A multi-purpose microprocessor-based electrochemical apparatus

D. GOSDEN

Tasmanian College of Advanced Technology, Launceston, Tasmania, Australia

M. HAYES, A. T. KUHN

Department of Chemistry and Applied Chemistry, University of Salford, Salford, Lancs., UK

D. WHITEHOUSE

Department of Electrical Engineering, Salford University, Salford, Lancs., UK

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A microprocessor-linked programmable calculator instrument is described. Current–voltage readings taken at predetermined intervals of time can be read, stored and passed to the calculator where they may be processed to yield Tafel slope data, ohmic drops, areas under curves (for cyclic voltammetry) or used in open-circuit decay calculations. The results may also be fed to a paper-tape punch for storage or graph-plotting using a larger computer.

1. Introduction

The use of a digital computer in the electrochemical laboratory is far from novel, indeed it forms the subject of a book devoted exclusively to the topic [1]. However, the years intervening since its publication have not seen the proliferation of this application that some might have predicted. Reeves [2] has highlighted some of the problems of the field, many of which seem at first sight to be trivial and only first-hand experience shows how real these are, and he testifies to the fact that on-line operation of a computer in a chemical laboratory is a difficult task, as well as being extremely costly.

The present paper describes one approach to the problem taken from the starting point of low cost and the acceptance of a limited range of applications. The focal point of the approach is the desk-top programmable calculator, preferably with tape-printer output. Such machines are now well within the reach of most educational establishments and their real prices are still falling.

Since many current programmable calculators have relatively slow reading rates (the Compucorp 327 has a maximum speed of 5 characters per

second), they can only be used 'on-line' to very slowly occurring processes. The solution, as described here, is to use a high-speed microprocessor unit (MPU) to acquire and store the data and then allow the calculator to call for the data from the store at its own speed. Our principle has been that this procedure allows a useful range of functions to be performed; furthermore, the software was arranged so that the whole assembly could largely be commanded through the keyboard of the programmable calculator, thus avoiding the well-known difficulty of programming or varying the functioning of the MPU.

The system described here records and stores electrode kinetic data in the form of current–voltage pairs. These pairs are then fed automatically into the calculator which processes them in the desired manner. The original intention was to analyse data taken in a Tafel region where the ohmic error was significant; under these conditions the Tafel equation becomes

$$\eta = a + b \log I + IR.$$

The procedure for solving this equation (using keyboard, i.e. manual, input of data) has already been described by some of us [3]. The Tafel slope,

exchange current density and ohmic drop are all obtained, together with a statistical analysis of the worth of the results. The usefulness of this equation is greatly extended by a more precise determination of I and V (or η), and on-line digital data processing as described here eliminates the errors due to transfer of data from conventional analog recorders by visual inspection and thence to the keyboard. With the same hardware and almost identical software, cyclic voltammetric data can be handled, and in particular the area under the peaks calculated between predetermined limits. Lastly, the equipment can be used to record chrono-potentiometric data and derive simple information from it such as in the open-circuit transient method used by Ord *et al.* [4]. In addition, the system allows the ready addition of a paper-tape punch to record the data either for permanent storage or for subsequent transmission to a graph-plotter. In this way, the tedium of plotting data by hand is eliminated. Digital techniques mean that data can be far more accurately obtained (and. thus operated upon) than is possible with conventional methods using $x-y$ chart recorders, for example.

2. Description of Equipment

The analog signals (current and voltage) which form the basis of the electrochemical data are converted into digital form by an analog/digital (A/D) converter. This can be achieved either by a separate A/D converter which then becomes a 'dedicated' item or by use of a digital voltmeter having a BCD output: the latter not only provides a visual display of the parameter being measured, but may also be used independently of the MPU system, especially if its output is taken out via detachable multipole connectors. Another point in the favour of a separate digital meter is that (at least at the present) digital panel meters are scarcely more expensive than the comparable individual A/D converter alone, (fast response A/D converters are much more expensive). Of the commercially available DPMs, those made by Normalair Garrett Ltd (NGL) have the fastest reading rate, being selectable up to 50 readings per second.

