Electroreduction of Molybdate and Tungstate Ions in Sodium Tungstate Melt Containing Li^+, Ba^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+}, and Al^{3+} Cations*

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The influence of highly polarizable metal cations on the process of tungstate (molybdate) ion electroreduction in sodium tungstate has been studied. The cation composition of oxide melt has been found to significantly influence the form of electrochemically active particles and the character of tungstate (molybdate) ion electroreduction in sodium tungstate melt.

In [1—4] it was thought, when describing the electrode processes occurring in sodium tungstate melt, that addition of Li_2MO_4 or $ZnMO_4$ and MO_3 gives rise to the formation of more complex tungsten (molybdenum)-oxygen species and to a lower activity of the oxygen ions, according to the following reaction

$$2MO_4^{2-} + xLi^+ \rightleftarrows Li_xO^{-(2-x)} + M_2O_7^{2-} \qquad (1)$$

where M = W, Mo. On this basis it was assumed that regardless of the cations in the melt, metal only exists in the form MO_4^{2-} and $M_2O_7^{2-}$ ions, while the electrode process can be described by the overall reaction

$$4M_2O_7^{2-} + 6e^- \rightleftarrows M + 7MO_4^{2-} \qquad (2)$$

It appears to us that cations in the melt – as shown for oxide—chloride melts [5, 6] – should strongly influence both the ionic forms of the anions in the melt and the composition of the electrochemically active anionic particles (those involved in the electrochemical process within the potential range being considered, in contrast to the ionic forms which are in the equilibrium with them) and hence also the parameters of the electrode reaction. The influence of the melt cation on the electrode reaction is demonstrated in the present work in the case of tungstate (molybdate) ion electroreduction in sodium tungstate melts.

EXPERIMENTAL

The tungstate (molybdate) ion electroreduction has been examined against the background of sodium tungstate at 1173 K, the latter containing cations Li^+, Ba^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+} The cations were added to the melt in the form of anhydrous tungstates and molybdates of the "chemically pure" class. The stoichiometry of the ordinary tungstates and molybdates was verified by chemical analysis. All chemicals were dried for 5 h under vacuum at 423—473 K, and calcined for another 5 h at 673—773 K. The potentiometry and voltammetry with a single and cyclic potential sweep were used as analysis means. A PJ-50-1 pulse potentiostat was used to obtain VA dependences. A platinum crucible was used as an anode and as a container for melt. Pin platinum semidipped electrodes sealed in quartz were used as indicator electrodes. The platinum-oxygen electrode Pt, O_2 ($p \approx 0.021$ MPa), Na_2WO_4—0.2 WO_3 was used as a reference electrode [7, 8].

RESULTS AND DISCUSSION

As shown in Refs. [3, 4], polytungstate and polymolybdate melts Na_2MO_4—MO_3 may be considered, as far as the structure is concerned, to be Na_2MO_4 $Na_2M_2O_7$ eutectic melts representing a mixture of ions Na^+, MO_4^{2-}, $M_2O_7^{2-}$ The relation between the MO_4^{2-} and $M_2O_7^{2-}$ ion concentrations is governed by the equilibrium

$$2MO_4^{2-} \rightleftarrows M_2O_7^{2-} + O^{2-} \qquad (3)$$

However, when using this concept for analysis of molten mixture containing tungstates or molybdates of highly polarizable cations certain contradictions originate. First, the addition of highly polarizable cations should result in binding oxygen ions and shifting equilibrium (*1*) to the right. Then, it is impossible to obtain tungstates and molybdates of normal highly polarizable cations, *e.g.* Ca^{2+}, Mg^{2+}, Zn^{2+} On the other hand, potassium, magnesium, and zinc

