The electrochemistry of tungsten (V), (IV) and (III) in molten LiCl-KCl eutectic was studied using cyclic voltammetry. Tungsten (V) exhibited a reversible one electron reduction, $\text{W(V)} + e^- \rightarrow \text{W(IV)}$, an irreversible reduction, $\text{W(IV)} + 2e^- \rightarrow \text{W(II)}$, and a broad reduction wave near the cathodic limit, $\text{W(II)} + 2e^- \rightarrow \text{W(0)}$. A disproportionation, $\text{W(II)} \rightarrow \text{W(IV)} + \text{W(0)}$ occurred, as shown by the deposition of powdery tungsten at any potential beyond that leading to the formation of W(II).

Tungsten (IV), added as $\text{K}_2\text{WCl}_6$, exhibited oxidation to W(V), reduction to W(II), and other W(II) related peaks. However, on continued electrolysis, a continuous tungsten "mirror" was deposited on all cell surfaces. This was apparently due to the effect of the high W(IV) concentration on the disproportionation of W(II).

Tungsten (III), added as $\text{K}_2\text{WCl}_6$, exhibited a complex electrochemical behavior. Electrolysis at a platinum flag resulted in the formation of resistive film which prevented the deposition of tungsten metal. Electrolysis at a tungsten flag yielded a dendritic tungsten deposit.

The purpose of this work was to elucidate the electrochemistry of tungsten (III), (IV), and (V) in molten LiCl-KCl eutectic. Information of this type is central in the development of new tungsten electroplating and electrowinning techniques and furthers the understanding of the chemistry of tungsten halides as well. While this
has been attempted before, first by Balko (1), and then by Johnston (2), the results have been neither complete nor conclusive. Balko's work relied mostly on chronopotentiometry as the electroanalytical tool, a technique whose results are often difficult to interpret. He also often suggested that further study was needed. Several of his products were either unidentifiable or admittedly produced under less than rigorous conditions. The later study, by Johnston, was of a narrower scope. It included only studies of tungsten (III). To further complicate matters, some of his results were in direct contradiction of earlier, carefully performed work (3). These difficulties indicated that further study was necessary to clarify the electrochemistry of this important chemical system.

EXPERIMENTAL

The LiCl-KCl eutectic was prepared by pre-drying the components at 150° in a vacuum oven. After mixing, the eutectic was ball-milled and re-dried. The mixture was then purified and made anhydrous by sparging with dry HCl as the temperature was raised to 425° over four hours. The melt was then sparged with nitrogen to remove the HCl. Magnesium turnings were added to remove the last trace of HCl, and the melt was then filtered and solidified. Remelting under vacuum completed the process and routinely gave melts having low residual currents. Background voltammograms were recorded to ascertain melt purity and the melt was discarded if these were unsatisfactory.

The electrochemical cell used in this study is shown schematically in Figure 1. A head (not shown) was clamped on the top of the cell to provide a hermetic seal as well as the necessary pass-throughs for gases, electrical leads and sample addition. Measurements were made at 450°C.

The tungsten species studied were prepared as follows: Tungsten (V) was added as WBr₅, as obtained from Alpha Products. Tungsten (IV) was added as K₂WC₁₇ prepared by the method of Kennedy and Peacock (4). Tungsten (III) was added as K₃W₂Cl₄ prepared by the method of Saillant et al. (5)

RESULTS AND DISCUSSION

Tungsten (V)

Tungsten (V) was added to the melt as WBr₅. The bromide was chosen over the chloride due to its higher boiling point (333° vs. 276°). It was added as pellets pressed in a die in a glove box filled with dry nitrogen. It was felt that the slight amount of bromide present would not affect the electrochemistry due to the five hundredfold excess of
chloride in the melt. The pellets dissolved rapidly to form a blue green solution which later became yellow green, particularly at higher concentration. Measurements on the W(V) system were complicated by its high volatility at 450° C. Brown vapor was often noted above the melt. While the solubility of W(V) in the melt was sufficient to allow electrochemical measurements, the conclusion was reached that the concentration of W(V) in the melt could not have been held constant, nor would an exact analysis of the melt for tungsten after cooling have been of any use. Similarly, peak heights from the voltammograms would be of only qualitative use when compared with other such measurements.

