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LITHIUM-MOIST AIR BATTERY

FINAL REPORT

by

Jorge E. A. Toni and R. L. Zwaagstra

July 1967

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Research & Development Procurement Office
U. S. Army Mobility Equipment Research and Development Center
Fort Belvoir, Virginia 22060

DA-44-009-AMC-1552(T)

Globe-Union Inc.
Corporate Applied Research Group
5757 North Green Bay Avenue
Milwaukee, Wisconsin 53201

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SUMMARY

The principal objective of this program is the study of the feasibility of the lithium moist-air high energy storage battery for use as the power system in vehicles. An overall equation which can be written for the reaction expected for this system is:

$$2Li + 1/2\ O_2 + H_2O \rightleftharpoons 2LiOH$$

Since considerable information is already available on the primary and secondary performance of the lithium anode in a variety of electrolytes, the primary effort was directed to the characterization of the performance of the air electrode in nonaqueous electrolytes. Oxygen has been found to be reducible on platinum and silver in non-aqueous media. Linear and cyclic sweep voltammetry have been used to study the electrochemical reduction of oxygen on smooth platinum electrodes for the lithium perchlorate-nitrosodimethylamine (NDA) and phenyltrimethylammoniumhexafluorophosphate (ϕMe_3NPF_6) - nitrosodimethylamine systems. The reduction of oxygen studied in both of the above systems occurs in two main steps: At -0.6V and -1.75V vs Ag/AgCl for $LiClO_4$-NDA and at -1.0V and -1.85V vs Ag/AgCl for ϕMe_3NPF_6-NDA. The mechanism of the electrode processes are complex; adsorption effects and chemical kinetics complications have been determined. The effect of the presence of water on the electrochemical reduction of oxygen in ϕMe_3NPF_6-NDA was studied extensively. The results appear to show that the reduction of oxygen might pass from a one electron reaction in the complete absence of water to a four electrons reaction, as in aqueous media, for concentrations of water over 1.2% by volume. A complex series of different mechanisms were postulated for intermediate values of water concentration.

The present report also covers the evaluation of the current capability of the proposed components of the cell: air electrode and lithium anode. It was shown that the oxygen electrode in phenyltrimethylammonium hexafluorophosphate-NDA can support a current of 20 ma/cm^2 for 21 hours at voltages of -1.15 to -0.92 Ag/AgCl using the American Cyanamid electrode AA (Pt load 50 mg/cm^2).

On an Allis-Chalmers sintered silver electrode the steady state current for 23 hours was 30 ma/cm^2 in a voltage range from -0.77 to -1.10 vs Ag/AgCl. The lithium electrode in the same electrolyte has demonstrated steady state capability in exploratory experiments at 30 ma/cm^2 and -2.5V vs Ag/AgCl. Also, small lithium moist-air cells have shown that they can operate at 5 ma/cm^2 with cell voltages of approximately 2.0V for short times.

The present report also includes the study of an analytical method for oxygen determination in non-aqueous media and experiments with the purpose of determining the diffusion coefficient for oxygen and the number of electrons which participate in the reduction.

FOREWORD

This is the Final Report of a research program conducted by Globe-Union Inc. under contract with the U. S. Army Mobility Equipment Research and Development Center (USAMERDC). The purpose of this program was to investigate the feasibility of the lithium-moist air high energy storage battery for use as a power source in vehicles. The research program was done under Contract DA-44-009-AMC-1552(T).

During the sixteen-month period of the contract two semi-annual reports (October, 1966 AD642248 and March, 1967 AD) and the present final report were issued. The technical contents were reviewed by USAMERDC prior to publication. The authors gratefully acknowledge the valuable discussions with Prof. Irving Shain, and the collaboration of William E. Elliott and Dr. Guy D. McDonald during parts of this contract. The gift of platinum fuel-cell electrodes from American Cyanamid is acknowledged.

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INTRODUCTION

The main purpose of this research program is the determination of the feasibility of a high energy electrochemical storage device for use as the main power system in vehicles.

Many electrode couples suggest themselves as being possible systems to produce sufficient energy density to keep the weight of a vehicle moderate and yet allow a reasonable range of operation. It is very difficult simply from the free energy of reaction to determine which of these various systems will be the best, not only with respect to energy density but also with respect to practical adaptability to sound engineering. The lithium-moist air battery has been selected as a system which appears to have many advantages over other systems. Among its advantages are its extremely high theoretical energy density (2566 watt-hours per pound), the possibility of ambient temperature operation and general simplicity. An overall equation which can be written for the reaction expected for this couple is:

$$2\ Li + 1/2\ O_2 + H_2O \rightleftharpoons 2\ LiOH$$

The review of the literature available with respect to the components of the proposed cell showed that considerable information was available about the primary and secondary characteristics of the lithium anode, but in contrast, very few studies had been done at that time covering the kinetics of oxygen reduction in non-aqueous media. This situation suggested that the main effort at the beginning of the contract should be dedicated to the characterization of the air electrode in non-aqueous solutions. In order to find the optimum conditions for the study of the air electrode in non-aqueous systems, screening of different solvents, solutes and electrode materials was done. Nitrosodimethylamine(NDA) showed advantages over propylene carbonate (PC) with all of the solutes used, and it was chosen as the solvent for the present research work. Platinum was considered the best catalyst material for use as an electrode in the initial studies. Lithium perchlorate and phenyltrimethylammonium hexafluorophosphate ($\emptyset Me_3NPF_6$) were the two best solutes for the electrode process investigations. Therefore, $LiClO_4$-NDA and $\emptyset Me_3NPF_6$-NDA were the two electrolytes chosen to study the mechanism of the electrochemical reduction of oxygen on smooth platinum electrodes during the first year of this program. Linear and cyclic sweep voltammetry were the principal electrochemical techniques used for the studies of the oxygen reduction mechanism. The effect of increasing concentration of water on the over-all reaction was also investigated.

The study of the air electrode was completed with experiments of current capabilities of half cells. They showed promising results with a current density of the order of 30 ma/cm^2. Finally, a relatively short part of the contract was dedicated to the lithium anode. This included linear sweep and half cell constant current experiments.

As a proof that both proposed components of the battery were compatible with each other, laboratory scale lithium-moist oxygen cells were run at low current density. The data were promising and did not show any immediate fundamental problems in the system.

During the development of the research contract two parallel problems, which had fundamental importance in the whole investigation, were studied. They included the development and reversibility study of a Ag/AgCl reference electrode for non-aqueous media and an analytical method for oxygen determination in non-aqueous solutions. The latter is discussed in the Appendix.

The discussion of the present final report will follow the main points expressed above. The sections which have been reported before will be only summarized and for the details the reader will be referred to previous reports.

The present report covering the sixteen-month period of the contract will be divided into the following sections:

Literature Review
Materials and Equipment
Exploratory Studies
Reference Electrode
Air Electrode
Lithium Anode
Laboratory Scale Lithium-Moist Oxygen System
Conclusions
Appendix

RESULTS AND DISCUSSION

LITERATURE REVIEW

An exhaustive analysis was completed of all the research available related to both the air electrode and lithium anode components of the proposed cell.

The discussion and list of the references was included in the First Semi-Annual Report, October 1966 AD642243.

MATERIALS AND EQUIPMENT

The description of the methods for purification of the different materials utilized in this program was given in the two previous semi-annual reports.

The potentiostatic equipment available in our laboratories consists of a combination of operational amplifier circuits. It was discussed in the First Semi-Annual Report, October 1966. A block diagram of the instrument and a circuit configuration for controlled potential methods are shown in Figures 1 and 2.

