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LITHIUM-MOIST AIR BATTERY

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FIRST SEMI-ANNUAL REPORT

by

Jorge E.A. Toni, Guy D. McDonald and William E. Elliott

CONTRACT NO. DA-44-009-AMC-1552(T)

U. S. Army Engineer Research and Development Laboratories Fort Belvoir, Virginia 22060

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FIRST SEMI-ANNUAL REPORT

LITHIUM-MOIST AIR BATTERY

Interim Report

by

Jorge E. A. Toni, Guy D. McDonald and William E. Elliott

October 1966

Department of the Army
Research & Development Procurement Office
U. S. Army Engineer Research & Development Laboratories
Fort Belvoir, Virginia 22060

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Applied Research Laboratories
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SUMMARY

The primary objective of this 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:

$$2\ \mathrm{Li} + 1/2\ \mathrm{O_2} + \mathrm{H_2O} \rightleftarrows 2\ \mathrm{LiOH}$$

The purpose of the first six months work in this program was to determine, insofar as possible, the feasibility of the three principle components of a lithium-moist air battery system, i.e., anode, cathode, and electrolyte.

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. The first problem encountered was that of establishing a stable reference electrode. A silver wire reference electrode was found to be unsatisfactory and a compact aqueous Ag/AgCl reference electrode protected from the electrolyte by a nonaqueous salt bridge was developed. Using this reference electrode, the potentials at which oxygen is reduced in various electrolytes was determined using linear scan and cyclic voltammetry.

The solvents (nitrosodimethylamine and propylene carbonate) for this study were chosen on the basis of their previously established ability for giving relatively highly conductive solutions compatible with lithium and silver. The solutes originally planned for use in these solvents were the quaternary ammonium hydroxides because of the desirability of having a relatively high hydroxide concentration in solution. A high hydroxide concentration would insure the formation of lithium hydroxide on the anode surface, thus aiding in the regeneration of the anode and protecting the air electrode from becoming extensively covered with lithium hydroxide. Tetramethylammonium hydroxide failed to have sufficient solubility to be used alone and the evaluation of other quaternary ammonium hydroxide with larger groups substituted on the nitrogen (which would be expected to have greater solubility) were hampered by procurement problems. In lieu of the

quaternary ammonium hydroxides, lithium perchlorate and phenyltrimethylammonium hexafluorophosphate were used.

The oxygen reduction was found to occur in two steps. On a platinum electrode in 1m lithium perchlorate-nitrosodimethylamine these reactions occur at -0.6V and -1.75V versus Ag/AgCl. The current obtainable with air electrode appears to be determined by the rate of adsorption of oxygen at the electrode surface and by the rate of mass transport of oxygen to the electrode surface. Unfortunately, these studies have been somewhat impeded by the presence of some electrochemically active species in the electrolyte which competes with oxygen for sites on the electrode surface. The work carried out in the first six months is largely preliminary in nature and more detailed studies are required before the air electrode in nonaqueous electrolyte will be completely characterized as feasible.

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LIST OF TABLES AND FIGURES

(Continued)

INTRODUCTION

The objective of this program is to determine experimentally the feasibility of a lithium-moist air battery. Three questions required immediate answers:

1. Can lithium perform satisfactorily as an anode in nonaqueous electrolytes?
2. Can oxygen be reduced in nonaqueous electrolytes, or, in other words, will the air electrode perform in organic electrolyte systems?
3. If the answer to both of these questions is affirmative, can the lithium air battery operate satisfactorily as a unit in these same organic electrolytes?

Based both on our own work and that of other investigators these questions were affirmatively answered. The feasibility of the lithium anode in nonaqueous electrolytes has already been well established.* Other investigators, as well as ourselves, have shown that the reduction of oxygen could be carried out electrochemically in nonaqueous electrolytes**, as will be further discussed later in the report. However, to our knowledge, no lithium-air battery has ever been described. Prior to this report a small laboratory lithium-air battery was operated at low current densities.

The purpose of the experimental program under this contract was to provide more detailed information in the following areas:

1. General Performance:

   What levels of current density, potential, etc., or, in other words, performance, can be expected from the air electrode? (Will it be comparable to fuel cell air electrodes?)

2. Effect of Materials:

   a. What organic electrolyte should be selected for optimum operation of the lithium-air cell?

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* See references 1 to 7, page viii.

** See references 8 to 17, page viii.

b. Since it is contemplated that moisture will be used with the air electrode, can it be shown that this is advantageous to the performance of the air electrode in nonaqueous media, or will the air electrode perform just as satisfactorily without the addition of moisture?

c. Are the catalysts which are utilized for oxygen or air electrodes in fuel cells satisfactory, or do they need modification for operation in nonaqueous media?

d. Will impurities in the electrolyte systems cause deterioration of electrode performance?

3. Compatibility (Chemical and Electrochemical):

Will the lithium electrode be compatible with the moist air electrode both chemically and electrochemically?

The above areas are of significance in determining the feasibility of the lithium-air battery, but it is recognized that the list is not complete.

This report covering the work accomplished in the first six months of this contract is divided into the following sections for ease in following the work:

A. REFERENCE ELECTRODE
B. LITHIUM ANODE
C. ELECTROLYTE
D. AIR ELECTRODE
E. IMPURITY STUDIES
F. FUTURE WORK

LITERATURE REVIEW

Research with lithium electrodes has been carried on by many investigators[1-7] and a great deal of information on the performance characteristics of this electrode is already known. Investigators who have studied the secondary characteristics of the lithium electrodes have claimed that it can be completely and efficiently recharged.[1]

While there is a vast amount of information scattered throughout the literature on the reduction of oxygen in aqueous media, there is very little which covers the kinetics of oxygen reduction in nonaqueous systems. In the aqueous system, it is generally considered that the reduction takes place in two steps, usually involving formation of the peroxide ion in the first step and reduction of the peroxide ion in the second step. Several investigators[8-10] have noted similar behavior in the reduction or oxygen in nonaqueous solutions, although the potentials are generally more negative than those in water. This negative shift in potential has been attributed to the lack of available protons in the nonaqueous media. Addition of proton containing materials to aprotic electrolytes has resulted in shifts to more positive potentials closer to aqueous values. More recent studies in nonaqueous media[11-17] have postulated that a single electron reduction of oxygen occurs for which the product is superoxide. At least two groups of investigators[11,14,17] have examined the product of this reaction by electron spin resonance to try to confirm the presence of the superoxide species. Chemical methods have also been used.[11] The solvents which have been used in the above studies include: acetonitrile, dimethylsulfoxide, N-methylacetamide, pyridine, methylene chloride, acetone and N,N-dimethylformamide. Among the salts which have been used as solutes was tetrabutylammonium perchlorate. The electrochemical methods which have been used include the use of polarography, AC polarography, voltammetry and chronopotentiometry. While the latest papers[11-17] are much more sophisticated than the earlier ones, they appear to ignore, in most cases, adsorption as a factor in the reduction of oxygen and our experimental work indicates that this may be a very important factor in oxygen electrode performance.

---

[1] Selim, R. G.; Hill, K. R. and Rao, M.L.B.; Mallory Co., Inc., Final Reports, NASA Contracts NAS3-6017 and NAS3-2780.

[2] Globe-Union Inc., Third to Eighth Quarterly Reports, NASA Contract NAS3-6015.

[3] McCallum, J.; Semones, D.E.; Trevethan, D.G.; and Faust, G.L.; Battelle Memorial Institute, First and Second Quarterly Report, Air Force Aero-Propulsion Laboratories, Contracts AF33(615)-2619 and AF33(615)-1195.

[4] Bauman, J.F.; and Adams, G.V.; Lockheed Missiles & Space Co., Final Report, Air Force Aero-Propulsion Laboratory, Contract AF33(657)-11709.

[5] Selim, R.G.; and Hill, K.R.; Mallory Co., Inc., Final Report NASA Contract NAS3-2780.

[6] Allison, Paper presented at Electrochem. Soc. Mtg., S.F., May 1965.

[7] Livingston, NASA Contracts NAS3-7632, NAS3-6004, and NAS3-2775.

[8] Coetzee, J.F. and Kolthoff, I.M., J.Am.Chem.Soc., 79, 6110 (1957)

[9] Kolthoff, I.M. and Reddy, T.B., J. Electrochem. Soc., 108, 980 (1961)

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[11] Maricle, D.L. and Hodgson, W.G., Anal. Chem., 37, 1562 (1965)

[12] Maricle, D.L., Office of Naval Research & Advanced Research Project Agency Contract NONR 4200(00), Tech. Rept. 4 (July 1964)

[13] Peover, M.E. and White, B.S., Chem. Comm. No. 10, 183 (1965)

[14] Slough, W., Chem. Comm. No. 10, 184 (1965)

[15] Johnson, E.L.; Pool, K.H. and Hamm, R.E., Anal. Chem., 38, 183 (1966)

[16] Sawyer, D.T. and Roberts, J.L., Jr., J. Electroanal. Chem., 12, 90 (1966)

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A. REFERENCE ELECTRODE

A. REFERENCE ELECTRODE

Silver electrodes are widely used as reference electrodes in nonaqueous solutions. The stability of the potential of these electrodes is in doubt. An alternative electrode was constructed which had the simplicity and versatility of the silver electrode, but which demonstrated considerably greater potential stability than the silver electrode. This electrode will be used in place of silver whenever precise potential measurements are required.

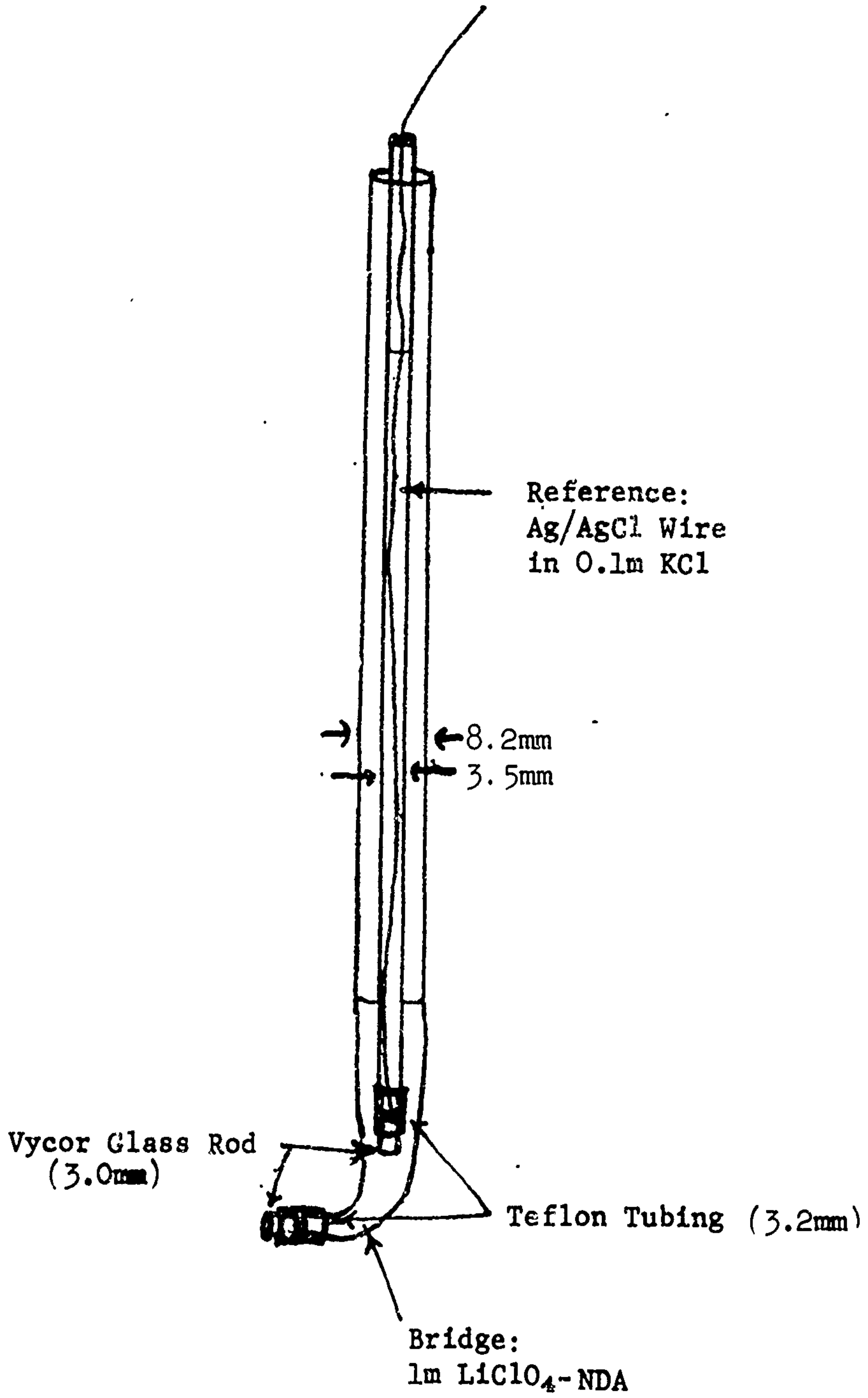
Figure 1, page 2, is a schematic drawing of this alternative reference electrode. It consists of a conventional silver-silver chloride electrode in an aqueous 0.1M KCl solution separated from the working electrolyte by a nonaqueous salt bridge (1m $LiClO_4$-Nitrosodimethylamine). A small piece of porous glass rod (Vycor No. 7930) is used to isolate the KCl solution from the salt bridge and the salt bridge from the solution of interest. The lower end of the salt bridge is curved to permit positioning of the reference electrode very close to the working electrode. The appropriate adjustment of the levels of the KCl and the salt bridge solutions will minimize the possibilities of diffusion of NDA in the reference electrode. The salt bridge is designed for easy cleaning after it has been contaminated by ions from the working electrolyte and the reference electrode.

The reversibility of this reference electrode was investigated using the classical method of applying small overpotentials to both sides of the equilibrium values and determining if there is any hysteresis. For this experiment, the cell consisted of the electrode shown in Figure 1, page 6, as the working electrode, a saturated Calomel Electrode (Beckmann 39170) as reference, a pyrolytic graphite rod as counter electrode and 1M $LiPF_6$-N-nitrosodimethylamine as electrolyte. The overpotentials were applied using potentiostatic equipment and were measured using a digital voltmeter through the use of a load resistor. The overpotentials were applied manually and the measurements were made within 10-20 seconds (after a steady value was achieved). The results are shown in Figure 2, page 3.

On the first run, a maximum hysteresis of only 0.6mv was observed. All other determination coincided. The potential as determined from Figure 2, page 3, of the Ag/AgCl (0.1M KCl), 1M $LiClO_4$-Nitrosodimethylamine reference electrode is -0.0249 ± 0.0003 volts relative to the saturated Calomel Electrode (SCE). For our experiment, a value of -0.025 volts versus SCE will be used.

The same reversibility test was attempted with a silver electrode. No steady potential value could be obtained so that it was impossible to determine its reversibility or its potential.

FIGURE 1. SILVER-SILVER CHLORIDE REFERENCE ELECTRODE



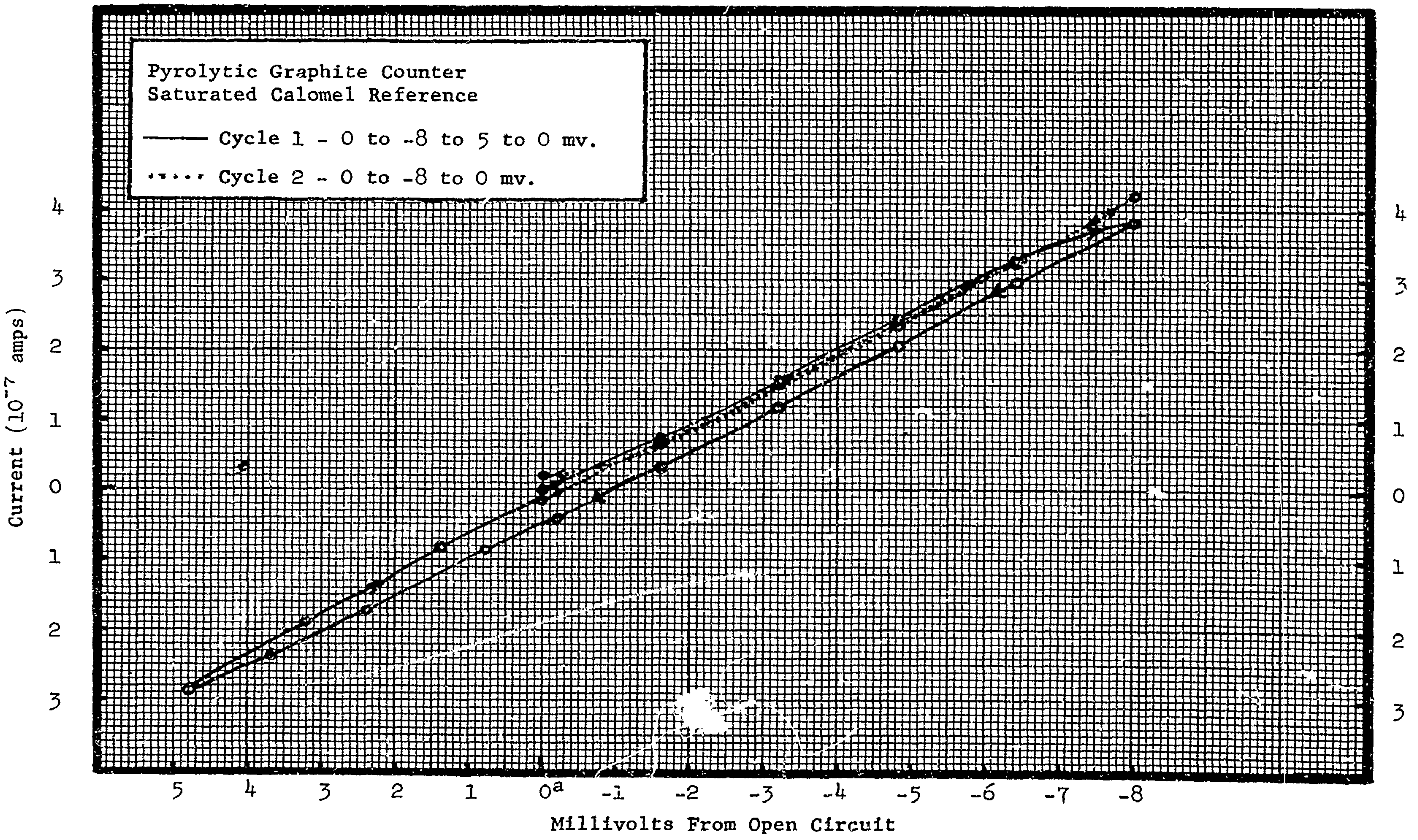


FIGURE 2. <u>REFERENCE ELECTRODE STUDY - HYSTERESIS OF SILVER-SILVER CHLORIDE ELECTRODE</u>

[a] Open circuit value of this reference electrode is -24.9mv versus a saturated calomel reference electrode.

B. LITHIUM ANODE

The selection of the lithium anode is based upon the high energy and low equivalent weight possessed by the metal. In fact, lithium should produce one of the lightest weight practical anodes. It has already been established[1-7] that lithium metal will exhibit a potential very close to the thermodynamic reversible potential, i.e., approximately three volts versus the standard hydrogen electrode in organic nonaqueous electrolytes. It has also been demonstrated that lithium can carry adequate current densities in this type of electrolyte. Thus, lithium becomes the obvious choice for an anode material. The postulated electrode reaction for lithium in the proposed battery is as follows:

$$\mathrm{Li} + \mathrm{OH}^- \rightleftarrows \mathrm{LiOH} + e^-$$

Considerable work has already been done on lithium in nonaqueous electrolytes as has been indicated in the literature section.

Possibly the greatest problem arising from the use of the lithium electrode is its chemical reactivity in the electrolyte systems. It is obvious that since it reacts with any protonic solvent to release hydrogen that it would be unstable in such media. We have already found several solvents sufficiently aprotic to be used with a secondary lithium electrode. Most of the work in attempting to establish information on rechargeability has been done in the cyclic ester propylene carbonate[1] However, lithium appears to be satisfactorily stable, at least for primary batteries, in a solvent discovered here--nitrosodimethylamine (NDA). Therefore, because the amine forms solutions of higher conductance than propylene carbonate (PC), it is the solvent of first choice in this program.

Preliminary exploratory tests run on lithium anodes using cell design 2, Figure 3, page 5, with pyrolytic graphite replaced by lithium, have demonstrated that even if the lithium electrode is coated with a layer of lithium hydroxide it is capable of satisfactory performance at low current density for extended periods of exposure as shown in Table I, page 6.

---

[1] Selim, R.G.; Hill, K.R. and Rao, M.L.B.; Mallory Co., Inc., Final Reports, NASA Contracts NAS3-6017 and NAS3-2780.

[2] Globe-Union Inc., Third to Eighth Quarterly Reports, NASA Contract NAS3-6015.

[3] McCallum, J.; Semones, D.E.; Trevethan, D.G.; and Faust, G.L.; Battelle Memorial Institute, First and Second Quarterly Report, Air Force Aero-Propulsion Laboratories, Contracts AF33(615)-2619 and AF33(615)-1195.

[4] Bauman, J.F.; and Adams, G.V.; Lockheed Missiles & Space Co., Final Report, Air Force Aero-Propulsion Laboratory, Contract AF33(657)-11709.

[5] Selim, R.G.; and Hill, K.R.; Mallory Co., Inc., Final Report NASA Contract NAS3-2780.

[6] Allison, Paper presented at Electrochem. Soc. Mtg., S.F., May 1965.

[7] Livingston, NASA Contracts NAS3-7632, NAS3-6004, and NAS3-2775.

FIGURE 3. TEST CELL DESIGN NO. 2

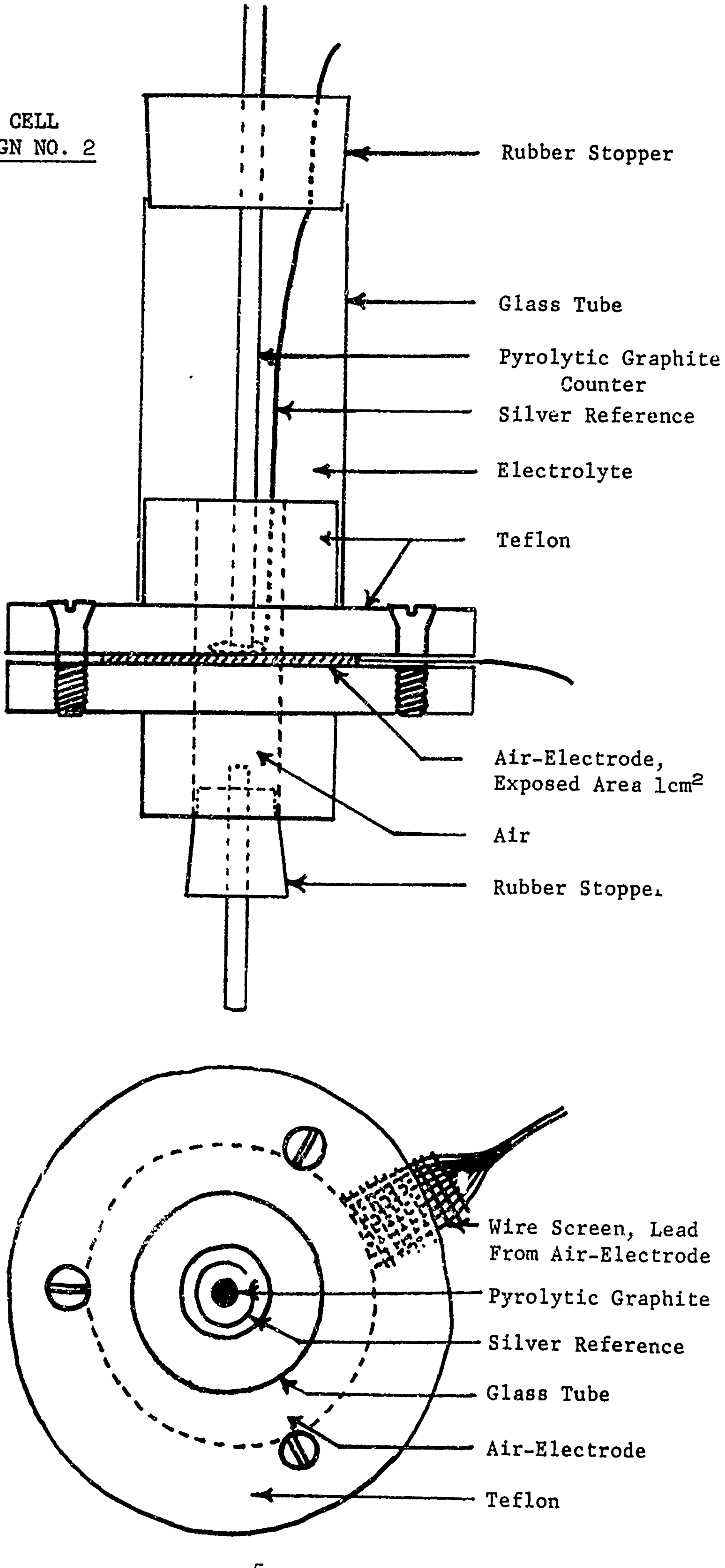


TABLE I. SILVER-AIR DISCHARGES IN LiClO$_4$-NITROSODIMETHYLAMINE

Time (Hours)	Current (ma/cm^2)	Voltages versus Ag-Reference	
		Cathode	Anode
	Spontaneous Discharge of Fresh Ag-Air Electrode		
42	1.0 to 0.7	0.00 to -0.30	-2.70 to -2.50
24	0.7 to 0.5	-0.30 to -0.80	-2.50
36	0.5 to 0.4	-0.80 to -1.10	-2.50
102			
	Forced Discharge of Cleaned Ag-Air Electrode		
37	1.0	0.0 to -0.30	-2.9 to -2.6
0.5	1.0	-0.3 to -0.80	-2.6
11	1.0	-0.8 to -1.10	-2.6
0.5	1.0	-1.1 to -2.10	-2.6
49.0			

C. ELECTROLYTE

The desired qualities for an electrolyte are high conductivity, electrochemical stability and compatibility with other components of the system. It is now generally recognized that properties such as solution viscosity, dielectric constant, concentration and solvent-solute interactions are important factors contributing to the conductance of electrolytes. Previous investigations[2] of over 200 solute-solvent systems led to the discovery of 100 systems with specific conductivity greater than 10^{-2} $\text{ohm}^{-1}\ \text{cm}^{-1}$. This conductivity while being about one order of magnitude lower than that found in aqueous electrolytes was found to be adequate for battery systems. Also, during the course of the above studies, it was possible to correlate several of the physical properties of the electrolyte into the empirical relationship given below:

$$L = \frac{k \cdot C \cdot \epsilon^m}{1000\eta}$$

where L = specific conductance in $\text{ohm}^{-1}\ \text{cm}^{-1}$.

C = concentration in terms of normality (or molarity where 1:1 electrolytes are involved).

ϵ = dielectric constant of the solvent.

m = exponent on the dielectric constant.

η = viscosity in centipoises of the solution at concentration C.

k = arbitrary constant with the units centipoise cm^2/ohm-equivalent.

This expression has several limitations, one being that it does not include any term to account for temperature effects.

Another is that the solubility of compounds is not considered. This is obviously a matter of essential importance in conductance. However, the solubility of the compounds is relatively easily determined separately. In fact, a single determination of the conductance at a given concentration can be decisive in determining whether satisfactory conductivity can be with a system. In addition, some general factors are known to contribute to solubility, such as:

1. Materials possessing similar structures are usually soluble in each other.

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[2] Globe-Union Inc., Third to Eighth Quarterly Reports, NASA Contract NAS3-6015.

2. Crystalline substances of low lattice energy are more soluble than those possessing high lattice energies. This is generally the case for salts possessing at least one large ion.

3. Certain solvent functional groups promote solubility.

From a consideration of these general empirical relations, an ideal electrolyte would consist of a solvent of low molecular weight, low molar volume, high dielectric constant, and appropriate solvating functional groups to promote solubility and dissociation. The solute should have low lattice energy, i.e., low charge density, ions or solvated ions of high mobility, and be chemically stable. The system should be electrochemically stable (high decomposition potentials), and have a low temperature coefficient of conductance.

One of the first solvents investigated on a previous contract was dimethylformamide $(CH_3)_2NCHO$. This compound had low viscosity, high dielectric constant, and good coordination ability. Unfortunately, this solvent appears to have an active hydrogen which means that lithium is unstable in it. Tetramethylurea, $(CH_3)_2NCON(CH_3)_2$, was next investigated. This solvent exhibited exceptionally good coordinating ability but its solutions had high viscosity. Acetonitrile, $(CH_3)CN$, with low viscosity and high dielectric constant gave highly conductive solutions. However, the keto-enol equilibrium in acetonitrile led to low lithium stability. N-nitrosodimethylamine, $(CH_3)_2NNO$, had a higher dielectric constant than the previously mentioned solvents, a low viscosity and good coordinating ability. Solutions made with N-nitrosodimethylamine were found to have higher conductivities than those made with the other organic solvents and lithium is apparently stable in this solvent. For this reason, N-nitrosodimethylamine is the solvent of choice for this project. For comparison purposes, the cyclic ether propylene carbonate, CH_3CHCH_2OCO, was also studied since this solvent has been extensively used by other researchers[1]. The physical properties of these solvents are tabulated below. The techniques used for purifying and characterizing these solvents are given in Appendix I.

Physical Properties of Nonaqueous Solvents

	N-Nitrosodimethylamine	Propylene Carbonate
Boiling point	27°C	83°C
Boiling pressure	1mm	1mm
Specific conductances, 1 molal, 26°C	2.37×10^{-5} ohm^{-1} cm^{-1}	1.1×10^{-5} ohm^{-1} cm^{-1}
Index of refraction, 28°C	1.434	1.419
Density, 25°C	0.995 g/cc	1.201 g/cc
Viscosity, 25°C	0.865 centipoises	2.52 centipoises
Dielectric constant (23°C)	53.0	69.0

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[1] Selim, R.G.; Hill, K.R. and Rao, M.L.B; Mallory Co., Inc., Final Reports, NASA Contracts NAS3-6017 and NAS3-2780.

Since it is desirable to form lithium hydroxide on the anode surface, a source of hydroxide ions must be present in the electrolyte. It was proposed that quaternary ammonium hydroxides would provide a supply of hydroxide ions. To date, only tetramethylammonium hydroxide has been investigated because of procurement problems. It was found that this material lacks appreciable solutility (soluble to less than 0.2 molal) in nitrosodimethylamine to be used by itself. The effect of adding this material to a solution containing another solute, phenyltrimethylammonium hexafluorophosphate, will be discussed in a later section. Other quaternary ammonium hydroxides with larger alkyl groups will be investigated. In place of the desired quaternary ammonium hydroxides, lithium perchlorate, lithium hexafluorophosphate and phenyltrimethylammonium hexafluorophosphate have been studied.

The specific conductivity of one molal solutions of these solutes were determined using the equipment described in Appendix I.

Specific Conductance of Electrolytes (ohm^{-1} cm^{-1})

Solute/Solvent	N-Nitrosodimethylamine	Propylene Carbonate
Lithium perchlorate	1.61×10^{-2} (28°C)	4.63×10^{-3} (28°C)
Lithium hexafluorophosphate	2.06×10^{-2} (28°C)	1.58×10^{-3} (28°C)
Phenyltrimethylammonium hexafluorophosphate	2.12×10^{-2} (27°C)	0.97×10^{-3} (28°C)
*Tetramethylammonium hydroxide	6.03×10^{-4} (28°C)	------
*Tetramethylammonium hydroxide, phenyltrimethylammonium hexafluorophosphate	1.84×10^{-2} (30°C)	------

* Solubility of tetramethylammonium hydroxide is less than 0.2 molal.

D. AIR ELECTRODE

In order to determine the feasibility of the air electrode, the kinetics of oxygen reduction must be investigated.

The kinetic studies were performed using voltammetry (linear scans and cyclic scans of potential). In certain circumstances the potentials were held constant at given values and given lengths of time to study the effect of potentiostatic holds on the peak current and potentials of the oxygen reduction waves and of any other reducible electroactive species present in the system. The methods utilized are based on those developed by Shain et al.[18-21]

The voltammetric results can be quite diagnostic of the kinetics when data are obtained at various scan rates so that the ratio of the peak current to the square root of the rate of scan is plotted against the scan rate. For example, it is possible by these methods to determine the presence of adsorbed species and the presence of chemical reactions preceding or following the electron transfer reaction. From the studies made to date, it appears that the oxygen reduction is limited on smooth platinum by a slow adsorption process. There also appears to be under certain conditions mass transport limited reactions (see Page 15). The reduction of oxygen in both anhydrous nonaqueous electrolytes and in the presence of moisture exhibited a two-step reduction; (peak potentials were about -0.6 volts and -1.75 volts versus Ag/AgCl). Unfortunately, all of the above conclusions cannot be stated definitively at this time because an impurity was found which interacts with the oxygen on the electrode surface causes spurious effects. The addition of water to the systems was found to increase the oxygen reduction peaks and cause them to shift to more positive potentials. While there still remains a substantial amount of work to be done to characterize the air electrode in nonaqueous media, the conclusions reached to date are significant since they point out factors which are limiting this electrode's performance and even in the presence of these effects it is possible to operate the air electrode for long periods of time at low current densities (1ma/cm^2). It should therefore be expected that when some of the impeding processes or products are removed from the system, the electrode will perform at a much higher level.

