Materials Science Forum Vols. 44 & 45 (1989) pp. 123-138

A LOW COST COMPUTER-CONTROLLED ELECTROCHEMICAL MEASUREMENT SYSTEM FOR EDUCATION AND RESEARCH

R.A. Cottis
Corrosion and Protection Centre, UMIST, P.O. Box 88,
Manchester M60 1QD

Abstract

With the advent of low cost computers of significant processing power, it has become economically attractive, as well as offering practical advantages, to replace conventional electrochemical instrumentation with computer-based equipment. For example, the equipment to be described can perform all of the functions required for the measurement of a potentiodynamic polarization curve, replacing the conventional arrangement of sweep generator, potentiostat and chart recorder, at a cost (based on the purchase cost of parts) which is less than that of most chart recorders alone. Additionally the use of computer control at a relatively low level provides a versatility (assuming the development of suitable software) which cannot easily be matched by conventional instruments.

As a result of these considerations a simple computer-controlled electrochemical measurement system has been developed, with a primary aim being its use in teaching an MSc class in corrosion science and engineering, with additional applications in MSc and PhD research. For educational reasons the design of the user interface has tried to make the internal operation of the unit as obvious as possible, and thereby minimize the tendency for students to treat the unit as a 'black box' with incomprehensible inner workings. This has resulted in a unit in which the three main components of function generator, potentiostat and recorder are presented as independent areas on the front panel, and can be configured by the user in exactly the same way as conventional instruments.

As with most computer systems the software is of as great an importance as the hardware in determining the performance of the unit and the usability of the system. To a great extent performance (as measured particularly by the speed of operation) and ease of use are incompatible, as fast data acquisition produces problems such as mains frequency interference which cannot be hidden from the user. Consequently the first general-purpose control program which has been developed for this unit stresses ease of use, and has a rather restricted performance, the maximum frequency of reading being 1 Hz, compared to the maximum digitization rate of 40 kHz. In compensation for this restriction all readings are integrated over one mains cycle in order to reduce mains frequency interference, and all readings (both of voltage and current) are fully autoranging.

Introduction

A range of computer interfaces have been used for the computer-control of electrochemical measurements. Many of these have been based on commercial digital multimeters, and consequently, while giving very high accuracy, tend to be rather expensive. Other, special purpose devices tend to have a rather limited range of capabilities, and, because of their relatively small market, remain rather expensive. It recently became clear that a simple, general-purpose device could perform the functions of sweep-function generator, potentiostat, log converter and X-Y recorder for a cost less than that of the cheapest conventional units, and with significantly enhanced flexibility. This paper describes the design of this unit, and outlines some of its modes of operation. Further information on the practical aspects of the construction of the unit, and sources of components, is available from the author.

Design Philosophy

Component selection.

Wherever possible readily-available components have been used, the normal criterion for acceptability being the listing of the device in the RS Components catalogue. The design has also been kept as simple as possible, using more expensive components intended for the required task, rather than more complex circuits using less expensive (but less suitable) components. (In this respect the author has, almost inevitably, been somewhat overtaken by the pace of developments in electronic devices).

At the time of writing the total component cost is around £300.

Computer interface.

The unit has been designed with a very simple computer interface, with a small adapter board being used to connect the computer to the unit. Computer interfaces have been designed for Amstrad and IBM computers. A small

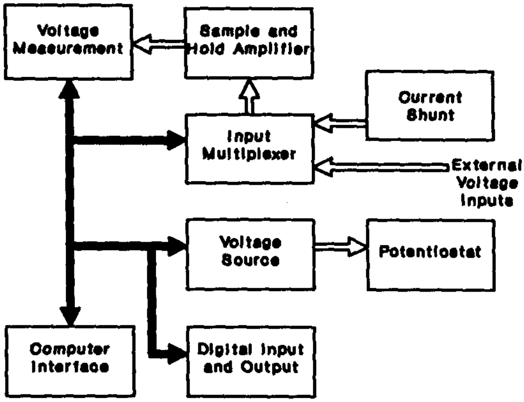

Figure 1 Block Diagram of Measurement System

microprocessor interface to permit use with any computer having an RS 232 interface is currently being designed.

