INFORMATION TO USERS

While the most advanced technology has been used to photograph and reproduce this manuscript, the quality of the reproduction is heavily dependent upon the quality of the material submitted. For example:

- Manuscript pages may have indistinct print. In such cases, the best available copy has been filmed.
- Manuscripts may not always be complete. In such cases, a note will indicate that it is not possible to obtain missing pages.
- Copyrighted material may have been removed from the manuscript. In such cases, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, and charts) are photographed by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps. Each oversize page is also filmed as one exposure and is available, for an additional charge, as a standard 35mm slide or as a 17"x 23" black and white photographic print.

Most photographs reproduce acceptably on positive microfilm or microfiche but lack the clarity on xerographic copies made from the microfilm. For an additional charge, 35mm slides of 6"x 9" black and white photographic prints are available for any photographs or illustrations that cannot be reproduced satisfactorily by xerography.

Order Number 8717723

Electrochemical studies of Na_2CrO_4 - Na_2SO_4 melts at 1200 K

Shi, Dingzhu, Ph.D.

The Ohio State University, 1987

U·M·I
300 N. Zeeb Rd.
Ann Arbor, MI 48106

PLEASE NOTE:

In all cases this material has been filmed in the best possible way from the available copy.
Problems encountered with this document have been identified here with a check mark ✓.

1. Glossy photographs or pages _____
2. Colored illustrations, paper or print _____
3. Photographs with dark background _____
4. Illustrations are poor copy _____
5. Pages with black marks, not original copy _____
6. Print shows through as there is text on both sides of page _____
7. Indistinct, broken or small print on several pages ✓
8. Print exceeds margin requirements _____
9. Tightly bound copy with print lost in spine _____
10. Computer printout pages with indistinct print _____
11. Page(s) _____ lacking when material received, and not available from school or author.
12. Page(s) _____ seem to be missing in numbering only as text follows.
13. Two pages numbered _____. Text follows.
14. Curling and wrinkled pages _____
15. Dissertation contains pages with print at a slant, filmed as received _____
16. Other _____

University
Microfilms
International

ELECTROCHEMICAL STUDIES OF Na_2CrO_4 - Na_2SO_4 MELTS
AT 1200 K

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Graduate School of
The Ohio State University

By

Dingzhu Shi, B.S., M.S.

* * * * *

The Ohio State University

1987

Dissertation Committee:

Prof. R. A. Rapp

Prof. S. Smialowska

Prof. W. B. Johnson

Approved by

Adviser

Department of Metallurgical
Engineering

To my husband, Zhengyu, for his love, support, and
encouragement.

ACKNOWLEDGEMENTS

First of all, I would like to express my appreciation to my advisor, Professor R. A. Rapp, for his invaluable guidance and advice during this research, and for the critical reading of this manuscript.

I would like to thank my co-worker, Juan C. Nava, for his helpful discussion and assistance, and acknowledge Y. S. Zhang and Y. S. Hwang for their help and support.

This research was supported by the Department of Metallurgical Engineering, the Ohio State University.

VITA

JULY 20, 1958

Born at Changsha, China

Jan. 1982

B.S. in Chemistry, Fudan
University, Shanghai,
China

Mar. 1986

M.S. in Metallurgical
Eng.,
The Ohio State University
Columbus, Ohio, U.S.A.

FIELD OF STUDY

Major Field:

Metallurgical Engineering

Corrosion

Drs. W. Johnson,
S. Smialowska, R. Rapp

Chemical Metallurgy

Drs. G. St. Pierre,
W. Johnson, R. Rapp,
Y. Sahai

Physical Metallurgy

Drs. P. Shewmon,
G. Powell, G. Meyrick,
W. Clark

Mechanical Metallurgy

Drs. J. Hirth,
R. Wagoner, R. Hoagland

Electron Microscopy

Dr. W. Clark

Solidification

Dr. C. Mobley

TABLE OF CONTENTS

	Page
Acknowledgements	III
Vita	IV
List of Tables	VIII
List of Figures	X
 Chapter	
I. Introduction	1
1. Hot Corrosion	1
2. Chemistry of Chromium	7
II. Thermodynamic Phase Stability Diagrams	10
1. PhaseStability Diagram for Na-S-O System and Na-Cr-S-O System at 1200 K	10
2. Application of the Phase Stability Diagram in Electrochemical Studies	20
III. Electrochemical Techniques	22
1. Cyclic Voltammetry	22
2. Chronopotentiometry	29
3. Chronoamperometry	35
4. Dynamic Polarization	38
IV. Experimental Apparatus and Procedures	41

	Page
1. Electrochemical Cell	41
2. Experimental Apparatus	46
3. Experimental Procedures	48
V. Results and Discussion. Electrochemical Studies of Na_2CrO_4 - Na_2SO_4 Melts in Neutral Condition in Pure O_2 Gas	50
1. Cyclic Voltammetry Studies	51
1.1 Detailed Studies of the Reduction Reaction Corresponding to Peak I_c in Pure O_2	58
1.2 Studies of Peak II_a and V_a in O_2 Gas ...	76
1.3 Melt Basicity and Oxygen Pressure Trace During Cyclic Voltammetry Measurements .	80
2. Chronopotentiometry	83
3. Summary of Experimental Results From Cyclic Voltammetry and Chronopotentiometry Studies of Reactions for Na_2CrO_4 in a Neutral Melt in O_2	103
4. Chronoamperometry Studies	109
5. Dynamic Polarization Studies	114
6. Reaction Mechanisms for Molten Na_2CrO_4 - Na_2SO_4 Salts in Neutral Melt in O_2 at 1200 K	120
VI. Results and Discussion. Electrochemical Studies of Na_2CrO_4 - Na_2SO_4 Melt in Basic	

	Page
Conditions	125
1. Cyclic Voltammetry Studies	125
2. Chronopotentiometry Studies	146
3. Chronoamperometry and Dynamic Polarization Studies	158
4. Reaction Mechanism for Peak I_C	166
VII. Results and Discussion. Electrochemical Studies of 8 m/o Na_2CrO_4 - Na_2SO_4 Solution in Acidic Condition	170
1. Cyclic Voltammetry Studies	171
2. Chronopotentiometry Studies	176
3. Chronoamperometry and Dynamic Polarization Studies	180
VIII. Conclusions	185
References	188

LIST OF TABLES

Table	Page
1 Thermodynamic data for Na-S-O and Na-Cr-S-O systems at 1200 K	12
2 List of chemical reactions involved in the construction of the phase stability diagrams	13
3 Eight reaction mechanisms for diagnostic plots in Figure 9	28
4 Effects of scan rate on cyclic voltammogram parameters for peak I_C for 12.5 m/o Na_2CrO_4 at 1200 K in O_2 gas	63
5 Electron transfer number and quarter-wave potential for reaction at transition τ_f for 10 m/o Na_2CrO_4 in O_2 gas	96
6 Calculated number of electron transferred for reaction at peak I_C at different scan rates and Na_2CrO_4 concentrations in O_2 gas	104
7 Calculated $E_{1/2}$ ($E_{\tau/4}$) from CV and chronopotentiometry for Na_2CrO_4 - Na_2SO_4	

	Page
solutions in O ₂ gas	108
8 Cathodic Tafel slope and electron transfer number for Na ₂ CrO ₄ -Na ₂ SO ₄ solutions in O ₂ gas	121
9 Comparison of characteristics of peak V _a for 8 m/o Na ₂ CrO ₄ in neutral melt in O ₂ and in basic melt	137
10 Calculated E _{τ/4} from CV and chronopotentiometry studies for Na ₂ CrO ₄ -Na ₂ SO ₄ solutions at 1200 K	154
11 Cathodic Tafel slope and electron transfer number for Na ₂ CrO ₄ -Na ₂ SO ₄ solutions in basic condition	165
12 Summary of electrochemical behavior and reaction mechanisms for peak I _C in neutral condition and in basic condition.....	187

LIST OF FIGURES

Figure		Page
1.	Calculated Na_2SO_4 - Na_2CrO_4 binary phase diagram	9
2.	Phase stability diagram for the Na-S-O system with superimposed isopotential lines at 1200 K	14
3.	Phase stability diagram for the Na-Cr-S-O system at 1200 K	16
4.	Thermodynamic phase stability diagram for the Na-Cr-S-O system with superimposed isoactivity lines at 1200 K	17
5.	Dominant chromium solute species in Na_2SO_4 - Cr_2O_3 system at 1200 K	18
6.	Solubility of Cr_2O_3 in fused Na_2SO_4 at 1200 K and 1 atm oxygen	19
7.	Cyclic Voltammetry	23
8.	Apparatus arrangement	24
9.	Diagnostic plots for eight different kinetic cases	27
10.	Chronopotentiometry	30
11.	Diagnostic plot	33

	Page
12. Chronoamperometry	36
13. Sampled-current voltammetry	37
14. Schematic cathodic polarization curve	39
15. Experimental setup for electrochemical studies at 1200 K	42
16. Experimental setup for coulometric titration of oxide ions in fused Na ₂ SO ₄ at 1200 K	45
17. Cyclic voltammograms of Na ₂ SO ₄ and 8 m/o Na ₂ CrO ₄ in O ₂ at 50 mV/sec	52
18. Cyclic voltammograms of Na ₂ SO ₄ and 8 m/o Na ₂ CrO ₄ in O ₂ at different cathodic switching potentials	53
19. Cyclic voltammograms of 0.5 m/o and 3 m/o Na ₂ CrO ₄ in O ₂ at 1200 K (-log a _{Na₂O} =10.1)	56
20. Cyclic voltammograms of 10 m/o and 12.5 m/o Na ₂ CrO ₄ in O ₂ at 20 mV/sec and 1200 K	57
21. Superimposed cyclic voltammograms of 8 m/o Na ₂ CrO ₄ in O ₂ for the first cycle and for the steady state in a potential range of -2140 mV to 460 mV at 1200 K and 120 mV/sec	59
22. Schematic diagnostic plot for cyclic voltammetric measurements	61
23. Proportionality of peak current to scan rate for peak I _C for 12.5 m/o Na ₂ CrO ₄ in O ₂	64

24. Proportionality of peak current to square root of scan rate for peak I_C for 8 m/o Na_2CrO_4 in O_2 65
25. Superimposed cyclic voltammograms of 3 m/o Na_2CrO_4 in O_2 for the 1st cycle and for the 2nd cycle in a potential range of -2200 mV to 370 mV at 100 mV/sec and 1200 K69
26. Open circuit oxygen pressure and melt basicity for 10 m/o and 20 m/o Cr_2O_3 on Na-Cr-S-O phase stability diagram with superimposed regions of dominant chromium solute species at 1200 K70
27. Cyclic voltammograms of 10 m/o and 20 m/o Cr_2O_3 in O_2 at 1200 K71
28. Dependence on scan rate of the current function of peak I_C for 8 m/o and 12.5 m/o Na_2CrO_4 in O_2 74
29. Rate of shift of half peak potential as a function of scan rate for peak I_C for 8 m/o and 12.5 m/o Na_2CrO_4 in O_2 75
30. Cyclic voltammograms of 12.5 m/o Na_2CrO_4 in different potential ranges in O_2 at 1200 K ($-\log a_{\text{Na}_2\text{O}} = 9.5$)77
31. Phase stability diagram with superimposed trace of melt basicity on working electrode surface

	during cyclic voltammetry measurements for 12.5 m/o Na_2CrO_4 at 1200 K	82
32.	Chronopotentiograms of 3 m/o and 8 m/o Na_2CrO_4 in O_2 at 1200 K (open-circuit basicity 10)	85
33.	Chronopotentiogram of pure Na_2CrO_4 in O_2 with 200 mA applied current at 1173 K	87
34.	Chronopotentiograms of 10 m/o and 12.5 m/o Na_2CrO_4 in O_2 at 1200 K (open-circuit melt basicity 9.8)	88
35.	Chronopotentiograms of 8 m/o Na_2CrO_4 with 400 mA applied current in O_2 at 1200 K (open-circuit melt basicity 10)	90
36.	Plots of chronopotentiometric data according to Eq. (20) and Eq. (21) for τ_f in Fig. 32(b)	94
37.	Plots of chronopotentiometric data according to Eq. (20) for τ_f in Fig. 32(a) and 34 (b)	97
38.	Dependence of $i\tau^{1/2}$ on current for τ_f for 3 m/o and 8 m/o Na_2CrO_4 in O_2 at 1200 K	99
39.	Superimposed chronoamperograms of 8 m/o Na_2CrO_4 in O_2 at different potential steps	110
40.	Dependence of cathodic $i\tau^{1/2}$ on time for 8 m/o Na_2CrO_4 in O_2 at -1500 mV	112
41.	Superimposed dependence of sampled-current on applied potential steps for pure Na_2SO_4 and	

	Page
8 m/o Na_2CrO_4 in O_2	113
42. Cathodic polarization curves of 3 m/o and 12.5 m/o Na_2CrO_4 in O_2 at scan rate of 10 mV/sec ...	115
43. Cathodic polarization curve recorded by a porous Pt painted ZrO_2 working electrode in 18 m/o Na_2CrO_4 in O_2 at scan rate of 10 mV/sec (open- circuit basicity 10.2)	117
44. Superimposed basicity trace on Na-Cr-S-O phase stability diagram during dynamic polarization measurements for 18 m/o Na_2CrO_4 in O_2 at 1200 K	119
45. Cyclic voltammograms of pure Na_2SO_4 and 3 m/o Na_2CrO_4 in basic condition	126
46. Cyclic voltammograms of 8 m/o and 10 m/o Na_2CrO_4 in basic condition at 1200 K	128
47. Cyclic voltammogram of Na_2SO_4 in the potential range of -2200 mV to 780 mV at 20 mV/sec and 1173 K. (melt basicity 6.66)	129
48. Cyclic voltammogram of 10 m/o Na_2CrO_4 in the potential range of -1950 mV to 700 mV at 80 mV/sec and 1200 K. (Melt basicity 7.6)	130
49. Cyclic voltammograms of pure Na_2SO_4 and Na_2CrO_4 - Na_2SO_4 solutions in a series of cathodic switching potentials in basic condition	133

	Page
50. Proportionality of peak current to scan rate for peak I_C of 8 m/o Na_2CrO_4 in basic condition ...	140
51. Proportionality of peak current to square root of scan rate for peak I_C in basic condition ...	141
52. Dependence on scan rate of the current function of peak I_C for 3 m/o and 10 m/o Na_2CrO_4 in basic conditions	143
53. Rate of shift of half peak potential as a function of scan rate for peak I_C of 3 m/o and 10 m/o Na_2CrO_4 in basic condition	144
54. Phase stability diagram with superimposed melt basicity trace on working electrode surface during cyclic voltammetry measurements for 8 m/o Na_2CrO_4 at 1200 K	145
55. Chronopotentiograms of 3 m/o and 8 m/o Na_2CrO_4 in basic condition at 1200 K (open-circuit melt basicity 6.7)	147
56. Chronopotentiograms of 10 m/o Na_2CrO_4 and pure Na_2SO_4 in basic condition	148
57. Plots of chronopotentiometric data according to Eq. (20) for τ_f of 3 m/o and 10 m/o Na_2CrO_4 shown in Fig. 55(a) and 56(a)	150
58. Plots of chronopotentiometric data according to Eq. (20) and (21) for τ_f of 8 m/o Na_2CrO_4 shown	

	Page
in Fig. 55(b)	151
59. Dependence of $i\tau^{1/2}$ on current for τ_f of 8 m/o Na ₂ CrO ₄ in basic condition	153
60. Chronopotentiogram of 8 m/o Na ₂ CrO ₄ with 400 mA applied current in basic condition ($-\log a_{\text{Na}_2\text{O}}$ = 6.3)	156
61. Superimposed chronoamperograms of 8 m/o Na ₂ CrO ₄ in basic condition at different potential steps at 1200 K	159
62. Superimposed sampled-current voltammograms of pure Na ₂ SO ₄ and 8 m/o Na ₂ CrO ₄ in basic condition	160
63. Dependence of cathodic $it^{1/2}$ on time for 8 m/o and 10 m/o Na ₂ CrO ₄ in basic condition	162
64. Superimposed cathodic polarization curve of pure Na ₂ SO ₄ and Na ₂ CrO ₄ -Na ₂ SO ₄ solutions in basic conditions	163
65. Cathodic polarization curve of 8 m/o Na ₂ CrO ₄ in basic condition at 10 mV/sec in the potential range of -700 mV to -2300 mV at 1200 K	164
66. Superimposed cyclic voltammograms of 8 m/o Na ₂ CrO ₄ in a potential range of -1520 mV to 1200 mV at various scan rates and 1200 K	172
67. Phase stability diagram with superimposed trace	

	Page
of melt basicity on working electrode surface during cyclic voltammetry for 8 m/o Na_2CrO_4 in acidic condition at 1200 K	174
68. Chronopotentiometry measurements for 8 m/o Na_2CrO_4 in acidic condition at 1200 K	177
69. Plots of chronopotentiometric data according to Eq. (20) and (21) for forward transition in Fig. 68	179
70. Superimposed chronoamperograms of 8 m/o Na_2CrO_4 in acidic condition at different potential steps	181
71. Plots of chronoamperometric results of 8 m/o Na_2CrO_4 in acidic condition at 1200 K	182
72. Cathodic polarization curve of 8 m/o Na_2CrO_4 in acidic condition at 1200 K	184

I. INTRODUCTION

Chromium is an important alloying element commonly added to high temperature materials because of its well known resistance to high temperature corrosion of various types (1). Even in the presence of a thin fused salt film (often sodium sulfate and/or sodium chloride) at elevated temperatures in an oxidizing gas environment, chromium still provides alloys with relatively good corrosion resistance by forming a dense continuous Cr_2O_3 oxide layer on alloy surfaces (2-4). The environmental attack caused by thin fused oxyanion salt films is called "hot corrosion".

1.HOT CORROSION

To a given extent, the exact mechanisms of hot corrosion are still uncertain. However, several models for hot corrosion have been established during the past years: (a) sulfidation model proposed by Simons et

al(5), (b) acidic-basic fluxing model by Goebel, Pettit, and Goward(2,6), and (c) dissolution-reprecipitation model by Rapp and Goto (7).

In the sulfidation model, sodium sulfate is considered as a reactant, and the hot corrosion mechanism is illustrated as a reduction reaction of sulfate to form a sulfide with the alloying element. Thus, accelerated corrosion will occur because of the sulfidation process.

The basic fluxing mechanism has been demonstrated by Bornstein and DeCrescente (8-10), and by Goebel et al. (2) for several different Ni-base alloys. In this model, it is the destructive basic dissolution of the normally protective oxides by excess oxide ions in sodium sulfate melt that causes the accelerated corrosion of the materials. Acidic fluxing, on the other hand, is a mechanism for the hot corrosion of alloys containing Mo, W, or V as alloying elements. In Na_2SO_4 -induced catastrophic oxidation, oxides of these alloying elements complex with oxide ions in the fused salt to form molybdate, tungstate, and vanadate ions which decrease the basicity of the melt and thus cause the acidic dissolution of the protective oxides. In the case of the basic fluxing, good corrosion resistance was

able to be achieved when Cr_2O_3 was present as the protective oxide to prevent alloy sulfidation. Perhaps, Cr is protective because Cr_2O_3 can buffer the Na_2SO_4 melt basicity by forming chromate CrO_4^{2-} ions, and as a result of this buffering effect, the hot corrosion attack to Ni can be avoided. Good resistance of Cr_2O_3 to acidic fluxing is also expected because its minimum solubility is observed near the acidity encountered in gas turbine environments (11).

The electrochemical model proposed by Rapp and Goto illustrates the hot corrosion mechanisms by considering half-cell reactions which may take place at the oxide/salt interface or at the salt film/gas interface, depending upon the presence of aliovalent transition metal ion concentrations in the salt film. This model can also incorporate the acidic-basic fluxing model discussed above to obtain a better understanding of the hot corrosion mechanisms.

The effect of Cr-addition on hot corrosion resistance of alloys has been studied by many authors (2-4,8-10,12-15) at temperatures both above and below the melting point of Na_2SO_4 salt. For Ni-base alloys, a much better corrosion resistance was often obtained for a higher Cr content alloy than for a low Cr alloy.

