ELECTROREDUCTION OF POTASSIUM FLUOROZIRCONATE ON THE BACKGROUND OF CHLORIDE AND CHLORIDE-FLUORIDE MELTS

Victor MALYSHEV, [a, b] Angelina GAB,[a,b] Alevtina IZVARINA,[a,b] Ana-Maria POPESCU[c]* and Virgil CONSTANTIN[c]

[a]National Technical University of Ukraine "Kyiv Polytechnic Institute", Faculty of Chemistry & Technology,
37 Peremoga Ave., Kyiv 05056, Ukraine
[b]Open International University of Human Development "Ukraine"
1g Khoriva St., Kyiv 04071, Ukraine; Email: victor_malyshev@mail.ru; lina_gab@mail.ru
[c] Roumanian Academy, "Ilie Murgulescu" Institute of Physical Chemistry, Laboratory of Molten Salts,
Splaiul Independentei 202, Bucharest-006021, Roumania

Electrochemical reduction of zirconium in chloride-fluoride melts was shown to proceed by the auto inhibition scheme and via reversible one-step four-electron transfer at low and high concentration of fluoride ions, respectively.

INTRODUCTION

Electrochemical behavior of zirconium was studied in fluoride, oxide-fluoride, fluoride-chloride, and chloride melts. The most reliable data were obtained in the fluoride-chloride systems used for electrolytic refining of zirconium.[1,2]

The KC1-NaCl-K_2ZrF_6 molten system was investigated in connection with high-temperature electrochemical synthesis of zirconium compounds from commercially available, stable in air potassium fluorozirconate. Despite extended studies on the mechanism of cathodic reduction of K_2ZrF_6 in chloride melts, there is still considerable disagreement on potentials, sequence of steps, and other aspects. Several mechanistic schemes were proposed for electroreduction of the KC1-NaCl-K_2ZrF_6 system. Some of the researchers assumed that an intermediate step precedes the discharge of zirconium ions to metal.[3-10] The step was supposed to involve[3] $nMF \cdot ZrF_2$, K_2ZrF_6 in different forms,[4,5] or very low soluble complex salts of zirconium in intermediate valent

states, *i.e.*, ZrF or $MZrF_4$ (M = Na, K).[6-10]

Other authors proposed three-, two,[11-14] or one-step[15-18] mechanisms for electroreduction of ZrF_6. These studies were performed under different atmosphere (air, argon, purging with argon) and different working electrodes (WE= Pt, W, Mo, and Zr, pyropolymers, and glassy-carbon) to follow cathodic reduction. Cyclic voltammetry was not employed. All this brought about a good deal of discrepancy between the experimental results.

In the present work we studied electrochemical behavior of zirconium in chloride-fluoride melts to evaluate the applicability of the system to high-temperature electrochemical synthesis of zirconium compounds.

RESULTS AND DISCUSSION

A reduction wave was observed in voltammetric curves at potentials of -1.5 to -1.8 V for KC1-NaC1 melts containing $1 \times 10^{-5} – 4 \times 10^{-4}$ mol/cm^3 K_2ZrF_6 (Fig. 1, curve 2). On the reverse (anodic) going scan, an oxidation wave due to the

cathodic product was found in the region much

more positive of the cathodic wave, *i.e.*, about -0.9 − -1.1 V.

Changing the tungsten indicator electrode to the platinum or glassy-carbon as well as the use of the air atmosphere or purging the system with

