CCA-559

541.138:546.791
Original Scientific Paper

Contribution to the Electrochemistry of Uranium(V) in Carbonate Solutions*

J. Čaja and V. Pravdić

Laboratory of Electrochemistry, Institute »Ruđer Bošković«,
Zagreb, Croatia, Yugoslavia

Received September 19, 1969

Oxidation — reduction reactions of uranium(V) and (VI) in sodium and caesium carbonate solutions at high *p*H were studied using the chronopotentiometric technique. Uranium(V) formed by electrolysis of uranium(VI) at constant potential is stable, its rate of disproportionation negligible. The apparent standard redox potential (uncorrected) of the U(VI)/U(V) couple was found to be — 0.760V vs. S. C. E. in 1 *M* Na_2CO_3 and $pH = 11.5$. The uncorrected overall transfer coefficients for the oxidation of U(V) and re-reduction of U(VI) were: 0.64 and 0.42 in 1 *M* Na_2CO_3, and 0.47 and 0.47 in 0.5 *M* Cs_2CO_3. The formal rate coefficients for the oxidation and re-reduction of 1 m*M* bulk U(V), referred to the N. H. E. were: 2.1×10^{-9} and 2.7×10^{-8} cm/sec in 1 *M* Na_2CO_3, and 8.0×10^{-9} and 1.1×10^{-8} cm/sec in 0.5 *M* Cs_2CO_3. Narrow concentration limits for the solubility of uranium complexes and the relatively low concentration sensitivity of the chronopotentiometric technique render precise quantitative calculations and corrections for double layer effects or counter-ion association rather difficult.

INTRODUCTION

There have been several studies on the electrochemistry of uranium carbonate complexes in this laboratory[1-3]. The interest in this field is due not only to the importance of uranium carbonate solutions in the hydrometallurgical processes of uranium dioxide[4,5], but nonetheless also due to the interesting properties of uranium complexes from the theoretical point of view. Several oxidation states of uranium ions are sufficiently stable for the purpose of electrochemical studies. Fig. 1 illustrates the present field of interest. The writing of the electrochemical and chemical reactions has been simplified, since it is known that almost each step involves some structural rearrangement[6]. Most of the complex equilibria belong to the domain of fast reactions, and none of the electrochemical reactions are reversible. The most closely reversible reaction in this system is the presently described oxidation-reduction reaction of uranium(V) in Cs_2CO_3.

The uranium(V) state is especially important as an intermediate state occurring in the reduction process of uranium(VI) into the uranium(IV) state, which, in turn, is the starting material for hydrolytic precipitation of UO_2.

---

* Taken in part from the Dissertation of J. Čaja, submitted to the Faculty of Science, University of Zagreb, 1967. Presented at the 1st *Yugoslav Symposium on Electrochemistry,* Belgrade 1968.

