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RESEARCH ON ORGANIC DEPOLARIZERS

Report No. 6
Contract No. DA36-039-SC-87336
DA Project No. 3A-99-09-002

Sixth Quarterly Progress Report
1 October 1962 to 31 December 1962

U. S. Army Electronics Research and Development
Laboratory
Fort Monmouth, New Jersey

MONSANTO RESEARCH CORPORATION
BOSTON LABORATORIES
EVERETT 49, MASSACHUSETTS

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The object of this work is to develop new organic compounds and systems that will lead to organic-depolarized primary cells with higher voltages and capacities than the present $\text{Mg}/\text{MgBr}_2/\underline{\text{m}}\text{-DNB}$ systems (m-DNB will be used throughout as an abbreviation for m-dinitrobenzene). Any new system so developed should have the flat discharge and high capacity of the $\text{Mg}/\text{MgBr}_2/\underline{\text{m}}\text{-DNB}$ cell.

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I. PURPOSE

The purpose of this work is to develop new organic compounds and systems that will lead to organic-depolarized primary cells with higher voltages and capacities than the present Mg/MgBr₂/m-DNB systems (m-DNB will be used throughout as an abbreviation for m-dinitrobenzene). Any new system so developed should have the flat discharge and high capacity of the Mg/MgBr₂/m-DNB cell.

II. ABSTRACT

Half-cell measurements on all depolarizers tested during the contract have been tabulated. From these data, depolarizers meeting certain specifications were segregated.

No consistent quantitative correlations were found between half-cell characteristics and the electronic strengths of substituents on nitrobenzenes or on other type depolarizers. The magnitude of the electronic effects of substituents on depolarizer activity is discussed and half-cell characteristics are compared to polarographic data from the literature.

Stable halogen addition compounds of heterohalides and of chlorine were prepared and tested. Various halogen addition compounds with the structure —NHXX₂ have proved stable in dry storage and in electrolyte for extended periods.

Inhibition of corrosion of magnesium by tetrasodium dinitropyromellitate and other similar soluble nitro compounds was confirmed by extended corrosion tests.

A slight increase in reduction efficiency of benzoquinone was realized in benzoquinone o-DNB mixes. Methanol (10 and 25% concentration) in ammonium bromide electrolyte lowered the reduction efficiency of m-DNB.

III. SUMMARY AND CONCLUSIONS

Half-cell measurements on all depolarizers tested so far were tabulated and the data analysed in an effort to correlate half-cell characteristics with chemical structure. The various half-cell characteristics such as open circuit potential, coulombic efficiency, and average operating potential were found to give no consistent quantitative correlation with the electronic strengths of substituents. A review of polarographic data in the literature was made to determine the relationship of the electronic strengths of substituents to half-wave potentials. Several series of reductions were found that gave quantitative correlation (pH dependent). The magnitude of the effect of substituents on half wave potential was found to be small. Thus, these electronic substituent effects are overshadowed in half cell tests where physical effects (such as solubility and absorbency on carbon are large.

Tests with halogen addition compounds were extended to obtain compounds with higher capacities and good storage stability. Compounds with the structure $>N\text{HXX}_2$ were the most stable and compounds such as quinolinium chloride perbromide were stable for a month both in electrolyte and in dry storage. A stable perchloride, quinolinium iodide perchloride, was also found. Stable heterohalide compounds such as quinolinium chloride iodine trichloride, trimethylammonium chloride iodine bromide, etc. were found to reduce with high efficiencies but with greater polarization than the perbromides. Additional tests at high drain rates with quinolinium chloride perbromide confirmed earlier tests by demonstrating its very low polarization at high drain rates (0.4 amp/g or 1.0 amp/in²).

The inhibition of corrosion of AZ-10 magnesium cans by tetrasodium dinitropyromellitate was confirmed by extended corrosion tests. Other soluble nitro compounds were also found to be effective inhibitors. Inhibition was effective both in the presence and absence of chromate inhibitors.

Two systems involving a combination of electrochemical reductions and chemical reaction of components in a depolarizer mixture were tested. In the first, *o*-DNB mixed with benzoquinone was found to give a slight improvement in the capacity of benzoquinone by a regeneration reaction. In the second system, sulfides added to iodine proved ineffective in increasing the reduction potential of iodine.

The efficiency of reduction of *m*-DNB was lowered by the addition of methanol to the electrolyte. The lowering was probably caused by reduction of absorbency of *m*-DNB on the carbon in the presence of methanol.

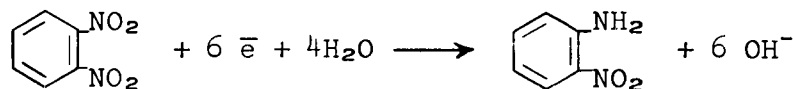
Screening tests with peroxides were continued. Peroxides tested thus far have polarized badly at low current drain.

IV. RESULTS AND DISCUSSION

A. CORRELATION OF HALF-CELL DATA WITH CHEMICAL STRUCTURE

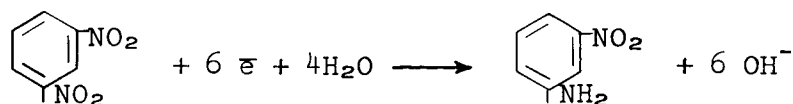
Correlation of depolarizer activity with chemical structure falls into two groups: first, correlation with the structure of the active group, and second, correlation of the effect of added substituents on activity of a given reactive group. The first correlation requires an involved quantum mechanical treatment and has not been attempted. Empirically, it can be seen that depolarizers reducing at high potentials generally have structures where a relatively weak bond is broken on reduction (e.g. halogens) and poor depolarizers have structures where a relatively strong bond is broken (e.g. $-\text{C}\equiv\text{C}-$). However, bond energy of the reactive group is not the only important factor in half cell performance since no correlation of bond energies with cell characteristics of depolarizers has been found. Indeed, some mechanisms of reduction may involve bond formation as the activation step.

There is a vast background of work on the effect of substituents on chemical reactivity. However, thermodynamic data are scanty. The magnitude of the effect of substituents on the theoretical reduction potential of a depolarizer can be calculated from the free energies of formation of reactants and products. Experimental values of free energy of formation for *o*-DNB, *m*-DNB, *o*-nitroaniline and *m*-nitroaniline are given by Parks and Huffman (Ref. 1).



49,400 cal

41,400 cal



42,900 cal

40,400 cal

The difference in free energy for the reactions are:

$$\Delta F^\circ \text{ ortho} = (49,400 - 41,400) + 4 \Delta F^\circ (\text{H}_2\text{O}) - 6 \Delta F^\circ (\text{OH}^-)$$

$$\Delta F^\circ \text{ meta} = (42,900 - 40,400) + 4 \Delta F^\circ (\text{H}_2\text{O}) - 6 \Delta F^\circ (\text{OH}^-)$$

$$\Delta \Delta F^\circ = 8000 - 2500 = 5500 \text{ cal}$$

Therefore, the increase in reduction potential, E_o , that can be expected for reduction of *o*-DNB compared to *m*-DNB is $5500/6(23,060) = 0.0398$ volt.

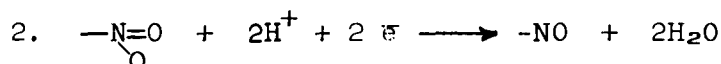
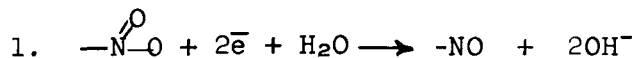
This is a very small increase in potential although the nitro group is one of the strongest electron-withdrawing substituents when in the ortho (or para) position. The low value indicates that only minor changes in theoretical reduction potential can be expected from substitution effects.

However, the reduction potentials of most depolarizers are limited kinetically where substituent effects may be more important. Polarographic measurements (e.g. half-wave potentials) illustrate the magnitude of effect of substituents on depolarizer groups since such measurements are not complicated by the physical variables that influence half-cell discharge measurements. Polarographic data for substituted nitrobenzenes (Ref. 2) show that the magnitude of the effect of substituents on reduction potential is dependent upon pH:

	pH 1	pH 3	pH 6	pH 10
$E_{\frac{1}{2}}$ (vs. S.C.E.) Nitrobenzene	-0.220	-0.340	-0.535	-0.740
$E_{\frac{1}{2}}$ p-COOCH ₃ Nitrobenzene	-0.125	-0.250	-0.400	-0.610
$\Delta E_{\frac{1}{2}}$	0.105	0.090	0.135	0.130

The electron-withdrawing substituent, $-\text{COOCH}_3$, has a stronger effect on reduction of the nitro group in base than in acid. Substituents that change chemically with pH (e.g. COOH , OH) show even greater differences.

The mechanism of reduction of the nitro group even in the first step is not simple and is dependent upon pH:



Therefore, the changes in $E_{1/2}$ at low pH reflect the effectiveness of the substituent on reaction 2 and, at high pH, on reaction 1.

This change in half-wave potential (0.09 to 0.135) caused by introduction of the $p\text{-COOCH}_3$ group in nitrobenzene gives an indication of the magnitude of change that can be expected since this group is a relatively strong electron-attracting substituent.

There also have been quantitative correlation of polarographic data with Hammett's sigma (σ) constants (Refs. 3,4). The Hammett equation was modified to give the relationship of half-wave potential to σ :

$$\log k/k^0 = \sigma \rho = \Delta E_{1/2}$$

$\Delta E_{1/2}$ is the shift in half-wave potential caused by a substituent, σ is the polar substituent constant, dependent upon the kind and position of substituent, and ρ is a constant characteristic of the reaction series.

This relationship is valid only for reaction series where the shift in half-wave potential is due to polar effects. (inductive and resonance) of substituents. Where resonance and steric effects are significant, there will be deviation from the linear relationship of $\Delta E_{1/2}$ with σ (e.g. OH on nitrobenzenes) since $\Delta E_{1/2}$ is equal to the sum of the polar, resonance, and steric energies?

The σ constants have been correlated with several series of reduction reactions (Refs. 3,4). The magnitude of ρ is a measure of the susceptibility of the given reaction series to substituents. For example, substituted diphenyliodonium derivatives ($\rho = 0.02$) (Ref. 1,4) reduce at practically the same potential irrespective of the substituent. Nitrobenzenes (Ref. 3,4) are slightly affected by substituent groups. At $\text{pH} < 3$, $\rho = 0.16$; at $\text{pH} 5-8$, $\rho = 0.14$; and at $\text{pH} > 11$, $\rho = 0.24$.

These values of ρ reflect the influence of substituents on the relative change in activation free energy between the reactant state and the transition state since in irreversible reductions

$$\Delta E_{\frac{1}{2}} \approx \Delta \Delta F^*.$$

[Effects that change the free energy of the original state and the transition state simultaneously and by the same amount are not detected.] Thus, polarographic data indicate that the magnitude of electronic effects of even relatively strong electron withdrawing substituents on reduction potential of aromatic nitro compounds is not large.

Zuman (Ref. 4) also reported a linear relationship of ρ with $\Delta E_{\frac{1}{2}}$ for some aliphatic nitro compounds (only four substituents correlated). ρ values were 0.20 at pH 10.9 and -0.9 in 0.05 M H_2SO_4 . The negative value of ρ in acid indicates that the mechanism of reduction of the aliphatic nitro compounds is different from that of aromatic nitro compounds, which have a positive value of ρ in acid.

The negative ρ value indicates that electron donating substituents favor the reduction. Thus, the activation step is predominately direct dissociation of a N-O bond (SN_1) whereas in the reduction of aromatic nitro compounds (where ρ is positive) the SN_2 mechanism predominates.

In summary, the data on the relationships of ρ constants of substituents to $\Delta E_{\frac{1}{2}}$ can be used to indicate the magnitude of the polar effect of substituents on the reduction (ρ), points out what substituents affect the reduction by steric or resonance interactions (deviation of $\Delta E_{\frac{1}{2}}$ from $\Delta E_{\frac{1}{2}}$ vs. ρ plot), and indicate the type of mechanism involved in reduction (positive or negative ρ).

Attempts to correlate half-cell measurements such as open circuit potentials, average operating potential, and coulombic efficiency with ρ constants were not successful. Apparently, other factors, such as variations in solubility of depolarizers in electrolyte or their absorbance on carbon overshadowed the effects due to polarity of the substituents.

The data collected to date from half cell tests, which reflect the total effect of the substituent, have been coded to enable compounds with certain characteristics to be separated.

Data from half-cell measurements of compounds tested during the first four quarters are summarized in Table 1 and of those tested during this quarter in Tables 2 and 3. Following are descriptions of the methods used to measure the properties tabulated.

Energy Capacity in watt-min/g was determined by direct measurement with a planimeter of the area under the discharge curves on the chronopotentiometric plots to a cut-off voltage of -0.6 v. In cell "D" tests, capacity was measured for both "A" and "B" levels. The value thus measured at level "A" strictly speaking does not have the dimensions, watt-min/g since current density is higher at this level. The value given, however, gives a good indication of the susceptibility of the depolarizer to polarization.

Coulombic Capacity in amp-min/g was taken directly from the chronopotentiometric plots at a cut-off voltage of -0.6 v. Capacities for both levels "A" and "B" in cell "D" are tabulated.

Coulombic Efficiency in % refers to the percentage of the theoretical coulombic capacity realized in the half-cell test up to the cut-off voltage of -0.6 v.

O.C.V. vs NHE (Volts) is the open circuit potential of the depolarizer in the cell after predischage of absorbed oxygen on the carbon. A 20- min. wait on open circuit followed the predischage period. Values in the tables that are starred (*) are open circuit potentials of undischarged samples.

$\frac{-\Delta E}{\log \Delta i}$ was obtained between open circuit and the operating potential for the given test. For tests in cell "D" operating current is usually 0.025 amp and in cell "C" 0.100 amp. Starred values (*) refer to tests where there was no predischage of absorbed oxygen.

Ave. Operating Potential (volts) was obtained by dividing the energy capacity by the coulombic capacity and subtracting 0.6 v from this value.

Drop in Potential in Each Quarter Time Period, %, is the percentage of the total drop in potential from the potential realized at start-up (at attaining operating potential) to -0.6 v.

Compounds are grouped below according to certain standards. For comparison, m-DNB has the following characteristics:

	<u>Ave. Operating Potential (volts)</u>	<u>Energy Cap. (Watt-min/g)</u>	<u>Coulombic Efficiency</u>	<u>Open Circuit Potential (volts)</u>
in cell "C"	-0.29	18.7	52.2	-0.08
in cell "D" (level B)	-0.10	over 10	over 17	—

1. Compounds with average operating potential over zero volts and energy capacity over 11 watt-min/g (cell "C" or "D"). Most of the active halogen (e.g. trichloroisocyanuric acid, *t*-butyl hypochlorite) and halogen addition compounds fall into this group. The only other compounds are two acids: 3,6-dinitrophthalic acid (and its anhydride which hydrolyses to the acid in electrolyte) and 1-carboxymethyl-3,3,5,5-tetranitropiperidine.

2. Compounds which have an energy capacity over 20 watt-min/g in cell "C". The group included the active halogen compounds plus the following nitro compounds:

2,5-dinitropyrrole
1,4,5-trinitronaphthalene
picric acid
o- and *p*-DNB

3. Nitro compounds which have average operating potential, energy capacity and coulombic efficiency greater than *m*-DNB when tested under the same conditions.

2,5-dinitrobenzoic acid
3,6-dinitrophthalic acid and its anhydride
1,4-dinitropyromellitic acid and its silver salt
o- and *p*-DNB
4-nitropyridine
picric acid
1,4,5-trinitronaphthalene

4. Nitro compounds which were above *m*-DNB in average operating potential and energy capacity (but not coulombic efficiency) when tested under the same conditions.

1,4,5,8-tetranitronaphthalene
2,5-dinitropyrrole

5. Compounds with open circuit potentials over +0.5 v. Most of the peroxides, active halogen compounds and halogen addition compounds are in this group.

In addition, iodosobenzene, iodoxybenzene, 1,4-dinitropyromellitic acid, its anhydride and its silver salt, 3,6-dinitrophthalic acid and its anhydride, picric acid, hexylnitrolic acid, benzoquinone and 2,5-dinitropyrrole fall into this category.

B. EXPERIMENTAL PROCEDURE

The standard procedures for operation of cell "C" are given in the Third Quarterly Report and of cell "D" in the Fourth Quarterly Report. Oxygen was pre-discharged from the carbon except in tests where the open circuit value was over 0.60 v (vs. N.H.E.). The period of discharge was 5 min. at 0.1 amp in cell "C" or 20 min. at 0.025 amp in cell "D"

and was followed by a 20 min. recovery period on open circuit before the start of the test. The standard cathode sample consists of 0.5 g of depolarizer and 0.25 g of Shawinigan Acetylene Black (50% compressed).

Methods used to prepare depolarizers are given in the Appendix.

C. HALF-CELL TESTS

1. Halogen Addition Compounds Methods used to prepare these compounds and a summary of their physical properties are given in the appendix. Data on shelf stability, both dry and in electrolyte, are given in Section D. The new compounds prepared were selected on the basis of expected improvements in stability and increased capacity. The capacity can be increased by addition of more than one molecule of halogen to the parent and by minimizing the molecular weight of the parent so that capacity approaches that of the free halogen.

Not all heterocyclics form stable addition compounds. For example, imidazole,



which contains two possible acceptor atoms for

halogen, does not form addition compounds. Two heterocyclic compounds, 1,10-phenanthroline and quinoxaline, were found to form relatively stable polyaddition compounds. The discharge characteristics of both the simple addition compounds and of their salts were very similar to other perbromides tested (Figures 1-8). Both quinoxalinium chloride perbromide and 1,10-phenanthroline perbromide have slightly higher energy and coulombic capacities than quinoline hydrochloride perbromide. The quinoxaline nucleus also reduced partially at about 0.1 volt in both compounds, (Figures 2 and 4). 1,10-Phenanthroline also appears to be reduced partially at lower potentials, (Figures 6 and 8). The values for coulombic efficiency and energy capacity in Table 2 for both compounds are for reduction of the halide only. It is possible that compounds of this type with higher capacities could be prepared by more efficient packing of halogen onto the parent nucleus.

The perchlorides have higher theoretical capacities than the perbromides, but perchlorides prepared earlier had limited stability. Quinolinium iodide perchloride, however, has been found to be stable. Its open circuit potential, (Figure 9), is slightly higher than those of the perbromides and also higher than those of any of the less stable perchlorides tested previously. This perchloride also reduces with high efficiency and has one of the highest capacities of the perhalogen compounds, (Figure 10). The compound polarizes during discharge more than the perbromides, however, with the result that its average operating potential is only 0.61 v vs. NHE.

Several addition compounds (Figures 11-23) of heterohalides were prepared since stability is expected to be higher for these compounds than for homogeneous perhalides. The open circuit values of the heterohalide compounds, IBr and ICl, on different parents varied more than the perbromides (Table 2). The addition compounds with ICl₃ had higher open circuit potentials, higher average operating potentials, and higher

capacities (Figures 11,13,15,18,19,20, and 23) than those of ICl and IBr, (Figures 11,12,14,15,16,17,20,21 and 22). Capacities of the ICl₃ compounds are also superior to the perbromides (Figure 13,19, and 23). All the heterohalides polarized more than the perbromides, with the result that average operating potentials are lower.

A series of half-cell tests in cell "D" at successively higher current drains were run with quinolinium chloride perbromide (Figures 25-27). Comparison of the data in the figures and in Table 2 shows that at level "B" very little polarization occurred on increasing the current drain eight-fold. Energy capacity dropped about 13%, but coulombic capacity was maintained. The average operating potential was lowered from 0.93 v to 0.7 v, but the discharge curve was still flat; 94.8% of the drop in current in the test at 0.4 amp/g occurred in the last quarter time period. Capacity and potential level at the bottom dropped sharply at current drains over 0.3 amp/g (0.75 amp/in²). This is in contrast to the result with quinolinium bromide perbromide (Figure 28 and Table 3) where level "A" maintained its potential for the entire run at 0.392 amp/g. Level "A" in a test in MgBr₂ was low (Figure 29). In this test, however, level "B" was not functioning properly owing to accumulation of gas bubbles. The discrepancy is probably caused by local accumulation of gas, which interferes with electrode readings. These readings then may not reflect the true condition of the cathode at that point. In the test with quinoline perbromide (Table 3 and Figure 30) gas accumulation also interfered with electrode reading at level "A". However, the data illustrate the ability of the perbromides to reduce with high efficiency at high current drains. This is illustrated particularly in Figures 31 and 32 where capacity is plotted against current drain for the quinolinium chloride perbromide series.

Silver oxide and the silver salt of dinitropyromellitic acid were also tested at high current drains (Figures 30 and 33 and Table 3). The perhalogen compounds have much higher operating potentials. The silver salt of dinitropyromellitic acid has the advantage of discharging with relatively high efficiency, but its operating potential is low. The perhalides are superior to silver oxide in both operating potential and capacity in ammonium bromide electrolyte. (Silver oxide operates better in 30% KOH than in ammonium bromide. Tests in KOH electrolyte will be reported in the next period.)

2. Aromatic Nitro Compounds

a. Substituent Effects on Nitrobenzenes. Several substituted nitrobenzenes were tested in cell "D" since earlier tests with this class had been run in a variety of test cells and electrolytes, thus making comparison of cell characteristics with changes in electron density at the nitro substituent impossible. Some of the cell characteristics of the compounds tested are given below. Data are also given in Table 2 and Figures 34-45.

Compound	O.C.V. vs N.H.E. volts	Average Operating Potential at Level B volts	Coulombic Efficiency of Level B %	Energy Capacity at Level B watt-min/g
Sodium <u>p</u> -nitrophenolate	0.03	-0.46	24.3	2.08
<u>p</u> -Nitrophenol	0.07	-0.33	~ 27.4	~ 5.2
Nitrobenzene	-0.07	-0.34	29.3	5.92
<u>p</u> -Nitrobenzotrile	-0.01	-0.33	30.7	5.38
Sodium <u>o</u> -nitrobenzoate	0.01	-0.30	28.0	4.22
Disodium nitroterphthalate	0.04	-0.25	38.5	4.32

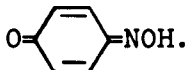
The extremes in open circuit potential are separated by only 0.14 v. Sodium p-nitrophenolate has a higher open circuit potential than nitrobenzene, although the -ONa substituent is an electron donor and would be expected to lower reduction potential. The values of open circuit obtained in the cell, therefore, do not accurately reflect changes in electron density at the nitro groups. There are probably several reasons for this. Test conditions require predischage of adsorbed oxygen on the carbon and in most cases small amounts of depolarizers are also reduced during this predischage period. Thus, open circuit values reflect the presence of reduction products. Also variability of solubility of depolarizers and their absorbence characteristics on the carbon electrode would affect their open circuit values.

Average operating potentials have a spread of 0.21v. Sodium p-nitrophenolate discharged at a lower potential than nitrobenzene and the sodium carboxylates at higher potentials. This would be expected from consideration of their electronic effects. However, p-nitrobenzotrile discharged at about the same average potential as nitrobenzene although the nitrile group is a relatively strong electron acceptor. This discrepancy again suggests that other factors affecting the reduction of nitro groups are masking the electronic effects of the substituent groups. As noted previously, (Section IV, A) the electronic effects are small.

The reduction efficiencies of these compounds range from 24 to 30% except for disodium nitroterphthalate, (Figure 45), which has a higher efficiency.

The energy capacity of nitrobenzene is higher than that of any of the substituted compounds. Thus, although the compounds containing electron-withdrawing substituents in some cases were reduced with slightly higher efficiency at higher potentials, the increase was not enough to compensate for the reduction in capacity caused by their higher molecular weights.

p-Nitrophenol was tested for comparison with the sodium phenolate. The hydroxy substituent is usually an electron donor, but in this molecule tautomerization involving the nitro substituent in neutral and acid media, results in a compound with a quinoid structure,

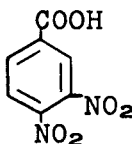


It was found in previous tests (Third Quarterly Report) in cell "D" that o-DNB was about equivalent to m-DNB although the electronic effect of the nitro group in the ortho position would be expected to exert a greater influence than in the meta position. p-DNB, (Figures 46 and 47) was also tested in cell "D". Its cell characteristics in cell "D" are similar to those in cell "C", tested earlier: initially, potential is higher than m-DNB, but potential drops more sharply with the result that the average operating potential and energy capacity at level "B" in cell "D" is lower for the para isomer.

The above data together with data on dinitrobenzenes with carboxylate substituents in section "C" of this report indicate that the overall electronic effect of the substituents on reduction of the nitro group is minor and is often masked by other influences. Thus, experimental data agree with the conclusions reached in Section IV, A.

b. Aromatic Nitro-Substituted Carboxylic Acids. Testing of compounds in this group was extended. During the last quarter, it was found that compounds containing one (or more) carboxylic acid groups ortho to each nitro substituent were superior to compounds containing carboxylic acid groups in the meta position. For comparison of compounds with carboxylic acid groups ortho and para, o- and p-nitrobenzoic acid were tested (Figures 48, 49, 50 and Table 2). The ortho isomer is slightly superior in discharge potential, but the para isomer is the superior depolarizer when judged by discharge level over the entire test.

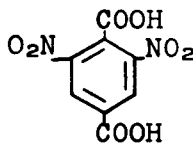
3,4-Dinitrobenzoic acid,



, (Figures 51 and 52)

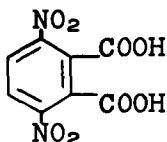
3,4-Dinitrobenzoic Acid

is about comparable to 2,6-Dinitroterephthalic acid,



2,6-Dinitroterephthalic Acid

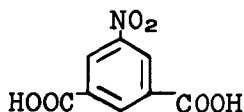
tested during the last quarter. Apparently the lower molecular weight of 3,4-dinitrobenzoic acid balances the slight beneficial effect of the additional meta carboxylic acid group in the second compound. Both compounds are inferior to 3,6-dinitrophthalic acid,



3,6-Dinitrophthalic Acid

which has a carboxylic acid group ortho to each nitro substituent.

The relative ineffectiveness of carboxylic acid groups in the meta position is also shown in the data for 5-nitroisophthalic acid,

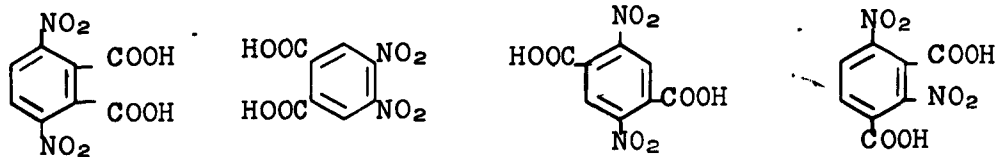


, (Figures 53 and 54).

5-nitroisophthalic Acid

The compound is inferior to p-nitrobenzoic acid and about equivalent to o-nitrobenzoic acid, both of which have one less carboxylic acid substituent.

The data indicate that the most favorable configurations are those where the nitro and carboxylic acid substituents are ortho or para to each other and where there is at least one carboxylic acid group per nitro substituent. Para substituents may be slightly superior to ortho substituents. Examples of compounds that should be or are known to be superior depolarizers include:



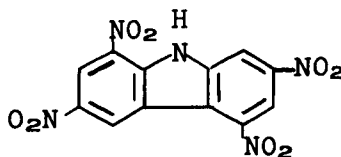
Use would probably be determined by availability of the compound.

c. Nitro-and Dinitrobenzenes substituted with Carboxylates or Sulfonates

Several salts in this group have been tested. Data for carboxylates of nitrobenzene were given in paragraph a. above. Data for disodium 3,6-dinitrophthalate (Figures 55 and 56) and potassium 2,4-dinitrobenzenesulfonate, (Figures 57 and 58) are listed in Table 2. There is little difference in cell characteristics of the salts compared to the corresponding dinitrobenzenes. All of the salts discharge at higher potentials initially, but potential generally drops more sharply during the test. Theoretical capacity of the salts is necessarily lower than that of the parent compound, and it is found that the gains in efficiency from use of the salts are not enough to give any significant improvement in experimental capacity over the parent compound since the efficiency gain just about balances the loss due to higher molecular weights. There is an advantage in use of the salts in cells with magnesium anodes since as noted later in Section E, the salts inhibit the corrosion of magnesium.

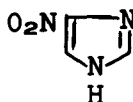
3. Trinitro- β -naphthoic Acids The three products isolated from the nitration of β -naphthoic acid (see Appendix) were tested separately in cell "D" (Figures 59-64). The discharge characteristics of the three products were very similar. The open circuit potentials were identical, (0.27 to 0.29 v). On discharge, Products 1 and 2 gave practically identical chronopotentiometric relationships (Figures 60 and 62). Product 3 differed only in that potential dropped more steeply in the first quarter time period but leveled out to a flatter discharge during the remaining time than did products 1 and 2. All products are better depolarizers than 1,4,5-trinitronaphthalene, which was tested in cell "C" during the Fourth Quarter. Both average operating potentials and open circuit potentials are higher. The data indicate that the increase in potential due to the carboxylic acid group is probably mostly a pH effect since the different isomers had very similar discharge characteristics. The products are only very slightly superior to m-DNB.

4. 1,3,6,8-Tetranitrocarbazole



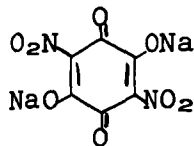
Samples, which were obtained commercially, were tested in cell "C" (Figures 65 and 66). The compound has a theoretical capacity about equivalent to that of m-DNB and reduced with 40% coulombic efficiency, but the average discharge potential was only -0.44 v.

5. 4-Nitroimidazole



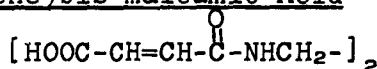
A sample of 4-nitroimidazole had been tested earlier in cell "C" (Fourth Quarterly Report). Partially reduced intermediates had leached out of the cathode and reacted with the bromine at the anode, causing an early shut down of the test. This test in cell "D", (Figures 67 and 68) shows that 4-nitroimidazole is inferior to m-DNB and also operates at a lower potential than nitrobenzene. This is in contrast to 4-nitropyridine, which is a superior depolarizer. The imidazole nucleus is more acidic than the pyridine nucleus and the 4-position is relatively electronegative with respect to the nitrogen atom.

6. Sodium Salt of Nitranilic Acid



This compound, which was obtained commercially, was tested in cell "D" (Figures 69 and 70). It can not be said definitely whether both types of active groups or only the nitro groups are being reduced. The coulombic capacity is slightly higher than theoretical for reduction of the quinone linkage alone (11.7 amp-min/g). Since the discharge curve is flat with no break in potential, it is possible that the entire discharge is from reduction of the nitro substituents. The discharge characteristics, however, are inferior to those of m-DNB.

7. N,N'-(1,2-Ethylene)bis maleamic Acid



This depolarizer, obtained from the Sample Recording Center of Monsanto Chemical Company, was tested in cell "C" (Figures 71 and 72). Each unsaturated carbon-carbon linkage in this compound is activated by the adjacent electron-withdrawing carboxylic acid and amide groups. Both reduction potential and efficiency were low and are inferior to those of tetracyanoethylene, which was tested previously. The four nitrile groups in the later compound are therefore more effective in activating the unsaturated linkage than one carboxylic acid plus one amide group.

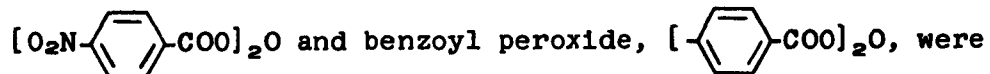
8. Phosphomolybdic Acid



The commercial sample has the above empirical formula. The sample weight used for the test was adjusted to compensate for the water of hydration: 0.62 g of the salt corresponding to 0.5 g of anhydrous $20 \cdot \text{MoO}_3 \cdot 2\text{H}_3\text{PO}_4$ was used in the test in cell "D" (Figures 73 and 74). The compound has a high open circuit potential, 0.69 v, and polarized very little on increasing the current to operating potential (Figure 73). However, the potential dropped sharply after a short time at 0.05 amps/g with the result that both coulombic capacity and energy capacity were lower than those of m-DNB.

9. Peroxides

Several peroxides were tested in cell "C" during the Fifth Quarter. Open circuit potentials of peracetic acid, CH_3COOH , p-nitrobenzoyl peroxide,



high, but all polarized appreciably at even moderate current drains. These peroxides have been retested this quarter in cell "D" (Figures 75 through 78).

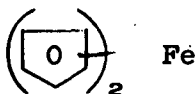
Polarization of both p-nitrobenzoyl- and benzoyl peroxides was the same at 0.025 amp, (0.127 amp/in²) (Figure 75). However, the unsubstituted compound was more polarized at lower currents. Therefore, it is possible that another substituted benzoyl peroxide might reduce at higher current drains with less polarization. Peroxides have the advantage of high initial potentials and the disadvantage of low coulombic capacities since reduction involves only a 2- electron change.

10. m-Dinitrobenzene in Electrolyte with Added Methanol

An attempt was made to improve the cell characteristics of m-DNB by increasing its solubility in electrolyte. A previous attempt had been made in cell "C" (Second Quarterly Report). Reduction efficiency was found to be lower in the presence of methanol. This lowering of efficiency was attributed to loss of m-DNB from the electrode site by leaching out into the large volume of electrolyte used in cell "C".

Tests in cell "D" with standard ammonium bromide electrolyte containing 10% and 20% methanol (Figures 79 through 82) show that the added methanol caused lower cell efficiencies, with the greater decrease in efficiency in the 20% methanol test. Apparently the methanol exerted a greater detrimental effect on some phase in the reduction mechanism than the beneficial effect on the mechanism by increased solubility of the m-DNB. It is probable that the absorbance of m-DNB on the carbon was lowered by preferential absorption of methanol by the carbon.

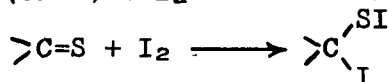
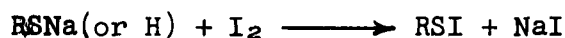
11. Ferrocene



Ferrocene was not reduced in a test in cell "D" (Figure 83). It was difficult to wet, and the sample had to be shaken with electrolyte and carbon containing a few drops of methanol before loading into the cell. The ferrocene is probably not absorbed by the carbon efficiency.

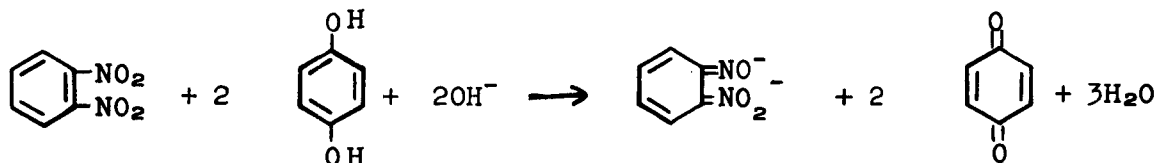
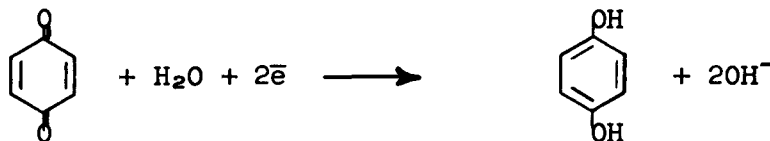
12. Depolarizer Mixtures

Two depolarizers with different discharge characteristics when mixed together were found earlier (Fifth Quarterly Report) to discharge independently of each other. Two systems where there is a combination of electrochemical reduction and chemical reaction of components in a mixture have been tested. The first system was chosen because it offered the possibility of increasing the discharge potential of iodine (and possibly bromine). Compounds of the type RSI are known to be reactive oxidizing agents, but have limited stability. Discharge potential is expected to be high based on discharge potentials of other compounds tested containing halogen in the +1 valence state. These compounds can be prepared in situ by several routes:



Only a small amount of the sulfur compound is required since it is regenerated on electrochemical reduction of RSI. Two tests were made with iodine, one with 0.1 g of CdS added and the other with carbon disulfide added. The data for iodine (Figures 84 and 85) and the CdS-I₂ mixture (Figures 86 and 87) show that the added sulfide did not increase the discharge potential, but caused a lowering in efficiency of reduction. Carbon disulfide, also, gave no increase in discharge potential. It is possible that the concentration of RSI is too low compared to the concentration of iodine to be detected. A system operating at very low current drains might be able to take advantage of this mixture. Also, a special cell where iodine concentration at the electrode is minimized (e.g. by continuous addition) should be operable.

The second system was designed to increase the capacity of a depolarizer by use of a mixture of depolarizer (quinone) with a chemical (o-DNB) that regenerates the depolarizer by chemical oxidation of its reduced form. The system operates since the depolarizer (quinone) reduces at a higher potential than the oxidant (o-DNB) under these cell conditions.

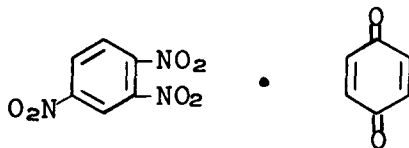


For each mole of o-DNB, 3 moles of quinone can be reduced with a total change of 6 electrons. The capacity of a 2:1 mixture of benzoquinone o-DNB is thus 83.9 amp-min./g compared to 30.7 amp-min./g for benzoquinone alone. (This does not include the additional capacity from complete reduction of o-DNB, but assumes complete utilization of o-DNB in the regeneration reaction.)

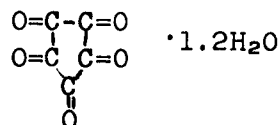
Tests in cell "D" with benzoquinone (Figures 88 and 89) and with a mixture of benzoquinone and o-DNB (Figures 90 and 91) indicated that the regeneration system was operating slightly since the mixture, containing 0.28 g of benzoquinone remained above zero volts (at electrode level C) for 135 minutes, which is the same time as in the test of benzoquinone (0.5 g) alone. The mixture then discharged at the level of o-DNB without completing the regeneration reaction. A test with chloranil was less successful. A test of chloranil, alone, in cell "D" is illustrated in Figures 92 and 93.

The chemical regeneration may be slow at room temperature. Therefore, tests in cell "C" at 50°C were run. (Figures 94 and 95). However, under these conditions benzoquinone polarized very quickly (Figure 95). The discharge curve of the mixture is close to that of o-DNB. There is a possibility that this system could be developed by improving the cell conditions to promote the chemical regeneration reaction. Slight changes in pH of the electrolyte (high pH may favor regeneration) may be advantageous. Also, improvement in contact of reagents is probably necessary. A higher ratio of o-DNB in the mix may be necessary. More efficient methods of mixing the reagents should be tried. For example, an ether or alcohol solution of benzoquinone could be mixed with the carbon, the solvent evaporated, and o-DNB added to the carbon and mixed.

Polynitrobenzenes form molecular complexes with most aromatic compounds. Use of a compound such as the one shown below would insure reagent contact.



13. Leuconic Acid



The preparation of this compound is described in the Appendix. A sample was tested in cell "D" (Figures 96 and 97). Although complete reduction of the five carbonyl groups to hydroxyl groups is possible, the half-cell data indicate that probably only the first one or two are reactive under these cell conditions.

D. STABILITY OF HALOGEN ADDITION COMPOUNDS IN DRY STORAGE AND IN ELECTROLYTE

Stabilities of most of the halogen addition compounds have been measured after periods of storage both dry and in 1:1 $\text{MgBr}_2 \cdot 6\text{H}_2\text{O}:\text{H}_2\text{O}$. Stability was determined by analysis for active halogen content by the standard iodometric method. Aqueous ethanol was used for the solvent during reaction of potassium iodide with the sample. The data are summarized in Tables 4 and 5. These data and those obtained previously lead to the following conclusions:

1. Addition compounds of halogens on strong bases are stable to simple dissociation, but may be susceptible to intramolecular reactions with resulting loss of activity. This is illustrated by the decomposition of pyridine perbromide through intramolecular reaction.
2. Electron-withdrawing substituents on the parent stabilize the addition compound against intramolecular reactions, but decrease stability from simple dissociation, especially in aqueous solution. Thus, 6-nitroquinoline perbromide is stable in dry storage, but dissociates slowly in aqueous solution.
3. Complexes of the type >NHXX_2 , where X is any halogen are the most stable both in dry storage and in electrolyte. Addition compounds such as trimethylammonium chloride perbromide, quinolinium chloride perbromide and quinolinium chloride perchloride are very stable. Compounds with a weak base as holder, such as quinoxalinium chloride perbromide, are more stable than the simple addition compound, i.e. quinoxaline perbromide, but do not have unlimited stability.

E. CORROSION TESTS

Further tests to ascertain the inhibitory effect of tetrasodium dinitropyromellitate on magnesium have confirmed the earlier results, reported in the Fifth Quarterly Report, that the salt is a strong inhibitor of corrosion of magnesium. It has also been found that other water soluble nitro compounds such as potassium 2,4-dinitrobenzene sulfonate and disodium dinitrophthalate also inhibit corrosion of magnesium.

Extension of the first tests reported previously to two months showed a greater contrast in the Az-10 magnesium cans that had been immersed in:

- (1) magnesium perchlorate electrolyte containing lithium and barium chromate inhibitors,
- (2) the electrolyte described in (1) saturated with m-DNB, and
- (3) the electrolyte described in (1) containing 25% by weight tetrasodium dinitropyromellitate.

The results are illustrated in Figures 98. The can treated as in (1) above was extensively corroded so that it had broken open. The can treated as in (2) above was almost as bad as can (1), although corrosion was not quite as extensive. The can in (3) showed very little indication of corrosion. Only minor pitting was visible.

Shorter time tests with potassium dinitrobenzenesulfonate and disodium dinitrophthalate show that these compounds are also effective inhibitors.

Tests were also run in the absence of chromate inhibitor. Under these conditions magnesium cans in 2M perchlorate are completely converted to magnesium hydroxide so that no water was left within 12 days. Corrosion of cans in solutions saturated with m-DNB was the same. A can immersed in the same electrolyte containing tetrasodium dinitropyromellitate (without any chromate inhibitors) showed only minor pitting after 12 days exposure. Thus, inhibition is effective in the absence of chromates, although the presence of both chromates and soluble nitro compounds affords the maximum protection. (Figure 99).

F. REFERENCES

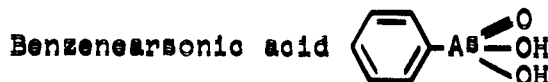
1. G. S. Parks and H. M. Huffman, "The Free Energies of Some Organic Compounds," The Chemical Catalog Co., Inc., New York, 1932.
2. J. E. Page, J. W. Smith and J. G. Walker, J. Phys. Chem. **53**, 545 (1949)
3. H. H. Jaffe', Chem. Revs., **53**, 191 (1953)
4. P. Zuman, Ricerca Scientifica, **30**, Suppl. No. 5, 229 (1960).

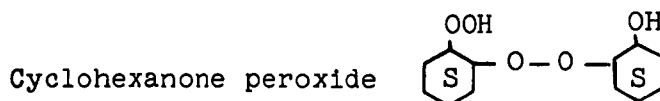
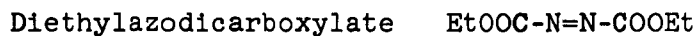
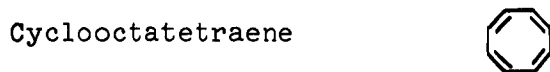
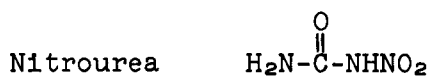
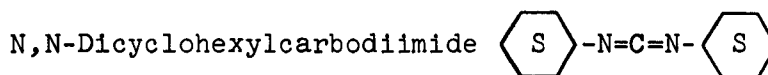
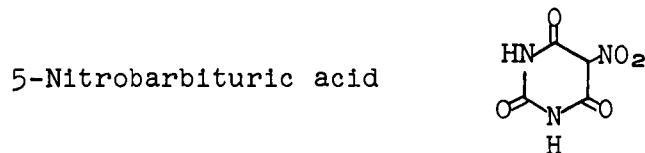
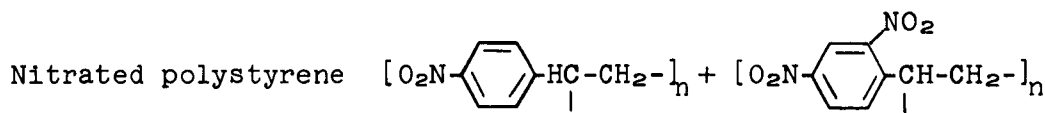
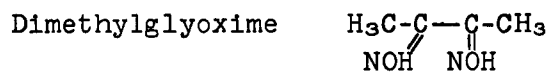
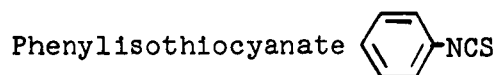
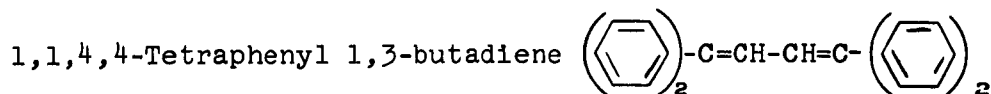
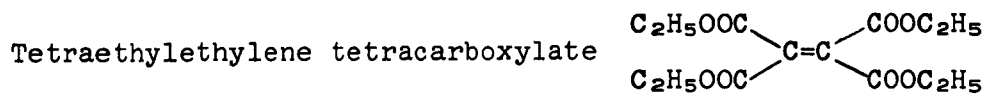
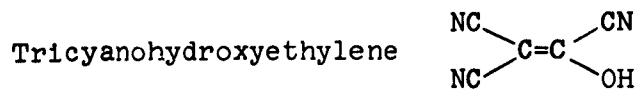
V. PROGRAM FOR NEXT QUARTER

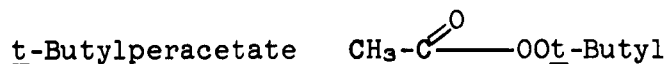
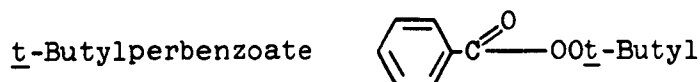
The absorbence of several nitro compounds by Shawinigan Black will be measured to determine if depolarizer structure correlates with magnitude of absorbence. Compounds with conjugated structures similar to the carbon skeleton, such as nitroanthracene, nitropyrene and nitrotriphenylene will be compared to nitro compounds with simpler structures such as m-DNB, tetrasodium dinitropyromellitate, and nitropropane.

For the screening program, nitro-substituted aromatic carboxylic acids such as the nitrobenzoic acids, 3,6-dinitrophthalic acid, and 1,4-dinitropyromellitic acid will be esterified to determine whether these compounds are superior to the sodium salts as depolarizers.

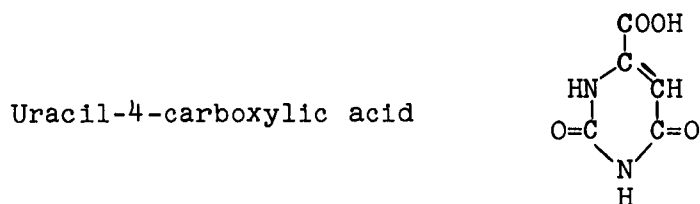
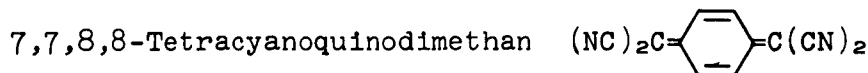
The following compounds listed are on hand for testing:







Methylethyl ketone peroxide



VI. CONFERENCES

6 November, 1962

Mr. S. J. Bartosh of the U. S. Army Electronic R/D Laboratory visited the Boston Laboratories of Monsanto Research Corporation to review the previous quarter's work and also to plan the future program.

14 December, 1962

Mr. B. A. Gruber, Dr. J. O. Smith and Mr. F. J. Winslow of the Boston Laboratories of Monsanto Research Corporation visited the U. S. Army Electronic R/D Laboratory to review current work.

VII. IDENTIFICATION OF PERSONNEL

<u>Name</u>	<u>Job Title</u>	<u>Hours Worked</u>
B. A. Gruber	Project Leader	108
J. O. Smith	Manager, Physical Chemistry and Engineering	20
J. E. Harris	Senior Research Chemist	56
E. A. McElhill	Research Chemist	436
J. H. Him	Laboratory Technician	431
Other Personnel		7
	Total	<u>1058</u>

Table 1

CELL CHARACTERISTICS OF 0.5g. SAMPLES OF DEPOLARIZERS IN CELL "C" AT 0.100 amp. IN 168 g/l NH₄Br ELECTROLYTE OR IN CELL "A" AT 0.025 amp. IN 250 g/l MgBr₂ · 6H₂O ELECTROLYTE

Ref. No.	Compound	Energy Cap. Mate-Min. g.		Coulombic Capacity Amp-Min/g.		Coulombic Efficiency (%)	O.C.V. (Volts) (1)	$\frac{\Delta \bar{E}}{\log \Delta I}$	Average Operating Potential (Volts) (1)	Drop in Potential by Quarters (%)				Comments
		Theor.	Found	Theor.	Found					1st	2nd	3rd	4th	
Substituted Mononitrobenzenes														
30201	Nitrobenzene	2.2		78.6	13.6	17.3	0.20*	2.9*	-0.44	12	16	24	36	Cell A
31406A	Nitrobenzene	11.5		78.6	4.6	58.5	0.50*	0.7*	-0.35	15	8.5	25	51	
27700	o-Fluoronitrobenzene	2.93		68.5	17	24.9	0.28*	3.1*	-0.43	—	—	—	—	Cell A
30250	2,4-Difluoronitrobenzene	8.8		60.9	30	49.3	0.38*	0.6*	-0.31	8.6	11.4	28.6	51.4	
31406B	2,4,5-Trifluoronitrobenzene	12.0		54.6	38	69.8	0.58*	0.7*	-0.28	23	7.7	25	44	
Substituted Dinitrobenzenes														
Ave. 27667, 69, 70, 71	m-Dinitrobenzene	5.54		114.8	22	19.2	0.38*	5.5*	-0.35	12.5	10	17.5	60	Cell A
Ave. 30233, 25	m-Dinitrobenzene	18.74		114.8	60	52.2	0.23*	0.33*	-0.29	13.4	11.1	17.8	53.7	
31435	m-Dinitrobenzene						-0.08	0.09						
31407	o-Dinitrobenzene	26.36		114.8	68	59.3	0.45*	0.45*	-0.21	12.1	17.3	24.2	46.7	
31408	p-Dinitrobenzene	25.14		114.8	64	55.8	0.34*	0.34*	-0.21	9.0	18	18	55.4	
27696	2,4-Dinitrofluorobenzene	4.99		104	17	16.3	0.43*	3.44*	-0.31	20	15	15	50	Cell A
27699	2,5-Dichloro-1,3-dinitrobenzene	3.81		81.7	13	15.9	0.28*	13.8*	-0.29	23.8	25.5	22.1	28.9	Cell A
27697	1,4-Dichloro-2,3-dinitrobenzene	2.91		81.7	14.7	18.0	0.32*	2.2*	-0.40	17	19	12.7	51	Cell A
30203	1,2,4,5-Tetraethyl-3,6-dinitrobenzene	0.3		86.3	5	5.8	0.32*	4.6*	-0.54	—	—	—	—	Cell A
27687, 8	2,5-Dinitrobenzoic Acid	9.1		91.2	17.8	19.5	0.55*	2.4*	-0.09	30	2.6	26	41.7	Cell A

Table 1 (cont'd.)

Ref. No.	Compound	Energy Cap. Watt-Min./g.	Coulombic Capacity Amp-Min./g. Theor. Found	Coulombic Efficiency (%)	O.C.V. (Volts)	$-\Delta E$ $-\log \Delta I$	Average Operating Potential (Volts)	Drop in Potential by Quarters (%)				Comments
								1st	2nd	3rd	4th	
30208B	1,4-Dinitroprocellitic Acid	7.0	56.2	31.7			-0.21	31	21	21	27	Cell A
34913	3,6-Dinitrophthalic Acid	13.2	75.6	38	0.47	0.19	-0.25	21	32	16.5	30.5	
34911	N-(2,4-Dinitrophenoxy)-2- benzoquinonamine	15.9	78.2	35	0.16	0.26	-0.15	38	8.4	6.3	43	Quinone linkage also reduces
	<u>SUBSTITUTED POLYMERO- BENZAZINES</u>											
36204	Picric Acid	26.1	126.4	80	0.58	0.34	-0.27	53	8.7	4.9	34.6	
33462	Diphenylpicrylhydrazine	2.4	73.4	20	-0.06	0.37	-0.48	20	5	38	38	
	<u>NITROGEN HETEROCYCLES CONTAINING NITRO GROUPS</u>											
33464	4-Nitroimidazole		85.5		-0.06	0.16						Early shut down
33490	3-Nitroindole	5.12	59.7	40	0.04	0.23	-0.47	28.6	19	19	33.3	
33497	2-Nitropyrrole	6.06	96.7	40	-0.06	0.28	-0.45	20	4	20	56	
33499	3-Nitroimidoline	12.64	55.2	43	0.05	0.01	-0.31	16.7	8.3	41.7	33.3	
33490	5-Nitro-1-thiadiazole	9.84	53.3	33	-0.10	0.1	-0.30	14	4.5	11.6	70	
33498	2,5-Dinitropyrrole	20.3	133	47	0.40	0.22	-0.17	41.7	3.9	7.8	46.8	
33475	2,4-Dinitrophenoxazine	3.30	70.7	23	-0.03	-0.30	-0.46	37.1	14.8	14.8	33.4	
	<u>CONDENSED RING AND CONDENSED RING HETEROCYCLES CONTAINING O OR S WITH NITRO SUBSTITUENTS</u>											
31438	2-Nitrofluorene	5.06	45.8	23	0.44*	0.68*	-0.38	10.5	2.1	4.2	81.3	
31437	9-Nitroanthracene	1.92	43.3	10	0.50*	0.80*	-0.41	—	33	33	33	
31436	1-Nitroanthraquinone	6.90	5.08	32	0.44*	0.49*	-0.36*	55.7	5.6	7.4	29.6	Quinone linkage also reduces
33477B	5-Nitro-1,3-Benzodioxane	7.90	53	36	0.005	0.27	-0.38	24.1	6	6	63	

Table 1 (cont'd.)

Ref. No.	Compound	Energy Cap. Watt-Min./g.	Coulombic Capacity Amp-Min./g. Theor. Found	Coulombic Efficiency (%)	O.C.V. (Volts)	$\frac{\Delta \Sigma}{\text{Total}}$	Average Operating Potential (Volts)	Drop in Potential by Quarters (%)				Comments	
								1st	2nd	3rd	4th		
31447	2,7-Dinitrofluorene	---	75.4	4	5.3	0.41*	---	---	---	---	---	---	---
31449	1,8-Dinitronaphthalene	9.62	89	25	28.1	0.49*	-0.21	15.8	15.8	5.3	63.2	---	---
31446	1,5-Dinitronaphthalene	5.16	89	20	22.5	0.51*	-0.34	20.0	24.9	8.6	48.7	---	---
33465	2,8-Dinitrophenothiazin-10- Dioxide	1.62	60.2	7	11.6	0.0	-0.37	---	33	35.2	27.8	---	---
33456	1,4,5-Trinitronaphthalene	23.64	110	70	63.7	0.53*	-0.26	47.7	6.6	1.7	43.2	---	---
33458	1,4,5,8-Tetranitronaphthalene	20.23	125	50	40.0	0.38*	-0.19	1.0	0.3	42.3	42.3	---	---
33470	2,4,7-Trinitro-9-Fluorenone	9.88	91.9	36	39.2	0.06	-0.33	18.6	14.0	18.6	48.8	---	---
<u>NITRATES</u>													
33467	Propyl Nitrate	0	30.7	0	0	-0.2	---	---	---	---	---	---	---
33468	Benzyl nitrate	1.76	21.1	16	75.8	0	-0.35	23.1	15.4	15.4	30.8	---	---
33469	p-Nitrobenzyl nitrate	6.30	65.2	37	56.8	-0.02	-0.43	22.9	22.9	20.0	28.6	---	Nitro Group also reduced
<u>ACTIVATED UNSATURATED COMPOUNDS</u>													
33487	Fumaric Acid	1.5	27.7	15	54.2	-0.02	-0.50	15	20	25	40	---	---
33492	Maleic Anhydride	2.1	32.8	10	30.5	0.14	-0.39	---	31.7	15.8	52.8	---	---
31419	Tetracyanoethylene	9.14	25.2	15	59.5	0.49*	+0.08	1	38	40	20	---	---
33478	1-Nitropropene	2.78	148	15	10.1	0.14	-0.41	42.2	15.8	18.4	23.7	---	Nitro Group also reduced
31403	Diphenylacetylene	---	36.2	0	0	0.40*	---	---	---	---	---	---	---

Table 1 (cont'd.)

Ref. No.	Compound	Energy Cap. Watt-Min g	Coulombic Capacity Amp-Min/g Theor. Found	Coulombic Efficiency %	O.C.V. (Volts)	ΔE 100 A.I.	Ave Operat- ing Potential (Volts)	Drop in Potential by Quarters ($\frac{\$}{1st}$, $\frac{\$}{2nd}$, $\frac{\$}{3rd}$, $\frac{\$}{4th}$)	Comments
PEROXIDES									
31414	t-Butyl Peroxide	-	22.1	0	0.68*	1.3*	-	-	
31905	t-Butyl Hydroperoxide	-	35.8	0	0.05	6.5	-	-	
31909	Ascaridole	3.14	19.2	12	0.3	0.52	-0.34	22.2	11.1 5.6 61
31903	Benzoyl Peroxide	4.7	13.3	5	0.93	0.54	0.18	0	41 0 59
31904	p-Nitrobenzoyl Peroxide	13.56	44.8	33	0.94	0.84	-0.19	48	1.5 3 48
	Peracetic Acid (0.5 g 40%)	5.46	16.8	9	1.1	0.42	0.07	0	51.7 15.1 23.1
31906	Peracetic Acid (1.25 g of 40%)		42.3	9-19	1.08*	0.30	-	-	-
SULFOXIDES AND SULFONES									
31402	Dimethyl Sulfoxide	0	41.3	0	0.17*	1.2*	-	-	-
30204	Phenyl Sulfoxide	0	15.9	0	0.4*	6.9*	-	-	-
30205	Phenyl Sulfone	0	29.4	0	0.77*	10.3*	-	-	-
31409B	p-Tolylidissulfone	-	41.7	3	0.59*	0.79*	-	-	-
31927	4-Oxathiane-4,4-dioxide	0	47.3	0	-0.22	0.78	-	-	-
NITROSO COMPOUNDS									
31910	1,3,5-Trinitrosobenzene- hydro-s-triazine	1.34	111	9	0.13	0.38	-0.45	-	-

Table 1 (cont'd.)