argon considerably complicate interpretation of the voltammetric curves due to appearance of additional waves. The cathodic reduction wave is extended along the potential axis (over 250 mV) and has no inflections.
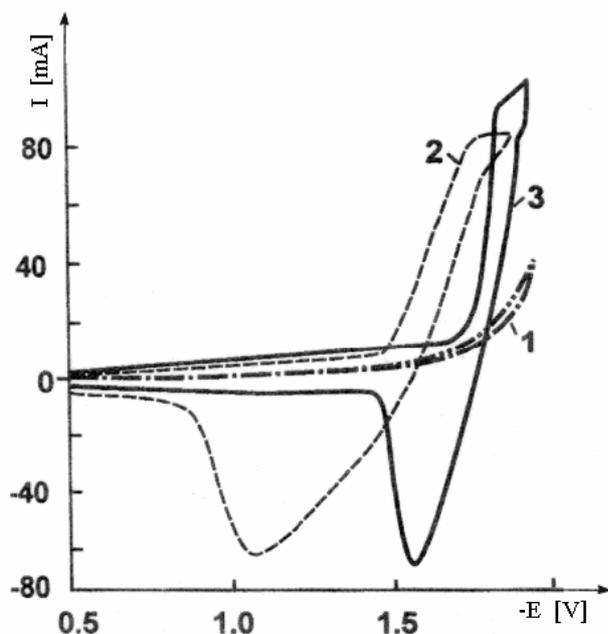

Fig. 1 – Cyclic voltammograms recorded with v=0.1V/s at the WE (1023 K) for melts: 1 – KCl-NaCl; 2 – KCl-NaCl- 8 *10^{-5} mol/cm^3 K$_2$ZrF$_6$; 3 – KCl-NaCl-8 *10^{-5} mol/cm^3 K$_2$ZrF$_6$-3.2*10^{-3} mol/cm^3 NaF [Zr(IV)]:[F] = 1:40.

The increase in the polarization rate to 10 V/s makes impossible the observation of intermediate steps. The potentials of the peak and half-peak are

shifted to the negative region as the fluorozirconate concentration increases whereas the discharge potential remains nearly constant (Table 1).

Table 1

Parameters of K$_2$ZrF$_6$ electro-reduction in NaCl-KCl- K$_2$ZrF$_6$ melt (S_{WE} = 0.385 cm^2, v = 0.1 V/s, Ag$^+$/Ag reference electrode, T = 1023 K)

C (K$_2$ZrF$_6$) x10^4 [mol/cm^3]	I$_p^c$ x 10^{-2} [A/cm^2]	-E$_d^c$	-E$_{p/2}^c$	-E$_p^c$	E$_p^a$	*ΔE$_p^{a-c}$
		[V]				
0.5	3.6	1.43	1.49	1.60	1.20	0.40
1.0	7.4	1.43	1.55	1.70	1.15	0.55
1.5	11.1	1.44	1.57	1.72	1.08	0.65
2.0	14.7	1.45	1.58	1.74	1.04	0.70
2.5	18.4	1.46	1.58	1.75	1.03	0.72
3.0	22.1	1.48	1.59	1.76	0.94	0.82
3.5	25.8	1.49	1.60	1.80	0.87	0.93

*E$_p^{a-c}$ =E$_p^a$-E$_p^c$

The potentiostatic electrolysis at potentials of the wave observed gives zirconium metals as unique product. The relationship between the peak current and concentration of K$_2$ZrF$_6$ is linear in the sweep-rate and concentration ranges studied.

The criterion for diffusion control is that $i_p/v^{1/2}$

(v=scan rate) must be constant only for planar electrodes and for a given concentration of the electroactive species.[19] Taking in account that criterion we found that the ratio $i_p/v^{1/2}$ is almost constant over the wide range of polarization rates (from 0.1 to 100 V/s). This constancy is observed

within the range of K_2ZrF_6 concentrations 5×10^{-5} to 4×10^{-4} molcm^{-3}. The mass-transfer rate i_p/nFC $(1.39-1.68 \times 10^{-3})$ cm/s for steady - state waves characterizing the transport of the reactants to the electrode surface is comparable in value to the rate of diffusion transfer. The directly proportional relationship between the current and K_2ZrF_6 concentration, the constancy of the ratio $i/v^{1/2}$ and the values of i_p/nFC indicate that the electrode process is limited by diffusion of electroactive species to the electrode surface.

