

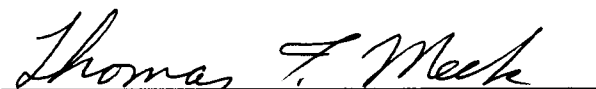
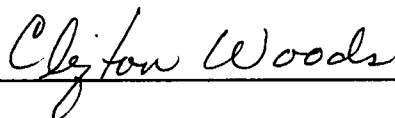
To the Graduate Council:

I am submitting herewith a dissertation written by Karl Dale Sienerth, entitled "Electrochemical Studies of Niobium(V) in Sodium Chloroaluminate and Fluorochloroaluminate Melts." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.



Gleb Mamantov, Major Professor

We have read this dissertation
and recommend its acceptance:



Accepted for the Council:



Associate Vice Chancellor
and Dean of The Graduate School

STUDIES OF THE ELECTROCHEMISTRY OF NIOBIUM(V) IN SODIUM
CHLOROALUMINATE AND FLUOROCHLOROALUMINATE MELTS

A Dissertation
Presented for the
Doctor of Philosophy Degree
The University of Tennessee, Knoxville

Karl Dale Sienerth

December, 1992

This work is dedicated to my wife, Sonya Dial Sienerth, for her patient and loving support, and to my son Nicholas Allen Sienerth, who refrained from driving his mother completely mad as she cared for him alone on the many nights the author spent completing this dissertation.

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ABSTRACT

Studies pertaining to the contamination of some molten salts by oxide impurities were conducted. Tantalum(V) was used as a Raman spectroscopic probe ion to determine the level of oxide contamination of FLiNaK; it was determined that, of the several methods examined, slow recrystallization was by far the best method for removal of oxide from the melt. Carbonyl chloride and carbon tetrachloride were found to be effective agents for removing oxide from sodium chloroaluminates. Of these two reagents, carbon tetrachloride showed greater advantages in its ability to react with oxide at lower temperatures and shorter times.

The electrochemistry of Nb(V) in sodium chloroaluminates at 178°C was examined, and it was determined that previously published studies were conducted in solutions of high oxide content. The reduction of NbCl₅ in COCl₂- and CCl₄-treated melts was found to proceed via essentially four steps at short times and low concentrations. At higher concentrations and long times, the reduction sequence was complicated by the appearance of an additional process which was due the reduction of the product of a chemical reaction which followed the initial reduction step.

The effect of temperature on the electrochemistry of Nb(V) in sodium chloroaluminates and fluorochloroaluminates was examined; temperature had a marked effect on the

reduction of Nb(V) in these melts, but no great differences were observed between melts with and those without fluoride.

Attempts to electrolytically produce niobium metal from Nb(V) in chloroaluminates and fluoro-chloroaluminates were made. While varying several parameters (such as temperature, fluoride content, and applied current density), deposition of the metal was achieved in only a few cases. The best deposit was obtained using a tungsten cathode at 550°C from a chloroaluminate melt in the absence of fluoride.

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CHAPTER I

INTRODUCTION

Molten salts (1-13) have long been of interest as solvents for uncommon chemical reactions, as well as for use in many technological applications. They generally exhibit large decomposition potentials and high electrical conductivities, making them useful in electrochemical studies. The transparency of molten salts over large regions of the electromagnetic spectrum is often a great advantage in spectroscopic investigations.

Alkali halides (especially fluorides and chlorides) have been utilized extensively in the study of the chemistry and electrochemistry of refractory metals (the nine transition elements of Groups IV-B, V-B, and VI-B of the periodic table). Similarly, melts composed of aluminum halides combined with alkali or organic halides, the so-called haloaluminate melts, have been used in electrochemical and spectrochemical investigations of these important metals. Electrodeposition of the refractory metals is feasible in alkali fluorides and chlorides, although coherent deposits of these metals have been attained only in the former melts, and this requires rather high temperatures ($>700^{\circ}\text{C}$). Furthermore, some controversy exists as to the true nature of the electrode reactions during reduction of some refractory metals in these melts; this may be related to the difficulty

in removing melt impurities, particularly oxide-containing species. The reduction of refractory metals in haloaluminates generally results in the formation of low-oxidation state cluster species. Melts of intermediate form, namely fluorochloroaluminates, might facilitate the electrolytic production of certain refractory metals at temperatures below those required in the molten alkali halides.

A. A Review of the Literature

This review describes the characterization and applications of molten halides and haloaluminates. The electrochemistry of niobium in these media will be discussed. Since the chemistry and electrochemistry of tantalum is often similar to that of niobium, and thus some analogies may be drawn thereto, studies regarding this metal are also included. Finally, investigations of the effect of oxide on the electrochemistry and spectroscopy of niobium and tantalum in various melts will be reviewed.

A variety of reference electrodes have been used in the studies reviewed here; this can cause some confusion when one tries to compare results reported by different authors. To assist the reader in such comparisons, a list of redox potentials with respect to selected "standard" reference couples is given in Table I.

Table I. Some Redox Potentials for Reference Couple Conversion.

Redox Couple	Reference Couple ^a	
	Ag(I)/Ag	Ni(II)/Ni
Ag(I)/Ag	-----	+0.64 ^d
Al(III)/Al Cl ₂ /Cl ⁻	-1.04 ^f , m	-1.50 ^d , m
	+1.033 ^b , m	
	+0.838 ⁱ , X	
	-0.068 ^b , m	
Ni(II)/Ni	-0.134 ⁱ , X	-----
	+0.727 ^b , m	
Pt(II)/Pt	+0.672 ⁱ , X	
		+1.65 ^k , X

a. Unless otherwise specified, data are taken from reference 14. X = mole fraction scale, M = molar scale, m = molal scale. Potentials are given in volts, and are standard or formal potentials (E° or E°'), with the standard conditions (solvent and temperature) given in following notes.

b. Potentials given are vs. Al(III)/Al in AlCl₃-NaCl_{sat} (basic) melt.

c. In AlCl₃-NaCl_{sat}, 175°C.

d. In NaF-KF eutectic (40-60 mole %), 850°C.

e. In AlCl₃-NaCl-KCl eutectic (66-20-14 mole %), 135°C.

f. In AlCl₃-NaCl (2-1 molar ratio), 175°C.

g. Potential of an Al wire in 2-1 AlCl₃-NaCl vs. that of Al in AlCl₃-NaCl_{sat}, from reference 15.

h. In LiCl-KCl eutectic (59-41 mole %), 450°C.

i. In NaCl-KCl eutectic (50-50 mole %), 727°C (1000K).

j. In AlCl₃-NaCl-KCl eutectic (66-20-14 mole %), 150°C.

k. In FLiNaK, 500°C.

1. Molten Fluoride Media

Molten fluoride media have been used for over 100 years in various research and commercial applications. Certainly one of the most recognized applications for molten fluorides is the electrowinning of aluminum metal in the Hall-Heroult process (16), in which refined bauxite (Al_2O_3) is dissolved and electrochemically reduced in a cryolite (Na_3AlF_6) bath. Fluoride melts also facilitate the electrolytic production of many of the alkali, alkaline earth and transition metals (3,13,17), including the refractory metals (18-20). The wide spectroscopic window of these media, especially the alkali fluoride melts, makes them good solvents for obtaining vibrational and UV-visible spectra of solute species (21-24). Molten fluorides have been investigated as possible coolants and fuel solvents in nuclear reactor technology (24). Reviews on chemistry and spectroscopy in molten fluorides are available (21,23,24).

Alkali metal and alkaline earth fluoride melts have desirable characteristics, such as high conductivity and wide electrochemical windows (1-3). Pizzini et al. determined electrode overvoltages of nickel electrodes in oxide-containing binary alkali fluoride melts (25), and this group also studied (26) oxygen and hydrogen electrodes in the ternary eutectic melt LiF-NaF-KF (46.5-11.5-42.0 mole %), hereafter referred to as FLiNaK . Jenkins et al. (27,28) conducted electromotive force (EMF) measurements on the

Ni(II)/Ni couple in FLiNaK and molten LiF-BeF₂-ZrF₄ (65.6-29.4-5.0 mole %); this couple has been widely employed in stable reference electrodes for many electrochemical studies using molten fluorides. Jenkins et al. (29) have also determined the electrode potentials (with respect to the Ni(II)/Ni reference) for Be(II)/Be, Zr(IV)/Zr, Cr(III)/Cr(II), Cr(II)/Cr, Fe(III)/Fe(II) and Fe(II)/Fe in LiF-BeF₂-ZrF₄, and for Fe(III)/Fe(II) and Fe(II)/Fe in FLiNaK. Mamantov and coworkers (30-32) studied extensively the electrochemistry of uranium in LiF-BeF₂-ZrF₄. Clayton (33) performed electrochemical studies of titanium in FLiNaK, LiF-BeF₂-ZrF₄, and NaBF₄, as well as of uranium and thorium in FLiNaK. Bowman (34) investigated the electrochemistry of aluminum in LiF-NaF-CaF₂ (53-36-11 mole %). The highly complexing nature of fluoride media makes it feasible to generate high oxidation states, as demonstrated by the formation of Mn(III) and Co(III) (22) in FLiNaK. Applications and techniques of electrochemistry in molten fluorides have been reviewed (23,24,35-39).

Various difficulties are encountered when working with molten fluorides (35,40). In general, the fluorides are toxic, and proper care must be taken when preparing melts and solutions. The operation of most fluoride baths requires high temperatures, frequently in excess of 600°C; this, coupled with their chemically aggressive nature, imposes rather strict limitations on the materials usable for

containment. Some alkali fluorides are very moisture sensitive; rigorous care is required in the preparation, purification, and use of melts containing these salts.

2. The Electrochemistry of Niobium and Tantalum in Molten Alkali Fluorides

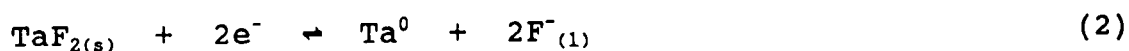
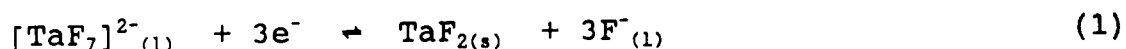
In the 1960's, Mellors and Senderoff published several articles describing the deposition of nearly all of the refractory metals from molten FLiNaK, the only exception being titanium, which could not be deposited to any appreciable thickness due to the concurrent reduction of potassium (18,35,41-45). The solutes used in these deposition studies were generally of the form $M\text{MrF}_x$, where M is an alkali metal, and Mr is the refractory metal (for instance, K_2TaF_7 and K_2NbF_7 were used for the deposition of Ta and Nb, respectively). At the time these studies were conducted, the importance of oxide impurities in molten salts was not established, and these authors did not report the purity of the melts with respect to oxide. One definite result of these studies was the ability to obtain thick, coherent deposits of eight of the nine refractory metals; Mellors and Senderoff reported the electroplating of large items (such as steel valves, and sheets as large as 3000 cm^2), and the ability to electroform items of complex shape and design by depositing the refractory metal on copper followed by removal of the copper by dissolution in nitric acid (44). The

purity of the deposits, determined by chemical analysis, generally exceeded 99.98 percent (44).

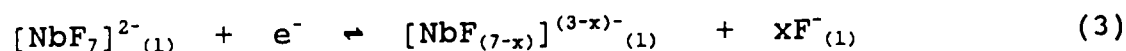
Some researchers have reproduced the studies of Mellors and Senderoff (46,47), and many have extended the investigations of the electrodeposition of refractory metals from the ternary eutectic to studies in binary salt mixtures such as LiF-NaF (50-50 mole %) (48,49) and the KF-NaF eutectic (46); studies in molten KF-K₂MrF₇ (where Mr=Ta,Nb) (50); and the electrowinning of refractory metal alloys, particularly Ta-Cr (51), tantalum silicide (52), tantalum carbides (53), and Ta/Ni and Nb/Ni (49). Cohen studied the use of periodic current reversal to enhance the quality of niobium electrodeposited from molten fluorides (47). Little doubt exists concerning the ability to form thick, coherent electrodeposits of these metals from selected fluoride baths.

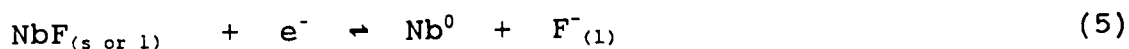
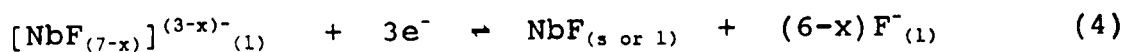
Using chronopotentiometry, Mellors and Senderoff attempted to elucidate the electrode processes involved in the electrodeposition of tantalum (41) and niobium (43) from FLiNaK. These workers proposed the mechanisms given in Equations 1 and 2 for tantalum and in Equations 3-5 for

Tantalum:



Niobium:





niobium. The first step in the tantalum reduction was considered to be diffusion controlled and reversible, and the second step was found to be highly irreversible (41). In the case of niobium (43), the first two steps in the reduction scheme were believed to be reversible and diffusion controlled, while the last step was neither. It was demonstrated that the initial step in the mechanism for niobium occurs spontaneously in the presence of niobium metal due to a reaction between the pentavalent niobium and the metal to form the tetravalent moiety. Indeed, electrolysis in a solution containing a significant amount of $[\text{NbF}_7]^{2-}$ exhibited a current efficiency near zero; this, according to Mellors and Senderoff (43), was due to a reaction between NbF_5 and $[\text{NbF}_7]^{2-}$ to regenerate the tetravalent niobium fluoride species.

Mellors and Senderoff suggested (43) that the presence of an irreversible step in the reduction schemes for tantalum, niobium and zirconium was an important factor in the ability to obtain coherent deposits of each of the refractory metals from fluoride melts. Support for this suggestion was obtained in the cases of molybdenum and tantalum (45). By comparison, the more easily dissociated chloro-complexes of these metals (in alkali chloride melts) allowed

for high concentrations of the "free" metal cation at the electrode surface, and thus led to the formation of powdery or dendritic deposits (18).

Yoko and Bailey (54) studied the electroreduction of niobium in FLiNaK using chronopotentiometry and cyclic voltammetry. Their work indicated the presence of a two-step process, shown in Equations 6-7.



Taxil and others (48,49) have investigated the reduction mechanisms for both tantalum and niobium in FLiNaK and NaF-LiF, and proposed the mechanisms shown in Equations 8 and Equations 9-10, respectively.

Tantalum:



Niobium:



Decroly et al. (50) conducted a study of the electro-deposition of niobium and tantalum from the binary salts $\text{KF-K}_2\text{MrF}_7$ ($\text{Mr} = \text{Nb}, \text{Ta}$), determining the effect of variations in cathodic current density, length of electrolysis time, concentration of K_2MrF_7 , and temperature on current efficiency. Furthermore, these workers constructed cathodic po-

larization curves, from which they hypothesized that, as the deposition proceeds, some portion of the deposit is redissolved into the solvent, giving rise to lower oxidation state species. Some fraction of these latter species is reduced again at the cathode, and some diffuse to the anode to be oxidized. This effect was more evident in the case of niobium than for tantalum.

The discrepancies in the reported mechanisms for the reduction of niobium and tantalum have not been addressed in detail in the literature. The mechanisms proposed by Mellors and Senderoff could be considered questionable due to the proposed formation of divalent tantalum fluoride and monovalent niobium fluoride; such species have not been observed by other means, and their existence in these melts has not been confirmed (although Mellors and Senderoff claim to have isolated a divalent tantalum species from sludge removed from melts used for deposition (41)). An inspection of the cyclic voltammograms presented by Yoko and Bailey (54) reveals, in fact, at least three reduction waves rather than the two reported by these workers.

The basis of this disagreement may lie in the assumption that solvents and solutes are pure, or at least pure to the extent that any impurities cannot significantly interfere with the studies underway. High purity fluoride melts are difficult to achieve, due to the extreme hygroscopicity of the alkali fluorides. However, as noted previously, the

melts used by these workers likely contained high concentrations of oxide impurities.

One group in particular (55,56) has taken issue with the mechanism proposed by Senderoff et al. (41) for the reduction of tantalum in FLiNaK, and fluoride-containing melts in general. Polyakov and coworkers (56) found that the voltammetric response observed during the reduction of Ta(V) in fluoride-containing melts is drastically altered by the presence of oxide species (cf., pp. 30-31). These workers proposed (55) that the behavior observed by Senderoff et al. (41) was in fact due to tantalum oxyfluoride species, or a mixture of fluoride and oxyfluoride species, rather than pure fluoride species. Polyakov and coworkers (57) observed similar dependence of the voltammetric response on oxide species in the reduction of Nb(V) in fluoride melts (cf., pp. 31-32).

3. The Electrochemistry of Niobium and Tantalum in Molten Alkali Chlorides and Chloride-fluorides

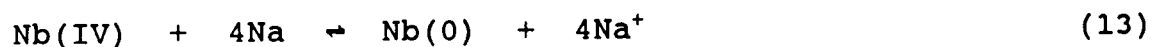
Studies of tantalum and niobium in pure alkali chloride systems (i.e., in the complete absence of fluoride ion) have not been common; such work is hindered by the generally high volatility of high valence tantalum and niobium chlorides. Johnson and coworkers (58) succeeded in preparing solutions of Nb(III) [low current density] and Nb(IV) [high current density] in NaCl-KCl and a solution of Nb(IV) in LiCl-KCl melts by anodization of niobium metal. When deposition of

niobium was attempted using solutions prepared in this manner, the cathode product was not coherent and was found to be a mixture of niobium metal and NbCl_3 . These workers proposed the following mechanisms for reduction to the metal which differed depending on the solvent and the species in solution:

Nb(III) in NaCl-KCl: (the electrochemistry of Nb(IV) in NaCl-KCl was not reported)



Nb(IV) in LiCl-KCl:



The latter mechanism proceeded through an intermediate step which involved the reduction of sodium. Caton and Freund (59) conducted similar studies in the LiCl-KCl eutectic, and concluded that the predominant species in melts prepared by anodization of Nb metal were Nb(IV) and Nb(III), in a ratio of approximately 3:1. Voltammograms conducted after the anodization indicated an initial one-electron reduction of Nb(IV) to Nb(III), followed by a 2 or 3 electron reduction step.

Saeki and Suzuki (60) examined niobium subchloride in the LiCl-KCl eutectic and compared solutions prepared by anodization of niobium metal and by addition of Nb_3Cl_8 . Their results indicated that the apparent valence of niobium

in the melt after anodization (regardless of the current density) was invariably about 3, and that the species generated by this method showed characteristics identical to those of Nb_3Cl_8 throughout a range of Nb_xCl_y concentrations and a range of temperatures from 500 to 650°C.

Pimenov and Baimakov (61) determined the temperature dependence of the diffusion coefficients for Nb(III) and Nb(II) in NaCl-KCl and for Nb(III) in LiCl-KCl as shown in Equations 14, 15, and 16, respectively.

$$\log[D_{\text{Nb(III)}}] = -2.36 - 2780/T \pm 0.03 \quad (14)$$

$$\log[D_{\text{Nb(II)}}] = -2.04 - 2000/T \pm 0.03 \quad (15)$$

$$\log[D_{\text{Nb(III)}}] = -2.66 - 1530/T \pm 0.02 \quad (16)$$

Suzuki's (62) studies of the species generated by anodization of niobium and tantalum in LiCl-KCl suggest that the predominant niobium species is likely Nb_3Cl_8 , and that Ta(IV) is certainly formed. A later report by Suzuki (63) involved the chronopotentiometric analysis of a Ta(IV) solution prepared by anodization of the metal; the results indicated that Ta(IV) was reduced in a one-step, two electron process to Ta(II), the form of which could not be determined. The Ta(II) was reduced to the metal in a complex process which was not studied. Anodic chronopotentiometry revealed that the Ta(IV) could be oxidized in a reversible one electron step to Ta(V).

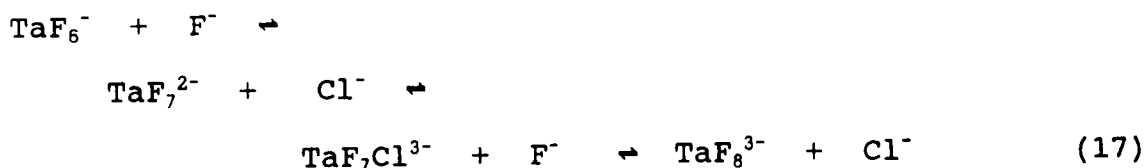
Barhoun (64) studied the reduction of Nb(V) in LiCl-KCl

at temperatures ranging from 400 to 650°C. He observed essentially two waves in the LiCl-KCl eutectic, and assigned these to the Nb(V)/Nb(IV) and the Nb(IV)/Nb(III) couples, respectively. However, the average valence of the product of the last step ranged from 2.4 to 2.9, depending upon the temperature and the potential applied; at the highest temperatures (>600°C), niobium metal was produced at the working electrode. This worker also studied Ta(V) in NaCl-KCl at 720°C; he observed a single, 5-electron, reversible reduction to the metal.

Picard and Bocage (65) conducted electrochemical experiments at 450°C using LiCl-KCl solutions in which a niobium rod had been anodized at various current densities. They reported the standard potentials (vs. the standard Cl_2/Cl^- reference) for the Nb(0)/Nb(III) couple as -1.44 V; for the Nb(III)/Nb(IV) couple as -1.12 V; and for the Nb(IV)/Nb(V) couple as -0.32 V.

Many studies involving the electrochemistry of niobium and tantalum in molten alkali chlorides utilized K_2NbF_7 and K_2TaF_7 as the solute species. It might be argued that such melts be considered of the chloride-fluoride genre; however, Inman and White (19) have suggested that fluoride ions will complex high-valent refractory metals more strongly than chloride ions, and will in fact tend to replace chlorides in tantalum or niobium complexes even in alkali chloride solvents such as LiCl-KCl, exhibiting equilibria such as

demonstrated in Equation 17. Thus, systems involving K_2MrF_7



(Mr=Ta,Nb) in alkali chloride melts may be considered simply as solutions of the fluorometallate in the chloride solvent.

Chemla and Grinevitch (66) examined the electrochemistry of K_2NbF_7 in alkali chloride melts of the type NaCl-KCl. They proposed a two step reduction to the metal, with the reduction of Nb(V) to Nb(IV) occurring at -0.70 V (vs. Cl_2), and the following four-electron reduction to niobium occurring at -1.5 V.

Barhoun et al. (67) studied the reduction of K_2NbF_7 in the NaCl-KCl eutectic at 720°C. They observed two well-defined waves, and attributed them to Nb(V)/Nb(IV) and Nb(IV)/Nb(0). They determined the diffusion coefficients of the Nb(V) and the Nb(IV) ions as 1.83×10^{-5} and 2.34×10^{-5} cm^2/s , respectively.

Similarly, Berghoute (68) studied the electrochemical reduction of K_2NbF_7 in NaCl-KCl at 720°C and observed behavior identical to that seen by Barhoun (67). Berghoute reported the standard reduction potential, E° , vs. Ni(II)/Ni for the Nb(V)/Nb(IV) reversible couple as 0.394 V, and for the Nb(IV)/Nb(0) quasi-reversible couple as -0.178 V.

Bailey et al. (69) reported the production of Ta(V),

Ta(IV), and Ta(II) by anodization of a tantalum electrode in the LiCl-KCl eutectic. They determined that Ta(V) was reduced in a reversible reaction to Ta(IV) at -0.67 V (vs. Pt(II)/Pt), and that Ta(IV) and Ta(II) were reduced to the metal at -1.7 V and -2.2 V, respectively.

Polyakova et al. (55) studied the reduction of Ta(V) in the CsCl-KCl-NaCl eutectic in the temperature range 550 to 780°C. When Ta(V) was added as TaCl₅, cyclic voltammetry revealed two waves with peaks at approximately 0.25 and -0.6V, vs. Ag(I)/Ag. They determined that these waves corresponded to a one-electron charge transfer (Ta(V)/Ta(IV)), and a four-electron transfer (Ta(IV)/Ta(0)), respectively. However, when fluoride was introduced, either by adding K₂TaF₇ or NaF, only one reduction wave was observed at approximately -0.9V, corresponding to a five-electron reduction of Ta(V) to the metal.

4. Chloroaluminate and Fluorochloroaluminate Melts

Aluminum halide based melts have been of considerable interest for many years now. These melts exhibit several desirable characteristics which make them interesting solvents for performing unusual synthetic and redox chemistry, as well as for conducting electrochemical and spectroscopic investigations. Although a wide variety of these melts are possible and have been utilized, emphasis here will be given to the aluminum chloride based melts.

Chloroaluminate melts, like many other molten salts, exhibit high conductivities and wide spectroscopic windows in the UV-visible and infrared ranges. The electrochemical window is generally more limited than that for alkali fluorides due to the more facile reduction of aluminum (compared to the alkali cations) and oxidation of chloride (than fluoride). However, one distinct property that chloroaluminates (and all aluminum halide based melts) possess is the wide range of acidities available. By varying the molar ratio of aluminum chloride, which is deemed a Lewis acid, to other melt components (typically alkali halides or organic halides), one can prepare melts which are highly basic, neutral, or highly acidic in nature. Several reviews are available concerning the preparation and use of haloaluminate melts (38,70-73).

5. Electrochemistry of Niobium and Tantalum in Chloroaluminates

Ting (74) has reviewed the electrochemistry of niobium, and McCurry (75) that of niobium and tantalum in alkali chloroaluminate melts. Only studies of these two workers (and their coworkers) and some more recent investigations will be discussed here.

Ting et al. (74,76) studied the electrochemistry of niobium in the acidic and basic (NaCl saturated) sodium chloroaluminate melts; hereafter, the NaCl-saturated sodium chloroaluminate melt (but not the acidic melt) will be re-

ferred to as SCA (for sodium clhoroaluminate). In SCA they determined that at long times (slow voltammetric scan rates, and chronoamperometric (CA) sampling on the order of 5 s) the reduction of Nb(V) progressed through a rather complex series of electrochemical and chemical steps, as shown in Equations 18-22. The reduction did not proceed beyond the



formation of Nb_3Cl_8 due to the high stability of this cluster in SCA. At shorter times (fast scan rates and CA sampling time of 0.1 sec.), the chemical reaction following the first reduction could be outrun, and only two simple reversible one electron transfer reactions were observed as $\text{Nb(V)} \rightleftharpoons \text{Nb(IV)} \rightleftharpoons \text{Nb(III)}$. A third reduction step observed in voltammetric and chronopotentiometric experiments at fast scan rates and high current densities, respectively, was attributed to a second order electrode process involving the reduction of Nb^{3+} . Electrochemical results obtained in the acidic melt indicated that the reduction occurs via the formation of Nb^{4+} , followed by dimerization and reduction to Nb_2^{6+} . A wave attributed to a higher order reduction involving Nb^{3+} was also observed.

Several reports of the investigation of the electrochemistry of tantalum in $\text{AlCl}_3\text{-NaCl}$ melts can be found in the literature (75,77,78). In a slightly acidic melt (51-49 mole % $\text{AlCl}_3\text{-NaCl}$), two reduction waves at approximately 0.37 and 0.25 V (vs. Al(III)/Al) were observed. Analysis of the voltammetric response and the results of controlled potential coulometry suggested that a series of electrochemical and chemical steps were involved in the reduction of Ta(V) to a tantalum chloride cluster species, $\text{Ta}_6\text{Cl}_{14}$, as depicted in Equations 23-26. Tantalum metal could not be



obtained by electrochemical reduction in this melt due to the formation of stable cluster species. Results observed in the acidic melts were similar to those for niobium in the same melt.

A compilation of the redox chemistry of tantalum and niobium in fluoride, chloride, chloroaluminate and mixed melts, along with redox potentials, is given in Table II. Table III lists some reported diffusion coefficients for various tantalum and niobium ions in these melt systems.

Table II. Reduction/Oxidation Chemistry of Tantalum and Niobium in Various Halide Melt Systems.

Redox Couple	Reversibility	System/temp (°C)	Type of Experiment	Reference Electrode	Potential (V)	Ref.
Fluoride Systems						
Ta(V)/Ta(II)	R ^a	FLiNaK / 750	CP ^b	Ni(II)/Ni	-1.03 (E _{1/4})	41
Ta(II)/Ta(O)	I ^c	" "	" "	" "	-1.26 (E _{1/4})	41
Nb(V)/Nb(IV)	R	FLiNaK / 750	CP	Ni(II)/Ni	-0.11 (E _{1/4})	43
Nb(IV)/Nb(I)	R	" "	" "	" "	-0.76 (E _{1/4})	43
Nb(I)/Nb(O)	I	" "	" "	" "	-1.02 (E _{1/4})	43
Ta(IV)/Ta(V)		FLiNaK / 750	CP	Ni(II)/Ni		34
Ta(V)/Ta(O)	QR ^d	FLiNaK / 560-800	CV/CP	Ta wire	-0.05 (E _{1/2})	49
Nb(V)/Nb(III)	QR	FLiNaK / 612	CV/CP	Pt QRE	-0.83 (E _{1/2})	54
Nb(III)/Nb(O)	QR	" "	" "	" "	-1.03 (E _{1/2})	54
Nb(V)/Nb(IV)	R	LiF-NaF / 750	CP/CA ^e /CV	Ni(II)/Ni	-0.06 (E _{1/2})	48
Nb(IV)/Nb(O)	QR	" "	" "	" "	-0.17 (E _{1/2} , E _{1/4})	48
Nb(V)/Nb(III)		LiF-BeF ₂ -ZrF ₄ 500	CP/CV/NPV ^g	Ni(II)/Ni	~-0.6 (E _{1/2})	74
[NbO ₂]/[NbO ₂] ^h						
Nb(III)/Nb(II)		LiF-BeF ₂ -ZrF ₄ 500	" "	" "	~-0.8 (E _{1/2})	74
[NbO ₂]/[NbO]						
Nb(V)/Nb(II)		LiF-BeF ₂ -ZrF ₄ 500	" "	" "	~-1.16 (E _{1/2})	74
[Nb ₂ O ₅]/[NbO]						
Alkali Chloride Systems						
Nb(III)/Nb		LiCl-KCl / 530	i-E plot	Cl ₂ /Cl ⁻	-1.5	58
Nb(IV)/Nb		NaCl-KCl / 650	i-E plot	Cl ₂ /Cl ⁻	-1.17	58
Nb(IV)/Nb(III)	R	LiCl-KCl / 450	NPV	Pt(II)/Pt	~-0.85 (E _{1/2})	58
Ta(IV)/Ta(II)	R	LiCl-KCl / 600	CP	Ag(I)/Ag	-0.45 (E _{1/4})	63
Ta(II)/Ta(O)	I	" "	" "	" "	-0.6 (E _{1/4})	63
Ta(IV)/Ta(V)		" "	" "	" "	+0.28 (E _{1/4})	63
Nb(V)/Nb(IV)	R	LiCl-KCl / 450	CV/CP	Cl ₂ /Cl ⁻	-0.32 (E ^o)	64
Nb(IV)/Nb(III)	I	" "	" "	" "	~-1.1 (E ^o)	64
Nb(III)/Nb(O)		" " / >500	" "	" "	-1.46 (E ^o)	64

Table II. (continued)

Redox Couple	Revers- ibility	System/temp (°C)	Type of Experiment	Reference Electrode	Potential (V)	Ref.
Alkali Chloride Systems (continued)						
Nb(V)/Nb(IV)	R	NaCl-KCl / 720	CV/CP	Ni(II)/Ni	+0.40 ($E_{1/2}$)	64
Nb(IV)/Nb(O)		" "	" "	" "	-0.12 ($E_{1/2}$)	64
Ta(V)/Ta(O)		NaCl-KCl / 720	CV	Ni(II)/Ni	-0.60 (E_p)	64
[TaF ₆] ⁻		" "	" "	" "	" "	" "
Ta(V)/Ta(O)		NaCl-KCl / 720	CV	Ni(II)/Ni	-0.80 (E_p)	64
[TaOF ₆] ⁻		" "	" "	" "	" "	" "
Nb(V)/Nb(IV)		LiCl-KCl / 450	CP	Cl ₂ /Cl ⁻	-0.32 ($E_{1/2}$)	65
Nb(IV)/Nb(III)		" "	" "	" "	-1.12 ($E_{1/2}$)	65
Nb(III)/Nb(O)		" "	" "	" "	-1.44 ($E_{1/2}$)	65
Nb(V)/Nb(IV)		NaCl-KCl / 800	CV/CP/NPV	Cl ₂ /Cl ⁻	-0.9 ($E_{1/2}$)	66
Nb(IV)/Nb(O)		" "	" "	" "	-1.5 ($E_{1/2}$)	66
Nb(V)/Nb(II)		" "	" "	" "	-1.3 ($E_{1/2}$)	66
[NbOF ₅] ⁻ /[NbO]		" "	" "	" "	" "	" "
Nb(V)/Nb(IV)	R	NaCl-KCl / 720	CV/CP	Ni(II)/Ni	+0.39 (E_o')	67, 68
Nb(IV)/Nb(O)	QR	" "	" "	" "	-0.18 (E_o')	67, 68
Ta(V)/Ta(IV)		LiCl-KCl / 450	CV/CP/NPV	Pt(II)/Pt	-0.67 ($E_{1/2}$)	69
Ta(IV)/Ta(O)		" "	" "	" "	-1.7 ($E_{1/2}$)	69
Ta(II)/Ta(O)		" "	" "	" "	-2.2 ($E_{1/2}$)	69
Alkali Fluoride-Chloride Systems						
Nb(V)/Nb(IV)	R	KCl-KF / 700	CV/NPV	Ag(I)/Ag	-0.5 ($E_{1/2}$)	57
Nb(IV)/Nb(O)	R	" "	" "	" "	-1.3 ($E_{1/2}$)	57
Nb(V)/Nb(O)		" "	" "	" "	-1.1 ($E_{1/2}$)	57
[NbOF ₅] ⁻		" "	" "	" "	" "	" "
Ta(V)/Ta(O)		KCl-KF / 700	CV/NPV	Ag(I)/Ag	-1.3 ($E_{1/2}$)	56
Ta(IV)/Ta(O)		" "	" "	" "	-1.4 ($E_{1/2}$)	56
[TaOF ₆] ⁻		" "	" "	" "	" "	" "
Ta(V)/Ta(O)		" "	" "	" "	-1.6 ($E_{1/2}$)	56
[TaO ₂ F ₄] ⁻		" "	" "	" "	" "	" "

Table II. (continued).

Redox Couple	Reversibility	System/temp (°C)	Type of Experiment	Reference Electrode	Potential (V)	Ref.
<u>Chloroaluminate Systemsⁱ</u>						
Nb(V)/Nb(IV)	R	AlCl ₃ -MEIC ^j / 40	CV	Al(III)/Al	+0.17 (E _{1/2})	79
Nb(IV)/Nb(III)	R	" "	" "	" "	-0.93 (E _{1/2})	79
Nb(V)/Nb(IV) [NbOCl ₂] ²⁻	QR	" "	" "	" "	-0.52 (E _{1/2})	79
Ta(V)/Ta(IV)	R	AlCl ₃ -MEIC / 40	CV	Al(III)/Al	-0.49 (E _{1/2})	80

a. Refers to a reversible electron transfer reaction.

b. Chronopotentiometry.

c. Refers to an irreversible reaction.

d. Quasireversible.

e. Cyclic voltammetry.

f. Chronoamperometry.

g. Normal pulse voltammetry.

h. Square brackets, [], give the form of the species involved in the electrode reaction.

i. Note: Reduction processes of Ta(V) and Nb(V) in alkali chloroaluminates are very complex.

For details, see the related text of Chapter I, and references 72-74 (niobium); and 73, 75, and 76 (tantalum).

j. 1-Methyl-3-ethylimidazolium chloride.

Table III. Diffusion Coefficients for Some Tantalum and Niobium Species in Halide Melts.

Species	System/Temp. (°C)	Type of Experiment	Diffusion Coefficient (cm ² /sec)	Reference
Ta (V)	FLiNaK / 750	CP ^a	1.5×10^{-5}	41
[NbF ₇ ²⁻]	FLiNaK / 750	CP	2.03×10^{-5}	43
Nb (V)	LiF-NaF / 750	CP/CV ^a /CA ^a	4.0×10^{-6}	48
Ta (V)	FLiNaK / 560	CV/CP	1.7×10^{-7}	49
Ta (V)	" / 800	CV/CP	2.8×10^{-6}	49
Nb (III)	LiCl-KCl / 600	EMF measurements	3.87×10^{-5}	61
Nb (III)	NaCl-KCl / 800	EMF measurements	5.18×10^{-5}	61
Ta (IV)	LiCl-KCl / 600	CP ^b	2.5×10^{-4}	63
Ta (IV)	" "	CP ^c	1.4×10^{-4}	63
Nb (III)	LiCl-KCl / 510	CV/CP	1.92×10^{-2}	64
Ta (V)	NaCl-KCl / 720	CV/CP	1.45×10^{-5}	64
Nb (V)	NaCl-KCl / 720	CV/CP	1.83×10^{-5}	67
Nb (IV)	" "	" "	2.34×10^{-5}	67
Ta (V)	AlCl ₃ -NaCl (51-49 m/o) 600	CV	3.3×10^{-6}	75
Nb (V)	AlCl ₃ -NaCl _{sat} / 180	CV	$5.8 - 7.1 \times 10^{-6}$	76
Nb (V)	" " "	CP	$4.5 - 4.9 \times 10^{-6}$	76
Nb (V)	" " "	CA	$\approx 4.8 \times 10^{-6}$	76
Ta (V)	AlCl ₃ -MEIC ^a / 40 (44.4-55.6)	CV	5.14×10^{-7}	80
		CA	5.61×10^{-7}	80
		RDE ^d	5.03×10^{-7}	80
Ta (IV)	AlCl ₃ -MEIC / 40 (44.4-55.6)	CV	2.83×10^{-7}	80
		CA	3.23×10^{-7}	80
		RDE	3.05×10^{-7}	80

Table III. (continued).

Species	System/Temp. (°C)	Type of Experiment	Diffusion Coefficient (cm ² /sec)	Reference
Ta(V)	AlCl ₃ -MEIC / 40 (49.0-51.0)	CV	7.96 X 10 ⁻⁷	80
		CA	9.37 X 10 ⁻⁷	80
		RDE	8.18 X 10 ⁻⁷	80
Ta(IV)	AlCl ₃ -MEIC / 40 (49.0-51.0)	CV	4.06 X 10 ⁻⁷	80
		CA	4.46 X 10 ⁻⁷	80
		RDE	4.10 X 10 ⁻⁷	80
Nb(V)	AlCl ₃ -MEIC / 40 (44.4-55.6)	CV/CA/RDE	4.98 X 10 ⁻⁷	79
[NbCl ₆]	" "	" "	3.02 X 10 ⁻⁷	79
Nb(IV)	" "	" "	"	"
[NbCl ₆] ²⁻	" "	" "	"	"
Nb(III)	" "	" "	"	"
[NbCl ₆] ³⁻	" "	" "	"	"
Nb(V)	AlCl ₃ -MEIC / 40 (44.4-55.6)	CA/RDE	2.82 X 10 ⁻⁷	79
[NbOCl ₅] ²⁻	" "	" "	"	"
Nb(IV)	" "	" "	2.01 X 10 ⁻⁷	79
[NbOCl ₅] ²⁻	" "	" "	"	"
Nb(V)	AlCl ₃ -MEIC / 40 (49.0-51.0)	CV/CA/RDE	8.21 X 10 ⁻⁷	79
Nb(IV)	" "	" "	4.92 X 10 ⁻⁷	79
Nb(III)	" "	" "	>2.59 X 10 ⁻⁷	79

a. Refer to notes in Table I for explanation of this abbreviation.

b. From cathodic chronopotentiometry: Ta(IV)/Ta(II).

c. From anodic chronopotentiometry: Ta(IV)/Ta(V).

d. Rotating disk electrode.

6. Fluorochloroaluminate Melts

Very little research has been conducted in mixed fluorochloroaluminate systems. Tremillon and Duchange (81) examined the effect of additions of small quantities of fluoride ions on chloroaluminate melts. They proposed the monobasic action of fluoride in the formation of mixed haloaluminate moieties of the form $\text{Al}_2\text{Cl}_6\text{F}^-$, AlCl_3F^- , as well as dibasic behavior in the formation of the unusual species $\text{AlCl}_4\text{F}^{2-}$, although no supporting evidence for the existence of this latter species has been offered.

Gilbert et al. (82) conducted an intensive study of the Raman spectra of fluoride-containing SCA (hereafter referred to as SFCA, for sodium fluorochloroaluminate) melts. These workers determined that, in the liquid state at 800°C, the previously unknown mixed fluorochloroaluminate species AlCl_3F^- , $\text{AlCl}_2\text{F}_2^-$, and AlClF_3^- , as well as the AlF_4^- moiety were observed in the basic melt. Spectra of acidic fluoride-containing melts obtained at 200°C suggested the presence of a species of the form $\text{Al}_2\text{Cl}_6\text{F}^-$. No evidence of any of these mixed species could be found in solidified melts.

7. Oxide Contamination of Molten Salts: Determination and Purification of Melts

Prior to the early 1970's, the possible influence of dissolved oxide species on solutes in molten salts was not

considered in most investigations. It was not until the 1980's that researchers began to realize that even fairly low levels of oxide species present in the melts could have a marked effect on solute chemistry and electrochemistry, especially when work at low solute concentrations was attempted.

a. Molten fluoride media. Mamantov (36) reported several methods useful for removal of impurities from these melts, and concluded that no single method is sufficient to prepare melts of purity equal to that attainable in molten chlorides after treatment with HCl gas. Most methods utilized for fluoride melt purification are aimed toward eliminating dissolved metal species which can be introduced during salt preparation, but some of these are also amenable to removal of oxide impurities. One of the most efficient methods of removing metallic and oxidic impurities from fluoride melts is by sparging the melt with a mixture of HF and H₂ (34,36) ; however, this requires rather costly, specialized apparatus for handling of the toxic and reactive gases. Senderoff and coworkers (41-45) generally purified their FLiNaK melts using NH₄HF₂ (which decomposes to HF and NH₃) and H₂. Other purification methods include simply melting a eutectic in air to "expel moisture" (83-85); heating a eutectic or individual fluoride salt (usually to melting) under vacuum (25,26,54); heating under a flow of argon or

sparging with argon (48,49,51); and electrolysis of the molten eutectic (46,86). von Barner et al. (40) found that fairly high quality melts could be obtained by slow recrystallization of the constituent fluoride salts prior to their combination.

No reliable method for the direct detection of oxidic contaminants in molten fluoride media has been proposed to date.

b. Chloroaluminate melts. Various indirect electrochemical and spectroscopic methods for detection of oxidic impurities in chloroaluminate melts have been proposed (77,87,88). Mamantov and coworkers (89, 90) developed a method for the direct determination of melt oxide concentration based on the infrared absorption of aluminum oxychloride in the region 680-800 cm^{-1} . Flowers has reviewed many aspects of oxide chemistry in molten chloroaluminates (91).

For many years, melts were considered sufficiently pure if the individual salts (e.g., NaCl and AlCl_3) were purified. Generally, the alkali chloride would be dried under vacuum at a temperature lower than its melting point; for ultra pure salt, the chloride would be melted and sparged with HCl gas. Aluminum chloride was purified by multiple distillation or sublimation in Pyrex or quartz vessels. In more recent years, however, it has been shown that even when

the worker is careful in the extreme, fairly significant levels of oxide exist in the melt (90-93). For example, Flowers and Mamantov (90) showed that the concentration of adventitious oxide impurities in sodium chloroaluminate melts was on the order of 10 mM. Similarly, Sun and Hussey (79) found that their ambient temperature molten salts were contaminated by small amounts of water adsorbed to even rigorously dried glassware.

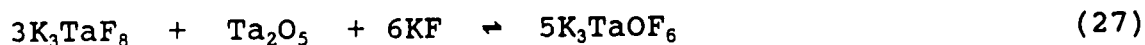
Melt purification with HCl has been proposed and studied (89), but this method was found to be limited by the establishment of an equilibrium between oxidic species in the melt, HCl, and H₂O. Hussey and coworkers (79,80,92) showed that oxide could be essentially eliminated from the ambient temperature molten salt AlCl₃-1-methyl-3-ethylimidazolium chloride by treatment with phosgene (COCl₂).

8. Oxide Contamination of Molten Salts: Effect on the Electrochemistry of Niobium and Tantalum

a. Molten chloride/fluoride media. Two studies were conducted by Konstantinov et al. on the electrochemistry of tantalum (56) and niobium (57) in chloride-fluoride melts to which quantitative amounts of the metal pentoxides were added. The melt used was KCl-KF (55-45 mole %), with the heptafluorometallates added as solute species.

