

CHEAP EFFICIENT ENERGY FROM THE
ELECTROLYSIS OF CARBON AND WATER

by

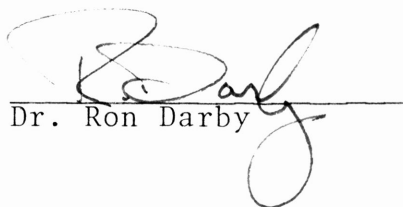
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ABSTRACT

The effects of loading six to eight weight per cent carbon black in 4.15 N H_2SO_4 electrolyte on the cell performance and reaction products from water electrolysis were studied.

When only the anodic reaction is depolarized with carbon, a reduction in the open circuit potential by a factor of six is predicted theoretically, indicating that carbon slurry electrolysis consumes only 17% of the electrical energy that water electrolysis does. Experimental results confirm these thermodynamic predictions.

If carbon is also present at the cathode, it is also possible theoretically to produce various organic compounds. Experimental evidence was obtained for the production of methane under this condition.

All products can be produced at high current efficiencies but, only at high carbon reactivity. The feasibility of any such cell will be dependent upon significant additional research.

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INTRODUCTION

In our present society, where energy is the key to affluent existence, a clean efficient fuel that is readily available is desperately needed. Hydrogen gas has long been sought after for precisely these reasons. It is used extensively in the refining and purification of both coal and petroleum as well as in the fuel cells used to power many space vehicles.

Conventional production of hydrogen for use in petroleum refining occurs in the catalytic reforming process, which cracks high molecular weight organic compounds into high grade gasoline products. The hydrogen is utilized later in the alkylation process to make low molecular weight straight chain molecules from cyclic ones. However, the hydrogen produced in the cracking unit does not adequately meet the demands of the alkylation unit. Therefore, a crucial portion of a refinery is the hydrogen plant. One method used to produce hydrogen gas involves the reaction of steam and carbon in a highly endothermic mechanism yielding synthesis gas (CO and H₂). This reaction must be conducted at temperatures in the range of 800^o C and consumes great quantities of energy. Synthesis gas however contains impurities and must be purified.

Pure hydrogen gas can also be produced in electrolytic processes. The simple electrolysis of water however consumes a large quantity of electricity and is therefore seldom used

as a means of hydrogen production. Recent developments in this area suggest that coal slurries might be electrolysed to liberate pure hydrogen and carbon dioxide gases with low energy inputs.

Electrochemical reactions employ the transfer of electrons to accomplish a reduction reaction (the addition of electrons) at the cathode (negative electrode) and an oxidation reaction at the anode (positive electrode). In water electrolysis hydrogen ions are reduced at the cathode to H_2 gas while H_2O is oxidized at the anode forming O_2 gas.

If carbon is present at the anode, it is possible for it to react with the liberated oxygen producing carbon oxides. This action "depolarizes" the anode allowing the overall electrolysis to proceed at a lower driving potential. This is the basis for the electrochemical gasification of coal slurries. The lower cell potential and consequent reduction in energy usage is achieved at the expense of carbon being depleted. Research on this phenomenon by Robert W. Coughlin and Mohamad Farooque^{2,3,4} suggests that the electrolysis of coal slurries might prove to be a viable method of producing hydrogen gas. The combination of fossil fuel and electrical energy has not been investigated or applied before according to Coughlin and Farooque². Because this is a unique reaction mechanism a large number of parameters must be evaluated for their consequences. Coughlin and Farooque have found that:

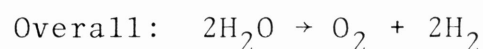
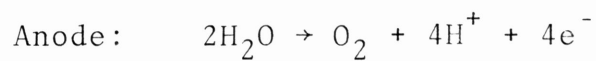
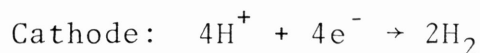
- 1) Coal reactivity is dependent upon particle size, i.e., small particles yield high oxidation rates.
- 2) Contact between the coal and the anode is necessary for the reaction to occur at reasonable rates.
- 3) Retardation of the reaction occurs as time progresses owing to the deposition of surface oxides on the coal.
- 4) The supporting electrolyte is not consumed in the reaction.

These conclusions will be considered in the present investigation.

The work of Coughlin and Farooque^{2,3,4}, as well as others⁶ considers contact of coal only with the anode. Even more interesting results might be obtained when coal is present at both electrodes. It should be possible to produce a variety of organic compounds from the combination of carbon with the hydrogen at the cathode.

THEORY

When water is electrolyzed, hydrogen gas is evolved at the cathode and oxygen at the anode according to the following mechanism:



The theoretical energy available for doing work in any reaction is related to the change in Gibb's free energy resulting from the reaction (ΔG). The change in Gibb's free energy for a reaction is equal to the summation of the Gibb's free energies of formation of the products minus the reactants. Or:

$$\Delta G = \sum \Delta G_f (\text{products}) - \sum \Delta G_f (\text{reactants}) \quad (1)$$

where the free energy of formation is the energy change of the reaction necessary to form the compound from its constituent elements. If all the free energies of any substance are derived from an arbitrary standard state, the change in free energy is defined as the standard free energy change denoted by ΔG^0 . The choice of standard states is usually for all elements and compounds except carbon to be perfect gases at one atmosphere pressure and the specified temperature. Carbon is to be in its graphite form at one atmosphere pressure and the specified temperature.