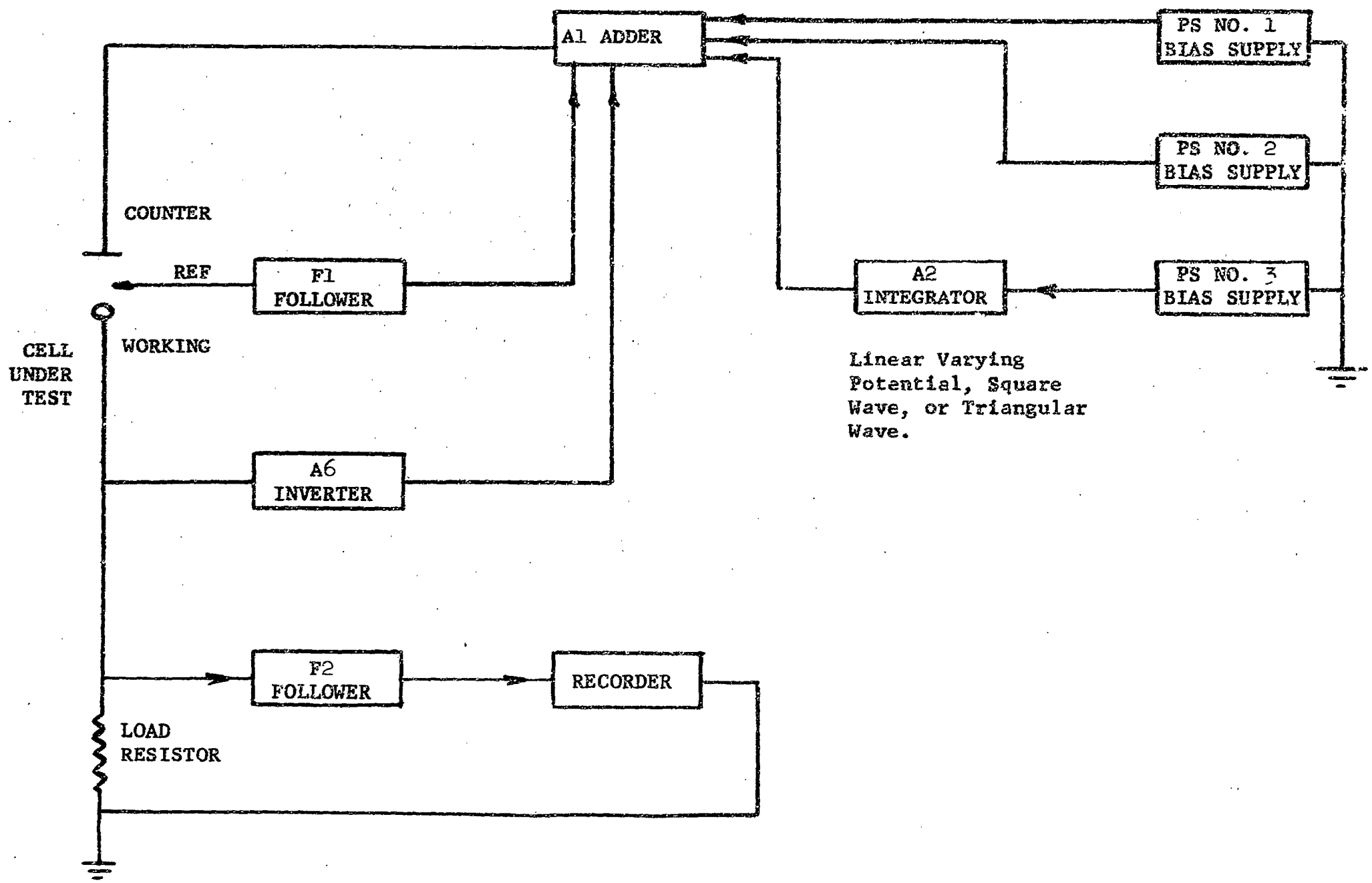
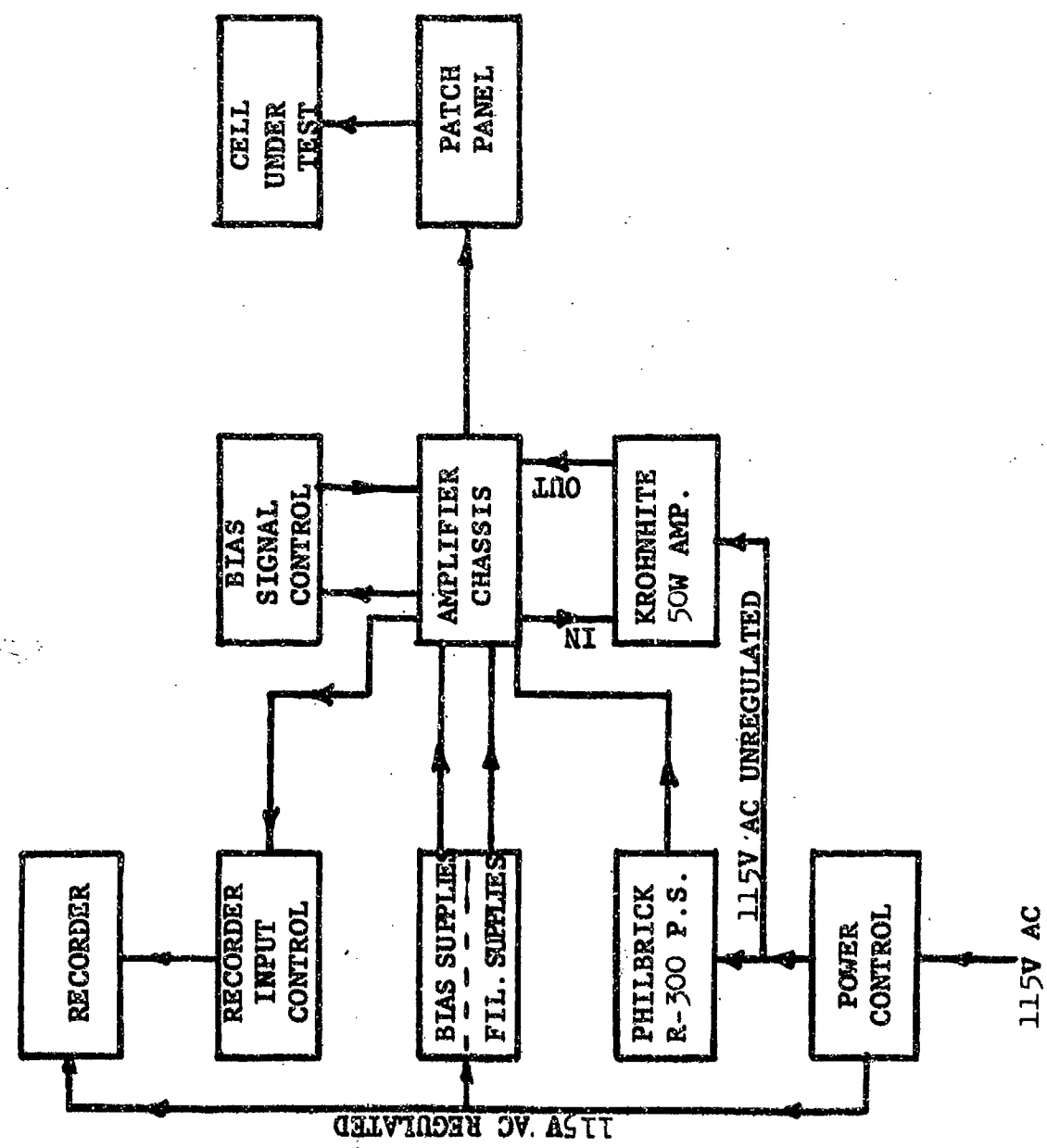


FIGURE 1. BLOCK DIAGRAM OF THE INSTRUMENT FOR ELECTROCHEMICAL STUDIES

FIGURE 2. CIRCUIT CONFIGURATION FOR CONTROL POTENTIAL METHODS



EXPLORATORY STUDIES

The First Semi-Annual Report, October 1966 AD642248 included exploratory studies related with the air electrode in the following electrolyte systems:

a. 1m phenyltrimethylammonium hexafluorophosphate, saturated tetramethylammonium hydroxide-N-nitrosodimethylamine.

b. 1m phenyltrimethylammonium hexafluorophosphate, saturated tetramethylammonium hydroxide - propylene carbonate.

c. 1m lithium perchlorate-propylene carbonate.

d. 1m lithium perchlorate-N-nitrosodimethylamine.

e. 1m phenyltrimethylammonium hexafluorophosphate-N-nitrosodimethylamine.

f. 1m phenyltrimethylammonium hexafluorophosphate-propylene carbonate.

These studies were performed with platinum black American Cyanamid Type AA-1 electrodes and they have shown better current capabilities for all the systems with N-nitrosodimethylamine as solvent than with propylene carbonate. This was the principal reason for choosing N-nitrosodimethyamine as the solvent for further studies.

REFERENCE ELECTRODE

At the beginning of this research program, it was found that the silver wire was unsatisfactory as a reference electrode, and a compact aqueous Ag/AgCl reference electrode protected from the electrolyte by a non-aqueous salt bridge was developed. The application of small overpotentials at both sides of the equilibrium potential did not result in any significant hysteresis effect. The electrode was stable and reversible.

The details of the preparation and hysteresis study of the reference electrode were explained in the First Semi-Annual Report, October 1966.

AIR ELECTRODE

REDUCTION OF OXYGEN IN NON-AQUEOUS MEDIA

The first year of research work on the contract was mainly dedicated to the study of the mechanism of the electrochemical reduction of oxygen on smooth platinum electrodes in nitrosodimethylamine (NDA) solutions. Two different solutes were used: lithium perchlorate and phenyltrimethylammonium hexafluorophosphate ($\emptyset Me_3NPF_6$). The study of both systems has shown that oxygen is electro-reduced in two principal steps. Surface adsorption and chemical kinetics complications were also observed. The experimental details of the studies have been covered in the First Semi-Annual Report, October 1966, for the $LiClO_4$-NDA system and in the Second Semi-Annual Report, March 1967, for the $\emptyset Me_3NPF_6$-NDA system.

a. Lithium Perchlorate - Nitrosodimethylamine System

It was demonstrated that the electrochemical reduction of oxygen in this media occurs in two steps: The first a -0.6V vs Ag/AgCl and the second at -1.75V vs Ag/AgCl. The current observed with the air electrode appeared to be limited by a surface interaction, adsorption of oxygen on the platinum electrode, and by mass transport of the active species.

b. Phenyltrimethylammonium hexafluorophosphate-nitrosodimethylamine System

b-1 Work during the second reporting period covered the study of the mechanism of the oxygen reduction in the electrolyte phenyltrimethylammonium hexafluorophosphate-nitrosodimethylamine.

Using this electrolyte an extensive study was made of the kinetics of the oxygen reduction on smooth platinum electrodes for a wide range of concentration of protons. The research has covered systems with extremely low concentrations of water (20-30 ppm) to concentration levels at which its effect on the mechanism was a maximum (> 1.2% by volume). The overall mechanism is a complex process which includes, first, a series of surface processes on the electrode (adsorption, interaction between oxygen and platinum, reduction of the film formed) and second, two partially mass transport dependent steps.

