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Improvements to the marker pulse technique of characterizing electrochemical reactors

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In the marker-pulse method of characterizing electrochemical reactors, unwanted coupling often occurs between the marker and detector electrodes. This makes the transient response hard to analyse and the continuous cross-correlation of input and output signals virtually impossible. The origins of the problem have been investigated and methods of minimizing the effect are described which produce clean transients and acceptable correlograms.

1. Introduction

A common technique of chemical reaction engineering [1] is the injection of dye into a chemical reactor; this may be as a pulse, a step or a sinusoidal oscillation in concentration. The response of a detector at the exit from the reactor, in general, will then be a skew Gaussian, a sigmoid, or a sinusoid of different phase and amplitude to the input. With the aid of a suitable mathematical model, the mean residence time and distribution of residence times in the reactor may be obtained by moment analysis or curve fitting. This principle has been extended to electrochemical reactors [2] in a form particularly suitable for electronic processing of the data. A pair of electrodes are positioned at the inlet and a pulse or step in voltage is applied to them; electro-active species, such as Cu^{2+} or Zn^{2+}, are injected into the fluid as a discrete concentration pulse or step at the anode. Downstream a similar pair of electrodes are held at the potential of the diffusion limiting current of the electroactive species, such that the current drawn is proportional to its concentration; the output of a current follower then gives the response to the input pulse or step. Since both input and output are in electrical analogue form, data acquisition is simple by strip chart, tape recorder or computer. This technique has been applied with reasonable success to short fluidized beds [2], packed beds [2, 3], bipolar trickle towers [4], capillary gap (disc stack) and pump cells [5, 6], and to battery systems [7], nevertheless certain deficiencies are apparent in the basic technique. These become particularly significant when the stimulus and the response are directly cross-correlated [8, 9].

Fig. 1a shows an idealized response at a detector to a concentration pulse injected upstream. The centroid of the distribution (normalized first moment) is a measure of the mean residence time, τ, of the injected material, while in principle the axial dispersion can be obtained from the first and second moments [1]. However, Figs. 1b and c show typical forms of observed transients; interference occurs at the detector simultaneously with the injection pulse. This may take the form of a voltage spike (Fig. 1b) or its differential (Fig. 1c). The form of the interference has been observed to be strongly dependent on the nature of the electrode–electrolyte system [3–5]. If the time delay before the marked material reaches the detector is long, then overlapping is not a problem, but if the moving phase is fast, or the distance between injector and detector short, then the overlap between the starting pulse and response causes error in the analysis [3]; if moment analysis is used then the errors in the zeroth and first moments can be appreciable, while curve fitting is always difficult. This interference also makes it impossible to cross-correlate input and output directly since the correlation at zero time delay is large and all other contributions (which contain the desired information) vanishingly small. The insertion of a time delay before recording the

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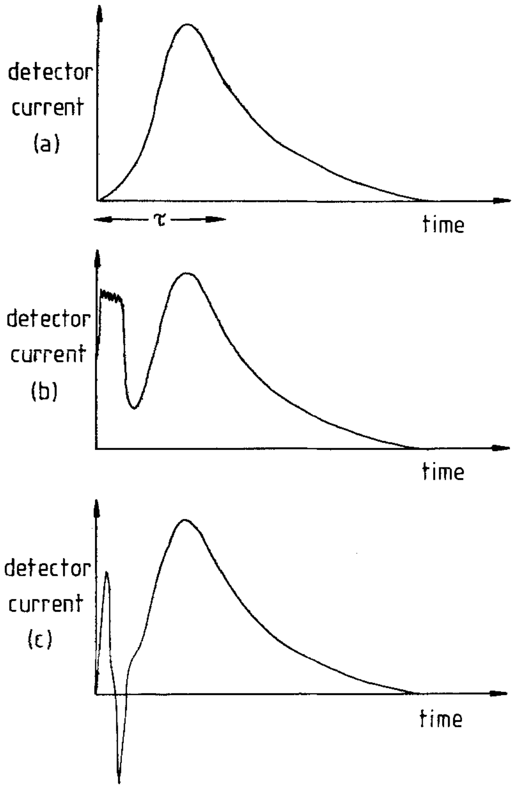

Fig. 1. (a) Idealized response curve to a δ-function input of marker. (b) and (c) Experimental responses showing interference at short time delays.

response to a discrete pulse, or of a pre-computational delay in correlator or computer, helps in some cases, but is clearly undesirable when some real information arrives at short times (e.g. break-through in a fluidized bed). This paper is concerned with the identification of the origin of the interference and its suppression.