The work of an electrochemical process is the work necessary to transfer the necessary charge. This work is equal to the product of the charge and the voltage necessary to push that charge:

$$\text{Work} = QE = mFE \quad (2)$$

The charge Q is equal to the product of the moles of electrons transferred (m) and the charge of one mole of electrons (F). Thus the electrical work is related to the chemical work for a reaction in its standard state by:

$$mFE^{\circ} = -\Delta G^{\circ} \quad (3)$$

The standard cell potential (E°) is therefore:

$$E^{\circ} = -\Delta G^{\circ}/mf \quad (4)$$

For water electrolysis the change in free energy at room temperature (25°C) is 113.374 kcal^1 . The number of moles of electrons in this reaction is 4 moles and the charge of one mole of electrons is $23.06 \text{ kcal volt}^{-1} \text{ mole}^{-1}$. Therefore

$$E^{\circ} = -(113.374 \text{ kcal}) / (23.06 \text{ kcal volt}^{-1} \text{ mole}^{-1})(4 \text{ mole})$$

$$E^{\circ} = -1.23 \text{ volts}$$

where the negative potential means that energy must be supplied to the cell.

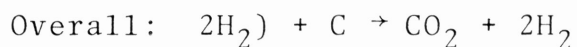
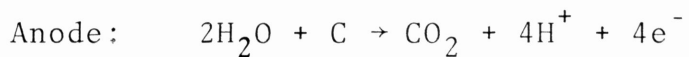
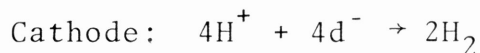
Another useful quantity is the energy density. The energy required to produce one pound of product, H_2 in this case is:

$$E.D. = (F)(\text{moles of } H_2/\text{mole of } e^-)(E^0)(1/Ml./H_2) . \quad (5)$$

For the case under consideration the $E.D. = .033 \text{ kw.hr./lb.}H_2$.

The electrolysis of water has a standard cell potential of 1.23 volts and an energy density of $.033 \text{ kw.hr./lb.}H_2$.

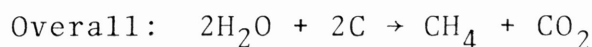
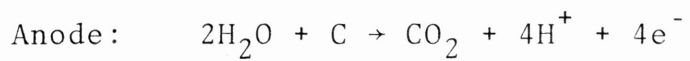
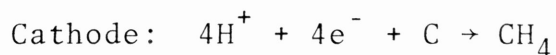
On the other hand the oxidation of coal slurries:



has a standard cell potential of only 0.21 volts and an energy density of $5.6 \times 10^{-3} \text{ kw.hr./lb.}H_2$. The addition of carbon to the anode thus reduces the standard cell potential by a factor of six. This translates to a savings of 83% on the cost of electricity required to produce one pound of hydrogen by coal electrolysis over the cost of water electrolysis.

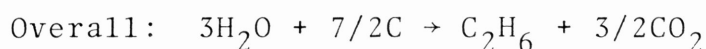
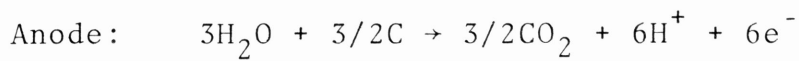
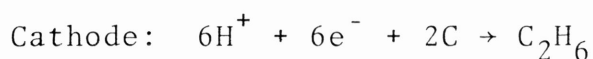
If carbon particles are present at both the anode and cathode a full range of organic compounds might theoretically be evolved. Several possible mechanisms are presented below:

Methane might be produced by the following reaction scheme:



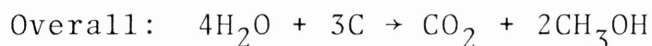
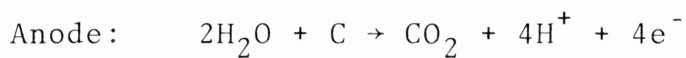
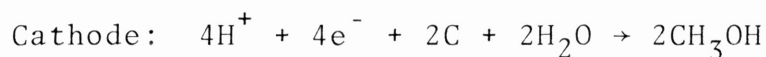
which has an open circuit voltage of 0.075 volts and an energy density of 5.0×10^{-4} kw.hr./lb. CH_4 .

Ethane could be manufactured by:



which demonstrates an open circuit voltage of 0.201 volts and an energy density of 1.08×10^{-3} kw.hr./lb. C_2H_6 .

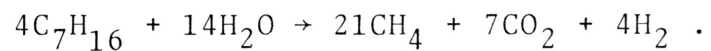
Methanol might also be produced.



which displays an open circuit voltage of 0.573 volts and an energy density fo 9.6×10^{-4} kw.hr./lb. CH_3OH .

The prospect of possibly being able to produce any of these compounds as well as others from carbon, water, and electrons is very significant. For instance the present use of coal for the formation of methane utilizes thermal

processes. The steam reformer produces methane from naphtha and steam:



This reaction occurs only at a temperature of 850^o F and a pressure of 30 ATM⁸ while the electrolysis reaction is carried out at ambient conditions.

EXPERIMENTAL

The cell used in this study is illustrated in Figure 1. The reaction vessel has a volume of 700 ml. The electrode used as the anode was expanded titanium metal coated with ruthenium oxide catalyst. The cathode is strip platinum surrounded by a glass cylinder equipped with a glass frit at its base so that carbon and cathode were separated. A reference electrode was used in potential measurements.

An electrolyte concentration of 4.15 N sulfuric acid was used because of high electrical conductivity. The electrolyte was loaded with N220 carbon black (-220 mesh) to concentrations of six-to-eight weight percent to conform to the findings of Coughlin and Farooque² (Number 1). Carbon black was employed in this investigation because of its simple composition.

Evolved gases were analyzed with a gas chromatograph.

DISCUSSION OF RESULTS

The procedure used in an attempt to substantiate the predicted values of E° was to pass a given current through a pure H_2SO_4 solution, indicative of water electrolysis, and measure the voltage of each electrode with respect to a reference.