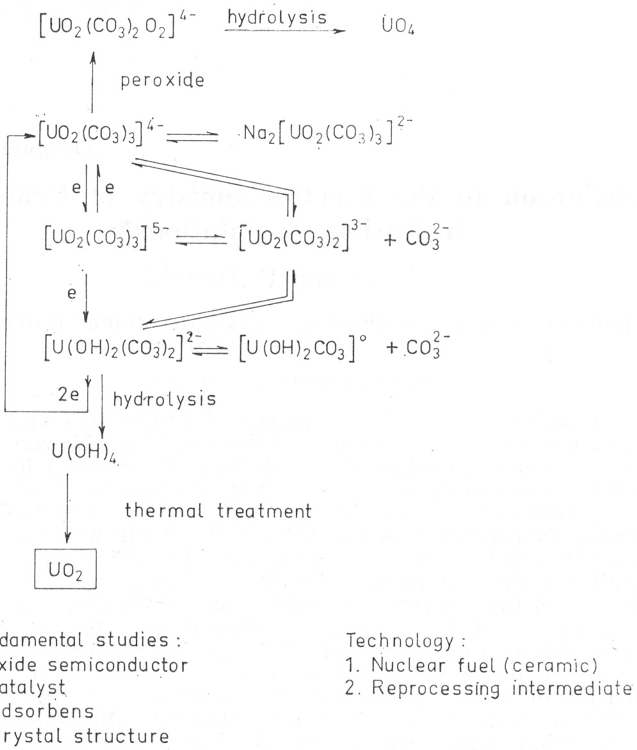

Fig. 1. The general chart of the uranium-carbonate system in aqueous solution. The uranium(V) carbonate complex is shown in its central position in the series, connected to other oxidation states by quasi-reversible and irreversible electrochemical reactions, as well as complex equilibria preceding the disproportionation reaction.

This state undergoes rapid disproportionation in acidic solutions, but is comparatively stable in alkaline. Most of the chemical equilibria in the uranium carbonate complex system compete with irreversible hydrolysis[7,8]. Hydrolyzed species are often specifically adsorbed at mercury electrodes and sometimes accelerate an electrode reaction. Therefore a study of the type described in the paper requires some precautions to prepare a stable uranium(V) solution. This will be achieved in the case of solutions with high concentrations of carbonate (in ecxess of 0.5 *M*) and low (as practicable) concentrations of uranium (upper limit 10 m*M*). Considering the above mentioned limits of sensitivity of the chronopotentiometric method in elucidating electron transfer reactions, the lower practicable limit of the uranium(V) concentration will be at 0.5 m*M*. This results in very narrow concentrations »windows«. As a result, studies requiring measurements of concentration dependence of some kinetic parameter will be severely limited. However, quite useful information can still be obtained.

The present state of the theory of electrochemical kinetics[9–11], would require corrections of data obtained for the effect of the double layer and for the ionic association phenomena. The present data, limited to narrow concentration ranges and a constant pH are presented without corrections. There are two reasons justifying this. Firstly, although no conclusive adsorption data have been obtained, it is still uncertain whether or not the uranium carbonate complexes are specifically adsorbed at the mercury electrode. Secondly, counter-ion association of highly charged anionic complexes has been proved[10,11], although there is no convincing evidence whether or not the associated complex itself is discharged. In view of these ambiguities it seems that the presentation of direct experimental evidence offers the soundest basis for any future use of these results.

EXPERIMENTAL

The cell

Preparation of uranium(V) from the starting uranium(VI) solutions and the chronopotentiometric experiments were both done in a single, combined, water jacketed cell of 250 ml volume, shown in Fig. 2.[12] At the bottom of the cell a single large mercury pool could be maintained (stirred with a glass propeller) for the constant potential electrolysis. Alternatively a smaller mercury pool, contained in the cylindrical cup, with a highly reproducible surface area of 3.30 cm^2 could be created. Two counter electrodes, both platinum foils of approximately 2 cm^2 surface area, were held in two small compartments separated from the main compartment by fritted glass. One of these was used in the preparative part of the work, in constant potential electrolysis. The other, used in chronopotentiometric measurements, was located close to, and above the center, of the mercury cup electrode to ensure uniform current distribution. A single saturated calomel electrode was used in both types of electrolysis. Calibration of the surface area of the mercury cup electrode was performed by measuring the transition time for Cd^{2+} in KNO_3, as recommended by Reilley *et al.*[13] Reproducible data on transition times in experiments with alkaline solutions were obtained only after careful treatment of the cylindrical cup with a silicone water repellant fluid. After 5 to 6 hours of contact of the siliconized walls with the alkaline carbonate solution signs of release of surface active contaminants were observed. The most pronounced indicatory of silicone film dissolution was the unusual dependence of the transition time for the oxidation of uranium(V) on the time of contact of the mercury electrode with the solution prior to measurement[12].

