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A SIMPLE MODEL OF THE BATCH ELECTROCHEMICAL REDUCTION OF NITRATE/NITRITE WASTE (U)

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A Simple Model of the Batch Electrochemical Reduction of NO_3^-/NO_2^- Waste

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Abstract

A model of a divided parallel plate electrochemical cell operated in a batch mode for the destruction of NO_3^-/NO_2^- in alkaline waste streams is presented. The model uses boundary layer approximations at each electrode and at the separator to minimize computation time. Five competing electrochemical reactions are included at the cathode. The model uses either an explicit Runge-Kutta routine with empirically determined current efficiencies or an implicit stepping routine for each electrode if the current efficiencies are to be predicted. Time dependent changes of the concentration, temperature, and cell voltage are predicted for constant current operation. Model predictions are compared with experimental data.

Introduction

The electrochemical treatment of liquid radioactive wastes has become a topic of scientific and environmental interest in recent years. In particular, methods of electrochemically reducing NO_3^-/NO_2^- wastes to NaOH holds promise in decreasing the waste volume and the possible reuse, after evaporation, as a pure stream of concentrated NaOH [1]. Preliminary experimental data has been collected [2] using a parallel plate electrolyzer with a divided cell configuration. Here, a simple model has been developed to predict concentration and temperature changes in this parallel plate cell using empirical correlations and assumptions generated from the experimental data.

The anolyte and catholyte are recirculated through the cell and into mixing reservoirs. Typically the residence time is short and conversions per pass are small in the reactor due to the goal of operating at a high limiting current. At the start of batch operation, the catholyte is a synthetic waste stream composed of 1.95 M $NaNO_3$, 0.60 M $NaNO_2$, and 1.33 M NaOH and the anolyte is approximately 5.0 M NaOH. In the model,

the well-mixed reservoirs of the anolyte and catholyte and the parallel plate cell are lumped together and treated as batch reactors with gas generation. Material balances are solved for these reservoirs using an explicit Runge-Kutta or an implicit stepping routine to integrate the equations. The model predicts the concentration, voltage and temperature changes during a batch operation. Energy balances are solved to predict temperature changes due to heat transfer and voltage losses within the electrochemical cell. The model considers five competing electrochemical reactions at the cathode and only the oxidation of OH^- at the anode. An alternative to the model presented here is a more rigorous single-pass model [3].

Figure 1 is a schematic diagram of the experimental apparatus in which storage tanks #1 and #2 correspond to the anolyte and catholyte reservoirs respectively. For batch operation, storage tanks #3 and #4 are not used and the solutions are returned to tanks #1 and #2 through valves throughout the run. In a typical experiment, anolyte and catholyte solutions are charged into the system. The pumps are then turned on and the rotameters adjusted to the desired flowrates. A constant current is then applied to the electrochemical cell. Anolyte and catholyte samples are collected during the course of the experiment from which concentration data is obtained for the major components. Reservoir temperatures are recorded for the duration of the experiment. The experiment is terminated when approximately 95% of the initial NO_3^- and NO_2^- is destroyed.

Theory and Mathematical Model

Model Equations

The voltage of the cell depends on the open circuit potential of the cell (V_o), the resistances of the anolyte, catholyte, and separator (R_a, R_c, and R_s), the current density through the cell (i), and the kinetic and concentration overpotentials at the anode and cathode (η_a and η_c):

$$V = V_o + iAR_{cell} + |\eta_a| + |\eta_c| \qquad (1)$$

where, A, is the projected electrode area in the parallel plate cell. The open circuit potential of the cell is the difference between the thermodynamic potential of the anode (U_a) and the mixed potential of the cathode (E_c):

$$V_o = E_c - U_a \qquad (2)$$

The anodic reaction is the oxidation of OH^- to form O_2 and the thermodynamic voltage should deviate from an initial anode voltage as the activities of the anolyte and the temperature change:

$$U_a = U_a^{\theta} - \frac{RT}{4F}\ln\left(\frac{a_{H_2O}^2 P_{O_2}}{a_{OH^-}^4}\right) \quad (3)$$

The voltage of the cathode (E_c) is a mixed potential corresponding to the combined effects of thermodynamics and kinetics of NO_3^-/NO_2^- reduction and the water reduction reaction. These reactions can be written:

	U^{θ}(V)	
$1/2NO_3^- + 1/2H_2O + e^- \rightleftharpoons 1/2NO_2^- + OH^-$	0.011	(4)
$1/6NO_2^- + 5/6H_2O + e^- \rightleftharpoons 1/6NH_3 + 7/6OH^-$	-0.165	(5)
$1/3NO_2^- + 2/3H_2O + e^- \rightleftharpoons 1/6N_2 + 4/3OH^-$	0.406	(6)
$1/2NO_2^- + 3/4H_2O + e^- \rightleftharpoons 1/4N_2O + 3/4OH^-$	0.151	(7)
$H_2O + e^- \rightleftharpoons 1/2H_2 + OH^-$	-0.828	(8)

The resistance in the cell depends on the conductivity of the anolyte, catholyte, and separator (κ_i). It is also directly dependent on the perpendicular distances (S_i) through the electrolytes and separator between the parallel plates of the cell:

$$R_{cell} = \frac{1}{A}\left(\frac{S_a}{\kappa_a} + \frac{S_s N_M}{\kappa_s} + \frac{S_c}{\kappa_c}\right) \quad (9)$$

The constant, A, is the projected area of the electrodes and N_M, the MacMullin number [4], is a property of the separator which may be defined as the ratio of the porosity to the tortuosity. Experimental data are used to develop empirical correlations for the conductivity which is a function of concentrations and temperature.