Ref. No.	Compound	Energy Cap. Matt-Min/g	Coulombic Capacity		Coulombic Efficiency %	O.C.V. (Volts)	ΔE (Volts)	Ave. Operating Potential (Volts)	Drop in Potential by Quarters, (5)				Comments
			Theor. Found	Amper-Min/g					1st	2nd	3rd	4th	
34921	p-Nitro-N-Nitrosodiphenylamine	3.78	66.3	20	30.2	0.06	0.36	-0.11	5	20	13	13	Nitro group also
34931	4-Ethoxy-4'-nitro-N-nitrosophenylamine	1.2	56.2	16.5	29.4	0.05	0.45	-0.53	-0	20	15	25	Nitro group also
34933	4,4'-(N-methyl-N-nitroso)-azobenzene	0	71.3	0	0	-0.15	0.35	-	-	-	-	-	-
36207	N-Nitrosophenyl-N'-nitrosocyanethyl-p-phenylenediamine	-	43.7	2.5	5.7	0.03	0.43	-	-	-	-	-	-
36233	p-Nitrosophenol	16	51.3	29	55.8	0.22	0.08	-0.04	16	12	12	60	-
	NITRO GROUPS ON SATURATED SYSTEMS												
33472	Nitroguanidine	1.76	96.8	26	28.1	-0.08	0.34	-0.53	40.3	22.7	13.2	13.2	-
30249	Nitrocyclohexane	1.0	75.0	10	13.3	-	-	-0.50	42	3	10	42	-
31412	Methyl-3,3,5,5-tetranitropiperidinoacetate	9.56	114.8	26	22.7	0.45*	0.40*	-0.23	13.3	13.3	23.4	-0.2	-
31411	1-Carboxyethyl-3,3,5,5-tetranitropiperidine	12.5	119.5	18	15.1	0.55*	0.40*	+0.09	1.4	1.4	5.6	92.3	-

Table 1 (cont'd.)

Ref. No.	Compound	Energy Cap. Mete-Min. g.	Coulombic Capacity $\frac{amp-hr}{g.}$		Coulombic Efficiency (%)	O.C.V. (Volts)	$\frac{\Delta \Sigma}{\log \Delta I}$	Average operating Potential (Volts)	Drop in Potential by Quarters, (g)				Comments
			Theor.	Found					1st	2nd	3rd	4th	
NITROLIC ACIDS													
31442	Acetonitric Acid	-	154.6	>12	-	0.77*	0.70	-	-	-	-	-	-
33477A	Propylpseudonitrole	2.94	136.4	13	9.54	0.44	0.62	-0.37	15	22.5	25	37.5	
33493	Hexylnitric Acid	4.42	100.5	15	14.9	0.62	0.66	-0.31	10	74	16.7		
ACTIVE HALOGEN COMPOUNDS													
34902	1-Butyl Hypochlorite	22.56	33.9	19	56	1.05	0.23	0.59	0	0.7	7.1	92.2	in perchlorate
31420	Trichloroisocyanuric Acid	27.1	43.6	22	50.7	1.40*	0.24*	0.63	7.2	26.5	54.2	12	in perchlorate
31424	Trichloroisocyanuric Acid	26.7	43.6	22	50.7	-	-	0.62	3.9	18.2	20.8	57.2	in perchlorate
31441	Trichloroisocyanuric Acid	43.8	43.6	31	71.2	1.01*	0.02	0.81	3.3	6.5	11.7	78.5	in MgBr ₂
31421	1,3,4,6-Tetrachloroglycoluril	32.4	46.1	29.5	64.2	0.91*	0.25	0.50	20.5	4.1	6.9	69	in perchlorate
31418	1,3,4,6-Tetrachloroglycoluril	30.6	46.1	24	52.2	0.95*	0.15*	0.68	2.9	1.5	2.9	96.8	in MgBr ₂
31440	7,8-Diphenyl-1,3,4,6-tetra-chloroglycoluril	13.32	34.3	16	46.7	0.95*	0.38*	0.23	0	31.6	36.9	31.6	in perchlorate
31445	7,8-Diphenyl-1,3,4,6-tetra-chloroglycoluril	12.8	34.3	12	35.1	0.97*	0.17*	0.47	12.1	10.4	15.3	61.2	in MgBr ₂
33493	N,N'-Dichloroquinonediimine	5.8	55.2	12	21.7	0.40	0.37	-0.12	11.5	21.3	34.5	32.8	in perchlorate

Table 1 (cont'd.)

Ref. No.	Compound	Energy Cap. (kWh/MWh)	Coulombic Capacity (amp-hr/lb)	Coulombic Efficiency (%)	O.C.V. (Volts)	ΔE (log I)	Average Operating Potential (Volts)	Drop in Potential by Quarters (g)			Comments	
								1st	2nd	3rd		
	MISCELLANEOUS COMPOUNDS											
33495	4,4'-Dichloroxybenzene	--	36.1	2	5.55	-0.18	0.16	-	-	-		
31401	Benzonitrile	0	62.7	0	0	0.29*	1.3*	-	-	-		
33473	2-Nitrobenzenediazonium fluoroborate	0	54.3	0	0	-0.06	0.40	-	-	-		
33479	2,4,6-Triphenylbenzene-diazonium sulfate	0	8.53	0	0	-0.19	0.98	-	-	-		
34929	Ferric salt of 2-mercapto-benzothiazole	0	5.8	0	0	-0.12	0.62	-	-	-		
33481	Trichloroacetic acid	2.08	19.7	10	50.8	0.3	0.60	-0.39	0	10	23	67
31413	Iodobenzene	--	14.6	2	13.7	0.94*	0.7*	-	-	-	-	-
31409	Iodobenzene	--	27.1	3	11.1	0.93*	0.93*	-	-	-	-	-
33494	Benzyl-N-(2-chloroallyl)dithiocarbonate	0	12.5	0	0	-0.23	0.76	-	-	-	-	-
30206	Triphenylphosphine oxide	0	11.6	0	0	0.50*	2.75*	-	-	-	-	-
34919	3,3'-Bis(2,3-dichloroallyl)cyanoinododithiocarbonate	0	28.7	0	0	-0.1	0.54	-	-	-	-	-
34924	N,N'-Diphenylsulfonylquinonediimine	4.0	8.35	5	59.8	0.41	0.11	0.2	-	-	-	-
34929	Potassium cyanodithioimidocarbonate	0	49.7	0	0	-0.19	0.80	-	-	-	-	-

(1) * indicates sample not predischarged vs N.H.S.

Table 2

CELL CHARACTERISTICS OF 0.5 g. SAMPLES OF DEPOLARIZERS TESTED DURING SIXTH QUARTER
 IN CELL "D" AT 0.025 AMP-MIN/G OR IN CELL "C" AT 0.0100 AMP-MIN/G
 IN 168 g/l. NH₄Br ELECTROLYTE

Ref. No.	Compound	Energy Capacity (watt-min/g)		Coulombic Capacity (amp-min/g)		Coulombic Efficiency	O. C. V. in volts vs. N. H. E.	ΔE		Drop in Potential of Level B by Quarters, %	Ave. Operating Potential in volts vs. N. H. E.	Values of capacity for Br ₂ only. The parent compound also reduces at lower potential					
		Level A	Level B	Level A	Level B			Level C	Level A				Level B	1st	2nd	3rd	4th
36244	Quinoxaline perbromide (52.5% Br)	6.1	7.0	10.98*	4.7	4.2	57.7	66.2	0.98	0	0.1	0.70	0.85	0.6	1.9	4.4	93.2
36248	Quinoxalium chloride perbromide 34.1% Br	5.60	6.1	6.87*	4	4	58.2	58.2	0.98	0.012	0.04	0.80	0.92	3.2	50.3	11.6	34.8
37203	Quinoxalium chloride perbromide 59% Br	13.17	13.9	11.87*	8.8	8.8	74.2	74.2	1.01	0	0.02	0.90	0.98	1.2	1.2	3.7	93.9
37201	1,10-Phenanthroline perbromide 39% Br	10.48	11.03	7.87*	7.8	7.8	100	100	1.00	0	0.01	0.75	0.82	1.3	1.3	2.6	94.8
37202	1,10-Phenanthroline chloride perbromide 48.8% Br	11.9	13.1	9.84*	8.6	8.6	87.3	87.3	1.01	0.006	0.03	0.79	0.92	1.3	1.9	1.3	95.5
37214	Iodine	12.4	12.4	12.7	11.5	11.5	90.6	90.6	0.87	0.012	0.025	0.48	0.48	4.9	3.3	7.3	84.5
37226	Iodine + 0.1 g CdS	9.4	10.3	12.7	12.0	11.0	94.4	86.5	0.60	0	0.01	0.14	0.34	1.7	2.6	80.1	15.6
37233	Quinoxaline hydrochloride perchloride	11.8	14.7	11.8*	10.7	11.2	90.8	95.0	1.07	0.02	0.09	0.50	0.61	1.2	14.6	12.8	71.4
38406	Triethylammonium chloride moniodide	9.8	11.2	12.5*	8.4	9.0	67.2	72.0	0.97	0.01	0.01	0.57	0.65	4.5	8.3	10.8	76.4
38407	Triethylammonium chloride iodine tri-chloride	16.9	17.6	18.6*	12.9	13.2	69.3	71.0	1.10	0.006	0.01	0.71	0.73	2.4	9	16.8	71.9

Table 2 (cont'd.)

Ref. No.	Compound	Energy Capacity (whr-min/g)		Coulombic Capacity (amp-hr/g)		Coulombic Efficiency		O. C. V. in volts		Ave. Operating Potential in volts		Drop in Potential of Level B by Quarters		Comments				
		A	B	Theor.	A	B	A	B	A	B	A	B	A		B			
38408	Trimethylammonium chloride iodine bromide	11.5	11.7	10.6*	9.5	9.5	89.7	89.7	0.88	0.006	0.02	0.61	0.63	2.1	10	8.9	78.8	
38401	Quinoline iodine chloride	11.7	12.4	11.2*	11.2	10.0	100	100	0.77	0.03	0.09	0.45	0.51	4.6	5.4	8.4	81.7	
38402	Quinoline iodine trichloride - A	14.6	16.10	15.1*	13.1	13.7	86.9	90.8	1.06	0.02	0.04	0.52	0.58	8.9	13.2	13.2	65.7	
38403	Quinoline iodine trichloride - B	16.4	17.12	13.6*	13.7	13.7	100	100	1.02	0.006	0.006	0.60	0.65	5.0	11.2	21.2	62.6	
36693	Quinoline iodine bromide	10.1	10.7	9.4*	9.9	10.0	100	100	0.75	0.03	0.08	0.44	0.47	4.7	6.2	7.7	81.4	
38409	Quinolinium chloride iodine chloride	9.3	9.6	8.35*	8.7	8.7	100	100	0.81	0.006	.04	0.47	0.50	5.8	8.7	9.4	76.2	
38410	Quinolinium chloride iodine trichloride	17.4	18.1	15.8*	13.5	14	85.3	88.7	1.08	0	-.04	0.69	0.69	3.1	10.5	14.8	71.6	
38412	Quinolinium chloride iodine bromide	9.4	10.1	7.72*	(9.3)	(9.5)	100	100	0.81	0.006	0.03	0.46	0.41	6.5	10.0	19.4	64.1	
37222	Quinolinium chloride perbromide	12.6	12.6	9.96*	8.25	8.25	82.7	82.7	0.99	0.006	0.006	0.93	0.93	1.2	0.6	0.6	97.5	Standard 0.05 amp/g
37235	Quinolinium chloride perbromide	11.4	12.7	9.98	8.2	8.2	82.2	82.2	1.00	--	--	0.79	0.95	1.2	1.2	1.2	96.4	0.100 amp/g
37236	Quinolinium chloride perbromide	8.7	11.1	9.98	7.2	7.5	72.2	75.2	1.01	--	--	0.61	0.88	0.6	1.2	3.2	95.0	0.150 amp/g
37237	Quinolinium chloride perbromide	8.6	11.5	9.98	7.8	8.1	78.2	83.2	1.00	--	--	0.50	0.82	0	0.7	2.6	96.7	0.250 amp/g
37238	Quinolinium chloride perbromide	8.4	10.8	9.98	7.8	8.1	65.2	73.2	1.00	--	--	0.47	0.73	2.0	2.0	8.5	87.5	0.300 amp/g
37239	Quinolinium chloride perbromide	5.5	9.9	9.98	6.3	7.4	63.2	74.2	1.00	--	--	0.27	0.74	1.3	2.0	4.6	92.1	0.350 amp/g
37240	Quinolinium chloride perbromide	0.6	10.9	9.98	2.5	8.4	25.1	84.2	1.00	--	--	-0.36	0.70	2.7	2.1	1.4	94.8	0.400 amp/g

Table 2 (cont'd.)

Ref. No.	Compound	Energy Capacity (watt-min/g)		Coulombic Capacity (amp-min/g)		Coulombic Efficiency		O. C. V. in volts vs. H. H. E.		-ΔX Level		Ave. Operating Potential in volts vs. H. H. E.		Drop in Potential of Level B by Quartz, g		Comments		
		A	B	Theor.	A	B	A	B	A	B	A	B	A	B	1st		2nd	3rd
37241	Nitrobenzene	(.53)	5.92	78.6	(4)	~83	5.2	~89.3	-0.07	0.09	0.22	-0.47	-0.34	18.4	5.6	10.5	65.8	Sample attacked plastic cell
37245	p-Nitrobenzonitrile	2.90	5.38	65.2	12.8	~20	19.7	30.7	-0.01	0.06	0.14	-0.37	-0.33	12.8	17.0	23.4	46.8	
37244	p-Nitrophenol	3.58	5.2	69.5	14.5	~19	20.9	27.4	0.07	0.14	0.17	-0.35	-0.33	4.3	12.8	19.2	64	
38418	p-Nitrophenol Sodium salt	1.25	2.08	60.0	7.6	14.6	12.6	24.3	0.03	0.08	0.12	-0.44	-0.46	14.3	17.8	25.0	43.2	
37224	o-Nitrobenzoic acid	4.02	5.98	57.8	9.5	16.5	16.4	28.5	0.32	0.18	0.23	-0.18	-0.24	6.6	16.4	47.7	29.5	
37225	p-Nitrobenzoic acid	~5.8	~5.8	~5.8	~5.8	~5.8	~5.8	~5.8	0.19	0.09	0.18	-0.29	-0.23	3.5	33.4	14	49.2	
37249	Sodium o-nitrobenzoate	3.29	4.22	51.2	11.5	14.3	22.5	28.0	0.01	0.12	0.14	-0.31	-0.30	7.1	9.5	35.7	47.7	
37248	Diacidum Nitroterephthalate	3.21	4.32	32.2	10.3	12.4	32.0	38.5	0.04	0.10	0.12	-0.29	-0.25	4.7	4.7	11.6	79.1	
37250	Potassium 2,4-di-nitrobenzene sulphonate	3.27	7.15	67.6	8	~83	11.8	34.1	0	0.02	0.05	-0.29	-0.19	7.3	29.1	29.1	34.5	
33488	Tetraodium 1,4-Dinitropropanoate	4.0	6.1	44.8	9.5	15	21.2	33.5	0.12	0.05	0.11	-0.35	-0.18	9.7	11.3	40.3	36.7	Previous test
38417	Diacidum 3,6-Di-nitro phthalate	4.9	7.8	64.3	9.5	18.8	14.7	29.2	0.12	0.01	0.06	-0.08	-0.19	6.0	14.9	37.4	41.8	
33453	p-Dinitrobenzene	2.97	10	114.8	11.8	20	10.5	17.4	0.38*	--	--	-0.35	-0.2	--	--	--	--	Previous test
37246	p-Dinitrobenzene	4.0	6.23	114.8	10.5	17	9.14	14.8	0.12	0.02	0.05	-0.23	-0.22	3.5	15.8	35.1	45.7	
37205	p-NBS in 1:9 H ₂ O-0.1M KCl electrolyte	1.76	3.76	114.8	7.2	14.3	6.3	12.4	-0.03	0.08	0.13	-0.35	-0.34	9.5	21.5	31.0	36.2	
37206	p-NBS in 1:4 H ₂ O-0.1M KCl electrolyte	1.03	2.33	114.8	4.2	9.5	3.7	8.3	-0.03	0.08	0.15	-0.35	-0.32	4.8	28.5	42.8	23.8	
37223	2,4-Dinitrobenzoic Acid	5.78	9.34	94.2	11.8	16	13	17.6	0.34	0.09	0.14	-0.18	-0.02	12.8	5.1	21.8	60.3	

Table 2 (cont'd.)

Ref. No.	Compound	Energy Capacity (amp-min/A)		Coulombic Capacity (amp-min/A)		O. C. V. in volts vs. N. H. E.	$\frac{\Delta E}{\log \frac{A}{C}}$	Ave. Operating Potential in volts vs. N. H. E.		Drop in Potential of Level B by								
		Theor.	Found	Theor.	Found			Level A	Level B	15% current	25% current	100% current						
37207	5-Nitroisophthalic acid	4.38	7.3	45.8	14.5 ~ 19.5	31.7 ~ 43	0.24	0.12	0.19	-0.29	-0.22	31.7	12.3	8.8	47.5			
37210	Trinitro- <i>o</i> -Naphthoic acid ¹	7.18		94.5	11.8	13	12.5	13.8	0.28	0.05	0.11	-0.11	-0.05	3.9	6.4	14	75.8	
37211	Trinitro- <i>o</i> -Naphthoic acid ²	7.10		94.5	10.1 ~ 14.5	10.6 ~ 16	0.29	0.02	0.11	-0.10	-0.12	3.9	32.1	36.5	25.7			
37213	Trinitro- <i>o</i> -Naphthoic acid ³	4.37	9.19	94.5	10.5 ~ 17	11.1 ~ 18	0.27	0.06	0.23	-0.18	-0.06	18.5	7.9	13.2	60.8			
37209	4-Nitroindazole	0.90	1.35	85.5	7.2	9.5	8.4	11.1	-0.15	0.09	0.16	-0.48	-0.46	4.0	12.0	32.0	52.0	
37208	Sodium salt of nitranilic acid	0.94	1.85	82.3	8.4	12.5	10.2	15.2	-0.16	0.08	0.15	-0.49	-0.45	10	15	65		
37228	Benzoquinone	4.8	6.2	29.9	9.1	11.1	30.4	37.1	0.62	0.17	0.24	-0.17	-0.04	13.6	18.2	20.5	47.8	
37229	0.282 g Benzoquinone + 0.218 g DMB	4.5	7.5		10.3	17.3	33.9	57.8	0.62	0.11	0.24	-0.16	-0.17	26.9	24.7	8.6	39.8	
37218	Chloranil	6.0	7.8	13.0	9.9	10.5	76.2	80.8	0.30	0.01	0.06	0.01	0.14	3.5	6.9	9.2	80.6	
36246	Peracetic acid	5.76	6.95	42.3	10.2	10.5	24.1	24.8	1.08	0.07	0.49	-0.04	0.06	4.8	7.3	30.1	58.1	in perchlorate
36249	2-Nitrobenzoyl peroxide	6.23 ~ 9.5	44.8		11.0 ~ 45	24.5 ~ 33	0.96	0.32	0.42	-0.03	0.03	--	--	--	--	--	--	
36245	Benzoyl peroxide	2.63	3.14	13.3	3.8	3.8	28.6	28.6	0.93	0.30	0.41	0.09	0.23	8.6	9.5	15.2	56.7	
36119	Leuconic Acid-1.2H ₂ O	2.3	4.6	99.3	6.8	12.0	6.9	12.1	0.21	0.03	0.13	-0.26	-0.22	16	30.6	26.6	26.6	
36114	Ferrocene	0	0	0	0	0	0	0	-0.16	0.62	0.69	--	--	--	--	--	--	
37234	Phosphomolybdic acid	3.98	4.00	20.3	7.8	9	38.4	44.4	0.69	0.08	0.08	-0.16	-0.09	37	33.4	20.4	9.3	0.62 g hydrate
Tests in Cell "C"																		
36250	N,N'-(1,2-Ethylene)-bis maleamic acid		0.64	25.0		9		36.0	-0.06	0.32		-0.54	15.3	15.3	15.3	54.1		
37212	1,3,6,8-Tetranitro-carbazole		7.2	111		45		40.7	0.14	0.40		-0.44	29.5	20.6	23.5	26.5		

*Capacity calculated from active halogen analysis

Table 3

COMPARISON OF CELL CHARACTERISTICS OF DEPOLARIZERS
TESTED AT HIGH AND LOW DRAIN RATES IN CELL "D"

Ref. No.	Compound	Energy Cap. Mvt-Min. g.		Coulombic Capacity $\frac{\text{amp-hr}}{\text{g}}$		Coulombic Efficiency (%)		O.C.V. (Volts)	$\frac{\Delta E}{\log \Delta I}$	Ave. Operating Potential (Volts)		Drop in Potential by Current for Electrode B				Comments
		A*	B	Theor. g.	Found g.	A	B			A	B	1st	2nd	3rd	4th	
37217	Quinoline Hydrobromide Perbromide	9.70	(7.76) (C=9.78)	8.73	7.84	7.25	83.1	0.99	—	.63	(.47)	10.	21.9	20.4	47.7	0.196 amps in NH ₄ Br = 1 amp/in ² = 0.292 amps/g.
36238	Quinoline Hydrobromide Perbromide	13.2		8.73	8.7	8.7	100	0.99	—	0.97		1	1	1	96.8	0.025 amps in NH ₄ Br = 0.127 amps/in ² = 0.05 amps/g.
37220	Quinoline Hydrobromide Perbromide	9.94		8.73	7.1-9.4	7.1-9.4	100	0.99	—	.54	.93	3.1	1.9	4.3	90.7	0.196amps in MgBr ₂
34945	Quinoline Perbromide	(C=11.7) A-sub-bias		11.1	—	8.23	—	74.2	1.01	—	0.67	14.4	4.4	3.8	42.7	0.196 amps in NH ₄ Br
34941	Quinoline Perbromide	12.0		11.1	8.8	8.8	79.2	1.00	—	0.84		0	1.5	5.2	93.5	0.025 amps in NH ₄ Br
37219	AgO	~4.2	(-6.97)	13 or 26	-7.4	(C=7.36) B over 10	56.8 or 28.9	0.63	—	-0.03	(-.03)	35	2.7	4.5	58	0.196 amps in NH ₄ Br
36237	AgO	6.7		13 or 26	11	13	84.7 or 42.4	0.70	—	0.01	0.22	26.2	2.4	6.3	65.1	0.025 amps in NH ₄ Br
34947	Silver Salt of Dinitro-pyromellitic Acid	5.33	over 10.6	31.7	13.7	over 15	41.8	0.65	—	-.21	(-0)	—	—	—	—	0.196 amps in NH ₄ Br
34946	Silver Salt of Dinitro-pyromellitic Acid	8.6	10	31.7	15.2	18	45	0.61	—	-.05	(-.04)	—	—	—	—	0.025 amps in NH ₄ Br

*A and B refer to the electrode level in cell
1. vs. M.H.E.

Table 4

STABILITY OF PERHALOGEN COMPOUNDS IN DRY STORAGE
(Room Temperature)

COMPOUND	Initial %	(% of Initial Active Halogen Present After X Days in Dry Storage)				Over 40 Days %		
		1-10 Days %	10-19 Days %	Over 20 Days %	Over 40 Days %			
Pyridine perbromide	-	1	Very Low					
Pyridine bromide perbromide 2H ₂ O	43.7 ¹			56	97.3	146	95.2	
Quinoline perbromide	Varies		15	82.3	26	66.3	49	52.3
Isoquinoline perbromide	55.3 ¹			60	72.2	150	66.2	
6-nitroquinoline perbromide	47.8 ¹			29	100			
8-nitroquinoline perbromide	47.8 ¹			30	87.			
Quinolinium bromide perbromide	43.3		11	100				
Quinolinium chloride perbromide	42.9			30	100			
Quinolinium iodide perchlorate	26.2			21	100			
Quinoxaline perbromide	56.8	8	93	13	92			
Quinoxalinium chloride perbromide	59.0							
1,10-Phenanthroline chloride perbromide	48.8					70	100	
Trimethylammonium chloride iodine trichloride	67.7			31	98.7			
Trimethylammonium chloride iodine bromide	68.3			31	100			
Trimethylammonium chloride iodine chloride	62.7			31	100			
Quinoline iodine chloride	56.7			31	100			
Quinoline iodine trichloride	54.7			31	100			

1 Theoretical for formula given; no initial value obtained.

Table 5

STABILITY OF PERHALIDES IN ELECTROLYTE

% OF ACTIVE HALOGEN RETAINED AFTER X DAYS IN
1:1 MgBr₂ · 6H₂O : H₂O

COMPOUND	Room Temperature					
	Days	% Retentive	Days	% Retentive	Days	% Retentive
Pyridinium bromide perbromide	1	92	11	91		
Quinoline perbromide	1	100	4	86.5	11	69.8
6-Nitroquinoline perbromide*	1	82,100	4	81.2	10	59
Quinolinium bromide perbromide	1	100	4	100	10	97.5
Quinolinium chloride perbromide			6	100	30	98
Quinolinium iodide perchlorate			6	100	30	100
Trimethylammonium chloride iodine trichloride	3	100				
Trimethylammonium chloride iodine chloride	3	100				
Quinoxaline perbromide	1	Almost none				
Trimethylammonium chloride iodine bromide	3	100				
Quinoxalinium chloride perbromide	1	81.3				
1,10-Phenanthroline perbromide	1	100				
Quinoline iodine trichloride	3	100				

* Note in water (without salt) 6-nitroquinoline retained 87.6% after (1 day) and Quinolinium bromide perbromide retained only 44.7%.

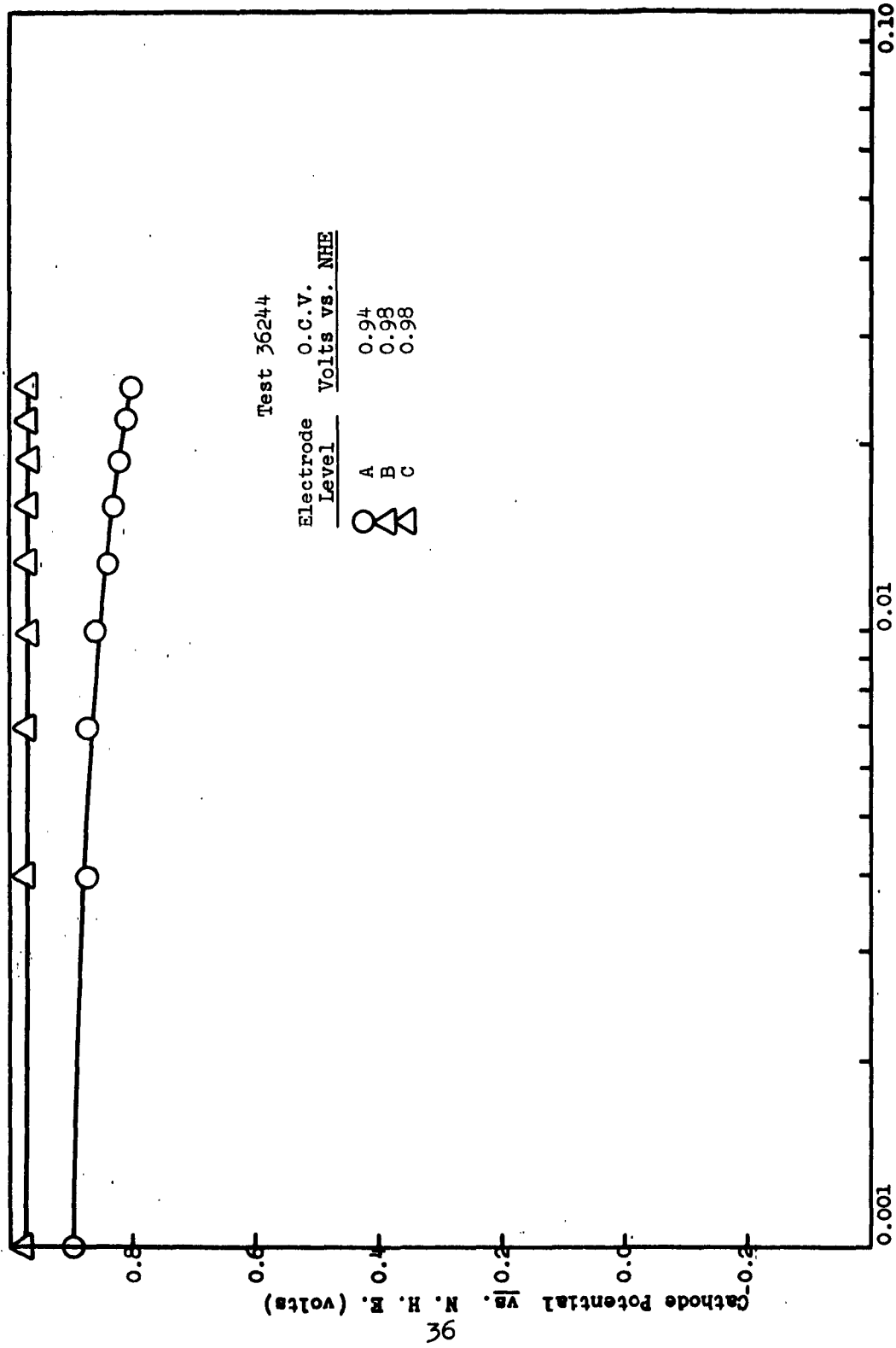


Figure 1 Voltage-current relationship of 0.5 g. samples of quinoxaline perbromide in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

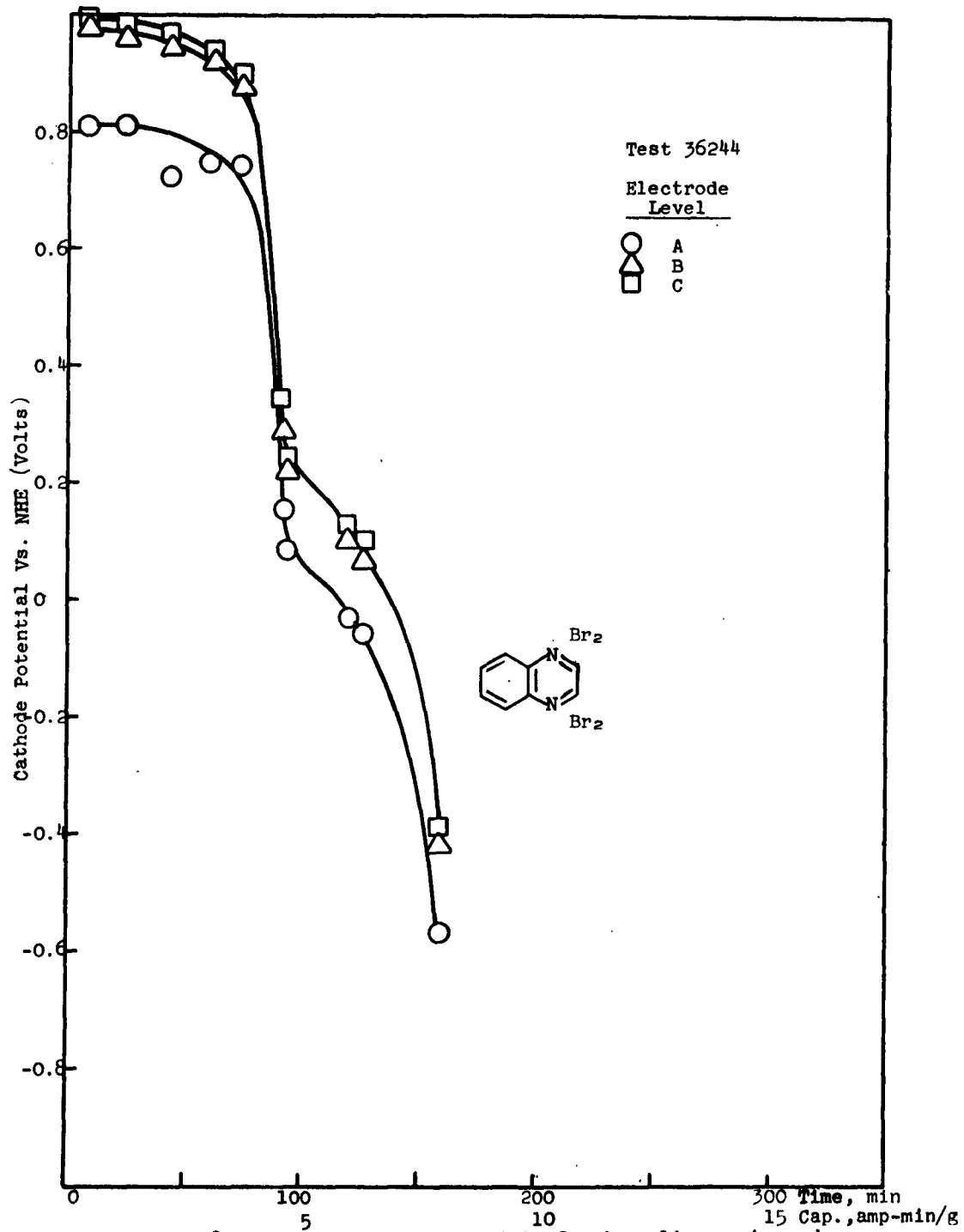


Figure 2 Chronopotentiometric plot of quinoxaline perbromide in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

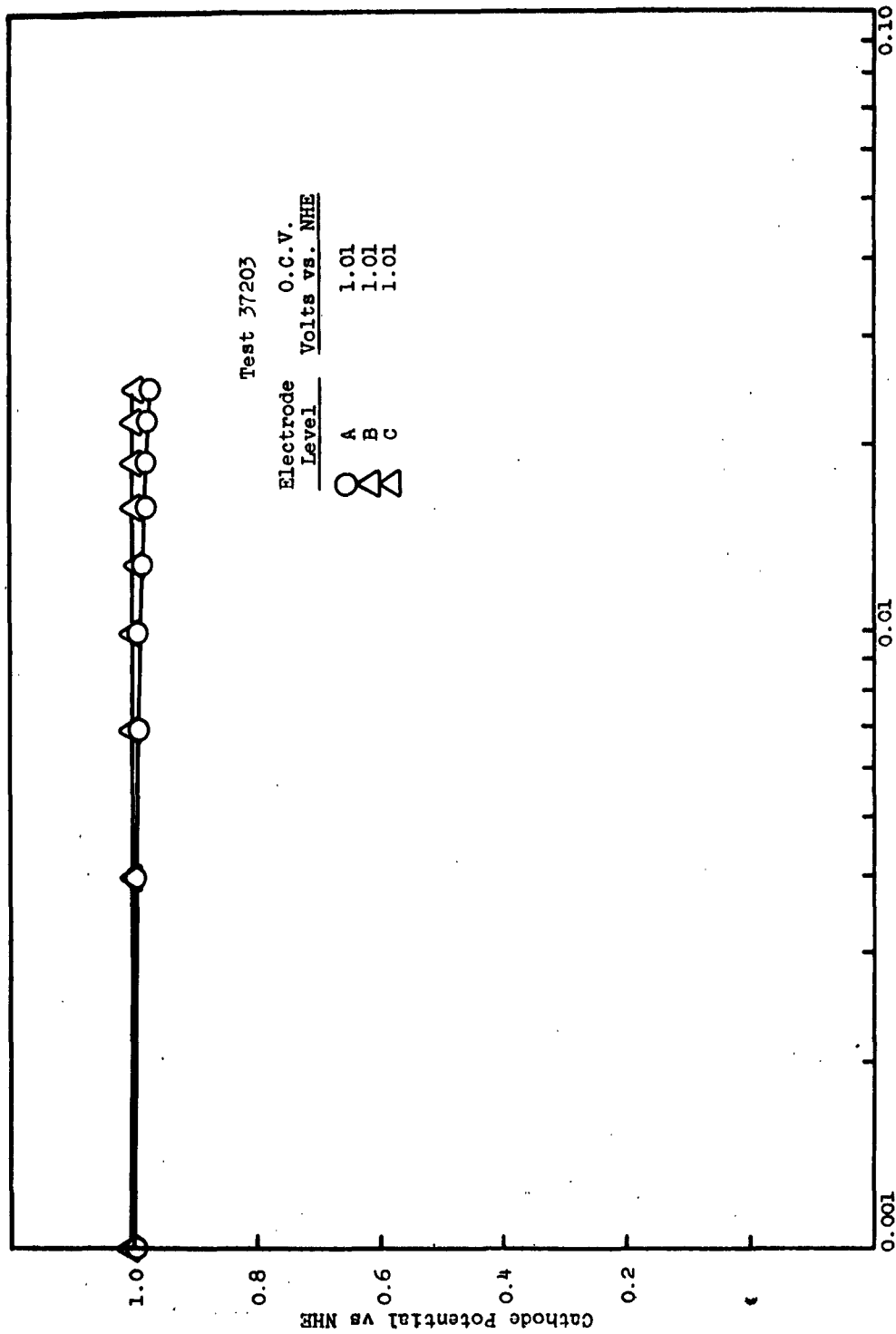


Figure 3 Voltage-current relationship of 0.5 g. sample of quinoxalium chloride perbromide in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

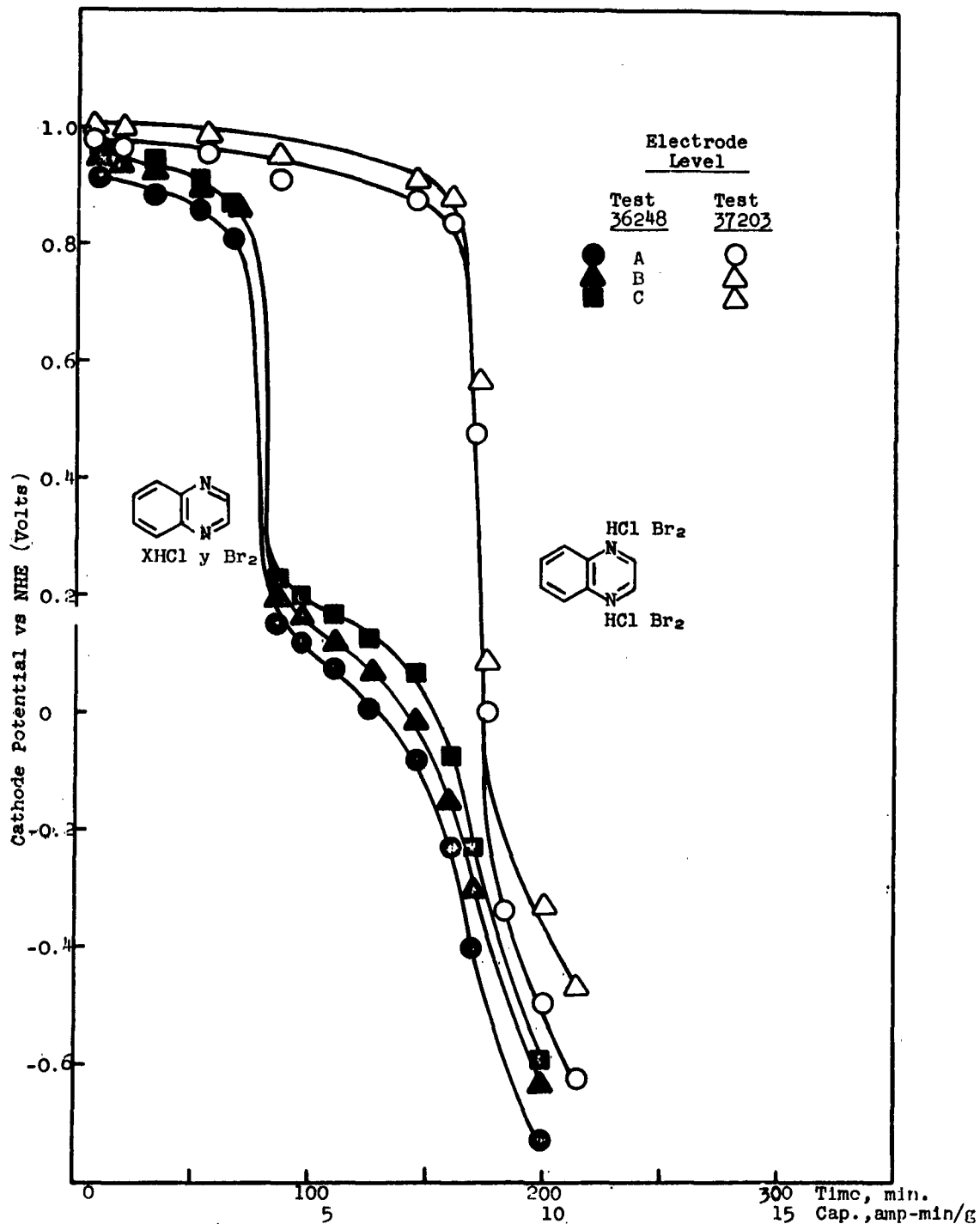


Figure 4 Chronopotentiometric plot of quinoxalinium chloride perbromide in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

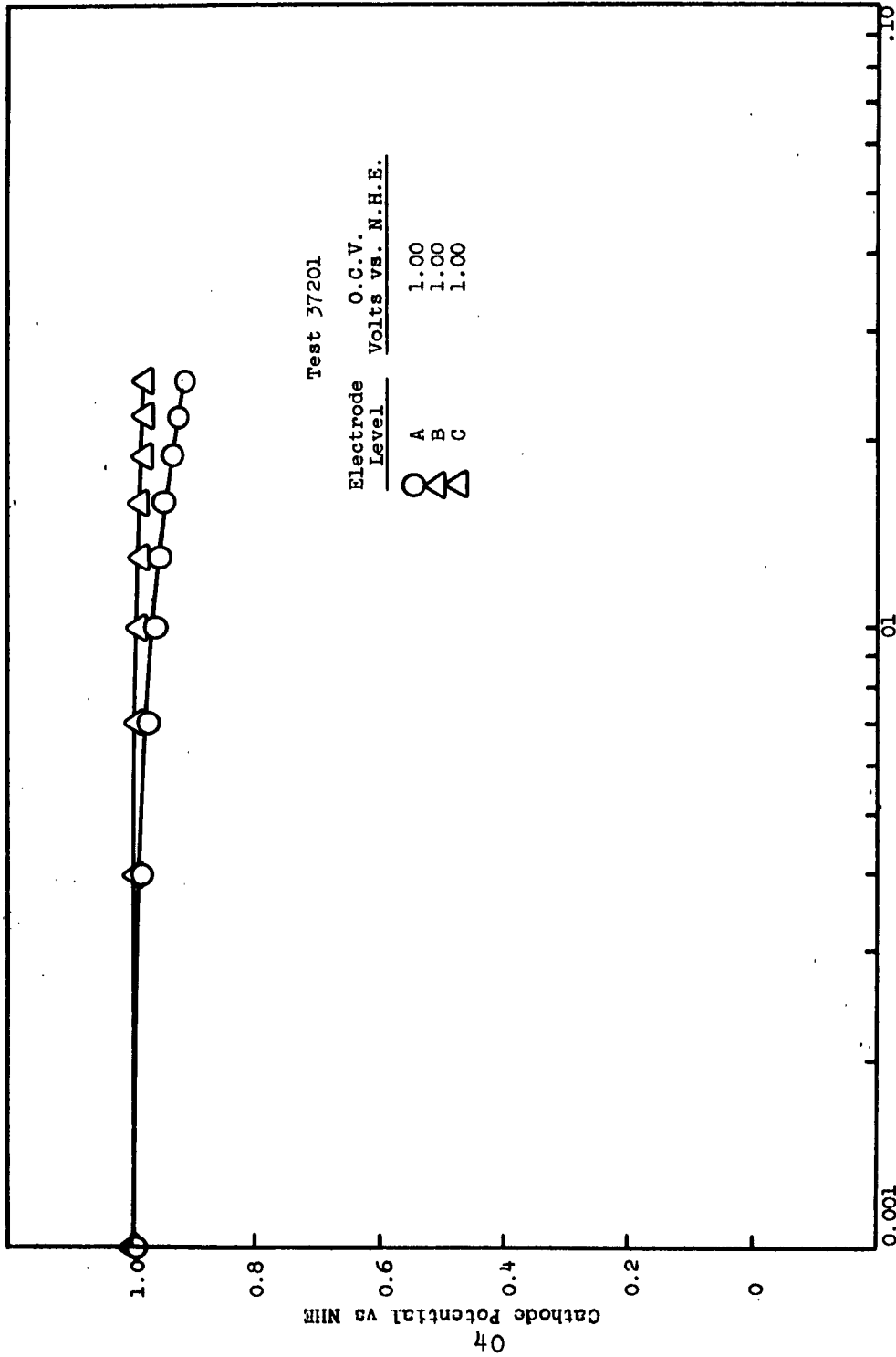


Figure 5 Voltage-current relationship of 0.5 g. sample of 1,10-phenanthroline perbromide in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

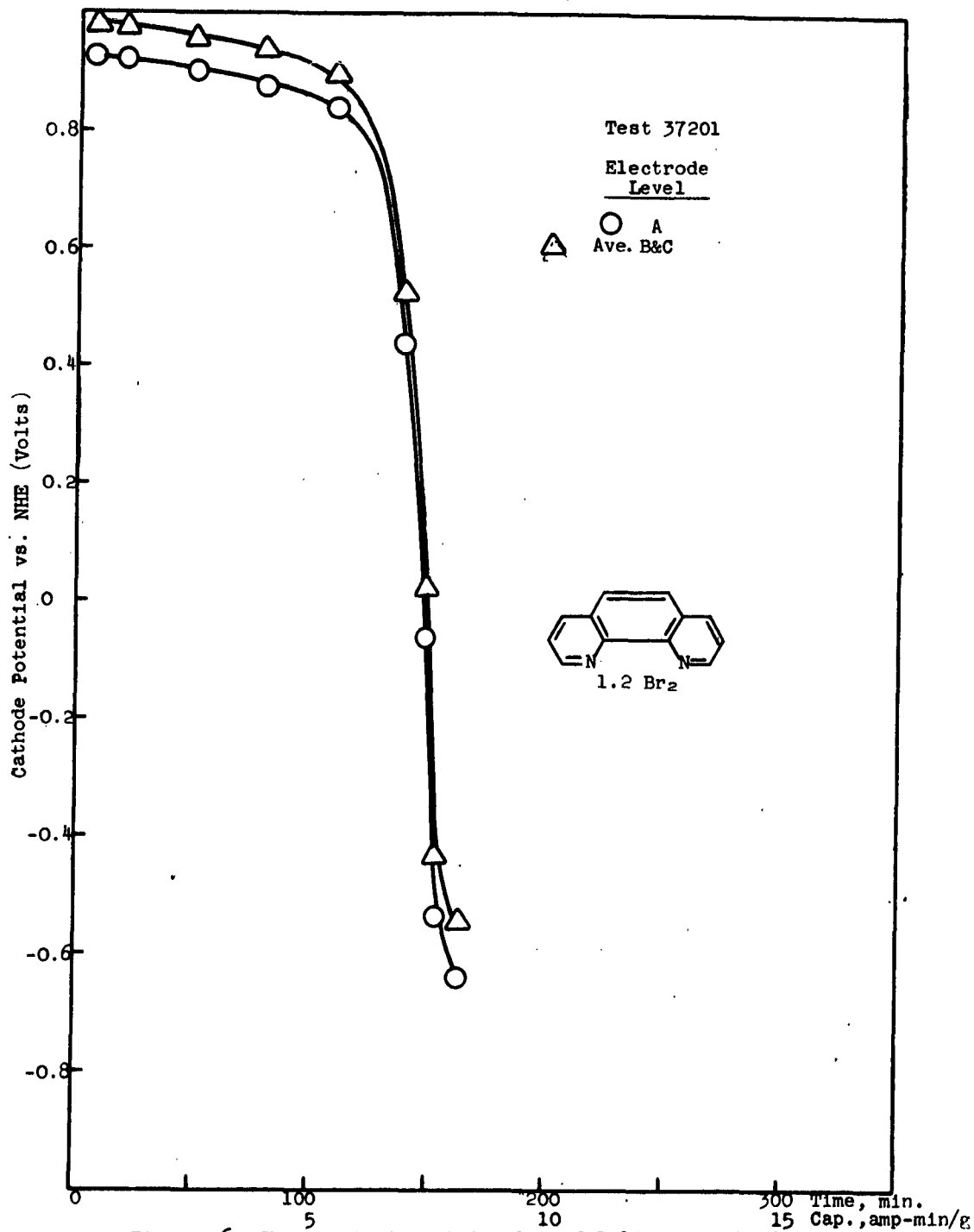


Figure 6 Chronopotentiometric plot of 1,10-phenanthroline perbromide in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

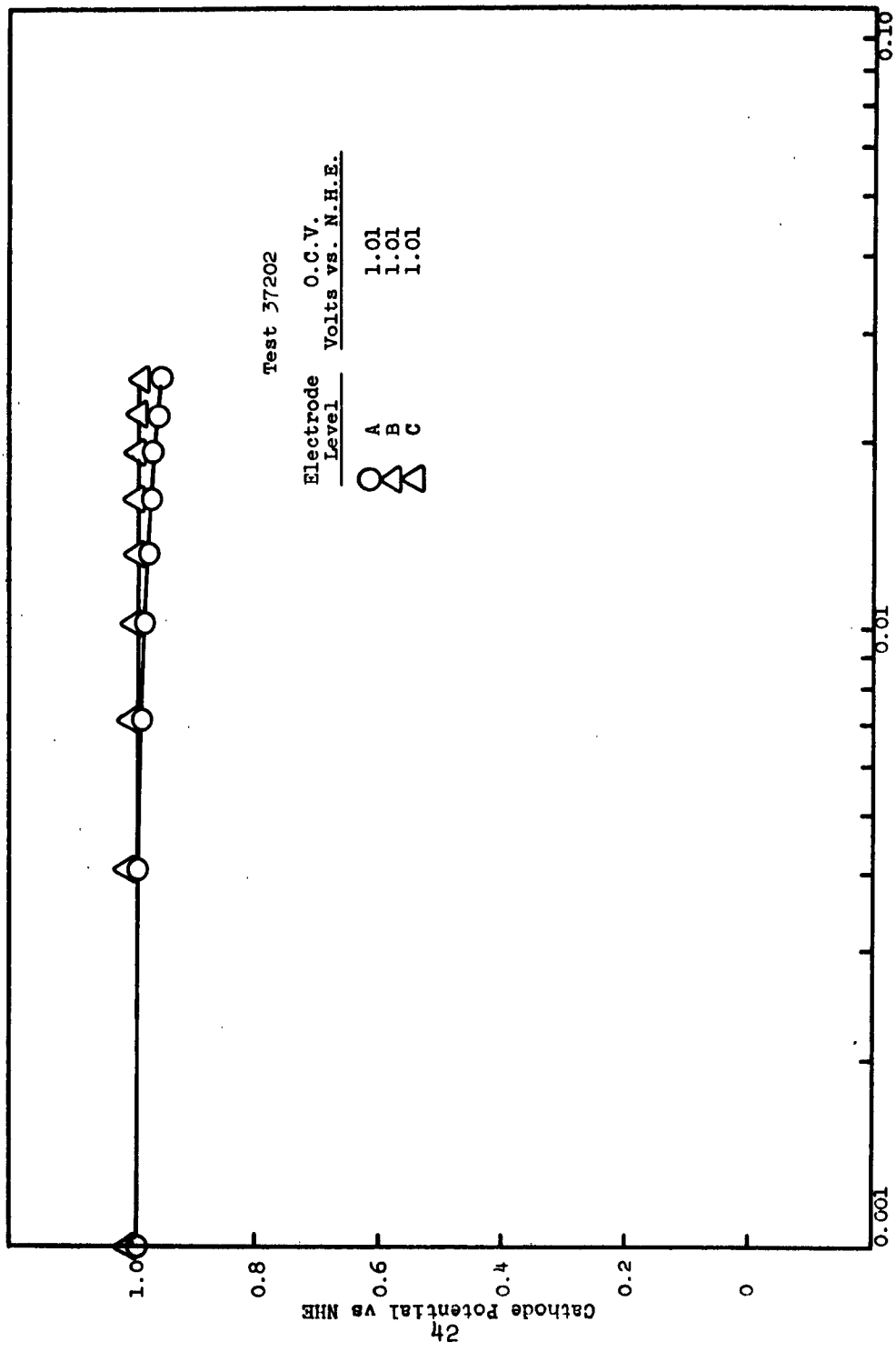


Figure 7 Voltage-current relationship of 0.5 g. sample of 1,10-phenanthroline chloride perbromide in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

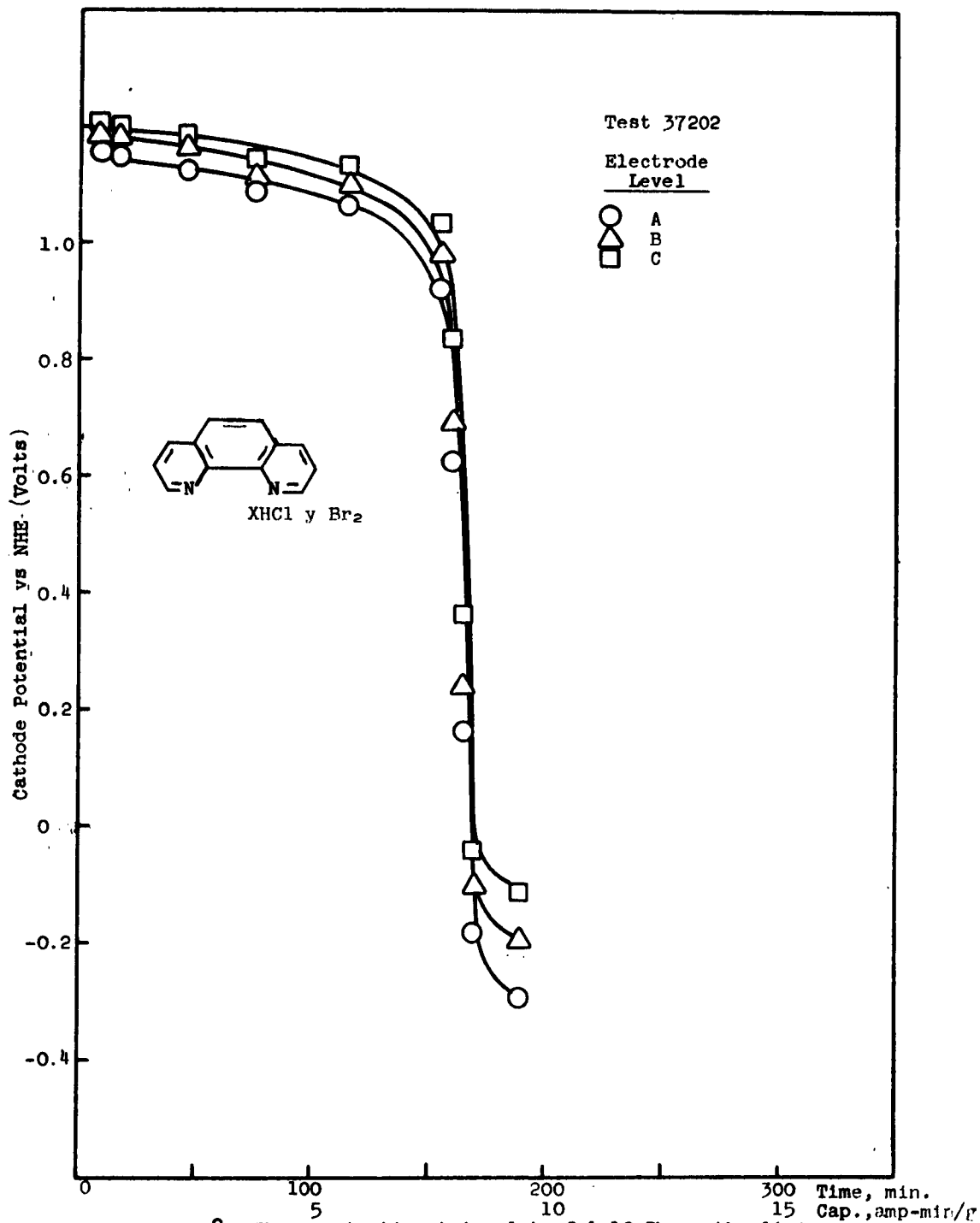


Figure 8 Chronopotentiometric plot of 1,10-Phenanthroline
 chloride perbromide in cell "D" in 168 g/l NH₄Br
 electrolyte at 0.05 amp/g.