2. Experimental investigation and discussion

The electrolyte used throughout this investigation was cupric sulphate (typically 10^{-3} M) in aqueous sulphuric acid (pH $\simeq$ 1). The cupric ion concentration was monitored by a copper wire cathode with a copper gauze as counter electrode, the cathodic overpotential being raised until the current flowing in the detector circuit was mass transfer limited. Under these conditions, the current flowing in the detector circuit was an analogue of local cupric ion concentration. The marker electrodes were both copper gauzes (40 gauge).

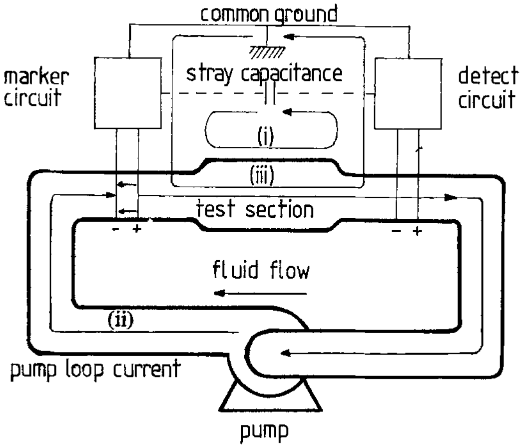

Fig. 2. Schematic diagram of possible current paths: (i) by stray capacitance; (ii) by electrolyte loop; (iii) by common electrical ground.

Three sources of interference between input and output were identified: stray capacitance, the electrolyte loop, and the common electrical ground between marker and detector units (Fig. 2). These were investigated empirically.

Stray capacitance between marker and detector units can be minimized by careful layout of the electrical circuit. This brings about a significant improvement, but does not eliminate the problem entirely.

The closed loop recirculation path of the electrolyte is responsible for a second contribution. Most of the current in the marker circuit flows between the electrodes by the shortest path, but a fraction, albeit small, flows between the electrodes in the opposite direction, via the pump in a closed loop system (Fig. 2). This produces a potential drop between the detector and its counter electrode which perturbs the output current of the detector circuit (since, even with differential area electrodes, it is impossible to obtain a completely flat diffusion plateau for copper deposition). The effect of a pulse at the marker is then to give a response at the detector which has nothing to do with the convection of the marker ions and therefore carries no hydrodynamic information. The sense of the pseudo-response can be positive or negative, depending on the relative arrangements of the marker and detector anodes and cathodes.

Provided that the marker circuit was floated electrically (see below), it was found possible to eliminate this effect by using a pair of gauze