The overpotentials at the anode or cathode may be determined by using the Butler-Volmer equation:

$$\frac{i_j}{i_{oj_{ref}}} = \prod_k \left(\frac{C_k}{C_{k_{ref}}}\right)^{p_{kj}} \exp\left(\frac{\alpha_{aj} F}{RT}\eta_j\right) - \prod_k \left(\frac{C_k}{C_{k_{ref}}}\right)^{q_{kj}} \exp\left(\frac{-\alpha_{cj} F}{RT}\eta_j\right) \quad (10)$$

In which k is the ionic species and j is the corresponding reaction. The overpotential (η_j), in equation 10, is the difference between the voltage of the electrode, the solution potential at the electrode surface, and the reference electrode potential. For a single reaction, the boundary layer assumption results in an expression for the ratio of the surface concentration, C_k, to the reference concentration, C_{kref}, in terms of the limiting current [5]:

$$\frac{C_k}{C_{k_{ref}}} = \left(1 - \frac{i}{i_{Lk}}\right)\frac{C_{k,b}}{C_{k_{ref}}} \tag{11}$$

where the limiting current density for species k at the anode and cathode may be calculated:

$$i_{Lk} = \frac{Nu_k D_k F C_k n}{s_k L} \tag{12}$$

Newman [6] gives an expression for the average Nusselt number for flow between two planar electrodes:

$$Nu_k = 1.8488\left(\frac{Re\,Sc_k d_e}{L}\right)^{1/3} - 0.4 \tag{13}$$

in which

$$Re = \frac{d_e v}{\nu} \tag{14}$$

and

$$Sc_k = \frac{\nu}{D_k} \tag{15}$$

For multiple reactions, the concentration ratio includes the sum of the partial current densities since the flux of species k at the surface depends on all of the j reactions:

$$\sum \frac{-s_{ij} i_j}{n_j F} = N_k = -k_{m_k}(C_{kb} - C_k) \tag{16}$$

where k_{mk} is the mass transfer coefficient for species k, C_{kb} is the bulk concentration and C_k is the surface concentration of species k. The mass transfer coefficient can be calculated from the following equation:

$$k_{m_k} = \frac{Nu_k D_k}{2S} \tag{17}$$

Thus the concentration ratio in the Butler-Volmer equation can be written:

$$\frac{C_k}{C_{k_{ref}}} = \left(1 - \frac{\sum \frac{s_{ij} i_j}{n_j F}}{k_{mk} C_{kb}} \right) \frac{C_{kb}}{C_{k_{ref}}} \tag{18}$$

These concentration ratios are then included in the Butler-Volmer equation with the assumed fractional reaction orders shown in Table I. As discussed below the prediction of the partial current densities for multiple reactions using this boundary layer approximation results in a set of nonlinear ordinary equations which must be solved at each time step. These equations can be contrasted to the equations of the more rigorous model which requires solution of a set of nonlinear equations at each spatial position.

Mass Balances

The change in the liquid phase molar concentration of species i is governed by a time dependent mole balance which may be written in a form:

$$\frac{d(VC_k)}{dt} = Q_{in} C_{k,in} - Q_{out} C_{k,out} - \sum_j \frac{s_{kj} i A \varepsilon_j}{n_j F} + R_k \tag{19}$$

The first two terms on the right hand side of equation (19) correspond to the inlet and outlet molar flows which may be set equal to zero since the reservoirs of the electrochemical cell are considered to be batch reactors. The third term is the electrochemical production of species i and the fourth term is the homogeneous production rate which may be set equal to zero. The change in concentration of each species depends only on the volume change in the reactor and the partial current densities which can be written as the product of the total applied current and reaction efficiencies or as the partial current densities as determined from the solution of the Butler Volmer Equations:

$$\frac{d(VC_k)}{dt} = -\sum_j \frac{s_{kj} i A \varepsilon_j}{n_j F} = -\sum_j \frac{s_{kj}\, i_j\, A}{n_j F} \tag{20}$$

In equations 4-8 the liquid species of interest are NO_3^-, NO_2^-, and OH^- and the off-gas species N_2, NH_3, N_2O, H_2, and O_2. The stoichiometric coefficients (s_{ij}) may be obtained by placing the electrochemical reactions in a generalized form (see Newman [6]). The efficiencies, ε_j, would typically be determined from empirical expressions but this empiricism is not needed if the partial current densities are obtained by solving simultaneously the partial current density equations (10) and an equation which requires the sum of the partial current densities to equal the total applied current at an electrode. The dependent variables in this problem are the solution potential at the electrode surface

and the five partial current densities corresponding to equations 4-8. During this calculation, the bulk concentrations are held constant at the inlet concentrations at that instant in time.

Energy Balance

The energy balance for the batch reactor system can be written to include the enthalpies of the gas streams leaving the reservoirs:

$$V\rho C_p \frac{dT}{dt} = -(|\eta_a|i + \sum_{j=1}^{M} |\eta_{cj}|i_{cj})A - (iA)^2 R_{cell} + UA(T_{Air} - T) - QC_{pgas}T \quad (21)$$

The first term on the right hand side corresponds to the summation of the energy losses at the anode and cathode due to kinetics and mass transfer. The second term corresponds to internal resistance losses due to the anolyte, catholyte, and separator. The third and fourth terms are the energy loss due to heat transfer to the atmosphere and the off gas leaving the reservoirs, respectively.

The variables C_p and κ_i are calculated using empirical expressions that are a function of concentration and temperature. Other physical parameters may be correlated to empirical equations as more experimental data becomes available.

Results and Discussion

The simple model presented here differs from the differential [3] model in that it does not account for the effects of migration in the electrochemical cell. However, it does predict temperature which has a pronounced effect on reaction kinetics due to the dependency of the diffusion coefficients, reference potentials, limiting current densities, and electrical conductivities on temperature. The assumption of Tafel kinetics in the Butler-Volmer equation showed acceptable qualitative agreement with the rigorous model. The simple model converges rapidly with a computer run time of less than two minutes in most cases and may be adapted to spreadsheet software. Future use of the model includes the calculation of kinetic parameters from experimental data collected.

The physical and kinetic properties used in the model are shown in Table 1. Some values such as the exchange current densities and transfer coefficients are approximated due to the lack of experimental data. The initial concentrations of NO_3^-, NO_2^-, and OH^- correspond to zero time in the simple numerical model.

Figures 3 and 4 show the current efficiencies of the cathodic reactions as a function of the charge passed through the electrochemical cell at current densities of 0.35 A/cm^2 and 0.45 A/cm^2 respectively. In the predictions the current efficiency for the reduction of NO_3^- reduces rapidly to zero. As the concentration of NO_3^- decreases, the concentration of NO_2^- builds which influences the kinetics of the three NO_2^- reduction

reactions. Later in the model predictions, the current efficiencies of the NO_2^- reduction reactions fall due to low concentrations. This coincides with an increase in the rate of water reduction. The effect of the increase in current density from 0.35 to 0.45 A/cm^2 shows an increase in the kinetic rate of the cathodic reactions.

