Document Number
TRACOR 66-104-U

AD626211

QUARTERLY STATUS REPORT NO. 11

1 July - 30 September 1965

ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

Contract No. Nonr-4054(00)
Research Project No. RR001-06-02
ARPA Order No. 399, Program Code No. 2910

January 5, 1966

TRACOR
4525 ED BLUESTEIN BOULEVARD • AUSTIN, TEXAS 78721 • 512 WA 6-2800

TRACOR, INC. 4525 ED BLUESTEIN BLVD., AUSTIN, TEXAS 78721

QUARTERLY STATUS REPORT NO. 11

1 July - 30 September 1965

ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

Contract No. Nonr-4054(00)
Research Project No. RR001-06-02
ARPA Order No. 399, Program Code No. 2910

January 5, 1966

Prepared by:

Larry G. Spears

Larry D. Fiel

James L. Lindgren

Approved by:

Earl S. Snavely Jr

Earl S. Snavely, Jr.
Director of Chemical
Research

TABLE OF CONTENTS

DISTRIBUTION LIST

DD Form 1473

LIST OF ILLUSTRATIONS

LIST OF TABLES

Abstract

The electrolysis of NH_4F in anhydrous HF at various concentrations and anode potentials was studied during the past quarter.

If water is present in the electrolyte, the proportion of N_2F_2 is decreased and OF_2 and NF_3 are increased. It is apparent that water has a large effect on the electrode reactions and thus cannot be used as a passivator to decrease attack of the anode during electrochemical fluorinations.

Additional studies were made to determine the conditions required for passivation of electrodes in liquid HF electrolytes.

ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

I. INTRODUCTION

Past work on this project has shown that the fluorination of NH_4^+ in AHF does not occur by a potential-dependent stepwise reaction. In anhydrous HF electrolytes, corrosion of the anode material, nickel and Monel, occurs to the extent of about 10% of the current passed. The corrosion products accumulate on the electrode surface and strongly absorb quantities of fluorine evolved by the anode. Thus, the fluorination of species in the electrolyte probably occurs by chemical fluorination by fluorine trapped in the anode film. The increase in diffusion control through the anode film, the occurrence of both chemical and electrochemical oxidations, and changes in electrode character make the electrode kinetics exceedingly complicated.

Recent work has shown that nickel anodes can be passivated by the presence of as little as 0.01% H_2O in the electrolyte. Moreover, the passivity persists after passage of sufficient current to decompose all the water. Current work given in this report shows that the presence of water has a large effect on the relative proportion of various species in the volatile products formed by electrochemical fluorination of NH_4^+; however, the persistence of passivity after decomposition of the water present makes it possible to use prepassivated electrodes for electrochemical fluorinations thereby decreasing the amount of current contributing to anode corrosion. It is also expected that the use of passive electrodes, which do not form bulky fluorine-saturated coatings, will allow observations of the true electrode behavior of anodic oxidation reactions in HF solutions.

Current work is devoted to obtaining quantitative analyses of the volatile and soluble products of electrochemical fluorinations of NH_4^+ in HF. Volatile product analyses are obtained by gas chromatography complemented by IR and mass spectra verifications of the species observed. Solution analyses are obtained by IR spectroscopy utilizing cells developed for this project. Additional work on electrode passivity is being performed to obtain the mode of electrical conduction through the fluoride film and to identify the species responsible for passivation of the electrode.

TABLE I

RELATIVE AMOUNTS OF VOLATILE PRODUCTS FORMED FROM THE ELECTROLYSIS OF NH_4F IN AHF

NH_4F CONCENTRATION	APPLIED CONSTANT POTENTIAL	%[a] F_2	% OF_2	% NF_3	% *trans*-N_2F_2	% α[b]
0.04M	8.0 V	96.1%	~ 1.8%	1.1%	1.0%	------
0.05M	10.0 V	95.0%	~ 0.1%	0.3%	4.6%	------
0.10M	6.0 V	99.6%	------	-----	0.4%	------
0.10M	8.0 V	91.1%	~ 0.12%	0.1%	8.66%	~ 0.12%
0.10M	10.0 V	91.5%	~ 0.01%	~0.03%	8.46%	------
0.87M	7.7 V	66.2%	~ 0.1%	0.14%	33.5%	~ 0.06%
1.0M	8.0 V	77.2%	~ 2.4%	2.1%	18.3%	~ 0.2%
2.0M	10.0 V	63.0%	~18.0%	12.8%	4.2%	------

---

[a] % = percentage of product as found in the gas sample analyzed.

[b] α = unidentified product.

II. ANALYSIS OF ELECTROLYSIS PRODUCTS

A major portion of the work this past quarter has been devoted to the analysis of the volatile products formed from the electrolysis of NH_4F in HF. The products obtained were identified by gas chromatography and infrared and mass spectroscopy. The yields of the various products were studied as a function of both the applied potential and NH_4F concentration.

