JOURNAL OF APPLIED ELECTROCHEMISTRY **10** (1980) 473–479

A multi-electrode charge injector for selective metal deposition

CH. YARNITZKY, M. ARIEL, C. ZUR

Department of Chemistry, Technion IIT, Haifa, Israel

Received 7 August 1979

The design of a charge injector potentiostat for the correction of *iR* drops in a multi-electrode system is described. The quality of performance obtainable with this instrument is demonstrated by using it to control the potentials of two working electrodes in a flow system, in which the *iR* drops are interdependent and potential control with an ordinary dual electrode potentiostat is therefore ineffective. The instrument supplies driving currents up to 200 mA to each of the electrodes, by applying pulses of 800 mA amplitude and 10 μs width; its lowest charge pulse is of the order of 4×10^{-8} C. Additional charge injector stages may be introduced to control the potential of any desired number of working electrodes. The schematic diagram of the instrument and results of performance tests carried out with a dummy cell and both batch and flow electrochemical cells are reported. In the flow cell, with its twin graphite cloth electrodes held at potentials suitably controlled by the instrument, Cu and Cd were successfully electroseparated.

---

1. Introduction

Flow systems employing several electrodes on which different metals may be accumulated have been proposed as a useful device for water purification [1]. Their adaptation to the continuous electroseparation of metals on an array of stacked electrodes has also been considered [2]. The success of such direct separations hinges on the adequate control of the potential of the electrodes during the electrolysis step. The problem of multi-electrode potential control [3] is complicated by the high potential drops usually encountered in such systems (of the order of a few hundred millivolts); with inadequate control, separation is incomplete and the metal deposits become impure.

Among the hitherto unsuccessful attempts to solve this problem, the use of individual Luggin capillaries reaching down to every electrode and manually controlled positive feedback is clearly most unfavourable for any sort of scaled up operation. The dynamic compensation technique [4], so useful in compensating *iR* drops in many situations also fails here; the technique employs a small alternating voltage signal superimposed on a variable potential. In the multi-electrode system this signal must be applied to each of the electrodes independently and the resulting alternating currents influence each other; improper opening of the electronic gate, resulting in compensator instability and low-frequency oscillations, occurs. In addition, quite often, hydrogen gas bubbles collect on the electrodes, abruptly changing cell resistance and leading to potential drops exceeding the scope of the compensator.

In this paper a definite solution of the problem is described, based on an adaptation of the digipotentiogratör suggested by Goldworthy and Clem, which injects or extracts the charge required to maintain the working electrodes at the desired potential [5]. The potentials of the working electrodes are measured intermittently under open circuit conditions and compared to the potentials applied to each; if too high, negative charge is injected and vice versa. A simple synchronization circuit ensures that charge injection, where required, takes place in the intervals between potential measurement.

2. Design philosophy

The specifications for the new instrument: maximum driving potential 40 V and maximum current

