Influence of Second Coordination Sphere on the Kinetics of Electrode Reactions in Molten Salts

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The influence of the second coordination sphere on the electroreduction of hafnium complexes to hafnium metal, and the redox reaction Eu(III) + e^- $\Leftrightarrow$ Eu(II) in alkali halide melts was studied. It is shown that the large caesium cations in the melt reduce the transfer and the diffusion coefficients as well as the heterogeneous rate constants for charge transfer of hafnium complexes. The standard rate constants for the europium redox reaction increase when going from NaCl-KCl to CsCl. The different influence of the second coordination sphere on the electrode reactions is explained by different limitation stages for electron transfer.

Key words: Melts; Second Coordination Sphere; Cyclic Voltammetry; Heterogeneous Rate Constants; Standard Rate Constants.

Introduction

A change in the cationic composition of a melt, which determines the composition of the second coordination sphere, allows one to monitor and control electrodeposition of metals [1]. Therefore it is important to study this effect. There are many data concerning the influence of the cationic composition on diffusion coefficients [2]. But there exist practically no data on the effect of the second coordination sphere on the kinetics of electrode reactions. Only in [3] the effect of the second coordination sphere on the electroreduction of hafnium and rhenium complexes in molten alkali halide melts was discussed.

Experimental

The preparation of hafnium and europium halide salts and alkali chloride melts was described in details in [3, 4].

Our study was performed employing linear sweep voltammetry (LSV) and cyclic voltammetry (CV), using a VoltaLab-40 potentiostat with packaged software “VoltaMaster 4". The scan rate was varied between $5{\cdot}10^{-3}$ and 5.0 Vs^{-1}. The experiments were carried out at 973 - 1173 K. The cyclic voltammetric curves were recorded at 0.8 - 2.0 mm diameter glassy carbon, molybdenum, tungsten, and platinum electrodes with respect to a glassy carbon plate as a quasi-reference electrode, and to a silver reference electrode, Ag/NaCl-KCl-AgCl (2 wt%). The glassy carbon ampoule served as the counter electrode.

Results and Discussion

Chloride and fluoride complexes of hafnium in halide melts discharge irreversibly with hafnium formation at the cathode [5, 6]. Kinetic parameters for electroreduction of hafnium complexes in molten salts of various cationic composition are presented in Table 1.

The transfer coefficients times the number of electrons in the rate-controlling step of the electrode process were found by the Matsuda-Ayabe equation [7]

$$E_{\mathrm{p}}^{\mathrm{C}} - E_{\mathrm{p}/2}^{\mathrm{C}} = -1.857RT/\alpha n_{\alpha}F, \qquad (1)$$

where $E_{\mathrm{p}}^{\mathrm{C}}$ is the potential of the cathodic peak, $E_{\mathrm{p}/2}^{\mathrm{C}}$ the potential of the half-peak, α the electrochemical transfer coefficient and n_{α} the number of electrons transferred.

The diffusion coefficients were calculated by an equation which is valid for the irreversible electroreduction [8]:

$$I_{\mathrm{p}}^{\mathrm{C}} = 0.496nFCAD^{1/2}(\alpha n_{\alpha}F\nu/RT)^{1/2}, \quad (2)$$

Table 1. Heterogeneous charge transfer rate constants of hafnium complexes in molten salts.

Melt, electrode process	T, K	$-E_p^C$, V	αn_α	$D\times10^5$, cm^2/s	k^0_{fh}, cm/s Eq. (3)
NaCl-KCl-$HfCl_2$,	973	1.245	1.45	3.35	$7.9\cdot10^{-12}$
$HfCl_4^{2-}$ + 2e	1023	1.224	1.48	4.23	$2.4\cdot10^{-11}$
→Hf + $4Cl^-$	1073	1.214	1.52	5.23	$4.8\cdot10^{-11}$
CsCl-$HfCl_4$,	973	1.397	1.54	0.88	$0.9\cdot10^{-13}$
$HfCl_6^{2-}$ + 4e	1023	1.374	1.62	1.24	$1.5\cdot10^{-13}$
→Hf+$4Cl^-$	1073	1.356	1.71	1.69	$2.7\cdot10^{-13}$
NaCl-KCl-K_2HfF_6,	973	1.568	1.43	1.60	$3.6\cdot10^{-14}$
HfF_6^{2-} + 4e	1023	1.574	1.47	2.16	$7.1\cdot10^{-14}$
→Hf + $6F^-$	1073	1.582	1.53	2.84	$8.8\cdot10^{-14}$
NaCl-KCl-CsCl-K_2HfF_6,	973	1.681	1.33	0.76	$2.6\cdot10^{-14}$
HfF_6^{2-} + 4e	1023	1.677	1.38	1.09	$4.8\cdot10^{-14}$
→ Hf + $6F^-$	1073	1.671	1.45	1.53	$6.2\cdot10^{-14}$