The procedure used for the GC work is described in Quarterly Reports 9 and 10 (1,2). The samples used for the IR and mass spectra were trapped from the GC exit line in 3 and 5 cc bombs immersed in liquid nitrogen. The IR spectrophotometer used is a Beckman IR 5-A, and the mass spectrograph used is a modified Electrodynamics Model 21-620 (m/e range of 2 to 150).

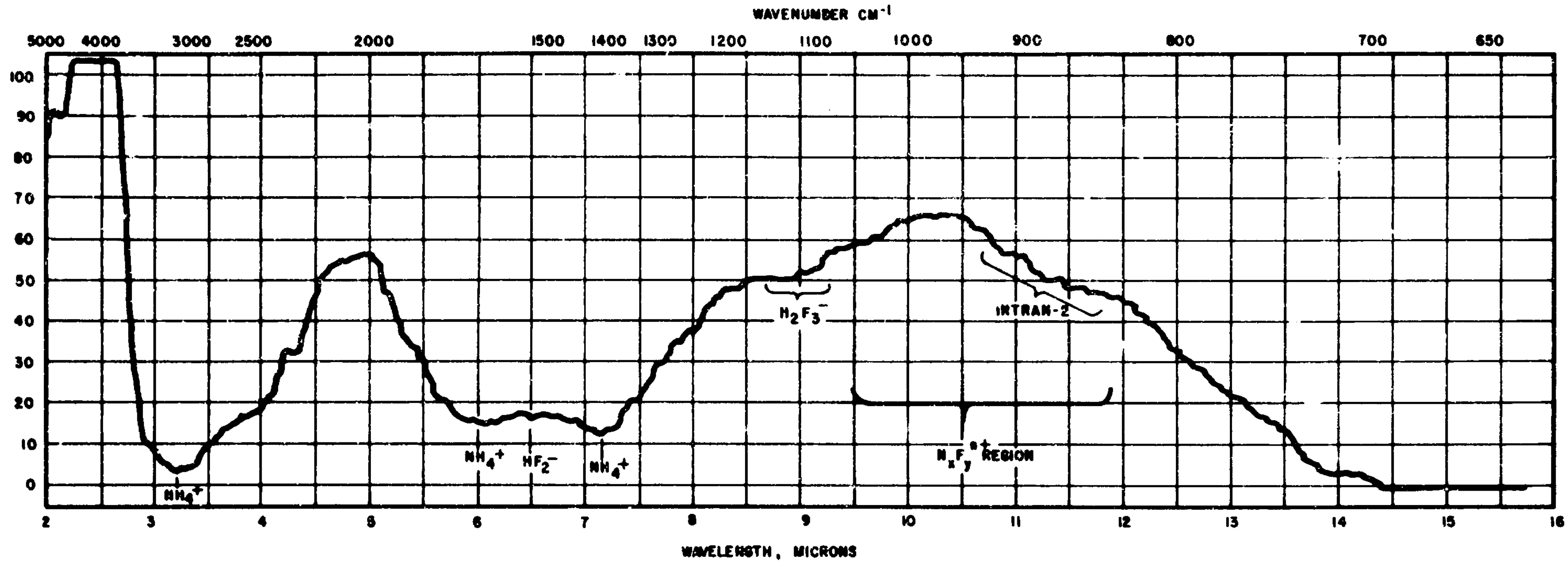
Table I shows the concentrations of the various species present in the volatile cell products as a function of applied potential and NH_4F concentration. The relative proportion of <u>trans</u>-N_2F_2 is affected by at least three factors:

1. The NH_4F concentration
2. The anode potential
3. The presence of H_2O in the electrolyte as indicated by the amount of OF_2 formed (3).

An IR spectrum of a liquid electrolyte sample taken during an electrolysis of 5M NH_4F in AHF at 8.0 volts is shown in Figure 1. The spectrum has no absorption bands between 9.5 and 11.8 microns which can be attributed to $N_xF_y^{n+}$. The broad, strong NH_4^+ bands are easily seen at 3.2, 6.0, and 7.15 microns. The weak HF_2^- band is seen at 6.5 microns and the broad, weak $H_2F_3^-$ band between 8.6 and 9.2 microns. The portion of the spectrum between 10.8 and 11.9 microns is part of the background spectrum due to Irtran-2.

The presence of the various species in the volatile cell products was confirmed by IR and mass spectra. A portion of each sample trapped was used to obtain an IR spectrum which corresponded to the mass spectra identification. It should be noted that both the IR and MS (4) distinguish between *cis*- and *trans*-N_2F_2. Two strong absorption bands are obtained for *cis*-N_2F_2 between 6.15 and 6.3 microns, while *trans*-N_2F_2 has two strong bands at 10.1 and 10.3 microns. In the mass spectra, the strongest peak for *cis*-N_2F_2 is mass 47 and the strongest peak for *trans*-N_2F_2 is mass 28.