Power consumption.

The power supply is a significant factor in terms of the cost and size of the unit, and as far as possible low power devices have been used. The power consumption of the unit is dominated by the power required by the potentiostat.

Required Functions

Discussion with other colleagues involved in a range of electrochemical corrosion studies suggested that the following minimum requirements should be provided:

Voltage Source, ±4 to 5 V, better than 1 mV resolution.

Current Measurement Input, Range 10^{-7} to 1 A

Voltage Measurement Input, Ranges ±10 mV to 10 V (more sensitive ranges might have been considered desirable, but this specification was tempered by the known difficulties of the amplification of small dc signals). Fully differential inputs.

Potentiostat circuit ±10 V, ±300 mA (again this specification is based on realism more than an ideal).

The block diagram which results from this specification is shown in figure 1, and the individual components of this design are discussed further below.

Voltage Source

In order to provide a good voltage resolution, thereby ensuring the possibility of obtaining a smoothly changing voltage, a 16-bit digital-to-analogue converter (DAC) was used. Using a voltage range of ± 4.096 V, this gives a voltage resolution of 1/8 mV. The DAC circuitry is shown in figure 2. The circuit is based

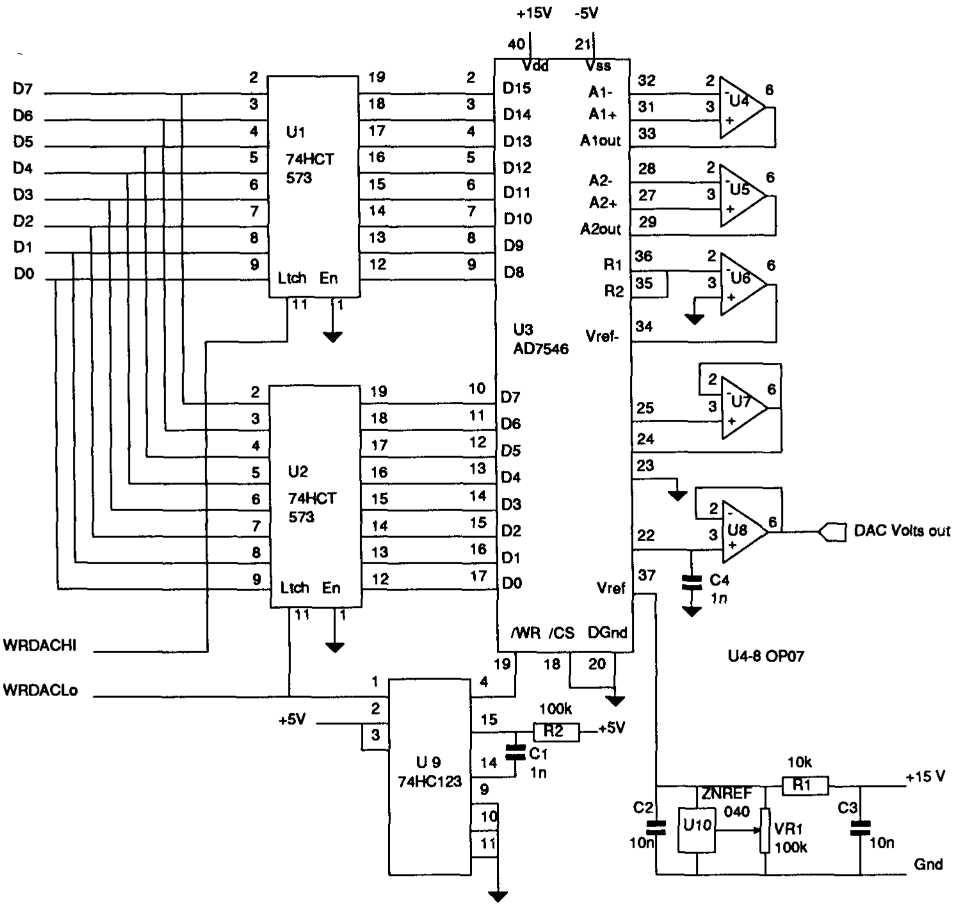

Figure 2 Voltage Source

on the AD 7546, which is designed to offer 16-bit monotonicity. (A DAC is described as having a monotonic output if a single bit increase in the digital input always results in an increase in the analogue output voltage).