The reactive dissolution of Cr_2O_3 , which is the oxidation product of Cr, in sodium sulfate melt to form sodium chromate was also confirmed from both the hot corrosion studies and a Cr_2O_3 solubility study (16). It is believed that the excellent corrosion resistance provided by chromium oxide, Cr_2O_3 , is partially due to its ability to buffer the melt basicity via the formation of chromate. Considering the different valance states for chromium in its compounds, it is reasonable to believe that chromium could also be able to stabilize the oxygen potential in the fused salt film by changing from one valance state to another. Kinetic studies of type II hot corrosion by Co-Cr-Al alloys conducted by Luthra (13) demonstrated that the improvement in corrosion resistance for these alloys with the addition of Cr is offered by the rapid growth of $\text{CoCr}_2\text{O}_4/\text{Cr}_2\text{O}_3$ films which separate the substrate material from the corrosive salt medium and consequently lower the corrosion rates. However, the exact roles of chromium in Na_2SO_4 -induced hot corrosion are still not very clear.

The influence of chromium on alloy hot corrosion by fused sodium sulfate in oxidizing gas environments has been studied by kinetic, microscopic and diffraction methods and by chemical analyses. But all the results

obtained from these studies apply only for thermodynamically stable substances, and any transient reaction intermediates or the metastable reaction products which may be important to understanding detailed hot corrosion reaction mechanism are actually not detectable.

As pointed out by Rapp and Goto (7) and Kawakami et al. (17), in analog to the atmospheric corrosion of metals by a thin aqueous electrolyte at room temperature, electrochemical reactions must play an important role in hot corrosion. The fused salt film is an ionic conductor, and is therefore an electrolyte at high temperatures. The alloy is physically separated from the gas phase by the salt film in hot corrosion. Therefore, the possible reaction intermediates and the hot corrosion reaction mechanisms should be best studied and clarified by electroanalytical chemistry techniques.

Only cyclic voltammetry and chronopotentiometry studies for Na_2SO_4 melt with Cr_2O_3 additions have been previously attempted by Tsai (18). But the experimental conditions explored in Tsai's work were mostly in the center of Cr_2O_3 phase stability field where the concentration of soluble Cr-species in molten Na_2SO_4 is so low that the electrochemical response from the

Cr-solutes was too weak to be detected experimentally.

The purpose of this research was to evaluate the electrochemical reaction steps and any coupled chemical reactions of Cr-species in fused sodium sulfate. Because chromium oxide Cr_2O_3 dissolves into sodium sulfate melt as sodium chromate in the basic dissolution reaction (16), Na_2CrO_4 solute was added to fused Na_2SO_4 to provide the Cr-species in the electrolyte. All the experiments were conducted under controlled and electrochemically measured values of Na_2SO_4 melt basicity, which is very important for determining and explaining of the experimental results obtained. Because the study of Cr or Cr-alloys as reactive electrodes is quite difficult, and relatively unexplored, the electrochemical reactions of the chromate-doped Na_2SO_4 was studied using a Pt electrode.

The electrochemical methods employed in this study consist of cyclic voltammetry, chronopotentiometry, chronoamperometry, and dynamic polarization. All tests were carried out at a Pt working electrode in a Na_2SO_4 melt with additions of known amounts of Na_2CrO_4 powder at 1200 K in O_2 and/or O_2 - SO_2 gas environments. A traditional three-electrode arrangement was adopted for the high temperature electrochemical cell.

Studies of the pure Na_2SO_4 melt at 900 C using the same techniques as this research were reported by Nava (19) recently. The reaction mechanisms for pure fused Na_2SO_4 concluded from his work were somewhat different from the other studies reported previously (12-14). Because of the similarity in experimental conditions (including the working electrode geometry and melt basicity), the results from Nava's study will be used to interpret the possible reaction mechanisms for the Na_2CrO_4 - Na_2SO_4 system where influence from the Na_2SO_4 melt needs to be considered. The interpretation will be based mainly on the thermodynamic phase stability diagrams for the Na-S-O and Na-Cr-S-O systems at 1200 K, and the chemistry of Cr compounds will be used to support and decide the electrochemical results when thermodynamic data are insufficient.

2. CHEMISTRY OF CHROMIUM

As a typical transition element, chromium forms many compounds. Its oxidation states can vary from 2- to 6+; the highest oxidation state, 6+, corresponds to the sum of the numbers of 3d and 4s electrons. The most common and stable oxidation states are 2+, 3+, and 6+ (23). Among the highly oxidized Cr(6+) compounds, sodium chromate and dichromate are two very important

ones from which most other chromium compounds are produced (24). The chromate can be converted to dichromates by increasing the solution acidity. As an aqueous solution is made more basic or acidic, this equilibrium is shifted as indicated in the following reaction

If the aqueous solution contains a high Cr(6+) concentration, polychromates may also form (23).

The binary phase diagram for the Na_2CrO_4 - Na_2SO_4 system was calculated by Liang, Lin, and Pelton (25) through an interactive computer program from the thermodynamic properties of the various phases. The resulted binary phase diagram is shown in Fig. 1. Because of the similarity in chemical behavior of the sulfate and the chromate, the Na_2CrO_4 - Na_2SO_4 binary is totally miscible, forming solid and liquid solutions. At the experimental temperature of 927 C (i.e., 1200 K), a salt mixture of Na_2CrO_4 and Na_2SO_4 in any proportion is completely liquid.

Figure 1 Calculated Na_2SO_4 - Na_2CrO_4 binary phase diagram (25).

II THERMODYNAMIC PHASE STABILITY DIAGRAMS

In order to elucidate the reaction mechanisms of Cr species in a sodium sulfate melt, a knowledge of the possible reactant and product compounds in the system under the experimental conditions is needed. In this thesis, the thermodynamic phase stability diagrams for the Na-S-O and Na-Cr-S-O systems at 1200 K were constructed to assist the interpretation and understanding of the results of electrochemical studies for Na_2CrO_4 - Na_2SO_4 solutions.

1. PHASE STABILITY DIAGRAMS FOR THE Na-S-O SYSTEM AND Na-Cr-S-O SYSTEM AT 1200 K

For the pure sodium sulfate melt, there exists a formation-decomposition equilibrium:

The interrelationship of the activities of the species involved in this reaction can be obtained from the standard Gibbs energy of formation:

$$\log K = \log P_{\text{SO}_3} + \log a_{\text{Na}_2\text{O}} = -1/(2.303 RT)(\Delta G^\circ_{\text{Na}_2\text{O}} + \Delta G^\circ_{\text{SO}_3} - \Delta G^\circ_{\text{Na}_2\text{SO}_4}) \quad (3)$$

The basicity of the Na_2SO_4 melt is defined as the negative logarithm of the Na_2O activity, $-\log a_{\text{Na}_2\text{O}}$, and the acidity by the negative logarithm of SO_3 partial pressure, $-\log P_{\text{SO}_3}$. The log-log stability diagrams are constructed by plotting oxygen pressure P_{O_2} as the ordinate versus redundantly the $\log P_{\text{SO}_3}$, and the melt basicity, $-\log a_{\text{Na}_2\text{O}}$. The diagrams represent an analogy to the Pourbaix potential-pH diagrams of aqueous solution corrosion, except that the sense for the acid/base abscissa has been reversed.

The thermodynamic data needed for the calculation are given in Table 1. The reactions involved in the stability diagram construction are listed in Table 2. The activities for coexistence of stable condensed phases were taken as unity; thus the equilibria are described by combinations of values for the partial pressure of oxygen, P_{O_2} , together with either the partial pressure of sulfur trioxide P_{SO_3} , or the basicity of the melt. The $-\log a_{\text{Na}_2\text{O}}$ axis applies only within the stability field for the Na_2SO_4 solvent phase.

Figure 2 is the phase stability diagram for Na-S-O system at 1200 K; the regimes of the dominant minority anion species as well as the iso-sodium

TABLE 1 THERMODYNAMIC DATA FOR Na-Cr-S-O SYSTEM AT 1200 K

<u>COMPOUNDS</u>	<u>ΔG°(Kcal/mole)</u>	<u>REFERENCE</u>
NaO ₂ (l)	-23.848	26
Na ₂ O(s)	-59.832	26
Na ₂ O ₂ (s)	-60.642	26
Na ₂ SO ₄ (l)	-213.612	26
Na ₂ S(s)	-67.489	26
SO ₂ (g)	-65.582	26
SO ₃ (g)	-62.360	26
Cr ₂ O ₃ (s)	-195.807	26
NaCrO ₂ (s)	-148.922	27
Na ₂ CrO ₄ (l)	-222.308	28
CrS(s)	-32.440	29
Cr ₂ (SO ₄) ₃ (s)	-307.447	30
Na ₂ S ₂ O ₇ (l)	-278.670	31

TABLE 2. LIST OF CHEMICAL REACTIONS INVOLVED IN THE CONSTRUCTION OF THE PHASE STABILITY DIAGRAMS

A. Na-S-O SYSTEM

<u>NUMBER</u>	<u>CHEMICAL REACTION</u>
1	$3/2 \text{ O}_2(\text{g}) + \text{Na}_2\text{SO}_4(1) = 2 \text{ NaO}_2(1) + \text{SO}_3(\text{g})$
2	$2 \text{ NaO}_2(1) = \text{Na}_2\text{O}_2(\text{s}) + \text{O}_2(\text{g})$
3	$\text{Na}_2\text{O}_2(\text{s}) = \text{Na}_2\text{O}(\text{s}) + 1/2 \text{ O}_2(\text{g})$
4	$\text{Na}_2\text{O}(\text{s}) + \text{SO}_3(\text{g}) = \text{Na}_2\text{S}(\text{s}) + 2 \text{ O}_2(\text{g})$
5	$\text{Na}_2\text{O}(\text{s}) + \text{SO}_3(\text{g}) = \text{Na}_2\text{SO}_4(1)$
6	$\text{Na}_2\text{O}_2(\text{s}) + \text{SO}_3(\text{g}) = \text{Na}_2\text{SO}_4(1) + 1/2 \text{ O}_2(\text{g})$
7	$\text{Na}_2\text{S}_2\text{O}_7(1) = \text{Na}_2\text{SO}_4(1) + \text{SO}_3(\text{g})$
8	$3/2 \text{ O}_2(\text{g}) + \text{Na}_2\text{S}_2\text{O}_7(1) = 2 \text{ NaO}_2(1) + 2 \text{ SO}_3(\text{g})$
9	$\text{Na}_2\text{S}_2\text{O}_7(1) = \text{Na}_2\text{S}(\text{s}) + \text{SO}_3(\text{g}) + 2 \text{ O}_2(\text{g})$
10	$\text{Na}_2\text{SO}_4(1) = \text{Na}_2\text{S}(\text{s}) + 2 \text{ O}_2(\text{g})$
11	$\text{Na}_2\text{SO}_4(1) = \text{Na}_2\text{O}(\text{s}) + \text{SO}_3(\text{g})$

B. Na-Cr-S-O SYSTEM

<u>NUMBER</u>	<u>CHEMICAL REACTION</u>
1	$\text{Na}_2\text{CrO}_4(1) = \text{NaCrO}_2(\text{s}) + 1/2 \text{ Na}_2\text{O}(\text{s}) + 3/4 \text{ O}_2(\text{g})$
2	$\text{Na}_2\text{CrO}_4(1) = \text{Na}_2\text{O}(\text{s}) + 1/2 \text{ Cr}_2\text{O}_3(\text{s}) + 3/4 \text{ O}_2(\text{g})$
3	$3 \text{ Na}_2\text{SO}_4(1) + 2 \text{ Na}_2\text{CrO}_4(1) = \text{Cr}_2(\text{SO}_4)_3(\text{s}) + 5 \text{ Na}_2\text{O}(\text{s}) + 3/2 \text{ O}_2(\text{g})$
4	$\text{Cr}_2\text{O}_3(\text{s}) + 3 \text{ Na}_2\text{SO}_4(1) = \text{Cr}_2(\text{SO}_4)_3(\text{s}) + 3 \text{ Na}_2\text{O}(\text{s})$
5	$\text{Cr}_2\text{O}_3(\text{s}) + 2 \text{ Na}_2\text{SO}_4(1) = 2 \text{ CrS}(\text{s}) + 2 \text{ Na}_2\text{O}(\text{s}) + 9/2 \text{ O}_2(\text{g})$
6	$\text{Cr}_2\text{O}_3(\text{s}) + \text{Na}_2\text{O}(\text{s}) = 2 \text{ NaCrO}_2(\text{s})$
7	$\text{NaCrO}_2(\text{s}) + \text{Na}_2\text{SO}_4(1) = \text{CrS}(\text{s}) + 3/2 \text{ Na}_2\text{O}(\text{s}) + 9/4 \text{ O}_2(\text{g})$
8	$\text{Cr}_2(\text{SO}_4)_3(\text{s}) + \text{Na}_2\text{O}(\text{s}) = 2 \text{ CrS}(\text{s}) + \text{Na}_2\text{SO}_4(1) + 9/2 \text{ O}_2(\text{g})$

Figure 2 Phase stability diagram for the Na-S-O system with superimposed isopotential lines at 1200 K.

activity lines with respect to the $\text{Ag}/\text{Ag}^+/\text{mullite}$ reference electrode have been superimposed with dotted lines. The phase stability diagram for the Na-Cr-S-O system at 1200 K is shown in Fig. 3. This diagram is obtained by superposition of the corresponding diagrams for the Na-S-O and Cr-S-O systems at the same temperature. For both Fig. 2 and Fig. 3, within each region, the labelled species represents the stable condensed phase (corrosion product) in equilibrium with the O_2 - SO_3 gas mixtures. The stable Cr-compounds coexisting with sodium sulfate system are also presented in the Na-Cr-S-O stability diagram.

Figure 4 is a phase stability diagram for the Na-Cr-S-O system at 1200 K with superimposed isoactivity lines for the pertinent species. The possible dissolution products for Cr_2O_3 in fused Na_2SO_4 are shown in Fig. 5, where the dominant regimes of each solute are indicated. The latter diagram results from measurements of the Cr_2O_3 dissolution behavior in fused Na_2SO_4 at 1200 K (16). Experimentally, the Cr_2O_3 solubility in Na_2SO_4 melt was measured in oxygen gas at 1200 K by Zhang (16). Figure 6 shows Zhang's results for 1 atm oxygen pressure. Very good agreement between the experiments and the thermodynamic predictions has been achieved. Figure 6 shows that the minimum

Figure 3 Phase stability diagram for the Na-Cr-S-O system at 1200 K.

Figure 4 Thermodynamic phase stability diagram for the Na-Cr-S-O system with superimposed isoactivity lines at 1200 K (16).

Figure 5 Dominant chromium solute species in Na_2SO_4 - Cr_2O_3 system at 1200 K (16).

Figure 6 Solubility of Cr_2O_3 in fused Na_2SO_4 at 1200 K and 1 atm. oxygen (16).

solubility for Cr_2O_3 in fused Na_2SO_4 at 1 atm P_{O_2} at about $-\log a_{\text{Na}_2\text{O}} = 15.4$. To estimate the reaction mechanism for Cr-solutes in Na_2SO_4 by electrochemical methods, experimental conditions far from the minimum solubility region should be adopted so that a reasonably strong response can be obtained from the dissolved Cr-solutes.

2. APPLICATION OF THE PHASE STABILITY DIAGRAM IN ELECTROCHEMICAL STUDIES

The stability diagram for Na-Cr-S-O system is used in this research as an aid to the interpretation of the kinetic results obtained from the electrochemical experiments. The diagram specifies which phases are thermodynamically in equilibrium with the gas mixtures when the oxygen pressure and melt basicity are specified. One can also trace the reaction process for Na_2SO_4 -related hot corrosion by measuring combined values for P_{O_2} and $a_{\text{Na}_2\text{O}}$ in the system during reaction. Experimentally, this is done by measuring simultaneously the oxygen pressure and melt basicity at the working electrode surface under study. The potential differences of the working electrode with respect to the $\text{Ag}/\text{Ag}^+/\text{mullite}$ reference electrode as well as with respect to stabilized zirconia oxygen sensor are

recorded. The combination of these two measurements provides the trace of melt basicity and oxygen activity during an electrochemical or chemical reaction.

However, the phase stability diagram represents only the thermodynamic equilibrium conditions. In the examination of the electrochemical reaction mechanisms, the phase stability diagrams can only serve as an auxiliary means for the interpretation of the possible reaction products involved. Moreover, because of the lack of certain thermodynamic data for the Na-Cr-S-O system at 1200 K, the presently calculated phase stability diagram may be incomplete, and some stable Cr compounds other than those shown in the diagram could exist. Complications from kinetic effects which are not encountered in the thermodynamic calculations can also occur experimentally. Nevertheless, the phase stability diagram presented in Fig.2.2 may still be a useful tool for the general understanding of the possible reaction processes in the system.

III ELECTROCHEMICAL TECHNIQUES

1. CYCLIC VOLTAMMETRY (CV)

In cyclic voltammetry the potential applied to an electrode (by means of a potentiostat) is changed linearly with time. The current is measured as a function of potential during CV. Figure 7 shows schematically the potential change in cyclic voltammetry scan. The triangular potential cycle can be represented by the following equation:

$$E = E_i - vt \quad (4)$$

where E_i is the initial potential, v is the scan rate in volts per second, and t is the polarization time. In cyclic voltammetry, the experiment is conducted in unstirred solutions, where convection is eliminated as much as possible. Figure 8(a) shows the schematic experimental arrangement for cyclic voltammetry experiments.

The basic feature of a voltammogram is the

(a)

(b)

Figure 7 Cyclic Voltammetry. (a) Cyclic potential sweep. (b) Resulting cyclic voltammogram.

Figure 8 Apparatus Arrangement
 (a) Cyclic Voltammetry (b) Chronopotentiometry

appearance of a current peak at a potential characteristic of the electrode reaction taking place. A typical cyclic voltammetry current-potential curve is depicted in Fig. 7(b). The position and shape of a given peak depends on such factors as sweep rate, electrode material, switching potentials, solution composition, and the concentration of reactants. Generally, cyclic voltammetry is very useful for the identification of steps in the overall reaction and new species which appear in solution during electrolysis as a result of combined electrochemical and chemical reactions. Experimentally, for the determination of reaction mechanisms, peak currents and peak potentials are measured in dependence on scan rate.

The mathematical description of the i - E curve in cyclic voltammetry for a reversible reaction is based on the Nernst equation (32). For the equilibrium

where O and R represent the oxidized and reduced species, respectively, at any time during the potential scan, the Nernst equation can be written as:

$$\frac{C_O(0,t)}{C_R(0,t)} = \exp[(nF/RT)(E-E^0)] = \exp[(nF/RT)(E_i - vt - E^0)] \quad (6)$$

where the concentrations of O and R are expressed as a function of the instantaneous electrode potential.

Randles, Sevcik, and Delahay (33-35) derived equations describing the diffusion-controlled peak current, i_p , which for both a reversible and totally irreversible wave, is proportional to C_0 and $v^{1/2}$ if the reaction $O + ne = R$ is assumed:

$$i_p \propto C_0 v^{1/2} \quad (7)$$

where C_0 is the bulk concentration of species O, and v is the scan rate.

For semi-infinite one-dimensional diffusion, $i_p/v^{1/2}$ is a constant at different scan rates. However, when preceding, following, or catalytic chemical reactions are coupled with reversible or irreversible charge transfers in the system, the mathematical treatment is more complicated, and the $i_p/v^{1/2}$ ratio becomes a function of scan rate. Nicholson and Shain (35) considered the kinetic complications for various electrode processes, and established diagnostic criteria diagrams for the eight possible kinetic cases examined. These diagrams are shown in Fig. 9. The description of the corresponding reaction mechanism is listed in Table 3. By comparing the diagnostic criteria with the experimental results, one can identify the unknown kinetic case by assuming the same reaction mechanism occurs if the experimental behavior shows the same trend

Figure 9 Diagnostic Plots for Eight Different Kinetic Cases (36).
 (a) Dependence of cathodic current function $i_p^c/v^{1/2}$ on scan rate. (b) Dependence of the change in cathodic half peak potential $\Delta E_{p/2}/\Delta \log v$ on scan rate.

TABLE 3 EIGHT REACTION MECHANISMS FOR DIAGNOSTIC PLOTS IN FIG. 9

I. Reversible Charge Transfer:

II. Irreversible Charge Transfer:

III. Chemical Reaction Preceding
A Reversible Charge transfer: IV. Chemical Reaction Preceding An
Irreversible Charge Transfer: V. Charge Transfer Followed By A
Reversible Chemical Reaction: VI. Charge Transfer Followed By An
Irreversible Chemical Reaction: VII. Catalytic Reaction With
Reversible Charge Transfer: VIII. Catalytic Reaction With
Irreversible Charge Transfer:

as the theoretical description.

2. CHRONOPOTENTIOMETRY

Chronopotentiometry is an electrochemical technique in which a controlled current is caused to flow between two electrodes (usually the working electrode and the counter electrode), and the potential of the working electrode is monitored as a function of time with respect to a reference electrode. The solution is unstirred and contains an excess of a supporting electrolyte so that diffusion of the electroactive reactant or product is the principal mechanism of mass transport (37). Figure 8(b) is a simplified block diagram of apparatus for chronopotentiometry measurements.

