THEORETICAL AND EXPERIMENTAL FLOW CELL STUDIES OF A HYDROGEN-BROMINE FUEL CELL

NASA Contract NAG 3-500

Final Report - Part I

by

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ABSTRACT

There is increasing interest in hydrogen-bromine fuel cells as both primary and regenerative energy storage systems. One promising design for a hydrogen-bromine fuel cell is a negative half cell having only a gas phase, which is separated by a cationic exchange membrane from a positive half cell having an aqueous electrolyte. The hydrogen gas and the aqueous bromide solution are stored external to the cell.

In order to calculate the energy storage capacity and to predict and assess the performance of a single cell, the open circuit potential (OCV) must be estimated for different states of charge, under various conditions.

Theoretical expressions were derived to estimate the OCV of a hydrogen-bromine fuel cell. In these expressions temperature, hydrogen pressure, bromine and hydrobromic acid concentrations were taken into consideration. Also included are the effects of the Nafion membrane separator and the various bromide complex species. Activity coefficients were taken into account in one of the expressions. The sensitivity of these parameters on the calculated OCV was studied.

Experiments were completed to measure the OCV of a hydrogen-bromine fuel cell at various states of charge of a cell with initial charge capacities of 35% HBr and 48% HBr. Rates of membrane and solution equilibrium were also studied.

The theoretical expressions were useful in assessing the effects of various parameters on the OCV. The variables which were found to have a significant effect on the OCV through either experimental or theoretical study were: hydrogen pressure, temperature, hydrobromic acid and bromine concentrations. The type of Nafion membrane separator had an insignificant influence on the OCV. The agreement between the predicted and the actual OCV might be improved with knowledge of the activity coefficients, and of the chemistry of bromide species in concentrated solutions.

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NOMENCLATURE

a_i = activity of species i, moles/liter

$a_i^{\bar{\theta}}$ = property expressing secondary reference state, liter/mole

a_1 = mole fraction tribromide formed from elemental bromine

b_1 = mole fraction pentabromide formed from elemental bromine

c_1 = mole fraction of free bromine

C_i = initial concentration of species i, moles/liter

$\bar{C}_i$ = equilibrium concentration of species i, moles/liter

C_o = concentration of solvent, moles/liter

C_R = fixed anion concentration of membrane, moles/liter

d_e = density of electrolyte absorbed by membrane, g/cc

F = Faraday's constant, 96,487 c/equiv.

f_e = weight fraction of electrolyte absorbed by membrane

f_i = fraction of membrane ion groups in ion clusters

f_w = fraction of membrane electrolyte in ion clusters

K = equilibrium constant

m_i = molality of species i, moles/kg

M_o = molecular weight of solvent, g/mole

r^2 = parameter which represents goodness of a linear regression

R = universal gas constant, 8.314 J/gmole-K

T = temperature, K

U = open circuit potential, volts

U^{θ} = open circuit potential at standard state, volts

W_i = weight of species i in solution, g

X_i = weight fraction of species i in solution

γ_i = molal activity coefficient of species i

λ_i = absolute activity of species i

λ_i^{θ} = property expressing secondary reference state, kg/mole

ϕ = electric potential, (or quasielectrostatic potential), volts

μ_i = electrochemical potential of species i, J/mole

$\mu_{H_2}^{*}$ = chemical potential of hydrogen referred to ideal gas state, J/mole

Superscripts

α = hydrogen electrode phase

α' = bromine electrode current collector

β = membrane phase

δ = solution phase

θ = standard state

Subscripts

n = reference ion, hydrogen ion

s = supporting electrolyte

e = electron

CHAPTER I

INTRODUCTION AND BACKGROUND

There has been increasing interest in recent years in hydrogen-halogen rechargeable fuel cells as both primary and regenerative energy storage systems. They can be coupled with solar cell systems to provide the power necessary to charge the hydrogen-halogen battery [1]. This, along with the high energy densities of these systems, make them candidates for space power applications.

The types of hydrogen-halogen batteries that have been studied are the hydrogen-chlorine, hydrogen-bromine, and hydrogen-iodine. The hydrogen-chlorine and hydrogen-bromine systems are comparable in terms of efficiency and heat rejection, but the hydrogen-iodine is less efficient [2]. The advantage the hydrogen-bromine system has over the hydrogen-chlorine system is the high solubility of bromine in hydrobromic acid, whereas chlorine has a low solubility in hydrochloric acid.

The electrochemical reactions for the hydrogen-bromine system are reversible, and the use of polymer electrolytes has eliminated cell gaps. Consequently, good energy storage efficiencies can be obtained even at high current density operation.

A high power density system, where there is a high rate of energy delivery, is important because it is useful for situations requiring either high or low power. The power density of a system is directly proportional to its current density, so high current density operation is desirable.

Operation at high current densities requires reactor designs which enhance mass transfer rates. A flow system is necessary to improve mass transfer performance and aid in thermal management.

1.1 Hydrogen-Bromine Fuel Cells

The flow system design for a hydrogen-bromine cell is a negative half-cell having only a gas phase which is separated by a solid polymer ionic conducting membrane from a positive half-cell having a flowing aqueous electrolyte. Figure 1 shows a schematic of the hydrogen-bromine energy storage system. The hydrogen and bromine formed are stored external to the cell, the hydrogen stored in the form of a metal hydride.

1.1.1 Reactions and Battery Operation

The overall reaction taking place in the cell during charge can be written as:

$$HBr(aq.) + \text{electrical energy} \rightarrow 1/2H_2(g) + 1/2Br_2(l)$$

The energy is stored in the form of bromine in the

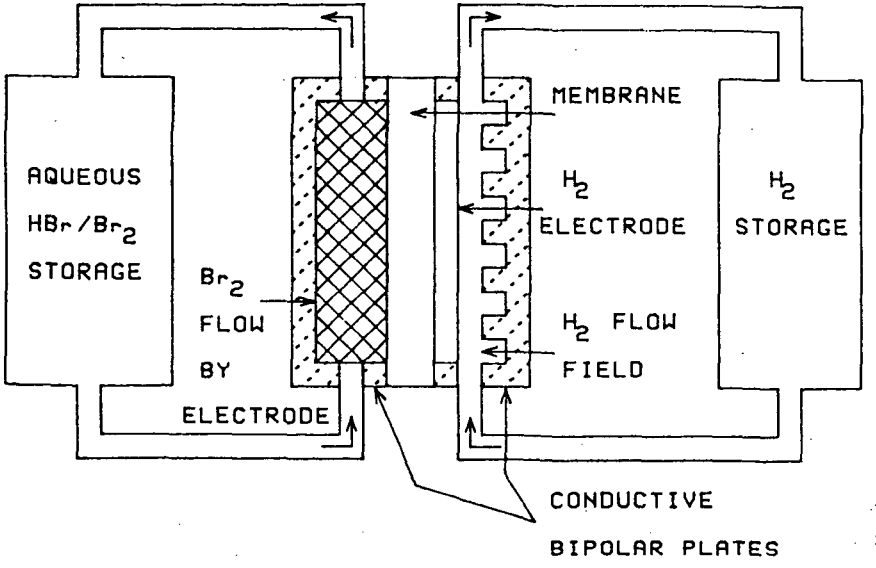


Figure 1. Schematic of a hydrogen-bromine energy storage system.

electrolyte reservoir and as hydrogen gas in the hydrogen reservoir. Because of this, the total energy storage as watt-hours depends primarily on the reservoir size, rather than on the size of the cells [3].

The use of solid polymer electrolytes combined with electrodes promoting good mass transfer make it possible to operate the cell with current densities in the range of 300 mA/cm^2 [4]. In practice, the configuration for a multicell battery is bipolar construction, with the electrodes in direct contact with the solid polymer electrolyte, which is a proton conducting membrane.

1.1.2 Advantages and Disadvantages of Hydrogen-Bromine Fuel Cells

The major advantage that the hydrogen-bromine battery has over other fuel cell systems is that the positive electrode overpotential during the charge reaction is negligible, as is its polarization during the discharge reaction. Therefore, the reaction

$$Br^- \rightleftarrows 1/2\ Br_2 + e$$

approaches thermodynamic reversibility [3].

Other advantages the hydrogen-bromine system possesses are:

1. fast electrode kinetics cause a high electric to electric efficiency [5];
2. the cells can be operated at high current densities;

3. a flow system improves mass transfer performance and aids in thermal management;

4. because of the high solubility of bromine in hydrobromic acid, there is less concern regarding mass transfer limitations; and

5. the fuel cell can be operated with shallow discharges, and can tolerate both over charge and under discharge [5].

Another advantage is that the use of a solid polymer electrolyte (SPE) allows the anode and the cathode to be operated at different pressures. This means that hydrogen can be produced at a pressure high enough for storage as a metal hydride or as a compressed gas without further compression.

A major disadvantage to any flow cell system is the external pumping energy necessary for operation and the associated efficiency loss.

There are also some disadvantages specific to the hydrogen-bromine system. They are:

1. the weight of the aqueous phase containing bromine, and its solubilizer;

2. the high corrosivity of bromine and hydrobromic acid; and

3. the open circuit voltage is dependent on the state of charge of the bromine reservoir [3].

Another disadvantage to the system is the complexities inherent to the lack of knowledge regarding the mechanism of charge transport within the cation exchange membrane used as the solid polymer electrolyte.

1.2 Background on the Development of the Hydrogen-Bromine Fuel Cell

The major components of a hydrogen-bromine fuel cell were studied for the development of a reliable, long-lived system. The areas studied include electrodes, materials of construction, electrolytes, and membranes.

Long-lived electrodes with high current density operation are desired. Teflon-bonded platinum black gas diffusion anodes and porous carbon or graphite cathodes have been found to be capable of long term, high current density operation with no significant degradation [7].

Because of the corrosive behavior of bromine and hydrobromic acid, materials that could be used for cell construction were determined by soaking samples in aqueous concentrated HBr / Br_2 solutions [6]. It was found that the acceptable metals include platinum, platinum-iridium, titanium-palladium, tantalum, and niobium. The tri- or tetra-fluoroethylene polymers, Teflon, Kynar, and Halon, were also found to be bromine resistant.

Besides being resistant to the corrosive properties of bromine, the SPE used must permit transport of hydrogen ions and prevent the transport of the bromine containing

species. The transport of bromine species would cause the discharge reactions to occur without electrochemical benefit, and also causes the degradation of the hydrogen electrode due to bromine attack. Perfluorinated sulfonic acid membranes, Nafion, have been used since they are chemically inert, highly permeable to cations, and preclude passage of anions [4].

Because the electrode kinetics of a hydrogen-bromine fuel cell are fast, the voltage and coulombic efficiencies are primarily determined by the voltage drop across the membrane. This means that the efficiency is strongly related to the membrane conductivity and reactant permeation across the membrane. Good conductivity can be achieved by boiling the membrane in water to swell the polymer matrix, but the effects of this do not last if the membrane is allowed to dry [5].

Bromine has a very low solubility in water, so a solubilizer must be present in the system. The bromine needs to be dissolved in as little unreacting solvent as possible due to the weight considerations for aerospace applications.

A study showed that the cell resistance was three to eight times higher in the charged state for a cell with a salt solubilizer, (e.g., NaBr, KBr, LiBr, NH_4Br, CsBr, NaCl or $SrBr_2$), than for a cell with an HBr solubilizer [6]. This was believed to be due to fewer available

hydrogen ions within the membrane for charge transport. For cells that were substantially discharged, the salt solubilizers had little impact on the cell resistance. For these reasons, HBr is the preferred solubilizer for bromine.

1.3 Goal of this Research

Since the open circuit voltage is dependent on the state of charge of the electrolyte, multicell systems use switches to control the number of cells being used to meet the requirements at any given time. Therefore, the open circuit potential must be known as a function of the state of charge of the bromine solution reservoir.

This research was done to develop a theoretical expression capable of finding the open circuit potential of the hydrogen-bromine cell for a given hydrogen partial pressure, hydrobromic acid and bromine concentrations, operating temperature, and type of membrane separator.

Experimental work was done to confirm the theoretical development. The rates of membrane and solution equilibrium were measured to determine the length of time required for the membrane to come into equilibrium with the solution.

CHAPTER II

LITERATURE REVIEW

2.1 Reported Values of the Open Circuit Potential

Work had been done previously to determine the open circuit potential of a hydrogen-bromine fuel cell. The details of this work were either not thoroughly reported, or the system was significantly different, causing the reported values to be unusable for the system presently being studied.

Yeo and Chin [5] reported an empirical equation which can be used to calculate the open circuit cell voltage. The open circuit voltage, E_o, is expressed as:

$$E_o = \pm \left\{ \phi - (T-298) \left[4.3+1.86 \ln \frac{12.36 X_{HBr}}{1-X_{HBr}} \right] \times 10^{-4} + 4.31 \times 10^{-5} T \left(\ln f_{H_2} + \ln a_{Br_2} \right) \right\} \qquad (2\text{-}1)$$

where

$$\phi = \begin{cases} 1.073 - 0.0567 \ln \dfrac{12.36 X_{HBr}}{1-X_{HBr}} & (0.016 < X_{HBr} < 0.11) \\ 1.095 - 0.1042 \ln \dfrac{12.36 X_{HBr}}{1-X_{HBr}} & (0.11 < X_{HBr} < 0.28) \\ 1.336 - 0.2581 \ln \dfrac{12.36 X_{HBr}}{1-X_{HBr}} & (0.28 < X_{HBr} < 0.58) \end{cases} \qquad (2\text{-}2)$$

where

T - temperature in ^{o}K

X_{HBr} - weight fraction of hydrobromic acid

f_{H_2} - fugacity of hydrogen gas

a_{Br_2} - activity of Br_2 in the electrolyte

This equation was determined through experiments where the electrolyte was aqueous HBr, rather than an aqueous solution of bromine and hydrobromic acid. The hydrogen and bromine terms used in this expression are the theoretical Nernst-type terms added to approximate the effects these values would have on the open circuit voltage [8]. Note that the expression

$$\frac{R}{2F} = 4.31 \times 10^{-5} \qquad (2\text{-}3)$$

follows the Nernst expression form. They state that the activity of the bromine can be taken as unity for bromine present as a liquid phase. It seems that these expressions assume that bromine is saturated in the hydrobromic acid solution for all states of charge. However, this is only true for high states of charge. Therefore, this equation does not accurately reflect the open circuit potentials where the bromine content is below its solubility limit in the hydrobromic acid solution.

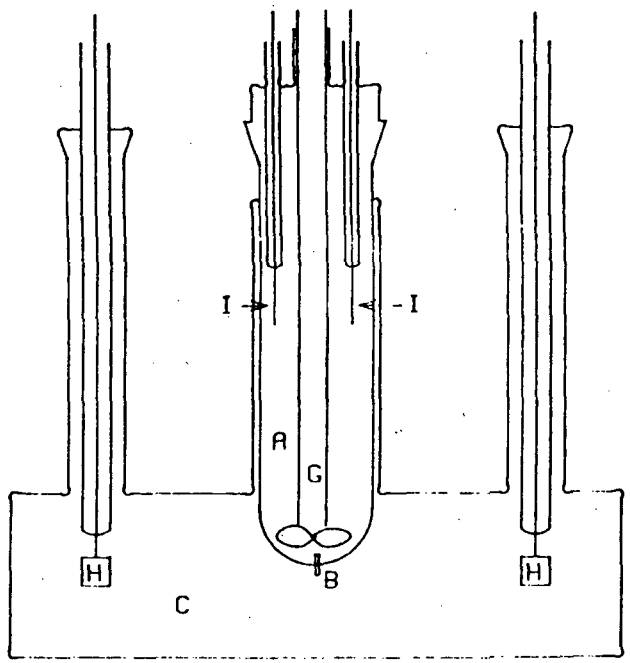
Analysis of the term $12.36X_{HBr}/(1-X_{HBr})$ reveals that it is a conversion of the weight fraction of HBR to its molality. This means that expressions (2-1) and (2-2)

are Nernst-type expressions in terms of hydrobromic acid concentration. The first and second terms of (2-1) contain numerical values found through a regression of data, and are assumed to represent the activity coefficient effects on the activity of hydrobromic acid, as would be found in a theoretical Nernst expression.

This correlation was determined using temperature studies, but not through experiments of hydrogen pressures. A Nafion 115 membrane was used as the solid polymer electrolyte for these experiments. A computer program that calculates the open circuit voltage using this correlation is given in Appendix A.

Some General Electric open circuit voltage data were given [9]. That report provides the temperature and pressure used in the experiments and the measured open circuit potential at four different states of charge. The initial and final HBr concentrations were given. The concentrations were reported in weight percentages, and it is unclear whether these values include the weight of the bromine present in the solution. Furthermore, no information on the membrane was provided.

Experimental work to measure the open circuit potential of a hydrogen-bromine cell was done by Glass and Boyle [3,6] using the system shown in Figure 2. A hydrobromic acid solution was prepared, and half was placed in the hydrogen half cell, compartment C. Bromine was



A = BROMINE HALF CELL
B = WICK
C = HYDROGEN HALF CELL
G = STIRRER
H = HYDROGEN ELECTRODES
I = PLATINUM ELECTRODES (BROMINE)

Figure 2. Schematic of experimental cell used by Glass and Boyle [3,6] to measure open circuit voltage of a hydrogen- bromine fuel cell.

mixed with the remaining acid, and placed in the bromine half cell, compartment A. The hydrogen electrodes were platinized platinum, and the bromine electrode was shiny platinum. The values reported for the open circuit voltage were referenced against a hydrogen electrode. It is not clear whether the reported potentials were corrected to standard conditions of a normal hydrogen reference electrode, i.e., 1 atm. hydrogen pressure, and unit activity of hydrogen ions. Also, no membrane was used in their system, therefore the values found in these experiments may not adequately represent those of the flow cell SPE system considered in this research.

2.2 Nafion Membranes as Solid Polymer Electrolytes

The Nafion membrane is an ion containing polymer. Nafion has a perfluorinated ethylene backbone with side chains of the form

$$-(O-CF_2-\underset{\displaystyle CF_3}{\underset{|}{CF}})_x OCF_2CF_2SO_3H$$

where x is usually one [4, 24].

The hypothesis that the ions in Nafion are clustered is generally accepted, but has not been verified, especially in acidic electrolytes [4].

Yeo [10] states that the structure of the membrane can be described as a microphase-separated system in which a matrix of low ion content is interspersed with ion

clusters. Part of the water contained in the membrane is associated with the sulfonic acid groups, part with the organic matrix, and the remainder forms hydrophilic ion clusters.

Yeo and McBreen [4] found that the membrane resistivity is permanently reduced after it has been heated once, so the membrane should be preheated to at least 70°C before it is used. This is apparently due to an increase in the water content of the membrane. They also found that the membrane conductivity is about one order of magnitude less than the conductivity of the free electrolyte.

Yeo and McBreen [4] also studied the permeation of bromine through Nafion. They found that the bromine diffusivity in the membrane decreased with increasing acid concentration. This is due to the decrease of the water content of the membrane with high acid concentrations. The rates of bromine permeation were lower than they expected, and this is believed to be due to the complexing of bromine to form tribromide and pentabromide ions.

2.3 Equilibria of Aqueous Bromine and Hydrobromic Acid Solutions

The equilibria present in aqueous solutions of hydrobromic acid and bromine were studied by Jones and Baeckstrom [11]. The equilibrium constants of the reactions

$$Br_2 + H_2O \rightleftarrows H^+ + Br^- + HBrO$$

$$Br_2 + Br^- \rightleftarrows Br_3^-$$

$$2Br_2 + Br^- \rightleftarrows Br_5^-$$

were determined from conductance measurements. The equilibrium constant for the hydrolysis reaction was found to be 5.8×10^{-9}. For the complexing reactions forming tribromide and pentabromide, the equilibrium constants were found to be 16 and 40, respectively. These values were determined at the solubility of bromine in water at 25°C, which is equivalent to 0.2141 molar, of which 0.2098 mole is present as Br_2.

Work was done by Will [12] to determine the tribromide concentrations in aqueous solutions made using high concentrations of bromide ions and bromine. He found that essentially all of the bromine originally added reacted to form tribromide.

CHAPTER III

THEORY

The open circuit potential of a fuel cell is the potential of the cell at equilibrium, where no current is flowing through the cell. The properties a fuel cell possesses at the open circuit condition can be determined theoretically through thermodynamic relationships and material properties.

3.1 Derivation of the Open Circuit Potential Expression

A theoretical expression was derived to determine the open circuit potential for the SPE hydrogen-bromine fuel cell depicted in Figure 3. The open circuit potential for this hydrogen-bromine cell can be expressed as:

$$FU = -F(\Phi^{\alpha} - \Phi^{\alpha'}) = \mu_e^{\alpha} - \mu_e^{\alpha'} \qquad (3\text{-}1)$$

The symbol μ_i represents the electrochemical potential of species i.

In the α phase, the reaction is

$$1/2\ H_2 \rightleftharpoons H^+ + e$$

so

$$\mu_e^{\alpha} = 1/2\ \mu_{H_2}^{\alpha} - \mu_{H^+}^{\alpha} \qquad (3\text{-}2)$$

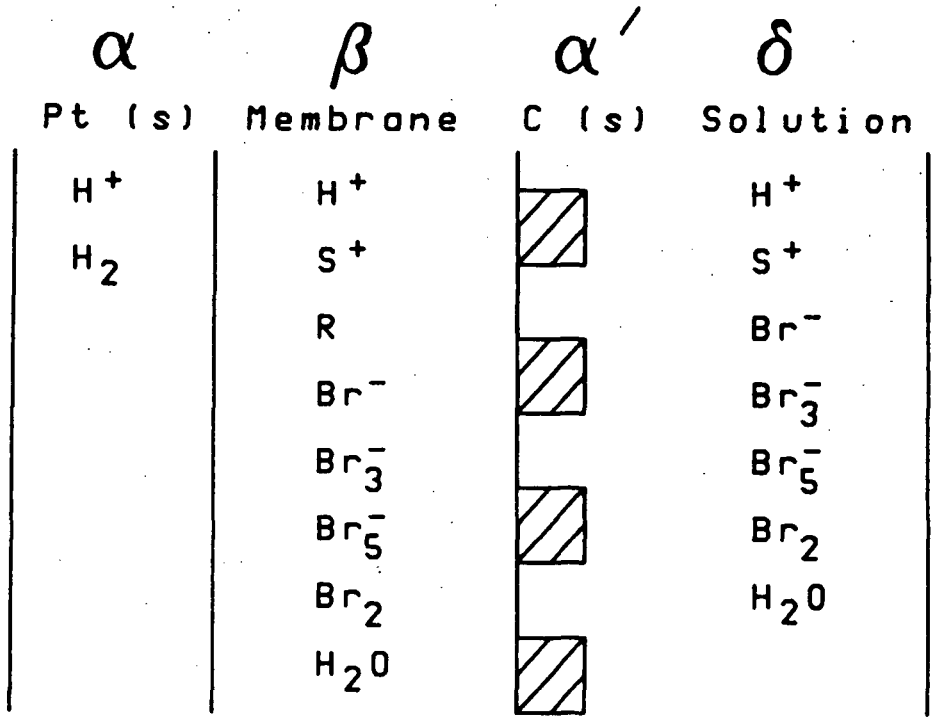


Figure 3. Diagram of species present in each phase of the SPE hydrogen-bromine fuel cell.

At equilibrium, the electrochemical potentials of the hydrogen ion in the α and β phases are equal, therefore

$$\mu^{\alpha}_{H^+} = \mu^{\beta}_{H^+} \qquad (3\text{-}3)$$

The reactions taking place at the α′ electrode are:

$$1/2\ Br_2 + e^- \rightleftarrows Br^-$$
$$3/2\ Br_2 + e^- \rightleftarrows Br_3^-$$
$$5/2\ Br_2 + e^- \rightleftarrows Br_5^-$$
$$1/2\ Br_3^- + e^- \rightleftarrows 3/2\ Br^-$$
$$1/4\ Br_5^- + e^- \rightleftarrows 5/4\ Br^-$$
$$3/2\ Br_5^- + e^- \rightleftarrows 5/2\ Br_3^-$$

The hydrolysis reaction of bromine is neglected due to its extremely low equilibrium constant [11].

By combining the equations in such a way as to eliminate dependent reactions, three independent reactions are found. They are:

$$Br_2 + Br^- \rightleftarrows Br_3^-$$
$$2Br_2 + Br^- \rightleftarrows Br_5^-$$
$$1/2\ Br_2 + e^- \rightleftarrows Br^-$$

These equations describe the solution phase chemistry of the δ phase.

The electrochemical potentials of the electrons in the α′ and δ phases are equal.

$$\mu_e^{\alpha'} = \mu_e^{\delta} \tag{3-4}$$

The bromine oxidation reaction can then be described by

$$\mu_e^{\delta} = \mu_{Br^-}^{\delta} - 1/2\ \mu_{Br_2}^{\delta} \tag{3-5}$$

Because some of the bromine reacts to form tribromide and pentabromide, the electrochemical potential of bromine can be written as

$$\mu_{Br_2}^{\delta} = a_1(\mu_{Br_3^-}^{\delta} - \mu_{Br^-}^{\delta}) + 1/2b_1\ (\mu_{Br_5^-}^{\delta} - \mu_{Br^-}^{\delta}) + c_1\mu_{Br_2}^{\delta} \tag{3-6}$$

following the stoichiometry of the reactions, where a_1, b_1, and c_1 are the mole fractions of the Br_3^-, Br_5^-, and Br_2 formed in their respective orders. Also, by definition,

$$a_1 + b_1 + c_1 = 1 \tag{3-7}$$

where

$$a_1 = \frac{\overline{C}_{Br_3^-}^{\delta}}{\overline{C}_{Br_2}^{\delta} + \overline{C}_{Br_3^-}^{\delta} + \overline{C}_{Br_5^-}^{\delta}} \tag{3-8}$$

$$b_1 = \frac{\overline{C}_{Br_5^-}^{\delta}}{\overline{C}_{Br_2}^{\delta} + \overline{C}_{Br_3^-}^{\delta} + \overline{C}_{Br_5^-}^{\delta}} \tag{3-9}$$

$$c_1 = \frac{\overline{C}_{Br_2}^{\delta}}{\overline{C}_{Br_2}^{\delta} + \overline{C}_{Br_3^-}^{\delta} + \overline{C}_{Br_5^-}^{\delta}} \tag{3-10}$$

The open circuit potential becomes

$$FU = 1/2\ \mu^{\alpha}_{H_2} - \mu^{\beta}_{H^+} - \mu^{\delta}_{Br^-} + 1/2[a_1(\mu^{\delta}_{Br^-_3} - \mu^{\delta}_{Br^-}) + 1/2\ b_1(\mu^{\delta}_{Br^-_5} - \mu^{\delta}_{Br^-}) + c_1\ \mu^{\delta}_{Br_2}] \quad (3\text{-}11)$$

Using the definitions given by Newman [13],

$$\mu^{\alpha}_{H_2} = \mu^{*}_{H_2} + RT\ln\ \rho^{\alpha}_{H_2} \quad (3\text{-}12)$$

$$\mu^{\beta}_{H^+} = RT\ln(\lambda^{\theta}_{H^+}) + RT\ln(m^{\beta}_{H^+}\gamma^{\beta}_{H^+}) \quad (3\text{-}13)$$

$$\mu^{\delta}_{Br^-_3} = RT\ln(\lambda^{\delta}_{Br^-_3}) \quad (3\text{-}14)$$

$$\mu^{\delta}_{Br^-} = RT\ln(\lambda^{\delta}_{Br^-}) = RT\ln(\lambda^{\theta}_{Br^-}) + RT\ln(m^{\delta}_{Br^-}\gamma^{\delta}_{Br^-}) \quad (3\text{-}15)$$

$$\mu^{\delta}_{Br^-_5} = RT\ln(\lambda^{\delta}_{Br^-_5}) \quad (3\text{-}16)$$

$$\mu^{\delta}_{Br_2} = RT\ln(\lambda^{\delta}_{Br_2}) = RT\ln(\lambda^{\theta}_{Br_2}) + RT\ln(m^{\delta}_{Br_2}\gamma^{\delta}_{Br_2}) \quad (3\text{-}17)$$

Substituting these expressions into the equation for the open circuit potential gives

$$FU = 1/2\ \mu^{*}_{H_2} - RT\ln\lambda^{\theta}_{H^+} - RT\ln\lambda^{\theta}_{Br^-} + RT\ln\left(\frac{p^{\alpha\ 1/2}_{H_2}}{m^{\beta}_{H^+}\ \gamma^{\beta}_{H^+}\ m^{\delta}_{Br^-}\ \gamma^{\delta}_{Br^-}}\right)$$

$$+ 1/2\left[a_1 RT\ln\left(\frac{\lambda^{\delta}_{Br_3^-}}{\lambda^{\delta}_{Br^-}\lambda^{\delta}_{Br_2}}\right) + 1/2 b_1 RT\ln\left(\frac{\lambda^{\delta}_{Br_5^-}}{\lambda^{\delta}_{Br^-}\lambda^{\delta\ 2}_{Br_2}}\right)\right.$$

$$\left. + a_1 RT\ln\lambda^{\delta}_{Br_2} + b_1\ RT\ln\lambda^{\delta}_{Br_2} + c_1\ RT\ln\lambda^{\delta}_{Br_2}\right] \qquad (3\text{-}18)$$

By definition [13] there is the relationship

$$m_i \gamma_i = a_i \qquad (3\text{-}19)$$

The equilibrium relationships also exist [11]:

$$\frac{\lambda^{\delta}_{Br_3^-}}{\lambda^{\delta}_{Br^-}\lambda^{\delta}_{Br_2}} = K_1 = 16 \qquad (3\text{-}20)$$

$$\frac{\lambda^{\delta}_{Br_5^-}}{\lambda^{\delta}_{Br^-}\lambda^{\delta 2}_{Br_2}} = K_2 = 40 \qquad (3\text{-}21)$$

By combining the above equations, the open circuit potential expression becomes:

$$FU = 1/2\ \mu^{*}_{H_2} - RT\ln\lambda^{\theta}_{H^+} - RT\ln\lambda^{\theta}_{Br^-} + 1/2\ RT\ln\lambda^{\theta}_{Br_2}$$

$$+ RT\ln\frac{p^{\alpha\ 1/2}_{H_2}\ a^{\delta\ 1/2}_{Br_2}}{a^{\beta}_{H^+}\ a^{\delta}_{Br^-}} + 1/2\left[a_1\ RT\ln K_1 + 1/2\ b_1 RT\ln K_2\right] \qquad (3\text{-}22)$$

The standard potential is defined to be

$$FU^{\theta} = 1/2\ \mu^{*}_{H_2} - RT\ln\lambda^{\theta}_{H^+} - RT\ln\lambda^{\theta}_{Br^-} + 1/2\ RT\ln\lambda^{\theta}_{Br_2} \qquad (3\text{-}23)$$

so the open circuit potential expression now becomes:

$$FU = FU^{\theta} + RT\ln \frac{p_{H_2}^{\alpha\ 1/2}\ a_{Br_2}^{\delta\ 1/2}}{a_{H^+}^{\beta}\ a_{Br^-}^{\delta}} + 1/2[a_1 RT\ln K_1 + 1/2 b_1 RT\ln K_2] \qquad (3\text{-}24)$$

Neglecting activity coefficients of the ions gives the following expression:

$$FU = FU^{\theta} + RT\ln \frac{p_{H_2}^{\alpha\ 1/2}\ a_{Br_2}^{\delta\ 1/2}}{m_{H^+}^{\beta}\ m_{Br^-}^{\delta}} + 1/2[a_1 RT\ln K_1 + 1/2 b_1 RT\ln K_2] \qquad (3\text{-}25)$$

The molalities can be expressed in terms of molarity units by the relationship

$$m_i = \frac{C_i}{C_o M_o} \qquad (3\text{-}26)$$

where C_o and M_o are the concentration and molecular weight of the solvent, respectively.

The concentrations of the bromide species in the solution and of the hydrogen ion concentration in the membrane must be determined in order to calculate the open circuit voltage of the system.

3.2 Calculation of Equilibrium Bromide Concentrations

The equilibrium concentrations of the bromide compounds for the solution or δ -phase are calculated using the symbols

$\overline{C}_i \equiv$ concentration at equilibrium of species i

$C_i \equiv$ initial concentration of species i

where the subscript s refers to a uni-univalent supporting electrolyte (e.g. NaBr, LiBr).

The principle of electroneutrality requires that:

$$\overline{C}_{H^+} + \overline{C}_s = \overline{C}_{Br^-} + \overline{C}_{Br_3^-} + \overline{C}_{Br_5^-} \qquad (3\text{-}27)$$

It is assumed that the cation concentration in the δ-phase *is unchanging and known.*

$$\overline{C}_{H^+} = C_{H^+} \qquad (3\text{-}28)$$

$$\overline{C}_s = C_s \qquad (3\text{-}29)$$

The various anion concentrations change during equilibration, but are subject to the condition that bromine atoms in unit volume are conserved.

$$C_s + C_{H^+} + 2C_{Br_2} = \overline{C}_{Br^-} + 2\overline{C}_{Br_2} + 3\overline{C}_{Br_3^-} + 5\overline{C}_{Br_5^-} \qquad (3\text{-}30)$$

These changes are due to the complexing reactions

$$Br_2 + Br^- \rightleftarrows Br_3^-$$

$$2Br_2 + Br^- \rightleftarrows Br_5^-$$

where the equilibrium constants are simplified from (3-20) and (3-21) to be:

$$\frac{\overline{C}_{Br_3^-}}{\overline{C}_{Br^-}\,\overline{C}_{Br_2}} = K_1 = 16 \qquad (3\text{-}31)$$

$$\frac{\overline{C}_{Br_5^-}}{\overline{C}_{Br^-}\,\overline{C}_{Br_2}^2} = K_2 = 40 \qquad (3\text{-}32)$$

Combining equations (3-27) through (3-32) gives a cubic equation which can be used to solve for the equilibrium bromine concentration:

$$0 = 2C_{Br_2} + (32C_{Br_2} - 32C_s - 32C_{H^+} - 2)\,\overline{C}_{Br_2} + (80C_{Br_2} - 160C_{H^+} - 160C_s - 32)\,\overline{C}_{Br_2}^2 - 80\overline{C}_{Br_2}^3 \qquad (3\text{-}33)$$

The root of this equation can be found using the bisection technique, as this method will insure a reasonable value to the root calculated. After the equilibrium bromine concentration is known, the bromide, tribromide, and pentabromide concentrations are found as follows:

$$\overline{C}_{Br^-} = \frac{C_s + C_{H^+}}{1 + 16\overline{C}_{Br_2} + 40\overline{C}_{Br_2}^2} \qquad (3\text{-}34)$$

$$\overline{C}_{Br_3^-} = 16\overline{C}_{Br_2}\,\overline{C}_{Br^-} \qquad (3\text{-}35)$$

$$\overline{C}_{Br_5^-} = 40\overline{C}_{Br_2}^2\,\overline{C}_{Br^-} \qquad (3\text{-}36)$$

For the high states of charge, where two liquid phases are present in the δ-phase, the equilibrium concentrations are found by assuming the second liquid phase is pure bromine with unit activity [5]. This reduces equations (3-20) and (3-21) to be

$$\frac{\overline{C}_{Br_3^-}}{\overline{C}_{Br^-}\, a_{Br_2}} = K_1 = 16 \qquad (3\text{-}37)$$

$$\frac{\overline{C}_{Br_5^-}}{\overline{C}_{Br^-}^{\,2}\, a_{Br_2}} = K_2 = 40 \qquad (3\text{-}38)$$

thus allowing the concentrations of bromide, tribromide, and pentabromide to be readily calculated.

3.3 Derivation of Expression to Estimate Hydrogen Ion Concentration in Membrane

A potential difference develops between two phases of adjoining electrolytes at equilibrium if the phase boundary is not permeable to all ions [14]. The hydrogen-bromine fuel cell has a cation exchange membrane, which restricts the passage of anions. This potential difference is expressed in terms of concentrations in the derivation of the open circuit potential expression where

$$\mu_{H^+}^{\delta} \neq \mu_{H^+}^{\beta} \qquad (3\text{-}39)$$

This inequality is accounted for by use of Donnan principles, and is derived as follows.

The concentration of the hydrogen ion in the membrane was found using the conditions of electroneutrality in the β and δ-phases, and the fact that the electrochemical potentials of an ion in the β and δ-phases are equal at equilibrium.

Following the definitions of equilibrium in Newman [13], the electrochemical potential of a reference ion in solution can be written as

$$\mu_n = RT\ln C_n + z_n F\Phi \tag{3-40}$$

and for all other ions present,

$$\mu_i = RT\ln \bar{C}_i + z_i F\Phi + RT(\ln f_i - \frac{z_i}{z_n}\ln f_n) + RT(\ln a_i^{\theta} - \frac{z_i}{z_n}\ln a_n^{\theta}) \tag{3-41}$$

Since the electrochemical potentials of an ion at the phase boundary are equal, the term $RT(\ln a_i^{\theta} - \frac{z_i}{z_n}\ln a_n^{\theta})$ cancels out, because it is independent of phase. The approximation that the $RT(\ln f_i - \frac{z_i}{z_n}\ln f_n)$ terms are equal for the β and δ-phases is made. Therefore, for the hydrogen ion,

$$RT\ln C_{H+}^{\delta} + F\Phi^{\delta} = RT\ln C_{H+}^{\beta} + F\Phi^{\beta} \tag{3-42}$$

$$RT\ln \bar{C}_{Br_3^-}^{\delta} - F\Phi^{\delta} = RT\ln \bar{C}_{Br_3^-}^{\beta} - F\Phi^{\beta} \tag{3-43}$$

Similar equations were written for all ions in the system. Combination of these equations leads to the relationships

$$\frac{C^{\delta}_{H+}}{C_{H+}{}^{\beta}} = \frac{\overline{C}^{\beta}_{Br_3^-}}{\overline{C}_{Br_3^-}{}^{\delta}} = \frac{C^{\delta}_{s}}{C^{\beta}_{s}} = \frac{\overline{C}^{\beta}_{Br_5^-}}{\overline{C}_{Br_5^-}{}^{\delta}} = \frac{\overline{C}^{\beta}_{Br^-}}{\overline{C}_{Br^-}{}^{\delta}} \qquad (3\text{-}44)$$

The conditions of electroneutrality are:

$$\beta\text{-phase} \quad C^{\beta}_{H+} + C^{\beta}_{s} = \overline{C}^{\beta}_{Br^-} + \overline{C}^{\beta}_{Br_3^-} + \overline{C}^{\beta}_{Br_5^-} + C_R \qquad (3\text{-}45)$$

$$\delta\text{-phase} \quad C^{\delta}_{H+} + C^{\delta}_{s} = \overline{C}^{\delta}_{Br^-} + \overline{C}^{\delta}_{Br_3^-} + \overline{C}^{\delta}_{Br_5^-} \qquad (3\text{-}46)$$

with the assumption that the amount of solution absorbed by the membrane is negligible.

Combining equations (3-44), (3-45), and (3-46) leads to the equation

$$C^{\beta}_{H+} = \frac{C_R + \sqrt{C_R{}^2 + 4(C^{\delta}_{H+} + C^{\delta}_{s})^2}}{2} \quad \frac{C_{H+}{}^{\delta}}{C^{\delta}_{H+} + C^{\delta}_{s}} \qquad (3\text{-}47)$$

where C_R is the fixed anion concentration of the membrane.

CHAPTER IV

EXPERIMENTAL SYSTEM AND PROCEDURE

An experimental system was designed and built to measure the open circuit potential of a hydrogen-bromine fuel cell. The variables to be studied were HBr and Br_2 concentration, hydrogen partial pressure, and type of Nafion membrane. Estimated rates of membrane and solution equilibrium were also measured with this system.

4.1 Equipment

4.1.1 Experimental System

Figure 4 is a schematic of the system used for experimental measurements. A listing of the equipment used is given in Appendix C. All parts were constructed of Teflon or glass due to the high corrosivity of hydrobromic acid and bromine.

The hydrobromic acid solution was sparged with nitrogen to remove oxygen from the system to obtain more reproducible results. The solution was mixed in a storage tank that was immersed in a water bath. The solution was pumped through the cell, using a Teflon piston pump chosen because of the low flow rates. A standard calomel reference electrode was inserted into this line. A

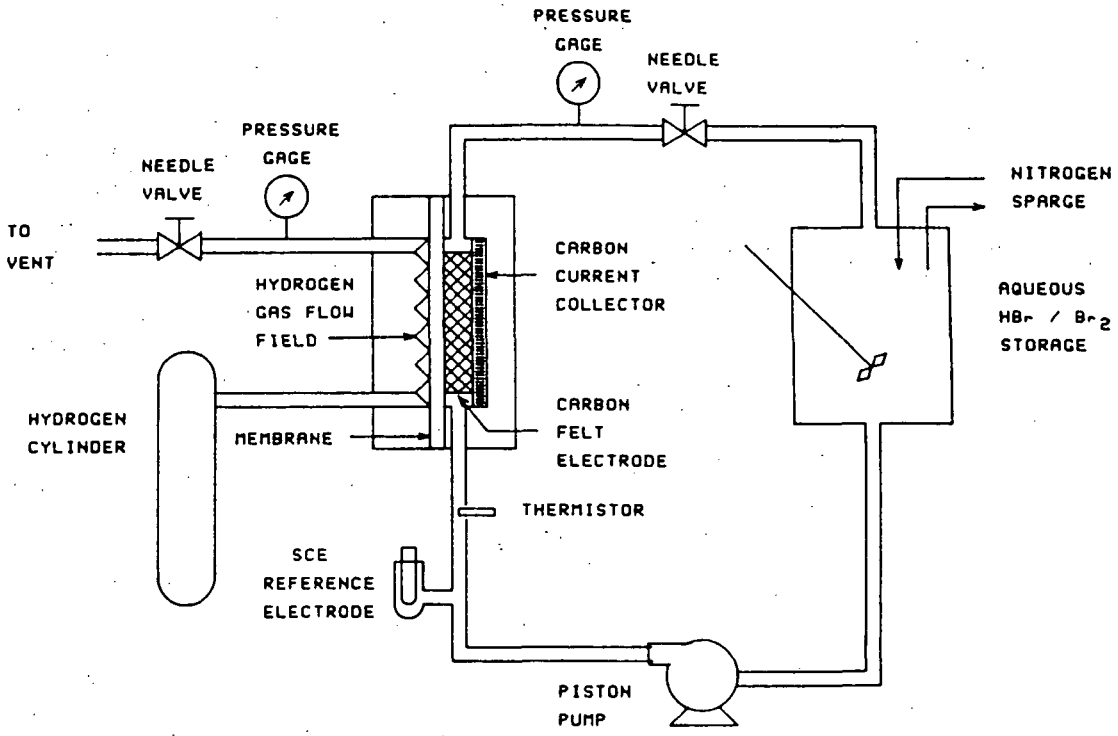


Figure 4. Diagram of experimental system for measuring open circuit voltage.

thermistor at the cell entrance measures the solution temperature to determine as closely as possible the actual cell temperature. There are pressure gages at the cell outlets, followed by needle valves to maintain equal pressure in each half cell.

Detailed diagrams of the half cells are shown in Figures 5 and 6. Both half cells were machined of TFE Teflon blocks. The cell was designed around the constraint of the size of the catalytically active region of the SPE membrane electrode assembly. A drawing of the membrane electrode assembly is shown in Figure 7. The electrode materials bonded to the membrane are a platinum black catalyst on the hydrogen side and a proprietary catalyst of Electrochem. Inc. bonded to the Nafion 120 membrane on the bromine side [15].

For some experiments, the Nafion 120 SPE membrane electrode assembly was replaced by a Nafion 117 film (equivalent weight 1100, thickness 0.178 cm. [12]). The Nafion 117 film does not have an electrode bonded to it. In either case, a 52 mesh platinized platinum screen was pressed against the membrane on the gas side, with a 52 mesh shiny platinum screen placed behind it, which was spot welded to a platinum lead wire.

The hydrogen flow field was designed to provide the most support for the platinum screens and membrane with minimal contact area. This was done by cutting v-shaped

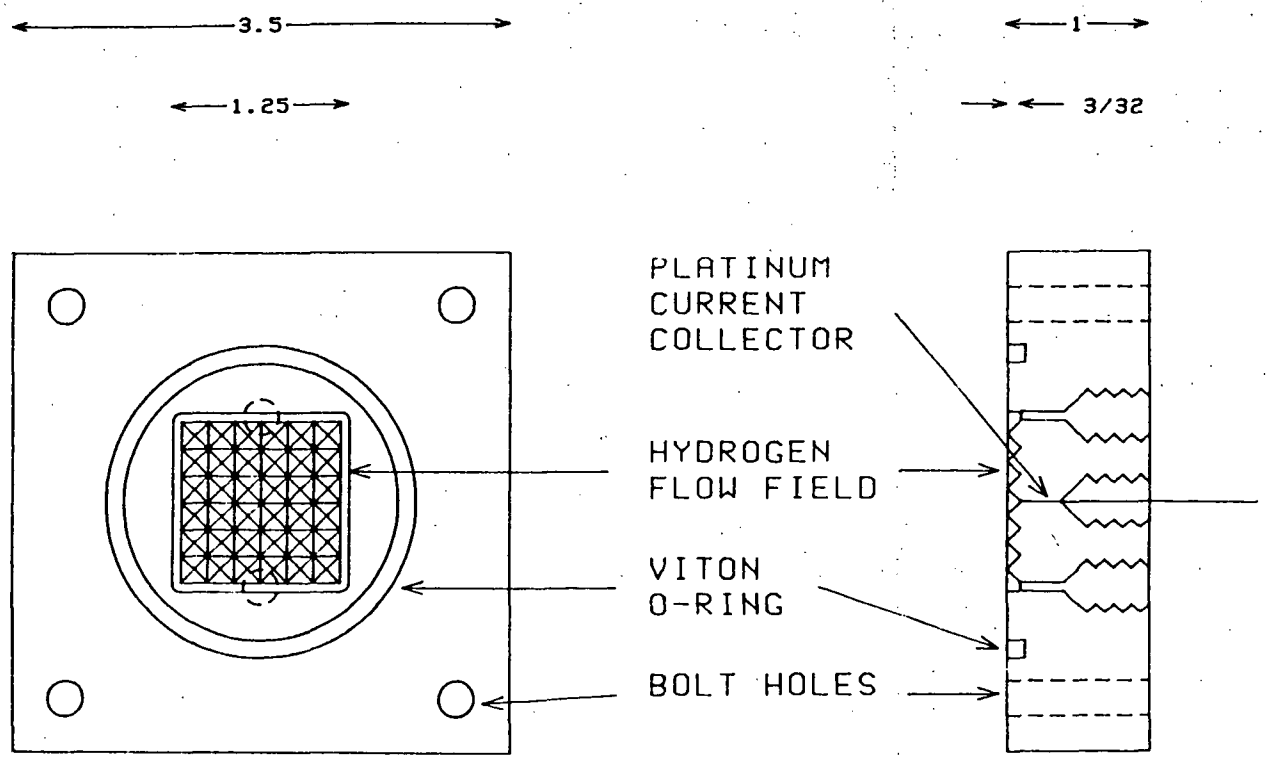


Figure 5. Diagram of hydrogen half cell. The dimensions of drawing are inches, and the drawing is to 75% of scale.