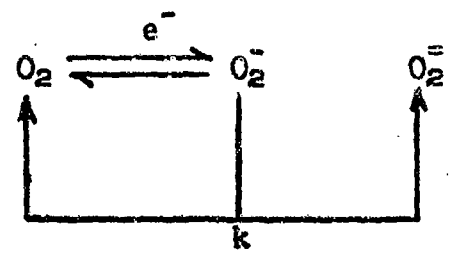
The first of these mass transport controlled steps includes an ECE mechanism complicated by disproportionation and apparently is the reduction of oxygen to peroxide with superoxide as an intermediate. The second step is a highly irreversible one and possibly is the reduction of peroxide to hydroxide when protonic materials (water, etc.) are available. Detailed studies using various levels of water concentration have demonstrated that water (protons) affects each step of the mechanistic process, and that increasing amounts of water yield more favorable reduction conditions and increase the level of the peak current in each step.

The interpretation of the data obtained during this second six months research led to the postulation of a hypothetical overall mechanism:

1. O_2 solution $\rightleftharpoons$ O_2 surface

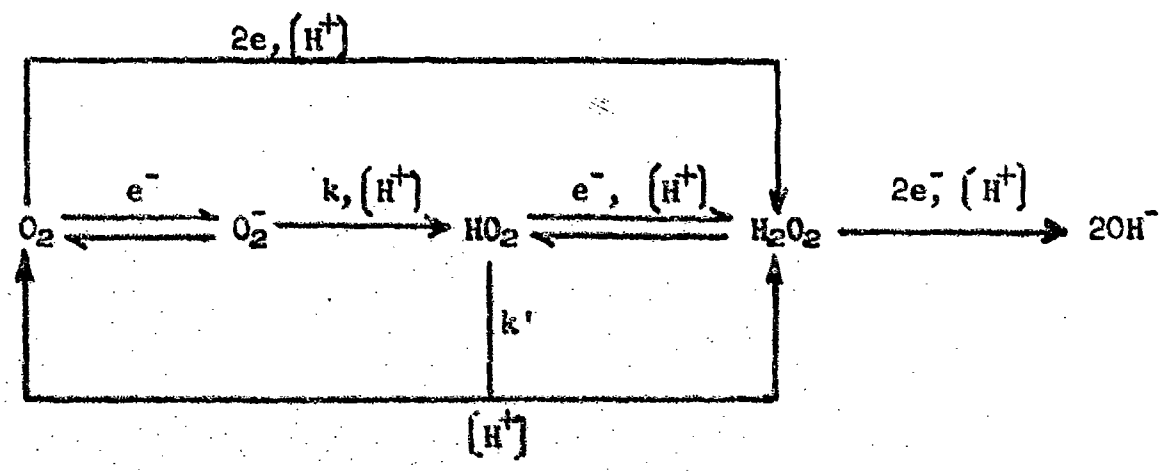
2. O_2 surface + Pt $\longrightarrow$ Pt_xO_y

3. No protons available:



where $2O_2^- \xrightarrow{k} O_2 + O_2^=$

4. Protons Available:



b-2 <u>Potentiostatic studies in order to determine the diffusion coefficient of oxygen and the number of electrons involved in the reaction</u>

The kinetics of the oxygen reduction on smooth platinum electrodes in the ϕMe_3NPF_6-NDA systems contained in the Second Semi-Annual Report of the present contract has just been summarized in the above section. The investigation of the postulated mechanism needs to be completed by the determination of the number of electrons exchanged in the different postulated reactions or by the identification of their products.

Both of these determinations encounter serious difficulties because of the complex system involved and the absence of suitable methods available. However, we made some attempts to determine the number of electrons and the diffusion coefficient of O_2 in the system studied. The method chosen for these objectives was a potentiostatic electrolysis at short times and analysis of the current-time curves (1,2).

If the potentiostatic reduction of a substance O to a substrate R is considered at potentials sufficiently cathodic that the current is controlled entirely by the diffusion of O to a spherical electrode surface, but without complication by kinetic effects, the equation for the current-time curve is:

$$i = n\,FAD_oC_o^* \left[\frac{1}{(\pi D_o t)^{1/2}} + \frac{1}{r_o} \right]$$

where i is the current flowing, n is the number of electrons involved in the electrode reaction, F is the Faraday, A is the area of the spherical electrode, D_o is the diffusion coefficient of substance O, C_o^* is the bulk concentration of substance O, t is the time after the sudden application of the constant potential and r_o is the radius of the electrode.

From the above equation, it is clear that if current is plotted as a function of $1/t^{1/2}$ a straight line has to be obtained and from the values of the intercept and the slope the variables n and D_o can be calculated.

We decided to apply the method to our system for cases with different concentrations of water added, while recognizing that for some of those cases it would not be useful for the kinetic complication studied. Nevertheless, any failure of the application of the potentiostatic method for these cases might be considered a support of our previous postulation. We hoped that for the reduction of oxygen at concentrations of water over 1.2% by volume the method could be useful if the kinetic mechanism of O_2, being similar to that in aqueous media, did not have kinetics complications.

The experiments were run with the same system used before, 0.5m phenyltrimethylammonium hexafluorophosphate-NDA saturated with O_2 (5×10^{-3}M) at different points in the range of concentration of water added. (Second Semi-Annual Report) The study was concentrated on the first reduction peak with the transformations known when water is added. In order to apply the equation a spherical platinum (bead) electrode was used. One of the first problems observed was the selection of a sufficiently cathodic potential. Additions of water shift the second peak to more positive values and the separation between peaks I and II is decreased.

Several experiments were run at concentrations of water from 45 ppm to 1.6% by volume, but although straight lines were obtained, the results were not reproducible and did not show values for n and D which could be expected. With no water added, the values of n covered results between 0.5 and 0.7, and for 1.6% of water they were between 1.3 and 1.7. The results for the diffusion coefficient were apparently too high; they oscillated between 1 and 2×10^{-4} cm^2/sec. Time did not permit a continuation of these experiments which could have involved other techniques such as exhaustive constant potential electrolysis which could perhaps, by coulometry give values for n.

HALF CELL CONSTANT CURRENT EXPERIMENTS

The introduction explained that one of the main efforts was dedicated to obtaining information about current capabilities of the air electrode and lithium anode.

To perform these experiments in a suitable way, the floating type electrode cell was used for the air electrode.

The floating electrode was suggested by Giner and Smith (3) and it consists of suspending a porous electrode just in the interphase between the gas and the liquid. The behavior of this method simulates a practical fuel cell electrode. The cell is shown in Figure 3. Different types of American Cyanamid platinum black electrodes and an Allis-Chalmers sintered silver electrode were held by a platinum spatula contact just on the electrolyte surface, efforts always being made to eliminate any flooding. The counter electrode was a bright platinum sheet electrode parallel to the working electrode. The reference electrode (Ag/AgCl) was located on one side between the other electrodes. Oxygen saturated with moisture was passed continuously over the solution.

The source of constant current was our operational amplifier equipment described previously (First Semi-Annual Report). Tables I and II are a summary of our data.

Two different solutions ($LiClO_4$-NDA and $\emptyset Me_3NPF_6$-NDA) were tested. In both cases we added 1% H_2O by volume. The results from Table I which correspond to $LiClO_4$ can be considered poor. No lasting steady potentials were observed. But, the results obtained with the $\emptyset Me_3NPF_6$ (Table II) can be considered promising. Six different fuel cell platinum black electrodes were studied. The range of platinum loading varied widely from 2.5 mg/cm^2 to 50 mg/cm^2. The Allis-Chalmers silver electrode was also studied.

The experiments were not meant to be exhaustive; they were run until the potential of the working electrode reached values low enough to be interesting for preliminary screening or until the time of the experiment was considered long enough to show capability of the electrode under study. The current density was changed at different intervals to obtain information about the current capability for each individual electrode. These experiments at different current densities were continuous without holding the electrodes at open circuit before changing current.

The best result was with the silver electrode in $\emptyset Me_3NPF_6$-NDA: 23 hours at 30 ma/cm^2 gave a polarization of 0.3V (-0.77 to -1.10V vs Ag/AgCl). The experiments with platinum black electrodes showed the effect of the platinum loading. The best current capability for platinum electrodes was obtained with the Type AA 50 mg/cm^2.