The speed of response and linearity of the DAC depends upon the external operational amplifier buffers used. In this application speed of response was not considered to be of primary importance, and in order to give good linearity without the need to trim the amplifiers the 0P-07 was used for its low noise and input offset voltage.

The AD7546 is designed for 16 bit input, whereas, for generality, the computer interface is designed for 8-bit input. Therefore two 74HCT573 latches are used to store the input data. This is loaded into the AD7546 when the least significant byte has been loaded. Because of the rather limited high frequency response of the

0P-07 a rather large output glitch is obtained when the most significant bits change. In order to eliminate this the write enable pulse to the AD 7546 is stretched by the monostable (U9, R2 and C1), and the deglitch switch built into the AD7546 is used to activate a sample-and-hold amplifier (C4 and U8).

Voltage Measurement

The measurement of voltage provides one of the main design decisions for this unit. The four major characteristics which are set by this decision are speed, measurement accuracy, interference rejection (particularly mains frequency interference) and costs. Unfortunately these factors tend to be mutually incompatible. For this particular unit it was anticipated that reasonably fast operation would be required for use in transient studies, and to permit measurements to be made on several channels, therefore a successive-approximation analogue to digital converter (ADC) was selected. The highest resolution of readily available ADCs at reasonable cost is 12 bits. This is significantly better than a typical X-t recorder, and was felt to be adequate for the majority of electrochemical measurements. In order to increase the dynamic range of the measurements a programmable-gain amplifier was used ahead of the ADC to give a number of computer-selectable measuring ranges (see table 1). The device selected is capable of making one conversion every 40 μs, and for most applications this will be as fast as the controlling computer can handle.

Amplifier Gain	ADC Range	Measuring Range	Resolution
1	10 V	10 V	4.9 mV
1	5 V	5 V	2.4 mV
10	10 V	1 V	0.49 mV
10	5 V	500 mV	0.24 mV
100	10 V	100 mV	49 μV
100	5 V	50 mV	24 μV
1000	10 V	10 mV	4.9 μV
1000	5 V	5 mV	2.4 μV

Table 1 Measuring Ranges

In order to provide for the measurement of both voltage and current an analogue multiplexer was used to switch between a range of alternative voltage inputs. Many of the students who were expected to use this unit have little training in electronics, and could not be expected to appreciate the significance of single-ended voltage measuring inputs. This would, in any case, somewhat limit the application of the unit. Consequently two multiplexers are used to give 8 differential voltage inputs, four of which are used for current measurements (see below), and four of which are available for general purpose voltage measurements.

