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Conference Paper

## The Mechanism of Electro-Reduction of Chromate in Molten LiCl-KCl\*

H. A. Laitinen and L. R. Lieto\*\*

Roger Adams Laboratory, The University of Illinois, Urbana-Champaign,  
Illinois 61801, U.S.A.

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When chromate ion is electro-reduced in molten LiCl-KCl in the presence of Mg(II), Zn(II) or Ni(II), the product is typically of composition  $\text{Li}_X\text{M}_Y\text{CrO}_4$ , in which  $X + 2Y = 5$ . Variations in composition accompany variations in experimental conditions, except in the case of Zn(II), for which  $X = 1$  and  $Y = 2$ . With Co(II), the product is either  $\text{Li}_X\text{Co}_Y\text{CrO}_4$  or  $\text{Co}_2\text{CrO}_4$  or a mixture of the two, depending upon the conditions. A mechanism involving a first two-electron reduction followed by a competition between further one-electron reduction and an internal chemical redox reaction accounts satisfactorily for the variation of product with changes in experimental conditions.

### INTRODUCTION

The electrochemical reduction of chromate in molten (Li, K) Cl was first reported by Black and DeVries in 1955.<sup>1</sup> These authors presented the reduction as a two-step process. Later work by Ferguson<sup>2</sup> and Bhatia<sup>3</sup> clearly showed that the reduction proceeded in a single, three electron step. The product of the reduction was not identified by them; however Laitinen and Bankert<sup>5</sup> were able to establish the composition of the product. Further, they showed that the reduction pathway was significantly altered by the presence of alkaline earth cations. These results were a confirmation of some early work by Laitinen<sup>6</sup> and represent the second stage in the study of the electroreduction of chromate. Several workers<sup>4-9</sup> have examined the reduction mechanism of chromate in the presence of a variety of divalent metal ions. Recently, Hanck and Laitinen<sup>9</sup> have examined the mechanism in the presence of added  $\text{CoCl}_2$ . This ion, because of the possibility of oxidation of the +3 state, can cause the reduction of chromate to proceed by either one or both of two pathways depending on the nature of the experiment.

### EXPERIMENTAL

The experimental apparatus and techniques were the same as have been described previously<sup>9,10</sup>.

All chemicals used were analytical reagent grade and used without purification except the  $\text{CoCl}_2$  which was purified by sublimation before use. (Li,K)Cl eutectic was obtained from Anderson Physics Laboratories, Inc., Urbana, Illinois.

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\*\* Present address: Illinois State University, Normal, Illinois 61761, U.S.A.

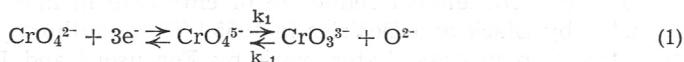
Controlled potential electrolysis experiments were made using a Heath EUA-19-2 chopper stabilized polarograph with an additional Heath EUW-19B current amplifier, as a potentiostat. The maximum current which this system can handle is 20 ma. The current was integrated by measuring the voltage drop across a standard resistor placed in series with the cell using a Heath EU-805A Universal Digital Instrument. The output of the digital voltmeter mode of the instrument is a frequency which is proportional to the input voltage. This frequency was input to the events counter mode of the instrument and the display was set to record the running sum of the events counter. The net result is a response which is a linear function of the number of coulombs passing through the resistor and hence the electrolysis cell.

X-ray powder diffraction data was obtained using an 11.47 cm Debye-Scherrer camera exposed to Ni filtered CuK $\alpha$  radiation from a Norelco X-ray unit.

Dissolution of the electrode deposit was accomplished with boiling HClO<sub>4</sub>. Determination of the lithium content was performed using flame emission spectroscopy. Chromate was determined by amperometric titration with standard Fe(II) using a rotating Pt electrode polarized at -1.0 V vs. S.C.E. Analysis for Co(II) was performed as follows. The acidic sample was treated with an excess of ascorbic acid and then heated. An excess of standard EDTA solution was added and the pH adjusted to 4-5 with NH<sub>4</sub>OH. After 5-10 minutes of additional heating the pH was adjusted to 9-10 with concentrated NH<sub>4</sub>OH and the excess EDTA was titrated with standard Zn(II) solution using eriochrome black to indicate the end point. The results are the sum of cobalt and chromium.