It was recognised that current—voltage data might be obtained either with two separate A/D converters or by multiplexing the output of a single A/D converter. Two NGL type 6030ER DPMs were already available and since their settling time is around 150 ms, multiplexing would restrict the application to relatively slowly changing $I-V$ inputs. These meters are of the $3\frac{3}{4}$ digit type, i.e. the maximum reading is 3·999 V. An A/D converter would have to have a resolution of 14 bits to do this and at present these are much more expensive than the DPM used here. If a 3-digit reading (999) is acceptable, then a 12-bit converter could be used, and these are available cheaply. It should be remembered that the digital output needs to be in BCD form, and also, the conversion process should preferably be by the dual slope integration method because of its excellent noise rejection characteristics.

The more cost-effective solution was thus two separate DPMs to be read simultaneously. The output signals from these were fed to the microprocessor unit with ancillary memory stores, and thus to the programmable calculator (Compucorp Scientist 327) which provided a printed record of data and calculated results. Figs. 1 and 2 show a block diagram and simplified flow-chart. The circuitry is shown in Figs. 3 and 4. The operating program is stored in an ROM and occupies 502 locations. The data memory is a RAM of 2048 bits split into 256 eight-bit words (bytes). Working on a basis of four significant figures for the I and V inputs, this allows for a total of 100 $I-V$ data pairs to be stored prior to any operation. This has been found to suffice for most purposes, though it should be stressed that addition of greater storage capacity is both simple and inexpensive to implement. A small amount of memory is required on a temporary basis for the program to operate and the RAM described above suffices for this. The apparatus also incorporates a four-digit LED display and this serves either to read out the desired time interval between readings of $I-V$ data pairs (which can be set up with push-buttons on the equipment, or varied by a command from the programmable calculator). Alternatively, the display can be used to read out the value of I and V held in each store location. While the MPU with its ancillaries suffices to read and store the electrochemical data, its connection to the programmable calculator via a standard 20 mA interface (Fig. 4) permits not only operations on the data by the calculator, together with hard-copy output, but
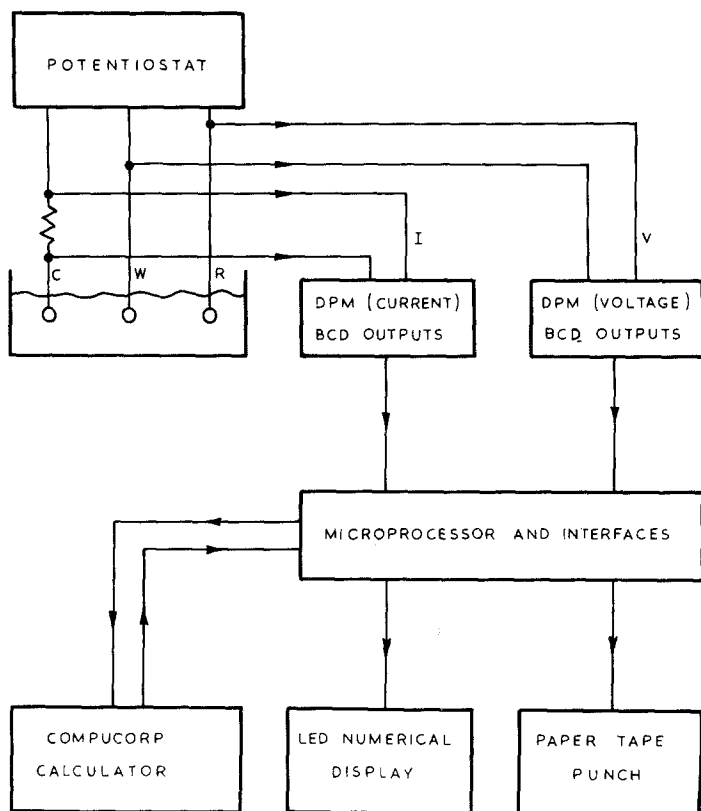
Fig. 1. Block diagram of the system.

also allows easy access (though the keyboard) to the MPU. In the present case, the calculator manufacturers produce their own interface unit designed to accept data in the ASCII (teletype) code.