0021–891X/80/040473–07$02.70/0

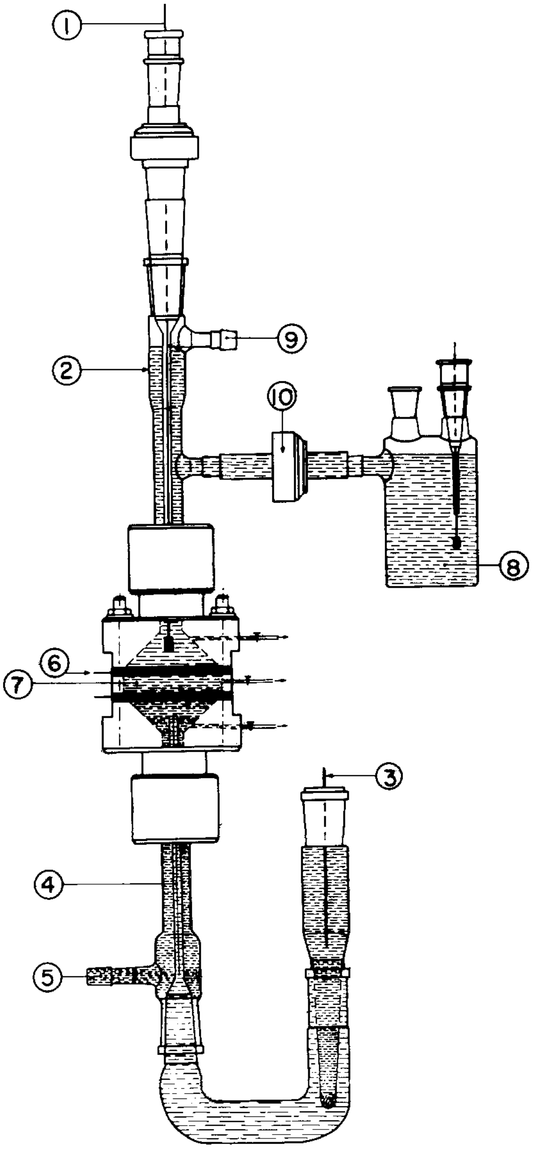


Fig. 1. Flow cell: (1) counter electrode; (2) flow tube; (3) reference electrode; (4) Luggin capillary; (5) flow inlet; (6) single screen; (7) spacer; (8) second counter electrode; compartment used during electrodissolution of deposited films; (9) flow outlet; (10) ion-exchange membrane holder.

supplied to each electrode 200 mA, necessitated major changes in its circuit. Further changes resulted from dispensing with digital read out.

To meet the demands of the flow cell (Fig. 1), the charge injected in each pulse was increased: minimum and maximum charges are 4×10^{-8} and 8×10^{-6} C, respectively; pulse width is 10 μs and maximum duty cycle 0.25.

Since at least two working electrodes are employed, the counter electrode is grounded; the potential difference between each working electrode and the reference electrode is compared to the desired potential, by means of an electronic comparator. The amplified output of the latter is fed through sample and hold circuits into two driver transistors which trigger the positive and negative pulse current generators. If the input of the comparator is less than ± 2 mV no charge is injected; this constituted the only source of error in the potential control.

The instrument is divided into three parts: (a) a power supply and pulse generator which drive all stages of the charge injection system; (b) a charge injection driving system for each of the working electrodes employed (the present instrument demonstrates the principle with two working electrodes, but more may be added as required); (c) power pulse charge generators driven by the charge injection systems.

3. The electronic circuit

The schematic diagram of the power supply is shown in Fig. 2. The timer 555 forms a square wave which is fed into a simple flip-flop. The direct and complementary outputs of the flip-flop and the square wave are connected to gates to give the waveforms shown in Fig. 3. As will become apparent later, G_1 isolates the S and H circuit from fast transients appearing at the output of the comparator stage, while G_2 triggers the univibrators driving the pulse currents. The schematic diagram of the charge injection stages are shown in Fig. 4. O.A.$_1$ is a simple follower, used to measure the working electrode potential; its input is clamped by diodes to + 5–5 V and may lead to an error up to 3% in the low current ranges; on the other hand, in these ranges and at the usual cell resistances encountered (of the order of 1 kΩ) the *iR* potential drops requiring compensation are small and do not exceed 5 V. O.A.$_R$ is another follower, connected to the reference electrode (*one* only, whatever the number of working electrodes). The comparator is, in effect, an operational amplifier O.A.$_2$, which adds the input and reference potentials and subtracts the working electrode potential.