The results obtained are plotted in Figure 2. If the respective loci for both electrodes are extrapolated to the limiting value of zero current the standard cell potential can be generated. The consequential E° is approximately 1.26 volts. The excessive curvature of the cathode function in the high current region is connotative of the limitation of the cathode reaction at increasing current density. The overpotential of a reaction is the voltage above the open circuit voltage necessary to drive the reaction at a given rate. Overpotential is a function of current density as well as other parameters.⁷ The rapid production of H_2 on the cathode increases the current density by decreasing the available surface area for the reaction, thus increasing overpotential.

Figure 3 depicts equivalent results for both water and carbon slurry electrolysis. The cathode function is identical for both cases since carbon is present only at the anode. The lower anode potential curve carbon electrolysis is as predicted. The open circuit potential for this curve is on the order of 0.25 - 0.3 volts (see Figure 5, Appendix page 22). This value is above that expected

from thermodynamics but still well below that for water electrolysis. The upward curvature of the carbon anode curve is due to a production of O_2 in greater amounts than can be captured by the carbon.

Numerous experiments of this type were conducted to determine the reproducibility of these results. The effect of stirring on the case of water electrolysis was also investigated and determined to be negligible (see Figure 6, Appendix page 23). The selection of a reference electrode on the overall cell potential was also found to be negligible. All of the experimentally gathered information agrees with the thermodynamic estimates.

Chromatographic analysis of the reaction gases at various times and applied currents manifested a cathodic current efficiency for hydrogen production of 100%. Current efficiency is the ratio of the current that forms a specific product to the current passed. A current efficiency of 100% necessitates that all current passed yields the compound in question. The anodic efficiency ranged from 0 to 100%. In other words, with a fresh suspension only CO_2 was generated but as time progressed and the reactivity of the carbon diminished CO_2 was replaced by O_2 . There was no evidence of any other carbon oxides being composed. This implies that the reactivity of the carbon must be maintained at a maximum. Accomplishment of this objective can be achieved either by regenerating the carbon as suggested by

Coughlin and Farooque² or by introducing unreacted carbon while simultaneously extracting spent carbon. Therefore the preservation of high reactivity over a period of time is insured thereby guaranteeing carbon slurry electrolysis and low potential demands.

The research continued by first removing the now extraneous glass frit from the cathode. The resulting products were analyzed using gas chromatography. As hoped, methane gas was found to be present in the product gases. However it was produced only from a fresh solution. The current efficiency for methane ranged from 100% to 9% (see Table I, Appendix page 25). The creation of CH₄ was found to be extremely sensitive to carbon reactivity.

No organic phase was detected in the solution. On the assumption that these compounds might compose a portion of the deposits retarding carbon reactivity the decanted carbon solid was heated to drive off these deposits. The condensed vapors were analyzed in a liquid chromatograph but no methanol was found to be present.

The specific products and distributions which might be obtained from carbon reduction is a very complex function of a number of parameters. It is believed that the electrocatalytic nature of the electrode surfaces will play an important role in that function.

CONCLUSIONS

The use of carbon to depolarize both anode and cathode reactions in water electrolysis is a potentially significant combination of fossil fuels and electrochemistry. The electrolysis of carbon slurries can proceed at ambient conditions, as opposed to conventional thermal mechanisms, and at lower energy expenditures than water electrolysis.

Carbon slurry electrolysis manifests a standard cell potential only one-sixth as large as that of water electrolysis. This represents a savings of 83% in terms of energy consumption per pound of H_2 liberated.

If carbon is present at the cathode as well as the anode an entire array of organic compounds might result. The specific product distribution in this instance is likely to be a sensitive function of the electrocatalytic nature of the electrodes, the operating temperature, etc.

The simplest hydrocarbon, methane, was evolved using the experimental design presented herein. The experimental current efficiencies ranged from 100 to 0%.

The current efficiencies of all products changes with time. CO_2 is replaced by O_2 at the anode and CH_4 is replaced by H_2 at the cathode.

The current efficiencies are related directly to the reactivity of the carbon. As time progresses the reactivity of the carbon retards, owing to surface depositions making it first more difficult to evolve CH_4 and then more difficult to evolve CO_2 .

Since high current efficiencies are warranted, it is evident that some method to maintain reactivity is desirable. The most obvious approach to this problem is the design of a flow reactor. One possibility is illustrated in Figure 4. The object is to continuously pump a carbon slurry through the cell and either regenerate it or replenish it in an external loop. Since high current efficiencies represent minimum energy costs and maximum raw material costs (C) an optimum operating condition can be obtained.

NOMENCLATURE

<u>Symbol</u>	<u>Description</u>	<u>Units</u>
E°	Standard open cell potential	Volts
F	Faraday's constant	$\frac{C}{\text{mole}}$
G°	Standard Gibbs Free Energy Change	$\frac{\text{kcal}}{\text{mol}}$
n	Number of electrons transferred	mole-
Q	Charge transfe-red	C

