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Electrochemical reduction of $ZrCl_4$ in molten NaCl, CsCl and KCl-LiCl and chemical reactions coupled to the electrodeposition of zirconium

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Cyclic voltammetry is used to study the reduction of $ZrCl_4$ in molten NaCl, KCl–LiCl or CsCl and the nature of the various electrochemical processes. The chemical reactions between Zr metal and the M_2ZrCl_6 complex occurring in the bath are also studied.

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1. Introduction

The morphology of the deposits of refractory metals such as Ti, Zr or Hf, produced by electrochemical reduction of their tetrachlorides, depends on several parameters, e.g. temperature, current density, applied voltage, stirring, purity of the melts, etc. However, the nature of the alkali halides in the bath is also a very important factor. Indeed, when the electrowinning of Zr from $ZrCl_4$ was studied, a crystalline deposit was obtained in CsCl melts, whereas in NaCl melts the deposits were powdery and poorly adherent. In the latter case, when fluoride ions (which according to Pint and Flengas [1] enhance the average valency of the dissolved Zr species as in CsCl melts) were added, more compact, crystalline dendritic deposits were obtained.

The nature of the anions and cations in the molten baths affects the composition and stability of the complexes of Zr in its various oxidation states. In order to define the optimum conditions for the electrocrystallization of Zr, the factors which affect the stability of the complexes of Zr in the baths were studied. First of all we characterize the reduction steps of $ZrCl_4$ in various alkali chlorides such as NaCl, CsCl and KCl–LiCl. Then we identify the disproportionations and redox reactions occurring during electrolysis because of the simultaneous presence of several oxidation states of Zr.

2. Reduction of $ZrCl_4$ in various molten salts

2.1. *Experimental procedure*

According to the temperature, we used either a Pyrex (less than 580° C) or a quartz (higher than 580° C) cell. These types of cell have been described previously [2]. The salt was placed in a crucible of Pyrex or quartz and then sealed inside the cell. A viton joint between the ground flats of the Pyrex cover and the cell ensured good sealing. The cover included various ports for the introduction of the electrodes and the thermocouple and for argon circulation. It also included a lock for the addition of $ZrCl_4$ pellets. The zirconium tetrachloride, twice sublimed, was stored in a dry-box under argon. The auxiliary electrode was a graphite rod (6mm in diameter).

The reference electrode was a silver wire immersed in a 1 mol% solution of AgCl in the melt under study. In this work all the potentials are related to a chlorine reference potential. According to the potential range studied, the working electrode was either a tungsten or a vitreous carbon rod (working area: $1\,cm^2$).

The pure alkali chlorides or the eutectic mixture were melted under vacuum. The melts were then purified by bubbling a dry HCl stream through them. Cyclic voltammetry with scan rates from $0.02\,V\,s^{-1}$ to $1\,V\,s^{-1}$ was used for this study.

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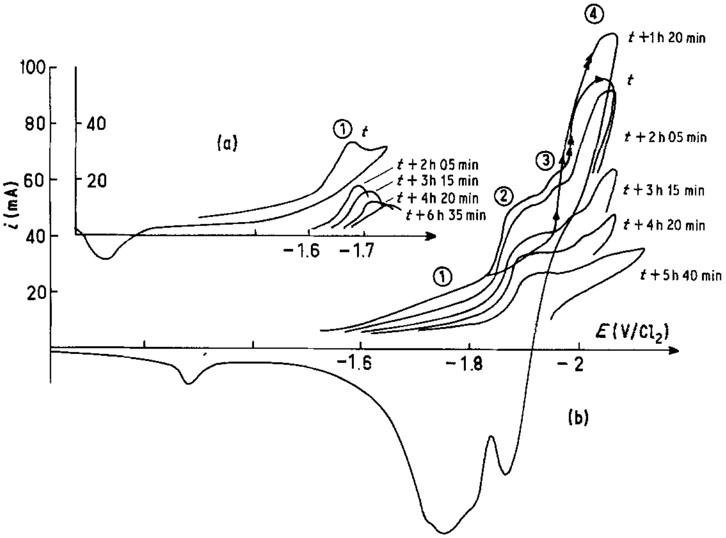

Fig. 1. Current–potential curves drawn as a function of time for $ZrCl_4$ in molten NaCl at 820° C. (a) On a vitreous carbon electrode, (b) on a tungsten electrode.