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[18] Nicholson, R.S. and Shain, I., Anal. Chem., 36, 706 (1964)
[19] Nicholson, R.S. and Shain, I., Anal. Chem., 37, 178 (1965)
[20] Polcyn, D.S. and Shain, I., Anal. Chem., 38, 370 (1966)
[21] Polcyn, D.S. and Shain, I., Anal. Chem., 38, 376 (1966)

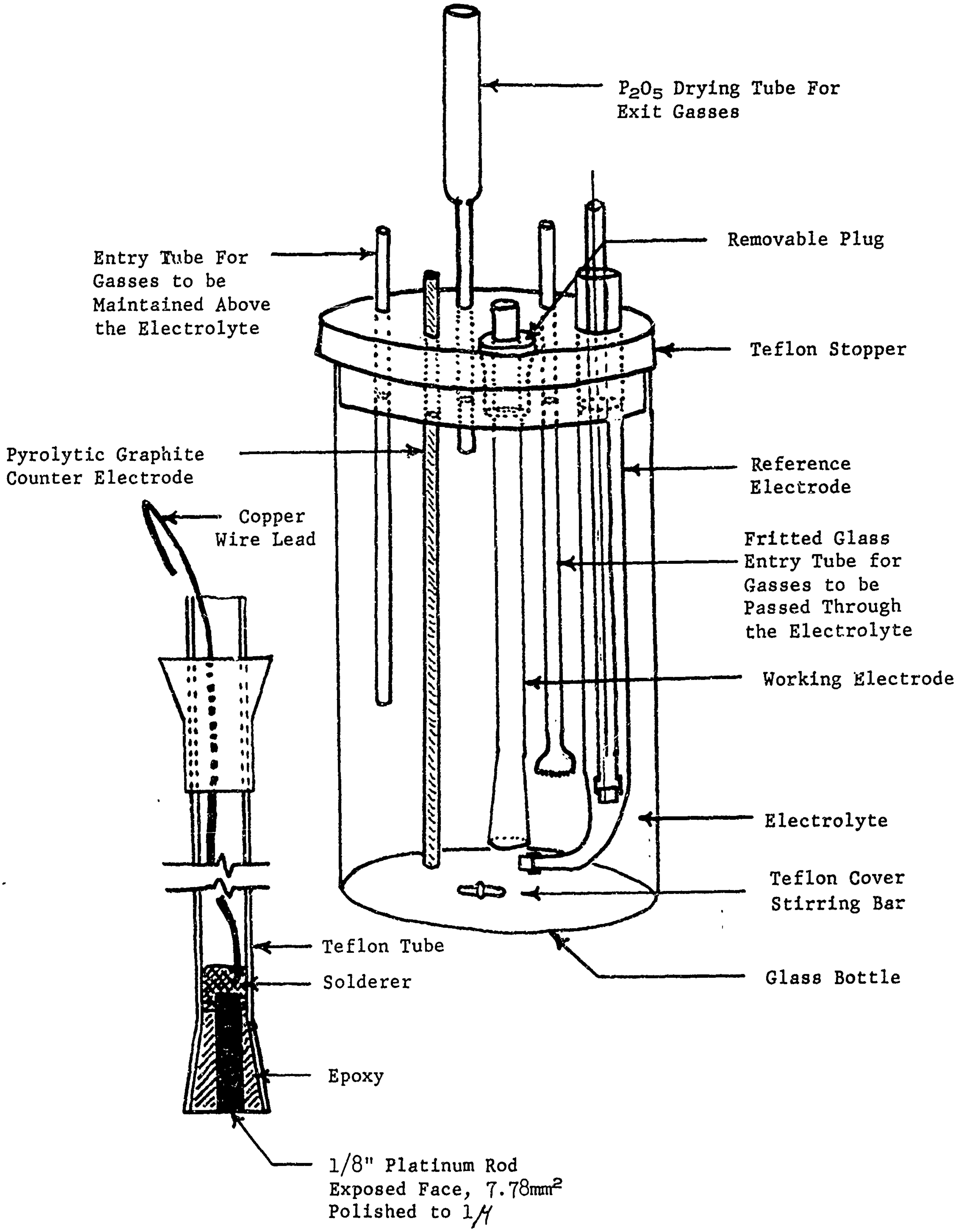
A cell similar in design to a polarographic cell (Figure 4, page 12, cell No. 3) was used for the kinetic study of the oxygen reduction. The electrodes could be easily interchanged and the electrolyte in the cell could be purged with nitrogen to eliminate the oxygen content or could be saturated with oxygen, depending upon the experiment. The electrolyte could be agitated if desired. The working electrode used in this cell was a bright platinum disc (Figure 4, page 12). The reference electrode used a Ag/AgCl with a salt bridge containing one molal lithium perchlorate-nitrosodimethylamine (see "Reference Electrode" section). A pyrolytic graphite counter electrode was used. Based on the exploratory experiments (see Appendix II) the electrolyte which gave the best performance was lithium perchlorate-nitrosodimethylamine and it was therefore used for the kinetic study.

Bright platinum disc electrodes were used as working electrodes during the course of this investigation in an attempt to minimize the problems encountered previously while using the platinum black electrodes, namely, lack of reproducibility, contamination, and uncertainty as to the condition of the surface (see Appendix II). The currents from these bright platinum electrodes, as would be expected, were considerably lower than for the corresponding black platinum electrodes of the same geometric area. In our experiments with the bright platinum electrode, currents were approximately 20-25 times lower than for the American Cyanamid platinum electrode.

The objective of these studies was to determine whether oxygen reduction waves could be observed and at what potentials they would occur. In addition, we were interested in finding out whether the oxygen reduction would take place in two steps in the nonaqueous electrolyte. Indeed, two peaks were observed in the solution one molal in lithium perchlorate with nitrosodimethylamine as the solvent, Figure 5-a, page 13. The cyclic voltammetric sweep shown in this figure could be considered typical of the two-step oxygen reduction at the platinum electrode. The first wave has a peak potential at -0.63 volts versus Ag/AgCl and the second one at -1.75 volts versus Ag/AgCl. An anodic peak was also observed on the reverse scan at approximately -1.0 volts but it is not well-defined and possibly due to an impurity. This peak did not seem to be directly related to any of the reduction peaks.

One of the most pronounced effects noted with oxygen saturated solutions was the effect of a prior potentiostatic hold of the initial potential on the resulting current-potential curves. A comparison of the curves obtained showed that much larger peak currents were obtained in the cases where a hold at zero volts versus Ag/AgCl was made prior to the scan, than for the curves obtained without a prior potentiostatic hold. Figures 5-a and 5-b, pages 13 and 14, show the curves obtained with and without potentiostatic holds and also show the corresponding residual current due to an impurity present in the electrolyte.

FIGURE 4. TEST CELL DESIGN NO. 3



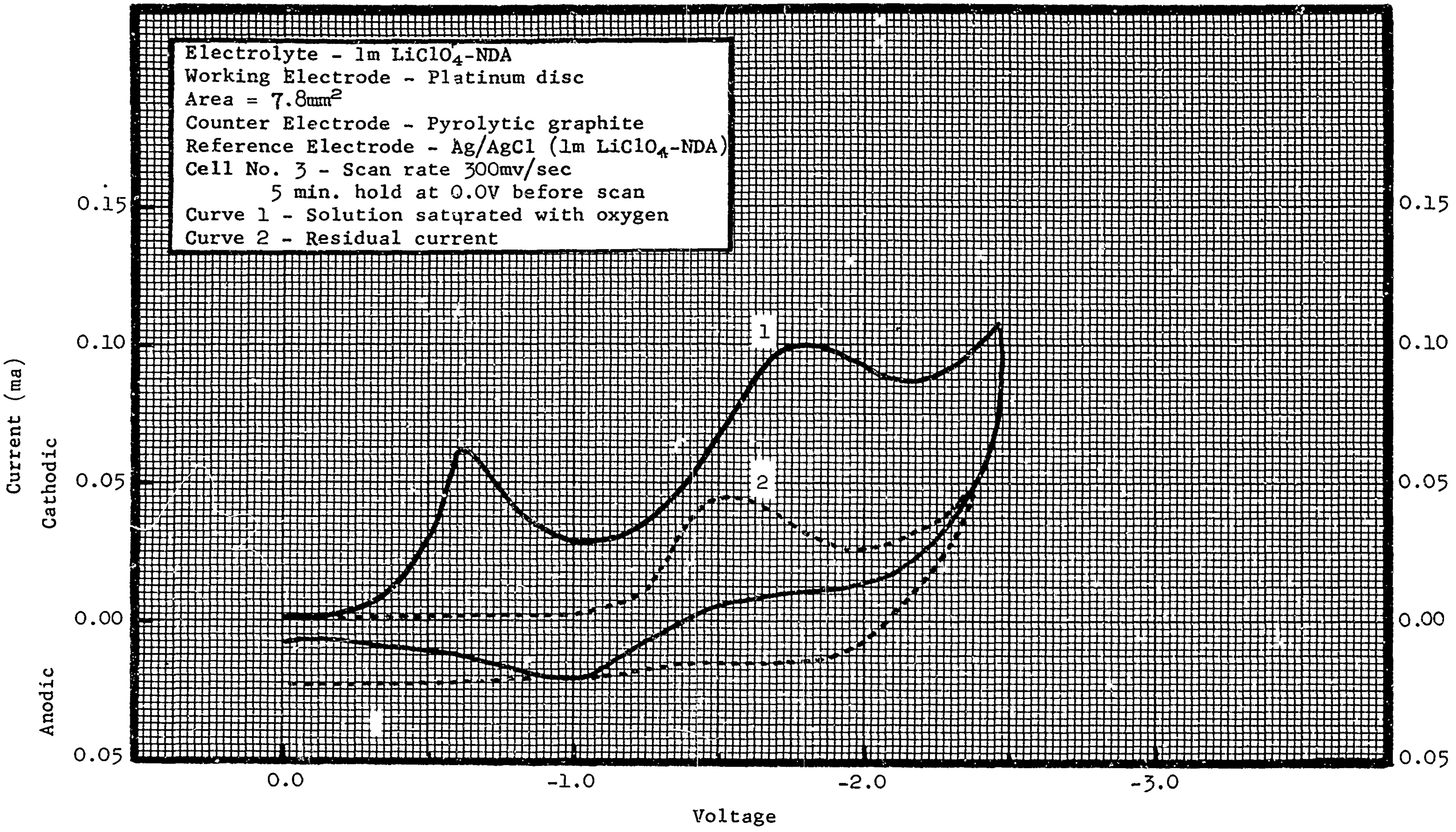


FIGURE 5. CYCLIC VOLTAMMOGRAM OF OXYGEN WITH A SMOOTH PLATINUM DISC ELECTRODE IN 1m $LiClO_4$-NDA

Figure 5-a. 5 minute hold at 0.0V prior to scans.

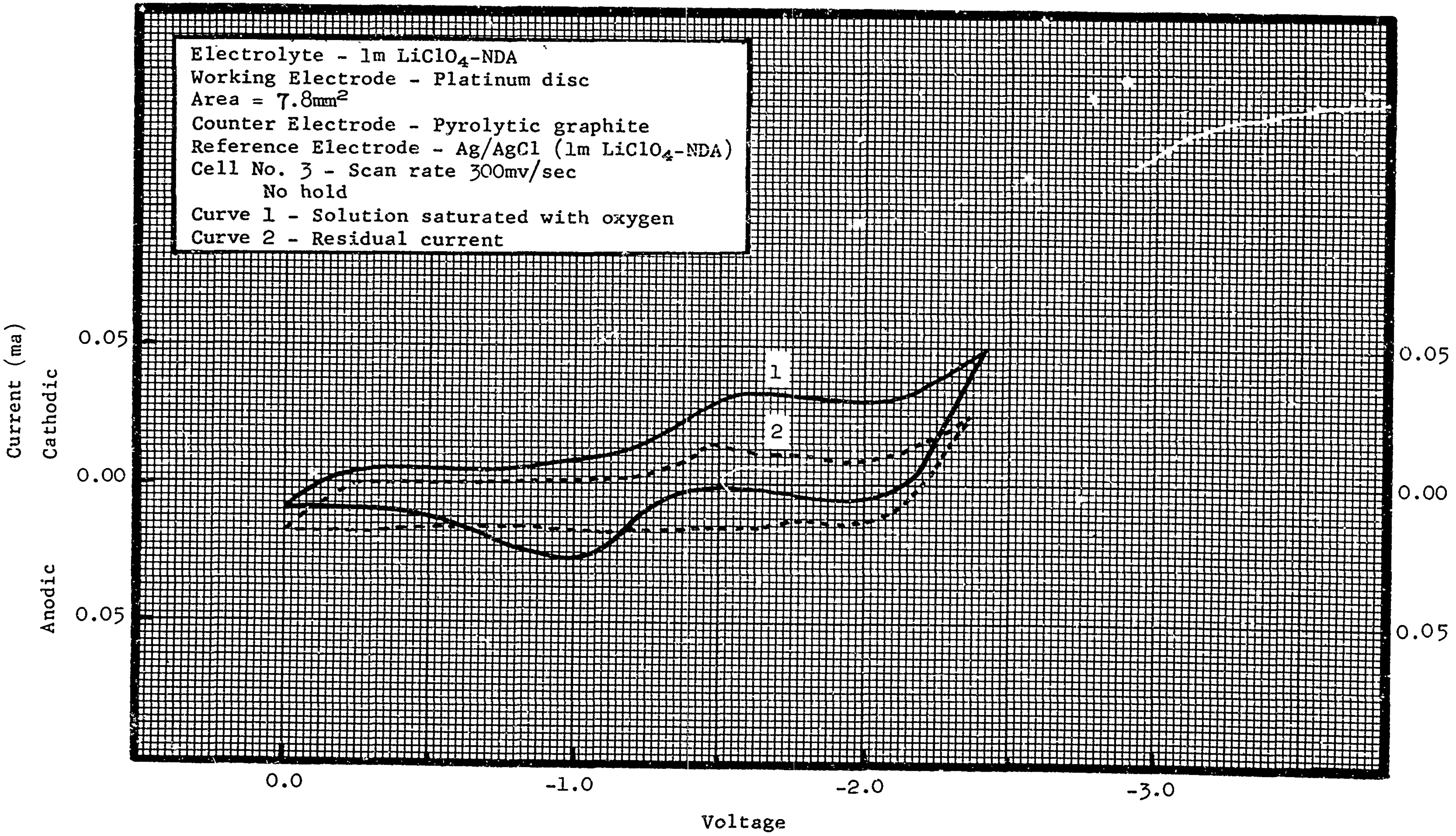


FIGURE 5. CYCLIC VOLTAMMOGRAM OF OXYGEN WITH A SMOOTH PLATINUM DISC ELECTRODE IN 1m $LiClO_4$-NDA

Figure 5-b. No hold prior to scans.

The peak current obtained after a potentiostatic hold depends upon the length of time the electrode is held at that potential. The highest peak current is a steady state value which is obtained after an approximately 5-minute hold (Figure 6, pages 16 and 17). The first peak in each scan shown in Figure 6 is larger and sharper than those shown in Figure 5, pages 13 and 14, because the second series was run on an electrolyte containing a larger amount of the impurity. A comparison of the two electrolytes will be made later.

During the time the potential was held constant, the current was very close to zero. The number of coulombs involved in the potentiostatic hold is much smaller than the number of coulombs under the subsequent residual current curve. This suggests that an adsorption process occurs during the hold. The effect of agitation during the hold on the subsequent scan as shown in Figure 7, page 18, provides additional evidence for this hypothesis. The curve with the larger peaks was obtained with agitation. (Agitation did not affect the current while the initial potential was held constant.) The same behavior is shown in Figure 8, page 19. In this figure, there are three curves, one without a prior hold, one with a hold without agitation and one with a hold with agitation. The difference between the last two curves is quite pronounced with agitation causing a considerable increase in the peak height found on the subsequent scan. Thus, the above data would indicate that the chemisorption rate was limited mainly by the rate of transport of the adsorbing species through the solution by diffusion and convection.

There is also evidence that the mass transport process affects the rate of the oxygen reduction as expected. When the electrolyte is agitated during the scan itself, the oxygen peaks are also considerably larger (Figure 9, page 20). These experiments suggest that there are two sources limiting the oxygen reduction current, one attributable to the rate the species is adsorbed and the other being the rate of mass transport of oxygen to the electrode.

The effect of scan rate on the oxygen reduction wave was investigated in two series of experiments. The main difference between the two series was the concentration of the impurity in the electrolyte. If the concentration of the impurity is proportional to the peak height, then the impurity in series II, Figure 11-a, page 28, would be approximately four times larger than that found in series I, Figure 10-a, page 21. The only other difference between series I in Figure 10, pages 21 to 27, and series II, Figure 11, pages 28 to 33, is the length of the constant potential hold prior to scanning and the length of time the electrolyte was allowed to rest prior to the scan. For series I, a three minute initial potential hold with agitation was used, no rest period, and for series II a 5-minute hold with agitation was used, followed by a 30-second rest at 0.0V vs. Ag/AgCl. A comparison of series I and series II revealed several prominent features. The ratio between the first and second peaks is larger for series II than for series I, the currents are much larger for all peaks in series II, and the first peak was shifted to more positive values in the second series relative to the first series. These studies show the enormous influence which the impurity had on the oxygen reduction.

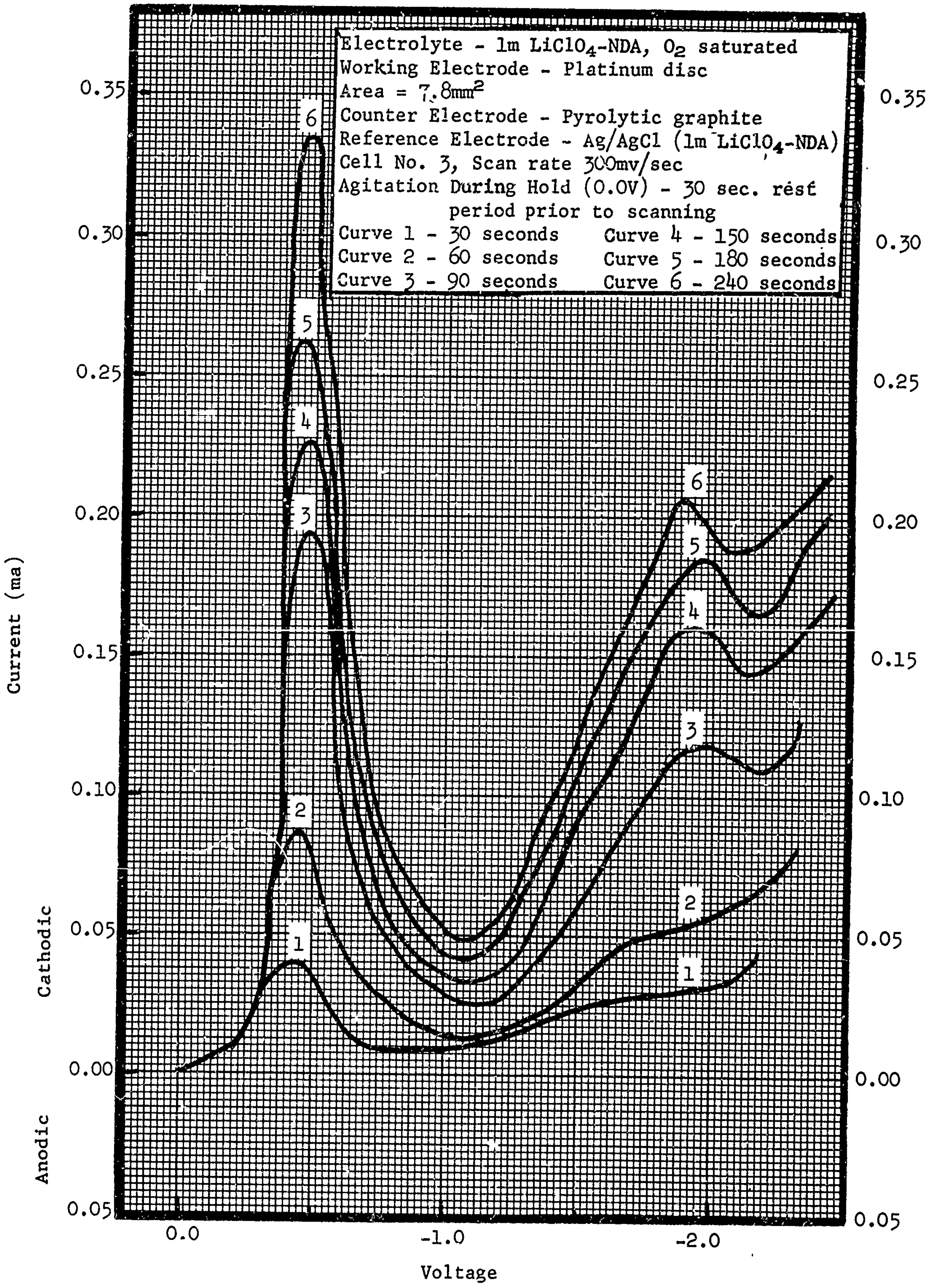


FIGURE 6. EFFECT OF HOLDING AT OV ON OXYGEN REDUCTION

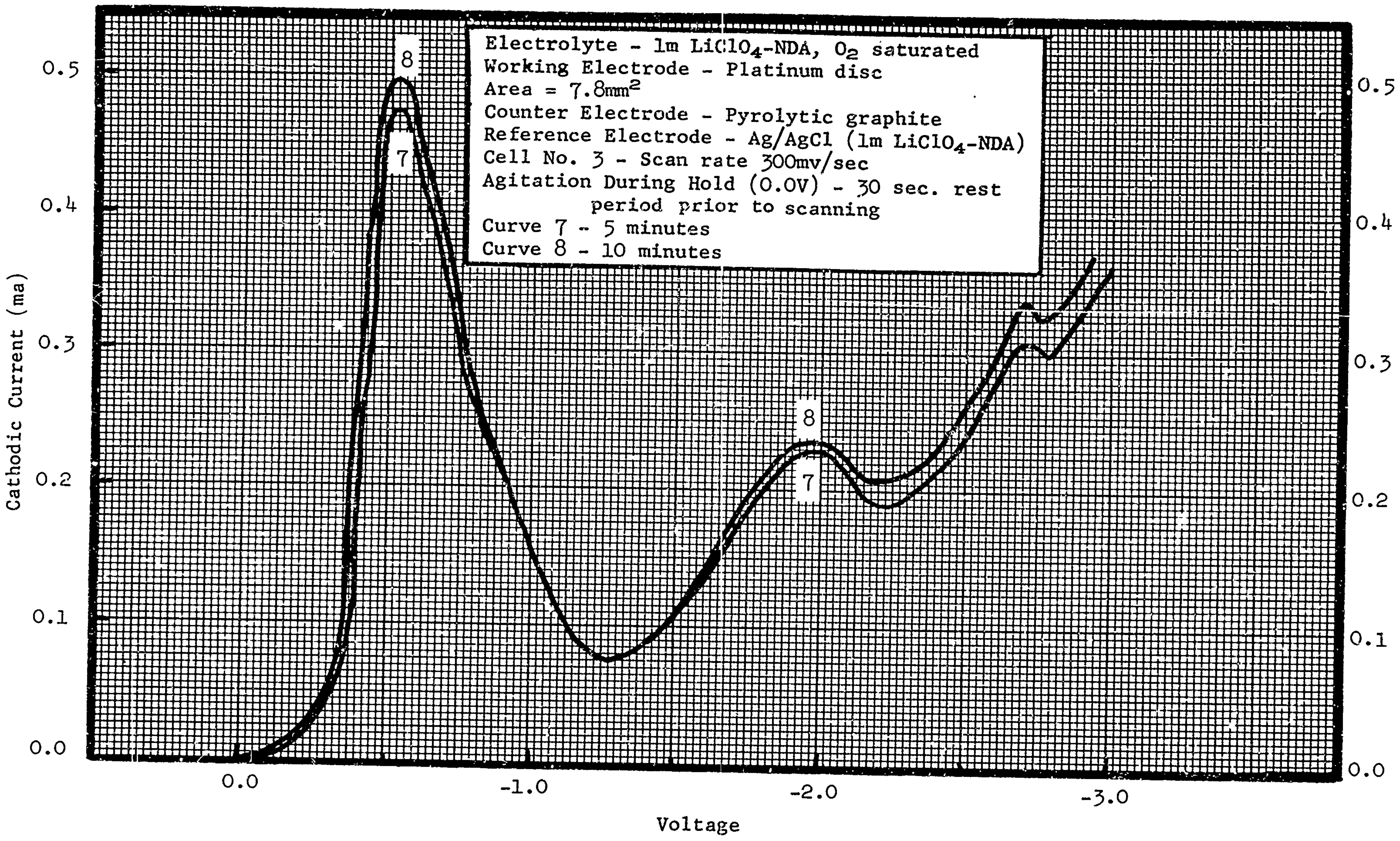


FIGURE 6. EFFECT OF HOLDING AT OV ON OXYGEN REDUCTION (Continued)

(Continued)

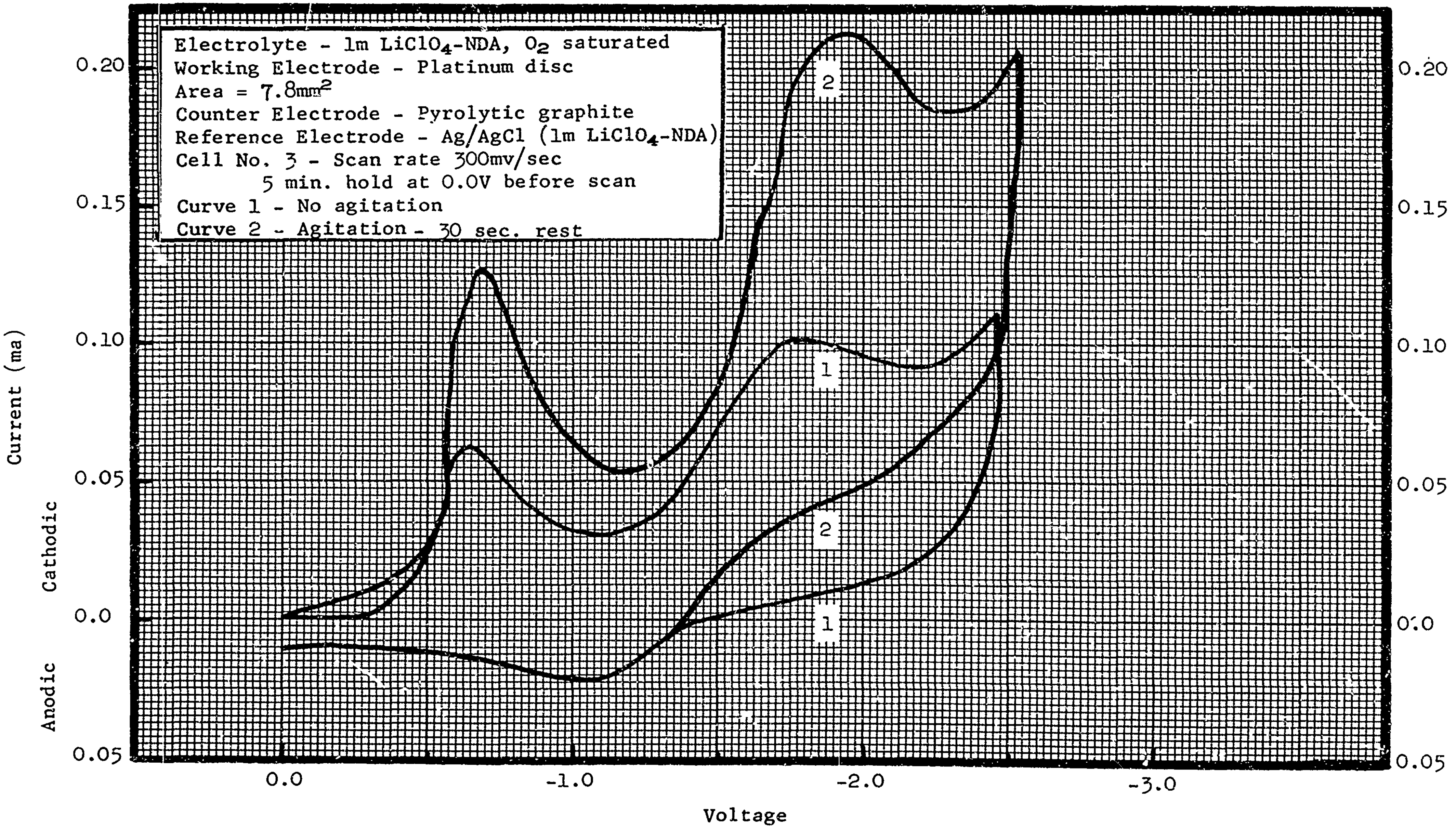


FIGURE 7. EFFECT OF AGITATION DURING THE HOLD

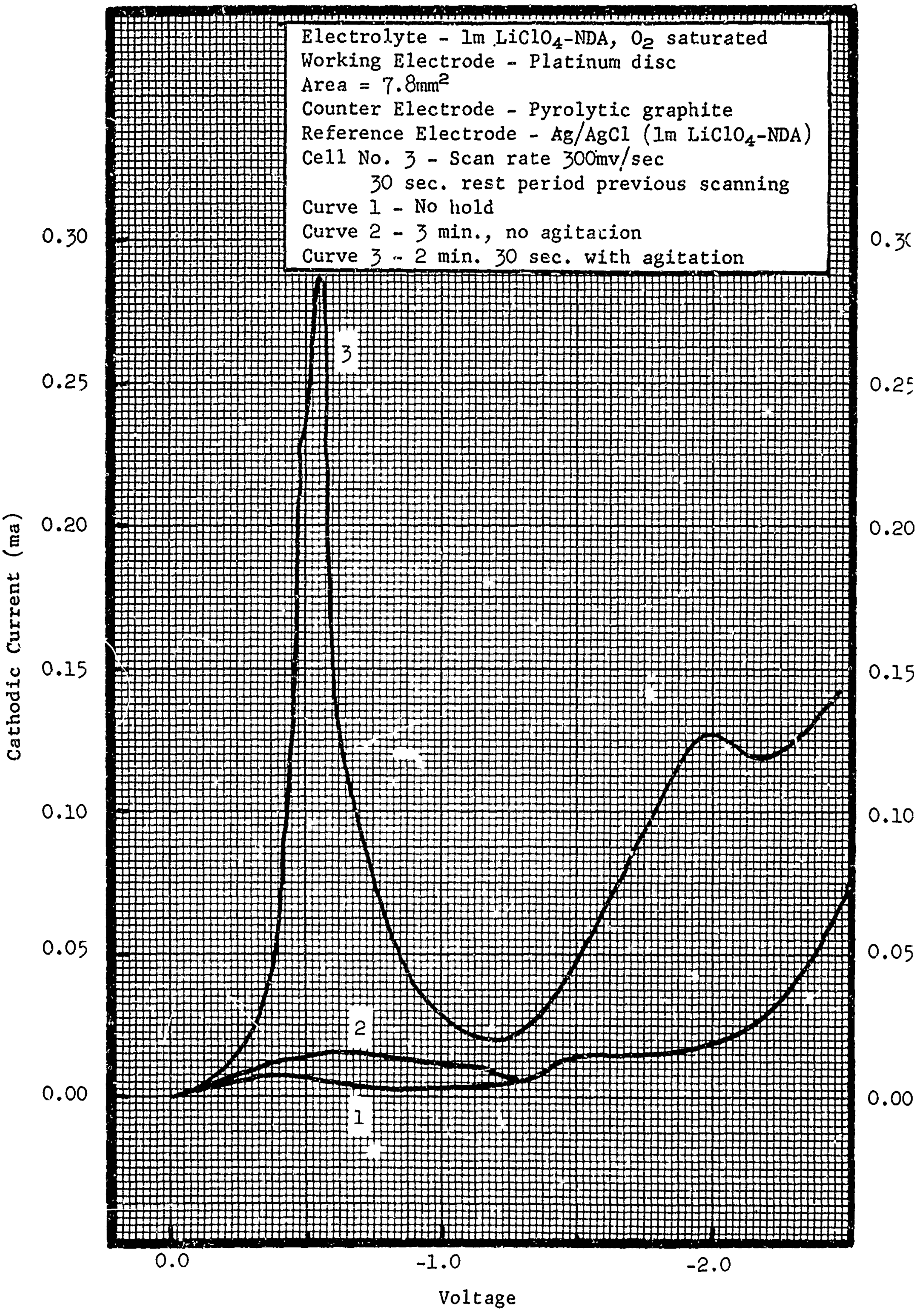


FIGURE 8. <u>EFFECT OF AGITATION DURING HOLD AT OV ON OXYGEN REDUCTION</u>

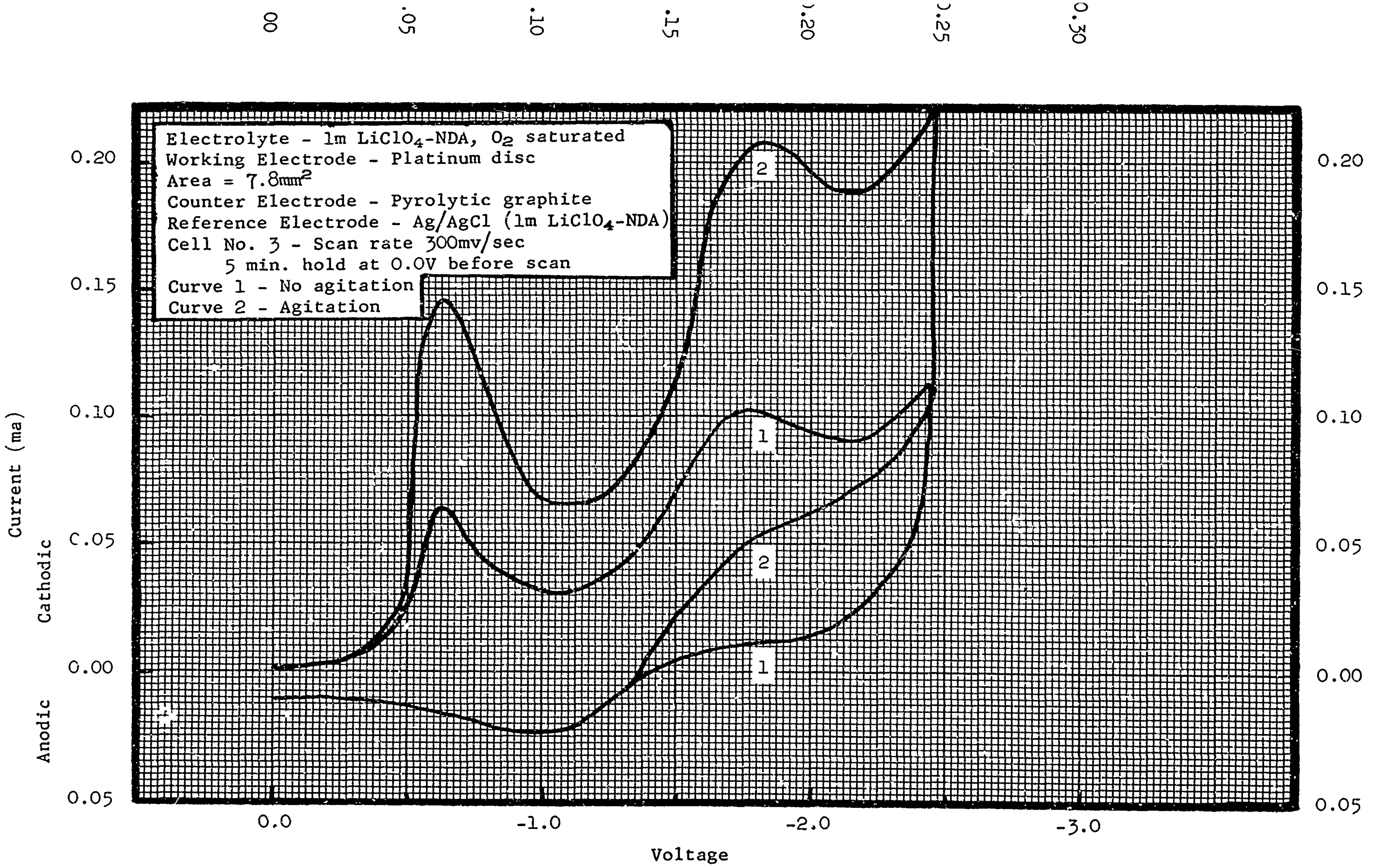


FIGURE 9. **EFFECT OF AGITATION DURING SCANNING ON OXYGEN REDUCTION**

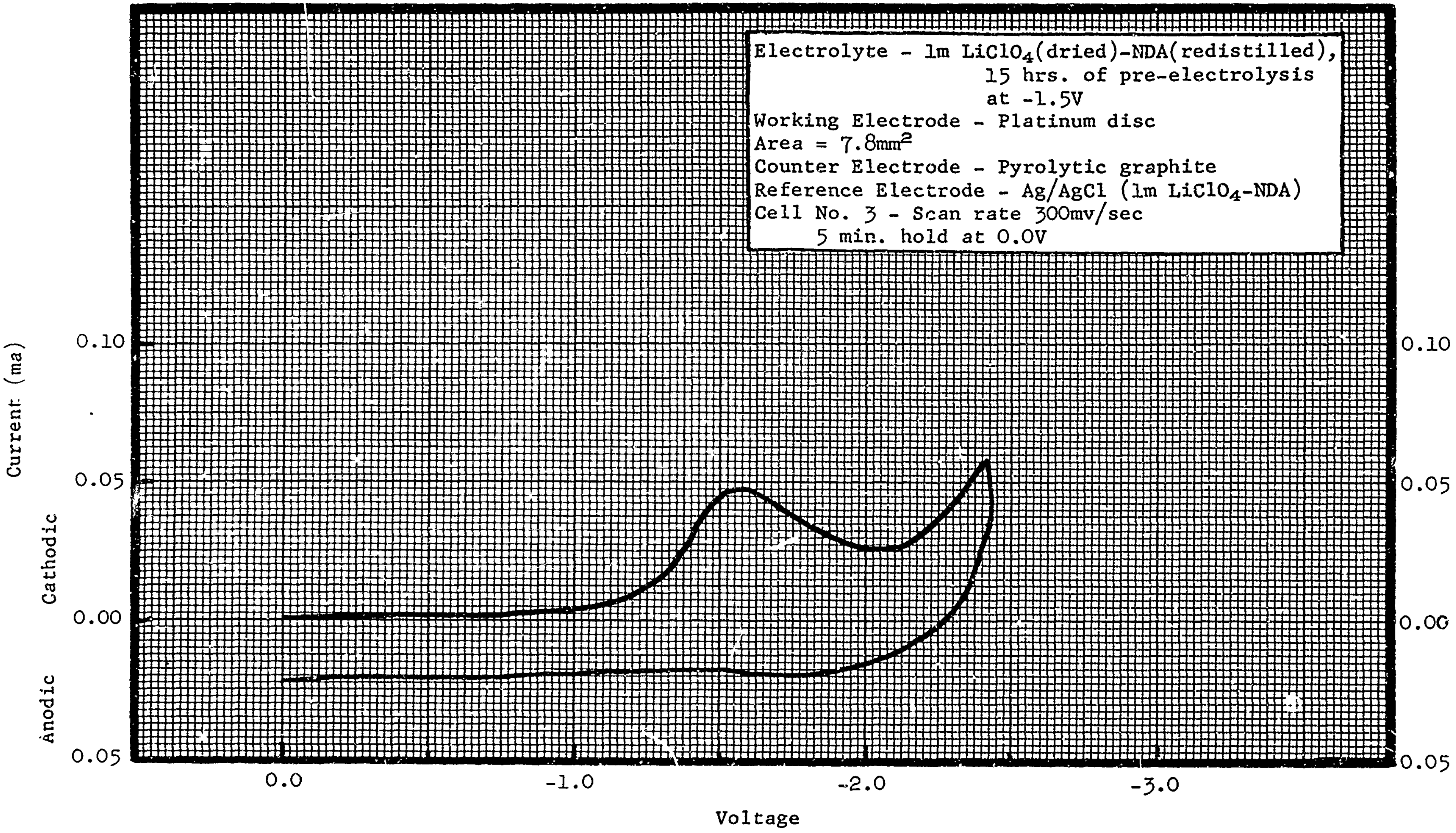


FIGURE 10. SERIES I - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 10-a. Residual Current.

