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SHORT COMMUNICATION

Problem of scale-up in electrochemical systems

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1. Introduction

The word 'scale-up' is rather difficult to define. A process which is feasible on a laboratory scale can, in principle, be commercialized as a large-scale industrial plant. However, in this eventuality, the process may have to be modified to allow for changes in the size of the apparatus. The principle governing this modification is called scale-up.

The scale-up of an electrochemical system is primarily concerned with the voltage drop across the cell, the cell resistances and the current density. The voltage drop across an electrolytic cell consists, mainly, of three components arising out of three resistances, namely, the resistance of the electrolyte (R_E), the resistance due to concentration polarization (R_C) and the resistance due to activation polarization (R_A). When working at moderate current densities and below the limiting current, conditions which are normally used in industry, the resistance due to activation polarization (R_A), can be neglected. With this assumption the scale-up problem can be considered under two headings:

I. *Ohmic resistance controlling regime*

The voltage drop in this regime is dependent only on R_E. Then obviously from Ohm's law we have

$$i = \frac{VK}{d} \tag{1}$$

where

i = current density A cm^{-2}
K = Specific conductivity ohm^{-1} cm^{-1} of the electrolyte
d = the distance of separation of electrodes, (cm)
V = Voltage drop across the cell, (volts)

For scale-up as indicated by Agar and Hoar [1], the model and the prototype should obey Equation 1 and should have the same $\frac{K}{d}$ ratio while operating at constant i and V.

II: *Mass transfer or natural convection controlling regime*

If it is assumed that there is no forced convection (movement of electrolyte by artificial stirring), then the voltage drop in this regime is dependent upon R_E and R_C. Unfortunately, however, the exact contributions of R_E and R_C cannot be predicted from the present state of theoretical knowledge. However, the variables which are involved in such a situation are known. Hence, an empirical approach has been adopted by applying the Buckingham Pi theorem [2, 3]. Eight variables, namely, V, I, θ, d, D, h, $g\,\frac{\Delta\rho}{\rho}$ and ν seem to be influencing mass transfer phenomena in the system. These variables have been defined and listed in Table 1. We have eight variables expressed in terms of four fundamental dimensions, namely, unit mass M, unit length L, unit time T and unit charge Q. Hence, we should get four dimensionless groups, which

Table 1. Nomenclature

Variable	*Symbol*	*Fundamental dimensions*
Current density	i	$L^{-2}\ T^{-1}\ Q$
Current per unit width	I	$L^{-1}\ T^{-1}\ Q$
Voltage across the cell	V	$ML^{-2}\ T^{-2}\ Q^{-1}$
Specific resistivity	θ	$ML^{3}\ T^{-1}\ Q^{-2}$
Distance of separation of electrodes	d	L
Height of the electrode	h	L
Diffusivity of electrolyte	D	$L^{2}\ T^{-1}$
Kinematic viscosity	ν	$L^{2}\ T^{-1}$
Quantity governing buoyancy force	$\frac{g\Delta\rho}{\rho}$	$L\ T^{-2}$
Specific conductivity	K	$M^{-1}\ L^{-3}\ TQ^{-2}$

Table 2. Dimensionless groups

Group		*Remarks*
Grashof number	$\frac{g\Delta\rho h^3}{\rho\nu^2}$	*Ratio of* (Characteristic buoyancy force) *to* (Characteristic viscous force)
Schmidt number	ν/D	(Mass transport by momentum *to* Mass transport by diffusion)
Ohmic resistance controlling group	$\frac{V}{i\theta d}$	—
Group dependant on geometry	d/h	—

are listed in Table 2. By rearrangement of these dimensionless groups one obtains by mathematical simplification:

$$i = \frac{V}{\theta d}(\text{Gr.Sc.})^m\ (d/h)^n \tag{2}$$

Noting that $\frac{1}{\theta} = K$ the above equation becomes

$$i = i_{(\text{ohmic})}(\text{Gr.Sc.})^m\ (d/h)^n \tag{3}$$

Equation 3 can be further simplified as follows: For a constant potential gradient, $i_{(\text{ohmic})}$ is proportional to the bulk concentration C_0 hence

$$i_{(\text{ohmic})} = k\ C_0$$

$$i = k\ C_0\ (\text{Gr. Sc.})^m\ (d/h)^n \tag{4}$$

Equation 4 relates current density to the bulk concentration, cell geometrical variables d and h, and to mass transfer dimensionless groups, namely, Gr and Sc numbers.

