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TITLE

OXYGEN ELECTRODES AS DEPOLARIZED CATHODES IN CHLOR-ALKALI CELLS

13

V. EFFECT OF SILVER LOADING ON PERFORMANCE

PAGES
IN FULL
REPORT

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REVIEWER'S SIGNATURE

*J. R. Meyer*This
report
is:☒

INTERIM

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FINAL

and mainly:

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NEW

☐

REVIEW

DESCRIPTIVE SUMMARY
WITH CONCLUSIONS:

(Include in this space references to data books, and to earlier related reports, patents and publications.)

Silver plated 3 micron pore size porous nickel has been shown to give excellent performance as an oxygen electrode in lab chlor-alkali cells using asbestos flow-through diaphragms.

SAFETY: Normal precautions for handling hot caustic and brine were taken.

ECOLOGY: Cathodes of this type would not cause changes from current practice with respect to ecology.

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INTRODUCTION

In several reports¹⁻⁴ we have discussed the use of oxygen electrodes as cathodes in chlor-alkali cells, and have described the preparation and evaluation of several different types of electrodes. In the last report⁴ we gave evidence for the electrode performance relative to our goal of >0.6 volts depolarized at 0.5 amp/in² being limited by the available surface area of the electrodes. Consequently we have obtained porous nickel with a higher surface area than that used previously and, using electrolessly deposited silver as catalyst, have fabricated and evaluated several electrodes. The results of this work are reported here.

EXPERIMENTAL

Electroless plating was used to deposit the catalyst. This was accomplished by immersing the nickel substrate (Gould, Inc., 3 micron pore size, 10 mils thick) in a conventional cyanide silver plating bath, which also contained free silver metal. Two sets of electrodes were then constructed - "small" electrodes (0.11 in²) and our standard 3 in² electrodes. Silver loadings on the small electrodes were⁵: A, 0 oz/ft²; B, 0.50 oz/ft²; C, .79 oz/ft²; D, .89 oz/ft²; E, 1.21 oz/ft² and about 0.5-0.8 oz/ft² for the large electrodes, GMD 1 and GMD 2.

The small electrodes were evaluated using a modified version of the apparatus described previously.³ Figure 1 shows the details of this apparatus. The gas electrodes are mounted in milled Swazelock nuts,³ but a second section of stainless steel tubing has been added. Previously, the electrodes studied were relatively porous, allowing oxygen to bubble through freely. Under those conditions, no problems were experienced due to a build-up of the residual inert gases in the oxygen, and switching from operation on oxygen to nitrogen was straightforward. However, the electrodes studied here allow no gas bubbling under most of the pressures used, and consequently, it was necessary to add an auxiliary gas outlet tube. The outlet end of this tube contains a metering valve which allows for fine adjustment of flow rate. The gas pressure on the back of the electrode can be measured accurately by means of the Wallace-Tiernan gauge. The PAR Model 373 potentiostat was used as before, with the stainless steel tubing used both for the electrical lead and gas supply to the gas electrode. The reference electrode is a Beckman Lazaran Ag/AgCl electrode, and the auxiliary electrode is a 1" x 2" platinum screen.

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It is not necessary to insulate the stainless steel tubing since a) the rate of the oxygen reduction reaction on steel is negligible under these conditions and b) we generally operate at potentials well below those at which significant hydrogen evolution occurs on stainless steel (>-1.1 volts vs Ag/AgCl). Thus there are no interfering reactions taking place on the tubing.

The large electrodes were operated in the usual way,^{4,5} one with a duPont Nafion ion exchange membrane, and one with a conventional asbestos flow-through diaphragm.

RESULTS AND DISCUSSION

In an earlier report⁴ we described the operation of gas diffusion electrodes in some detail, and indicated that for these types of electrodes (with our test conditions), the surface area and oxygen pressure could be limiting factors. Further, we argued that an insensitivity of the voltage-current relationship to changes in the oxygen pressure was indicative of activation control and that, for a given catalyst, performance could be improved only by increasing the surface area of the electrode. However, a change in performance due to a change in oxygen pressure does not rule out the possibility of partial activation control, i.e., a state of mixed activation-mass transfer control.

Increasing the gas pressure can have two effects. One is to increase the mass transfer rate of oxygen (through the thin electrolyte films which exist in the pores of the electrode) to the surface where reaction occurs. The second is to vary the position of the gas-liquid interface within the electrode. This effect is important if the catalyst is not distributed uniformly throughout the structure, as is the case here where the silver has been deposited primarily on the electrolyte face of the electrode.