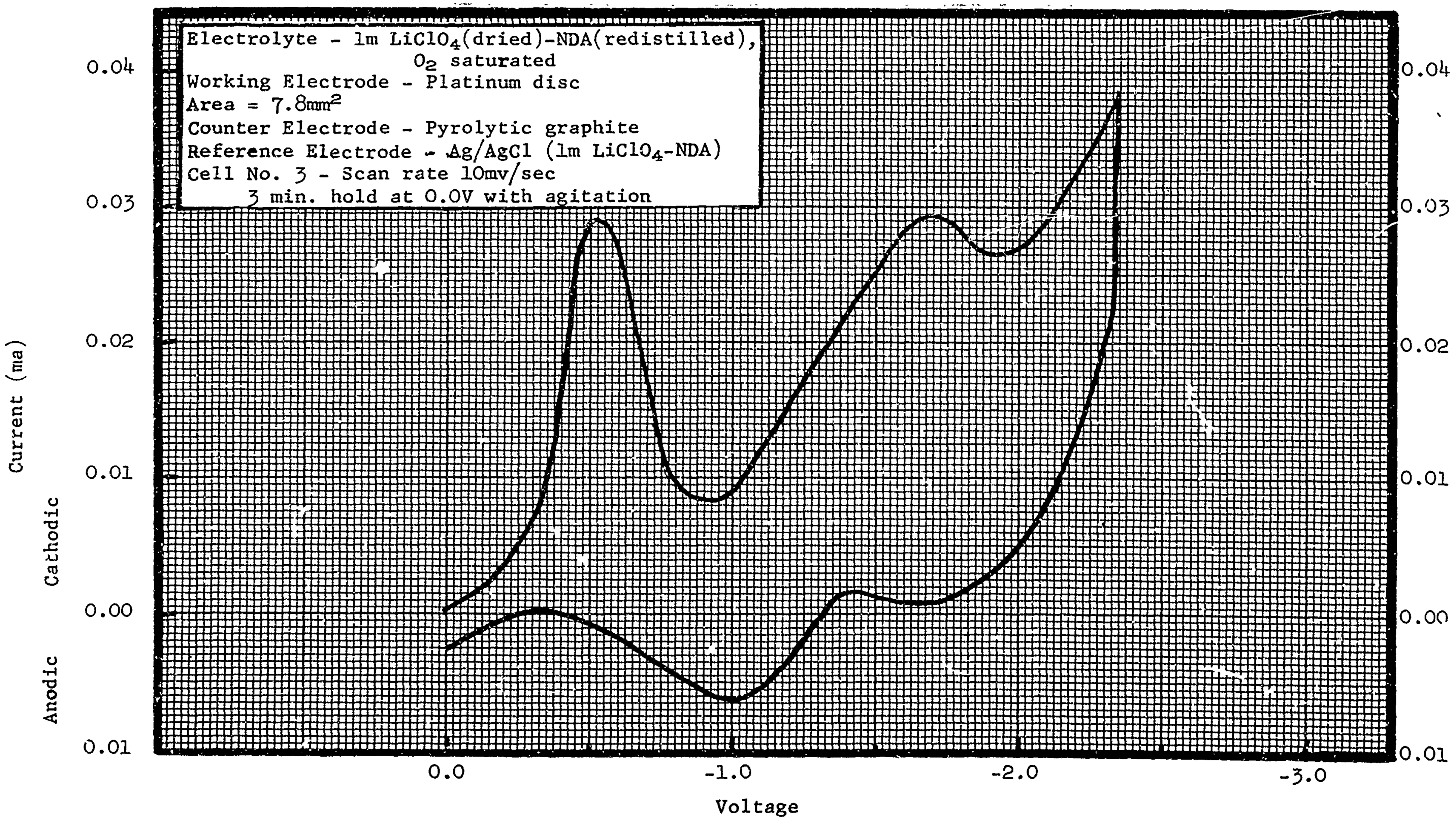
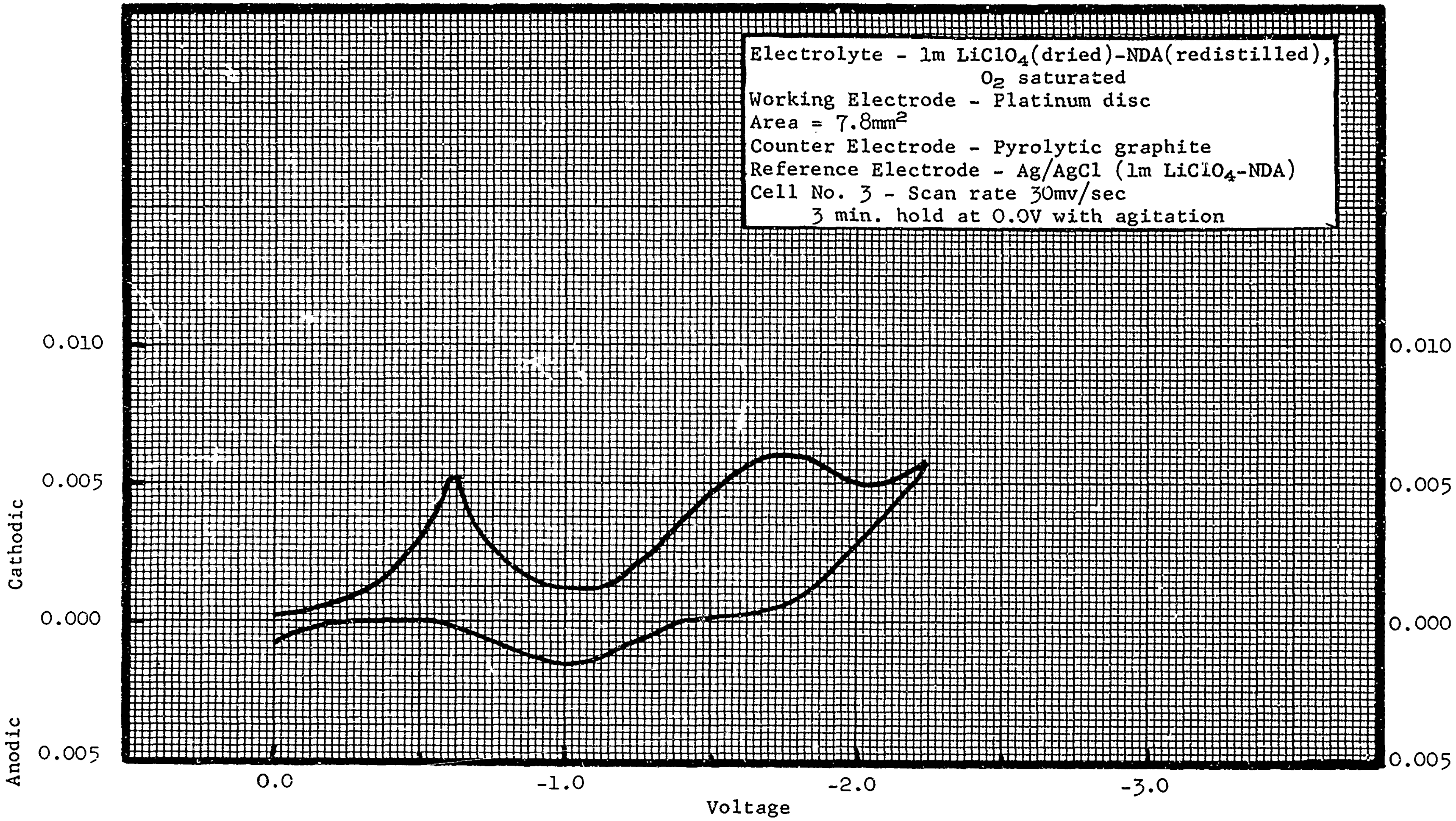


FIGURE 10. SERIES I - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 10-b. Scan Rate 10mv/sec.



Electrolyte - 1m $LiClO_4$(dried)-NDA(redistilled),
O_2 saturated
Working Electrode - Platinum disc
Area = 7.8mm^2
Counter Electrode - Pyrolytic graphite
Reference Electrode - Ag/AgCl (1m $LiClO_4$-NDA)
Cell No. 3 - Scan rate 30mv/sec
3 min. hold at 0.0V with agitation

FIGURE 10. SERIES I - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 10-c. Scan Rate 30mv/sec.

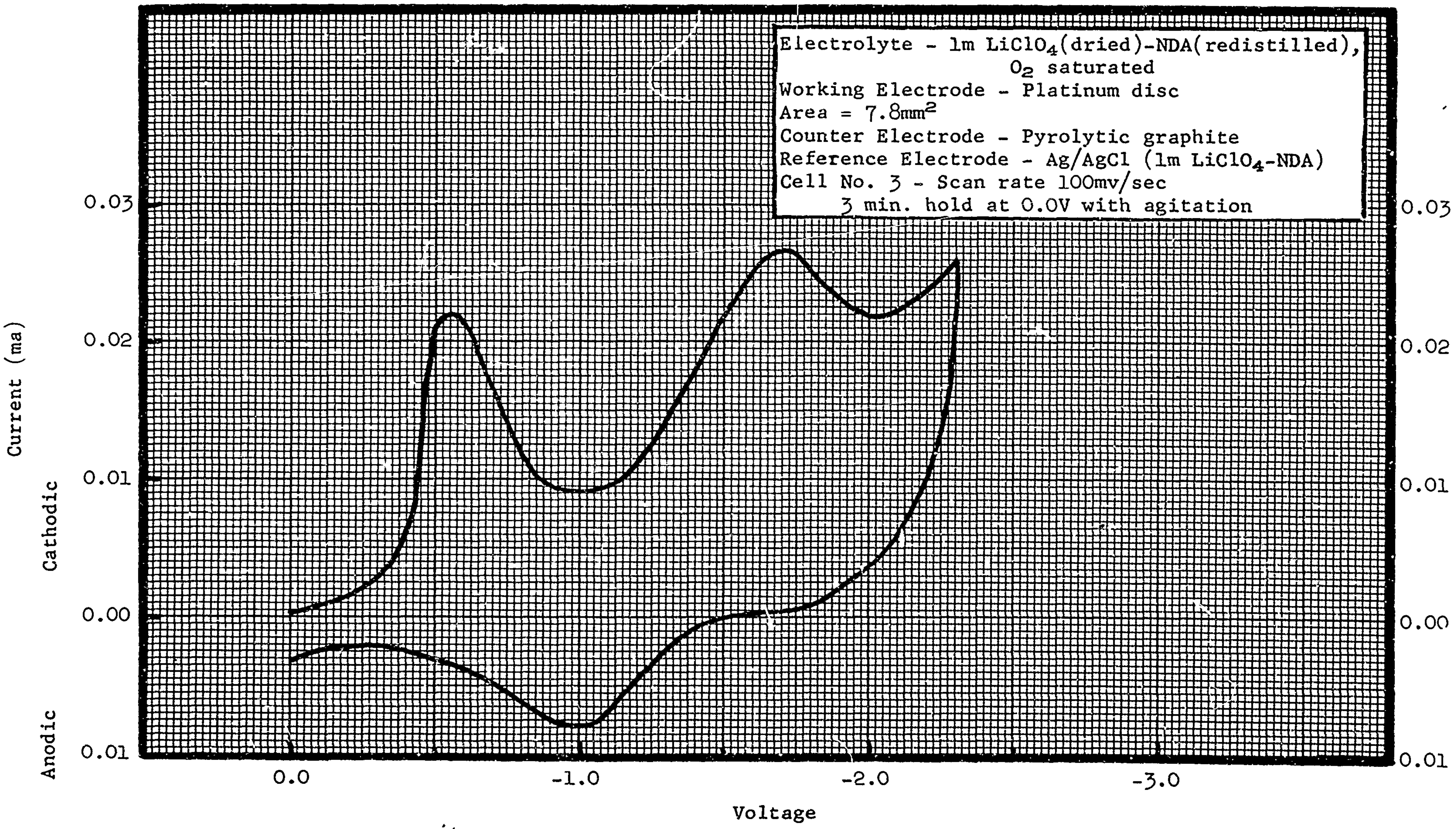


FIGURE 10. SERIES I - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 10-d. Scan Rate 100mv/sec.

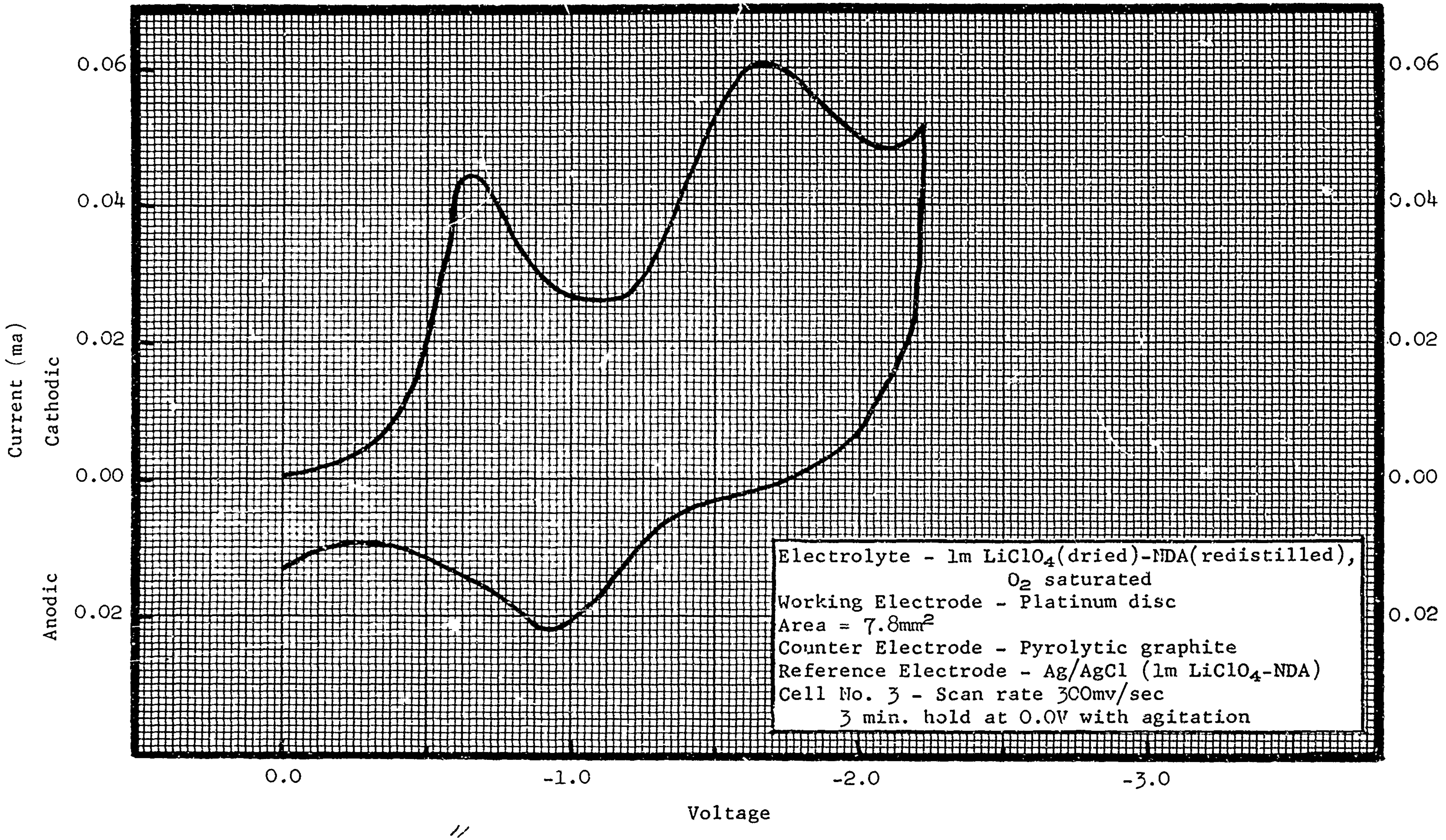


FIGURE 10. <u>SERIES I - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION</u>

Figure 10-e. Scan Rate 300mv/sec.

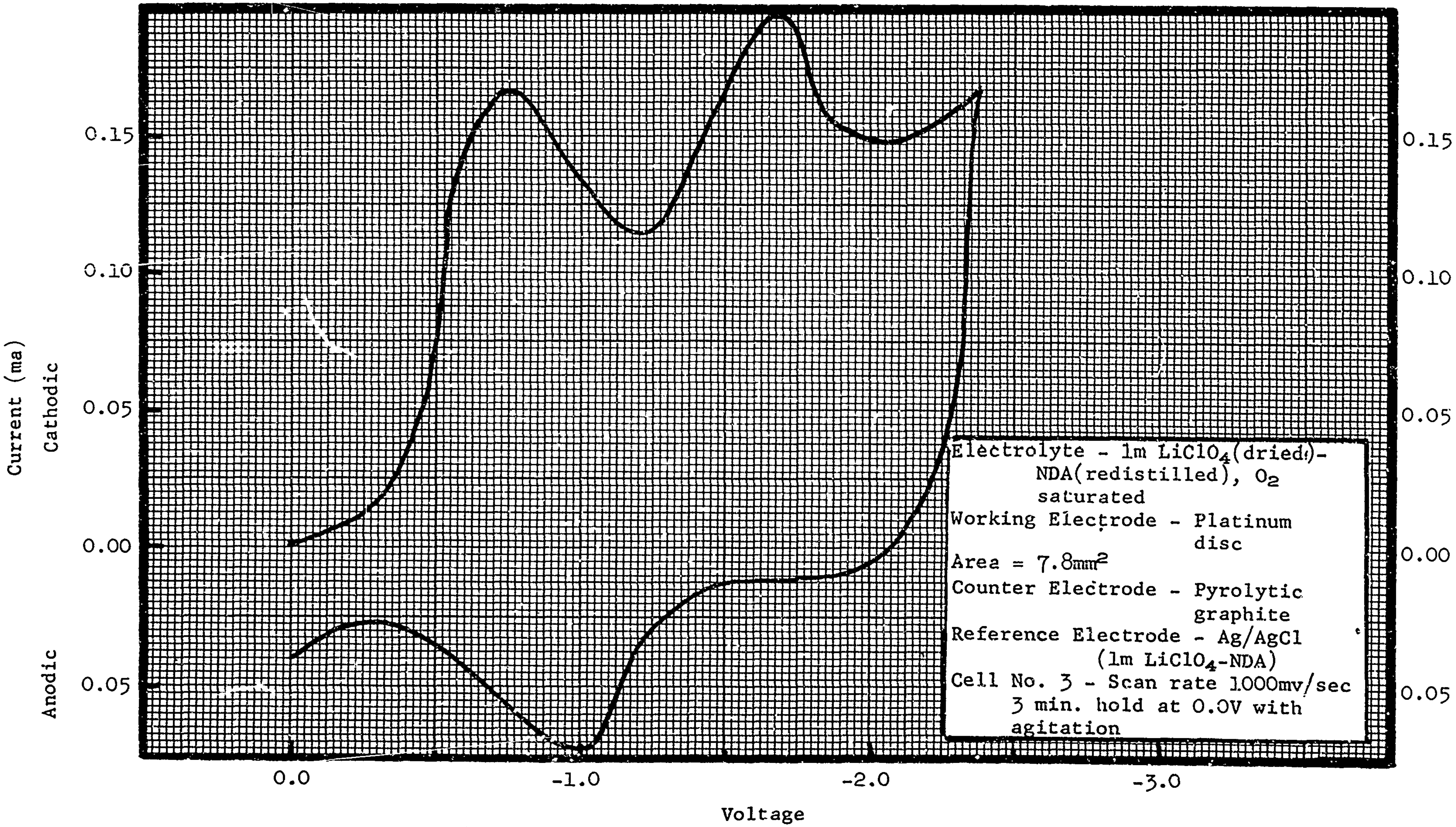


FIGURE 10. SERIES I - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 10-f. Scan Rate 1000mv/sec.

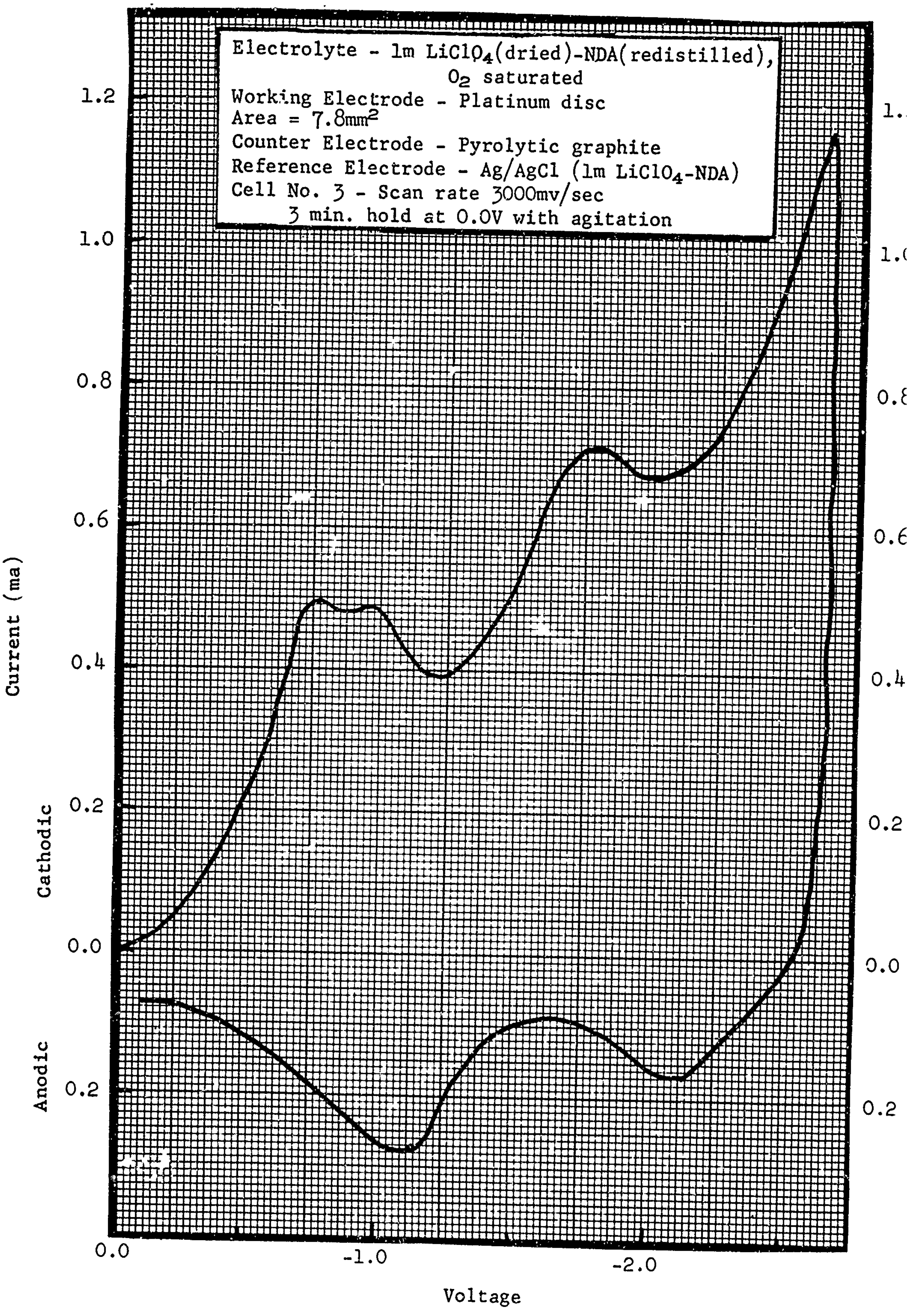


FIGURE 10. SERIES I - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 10-g. Scan Rate 3000mv/sec.

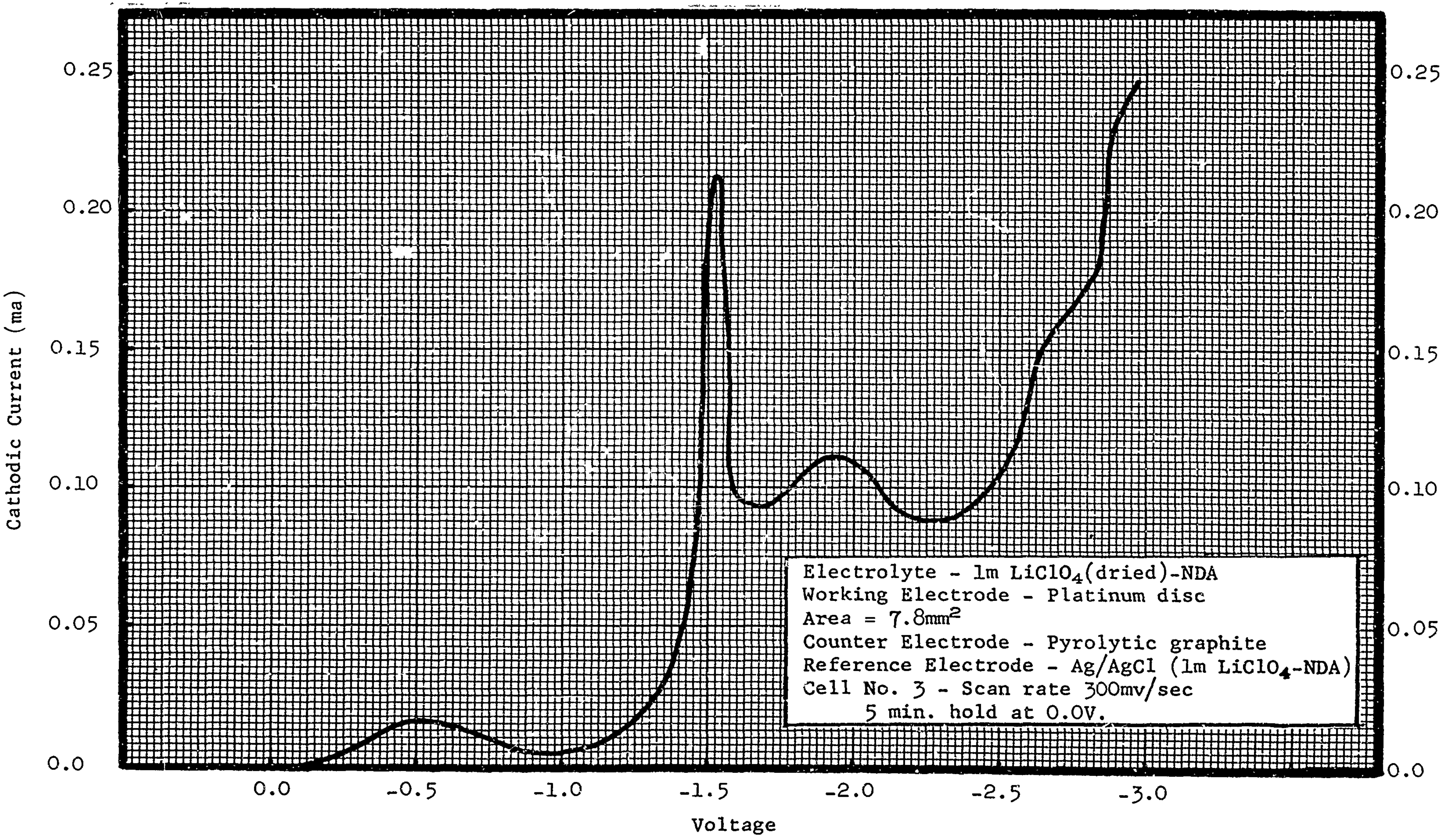


FIGURE 11. SERIES II - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 11-a. Residual Current.

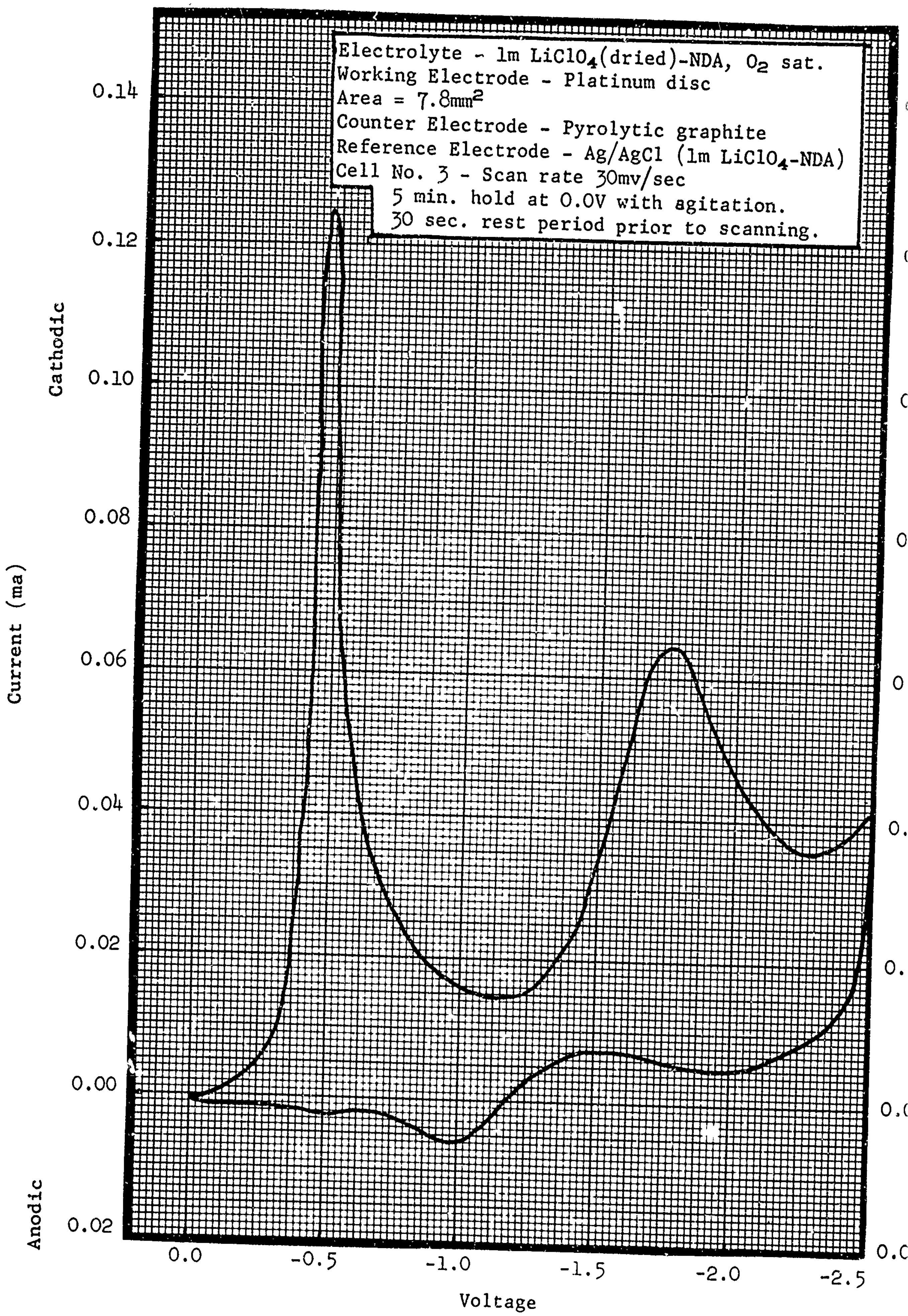

Electrolyte - 1m $LiClO_4$(dried)-NDA, O_2 sat.
Working Electrode - Platinum disc
Area = 7.8mm^2
Counter Electrode - Pyrolytic graphite
Reference Electrode - Ag/AgCl (1m $LiClO_4$-NDA)
Cell No. 3 - Scan rate 30mv/sec
5 min. hold at 0.0V with agitation.
30 sec. rest period prior to scanning.