In the investigation of the Ta(V) reduction (56), these

workers observed a single, sharp voltammetric wave at approximately -1.3 V (vs. Ag(I)/Ag) when only K_2TaF_7 was present in solution. However, upon the addition of successive aliquots of Ta_2O_5 , additional waves began to grow in; a wave at -1.4 V was observed with the initial oxide additions, and with more additions, one at -1.6 V was seen. It was proposed that the initial wave (-1.3 V) was due to the 5 electron reduction of $[TaF_8]^{3-}$, the second (-1.4 V) due to the reduction of $[TaOF_6]^{3-}$; the final reduction was attributed to $[TaO_2F_4]^{3-}$. The $[TaF_8]^{3-}$ wave disappeared entirely when the Ta_2O_5/K_2TaF_7 ratio reached 1/3, or when the Ta/O ratio was 1/1. From these results, the authors postulated an equilibrium reaction such as that given in Equation 27.

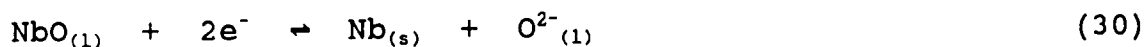
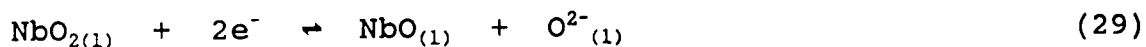
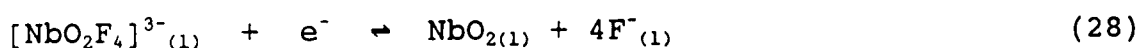


Furthermore, they noted that when the Ta/O ratio was 1/1, the peak currents for the second and third waves reached maximum values, and further additions of Ta_2O_5 had no effect. Addition of K_2TaF_7 allowed the observation of the first reduction wave again.

In the case of niobium (57), linear sweep voltammetry and normal pulse voltammetry revealed two reduction waves at -0.5 V and -1.3 V (vs. Ag(I)/Ag) in solutions of K_2NbF_7 in KCl-KF; the diffusion limited currents for these waves gave a ratio, I_{d2}/I_{d1} , of 4. Both waves were found to be reversible. Analysis of the voltammetric responses indicated

that the reduction of Nb(V) in this melt follows a two-step process in which Nb(V) is first reduced to Nb(IV), followed by a four-electron reduction to the metal.

The addition of oxide in the form of Nb₂O₅ produced more complicated results than in the case of tantalum. Initial small quantities of oxide caused the two waves due to the reduction of [NbF₇]²⁻ to decrease, and a new wave with a peak potential of -1.1 V was observed. When the K₂NbF₇:Nb₂O₅ ratio reached 3:1, the peaks at -0.5 V and -1.3 V had disappeared completely, and only the wave at -1.1 V was noted. Analysis of this wave revealed that it corresponded to a five-electron reduction of Nb(V) to the metal, and this was supported by x-ray diffraction studies of the cathode product. Further addition of oxide caused the peak due to the reduction of [NbOF₆]³⁻ to decrease in height, and three new peaks were observed at more negative potentials. At a Nb₂O₅/K₂NbF₇ ratio of 2/1, this transformation ended with the complete elimination of the peak at -1.1 V. These workers proposed a three step mechanism for the reduction of [NbO₂F₄]³⁻ as given in Equations 28-30. Additions of oxide



beyond the 2/1 ratio caused the appearance of a new peak at about -0.65 V, which the authors attribute to the reduction

of NbO_3^- . No dissolution of Nb_2O_5 occurred beyond the 3/1 ratio. However, the peak at -0.65 V was observed with solutions of Nb_2O_5 in the melt in the absence of K_2NbF_7 .

Barhoun (64) studied the effect of oxide added to a LiCl-KCl solution of Nb(V), where he initially observed two waves (Nb(V)/Nb(IV) and Nb(IV)/Nb(III)). Upon the addition of oxide, both waves decreased in height, and finally completely disappeared when the O^{2-}/Nb ratio had reached approximately 2.

Barhoun (64) also studied the effect of oxide on the cyclic voltammetry in NaCl-KCl solution of Ta(V). Initially, only one wave was observed (Ta(V)/Ta(0)); when a small quantity of oxide was added, a new wave positioned approximately 0.25 V negative of the first began to grow in. When the O^{2-}/Ta ratio had reached unity, the initial wave had disappeared entirely, and the new, more cathodic wave was the only feature observed.

b. Chloroaluminate melts. McCurry *et al.* (75,77) studied the electrochemistry of Ta(V) in sodium chloroaluminate melts, and the effect of the addition of oxide to the melt. They observed a single reduction peak, attributed to the reduction of TaCl_6^- to TaCl_6^{2-} , at approx. +0.65 V (vs. Al(III)/Al in $\text{AlCl}_3\text{-NaCl}_{\text{sat}}$ melt) when the $\text{O}^{2-}/\text{Ta(V)}$ ratio was low. However, when the oxide level was increased, a second peak at +0.45 V became evident. These workers showed that

TaCl_6^- underwent a stoichiometric reaction with oxide in the melt to produce TaOCl_4^- , which was reduced at the less positive potential. The Ta(V)/Ta(IV) system was proposed as a probe for the voltammetric determination of oxide in these melts (77).

Sun and Hussey (79) examined the electrochemistry of niobium chloride and oxychloride in basic AlCl_3 -1-methyl-3-ethylimidazolium chloride room temperature melts. They found that $[\text{NbCl}_6]^-$ could be reduced in two one electron reversible steps to $[\text{NbCl}_6]^{2-}$ and $[\text{NbCl}_6]^{3-}$, with E_1 's of 0.17 and -0.93 V, respectively (vs. Al(III)/Al). Upon the addition of oxide to the melt, $[\text{NbCl}_6]^-$ was converted to $[\text{NbOCl}_5]^{2-}$, and this oxychloride moiety could be reduced to $[\text{NbOCl}_y]^{2-y}$ in a one-electron quasi-reversible reaction with a formal potential of -0.521 V. These workers found that the oxychlorides could be converted easily to their respective chlorides in this melt by reaction with phosgene.

Barnard and Hussey (80) studied the electrochemistry of Ta(V) in the same melt. They determined that $[\text{TaCl}_6]^-$ was reduced to $[\text{TaCl}_6]^{2-}$ in a reversible one-electron step at -0.49 V (vs. Al(III)/Al), and that the Ta(V) species, but not the Ta(IV) species, could be converted to an oxychloride by the addition of oxide to the melt. This oxychloride could be reconverted to the chloride species by treatment with phosgene. Ta(IV) could be further reduced at -1.70 V, but this reduction was complicated by coupled chemical

but this reduction was complicated by coupled chemical reactions. The number of electrons involved in this latter step was found to be two at slow voltammetric rates, but at faster rates the reaction simplified to a one-electron quasi-reversible process.

B. Proposed Research

Several methods of FLINAK purification will be investigated to determine which can be used to produce the lowest level of oxide contamination. Vibrational (infrared and Raman) spectroscopy will be used to examine the fluoride and oxyfluoride chemistry of Ta(V) in FLINAK; these results will be used to ascertain the feasibility of using Ta(V) as a probe for oxide contamination of FLINAK.

Methods for removal of oxide impurities from chloroaluminate and fluorochloroaluminate melts will be investigated, in order to obtain melts of highest quality in which to conduct further studies.

The electrochemistry of Nb(V) in chloroaluminate melts will be reinvestigated in oxide-free melts; a study of the electrochemistry in fluorochloroaluminate melts will be undertaken for comparison with that in the chloroaluminates, as well as to estimate the possibility of utilizing either melt as a means of electroplating refractory metals.

CHAPTER II

EXPERIMENTAL

A. Chemicals

1. Materials Used in the Preparation of Melts

a. FLiNaK. Lithium fluoride (Fluka, purum, >99%), sodium fluoride (Fluka, purum, >99.0%), and potassium fluoride (Fluka, puriss, >99.0%), used for the preparation of FLiNaK, were not further purified prior to mixing. Ammonium bifluoride (Aldrich, 98%) also was used as received. Nitrogen (99.999%, prepurified), argon (standard grade) and hydrogen (MG, 99.998%), used to maintain an inert atmosphere and for melt sparging, were used as received.

b. SCA and SFCA melts. Sodium chloride (Mallinkrodt, Analytical reagent grade) was dried under vacuum (<50 mTorr) at 450°C in a Pyrex tube for >48 hours. The tube was then torch-sealed and taken into a drybox; the NaCl was transferred to a large Erlenmeyer flask and stored in a drybox until used.

Anhydrous aluminum chloride (Fluka, puriss grade, >99%) was purified by distillation from an approximately 100-1 weight ratio mixture of AlCl_3 and NaCl, to which had been added aluminum metal (Aesar, 99.999%). The purification procedure is described in detail in reference 91.

Sodium fluoride (Alfa, puratronic, 99.995%) was used as received in the preparation of SFCA melts.

Carbonyl chloride (Matheson Gas, 99.0%) and carbon tetrachloride (Mallinkrodt, 99.9%) were used as received.

2. Solute Compounds

Potassium heptafluorotantalate (Alfa, 99.9%) was used as received without purification. However, while most of the received material appeared as clear white flakes, some portions contained chunks which were visibly opaque. Raman spectroscopy of the two visibly different materials showed that the opaque matter exhibited higher oxide contamination (compare the band at 878 cm^{-1} (94) in Figures 1a and 1b); these portions of K_2TaF_7 were avoided during solution preparation.

Tantalum pentachloride (Alfa, 99.9%) and NbCl_5 (Alfa, 99.9%) were purified by sublimation. The metal chloride was placed in a Pyrex tube (approximately 25 cm in length) in a drybox, and the tube was transferred to a vacuum line and torch sealed under vacuum. The tube was then placed in a vertical furnace with about 3 cm elevated above the top of the furnace. Pyrex wool was packed around the tube at the top of the furnace, and a stream of air was directed at the end projecting out. The temperature in the furnace was then increased to 210°C in the case of TaCl_5 , or 125°C in the case of NbCl_5 , and sublimation proceeded for approximately

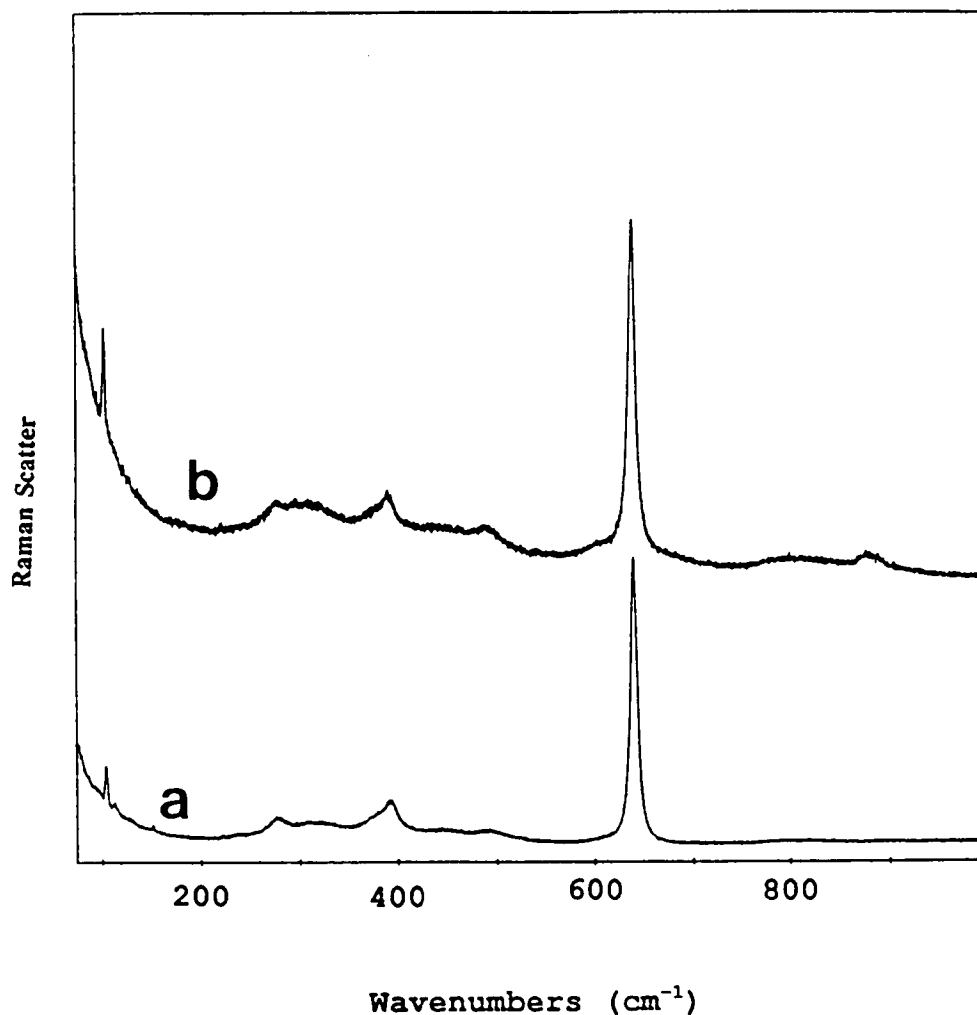


Figure 1. Raman spectra of K_2TaF_7 powder, obtained in sealed quartz tubes at room temperature. Excitation source was a 488 nm Ar ion laser operating at 400 mW. The strong band at 640 cm^{-1} is due to $[TaF_7^{2-}]$, and the weak band at 878 cm^{-1} is due to tantalum oxyfluoride (94).

- a. Clear portion of K_2TaF_7 , as received.
- b. Opaque portion of K_2TaF_7 , as received.

24 hours. After the tube was cooled, the lower end of the tube, which contained a white powder (probably MOCl_3 , $\text{M}=\text{Ta}, \text{Nb}$ (74,75)), was removed by sealing with a torch. Raman spectra and X-ray diffraction spectra of the metal chlorides revealed no bands due to oxide (75,94).

Niobium oxide (Nb_2O_5 , Aldrich, 99.99%) was used as received.

Niobium oxide trichloride was prepared by the procedure described in reference 95. A stoichiometric ratio of NbCl_5 and Nb_2O_5 was placed in a quartz ampule and sealed under vacuum. The quartz tube was placed in a Lindberg furnace and heated to 300°C for 12 hours. After cooling, the quartz tube was observed to contain a white solid (NbOCl_3) with a small quantity of yellow solid (unreacted NbCl_5). The white solid was divided into three portions, each of which was placed in a Pyrex tube (approx. 20 cm long). The tubes were torch sealed under vacuum and placed in a horizontal furnace with three temperature zones (350 , 250 , and 25°C); the end of the tube containing the white solid was positioned in the hottest zone. After the sublimation had proceeded for three days, the tubes were removed from the furnace. Four distinct regions could be observed in each tube: at the end of the tube which had been in the 350°C zone was a small quantity of coarse grey powder; in the 250°C zone was a large quantity of opaque white material; in the region between the 350 and 250°C zones was a small amount of pale blue solid;

and, finally, in the ambient temperature zone were bright yellow crystals. Raman spectra of each solid were obtained, and the yellow crystals and the white matter were determined to be NbCl_5 and NbOCl_3 , respectively. The Raman spectra of the other two substances matched none that could be found in the literature, but their identity can be inferred from reference 96 as NbO_2Cl and $\text{Nb}_3\text{O}_7\text{Cl}$ for the grey and blue solids, respectively.

In the preparation of Nb(IV) solutions for deposition experiments, solutions of Nb(V) were prepared by adding either NbCl_5 or K_2NbF_7 to the SCA or SFCA melt, and to these solutions were added either Nb metal in a 1:1 (Nb(V):Nb) molar ratio, or aluminum metal in a 3:1 (Nb(V):Al) molar ratio. The solutions were heated to 450°C in sealed Pyrex ampoules and allowed to react for >12 hours.

Sodium carbonate (Mallinkrodt, analytical reagent grade) was dried under vacuum at 300°C for >48 hours, and then was transferred to drybox and stored until used.

3. Electrode Materials

Working electrodes for electrochemistry in SCA and SFCA were constructed from tungsten wire (Aesar, 99.95%, 0.75 mm ϕ), platinum wire (Aesar, 99.999%, 0.5 or 0.25 mm ϕ), or glassy carbon rod (Sigri, grade K, 1 mm ϕ). Quasi-reference electrodes were constructed using the 0.25 mm ϕ Pt wire. Counter electrodes were made from glassy carbon rod (Sigri,

grade K, 3 mm ϕ) or from platinum foil. Reference electrodes were prepared by sealing a silver wire (Aesar, 99.9985%) electrode in a thin glass bulb to which a SCA solution saturated in AgCl (Aesar, 99.9%) was added.

Cathodes in the electrodeposition experiments were constructed either of nickel plates (Aesar, 99.9%, 2X.5X.25 cm) or tungsten foil (Aesar, 99.99%, 2 X .5 X 0.05 cm). Anodes were of niobium metal, either coiled wire (Aesar, 99.9%, 1 mm ϕ) or plates (Aesar, 99.9%, 2 X 1 X 0.25 cm).

For electrolytic purification of FLiNaK, a nickel plate (4 X 1.5, X .25 cm) cathode, a glassy carbon rod (4 mm ϕ) anode, and a Pt wire (0.5 ϕ) quasi-reference were used.

Cleaning of the electrodes is described in the Procedures section.

B. Apparatus

1. Dryboxes and Vacuum Lines

All melt components and solute species used in these studies are highly hygroscopic in nature, and thus require special care in handling in order to avoid contamination from atmospheric oxygen and water. Unless otherwise stated, all work was conducted either in a nitrogen-atmosphere dry-box (water level typically <2 ppm), in evacuated and sealed cells or ampules, or in nitrogen or argon purged steel or glass cells.

In most cases, the vacuum lines used were of Pyrex;

they could be evacuated to a pressure of <50 mTorr, and were separated from the pump by a vacuum trap immersed either in liquid nitrogen or an acetone-dry ice bath. Except for the COCl_2 line, which is described below, the Pyrex vacuum lines were constructed in-house, and utilized stopcocks and AceThred connectors (#15) to facilitate connection of sample vessels to the line. The stainless steel vacuum line used in working with FLiNaK was connected at one port to a combination rough pump-diffusion pump which could attain a pressure of 50 mTorr with the diffusion pump off-line, and a pressure as low as 0.2 mTorr with the diffusion pump enabled. This line also had a port through which argon or nitrogen could be introduced for purging or sparging.

Transfer of glassware from a drybox to a vacuum line was usually accomplished by forcing a tightly-fitting piece of Tygon tubing over the glass tube end and clamping the Tygon closed with a pinch clamp. Upon removal from the drybox, a length of copper wire was secured around the Tygon tube where it overlapped the glass tube, a fritted Pyrex adapter was fitted into the open end of the Tygon tube, and the adapter was connected to the vacuum line via an AceThred adapter.

2. Apparatus Used in Working with FLiNaK Melts and Solutions

A Lindberg (Model 56622) furnace was used in prep-

aration of FLiNaK melts; the temperature was controlled manually by providing the appropriate voltage from an AC transformer (220V, 20A, built in-house) or by a Lindberg (Model 59344) Digital Temperature Controller. The temperature was measured inside the cell whenever possible using a chromel-alumel (Omega, K-type) thermocouple, which was sheathed in a nickel tube and connected to a digital readout (Omega). Alternatively, the temperature would be measured by inserting a chromel-alumel thermocouple between the outer surface of the cell and the inner wall of the furnace.

The cell assembly used in the preparation of FLiNaK melts is shown in Figure 2. The body of the cell (Figure 2a) was constructed in-house from 304 stainless steel. A circular groove was cut into the underside of each cell top approximately $3/8$ " from the outer edge to accommodate a Viton O-Ring. The high-vacuum top (Figure 2b), also constructed in-house, was of 304 stainless steel, and consisted of a flat round plate $1/2$ " thick, a $5/8$ inch tube to which was welded a high vacuum ball valve, and a $1/4$ inch tube to which was welded a high vacuum rotary valve. With this top in place and the diffusion pump enabled, the cell could be evacuated to <0.2 mTorr. The top shown in Figure 2c was used for addition of NH_4HF_2 and for electrolytic purification. It consisted of a flat round plate ($1/2$ " thick) with a centered $5/8$ " tube welded to a $3/4$ " Swagelok fitting; this tube was either closed with a Swagelok blank or was

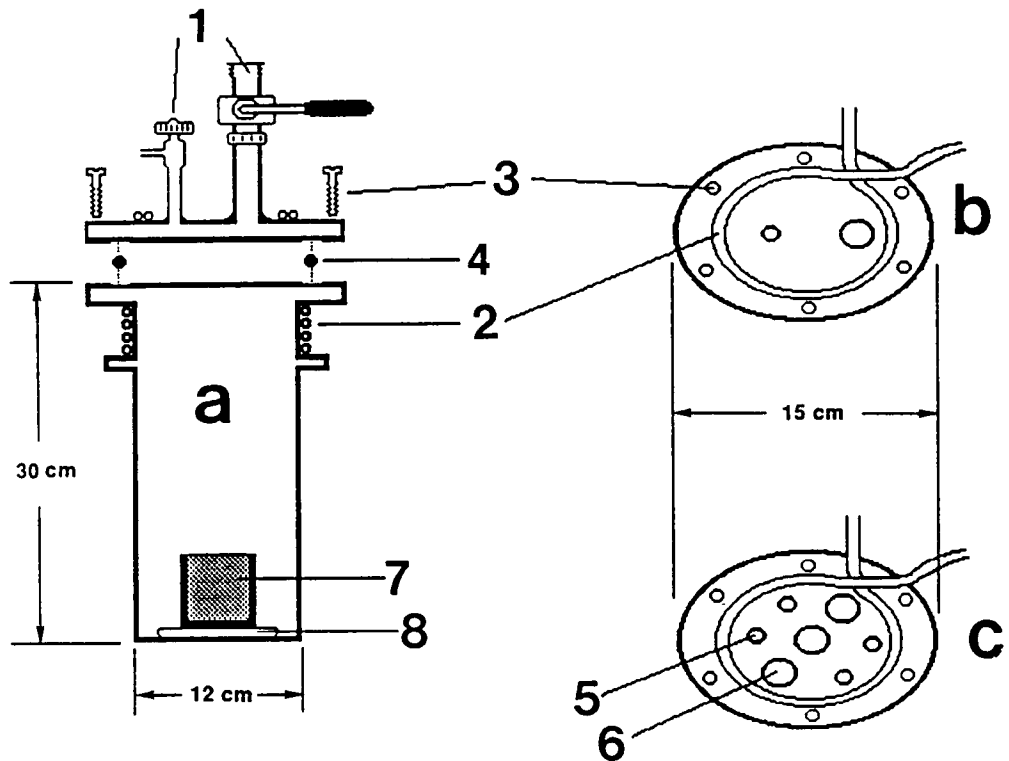


Figure 2. Stainless steel cell used for work with FLiNaK.

- a. Cell body
- b. High vacuum cell top
- c. General purpose cell top

- | | |
|--------------------------------|-----------------------|
| 1. Evacuation and purge valves | 5. 1/4" Cajon fitting |
| 2. Copper cooling coils | 6. 1/2" Cajon fitting |
| 3. Fastening bolts | 7. Carbon crucible |
| 4. Viton O-ring | 8. Alumina plate |

fitted with a ball valve, depending on what was needed. Surrounding the central tube were four 1/4" Cajon and two 1/2" Cajon fittings, which were used for introduction of N₂ or Ar, H₂, NH₄HF₂, or the electrode assemblies for electrolytic purification. The cell could be evacuated to <50 mTorr with this top in place, but was usually under N₂ or Ar purge in such a case.

Sparging of melts was accomplished using a nickel tube to which had been soldered a 6 cm length of platinum tube. Only the platinum tube came in contact with the melt.

Diagrams of the electrodes used for electrolytic purification of FLiNaK are shown in Figure 3. Nickel rods, 1/8" diameter, sheathed in quartz tubes (Quartz Plus or Quartz Scientific) were used as electrode leads. The quartz was sealed to the rod at the top using Varian Torr-seal epoxy. The platinum quasi-reference electrode was spot-welded directly to the nickel rod, which, in order to obtain a good spot-weld, had to be filed down to a thickness of approximately 1 mm. The thickness of the nickel plate prevented the use of spotwelding in the case of the cathode; the nickel rod was flattened slightly to provide better contact with the nickel plate. Next, a diagonal cut was made at the top of the flattened area, and the top of the nickel plate was folded to fit into this cut. The area of contact was wrapped tightly with copper foil, followed by a tight coil of copper wire. Proper contact was ascertained by measuring

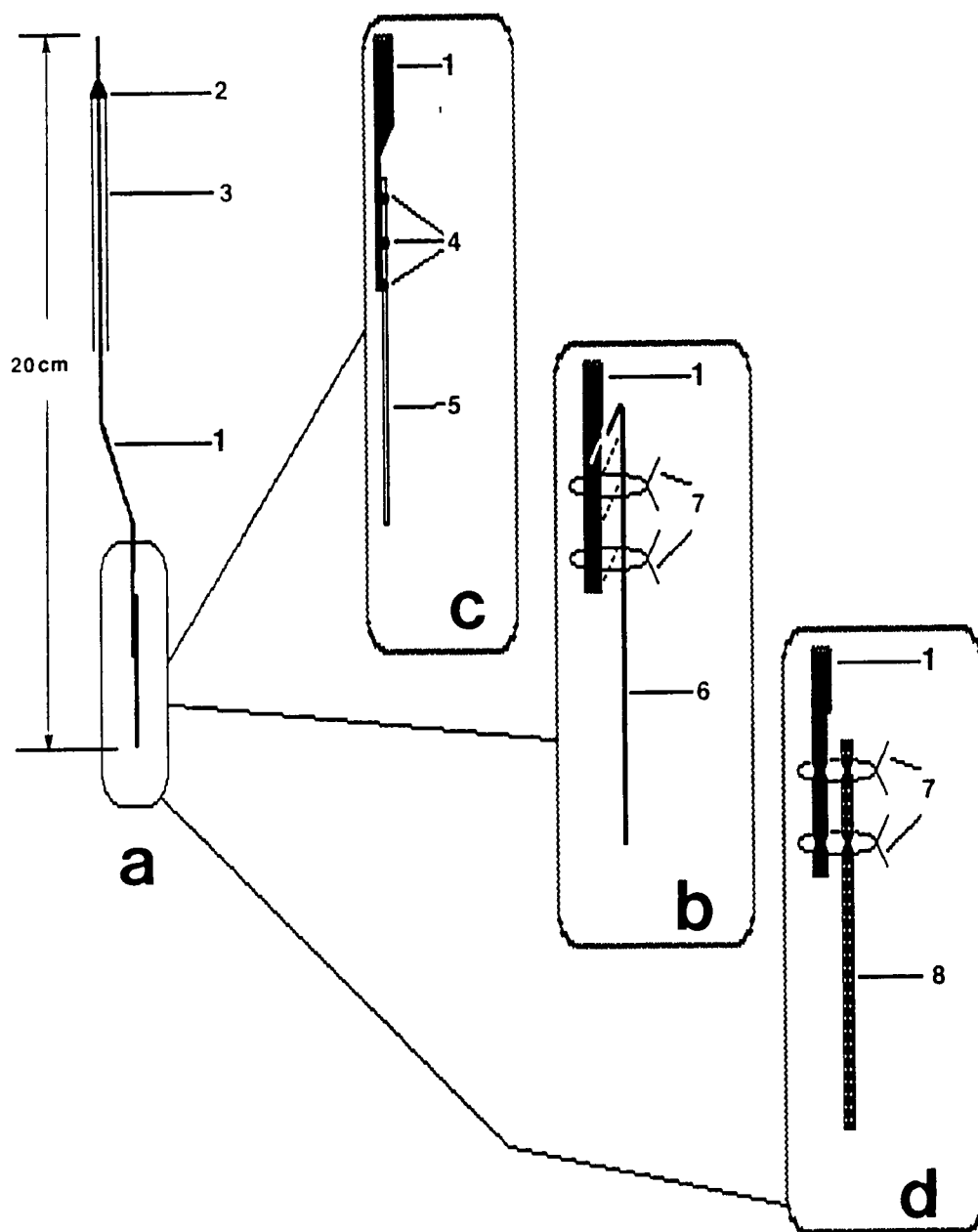


Figure 3. Diagrams of electrode assemblies used in electrolytic purification of FLiNaK melts.

- | | | |
|---|--------------------------------------|------------------|
| a. Complete electrode | b. Expanded view of Ni-plate cathode | |
| c. Expanded view of Pt wire quasi-reference | d. Expanded view of GC rod anode | |
| 1. Ni rod lead | 4. Spot-weld | 7. Cu wire twist |
| 2. TorrSeal epoxy | 5. Pt wire | 8. GC rod |
| 3. Quartz sheath | 6. Ni plate | |

the resistance from the top of the nickel rod to the bottom of the nickel plate. To construct the glassy carbon anode, both the bottom of the nickel rod and the top of the glassy carbon rod were flattened, and two shallow grooves were made around the circumference of each. Both were wrapped with thin copper foil and pressed together, and then copper wire was wrapped around them into each groove to prevent the glassy carbon from slipping away from the nickel lead.

Recrystallization of FLiNaK was conducted in a glassy carbon cup (Sigri, Grade K, 50 ml capacity) enclosed in a quartz ampoule. "Low-grade" FLiNaK (see Procedures section) was loaded into the cup inside a drybox, and the cell was transferred to a vacuum line, evacuated and sealed.

Premelting of K_2TaF_7 -FLiNaK solutions was accomplished using the apparatus depicted in Figure 4. The apparatus consists of a glassy carbon (Sigri) or graphite (Alfa) cup (approximately 1 ml capacity) inside a quartz tube with inner diameter slightly larger than the outer diameter of the cup. The tube was capped with the adapter shown in Figure 4, which was designed to connect easily to a vacuum line. Details of Raman sample preparation can be found in the Procedures section.

Raman spectroscopic measurements of Ta(V)-FLiNaK solutions were obtained using "windowless" cells (97) enclosed in quartz tubes. The top of the quartz tubes were closed with adapters similar to that shown in Figure 4.

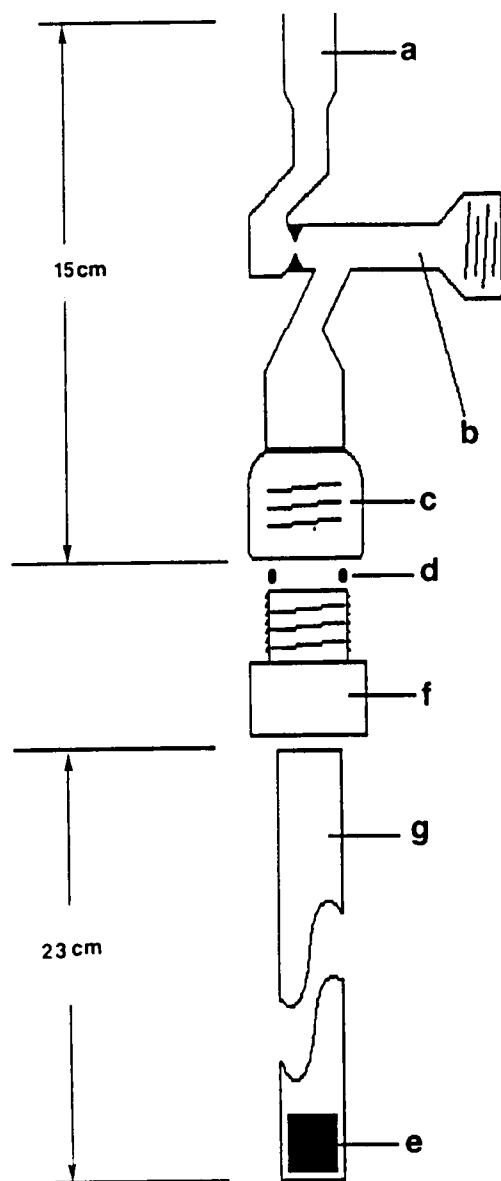


Figure 4. Apparatus used for premelting FLiNaK solutions.

- | | |
|---------------------------|--------------------|
| a. Vacuum line connection | e. Carbon crucible |
| b. Ace Glass stopcock | f. Teflon bushing |
| c. AceThred adapter | g. Quartz tube |
| d. FETFE O-ring | |

3. Apparatus Used in Working with SCA and SFCA Melts

Unless otherwise stated, Lindberg crucible furnaces were used in conjunction with Lindberg temperature controllers in working with SCA and SFCA melts at elevated temperatures. Temperature control was achieved by connecting the lead of a chromel-alumel thermocouple which is built into the furnace to an adaptor which is built into the controller. In all cases, the temperature was monitored using a second thermocouple positioned next to the cell or reaction vessel and connected to a digital readout. When samples of expected high vapor pressure were heated, the furnace was located inside a fume hood in case of cell breakage.

Treatment of melts with COCl_2 was accomplished using a dedicated vacuum line (Figure 5) constructed of Pyrex, with ground glass joint stopcocks lubricated with Silicone grease. Connection of a cell or reaction vessel to the vacuum line was via a ground glass ball joint (Figure 6). Vessels attached to the vacuum line were heated using a furnace, constructed in-house, which consisted of nichrome ribbon wrapped around a 60 mm inner diameter Pyrex tube.

Treatment of melts with CCl_4 was accomplished using an apparatus like that shown in Figure 7a. The apparatus consisted of a septum port, an Ace Glass stopcock, and an AceThred adapter, the latter of which was used for attachment to the treatment vessel, which could be a melt tube or

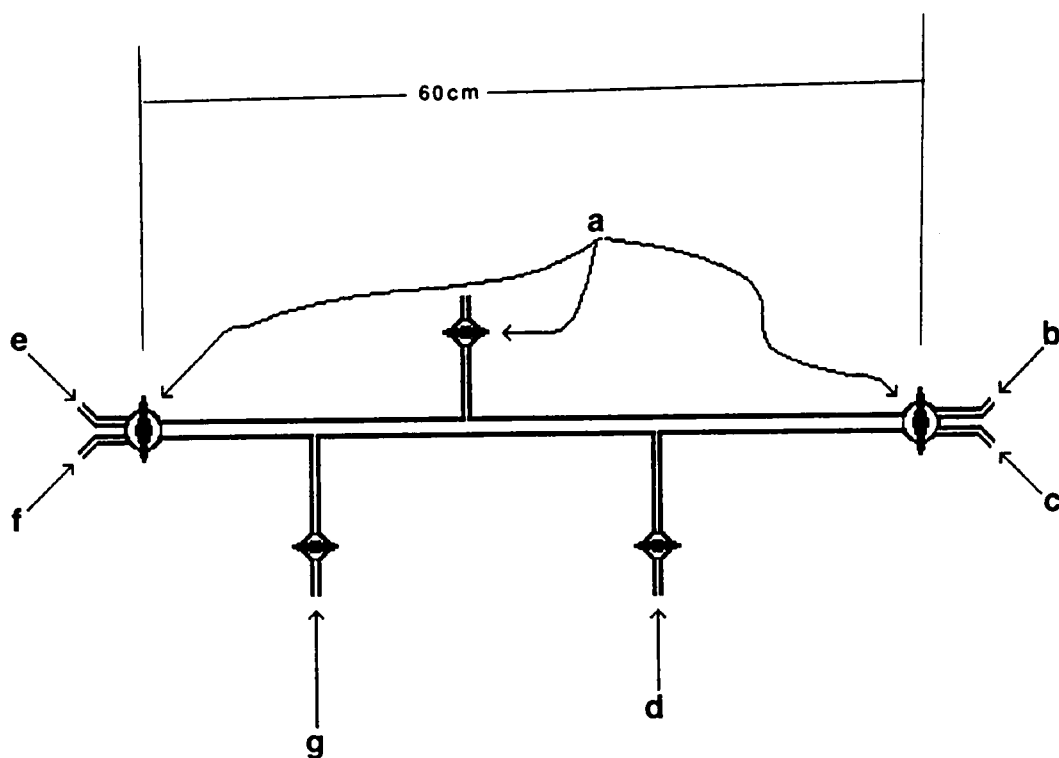


Figure 5. Pyrex vacuum/gas line dedicated to COCl_2 treatment of SCA melts.

- | | |
|----------------------------|-------------------------------|
| a. Ground glass stopcocks | e. Nitrogen inlet |
| b. Connection to NaOH trap | f. Hg column |
| c. Connection to vacuum | g. Connection to Hg manometer |
| d. Cell/tube connection | |

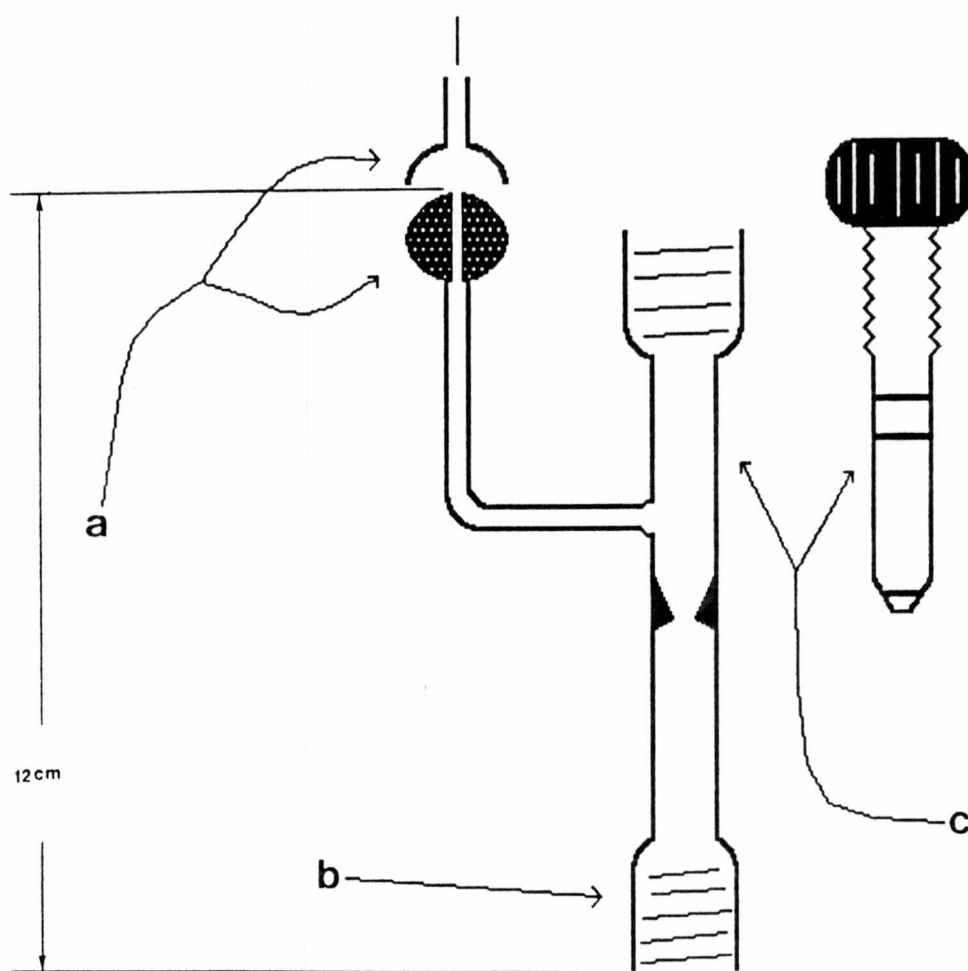


Figure 6. Apparatus used to connect a cell or melt tube to the COCl_2 gas/vacuum line.

- a. Ground glass ball joint
- b. AceThred adapter
- c. Ace Glass stopcock

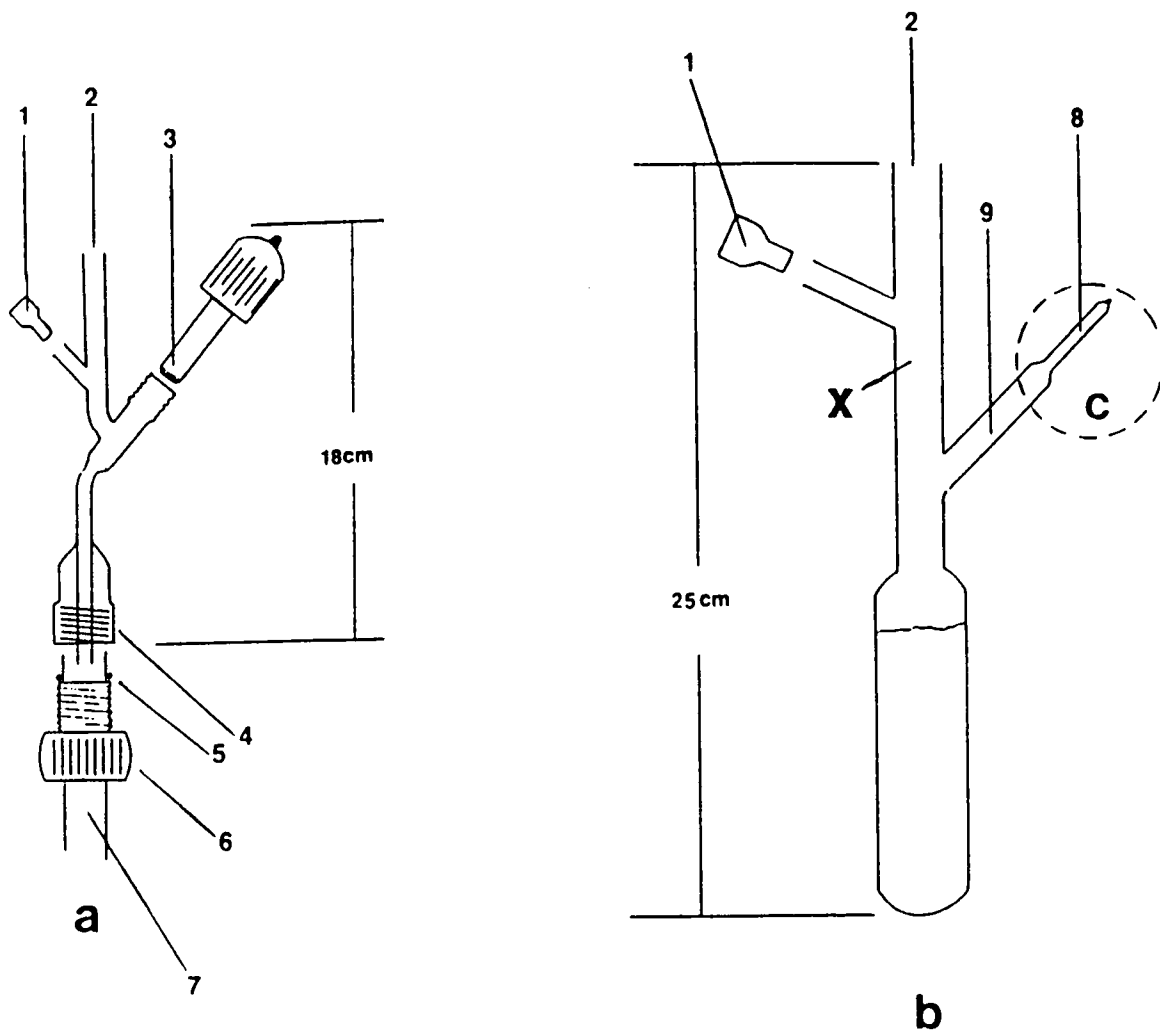


Figure 7. Apparatus used in treating SCA and SFCA melts with CCl_4 .

- a. Used for treatment of melts in cells or melt tubes
- b. Used for bulk treatment of large quantities of melt
- c. Evacuation port

- 1. Rubber septum
- 2. Connection to vacuum
- 3. Kontes Teflon stopcock
- 4. AceThred adapter
- 5. FETFE O-ring

- 6. Teflon bushing
- 7. Cell or melt tube
- 8. 3 mm tube
- 9. 7 mm tube

a pre-fabricated cell. Alternatively, a tube like that depicted in Figure 7b could be used for bulk melt treatment. The procedure for the addition, reaction, and removal of CCl_4 is described in the Procedures section of this chapter.

Infrared spectra of liquids were obtained using a cell similar to that described by Flowers and Mamantov (98). The cell utilized silicon windows which were torch-sealed to the Pyrex body of the cell. Two AceThred adapters on the top of the cell provided access for loading and sample addition, and produced an airtight seal when closed. A furnace with diametrically opposed holes, which was constructed in-house, allowed heating of the melt inside the sample chamber of the FTIR instrument.