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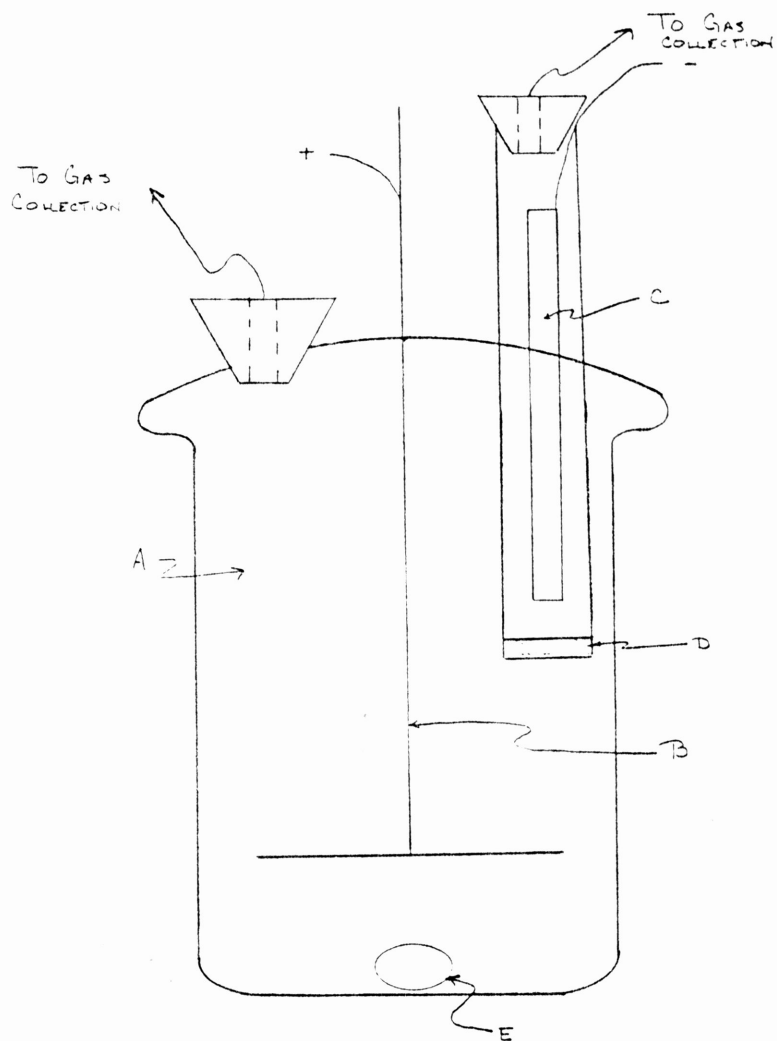
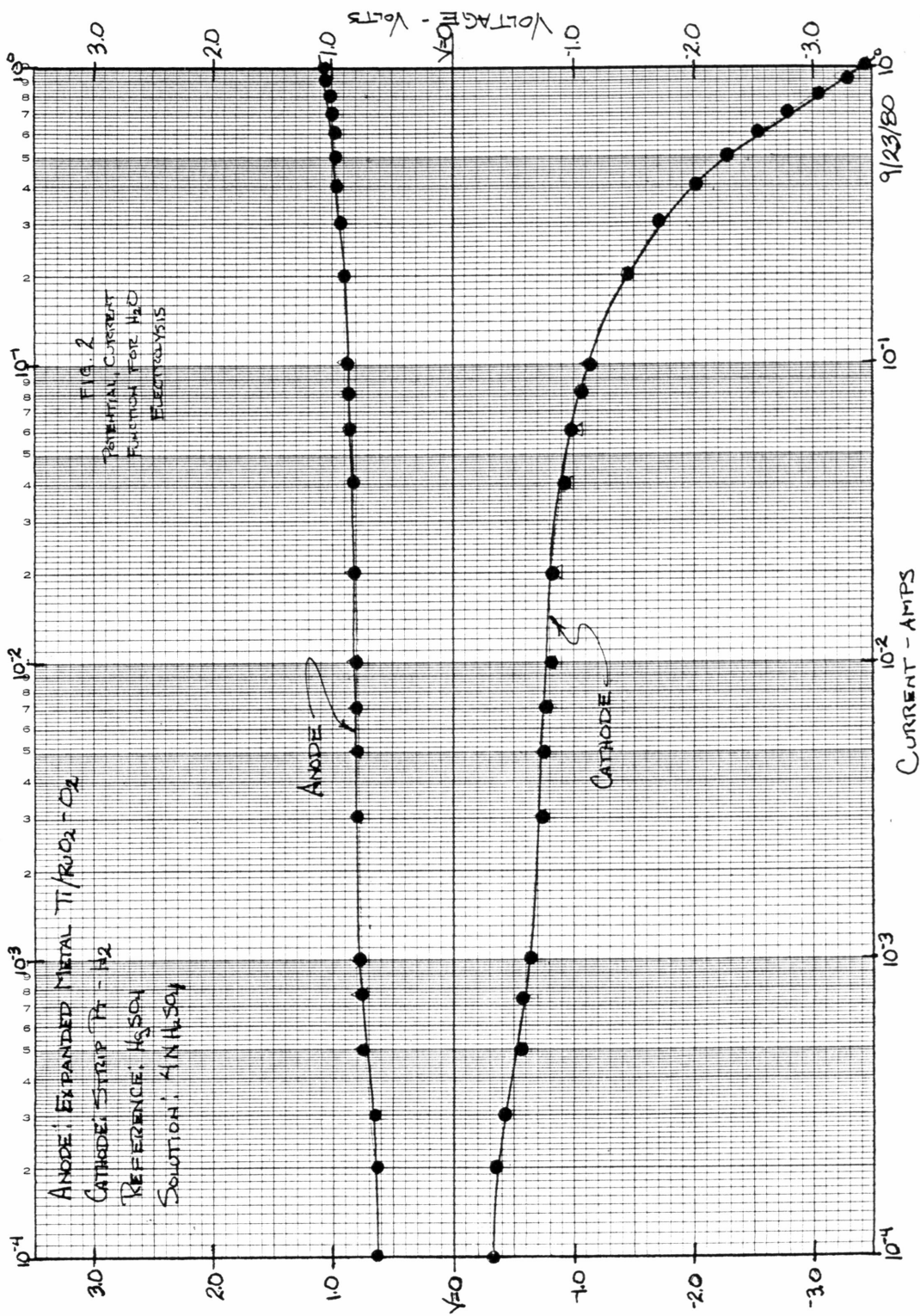