FIGURE 11. SERIES II - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 11-b. Scan Rate 30mv/sec.

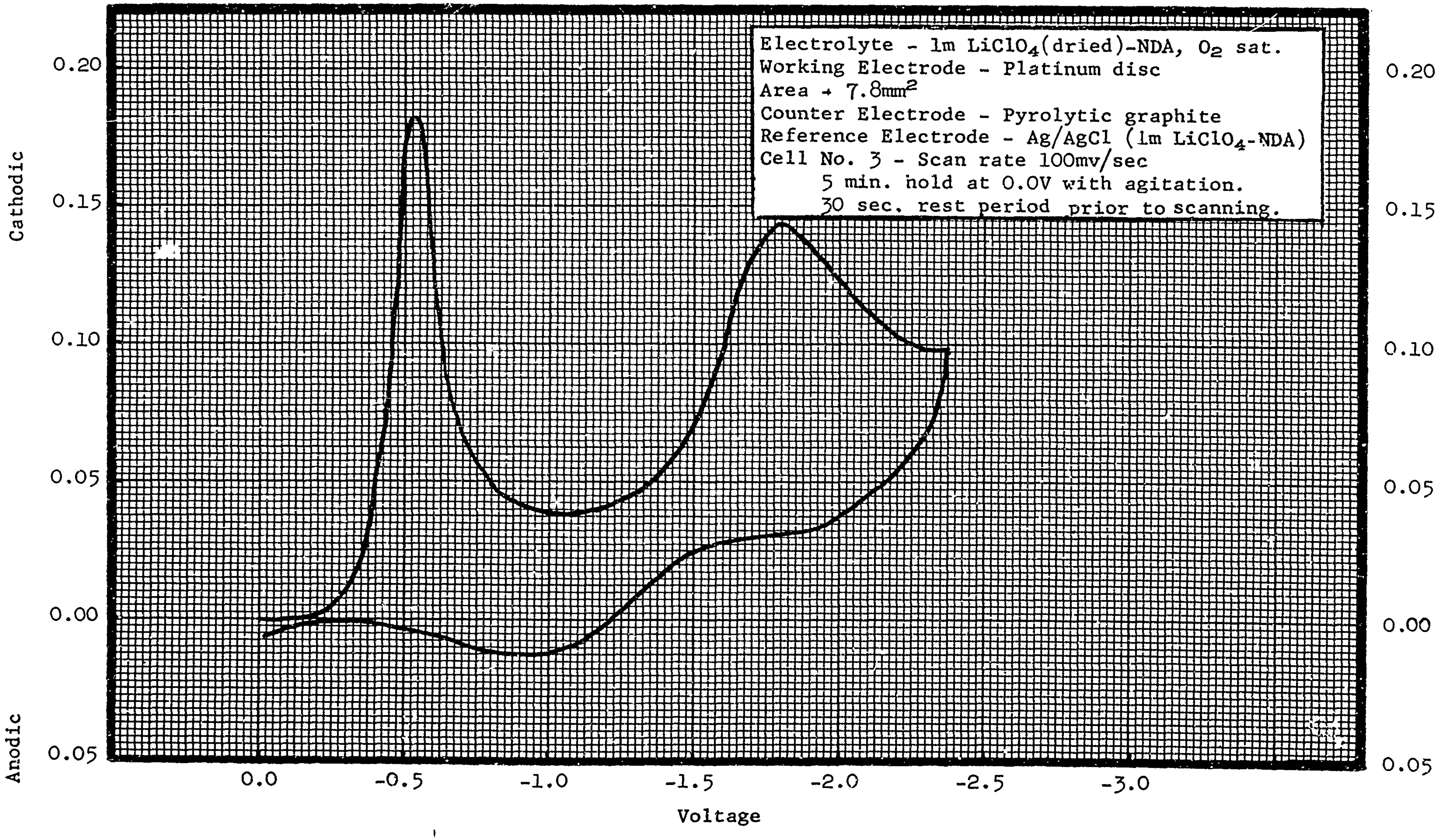


FIGURE 11. <u>SERIES II - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION</u>

Figure 11-c. Scan Rate 100mv/sec.

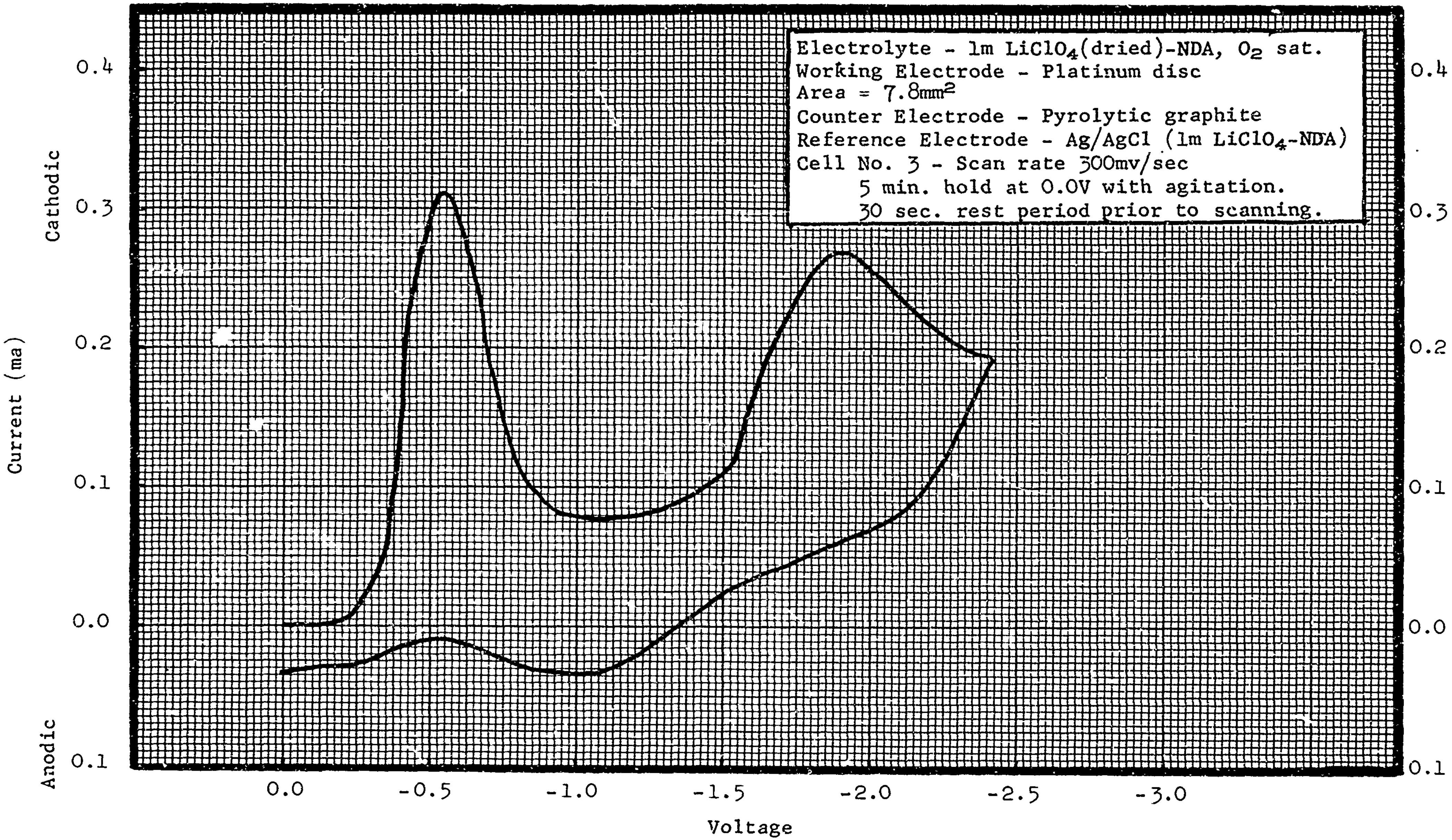


FIGURE 11. SERIES II - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

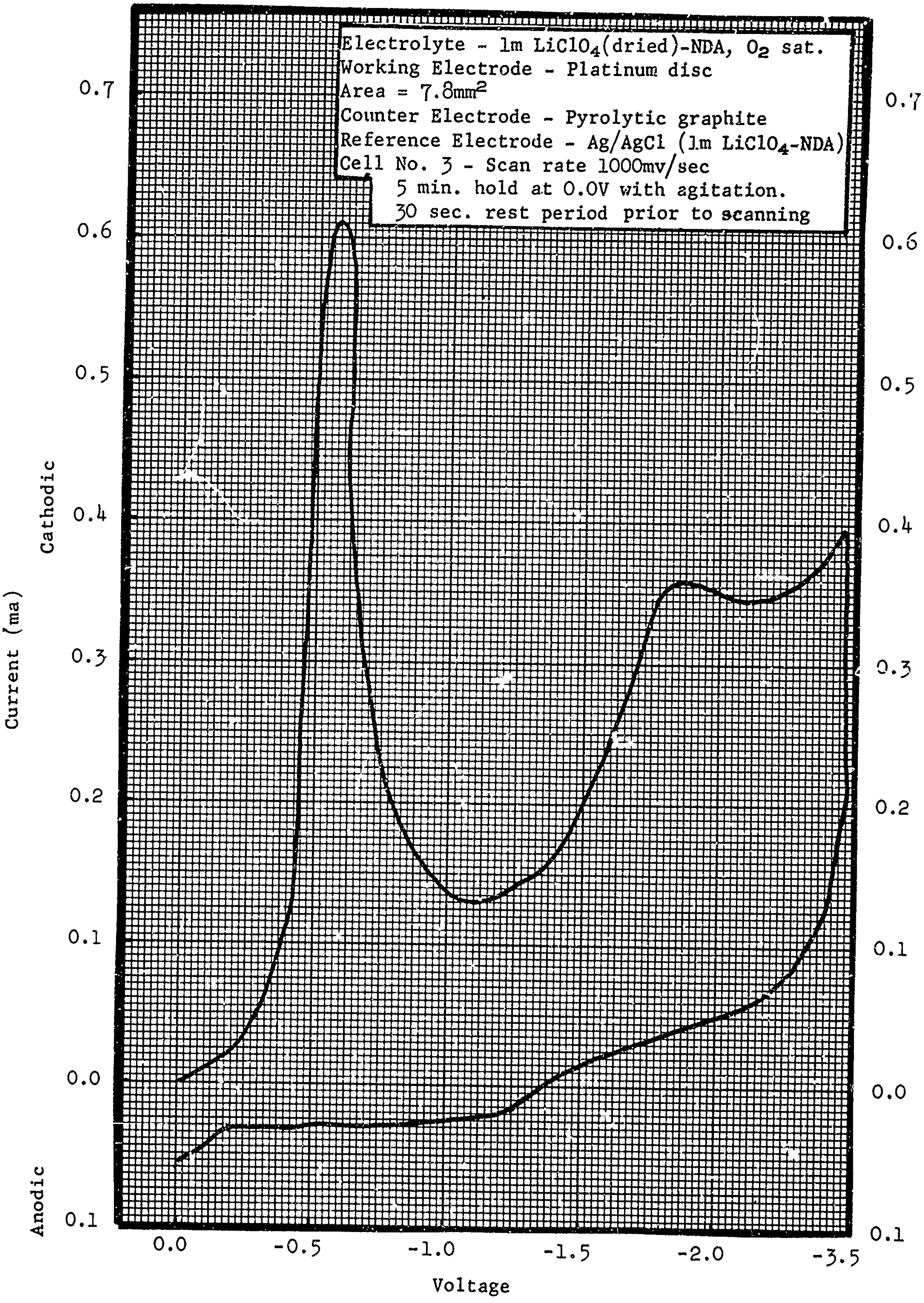


FIGURE 11. SERIES II - CYCLIC VOLTAMMOGRAM OF OXYGEN REDUCTION

Figure 11-e. Scan Rate 1000mv/sec.

Figure 11-d. Scan Rate 300mv/sec.

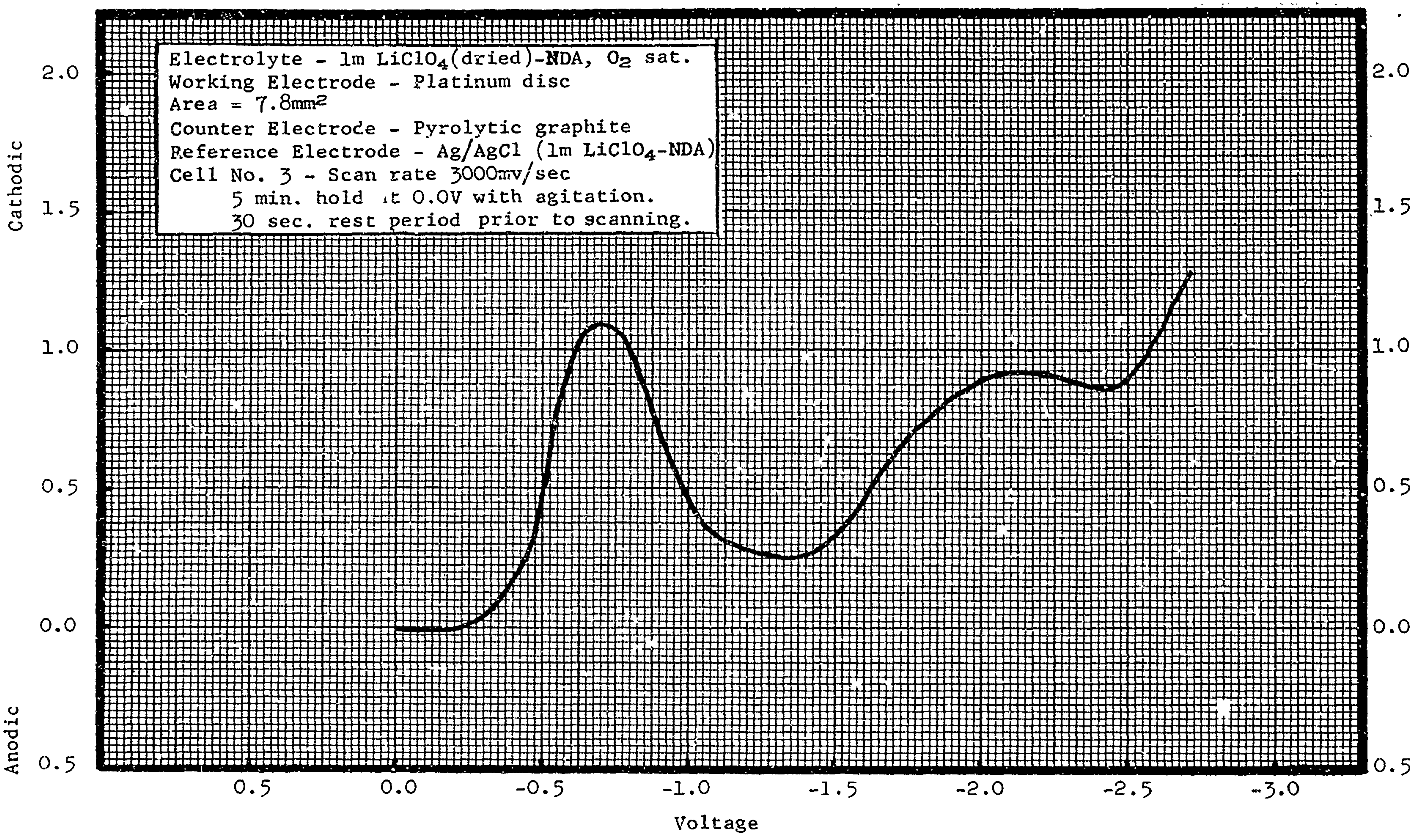


FIGURE 11. <u>SERIES II - VOLTAMMOGRAM OF OXYGEN REDUCTION</u>

Figure 11-f. Scan Rate 3000mv/sec.

The influence of water on the oxygen reduction is shown in Figure 12, pages 35 and 36. When one drop of water was added (approximately 0.25 volume percent) both peaks were approximately doubled and there was a slight shift of the first wave to more positive potentials. This is in agreement with previous observations made by other researchers on the change of the mechanism for oxygen reduction when protons are available.

The presence of some type of electrochemically reducible species in this electrolyte was found during the course of these studies. This species could be reduced at -1.5 volts relative to the Ag/AgCl reference and therefore created some uncertainty about the second reduction wave for oxygen which occurs at about this potential. A detailed study was made on this impurity and will be reported in the following section. Some of the experiments which have been performed on this electrolyte seem to indicate that moisture may at least be in part responsible for this problem. Additional work would be required however before the identity of this impurity can be determined.

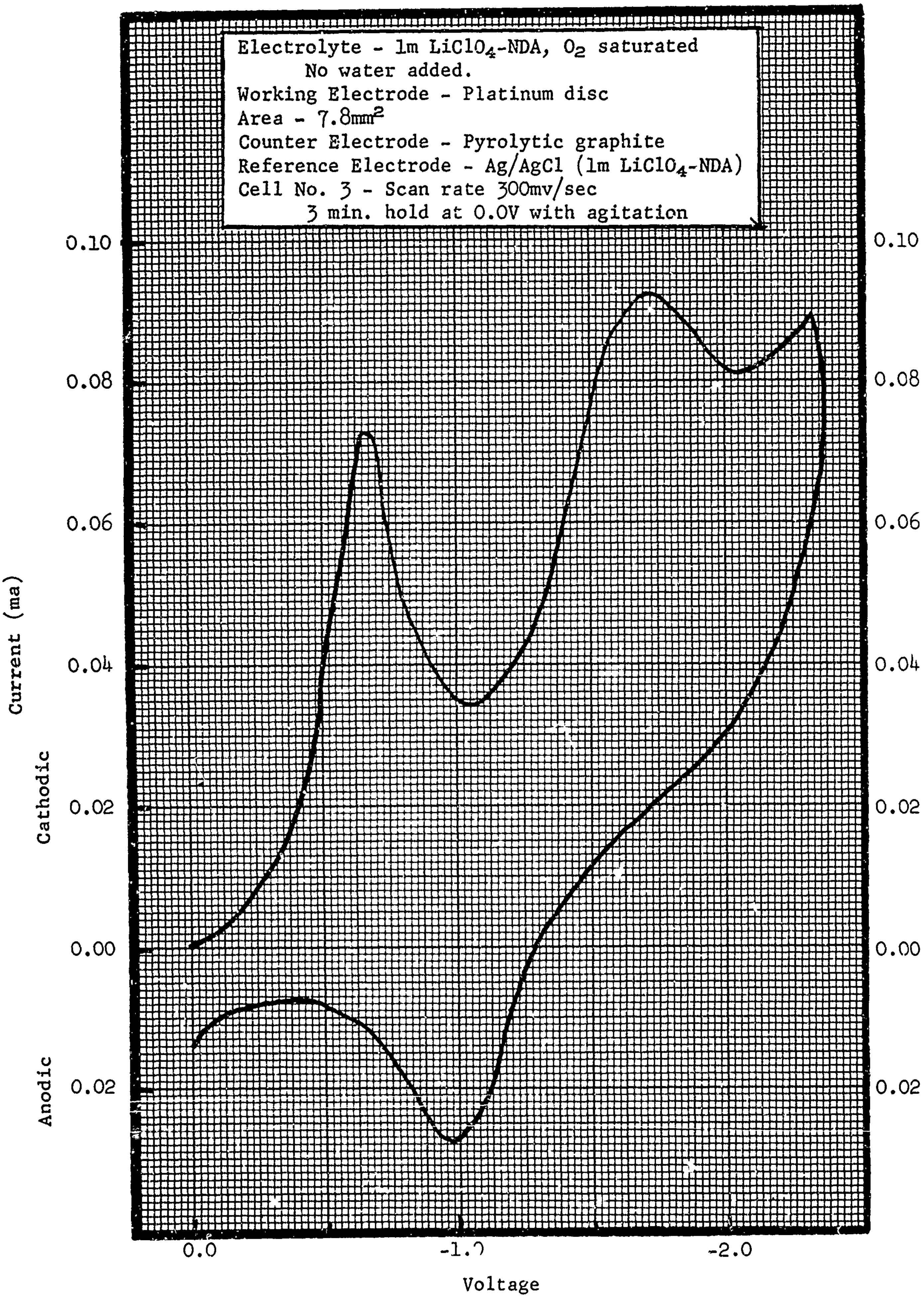


FIGURE 12. EFFECT OF WATER ON THE REDUCTION OF OXYGEN

Figure 12-a. Scan in Absence of Water

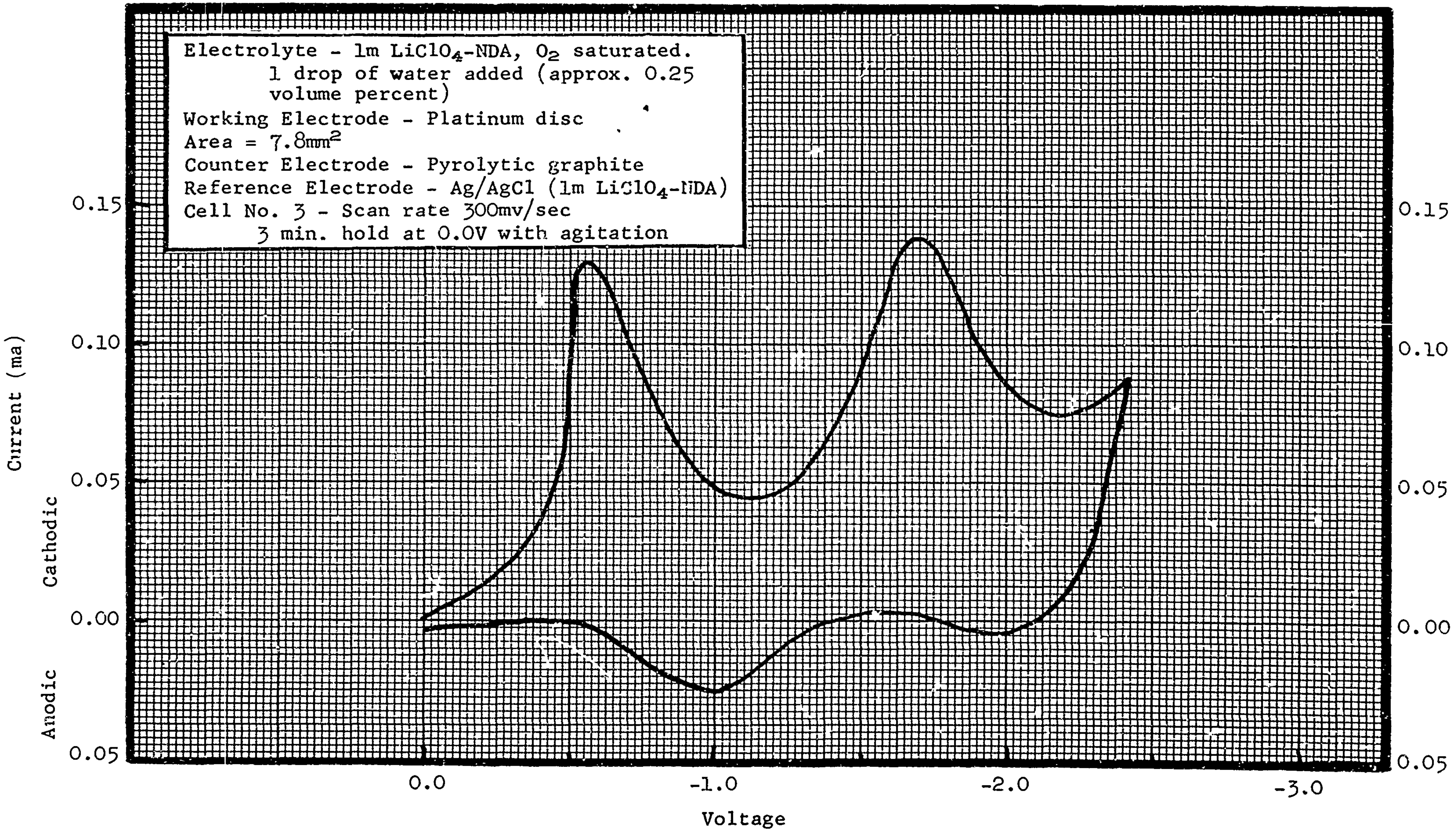


FIGURE 12. EFFECT OF WATER ON THE REDUCTION OF OXYGEN

Figure 12-b. Scan with Water Added.

E. IMPURITY STUDIES

In the voltammetric studies which were carried out to get an understanding of the oxygen reduction process in nonaqueous electrolytes, it was observed that under certain conditions there were impurities present which were electroactive and reducible in the region of the oxygen reduction waves. An impurity peak was observed at -0.5 volts versus the silver-silver chloride electrode. This impurity did not appear to be present in significant quantities and in some cases was not observed to be present at all. The second peak, however, which occurs at -1.5 volts versus the silver-silver chloride reference, was continuously causing difficulties in our studies.

The -1.5 volt impurity peak is so close to that of the second reduction wave for oxygen that it interferes with this wave. It also was observed that oxygen and this impurity were interacting in some fashion at the electrode surface. The tests run seem to indicate that the impurity competes with oxygen for sites on the electrode surface.

Some preliminary work to eliminate the impurity has already been carried out. This includes pre-electrolysis, addition of adsorbent materials such as silica gel, and prepurification of the electrolyte components. The above experiments were not completely successful in removing the impurity, and further work is required.

Furthermore, it has been recognized that the systems in which the impurities have been observed have always included, in addition to the platinum disc working electrode, the following materials:

Nitrosodimethylamine
Lithium Perchlorate
Pyrolytic Graphite

A systematic elimination of each of these materials from the system will be attempted in order to isolate the source of the impurity. A series of experiments in dimethylformamide indicated that with only two components present, i.e., lithium perchlorate and pyrolytic graphite, that the problem exists even in this solvent.

It is also possible, of course, that the problem is related to the moisture content of materials, since, in the presence of moisture, the impurity peaks are enhanced, but the results to date are not definitive in this regard since oxygen peaks are also enhanced by the presence of moisture. These studies are being continued.

Typical waves for the impurity species are found in the cyclic voltammetric scans run on the one molal lithium perchlorate-nitrosodimethylamine electrolyte (Figure 13, pages 38 and 39). It was noted previously that two impurity peaks have been observed, one at -0.5 volts and one at -1.5 volts versus the Ag/AgCl electrode. The most important of these two impurity peaks appears to be the second, which

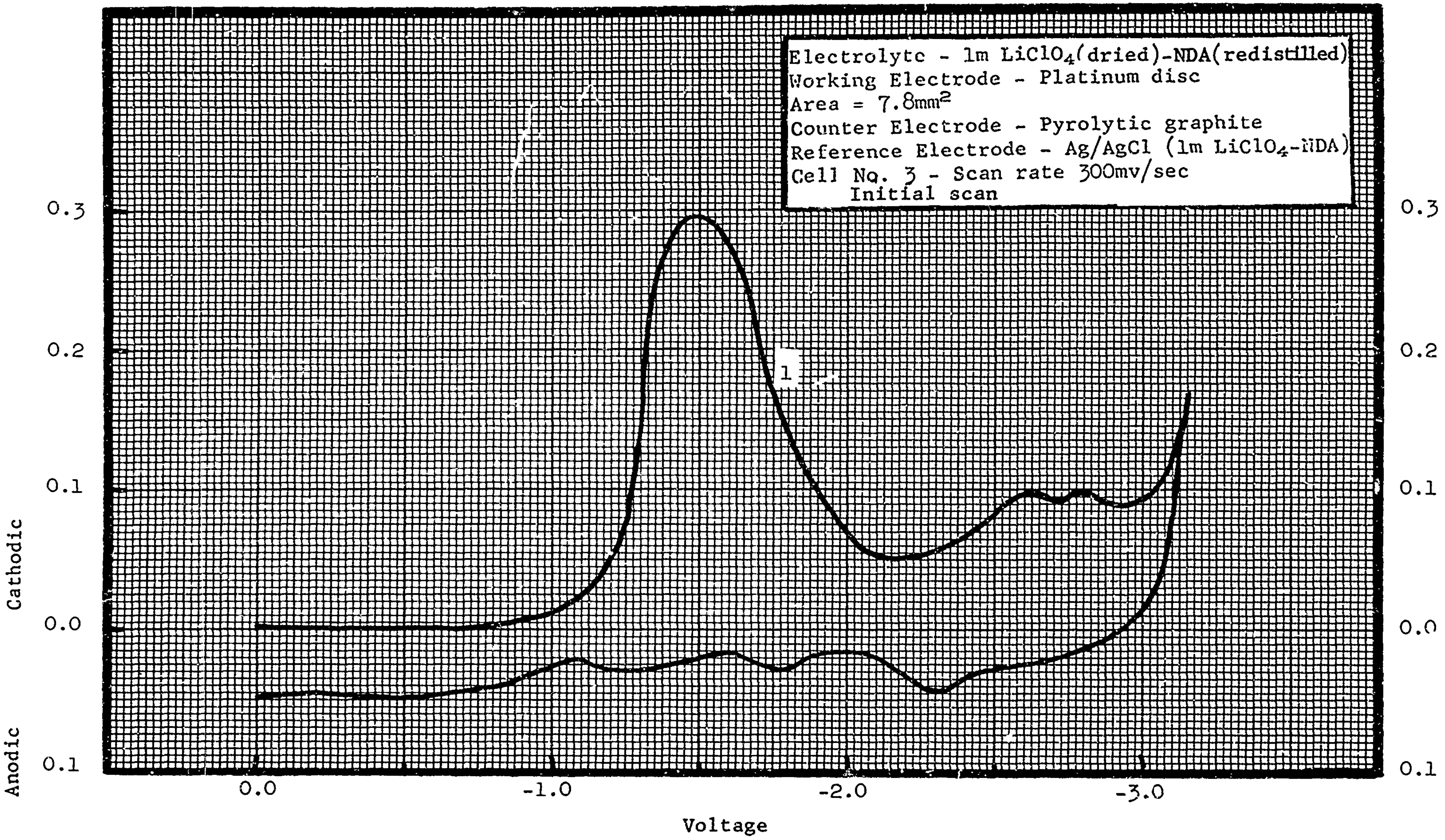


FIGURE 13. TYPICAL VOLTAMMETRY OF THE IMPURITY

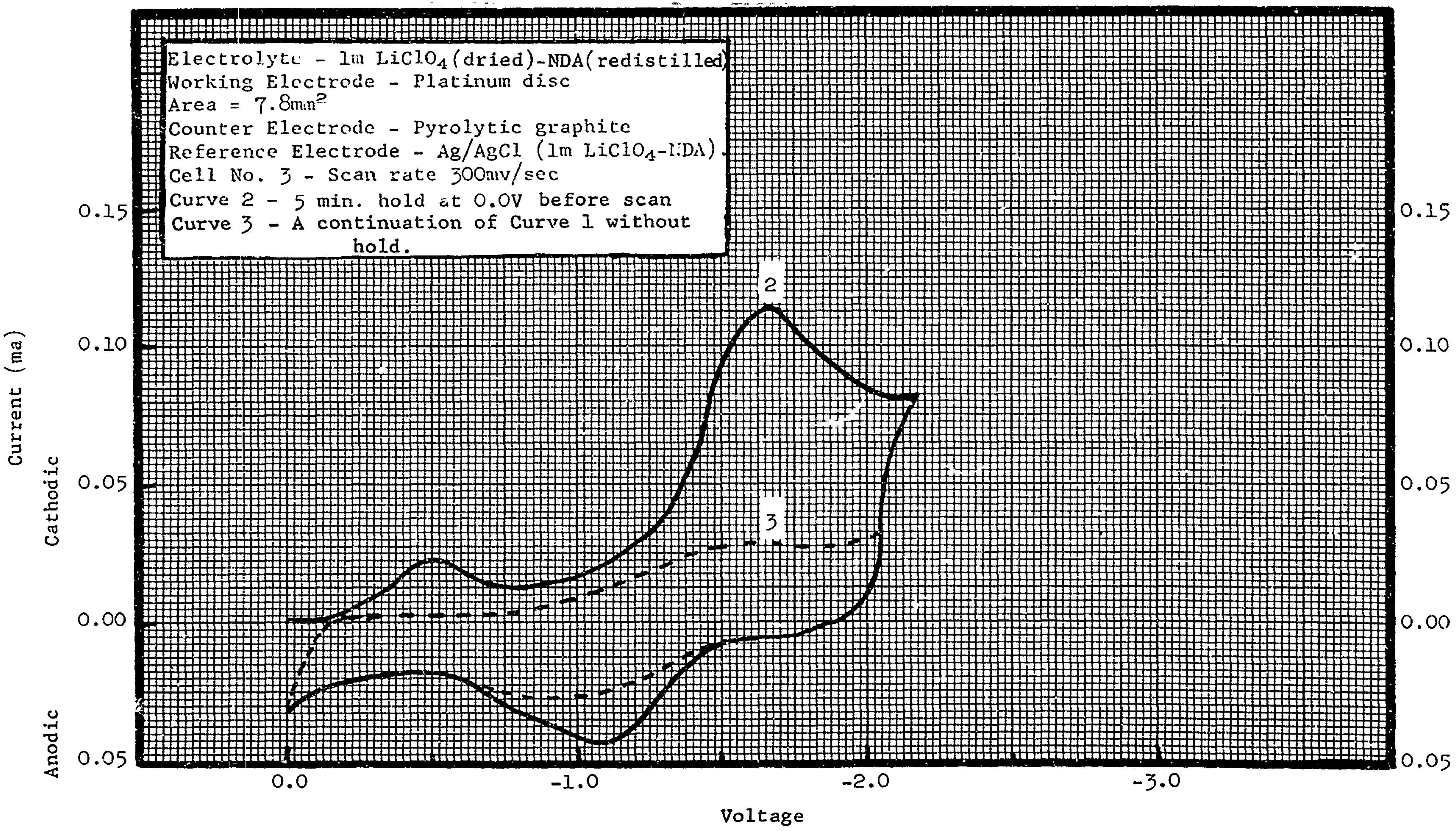


FIGURE 13. <u>TYPICAL VOLTAMMETRY OF THE IMPURITY</u>
(Continued)

occurs at -1.5 volts during cathodic scans. Anodic scans show another impurity peak at approximately -1.1 volts which may be related to the -1.5 volt cathodic peak. On occasion, the second impurity peak has been observed to be considerably sharper than in other cases (Figures 10-a and 11-a, pages 21 and 28, respectively).