Table 1: Physical, Mass Transfer, and Kinetic Properties (Temperature = 298.15 K)

Catholyte Volume:	700 ml
Anolyte Volume:	7000 ml
Electrode Gap:	0.6 cm
Separator Thickness:	0.05 cm
MacMullin Number (N_M):	5.0
Volumetric Flowrate:	10.5 cm^3/sec
Kinematic Viscosity (ν):	1 cS
Solution Density (ρ):	1 gm/cm^3
Initial NO_3^- Concentration:	1.95×10^{-3} moles/cm^3
Initial NO_2^- Concentration:	0.60×10^{-3} moles/cm^3
Initial OH^- Concentration:	1.33×10^{-3} moles/cm^3
Transfer Coefficient (α):	0.5 all reactions
Exchange Current Densities-	
reaction 4:	1.6×10^{-10} A/cm^2
reaction 5:	2.0×10^{-11} A/cm^2
reaction 6:	6.6×10^{-15} A/cm^2
reaction 7:	3.1×10^{-13} A/cm^2
reaction 8:	3.0×10^{-6} A/cm^2
anodic reaction:	1.9×10^{-11} A/cm^2
Electrons Transferred per Reaction-	
reaction 4:	1
reaction 5:	1
reaction 6:	1
reaction 7:	1
reaction 8:	1
anodic reaction:	4
Diffusion Coefficients-	
NO_3^- species	1.902×10^{-5} cm^2/sec
NO_2^- species	1.902×10^{-5} cm^2/sec
OH^- species	5.260×10^{-5} cm^2/sec

Figure 5 shows the how the concentrations of NO_3^-, NO_2^-, and OH^- in the catholyte change during the course of the experiment at current densities of 0.35 and 0.45 A/cm^2. The concentration of NO_3^- decreases through the entire experiment while the concentration

of NO_2^- first increases, due to the rapid rate of NO_3^- reduction, then decreases. The concentration of OH^- increases to a steady value as the concentration of NO_3^- and NO_2^- fall. The final concentration of the OH^- will depend on the rate of mass transport of H_2O across the separator which is not calculated in this model.

Figures 6 and 7 show how the total cell potential and its components change during the experiment. In figure 6 the reference potential for the reduction of water, the anodic reference potential, and the anodic potential remain constant through the entire experiment. The cathodic potential decreases due to the kinetics of the cathodic reactions and the resistance losses increase due to the increase in the temperature of the cell. The total cell potential decreases to a steady value then increases slightly at the end of the experiment. This increase in the cell potential coincides with the onset of the water reduction reaction. This effect is more pronounced at lower current densities as shown in figure 7.

Figure 8 shows how the temperature of the cell is influence by current density. At current densities of 0.35, 0.45, and 0.55 A/cm^2 a strong dependency of the temperature on the current density is apparent. The final temperature depends on the value of the heat transfer coefficient, U, which was assumed to be zero for this figure.

Figures 9 and 10 compare the model predictions with the experimental data taken in the apparatus shown in figure 1 with the current density of 0.5 A/cm^2. Physical and Kinetic parameters shown in Table 1 were used. Comparison is quite good especially for the nitrate and nitrite species. It is interesting to note that the cell voltage drop for Celgard was higher than that for Nafion.

Conclusions

A boundary layer model has been presented for the electrochemical reduction of nitrate and nitrite species in a parallel plate reactor. The model neglects migration but includes the dependency of simultaneous reactions on the surface concentration. The model agrees favorably with experimental data.

Acknowledgement

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Figure 1: **Schematic Diagram**