Apparatus

The current source was an all electronic unit capable of maintaining the current constant to within 0.2% of the set value. It consisted of a Philbrick K2WA/K2PA operational amplifier pair connected as a cathode follower and regulating the current through a Helipot and metal-film high stability resistors. The ± 300V D. C. power suply unit was an all-electronic device of high stability (0.1%). Chronopotentiograms were recorded on a strip chart recorder (Nesco, Costa Mesa, California) with a paper speed of 8 in/min. whenever the transition time exceeded 5 sec. Shorter transition times were recorded by taking photographs off the screen of a Tektronix 564 storage oscilloscope. The graphical method of Reimuth[14] was used in determining the transition times.

Chemicals

Analytical grade chemicals were used (Merck, Darmstadt, Germany). Carbonates of sodium and caesium were purified by heating to 450° C for several hours, and then recrystallized. Triply distilled water and doubly distilled mercury were used. Uranium(VI) stock solutions (roughly 0.1 *M*) were prepared from analytical grade ammonium diuranate dissolved in sodium bicarbonate solution at $p\mathrm{H} = 8.4$. The concentration of uranium in the stock solution was determined by precipitating with ammonia, filtering, washing and heating in air to constant weight (U_3O_8).

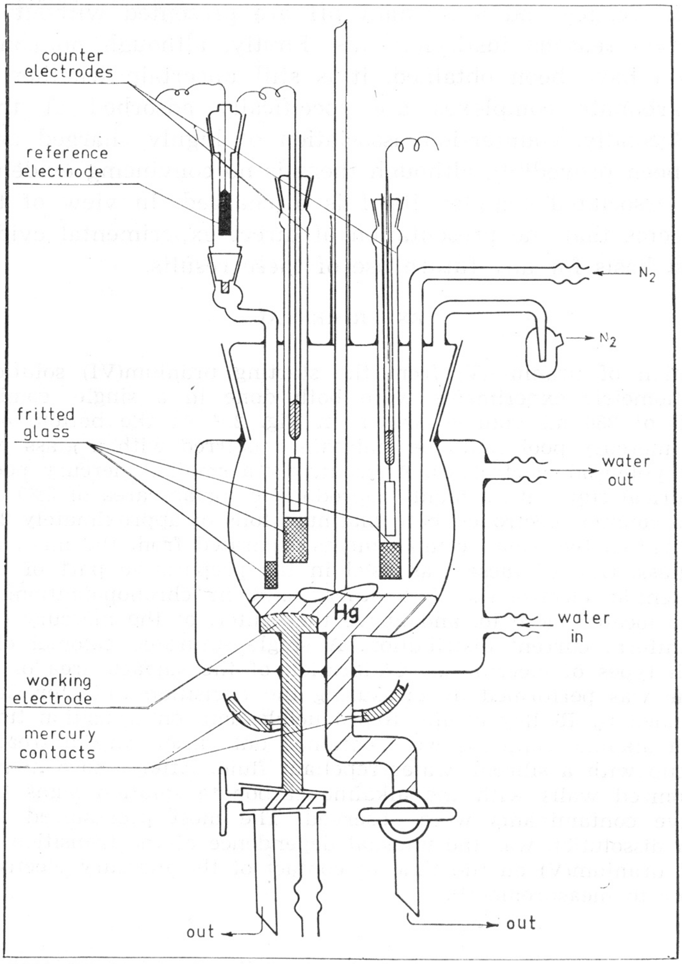

Fig. 2. The electrolysis cell for combined pre-electrolysis and chronopotentiometry at the mercury pool electrode. The large pool of mercury is used for preparative work (pre-electrolysis) the smaller one, in a cylindrical insert, is for chronopotentiometry.

Dilutions of the stock solution were made immediately before each experiment. The pH of the experimental solution was determined and adjusted to the desired value by additions of hydroxide or introduction of CO_2. Prepurified nitrogen was further deoxygenated by passing it first through a heated column filled with copper catalyst (BTS Catalyst, BASF), and then through a carbonate solution of the same *p*H and concentration of carbonate as that in the cell.