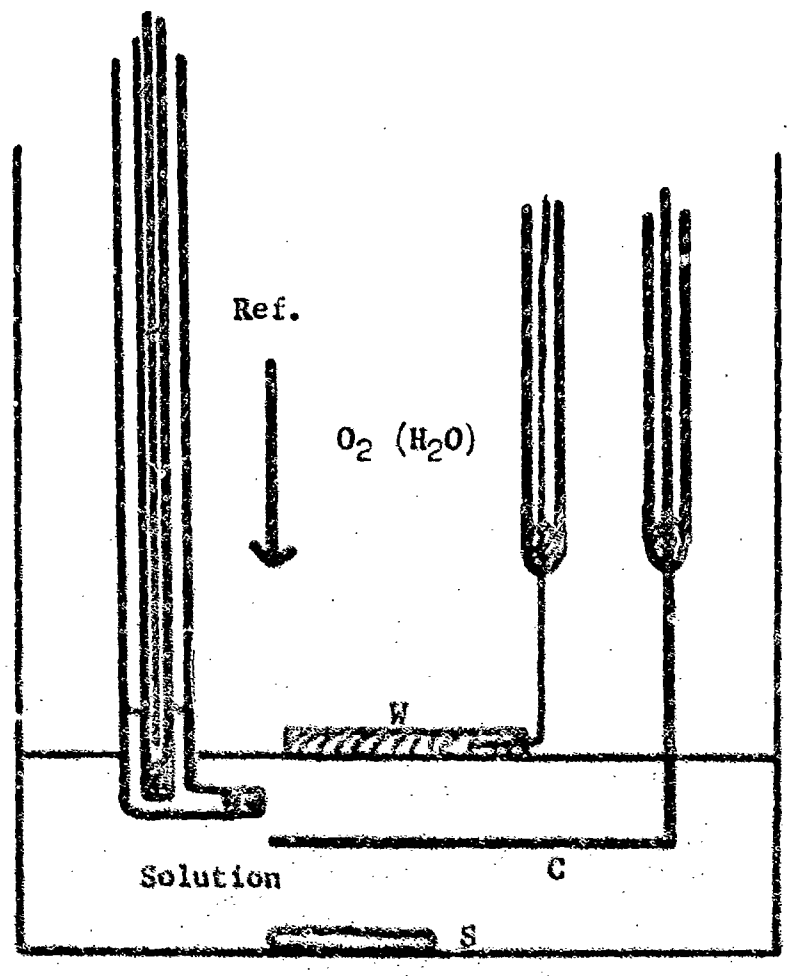
We considered that the experiments summarized in Tables I and II show in some extent the possibilities of the oxygen electrode. They are not conclusive but creat some optimism about the future development of the complete system.

W - Working electrode, geometrical area in contact with solution 1 cm^2.

Ref - Reference electrode, Ag/AgCl (0.1M KCl) with bridge solution 1m $LiClO_4$-NDA.

C - Counter Electrode, Pt. Area 6 cm^2.

S - Stirring bar.



FLOATING ELECTRODE CELL

FIGURE 3

TABLE I

OXYGEN ELECTRODE - CONSTANT CURRENT EXPERIMENT

(FLOATING ELECTRODE CELL) Volts vs Ag/AgCl

0.5m $LiClO_4$ - NDA + 1% H_2O

ELECTRODE	CURRENT DENSITY ma/cm^2	DURATION OF TEST	OPEN CIRCUIT POTENTIAL BEFORE TEST Volts vs Ag/AgCl	CLOSED CIRCUIT VOLTAGE Volts vs Ag/AgCl	
				After Current Applied	At the End of the test
Ag (Allis-Chalmers)	a. 30	30 sec.	+0.32V	-1.26	-2.06
	b. 20	2 min.10 sec.		-1.00	-1.70
	c. 10	18 min.		-0.66	-1.92
Pt Type LAA-25 $25mg/cm^2$	15.4	24 min.	+0.5	-0.51	-1.98
Pt Type AA $50\ mg/cm^2$	a. 15	7 hrs. 28 min.	+0.52	-1.16	-1.12
	b. 20	24 min.		-0.42	-1.66

TABLE II

OXYGEN ELECTRODE - CONSTANT CURRENT EXPERIMENT

(FLOATING ELECTRODE CELL) Volts vs Ag/AgCl

0.5m $(Me_3NH)PF_6$-NMA + 1% H_2O

ELECTRODE	CURRENT DENSITY ma/cm^2	DURATION OF TEST	OPEN CIRCUIT POTENTIAL BEFORE TEST Volts vs Ag/AgCl	CLOSED CIRCUIT VOLTAGE Volts vs Ag/AgCl	
				After Current Applied	At the End of the Test
Ag (Allis-Chalmers)	30	23 hrs.	+0.15	-0.77	-1.10
Pt Type ESE 2.5 mg/cm^2	10	10 min.	+0.08	-1.25	-1.79
Pt Type LBB-3C 2.5 mg/cm^2	10	75 min.	+0.32	-1.25	-1.27
Pt Type LAB-6 9 mg/cm^2	a. 10 b. 20 c. 30	50 min. 68 min. 11 min.	+0.37	-0.70 -0.88 -1.77	-0.77 -1.10 -1.88
Pt Type LAA-1 9 mg/cm^2	a. 30 b. 30	8 hrs., 36 min. 7 hrs.,	+0.42 +0.35	-1.27 -1.25	-1.20 -1.31
Pt Type LAA-25 25 mg/cm^2	a. 10 b. 14.8 c. 20	3 hrs., 15 min. 1 hr., 15 min. 1 hr., 10 min.	+0.42	-1.00 -1.10 -1.17	-1.00 -1.10 -1.17
Pt Type AA 50 mg/cm^2	a. 20 b. 30 c. 40	21 hrs., 10 min. 4 hrs., 14 min. 30 min.	+0.42	-1.15 -1.15 -1.25	-0.92 -1.08 -1.27

LITHIUM ANODE

The first semi-annual report included a bibliography and a review of the properties of the lithium anodes. The present report details some experiments designed to obtain a better understanding of the behavior of lithium as an anode in systems which have been studied previously with the air electrode. We have to recognize that the time dedicated to the anode was very short compared to that used to study the oxygen electrode. The principal interest in this case was only to demonstrate that lithium can be oxidized in the non-aqueous electrolyte in which oxygen is reduced and that its current capabilities can be compatible with the air electrode.

The study can be separated in two parts: linear sweep voltammetry and half cell constant current experiments. In these studies small pieces of lithium were pressed in a cup electrode. Mounting the metal in this manner prevented any gross changes in the area of the lithium electrode during the tests which might affect the results. The cup was made from a small piece of 1/8" teflon tubing (Figure 4) and a glass rod containing a platinum contact sealed inside it. This cup electrode filled with lithium performed satisfactorily and is easily fabricated.

LINEAR SWEEP VOLTAMMETRY EXPERIMENTS

Figure 5 shows a typical oxidation of the lithium cup electrode in 0.5m $\emptyset Me_3NPF_6$-NDA. The experiment was started at the zero current potential (-2.77V vs Ag/AgCl) and scanned to positive values at 3 mv/sec. The slope of the i-E curve is very high and reversal during the vertical anodic portion of the curve followed exactly the previous trace. Agitation did not show any effect on the currents observed. These experiments appear to show, at least qualitatively, that the electro-oxidation of lithium in $\emptyset Me_3NPF_6$-NDA is a nearly reversible reaction without strong chemical effects from possible reactions with the electrolyte which could passivate the oxidation of the metal anode.

HALF CELL CONSTANT CURRENT EXPERIMENTS

The constant current experiments with lithium were also run with the cup electrode described in Figure 4. The other electrodes were located appropriately to obtain a uniform current distribution. The test electrolyte was 0.5m $\emptyset Me_3NPF_6$-NDA with the addition of 0.4% by volume of water. This order of concentration of water appears to be the maximum tolerable level without serious gassing problems. The experiment was run at 30 ma/cm^2 for 3 hours 30 minutes showing a steady potential close to -2.5V vs Ag/AgCl.

It should be pointed out here that the maximum tolerable level of water concentration (0.4%) for lithium is far below the minimum water concentration level (1.2%) necessary for maxima current capability of the oxygen electrode. This problem has to be considered in future studies.