Pure WCl₅ was shown to be stable with respect to disproportionation into WCl₃ and WCl₃ by Drobot and Nikolaev (6). This was determined from measurements leading to a WCl₅-WCl₃ phase diagram. While extrapolation of this information from the pure system to a dilute molten salt solution may have been risky, the results of this study did not indicate W(V) disproportionation.

A sample voltammogram of W(V) is given in Figure 2. The results indicated a reversible couple believed to be W(V) + e⁻ → W(IV). The average potential of the cathodic and anodic peaks were 0.86 ± 0.04 and 1.02 ± 0.04 V respectively*. Neither peak, nor obviously, their separation, 0.15 ± 0.03 V, changed with varying scan rate. From this value, n, the number of electrons transferred can be calculated from the equation:

$$E_{pc} - E_{pa} = -(0.059/n)(T/298)$$

The resulting value, n = 0.9 ± 0.2, clearly indicated a one electron transfer. It must be noted that the reduced species appeared to be insoluble because $$i_{pa} > i_{pc}$$. This agreed with the observation that K WCl₅, a plausible analog to an electrochemically produced W(IV) species, dissolved slowly and incompletely, even with agitation of the melt.

An irreversible cathodic peak was observed at Eₚ = 0.40 V at a scan rate of 0.867 V/sec. This peak shifted anodically with decreasing scan rate. When Eₚ was plotted versus log v, a value for the product an can be determined from the slope according to the equation:

$$cn = (30/m)(T/298)$$

where v was the scan rate in mV/sec and m was the slope in mV/decade.

*All potentials given vs. mole fraction Ag/Ag⁺
and α, the charge transfer coefficient. In this case α = 1.1 ± 0.4. If as was later assumed, n = 2, then α = 0.5 ± 0.2. The reaction giving rise to this peak has been assigned to be \( \text{W(IV)} + 2e^- \rightarrow \text{W(II)} \) and was common to all the tungsten halide species studied.

A broad peak of variable shape and position occurred at negative potentials near the cathodic limit of the scan. The potential range of this peak was from -0.70 to -1.00V. While this peak could not be well characterized numerically, it was common to all tungsten halide species studied and has been assigned to be \( \text{W(II)} + 2e^- \rightarrow \text{W(0)} \) for reasons discussed below.

Two other peaks were found; a cathodic peak at 0.10V and a broad anodic peak at -0.02V. These could not simply be the reverse of each other and may involve various tungsten cluster ions of compounds such as \( \text{WC}_1 \) or \( \text{WC}_1^4 \) (7).

Controlled potential electrolysis was performed at two potentials to identify the products of the respective cathodic reactions. In the first case, the potential was controlled at a value just above the cathodic limit. A platinum flag was used as the working electrode. A black deposit was collected after overnight electrolysis. The deposit was insoluble in water. X-ray diffraction showed that the product was tungsten metal (8) with an impurity of \( \beta \)-tungsten (9). The \( \beta \)-tungsten was probably formed due to the presence of oxide or oxygen from atmospheric contamination of the melt overnight. While the melt initially was oxygen and oxide free, as shown by a background voltammogram, slow contamination was inevitable unless the cell was totally sealed. In the second case, the potential was controlled at +0.47V, just past the potential necessary for the reaction assigned to be \( \text{W(IV)} + 2e^- \rightarrow \text{W(II)} \). A black material was produced which was denser than the melt and insoluble in water and also appeared to be tungsten metal. The formation of the same product from both reduction steps is accounted for by a disproportionation of \( \text{W(II)} \) as discussed later. Analyses of the product were not made.

**Tungsten (IV)**

Tungsten (IV) was added to the melt as \( \text{K}_2 \text{WC}_1 \). This was found to be more practical than the addition of \( \text{WC}_1^4 \), the next most likely source. It was assumed that the electrochemical behavior of \( \text{K}_2 \text{WC}_1 \) was identical with that of \( \text{WC}_1 \), due to the favorable chloride ion affinity of \( \text{WC}_1 \) (10). Thus any \( \text{WC}_1 \) added to the large excess of chloride present in the melt would have reacted to form \( \text{WC}_1^4^- \).