Procedure

A measured portion of the test solution (normally 150 ml) was introduced into the cell, deoxigenated with nitrogen, and electrolysed at constant potential of — 1.25V vs. S. C. E. until the current decreased to a value below 0.5% of the initial value. The total charge passed was 3—5% above the theoretically required one, in accordance with the previously determined current efficiency[15]. After completing the electrolysis mercury, still under polarization, was released through both stopcocks. Then the cylindrical cup was filled with mercury to the predetermined, calibrated level and kept in contact with the solution at least three minutes before applying the constant current for the chronopotentiometric experiment. With one filling of mercury only one current reversal chronopotentiogram was recorded. Up to 10 experiments were made on the same solution. If additional experiments were needed, the procedure of pre-electrolysis was repeated with the same solution.

RESULTS

Chronopotentiograms of the oxidation of U(V) are shown in Fig. 3. The chronopotentiogram for the 3 m*M* solution is well defined (curve 1), but irreproducible phenomena set in if electrolysis is prolonged beyond the transition time. Care is to be exercized, therefore, in current reversal expe-

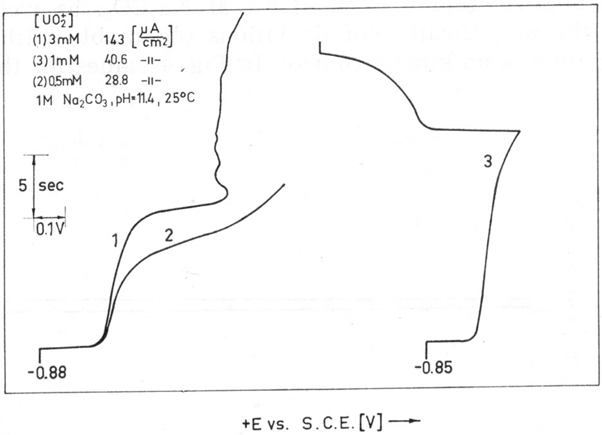

Fig. 3. Chronopotentiograms of uranium(V) in 1 *M* Na_2CO_3: (1) for a 3 m*M* solution showing irreproducible effects on prolonging electrolysis beyond the transition time; (2) for a 0.5 m*M* solution and (3) current reversal (oxidation and rereduction) chronopotentiogram for a 1 m*M* solution.

TABLE I

*Kinetic Parameters for the Oxidation and Re-reduction Reactions of 1 m*M* Uranium(V) in Sodium and Caesium Carbonate Solutions at* pH = *11.4 ± 0.15 at* $t = 25^0$ *C.*

	1 *M* Na_2CO_3		0.5 *M* Cs_2CO_3	
	oxidation	re-reduction	oxidation	re-reduction
$E_{\tau/4}$, $E_{0.215\ t}$ V/S. C. E.	— 0.674	— 0.863	— 0.770	— 0.833
$E_{t=0}$ V/S. C. E.	— 0.701	— 0.791	— 0.820	— 0.804
transfer coefficient	0.64	0.41	0.47	0.47
log k_h^o cm/sec	— 8.68	— 7.37	— 8.10	— 7.97