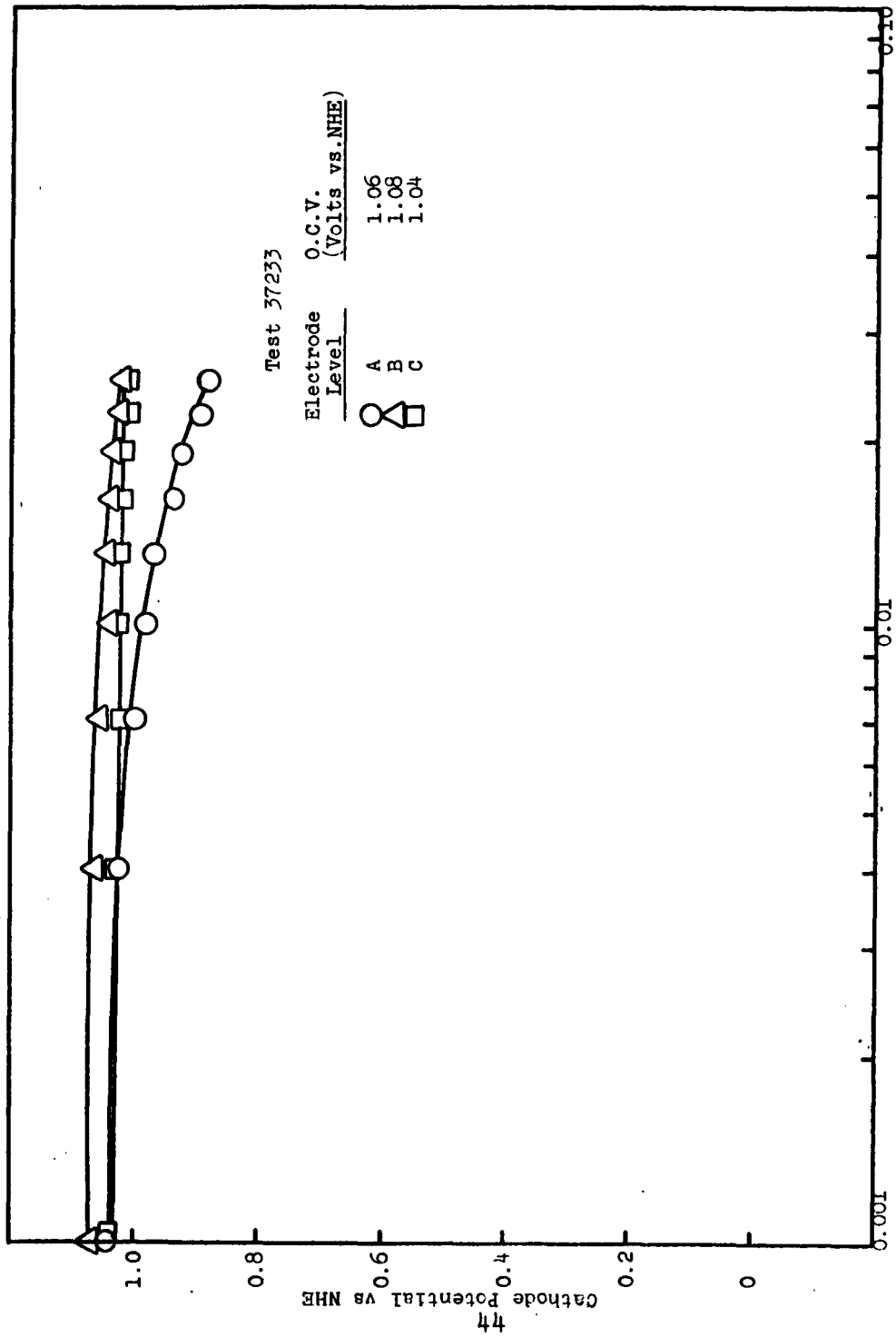


Figure 9 Voltage-current relationship of 0.5 g. sample of quinolinium iodide perchloride in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

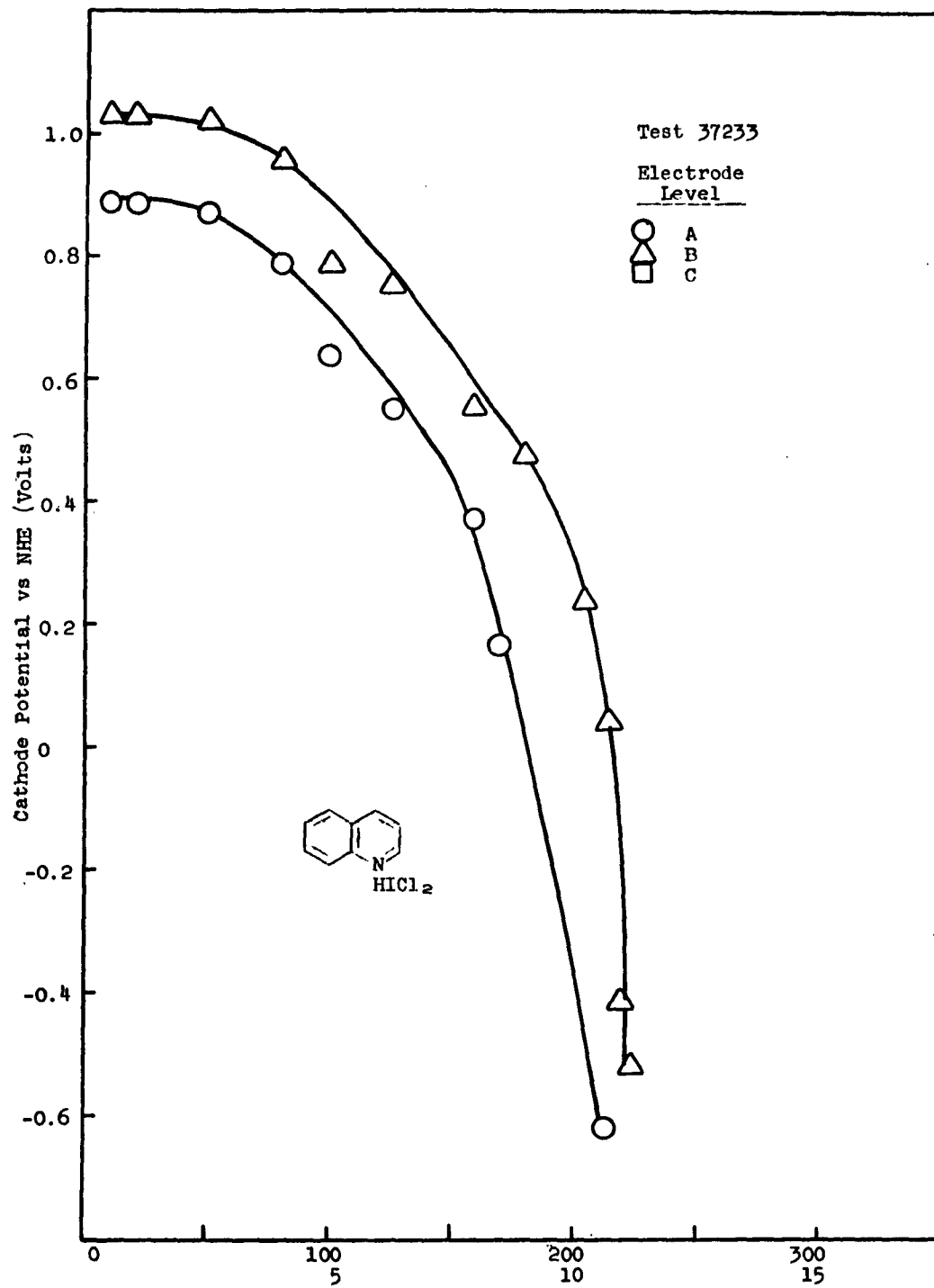


Figure 10 Chronopotentiometric plot of quinolinium iodine perchlorate in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

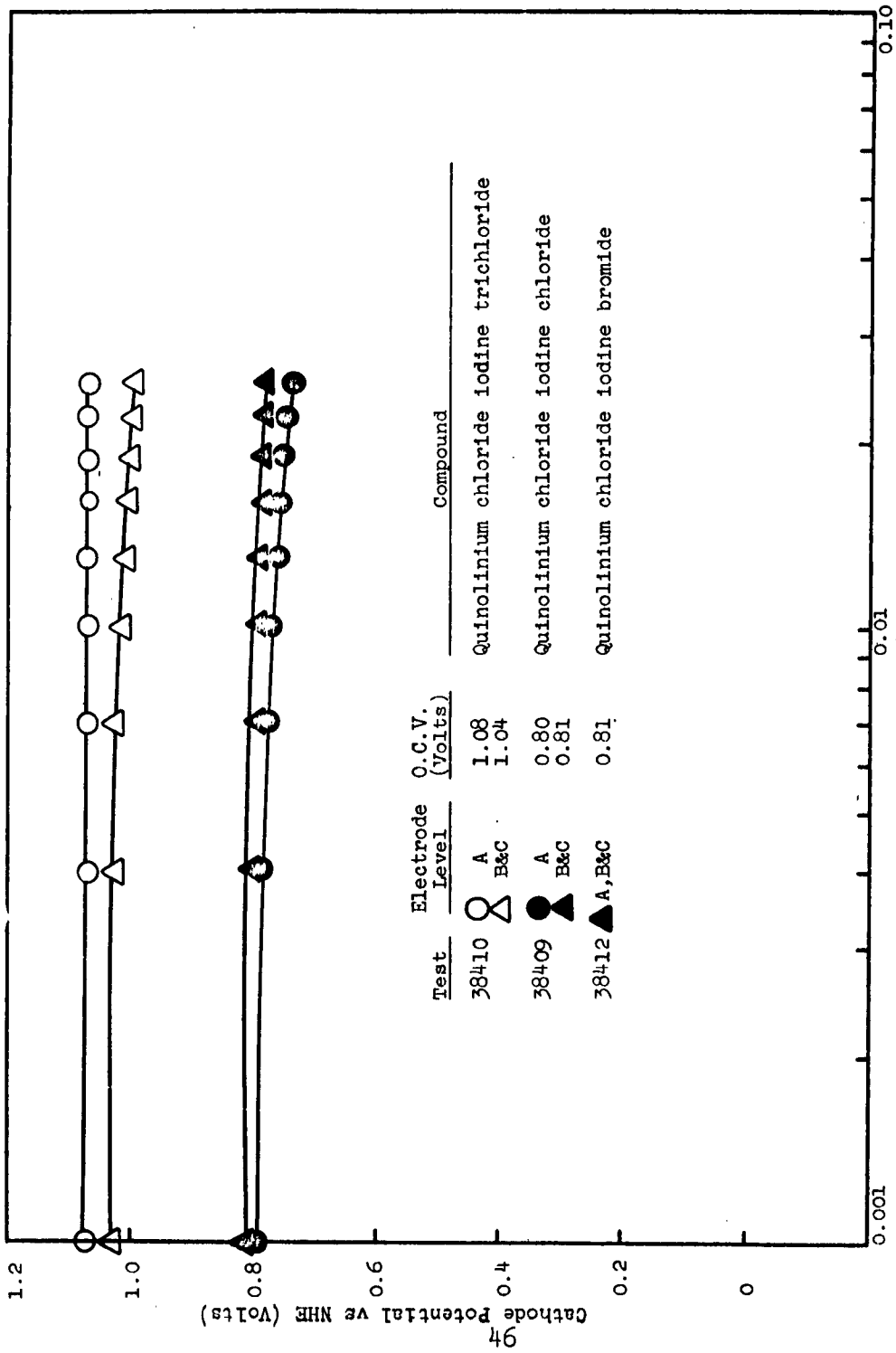


Figure 11 Voltage-current relationship of 0.5 g. samples of the addition compounds of quinolinium chloride with iodine bromide, iodine chloride and iodine trichloride in cell D in 168 g/l NH₄Br to 0.025 amps.

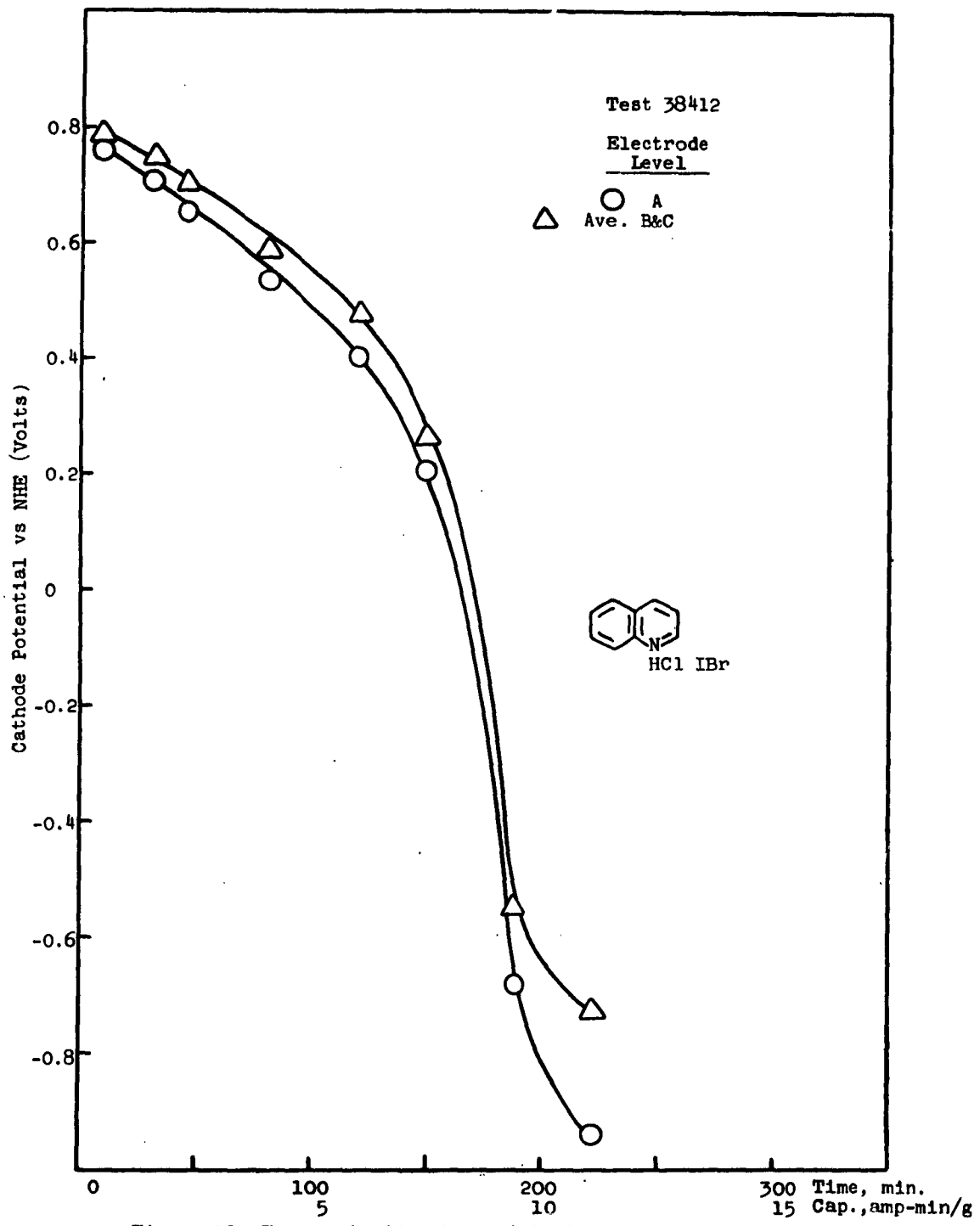


Figure 12 Chronopotentiometric plot of quinolinium chloride iodine bromide in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g

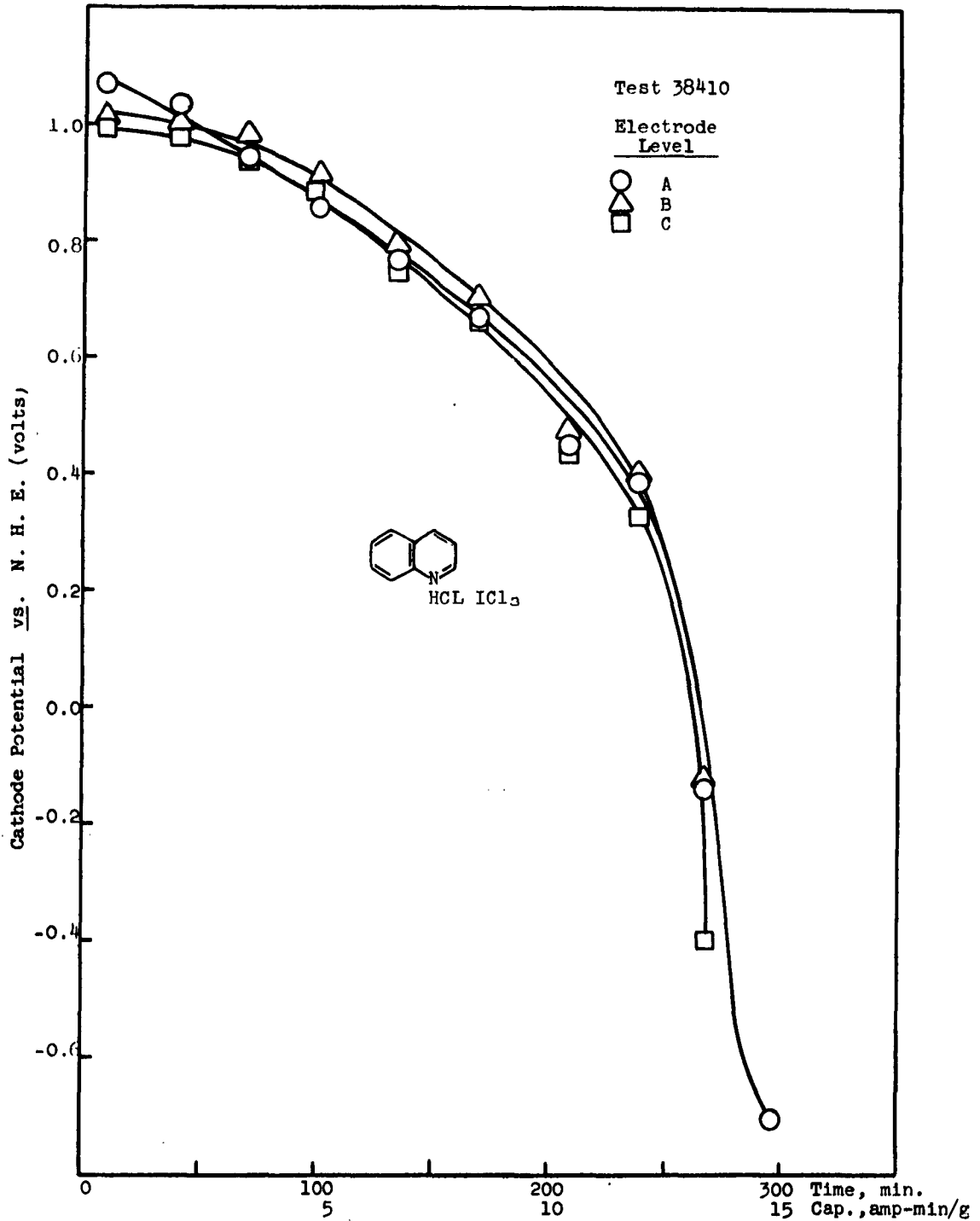


Figure 13 Chronopotentiometric plot of quinolinium chloride iodine trichloride in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g

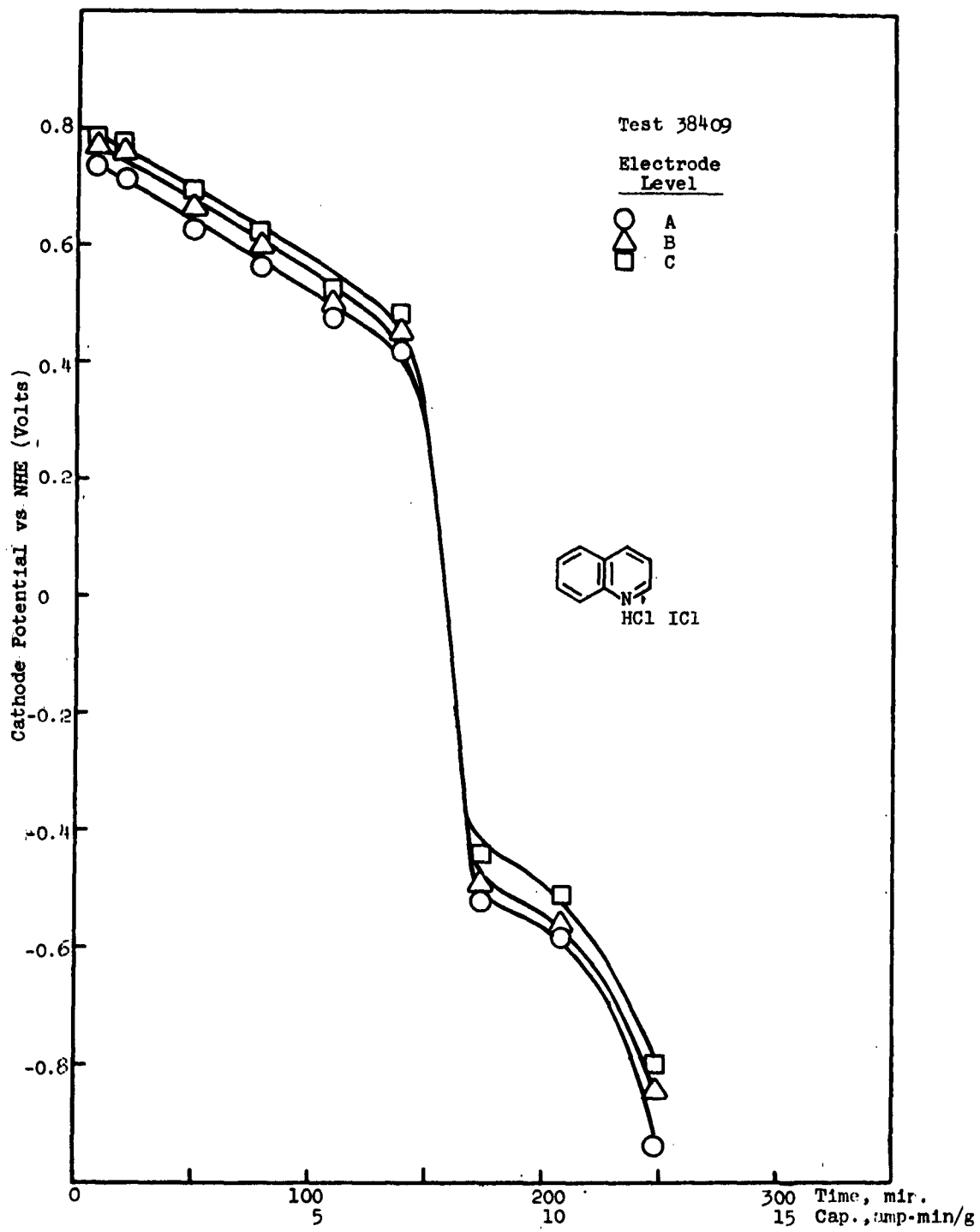


Figure 14 Chronopotentiometric plot of quinolinium chloride iodine chloride in cell "D" in 168 g/l NH_4Br electrolyte at 0.05 amp/g

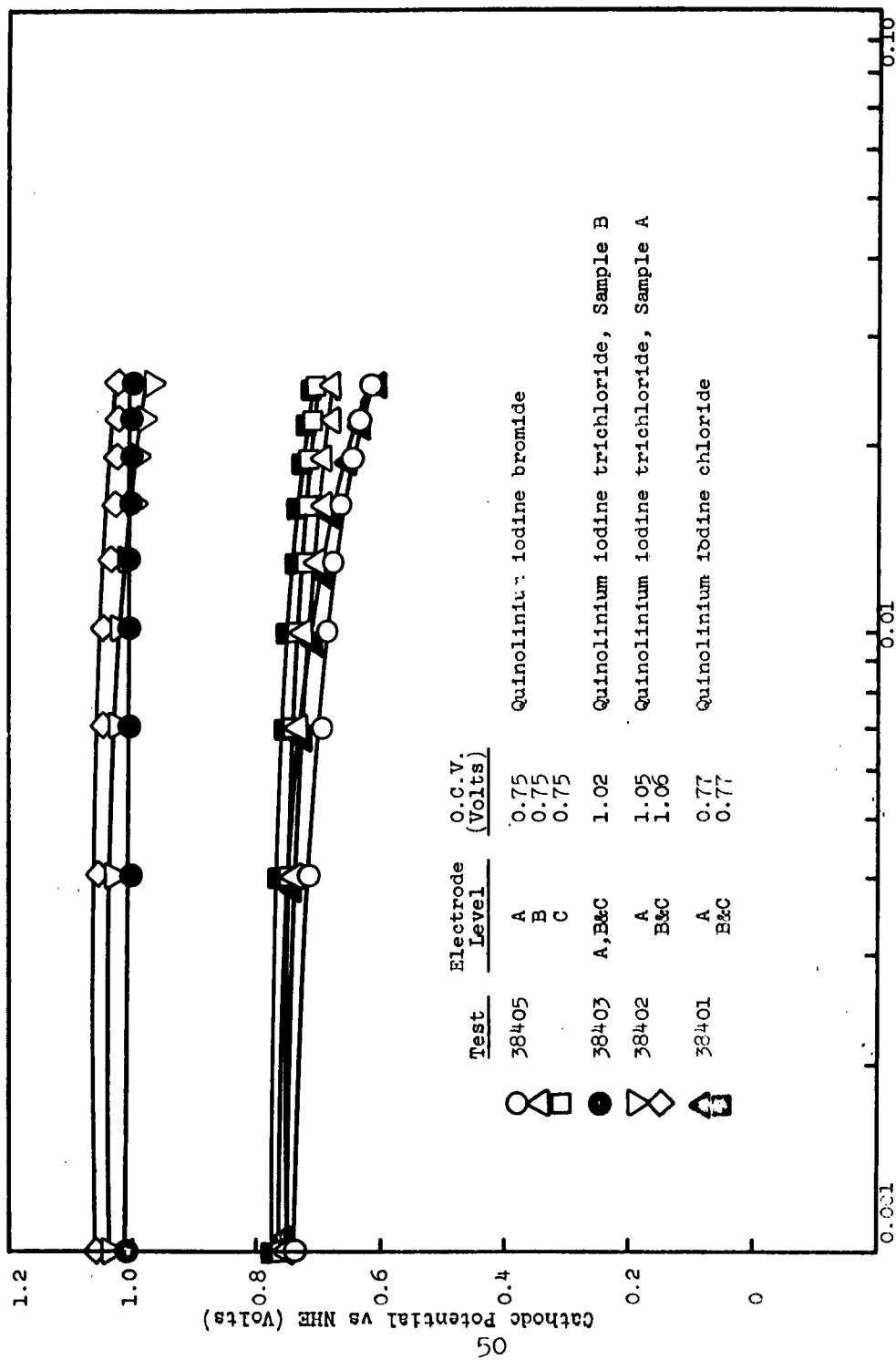


Figure 15 Voltage-current relationship of 0.5 g. samples of addition compounds of quinoline with iodine bromide, iodine chloride, and iodine trichloride in cell "D" in 168 g/l NH₄Br to 0.025 amps.

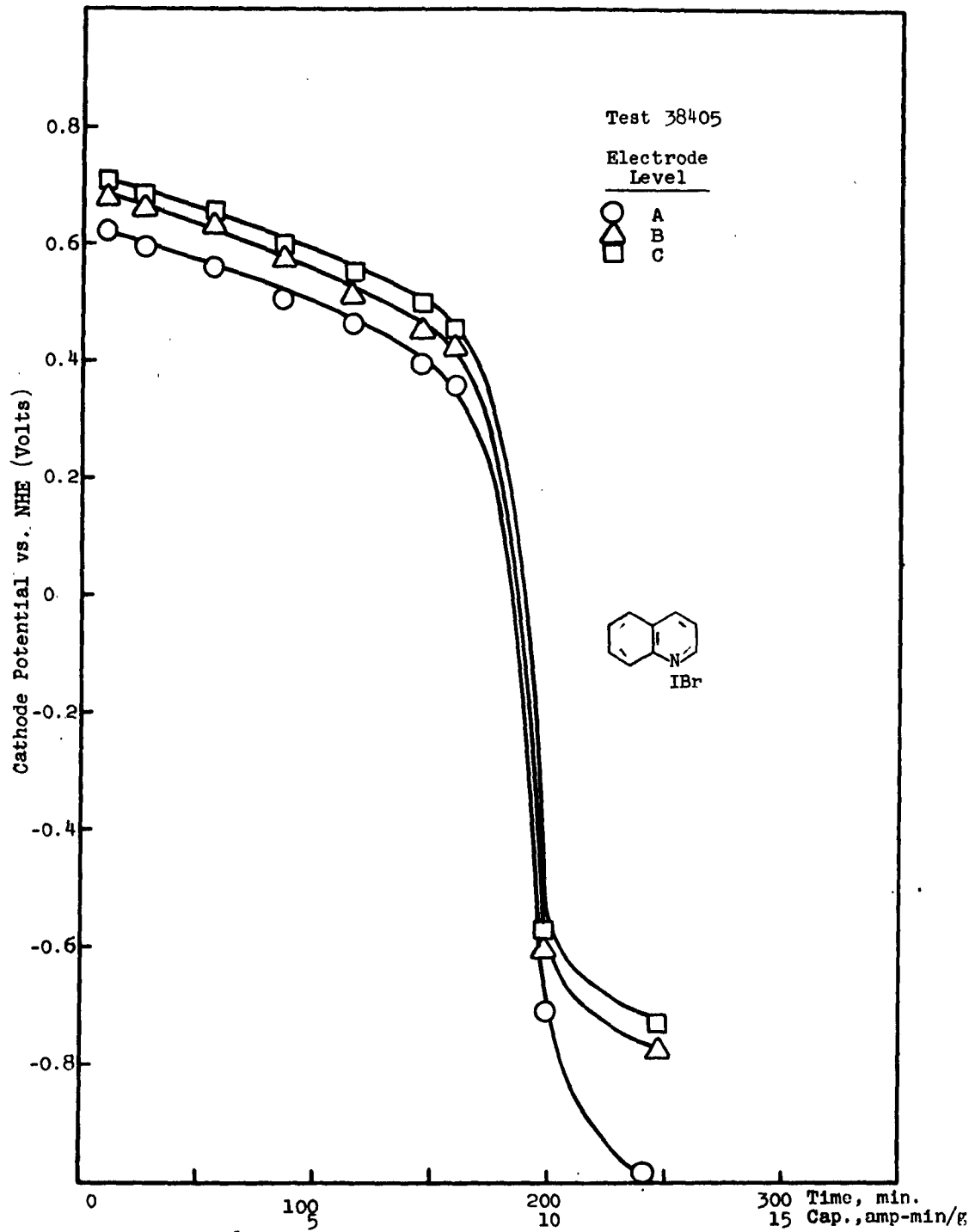


Figure 16 Chronopotentiometric plot of quinoline iodine bromide in cell "D" in 168 g/l NH_4Br electrolyte at 0.05 amp/g

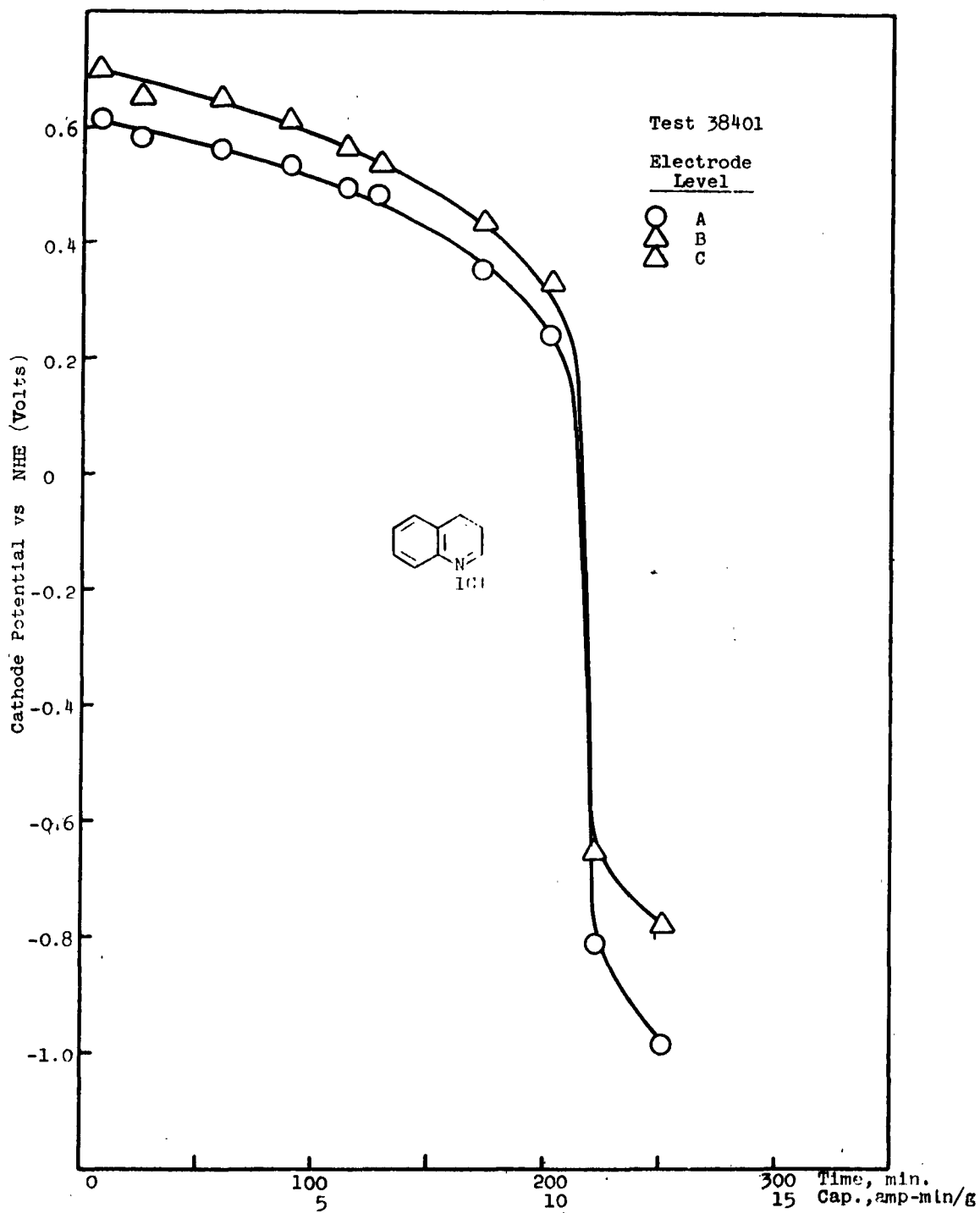


Figure 17 Chronopotentiometric plot of quinoline iodine chloride in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g

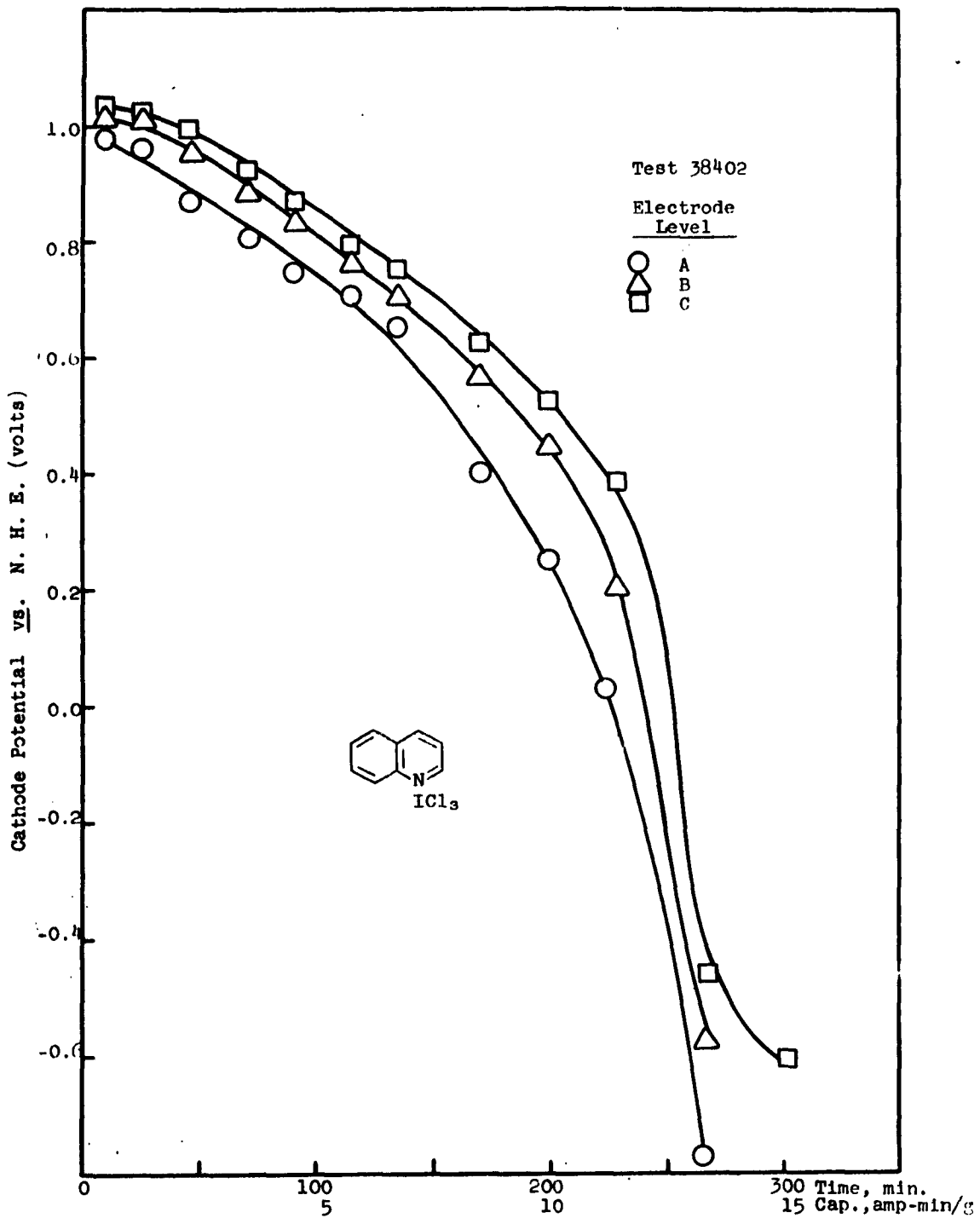


Figure 18 Chronopotentiometric plot of quinoline iodine trichloride (Sample A) in cell "D" in 168 g/l electrolyte at 0.05 amp/g

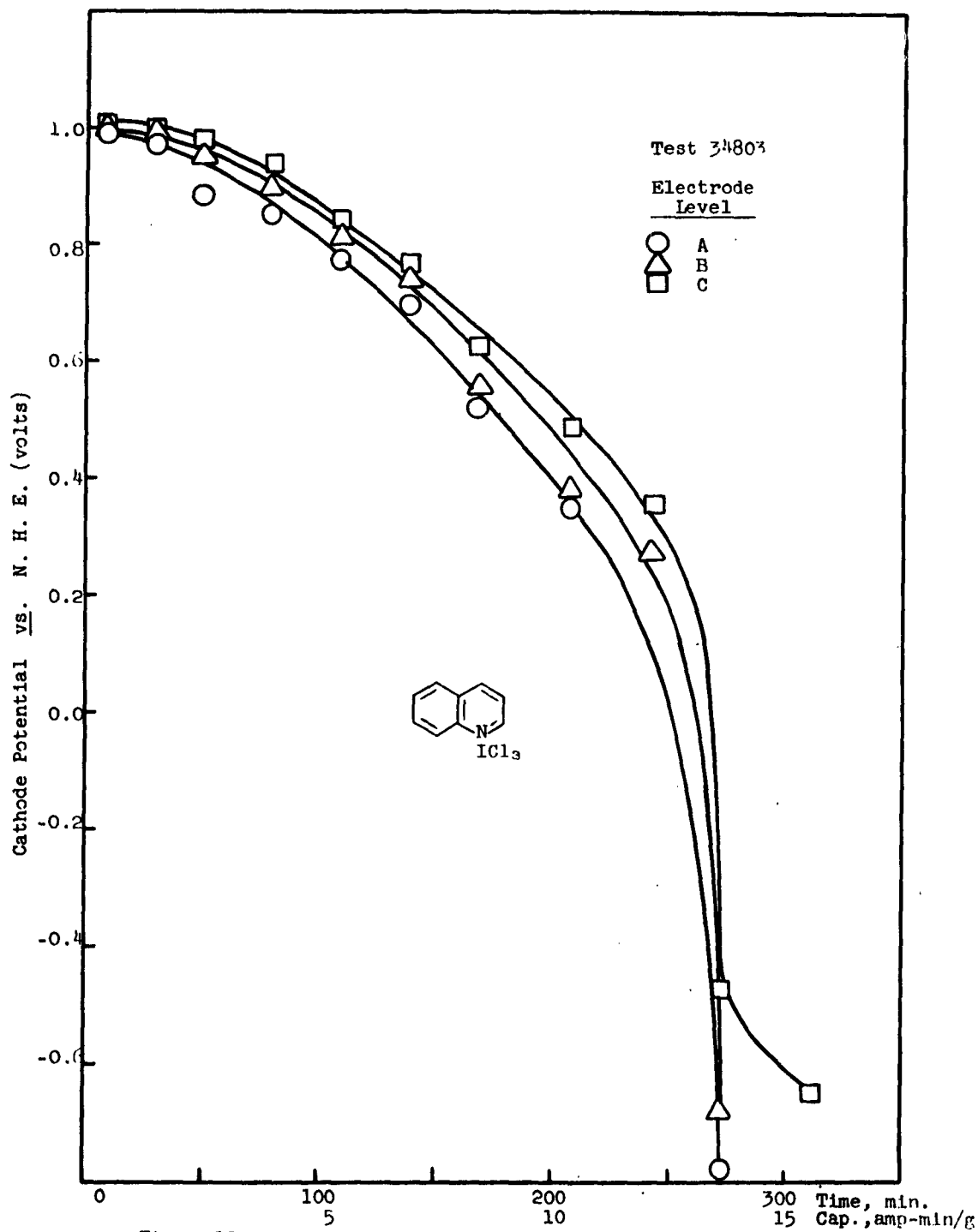


Figure 19 Chronopotentiometric plot of quinoline iodine tri-chloride (Sample B) in cell "D" in 168 g/l NH_4Br electrolyte at 0.05 amp/g

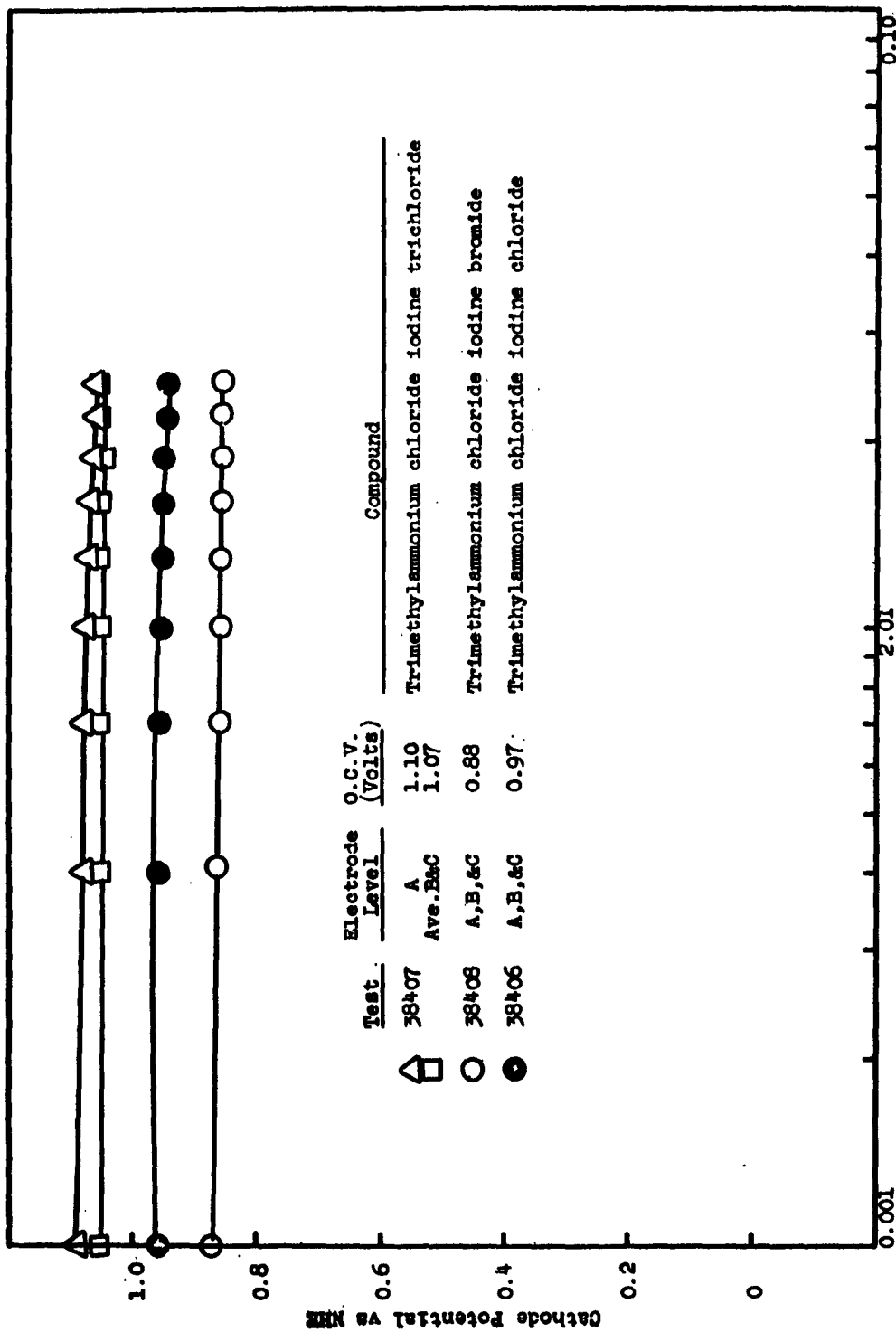


Figure 20 Voltage-current relationship of 0.5 g. samples of addition compounds of trimethylammonium chloride with iodine bromide in cell "D" in 169 g/l NH₄Br to 0.025 amps.

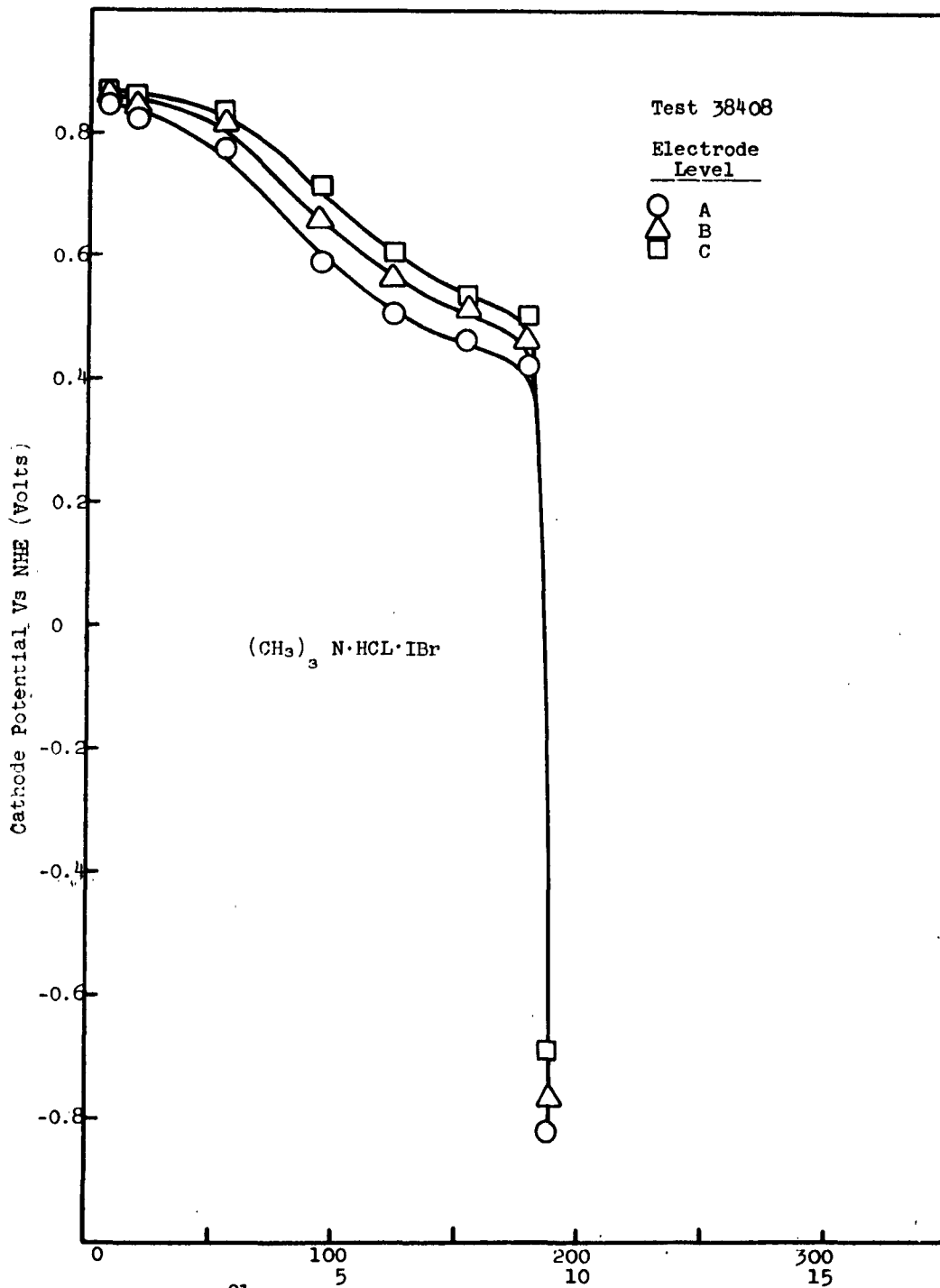


Figure 21 Chronopotentiometric plot of trimethylammonium chloride iodine bromide in cell "D" in 168 g/l NH_4Br electrolyte at 0.05 amp/g.

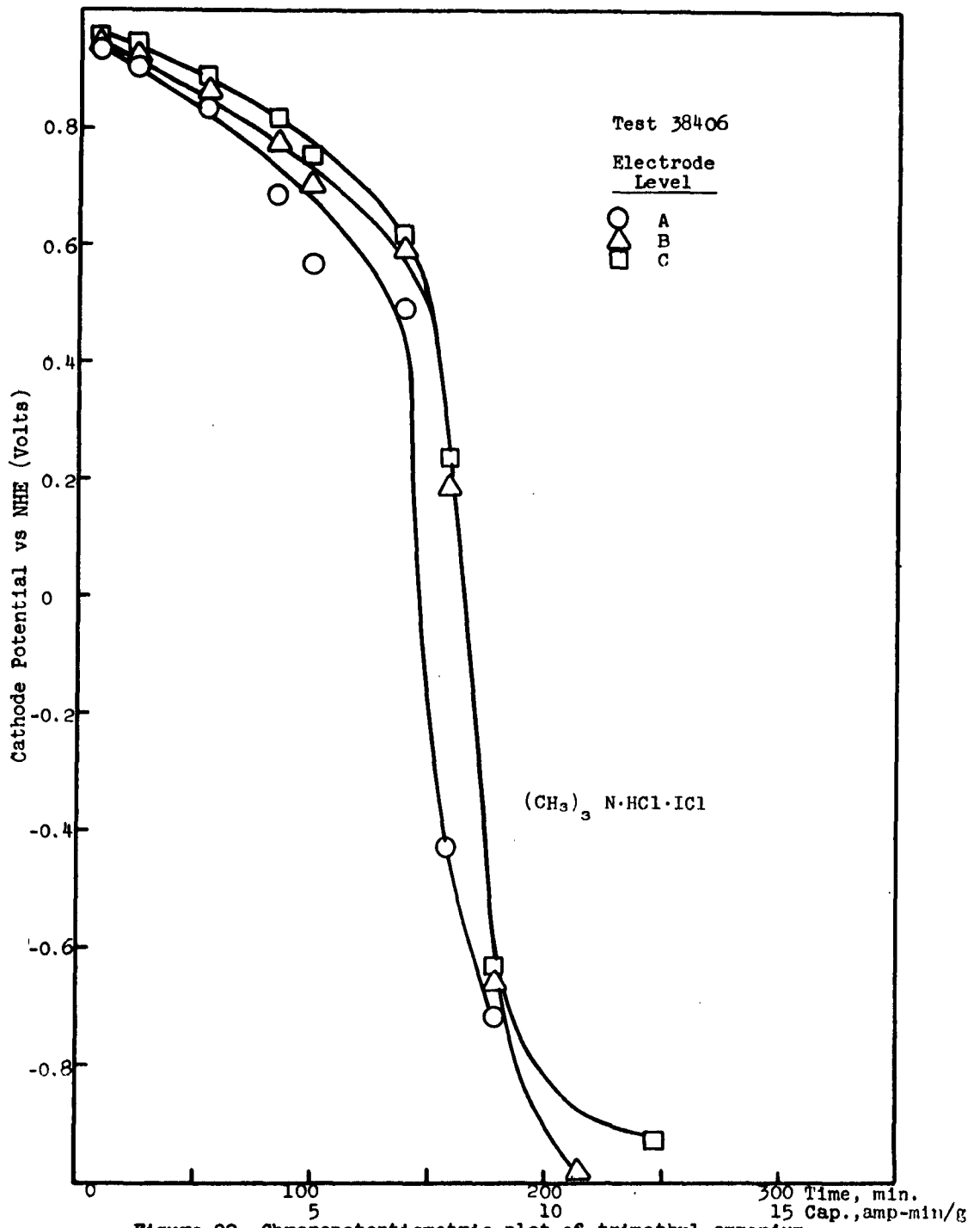


Figure 22 Chronopotentiometric plot of trimethyl ammonium chloride iodine chloride in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

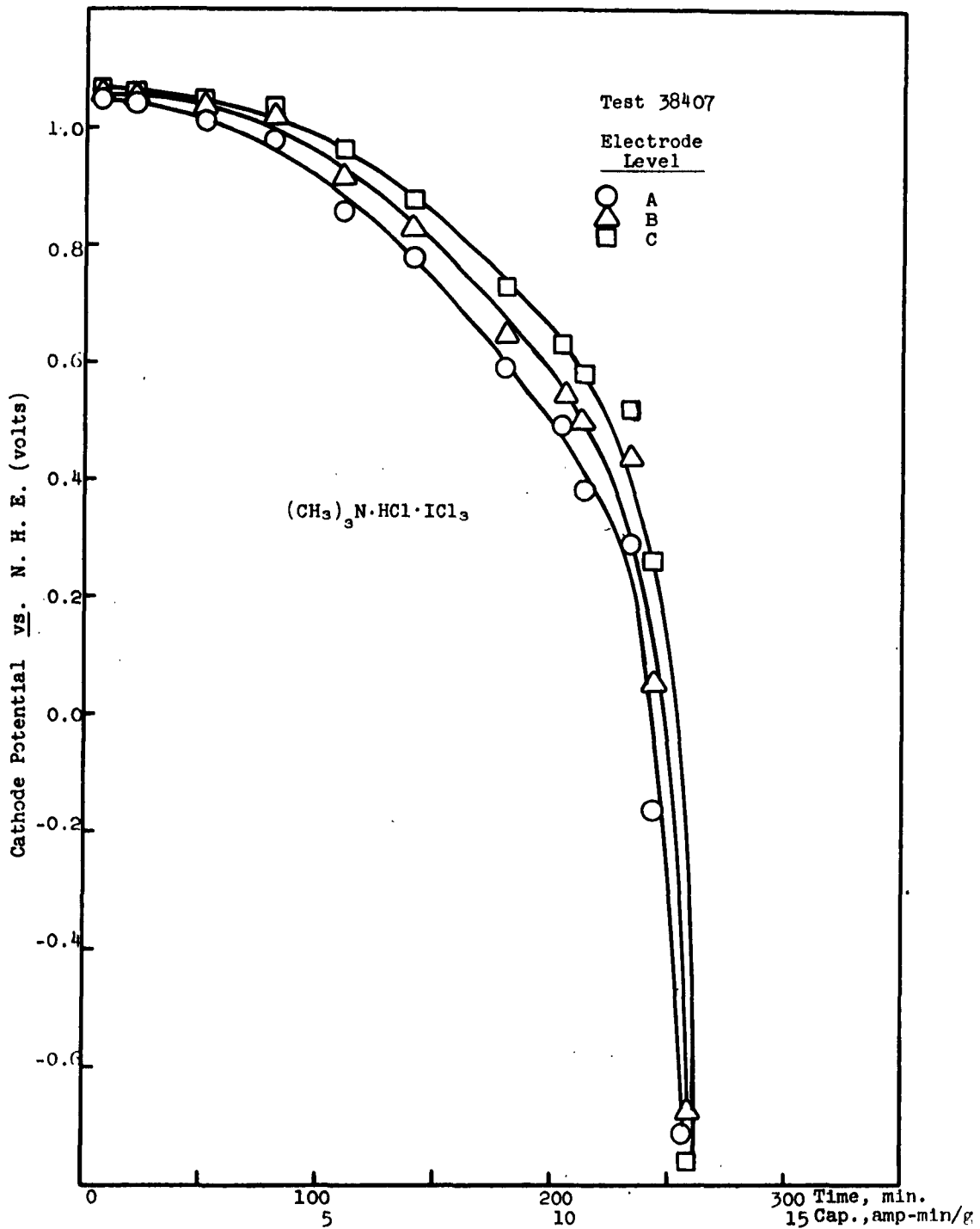


Figure 23 Chronopotentiometric plot of trimethylammonium chloride iodine trichloride in cell "D" in 168 g/l NH_4Br electrolyte at 0.05 amp/g.