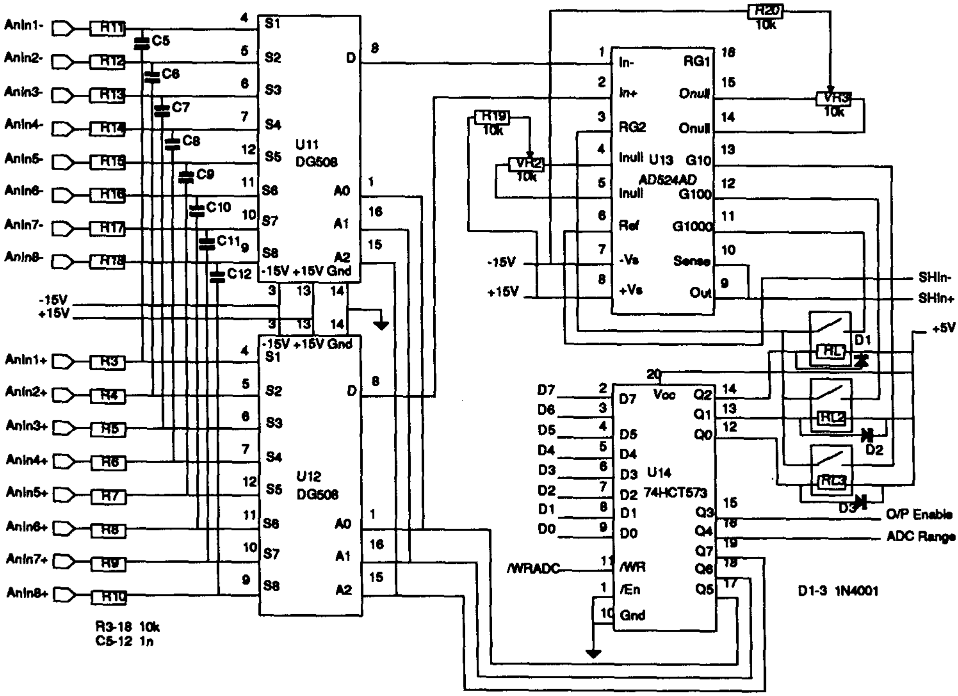

Figure 3 Input Filter, Multiplexer and Amplifier

Input Filter and Multiplexer

The input multiplexer is based on two DG508 eight input analogue multiplexers (figure 3). A measure of input protection for these and subsequent devices is provided by the input resistors (R3 to R18), which will limit the current passing through the input protection diodes of the multiplexers in the event of voltages outside the range of the supply voltage being applied to the input. Capacitors C5 to C12 limit the input cut-off frequency in order to reduce problems of high frequency noise. The value of these capacitors may be varied according to the intended application, but a minimum of 1 nF is suggested, which gives a high frequency roll-off starting at 5 kHz. In situations where mains frequency noise presents problems the roll-off frequency may be reduced to 5 Hz by using 100 nF capacitors, with 100 kΩ resistors for R3 to R18. When spectral measurements are being made (e.g. electrochemical noise measurements) these components will act as anti-aliasing filters, but the roll-off is relatively shallow, and for low frequency measurements it is probably better to over-sample the input signal (i.e. take more frequent readings than is necessary for the spectral analysis) and use digital filtering techniques to give a more effective reduction in the frequencies above the band of interest.

Instrumentation Amplifier

The instrumentation amplifier is based on the AD524 (figure 3). By means of a simple external connection this provides selectable gains of 1, 10, 100 or 1000, thereby providing a wide dynamic range. The switched resistor for the gain of 1000 is only 40 Ω, therefore the gain switching device must be low resistance, and semi-conductor analogue switches cannot be used. Consequently this function is served by three reed relays (RL1 to RL3), which switch in the gain selection resistors for gains of 10, 100 and 1000. The AD524 provides a separate output reference terminal, and this is taken, via the ground end of the sample-and-hold capacitor, directly to the ADC ground terminal, in order to minimize ground loop problems. VR2 and VR3 provide for nulling of the input and output errors of the amplifier.