Consider a simple reversible charge-transfer process:

The potential of the working electrode is related to the surface concentrations by the Nernst equation

$$E = E_0 + (RT/nF) \ln(C_O/C_R) \quad (9)$$

When a constant current is applied, a typical variation of potential with time will be obtained as shown in Fig. 10(b), where τ is the time required to reach the potential shift, and is called the transition time.

Figure 10 Chronopotentiometry. (a) Current vs. time input.
(b) Potential vs. time response.

Although the change in bulk concentrations is negligible during the transition, the surface concentrations of both the reactant and product species vary markedly and their ratio determines the potential observed. This ratio varies rapidly at the beginning of the transient, where R is generated in a solution which is initially free of it, slowly when the two surface concentrations are about equal, and then rapidly again towards the end of the transient when the surface concentration of O is dropped to zero. At this time, the flux of O to the surface is insufficient to accept all of the electrons being forced across the electrode-solution interface so that the potential of the electrode will shift to a more negative value where a new, second reduction process can take place. In Fig. 10(b) the transition time τ is measured from the extrapolated initial trace to the point of collinearity of the final tangent with the E-t curve, a method suggested by Kuwana (38-39), and also the method adopted in this study for the transition time measurement.

The basic equation for chronopotentiometry was first derived by Sand (40). For an unstirred solution and under the assumption of semi-infinite linear diffusion, the Sand equation is given by:

$$i\tau^{1/2} = nFA(\pi D_O)^{1/2}C_O/2 \quad (10)$$

where i is the applied constant current. The measured values of $i\tau^{1/2}$ for various currents can be used to determine the reaction mechanisms by comparing with the diagnostic plots shown in Fig. 11. A lack of constancy of the $i\tau^{1/2}$ values with i for a given C_0 indicates complications in the electrode reaction from coupled homogeneous chemical reactions or adsorption.

For a reversible electron transfer process, the Nernst equation applies. The shape of a reversible chronopotentiogram is described by the potential-time relation as shown in the following equation:

$$E = E_{\tau/4} + (RT/nF) \ln[(\tau^{1/2} - t^{1/2})/t^{1/2}] \quad (11)$$

where $E_{\tau/4}$, the quarter-wave potential is

$$E_{\tau/4} = E^{0'} - (RT/2nF) \ln(D_O/D_R) \quad (12)$$

and is numerically equivalent to $E_{1/2}$, the polarographic half-wave potential in cyclic voltammetry.

For a totally irreversible reaction wave, the equivalent expression can also be obtained:

$$E = E^{0'} + (RT/\alpha n_a F) \ln[2k_O/(\pi D_O)^{1/2}] + \\ (RT/\alpha n_a F) \ln(\tau^{1/2} - t^{1/2}) \quad (13)$$

Thus the whole E - t wave will shift toward more negative potentials when the applied current is increased. Experimentally, the reversibility of an electrode reaction is tested by repeating the experiment over a

Figure 11 Diagnostic plot.

range of applied currents and determining the apparent n value in each case. The linearity of the plots of E vs $\ln[(\tau^{1/2} - t^{1/2})/t^{1/2}]$ and the constancy of n value calculated for the applied current range are indicative of reversible behavior (41).

A modification of chronopotentiometry is introduced by the current reversal technique. In this case, the current is reversed at or before the forward transition time, i.e., $t_f < \tau_f$. Mathematically, it has been shown that for the stable product R , the reverse transition time is always $1/3$ that of the forward time up to and including τ_f (32, 37), independent of D_O , D_R , C_O and the rate of the electron transfer. The factor of $1/3$ means that of the total amount of R generated during the forward step, only $1/3$ returns to the electrode during the backward step up to τ_b , with a large amount of R diffusing into the bulk solution. If the reaction product R is unstable, the τ_b/t_f ratio will be decreased because the reverse time will be shortened. On the other hand, if the product is insoluble or adsorbed on electrode, this ratio will be increased and the reverse time will be lengthened. Experimentally, the measured τ_b/t_f ratio can be used as an auxiliary means to identify the possible kinetic complications shown in chronopotentiometry studies. The lower curve in Fig.

10(b) is a typical example of current-reversal chronopotentiogram (41).

3. CHRONOAMPEROMETRY

In chronoamperometry, the potential is initially kept at some value E_1 where no electrochemical reaction is proceeding and then stepped to a new value, E_2 , at time equal zero, where the species O is reduced at a diffusion-limited rate, the corresponding current response is recorded as a function of time. Figure 12(a) is a diagram of the wave form applied in the chronoamperometry experiment. The current flow versus time is shown in Fig. 12(b).

Experimentally, a series of potential steps is applied. The initial potential E_1 is always chosen to be at a constant value where no electron exchange reaction, or faradaic process occurs so that the change from experiment to experiment is induced by the step potential E_2 , as depicted in Fig. 13(a). The current at some fixed time t_1 in each of these current-time curves is sampled, and then plotted vs. the potential step at which the step takes place. Figure 13(c) shows the sampled-current voltammogram obtained. The plateau in current indicates the mass transfer-limited region, where the surface concentration of reactant O is zero,

Figure 12 Chronoamperometry. (a) Potential vs. time input.
(b) Current vs. time response.

Figure 13 Sampled-current voltammetry. (a) Step waveforms applied in a series of experiments. (b) Current-time response to the steps. (c) Sampled-current voltammetry.

and the current is limited by diffusion of O from the bulk of solution to the electrode surface where it undergoes the reduction reaction.

The experimental arrangement for chronoamperometry measurement is essentially the same as that for cyclic voltammetry except that instead of a triangular potential wave, a constant potential is applied in each experiment.

4. DYNAMIC POLARIZATION

Potentiodynamic polarization is the electrochemical characterization of a system by its current-potential relationship. The potential of the working electrode is scanned slowly in the desired direction, cathodic or anodic, so the electrochemically active species on and/or around the working electrode surface are forced to a potential range where the electrochemical reaction can take place. Experimentally, the polarization characteristics are measured by plotting the current response as a function of the applied potential. Figure 14 is a schematic of the typical cathodic polarization curve obtained from aqueous solution. The curve is characterized by a linear activation controlled part followed by a constant limiting current, where the diffusion of the reacting

Figure 14 Schematic cathodic polarization curve.

species in the solution is the rate-limiting step. By studying and analyzing the observed current-potential behavior, and comparing with that from cyclic voltammetry, one would understand more clearly the specific reaction mechanisms present in the system. Meanwhile, several important experimental parameters, such as the electron transfer number n , and the diffusion coefficient of the reactant, D_0 , can be calculated from the i - E response if the concentration of the reactant is known and proper value for α in the system is chosen.

IV EXPERIMENTAL APPARATUS AND PROCEDURES

1. ELECTROCHEMICAL CELL

The experimental apparatus used for the electrochemical studies in this work is illustrated in Fig. 15. The working electrode was a platinum (99.9%) thin foil which was spot-welded to a platinum lead wire. The area of the working electrode was about 0.13 cm^2 . The counter electrode made of a loop of platinum wire centered around the working electrode so that a uniform current distribution in the system could be ensured. Both the working and counter electrodes were sealed in alumina tubes with high-temperature ceramic cement (Ceramabond #552) so that the working electrode would have a known area and geometry, and at the same time, the platinum wires could be prevented from being attacked by the highly corrosive mixed salt media. The reference electrode was the $\text{Ag}/\text{Ag}^+/\text{mullite}$ electrode (McDaniel MV-30), which was made of a pure silver wire spot-welded to a platinum lead wire and dipped into a 10

Figure 15 Experimental setup for electrochemical studies at 1200 K.

m/o Ag_2SO_4 -90m/o Na_2SO_4 mixture contained in a one-end closed McDaniel MV-30 mullite tube. The mullite tube was also sealed with Ceramabond at the top to maintain a constant composition for the Ag_2SO_4 - Na_2SO_4 melt. A 3.5 wt% CaO-doped partially stabilized zirconia tube served as a second reference electrode. This electrode was prepared by painting platinum paste onto the inside surface at the closed end of the zirconia tube and heated at 1200 C for three days. The porous platinum layer thus formed on the inside ZrO_2 tube surface served as an electrode in contact with an inserted platinum lead wire. By measuring the potential difference between the working electrode and the ZrO_2 electrode, the oxygen pressure at the working electrode surface could be obtained. The basicity of the melt was established using the zirconia electrode together with the $\text{Ag}/\text{Ag}^+/\text{mullite}$ reference electrode. The composition and voltages of these cells for measuring the oxygen pressure and melt basicity at 1200 K are shown below:

CELL I (OXYGEN PRESSURE MEASUREMENTS)

$(-)\text{Pt,air}/\text{ZrO}_2(\text{CaO}), \text{O}^{2-}/\text{Na}_2\text{SO}_4+\text{Na}_2\text{CrO}_4,\text{O}_2,\text{SO}_3,\text{Pt}(+)$

R.E. ($P_{\text{O}_2}=0.21\text{atm.}$)

$$E_I = (RT/4F) \ln [P_{\text{O}_2}(\text{W.E})/0.21] = 0.0404 + 0.0595 \log P_{\text{O}_2} \quad (14)$$

CELL II (MELT BASICITY MEASUREMENTS)

$(-)\text{Pt,air}/\text{ZrO}_2(\text{CaO}), \text{O}^{2-}/\text{Na}_2\text{CrO}_4-\text{Na}_2\text{SO}_4, \text{O}^{2-}$

/mullite(Na^+)/10m/o Ag_2SO_4 - Na_2SO_4 , Ag(+)

The reaction and the voltage for cell II are:

$$E = 1.475 + 0.119 \log a_{\text{Na}_2\text{O}} \quad (16)$$

Thus, as explained in detail by Park and Rapp (21), by measuring the voltages of cell I and cell II, the $a_{\text{Na}_2\text{O}}$ and P_{O_2} at the ZrO_2 /melt interface can be calculated.

In the experiments, the electrodes were immersed into the fused electrolyte held in an alumina crucible within a closed-end mullite chamber sealed with a brass flange. After the temperature reached 1200 K, pure dried oxygen gas or an O_2/SO_2 gas mixture was introduced into the system through the gas inlet, which was filled with a platinized ceramic catalyst to ensure equilibrium among SO_2 , O_2 , and SO_3 at the experimental temperature.

The experiments were conducted under conditions of various melt basicity. The change in melt basicity was achieved by either adding Na_2O_2 powder into the melt for a very basic melt ($-\log a_{\text{Na}_2\text{O}} = 7$), or by introducing a O_2/SO_2 gas mixture combined with use of an electrochemical titration method to obtain a very acidic melt ($-\log a_{\text{Na}_2\text{O}} = 16$). Figure 16 illustrates the coulometric titration method of Deanhardt and Stern (42). The CaO-stabilized zirconia electrode in this

Figure 16 Experimental setup for coulometric titration of oxide ions in fused Na_2SO_4 at 1200 K.

arrangement serves as a titrating electrode which, in combination with the Na-conducting mullite electrode (Pt/Na₂SO₄/mullite) withdraws oxide ions (and Na⁺ ions) from the Na₂SO₄ melt when a positive dc current is applied. The equilibrium activity of Na₂O in the melt was calculated from the measured voltage between a second zirconia electrode and a Ag/Ag⁺/mullite reference electrode as shown in Fig. 16.

When a basicity trace during the reaction process was desired, a second working electrode made of platinum wire connected to a porous platinum layer on the outside surface of the ZrO₂ tube was introduced in the assembly shown in Fig. 15. According to the electrochemical studies in a Na₂SO₄ melt conducted by Park and Rapp (21), only when such an arrangement is used for the working electrode can the local basicity change resulting from any reaction taking place at the working electrode surface be detected. A working electrode remote from the ZrO₂ electrode would only provide the value of the basicity locally at the zirconia/melt interface rather than that at the working electrode surface.

2. EXPERIMENTAL APPARATUS

The schematic experimental arrangements for

controlled potential and controlled current experiments are shown in Fig. 8(a) and (b).

In electrochemical studies of the sodium chromate-sodium sulfate solutions, an Aardvark Model V potentiostat was used to control the potential of the working electrode in cyclic voltammetry measurements, a Bioanalytical Systems generator (model CV-1B-120) was used to produce the triangular potential wave, and a Houston Instrument omnigraphic X-Y recorder was employed for recording the cyclic voltammograms obtained. In chronopotentiometry measurements, a Bascom-Turner data acquisition and management system (model 4120) served as the recorder for tracing the potential-time response, and a Ministat precision potentiostat (model 251) together with a resistance box functioned as a current generator to supply the constant current required by these experiments. A model 350 corrosion measurement system (by EG&G) was used in both chronoamperometry and dynamic polarization measurements. When the coulometric titration method was used to obtain a very acid melt, a model 70HP10 Wenking potentiostat was adopted to supply the required potential to the ZrO_2 titrating electrode.

For the measurements of various electrode potentials, a Keithley model 177 digital multimeter was

used.

3. EXPERIMENTAL PROCEDURES

Anhydrous sodium sulfate (Na_2SO_4), 99.8% pure, was dried at 110 C. For each experiment, 40 g Na_2SO_4 and various amounts of anhydrous sodium chromate (Na_2CrO_4) were charged into the crucible to obtain the desired chromate concentration. The electrodes were placed at such a depth to provide sufficient coverage of the electrodes by the molten salt. The relative positions of the electrodes were held constant in each experiment by fixing them with platinum wire; thus the working electrode was ensured to be in the center of the crucible and symmetrical with respect to the counter electrode, and the distance between the working and the $\text{Ag}/\text{Ag}^+/\text{mullite}$ reference electrode was minimized and kept constant.

After the furnace was heated to 1200 K, either pure dried oxygen gas or a dried O_2/SO_2 gas mixture was introduced into the mullite chamber through the gas inlet. When Na_2O_2 powder was added to increase melt basicity, the chamber was closed and left to equilibrate with the applied gas, while the voltages between the working electrode and the $\text{Ag}/\text{Ag}^+/\text{mullite}$ reference electrode as well as that between the working electrode

and the ZrO_2 reference electrode were recorded. After the measured potentials became constant, electrochemical measurements were initiated. The electrochemical techniques used in this study included cyclic voltammetry, chronopotentiometry, chronoamperometry, and dynamic polarization measurements.

V. RESULTS AND DISCUSSION
ELECTROCHEMICAL STUDIES OF Na_2CrO_4 - Na_2SO_4 MELT
IN NEUTRAL CONDITION IN PURE O_2 GAS

The electrochemical behavior of Na_2CrO_4 - Na_2SO_4 melt was first studied in neutral condition in pure O_2 gas at 1200 K. For all electrochemical measurements to be discussed in the following chapters, unless otherwise specified, the potential were always measured referring to the Ag/10 m/o Ag_2SO_4 -90m/o Na_2SO_4 / mullite reference electrode. In all experiments, various amounts of anhydrous Na_2CrO_4 powder were mixed with Na_2SO_4 powder before heating, and the open-circuit melt basicity was measured for each test before the electrochemical measurements began. The Na_2CrO_4 bulk concentrations studied under these experimental condition were: 0.5 m/o, 3.0 m/o, 8.0 m/o, 10.0 m/o, 12.5 m/o, and 18.0 m/o. Except for the 0.5 m/o and 18.0 m/o concentrations, the other four concentrations were tested by cyclic voltammetry, chronopotentiometry, chronoamperometry, and dynamic polarization techniques. Only cyclic

voltammetry studies were performed for 0.5 m/o, and only two polarization curves were able to be obtained from the 18.0 m/o melt because of the experimental difficulties encountered. For all the Na_2CrO_4 - Na_2SO_4 solutions studied, the open-circuit potential is in the Na_2CrO_4 phase stable region where the chromate and the sulfate are liquid.

1. CYCLIC VOLTAMMETRY STUDIES

Cyclic voltammetry studies were used to evaluate the overall redox reactions involved in the Na_2CrO_4 - Na_2SO_4 melt in neutral condition in pure O_2 . Figure 17(a) shows a cyclic voltammogram recorded by a pure Pt foil working electrode immersed in pure Na_2SO_4 at 50 mV/sec at 900 C equilibrated with O_2 . A typical cyclic voltammogram recorded for the 8.0 m/o Na_2CrO_4 addition at the same working electrode in O_2 gas at 50 mV/sec is shown in Fig. 17(b). Figure 18(a) is the cyclic voltammetry i-E response measured for pure Na_2SO_4 when the cathodic switching potential E_λ is gradually increased from about -830mV to -1810mV. No significant current change with the decreasing potential occurs until the cathodic E_λ reaches -1810 mV, where an increase in cathodic current is observed. Similar tests

Figure 17 Cyclic voltammograms for Na_2SO_4 and 8 m/o Na_2CrO_4 at 50 mV/sec. (a) Pure Na_2SO_4 in a potential range of -2300 mV to 575 mV with $-\log a_{\text{Na}_2\text{O}}=10.1$ at 1173 K. (b) 8 m/o Na_2CrO_4 in a potential range of -2330 mV to 547 mV with $-\log a_{\text{Na}_2\text{O}}=9.5$ at 1200 K.

Figure 18 Cyclic voltammograms of Na_2SO_4 and 8 m/o Na_2CrO_4 in O_2 at different cathodic switching potentials ($-\log a_{\text{Na}_2\text{O}}=10$). (a) Pure Na_2SO_4 at 50 mV/sec and 1173 K. (b) 8 m/o Na_2CrO_4 at 20 mV/sec and 1200 K.

for 8 m/o Na_2CrO_4 - Na_2SO_4 melt were performed and the results are shown in Fig.18(b). In this case, with the addition of chromate, a rise in cathodic current was obtained at potentials as high as -1340 mV, and when the cathodic E_λ was decreased to -1640 mV, a well defined cathodic peak I_C was revealed, with its peak potential at about -1550 mV. Hence, it is very clear that the observed peak I_C in the Na_2CrO_4 - Na_2SO_4 system results from some reduction reaction of the chemical species related to the sodium chromate additions.

A very important feature should be pointed out here: the cyclic voltammograms recorded in Fig. 18(b) reveal no anodic peak up to a cathodic switching potential of $E_\lambda = -1.6$ V, but there is a rise in cathodic current which begins as early as about -1.3 V indicating a reduction reaction taking place in the system. There is also an increase in anodic current when the scanning potential is switched at cathodic E_λ . This rise in anodic current after the cathodic E_λ potential implies that an oxidation reaction exists in the system. Obviously, whatever is being reduced in the potential range of about -1.3 to -1.55 V does undergo an oxidation reaction when the sweeping potential is reversed, but the species available for the anodic reaction are too little that a clearly defined anodic

peak is not able to be developed. A possible explanation for this missing anodic peak is that there is a very fast chemical reaction following the cathodic process which consumes most of the reduced product of the forward cathodic scan and to form some electro-inactive species. Thus, when the potential is reversed, only a small amount of the reduced product is reoxidized, so that a well defined anodic peak can not be detected. The validity of this explanation is tested later by other electrochemical technique.

Figure 19 to 20 are the cyclic voltammograms recorded by a Pt foil working electrode for Na_2CrO_4 concentrations of 0.5, 3.0, 10.0, and 12.5 m/o in O_2 gas. All these voltammograms were obtained by starting the cyclic voltammetry scans at the open-circuit potential for the given system. The cross marked on the voltammograms represents the zero applied potential position. The scan rate and the open-circuit melt basicity for each plot are given in the corresponding figures.

There are, therefore, several anodic peaks shown in the Na_2CrO_4 - Na_2SO_4 system. Peak III_a (at about -300 to -600 mV) and IV_a (about -1050 to -1160 mV) probably result from reactions by the Na_2SO_4 supporting

Figure 19 Cyclic voltammograms of 0.5 m/o and 3 m/o Na_2CrO_4 in O_2 at 1200 K. (a) 0.5 Na_2CrO_4 in a potential range of -2080 mV to 700 mV with melt basicity of 10.1 at 40 mV/sec. (b) 3 m/o Na_2CrO_4 in a potential range of -2040 mV to 400 mV with melt basicity of 10.1 at 20 mV/sec.

Figure 20 Cyclic voltammograms for 10 m/o and 12.5 m/o Na_2CrO_4 in O_2 at 20 mV/sec and 1200 K. (a) 10 m/o Na_2CrO_4 in a potential range of -1990 mV to 350 mV with melt basicity of 10.2. (b) 12.5 m/o Na_2CrO_4 in a potential range of -2380 mV to 500 mV with melt basicity of 9.7.

electrolyte because their peak potentials are very close to those observed for the pure Na_2SO_4 melt. Close examination of peak III_a and IV_a in both the Na_2CrO_4 - Na_2SO_4 and Na_2SO_4 systems reveals some differing characteristics. For example, the peak shape and the exact peak potentials are changed after adding Na_2CrO_4 . These differences could result from some kind of interaction, either chemical and/or physical, between the species related to sodium chromate and sodium sulfate.