\( \text{K}_2 \text{WC}_1 \) did not dissolve as readily as the other tungsten species studied. Upon mixing with bubbling nitrogen, a yellow green solution was produced. Complete dissolution of the material added was not always
The electrochemical results for this system were striking. Voltammetry at first appeared to give normal results. Subsequent scans showed the current growing rapidly to values above the capabilities of the potentiostat. Upon disassembly, the working electrode invariably had a conductive coating on the glass surrounding the platinum microelectrode. This increased the area of the electrode so greatly that voltammetry was no longer possible. The initial voltammogram, for example Figure 3, indicated a pattern of two cathodic peaks and two anodic peaks. The first cathodic peak was an irreversible reduction occurring at about +0.5V. This was believed to be the result of the reaction \( \text{W(IV)} + 2e^- \rightarrow \text{W(II)} \). The second peak occurred at about -1.0V and was believed to show the reaction \( \text{W(II)} + 2e^- \rightarrow \text{W(0)} \). These two cathodic peaks were common to all the tungsten halide systems studied. The anodic peak which occurred around +1.0V was believed to indicate the reaction \( \text{W(V)} \rightarrow \text{W(IV)} + e^- \). Another anodic wave at +0.32V probably indicated oxidation of \( \text{W(II)} \) to a tungsten species with a valence around 3. These peaks were also common to all the tungsten halide voltammograms. The exact peak currents associated with the various reactions could not be determined due to the rapid increase in electrode size with time. This size increase also tended to reduce the resolution of the technique thus making the potential of the peak difficult to estimate.

By far, the most striking result of the study of this system came from controlled potential electrolysis. Electrolysis of the solution on a platinum flag at +0.46V gave an initial current of about 3mA/cm². After overnight electrolysis, the current had increased to 6mA/cm². When the cell was shaken gently, the current dropped to 1mA/cm² and then began to increase again. The electrolysis was carried on for another half hour and then was stopped. Upon solidification the melt was white and a metallic mirror was deposited on all the glass surfaces. Explanation of this behavior, which was unique to the \( \text{W(IV)} \) system, was the key to understanding the electrochemistry of tungsten halides in the melt.

The widespread deposition of tungsten on all surfaces in contact with the melt suggested a chemical reaction rather than a purely electrochemical deposition process. Electrodeposition would be expected to produce a smooth coating, dendrites or a powder only on the electrode surface. Some means of transport of a reduced tungsten species must be postulated in this actual case. To explain the phenomenon, it was proposed that disproportionation of \( \text{W(II)} \) gave rise to the tungsten film on all cell surfaces. This reaction was well documented (7). A film was formed instead of powder or dendrites due apparently to the equilibrium:

\[
2\text{W(II)} \rightarrow \text{W(0)} + \text{W(IV)}
\]
Tungsten (IV) was in much higher concentration here than in any of the other systems in this study. This would allow a higher equilibrium concentration of soluble W(II) which could migrate further from the electrode before disproportionating. Thus an extensive film was formed rather than a local product. The film was continuous, conductive, grew out from the electrode, and was fragile, as shown by the sudden decrease in current when the cell was shaken, followed by the gradual increase in current as the film was reestablished. In the absence of an electrolysis current, no film formed and no metallic deposit or precipitate was observed.

Dalko also found a 2-step reduction for this system by chronopotentiometry, though on the basis of less data he believed that the first product was W(III). This species seems unlikely to exist without disproportionating. He found no evidence of film formation but the use of a platinum flag electrode for the relatively short period of time necessary to record a chronopotentiogram would have made the additional area due to film formation less apparent in the electrochemical results.

Tungsten (III)

Tungsten (III) was added to the melt as K$_3$WCl$_4$. This cluster compound was chosen because no simple W(III) halide or alkali metal halide was stable under the conditions of this study. Attempts to synthesize WC$_1$ by disproportionation of other tungsten halides have yielded only WC$_{1.4}$ (11) or WC$_{1.5}$ (7). These non-stoichiometric halides probably have a cluster structure as well.