Figure 8 depicts the cells in which niobium deposition experiments were conducted. In general the cells consisted of a single niobium coil or plate anode and one or more cathodes made from either nickel plate or tungsten foil. The electrode leads were tungsten wires (0.75 mm ϕ), and connection of the leads to the electrode material was made by spotwelding each to a short length of Pt wire (0.5 mm ϕ). If the experiment were to be conducted at temperatures below 550°C, the cell would be constructed of Pyrex, and direct Pyrex-to-tungsten seals were utilized to ensure hermetic conditions. Quartz cells were used for higher temperature experiments. Since the tungsten leads would not form a strong and hermetic bond with quartz, the glass shop con-

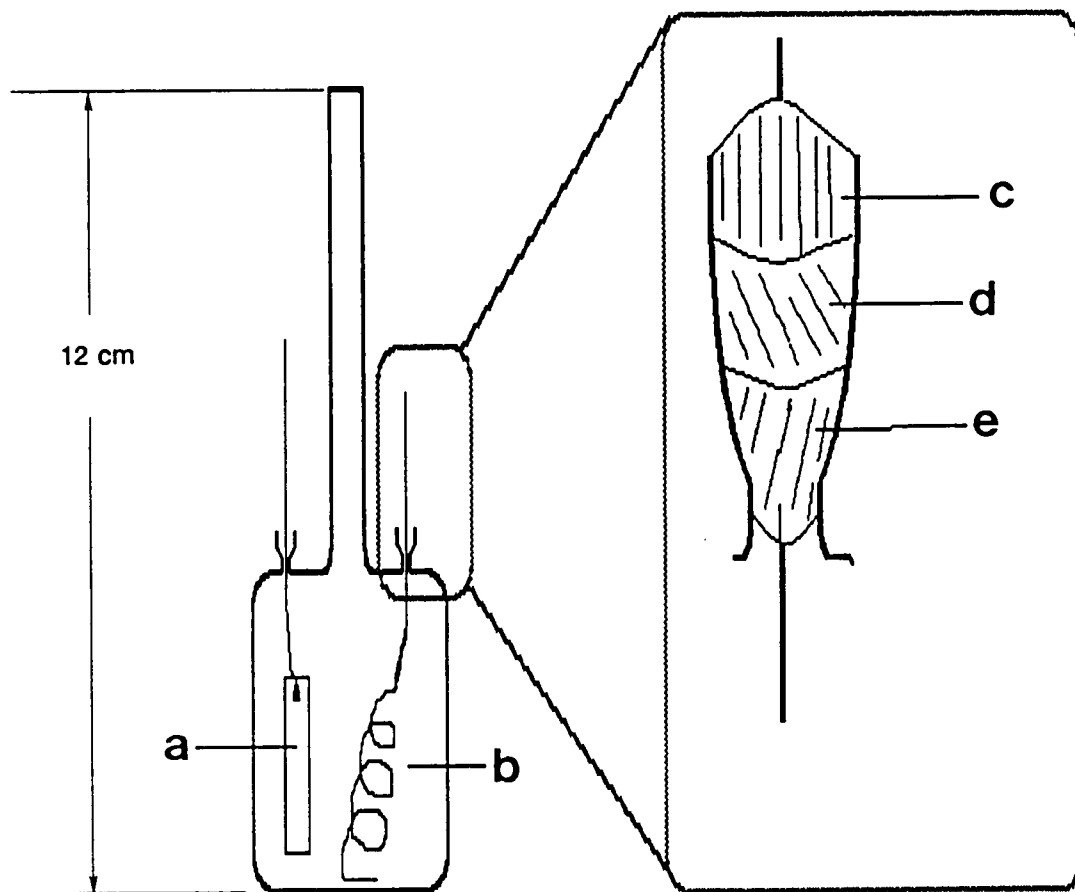


Figure 8. Quartz or Pyrex deposition cell. If the cell was of Pyrex, the cement was not necessary, and direct Pyrex-to-tungsten seals were made between the cell and a tungsten wire electrode lead.

- a. Nickel or tungsten plate cathode
- b. Niobium coil or plate anode
- c. Saureisen No. 2 Aluseal Cement
- d. Cotronics Thermeez high temperature ceramic epoxy
- e. Cotronics #905 Quartz low expansion ceramic binder

structed the cells with the electrodes in place, but without attempting to close the tube around the tungsten leads. Sealing of these gaps was attempted using various ceramic high-temperature cements; hermetic seals could not always be made, but the best results were obtained by layering three different types of cement into the electrode well, as shown in Figure 8.

Electrochemical measurements were conducted using Pyrex cells (see Figure 9) which were evacuated and sealed after addition of melt or solute. The reference electrode consisted of a silver wire immersed in an AgCl-saturated SCA melt, contained in a thin glass bulb completely isolated from the rest of the cell. Since the ohmic drop across the glass membrane is very large, a quasi-reference electrode, consisting of a platinum wire separated from the bulk melt via a medium-porosity frit, was used. Note that the quasi-reference electrode compartment contained the same melt composition as the bulk melt, and that a hole was cut into the compartment, above the melt line, for pressure equilibration. The other electrodes were described in the Materials section. The electrodes were arranged (Figure 9, top view) such that the quasi-reference electrode would be isolated from the bulk melt, as well as from any products of working/counter electrode reactions, even during long-time experiments. Finally, attached to the cell body were two branched tubes used for solute addition.

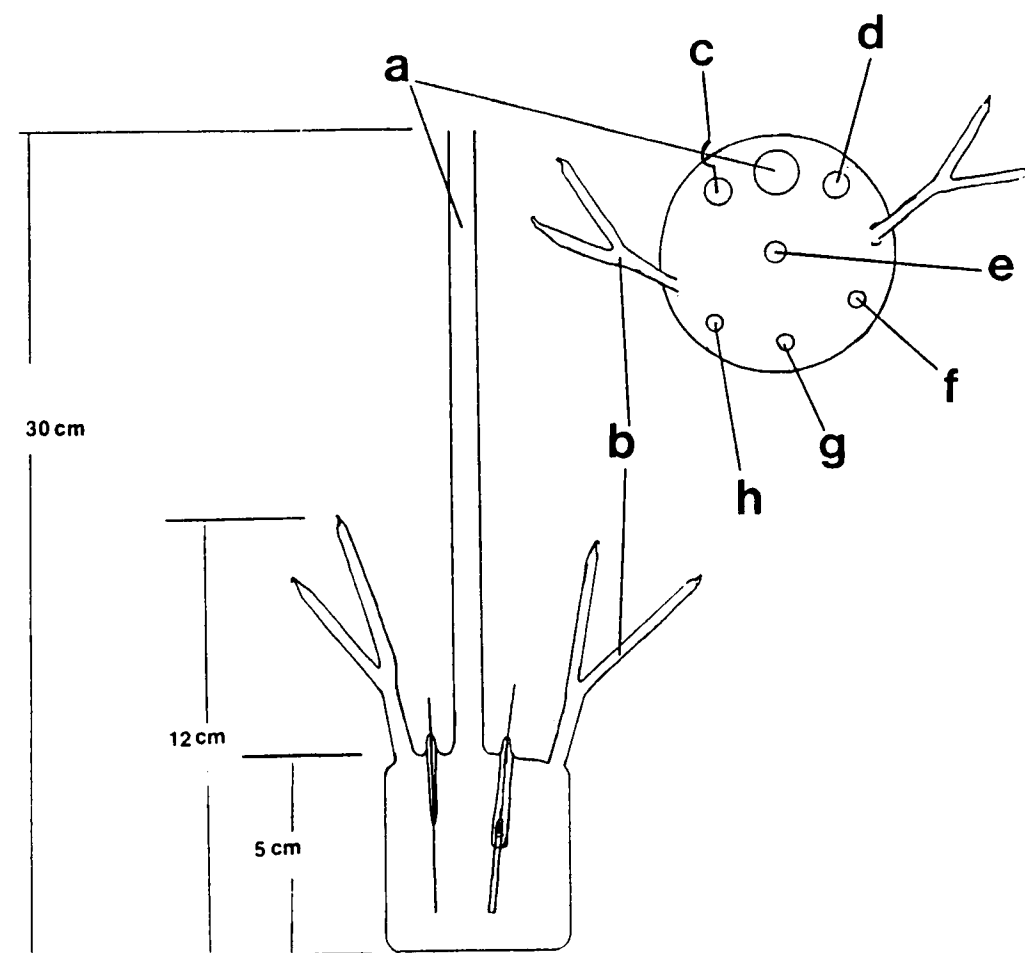


Figure 9. Diagram of the cells used in electrochemical studies of Nb(V) in SCA and SFCA.

- | | |
|---|------------------------------|
| a. Fill tube | e. GC counter electrode |
| b. Solute addition tubes | f. W wire working electrode |
| c. Pt quasi-reference electrode in a fritted (medium porosity) tube | g. Pt wire working electrode |
| d. AgCl/Ag reference electrode in a thin glass bulb | h. GC working electrode |

4. Instrumentation

a. Electrochemical instruments. Constant current and constant potential electrolysis experiments were performed using either Princeton Applied Research Model 273 Potentiostat/Galvanostat (PAR 273) in the stand alone mode, or a PAR Model 173/179 Potentiostat. Pulsed electrolysis experiments were conducted using the PAR 273 in the stand alone mode, or the PAR 173/179 in conjunction with a PAR Model 175 Programmer.

Other electrochemical measurements (voltammetry and coulometry) were made using the PAR 273, which was controlled via a IEEE-488 GPIB interface by a IBM PS/2 Model 70-A21 microcomputer running the PAR M270 software. The IBM PS/2 M70-A21 is an 80386-based computer which operates at a speed of 25 MHz, and which utilizes the MicroSoft Disk Operating System (MS-DOS, versions 3.0 to 3.3) or Digital Research DOS (DR-DOS, version 6.0). The software, obtained from PAR, is capable of controlling the PAR 273 in a wide variety of electrochemical methods, and also provides some minor data manipulation facilities such as smoothing, baseline correction, peak location, and linear line-fitting.

Chronoamperometry experiments were conducted using the PAR 273, which was controlled by the IBM PS/2 running a program (CA.EXE) written and compiled in QuickBasic (Microsoft, version 4.5) specifically for that purpose. This program collected current-time data and stored it in a disk file.

At a later time a second program (CAFILT.EXE) was used to reconfigure the data in a series of current vs. potential sequences, which were stored in a format readable by either Lotus 1-2-3 (version 2.2) or QuattroPro (Borland, version 3.0).

Voltage measurements, such as that of the potential of the Pt quasi-reference electrode vs. the Ag(I)/Ag reference, were made using a Keithley 616 high impedance electrometer, when it was available, or a Keithley 173A digital multimeter. It was found that both the electrometer and the voltmeter provided the same result, but that the voltmeter required more time to reach a steady value.

b. Spectroscopic instruments. Raman spectra of prepared samples were obtained by Anna G. Edwards in the UTK Raman laboratory. The excitation source was a Coherent Innova Model I-100-15 argon ion laser, most frequently using the 514.5nm line; a Jobin-Yvon (J-Y) 2000M monochromator, and a RCA Model C31034 photomultiplier tube (PMT) mounted in a Products for Research thermoelectrically cooled PMT housing equipped with a PR-201 no-dew attachment constituted the Raman scattering collection system. The monochromator was scanned using an Instruments S.A. (ISA) Model 980015 stepping motor, controlled via an analog/digital/analog converter installed in a IBM PS/2 Model 50-SX microcomputer running the BGRaman software developed by Professor Bernard Gilbert (University of Liege, Belgium).

Infrared spectra were obtained with a Bio-Rad FTS-7 Fourier transform infrared (FTIR) spectrometer which was controlled via parallel interfacing by a microcomputer system based on the Motorola 68000 family of CPU chips. The FTS-7 is a mid-range instrument ($4400 - 400 \text{ cm}^{-1}$) with a ceramic source, a KBr-GaSe beamsplitter and a DTGS detector. It is capable of obtaining spectra at resolutions ranging from 16 cm^{-1} to 1 cm^{-1} . The computer utilizes the Idris operating system (Whitesmiths, LTD), which is a micro-computer version of the mainframe operating system UNIX, and Digital Data Systems (DDS, BioRad, release 4.33) software to obtain spectra from the FTS-7. The DDS software provides means for various data manipulation techniques, including spectral subtraction, multipoint baseline correction, and multiple spectrum overlays.

A Hewlett-Packard Model 8452A Diode Array spectrometer was used to obtain UV-visible spectra. The HP8452A has a maximum spectral range of 190 to 800 nm, and can function at a resolution of either 1 nm or 2 nm, depending upon an internal switch setting selected by the user. The spectrometer was linked to a Intel 80286-based microcomputer via an HPIB interface (HPIB is the Hewlett Packard equivalent of the IEEE-488 General Purpose Interface Bus (GPIB) standard interface). The HP 8452 software was used to control the spectrometer and for data analysis.

High temperature spectra were obtained using the

HP8452A spectrometer with a water-cooled furnace/cell holder, which was designed and constructed in-house. The cell holder had an aluminum water-cooled base (1/4" thick), on top of which rested a low-thermal-conductivity ceramic block (Cotronics, type 360-HS). The cell holder itself was fastened to the top of the ceramic block via a metal plate. Heating of the cell holder was accomplished using a furnace composed of nichrome wire wound around a 45-mm inner diameter quartz tube (Quartz Plus); the furnace was water cooled, and included an insulating layer of ceramic blanket (Cotronics, type 370) between the heating coils and the water-cooling copper tubes. The furnace could be used only to temperatures as high as 600°C, since the cell holder and top plate were of aluminum (which melts at approx. 650°C). However, if these pieces were replaced with stainless steel or nickel equivalents, the furnace could be safely used inside the spectrometer at temperatures $\geq 1000^{\circ}\text{C}$.

A Perkin-Elmer PHI5000 ESCA (Electron Spectroscopy for Chemical Analysis) instrument was used for analysis of deposits and products of electrolysis experiments. The instrument was periodically calibrated using gold and copper foil standards.

A Siemens D-500 X-Ray Diffraction spectrometer was used for analysis of deposits and synthesized reagents. The spectrometer was controlled by a minicomputer, which could be accessed by a PC (DOS-based) computer or a Tektronix ter-

minal for control and data analysis. The software included an on-line library of JCPDS files for comparison with spectra obtained on the instrument.

C. Procedures

1. Melt Preparation

a. Initial preparation of FLiNaK. FLiNaK was prepared by first mixing the proper quantities of LiF, NaF, and KF in a large glassy carbon crucible. The crucible was carefully lowered into the body of a stainless steel cell (Figure 2a, p. 42), the cell was sealed with a high-vacuum top (Figure 2b, p. 42) and then placed in a Lindberg furnace. The outlet of the ball valve was then connected to a stainless steel vacuum line, and the cell was evacuated slowly to avoid spillage of the mixture. The pressure was monitored with a high vacuum gauge that was connected to the vacuum line. When the pressure had decreased to <200 mTorr, the temperature was slowly raised to 525°C to melt the eutectic mixture. Usually, as the temperature increased, the pressure increased to a maximum of about 500 mTorr, and then began to decrease again as the temperature reached $\approx 500^\circ\text{C}$. After the pressure had decreased to 1-5 mTorr, the diffusion pump was engaged, and the cell was left to evacuate for 12-16 hours. The pressure generally decreased to <0.2 mTorr

after this period. Melt at this stage of preparation was considered "low-grade" FLiNaK.

Several methods for further purification of "low-grade" FLiNaK were utilized in order to judge the relative efficiency of each. These methods included those described in the literature (40-46,48,49,51,86) which concerned the use of FLiNaK as a solvent for electrochemical studies (usually of refractory metals).

b. Purification of "Low-grade" FLiNaK with NH_4HF_2 (41-45). Working in a drybox, approximately 200 grams of "low-grade" FLiNaK were placed in a large glassy carbon crucible, which was gently lowered into the stainless steel cell (see Figure 2a, p. 42). The cell top depicted in Figure 2c (p. 42) was placed atop the cell and fastened into place. A 6 mm diameter nickel tube was inserted into the cell through one of the Cajon fittings, and the top end of the tube was closed with a piece of Tygon tubing sealed with a pinch clamp. The cell was then carefully placed in the antechamber of a drybox such that it lay at an angle of approx. 30° (so that the melt would not spill out of the crucible).

The cell was removed from the antechamber and placed in the furnace. The Tygon tubing was connected to the vacuum/nitrogen line, and the cell was evacuated to a pressure of <50 mTorr, and then back-filled with nitrogen. Under fast

nitrogen purge, two large stainless steel tubes were inserted into the large Cajon fittings, and these were then connected to the exigent gas apparatus, which consisted of backflow traps followed by bubblers containing an aqueous solution of NaHCO_3 . The nitrogen flow was then reduced such that the bubbling rate was approximately 1 bubble per second.

The cell was then heated to 525°C , and ample time was allowed for complete melting of the FLiNaK . Next a quantity of NH_4HF_2 was weighed out in an addition vessel in an amount of approximately 3 weight percent of the total mass of FLiNaK (this method for adding reagents to molten fluorides is described in reference 23). The vessel was attached to the vacuum/nitrogen line with Tygon tubing, and was purged for several minutes with nitrogen. The nitrogen flow was increased to provide a fast purge, the central valve on the cell top was opened, the addition tube was inserted through the valve, and the NH_4HF_2 was added. Extreme care had to be taken at this point, as there was inevitably an initial burst of vapors due to the decomposition of the NH_4HF_2 into NH_3 and HF . After the addition was made, the addition tube was withdrawn, the valve was closed quickly, and the nitrogen flow was again decreased. The intensity of the reaction could be estimated by observation of the amount of vapor and solid material flowing through the exigent gas apparatus. After about 30 minutes, the reaction had generally subsided

sufficiently to proceed with another addition. This procedure was repeated until 18-24 weight percent NH_4HF_2 had been added. It should be noted that the steel and Tygon tubes generally had to be replaced once or twice during the procedure in order to prevent clogging by solid matter (probably NH_4F).

After the final aliquot of NH_4HF_2 had been added and sufficient time for the reaction to subside had passed (1/2 to 1 hour), the temperature was slowly increased to 750°C in order to ensure that the reaction was complete. The cell was purged with nitrogen during this time, and a rapid increase in the exigent gas flow would occur at a temperature of approximately 650°C ; this was probably due to the decomposition of residual NH_4HF_2 which had condensed on the upper portions of the cell walls. It was extremely important to increase the temperature slowly, and to monitor the cell during that time. After the temperature had been maintained at 750°C for approximately 2 hours, a sparge tube was inserted through the addition port. The sparge tube was described previously (p. 43). A mixture of approx. 1:4 $\text{H}_2:\text{N}_2$ was directed through the sparge tube, which was then lowered and positioned such that the platinum tube was just above the bottom of the carbon crucible. The melt was thus sparged for a period of 12-16 hours. The flow of H_2 was then stopped, and the melt was sparged with N_2 for a period of several hours in order to remove any residual H_2 from the

melt. Finally, the flow of nitrogen was stopped, the cell was evacuated to a pressure of <50 mTorr, followed by cooling of the cell and transfer into a drybox for removal and crushing of the melt.

c. Purification of "low-grade" FLiNaK by electrolysis (46,86). Approximately 50g of "low-grade" FLiNaK were placed in a small (30 ml) glassy carbon crucible, which was then placed into a stainless steel cell, with a piece of alumina plate placed between the crucible and the cell bottom to provide electrical insulation. The cell top was fixed in place, and the cell was removed from the drybox. A nitrogen purge was introduced to the cell, with the effluent gas bubbled through glycerin. Three electrodes were inserted under fast nitrogen purge: a large nickel plate electrode to be used as cathode; a 5 mm OD glassy carbon rod electrode for use as the anode; and a 0.25 mm diameter platinum wire electrode for use as a quasi-reference for potential control.

The cell was heated to 500°C, and time was allowed for the melt to completely liquefy. The electrodes were then lowered into the melt under fast nitrogen purge, with the anode lowered sufficiently that it made firm contact with the bottom of the glassy carbon cup. A potential of -1.7V was applied across the cathode and anode, and the current was measured with time. When the measured current had decayed to <2 mA (after 36 hours), the cell was disconnected

from the potentiostat, the electrodes raised above the melt, and the furnace turned off. After the cell had cooled, it was taken into a drybox, and the melt was removed and crushed.

d. Purification of "low-grade" FLiNaK by recrystallization (40). Approximately 100 g of "low-grade" FLiNaK were loaded into a glassy carbon crucible, which was placed in a quartz cell similar to that used for premelting of FLiNaK solutions (see Fig. 4, p. 46). The cell top was attached, and the cell was removed from the drybox. The cell was evacuated, and then closed off from the vacuum line using the stopcock on the cell top.

The lower portion of the cell was heated to 500°C, while the cell head was cooled by directing compressed air at it. After two hours, the cell was raised only long enough to ensure that all of the FLiNaK was molten. The temperature was then decreased to 480°C, and sufficient time for temperature equilibration was allowed (approx. 1hr). The temperature was then decreased at a rate of 2-5°C per hour, until a temperature of 430°C had been reached, after which the temperature decrease was accelerated until the cell was at approximately 100°C. After taking the cell into a drybox, the impure core was removed, and the remainder of the melt was stored for later use.

e. Preparation of SCA melts. Unless otherwise specified, all sodium chloroaluminate melts used were SCA melts. Preparation of the melts has been described previously (74,75,91), and so will be discussed only briefly here. Typically, a melt would be prepared by mixing equimolar amounts of purified AlCl_3 and NaCl in a large (approximately 200ml) ampule. Approximately 5% excess NaCl would then be added to the ampule; also, several pieces of aluminum metal (4N) would be placed into the ampule. The ampule would be capped with Tygon tubing, which was clamped closed, and then removed from the drybox and sealed under vacuum. The ampule was then placed in a rocking horizontal furnace and heated to 170°C until the contents were molten. The temperature was then increased to 190°C and the tube was allowed to rock overnight. After the salts were fused in this manner, the tube was removed from the furnace and allowed to cool rapidly (after the solid particles had settled into the neck of the ampule).

f. Preparation of SFCA melts. Sodium fluorochloroaluminate melts were prepared by first preparing a bulk quantity of SCA melt. The SCA melt was then crushed to a coarse powder, and a weighed amount was placed into a quartz or Pyrex ampule (quartz was used when preparing melts of $R = \text{mole ratio of F:Al} > 0.25$). The molar mass of this quantity of SCA was approximated as that of NaAlCl_4 , and an

appropriate quantity of high purity NaF was then added in order to prepare a melt of the desired R value. The tube was capped with Tygon tubing, which was clamped, and then removed from the drybox and sealed under vacuum. If the melt was of low R (<0.75), the ampule was then placed into a Lindberg furnace and slowly heated until completely liquid, and then allowed to cool fairly rapidly upon removal from the furnace. Higher R-value melts were heated to melting in a high-temperature horizontal furnace, and were allowed to cool slowly after the power to the furnace was disconnected. This was found necessary, since the melts of higher R tended to expand considerably upon cooling, and the tubes were invariably broken if cooled vertically.

g. Treatment of SCA melts with COCl_2 . Melts would be treated with COCl_2 either before or after having been placed into an electrochemical or spectroscopic cell. In general, an apparatus similar to that shown in Figure 6 (p. 49) was affixed to the vessel via an AceThred adapter. The vessel was then connected to the COCl_2 line and evacuated to a pressure of <25 mTorr. The contents of the vessel were melted, and then COCl_2 was introduced (as the gas), and the pressure was regulated manually at 20-40 Torr above atmospheric for four hours. Next, the vessel was slowly evacuated to a pressure of <25 mTorr; the evacuated COCl_2 was condensed and frozen into a liquid nitrogen cooled Pyrex

trap. After the vessel had been kept under dynamic vacuum for three hours, the melt was allowed to cool, the stopcock was closed, and the vessel was either torch sealed or transferred to a drybox. After removal of the vessel, the entire vacuum/gas line was purged with N_2 , with the exigent gas passed through first a NaOH solution, and then through water. The frozen $COCl_2$ was allowed to come to room temperature, and was carried with the N_2 through the bubblers.

h. Treatment of SCA and SFCA melts with CCl_4 . When the melt was treated after it was in the electrochemical or spectroscopic cell, an apparatus like that depicted in Figure 7a (p. 50) would be attached to the fill tube of the cell via the AceThred adapter. The septum would be set into place with a threaded cap, and the stopcock would be closed. After removal from the drybox, the cell would be attached to the vacuum via the stopcock port. The cell was evacuated to a pressure <50 mTorr, and then the body of the cell was chilled with liquid nitrogen. The stopcock was then closed, and an appropriate amount of CCl_4 was added using a gastight microsyringe through the septum; this addition had to be accomplished quickly to prevent air from entering the cell through the syringe. After several minutes, during which the CCl_4 would be frozen in the cell body, the cell was torch sealed at a point beneath the AceThred adapter.

The cell was then placed into a furnace and heated to 165°C for several hours, and then was allowed to cool and was taken back into a drybox. The fill tube was broken, and an apparatus like that shown in Figure 6 (p. 49), sans the ball joint, was attached. Upon removal from the drybox, the cell was evacuated, and then slowly heated to 165°C. The evacuation was continued for several hours, or until the melt had lost the yellowish tinge that generally occurred after treatment with CCl_4 , and then the cell was torch sealed.

When treating bulk quantities of melt (not in a cell), a tube like that shown in Figure 7b (p. 50) was used. The vessel was loaded with melt through the fill tube; a septum was affixed to the injection port. The fill tube was capped with Tygon tubing, and then the vessel was removed from the drybox and attached to the vacuum line. After evacuation to <50 mTorr, the vessel was cooled with liquid nitrogen, and then the Tygon tube was clamped closed. An appropriate amount of CCl_4 was injected through the septum, and the tube was sealed (at point X, in Figure 7b, p. 50) after several minutes. The vessel was then heated to 165°C for several hours, and then the melt was allowed to solidify.

Next, a section of Tygon tubing was placed over the evacuation port (labelled C, in Figure 7b, p. 50) such that it extended past the 3mm Pyrex tube and could be affixed to the 7mm Pyrex tube. The vessel was connected to a vacuum

line via the Tygon tubing, and was then evacuated to <50 mTorr. Next, the 3mm Pyrex tube was crushed, and the vessel allowed to evacuate to <50 mTorr. The vessel was heated to 165°C in order to melt the contents and affect the complete removal of the CCl_4 .

2. Raman Spectroscopy of FLiNaK Solutions

a. Preparation of samples. For individual samples, solutions of Ta(V), or of Ta(V) with Na_2CO_3 , would be prepared by mixing appropriate quantities of K_2TaF_7 and purified FLiNaK inside a drybox; premelting was accomplished using the apparatus depicted in Figure 4 (p. 46). When several samples were to be prepared at one time, each would be placed inside a small carbon cup, and then the several cups would be arranged inside a large (30-60 ml) graphite cup. This large crucible would be inserted into a large quartz tube (45 mm inner diameter), which was capped with a 50mm AceThred adapter with a stopcock attachment.

The premelting vessel would then be removed from the drybox, evacuated to a pressure of approximately 500 mTorr, and then closed off and removed from the vacuum line. Next, the bottom of the vessel was inserted into a Lindberg furnace, and compressed air was directed at the vessel cap for cooling. The temperature in the furnace was then increased to 500°C, and enough time was allowed for the sample(s) to melt (at least 30 min.). The temperature was

then increased to 750°C (850°C in some cases), and remained at this point for 30-60 minutes in order to allow complete dissolution of the solutes. The vessel was then removed from the furnace and allowed to cool rapidly in air, and then was taken into a drybox.

b. Sample characterization using Raman spectroscopy.

After premelting the Ta(V) solutions, the samples were broken into large (3-5 mm) pieces using an agate mortar and pestle. One or two of these pieces, having a total mass of approximately 0.250-0.300 g, would be placed inside a graphite or nickel windowless cell (97), which would then be placed in a 12 mm OD quartz tube. The tube was capped with either Tygon tubing or a AceThred-Stopcock adapter.

Upon removal from the drybox, the sample tube was inserted into a furnace which was designed specifically for high-temperature Raman measurements. The sample was irradiated with a 514.5nm Ar ion laser line, and the Raman scattering was collected at 90° and directed through the monochromator. The temperature was rapidly increased to 500°C, and then raised more slowly until the sample was observed to melt. As soon as the sample was clearly melted, a spectrum was obtained in the region from 500-1000 cm^{-1} ; samples tended to fog the quartz cell "window" to various degrees over time, depending upon the temperature, oxide level, and

Ta(V) concentration. If possible, a spectrum was also obtained over a larger region, generally 75-1200 cm^{-1} .

3. Raman Spectroscopy of SCA and SFCA Samples

The preparation of samples and acquisition of Raman spectra for SCA and SFCA samples were much simpler than in the case of FLiNaK samples. Sample preparation required only the mixing of the proper quantities of melt with solute in 7-12 mm OD Pyrex or quartz tubes (Pyrex for low-fluoride melts), sealing the tube under vacuum, and measuring the Raman spectrum as described in the case of Ta(V) solutions in FLiNaK.

4. Deposition (Electrolysis) in SCA and SFCA Melts

A solution was prepared and loaded into a cell inside a drybox. The cell was then capped with Tygon tubing, removed from the drybox, and sealed under vacuum. Heavy copper wire (16 gauge) leads were soldered onto the tungsten electrode leads using high-temperature silver/tin solder. The copper wires were covered with 3mm OD Pyrex or quartz tubing (Pyrex for use below 525°C) in order to prevent shorting of the leads and for protection against high-temperature oxidation.

The cell was then lowered into a Lindberg furnace, and the temperature was slowly raised to the desired level. The PAR 273 electrochemical cell connectors were then attached to the proper copper leads; the cell was allowed to remain

at open circuit until a stable potential had been reached, indicating that solute dissolution was complete and the solution was at equilibrium. Next, a desired current was applied to the cathode, and the potential across the cathode and anode was monitored with time.

If the cell contained multiple cathodes, and the experiment involved several applied current densities, the lowest current density was applied first in order to minimize the effect of early experiments on later ones.

If pulsed current electrolysis was being performed, the cell was set up as described above, and then the pulse program would be applied to the cathode.

5. UV-visible Spectroscopy of SCA and SFCA Solutions of Niobium

Solutions were prepared and loaded into 0.025-cm or 0.3-cm pathlength quartz cells, which were then capped, removed from the drybox, and vacuum sealed. Pure SCA or SFCA melts, in cells of pathlength equal to that of the solution cell, were used as references.

Loaded and sealed cells were placed inside the high temperature UV-visible furnace, heated to the desired temperature, and spectra were obtained. Generally, spectra were obtained at various temperatures from 160 to 525°C, and then were again obtained as the temperature was decreased to determine if any permanent changes in the solutions had occurred.

6. X-Ray Methods -- ESCA and X-ray Diffraction

ESCA and X-ray diffraction were used for chemical analysis of synthesized reagents and electrolysis products. Metallic samples, or samples on metallic substrates, were analyzed directly. Non-metallic samples were ground to fine powders; for ESCA, the powder was pressed into indium foil prior to analysis; for X-ray diffraction, the sample was tightly packed into a sample holder constructed of a 0.5 cm thick Pyrex plate with a 0.3 cm deep x 1 cm diameter hole drilled into it. If the sample to be analyzed was air-sensitive, it was transferred to the ESCA sample chamber using an inert atmosphere transfer unit. X-ray diffraction of air-sensitive compounds was accomplished by simply covering the sample holder with a strip of Scotch tape (3-M, 1"); this method sufficiently protected the sample for the time period needed to obtain the spectrum.

7. Electrochemical Experiments

a. Cell preparation. All of the cell electrodes, except the reference, were cleaned using the following procedure, which was designed primarily to clean tungsten, but which was sufficient for proper cleaning of all other materials in the cell. After a cell had been constructed and annealed in the glass shop, the tungsten has a dark grey to black surface coating. The cleaning procedure involved first filling the cell with an aqueous solution of

$\text{NaNO}_2\text{:NaOH}$ (5:40 weight %) and heating in boiling water just until the tungsten became dull grey in color, followed by thorough rinsing with distilled water. The cell would then be filled with a mixture of concentrated $\text{HF:HNO}_3\text{:HCl:H}_2\text{O}$ (0.25:1:1:10 ratio by volume) and again heated in boiling water until the tungsten acquired a thin pale-yellow surface coating. After rinsing with distilled water, the cell would be made approximately 3/4 full with distilled water, and then a few milliliters of the $\text{NaNO}_2\text{:NaOH}$ solution would be added. The yellow coating on the tungsten would turn blue, and then would dissolve, leaving a shiny silvery surface. The cell would be rinsed thoroughly with distilled water. If the cell contained any frit material, it would be placed in a vacuum oven (130°C) for several hours and then rinsed again with distilled water; it was found that this additional step was needed to completely remove from the frit any residue of the cleaning solutions. After the final rinsing with distilled water, the cell was rinsed first with 100% ethanol, and then with 100% methanol.

Next, the cell was evacuated to a pressure of <50 mTorr for at least 1 hour, and then heated slowly under vacuum to 525°C . After several hours at this temperature, the furnace was turned off and the cell was allowed to come to room temperature, while still under vacuum. The electrodes would then be inspected, and if any discoloration was observed, the entire cleaning procedure would be repeated. If the

electrodes were in good condition, and the cell was not to be used immediately, it would be torch sealed under vacuum and stored until needed.

b. Voltammetry. Normal pulse (NPV) and square wave (SWV) voltammetries were performed using the PAR Model 273 controlled by the IBM PS/2-70 running the M270 software. The raw data obtained during NPV experiments were sometimes differentiated to obtain differential normal pulse (DNPV) results. Cyclic voltammetry (CV) was performed using either the M273 setup, or with a Model 173/179 controlled by the PAR 175 programmer.

c. Chronoamperometry and chronocoulometry. Chronoamperometric data were obtained using the CA273 software mentioned above (p. 55). The data were arranged into a form readable by QuattroPro or LOTUS using the CAFILT program, also mentioned above (p. 56). After extracting the data into a spreadsheet, the data were either plotted and analyzed in the form of a chronoamperometric experiment, or the current was integrated with time, and chronocoulometric analysis was conducted.

CHAPTER III

RESULTS AND DISCUSSION

REMOVAL OF OXIDE IMPURITIES FROM FLiNaK AND SCA

A. Oxide Determination in FLiNaK

No methods for direct determination of oxide impurities in FLiNaK have been reported. However, von Barner *et al.* (40) showed that the Raman spectrum of Nb(V), added as K_2NbF_7 , changed dramatically as oxide (Na_2O) was added. These workers determined that the band due to niobium fluoride, present as NbF_7^{2-} , decreased in intensity as oxide was added, and several other bands became evident; these latter bands were attributed to $NbOF_5^{2-}$, $NbO_2F_4^{3-}$, and NbO_2 .

Present studies show similar results in the case of Ta(V) in FLiNaK. Figure 10 shows the Raman spectra of solutions of K_2TaF_7 in FLiNaK purified using NH_4HF_2 . In the region between 500 and 1000 cm^{-1} , only two main bands are observed, at 640 and 904 cm^{-1} ; these bands have been attributed (99) to scattering by tantalum fluoride species (probably TaF_7^{2-}) and tantalum oxyfluoride species (probably $TaOF_5^{2-}$), respectively. It is apparent that as the concentration of K_2TaF_7 is decreased, the relative intensity of the band at 904 cm^{-1} to that at 640 cm^{-1} increases. Changes in a weaker and broader band which occurs at lower frequen-

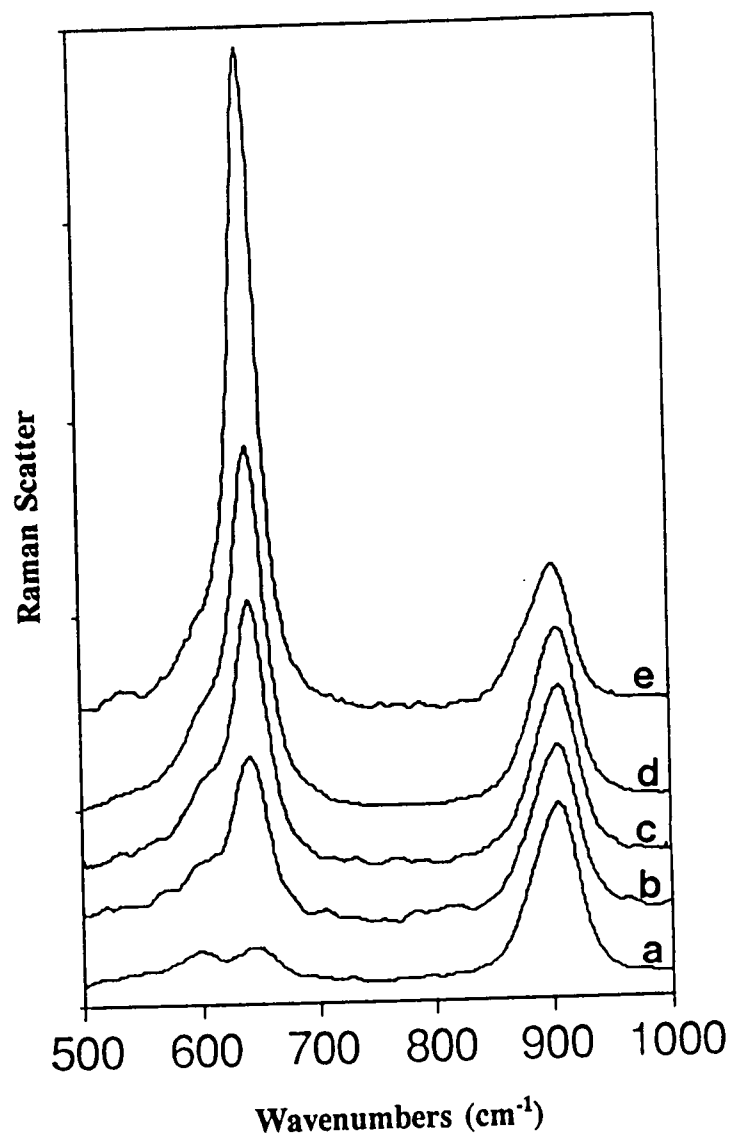


Figure 10. Raman spectra of solutions of different K_2TaF_7 concentrations in FLiNaK. The band at 640 cm^{-1} is due to TaF_7^{2-} (99), and that at 904 cm^{-1} is due to tantalum oxyfluoride species. All curves were normalized by the intensity of the band at 904 cm^{-1} .

- | | |
|---|--|
| a. 0.511 mole% K_2TaF_7 , 610°C | d. 2.07 mole% K_2TaF_7 , 590°C |
| b. 0.988 mole% K_2TaF_7 , 590°C | e. 3.84 mole% K_2TaF_7 , 580°C |
| c. 1.20 mole% K_2TaF_7 , 570°C | |

cies (with maxima in the range 275-315 cm^{-1}) are also seen. The changes in the spectra are attributed to the decrease in the ratio of fluoride to oxyfluoride species in the melt. To verify this assertion, solutions of K_2TaF_7 were prepared in which oxide was introduced in the form of Na_2CO_3 . Figure 11-a shows a spectrum of K_2TaF_7 in FLiNaK to which no oxide was added; the spectrum in Figure 11-b is that of a FLiNaK solution to which equimolar amounts of K_2TaF_7 and Na_2CO_3 were added. It is apparent that when oxide is added, the intensity of the band at 640 cm^{-1} decreases significantly, while the band at 904 cm^{-1} increases in intensity. A detailed study of the Ta(V) fluoride and oxyfluoride system in FLiNaK, using Raman spectroscopy, is currently underway (100). It is sufficient to this report to understand that the band at 640 cm^{-1} is due to the tantalum fluoride species, the band at 904 cm^{-1} is due to a tantalum oxyfluoride species, and that the relative intensities of these bands are an indication of the relative concentrations of these two species in solution.

B. Analysis of Methods of FLiNaK Purification

Many methods for FLiNaK purification have been reported in the literature (25,26,34,36,40-54,83-86). The methods used in this work (described in Chapter II, pp. 60-65), were selected due to the frequency of their appearance in the literature.

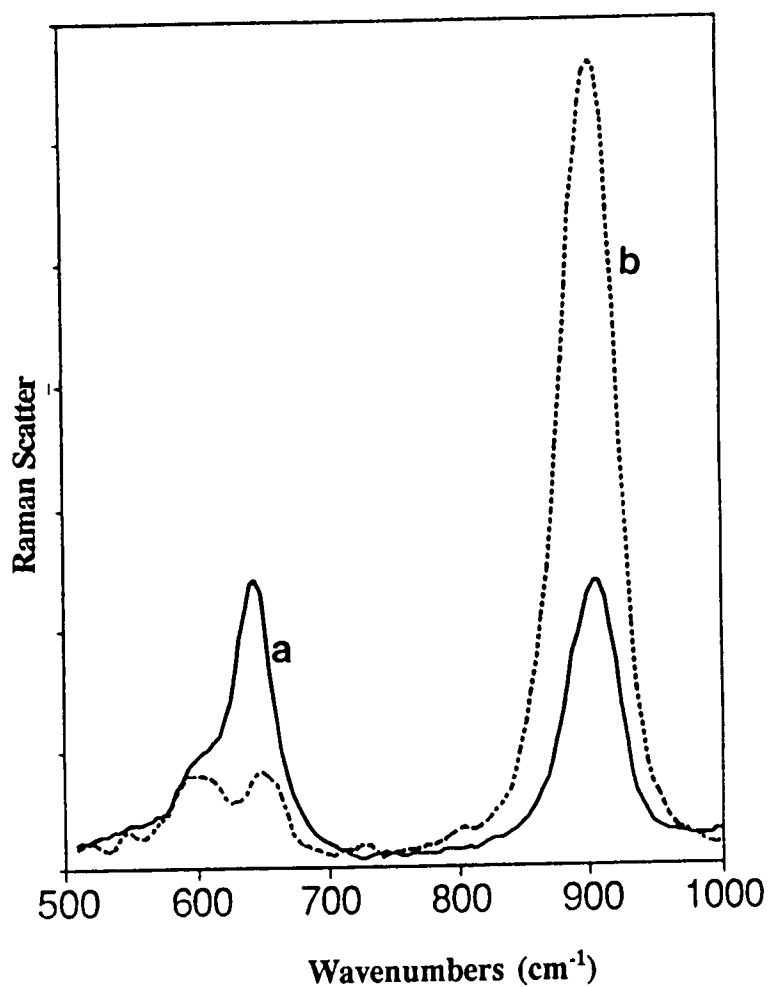


Figure 11. Raman spectra of FLiNaK solutions of K_2TaF_7 , with and without added oxide. $T = 600^\circ C$.

- a. (—) 1.0 mole % K_2TaF_7 , no oxide added
- b. (---) 1.0 mole% K_2TaF_7 , 0.98 mole% Na_2CO_3

1. Purification of FLiNaK with NH_4HF_2

The details of this method of purification are given in Chapter II (pp. 61-63). Figure 12 shows the Raman spectrum of a solution of K_2TaF_7 in FLiNaK which had been treated only once with the NH_4HF_2 method. It is apparent that this solution contains a high level of oxide contamination, as indicated by the relative intensities of the oxide and fluoride bands. Better results were obtained when the treatment was repeated several times (Figure 13), but no improvement beyond the level observed in Figure 13 could be obtained using this method.

Treating melts with NH_4HF_2 appeared to be the method of choice for Senderoff and coworkers (18,35,41-45). The fact that this technique does not produce oxide-free FLiNaK strongly supports the contention by Polyakov and coworkers (55-57) that the studies reported by Senderoff and coworkers were conducted in solutions rich in oxide impurities. In the case of tantalum and niobium, this suggests that the transition times observed by these workers in their chronopotentiograms were due to one or more oxide species, and that it was probably unnecessary to invoke the existence of such uncommon species as NbF and TaF_2 .