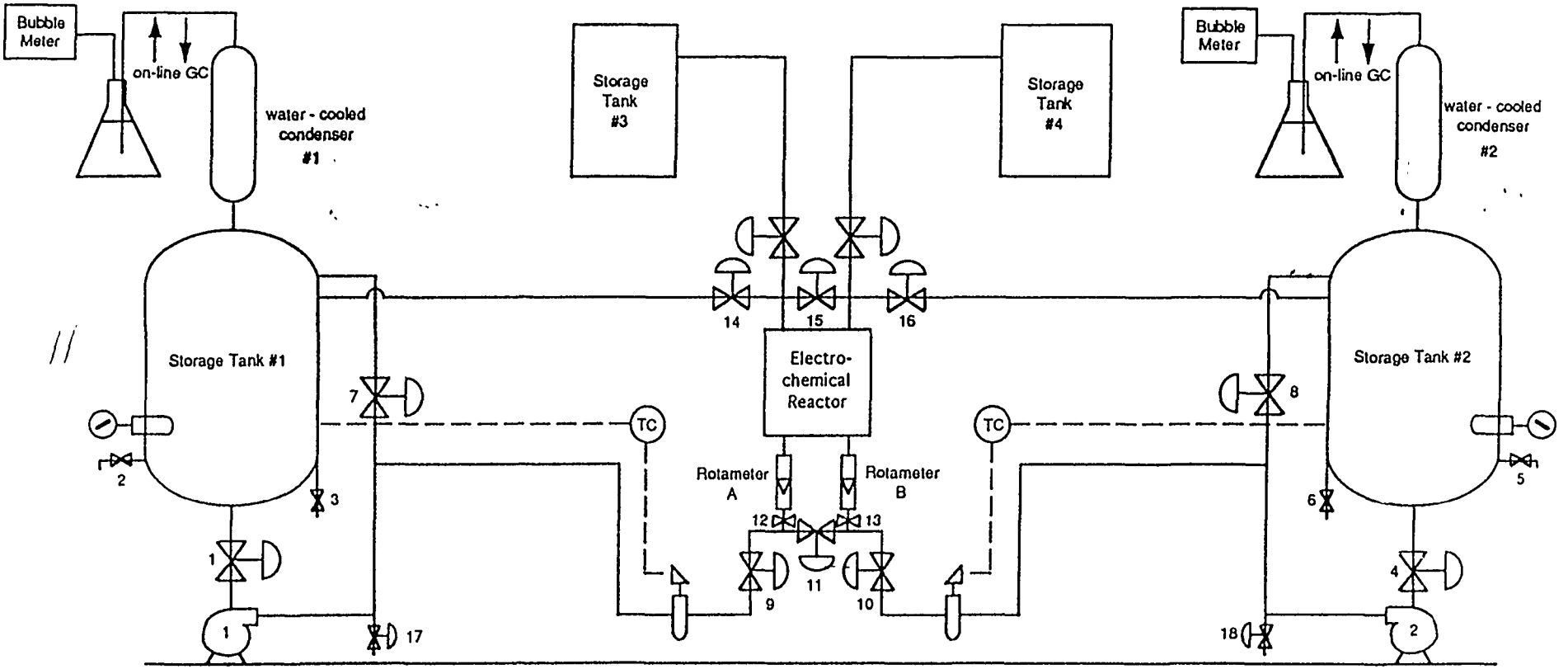

Figure 2: MP Electrochemical Cell

Cross-Sectional Side View

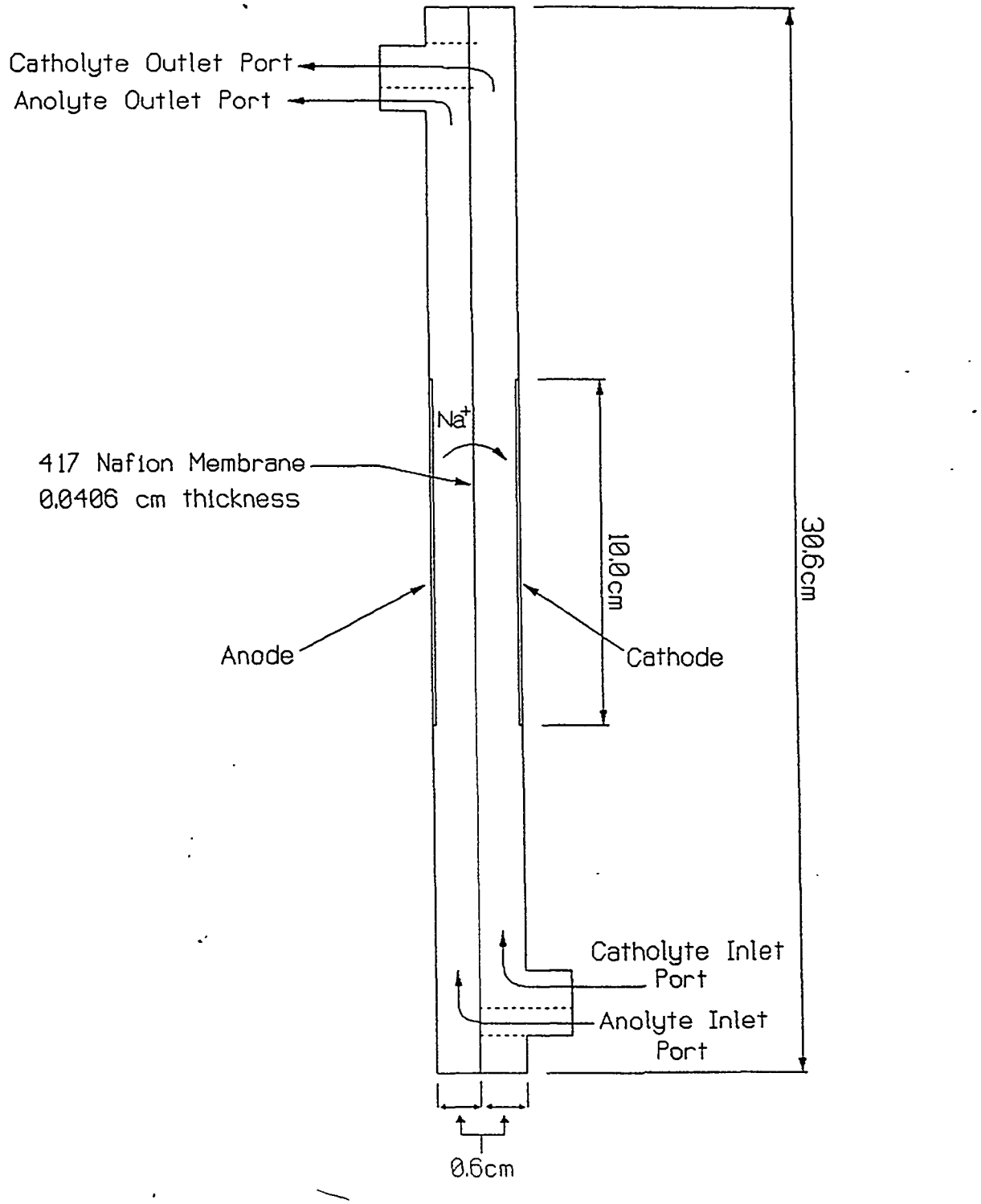

Figure 3: Electrolysis Current Efficiencies of NO_3/NO_2 Reduction Process, i = 0.35 A/cm^2