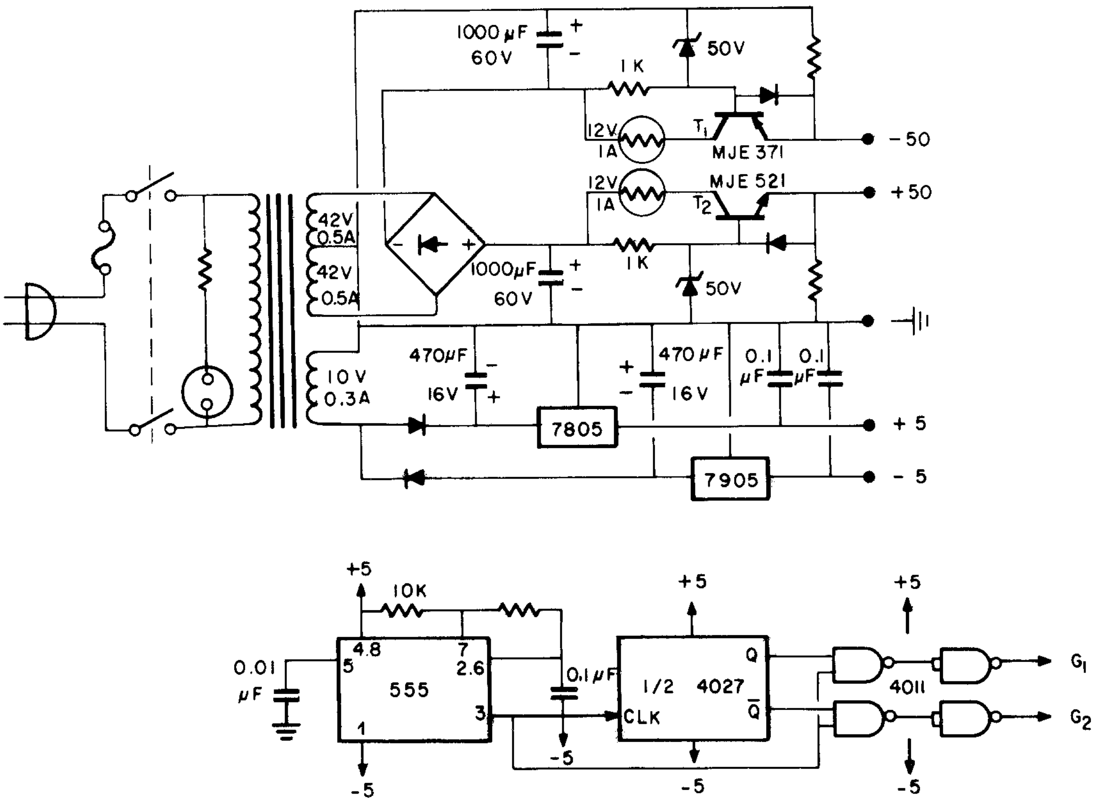


Fig. 2. Schematic diagram of the power supply.