Consider now the voltage-current curves for electrodes A-E, shown in Figures 2-6.

Electrode A, Figure 2, contains no silver, and shows little depolarization in the 0.5 amp/in^2 region. Note that, above about 0.15 amp/in^2 , increasing gas pressure has little effect on the depolarization, which is consistent with activation control, the expected rate limiting step in the absence of a catalyst.

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Electrodes B and C, Figures 3 and 4, perform somewhat similarly to each other, although it is necessary to operate at slightly higher pressures for C to achieve the same performance as B. In both cases the depolarization is of the order of 0.6-0.7 volts at 0.5 amp/in².

The performance of electrodes D and E is poorer than B and C, even at significantly higher gas pressures (Figures 5 and 6). The maximum depolarization is about 0.55 volts for electrode D, and about 0.45 volts for electrode E.

For each of electrodes B-E, increasing the oxygen pressure increases the performance significantly at the highest current densities, which demonstrates that mass transfer is a limiting factor in that region. At 0.5 amp/in², however, the effect of pressure is relatively small (for electrode E, the actual variation in depolarization is large, but note that the range of pressures used is much larger than for the other electrodes). In all cases the highest pressure used was that at which significant gas bubbling through the electrode occurred. This relatively small degree of dependence of the depolarization on the oxygen pressure (for each electrode) again argues for activation control being predominant in the 0.5 amp/in² and lower region, assuming a reasonable explanation can be offered for the necessity of using higher pressures to obtain similar performance on going from electrode B to E. That is, the performance at 7-8 psi is different for each electrode, whereas the mass transfer rate of oxygen should be the same at the same pressure.

The explanation of these differences is based on the effect that the silver plating has on the pore structure. Figure 7 shows three photomicrographs of porous nickel containing 0, 0.5, and 1.2 oz/ft² of silver, i.e., equivalent to electrodes A, B, and E. The black areas are pores, which are shadowed under the lighting conditions used. As the silver loading is increased, the black areas "fill-up", i.e., the pore size becomes smaller. The capillary pressure, which is the pressure of the electrolyte in a pore, is inversely proportional to the pore size, and can become quite large for small pores,⁴ e.g., ~15 psi for 1.5 micron radius pores. Since the silver is located predominantly near the electrolyte side of the electrode, and the gas pressure must be large enough to keep the liquid-gas interface near the catalyzed area in order to obtain acceptable performance, then the gas pressure required increases with increasing silver loading (i.e., decreasing pore size). Thus for these electrodes the minimum pressure needed for operation should also increase with increased silver loading, which is consistent with the experimental results.

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In addition, the surface area of a pore decreases as the radius decreases. Thus, as we decrease the size of the pores due to the extra silver loading, the effective surface area is reduced. This increases the true current density (based on actual surface area rather than geometric area) and thus increases the activation overvoltage. This explains the poorer performance of electrodes D and E even at the higher pressures where the capillary pressure effect has been compensated for.

The current-voltage curves for the two larger electrodes are shown in Figure 8, with the results for electrodes B and D replotted for comparison. GMD 1 and GMD 2 were electrolessly silver plated for 60 minutes each, but on different days. It appears that GMD 1 was more heavily silver plated than GMD 2, since it operated at a higher pressure (~12 psi vs 9 psi) and the performance fell off at higher current densities. This indicates one of the problems of electroless plating - the necessity of maintaining very constant conditions in order to get reproducible results. Note that GMD 1 behaved more like the highly silver loaded electrode D, and GMD 2 like electrode B. GMD 2 and electrode B both show relatively flat voltage-current curves, with some scatter in the data.

Electrodes GMD 1 and GMD 2 were run mainly in order to determine the lifetime of these types of electrodes. GMD 1, with an ion exchange membrane as diaphragm failed after 23 days due to failures in the caustic recirculation system. Electrode GMD 2, with an asbestos flow-through diaphragm, has operated at >0.7 volts depolarized for over 90 days. After 87 days the cell was disassembled for gasket replacement and inspection of the electrode showed no evidence of deterioration.