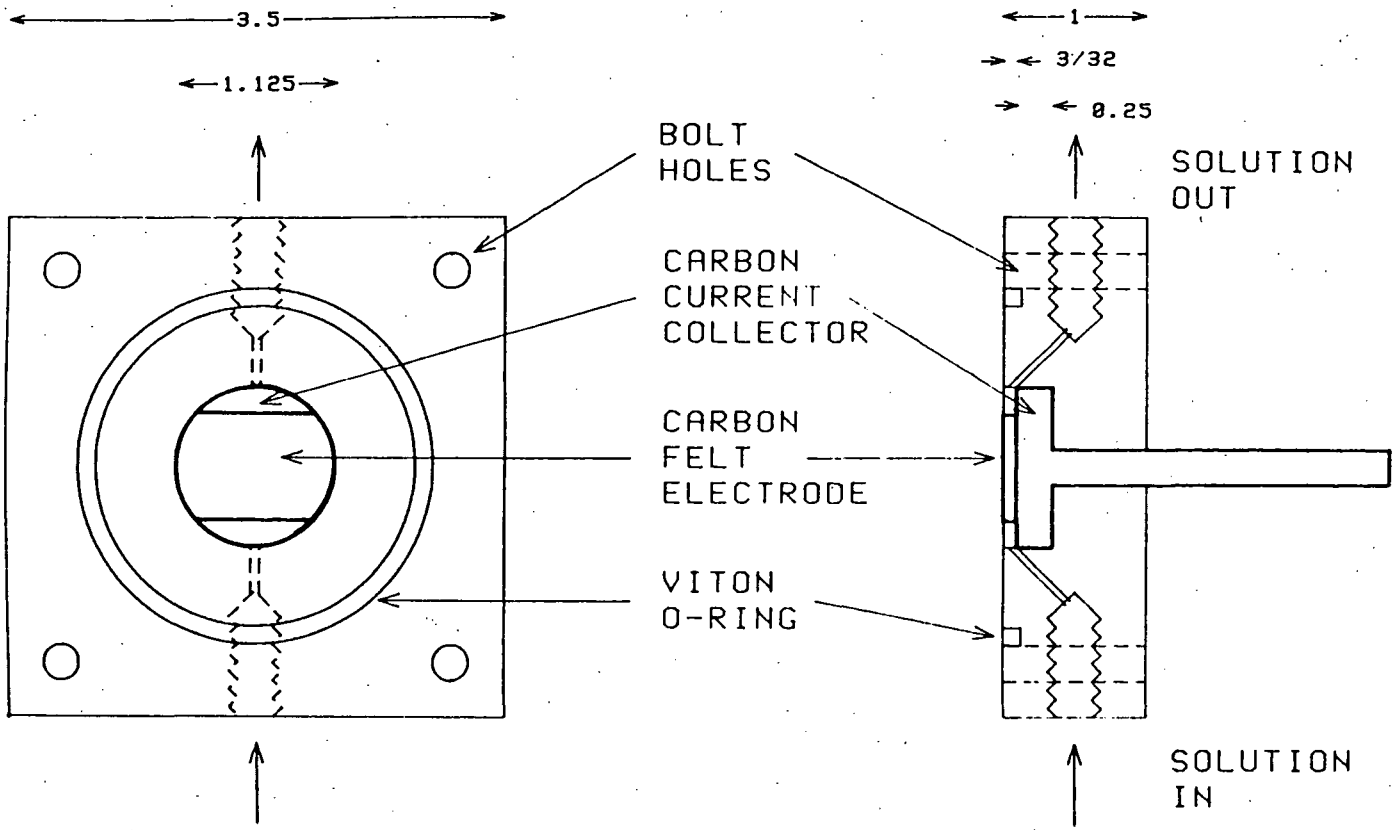


Figure 6. Diagram of bromine half cell. The dimensions of drawing are inches, and the drawing is to 75% of scale.

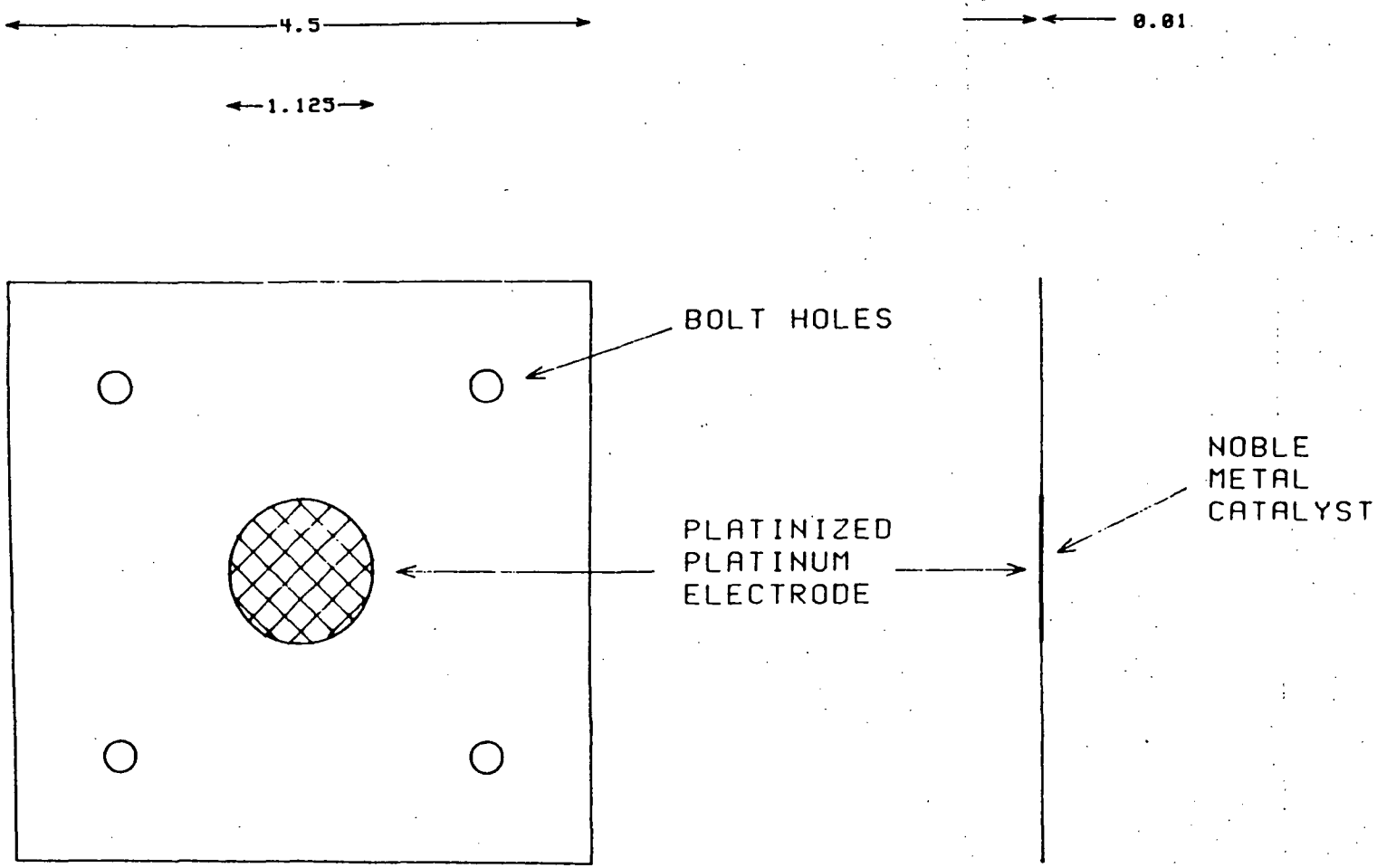


Figure 7. Diagram of Nafion 120 membrane electrode assembly. Dimensions are given in inches, and drawing is to 75% of scale.

grooves perpendicular to each other across the surface of the cell. This creates pyramids which were subsequently machined down 0.012" to allow placement of the platinum screens.

The bromine half cell contains a carbon felt electrode and a graphite block current collector. The geometry of the carbon felt electrode is as shown in Figure 6. This design allows for open regions at the chamber entrance and exit, to prevent solution hold up in the cell, and thus maintain constant and uniform concentration throughout the electrode.

4.1.2 Electrometer and Data Acquisition System

Voltage measurements were taken with a Keithley 617 Programmable Electrometer which was controlled by an IBM PC. The software used for this was the Keithley DAS Plus 500. This electrometer was chosen for these measurements because of its high impedance (> 200 x 10^{12} ohms) and its high accuracy (about 0.05%) [16]. In order to measure the cell voltage and the voltage from the reference electrode to a half cell, a relay was built. A schematic of the relay circuit is shown in Appendix C.

A program was written using Keithley DAS Plus 500 software to measure the required voltage readings. A flowchart of the program is shown in Figure 8 and the Basic code of the program is listed in Appendix E.

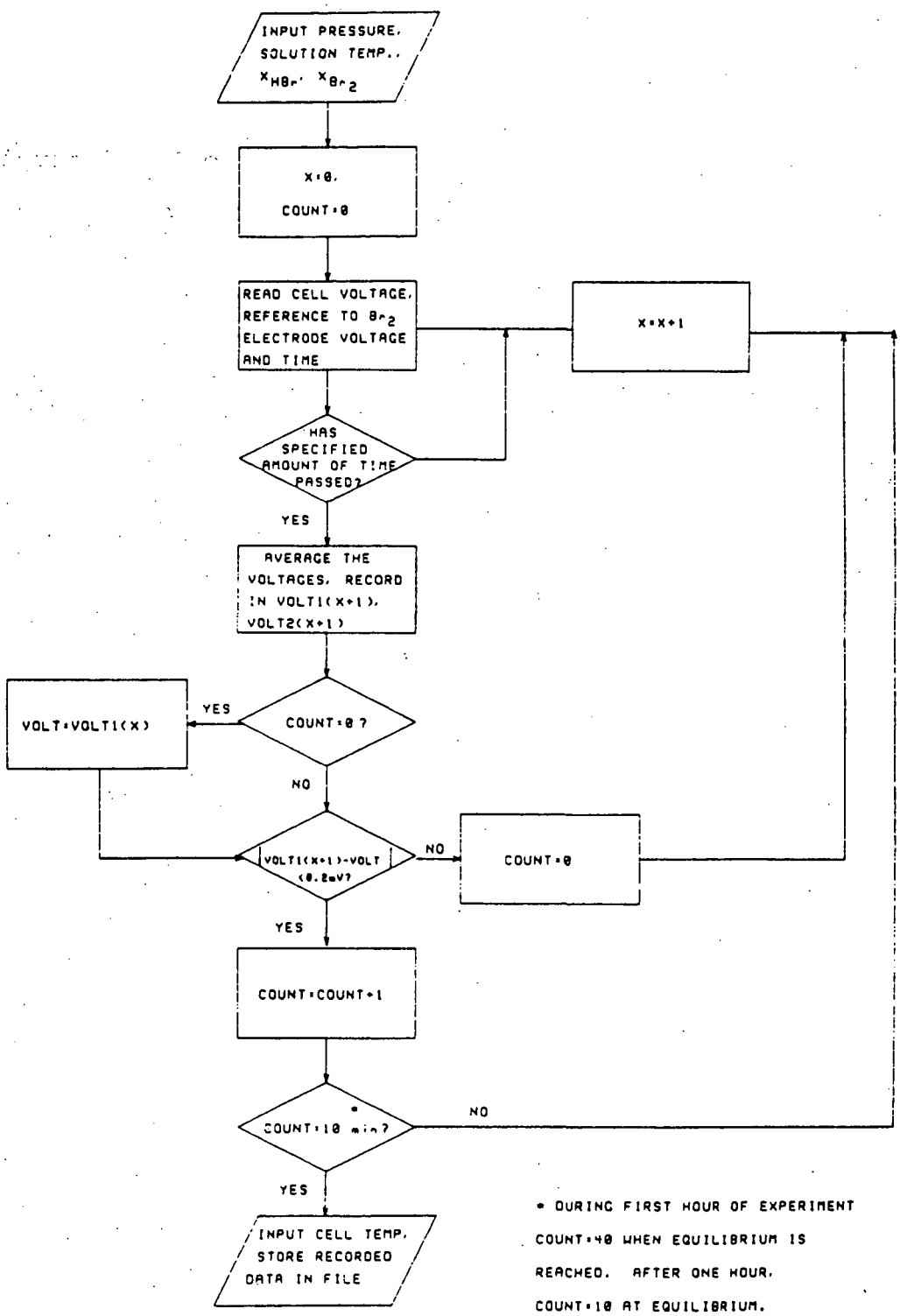


Figure 8. Flowchart of data acquisition program.

4.2 Experimental Procedure

All solutions used in this study were prepared from Fisher Scientific analytical grade chemicals and from deionized and distilled water. Ultra-high purity hydrogen and nitrogen from Linde Co. were used.

The hydrobromic acid solution was placed in the storage reservoir, then nitrogen sparged for at least two hours. Then, the acid solution was drawn into the reference electrode holder, and a sample of the HBr solution was taken for titration. (See Appendix F.) Bromine was added to the storage tank, and then the experiment could be started. Before each experiment, the solution was titrated to insure that the bromine concentration was unchanged. (See Appendix F.) The same solution could be used for all experiments involving the same concentrations of hydrobromic acid and bromine.

The complete experimental start up procedure is outlined in Appendix D. The solution was mixed throughout each experiment. During each experiment, voltage measurements were taken across the cell and between the bromine and reference electrodes.

The cell voltage was measured by the electrometer with the hydrogen electrode was common. In the bromine electrode measurements, the bromine electrode was held as common and the potential was measured with respect to a reference electrode. (See wiring diagram in Appendix C.)

This procedure allowed correct readings of the magnitude of the potential although the sign convention must carefully be interpreted.

Voltage measurements were taken every second. During the first hour of each experiment, the average value of these measurements was recorded every fifteen seconds. For the remainder of the experiment, the average voltages were recorded every minute. The median time between the reported measurements was also recorded.

4.2.1 Determination of Equilibrium Conditions

Equilibrium was considered to be reached when the recorded cell voltages differed by less than 0.0002V over the past ten minutes. Because of the way in which the program was written, this condition could be met for more than ten minutes before equilibrium was considered to be reached. (See Figure 8.)

After the equilibrium condition was met, the temperature at the cell entrance was placed into the data file by the operator, and a titration was done to verify that the bromine concentration had not changed during the experiment. This was necessary because of the high vapor pressure of bromine.

4.2.2 Measurement of Rates of Solution and Membrane Equilibrium

In order to measure the rates of solution and membrane equilibrium, the hydrobromic acid and bromine

solution in the storage reservoir was spiked with bromine after the equilibrium condition had been met for at least seven minutes. This was done by pouring bromine into the storage flask. The system was then allowed to equilibrate. The transient voltages after the addition of bromine provide information on the rates at which the system reaches equilibrium after the solution concentration is altered.

CHAPTER V

RESULTS AND DISCUSSION

The open circuit voltage of a hydrogen-bromine fuel cell was determined both theoretically and experimentally. These studies were done to determine the effects of electrolyte concentration, type of Nafion membrane, operating temperature, and pressure.

5.1 Computation of Open Circuit Voltage

5.1.1 Calculation Procedure

Computer programs were written to calculate the open circuit potential of a hydrogen-bromine fuel cell using the theoretical expression derived in Chapter III. The algorithm used in these programs is shown in Figure 9, and their FORTRAN listings are given in Appendix B.

These programs, OCV1 and OCVACT, calculate the open circuit voltage of the hydrogen-bromine cell for a given temperature, hydrogen pressure, bromine and hydrobromic acid concentrations. These concentrations can be given in terms of weight percentages or molalities. The programs can calculate the open circuit voltage with or without a Nafion membrane present. If a uni-univalent supporting

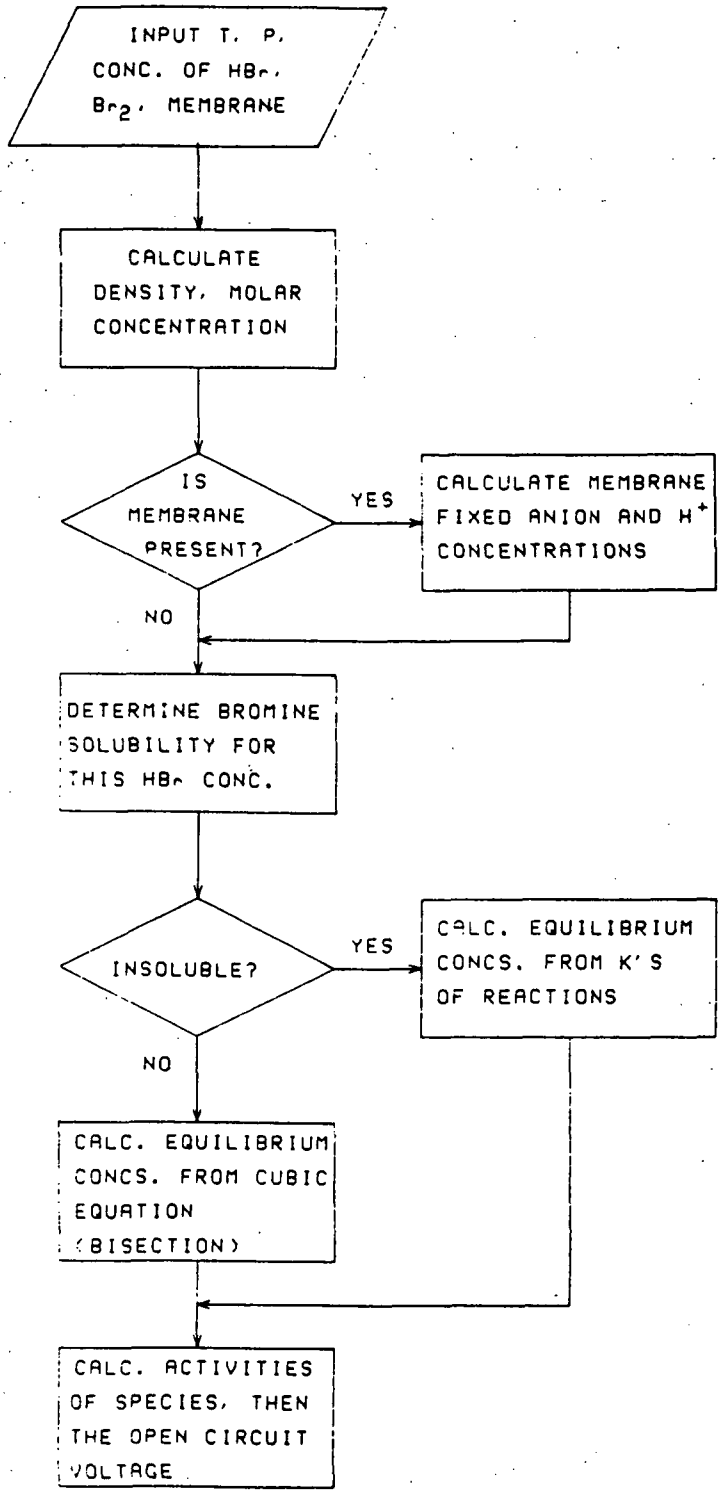


Figure 9. Flowchart of method used to calculate the open circuit voltage of a hydrogen-bromine fuel cell.

electrolyte (e.g., NaBr, KBr) is present in the system, its concentration and molecular weight must also be provided.

If the concentrations are given in weight percentages, the molal concentrations are calculated. Then, the density of the solution-phase electrolyte is determined from a curve fit of the milliequivalents of bromine atoms per gram of water versus solution density data of Glass and Boyle [3]. The equation is

$$\rho = 1.017686873 + 0.04488363995EQ - 0.0004914449546EQ^2 \quad (5\text{-}1)$$

where

ρ - solution density (g/cc)

EQ - equivalents of bromide ions, defined by

$$EQ = m_{Br^-} + 2m_{Br_2} + 3m_{Br_3^-} + 5m_{Br_5^-} \quad (5\text{-}2)$$

where the concentration terms are the molal bromide, bromine, tribromide and pentabromide concentrations. For this correlation it does not matter if the bromine is present as Br^-, Br_3^-, Br_5^-, or Br_2. For calculation of solution density with a supporting electrolyte present, the assumption is made that the size of the cation is small compared to the size of the bromide ion. This allows the bromide ion of the supporting electrolyte to be included in the solution density calculation.

For systems with a membrane, the fixed anion concentration of the membrane can be calculated using the

ion cluster model of Nafion, discussed in Chapter II. Using this model, the fixed ion concentration of the membrane, C_R, is given by [10]

$$C_R = \frac{1000 d_e}{EW} \frac{f_i}{f_e f_w} \tag{5-3}$$

where

EW - equivalent weight of the membrane

d_e - density of electrolyte absorbed by the membrane

f_e - weight fraction of electrolyte absorbed by the membrane

f_i - fraction of ionic groups in ion clusters

f_w - fraction of electrolyte in ion clusters

Due to the hydrophilic nature of the ionic groups the ratio of f_i/f_w is assumed to be one [10].

For calculation of the fixed anion concentration of the membrane, the density of the electrolyte absorbed in the membrane is assumed to be the same as the density of the solution phase. The weight fraction of the electrolyte absorbed can be determined by an empirical expression given by Yeo and Chin [5]

$$f_e = \frac{0.323}{1 + 0.068 C_{HBr}} \tag{5-4}$$

where C_{HBr} is the molarity of the charged bromide species in the solution phase, or the molarity of the hydrobromic

acid given as input to the program. This equation was determined for a system using a Nafion 115 membrane, with an equivalent weight of 1200, and was assumed to be valid for any type of Nafion membrane.

After calculating the fixed ion concentration of the membrane, the hydrogen ion concentration of the membrane can be found using equation (3-47). If no membrane is present in the system, the hydrogen ion concentration used in equation (3-25) is that of the solution phase.

A curve fit of the data of Glass [6] is used to determine whether the bromine concentration in the solution is above the solubility limit. The second order polynomial used to describe this data is

$$\text{CURVE} = 0.2526794598 + 1.057577737C_{H+} + 0.0487321524C_{H+}^2 \qquad (5\text{-}5)$$

where

CURVE - solubility limit of bromine (molar concentration)

C_{H+} - molar hydrogen ion concentration of solution phase

Two liquid phases are present when

$$C_{Br_2} > \text{CURVE} \qquad (5\text{-}6)$$

If two liquid phases are present, the second phase is considered to be pure bromine, with unit activity, and the

equilibrium distribution of the bromide species is found directly from equations (3-37) and (3-38).

If the bromine concentration is below the solubility limit, the bisection method is used to determine the equilibrium bromine concentration from the cubic equation (3-33). This method insures that the root calculated is of a reasonable value. Once the equilibrium bromine concentration is known, the others are easily calculated.

The program OCV1 determines the open circuit potential of a hydrogen-bromine fuel cell using equation (3-25), which neglects activity coefficients of all species. The program OCVACT determines the open circuit voltage of the fuel cell using equation (3-24) using the approximation that

$$\gamma_{HBr}^{\delta} = \gamma_{Br^-}^{\delta} = \gamma_{H^+}^{\beta} \tag{5-7}$$

where γ_{HBr}^{δ} is evaluated at the concentration of charged bromide species in the solution phase. The polynomial used to calculate the hydrobromic acid activity coefficient was determined through a third order curve fit of the activity coefficients given by Balko [2]

$$\gamma_{HBr} = 0.9418152476 - 0.03224218452 m_{H^+} + 0.045343504 m_{H^+}^2 + 0.015525929 m_{H^+}^3 \tag{5-8}$$

5.1.2 Comparison of Calculations with Literature Data

The values calculated from the open circuit voltage equations (3-24) and (3-25) were compared to the values given by G.E. [9]. For these cases, the weight percentages of HBr and Br_2 were calculated two ways. First, it was assumed that the weight of Br_2 was not used in the determination of the given initial and final values of the weight percentages of hydrobromic acid. Second, it was assumed that the weight of bromine was included in the given weight percentages.

The equilibrium voltage was also calculated using the empirical correlation (2-1) and (2-2) of Yeo and Chin [5]. The concentrations used in the calculations were found by the same two methods as described earlier, for comparison of these values to the data of G.E. and the values found by the theoretical expressions, (3-24) and (3-25). The results are tabulated in Table 1 and in Figures 10 through 12, where the 45 degree line signifies where perfect agreement with the reported data would lie.

In general, the values calculated by OCV1 are greater than the data of G.E. or of the correlation of Yeo and Chin. This result was attributed to the fact that OCV1 neglects the activity coefficients, which seems plausible, since this system is of concentrated solutions. For the lower states of charge, the values calculated by OCVACT are lower than the values calculated by OCV1, but larger than

Table 1. Comparison of values calculated from open circuit potential equation to those given by G. E. [9] and values calculated from empirical correlation of R.S. Yeo and D-T. Chin [5]. The temperature is 23 C, pressure is 1 bar for all cases. In the calculations, U^{θ} is taken to be 1.088V according to [17]. Voltages in parantheses include estimated activity coefficients.

Case	Method 1	Method 2	Yeo & Chin	G. E.
Start at 48% HBr 40% HBr at eq.	0.976V (0.876V)	0.955V (0.827V)	0.793V (1) 0.749V (2)	0.74V
Start at 48% HBr 20% HBr at eq.	1.157V (1.151V)	1.043V (1.015V)	0.978V (1) 0.946V (2)	0.96V
Start at 48% HBr 10% HBr at eq.	1.183V (1.186V)	1.167V (1.166V)	1.056V (1) 1.006V (2)	1.20V
7% HBr 7% Br_2	—	1.066V (1.068V)	1.094V	1.02V

(1) $X_{HBr} = \frac{W_{HBr}}{W_{HBr} + W_{H_2O}}$ (2) $X_{HBr} = \frac{W_{HBr}}{W_{HBr} + W_{Br_2} + W_{H_2O}}$

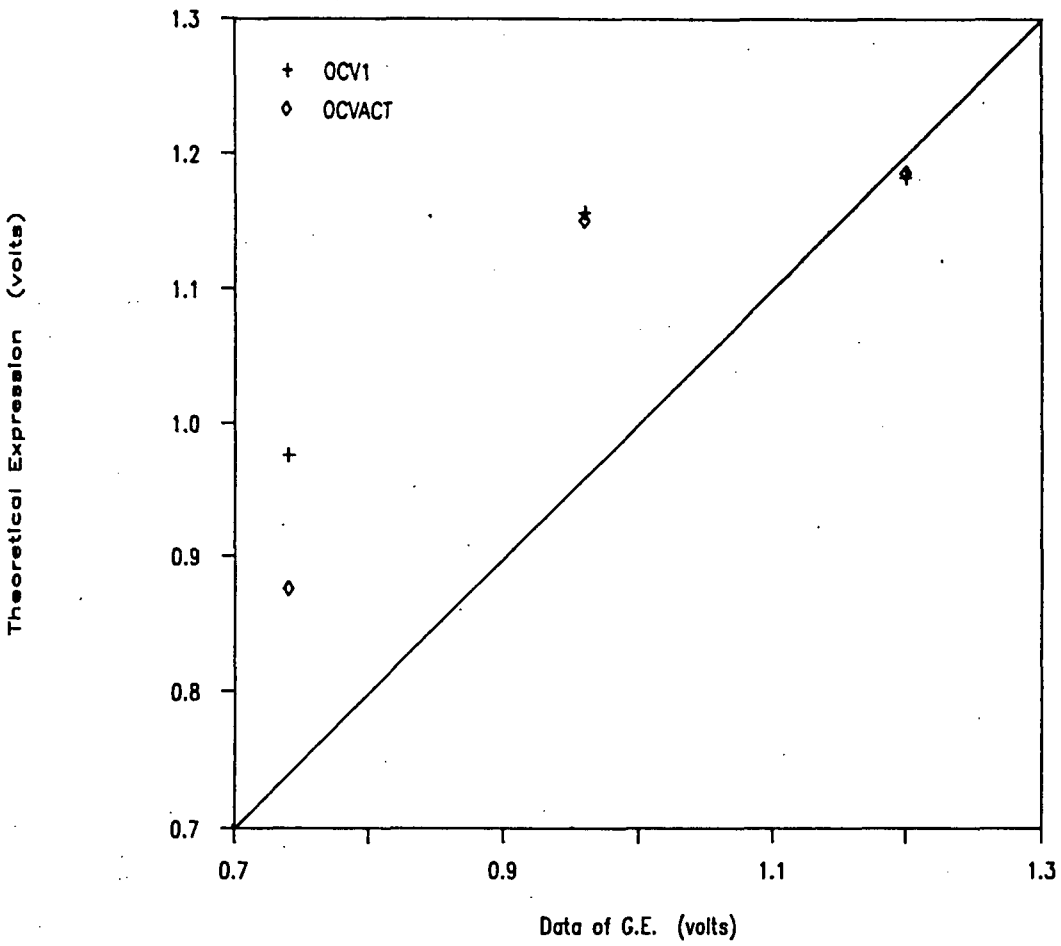


Figure 10. Comparison of theoretically determined open circuit voltages using OCV1 and OCVACT to data of G. E. [9], assuming weight of bromine was excluded from given weight fractions.

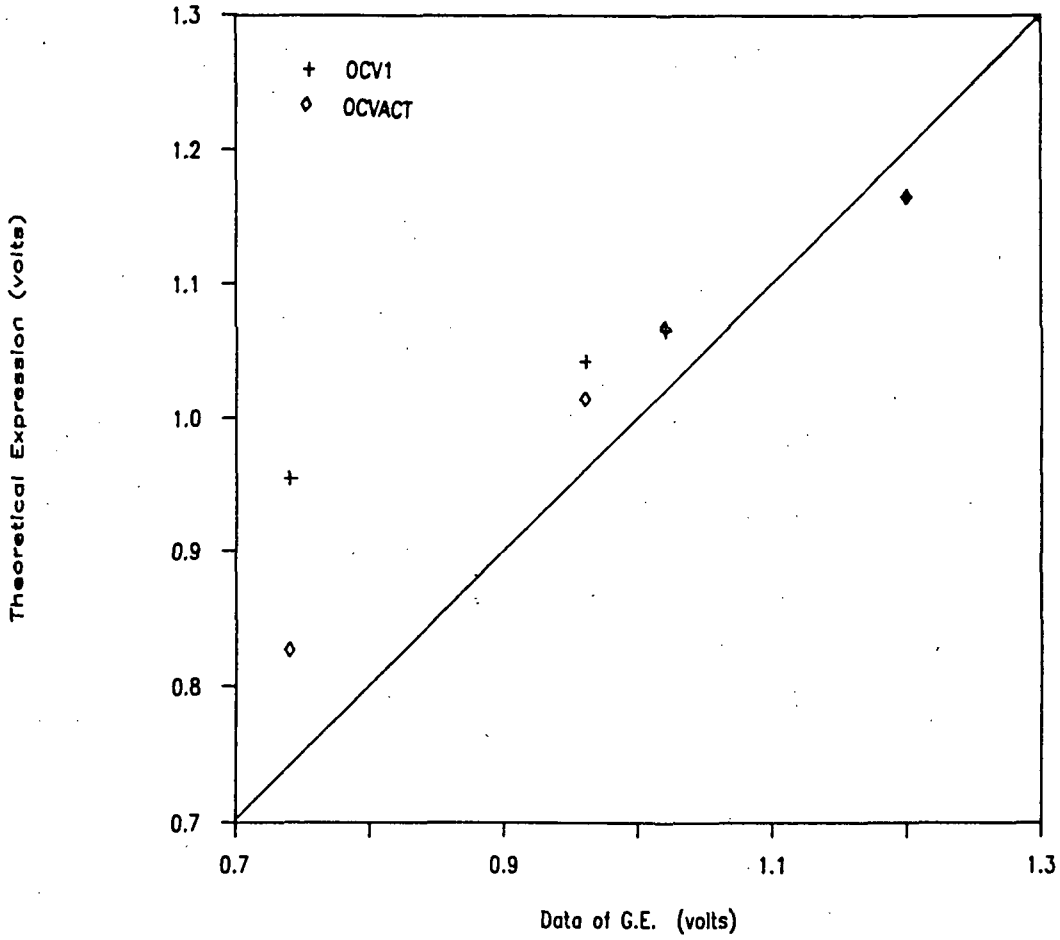


Figure 11. Comparison of theoretically determined open circuit voltages using OCV1 and OCVACT to data of G. E. [9], assuming weight of bromine was included in given weight fractions.

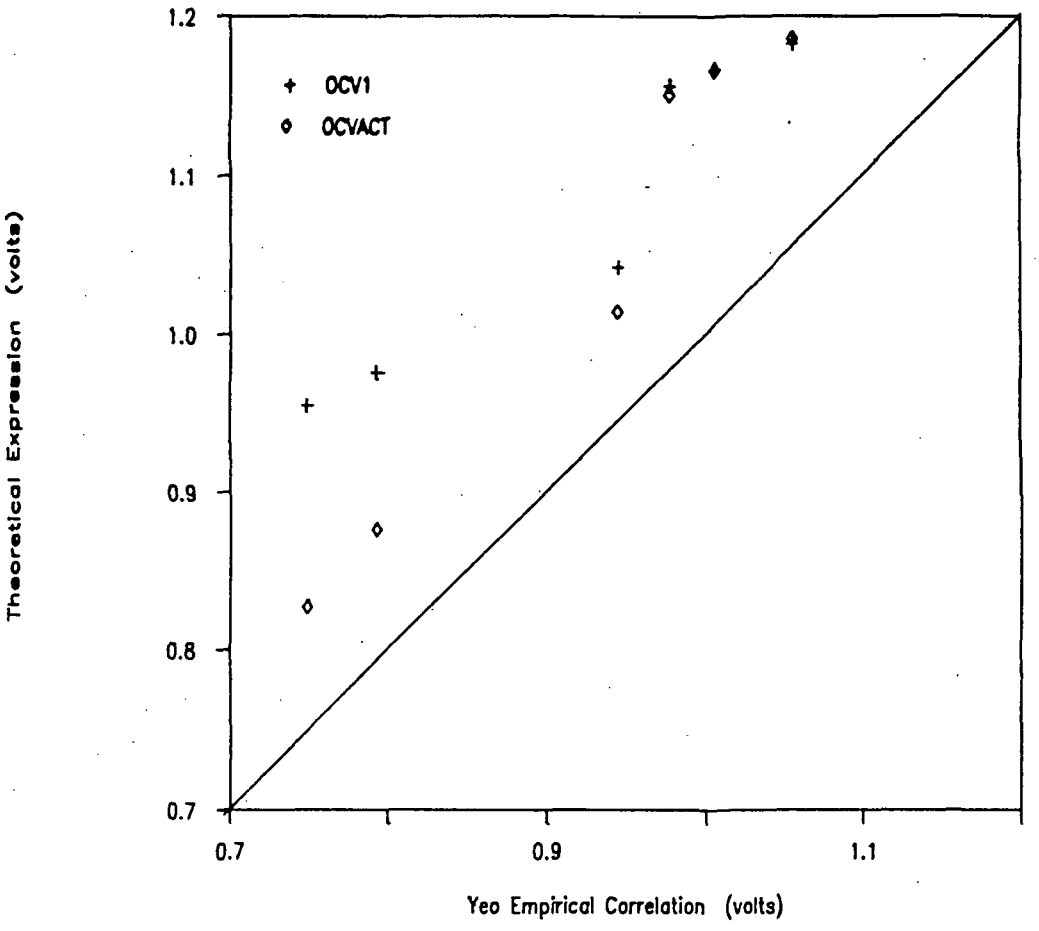


Figure 12. Comparison of theoretically determined open circuit voltages calculated by OCV1 and OCVACT to empirical correlation of Yeo and Chin [5].

the data of G. E. At the higher states of charge, there is little effect from the activity correction. For the highest state of charge, the open circuit voltages calculated by OCV1 and OCVACT are somewhat lower than those measured by G.E.

Figure 12 is a comparison of the open circuit voltages calculated by OCV1 and OCVACT to those calculated by the correlation of Yeo and Chin [5]. At the lowest state of charge, the voltages calculated by OCVACT were lower than the voltages calculated by OCV1, but larger than the values calculated from the correlation of Yeo and Chin. At the high states of charge, where two solution phases are present, the open circuit voltages calculated by OCVACT and OCV1 are nearly equal.

The calculated results of OCVACT provide reasonable estimates considering the fact that the true activity coefficients of bromide ions in this ternary solution are not known, nor are the activity coefficients of hydrogen ion in the Nafion membrane. At high concentrations of hydrobromic acid, the activity coefficients of HBr are large, and might be larger in a solution with bromine present. Also, the activity coefficient of protons in the membrane is unknown. At higher states of charge, the activity coefficient of aqueous hydrobromic acid decreases. At concentrations less than one molal, the activity coefficient of hydrobromic acid is less than unity [18].

In the case of comparing the calculated values with the G.E. data at the high bromine concentration, the calculated values are less than the experimental value of G.E. This may be due to the fact that the equilibrium constants for the bromine complexing reactions are for dilute solutions, and may not be valid in solutions of high bromine concentrations.

The effects of these equilibrium constants were studied through use of the computer program OCKEFF, listed in Appendix B. It allows the open circuit voltage to be calculated using equilibrium constants of the complexing reactions other than those in equations (3-31) and (3-32). The results of this program are shown in Figures 13 and 14. They show that the effects of the equilibrium constants are negligible at low states of charge, where the bromine concentration is small, and increase with increasing bromine concentration. The magnitude of the effect of multiplying or dividing the equilibrium constants by five at 79.2% of charge was about one hundred millivolts.

The open circuit voltages of a hydrogen-bromine fuel cell with no solid polymer electrolyte were calculated for comparison to the values of Glass and Boyle [3] using programs OCV1 and OCVACT. The results are shown in Table 2 and Figure 15. For solutions with high HBr concentrations, the voltages calculated by OCV1 are significantly higher than the data of Glass and Boyle. However, the values

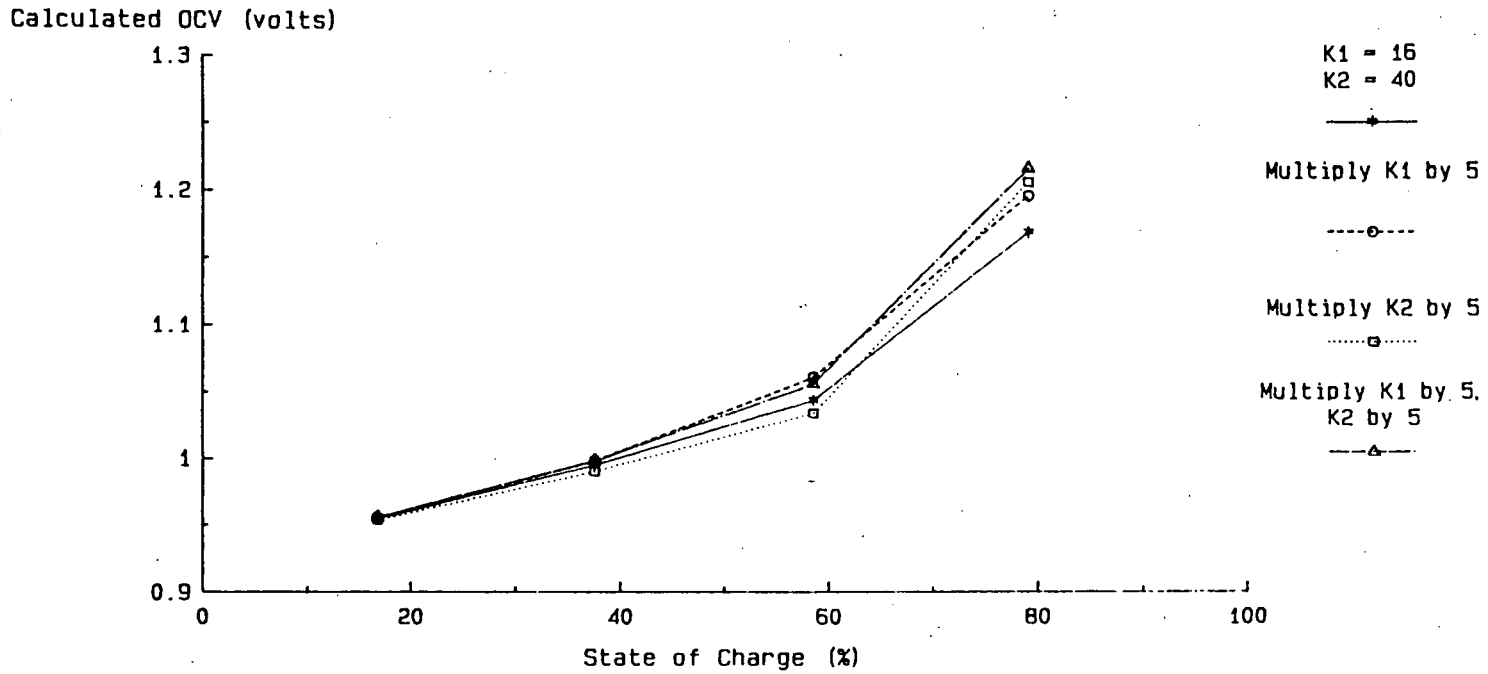


Figure 13. Effects of larger equilibrium constants of complexing reactions on the calculated open circuit voltage using OCV1.

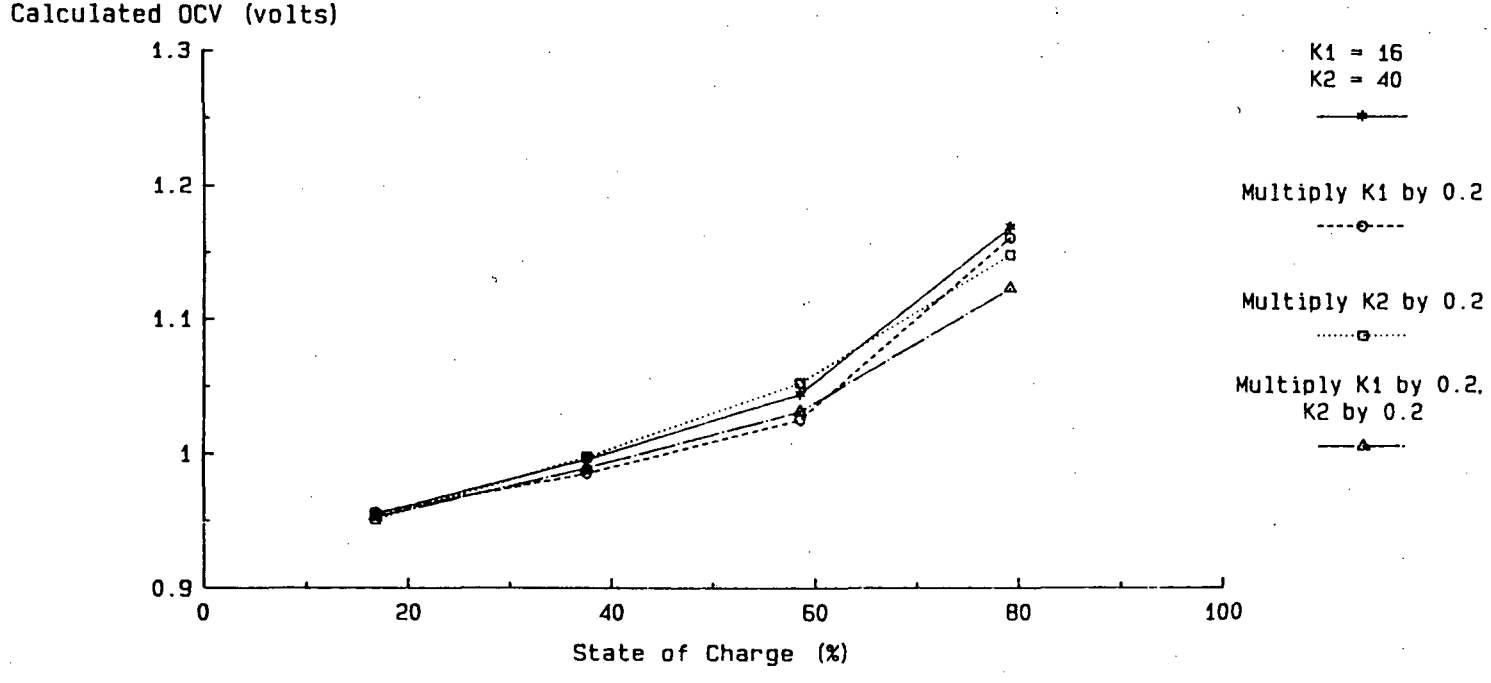


Figure 14. Effects of smaller equilibrium constants of complexing reactions on the calculated open circuit voltage using OCV1.

Table 2. Comparison of values calculated from theoretical open circuit potential expression to those found by Glass and Boyle [3] at 30 C, 1 atm. U^{θ} is taken to be 1.084V according to [17]. Voltages in parentheses include estimated activities.

Case	Calculated from Theory	Glass and Boyle
$m_{HBr} = 11.19$ $m_{Br_2} = 0.478$	0.940V (0.766V)	0.692V
$m_{HBr} = 8.95$ $m_{Br_2} = 0.499$	0.949V (0.810V)	0.748V
$m_{HBr} = 5.74$ $m_{Br_2} = 0.538$	0.978V (0.892V)	0.884V
$m_{HBr} = 1.60$ $m_{Br_2} = 2.04$	1.108V (1.104V)	1.076V
$m_{HBr} = 11.20$ $m_{Br_2} = 3.53$	0.978V (0.803V)	0.704V
$m_{HBr} = 5.67$ $m_{Br_2} = 3.59$	1.019V (0.935V)	0.880V
$m_{HBr} = 2.64$ $m_{Br_2} = 3.57$	1.084V (1.065V)	1.032V
$m_{HBr} = 11.25$ $m_{Br_2} = 6.73$	0.990V (0.815V)	0.729V
$m_{HBr} = 5.68$ $m_{Br_2} = 6.97$	1.038V (0.953V)	0.895V
$m_{HBr} = 6.67$ $m_{Br_2} = 9.01$	1.032V (0.928V)	0.888V

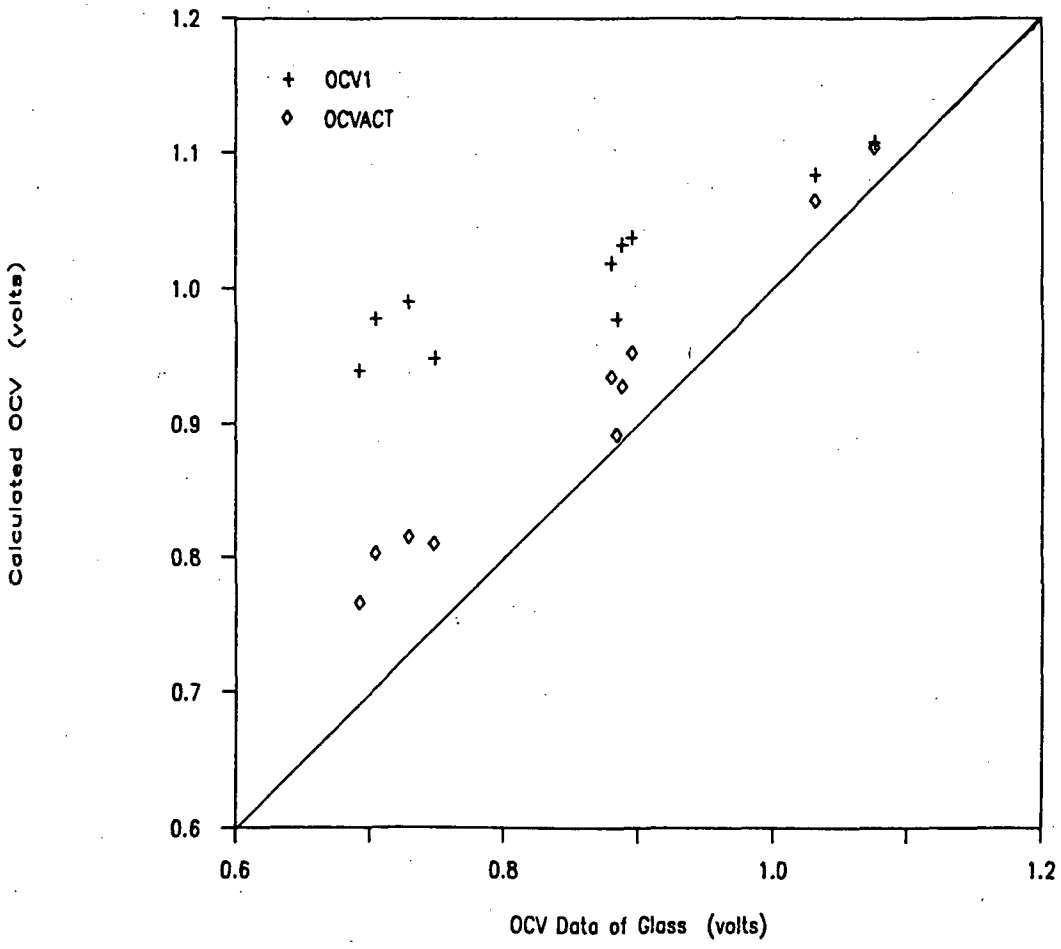


Figure 15. Comparison of open circuit voltages calculated by OCV1 and OCVACT to the data of Glass [3,6].

calculated by OCVACT are much closer to the experimental data. At intermediate bromine concentrations, the results are similar, but the calculated values are in better agreement with the reported data. At high bromine concentrations, the values calculated by both programs approach measured values. This comparison at different states of charge shows that the activity coefficients have a significant effect on the open circuit potential, especially at high HBr concentrations. Also, the agreement between OCVACT estimates and reported data is surprisingly good considering that activity coefficient data for this system are not accurately known.