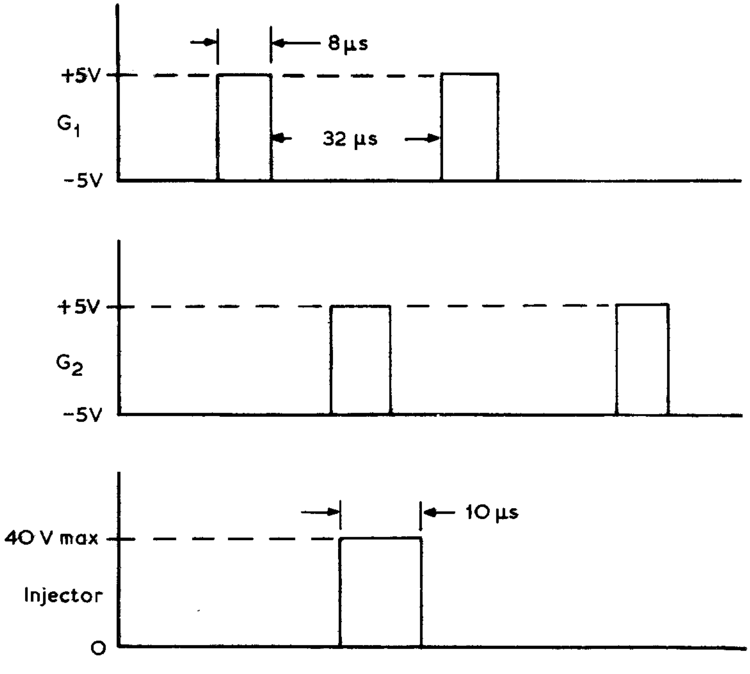
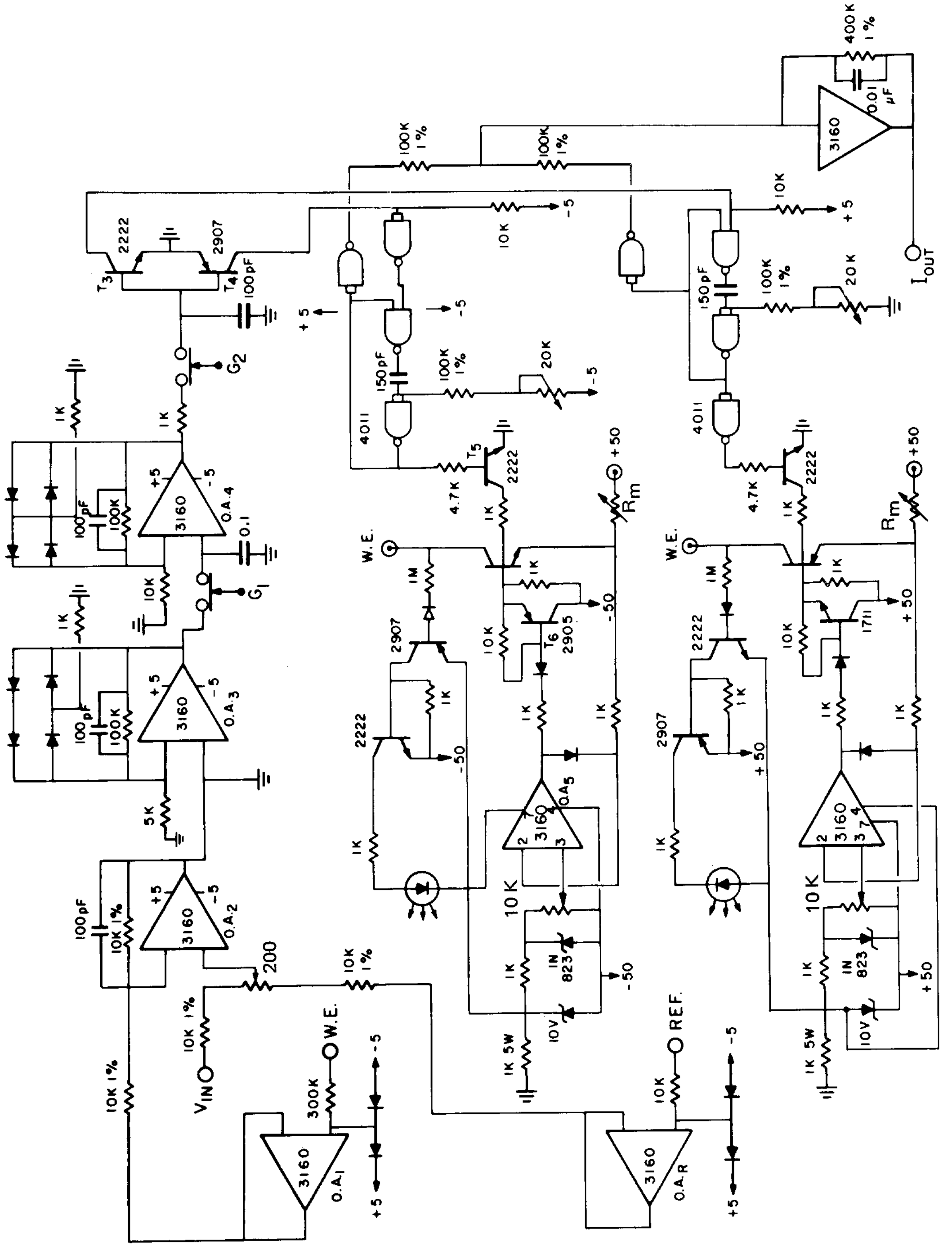


Fig. 3. Waveforms of various stages.