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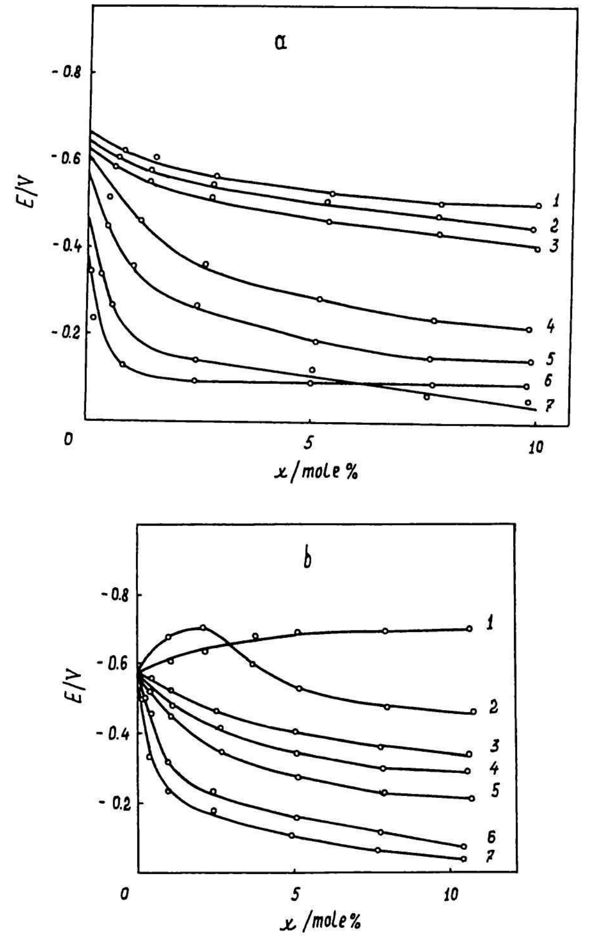

Fig. 1. Dependence of equilibrium potentials of platinum-oxygen electrode on the concentration of different tungstates and tungsten(VI) oxide (*a*) and different molybdates and molybdenum(VI) oxide (*b*) in the sodium tungstate melt (T = 1173 K): *a*) *1*. $SrWO_4$, *2*. $BaWO_4$, *3*. $LiWO_4$, *4*. $MgWO_4$, *5*. $ZnWO_4$, *6*. $Al_2(WO_4)_3$, *7*. WO_3; *b*) *1*. Na_2MoO_4, *2*. $CaMoO_4$, *3*. $BaMoO_4$, *4*. Li_2MoO_4, *5*. $MgMoO_4$, *6*. $Al_2(MoO_4)_3$, *7*. MoO_3.

tungstates and molybdates are actually congruently melting compounds formed in the exchange reaction with alkali metal tungstates and molybdates or in melting of their oxides. With the increase in cation specific charge, the solubility of highly polarizable tungstates and molybdates in sodium or potassium tungstate decreases [9]. This very fact indicates an increase in Me—MO_4^{2-} bond strength with increasing specific charge and, in molten mixtures, it shows a decrease in oxygen ion concentration, *i.e.* the acidification of the melt.

This is verified by the data shown in Fig. 1. The additions of highly polarizable cation tungstates (Fig. 1*a*) and molybdates (Fig. 1*b*) shift the oxygen electrode potential to the region of more positive values, that is, reduce the oxygen ion activity. With the increase in specific charge of cations in the Ba^{2+}, Sr^{2+}, Li^{+}, Mg^{2+}, Zn^{2+}, Al^{3+} series, a more pronounced shift is observed.

In the case of addition of aluminium tungstate and tungsten trioxide (aluminium molybdate and molybdenum trioxide), the oxygen electrode potential—concentration dependences display close values. This allows the assumption that, with a highly polarizable cation present in the melt, an acid-base dissociation of the tungstate (molybdate) ion is possible

$$2Al^{3+} + 3MO_4^{2-} \rightleftarrows 3MO_3 + Al_2O_3 \qquad (4)$$

The data given in [10] favour the occurrence of reaction (*4*) against the background of chloride melts.

