LETTER

Comments on the paper 'The performance of a forced-flow parallel plate electrochemical reactor with dilute solutions' by A. T. Kuhn and B. Marquis

The recent paper by Kuhn and Marquis [1] is an interesting study of a parallel plate electrochemical reactor which broadly corresponds to work done elsewhere [2, 3, 4], the latter two references being reports of an extensive theoretical and experimental investigation of cells having short hydrodynamic entrance lengths.

There are a number of points raised that are worthy of note. The first is rather minor and concerns the validity of the equation

$$\frac{V dC}{dt} = -k_L A C \qquad (1)$$

in describing the change in concentration of reactant with time in a batch system with continuously recirculating electrolyte. The concentration is more correctly described by the differential equation

$$\frac{MV}{R^2}\frac{d^2C}{dt^2} + \frac{1}{R}\left\{M + V\frac{(1+k_L A)}{R}\right\}\frac{dC}{dt} + \frac{k_L A C}{R} = 0 \qquad (2)$$

where M is the cell volume, V the total electrolyte volume less the cell volume, and R the flow rate. For $V \gg M$ and $1 \gg k_L A/R$ Equation (2) reduces to Equation (1) which under Kuhn and Marquis's experimental conditions ($V/M \approx 60$ for a 7 mm electrode separation) is a very good approximation. A paper fully discussing the behaviour of batch cells with recirculating electrolyte is under preparation [5].

A second point concerns the use of the Chilton–Colburn relationship expressed by

$$\frac{k_L}{u}\left(\frac{P_{BM}}{P}\right)\left(\frac{\mu}{\rho D}\right)^{0.56} = 0.023 \ Re^{-0.17} \qquad (3)$$

The above equation (which appears to have two misprints in Kuhn and Marquis's paper) is only applicable as such to correlate gas phase mass transfer data, hence the inclusion of the drift factor term P_{BM}/P to account for non-equimolecular counter diffusion. The liquid-phase equivalent to Equation (3) would have an analogous C_{BM}/C term, but it is better to use the original Chilton–Colburn relationship [6]

$$j_m = \frac{k_L}{u}\left(\frac{\mu}{\rho D}\right)^{\frac{2}{3}} = 0.023 \ Re^{-0.2} \qquad (4)$$

which has been successfully used by many workers for correlating electrolytic mass transfer data, in particular by Hubbard and Lightfoot [7] and Pickett and Ong [4] for parallel plate cells.

A better equation to predict data for short hydrodynamic entrance lengths and with an electrode length, L, less than twelve equivalent diameters of the cell, is

$$j_m = \frac{k_L}{u}\left(\frac{\mu}{\rho D}\right)^{\frac{2}{3}} = 0.125\left(\frac{L}{de}\right)^{0.2} Re^{-\frac{1}{3}} \qquad (5)$$

For $L/de = 10$ and $Re = 2000$, k_L predicted by Equation (5) is about three times greater than that of Equation (4) which is consistent with Kuhn and Marquis's observations.

The effect of nodules of copper formed at the cathode on the flow is in general less than postulated by the authors. A surface is defined as hydraulically smooth if [8]

$$\frac{u h \rho}{\mu} < 100 \qquad (6)$$

where u is the mean velocity and h the height of a projection. For the above condition, friction factors and mass transfer coefficients should be substantially unaffected by projections. For laminar flow, roughness has little effect in any event, effects being confined more to turbulent

conditions. It is conceivable that roughness effects are less than postulated over the range of Reynolds numbers used.

In the opinion of the writer two other explanations of some mass transfer enhancement are possible. The first is the presence of a very short hydrodynamic exit length. Studies [9] have revealed that equal or greater mass transfer rates are obtainable near the cell exit compared with the inlet. There could also be an enhancement due to the disruption of the mass transfer boundary layer at the cathode by hydrogen evolution. Such results have been obtained in a continuous flow parallel plate gas electrolyser [10] with a long hydrodynamic entrance length. Verification of this might be seen as increasing the deviation from the concentration/time relationship implied by Equation (1) as hydrogen evolution becomes more significant.

Notwithstanding the above observations, the writer concurs with a number of opinions and conclusions of Drs Kuhn and Marquis concerning the design of electrochemical cells in general.

