

KINETICS OF ELECTRODE PROCESSES IN LiCl-KCl-UCl₄ MELT

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The electrochemical behavior of uranium was investigated in numerous studies, but up to now no data were available on the standard rate constants of charge transfer for electrode processes



Analysis of literature data showed also that diffusion coefficients (D) are larger for U(IV) than for U(III) oxidation state. In our opinion, these results are erroneous, because they are in disagreement with numerous data on the influence of oxidation state of central atoms on diffusion coefficients.

The main goal of the present study is the determination of parameters for U(IV) and U(III) complexes such as: diffusion coefficients and standard rate constants of charge transfer.

The diffusion coefficients of U(IV) and U(III) were determined by cyclic voltammetry, chronopotentiometry and chronoamperometry methods. The resulting values of diffusion coefficients are in a good agreement and in the temperature range 723-823 K diffusion coefficients of U(III) are larger than those of U(IV). The diffusion coefficients are described by the following empirical equations

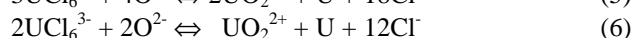
$$\log D_{\text{U(IV)}} = -2.46 - 1956/T \pm 0.03 \quad (3)$$

$$\log D_{\text{U(III)}} = -2.64 - 1700/T \pm 0.02 \quad (4)$$

The charge transfer standard rate constants (k_s) were calculated on the basis of cyclic voltammetry data for the redox reaction (1) and using impedance spectroscopy method for electrodeposition process (2). Influence of the temperature on the standard rate constants of process (1) and (2) are presented in Table 1.

The values of constants testify that the redox process proceeds quasi-reversibly, mostly under diffusion control, but the process of electrodeposition is mainly controlled by the rate charge transfer.

Interaction of oxide materials (pyrex and alumina) with LiCl-KCl-UCl₄ and LiCl-KCl-UCl₃ melts was studied. The following chemical reactions were found to occur in the melts



In all those studies, for instance [1-3], which were performed with electrochemical cells made of oxide

materials, such interaction was likely and may have played a significant role on the kinetic parameters and hence on the experimental data.

Table 1. Temperature dependence of the standard rate constant (k_s , cm s⁻¹) in LiCl-KCl eutectic melt

Process	k_s , 723 K	k_s , 773 K	k_s , 823K
(1)	$1.60 \cdot 10^{-2}$	$2.85 \cdot 10^{-2}$	$4.79 \cdot 10^{-2}$
(2)	$1.8 \cdot 10^{-4}$	$2.6 \cdot 10^{-4}$	$3.4 \cdot 10^{-4}$

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References

- [1] A. Leseur, CEA Report No 3793, 98 (1969).
- [2] F. Kaligara, L. Martinot, G. Duyckaerts, Bull. Soc. Chim. Belges **75**, 15 (1967).
- [3] L. Martinot, G. Duyckaerts, Inorg. Nucl. Chem. Lett. **6**, 587 (1970).