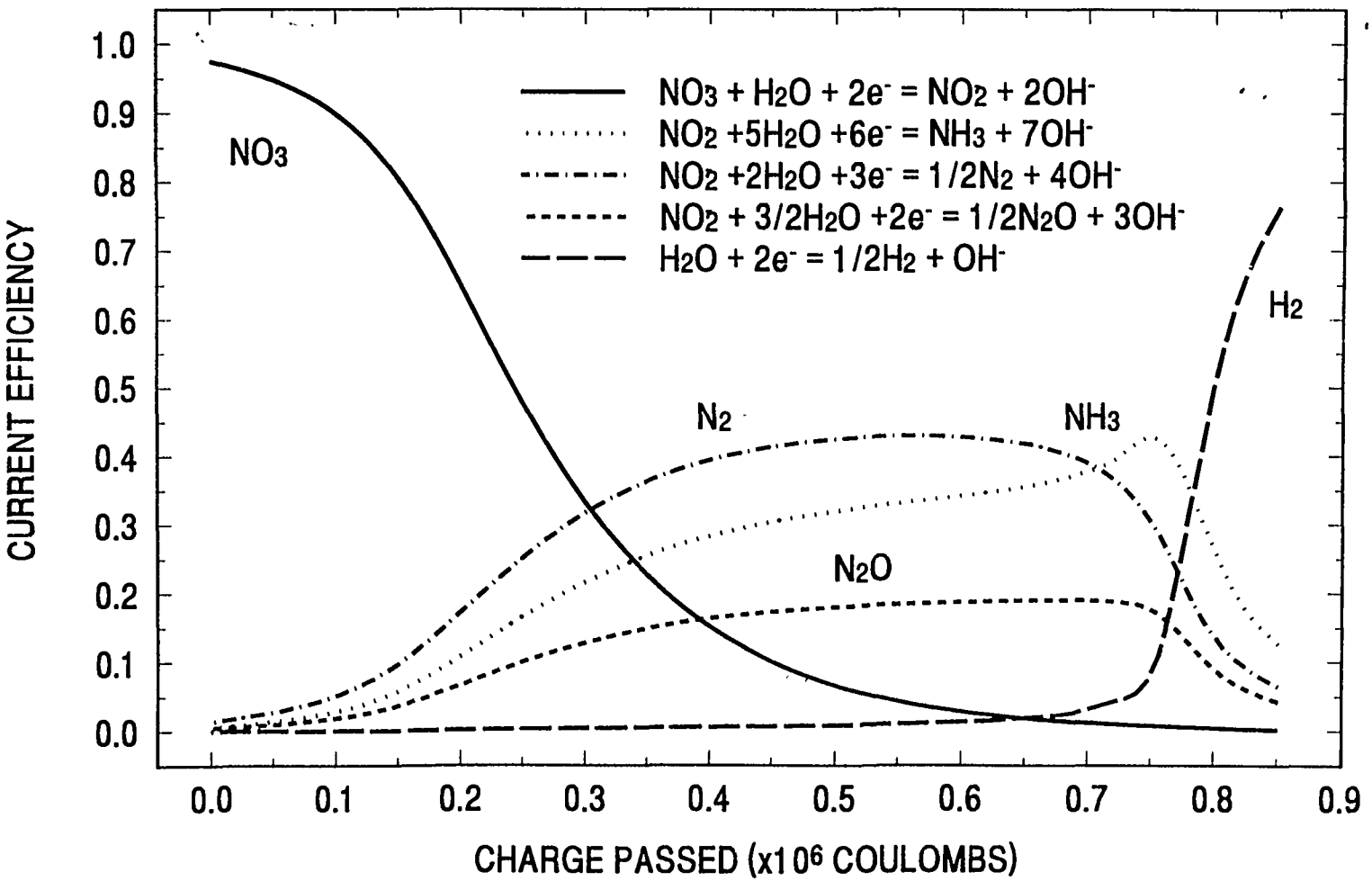

Figure 4: Electrolysis Current Efficiencies of NO_3/NO_2 Reduction Process, i = 0.45 A/cm^2

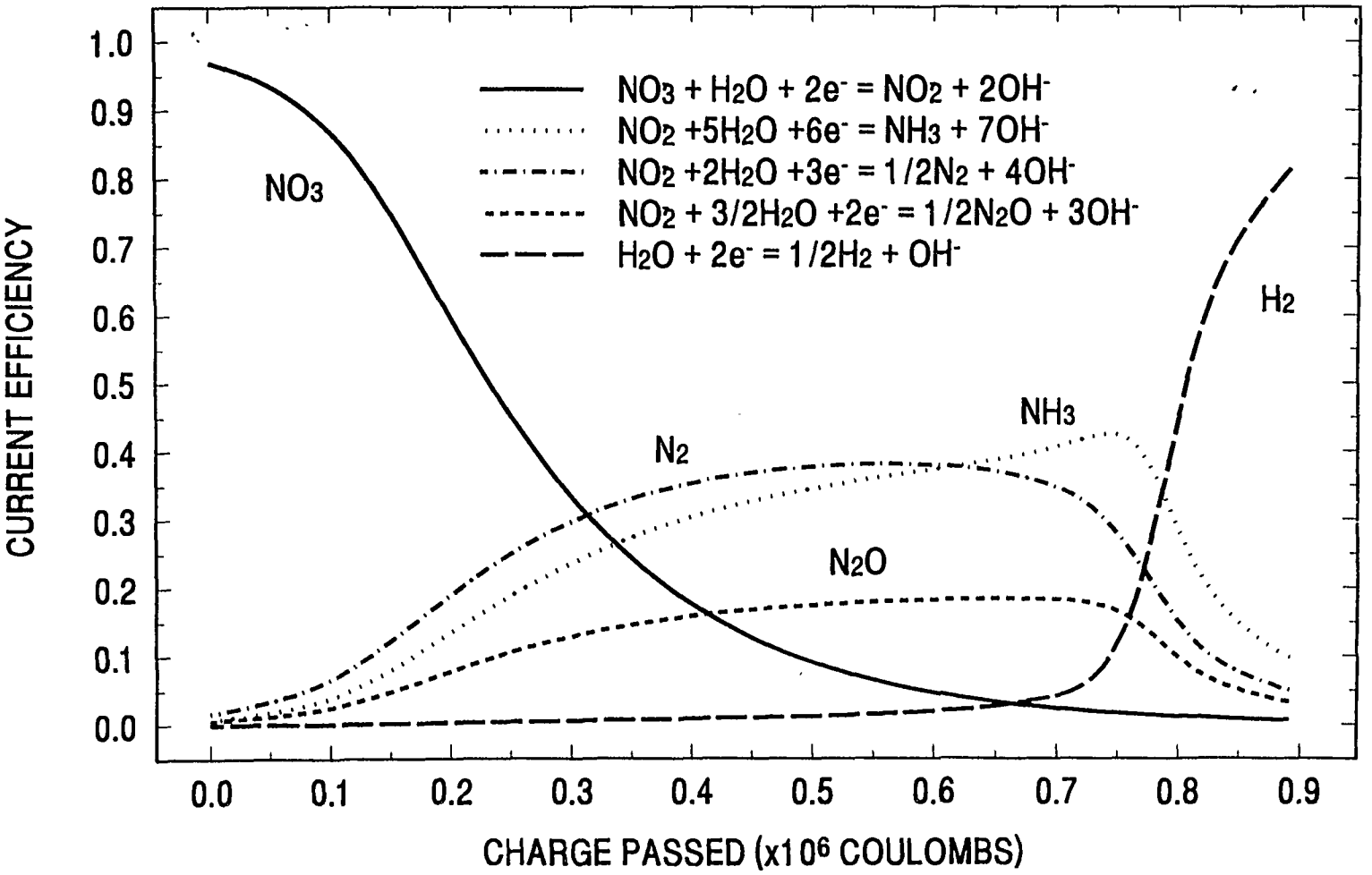

Figure 5: Catholyte Compositions of Major Components
at i = 0.35 A/cm^2 and i = 0.45 A/cm^2

