Electronic Conductivity of NaCl-KCl Equimolar Melt Containing Eu(III) and Eu(II) Complexes by Electrochemical Impedance Spectroscopy

Sergey A. Kuznetsov^{a,b} and Marcelle Gaune-Escard^b

^a Institute of Chemistry, Kola Science Centre RAS, 14 Fersman Str., 184209 Apatity, Murmansk Region, Russia

^b Ecole Polytechnique, Mecanique Energetique, Technopole de Chateau Gombert, 5 rue Enrico Fermi, 13453 Marseille Cedex 13, France

Reprint requests to M. G.-E.; Fax: +33(0)4 91 11 74 39; E-mail: mge@polytech.univ-mrs.fr

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The electronic conductivity of molten equimolar NaCl-KCl containing Eu(III) and Eu(II) complexes was studied by electrochemical impedance spectroscopy. The ratio between electronic and electrolyte resistance as a function of the electrode potential was determined. The electronic conductivity was found to be maximal when the amounts of Eu(III) and Eu(II) are about equal. The electronic conductivity of this melt does not exceed 2.3% of the ionic conductivity. Deviation from the molar ratio Eu(III)/Eu(II) = 1 led to a considerable diminution of the electronic conductivity.

Key words: Complexes of Europium; Cyclic Voltammetry; Impedance Spectra; Equivalent Circuit; Electronic and Ionic Conductivity.

1. Introduction

Rare-earth metals and their alloys are widely used in modern techniques. Electrowinning and electrorefining are promising methods for the production of high-purity rare-earth metals [1–4]. In order to achieve optimal electrolysis parameters in these processes knowledge of the electronic and ionic partial conductivities is necessary.

It was shown in [5–8] that the conductivity of the redox couples Nb(V)-Nb(IV) and Ta(V)-Ta(IV) in alkali chloride melts is partly electronic. The electronic conductivity of molten systems can be determined by the Wagner-Hebb method, utilizing a blocked working electrode and a reversible counter electrode, using potentials where the Faraday process does not exist [8]. This method allows to separate electronic and ionic conductivity contributions of the molten electrolyte. The electronic conductivity can also be determined by electrochemical impedance spectroscopy. In many cases, the impedance spectra are characterized by a Warburg transport impedance and are well fitted by an equivalent circuit of the Randles type [9]. The results reported in [5–8] have shown that a perfect fit can be obtained at low frequencies by coupling a resistive element in parallel with the element representing

the ionic transfer (Ohmic resistance) of the electrolyte. This parallel resistor may be assigned to an electronic contribution to the electrolyte conductivity [6].

Electronic conductivity in ionic melts containing EuCl_3 appears due to EuCl_3 decomposition [10–12]. Thus in these melts the electronic conductivity would arise from the exchange of the valence electrons between complexes of Eu(III) and Eu(II).

In this article the electronic conductivity in an NaCl-KCl equimolar melt containing complexes of Eu(III) and Eu(II) was determined by the electrochemical impedance spectroscopy method.

2. Experimental

2.1. Chemicals and Preparation of Salts

Europium trichloride was synthesized from the oxide Eu_2O_3 (Johnsen Matthey, 99.9%). Thionyl chloride (Johnsen Matthey, 99%) was used as a chlorinating agent. The SOCl_2 vapour was passed through solid Eu_2O_3 at 823 K using argon as a carrier gas during 6 h. Chemical analysis of the prepared EuCl_3 was performed by use of mercurimetric (chloride) and complexometric (EDTA in the presence of xylenol orange-europium) methods. The results of the anal-

Table 1. Chemical analysis of EuCl_3 .

mass%			
$\text{Cl}_{\text{experimental}}$	$\text{Cl}_{\text{theoretical}}$	$\text{Eu}_{\text{experimental}}$	$\text{Eu}_{\text{theoretical}}$
41.18	41.17	58.82	58.83

ysis did show that the molar ratio Cl/Eu was essentially three. The chemical analysis of EuCl_3 is given in Table 1. Being highly hygroscopic, EuCl_3 was stored in sealed glass ampoules under vacuum. All further handling of europium trichloride was performed in a controlled purified argon atmosphere glove-box (water content less than 2 ppm). Continuous argon purification was achieved by forced recirculation through external molecular sieves.

NaCl and KCl were purchased from Prolabo (99.5% min.). They were dehydrated by continuous and progressive heating just above the melting point under gaseous HCl atmosphere in quartz ampoules. Excess HCl was removed from the melt by argon bubbling. The salts were handled in the glove-box and stored in sealed glass ampoules, as explained above.

The total concentration of europium was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES). Determination of Eu(II) in quenched samples was performed by potentiometric titration with potassium dichromate.