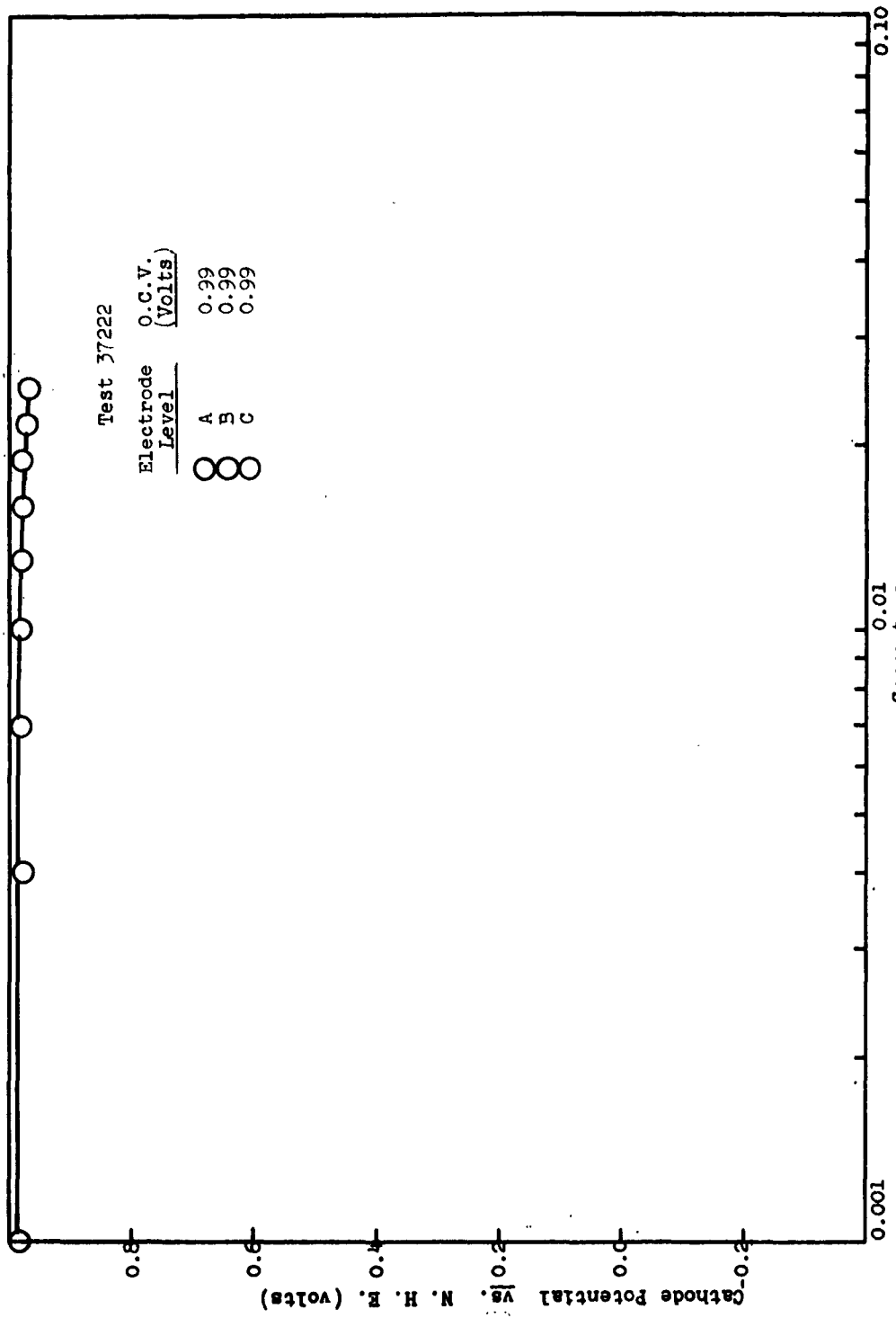


Figure 24 Voltage-current relationship of 0.5 g. sample of quinolinium chloride perbromide in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

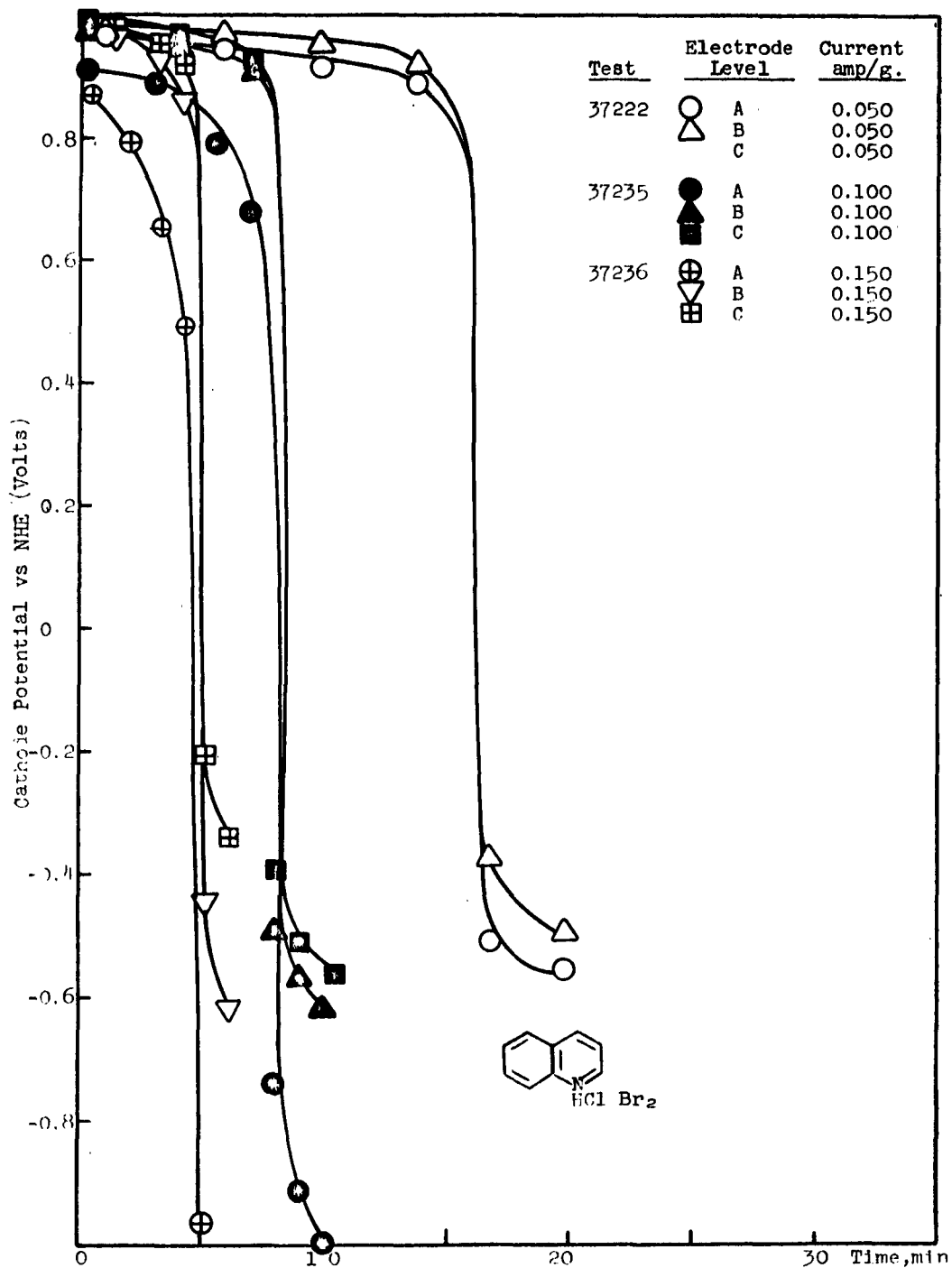


Figure 25 Chronopotentiometric plots of quinolinium chloride in cell "D" in 163 g/l NH₄Br electrolyte at 0.050, 0.100 and 0.150 amp./g.

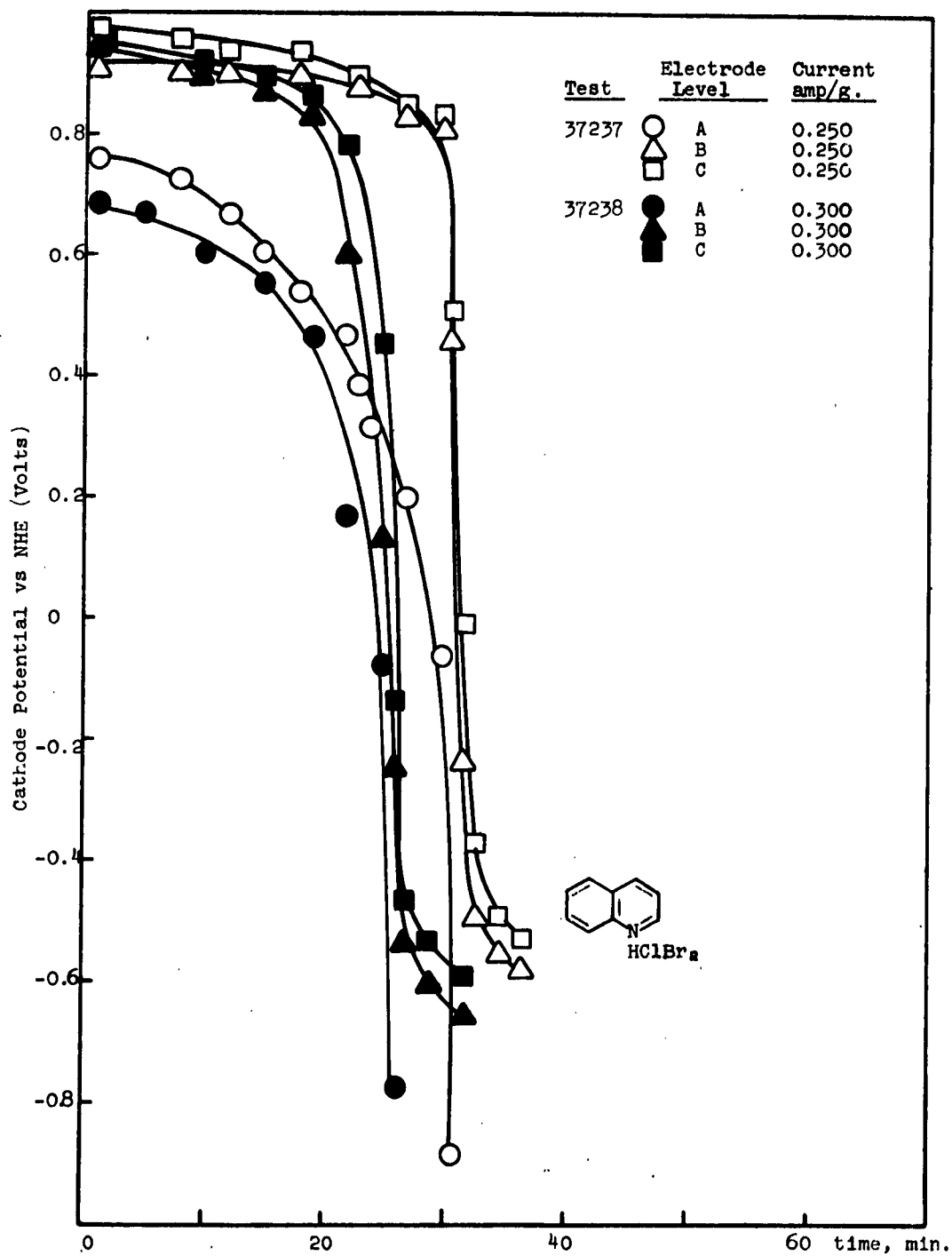


Figure 26 Chronopotentiometric plots of quinolinium chloride perbromide in cell "D" in 168 g/l NH₄Br at 0.250 and 0.300 amp/g.

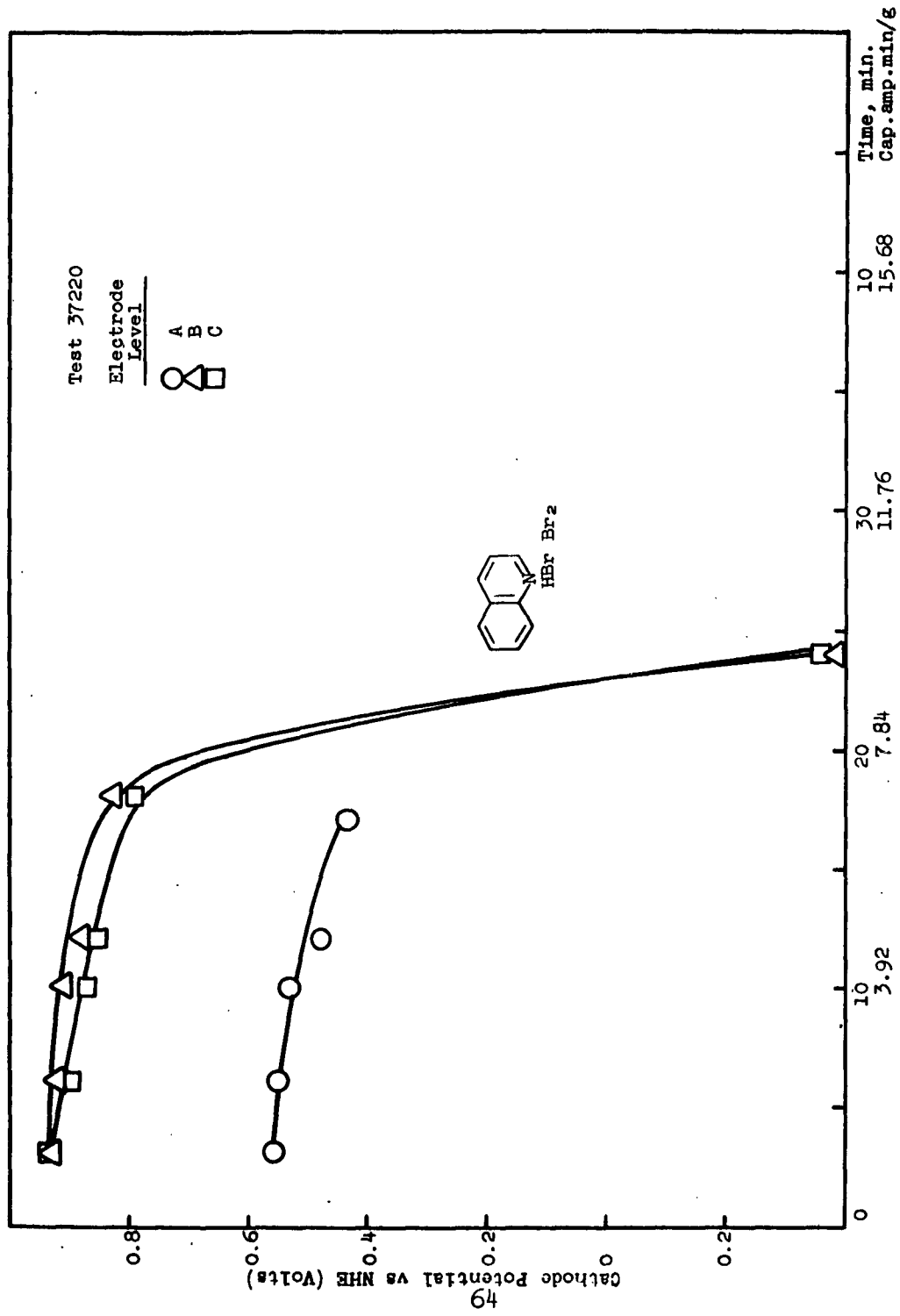


Figure 29 Chronopotentiometric plots of quinolinium bromide perbromide in cell "D" in 250 g/l MgBr₂·6H₂O at 0.392 amp/g.

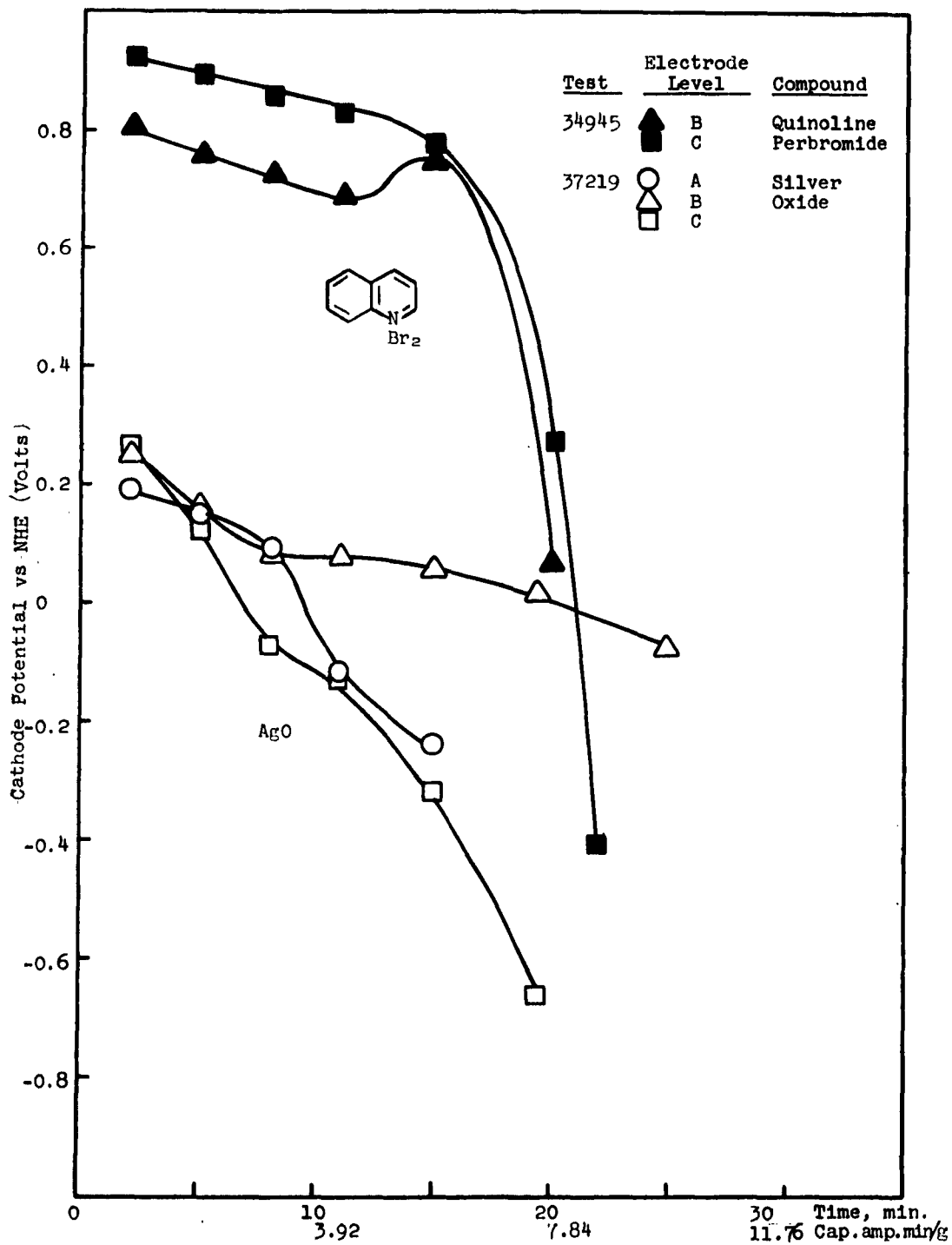


Figure 30 Chronopotentiometric plots of quinoline perbromide and silver oxide in cell "D" in 168 g/l NH_4Br electrolyte at 0.392 amp/g.

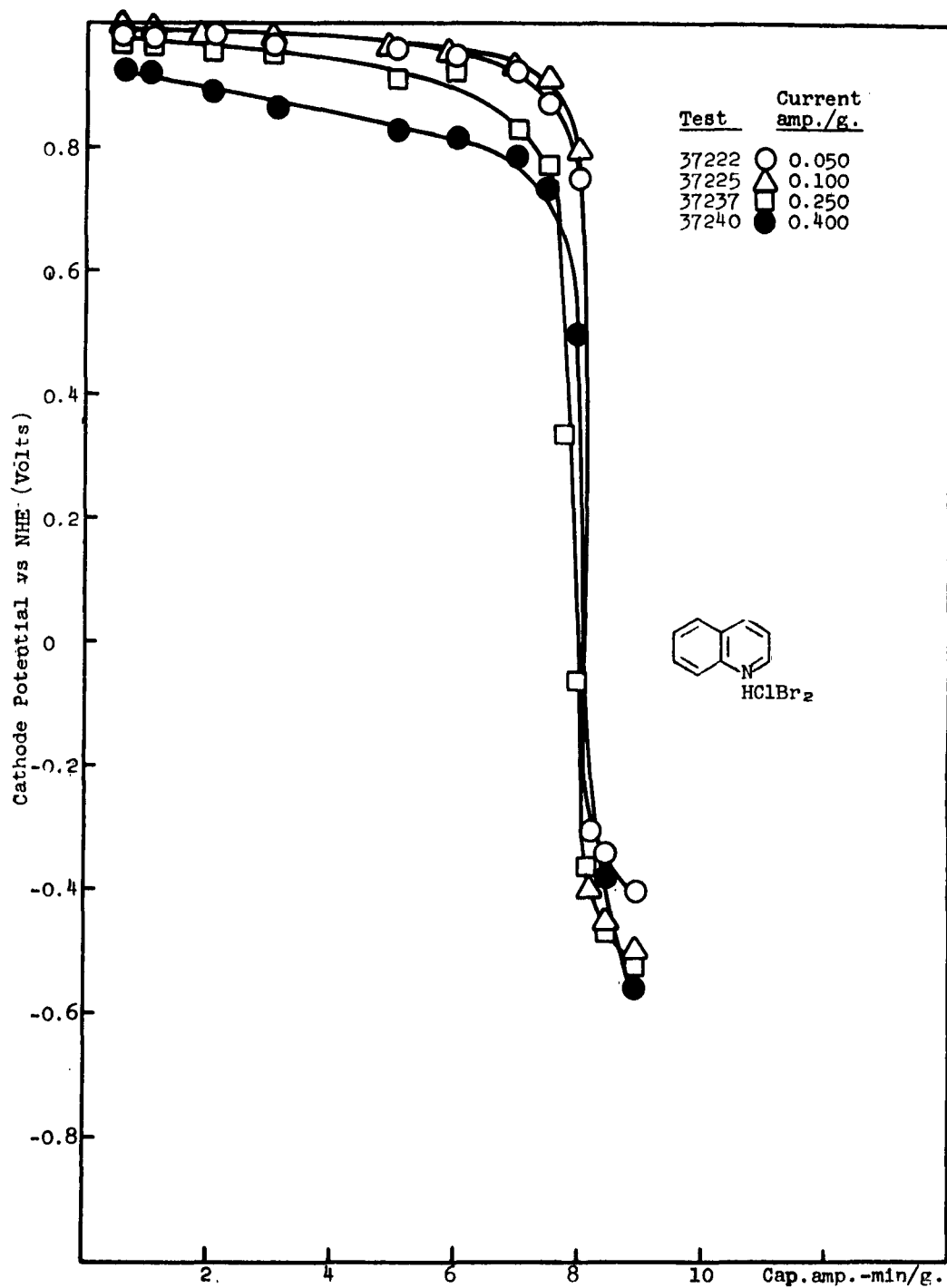


Figure 31 Effect of increase in current on coulombic capacity of quinolinium chloride perbromide at level C in cell "D" in 168 g/l NH₄Br

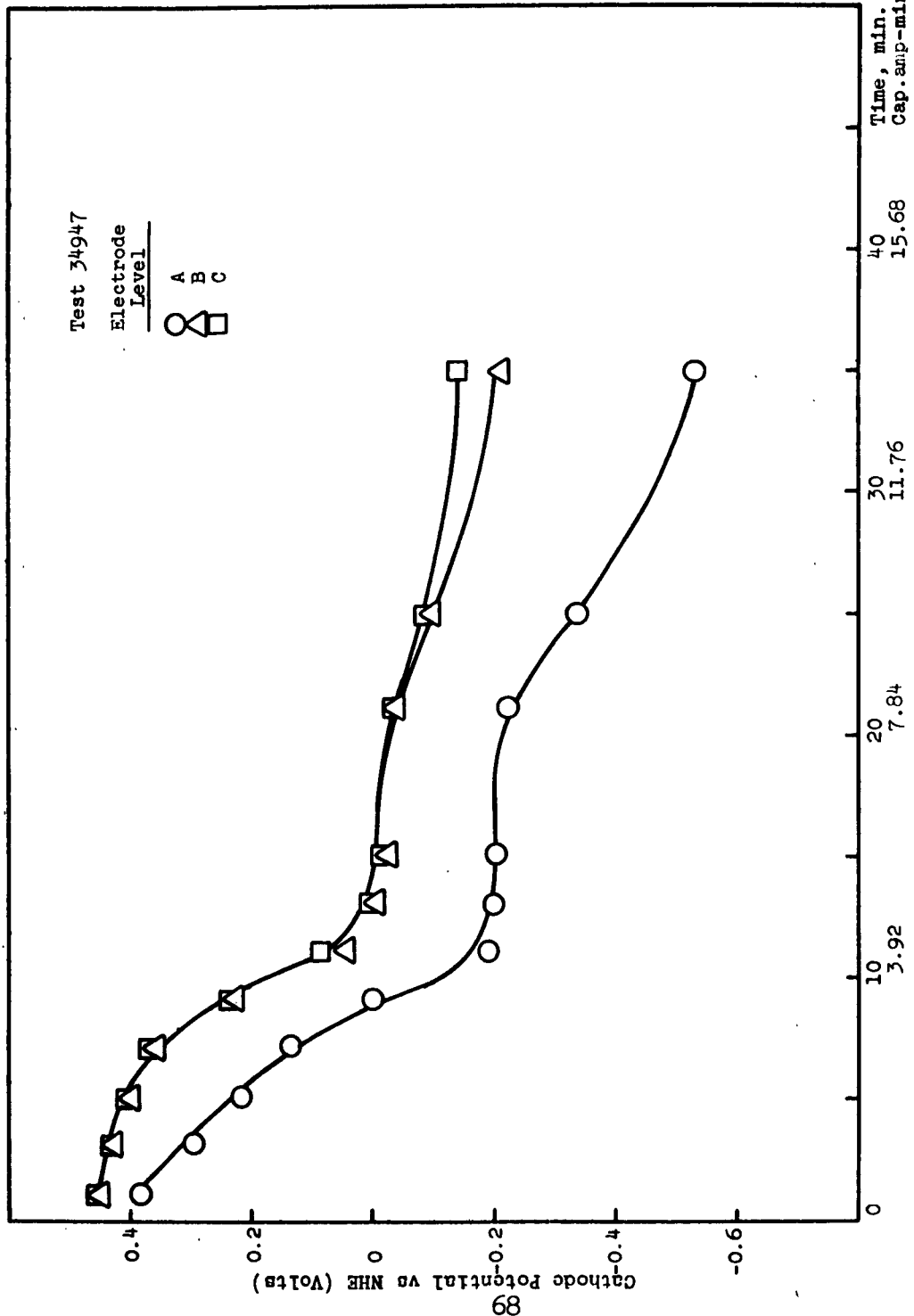


Figure 33 Chronopotentiometric plot of the silver salt of 1,4-dinitropyromellitic acid in cell "D" in 168 g/l NH₄Br at 0.392 amp/g.

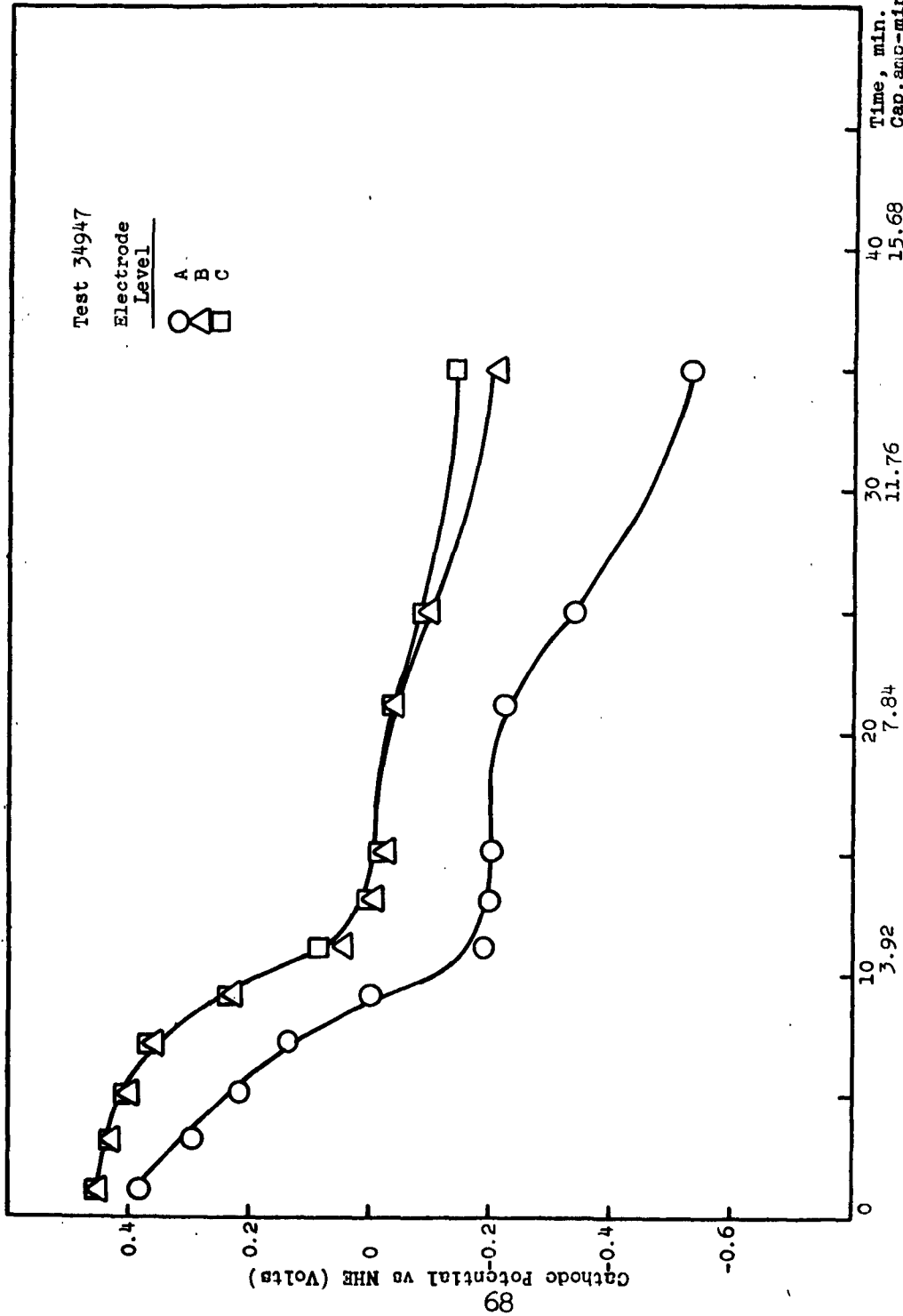


Figure 33 Chronopotentiometric plot of the silver salt of 1,4-dinitropyromellitic acid in cell "D" in 168 g/l NH₄Br at 0.392 amp/g.

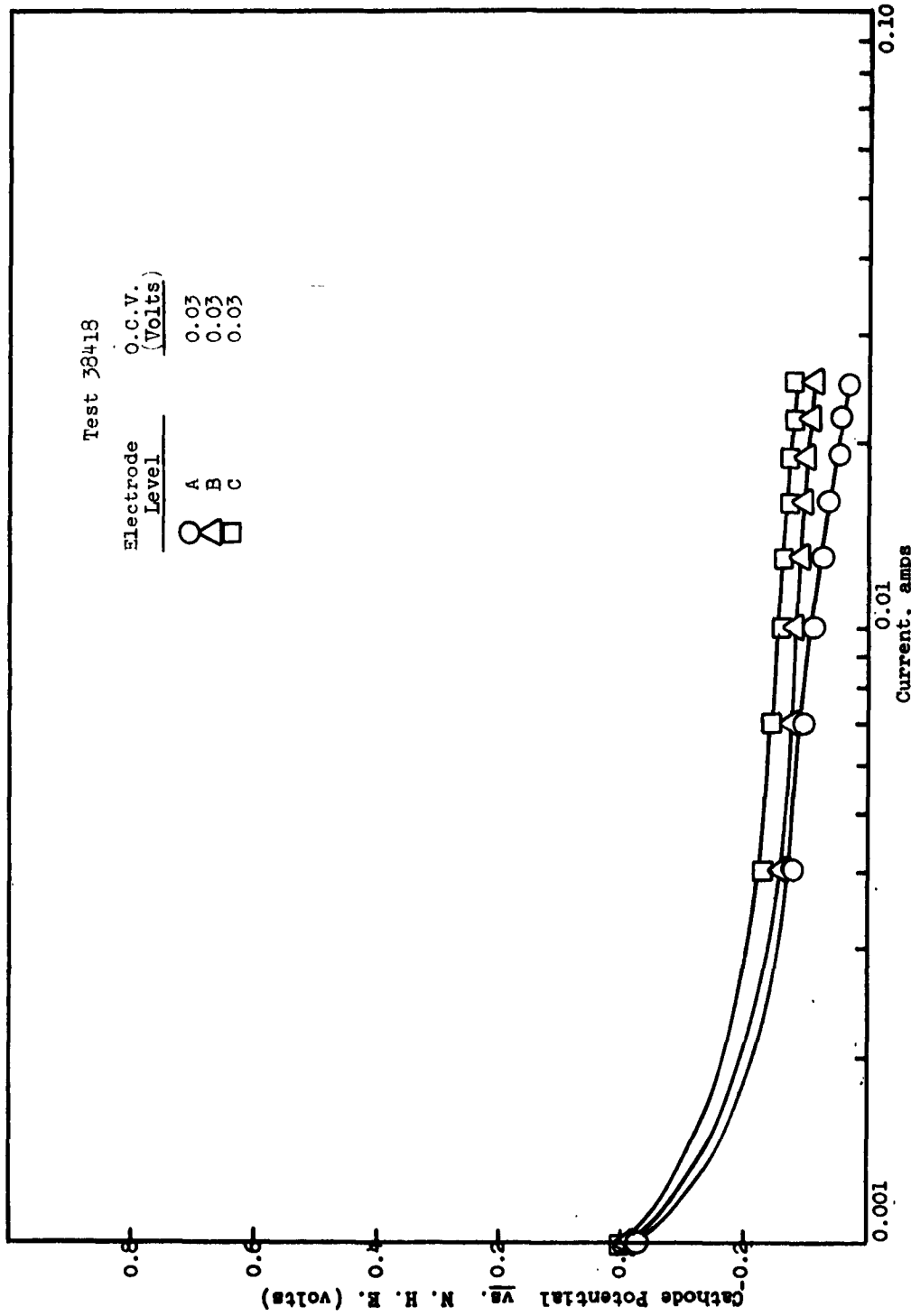


Figure 34 Voltage-current relationship of 0.5 g. sample of sodium p-nitrophenolate in cell "D" 168 g/l NH₄Br electrolyte to 0.025 amps.

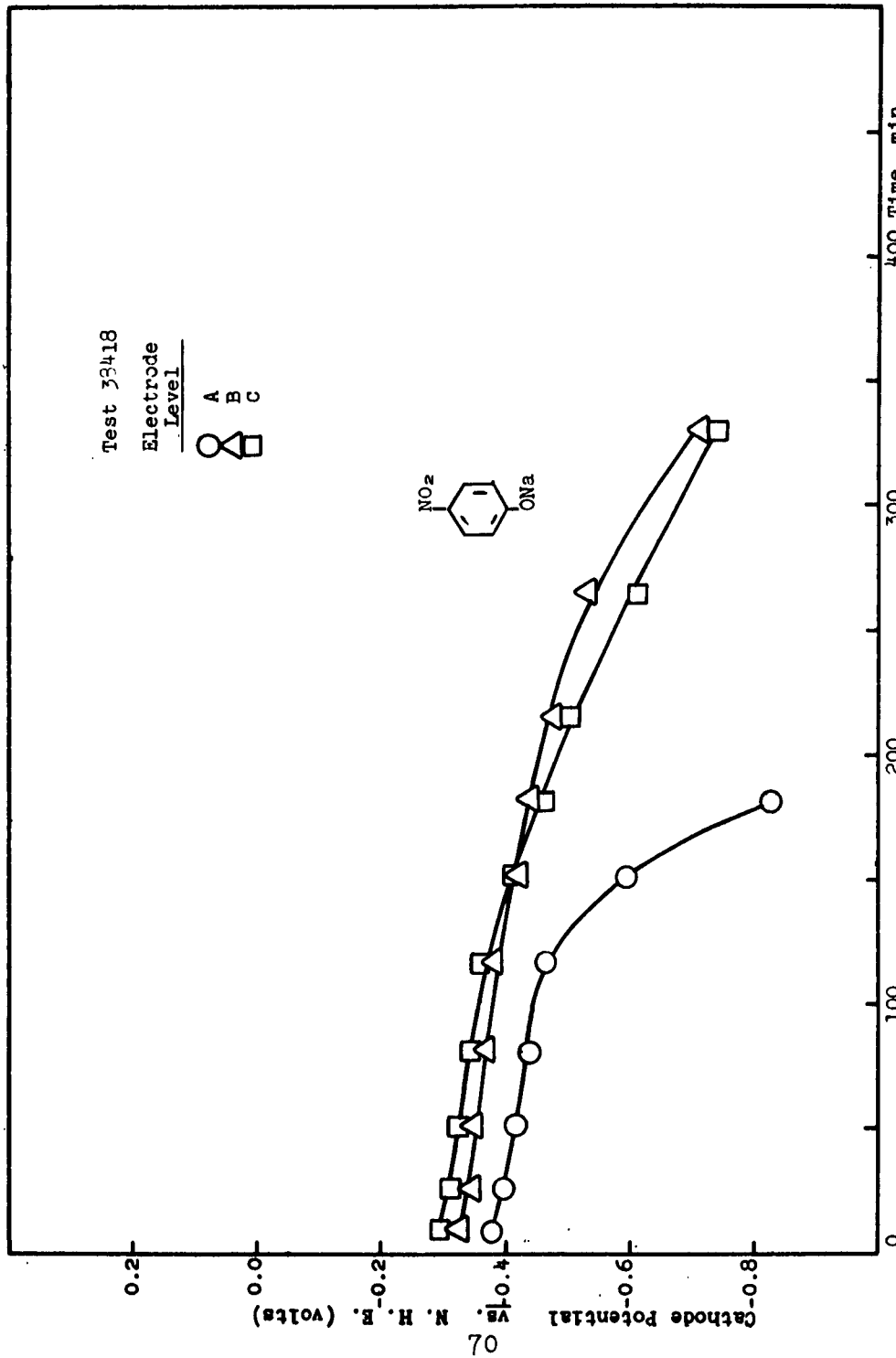


Figure 35 Chronopotentiometric plot of sodium p-nitrophenolate in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

Test 37244

Electrode Level	O.C.V. (Volts)
A	0.06
B	0.07
C	0.07

○
□

○
□

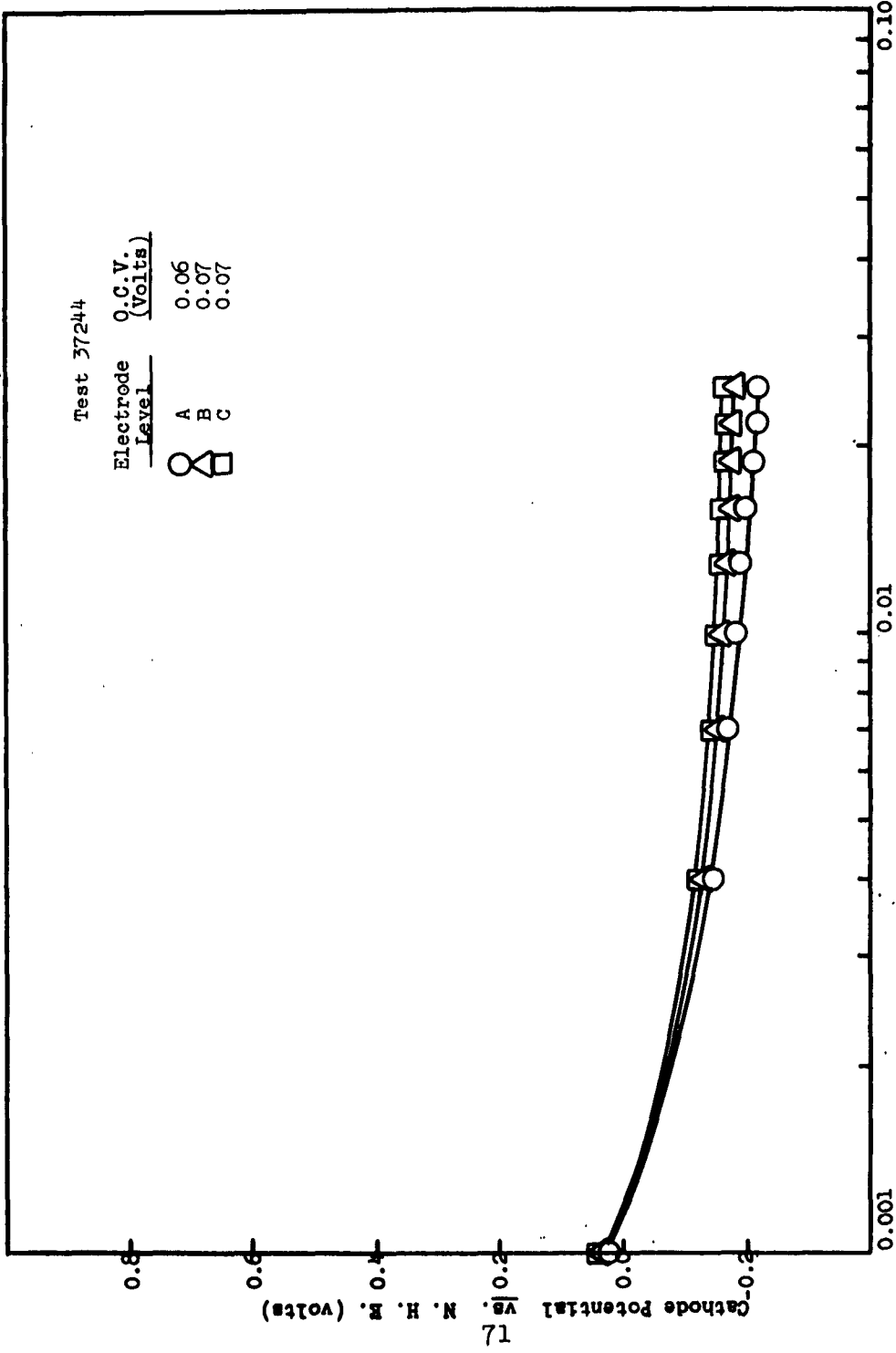


Figure 36 Voltage-current relationship of 0.5 g. sample of p-nitrophenol in cell "D" in 168 g/l NH₄Et electrolyte to 0.025 amps.

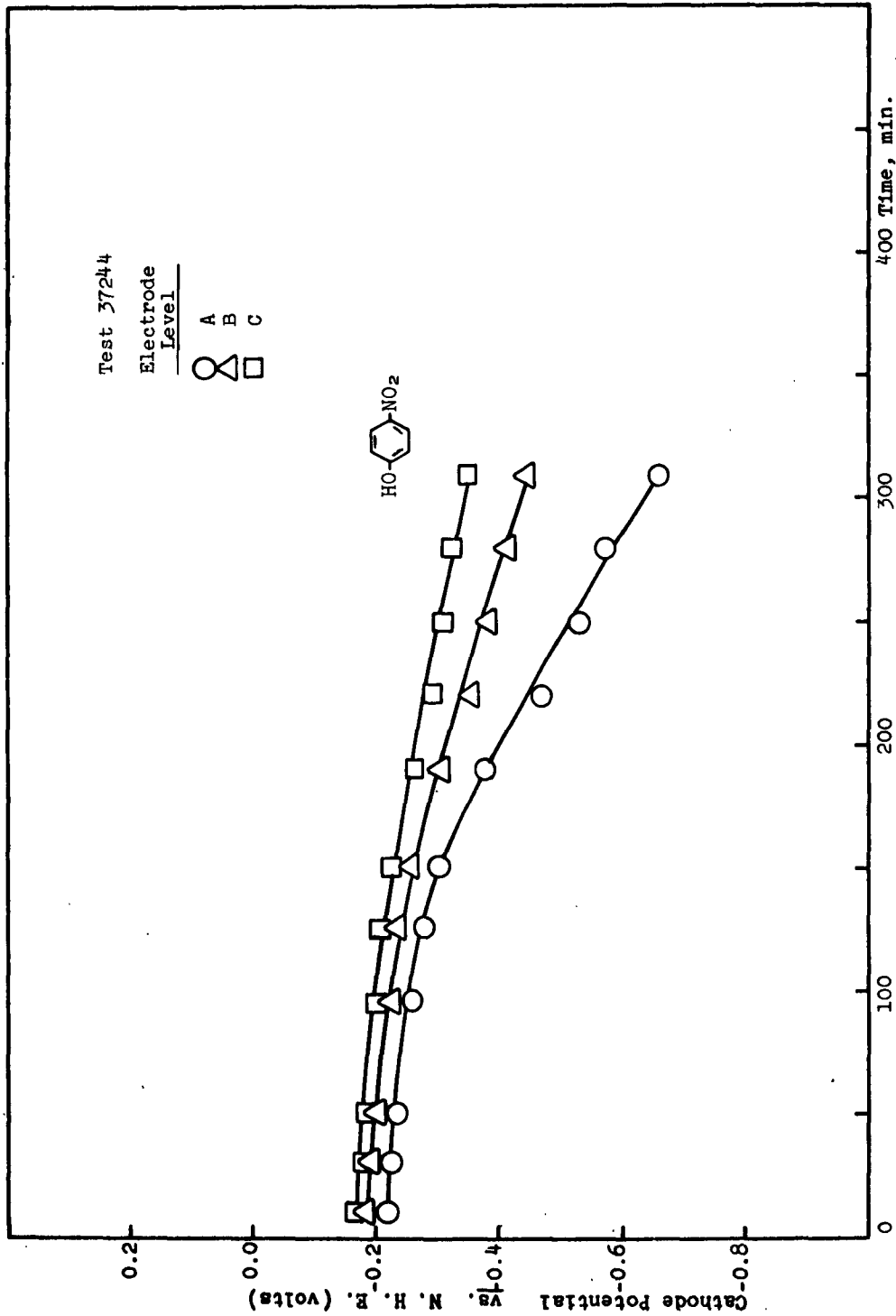


Figure 37 Chronopotentiometric plot of p-nitrophenol in cell "D" in 168 g/l NH₄Br electrolyte at 3.05 amp/g.

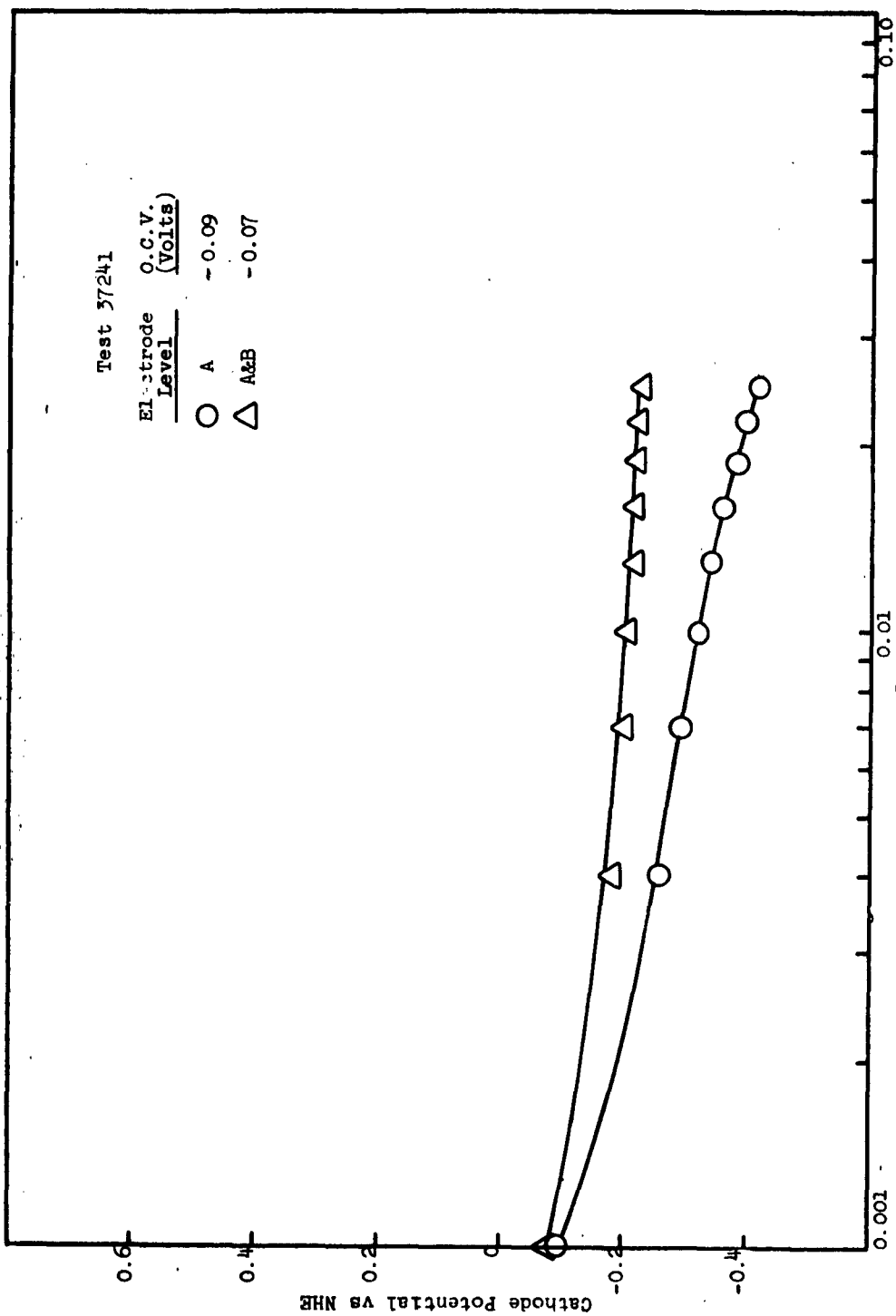


Figure 38 Voltage-current relationship of 0.5 g. sample of nitrobenzene in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

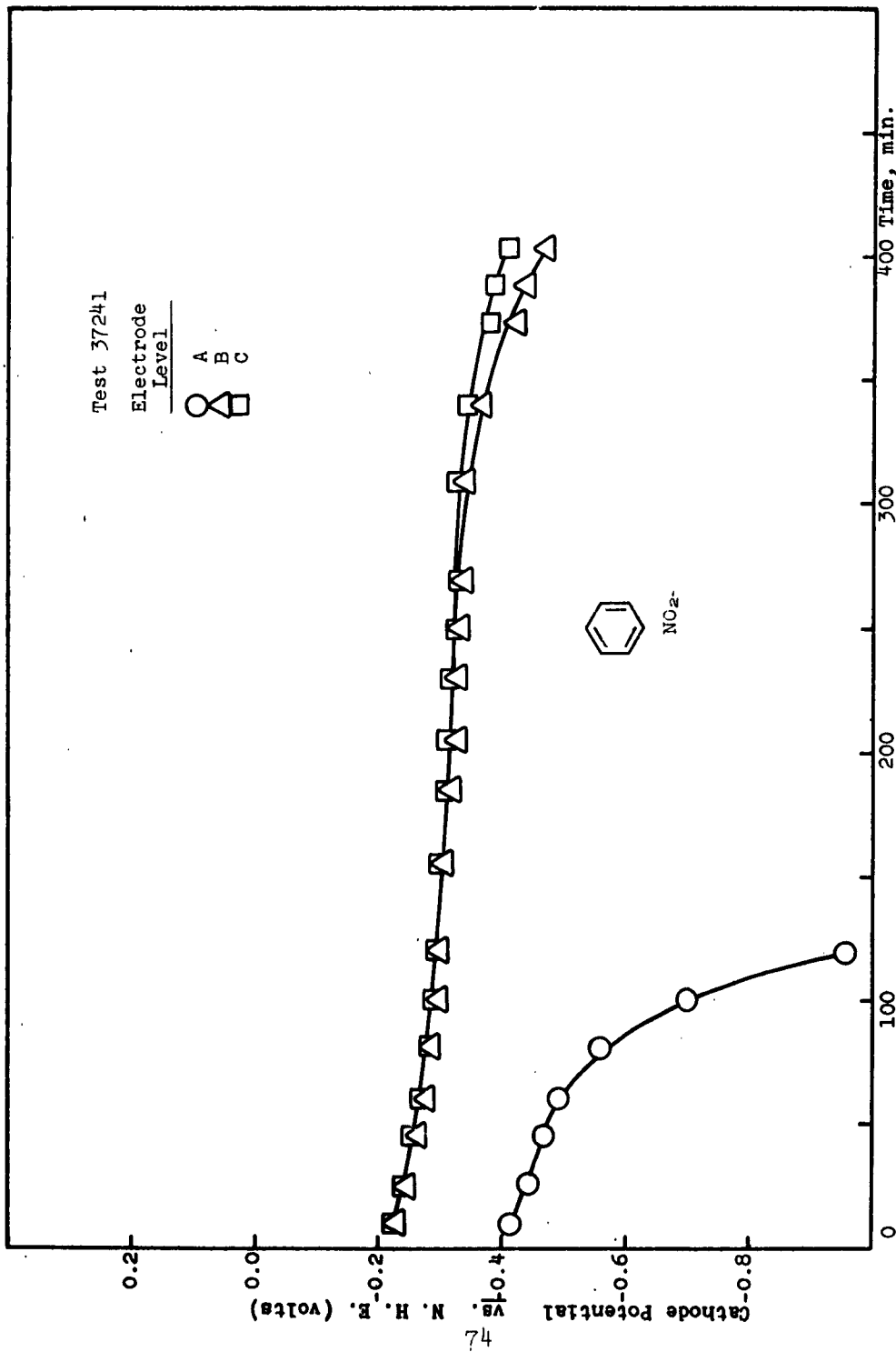


Figure 39 Chronopotentiometric plot of nitrobenzene in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

Test 37245

Electrode Level	Q.C.V. (Volts)
A	-0.04
B	-0.03
C	-0.01

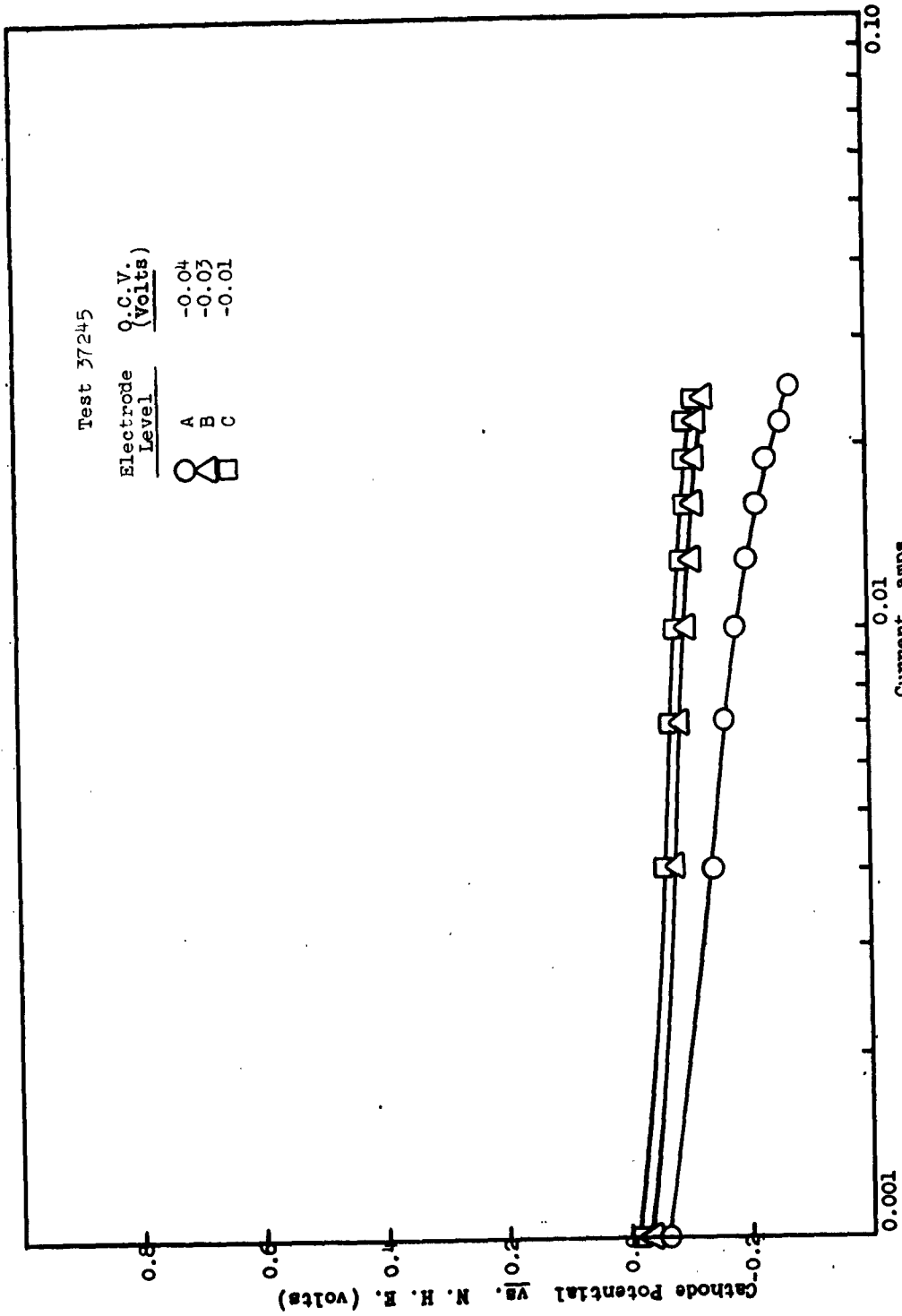


Figure 40 Voltage-current relationship of 0.5 g. sample of p-nitrobenzotrile in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

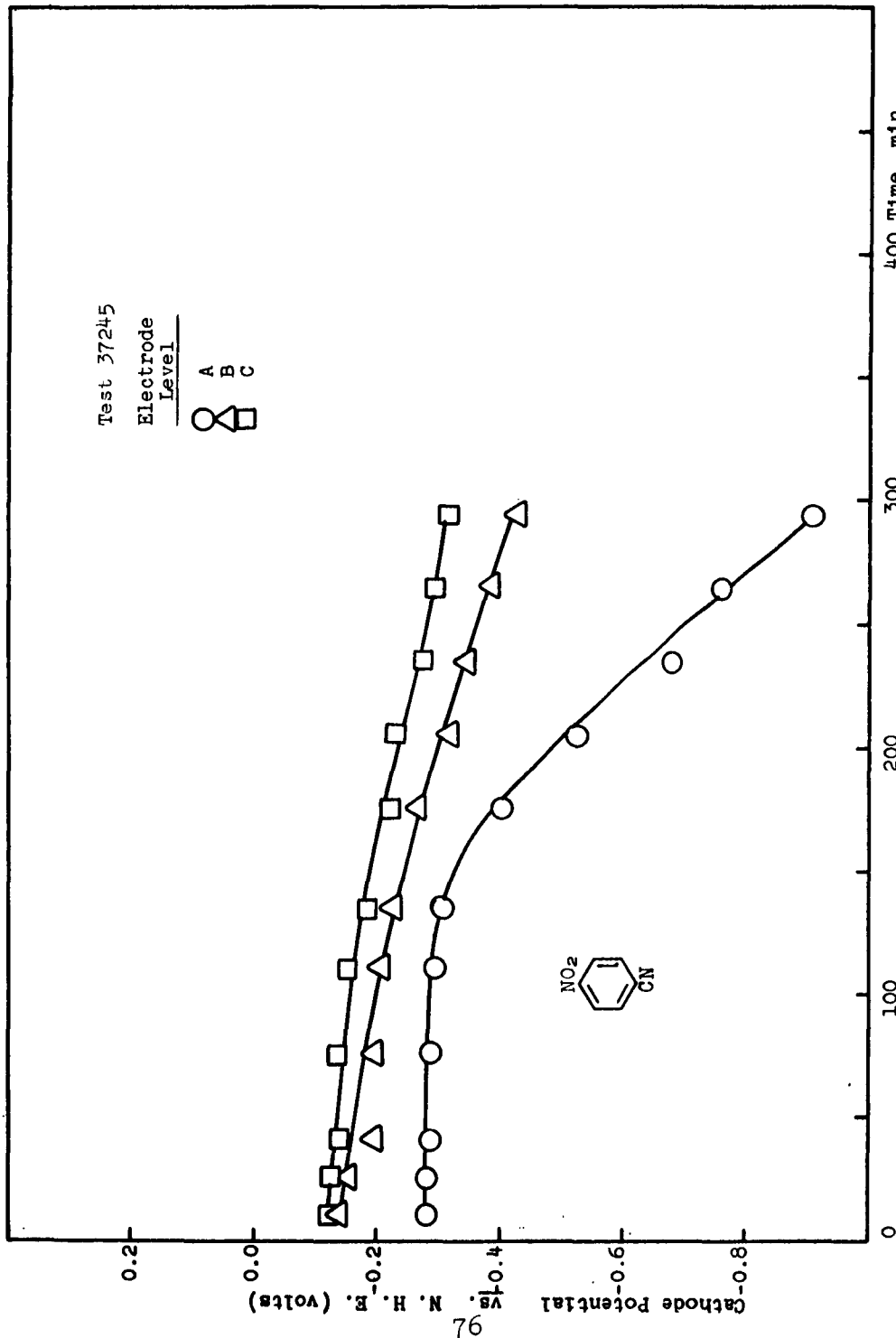


Figure 41 Chronopotentiometric plot of p-nitrobenzonitrile in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

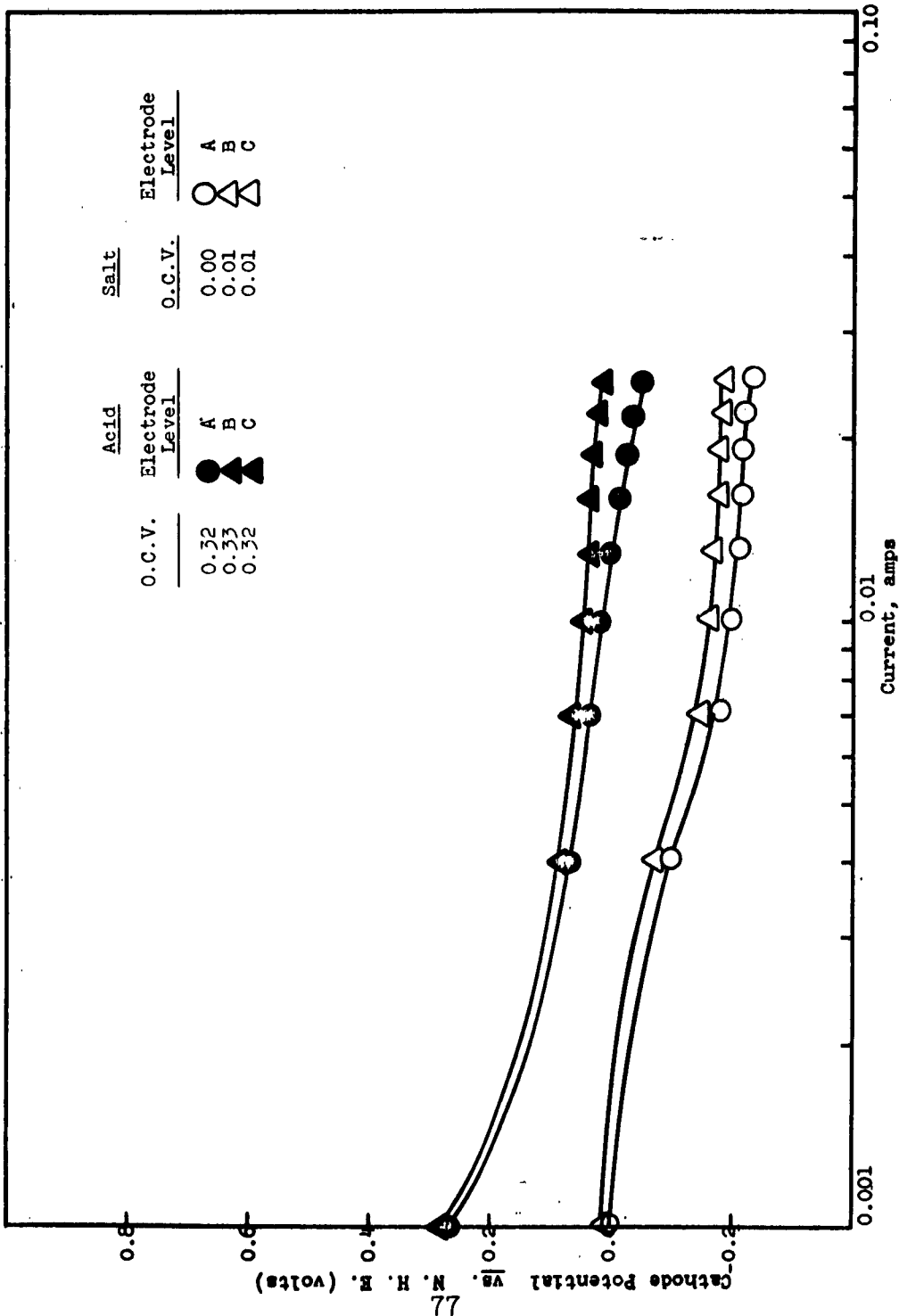


Figure 42 Voltage-current relationships of 0.5 g. sample of o-nitrobenzoic acid and sodium o-nitrobenzoate in cell D^{10} in 168 g/l NH_4Br electrolyte to 0.025 amps.