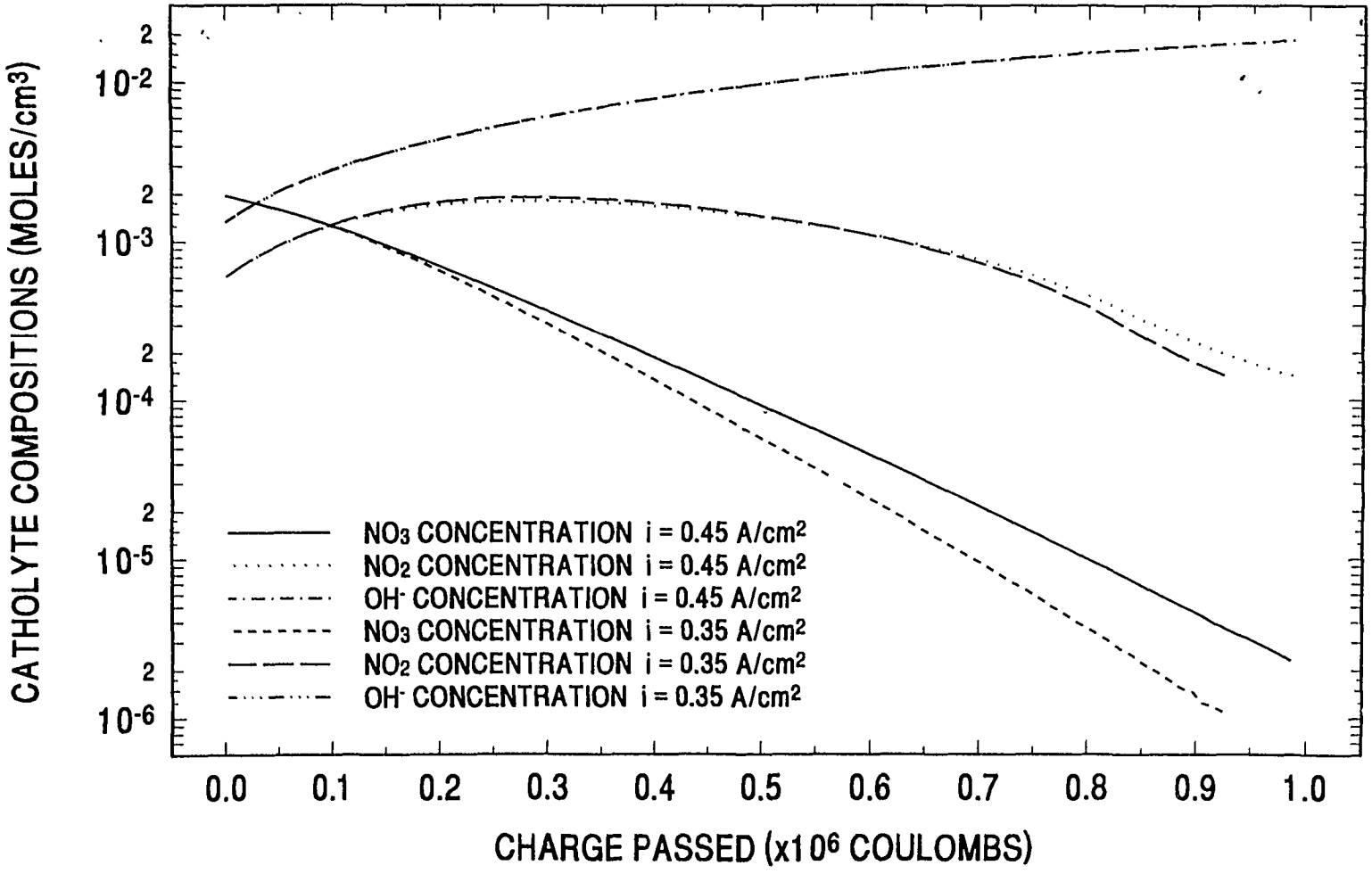

Figure 6: Components of the Cell Potential
as a Function of Charge Passed

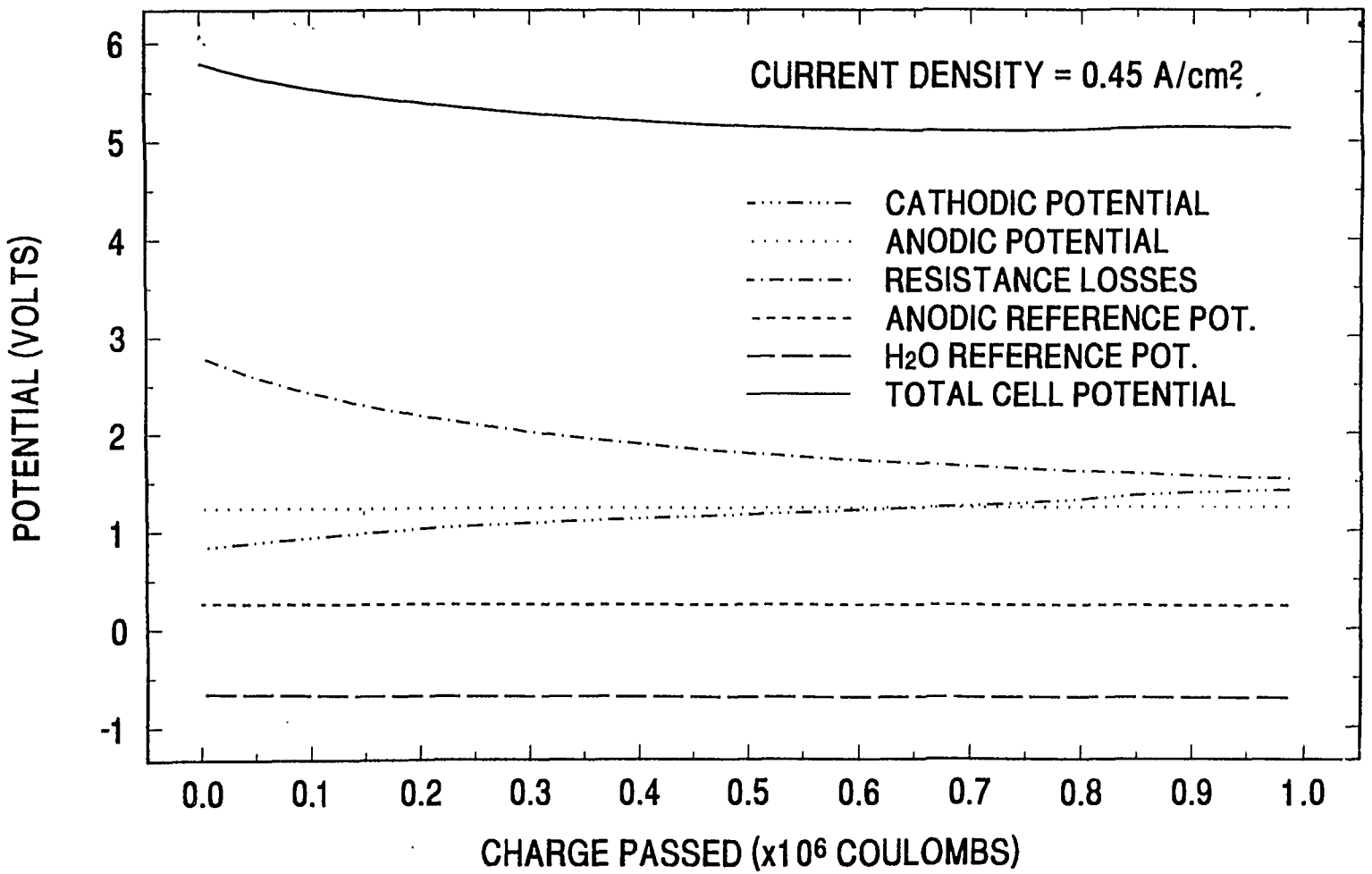

Figure 7: Effect of Current Density
on Total Cell Voltage