5.1.3 Effects of Parameters on Open Circuit Voltage

The effects of several parameters on the open circuit voltage of the hydrogen-bromine fuel cell were studied using the program OCV1. The results of these calculations were to help identify which parameters produce a significant effect which could then be experimentally observed using the system described in chapter 4.

The open circuit voltages were calculated for 25, 45, and 75°C. From equation (3-25) the temperature dependence of the U^{θ} term is given by the equation

$$U^{\theta} = 1.0873 - (T-298.15)x541x10^{-6} \qquad (5-9)$$

where

U^{θ} - standard potential

T - Kelvin temperature

The other terms of (3-25) are also dependent on the temperature. The results of these calculations are shown in Figure 16. The temperature effect is greatest at low states of charge. At high states of charge, the second term of equation (3-25) increases, causing a lesser temperature dependence. An increase in temperature causes a decrease in the open circuit voltage, as predicted by equation (5-9).

The effects of membrane equivalent weight on the open circuit voltage were examined. The results are shown in Figure 17. Membrane equivalent weights of 1100, 1200 and 1500 were studied, using the assumption that equation (5-4) is valid for any type of Nafion membrane. The equivalent weight of the membrane was determined to have little effect on the open circuit voltage.

Also, the effects of varying the hydrobromic acid and bromine concentrations were calculated using OCV1. The results of these studies are shown in Figures 18 and 19. In Figure 18, open circuit voltage is plotted against the bromine concentration with constant hydrobromic acid concentration. For a given hydrobromic acid concentration, the open circuit voltage increases with increasing bromine concentration. Also, the voltages are lower for the

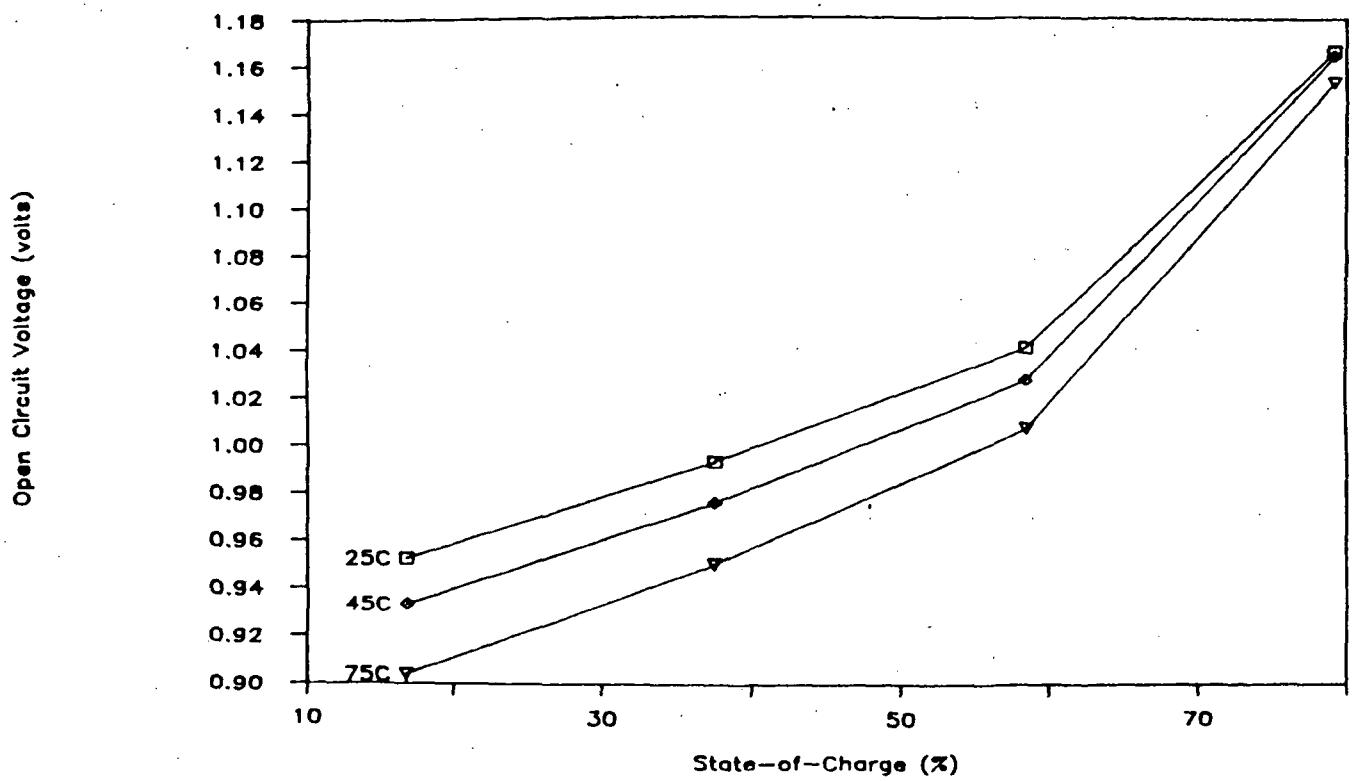


Figure 16. Effects of temperature on the open circuit voltage calculated by OCV1 for various states-of-charge.

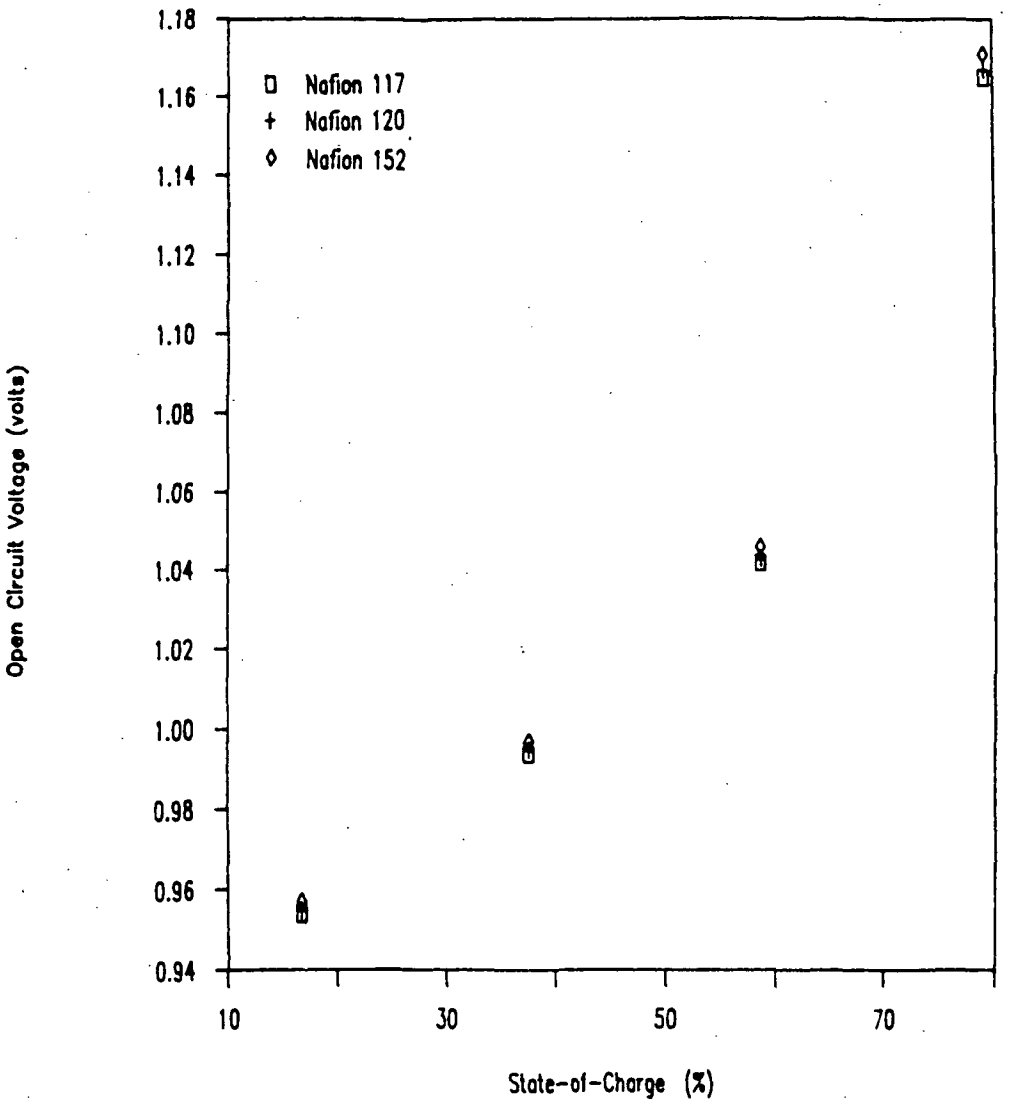


Figure 17. Effects of types of Nafion membranes on the open circuit voltage calculated by OCV1.

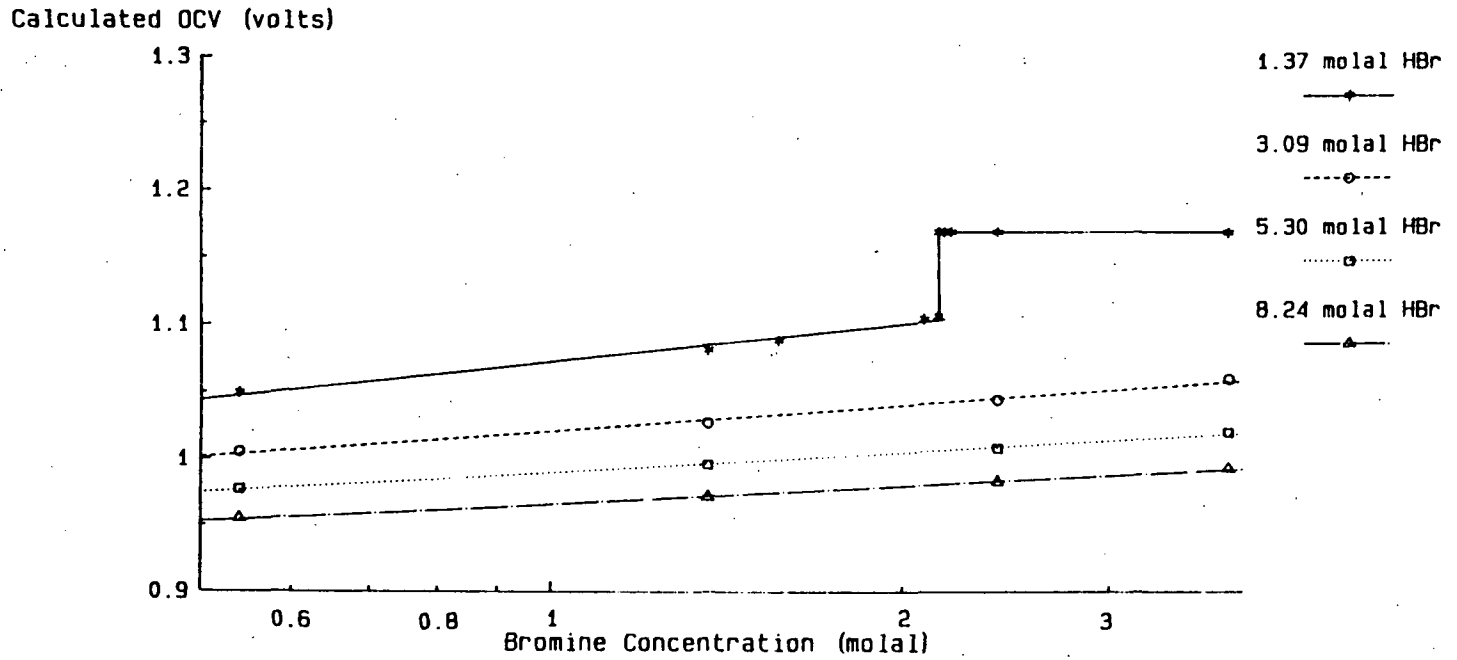


Figure 18. Semilog plot of effects of bromine concentration on the open circuit voltage calculated by OCV1.

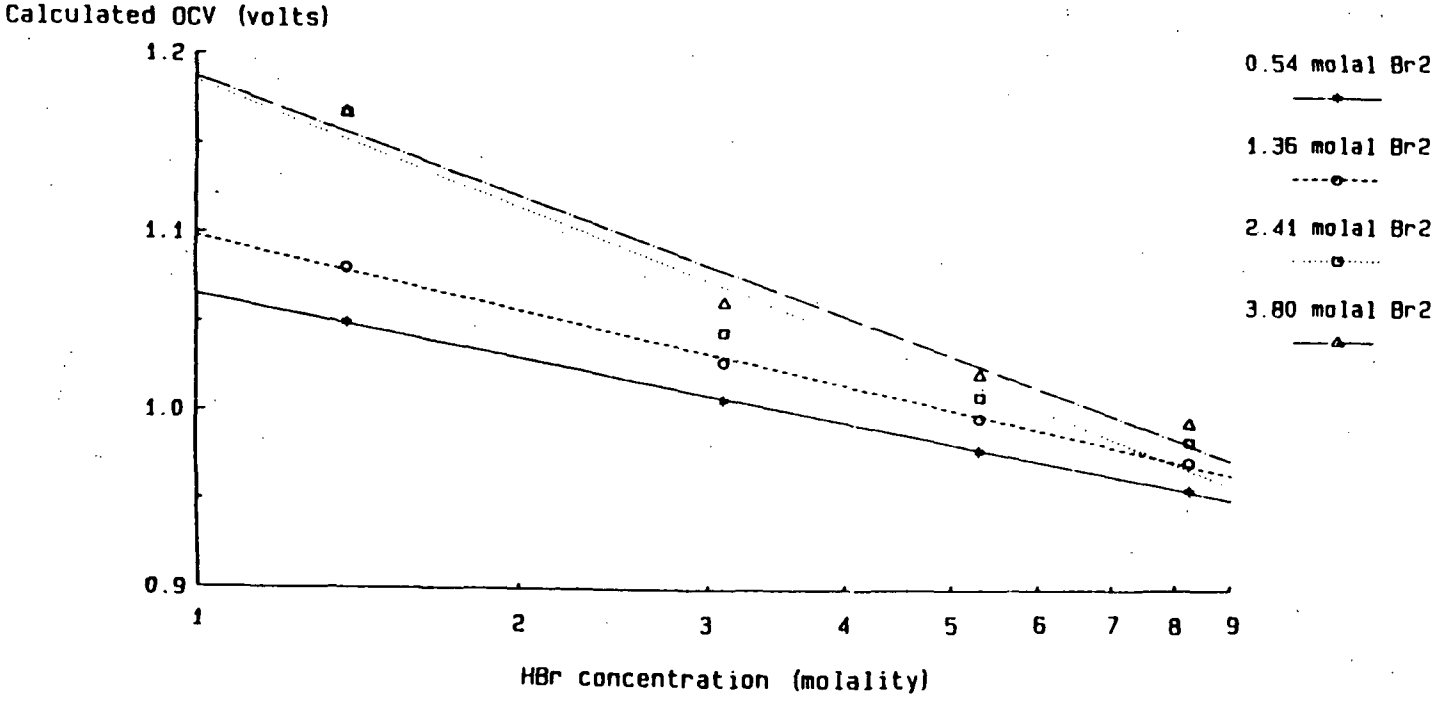


Figure 19. Semilog plot of effects of hydrobromic acid concentration on the open circuit voltage calculated by OCV1.

solutions with higher hydrobromic acid concentrations. The curve for a solution with 10% HBr (1.37 molal HBr) shows that at higher bromine concentrations, the solution forms two phases, causing the bromine concentration to have no effect on the open circuit voltage, since the activity of the bromine is constant with a value of unity.

The step change in the 1.37 molal HBr curve of Figure 18 indicates the presence of a two phase solution, and is an artifact of the method used to define the activity of bromine. Prior to the presence of a second, pure bromine phase in the solution, the majority of the bromine complexed to form tribromide and pentabromide. Therefore, the molality of the bromine after equilibration was significantly less than unity, and was defined to be equal to the bromine activity. When two liquid solution phases where present, the bromine activity was assumed to be unity in calculation of the open circuit voltage, causing the discontinuity in the calculated open circuit voltages.

Figure 19 shows the open circuit voltage as a function of hydrobromic acid concentration for constant bromine concentrations. The open circuit voltage decreases with increasing HBr concentrations. Higher voltages were calculated for the solutions with higher bromine concentrations.

Both Figures 18 and 19 reflect the trends expected from the first two terms of (3-25). If complexing of the bromine to form tribromide and pentabromide ions did not occur, these would be the only two terms needed to describe the open circuit voltage. To determine the effects of the complexing reactions on the open circuit voltage, a relationship between the open circuit voltage and the molal hydrobromic acid concentration for a constant bromine concentration was examined. This result should be a line with a slope of -59 mV at 23°C if the effects of the complexing reactions on the open circuit voltage are insignificant.

Table 3 shows the results of a linear regression and r^2, which represents the goodness of fit of the line, where perfect fit is represented by r^2 equal to one, and a poor fit by r^2 of zero. The results indicate that the complexing reactions are less significant for lower bromine concentrations, and more significant when the bromine concentrations are high. The linearly regressed lines are shown in Figure 19.

The effects of the complexing reactions on the open circuit voltage can also be seen in Figure 18. If complexing reactions of the bromine species do not occur, a plot of the open circuit voltage versus the bromine concentration would give a line with a slope of -30 mV. Table 4 shows the results of a linear regression on the

Table 3. Results of a linear regression of $\ln(m_{HBr})$ versus the open circuit voltage calculated by OCV1 for constant bromine concentrations.

Bromine Concentration	Linear Equation that Describes OCV	r^2 Goodness of Fit
7.95%	$1.06511-0.052557 \ln(m_{HBr})$	0.993450
17.88%	$1.09757-0.060954 \ln(m_{HBr})$	0.993030
27.82%	$1.18477-0.103431 \ln(m_{HBr})$	0.944587
37.76%	$1.18729-0.098084 \ln(m_{HBr})$	0.967060

Table 4. Results of a linear regression of $\ln(m_{Br2})$ versus the open circuit voltage calculated by OCV1 for constant hydrobromic acid concentrations.

Hydrobromic Acid Concentration	Linear Equation that Describes OCV	r^2 Goodness of Fit
10% *	1.07171+0.039961 $\ln(m_{Br2})$	0.98124
20%	1.02017+0.027412 $\ln(m_{Br2})$	0.98961
30%	0.98935+0.021273 $\ln(m_{Br2})$	0.99565
40%	0.96601+0.018838 $\ln(m_{Br2})$	0.99717

* Regression only includes points prior to the solubility limit of bromine in 10% HBr.

calculated open circuit voltages, at concentrations below the solubility limit of bromine in solution, and the goodness of fit parameter, r^2. These regressions show that due to the complexing reactions, the slope is near 30 mV in the first two cases, however the line fit is not as good, thus indicating that a significant quantity of the bromine complexes to form tribromide and pentabromide.

5.2 Experimentally Determined Open Circuit Voltages

Open circuit voltage measurements were made for four states of charge of solutions with initial charge capacities of 48% and 35% HBr. The effects of pressure and membrane equivalent weights were also studied. Experimental results are tabulated in Appendix H, along with samples of experimental data.

The effects of the membrane types on the open circuit voltage of a hydrogen-bromine fuel cell were determined experimentally. A comparison was made of two type of membranes. They were a Nafion 117 membrane with an equivalent weight of 1100, and a catalyzed Nafion 120 membrane with an equivalent weight of 1200. These membranes were chosen for comparison because, although Nafion 120 is no longer commercially available and has been replaced by Nafion 117, Nafion 120 was the type that was purchased from General Electric with electrodes bonded to it; platinized platinum on the hydrogen side, and a

proprietary noble metal catalyst of Electrochem Inc. on the bromine side.

Figure 20 shows experimental results for the two membrane types at concentrations corresponding to 58.5% state of charge for an electrolyte capacity of 48% HBr. It shows reproducibility within the limits of experimental error. Similar equilibrium voltages for the two systems are predicted. This is because the ratio of the equivalent weights is close to unity in equation (5-3), so the fixed ion concentrations of the membranes are about the same. This means that the difference in the hydrogen ion concentrations of the membrane will be small, having little effect on the open circuit voltage.

Table 5 shows the open circuit voltages determined for a system with a Nafion 117 membrane, a pressure of 2 psig, and room temperature operation. These experiments were done for a 16.7% state of charge of a solution with a capacity of 48% HBr. The open circuit voltages found in these experiments have an average value of 0.733V, with a standard deviation of 0.034V.

Table 5 also shows the results of four experiments done for the same conditions of concentration, temperature and pressure, except the Nafion 120 membrane electrode assembly was used. The average open circuit voltage of these experiments is 0.737V, with a standard deviation of 0.006V. Thus, the effects of different Nafion membranes

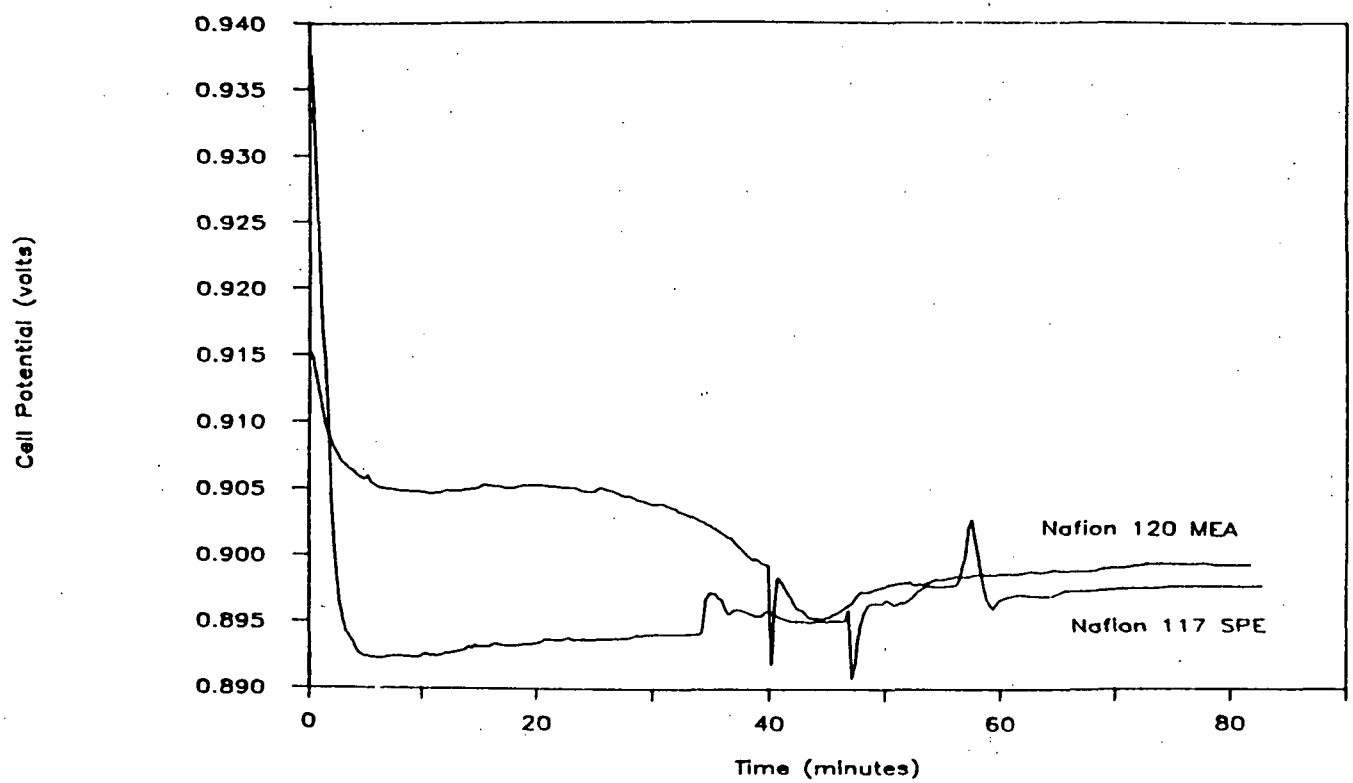


Figure 20. Comparison of experimental results obtained using Nafion 117 membrane (T=26.1C) to those of catalyzed Nafion 120 catalyzed membrane (T=25.5C). The experiments were conducted at 2 p.s.i. and concentrations of 20% HBr and 27.82% Br_2.

Table 5. Open circuit voltages for 16.7% state of charge of solution with an initial charge capacity of 48% HBr. All experiments conducted at room temperature, and pressure of 2 p.s.i. The SPE used in these studies was either a Nafion 117 membrane, or a Nafion 120 membrane electrode assembly.

Membrane	Open Circuit Voltage (V)
Nafion 117	0.745
Nafion 117	0.780
Nafion 117	0.688
Nafion 117	0.719
Nafion 120 MEA	0.744
Nafion 120 MEA	0.740
Nafion 120 MEA	0.732
Nafion 120 MEA	0.731

are negligible, although these experiments appear to be more reproducible than those with the Nafion 117 membrane.

The reason for less reproducible data with the Nafion 117 system could be related to slow deactivation of the platinized platinum electrode in that system. (e.g., caused by the dry environment). The high surface area platinum catalyst on the Nafion 120 membrane is less likely to deactivate. Also, the precious metal catalyst on the bromine side of the Nafion 120 membrane may keep bromine species from diffusing across the separator. Therefore, deactivation of the platinum hydrogen electrode in the Nafion 120 system is less likely.

Experiments were also done to determine the magnitude of the effects of the hydrogen pressure and the bromide solution pressure on the open circuit voltage. This was accomplished by altering the hydrogen or bromine pressure during an experiment; 2 psig to 4 psig. The effects of altering the hydrogen pressure are shown in Figure 21. The results show that for pressure increases, the voltage sharply rises a couple of millivolts, then falls to a value higher than that prior to the change. When the pressure is reduced to 2 psig, the voltage drops a few millivolts, then rises rapidly to a value less than that before the change.

The effect of pressure changes in the aqueous electrolyte for one experiment is shown in Figure 22.

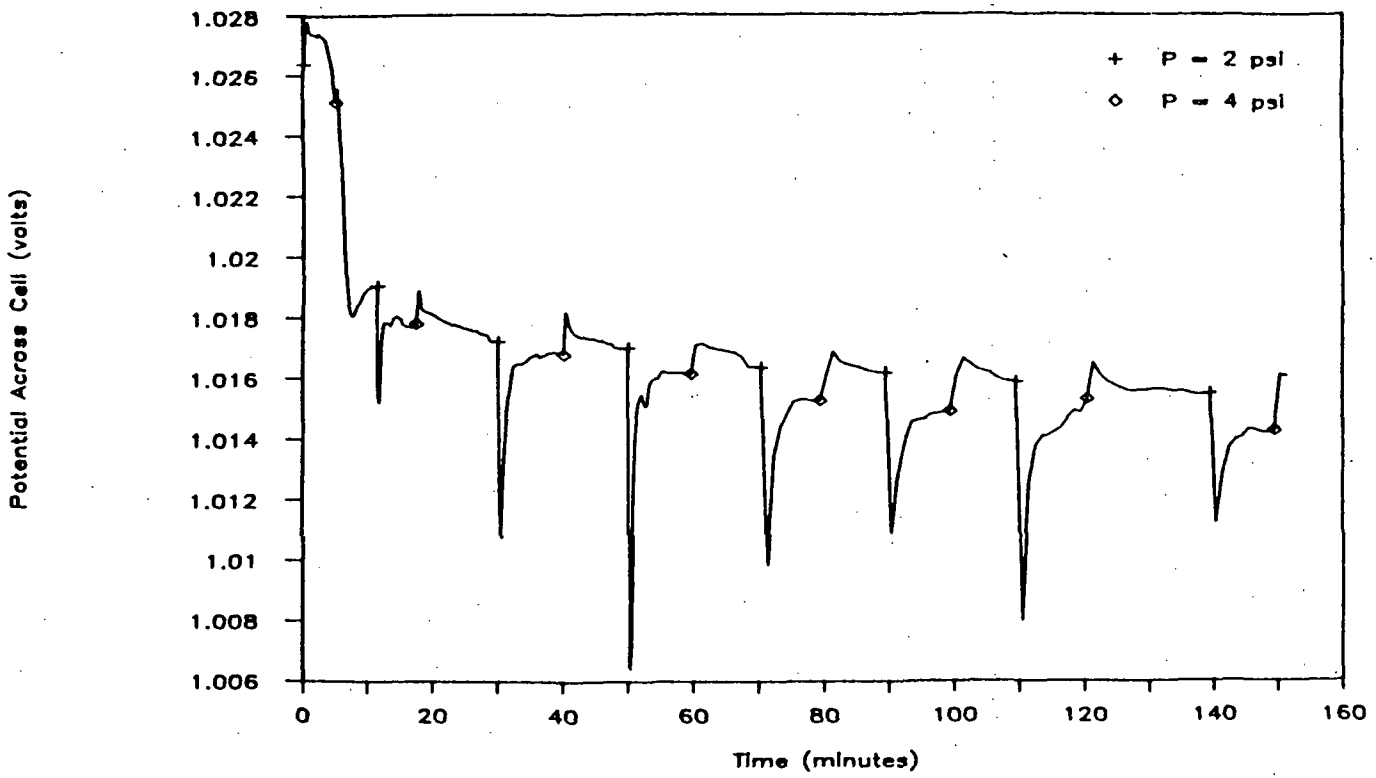


Figure 21. Effects of altering hydrogen pressure during an experiment conducted at 27C, solution pressure of 2 p.s.i. and concentrations of 10% HBr and 7.95% Br_2.

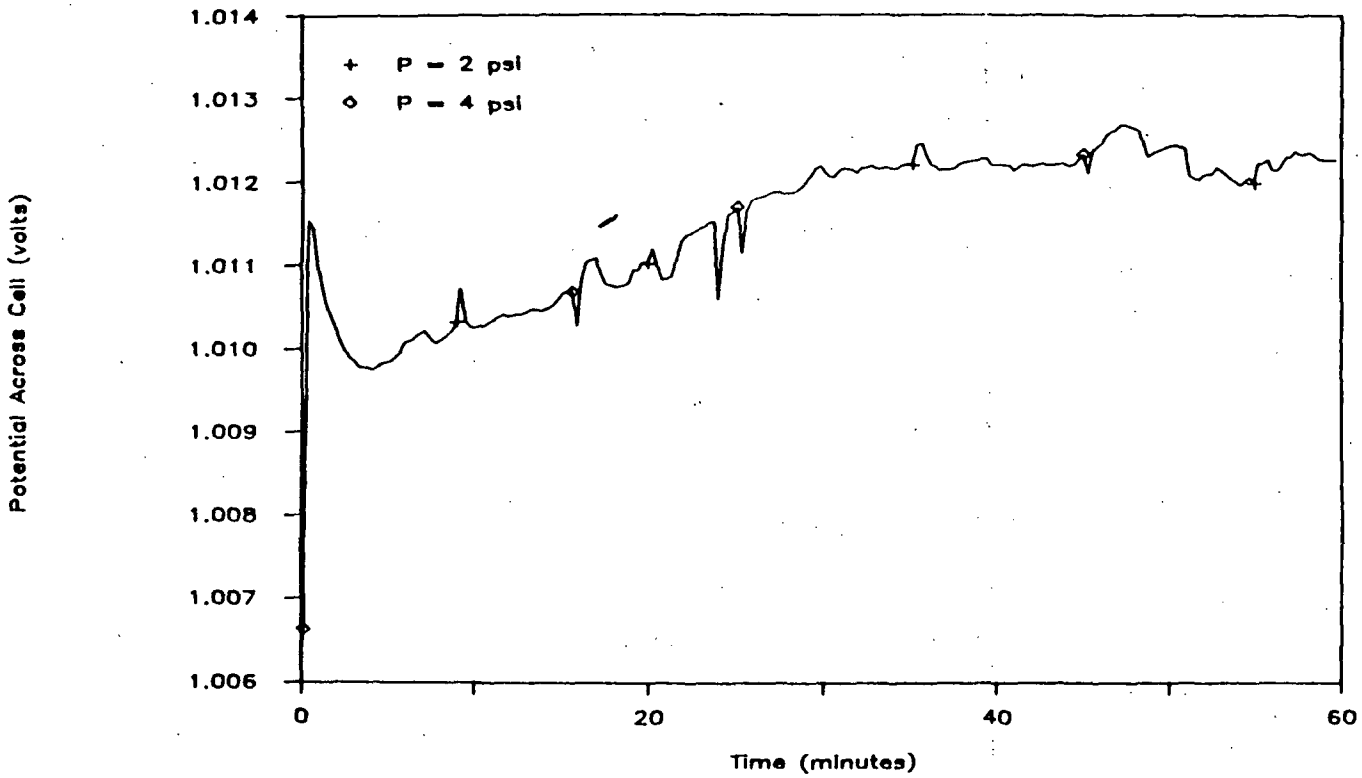


Figure 22. Effects of altering solution pressure during an experiment conducted at 27C, hydrogen pressure of 2 p.s.i. and concentrations of 10% HBr and 7.95% Br_2.

The effects of liquid pressure changes are not as pronounced as for those of the hydrogen. When the solution pressure is increased, the voltage increases slightly, then oscillates to a value close to that prior to the change. For a decrease in the pressure, the voltage decreases slightly, then oscillates to a value close to that prior to the change. In one of the experiments, equilibrium was reached, even though the solution pressure was being altered.

A detailed analysis of the effects of altering the half cell pressures during operation is beyond the scope of this research. However, the theoretical expression (3-24) does not depend on the bromine pressure, so the effect of changing the solution pressure value is expected to be negligible, as was shown. Since the hydrogen pressure is a term in the expression, the effect of altering this value is expected to be more significant, and this was shown to be true.

The effect of the hydrogen pressure on the open circuit potential of the hydrogen-bromine cell at 16.7% state of charge was determined for three pressures. The open circuit voltage of the cell was plotted against the log of the square root of the pressure. The resulting graph should be a line with a positive slope of 30 mV/atm. This plot is shown in Figure 23, which shows that a regression would be meaningless. Because the experimental

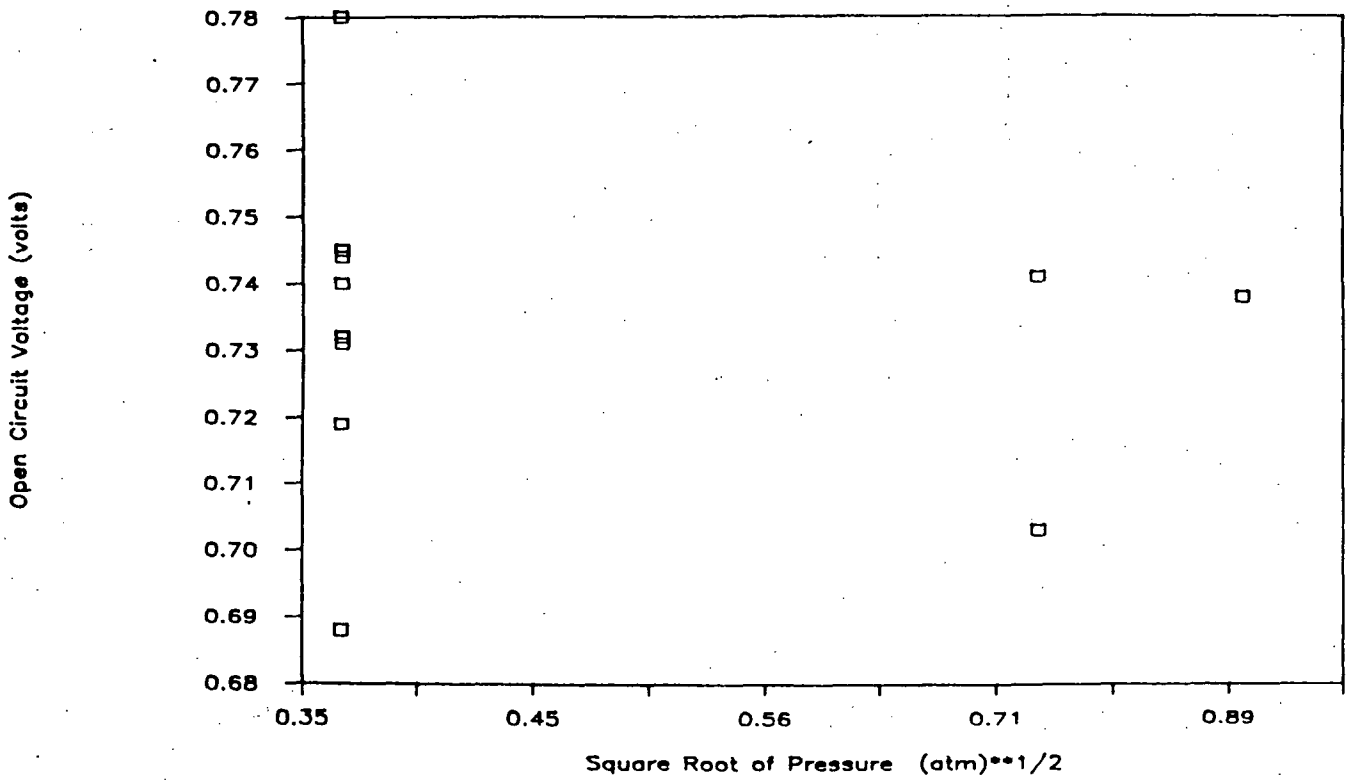


Figure 23. Semilog plot of effects of hydrogen pressure on the open circuit potential. Experiments were conducted at room temperature, concentrations of 40% HBr and 7.95% Br_2.

inaccuracies involved in measuring the open circuit potential of this system, are on the order of the differences expected due to the pressures studied, this trend could not be detected. However, due to safety considerations, operation at higher pressures was not attempted. Therefore, the remainder of the experiments were conducted at a pressure of 2 psig. Also, due to safety considerations, all experiments were conducted at room temperature.

The experimentally determined open circuit voltages of hydrogen bromine fuel cells with initial charge capacities of 48% and 35% are given in Tables 6 and 7. Although the experiments were not completed at the same temperature, the expected effect of the temperature difference on the open circuit voltage is less than 3 mV., and was considered to be insignificant.

The mean experimental values and the error incurred in the estimation of the mean within a 95% confidence interval [19] are shown in Figure 24. Note that the results of the experiments with a charge capacity of 35% HBr are much more reproducible than those with an electrolyte capacity of 48% HBr.

For both the 35% HBr and 48% HBr electrolyte capacity solutions, the 79.2% state of charge electrolyte was a two phase liquid, where the second phase is considered to be pure bromine. For these experiments at

Table 6. Open circuit potentials determined experimentally for an electrolyte capacity of 35% HBr, Nafion 120 membrane electrode assembly, room temperature, 2 p.s.i. Reported error is that in estimation of mean within a 95% confidence level.

State-of-Charge (%)	N	Mean (V)	Error (V)
16.7	4	0.854	0.001
37.5	2	0.916	0.000
58.5	3	0.988	0.001
79.2	2	1.107	0.013

N = number of experimental values

All experiments were done at a pressure of 2 psig, and temperatures between 23.7 and 25.4 C.

Table 7. Open circuit voltages determined experimentally for an electrolyte capacity of 48% HBr, room temperature, and 2 p.s.i. Reported error is the error incurred in estimation of the mean within a 95% confidence interval.

State-of-Charge (%)	Membrane (Nafion)	N	Mean (V)	Error (V)
16.7	120 MEA	4	0.737	0.009
16.7	117	4	0.733	0.054
37.5	120 MEA	3	0.802	0.023
58.5	120 MEA	2	0.897	0.022
58.5	117	1	0.898	-
79.2	120 MEA	2	1.068	0.000

For all experiments, the pressures were 2 psig, and the temperatures were 24.4 C to 27.4 C.

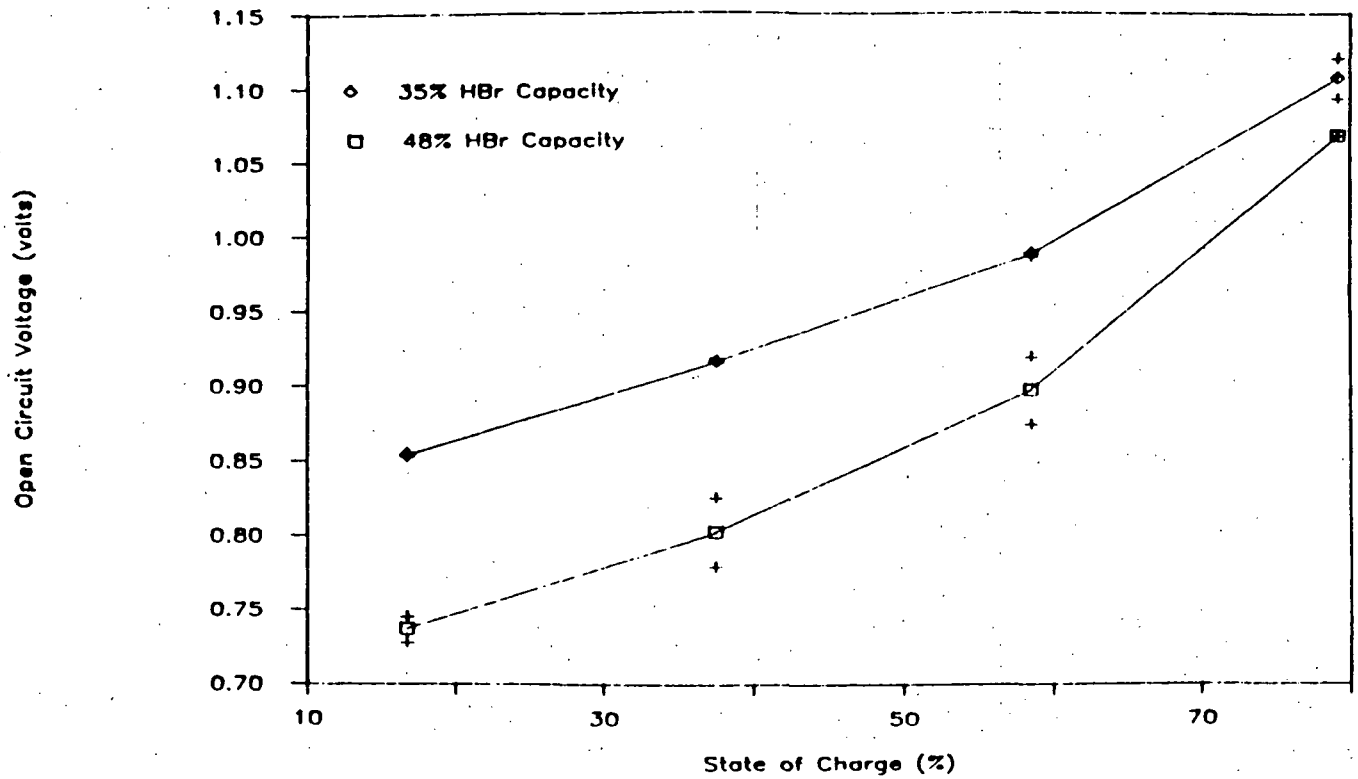


Figure 24. Estimated means of experimental results for experiments with Nafion 120 catalyzed membrane. Error incurred in estimation of mean is in the 95% confidence interval [19].

the 48% capacity electrolyte, equilibrium was not reached, although the voltage stayed fairly constant at 1.068V, but then began to decline. See Figure 25. In one experiment for the 79.2% state of charge determined from a 35% HBr solution, equilibrium appeared to be reached at 1.108V. However, in the other experiment, the voltage stayed constant for several minutes at 1.106V, then began to decline.

Because this is the only state of charge where equilibrium was not achieved, the cause may be related to the presence of a two phase electrolyte, or perhaps catalyst deactivation due to the high bromine concentration. These experiments suggest that the more concentrated solutions are not as stable as the less concentrated solutions.

5.3 Comparison of Experimental Data to Previously Reported and Theoretical Open Circuit Voltages

The open circuit voltages predicted by others and the theoretical expression were compared to the results measured experimentally in this research.