2. Purification of FLiNaK by Electrolysis

Some authors (46,86) have reported success in eliminating metallic and oxide-containing impurities from FLiNaK

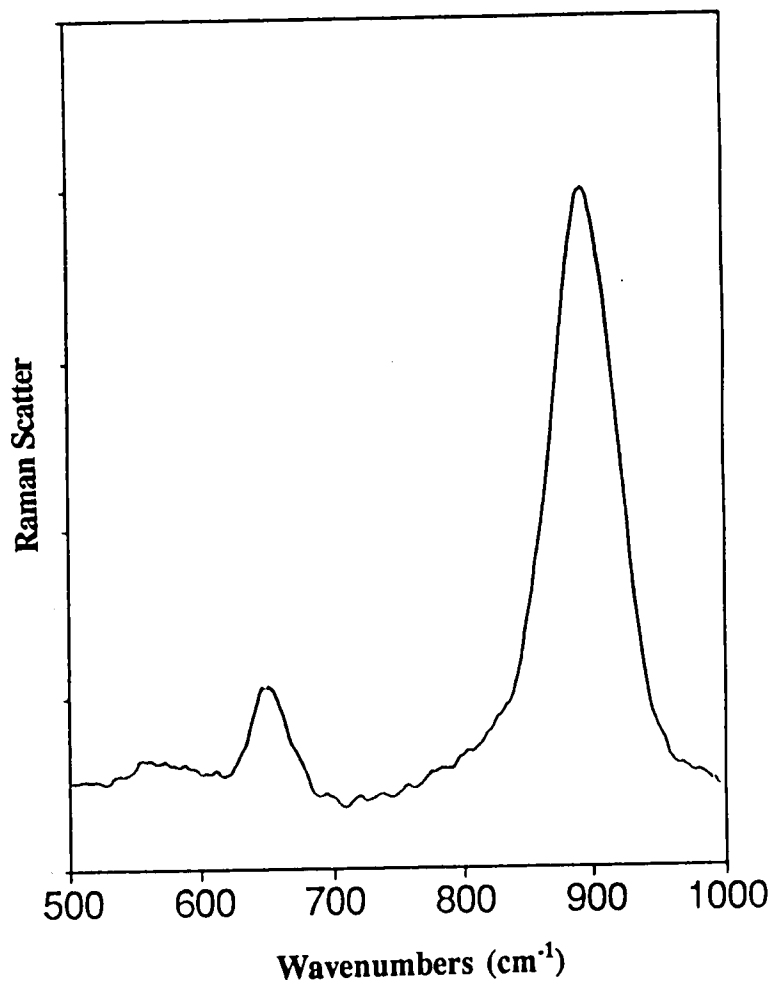


Figure 12. Raman spectrum of 2.0 mole% K_2TaF_7 in FLiNaK at 600°C . FLiNaK was purified by a single treatment with NH_4HF_2 , followed by sparging with H_2/N_2 (1/4 ratio), and evacuation to 0.20 mTorr.

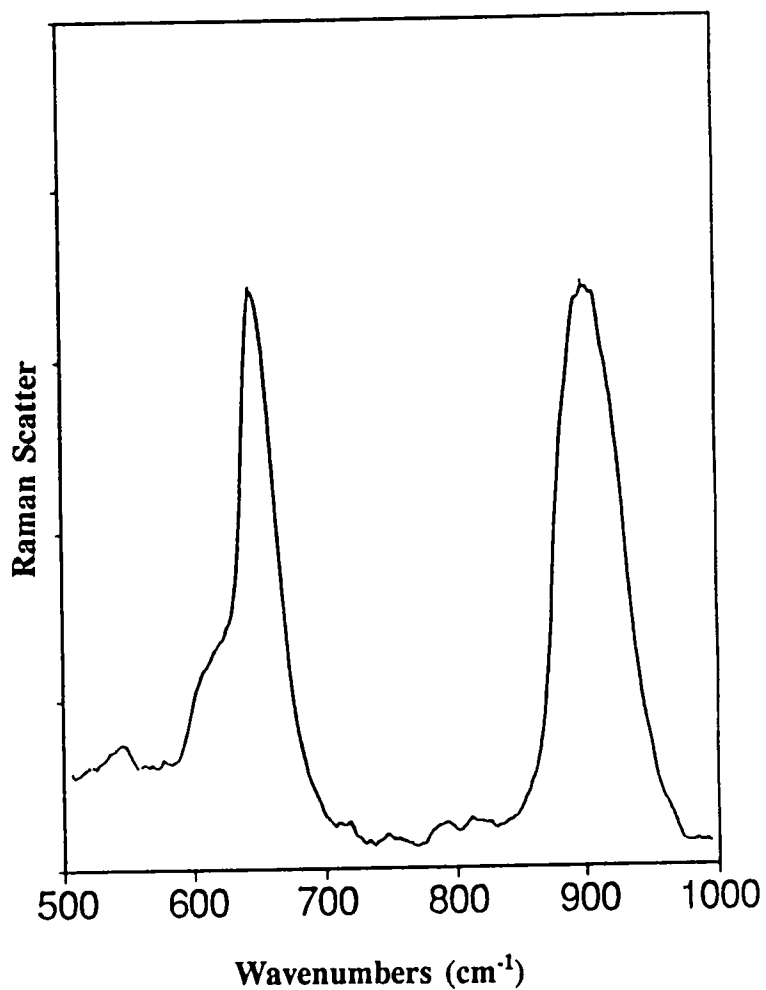


Figure 13. Raman spectrum of 2.0 mole% K_2TaF_7 in FLiNaK at 580°C . FLiNaK was purified by three treatments with NH_4HF_2 , followed by sparging with H_2/N_2 (1/4 ratio), and evacuation to 0.20 mTorr.

melts using electrolysis. Details of this purification method as used in this work are given in Chapter II (pp. 63-64).

Figure 14 shows a Raman spectrum of a K_2TaF_7 solution in FLiNaK which had been purified by electrolysis using a nickel cathode and a carbon anode. An improvement compared to the melt treated only once with NH_4HF_2 (Figure 12, p. 81) is apparent, but the purity is lower than that of a melt which was treated several times with NH_4HF_2 (Figure 13, p. 82).

3. Purification of FLiNaK by Recrystallization

Slow recrystallization of the constituent salts (LiF, NaF, and KF) of FLiNaK to obtain high quality melts was reported by von Barner et al. (40). Such procedures can be quite tedious, and require very high temperatures (the melting point of NaF, for instance, is $996^\circ C$). To date, no report of an attempt to zone refine or recrystallize FLiNaK directly has appeared. The studies presented here indicate that excellent results can be obtained by treating "low-grade" FLiNaK with the method described in Chapter II (pp. 64-65).

Figure 15 shows the Raman spectrum of a K_2TaF_7 solution prepared with FLiNaK that had been recrystallized. It is apparent that, although the concentration of the Ta(V) in this sample was less than half that of the solutions repre-

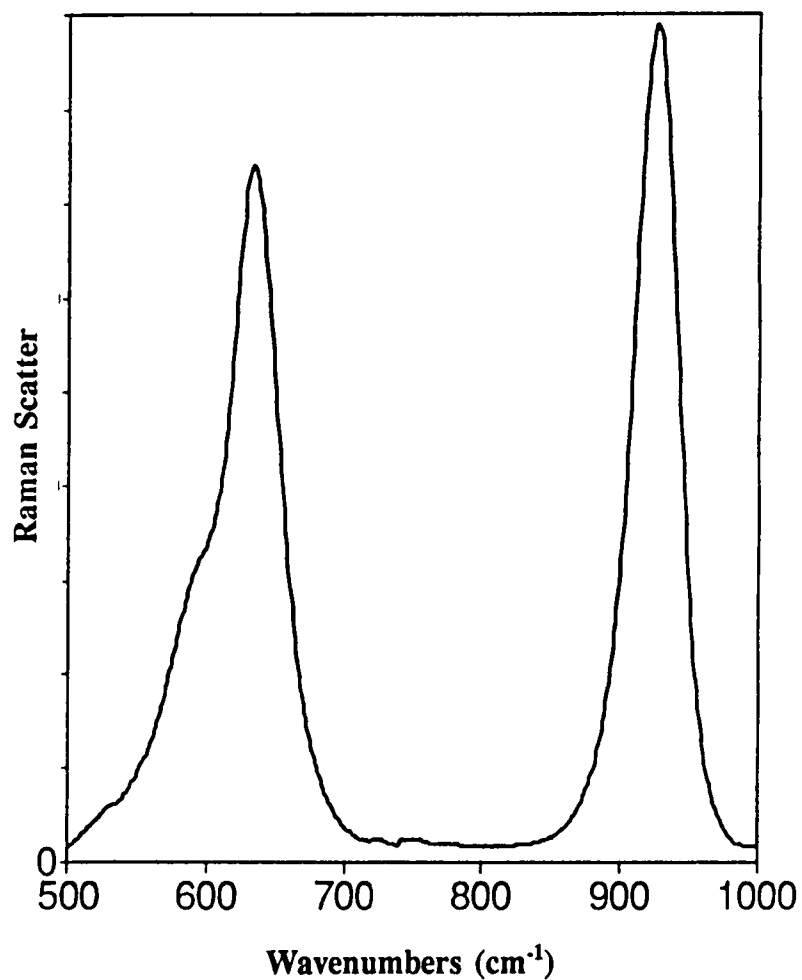


Figure 14. Raman spectrum of 2.12 mole% K_2TaF_7 in FLiNaK at 590°C. FLiNaK was purified by electrolysis using a nickel cathode and a glassy carbon anode. A potential of -1.7 V (vs a Pt quasi-reference electrode) was applied for 36 hr.

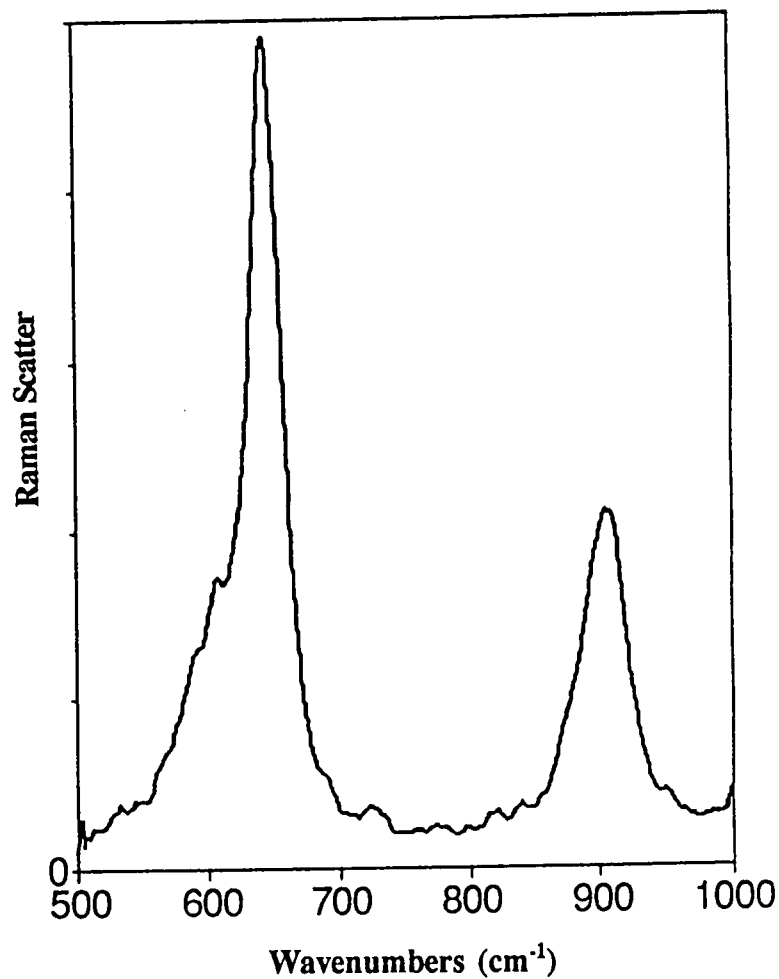


Figure 15. Raman spectrum of 0.998 mole% K_2TaF_7 in FLiNaK at 580°C. FLiNaK was purified by slow recrystallization in glassy carbon. The temperature was decreased at a rate of 3°C per hour.

sented in Figures 12-14, the relative intensity of the fluoride peak to that of the oxyfluoride peak is higher.

Table IV gives some pertinent data which indicate the relative effectiveness of the purification methods described here. Of particular interest is column 4, which gives the ratio of the peak intensities of the fluoride and oxyfluoride bands, normalized by (divided by) the concentration of added K_2TaF_7 ; the higher the value of this parameter, the greater the degree of oxide removal caused by the indicated purification method. An examination of Table IV demonstrates the relative effectiveness of recrystallization with respect to the three other methods used for purification.

C. Oxide Determination in SCA

Two methods for the determination of oxide in sodium chloroaluminate molten salts have been reported. Laher et al. (77) described the use of voltammetric analysis of a solution of Ta(V) in SCA, in which the tantalum chloride and tantalum oxychloride species are reduced at different potentials. By examination of the relative peak heights of the waves due to these two species, one can calculate the level of oxide impurity present in the melt. Flowers and Mamantov (90) described the FTIR spectroscopic investigation of oxide in SCA. Bands at 680 and 801 cm^{-1} were found to be attributable to the presence of aluminum oxychloride species, and the variation of the intensities of these bands as consec-

Table IV. Comparison of Several Methods of FLiNaK Purification.

Method	K ₂ TaF ₇		R(F:O) (normalized) ^b
	Concentration (mole %)	R(F:O) ^a	
NH ₄ HF ₂ addition	2.0	0.18	0.09
Multiple NH ₄ HF ₂ additions	2.0	0.97	0.48
Electrolysis	2.1	0.88	0.42
Recrystallization	1.0	2.5	2.5

a. The ratio of the peak intensity of the fluoride (TaF₇²⁻) band to that of the oxyfluoride (TaOF₅²⁻) band.

b. Same as Column 3, except normalized to account for differences in the K₂TaF₇ concentration by dividing the value in Column 3 by that in Column 2.

utive aliquots of water were injected into the cell was used to determine the original oxide concentration in the melt.

D. Removal of Oxide from SCA Melts Using Phosgene

Sun et al. (92) reported the use of phosgene (COCl_2) for removal of oxide impurities from AlCl_3 -MEIC ambient temperature melts; however, no studies had yet been undertaken to determine the effectiveness of this method in sodium chloroaluminate systems.

Figure 16a shows an infrared spectrum covering the region from 850 to 650 cm^{-1} for a SCA melt containing approximately 15 mM oxide. The absorption bands at 680 and 801 cm^{-1} , attributed by Flowers and Mamantov (90) to aluminum oxychloride species, are observed. When COCl_2 was introduced into the cell and allowed to react at a pressure of one atmosphere and a temperature of 200°C for four hours, both of these bands disappeared (the spectrum in Figure 16b was recorded after the excess COCl_2 had been evacuated). Prior to evacuation of the COCl_2 , additional bands at 1802 and 886 cm^{-1} could be observed in the infrared spectrum, and these were attributed to the presence of excess COCl_2 dissolved in the melt (94). It is important to note, therefore, that any unreacted COCl_2 could be removed completely from the melt by evacuation; this species is reduced irreversibly in the melt ($E_p = -0.35$ V vs. Al(III)/Al), and could interfere with electrochemical studies of other

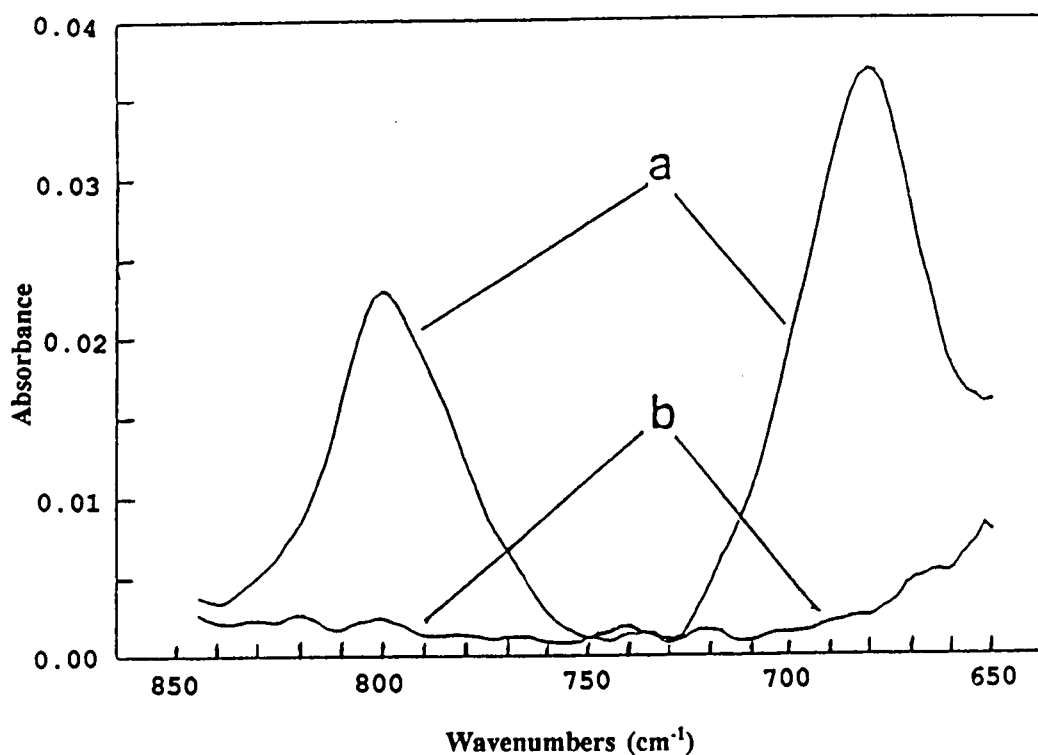


Figure 16. FTIR spectra of SCA melt before (a) and after (b) treating with 1 atm COCl_2 and 200°C for 4 hours, followed by evacuation for 1 hour. Spectra were obtained at 175°C. Solution (a) contained approximately 15 mM oxide, added as Na_2CO_3 .

solutes. Similar experiments were conducted at 165°C, but unsatisfactory results were obtained.

The results of these studies have been published recently (101).

E. Removal of Oxide from SCA by Carbon Tetrachloride

The use of phosgene for oxide removal from SCA melts poses some problems:

1. the gas is a poison, and must be handled with extreme caution, using a dedicated vacuum line, pump, and hood;
2. COCl_2 is expensive -- a one-pound tank costs on the order of \$175;
3. treating melts with COCl_2 is difficult and tedious (see Chapter 2, pp. 47, 65-66);
4. treating solutions of volatile compounds is not feasible, due to the high temperatures $\geq 200^\circ\text{C}$ required, and the impracticality of having a closed system during treatment.

The items enumerated above give sufficient cause to consider other possible methods for removal of oxide from SCA melts.

Present studies have shown that carbon tetrachloride (CCl_4) also facilitates the removal of oxide impurities from SCA melts. In an experiment similar to that conducted using COCl_2 , CCl_4 was added to oxide-containing melts, and the infrared spectra were recorded. Figure 17 shows the decrease

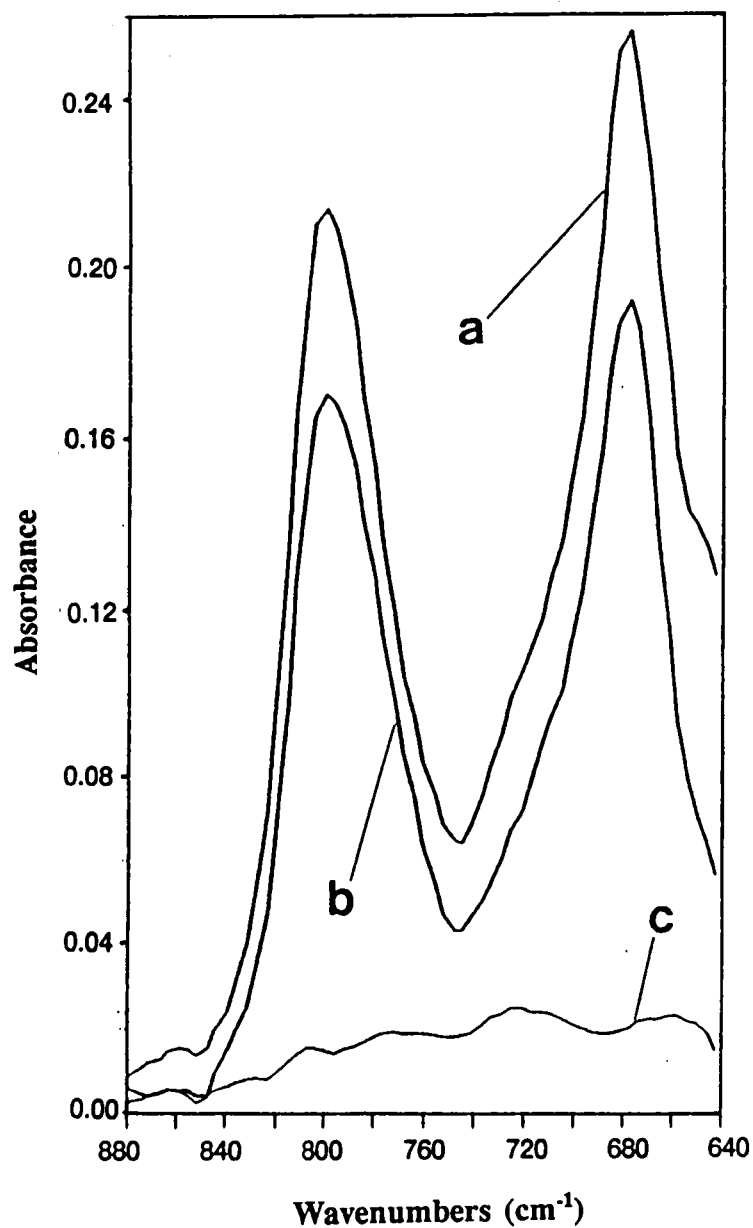
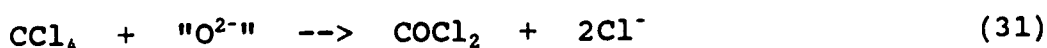


Figure 17. FTIR spectra of SCA melt at 200°C showing the effect of adding CCl_4 .

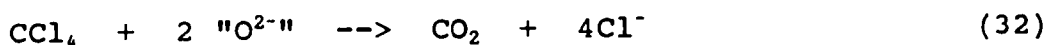
- a. Melt contains 20.3 mM oxide (Na_2CO_3); no CCl_4 added
- b. 30 min. after the addition of 150 μL CCl_4
- c. 120 min after the addition of 450 μL CCl_4

in the two oxide bands (at 680 and 801 cm^{-1}) with time and added CCl_4 . Note that an approximately 4-fold excess of CCl_4 was required (450 μL) in order to completely remove the oxide, present at approximately 20 mM, from the melt.

It was initially postulated that the reaction between CCl_4 and melt oxide might result in carbonyl chloride as a product or byproduct, as shown in Equation 31. However,



this was not the case; no indication of a band at 886 cm^{-1} was observed, nor were bands in the region of 1800 cm^{-1} observed. Rather, a doublet, indicative of dissolved CO_2 , was observed to grow in with time in the region of 2400-2300 cm^{-1} . These observations suggest that the reaction of CCl_4 with oxide species in the melt tends to go to completion, as shown in Equation 32.



It is apparent from Equation 32 that the presence of excess CO_2 in the system would tend to limit the effectiveness of CCl_4 in its reaction with oxide impurities, due to Le Chatelier's Principle. In the experiment described above, oxide was added to the melt in the form of Na_2CO_3 , which reacts with SCA to form dissolved oxide species, NaCl , and CO_2 . A better test for the effectiveness of CCl_4 on oxide removal would involve an oxide source that did not

result in the formation of CO_2 ; Flowers and Mamantov (90,91) used water as a source of oxide, and observed a linear dependence of the intensities of the bands at 680 and 801 cm^{-1} on the volume of water added.

A brief study was undertaken in which the infrared spectra of a melt containing approximately 24 mM oxide, added as water, were recorded at 175°C, before and after the addition of CCl_4 . Before CCl_4 was added (after water had been added), two bands at 680 and 801 cm^{-1} were observed, as in the studies described above (Figures 16, p. 89 and 17, p. 91). Just 30 minutes after 250 μL CCl_4 was injected into the spectroscopic cell, however, both of these bands had been completely eliminated from the spectrum, indicating that essentially all of the oxide had reacted with the CCl_4 . These results demonstrate that CCl_4 is a better agent than COCl_2 for oxide removal from SCA melts, in that it reacts more rapidly (30 minutes, vs 4 hours for COCl_2), and that it reacts at a lower temperature (175°C vs a minimum of 200°C for COCl_2).

CHAPTER IV

RESULTS AND DISCUSSION

ELECTROCHEMISTRY OF Nb(V) IN SCA AND SFCA

A. Studies Conducted in the Presence of Oxide

1. A Brief Review of Results Obtained by Previous Workers.

The Ph.D. dissertation by Ting (74) deals with the electrochemistry of Nb(V) in various compositions of sodium chloroaluminate melts. Only those results obtained in the so-called "50-50" AlCl_3 -NaCl melts will be reviewed here, for the sake of brevity and due to the fact that they more directly relate to recent studies. Note that, although Ting used an Al(III)/Al (in 63-37 AlCl_3 -NaCl) reference electrode, all potentials cited here are with respect to the Ag(I)/Ag electrode for direct comparison with current results. The Al(III)/Al (in 63-37 AlCl_3 -NaCl) reference electrode has a potential 0.513 V more negative than the Ag(I)/Ag reference (14); as given in Table I (p. 3), the redox potential of the Ag(I)/Ag couple vs an Al(III)/Al (in the NaCl-saturated melt) is 1.086 V, and the potential difference of the Al(III)/Al couple in the basic and acidic melts is 0.573 V.

Ting (74) observed cyclic voltammograms like that shown in Figure 18, in which he noted the presence of four waves with cathodic peaks at -0.09, -0.24, -0.46, and -0.75 V, re-

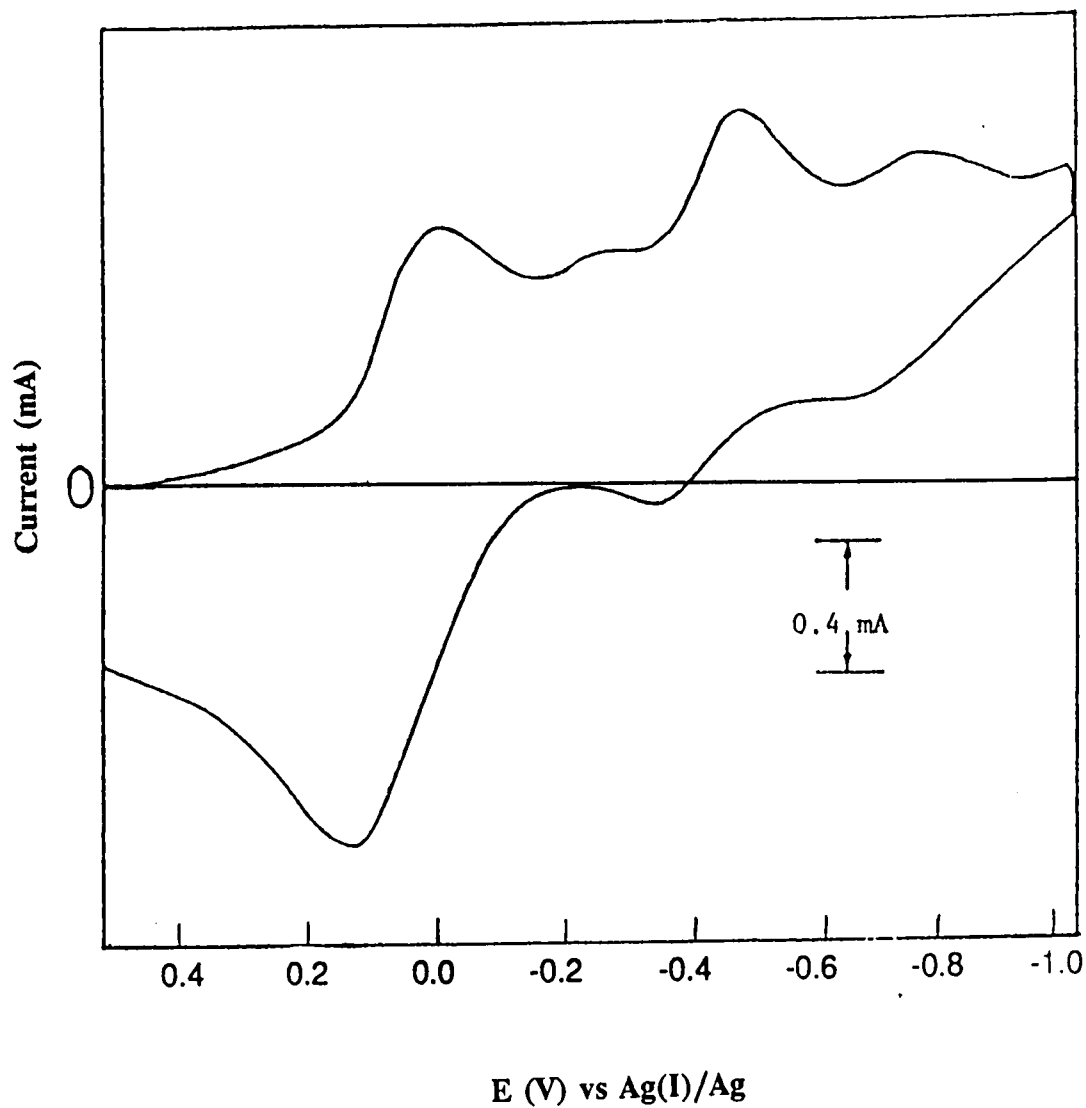


Figure 18. CV obtained by Ting (74) for a 5.2×10^{-2} M NbCl_5 solution in "50-50" AlCl_3 - NaCl . Working electrode was a Pt wire; $T = 160^\circ\text{C}$; scan rate = 0.1 V/s. Reproduced from reference 74.

spectively. He observed similar behavior among solutions having a range of Nb(V) concentrations from as low as 6 mM to as high as 50 mM, although the potential of the first wave shifted anodically with increasing concentration. Differential pulse voltammetry (DPV) gave curves like that presented in Figure 19; again, four waves were observed, with maxima ($E_{1/2}$'s) at -0.05, -0.31, -0.43, and -0.79 V, respectively. Using a variety of experimental techniques, he proposed the mechanism given in Equations 18-22 in the Introduction section (p. 18).

McCurry (75) obtained curves similar to Ting's for the reduction of Nb(V) in SCA, although his work was conducted primarily using solutions of low concentrations (<10 mM).

Harward (102) attempted to reproduce Ting's results, with limited success (Harward utilized a Al(III)/Al in NaCl saturated melt as a reference, which has a potential 1.086 V more negative than Ag(I)/Ag (14)). At low concentrations (<12 mM), he observed cyclic voltammetric curves similar to those reported by Ting. However, when the concentration was increased (>20 mM), the appearance of the voltammetric curve began to change (see Fig. 20), and he observed four waves with peaks at 0.12, -0.08, -0.33, and -0.52 V. A DPV obtained by Harward (Fig. 21) shows the discrepancy more clearly (maxima occur at 0.14, -0.04, -0.28, and -0.50 V). Harward did not pursue studies of Nb(V) in much detail, nor did he address the deviation from previously reported re-

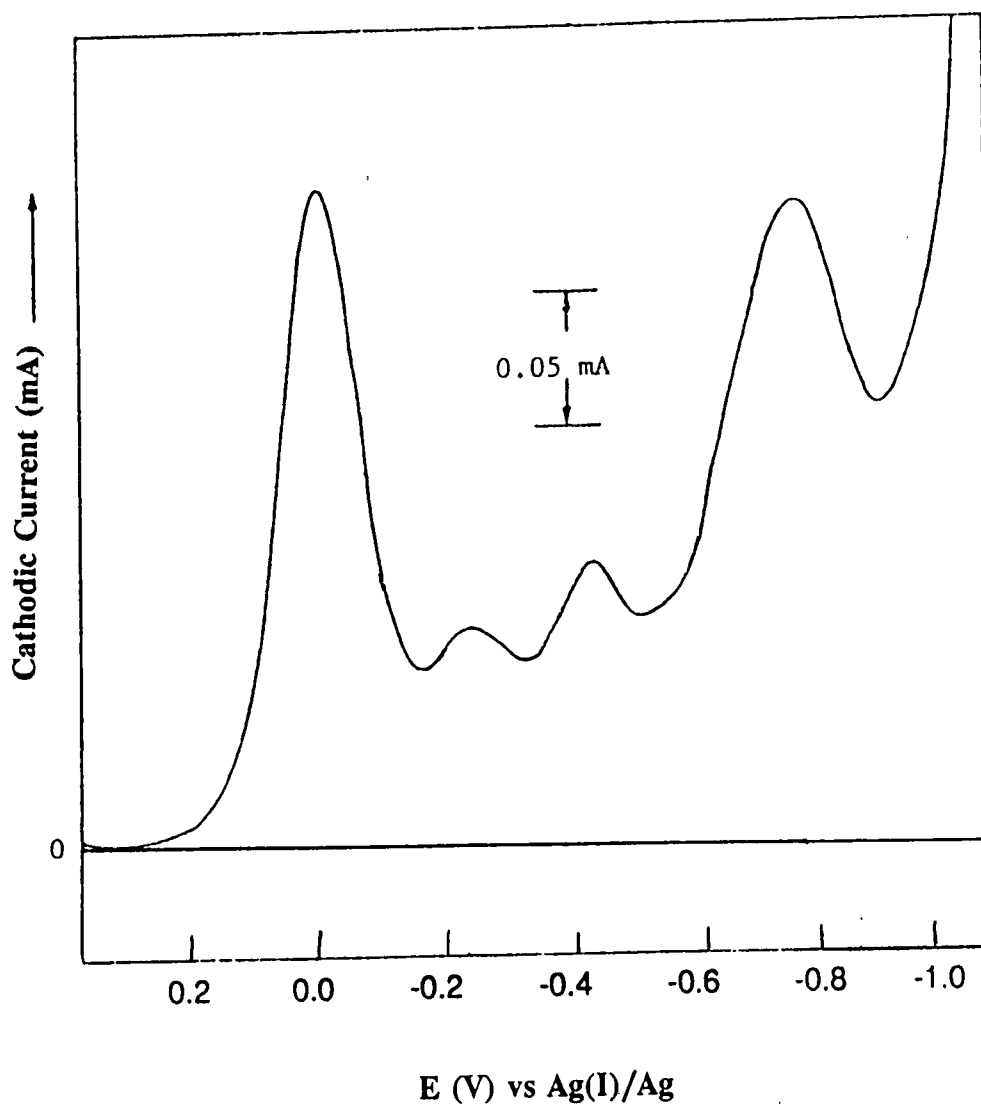


Figure 19. DPV obtained by Ting (74) for a 6.8×10^{-3} M NbCl_5 solution in "50-50" AlCl_3 - NaCl . Working electrode was a Pt wire; $T = 160^\circ\text{C}$; scan rate = 0.01 V/s; pulse amplitude = 5 mV.

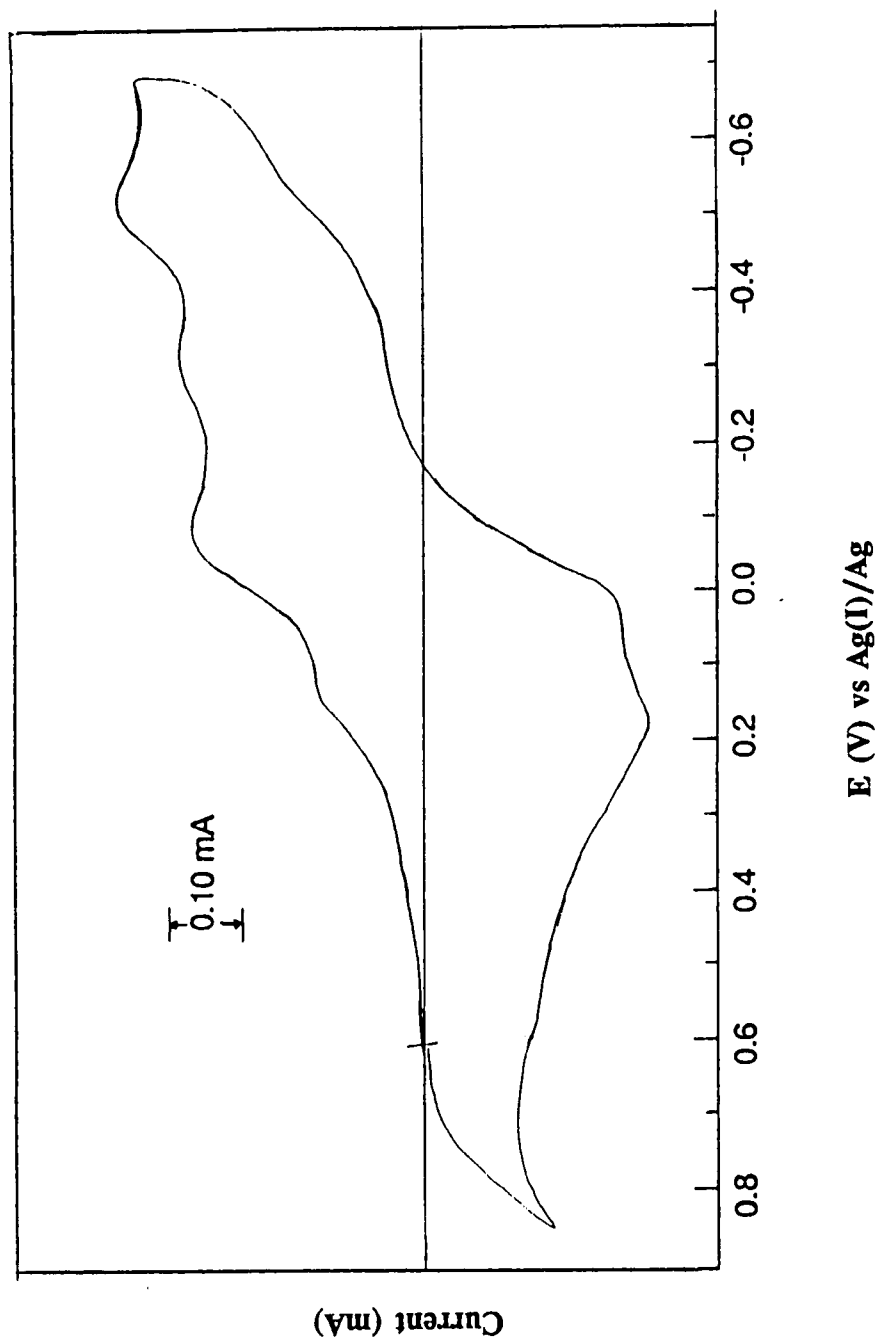


Figure 20. CV obtained by Harward (101) for a 2.62×10^{-2} M NbCl_5 solution in SCA. Working electrode was a Pt wire; $T = 180^\circ\text{C}$; scan rate = 0.1 V/s .

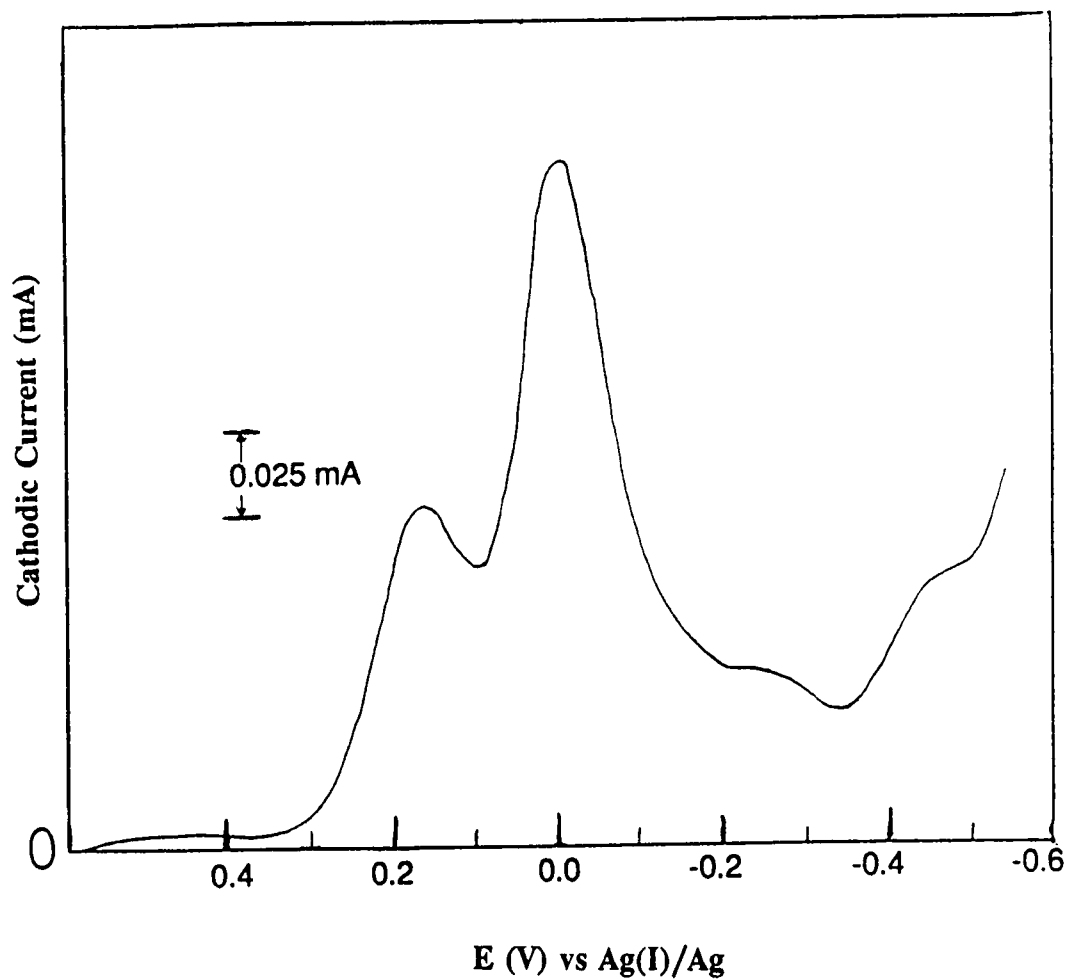


Figure 21. DPV obtained by Harward (101) for a 2.62×10^{-2} M NbCl_5 solution in SCA. Working electrode was a Pt wire; $T = 180^\circ\text{C}$; scan rate = 0.01 V/s.

sults; his dissertation primarily dealt with a different subject.

2. Presentation and Comparison of Some Current Results

It is common, when continuing a project begun by another person, to first attempt to reproduce the previous results in order to both ascertain the accuracy of the results and develop the technique of the more recent experimenter. Repeated attempts to reproduce the results obtained by Ting led to frustration; reproduction did not seem possible. Out of the frustration grew the ability, indeed the necessity, to take meticulous care in the preparation of melts and reagents, beyond the standard methods. It was only with the development of the oxide-removal methods discussed in Chapter 3 that some certainty of the inaccuracy of Ting's results was attained. In such a situation, it is incumbent upon the more recent researcher to definitively demonstrate that prior results are incorrect. The results presented below were obtained by the author, and are intended to accomplish such a demonstration.

Cyclic voltammetric curves obtained using SCA solutions of Nb(V) were invariably unlike those reported by Ting. Figure 22 shows a typical CV obtained at platinum in a 11 mM Nb(V) melt. Five waves are observed with peak potentials of 0.114, -0.092, -0.374, -0.531, and (-0.87) V. With the exception of the final wave, these values more closely resemble those obtained by Harward (102) at high concentration

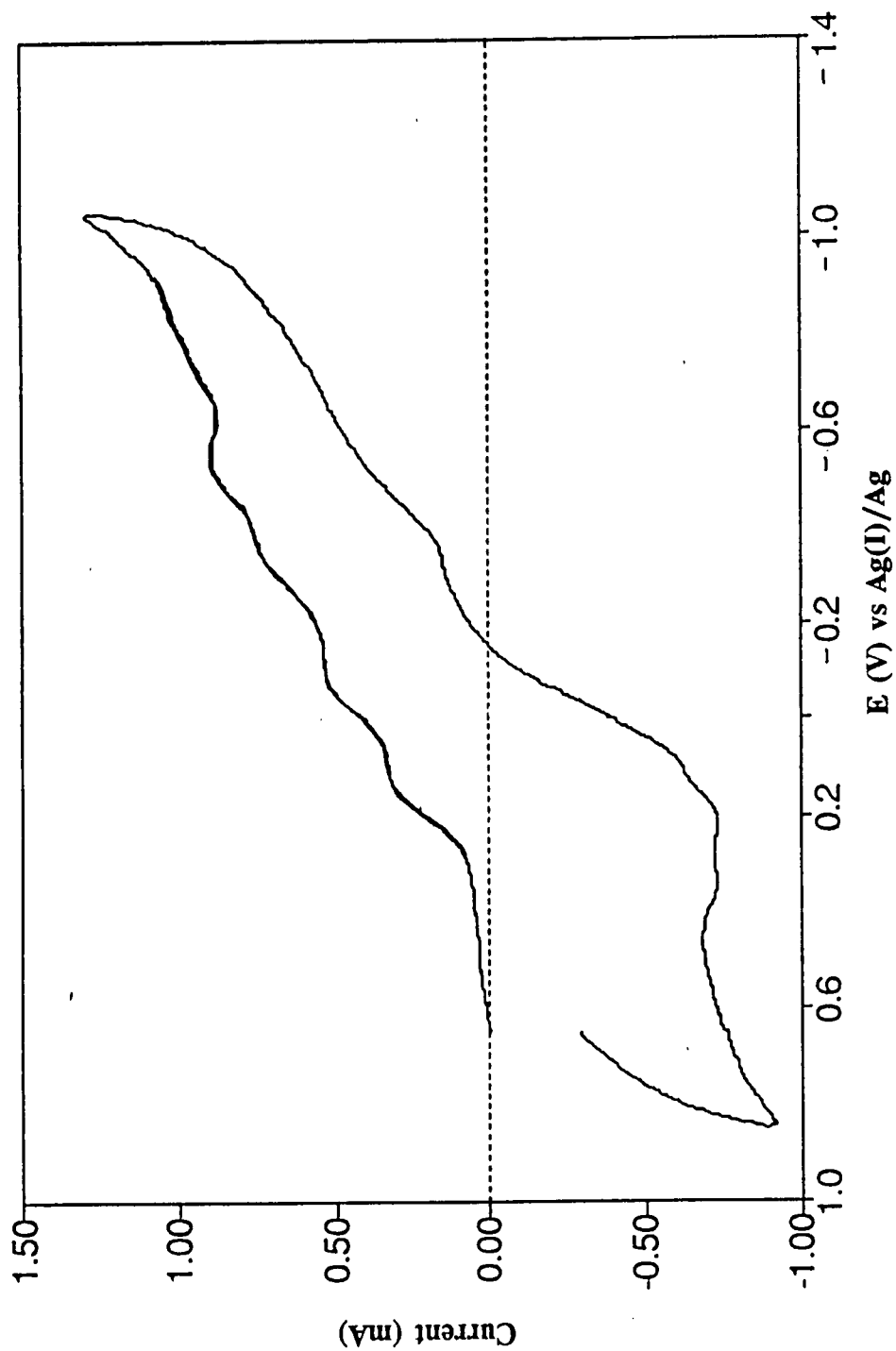


Figure 22. CV obtained for a 1.11×10^{-2} M NbCl_5 solution in SCA. The melt had been treated with COCl_2 prior to use; working electrode was a Pt wire; $T = 178^\circ\text{C}$; scan rate = 0.5 V/s .

than those of Ting (74,76). Also in common with Harward's results is the fact that the appearance of the curve changed with increasing concentration; Figure 23 shows a CV of the same melt with 25 mM Nb(V), in which the first wave appears to have increased with respect to the second wave.