2.2. Procedures and Electrochemical Cell

NaCl and KCl were mixed in the required ratio, placed in an ampoule made of glassy carbon (GC) of the SU-2000 type and transferred to a hermetically sealed retort of stainless steel. The latter was evacuated to a residual pressure of 0.7 Pa, first at room temperature and then at higher temperatures (473, 673 and 873 K). After this, the retort was filled with high-purity argon and the electrolyte was melted.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were employed, using a VoltaLab-40 potentiostat operated with the packaged software “VoltaMaster 4”, version 6 and the complementary Zahner Im 6d unit. The potential scan rate (v) was varied between $5 \cdot 10^{-3}$ and 5 V s^{-1} . The impedance spectra were recorded from 100 mHz up to 100 kHz, and an amplitude of 10 mV was applied. The experiments were carried out at 973 K. The cyclic voltammetric curves and impedance spectra were recorded at a glassy carbon working electrode (1 mm diameter, type SU-2000) with respect to a glassy carbon rod (2 mm diameter, type SU-2000)

as a quasi-reference electrode. The glassy carbon plate (surface area 3.6 cm^2 , type SU-2000) served as the counter electrode. While the potential of this quasi-reference electrode does not constitute a thermodynamic reference, the use of this electrode was preferred in order to avoid any contact between the melt and oxygen-containing material as used in classical reference electrodes. The potential of the chlorine evolution on the glassy carbon working electrode was used as internal reference potential [13]. During the experiments, the electrochemical cell was kept under an inert argon atmosphere (99.999%, Air Liquide).

The content of EuCl_3 introduced into the NaCl-KCl melt was 2 mol%. A relatively high content was chosen because the electronic conductivity is practically not revealed in diluted solutions containing complexes of mixed valency, due to the shielding influence of cations and anions in the solvent.

3. Results and Discussion

A typical cyclic voltammetric curve of an NaCl-KCl melt after addition of EuCl_3 , as obtained at the glassy carbon electrode, is presented in Figure 1. Wave 1 is observed in the cathodic-anodic region and is indicative of the appearance of Eu(II) in the melt due to the reaction [10–12]

The ratio of Eu(III) to Eu(II) at each potential can be calculated from the equation

$$c_{\text{Eu(III)}} c_{\text{Eu(II)}} = I_p^c \cdot D_{\text{Eu(II)}}^{1/2} / I_p^a \cdot D_{\text{Eu(III)}}^{1/2}, \quad (2)$$

where $c_{\text{Eu(III)}}$ and $c_{\text{Eu(II)}}$ are the concentrations of Eu(III) and Eu(II) complexes in the melt; $D_{\text{Eu(III)}}$ and $D_{\text{Eu(II)}}$ are the diffusion coefficients and I_p^c and I_p^a the cathodic and anodic currents.

The kinetics of the redox electrode reaction

was studied in detail [10–11]. It was shown that the process at $v = 0.3 \text{ V s}^{-1}$ proceeds quasi-reversibly mostly under diffusion control, and the standard rate constant at 973 K was determined as $8 \cdot 10^{-3} \text{ cm s}^{-1}$. The diffusion coefficients of the Eu(III) and Eu(II) complexes at the temperature 973 K were $2.25 \cdot 10^{-5}$ and $4.36 \cdot 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, respectively.

Figure 2 displays the Nyquist plot and Fig. 3 the Bode plot, obtained at the potential +0.1 V vs. the

Fig. 1. Cyclic voltammetric curve at the glassy carbon electrode after addition of 2 mol% of EuCl_3 to an NaCl-KCl melt. Area: 0.32 cm^2 ; sweep rate: 0.3 V s^{-1} ; temperature: 973 K; quasi-reference electrode: glassy carbon.

Fig. 2. Nyquist plot of the impedance after addition of 2 mol% of EuCl_3 to an NaCl-KCl melt. Working electrode: glassy carbon; the potential +0.1 V vs. the glassy carbon quasi-reference electrode; temperature: 973 K; Δ : modulus of the impedance.

GC quasi-reference electrode. It is well known that the Randles equivalent circuit usually simulates effectively the impedance characteristics of a fast charge transfer reaction at a planar electrode [14]. This circuit includes a parallel combination of the charge transfer resistance in series with the Warburg diffusion impedance and the double layer capacitance. This parallel combination is in series with the electrolyte resistance. A Nyquist plot of the impedance represents a circular arc at high frequencies and a linear behaviour with negative slope -1 at lower frequencies, because the diffusion becomes dominant. The latter is described by the Warburg el-

Fig. 3. Bode plot of the impedance after addition of 2 mol% of EuCl_3 to an NaCl-KCl melt. Working electrode: glassy carbon; the potential +0.1 V vs. the glassy carbon quasi-reference electrode; temperature: 973 K; Δ : modulus of the impedance; $\circ$: values of the phase angle.