where I_p^C is the peak cathodic current (A), A the area of the electrode (cm^2), C the bulk concentration of the active species (mol cm^{-3}), D the diffusion coefficient (cm^2 s^{-1}), ν the potential sweep rate (V s^{-1}) and n the number of electrons involved in the reaction.

The heterogeneous charge transfer rate constants for hafnium complexes (k^0_{fh}) in melts relative to the silver reference electrode were determined by Delahay's equation [9]

$$E_p^C = -1.14\frac{RT}{\alpha n_\alpha F} + \frac{RT}{\alpha n_\alpha F}\ln\frac{k^0_{fh}}{\sqrt{D_{ox}}} - \frac{RT}{2\alpha n_\alpha F}\ln \alpha n_\alpha . \qquad (3)$$

As can be seen from Table 1, the occurrence of the large cesium cations in the melt reduces the transfer and diffusion coefficients as well as the heterogeneous rate constants for charge transfer. In some cases the CsCl-$HfCl_4$ melt causes a change in the number of steps of the electroreduction process and stabilizes a higher oxidation state [3].

It was found [4, 10] that in alkali chloride melts the peak current of the electroreduction process

$$\text{Eu(III)} + e^- \rightarrow \text{Eu(II)} \qquad (4)$$

is directly proportional to the square root of the polarization rate, while the peak potential does not depend on the polarization rate up to ν = 0.1 Vs^{-1}. The peak current of the electroreduction process is linearly dependent on the $EuCl_3$ concentration, while the peak potential of the first stage does not depend on the concentration of europium trichloride in the melt. According to the theory of linear sweep voltammetry [11], up to a polarization rate of 0.1 V s^{-1} the electrode process is controlled by the rate of the mass transfer and yields a reduced form, soluble in the melt.

Table 2. Diffusion coefficients of Eu(III) complexes using (7) and activation energies for diffusion (ΔU) in alkali chloride melts.

Melt	A	B	Δ	D, cm^{2}s$^{-1}\cdot10^5$ 1100 K	ΔU, kJmol^{-1}
NaCl-KCl	2.42	2152	0.03	4.20	41.2
KCl	2.37	2243	0.04	3.90	42.9
CsCl	2.29	2584	0.02	2.30	49.5

Table 3. Diffusion coefficients of Eu(II) complexes using (7) and activation energies for diffusion (ΔU) in alkali chloride melts.

Melt	A	B	Δ	D, cm^{2}s$^{-1}\cdot10^5$ 1100 K	ΔU, kJmol^{-1}
NaCl-KCl	2.31	1983	0.02	7.71	38.0
KCl	2.29	2057	0.04	6.92	39.4
CsCl	2.25	2364	0.02	3.99	45.3

The diffusion coefficients (D) for the chloride complexes of Eu(III) in alkali chloride melts were determined at ν = 0.1 Vs^{-1} using of the Randles-Shevchik equation [9]

$$I_p^C = 0.4463F^{3/2}R^{-1/2}T^{-1/2}n^{3/2}ACD^{1/2}\nu^{1/2}. \qquad (5)$$

Equation (5) was employed for the calculation of $D_{Eu(II)}$ in the NaCl-KCl-$EuCl_2$, KCl-$EuCl_2$ and CsCl-$EuCl_2$ melts on the basis of the peak current determined for the process

$$\text{Eu(II)} - e \rightarrow \text{Eu(III)} \qquad (6)$$

The coefficients of the equation

$$\log D = -A - \frac{B}{T} \pm \Delta \qquad (7)$$

and D at 1100 K for Eu(III) and Eu(II) in NaCl-KCl, KCl and CsCl are given in the Tables 2 and 3. These tables also include the activation energies for diffusion (ΔU) of Eu(III) and Eu(II), which are calculated from the equation