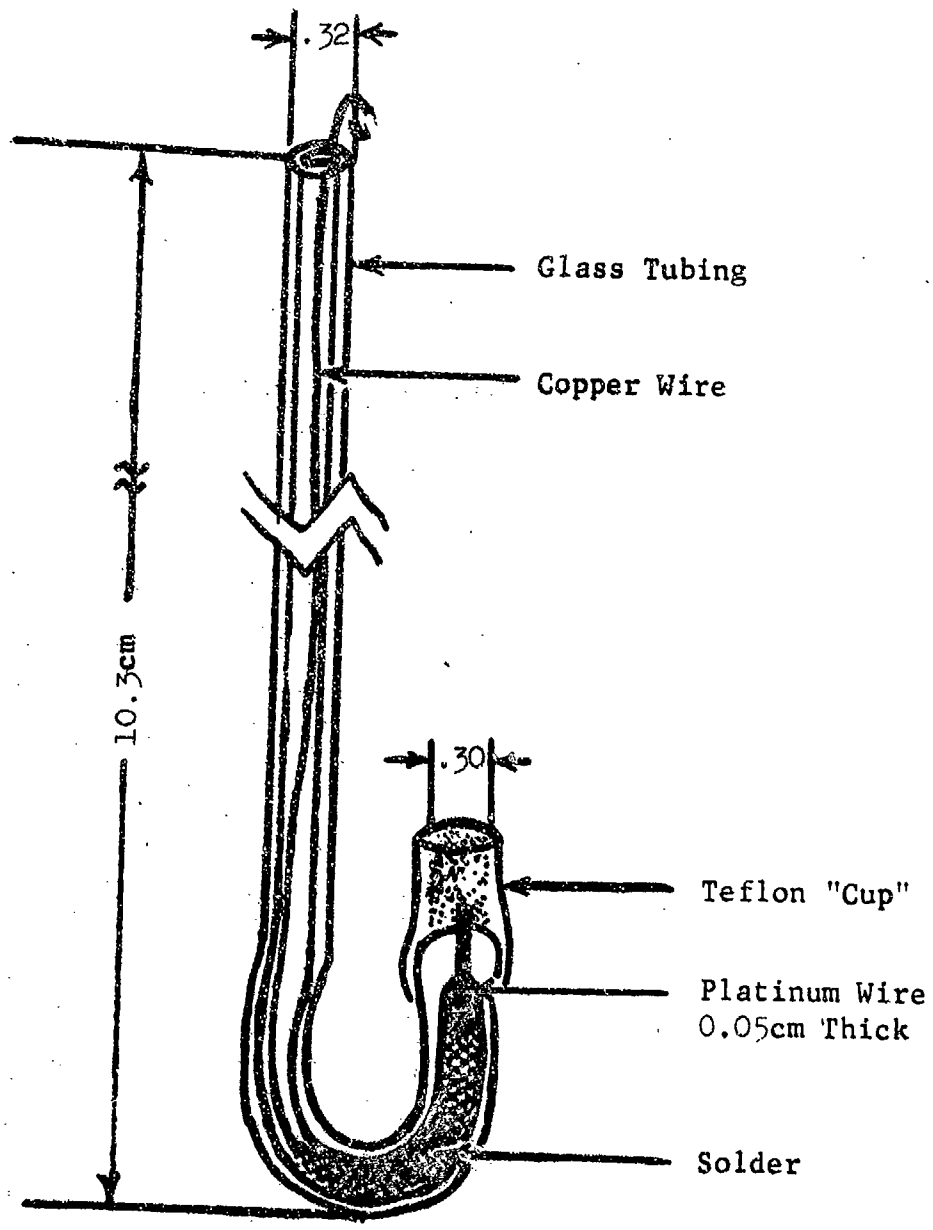


FIGURE 4. THE CUP ELECTRODE

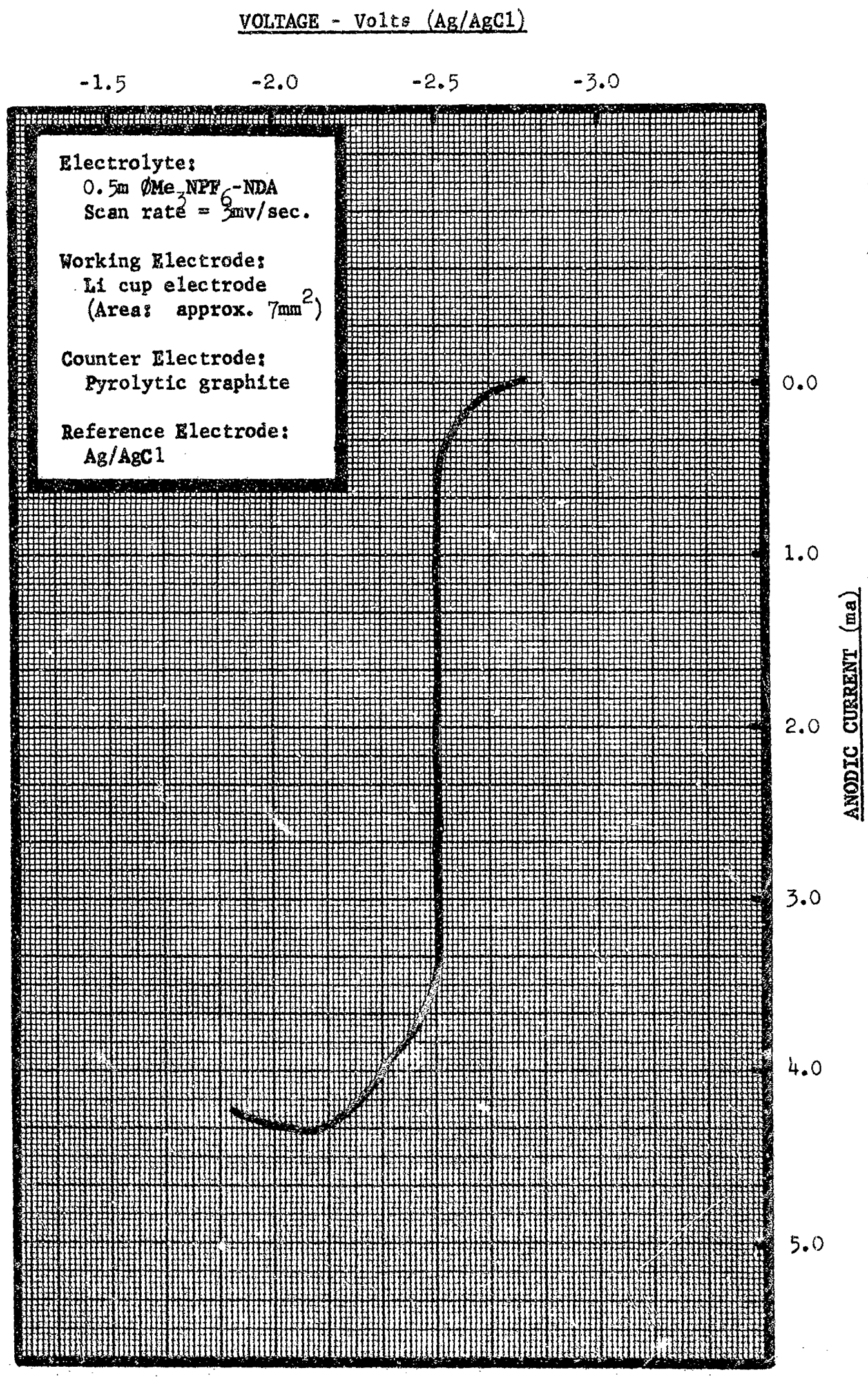


FIGURE 5

TYPICAL OXIDATION OF THE LITHIUM CUP ELECTRODE

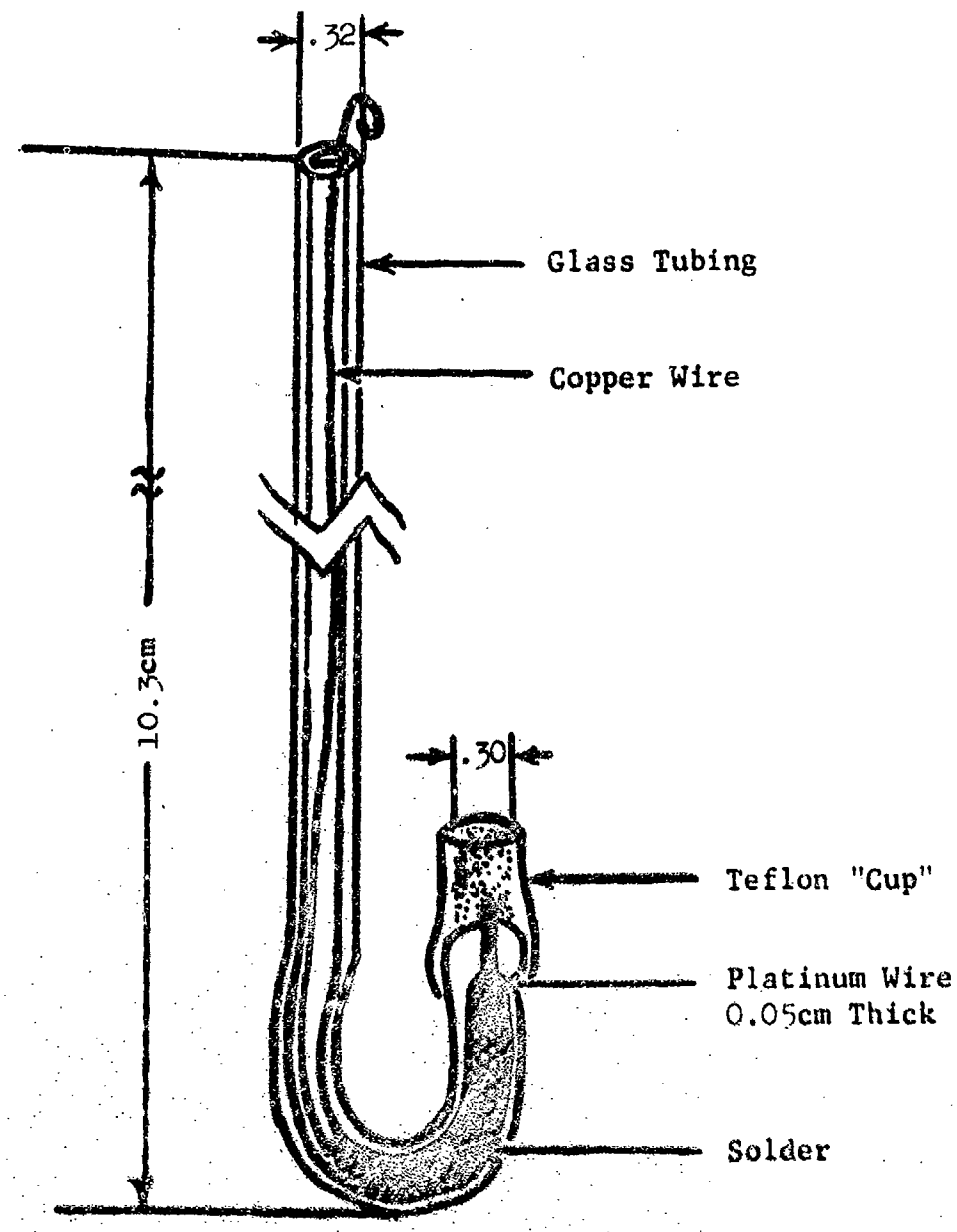


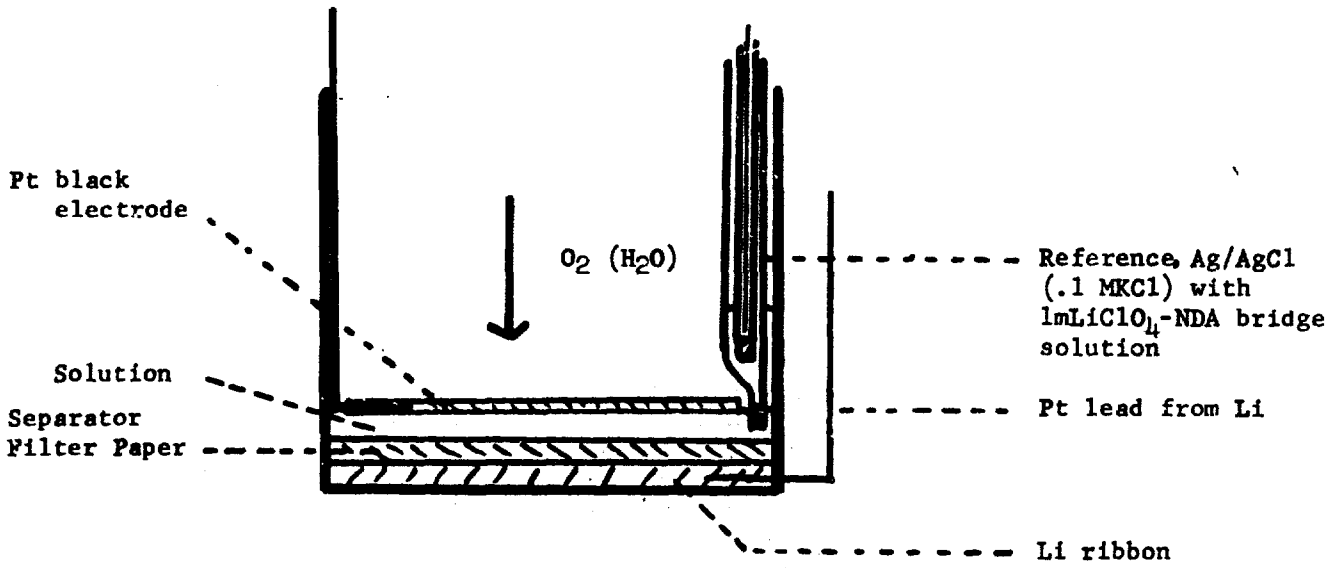
FIGURE 4. THE CUP ELECTRODE

LABORATORY SCALE LITHIUM-MOIST OXYGEN SYSTEM

After the results described in the previous sections were obtained, it appeared relevant to spend some effort in trying a complete cell on laboratory scale. Similar experiments were run at the beginning of the contract (First Semi-Annual Report) but with $LiClO_4$-NDA. In this case we chose phenyltrimethylammonium hexafluorophosphate-NDA which has shown better performance than $LiClO_4$ (Tables I and II) and has been studied extensively during the second part of the present contract. While we realize that any results would not be conclusive, we felt they would at least indicate whether any immediate difficulties results when the individual components were combined in phenyltrimethylammonium hexafluorophosphate-NDA to form the complete system.

Two types of cells were used for the experiments. They appear in Figure 6. Cell 2 has been described previously in the First Semi-Annual Report, and Cell 1 is a very simple design in which application of the floating electrode idea is attempted. The results are summarized in Table III. Two catalyst air electrodes were tested: American Cyanamid Type AA and the silver Allis-Chalmers electrode. There are experiments at 5 ma/cm^2 and 2.8 ma/cm^2 and they were run for very short times, mainly because difficulties in the construction of the systems have created experimental problems. However, some observations can be made about the complete system. First, the stability of the lithium anode electrode was demonstrated, and secondly, the possibility of a 2V battery is promising.

CELL I



CELL II

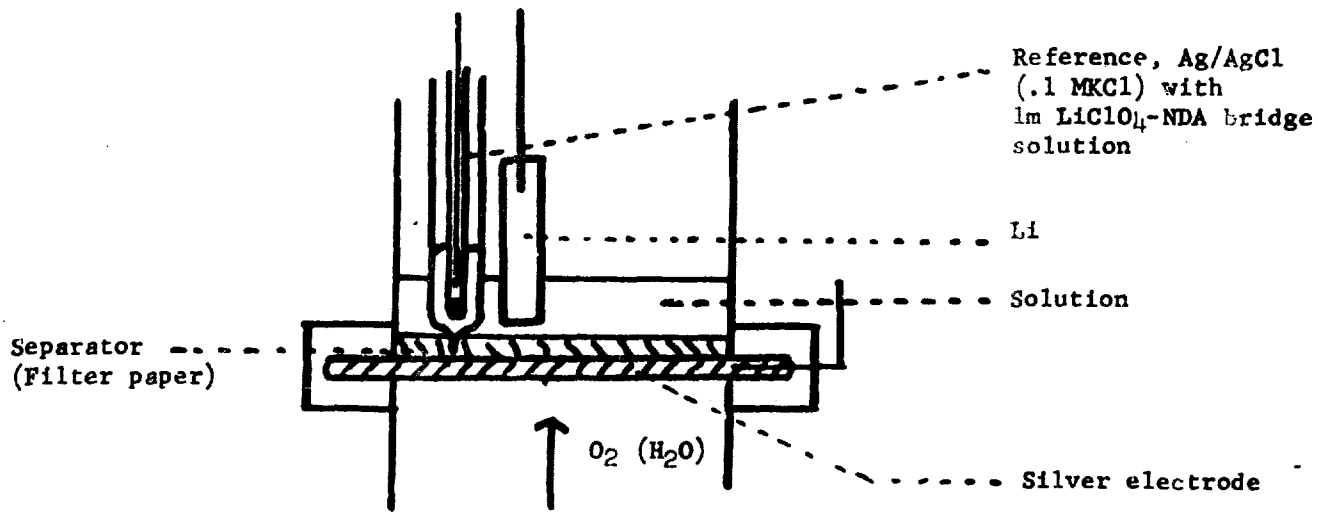


FIGURE 6

CELLS USED FOR THE CONSTANT CURRENT EXPERIMENTS WITH THE

LITHIUM-MOIST OXYGEN SYSTEM

TABLE III