References

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The authors are grateful to Dr Pickett for pointing out the error (use of P_{BM} in place of C_{BM}) in the paper. However since this factor was actually set at unity—as stated in the paper—the results are not affected. They also take this opportunity of pointing out that the figure captions to Figs. 8 and 9 were reversed.

The other points find less sympathy with the authors. The aim of chemical engineering should be to provide the tools with which results can be explained, extrapolated or predicted in as reliable a way as possible. Nevertheless a simplified approach has certain advantages in the industrial context and such was the spirit in which the paper was written, indeed this point was explicitly made in the text. This dichotomy is well-illustrated by Dr Pickett's first set of Equations (1) from Marquis and Kuhn and (2)—presumably his own. In the pedantic sense, Equation (2) is undoubtedly the full and correct one. But in so far as the design and operation of the actual experiment in question is concerned (and Pickett admits this himself) the added complexities of Equation (2) are not necessary. The authors considered this before writing the paper (indeed while designing the experiment) and Equation (1) was employed on this basis alone.

In the same spirit, the use of the Chilton–Colburn analogy was felt to possess an inherent simplicity which was desirable while (again as stated in the paper) neither the design of the cell, with its short entry length, nor its operation, during which the cross-sectional area decreased significantly, merited a more complex interpretation. Though the ×4 agreement between prediction and results was felt to be satisfactory in these circumstances, a better agreement could obviously be found using more complex formulae. Jennings [1] has taken the formula:

$$I_{L,av} = 0.666 n F C_0 D (v/D)^{0.33} (U_c/vL)^{0.5}$$

described by Tobias et al. [2] in 1952 for use in entry regions of parallel plate cells and applied it over the whole range of the data of this paper. He finds the agreement to be ×2 or better, mainly within 50% as shown in Table 1 below. It would be instructive to compare the results obtained with this equation with those obtained by the use of Equation (5) from Pickett, perhaps using the data from this or some other paper. However, as Jennings has shown, very little

Table 1. Laminar flow of the electrolyte between parallel flat electrodes

Electrode separation (cm)	Av. linear velocity of electrolyte (U)	Hydro-dynamic entrance length L_e	Calculated $I_{L,av}$ A dm^{-2}				Actual $I_{L,av}$ A dm^{-2}			
			100 ppm	75 ppm	50 ppm	25 ppm	100 ppm	75 ppm	50 ppm	25 ppm
0·7	1·7 cm s^{-1}	3·3 cm	0·124	0·093	0·062	0·031	0·060	0·050	0·035	0·015
0·7	7·8 cm s^{-1}	15·3 cm	0·292	0·218	0·146	0·073	0·100	0·080	0·050	0·020
0·7	15·8 cm s^{-1}	40·0 cm	0·425	0·319	0·213	0·106	0·210	0·160	0·110	0·060
0·7	24·8 cm s^{-1}	49·0 cm	0·536	0·402	0·268	0·134	0·300	0·210	0·140	0·080
0·35	18·4 cm s^{-1}	9·2 cm	0·460	0·345	0·230	0·115	0·190	0·170	0·100	0·080
0·35	37·7 cm s^{-1}	18·9 cm	0·610	0·459	0·305	0·153	0·350	0·260	0·190	0·100
0·35	47·8 cm s^{-1}	23·6 cm	0·738	0·555	0·369	0·185	0·550	0·415	0·290	0·130

room for improvement exists. Also, one gets the impression from Equation (5) (as given by Pickett in his comments) that $k_L \propto L^{0.2}$ and that as $L \to 0$, so does k_L. At first sight these are rather surprising conclusions.

As regards the remainder of the comments, the original statement of the authors that the growth of copper nodules was so extensive that the cell cross-sectional area was *significantly* reduced with commensurate effects on N_{Re}, overrides any consideration of 'hydraulic smoothness'. Lastly, with regard to Dr Pickett's forthcoming publications, in the light of Jennings's calculations, there appears to be little enhancement over and above that predicted by Tobias *et al.* [2] to be accounted for. Enhancement due to cathodic gas evolution was mentioned in the original paper and it is not clear what Dr Pickett is trying to add in this respect.

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