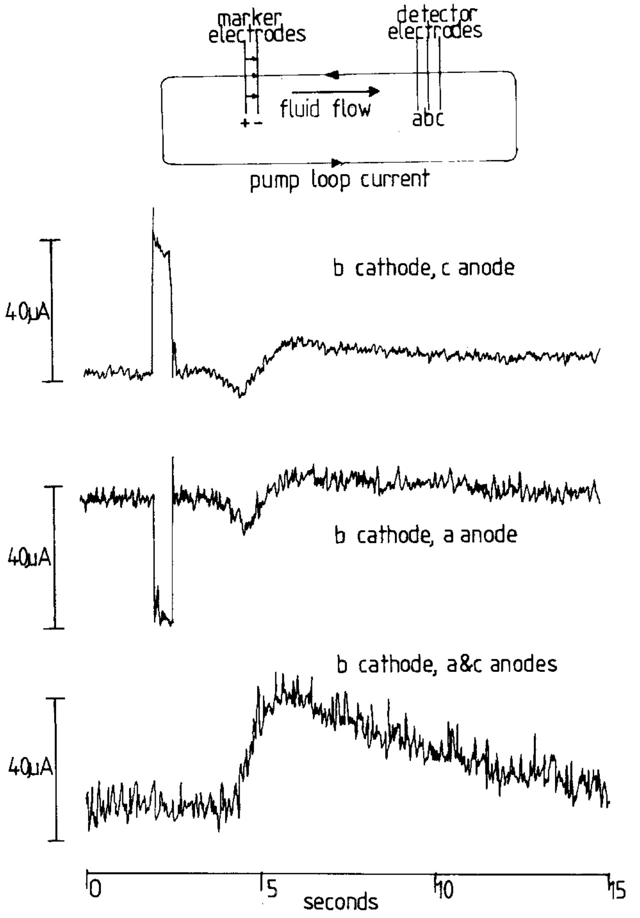

Fig. 3. Effect of detector electrode configuration.

counter electrodes as screens. Fig. 3 shows the effect of anode placement on the response; in each case electrode b is the cathode. When the detector anode is downstream of its cathode the recirculating pulse current augmented the detector potential and a positive spike is seen (Fig. 3a). Conversely when the detector anode is upstream of its cathode, the pseudo-response is negative (Fig. 3b), but if a pair of anodes (a and c) are used to screen the detector cathode, the initial pulse disappeared into the noise (Fig. 3c). Unfortunately this technique is not applicable when the detector electrodes are set into the wall (e.g. planar electrode) of a cell [7].

By far the most important source of interference is the direct electrical link when the marker and detector units have a common ground (Fig. 2). In this case current can flow from the marker, through the electrolyte, into the detector and return via the ground path. It is simple to break the electrical ground loop in the case of discrete pulse excitation; for example the marker circuit can be supplied by a floating voltage source such as dry cell batteries, but this procedure is not directly applicable to the direct cross-correlation of detector response with continuous input to the market (such as random binary noise), since a digital correlator or computer requires a common reference point for the two analogue voltage signals. The correlation technique is also sensitive to the nature of the marker electrode system; a copper marker counter electrode (cathode) tends partially to nullify the effect of the marker anode ('mirroring'), since only the difference between the copper dissolved and deposited serves to 'mark' the solution. Increasing the amplitude of the pulse applied from the floating source helps, but this also increases the electrical interference described above.

Cross-correlation experiments using a platinum

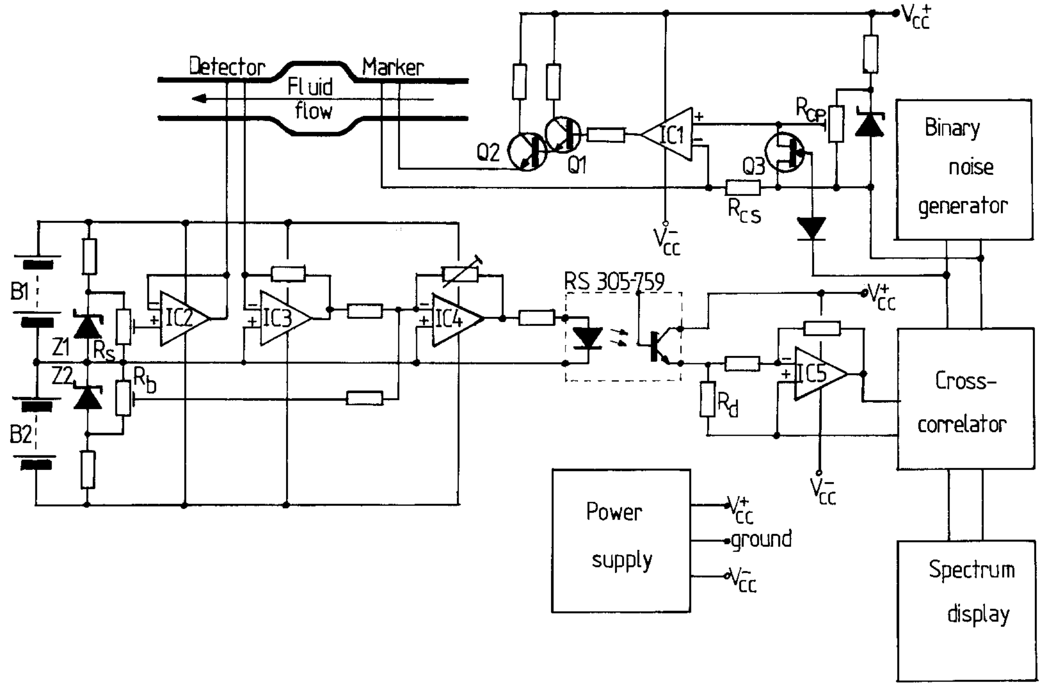

Fig. 4. Optically coupled detector and marker circuits.