Figure 1- Electrlytic Cell

- A- Reaction Kettle (700ml)
- B- Expanded Metal Titanium
Electrode- RuC_2 Catalyzed
- C- Strip Platinum Cathode
- D- Glass Frit
- E- stirring Bar

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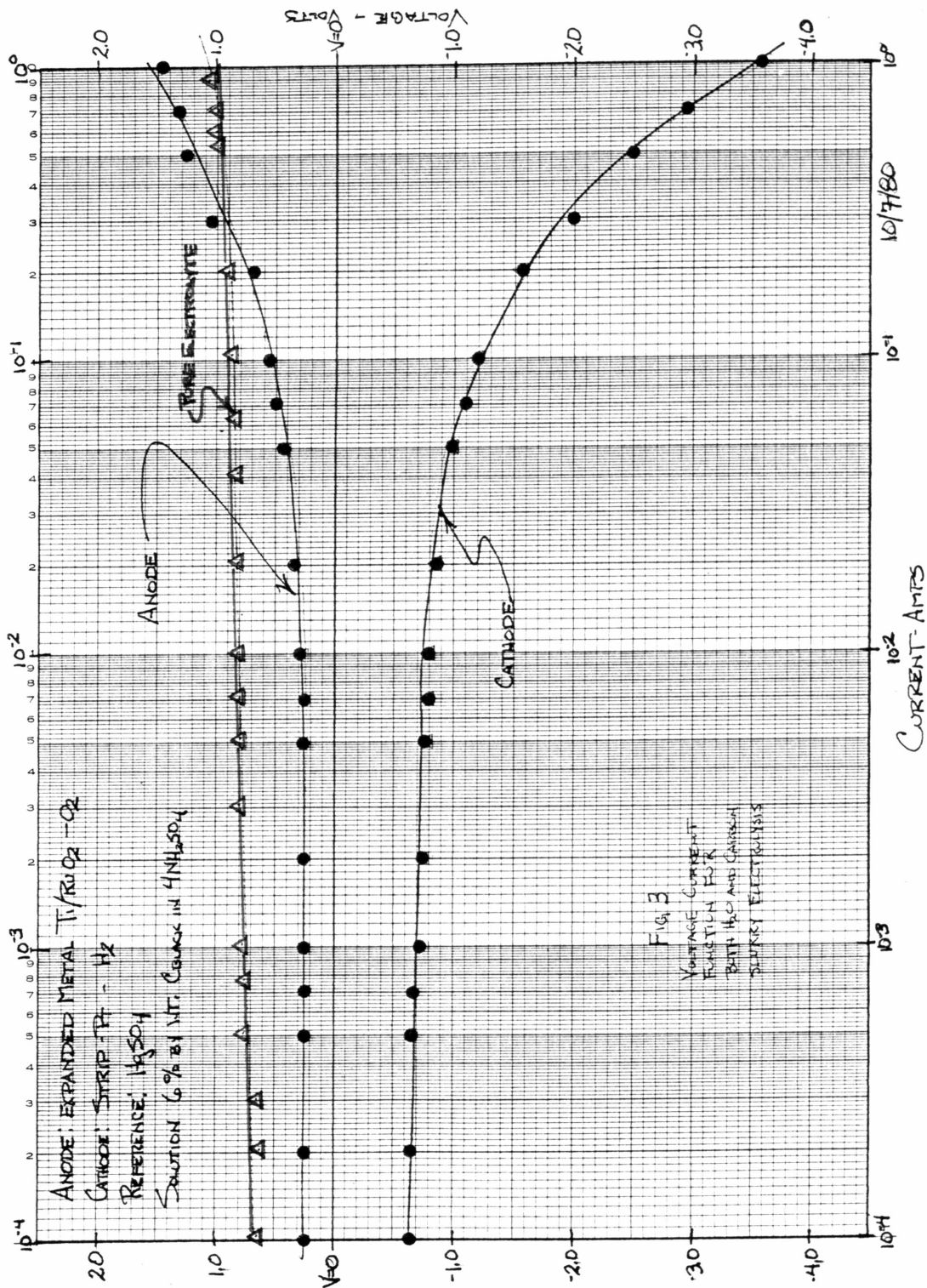