The comparison of stability constants for Al_2O_3 and WO_4^{2-} (MoO_4^{2-}) does the same. If equilibria (*1*) and (*2*) are true, then the tungsten (molybdenum) electroreduction potentials should be practically independent of cation composition in the equal-acidity (pO^{2-}) melts. Thus, for example, sodium tungstate melts containing 5 mole % $MgWO_4$ and 0.5 mole % $Al_2(WO_4)_3$ or 7.5 mole % $MgWO_4$ and 1.0 mole % $ZnWO_4$ have equal acidity (Fig. 1*a*), and hence the tungstate-ion electroreduction process should exhibit similar parameters. Similarly, sodium tungstate melts with 5 mole % $MgMoO_4$ and 1.5 mole % $Al_2(MoO_4)_3$ or with 2.5 mole % $MgMoO_4$ and 7.5 mole % $BaMoO_4$ have identical acidities (Fig. 1*b*), so that identical parameters should govern the electroreduction of molybdate ions in these melts. To verify this assumption and clarify the influence of cationic composition on tungstate (molybdate)-ion electroreduction, a voltammetric analysis has been made for the Na_2WO_4—$Me^{n+}_{2/n}MO_4$ system (where Me^{n+} is Li^{+}, Ba^{2+}, Sr^{2+}, Mg^{2+}, Zn^{2+}, Al^{3+}). Fig. 2 shows VA-diagrams for sodium tungstate melt to which barium, magnesium, zinc, and aluminium tungstates were added in succession. The addition of Li_2WO_4 does not bring about reduction waves, while other tungstates bring them about but at different potentials. Potentiostatic electrolysis at the reduction wave potentials detects a metallic tungsten precipitate. The observed electroreduction waves are characterized by the following peculiarities. With the increase in cation specific charge, the electroreduction wave shifts to the positive potential region. Thus, in going from Ba^{2+} and Sr^{2+} to Zn^{2+} and Al^{3+} cations, the shift approaches 1.0 V. The lower limit of tungstate concentration at which the reduction wave is detected depends on the cation specific charge. With the increase in cation specific charge, the reduction wave transforms from S- to L-shaped one. Fig. 3 shows voltammograms for sodium tungstate melt to which molybdates of lithium, barium, magnesium, and aluminium were added consecutively. Added Na_2MoO_4 does not exhibit reduction waves. The electroreduction waves which are observed have the following special features: (i) the