marker counter electrode were unsuccessful due to the evolution of gas bubbles, which altered the hydrodynamic conditions in the cell and also caused extra noise in the detector signals. Marshall [7] has shown that the presence of bubbles in a parallel plate reactor can increase the apparent dispersion by two orders of magnitude. Attempts to place the marker counter electrode in a side arm were abandoned, since it was found impossible to achieve a uniform current distribution across the marker electrode, and thereby a uniform distribution of marker species in the fluid.

Nevertheless correlograms can be obtained if the electrical circuit is broken by driving one circuit from a floating source and coupling the signal to the main network by means of an optical link (Fig. 4). The current generator driving the marker electrodes is referenced to mains ground. The high gain of the operational amplifier (IC1) with the Darlington coupled output transistors (Q1, Q2) maintains a current between the marker electrodes such that the voltage dropped across R_{CS} is equal to that set by potentiometer R_{CP}. This current can be turned on and off, via the FET switch (Q3), by a binary noise generator. The detector circuit is driven from floating voltage supplies (batteries B1, B2) and is thus electrically isolated from mains ground. Potentiometer R_s across the zener, Z1, sets the voltage applied to the electrode pair via a voltage follower buffer (IC2). The current follower (IC3) output is biased with a voltage derived from zener, Z2, and potentiometer, R_{B}, by summing amplifier (IC4) in order to operate the LED in a reasonably linear region. The phototransistor in the optical coupler (RS 305-759) drives current through and a voltage drop develops across R_{D} referenced to the mains ground. This is amplified by IC5 and presented to one channel of the cross-correlator. This arrangement [8] was used to measure the impulse response of a model cell containing a bed of dumped glass beads, separated from the counter electrode by a Nafion membrane (Fig. 5). The counter electrode of the marker circuit was placed on the far side of the membrane, thus eliminating the 'mirroring' effect described above. Marking was achieved by using a 200 mA current source switched by a random binary signal from a Hewlett-Packard generator (3722A) clocked at 10 Hz. The correlograms (average of 2048 samples) computed using a Hewlett-Packard digital correlator (3721A) are presented for three flow rates in Fig. 6. Even

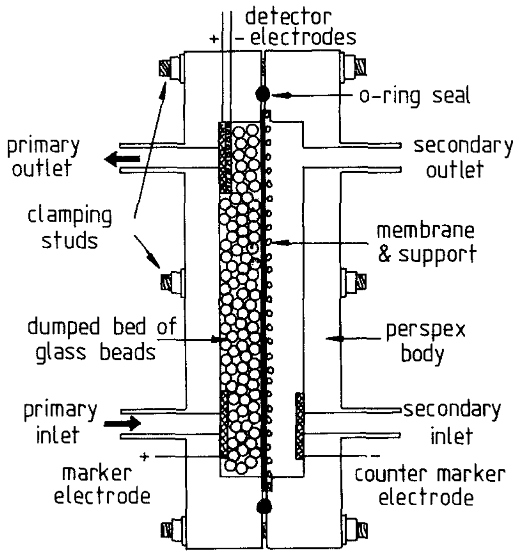

Fig. 5. Model two-dimensional packed bed cell.

though the quality of the data is still not good, it is clear that the shape of the response is a function of flow velocity; in principle the quality of the data can be improved by taking more samples at the cost of increased time. For comparison, a correlation is also shown which was obtained for the same system but with the common ground link unbroken. Note the change in vertical scale; the difference is dramatic. Without the optical isolator only the spurious response at zero time delay due to the artefacts described above, is significant and no meaningful information can be obtained.