The effect of oxygen on the electrochemical reduction of the impurity can be seen by comparing the scans shown in Figure 8, page 19, of the previous section, and Figure 14, page 41. The experimental conditions under which the curves found in Figure 14, page 41, were obtained are exactly the same as those used to obtain the curve shown in Figure 8, page 19, except that prior to the scans shown in Figure 8 the electrolyte was saturated with oxygen. The reduction peak of the impurity found in Figure 14 has disappeared and only the reduction peaks of oxygen are observed. When the solution was purged with nitrogen to eliminate oxygen, the curves shown in Figure 14 are again obtained.

Another experiment demonstrating the effect of oxygen on the performance of the impurity on a platinum electrode was one in which the scans were run while the solution was being saturated with oxygen (Figure 15, page 42). The scan run after oxygen had been passed through the solution for 30 seconds showed only the impurity waves. After oxygen had been passed through the solution for two minutes the impurity peak was substantially decreased and peaks attributable to oxygen started to appear. An interesting observation can be made by comparing Figures 16-a, page 43 and 16-b, page 44. The concentration of the impurity in these solutions was quite high and the solution was saturated with oxygen before use. After a one-minute potentiostatic hold at zero volts, the oxygen reduction waves at -0.6 and -1.75 volts were obtained with only a very small wave at -1.3 volts versus Ag/AgCl from the impurity. When a five-minute hold at zero volts was made prior to the scan, peaks of about the same size were obtained. This would appear to indicate a competition between the oxygen and the impurity for the electrode surface. Oxygen appears to be more strongly adsorbed on the electrode than the impurity. The ratio of the concentration of the adsorbed species on the electrode surface however can be altered by changing the relative concentration of the species in solution.

Several attempts were made to identify the impurity and to eliminate it. The possibility that the reducible species found in the lithium perchlorate-nitrosodimethylamine electrolyte was water was investigated. It was noted that the addition of water substantially increased the reduction wave obtained. Figure 17, pages 45 and 46, shows the cycles obtained on this electrolyte before and after water was added. It was also noted that when a drying agent such as silica gel was added to the electrolyte, the impurity wave was decreased (Figure 18, page 47). This decrease of the impurity wave was only temporary and after the solution was allowed to stand for some time it increased again. The use of doubly distilled nitrosodimethylamine and carefully dried lithium perchlorate did not seem to affect the reduction waves obtained as has been shown

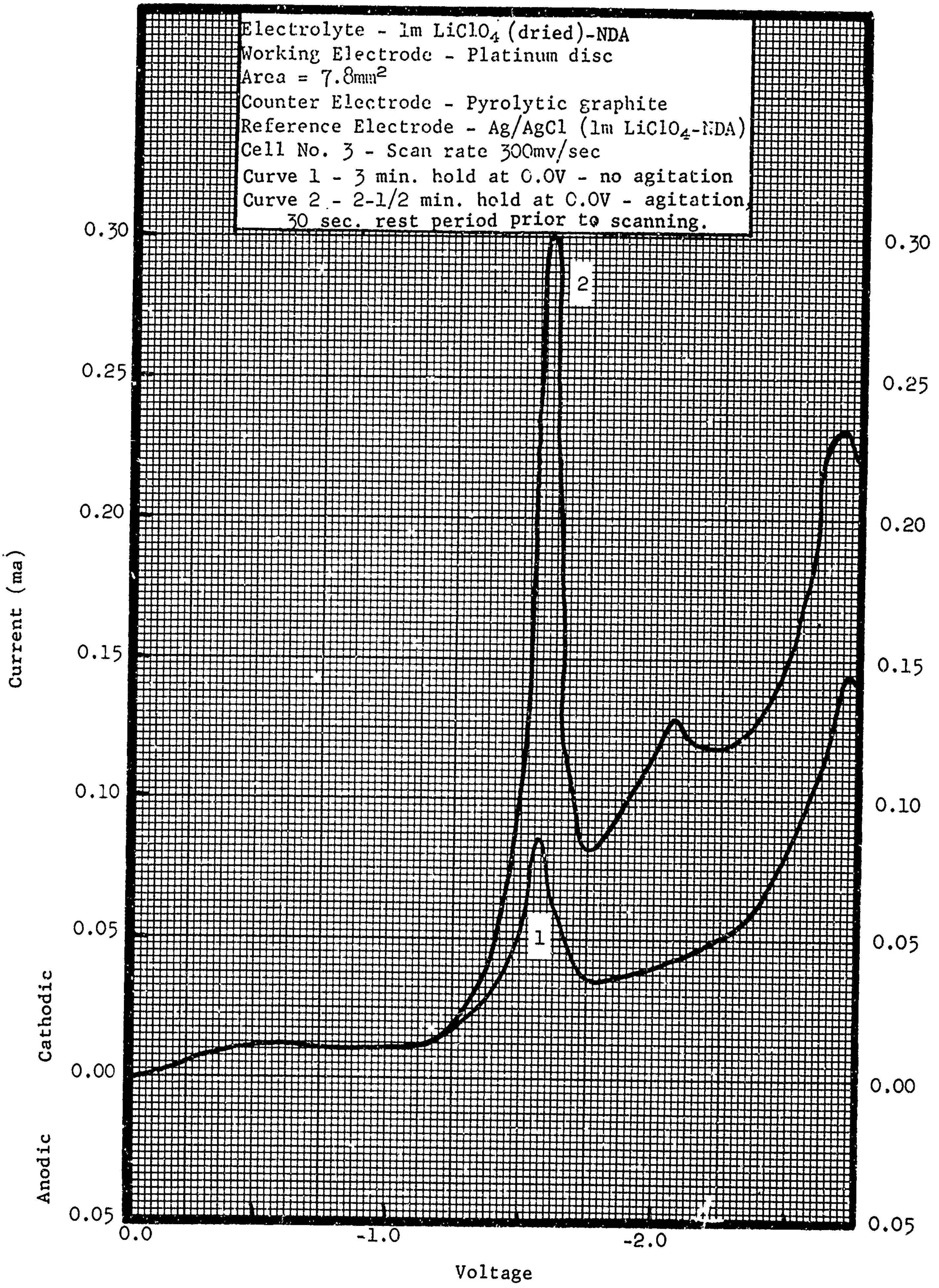


FIGURE 14. EFFECT OF AGITATION DURING HOLD ON SUBSEQUENT SCAN

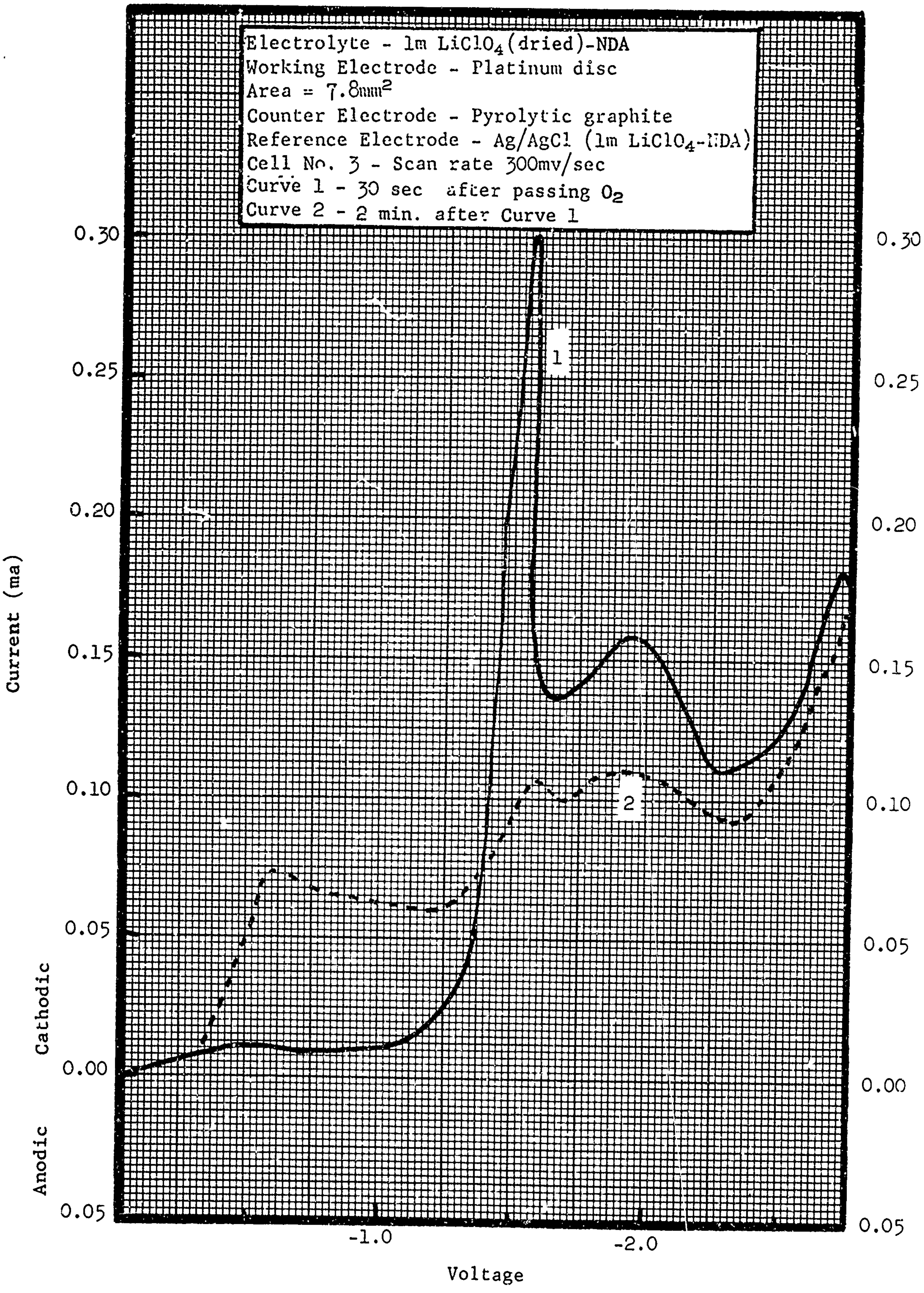


FIGURE 15. SCANS OF SOLUTIONS PARTIALLY SATURATED WITH OXYGEN

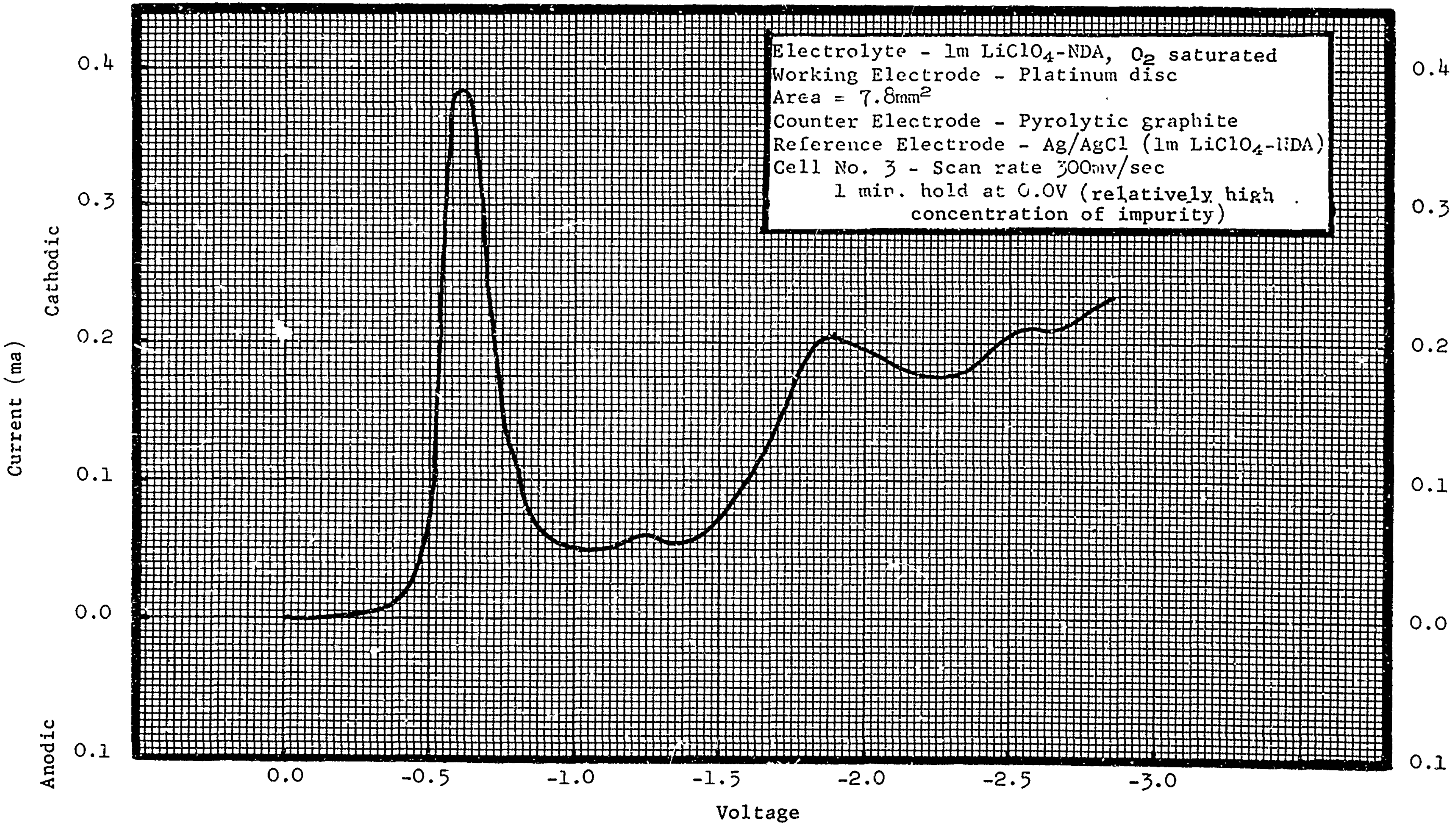


FIGURE 16. <u>STUDY OF THE ELECTROACTIVE IMPURITIES</u>

Figure 16-a. One Minute Hold at OV Before Scan.

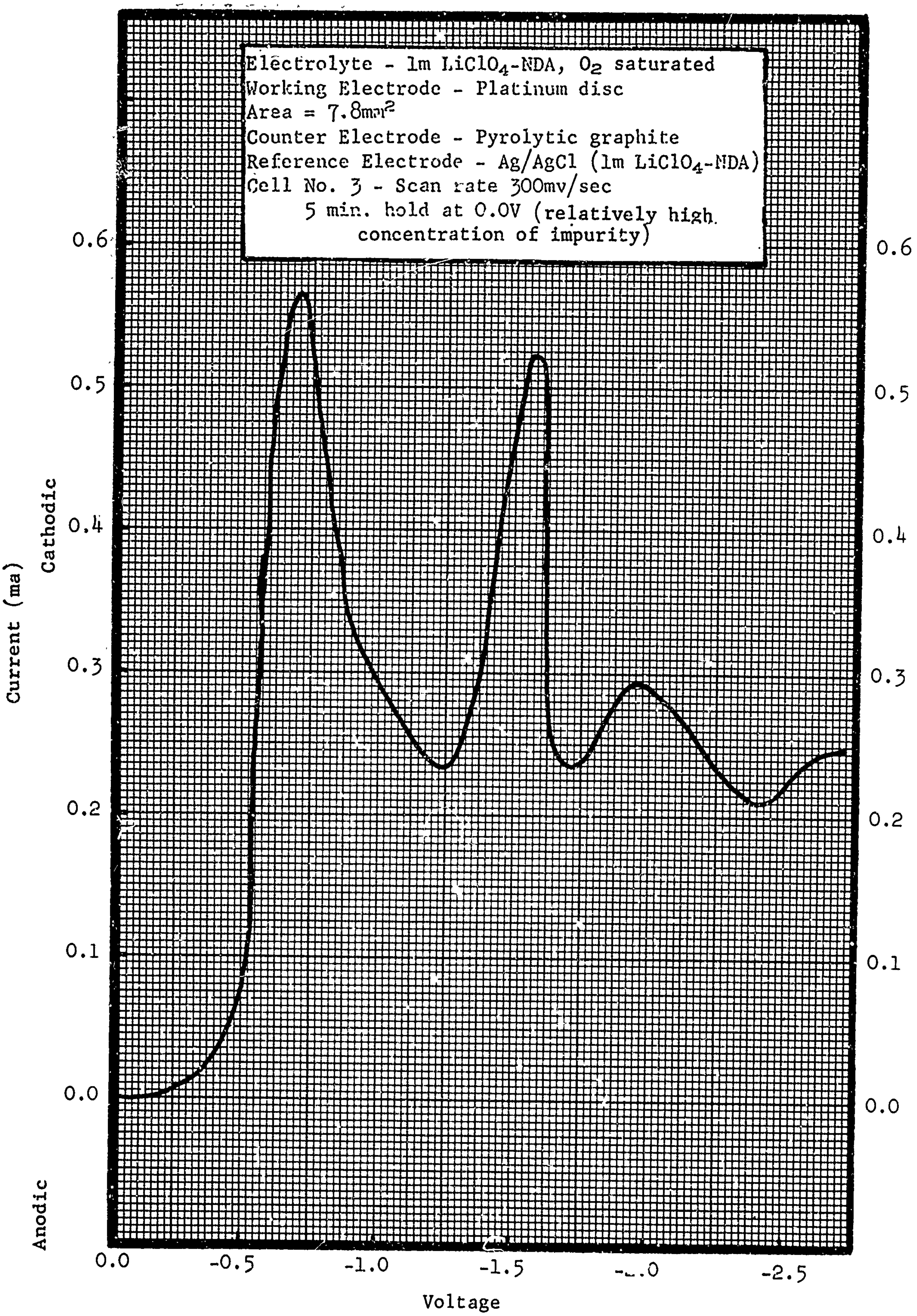


FIGURE 16. STUDY OF THE ELECTROACTIVE IMPURITIES

Figure 16-b. Five Minute Hold at 0V Before Scan.

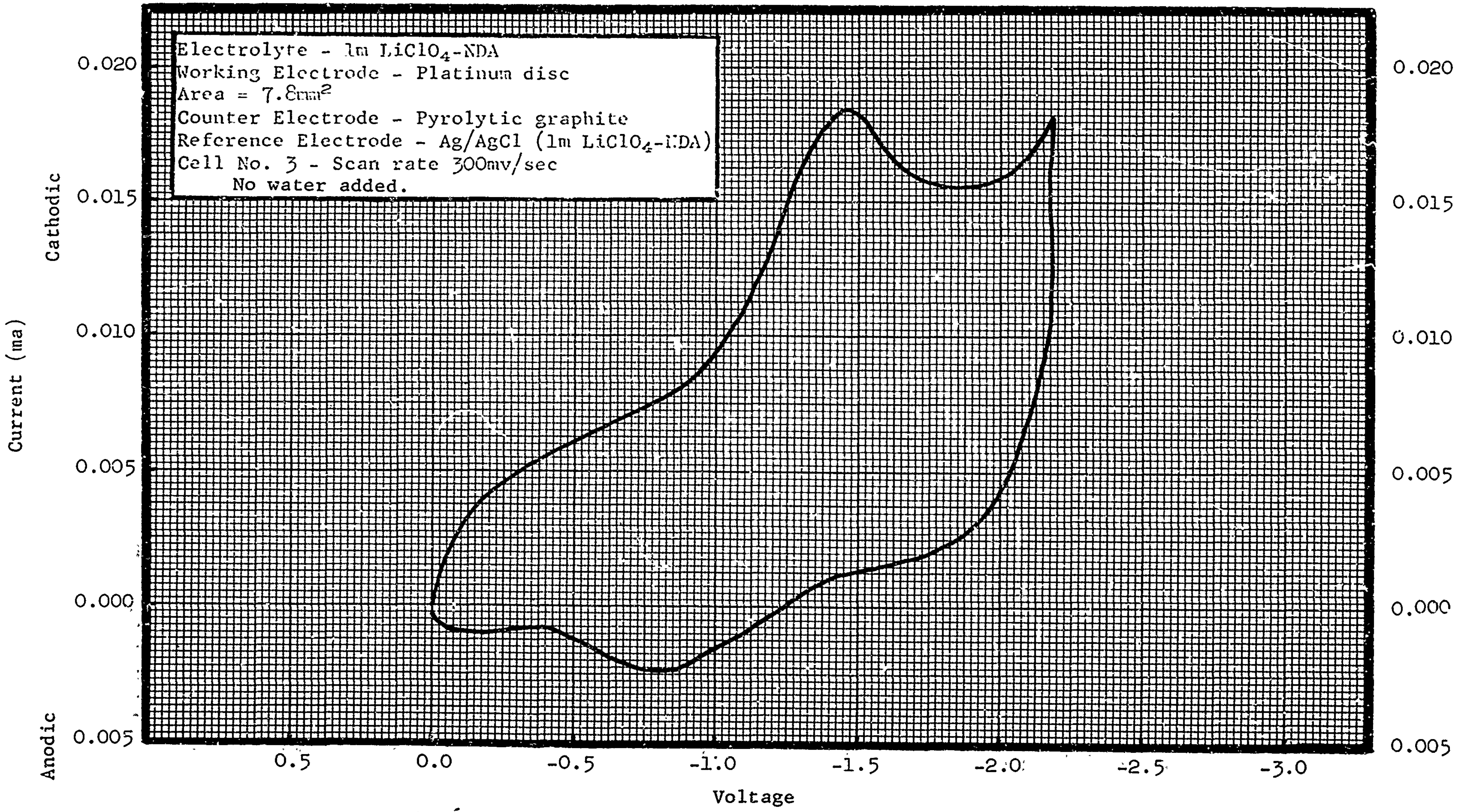
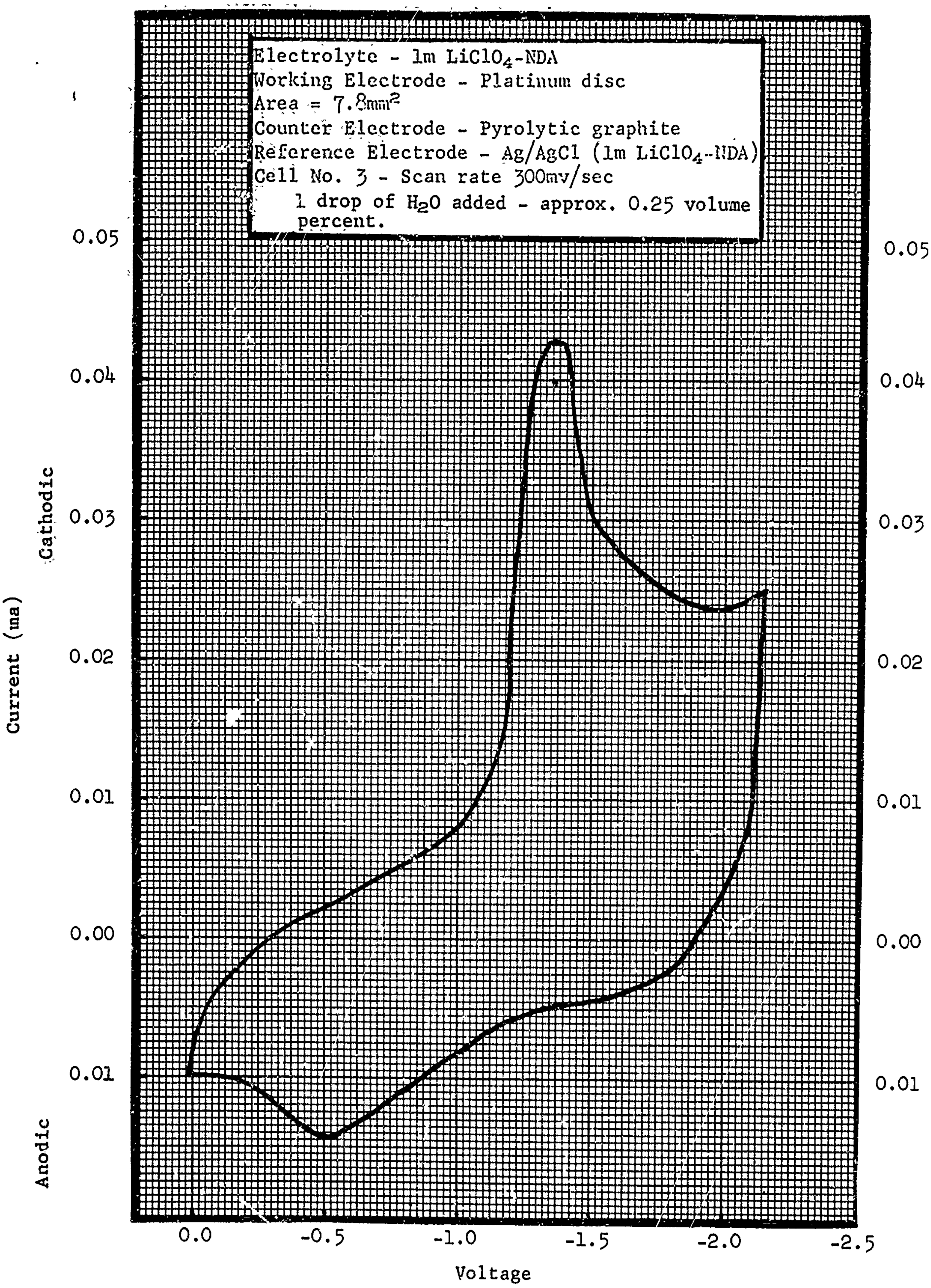


FIGURE 17. <u>EFFECT OF WATER ADDITION ON THE REDUCTION OF THE IMPURITIES</u>

Figure 17-a. Scan in Absence of Water.



Electrolyte - 1m $LiClO_4$-NDA
Working Electrode - Platinum disc
Area = 7.8mm^2
Counter Electrode - Pyrolytic graphite
Reference Electrode - Ag/AgCl (1m $LiClO_4$-NDA)
Cell No. 3 - Scan rate 300mv/sec
1 drop of H_2O added - approx. 0.25 volume percent.

FIGURE 17 EFFECT OF WATER ADDITION ON THE REDUCTION OF THE IMPURITIES

Figure 17-b. Scan With Water Present.

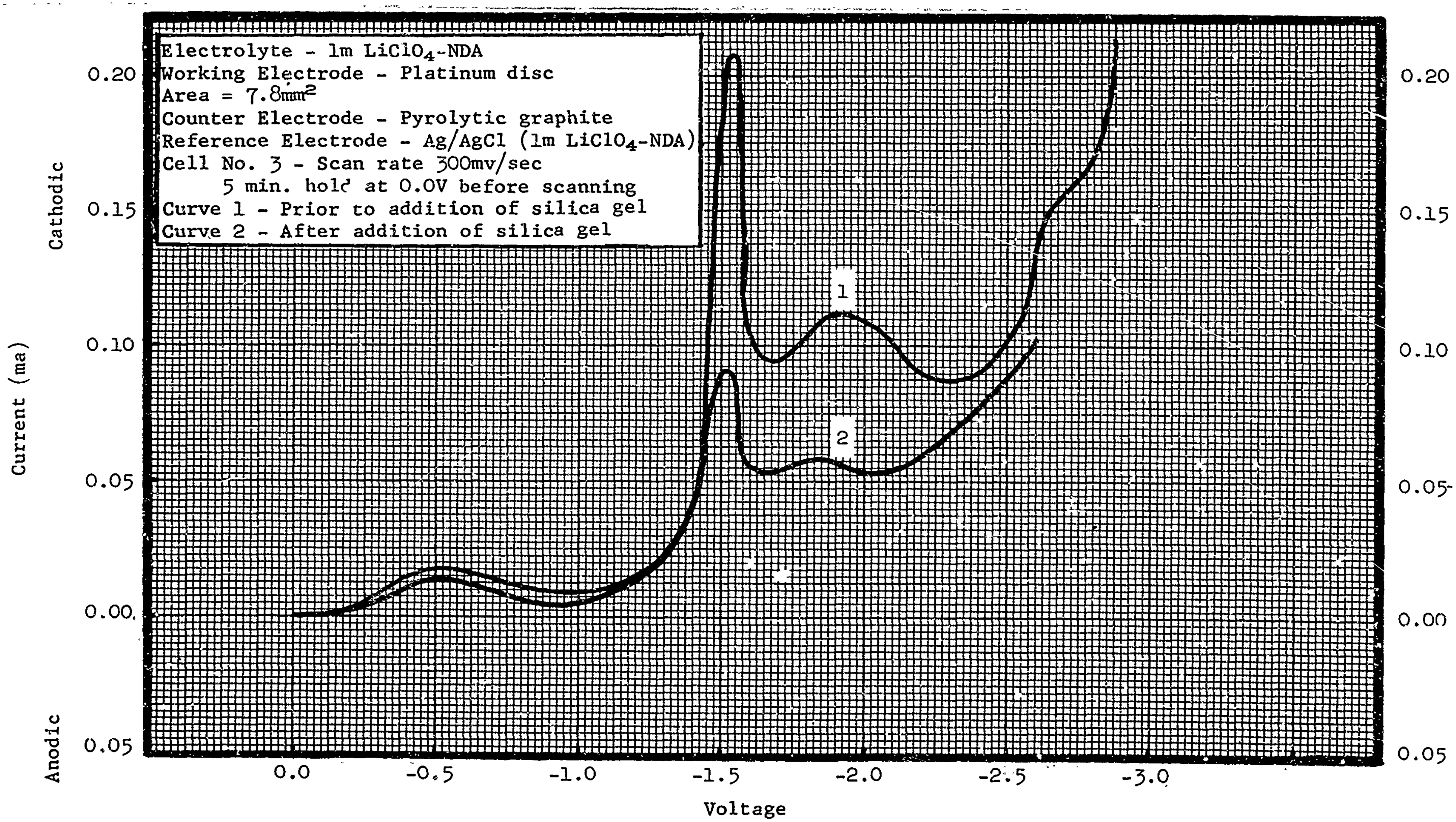


FIGURE 18. EFFECT OF SILICA GEL ADDITION ON THE REDUCTION OF THE IMPURITIES

previously in Figure 13, page 38. A comparison of Figures 13, page 39 and 10-a, page 21, of the previous section, shows that pre-electrolysis of the agitated solution with 1cm^2 platinum electrodes for 15 hours can decrease the impurity wave. The platinum electrodes used for this pre-electrolysis were covered with a brown film after electrolysis.

Experiments run with lithium perchlorate in dimethylformamide have shown similar behavior (Figure 19-a, page 49) to that obtained in lithium perchlorate nitrosodimethylamine. Addition of nitrosodimethylamine did not alter the curves obtained (Figure 19-b, page 50). However, water addition did increase the size of the impurity peak (Figure 19-c, page 51). At the present time there is insufficient information available to positively identify this impurity. While some of the experiments suggest that moisture is a contributing factor to this problem, additional experiments run under more rigorous conditions must be made.