The product previously identified as *cis*-N_2F_2 has been identified by its IR and mass spectra to be SiF_4.



SPECTRUM # 10-15-65 A

DATE - OCT. 15, 1965

SAMPLE - +8.0 V ELECTROLYSIS SAMPLE FROM 5 M NH_4F IN AHF SOLUTION

SOURCE -

STRUCTURE -

PATH - .015 mm

SOLVENT - HF

CONCENTRATION -

PHASE - LIQUID

COMMENTS - SLOW SCAN, TEMPERATURE ≈ - 65° C

ANALYST - Larry L. Spears

FIG. 1- IR LIQUID SPECTRUM OF PRODUCTS OBTAINED FROM THE ELECTROLYSIS OF 5M NH_4F IN AHF AT +8.0 V.

TRACOR, INC | DWG 6581
AUSTIN, TEXAS 1-4-66 | LS-SJN

III. ELECTROCHEMICAL STUDIES ON NICKEL

Differential capacity measurements were made on nickel electrodes in AHF and in HF plus 0.01% and 0.10% H_2O. The method of charging curves based on the application of a square-wave signal was used for making the measurements (5). This method is suitable for solid metal electrodes having geometrical areas as large as 2 to 3 cm^2. All data reported here were taken on nickel electrodes with an area of 1 cm^2. With this small electrode size and the circuit parameters listed below, differential capacities up to 10 $\mu F/cm^2$ are readily obtained with good accuracy. A block diagram of the electronic setup is shown in Figure 2. The pulse generator delivers a push-button triggered 10 mA, 15 μsec pulse with a rise time of < 1 μsec. The potential-time trace displayed on the oscilloscope (Tektronix 535A with a Type H preamp) was recorded with a Polaroid camera. The differential capacity is then calculated from the equation

$$c = I/\left(\frac{dE}{dt}\right)_{t=0}$$

where $\frac{dE}{dt}$ = the slope of the potential-time trace.

Capacity data were taken during galvanostatic polarization runs. The polarization curves and differential capacity measurements are shown in Figures 3 and 4.

The current density during anodic polarization of nickel in AHF using a constant current source is somewhat higher than when using a constant potential source (1), but the general shape of the curves are the same. However, upon the addition of H_2O, the galvanostatic curves exhibit a behavior typical of a passivating electrode (i.e., a large increase in potential at a fixed current density until electrolyte decomposition occurs) (5). The current