FIG. 3
 VOLTAGE-CURRENT
 FUNCTION FOR
 BOTH H₂O AND CATHODIC
 SURFACE ELECTROLYSIS

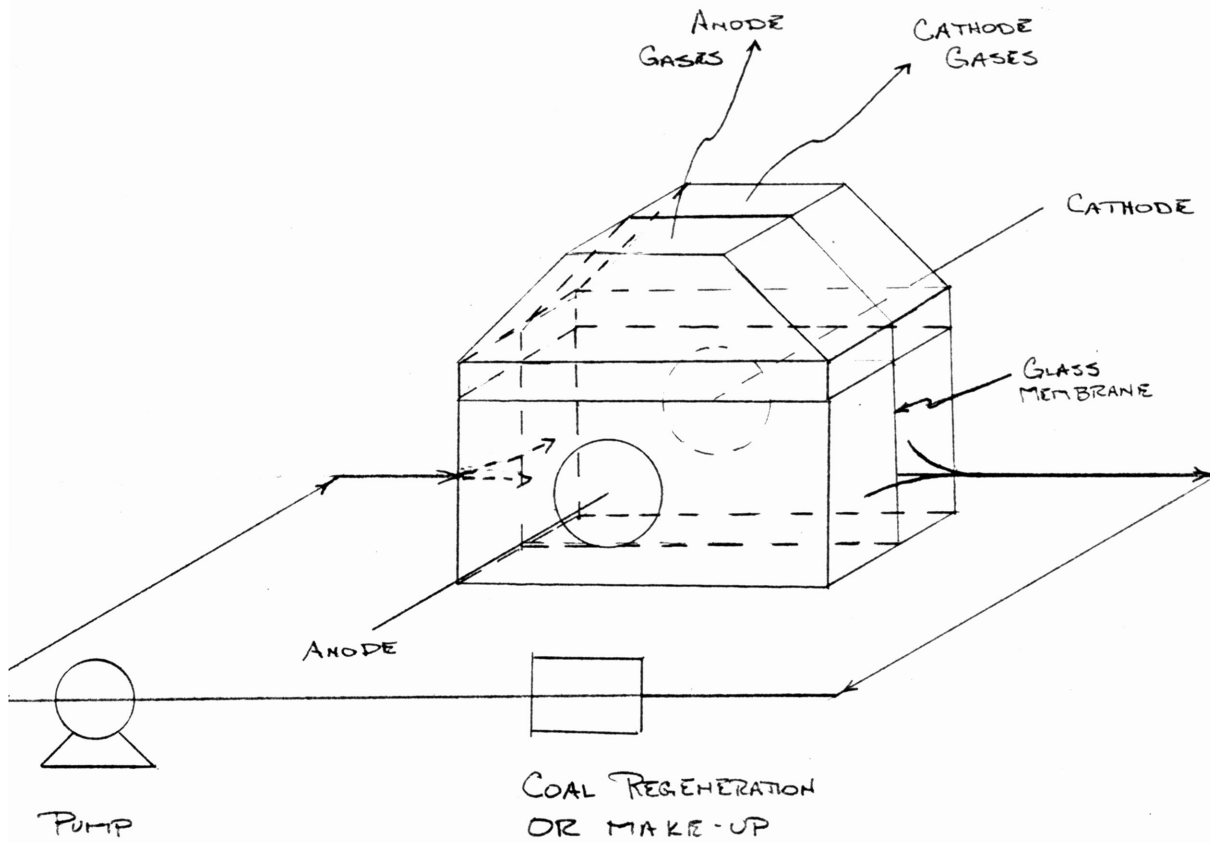


FIGURE 4. ELECTROCHEMICAL FLOW PROCESS

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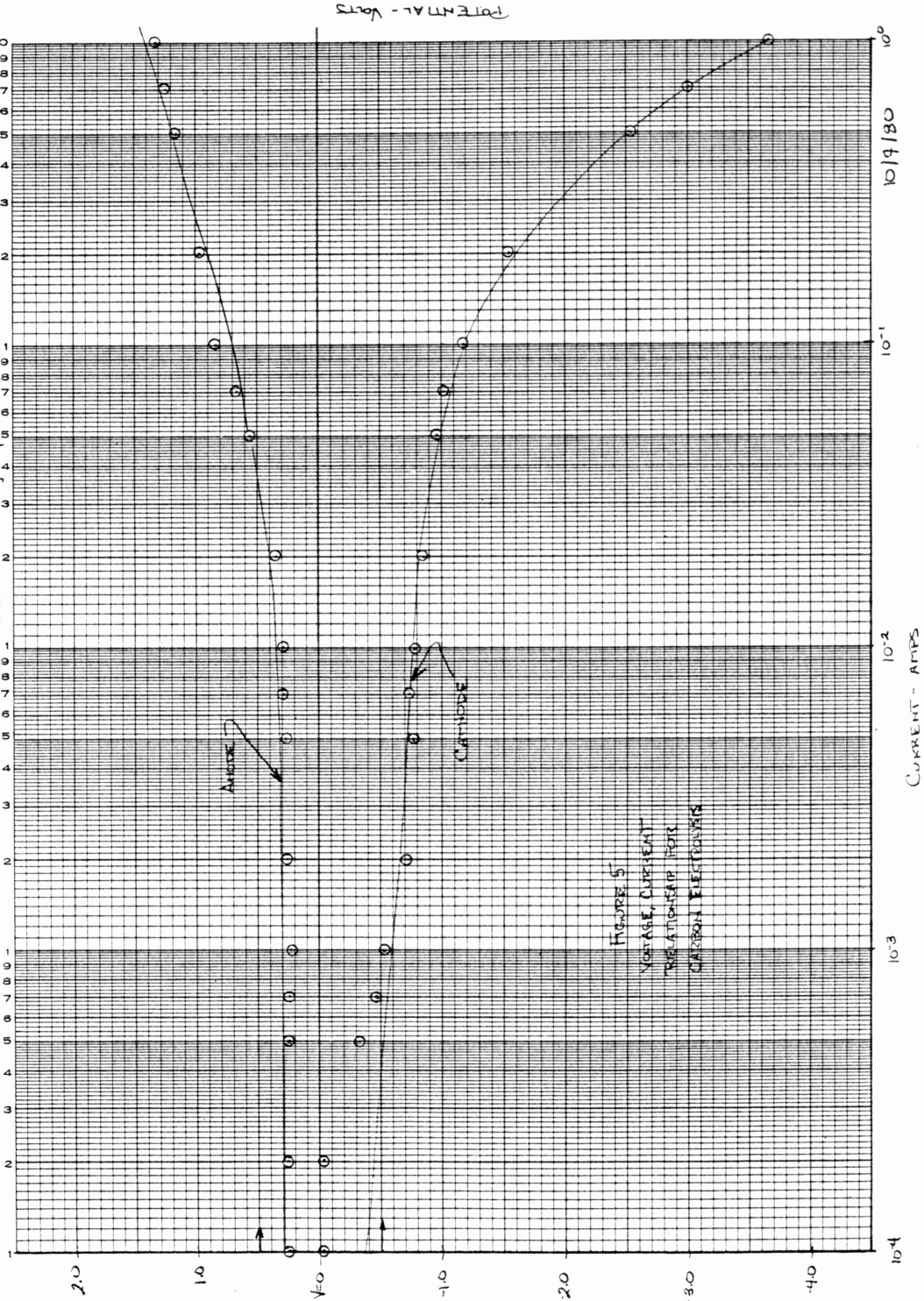
TEMP = 22.9°C