2.2. *Results*

2.2.1. Reduction of $ZrCl_4$ in NaCl at 820° C. The current–potential curves (Fig. 1) indicate a complicated mechanism for the reduction of $ZrCl_4$. Indeed, on a tungsten cathode (Fig. 1b) it is a four-step reduction, the first of which is more pronounced on the vitreous carbon electrode (Fig. 1a). As shown by the curves recorded at various time intervals after the addition of $ZrCl_4$, the limiting currents evolve with time (Fig. 2). For waves 1, 3 and 4 the limiting currents decrease with time. Therefore these waves may be attributed to the reduction of the same species, the concentration of which decreases with time. On the other hand, the limiting current for the second wave, which was zero at the beginning, increases progressively and then decreases after two hours: the origin of this wave is thus not the same as for the other three.

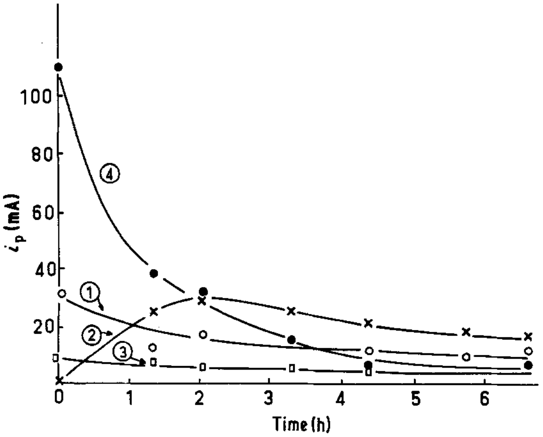

Fig. 2. Peak current versus time for each reduction wave of $ZrCl_4$ in NaCl at 820° C.

To determine the nature of the electrode processes leading to these waves we have calculated the potentials of the possible reductions for the various oxidation states of zirconium. Each compound is considered in its three physical states. The thermodynamic data used, ΔG, ΔH and ΔS, are those of Barin and Knacke [3] for the zirconium chlorides and of Morozov and Toptygin [4] for the complexes.

Each calculated value of E_0 may be compared to the potential $E_{1/2}$ measured by voltammetry, assuming the reactions to be reversible and the diffusion coefficients of the oxidized and reduced forms to be the same. $E_{1/2}$ corresponds to the potential for which i is 85.17% of i_p, the peak current.

As the four reduction steps are very close, we cannot confirm their nature by comparison of experimental and calculated potentials (Table 1). In any case, these calculated values of E_0 cannot quantitatively be compared to the experimental $E_{1/2}$ values because of the overpotentials associated with the nucleation of the deposition reactions. Moreover, the electron transfers are not reversible and we cannot calculate the number of electrons involved. It is, however, possible to study and compare these reduction steps with those observed

Table 1. Comparison of experimental and calculated potentials for reduction of $ZrCl_4$ in NaCl

Potential	Wave 1	Wave 2	Wave 3	Wave 4
$E_{1/2}$ (exp.) (V)	−1.74	−1.88	−1.93	−2.03
E_0 (calc.)† (V)	−1.72 4(C) → 2(s) −1.78 4(g) → 2(s)	−1.92 4(g) → 0 −1.78 4(g) → 2(s) −1.72 4(C) → 2(s) −1.89 4(C) → 0	−1.89 4(C) → 0 1.92 4(g) → 0	−2.06 2(s) → 0

† 4(C) = Zr^{4+} complexed, 4(g) = $ZrCl_4$ in gaseous state, 2(s) = $ZrCl_2$ in solid state.

in lower melting point baths, i.e. KCl–LiCl and CsCl, where the intermediate compounds can be identified by physical chemical data.