The analysis of the voltammograms in semi-log coordinates $log(i_d - i) - E$ and $log[i/(i_d - i)] - E$

(Fig.2a), polarization curves for zirconium electrode in the log $(i_d - i) - E$ coordinates (Fig. 3,

curve 3), the data of nonstationary measurements by the criteria of Matsuda-Ayabe and Delahey, and cyclic voltammograms shows that the number of electrons transferred in the electrode process is not equal to 4 [Value of coefficient $3.2RT/4F$ for four electrons reversible charge transfer under experimental conditions (T=1073K) is 0.074V. Therefore, ΔE_p^{a-c} measured experimentally (0.650-0.700V) is much larger then this value which can be indicated as: ΔE_p^{a-c} (0.650-0.700 V) $\gg \frac{3.2RT}{4F}$
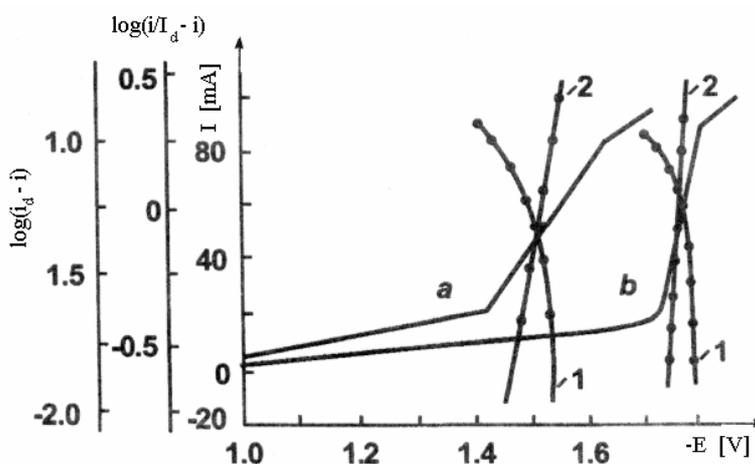
(0.074 V)].

Fig. 2 – Stationary voltammograms at the WE (1023 K) for KC1-NaC1-1×10^{-4} mol/cm^3 K_2ZrF_6 (a); KCl-NaC1-8×10^{-5} mol/cm^3 K_2ZrF_6-3.2×10^{-3} mol/cm^3 NaF (b) melts, and corresponding diagrams in semi-log coordinates $log(i_d - i)$ vs. E (1) and $log [i/(i_d - i)]$ vs. E (2); Scan rate 20 mV/s.

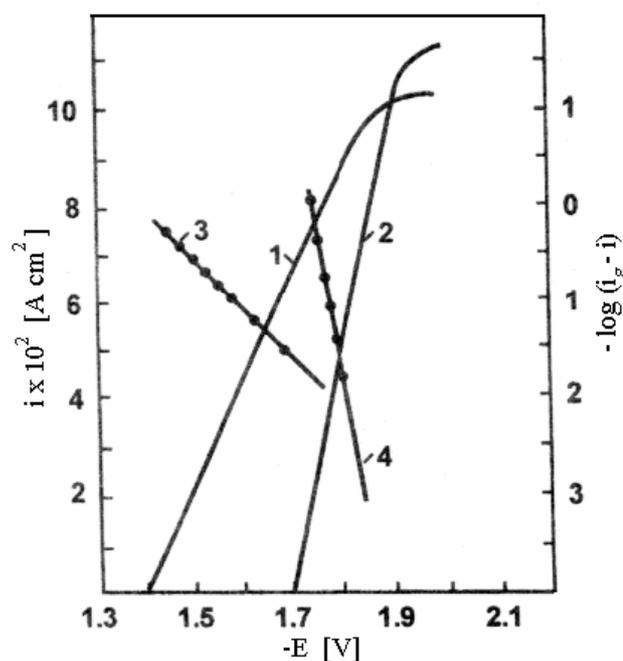Fig. 3 – Polarization of zirconium electrode in KC1-NaC1-8×10^{-5} mol/cm^3 K_2ZrF_6 (1); and KCl-NaC1- 8×10^{-5} mol/cm^3 K_2ZrF_6 –3.2×10^{-3} mol/cm^3 NaF (2) melts and corresponding diagrams in coordinates $log(i_d - i)$ vs. E coordinates (3 and 4 respectively). Scan rate 20 mV/s; T = 1073 K.
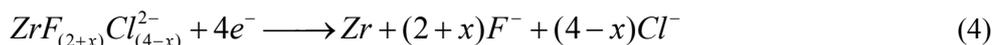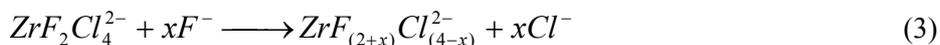
The study of the effect produced by [F⁻] ions on electroreduction of K_2ZrF_6 made it possible to elucidate the true reason for the apparent irreversibility and the influence of the mole ratio [Zr(IV)] : [F⁻] on the reduction mechanism and the nature of zirconium species in the melt as well as to find out the optimum composition of the electrolyte providing the one-step reversible transfer. The fluoride ions were introduced to the melt in the form of sodium fluoride.