### *The Electro-Reduction of Chromate and the Effects of Divalent Metal Ions*

The reduction of chromate ion at a platinum electrode in molten (Li, K) Cl proceeds quasi-reversibly, in a single three-electron step. If more than a few millicoulombs per cm<sup>2</sup> are used for the electrolysis, the major product is the compound Li<sub>5</sub>CrO<sub>4</sub>. However, if the quantity of electricity used is less than that required for the formation of an insoluble deposit, the electrode reaction can be shown<sup>5</sup> to proceed along the following path.



Upon addition of various divalent metal ions, the reduction potential of chromate is shifted anodically by 400 to 1000 mv depending on the nature of M(II) and the chemical portion of the above sequence is changed to yield a new product, Li<sub>x</sub>M<sub>y</sub>CrO<sub>4</sub><sup>7-9</sup>.

This product has been observed for Mg(II), Ni(II) and Zn(II). The exact composition of the product depends on experimental conditions, but the number of Faradays per mole of product is always three as in (1). In general it has been observed that X + 2 Y = 5. For the Mg(II) and Ni(II) compounds the mole fraction of lithium varies from 0.25 to 0.5 and from 0.6 to 0.8, respectively while the Zn(II) compound has always been observed to be stoichiometric with X equal to 1.0. Where the composition of the product is variable it always follows the same relationship with respect to experimental parameters. The general trend is for the mole fraction of lithium in the product to increase as the temperature of preparation is increased and to decrease as the current density or the concentration of divalent metal ion is increased. The product with Zn(II) ion is unaffected by changes in preparative conditions for the range of conditions examined<sup>9</sup>. In addition to being very thermally stable, these compounds are very resistive to oxidation. The Zn(II) product is the only one which can be at least partially electrochemically reoxidized.

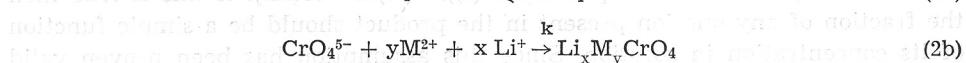
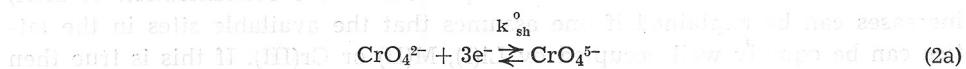
All three of the compounds mentioned are closely related, structurally. They are face centered cubic lattices with a unit cell edge of approximately

4.2 Å. A detailed analysis of the X-ray powder pattern data for the Zn(II) compound indicates that it is a disordered lattice in which the Li(I), Zn(II) and Cr(III) ions are randomly distributed among the available cation sites. The Mg(II) and Ni(II) compounds probably have similar structures. When heated in the absence of air all three materials undergo a decomposition which yields the metal chromite,  $MCr_2O_4$ , which is readily identified by its diamond cubic (spinel) structure, as well as  $Li_2O$  and  $MO$ .

