDE) after Kemula[4] was used. Cyclic voltammetric curves were recorded using a Radiometer Polarograph (PO-4). Purified nitrogen was passed through the solution for 20 minutes. As a reference electrode a saturated calomel electrode was used, and all potentials are referred against this electrode. All plutonium solutions were handled in a glove box.

RESULTS AND DISCUSSION

The cyclic voltammetric curves on HMDE, shown in Figs. 1 and 2, were recorded from solutions of approx. 1 m*M* Pu (IV) in 1 *M* Na_2CO_3 and 0.5 m*M* Pu (IV) in 0.5 *M* Na_2CO_3 + 0.5 *M* $NaHCO_3$, respectively.

Cathodic peak potentials were found at — 1.17 V and — 1.12 V, the anodic potentials at — 0.10 V and — 0.12 V.

In Figs. 3 and 4 the cyclic voltammetric curves are shown for 1 m*M* and 0.5 m*M* U (VI) in the same carbonate solutions as those for plutonium. Cathodic peak potentials at — 1.05 and — 1.06 V, and anodic peak potentials

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* Experiments with Pu-239 were done in the Hot-Laboratory of the Institute »Boris Kidrič«, Vinča, Belgrade.

at — 0.52 and — 0.53 V for 1 M Na$_2$CO$_3$ and 0.5 M Na$_2$CO$_3$ + 0.5 M NaHCO$_3$, respectively, were observed. On the basis of these results the constant potential selective reduction of U (VI) in a mixed carbonate solution of Pu (IV) and U (VI) should be possible.
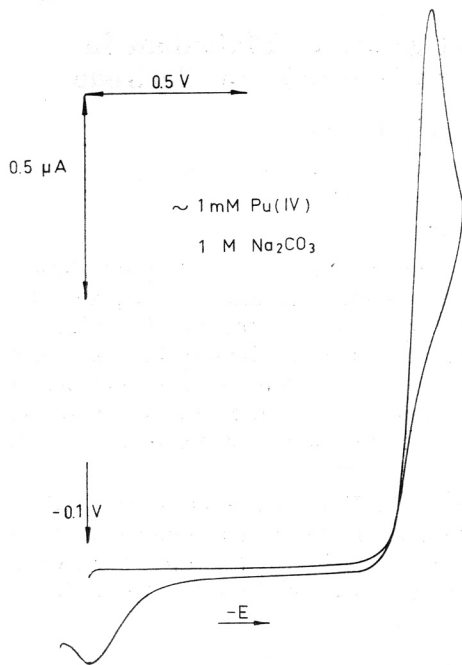

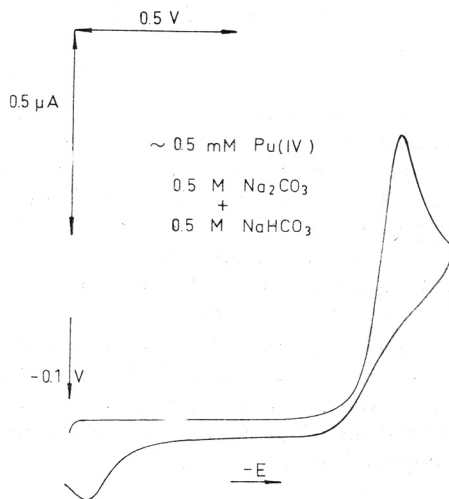Fig. 1. Cyclic voltammetric curve of ~ 1 mM Pu (IV) in 1 M Na$_2$CO$_3$.

Fig. 2. Cyclic voltammetric curve of ~ 0.5 mM Pu (IV) in 0.5 M Na$_2$CO$_3$ + 0.5 M NaHCO$_3$.

The very pronounced separation of the cathodic and anodic peak potentials indicates that the reduction of Pu (IV) is an irreversible process. Comparing the cyclic voltammetric curves it is obvious that the reduction of Pu (IV) shows a higher degree of irreversibility than the reduction of U (VI) in carbonate solutions.

Matsuda's[5] equation for an irreversible electrode reduction is:

$$E_{p/2} - E_p = 1.85 \frac{RT}{\alpha \, nF}$$

where E_p and $E_{p/2}$ are peak and half-peak potentials. Assuming one electron transfer, the transfer coefficients (α) from the reduction peak were calculated using this equation. The obtained results are given in the Table.

