ELECTROCHEMICAL BEHAVIOUR AND LINEAR VOLTAMMETRIC DETERMINATION OF OXYGEN IN HALIDE MELTS

L.POLYAKOVA, Z.KONONOVA AND E.POLYAKOV

INSTITUTE OF CHEMISTRY KSC RAS, 14 FERSMAN ST.,
APATITY 184200 RUSSIA

SUMMARY

Voltammetric studies were carried out using a glassy carbon working electrode to determine the concentration of oxide ion in a CsCl-KCl-NaCl eutectic melt. The mechanism of electrode process and some kinetic parameters were established. The oxidation of O^{2-} is irreversible two-stage process complicated by adsorption. The diffusion coefficient of oxide ions changes from $5.62 \cdot 10^{-6}$ to $1.99 \cdot 10^{-6} cm^2 \cdot s^{-1}$ at $750-590^0C$. The equation for the calculation of oxide ion concentration was derived.

KEY WORDS: Molten halides, Voltammetry, Oxide ion determination

INTRODUCTION

Halide melts are widely used in production of metals, surface treatment, inorganic synthesis and nuclear technology. For many of them an oxygen content in the melt is vital importance. Among various methods for oxygen determination linear voltammetry probably is the most acceptable technique [1]. In this paper linear voltammetry was used for determination of oxide ion concentration in a CsCl-KCl-NaCl ternary eutectic melt (m.p.480^0C).

RESULTS AND DISCUSSION

Alkali metal chlorides were recrystallized, dried and calcinated at the temperature of 600^0 C. In some cases they were purified by zone melting. Sodium oxide (Aldrich, pure 98%) was used as O^{2-} donor. Experiments were carried out under argon atmosphere at temperatures 590 - 750^{0}C in a three-electrode cell with a glassy carbon rod as a working electrode [2].

Fig.1 presents typical voltammograms of the background melt, which was not purified by zone melting. The discharge of impurity ions gives a peak at 0,6 V against silver electrode or 1,37 V against glassy carbon.
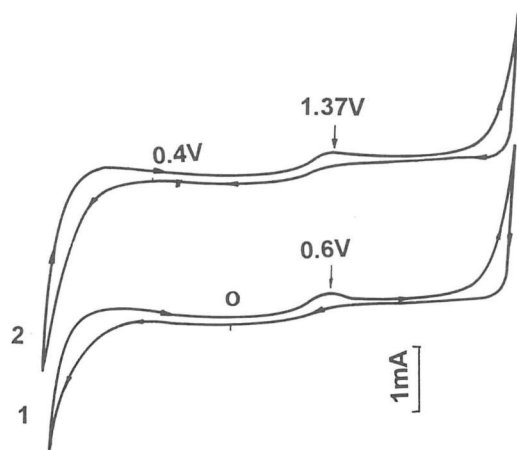

Fig.1. ' Linear sweep voltammograms of a CsCl-KCl-NaCl background melt, 698^{0}C, 0.1 V·s^{-1}, A_{GC}=0.18 cm^2. Reference electrode:(1) Ag/AgCl-RE; (2) glassy carbon quasi-reference electrode (GC-QRE).

Small additions of sodium oxide into the melt led to growth of this peak and a shoulder before it. Next additions increased a height of the peak, the

shoulder became more pronounced. This behaviour allows to associate these peaks with the discharge of oxide ions.

It is difficult to measure accurately the potential of the shoulder at a temperature of 700^{0}C and higher (Fig2).
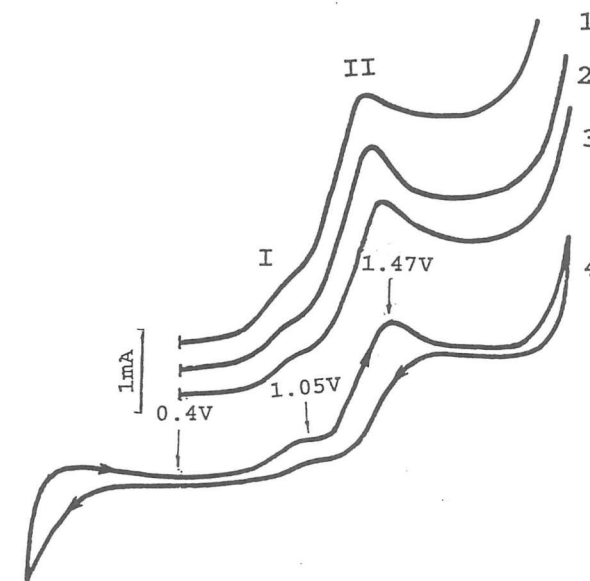

Fig.2. Voltammograms of CsCl-KCl-NaCl-Na$_2$O (0.172m/o) melt, GC-QRE, 0.1 V·s^{-1}, A_{GC}=0.18 cm^2, T (^{0}C): (1) 747; (2) 698; (3) 642; (4) 590.

Decreasing in the temperature makes this wave more pronounced and shifts both peaks to more negative potentials. The difference in potentials between the first and the second peak is about 300 - 350 mV. The dependence of the second peak current against a scan rate is linear and I /V$^{1/2}$ ratio remains constant in the rate range covered. The peak potential of the second stage shifts to the anodic region with an increase in the scan rate and the

dependence of E versus logV is linear. At a temperature of 971 K the shift of E with a change in the scan rate by an order of magnitude is 81 mV. These data indicate that this process is irreversible.

The half-width of the first peak (E^1_p- $E^1_{p/2}$) was found practically the same as for the second stage of oxidation. The values of a βn parameter higher than unity shows that both stages proceed with the participation of two electrons. The investigation of the concentration effect on the currents and potentials of both peaks confirmed the irreversible nature of the second peak. At the same time a nonlinear plot of the first peak current against the concentration is indicative of adsorption effect. The value of ratio of the peak current to the sodium oxide concentration decreased when concentration grown.

All the data obtained [3] allows to identify the anodic process observed as the two-stage scheme known for the cryolite-alumina melts. Nekrasov described it for oxochloride melts as follows [4]:

$$O^{2-}_{(dis)} + xC - 2e \rightarrow C_xO_{(ads)} \qquad (1)$$

$$O^{2-}_{(dis)} + C_xO_{(ads)} - 2e \rightarrow CO_{2(g)} + (x-1)C \qquad (2)$$

However the peak currents of the first and the second stages are incomparable in magnitude. This allows to suggest that the reaction

$$O^{2-}_{(dis)} + 1/2C - 2e \rightarrow 1/2CO_{2(g)} \qquad (3)$$

occurs in parallel with the reaction (2) at the second stage of anodic process. This model was used to determine the diffusion coefficient of oxide ion.

The total current of both stages found from the foot of the first wave to the top of the second one was proportional to the concentration of sodium oxide added. The plot of log D as a function of temperature is expressible by

the following empiric equation:

$$\log D = -2,680 - 2619/T \pm 0,003 \qquad (4)$$

Using the formalism of linear voltammetry method and the experimental data obtained one can express the concentration of oxide ion as a function of a peak current and experimental conditions in equation:

$$C_{O^{2-}} = 1,94 \times 10^{-6} \frac{j_p \cdot T^{1/2}}{V^{1/2}} \exp\frac{3016}{T} \qquad (5)$$

where j_p is the current density of anodic process, T - temperature, v - sweep rate.

The efficiency of purification of alkali metal halides by zone melting was evaluated using this equation. Compared to the initial salts, this method makes it possible to reduce the concentration of oxide ions from $(3-5) \times 10^{-2}$ to $(1-3) \times 10^{-3}$ m/o in a single pass.

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