CONSTANT CURRENT EXPERIMENT WITH LABORATORY SCALE

Li - Moist O_2 System

Electrolyte: 0.5m $\emptyset Me_3NPF_6$-NDA + 1% H_2O
Volts vs Ag/AgCl

CELL 1

Li - Pt (Type AA 50mg/cm^2)
Current Density: 5 ma/cm^2
Duration of test: 45 min.

ELECTRODE COUPLE	OPEN CIRCUIT POTENTIAL BEFORE TEST Volts vs Ag/AgCl	CLOSE CIRCUIT VOLTAGE Volts vs Ag/AgCl	
		After Current Applied	At the End of the Test
Li - Pt	+3.15	+2.00	+1.75
Pt - Ref.	+0.25	-0.50	-0.70
Li - Ref.	-2.85	-2.37	-2.37

CELL 2

Li - Ag (Allis-Chalmers)
Current Density: 5 ma/cm^2
Duration of Test: 28 min.

ELECTRODE COUPLE	OPEN CIRCUIT POTENTIAL BEFORE TEST Volts vs Ag/AgCl	CLOSE CIRCUIT VOLTAGE Volts vs Ag/AgCl	
		After Current Applied	At the End of the Test
Li - Ag		+1.32	+1.18
Ag - Ref.		-1.28	-1.40
Li - Ref.		-2.50	-2.50

Current Density: 2.8 ma/cm^2
Duration of Test: 2 hrs. 46 min.

Li - Ag	+3.25	+1.92	+1.76
Ag - Ref.	+0.05	-0.85	-0.92
Li - Ref.	-3.15	-2.55	-2.55

CONCLUSIONS

The principal conclusions reached at the end of the present contract are described below:

I. Oxygen has been found to be electrochemically reducible on platinum and silver in the non-aqueous solvents propylene carbonate and N-nitrosodimethylamine.

A. The reduction can be carried out at much higher rates in nitrosodimethylamine solutions than in propylene carbonate solutions.

B. The reduction of oxygen occurs in two main steps. At -0.6V and -1.75 vs Ag/AgCl in lithium perchlorate-nitrosodimethylamine and at -1.0V and -1.85V vs Ag/AgCl in phenyltrimethylammonium hexafluorophosphate-nitrosodimethylamine.

C. It has also been established that oxygen in non-aqueous media can be accumulated on the platinum electrode surface by a relatively slow adsorption process.

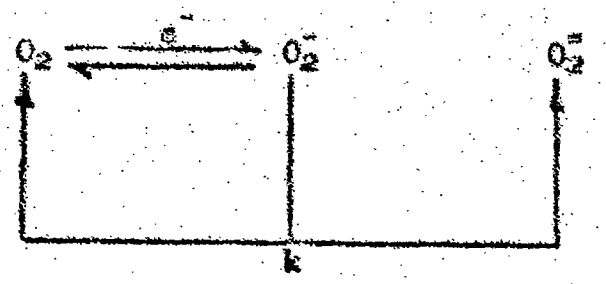
D. The oxygen reduction mechanism on smooth platinum in ϕMe_3NPF_6-NDA appears to be quite complex. The tests indicated that moisture can cause increases which more than double the oxygen reduction current and is therefore highly important to the reduction of oxygen even in non-aqueous media.