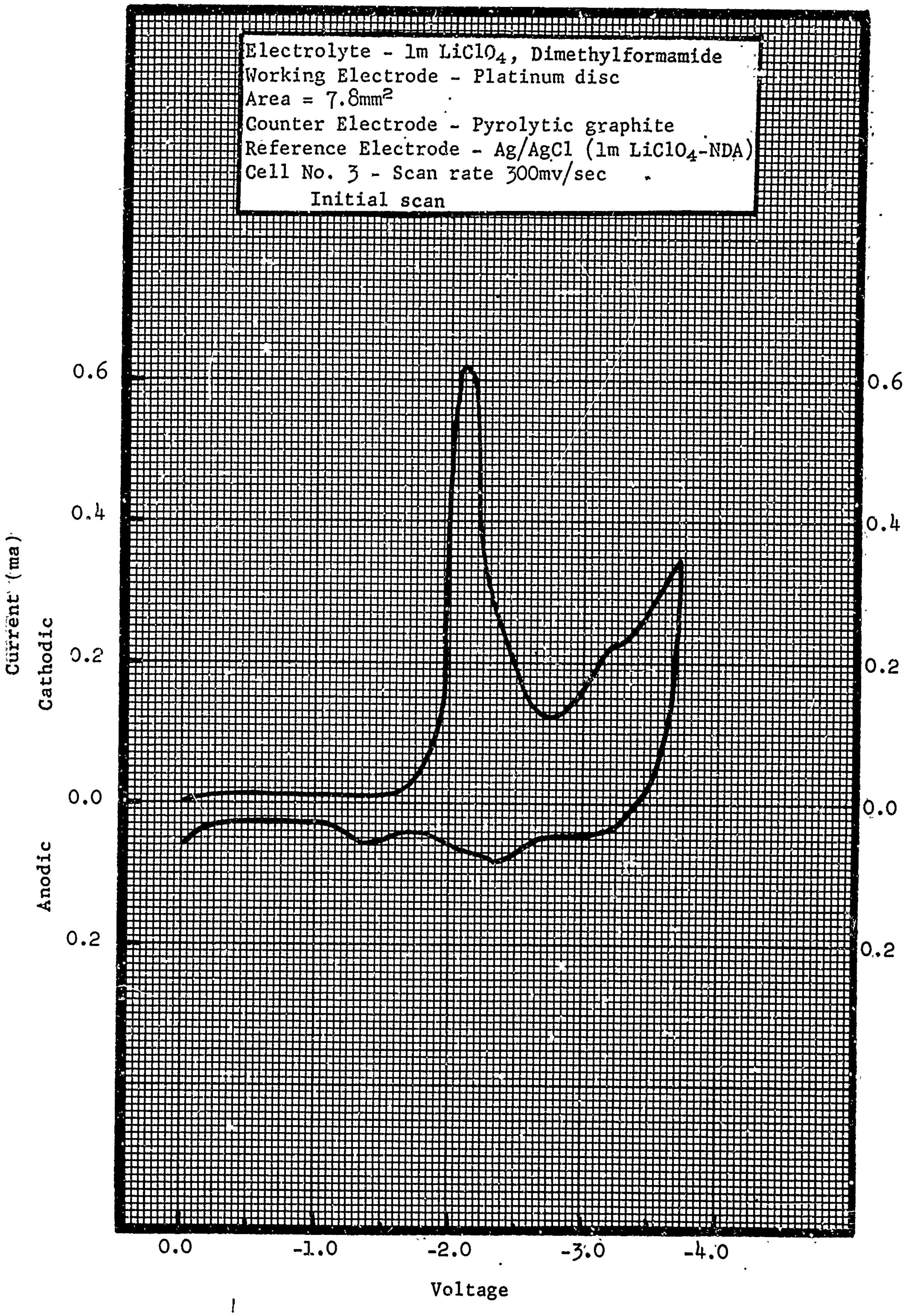


FIGURE 19. VOLTAMMETRY IN 1m $LiClO_4$-DIMETHYLFORMAMIDE

Figure 19-a. Initial Scan

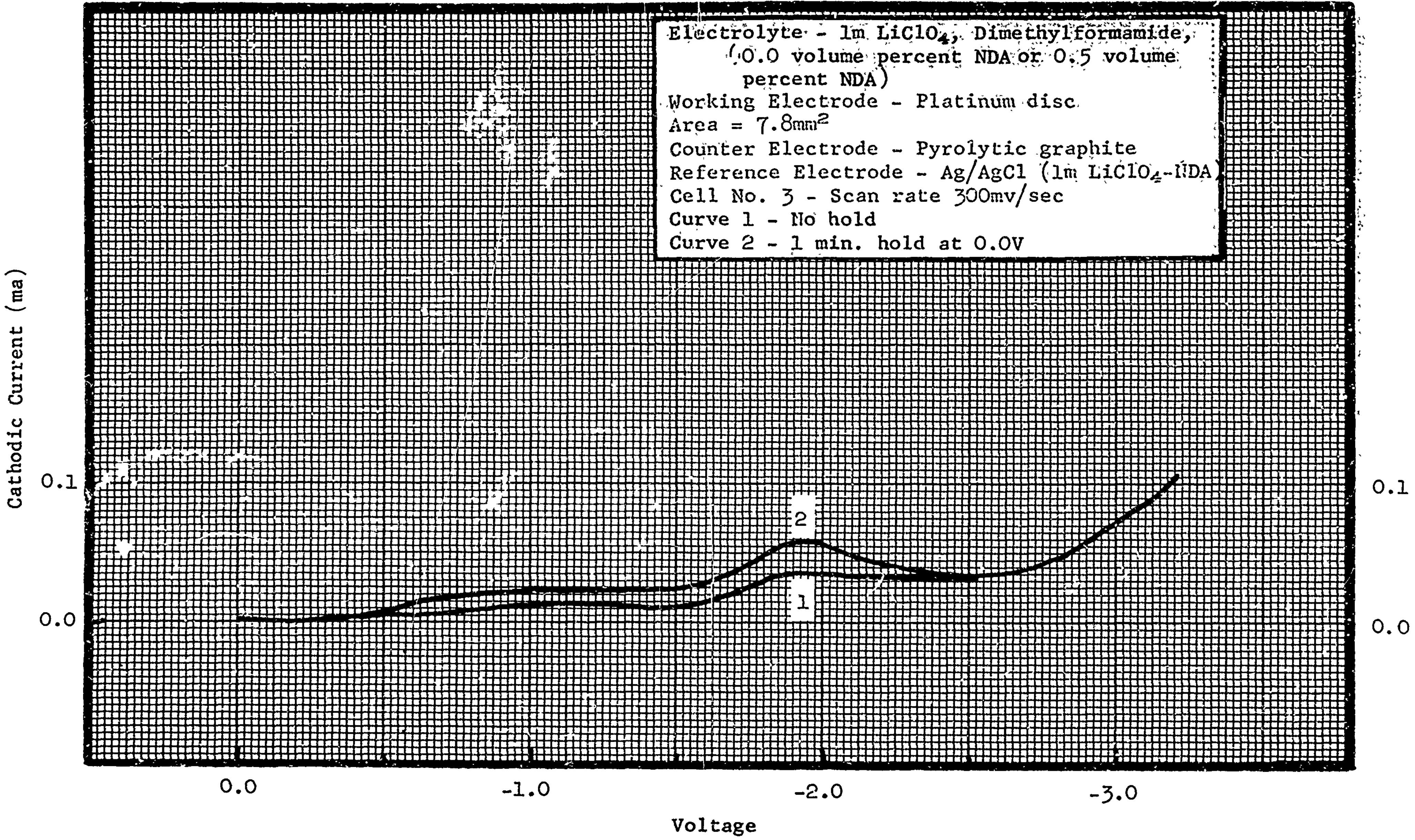


FIGURE 19. <u>VOLTAMMETRY IN 1m $LiClO_4$-DIMETHYLFORMAMIDE</u>

Figure 19-b. Effect of Holding at OV Before Scanning.

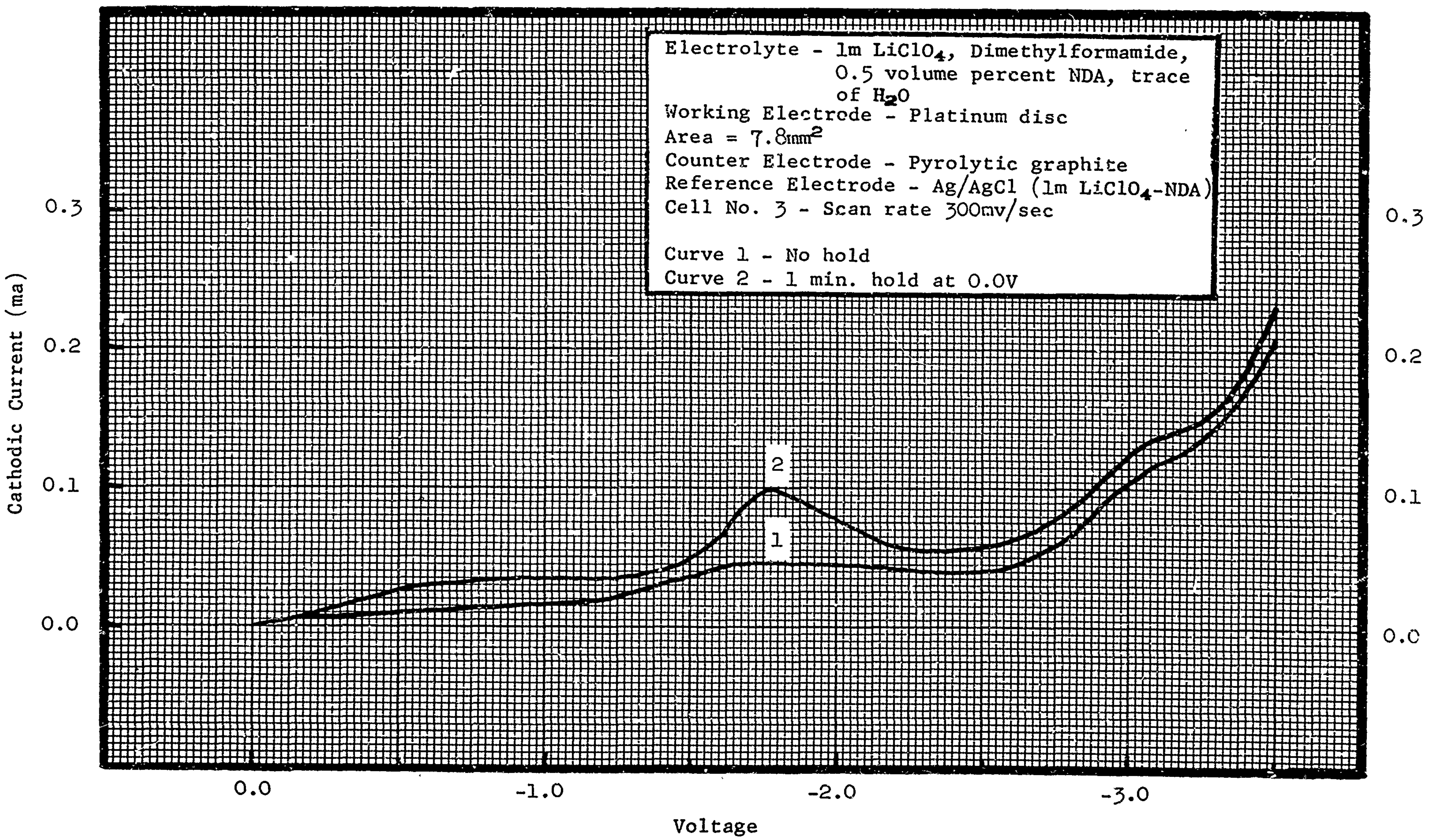


FIGURE 19. VOLTAMMETRY IN 1m $LiClO_4$-DIMETHYLFORMAMIDE

Figure 19-c. Effect of Adding Water.

F. FUTURE WORK

The future work will be directed to the following area:

1. The identification and/or elimination of the electrochemical reducible species found in our systems.
2. The determination of the effect of moisture on oxygen reduction.
3. The effect of the presence of hydroxide ion in the form of a tetraalkylammonium hydroxide on the performance of an air electrode.
4. The investigation of the decomposition potentials of the electrolytes used.
5. The determination of the relationship between oxygen concentration on the air electrode's current producing capability.
6. The electrochemical characterization of oxygen reduction on a silver electrode.

APPENDIX I

Materials & Equipment

The solvents which were utilized in this program and the solutes were purified to insure consistent results in the experimental program, as well as to remove impurities which might affect performance and, hopefully, to increase the ability of other laboratories to reproduce our results.

All the solvents used were purified by vacuum distillation. The vacuum distillation apparatus used included a 1000ml distilling flask, a vacuum-jacketed fractionating column which is strip-silvered, and a vacuum fraction collector. The column has an internal diameter of 2.5cm and is packed with a 90cm bed of 1/8" diameter glass helices. A 1:1 reflux ratio is maintained by means of a swinging funnel fitted with a soft iron core mounted in the distillation head. An electromagnet regulated by a General Electric Type TSA-14 timing device moves this funnel into position for either total reflux or collection. The timer cycle of 20 seconds is divided into the desired ratio of total reflux to collection, in this case 1:1. Vacuum is maintained with a No. 1400B Welch Duoseal vacuum pump capable of achieving a pressure of one micron. The vapor pressure is measured by an open ended manometer. The pressure in the system during distillation was kept as low as permitted by proper reflux conditions. For each solvent purified, 700ml were distilled. The first and last 100ml fractions were discarded. The purity of the distilled solvents were characterized by determining their refractive index, specific conductance, density and viscosity. The refractive indices were determined on a thermostated 28°C Bausch and Lomb "ABBE-56" refractometer. Conductances were determined using a dipping type conductance cell with black platinized platinum electrodes and a General Radio Type 1650-A impedance bridge. Densities were determined using a Westphal balance and viscosities with an Ostwald viscometer.

Both propylene carbonate and nitrosodimethylamine have been investigated for impurities using the vapor phase chromatograph (VPC). At the present time, VPC analysis is not routinely run on every batch of solvent but in the near future it will be incorporated into our routine solvent characterization.

The following solutes were investigated for use with the previously described solvents: lithium perchlorate, lithium hexafluorophosphate, trimethylphenylammonium hexafluorophosphate, and tetramethylammonium hydroxide. The lithium perchlorate obtained from Foote Chemical Company was dried at 120°C before use. The trimethylphenylammonium hexafluorophosphate from Ozark-Mahoning, tetramethylammonium hydroxide pentahydrate from City Chemical Company and the lithium hexafluorophosphate from Ozark Mahoning Company was used as received.

:3

The voltammetric equipment available in this laboratory consists of combinations of operational amplifier circuits originally suggested by Professor DeFord[22] of Northwestern University and modified by Professor I. Shain[23] and associates at the University of Wisconsin. This equipment can be utilized to carry out electrochemical studies involving all electrochemical methods presently in use, with the exception of very high frequency techniques and it can be modified to handle these. A block diagram of the instrument and a circuit configuration for controlled potential methods are shown in Figures 20 and 21, pages 55 and 56.

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[22] DeFord, D.D., Division of Anal. Chem., 133rd Meeting ACS, S.F., Calif., April 1958.

[23] Underkofler, W.L. and Shain, I., Anal. Chem., 35, 1778 (1963).

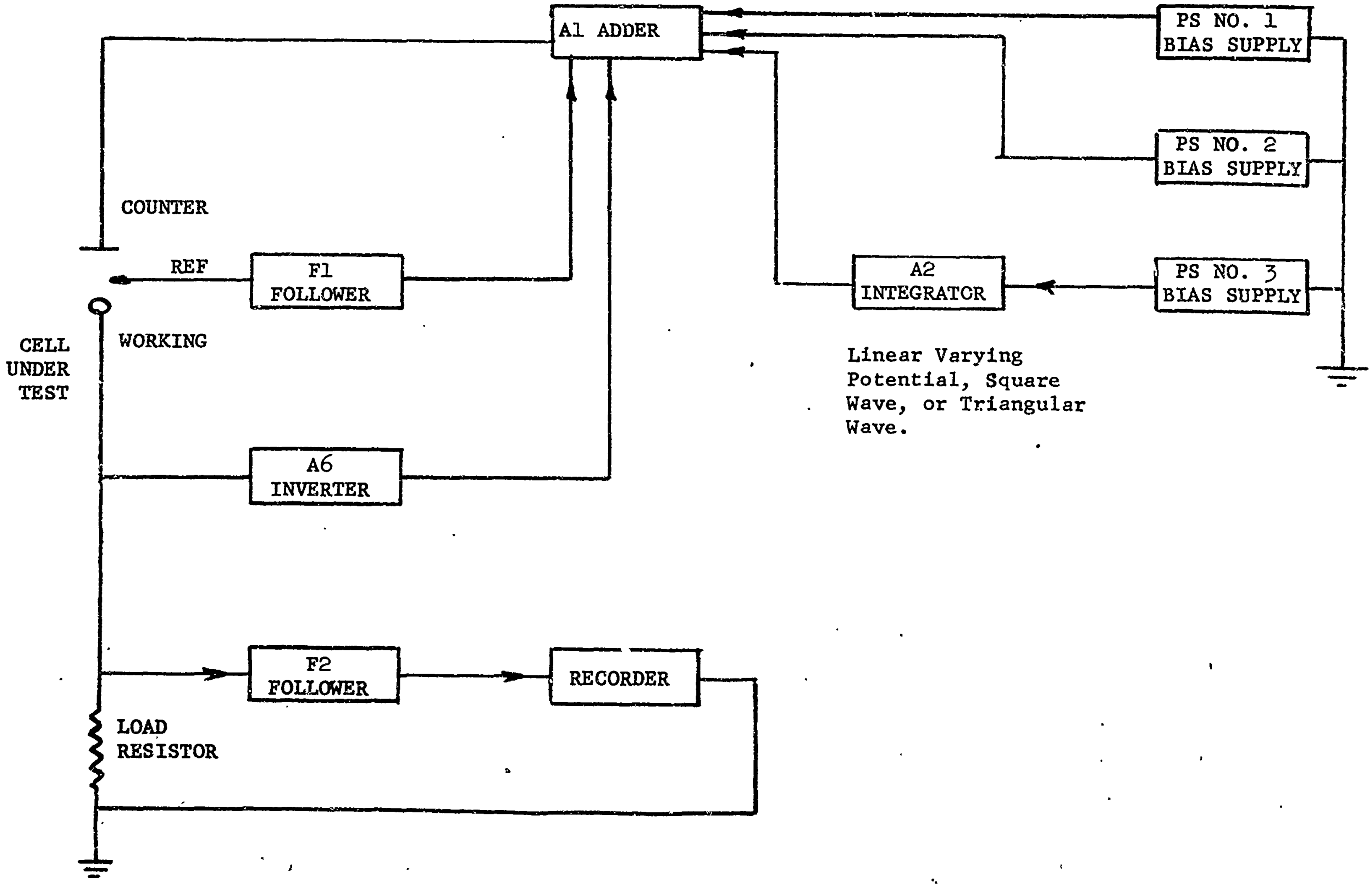
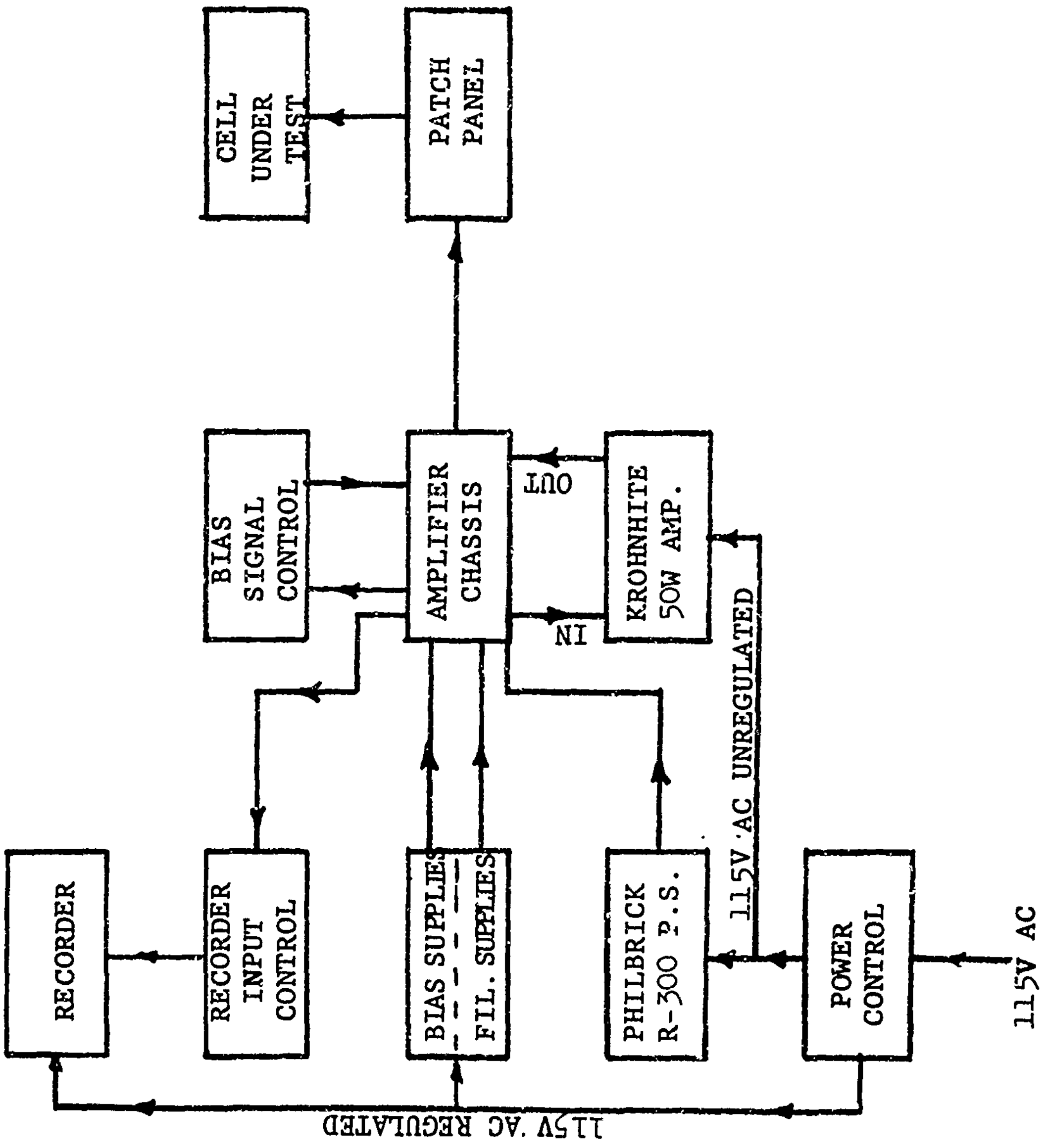


FIGURE 20. BLOCK DIAGRAM OF THE INSTRUMENT FOR ELECTROCHEMICAL STUDIES

FIGURE 21. CIRCUIT CONFIGURATION FOR CONTROL POTENTIAL METHODS



APPENDIX II

Exploratory Studies

In our preliminary studies for this program, it was necessary to do some exploratory experimental work to select the methods and materials which would be used and to define specific problem areas experimentally. In the electrochemical area it was necessary to run preliminary experiments with voltammetric techniques, various electrode materials, electrolytes, reference electrodes and different cell designs in order to make the proper selections for further studies. From this work certain conclusions were reached as to the problem areas in this program. The preliminary experiments demonstrated that voltammetry would be highly sensitive and diagnostic of electrochemical reactions which occur at the air electrode. The preliminary experiments were carried out with the American Cyanamid platinized platinum electrode No. AA-1 in a solution consisting of nitrosodimethylamine saturated with tetramethylammonium hydroxide and one molal in phenyltrimethylammonium hexafluorophosphate. The earliest curves obtained in this program demonstrating the reduction of oxygen are shown in Figure 22, page 58. In addition, some early curves were obtained with constant potential holds at potentials more positive than zero versus a silver strip reference prior to the scan (Figure 23, page 59). This set of data indicated that it was possible to passivate the platinum electrode at potentials more positive than zero volts versus the silver strip reference electrode. It was also learned, however, that the passivation could be removed by treating the electrode in aqueous media and evolving hydrogen at its surface. Another electrode which was examined without obtaining satisfactory reproducibility was the Allis-Chalmers silver fuel cell air electrode. Because of the above problems with these two fuel cell electrodes, it was decided that more detailed studies would be performed with a smooth platinum disc electrode.

In the process of obtaining the preliminary voltammetric data, several materials, methods and cell designs were studied. For example, the electrochemical tests were tried in three different cell designs, shown in Figures 24, 3 and 4, pages 60, 5 and 12, respectively. Several electrolytes were also utilized and will be discussed later. In addition, it was found that the silver strip reference electrode was not sufficiently poised to be a good stable reference electrode, whereas a specially designed silver-silver chloride electrode (Figure 1, page 2) performed very satisfactorily.

While most of the exploratory work involved electrochemical studies, the need for chemical tests became apparent. Two of the species which will have to be determined quantitatively are moisture and oxygen. Present plans are to determine moisture content by either vapor phase chromatography or the Karl Fischer method. Presently, methods for the determination of oxygen in solution are being investigated since the only commonly used test, the Winkler test, is tedious and complex. The possibility of using the method devised by Kolthoff and his associates[8] is now being explored. Preliminary experiments with his method have been promising and work is continuing on this technique.

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[8] Coetzee, J.F. and Kolthoff, I.M., J. Am. Chem. Soc., 79, 6110, (1957)

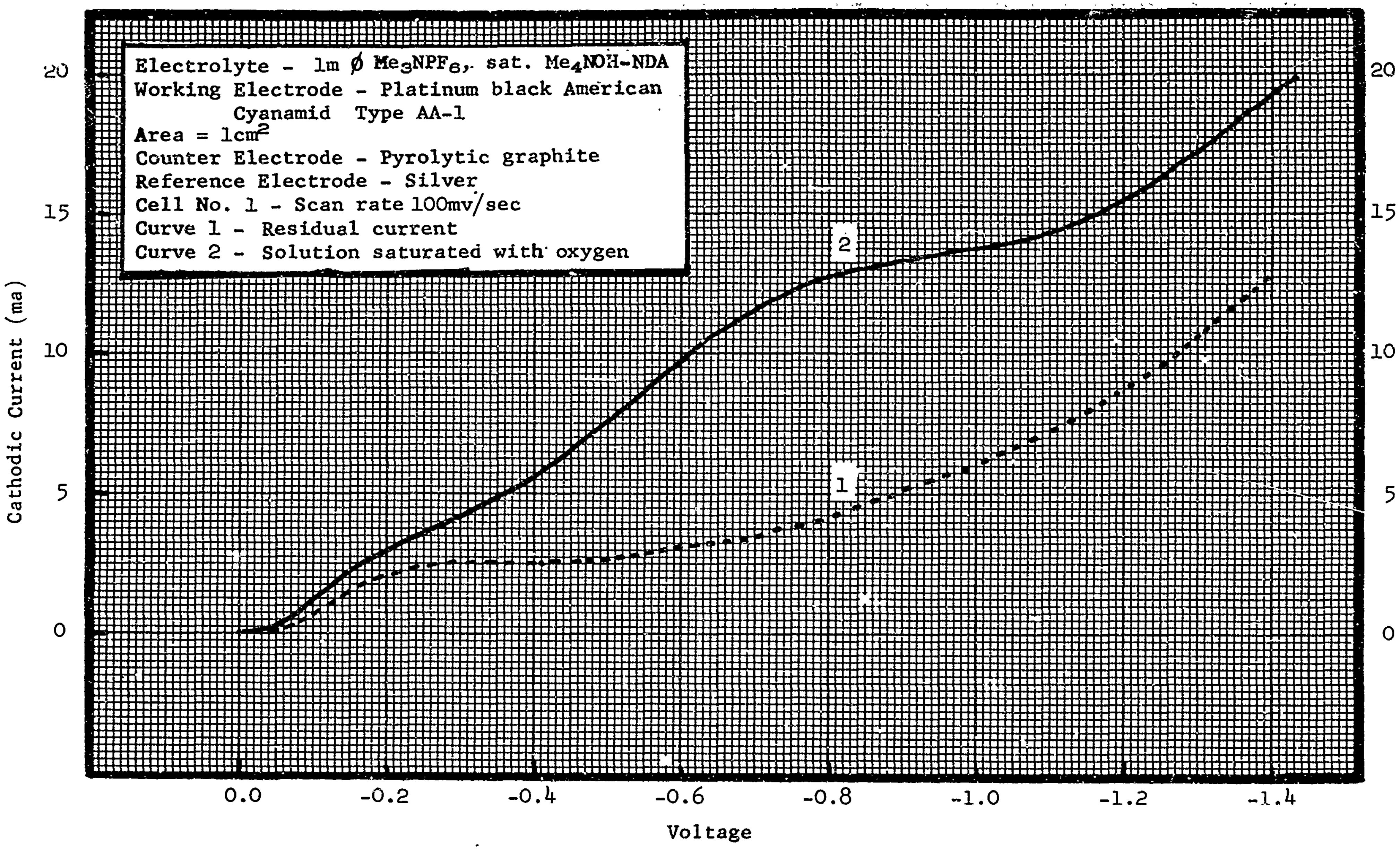


FIGURE 22. REDUCTION OF OXYGEN USING CELL NO. 1

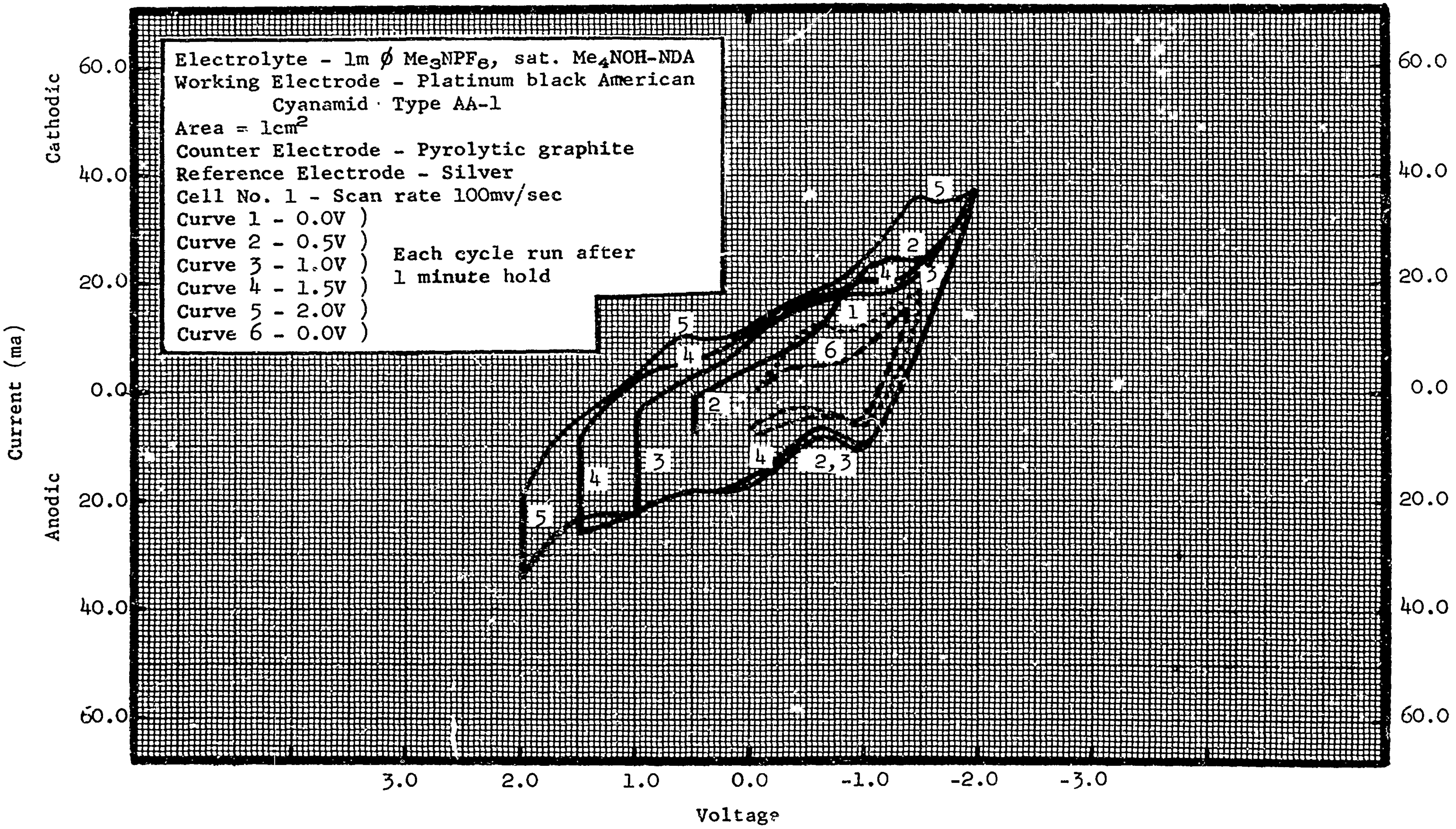
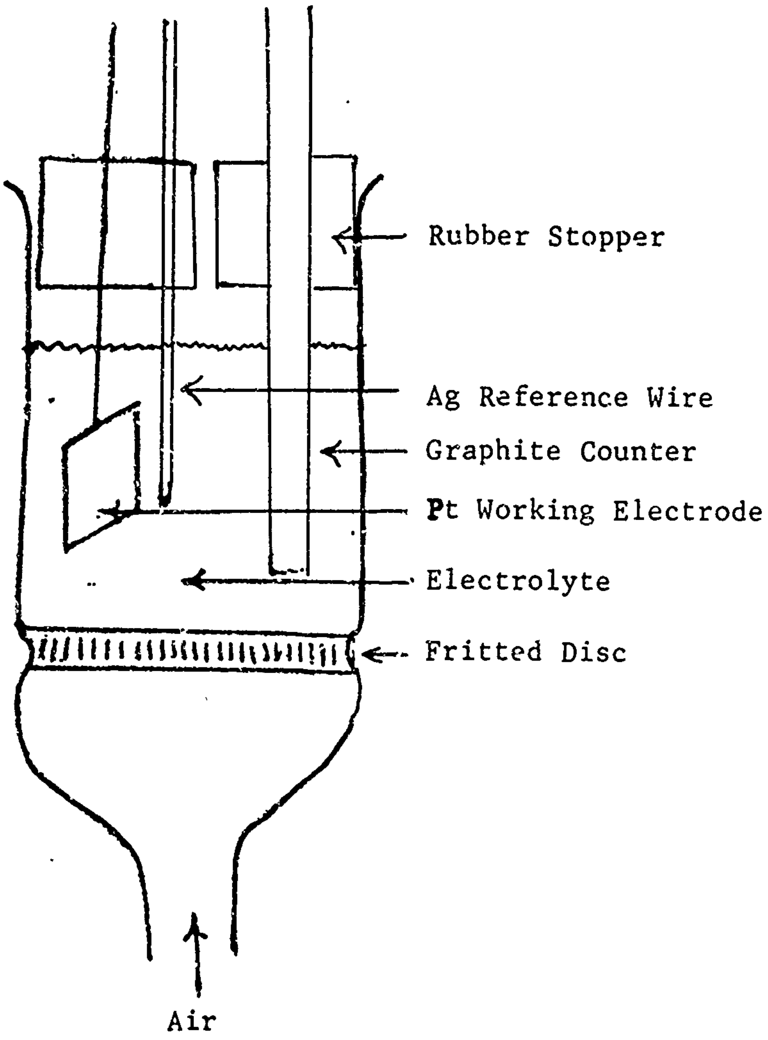


FIGURE 23. PASSIVATION OF THE PLATINUM AMERICAN CYANAMID ELECTRODE

FIGURE 24. TEST CELL DESIGN NO. 1



In addition to the above considerations, it was also felt necessary to do some preliminary work with a small lithium air cell to simply examine the level of performance that could be obtained and any sources of deterioration that might be observed. This cell ran at low current densities for approximately 102 hours, at which time the cell performance had deteriorated to the point where it was felt that it should be torn down and examined. When it was examined it was found that moisture had reacted with the lithium and also that a deposit had formed on the surface of the air electrode which was determined to be lithium hydroxide monohydrate and lithium carbonate. Thus it is recognized that the lithium ion must be prevented from reaching the cathode in an operating cell. By the same token, it was also found that the air electrode was quite durable in that it could be cleaned to remove deposits and then again operated as an air electrode for a substantial length of time (approximately 30 hours). Based on this exploratory work, it was determined that much better characterization of the performance of the oxygen or air electrode in nonaqueous electrolytes would be necessary.

Initial work was devoted to the determination of the oxygen reduction potential region in nonaqueous electrolytes. The linear scan and cyclic voltammetry was run on solutions which had been purged with nitrogen or on solutions which were saturated with oxygen. For these studies the cell design shown in Figure 24, page 60, was used (cell No. 1). At the time of these experiments, the reversibility studies of the Ag/AgCl reference electrode had not been performed and a sheet silver reference was used. The working electrode was the American Cyanamid platinum black electrode (AA-1). The cell was completed with a pyrolytic graphite counter electrode. The electrolyte generally used consisted of nitrosodimethylamine, which was saturated with tetramethylammonium hydroxide and one molal in phenyltrimethylammonium hexafluorophosphate.

One of the earliest curves obtained for the reduction of oxygen is shown in Figure 22, page 58. The first curve which is shown is the residual current obtained with nitrogen passing through the solution. The second curve shows the reduction of oxygen after the solution had been saturated with oxygen. If the solution was subsequently purged with nitrogen for 15 minutes, the first curve was again obtained. The general shape of the oxygen reduction wave is a very broad wave which started at approximately zero volts and reached a plateau of about -0.5 volts.