riments. Less well defined is the chronopotentiogram obtained for an 0.5 m*M* solution (curve 2), but on the other hand there are no post-waves or interferences. The most suitable concentration is 1 m*M* for which well defined chronopotentiograms are obtained. Curve 3 is an example of such a complete current reversal experiment. Most of the subsequent data refer to experiments with 1 or 3 m*M* solutions of uranium(V). The shape of the chronopotentiograms, as well as the large difference between the »half-wave« potentials for oxidation and reduction (Table I), $E_{\tau/4}$ and $E_{0.215}$ indicate highly irreversible electrochemical charge transfer reactions. Besides, within the limits of the sensitivity of the present method, the processes are purely diffusion controlled: the ratio between the reverse and forward transition times is 0.33 for all the concentrations studied, and for 1 and 0.5 *M* Na_2CO_3, as well as for 0.5 *M* Cs_2CO_3. Even the amplification of deviations obtainable with cyclic chronopotentiometry[6] reveals no kinetic control. In Fig. 4 values for the characteristic chronopotentiometric parameter, $i\tau^{1/2}/C$ *vs.* current density are shown, for two concentrations of uranium in 1 *M* Na_2CO_3. The statistical analysis shows that this parameter equals 155 ± 3 as calculated from 21 independent measurements for three concentrations of uranium, 0.5, 1.0, and 3.0 m*M*. The diffusion coefficient of uranium(V) in 1 *M* Na_2CO_3 is

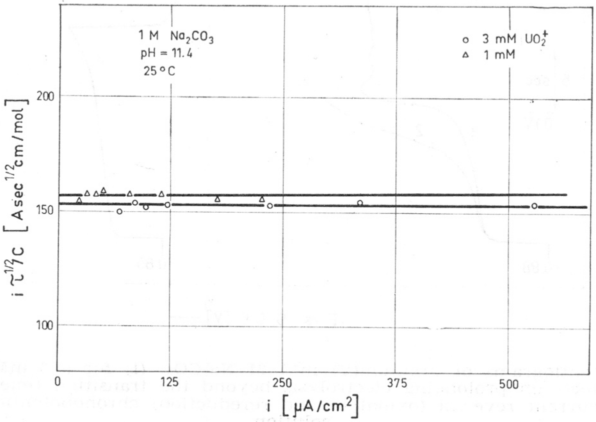

Fig. 4. The dependence of the characteristic chronopotentiometric parameter, $i\,\tau^{1/2}/C$ on current density for the oxidation of uranium(V). No kinetic complications are observable within the present experimental range of current densities.

$$D_5 = (3.30 \pm 0.06) \times 10^{-6}\ \text{cm}^2/\text{sec}$$

which is significantly lower than the value reported for uranium(VI)[1], $D_6 = (4.35 \pm 0.43) \times 10^{-6}$ cm²/sec in the same supporting electrolyte.

The determination of the apparent overall transfer coefficient for the oxidation of uranium(V) complex was done using the equation of Delahay and Berzins[16]

$$E = (RT/\beta n_a F)\ \ln\ (nFCk_{f,h}/i) + (RT/\beta n_a F)\ \ln\ [1 - (t/\tau)^{1/2}] \qquad (1)$$

where β is the transfer coefficient for the oxidation step. Both the number of electrons in the rate determining step, n_a, and the overall number of electrons exchanged, n, were taken as unity. The usual procedure was used in extrapolating the E *vs.* ln $1-(t/\tau)^{1/2}$ line to $t = 0$. From this potential, and the slope of the plot the rate coefficient, $k_{f,h}$ (referred to the normal hydrogen electrode potential) and the transfer coefficients were determined. The mean value for 24 independent measurements for 1 and 3 m*M* solutions of uranium(V) in 1 *M* Na_2CO_3 was

$$\beta = 0.64 \pm 0.02$$

Data for two experiments are shown in Fig. 5. The same treatment applied to the data obtained in 0.5 *M* Cs_2CO_3 gives

$$\beta = 0.47 \pm 0.02$$

These β values are uncorrected experimental data.