Figure 26 is a comparison between the experimentally measured open circuit voltage of this work and the open circuit voltage reported by G.E. [9]. This comparison is made assuming that the weight fractions of HBr that correspond to the reported open circuit voltages included the weight of bromine in the solution. The 45 degree line

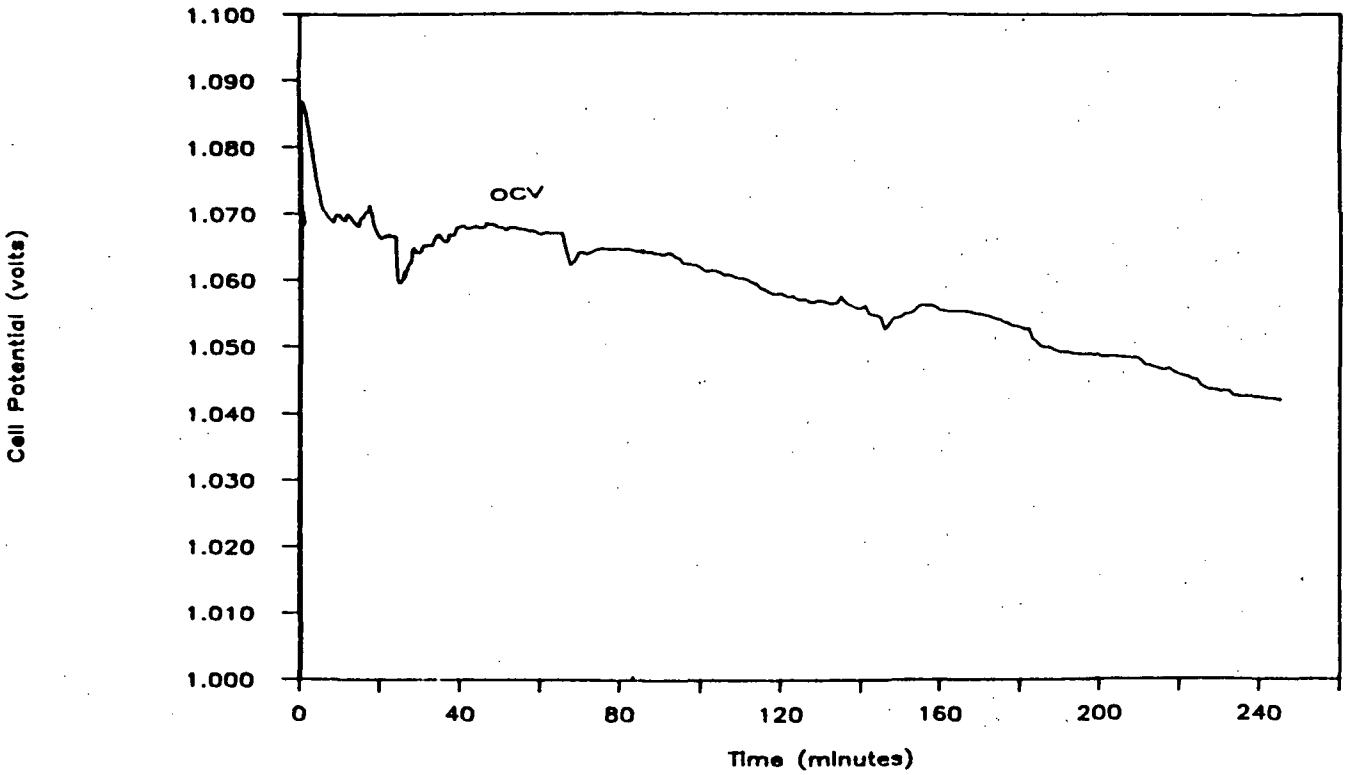


Figure 25. Results of an experiment to determine open circuit voltage of a solution of 10% HBr, 37.76% Br_2, pressure of 2 p.s.i., and Nafion 120 catalyzed membrane.

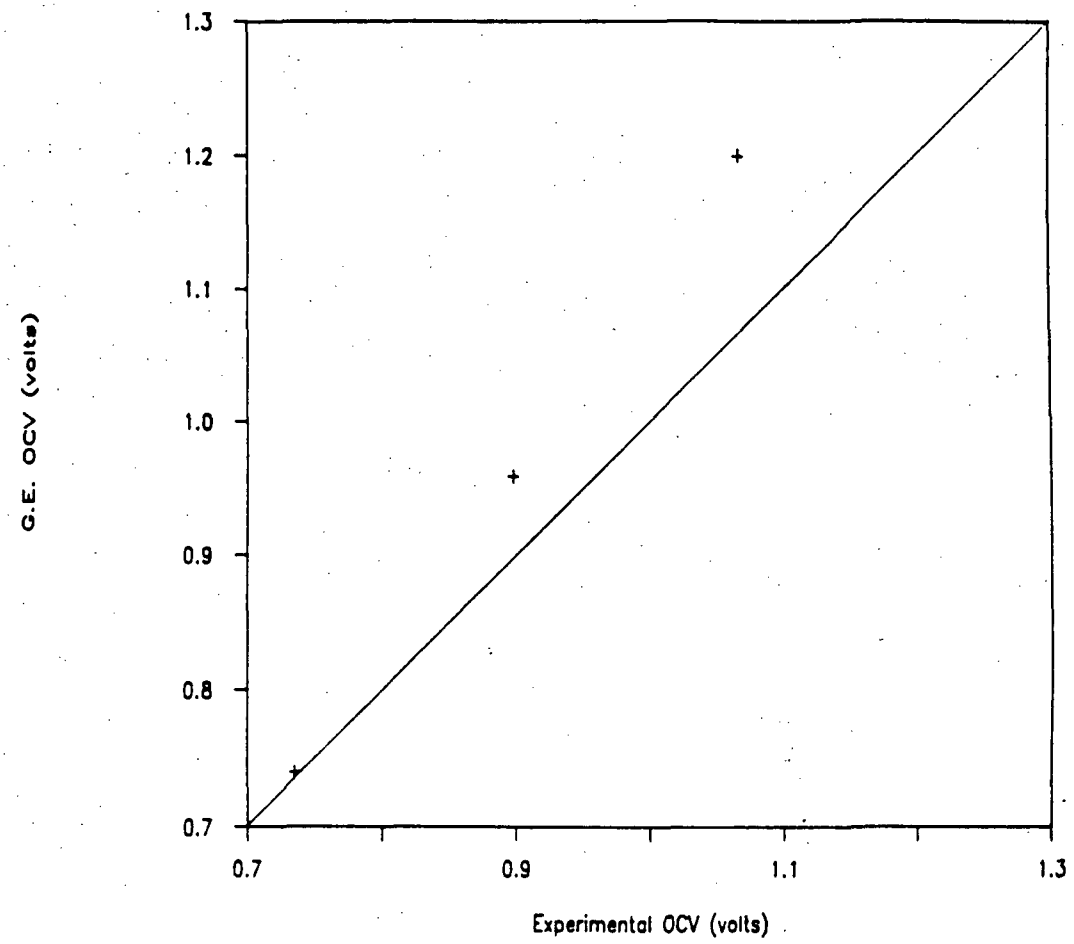


Figure 26. Comparison of experimental results to the open circuit voltages reported by G. E. [9].

C-2

represents perfect agreement between the data of G.E. and the open circuit voltages measured here. The values reported by G.E. are greater than those determined experimentally. This could be due to the reported HBr fractions not including the weight of bromine.

Figures 27 and 28 are comparisons of the open circuit voltages measured experimentally to those calculated from the semi-empirical correlation of Yeo and Chin [5] for solutions with initial charge capacities of 35% HBr and 48% HBr. The correlation predicts somewhat greater open circuit voltages than those found experimentally at the lower states of charge. At the highest state of charge, the open circuit voltage predicted by Yeo and Chin was less than that found experimentally. These differences are thought to be due to the absence of bromine in the experiments performed by Yeo and Chin [8] when developing their correlation (2-1); they treated the bromine effects theoretically. Their correlation also neglected the effects of tribromide and pentabromide formation.

Figures 29 and 30 show a comparison of the experimentally measured open circuit voltages to the calculated values for cells with initial charge capacities of 35% and 48% HBr. The voltages calculated by neglecting the activity coefficients (program OCV1) are greater than the measured values. At the lower states of charge

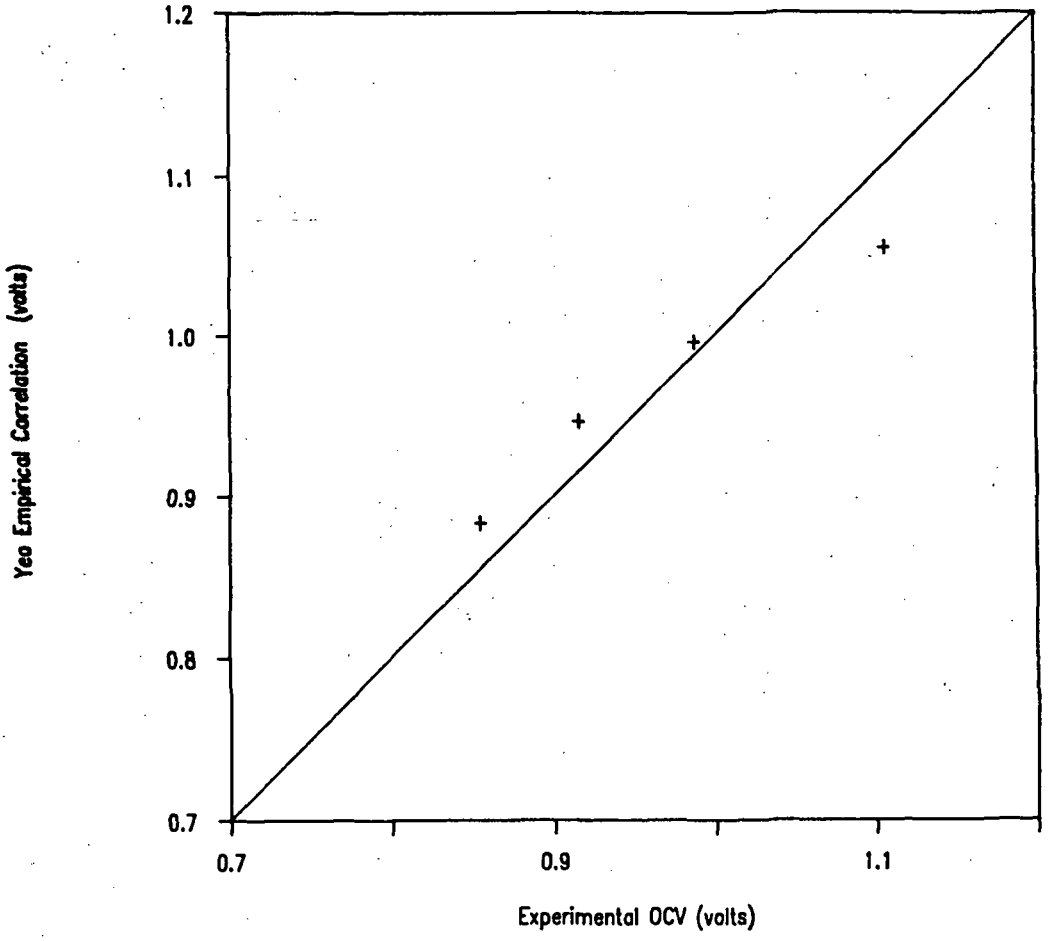


Figure 27. Comparison of experimental results for solutions with charge capacity of 35% HBr to open circuit voltages determined by correlation of Yeo and Chin [5].

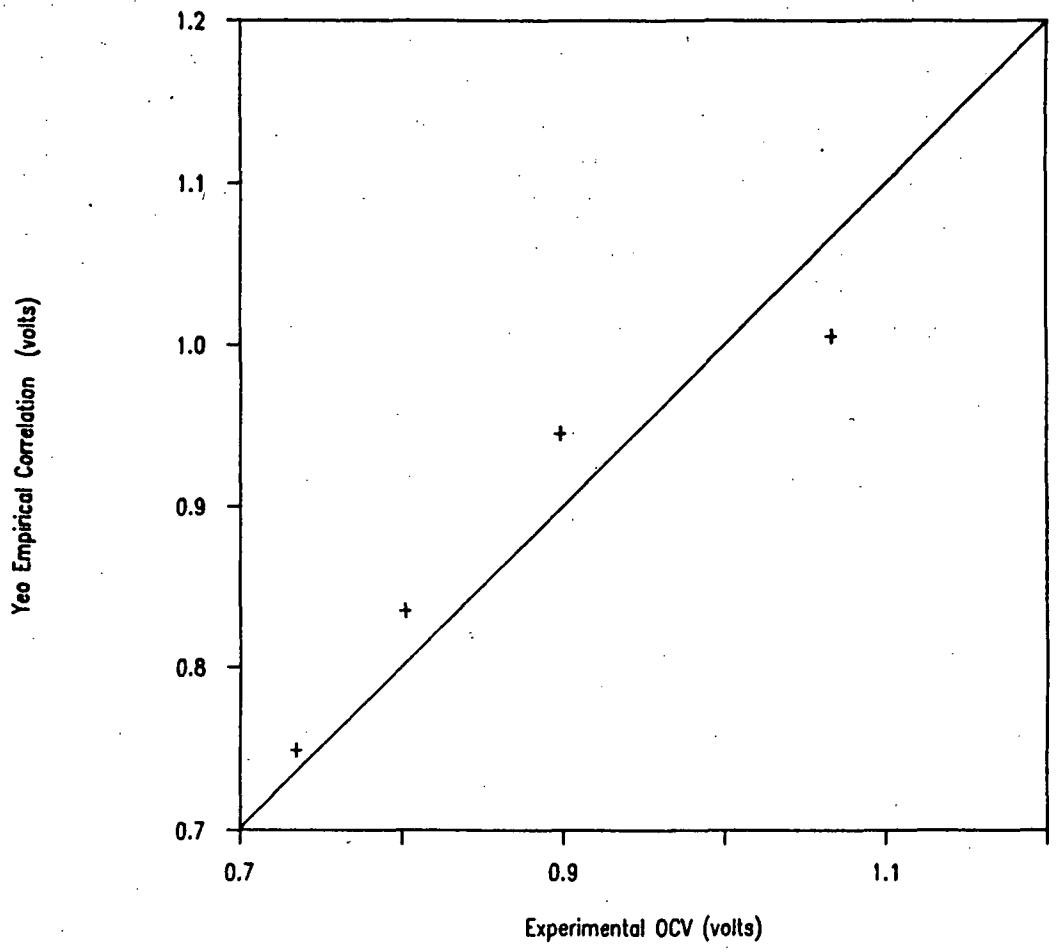


Figure 28. Comparison of experimental results for solutions with charge capacity of 48% HBr to open circuit voltages determined by correlation of Yeo and Chin [5].

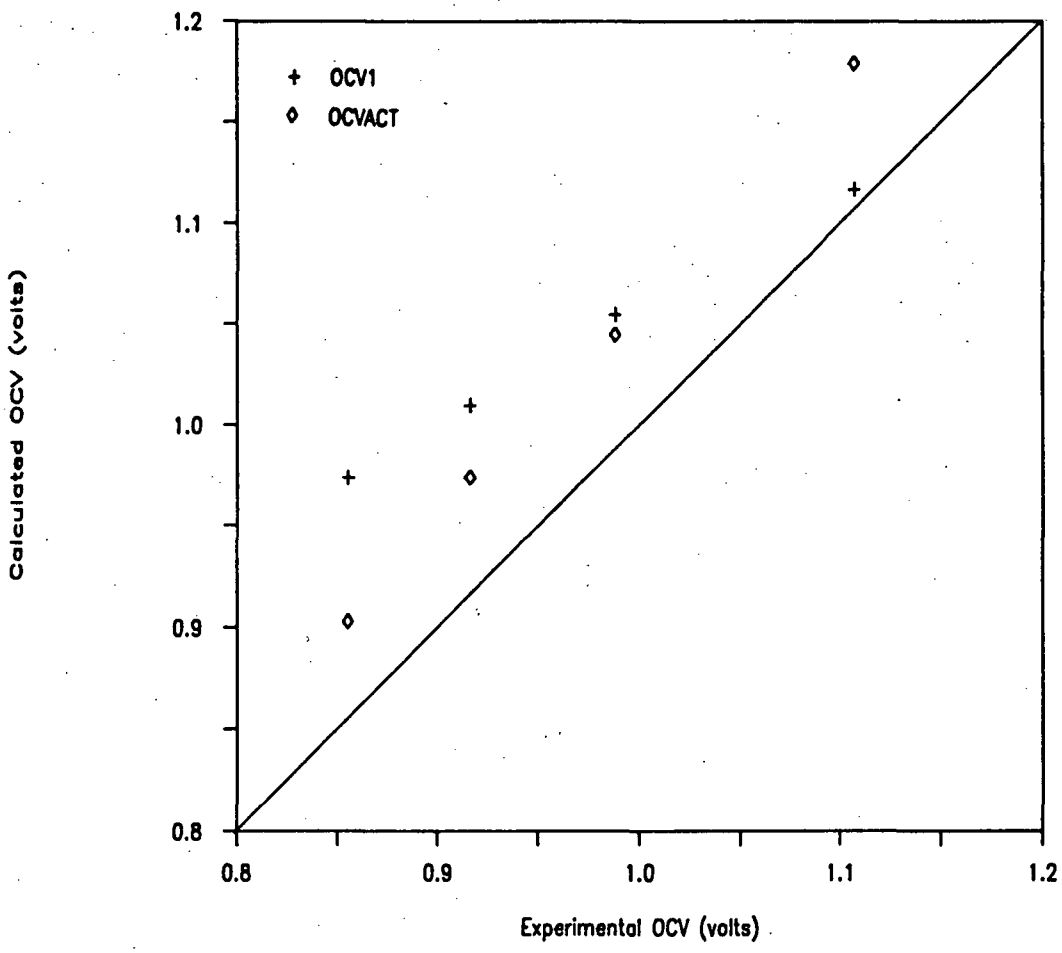


Figure 29. Comparison of open circuit voltages calculated by OCV1 and OCVACT to those found experimentally for solutions with a charge capacity of 35% HBr.

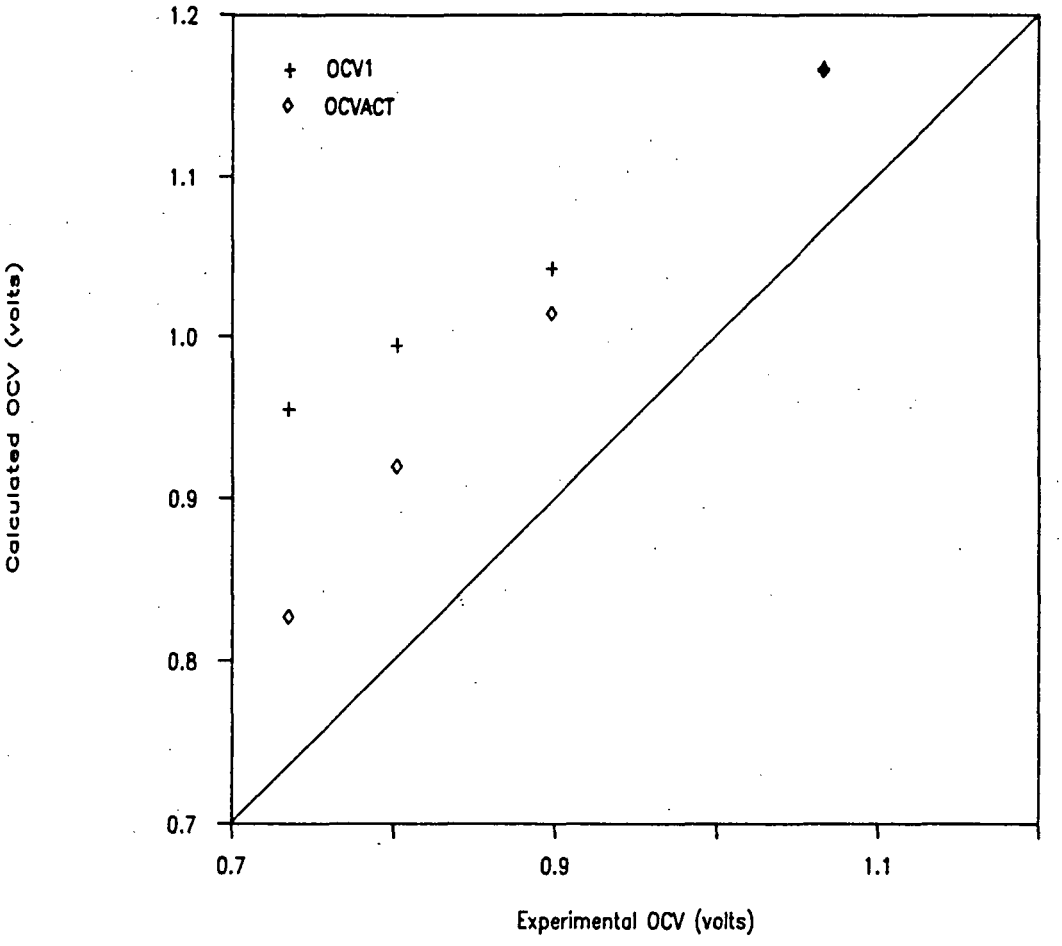


Figure 30. Comparison of open circuit voltages calculated by OCV1 and OCVACT to those found experimentally for solutions with a charge capacity of 48% HBr.

program OCVACT, with estimated HBr activity coefficients, calculates voltages closer to those found experimentally. However, the agreement is not as good as shown earlier in comparison to the data of Glass, (section 5.1.2). This indicates that the uncertainty of accounting for activity of protons in the membrane may be the cause of the discrepancy. As the state of charge increases, the effects of the activity coefficients decrease, so at the highest state of charge, the voltages calculated by OCVACT are actually greater than those found experimentally.

These comparisons accentuate the fact that knowledge of the actual bromine, hydrogen ion, and bromide ion activity coefficients are necessary for a theoretical expression to accurately predict the open circuit voltages of a hydrogen bromine fuel cell.

5.4 Rates of Solution and Membrane Equilibrium

To qualitatively determine the rates of solution and membrane equilibrium, experiments were done where additional bromine was added to the solution after equilibrium was practically reached. The resulting transient voltages across the cell and of the bromine electrode relative to a reference electrode were analyzed. The cell voltages during these experiments are shown in Figure 31. These experiments were conducted for 16.7% state of charge for a solution with a capacity of 35% HBr.

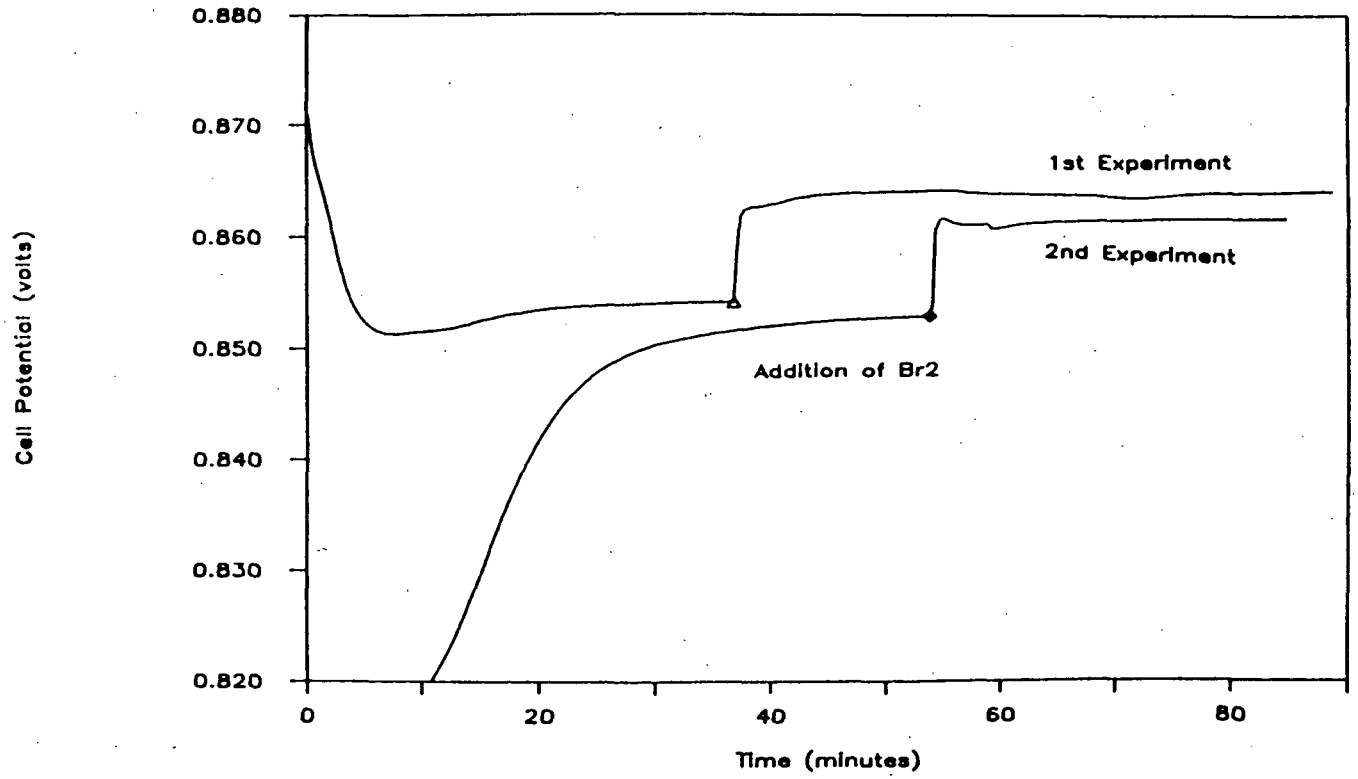


Figure 31. Results of experiments where bromine was added to solution near equilibrium for initial solution concentration of 29.17% HBr, 5.78% Br_2. Final solution concentration was 27.58% HBr, 10.93% Br_2.

For about the first minute after the bromine addition, the increases in the voltage across the cell and the voltage of the bromine electrode relative to the reference electrode were equal. Figure 32 is a plot of the transient voltages (potential minus the potential prior to bromine addition). The short-time transient may be due to mixing effects and kinetic effects of formation of bromide complexes.

Then, the transient potential difference of the bromine electrode began to increase faster than the transient potential difference across the cell. After several minutes, the transient potential difference of the bromine electrode was two millivolts higher than the transient potential difference across the cell. This difference is believed to be due to the liquid junction between the solution and the membrane.

The junction potential is caused by the difference of electrochemical potentials for an ionic species between the solution phase and the membrane phase. This is caused by the diffusion of ions in the membrane. The cause, magnitude and time dependence of this effect cannot be verified theoretically without knowledge of the transport properties in the membrane [20].

Figure 33 is a plot of the rate of the voltage changes after the addition of the bromine. It shows that the rate of cell and bromine electrode transient potentials

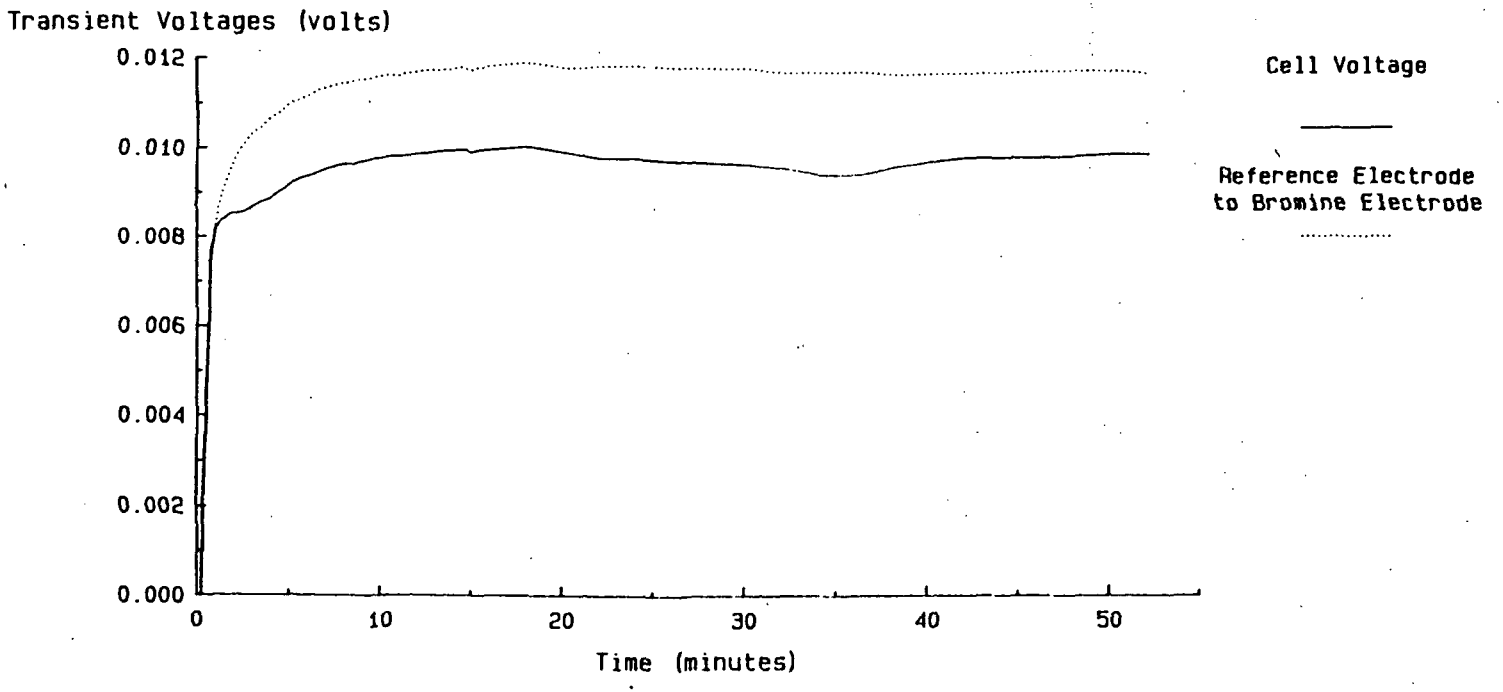


Figure 32. Transient voltages after addition of bromine.

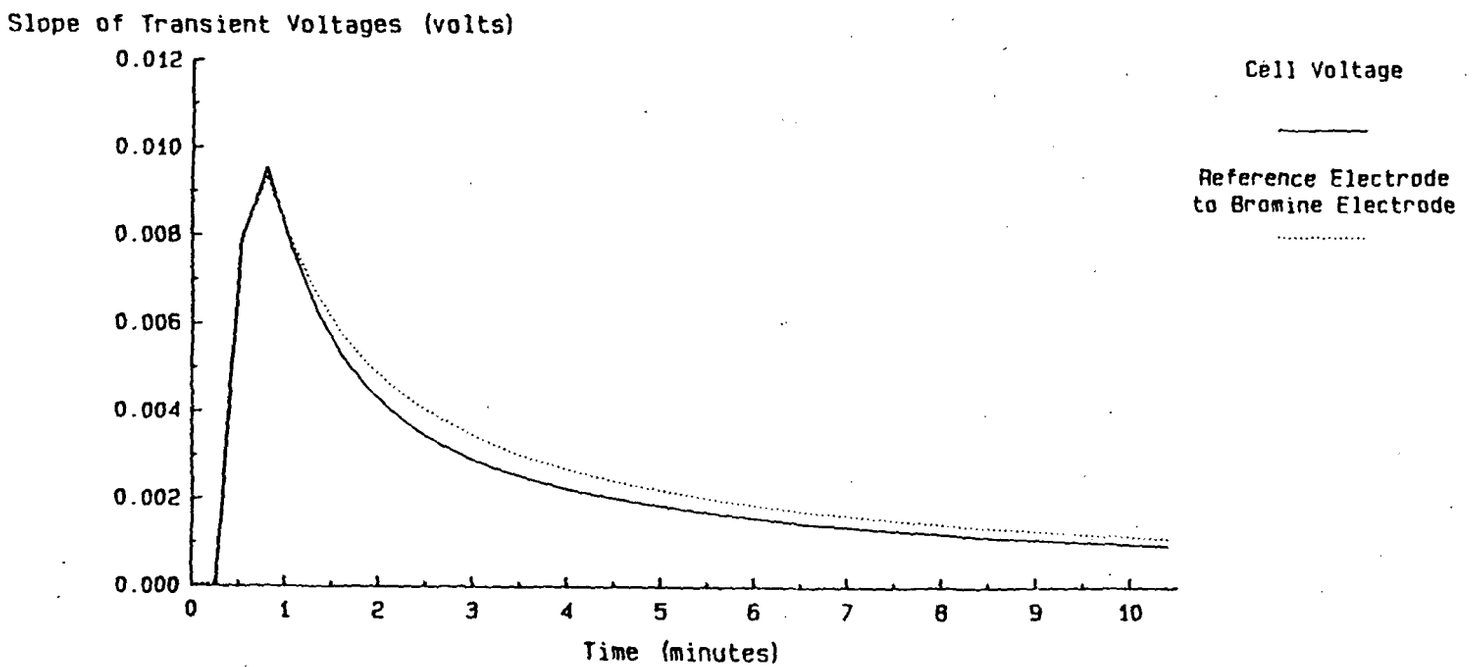


Figure 33. Slopes of transient voltages after addition of bromine.

are equal during the first minute. This suggests that the membrane does not act as a capacitor, otherwise there would be evidence of a time delay in the cell potential.

CHAPTER VI

SUMMARY

6.1 Conclusions

The following conclusions based on this research can be made:

1. An expression was derived for predicting the open circuit voltage of a hydrogen-bromine fuel cell and is useful for assessing the effects of various parameters.

2. Analysis of the literature data and this data suggests that proton activity in the membrane may have a significant influence on the open circuit voltage.

3. Knowledge of the actual activity coefficients, especially of protons in the membrane, should improve the agreement between the predicted and actual open circuit voltages.

4. The effects of the complexing reactions, in which tribromide and pentabromide ions are formed from the bromide ions and bromine, are significant at high states of charge, so that knowledge of the equilibrium constants of these reactions may improve the prediction of the open circuit voltage at higher states of charge.

5. The effect of membrane type was determined experimentally using Nafion 117 and Nafion 120, the latter

having electrode materials bonded to it. Although the mean open circuit voltages found using these two systems were similar (0.733V and 0.737V, respectively), the error in the measurements taken with the Nafion 120 membrane electrode was considerably less ($\pm$0.054V for Nafion 117 vs. $\pm$0.009V for Nafion 120, respectively).

6. The effect of fluctuations in hydrogen pressure on the open circuit voltage was found to be significant. The effects of pressure on the bromide solution were found to be negligible.

7. The open circuit voltages for solutions with a charge capacity of 48% HBr have a lower open circuit voltage (order of 100 mV) than those found for solutions with a charge capacity of 35% HBr. This means that there is a trade off between the open circuit voltage and the charge capacity.

8. The effect of operating temperature was determined theoretically. The open circuit voltage decreases with increasing temperature. The magnitude of this temperature effect is greatest at low states of charge, and is considerably less at high states of charge.

9. The variables which were found to have a significant effect on the open circuit voltage through either experimental or theoretical study are: hydrogen pressure, temperature, hydrobromic acid and bromine concentrations.

6.2 Recommendations

The following recommendations can be made:

1. Experimental work should be done to measure the activity of protons in Nafion membranes in contact with concentrated aqueous hydrobromic acid and bromine solutions.

2. Experimental work should be done to measure the activity coefficients of bromide ion and bromine in aqueous hydrobromic acid and bromine solutions within the concentration ranges of interest for this energy storage system.

3. The equilibrium constants of the complexing reactions of bromide ions and bromine to form tribromide and pentabromide ions should be experimentally measured in these concentrated solutions.

4. After acquiring necessary experimental thermodynamic data of this system, the expression for predicting the open circuit potential of the hydrogen-bromine fuel cell should be tested rigorously and refined to account for concentrated solution behavior.

5. Experimental work should be done to measure the effects of larger hydrogen pressures and higher operating temperatures on the hydrogen-bromine fuel cell.

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APPENDICES

APPENDIX A

COMPUTER PROGRAM TO CALCULATE OCV FROM EMPIRICAL CORRELATION OF YEO AND CHIN [5]

```
list
 10 C     PROGRAM YEO AND CHIN
 20 C
 30 C     PROGRAMMER: SHARON FRITTS
 40 C
 50 C     THIS PROGRAM CALCULATES THE OCV OF THE H2-BR2 BATTERY USING THE
 60 C     CORRELATION OF R.S. YEO AND D-T. CHIN. THE INPUTS TO THIS PROGRAM
 70 C     ARE THE TEMPERATURE, H2 PRESSURE AND WIEGHT PERCENTAGES OF HBR AND
 71 C     BR2
 72 C
 80       REAL MBR2, MHBR
 90       WRITE (6,100)
100   100 FORMAT(5X,'WEIGHT PERCENTAGE OF HBR')
110       READ (5,*) XHBR
120       WRITE (6,101)
130   101 FORMAT(5X,'WEIGHT PERCENTAGE OF BR2')
140       READ (5,*) XBR2
150       WRITE (6,102)
160   102 FORMAT(5X,'TEMPERATURE, CENTIGRADE')
170       READ (5,*) T
180       WRITE (6,103)
190   103 FORMAT(5X,'HYDROGEN PRESSURE')
200       READ (5,*) PH2
210 C
220 C     CALCULATE HBR AND BR2 MOLALITIES TO CALCULATE DENSITY  THEN
230 C     CALCULATE MOLARITIES
240 C
250       MBR2=1000*XBR2/(159.818*(100-XBR2))
260       MHBR=1000*XHBR/(80.917*(100-XHBR))
270       EQ=2*MBR2+MHBR
280       DENS=1 -0 04983275934*EQ+0 08197743373*EQ**2-0.02473400994*EQ**3
290      &+0.003635063042*EQ**4-0 0002914127657*EQ**5+0 00001296501373*EQ
300      &**6-3.001481576E-7*EQ**7+2.817081558E-9*EQ**8
310       CHBR=1000*DENS*MHBR/(1000+80.917*MHBR)
320       CBR2=1000*DENS*MBR2/(1000+159 818*MBR2)
330       R=8.3143
340       T=T+273
350       F=96487
360 C
370 C     CHECK TO SEE IF BR2 IS SEPARATE PHASE
380 C
390       CURVE=0.08733789318+2.394484059*CHBR-4.445906568*CHBR**2+
400      &7.722716276*CHBR**3-7 001672287*CHBR**4+3.348377237*CHBR**5-
410      &0.7771662813*CHBR**6+0.05887092684*CHBR**7+.002968743831*CHBR**8
420       IF((CBR2-CURVE).GE.0) ABR2=1
430       IF ((CBR2-CURVE).LT.0) ABR2=CBR2*1000/(1000*DENS-159.8*CBR2)
431 C
432 C     THIS CORRELATION USES WEIGHT FRACTIONS OF HBR EXCLUDING THE WEIGHT
433 C     OF BROMINE. SO A NEW WEIGHT FRACTION OF HBR IS CALCULATED.
434 C
435       XH2O=100-XHBR-XBR2
436       XHBR=100*XHBR/(XH2O+XHBR)
440       VAL=ALOG(12 36*XHBR/100/(1-XHBR/100))
450       IF((XHBR/100).LT.0 11) PHI=1.073-0 0567*VAL
460       IF((XHBR/100).GE.0.11.AND.(XHBR/100).LT.0.28) PHI=1.095-.1042*VAL
470       IF((XHBR/100).GE 0 28) PHI=1.336-0.2581*VAL
480       OCV=PHI-(T-298)*(4.3+1 86*VAL)*1E-4+4.31E-5*T*ALOG(PH2*ABR2)
490       WRITE (6,105) ABR2
500   105 FORMAT(5X,'BROMINE ACTIVITY',F6 3)
510       WRITE (6,106) OCV
520   106 FORMAT(5X,'OPEN CIRCUIT VOLTAGE IS', F8.4)
530       END
```

Example Output of YEO

```
run
YEO 01/02/86 13:27.42
    WEIGHT PERCENTAGE OF HBR
?40
    WEIGHT PERCENTAGE OF BR2
?7.95
    TEMPERATURE, CENTIGRADE
?23
    HYDROGEN PRESSURE
?1
    BROMINE ACTIVITY 0.540
    OPEN CIRCUIT VOLTAGE IS  0.8543
STOP
TIME 0.1 SECS
```

APPENDIX B

FORTRAN LISTINGS OF OCV1, OCVACT AND OCKEFF

```
list
  10 C     OCV1
  20 C
  30 C     PROGRAMMER:  SHARON FRITTS
  40 C
  50 C     THIS PROGRAM CALCULATES THE OPEN CIRCUIT POTENTIAL OF THE HYDROGEN-
  60 C     BROMINE CELL FOR A GIVEN TEMPERATURE, HYDROGEN PRESSURE,
  70 C     BROMINE AND HYDROGEN BROMIDE CONCENTRATION.  IT ALSO INCLUDES THE
  80 C     EFFECTS OF A SUPPORTING ELECTROLYTE, IF PRESENT.  IF A MEMBRANE
  90 C      IS PRESENT, THE DONNAN EFFECTS ON THE HYDROGEN ION CON-
 100 C     CENTRATION IS USED IN THE EXPRESSION.
 110 C
 120       REAL MBR2, MHBR, HBR, NERNST,MSE
 130       WRITE (6,99)
 140    99 FORMAT(2X,'TEMPERATURE, C')
 150       READ (5,*) T
 160       WRITE (6,100)
 170   100 FORMAT(2X,'HYDROGEN PRESSURE, ATM')
 180       READ (5,*) PH2
 190       WRITE (6,101)
 200   101 FORMAT(2X,'IF THE CONCENTRATIONS OF BR2 AND HBR ARE GIVEN IN')
 210       WRITE (6,102)
 220   102 FORMAT(2X,'WEIGHT PERCENT, INPUT 1; IF THEY ARE IN MOLALITY,')
 230       WRITE (6,103)
 240   103 FORMAT(2X,'INPUT 2.')
 250       READ (5,*) I
 260       WRITE (6,104)
 270   104 FORMAT(2X,'BROMINE CONCENTRATION')
 280       READ (5,*) BR2
 290       WRITE (6,105)
 300   105 FORMAT(2X,'HYDROGEN BROMIDE CONCENTRATION')
 310       READ (5,*) HBR
 320       WRITE (6,122)
 330   122 FORMAT(2X,'IS MEMBRANE PRESENT? (1 FOR YES, 0 FOR NO)')
 340       READ (5,*) J
 350       IF (J.EQ.0) GO TO 11
 360       WRITE (6,123)
 370   123 FORMAT (2X,'MEMBRANE EQUIVALENT WEIGHT')
 380       READ (5,*) EW
 390    11 WRITE (6,115)
 400   115 FORMAT(2X,'CONCENTRATION OF SUPPORTING ELECTROLYTE, MOLARITY')
 410       READ (5,*) SE
 420       IF (SE.EQ.0.) GO TO 10
 430       WRITE (6,120)
 440   120 FORMAT(2X 'SUPPORTING ELECTROLYTE')
 450       READ (5,121)
 460   121 FORMAT(A5)
 470       WRITE (6,116)
 480   116 FORMAT(2X,'MOLECULAR WEIGHT OF SUPPORTING ELECTROLYTE')
 490       READ (5,*) WT
 500 C
 510 C     THE CONSTANTS ARE DEFINED
 520 C
 530    10 R=8.3143
 540       T=273.15+T
 550       F=96487.
 560       IF (I.EQ.1) GO TO 1
 570       IF (I.EQ.2) GO TO 2
 580 C
 590 C     FOR THE CONCENTRATIONS GIVEN IN WEIGHT PERCENTAGES, THE
 600 C     MOLALITIES OF HBR AND BR2 ARE FOUND FOR USE IN LATER CALCULATIONS
 610 C
```

```
  620      1 XBR2=BR2
  630        XHBR=HBR
  640        XSE=SE
  650        MBR2=1000*XBR2/(159.818*(100.-XBR2))
  660        MHBR=1000*XHBR/(80.917*(100.-XHBR))
  670        IF(XSE.EQ.0) GO TO 3
  680        MSE=1000*XSE/(WT*(100.-XSE))
  690        GO TO 3
  700 C
  710 C      FOR THE CONCENTRATIONS GIVEN IN MOLALITIES, THE CONCENTRATIONS
  720 C      ARE FOUND IN WEIGHT PERCENTAGES FOR USE IN LATER CALCULATIONS
  730 C
  740      2 MBR2=BR2
  750        MHBR=HBR
  760        MSE=SE
  770        XHBR=100.*80.917/(1000.+MHBR*80.917)
  780 C
  790 C      THE EQUIVALENTS OF BROMINE ATOMS PER KG SOLUTION ARE FOUND FOR
  800 C      USE IN CALCULATION OF THE SOLUTION DENSITY USING A SECOND
  810 C      ORDER POLYNOMIAL CURVE FIT OF THE DATA OF GLASS AND BOYLE,
  820 C      "PERFORMANCE OF HYDROGEN BROMINE FUEL CELLS", FUEL CELL SYSTEMS,
  830 C      ACS ADVANCES IN CHEMISTRY SERIES #47, P.203, (1965).
  840 C
  850      3 EQ=2*MBR2+MHBR+MSE
  860        DENS=1.017686873+0.04488363995*EQ-4.914449546E-4*EQ**2
  870 C
  880 C      THE MOLAR CONCENTRATIONS OF THE SOLUTION ARE CALCULATED AFTER
  890 C      THE DENSITY OF THE SOLUTION IS KNOWN
  900 C
  910        CHBR=1000.*DENS*MHBR/(1000.+80.917*MHBR)
  920        CBR2=1000.*DENS*MBR2/(1000.+159.818*MBR2)
  930        CSE=1000.*DENS*MSE/(1000.+WT*MSE)
  940        CH=CHBR
  950 C
  960 C      IF A MEMBRANE IS PRESENT IN THIS CELL, SOME EXTRA CALCULATIONS
  970 C      REQUIRED.  THEY ARE, THE WEIGHT FRACTION OF ELECTROLYTE ABSORBED
  980 C      BY THE MEMBRANE, THE FIXED ANION CONCENTRATION OF THE MEMBRANE,
  990 C      THE HYDROGEN ION CONCENTRATION IN THE MEMBRANE, AND ITS ACTIVITY
 1000 C      IF NO MEMBRANE IS PRESENT, THESE CALCULATIONS ARE SKIPPED.
 1010 C
 1020        IF (J.EQ.0) GO TO 6
 1030 C
 1040 C      THE WEIGHT FRACTION OF THE ELECTROLYTE ABSORBED BY THE MEMBRANE
 1050 C      WAS EMPIRICALLY DETERMINED AS A FUNCTION OF THE MOLAR CONCENTRATION
 1060 C      BY R.S. YEO AND D-T. CHIN IN "A HYDROGEN-BROMINE CELL FOR ENERGY
 1070 C      STORAGE APPLICATIONS," J. ELECTROCHEM. SOC., 127, P. 549 (1980)
 1080 C
 1090        WTF=0.323/(1+0.068*CHBR)
 1100 C
 1110 C      THE FIXED ANION CONCENTRATION OF THE MEMBRANE IS CALCULATED BY
 1120 C      AN EQUATION REPORTED BY R.S. YEO, "ION CLUSTERING AND PROTON
 1130 C      TRANSPORT IN NAFION MEMBRANES ..." J. ELECTROCHEM. SOC.,130,
 1140 C      P.533, (1983)
 1150 C
 1160        CR=1000.*DENS/WTF/EW
 1170 C
 1180 C      THE HYDROGEN ION CONCENTRATION IN THE MEMBRANE IS CALCULATED FROM
 1190 C      AN EQUATION DERIVED THROUGH USE OF DONNAN PRINCIPLES, AND THE
 1200 C      ACTIVITY OF THE HYDROGEN ION IS FOUND FOR USE IN THE NERNST
 1210 C      EXPRESSION
 1220 C
```

```
      CHM=(CR+SQRT(CR**2+4*(CH+CSE)**2))/2*CH/(CH+CSE)
      AHM=CHM*1000/(1000*DENS-1.008*CHM)
      WRITE (6,112) CHM
  112 FORMAT (/2X,'MEMBRANE PROTON CONCENTRATION',F8.4,' MOLES/LITER')
      GO TO 7
C
C     IF NO MEMBRANE IS PRESENT, THE ACTIVITY OF THE HYDROGEN ION IN THE
C     SOLUTION PHASE IS FOUND FOR USE IN THE NERNST EXPRESSION
C
    6 AHM=CH*1000/(1000*DENS-1.008*CH)
C
C     THESE CALCULATIONS DETERMINE WHETHER THE BROMINE CONCENTRATION IS
C     ABOVE THE SOLUBILITY LIMIT, USING A CURVE FIT OF THE DATA OF GLASS,
C     "HYDROGEN-BROMINE FUEL CELL", IONICS,INC., CAMBRIDGE, MASS.,
C     CONTRACT NO. AF19(604)-8508, (1964)
C
    7 CURVE=0.2526794598+1.057577737*CH+0.0487321524*CH**2
C
C     IF THE DATA IS BELOW THE SOLUBILITY LIMIT, THE EQUILIBRIUM BROMIDE
C     COMPOUND CONCENTRATIONS MUST BE DETERMINED BY THE BISECTION METHOD
C     WHICH SOLVES THE CUBIC EQUATION FOUND THROUGH COMBINATION OF THE
C     REACTION EQUILIBRIUM CONSTANTS AND ELECTRONEUTRALITY CONDITIONS.
C     THE EQUILIBRIUM CONCENTRATIONS CAN BE EASILY FOUND IF THE BROMINE
C     CONCENTRATION IS ABOVE THE SOLUBILITY LIMIT, THROUGH USE OF THE
C     EQUILIBRIUM CONSTANTS OF THE COMPLEXING REACTIONS.
C
      IF((CBR2-CURVE).LT.0) GO TO 4
      ABR2=1
      WRITE (6,200)
  200 FORMAT(2X/2X,'BROMINE IS IN SEPARATE PHASE')
      CBREQ=(CH+CSE)/57
      CBR3EQ=16*CBREQ
      CBR5EQ=40*CBREQ
      CBR2EQ=CURVE
      GO TO 5
    4 CALL BISECT(CBR2,CH,CBR2EQ,CSE)
      CBREQ=(CH+CSE)/(1.0+16.*CBR2EQ+40.*CBR2EQ*CBR2EQ)
      CBR3EQ=16.*CBR2EQ*CBREQ
      CBR5EQ=40.*CBREQ*CBR2EQ*CBR2EQ
      ABR2=CBR2EQ*1000/(1000*DENS-159.818*CBR2EQ)
C
C     THE POTENTIAL DUE TO COMPLEXING OF THE BROMIDE IONS AND BROMINE
C     TO FORM TRIBROMIDE AND PENTABROMIDE IONS IS FOUND
C
    5 SUM=CBR2EQ+CBR3EQ+CBR5EQ
      COMP=0.5*(CBR3EQ/SUM*R*T/F*(ALOG(16.))+0.5*CBR5EQ/SUM*R*T/F*(ALOG(
     &40.)))
C
C     THE ACTIVITY OF THE BROMIDE ION IS FOUND, AND THE NERNST POTENTIAL
C     IS CALCULATED, USING THE STANDARD POTENTIAL OF 1.0873-541E-6*(T-
C     298.15) GIVEN BY MILAZZO AND CAROLI, TABLES OF STANDARD ELECTRODE
C     POTENTIALS, WILEY, NY, 1977, P.284-5.
C
      ABR=CBREQ*1000/(1000*DENS-79.909*CBREQ)
      NERNST=1.0873+ALOG(SQRT(PH2)*SQRT(ABR2)/AHM/ABR)*R*T/F+(T-298.15)*
     &(-541E-6)
C
C     THE OUTPUT OF THE PROGRAM IS GIVEN
C
      WRITE (6,106) DENS
  106 FORMAT(2X/2X,'DENSITY OF DELTA PHASE',F10.6,' G/ML')
```

```
      WRITE(6,107) CBR2EQ
  107 FORMAT(2X,'EQUILIBRIUM BROMINE CONCENTRATION',F9.6,' MOLES/LITER')
      WRITE (6,108) CBREQ
  108 FORMAT(2X,'EQUILIBRIUM BROMIDE CONCENTRATION',F9.6,' MOLES/LITER')
      WRITE(6,109) CBR3EQ
  109 FORMAT(2X,'EQUILIBRIUM TRIBROMIDE CONCENTRATION',F10.6,' MOLES/LIT)
     &ER')
      WRITE (6,110) CBR5EQ
  110 FORMAT(2X,'EQUILIBRIUM PENTABROMIDE CONCENTRATION',F10.6,' MOLES/L)
     &ITER')
      WRITE (6,111) NERNST
  111 FORMAT(2X,'NERNST POTENTIAL',F10.6,' VOLTS')
      WRITE(6,113) COMP
  113 FORMAT(2X,'POTENTIAL DUE TO COMPLEX FORMATION',F10.6,' VOLTS')
      TOTAL=NERNST+COMP
      WRITE (6,114) TOTAL
  114 FORMAT(2X,'TOTAL POTENTIAL',F10.6,' VOLTS'/)
      END
C
C     THIS SUBROUTINE USES THE BISECTION METHOD TO DETERMINE THE
C     EQUILIBRIUM BROMINE CONCETRATION WHICH IS THE ROOT OF A CUBIC
C     EXPRESSION
C
      SUBROUTINE BISECT(CBR2,CH,CBR2EQ,CSE)
      REAL MID
      A=0.
      B=2.
      FA=2*CBR2 -
    1 MID=(A+B)/2.
      FM=2.*CBR2+(32.*CBR2-32.*CH-32.*CSE-2.)*MID+(80.*CBR2-160.*CH-32.
     C-160.*CSE)*MID**2-80*MID**3
      IF (FA*FM.LE.0.) GO TO 2
      A=MID
      FA=FM
      GO TO 3
    2 B=MID
    3 IF (ABS(B-A).LE.0.000001) GO TO 4
      GO TO 1
    4 CBR2EQ=(A+B)/2
      RETURN
      END
```