All diodes are IN 914 unless otherwise indicated.

Fig. 4. Schematic diagram of charge injection stage. R_m is the current range resistor.

When balanced,

$$V_{\mathrm{O.A.}_2} = V_{\mathrm{in}} + V_{\mathrm{ref}} - V_{\mathrm{work}} = 0$$

or

$$V_{\mathrm{in}} = V_{\mathrm{work}} - V_{\mathrm{ref}}.$$

$\mathrm{O.A.}_3$ amplifies the signal of $\mathrm{O.A.}_2$ by a factor of 20.

$\mathrm{O.A.}_4$ acts both as a sample and hold circuit and amplifier; the signal is sampled, by means of gate G_1, after all potential transients due to charge injection have practically decayed to zero. The output of $\mathrm{O.A.}_4$ is transferred to the univibrators through transistors T_3, T_4 and a second gate G_2. The time constant of the resistor–capacitor connected to this gate is sufficiently short to ensure repetitive operation when needed. The univibrator circuits utilize NAND gates in the configuration suggested by the manufacturer of CMOS devices.

The driving pulse is transferred to the base of the appropriate power transistor. The combination of the $\mathrm{O.A.}_5$ and the transistor T_6 maintains a constant potential across the range resistor; this potential, divided by the resistor value, determines the pulse current. Part of this current (about 1%) flows through the base and varies with temperature and current range; overall stability is about 0.3% which is acceptable for most applications.

4. Performance tests

4.1. *Dummy cell*

The usual combination of two resistors in series with a capacitor connected to a resistor in parallel is used in the final test. Fig. 5a shows voltammograms recorded with a dummy cell connected to the new system as compared to Fig. 5b, where it is shown connected to a common potentiostat.

Some care must be expended in the choice of current range. Unlike the regular current to voltage converter, in which electrochemical parameters need not be considered, the charge injection technique depends on double layer capacitance and cell resistance. Ideally the charge injected should not alter the potential across the double layer appreciably (i.e. more than a fraction of a millivolt; in the instrument described, the gap between positive and negative charge injection is a few millivolts).

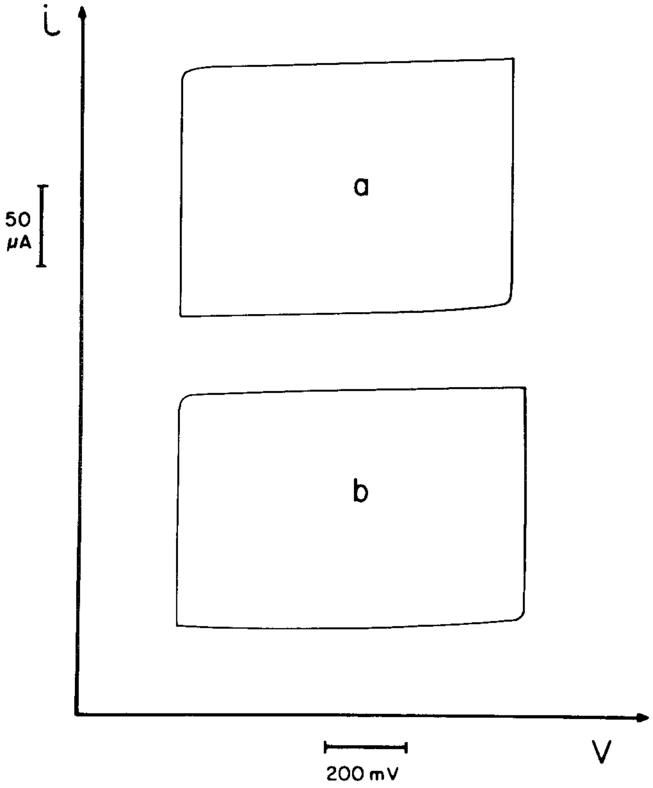


Fig. 5. Comparison of voltammograms recorded with a dummy cell; (a) with charge injector; (b) with common potentiostat; scan rate 20 mV s^{-1}.