$$ZrF_6^{2-} + 4Cl^- \longrightarrow ZrF_2Cl_4^{2-} + 4F^- \qquad (1)$$
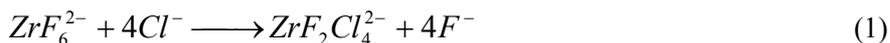
The existence of such complexes was confirmed by IR spectroscopy.[20]

$$ZrF_2Cl_4^{2-} + 4e^- \longrightarrow Zr + 2F^- + 4Cl^- \qquad (2)$$

build up at the electrode surface resulting in formation of complexes with a higher number of

$$ZrF_2Cl_4^{2-} + xF^- \longrightarrow ZrF_{(2+x)}Cl_{(4-x)}^{2-} + xCl^- \qquad (3)$$

$$ZrF_{(2+x)}Cl_{(4-x)}^{2-} + 4e^- \longrightarrow Zr + (2+x)F^- + (4-x)Cl^- \qquad (4)$$

The reduction wave in this case is extended along the potential axis and the process looks like an irreversible one. So one can see that with F⁻ ions addition to the melt, Cl⁻ ions substitution for F⁻ ions in $ZrF_2Cl_4^{2-}$ complex with subsequent formation of complexes with F⁻ number >2.

The scheme outlined above is confirmed by the $i_p/v^{1/2}$- $v^{1/2}$ relationship which gives information about the effect of a preceding step on the electron transfer. The analysis of the relationship shows that the decrease in the polarization rate leads to a lesser contribution from the electrochemically active complexes and to a corresponding rise of the current.

The linearity of the i_p – C_{Zr} curve indicates the absence of coupled processes under these conditions. The increase in basicity of the KC1- NaCl-K_2ZrF_6 melt due to addition of [F⁻] ions causes the inhibition of reaction (1), acceleration of reaction (3), and the shift of the wave to more negative potentials with a small enhancement of the limit current (Fig. 1, curve 3). These effects are especially pronounced with a large excess of [F⁻] ions. At the mole ratio of [Zr(IV)]: [F] = 1:40, the shift in the half-wave potential is 0.17-0.18 V and that in the discharge potential is 0.23-0.25 V. During F⁻ ions concentration increase, zirconium fluoride complexes composition shift toward increase of F⁻ ions number in complex takes place. As a consequence, potential shift (0.17-0.18 V) associated with complex composition change is observed.

It was supposed in earlier studies that in KC1-NaC1 melts containing K_2ZrF_6 in small quantities zirconium exists in the form of ZrF^{2-} ions.[4-6, 8, 9]

However the formation of mixed chloride-fluoride complexes was proved later.[14, 17, 18]

Taking into account that upon titration of purely chloride melts with fluoride ions the reduction mechanism changes at [Zr(IV)]:[F⁻]>>1:2, the researchers assumed the intermediacy of $ZrF_2Cl_4^{2-}$ species:

The fluoride ions released during electrolysis of the KC1-NaCl-K_2ZrF_6 melts by the reaction:

ligands and in the auto-inhibition of the process:

To clear up the change in the charge-transfer step and to determine the number of electrons transferred in the electrode process, we calculated stationary (Fig.2*b)* and non-stationary voltammetric parameters (Table 2) under conditions of increasing mole ratio [F]:[Zr(IV)]. As may be seen, the number of electrons increases and reaches the value of 4 at [F]/[Zr(IV)] = 30 by all the calculation criteria used.