Cathodic peak II_c and anodic peak I_a are always present in cyclic voltammograms with or without the addition of Na_2CrO_4 . These two peaks are identified as the cathodic and anodic current limits resulting from the decomposition of the Na_2SO_4 melt (43,44).

The following discussion will be focused mainly on the cathodic peak I_c and anodic peak V_a , which are the peaks resulting from electrochemical processes involving Cr-compounds.

1.1 DETAILED STUDIES OF THE REDUCTION REACTION CORRESPONDING TO PEAK I_c IN NEUTRAL MELT IN PURE O_2

Figure 21 shows two cyclic voltammograms measured in a potential range of -2140 mV to +460 mV at a scan

Figure 21 Superimposed cyclic voltammograms of 8 m/o Na_2CrO_4 in O_2 for the first cycle and for the steady state in a potential range of -2140 mV to 460 mV at 120 mV/sec and 1200 K.

rate of 120 mV/sec. The solid curve is the first scan, and the dashed one is the scan obtained after a number of continuous cycles until no obvious change in the cyclic voltammogram with time was displayed. This "steady state" curve shows a decrease in peak current for peak I_C and a shift in potential toward a more anodic value. These changes in peak current, position and shape with time indicate a complicated reaction mechanism with coupled chemical reactions and/or adsorption processes.

In order to determine whether peak I_C is a diffusion-controlled electron transfer reaction or an adsorption process, a number of different scan rates were used in cyclic voltammetry studies for a given scanning potential range. The scan rate is probably the most important experimental parameter for differentiating between the effects arising from adsorbed reactant and those due to species arriving at the electrode by diffusion (45). The maximum current (peak current) for a diffusion-controlled reaction is proportional to the square root of the scan rate, while that for an adsorption process increases linearly with the scan rate. Furthermore, the adsorption peak usually does not appear at slower scan rates. A diagnostic plot for the change in peak current with the square-root of

Figure 22 Schematic diagnostic plot for cyclic voltammetric measurements.

scan rate is given in Fig. 22. However, in the presence of a weakly adsorbed material, a separate peak cannot be observed, because the diffusion-controlled and the adsorption-controlled peaks occur at nearly the same potential thus the cyclic voltammograms may exhibit enhancement of the peak current because the electron transfer reaction also involves the adsorbed material at nearly the same potential as that for the "normal" diffusion-controlled electron transfer process (46,47).

Table 4 shows the experimental parameters for peak I_c in a 12.5 m/o Na_2CrO_4 melt when the scan rate varies from 4 to 800 mV/sec. The scanning potential range in this case is from -2380 mV to +506 mV. The open-circuit melt basicities are in the range of 9.4 to 9.5. Figures 23(a) and (b) are the corresponding plots of I_p vs. $v^{1/2}$ and I_p vs. v for the data shown in Table 4. Obviously, a linear relationship between the peak current and the scan rate is not observed. Instead, a fairly good linear dependence of I_p on the square root of the scan rate indicates that the peak current of I_c is mainly generated by a diffusion-controlled electron transfer reaction process. The I_p vs. $v^{1/2}$ relationship calculated for the 8 m/o Na_2CrO_4 concentration in O_2 gas is shown in Fig. 24. A linear behavior for the change in peak current with square root of scan rate is also

TABLE 4 Effects of Scan Rate on Cyclic Voltammogram
Parameters for Peak I_c for 12.5 m/o Na_2CrO_4 at 1200K
in O_2 Gas.

$(-\log a_{\text{Na}_2\text{O}} = 9.4-9.5)$

v (mV/sec)	$v^{1/2}(\text{mV/sec})^{1/2}$	E_p (mV)	I_p (mV)
4	2.00	-1430	47.4
10	3.16	-1450	69.7
20	4.47	-1465	77.4
50	7.07	-1500	108.3
80	8.94	-1540	152.6
200	14.14	-1550	155.5
500	22.36	-1625	228.5
800	28.28	-1650	271.7

Figure 23 Proportionality of peak current to scan rate for peak I_c for 12.5 m/o Na_2CrO_4 in O_2 . (a) Peak current vs. square root of scan rate. (b) Peak current vs. scan rate.

Figure 24 Proportionality of peak current to square root of scan rate for peak I_c for 8 m/o Na_2CrO_4 in O_2 .

observed for this plot, but again a positive ordinate intercept is observed.

Table 4 also reveals a change in potential E_p with change in scan rate. If peak I_c represents a purely diffusion-controlled process, the peak potential should not be scan-rate dependent (32). Thus, the shift in E_p in the more cathodic direction with increase in scan rate may imply some kinetic complications such as coupled chemical reactions and/or a weak adsorption process involved in the electron transfer step. Wopschall and Shain(45) examined several cases of possible weak adsorption. From their examples, it is proper to conclude that weak adsorption which may be present in the cathodic process is a weak adsorption of reactant, because weak adsorption of the product has little effect on the cathodic scan. It will cause the cathodic peak to shift anodically and exhibit a decrease rather than an increase in peak current with the increase in scan rate. This behavior is opposite to that observed here.

With the assumption of weak adsorption of reactant for the cathodic peak I_c , the shift of peak potential E_p with scan rate can be explained as follows: compared to unadsorbed species, the adsorbed reactant is more

difficult to reduce because there is a free energy of adsorption $-\Delta G^0$ involved. The adsorbed reactant tends to be more stable at the electrode surface and hence a higher driving force is needed to undergo a reduction reaction. As a result, the reduction will occur at a more cathodic potential than that for a normal, pure diffusion-controlled cathodic process. Furthermore, the flux of species diffusing to the electrode surface is time-dependent, and it becomes small at sufficiently fast scan rates relative to the amount of adsorbed species reacting at the electrode surface. Thus, when the scan rate is increased, the weak adsorption of reactant becomes a very important process and the cathodic peak potential will shift cathodically at higher scan rates.

The effects of cathodic and anodic switching potentials on the peak I_C were also studied. For cathodic E up to -2380 mV and anodic E up to $+910$ mV, no significant influence in the switching potentials on the cathodic peak potential was observed. There is, however, an increase in peak current for peak I_C as the cathodic E was brought to more negative values. This is probably an indication of the involvement of the species formed at the very cathodic potentials in the forward cathodic process at peak I_C .

In the cyclic voltammograms shown in Fig. 17 and Figure 19 to 20, the peak current I_C is only well defined when the Na_2CrO_4 concentrations exceed a certain value. For 0.5 m/o Na_2CrO_4 addition, this cathodic peak is totally missing. When the Na_2CrO_4 concentration is increased to 3 m/o, the cathodic peak is still not seen unless a very low cathodic E_λ (-2350 mV) is used, and the peak I_C shows up in the second scanning cycle only (as shown in Fig. 25). Very well defined peaks I_C are always observable for 8, 10, and 12.5 m/o Na_2CrO_4 concentrations. For the purpose of comparison, cyclic voltammetry studies for 10 and 20 m/o Cr_2O_3 in pure O_2 gas are briefly mentioned here. The measured open-circuit P_{O_2} (close to 1 atm.) and melt basicity (about 10.5) indicated that the Cr_2O_3 - Na_2CrO_4 mixtures were in the phase region where the Cr_2O_3 solubility in Na_2CrO_4 melt was 10^4 mole ppm, as shown in Fig. 26. The yellow-colored melt obtained after each experiment also proves the presence of a significant amount of Na_2CrO_4 , but there was no peak I_C detectable in cyclic voltammetry scan for any Cr_2O_3 concentrations studied up to as high as 20 m/o. The cyclic voltammograms recorded from 10m/o and 20m/o Cr_2O_3 - Na_2SO_4 in O_2 are given in Fig. 27.

If the reduction peak I_C result from the cathodic

Figure 25 Superimposed cyclic voltammograms of 3 m/o Na_2CrO_4 in O_2 for the 1st cycle and for the 2nd cycle in a potential range of -2200 mV to 370 mV at 100 mV/sec and 1200 K.

Figure 26 Open circuit oxygen pressure and melt basicity for 10 m/o and 20 m/o Cr_2O_3 on Na-Cr-S-O phase stability diagram with superimposed regions of dominant chromium solute species at 1200 K.

• o.c.p. for 10 m/o Cr_2O_3 .

• o.c.p. for 20 m/o Cr_2O_3 .

(a)

(b)

Figure 27 Cyclic voltammograms of 10 m/o and 20 m/o Cr_2O_3 in O_2 at 1200 K. (a) 10 m/o Cr_2O_3 in a potential range of -2140 mV to 400 mV at 500 mV/sec. $-\log a_{\text{Na}_2\text{O}}=11$. (b) 20 m/o Cr_2O_3 in a potential range of -2400 mV to 775 mV at 500 mV/sec. $-\log a_{\text{Na}_2\text{O}}=11.2$.

reaction of CrO_4^{2-} ions, as long as the amount of CrO_4^{2-} is high enough to be detected electrochemically, the peak should be present for a lower Na_2CrO_4 concentration as well, although the peak current might be low. Based on the present experimental results, it is reasonable to conclude that the peak I_c is not formed by a reduction reaction involving CrO_4^{2-} species, but rather there must be a chemical reaction in the melt, which upon equilibration, produces another Cr-related chemical species that undergoes the electron transfer reaction when the cathodic potential is applied. This chemical reaction must directly involve Na_2CrO_4 , and probably the chemical species produced at the cathodic limit, and the resulting product should maintain some equilibrium with the chromate. Thus, when the concentration of Na_2CrO_4 is not high enough, the content of the species formed by the chemical reaction is at an even lower level. Then the cathodic current resulting from the reduction of this chemically formed species will be too low to be detected, and the peak I_c is therefore, not observed. In case of 3 m/o Na_2CrO_4 , when the low cathodic E_λ was used, the amounts of O^{2-} ions and SO_2 molecules, both of which are the decomposition products for the Na_2SO_4 melt at the cathodic limit, were increased. These species could in turn shift the chemical equilibrium in the

$\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ melt such that the species responsible for the cathodic peak I_c are formed. Thus, when the potential was scanned back from anodic to cathodic in the second cycle, a peak I_c was able to be observed. The possible chemical reaction of the CrO_4^{2-} with the decomposition products SO_2 and the O^{2-} are as follows:

Because the calculation of the electron transfer number and the evaluation of the reversibility for peak I_c are interrelated, it is not possible to proceed into these calculations at the present moment. Figure 28 shows the current function ($I_p/v^{1/2}$) vs. scan rate plots for the peak I_c for 8 and 12.5 m/o $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ melt with O_2 gas. For all Na_2CrO_4 concentrations, the $I_p/v^{1/2}$ term decreases with the increase in scan rate and the $I_p/v^{1/2}$ vs. v behavior obtained is similar to type VI, VII, and VIII reaction mechanisms as described in the diagnostic criteria of Nicholson and Shain (36). The $\Delta E_{p/2}/\Delta \log v$ vs. v plots for the same peak from the 8 and 12.5 m/o $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ melts in O_2 gas, as shown in Fig. 29(a) and (b), display a small, gradual increase in the $\Delta E_{p/2}/\Delta \log v$ term with the scan rate, and the values for the $\Delta E_{p/2}/\Delta \log v$ term are always in the negative region. To discuss further the possible

Figure 28 Dependence on scan rate of the current function of peak I_c for 8 m/o and 12.5 m/o Na_2CrO_4 in O_2 . (a) 8 m/o Na_2CrO_4 . (b) 12.5 m/o Na_2CrO_4 .

Figure 29 Rate of shift of half peak potential as a function of scan rate for peak I_c for 8 m/o and 12.5 m/o Na_2CrO_4 in O_2 .
 (a) 8 m/o Na_2CrO_4 . (b) 12.5 m/o Na_2CrO_4 .

reaction mechanism for this cathodic reaction step, more information is needed. In a later section, the results from a second, independent electrochemical method will be discussed.

1.2 STUDIES OF PEAK II_a AND V_a IN NEUTRAL MELT IN O_2 GAS

Figure 17(a) is a cyclic voltammogram for pure Na_2SO_4 melt in O_2 gas in a potential range of -2250 mV to +575 mV at a scan rate of 50 mV/sec. There are four anodic peaks: they are designated as peak II_a , peak III_a , peak IV_a and peak V_a . Figure 30(b) shows a cyclic voltammogram obtained under similar experimental conditions for a 12.5 m/o Na_2CrO_4 - Na_2SO_4 melt in O_2 gas in the potential range of -2270 mV to +510 mV at a scan rate of 50 mV/sec. In this case, only two anodic peaks are present. Peak II_a and V_a are totally missing from the i -E response. Close examination of these two voltammograms reveals that the peak I_a is very shifted cathodically when Na_2CrO_4 is present; it begins at potentials of about 0 mV, approximately 300 mV more negative than that for pure Na_2SO_4 melt. This may explain why peak II_a is not observed in the Na_2CrO_4 - Na_2SO_4 system because the peak potential for peak II_a was at +200 mV, just within the potential range of peak I_a for the solution melt. Probably, peak II_a

Figure 30 Cyclic voltammograms of 12.5 m/o Na_2CrO_4 in different potential ranges in O_2 at 1200 K. $-\log a_{\text{Na}_2\text{O}} = 9.5$.
 (a) From -2380 mV to 500 mV at 120 mV/sec. (b) From -2270 mV to 500 mV at 50 mV/sec.

was simply merged with peak I_a so that it would not be detected as a separate peak; otherwise, it might have completely disappeared due to some kind chemical interaction between the Cr- related species with the Na_2SO_4 melt during the cyclic voltammetry scan process. For peak V_a , the situation is different. It vanishes gradually as the scan rate is increased and/or as the cathodic switching potential is shifted towards more anodic values. For example, in the 12.5 m/o Na_2CrO_4 - Na_2SO_4 melt, when cathodic $E_\lambda = -2380\text{mV}$, a trace of peak V_a was still observable for a scan rate of 120 mV/sec; but when the cathodic E_λ was raised to -2270 mV , the peak disappeared completely at a scan rate of only 50 mV/sec (see Fig. 30(a) and (b)). There was also a concentration dependence for this peak. For the same cathodic switching potential, a higher Na_2CrO_4 concentration melt will have a higher scan rate limit above which the peak V_a will not occur. In any case, the peak height of V_a is much smaller compared to that for pure Na_2SO_4 . In addition, the detailed shape of peak V_a is also quite different; only one peak was found for the pure Na_2SO_4 melt, but two adjacent peaks were found for Na_2CrO_4 -contained Na_2SO_4 melts when the cathodic switching potential is very negative (see Fig. 20(b)). All these differences suggest again that

there must be some sort of interactions between the chromate and the sulfate under the experimental conditions. The total disappearance of peak V_a in case of relatively high scan rates and/or relatively high cathodic E_λ values indicates that the species oxidized at the potential range for peak V_a no longer result from the decomposition product of the Na_2SO_4 melt at the cathodic limit II_C ; instead, Cr-related species must be responsible for the designated oxidation reaction steps. According to the diagnostic criteria given by Fig. 22, the obvious decrease in peak current with scan rate for peak V_a indicates a preceding chemical reaction for the anodic process. Hence the observed peak current dependence on the cathodic switching potential can be explained as follows: For a very low cathodic E_λ value, a longer time will elapse between the reverse of the scan and the anodic process, so that the chemical reaction will occur to a greater extent, and as a result, more electroactive species which are oxidized in the potential range of -1960 mV to -1820 mV will be produced. Based on this discussion, the following possible reaction mechanism is proposed for the anodic process V_a :

Where Y is the Cr-related species, X is the

decomposition product generated at peak II_c , R is the electroactive component produced by the chemical reaction, and O is the oxidation product formed at peak V_a . According to this proposed mechanism, a preceding chemical reaction between Y and X produces the electroactive species R which then undergoes the oxidation reaction at peak V_a to form species O. Because the peak potential is so close to the cathodic decomposition limit of the melt, it is difficult to determine the base line necessary for the peak current measurements, and quantitative calculations of the electron transfer number for this process cannot be made. Therefore, it is only possible to give the above qualitative scheme for the reaction mechanism. Further identification of the chemical species taking part in the anodic reaction will require other electrochemical techniques.

1.3 MELT BASICITY AND OXYGEN PRESSURE TRACE DURING CYCLIC VOLTAMMETRY MEASUREMENTS

For all the Na_2CrO_4 concentrations studied in O_2 gas by the cyclic voltammetry technique, the melt basicities and oxygen pressure on the working electrode surface were traced simultaneously during cyclic voltammetry scans. The Pt-painted ZrO_2 tube connected

to a Pt wire on the outer tube surface was used as the working electrode so that the recorded basicity and oxygen pressure trace in this study would reflect the situation exactly in the vicinity of the working electrode surface. Such a basicity trace measured for the 12.5 m/o Na_2CrO_4 - Na_2SO_4 melt in O_2 gas is shown in Fig. 31 for a scan rate of 50 mV/sec. As the potential is scanned to more negative values, the melt basicity on the working electrode surface changes gradually from the open-circuit value of 9.3 towards a more basic condition, being 8.5 at the cathodic peak I_C , and 7.7 at the cathodic switching potential. After that, the scanning potential is reversed, and the corresponding measured basicity follows a new path different from the cathodic path tending gradually towards the more acidic values at very anodic potentials. The maximum change in basicity during the whole scan is about 1.6, i.e., more than one order of magnitude. By plotting this basicity trace onto the Na-Cr-S-O phase stability diagram, Fig. 31 is obtained. On Fig. 31, the reaction at peak I_C occurs at conditions near the $\text{Cr}_2\text{O}_3/\text{CrS}$ boundary line. But no CrS formation was detected. Examination of precipitates after experiments only reveals chromium oxide. The same basicity measurements were conducted for the same melt but for a scan rate of 20 mV/sec. In this case, the maximum change in basicity during the

Figure 31 Phase stability diagram with superimposed trace of melt basicity on working electrode surface during cyclic voltammetry measurements for 12.5 m/o Na_2CrO_4 at 1200 K. Thicker solid line standing for peak I_c .

whole scan is 2.3, over 2 orders of magnitude. With an open-circuit basicity at 9.5, 7.2 was the most basic value achieved at the cathodic E_{λ} for a scan rate of 20 mV/sec. The change in basicity for I_C is shown in Fig. 31 by a segment of heavy solid line, the beginning of which denotes the initial current rise observed for peak I_C , and the end corresponds to the maximum current I_p position for peak I_C . On the Na-Cr-S-O phase stability diagram, the start of the cathodic sweep passes through the regime where Na_2CrO_4 becomes increasingly insoluble in Na_2SO_4 , and where NaCrO_2 solute should become more important than the Na_2CrO_4 solute. No cathodic reaction corresponding to a chromate to chromite reduction was observed. Similar results were obtained for melts with other Na_2CrO_4 concentration. Obviously, any "double buffering" effect of Cr with respect to both redox and acid-base change was not observed for $\text{CrO}_4^{2-}/\text{CrO}_2^-$ conversion from the present experiments. The observed kinetic behavior is different from the thermodynamic prediction according to the phase stability diagram of Na-Cr-S-O system. The implication and significance of this observed basicity trace will be discussed later when the reaction mechanism of the system is considered.

2. CHRONOPOTENTIOMETRY STUDIES

For reasons discussed previously, a second

electrochemical technique must be employed to acquire certain needed information. Chronopotentiometry measurements were used as an independent but complementary method from which the reversibility of the reaction and the electron transfer number can be evaluated.

Figure 32(a) is a chronopotentiogram recorded for a Pt foil working electrode immersed in 3.0 m/o $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ melt at 1200 K in O_2 gas with an applied current of 400 mA. Only one forward transition τ_f was found for the cathodic reaction, and two short backward transitions τ_{b3} and τ_{b4} were found when the current was reversed shortly after the forward transient. The potential range for the forward transition was at about -1250 mV to -1450 mV, and those for the backward transitions were at -1250 mV to -1150 mV, and -600 mV to -500 mV, respectively.

Obviously, despite the fundamental differences between the chronopotentiometry and the cyclic voltammetry measurements, the results obtained from these two techniques for a given melt are still comparable. As can be seen clearly from Fig. 17 and Fig. 19 to 20, the peak potentials for peak I_c , III_a , and IV_a in cyclic voltammograms for $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ melts are in close agreement with the potential ranges over

(a)

(b)

Figure 32 Chronopotentiograms for 3 m/o and 8 m/o Na_2CrO_4 in O_2 at 1200 K. (Open-circuit basicity 10). (a) 3 m/o Na_2CrO_4 with 400 mA applied current. (b) 8 m/o Na_2CrO_4 with 300 mA applied current.

which the cathodic transient τ_f , and the anodic transients τ_{b3} and τ_{b4} are observed.