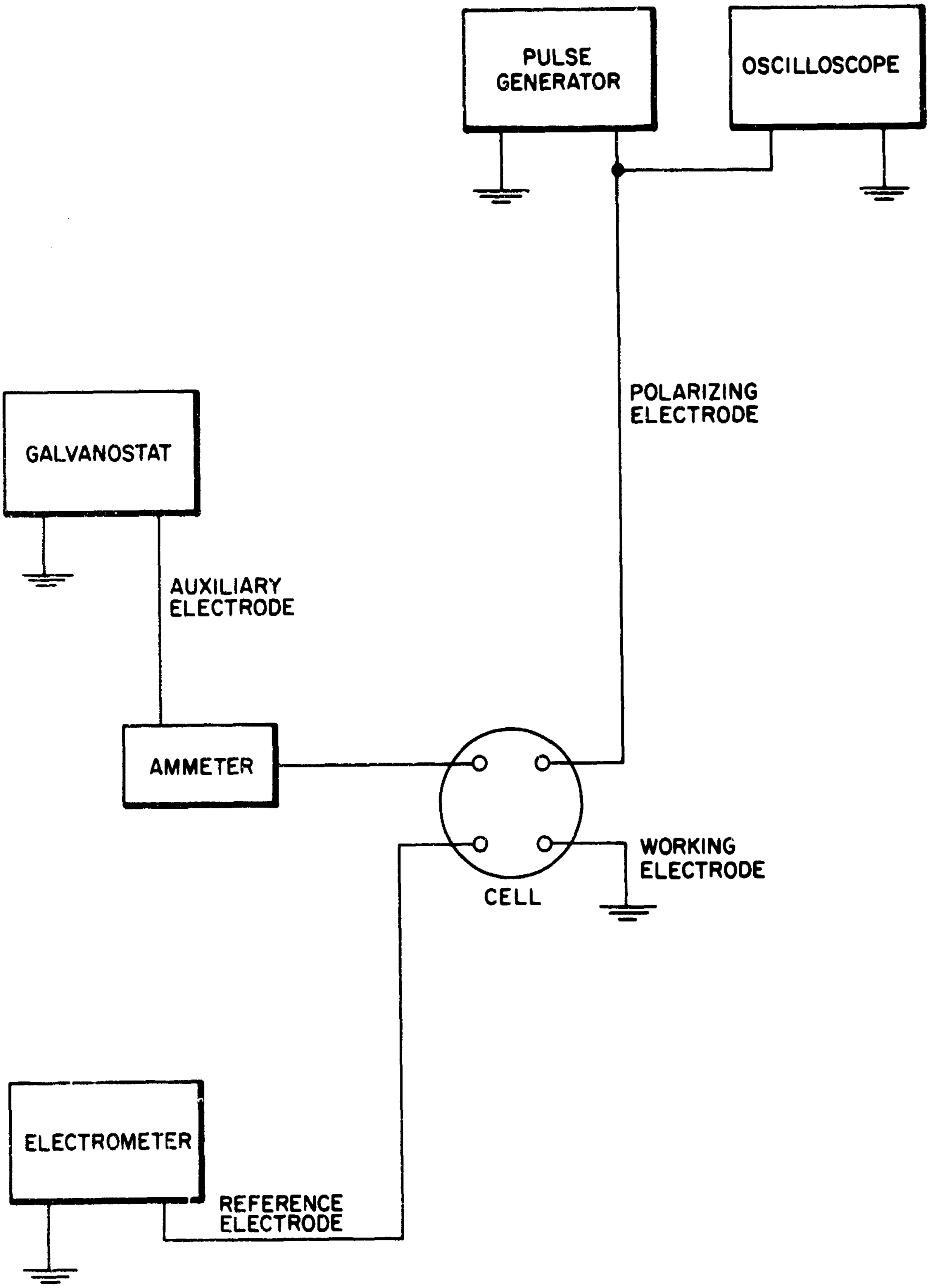


FIG. 2- BLOCK DIAGRAM OF PULSING CIRCUIT

TRACOR, INC | DWG 6544
AUSTIN, TEXAS 12-22-65 LF-DJK

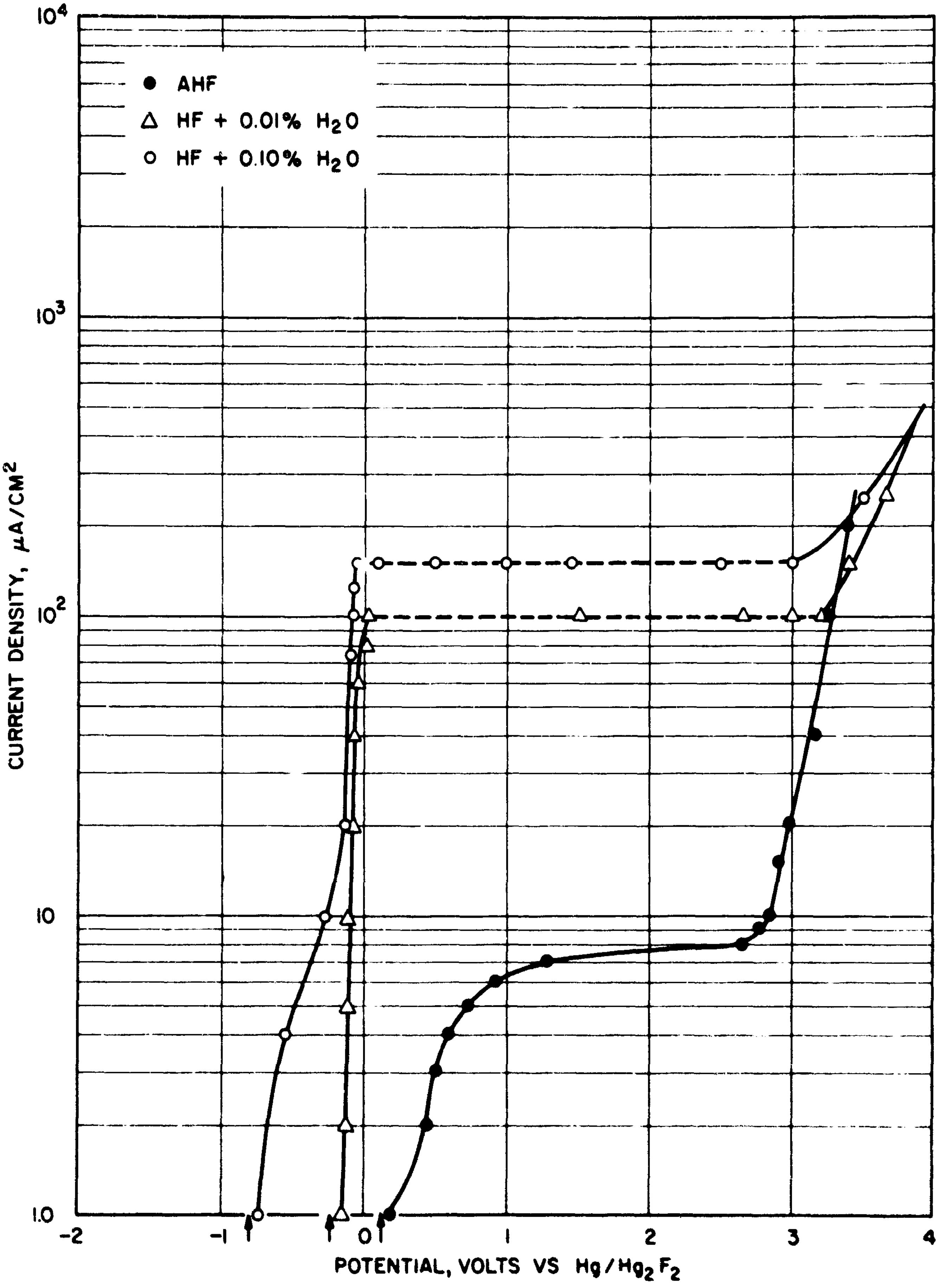


FIG. 3 - GALVANOSTATIC POLARIZATION CURVES OF NICKEL IN HF + 0.01 M NaF

TRACOR, INC | DWG 6545