CONCLUSIONS

Porous nickel with 3 micron pores is a good substrate for fabricating silver catalyzed oxygen electrodes. It is important to keep silver loadings low (0.5 oz/ft² or less) in order to prevent too great a pore size reduction, which results in poor electrochemical performance. A 3 in² electrode operating with an asbestos flow-through diaphragm has been operating for over 90 days with no signs of deterioration.

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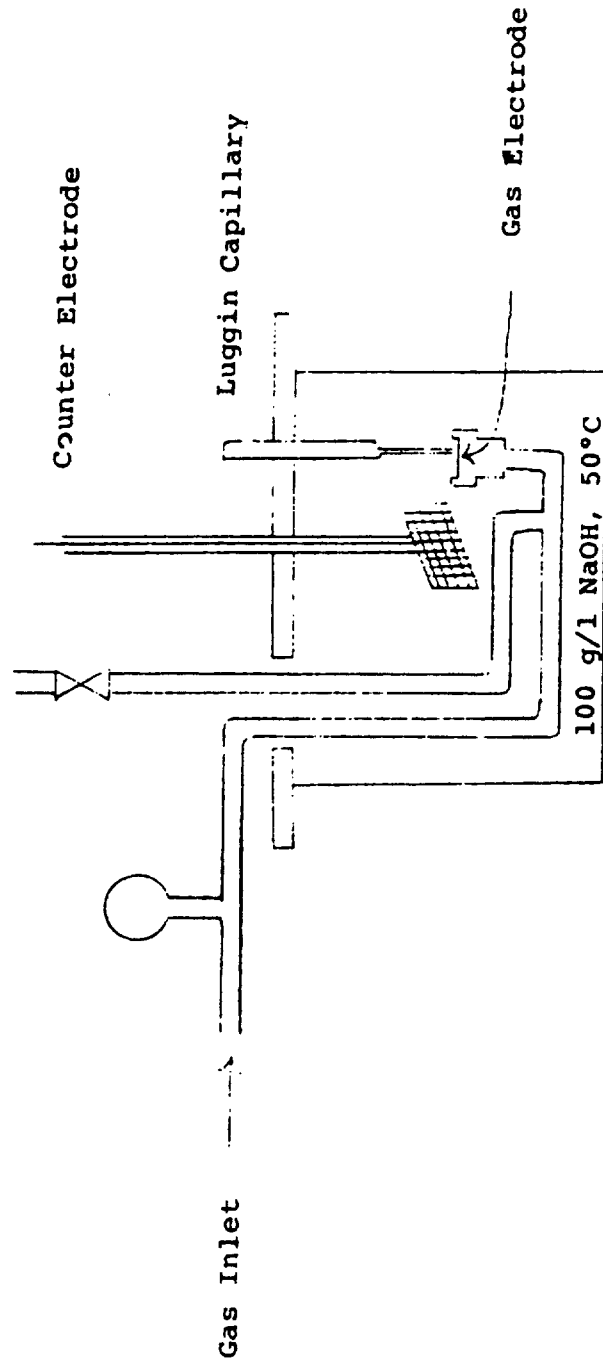
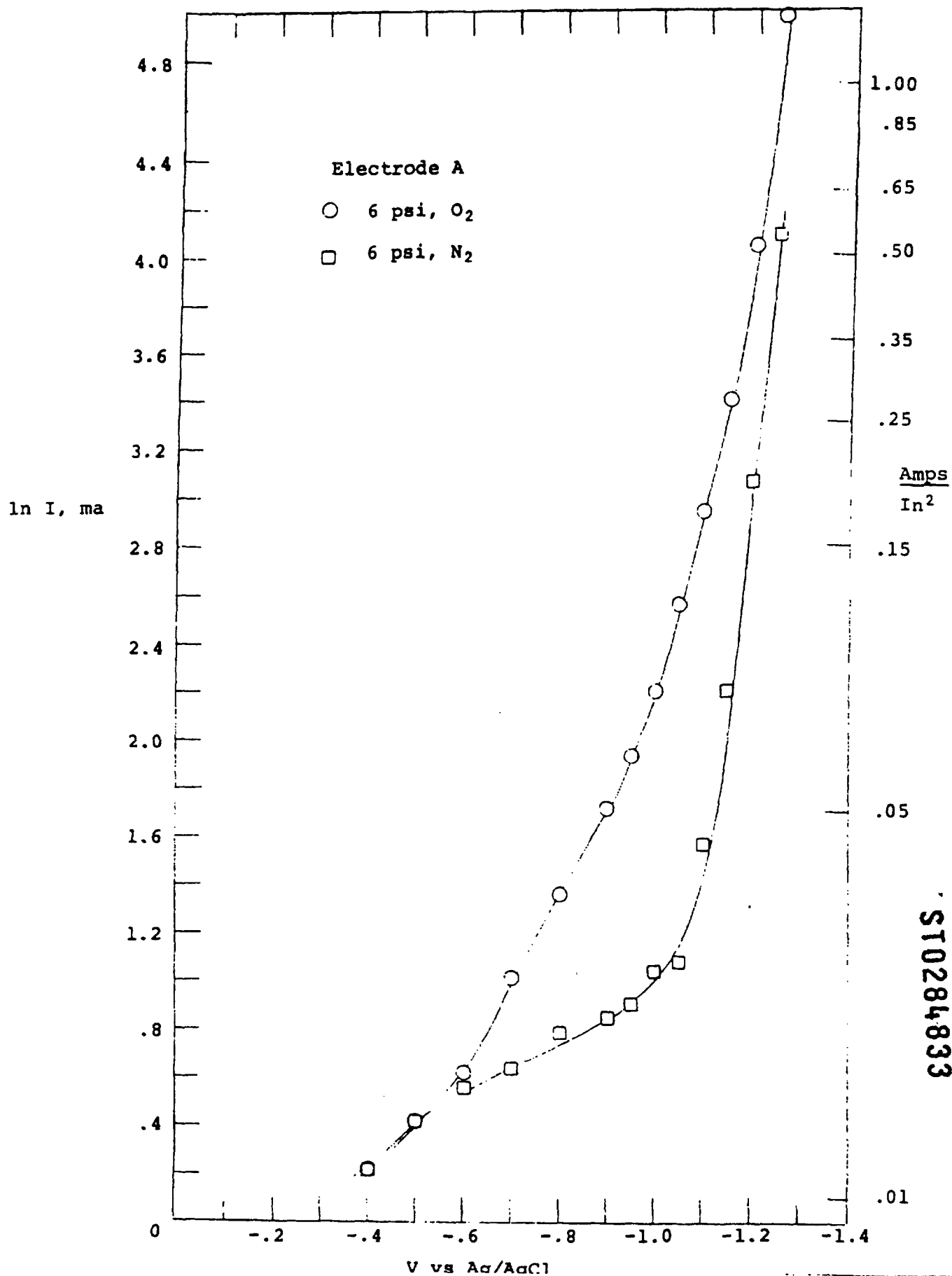
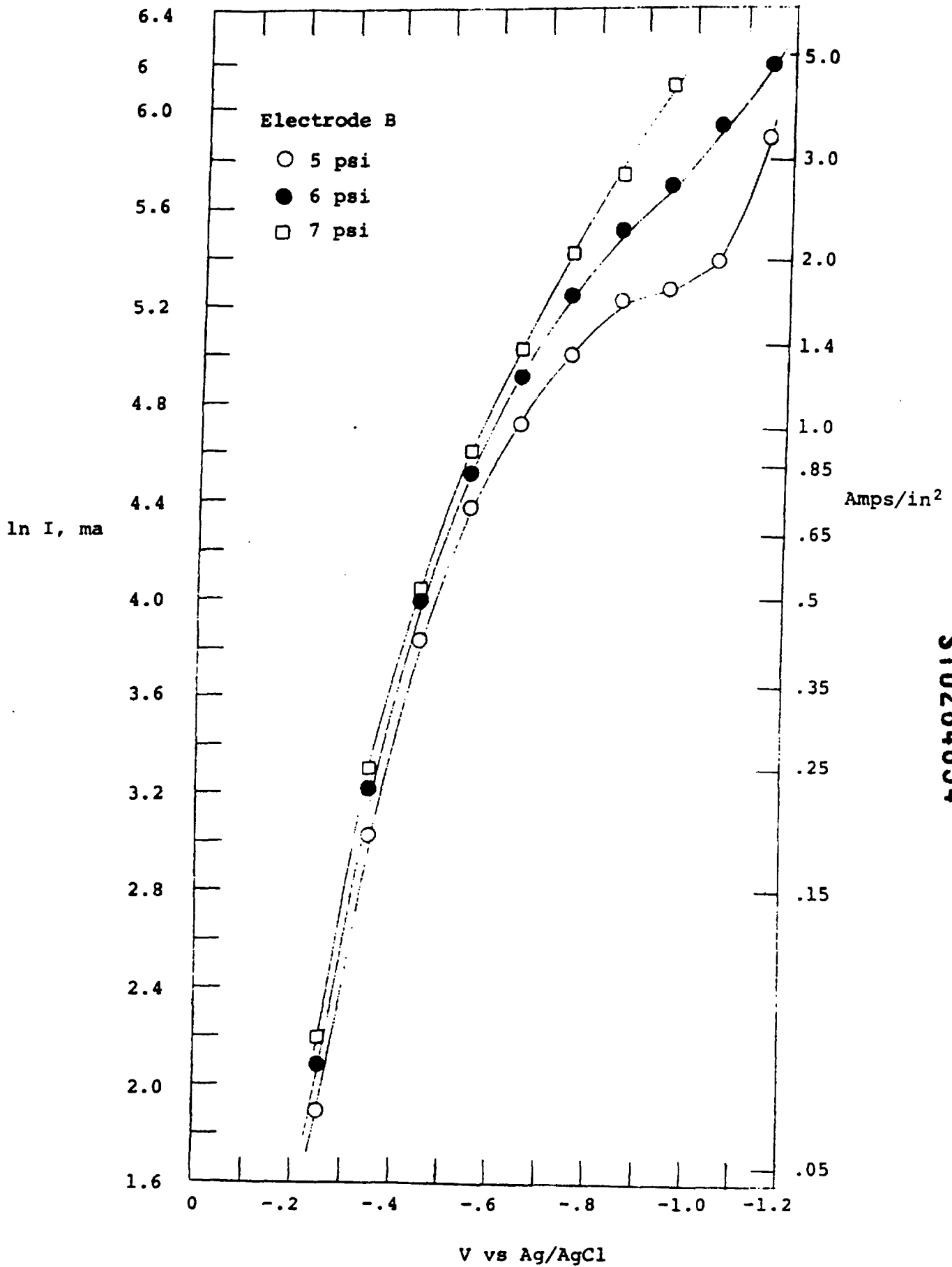