The [$\log(i_d - i)vs.E$] curve for polarization of the zirconium electrode (Fig. 3, curve 4*)* presents a straight line with the theoretical slope corresponding to the four-electron reversible process.

The fluoride ions added to the KC1-NaC1 melt replace [Cl⁻] ions in complexes, resulting thereby in their strengthening. It seemed of interest to determine the composition of the complexes with excess [F⁻] ions.

The coordination number was estimated by the shift in the discharge potential upon titration of the melt with F ions (Fig. 4), using the following equation:[21]

$$\frac{dE_d^c}{d\ln C(F^-)} = \frac{NRT}{nF} \qquad (5)$$

where: E_d^c = cathode discharge potential, N = ligands number bonded to zirconium in the course of titration, n = transferred electrons number, C = concentration, T = absolute temperature and R,F are the classical well known constants (Table 2).

Table 2

The effect of F ions on voltammetric characteristics in the NaF-KC1-NaCl-K_2ZrF_6 system at 1023 K

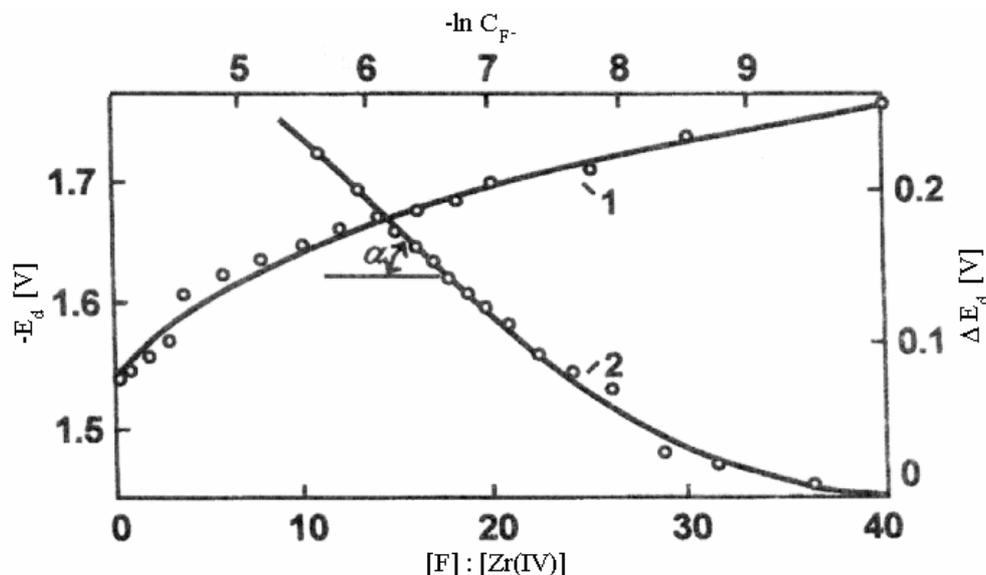| C (NaF) x 10^4 [mol/cm^3]	[F⁻]:[Zr]	i_p x 10^{-2} [A/cm^2]	$i_p/v^{1/2}$ x 10^2	$-E_p^c$	$-E_{p/2}^c$	$-E_d^c$	E_p^a	$E_{p/2}^c - E_p^c$	$E_p^a - E_p^c$
						[V]			
0	0	16.52	5.224	1.80	1.64	1.54	1.10	0.16	0.70
2.4	3	16.61	4.468	1.82	1.67	1.57	1.15	0.15	0.67
6.4	8	16.83	3.848	1.80	1.71	1.62	1.31	0.09	0.49
12.8	16	16.92	3.643	1.81	1.74	1.68	1.44	0.07	0.37
20.0	25	17.06	3.368	1.80	1.74	1.71	1.48	0.06	0.32
32.0	40	17.15	3.643	1.86	1.81	1.77	1.57	0.05	0.29

Fig. 4 – The effect of F⁻ ions on discharge potential of Zr-containing complexes: 1 – the plot of E_d vs. [F]:[Zr(IV)] for KCl-NaCl-K$_2$ZrF$_6$-NaF melt; 2 – the plot of discharged potential shift ΔE_d vs. $1nC_{(F-)}$ [$C_{(F-)}$ is the concentration of F⁻ ions, mol/cm³], T = 1023 K, WE=cathode.