3. Mode of operation

The system operates in three modes, and these are:
  (a) read from DPMs (Section 3.1)
  (b) display data (I or V) from store (Section 3.2)
  (c) transfer data from RAM to calculator (Section 3.3).

3.1. Read from DPM

In this mode up to 100 I–V pairs are read from the DPM and stored in the RAM. Prior to this, the time interval between samplings must be set. While the true goal is to sample at predetermined potential intervals, it was found easiest (using cyclic voltammetry as the basis) to work on the

basis of potential increasing linearly with time, and then to select an appropriate time interval. (This mode also makes chronopotentiometry much easier to carry out with the same hardware and software). The MPU was programmed to provide a delay of from 20 ms–100 s in steps of 20 ms between readings. Having set this value, the reading operation can commence. The MPU applies a 'hold' signal to both DPMs until fresh data is required. The 'hold' is then lifted and reapplied 15 ms later to start the conversion cycles in the DPMs and simultaneous readings of voltage and current are obtained. To establish that the voltage conversion is complete, the MPU interrogates the appropriate 'DPM ready' signal. When the reading process is complete the polarity and numerical data are read by the MPU and stored in two successive memory bytes. The current reading is then treated in the same manner. After elapse of the specified time interval, the cycle is repeated and both DPMs are read again. When 100 I–V pairs have been obtained, the reading operation is automatically halted.

START

START CONVERSION
ON BOTH DIGITAL
PANEL METERS.

PROCESS RESULTS IN
COMPUCORP. USING ITS
OWN PROGRAMME.

CHECK VOLTAGE
CONVERSION COMPLETE
STORE POLARITY AND
BCD DATA IN TWO
MEMORY LOCATIONS

AS DIRECTED RETURN
TO TAKE FRESH DATA
OR PRODUCE PAPER
TAPE ETC.

CHECK CURRENT
CONVERSION COMPLETE.
STORE POLARITY AND
BCD IN TWO MEMORY
LOCATIONS.

END OF
RECORDING
SEQUENCE

NO

YES

CHECK READY STATUS
OF CALCULATOR.
CHECK POLARITY OF
VOLTAGE READING AND
TRANSMIT APPROPRIATE
ASC II CODE AT 110
BAUD. CONVERT EACH
BCD DECADE TO ASCII
FORMAT AND TRANSMIT
TO CALCULATOR.

