

The transient behaviour of a class of semicontinuous tank electrolyzers

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Received 11 May 1987; revised 3 September 1987

The transient behaviour and figures of merit of an isothermal electrolyser consisting of a perfectly mixed-flow compartment and a batch compartment separated by an ion-selective membrane are analysed by means of its governing balance equations solved on a microcomputer.

Nomenclature

c	acid concentration	V	magnitude of the imposed voltage
E	conversion of the oxidized to the reduced species at the cathode	x_1^0	magnitude of the inlet concentration of the oxidized species
F	Faraday's constant (96 487 C mol ⁻¹)	w	acid concentration in the anolyte
i	current density	α	lumped parameter, defined as $1 + k_m^{A_i}/Q_c$
K	cost of operation	$\hat{\theta}_0, \hat{\theta}_1$	sample linear regression parameters (Table 5)
k_1, k_2	cost coefficients (specific costs)	λ	fractional concentration of the oxidized species defined as (concentration – surface concentration)/concentration
Q_s	charge density; \hat{Q}_s its sample regression	τ_c	mean residence time defined as V_c/Q_c
S_0	initial slope of the conversion-time curve (Fig. 3)		
t	time		
t_H	transport (transference) number of hydronium ions		

Special symbols

MU arbitrary monetary unit
* steady-state

The majority of symbols is defined in Table 1.

1. Introduction

A tank electrolyser consisting of two compartments separated by a membrane such that one of the compartments behaves as a static batch and the other compartment behaves as a flow system, is called a semicontinuous tank electrolyser. This mode of operation may be desirable if at least one reactant, e.g. hydronium-ion concentration in the continuous-flow compartment has to be kept under control via H₃O⁺ ion diffusion through the separating membrane. While semicontinuous chemical reactors (often called semi-batch reactors) are well known in chemical reaction engineering [1–4], their electrochemical counterpart has received limited attention in the electrochemical engineering literature. Pickett [5] examined in detail the semicontinuous system where the anode compartment behaves as a continuous-flow stirred tank electrochemical reactor (CSTER) and the cathode compartment as a static batch: at limiting current conditions analytical solutions for the residence time required to reach a certain conversion of the electrolyte can be obtained by assuming a constant transport number for the ionic species diffusing through the membrane which separates the catholyte from the anolyte. As shown by Pickett [5], the analysis becomes rather cumbersome for sub-limiting current conditions, where numerical integration is required

for the computation of concentration profiles, current and energy efficiencies etc. Departure from isothermal conditions necessitates numerical solutions even at limiting-current operation as electrolyte conductivity and density become time-dependent functions.

The purpose of this paper is to describe a numerical framework of semicontinuous electrolyser analysis which permits a relatively straightforward simulation of electrolyser transients via microcomputers. The system chosen for equation 6 is somewhat different from Pickett's. The cathode compartment is assumed to behave as a CSTER: the cathode reaction is the reduction of an oxidized species and the anodic department is a static batch system separated from the cathode department by a membrane through which hydronium ions migrate into the cathode compartment. The anode reaction is water decomposition producing oxygen gas and hydronium ions. The electrolyser operates at an essentially constant temperature, and gassing as well as evaporation effects are neglected; however, the variation of the transport number of hydronium ions with the monoprotic acid concentration is considered.

2. Theory

The mass balance set for the isothermal electrolyser in Fig. 1 consists of the following four constituent

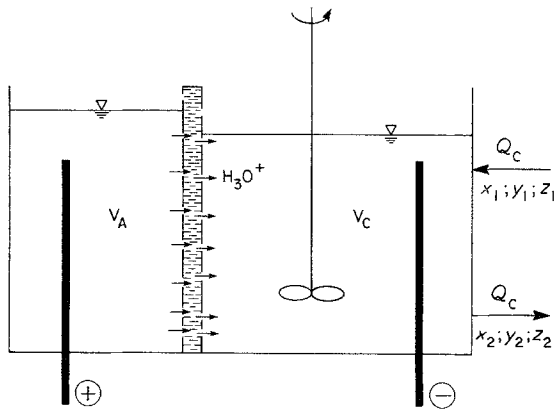


Fig. 1. Sketch of a semicontinuous tank electrolyser.

