

On the Nature of the Species Reduced During the Electrochemical Synthesis of Tungsten Bronzes†

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Although the electrolysis of polytungstate melts has been in use for a century as a means of preparing tungsten bronzes, including large single crystals, the nature of the electroreduction has received little study. Voltammetric studies at 750°C were conducted on a series of $\text{Na}_2\text{WO}_4\text{-WO}_3$, $\text{Li}_2\text{WO}_4\text{-WO}_3$, and $\text{K}_2\text{WO}_4\text{-WO}_3$ melts, using a $\text{Ag/Ag}_2\text{WO}_4$ reference electrode. It was determined that the species reduced in $\text{Na}_2\text{WO}_4\text{-WO}_3$ and $\text{Li}_2\text{WO}_4\text{-WO}_3$ melts containing 0-15% WO_3 is monomeric. Between 25-50% WO_3 in the $\text{Na}_2\text{WO}_4\text{-WO}_3$ melts and 35-46% WO_3 in the $\text{K}_2\text{WO}_4\text{-WO}_3$ melts, a tetramer is the predominant reducible species. At greater concentrations of WO_3 higher polymers predominate, perhaps up to $(\text{WO}_3)_{18}$. The observed changes in slope of the plots of half-wave potential versus $\log C^0$, which lead to the conclusion, correlate exactly with the occurrence of eutectic points in the phase diagram.

Introduction

The electrolysis of polytungstate melts has been employed since the 1860's as a means of preparing tungsten bronzes (1)-(3). The use of controlled current to promote the growth of large single crystals was first published by Brown and Banks (4) and has subsequently been widely used in improved versions for the growth of crystals of large classes of reduced oxides (5) and (6). In all these studies, little was accomplished in the way of understanding the nature of the electroreduction process. Empirical observations as to current, voltage temperature, and composition are frequently found, but generally consist of statements that a bronze of a particular composition was obtained from a melt of a certain composition at some temperature. There are some statements describing trends, such as the fact that bronzes of higher alkali content are obtained from melts high in alkali tungstates, and that higher temperatures lead to higher x values for a given melt composition.

In an effort to understand the basis of these observations, we carried out a detailed voltammetric

study of electrode processes in these melts. The detailed study will be published elsewhere (7). Some observations pertinent to the nature of the species which are reduced to form bronzes are given in this report.

Experimental

The polytungstate melts were prepared by fusing reagent-grade alkali tungstate or carbonate with tungsten trioxide. Voltammograms were obtained for the melts at 750°C, under argon, at Pt bead electrodes against a $\text{Ag/Ag}_2\text{WO}_4$ reference half-cell that was separated from the study melt by a non-porous porcelain separator. The latter was found to be conductive at the operating temperature. A wave for the reduction of WO_3 was identified which was proportional to the concentration of WO_3 . The half-wave potential, $E_{1/2}$, for this wave increased with the amount of WO_3 in the melt. Maintaining a potential on this wave resulted in the deposition of tungsten bronze at the electrode.

Values of $E_{1/2}$ were determined and plotted as a function of the log of the formality of WO_3 , Figs. 1 and 2. At concentrations above 2% WO_3 †, convective effects prevented a stable current plateau, and only the rising portion of the wave could be

† All concentrations are in mole%.

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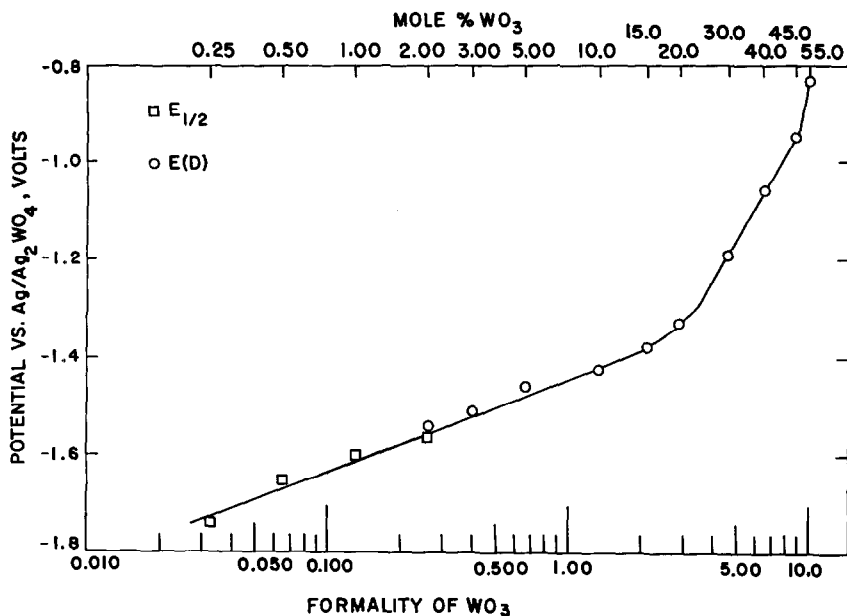