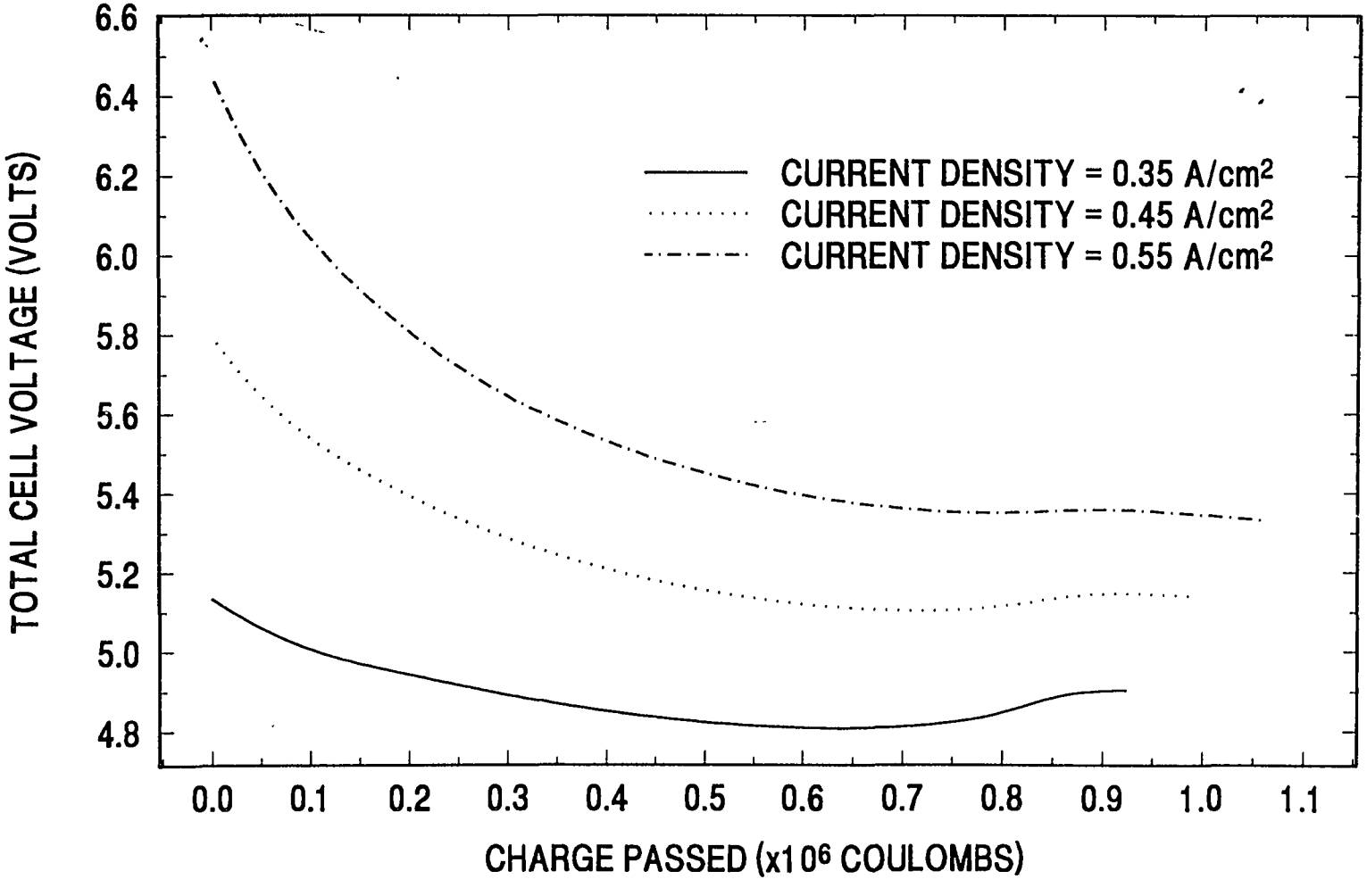

Figure 8: Effect of Current Density
on Cell Temperature

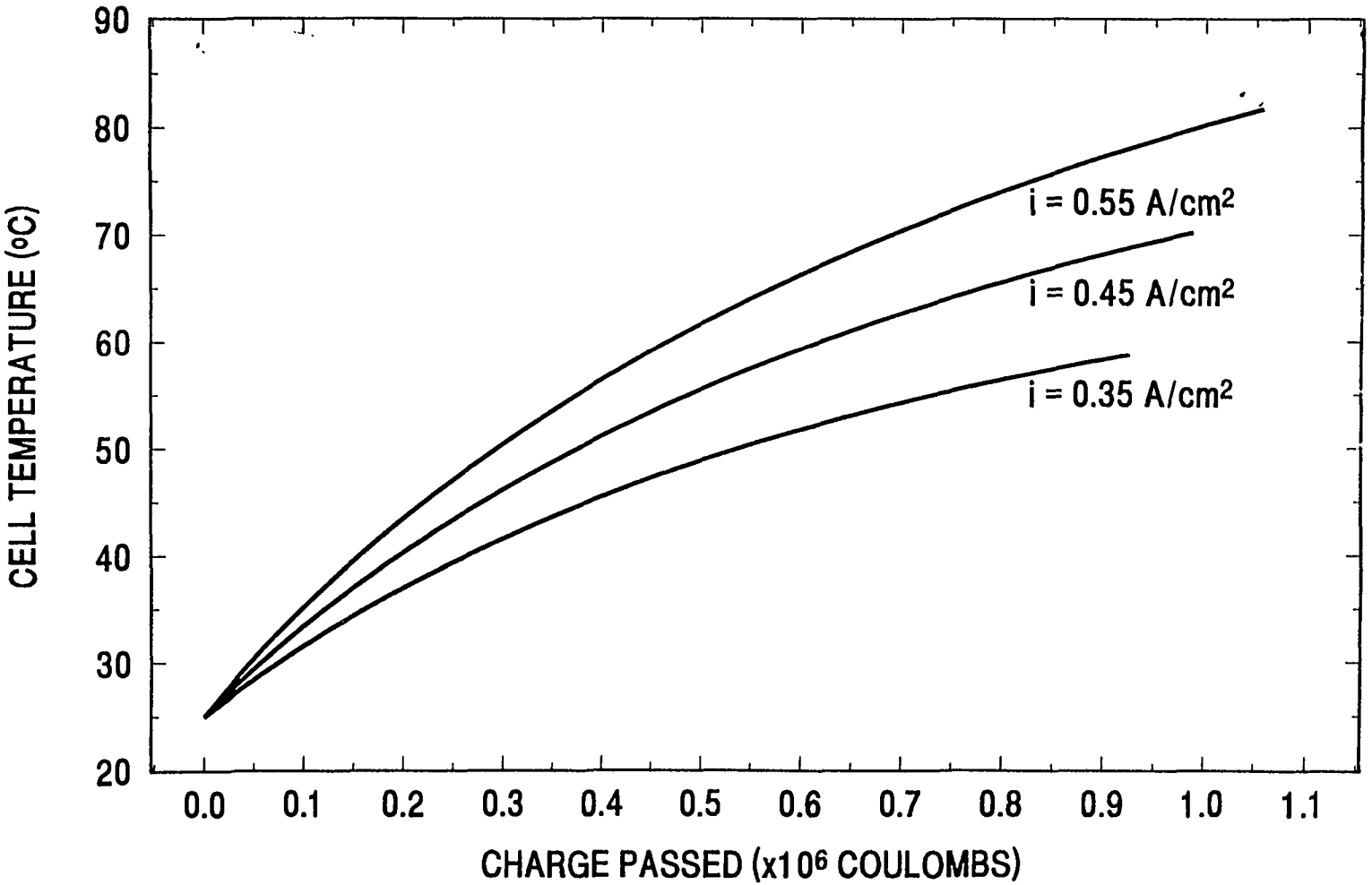

Figure 9: Compositions of Ionic Species in Run-3