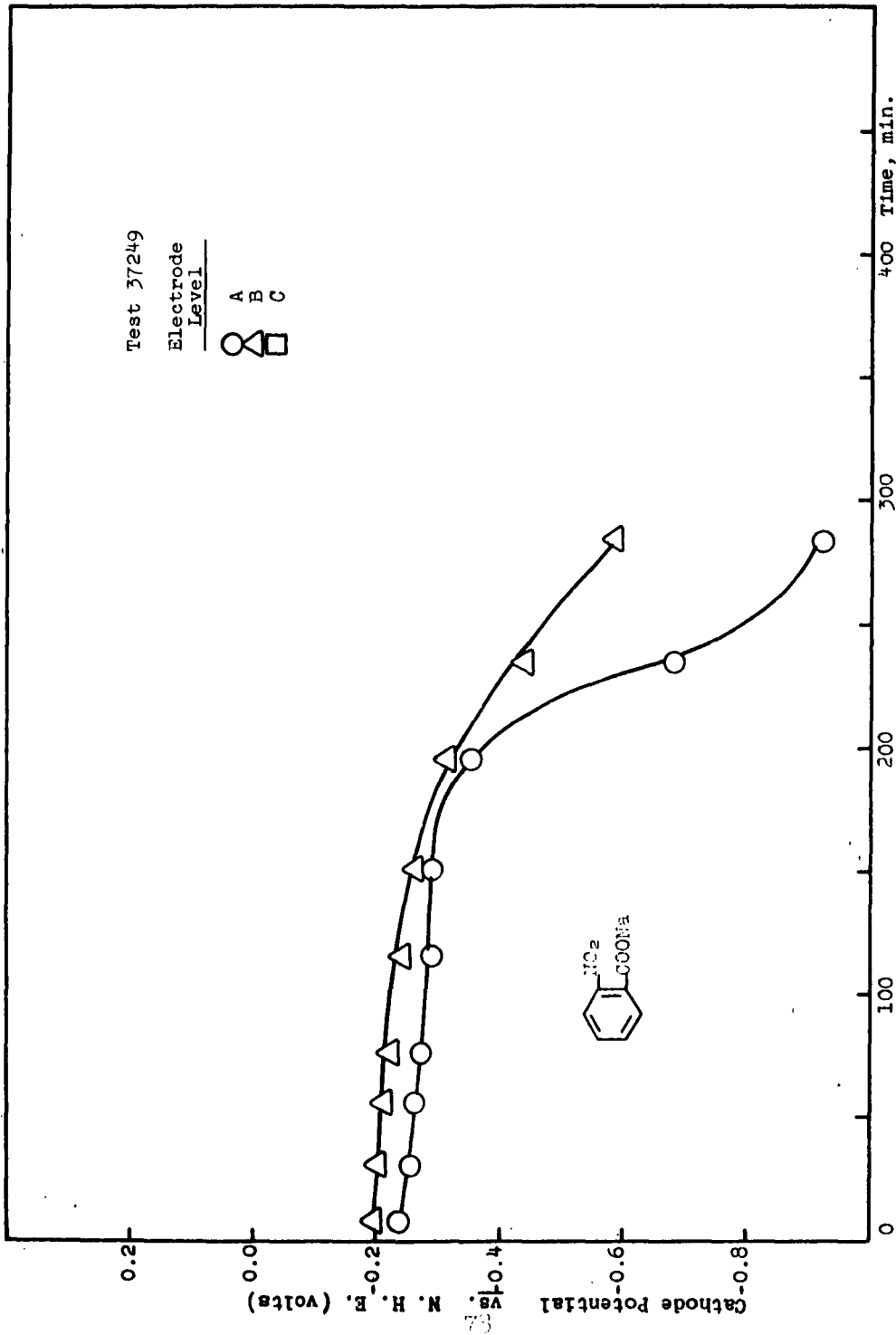


Figure 43 Chronopotentiometric plot of sodium o-nitrobenzoate in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g

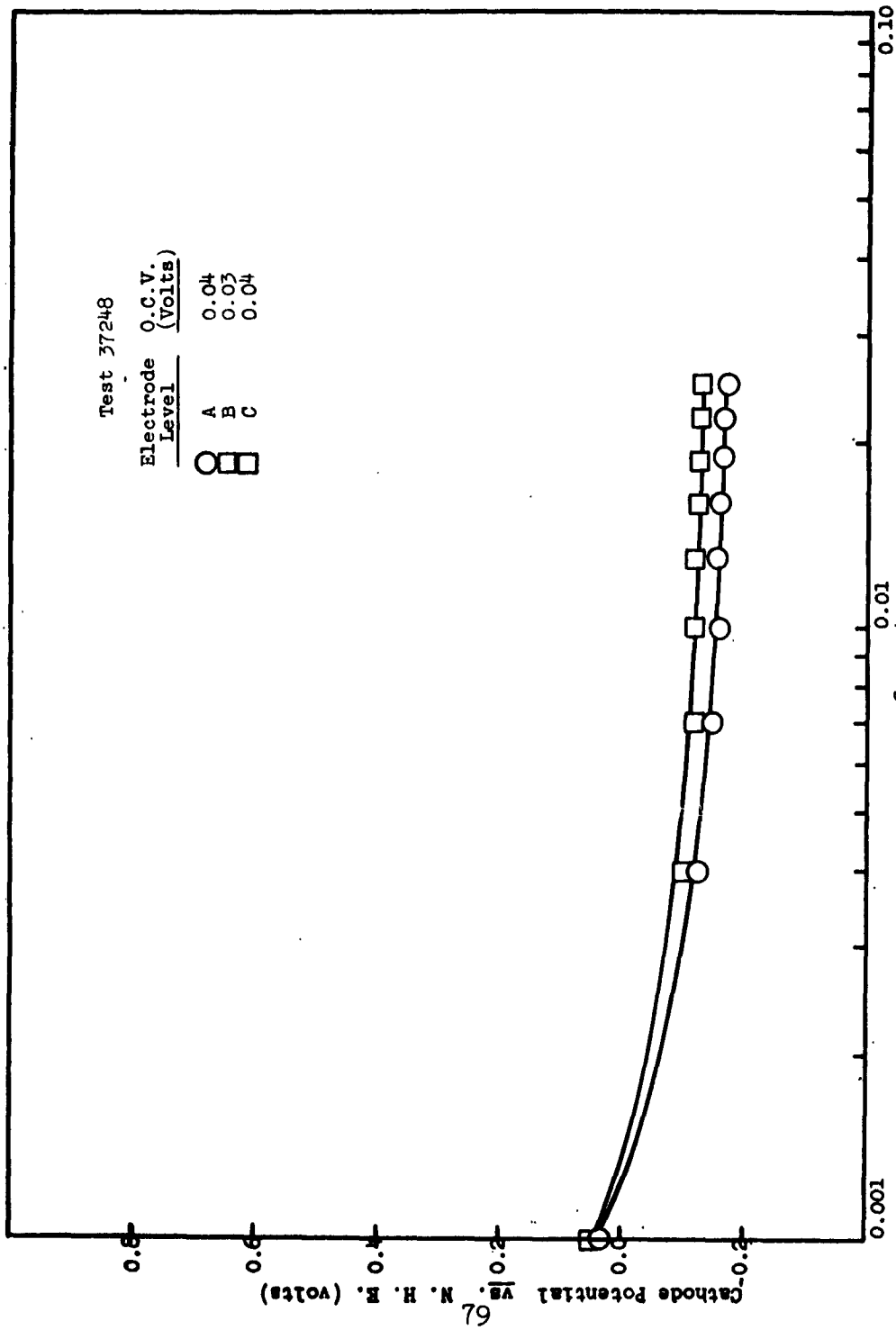


Figure 44 Voltage-current relationship of 0.5 g. sample of disodium nitroterephthalate in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

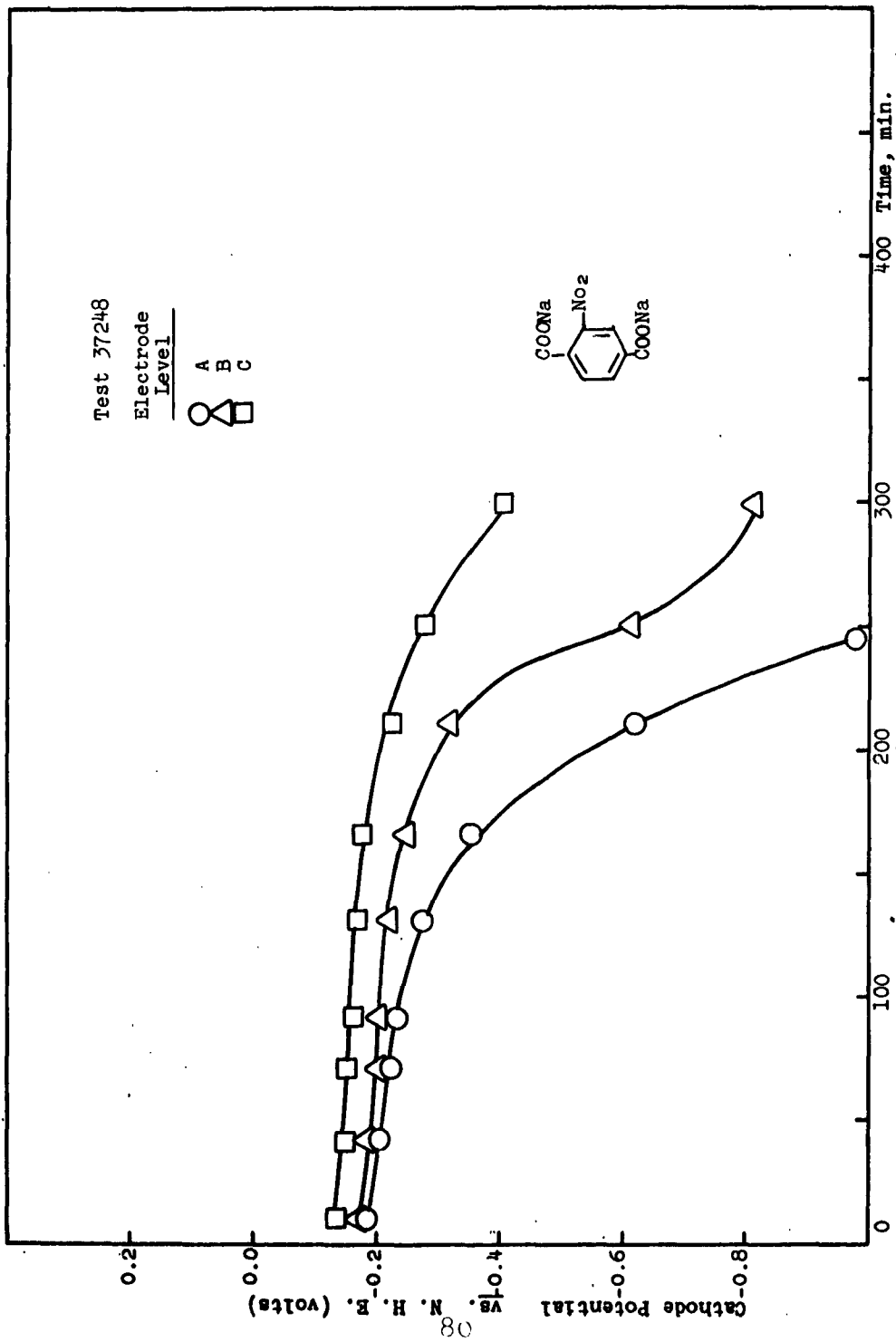


Figure 45 Chronopotentiometric plot of disodium nitroterephthalate in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

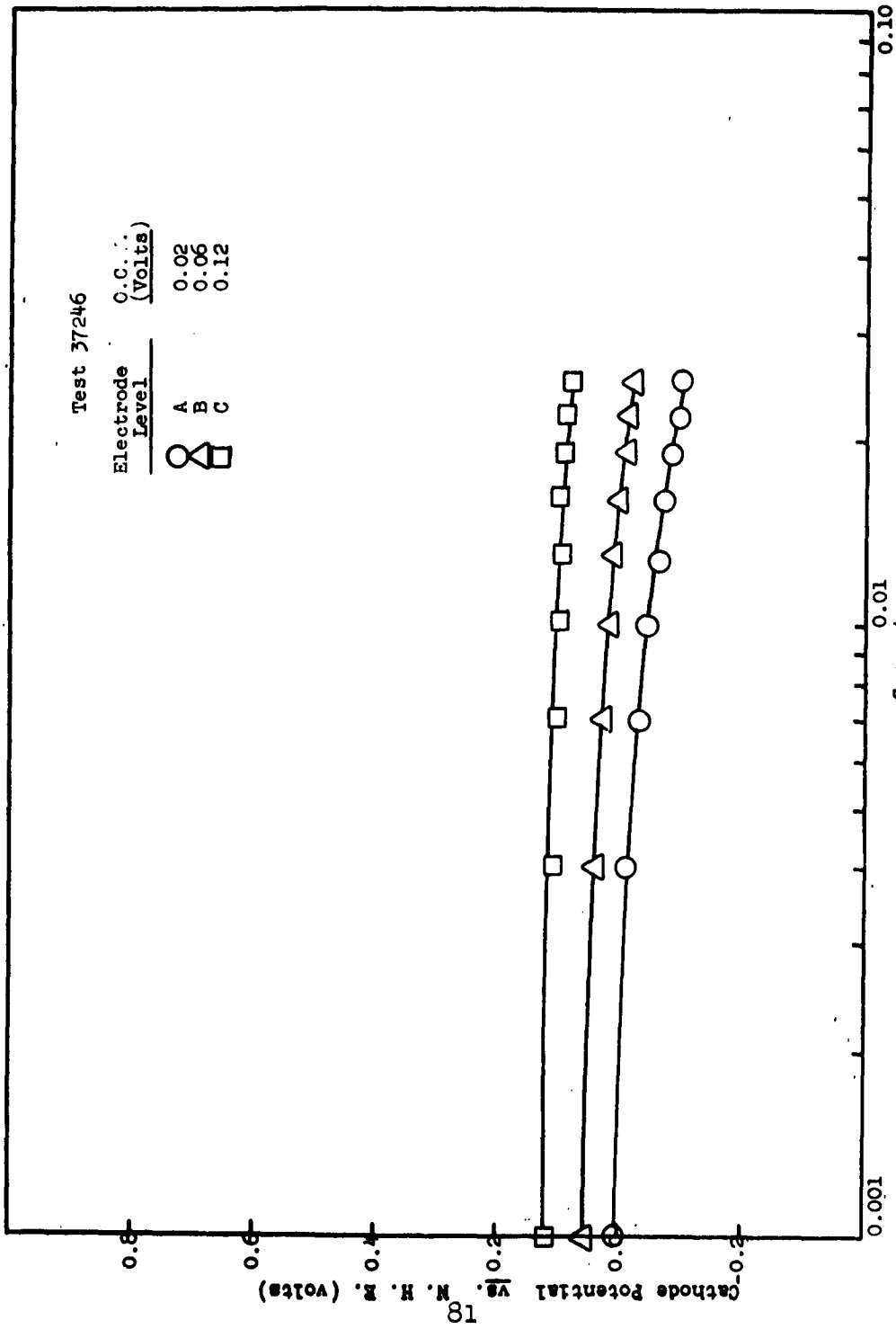


Figure 46 Voltage-current relationship of 0.5 g. sample of p-Dinitrobenzene in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

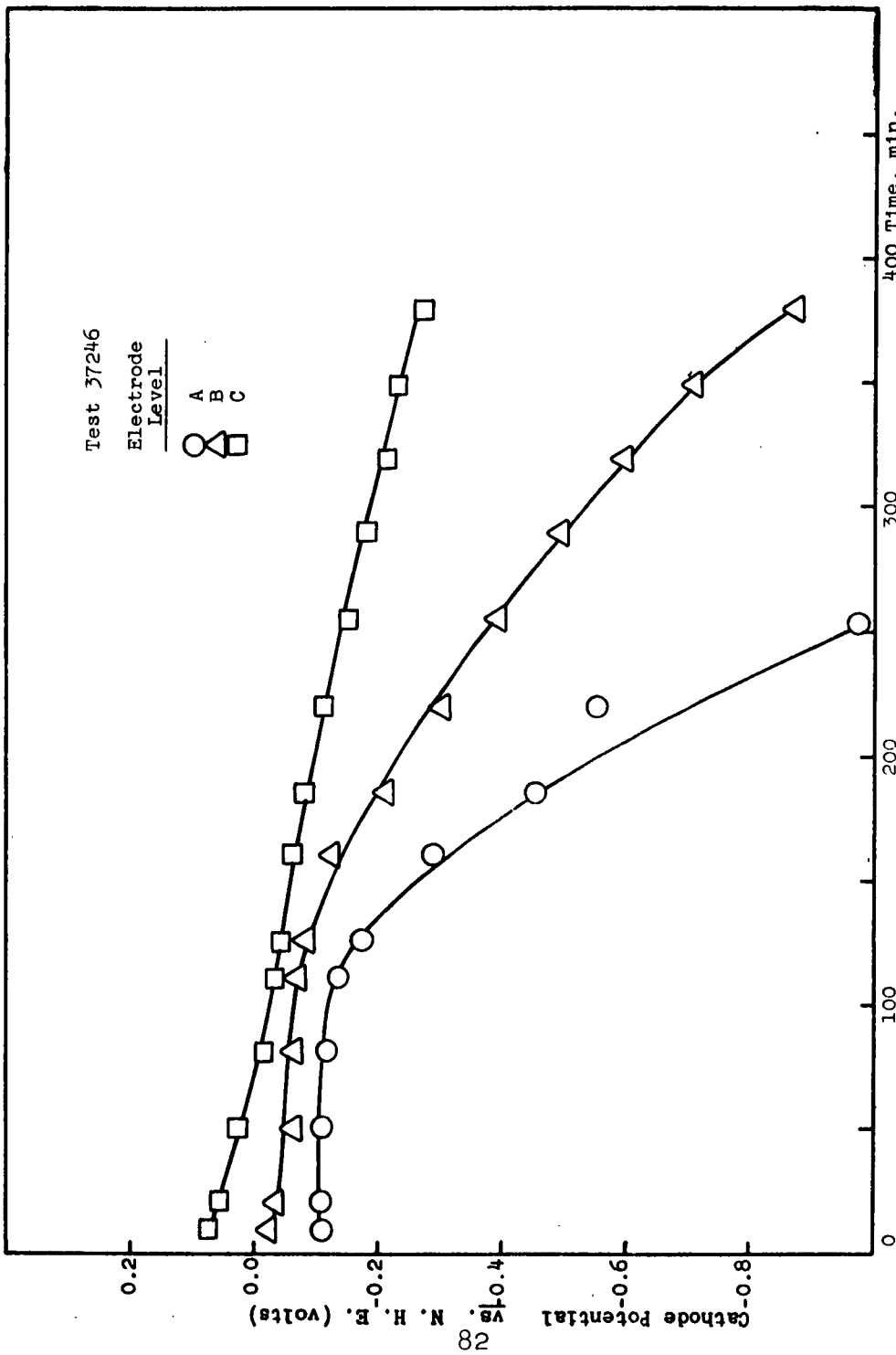


Figure 47 Chronopotentiometric plot of p-dinitrobenzene in cell "D" in 168 g/l NH_4Br electrolyte at 0.05 amp/g.

Test 37225

Electrode Level	O.C.V. (Volts)
A	0.18
B	0.19
C	0.19

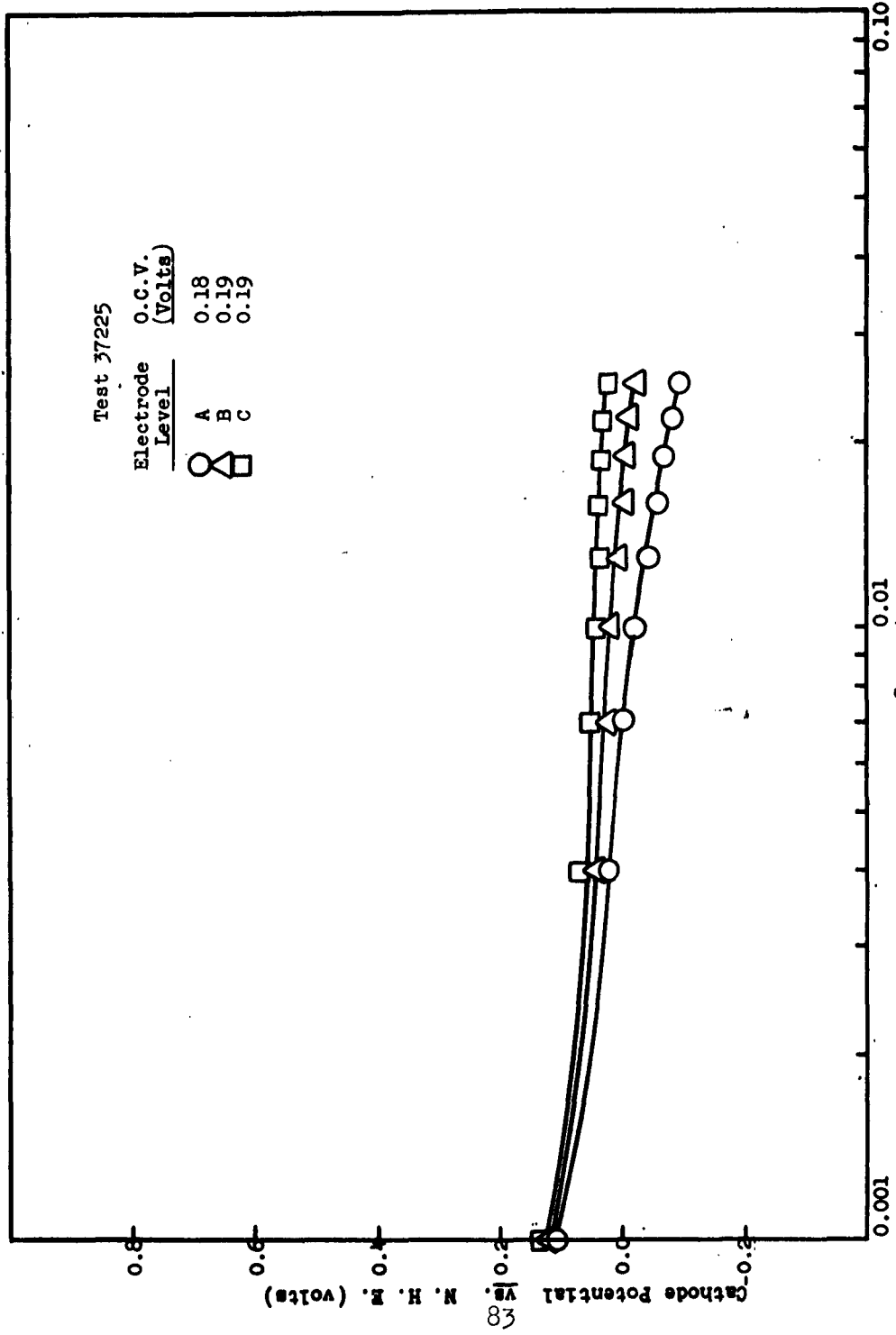


Figure 48 Voltage-current relationship of 0.5 g sample of p-nitrobenzoic acid in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

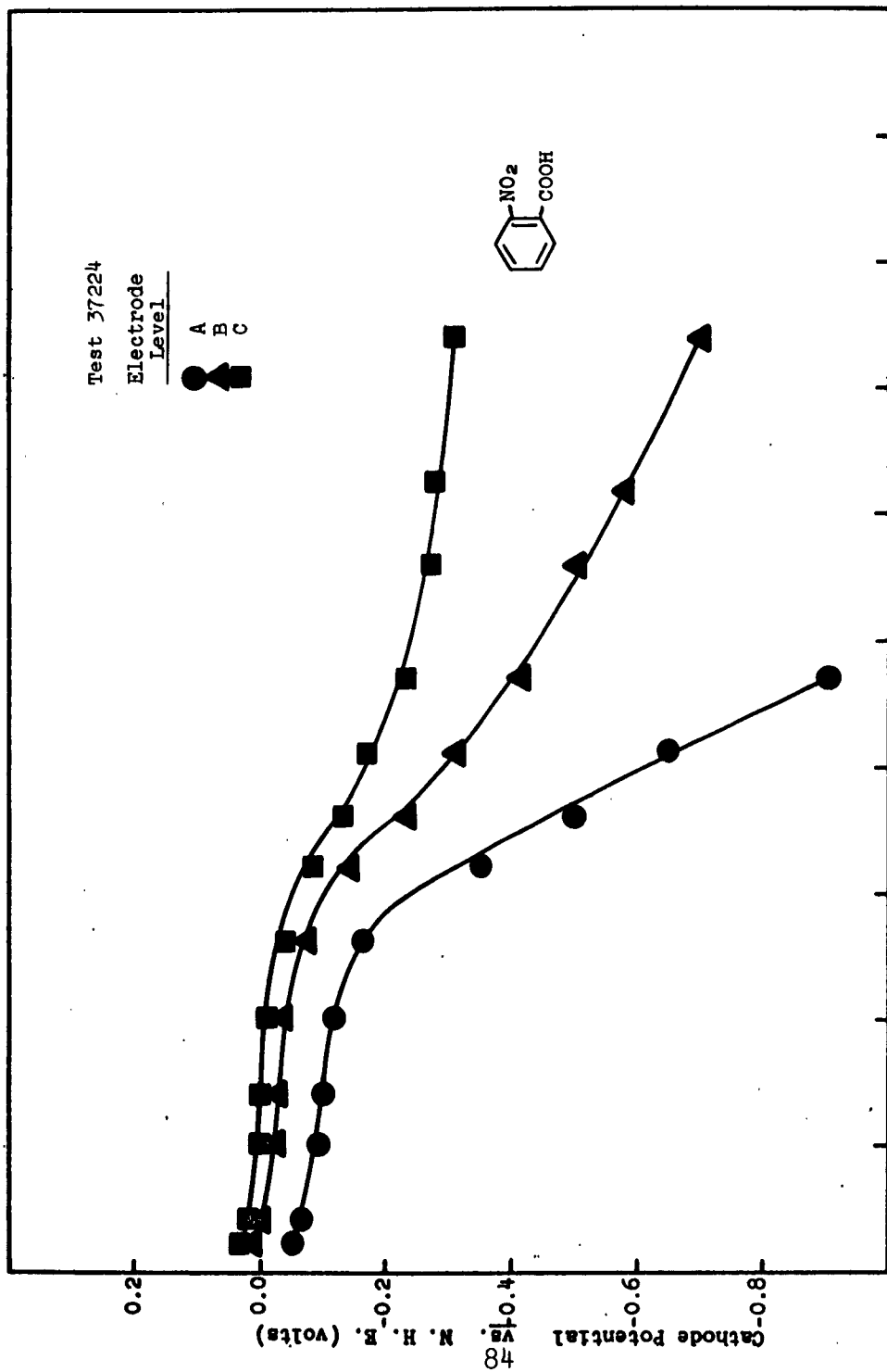


Figure 49 Chronopotentiometric plot of o-nitrobenzoic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g

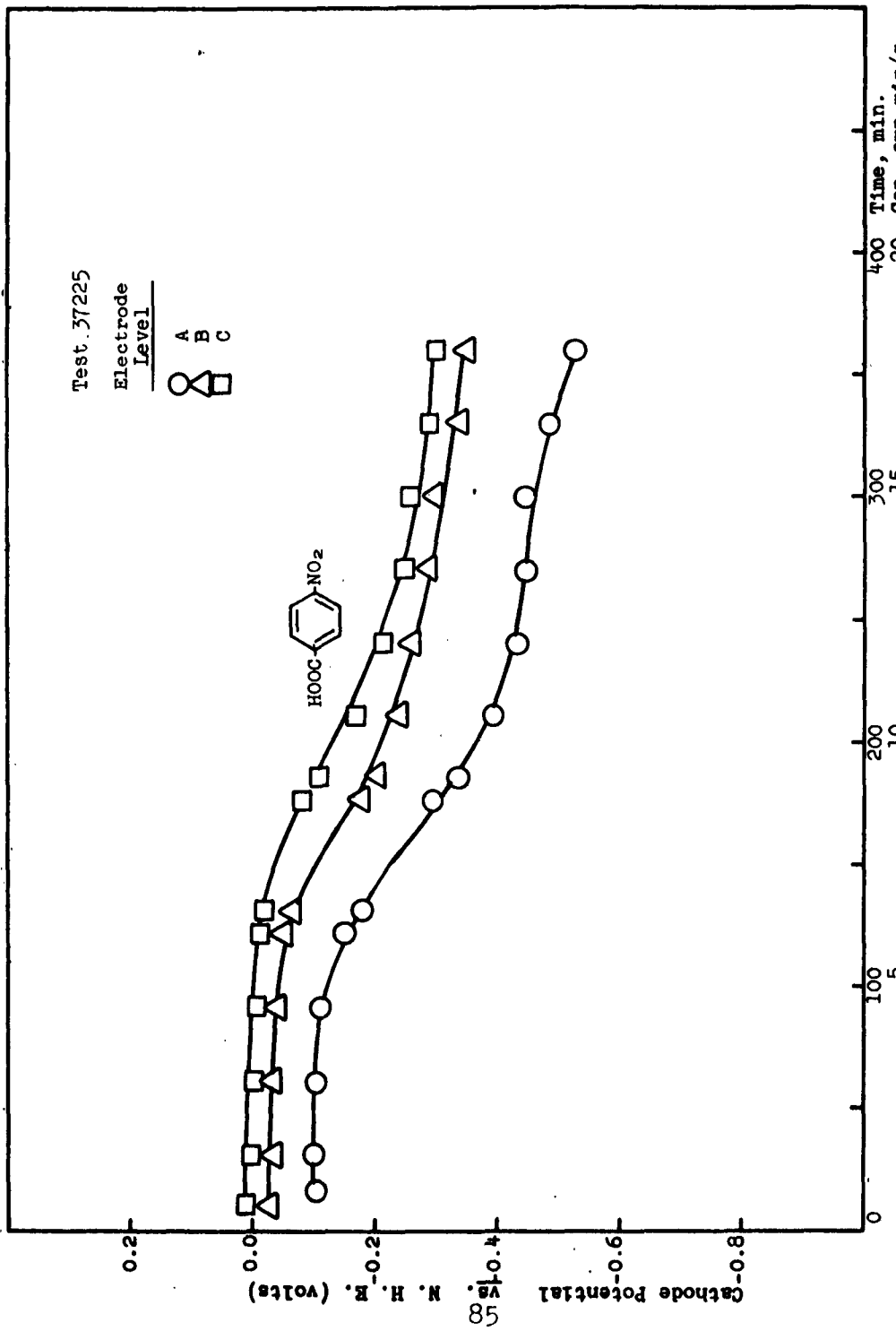


Figure 50 Chronopotentiometric plot of p-nitrobenzoic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g

Test 37223

Electrode Level	O.C.V. Volts vs. NHE
A	0.34
B	0.34
C	0.34

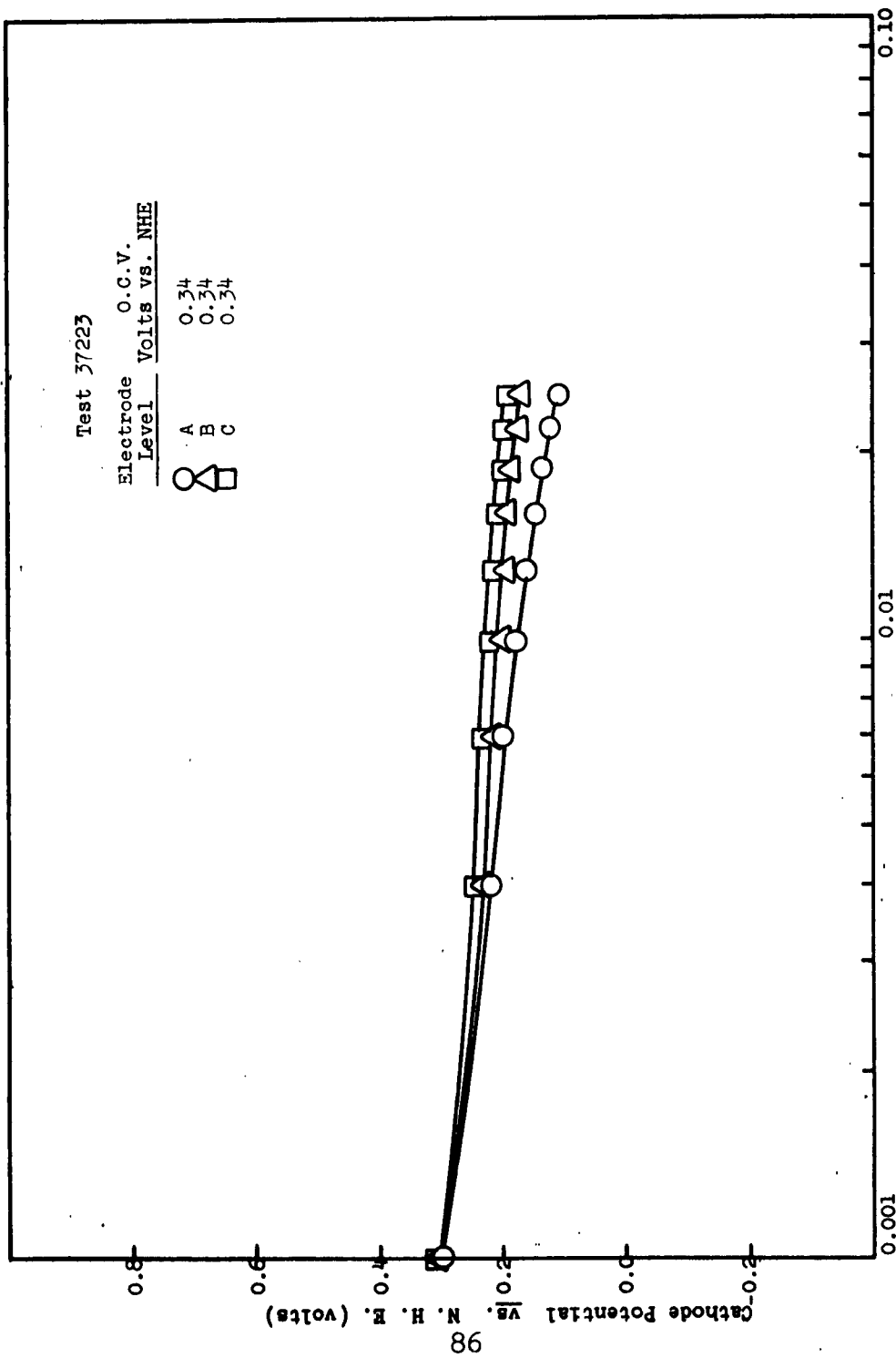


Figure 51 Voltage-current relationship of 0.5 g. sample of 3,4-dinitrobenzoic acid in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

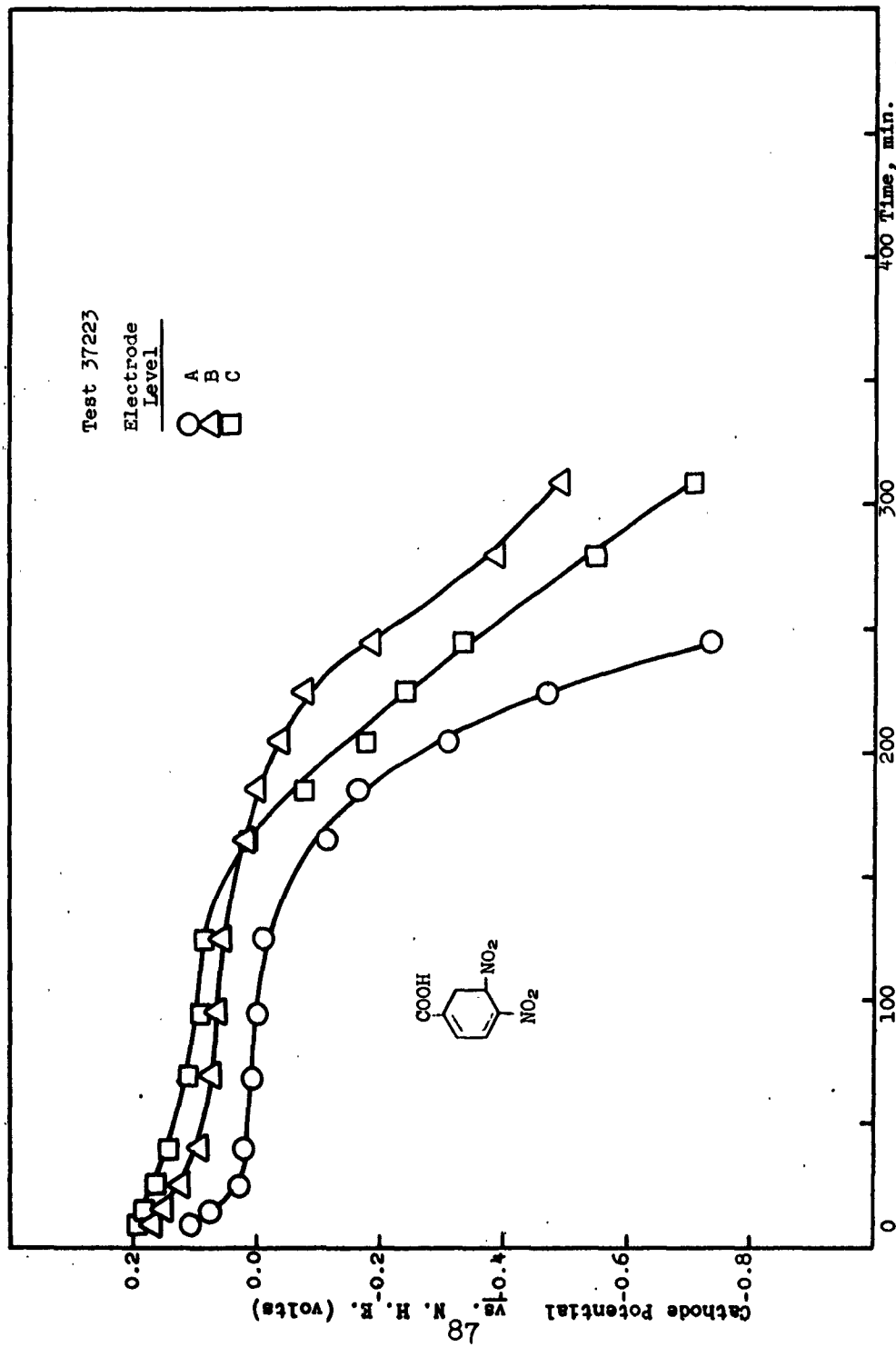


Figure 52 Chronopotentiometric plot of 3,4-dinitrobenzoic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

Test 37207

Electrode Level	O.C.V. Volts vs. NHE
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○	A	0.24
□	B	0.24
△	C	0.24

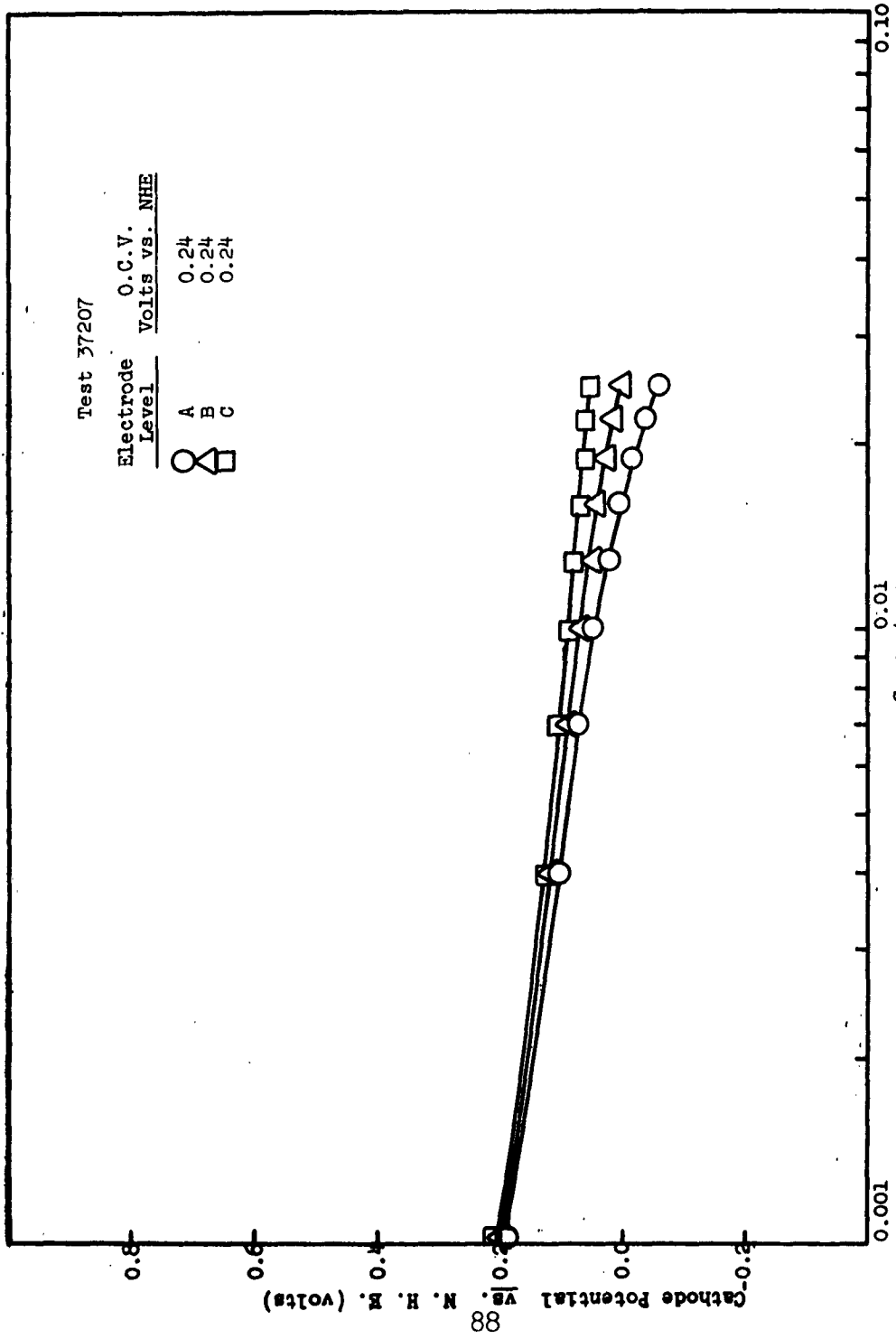


Figure 53 Voltage-current relationship of 0.5 g. samples of 5-nitroisophthalic acid in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

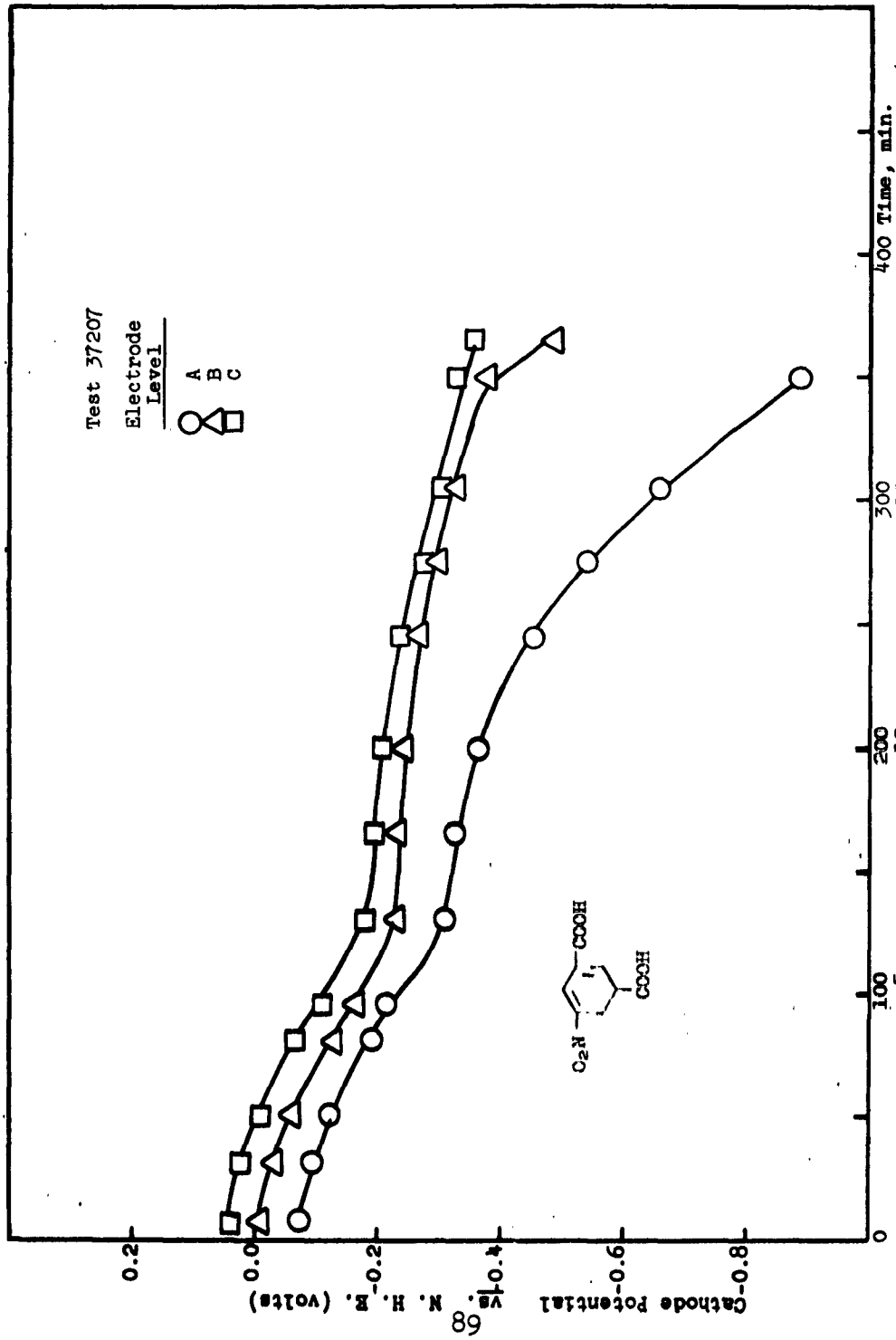


Figure 54 Chronopotentiometric plot of 5-nitroisophthalic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g

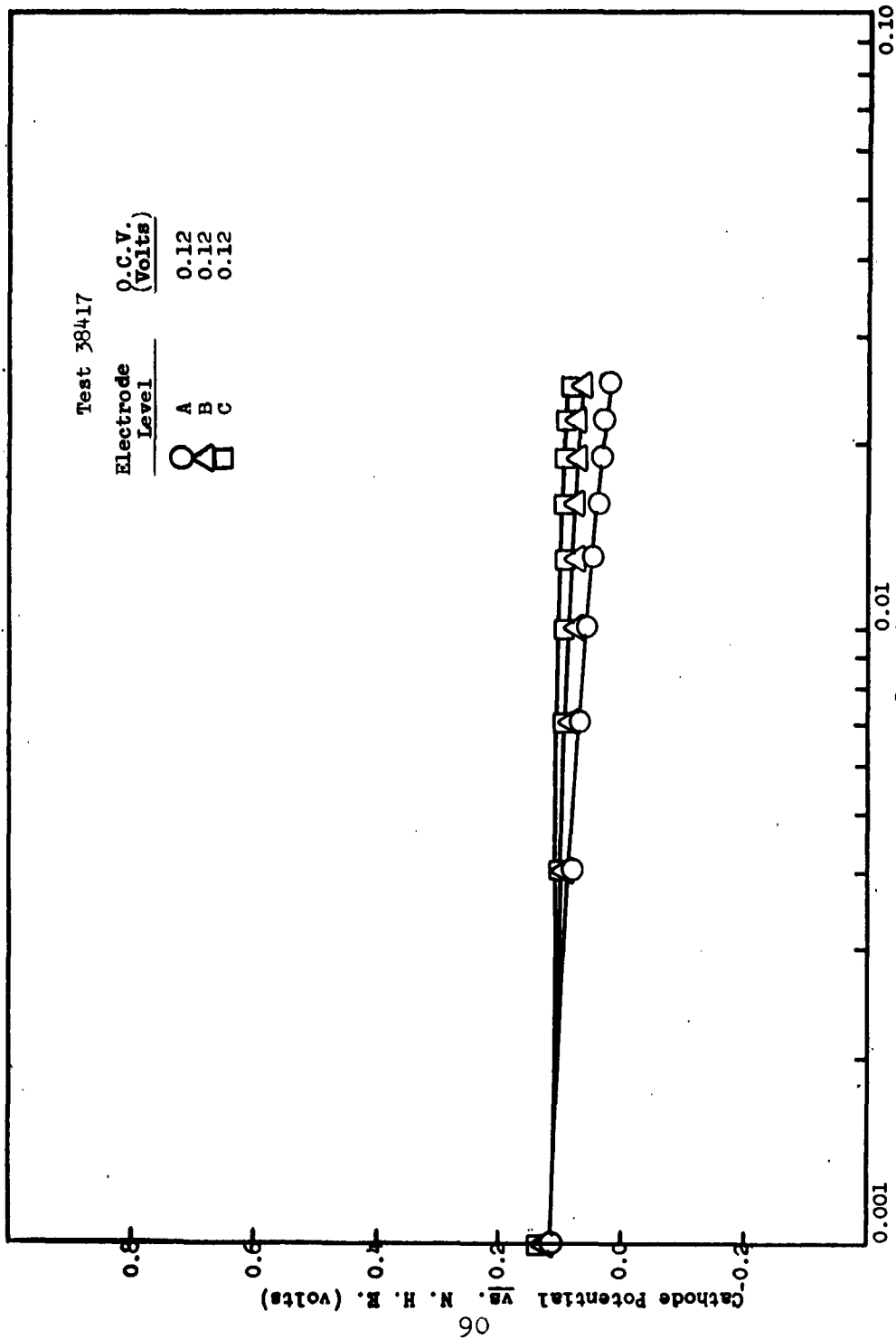


Figure 55 Voltage-current relationship of 0.5 g. sample of disodium 3,6-dinitrophthalate in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

