1970

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**Publication Info**

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http://www.electrochem.org/  
DOI: 10.1149/1.2407546  
http://dx.doi.org/10.1149/1.2407546

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Electrochemical Reduction of Chromate in the Presence of Nickel Chloride in Molten Lithium
Chloride-Potassium Chloride Eutectic

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ABSTRACT

Chronopotentiometry of chromate in the presence of NiCl₂ in molten LiCl-KCl eutectic reveals a diffusion controlled, three electron reduction step. In the presence of excess NiCl₂, chromate is reduced at --0.35V vs. Pt(II)/Pt reference electrode and the electroactive species responsible for the chronopotentiometric wave is estimated to have a diffusion coefficient of 1.06 × 10⁻⁵ cm² sec⁻¹ at 450°C. The stoichiometry of the reduction product depends mainly on the temperature at which the deposit is formed. At 500°C the deposit approaches the composition LiNi₂CrO₄. X-ray powder diffraction shows the deposit to be a single compound with a face centered cubic lattice. The length of the unit cell edge is estimated to be 4.14Å. At 1400°C a weight loss of the deposit is observed. X-ray powder diffraction shows the presence of two phases, which are identified as NiO and NiCr₂O₄. The weight loss is attributed to volatilization of Li₂O.

Laitinen and Propp (1) have shown that the electrochemical reduction product of K₂CrO₄ in LiCl-KCl eutectic containing dissolved MgCl₂ is a single unstiochiometric compound of formula Li₂MgₓCrO₄, where x + 2y = 5. The values of x and y depended on the conditions of the electrolysis, namely current density, temperature, and the molar ratio of Mg(II) to Cr(VI) dissolved in the melt. Typical values of x ranged between 0.8 and 0.5.

Hanck (2) observed that the reduction of chromate in the presence of Zn(II) was shifted from --1.0V vs. Pt(II)/Pt reference electrode to --0.55V. Analysis of the deposit indicated the composition to be LiZnₓCrO₄. The stoichiometry of the compound was not affected by the electrolysis conditions.

The present investigation was undertaken to determine whether the reduction of K₂CrO₄ is affected by the presence of NiCl₂ and to establish the composition of the reduction product. Spectrophotometric measurements failed to indicate any interaction between Ni(II) and chromate in the melt (3). Ni(II) is known to exist as stable chlorocomplexes (4) in chlorides melts, and it was of interest to determine whether any chloride is contained in the deposit. Also the reduction potential of Ni(II) lies about 0.2V below that of chromate in the absence of divalent ions and it was of interest to determine whether the deposition of metallic nickel could be avoided.

Experimental
Apparatus.—A Hevi-Duty MK 3012-S vertical split tube furnace (Hevi-Duty Electric Company, Water- town, Wisconsin) was utilized in this work. The temperature sensing element was a chromel alumel thermocouple (Omega Engineering, Inc., Springdale, Connecticut). All experiments were made at 450°C except as noted.

A Sargent Model IV coulometric current source was used for the electrolytic preparation of the electrode deposits. The constant current source for the chronopotentiometric studies has been described previously (1).

A Tektronix 503 oscilloscope served to record chronopotentiograms and to monitor the potential of the working electrode continuously during the preparation of the electrode deposits. The Pyrex cell and envelope have been described previously (5).

Electrodes.—The Pt indicator electrode used in this study has been previously described (6). The electrode had a geometric area of 0.5 cm² and was constructed so that the glass metal seal was always kept above the level of the melt. The Pt(II)/Pt reference electrode was constructed as described by Ferguson (8).

The platinum gauze electrodes used to prepare samples of the film, as well as the carbon electrode which served as the counterelectrode in all electrochemical investigations in the melt, were constructed as described by Propp (1).

Chemicals.—All chemicals used in this study were reagent grade. Potassium chromate (J. T. Baker Chemical Company, Phillipsburg, New Jersey) was vacuum dried at 150°C before use. Anhydrous NiCl₂ was prepared by heating the hexahydrate (J. T. Baker Chemical Company) in vacuum to 180°C over a three day period. Analysis indicated it to be 99.3% pure.

The LiCl-KCl eutectic was obtained from Anderson Physics Laboratories, Inc., Champaign, Illinois. The method of purification has been described (7).

Solid chemicals were added to the melt by means of a small glass spoon. A blanket of argon was kept over the melt at all times to exclude oxygen and water vapor. The purification train used in purifying the argon has been described (8).