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ANODE: EXPANDED METAL TiRu₂O₂O_x

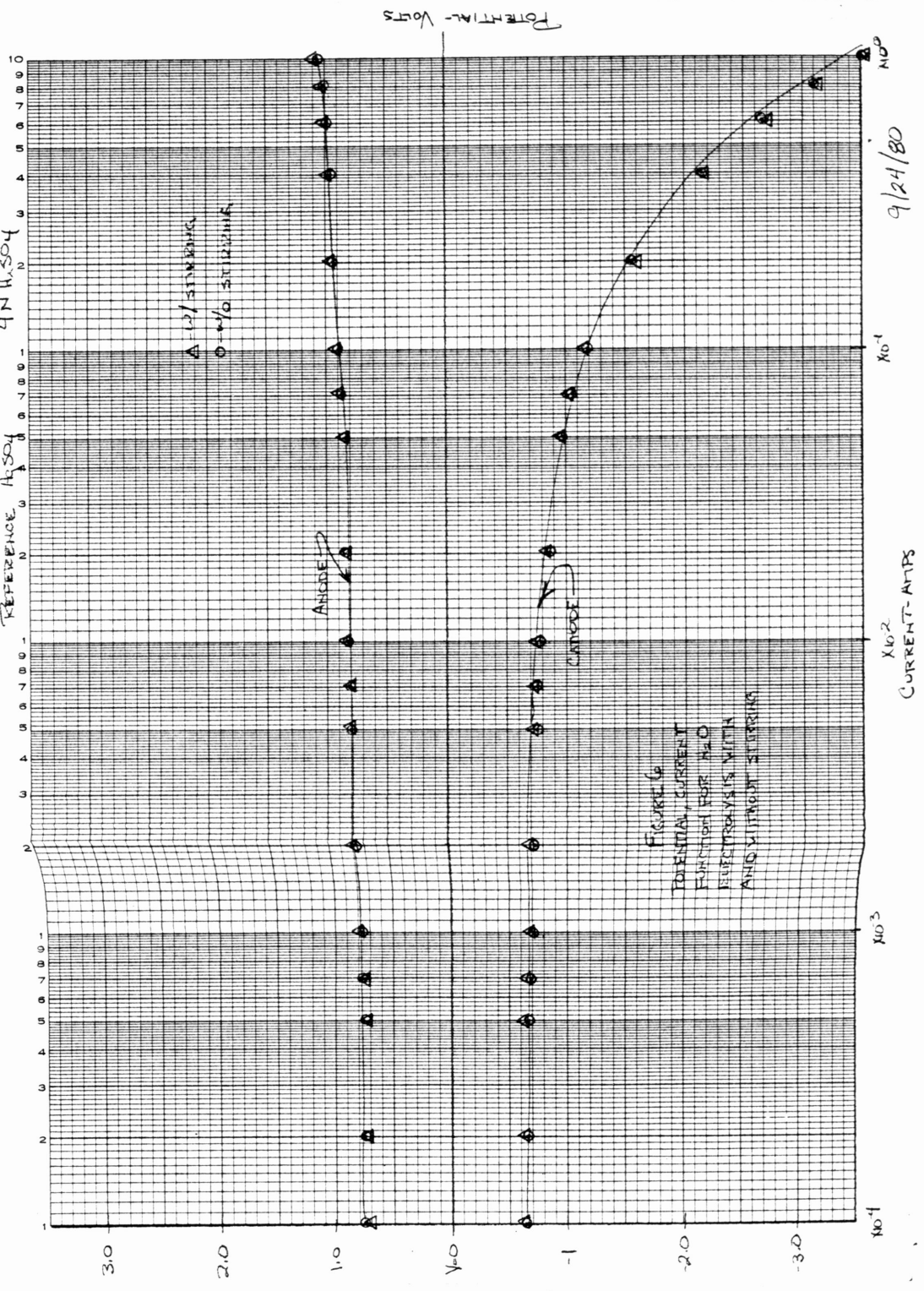
CATHODE: STRIP - H₂

REFERENCE: H₂SO₄ SOLUTION .06wt% C in H₂SO₄ (4N) N330



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SEMI-LOG DIVISIONS PER INCH
4 CYCLES X

DIETZEN CORPORATION
MADE IN U.S.A.
ANODE: EXPANDED METAL Ti/RuO₂-O₂
CATHODE: STAIN - H₂
REFERENCE: H₂SO₄ 4N H₂SO₄



NO. 340-L410 DIETZEN GRAPH PAPER
SEMI-LOGARITHMIC
4 CYCLES X 10 DIVISIONS PER INCH

DIETZEN CORPORATION
MADE IN U.S.A.