The K$_3$WCl$_4$ dissolved rapidly in the melt to give a tan-orange solution. In the absence of electrolysis, a reaction slowly occurred leading to an orange precipitate, which turned brown overnight at 450°C. After this solution was frozen, it was leached with water. No heavy metallic particles were observed and only a yellow precipitate remained insoluble. Thus, while K$_3$WCl$_4$ may have disproportionated or reacted with the melt at 450°C, the final product was not observed to be tungsten metal.

Johnston did not agree with this (2). He found that solid K$_2$W$_2$Cl$_9$ was thermally unstable at this temperature. He postulated that:

$$K_2W_2Cl_9 \rightarrow 3KC1 + WCl_2 + WCl_4$$

This was based on the observation that a sample of the alkali tungsten halide held at 450°C in an argon atmosphere decomposed to leave only a KCl residue. This was odd because a thermogravimetric study has shown that solid WC$_1$ is stable to 600°C in an inert atmosphere. WCl$_4$ was not
stable at $450^\circ$ but decomposed to $\text{WC}_1$ and $\text{WC}_3$ (7). He did not note any condensation of volatile tungsten species on the cooler portions of the cell. Poor temperature control or high rates of inert gas purge may have driven the above reaction to the right, but in this study, this decomposition did not appear to be a problem. Johnston also claimed that $\text{K}_2\text{W}_2\text{Cl}_6$ disproportionated in the melt to form tungsten metal and higher tungsten halides. His X-ray diffraction pattern of the insoluble reaction product did not indicate tungsten, nor did those of Balko for a similar experiment. Johnston noted the formation of a tungsten mirror on cell surfaces similar to that formed by $\text{W(IV)}$ in this study. This phenomenon did not occur during any experiment with $\text{W(III)}$ in this study. No mention of $\text{WC}_1$ evolution was made during any of these disproportionation experiments. While this study suggested that disproportionation occurred, it is doubtful that it proceeded to the ultimately stable products, $\text{WC}_1$ and tungsten metal. Neither a metallic precipitate nor distillation of volatile tungsten species were ever noted. It was more likely that insoluble tungsten cluster compounds of valence less than three were formed along with soluble $\text{WC}_1$. The electrochemical evidence supports this rather than the conclusions reached by Johnston.

The electrochemical investigation of $\text{WCl}_3^-$ began with cyclic voltammetry performed on a platinum microelectrode. This resulted in a complicated pattern of peaks which changed greatly with scan rate. The slow disproportionation of $\text{WC}_1$ into insoluble products prevented accurate knowledge of the concentration of various tungsten species in the melt. A typical voltammogram of $\text{WCl}_3^-$ at various scan rates is shown in Figure 4. The cathodic portion of the scan showed only one irreversible peak at $E_p = +0.45V$ at a scan rate of 100mV/sec. The peak shifted cathodically with increasing scan rate. The value of $n$ was determined from a plot of $E_p$ versus log $v$ to be $-2.3 \pm 2$. The similarity of potential between this peak and those present in other systems has led to its assignment as $\text{W(IV)} + 2e^- \rightarrow \text{W(II)}$. However, unlike the other systems, controlled potential electrolysis at a potential slightly cathodic of this peak did not produce tungsten metal on a platinum flag electrode. A dependence of $i_p$ on $v$ also suggested something other than a simple charge transfer. Instead, it appeared that an insoluble film, probably composed of lower tungsten halide clusters, was formed. This essentially insulated the platinum and stopped continued reduction to tungsten metal, even at the cathodic limit of the melt. It was therefore assumed that the $\text{W(II)}$ produced at the electrode reacts with some lower tungsten species not found in the other systems. Otherwise, it would have disproportionated to tungsten as it did in every other case. Johnston also found that a resistive film formed on his platinum electrodes under some conditions while studying $\text{K}_2\text{W}_2\text{Cl}_6$. He found that the film could be produced in quantities sufficient for analysis and that it was actually tungsten metal (which should not be resistive). The results of this study do not agree with this. While sufficient product was not collected for chemical analysis, when voltammetry was performed on a tungsten
electrode, the results were far different from the simple ohmic curve which Johnston obtained on his platinum, film covered electrode. These results will be discussed later in this section.