AUSTIN, TEXAS 12-22-65 LF-DJI

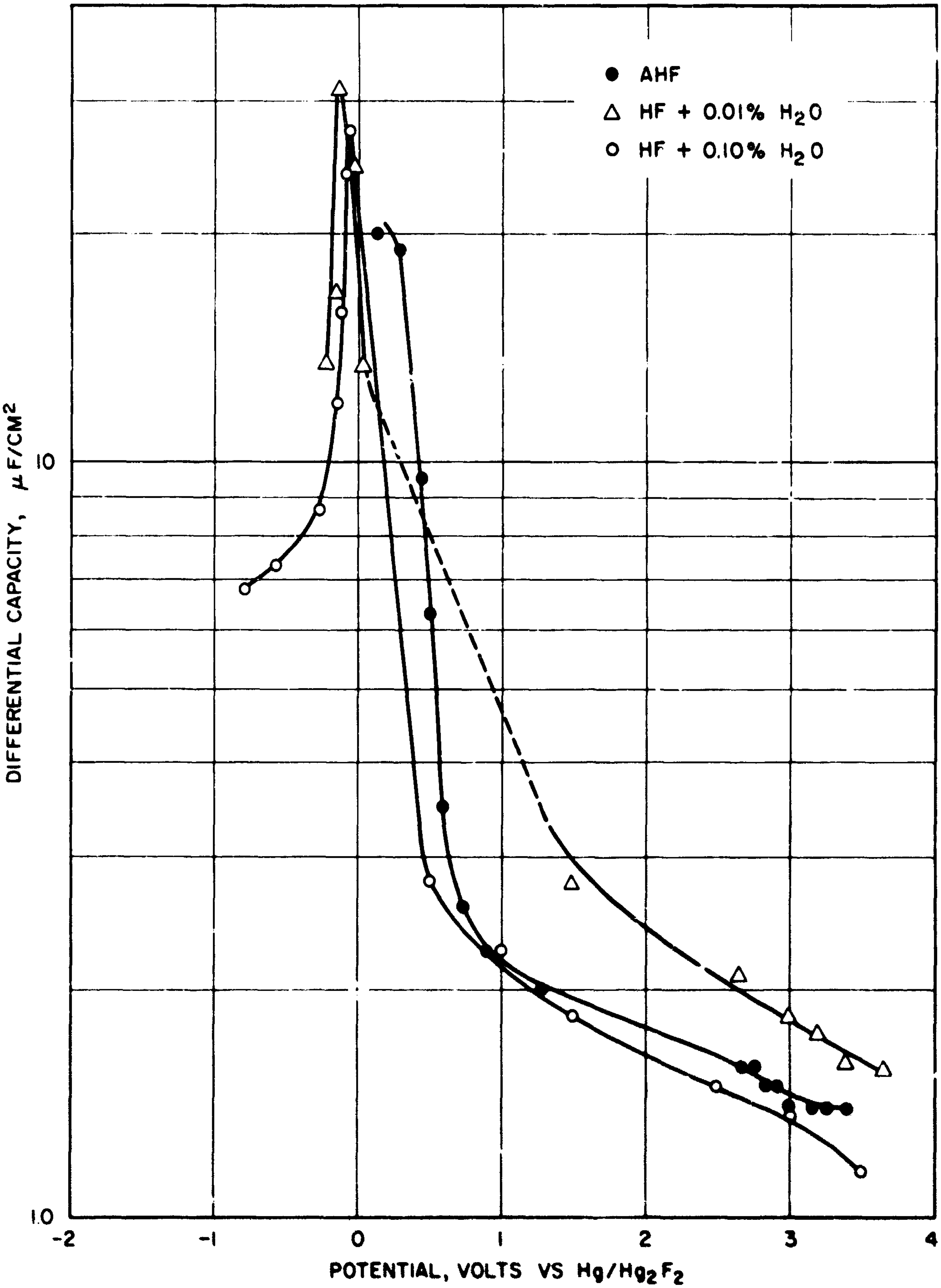


FIG. 4 - DIFFERENTIAL CAPACITY OF NICKEL IN HF + 0.01 M NaF

TRACOR, INC | DWG 6546
AUSTIN, TEXAS 12-22-65 LF-DJK

density increases with increasing water concentration as it did in the potentiostatic runs.