REPEAT PROCESS FOR
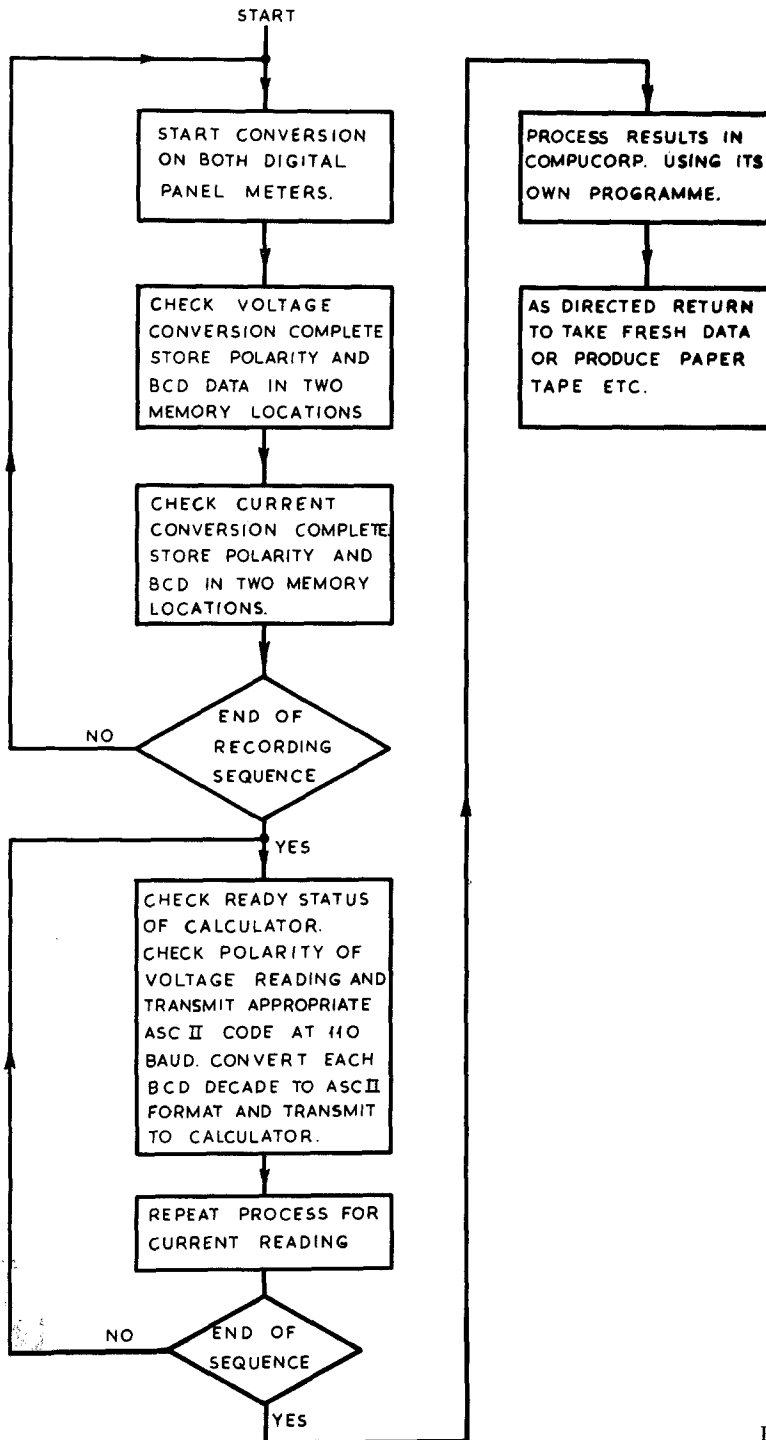CURRENT READING

END OF
SEQUENCE

NO

YES

Fig. 2. Flow chart for logging process.