Example Output of OCV1

```
run
OCV1 01/02/86 13:07:41
 TEMPERATURE, C
?23
 HYDROGEN PRESSURE, ATM
?1
 IF THE CONCENTRATIONS OF BR2 AND HBR ARE GIVEN IN
 WEIGHT PERCENT, INPUT 1, IF THEY ARE IN MOLALITY
 INPUT 2.
?1
 BROMINE CONCENTRATION
?7 95
 HYDROGEN BROMIDE CONCENTRATION
?40
 IS MEMBRANE PRESENT? (1 FOR YES  0 FOR NO)
?1
 MEMBRANE EQUIVALENT WEIGHT
?1200
 CONCENTRATION OF SUPPORTING ELECTROLYTE  MOLARITY
?0

 MEMBRANE PROTON CONCENTRATION 10 0001 MOLES/LITER

 DENSITY OF DELTA PHASE  1.391439 G/ML
 EQUILIBRIUM BROMINE CONCENTRATION 0.006682 MOLES/LITER
 EQUILIBRIUM BROMIDE CONCENTRATION 6.204001 MOLES/LITER
 EQUILIBRIUM TRIBROMIDE CONCENTRATION  0 663274 MOLES/LITER
 EQUILIBRIUM PENTABROMIDE CONCENTRATION  0 011080 MOLES/LITER
 NERNST POTENTIAL  0.920367 VOLTS
 POTENTIAL DUE TO COMPLEX FORMATION  0 034837 VOLTS
 TOTAL POTENTIAL  0 955205 VOLTS

STOP
TIME 0.2 SECS
```

```
list
 10 C     OCVACT
 20 C
 30 C     PROGRAMMER:  SHARON FRITTS
 40 C
 50 C     THIS PROGRAM CALCULATES THE OPEN CIRCUIT POTENTIAL OF THE HYDROGEN-
 60 C     BROMINE CELL FOR A GIVEN TEMPERATURE, HYDROGEN PRESSURE,
 70 C     BROMINE AND HYDROGEN BROMIDE CONCENTRATION.  IT ALSO INCLUDES THE
 80 C     EFFECTS OF A SUPPORTING ELECTROLYTE, IF PRESENT.  IF A MEMBRANE
 90 C     IS PRESENT THE DONNAN EFFECTS ON THE HYDROGEN ION CONCENTRATION
100 C      IS USED IN THE EXPRESSION.  ESTIMATES OF ACTIVITY COEFFICIENTS
110 C     OF HBR ARE INCLUDED.
120 C
130       IMPLICIT REAL (A-H,O-Z)
140       DOUBLE PRECISION MBR2, MHBR, MBR, NERNST,MSE
150       WRITE (6,99)
160    99 FORMAT(2X,'TEMPERATURE, C')
170       READ (5,*) T
180       WRITE (6,100)
190   100 FORMAT(2X,'HYDROGEN PRESSURE, ATM')
200       READ (5,*) PH2
210       WRITE (6,101)
220   101 FORMAT(2X,'IF THE CONCENTRATIONS OF BR2 AND HBR ARE GIVEN IN')
230       WRITE (6,102)
240   102 FORMAT(2X,'WEIGHT PERCENT, INPUT 1; IF THEY ARE IN MOLALITY,')
250       WRITE (6,103)
260   103 FORMAT(2X,'INPUT 2.')
270       READ (5,*) I
280       WRITE (6,104)
290   104 FORMAT(2X,'BROMINE CONCENTRATION')
300       READ (5,*) BR2
310       WRITE (6,105)
320   105 FORMAT(2X,'HYDROGEN BROMIDE CONCENTRATION')
330       READ (5,*) HBR
340       WRITE (6,122)
350   122 FORMAT(2X,'IS MEMBRANE PRESENT? (1 FOR YES, 0 FOR NO)')
360       READ (5,*) J
370       IF (J.EQ.0) GO TO 11
380       WRITE (6,123)
390   123 FORMAT (2X,'MEMBRANE EQUIVALENT WEIGHT')
400       READ (5,*) EW
410    11 WRITE (6,115)
420   115 FORMAT(2X,'CONCENTRATION OF SUPPORTING ELECTROLYTE, MOLARITY')
430       READ (5,*) SE
440       IF (SE.EQ.0.) GO TO 10
450       WRITE (6,120)
460   120 FORMAT(2X,'SUPPORTING ELECTROLYTE')
470       READ (5,121)
480   121 FORMAT(A5)
490       WRITE (6,116)
500   116 FORMAT(2X,'MOLECULAR WEIGHT OF SUPPORTING ELECTROLYTE')
510       READ (5,*) WT
520 C
530 C     THE CONSTANTS ARE DEFINED
540 C
550    10 R=8.3143
560       T=273.15+T
570       F=96487.
580       IF (I.EQ.1) GO TO 1
590       IF (I.EQ.2) GO TO 2
600 C
```

```
C     FOR THE CONCENTRATIONS GIVEN IN WEIGHT PERCENTAGES, THE
C     MOLALITIES OF HBR AND BR2 ARE FOUND FOR USE IN LATER CALCULATIONS
C
    1 XBR2=BR2
      XHBR=HBR
      XSE=SE
      MBR2=1000*XBR2/(159.818*(100.-XBR2))
      MHBR=1000*XHBR/(80.917*(100.-XHBR))
      IF(XSE.EQ.0) GO TO 3
      MSE=1000*XSE/(WT*(100.-XSE))
      GO TO 3
C
C     FOR THE CONCENTRATIONS GIVEN IN MOLALITIES, THE CONCENTRATIONS
C     ARE FOUND IN WEIGHT PERCENTAGES FOR USE IN LATER CALCULATIONS
C
    2 MBR2=BR2
      MHBR=HBR
      MSE=SE
      XHBR=100.*80.917/(1000.+MHBR*80.917)
C
C     THE EQUIVALENTS OF BROMINE ATOMS PER KG SOLUTION ARE FOUND FOR
C     CALCULATION OF THE DENSITY OF THE SOLUTION USING A SECOND ORDER
C     CURVE FIT OF THE DATA OF GLASS AND BOLYLE IN THE ARTICLE
C     "PERFORMANCE OF HYDROGEN BROMINE FUEL CELLS", FUEL CELL SYSTEMS,
C     ACS ADVANCES IN CHEMISTRY SERIES #47, P.203, (1965).
C
    3 EQ=2*MBR2+MHBR+MSE
       DENS=1.017686873+0.04488363995*EQ-4.914449546E-4*EQ**2
C
C     THE MOLAR CONCENTRATIONS OF THE SOLUTION ARE CALCULATED AFTER
C     THE DENSITY OF THE SOLUTION IS KNOWN
C
      CHBR=1000.*DENS*MHBR/(1000.+80.917*MHBR)
      CBR2=1000.*DENS*MBR2/(1000.+159.818*MBR2)
      CSE=1000.*DENS*MSE/(1000.+WT*MSE)
      CH=CHBR
C
C     IF A MEMBRANE IS PRESENT IN THIS CELL, SOME EXTRA CALCULATIONS
C     REQUIRED.  THEY ARE, THE WEIGHT FRACTION OF ELECTROLYTE ABSORBED
C     BY THE MEMBRANE, THE FIXED ANION CONCENTRATION OF THE MEMBRANE,
C     THE HYDROGEN ION CONCENTRATION IN THE MEMBRANE, AND ITS ACTIVITY.
C     IF NO MEMBRANE IS PRESENT, THESE CALCULATIONS ARE SKIPPED.
C
      IF (J.EQ.0) GO TO 6
C
C     THE WEIGHT FRACTION OF THE ELECTROLYTE ABSORBED BY THE MEMBRANE
C     WAS EMPIRICALLY DETERMINED AS A FUNCTION OF THE MOLAR CONCENTRATION
C     BY R.S. YEO AND D-T. CHIN IN "A HYDROGEN-BROMINE CELL FOR ENERGY
C     STORAGE APPLICATIONS," J. ELECTROCHEM. SOC., 127, P. 549 (1980)
C
      WTF=0.323/(1+0.068*CHBR)
C
C     THE FIXED ANION CONCENTRATION OF THE MEMBRANE IS CALCULATED BY
C     AN EQUATION REPORTED BY R.S. YEO, "ION CLUSTERING AND PROTON
C     TRANSPORT IN NAFION MEMBRANES ..." J. ELECTROCHEM. SOC.,130,
C     P.533, (1983)
C
      CR=1000.*DENS/WTF/EW
C
C     THE HYDROGEN ION CONCENTRATION IN THE MEMBRANE IS CALCULATED FROM
```

```
1210 C     AN EQUATION DERIVED THROUGH USE OF DONNAN PRINCIPLES, AND THE
1220 C     ACTIVITY OF THE HYDROGEN ION IS FOUND FOR USE IN THE NERNST
1230 C     EXPRESSION
1240 C
1250       CHM=(CR+SQRT(CR**2+4*(CH+CSE)**2))/2*CH/(CH+CSE)
1260       AHM=CHM*1000/(1000*DENS-1.008*CHM)
1270       GO TO 7
1280 C
1290 C     IF NO MEMBRANE IS PRESENT, THE ACTIVITY OF THE HYDROGEN ION IN THE
1300 C     SOLUTION PHASE IS FOUND FOR USE IN THE NERNST EXPRESSION
1310 C
1320     6 AHM=CH*1000/(1000*DENS-1.008*CH)
1330 C
1340 C     THESE CALCULATIONS DETERMINE WHETHER THE BROMINE CONCENTRATION IS
1350 C     ABOVE THE SOLUBILITY LIMIT, USING A CURVE FIT OF THE DATA OF GLASS,
1360 C     "HYDROGEN-BROMINE FUEL CELL", IONICS,INC., CAMBRIDGE, MASS.,
1370 C     CONTRACT NO. AF19(604)-8508, (1964)
1380 C
1390     7 CURVE=0.2526794598+1.057577737*CH+0.0487321524*CH**2
1400 C
1410 C     IF THE DATA IS BELOW THE SOLUBILITY LIMIT, THE EQUILIBRIUM BROMIDE
1420 C     COMPOUND CONCENTRATIONS MUST BE DETERMINED BY THE BISECTION METHOD
1430 C     WHICH SOLVES THE CUBIC EQUATION FOUND THROUGH COMBINATION OF THE
1440 C     REACTION EQUILIBRIUM CONSTANTS AND ELECTRONEUTRALITY CONDITIONS.
1450 C     THE EQUILIBRIUM CONCENTRATIONS CAN BE EASILY FOUND IF THE BROMINE
1460 C     CONCENTRATION IS ABOVE THE SOLUBILITY LIMIT, THROUGH USE OF THE
1470 C     EQUILIBRIUM CONSTANTS OF THE COMPLEXING REACTIONS.
1480 C
1490       IF((CBR2-CURVE).LT.0) GO TO 4
1500       ABR2=1
1510       WRITE (6,200)
1520   200 FORMAT(2X/2X,'BROMINE IS IN SEPARATE PHASE')
1530       CBREQ=(CH+CSE)/57
1540       CBR3EQ=16*CBREQ
1550       CBR5EQ=40*CBREQ
1560       CBR2EQ=CURVE
1570       GO TO 5
1580     4 CALL BISECT(CBR2,CH,CBR2EQ,CSE)
1590       CBREQ=(CH+CSE)/(1.0+16.*CBR2EQ+40.*CBR2EQ*CBR2EQ)
1600       CBR3EQ=16.*CBR2EQ*CBREQ
1610       CBR5EQ=40.*CBREQ*CBR2EQ*CBR2EQ
1620       ABR2=CBR2EQ*1000/(1000*DENS-159.818*CBR2EQ)
1630 C
1640 C     THE POTENTIAL DUE TO COMPLEXING OF THE BROMIDE IONS AND BROMINE
1650 C     TO FORM TRIBROMIDE AND PENTABROMIDE IONS IS FOUND
1660 C
1670     5 SUM=CBR2EQ+CBR3EQ+CBR5EQ
1680       COMP=0.5*(CBR3EQ/SUM*R*T/F*(ALOG(16.))+0.5*CBR5EQ/SUM*R*T/F*(ALOG(
1690      &40.)))
1700 C
1710 C     THIS SECTION DETERMINES THE ACTIVITY COEFFICENT OF HBR FOR THE
1720 C     CONCENTRATION OF BROMIDE IONS DETERMINED TO BE PRESENT AFTER
1730 C     SOLUTION EQUILIBRATION FROM A CUBIC CURVE FIT OF THE DATA REPORTED
1740 C     BY E.N. BALKO
1750 C
1760       MBR=MHBR
1770       GAMMA=0.9418152476-0.03224218452*MBR+0.045343504*MBR*MBR
1780      &+0.015525929*MBR**3
1790 C
1800 C     THE ACTIVITY OF THE BROMIDE ION IS FOUND, AND THE NERNST POTENTIAL
```

```
1810 C      IS CALCULATED  USING THE STANDARD POTENTIAL OF 1.0873-541E-6*(T-
1820 C      298.15) GIVEN BY MILAZZO AND CAROLI, TABLES OF STANDARD ELECTRODE
1830 C      POTENTIALS, WILEY, NY, 1977, P.284-5.
1840 C
1850        ABR=1000*CBREQ/(1000*DENS-CBREQ*79.909)*GAMMA
1860        AHM=AHM*GAMMA
1870        NERNST=1.0873+ALOG(SQRT(PH2)*SQRT(ABR2)/AHM/ABR)*R*T/F+(T-298.15)*
1880       &(-541E-6)
1890 C
1900 C      THE OUTPUT OF THE PROGRAM IS GIVEN
1910 C
1920        WRITE (6,106) DENS
1930    106 FORMAT(2X/2X,'DENSITY OF DELTA PHASE',F10.6,' G/ML')
1940        WRITE(6,107) CBR2EQ
1950    107 FORMAT(2X,'EQUILIBRIUM BROMINE CONCENTRATION',F9.6,' MOLES/LITER')
1960        WRITE (6,108) CBREQ
1970    108 FORMAT(2X,'EQUILIBRIUM BROMIDE CONCENTRATION',F9.6,' MOLES/LITER')
1980        WRITE(6,109) CBR3EQ
1990    109 FORMAT(2X,'EQUILIBRIUM TRIBROMIDE CONCENTRATION',F10.6,' MOLES/LIT
2000       &ER')
2010        WRITE (6,110) CBR5EQ
2020    110 FORMAT(2X,'EQUILIBRIUM PENTABROMIDE CONCENTRATION',F10.6,' MOLES/L
2030       &ITER')
2040        WRITE (6,111) NERNST
2050    111 FORMAT(2X,'NERNST POTENTIAL',F10.6,' VOLTS')
2060        WRITE(6,113) COMP
2070    113 FORMAT(2X,'POTENTIAL DUE TO COMPLEX FORMATION',F10.6,' VOLTS')
2080        TOTAL=NERNST+COMP
2090        WRITE (6,114) TOTAL
2100    114 FORMAT(2X,'TOTAL POTENTIAL',F10.6,' VOLTS'/)
2110        END
2120 C
2130 C      THIS SUBROUTINE USES THE BISECTION METHOD TO DETERMINE THE
2140 C      EQUILIBRIUM BROMINE CONCETRATION WHICH IS THE ROOT OF A CUBIC
2150 C      EXPRESSION
2160 C
2170        SUBROUTINE BISECT(CBR2,CH,CBR2EQ,CSE)
2180        REAL MID
2190        A=0.
2200        B=2.
2210        FA=2*CBR2
2220      1 MID=(A+B)/2.
2230        FM=2.*CBR2+(32.*CBR2-32.*CH-32.*CSE-2.)*MID+(80.*CBR2-160.*CH-32.
2240       C-160.*CSE)*MID**2-80*MID**3
2250        IF (FA*FM.LE.0.) GO TO 2
2260        A=MID
2270        FA=FM
2280        GO TO 3
2290      2 B=MID
2300      3 IF (ABS(B-A).LE.0.000001) GO TO 4
2310        GO TO 1
2320      4 CBR2EQ=(A+B)/2
2330        RETURN
2340        END
```

Example Output of OCVACT

```
run
OCVACT 01/15/86 13:58:53
 TEMPERATURE, C
?23
 HYDROGEN PRESSURE, ATM
?1
 IF THE CONCENTRATIONS OF BR2 AND HBR ARE GIVEN IN
 WEIGHT PERCENT, INPUT 1; IF THEY ARE IN MOLALITY,
 INPUT 2.
?1
 BROMINE CONCENTRATION
?7.95
 HYDROGEN BROMIDE CONCENTRATION
?40
 IS MEMBRANE PRESENT? (1 FOR YES, 0 FOR NO)
?1
 MEMBRANE EQUIVALENT WEIGHT
?1200
 CONCENTRATION OF SUPPORTING ELECTROLYTE, MOLARITY
?0

 DENSITY OF DELTA PHASE  1.393303 G/ML
 EQUILIBRIUM BROMINE CONCENTRATION 0.006683 MOLES/LITER
 EQUILIBRIUM BROMIDE CONCENTRATION 6.212220 MOLES/LITER
 EQUILIBRIUM TRIBROMIDE CONCENTRATION  0.664248 MOLES/LITER
 EQUILIBRIUM PENTABROMIDE CONCENTRATION  0.011098 MOLES/LITER
 NERNST POTENTIAL  0.791697 VOLTS
 POTENTIAL DUE TO COMPLEX FORMATION  0.034838 VOLTS
 TOTAL POTENTIAL  0.826535 VOLTS

STOP
TIME 0.2 SECS
```

```
list
C     OCKEFF
C
C     PROGRAMMER:  SHARON FRITTS
C
C     THIS PROGRAM CALCULATES THE OPEN CIRCUIT POTENTIAL OF THE HYDROGEN-
C     BROMINE CELL FOR A GIVEN TEMPERATURE, HYDROGEN PRESSURE,
C     BROMINE AND HYDROGEN BROMIDE CONCENTRATION.  IT ALSO INCLUDES THE
C     EFFECTS OF A SUPPORTING ELECTROLYTE, IF PRESENT.  IF A MEMBRANE
C     IS PRESENT, THE DONNAN EFFECTS ON THE HYDROGEN ION CONCENTRATION
C     IS USED IN THE EXPRESSION.  THE K VALUES FOR THE COMPLEXING
C     REACTIONS ARE VARIED.
C
      REAL MBR2, MHBR, HBR, NERNST
      WRITE (6,99)
   99 FORMAT(2X,'TEMPERATURE, C')
      READ (5,*) T
      WRITE (6,100)
  100 FORMAT(2X,'HYDROGEN PRESSURE, ATM')
      READ (5,*) PH2
      WRITE (6,101)
  101 FORMAT(2X,'IF THE CONCENTRATIONS OF BR2 AND HBR ARE GIVEN IN')
      WRITE (6,102)
  102 FORMAT(2X,'WEIGHT PERCENT, INPUT 1; IF THEY ARE IN MOLALITY,')
      WRITE (6,103)
  103 FORMAT(2X,'INPUT 2.')
      READ (5,*) J
      WRITE (6,104)
  104 FORMAT(2X,'BROMINE CONCENTRATION')
      READ (5,*) BR2
      WRITE (6,105)
  105 FORMAT(2X,'HYDROGEN BROMIDE CONCENTRATION')
      READ (5,*) HBR
      WRITE (6,122)
  122 FORMAT(2X,'IS MEMBRANE PRESENT? (1 FOR YES, 0 FOR NO)')
      READ (5,*) J
      IF (J.EQ.0) GO TO 11
      WRITE (6,123)
  123 FORMAT (2X,'MEMBRANE EQUIVALENT WEIGHT')
      READ (5,*) EW
   11 WRITE (6,127)
  127 FORMAT (2X,'FACTOR TO MULTIPLY K FOR TRIBROMIDE REACTION BY')
      READ (5,*) TRI
      WRITE (6,128)
  128 FORMAT (2X,'FACTOR TO MULTIPLY K FOR PENTABROMIDE REACTION BY')
      READ (5,*) PENTA
C
C     THE CONSTANTS ARE DEFINED
C
      R=8.3143
      T=273.15+T
      F=96487.
      IF (J.EQ.1) GO TO 1
      IF (J.EQ.2) GO TO 2
C
C     FOR THE CONCENTRATIONS GIVEN IN WEIGHT PERCENTAGES, THE
C     MOLALITIES OF HBR AND BR2 ARE FOUND FOR USE IN LATER CALCULATIONS
C
    1 XBR2=BR2
      XHBR=HBR
      MBR2=1000*XBR2/(159.818*(100.-XBR2))
```

```
      MHBR=1000*XHBR/(80.917*(100.-XHBR))
      GO TO 3
C
C     FOR THE CONCENTRATIONS GIVEN IN MOLALITIES, THE CONCENTRATIONS
C     ARE FOUND IN WEIGHT PERCENTAGES FOR USE IN LATER CALCULATIONS
C
    2 MBR2=BR2
      MHBR=HBR
      XHBR=100.*80.917/(1000.+MHBR*80.917)
C
C     THE EQUIVALENTS OF BROMINE ATOMS PER KG SOLUTION ARE FOUND FOR
C     USE IN CALCULATION OF THE SOLUTION DENSITY USING A SECOND
C     ORDER POLYNOMIAL CURVE FIT OF THE DATA OF GLASS AND BOYLE,
C     "PERFORMANCE OF HYDROGEN BROMINE FUEL CELLS", FUEL CELL SYSTEMS,
C     ACS ADVANCES IN CHEMISTRY SERIES #47, P.203, (1965).
C
    3 EQ=2*MBR2+MHBR
      DENS=1.017686873+0.04488363995*EQ-4.914449546E-4*EQ**2
C
C     THE MOLAR CONCENTRATIONS OF THE SOLUTION ARE CALCULATED AFTER
C     THE DENSITY OF THE SOLUTION IS KNOWN
C
      CHBR=1000.*DENS*MHBR/(1000.+80.917*MHBR)
      CBR2=1000.*DENS*MBR2/(1000.+159.818*MBR2)
      CH=CHBR
C
C     IF A MEMBRANE IS PRESENT IN THIS CELL, SOME EXTRA CALCULATIONS
C     REQUIRED.  THEY ARE, THE WEIGHT FRACTION OF ELECTROLYTE ABSORBED
C     BY THE MEMBRANE, THE FIXED ANION CONCENTRATION OF THE MEMBRANE,
C     THE HYDROGEN ION CONCENTRATION IN THE MEMBRANE, AND ITS ACTIVITY.
C     IF NO MEMBRANE IS PRESENT, THESE CALCULATIONS ARE SKIPPED.
C
      IF (J.EQ.0) GO TO 6
C
C     THE WEIGHT FRACTION OF THE ELECTROLYTE ABSORBED BY THE MEMBRANE
C     WAS EMPIRICALLY DETERMINED AS A FUNCTION OF THE MOLAR CONCENTRATION
C     BY R.S. YEO AND D-T. CHIN IN "A HYDROGEN-BROMINE CELL FOR ENERGY
C     STORAGE APPLICATIONS," J. ELECTROCHEM. SOC., 127, P. 549 (1980)
C
      WTF=0.323/(1+0.068*CHBR)
C
C     THE FIXED ANION CONCENTRATION OF THE MEMBRANE IS CALCULATED BY
C     AN EQUATION REPORTED BY R.S. YEO, "ION CLUSTERING AND PROTON
C     TRANSPORT IN NAFION MEMBRANES ..." J. ELECTROCHEM. SOC.,130,
C     P.533, (1983)
C
      CR=1000.*DENS/WTF/EW
C
C     THE HYDROGEN ION CONCENTRATION IN THE MEMBRANE IS CALCULATED FROM
C     AN EQUATION DERIVED THROUGH USE OF DONNAN PRINCIPLES, AND THE
C     ACTIVITY OF THE HYDROGEN ION IS FOUND FOR USE IN THE NERNST
C     EXPRESSION
C
      CHM=(CR+SQRT(CR**2+4*(CH)**2))/2*CH/(CH)
      AHM=CHM*1000/(1000*DENS-1.008*CHM)
      WRITE (6,112) CHM
  112 FORMAT (/2X,'MEMBRANE PROTON CONCENTRATION',F8.4,' MOLES/ LITER')
      GO TO 7
C
C     IF NO MEMBRANE IS PRESENT, THE ACTIVITY OF THE HYDROGEN ION IN THE
```

```
1210 C     SOLUTION PHASE IS FOUND FOR USE IN THE NERNST EXPRESSION
1220 C
1230      6 AHM=CH*1000/(1000*DENS-1.008*CH)
1240 C
1250 C     THESE CALCULATIONS DETERMINE WHETHER THE BROMINE CONCENTRATION IS
1260 C     ABOVE THE SOLUBILITY LIMIT, USING A CURVE FIT OF THE DATA OF GLASS,
1270 C     "HYDROGEN-BROMINE FUEL CELL", IONICS,INC., CAMBRIDGE, MASS.,
1280 C     CONTRACT NO. AF19(604)-8508, (1964)
1290 C
1300      7 CURVE=0.2526794598+1.057577737*CH+0.0487321524*CH**2
1310 C
1320 C     IF THE DATA IS BELOW THE SOLUBILITY LIMIT, THE EQUILIBRIUM BROMIDE
1330 C     COMPOUND CONCENTRATIONS MUST BE DETERMINED BY THE BISECTION METHOD
1340 C     WHICH SOLVES THE CUBIC EQUATION FOUND THROUGH COMBINATION OF THE
1350 C     REACTION EQUILIBRIUM CONSTANTS AND ELECTRONEUTRALITY CONDITIONS.
1360 C     THE EQUILIBRIUM CONCENTRATIONS CAN BE EASILY FOUND IF THE BROMINE
1370 C     CONCENTRATION IS ABOVE THE SOLUBILITY LIMIT, THROUGH USE OF THE
1380 C     EQUILIBRIUM CONSTANTS OF THE COMPLEXING REACTIONS.
1390 C
1400        IF((CBR2-CURVE).LT.0) GO TO 4
1410        ABR2=1
1420        WRITE (6,200)
1430    200 FORMAT(2X/2X,'BROMINE IS IN SEPARATE PHASE')
1440        CBREQ=(CH)/(1+16*TRI+40*PENTA)
1450        CBR3EQ=16*CBREQ*TRI
1460        CBR5EQ=40*CBREQ*PENTA
1470        CBR2EQ=CURVE
1480        GO TO 5
1490      4 CALL BISECT(CBR2,CH,CBR2EQ,TRI,PENTA)
1500        CBREQ=(CH)/(1.0+16.*CBR2EQ*TRI+40.*CBR2EQ*CBR2EQ*PENTA)
1510        CBR3EQ=16.*CBR2EQ*CBREQ*TRI
1520        CBR5EQ=40.*CBREQ*CBR2EQ*CBR2EQ*PENTA
1530        ABR2=CBR2EQ*1000/(1000*DENS-159.818*CBR2EQ)
1540 C
1550 C     THE POTENTIAL DUE TO COMPLEXING OF THE BROMIDE IONS AND BROMINE
1560 C     TO FORM TRIBROMIDE AND PENTABROMIDE IONS IS FOUND
1570 C
1580      5 SUM=CBR2EQ+CBR3EQ+CBR5EQ
1590        COMP=0.5*(CBR3EQ/SUM*R*T/F*(ALOG(16.*TRI))+0.5*CBR5EQ/SUM*R*T/F*
1600       &(ALOG(40.*PENTA)))
1610 C
1620 C     THE ACTIVITY OF THE BROMIDE ION IS FOUND, AND THE NERNST POTENTIAL
1630 C     IS CALCULATED, USING THE STANDARD POTENTIAL OF 1.0873-541E-6*(T-
1640 C     298.15) GIVEN BY MILAZZO AND CAROLI, TABLES OF STANDARD ELECTRODE
1650 C     POTENTIALS, WILEY, NY, 1977, P.284-5.
1660 C
1670        ABR=CBREQ*1000/(1000*DENS-79.909*CBREQ)
1680        NERNST=1.0873+ALOG(SQRT(PH2)*SQRT(ABR2)/AHM/ABR)*R*T/F+(T-298.15)*
1690       &(-541E-6)
1700 C
1710 C     THE OUTPUT OF THE PROGRAM IS GIVEN
1720 C
1730        WRITE (6,106) DENS
1740    106 FORMAT(2X/2X,'DENSITY OF DELTA PHASE',F10.6,' G/ML')
1750        WRITE(6,107) CBR2EQ
1760    107 FORMAT(2X,'EQUILIBRIUM BROMINE CONCENTRATION',F9.6,' MOLES/LITER')
1770        WRITE (6,108) CBREQ
1780    108 FORMAT(2X,'EQUILIBRIUM BROMIDE CONCENTRATION',F9.6,' MOLES/LITER')
1790        WRITE(6,109) CBR3EQ
1800    109 FORMAT(2X,'EQUILIBRIUM TRIBROMIDE CONCENTRATION',F10.6,' MOLES/LIT
1810       &ER')
```

```
1820        WRITE (6,110) CBR5EQ
1830    110 FORMAT(2X,'EQUILIBRIUM PENTABROMIDE CONCENTRATION',F10.6,' MOLES/L
1840       &ITER')
1850        WRITE (6,111) NERNST
1860    111 FORMAT(2X,'NERNST POTENTIAL',F10.6,' VOLTS')
1870        WRITE(6,113) COMP
1880    113 FORMAT(2X,'POTENTIAL DUE TO COMPLEX FORMATION',F10.6,' VOLTS')
1890        TOTAL=NERNST+COMP
1900        WRITE (6,114) TOTAL
1910    114 FORMAT(2X,'TOTAL POTENTIAL',F10.6,' VOLTS'/)
1920        END
1930 C
1940 C      THIS SUBROUTINE USES THE BISECTION METHOD TO DETERMINE THE
1950 C      EQUILIBRIUM BROMINE CONCETRATION WHICH IS THE ROOT OF A CUBIC
1960 C      EXPRESSION
1970 C
1980        SUBROUTINE BISECT(CBR2,CH,CBR2EQ,TRI,PENTA)
1990        REAL MID
2000        A=0.
2010        B=2.
2020        FA=2*CBR2
2030      1 MID=(A+B)/2.
2040        FM=2*CBR2+(32*CBR2*TRI-32*CH*TRI-2)*MID+(80*CBR2*PENTA-160*PENTA
2050       &*CH-32*TRI)*MID**2-80*PENTA*MID**3
2060        IF (FA*FM.LE.0.) GO TO 2
2070        A=MID
2080        FA=FM
2090        GO TO 3
2100      2 B=MID
2110      3 IF (ABS(B-A).LE.0.000001) GO TO 4
2120        GO TO 1
2130      4 CBR2EQ=(A+B)/2
2140        RETURN
2150        END
```

Example Output of OCKEFF

```
run
OCKEFF 01/02/86 13:24:18
 TEMPERATURE, C
?23
 HYDROGEN PRESSURE, ATM
?1
 IF THE CONCENTRATIONS OF BR2 AND HBR ARE GIVEN IN
 WEIGHT PERCENT, INPUT 1; IF THEY ARE IN MOLALITY,
 INPUT 2.
?1
 BROMINE CONCENTRATION
?7.95
 HYDROGEN BROMIDE CONCENTRATION
?40
 IS MEMBRANE PRESENT? (1 FOR YES, 0 FOR NO)
?1
 MEMBRANE EQUIVALENT WEIGHT
?1200
 FACTOR TO MULTIPLY K FOR TRIBROMIDE REACTION BY
?5
 FACTOR TO MULTIPLY K FOR PENTABROMIDE REACTION BY
?5

 MEMBRANE PROTON CONCENTRATION 10 0001 MOLES/ LITER

 DENSITY OF DELTA PHASE  1.391439 G/ML
 EQUILIBRIUM BROMINE CONCENTRATION 0 001385 MOLES/LITER
 EQUILIBRIUM BROMIDE CONCENTRATION 6 190020 MOLES/LITER
 EQUILIBRIUM TRIBROMIDE CONCENTRATION  0 685959 MOLES/LITER
 EQUILIBRIUM PENTABROMIDE CONCENTRATION  0 002375 MOLES/LITER
 NERNST POTENTIAL  0.900371 VOLTS
 POTENTIAL DUE TO COMPLEX FORMATION  0.055725 VOLTS
 TOTAL POTENTIAL  0.956096 VOLTS

STOP
TIME 0.2 SECS
```

APPENDIX C

EXPERIMENTAL EQUIPMENT

A listing of the experimental equipment is given in Table 8. It specifies the manufacturer and catalog number of all major pieces of equipment. The types of tubing used were FEP Teflon flexible tubing, and machined TFE Teflon tubing. The fittings were either injection molded PFA Teflon or machined TFE Teflon.

Figure 34 shows the wiring diagram for experimental data acquisition. The relay circuit shown in Figure 35 was constructed for this research.

Table 8. Experimental Equipment

Bromide Solution Storage Flask:	6954-77 Ace Glass, 1000 ml. Flask, Flask, Four Necks, One Threaded, Thermometer neck internally threaded, Teflon bushing to hold 7mm thermometer, and Viton O-rings. Side Necks T 20/40 - fitted with 5031-10 Twin Ace-Thread adapators, T 24/25 joint, Teflon bushing and Viton O-rings to hold 7 mm tubing. Center neck, T 20'40, fitted with stirrer.
Bromide Solution Stirrer:	Cole Parmer R-4740-00. Closed system stirrer with T 24/40 joint. Has glass shaft, Teflon blades and seal assembly, Viton O-ring. Used with Cole Parmer's variable-speed stirrer, R-4335-00 with speed range of 500-7500 rpm, up to 5 gal. bath.
Constant Temperature Bath:	Neslab Instruments Co., T 9/10 W, heats to 100 C.
Thermistor Thermometer:	Cole-Parmer R-8110-20 digital thermistor thermometer. Resolution to 0.1 degree in both Celsius and Fahrenheit with accuracy of $\pm$0.1% of reading. For 0 to 50°C operating temperature.
Thermistor Probe:	Cole-Parmer Liquid Immersion Probe R-8110-20. 5" Pyrex Glass probe with time constant of 4.2 sec.
Bromine Solution Pump:	All-Teflon piston pump, model no. 7149-10 Cole Parmer 0.0-2.4 l/min., pressure to 14.9 psi, -40 to 150 C.
Needle Valves:	Teflon TFE Needle valves, Cole Parmer R-6393-60. 0.2 gpm maximum flow at 1 psig. 75 psig. maximum pressure.
Pressure Gages:	0 to 30 psi gage with Fluorocarbon Co. GPO-42 all Teflon body protector.
Reference Electrode:	Standard Calomel Reference Electrode, Fisher Scientific 13-639-52. Prefilled with saturated KCl solution.

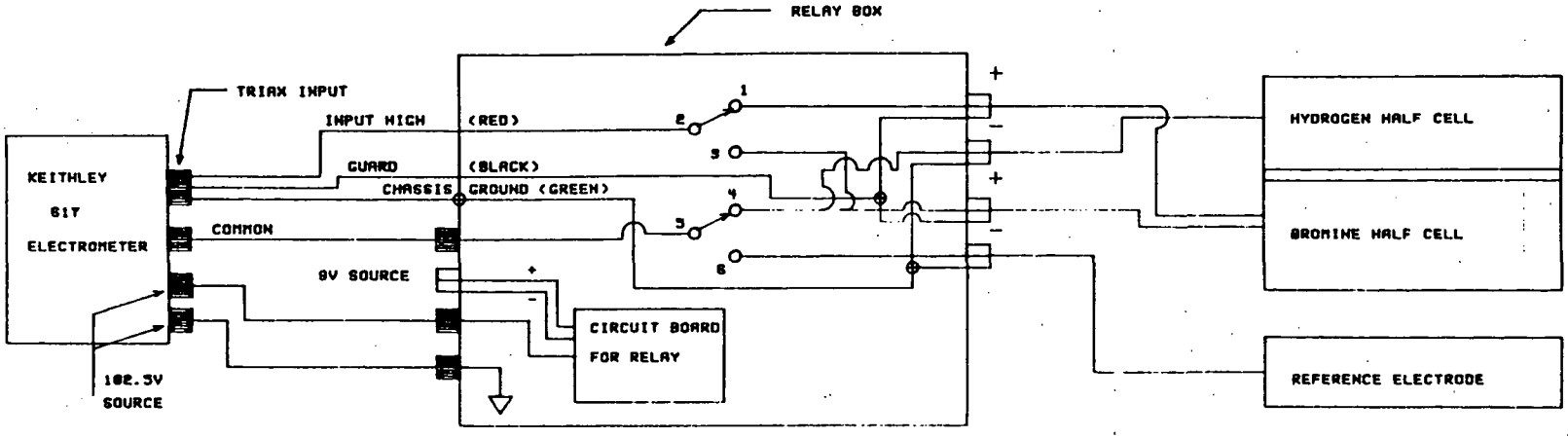

Figure 34. Schematic of wiring for experimental data acquisition.

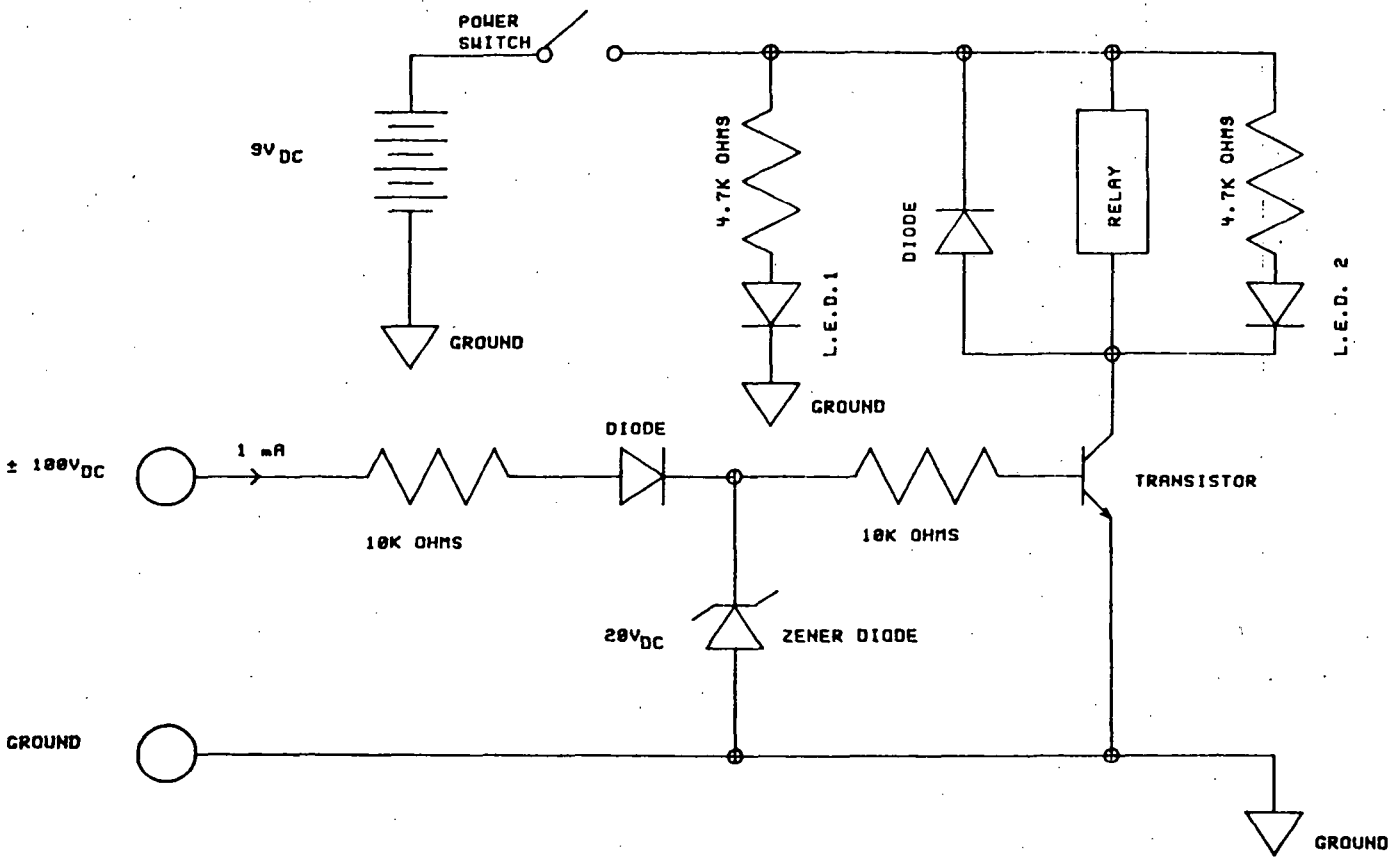

Figure 35. Diagram of relay circuit.

APPENDIX D

EXPERIMENTAL PROCEDURE

The steps taken to begin an experiment after the solutions are prepared as described in Chapter IV are listed below:

1. Turn electrometer on three hours before experiment is to begin.

2. Turn on water bath one hour before experiment is to begin.

3. Activate the platinized platinum screen by the method described in Appendix F. (When necessary, strip the platinum screen and platinize it again.)

4. Place platinized platinum screen in the hydrogen half cell, then place platinized side of membrane (when catalyzed Nafion 120 separator is used) between half cells, and bolt the cell together.

5. Connect cell to line, and connect leads.

6. Turn on stirrer, and collect solution sample for titration to determine bromine content. See Appendix F.

7. Enter storage solution temperature, pressure, and solution concentration into computer program.

8. Set the hydrogen flow to the desired pressure.

9. Prime the pump, then begin pumping solution.

10. Wait fifteen seconds for the solution to flow through cell, then begin data acquisition.

At the completion of an experiment:

1. Turn off the hydrogen.

2. Turn off the pump. Disconnect the cell, rinse the membrane and platinized platinum with distilled deionized water, then place both in a beaker of distilled deionized water.