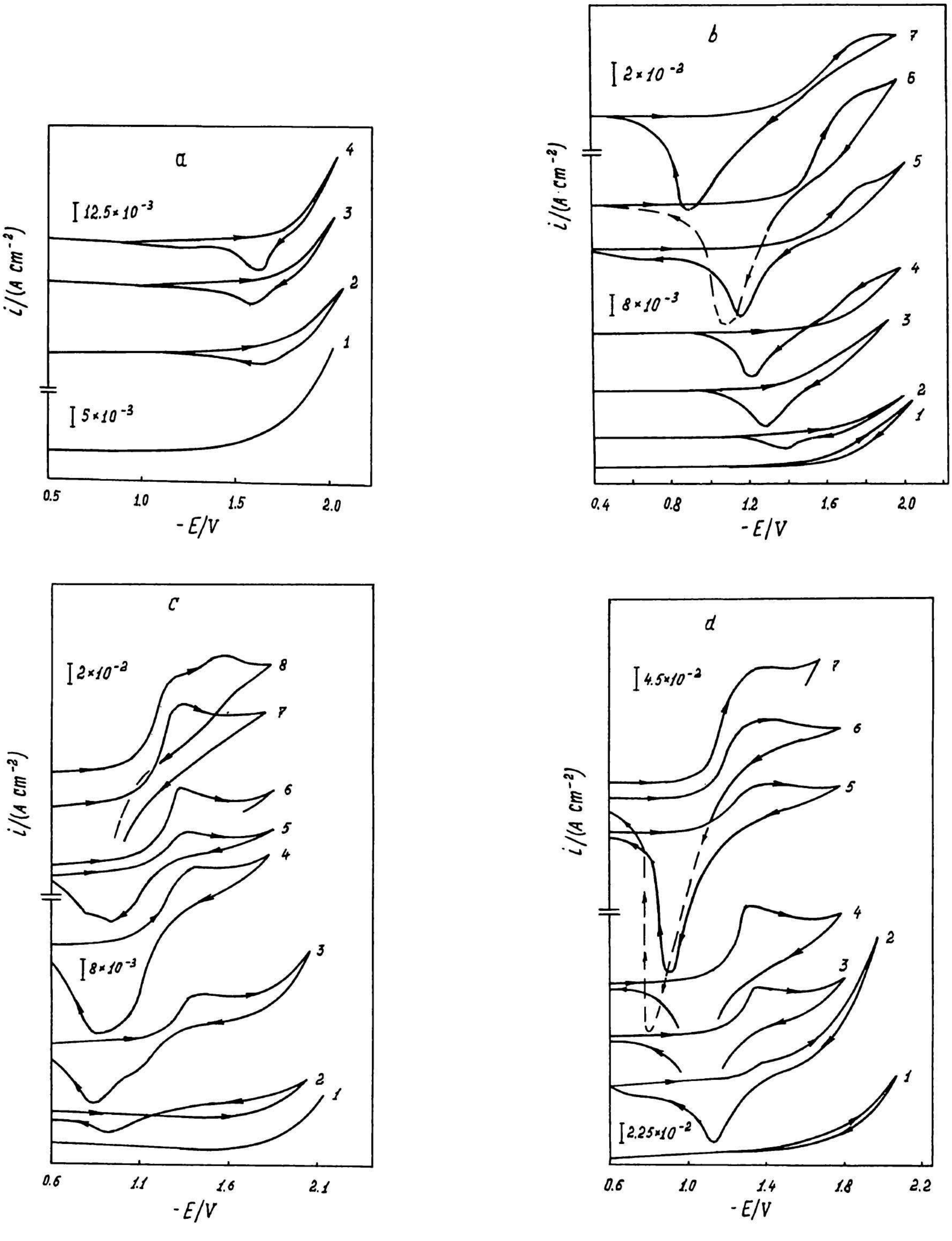

Fig. 2. Voltammograms of Na_2WO_4 melt recorded when adding tungstates $BaWO_4$ (*a*), $MgWO_4$ (*b*), $ZnWO_4$ (*c*), and $Al_2(WO_4)_3$ (*d*) of the concentration/(10^{-4} mol cm^{-3}): *a*) *1.* 0, *2.* 20, *3.* 30, *4.* 40; *b*) *1.* 0, *2.* 0.5, *3.* 2.0, *4.* 4.0, *5.* 6.0, *6.* 9.0, *7.* 20; *c*) *1.* 0, *2.* 0.25, *3.* 0.5, *4.* 0.75, *5.* 1.0, *6.* 20, *7.* 3.0, *8.* 4.0; *d*) *1.* 0, *2.* 0.25, *3.* 0.5, *4.* 0.75, *5.* 1.0, *6.* 2.0, *7.* 3.0. $T = 1173$ K, cathode Pt, $V = 0.1$ V s^{-1}

electroreduction wave shifts in the positive direction when the cation specific charge is higher (thus, the shift is about 1.2 V when going from Na^+ to Al^{3+} ions); (ii) the lower limit of the molybdate concentration for which a reduction wave can be observed depends on the cation specific charge; (iii) the reduction wave changes from S-shaped to L-shaped one with increasing specific charge of the cation. Electrol-