The differential capacity of the nickel electrode in AHF is about 20 $\mu F/cm^2$ at open circuit (Figure 4). This value is typical of those found on many metals in aqueous systems (6). Upon anodic bias, the differential capacity decreases rapidly to a value of about 1.5 $\mu F/cm^2$. The addition of water causes the open circuit potential to shift cathodic and the differential capacity is lower at open circuit. Also a peak in the capacity curve is noted at about 0 volts vs Hg/Hg_2F_2. The initial low capacities may be due to adsorption of a cation (e.g., H_3O^+) which is reduced upon anodic bias causing the capacity to increase until initiation of the film formation. The differential capacity curves from 0 volts to the fluorine evolution potential show no consistent significant changes with water concentration.

The low capacities are attributed to the formation of a stable film on the electrode. The stability of the film is evidenced by the length of time required for the differential capacity to reattain its initial value. Figure 5 shows the change in capacity with time at open circuit. After 20 hours the capacities of the electrodes were still below their original values, and in the solution containing 0.10% water, even after several days, the capacity was below its original value.

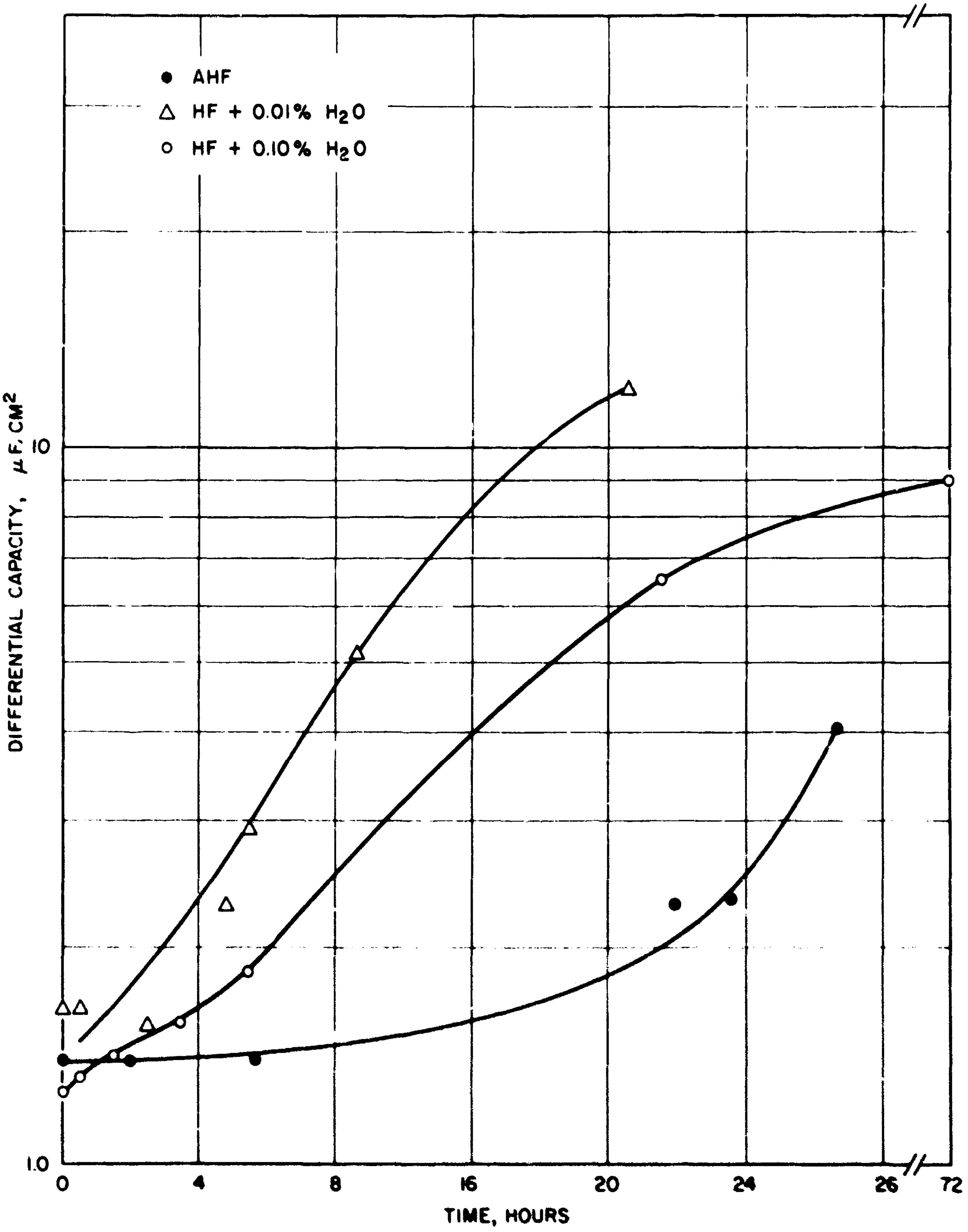


FIG.5 - CHANGE OF CAPACITY WITH TIME

TRACOR, INC | DWG 6547
AUSTIN, TEXAS 12-22-63 LF-DJK

IV. DISCUSSION

Analysis of the electrolysis products formed in both vapor and liquid phases will be continued to obtain balances between current passed and the amount of products formed. The data obtained for the vapor phase are reproducible and accurate. Analyses of volatile cell products showing large proportions of N_2F_2 under same conditions imply a strong possibility that intermediate ionic species exist during the electrochemical fluorination of NH_4^+. Confirmation of the existence of the intermediates may be accomplished by optimizing the yield of fluorinated nitrogen products (possibly by using passive electrodes) and by operating the cell at lower temperatures to prolong the life of the intermediates.

Differential capacity measurements on nickel electrodes in AHF plus 0.01M NaF show a value of about 20 $\mu F/cm^2$ at the open circuit. The capacity decreases rapidly upon anodic polarization to a steady reading of about 1.5 $\mu F/cm^2$, indicating the formation of a film on the electrode. Addition of water lowers the differential capacity at open circuit, but the same behavior is observed upon anodic polarization. Galvanostatic polarization curves are typical of a passivating electrode when H_2O is present. However, the low capacity film is present in AHF as well as when water is present, indicating that the passivating film (formed with H_2O plus HF) and the film formed in AHF are at least similar in some respects.

V. FUTURE WORK