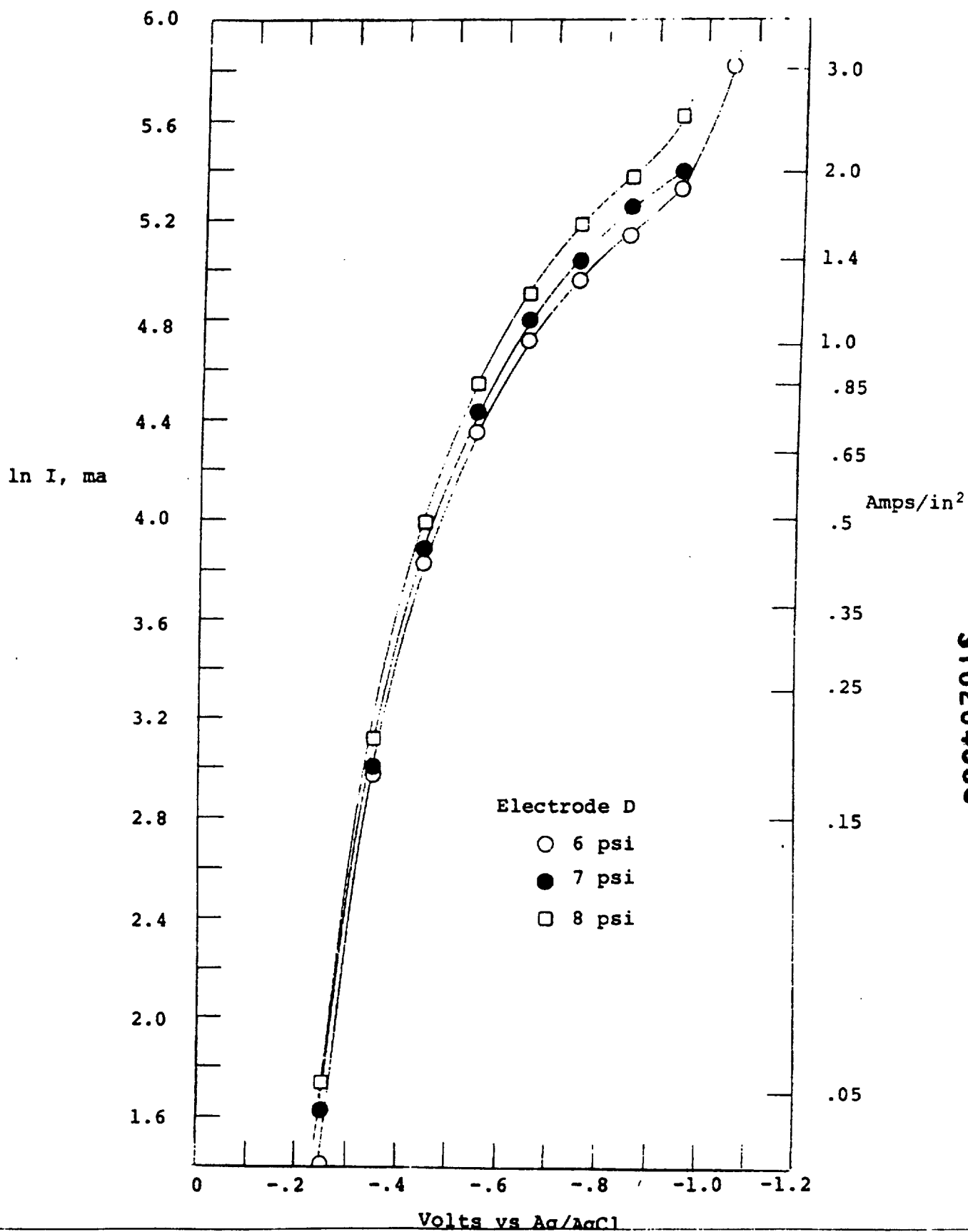
Figure 1. APPARATUS FOR EVALUATION OF SMALL GAS ELECTRODES