2.2.2. *Reduction of $ZrCl_4$ in KCl–LiCl at 520° C.*

As shown in Fig. 3 the *I–E* curve for this reduction is different from that for the NaCl melt and occurs in two steps (Fig. 3a). By electrolysis at controlled potentials we have shown that deposition of metal can be obtained at potentials more negative than −2.2 V. As Zr^{3+} is not stable at temperatures higher than 400° C, the addition of Zr reduces the Zr^{4+} ions in the melt to Zr^{2+} according to the reaction:

$$Zr + Zr^{4+} \rightleftharpoons 2Zr^{2+}.$$

Excess Zr leads to an increasing concentration of Zr^{2+}; thus it should enhance the reduction wave

$$Zr^{2+} + 2e \rightarrow Zr^0.$$

Indeed only one wave remains after adding an excess of Zr (Fig. 3b), and it may be attributed to the second reduction step of $ZrCl_4$. Therefore the first wave is related to the reduction of $(ZrCl_6)^{2-}$ to $ZrCl_2$.

2.2.3. *Reduction of $ZrCl_4$ in CsCl at 700° C.*

In this bath the reduction of $ZrCl_4$ is more complicated than in KCl–LiCl (Fig. 4). There are four waves, the third being the most important. When the concentration of the Zr^{2+} species is increased by adding metallic Zr to the melt, the height of the last wave increases. Thus it is related to the stage 2(s) → 0. Moreover, electrolysis at $E_{1/2} = -2.08$ V on a tungsten cathode gives a deposit with an X-ray pattern of zirconium. This metal comes from the direct reduction of Cs_2ZrCl_6. As the stability of the hexachlorozirconate M_2ZrCl_6 increases with the radius of the alkali cation M, its reduction potential becomes more and more cathodic. For Cs_2ZrCl_6, the highly negative value for this poten-

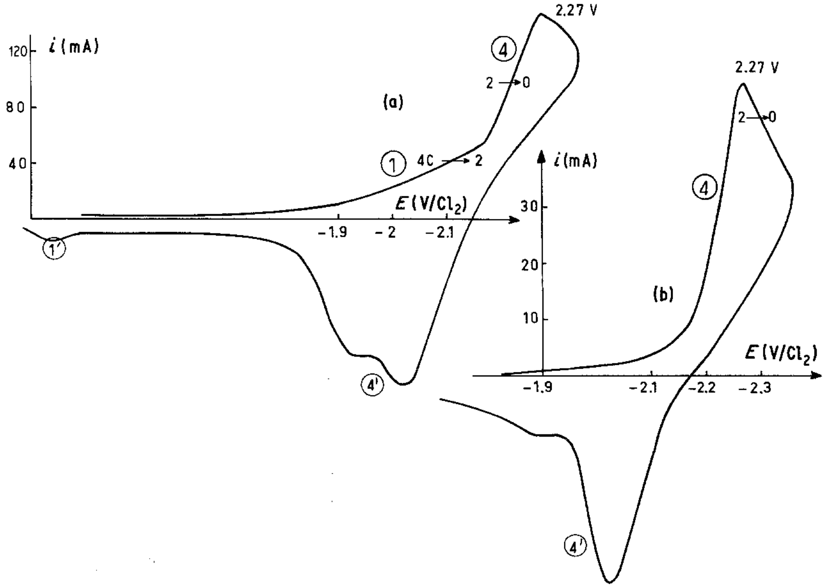

Fig. 3. Current–potential curves for the reduction of $ZrCl_4$ in KCl–LiCl bath at 520° C. (a) Without Zr, (b) with Zr.