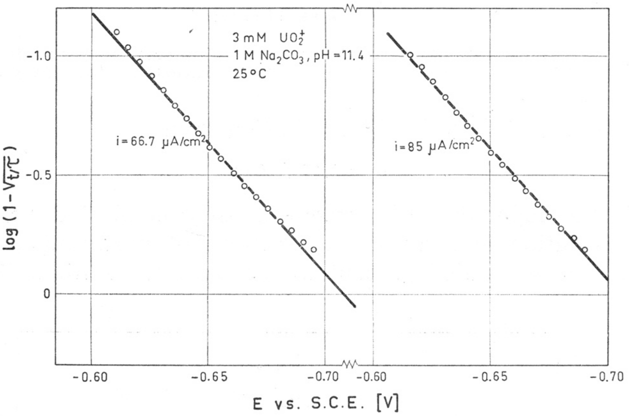

Fig. 5. Plot of equation (1) for the oxidation of 3 m*M* uranium(V) at two current densities. The slopes yield the transfer coefficient $\beta = 0.64 \pm 0.02$.

When studying the re-reduction of uranium(VI) from the experiments with uranium(V) in bulk of the solution, different current densities were used in the forward and reverse direction. This technique offers the advantage of being more precise, in view of the extended time scale in the reverse direction. Macero and Anderson[17] have developed the following equation for this case

$$E = (RT/\alpha n_b F) \ln (i_f/nFCk_{b,h}) + (RT/\alpha n_b F) \ln [\tau^{1/2}/(\tau - t)^{1/2} - (1 + a)\, t^{1/2}] \quad (2)$$

where $a = i_b/i_f$, the ratio of the reverse to forward current densities, α is the transfer coefficient for the reduction reaction, and subscript b refers to the reverse (re-reduction) step. All the other symbols have their conventional meaning. On plotting the $f(\tau) = \log [\tau^{1/2}/(\tau + t)^{1/2} - (1 + a)\, t^{1/2}]$ *vs.* E, the transfer coefficient, α, and rate coefficient, $k_{b,h}$, for the re-reduction reaction were again obtained. Fig. 6. shows the data for three different values of $a = i_b/i_f$ at constant $i_f = 32.1$ μA/cm². There is a higher dispersion of data in this case, than for the forward reaction. The estimate from 18 independent measurements at the same three concentrations of uranium(V) in 1 *M* Na_2CO_3 was

$$\alpha = 0.41 \pm 0.02$$

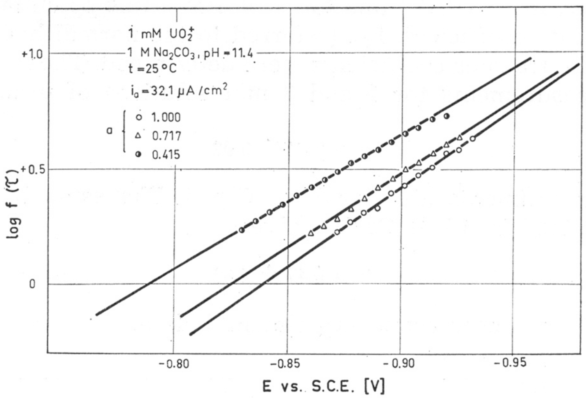

Fig. 6. Plots of equation (2) for the re-reduction of uranium(VI), with uranium(V) in the bulk of solution, for three different current density ratios $a = i_b/i_f$, at constant i_f.

The same treatment of data for 0.5 *M* Cs_2CO_3 gives

$$\alpha = 0.47 \pm 0.02$$

In Fig. 7. the logarithm of current density is plotted *vs.* the potential for both the oxidation and reduction reactions of uranium(V) and (VI) each time with the species studied present in the bulk of solution. Data locate the apparent standard potential of the U(VI)/U(V) couple in 1 *M* Na_2CO_3 solution at — 0.760V *vs.* S. C. E. As the preceding ones these data are also uncorrected.

