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

V. V. MALYSHEV

Institute of General and Inorganic Chemistry, National Academy of Sciences of Ukraine, Kiev

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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$_2$MO$_4$ 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

$$2\text{MO}_2^{2-} + x\text{Li}^+ \Leftrightarrow \text{Li}_x\text{O}^{-(2-x)} + \text{M}_2\text{O}_7^{2-} \quad (1)$$

where $M = \text{W, Mo}$. 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$_2$O$_7^{2-}$ ions, while the electrode process can be described by the overall reaction

$$4\text{M}_2\text{O}_7^{2-} + 6\text{e}^- \Leftrightarrow \text{M} + 7\text{MO}_4^{2-} \quad (2)$$

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.

RESULTS AND DISCUSSION

As shown in Refs. [3, 4], polytungstate and poly-molybdate melts Na$_2$MO$_4$—MO$_3$ may be considered, as far as the structure is concerned, to be Na$_2$MO$_4$ Na$_2$M$_2$O$_7$ eutectic melts representing a mixture of ions Na$^+$, MO$_2^{2-}$, M$_2$O$_7^{2-}$. The relation between the MO$_2^{2-}$ and M$_2$O$_7^{2-}$ ion concentrations is governed by the equilibrium

$$2\text{MO}_4^{2-} \Leftrightarrow \text{M}_2\text{O}_7^{2-} + \text{O}^{2-} \quad (3)$$

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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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 melts decreases [9]. This very fact indicates an increase in 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. 1a) and molybdates (Fig. 1b) 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

$$2\text{Al}^{3+} + 3\text{MoO}_4^{2-} \rightleftharpoons 3\text{MoO}_3 + \text{Al}_2\text{O}_3 \quad (4)$$

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

The comparison of stability constants for Al$\text{L}_2\text{O}_3$ and WO$\text{L}_4^{2-}$ (MoO$\text{L}_4^{2-}$) 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$\text{L}_4$ and 0.5 mole % Al$\text{L}_2$ (WO$\text{L}_4$)$_3$ or 7.5 mole % MgWO$\text{L}_4$ and 1.0 mole % ZnWO$\text{L}_4$ have equal acidity (Fig. 1a), and hence the tungstate-ion electroreduction process should exhibit similar parameters. Similarly, sodium tungstate melts with 5 mole % MgMoO$\text{L}_4$ and 1.5 mole % Al$\text{L}_2$(MoO$\text{L}_4$)$_3$ or with 2.5 mole % MgMoO$\text{L}_4$ and 7.5 mole % BaMoO$\text{L}_4$ have identical acidities (Fig. 1b), 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$\text{L}_2$WO$\text{L}_4$—Me$^{\text{n+}}$WO$_\text{L}_4$ system (where Me$^{\text{n+}}$ 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$_2$WO$\text{L}_4$ 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$_2$MoO$_4$ does not exhibit reduction waves. The electroreduction waves which are observed have the following special features: (i) the...
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-
ysis at the potentials where waves appear in voltamograms 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$_2$W$_4$O$_{12}$ melt recorded when adding different tungstates of the concentration/(mol cm$^{-3}$): 1. Na$_2$W$_4$O$_{12}$ base melt, 2. $2 \times 10^{-3}$ BaWO$_4$, 3. $4 \times 10^{-3}$ BaWO$_4$ + $1 \times 10^{-4}$ ZnWO$_4$, 4. $5 \times 10^{-5}$ Al$_2$(WO$_4$)$_3$ + $1 \times 10^{-4}$ ZnWO$_4$, 5. $5 \times 10^{-4}$ MgWO$_4$, 6. $5 \times 10^{-4}$ MgWO$_4$ + $5 \times 10^{-5}$ Al$_2$(WO$_4$)$_3$, 7. $7.5 \times 10^{-4}$ MgWO$_4$ + $1 \times 10^{-4}$ Al$_2$(WO$_4$)$_3$. T = 1173 K, cathode Pt, V = 0.1 V 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 MgW$_2$O$_7$, Al$_2$(W$_2$O$_7$)$_3$, 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$_2$(Mo$_2$O$_7$)$_3$ 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$_2$O$_7^{2-}$ (Mo$_2$O$_7^{2-}$) 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$_2$O$_7^{2-}$ (Mo$_2$O$_7^{2-}$) 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 MgMoO$_4$ display tungsten (molybdenum) reduction occurring with a noticeable overvoltage. However, with the increase in concentration the overvoltage value decreases. In
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Fig. 7. Polarization of a molybdenum electrode in Na$_2$WO$_4$ 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 $E - \ln\{(i_4 - i)\}$ 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.

REFERENCES