3.2. *Display data*

This facility is built in to allow the recorded $I-V$ data to be inspected. However, access is sequential, and 99 values of I or V will have to be displayed before the 100th one is exhibited. At any time during the display process, the MPU can be returned to the 'read DPM' mode when the new
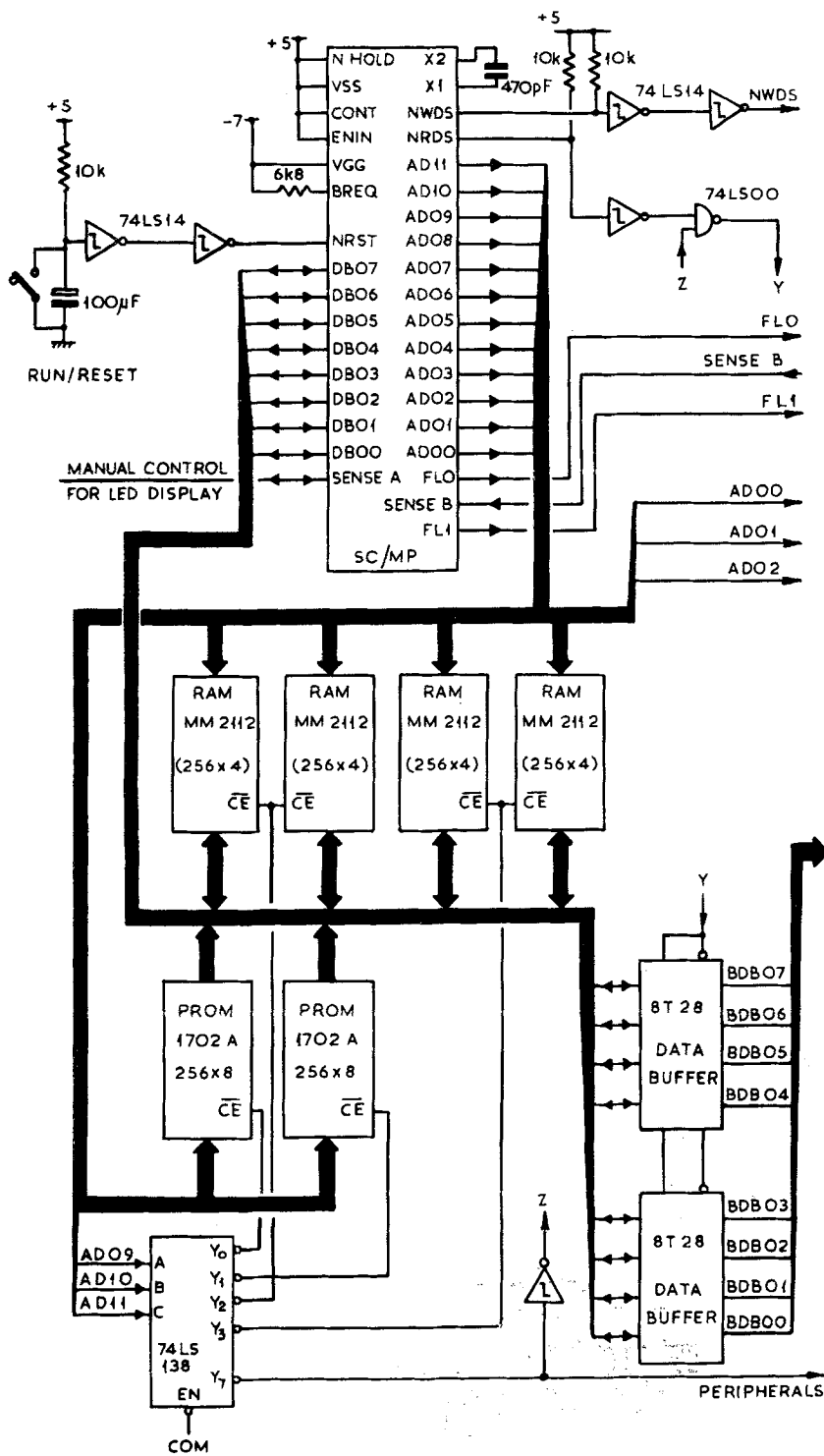
Fig. 3. Basic microprocessor.