Experimental techniques.—Samples of the electrode deposit resulting from the reduction of chromate in the presence of NiCl₂ were obtained by constant current electrolysis using platinum gauze electrodes. The gauze electrodes were cleaned in boiling HClO₄ rinsed with distilled water, dried at 120°C for 18 hr, and weighed before their insertion into the molten salt solution. After electrolysis the gauze electrodes were
washed with deionized water, dried at 120°C, and reweighed. The electrode deposits were dissolved in boiling 72% perchloric acid. The nickel content of the deposit was determined by an EDTA titration using a murexide indicator. The method chosen for the chromium determination is a modification of that of Meier, Myers, and Swift (9). The procedure used has been previously described (1). Lithium was quantitatively determined by flame photometry.

Results and Discussion

Chronopotentiometry of $K_2CrO_4-NiCl_2-LiCl-KCl$ systems.—The effect of Ni(II) on the reduction of chromate was demonstrated by successively increasing the concentration of Ni(II) at constant chromate concentration. Figure 1 shows that at a Ni(II) concentration of $7.29 \times 10^{-3}M$, two transitions were obtained: one at $0.35V$ vs. Pt(II)/Pt reference and the other at $-1.0V$. Additional increases in the nickel concentration caused the wave at $-0.35V$ to grow larger. At $-1.0V$, the nickel concentration had no influence on the first reduction step. This can be seen from the fact that identical transition times were obtained for $1.56 \times 10^{-2}M K_2CrO_4$ solution containing $3.28 \times 10^{-2}M NiCl_2$ and for one containing $5.8 \times 10^{-2}M NiCl_2$.

According to the Sand equation the product of $I \frac{1}{2}$ on $t$ is independent of $i$ for a semi-infinite linear diffusion controlled process. The dependence of $I \frac{1}{2}$ on $i$ is demonstrated in Table I for the reduction of $K_2CrO_4$.

Table I. Chronopotentiometry of $K_2CrO_4$ in the presence of $NiCl_2$

<table>
<thead>
<tr>
<th>$C_{CrO_4} (M)$</th>
<th>$C_{NiCl_2} (M)$</th>
<th>$i$ (mA)</th>
<th>$t \frac{1}{2}$ (sec/1/2)</th>
<th>$I \frac{1}{2}$ (sec/1/2)</th>
<th>$I \frac{1}{2}/C$ (sec/1/2 cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$7.8 \times 10^{-4}$</td>
<td>$1.34 \times 10^{-4}$</td>
<td>$6.025$</td>
<td>$0.497$</td>
<td>$3.29 \times 10^{-4}$</td>
<td>$492$</td>
</tr>
<tr>
<td>$9.0 \times 10^{-4}$</td>
<td>$6.65$</td>
<td>$3.25 \times 10^{-4}$</td>
<td>$486$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$10.0 \times 10^{-4}$</td>
<td>$8.50$</td>
<td>$3.40 \times 10^{-4}$</td>
<td>$490$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$15.0 \times 10^{-4}$</td>
<td>$1.00$</td>
<td>$3.33 \times 10^{-4}$</td>
<td>$490$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$20.0 \times 10^{-4}$</td>
<td>$1.605$</td>
<td>$3.20 \times 10^{-4}$</td>
<td>$490$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

While holding the current density and the Ni(II) to Cr(VI) ratio constant, a series of deposits was prepared at 400°C, 450°C, and 500°C. The results of chemical analyses of these deposits are shown in Table II. From this table one can see that Li(I) content increases and the Ni(II) content correspondingly decreases as the temperature of the molten salt bath is increased. Table II also shows that the sum of the weight percentages of the three oxides, NiO, Li₂O, and Cr₂O₃ is very close to 100%, indicating that the chromium in the deposit is in the +3 oxidation state, and that no chloride or potassium ion is present. The absence of chloride in the deposit requires that the nickel chlorocomplex dissociate before the Ni(II) is incorporated into the deposit. That such a dissociation occurs rapidly enough to prevent inclusion of chloride in the deposit is remarkable. From Table II it is also obvious that in spite of the fact that the reduction potential of Ni(II) lies about 0.2V below that of chromate in the absence of divalent metal ions, no evi-

in the range of $7.0 \times 10^{-3}M$ to $2.75 \times 10^{-2}M$. The results indicate that the reduction of chromate in the presence of Ni(II) is diffusion controlled over the time interval investigated. Using $n = 3$ from the controlled current coulometry, a value of $4.19 \pm 0.010 \times 10^{2} A sec^{1/2} cm^{2} mol^{-1}$ for the transition time constant and $0.3 cm^{2}$ for the area of the electrode, we calculate $D = 1.06 \pm 0.06 \times 10^{-5} cm^{2} sec^{-1}$ for the chromate reduction in the presence of Ni(II) at 450°C. From the slope in Fig. 2 (plot of $I \cdot t^{1/2}$ vs. $C$) the same value for the diffusion coefficient was obtained.