The current of the pulse, multiplied by cell resistance, clearly must not exceed 40 V; if it does, false current readings will result.

4.2. *Electrochemical cells*

4.2.1. Batch cell – $K_3Fe(CN)_6$. A batch cell containing a Pt working and counter and an Ag/AgCl/KCl reference electrode and filled with 10^{-3} M $K_3Fe(CN)_6$, 0.5 M KCl (pH 8–9) solution, was next used to test the instrument. Perfectly matched cyclic voltammograms, undistinguishable from those recorded with a potentiostat–positive feedback combination, were obtained, whatever the mode of operation: each control unit alone or both working simultaneously. The linear correlation between current peak height and the square root of the rate of potential scan was maintained in the 10–200 mV s^{-1} range.

4.2.2. Multiscreen flow cell – $K_3Fe(CN)_6$; Cu^{2+} + Cd^{2+}. The flow cell with its twin graphite cloth electrodes (diameter 35 mm) and its Ag/AgCl/KCl references and Pt gauze counter electrodes shown in Fig. 1, was next connected to the instrument and the $K_3Fe(CN)_6$ solution streamed through it. Cyclic voltammograms recorded with this cell again showed the two control units yielding identical results and capable of working simultaneously without affecting each other's performance.

Cyclic voltammograms run on a 10^{-3} M Cu^{2+}, 10^{-3} M Cd^{2+}, 0.5 M KCl, pH 3 solution, compared with those obtained in this cell and under equivalent flow conditions with a potentiostat–dynamic *iR* drop compensator set up, are slightly improved: the current peaks are sharper (Fig. 6).

4.2.3. Multiscreen flow cell – Cu, Cd deposition. The performance of the instrument was next tested in a more complex situation, where it was shown to provide excellent potential control while the potentiostat–compensator combination failed.

Selective separation of two metals by electrodeposition on stacked (in our case: twin) electrode screens required the independent potential control of the electrodes, at values dictated by the metals to be separated and the medium employed. One of the principal factors governing separation efficiency is the difference in deposition potentials; in the model system employed, 10^{-3} M Cd^{2+} + 10^{-3} M Cu^{2+}, 0.5 M KCl, pH 3, this is about 0.5 V.

As a first step, the independent potential control of each screen electrode was checked. In the flow cell, since each screen may be regarded as interposed between the solutions (and, as the

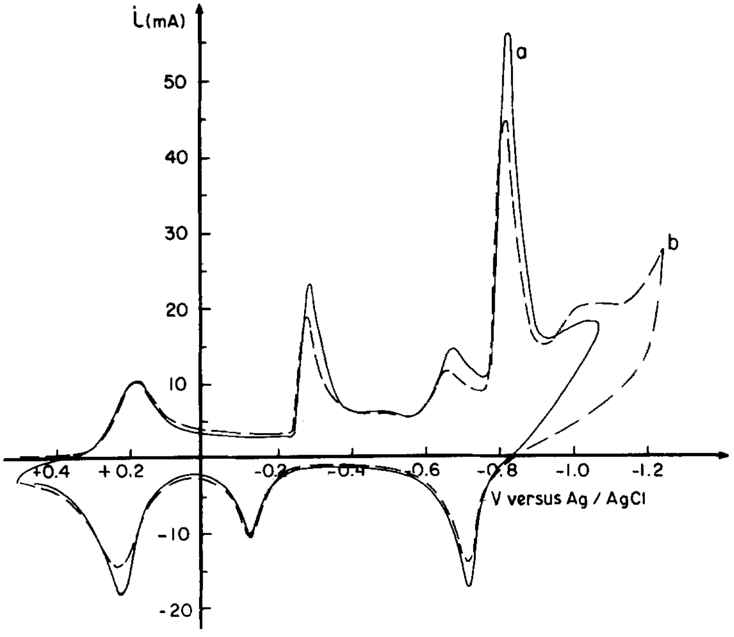


Fig. 6. Comparison of cyclic voltammograms run on a 10^{-3} M Cu^{2+} + 10^{-3} Cd^{2+} in 0.5 M KCl, pH 3 solution; scan rate 20 mV s^{-1}: (a) with charge injector; (b) with a potentiostat connected to an *iR* compensator.

case may be, additional screens) up and downstream from it, the question of electrical masking must arise.