The resultant waveform of square wave voltammetry (SWV) is similar to that of DPV; the two methods themselves are similar (SWV is inherently a differential technique), and both are expected to yield symmetrical peaks with maxima very near the $E_{1/2}$ of the redox process. Figure 24 shows a SWV obtained for a 11 mM solution of Nb(V); peaks occur at 0.160, -0.037, -0.280, -0.485, and -0.803 V. The shapes, relative intensities, and positions of the first four waves of Figure 24 resemble those observed by Harward using DPV (Fig. 21, p. 99). Furthermore, these same parameters for the last four waves in Figure 24 agree particularly well with those observed by Ting in DPV (Fig. 19, p. 97). Table V lists the above results for ease of comparison.

Figures 22 (p. 101) and 23 demonstrate the change observed in the CV when the concentration of NbCl₅ was increased. The SWV exhibits this change to a greater degree in the relative intensities of the first and second peaks. Any voltammetric response due to an uncomplicated redox process is expected to increase linearly with the concentration of the redox species; in other words, the quantity i_p/C , where i_p is the peak current and C is the con-

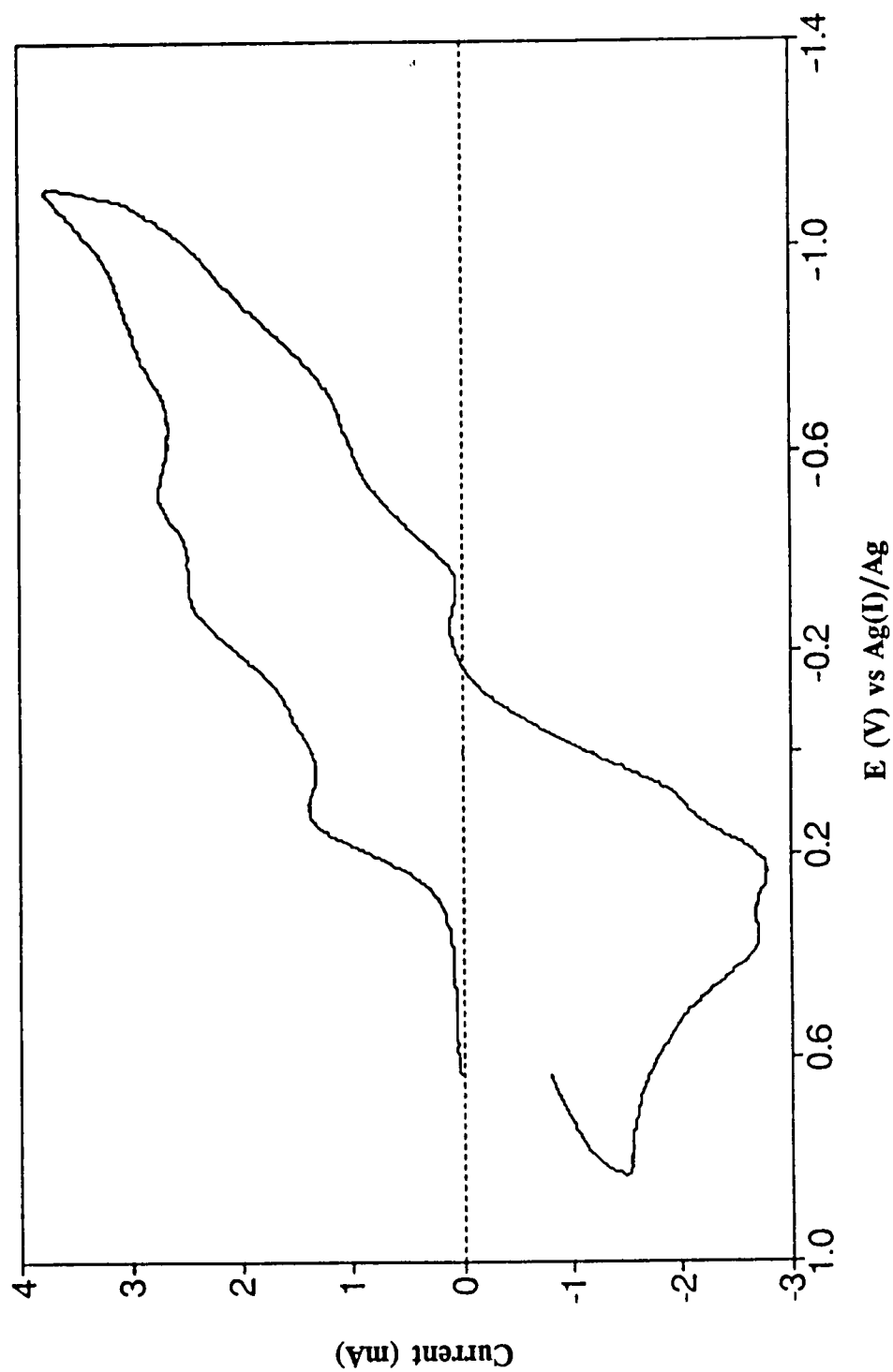


Figure 23. CV obtained for a 2.5×10^{-2} M NbCl_5 solution in SCA. The melt had been treated with COCl_2 prior to use; working electrode was a Pt wire; $T = 178^\circ\text{C}$; scan rate = 0.5 V/s .

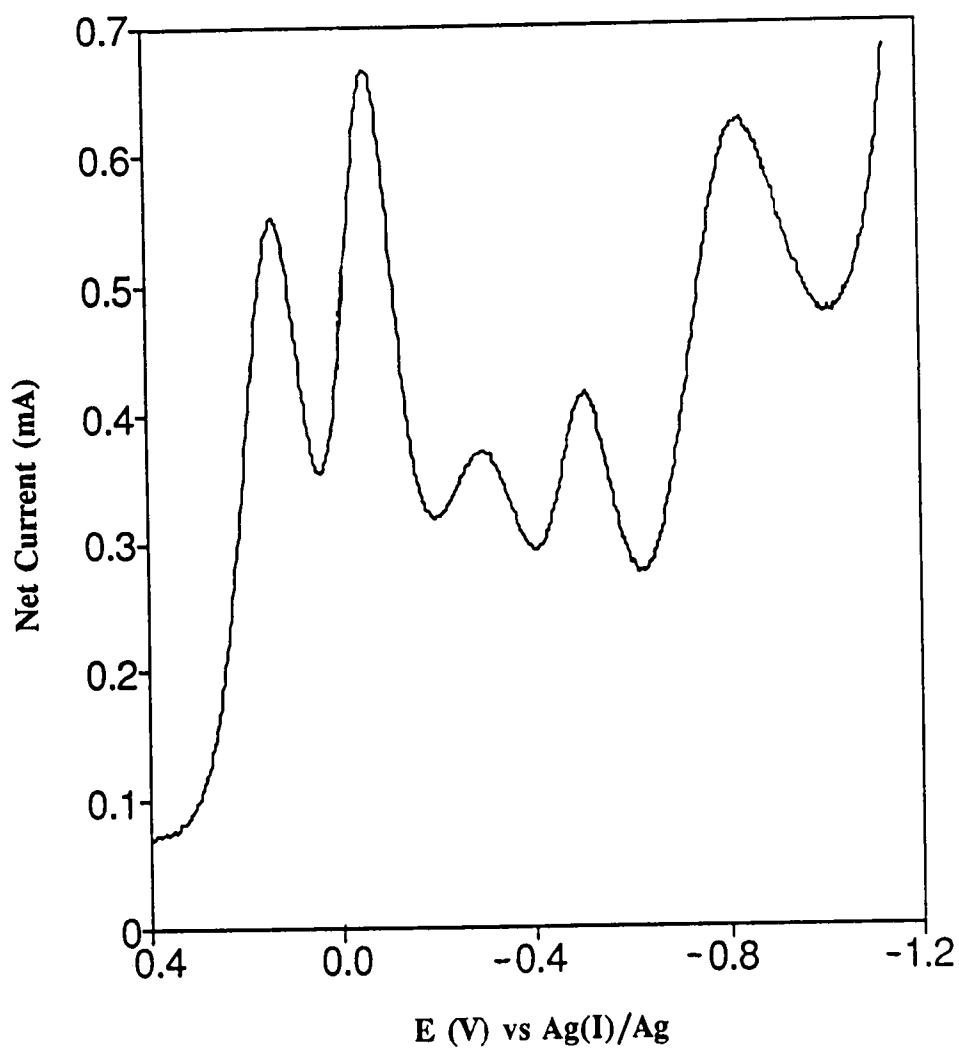


Figure 24. SWV obtained for a 1.11×10^{-2} M NbCl_3 solution in SCA. The melt had been treated with COCl_2 prior to use; working electrode was a W wire; $T = 178^\circ\text{C}$; frequency = 60 Hz; pulse height = 25 mV.

Table V. Peak Potentials from Voltammetry of Nb(V).

Method	$E_{p,0}$	$(E_{1/2})_0$	$E_{p,1}$	$(E_{1/2})_1$	$E_{p,2}$	$E_{p,3}$	$E_{p,4}$	Ref.
CV ^a			-0.09	0.03	-0.24	-0.46	-0.75	74
DPV ^b			-0.05		-0.31	-0.43	-0.79	74
CV ^c	0.12	0.15	-0.08	-0.03	-0.33	-0.52		102
DPV ^d	0.14		-0.04		-0.29	-0.50		102
CV ^e	0.114	0.161	-0.092	-0.032	-0.374	-0.531	(-0.8) ^f	this work
SWV ^g	0.160		-0.037		-0.280	-0.485	-0.803	this work
CV ^h			-0.081	-0.031	-0.320	-0.511	-0.80	this work
SWV ⁱ			-0.036		-0.301	-0.482	-0.783	this work

All potentials are given vs. Ag(I)/Ag; where necessary, the potential shift was determined using values from Table I (p. 3).

a. Al(III)/Al in 63-37 AlCl₃-NaCl melt reference used; 5.19x10⁻² M NbCl₅; 160°C; 0.10 V/s scan rate.

b. Al(III)/Al in 63-37 AlCl₃-NaCl melt reference used; 6.8x10⁻³ M NbCl₅; 160°C; 0.01 V/s.

c. Al(III)/Al in AlCl₃-NaCl_{sat} reference used; 2.62x10⁻² M NbCl₅; 175°C; 0.10 V/s.

d. Same as note (c), except the scan rate was 0.01 V/s.

e. Ag(I)/Ag reference used; 1.11x10⁻² M NbCl₅; 178°C; 0.10 V/s.

f. Due to the low intensity and broadness of this wave, only an approximate value could be measured for peak potential.

g. Same conditions as note (e); the frequency was 60 Hz.

h. Ag(I)/Ag reference used. The solution contained excess oxide; 3.51x10⁻² M NbCl₅; 178°C; 0.10 V/s.

i. Same conditions as note (h); the frequency was 60 Hz.

centration, should remain constant for all concentrations studied. However, the i_p/C values for the first reduction wave were found to be 0.085 and 0.140 mA/mM for the 11 mM and 25 mM solutions, respectively. The fact that the value for the 11 mM solution was significantly lower than that for the 25 mM solution indicates that some species (X) in solution had reacted with the $NbCl_5$ to diminish the effective concentration. Furthermore, species X must have been present in some finite amount which was lower than the amount of $NbCl_5$ added initially. Some simple algebraic manipulation (see the Appendix) can be used to determine the ratio of the concentration of species X to that of unreacted $NbCl_5$, as $C_X:C_{NbCl_5} = 1.17$, in the 11 mM solution.

To determine which of the two peaks is due to unreacted $NbCl_5$, and which is due to the product of the reaction with X, it is simply necessary to determine the ratio of the peak heights of the first two waves and compare it with the value of $C_X:C_{NbCl_5}$. However, the peak heights for the two waves are not immediately available with any certainty, since the two waves are not completely resolved.

It is possible to resolve the waves. The theory of SWV (103) predicts that a peak due to a reversible process will be symmetrical about the peak maximum. It is therefore feasible to determine the "backside" (more negative side) of a wave if one has only the "frontside" of it unhindered by other waves. Having determined the resolved first peak,

then, it is possible to subtract any contribution made by the first wave to the height of the second wave. This method was used with a SWV obtained in the 11 mM solution, making it possible to ascertain that the peak current of the second wave is indeed higher than that of the first wave (Figure 25). The ratio of the second wave peak height to that of the first was determined to be 1.22, which is in good agreement with the value of the relative concentrations of species X and NbCl_5 . In view of the above results, one is left with the rather surprising inference that the second wave is in fact that due to the product of the reaction between species X and NbCl_5 . It follows, then, that the results reported by Ting were probably erroneous in the assumption that the species under study was NbCl_5 .

It was necessary to determine the identity of species X. In recent years, it has become understood that oxide impurities can play a major role in the electrochemical behavior of some transition metals in chloroaluminate melts, and that adventitious oxide is, in fact, the primary impurity in these melts (77,79,80,87-93). If species X were oxide, then the addition of a slight excess of oxide to a melt containing NbCl_5 would be expected to cause the elimination of the first wave in Figure 24 (p. 104).

Oxide was added to a 35 mM NbCl_5 solution in the form of Na_2CO_3 , which reacts with the melt to produce dissolved oxide and CO_2 (75,92). Figure 26 shows a typical CV ob-

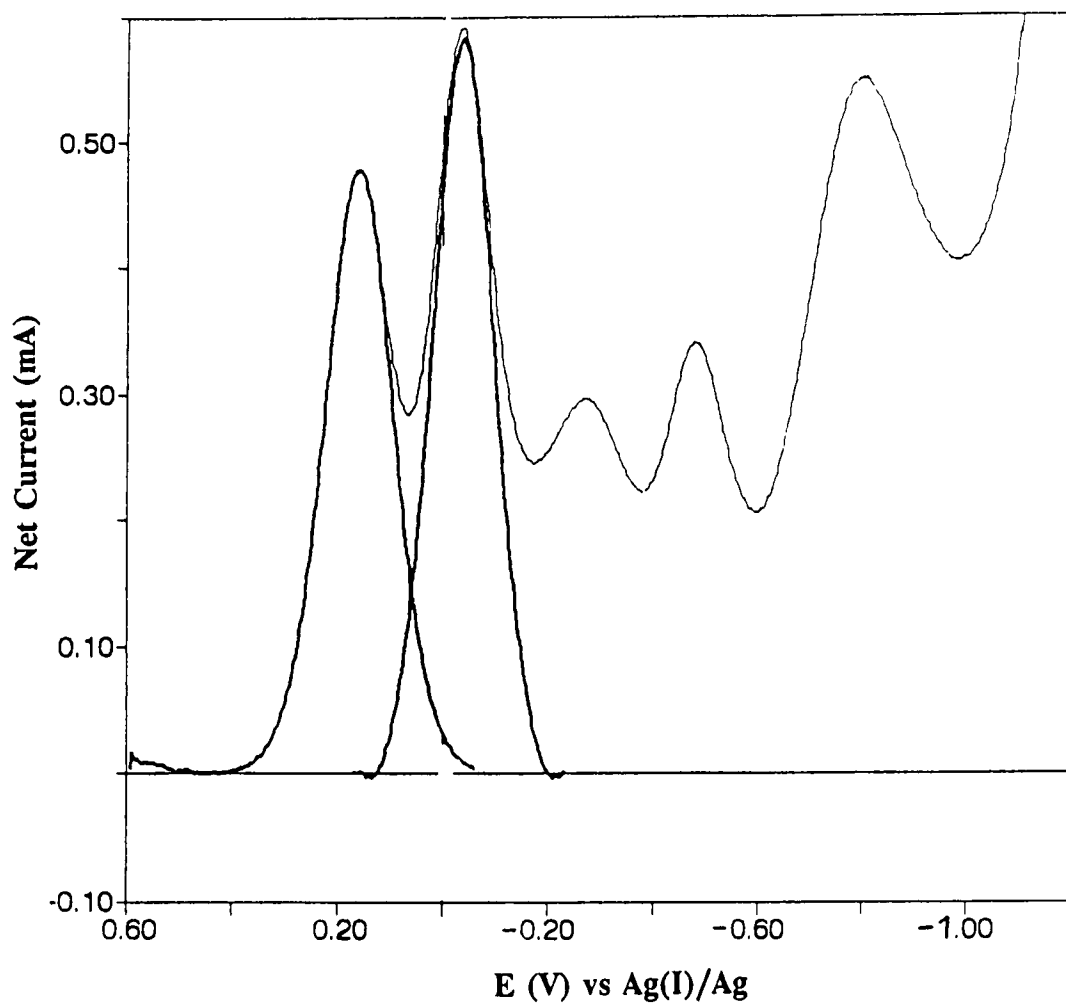


Figure 25. SWV with first and second peaks extracted by symmetrical reflection across the peak maxima. This is the same SWV as presented in Figure 24, with the peaks extracted as described in the text.

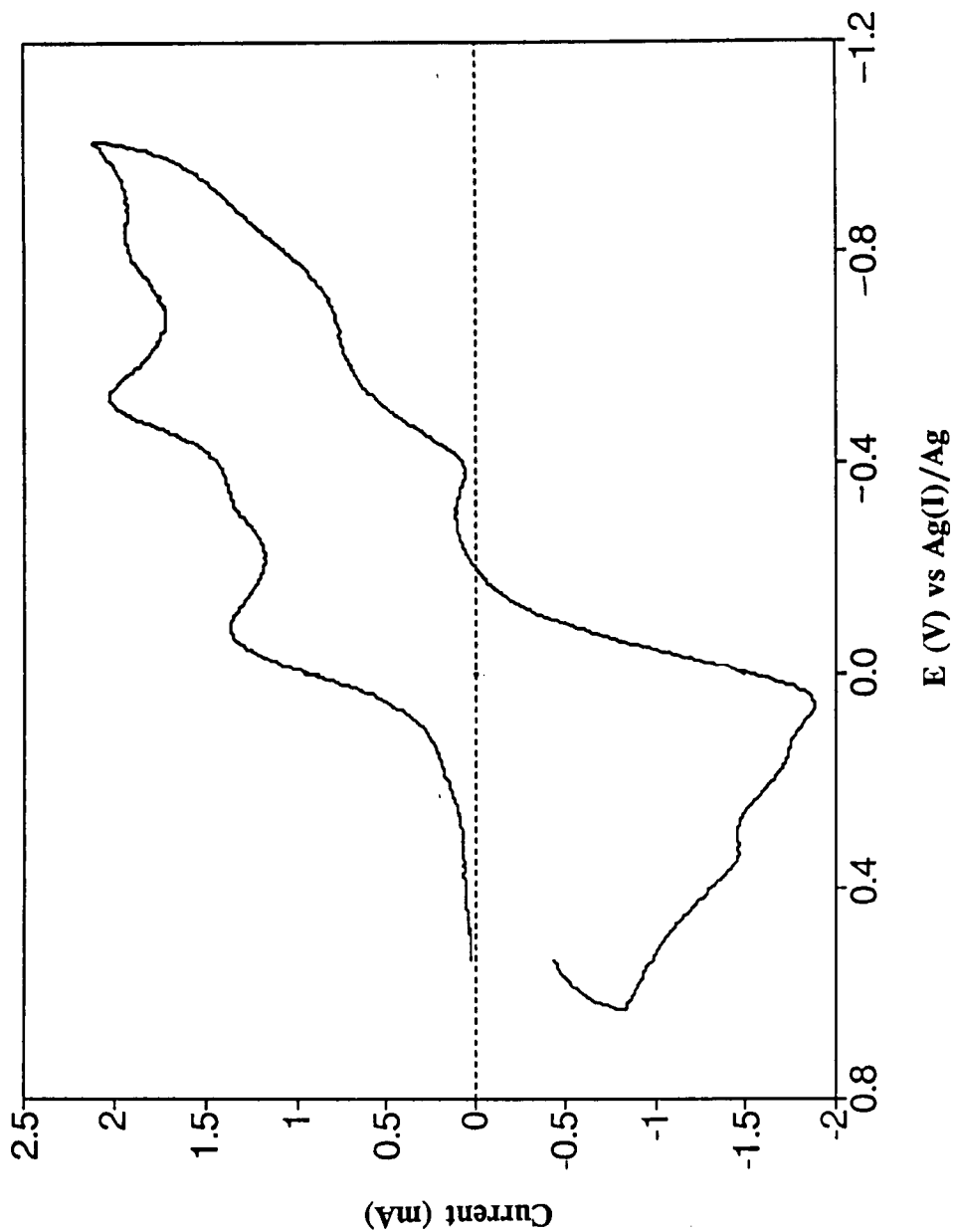


Figure 26. CV obtained for a 3.5×10^{-2} M NbCl_5 solution in SCA in the presence of excess oxide. Oxide had been added in the form of Na_2CO_3 ; working electrode was a W wire; $T = 178^\circ\text{C}$; scan rate = 0.1 V/s .

tained for the resulting solution. The form of this curve bears a striking resemblance to that obtained by Ting (Figure 18, p. 95); peak potentials in the CV in Figure 26 are -0.081, -0.320, -0.511 and -0.80 V. The SWV of the solution containing excess oxide is nearly identical to that shown in Figure 25 (p. 108), sans the first wave; reduction peaks occur at -0.036, -0.301, -0.482, and -0.783 V in the SWV. These values are very close to those reported by Ting for DPV (see Table V, p. 105).

Electronic spectra were obtained for NbCl_5 solutions with and without oxide added. Figure 27a shows a UV-visible spectrum of a 15 mM NbCl_5 solution, prepared using a COCl_2 -treated melt, at 200°C; two main bands are observed with maxima at 238 and 284 nm, respectively; a third band can be seen as a shoulder to the higher wavelength band. A solution of low NbCl_5 concentration was prepared with excess oxide. Figure 27b shows a spectrum of that solution; bands are observed with maxima at 222, 276, and 310 nm. Table VI compares these data with some reported by other workers. It is clear that Figure 27b is the spectrum of a niobium(V) oxychloride species, probably NbOCl_3 (or NbOCl_5^{2-}). On the other hand, the solution with which Figure 27a was obtained probably contained primarily NbCl_5 , but also contained some oxide as an impurity (by the shoulder observed at higher wavelength).

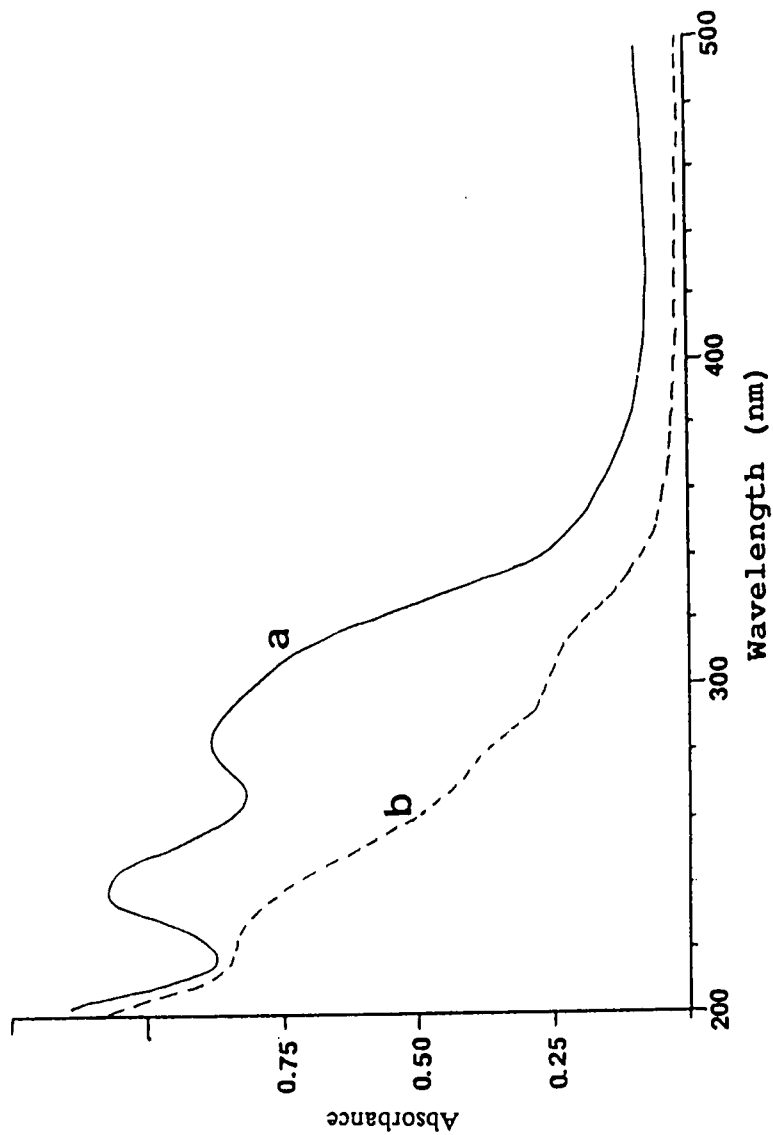


Figure 27. UV-visible spectra for NbCl_5 solutions in SCA at 200°C . The melt had been treated with COCl_2 prior to use. Cell path lengths were 0.3 cm.

a. (—) 1.5×10^{-2} M NbCl_5 .
b. (---) 2.88×10^{-3} M NbCl_5 , with > 10 mM oxide present. The absorbance scale for this spectrum is half that for (a).

Table VI. Maxima of Electronic Spectra for Nb(V).

Species	Solvent	Maxima, nm (ϵ , M ⁻¹ cm ⁻¹)	Ref.
NbCl ₅	(gas, 100°C)	240 (1.0x10 ⁴), 285 (1.0x10 ⁴)	75
NbCl ₅	SCA ^a , 175°C	235 (5.7x10 ³), 297 (4.6x10 ³)	75
NbCl ₅	SCA ^b , 175°C	240 (1.1x10 ⁴), 288 (1.3x10 ⁴)	105
NbCl ₅	SCA ^c , 200°C	238 ($\approx$ 7x10 ³), 284 ($\approx$ 6x10 ³)	this work
[NbCl ₆] ⁻	49/51 mole%		
	AlCl ₃ -MEIC, 25°C	291 (3.2x10 ⁴), 316 (1.7x10 ⁴), 360 (4.1x10 ³)	79
[NbOCl ₅] ²⁻	12 M HCl, 25°C	228 (3.6x10 ³), 280 (1.1x10 ⁴), 320 (1.3x10 ³)	79
[NbOCl ₅] ²⁻	CH ₃ CN, 25°C	205 (3.0x10 ⁴), 228 (4.0x10 ³), 278 (1.6x10 ⁴), 313 (1.1x10 ³)	79
[NbOCl ₅] ²⁻	49/51 mole%		
	AlCl ₃ -MEIC, 25°C	280 (1.4x10 ⁴), $\approx$ 320 (1.2x10 ³)	79
NbCl ₅ , excess oxide	SCA ^d , 200°C	222, 276, 310	this work

- NbCl₅ concentration was 2.8 mM.
- NbCl₅ concentration was 1.78 mM, and melt was treated with CCl₄ prior to use.
- NbCl₅ concentration was 15 mM, and melt was treated with COCl₂ prior to use.
- NbCl₅ concentration was 2.88 mM, and >10 mM oxide was added.

3. Discussion of Results from Oxide Studies

The results presented above lead one to the conclusion that the previously reported studies by Ting (74) were inaccurate in that they did not deal with the electrochemical behavior of niobium chloride species in SCA melts, but must have instead dealt with the corresponding behavior of niobium oxychloride species. It must be stressed, however, that the previous studies were conducted at a time when the importance of oxide impurities in these melts was not fully comprehended. The results presented by Ting assumed that the "50-50" $\text{AlCl}_3\text{-NaCl}$ was of relatively high purity. It was only with the more recently developed methods of melt preparation and purification that it was possible to realize this error. It should be noted also, that even at present, it is often difficult to obtain melts with essentially no oxide impurities; oxide sources abound throughout the preparation process, and even when solutions are treated in situ, impurities can be present. Such difficulties in working with molten salts are common, and indeed, expected.

B. Studies of the Electrochemical Behavior of NbCl_5 in SCA at 178°C

The studies discussed in the following sections were conducted in melts which had been treated in situ with CCl_4 or COCl_2 to remove oxide impurities. Much of the data pre-

sented were extracted from experiments conducted using solutions of relatively high concentration (≈ 20 mM) in order to minimize the effects of any oxide which remained after treatment, or which might have been inadvertently introduced via melt handling.

1. Cyclic Voltammetric Studies

Cyclic voltammetric studies were conducted at a temperature of $178 \pm 2^\circ\text{C}$ using solutions of NbCl_5 , concentration ranging from 5 to 30 mM. Scan rates ranging across three decades (0.05 V/s to 50 V/s) were used, and the studies were conducted at various working electrode materials, but primarily at tungsten and platinum. Some studies were conducted using glassy carbon electrodes, but over the course of long-term experiments, some spanning several weeks using the same cell, that electrode was often incapacitated. The reasons for this are not certain, but one likely cause is that melt crept between the glassy carbon and the glass in which it was sealed, and through numerous melting and cooling cycles, forced a break in connection between the glassy carbon and the tungsten lead.

Figure 28 shows a typical CV obtained in a 29 mM NbCl_5 solution at a scan rate of 0.2 V/s. Essentially four cathodic waves were observed at peak potentials of 0.114,

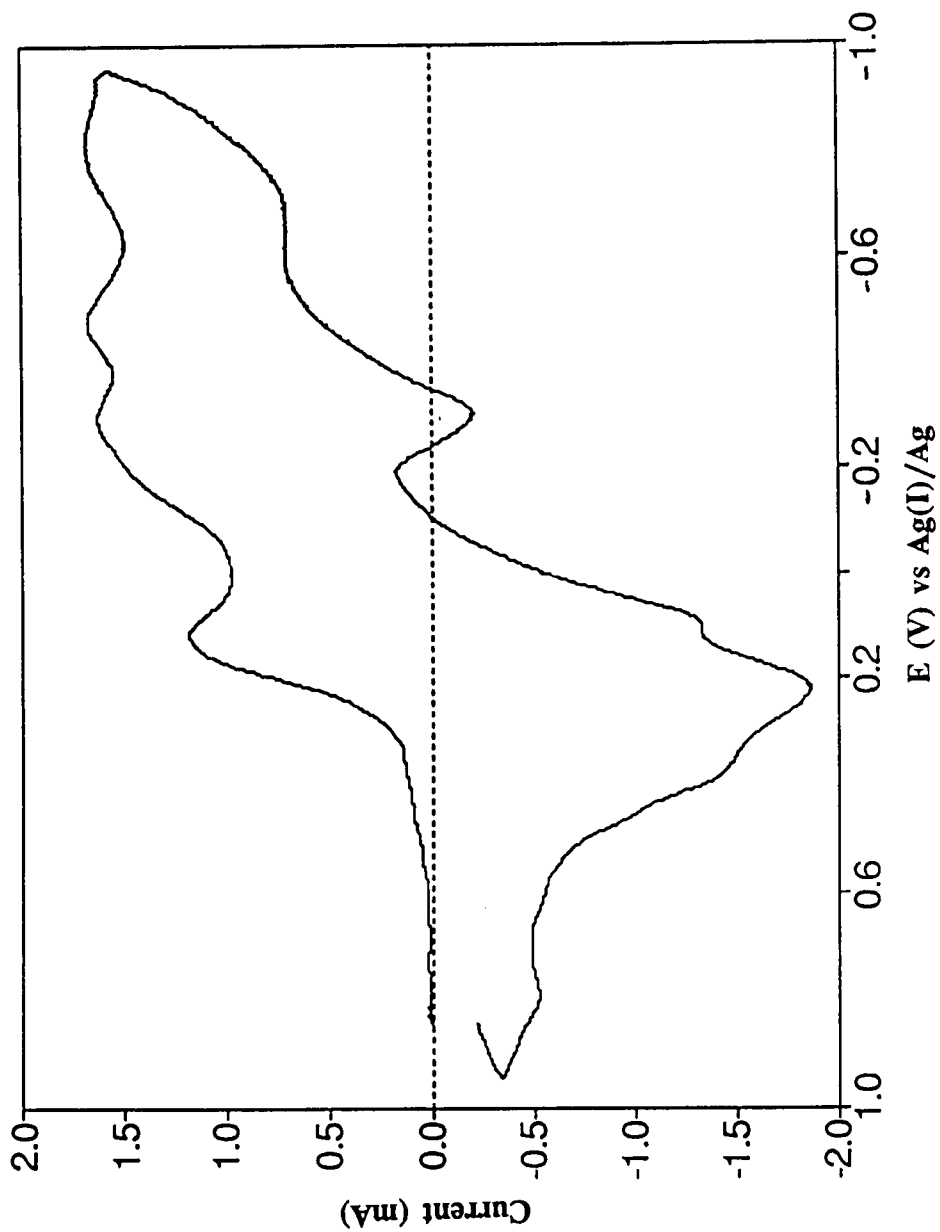


Figure 28. CV obtained using a 2.9×10^{-2} M NbCl_5 solution in SCA. The solution had been treated in situ with CCl_4 ; working electrode was a W wire; $T = 178^\circ\text{C}$; scan rate = 0.2 V/s .

-0.293, -0.482, and -0.809 V. A small wave was observed immediately preceding the second reduction wave (seen as a shoulder on the second wave in Figure 28) in solutions of relatively high concentration (>20 mM).

a. Analysis of the first wave in the cyclic voltammogram. Figure 29 shows a series of CV's in which the potential sweep was reversed immediately after the first wave. Table VII gives some pertinent data, which were extracted from CV curves, concerning the initial reduction wave. The values for n in column 6 of Table VII were determined using Equation 33 (105) where R is the ideal gas con-

$$(E_p^c - E_{p/2}) = 2.2RT/nF \quad (33)$$

stant, T is the temperature, and F is Faraday's constant. The $E_{1/2}$ values in column 9 of the table were determined from the midpoint between the cathodic and anodic peak potentials (105); those in column 10 were determined using Equation 34

$$E_{p/2} = E_{1/2} + 1.09 RT/nF \quad (34)$$

with $n=1$ (105). The peak potentials for CV's obtained at 50 V/s at higher concentrations appeared to differ significantly from values obtained at slower scan rates. This is likely due to the fact that at 50 V/s, one has approached the upper

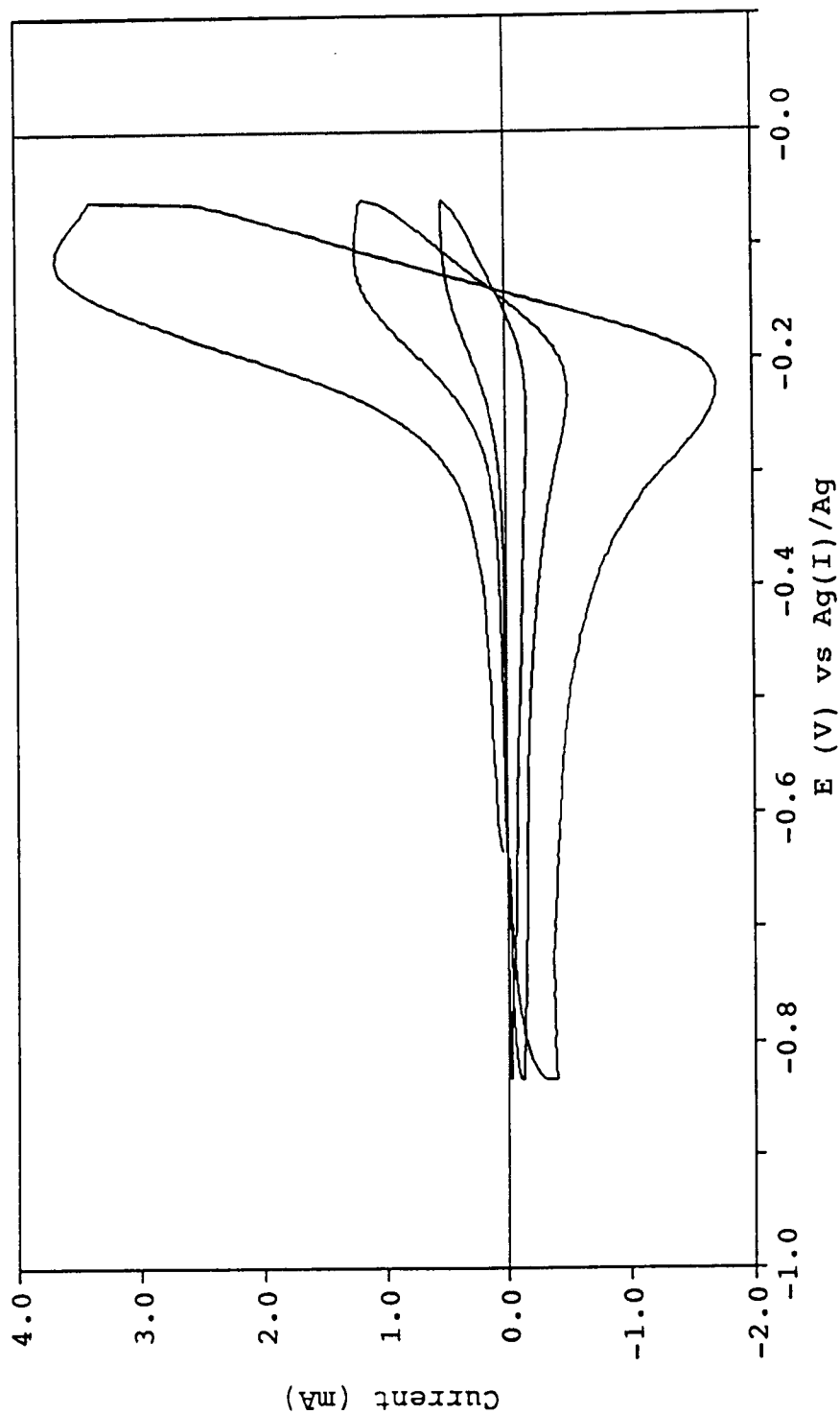


Figure 29. CV's obtained for a 1.88×10^{-2} M NbCl_5 solution in SCA which had been treated with CCl_4 . Working electrode was a W wire; $T = 178^\circ\text{C}$; the scan rate was varied as follows:
a. 0.05 V/s b. 0.5 V/s c. 5.0 V/s

Table VII. Some CV Data Pertaining to the First Wave in the CV of Nb(V) in SCA at 178°C.¹

Conc. NbCl ₅ (mM)	Scan Rate (V/s)	E_p^c (V)	$E_{p/2}$ (V)	$E_p^c - E_{p/2}$ (V)	n	E_p^a (V)	$(E_p^a - E_p^c)$ (V)	$E_{1/2}^2$ (V)	$E_{1/2}^3$ (V)	$i_p^{a,c}$ ----- i_p^c
5.1	0.05	0.104	0.197	-0.093	0.92	0.230	0.126	0.167	0.155	1.04
	0.10	0.104	0.194	-0.090	0.95	0.218	0.114	0.161	0.152	1.05
	0.20	0.105	0.194	-0.089	0.96	0.220	0.115	0.162	0.152	1.02
	0.50	0.105	0.202	-0.097	0.88	0.222	0.117	0.164	0.160	1.00
	5.0	0.113	0.205	-0.092	0.93	0.209	0.106	0.161	0.163	1.05
	50.0	0.108	0.195	-0.087	0.98	0.217	0.109	0.162	0.153	-----
18.8	0.05	0.105	0.204	-0.089	0.96	0.245	0.140	0.175	0.162	0.92
	0.10	0.102	0.196	-0.094	0.91	0.221	0.119	0.162	0.154	0.94
	0.20	0.103	0.198	-0.095	0.90	0.224	0.121	0.164	0.156	0.96
	0.50	0.105	0.205	-0.100	0.86	0.227	0.122	0.166	0.163	0.95
	5.0	0.105	0.202	-0.097	0.88	0.229	0.124	0.167	0.160	0.99
	50.0	0.079	0.180	-0.101	0.86	0.257	0.178	0.168	0.138	1.02
29.1	0.05	0.109	0.203	-0.094	0.91				0.161	
	0.10	0.108	0.201	-0.093	0.92				0.159	
	0.20	0.116	0.206	-0.090	0.95				0.164	
	0.50	0.123	0.212	-0.089	0.96				0.170	
	5.0	0.119	0.211	-0.092	0.93				0.169	
	50.0	0.070	0.204	-0.134	0.65				0.162	

1. Potentials are reported to three significant figures; the potential resolution of the PAR Model 273 is ± 0.002 V.
2. $E_{1/2}$ in this column determined from the midpoint between E_p^c and E_p^a .
3. $E_{1/2}$ in this column determined from Equation 34, p. 116.
4. Determined using Nicholson's criterion, as described in reference 106.

limit in scan rate obtainable with the PAR273/M270; for a full CV from +1V to -1V and back, less than 200 points could be recorded. Under such conditions, the potential resolution becomes quite low, and reliable values cannot always be obtained. Another consideration is the increase in the effect of iR drop (the difference in the applied voltage and the voltage measured at the reference electrode, caused by uncompensated solution resistance). The PAR273/M270 has a function which determines uncompensated solution resistance; although a value of 1 ohm, which is quite low, was obtained using this function, at high concentrations (and therefore, high currents), the iR drop can become significant.

Several characteristics of the data presented in Table VII (p. 118) indicate that the first wave in the reduction of $NbCl_5$ in SCA at 178°C is a reversible, one-electron transfer process. The cathodic peak potential, which should be independent of scan rate and concentration, does not shift in any regular fashion with either of these parameters. The ratio of the cathodic peak current to the anodic peak current (i_p^c/i_p^a), determined using Nicholson's criterion (105), remains very close to unity throughout the range of scan rates studied at two concentrations. The number of electrons transferred (n), as calculated by Equation 34, remains close to unity (disregarding the possibly faulty values for the 50 V/s scan rate).

Equation 35 (105) applies to reversible redox systems.

$$i_p = (2.69 \times 10^5) n^{3/2} A (D_o v)^{1/2} C_o^* \quad (35)$$

Therefore, a plot of i_p vs. the square root of the scan rate ($v^{1/2}$) should be linear, with an intercept of zero and a slope of $(2.69 \times 10^5) n^{3/2} A (D_o v)^{1/2} C_o^*$. Figure 30 shows such plots for each of the three concentrations studied. In each case, the plot is linear, and has an intercept near zero. From the slopes of the plots obtained for the 5.1 mM, 19 mM, and 29 mM solutions, the diffusion coefficient (D_o) for Nb(V) at 178°C was determined to be 1.31×10^{-6} , 1.72×10^{-6} , and 1.68×10^{-6} cm²s⁻¹, respectively.