Figure 33 shows a chronopotentiogram for pure Na_2SO_4 in O_2 as a comparison. The applied current in this case is 200 mA. No forward transition was found for Na_2SO_4 until the cathodic potential reached about -1500mV. The end of forward transient was at about -1900 mV. There were three backward anodic transitions with the potential ranges: -1850 mV to -1800 mV; -1150 mV to -1000 mV; and -300 mV to -100 mV, respectively. Figures 32(b) and 34(a, b) are the chronopotentiograms for 8.0, 10.0 and 12.5 m/o Na_2CrO_4 - Na_2SO_4 mixtures in O_2 gas. The applied current and the open-circuit melt basicity for each case are given in these plots and equal approximately 10. For all the Na_2CrO_4 concentrations studied, an applied current of 120 mA was required in order to observe the forward cathodic transition. When a lower current was used, no transition behavior could be detected within 100 seconds. Practically, this time scale is impractically long because possible complication from convection may occur in longer time electrolysis. All the calculations in the present work for chromopotentionetry studies are therefore based on the results obtained at higher currents where the boundary conditions required by the

Figure 33 Chronopotentiogram of pure Na_2SO_4 in O_2 with 200 mA applied current at 1173 K. Open-circuit melt basicity 10.

Figure 34 Chronopotentiograms of 10 m/o and 12.5 m/o Na_2CrO_4 in O_2 at 1200 K. (Open-circuit basicity 9.8) (a) 10 m/o Na_2CrO_4 with 200 mA applied current. (b) 12.5 m/o Na_2CrO_4 with 300 mA applied current.

Sand equation are satisfied.

To study the transition behavior corresponding to peak V_a observed in cyclic voltammetry, the cathodic current was maintained past the cathodic transition τ_f in the Na_2CrO_4 - Na_2SO_4 melt until the potential reached -2130 mV where substantial decomposition of the Na_2SO_4 melt had taken place. Figure 35 shows the chronopotentiograms thus obtained for the 8 m/o Na_2CrO_4 - Na_2SO_4 melt in O_2 gas. In Fig. 35(a), the cathodic current was kept at -2130 mV for about 5 seconds. When the current was reversed, no new anodic transition was observed except τ_{b3} and τ_{b4} . The current was then kept at -2130 mV for about 13 seconds in Fig. 35(b). In this case, a clearly defined anodic transition τ_{b1} did show in the range of -1950 mV to 1800 mV, when the current was reversed, and a very short second anodic τ_{b2} adjacent to the first one was also observed. This observation supports the argument put forward in the discussion of peak V_a of the cyclic voltammogram: there is a chemical reaction between the sodium chromate and the decomposition products of the sodium sulfate melt preceding the anodic process. This chemical reaction generates the electroactive species oxidizable at the potential range of -1960 mV to -1800 mV as seen in Fig. 35(a) and (b). When the current was

Figure 35 Chronopotentiograms of 8 m/o Na_2CrO_4 with 400 mA applied current in O_2 at 1200 K. Open-circuit basicity 10. (a) Current reversed after 5 sec at -2100 mV. (b) Current reversed after 13 sec at -2100 mV.

reversed shortly after the decomposition of the Na_2SO_4 melt, the time allowed for the chemical reaction to take place and the amount of decomposition products were both relatively small, so that the E-t response from the electroactive components generated by the chemical reaction was too weak to be identified. A longer decomposition time with the chemical reaction for the Na_2SO_4 melt provided more reactants for a longer subsequent reaction time. As a result, a significant local concentration of electroactive species were produced which gave rise to the observed anodic transitions τ_{b1} and τ_{b2} . A point worth mentioning here is that the differences in the magnitudes of the forward transition times shown in Fig. 32, 34, and 35. Although the potential range over which τ_f appeared is about the same, the τ_f values in Fig. 35 are much smaller than those in Fig. 34 and 34. The only difference involved in the experimental conditions for these chronopotentiograms was surface condition of the Pt working electrode. The chronopotentiograms of Fig. 35 were obtained from a fresh melt, but those in Figs. 32 and 34 were from a melt previously studied by cyclic voltammetry measurements where the Pt working electrode had been repeatedly polarized. According to Gilman (48), an oxygen-containing film will be formed on the Pt

electrode surface at anodic potentials where oxygen evolution occurs. Because the formation of this oxygen film is slow and irreversible, the surface condition of the Pt working electrode after considerable polarization will be quite different from that in the fresh solutions. Thus, the electrochemical response measured from the Pt electrode will also be different. Detailed discussion of the possible influence of the Pt electrode on electrochemical measurements because of the change in its surface condition by anodic film formation due to alternating-polarization can be found in Ref.(48).

Theoretically, for both cathodic and anodic transitions, the potential-time relation for either the reversible or irreversible reaction involving a soluble species can be quantitatively calculated (32). These equations are given as follows:

$$E = E_{\tau/4} + (RT/nF) \ln[(\tau^{1/2} - t^{1/2})/t^{1/2}] \quad (20)$$

for reversible reactions; and

$$E = E^{\circ'} + (RT/\alpha n_a F) \ln\{2k^0/\pi D_O\}^{1/2} + (RT/\alpha n_a F) \ln(\tau^{1/2} - t^{1/2}) \quad (21)$$

for irreversible reactions, where α is the transfer coefficient, k^0 is the rate constant for a homogeneous reaction, and αn_a is the number of electron involved in the rate-determining step.

The $E_{\tau/4}$ in Equation 20 is the so-called quarter-wave potential and is measured at time $t=\tau/4$.

A plot of the potential E versus $\ln[(\tau^{1/2}-t^{1/2})/t^{1/2}]$ according to Equation 20 for τ_f for 8 m/o $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ in O_2 is given in Fig. 36(a). The dots represent the actual experimental data, and the line is fit via a linear regression analysis by least squares method. As can be seen, a very good linear log plot is obtained. The electron transfer number n calculated from the slope of Fig. 36(a) is 0.8, normalized 1. In order to prove that the obtained good linear fit to Equation 20 does result from the reversible nature of the electrode reaction rather than from some possible special combination of α and n values, the similar calculation for τ_f based on Equation 21 has also been conducted. The results are shown in Fig. 36(b). Clearly, much better linear behavior was obtained for Equation 20, the linear regression parameter for which, in this particular case, is 0.999. For the irreversible E - t relation, this parameter is only 0.98. Similar procedures were followed to interpret τ_f for all the other experimental conditions studied. As a result, a very good linear regression parameter, ranging from 0.995 to 1.00, and a constant quarter-wave potential

Figure 36 Plots of chronopotentiometric data according to Eq. (20) and Eq. (21) for τ_f in Fig. 32(b). (a) Plot according to Eq. (20). (b) Plot according to Eq. (21).

$E_{\tau}/4$ at different applied constant currents for a given melt composition were always obtained for the expression describing the reversible reaction. But a poorer linear behavior was generally displayed when the totally irreversible expression was used, giving a linear regression parameter varying from 0.95 to 0.98. Thus, the validity of Equation 20 for τ_f is verified.

To test further the reversibility of the cathodic process in $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ melts, the method suggested by Gileadi et al.(41) was adopted. Following their criteria by repeating the experiment over a range of applied currents and determining the apparent n value in each case, no decrease in the n value with increasing current was observed for the experimentally tested current range of 150 mA to 500 mA. Table 5 summarizes the calculation for apparent n value of τ_f for 10 m/o $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ melts in O_2 by using Equation 20. The relative constancy in n value with the increase in current also proves the validity of Eq.20. Therefore, based on the above discussion for the chronopotentiometry measurements, it is concluded that the cathodic electrode reaction in $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ solution at potentials of about -1450 mV is a reversible electrochemical process with an electron transfer number of one.

Figure 37(a) and 37(b) are the linear log plots

TABLE 5 Electron Transfer Number And Quarter-wave Potential

For Reaction at Transition τ_f For 10 m/o Na_2CrO_4 In O_2 Gas

<u>i (mA)</u>	<u>n</u>	<u>E_{τ_4} (Volt)</u>
200	1.2	-1.33
300	1.4	-1.32
400	1.3	-1.32
500	1.3	-1.33

Figure 37 Plots of chronopotentiometric data according to Eq. (20) for τ_f in Fig. 32(a) and 33(b). (a) 3 m/o Na_2CrO_4 , Fig. 32 (a). (b) 12.5 m/o Na_2CrO_4 , Fig. 33(b).

according to Eq.20 for 3 and 12.5 m/o Na_2CrO_4 - Na_2SO_4 solutions in O_2 gas. A very well behaved linear fit is displayed for each of the Na_2CrO_4 concentrations.

Similar procedures could not be applied to transitions τ_{b1} and τ_{b2} to evaluate the reversibility and electron transfer number for the anodic electrode reactions because the transition times for these processes are too short. The same situation also applies to transition τ_{b4} . For τ_{b3} , however, the transition time over which the potentials covered is long enough to proceed with the calculation. The results show that this anodic reaction step is also reversible, and the number of electron transferred is calculated to be between 0.90 and 1.10, normalized 1. Since the electrode reaction corresponding to this transition, as is for peak IV_a in cyclic voltammetry, is considered to be an oxidation reaction of the species from Na_2SO_4 melt, this result does agree very well with the calculation for Na_2SO_4 (19). There is no change in n value with the change of Na_2CrO_4 concentration for both the anodic and cathodic electrode reactions quantitatively evaluated.

The dependence of the transition time on the applied current was also evaluated for the cathodic

Figure 38 Dependence of $i\tau^{1/2}$ on current for τ_f for 3 m/o and 8 m/o Na_2CrO_4 in O_2 at 1200 K. (a) 3 m/o Na_2CrO_4 . (b) 8 m/o Na_2CrO_4 .

process by plotting $i\tau_f^{1/2}$ versus i for a given Na_2CrO_4 concentration. Figure 38(a) and (b) are such plots for 8 m/o and 3 m/o Na_2CrO_4 - Na_2SO_4 melts. The dependence of the $i\tau^{1/2}$ product on current becomes very pronounced after i exceeds 200 mA. The positive deviation from the constant $i\tau^{1/2}$ product indicates the presence of adsorption in the cathodic process. Thus the prediction based on cyclic voltammetry studies is verified: the diffusion-controlled cathodic electrode reaction is accomplished by an adsorbed reactant species on the platinum working electrode.

Similar to the observation in cyclic voltammetry studies, the cathodic response for 3 m/o Na_2CrO_4 - Na_2SO_4 melt in chronopotentiometry measurements is not as well defined as those obtained from higher Na_2CrO_4 content solutions. As is shown in Fig. 32(a), in the second cycle, the end the of cathodic transition is hardly observable, although the potential range for the beginning of a plateau in E - t response still indicates that there are some electrochemical reactions involving the added Cr-compound going on in the system. This behavior agrees very well with the experimental observation in cyclic voltammetry studies.

One of the most significant applications of chronopotentiometry is to study of systems in which

chemical reactions precede, follow, or are in parallel with the electron-transfer processes(37). Equations 22 through 24 are examples for each of these processes:

Generally, for a preceding chemical reaction, the observed transition time is lower than that predicted by the Sand Equation, and the $i\tau^{1/2}$ value decreases linearly with increasing applied current. This behavior is explained in Fig. 11. For a following chemical reaction, however, the forward transition time will not be affected by the kinetic process because Y is not electroactive, and O is not involved in the following chemical reaction. Thus, the characteristic feature which distinguishes this process from the others is not the $i\tau^{1/2}$ vs. i behavior, but rather the ratio of the forward to reverse transition times. This ratio is equal to 3 for up to and including τ_f for a pure diffusion-controlled process. In the presence of a following reaction, the t_f/τ_b ratio will be greater than 3 because upon current reversal the wave will be shortened as some of the reduced products are transformed into electroinactive Y. In case of the catalytic reaction, the chronopotentiometry measurements

will display an increase in the $i\tau^{1/2}$ term with i at low applied currents, and a constant $i\tau^{1/2}$ product numerically equal to the value predicted from Sand Equation, at high currents.

Generally the t_f/τ_b ratio discussion applies only to a redox pair. For the $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ solution in the neutral melt in O_2 , the ratio of t_f/τ_b found for $t_f \leq \tau_f$ is always > 5 , which does indicate the presence of a following chemical reaction. Such a reaction would convert a large amount of reduction product to electroinactive species. Obviously, the preceding and catalytic reactions do not describe what was found for the cathodic reaction for the molten $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ salt. Thus the reaction mechanisms in Nicholson and Shain's diagnostic criteria involving proceeding (III & IV) and/or catalytic reactions (VII and VIII) do not fit the observations. Case I and II of the criteria are also excluded because a simple charge transfer reaction was not observed. As a result, only case V (charge transfer followed by a reversible chemical reaction) and VI (charge transfer followed by an irreversible chemical reaction) are left as the possible cathodic reaction mechanisms for the fused $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ binary in the neutral melt in O_2 gas at 1200 K. Calculations for cyclic voltammetry measurements plotted

in Fig. 28 to 29 for several Na_2CrO_4 concentrations show that both the $i_p/v^{1/2}$ -scan rate behavior and the $\Delta E_{p/2}/\Delta \log v$ -scan rate behavior for reaction at peak I_C can be correlated to case VI: reversible charge transfer followed by an irreversible chemical reaction. Considering all the information acquired thus far from electrochemical studies, this mechanism fits the experimental results quite well.

3. SUMMARY OF EXPERIMENTAL RESULTS FROM CYCLIC VOLTAMMETRY AND CHRONOPOTENTIOMETRY STUDIES OF REACTIONS FOR Na_2CrO_4 IN A NEUTRAL MELT IN O_2

Because the reversibility of the reaction at peak I_C has already been determined by chronopotentiometry studies, the electron transfer number for this cathodic reaction can also be evaluated through cyclic voltammetry measurements by the following equation:

$$n = 2.2RT/[(E_p - E_{p/2})F] \quad (25)$$

where $E_{p/2}$ is the half peak potential. This equation is only valid for a reversible charge transfer process. The number n calculated from this equation for peak I_C is between 0.8 and 1.08, normalized as 1. Table 6 are the results of the calculation of n for the reaction at peak I_C for 8 m/o and 12.5 m/o Na_2CrO_4 melts.

TABLE 6 Calculated Number of Electron Transferred for
Reaction at Peak I_C at Different Scan Rates and Na_2CrO_4
Concentrations in O_2 Gas

v (mV/sec)	n
8 m/o Na_2CrO_4	
10	0.80
20	0.84
50	0.84
80	0.80
120	0.80
12.5 m/o Na_2CrO_4	
4	1.08
10	1.06
20	1.03
50	0.95
80	0.83
200	0.80

There is no trend in the calculated n with scan rate for 8 m/o Na_2CrO_4 , but a noticeable decrease in n with increase in scan rate for the 12.5 m/o Na_2CrO_4 melt is obvious. The average calculated values of n for 8 m/o and 12.5 m/o Na_2CrO_4 melts are, respectively:

$$n = 0.82; \quad 8 \text{ m/o}$$

$$n = 0.96; \quad 12.5 \text{ m/o}$$

These results are consistent with what has been found from the chronopotentiometry studies, and it verifies the conclusion that the charge transfer step for reaction at peak I_C is reversible.

The following is a brief summary of the electrochemical studies for the Na_2CrO_4 - Na_2SO_4 melts in a neutral melt in O_2 .

I. Cathodic reaction at peak I_C and transition τ_f

1.1 The electroactive species reducible at the potentials for peak I_C and transition τ_f is not Na_2CrO_4 , but some other Cr-compound formed through an equilibrium from Na_2Cr_4 - Na_2SO_4 melt.

1.2 There is a weak adsorption of reactant on the Pt working electrode in the cathodic process.

1.3 The charge transfer reaction is reversible and is followed by a very fast, irreversible chemical reaction.

One electron is transferred during charge transfer step.

1.4 The cathodic reaction is accompanied by an increase in melt basicity of about two orders of magnitude.

II Anodic reaction at peak V_a and transition τ_{b1} and τ_{b2}

2.1 An oxidation reaction of some Cr-compound associated with a preceding chemical reaction probably consumes O^{2-} ions, the oxidation of which is believed to be responsible for peak V_a in the Na_2SO_4 melt.

2.2 The reversibility and electron transfer number is uncertain because of the difficulties encountered in determining the base line for the peak as well as in estimating the E-t relations.

III Anodic reactions at peaks IV_a , III_a , and transition times τ_{b3} , and τ_{b4} .

3.1 There are basically the same responses as those in Na_2SO_4 for these particular potential ranges.

3.2 There are some minor changes in peak potential and peak shape indicating some kind of interaction between the Na_2SO_4 melt and the Cr-compound.

3.3 The electron transfer number calculated for the reaction at peak IV_a and the transition time τ_{b3} is 1, and the charge transfer reaction is reversible, in agreement with the results for Na_2SO_4 for the same

electrode process.

3.4 The number of electrons transferred and the reversibility of the reaction at peak III_a and the transition time τ_{b4} could not be determined because of the very short transition time observed.

Table 7 summarizes the calculated results for $E_{1/2}$ (or $E_{\tau/4}$, as it is called in the controlled current experiment) from cyclic voltammetry and chronopotentiometry studies for the cathodic reaction. Considering that the calculation shown in Table 7 is based on measurements from two different experiments, it is reasonable to assume that the $E_{1/2}$ and $E_{\tau/4}$ potentials are numerically equal for each Na_2CrO_4 concentration. The data listed in Table 7 also show that except for the 8 m/o Na_2CrO_4 , which displayed a value for $E_{1/2}$ about 100 mV more negative than -1400 mV, there is no trend for $E_{1/2}$ or $E_{\tau/4}$ with the change in Na_2CrO_4 concentrations. All the polarographic half-wave potentials (as they are called in cyclic voltammetry) and the quarter-wave potentials (as they are called in chronopotentiometry) fall between -1.33 Volts and -1.40 Volts, and the calculated differences between each experiment are within 70 mV. Taking into account that the variation in Na_2CrO_4 concentration may influence the D_O/D_R ratio, and that experimental errors may be

TABLE 7 Calculated $E_{1/2}$ ($E_{\tau/4}$) From CV And
Chronopotentiometry For Na_2CrO_4 - Na_2SO_4 solutions
In O_2 Gas

m/o of Na_2CrO_4	$E_{1/2}$ from C.V. (Volts) ($E_{1/2} = E_{p/2} - 1.09RT/nF$)	$E_{\tau/4}$ from chronopotentiometry (Volts)
3	-1.38 ± 0.02	-1.40 ± 0.01
8	-1.50 ± 0.02	-1.52 ± 0.01
10	-1.37 ± 0.01	-1.33 ± 0.01
12.5	-1.40 ± 0.01	-1.36 ± 0.01

introduced from the electrochemical measurements, the observed discrepancy for $E_{1/2}$ values is acceptable.

Examination of Pt working electrode after the experiments often showed green-colored precipitates present on the working electrode surface beneath the Ceramabond layer. These precipitates were insoluble in water and are believed to be chromium oxide. Because the amount of the precipitates was too little, X-ray diffraction analysis could not be performed.

Noticeable vaporization of species from the $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ was also observed. After each experiment, white chemical deposits were found on the top inner surface of the brass flange resulting from condensation of the vaporized species. These species could be formed from Na_2CrO_4 and/or Na_2SO_4 directly, and/or from some other compounds which were formed by reactions taking place in the $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ system under the experimental temperature.

4. CHRONOAMPEROMETRY STUDIES

To verify the arguments put forward in the discussion of cyclic voltammetry studies, chronoamperometry tests were carried out in the electrochemical studies of the $\text{Na}_2\text{CrO}_4\text{-Na}_2\text{SO}_4$ solutions.

Figure 39 Superimposed chronoamperograms of 8 m/o Na_2CrO_4 in O_2 at different potential steps.

Figure 39 is a set of superimposed chronoamperograms recorded from a Pt foil working electrode immersed in a 8 m/o Na_2CrO_4 - Na_2SO_4 solution in O_2 gas. Each curve corresponds to a given applied potential step, E_{step} . As the applied cathodic potential is increased, a higher current response is observed because of an electrochemical process taking place at the Pt working electrode in the Na_2CrO_4 - Na_2SO_4 solution. An $it^{1/2}$ vs. t plot calculated from the chronoamperogram for the 8 m/o Na_2CrO_4 - Na_2SO_4 solution between the open-circuit potential and -1500 mV is shown in Fig. 40. In this potential range, the cathodic current first increased rapidly with time, then gradually approached a plateau, indicating that a diffusion-controlled electrode process was present in the system. For the chronoamperograms shown in Fig. 39, the initial potential E_1 was always the open-circuit potential. Figure 41 is the i vs. E plot for the 8 m/o Na_2CrO_4 - Na_2SO_4 melt onto which the i - E response from the pure Na_2SO_4 melt is superimposed. The abscissa E here stands for the final potential E_2 which was imposed intentionally during the experiments. Clearly, at the applied potential steps between -1200 mV and -1600 mV, the observed current response results mainly from reactions of chromium components, because in this

Figure 40 Dependence of cathodic $i t^{1/2}$ on time for 8 m/o Na_2CrO_4 in O_2 at a potential step of -1500 mV.