The anodic sweep of the cyclic voltammogram displayed a complicated pattern of oxidations. The first anodic wave was often resolved into two peaks, particularly at low scan rates. The peaks tended to shrink with increasing scan rate, suggesting that this was an oxidation of a species produced by the reaction of W(II) with another tungsten species present in the melt. It could not, however, simply be the reverse of \( \text{W(IV)} + 2e^- \rightarrow \text{W(II)} \) because the peak occurred at a potential cathodic to this reaction. “Window opening” experiments with an increasingly cathodic vertex potential, \( E^\alpha \), showed an increase in \( i_p \) as \( E^\alpha \) became more negative. A more cathodic \( E^\alpha \), or a slower scan rate would have allowed more time at potentials cathodic of the production of W(II). Thus more reactant for the oxidation indicated would be present, allowing a higher peak current and easier resolution of the peaks. The peaks did not shift significantly with scan rate; \( E_p^1 = +0.30 \), \( E_p^2 = +0.37 \), and \( i_p^1 > i_p^2 \). Two peaks of similar potential in this case indicated either that two similar oxidations were taking place or that an adsorption of either the product or reactant occurred. The existence of non-stoichiometric lower tungsten chlorides gave credence to the former, while the lack of a continued high reduction current at very cathodic potentials supported the latter, whereby an adsorbed species may “poison” the platinum surface preventing electrodeposition of tungsten metal. Sufficient information was not available to discriminate between these two mechanisms and subtle changes could cause the peaks to merge in either case as was occasionally observed. Due to the similarity in potential to the peak observed in the study of WC\(^{12-}\), which was characterized by a high concentration of W(II), the peaks have been assigned as:

\[
\text{W(II)} \rightarrow \text{W(\sim III) clusters} + \sim e^- 
\]

The concentration of W(II) in this case must have been low due to its reaction with other tungsten components in the melt, or tungsten metal deposition would have occurred. This would also account for the low peak currents observed for the above reactions.

The next anodic peak also did not correspond to any cathodic peak. It was characterized by narrow width and high peak current compared to all other peaks recorded by this study. The high peak current suggested the oxidation of an insoluble reduced species that was adherent to the electrode. The peak potential, \( E_p \), shifted anodically with increasing scan rate. At a 100mV/sec scan rate, \( E_p = 0.85V \). The slope of a plot of \( E_p \) versus \( \log v \) was 43±3mV/decade. This corresponded to a value of \( n = 1.7\pm1 \). As no independent evaluation of \( n \) was available, the value of \( n \) could not be determined. Window opening experiments were performed to evaluate the effect of varying \( E^\alpha \) on the peak current. The behavior
clearly indicated that this oxidation involved the product of the cathodic reaction which occurred at +0.47V when scanned at 33mV/sec. When \( E_A \) was anodic of 0.47V, the anodic peak disappeared. The anodic peak grew steadily as \( E_A \) was made more cathodic. In light of this information about the reactant for the oxidation, and the existence of still more anodic waves at higher potentials, the peak has been assigned to the reaction:

\[
\begin{align*}
W(II) + W(III) & \rightarrow W(II-III) \text{ clusters} \\
W(II-III) \text{ clusters} & \rightarrow W(IV) + (1-2)e^-
\end{align*}
\]

The next anodic peak was present only when the potential scan included the region at or near the cathodic limit of the melt. The peak vanished in scans with a more anodic \( E_A \). The peak occurred at around +1.01V at a scan rate of 33mV/sec. Faster scan rates tended to shrink the peak and the peak was never observed at 1000mV/sec. This could have been due to slight variations of \( E_A \) with different settings of \( v \) due to imperfect instrumentation, but more likely was a result of the minimal time spent in the region at the cathodic limit at high scan rates. It may represent oxidation of a different insoluble tungsten halide cluster, perhaps even one incorporating lithium generated at the cathodic limit. The data obtained were too variable to make a more rigorous mathematical analysis for comparison with the diagnostic criteria for peak identification.