2. Experimental results

Constants k, m and n were evaluated using the experimental data published by Wilke *et al.* [4] on the electrodeposition of copper from the acid copper sulphate bath under natural convection conditions.

The results are:

$$i = 0{\cdot}825\ (\text{Gr. Sc.})^{0{\cdot}16}\ (d/h)^{0{\cdot}75} \tag{5a}$$

and

$$i = 0{\cdot}412\ (\text{Gr. Sc.})^{0{\cdot}16}\ (d/h)^{0{\cdot}75} \tag{5b}$$

Limitations:

(a) Equation 5 (a) for high copper sulphate concentrations

$$0{\cdot}25 < C_0 < 0{\cdot}75 \text{ molality } CuSO_4$$

(b) Equation 5 (b) for low copper sulphate concentration about

$$0{\cdot}050 \text{ molality } CuSO_4$$

(c) for both 5(a) and 5(b): $6{\cdot}0 \times 10^6 < \text{Gr} < 10^9$
$2000 < \text{Sc} < 3000$

3. Discussion

The problems involved in scale-up are simple and direct in the first case where the ohmic resistance-controlling regime is operative. This is because the equation governing the scale-up is the well-known Ohm's law. But often one encounters electrochemical systems of the second kind, where a natural convection regime is controlling. Correlations useful for the scale-up of electrolytic cells have been derived and tested with experimental data on the electrodeposition of copper (see Table 3). The results are in very good agreement with the theoretical relationships. The average absolute deviation of Equation 5 is only 6·5% (Table 3). Although errors were of the order 10% to 15% in a few cases, the equations

Table 3. Electrodeposition of copper under natural convection

No.	*h*(cm)	*d*(cm)	*d/h*	C_0 *Molality*	Sc	*Gr* 10^{-9}	*i expt.* mA cm^{-2}	*i calc.* (*Eq.* 5 (a) or (b)) mA cm^{-2}	*Deviation* %	*Authors and references*
1	10	15	1·500	0·051	2524	0·0845	1·90	1·84	−3·16	Fouad and Ahmed [5]
2	20	15	0·750	0·051	2232	0·673	1·55	1·53	−1·33	
3	30	15	0·500	0·051	2814	1·852	1·38	1·35	−2·19	
4	40	15	0·375	0·051	2814	4·389	1·30	1·28	−1·54	
5	50	15	0·300	0·051	2814	8·572	1·201	1·165	−3·00	
6	0·635	10	15·75	0·0498	1943	0·00001167	4·20	4·85	+15·50	Wilke *et al.* [4]
7	7·620	10	1·31	0·0498	2117	0·01859	2·09	1·80	−13·90	
8	10	15	1·500	0·247	1863	0·2250	20·0	20·0	—	Fouad and Ahmed
9	20	15	0·750	0·247	1863	1·806	15·50	16·52	+6·5	
10	30	15	0·500	0·247	1902	6·011	14·33	14·81	+3·35	
11	40	15	0·375	0·247	1863	14·45	13·00	14·00	+7·70	
12	50	15	0·300	0·247	1902	27·82	12·80	12·92	+0·93	
13	0·635	10	15·75	0·247	2369	0·00004575	27·55	31·20	+13·20	Wilke *et al.*
14	3·81	10	2·62	0·247	2186	0·01018	16·60	19·50	+17·50	
15	7·62	10	1·31	0·247	2207	0·08403	14·05	15·70	+11·80	
16	0·635	10	15·75	0·660	2878	0·0001006	94·65	97·00	+2·48	Wilke *et al.*
17	2·54	10	3·94	0·660	2464	0·007437	66·30	66·70	+0·63	
18	7·62	10	1·31	0·660	2763	0·1797	44·1	49·40	+12·00	

Average absolute deviation = 6·5%

Note. Data reported by Fouad and Ahmed pertains to vertical electrodes with angle of inclination = 90°, Table V of reference 5.

seem to predict the experimental data reasonably well, notwithstanding the large variations in d/h from 0·3 to 15·75.

Scale-up criteria in electrochemical systems should probably be based on two factors:

(i) To first determine precisely the regime of the controlling mechanism.

(ii) To determine and to preserve (or alter if necessary) the geometric and transport parameters in accordance with the relationships derived above.

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