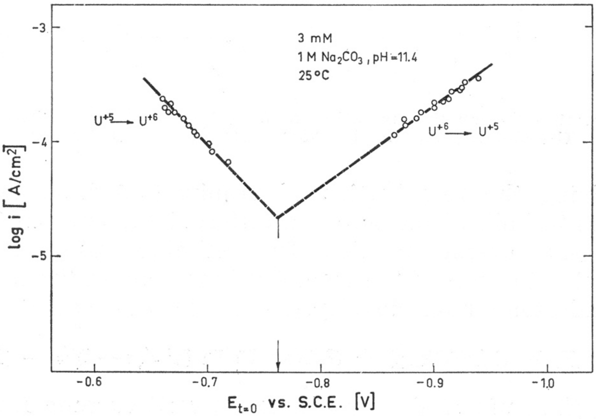

Fig. 7. Plots of logarithm current density vs. potential extrapolated to zero time for the oxidation of uranium(V) and reduction of uranium(VI) in 1 *M* Na_2CO_3 solution.

DISCUSSION

It seems fairly well established that the transition times of the reactions of oxidation and re-reduction studied in the present work are controlled by diffusion alone. Experiments failed to reveal any specific adsorption of either the penta- or hexavalent uranium species. There is however evidence from the differences in the diffusion coefficients of the two species that there is a difference in the association state. Both species have been claimed to possess identical stereochemistry[18], the tri-carbonate form, $[UO_2(CO_3)_3]^{4-}$ and $[UO_2(CO_3)_3]^{5-}$. Up to this point the experimental data are hard facts, beyond this only some speculation can help in understandig the mechanism of electrochemical reactions.

Gierst[10] has determined the effective charge of the associated uranium(VI) tri-carbonate complex as 1.4 ± 0.3. Further on, the actual form is claimed to be $[Na_2UO_2(CO_3)_3]^{2-}$, a reasonable assumption based on several references on anionic complexes in aqueous solutions[11,19]. The effective value therefore would support the idea of parallel or series mechanisms, by which one ligand is dissociated prior to electron transfer with simultaneous or subsequent changes in the degree of counter ion association. The rate of these reactions is probably very high. Vandenberghen (Ref. 11 p. 247) claims that parallel reduction of anions and ionic pairs occurs and that this is possible since both species, have »identical kinetic characteristics«. Whichever mechanism is operative it is highly probable that some association-dissociation reactions are taking place in the double layer, that they are very fast[20] beyond the capabilities of detection by chronopotentiometric techniques[21]. The large differences in the diffusion coefficients give weight to the idea that the two complex forms exist with different degrees of association. The determination of the diffusion coefficients is quite precise and does not involve any assumptions on the structure of the double layer or on the actual potential.

Corrections for the double layer potential

Estimation of the magnitude of corrections for the influence of the φ_2 potential of the double layer. According to Russell[22] and taking an extrapolation for 2 gion Na^+ the best estimate for the slope d $\varphi_2/dE = 0.06$ in the range of potentials involved in the oxidation (— 0.75 to — 0.55 V) and re-reduction reactions (— 0.85 to — 1.20 V *vs.* S. C. E.). The application of the Frumkin relation[9] to determine the »true« transfer coefficient:

$$\alpha n_t = (\alpha n_a - z\, d\varphi_2/dE)/(1 - d\varphi_2/dE) \qquad (3)$$

yields for the transfer coefficient, β, related to the oxidation of uranium(V), and the two probable actual charges of the associated complex:

$z = 1$ $\beta n_t = 0.62$ $\Delta\beta n = 0.02$

$z = 2$ $\beta n_t = 0.55$ $\Delta\beta n = 0.09$

Calculating the change in the overvoltage due to the variation of φ_2 and using the »true« values of the transfer coefficient, one obtains with the help of the expression (Ref. 9 p. 199):

for

$$\Delta\eta = (1 - z/\alpha n)\, \Delta\varphi_2 \qquad (4)$$

$z = 1$ $\Delta\eta = 19$ mV

$z = 2$ $\Delta\eta = 18$ mV

These corrections, are small and do not alter the basic information obtained from the experiments. Further experimental evidence, presently sought in the application of cyclic chronopotentiometry, is needed before definite conclusions could be reached about the actual mechanism of the reduction and oxidation reactions of uranium carbonate complexes.