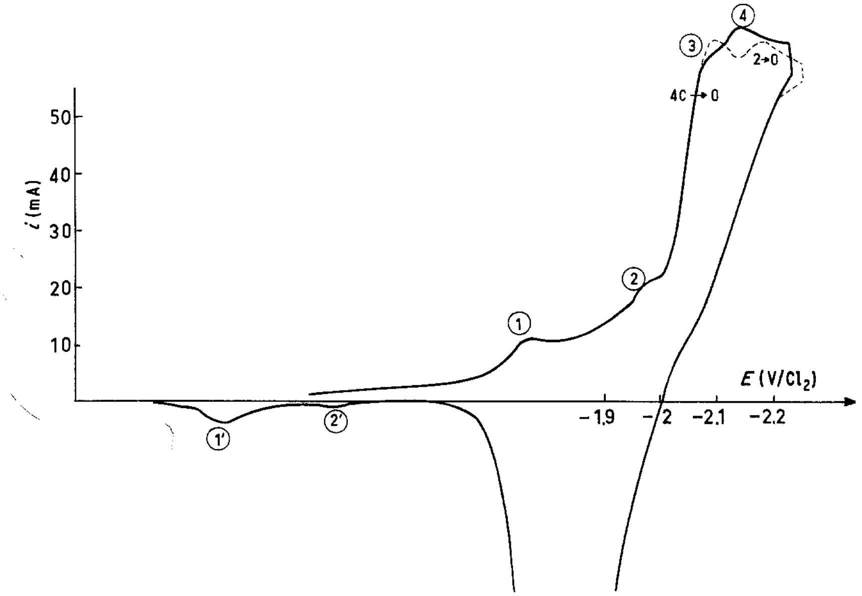

Fig. 4. Current–potential curve for the reduction of $ZrCl_4$ in molten CsCl at 700° C. ——— without Zr, – – – with Zr.

tial allows a direct reduction 4(C) → 0. The reduction of less stable complexes such as K_2ZrCl_6 occurs at more positive potentials and another step, 4(C) → 2(s), may appear, as in the KCl–LiCl eutectic.

Experimental and calculated potentials related to the various waves are collected in Table 2. By their comparison we may conclude that the first two waves are related to the transitions: 4(g) → 2(s) and 4(g) → 0, respectively. The dissolution of the M_2ZrCl_6 complex in the melt is achieved according to the equilibrium reaction:

$$M_2ZrCl_6 \rightleftharpoons ZrCl_4(g) + 2MCl. \qquad (1)$$

The dissociation depends on the partial pressure of $ZrCl_4$ over the bath and the nature of the alkali cation M^+. Increasing the radius of M^+, that is, going from lithium to caesium, enhances the stability of M_2ZrCl_6. Increasing the temperature favours its dissociation. Therefore at high temperatures and with alkali cations such as Na, Equilibrium 1 is shifted towards the right-hand side and the concentration of gaseous $ZrCl_4$ in the melt is greater. Likewise for caesium, for which the complex $ZrCl_6^{2-}$ is rather stable, the concentration of gaseous $ZrCl_4$ is no longer negligible when the temperature is raised to 700°C.

Table 2. Comparison of experimental and calculated potentials for reduction of $ZrCl_4$ in CsCl

Potential	*Wave*			
	1	2	3	4
$E_{1/2}$ (exp.) (V)	−1.75	−1.95	−2.08	−2.17
E_0 (calc.) (V)	−2 4(C) → 2(s) −1.76 4(g) → 2(s)	−2 4(C) → 2(s) −1.95 4(g) → 0	−2.07 4(C) → 0	−2.14 2(s) → 0

This hypothesis explains the origin of the waves observed during the reduction of $ZrCl_4$ in molten NaCl at 820°C or in CsCl at 700°C.

2.2.4. *Interpretation of the reduction steps of $ZrCl_4$ in NaCl.*

For this interpretation we have used the results obtained in the investigation of the reduction of $ZrCl_4$ in KCl–LiCl and CsCl. In Fig. 5 the curves recorded for the three melts studied are shown: these allow a comparison of the positions of the reduction waves. Table 3 summarizes the data collected for the various steps in these melts.

As the stability of Na_2ZrCl_6 is low, it is reduced to $ZrCl_2$ at a rather positive potential. The first wave is thus related to the stage 4(C) → 2(s), as confirmed by the comparison between theoretical and experimental potentials. When comparing the