Finally, Equation 35 predicts that for a simple reversible redox process, the peak current will increase linearly with the concentration of solute. Figure 31 shows a plot of voltammetric peak current vs. the concentration of NbCl₅. The plot is linear, with an intercept near zero.

b. Subsequent waves in the CV of NbCl₅. In solutions of low concentration (< 20 mM), only four reduction waves are observed in the CV of NbCl₅; the shoulder observed to precede the second wave (see Fig. 28, p. 115) only becomes significant at concentrations higher than 20 mM. Furthermore, even at high concentrations, the shoulder essentially disappears at high scan rate (compare Figures 28 and 32). Voltammetric data such as peak potential and current could not be obtained for this shoulder.

The behavior of the shoulder to the second wave indicates that it involves some reaction which is only signi-

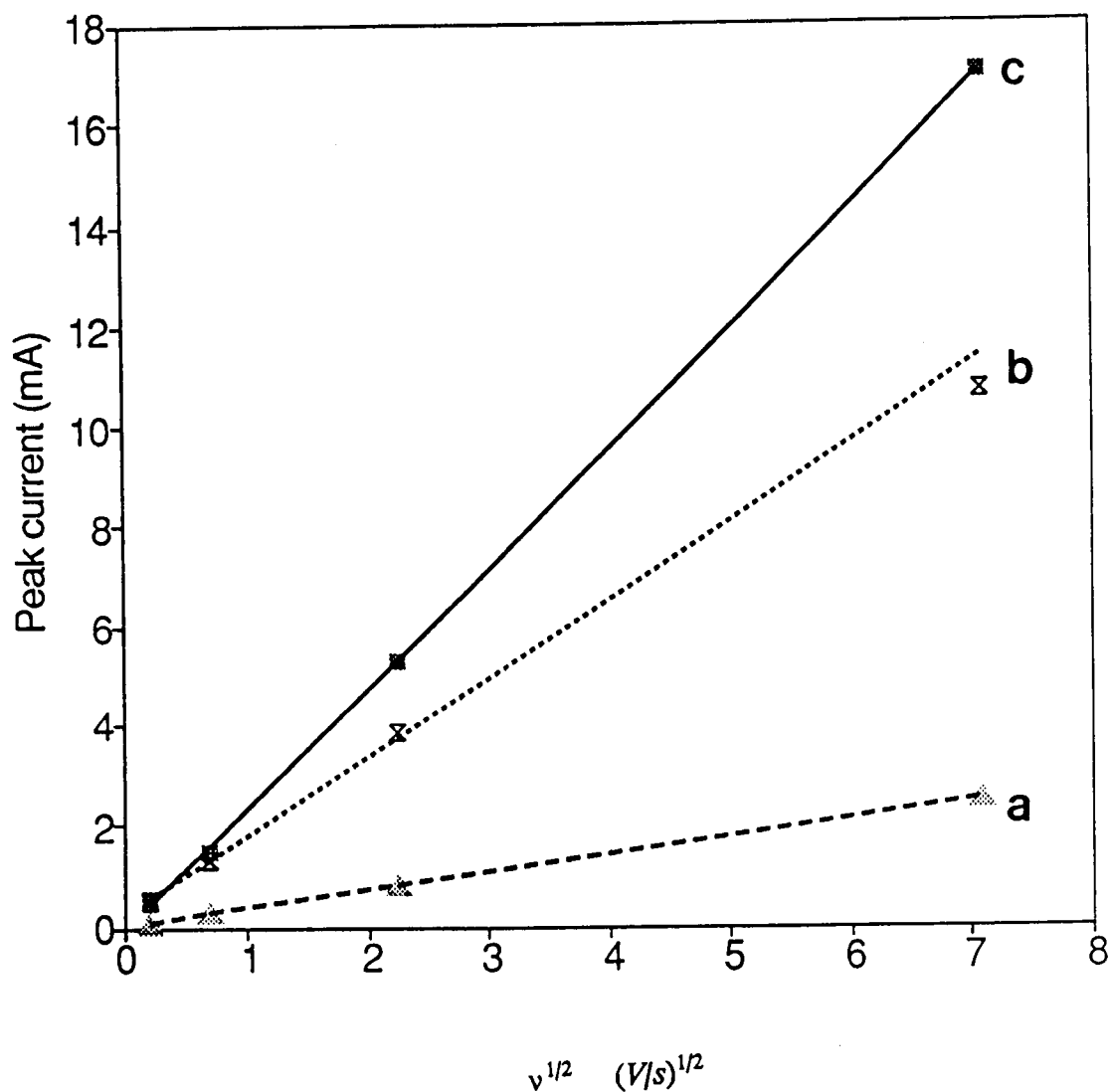


Figure 30. Plots of peak current vs. $v^{1/2}$ for the first wave in the CV obtained in solutions of $NbCl_5$ in CCl_4 -treated SCA. Working electrode was a W wire; $T = 178^\circ C$; the solution concentrations were

a. $5.1 \times 10^{-3} M$

b. $1.88 \times 10^{-2} M$

c. $2.91 \times 10^{-2} M$

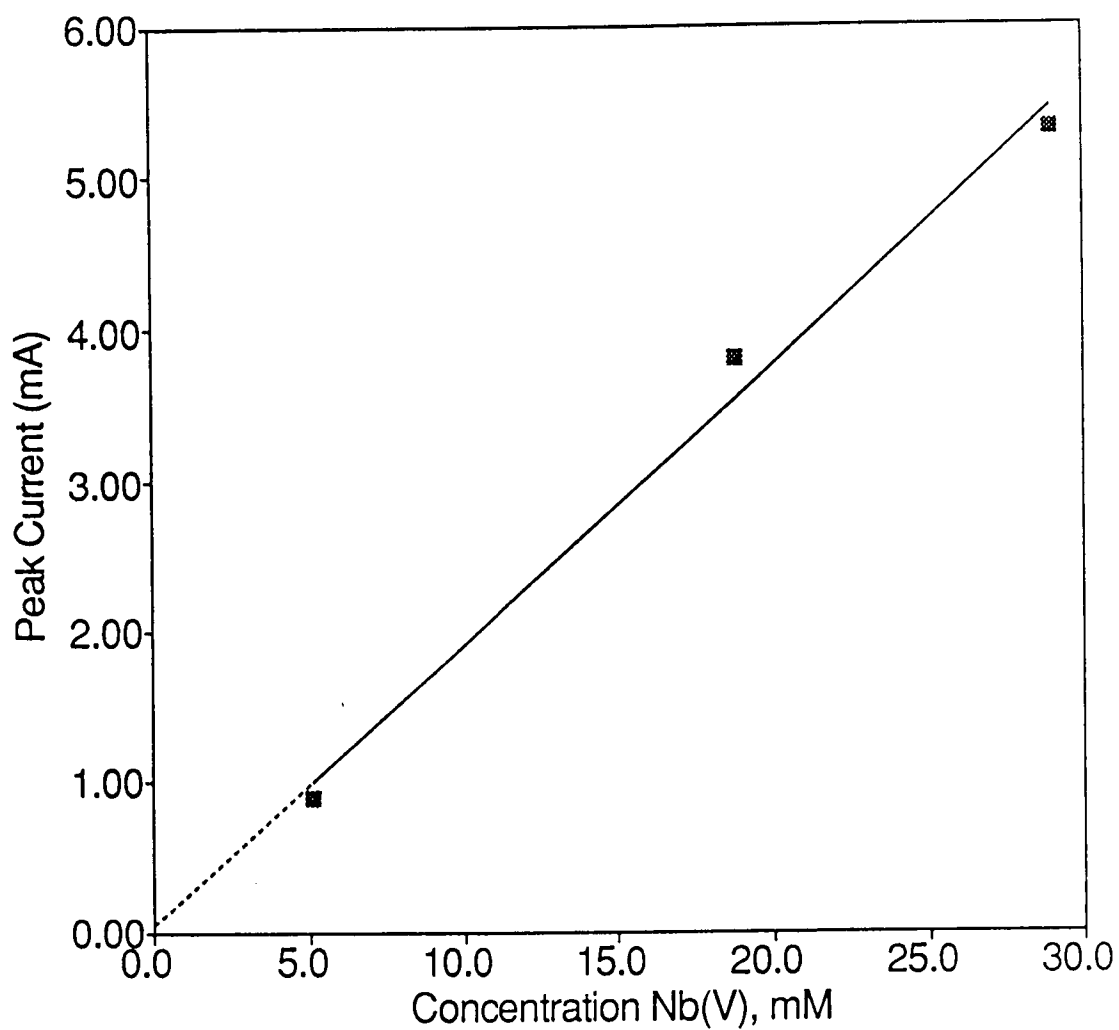


Figure 31. Plot of peak current vs. the concentration of NbCl_5 added to CCl_4 -treated SCA. Working electrode was a W wire; $T = 178^\circ\text{C}$; scan rate was 0.5 V/s.

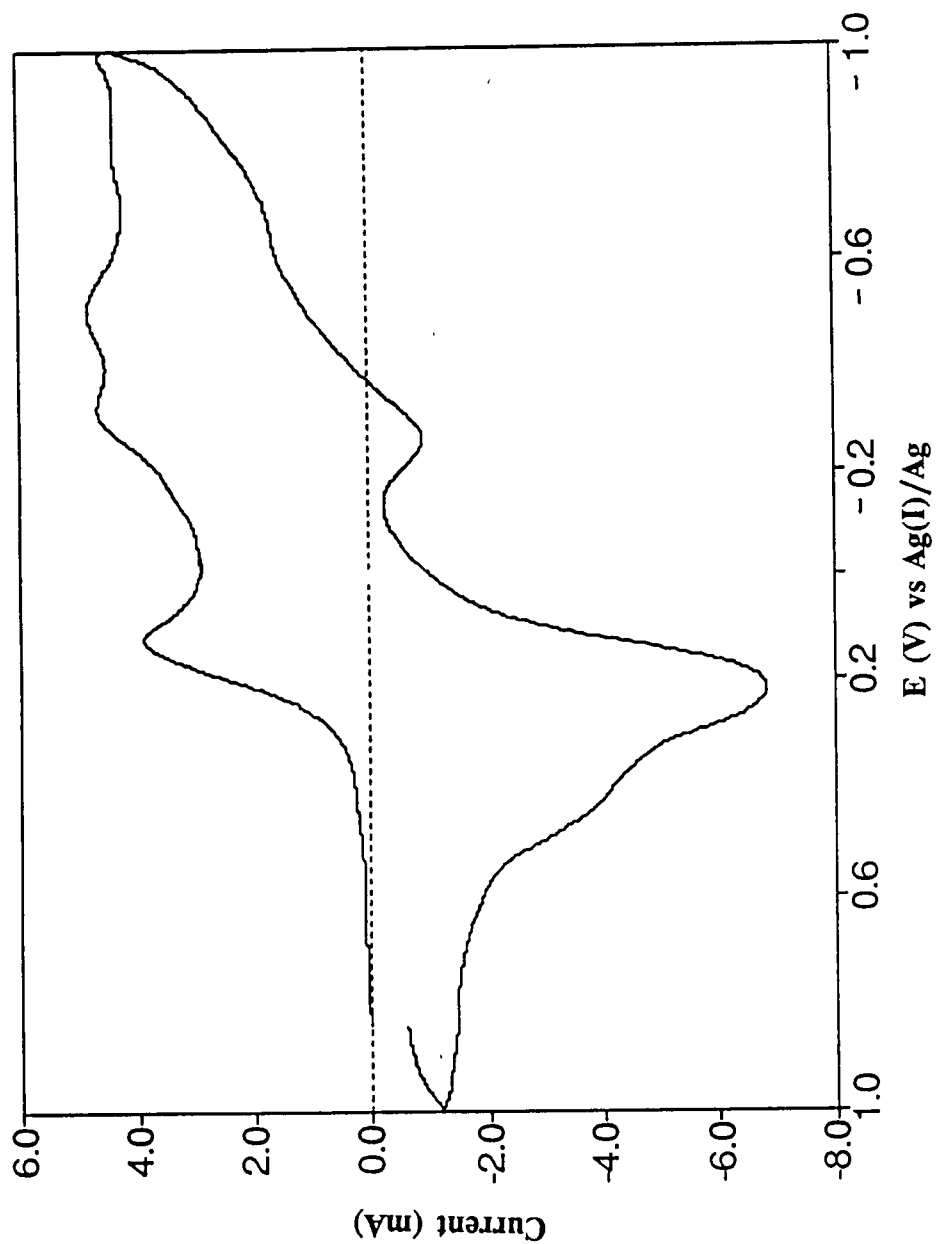


Figure 32. CV obtained for a 2.91×10^{-2} M NbCl_5 solution in CCl_4 -treated SCA. Working electrode was a W wire; $T = 178^\circ\text{C}$; scan rate = 2.0 V/s.

ficant at long times (slow scan rates) and high concentrations. The voltammetric data pertaining to the first reduction wave ($E_p \approx 0.11$ V) do not indicate that it is complicated by a following chemical reaction. However, the methods discussed in the preceding section are not sensitive to small deviations from ideality. More sensitive methods to probe such behavior are described in the literature (106); these methods consider the dependence of certain parameters related to i_p and $E_{p/2}$ with scan rate. Figure 33 shows a plot of the current function given in Equation 36

$$\psi_p = \frac{i_p}{nFAD^{1/2}C^o \left(\frac{nFv}{RT} \right)^{1/2}} \quad (36)$$

vs the scan rate (plotted on a logarithmic scale). The shape of the curve in Figure 33 is indicative of a following chemical reaction which regenerates the initial redox species (Case VII in reference 106). Figure 34 shows a plot of $(\Delta E_{p/2})/(\Delta \log v)$ vs. the scan rate (plotted on a logarithmic scale); this curve also indicates that a following chemical reaction regenerates the original redox species. Furthermore, the shapes of the curves observed in Figures 33 and 34 strictly exclude the occurrence of an EC mechanism (electrochemical step followed by a chemical reaction), and do not support dimerization of the redox product.

Some pertinent voltammetric data for the second, third and fourth waves in the CV are given in Table VIII. The

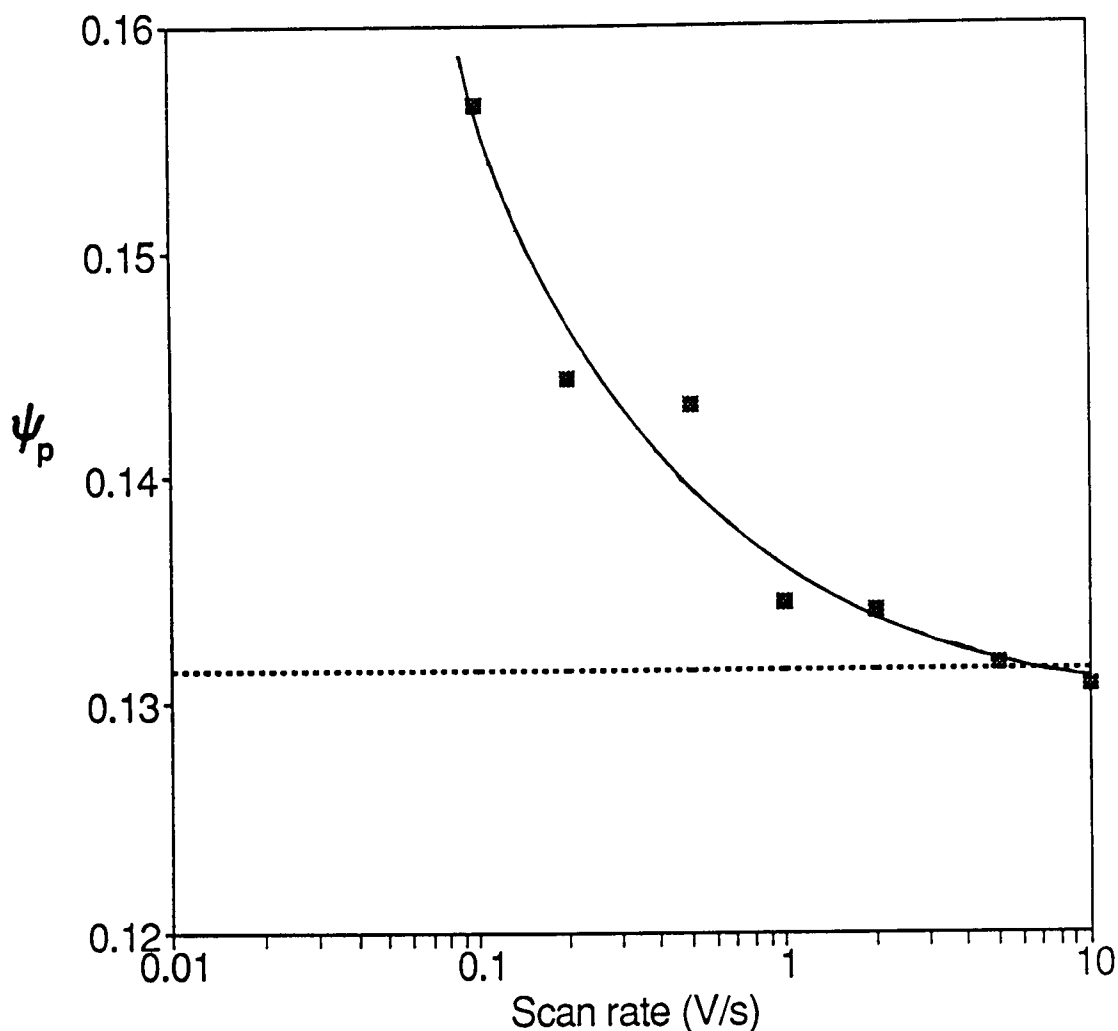


Figure 33. Plot of the dimensionless current function (ψ_p) vs. the scan rate (on a logarithmic scale) for the first reduction wave obtained by CV for a 2.91×10^{-2} M solution of NbCl_5 in SCA. The dotted line represents the theoretical current expected for this concentration, using $D_0 = 1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. Working electrode was a W wire; $T = 178^\circ \text{C}$; scan rate ranged from 0.1 to 10 V/s.

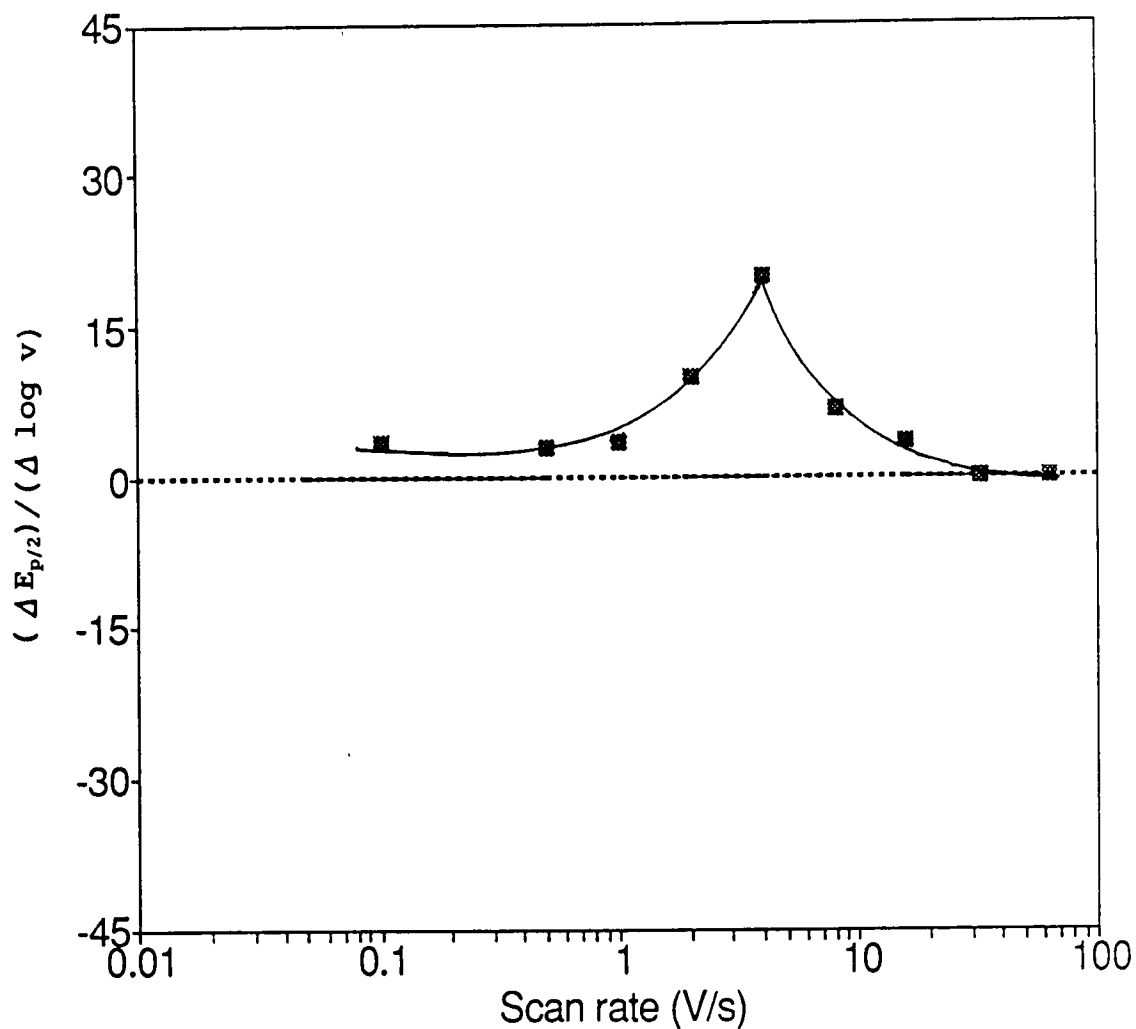


Figure 34. Plot of the function $(\Delta E_{p/2})/(\Delta \log v)$ vs the scan rate (on a logarithmic scale) for the first reduction wave obtained by CV for a 2.91×10^{-2} M solution of NbCl_5 in SCA. The dotted line represents the curve expected in the complete absence of complicating behavior. Working electrode was a W wire; $T = 178^\circ\text{C}$; scan rate ranged from 0.1 to 50 V/s.

Table VIII. Voltammetric Data Pertaining to the Final Three Waves.

Scan Rate (V/s)	$E_{p,2}$ (V)	$E_{p,3}$ (V)	$E_{p,4}$ (V)	$E_{p,2}-E_{p,3}$ (V)
0.04	----	-0.473	-0.717	----
0.20	-0.293	-0.482	-0.809	0.189
0.40	-0.306	-0.496	-0.803	0.190
2.0	-0.324	-0.504	(-0.830)	0.180
4.0	-0.339	-0.522	(-0.839)	0.183
20.0	-0.395	-0.548	(-0.879)	0.153
40.0	-0.421	-0.568	(-0.919)	0.147

Data were extracted from CV's obtained from a 29 mM NbCl₅ solution in SCA. The temperature was 178°C, and a tungsten working electrode was used.

peak potentials of the second and third waves shifted to more negative values as the scan rate was increased; the amount by which they were separated became smaller. At none of the scan rates studied were the two waves sufficiently resolved that peak current determination for the third wave could be accomplished. Complications from the shoulder preceding the second wave prevented the extraction of meaningful data for the second wave at low scan rate, and the proximity of the third wave caused similar difficulties at higher scan rates.

The cyclic voltammetric experiments did not yield results of any significance for the second and third waves; however, it was observed that during a negative sweep of the potential, a dark film was formed on the electrode surface as the potential passed that of the third reduction wave. Unfortunately, attempts to obtain X-ray powder diffraction data of this film were fruitless; no significant lines were noted other than a broad band in the regions of high d-spacing. At high concentrations (>20 mM), this film presented some definite problems; when the potential was swept past the third wave in the CV, a fairly sharp cathodic wave was observed between the first and second waves (-0.27 V) in the next CV obtained. This new cathodic wave grew in intensity each time the potential was consecutively scanned past the third wave. In order to obtain meaningful results in concentrated solutions, it was often necessary to

cycle the potential between the E_{initial} and the second reduction wave, reversing the potential sweep before the onset of the third wave, for 10 - 50 times until the wave at -0.27 V had diminished into the background.

The most negative wave ($E_p \approx -0.8$ V) in the CV was small and broad at all scan rates studied. The potential of this wave, like those of the second and third waves, shifted to more negative values with increasing scan rates (see Table VIII, p. 128).

2. Chronoamperometry and Chronocoulometry

Chronoamperometry (CA) can be useful for further characterization of a redox process; this technique has also been used often to estimate the diffusion coefficient of electroactive species (107). Chronocoulometry (CC) is considered to be superior to CA due to the inherent minimization of noise and transient current-time effects.

Figure 35 shows the current vs. time plots for several chronoamperometric experiments conducted at potentials just negative of each peak potential observed in the CV's (see Fig. 28, p. 115). Each of the curves in Fig. 35 appears as expected from the theory, with no apparent complications.

The Cottrell equation (Equation 37, from ref. 105) pre-

$$i_t = \frac{nFAC_oD_o^{1/2}}{\pi^{1/2}t^{1/2}} \quad (37)$$

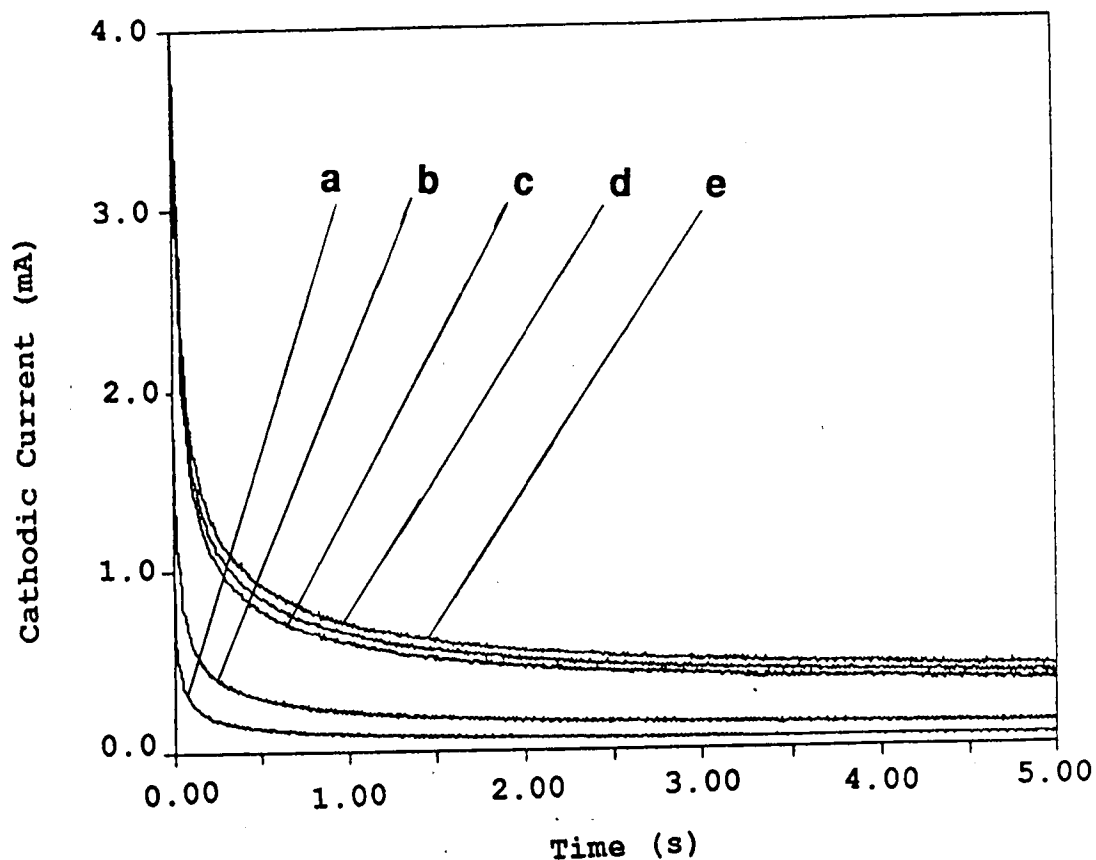


Figure 35. Current vs. time curves for chronoamperometric data obtained at various potential steps for a 5.1×10^{-3} M NbCl_5 solution in SCA. Working electrode was a W wire, $T = 178^\circ\text{C}$. The potential was stepped to the following values:

- | | |
|------------|------------|
| a. 0.05 V | d. -0.60 V |
| b. -0.20 V | e. -0.82 V |
| c. -0.30 V | |

dicts that, when dealing with a reversible reaction, a plot of CA current vs. $t^{-1/2}$ should be linear and will exhibit a slope of $(nFAC_0^*D_0^{1/2}\pi^{-1/2})$ and an intercept of zero. Figure 36 shows such a plot for data obtained after the potential was stepped to a potential (0.05 V) just past the first wave reduction potential in a 5.1 mM Nb(V) solution. The plot is linear, as expected for a Nernstian reaction. A linear plot, with a zero intercept, was obtained when an identical experiment was conducted using a solution of higher concentration (19 mM). From the slopes of these plots, and assuming that $n=1$, the diffusion coefficient for Nb(V) was found to be 1.5×10^{-6} and $2.4 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ at 178°C , respectively.

The Cottrell equation also predicts that the quantity $it^{1/2}$ will be constant for all times of a CA experiment. The Cottrell equation as given in Equation 37 was derived with only diffusion to a planar electrode considered. Over long periods of time, some deviation in the parameter $it^{1/2}$ is expected for non-planar electrodes (e.g. cylindrical electrodes); the effects of non-planar contributions are minimized for sampling times less than 1 second (107). Furthermore, at sufficiently long times, convection can cause a positive deviation in the value of $it^{1/2}$. With these factors considered, the parameter $it^{1/2}$ was found to be reasonably constant with t , with only a small deviation. The average value of $it^{1/2}$ determined from the 0.01 s to 0.75 s region of

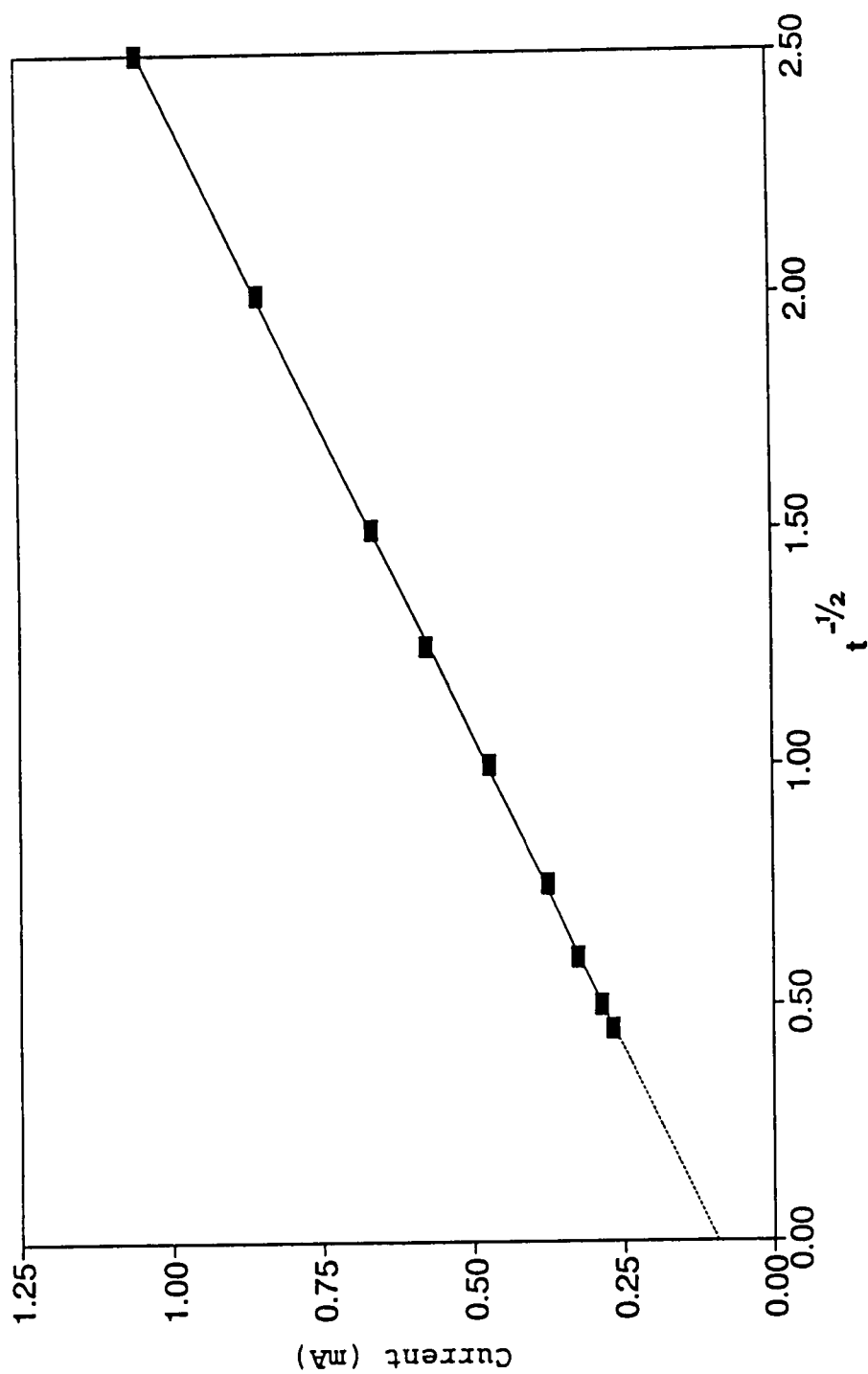


Figure 36. Plot of current vs. $t^{-1/2}$ for a chronoamperometric potential step to 0.05 V vs. Ag(I)/Ag in a 5.1×10^{-3} M NbCl₅ solution in SCA. The working electrode was a W wire; T = 178°C.

CA obtained in the 5.1 mM solution is $1.0 \times 10^{-4} \text{ As}^{1/2}$; this yields a value for D_0 for Nb(V) at 178°C of $2.24 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$.

Integration of the current with respect to time for a CA experiment yields the charge involved; integration of the Cottrell Equation 36 yields Equation 38, from which it is

$$Q = \frac{2nFAD_0^{1/2}C_0^*t^{1/2}}{\pi^{1/2}} \quad (38)$$

apparent that a plot of Q vs. $t^{1/2}$ should be linear for a reversible process. Figure 37 shows a plot of Q vs. $t^{1/2}$ determined from CA experiments conducted using the 5.1 mM solution; similar results were obtained for the 19 mM solution. The reason for the negative intercept is not clear. The diffusion coefficient (D_0) for Nb(V) at 178°C was determined to be 2.0×10^{-6} and $2.8 \times 10^{-6} \text{ cm}^2\text{s}^{-1}$ using the 5.1 and 19 mM solutions, respectively.

3. Normal Pulse Voltammetry (NPV)

Normal pulse voltammograms (NPV's) were obtained with the 5.1 mM and 19 mM solutions using pulse widths from 0.05 to 2.5 s. In general, the shorter pulse widths afforded better resolution among the observed waves; at pulse widths greater than 1.0 s no discrete waves could be resolved throughout the voltammogram. Regardless of the pulse width used, it was only possible to resolve the first wave.

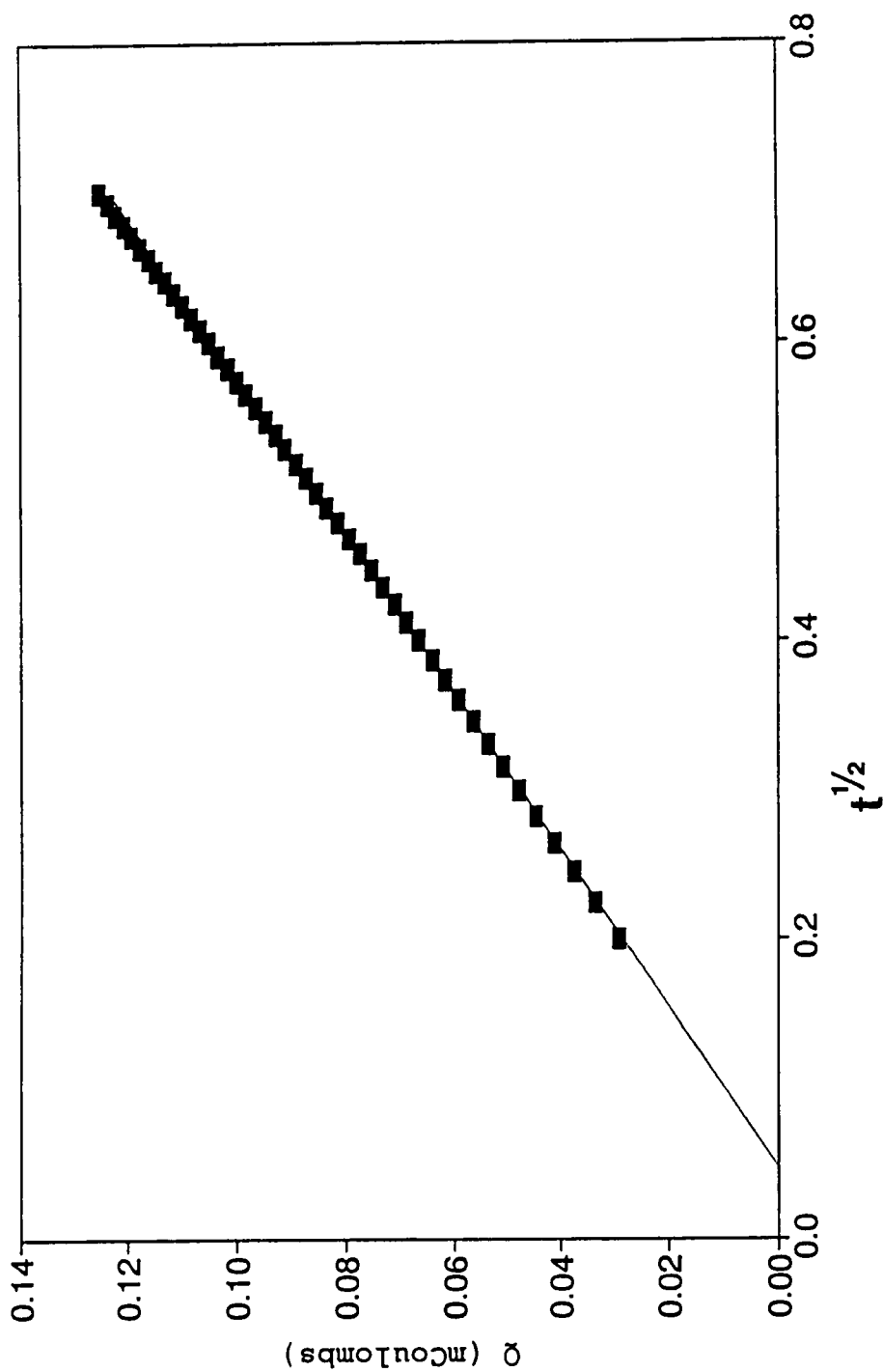


Figure 37. Plot of charge vs. $t^{1/2}$ for a potential step to 0.05 V. The charge was obtained from the integration of the data shown in Figure 36 (p. 130).

Figure 38 shows NPV's obtained for the 19 mM solution using pulse widths of 0.05 s and 1.0 s; only the first wave is shown in these NPV's. Both curves have the general appearance expected of a well-behaved, reversible charge transfer process. The current-potential relationship of a reversible redox couple should follow Equation 39 (105), in

$$E = E_{1/2} + \frac{RT}{nF} \ln \frac{i_d(\tau) - i(\tau)}{i(\tau)} \quad (39)$$

which τ is the current-sampling time, or pulse width. It is apparent that a plot of E vs. $\ln(i_d - i)/i$ should result in a straight line, with a slope of RT/nF and an intercept of $E_{1/2}$, if the process under study is Nernstian. The number of electrons (n) involved in the redox process can be determined from the slope of such a plot.

Figure 39 shows plots of E vs. $\ln(i_d - i)/i$ for the NPV experiments depicted in Figure 38. The plots are linear for both the 0.05 s and 1.00 pulse widths. From the slopes of these plots, n values were found to be 0.98 and 0.94, respectively; the intercepts ($E_{1/2}$) were found to be 0.167 V and 0.177 V, respectively. Both the calculated n values and the values of $E_{1/2}$ are in excellent agreement with those determined from the CV experiments (Table VII, p. 118).

Normal pulse voltammograms spanning the full potential range for the Nb(V) reduction are given in Figure 40 for pulse widths of 0.05 s and 1.00 s. As stated above, only the first reduction wave can be resolved sufficiently for

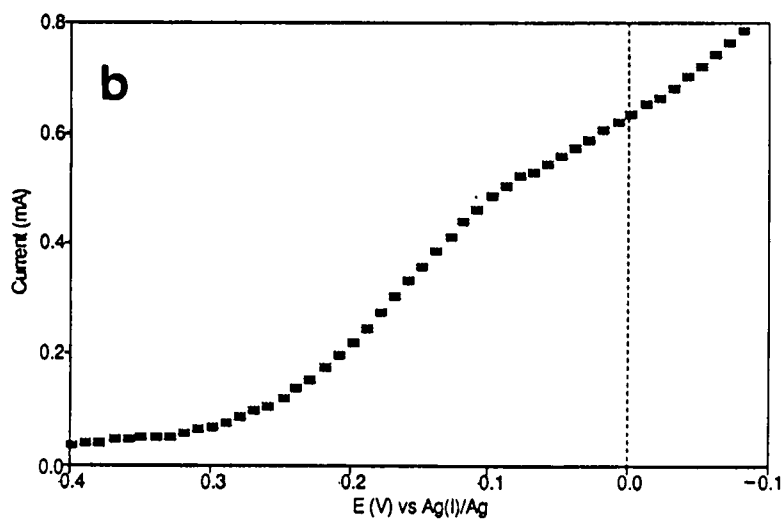
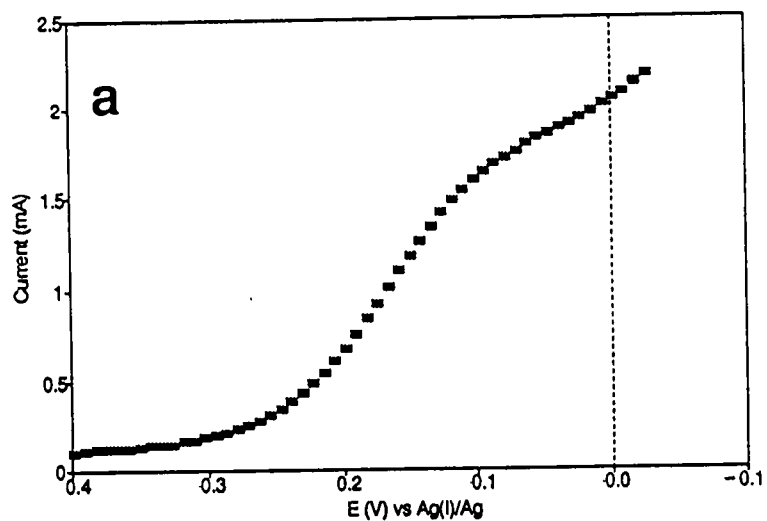


Figure 38. NPV curves for the first wave in the reduction of NbCl_5 (1.88×10^{-2} M) in SCA at 178°C at a W working electrode.

a. Pulse width = 0.05 s

b. Pulse width = 1.0 s

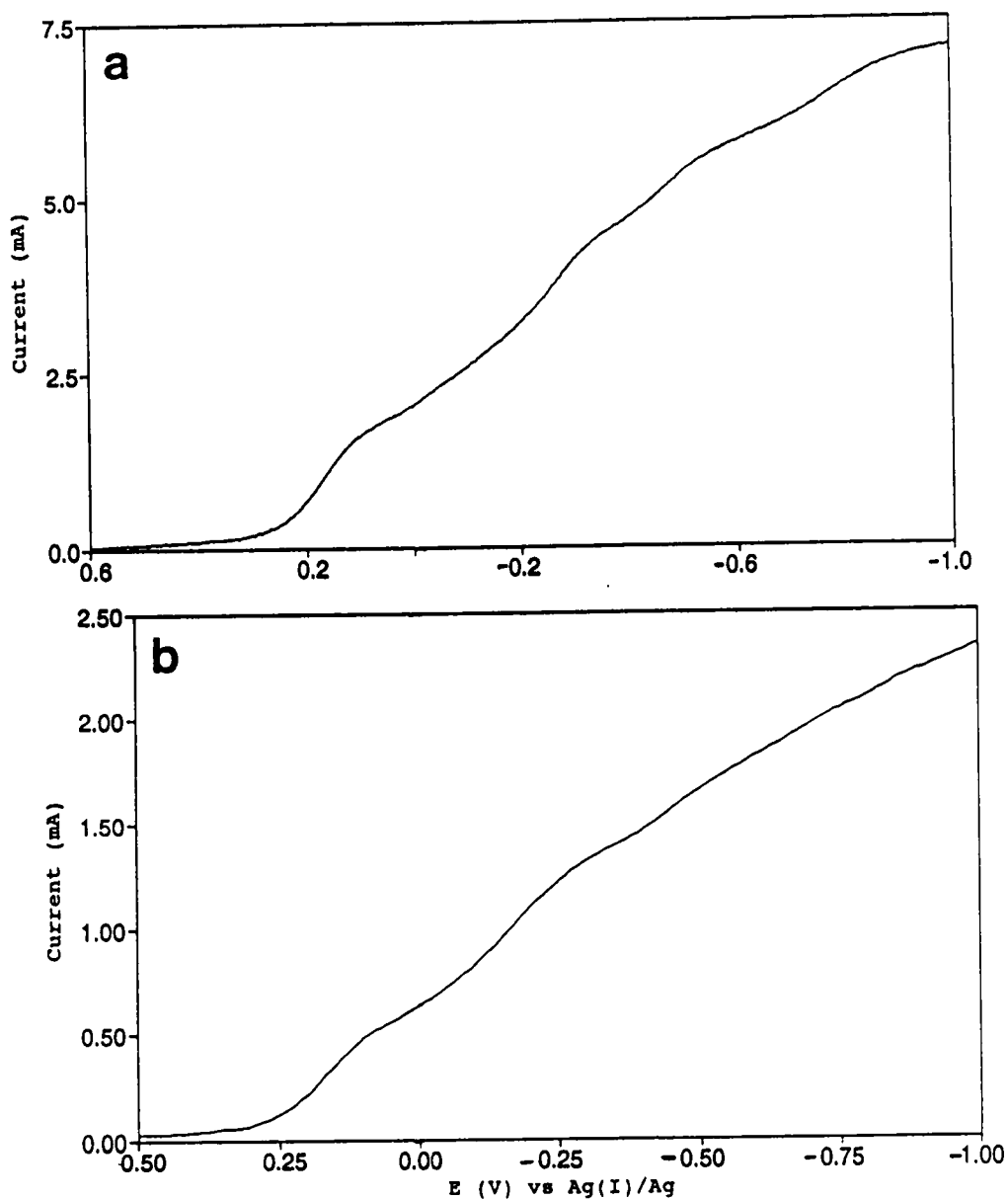


Figure 40. Full-range NPV curves obtained using a 1.88×10^{-2} M NbCl_5 solution in SCA. Working electrode was a W wire, $T = 178^\circ\text{C}$.