ANODE: EXPOSED METAL Ti/KO₂O₂
CATHODE: STEEL-H₂

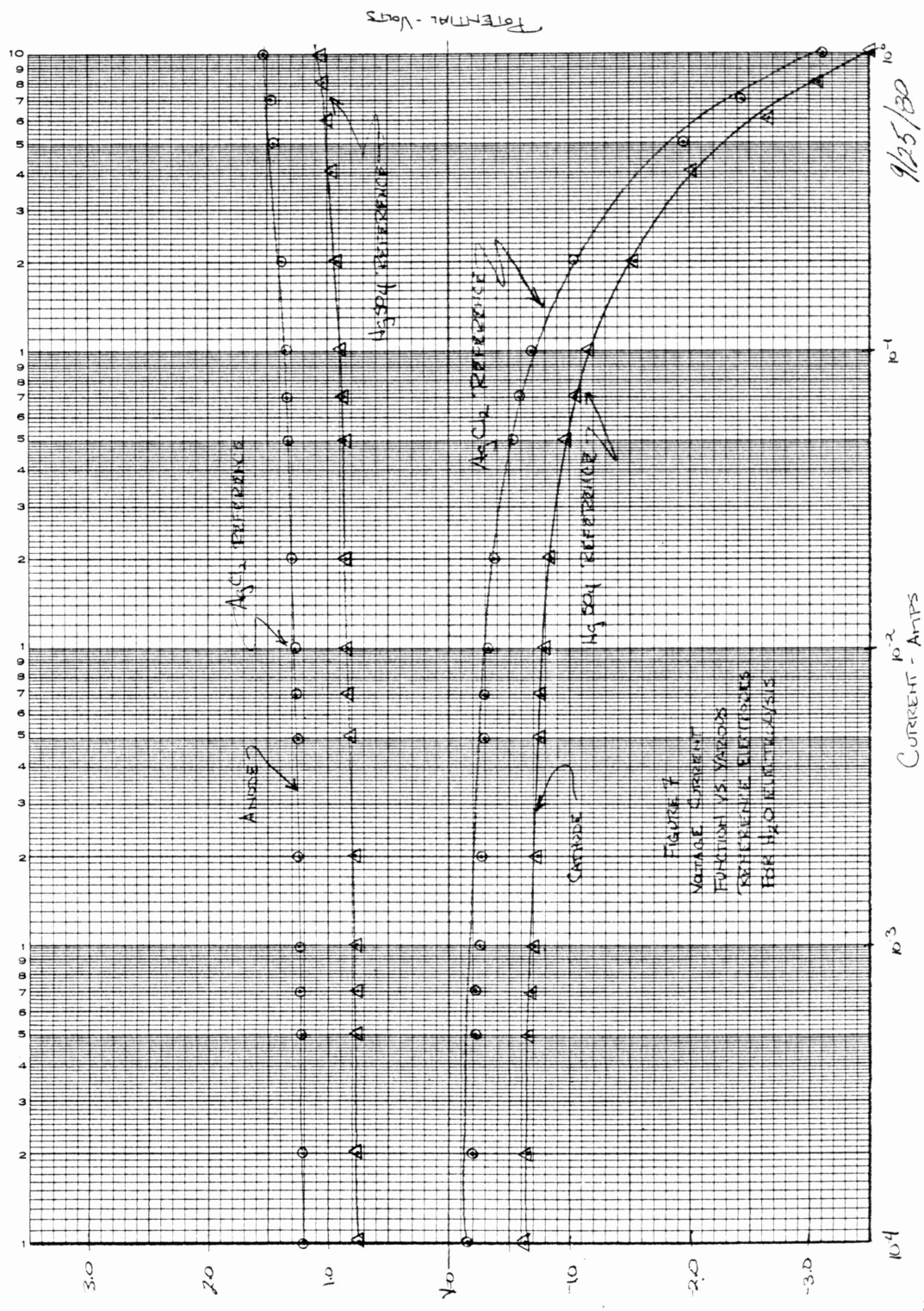


TABLE I
CHROMATOGRAPH RESULTS

SAMPLE #	DESCRIPTION	CURRENT (AMPS)	TIME (HRS.)	ELECTRODE	COMPOSITION	CURRENT EFFICIENCY
1	NEW SOLN. 6wt.% C IN 4.15N H ₂ SO ₄	1	8	ANODE	CO ₂	100%
				CATHODE	H ₂	100%
2	SAME AS #1	1	1	ANODE	CO ₂ /O ₂	50/50%
				CATHODE	H ₂	100%
3	SAME AS #1	1	1	ANODE	CO ₂ /O ₂	265/97.35%
				CATHODE	H ₂	100%
4	NEW SOLN. 6wt.% C IN 4.15N H ₂ SO ₄	1	3	ANODE	CO ₂	100%
				CATHODE	H ₂	100%
5	SAME AS #4	3	3	ANODE	CO ₂ /O ₂	42.5/57.5%
				CATHODE	H ₂	100%
6	SAME AS #4	3	3	ANODE	CO ₂ /O ₂	239/97.61%
				CATHODE	H ₂	100%
7	NEW SOLN. 6wt.% C IN 4.15N H ₂ SO ₄	3	.13	ANODE	CO ₂ /O ₂	100/0%
				CATHODE	H ₂	100%
8	NEW SOLN. 6wt.% C IN 4.15N H ₂ SO ₄	1	8	ANODE	CO ₂	100%
				CATHODE	CH ₄	100%
9	NEW SOLN. 6wt.% C IN 4.15N H ₂ SO ₄	3	3	ANODE	CO ₂	100%
				CATHODE	CH ₄	100%
10	NEW SOLN. 6wt.% C IN 4.15N H ₂ SO ₄	3	3	ANODE	CO ₂	100%
				CATHODE	CH ₄ /H ₂	80/20%