ement. The Warburg impedance is expressed by the equation [9]

$$Z_W = (1 - j)RT(nF)^{-2}(2)^{-1/2}w^{1/2} \cdot [1/(c_{\text{Eu(III)}}D^{1/2}_{\text{Eu(III)}}) + 1/(c_{\text{Eu(II)}}D^{1/2}_{\text{Eu(II)}})]. \quad (4)$$

Equation (4) applies strictly to semi-infinite diffusion to a planar surface and if the system is not quiescent, the Warburg impedance takes a different form [15, 16]:

$$Z_W = R_{CT} [1 + \{k_f \text{th}(\delta_N j^{1/2} w^{1/2} D^{-1/2}_{\text{Eu(III)}})/(jw D_{\text{Eu(III)}})^{1/2} + (k_b \text{th}(\delta_N j^{1/2} w^{1/2} D^{-1/2}_{\text{Eu(II)}})/(jw D_{\text{Eu(II)}})^{1/2})\}], \quad (5)$$

Fig. 4. Equivalent circuit. Description in the text (Results and Discussion).

where R_{CT} is the charge transfer resistance, th the hyperbolic tangent operator, δ_N the ideal Nernst diffusion layer thickness, k_f and k_b are the rate constants in the forward and reverse direction.

Analysis shows that at $\omega \rightarrow 0$, $Z_W \rightarrow R_{CT}(k_f \delta_N / D_{\text{Eu(III)}})$, and if the diffusion layer has a finite thickness, the impedance at low frequencies lies below the Warburg impedance [16]. Probably this is the reason for the deviation from the slope -1 in our case (Fig. 2). Nevertheless, utilization of the Nernst diffusion element did not provide a good fit of our experimental data.

After the abovementioned analysis for the simulation of the impedance characteristics, an equivalent circuit similar to that reported in [6] was used (Fig. 4). In this circuit: L is the inductivity in cables, R_1 represents the Ohmic resistance of the electrolyte, R_{CT} the charge transfer resistance, the Warburg impedance Z_{W1} represents the diffusion of ionic species, C_{DL} the capacitance of the double layer, R_2 the electronic resistance and Z_{W2} a Warburg-like element which constitutes diffusion of electrons.

The connection of elements R_2 and Z_{W2} parallel to the ionic elements R_1 , R_{CT} , Z_{W1} and C_{DL} indicates that the charge transfer through the electrochemical cell occurs due to an ionic process or to electronic conductivity. The full lines in Fig. 2 and 3 correspond to the equivalent circuit (Fig. 4), and the dashed lines show fits without taking into consideration the electronic conductivity (element R_2 of the circuit).

As can be seen from Fig. 2 and Fig. 3, the experimental data and simulated curves agree well. It was found that the resistance due to diffusion of electrons is negligible, because the equivalent circuit Z_{W2} has values in the pico capacity range.

In particular, significant for our study are the values of R_2 and R_1 in the equivalent circuit, which correspond to electronic and electrolyte resistance. At the potential $+0.1$ V relative to the GC quasi-reference

Fig. 5. Ratios between electronic resistance and electrolyte resistance as a function of electrode potentials for an initial content of 2 mol% EuCl_3 in NaCl-KCl melt. Working electrode: glassy carbon; quasi-reference electrode: glassy carbon; temperature: 973 K.

electrode, the values 0.967Ω and 124Ω were determined for the electronic and electrolyte resistance, respectively. Thus at this potential the fraction of electronic conductivity is less than 1% of the ionic conductivity. However, this value cannot be neglected because including electronic conductivity to the equivalent circuit significantly improves the fitting of the experimental data (Figs 2, 3) and suggests that the model agrees with the electrical analogues.

The ratio between electronic resistances and electrolyte resistances as a function of electrode potentials is shown in Figure 5. It is necessary to note that after each impedance measurement the rest potential of the GC quasi-reference electrode was controlled. The most appropriate method for doing so is the determination of the chlorine evolution potential. The reason of the shift rest potential is the change of the molten salt composition, because the $\text{Eu(II)}/\text{Eu(III)}$ molar ratio may increase during the experiment because of reaction (1). Another melt with the same initial composition was used for measurements if the shift of the rest potential exceeds 20 mV.

As can be seen from Figs. 1 and 5, a relatively sharp maximum of the electronic conductivity was observed for the melts with the $\text{Eu(III)}/\text{Eu(II)}$ molar ratio close to unity. The values of electronic conductivity for these melts were around 2.0–2.3% of the ionic conductivity. The deviation of the $\text{Eu(III)}/\text{Eu(II)}$ molar ratio from

unity led to a significant diminution of the electronic conductivity.

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