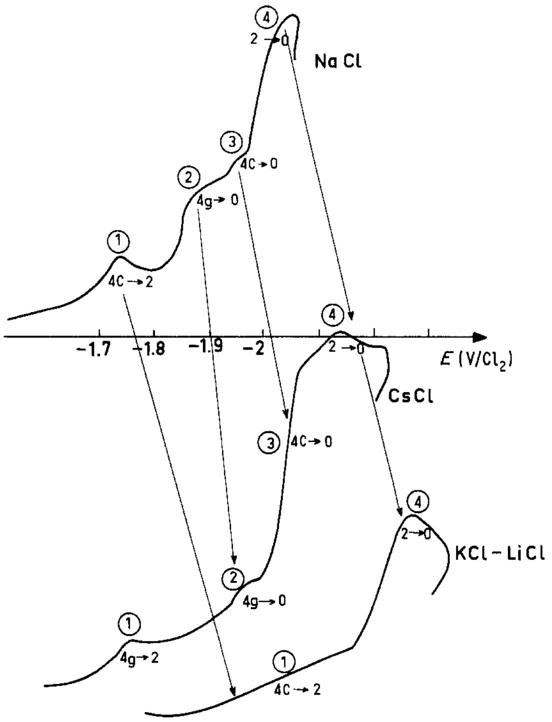

Fig. 5. Comparison of the reduction stages of $ZrCl_4$ in NaCl, CsCl and KCl–LiCl.

half-wave potentials in CsCl and NaCl, we may assign the third step to a transition 4(C) → 0. When the complex is first reduced into 2(s), this third wave is very low.

As in KCl–LiCl and CsCl baths the last step is a reduction 2(s) → 0. Waves 1, 3 and 4 are all related to the reduction of the complex Na_2ZrCl_6. This confirms the hypothesis made by considering the change with time of the heights of the waves (Fig. 1). On the other hand, Na_2ZrCl_6 at 820°C is in equilibrium with $ZrCl_4$ according to Reaction 1. As the stability of this complex compound is rather low, the concentration of $ZrCl_4$ may be high. By comparing experimental and calculated potentials we may attribute the second wave to a 4(g) → 0 reduction. Its origin is thus different from the other ones. We may now explain the curves of peak currents versus time (Fig. 2) for waves 1 and 4 (related to the 4(C) → 2(s) and 2(s) → 0 transitions) and why they cross, $i_p(4)$ becoming less than $i_p(1)$. Indeed $ZrCl_2$ tends to disproportionate according to the reaction

$$2ZrCl_2 \rightleftharpoons ZrCl_4 + Zr. \qquad (2)$$

At the beginning, when the $ZrCl_4$ concentration is high, Reaction 2 is shifted towards the left-hand side and $ZrCl_2$ is stable. Then the peak heights $i_p(1)$ and $i_p(4)$ evolve normally. After a few hours the concentration of $ZrCl_4$ decreases, electrochemically formed $ZrCl_2$ tends to disproportionate and wave 4, related to a 2(s) → 0 transition, decreases in height more rapidly than wave 1.

3. Chemical reactions between zirconium and its various oxidation states in the electrolysis melts

In a parallel study to the preceding work we have

Table 3. Calculated and experimental potentials in various melts

Melt	*Potential*	*Wave*			
		1	2	3	4
NaCl	$E_{1/2}$ (exp.) (V)	−1.74	−1.88	−1.93	−2.03
	E_0 (calc.) (V)	−1.78 4(g) → 2(s) −1.72 4(C) → 2(s)	−1.92 4(g) → 0 −1.78 4(g) → 2(s)	−1.89 4(C) → 0	−2.06 2(s) → 0
CsCl	$E_{1/2}$ (exp.) (V)	−1.75	−1.95	−2.08	−2.17
	E_0 (calc.) (V)	−1.76 4(g) → 2(s)	−1.95 4(g) → 0	−2.07 4(C) → 0	−2.14 2(s) → 0
KCl–LiCl	$E_{1/2}$ (exp.) (V)	−2.06			−2.27
	E_0 (calc.) (V)	−2.04 4(C) → 2(s)			−2.27 2(s) → 0

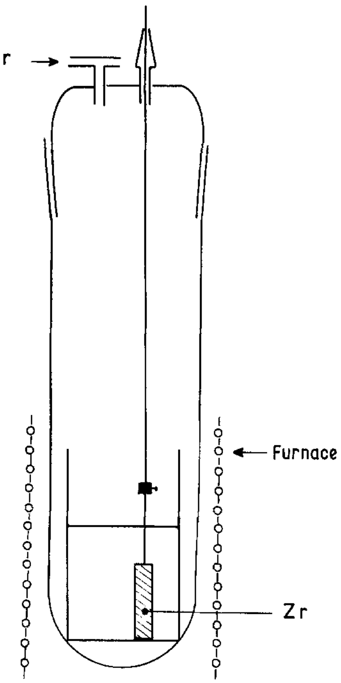

Fig. 6. Cell used for studying the oxidation of a Zr sheet in molten NaCl, KCl or CsCl with 5 wt% M_2ZrCl_6 (M, alkali metal cation of the bath).

