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Electrochemical Reduction of Uranium (VI) to Uranium (IV) in Carbonate Solutions*

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The purpose of this work was to investigate the possibility of preparation of uranium dioxide by electrochemical reduction of uranium(VI) from alkali carbonate solutions. There are many interesting features in deciding whether or not the electrochemical process is applicable to certain conditions of solution equilibria in the uranium-carbonate system. The study of the reduction of uranium(VI) from carbonate solutions has been undertaken to determine the reduction potential-current density relationship, the current efficiency, and the O/U ratio in the precipitated uranium dioxide, for which only scarce data are available in the literature.^{1,2}

The reduction of uranium (VI) compounds has been performed in an H-shaped glass cell with mercury as cathode. The anodic compartment has been

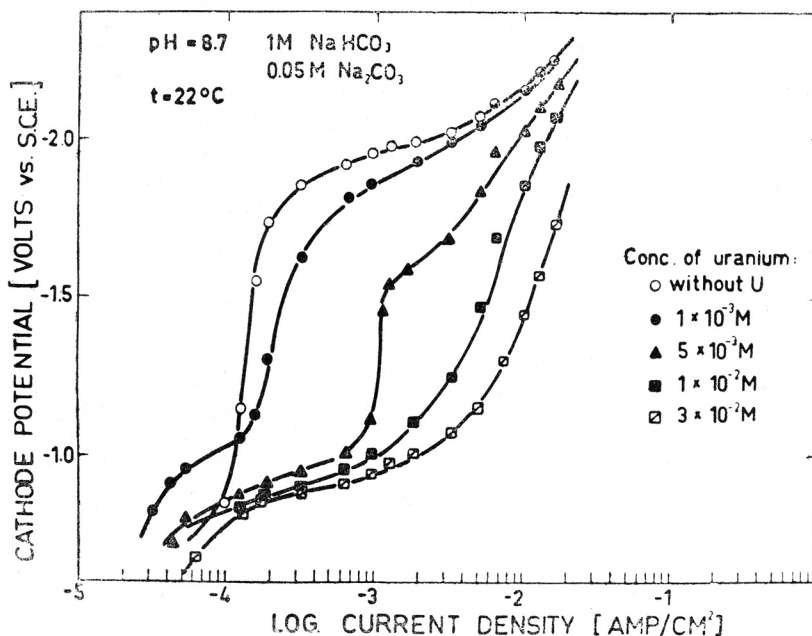


Fig. 1. Plot of current density vs. the potential of the mercury cathode in solution of 1.0 M $\text{NaHCO}_3 + 0.05 \text{ M Na}_2\text{CO}_3$, pH 8.7, for 4 different concentrations of uranium(VI).

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separated from the cathodic by a cation exchange membrane, Zerolit C-20 (The Ionics Inc. USA). The cross section of the mercury cathode was about 16 cm^2 . A piece of platinum foil of an area of 2 cm^2 served as anode. The electrolysis was performed at ambient temperature. As a source of the electric current a multipurpose servo instrument was used by means of which a constant potential was automatically maintained during the electrolysis. Current integration was performed by a precision low inertia D. C. motor (Electromethods, Stevenage, England) with an error of 0.7%.

In Fig. 1. the current density-cathode potential diagram is given for the solution of $1 \text{ M NaHCO}_3 + 0.05 \text{ M Na}_2\text{CO}_3$, pH 8.7 and four uranium concentrations ranging from $1 \times 10^{-3} \text{ M}$ to $3 \times 10^{-2} \text{ M}$. The well defined current plateau was found between -1.00 and -1.50 V vs. SCE . At higher current densities a simultaneous reduction of uranium and sodium ions occurs, thus causing a lowering of the current efficiency for the reduction of uranium (VI).

Fig. 2. illustrates the current efficiency vs. the initial uranium (VI) concentration for the controlled potential of -1.20 and -1.55 V vs. SCE . The data show that a maximum at about $5 \times 10^{-3} \text{ M}$ uranium is likely to exist.

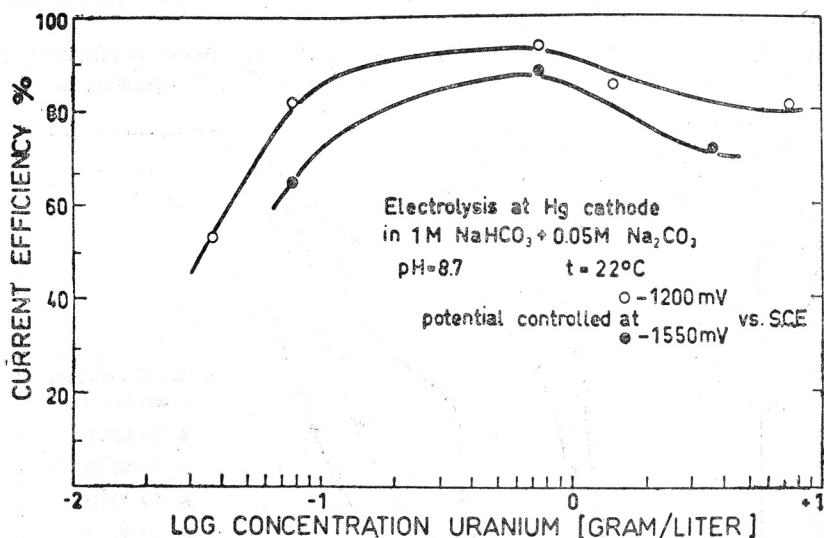


Fig. 2. Plot of current efficiency for the reduction of uranium(VI) into uranium(IV) on the mercury cathode vs. the initial concentration of uranium in solution of $1.0 \text{ M NaHCO}_3 + 0.5 \text{ M Na}_2\text{CO}_3$, pH 8.7, for constant controlled potentials of -1.20 and $-1.55 \text{ Volts vs. the saturated calomel electrode}$.

The O/U ratio of uranium dioxide, precipitated at pH 10.7 by addition of sodium hydroxide to the electrolysed solution, was coulometrically³ determined to be 2.01.

Further experiments to elucidate the influence of pH, the composition of solution and temperature, on the yield of precipitable uranium reduced are in progress.

REFERENCES

1. L. A. McClaine, E. P. Bullwinkel, and J. C. Huggins, *Proc. Int. Conf. on Peaceful Uses of Atomic Energy*, Geneva 1955, Vol. 8, p. 26, No. P/525.
2. M. Perec, *Nukleonika* 6 (1961) 357.
3. R. W. Stromatt and R. E. Connally, *Anal. Chem.* 33 (1961) 345.

IZVOD

Elektrokemijska redukcija urana(VI) u uran(IV) u karbonatnim otopinama

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Ispitivani su uvjeti elektrokemijske redukcije urana(VI) do urana(IV) u otopini 1,0 M NaHCO₃ + 0,05 M Na₂CO₃ za 4 razne koncentracije urana. Određen je odnos gustoće struje prema potencijalu živine katode, kao i iskorištenje struje za elektrolizu kod konstantnih potencijala od -1,20 i -1,55 V prema zasićenoj kalomel elektrodi. Nastali uran(IV) istaložen je dodatkom NaOH kao oksid, za koji je kulometrijski određen odnos O/U od 2,01.

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ZAGREB

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