For orientation purpose the formal redox potential could be calculated from the cathodic and anodic peaks as proposed by Randles[7] and is about — 0.6 V. The shift from + 0.74 to — 0.6 V is due to the complexation of plutonium with carbonate, and the shift of the cathodic and anodic peaks from — 0.6 V may be the result of the irreversibility of the electrode process.

The conclusion is drawn that polarography is a suitable tool for further electrochemical investigations of plutonium carbonate complexes.
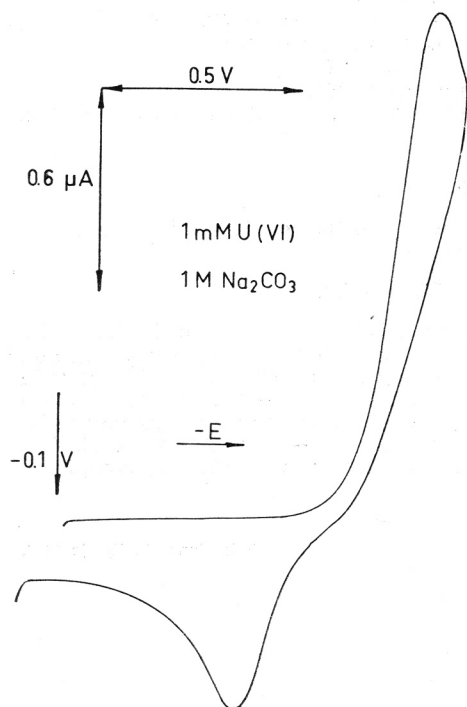

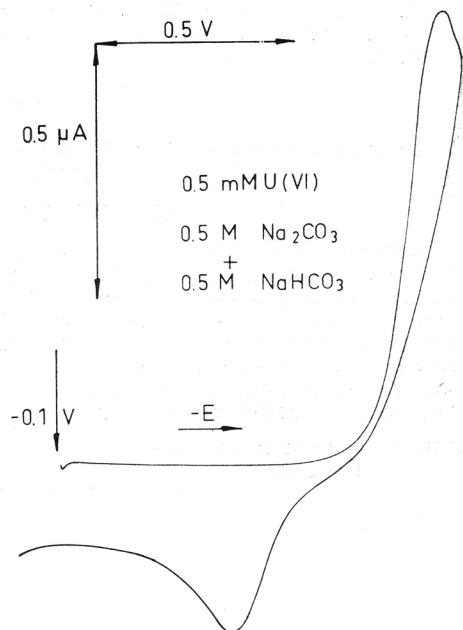Fig. 3. Cyclic voltammetric curve of 1 mM U (VI) in 1 M Na₂CO₃.

Fig. 4. Cyclic voltammetric curve of 0.5 mM U (VI) in 0.5 M Na₂CO₃ + 0.5 M NaHCO₃.

TABLE

Transfer Coefficients (α) for Reduction of Pu (IV) and U (VI) in Carbonate Solutions

	Plutonium		Uranium	
	1 M Na₂CO₃	0.5 M Na₂CO₃ + 0.5 M NaHCO₃	1 M Na₂CO₃	0.5 M Na₂CO₃ + 0.5 M NaHCO₃
Present work	0.68	0.67	0.45	0.45
Lemaire[6]	—	—	0.48	0.48

By analogy with uranium the electrochemistry of plutonium carbonate system is expected to show a complicated pattern, *i. e.* several electrode and coupled chemical reactions may exist, the whole problem warranting extended studies.

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IZVOD

Prethodna elektrokemijska ispitivanja plutonija u karbonatnim otopinama na visećoj živinoj kapi

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Ispitane su osnovne elektrokemijske karakteristike plutonija u karbonatnim otopinama. Val redukcije Pu (IV) na visećoj živinoj kapi u otopinama karbonata ima potencijal vrha oko — 1,1 V prema Z. K. E. a potencijal vrha oksidacijskog vala nastalog Pu (III) je oko — 0,10 V prema Z. K. E. Izračunat je koeficijent prijelaza (α) za proces redukcije i iznosi 0,67. Također je izračunat formalni redoks potencijal Pu (IV)/Pu (III) u karbonatnim otopinama i iznosi oko — 0,60 V prema Z. K. E. Može se zaključiti da plutonij (IV) tvori u karbonatnim otopinama stabilne komplekse i da je redoks proces ireverzibilan.

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