3. Cap tubing at cell entrance and exit to prevent evaporation of bromine from storage.

4. Take a solution sample for titration, then turn off the stirrer and electrometer.

APPENDIX E

BASIC CODE OF DATA ACQUISITION PROGRAM FOR KEITHLEY PLUS 500 DATA ACQUISITION SYSTEM

```
10 REM Program used in data acquisition of hydrogen-bromine cell open circuit
20 REM voltage and rates of solution and membrane equilibrium data.
30 REM
40 REM Programmers:  Sharon Fritts, Doug Smith and Gail Lance
50 REM
60 REM Note: An uncommented version of this program was used to collect
70 REM experimental data since comments slow running time considerably.
80 REM
90 PRINT "IF CONTROL UP IS PRESSED THE PROGRAM IS TO STOP"
100 REM
110 REM These lines initialize the Plus500 software system.
120 REM
130       CLEAR   ,63000!         ' GPIB-PC Rev. B.1
140       IBINIT1 = 63000!        ' BASICA Declaration File
150       IBINIT2 = IBINIT1 + 3   '
160       BLOAD "bib.m",IBINIT1
170       CALL IBINIT1(IBFIND,IBTRG,IBCLR,IBPCT,IBSIC,IBLOC,IBPPC,IBBNA,IBONL,IB
RSC,IBSRE,IBRSV,IBPAD,IBSAD,IBIST,IBDMA,IBEOS,IBTMO,IBEOT)
180       CALL IBINIT2(IBGTS,IBCAC,IBWAIT,IBPOKE,IBWRT,IBWRTA,IBCMD,IBCMDA,IBRD,
IBRDA,IBSTOP,IBRPP,IBRSP,IBDIAG,IBXTRC,IBSTA%,IBERR%,IBCNT%)
190 NA$="gpib0":CALL IBFIND(NA$,INTERF1%)
200 NA$="dev15":CALL IBFIND(NA$,ELECTR%)
210 V%=&H102:CALL IBPOKE(BRD0%,V%)
220 V%=27:CALL IBPAD(ELECTR%,V%)
230 V%=1:CALL IBSRE(INTERF1%,V%)
240 REM
250 REM This command locks out the front panel of the electrometer.
260 REM
270 CMD$=CHR$(&H11):CALL IBCMD(INTERF1%,CMD$)
280 CLS
290 REM
300 REM Initialize pressure, temperature and concentration arrays.
310 REM
320 DIM PT(5)
330 REM
340 REM Initialize the voltage and time storing arrays.
350 REM
360 DIM VOLT1(2048)
370 DIM VOLT2(2048)
380 DIM TIME(2048)
390 INPUT "WHAT IS THE PRESSURE";PT(1)
400 INPUT "WHAT IS THE TEMPERATURE";PT(2)
410 INPUT "WHAT IS CONCENTRATION OF HBr"; PT(3)
420 INPUT "WHAT IS CONCENTRATION OF Br2"; PT(4)
430 REM
440 REM Sets the clock to zero.
450 REM
460 X$="00"
470 TIME$=X$
480 REM
490 REM Initialize time buffer, number of voltages read.
500 REM
510 TBUF=0:D=0
520 REM
530 REM Clears the electrometer
540 REM
550 CALL IBCLR(ELECTR%)
560 REM
570 REM Command that sets the function and range for measuring VOLT1
580 REM
590 CMD$="R2F0C0T5X"
```

```
600 REM
610 REM Sets voltage source to be used to trip the relay, and then
620 REM command string that sets function and range for measuring VOLT2
630 REM
640 V$="D1V+10201X"
650 CME$="R2FOCOT501X"
660 REM
670 REM Command string that turns off voltage source.
680 REM
690 V1$="O0X"
700 REM
710 REM Intialize the checks to be used throughout the program.
720 REM
730 X=0:SCOUNT=0:LCOUNT=0:CHK=59
740 REM If cursor up key is pressed, go to routine that saves data
750 REM
760 ON KEY(11) GOSUB 2550:KEY(11) ON
770 REM
780 REM Turn off voltage source, then insert a time delay of 130msec.
790 REM read voltage to be used to find VOLT1 with electrometer, then convert
800 REM it to a numerical value.  If this voltage is about 0V then beep.
810 REM
820 CALL IBWRT(ELECTR%,V1$)
830 CALL IBWRT(ELECTR%,CMD$)
840 V%=9:CALL IBTMO(BRD0%,V%)
850 V%=8
860 CALL IBTMO(BRD0%,V%)
870 RD$=SPACE$(50)
880 CALL IBRD(ELECTR%,RD$)
890 RD=VAL(MID$(RD$,5,16))
900 IF ABS(RD)<6.000001E-04 THEN BEEP
910 REM
920 REM Turn on voltage source to trip the relay, then insert a time delay
930 REM of 130msec, read voltage used to find VOLT2, then convert reading
940 REM to a numerical value.  If this voltage is about 0V then beep.
950 REM
960 CALL IBWRT(ELECTR%,V$)
970 CALL IBWRT(ELECTR%,CME$)
980 V%=9
990 CALL IBTMO(BRD0%,V%)
1000 V%=8
1010 CALL IBTMO(BRD0%,V%)
1020 RE$=SPACE$(50)
1030 CALL IBRD(ELECTR%,RE$)
1040 RE=VAL(MID$(RE$,5,16))
1050 IF ABS(RE)<6.000001E-04 THEN BEEP
1060 REM
1070 REM Reads the time into minutes, and calls it SBUF
1080 REM
1090 T$=TIME$
1100 A=VAL(MID$(T$,1,2))*60
1110 B=VAL(MID$(T$,4,2))
1120 C=VAL(MID$(T$,7,2))/60
1130 SBUF=A+B+C
1140 REM
1150 REM Increment number of voltages read, and sum voltages to find VOLT1 and
1160 REM VOLT2 into V1BUF and V2BUF as they are being read for averaging later.
1170 REM
1180 D=D+1
1190 V1BUF=V1BUF+RD
```

```
1200 V2BUF=V2BUF+RE
1210 REM
1220 REM If the time since the last time a voltage has been averaged and
1230 REM recorded is less than 15 seconds, go to 740 for more voltage readings
1240 REM
1250 IF(SBUF-TBUF)<=.25 GOTO 760
1260 REM
1270 REM Find median time between sets of recorded voltages, and average the
1271 REM during this time and store them in arrays Volt1 and Volt2
1280 REM
1290 TIME(X+1)=(SBUF+TBUF)/2
1300 TBUF=SBUF
1310 VOLT1(X+1)=V1BUF/D
1320 VOLT2(X+1)=V2BUF/D
1330 REM
1340 REM Reset number of voltages used in averaging to zero, print recorded
1350 REM voltages on screen
1360 REM
1370 D=0
1380 PRINT "THE VOLTAGES AND TIME ARE",VOLT1(X+1), VOLT2(X+1), TIME(X+1),X ,SCOU
NT
1390 REM
1400 REM If number of times equilibrium condition has been met is zero, set
1410 REM last recorded voltage to be that used for determining equilibrium
1420 REM criteria
1430 REM
1440 IF SCOUNT =0 THEN VOLT=VOLT1(X)
1450 REM
1460 REM If equilibrium condition is met, increment SCOUNT, otherwise, set
1470 REM SCOUNT to be zero
1480 REM
1490 IF ABS(VOLT1(X+1)-VOLT)<.0002 THEN SCOUNT=SCOUNT+1 ELSE SCOUNT=0
1500 REM
1510 REM Increment space number in storage array, and check to see if equil.
1520 REM condition has been met for ten minutes.  If so, go to data storage.
1530 REM
1540 X=X+1
1550 IF SCOUNT=40 THEN GOTO 2550
1560 REM
1570 REM Reset voltage buffers, and if experiment has been running less than one

1580 REM hour, return to line 740 to read more data.
1590 REM
1600 V1BUF=0:V2BUF=0
1610 IF (SBUF<60) THEN GOTO 760
1620 REM
1630 REM Calculate the number of minutes the equilibrium criteria has been met.
1640 REM Check to see if the cursor up key has been hit to stop the program and
1650 REM store the data.
1660 REM
1670 LCOUNT=SCOUNT\4
1680 ON KEY(11) GOSUB 2550:KEY(11) ON
1690 REM
1700 REM Turn off voltage source, then insert a time dalay of 130 msec.  Read
1710 REM voltage to be used in determining VOLT1 with electrometer, then
1720 REM convert voltage to a numerical value.  Make sure voltage is not zero.
1730 REM
1740 CALL IBWRT(ELECTR%,V1$)
1750 CALL IBWRT(ELECTR%,CMD$)
1760 V%=9:CALL IBTMO(BRD0%,V%)
```

```
1770 V%=8
1780 CALL IBTMO(BRD0%,V%)
1790 RD$=SPACE$(50)
1800 CALL IBRD(ELECTR%,RD$)
1810 RD=VAL(MID$(RD$,5,16))
1820 IF ABS(RD)<6.000001E-04 THEN BEEP
1830 REM
1840 REM Turn on voltage source to trip the relay, then insert a time delay
1850 REM of 130 msec, read voltage to be used to find VOLT2, then convert it
1860 REM to a numerical value.  Make sure this voltage is not zero.
1870 REM
1880 CALL IBWRT(ELECTR%,V$)
1890 CALL IBWRT(ELECTR%,CME$)
1900 V%=9
1910 CALL IBTMO(BRD0%,V%)
1920 V%=8
1930 CALL IBTMO(BRD0%,V%)
1940 RE$=SPACE$(50)
1950 CALL IBRD(ELECTR%,RE$)
1960 RE=VAL(MID$(RE$,5,16))
1970 IF ABS(RE)<6.000001E-04 THEN BEEP
1980 REM
1990 REM Reads the time into minutes, and call it SBUF
2000 REM
2010 T$=TIME$
2020 A=VAL(MID$(T$,1,2))*60
2030 B=VAL(MID$(T$,4,2))
2040 C=VAL(MID$(T$,7,2))/60
2050 SBUF=A+B+C
2060 REM
2070 REM Increment number of voltages read, and sum voltages to be used to
2080 REM determine VOLT1 and VOLT2 into V1BUF and V2BUF as they are being read
2090 REM for averaging later.
2100 REM
2110 D=D+1
2120 V1BUF=V1BUF+RD
2130 V2BUF=V2BUF+RE
2140 REM
2150 REM If it has been a minute since the last time a voltage has been
2160 REM recorded or averaged, go to 1660
2170 REM
2180 IF(SBUF-TBUF)<1 THEN GOTO 1680
2190 REM
2200 REM Find median time between recorded voltages, and average voltage during
2210 REM this time and store in VOLT1 and VOLT2 arrays. Reset voltage counter
2220 REM to zero, and put recorded voltages and time on the screen.
2230 REM
2240 TIME(X+1)=(TBUF+SBUF)/2
2250 TBUF=SBUF
2260 VOLT1(X+1)=V1BUF/D
2270 VOLT2(X+1)=V2BUF/D
2280 D=0
2290 PRINT"THE VOLTAGES AND TIME ARE",VOLT1(X+1),VOLT2(X+1), TIME(X+1),X,LCOUNT
2300 IF LCOUNT =0  THEN VOLT=VOLT1(X)
2310 REM
2320 REM If number of times equilibrium condition has been met is zero, set
2330 REM last recorded voltage to be that used for determining equilibrium
2340 REM criteria in the next reading
2350 REM
2360 REM If equilibrium condition is met increment LCOUNT, otherwise, set it to
2370 REM be zero.
```

```
2380 REM
2390 IF ABS(VOLT1(X+1)-VOLT)<.0002 THEN LCOUNT=LCOUNT+1 ELSE LCOUNT=0
2400 X=X+1
2410 REM
2420 REM If equilibrium condition has been met for ten minutes, go to data
2430 REM storage section of program.
2440 REM
2450 IF LCOUNT=10 THEN GOTO 2550
2460 V1BUF=0:V2BUF=0
2470 REM
2480 REM If it has been one hour since the electrometer was zeroed, rezero the
2490 REM electrometer, otherwise continue reading data.
2500 REM
2510 IF CHK<59 THEN CHK=CHK+1 ELSE CHK=0
2520 IF CHK>0 GOTO 2540
2530 CHK$="Z0XC1XZ1XC0X": CALL IBWRT(ELECTR%,CHK$)
2540 GOTO 1680
2550 V%=0:CALL IBONL(INTERF1%,V%)
2560 CALL IBONL(ELECTR%,V%)
2570 REM
2580 REM Store data in file.
2590 REM
2600 CMD$=CHR$(&H14):CALL IBCMD(INTERF1%,CMD$)
2610 INPUT"WHAT DO YOU WANT TO NAME THIS RUN";A$
2620 INPUT"WHAT IS THE FINAL TEMPERATURE";PT(5)
2630 B$=".prn"
2640 C$=A$+B$
2650 Y1$="  VOLT1"
2660 Y2$="  VOLT2"
2670 Z$="MINUTES"
2680 OPEN "o",#1,C$
2690 PRINT #1,Y1$,Y2$,Z$
2700 CLOSE #1
2710 OPEN C$ FOR APPEND AS #1
2720 FOR Y=1 TO X+1
2730 PRINT #1,VOLT1(Y), VOLT2(Y),TIME(Y)
2740 NEXT Y
2750 CLOSE #1
2760 OPEN C$ FOR APPEND AS #1
2770 PRINT #1,PT(1),PT(2),PT(3),PT(4),PT(5)
2780 CLOSE #1
2790 END
```

APPENDIX F

TITRATIONS AND OTHER EXPERIMENTAL PROCEDURES

A. Mohr Titration for Hydrobromic Acid Concentration

The hydrobromic acid concentration was determined after sparging the aqueous hydrobromic acid solution in the storage tank with nitrogen, to insure that the correct concentration was still present in the solution. The Mohr titration method was used [21]. This method involves titration with silver nitrate, with a sodium chromate indicator.

B. Titration for Bromine

The bromine concentration was measured before and after each experiment to determine whether any bromine had evaporated from the aqueous hydrobromic acid and bromine solution. This was done through titrations with sodium thiosulfate and a potassium iodide indicator. The method used is the same as the method used by LaHurd [22] for determination of chlorine concentration, except the sodium thiosulfate concentration for titration was 0.1 molar and 0.2 ml solution samples were used.

C. Platinizing the Platinum Screen

The platinum hydrogen electrode was platinized and activated using the electrochemical method of Gileadi [23]. The electrode was activated by polarizing anodically and cathodically dilute sulfuric acid prior to each experiment.

APPENDIX G

SAMPLE CALCULATIONS

I. Bromide Solution Concentrations

The bromide species concentrations were calculated for a 48% HBr charge capacity solution in the following manner.

The basis used in these calculations was 100 g. of solution. This initial solution is composed of 48 g. HBr, and 52 g. water. The solution was then hypothetically charged to form bromine, with the assumption that all of the hydrogen ions released in the reaction

$$HBr \rightleftarrows 1/2\ H_2 + 1/2\ Br_2$$

had been transported through the membrane and were no longer present in the solution. It was also assumed that the amount of water in the solution is unchanging. The concentrations were determined for solutions where the reported weight fractions excluded the weight of bromine, and for solutions where the reported weight fraction included the weight of bromine.

The molecular weights used in the calculations are 80.917 for HBr and 159.818 for bromine.

1.1 Reported Concentrations Excluding Bromine Weight

Because computer programs OCV1, OCVACT, and OCKEFF require the weight fraction of bromine as input to the program, reported concentrations which excluded the weight of bromine were treated in the following manner.

The initial solution was found to have 0.593 moles of HBr. The weight of HBr in the solution was found through iteration by

$$W_{HBr} = X/(X+52) \qquad (G-1)$$

where X is the reported weight fraction of HBr [9]. The quantity of bromine in the reported solution was found through conservation of bromide ions in the equation

$$1/2(0.593 \text{ moles Br} - W_{HBr}/80.917)\ 159.818 = W_{Br2} \qquad (G-2)$$

where W_i = weight of species i.

Then, the weight fraction of HBr in a solution which includes the weight of Br_2 must be found, so both the HBr and Br_2 concentrations input to the program are defined by the same method. The weight percentage of HBr input to the program was given by

$$X_{HBr} = W_{HBr}/(W_{HBr}+W_{Br_2}+W_{H_2O}) \qquad (G-3)$$

where X_i is the weight fraction of species i. The weight

fraction of Br_2 is found in the same manner. The solution concentrations found by this method are listed in Table 9.

1.2 Reported Concentrations Including Bromine Weight

Open circuit voltages were calculated for comparison to the data of G. E. [9], using the assumption that the reported weight fractions of HBr included the weight of bromine. These were also the concentrations used in the experimental measurement of the open circuit voltage for various states of charge of a system with a charge capacity of 48% HBr.

The weights of bromine and HBr were calculated from a solution with a known weight percentage of HBr, through the equation

$$X_{HBr} = \frac{W_{HBr}}{1/2(48-W_{HBr})159.818/80.917+W_{HBr}+52} \qquad (G-4)$$

which combines the definition of weight fraction with conservation of bromide ions and the first term of the denominator is W_{Br2}. Because X_{HBr} was reported, W_{HBr} was found by iteration. The total solution weight is then calculated, along with X_{Br2}. The solution concentrations calculated by this method are listed in Table 10.

The solution concentrations used in determining the open circuit voltage of a cell with a charge capacity of 35% HBr were calculated using an equation similar to (G-4). The solution concentrations are given in Table 11.

Table 9. Solution concentrations calculated from weight fractions of HBr that exclude weight of bromine for comparison to data of G. E. [9].

	X_{HBr}	X_{Br_2}
Start with 48% HBr 40% HBr at eq.	34.7	13.2
Start with 48% HBr 20% HBr at eq.	13.1	34.7
Start with 48% HBr 10% HBr at eq.	5.8	41.9

Table 10. Solution concentrations for various states of charge from 48% HBr charge capacity.

State of Charge	X_{HBr}	X_{Br_2}
16.7	40	7.95
37.5	30	17.88
58.5	20	27.82
79.2	10	37.76

Table 11. Solution concentrations for various states of charge from 35% HBr charge capacity.

State of Charge	X_{HBr}	X_{Br_2}
16.7	29.17	5.78
37.5	21.88	13.02
58.5	14.54	20.21
79.2	7.29	27.49

II. State-of-Charge

The states-of-charge reported in Tables 10 and 11 are calculated from the weight fractions of HBr in solutions which include the weight of Br_2. The equation used for this calculation is

$$S.O.C. = 100(1-X_{HBr}/X_{HBr}^{o}) \qquad (G-5)$$

where X_{HBr}^{o} is the charge capacity of the solution.

III. Curve fits of Data

Polynomials were estimated from regression of the data of Glass and Boyle [3], and of Glass [6] and Balko [2] to estimate the solution density, bromine solubility limit and activity coefficients of hydrobromic acid. These curve fits were done in APL, and are attached. The vectors given as output are the polynomial coefficients for the equation with the dependent variable to the zeroth, first, second, and, when necessary, third power.

CURVE FIT OF SOLUTION DENSITY TO MOLAL CONCENTRATION OF BROMIDE SPECIES OF GLASS AND BOYLE [3]

```
      MEQBR ← 0 2 5 10 12 15 20 25 27.5

      RHO ← 1 1.108 1.25 1.42 1.5 1.57 1.7 1.82 1.9

      DENS ← RHO ⌹ MEQBR ∘.* 0 1 2

      DENS
1.017686873 0.04488363995 ¯4.914449546E¯4
```

CURVE FIT OF GLASS' [6] SOLUBILITY DATA

OF BROMINE IN AQUEOUS HBR

```
      CHBR ← 0.2 0.4 0.6 0.8 1.0 1.5 2.0 2.5 3.0

      CBR2 ← 0.44 0.68 0.91 1.15 1.39 1.95 2.55 3.15 3.90

      CURVE ← CBR2 ⌹ CHBR ∘.* 0 1 2

      CURVE
0.2526794598 1.057577737 0.0487321524
```

CURVE FIT OF BALKO [2] ACTIVITY COEFFICIENT DATA IN AQUEOUS HBR

```
      MHBR ← 0 1 2 3 5 6 7 8 9

      LOGGAM ← 0 ¯0.055 0.073 0.229 0.565 0.788 0.915 1.049 1.199

      GAMMA ← 10 * LOGGAM

      GAMMA
1 0.881048873 1.183041556 1.6943378 3.672823005 6.137620052 8.222426499
      11.19437883 15.81248039

      GAMHBR ← GAMMA ⌹ MHBR ∘ . * 0 1 2 3

      GAMHBR
0.9418152476 ¯0.03224218452 0.045343504 0.015525929
```

APPENDIX H

EXPERIMENTAL DATA

The results of the experiments to measure the equilibrium of the hydrogen-bromine fuel cell with a charge capacity of 48% HBr are listed in Table 12. They are listed in the order of descending states of charge. The results of the studies to determine the effect of pressure on the open circuit voltage are also included. This Table combines the results obtained using the Nafion 120 membrane electrode assembly and the Nafion 117 membrane.

The results of the experiments to measure the open circuit voltages at various states of charge of a solution with a charge capacity of 35% HBr are listed in Table 13 in the order of descending states of charge. The experiments SPIKE3 and SPIKE4 are included here with the open circuit voltages measured before the addition of bromine.

Experiments SPIKE3 and SPIKE4 were conducted to measure the rates of solution and membrane equilibrium, and the results are given in Table 14. The voltage-time output of the data acquisition program is also given in Table 15. The first column of data is the cell voltage, the second column is the reference to bromine electrodes voltage, and the third column is the time in minutes. The last row of

each data set reported here records the pressure (psig), solution storage temperature (C), weight fractions of HBr and Br_2, and the temperature at the cell inlet at the completion of the experiment.

The output of experiments PRESCHG, BRPCHG, BRPCHG1, and BRPCHG2 are given in Table 16. In PRESCHG, the hydrogen pressures were changed during operation. In BRPCHG, BRPCHG1, and BRPCHG2 the solution pressures were changed during operation. Equilibrium was reached in experiment BRPCHG1.

The outputs of the experiments LLMMM1 and LLMMS1 are given in Table 17. These experiments compare the effects of a Nafion 120 catalyzed membrane to a Nafion 117 membrane for experiments conducted at 59.2% state of charge of a solution with a charge capacity of 48% HBr.

The data of experiments LLLHM1 and NLHM2 are given in Table 18. LLLHM1 is an experiment for a solution at 79.2% state of charge from a solution with charge capacity of 48% HBr. Equilibrium was not reached during this experiment. NLHM2 is an experiment representing 79.2% state of charge of a solution with a charge capacity of 35% HBr. This was the only experiment conducted at 79.2% state of charge (two liquid phases are present) where equilibrium was reached.

The data of experiments LLHLS, MLHLS3, and HLHLS are given in Table 19. These experiments are for a Nafion 117 membrane, solutions with 40% HBr and 7.95% Br_2. The experiments were conducted at hydrogen pressures of 2 psig, 8 psig, and 12 psig.

Table 12. Results of experiments to measure OCV of hydrogen-bromine fuel cell with charge capacity of 48% HBr.

Name	Nafion	P	T	X HBr	X Br2	OCV	Ref.	Time
	(psi)		(C)	(%)	(%)	(V)	(V)	(min.)
LLLHM1	120	2	24.4	10	37.76	1.062	1.032	175
LLLHM2	120	2	24.4	10	37.76	1.064	1.032	90
LLLLS	117	2	26.5	10	7.95	1.014	0.788	93.5
LLLLS2	117	2	27.2	10	7.95	1.017	0.789	80.5
LLMMM1	120	2	25.5	20	27.82	0.899	0.898	81.8
LLMMM2	120	2	26.2	20	27.82	0.894	0.889	144.2
LLMMS1	117	2	26.1	20	27.82	0.898	0.895	82.7
LLNNM1	120	2	24.2	30	17.88	0.815	0.818	31.1
LLNNM2	120	2	24.7	30	17.88	0.795	0.816	135.2
LLNNM3	120	2	25.4	30	17.88	0.796	0.825	150.9
LLHLM	120	2	27.4	40	7.95	0.744	0.611	57.4
LLHLM4	120	2	26.8	40	7.95	0.74	0.628	117.8
LLHLM5	120	2	26.2	40	7.95	0.732	0.666	90.7
LLHLM7	120	2	25.6	40	7.95	0.731	0.75	53.4
LLHLS	117	2	26.5	40	7.95	0.745	0.55	28.5
LLHLS1	117	2	26.8	40	7.95	0.78	0.642	149.7
LLHLS4	117	2	26.2	40	7.95	0.688	0.641	194.9
LLHLS7	117	2	25.5	40	7.95	0.719	0.752	125.9
MLHLM	120	8	27.8	40	7.95	0.741	0.611	210
MLHLS	117	8	26.8	40	7.95			
MLHLS2	117	8	26.6	40	7.95			
MLHLS3	117	8	25.4	40	7.95	0.703	0.615	81.5
HLHLS	117	12	25.6	40	7.95	0.738	0.615	76.5

Table 13. Results of experiments to measure OCV of hydrogen-bromine fuel cell with charge capacity of 35% HBr.

Name	Nafion	P (psi)	T (C)	X HBr (%)	X Br2 (%)	OCV (V)	Ref. (V)	Time (min.)
NLHM1	yes	2	25	7.29	27.49	1.105	1.051	40
NLHM2	yes	2	24.6	7.29	27.49	1.108	1.045	40.8
NMMM1	yes	2	24.2	14.54	20.21	0.963	0.95	24.1
NMMM4	yes	2	24.6	14.54	20.21	0.988	0.939	15.6
NMMM6	yes	2	24.7	14.54	20.21	0.988	0.937	39.7
NMMS1	no	2	25.4	14.54	20.21	0.978	0.94	25.4
NNNM1	yes	2	24.2	21.84	13	0.916	0.876	12.7
NNNM2	yes	2	23.9	21.88	13.02	0.916	0.878	47.4
NHLM1	yes	2	23.7	29.17	5.78	0.854	2.003	57
NHLM2	yes	2	22.9	29.17	5.78	0.855	0.835	12.1
SPIKE3	yes	2	24.2	29.17	5.78	0.853	0.837	53.5
SPIKE4	yes	2	24.4	29.17	5.78	0.854	0.826	36.5

Table 14. Results of rates of solution and membrane equilibrium experiments.

	SPIKE3	SPIKE4
Before Bromine Addition		
X HBr	29.17	29.17
X Br2	5.78	5.78
OCV (V)	0.853	0.854
Ref. (V)	0.837	0.826
Time at Br2 Spike	53.5	36.5
After Bromine Addition		
X HBr	27.58	27.58
X Br2	10.93	10.93
OCV (V)	0.862	0.864
Ref. (V)	0.849	0.837
Time at Equilibrium	84.7	88.7
Temperature (C)	24.6	25
Pressure (psi)	2	2

Table 15. Voltage-time data of experiments SPIKE3 and SPIKE4.

SPIKE3

VOLT1	VOLT2	MINUTES
0.597283	-0.83569	0.133333
0.649222	-0.83603	0.4
0.697559	-0.83622	0.666666
0.735564	-0.83640	0.933333
0.760565	-0.83657	1.2
0.777463	-0.83677	1.466667
0.784835	-0.83692	1.733333
0.788857	-0.83702	2
0.79168	-0.83709	2.266667
0.793963	-0.83713	2.533333
0.795773	-0.83715	2.8
0.797371	-0.83718	3.066667
0.7992	-0.83718	3.333334
0.800947	-0.83718	3.6
0.802416	-0.83718	3.866667
0.803625	-0.83717	4.133333
0.804752	-0.83716	4.4
0.80573	-0.83714	4.666667
0.806640	-0.83713	4.933334
0.807466	-0.83712	5.2
0.808245	-0.83710	5.466667
0.808967	-0.83708	5.733334
0.809636	-0.83706	6
0.810305	-0.83704	6.275
0.810929	-0.83703	6.55
0.811518	-0.83701	6.816667
0.812101	-0.83699	7.091666
0.812683	-0.83697	7.366667
0.813423	-0.83696	7.633333
0.814227	-0.83695	7.9
0.814967	-0.83693	8.166667
0.815644	-0.83693	8.433333
0.816272	-0.83693	8.7
0.816843	-0.83692	8.966667
0.817363	-0.83689	9.233334
0.817842	-0.83689	9.5
0.818330	-0.83690	9.766666
0.818792	-0.83690	10.03333
0.819285	-0.83690	10.3
0.819751	-0.83690	10.56667
0.820225	-0.83690	10.83333
0.820732	-0.83689	11.1
0.821227	-0.83687	11.36667
0.821733	-0.83687	11.63333
0.822263	-0.83687	11.9
0.822808	-0.83686	12.16667
0.823353	-0.83689	12.43333
0.823959	-0.83688	12.7
0.824563	-0.83688	12.96667
0.825208	-0.83689	13.23333
0.825846	-0.83690	13.5
0.826538	-0.83692	13.76667
0.827266	-0.83692	14.03333
0.828000	-0.83692	14.3
0.828720	-0.83692	14.56667
0.829441	-0.83691	14.83333
0.830175	-0.83690	15.1
0.830912	-0.83688	15.36667
0.831657	-0.83687	15.63333
0.832396	-0.83685	15.9

0.833132	-0.83685	16.16667
0.833857	-0.83684	16.43333
0.834572	-0.83683	16.7
0.835257	-0.83684	16.96667
0.835935	-0.83684	17.23333
0.836577	-0.83685	17.5
0.837219	-0.83685	17.76667
0.837835	-0.83686	18.03333
0.838438	-0.83687	18.3
0.839034	-0.83689	18.56667
0.839612	-0.83690	18.83333
0.840161	-0.83691	19.1
0.840694	-0.83693	19.36667
0.841202	-0.83695	19.63333
0.841710	-0.83697	19.9
0.842169	-0.83698	20.16667
0.842633	-0.837	20.43333
0.84306	-0.83701	20.7
0.843470	-0.83702	20.96667
0.843874	-0.83704	21.23333
0.844243	-0.83705	21.5
0.844592	-0.83706	21.76667
0.844942	-0.83708	22.03333
0.845274	-0.83709	22.3
0.845584	-0.83709	22.56667
0.845874	-0.83710	22.83334
0.846169	-0.83710	23.1
0.846437	-0.83710	23.36667
0.846701	-0.83711	23.63333
0.846954	-0.83709	23.9
0.847207	-0.83709	24.16667
0.847449	-0.83708	24.43334
0.847674	-0.83706	24.7
0.847875	-0.83706	24.96667
0.848067	-0.83706	25.23333
0.848257	-0.83706	25.5
0.848430	-0.83705	25.76667
0.848593	-0.83704	26.03333
0.848766	-0.83703	26.3
0.848912	-0.83705	26.56667
0.849066	-0.83705	26.83334
0.849225	-0.83705	27.1
0.849359	-0.83705	27.36667
0.849487	-0.83704	27.63333
0.849607	-0.83702	27.9
0.849712	-0.83702	28.16667
0.849821	-0.83703	28.43334
0.849914	-0.83703	28.7
0.850003	-0.83703	28.96667
0.850106	-0.83705	29.23333
0.850218	-0.83706	29.5
0.850295	-0.83708	29.76667
0.850371	-0.83708	30.03333
0.850442	-0.83708	30.3
0.850513	-0.83709	30.56667
0.850572	-0.83709	30.83334
0.850632	-0.83709	31.10833
0.850686	-0.83709	31.38333
0.850751	-0.83709	31.65
0.850806	-0.83709	31.91667
0.850860	-0.83709	32.18334
0.850909	-0.83708	32.45
0.850954	-0.83709	32.71667
0.851008	-0.83709	32.98333
0.851072	-0.83709	33.25
0.851124	-0.83709	33.51667

0.851176	-0.83709	33.78333
0.851217	-0.83709	34.05
0.851249	-0.83710	34.31667
0.851306	-0.83710	34.58334
0.851367	-0.83711	34.85
0.851408	-0.83712	35.11667
0.851444	-0.83713	35.38333
0.851479	-0.83714	35.65
0.851519	-0.83716	35.91667
0.851550	-0.83716	36.18334
0.851594	-0.83717	36.45
0.851634	-0.83717	36.71667
0.851668	-0.83718	36.98333
0.851704	-0.83718	37.25
0.851743	-0.83719	37.51667
0.851782	-0.83720	37.78333
0.851837	-0.83721	38.05
0.851867	-0.83721	38.31667
0.851907	-0.83722	38.58334
0.851942	-0.83723	38.85
0.851972	-0.83723	39.11667
0.851999	-0.83723	39.38333
0.852022	-0.83724	39.65
0.852047	-0.83725	39.91667
0.852082	-0.83725	40.18334
0.852104	-0.83726	40.45
0.852135	-0.83726	40.71667
0.852163	-0.83728	40.98333
0.852186	-0.83728	41.25
0.852217	-0.83729	41.51667
0.852234	-0.83729	41.78333
0.852253	-0.83731	42.05001
0.852287	-0.83732	42.31667
0.852312	-0.83733	42.58334
0.852334	-0.83733	42.85
0.852355	-0.83736	43.11667
0.852377	-0.83736	43.38333
0.852397	-0.83737	43.65
0.852410	-0.83733	43.91667
0.852435	-0.83733	44.18334
0.852456	-0.83734	44.45
0.852483	-0.83734	44.71667
0.852510	-0.83735	44.98333
0.852528	-0.83736	45.25
0.852547	-0.83737	45.51667
0.852571	-0.83737	45.78334
0.852588	-0.83738	46.05001
0.852595	-0.83738	46.31667
0.852607	-0.83738	46.58334
0.852617	-0.83739	46.85
0.852640	-0.83739	47.11667
0.852660	-0.83739	47.38333
0.852673	-0.83740	47.65
0.852697	-0.83739	47.91667
0.852707	-0.83740	48.18334
0.852720	-0.83741	48.45
0.852740	-0.83741	48.71667
0.852752	-0.83742	48.98333
0.852769	-0.83742	49.25
0.852784	-0.83743	49.51667
0.852797	-0.83743	49.78334
0.852802	-0.83743	50.05001
0.852814	-0.83744	50.31667
0.852825	-0.83744	50.58334
0.852837	-0.83745	50.85
0.852847	-0.83745	51.11667

```
0.852854 -0.83745 51.38333
0.852863 -0.83746    51.65
0.852880 -0.83746 51.91667
0.852887 -0.83746 52.18334
0.852893 -0.83746    52.45
0.852900 -0.83747 52.71667
0.852914 -0.83747 52.98333
0.852927 -0.83747    53.25
0.852932 -0.83747 53.51667
0.852944 -0.83747 53.78334
0.854258 -0.83889 54.05001
0.860704 -0.84457 54.31667
0.861541 -0.84567 54.58334
0.861747 -0.84633    54.85
0.861668 -0.84676 55.11667
0.861509 -0.84709 55.38333
0.861363 -0.84734    55.65
0.861261 -0.84753 55.91667
0.861187 -0.84769 56.18334
0.861129 -0.84782    56.45
0.861099 -0.84793 56.71667
0.861085 -0.84802 56.98333
0.861080 -0.84809    57.25
0.861100 -0.84815 57.51667
0.861119 -0.84822 57.78334
0.861145 -0.84827 58.05001
0.861148 -0.84832 58.31667
0.861171 -0.84837 58.58334
 0.86121 -0.84841    58.85
0.860875 -0.84847 59.11667
0.860743 -0.84852 59.38333
0.860856 -0.84851    59.65
0.860937 -0.84853 59.91667
0.861038 -0.84856    60.55
0.861255 -0.84853    61.55
0.861318 -0.84858    62.55
0.861388 -0.84863 63.55001
0.861446 -0.84864    64.55
0.861461 -0.84867    65.55
0.861494 -0.84869    66.55
0.861530 -0.84870    67.55
0.861566 -0.84872    68.55
0.861556 -0.84874    69.55
0.861565 -0.84875    70.55
0.861586 -0.84875    71.55
0.861615 -0.84875    72.55
0.861651 -0.84875 73.55833
0.861667 -0.84877 74.56667
0.861628 -0.84878   75.575
0.861624 -0.84878 76.59167
0.861653 -0.84878 77.60834
0.861637 -0.84877   78.625
0.861645 -0.84877 79.64166
0.861612 -0.84877 80.65833
0.861618 -0.84877   81.675
0.861637 -0.84878 82.68333
0.861667 -0.84876 83.69167
0.861665 -0.84876     84.7
       0        0         0
       2     24.6     29.17      5.78      24.2
```

SPIKE4

VOLT1	VOLT2	MINUTES
0.870997	-0.82174	0.133333
0.868867	-0.82195	0.4
0.867330	-0.82221	0.666666
0.866037	-0.82235	0.933333
0.864981	-0.82242	1.2
0.863939	-0.82245	1.466667
0.862799	-0.82249	1.733333
0.861615	-0.82253	2
0.860405	-0.82252	2.266667
0.859240	-0.82255	2.533333
0.858095	-0.82253	2.8
0.857006	-0.82252	3.066667
0.856000	-0.82253	3.333334
0.855102	-0.82257	3.6
0.854359	-0.82260	3.866667
0.853722	-0.82268	4.141667
0.853230	-0.82276	4.416667
0.852781	-0.82287	4.683334
0.852450	-0.82298	4.95
0.852202	-0.82308	5.225001
0.851993	-0.82317	5.5
0.851777	-0.82326	5.766667
0.851607	-0.82335	6.033334
0.851507	-0.82347	6.3
0.851415	-0.82355	6.566667
0.851362	-0.82361	6.833333
0.851339	-0.82369	7.1
0.851317	-0.82374	7.375
0.851331	-0.82380	7.65
0.851330	-0.82385	7.916667
0.851381	-0.82389	8.183333
0.851409	-0.82392	8.45
0.851436	-0.82396	8.716667
0.851482	-0.82396	8.983334
0.85153	-0.82400	9.258333
0.851555	-0.82402	9.533333
0.851547	-0.82405	9.8
0.851533	-0.82407	10.06667
0.851602	-0.82408	10.33333
0.851655	-0.82410	10.6
0.851622	-0.82411	10.86667
0.851696	-0.82413	11.13333
0.851748	-0.82414	11.4
0.851765	-0.82415	11.66667
0.851817	-0.82416	11.93333
0.851809	-0.82416	12.2
0.85189	-0.82417	12.46667
0.851914	-0.82417	12.73333
0.852030	-0.82418	13
0.852067	-0.82419	13.26667
0.852154	-0.82420	13.53333
0.852196	-0.82419	13.8
0.852252	-0.82421	14.06667
0.852381	-0.82423	14.33333
0.852466	-0.82423	14.6
0.852532	-0.82422	14.86667
0.852587	-0.82423	15.13333
0.852620	-0.82424	15.4
0.852653	-0.82426	15.66667
0.852714	-0.82426	15.93333
0.852784	-0.82426	16.2
0.852899	-0.82427	16.46667
0.852930	-0.82429	16.73333

0.852994	-0.82429	17
0.853059	-0.82431	17.26667
0.853100	-0.82433	17.53333
0.853148	-0.82434	17.8
0.853141	-0.82437	18.06667
0.853161	-0.82439	18.33333
0.853246	-0.82439	18.6
0.853261	-0.82440	18.86667
0.853314	-0.82442	19.13333
0.853360	-0.82445	19.4
0.853400	-0.82448	19.66667
0.853445	-0.82448	19.93333
0.853481	-0.82449	20.2
0.853513	-0.82451	20.46667
0.853541	-0.82453	20.73333
0.853595	-0.82454	21
0.853622	-0.82454	21.26667
0.853644	-0.82455	21.53333
0.853660	-0.82456	21.8
0.853657	-0.82458	22.06667
0.853662	-0.82459	22.33334
0.853705	-0.82460	22.6
0.853735	-0.82460	22.86667
0.853743	-0.82460	23.13333
0.853768	-0.82463	23.4
0.853797	-0.82464	23.66667
0.853816	-0.82465	23.93334
0.853839	-0.82464	24.2
0.853715	-0.82456	24.46667
0.853852	-0.82465	24.73333
0.853876	-0.82466	25
0.853883	-0.82468	25.26667
0.85391	-0.82471	25.53333
0.853918	-0.82472	25.8
0.853932	-0.82473	26.06667
0.853946	-0.82474	26.33334
0.853930	-0.82476	26.6
0.853955	-0.82478	26.86667
0.853973	-0.82480	27.13333
0.853984	-0.82483	27.4
0.853978	-0.82485	27.66667
0.853984	-0.82487	27.93334
0.853991	-0.82489	28.2
0.854027	-0.82492	28.46667
0.854057	-0.82496	28.73333
0.854047	-0.82497	29
0.854060	-0.82501	29.26667
0.854067	-0.82504	29.53333
0.854083	-0.82508	29.8
0.854093	-0.82511	30.06667
0.854112	-0.82514	30.33334
0.854115	-0.82517	30.6
0.854118	-0.82520	30.86667
0.854127	-0.82522	31.13333
0.85413	-0.82525	31.4
0.854139	-0.82526	31.66667
0.854145	-0.82530	31.93333
0.854146	-0.82532	32.2
0.854150	-0.82536	32.46667
0.85417	-0.82538	32.73333
0.854169	-0.82540	33
0.854172	-0.82541	33.26667
0.854146	-0.82543	33.53333
0.854154	-0.82544	33.8
0.854184	-0.82547	34.06667
0.854175	-0.82549	34.33334

0.854187	-0.82551	34.6
0.854202	-0.82552	34.86667
0.854211	-0.82551	35.13333
0.854191	-0.82553	35.4
0.854175	-0.82555	35.66667
0.854212	-0.82557	35.93334
0.85419	-0.82555	36.2
0.854202	-0.82557	36.46667
0.854196	-0.82559	36.73333
0.858402	-0.82979	37
0.861833	-0.83303	37.26667
0.862390	-0.83389	37.53333
0.862575	-0.83443	37.8
0.862633	-0.83478	38.06667
0.862727	-0.83508	38.33334
0.862725	-0.83536	38.6
0.862737	-0.83556	38.86667
0.862784	-0.83572	39.13333
0.862830	-0.83586	39.4
0.862901	-0.83596	39.66667
0.862968	-0.83601	39.93334
0.863010	-0.83615	40.2
0.863047	-0.83623	40.46667
0.863155	-0.83630	40.73333
0.863227	-0.83637	41
0.863292	-0.83645	41.26667
0.863377	-0.83655	41.53333
0.863452	-0.83661	41.8
0.863514	-0.83664	42.06667
0.863554	-0.83670	42.33334
0.863580	-0.83673	42.6
0.863615	-0.83681	42.86667
0.863665	-0.83686	43.13333
0.863706	-0.83689	43.4
0.863752	-0.83692	43.66667
0.863777	-0.83694	43.93334
0.863816	-0.83699	44.2
0.863836	-0.83699	44.46667
0.863842	-0.83701	44.73333
0.863842	-0.83706	45
0.863890	-0.83708	45.26667
0.863907	-0.83709	45.53334
0.863924	-0.83710	45.80001
0.863961	-0.83711	46.06667
0.863963	-0.83716	46.33334
0.863985	-0.83715	46.6
0.863998	-0.83717	46.86667
0.864011	-0.83717	47.13333
0.864006	-0.83715	47.40834
0.86402	-0.83719	47.68334
0.864029	-0.83723	47.95
0.864046	-0.83723	48.21667
0.864061	-0.83724	48.48333
0.864081	-0.83725	48.75
0.864078	-0.83727	49.01667
0.864094	-0.83727	49.28334
0.864116	-0.83724	49.55001
0.864124	-0.83729	49.81667
0.864132	-0.83727	50.08334
0.864132	-0.83729	50.35
0.864141	-0.83732	50.61667
0.864152	-0.83734	50.88333
0.864138	-0.83729	51.15
0.864077	-0.83726	51.41667
0.864132	-0.83732	51.68334
0.864149	-0.83731	51.95

```
0.864149 -0.83736 52.21667
0.864152 -0.83738 52.48333
0.864148 -0.83740    52.75
0.864178 -0.83741 53.01667
0.864187 -0.83741 53.28334
0.864207 -0.83741 53.55001
0.864201 -0.83742 53.81667
0.864206 -0.83743 54.08334
0.864230 -0.83744    54.35
0.864218 -0.83744 54.61667
0.864249 -0.83742 54.88333
0.864220 -0.83739    55.15
0.864200 -0.83738 55.41667
0.864234 -0.83734 55.68334
0.864211 -0.83739    55.95
0.864155 -0.83738 56.21667
0.864117 -0.83734 56.48333
0.864053 -0.83729    56.75
0.864003 -0.83728 57.01667
0.863974 -0.83730 57.28334
0.863966 -0.83731 57.55001
0.863943 -0.83729 57.81667
0.863940 -0.83731 58.08334
0.863928 -0.83733    58.35
0.863918 -0.83734 58.61667
0.863905 -0.83732 58.88333
0.863912 -0.83733    59.15
0.863919 -0.83731 59.41667
0.863929 -0.83735 59.68334
0.863933 -0.83735    59.95
0.863930 -0.83734 60.58333
0.863900 -0.83733 61.59167
0.863866 -0.83729     62.6
0.863845 -0.83729     63.6
0.863815 -0.83726     64.6
0.863801 -0.83729     65.6
0.863782 -0.83727 66.60834
0.863749 -0.83723 67.61667
0.863691 -0.83717 68.61667
0.863635 -0.83713 69.61667
0.863552 -0.83720 70.61667
0.863504 -0.83724 71.61667
0.863556 -0.83721   72.625
0.863696 -0.83713 73.63333
0.863755 -0.83714 74.63333
0.863839 -0.83720 75.63333
0.863887 -0.83719 76.63333
0.863953 -0.83723 77.63333
0.863978 -0.83720 78.63333
0.863970 -0.83722 79.63333
0.863965 -0.83722 80.63333
0.863972 -0.83721 81.63333
0.863977 -0.83725 82.63333
0.863986 -0.83724 83.63333
0.864018 -0.83726 84.63333
0.864046 -0.83726 85.63333
0.864077 -0.83727 86.64166
0.864095 -0.83723    87.65
0.864069 -0.83720    88.65
       0        0        0
       2       25    29.17     5.78     24.4
```

Table 16. Voltage-time data of experiments PRESCHG, BRPCHG1, BRPCHG2 and BRPCHG.