REFERENCES

1. J. Čaja and V. Pravdić, *J. Electroanal. Chem.* **8** (1964) 390.
2. D. Čukman, J. Čaja, and V. Pravdić, *J. Electroanal. Chem.* **19** (1968) 267.
3. M. Branica and V. Pravdić, *Polarography* **1964** (Southampton) p. 435. G. H. Hills, Editor.
4. V. Pravdić, M. Branica, and Z. Pučar, *Electrochem. Techn.* **1** (1963) 312.
5. V. Pravdić, M. Branica, and Z. Pučar, *Proc. III Int. Conf. on Peaceful Uses of Atomic Energy,* Geneva 1964, **11** (1964) 370.
6. M. Vuković, *M. Sc. Thesis,* Univ. of Zagreb 1969. In course of publication.
7. M. Branica, V. Pravdić, and Z. Pučar, *Croat. Chem. Acta* **35** (1963) 281.
8. B. Tomažić, M. Samaržija, and M. Branica, *J. inorg. nucl. Chem.* **31** (1969) 1771.
9. P. Delahay, *Double Layer and Electrode Kinetics,* Interscience Publ. New York 1965. cf. Ch. 9, pp. 197 ff.
10. L. Gierst, L. Vandenberghen, E. Nicolas, and A. Fraboni, *J. Electrochem. Soc.* **113** (1966) 1025. also: *Symposium on Electrode Processes,* The Electrochemical Society, Cleveland 1966, p. 145.
11. L. Tytgat-Vandenberghen, *Thèse de doctorat,* Universite Libre de Bruxelles, 1969.
12. J. Čaja, *Dissertation,* Univ. of Zagreb 1967.
13. C. N. Reilley, G. W. Everett, and R. H. Johns, *Anal. Chem.* **27** (1955) 483.
14. W. H. Reinmuth, *Anal. Chem.* **33.** (1961) 485.
15. V. Pravdić, M. Branica, and Z. Pučar, *Croat. Chem. Acta* **33** (1961) 151.
16. P. Delahay, *New Instrumental Methods in Electrochemistry,* Interscience Publ. New York, 1954.
17. D. J. Macero and L. B. Anderson, *J. Electroanal. Chem.* **6** (1963) 221.
18. I. I. Chernyaeev (Editor), *Complex Compounds of Uranium* (in Russian), Nauka, Moscow 1964.
19. A. I. Stabrovskii, *Zh. Neorg. Khim.* **5** (1960) 811.
20. M. Eigen and G. Maas, *Z. Physik. Chem.* NF **49** (1966) 163.
21. R. L. Birke and D. K. Roe, *Anal. Chem.* **37** (1965) 450.
22. C. D. Russell, *J. Electroanal. Chem.* **6** (1963) 486.

IZVOD

Elektrokemijske reakcije uraniuma(V) u karbonatnim otopinama

J. Čaja i V. Pravdić

Proučavane su elektrokemijske reakcije uraniuma(V) i (VI) u otopinama natrium i cezium karbonata kod visokog $pH = 11.4$. U tim uslovima uranium(V) je stabilan. Određeni su koeficijenti prijenosa u otopinama 1 M Na_2CO_3 i 0.5 M Cs_2CO_3, formalni standardni potencijal para U(VI)/U(V), te koeficijenti brzine elektrokemijskih reakcija. Eksperimentalni podaci navedeni su bez korekcija za asocijaciju protuiona ili za potencijal elektrokemijskog dvosloja. Ustanovljeno je, da su sve proučavane elektrokemijske reakcije ireverzibilne, s time, da promjena protuiona osnovnog elektrolita od natriuma na cezium mijenja sve osnovne kinetičke parametre u smjeru reverzibilnije reakcije.

INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB

Primljeno 19. rujna 1969.