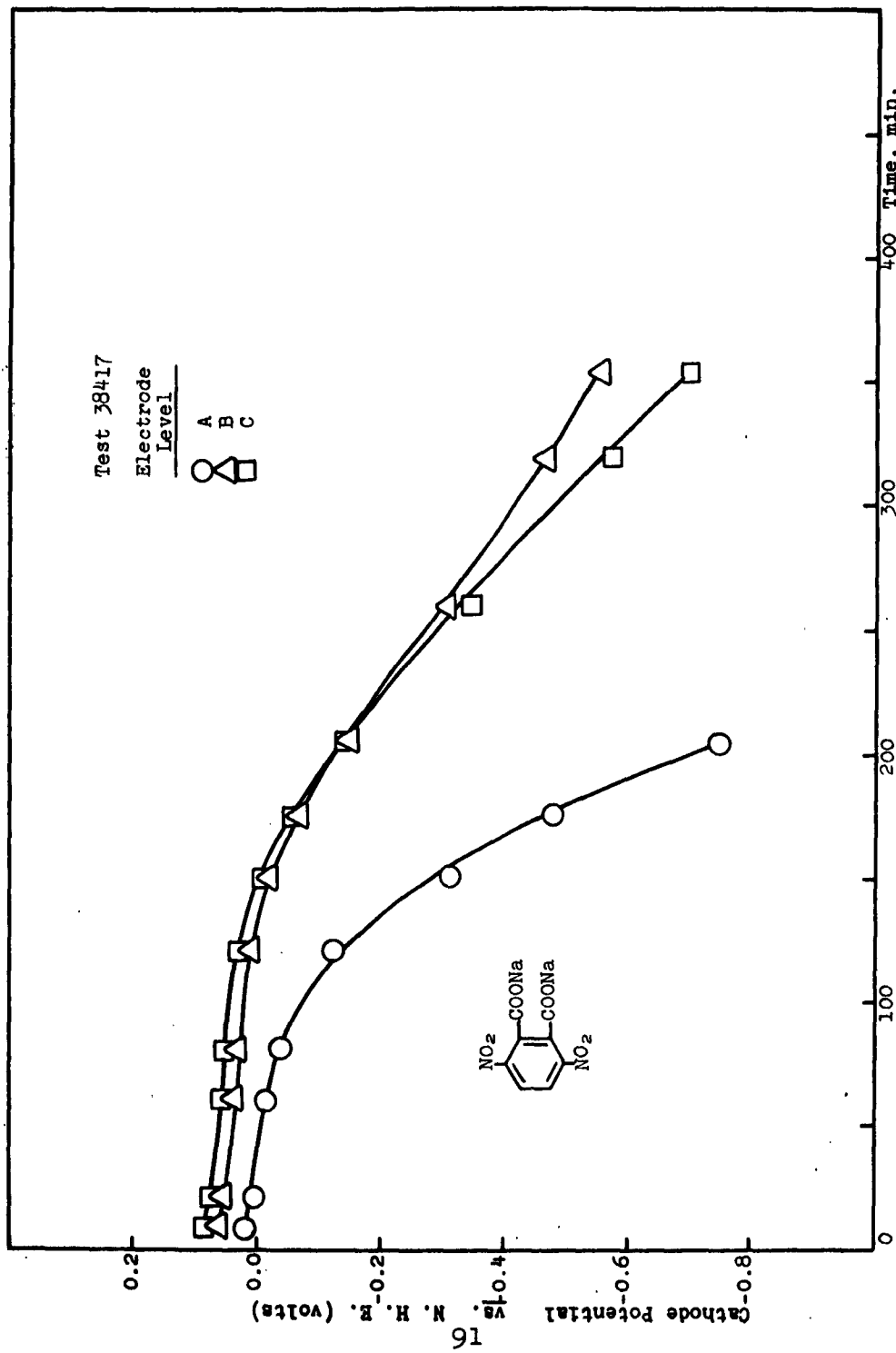


Figure 56 Chronopotentiometric plot of disodium 3,6-dinitrophenylate in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

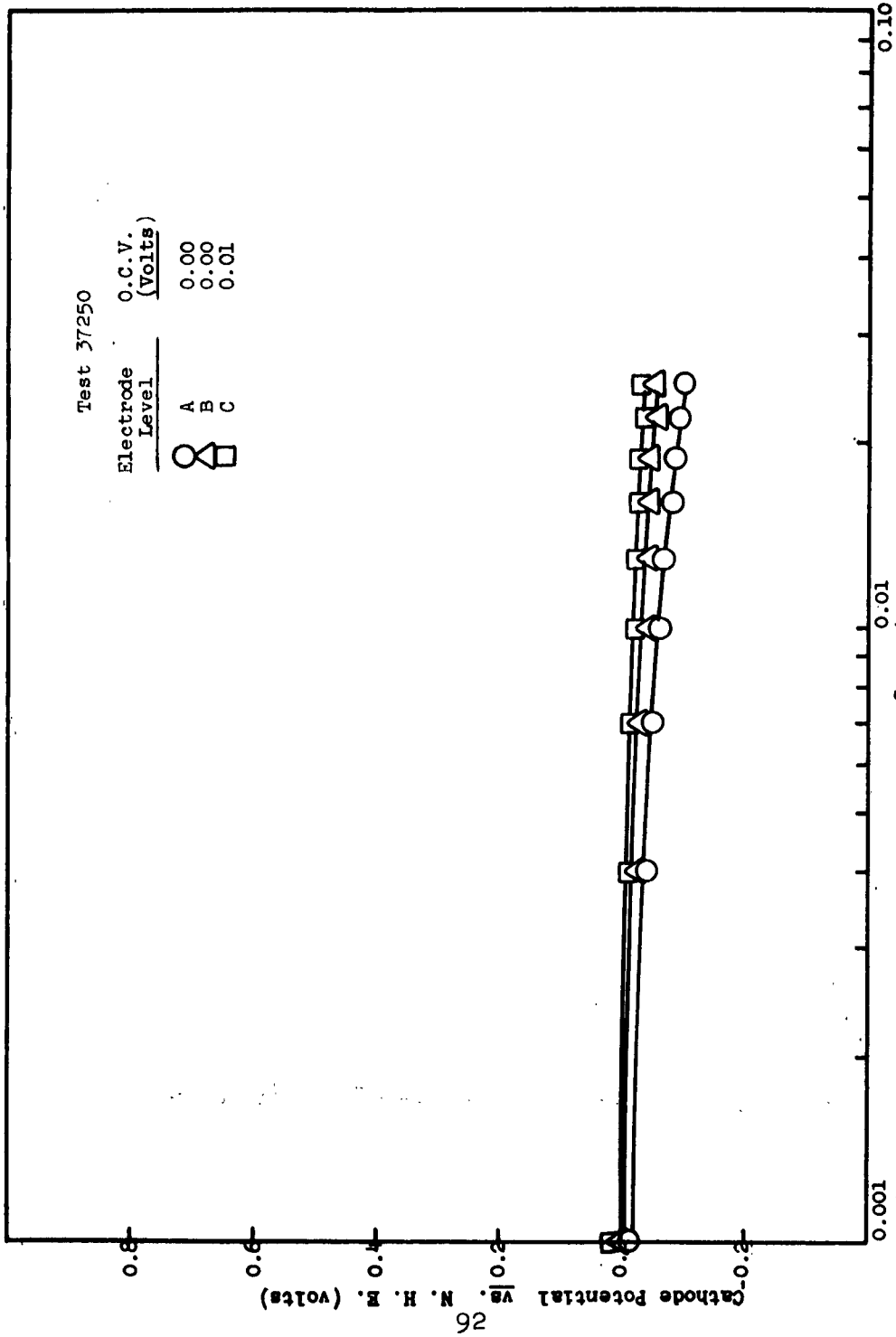


Figure 57 Voltage-current relationship of 0.5 g. sample of potassium 2,4-dinitrobenzene sulfonate in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

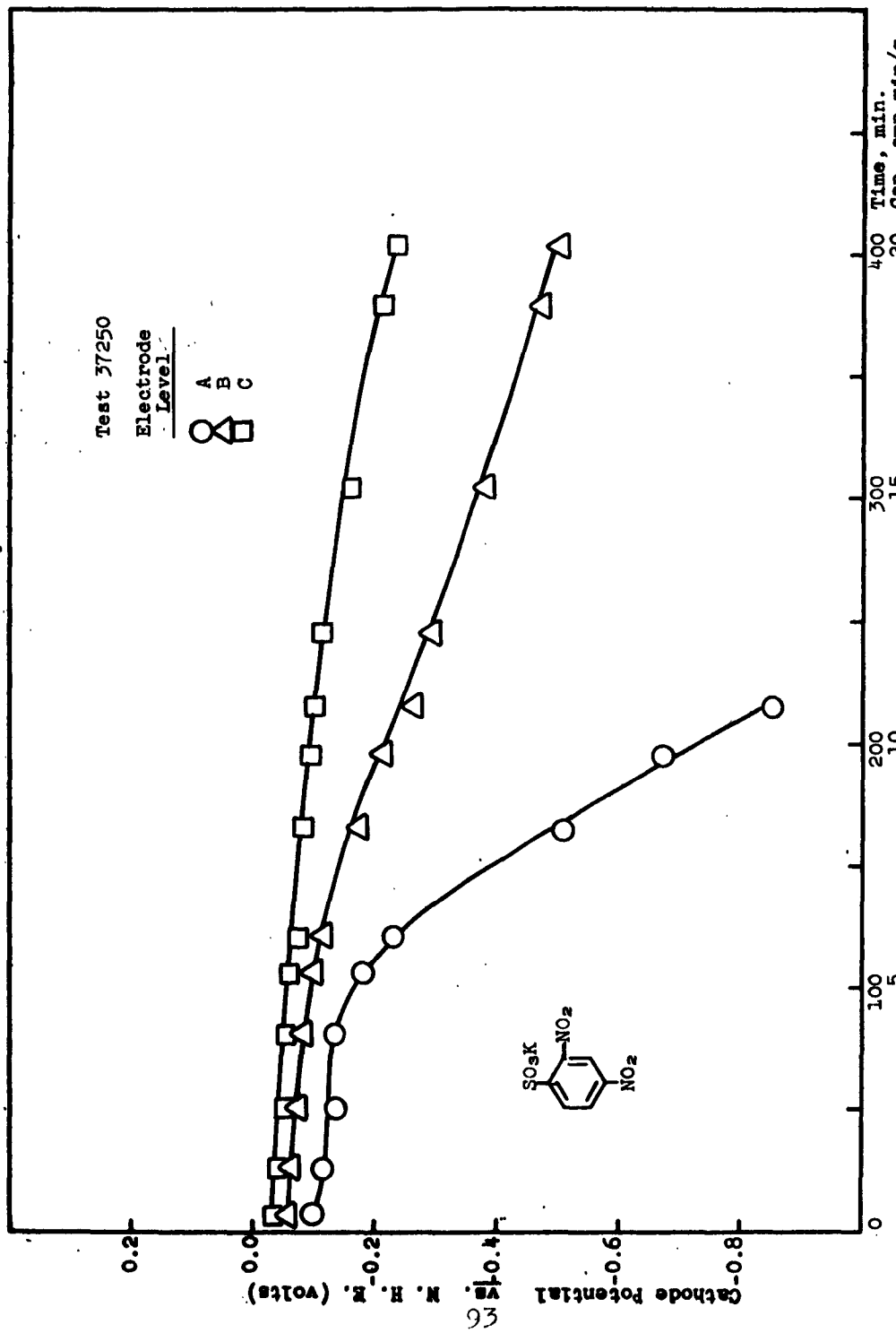


Figure 58 Chronopotentiometric plot of potassium 2,4-dinitrobenzene sulfonate in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

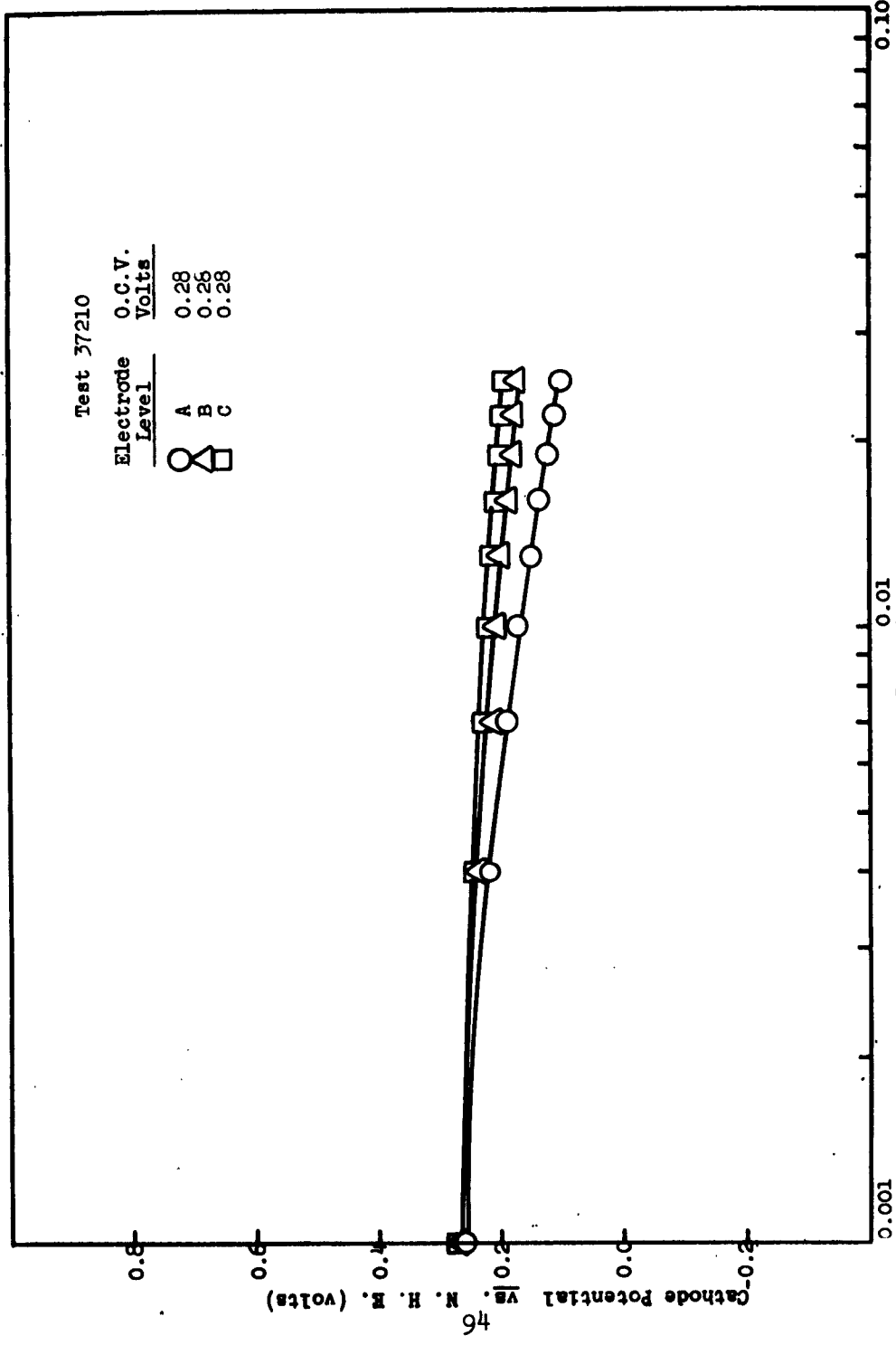


Figure 59 Voltage-current relationship of 0.5 g. sample of trinitro- β -naphthoic acid, product I in cell "D" in 168 g/l NH_4Br electrolyte to 0.025 amps.

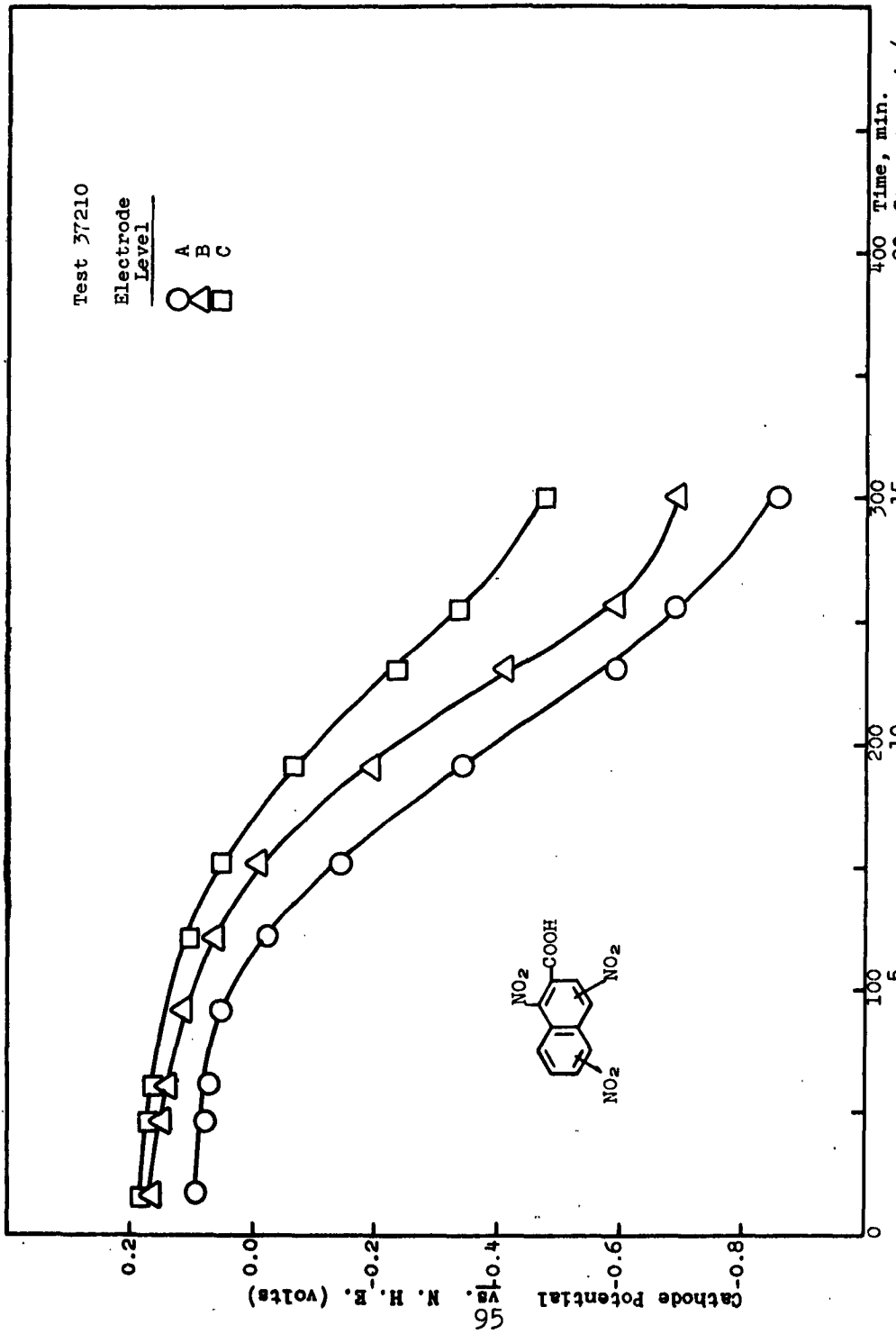


Figure 60 Chromopotentiometric plot of trinitro- β -naphthoic acid, Product 1, in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp./g.

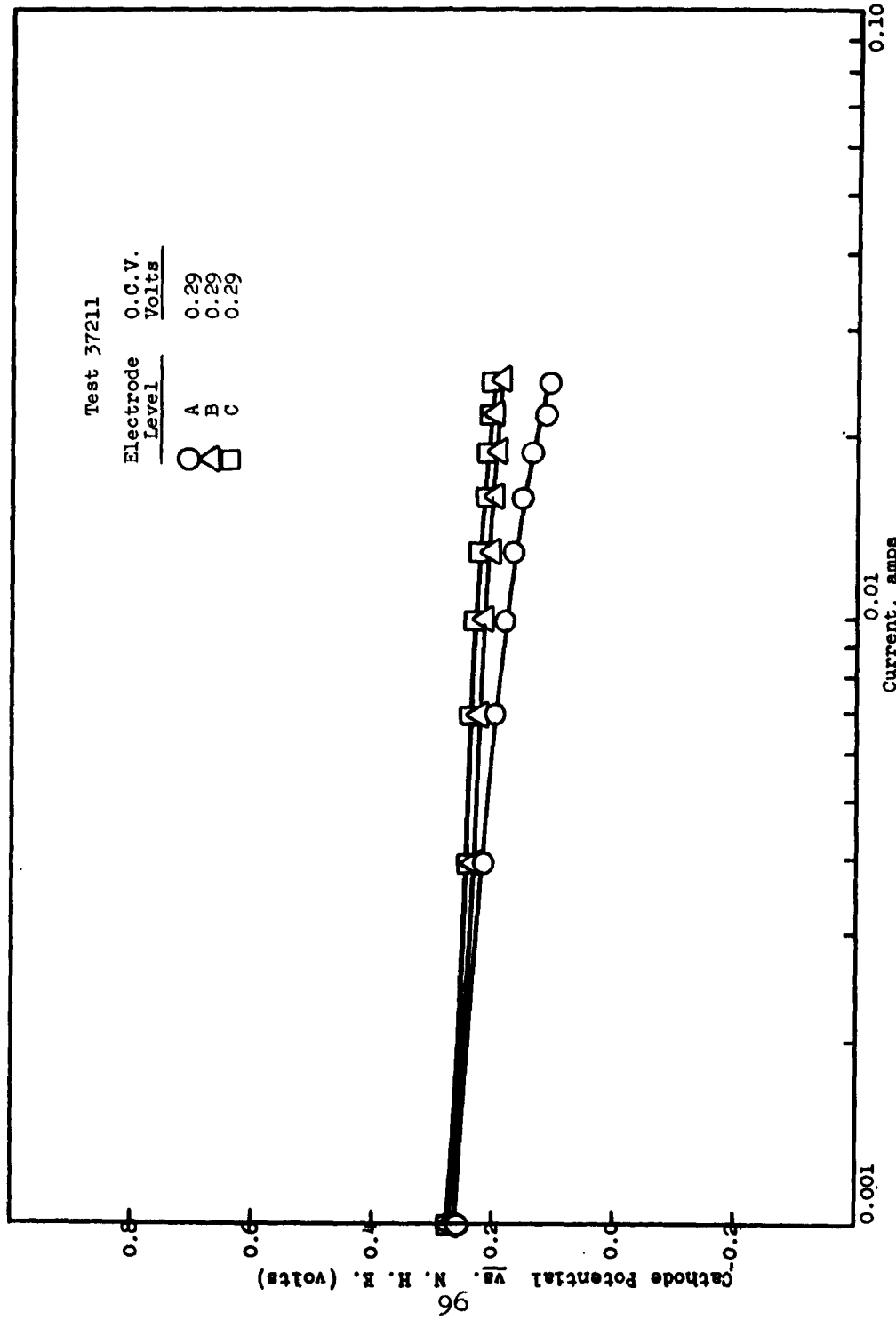


Figure 61 Voltage-current relationship of 0.5 g. sample of trinitro- β -naphthoic acid, product 2 in cell "D" in 168 g/l NH_4Br electrolyte to 0.025 amps.

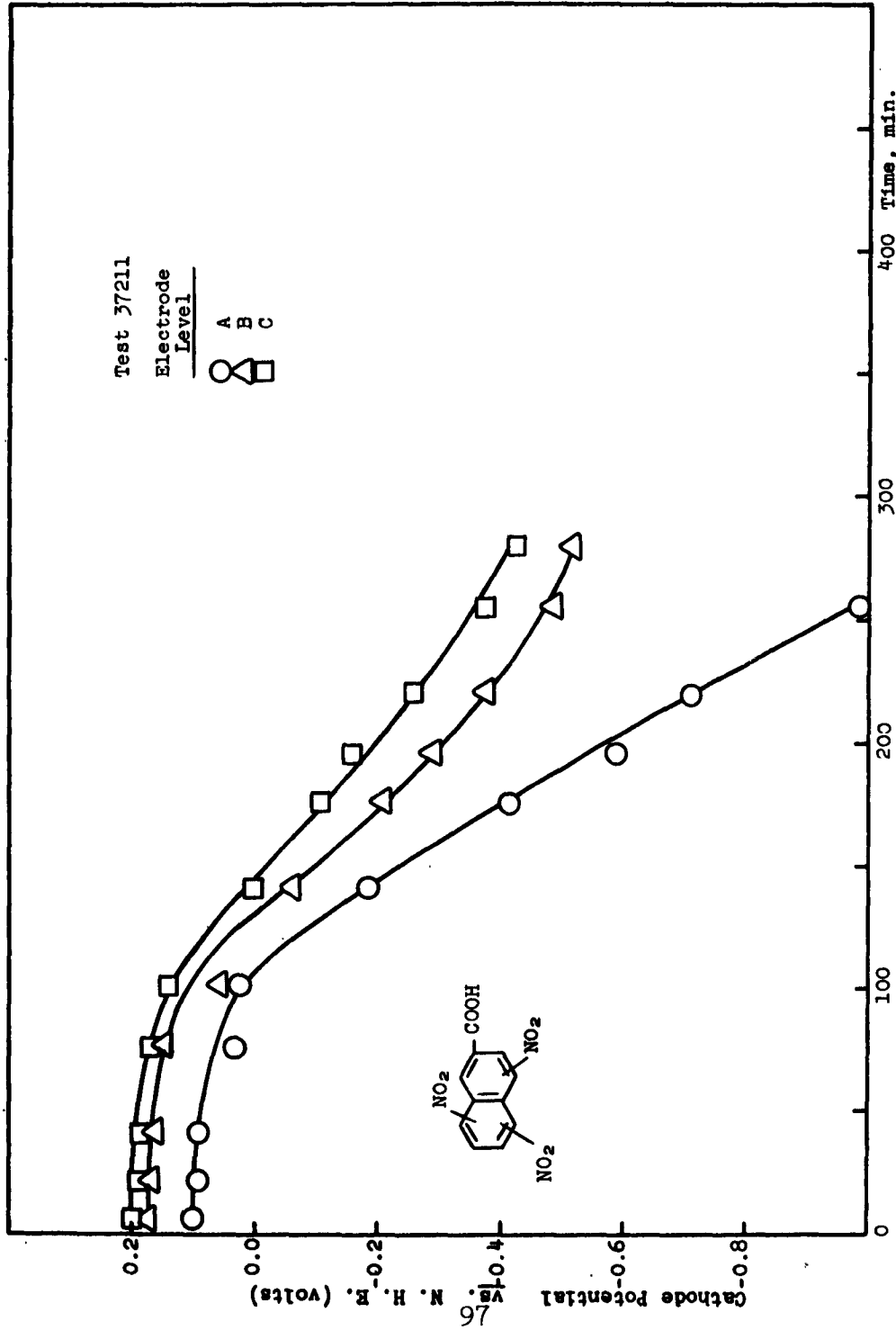


Figure 62 Chronopotentiometric plot of trinitro- β -naphthoic acid, Product 2, in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

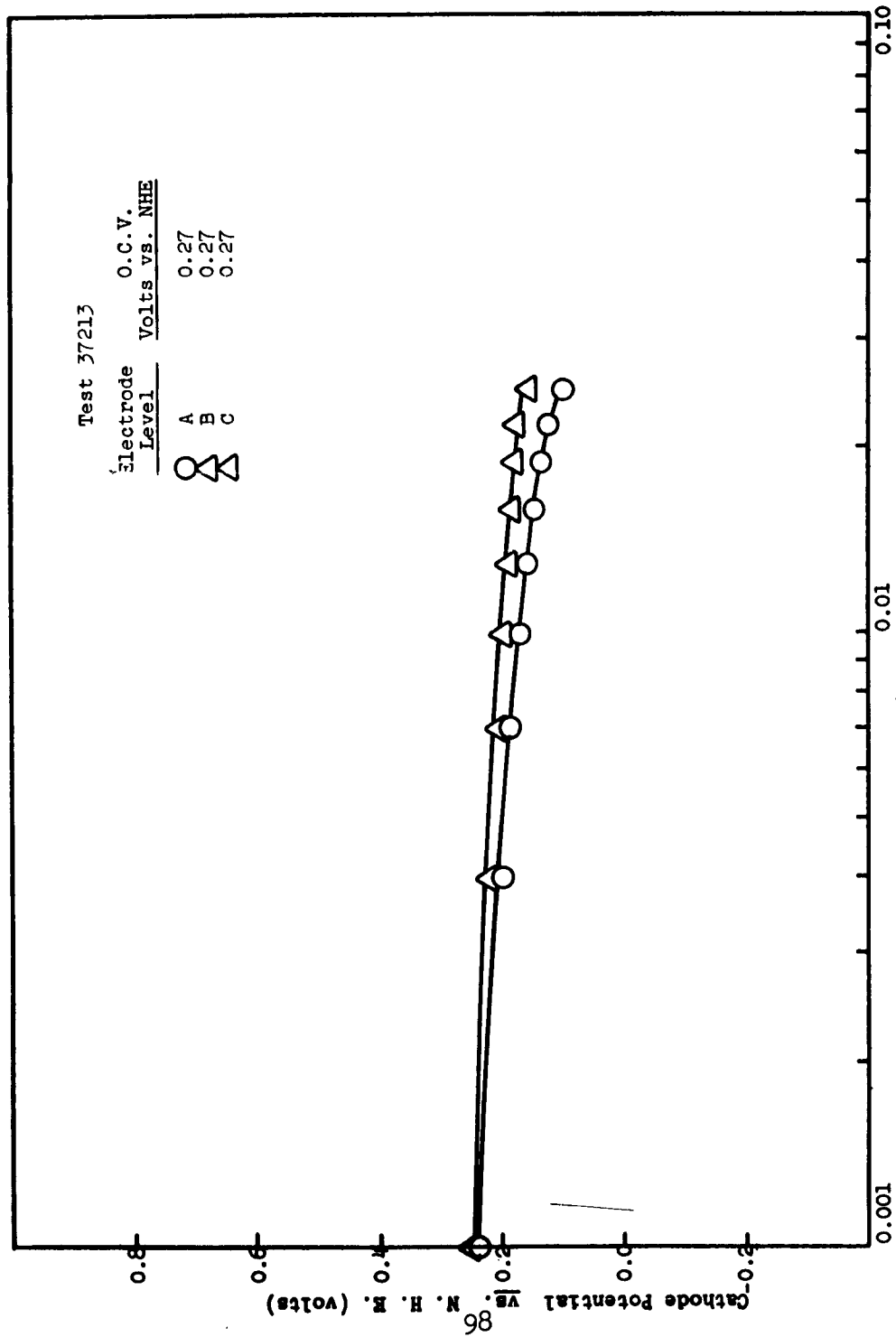


Figure 63 Voltage-current relationship of 0.5 g. sample of trinitro- β -naphthoic acid, product 3 in cell "D" in 168 g/l NH_4Br electrolyte to 0.025 amps.

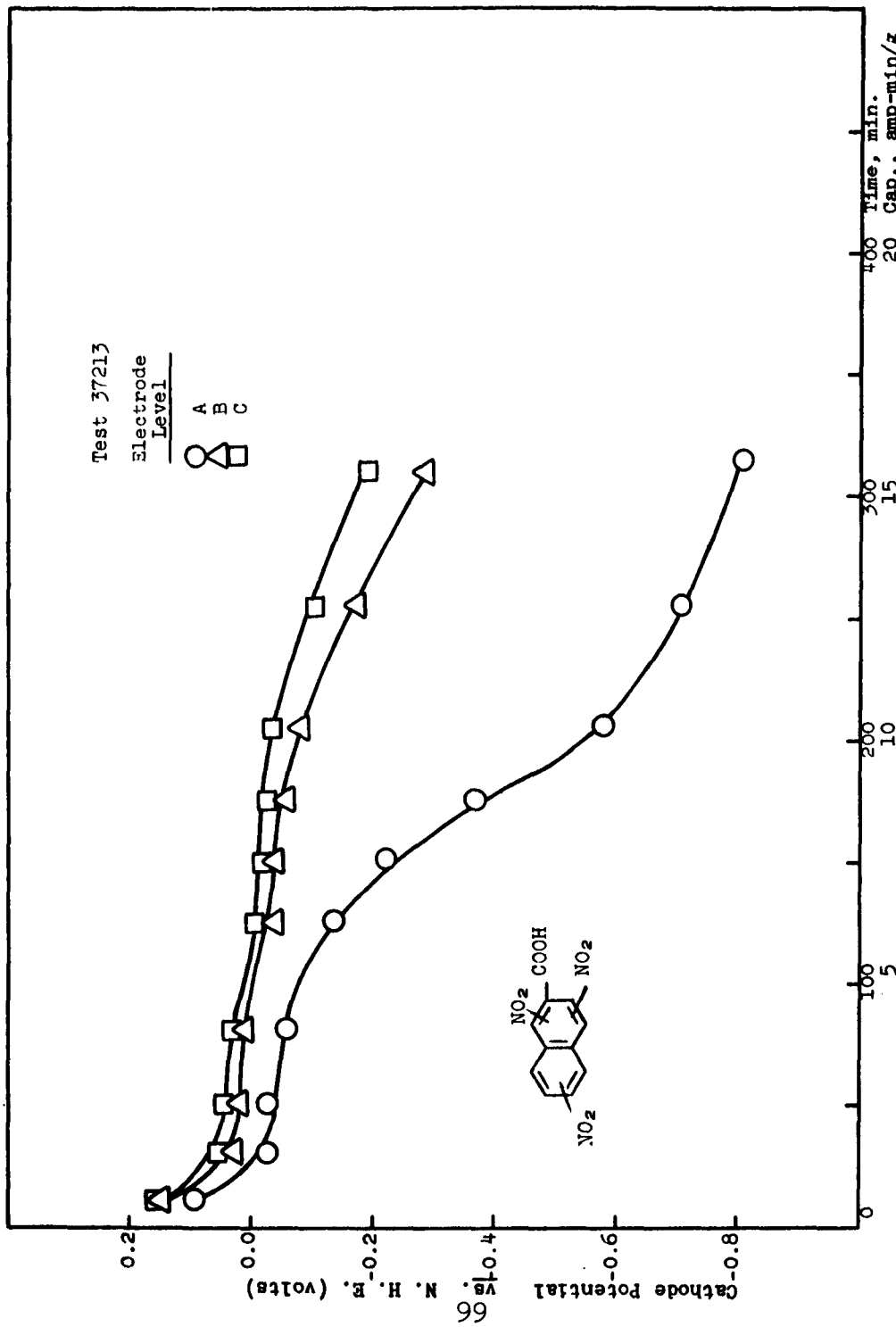


Figure 64 Chronopotentiometric plot of trinitro-β-naphthoic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

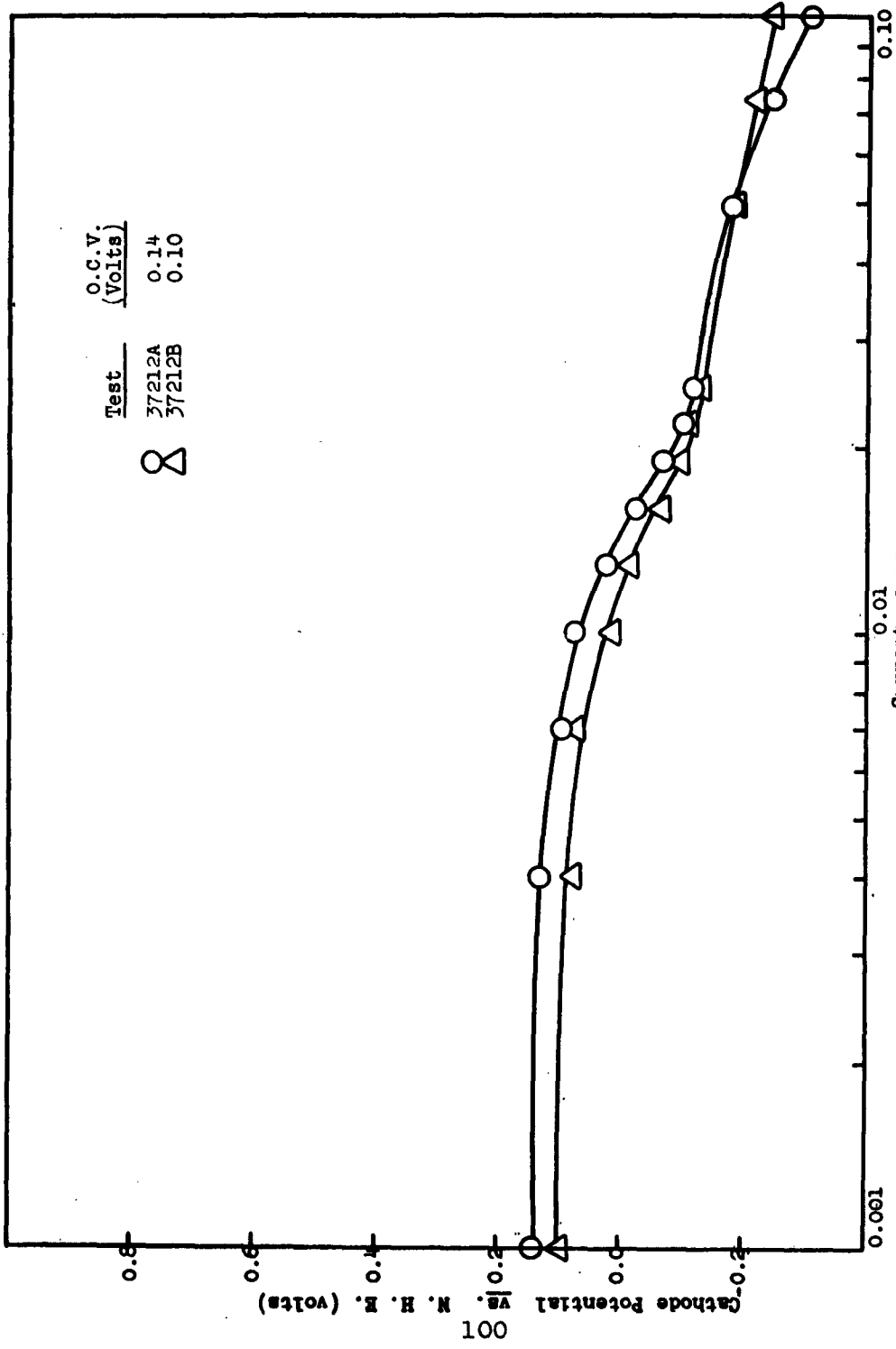


Figure 65 Voltage-current relationship of 0.5 g. samples of 1,3,6,8-tetranitrocarbazole in cell "C" in 168 g/l NH₄Br to 0.100 amps.

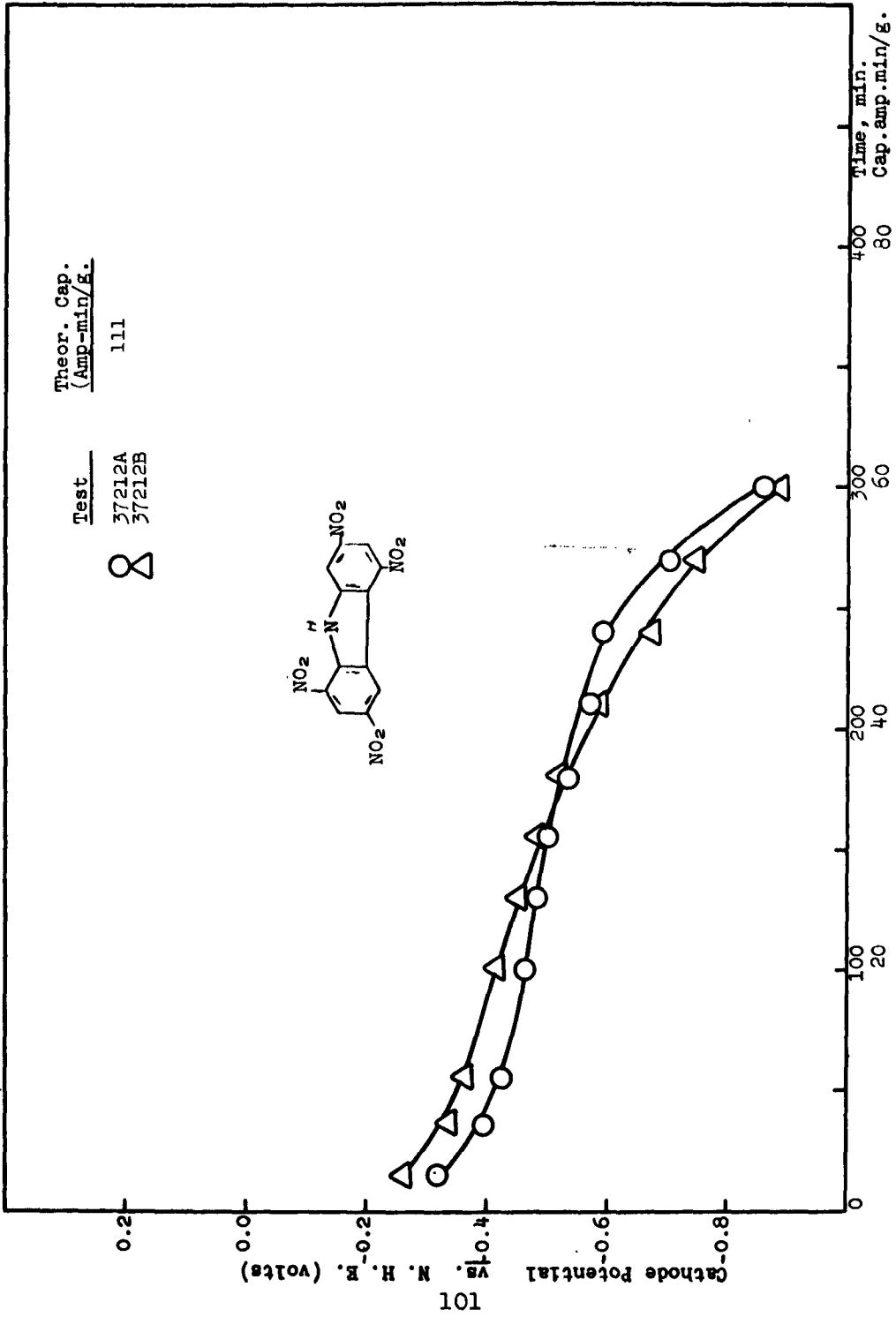


Figure 66 Chronopotentiometric plots of 1,3,6,8-Tetranitrocarbazole in cell "C" in 163 g/l NH₄Br electrolyte at 0.200 amp/g.

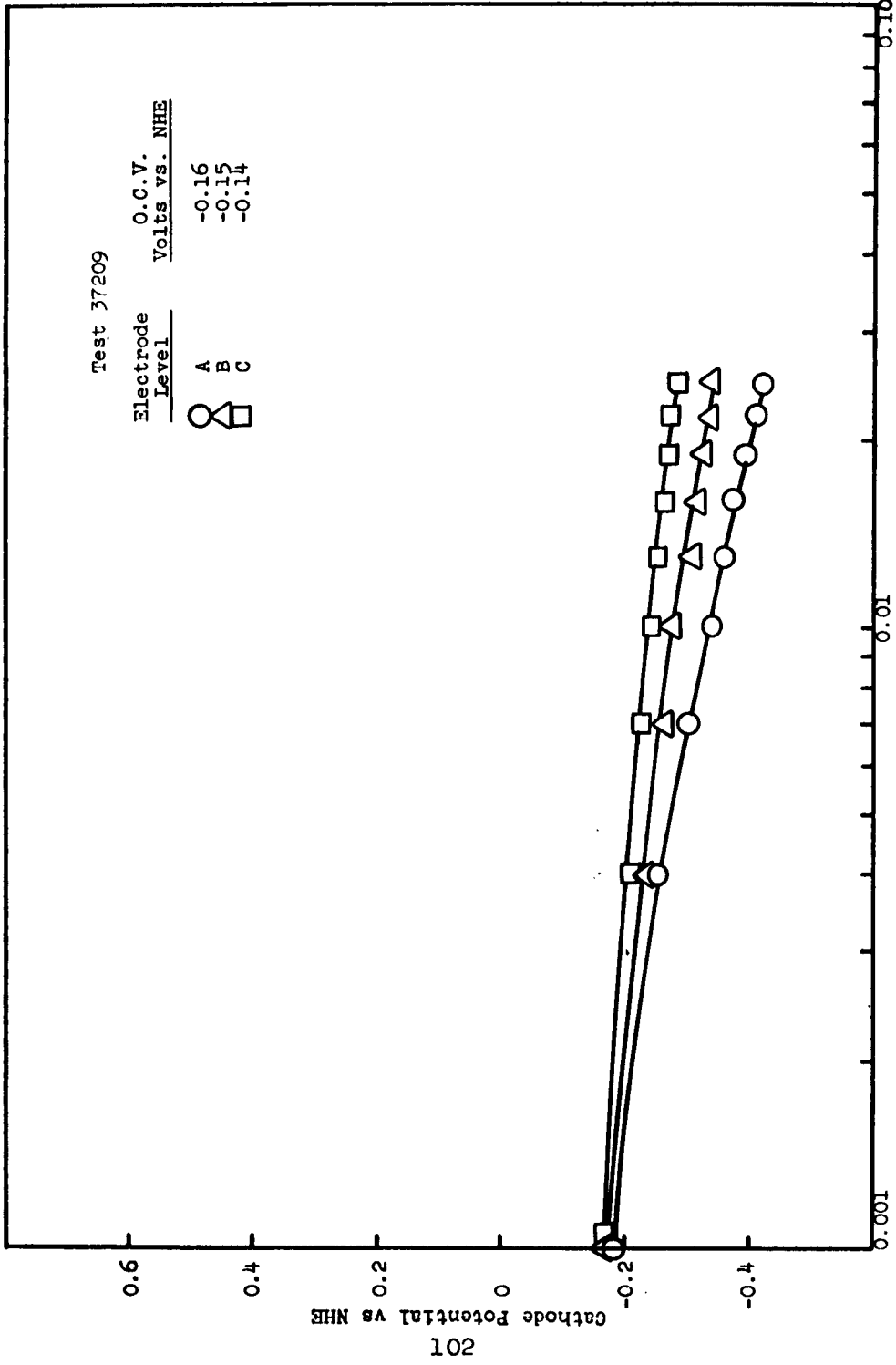


Figure 67 Voltage-current relationship of 0.5 g. sample of 4-nitroimidazole in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

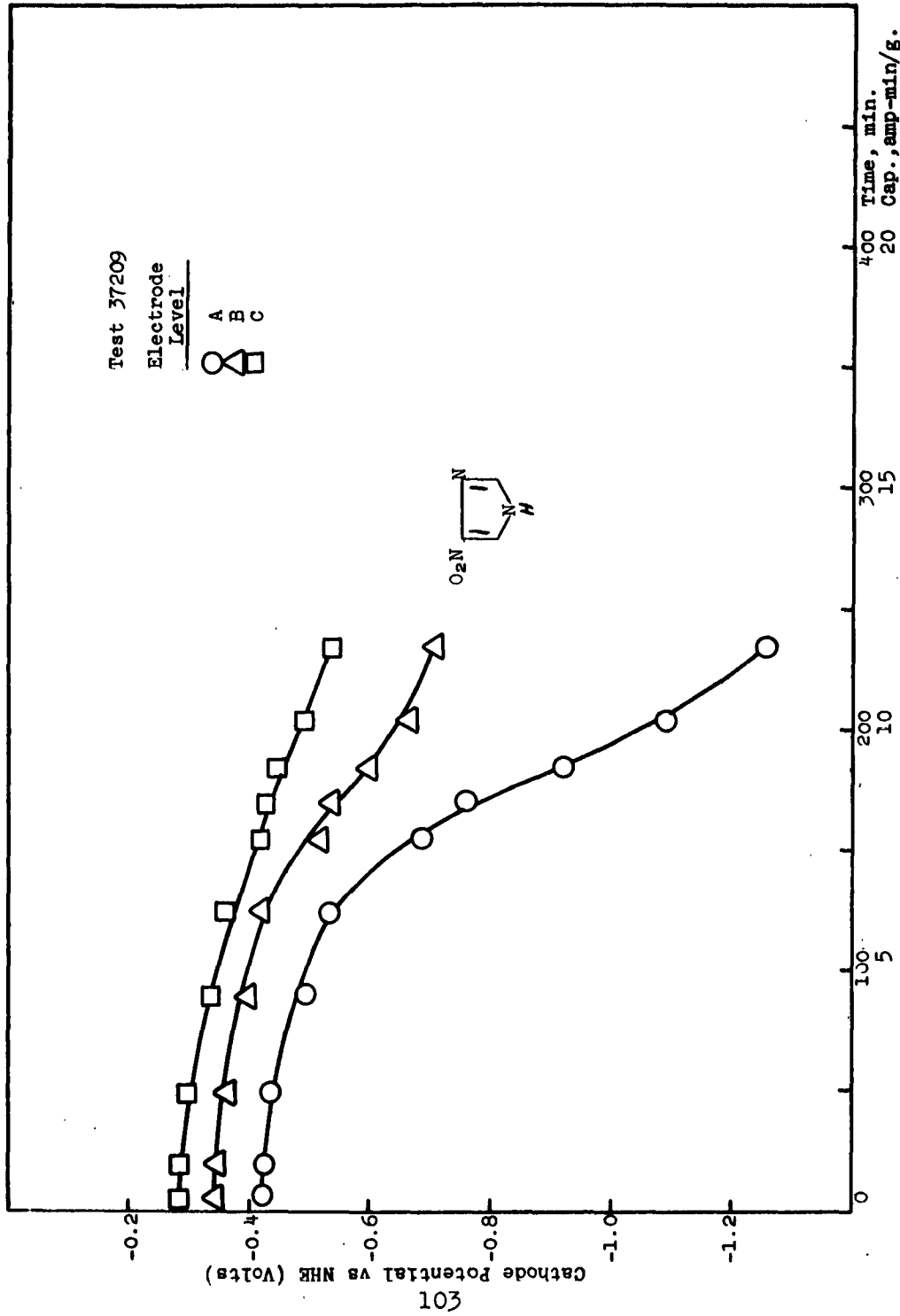


Figure 68 Chronopotentiometric plot of 4-nitroimidazole in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp./g.

Test 37208

Electrode Level	O.C.V. Volts
A	-0.16
B	-0.16
C	-0.16

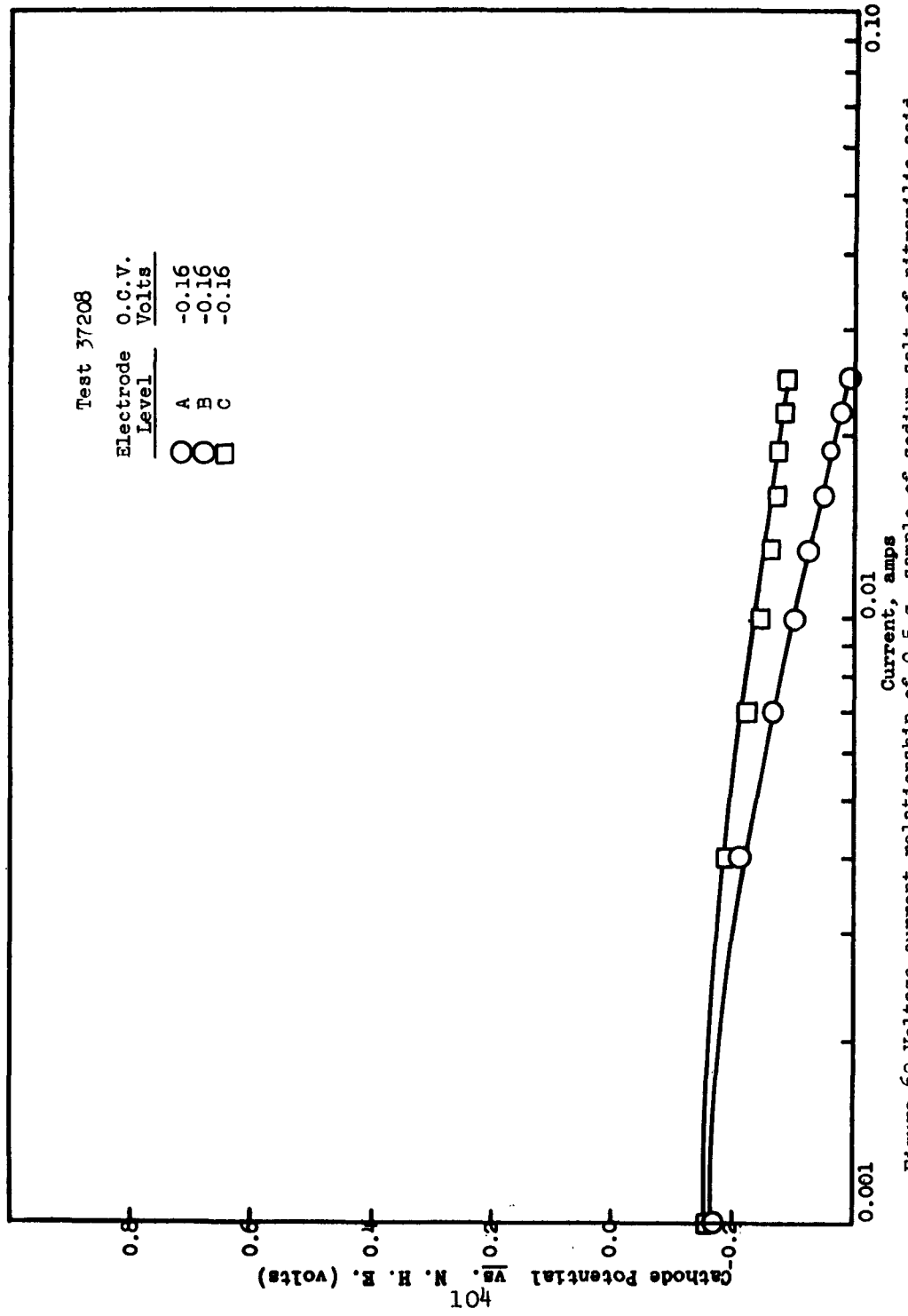


Figure 69 Voltage-current relationship of 0.5 g. sample of sodium salt of nitranillic acid in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

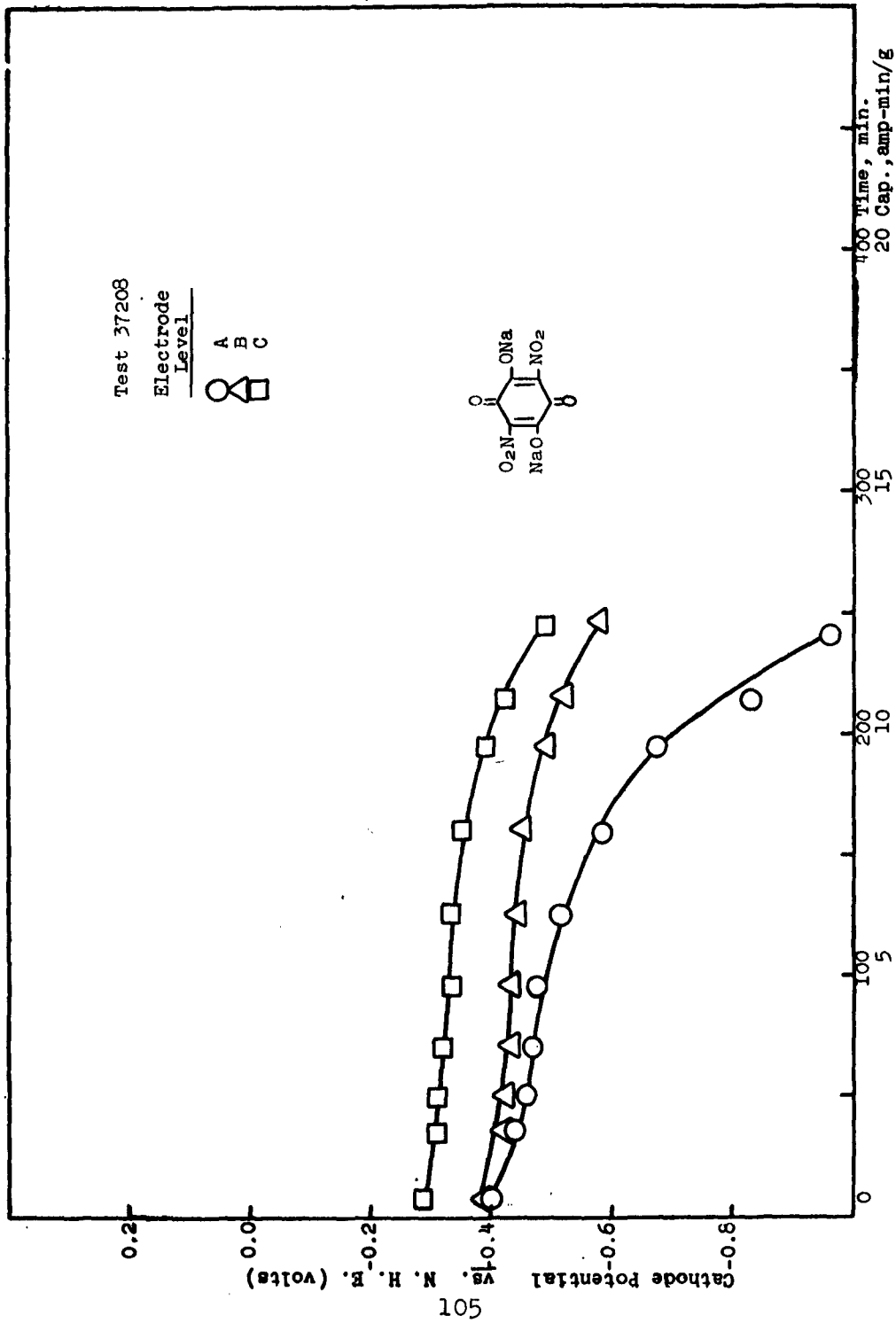


Figure 70 Chronopotentiometric plot of sodium salt of nitranilic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g

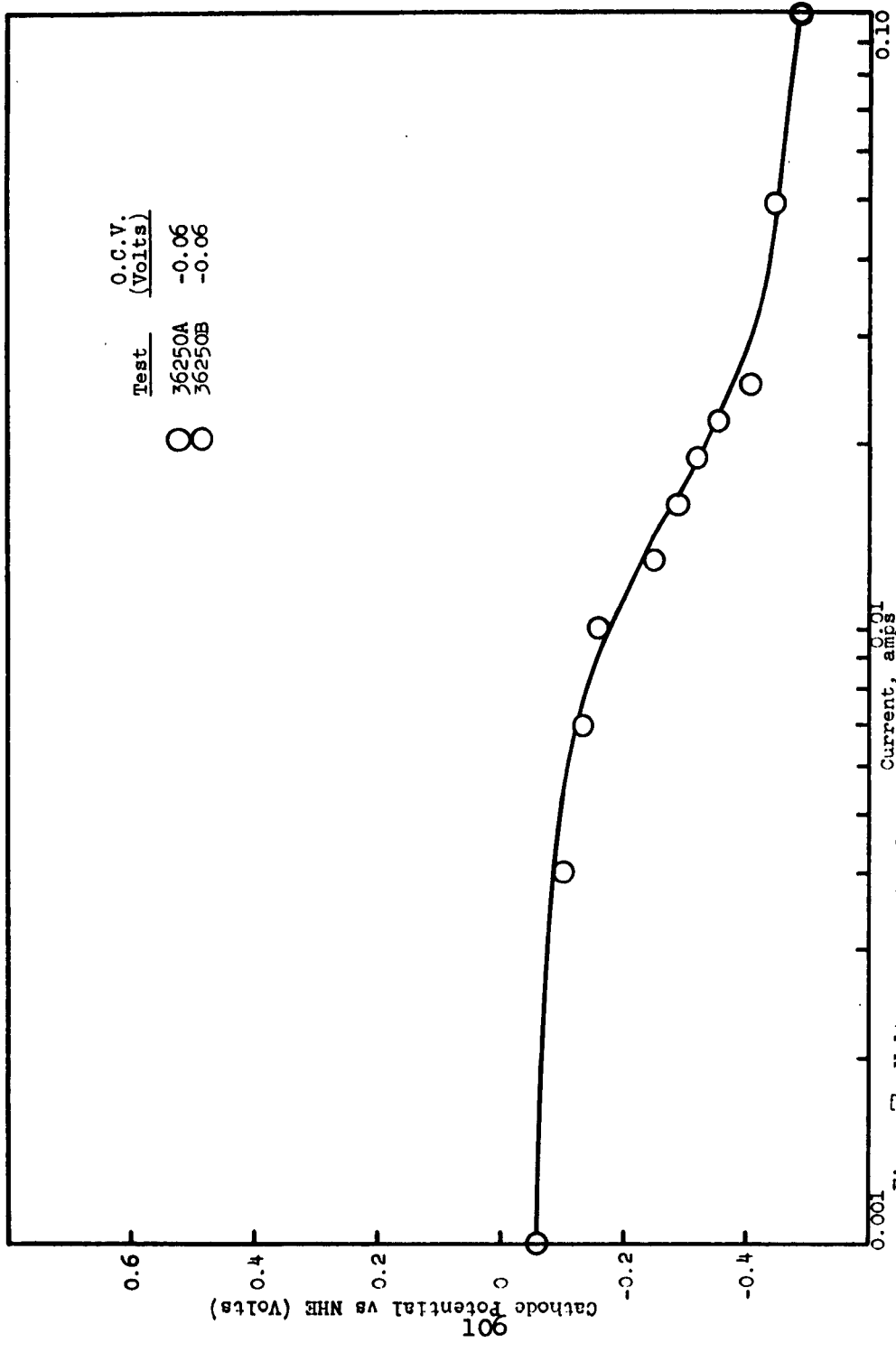


Figure 7. Voltage-current relationship of 0.5 g. N,N'-(1,2-ethylene) bis maleamic acid in cell "C" in 168 g/l NH₄Br electrolyte to 0.100 amps.