3. Summary and conclusions

While the marker-pulse technique is a powerful tool in electrochemical engineering [2–6] con-

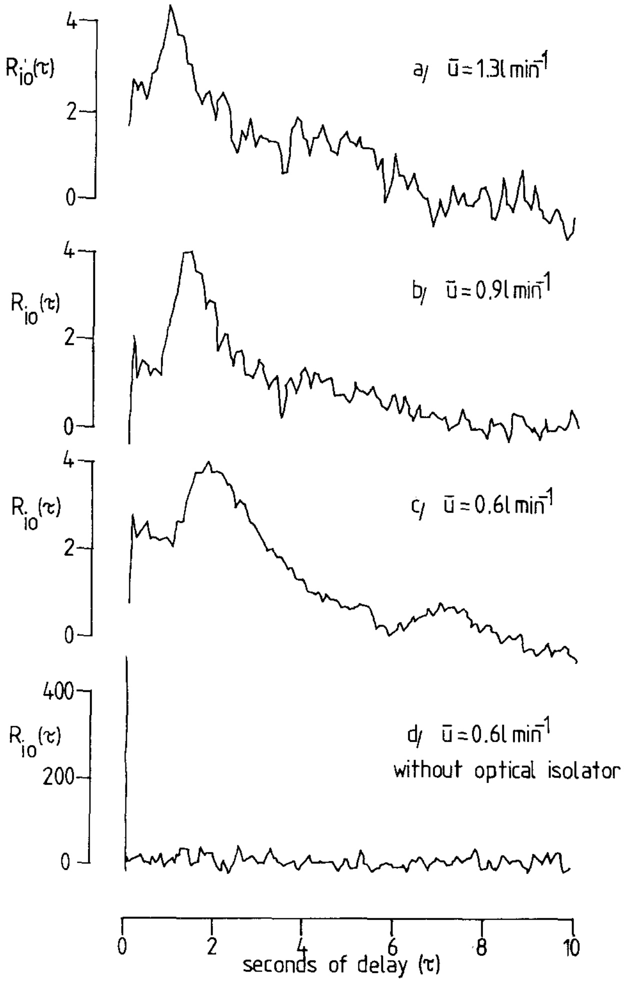

Fig. 6. Cross correlograms; (a), (b) and (c) with optical isolator, (d) without optical isolator showing spike at zero time delay.

siderable care must be taken when using electrochemical transducers as monitors of electrochemical systems. In the case of single pulse excitation, careful circuit design to eliminate stray capacitance, and the use of a floating source to eliminate a ground loop, may be adequate and good results can be obtained. However, the use of an optical isolator to decouple input from output electrically yields further improvement, and is essential when closely spaced arrays of detectors [7] are used, or the input and output are directly cross-correlated, as in the measurement of the transfer function of a reactor by continuous perturbation [8].

The optical isolator used in this investigation (RS 305-759) was developed for digital signal transmission and is subject to severe limitations when used for analogue signal transfer. This problem of non-linearity in the optical isolator can be circumvented by driving the marker rather than the detector electrodes from a floating source, since, in continuous perturbation experiments the marker is excited with a binary signal for which the optical isolator was designed. However, this is not always convenient, because there may be many detectors present which are mutually interactive. Also it is usually not feasible to drive the reactor electrodes themselves from a floating source, which would be required in the investigation of cell potential–concentration response functions by this technique. The approach of isolating the detector circuitry is thus considered to be of more general applicability.

The biasing circuitry necessary to operate the optical isolator in the restricted linear region can add to the problem of (uncompensated) drift already present in the detector system, as can be seen from the sloping baselines in Fig. 6. In control applications [8], stability over periods of thousands of seconds is necessary. Fig. 6, for example, shows that, even in a small model cell, the frequencies of significant processes predominantly are in the region of 0·1–1·0 Hz. Obviously as the scale increases the significantly time constants grow and the problem of differentiating a change in performance from spurious drift becomes crucial [8]. Considerable improvement is to be expected from the use of negative feedback around the matched dual channel optical isolators and single emitter/double detector optical isolators which are now available [10]. Work is progressing on these aspects of improving the quality of experimental data; the mathematical difficulties of extracting information from the data are discussed elsewhere [3, 6, 11].

The technique of optically isolating electrochemical concentration monitoring transducers, such as pH probes, is now employed routinely in this laboratory.

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