equations, assuming that the effective cathode and anode areas are equal:

$$\text{oxidized species: } V_c \frac{dx_2}{dt} = Q_c(x_1 - x_2) - \frac{iA}{nF} \quad (1)$$

$$\text{reduced species: } V_c \frac{dy_2}{dt} = Q_c(y_1 - y_2) + \frac{iA}{nF} \quad (2)$$

$$\text{anolyte acid: } V_A \frac{dw}{dt} = (1 - t_H) \frac{iA}{F} \quad (3)$$

$$\text{catholyte acid: } V_c \frac{dz_2}{dt} = Q_c(z_1 - z_2) + t_H \frac{iA}{F} \quad (4)$$

The current density may be expressed in terms of the mass transport coefficient k_m and the fractional concentration λ as

$$i = zFk_m\lambda x_2 \quad (5)$$

At limiting-current conditions $\lambda \rightarrow 1$, $i \rightarrow i_L = zFk_m x_2$ and the analytical solution

$$x_2(t) = \frac{1}{\tau_c} \exp\left(-\frac{\alpha}{\tau_c} t\right) \int_0^t x_1(t) \times \exp\left(\frac{\alpha}{\tau_c} t\right) dt + x_2^0 \exp\left(-\frac{\alpha}{\tau_c} t\right) \quad (6)$$

may be obtained [6] for inlet concentrations $x_1(t)$ of the oxidized species, if t_H is a constant. In the simplest case, when $x_{20} = 0$ and $x_1(t) = x_1^0$, straightforward integration of equation 6 yields the transient solution

$$x_2(t) = \frac{x_1^0}{\alpha} \left[1 - \exp\left(-\frac{\alpha}{\tau_c} t\right) \right] \quad (7)$$

with its associated steady state solution

$$\lim_{t \rightarrow \infty} x_2(t) = x_2^* = \frac{Q_c x_1^*}{Q_c + k_m A \lambda} \quad (8)$$

In a more realistic formulation, the variation of the transport number of hydronium ions with acid concentration is considered via interionic attraction

theory [7] or, more conveniently, via the semi-empirical relationship

$$t_H = t_H^0 + A_t \sqrt{c} \quad (9)$$

Consequently, t_H in equation 3 is computed with $c = w$ and since the exact acid distribution in the membrane is assumed to be unknown, t_H in equation 4 is computed with $c = \frac{1}{2}(w + z_2)$ as an approximation. Numerical values of the coefficient A_t are given for several electrolytes by Parsons [8]. The fractional concentration λ is related to the physical parameters of the electrolyser via the electric potential balance [5, 6]

$$V = V_D + \sum_{i=1}^2 |a_i + b_i \log_{10}(zFk_m \lambda x_2)| + q_1 |\log_{10}(1 - \lambda)| + zFk_m \lambda x_2 \times \left(\frac{h_A}{\sigma_A} + \frac{h_c}{\sigma_c} + \frac{h_M}{\sigma_M} \right) \quad (10)$$

The semicontinuous electrolyser is, therefore, described by model equations 1–5, 9 and 10 representing linear differential equations with nonlinear forcing functions which are interlocked by the nonlinear electric potential balance. This mathematical encumbrance is carried over into the steady state, as shown by equation 11:

$$x_2^* = \frac{Q_c x_1^*}{Q_c + k_m A \lambda^*}; \quad y_2^* = y_1^* + \frac{k_m A \lambda^*}{Q_c} x_2^* \quad (11)$$

The steady state concentration of the oxidized species requires an iterative or root-finding procedure, as λ^* is a function of x_2^* . The acid concentration does not reach a steady state in either compartment.

3. Computational aspects of the microcomputer solution

The model structure suggests an algorithmic scheme in which equations 1–4 are treated as a vector-matrix differential equation coupled with equation 10 as an algebraic nonlinear equation: the variables w , x_2 , y_2 and z are elements of a solution vector u ($u_0 = w$; $u_1 = x_2$; $u_2 = y_2$; and $u_3 = z$). Equation 10 may be solved conveniently by a root-finding procedure for a specified value of the imposed voltage V , which is imbedded appropriately in the u -solution routine. Numerical simulation was carried out on a DEC Rainbow 100+ microcomputer equipped with a C-compiler under the CP/M operating system [9] and the recently developed vector-matrix differential equation solver called C SIM [10, 11] was employed to execute the simulation. Equation 10 was handled via a standard interval-halving [12] root-finding procedure, and integration was carried out by a variable-size modified Adams-Bashforth procedure [13] built into C SIM. Transient profiles were obtained to the value of the oxidized-species concentration $5 \times 10^{-5} \text{ mol dm}^{-3}$ different from the steady state values.