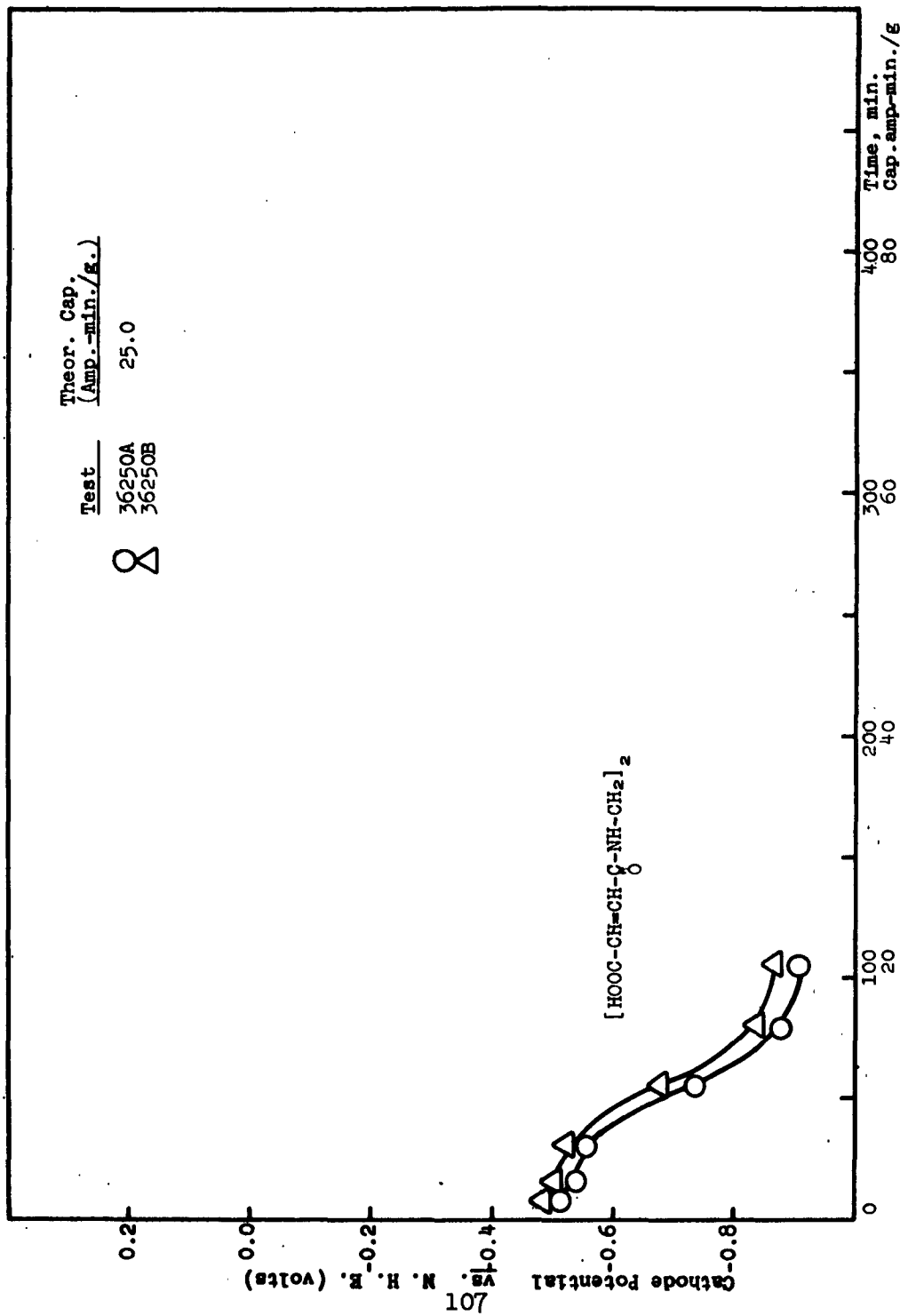


Figure 72 Chronopotentiometric plots of N,N'-(1,2-ethylene) bis maleamic acid in cell "C" in 168 g/l NH₄Br electrolyte at 0.200 amp./g.

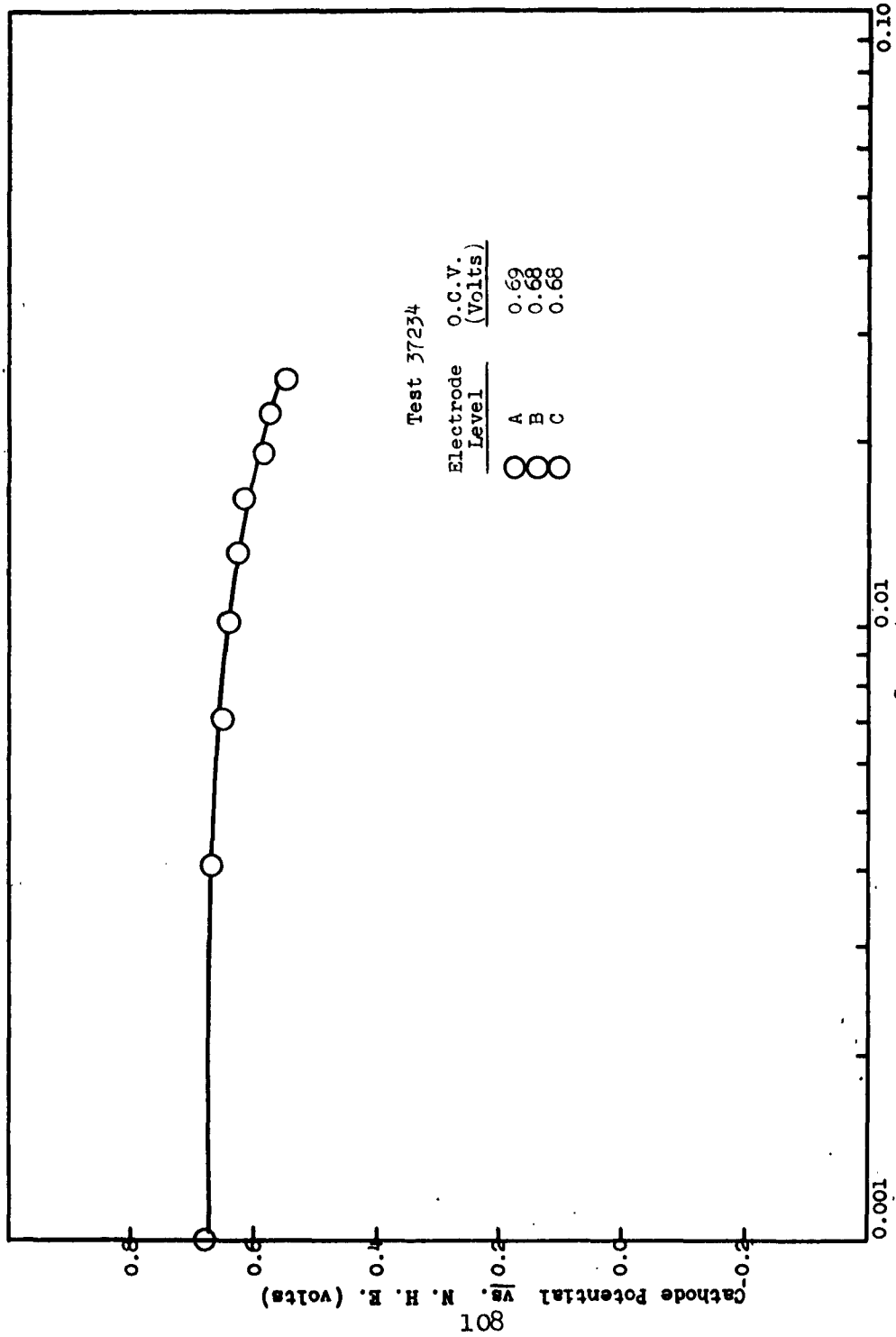


Figure 73 Voltage-current relationship of 0.62 g phosphomolybdic acid in cell "D" in 168 g/l NH₄Br to 0.025 amps.

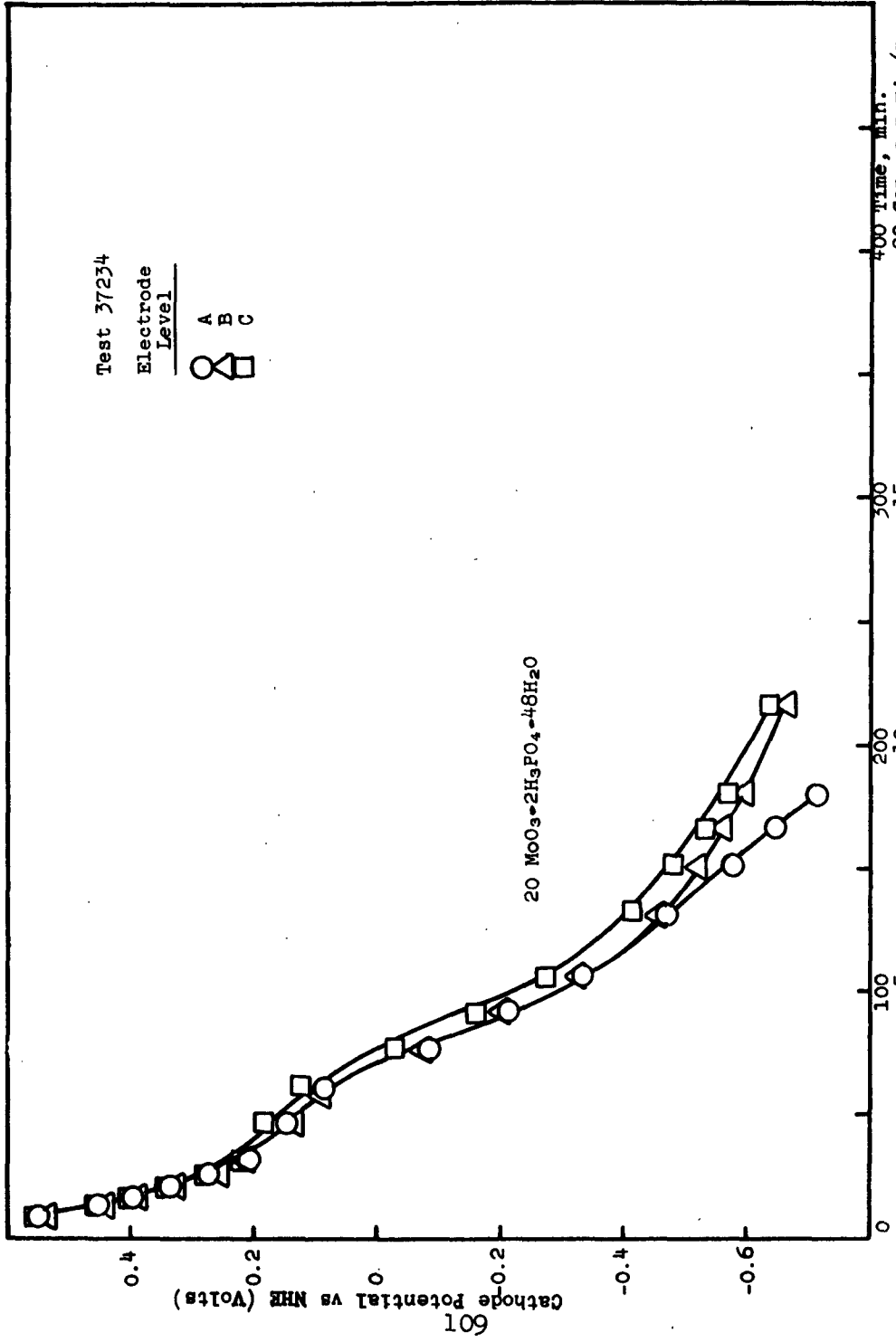


Figure 74 Chronopotentiometric plot of phosphomolybdic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

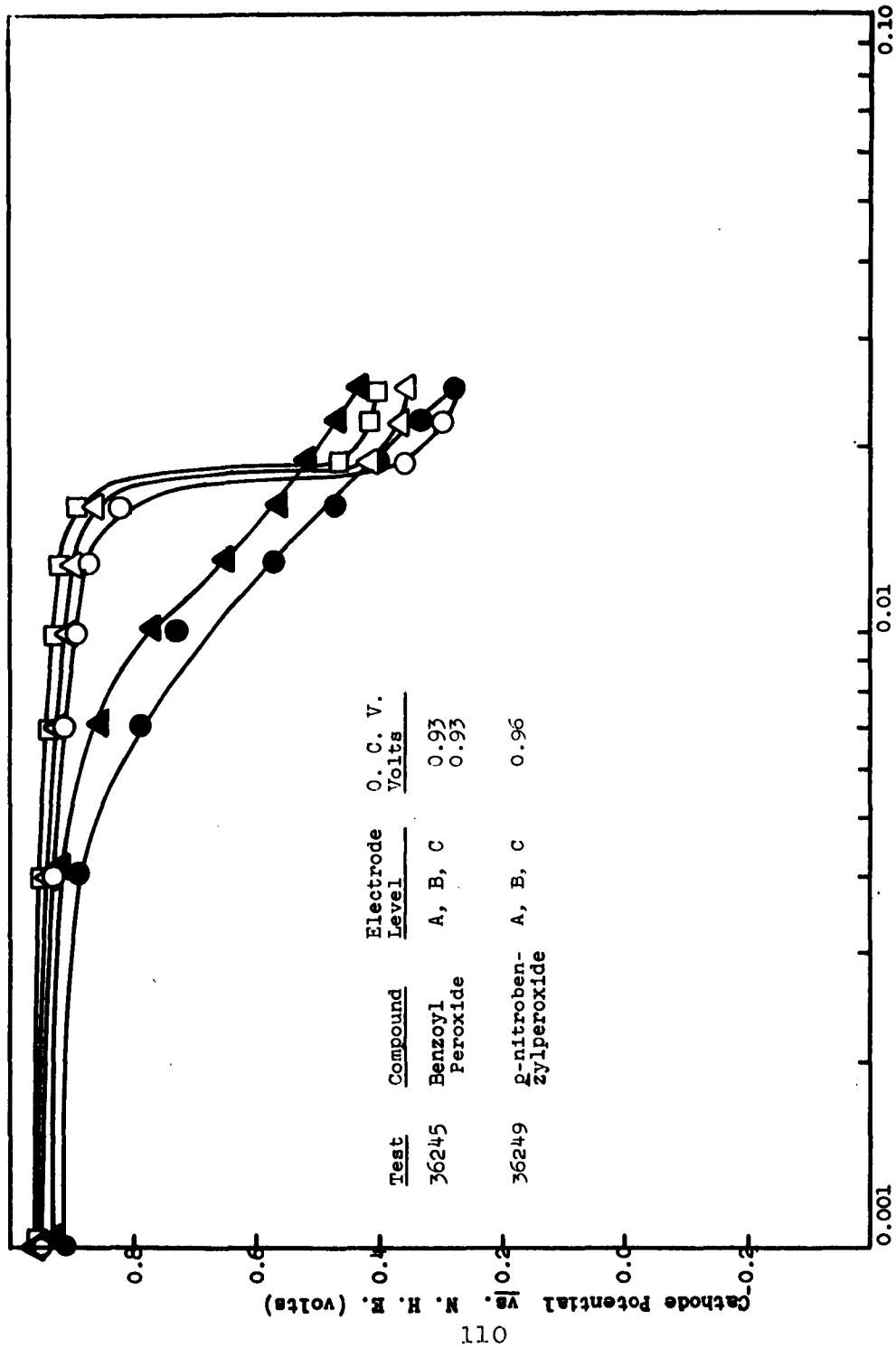


Figure 75 Chronopotentiometric plot of benzoyl peroxide and p-nitrobenzoyl peroxide in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp./g.

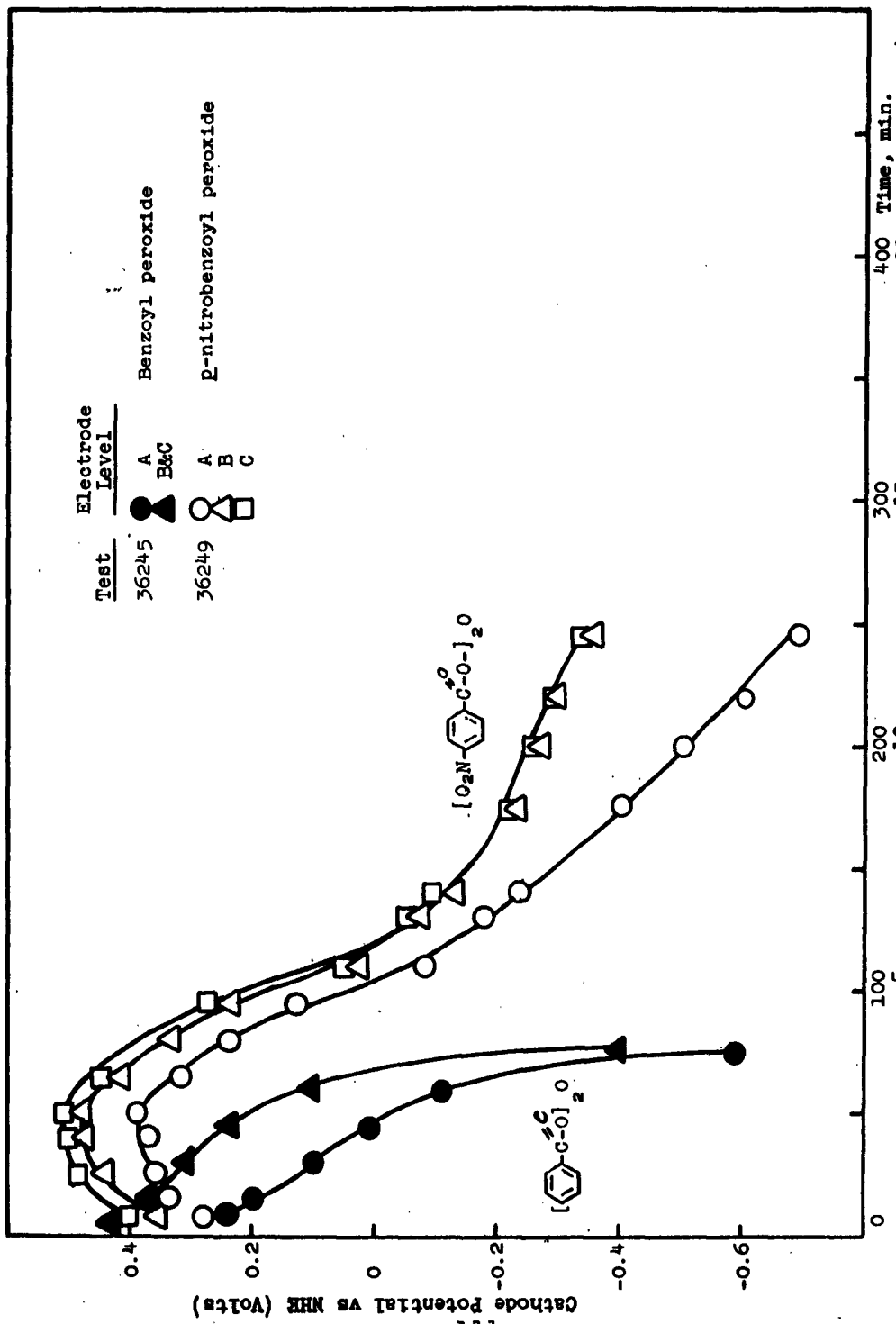


Figure 76 Chronopotentiometric plot of p-nitrobenzoyl peroxide and benzoyl peroxide in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp./g.

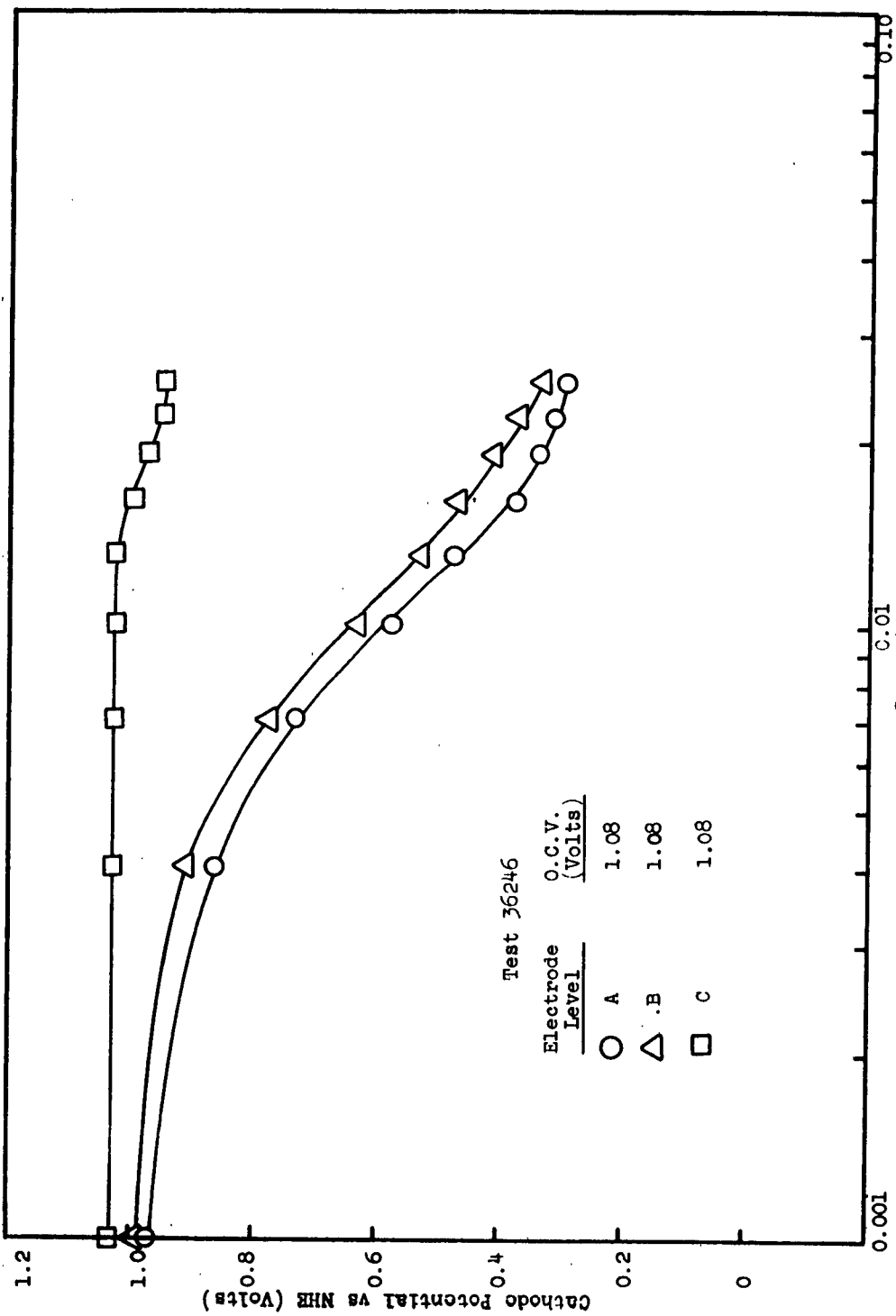


Figure 77 Voltage-current relationship of 1.25 g. of 40% peracetic acid in 2 M Mg(ClO₄)₂ electrolyte in cell "D" to 0.025 amps.

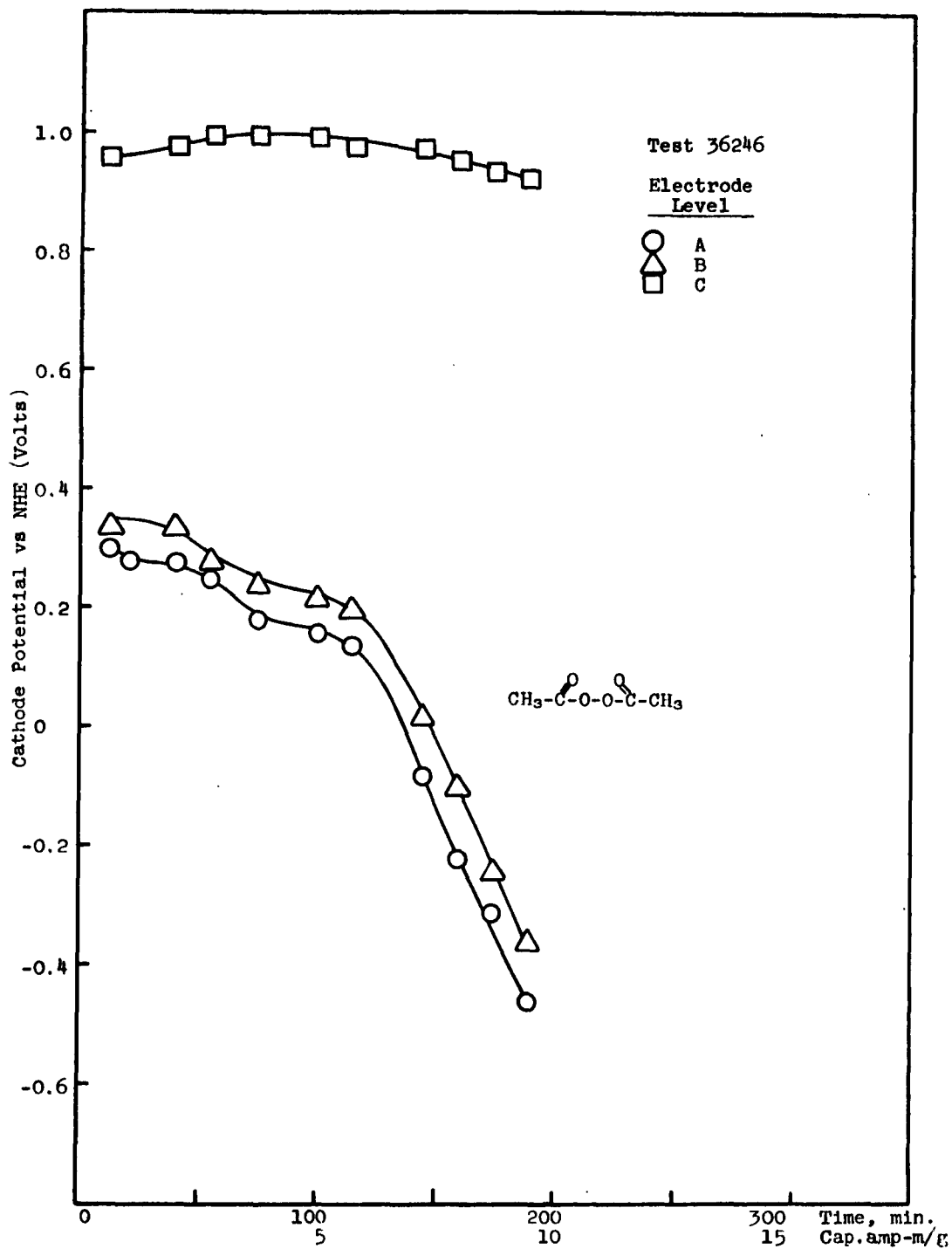


Figure 78 Chronopotentiometric plots of peracetic acid in cell "D" in 2M Mg(ClO₄)₂ electrolyte at 0.05 amp./g.

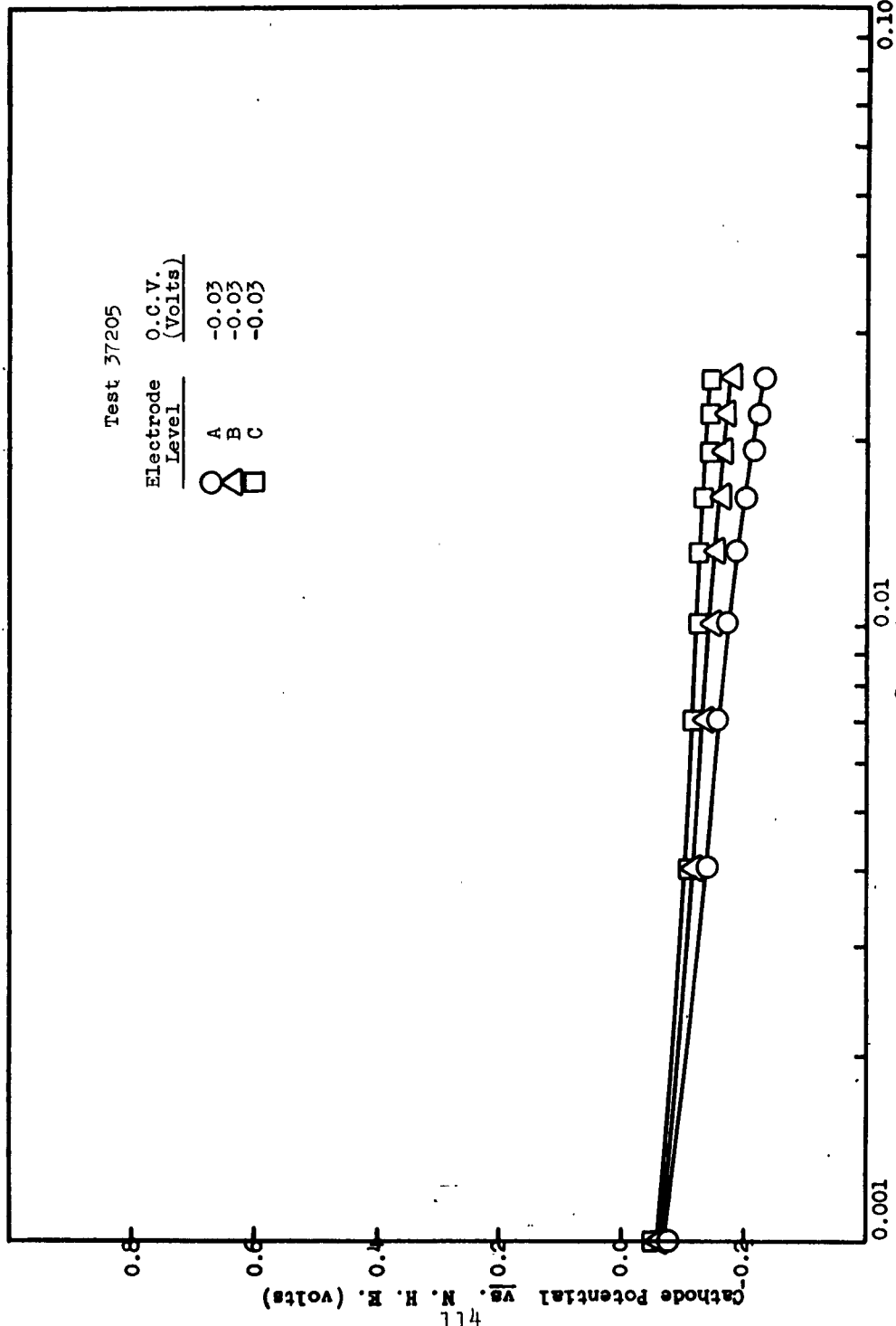


Figure 79 Voltage-current relationship of 0.5% sample of m-dinitrobenzene in cell "D" 1:9 methanol: 168 g/l aqueous NH₄Br electrolyte to 0.025 amps.

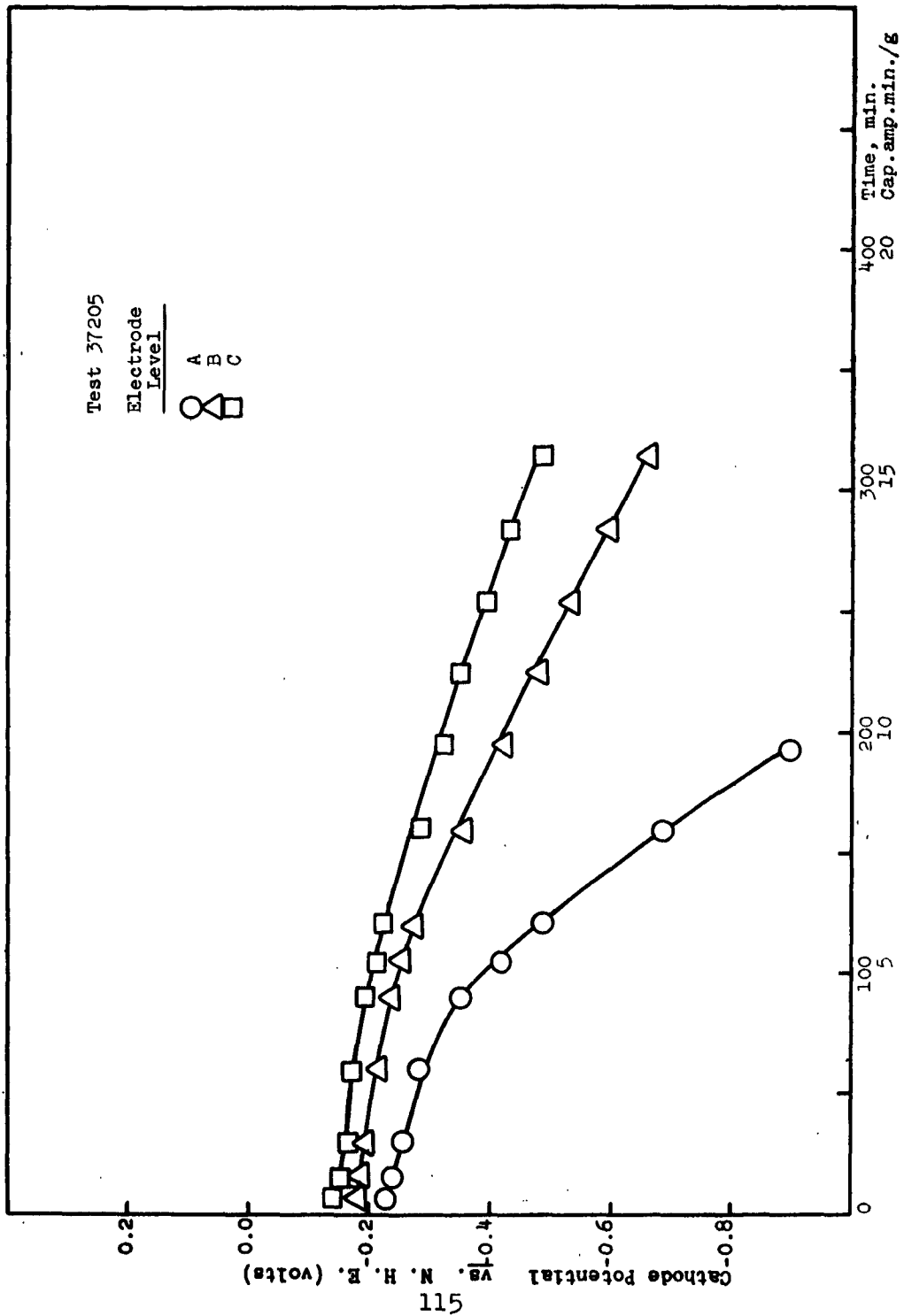


Figure 80 Chronopotentiometric plots of dinitrobenzene in cell "D" in 1:9 Methanol: 163 g/l aqueous NH_4Br electrolyte at 0.05 amp/g.

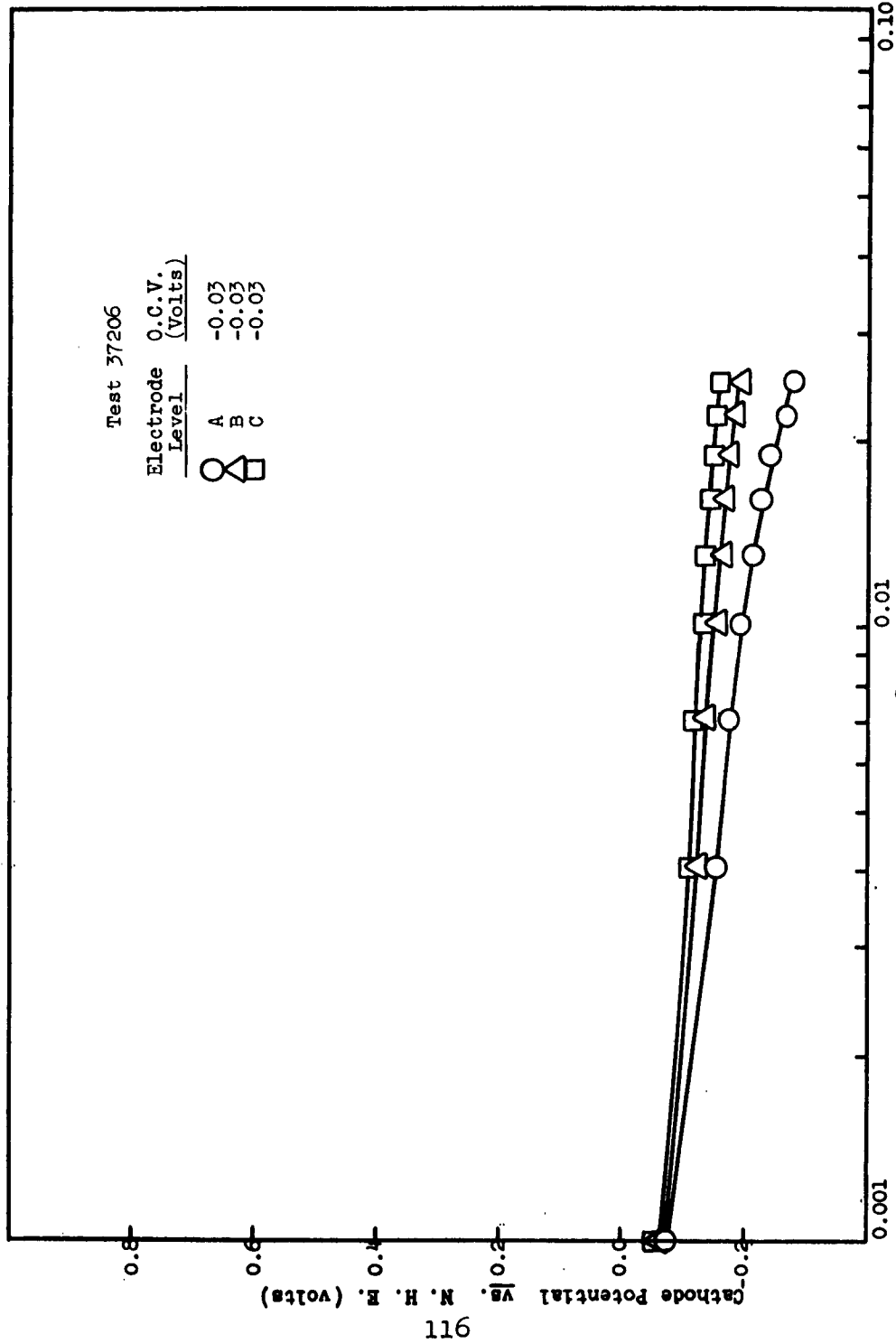


Figure 81 Voltage-current relationship of 0.5 g. m-dinitrobenzene in cell "D" in 1:4 methanol: 168 g/l aqueous NH_4Br to 0.025 amps.

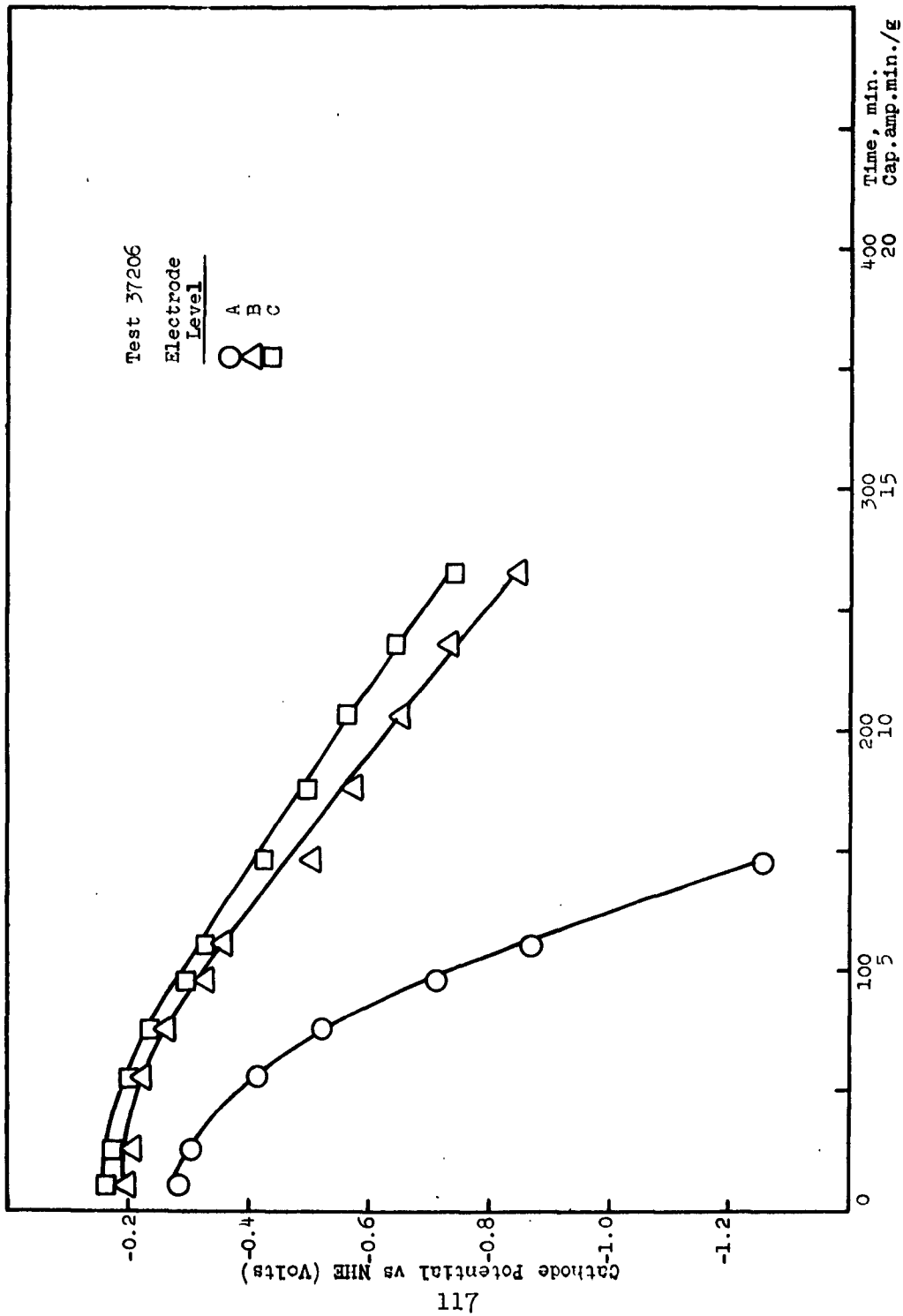


Figure Chronopotentiometric plots of *m*-dinitrobenzene in cell "D" in 1:4 methanol: 163 g/l aqueous NH_4Br at 0.05 amp/g.

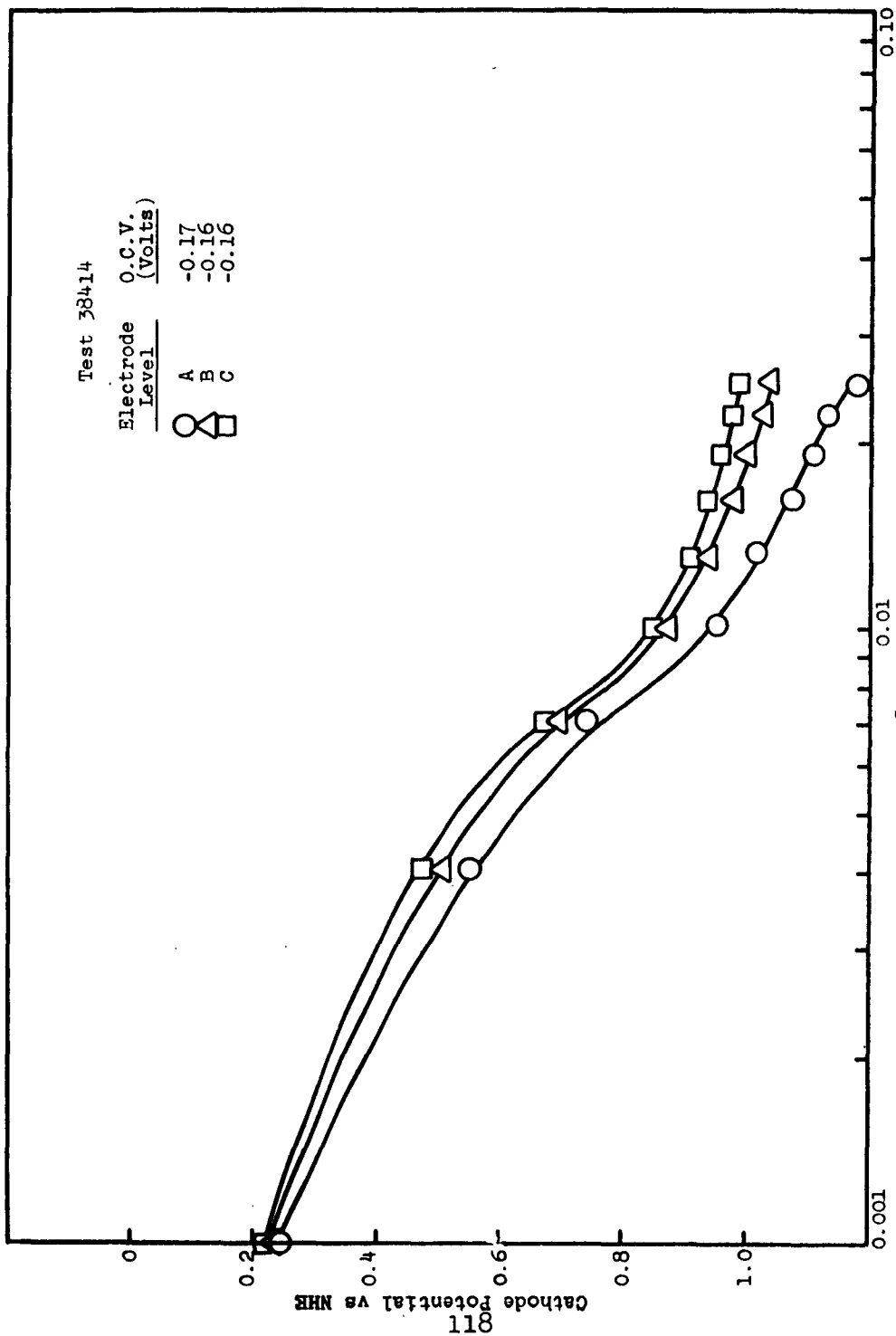


Figure 83 Voltage-current relationship of 0.5 g. sample of ferrocene in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

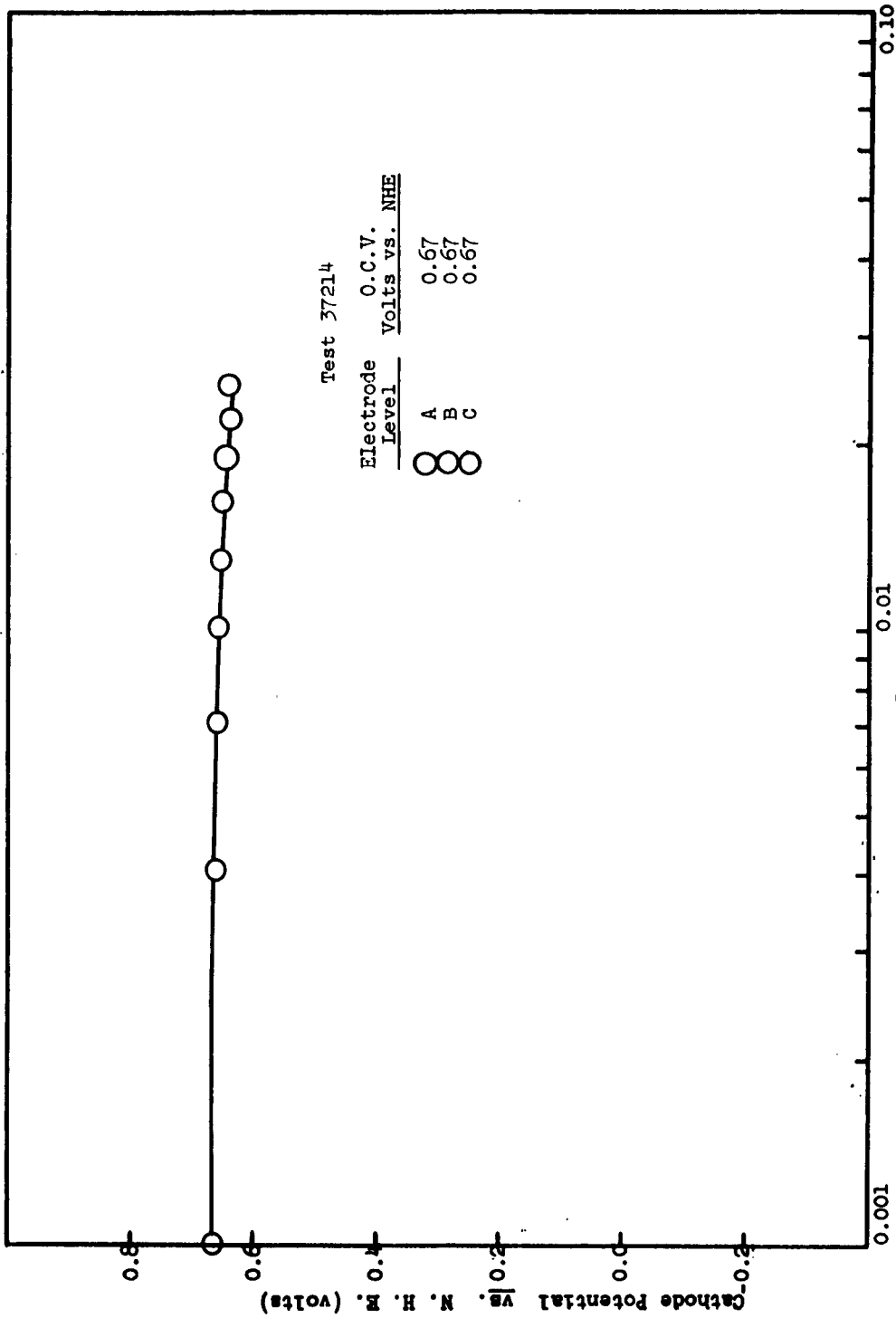


Figure 84 Voltage-current relationship of 0.5 g. samples of iodine in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

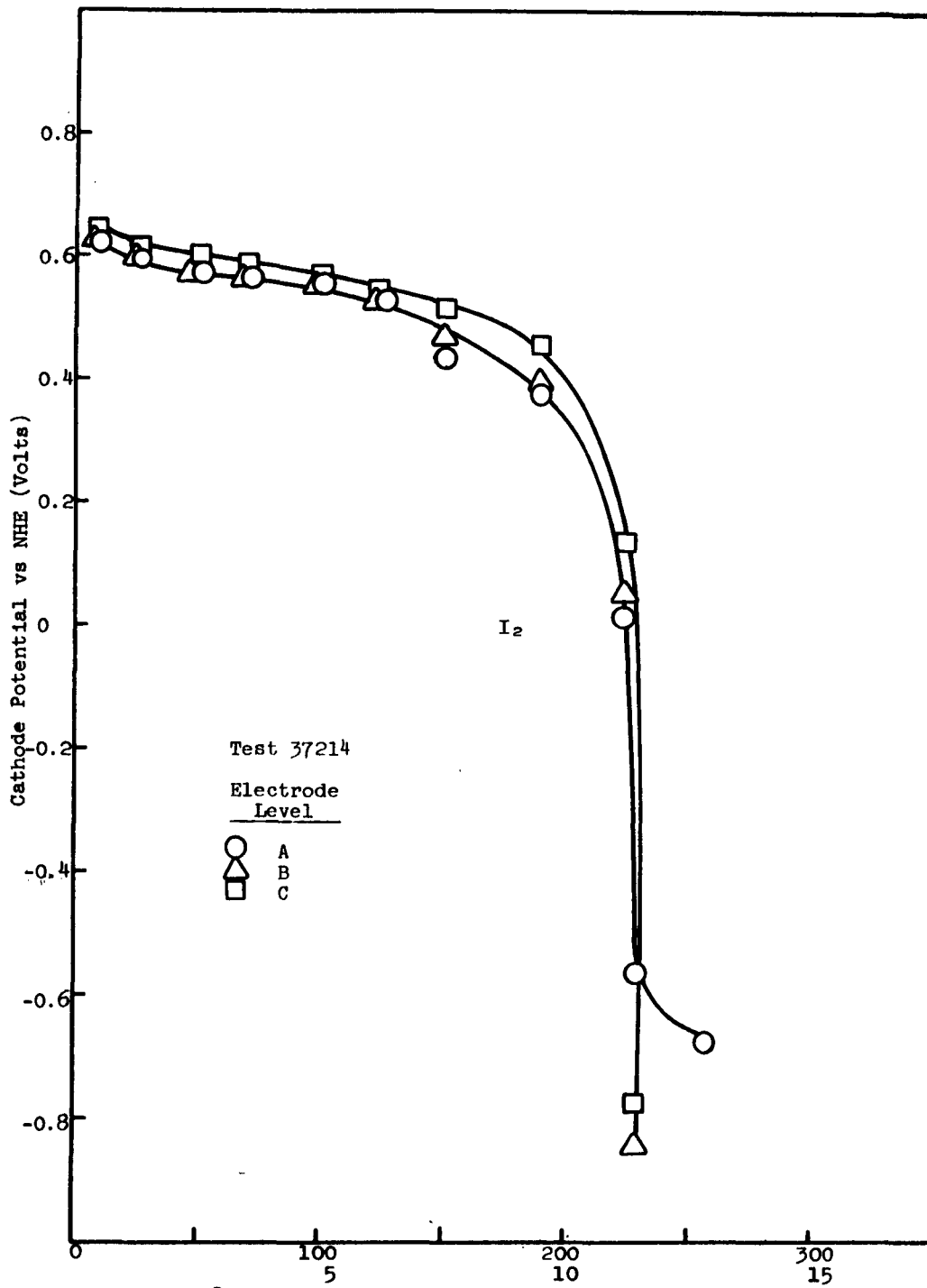


Figure 85 Chronopotentiometric plot of iodine in cell "D" in 168 g/l NH_4Br electrolyte at 0.05 amp/g

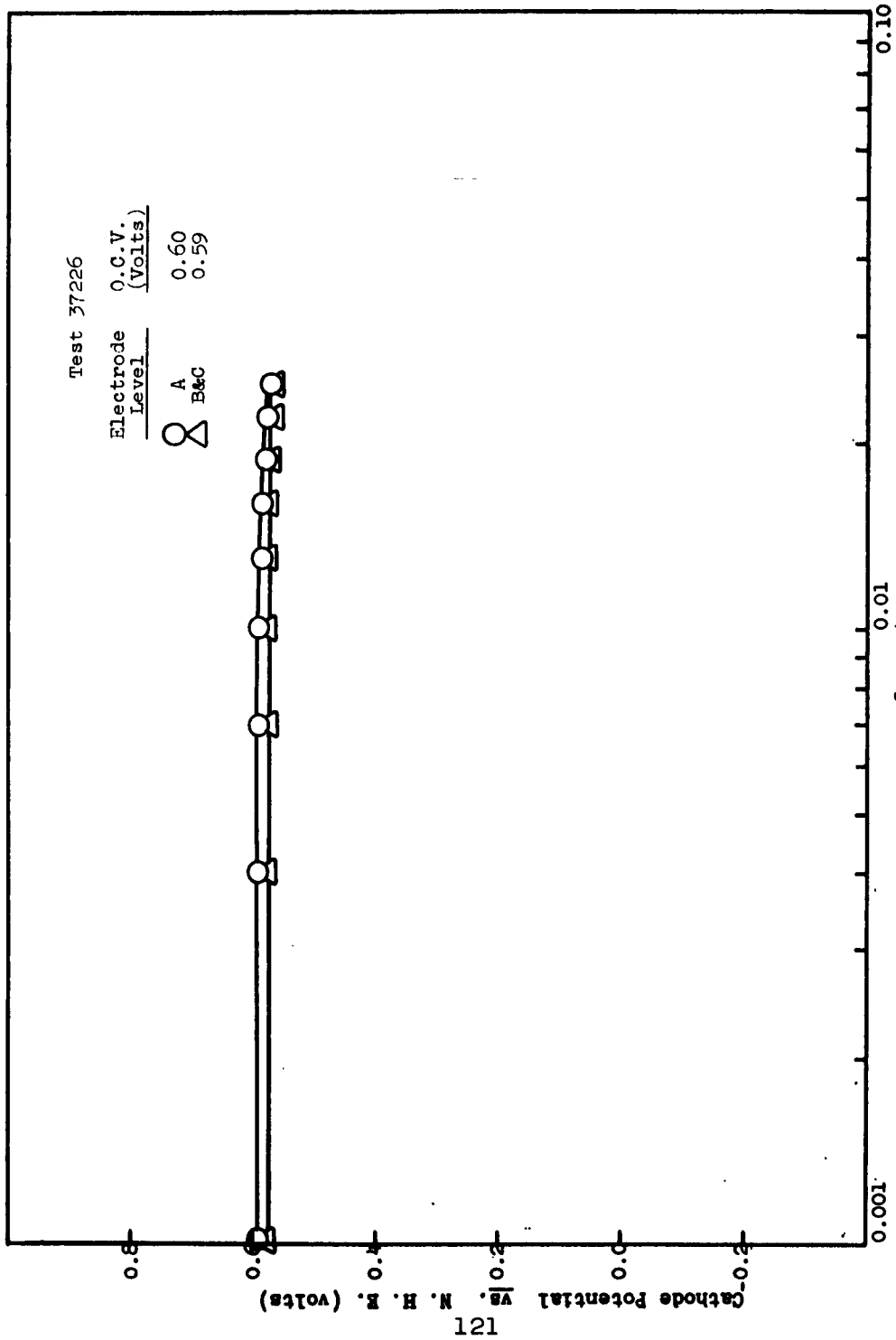


Figure 86 Voltage-current relationship of 0.5 g. iodine + 0.1 g. cadmium sulfide in cell "D" in 108 g/l NH₄Br to 0.025 amps.