Figure 41 Superimposed dependence of sampled-current on applied potential steps for pure Na_2SO_4 and 8 m/o Na_2CrO_4 in O_2 . (Current sampling time $t=0.77$ sec.)

potential range the Na_2SO_4 shows very little reaction, and its current response is, therefore, very low. By extrapolating the current from pure Na_2SO_4 to more negative potentials and subtracting it from the current for the Na_2CrO_4 - Na_2SO_4 solution, a well defined limiting current can be obtained for the Na_2CrO_4 - Na_2SO_4 melt in the potential range of -1400mV to -1600mV. This proves that the reduction reaction in the Na_2CrO_4 - Na_2SO_4 system in this specific potential range is certainly diffusion-controlled. The considerable current increase beyond -1800mV in Fig. 41 is brought about by the decomposition of the supporting electrolyte, i.e., sodium sulfate.

5. DYNAMIC POLARIZATION STUDIES

Dynamic polarization studies were carried out for 3, 8, 10, 12.5, and 18 m/o Na_2CrO_4 melt in O_2 . Figures 42(a) and (b) are the polarization curves obtained from 3 and 12.5 m/o Na_2CrO_4 salts. For 8 and 10 m/o Na_2CrO_4 concentrations, the polarization behavior is very similar to that shown in Fig. 42(b). As can be seen from Fig. 42, the current-potential behavior for 3 m/o Na_2CrO_4 differs from those for higher chromate concentrations: no limiting current was found for the 3 m/o Na_2CrO_4 melt, but well defined limiting currents with magnitudes of about 220 to 370 mA/cm^2 were always

Figure 42 Cathodic polarization curves of 3 m/o and 12.5 m/o Na_2CrO_4 in O_2 at scan rate of 10 mV/sec. Open-circuit basicity 10.
(a) 3 m/o Na_2CrO_4 . (b) 12.5 m/o Na_2CrO_4 .

obtained for Na_2CrO_4 concentrations of 8 to 12.5 m/o, with the higher limiting current densities corresponding to higher chromate contents. This result correlates very well with what was found in cyclic voltammetry studies. A quantitative correlation between the limiting currents and the solution concentrations is not possible. The preparation of exactly sized working electrodes, as well as the control of leakage of fused salts through the Ceramabond cement layer on the Pt foil and even into the aluminum tube around the Pt lead wire of the working electrode were difficult to control experimentally.

Figure 43 is the i - E curve for the 18 m/o Na_2CrO_4 solution obtained at open-circuit basicity of 10.17 using a painted platinum ZrO_2 working electrode. For this high chromate concentration only two polarization curves were measured in O_2 . After the second E - i curve was recorded, which is shown in Fig. 43, the electrochemical cell apparently insulated. No more measurements could be made and the potentiostat indicated overloading for any amount of current or potential applied. During the dynamic polarization, the local basicity on the working electrode was traced. When the potential of the working electrode was forced to shift cathodically during the scan, the melt basicity

Figure 43 Cathodic polarization curve recorded by a porous Pt painted ZrO_2 working electrode in 18 m/o Na_2CrO_4 in O_2 at scan rate of 10 mV/sec and 1200 K. Open-circuit basicity 10.2.

responded by changing rapidly from the open-circuit basicity of 10.17 to 6.13 where the applied cathodic potential was approximately -1800 mV. The basicity trace for the cathodic polarization of 18 m/o Na_2CrO_4 is shown in Fig. 44. After the furnace was cooled down, the Pt painted working electrode and Ag/Ag⁺/mullite reference electrode were found surrounded by green-colored precipitates. The same precipitates were also observed in the melt around the counter electrode. These green-colored products were analyzed by X-ray diffraction and verified as a cubic chromium oxide, but the chemical formula of is unknown. According to Laubengayer and McCune(49) who first identified and reported this X-ray pattern, the cubic chromium oxide is a metastable phase at temperatures above 419-424 C, and is probably the monotropic, as is the cubic $\gamma\text{-Fe}_2\text{O}_3$, of rhombohedral Cr_2O_3 oxide. Therefore, the failure of cell after two dynamic polarization scans results from the formation of a significant amount of this low conductive chromium oxide around the electrodes and in the melt. However, this experiment does indicate that the reduction reaction in this particular melt proceeds to a greater extent due to the very high Na_2CrO_4 concentration, and a substantial precipitation of the chromium oxide occurs.

Figure 44 Superimposed basicity trace on Na-Cr-S-O phase stability diagram during dynamic polarization measurements for 18 m/o Na_2CrO_4 in O_2 at 1200 K.

Both Fig. 42 and 43 showed a well behaved Tafel region. The slope of this linear region was calculated for all three polarization curves, and the number of electrons transferred in the cathodic scan was estimated for each case. The value for α in the calculation was assumed to be 0.5. Table 8 shows the results from the Tafel slope calculation for the dynamic polarization studies of Na_2CrO_4 - Na_2SO_4 binary solutions in O_2 .

No clearly defined limiting current was appeared on the current-potential curve for the 18 m/o Na_2CrO_4 melt, probably due to the high chromate concentration. This high chromate concentration increases the amount of the reactant for the reduction reaction to a much higher level so that depletion of the reactant at the working electrode was shifted to a more negative potential where the decomposition of the Na_2SO_4 supporting electrolyte already occurred. As a result, the diffusion-controlled limiting current could not be observed.

6. REACTION MECHANISMS FOR MOLTEN Na_2CrO_4 - Na_2SO_4 SALTS IN NEUTRAL MELT IN O_2 AT 1200K

Based on the electrochemical studies of rather neutral Na_2CrO_4 - Na_2SO_4 melts in O_2 , a possible reaction mechanism for the reduction reaction at peak I_c in

TABLE 8 Cathodic Tafel Slope and Electron Transfer
Number for Na_2CrO_4 - Na_2SO_4 Solutions in O_2 Gas

Na_2CrO_4 m/o	Tafel Slope($\alpha nF/2.3RT$)	n ($\alpha=0.5$)
3.0	2.205	1.05
12.5	2.783	1.32
18.0	2.960	1.41

cyclic voltammetry and transient τ_f in chronopotentiometry is proposed as follows:

(1) In the Na_2CrO_4 - Na_2SO_4 melt, the chromate may undergo some chemical reactions and create some other chromium compounds upon equilibrium with the melt. These equilibria exist in the melt before the electrochemical study begins:

The formation of CrO_3 vapor species is favored at high temperatures in oxidizing gas environments. Reaction 26(b) is proposed because a chromium compound different than Na_2CrO_4 is believed to be the electroactive species reducible at the potentials for peak I_c . The formation of CrO_4^{3-} thus explains the dependence of the peak I_c on the decomposition of the supporting electrolyte, Na_2SO_4 , and the lack of cathodic response for lower Na_2CrO_4 additions, less than 3 m/o. These reactions take place in the melt before the electrochemical studies get started.

(2) During cathodic scanning, a reversible one electron transfer reduction takes place and is followed by a very fast irreversible succeeding chemical reaction:

(reversible cathodic reduction reaction)

(irreversible chemical reaction)

The formation of Cr_2O_3 was verified by X-ray diffraction analysis. The release of oxide ions by reaction 27(b) explains the experimentally observed shift in melt basicity during cathodic scans. This succeeding chemical reaction is irreversible and takes place at a very fast rate, so that the reoxidation peak for CrO_3^{2-} to CrO_4^{3-} is virtually unobservable in the reverse scan. The oxide ions formed in reactions 27(a) and (b) will recombine with CrO_4^{2-} ions to form more CrO_4^{3-} species via Eq. 26(b). Other chemical reactions may also occur, consuming more oxide ions. For example, O_2^{2-} ions may be formed by reacting with oxygen gas:

The exact reaction mechanisms at the anodic peak V_a in the Na_2CrO_4 - Na_2SO_4 system could not be deduced from the present studies. But the substantial reduction in peak height for peak V_a , which is considered as the oxidation of O^{2-} to O_2^{2-} for Na_2SO_4 , does indicate that the preceding chemical reaction for peak V_a in the Na_2CrO_4 - Na_2SO_4 binary melt, must be a reaction between the O^{2-} ions and some chromium component. Thus the O^{2-}

ions are largely consumed by the chemical reaction so that the O^{2-} O_2^{2-} peak will virtually disappear in the presence of chromate additions:

(preceding chemical reaction)

(oxidation of R)

Reactions at peak IV_a and III_a are still considered to be the oxidation of O_2^{2-} ions and O_2^- ions, as were proposed for the pure Na_2SO_4 melt, because only minor changes are observed for these two peaks after introducing Na_2CrO_4 into the system. Apparently, the existence of O_2^{2-} and/or O_2^- ions in the melt is not affected much by the chromate additions. The O_2^{2-} ions will be present in the melt via the equilibrium between the O^{2-} ions and oxygen gas:

The proposed oxidation reactions for peaks IV_a and III_a are given below:

The proposed reaction mechanisms fit very well the results of electrochemical studies for Na_2CrO_4 - Na_2SO_4 melt in O_2 gas.

VI RESULTS AND DISCUSSION

ELECTROCHEMICAL STUDIES OF Na_2CrO_4 - Na_2SO_4 MELT IN BASIC CONDITIONS

To examine the dependence of the reaction mechanism on melt basicity, the electrochemical behavior of the Na_2CrO_4 - Na_2SO_4 binary was also studied under basic melt conditions, with $-\log a_{\text{Na}_2\text{O}}$ varying from about 6.0 to 7.5. The Na_2CrO_4 bulk concentrations under these basic conditions were varied from 3, 8, to 10 m/o. The open-circuit potentials for all the melts studied in the basic conditions are in the Na_2CrO_4 phase stable region. The electrochemical techniques used for the study consisted of cyclic voltammetry, chronopotentiometry, chronoamperometry, and dynamic polarization.

1. CYCLIC VOLTAMMETRY STUDIES

Figure 45(a) is a cyclic voltammogram for pure Na_2SO_4 in a basic melt with $-\log a_{\text{Na}_2\text{O}} = 6.66$. Compared

Figure 45 Cyclic voltammograms of pure Na_2SO_4 and 3 m/o Na_2CrO_4 in basic condition. (a) Na_2SO_4 in the potential range of -2130 mV to 750 mV at 40 mV/sec and 1173 K, melt basicity 6.66. (b) 3 m/o Na_2CrO_4 in the potential range of -2250 mV to 435 mV at 20 mV/sec and 1200 K, melt basicity 6.31.

to that in O_2 gas where the basicity was 10.1, there are a couple of new cathodic peaks seen for this condition: one peak is at the potential of about -410 mV (peak 1), and the other, -1600 mV (peak 2). The electrochemical reactions at these two peak potentials were interpreted by Nava as follows (19):

Figures 45(b) to 46 are cyclic voltammograms obtained in basic conditions for Na_2CrO_4 - Na_2SO_4 binaries with 3, 8, and 10 m/o Na_2CrO_4 bulk concentrations. The open-circuit melt basicity and the scan rate for each of these melts are specified in the respective Figures. Only one cathodic peak (peak I_C) appears at a potential of about -1420 to -1450 mV. the cathodic peak 1 at -410 mV for Na_2SO_4 melt was virtually missing. Because the height for this cathodic peak is very small, it is likely that the disappearance of peak 1 in the cyclic voltammograms for Na_2CrO_4 - Na_2SO_4 solutions simply results from differences in experimental conditions employed; the current scale used for the Na_2SO_4 melt is 4 times more sensitive than that for the Na_2CrO_4 - Na_2SO_4 solutions, and the anodic switching potential adopted for the Na_2SO_4 was more than 200 mV more positive than those for the binary salts. Figure 47 is another cyclic

Figure 46 Cyclic voltammograms of 8 m/o and 10 m/o Na_2CrO_4 in basic condition at 1200 K. (a) 10 m/o Na_2CrO_4 in the potential range of -2320 mV to 400 mV at 20 mV/sec and basicity of 7.10. (b) 8 m/o Na_2CrO_4 in the potential range of -2340 mV to 500 mV at 50 mV/sec and basicity of 6.80.

Figure 47 Cyclic voltammogram of Na_2SO_4 in the potential range of -2200 mV to 780 mV at 20 mV/sec and 1173 K, melt basicity 6.66 (19).

Figure 48 Cyclic voltammogram of 10 m/o Na_2CrO_4 in the potential range of -1950 mV to 700 mV at 80 mV/sec and 1200 K, melt basicity 7.6.

voltammogram for pure Na_2SO_4 with a less sensitive current scale. The small cathodic peak 1, in this case, was not observed. On the other hand, however, when a higher anodic potential limit and a higher sensitivity of current are used for the binary solution, a cathodic peak at about -180 mV does appear (Fig. 48). This peak is considered to be the same as peak 1 for Na_2SO_4 based on the following reasons:

1. They both appeared after the anodic decomposition of the Na_2SO_4 supporting electrolyte.
2. About one order of difference in melt basicity existed for these two measurements. The cyclic voltammogram shown in Fig. 45 for pure Na_2SO_4 was obtained in a melt basicity of 6.66, while that shown in Fig. 48 for the chromate-sulfate solution was measured for the melt basicity of 7.6.

Since the chemical species O_2 involved in the reaction at peak 1 is also in equilibrium with O^{2-} ions in the melt via the reaction $1/2 \text{O}_2 + \text{O}^{2-} = \text{O}_2^{2-}$, it is quite understandable that as the melt basicity changes, the reaction potential will also be changed. In this particular case, a decrease in melt basicity will shift the peak potential anodically.

Peak 2 of Fig. 45 at -1600 mV did not appear in

cyclic voltammograms for the chromate-sulfate solutions either. This peak must result from some kind of chemical reactions between the O_2^- ions produced at peak 1 and the product from the reaction at peak I_c . This latter reaction occurs at a potential more anodic than -1600 mV, which considerably decreases the available O_2^- species for the successive reduction reaction at peak 2.

To verify that the peak I_c designated in cyclic voltammograms of Na_2CrO_4 - Na_2SO_4 solutions does arise from Cr-species, a series of cyclic voltammetric scans with different cathodic switching potentials were recorded for both pure Na_2SO_4 and 8 m/o Na_2CrO_4 . The results are shown in Fig. 49, where plots (a) are for pure Na_2SO_4 , and plots (b) are with chromate additions. Although the scale used for recording the current response for Na_2SO_4 is more than 5 times more sensitive than that for the Na_2CrO_4 - Na_2SO_4 solution, a well defined cathodic peak can be observed for 8 m/o Na_2CrO_4 at about -1500 mV in Fig. 49(b), but no such peak can be found for pure Na_2SO_4 even at -1600 mV in Fig. 49(a).

A very shallow anodic peak IV_a' at about -1100 mV is revealed when the scanning potential is switched to anodic for the 8 m/o Na_2CrO_4 solution in Fig. 49(b). This anodic peak becomes better developed when the scan

Figure 49 Cyclic voltammograms of pure Na_2SO_4 and Na_2CrO_4 - Na_2SO_4 solutions in a series of cathodic switching potentials in basic condition. (a) Na_2SO_4 at 1173 K and 40 mV/sec. (b) 8 m/o Na_2CrO_4 at 1200 K and 50 mV/sec. (c) 10 m/o Na_2CrO_4 at 1200 K and 80 mV/sec.

rate is increased. Figure 49(c) is a cyclic voltammogram for 10 m/o Na_2CrO_4 in the potential range of -1610 mV to 375 mV at a scan rate of 80 mV/sec and a melt basicity of 6.8. Since the chosen potential range eliminates the decomposition and/or reaction from the background electrolyte, the anodic peak IV_a' observed at about -1100 mV is then clearly the reoxidation of the products produced at peak I_c in the cathodic scan. The dependence on scan rate of this anodic peak results from the following chemical reaction coupled with the cathodic charge transfer process. When a higher scan rate is employed, less time will elapse before the potential is switched to the anodic direction, so that the chemical reaction can only consume a smaller amount of the reduction reaction products, and hence, more species will be available for the reoxidation process. Experimentally, because this anodic peak IV_a' occurs in essentially the same potential range as peak IV_a of pure Na_2SO_4 , it is difficult to differentiate and analyze peak IV_a' of Na_2CrO_4 in further detail.

There is a noticeable shift (about 100 mV) in peak potential for peak I_c in Na_2CrO_4 - Na_2SO_4 solutions upon a change in basicity of the melt. Considering the 8 m/o Na_2CrO_4 - Na_2SO_4 solution as an example. For the same scan range of -2330 mV to +540 mV and the same scan rate

of 120 mV/sec, the peak potential in the more basic melt ($-\log a_{\text{Na}_2\text{O}} = 6.8$) occurs at -1410 mV, while that in the less basic melt ($-\log a_{\text{Na}_2\text{O}} = 9.5$) appears at -1585 mV. This potential shift is also understandable if an equilibrium involving the reactants for peak I_C with O^{2-} ions is considered.

Another noticeable change in the peak I_C is that this peak for 3 m/o Na_2CrO_4 melt is much better defined in the basic condition than in neutral melt in O_2 gas. A cathodic peak at the potential for peak I_C is showed in Fig. 46, but no such peak can be observed in Fig. 19. Obviously, the amount of the reducible components is quite dependent upon the basicity of the melt. With a higher melt basicity, the concentration of the reducible species will be increased, so a higher peak current, or a better developed cathodic peak will be observed. This change is consistent with the reaction mechanism for the reduction of Na_2CrO_4 in Na_2SO_4 melt proposed later here, where a chemical equilibrium of the CrO_4^{2-} ions with O^{2-} in the melt takes place before electrochemical measurements to form the electroactive species CrO_4^{3-} which is reducible at potentials of peak I_C :

With an increase in melt basicity, the above equilibrium

will shift to the right-hand side where more CrO_4^{3-} species can be formed. Thus, for a given Na_2CrO_4 concentration, more reactants for the reduction reaction at peak I_C will be present in the system when the melt basicity is made more basic.

The dependence of the cathodic peak I_C on the cathodic and anodic switching potentials were studied in basic melt. As for the less basic melt discussed in Chapter V, no influence of these switching potentials on the peak potential E_p was observed. Although there was some increase in peak current with an increase in cathodic E_λ , compared with what was observed in neutral melt in O_2 gas, the influence of cathodic switching potential on peak current for peak I_C in the basic melt was much smaller. Probably there were excess oxide ions present in the basic melt to react with CrO_4^{2-} ions and produce sufficient electroactive CrO_4^{3-} species for the cathodic process. Therefore, the decomposition reaction of sulfate at the cathodic E_λ to form O^{2-} ions became relatively less important to peak I_C in basic conditions.

The anodic peaks in the more basic melts are essentially the same as those in the less basic melts, except that peak III_a is almost missing, while the peak

currents for peaks IV_a and V_a are much enhanced. Table 9 shows the comparison between two different melt basicities for peak V_a and 8 m/o Na_2CrO_4 .

TABLE 9 COMPARISON OF CHARACTERISTICS OF PEAK V_a
FOR 8 m/o Na_2CrO_4 IN NEUTRAL MELT IN O_2 AND IN
BASIC MELT

Cathodic E (mV)	$-\log a_{Na_2O}=9.5$	$-\log a_{Na_2O}=6.8$
-2270	Disappeared at 50 mV/sec.	Observable for scan rate of 120 mV/sec.
-2340	A trace of the peak observable at the scan rate of 120 mV/sec.	Very clearly defined up to scan rate of 200 mV/sec.

As was discussed in the previous chapter, the electroactive species oxidized at peak V_a are believed to be formed by a chemical reaction with O^{2-} ions produced at the cathodic limit II_c . This conclusion is now very well demonstrated by the experimental results listed in Table 9. For the basic melt, there are more oxide ions present in the solution, thus the chemical reaction to form the oxidizable species for peak V_a will be considerably enhanced. As a result, the anodic peak

V_a is much better defined, and its dependence on scan rate and on negative switching potential becomes less pronounced.