Electrochemical fluorinations of NH_4^+ in anhydrous HF will be continued. Particular emphasis will be placed on the detection of soluble intermediate ionic species through the use of lower cell temperatures and optimum cell conditions. It is anticipated that the use of passive electrodes will result in a greater selectivity of product formation by control of the anode potential. The analytical methods and electrochemical techniques developed thus far will be applicable to investigations of the electrochemical fluorination of $N_2H_5^+$ in anhydrous HF.

Investigations of passive electrodes will be limited to attempts to identify the extremely thin films formed during anodic polarization. These experiments will utilize X-ray and/or electron diffraction patterns obtained from nickel electrodes after anodic polarization in HF containing trace amounts of water.

LIST OF REFERENCES

1. E. S. Snaverly, Jr., *et al*., "Electrochemical Studies in the Synthesis of N-F Compounds," Quarterly Status Report No. 9, TRACOR, Inc., Document No. TRACOR 65-224-U.

2. E. S. Snavely, Jr., *et al*., "Electrochemical Studies in the Synthesis of N-F Compounds," Quarterly Status Report No. 10, TRACOR, Inc., Document No. TRACOR 65-348-U.

3. American Oil Company, First Annual Report, February 1964, ARPA Order No. 402, Task 3, ARPA Program Code 3910, ARO-D Project 4135.

4. C. B. Colburn, J. Am. Chem. Soc. 81, 6397 (1959).

5. R. J. Brodd and N. Hackerman, J. Electrochem. Soc. 104, 704 (1957).

6. J. J. McMullen and N. Hackerman, J. Electrochem. Soc. 106, 341 (1959).

UNCLASSIFIED
Security Classification

DOCUMENT CONTROL DATA - R&D

(Security classification of title body of abstract and indexing annotation must be entered when the overall report is classified)

1 ORIGINATING ACTIVITY (Corporate author)
TRACOR, Inc.
1701 Guadalupe
Austin, Texas 78701

2a REPORT SECURITY CLASSIFICATION
UNCLASSIFIED

2b GROUP

3 REPORT TITLE
QUARTERLY STATUS REPORT NO. 11
1 July - 30 September 1965
ELECTROCHEMICAL STUDIES IN THE SYNTHESIS OF N-F COMPOUNDS

4 DESCRIPTIVE NOTES (Type of report and inclusive dates)
Quarterly

5 AUTHOR(S) (Last name, first name, initial)
Spears, Larry G.
Fiel, Larry D.
Lindgren, James L.
Snavely, Earl S., Jr.

6 REPORT DATE
5 January 1966

7a TOTAL NO OF PAGES
20

7b NO OF REFS
6

8a CONTRACT OR GRANT NO
Nonr-4054(00)

b PROJECT NO
RR001-06-02

c ARPA Order No. 399

d Program Code No. 2910

9a ORIGINATOR'S REPORT NUMBER(S)
66-104-U

9b OTHER REPORT NO(S) (Any other numbers that may be assigned this report)

10 AVAILABILITY LIMITATION NOTICES
"Qualified requesters may obtain copies of this report from DDC."

11 SUPPLEMENTARY NOTES

12 SPONSORING MILITARY ACTIVITY
Department of the Navy
Office of Naval Research
Power Branch, Washington, D.C. 2036

13 ABSTRACT

The electrolysis of NH_4F in anhydrous HF at various concentrations and anode potentials was studied during the past quarter.