- a. Scan rate = 5 mV/s, step time = 5 s, pulse width = 0.05 s
- b. Scan rate = 1 mV/s, step time = 10 s, pulse width = 1 s

analysis. Very little can be said about the NPV's in Figure 40; indeed, it is difficult even to determine the number of reduction steps present.

Derivative methods are often useful in resolving poorly defined waves such as those observed in Figure 40. The most common method for producing derivative (differential) normal pulse voltammograms (DNPV) is to plot the difference of the currents measured during two consecutive potential pulses vs the potential. The resultant waveform should be a symmetrical peak with a maximum near $E_{1/2}$. It is often necessary to utilize a large difference between the potential of one pulse and that of the consecutive pulse in order to maximize the signal-to-noise ratio. Alternatively, one can prepare DNPV's directly from NPV's by simply subtracting the current measured during one potential step (E_1) from that measured during a later (more negative) potential step (E_2). The resolution of the resulting DNPV depends upon the difference in potentials of consecutive pulses (defined as the scan increment or ΔE in the NPV); the height of the peaks produced depends upon the difference in the selected E_2 and E_1 . It is advantageous, then, to minimize the scan increment when conducting the NPV experiment, and to maximize ($E_2 - E_1$) when calculating the differential current.

Figure 41 shows the DNPV calculated from the data obtained in the NPV experiment which resulted in the 0.05 s pulse-width voltammogram shown in Figure 40 (p. 139). Four

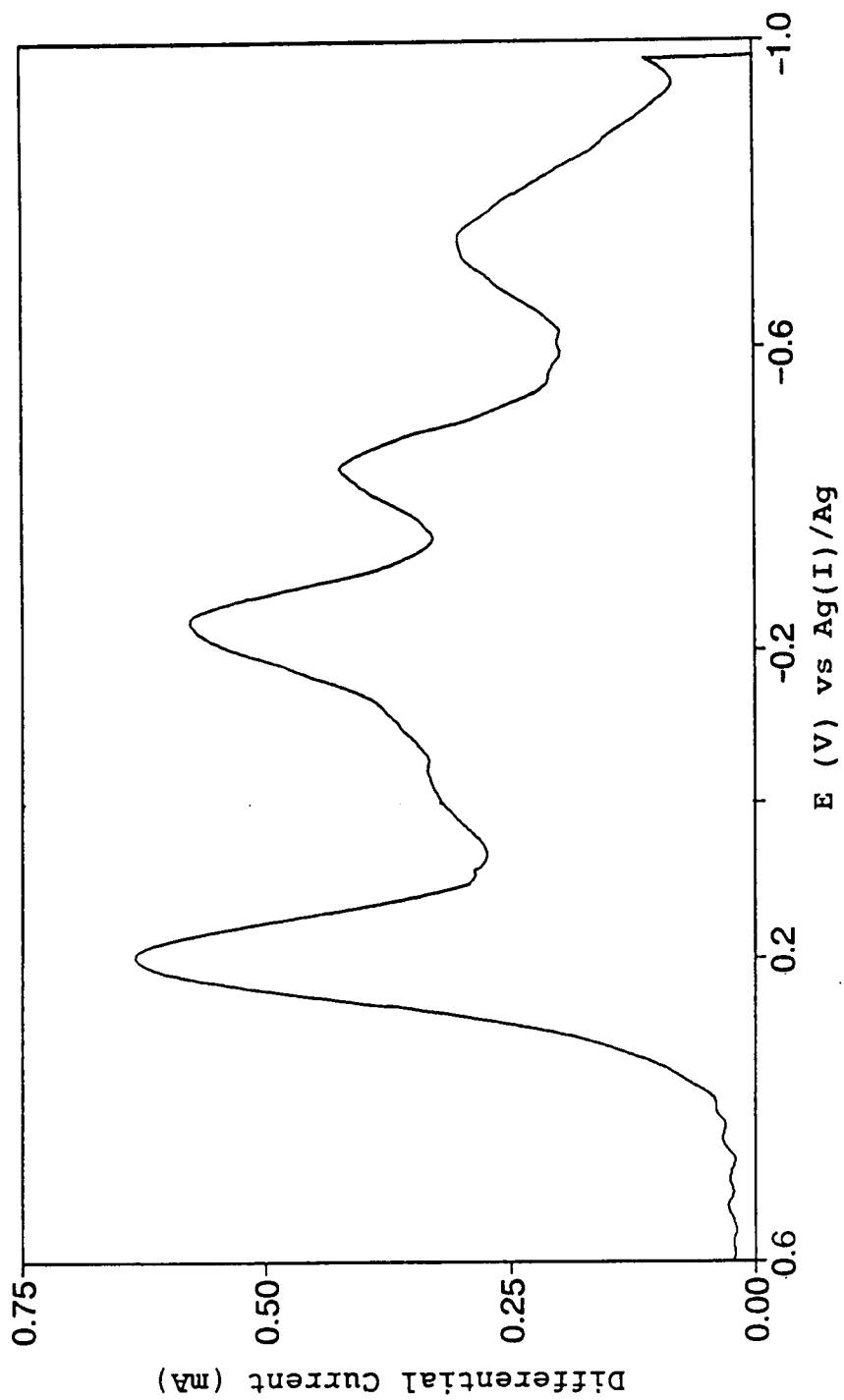


Figure 41. DNPV obtained from the NPV shown in Figure 40a.
($E_2 - E_1$) = 20 mV; other parameters are as given in Figure 40a.

waves are observed in Figure 41, with maxima at 0.18, -0.25, -0.44, and -0.78 V, respectively, which correspond to the four observed in CV (Fig. 32, p. 123). The shoulder to the second wave that was observed in CV (Figure 28, p. 115) can be seen in Figure 41, but it is quite small with respect to the four main waves; short pulse widths in NPV are analogous to fast scan rates in CV.

Figure 42 shows the DNPV derived from the NPV obtained at the longer pulse width (1 s) in Figure 40 (p. 139). Five peaks are seen; the first three have maxima at 0.17, -0.14, and -0.44 V, respectively. It is of interest to compare the appearance and the position of the second wave in Figures 41 and 42. In Figure 42, the wave is obviously broader than that in Figure 41; the peak potential of the second wave in Figure 42 is 0.11 V positive of that in Figure 41. It is reasonable to suggest that 1.0 second is sufficient time to allow the occurrence of the process which gave rise to the shoulder on the second wave in the CV; at small pulse widths (0.05 s), this process has less time to occur.

The DNPV shown in Figure 42 exhibits two additional waves with maxima at -0.61 and -0.81 V, respectively. The more negative of the two waves (-0.81 V) is likely identical to the fourth wave observed in CV (Figure 28, p. 115). The wave occurring at -0.61 V cannot be explained at this time.

4. Square Wave Voltammetry (SWV)

Advantages of SWV over many other voltammetric tech-

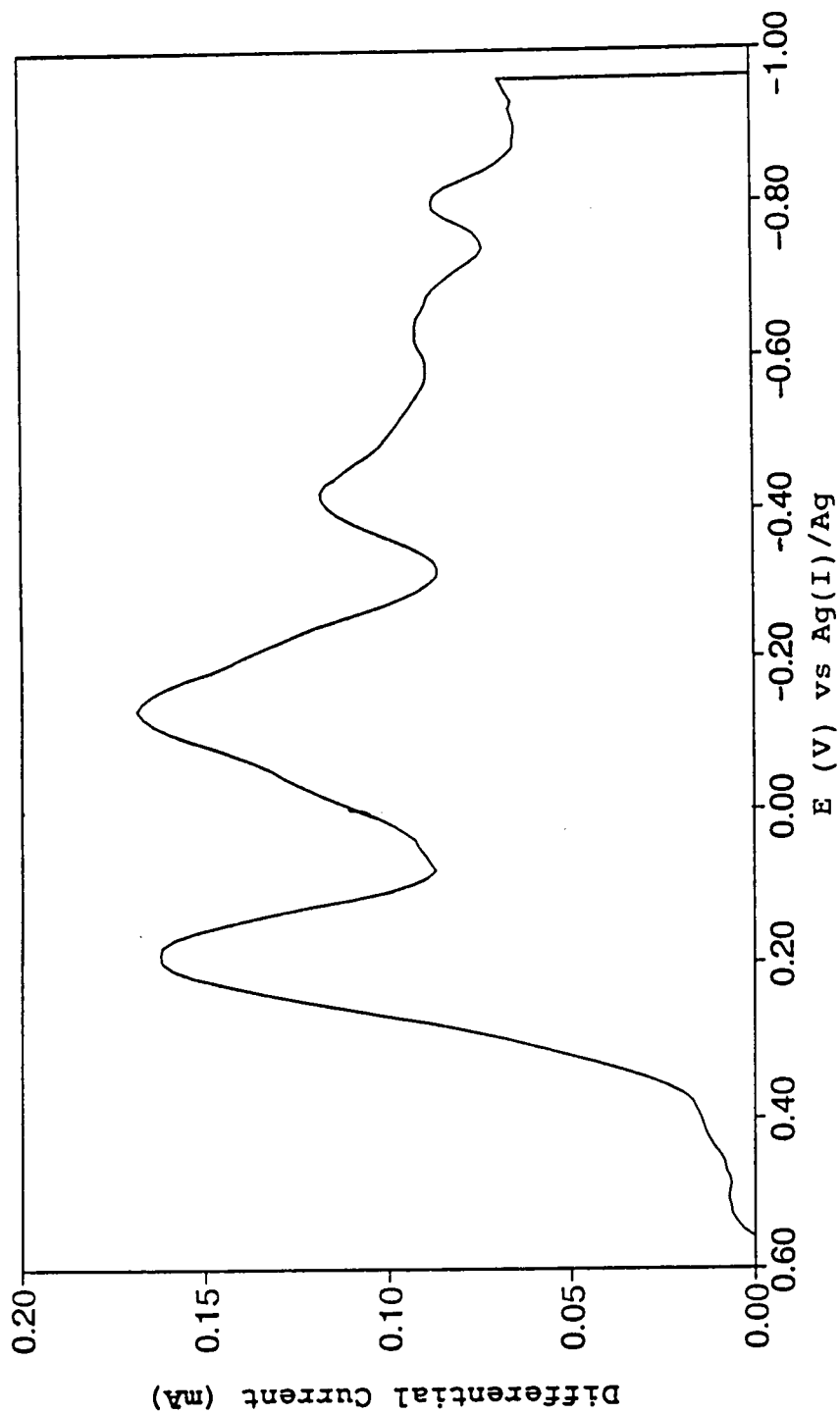


Figure 42. DNPV obtained from the NPV shown in Figure 40b.
 $(E_2 - E_1) = 20$ mV; other parameters are as given in Figure 40b.

niques include increased wave resolution, increased speed with which scans can be obtained, and the lack of problems which can develop when the potential remains negative of one or more reduction waves for extended periods of time (for instance, the cathodic wave that developed between the first and second wave during CV in concentrated solutions). In general, the peak current for a SWV wave is given by the function in Equation 40; i_p is the peak current, ω is the

$$i_p = [nFAC_o^*(\pi D_o)^{1/2}\omega^{1/2}] \psi_p \quad (40)$$

frequency, in hertz, and ψ_p is a dimensionless current function which depends on the pulse height and the magnitude of the square wave excitation signal.

Figure 43 shows a typical SWV obtained in the 29 mM solution at a frequency of 60 Hz and a pulse height of 25 mV (the wave at $\approx -0.1V$ may be due to residual oxide and/or due to the wave which appears in subsequent scans after scanning past the third wave; SWV is a more sensitive technique than CV); Table IX lists some pertinent voltammetric data. As in CV, four definite waves are present, with the second wave having a pre-wave shoulder. Also as in CV, this shoulder disappeared as the speed (frequency) of the experiment was increased. Figure 44 shows SWV's obtained using frequencies of 60, 120, 240 and 480 Hz; only the potential region from 0.0 to $-0.7 V$ (second and third waves) is shown to more

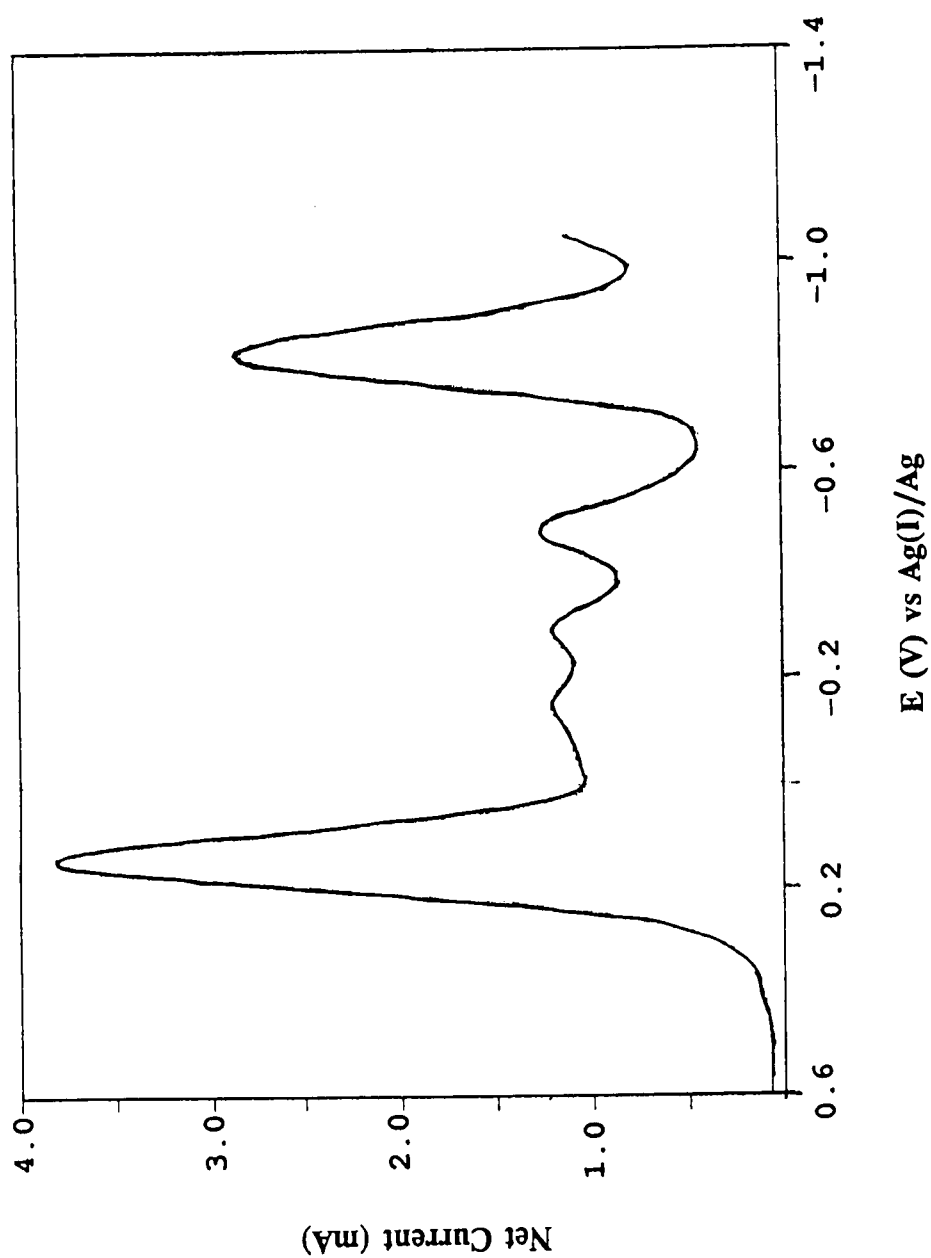


Figure 43. SWV obtained using a 2.91×10^{-2} M NbCl_5 solution in SCA. Working electrode was a W wire, frequency = 60 Hz, pulse height = 25 mV, $T = 178^\circ\text{C}$.

Table IX. Voltammetric Data for Four Main Waves in SWV.

Frequency (Hz)	$E_{p,1}$ (V)	$(E_{p,2})'$ (V)	$E_{p,2}$ (V)	$E_{p,3}$ (V)	$E_{p,4}$ (V)	$\frac{i_{p,2}}{i_{p,1}}$	$\frac{i_{p,3}}{i_{p,1}}$	$\frac{i_{p,4}}{i_{p,1}}$
60	0.172	-0.113	-0.266	-0.442	-0.791	-----	0.306	0.387
120	0.170	-0.126	-0.266	-0.458	-0.804	0.292	0.304	0.719
240	0.167	(-0.13)	-0.275	-0.464	-0.803	0.281	0.292	0.893
480	0.170	-----	-0.278	-0.479	-0.807	0.282	0.298	0.938

Data were extracted from SWV's obtained for a 2.91×10^{-2} M NbCl₅ solution in SCA at 178°C, using a tungsten working electrode.

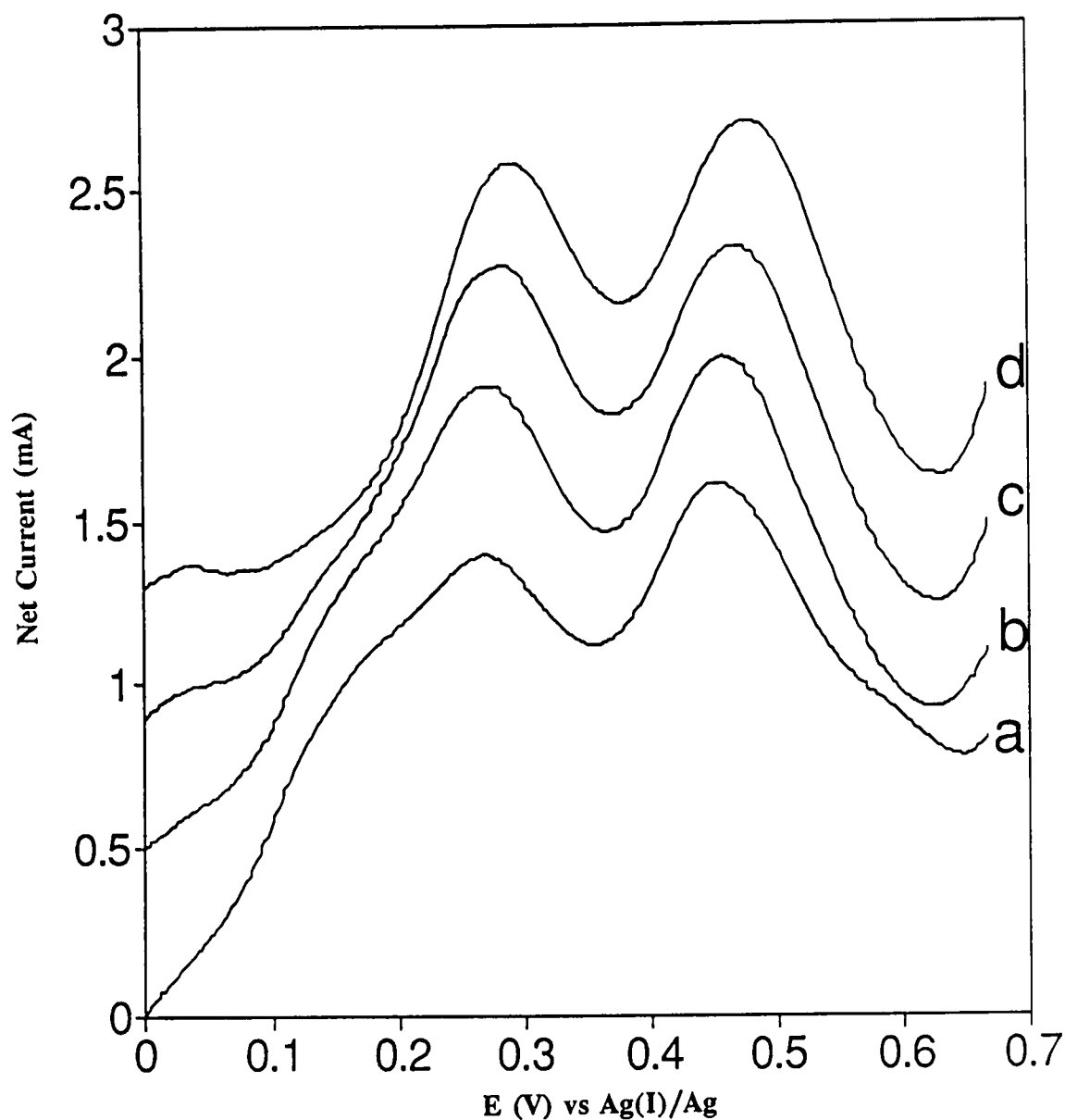


Figure 44. Detail of the region between 0.0 and -0.7 V for SWV's obtained for a 2.91×10^{-2} M solution of NbCl_5 in SCA. Working electrode was a W wire, $T = 178^\circ\text{C}$. In all cases, the pulse height was 25 mV.

a. Frequency = 60 Hz
b. Frequency = 120 Hz

c. Frequency = 240 Hz
d. Frequency = 480 Hz

clearly demonstrate the effect of frequency on the shoulder to the second wave. In Table IX, the parameters $i_{p,2}/i_{p,1}$, $i_{p,3}/i_{p,1}$, and $i_{p,4}/i_{p,1}$ give the ratio of the peak current of waves 2, 3, and 4, respectively, to that of wave 1. The approximate peak potentials for the shoulder of the second wave are given when possible in the column headed $(E_{p,2})'$.

It is clear that the peak potential for the first reduction wave remains constant with increasing frequency, as would be expected for a reversible process. All other peak potentials tend toward more negative values, just as in CV, but the shift is to a much lesser extent. Of particular interest are the last three columns. The values for $i_{p,2}/i_{p,1}$ and $i_{p,3}/i_{p,1}$ remain constant with changing frequency, but that for $i_{p,4}/i_{p,1}$ tends toward unity as the frequency is increased. Since the peak current of a SWV wave depends on D_o , n , and frequency, the ratio of peak heights can be considered to be a rough approximation of the relative number of electrons involved in each process, assuming other factors remain the same. If it is assumed that the first wave involves only one electron, then these ratios give an idea of the relative apparent number of electrons transferred, with consideration given, of course, to possible differences in reversibility, as well as other complications.

In considering reversibility, one must remember that the net current plotted in Figure 43 (p. 144) is actually the difference of the forward and reverse currents. It is

sometimes worthwhile to plot the forward and reverse currents directly, rather than their difference, in order to gain some insight into system characteristics. Figure 45 shows the plots of the forward and reverse currents for SWV's obtained using two different frequencies. These plots depict the changes in $i_{p,x}/i_{p,1}$ shown in Table IX (p. 145), with the relative intensities of the forward and reverse waves for peaks 2 and 3 remaining fairly constant with respect to those for peak 1, while the intensities of both the forward and reverse currents for wave 4 increase dramatically.

The SWV theory predicts (103) that the peak height should be linearly dependent upon the square root of the frequency; i.e., a plot of peak height vs. $\omega^{1/2}$ should be linear, and should have an intercept of zero. Figure 46 shows plots of i_p vs. $\omega^{1/2}$ for the four waves observed in Figures 43 (p. 144) and 45. The plots for waves 1, 2 and 3 are indeed linear, and have intercepts near zero; this is not the case for wave 4, probably due to the change in its relative peak height with frequency, as demonstrated in Table IX. The slopes of the plots for waves 1, 2, and 3 are 0.351, 0.099, and 0.102, respectively; normalized to the slope of the first wave (with the assumption that it involves a one-electron reduction process), these values are 1.00, 0.282, and 0.290, respectively. As with peak intensities, the relative magnitudes of the slopes of these

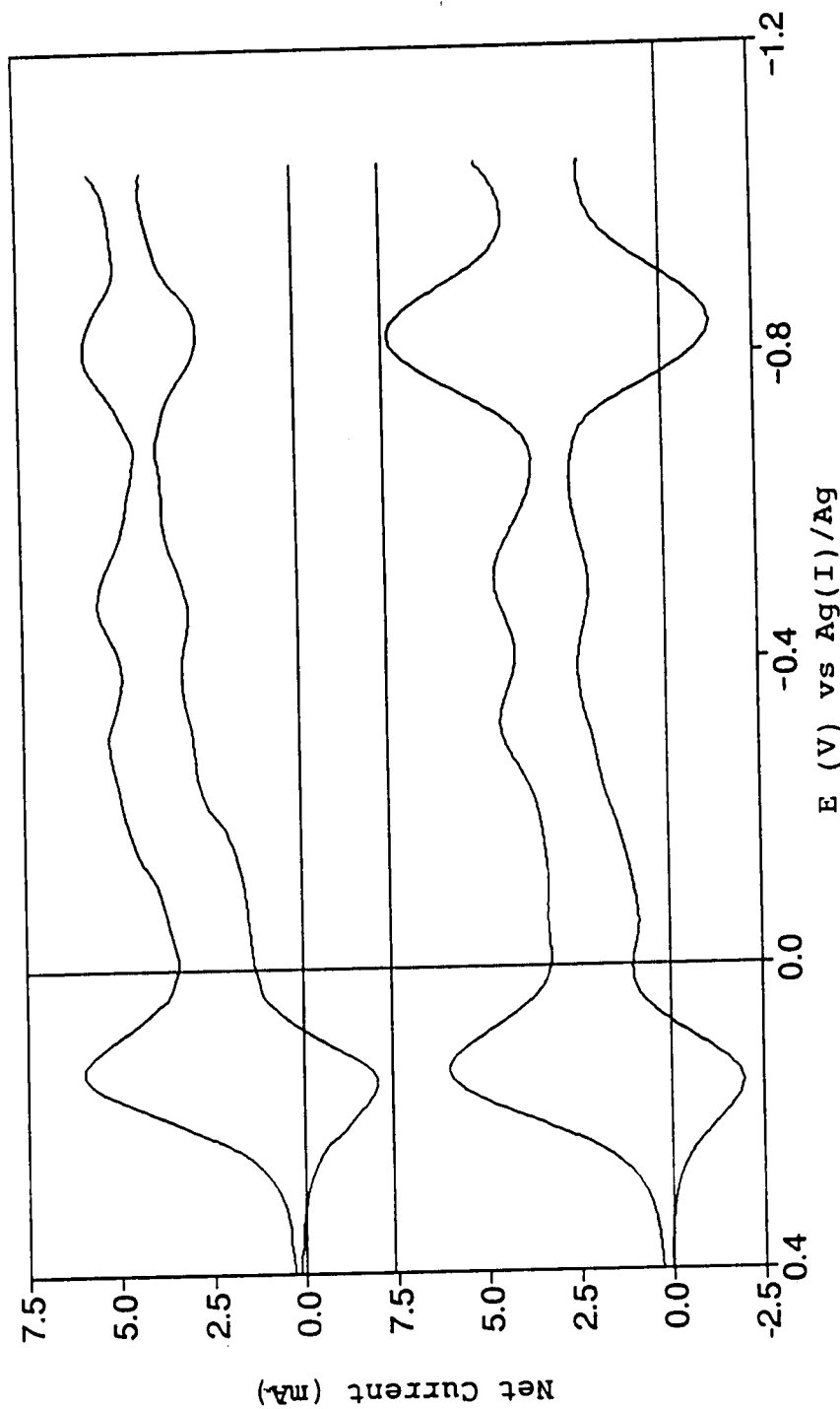


Figure 45. Demonstration of the variation in the forward and reverse currents from SWV as the frequency used in the experiment is altered. NbCl_5 concentration = $2.91 \times 10^{-2} \text{ M}$; working electrode was a W wire; $T = 178^\circ\text{C}$.

- a. Frequency = 60 Hz, pulse height = 25 mV
- b. Frequency = 480 Hz, pulse height = 25 mV

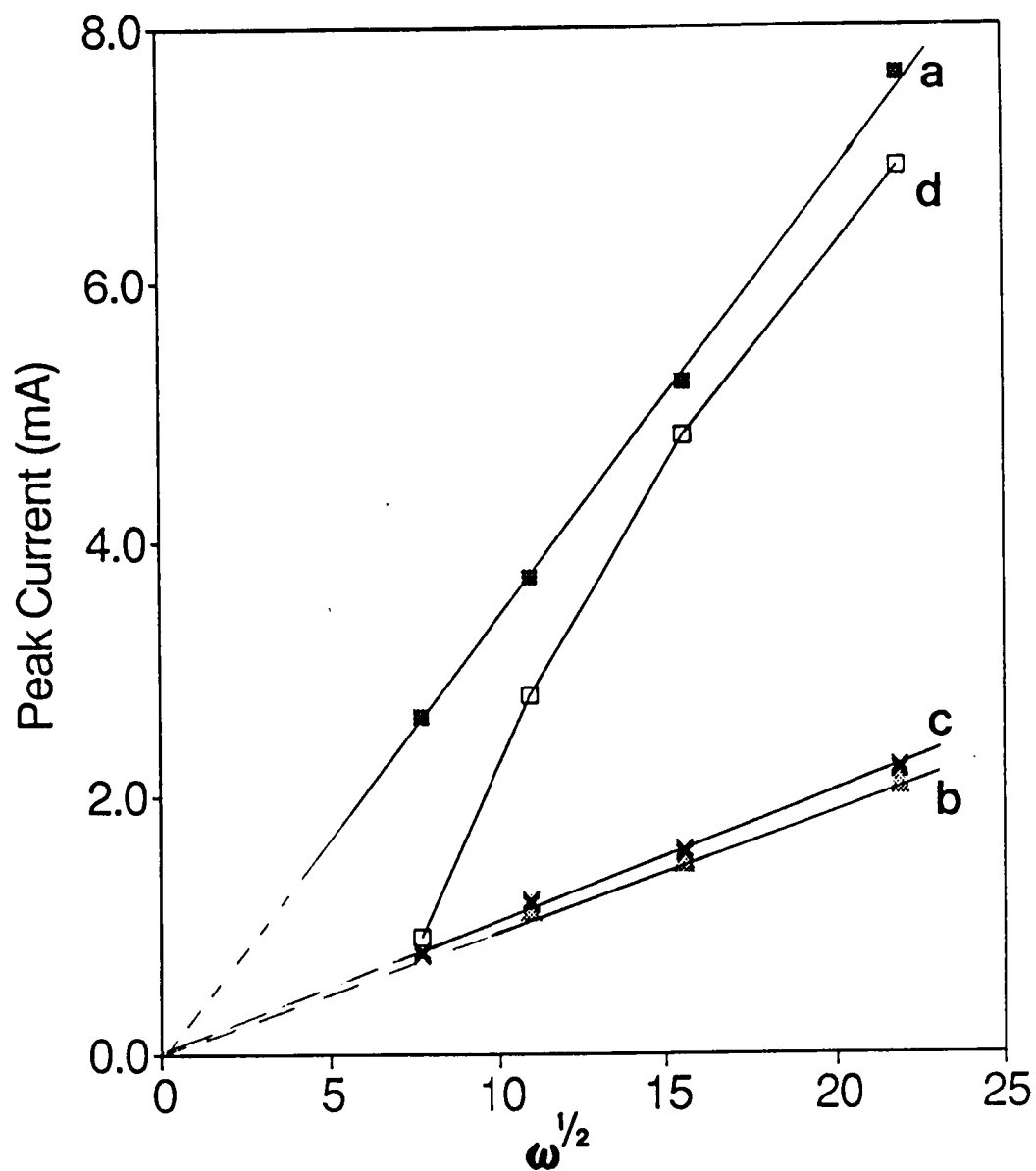


Figure 46. Plots of peak current vs. $\omega^{1/2}$ for the four primary waves in the SWV of NbCl_5 (2.91×10^{-2} M) in SCA. a. First, b. Second, c. Third, and d. Fourth wave

plots should be an indication of the relative apparent number of electrons involved in the redox processes, if only reversible processes are considered. In essence, the slopes are derived from the same data as those parameters given in Table IX (p. 145), so their ratios should be of the same order; such is the case.

5. Exhaustive Electrolysis (Constant Potential Coulometry)

One of the most definitive techniques for determining the number of electrons involved in a redox process is exhaustive electrolysis, in which a potential negative of the reduction wave of interest is applied to a working electrode of large surface area until the current decays to a small fraction of the initial current (107). It is important when doing this type of experiment to have good convection (stirring) to ensure thorough mixing of the solution as the electrolysis proceeds.

The first attempt to determine the n -value for the first wave in the reduction of NbCl_5 , gave incredible results. After many hours of electrolysis, the solution had not changed (in appearance, and by voltammetric analysis), but the equivalent of approximately 4 electrons per mole of Nb(V) had been passed. It was postulated that, while the Nb(V) was reduced at the working electrode, the counter electrode was producing Cl_2 (from the melt), which was diffusing through the frit separating the counter electrode

from the bulk solution and reacting with the reduced niobium species to produce Nb(V). This led to the realization that it is essential to use an aluminum counter electrode, separated from the bulk melt by a medium porosity frit, in exhaustive coulometry when working with the Nb(V) system; during the coulometric experiment, the aluminum is oxidized, rather than chloride, resulting in a slight change in the melt composition, but preventing the formation of chlorine.

Subsequent electrolysis experiments met with more success. When a potential of 0.05 V (corrected to the Ag(I)/Ag reference) was applied to a melt containing 2.97×10^{-4} moles of NbCl₅ (expected charge of 28.63 C for $n=1$), the charge passed, after the current had decayed to less than 1% of the initial current, was determined to be 27.89 C. From these data, an n -value of 0.974 was calculated, indicating that the first wave in the reduction of Nb(V) in SCA involves one electron. It should be noted that some portions of the aluminum counter and quasi-reference electrodes above the level of the melt were considerably blackened, presumably by the reaction with gas-phase NbCl₅; this reaction could partially account for the fact that the calculated n -value was slightly less than unity.

Upon completion of the electrolysis experiment, the solution was observed to be brown in color, with some small amount of particulate matter. As the melt cooled, the color

changed slowly, and it became deep purple on reaching room temperature.

A UV-visible spectrum of the resulting solution was obtained at 175°C, and is shown in Figure 47; maxima were observed at 206, 230, 252, 282, and 328 nm. These values are in excellent agreement with those reported by McCurry (75) for Nb(IV). It is reasonable to state that the product of the electrolysis at the first reduction wave is Nb(IV).

The next electrolysis was carried out at a potential (-0.15 V, corrected to the Ag(I)/Ag reference) that was estimated to be into the rising edge of the shoulder to wave 2 (Figs. 28, p. 115, and 42, p. 142). A solution containing 1.701×10^{-4} moles of NbCl₅ was electrolyzed until the current had dropped to below 1% of the initial current. The total number of coulombs passed was found to be 23.98, giving the total n-value for this prewave of 1.46. The solution was brownish-yellow after electrolysis, and attained a deep green color upon cooling to room temperature.

An electrolysis was carried out in a solution containing 1.93×10^{-4} moles of NbCl₅ at a potential (-0.33 V, corrected to the Ag(I)/Ag reference) just past the second wave in the voltammogram. The charge passed was found to be 40.76, giving the total n-value of 2.19. The solution after electrolysis was brown, with some fine dark particulate matter present; upon cooling, the solution was light brown.

An electrolysis was carried out in a solution

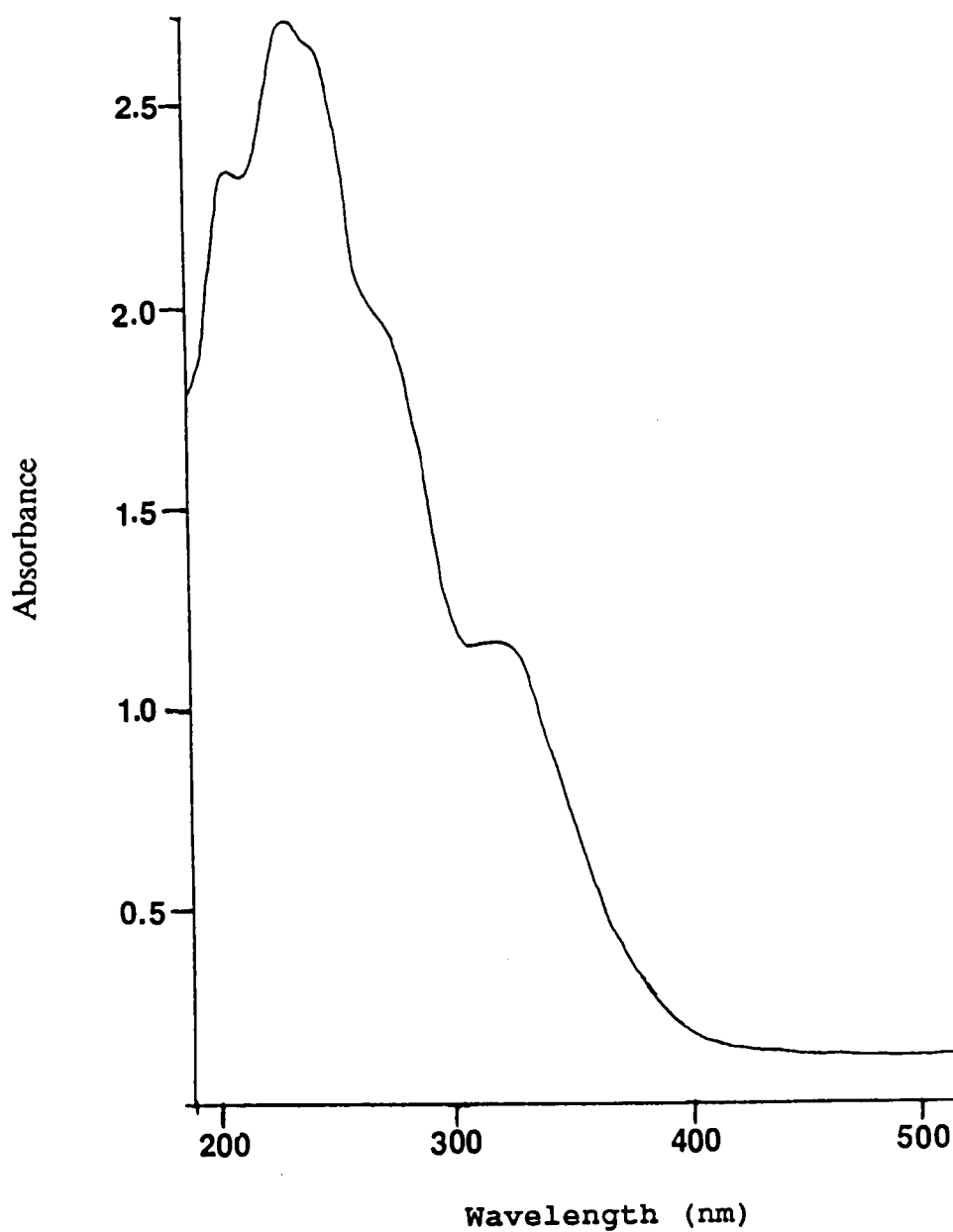


Figure 47. UV-visible spectrum obtained after exhaustive electrolysis at a potential of 0.05 V (after the first wave in the CV) in a SCA solution containing 2.97×10^{-4} moles of Nb(V). The experimental temperature was 178°C, and the spectrum was obtained at 175°C.

containing 1.69×10^{-4} moles of NbCl_5 at a potential (-0.54 V, corrected to the $\text{Ag(I)}/\text{Ag}$ reference) just past the third wave in the voltammogram. The charge passed after the current had dropped to below 1% of the initial current was determined to be 39.82, giving the total n -value for this wave of 2.44.

It should be noted that in every electrolysis experiment, the aluminum electrodes became blackened. Although these electrodes were separated from the bulk melt using medium porosity frits, it was necessary to have a small hole (≈ 4 mm diameter) in the counter and reference electrode compartments, above the melt level, for pressure equilibration. It was in the region of this hole that blackening of the electrode occurred. It must be considered that this reaction diminished the total amount of NbCl_5 available for experimental evaluation of the n -values.

6. Discussion of Results

a. First wave. No doubt remains that the first wave in the reduction of NbCl_5 in SCA at 178°C is essentially a reversible one-electron charge transfer process. Values for n near unity were determined by CV (0.93, average), NPV (0.96, average), and exhaustive electrolysis (0.974). Reversibility was verified by the following facts (types of experiments are given in parentheses):

- i. a plot of i_p vs. $v^{\frac{1}{2}}$ was linear and had a zero intercept (CV);
- ii. a plot of i_p vs. $[\text{NbCl}_5]$ was linear and had a zero intercept (CV);
- iii. plots of E vs. $\ln[(i_d - i)/i]$ were linear (NPV);
- iv. plots of current vs. $t^{-\frac{1}{2}}$ were linear, and had zero intercepts (CA);
- v. plots of Q_c vs. $t^{\frac{1}{2}}$ were linear (CC);
- vi. a plot of i_p vs. $\omega^{\frac{1}{2}}$ was linear and had a zero intercept (SWV).

The diffusion coefficient for the Nb(V) species in SCA at 178°C was determined by CV, CA, and CC experiments to be $1.87 \times 10^{-6} \text{ cm}^2/\text{s}$ (average). The $E_{1/2}$ of the redox process was found to be 0.167 V (average) vs. Ag(I)/Ag via CV, SWV and NPV experiments.

Indications of non-ideality were found, and are discussed below; these complications appeared to be rather small on the voltammetric time scale, but might have become more significant on the coulometric time scale.

b. Second wave and the preceding shoulder.

Unfortunately, studies as comprehensive as those conducted on the first wave could not be extended to the more negative waves due to their generally lower intensity and broader aspect. However, several characteristics were noted. In the voltammetric (CV, NPV, DNPV, and SWV) experiments, the

shoulder was most prominent at long times (slow scan rate, long pulse widths, and low frequencies); it tended to disappear entirely at very short times or in fast experiments. This behavior indicates that the shoulder was due to the reduction of some species being generated by a rather slow chemical reaction following the first reduction. The fact that there was no gross effect on the characteristics of the first reduction wave indicates that the chemical reaction was slow, and did not proceed to a great extent. It was possible, however, to perform exhaustive coulometry at the rising portion of the shoulder and determine a cumulative n -value of 1.46 electrons; subtracting the one electron due to the first reduction yields an n -value for this reduction of 0.46 electrons. Analysis of the voltammetric data from the first reduction wave using sensitive methods revealed that some complications were involved. These analyses indicated that the following chemical reaction involved the regeneration of the initial redox species (Nb(V) , in this case). Similar phenomena were observed by Mamantov and coworkers for the oxidation of U(IV) in $\text{LiF-Bef}_2\text{-ZrF}_4$ (108) and the reduction of U(IV) in FLiNaK (109). These workers proposed schemes involving the disproportionation of the redox product (U(V) and U(III) , respectively) to regenerate U(IV) .