The increase in peak current for peak IV_a with the increase in melt basicity is also expected. Generally, for a given melt, all the oxygen-related species in different valence states in the system are considered to be in equilibrium with each other. For the Na_2CrO_4 - Na_2SO_4 solution, the different oxygen species include O^{2-} , O_2^{2-} , and O_2^- ions, O atoms in the melt, and dissolved O_2 gas. The equilibria between these oxygen-related species can be represented by the equation:

$$[O_x^{-Y}] = f(P_{O_2}) \quad (36)$$

From the phase stability diagram shown in Fig. 2, for a given potential on the working electrode, when the concentration of O^{2-} ions is increased, the equilibria with other oxygen components will all shift in such a way that components such as O_2^{2-} ions will increase their concentrations as well. Thus, if these oxygen species are responsible for the reactions at a cathodic and/or anodic peak, the peak current for this specific peak will also be increased. Since the reaction at peak IV_a is the oxidation of O_2^{2-} ions, the enhancement in peak height for peak IV_a in basic conditions is therefore quite understandable.

The disappearance of peak III_a in basic conditions can be explained by taking into account its peak potential. In pure Na₂SO₄, this peak appeared at about 0 mV, but for Na₂CrO₄-Na₂SO₄ solutions, the decomposition peak I_a had already appeared at this potential. Therefore, these two peaks could simply be merged together.

The characteristics of the cathodic peak I_c in the basic melt condition were also evaluated. Figures 50(a) and (b) are plots of the change in peak currents with scan rate for the 8 m/o Na₂CrO₄ melt. A very good linear relationship is obtained when peak current is plotted against the square root of scan rate, but no such linear behavior is revealed when the scan rate is plotted directly. This indicates that the electrode process detected at peak I_c is still diffusion-controlled. The same results were obtained for 3 m/o and 10 m/o Na₂CrO₄-Na₂SO₄ solutions. Figures 51(a) and (b) are the current vs. $v^{1/2}$ plots for 3 and 10 m/o Na₂CrO₄, respectively.

Following the same procedures as in neutral melt and in O₂ gas, the dependence of current function ($i_p/v^{1/2}$) on scan rate for the cathodic peak I_c in basic melt was also calculated. As shown in Fig. 52(a) and

Figure 50 Proportionality of peak current to scan rate for peak I_c of 8 m/o Na_2CrO_4 in basic condition. (a) Peak current vs. square root of scan rate. (b) Peak current vs. scan rate.

Figure 51 Proportionality of peak current to square root of scan rate for peak I_c in basic conditions. (a) 10 m/o Na_2CrO_4 . (b) 3 m/o Na_2CrO_4 .

(b), the same behavior as was in neutral melt for peak I_C is observed in the basic melt. Furthermore, $\Delta E_{p/2}/\Delta \log v$ vs. v plots for 3 and 10 m/o Na_2CrO_4 in the basic melt as shown in Fig. 53(a) and (b) display a gradual increase in the $\Delta E_{p/2}/\Delta \log v$ term with the rise in scan rate, and thus indicate that essentially the same electrode process can be presumed for the reaction at peak I_C in the basic melt as in the O_2 gas.

The basicity trace measured for 8 m/o Na_2CrO_4 in cyclic voltammetry studies is shown in Fig. 54. Different from that obtained in O_2 gas, there is a small change (about 0.62) in melt basicity during the cathodic scan. No buffering effect resulting from a redox reaction is observed. In Fig. 54, the basicity change corresponding to the cathodic reaction at peak I_C is designated by a segment of thicker solid line, which lies essentially in the region of chromite stability. As is discussed previously, the reaction mechanism for peak I_C is presumably the same as was proposed in O_2 gas. Thus, in order to explain the observed basicity trace, a reaction between the O^{2-} ions produced in the cathodic reaction with some other components in the system must be considered. Such a chemical reaction is proposed as follows:

Figure 52 Dependence on scan rate of the current function of peak I_c for 3 m/o and 10 m/o Na_2CrO_4 in basic conditions.
 (a) 3 m/o Na_2CrO_4 . (b) 10 m/o Na_2CrO_4 .

Figure 53 Rate of shift of half peak potential as a function of scan rate for peak I_c of 3 m/o and 10 m/o Na_2CrO_4 in basic condition. (a) 3 m/o Na_2CrO_4 . (b) 10 m/o Na_2CrO_4 .

Figure 54 Phase stability diagram with superimposed melt basicity trace on working electrode surface during cyclic voltammetry measurements for 8 m/o Na_2CrO_4 at 1200 K. Thicker solid line standing for peak I_C .

where O^{2-} is the oxide ion formed in the cathodic process, and O_2^- is formed by reduction of O_2 at peak 1. Because of this chemical reaction, the basicity of the melt will be kept approximately constant and the O_2^- ions will be consumed before reaching the potential for peak 2 where the reduction reaction of O_2^- to O_2^{2-} will take place. As a result, the disappearance of peak 2 after introducing Na_2CrO_4 into the system as well as the relative constancy in basicity trace can be explained.

Solid precipitates were found after 3 m/o Na_2CrO_4 experiments both on Pt foil working electrode beneath the Ceramabond cover layer as well as around the Pt lead wire of the working electrode inside the alumina tube. Microscopic examination showed that the precipitates were a single phase compound, and semi-quantitative SEM analysis suggested the compound $NaCrO_2$, which is consistent with the basicity trace recorded during cyclic voltammetry scan for the Na_2CrO_4 - Na_2SO_4 melt in the basic conditions.

2. CHRONOPOTENTIOMETRY STUDIES

Chronopotentiometry measurements were also performed for the Na_2CrO_4 - Na_2SO_4 solutions under basic conditions to determine the reversibility and the charge transfer number of the reactions. Figures 55(a), (b),

(a)

(b)

Figure 55 Chronopotentiograms of 3 m/o and 8 m/o Na_2CrO_4 in basic condition at 1200 K (open-circuit melt basicity 6.7). (a) 3 m/o Na_2CrO_4 with 250 mA applied current. (b) 8 m/o Na_2CrO_4 with 300 mA applied current.

Figure 56 Chronopotentiograms of 10 m/o Na_2CrO_4 and pure Na_2SO_4 in basic condition. (a) 10 m/o Na_2CrO_4 with 400 mA applied current at 1200 K and basicity of 7.6. (b) Na_2SO_4 with 120 mA applied current at 1173 K and basicity of 6.66 (19).

and Fig. 56(a) are the chronopotentiograms recorded from a Pt working electrode immersed in 3, 8, and 10 m/o Na_2CrO_4 - Na_2SO_4 solutions, respectively, for the melt basicity of about 6.5 to 7.5. The constant current applied is specified in the corresponding chronopotentiogram.

For the basic melt, the chronopotentiograms are also very similar to those obtained for the neutral melt in O_2 gas. The forward cathodic transition occurred between the potential range of -1250 mV and -1430 mV, and above that, the decomposition of the Na_2SO_4 background electrolyte began. Figure 56(b) is a chronopotentiogram of pure Na_2SO_4 in a melt with basicity of 6.66, the applied current in this case is 120 mA. As can be seen, for Na_2SO_4 , no forward transition appeared in the first cycle, and no forward transition was observed in the second cycle until the potential reached about -1650 mV.

Figures 57(a), (b) and 58(a), (b) are the E vs. $\ln[(\tau^{1/2}-t^{1/2})/t^{1/2}]$ plots for chronopotentiograms shown in Fig. 55(a) and (b), and 56(a). The linear regression parameters are, 0.998, 0.995, and 0.999, respectively. The number of electrons transferred calculated from these plots is between 0.92 to 1.10,

Figure 57 Plots of chronopotentiometric data according to Eq. (20) for τ_f of 3 m/o and 10 m/o Na_2CrO_4 shown in Fig. 55(a) and 56(a). (a) 3 m/o Na_2CrO_4 . (b) 10 m/o Na_2CrO_4 .

(a)

(b)

Figure 58 Plots of chronopotentiometric data according to Eq.(20) and (21) for τ_f of 8 m/o Na_2CrO_4 shown in Fig. 55(b). (a) Plot according to Eq. (20). (b) Plot according to Eq. (21).

normalized as 1. As a comparison, the E vs. $\log(\tau^{1/2} - t^{1/2})$ plot for the irreversible relation for 8 m/o Na_2CrO_4 melt is also shown in Fig. 58(b), where a poor linearity is obtained. By following the same arguments that a good linear fit to the potential-time equation is obtained for reversible behavior, that the apparent n value calculated for a range of current does not decrease with increase in current, and that the quarter-wave potential $E_{\tau/4}$ obtained from the $E - \log[(\tau^{1/2} - t^{1/2})/t^{1/2}]$ plots is not changed with current for a given chromate concentration, the conclusion can be drawn that the reduction reaction is a reversible charge transfer process and the number of electron transferred in the reduction reaction is one.

Figure 59 is the $i\tau^{1/2}$ vs. i plot for the forward transition for 8 m/o Na_2CrO_4 in the basic melt. The current was varied from 50 mA to 500 mA. The rise in $i\tau^{1/2}$ with current at higher i values indicates the presence of adsorption associated with the charge transfer process.

The quarter-wave potentials $E_{\tau/4}$ calculated for the reduction reaction at different chromate concentrations are listed in Table 10, where the voltammetry half-wave potentials calculated from cyclic voltammetry studies

Figure 59 Dependence of $i\tau^{1/2}$ on current for τ_f of 8 m/o Na_2CrO_4 in basic condition.

for the corresponding melts are also given. Very good agreement is achieved between the chronopotentiometry and the cyclic voltammetry measurements.

TABLE 10 CALCULATED $E_{\tau/4}$ FROM CV AND
CHRONOPOTENTIOMETRY STUDIES FOR Na_2CrO_4 - Na_2SO_4 SOLUTIONS
AT 1200 K

Na_2CrO_4 m/o	$E_{1/2}$ FROM CV ($E_{1/2} = E_{p/2} - 1.09(RT/nF)$) (Volt)	$E_{\tau/4}$ FROM CHRONOPOTENTIOMETRY (Volt)
3	-1.39 ± 0.01	-1.42 ± 0.02
8	-1.31 ± 0.02	-1.30 ± 0.02
10	-1.29 ± 0.01	-1.29 ± 0.01

The backward transitions observed in the basic melts are essentially the same as those in O_2 . The transitions τ_{b3} and τ_{b4} are still present, and the calculation for τ_{b3} confirms that the same reversible, one-electron anodic reaction is taking place at this potential range as in the less basic neutral melt in O_2 , i.e.,

Comparison between the chronopotentiograms obtained for 8 m/o Na_2CrO_4 solution at two different melt basicities with the same applied current (300 mA) shows that the

backward transition τ_{b3} in the basic melt is much more pronounced than that in the neutral melt equilibrated with O_2 (see Fig. 33(b) and Fig. 55(b)). This increase in transition time τ_{b3} with melt basicity is consistent with the increase in anodic peak current for peak IV_a in the cyclic voltammogram. On the other hand, the much lower τ_{b4} value obtained in chronopotentiometry in the basic melt also agrees with the fact that the peak III_a in cyclic voltammetry is virtually missing in the basic melt.

The ratio of the forward to backward transition times calculated for all three chromate concentrations is higher than 4, indicating the presence of a following chemical reaction for the cathodic charge transfer process.

The behavior of the transition τ_{b1} in the basic melt was also tested. Figure 60 shows the chronopotentiogram recorded by a Pt foil working electrode immersed in an 8 m/o Na_2CrO_4 - Na_2SO_4 solution at a basicity of 6.1 with 400 mA applied current. In the first cycle, the current was kept at -2160 mV for about 2.4 seconds. When the current was reversed, no transition was observed in the potential range of -2000 mV to -1800 mV. After maintaining the cathodic current

Figure 60 Chronopotentiogram of 8 m/o Na_2CrO_4 with 400 mA applied current in basic condition ($-\log a_{\text{Na}_2\text{O}}=6.3$), 1200 K.

at -2160 mV for a longer time, a very well developed transition τ_{b1} showed up upon current reversal. For the chronopotentiogram in the second cycle of Fig. 60, the cathodic current was reversed after 12.4 seconds at -2160 mV where the decomposition of the supporting electrolyte Na_2SO_4 took place. Experimentally, at this melt basicity of 6.1, about 5 seconds of electrolysis of the fused salt solution at the Na_2SO_4 decomposition potential is needed for the 400 mA applied current in order to obtain a backward transition τ_{b1} when the applied current is reversed. Similar tests in the neutral melt equilibrated with oxygen demonstrated that an electrolysis time exceeding 9 seconds at this decomposition potential was necessary for an applied current of 400 mA in order to acquire a fairly well characterized τ_{b1} . This time difference again supports the model for the reaction at peak V_a that there is a preceding chemical reaction involving oxide ions taking place before the charge transfer process at this potential range. The lesser dependence for the reaction on melt decomposition in the basic melt is attributed to the presence of a relatively higher content of oxide ions in the solution. This observation also matches the results from cyclic voltammetry studies where a less pronounced dependence of peak V_a on the cathodic

switching potential and scan rate was obtained for the basic melt conditions.

3. CHRONOAMPEROMETRY AND DYNAMIC POLARIZATION STUDIES

Chronoamperometry and dynamic polarization techniques were applied to the Na_2CrO_4 - Na_2SO_4 system in the basicity range of 6.3 to 7.3 at 1200 K. The results are given in Fig. 61 to Fig. 65.

Figure 61 is the superimposed chronoamperograms of 8 m/o Na_2CrO_4 for a series of applied potential steps. All the measurements were started at open-circuit potential of the system. As the potential step is increased from -1400 mV to -1500 mV, the maximum current on the current-time curve is also increased. This maximum current value does not change significantly when the potential step is raised from -1500 mV to -1600 mV. The relatively constant cathodic current in the potential range of -1500 mV to -1600 mV corresponds to the reduction reaction for the chromate-sulfate solution at peak I_c . A considerable increase in current is observed when the applied potential step is changed to -1800 mV, indicating the beginning of electrolysis of the background electrolyte. Figure 62 illustrates the superimposed current-potential response of pure Na_2SO_4 and 8 m/o Na_2CrO_4 solution for a series of

Figure 61 Superimposed chronoamperograms of 8 m/o Na_2CrO_4 in basic condition at different potential steps at 1200 K.

Figure 62 Superimposed sampled-current voltammograms of pure Na_2SO_4 at 1173 K (19) and 8 m/o Na_2CrO_4 at 1200 K in basic condition (current sampling time $t=0.77$ sec.).

chronoamperometry experiments in basic conditions. Compared with the current response from pure Na_2SO_4 , for potentials up to -1800 mV, the i value from the Na_2CrO_4 - Na_2SO_4 solution is much higher, demonstrating that the cathodic response obtained from cyclic voltammetry in this potential range does result from Cr-species. The lack of a very clearly defined constant current region on the i - E plot in Fig. 62 for 8 m/o Na_2CrO_4 can be contributed to the noticeable amount of current resulting from the electrolysis of the background electrolyte, Na_2SO_4 . Figures 63(a) and (b) are plots of the $it^{1/2}$ dependence on time for 8 m/o and 10 m/o Na_2CrO_4 in basic conditions, respectively. A very well defined plateau is present for both figures for a longer electrolysis time, indicating that the reaction taking place in this potential range for both chromate concentrations is diffusion-controlled.

Figures 64 and 65 are the dynamic polarization curves for 3, 8, and 10 m/o Na_2CrO_4 - Na_2SO_4 solutions for basic melt conditions. As a comparison, the polarization curve for pure Na_2SO_4 at a similar melt basicity is superimposed in Fig. 64 (a) and (b). No limiting current is revealed by the current-potential response for pure Na_2SO_4 in the studied potential range, but a limiting current between -1400 mV and -1600 mV can

Figure 63 Dependence of cathodic $it^{1/2}$ on time for 8 m/o Na_2CrO_4 and 10 m/o Na_2CrO_4 in basic condition. (a) 8 m/o Na_2CrO_4 at potential step of -1400 mV. (b) 10 m/o Na_2CrO_4 at potential step of -1600 mV.

Figure 64 Superimposed cathodic polarization curves of pure Na_2SO_4 (at 1173 K and 1 mV/sec) (19) and Na_2CrO_4 - Na_2SO_4 solutions (at 1200 K and 10 mV/sec) in basic conditions. (a) Na_2SO_4 and 3 m/o Na_2CrO_4 . (b) Na_2SO_4 and 10 m/o Na_2CrO_4 .

Figure 65 Cathodic polarization curve of 8 m/o Na_2CrO_4 in basic condition at 10 mV/sec in the potential range of -700 mV to -2300 mV at 1200 K.

be found for both the 3 m/o and 10 m/o Na_2CrO_4 solutions. Figure 65 is the polarization curve for 8 m/o Na_2CrO_4 obtained by extending the cathodic potential to -2300 mV. The considerable increase in current after about -2100 mV signifies the decomposition of sodium sulfate supporting electrolyte.

The Tafel slope and the number of electrons transferred for all three polarization curves of Na_2CrO_4 - Na_2SO_4 were calculated, and the results are given in Table 11. In the calculation, the α value was chosen to be 0.5, which is the same as that used in calculations of the n value for the less basic melts discussed in the previous chapter.

TABLE 11 CATHODIC TAFEL SLOPE AND ELECTRON TRANSFER NUMBER FOR Na_2CrO_4 - Na_2SO_4 SOLUTIONS IN BASIC CONDITION

Na_2CrO_4 (m/o)	Tafel Slope ($\alpha nF/2.3RT$)	n ($\alpha=0.5$)
3.0	2.921	1.39
8.0	2.819	1.34
10.0	3.017	1.43

In summary, the chronoamperometry and dynamic

polarization experiments confirm the results obtained from cyclic voltammetry and chronopotentiometry measurements, and therefore can be used as support for the reaction mechanisms for the Na_2CrO_4 - Na_2SO_4 solutions in the basic condition, to be presented now.

4. REACTION MECHANISM FOR PEAK I_C

Based on the experimental results from several different solution compositions, the following reaction mechanisms can be deduced for the cathodic reaction at peak I_C for the Na_2CrO_4 - Na_2SO_4 solutions.

I. A chemical equilibrium exists between the chromate ions CrO_4^{2-} and the oxide ions O^{2-} in the system before the electrochemical measurements:

The product (CrO_4^{3-}) generated by reaction (39) supplies the electroactive species reducible in the potential range within which the peak I_C is observed. The presence of reaction (39) in the neutral melt in O_2 was demonstrated in Chapter V by the fact that electrochemical response was absent for Na_2CrO_4 additions of less than 3 m/o. The essential features of the electrochemical behavior are still the same in the basic conditions as they were in the neutral melt in O_2 ,

and the peak I_C and the forward transition time τ_f obtained from the cyclic voltammograms and the chronopotentiograms for the 3 m/o Na_2CrO_4 solution are still not very well developed in the basic solution when compared with higher chromate concentrations. However, it is reasonable to consider that the same chemical equilibrium existed in the system before any electrochemical studies are performed. On the other hand, since there are more oxide ions in the melt in the basic condition than in the neutral condition discussed in the previous chapter, the content of the electroactive species CrO_4^{3-} produced by reaction (39) will be higher in the basic melt for any given CrO_4^{2-} concentration. Experimentally, a shallow peak I_C was obtained for 3 m/o Na_2CrO_4 in the basic condition upon cathodic polarization, but no such peak was observable for the same melt composition in the neutral melt in O_2 gas. Enhancement in the peak current of peak I_C for 8 m/o and 10 m/o Na_2CrO_4 in the basic conditions also occurred.

II. The electrochemical reaction at the potential range of peak I_C is a reversible, one electron-transfer reaction followed by an irreversible chemical reaction. The basicity change during the cathodic process is small but the solution becomes more basic:

The electroactive species CrO_4^{3-} is reduced to CrO_3^{2-} according to reaction (40) at potentials of peak I_c . In this reversible charge transfer step, the Cr^{5+} is converted to Cr^{4+} by receiving one electron, and the reaction is accompanied by a release of an oxide ion for each CrO_3^{2-} ion generated. The irreversible following chemical reaction in the basic melt is different from that in the neutral melt. No chromium oxide precipitates were observed in the basic melt, and the basicity trace recorded in cyclic voltammetry during cathodic polarization passes through the stability field of NaCrO_2 .

The NaCrO_2 precipitates were found from the working electrode after electrochemical studies in basic melt. The CrO_3^{2-} ions produced in reaction (40) is consumed by this following chemical reaction so that the reoxidation of CrO_3^{2-} to CrO_4^{3-} cannot be detected as a well defined anodic peak as the applied potential is reversed.

To explain the absence of peak 2 after introducing chromate solutes into fused sodium sulfate, a chemical reaction is proposed in which the oxide ions will combine with the O_2^- ions formed at peak 1 as is given

by reaction (37):

Both the oxide ions O^{2-} and the superoxide ions O_2^- will be consumed in reaction (42). From a combination of reactions (39) through (42), the net change in the system is:

There is a release of one oxide ion in the cathodic process, which accounts for the observed small but positive change in the melt basicities.