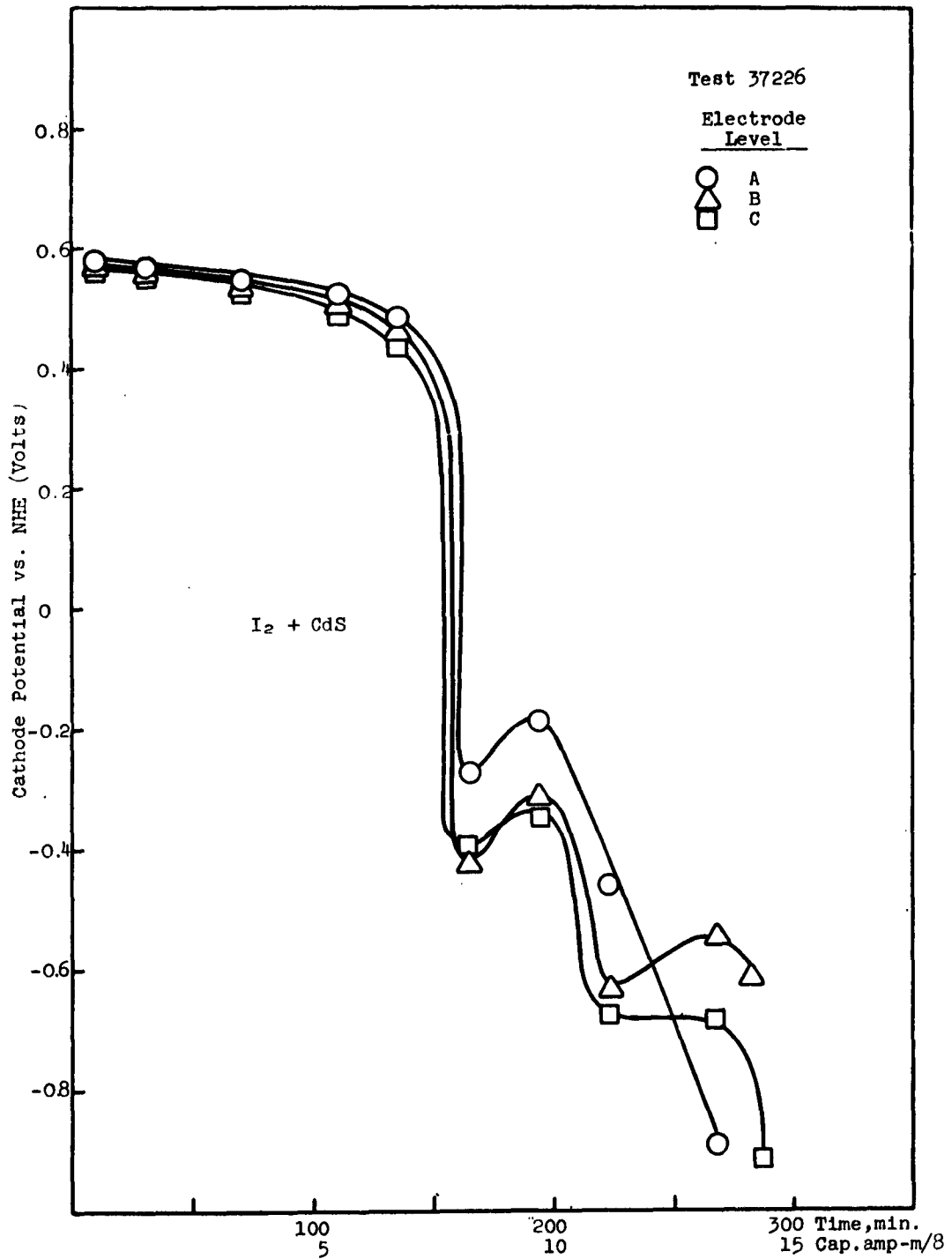


Figure 87 Chronopotentiometric plots of iodine with cadmium sulfide catalyst in cell "D" in 168 g/l NH₄Br at 0.05 amp/g.

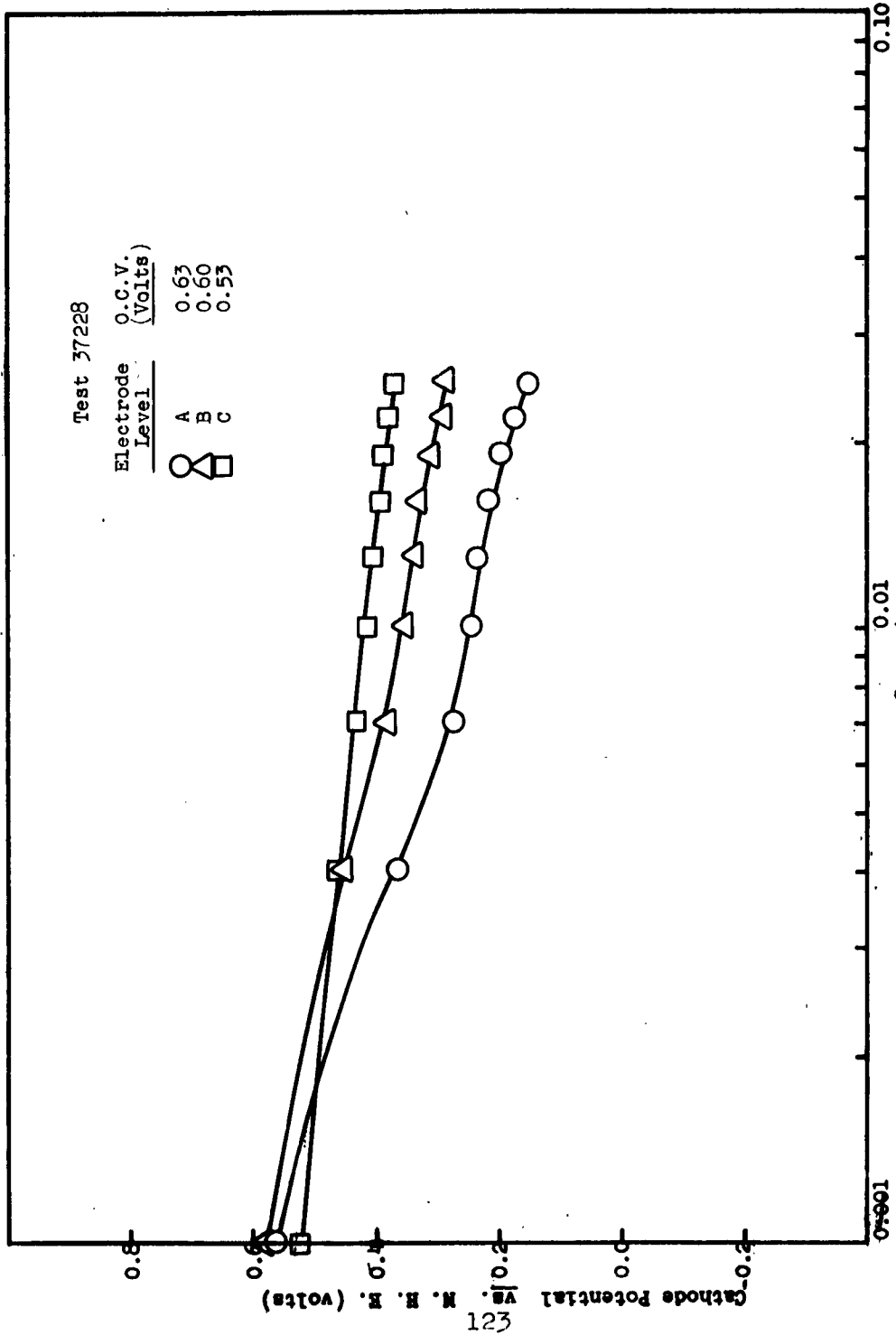


Figure 88 Voltage-current relationship of 0.5 g. sample of benzoquinone in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

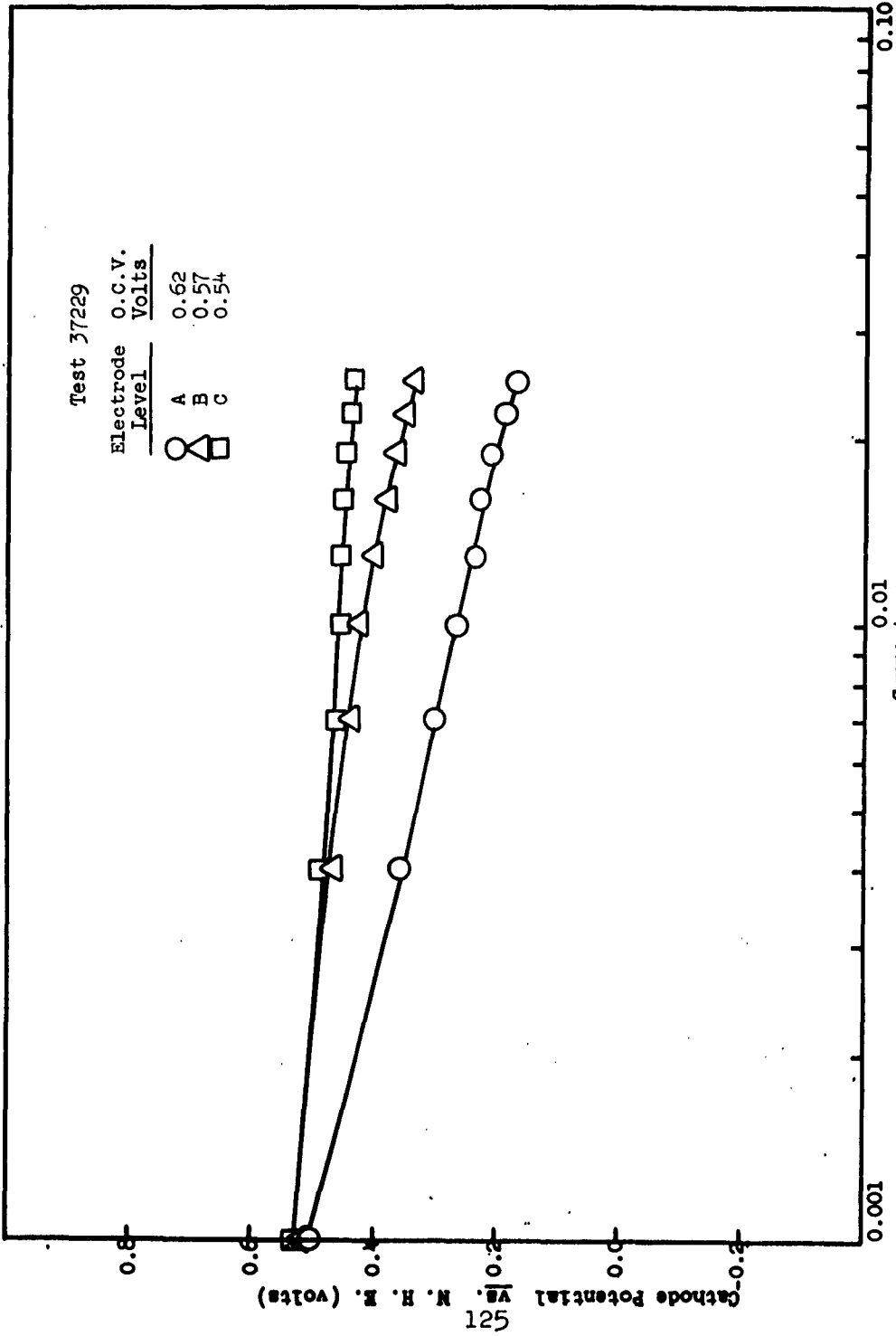


Figure 90 Voltage-current relationship of 0.262 g Benzoquinone plus 0.218 g o-DNB in cell "D" in 168 g/l NH₄Br to 0.025 amps.

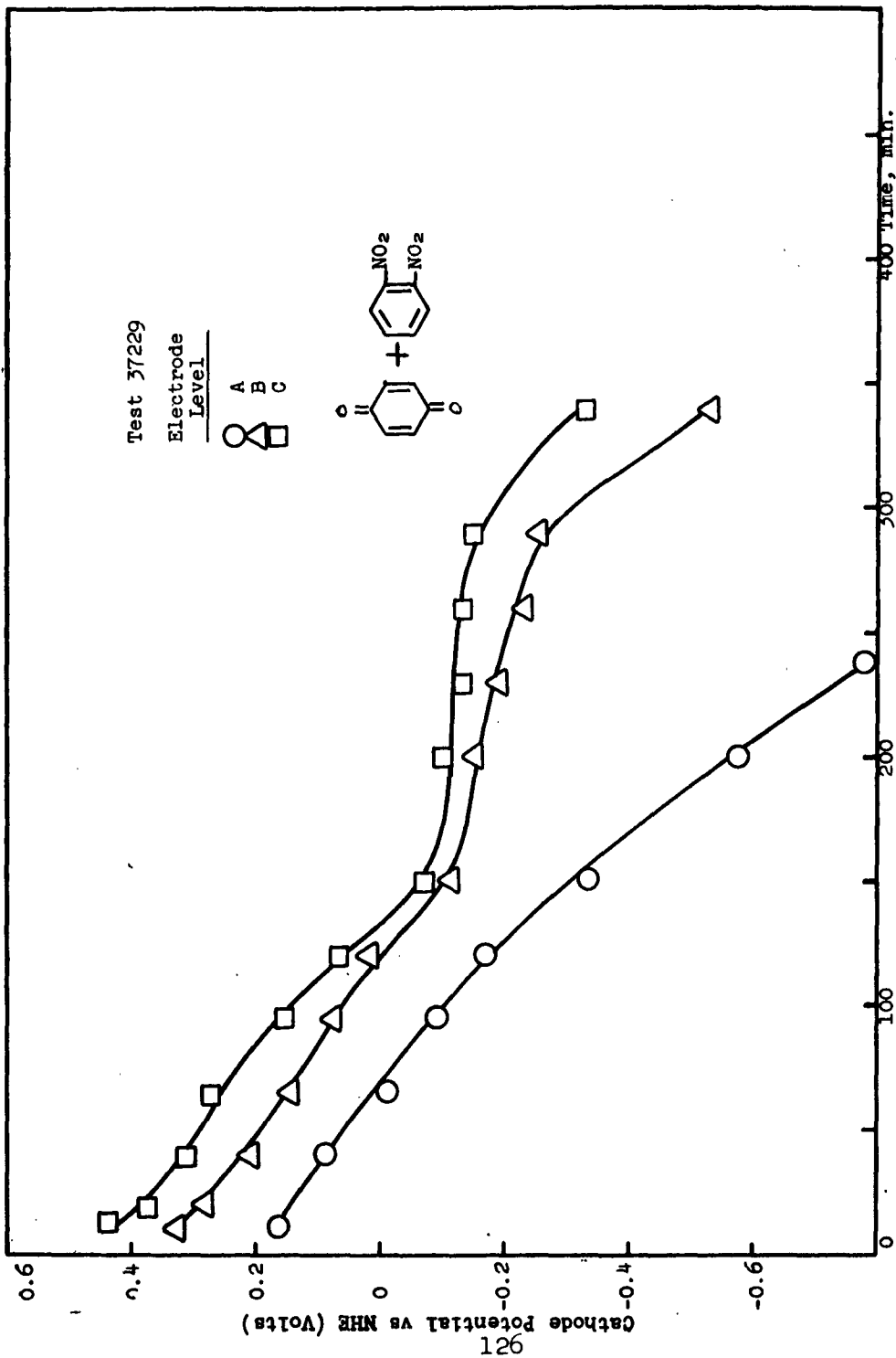


Figure 91 Chronopotentiometric plot of 0.28 benzoquinone plus 0.22 o-DNB in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

Test 37218

Electrode Level	O.C.V. (Volts)
A	0.30
B&C	0.30

○ A
△ B&C

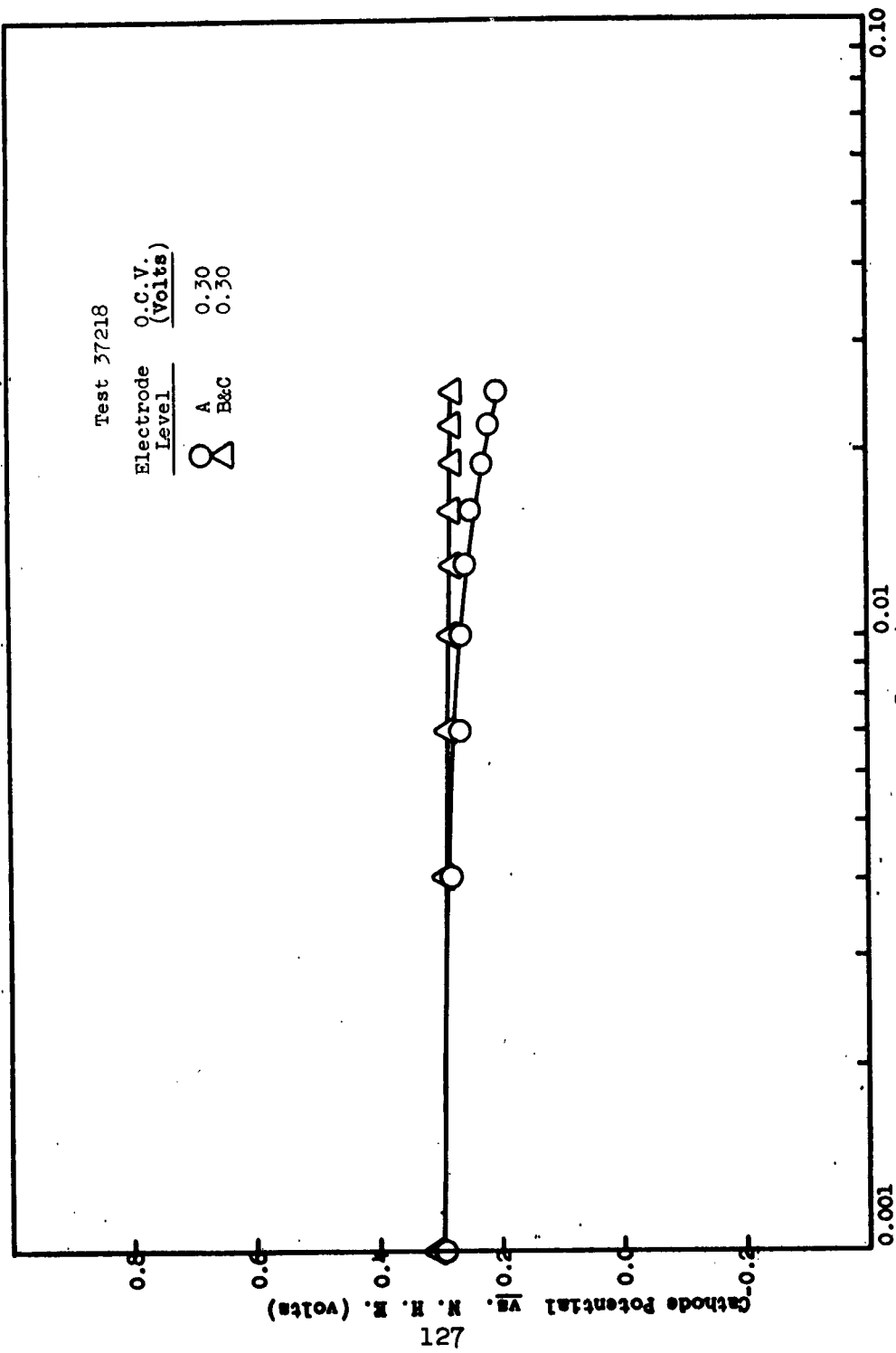


Figure 92 Voltage-current relationship of 0.5 g. sample of chloranil in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

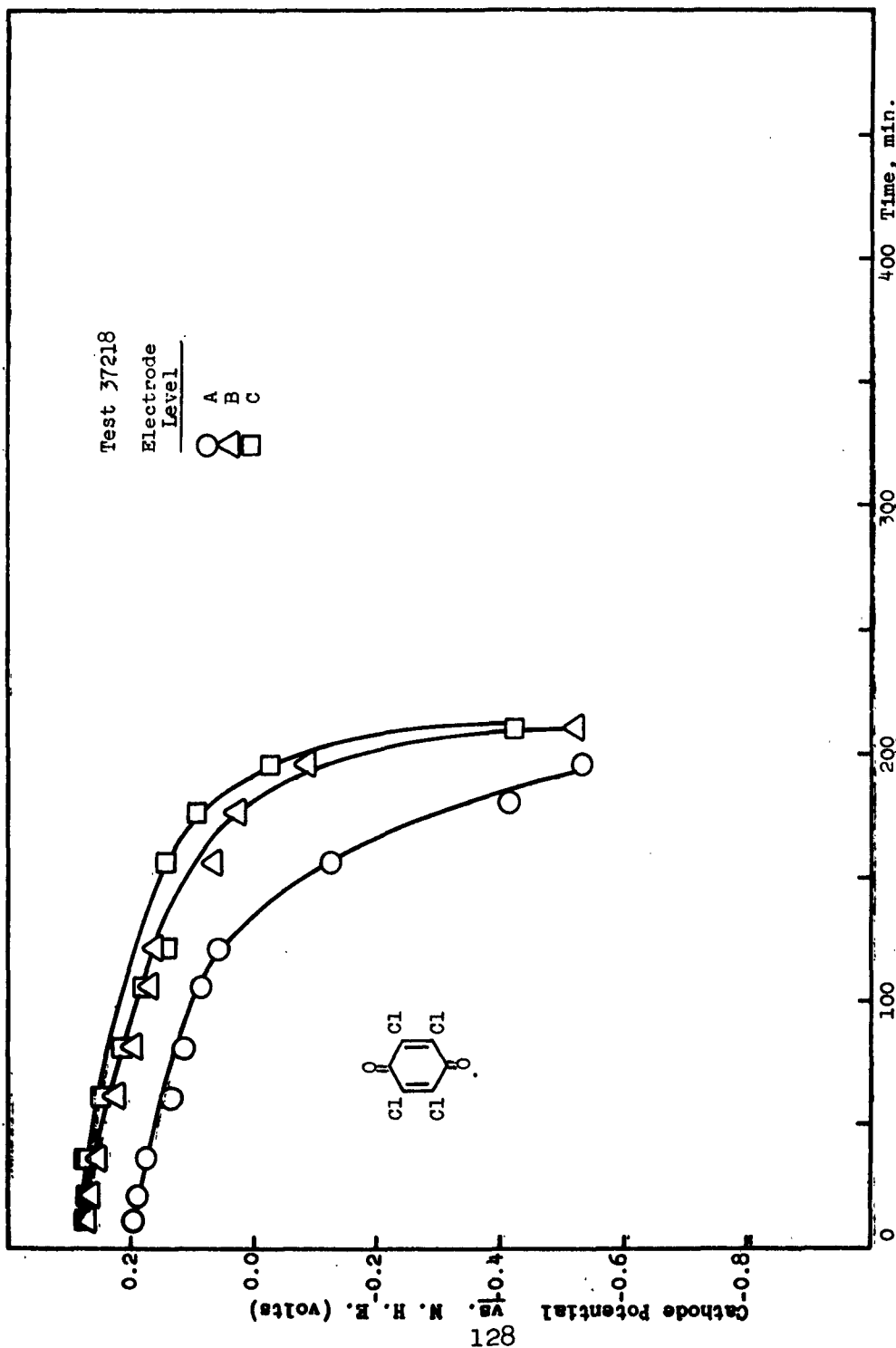
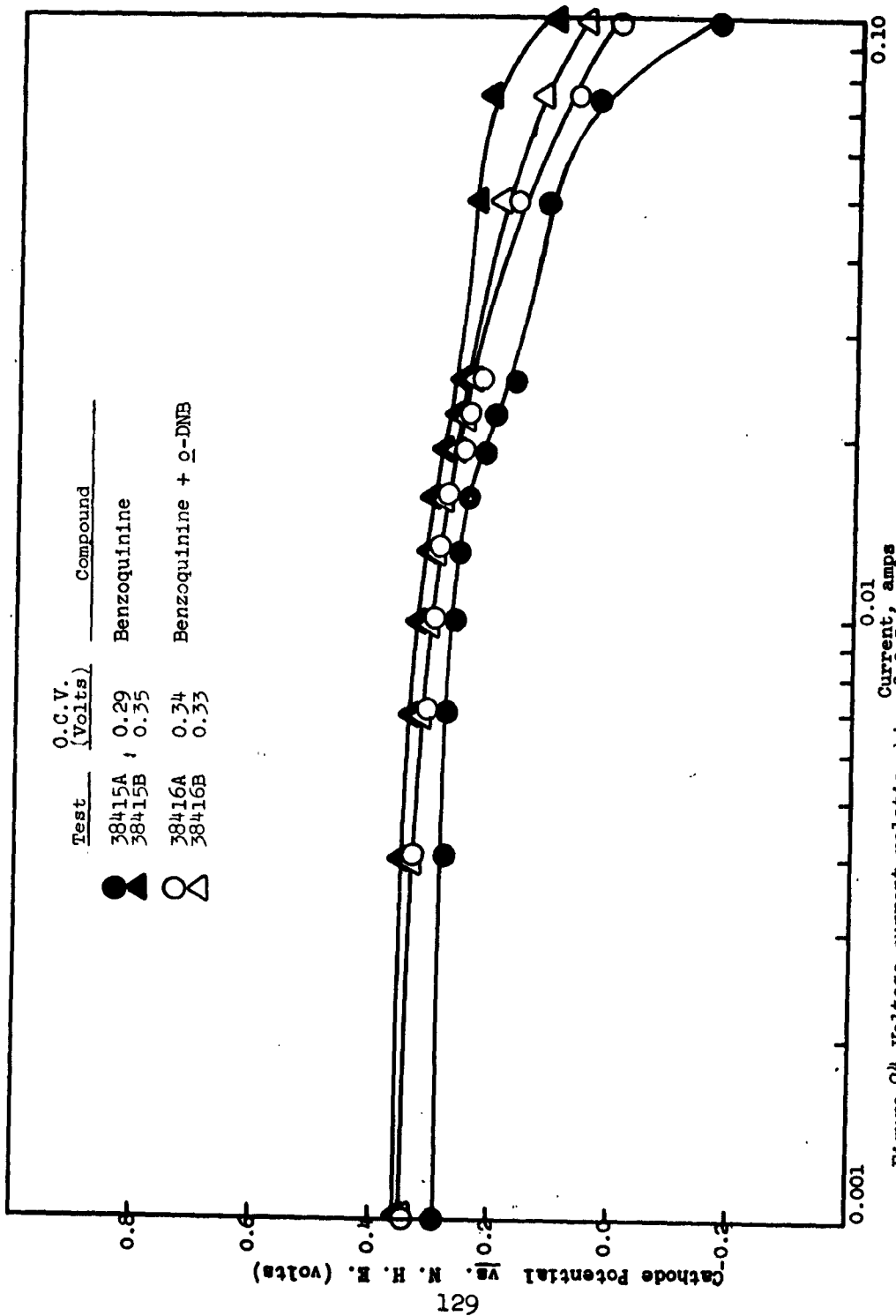


Figure 93 Chronopotentiometric plot of chloranil in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g



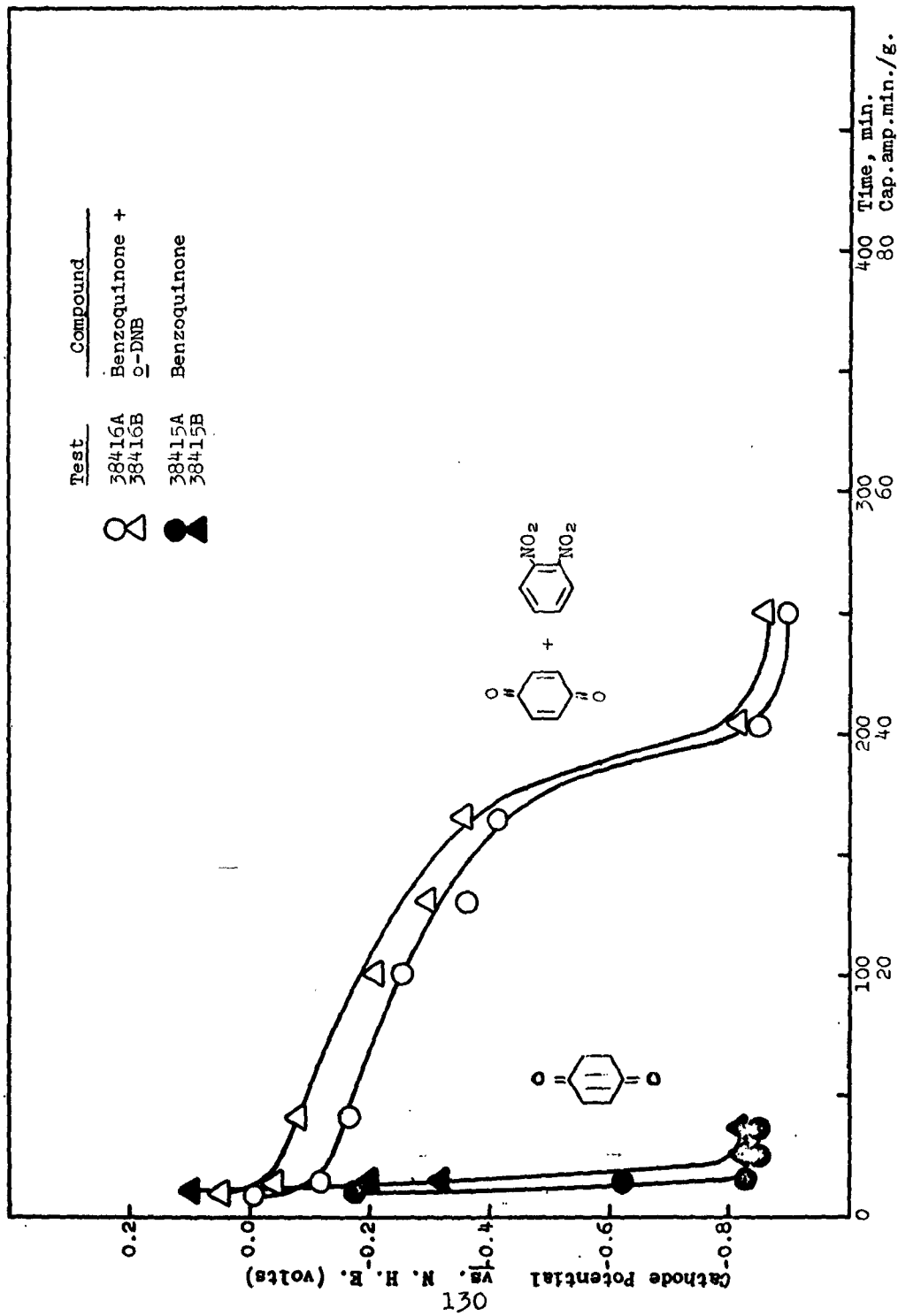


Figure 95 Chronopotentiometric plots of benzoquinone and .28 benzoquinone : .28 o-DNB in cell "C" at 50°C in 168 g/l NH₄Br at 0.200 amp/g.

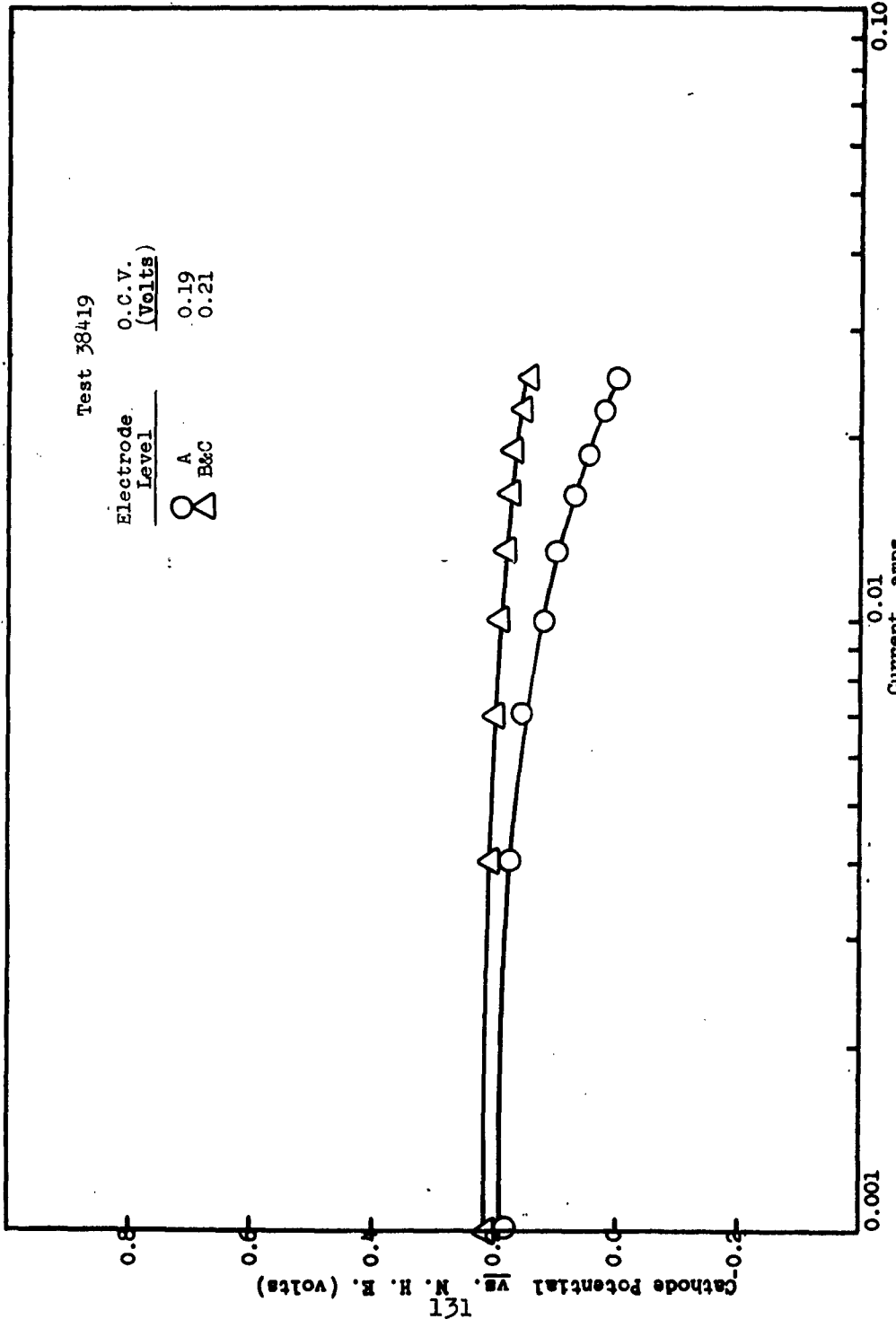


Figure 96 Voltage-current relationship of 0.5 g. sample of leuconic acid in cell "D" in 168 g/l NH₄Br electrolyte to 0.025 amps.

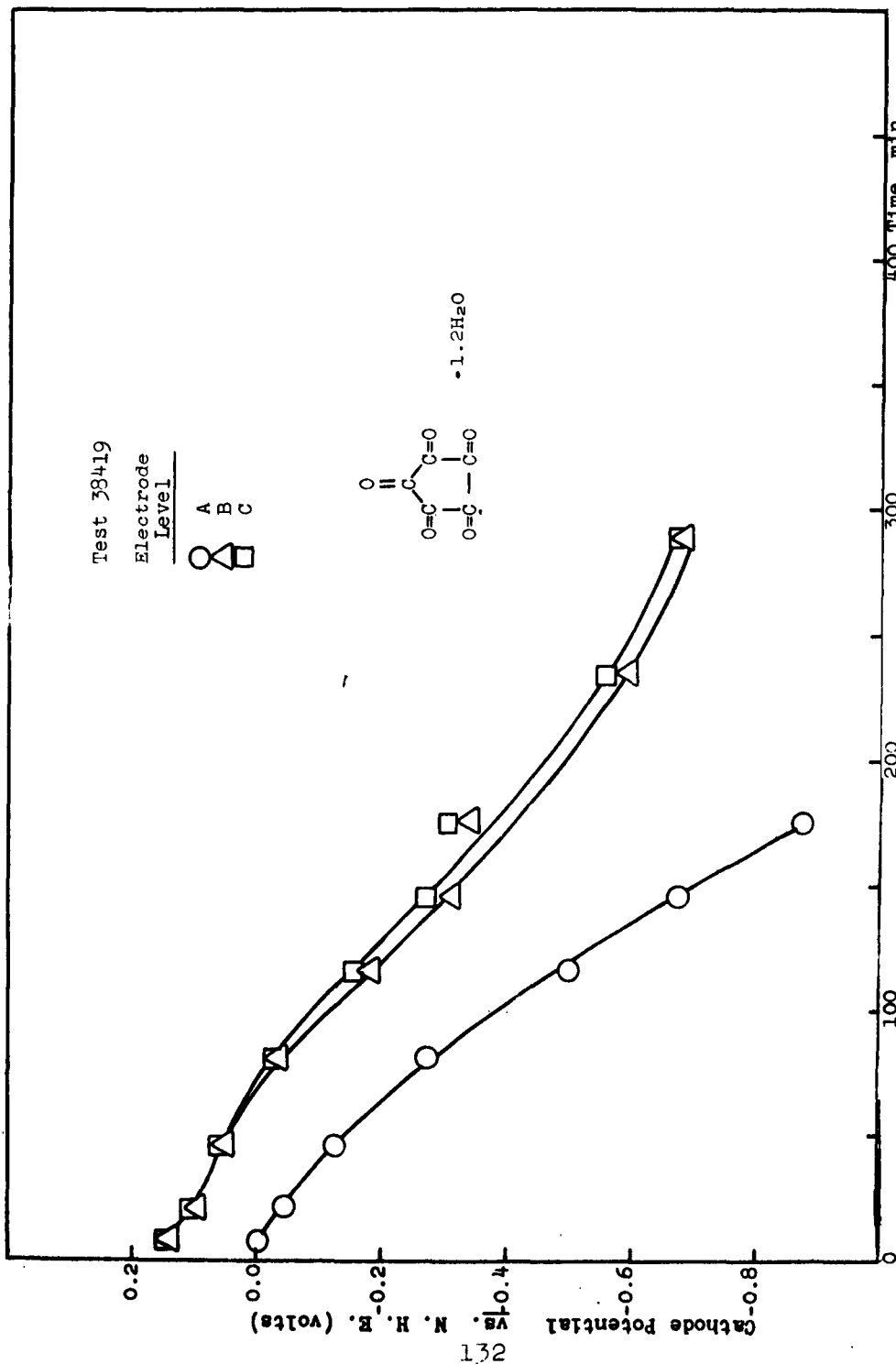


Figure 97 Chronopotentiometric plot of leuconic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

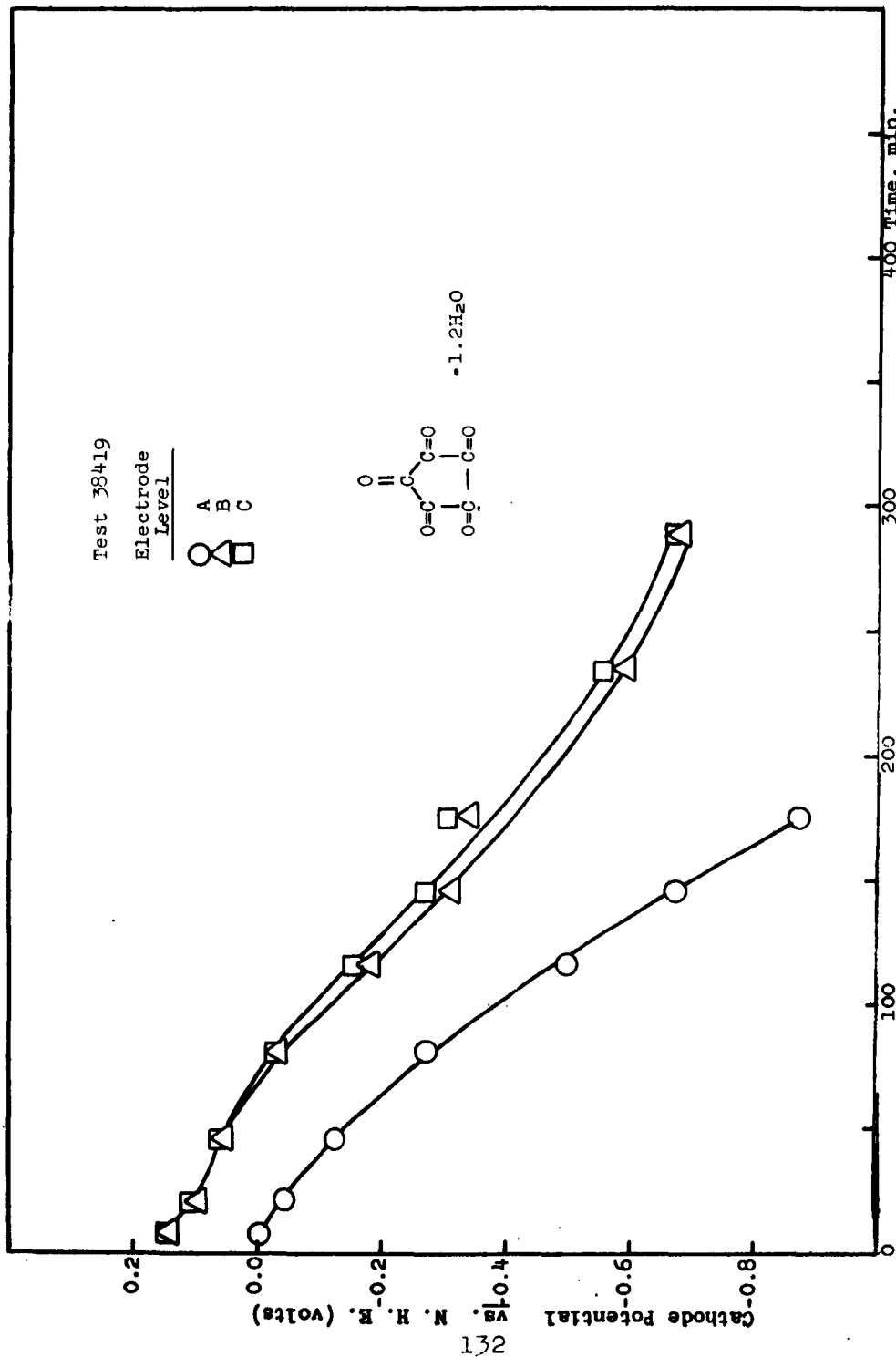


Figure 97 Chronopotentiometric plot of leuconic acid in cell "D" in 168 g/l NH₄Br electrolyte at 0.05 amp/g.

WITH CHROMATE INHIBITORS

Blank

Sat. with
m-DNB

25% Tetrasodium
Dinitropyro-
mellitate



1A

2A

3A

1 Week Exposure



1B

2B

3B

1 Month Exposure



1C

2C

3C

2 Months Exposure

Figure 98. Results of Corrosion Tests on AZ-10 Magnesium Size A Dry Cell Cans. With Inhibitor.

WITHOUT CHROMATE INHIBITORS

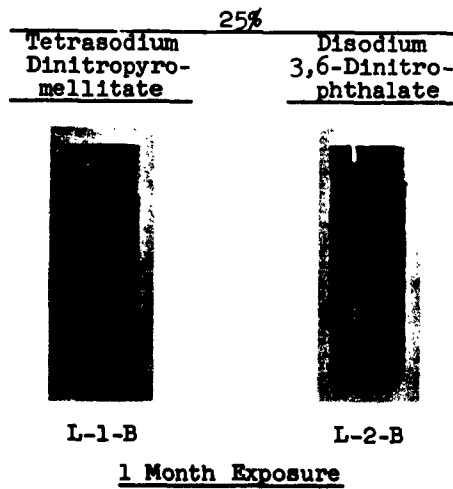
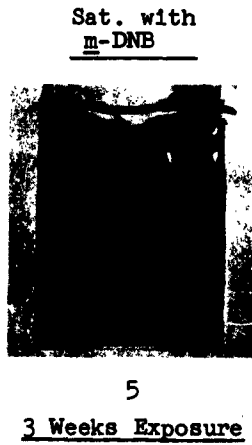
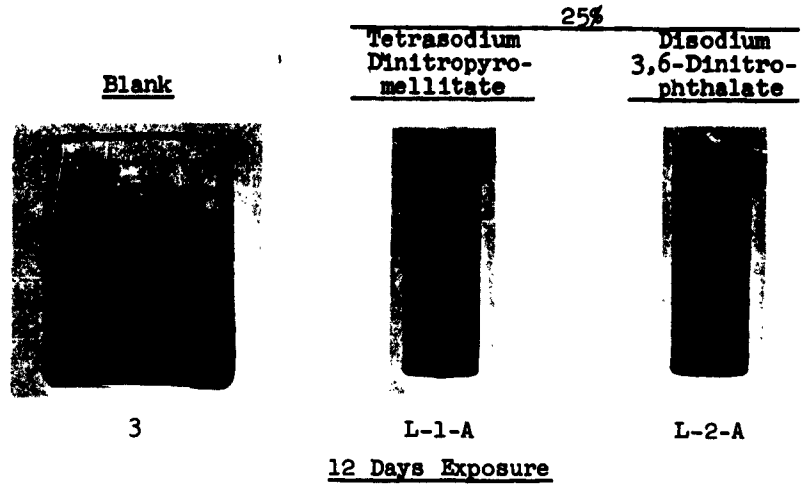


Figure 99. Results of Corrosion Tests on AZ-10 Magnesium Size A Dry Cell Cans. Without Inhibitor.

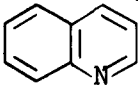
VIII. APPENDIX

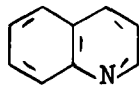
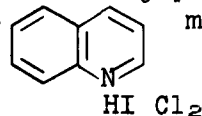
A. METHODS USED FOR PREPARATION OF COMPOUNDS TESTED

1. Halogen Addition Compounds

The simple addition compounds of the type $>NX_2$, where X is any halogen atom, were prepared by adding a slight excess of the halogen (as gas or in chloroform or carbon tetrachloride solution) to a chloroform or carbon tetrachloride solution of the free base, $>N$, at room temperature, filtering the resulting product, washing with solvent and drying at room temperature.

Compounds of the type $>NHXX_2$ were prepared in the same way by addition of the halogen to pulverized salt, $>NHX$, in carbon tetrachloride or chloroform and allowing the mixture to stand overnight. The product was recovered by filtering, and washed with solvent and dried at room temperature. The salts, $>NHX$, were prepared from the corresponding free bases by direct addition of HX to the free base in chloroform or carbon tetrachloride solution.

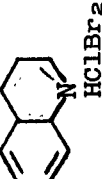
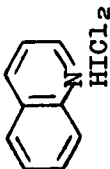

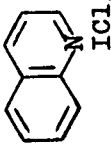

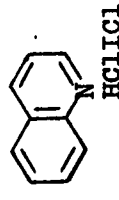
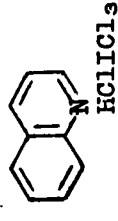
The addition compounds were analyzed for active halogen by reaction with KI. In some cases, the experimental value does not correspond to a 1:1 addition compound, in some cases being higher and in others lower. This difference could be caused by either retention of more or less than one mole of halogen by the carrier or by partial exchange of halogen in the HX of the carrier (e.g.  may contain some

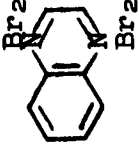

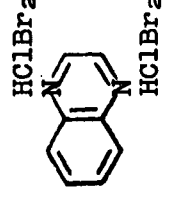
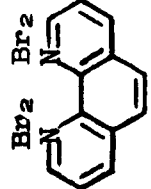
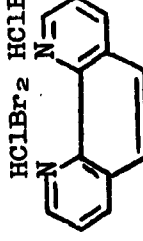



HClCl₂

). Analyses for total halogen in individual cases could

resolve the cause. The experimental values have been used for calculation of coulombic capacity. Data on compounds prepared this quarter follow (see next page). An attempt to prepare bromine addition compounds of 4-nitroimidazole was unsuccessful.

Compound	Theoretical 1:1 Structure	Color	mp, °C	Active Halogen, %	
				Calc. from 1:1 Compound	Found
Quinolinium chloride perbromide		yellow	60-90	49.3	42.9
Quinolinium iodide perchloride		yellow	140-58	21.7	26.1
Quinoline iodine chloride		tan	158-9	55.8	56.7
Quinoline iodine trichloride		yellow	97-125	64.5	54.7
Sample A			oil	64.5	49.4
Sample B					
Quinoline iodine bromide		gold	124-7	61.7	60.7
Quinolinium chloride iodine chloride		yellow-brown	98-101	49.7	42.2
Quinolinium chloride iodine trichloride		brown	oil	58.7	54.3

Compound	Theoretical 1:1 Structure	Color	mp, °C	Active Halogen, %	
				Calc. from 1:1 Compound	Found
Quinoxaline perbromide		yellow-green	104-8	71.2	52.8
Quinoxaliniun bromide perbromide		greenish-yel; turns red on standing	61-8	52.5	28.9
Quinoxaliniun chloride perbromide					
Sample A		yellow-brown	52-5	61.2	34.1
Sample B		brown	long range	61.2	59.0
1,10-Phenanthroline perbromide		orange	120-4	64.0	39.1
1,10-Phenanthrolinium chloride perbromide		yellow	136-45	55.8	48.8

<u>Compound</u>	<u>Theoretical 1:1 Structure</u>	<u>Color</u>	<u>mp, °C</u>	<u>Active Halogen, %</u>	
				<u>Calc. from 1:1 Compound</u>	<u>Found</u>
Quinolinium chloride iodine bromide	 HClBr	l. brown	56-92	55.7	49.7
Trimethylammonium chloride iodine chloride	$(\text{CH}_3)_3\text{NHClICl}$	yellow-brown	100-2	63.0	62.7
Trimethylammonium chloride iodine trichloride	$(\text{CH}_3)_3\text{NHClICl}_3$	dark yellow	180	71.0	67.7
Trimethylammonium chloride iodine bromide	$(\text{CH}_3)_3\text{NHClIBr}$	brown	~ 45	68.5	68.3

(1) Compound was prepared from aqueous HBr in CCl_4 . The product contained water of hydration and was unstable.

2. Leuconic Acid

Leuconic acid was prepared by oxidation of inositol with nitric acid, using the procedure of Contardi (Ref. 1). A mixture of 20 g. inositol in 60 ml 90% HNO₃ was refluxed for 30 minutes and then the solution evaporated to dryness on a steam plate. The product was dissolved in water, precipitated with ethanol, filtered and washed with ethanol. Solvent was removed by evacuation for 1 hour at 10 mm. followed by 90 minutes at 0.2 mm. at room temperature. The final product, a hydrate, had an elemental analysis corresponding to C₅O₅ · 1.2H₂O.

3. Salts of Acids

The salts of benzene carboxylic or sulfonic acids were prepared by titrating aqueous solutions of the acids to a phenolphthalein end point with sodium (or potassium) hydroxide, and recovering the salt by evaporation to dryness on a steam plate.

4. Trinitro-β-Naphthoic Acids

Dhar (Ref. 2) reported preparation of two, unidentified isomers of trinitro-β-naphthoic acid by nitration of β-naphthoic acid. Using Dhar's procedure, 125 ml. 70% HNO₃ was added to a slurry of 10 g. β-naphthoic acid in 200 ml. conc. H₂SO₄ slowly until the temperature reached 85°C and there was complete solution. The solution was cooled and kept at 30-40° until all the nitric acid was added and the solution allowed to sit 4 days. The solid product (product 1) which separated was removed by filtration and the filtrate poured onto ice. Product 2 was removed from the aqueous acid by filtration. Addition of more water to the filtrate precipitated product 3. Data on the products which were not analyzed or identified further, are below.

<u>Product</u>	<u>Color</u>	<u>mp, °C*</u>	<u>Weight Grams</u>	<u>Acid Equivalent **</u>
1	Yellow	259-61.	3.5	300
2	Pale Yellow	200-215 (d)	3.6	305
3	Yellow	190-215 (d)	3.1	310

* Dhar gives product 1, mp 220° and product 2, mp 215°.

** Calculated for trinitro substituted acid is 307.

IX. REFERENCES

- 1.) A. Contardi, Gazz. chim. ital. 51, I, 109 (1921); C.A. 15, 3073.
- 2.) S. N. Dhar, J. Chem. Soc. 117, 1001 (1920); C.A. 14, 3404.

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<p>AD- Monasanto Research Corp., Everett, Mass. RESEARCH ON ORGANIC DEPOLARIZERS, Rept. No. 6 1 October 1962 - 31 December 1962, by B. A. Gruber and E. A. McElhill 139 pages incl. illus, tables, & refs. Contract DA 36-039-SC-87336 DA Proj. 3A-99-09-002</p> <p>Unclassified Report</p> <p>Half-cell measurements on all depolarizers tested during the contract have been tabulated. No consistent quantitative correlations were found between half-cell characteristics and the electronic strengths of substituents on nitrobenzenes or on other type depolarizers. Stable halogen addition compounds of heterohalides and of chlorine were prepared and tested. Various halogen addition compounds with the structure -NHX₂ have proved stable in dry storage and in electrolyte for extended periods. Inhibition of corrosion of magnesium by tetrasodium dinitropyromellitate and other similar soluble</p> <p>(over)</p>	<p>UNCLASSIFIED</p> <p>1. Batteries</p> <p>2. Depolarizers</p> <p>I. Gruber, B. A.</p> <p>II. U. S. Army Electronics R/D Laboratories</p> <p>Contract DA 36-039-SC-87336</p>	<p>UNCLASSIFIED</p> <p>1. Batteries</p> <p>2. Depolarizers</p> <p>I. Gruber, B. A.</p> <p>II. U. S. Army Electronics R/D Laboratories</p> <p>Contract DA 36-039-SC-87336</p>	<p>UNCLASSIFIED</p> <p>1. Batteries</p> <p>2. Depolarizers</p> <p>I. Gruber, B. A.</p> <p>II. U. S. Army Electronics R/D Laboratories</p> <p>Contract DA 36-039-SC-87336</p>	<p>UNCLASSIFIED</p> <p>1. Batteries</p> <p>2. Depolarizers</p> <p>I. Gruber, B. A.</p> <p>II. U. S. Army Electronics R/D Laboratories</p> <p>Contract DA 36-039-SC-87336</p>	<p>UNCLASSIFIED</p> <p>1. Batteries</p> <p>2. Depolarizers</p> <p>I. Gruber, B. A.</p> <p>II. U. S. Army Electronics R/D Laboratories</p> <p>Contract DA 36-039-SC-87336</p>
<p>nitro compounds was confirmed by extended corrosion tests. A slight increase in reduction efficiency of benzoquinone was realized in benzoquinone o-DMB mixes. Methanol (10 and 25% concentration) in ammonium bromide electrolyte lowered the reduction efficiency of m-DMB.</p>	<p>UNCLASSIFIED</p> <p>nitro compounds was confirmed by extended corrosion tests. A slight increase in reduction efficiency of benzoquinone was realized in benzoquinone o-DMB mixes. Methanol (10 and 25% concentration) in ammonium bromide electrolyte lowered the reduction efficiency of m-DMB.</p>	<p>UNCLASSIFIED</p> <p>nitro compounds was confirmed by extended corrosion tests. A slight increase in reduction efficiency of benzoquinone was realized in benzoquinone o-DMB mixes. Methanol (10 and 25% concentration) in ammonium bromide electrolyte lowered the reduction efficiency of m-DMB.</p>	<p>UNCLASSIFIED</p> <p>nitro compounds was confirmed by extended corrosion tests. A slight increase in reduction efficiency of benzoquinone was realized in benzoquinone o-DMB mixes. Methanol (10 and 25% concentration) in ammonium bromide electrolyte lowered the reduction efficiency of m-DMB.</p>	<p>UNCLASSIFIED</p> <p>nitro compounds was confirmed by extended corrosion tests. A slight increase in reduction efficiency of benzoquinone was realized in benzoquinone o-DMB mixes. Methanol (10 and 25% concentration) in ammonium bromide electrolyte lowered the reduction efficiency of m-DMB.</p>	<p>UNCLASSIFIED</p> <p>nitro compounds was confirmed by extended corrosion tests. A slight increase in reduction efficiency of benzoquinone was realized in benzoquinone o-DMB mixes. Methanol (10 and 25% concentration) in ammonium bromide electrolyte lowered the reduction efficiency of m-DMB.</p>