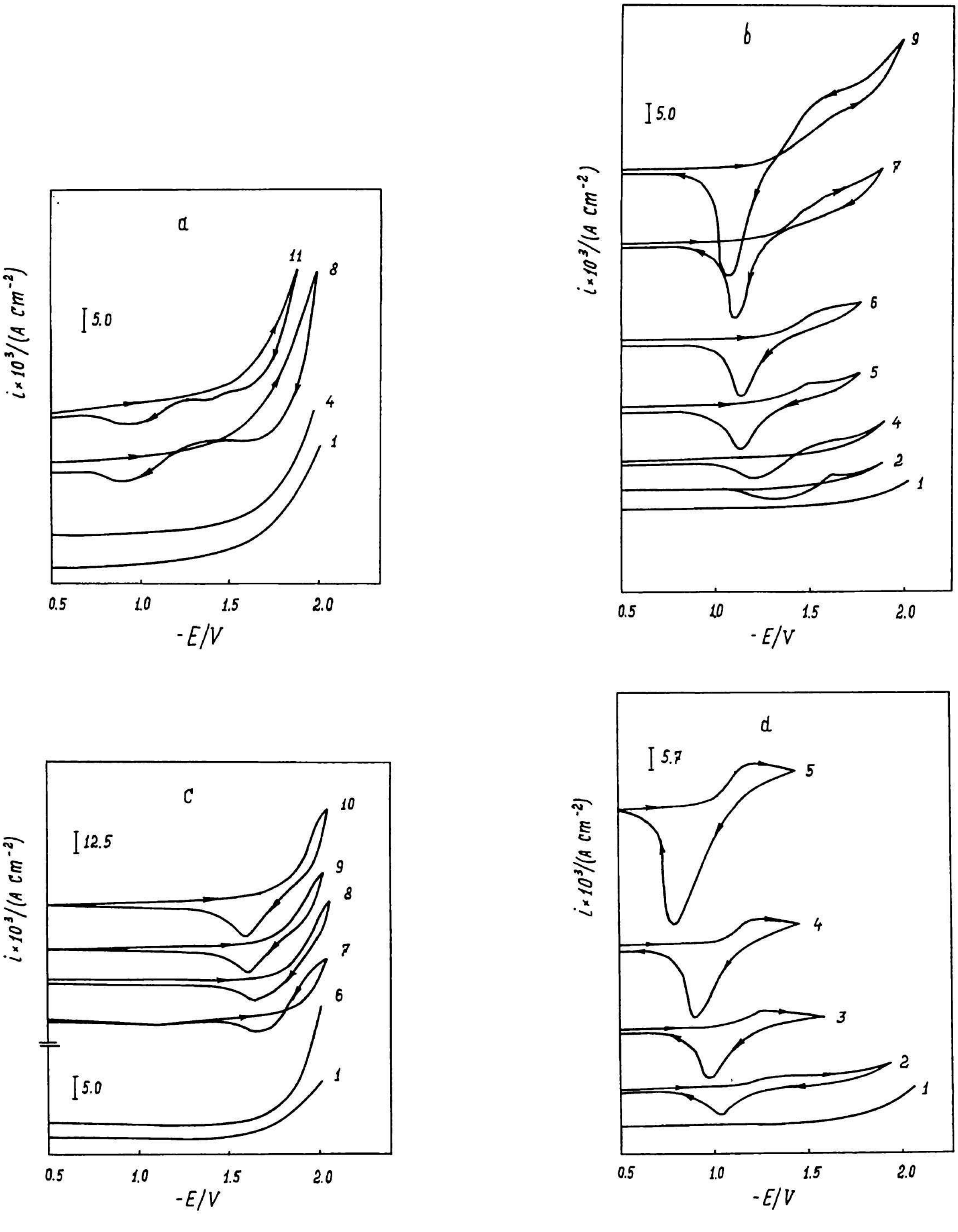

Fig. 3. Voltammograms of Na_2WO_4 melt recorded when adding molybdates Li_2MoO_4 (*a*), $MgMoO_4$ (*b*), $BaMoO_4$ (*c*), and $Al_2(MoO_4)_3$ (*d*) of the concentration/(10^{-4} mol cm^{-3}): *1.* 0, *2.* 0.5, *3.* 0.75, *4.* 1.0, *5.* 2.0, *6.* 3.0, *7.* 4.0, *8.* 5.0, *9.* 6.0, *10.* 7.0, *11.* 10.0. $T = 1173$ K, cathode Pt, $V = 0.1$ V s^{-1}.

ysis at the potentials where waves appear in voltammograms recorded in melts with different molybdates yields metallic molybdenum, while at current densities higher than the limiting current of molybdenum deposition, molybdenum-tungsten alloy is produced.

These peculiarities cannot be explained proceeding from the assumption that electrochemically active particle is formed by eqn (*1*) in a sodium tungstate melt containing highly polarizable tungstates. The results of voltammetric measurements do not support the assumption either that the electrode process should be characterized by equal parameters in equal-acidity melts (equilibria (*1*) and (*2*)). The cation specific charge exerts significant influence on the elec-