During this exploratory work, it was often difficult or impossible to reproduce the results. On occasion the same curves were obtained with or without oxygen. The abnormal behavior was found to be due to passivation of the platinum black electrode when it was held at potentials more positive than zero volts. This passivation of the electrode was encountered whenever we scanned the electrode in the region between +2 volts to -2 volts in an attempt to cover the whole polarization range of the electrolyte.

The scans shown in Figure 23, page 59, run on the same day using the same electrode and solution that had been used in the experiment shown in Figure 23 shows the effect of holding the platinum black electrode at various potentials on the subsequent scans. Curve 1 is the oxygen reduction after holding the potential of the electrode at zero volts for one minute. Curves 2 through 5 are the cycles after one minute holds at +0.5 volts, +1.0 volts, +1.5 volts and +2.0 volts, respectively. Curve 6 is the curve obtained after a one minute hold at zero volts but after the series had been completed. It is interesting to note the pronounced effect of the various holds on the subsequent reduction waves. The oxygen reduction was only obtained on the initial scan and all subsequent scans were considerably different. It should be pointed out that after Curve 6 it was impossible to obtain the oxygen reduction wave again by holding the electrode at zero volts versus a silver strip reference or at a potential more negative than zero volts.

A passivated electrode was found to be reactivated by the evolution of hydrogen on the electrode in an acidic aqueous solution, possibly by reduction of platinum oxides. This pretreatment may cause problems because of the possibility of altering the platinum surface by dissolution of H_2 into the platinum during hydrogen evolution.[24] It should also be pointed out that the working electrode used for these experiments was a porous platinum black fuel cell electrode. This type of electrode, after passivation, would be particularly difficult to reactivate because of its extremely large surface area.

A second cell (Figure 3, page 5) (cell No. 2) was designed in which the geometry of the electrodes was close to a possible configuration of a battery. Using this cell, it was noted that an increase in the current was obtained by increasing the air oxygen pressure applied to the electrode. The particular configuration of the American Cyanamid air electrode did not permit a wide range of pressure variation. Gas broke through the electrode at relatively low pressures. Figure 25, page 63, shows the residual current and the current obtained through the reduction of oxygen using the second cell design. The definition of the reduction wave using this cell design is noticeably poorer than that obtained using the first cell design. For this reason the first cell design was used for all subsequent voltammetric studies in the exploratory work.

A lithium-air test battery was assembled to determine the compatibility of the various components. The cell design used for this test is shown in Figure 3, page 5, with the graphite counter replaced with a lithium electrode. The silver air electrode (Allis-Chalmers No. 3860) was mechanically protected from the lithium anode by a Gelman glass fiber barrier. The electrolyte used was one molal lithium perchlorate-nitrosodimethylamine. The air supplied to the cell was saturated with moisture

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[24] Schuldiner, S. and Warner, T.B., Electrochim. Acta, 11, 307 (1960)

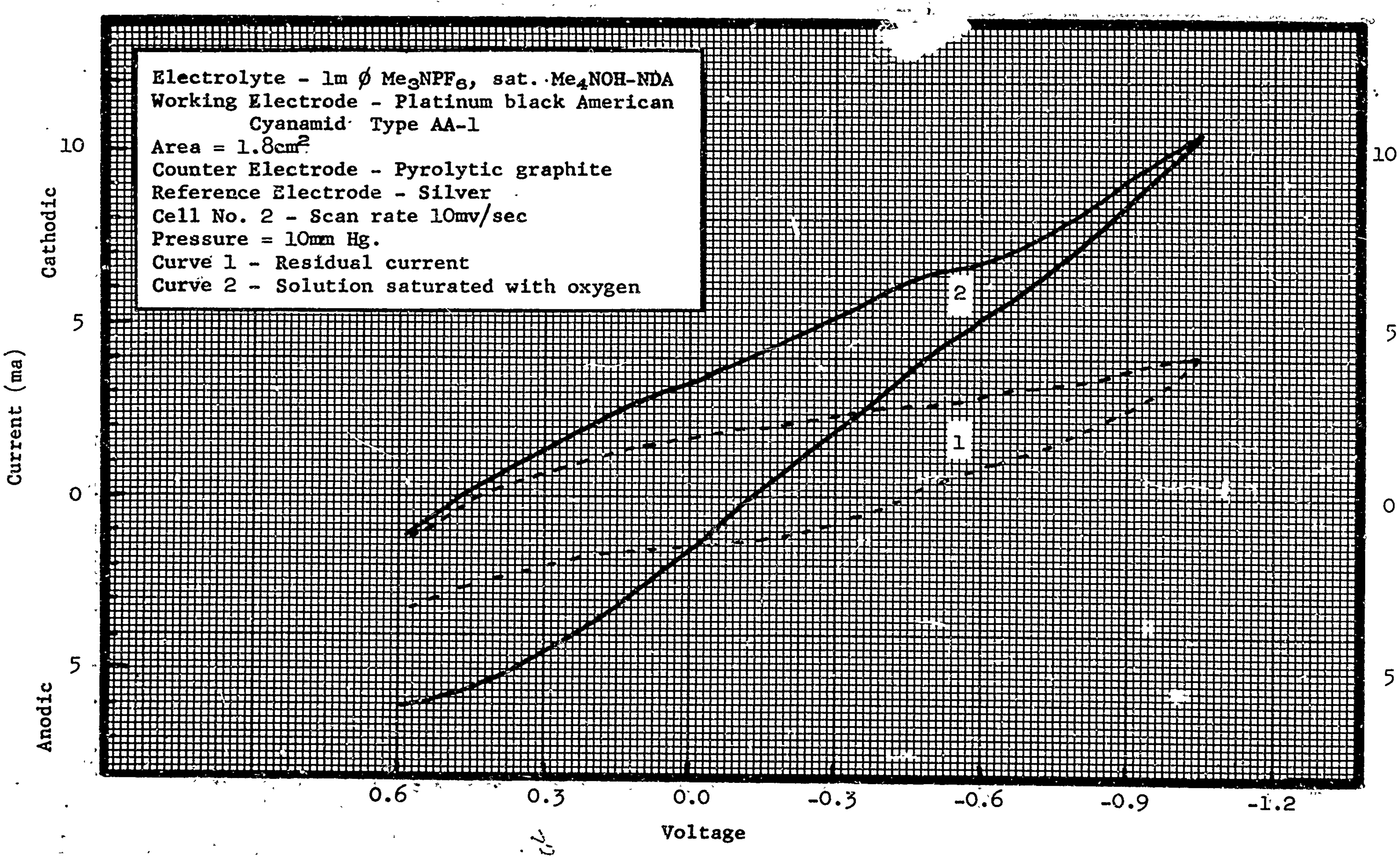


FIGURE 25. REDUCTION OF OXYGEN USING CELL NO. 2

by passing it through an aqueous bubbler. The potentials of the lithium and the air electrode for a 1ma/cm^2 spontaneous discharge are given in Table I, page 6. After 102 hours of discharge, the cell was disassembled. The air-electrode was found to be covered with a heavy deposit which was identified by X-ray diffraction as lithium hydroxide monohydrate and lithium carbonate. Cleaning the air electrode with a ten percent aqueous oxalic acid solution removed the basic deposit. A 1ma/cm^2 forced discharge, see Table I, page 6, showed that this treatment did restore the electrode's performance. This experiment shows that enhanced electrode performance could be obtained if the deposition of lithium hydroxide can be prevented from occurring on the air electrode's surface.

After the initial exploratory work, a series of experiments were performed to identify and locate the oxygen reduction potential region in a variety of different electrolytes. At present oxygen reduction waves have been observed in each of the following electrolytes:

> One molal phenyl-trimethylammonium hexafluorophosphate, saturated tetramethylammonium hydroxide - N-nitrosodimethylamine (NDA)
>
> One molal phenyl-trimethylammonium hexafluorophosphate, saturated tetramethylammonium hydroxide - propylene carbonate (PC)
>
> One molal lithium perchlorate - N-nitrosodimethylamine
>
> One molal lithium perchlorate - propylene carbonate
>
> One molal phenyl-trimethylammonium hexafluorophosphate - N-nitrosodimethylamine
>
> One molal phenyl-trimethylammonium hexafluorophosphate - propylene carbonate

Figures 26-31, pages 65 through 77 show the reduction waves attributable to oxygen in the electrolytes listed above. The oxygen was saturated with moisture before it was admitted to the cell. The effect of scan rate is also shown in these figures. The following conclusions can be drawn from a comparison of these figures. The current densities found in N-nitrosodimethylamine are usually larger than those found in propylene carbonate at a given potential and in the case of the lithium perchlorate containing electrolytes the current density at the peak is approximately ten times larger for the N-nitrosodimethylamine that the propylene carbonate solutions. Since well-defined oxygen waves were not obtained in most of these electrolytes, it is not possible to compare peak potentials or halfwave potentials. However, since higher currents are obtained in N-nitrosodimethylamine than propylene carbonate electrolytes it is the solvent of choice for further studies.

It is particularly interesting to note that when the electrolyte containing phenyl-trimethylammonium hexafluorophosphate was used alone, that is, without a quaternary ammonium hydroxide, the oxygen reduction wave appears to be approximately 0.5 volts more positive versus a silver strip reference than when the other electrolytes were used. The reason for this potential shift is not yet known and further study is required.

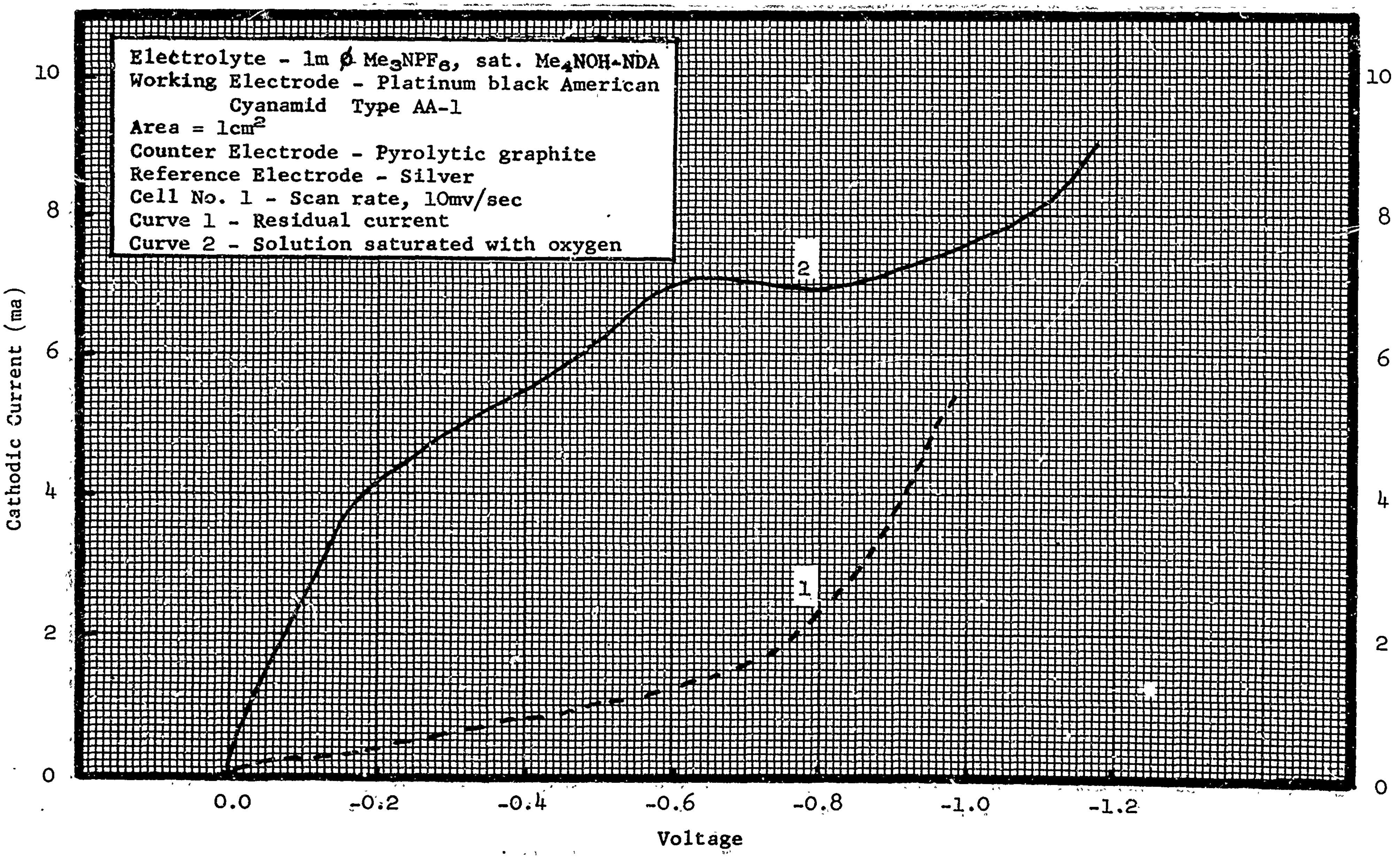


FIGURE 26. REDUCTION OF OXYGEN IN 1m ∅ Me$_3$NPF$_6$, SATURATED Me$_4$NOH-NDA

Figure 26-a. Scan Rate 10mv/sec.

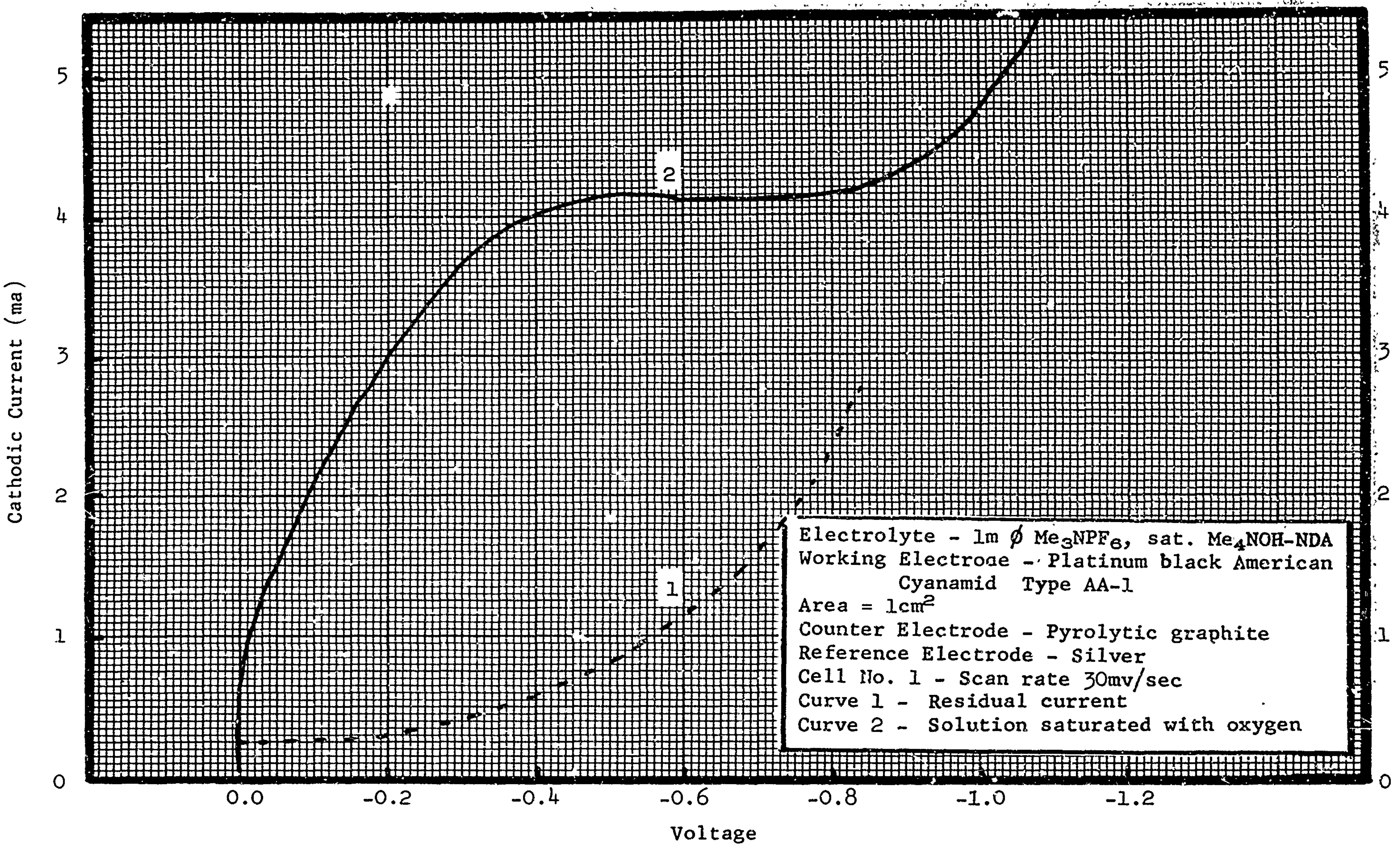


FIGURE 26. REDUCTION OF OXYGEN IN 1m ∅ Me_3NPF_6, SATURATED Me_4NOH-NDA

Figure 26-b. Scan Rate 30mv/sec.

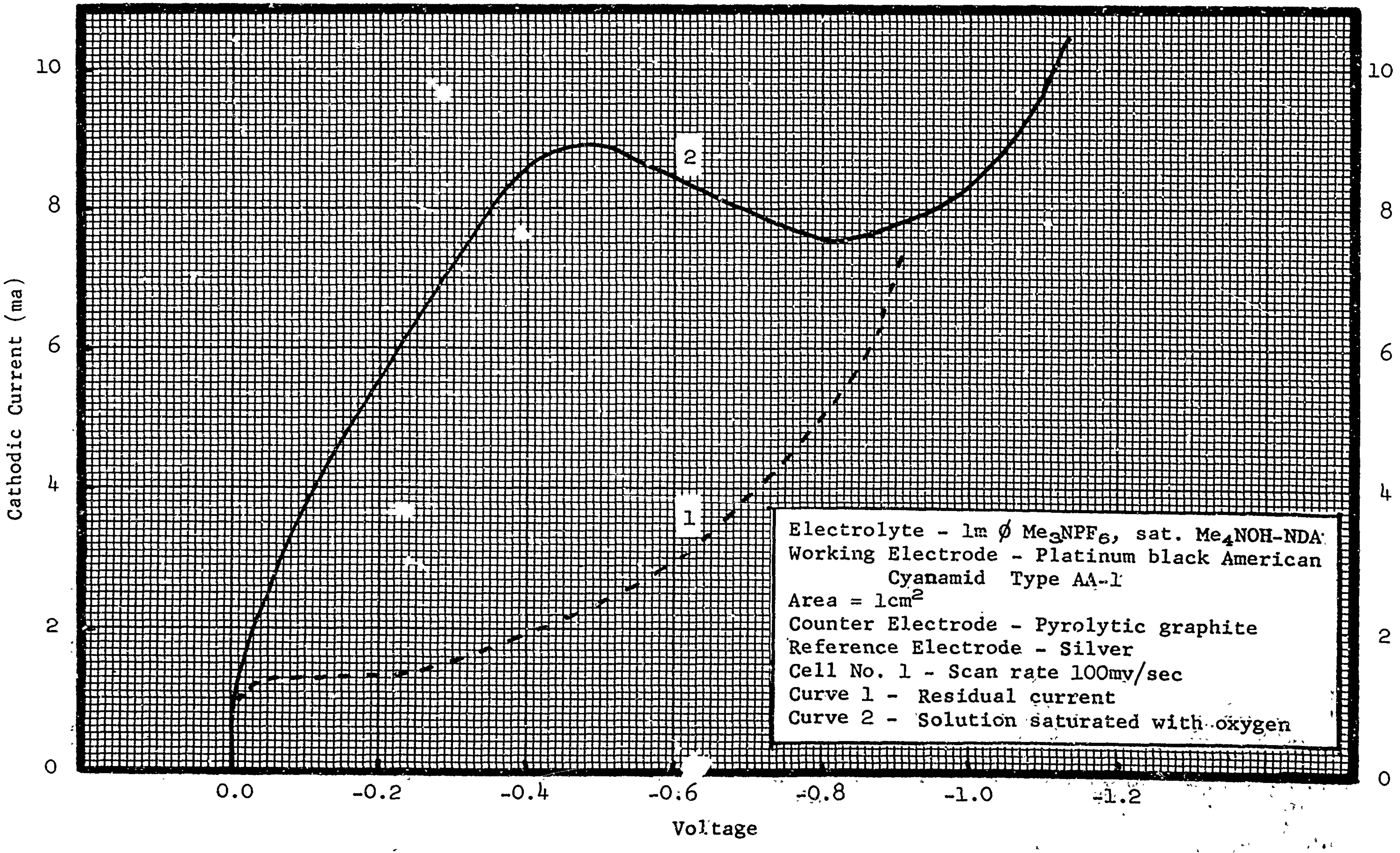


FIGURE 26. <u>REDUCTION OF OXYGEN IN 1m Ø Me_3NPF_6, SATURATED Me_4NOH-NDA</u>

Figure 26-c. Scan Rate 100mv/sec.

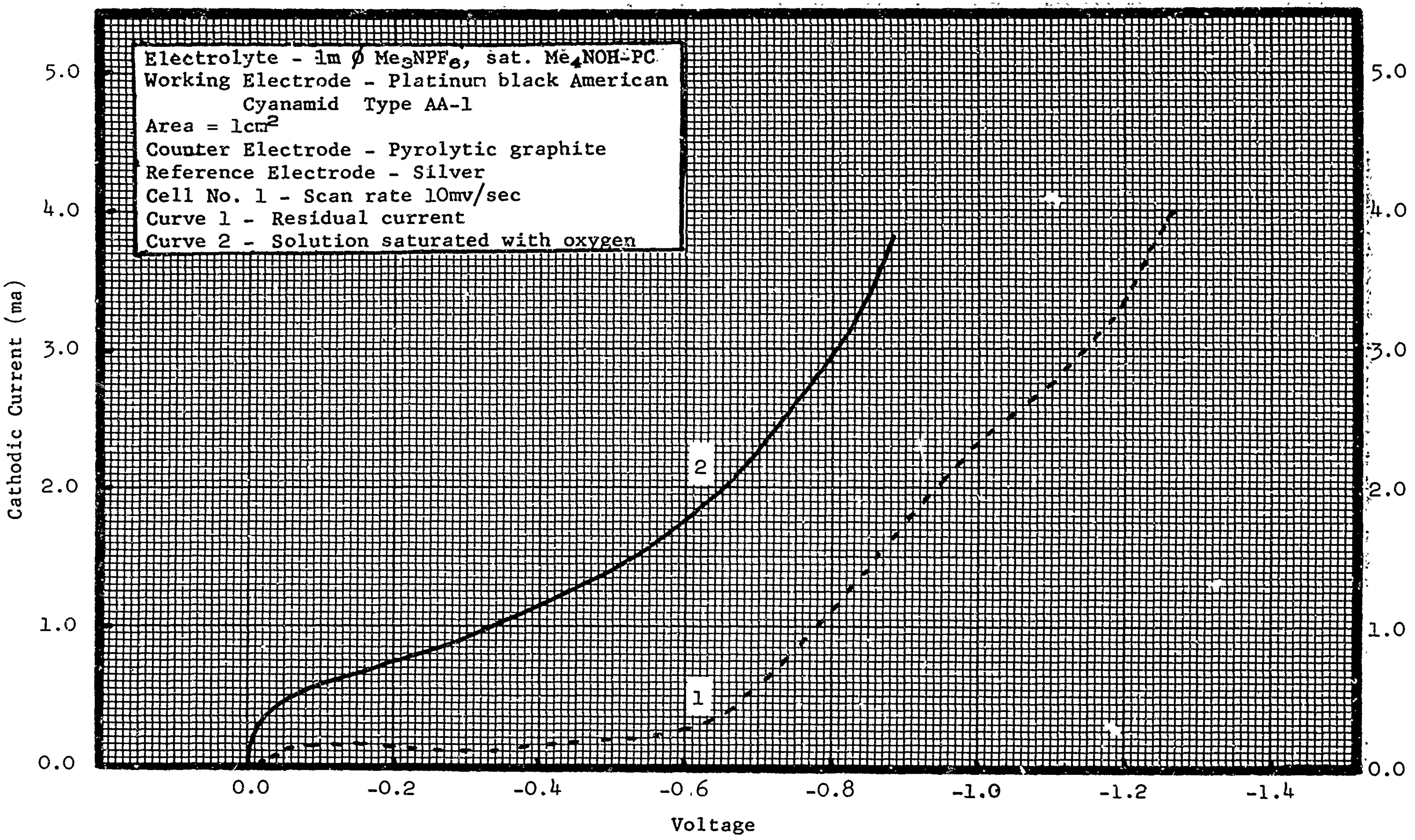


FIGURE 27. REDUCTION OF OXYGEN IN 1m Ø Me_3NPF_6, SATURATED Me_4NOH-PC

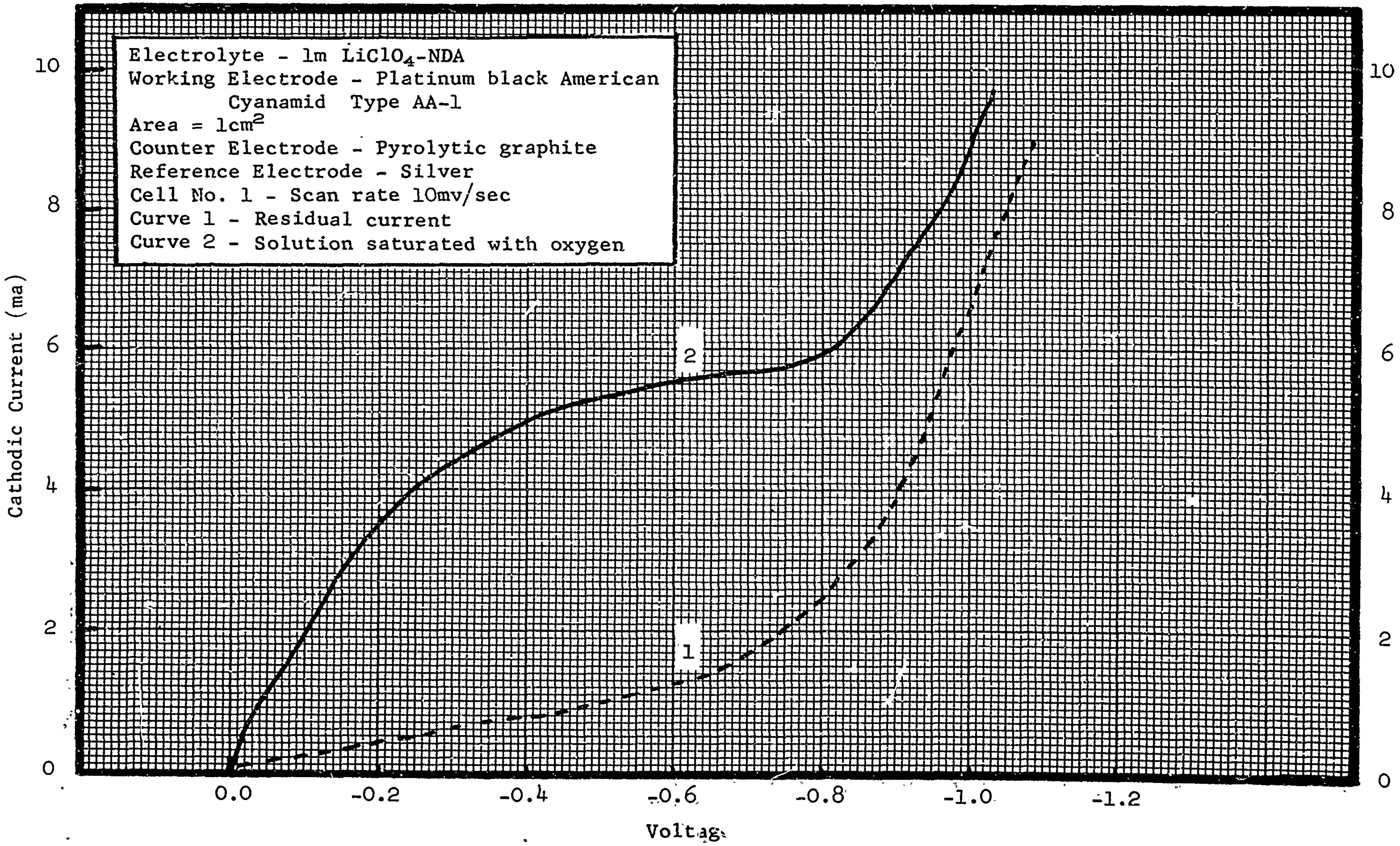


FIGURE 28. <u>REDUCTION OF OXYGEN IN 1m LiClO$_4$-NDA</u>

Figure 28-a. Scan Rate 10mv/sec.

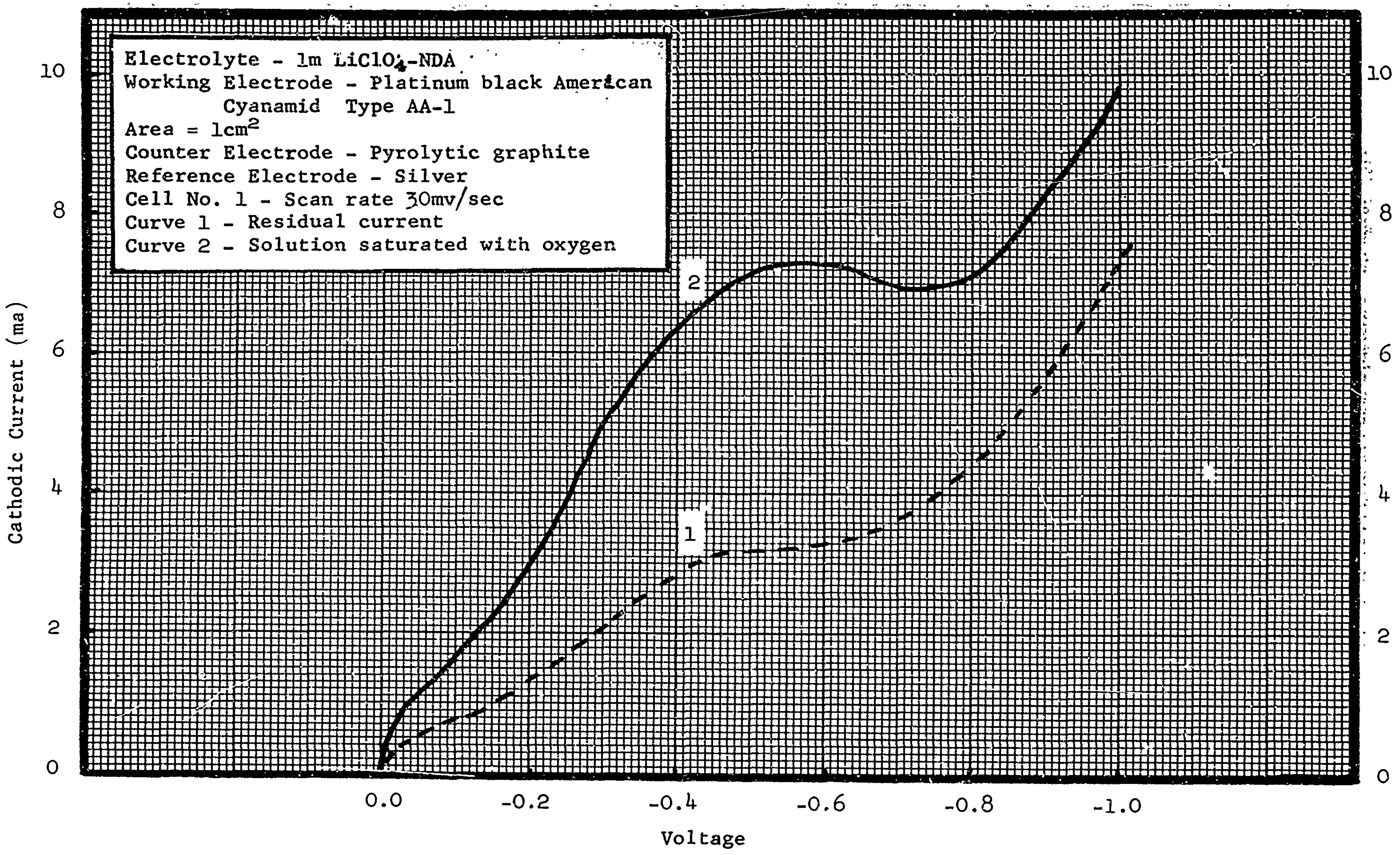


FIGURE 28. REDUCTION OF OXYGEN IN 1m LiClO$_4$-NDA

Figure 28-b. Scan Rate 30mv/sec.