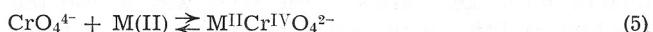
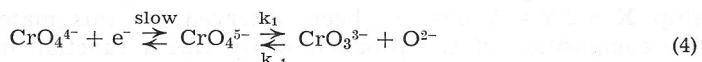
In the presence of Co(II) ions the product of the electrochemical reduction of chromate has been observed to be significantly different from that which is obtained for the other divalent metal ions. Under certain conditions a product having the general formula  $Li_xCo_yCrO_4$  was obtained but the relationship  $X + 2 Y = 5$  has not been observed for this material<sup>9,10</sup>. Furthermore, the composition of the product, while still a function of experimental parameters, no longer varies in the same way as did the other products. The mole fraction of lithium increases as the current density or concentration ratio of Co(II) to Cr(VI) increases. The value of X decreases as the potential of the cathode becomes more positive or as the temperature of the melt or the concentration of Co(II) increases. The number of Faradays per mole of product depends on the stoichiometry and hence on experimental conditions and is, in general, given by the relation  $n = 2 + X$ . Under conditions of low cathode potential and Co(II) / Cr(VI) concentration ratio, and high temperature and Co(II) concentration a limiting product is observed for which the composition is  $Co_2CrO_4$  and n equals two Faradays per mole. The reduction potential of chromate is shifted anodically by 620 mv when  $Co_2CrO_4$  is the product. Hanck and Laitinen<sup>11</sup> have shown that this compound has a diamond cubic lattice with a unit cell edge of 8.17 Å. A normal spinel structure in which Co(II) ions occupy the tetrahedral sites and Co(III) and Cr(III) ions share the octahedral sites has been proposed. This assignment is based on X-ray powder diffraction studies and by analogies with known compounds. In the light of recently published data<sup>12</sup> on the spinel Mn(II) [Co(III)Cr(III)]O<sub>4</sub> this structure seems to be confirmed.

Any proposed mechanism for the electroreduction of chromate in molten (Li, K) Cl must account for all of observations already noted in addition to some others. The diffusion coefficient of chromate is apparently unchanged by the addition of Ca(II), Mg(II), Ni(II) or Zn(II) and is estimated<sup>5,7,9</sup> at  $1.0 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup>. However, when  $Co_2CrO_4$  is the only product the apparent diffusion coefficient has been estimated at  $2.0 \times 10^{-5}$  cm<sup>2</sup> sec<sup>-1</sup> (ref. 10). While this fact might indicate the presence of a Co(II) —  $CrO_4^{2-}$  interaction, absorption spectrophotometric measurements of pure solutions of  $CoCl_2$  or  $NiCl_2$  and solutions of either salt with  $K_2CrO_4$  in molten (Li, K) Cl indicate that no observable interaction occurs<sup>10</sup>. Finally, the height of the voltammetric reduction wave of chromate is unchanged by the addition of Co(II) despite the fact that the former is a three electron process while the latter consumes only two electrons.

In an attempt to explain the reduction process<sup>10</sup> a following chemical reaction was proposed, viz.



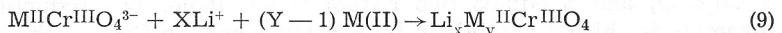
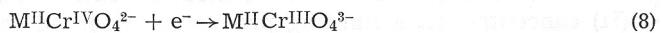
However, a detailed kinetic analysis<sup>10</sup> of this model has shown that for any acceptable value for the standard heterogeneous rate constant,  $k_{sh}^0$ , there exists no reasonable value for the rate constant,  $k$ , which will account for the shift in the reduction potential which was observed. Another reaction sequence has been proposed<sup>9,10</sup> which involves the interaction of the divalent metal ion with an intermediate oxidation state of chromium. This model provides for a distinction between the pathways for metal ions which can be oxidized and those which cannot.



### path 1



### path 2



The sequence of reactions starts with the facile addition of two electrons in either one or two steps to produce  $\text{CrO}_4^{4-}$ . In the absence of any divalent metal ions, this species can undergo a further, one electron, reduction to yield  $\text{CrO}_4^{5-}$ . This species then reacts to produce  $\text{CrO}_3^{3-}$  or  $\text{Li}_3\text{CrO}_4$  depending on experimental conditions. This reduction sequence seems reasonable in view of the well known fact that Cr(VI) and Cr(IV) are both tetrahedral whereas Cr(III) is octahedral. Hence, the reaction (3) should be faster than the electrochemical part of reaction (4). In the presence of non-oxidizable divalent metal ions,  $\text{CrO}_4^{4-}$  forms an ion pair complex with the metal ion which promotes the further electrochemical reduction of the chromium. The Cr(III) complex generated then precipitates as the compound  $\text{Li}_x\text{M}_y^{\text{II}}\text{Cr}^{\text{III}}\text{O}_4$ . This scheme is depicted under path 2 and probably represents the mechanism taken by all divalent metal ions, the only differences being in the relative rates of the reactions and the stabilities of the complex ions formed. The changes in the stoichiometry of the product with varying experimental conditions can be rationalized as follows. The increase in the value of  $X$  as a function of temperature is consistent with the invasion of the coordination sphere of either  $\text{M}^{\text{II}}\text{Cr}^{\text{IV}}\text{O}_4^{2-}$  or  $\text{M}^{\text{II}}\text{Cr}^{\text{III}}\text{O}_4^{3-}$  by  $\text{Li}^+$  as temperature increases. Such phenomena are well known in the case of Ni(II) ion in molten (Li, K) Cl eutectic<sup>13</sup>. The decrease of the lithium content of the product as the concentration of M(II) increases can be explained if one assumes that the available sites in the lattice can be equally well occupied by Li(I), M(II) or Cr(III). If this is true then the fraction of any one ion present in the product should be a simple function of its concentration in solution. Since this assumption has been proven valid