incoming data will be stored in memory locations beginning from the one reached in the preceding 'display' operation and continuing until the memory store is once again full. Providing no new data is being acquired, existing $I-V$ pairs are not erased during the display process.
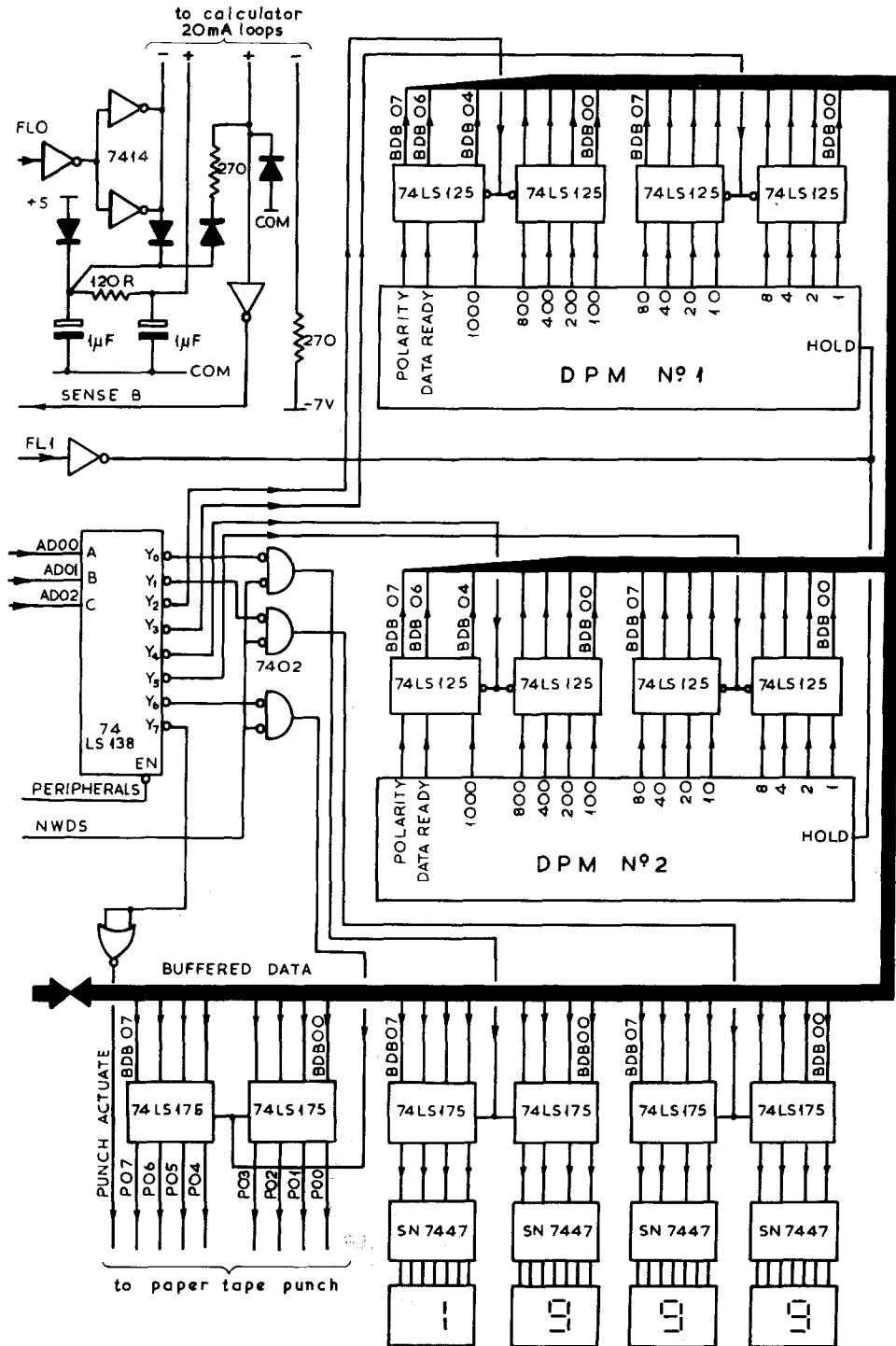
Fig. 4. Peripheral equipment.

3.3 *'Write to calculator'*

Transfer of data to the calculator is controlled by instructions in the program, the $I-V$ pairs being read in the order $I_1, V_1, I_2, V_2, I_3, V_3, I_4, V_4, \ldots$ etc. The program must contain some sort of subroutine (for instance, a simple counter) which will prevent it from trying to read more than 100 pairs of points. Other more sophisticated arrangements could include the use of data from a particular potential or current range. For charge $(I\,t)$ measurement, for example the determination of surface area by hydrogen adsorption, only currents above a preset value (the double-layer charging current) need be included, the potential range of measurement also being preset.

4. Further developments

In place of the commonly used potential ramp function used in cyclic voltammetry, one could readily envisage an MPU-generated 'voltage staircase'. The MPU could be arranged to read the current at each voltage level, compare current readings over a period of time, and move to a new voltage level when the 'steady-state' was reached, this last being defined at will as a given variation of current with time. In conclusion, while there is no doubt that computers can be made to operate in a much more sophisticated way in conjunction with electrochemical experiments, one faces the problem that there are then all manner of specialized problems which require individual attention. It is our contention that the apparatus described here, has sufficient universality to make it useful in all electrochemical laboratories.

References

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