The postulated mechanism in this system includes first, a series of surface processes on the electrode (adsorption, interaction between oxygen and platinum, reduction of the film formed) and second, two partially mass transport dependent steps with chemical kinetics complication (E.C.E. mechanism) thus, the following steps occur:

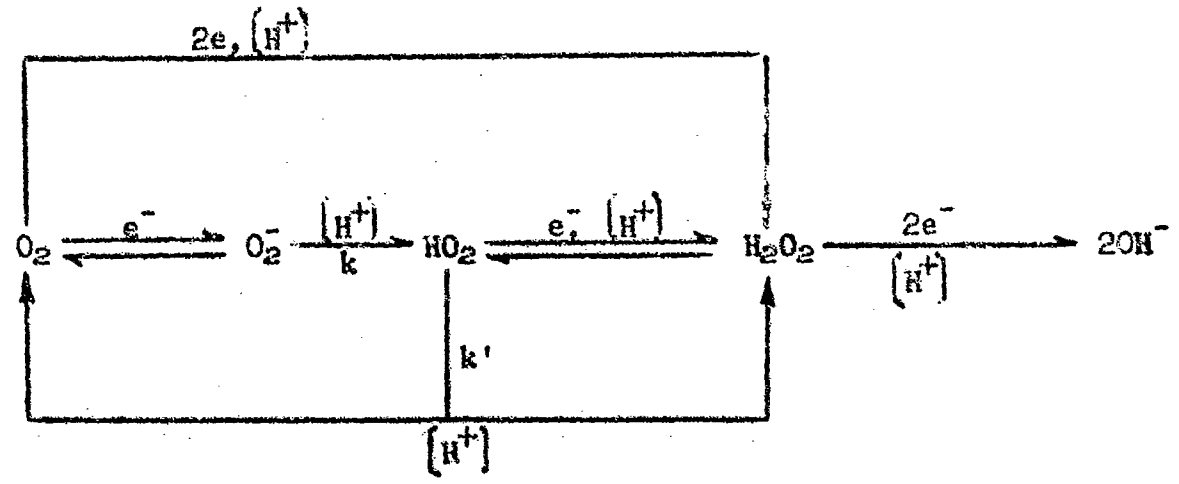
1. O_2 soln $\rightleftharpoons$ O_2 surface

2. O_2 surface + Pt $\longrightarrow$ Pt_xO_y

3. No protons available



4. Protons available



E. The oxygen electrode has shown steady state current delivering capability in ϕMe_3NPF_6-Nitrosodimethylamine (1.0% H_2O). On an American Cyanamid electrode AA (Pt load 50 ma/cm^2) the steady state current for 21 hours was 20 ma/cm^2 at voltages of -1.15 to -0.92V vs Ag/AgCl. On an Allis-Chalmers sintered silver electrode the steady state current for 23 hours was 30 ma/cm^2 in the voltage region from -0.77 to -1.10V vs Ag/AgCl.

II. The lithium electrode in the same electrolyte (but 0.4% H_2O) has demonstrated steady state capability in exploratory experiments at 30 ma/cm^2 and -2.5V vs Ag/AgCl.

III. A small lithium-moist air cell in $LiClO_4$-NDA was shown to operate for periods up to two weeks at low current density (1.0 to 0.5 ma/cm^2 with cell voltage 2.5 to 1.5V). In some recent exploratory cell tests at 5 ma/cm^2 the cell voltage was approximately 2.0V for 45 minutes. The electrodes were a lithium ribbon anode, 1 cm^2 in area, and an American Cyanamid AA cathode, 1 cm^2 in area. The electrolyte was ϕMe_3NPF-NDA (1.0% H_2O).

IV. The silver-silver chloride reference electrode utilized in this work was studied and it was established that it was nonpolarizable under the operating conditions of the tests performed in this program.

V. An analytical method for oxygen in non-aqueous solutions was studied to some extent and applied to determine the oxygen concentration in nitrosodimethylamine solutions. The concentration of oxygen saturated solutions was 5×10^{-3}M.

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APPENDIX

ANALYSIS FOR OXYGEN IN NON-AQUEOUS ELECTROLYTE

From the beginning of the contract we realized the necessity for determining the concentration of oxygen in the non-aqueous electrolytes studied during the progress of the present research. The knowledge of the concentration of oxygen is essential for any quantitative evaluation of the experiments performed.

The Winkler (4) method for determining oxygen concentration has special sources of error with organic materials being one of the most serious interferences. However, other researchers (5,6,7) have used it to evaluate the concentration of oxygen in non-aqueous solutions such as acetonitrile and dimethylsulfoxide.

Coetzee and Kolthoff (5) have proposed another volumetric titration which they claimed was successful for acetonitrile, but unfortunately a complete study is not available. We decided to extend the study of this method and apply it to our research program.

The method as it was reported, is a volumetric titration based on the reaction between oxygen and Fe^{++} in neutral or basic media,

$$pH \geq 7 \qquad O_2 + 4Fe^{++} + 2H_2O \longrightarrow 4Fe^{+++} + 4OH^-$$

and the back titration of the Fe^{++} excess with ceric (Ce^{+4}) in acid solutions:

$$pH = 2 \qquad Fe^{++} + Ce^{+4} \longrightarrow Fe^{+++} + Ce^{+3}$$

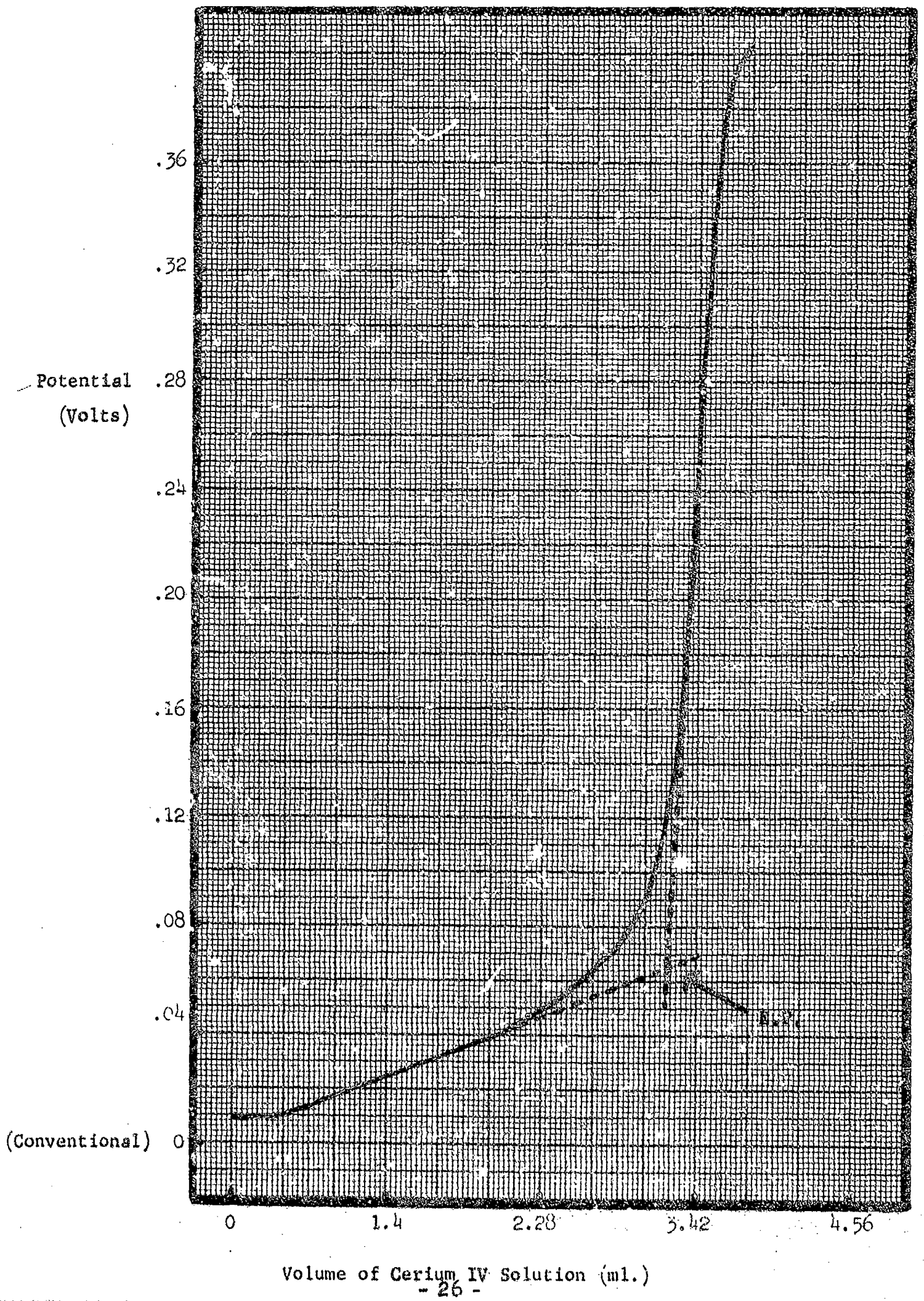
The first approach used was a conventional potentiometric titration using a platinum indicator electrode. However, when the end point of the titration was reached, it was not stable and it dropped down after several seconds making it very difficult to establish a real final value for the titration. This behavior could be explained by a post-reaction between the Ce^{+4} and the NDA solutions. This problem was resolved by the replacement of the conventional potentiometry by a continuous potentiometric titration. By addition of the titrant (Ce^{+4}) at an appropriate continuous flow rate the post-reaction could be minimized. We found that by using a titrant flow rate of 1.14 ml/min. a reproducible end point of the Fe^{+2} titration with Ce^{+4} could be achieved in presence of NDA. We also demonstrated that the end point of the titration of Fe^{++} corresponds to the intersection of the extrapolated lines before and after the sharp increase in potential as is shown in Figure 7.