MP Cell, Pb/SS electrodes, Nafion 350

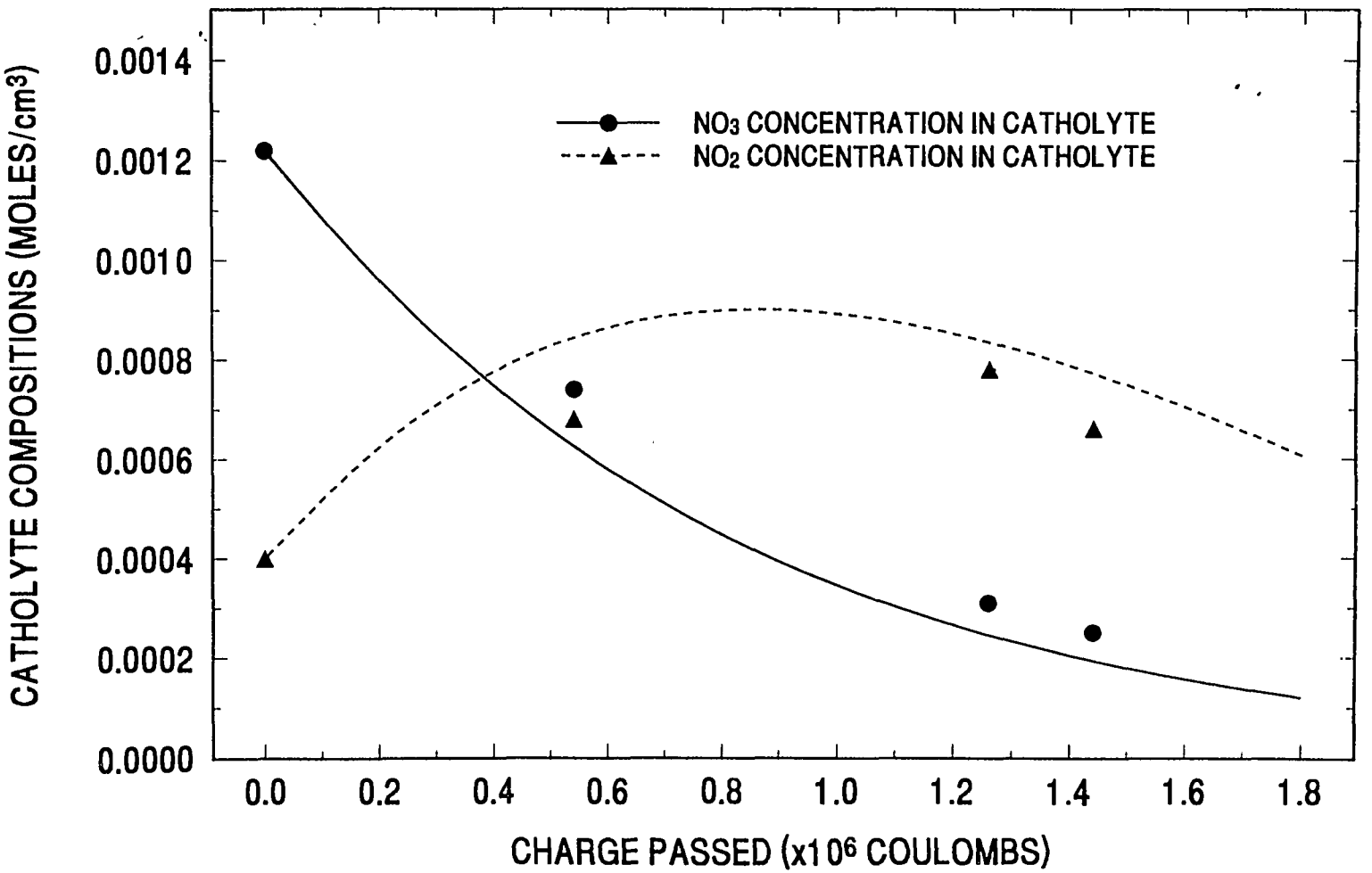

Figure 10: Model Predictions of Total Cell Voltage
Versus Total Cell Voltage in Run-1 and 3
MP Cell,Pb/SS electrodes,Nafion 350 and Celgard 3400