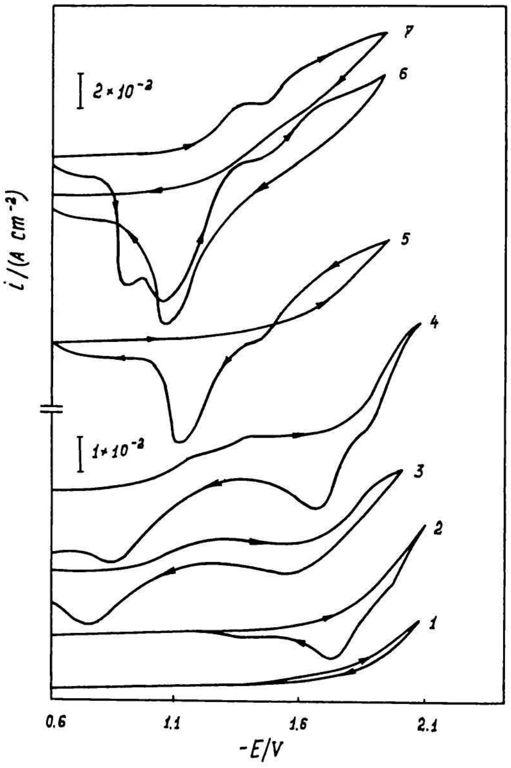

Fig. 4. Voltammograms of Na_2WO_4 melt recorded when adding different tungstates of the concentration/(mol cm^{-3}): *1.* Na_2WO_4 base melt, *2.* 2×10^{-3} $BaWO_4$, *3.* 4×10^{-3} $BaWO_4$ + 1×10^{-4} $ZnWO_4$, *4.* 5×10^{-5} $Al_2(WO_4)_3$ + 1×10^{-4} $ZnWO_4$, *5.* 5×10^{-4} $MgWO_4$, *6.* 5×10^{-4} $MgWO_4$ + 5×10^{-5} $Al_2(WO_4)_3$, *7.* 5×10^{-4} $MgWO_4$ + 1×10^{-4} $Al_2(WO_4)_3$. $T = 1173$ K, cathode Pt, $V = 0.1$ V s^{-1}.

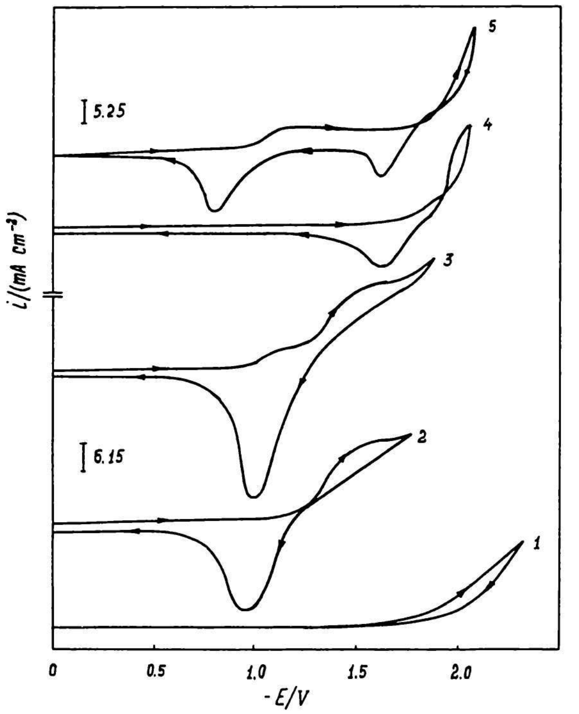

Fig. 5. Voltammograms of Na_2WO_4 melt recorded when adding different molybdates of the concentration/(mol cm^{-3}): *1.* Na_2WO_4 base melt, *2.* 8×10^{-4} $MgMoO_4$, *3.* 8×10^{-4} $MgMoO_4$ + 7.5×10^{-5} $Al_2(MoO_4)_3$, *4.* 7×10^{-4} $BaMoO_4$, *5.* 7×10^{-4} $BaMoO_4$ + 7.5×10^{-5} $Al_2(MoO_4)_3$. $T = 1173$ K, cathode Pt, $V = 0.1$ V s^{-1}.

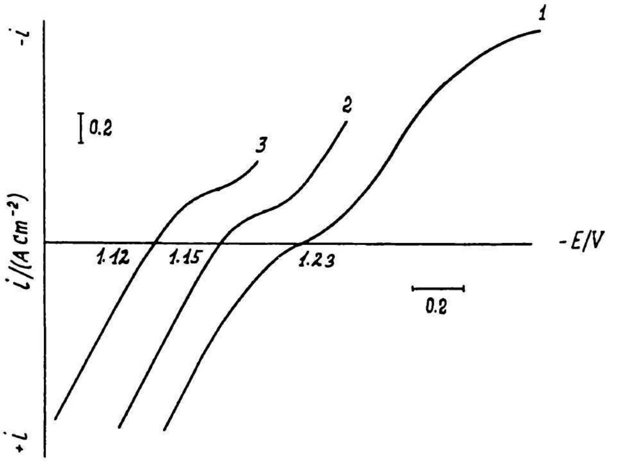

Fig. 6. Polarization of a tungsten electrode in Na_2WO_4 melts with tungstates $MgWO_4$ (*1*) and $Al_2(WO_4)_3$ (*2, 3*) added in concentration/(10^{-4} mol cm^{-3}): *1.* 20, *2.* 0.75, *3.* 1.25. $T = 1173$ K, $V = 20$ mV s^{-1}.