The technique of the method will be described shortly. The study of the method tool place in the following steps, in the sequence listed:

A. Titration of Fe^{++} with Ce^{+4} in aqueous solutions. Comparison of the end point obtained by conventional potentiometric titration using the method of the second derivative and those by the continuous titration.

FIGURE 7

TYPICAL END POINT OF A CONTINUOUS POTENTIOMETRIC TITRATION



B. Effect of Osmiumtetroxide (OsO_4) as catalyst of the reaction between Fe^{+2} and Ce^{+4}. The intention of the experiments was to improve the definition of the end point by accelerating the reaction and to increase the rise of the potential after the completion of the titration.

C. Effect of the presence of NDA and search for the appropriate flow rate of the titrant.

D. Determination of the concentration of oxygen from oxygen saturated water samples and comparison of the results with expected values found in standard tables.

E. Determination of the concentration of oxygen in NDA solutions.

Following the sequence just described, it was observed that the most important problem was the precipitation of $Fe(OH)_3$ after the reaction between Fe^{+2} and O_2. Apparently it can absorb Fe^{++} and if the $Fe(OH)_3$ is not completely dissolved, the results are erratic. This problem is more noticeable when NDA is present. Several methods were tried in order to minimize the errors. The principal points studied were the following:

1. pH at which the reaction with oxygen occurs.

2. Time during the reaction between O_2 and Fe^{++} in neutral or basic media.

3. Time after the addition of acid which should dissolve the $Fe(OH)_3$ and condition the solution for the back titration with Ce^{+4}.

4. pH in the acid media.

5. Complexing agents in order to eliminate the $Fe(OH)_3$ precipitation: EDTA, sodium tetraborate and sodium pyrophosphate were studied.

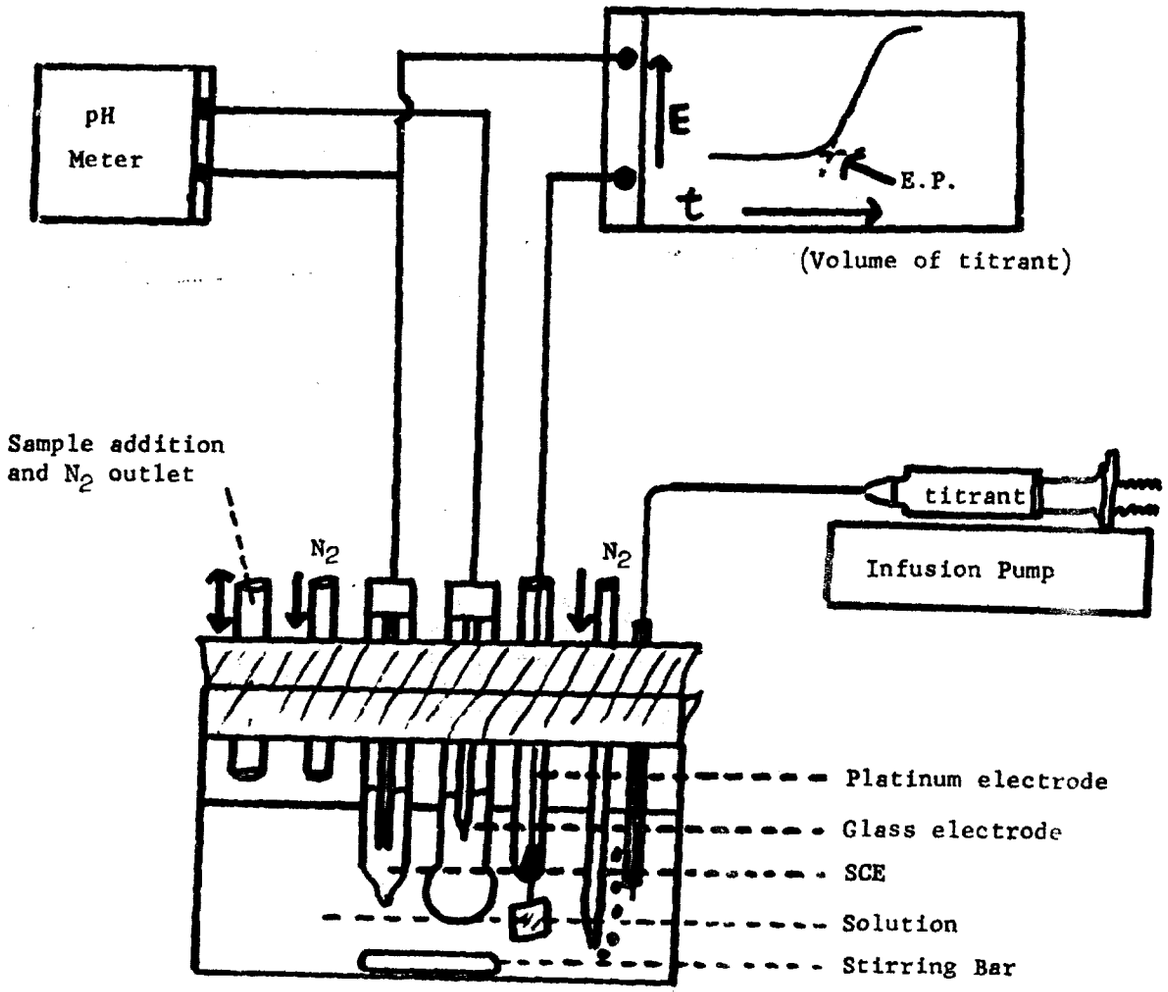
We do not consider that at this moment all the possible variables were studied and as a consequence the study was not finished. We believe that the method can be improved. However, using the method which will be described below we did determine the concentration of oxygen in NDA solution with and without the phenyltrimethylammonium hexafluorophosphate. There was not an appreciable difference, considering the error of the method in both cases. The value obtained from 32 titrations was $5 \pm 1\ 10^{-3}$M. (σ = .0013).

DESCRIPTION OF THE METHOD

Figure 8 describes the set up for the continuous potentiometric titration. Before the addition of the sample air was carefully removed from the solutions by bubbling nitrogen. The titrant was added in a constant flow rate by using a Harvard Apparatus infusion pump Model 975.

FIGURE 8

SETUP FOR THE CONTINUOUS POTENTIOMETRIC TITRATION



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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)*

Globe-Union Inc.
5757 N. Green Bay Avenue
Milwaukee, Wisconsin 53201

2a. REPORT SECURITY CLASSIFICATION

UNCLASSIFIED

2b. GROUP

3. REPORT TITLE

LITHIUM-MOIST AIR BATTERY

4. DESCRIPTIVE NOTES *(Type of report and inclusive dates)*

Final Report, March 1966 - July 1967

5. AUTHOR(S) *(Last name, first name, initial)*

Toni, Jorge E. A.
Zwaagstra, R. L.

6. REPORT DATE

July 1967

7a. TOTAL NO. OF PAGES

46

7b. NO. OF REFS

7

8a. CONTRACT OR GRANT NO.

DA-44-009-AMC-1552(T)

b. PROJECT NO.

1C622001A01202

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

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

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13. ABSTRACT

The principal objective of this program is the study of the feasibility of the lithium-moist air high energy storage battery for use as the power system in vehicles. The primary effort was directed to the characterization of the performance of the air electrode in non-aqueous electrolytes. Oxygen has been found to be reducible on platinum and silver in non-aqueous media. Linear and cyclic sweep voltammetry have been used to study the electrochemical reduction of oxygen on smooth platinum electrodes for the lithium perchlorate-nitrosodimethylamine (NDA) and phenyltrimethylammonium hexafluorophosphate ($\emptyset Me_3NPF_6$) nitrosodimethylamine systems. The reduction of oxygen studied in both of the above systems occurs in two main steps: at -0.6V and -1.75V vs Ag/AgCl for $LiClO_4$-NDA and at -1.0V and -1.85V vs Ag/AgCl for $\emptyset Me_3NPF_6$-NDA. The mechanism of the electrode processes are complex; adsorption effects and chemical kinetics complications have been determined. The effect of the presence of water on the electrochemical reduction of oxygen in $\emptyset Me_3NPF_6$-NDA was studied extensively. The results appear to show that the reduction of oxygen might pass from a one electron reaction in the complete absence of water to a four electron reaction, as in aqueous media, for concentrations of water over 1.2% by volume. A complex series of different mechanisms were postulated for intermediate values of water concentration. (U)

The present report also covers the evaluation of the current capability of the proposed components of the cell: air electrode and lithium anode. It was shown that the oxygen electrode in phenyltrimethylammonium hexafluorophosphate-NDA can support a current of 20 ma/cm^2 for 21 hours at voltages of -1.15 to -0.92 Ag/AgCl using the American Cyanamid electrode AA (Pt load 50 mg/cm^2). (U)

(Continued on next page)

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14. KEY WORDS	LINK A ROLE	LINK A WT	LINK B ROLE	LINK B WT	LINK C ROLE	LINK C WT
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On an Allis-Chalmers sintered silver electrode the steady state current for 23 hours was 30 ma/cm^2 in a voltage range from -0.77 to -1.10 vs Ag/AgCl. The lithium electrode in the same electrolyte has demonstrated steady state capability in exploratory experiments at 30 ma/cm^2 and -2.5V vs Ag/AgCl. Also, small lithium-moist air cells have shown that they can operate at 5 ma/cm^2 with cell voltages of approximately 2.0V for short times. (U)

The present report also includes the study of an analytical method for oxygen determination in non-aqueous media and experiments with the purpose of determining the diffusion coefficient for oxygen and the number of electrons which participate in the reduction. (U)