The most anodic voltammetric peak observed in the system occurred in the potential range of +1.17- +1.24V. Its closeness to the anodic limit sometimes prevented an adequate identification. It was felt that, in view of its similarity in potential with peaks in other systems, that it can be assigned to the reaction \( W(IV) \rightarrow W(V) + e^- \). It must be noted that no corresponding cathodic reaction has been recorded. This could have been due to the presence of a high concentration of reduced tungsten species which would quickly reduce any \( W(V) \) formed i.e. \( W(V) + W(III) \rightarrow W(IV) \).

The electrochemical investigation included a set of experiments similar to those above except that they were performed on a tungsten wire microelectrode or flag electrode instead of platinum. The resulting pattern of voltammetric peaks was far less complicated than those described above. Controlled potential electrolysis gave a non-adherent product which consisted of tungsten dendrites. Electrolysis at +0.21V gave a steady state current density of 0.26mA/cm², while at +0.01V, the current density was 2.3mA/cm². The voltammogram of \( W_2Cl^2- \) on a tungsten electrode is given in Figure 5. It showed one irreversible reduction, a reversible couple with an insoluble product and an irreversible oxidation. The irreversible cathodic wave occurred at a potential of +0.5V at 1000mV/sec scan rate. The peak current was very strongly dependent on scan rate, and tended to disappear at the lowest available rate (33mV/sec.) This suggested weak adsorption of the
reactant because \( i \propto v^{1/2} \) increased with increasing \( v \) (12). The peak current also tended to increase with time as the experiment proceeded. The potential shifted cathodically with increasing scan rate, as would be expected for an irreversible reduction. Insufficient data prevented a reliable determination of \( n \). Due to the similarity in potential between this peak and peaks observed in other systems, this peak has been assigned to the reaction:

\[
\begin{align*}
W(IV) + 2e^- & \rightarrow W(II) \\
\text{where} & \\
W(III) & \rightarrow W(IV) + W(II)
\end{align*}
\]

The increasing peak current suggested an increasing concentration of \( W(IV) \) in the melt due to continued disproportionation of \( W_Cl^+ \). Electrolysis at +0.21V yielded a steady but small current.

The next reaction was a reversible one. The peak anodic current was much greater than the peak cathodic current which indicated that the reduced species was insoluble. The peak potential did not display a significant shift with scan rate and occurred at +0.12\+0.02V. The corresponding anodic wave occurred at +0.22\+0.02V. The average value of \( E_{pa} - E_{pc} = 102\+4mV \), which corresponded to \( n = 1.4 \) electrons transferred. This reaction was believed to be:

\[
\begin{align*}
W(III) + e^- & \rightarrow W(II) \\
W(II) + W(III) & \rightarrow \text{insoluble clusters}
\end{align*}
\]

This case differed markedly from that observed at the platinum microelectrode. The corresponding reduction was irreversible. Moreover, on a tungsten electrode, tungsten metal was produced at a potential of +0.3V in quantities sufficient for analysis. On a platinum electrode, the electrolysis current was too low at accessible potentials to produce a significant amount of product. This may be due to some participation of the tungsten metal in the final disproportionation of \( W(II) \) to \( W(0) \) and \( W(IV) \). Perhaps the tungsten catalyzed the disproportionation by providing low-energy nucleation sites for tungsten crystallization. Or, alternatively, the following mechanism could be proposed:

\[
\begin{align*}
W(III) + e^- & \rightarrow W(II) \\
W(II) + 2 W(III) & \rightarrow \text{insoluble clusters} \\
\text{insoluble clusters} + W(0) & \rightarrow 4 W(II) \\
4 W(II) & \rightarrow 2 W(0) + 2 W(IV) \\
3 W(III) + e^- & \rightarrow W(0) + 2 W(IV)
\end{align*}
\]

Further study of this system must be made to determine the complicated
electrochemical mechanisms governing the reduction of $W_2Cl_6^-$ to the metal.