PRESCHG

VOLT1	VOLT2	MINUTES
1.026392	-0.78603	0.133333
1.027308	-0.78534	0.4
1.027814	-0.78508	0.666666
1.027563	-0.78494	0.933333
1.027407	-0.78485	1.2
1.027367	-0.78472	1.466667
1.027352	-0.78465	1.733333
1.027373	-0.78453	2
1.027277	-0.78445	2.266667
1.027406	-0.78424	2.533333
1.027309	-0.78414	2.8
1.027256	-0.78411	3.066667
1.027194	-0.78392	3.333334
1.027129	-0.78378	3.6
1.026898	-0.78366	3.866667
1.026626	-0.78355	4.133333
1.026408	-0.78341	4.4
1.026095	-0.78328	4.666667
1.025664	-0.78313	4.933334
1.025106	-0.78296	5.2
1.025589	-0.78275	5.466667
1.024862	-0.78255	5.733334
1.023406	-0.78239	6
1.021726	-0.78234	6.266667
1.020161	-0.78241	6.533334
1.019067	-0.78258	6.8
1.018451	-0.78271	7.066667
1.018149	-0.78280	7.333333
1.018046	-0.78287	7.600001
1.018091	-0.78292	7.866667
1.018227	-0.78296	8.133333
1.018366	-0.78299	8.408333
1.018517	-0.78302	8.691667
1.01865	-1.08299	8.966667
1.018779	-2.00232	9.233334
1.018855	-2.00233	9.5
1.018924	-2.00232	9.766666
1.018985	-2.00232	10.03333
1.019009	-2.00231	10.3
1.019038	-2.00232	10.56667
1.019065	-2.00229	10.83333
1.019066	-2.00229	11.1
1.019069	-2.00229	11.36667
1.015506	-2.00230	11.63333
1.015203	-2.00229	11.9
1.017225	-2.00226	12.16667
1.017796	-2.00229	12.43333
1.017889	-2.00229	12.7
1.017866	-2.00230	12.96667
1.017834	-2.00230	13.23333
1.017745	-2.00229	13.5
1.017886	-2.00229	13.76667
1.018013	-2.00229	14.03333
1.018066	-2.00227	14.3
1.018074	-2.00226	14.56667
1.018002	-0.75460	14.83333
1.017962	-0.78301	15.1
1.017786	-0.78299	15.36667
1.017763	-0.78297	15.64167

1.017722	-0.78298	15.91667
1.017721	-0.78299	16.18333
1.017727	-0.78297	16.45
1.017698	-0.78299	16.71667
1.017694	-0.78300	16.98333
1.017717	-0.78300	17.25
1.017831	-0.78300	17.51667
1.018917	-0.78303	17.78333
1.018482	-0.78307	18.05
1.018289	-0.78311	18.31667
1.018223	-0.78312	18.58333
1.018207	-0.78313	18.85
1.018189	-0.78314	19.11667
1.01817	-0.78314	19.38333
1.018146	-0.78315	19.65
1.018116	-0.78315	19.91667
1.018096	-0.78316	20.18333
1.018055	-0.78316	20.45
1.018019	-0.78316	20.71667
1.017982	-0.78317	20.98333
1.017962	-0.78317	21.25
1.017925	-0.78318	21.51667
1.017892	-0.78318	21.79167
1.017868	-0.78318	22.06667
1.01785	-0.78319	22.33334
1.017811	-0.78319	22.6
1.017782	-0.78320	22.86667
1.017779	-0.78320	23.13333
1.017764	-0.78319	23.4
1.017762	-0.78320	23.66667
1.01773	-0.78320	23.93334
1.017725	-0.7832	24.2
1.017709	-0.78319	24.46667
1.017682	-0.78320	24.73333
1.017654	-0.78320	25
1.017651	-0.78320	25.26667
1.017617	-0.78320	25.53333
1.017617	-0.78319	25.8
1.017581	-0.78320	26.06667
1.017574	-0.78320	26.33334
1.017574	-0.78320	26.6
1.017599	-0.78320	26.86667
1.017502	-0.7832	27.13333
1.017479	-0.78319	27.4
1.017486	-0.78319	27.675
1.017447	-0.78319	27.95
1.017439	-0.78319	28.21667
1.0174	-0.78319	28.48333
1.017261	-0.78317	28.75
1.017204	-0.78318	29.01667
1.017234	-0.78318	29.28333
1.017242	-0.78319	29.55
1.017244	-0.78320	29.81667
1.017228	-0.78320	30.08334
1.012796	-0.78326	30.35
1.010732	-0.78309	30.61667
1.012857	-0.78309	30.88333
1.013899	-0.78310	31.15
1.014767	-0.78307	31.41667
1.015298	-0.78305	31.68334
1.015605	-0.78301	31.95
1.016036	-0.78307	32.21667
1.016442	-0.78313	32.48333
1.016477	-0.78313	32.75
1.016501	-0.78314	33.01667
1.01651	-0.78314	33.28333

1.016488	-0.78316	33.55834
1.016509	-0.78317	33.83334
1.016556	-0.78317	34.1
1.016594	-0.78315	34.36667
1.016632	-0.78315	34.63333
1.016703	-0.78313	34.9
1.016736	-0.78312	35.16667
1.016759	-0.78312	35.43334
1.01679	-0.78311	35.7
1.016834	-0.78311	35.96667
1.016773	-0.78309	36.23333
1.016696	-0.78310	36.5
1.016757	-0.78312	36.76667
1.016769	-0.78312	37.03333
1.016794	-0.78312	37.3
1.016823	-0.78311	37.56667
1.016863	-0.78312	37.83334
1.016869	-0.78312	38.1
1.016878	-0.78312	38.36667
1.016905	-0.78312	38.63333
1.016905	-0.78312	38.9
1.016882	-0.78313	39.16667
1.016868	-0.78314	39.44167
1.016867	-0.78315	39.71667
1.016872	-0.78316	39.98333
1.016799	-0.78317	40.25
1.018202	-0.78317	40.51667
1.018019	-0.78315	40.78333
1.017737	-0.78315	41.05
1.01762	-0.78314	41.31667
1.017543	-0.78315	41.58334
1.01749	-0.78317	41.85
1.017447	-0.78318	42.11667
1.017421	-0.78319	42.38333
1.017387	-0.78321	42.65
1.017373	-0.78323	42.91667
1.017366	-0.78325	43.18334
1.017352	-0.78326	43.45
1.017331	-0.78326	43.71667
1.017329	-0.78327	43.98333
1.017309	-0.78329	44.25
1.017311	-0.78330	44.51667
1.017306	-0.78330	44.79167
1.017291	-0.78331	45.06667
1.017276	-0.78331	45.33334
1.017253	-0.78331	45.6
1.017255	-0.78332	45.86667
1.017236	-0.78332	46.13333
1.017203	-0.78332	46.4
1.017171	-0.78332	46.66667
1.017149	-0.78333	46.93334
1.017131	-0.78334	47.2
1.017151	-0.78335	47.46667
1.017096	-0.78335	47.73333
1.017029	-0.78334	48
1.017009	-0.78334	48.26667
1.016994	-0.78334	48.53334
1.016984	-0.78334	48.80001
1.016984	-0.78334	49.06667
1.016979	-0.78335	49.33334
1.016994	-0.78335	49.6
1.017	-0.78335	49.86667
1.017002	-0.78335	50.13333
1.006377	-0.78421	50.4
1.007279	-0.78383	50.66667
1.011962	-0.78349	50.94167

1.013806	-0.78333	51.21667
1.014791	-0.78328	51.48333
1.01518	-0.78328	51.75
1.015317	-0.78326	52.01667
1.015476	-0.78327	52.28334
1.015224	-0.78321	52.55001
1.015049	-0.78317	52.81667
1.015109	-0.78316	53.08334
1.015694	-0.78326	53.35
1.015897	-0.78329	53.61667
1.015981	-0.78329	53.88333
1.016019	-0.78330	54.15
1.015992	-0.78331	54.41667
1.015994	-0.78333	54.68334
1.016101	-0.78333	54.95
1.016211	-0.78332	55.21667
1.016266	-0.78331	55.48333
1.016221	-0.78331	55.75
1.016192	-0.78332	56.01667
1.016194	-0.78330	56.28334
1.016198	-0.78329	56.55001
1.01619	-0.78329	56.825
1.016199	-0.78327	57.1
1.016184	-0.78327	57.36667
1.016227	-0.78326	57.63333
1.016226	-0.78326	57.9
1.016199	-0.78326	58.16667
1.016199	-0.78326	58.43334
1.016162	-0.78327	58.7
1.016112	-0.78327	58.96667
1.016138	-0.78327	59.23333
1.016143	-0.78326	59.5
1.016158	-0.78325	59.76667
1.017097	-0.78323	60.4
1.01719	-0.78310	61.4
1.017023	-0.78312	62.4
1.01697	-0.78314	63.4
1.016935	-0.78316	64.4
1.016895	-0.78317	65.4
1.016848	-0.78317	66.4
1.016733	-0.78316	67.4
1.016391	-0.78313	68.4
1.016393	-0.78315	69.4
1.016365	-0.78315	70.4
1.009833	-0.78344	71.4
1.013445	-0.78297	72.4
1.014465	-0.78305	73.4
1.01482	-0.78304	74.4
1.015255	-0.78312	75.4
1.015339	-0.78312	76.40833
1.015327	-0.78311	77.41666
1.015252	-0.78312	78.41666
1.015285	-0.78313	79.41666
1.016114	-0.78312	80.41666
1.016903	-0.78301	81.41666
1.016592	-0.78300	82.41666
1.01648	-0.78303	83.41666
1.016427	-0.78309	84.425
1.016377	-0.78312	85.43333
1.01629	-0.78314	86.43333
1.016248	-0.78313	87.43333
1.016221	-0.78313	88.43333
1.016224	-0.78313	89.43333
1.010879	-0.78346	90.43333
1.012824	-0.78320	91.43333
1.013924	-0.78314	92.44167

```
1.014605 -0.78326     93.45
1.014657 -0.78327     94.45
1.014672 -0.78326     95.45
1.014848 -0.78324     96.45
1.014862 -0.78323     97.45
1.014904 -0.78320     98.45
1.014929 -0.78318  99.45833
1.016169 -0.78316  100.4667
1.016689 -0.78308  101.4667
1.016484 -0.78306  102.4667
1.016338 -0.78307  103.4667
1.016256 -0.78308  104.4667
1.016193 -0.78308  105.4667
1.016052 -0.78307  106.4667
1.015946 -0.78305  107.4667
1.015917 -0.78304  108.4667
1.015888 -0.78304  109.4667
1.007968 -0.78332   110.475
1.012509 -0.78299  111.4833
1.013806 -0.78304  112.4833
1.014125 -0.78306  113.4833
1.014139 -0.78304  114.4833
1.014283 -0.78306  115.4833
1.014402 -0.78303  116.4833
1.014742 -0.78310  117.4833
1.014976 -0.78315  118.4833
1.014878 -0.78312  119.4833
1.015329 -0.78310  120.4833
1.016515 -0.78302  121.4833
1.016127 -0.78301  122.4833
1.015934 -0.78301  123.4833
1.015805 -0.78301  124.4833
1.015714 -0.78300  125.4833
1.015624 -0.78299  126.4833
1.015577 -0.78298  127.4833
1.015627 -0.78298  128.4833
1.015608 -0.78297  129.4833
1.015651 -0.78296  130.4917
 1.01566 -0.78295     131.5
1.015626 -0.78295     132.5
1.015583 -0.78293     133.5
1.015577 -0.78293     134.5
1.015572 -0.78291     135.5
1.015503 -0.78290     136.5
1.015468 -0.78288  137.5083
1.015496 -0.78289  138.5167
1.015508 -0.78288  139.5167
1.011201 -0.78303  140.5167
 1.01294 -0.78284  141.5167
1.013738 -0.78293  142.5167
1.014003 -0.78298  143.5167
1.014079 -0.78298  144.5167
1.014353 -0.78303  145.5167
1.014291 -0.78302  146.5167
1.014222 -0.78302   147.525
1.014197 -0.78303  148.5333
1.014285 -0.78300  149.5333
1.016135 -0.78298  150.5333
1.016083 -0.78291  151.5333
       0        0         0
       2     28.3        10     7.95        27
```

BRPCHG1

VOLT1	VOLT2	MINUTES
1.014897	-0.78017	0.133333
1.014924	-0.78017	0.4
1.014926	-0.78019	0.666666
1.014923	-0.78019	0.933333
1.014936	-0.78019	1.2
1.014951	-0.78019	1.466667
1.014946	-0.78020	1.733333
1.015	-0.78020	2
1.015134	-0.78020	2.266667
1.015009	-0.78021	2.533333
1.015025	-0.78022	2.8
1.014974	-0.78021	3.066667
1.014969	-0.78022	3.333334
1.014954	-0.78022	3.6
1.014936	-0.78022	3.866667
1.015025	-0.78016	4.133333
1.01506	-0.78014	4.4
1.015151	-0.78015	4.666667
1.014987	-0.78015	4.933334
1.014834	-0.78020	5.2
1.014744	-0.78028	5.466667
1.014881	-0.78024	5.733334
1.014939	-0.78022	6
1.014919	-0.78021	6.266667
1.014901	-0.78020	6.541667
1.014886	-0.78018	6.816667
1.014863	-0.78016	7.083333
1.014802	-0.78015	7.35
1.014799	-0.78014	7.608334
1.014823	-0.78012	7.866667
1.014629	-0.78007	8.133333
1.014588	-0.78004	8.399999
1.014611	-0.78004	8.666667
1.014646	-0.78004	8.933333
1.014743	-0.78004	9.2
1.014876	-0.78005	9.466667
1.014774	-0.78004	9.733334
1.014787	-0.78005	10
1.014994	-0.77997	10.26667
1.015098	-0.77995	10.53333
1.014655	-0.77996	10.8
1.014546	-0.77997	11.06667
1.014506	-0.77997	11.33333
1.014434	-0.78000	11.6
1.014406	-0.78004	11.86667
1.014427	-0.78007	12.13333
1.01444	-0.78010	12.4
1.014481	-0.78011	12.66667
1.014184	-0.78006	12.93333
1.014147	-0.78005	13.2
1.014203	-0.78005	13.46667
1.014183	-0.78005	13.73333
1.014091	-0.78004	14
1.01406	-0.78003	14.26667
1.014059	-0.78001	14.54167
1.014079	-0.78001	14.81667
1.014083	-0.78001	15.08333
1.014044	-0.78002	15.35
1.014031	-0.78004	15.61667
1.014032	-0.78003	15.88333
1.014048	-0.78003	16.15
1.014042	-0.78003	16.41667
1.014062	-0.78003	16.68333

1.014063	-0.78003	16.95
1.01407	-0.78003	17.21667
1.014112	-0.78002	17.48333
1.014179	-0.78003	17.75
1.014149	-0.78003	18.01667
1.014245	-0.78003	18.28333
1.014213	-0.78004	18.55
1.015057	-0.78004	18.81667
1.015661	-0.78003	19.08333
1.015163	-0.78002	19.35
1.015392	-0.78002	19.61667
1.015387	-0.78000	19.88333
1.014888	-0.78000	20.15
1.013804	-0.78009	20.41667
1.014242	-0.78008	20.69167
1.014376	-0.78006	20.975
1.014523	-0.78006	21.25
1.014695	-0.78007	21.51667
1.014314	-0.78008	21.78333
1.014422	-0.78007	22.05
1.014225	-0.78008	22.31667
1.014116	-0.78008	22.58334
1.014179	-0.78009	22.85
1.014089	-0.78005	23.11667
1.014094	-0.78004	23.38333
1.014289	-0.78006	23.65
1.014238	-0.78003	23.91667
1.013796	-0.78003	24.18334
1.013809	-0.78003	24.45
1.01387	-0.78003	24.71667
1.014083	-0.78003	24.98333
1.01446	-0.78003	25.25
1.015062	-0.78004	25.51667
1.015349	-0.78005	25.78333
1.01553	-0.78006	26.05
1.015047	-0.78005	26.325
1.014673	-0.78007	26.6
1.015251	-0.78007	26.86667
1.014262	-0.78008	27.13333
1.014303	-0.78008	27.4
1.013443	-0.78009	27.66667
1.013551	-0.78009	27.93334
1.013501	-0.78009	28.2
1.013931	-0.78010	28.46667
1.014311	-0.78010	28.73333
1.013771	-0.78009	29
1.013394	-0.78011	29.26667
1.013377	-0.78013	29.53333
1.013435	-0.78015	29.8
1.013434	-0.78017	30.06667
1.013815	-0.78011	30.33334
1.013696	-0.78013	30.6
1.013601	-0.78015	30.86667
1.014727	-0.78015	31.13333
1.015285	-0.78018	31.4
1.013364	-0.78017	31.66667
1.013241	-0.78016	31.93333
1.013287	-0.78016	32.2
1.013428	-0.78016	32.475
1.014239	-0.78015	32.75
1.016074	-0.78015	33.01667
1.015179	-0.78015	33.28333
1.015146	-0.78016	33.55
1.014292	-0.78016	33.81667
1.013601	-0.78014	34.08334
1.013772	-0.78015	34.35

1.013638	-0.78015	34.61667
1.013433	-0.78016	34.88333
1.013427	-0.78015	35.15
1.014136	-0.78015	35.41667
1.013892	-0.78016	35.68334
1.013708	-0.78016	35.95
1.01391	-0.78016	36.21667
1.013596	-0.78016	36.48333
1.013218	-0.78015	36.75
1.013131	-0.78015	37.01667
1.013059	-0.78016	37.28333
1.013039	-0.78016	37.55
1.013078	-0.78017	37.81667
1.013144	-0.78018	38.09167
1.013255	-0.78021	38.36667
1.013147	-0.78021	38.63333
1.01302	-0.78028	38.9
1.013238	-0.78033	39.16667
1.013248	-0.78035	39.43334
1.013135	-0.78035	39.7
1.013138	-0.78035	39.96667
1.0129	-0.78042	40.23333
1.012924	-0.78040	40.5
1.012934	-0.78040	40.76667
1.012951	-0.78038	41.03333
1.012953	-0.78039	41.3
1.012926	-0.78041	41.56667
1.012937	-0.78042	41.83334
1.012929	-0.78042	42.1
1.012951	-0.78042	42.36667
1.012954	-0.78044	42.63333
1.012759	-0.78041	42.9
1.012964	-0.78041	43.16667
1.013064	-0.78041	43.44167
1.013097	-0.78042	43.71667
1.013118	-0.78040	43.98333
1.013131	-0.78038	44.25
1.013062	-0.78038	44.51667
1.013034	-0.78037	44.78334
1.013059	-0.78037	45.05001
1.01304	-0.78037	45.31667
1.012996	-0.78038	45.58334
1.012967	-0.78038	45.85
1.012954	-0.78039	46.11667
1.012986	-0.78038	46.38333
1.012979	-0.78038	46.65
1.012977	-0.78038	46.91667
1.012944	-0.78039	47.18334
1.01294	-0.78042	47.45
1.012933	-0.78041	47.71667
1.012921	-0.78041	47.98333
1.012937	-0.78041	48.25
1.012919	-0.78041	48.51667
1.012911	-0.78041	48.78334
1.012931	-0.78041	49.05834
1.012909	-0.78040	49.33334
1.012899	-0.78040	49.6
1.012896	-0.78040	49.86667
1.01292	-0.78039	50.13333
1.012665	-0.78018	50.4
1.012354	-0.78006	50.66667
1.012295	-0.78007	50.93334
1.012199	-0.78007	51.2
1.012202	-0.78008	51.46667
1.012084	-0.78006	51.73333
1.012097	-0.78007	52

1.01205	-0.78007	52.26667
1.011984	-0.78013	52.53334
1.011975	-0.78014	52.80001
1.011974	-0.78013	53.06667
1.011929	-0.78014	53.33334
1.011945	-0.78014	53.6
1.011955	-0.78014	53.86667
1.011957	-0.78016	54.13333
1.011886	-0.78014	54.4
1.011835	-0.78012	54.66667
1.011758	-0.78009	54.94167
1.011691	-0.78008	55.21667
1.011639	-0.78007	55.48333
1.011672	-0.78008	55.75
1.011605	-0.78008	56.01667
1.011609	-0.78008	56.28334
1.011629	-0.78008	56.55001
1.011587	-0.78008	56.81667
1.011578	-0.78008	57.08334
1.011524	-0.78007	57.35
1.011761	-0.78012	57.61667
1.011793	-0.78021	57.88333
1.011741	-0.78023	58.15
1.011746	-0.78025	58.41667
1.01171	-0.78026	58.68334
1.011711	-0.78025	58.95
1.011724	-0.78024	59.21667
1.011747	-0.78024	59.48333
1.011728	-0.78024	59.75
1.011819	-0.78027	60.39167
1.011974	-0.78036	61.4
1.012295	-0.78035	62.4
1.011999	-0.78035	63.4
1.011987	-0.78032	64.40833
1.011982	-0.78028	65.41666
1.01194	-0.78030	66.41666
1.0121	-0.78033	67.425
1.012304	-0.78044	68.43333
1.012236	-0.78040	69.43333
1.011821	-0.78033	70.44167
1.011979	-0.78032	71.45
1.011984	-0.78033	72.45
1.011736	-0.78021	73.45
1.011331	-0.78022	74.45
1.011355	-0.78027	75.45
1.011621	-0.78041	76.45
1.011566	-0.78045	77.45
1.011547	-0.78046	78.45833
1.011581	-0.78047	79.46667
1.01169	-0.78047	80.46667
1.011317	-0.78051	81.46667
1.01145	-0.78051	82.46667
1.011432	-0.78051	83.46667
1.011381	-0.78052	84.46667
1.01133	-0.78053	85.46667
1.011315	-0.78054	86.475
1.011324	-0.78055	87.48333
1.011217	-0.78057	88.48333
1.011301	-0.78058	89.48333
1.011355	-0.78057	90.48333
1.011353	-0.78059	91.49167
1.011319	-0.78060	92.5
1.011411	-0.78062	93.5
1.011474	-0.78062	94.5
1.011535	-0.78066	95.5
1.011551	-0.78063	96.50833

1.011267	-0.78064	97.51667
1.011428	-0.78066	98.51667
1.011391	-0.78069	99.51667
1.011259	-0.78073	100.5167
1.011174	-0.78073	101.5167
1.011185	-0.78074	102.5167
1.01122	-0.78074	103.5167
1.011125	-0.78074	104.5167
1.011203	-0.78075	105.5167
1.011294	-0.78076	106.5167
1.011219	-0.78077	107.5167
1.011295	-0.78077	108.5167
1.011392	-0.78077	109.5167
1.011387	-0.78077	110.5167
1.011043	-0.78080	111.5167
1.011274	-0.78080	112.5167
1.011325	-0.78080	113.5167
1.01156	-0.78080	114.5167
1.011552	-0.78079	115.525
1.011686	-0.78079	116.5333
1.011766	-0.78078	117.5333
1.011897	-0.78078	118.5333
1.011545	-0.78079	119.5333
1.011202	-0.78081	120.5333
0	0	0
2	26.7	10

7.95 26.6

BRPCHG2

VOLT1	VOLT2	MINUTES
1.006635	-0.78051	0.133333
1.011531	-0.78073	0.4
1.011434	-0.78085	0.666666
1.011061	-0.78093	0.933333
1.010758	-0.78097	1.2
1.010516	-0.78101	1.466667
1.010364	-0.78105	1.733333
1.010228	-0.78102	2
1.010101	-0.78098	2.266667
1.009986	-0.78097	2.533333
1.009894	-0.78097	2.8
1.009859	-0.78100	3.066667
1.009783	-0.78102	3.333334
1.009776	-0.78103	3.6
1.009776	-0.78104	3.866667
1.00975	-0.78104	4.133333
1.009787	-0.78104	4.4
1.009838	-0.78104	4.666667
1.00985	-0.78103	4.933334
1.009868	-0.78103	5.2
1.009918	-0.78103	5.466667
1.009976	-0.78103	5.733334
1.010091	-0.78102	6
1.010114	-0.78100	6.266667
1.010146	-0.78100	6.533334
1.010183	-0.78100	6.8
1.010226	-0.78099	7.066667
1.010161	-0.78100	7.333333
1.010099	-0.78099	7.600001
1.010073	-0.78099	7.866667
1.010124	-0.78101	8.133333
1.010164	-0.78101	8.408333
1.010228	-0.78099	8.683333

1.01033	-0.78097	8.95
1.010729	-0.78086	9.216667
1.010329	-0.78084	9.483334
1.010258	-0.78085	9.75
1.010261	-0.78085	10.01667
1.010281	-0.78085	10.28333
1.010283	-0.78083	10.55
1.010323	-0.78082	10.81667
1.010357	-0.78082	11.08333
1.010385	-0.78082	11.35
1.010418	-0.78081	11.61667
1.010387	-0.78081	11.88333
1.010405	-0.78080	12.15
1.010421	-0.78078	12.41667
1.010417	-0.78075	12.68333
1.010439	-0.78075	12.95
1.010475	-0.78074	13.21667
1.01047	-0.78072	13.48333
1.010444	-0.78068	13.75
1.010467	-0.78065	14.025
1.010496	-0.78063	14.3
1.010536	-0.78062	14.56667
1.010604	-0.78061	14.83333
1.010672	-0.78060	15.1
1.010699	-0.78058	15.36667
1.010683	-0.78055	15.63333
1.010263	-0.78058	15.9
1.010853	-0.78067	16.16667
1.011047	-0.78062	16.43333
1.011073	-0.78059	16.7
1.011092	-0.78055	16.96667
1.010892	-0.78047	17.23333
1.010771	-0.78043	17.5
1.010759	-0.78043	17.76667
1.010737	-0.78040	18.03333
1.010757	-0.78039	18.3
1.01077	-0.78036	18.56667
1.01079	-0.78032	18.83333
1.010951	-0.78033	19.1
1.010939	-0.78031	19.36667
1.011046	-0.78029	19.64167
1.011023	-0.78029	19.91667
1.011195	-0.78026	20.18333
1.011007	-0.78022	20.45
1.010826	-0.78023	20.71667
1.010849	-0.78021	20.98333
1.01087	-0.78022	21.25
1.011068	-0.78027	21.51667
1.011288	-0.78034	21.78333
1.011361	-0.78036	22.05
1.01139	-0.78036	22.31667
1.011424	-0.78036	22.58334
1.011456	-0.78035	22.85
1.011479	-0.78034	23.11667
1.011522	-0.78035	23.38333
1.011528	-0.78034	23.65833
1.010583	-0.78007	23.93334
1.011246	-0.78020	24.2
1.01161	-0.78032	24.46667
1.011639	-0.78036	24.73333
1.011701	-0.78039	25
1.011135	-0.78039	25.26667
1.01165	-0.78048	25.53333
1.01177	-0.78047	25.8
1.011802	-0.78046	26.06667
1.011816	-0.78046	26.33334

1.011832	-0.78045	26.6
1.011864	-0.78044	26.86667
1.011887	-0.78049	27.13333
1.011872	-0.78049	27.4
1.011842	-0.78049	27.66667
1.011868	-0.78047	27.93334
1.011869	-0.78046	28.20834
1.011899	-0.78045	28.48333
1.011951	-0.78044	28.75
1.012004	-0.78043	29.01667
1.012081	-0.78041	29.28333
1.012166	-0.78042	29.55
1.012196	-0.78046	29.81667
1.012109	-0.78050	30.08334
1.012056	-0.7805	30.35
1.01205	-0.78048	30.61667
1.01213	-0.78047	30.88333
1.012166	-0.78047	31.15
1.012154	-0.78045	31.41667
1.012138	-0.78043	31.68334
1.01211	-0.78042	31.95
1.012172	-0.78040	32.21667
1.01217	-0.78038	32.48333
1.012199	-0.78037	32.75833
1.012156	-0.78035	33.03333
1.012156	-0.78029	33.3
1.012179	-0.78030	33.56667
1.012166	-0.78031	33.83334
1.012158	-0.78030	34.1
1.012182	-0.78029	34.36667
1.012213	-0.78028	34.63333
1.012229	-0.78027	34.9
1.012207	-0.78026	35.16667
1.012449	-0.78021	35.43334
1.012466	-0.78019	35.7
1.012318	-0.78026	35.96667
1.012206	-0.78025	36.23333
1.012186	-0.78022	36.50833
1.01214	-0.78019	36.78333
1.012151	-0.78019	37.05
1.012159	-0.78017	37.31667
1.012164	-0.78015	37.58334
1.012214	-0.78014	37.85
1.01224	-0.78013	38.11667
1.012249	-0.78012	38.38333
1.012264	-0.78009	38.65
1.01226	-0.78008	38.91667
1.012289	-0.78009	39.18334
1.012278	-0.78008	39.45
1.012196	-0.78007	39.71667
1.01221	-0.78006	39.98333
1.012207	-0.78006	40.25
1.0122	-0.78005	40.51667
1.012195	-0.78004	40.79167
1.012129	-0.77999	41.06667
1.012193	-0.78000	41.33334
1.012214	-0.77999	41.6
1.012193	-0.77998	41.86667
1.012183	-0.77997	42.13333
1.012211	-0.77996	42.4
1.012234	-0.77994	42.66667
1.012204	-0.77994	42.93334
1.012206	-0.77995	43.2
1.012219	-0.77994	43.46667
1.012229	-0.77994	43.73333
1.012208	-0.77994	44.00833

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1.012188 -0.77994 44.28334
1.012218 -0.77992 44.55001
1.012285 -0.77993 44.81667
1.012331 -0.77991 45.08334
1.012098 -0.77992    45.35
1.012381 -0.77995 45.61667
 1.01244 -0.77994 45.88333
1.012474 -0.77993    46.15
1.012557 -0.77990 46.41667
1.012611 -0.77992 46.68334
1.012631 -0.77994    46.95
1.012687 -0.77994   47.225
1.012689 -0.77994     47.5
1.012654 -0.77991 47.76667
1.012644 -0.77990 48.03334
1.012609 -0.77988 48.30001
1.012463 -0.77981 48.56667
1.012297 -0.77973 48.83334
 1.01235 -0.77975     49.1
1.012376 -0.77979 49.36667
1.012401 -0.77979 49.63333
1.012421 -0.77980     49.9
1.012443 -0.77980 50.16667
1.012448 -0.77981 50.44167
1.012424 -0.77981 50.71667
  1.0124 -0.77979 50.98333
1.012071 -0.77972    51.25
1.012039 -0.77972 51.51667
1.012031 -0.77972 51.78334
1.012092 -0.77974 52.05001
1.012106 -0.77974 52.31667
1.012106 -0.77974 52.58334
1.012191 -0.77973    52.85
 1.01213 -0.77973 53.11667
1.012091 -0.77971 53.38333
1.012039 -0.77971 53.65834
   1.012 -0.77971 53.93334
1.011965 -0.77969     54.2
1.012024 -0.77972 54.46667
1.012061 -0.77974 54.73333
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1.012234 -0.77978 55.26667
1.012239 -0.77988 55.53334
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1.012151 -0.77992 56.06667
1.012135 -0.77991 56.33334
1.012204 -0.77991     56.6
1.012304 -0.77992 56.86667
1.012309 -0.77993 57.14167
1.012376 -0.77999 57.41667
1.012343 -0.78000 57.68334
1.012327 -0.77999    57.95
1.012363 -0.78000 58.21667
1.012319 -0.77997 58.48333
1.012276 -0.77993    58.75
1.012267 -0.77992 59.01667
1.012268 -0.77993 59.28334
1.012263 -0.77992 59.55001
1.012272 -0.77990 59.81667
0.993091 -0.76517    60.45
0.992800 -0.76484    61.45
0.993497 -0.76539 62.45834
0.993411 -0.76535 63.46667
       0        0        0
       2     27.5       10     7.95     26.8
```

BRPCHG

VOLT1	VOLT2	MINUTES
1.035629	-0.77984	0.133333
1.031636	-0.78057	0.4
1.029017	-0.78076	0.666666
1.027204	-0.78087	0.933333
1.026232	-0.78104	1.2
1.025317	-0.78106	1.466667
1.024494	-0.78101	1.733333
1.023693	-0.78097	2
1.022933	-0.78091	2.266667
1.022137	-0.78078	2.533333
1.021229	-0.78066	2.8
1.020289	-0.78057	3.066667
1.019267	-0.78050	3.333334
1.018489	-0.78050	3.6
1.017964	-0.78051	3.866667
1.017564	-0.78054	4.133333
1.017268	-0.78056	4.4
1.017092	-0.78054	4.666667
1.016887	-0.78051	4.933334
1.016793	-0.78047	5.2
1.016705	-0.78040	5.466667
1.016656	-0.78036	5.733334
1.016567	-0.78030	6
1.01653	-0.78024	6.266667
1.016426	-0.78018	6.533334
1.016347	-0.78013	6.808334
1.016348	-0.78008	7.083333
1.016261	-0.78003	7.35
1.016167	-0.77998	7.616667
1.016132	-0.77994	7.883333
1.016096	-0.77989	8.15
1.01604	-0.77985	8.416667
1.015997	-0.77982	8.683333
1.015956	-0.77979	8.95
1.015943	-0.77976	9.216667
1.015913	-0.77973	9.483334
1.015915	-0.77969	9.75
1.015905	-0.77967	10.01667
1.015846	-0.77966	10.28333
1.015849	-0.77967	10.55
1.015816	-0.77966	10.81667
1.015782	-0.77964	11.08333
1.015756	-0.77961	11.35
1.015715	-0.77959	11.61667
1.01554	-0.77953	11.88333
1.015528	-0.7795	12.15
1.015499	-0.77947	12.425
1.015501	-0.77946	12.7
1.015544	-0.77945	12.96667
1.015517	-0.77946	13.23333
1.015571	-0.77946	13.5
1.01551	-0.77944	13.76667
1.015523	-0.77944	14.03333
1.015426	-0.77942	14.3
1.015705	-0.77942	14.56667
1.015596	-0.77942	14.83333
1.015523	-0.77941	15.1
1.015419	-0.77939	15.36667
1.015542	-0.77937	15.63333
1.015555	-0.77937	15.90833
1.015332	-0.77937	16.18333
1.015184	-0.77936	16.45
1.015364	-0.77936	16.71667

1.015438	-0.77936	16.98333
1.015349	-0.77936	17.25
1.015269	-0.77935	17.51667
1.015446	-0.77936	17.78333
1.015355	-0.77936	18.05
1.015384	-0.77936	18.31667
1.01533	-0.77936	18.58333
1.015367	-0.77936	18.85
1.015497	-0.77936	19.11667
1.015699	-0.77936	19.39167
1.01591	-0.77936	19.66667
1.015654	-0.77937	19.93333
1.014947	-0.77934	20.2
1.014952	-0.77931	20.46667
1.014956	-0.77931	20.73333
1.014936	-0.77933	21
1.014887	-0.77934	21.26667
1.015013	-0.77935	21.53333
1.015001	-0.77936	21.8
1.015119	-0.77936	22.06667
1.015255	-0.77937	22.33334
1.015098	-0.77937	22.6
1.015094	-0.77938	22.86667
1.015209	-0.77937	23.13333
1.015201	-0.77937	23.40833
1.015218	-0.77934	23.68334
1.015249	-0.77935	23.95
1.015294	-0.77933	24.21667
1.015527	-0.77936	24.48333
1.015467	-0.77939	24.75
1.015205	-0.77937	25.01667
1.015297	-0.77937	25.28333
1.015244	-0.77936	25.55
1.015622	-0.77940	25.81667
1.015528	-0.77941	26.08334
1.015181	-0.77941	26.35
1.015364	-0.77939	26.625
1.015292	-0.77940	26.9
1.015349	-0.77947	27.16667
1.016075	-0.77944	27.43334
1.015382	-0.77945	27.7
1.014951	-0.77951	27.96667
1.014841	-0.77953	28.23333
1.014829	-0.77952	28.5
1.015614	-0.77955	28.76667
1.014764	-0.77956	29.03333
1.014731	-0.77955	29.3
1.014832	-0.77955	29.56667
1.014838	-0.77955	29.83334
1.014758	-0.77957	30.1
1.0147	-0.77959	30.36667
1.01484	-0.77970	30.63333
1.014892	-0.77970	30.90833
1.014854	-0.77969	31.18334
1.014771	-0.77970	31.45
1.01477	-0.77969	31.71667
1.01474	-0.77973	31.98333
1.014766	-0.77977	32.25
1.014718	-0.77970	32.51667
1.01469	-0.77971	32.78333
1.014726	-0.77969	33.05
1.014731	-0.77973	33.31667
1.014719	-0.77975	33.58334
1.014646	-0.77974	33.85
1.014632	-0.77978	34.125
1.014658	-0.77973	34.4

```
1.014609 -0.77975 34.66667
1.014617 -0.77978 34.93334
1.014624 -0.77981     35.2
1.014663 -0.77982 35.46667
1.014652 -0.77979 35.73333
1.014601 -0.77982       36
1.014595 -0.77982 36.26667
1.014564 -0.77982 36.53333
1.014576  -0.7798     36.8
 1.01459 -0.77978 37.06667
1.014574 -0.77980 37.33334
1.014556 -0.77980 37.60833
1.014463 -0.77980 37.88333
1.014433 -0.77983    38.15
1.014419 -0.77986 38.41667
1.014409 -0.77992 38.68334
1.014405 -0.77981    38.95
1.014348 -0.77982 39.21667
1.014441 -0.77982 39.48333
1.014544 -0.77982    39.75
       0         0        0
       2        26       10     7.95     26.7
```

Table 17. Voltage-time data of experiments LLMMM1 and LLMMS1.

LLMMM1

VOLT1	VOLT2	MINUTES
0.915172	-0.89539	0.133333
0.914685	-0.89610	0.4
0.913502	-0.89628	0.666666
0.912181	-0.89635	0.933333
0.910914	-0.89639	1.2
0.909819	-0.89642	1.466667
0.909042	-0.89644	1.733333
0.908435	-0.89645	2
0.907962	-0.89646	2.266667
0.907535	-0.89650	2.533333
0.907137	-0.89651	2.8
0.906857	-0.89653	3.066667
0.906652	-0.89654	3.333334
0.906410	-0.89656	3.6
0.906331	-0.89655	3.866667
0.906135	-0.89656	4.133333
0.905910	-0.89656	4.4
0.905796	-0.89656	4.666667
0.905656	-0.89656	4.933334
0.905941	-0.89654	5.2
0.905442	-0.89654	5.475001
0.905310	-0.89657	5.75
0.90513	-0.89660	6.016667
0.905034	-0.89665	6.283334
0.905008	-0.89669	6.55
0.904936	-0.89672	6.816667
0.904913	-0.89676	7.091666
0.904921	-0.89679	7.366667
0.904858	-0.89680	7.633333
0.904813	-0.89681	7.9
0.904784	-0.89682	8.166667
0.904841	-0.89684	8.441667
0.904805	-0.89686	8.716667
0.904747	-0.89687	8.983334
0.904763	-0.89689	9.25
0.904792	-0.89691	9.516666
0.904735	-0.89695	9.783333
0.904689	-0.89696	10.05
0.904692	-0.89697	10.31667
0.904599	-0.89700	10.58333
0.904610	-0.89701	10.85
0.904692	-0.89699	11.11667
0.904691	-0.89698	11.38333
0.904732	-0.89698	11.65
0.904862	-0.89700	11.91667
0.904902	-0.89700	12.18333
0.904825	-0.89703	12.45
0.904825	-0.89705	12.725
0.904817	-0.89706	13
0.904862	-0.89708	13.26667
0.904917	-0.89708	13.53333
0.904953	-0.89709	13.8
0.904981	-0.89710	14.06667
0.905032	-0.89712	14.33333
0.905000	-0.89715	14.6
0.905057	-0.89716	14.86667
0.905202	-0.89715	15.13333
0.905344	-0.89715	15.4
0.905332	-0.89716	15.66667
0.905247	-0.89716	15.93333

0.905164	-0.89718	16.2
0.905208	-0.89718	16.46667
0.905202	-0.89719	16.73333
0.905140	-0.89719	17
0.905041	-0.89722	17.26667
0.905060	-0.89724	17.53333
0.905090	-0.89725	17.8
0.905065	-0.89725	18.06667
0.905197	-0.89726	18.33333
0.905257	-0.89727	18.6
0.905301	-0.89726	18.86667
0.905274	-0.89726	19.13333
0.905274	-0.89727	19.4
0.905277	-0.89728	19.66667
0.905329	-0.89728	19.93333
0.905259	-0.89730	20.2
0.905239	-0.89731	20.46667
0.905237	-0.89732	20.73333
0.905190	-0.89732	21
0.905144	-0.89733	21.26667
0.905197	-0.89734	21.53333
0.905134	-0.89733	21.8
0.905082	-0.89733	22.06667
0.905075	-0.89734	22.33334
0.905067	-0.89735	22.6
0.905052	-0.89735	22.86667
0.905068	-0.89736	23.13333
0.905072	-0.89737	23.4
0.904924	-0.89737	23.66667
0.904802	-0.89738	23.93334
0.904771	-0.89739	24.2
0.904769	-0.89738	24.46667
0.904749	-0.89739	24.73333
0.904757	-0.8974	25
0.904990	-0.89738	25.26667
0.905141	-0.89735	25.53333
0.904967	-0.89738	25.8
0.904881	-0.89739	26.06667
0.904822	-0.89740	26.33334
0.904799	-0.89740	26.6
0.904683	-0.89742	26.86667
0.904577	-0.89742	27.13333
0.90444	-0.89742	27.4
0.904397	-0.89742	27.66667
0.904459	-0.89742	27.93334
0.904356	-0.89742	28.2
0.904235	-0.89743	28.46667
0.904097	-0.89745	28.73333
0.904082	-0.89747	29
0.904027	-0.89747	29.26667
0.903934	-0.89747	29.53333
0.903816	-0.89746	29.8
0.903791	-0.89746	30.06667
0.903796	-0.89747	30.33334
0.903847	-0.89745	30.6
0.903827	-0.89745	30.86667
0.903682	-0.89745	31.13333
0.903595	-0.89746	31.4
0.903520	-0.89746	31.66667
0.903470	-0.89746	31.94167
0.903233	-0.89746	32.21667
0.903184	-0.89746	32.48333
0.903094	-0.89747	32.75
0.902979	-0.89747	33.01667
0.902896	-0.89746	33.28333
0.902797	-0.89746	33.55

0.90266	-0.89747	33.81667
0.902561	-0.89745	34.08334
0.902464	-0.89746	34.35
0.902302	-0.89748	34.61667
0.9022	-0.89747	34.88333
0.902036	-0.89747	35.15
0.901930	-0.89747	35.41667
0.901745	-0.89746	35.68334
0.901635	-0.89746	35.95
0.901433	-0.89745	36.225
0.901291	-0.89744	36.5
0.901239	-0.89744	36.76667
0.900995	-0.89744	37.03333
0.900731	-0.89744	37.3
0.900509	-0.89744	37.56667
0.900242	-0.89746	37.83334
0.899990	-0.89749	38.1
0.899822	-0.89749	38.36667
0.899643	-0.89751	38.63333
0.899775	-0.89750	38.9
0.899570	-0.89751	39.16667
0.899367	-0.89755	39.44167
0.899316	-0.89754	39.71667
0.899215	-0.89756	39.98333
0.891774	-0.89797	40.25
0.895972	-0.89761	40.51667
0.898412	-0.89762	40.78333
0.898046	-0.89765	41.05
0.897639	-0.89766	41.31667
0.897205	-0.89769	41.58334
0.896904	-0.89768	41.85
0.896485	-0.89767	42.11667
0.896104	-0.89766	42.38333
0.895889	-0.89765	42.65
0.895855	-0.89763	42.91667
0.895657	-0.89764	43.18334
0.895344	-0.89764	43.45
0.895312	-0.89765	43.71667
0.895344	-0.89765	43.98333
0.89529	-0.89768	44.25
0.895246	-0.89775	44.51667
0.895320	-0.89774	44.78334
0.895432	-0.89773	45.05001
0.895434	-0.89774	45.31667
0.895625	-0.89774	45.58334
0.895669	-0.89774	45.85
0.895800	-0.89774	46.11667
0.895968	-0.89773	46.38333
0.896148	-0.89773	46.65
0.896308	-0.89774	46.91667
0.896432	-0.89776	47.18334
0.896862	-0.89776	47.45
0.897098	-0.89774	47.71667
0.897320	-0.89772	47.98333
0.897242	-0.89775	48.25
0.897240	-0.89777	48.51667
0.897342	-0.89776	48.78334
0.897484	-0.89772	49.05001
0.897522	-0.89771	49.31667
0.897577	-0.89771	49.58334
0.897664	-0.89773	49.85
0.897685	-0.89773	50.11667
0.897852	-0.89774	50.38333
0.897875	-0.89775	50.65
0.897902	-0.89776	50.91667
0.897909	-0.89776	51.18334

0.897950	-0.89776	51.45		
0.897982	-0.89777	51.71667		
0.898002	-0.89777	51.98333		
0.89806	-0.89777	52.25		
0.897779	-0.89778	52.51667		
0.897817	-0.89778	52.78334		
0.897932	-0.89777	53.05001		
0.897827	-0.89776	53.31667		
0.897877	-0.89775	53.58334		
0.898035	-0.89775	53.85		
0.898126	-0.89774	54.11667		
0.898253	-0.89776	54.38333		
0.898259	-0.89777	54.65		
0.898202	-0.89777	54.91667		
0.898262	-0.89777	55.18334		
0.898336	-0.89778	55.45		
0.898407	-0.89779	55.71667		
0.89838	-0.89779	55.98333		
0.898486	-0.89779	56.25833		
0.898489	-0.89779	56.53334		
0.898452	-0.89780	56.80001		
0.898416	-0.89780	57.06667		
0.898464	-0.89782	57.33334		
0.898552	-0.89782	57.6		
0.898625	-0.89783	57.86667		
0.898634	-0.89783	58.13333		
0.898558	-0.89783	58.4		
0.898626	-0.89782	58.66667		
0.898569	-0.89781	58.93334		
0.898580	-0.89779	59.2		
0.898568	-0.89779	59.46667		
0.898602	-0.89780	59.73333		
0.898670	-0.89778	60		
0.898693	-0.89778	60.63334		
0.898656	-0.89774	61.63334		
0.898887	-0.89775	62.63334		
0.898745	-0.89778	63.64167		
0.899000	-0.89776	64.65833		
0.898857	-0.89775	65.66666		
0.898901	-0.89778	66.66666		
0.898863	-0.89777	67.66666		
0.899039	-0.89777	68.66666		
0.899190	-0.89776	69.66666		
0.899147	-0.89777	70.675		
0.899307	-0.89776	71.69167		
0.899430	-0.89777	72.70833		
0.899474	-0.89778	73.725		
0.899446	-0.89782	74.73333		
0.899388	-0.89782	75.74167		
0.899388	-0.89785	76.75		
0.899506	-0.89784	77.75		
0.899298	-0.89786	78.75		
0.899344	-0.89786	79.75		
0.899329	-0.89786	80.75		
0.899356	-0.89788	81.75		
0	0	0		
2	26.8	20	27.82	25.5

LLMMS1

VOLT1	VOLT2	MINUTES
0.937486	-0.89026	0.133333
0.933187	-0.89044	0.4
0.927827	-0.89079	0.666666
0.922100	-0.89126	0.933333
0.916769	-0.89204	1.2
0.914635	-0.89260	1.466667
0.909874	-0.89281	1.733333
0.904217	-0.89317	2
0.900339	-0.89362	2.266667
0.897878	-0.89399	2.533333
0.896297	-0.89426	2.8
0.895114	-0.89444	3.066667
0.894202	-0.89461	3.333334
0.893782	-0.89484	3.6
0.893431	-0.89497	3.875
0.892973	-0.89502	4.15
0.892652	-0.89499	4.416667
0.892470	-0.89504	4.683334
0.892380	-0.89509	4.95
0.892381	-0.89518	5.216667
0.892265	-0.89526	5.483334
0.892273	-0.89531	5.75
0.892233	-0.89532	6.025
0.89225	-0.89536	6.3
0.89229	-0.89539	6.566667
0.892412	-0.89549	6.833333
0.892411	-0.89553	7.1
0.892462	-0.89555	7.366667
0.892472	-0.89558	7.633333
0.892478	-0.89560	7.9
0.892439	-0.89558	8.175
0.892392	-0.89557	8.45
0.892345	-0.89557	8.716667
0.892402	-0.89562	8.983334
0.892293	-0.89560	9.25
0.892375	-0.89561	9.516666
0.892412	-0.89562	9.783333
0.892610	-0.89565	10.05
0.892669	-0.89562	10.31667
0.892507	-0.89564	10.58333
0.892491	-0.89569	10.85
0.892505	-0.89570	11.11667
0.892515	-0.89568	11.38333
0.892564	-0.89571	11.65
0.892719	-0.89572	11.91667
0.892735	-0.89574	12.18333
0.892749	-0.89576	12.45
0.892794	-0.89577	12.71667
0.892836	-0.89577	12.98333
0.892881	-0.89579	13.25
0.892931	-0.89579	13.51667
0.893006	-0.89580	13.78333
0.893209	-0.89583	14.05
0.893016	-0.89586	14.31667
0.893292	-0.89584	14.58333
0.893117	-0.89585	14.85
0.893213	-0.89586	15.11667
0.893169	-0.89585	15.38333
0.893149	-0.89583	15.65
0.893214	-0.89586	15.91667
0.893361	-0.89584	16.18333
0.893390	-0.89584	16.45
0.893284	-0.89585	16.71667

0.893216	-0.89587	16.98333
0.893194	-0.89587	17.25
0.893214	-0.89588	17.51667
0.893246	-0.89587	17.78333
0.893257	-0.89588	18.05
0.893286	-0.89589	18.31667
0.893304	-0.89589	18.58333
0.893357	-0.89590	18.85
0.893339	-0.89590	19.11667
0.893343	-0.89590	19.38333
0.893406	-0.89590	19.65
0.893437	-0.89589	19.91667
0.893483	-0.89588	20.18333
0.893570	-0.89590	20.45
0.893772	-0.89586	20.71667
0.893691	-0.89588	20.98333
0.893652	-0.89592	21.25
0.89367	-0.89593	21.51667
0.893656	-0.89594	21.78333
0.893666	-0.89595	22.05
0.893688	-0.89596	22.31667
0.893867	-0.89595	22.58334
0.893796	-0.89595	22.85
0.893657	-0.89595	23.11667
0.893664	-0.89595	23.38333
0.893715	-0.89594	23.65
0.893676	-0.89594	23.91667
0.893676	-0.89594	24.18334
0.893649	-0.89592	24.45
0.893667	-0.89591	24.71667
0.893676	-0.89590	24.98333
0.893722	-0.89590	25.25
0.893769	-0.89591	25.51667
0.893749	-0.89591	25.78333
0.893747	-0.89591	26.05
0.893772	-0.89591	26.31667
0.893789	-0.89591	26.58334
0.893797	-0.89590	26.85
0.893795	-0.89590	27.11667
0.893830	-0.89591	27.38333
0.893872	-0.89590	27.65
0.893808	-0.89590	27.91667
0.893904	-0.89589	28.18334
0.893985	-0.89589	28.45
0.894088	-0.89588	28.71667
0.893934	-0.89586	28.98333
0.894109	-0.89586	29.25
0.894118	-0.89585	29.51667
0.894086	-0.89585	29.78333
0.894115	-0.89585	30.05
0.894165	-0.89582	30.31667
0.894129	-0.89582	30.58334
0.894110	-0.89582	30.85
0.894137	-0.89581	31.11667
0.894137	-0.89581	31.38333
0.894131	-0.89581	31.65
0.894111	-0.89580	31.91667
0.894113	-0.89580	32.18334
0.894138	-0.89579	32.45
0.894164	-0.89578	32.71667
0.894163	-0.89578	32.98333
0.894150	-0.89578	33.25
0.894147	-0.89578	33.51667
0.894173	-0.89577	33.78333
0.894139	-0.89576	34.05
0.894614	-0.89565	34.31667

0.896773	-0.89516	34.58334
0.897249	-0.89513	34.85
0.897255	-0.89516	35.11667
0.897142	-0.89519	35.38333
0.896808	-0.89525	35.65
0.896725	-0.89527	35.91667
0.896047	-0.89538	36.18334
0.895602	-0.89544	36.45
0.895679	-0.89541	36.71667
0.895917	-0.89536	36.98333
0.89598	-0.89535	37.25
0.895893	-0.89539	37.51667
0.895845	-0.89541	37.78333
0.895710	-0.89544	38.05
0.895610	-0.89545	38.31667
0.895538	-0.89549	38.58334
0.895434	-0.89552	38.85
0.895460	-0.89552	39.11667
0.895540	-0.89551	39.39167
0.895775	-0.89549	39.66667
0.895901	-0.89548	39.94167
0.895699	-0.89551	40.21667
0.895544	-0.89554	40.48333
0.895409	-0.89556	40.75
0.895296	-0.89557	41.01667
0.895239	-0.89560	41.28333
0.895165	-0.89561	41.55
0.895097	-0.89562	41.81667
0.895101	-0.89562	42.08334
0.895104	-0.89562	42.35
0.895138	-0.89562	42.61667
0.895118	-0.89562	42.88333
0.895094	-0.89562	43.15
0.894996	-0.89561	43.41667
0.895059	-0.89561	43.68334
0.895099	-0.89561	43.95
0.895141	-0.89561	44.21667
0.895146	-0.89561	44.48333
0.895062	-0.89562	44.75
0.895069	-0.89562	45.01667
0.895160	-0.89562	45.28334
0.89519	-0.89561	45.55001
0.895177	-0.89561	45.81667
0.895154	-0.89562	46.08334
0.895073	-0.89562	46.35
0.895225	-0.89561	46.61667
0.895915	-0.89557	46.88333
0.890759	-0.89601	47.15
0.891883	-0.89600	47.41667
0.893792	-0.89584	47.68334
0.894827	-0.89575	47.95
0.895683	-0.89568	48.21667
0.896168	-0.89566	48.48333
0.896431	-0.89566	48.75
0.896427	-0.89569	49.01667
0.896470	-0.89568	49.28334
0.896411	-0.89570	49.55001
0.896376	-0.89571	49.81667
0.896667	-0.89571	50.08334
0.896693	-0.89571	50.35
0.896442	-0.89571	50.61667
0.896243	-0.89573	50.88333
0.896367	-0.89575	51.15
0.896532	-0.89575	51.41667
0.896395	-0.89575	51.68334
0.896657	-0.89572	51.95

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0.896772 -0.89573 52.21667
0.897000 -0.89570 52.48333
0.897302 -0.89566    52.75
0.897459 -0.89563 53.01667
0.897610 -0.89561 53.28334
0.897708 -0.89561 53.55001
0.897800 -0.89561 53.81667
0.897687 -0.89561 54.08334
0.897665 -0.89561    54.35
0.897691 -0.89560 54.61667
0.897646 -0.89561 54.88333
0.897684 -0.89559    55.15
0.897779 -0.89559 55.41667
0.897749 -0.89560 55.68334
0.897740 -0.89559    55.95
0.897845 -0.89559 56.21667
0.898144 -0.89558 56.48333
0.899186 -0.89536    56.75
0.900054 -0.89510 57.01667
0.902147 -0.89500 57.28334
0.902690 -0.89494 57.55001
0.901218 -0.89504 57.81667
0.900097 -0.89513 58.08334
0.898684 -0.89531    58.35
0.897486 -0.89543 58.61667
0.896686 -0.89550 58.88333
0.896293 -0.89552    59.15
0.895954 -0.89558 59.41667
0.896379 -0.89552 59.68334
0.896742 -0.89545    59.95
0.896950 -0.89543 60.58333
0.897156 -0.89523 61.58333
0.897018 -0.89524 62.58333
0.896977 -0.89527 63.58334
0.897042 -0.89528 64.58334
0.897430 -0.89525 65.59167
0.897386 -0.89527 66.60834
0.897456 -0.89525 67.61667
0.897492 -0.89522 68.61667
0.897559 -0.89519 69.61667
0.897626 -0.89518 70.61667
0.897624 -0.89517 71.61667
0.897642 -0.89515 72.61667
0.897654 -0.89515 73.61667
0.897751 -0.89515 74.61667
0.897788 -0.89515 75.61667
0.897727 -0.89513   76.625
0.897725 -0.89512 77.64166
0.897725 -0.89513 78.65833
0.897722 -0.89511   79.675
0.897701 -0.89510 80.69167
0.897753 -0.89504     81.7
0.897715 -0.89504     82.7
       0        0         0
       2     27.3        20    27.82      26.1
```