Studies of the second wave were hindered by the appearance of the shoulder discussed above, as well as the close proximity of the third wave, and even by the appear-

ance of a new wave (see pp. 127-129) at high concentration. Some general tendencies were noted, however. The peak potential tended to shift to more negative values as the rate of the experiment (CV, SWV, DNPV) increased; this may have been due in part to the diminishing effect of the shoulder, which would have caused an apparent shift in the peak potential of the second wave to more negative values; the additive effect of two overlapping waves tends to shift the peak potentials of both waves toward a median value. Also, exhaustive electrolysis at the potential corresponding to the wave provided a value for n of 2.19 electrons cumulative from the initial potential. When the potential was stepped past the shoulder and into the second wave, the process which gave rise to the shoulder would have little effect if it were due to the product of a slow chemical reaction. Therefore, it is likely that the n -value for the second wave is 1.19 electrons. It should be stressed again, however, that the time scale of the coulometric experiments was as much as three orders of magnitude greater than that of the voltammetric experiments. This could be an important factor in the differences observed between the relative n -values obtained for the first and second waves in the two types of experiments.

c. Third wave. The third wave suffered from analysis problems similar to those discussed above for the second wave. In brief, it was noted that the peak potential for

this wave tended towards more negative values as the experiment rate increased; this was less obvious in the SWV studies than in the CV studies. Exhaustive electrolysis yielded a cumulative n-value of 2.44 electrons for this wave, which gives a value of 0.25 electrons for the wave alone.

d. Fourth wave. The fourth wave in the electrochemical reduction of Nb(V) in SCA proved to be the most difficult to analyze. Its appearance in CV was generally broad and small, making it difficult to even measure the proper peak potential, much less any other voltammetric parameters. In SWV, the wave appeared to have some reversible character, especially at high frequencies, when the intensity of this wave tended to be higher than that of the first wave. Results from NPV were not useful, and those from DNPV were unusual in that two waves were observed in the position of the fourth wave at long pulse times. It is possible that this was an anomaly caused by the derivative method used. As mentioned above, time in an experiment is an important factor. It is quite possible that the film formed on the electrode surface could have caused some passivation over the long experimental times, whereas at short times (high frequencies), passivation did not occur.

e. Proposed reaction sequence. The simplest case, that observed at short times and fast experiment rates, will

be discussed first. Under such conditions, only four reduction waves were observed in CV, DNPV and SWV. Based on the results presented and discussed in this chapter and previous results from the literature cited below, the reaction sequence for the reduction of NbCl_5 in SCA at 178°C is proposed to be as given in Equations 41-44.



Since the n-value of the first wave was found definitively to be unity, it follows that the first step (E1) in the reduction mechanism for NbCl_5 is the reduction of Nb^{5+} to Nb^{4+} .

An n-value of 1.19 was obtained by exhaustive coulometry for the second wave. The reduction equation proposed above for this step (E2) would be expected to exhibit an n-value of 1.33 per niobium atom. However, as noted previously, some reaction of NbCl_5 with the aluminum electrodes present in the cell was suggested, which would effectively diminish the concentration. Furthermore, the species Nb_3Cl_8 is known and has been characterized (96), and evidence of its existence in chloroaluminate melts has been reported (75,104,110).

The total number of electrons passed per mole of NbCl_5

in the electrolysis at the third wave was determined to be 2.44. The difference between this value and that found for the second wave is 0.25 electrons. The reduction of Nb_3^{8+} to Nb_6^{15+} should require 0.5 electrons; the direct reduction of Nb(V) to Nb_6^{15+} would require 2.5 electrons per mole of NbCl_5 in solution, which compares favorably with the value of 2.44 obtained. The substance $\text{Nb}_6\text{Cl}_{15}$ is known and has been characterized (96).

No direct evidence for the reduction represented in equation E4 was found; the apparent n-value could not be reliably determined in any case, but an apparent n-value close to unity can be inferred from the SWV data (Table IX, p. 145) at high frequencies. As for the third wave, the fourth wave results in the deposit of a film on the electrode surface. The identity of this film could not be determined, but it is unlikely that it is metallic Nb, as indicated by the lack of any definitive lines in the X-ray diffraction pattern. It is certain that a reduction takes place, and no niobium chloride species of lower oxidation state than 2.33 have been described in reliable reports (96). It is postulated, based on the assumption that the preceding steps occur (Equations 41-43), that the product of this reduction step is a film of $\text{Nb}_6\text{Cl}_{14}$. It should be noted, however, that no direct correlation between the fourth reduction wave and any of the preceding waves was

observed. In order to determine the product of this reduction process, further experimentation is required.

At long times, or slow experiment rates, an additional wave was observed as a shoulder to the second wave. Some of the voltammetric results suggest that the product of the first reduction undergoes some chemical reaction to regenerate the initial species (although the extent of this reaction must be small on the voltammetric time-scale, since no gross effects were seen); review section B.1, pp. 120 - 125 for details. McCurry (75) suggested that solutions of Nb^{4+} undergo disproportionation to Nb^{3+} and Nb^{5+} at temperatures above 200°C . From the results described above for the first wave, it is quite certain that Nb^{4+} was produced during the first reduction wave, and it is quite possible that it disproportionated to Nb^{3+} (and Nb^{5+} , of course), although the rate of the disproportionation would be expected to be slower at 178°C than at 200°C ; the effect of the process complicating the first wave was quite small, as would be expected from a slow following chemical reaction.

If the Nb^{3+} produced by Nb^{4+} disproportionation subsequently underwent a higher order reduction to a stable cluster species (Nb_3^{8+}), involving a net of $1/3$ electrons per atom of Nb^{3+} , then the n -value of 0.46 obtained by coulometry for this step would not be unreasonable. The number of electrons passed for the reduction of Nb^{3+} would be

expected to be 0.33; the excess charge likely accumulated due to reduction in the second wave, since it was impossible to truly isolate the shoulder from this wave. Such a proposal is not unreasonable. Studies involving the formation of subvalent niobium species in chloride media by reduction of Nb(V) (64) and anodization of niobium metal (60,62) indicated that the species produced had a valence of less than 3; the studies by Suzuki and coworkers (60,62) indicated that the predominant species was Nb_3Cl_8 . If Nb^{3+} were produced by disproportionation of Nb(IV), and it were less stable than Nb_3^{8+} , then it would be feasible that the reduction of Nb^{3+} would occur at a potential more positive than that of Nb_3^{8+} . Furthermore, a close inspection of Figure 44 (p. 146) shows that the relative peak intensity of the third wave does not vary with the speed of the experiment (frequency, in this case), while that of the second wave increases as the effect of the shoulder is diminished.

It is possible, then, that the reaction which gives rise to the shoulder competes for reactant with that which gives rise to the second wave, but that the products of the reactions are identical; this product is further reduced in the third wave. Based on these criteria, the steps given in equations (45) and (46) are proposed to occur between those



given in equations (41) and (42), at long experimental times.

C. Studies of the Electrochemistry of Nb(V) in SCA and SFCA at Elevated Temperatures

One of the goals of the research dealing with the study of the electrochemical behavior of Nb(V) in SCA and SFCA melts was to determine the feasibility of using these melts in the deposition of niobium metal. Previous studies (74-76) indicated that at low temperature ($<300^{\circ}\text{C}$), metal was not produced when Nb(V) was reduced in SCA melts due to the formation of stable niobium chloride clusters. Results reported in this text support that conclusion. However, attempts to electrodeposit niobium in chloroaluminates at higher temperatures have not been reported. This section deals with the studies of the electrochemical behavior of Nb(V) in SCA and SFCA melts, and attempts to electrodeposit niobium in these melts, at elevated temperatures.

1. Effect of Temperature on the Reduction of Nb(V) in SCA

Studies on the electrochemistry of Nb(V) in SCA were conducted in the temperature range of 160°C to 500°C . What follows is a brief, semi-quantitative description of the changes observed in the CV as temperature was increased.

Figures 48 and 49 show CV's obtained for a 32 mM solution of NbCl_5 in SCA at 160 and 240°C , respectively. It

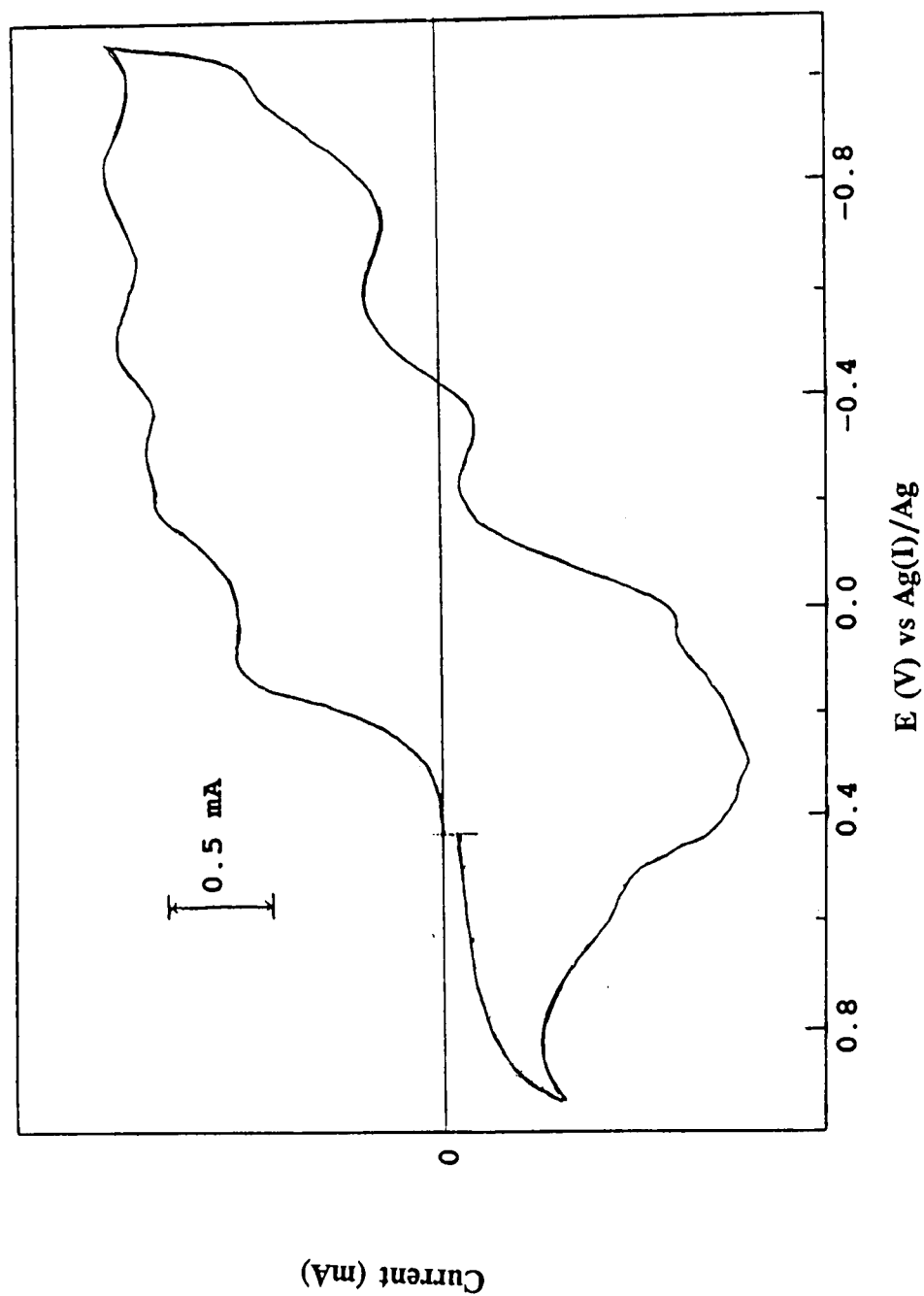


Figure 48. CV obtained in a 3.2×10^{-2} M solution of NbCl_5 in SCA at a temperature of 160°C . Working electrode was Pt wire, scan rate = 0.1 V/s .

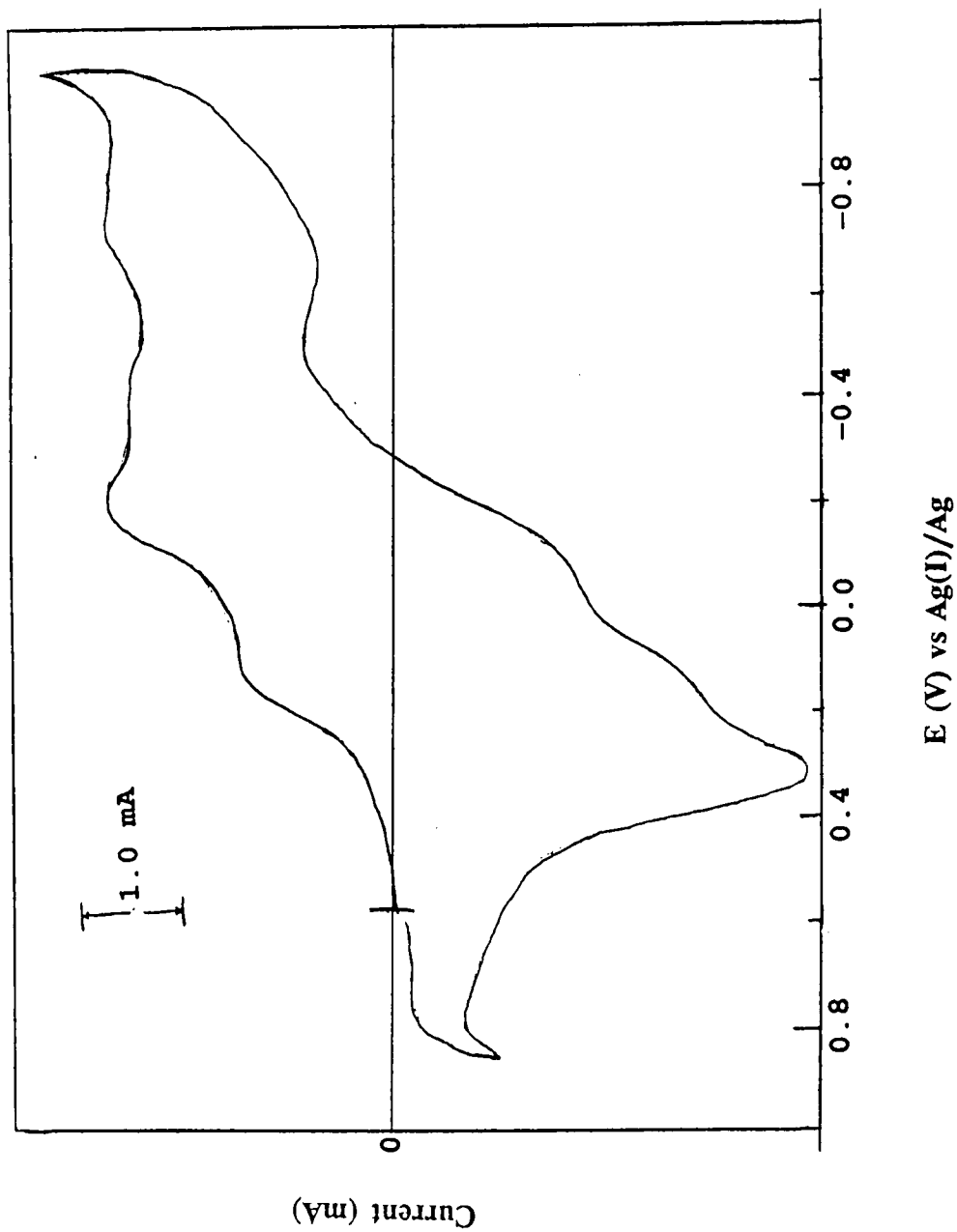


Figure 49. CV obtained for a 3.2×10^{-2} M solution of NbCl_5 in SCA at 240°C . Working electrode was a Pt wire, scan rate = 0.1 V/s .

is apparent that the shoulder that precedes the second wave in the CV at low temperature becomes more prevalent at higher temperatures, to the point that it masks the appearance of the second wave. This observation tends to support the proposed additional steps given in equations (45) and (46); the disproportionation of Nb(IV) would be expected to increase at higher temperatures, due to the greater volatility of NbCl₅ at higher temperatures.

Table X lists the peak potentials of the waves observed in the CV as the temperature was increased. Some general trends can be distinguished. As the temperature was increased from 160 to 240°C, E₁ (the peak potential for the first wave) shifted to more negative values, while E₃ and E₄ shifted to more positive values. At temperatures above 200°C, it became impossible to distinguish separate waves for the second wave and the preceding shoulder. Furthermore, at 325°C, no distinction between the second, third, and fourth waves could be seen; rather, only a large, broad wave was seen. The first wave ceased to be peak-shaped at temperatures above 325°C, as it became simply a broad, low plateau preceding the larger wave into which the second, third, and fourth wave had merged.

At temperatures $\geq 325^\circ\text{C}$, a new wave was observed near the cathodic limit of the melt. At temperatures below 400°C, this wave was generally difficult to resolve from the melt limit, but it became markedly observable above 400°C

Table X. Peak Potentials^a for CV Waves at Various Temperatures.

Temperature (°C)	$E_{p,1}^c$	$(E_{p,2}^c)^b$	$E_{p,2}^c$	$E_{p,3}^c$	$E_{p,4}^c$	$E_{p,5}^c$
160	0.11	-0.18	-0.29	-0.49	-0.80	-----
180	0.13	-0.15	-0.24	-0.44	-0.78	-----
200	0.13	---->	-0.17 <---- ^c	-0.42	-0.75	-----
240	0.14		-0.19	(-0.40) ^d	-0.75	-----
280	0.10	(-0.20)		---->(-0.45) <----		
325	0.88		----->	-0.50 <-----		(-1.2)
375	----- ^e			≈-0.30		-1.2
425				≈-0.30		-1.13
460				≈-0.26		-1.04
500				≈-0.25		-0.98

- a. All potentials given in V vs. the Ag(I)/Ag reference.
- b. This column refers to the shoulder preceding the second wave.
- c. Arrows indicate a merging of two or more waves into one.
- d. Parentheses indicate that the given value is approximate due to difficulty in determining peak potential.
- e. Could not determine a peak potential. After 325°C, the initial wave appeared only as a broad, flat plateau.

(Figure 50). This new wave was much larger than any observed in the more anodic region of the CV, and it tended to shift to more positive values with increasing temperature.

Figure 50 shows a CV obtained at a temperature of 500°C. The primary features are a broad wave at approximately -0.25 V, and a large, sharper wave nearer the cathodic melt limit (-0.98 V). Associated with the reduction wave at -0.25 V is an anodic wave observed at approximately 0.22 V. The two anodic waves observed at -0.92 and -0.12 V are associated with the more cathodic reduction wave.

When the electrode was observed during the process of a slow linear scan at 500°C, a black film was clearly seen to form on its surface as the potential was swept past -0.25 V, where the first wave appeared in Figure 50. No observable changes occurred on the electrode surface upon reaching the wave at -0.98 V, but "refractive" eddies appeared in the area of the electrode at that potential. During the reverse (anodic) scan, the film was removed upon reaching the most positive anodic wave (0.22 V). Using Equation 33 (p. 116) to determine the number of electrons associated with the reduction waves at -0.25 and -0.98 V gave n -values of 3.25 and 2.1, respectively. One might be tempted, based on these values, to assign a reaction sequence involving a reduction to Nb(II), followed by reduction to Nb metal. However, these are clearly not simple waves, and it is more likely that these values are simply erroneous, and result from any

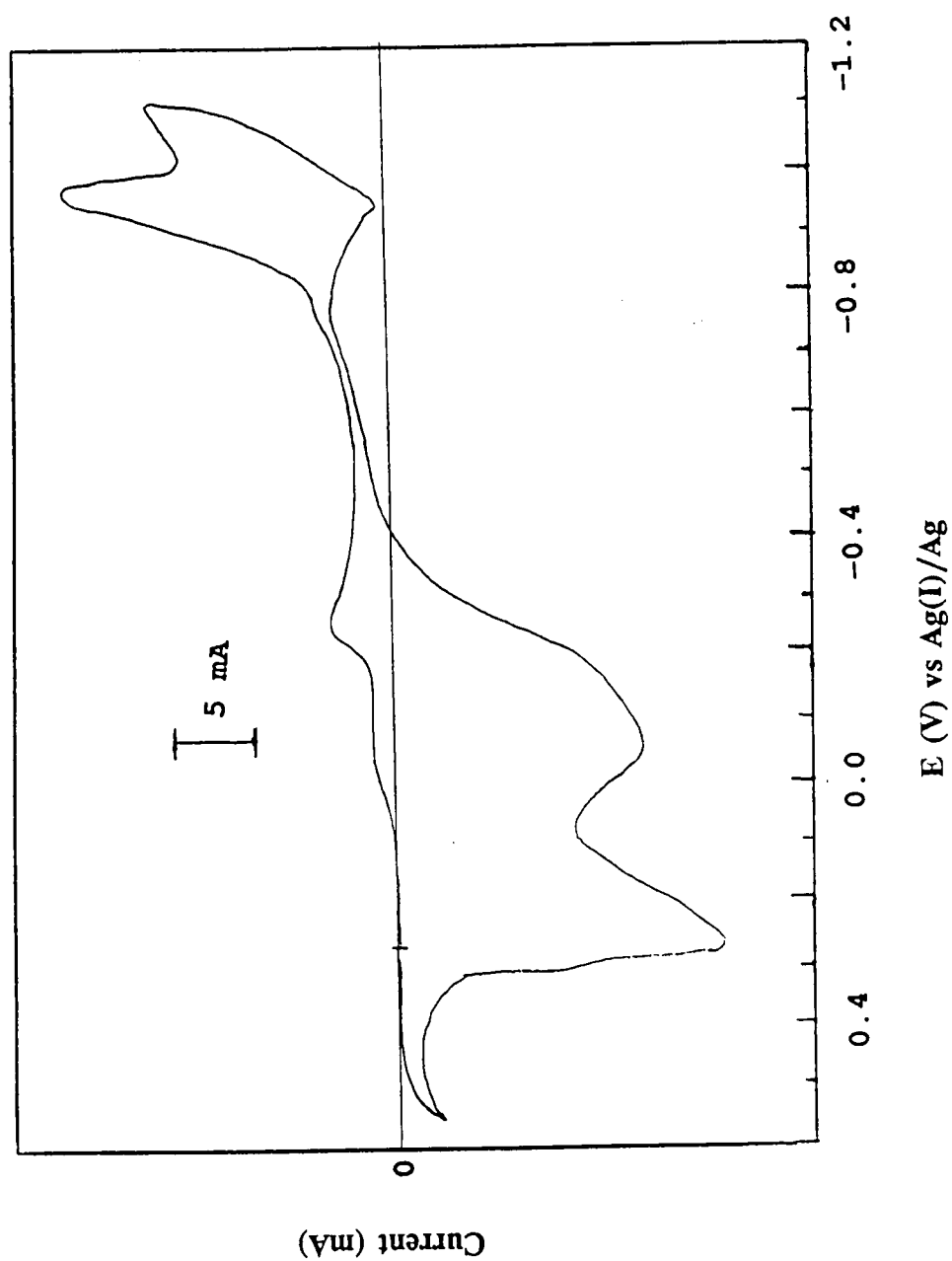


Figure 50. CV obtained for a 3.2×10^{-2} M NbCl_5 solution in SCA at 500°C . Working electrode was a W wire; scan rate was 0.1 V/s.

number of complications that might occur at these elevated temperatures (for instance, the formation of the film during the first reduction step).

2. Effect of Added Fluoride on the Electrochemistry of Nb(V)

Briefly stated, no significant differences were observed between CV's obtained from SCFA and SCA solutions of Nb(V). Figure 51 shows a CV obtained at 500°C in a 34 mM solution of NbCl₅ in SFCA (R = F/Al ratio = 0.11). The general appearance of the CV is very similar to that observed at the same temperature in SCA (Figure 50, p. 170). Two main reduction waves are seen at -0.27 and -0.97 V. As in the SCA melt, a film was formed on the electrode surface at the first reduction wave, and no changes in the appearance of the electrode surface were observed upon reaching the second wave. The film disappeared during the anodic scan after reaching the most positive anodic wave. There is clearly a difference in the behavior observed in the two melts during the anodic sweep, however.

3. Constant Current Electrolysis of Nb(V) in SCA and SFCA

A total of 26 experiments were conducted in attempts to produce niobium metal by constant current electrolysis of Nb(V) solution in SCA and SFCA melts (see Table XI). In these experiments, several parameters were varied, including the temperature, the Nb(V) concentration, the fluoride con-

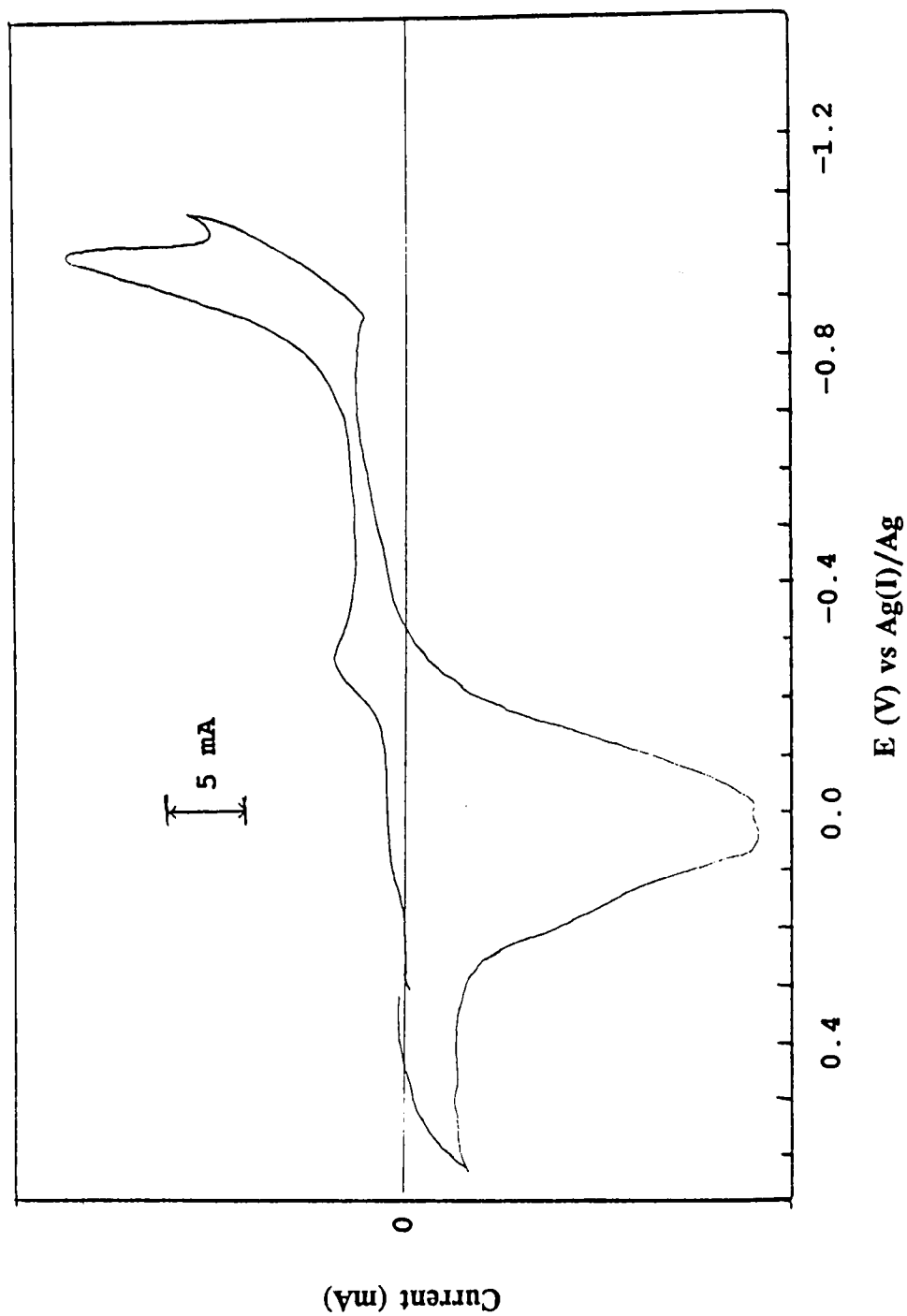


Figure 51. CV obtained for a 3.4×10^{-2} M NbCl_5 solution in SFCA ($R=0.11$) at 500°C . Working electrode was a W wire; scan rate was 0.1 V/s .

Table XI. Summary of Electrolysis Experiments.

C _{Nb} (V) (mole%)	R	T (°C)	Current		Time (min)	Results	Comments
			Density (mA/cm ²)				
12.5	0.99	625	11		12	none	Electrode lead "burned".
12.5	0.99	625	21		8	none	Electrode lead "burned".
12.5	1.0	625	25		60	no metal	
12.5	1.0	625	50		120	no metal	
12.6	1.0	600	45c/130a		150	no metal	Pulsed between 45 mA/cm ² cathodic and 130 mA/cm ² anodic for 60 and 6 seconds, respectively.
12.6	1.0	600	80c/330a		60	no metal	Pulsed as above; electrode broke.
12.5	1.0	550	20c/40a		120	no metal	Pulsed for 20 and 2 seconds.
"	"	"	40c/80a		120	<u>METAL</u>	Pulsed for 20 and 2 seconds.
							Smooth deposit on Ni cathode, but little niobium metal (by ESCA).
12.5	1.0	550	80c/160a		120	<u>METAL</u>	Pulsed for 20 and 2 seconds.
							Coarse, granular deposit of niobium (by ESCA) intermixed with non-metal deposit. Ni cathode.
11.8	0.9	629	---		---	none	Cell broke on heating.
9.0	0.5	580	250c/500a		120	no metal	Pulsed for 65 and 10 seconds.

Table XI. (continued)

C _{Nb(V)} (mole%)	R	T (°C)	Current		Time (min)	Results	Comments
			Density (mA/cm ²)				
8.6	0.6	580	100c/200a		600	no metal	Pulsed for 55 and 5 seconds.
8.0	0	580	---		---	none	Cell broke on heating.
7.4	1.0	600	---		---	none	Cell broke on heating.
3.3	0.6	550	---		---	none	Cell broke on heating.
3.0	1.0	560	200c/350a		60	no metal	Pulsed for 55 and 5 seconds.
3.0	1.0	560	100		360	no metal	
2.8	1.0	650	50		120	no metal	
2.8	1.0	650	100		240	no metal	
2.8	1.0	600	400c/2000a		90	no metal	Pulsed for 60 and 1 seconds.
2.8	1.0	600	200c/2000a		60	no metal	Pulsed for 60 and 1 seconds.
2.6	0	550	40		900	<u>METAL</u>	Best deposit (by ESCA/X-ray). W cathode.
2.5	0.25	550	100		120	no metal	
2.5	0.25	550	50		240	<u>METAL</u>	Very small amount of Nb metal (by ESCA and X-Ray). W cathode.
2.5	0.25	655	50		180	<u>METAL</u>	Very little Nb (ESCA). W cathode.
2.5	0.25	655	25		240	<u>METAL</u>	Very little Nb (ESCA). W cathode.

Note: The designations "c" and "a" indicate the cathodic and anodic currents, respectively, involved in the pulse program applied.

the temperature, the Nb(V) concentration, the fluoride content of the melt, the current density, and the cathode substrate material. The range of parameters was by no means exhausted, and much work remains in this area before definitive results can be reported. Discussed here are simply some general observations made in the process of attempting to reduce Nb(V) to the metal. In all but a few cases, no metal was obtained, at least none that could be observed using ESCA and X-ray diffraction spectral analysis. In all cases, at the end of an experiment the cathode was found to be covered with a thick coating of undissolved, dark-green colored material.

Current densities ranging from 5 to 250 mA/cm² were studied, and in some cases, the current was pulsed between some cathodic value and some anodic value, in an attempt to minimize the accumulation of non-metallic deposit (probably cluster species) on the electrode surface. In general, the best results were obtained at current densities below 50 mA/cm²; in such cases, the coating of undissolved material on the cathode was thinner and more evenly distributed. These experiments seemed to indicate that, when niobium metal was produced at all, it was only at low current densities. Furthermore, the pulsed method had no effect. The fluoride content of the melt was varied from R=0 to R=1.0. The variation of R appeared to have no significant effect on deposition. In fact, the best deposit was obtained from a melt containing no fluoride. The temperature at which

deposition was attempted was varied from 525 to 625°C. It was apparent that temperatures higher than 525°C were needed to allow the deposition of niobium metal. No distinct advantage to using temperatures higher than 550°C was seen. In fact, if any temperature advantage could be inferred at all, it was that temperatures below 580°C were at least safer, as the cell was less likely to leak or break due to high vapor pressure.

Tungsten foil and nickel plates were used as cathode materials. The smoothest deposit was obtained using a tungsten foil cathode, but experiments that produced niobium were few enough that no exact conclusion concerning the cathode material can be put forth.

Table XII lists the d-spacings determined from an X-ray diffraction pattern for a niobium deposit on a tungsten cathode, obtained from a melt with no fluoride added (item 22 in Table XI, p. 174). Weak lines attributed to niobium metal are observed, but these are very small in comparison to the lines due to tungsten metal. The data presented in Table XII represent the best (smoothest, and apparently the thickest) deposit formed in these studies. It should be understood that, while a thick, coherent plate has not yet been obtained, the production of niobium metal from chloroaluminate melts is unprecedented. It is possible that if a more systematic approach were taken in future studies, higher quality deposits might be obtained.

Table XII. X-Ray Powder Patterns for Niobium Deposited on Tungsten and for Niobium and Tungsten Metals.

<u>Nb Deposit^a</u>			<u>Nb Metal^b</u>		<u>W Metal^c</u>	
(Å)	I ^{Nb}	I ^W	(Å)	I	(Å)	I
2.31	100	2	2.33	100		
2.21		3			2.24	100
1.64	25	1	1.65	20		
1.34	25	1	1.34	30		
1.28		100			1.30	23
0.84		8			0.85	18

The values for I given in the table are the relative intensities for the observed lines, with the strongest given an arbitrary value of 100. I^{Nb} is the relative intensity for the niobium lines, with the strongest niobium line given an arbitrary value of 100. I^W is the relative intensity for all lines, with the strongest tungsten line given an arbitrary value of 100.

- Niobium metal deposited on a tungsten cathode at 550°C by constant current electrolysis in a SCA melt containing 2.6 mole% Nb(V); a current density of 40 mA/cm² was applied for 15 hours.
- From the JCPDS file (16-1) for niobium metal.
- From the JCPDS file (4-806) for tungsten metal.

CHAPTER V

SUMMARY AND CONCLUSIONS

A. Studies on the Removal of Oxide Contamination from FLiNaK and SCA Molten Salts

The use of Ta(V) as a Raman probe ion for oxide contamination of FLiNaK melts has been briefly discussed. It was shown that the relative intensities of two strong bands, one due to the tantalum fluoride moiety (649 cm^{-1}) and the other due to tantalum oxyfluoride species (904 cm^{-1}), can be utilized to estimate the level of oxide impurities in the melt. Several methods of melt purification, variations of which have been long used by many researchers, were examined to determine the relative facility with which they removed oxides. By far, the best of the methods studied was that of slow recrystallization of the FLiNaK eutectic mixture, which exhibited an effectiveness over five times greater than the best of the other methods.

Two methods for removing oxide impurities from SCA melts were examined. Treatment of the melt with phosgene proved to be effective, but required a dedicated vacuum line (see Chapter II, pp. 66-67) and hood, a temperature of 200°C or more, and several hours for the reaction to be completed. The use of carbon tetrachloride was found to be an excellent method for oxide removal. Furthermore, using CCl_4 , required

a lower working temperature, less complex handling procedures and materials, and shorter reaction times, compared to using phosgene. These advantages, in addition to the lower health risk of working with CCl_4 , compared to that of phosgene, strongly recommend that the former be considered the method of choice in the matter of oxide removal from SCA melts.

B. Studies on the Electrochemistry of Nb(V) in SCA Melts Containing Oxide

Results were presented which demonstrated that previous reports (74-76) on the electrochemistry of Nb(V) in SCA melts were in error. These previous workers analyzed their data and proposed a reaction sequence for the reduction of Nb(V) based on the assumption that the reacting species was NbCl_5 . It was shown here that the previous studies were conducted in melts which contained quite high concentrations of oxide impurities, and that the species under study was in fact niobium(V) oxychloride.

Using oxide removal methods described in Chapter 3 made it possible to prepare solutions of NbCl_5 in SCA which were essentially free of oxide impurities. Studies on the electrochemical behavior of NbCl_5 in SCA were conducted to determine the reduction scheme of Nb(V). Cyclic, square wave, and normal pulse voltammetries, as well as

chronoamperometry and controlled potential electrolysis, were used in these analyses.

It was determined that the reduction of Nb(V) in SCA at 178°C involved four steps in the simplest case, which was when the experiment rate was fast or experiment times were short. Experimental data suggested that Nb(V) was first reduced to Nb(IV) in a one-electron reversible charge transfer; following this, Nb(IV) was reduced to various sub-valent niobium chloride species which were quite stable in the melt; niobium metal was not produced at 178°C.

At long experimental times (slow rates), a complication was observed in the form of an additional wave between the first and second reduction waves. It was postulated, based on the analysis of experimental data, that this wave was due to the reduction of Nb(III), produced by the disproportionation of Nb(IV) formed in the first step.

An examination of the effect of temperature on the electrochemical behavior of Nb(V) in SCA and SFCA melts was undertaken. No significant difference in the Nb(V) electrochemistry in these two melts was observed. In general, as the temperature was increased from <200°C to 500°C, the first wave broadened and became almost indistinguishable, except as a broad, flat plateau. The final three (four) waves in the low-temperature voltammogram merged into a single large wave. Also, as the temperature was increased, a new wave was observed near the melt cathodic limit; the

peak potential of this new wave shifted to more negative values as the temperature was increased.

Some constant current electrolysis experiments were conducted in SCA and SFCA melts at temperatures $>400^{\circ}\text{C}$ in attempts to electrochemically produce Nb metal from Nb(V) solutions. Few positive results were obtained, but some general comments were made concerning the advantages and disadvantages of using various ranges of current density, temperature, and fluoride content. It was possible to produce smooth but thin coatings of Nb metal on both nickel and tungsten substrates.

C. Suggestions for Future Work

More definitive results concerning the electrochemistry of Nb(V) in SCA and SFCA would be useful, in that they would serve as a guide to conducting the search for the optimum conditions for metal deposition in these melts. Unfortunately, it does not seem that such results will be obtained using purely electrochemical means. It would be instructive to perform UV-visible spectroelectrochemical measurements in solutions of fairly high concentration; between 10 and 15 mM would probably be optimum to avoid hindrances by the shoulder that appears just before the second reduction wave in the CV at higher concentrations, and to avoid complications by any adventitious oxide species. Such an undertaking would be difficult, however,

as spectroelectrochemical cells of extremely small pathlength (<0.05 cm) would be required to obtain meaningful spectra. Attempting to insert an optically transparent electrode into such a small cell is not a trivial task.

Two other spectroscopic methods would be quite useful in characterizing the films formed at the surface of the electrode during the third and the fourth waves in the CV/SWV's. Although it was not possible in the studies reported here to obtain usable X-ray powder diffraction patterns for the films, it might be possible, using a large electrode and concentrated solutions, to obtain enough of the films to prepare an "independent" X-ray sample (i.e., one that is not simply supported on the electrode surface). The other spectroscopic method is FTIR, particularly in the far infrared (FIR) region. The halide cluster species of many of the refractory metals tend to have quite distinctive FIR spectra, and they should be more definitive than using UV-visible spectroscopy. Understanding the chemistry of these films (and of the cluster species in general) in the SCA and SFCA melts might provide means to avoid them, possibly leading to better quality metallic deposits.

Finally, a more detailed study of the chemistry and the electrochemistry of niobium oxychloride should be conducted. Ting (74) studied the effect of added oxide, but it was shown in this work that his melts were already rich in oxide. In alkali fluoride melt, at least, the addition of

oxide can actually be helpful in attempts to obtain good plates of refractory metals (19); the high level of oxide in the melts of Senderoff and Mellors did not deter them from obtaining very high quality metallic deposits (44). The author believes that the addition of a slight excess of oxide to the melt simplifies matters somewhat with respect to the electrochemistry of Nb(V); it is possible that the presence of oxide inhibits the growth of films to some extent, just as was expected in the case of added fluoride. Conducting studies in high-oxide melts would eliminate the need for constant vigilance in removing and avoiding oxide sources.

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APPENDIX

APPENDIX

DETERMINATION OF THE CONCENTRATION OF SPECIES X

This Appendix refers to the determination of the relative concentration of the unknown species (X) which was proposed to react with Nb(V) in the 11 mM solution (Chapter 4, p. 106). The discussion that follows describes the method by which the ratio of the concentration of X to the concentration of NbCl₅ was determined using data obtained from SWV conducted in 11 mM (actual, 11.11 mM) and 25 mM (actual 24.98 mM) solutions of NbCl₅ in SCA. This method is essentially identical to that applied to a standard addition experiment.

In these calculations, species X is assumed to react stoichiometrically with NbCl₅. Also, it is assumed that the initial wave in the SWV (Figure 24, p. 104) is due to the reduction of NbCl₅, and that the second wave is due to the reduction of the product of the reaction of NbCl₅ with X; these assumptions were shown to be accurate (Chapter 4, p. 106).

Since a reduction wave attributed to NbCl₅ was observed in the 11 mM solution of NbCl₅, and the reaction of X with NbCl₅ is stoichiometric, then all of X must have been consumed by reaction with 11 mM of NbCl₅, with an excess of the latter present in solution. Therefore none of the NbCl₅ added to increase the concentration to 25 mM reacted with X.

In SWV, the peak height of a wave is directly propor-

tional to the concentration of the substance. Therefore, the ratio of the peak heights for the first wave in the 25 and 11 mM solutions is a direct measure of the ratio of the actual concentrations of NbCl_5 (after reaction with X) in the two solutions. This ratio, $i_{P,25}:i_{P,11}$, was found to be 3.70.

For simplicity, the following variables are defined:

C_X = concentration of species X;

$C_{T,11}$ = theoretical concentration of NbCl_5 in the 11 mM solution (before reaction with X);

$C_{T,25}$ = theoretical concentration of NbCl_5 in the 25 mM solution (before reaction with X);

$C_{A,11}$ = actual concentration of NbCl_5 in the 11 mM solution (after reaction with X); and

$C_{A,25}$ = actual concentration of NbCl_5 in the 25 mM solution (after reaction with X).

With these variables defined, the assumptions made above, and the ratio $i_{P,25}:i_{P,11}$, equations (A1), (A2), and (A3) can be

$$C_{A,11} = C_{T,11} - C_X \quad (\text{A1})$$

$$C_{A,25} = C_{A,11} + (C_{T,25} - C_{T,11}) \quad (\text{A2})$$

$$C_{A,25} = 3.70C_{A,11} \quad (\text{A3})$$

defined. These equations can be combined and rearranged to give equation (A4). Since $C_{T,11}$ and $C_{T,25}$ are known quantities

$$\frac{C_X}{C_{A,11}} = \frac{3.70C_{T,11} - C_{T,25}}{C_{T,25} - C_{T,11}} \quad (\text{A4})$$

11.11 and 24.98 mM, respectively), then the ratio $C_X:C_{A,11}$ (or $C_X:C_{NbCl_5}$) can be determined directly as 1.17. It is straightforward, then, to determine the ratio of oxide to Nb(V) in the 11.11 mM solution as 0.54.

VITA

Karl Dale Sienerth was born in Phoenix, Arizona on November 28, 1963, the last of his parents' four children; after moving with his family to various places in the Southeast United States, he spent most of his youth growing up in Gold Hill and Rockwell, North Carolina. He attended East Rowan High School, and graduated valedictorian in May, 1981. He attended Pfeiffer College in Misenheimer, North Carolina, from which he graduated with honors with a Bachelor of Science degree in chemistry and mathematics in May, 1985. He entered graduate school in chemistry at the University of Tennessee, Knoxville, in August, 1985, and worked under the direction of Dr. Gleb Mamantov in the Molten Salt Group. He has accepted a position as Assistant Professor of Chemistry, with a commission of Major in the Virginia Militia, at the Virginia Military Institute in Lexington, Virginia. Karl now lives in Lexington with his wife of 2-1/2 years, Sonya Dial Sienerth, and his 4-month old son, Nicholas Allen Sienerth.