No electrochemical reaction involving the reduction of SO_4^{2-} species are observed until the cathodic limit II_c is reached where the decomposition of Na_2SO_4 melt takes place. The lack of electrochemical response from the CrO_4^{2-} species is verified by the fact that no electrochemical process can be detected for the Na_2CrO_4 additions of less than 3 m/o. No direct reduction of Na_2CrO_4 to NaCrO_2 is observed from the present experiments, only one reduction peak with one electron transfer is detected for the Na_2CrO_4 - Na_2SO_4 solutions in basic melt conditions.

VII. RESULTS AND DISCUSSION

ELECTROCHEMICAL STUDIES OF 8 m/o Na_2CrO_4 - Na_2SO_4 SOLUTION IN ACIDIC CONDITION

To compare and contrast the electrochemical behavior of Na_2CrO_4 at different melt basicities, the 8 m/o Na_2CrO_4 - Na_2SO_4 solution was also studied in acidic condition at $-\log a_{\text{Na}_2\text{O}} = 15.3$ to 16. The melt basicity was very close to the minimum solubility of Cr_2O_3 at 1 atm oxygen pressure. According to Zhang's solubility measurements (16), the chromium oxide will dissolve in Na_2SO_4 as Cr^{3+} ions in this acidic condition while the chromate solutes are less soluble in the Na_2SO_4 melt. The electrochemical techniques employed included cyclic voltammetry, chronopotentiometry, chronoamperometry, and dynamic polarization. A 1 % SO_2 - O_2 gas mixture was used together with the coulometric titration to achieve the desired high acidity of the melt. After about 48 hours, the applied titrating potential was removed, and the system was closed to the introduction of gas. The melt

was then left to equilibrate with the gas phase in the system until a stable melt basicity was attained. As was done for the neutral melt in O_2 gas, as well as in the basic melt, all the experiments in the acidic condition were started from the open-circuit potential of the melt. Because no experiments of pure Na_2SO_4 background electrolyte have been conducted near this acidic condition, only a brief presentation and discussion of the results of electrochemical studies of Na_2CrO_4 can be given here.

1 CYCLIC VOLTAMMETRY STUDIES

Figure 66 presents superimposed cyclic voltammograms for 8 m/o Na_2CrO_4 in a potential range of -1520 mV to +1200 mV at various scan rates. The open-circuit basicity of the melt was about 16. No clearly defined cathodic peak appeared in this potential range at lower scan rate of 20 mV/sec within the Na_2SO_4 decomposition limits. When the scan rate is increased, however, a well developed cathodic peak similar to the peak I_C in basic and neutral melt conditions appeared at a potential of about -870 mV. For up to a scan rate of 200 mV/sec, the dependence of the current function ($i_p/v^{1/2}$) and the rate of shift of half-peak potential on scan rate is random and cannot be fitted into the

Figure 66 Superimposed cyclic voltammograms of 8 m/o Na_2CrO_4 in a potential range of -1520 mV to 1200 mV at various scan rates at 1200 K. Open-circuit basicity 16.

reaction mechanisms given by Nicholson and Shain's criteria (36). Because this peak only appeared at higher scan rate, it probably results from a strong adsorption process.

The lack of a well developed cathodic peak for 8 m/o Na_2CrO_4 in acidic condition at lower scan rate is consistent with the reaction mechanism proposed for the Na_2CrO_4 - Na_2SO_4 solution in O_2 and in basic condition, where the electroactive species CrO_4^{3-} reducible at potentials of peak I_C are formed via chemical reaction between the CrO_4^{2-} and oxide ions. Since the content of the oxide ions in acidic melt is very low, the amount of the species would be too little to be detected even for a 8 m/o Na_2CrO_4 solution.

At higher scan rates no obvious dependence of the cathodic peak on anodic and/or cathodic switching potentials was observed.

The basicity trace recorded from a Pt painted ZrO_2 electrode immersed in this acid melt during cyclic voltammetry measurements is shown in Fig. 67. The scan rate was 50 mV/sec, and the very wide potential range scanned was from -1910 mV to +980 mV. Both iso- P_{SO_2} lines and constant $E(\text{Ag}/\text{Ag}^+)$ lines are plotted onto the diagram so that an idea of the chemical status of the

Figure 67 Phase stability diagram with superimposed trace of melt basicity on working electrode surface during cyclic voltammetry for 8 m/o Na_2CrO_4 in acidic condition at 1200 K.

working electrode during the cyclic voltammetry sweep can be obtained. As is shown in Fig. 67, the melt basicity is constant during the potential sweep, and the recorded trace follows a vertical line on the Na-Cr-S-O phase diagram. The SO_2 gas partial pressure is about 10^{-1} atm at the beginning of the scan, and becomes very high and Na_2S and CrS become stable as the potential sweeps to very negative values. The trace is near the $\text{Cr}_2\text{O}_3/\text{Cr}_2(\text{SO}_4)_3$ boundary, but no $\text{Cr}_2(\text{SO}_4)_3$ precipitates were found after the experiment. However, some green-colored Cr_2O_3 was detected by x-ray diffraction analysis. After the electrochemical studies the melt displayed a yellow-colored chromate-sulfate solution layer in the lower part of the crucible and a mixture of green-colored Cr_2O_3 precipitates and yellow-colored solution in the upper part of the crucible around the electrodes. The open-circuit potential also indicates that the acidic melt in equilibrium with the $\text{SO}_3/\text{SO}_2/\text{O}_2$ gas mixture is at the $\text{Na}_2\text{CrO}_4/\text{Cr}_2\text{O}_3$ boundary line where the chromate and the chromium oxide are coexisting with each other. The oxygen pressure of the system is above 1 atm at open-circuit potential. From the Na-Cr-S-O phase stability diagram, the Cr_2O_3 is the stable phase in this acidic melt condition at $P_{\text{O}_2} = 1$ atm, but the chromate is not. Therefore, thermodynamically the

chromate solutes should decompose chemically to form Cr_2O_3 without cathodic polarization. This explains the considerable precipitation of Cr_2O_3 from the solution melt in the acidic condition where no clearly defined cathodic peak can be observed at lower scan rates. Experimentally, because of the presence of excess amount of Na_2CrO_4 , the oxygen pressure of the system has to be raised to > 1 atm where the Na_2CrO_4 and the Cr_2O_3 can be in equilibrium with each other in the acidic melt. Repeated polarization of the melt will shift the open-circuit oxygen pressure to a lower value into the Cr_2O_3 stable field.

Orange-colored precipitates were found in the melt around the working electrode inside the alumina tube; although the amount of the precipitates was too little to be analyzed by x-ray diffraction, these precipitates were probably dichromates, the presence of which in acidic solution was expected according to the chemistry of chromium compound (23).

2. CHRONOPOTENTIOMETRY STUDIES

Figure 68(a) is a chronopotentiogram recorded by a Pt foil working electrode in the 8 m/o Na_2CrO_4 solution with basicity of 16 and 300 mA applied current. A forward transition in the potential range of -659 mV to

Figure 68 Chronopotentiometry measurements for 8 m/o Na_2CrO_4 in acidic condition at 1200 K ($-\log a_{\text{Na}_2\text{O}}=16$) (a) Chronopotentiogram with 300 mA applied current. (b) $i\tau^{1/2}$ dependence on current for the forward transition.

-900 mV is shown in Fig. 68(a). In agreement with the cyclic voltammetry results, for 8 m/o Na_2CrO_4 , this forward transition in the acid melt is not as well defined as the τ_f in the basic conditions. The plateau for the E-t response at potentials over -1000 mV corresponds to the decomposition of the Na_2SO_4 supporting electrolyte. Figure 68(b) is the $i\tau^{1/2}$ dependence on applied current for the forward transition of the solution melt in acidic condition. The positive deviation of the $i\tau^{1/2}$ product at higher currents indicates again the presence of adsorption in the cathodic process. Figure 69 shows the E vs. log plots for 8 m/o Na_2CrO_4 in acidic melt. Figure 69 (a) is plotted according to Eq. (20) for a reversible reaction, and (b) according to Eq. (21) for an irreversible reaction. A much better linear fit is obtained in Fig. 69(a), the linear regression parameter of which is 0.999. The apparent number of electrons transferred, calculated from the slope of Fig. 69(a), is 1.24, normalized to 1. Thus, the cathodic process in the acidic condition is concluded as a reversible, one-electron-transfer process.

Two very short backward transitions were observed in Fig. 68 when the current was reversed. Experimentally, two better defined two backward

Figure 69 Plots of chronopotentiometric data according to Eq. (20) and (21) for the forward transition in Fig. 68. (a) Plot according to Eq. (20). (b) Plot according to Eq. (21).

transitions were revealed when lower applied currents (180 mA) were used. The reversibility and electron transfer number for the backward transitions not evaluated because the potential ranges over which the backward transitions occurred are so narrow that meaningful calculation cannot be conducted.

3. CHRONOAMPEROMETRY AND DYNAMIC POLARIZATION STUDIES

Figures 70 to 72 are the experimental results obtained from chronoamperometry and dynamic polarization studies of the 8 m/o Na_2CrO_4 in the acidic melt. Figure 70 is the superimposed chronoamperograms for potential steps of -800 mV and -1400 mV; the open-circuit basicity for the measurements was 15.3. A constant current is obtained for the -800 mV potential step at long electrolysis times ($t > 50$ sec.) but the current response for the -1400 mV potential step constantly changed with time for up to 150 seconds, which is the electrolysis time adopted in all the chronoamperometry studies of Na_2CrO_4 - Na_2SO_4 solutions. Figure 71 (a) is the $it^{1/2}$ vs. t plot for the -800 mV potential step shown in Fig. 70. The $it^{1/2}$ product approaches to a constant value as the time increased. When plotting the maximum current response vs. the applied potential step, Fig. 71(b) is obtained. The current increased significantly

Figure 70 Superimposed chronoamperograms of 8 m/o Na_2CrO_4 in acidic condition at different potential steps. ($-\log a_{\text{Na}_2\text{O}}=15.3$)

Figure 71 Plots of chronoamperometric results of 8 m/o Na_2CrO_4 in acidic condition at 1200 K. (a) $it^{1/2}$ vs. t plot. (b) Sampled-current voltammetry.

after about -800 mV, and then became relatively unchanged with the potential until it reaches about -1200 mV, where a sudden increase in current was observed. The dash line in Fig. 71(b) represents an uncertainty in the exact shape of the sampled-current voltammetry plot in that particular potential range. The sudden increase in current after -1400 mV results from the decomposition of the Na_2SO_4 background electrolyte.

Figure 72 is a cathodic polarization curve in the potential range of the open-circuit potential ($+400$ mV) to -1500 mV at a basicity of 16 for the 8 m/o Na_2CrO_4 solution. The considerable increase in polarization current after -1200 mV in Fig. 72 again indicates the beginning of the decomposition of Na_2SO_4 .

As was mentioned at the beginning of this chapter, because of the lack of information of the electrochemical behavior of Na_2SO_4 background electrolyte in the acidic condition, it is difficult to further pursue the possible reaction mechanism of Na_2CrO_4 based on the present experimental results. Detailed electrochemical studies of Na_2SO_4 are necessary before a conclusion can be drawn for the chromate-sulfate solution.

Figure 72 Cathodic polarization curve of 8 m/o Na_2CrO_4 in acidic condition at 1200 K ($-\log a_{\text{Na}_2\text{O}} = 16$).

VIII. CONCLUSIONS

Electrochemical studies of Na_2CrO_4 solute in fused Na_2SO_4 at 1200 K deduced that the chromate ions, CrO_4^{2-} , are not electroactive within the potential range where the Na_2SO_4 background electrolyte is stable. Only one cathodic reaction is detected, and it is determined as a reversible charge transfer process with an electron transfer number of one. The electroactive species is believed to be CrO_4^{3-} , which is reducible at potentials of the cathodic peak corresponding to this cathodic reaction and is formed by a chemical reaction between the CrO_4^{2-} and O^{2-} ions in the solution. An irreversible following chemical reaction is present for the cathodic process, and the reaction product is chromium oxide, Cr_2O_3 , in the neutral melt; and sodium chromite, NaCrO_2 , in the basic melt.

The kinetic behavior of the chromate-sulfate binary is different from the thermodynamic prediction according to the phase stability diagram of Na-Cr-S-O

system. No chromium sulfide and/or sodium sulfide precipitates were found in the melt after the experiments. Although the basicity traces recorded by a porous Pt painted ZrO_2 electrode during cyclic voltammetry measurements both in neutral and basic melts indicate that the local chemical state of the working electrode is in the regime where NaCrO_2 solute should be more important than the Na_2CrO_4 solute, no cathodic reaction corresponding to a direct reduction of chromate to chromite was observed. Furthermore, any "double buffering" effects of chromium with respect to both redox and acid-base changes were not observed for $\text{CrO}_4^{2-}/\text{CrO}_2^-$ conversion from the present experiments.

No significant change in electrochemical behavior of Na_2CrO_4 - Na_2SO_4 solutions was observed either as the melt basicity was changed from neutral to more basic, or as the Na_2CrO_4 concentration was varied from 3 m/o to 12.5 m/o. No electrochemical response was detected for Na_2CrO_4 additions of less than 3 m/o. For a Na_2CrO_4 content of 18 m/o, however, the cathodic reaction was found associated with a considerable precipitation of the chromium oxide from the solution melt. The cell was insulated because of the precipitation of this oxide into the fused salt.

No electrochemical response was observed for the chromate-sulfate solution in very acidic condition where the solubility of Cr_2O_3 is very low (< 500 mole ppm). The precipitation of the chromium oxide out of the solution prior to cathodic polarization is expected because thermodynamically Cr_2O_3 is the stable phase under this acidic condition.

The electrochemical behavior and the reaction mechanisms for cathodic peak I_C in neutral condition and in basic condition are summarized in Table 12.

TABLE 12 Summary of Electrochemical Behavior and the Reaction Mechanisms for Peak I_C in Neutral and Basic Conditions

	Basic	Neutral
E range(mV)	-1250 to -1450	-1250 to -1510
n (Cal'd)	1	1
Reaction Type (Nicholson & Shain)	VI	VI
Basicity Trace (during CV)	~2 (E_{ocp} to E_λ)	<1 (E_{ocp} to E_λ)
Reaction Mechanisms	$\text{CrO}_4^{3-} + e \rightleftharpoons \text{CrO}_3^{2-} + \text{O}^{2-}$ $2 \text{CrO}_3^{2-} + 2 \text{Na}^+ \rightarrow 2 \text{NaCrO}_2 + 1/2 \text{O}_2 + \text{O}^{2-}$	$\text{CrO}_4^{3-} + e \rightleftharpoons \text{CrO}_3^{2-} + \text{O}^{2-}$ $2 \text{CrO}_3^{2-} \rightarrow \text{Cr}_2\text{O}_3 + 1/2 \text{O}_2 + 2 \text{O}^{2-}$

REFERENCES

1. J.Stringer, Ann. Rev. Mater. Sci., 7, 477,(1977).
2. J.A.Goebel, F.S.Pettit, and G.W.Goward, Met. Trans.,4, 261,(1973).
3. G.C.Fryburg, F.J.Kohl, C.A.Stearns, and W.L.Fielder, J. Electrochem. Soc., 129(3), 571,(1982).
4. G.C.Fryburg, F.J.Kohl and C.A.Stearns, J. Electrochem. Soc., 131(12), 2985,(1984).
5. E.L.Simons, G.V.Browning, and H.A.Liebhafsky, Corrosion, 11, 505t,(1955).
6. J.A.Goebel, F.S.Pettit, Met. Trans., 1, 1943,(1970).
7. R.A.Rapp and K.S.Goto, "Proc. 2nd Intern. Symposium on Molten Salts", J.Braunstein ed., The Electrochem. Soc., (1979).
8. N.S.Brostein and M.A.DeCrecente, Trans. AIME, 245, 1947,(1969).
9. N.S.Bornstein and M.A.DeCrecente, Corrosion, 26(7), 209,(1970).
10. N.S.Bornstein and M.A.DeCrecente, Met. Trans., 2, 2875,(1971).
11. R.A.Rapp, Mater. Sci. Eng., 85, 319,(1986).
12. K.L.Luthra and D.A.Shores, J. Electrochem. Soc.,

- 127(10), 2202,(1980).
13. K.L.Luthra, J. Electrochem. Soc., 132(6), 1293,(1985).
 14. N.S.Bornstein and M.A.DeCrescente, Metal. Trans., 2, 2875,(1971).
 15. Y.Bourhis and C.St.John, Oxid. Met., 9, 507,(1975).
 16. Y.S.Zhang, J. Electrochem. Soc., 133(3), 655,(1986).
 17. M.Kawakami, K.S.Goto, and R.A.Rapp, Transactions ISIJ, 29, 646,(1980).
 18. S.Y.Tsai, M.S. Thesis, The Ohio State University, 1984.
 19. J.C.Nava, Ph.D. Dissertation, The Ohio State University, 1987.
 20. E.E.Hellstrom, Corr. Sci., 23, 709,(1983).
 21. W.C.Fang and R.A.Rapp, J. Electrochem. Soc., 130, 2335,(1983).
 22. C.O.Park and R.A.Rapp, J. Electrochem. Soc., 133(8), 1636,(1986).
 23. C.L.Rollinson, "The Chemistry of Chromium, Molybdenum and Tungsten", Pergamon Press, Oxford, 1975.
 24. W.H.Hartford and R.L.Copson, "Chromium Compounds" in Encyclopedia of Chemical Technology, 5 Interscience, New York, 2nd edn., (1964), p.484.
 25. W.W.Liang, P.L.Lin, and A.D.Pelton, High Temp. Sci.,

- 12, 41,(1980).
26. JANAF Thermodynamic Tables, 2nd Ed., NB 535, U.S. Dept. of Commerce, (1970) and supplements.
27. B.F.Shain, P.C.S.Wu, and P.Chiotti, J. Nuc. Mat., 67, 13,(1977).
28. W.W.Liang and J.F.Elliot, J.Electrochem. Soc., 123, 617,(1976).
29. T.A.Ramanarayanan and W.L.Worrell, J. Electrochem. Soc., 127, 1717,(1980).
30. K.T.Jacob, D.B.Rao, and H.G.Nelson, Metall. Trans. A, 10, 327,(1979).
31. L.P.Kostin, L.L.Pluzhnikov, and A.N.ketov, Russ. J. Phys. Chem., 49, 1313,(1975).
32. A.F.Bard and L.R.Faulkner, "Electrochemical Methods", John Wiley and Sons, Inc., New York, (1980).
33. J.E.B.Randles, Trans. Faraday Soc., 44, 327,(1948).
34. A.Sevcik, Colledtion Czech. Chem. Commun., 13, 349, (1948).
35. P.Delarhay, J. Am. Chem. Soc., 75, 1190, (1953).
36. R.S.Nicholson and I.Shain, Anal. Chem., 36, 706, (1964).
37. P.J.Lingane, CRC Critical Reviews in Analytical Chem., Jan. 1971, pp 587-634.
38. W.H.Reinmuth, Anal.Chem., 33, 485,(1961).

39. D.G.Davis, Applications of Chronopotentiometry to Problems of Analytical Chemistry, in Electroanalytical Chemistry, vol.1, A.Bard Ed., Marcel Dekker, Inc., New York, 1966.
40. H.J.S.Sand, Phil. Mag., 1, 45,(1901).
41. E.Gileadi, E.Kirowa-Eisner, and J.Penciner, "Interfacial Electrochemistry", Addison-Wesley Publishing Co. Inc., Reading, Massachusetts, 1975.
42. M.L.Deanhardt and K.H.Stern, J. Phys. Chem., 84, 2831,(1980).
43. W.C.Fang and R.A. Rapp, J. Electrochem. Soc., 130, 2335,(1983).
44. K.H.Stern, M.L.Deanhardt, and R.M.Panayappan, J. Phys. Chem., 83, 2848,(1979).
45. R.H.Wopschall and I.Shain, Anal. Chem., 39(13), 1545,(1967).
46. R.A.Osteryoung, G.Lauer, and F.C.Anson, J. Electrochem. Soc., 110, 926,(1963).
47. C.A.Streuli and W.D.Cooke, Anal. Chem., 26, 963,(1954).
48. S.Gilman, The Anodic Film on Platinum Electrode, in Electroanalytical Chemistry, Vol.2, A.Bard Ed., Marcel Dekker, Inc., New York, 1967.
49. A.W.Laibergayer and H.W.McCune, J. Am. Chem. Soc., 74, 2362,(1952).