Table 18. Voltage-time data of experiments LLLHM1 and NLHM2.

LLLHM1

VOLT1	VOLT2	MINUTES
1.070117	-1.02576	0.133333
1.071407	-1.02764	0.4
1.071317	-1.02873	0.666666
1.070323	-1.02937	0.933333
1.069035	-1.02981	1.2
1.067576	-1.03002	1.466667
1.065995	-1.03007	1.733333
1.064391	-1.03007	2
1.062597	-1.03007	2.266667
1.061014	-1.03010	2.533333
1.059599	-1.03013	2.8
1.058268	-1.03018	3.066667
1.056986	-1.03021	3.333334
1.055319	-1.03020	3.6
1.053785	-1.03019	3.866667
1.052084	-1.03020	4.133333
1.051224	-1.03021	4.4
1.050381	-1.03022	4.666667
1.049301	-1.03021	4.933334
1.04957	-1.03026	5.2
1.049002	-1.03025	5.466667
1.048993	-1.03025	5.733334
1.049022	-1.03025	6
1.048364	-1.03022	6.266667
1.047549	-1.03019	6.533334
1.047431	-1.03022	6.8
1.047237	-1.03025	7.066667
1.046851	-1.03026	7.333333
1.045878	-1.03021	7.600001
1.045533	-1.03021	7.866667
1.045509	-1.03019	8.133333
1.046014	-1.03022	8.399999
1.046702	-1.03027	8.666667
1.045546	-1.03028	8.933333
1.044734	-1.03030	9.2
1.044724	-1.03026	9.466667
1.045052	-1.03028	9.733334
1.045112	-1.03011	10
1.04607	-1.03005	10.26667
1.045691	-1.03003	10.53333
1.046286	-1.03006	10.8
1.046517	-1.03004	11.06667
1.048147	-1.03002	11.33333
1.051166	-1.03009	11.6
1.051109	-1.03007	11.86667
1.050984	-1.03006	12.13333
1.050919	-1.03004	12.4
1.050954	-1.03003	12.66667
1.050804	-1.03002	12.93333
1.050813	-1.03000	13.2
1.050604	-1.02998	13.46667
1.050574	-1.02998	13.73333
1.050788	-1.03000	14
1.050797	-1.03000	14.26667
1.050686	-1.03000	14.53333
1.050733	-1.03000	14.8
1.050285	-1.02998	15.06667
1.049904	-1.02998	15.33333
1.049647	-1.02997	15.6
1.049214	-1.02998	15.86667

1.048976	-1.02998	16.13333
1.048918	-1.02998	16.4
1.048895	-1.02999	16.66667
1.049397	-1.02998	16.93333
1.050067	-1.03001	17.2
1.049252	-1.03007	17.46667
1.049182	-1.03008	17.73333
1.048486	-1.03008	18
1.04747	-1.03010	18.26667
1.047751	-1.03012	18.53333
1.047734	-1.03014	18.80833
1.047529	-1.03015	19.08333
1.047391	-1.03017	19.35
1.047667	-1.03021	19.61667
1.047641	-1.03022	19.88333
1.047628	-1.03023	20.15
1.047267	-1.03024	20.41667
1.047306	-1.03023	20.68333
1.047318	-1.03023	20.95
1.047111	-1.03024	21.21667
1.047976	-1.03025	21.48333
1.047903	-1.03024	21.75
1.04786	-1.03025	22.01667
1.047881	-1.03025	22.28333
1.047682	-1.03027	22.55
1.047469	-1.03027	22.81667
1.047419	-1.03028	23.08334
1.047389	-1.03030	23.35
1.047715	-1.03030	23.61667
1.047998	-1.03036	23.88333
1.048085	-1.03041	24.15
1.048034	-1.03039	24.41667
1.048749	-1.03020	24.68334
1.048793	-1.03014	24.95
1.048889	-1.03013	25.21667
1.049017	-1.03007	25.48333
1.048624	-1.03012	25.75
1.048753	-1.03014	26.01667
1.048695	-1.03016	26.28333
1.048576	-1.03017	26.55
1.048676	-1.03002	26.825
1.048684	-1.02999	27.1
1.04847	-1.03000	27.36667
1.048155	-1.03000	27.63333
1.047649	-1.03001	27.9
1.048116	-1.03003	28.16667
1.048594	-1.03003	28.43334
1.048431	-1.03004	28.7
1.048184	-1.03002	28.96667
1.049408	-1.03000	29.23333
1.048654	-1.02999	29.5
1.04936	-1.03003	29.76667
1.049543	-1.03003	30.03333
1.049006	-1.03002	30.3
1.048357	-1.03000	30.56667
1.048658	-1.03000	30.83334
1.048824	-1.02999	31.1
1.04836	-1.02999	31.36667
1.047799	-1.02998	31.63333
1.047266	-1.02997	31.9
1.046273	-1.03009	32.16667
1.046026	-1.03009	32.43334
1.046142	-1.03007	32.7
1.046879	-1.03009	32.96667
1.046386	-1.03008	33.23333
1.045883	-1.03006	33.5

1.045774	-1.03007	33.76667
1.045719	-1.03006	34.03333
1.045718	-1.03005	34.3
1.046878	-1.03006	34.56667
1.046986	-1.03007	34.83334
1.047059	-1.03008	35.1
1.047111	-1.03006	35.36667
1.047185	-1.03007	35.63333
1.04696	-1.03010	35.9
1.047044	-1.03014	36.16667
1.046944	-1.03016	36.43334
1.047623	-1.03018	36.7
1.048102	-1.03017	36.96667
1.048354	-1.03014	37.23333
1.048277	-1.03006	37.5
1.048178	-1.02999	37.76667
1.048264	-1.02994	38.03333
1.048154	-1.02987	38.3
1.047988	-1.02982	38.575
1.047889	-1.02976	38.85
1.04922	-1.02979	39.11667
1.050278	-1.02983	39.38333
1.052155	-1.02991	39.65
1.052875	-1.02991	39.91667
1.053119	-1.02991	40.18334
1.053076	-1.02989	40.45
1.052766	-1.02991	40.71667
1.052219	-1.02992	40.98333
1.051354	-1.02989	41.25
1.051009	-1.02983	41.51667
1.050412	-1.02982	41.78333
1.050532	-1.02980	42.05001
1.050616	-1.02979	42.31667
1.050589	-1.02977	42.58334
1.051124	-1.02975	42.85
1.051835	-1.02973	43.11667
1.051071	-1.02968	43.38333
1.051885	-1.02958	43.65
1.050945	-1.02935	43.91667
1.050009	-1.02935	44.18334
1.045506	-1.02942	44.45
1.037985	-1.02923	44.71667
1.035935	-1.02910	44.98333
1.037448	-1.02906	45.25
1.034841	-1.02898	45.51667
1.037377	-1.02900	45.78334
1.041146	-1.02914	46.05001
1.044544	-1.02922	46.31667
1.046229	-1.02918	46.58334
1.04725	-1.02918	46.85
1.048304	-1.02914	47.11667
1.048981	-1.0291	47.38333
1.049297	-1.02907	47.65
1.049622	-1.02904	47.91667
1.050778	-1.02895	48.19167
1.052408	-1.02885	48.46667
1.051683	-1.02892	48.73333
1.051141	-1.02895	49
1.050733	-1.02898	49.26667
1.050696	-1.02898	49.53334
1.050595	-1.02896	49.80001
1.050425	-1.02896	50.06667
1.050649	-1.02896	50.33334
1.050862	-1.02895	50.6
1.051042	-1.02894	50.86667
1.051129	-1.02896	51.13333

1.051285	-1.02895	51.4
1.051244	-1.02895	51.66667
1.051283	-1.02894	51.93334
1.051215	-1.02895	52.2
1.051104	-1.02896	52.46667
1.050786	-1.02897	52.73333
1.050788	-1.02896	53
1.050739	-1.02897	53.26667
1.050736	-1.02895	53.53334
1.050774	-1.02894	53.80001
1.050786	-1.02893	54.06667
1.051016	-1.02893	54.33334
1.051667	-1.02887	54.6
1.051683	-1.02879	54.86667
1.051064	-1.02879	55.13333
1.050939	-1.02883	55.4
1.050764	-1.02886	55.66667
1.051144	-1.02886	55.93334
1.050999	-1.02888	56.2
1.050844	-1.02888	56.46667
1.050354	-1.02891	56.73333
1.050096	-1.02891	57
1.050231	-1.02890	57.26667
1.050299	-1.02891	57.53334
1.050337	-1.02891	57.80834
1.05048	-1.02891	58.09167
1.050714	-1.02891	58.36667
1.050584	-1.02891	58.63333
1.05063	-1.02891	58.9
1.050574	-1.02891	59.16667
1.050704	-1.02889	59.43334
1.050736	-1.02888	59.7
1.051586	-1.02885	59.96667
1.051955	-1.02888	60.6
1.051112	-1.02871	61.6
1.051435	-1.02867	62.6
1.051155	-1.02864	63.6
1.051482	-1.02862	64.6
1.051725	-1.02858	65.6
1.052016	-1.02856	66.6
1.051706	-1.02851	67.6
1.05097	-1.02845	68.6
1.05102	-1.02840	69.6
1.051127	-1.02835	70.6
1.051189	-1.02830	71.6
1.051162	-1.02826	72.6
1.051286	-1.02824	73.6
1.051343	-1.02821	74.6
1.051548	-1.02818	75.6
1.051446	-1.02816	76.6
1.051551	-1.02815	77.6
1.051589	-1.02813	78.6
1.051774	-1.02814	79.6
0.65258	-1.03085	80.6
0.829189	-1.03375	81.6
0.901255	-1.03372	82.6
1.038101	-1.02928	83.6
1.058923	-1.02949	84.6
1.065687	-1.02974	85.6
1.06707	-1.02983	86.6
1.067918	-1.02997	87.6
1.06865	-1.03016	88.60834
1.069025	-1.03030	89.61667
1.068168	-1.03035	90.61667
1.068772	-1.03043	91.625
1.069227	-1.03055	92.63333

1.06878	-1.03071	93.63333
1.068571	-1.03092	94.63333
1.06877	-1.03088	95.63333
1.068437	-1.03104	96.63333
1.068204	-1.03122	97.63333
1.068069	-1.03130	98.63333
1.068611	-1.03118	99.63333
1.068617	-1.03118	100.6333
1.068355	-1.03133	101.6333
1.068373	-1.03142	102.6333
1.067849	-1.03163	103.6333
1.067932	-1.03158	104.6333
1.068206	-1.03148	105.6333
1.068338	-1.03141	106.6333
1.067938	-1.03147	107.6333
1.067469	-1.03159	108.6333
1.067225	-1.03168	109.6333
1.067505	-1.03164	110.6333
1.068459	-1.03133	111.6333
1.067689	-1.03156	112.6333
1.066994	-1.03179	113.6333
1.067394	-1.03178	114.6333
1.067575	-1.03175	115.6333
1.06724	-1.03188	116.6333
1.066784	-1.03218	117.6333
1.066804	-1.03222	118.6333
1.066686	-1.03230	119.6333
1.066511	-1.03230	120.6417
1.066812	-1.03205	121.65
1.066902	-1.03186	122.65
1.066772	-1.03179	123.65
1.067125	-1.03165	124.65
1.067687	-1.03136	125.65
1.068242	-1.03115	126.65
1.068476	-1.03103	127.6583
1.068443	-1.03103	128.6667
1.068598	-1.03090	129.6667
1.068618	-1.03089	130.675
1.068574	-1.03086	131.6833
1.068517	-1.03086	132.6917
1.068508	-1.03083	133.7
1.068427	-1.03082	134.7
1.068231	-1.03082	135.7083
1.067651	-1.03107	136.7167
1.068039	-1.03100	137.725
1.067679	-1.031	138.7333
1.067643	-1.03108	139.7417
1.067758	-1.03098	140.75
1.06776	-1.03105	141.7583
1.067796	-1.03101	142.775
1.067588	-1.03092	143.7833
1.067549	-1.03085	144.7833
1.067378	-1.03083	145.7917
1.067379	-1.03083	146.8
1.067225	-1.03092	147.8083
1.066766	-1.03111	148.8167
1.06658	-1.03120	149.825
1.066346	-1.03123	150.8333
1.066217	-1.03132	151.8333
1.066305	-1.03125	152.8333
1.066249	-1.03154	153.8333
1.065905	-1.03163	154.8333
1.065663	-1.03175	155.8333
1.065649	-1.03189	156.8333
1.065268	-1.03190	157.8333
1.065241	-1.03186	158.8333

1.065207	-1.03185	159.8333		
1.065215	-1.03175	160.8333		
1.065084	-1.03181	161.8417		
1.064853	-1.03192	162.85		
1.064404	-1.03197	163.85		
1.06444	-1.03186	164.85		
1.064297	-1.03179	165.85		
1.064252	-1.03188	166.8583		
1.064512	-1.03186	167.8667		
1.064496	-1.03187	168.8667		
1.064257	-1.03195	169.8667		
1.064066	-1.03204	170.875		
1.063666	-1.03208	171.8833		
1.062898	-1.03210	172.8917		
1.062567	-1.03219	173.9		
1.062602	-1.03215	174.9		
1.062489	-1.03215	175.9		
1.062004	-1.03234	176.9083		
1.061924	-1.03243	177.9167		
1.06212	-1.03243	178.9167		
1.062252	-1.03240	179.925		
1.062018	-1.03246	180.9333		
1.061564	-1.03261	181.9333		
1.061889	-1.03225	182.9333		
0	0	0		
2	27.5	10	37.76	24.4

NLHM2

VOLT1	VOLT2	MINUTES
0	0	0.183333
0	0	0.533333
1.114178	-1.03988	0.833333
1.113904	-1.04034	1.091667
1.113501	-1.04074	1.35
1.113023	-1.04114	1.616667
1.112648	-1.04152	1.883333
1.11237	-1.04191	2.15
1.111944	-1.04225	2.416667
1.111426	-1.04254	2.683334
1.110895	-1.04281	2.95
1.110487	-1.04301	3.216667
1.1101	-1.04323	3.483333
1.109759	-1.04341	3.75
1.109449	-1.04359	4.016667
1.109203	-1.04371	4.283334
1.108995	-1.04381	4.55
1.108802	-1.04391	4.816667
1.108634	-1.04401	5.083333
1.10847	-1.04410	5.35
1.108352	-1.04418	5.608334
1.108275	-1.04423	5.866667
1.108189	-1.04426	6.133333
1.108134	-1.04430	6.4
1.108081	-1.04434	6.666667
1.108049	-1.04437	6.933334
1.107974	-1.04440	7.2
1.107934	-1.04441	7.466667
1.107899	-1.04442	7.733334
1.107878	-1.04445	8
1.107856	-1.04447	8.266666
1.107846	-1.04449	8.533333
1.10782	-1.04452	8.8

1.107793	-1.04452	9.066667
1.107791	-1.04454	9.333333
1.107768	-1.04455	9.600001
1.107764	-1.04455	9.866667
1.107785	-1.04454	10.13333
1.107787	-1.04452	10.4
1.107811	-1.04451	10.66667
1.107818	-1.04449	10.93333
1.107813	-1.04449	11.2
1.107833	-1.04447	11.46667
1.107859	-1.04446	11.73333
1.107858	-1.04445	12
1.107863	-1.04444	12.26667
1.107852	-1.04443	12.53333
1.107377	-1.04469	12.8
1.06942	-1.04875	13.06667
1.107115	-1.04525	13.33333
1.107625	-1.04491	13.6
1.107706	-1.04482	13.86667
1.10775	-1.04476	14.13333
1.107787	-1.04471	14.4
1.107821	-1.04466	14.66667
1.107861	-1.04458	14.93333
1.107903	-1.04452	15.2
1.107934	-1.04447	15.46667
1.10803	-1.04442	15.74167
1.108104	-1.04440	16.01667
1.108139	-1.04437	16.28333
1.10802	-1.04438	16.55
1.107976	-1.04439	16.81667
1.107951	-1.04441	17.08333
1.107968	-1.0444	17.35
1.107904	-1.04441	17.61667
1.107853	-1.04443	17.88333
1.107831	-1.04445	18.15
1.107802	-1.04444	18.41667
1.107797	-1.04443	18.68333
1.107773	-1.04443	18.95
1.107747	-1.04445	19.21667
1.107749	-1.04446	19.48333
1.107757	-1.04448	19.75
1.107771	-1.04443	20.01667
1.10773	-1.04445	20.28333
1.107732	-1.04446	20.55
1.107726	-1.04448	20.81667
1.107763	-1.04448	21.08334
1.107784	-1.0445	21.35
1.107752	-1.04462	21.61667
1.107711	-1.04467	21.88333
1.107746	-1.04466	22.15
1.107761	-1.04467	22.41667
1.107765	-1.04469	22.68334
1.107759	-1.04470	22.95
1.107761	-1.04467	23.21667
1.107699	-1.04479	23.48333
1.107717	-1.04476	23.75833
1.107777	-1.04472	24.03333
1.10777	-1.04475	24.3
1.107662	-1.04491	24.56667
1.107414	-1.04529	24.83334
1.107399	-1.04532	25.1
1.107435	-1.04521	25.36667
1.107473	-1.04395	25.63333
1.10752	-1.04503	25.9
1.107535	-1.04510	26.16667
1.107644	-1.04504	26.43334

1.107746	-1.04497	26.7
1.107712	-1.04508	26.96667
1.107726	-1.04506	27.23333
1.107726	-1.04506	27.5
1.10777	-1.045	27.76667
1.107772	-1.04498	28.03333
1.10774	-1.04501	28.3
1.107806	-1.04494	28.56667
1.107953	-1.04479	28.83334
1.108212	-1.0446	29.1
1.108306	-1.04457	29.36667
1.108293	-1.04461	29.63333
1.108387	-1.04459	29.9
1.108498	-1.04461	30.16667
1.108492	-1.04464	30.43334
1.108456	-1.04465	30.7
1.108425	-1.04468	30.96667
1.108404	-1.04468	31.23333
1.108395	-1.04468	31.5
1.108399	-1.04468	31.76667
1.108407	-1.04463	32.025
1.108427	-1.04460	32.28333
1.108487	-1.04451	32.55
1.108599	-1.0444	32.81667
1.108567	-1.04443	33.08334
1.108501	-1.04447	33.35
1.108489	-1.04449	33.61667
1.108451	-1.04455	33.88333
1.108486	-1.04289	34.15
1.108438	-1.04459	34.41667
1.108412	-1.04461	34.69167
1.108469	-1.04456	34.96667
1.108447	-1.04459	35.23333
1.108406	-1.04467	35.5
1.108424	-1.04464	35.76667
1.108394	-1.04466	36.03333
1.108361	-1.04471	36.3
1.108359	-1.04472	36.56667
1.108356	-1.04471	36.83334
1.108348	-1.04473	37.1
1.108478	-1.04458	37.36667
1.108458	-1.04458	37.63333
1.108429	-1.04461	37.9
1.108391	-1.04465	38.16667
1.108345	-1.04468	38.43334
1.108366	-1.04465	38.7
1.108423	-1.04464	38.96667
1.108356	-1.04470	39.23333
1.108379	-1.04469	39.5
1.108437	-1.04463	39.76667
1.108464	-1.04465	40.03333
1.108491	-1.04462	40.3
1.108433	-1.04467	40.56667
1.108432	-1.04467	40.83334
0	0	0
2	24.4	7.29 27.49 24.6

Table 19. Voltage-time data of experiments LLHLS, MLHLS3 and HLHLS.

LLHLS

VOLT1	VOLT2	MINUTES
0.811803	-1.73595	0.133333
0.805872	-0.98662	0.4
0.798475	-1.00222	0.666666
0.793659	-0.95230	0.933333
0.789584	-0.92579	1.2
0.785684	-1.08882	1.466667
0.782044	-0.56780	1.733333
0.778240	-0.54860	2
0.774435	-0.54924	2.266667
0.770637	-0.54974	2.533333
0.767028	-0.55000	2.8
0.763878	-0.55027	3.066667
0.761187	-0.55060	3.333334
0.758977	-0.55086	3.6
0.757228	-0.86787	3.866667
0.755792	-0.95755	4.133333
0.754625	-0.55114	4.4
0.687455	-0.53156	4.666667
0.752886	-0.91059	4.933334
0.752280	-0.55123	5.2
0.751763	-0.94775	5.466667
0.751354	-0.95379	5.733334
0.750987	-0.55113	6
0.750680	-0.55109	6.266667
0.750417	-0.55106	6.533334
0.750172	-0.55103	6.8
0.74992	-0.55102	7.066667
0.749650	-0.55099	7.333333
0.748690	-0.6996	7.600001
0.748023	-1.10979	7.866667
0.749606	-1.13066	8.141666
0.750935	-1.07417	8.416667
0.754592	-1.00772	8.683333
0.754086	-1.12188	8.95
0.755327	-1.19589	9.216667
0.710437	-0.96209	9.483334
0.763462	-1.23558	9.75
0.766901	-1.13871	10.01667
0.769776	-1.33359	10.28333
0.769040	-1.26299	10.55
0.772940	-1.28776	10.81667
0.77513	-1.33776	11.08333
0.772417	-1.20634	11.35
0.776025	-0.95915	11.61667
0.776200	-1.14358	11.88333
0.778970	-1.28791	12.15
0.782823	-0.75161	12.41667
0.783650	-0.54638	12.69167
0.780738	-0.54579	12.96667
0.781225	-0.54645	13.23333
0.783468	-0.54843	13.5
0.780995	-0.54888	13.76667
0.731908	-0.54911	14.03333
0.7175	-0.54924	14.3
0.718464	-0.54930	14.56667
0.719015	-0.54937	14.83333
0.720300	-0.54961	15.1
0.752120	-0.54978	15.36667
0.788781	-0.54983	15.63333

```
0.776460 -0.54986     15.9
0.746245 -0.54985 16.16667
0.745286 -0.54982 16.43333
0.745174 -0.54981     16.7
0.745065 -0.54981 16.96667
0.744964 -0.54963 17.23333
0.744910 -0.54944     17.5
0.744862 -0.54938   17.775
0.744822 -0.54936    18.05
0.744791 -0.54933 18.31667
0.744769 -0.54931 18.58333
0.744755 -0.54929    18.85
0.744745 -0.54929 19.11667
0.744719 -0.54929 19.38333
0.744705 -0.54928    19.65
0.744713 -0.54926 19.91667
0.744729 -0.54926 20.18333
0.744741 -0.54875    20.45
0.744752 -0.54760 20.71667
0.744764 -0.54914 20.98333
0.744765 -0.54930    21.25
0.744778 -0.54926 21.51667
0.744770 -0.54925 21.78333
0.744737 -0.54924 22.05834
0.744730 -0.54925 22.33334
0.744731 -0.54922     22.6
0.744730 -0.54923 22.86667
0.744732 -0.54922 23.13333
0.744738 -0.54926     23.4
0.744752 -0.54932 23.66667
0.744753 -0.54930 23.93334
0.744755 -0.54931     24.2
0.744768 -0.54918 24.46667
0.744753 -0.54904 24.73333
0.744787 -0.54898       25
0.744782 -0.54893 25.26667
0.744792 -0.54933 25.53333
0.744775 -0.54950     25.8
0.744785 -0.54955 26.06667
0.744790 -0.54955 26.34167
0.744814 -0.54956 26.61667
0.744825 -0.54956 26.88333
0.744833 -0.54956    27.15
0.744833 -0.54962 27.41667
0.744846 -0.54964 27.68334
0.744830 -0.54965    27.95
0.744806 -0.54975 28.21667
0.744798 -0.55018 28.48333
       0         0        0
       2      26.5       40     7.95     26.5
```

MLHLS3

VOLT1	VOLT2	MINUTES
0.768033	-0.61781	0.133333
0.768873	-0.61732	0.4
0.765395	-0.61696	0.666666
0.753674	-0.61676	0.933333
0.727802	-0.61665	1.2
0.695912	-0.61659	1.466667
0.663237	-0.61656	1.733333
0.624117	-0.61655	2
0.586413	-0.61654	2.266667
0.555775	-0.61656	2.533333
0.535521	-0.61660	2.8
0.525135	-0.61660	3.066667
0.519522	-0.61661	3.333334
0.520449	-0.61664	3.6
0.525266	-0.61668	3.866667
0.537083	-0.61671	4.133333
0.543705	-0.61672	4.4
0.551175	-0.61673	4.666667
0.55869	-0.61676	4.933334
0.566124	-0.61678	5.2
0.57392	-0.61677	5.466667
0.581697	-0.61678	5.741667
0.589772	-0.61678	6.025
0.595322	-0.61677	6.3
0.600370	-0.61678	6.566667
0.606593	-0.61676	6.833333
0.610824	-0.61674	7.1
0.613812	-0.61672	7.366667
0.618863	-0.61671	7.633333
0.624402	-0.61670	7.9
0.625852	-0.61669	8.166667
0.628661	-0.61667	8.433333
0.631407	-0.61665	8.7
0.634586	-0.61663	8.966667
0.637081	-0.61661	9.233334
0.639188	-0.61660	9.5
0.630397	-0.61658	9.766666
0.632628	-0.61656	10.03333
0.635552	-0.61653	10.3
0.637723	-0.61652	10.56667
0.640181	-0.61650	10.83333
0.642367	-0.61649	11.1
0.644498	-0.61647	11.36667
0.646953	-0.61646	11.63333
0.648816	-0.61644	11.9
0.651541	-0.61642	12.175
0.653256	-0.61641	12.45
0.654778	-0.61638	12.71667
0.65639	-0.61635	12.98333
0.657980	-0.61633	13.25
0.659088	-0.61631	13.51667
0.660123	-0.61630	13.78333
0.661240	-0.61628	14.05
0.662305	-0.61626	14.31667
0.663347	-0.61625	14.58333
0.66443	-0.61623	14.85
0.665632	-0.61621	15.11667
0.666722	-0.61620	15.38333
0.667537	-0.61619	15.65
0.668306	-0.61617	15.91667
0.668847	-0.61615	16.18333

0.66943	-0.61615	16.45833
0.670367	-0.61613	16.73333
0.671912	-0.61611	17
0.672374	-0.61610	17.26667
0.672760	-0.61610	17.53333
0.673867	-0.61608	17.8
0.674805	-0.61607	18.06667
0.675651	-0.61606	18.33333
0.676377	-0.61605	18.6
0.677049	-0.61604	18.86667
0.677682	-0.61604	19.13333
0.678347	-0.61605	19.4
0.678949	-0.61604	19.66667
0.679539	-0.61603	19.93333
0.680067	-0.61602	20.2
0.680712	-0.61602	20.46667
0.681143	-0.61601	20.73333
0.681615	-0.61600	21
0.681785	-0.61599	21.26667
0.682367	-0.61599	21.53333
0.6829	-0.61598	21.8
0.683386	-0.61598	22.06667
0.683771	-0.61598	22.34167
0.684404	-0.61597	22.61667
0.684645	-0.61596	22.88333
0.685322	-0.61596	23.15
0.68579	-0.61595	23.41667
0.686243	-0.61595	23.68334
0.686666	-0.61594	23.95
0.687007	-0.61594	24.21667
0.687380	-0.61593	24.48333
0.687695	-0.61593	24.75
0.688112	-0.61592	25.01667
0.68842	-0.61591	25.28333
0.688787	-0.61591	25.55
0.688912	-0.61590	25.81667
0.689182	-0.61589	26.08334
0.689364	-0.61589	26.35
0.689311	-0.61589	26.61667
0.689465	-0.61588	26.89167
0.689655	-0.61588	27.16667
0.689784	-0.61587	27.43334
0.689837	-0.61586	27.7
0.689887	-0.61586	27.96667
0.690007	-0.61586	28.23333
0.689965	-0.61586	28.5
0.689892	-0.61585	28.76667
0.690079	-0.61585	29.03333
0.690255	-0.61584	29.3
0.690907	-0.61583	29.56667
0.691232	-0.61583	29.83334
0.691509	-0.61583	30.1
0.691629	-0.61582	30.36667
0.691775	-0.61582	30.63333
0.691904	-0.61582	30.9
0.69227	-0.61581	31.16667
0.692495	-0.61581	31.43334
0.692715	-0.61580	31.7
0.692841	-0.61580	31.975
0.693119	-0.61579	32.25
0.693336	-0.61580	32.51667
0.693537	-0.61579	32.78333
0.693674	-0.61579	33.05
0.6938	-0.61578	33.31667

0.694020	-0.61578	33.58334
0.693972	-0.61578	33.85
0.694138	-0.61577	34.11667
0.69431	-0.61576	34.38333
0.694419	-0.61575	34.65
0.694455	-0.61575	34.91667
0.694761	-0.61575	35.18334
0.694817	-0.61575	35.45
0.695061	-0.61575	35.71667
0.695164	-0.61574	35.98333
0.695125	-0.61575	36.25
0.695167	-0.61574	36.51667
0.695139	-0.61574	36.79167
0.695298	-0.61574	37.06667
0.695469	-0.61573	37.33334
0.695552	-0.61573	37.6
0.695564	-0.61573	37.86667
0.695666	-0.61573	38.13333
0.695827	-0.61573	38.4
0.695995	-0.61572	38.66667
0.695967	-0.61572	38.93334
0.696076	-0.61572	39.2
0.696117	-0.61572	39.46667
0.696178	-0.61572	39.73333
0.696407	-0.61572	40
0.696577	-0.61571	40.26667
0.696663	-0.61570	40.53333
0.696633	-0.61570	40.8
0.696660	-0.61571	41.06667
0.696685	-0.61570	41.34167
0.696877	-0.61570	41.61667
0.697025	-0.61570	41.88333
0.697057	-0.61569	42.15
0.697201	-0.61569	42.41667
0.697212	-0.61569	42.68334
0.697517	-0.61568	42.95
0.697592	-0.61568	43.21667
0.697553	-0.61568	43.48333
0.697652	-0.61568	43.75
0.697897	-0.61567	44.01667
0.697962	-0.61567	44.28334
0.698322	-0.61566	44.55001
0.698647	-0.61566	44.81667
0.698625	-0.61565	45.08334
0.698677	-0.61565	45.35834
0.698667	-0.61565	45.63333
0.698702	-0.61565	45.9
0.698820	-0.61564	46.16667
0.698802	-0.61564	46.43334
0.698926	-0.61563	46.7
0.699017	-0.61564	46.96667
0.699109	-0.61563	47.23333
0.699144	-0.61563	47.5
0.699353	-0.61562	47.76667
0.699544	-0.61562	48.03334
0.699600	-0.61562	48.30001
0.699613	-0.61562	48.56667
0.699719	-0.61561	48.83334
0.699722	-0.61561	49.1
0.699695	-0.61561	49.375
0.699681	-0.61560	49.65
0.699814	-0.61560	49.91667
0.700002	-0.61560	50.18334
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0.700098	-0.61560	50.71667
0.700083	-0.61559	50.98333
0.699992	-0.61559	51.25
0.700140	-0.61558	51.51667
0.700210	-0.61558	51.78334
0.700326	-0.61558	52.05001
0.700405	-0.61558	52.31667
0.70053	-0.61557	52.58334
0.700663	-0.61557	52.85
0.700682	-0.61557	53.11667
0.700672	-0.61557	53.38333
0.700798	-0.61557	53.65
0.700827	-0.61556	53.91667
0.700807	-0.61556	54.18334
0.700877	-0.61555	54.45
0.700825	-0.61555	54.71667
0.700967	-0.61555	54.98333
0.701050	-0.61555	55.25
0.701055	-0.61555	55.525
0.701101	-0.61554	55.80001
0.701220	-0.61554	56.06667
0.701250	-0.61554	56.33334
0.70129	-0.61554	56.6
0.701345	-0.61553	56.86667
0.701390	-0.61553	57.13333
0.701427	-0.61553	57.4
0.701588	-0.61552	57.66667
0.701752	-0.61552	57.93334
0.701807	-0.61552	58.2
0.701807	-0.61551	58.46667
0.701775	-0.61551	58.73333
0.701787	-0.61551	59
0.701876	-0.61551	59.26667
0.701929	-0.61551	59.53334
0.701897	-0.61551	59.80001
0.688594	-0.60389	60.43334
0.701579	-0.61539	61.43334
0.701589	-0.61539	62.43334
0.701783	-0.61538	63.43334
0.701942	-0.61538	64.44167
0.702174	-0.61537	65.45
0.702268	-0.61537	66.45
0.702355	-0.61536	67.45
0.702246	-0.61535	68.45
0.702502	-0.61533	69.45833
0.702697	-0.61531	70.46667
0.702815	-0.61532	71.46667
0.702663	-0.61532	72.46667
0.702777	-0.61531	73.46667
0.702881	-0.61530	74.46667
0.702817	-0.61530	75.46667
0.702733	-0.61529	76.46667
0.702675	-0.61529	77.46667
0.702674	-0.61529	78.46667
0.702754	-0.61529	79.46667
0.702811	-0.61529	80.46667
0.70285	-0.61529	81.475
0	0	0
8	26.4	40

7.95 25.4

HLHLS

VOLT1	VOLT2	MINUTES
0.821977	-0.62402	0.133333
0.792875	-0.59219	0.4
0.778423	-0.58229	0.666666
0.794878	-0.60208	0.933333
0.795601	-0.60500	1.2
0.796472	-0.60949	1.466667
0.798758	-0.61642	1.733333
0.794737	-0.61850	2
0.786735	-0.61858	2.266667
0.777674	-0.61826	2.533333
0.769612	-0.61765	2.8
0.764906	-0.61810	3.066667
0.762087	-0.61848	3.333334
0.760217	-0.61848	3.6
0.759032	-0.61833	3.866667
0.758282	-0.61817	4.133333
0.757882	-0.61807	4.4
0.757594	-0.61792	4.666667
0.757538	-0.61786	4.933334
0.757360	-0.61776	5.2
0.757258	-0.61771	5.466667
0.757257	-0.61773	5.733334
0.757253	-0.61768	6
0.757163	-0.61755	6.266667
0.757066	-0.61739	6.541667
0.757082	-0.61731	6.816667
0.757093	-0.61720	7.083333
0.757123	-0.61711	7.35
0.757163	-0.61705	7.608334
0.757107	-0.61701	7.866667
0.756696	-0.61693	8.133333
0.755925	-0.61682	8.399999
0.755006	-0.61671	8.666667
0.754094	-0.61667	8.933333
0.753258	-0.61662	9.2
0.752528	-0.61656	9.466667
0.751890	-0.61652	9.733334
0.751272	-0.61648	10
0.750688	-0.61644	10.26667
0.750176	-0.61635	10.53333
0.749573	-0.61632	10.8
0.748984	-0.61632	11.06667
0.748418	-0.61626	11.33333
0.747904	-0.61623	11.6
0.747372	-0.61618	11.86667
0.746802	-0.61613	12.13333
0.746482	-0.61607	12.4
0.746083	-0.61600	12.66667
0.745667	-0.61598	12.93333
0.745299	-0.61593	13.2
0.744915	-0.61576	13.46667
0.744074	-0.61505	13.74167
0.742691	-0.61392	14.01667
0.739164	-0.61048	14.28333
0.734637	-0.60617	14.55
0.676015	-0.55428	14.81667
0.703404	-0.57701	15.08333
0.709102	-0.57984	15.35
0.732343	-0.60486	15.61667
0.738805	-0.61049	15.88333
0.742090	-0.61358	16.15
0.74224	-0.61377	16.41667
0.742130	-0.61386	16.68333

0.742136	-0.61398	16.95
0.742649	-0.61466	17.21667
0.742873	-0.61490	17.48333
0.742923	-0.61499	17.75
0.742772	-0.61502	18.01667
0.74278	-0.61518	18.28333
0.742768	-0.61523	18.55
0.742788	-0.61536	18.81667
0.742884	-0.61543	19.08333
0.74319	-0.61545	19.35833
0.743204	-0.61547	19.63333
0.743100	-0.61553	19.9
0.743010	-0.61557	20.16667
0.743024	-0.61557	20.43333
0.743088	-0.61558	20.7
0.74315	-0.61558	20.96667
0.741374	-0.61559	21.23333
0.738932	-0.61561	21.5
0.738542	-0.61560	21.76667
0.738556	-0.61560	22.03333
0.738526	-0.61560	22.3
0.738857	-0.61560	22.56667
0.739255	-0.61560	22.83334
0.739168	-0.61561	23.1
0.738875	-0.61561	23.36667
0.739171	-0.61562	23.64167
0.739055	-0.61561	23.91667
0.739097	-0.61561	24.18334
0.738812	-0.61560	24.45
0.738509	-0.61561	24.71667
0.738645	-0.61561	24.98333
0.738616	-0.61562	25.25
0.738985	-0.61561	25.51667
0.739245	-0.61561	25.78333
0.739191	-0.61561	26.05
0.739144	-0.61560	26.31667
0.739360	-0.61561	26.58334
0.739024	-0.61561	26.85
0.739374	-0.61560	27.11667
0.739535	-0.61560	27.38333
0.739845	-0.61560	27.65833
0.739731	-0.61560	27.93334
0.739582	-0.61561	28.2
0.739384	-0.61561	28.46667
0.739275	-0.61560	28.73333
0.739197	-0.61560	29
0.739097	-0.61560	29.26667
0.739167	-0.61560	29.53333
0.739285	-0.61560	29.8
0.73924	-0.61560	30.06667
0.739335	-0.61560	30.33334
0.739786	-0.61559	30.6
0.740077	-0.61558	30.86667
0.74015	-0.61557	31.13333
0.74018	-0.61556	31.4
0.740302	-0.61556	31.66667
0.740256	-0.61557	31.93333
0.740442	-0.61557	32.2
0.740396	-0.61557	32.46667
0.740242	-0.61558	32.74167
0.740078	-0.61559	33.01667
0.740235	-0.61558	33.28333
0.740347	-0.61558	33.55
0.740435	-0.61558	33.81667
0.740572	-0.61559	34.08334
0.740674	-0.61559	34.35

0.740572	-0.61560	34.61667
0.740498	-0.61559	34.88333
0.740637	-0.61560	35.15
0.740575	-0.61560	35.41667
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0.740397	-0.61560	36.21667
0.740310	-0.61560	36.48333
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0.740415	-0.61559	37.81667
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0.739071	-0.61559	38.9
0.738667	-0.61559	39.16667
0.738218	-0.61559	39.43334
0.737657	-0.61559	39.7
0.737191	-0.61560	39.96667
0.736757	-0.61560	40.23333
0.736522	-0.61559	40.5
0.736297	-0.61559	40.76667
0.736162	-0.61559	41.03333
0.736235	-0.61559	41.3
0.736213	-0.61560	41.56667
0.736090	-0.61559	41.83334
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0.735942	-0.61558	42.9
0.73584	-0.61557	43.16667
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0.735848	-0.61557	43.71667
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0.735994	-0.61557	44.25
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0.736205	-0.61555	49.86667
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0.738248 -0.61530 76.49167
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