for  $\text{LiZn}_2\text{CrO}_4$ , it is a small matter to extend it to Mg(II) and Ni(II). The effects of current density on the stoichiometry of the product are not so straightforwardly explained.

Path 1 is represented as the mechanism which prevails in the presence of oxidizable metal ions such as Co(II). It is simply an internal oxidation-reduction reaction between M(II) and Cr(IV) with the subsequent precipitation of the resultant ion.

It is clear that if the proposed mechanism is the correct one, one can predict the formation of products other than  $\text{Co}_2\text{CrO}_4$  for the reduction of chromate with Co(II). Specifically, if the rates of reactions, (6) and (7), are or can be made slow compared to the ordinary electrochemical reaction, (8) then one would expect the product to be principally  $\text{Li}_x\text{Co}_y\text{CrO}_4$ . Since reactions (6) and (7) are chemical in nature their rates should be temperature dependent, whereas the rate of reaction (8) should not be nearly so sensitive to temperature changes but should be a sensitive function of cathode potential. Considerations of this nature led us to attempt the reduction of chromate in the presence of Co(II) under conditions which would favor the formation of  $\text{Li}_x\text{Co}_y\text{CrO}_4$  if that were possible. The experimental setup is substantially the same as previously described<sup>9</sup> and the conditions of the reduction were as follows.

$$\begin{aligned} E_{\text{cathode}} &= -1.07 \text{ vs. } 1 \text{ M Pt(II)/Pt} \\ \text{temperature} &= 390^\circ \text{ C} \\ \text{initial } [\text{CoCl}_2] &= 2.68 \times 10^{-2} \text{ M} \\ \text{initial } [\text{CoCl}_2] / [\text{K}_2\text{CrO}_4] &= 2.62 \end{aligned}$$

Since the deposit adheres to the electrode, an estimate of the equivalent weight of the product can be obtained by integration of the current flowing during electrolysis. This yielded a value of 77.4 grams per equivalent. Analysis of the deposit indicates that its empirical formula is  $\text{Li}_{1.11}\text{Co}_{2.22}\text{CrO}_{4.27}$  (I) with recovery of 100.3% of the weight of the sample as the oxides  $\text{Li}_2\text{O}$ ,  $\text{CoO}$  and  $\text{Cr}_2\text{O}_3$ . X-ray powder diffraction of the product is presented in Table I. The pattern is that of a face centered cubic lattice with a unit cell edge of 4.175 Å.

The physical properties of this material closely resemble those for the products obtained for the reduction in the presence of Mg(II), Ni(II) and Zn(II). Clearly, the reaction sequence previously postulated has been given added credibility by the success of the predictions based upon it. In addition, one may now explain some of the anomalies presented earlier. Since nominally