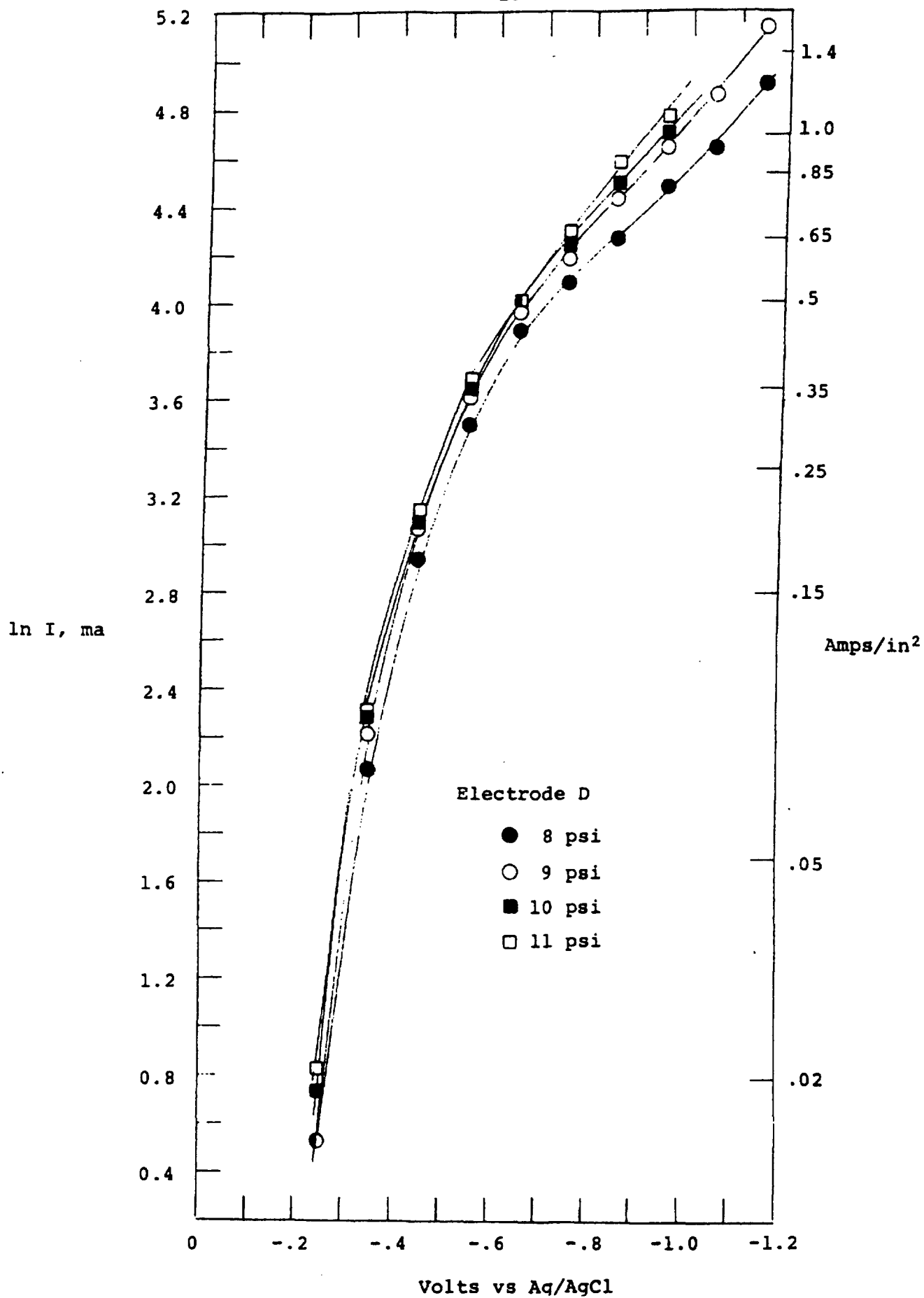
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