Table 1. Operating and physical parameters of a semicontinuous tank electrolyser (illustrative example)

Active area of each electrode $A = 25.0 \text{ dm}^2$
Mass transport coefficient $k_m = 1.0 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1}$
Catholyte flow rate $Q_c = 0.1 \text{ dm}^3 \text{ min}^{-1}$
Inlet concentration of oxidized species in catholyte $x_1 = 0.1 \text{ mol dm}^{-3}$
Inlet concentration of reduced species in catholyte $y_1 = 0.01 \text{ mol dm}^{-3}$
Inlet concentration of acid in catholyte $z_1 = 0.01 \text{ mol dm}^{-3}$
Active anolyte volume $V_A = 5.0 \text{ dm}^3$
Active catholyte volume $V_c = 10.0 \text{ dm}^3$
Valency of cathode reaction $n = 2$
Transport number of H^+ ions at infinite dilution $t_{\text{H}}^0 = 0.8209$
Empirical transport number coefficient (9) $A_t = 0.04507 (\text{dm}^3)^{1/2} \text{ mol}^{-1/2}$
Tafel-parameters: anode reaction $a = 0.70 \text{ V}$; $b = 0.03 \text{ V dec}^{-1}$ cathode reaction $a = 0.60 \text{ V}$; $b = 0.19 \text{ V dec}^{-1}$
Decomposition voltage $V_D = 1.70 \text{ V}$
Concentration overpotential factor $q_1 = 0.1 \text{ V}$
Anode/membrane distance $h_A = 7.0 \text{ cm}$
Cathode/membrane distance $h_C = 7.5 \text{ cm}$
Membrane width $h_M = 5.0 \text{ mm}$
Mean anolyte conductivity $\sigma_A = 0.55 \text{ S cm}^{-1}$
Mean catholyte conductivity $\sigma_C = 0.45 \text{ S cm}^{-1}$
Membrane conductivity $\sigma_M = 0.15 \text{ S cm}^{-1}$
Initial concentrations: oxidized species in cathode compartment $x_{20} = 0.1 \text{ mol dm}^{-3}$
reduced species in cathode compartment $y_{20} = 0.01 \text{ mol dm}^{-3}$
acid concentration in cathode compartment $z_{20} = 0.01 \text{ mol dm}^{-3}$
acid concentration in anode compartment $w_0 = 0.02 \text{ mol dm}^{-3}$

4. An illustrative example

Table 1 contains operating and physical parameters of a semicontinuous electrolyser whose transient response is shown in Fig. 2, and steady state in Table 2. The minimum imposed voltage required to maintain electrolysis is about 2.36 V, and at voltages higher than 2.6 V limiting current conditions are approached. The

Table 2. Steady state conditions in the semicontinuous tank electrolyser

Imposed voltage (V)	λ	Concentration (mmol dm^{-3})	
		Oxidized species	Reduced species
2.36	0.4122	94.177	15.823
2.40	0.5343	92.580	17.420
2.45	0.6953	90.555	19.445
2.50	0.8364	88.853	21.147
2.55	0.9294	87.765	22.235
2.60	0.9743	87.249	22.751
Limiting current	1	86.957	23.043

variation of acid concentration with time is illustrated in Table 3 over approximately 90% of the time span necessary to reach the steady state concentration of the oxidized species to a $5 \times 10^5 \text{ mol dm}^{-3}$ accuracy; this time span varies between 470 and 500 min in the illustrative example. The concentration of the oxidized specie at the cathode surface may readily be estimated via the λ -factor obtained at any arbitrary time instant from the voltage balance: the computation is illustrated in Table 4.