If water is present in the electrolyte, the proportion of N_2F_2 is decreased and OF_2 and NF_3 are increased. It is apparent that water has a large effect on the electrode reactions and thus cannot be used as a passivator to decrease attack of the anode during electrochemical fluorinations.

Additional studies were made to determine the conditions required for passivation of electrodes in liquid HF electrolytes.

DD FORM 1473

UNCLASSIFIED
Security Classification

14 KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Quantitative Chemical Analysis						
Electrochemistry						
Electrode Materials						
IR Spectrophometric Analysis						
Gas Chromatographic Analysis						
N-F Compounds						
Fluorine Compounds						

INSTRUCTIONS

1. ORIGINATING ACTIVITY: Enter the name and address of the contractor, subcontractor, grantee, Department of Defense activity or other organization *(corporate author)* issuing the report.

2*a*. REPORT SECURITY CLASSIFICATION: Enter the overall security classification of the report. Indicate whether "Restricted Data" is included. Marking is to be in accordance with appropriate security regulations.

2*b*. GROUP: Automatic downgrading is specified in DoD Directive 5200.10 and Armed Forces Industrial Manual. Enter the group number. Also, when applicable, show that optional markings have been used for Group 3 and Group 4 as authorized.

3. REPORT TITLE: Enter the complete report title in all capital letters. Titles in all cases should be unclassified. If a meaningful title cannot be selected without classification, show title classification in all capitals in parenthesis immediately following the title.

4. DESCRIPTIVE NOTES: If appropriate, enter the type of report, e.g., interim, progress, summary, annual, or final. Give the inclusive dates when a specific reporting period is covered.

5. AUTHOR(S): Enter the name(s) of author(s) as shown on or in the report. Enter last name, first name, middle initial. If military, show rank and branch of service. The name of the principal author is an absolute minimum requirement.

6. REPORT DATE: Enter the date of the report as day, month, year; or month, year. If more than one date appears on the report, use date of publication.

7*a*. TOTAL NUMBER OF PAGES: The total page count should follow normal pagination procedures, i.e., enter the number of pages containing information.

7*b*. NUMBER OF REFERENCES: Enter the total number of references cited in the report.

8*a*. CONTRACT OR GRANT NUMBER: If appropriate, enter the applicable number of the contract or grant under which the report was written.

8*b*, 8*c*, & 8*d*. PROJECT NUMBER: Enter the appropriate military department identification, such as project number, subproject number, system numbers, task number, etc.

9*a*. ORIGINATOR'S REPORT NUMBER(S): Enter the official report number by which the document will be identified and controlled by the originating activity. This number must be unique to this report.

9*b*. OTHER REPORT NUMBER(S): If the report has been assigned any other report numbers *(either by the originator or by the sponsor)*, also enter this number(s).

10. AVAILABILITY/LIMITATION NOTICES: Enter any limitations on further dissemination of the report, other than those imposed by security classification, using standard statements such as:

(1) "Qualified requesters may obtain copies of this report from DDC."

(2) "Foreign announcement and dissemination of this report by DDC is not authorized."

(3) "U. S. Government agencies may obtain copies of this report directly from DDC. Other qualified DDC users shall request through

____."

(4) "U. S. military agencies may obtain copies of this report directly from DDC. Other qualified users shall request through

____."

(5) "All distribution of this report is controlled. Qualified DDC users shall request through

____."

If the report has been furnished to the Office of Technical Services, Department of Commerce, for sale to the public, indicate this fact and enter the price, if known.

11. SUPPLEMENTARY NOTES: Use for additional explanatory notes.

12. SPONSORING MILITARY ACTIVITY: Enter the name of the departmental project office or laboratory sponsoring *(paying for)* the research and development. Include address.

13. ABSTRACT: Enter an abstract giving a brief and factual summary of the document indicative of the report, even though it may also appear elsewhere in the body of the technical report. If additional space is required, a continuation sheet shall be attached.

It is highly desirable that the abstract of classified reports be unclassified. Each paragraph of the abstract shall end with an indication of the military security classification of the information in the paragraph, represented as *(TS)*, *(S)*, *(C)*, or *(U)*.

There is no limitation on the length of the abstract. However, the suggested length is from 150 to 225 words.

14. KEY WORDS: Key words are technically meaningful terms or short phrases that characterize a report and may be used as index entries for cataloging the report. Key words must be selected so that no security classification is required. Identifiers, such as equipment model designation, trade name, military project code name, geographic location, may be used as key words but will be followed by an indication of technical context. The assignment of links, rules, and weights is optional.