FIG. 1. Half-wave potentials versus log formality of WO_3 , for sodium polytungstates. Half-wave potential, $E_{1/2}$, approximated by decomposition potential, $E(D)$, at higher WO_3 concentrations; see legend. Data at $750^\circ C$. Mole% WO_3 at top of figure.

recorded. The decomposition potential, $E(D)$, for WO_3 reduction was plotted in place of the $E_{1/2}$ value in Figs. 1 and 2 for concentrations of WO_3 above 2%. Potential measurements on independently prepared melts of the same composition were reproducible to ± 0.01 V.

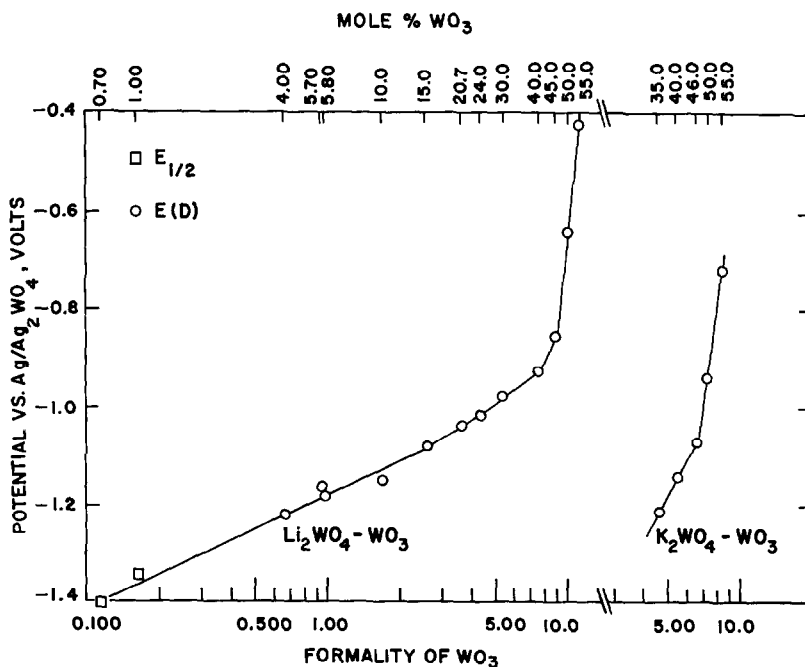


FIG. 2. Half-wave potentials versus log formality of WO_3 , for lithium and potassium polytungstates. Half-wave potential, $E_{1/2}$, approximated by decomposition potential, $E(D)$, at higher WO_3 concentrations; see legend. Data at $750^\circ C$. Mole% WO_3 at top of figure.

Discussion

The slopes of the plots in Fig. 1 and Fig. 2 were tested against the Kolthoff-Lingane relationships [Eqs. (1) and (2)] which apply to the reversible reduction to a product which does not diffuse away from the electrode.

$$E = \text{const} + (2.3RT/nF) \log(i_l - i). \quad (1)$$

$$\Delta E_{1/2} / \Delta \log C^0 = 2.3RT/nF. \quad (2)$$

These relationships between potential, E , and current, i , are well known (8). In Eqs. (1) and (2), i_l is used to represent the transport-limited current which is proportional to the bulk concentration, C^0 , of the reducible material. The number of electrons transferred is given by n and the other terms have their usual meanings. A plot of half-wave potential, $E_{1/2}$, vs $\log C^0$ has a theoretical slope of $2.3RT/nF$. It may be readily seen from Eq. (1) that when the bulk concentration is large and at the onset of reduction, i.e., when $i_l \gg i$ and at $E \simeq E(D)$, a plot of $E(D)$ vs $\log C^0$ has the same slope. Theoretical slopes were obtained for the one-electron reduction of WO_3 in sodium polytungstate and lithium polytungstate melts containing up to 15% WO_3 . The $\text{K}_2\text{WO}_4\text{-WO}_3$ system could not be examined in this range because it is not molten below 35% WO_3 . For concentrations above 15% WO_3 , slopes were obtained that correspond to the one-electron reduction of polymers of WO_3 . The slopes obtained for the $\text{Na}_2\text{WO}_4\text{-WO}_3$ melts containing 25–50% WO_3 and the $\text{K}_2\text{WO}_4\text{-WO}_3$ melts containing 35–46% WO_3 indicate that the tetramer is the predominant species reduced in these melts. At concentrations above 46% WO_3 in potassium polytungstate melts, the change in slope in Fig. 2 indicates that the reducible species is a much larger polymer, perhaps up to $(\text{WO}_3)_{18}$. Large polymers also occur in the $\text{Na}_2\text{WO}_4\text{-WO}_3$ and $\text{Li}_2\text{WO}_4\text{-WO}_3$ melts above 50% WO_3 .