$$-\Delta U/2.303R = \partial \log D/\partial(1/T). \qquad (8)$$

As can be seen from the Tables 2 and 3, a decrease of D was found when the composition of second coordination sphere of the cation changes from Na to Cs. Similar changes in D are well-known [2]. They are due to the decrease of the counter-polarizing effect of cations from Na to Cs and result in a decrease of the metal-ligand bond length. The diffusion coefficients decrease when the europium oxidation increases, while the activation energies for diffusion increase. So D decreases and ΔU increases with increase of the ionic moment of the diffusing species. These results agree with numerous data on the influence of oxidation of central atom on the diffusion coefficients and activation energies for diffusion of complexes [2]. The decrease in D is related to the increased strength of the complexes, and this in turn leads to a decrease in the contribution to the diffusion coefficient of the "hopping" mechanism, as discussed in [12].

A mixed diffusion and electron-transfer control was observed in alkali chloride melts [4, 10] at 0.1 $< \nu \leq 0.3$ Vs^{-1} for redox the reaction

$$\mathrm{Eu(III)} + \mathrm{e}^- \Leftrightarrow \mathrm{Eu(II)}. \tag{9}$$

The problem of kinetic parameters determining a quasi-reversible process on the basis of cyclic voltammetry was considered by Nicholson [13]. The standard rate constant of the electrode process is related to the function ψ as follows:

$$\psi = \frac{k_\mathrm{s}\left(\frac{D_\mathrm{ox}}{D_\mathrm{red}}\right)^{\alpha/2}}{\pi^{1/2} D_\mathrm{ox}^{1/2}\left(\frac{nF}{RT}\right)^{1/2}\nu^{1/2}} \tag{10}$$

Here ψ is a function related to the difference between the peak potentials $E_\mathrm{p}^\mathrm{A} - E_\mathrm{p}^\mathrm{C}$ (mV), k_s is the standard rate constant of the electrode process (cm s^{-1}) and $\alpha = 0.5$ the transfer coefficient.

The dependencies of $E_\mathrm{p}^\mathrm{A} - E_\mathrm{p}^\mathrm{C}$ on the function ψ reported in [13] for 298 K must be recalculated for the present working temperatures, as was shown in [4, 5]. This influence of the second coordination sphere and temperature on the standard rate constants of the electrode reaction (9) is presented in the Table 4.

Table 4. Standard rate constants (cm s^{-1}) of the electrode reaction Eu(III) + e$^-$ $\Leftrightarrow$ Eu(II) in alkali chloride melts at different temperatures.

Melt	973 K	1023 K	1073 K	1123 K	1173 K
NaCl-KCl	$0.80\cdot10^{-2}$	$1.25\cdot10^{-2}$	$2.27\cdot10^{-2}$	$2.98\cdot10^{-2}$	
KCl			$3.10\cdot10^{-2}$	$3.73\cdot10^{-2}$	$5.37\cdot10^{-2}$
CsCl	$1.92\cdot10^{-2}$	$2.91\cdot10^{-2}$	$3.97\cdot10^{-2}$	$5.45\cdot10^{-2}$	

As seen from the Table 4, the standard rate constants increase when going from NaCl-KCl to CsCl melt. To our best knowledge, no data concerning the influence of the second coordination sphere on the standard rate constants of redox electrochemical reactions in molten salts have been reported before.

The electron transfer itself, which in the condensed phase may occur on a time scale of 10^{-15} s, precedes the slower stage of complex rearrangement. According to the theory of elementary charge transfer, the smaller and stronger bond complexes require higher rearrangement energy, and in consequence the electroreduction proceeds with slower rate [14]. The complex size and metal-ligand bond length decreases from NaCl-KCl to KCl and CsCl. Therefore a decrease of the charge transfer constants would have been expected, which agrees with experimental results for hafnium (Table 1) and contradicts data for the europium redox reactions (Table 4). However, the previous approach is not valid for all electrochemical systems. Our experimental results allow to suggest that for the redox reaction (2) the limiting stage is not rearrangement of complexes but electron transfer over outer sphere cations. In this case the explanation of the larger values observed for the standard rate constants in CsCl melt is the larger polarizability of caesium.

Conclusion

The influence of the second coordination sphere on the electroreduction of hafnium complexes to the metal and the europium redox reaction was studied. Based on experimental data it is suggested that the limitation for discharge of hafnium complexes is rearrangement of complexes , but for the redox reaction of europium it is electron transfer over outer sphere cations.

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