troreduction potential in equal-acidity melts. Thus, the electroreduction potential of $BaWO_4$ and $SrWO_4$ is −1.9 to −2.0 V, those of $MgWO_4$, $Al_2(WO_4)_3$, and $ZnWO_4$ are −1.5 to −1.7 V, −1.1 to −1.2 V, and −1.0 to −1.1 V, respectively. Similarly, the electroreduction potentials of $BaMoO_4$, $MgMoO_4$, and $Al_2(MoO_4)_3$ are −1.8 to −1.9 V, −1.4 to −1.6 V, and −1.0 to −1.2 V, respectively. Such a large difference in tungstate (molybdate)-ion electroreduction potentials indicates that the form and composition of electrochemically active species depend on the melt cationic composition. With ditungstate (dimolybdate) ions $W_2O_7^{2-}$($Mo_2O_7^{2-}$) as the electrochemically active species, the shift of the deposition potential would be $2.3 \times 4RT/(6F) = 0.152$ V for a tenfold increase in $W_2O_7^{2-}$($Mo_2O_7^{2-}$) concentration. It is difficult to explain in terms of equilibria (*1*) and (*2*) that several electroreduction waves of tungstate (molybdate) ions appear when the sodium tungstate melt contains simultaneously tungstates (molybdates) of different, strongly polarizing cations (Figs. 4 and 5). The cation specific charge exhibits influence not only on the potential but on the electrode process character as well. Figs. 6 and 7 show the polarization of tungsten (molybdenum) electrode in a sodium tungstate melt containing magnesium and aluminium tungstates (molybdates). The melts containing $MgMO_4$ display tungsten (molybdenum) reduction occurring with a noticeable overvoltage. However, with the increase in concentration the overvoltage value decreases. In

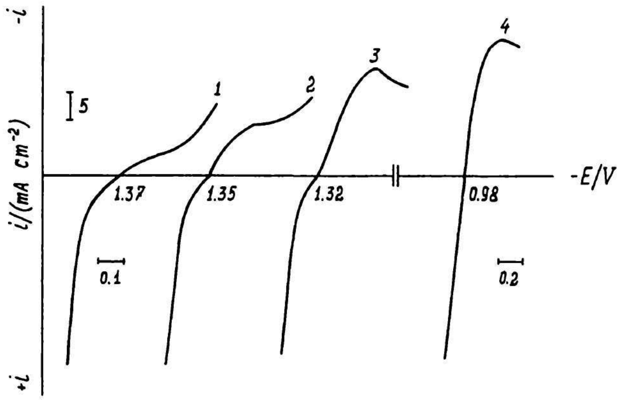

Fig. 7. Polarization of a molybdenum electrode in Na_2WO_4 melts with molybdates $MgMoO_4$ (*1*—*3*) and $Al_2(MoO_4)_3$ (*4*) added in concentration/(10^{-4} mol cm^{-3}): *1.* 1.0, *2.* 2.0, *3.* 4.0, *4.* 3.0. $T = 1173$ K, $V = 20$ mV s^{-1}.

the melts containing $Al_2(MO_4)_3$ tungsten (molybdenum) is reduced with practically no overvoltage. This along with limiting current directly proportional to the $Al_2(MO_4)_3$ concentration, speaks in favour of a reversible occurrence of the electroreduction process. In analysis of polarization curves in semilog coordinates $E - \ln\{(i_d - i)\}$ it has been found that the number of electrons transferred in the electrode process is 6.0 ± 0.25.

Thus, it is seen from potentiometric and voltammetric studies that in purely oxidic melts, the potential of tungsten (molybdenum) deposition can be controlled within a wide range of values, and the character of tungstate (molybdate)-ion electroreduction can be influenced by changes in the cationic composition of the melt.

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