The concept that the melt contains species such as WO_3 , $(\text{WO}_3)_4$, and higher polymers over different ranges of melt composition is supported by the following additional evidence.

Correlation to the Phase Diagrams (9)

According to the above treatment, the compositions at which the simplest reducible species begins to polymerize in the lithium and sodium polytungstates occurs at about 20% WO_3 , the composition of the major eutectic in the systems $\text{Li}_2\text{WO}_4\text{-WO}_3$ and $\text{Na}_2\text{WO}_4\text{-WO}_3$. The eutectic is deep in the latter system, and the transition to a higher polymer occurs over a narrow composition

range. In the lithium system the eutectic is shallow and the transition occurs over a broad composition range, and, at the higher concentrations of WO_3 , the polymerization number is higher than for the sodium system. This last result is not unexpected in view of the fact that the temperature at which the data were obtained, 750°C, is approximately at the melting point of those compositions containing about 50% WO_3 in the lithium system, whereas this temperature is over 10°C above the melting point for the same compositions in the sodium system. In the system $\text{K}_2\text{WO}_4\text{-WO}_3$, a sharp change in polymerization at 46% WO_3 is indicated by the electrochemical data. At exactly this composition, a deep eutectic occurs in this system. A second eutectic occurs at 55% WO_3 in the lithium and sodium systems. This eutectic is reflected by the electrochemical data for the sodium system. A change in slope for the lithium system at this composition may be hidden by the already large slope in this region.

Conductivity Data

Early conductivity data taken in sodium polytungstates (10) suggest that the melt undergoes increased polymerization with increased WO_3 content because the specific conductivity was found to fall off smoothly with increased WO_3 in the melt. These and other (9) workers were also able to obtain supercooled melts up to 75–80% WO_3 by long heating and vigorous stirring. Later conductivity data (11) on the alkali polytungstates, however, are not in agreement with the earlier results and suggest a much more complicated system.

Product Composition

It is well-known (5) that the metal content in the bronze deposited electrochemically from molten polytungstates increases as the concentration of the cation in the melt. Analysis of the data presented in the literature for the sodium (12) and (13) and copper (14) systems and our own analysis of the results from the sodium system suggest that the following relationship holds to a first approximation at 750–800°C:

$$m(\text{bronze}) = \frac{1}{2}m(\text{melt}),$$

where m is defined as

$$\frac{\text{atoms of metal}}{(\text{atoms of metal}) + (\text{molecules of } \text{WO}_3)}$$

According to the above polymerization concept, the species reduced at the cathode in a melt containing 50% WO_3 –50% Na_2WO_4 would be $(\text{WO}_3)_4^-$. If, after reduction, this species reacts with the

sodium ion, a bronze of composition $\text{Na}_{0.25}\text{WO}_3$ would be formed. It is well known that the bronze recovered at the cathode from a melt of 50% WO_3 -50% Na_2WO_4 is the violet cubic bronze of the approximate composition $\text{Na}_{0.5}\text{WO}_3$. In equilibrating with the melt to form the bronze $\text{Na}_{0.5}\text{WO}_3$, the initially produced $\text{Na}_{0.25}\text{WO}_3$ must go through the composition $\text{Na}_{0.37}\text{WO}_3$. This last species, however, is two-phased at 750°C (15). In three reductions in melts containing 50% WO_3 -50% Na_2WO_4 the usual product was obtained. In one reduction, however, small crystals of both a low-sodium blue tetragonal bronze and a higher-sodium red cubic bronze were recovered instead. Recovery of the two-phased product lends support to the postulated reduction species.

Conclusion

Interpretation of electrochemical data obtained in alkali polytungstates suggests that the species reduced at low concentrations of WO_3 polymerizes at higher concentrations but that species of particular polymerization numbers predominate over large concentration ranges which correlate to the phase diagrams of the systems.

Acknowledgment

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