TABLE I

X-Ray Powder Diffraction Pattern of  $\text{Li}_{1.11}\text{Co}_{2.22}\text{CrO}_{4.27}$ 

d (Å)	I/I <sub>0</sub>	hkl	a (Å)
2.425	30	111	4.164
2.082	100	200	4.167
1.4758	70	220	4.177
1.259	20	311	4.178
1.2053	20	222	4.178
0.9570	10	331	4.174
0.9341	20	420	4.180
0.8523	20	422	4.178

three electrons are transferred per mole of (I), we may now recalculate the diffusion coefficient of chromate based on this new value of n. Using chronoamperometric data the diffusion coefficient turns out to be  $0.91 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$  which is the same as has been observed in all of the other cases. In addition, since the path of the reduction is potential dependent it is clear that chronopotentiometry cannot yield a meaningful value for n. This also explains why the wave height for the voltammetric reduction of chromate is unaffected by the addition of Co (II), since both processes involve three electrons at potentials corresponding to the limiting current. Finally, the compositional trends for the case of added Co (II) can be rationalized quite well. Since the product can be a mixture of materials produced by two competing reaction mechanisms, anything which affects the relative rates of these two pathways will affect the product distribution. Thus increasing the temperature should favor path 1 over path 2 and making the cathode more negative should effect the opposite result.

### Problems and Projections

The proposed reaction sequence for the reduction of chromate in (Li, K)Cl eutectic rationalizes the available data very well. The mechanism has been observed to fail in cases where the metal ion chemically reacts with chromate ion either by reducing the chromate, as is the case with Fe (II), Mn (II), Ti (II) and Sn (II) or by a transfer of oxide ion such as with Al (III), and possibly Ru (III) and Ce (III). Titanium (III), V (III), Cr (III) and Th (IV) form precipitates with chromate ion which are quite possibly simply the metal chromates. No interaction has been observed when chromate is electrochemically reduced in the presence of univalent ions larger than Li (I). For example, no products have ever been obtained which contain potassium and when chromate is reduced in the presence of Cu (I), Tl (I) or Ag (I) the only product is  $\text{Li}_5\text{CrO}_4$ . Cadmium (II) is unique in its effect on the reduction of chromate in that the reduction potential is shifted cathodically. This may suggest that another reduction mechanism is operative but the rather low solubility of  $\text{CdCrO}_4$  in this solvent makes this system somewhat difficult to manage. Lanthanum (III) and Nd (III) do cause a shift in the reduction potential of chromate and studies on the nature of the products obtained and the electrode mechanism are presently under way.

The reduction of chromate in the presence of calcium (II) ion has been the most irreproducible system encountered. It was first observed twenty years ago<sup>6</sup> and later confirmed<sup>4,5</sup> that the reduction produces an intractable material containing Li (I), Ca (II), Cr (III) and oxide ion. Later attempts at obtaining self-consistent data were not successful. We have recently shown that the presence of trace quantities of moisture or hydroxide ion in the solvent drastically affects the nature of the reduction. This undoubtedly was the cause of some of the earlier problems but the present status concerning the Ca (II) —  $\text{CrO}_4^{2-}$  system is still quite unclear. Present efforts under consideration are directed towards finding a system in which the postulated  $\text{CrO}_4^{2-}$  ion can be isolated and unambiguously identified. In addition, the reduction of chromate in the presence of divalent ions other than simple metal ions, such as  $\text{VO}^{2+}$ , is also being considered.

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## IZVOD

**Mehanizam elektro-redukcije kromata u talinama LiCl—KCl***H. A. Laitinen i L. R. Lieto*

Proučavana je redukcija kromat iona u eutektičkoj talini LiCl—KCl. Pokazano je da tro-elektronском redukcijom nastaje  $\text{Li}_5\text{CrO}_4$ . Dodatak iona Mg(II), Ni(II) i Zn(II) u talinu dovodi do snižavanja prenapetosti redukcije za oko 0.4 do 1.0 V. Osim toga stvaraju se i kompleksni kromati tipa  $\text{Li}_x\text{M}_y\text{CrO}_4$  (M je dvovalentni ion navedenih metala). Opisana je i sinteza elektroredukcijom spoja  $\text{Li}_{1.11}\text{Co}_{2.22}\text{CrO}_{4.27}$  i određeni su njegovi kristalografski parametri. Predložena je i reakciona shema, koja vodi računa i o stehiometriji produkata i o pomacima elektrodnih potencijala.

ROGER ADAMS LABORATORY  
UNIVERSITY OF ILLINOIS  
URBANA-CHAMPAIGN

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