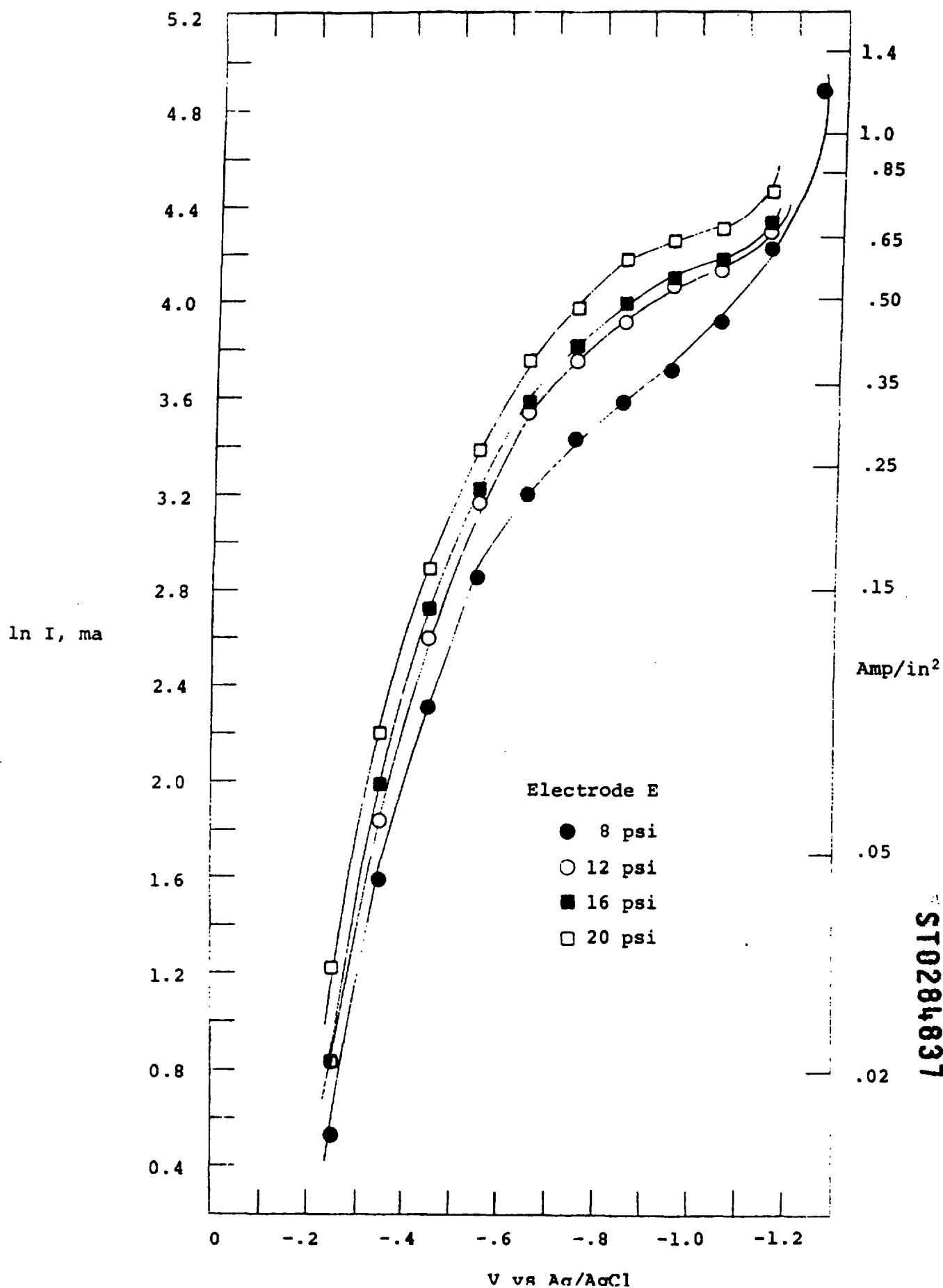