studied the reactions which occur simultaneously with the electrolysis, i.e. dismutations, redox reactions and complexing with the bath components. To this end, we have studied the oxidation of a sheet of zirconium immersed in melts of KCl, NaCl or CsCl with 5 wt% of hexachlorozirconate of the same alkali cation. An Inconel crucible containing the dehydrated salt and a known amount of hexachlorozirconate was inserted in a silica tube, under an argon stream. A sheet of zirconium of known weight was then totally immersed after the salt had fused (Fig. 6). To compare the results, all the runs were carried out at 850° C and the sheet of metal was removed after 2 or 4 days. In each case we examined the weight loss of the sheet and the nature of the insoluble products.

Table 4. Products obtained after two- and four-day oxidations of Zr in various melts

Melt	*Two days*	*Four days*
NaCl	Zr + $ZrCl_2$ (very weak)	Zr
KCl	Zr + $ZrCl_2$ (very weak)	Zr
CsCl	$ZrCl_2$ + Zr (very weak)	Zr

Table 5. Calculated and experimental weight losses

Melt	*Maximum calculated weight loss* (g)	*Experimental weight loss after two days* (g)
NaCl	0.483	1.571
KCl	0.34	1.323
CsCl	0.238	1.249

The X-ray patterns of the compounds precipitated at the bottom of the cell showed only the peaks for the alkali chlorides. Therefore we eliminated them by extracting the content of the crucibles with water. The X-ray pattern of the insoluble part obtained after filtration shows that it is a mixture of metallic zirconium and cubic ZrO_2. For this latter compound we think that the initial precipitate was amorphous $ZrCl_2$. Indeed, when putting this chloride in water, a dark brown colloidal solution is obtained which hydrolyses progressively into cubic ZrO_2 [5]. The compound which forms during a two-day oxidation of Zr in KCl or NaCl melts is different from the one formed in CsCl: in NaCl or KCl mostly Zr powder is collected whereas in CsCl it is principally $ZrCl_2$ (Table 4). Table 5 summarizes the calculated maximum possible and the experimental weight losses from the zirconium sheet after a two-day exposure. Pint and Flengas [1] made similar runs in sealed containers with baths such as KCl–NaCl, CsCl, etc. at 700° C. They do not mention the occurrence of a precipitate and they measured weight losses which are much lower than ours.

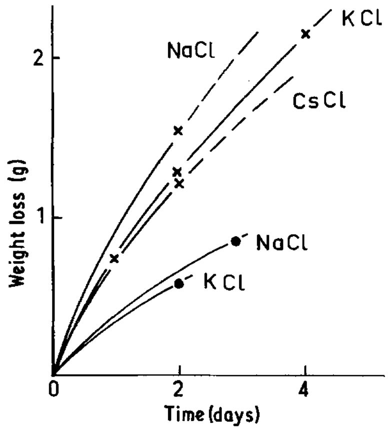

Fig. 7. Weight loss of Zr sheet immersed in various baths as a function of time. ●, Baths containing a hexachlorocomplex; ×, baths containing a hexafluorocomplex.

In Table 5 we can see that the weight loss of the sheet is much higher than that calculated using Reaction 3 which represents the attack of the metal by all the $ZrCl_4$ introduced as M_2ZrCl_6 in the melt:

$$ZrCl_4 + Zr \rightleftharpoons 2ZrCl_2. \quad (3)$$

This important difference cannot be attributed to an insufficient dehydratation of the melts. Indeed a melt with 5 wt% of fluoride complex gives a weight loss much lower than the same bath with 5 wt% of chloride complex (Fig. 7).

The results may be explained by considering Reaction 3. It is shifted to the right-hand side and as $ZrCl_2$ is insoluble it precipitates. However $ZrCl_2$ is unstable at this high temperature (850° C): its disproportionation gives zirconium powder and regenerates the complex M_2ZrCl_6, through which corrosion of the sheet continues.

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