Fig. 1. Effect of nickel chloride concentration on reduction of chromate. $1.56 \times 10^{-2}M K_2CrO_4$. A. No NiCl₂; B. $7.29 \times 10^{-3}M NiCl₂$. C. $3.28 \times 10^{-2}M NiCl₂$. 

Fig. 2. Dependence of $I \cdot t^{1/2}$ on concentration of $K_2CrO_4$. 0.5 cm² Pt flag electrode. $CNiCl_2/Cr_2O_4 > 2.1$. 

Table II. Composition of electrode deposit as function of temperature

<table>
<thead>
<tr>
<th>$C_{CrO_4}$</th>
<th>$0.0023M$</th>
<th>$C_{NiO}$</th>
<th>$0.198M$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>Wt %</td>
<td>Wt %</td>
<td>Wt %</td>
</tr>
<tr>
<td>(°C)</td>
<td>LiO</td>
<td>NIO</td>
<td>Cr₂O₃</td>
</tr>
</tbody>
</table>
400          | 3.75 | 66.8 | 31.6 | 102.0 | 102.0 | Li₂O·Ni₂O·Cr₂O₃·6NiCl₂ |
450          | 4.09 | 64.5 | 30.6 | 99.2 | 99.2 | Li₂O·Ni₂O·Cr₂O₃·6NiCl₂ |
500          | 5.10 | 64.0 | 31.9 | 101.0 | 101.0 | Li₂O·Ni₂O·Cr₂O₃·6NiCl₂ |
The empirical formula which best describes the deposit composition is $\text{Li}_x\text{Ni}_y\text{Cr}_z\text{O}_w$. As was observed by Propp (1) in his study of the MgCl$_2$-K$_2$CrO$_4$ system, $x + 2y = 2z$ indicating that no oxide is lost during the electrolysis. At high temperature the deposit approaches the composition $\text{Li}_x\text{Ni}_y\text{Cr}_z\text{O}_w$.

Table III indicates that there is only a small change in the composition of the electrode deposit on changing the molar ratio of Ni(II) to Cr(VI). There is a slight decrease in Li(I) content and an accompanying increase in Ni(II) content as the molar ratio of Ni(II) to Cr(VI) is increased. The effect of current density on the composition of the electrode deposit on holding the temperature and the molar ratio of Ni(II) to Cr(VI) constant was observed and is indicated in Table IV. Current density in the range 1-10 mA/cm$^2$ does not appear to be a significant factor in determining the chemical composition of the electrode deposit.

**X-ray powder diffraction studies.**—Table V indicates that the deposit is a single compound with a face centered cubic lattice. The length of the unit cell edge is estimated to be 4.14 Å.

**Thermal stability of electrode deposit.**—A sample of deposit, while still on the platinum gauze electrode, was heated in air and in an argon atmosphere to 1000°C for a period of 48 hr. Weight losses were only 0.5% in argon and 0.04% in air. Chemical analyses on the heated samples were in agreement with the previous analyses of unheated samples. The heated samples contained 3.87% Li$_2$O, 66.7% NiO, and 37.8% Cr$_2$O$_3$, corresponding to the empirical formula $\text{Li}_0.60\text{Ni}_2.10\text{Cr}_0.90\text{O}_3$. The x-ray powder pattern of the deposit appeared to change slightly after heating to temperatures above 950°C. The original face centered cubic lattice. The length of the unit cell $a = 4.169$ Å. The face centered cubic phase corresponds reasonably well to NiO ($a = 4.176$ Å) and the diamond cubic phase to NiCr$_2$O$_4$ ($a = 8.32$ Å). No lines were observed which could be assigned to the unheated nickel compound or to pure Li$_2$O.

Chemical analyses of the electrode deposit heated to 1400°C are in agreement with x-ray data. The deposit contained 67.01% NiO, 32.3% Cr$_2$O$_3$, and no Li$_2$O which corresponds to the empirical formula $\text{Ni}_2.10\text{Cr}_0.90\text{O}_3$.

The empirical formula of an unheated sample was found to be $\text{Li}_0.60\text{Ni}_2.10\text{Cr}_0.90\text{O}_3$. If the Li$_2$O is lost during heating, the remainder of the compound must have the empirical formula $\text{Ni}_2.10\text{Cr}_0.90\text{O}_3$ which is in agreement with chemical analyses of the heated sample.

Manuscript submitted Sept. 23, 1969; revised manuscript received ca. Dec. 1, 1969.

Any discussion of this paper will appear in a Discussion Section to be published in the December 1970 Journal.

**REFERENCES**

3. K. W. Hanck, Personal communication, unpublished results.