5. Discussion: figures of merit

The efficiency of a semicontinuous electrolyser may be measured by the relative variation with time of the conversion of the main reactant, in this case the conversion of the oxidized species to the reduced species at the cathode, defined as

$$E = 100(x_{20} - x_2)/x_{20} \text{ per cent} \quad (12)$$

As shown in Fig. 3, the electrolyser is most efficient at short time periods, where the slope of a tangent line drawn to the (E, t) curves is relatively large. On the other hand, the charge density, a figure of merit for

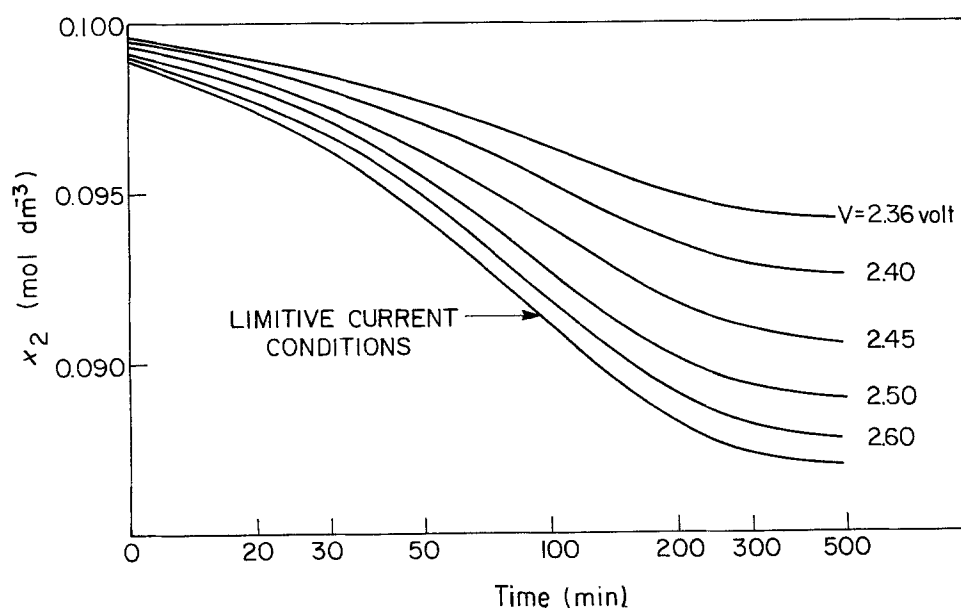


Fig. 2. Oxidized-species concentration transients (illustrative example).

Table 3. The variation of acid concentration with time in the semicontinuous tank electrolyser (A anolyte; C catholyte)

Time (min)	Acid concentration, mmol dm ⁻³													
	V = 2.36		2.40		2.45		2.50		2.55		2.60		Limiting current	
	A	C	A	C	A	C	A	C	A	C	A	C	A	C
0	20.00	10.00	20.00	10.00	20.00	10.00	20.00	10.00	20.00	10.00	20.00	10.00	20.00	10.00
10	20.30	10.70	20.39	10.90	20.51	11.17	20.62	11.42	20.70	11.61	20.74	11.71	20.77	11.78
50	21.82	13.51	22.59	14.89	23.35	16.31	24.04	17.62	24.55	18.57	24.83	19.10	25.01	19.44
100	24.02	16.11	25.15	17.82	26.49	19.94	27.97	22.09	28.84	23.44	29.34	24.19	29.77	24.75
150	26.04	17.51	27.73	19.61	29.93	22.34	31.89	24.75	33.25	26.40	33.96	27.25	34.40	27.75
200	28.05	18.36	30.28	20.68	33.18	23.68	35.64	26.26	37.49	28.05	38.39	28.93	38.93	29.45
300	32.04	19.17	35.87	21.71	39.64	24.96	43.36	27.74	45.87	29.56	47.12	30.44	47.87	30.95
400	34.03	19.36	40.42	22.09	46.07	25.41	50.93	28.24	54.16	30.06	55.76	30.93	56.70	31.43
450	38.01	19.54	42.95	22.17	49.26	25.52	54.69	28.35	58.28	30.17	60.05	31.04	61.09	31.53

energy expenditure;

$$Q_s = \frac{1}{E} \int_0^t i dt = \frac{nFk_m}{E} \int_0^t \lambda x_2 dt \quad (13)$$

remains remarkably linear with time, as seen in Table 5. Since the slope of the charge density/time relationship $\hat{\theta}_1$ as well as the initial slope of the conversion/time relationship S_0 increase with the imposed voltage the trade-off between energy costs and product value may be optimized if the cost of operation K may be expressed approximately as

$$K \simeq k_1 \hat{\theta}_1 + k_2/S_0 \quad (14)$$

where k_1 and k_2 are specific costs related to electric energy and electrolyser operation, respectively. The optimal imposed voltage is then obtained from the relationship

$$S_0^2 \frac{d\hat{\theta}_1}{dS_0} = \frac{k_2}{k_1} \quad (15)$$

Upon setting $dK/dS_0 = 0$; if, e.g. $k_1 = 2.5 \text{ MU dm}^2 \text{ A}^{-1}$ and $k_2 = 0.0111 \text{ MU min} (\% \text{ conversion})^{-1}$; equa-

tion 15 with data in Table 5 yields $S_0 \simeq 0.065$, hence $V_{\text{opt}} \simeq 2.4 \text{ V}$.