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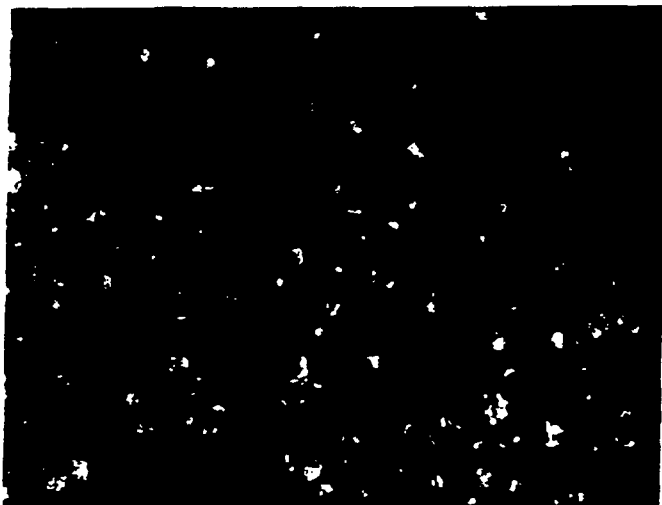




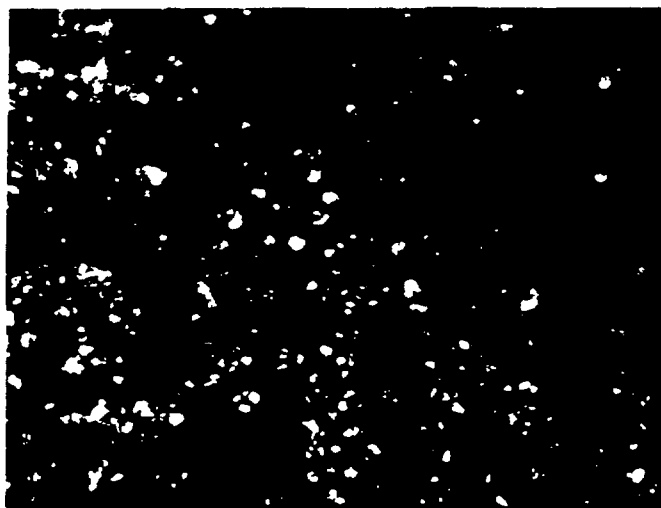
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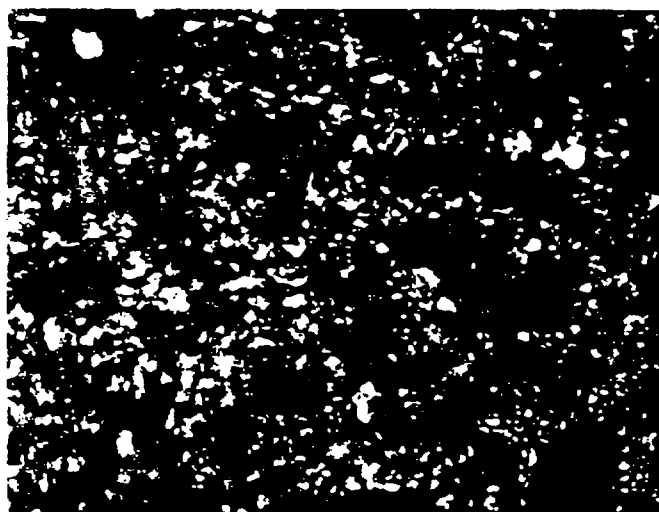
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0 oz/ft² Ag



0.5 oz/ft² Ag



1.2 oz/ft² Ag

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