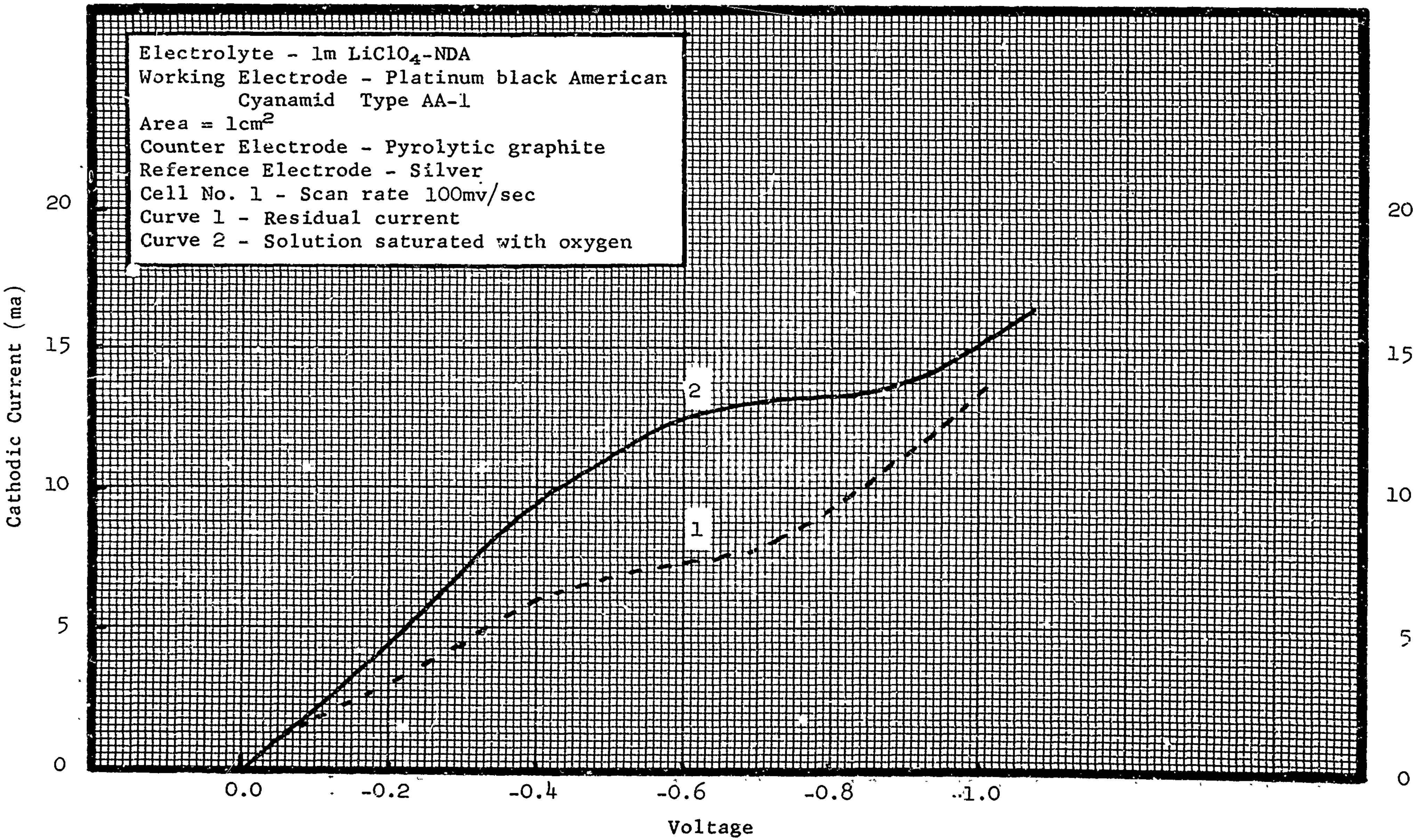


FIGURE 28. REDUCTION OF OXYGEN IN 1m $LiClO_4$-NDA

Figure 28-c. Scan Rate 100mv/sec.

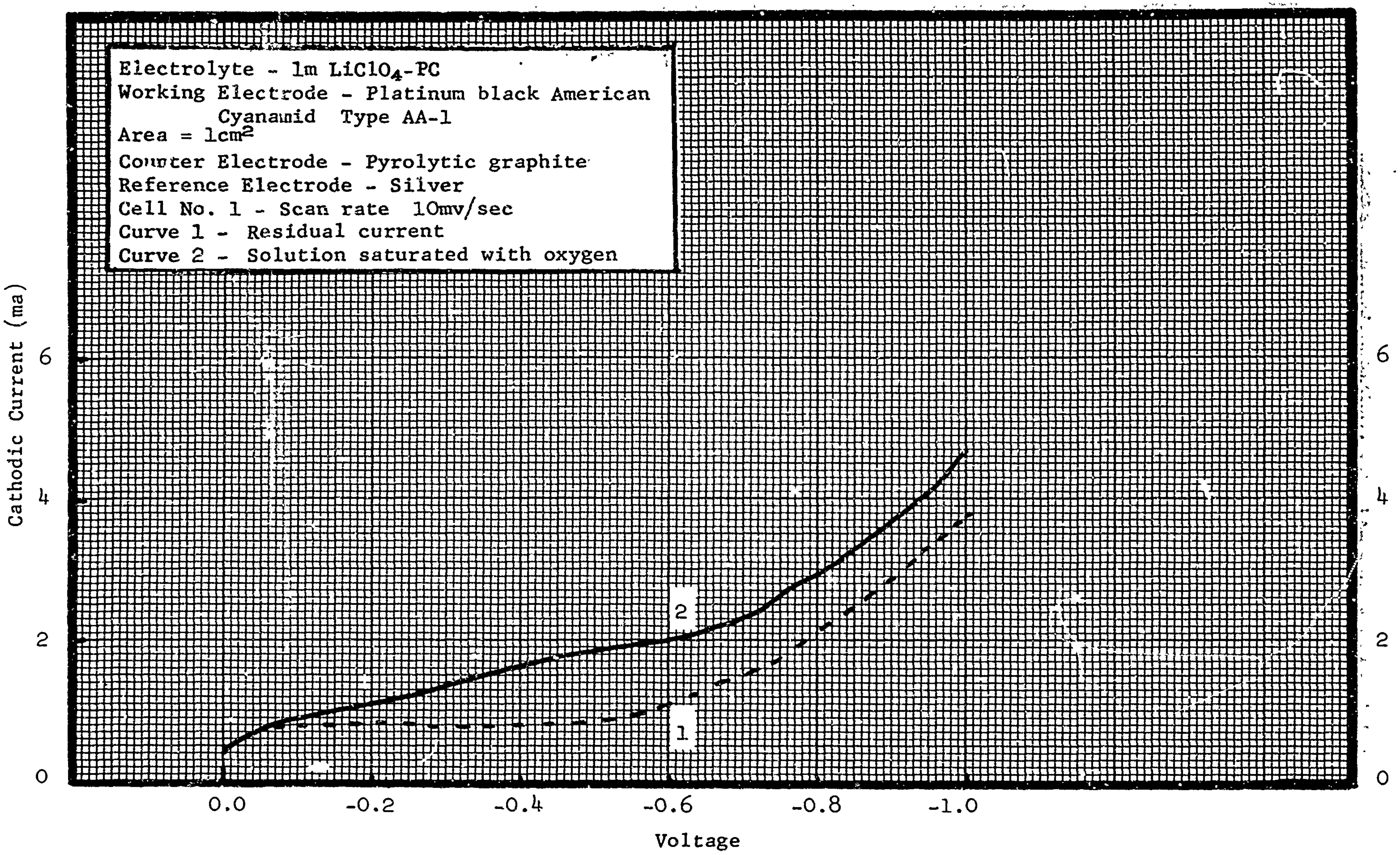


FIGURE 29. REDUCTION OF OXYGEN IN 1m $LiClO_4$-PC

Figure 29-a. Scan Rate 10mv/sec.

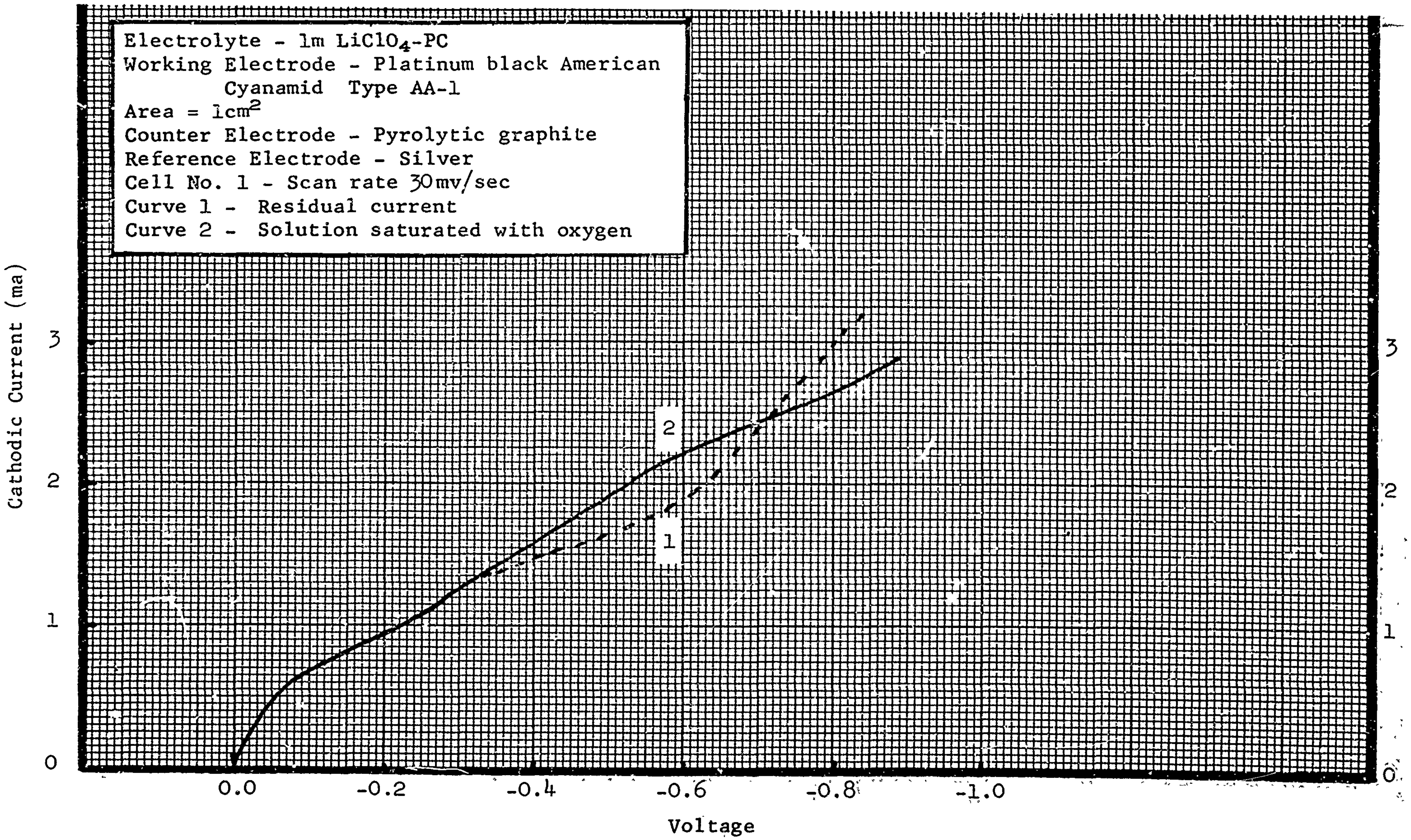


FIGURE 29. REDUCTION OF OXYGEN IN 1m $LiClO_4$-PC

Figure 29-b. Scan Rate 30mv/sec.

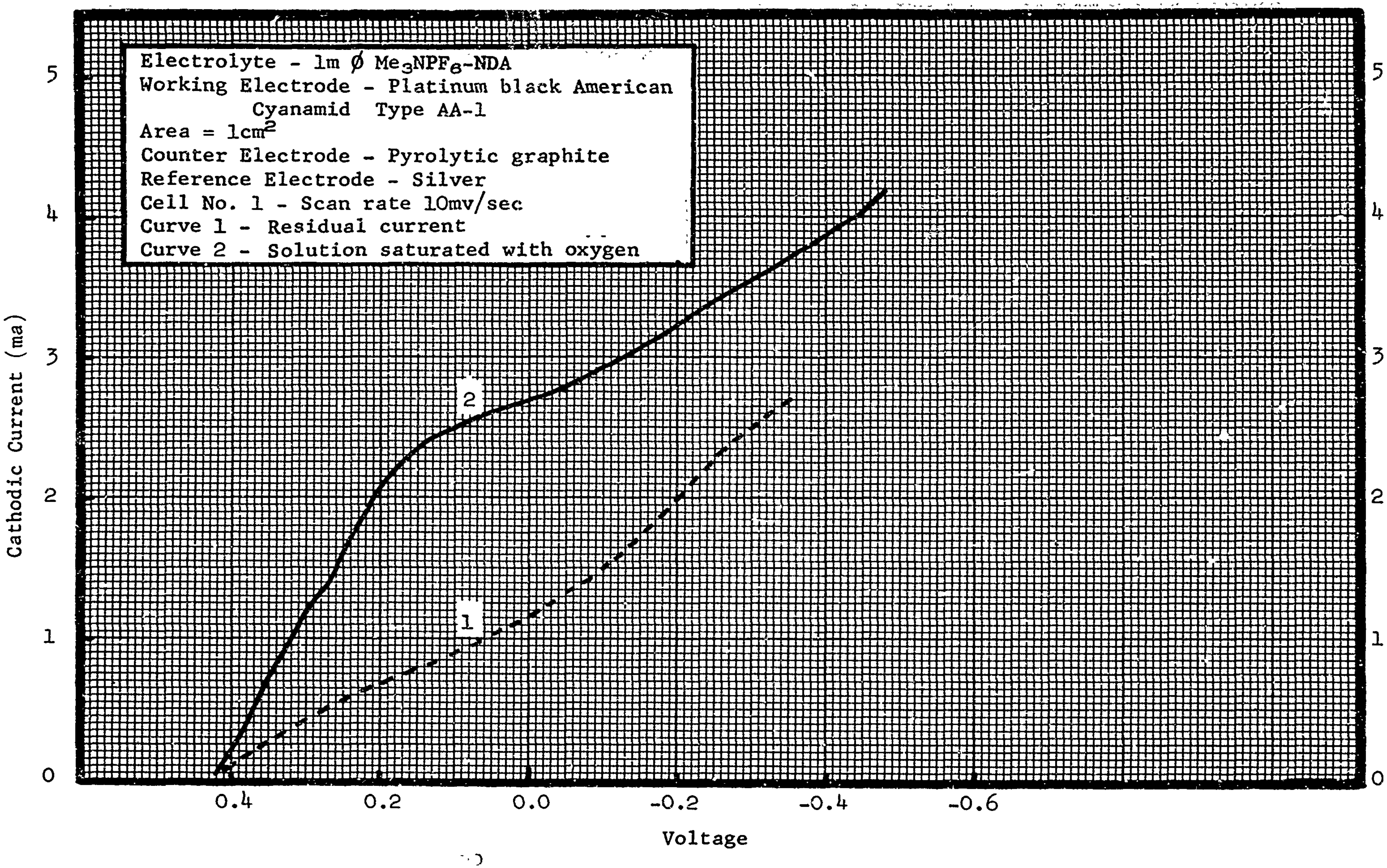


FIGURE 30. <u>REDUCTION OF OXYGEN IN 1m Ø Me_3NPF_6-NDA</u>

Figure 30-a. Scan Rate 10mv/sec.

Figure 30-a. Scan Rate 10mv/sec.

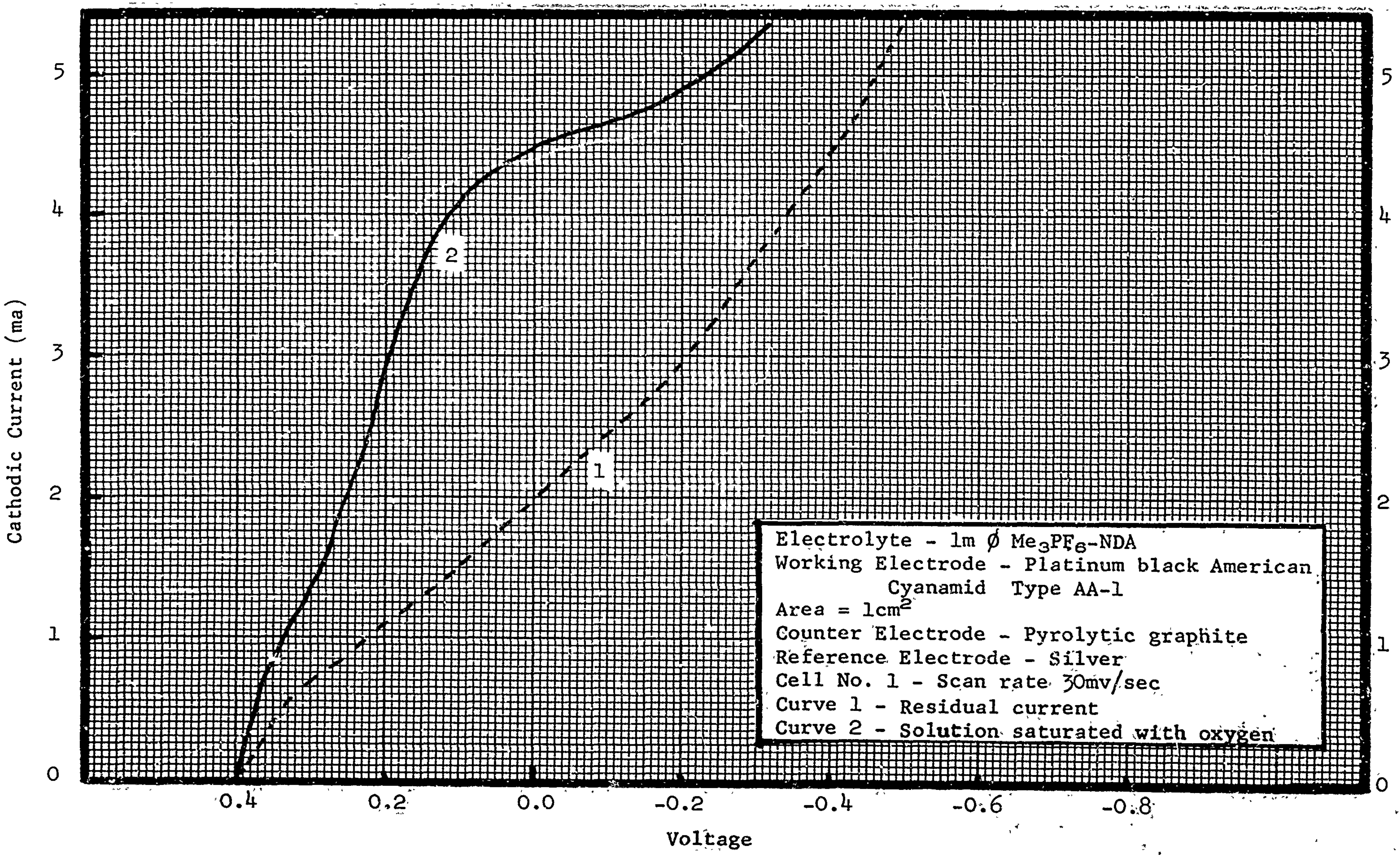


FIGURE 30. REDUCTION OF OXYGEN IN 1m ∅ Me_3PF_6-NDA

Figure 30-b. Scan Rate 30mv/sec.

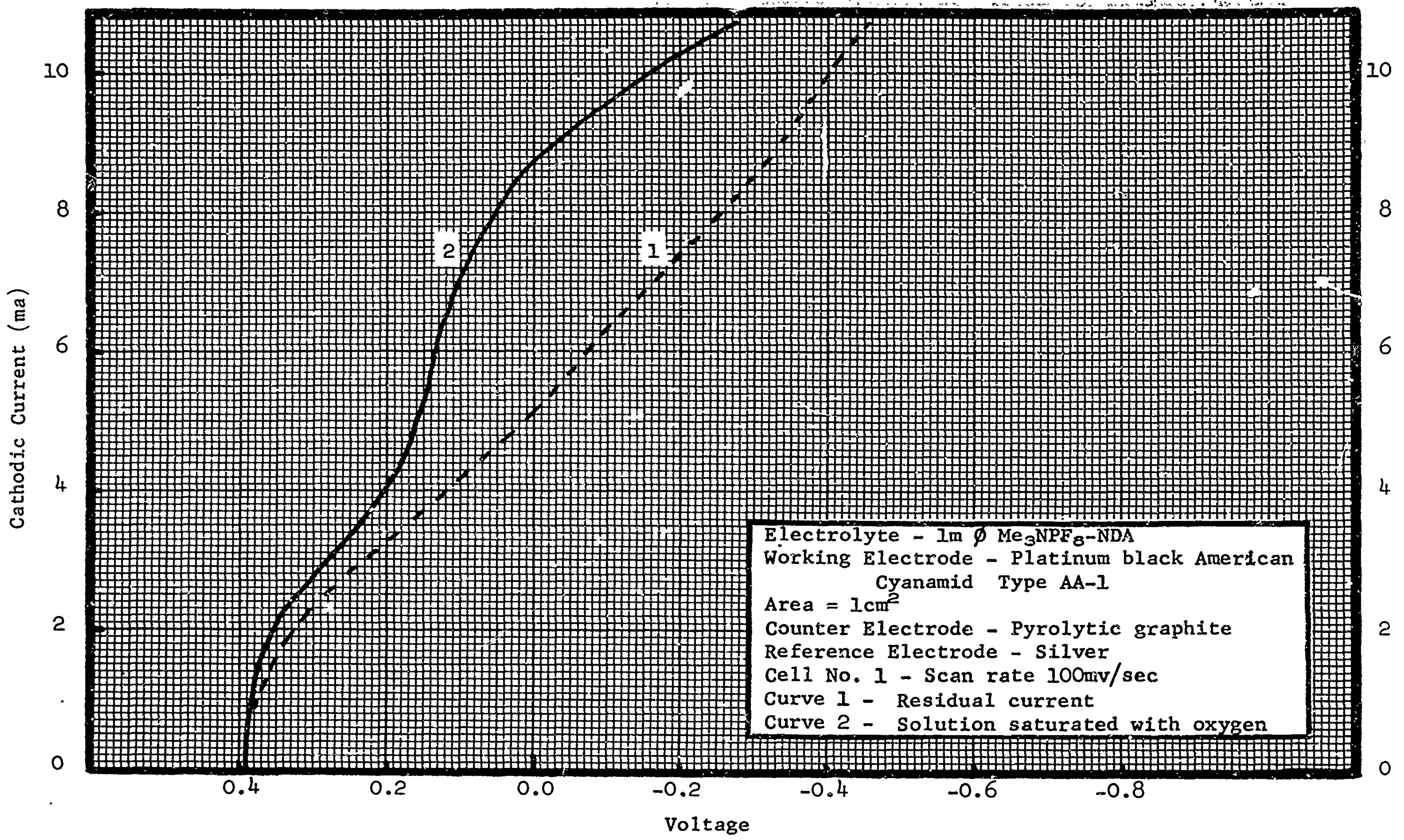


FIGURE 30. REDUCTION OF OXYGEN IN 1m ∅ Me_3NPF_8-NDA

Figure 30-c. Scan Rate 100mv/sec.

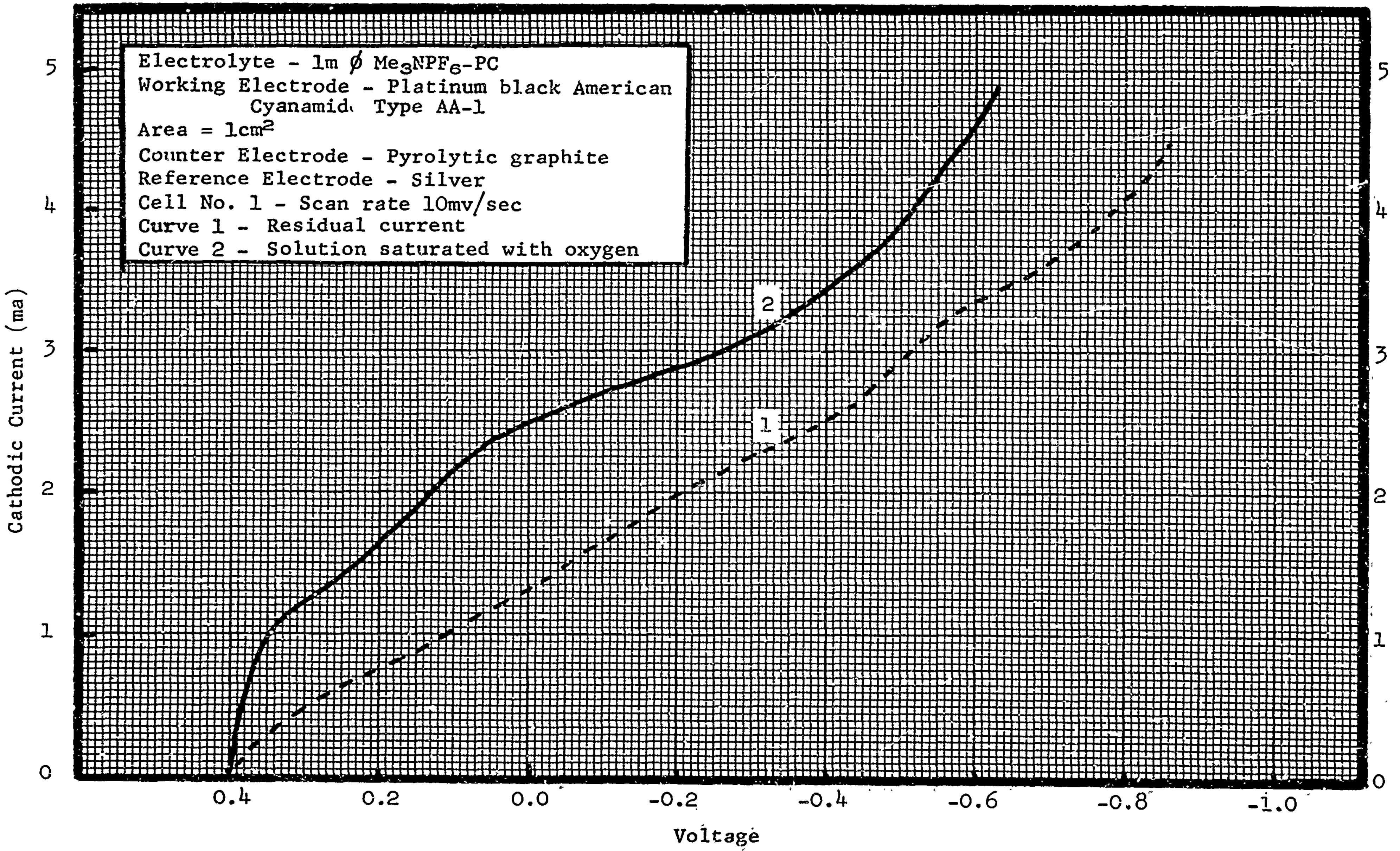
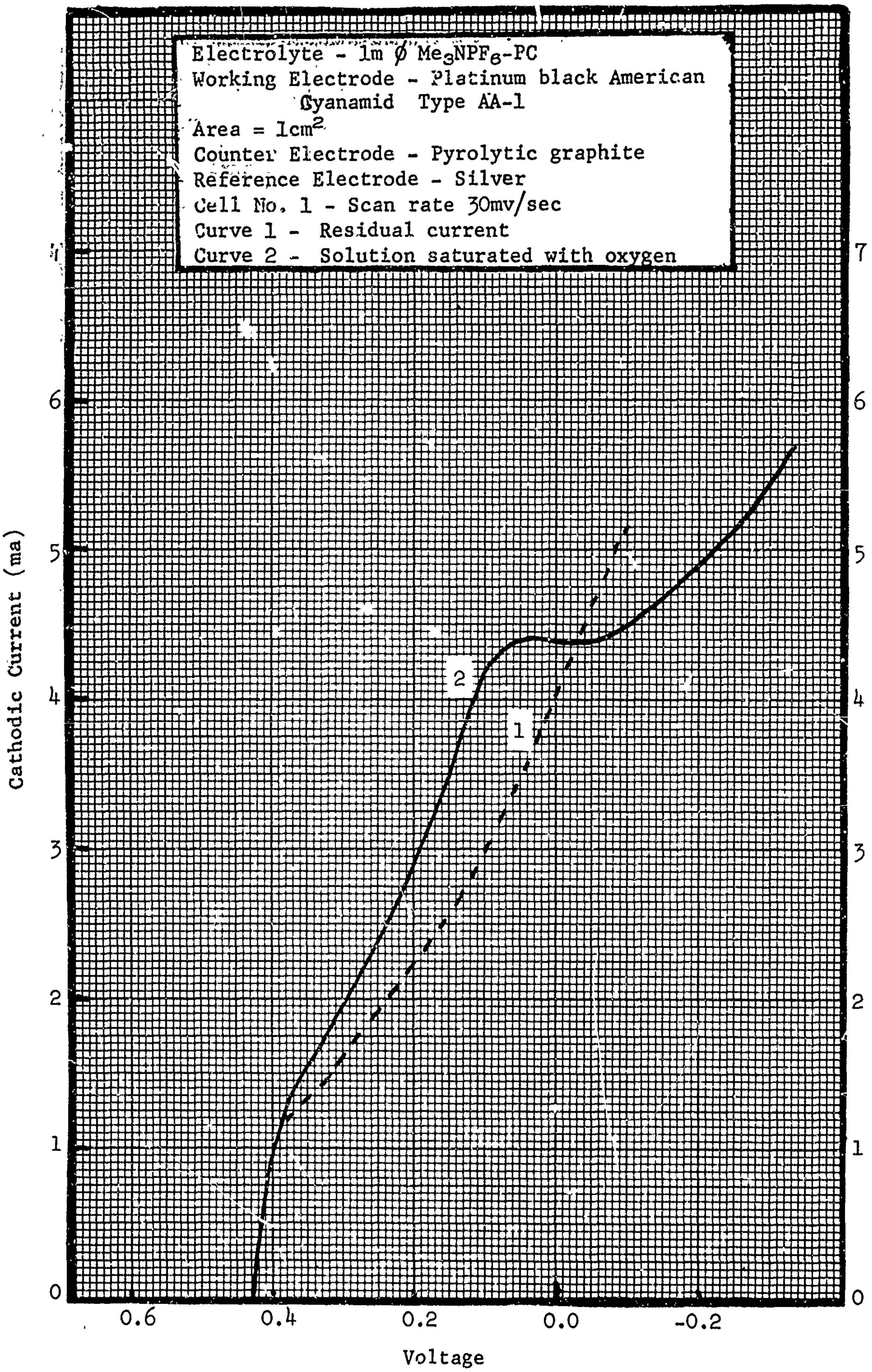


FIGURE 31. <u>REDUCTION OF OXYGEN IN 1m ∅ Me_3NPF_6-PC</u>

Figure 31-a. Scan Rate 10mv/sec.



Electrolyte - 1m ∅ Me_3NPF_6-PC
Working Electrode - Platinum black American
Cyanamid Type AA-1
Area = $1cm^2$
Counter Electrode - Pyrolytic graphite
Reference Electrode - Silver
Cell No. 1 - Scan rate 30mv/sec
Curve 1 - Residual current
Curve 2 - Solution saturated with oxygen

FIGURE 31. REDUCTION OF OXYGEN IN 1m ∅ Me_3NPF_6-PC

Figure 31-b. Scan Rate 30mv/sec.

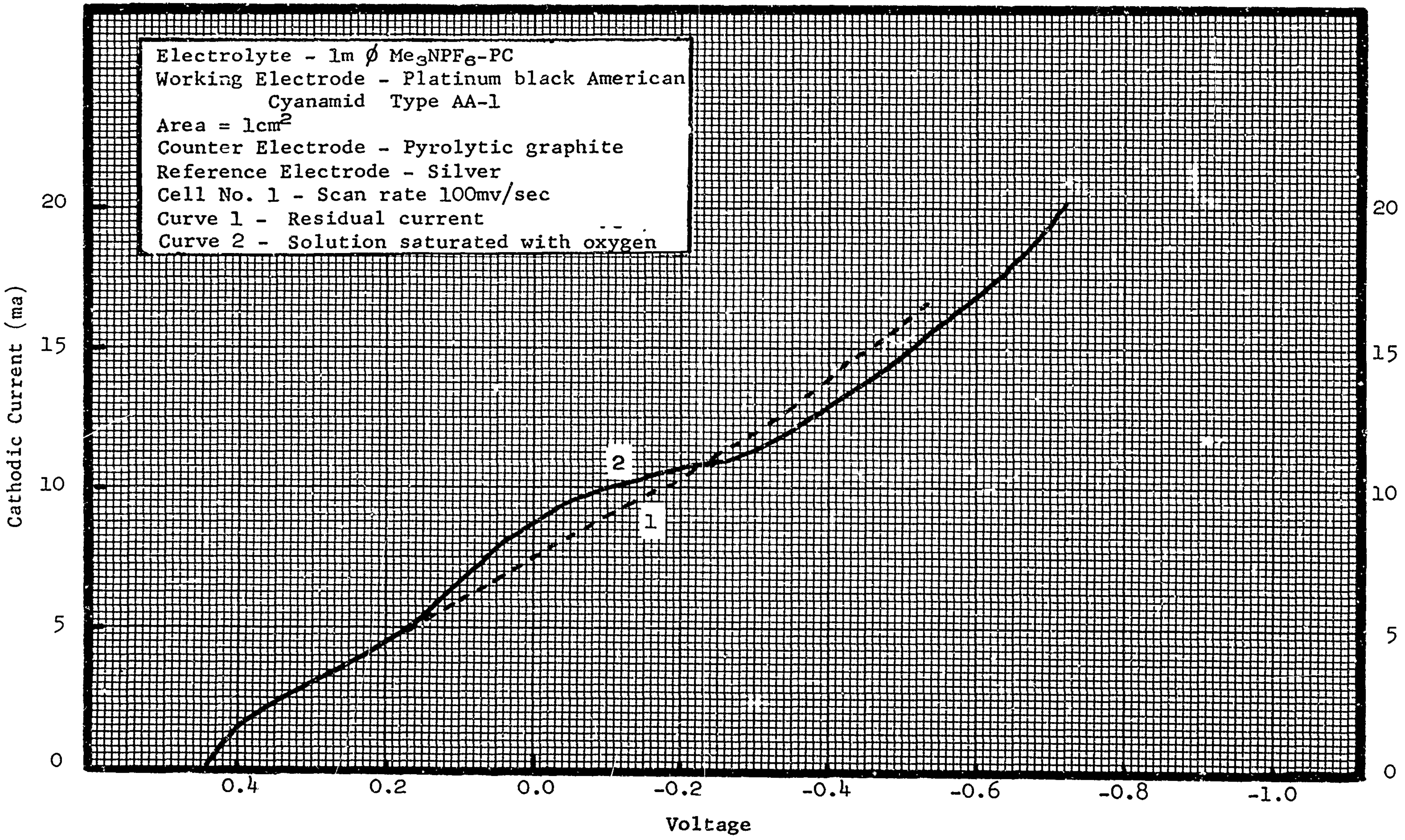


FIGURE 31. <u>REDUCTION OF OXYGEN IN 1m ∅ Me_3NPF_6-PC</u>

Figure 31-c. Scan Rate 100mv/sec.

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13 ABSTRACT

The purpose of the first six months work in this program was to determine, insofar as possible, the feasibility of the three principle components of a lithium-moist air battery system, i.e., anode, cathode, and electrolyte. From the work done during this period, it is concluded that at low current density lithium air cell is feasible. Oxygen reduction is shown to occur in two steps in 1m lithium perchlorate-nitrosodimethylamine on a platinum electrode, at -0.6V and -1.75V versus Ag/AgCl. The current obtainable with an air electrode appears to be determined by the rate of adsorption of oxygen at the electrode surface and by the rate of mass transport of oxygen to the electrode surface. Unfortunately, these studies have been somewhat impeded by the presence of some electrochemically active species in the electrolyte which competes with oxygen for sites on the electrode surface. The work carried out in the first six months is largely exploratory and more detailed studies are required before the air electrode in nonaqueous electrolyte will be completely characterized.

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14. KEY WORDS	LINK A		LINK B		LINK C	
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Air Electrode						
Nonaqueous Battery						
Oxygen Reduction						
Nonaqueous Electrolytes						
Nitrosodimethylamine						

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