As long as no current flows through the cell, no potential difference is measured between the tips of two identical reference electrodes bracketing the screen (whatever the voltage imposed between the latter and the counter electrode). The passage of current, i.e. the occurrence of electrode reactions at the screen, affects solution composition; the solutions before and after the screen are no longer identical, and potential differences across the screens result. These may, however, be minimized by employing fairly concentrated supporting electrolyte solutions; under the experimental conditions described (e.g. during the deposition of Cu^{2+} leading to a 97% decrease in $[Cu^{2+}]$ from one face of the screen to the other), these potential differences did not exceed 10 mV and were considered negligible. Significantly larger changes in the potential profile in the cell are due to the ohmic potential drops which accompany the passage of current. In the multiscreen cell their compensation is a complex problem, practically insoluble by conventional methods. Although that part of the drop relating to the solution resistance between the first screen and the counter electrode (and the current through the first) is easily dealt with, additional currents, flowing from other screens to the counter electrode complicate the picture; adequate potential control of the second (or any additional screens – if present) becomes problematic.

A further complication arises from the continuing change in electrode surface accompanying the deposition of metal films on the graphite screens; the increasing deposition currents again lead to changes in ohmic potential drops. Attempts to compensate for these constantly changing potential drops with a double potentiostat and two dynamic compensators (i.e. one for each screen) failed.

A flow cell equipped with a graphite cloth electrode has been used to establish optimum conditions (concentration range, solution flow rate and imposed potential) for the controlled potential electrodeposition of Cu from Cu^{2+} and of Cd from Cd^{2+} solutions [4]. These were adapted for the flow-cell shown in Fig. 1, i.e. solution flow rate was increased to 16 $cm^3\ min^{-1}$ to fit the increased electrode area; the multielectrode charge injector was used to impose screen potentials of -0.6 V and -1.1 V versus the reference electrode on the first and second screen for the successive deposition of Cu and Cd.

10^{-3} M Cu^{2+} and 10^{-3} M Cd solutions were first run separately, with only one screen operating at the appropriate potential. At the flow rate and potentials employed, a steady state of 97% recovery for both metals was achieved after a short initial period required for the build up of the first layers of metal films on the electrode. For Cu this takes about 5 min (during which Cu recovery is in the 60–70% range). The Cu deposit is dendritic; electrode area, deposition current and hence also ohmic potential drop in the cell increase with time. In the Cd deposition the initial stage lasts only 2 min, thereafter 97% recovery is sustained.

The simultaneous removal of Cu^{2+} and Cd^{2+} from a flowing solution containing both metal ions, with Cu depositing on the first and Cd on the second screen, was carried out as follows: a potential of -0.6 V was imposed on the first screen for 5 min to ensure complete coverage and 97% Cu recovery; the second screen is then activated at -1.1 V, to deposit Cd (with the first maintained at -0.6 V). This mode of operation prevents Cu from depositing on the second screen during the initial period).

The Cu deposited on the first screen was practically free of Cd metal (at least 99% pure); the Cd, on the second, obviously contained the 2–3% Cu which was not recovered by the first.

Accepted analytical methods were employed to check solution and metal deposit composition.

References

[1] D. Yaniv and M. Ariel, *J. Electroanalyt. Chem.* 79 (1977) 159.

[2] C. Zur, D.Sc. thesis, to be presented to the Senate of the Technion-I.I.T.

[3] D. T. Napp, D. C. Johnson and S. Bruckenstein, *Anal. Chem.* 39 (1967) 481.

[4] D. Yaniv, D.Sc. thesis, presented to the Senate of Technion-I.I.T. (1979).

[5] W. W. Goldsworthy and R. G. Clem, *Analyt. Chem.* 44 (1972) 1360.