6. Concluding remarks

The major utility of microcomputer-based simulation is in exploring (at least in a preliminary fashion) the effect of various design parameters and operation alternatives in electrolyser performance. The designer may, for instance consider the recycling of the effluent through a mixing tank into the catholyte in electrolysis at a low imposed voltage as an alternative to single-pass operation if the simulated response and subsequent results via equation 15 are unsatisfactory from a technological point of view. Simulation can also serve as a design tool for pilot-plant scale experiments by establishing the most attractive domain of the experimental variables and cost components.

Acknowledgement

This research was carried out on equipment obtained

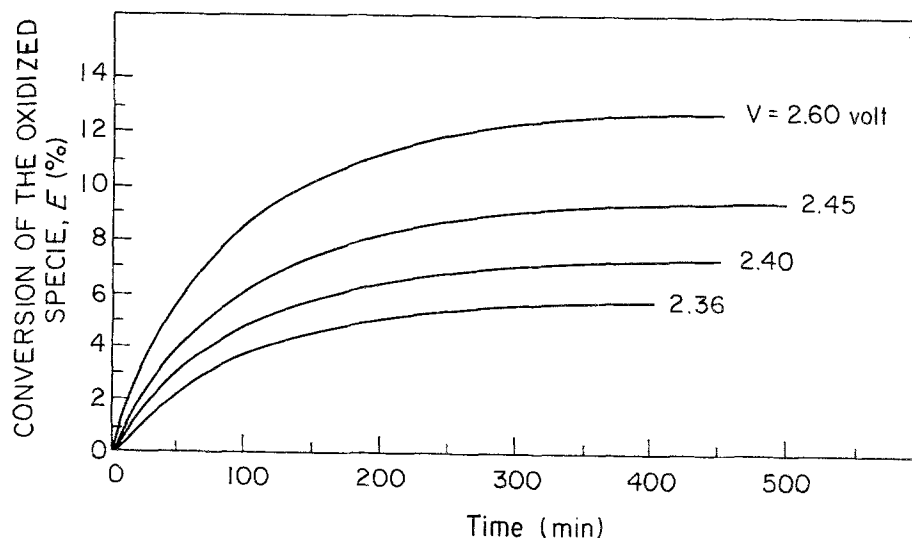


Fig. 3. Oxidized-species conversion transients (illustrative example).

Table 4. λ -factors and surface concentrations of the oxidized species during typical transients

Time (min)	Imposed voltage (V)			
	V = 2.36		V = 2.60	
	λ	$x_{2,E}$ (mmol dm ⁻³)	λ	$x_{2,E}$ (mmol dm ⁻³)
0	0.3928	60.72	0.9605	39.50
50	0.4003	58.59	0.9670	31.10
100	0.4041	57.52	0.9703	27.10
200	0.4095	56.07	0.9730	24.00
300	0.4112	55.62	0.9740	22.80
400	0.4118	55.45	0.9742	22.56
∞	0.4122	55.36	0.9743	22.40

Table 5. Charge densities and initial slopes of the conversion-time curves (Fig. 3)

Regression model: $\hat{Q}_s = \hat{\theta}_0 + \hat{\theta}_1 t$

Imposed voltage (V)	Regression parameters		Coefficient of determination r^2	Initial slope S_0 (min ⁻¹)
	$\hat{\theta}_0$ (C dm ⁻²)	$\hat{\theta}_1$ (A dm ⁻²)		
2.36	57.1403	0.61699	0.9966	0.047
2.40	54.9417	0.63150	0.9950	0.065
2.45	51.8807	0.64296	0.9948	0.122
2.60	53.9039	0.64797	0.9955	0.272

via a Digital Equipment Corporation – University of Waterloo Research Agreement, and supported by the Natural Sciences and Engineering Research Council of Canada.

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