The slope of the ΔE_d (ΔE_d is shift of cathode discharge potential during fluoride ion concentration - C_F^- - changing) vs. $\Delta 1nC_F^-$ curve (Fig. 4) is equal to NRT/nF from where N value is calculated. The plot is linear over the $1nC_F^-$ range of 5-8.5 and gives N=3.86-4.33 (according with equation (5)). Apparently, E_d^c means the discharged potential relevant to beginning of cathode wave at current-voltage dependency, which is referred to our eq.(5). Thus the composition of the zirconium-containing complex is ZrF$_6$²⁻.

For a better understanding of all the process and all the complexes formed into the melt we must say that during K$_2$ZrF$_6$ addition to KCl-NaCl melt, $ZrF_2Cl_4^{2-}$ complex take place.

Also further addition of F⁻ ions in melt leads to substitution of Cl⁻ ions by them and to ZrF_6^{2-} complex formation with NaF excess which is obvious from the next reaction (6). We failed to determine intermediate values of N by the method proposed in ref.[22]

The number of electrons participating electrode process, calculated from current-voltage dependencies for tungsten and zirconium electrodes are well illustrated in Table 3.

Table 3

The number of electrons participating to the electrode process, calculated from current-voltage dependencies for zirconium electrode

n calculated from	
Peak half- widths	Polarization of Zr electrode
1.21	0.923
1.29	0.948
2.15	1.562
2.77	2.670
3.23	3.625
3.88	4.413

The formation and discharge of electrochemically active complexes in the presence of excess NaF ([F⁻]/[Zr (IV)] > 30) can be presented as follows:

$$ZrF_2Cl_4^{2-} + 4F^- \longleftrightarrow ZrF_6^{2-} + 4Cl^- \quad (6)$$

$$ZrF_6^{2-} + 4e^- \longrightarrow Zr + 6F^- \quad (7)$$
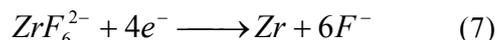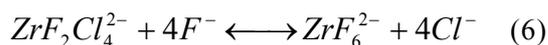
We did not study purely fluoride melts but the reported data on the four-electron reversible one-step reduction[23] are in good agreement with the present results.

EXPERIMENTAL

The main method used in the study was voltammetry at potential scan rates ranging from 20 mV/s to 10 V/s under stationary and non-stationary polarization conditions. The experiments were carried out at the temperature of 973 to 1073 K in a quartz reactor under the inert atmosphere. Argon was purified as described in ref.[18]

In a three-electrode cell, the platinum, glassy-carbon, and tungsten semi-dipped electrodes served as the working electrode and a glassy-carbon crucible as the anode and container for the melt. The reference electrode was KC1-NaCl-5 mol% AgCl/Ag protected against fluorides by a graphite cover. The design of the electrode and its use in different fluoride and chloride-fluoride melts were described in another ref.[20]

The electrolytes were prepared from thoroughly dehydrated salts of the "ultrapure" grade (sodium and potassium chlorides) by stepwise heating to 600 °C in vacuum and subsequent melting under the argon atmosphere. Commercial potassium hexafluorozirconate was re-crystallized prior to use.

CONCLUSIONS

Based on the linear and cyclic voltammetric measurements, we can assume that electrochemical reduction of zirconium in chloride-fluoride melts has different mechanisms at low and high concentration of F ions.

In the first case the reduction proceeds by the auto-inhibition scheme whereas in the second the four-electron reversible one-step process is observed.

By varying the $[F^-]:[Zr(IV)]$ ratio in the melt, it is possible to create conditions providing one-step four-electron discharge of zirconium.

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