The last voltammetric peak observed for $W_2Cl_6^-$ on a tungsten electrode was an irreversible oxidation which occurred at a potential of +1.10V. The peak appeared only late in the run, probably due to the increased concentration of reaction products of the disproportionation of $W_2Cl_6^-$. $W$(IV) has been postulated as one of these products as well as a product of the disproportionation of $W$(II) to tungsten metal. The potential of the peak was similar to the irreversible oxidation assigned to the reaction $W$(IV) $\rightarrow$ $W$(V) + e$ in other, previously discussed systems, and may be assigned to the above reaction.

Both Balko and Johnston observed the disproportionation of $W_2Cl_6^-$. Johnston found one irreversible cathodic peak and no anodic peaks. This did not seem plausible because disproportionation products should surely show their voltammetry pattern as well. Also, a substance which disproportionates should also be oxidizable, but he found no anodic peaks. Balko observed the presence of $W$(IV) and $W$(V) in the melt by spectroscopy as well as by electrochemical measurements, although he differed with this study on some of the peak assignments.

CONCLUSION

The electrochemical results obtained for tungsten (V), (IV) and (III) are summarized in the table below. The reaction scheme below agreed with the known chemical behavior of the various tungsten species and accounted for the various voltammetric peaks and types of tungsten deposits obtained through electrolysis.

**Summary of Electrochemical Results for Tungsten (III), (IV), (V)**

| Reaction | $\text{Pot}_\alpha$ | $P_{2+}$ | $P_{4+}$ | $P_{2+}$ | $P_{4+}$ |
|----------|-----------------|--------|--------|--------|--------|
| $W$(IV)+2e$^-\rightarrow W$(II) | +0.5 | + | + | + | + |
| $W$(II)$\rightarrow W$(IV) + $W$(0) | - | + | 1 | 2 | 3 |
| $W$(II)$\rightarrow W$(II-III) + (0-1)e$^- | +0.3 | + | + | 4 | 5 |
| $W$(II)+2e$^-\rightarrow W$(0) | -1.0 | + | + | - | - |
| $W$(II-III)$\rightarrow W$(IV) + (1-2)e$^- | +0.9 | - | - | + | - |
| $W$(II-III)$\rightarrow W$(IV) + (1-2)e$^- | +1.0 | - | - | + | - |
| $W$(IV)$\rightarrow W$(V) + e$^- | +1.1 | 5 | + | + | + |

1. tungsten mirror deposited on cell surfaces
2. no tungsten deposited, only resistive film

**tungsten electrode**

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3. complicated mechanism including tungsten clusters and tungsten participation
4. resolved into two peaks
5. reversible

The most significant finding of the study on tungsten halides was that tungsten was deposited at positive potentials by disproportionation of tungsten (II) rather than by direct reduction. However, further work, including product identification, is needed to bolster this conclusion. The disproportionation mechanism of tungsten deposition explains why tungsten deposited at a potential just cathodic of +0.5V when other reduction peaks were observed at potentials far more cathodic. It accounted for normal deposition of tungsten from W(V) via an unhindered disproportionation of W(II), the tungsten mirror from W(IV) via a hindered disproportionation which permitted W(II) diffusion, and the lack of deposition from W(III) due to a reaction of W(II) with tungsten species in the melt, except when a tungsten electrode was used whereby the deposition was catalyzed. The overall reaction scheme agreed with many documented disproportionation reactions and the formation of insoluble non-stoichiometric halide complexes. Direct reduction to tungsten as proposed by others does not explain the differences in tungsten deposition behavior.

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Figure 1: The Electrochemical Cell

The Electrochemical Cell; A-addition chute/gas bubbler, B-melt container, C-reference electrode compartment/working electrode, D-fill hole, E-silver flag reference electrode, F-10mm. fine porosity frit, G-flag type working electrode, H-thermocouple well, I-microelectrode type working electrode, J-platinum flag auxiliary electrode, K-level of melt, L-auxiliary electrode compartment/working electrode.
Figure 3: Voltammogram of Tungsten (IV)

Figure 4: Voltammogram of Tungsten (V)

Figure 5: Voltammogram of VCl$_3$ on a Tungsten Microelectrode

Figure 6: Voltammogram of FeCl$_3$ on a Platinum Microelectrode