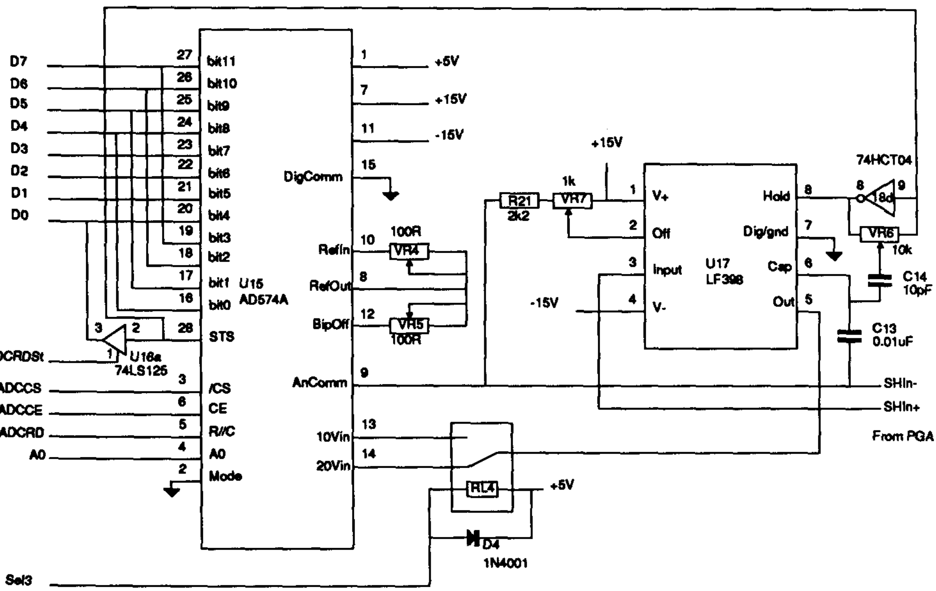

Figure 4 Sample-and-Hold Amplifier and ADC

Sample-and-Hold Amplifier

In order to minimize complications arising from changes in the input voltage while the analogue to digital conversion is being performed, the ouput from the instrumentation amplifier is passed through the sample and hold amplifier (U15 and associated components - figure 4). This is controlled by the status output from the ADC, which is high only while the conversion is being performed. Thus the input to the ADC is kept essentially constant while the actual conversion is being performed. VR6 and C14 provide for nulling of hold switching errors, while VR7 and R21 permit nulling of the input offset voltage. In order to avoid problems due to dielectric absorption (which results in drift of the held voltage with time) the hold capacitor (C13) should be a polystyrene type.

Analogue-to-Digital Converter

The ADC (figure 4) is based on the AD574A configured for bi-polar inputs (i.e. negative and positive voltages can be measured). The alternative voltage measuring ranges of ± 5 or ± 10 V are selected by means of RL4. The digital output from the ADC is configured for eight bit working, with the STATUS signal (which can be used to detect end-of-conversion) being connected as bit 0 of the least significant byte of output. VR4 and VR5 provide for adjustment of the measured voltage and the bipolar offset.

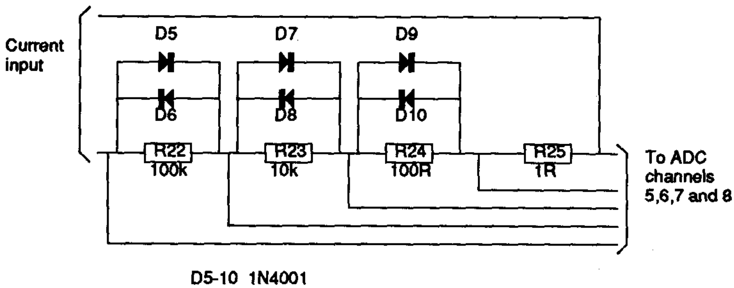

Figure 5 Current Shunt

Current Shunt

There are essentially two approaches to the measurement of current. Either a resistor can be placed in the current measuring circuit, and the voltage developed across the resistor measured, or a current amplifier (often referred to as a zero-resistance ammeter or ZRA) can be used to convert the current to a voltage without developing a voltage drop in the circuit being measured. The ZRA approach has two disadvantages for the instrument in question - the common power supply presents some rather subtle and difficult grounding problems, and the ZRA will draw the full measured current from the power supply, effectively doubling the power requirement for the internal potentiostat, and making the addition of external, higher current potentiostats much more difficult. Consequently simple resistive shunts have been used. A second problem with electrochemical current measurements is the very wide dynamic range which is required, an ideal range being about 10^{-8} to 1 amp. It is not possible to achieve this range with a single resistor, therefore some form of resistor switching is needed. (As an alternative the voltage drop across a forward- biased semi-conductor junction may be used to give a voltage which is approximately logarithmically related to the current. This could give a very economical solution to the problem, but careful correction for device linearity and temperature errors would be required to obtain accurate results). The solution devised (figure 5) is economical in terms of component costs, power consumption and software overhead, although it does result in a rather large voltage drop at high currents. Four measuring resistors are used (R22 to R25), each connected to one of the differential inputs of the input multiplexer. In order to limit the voltage drop across the larger-value resistors when large currents are being passed, these are by-passed with parallel connected diodes (D5-D10) which will start to conduct when the voltage drop exceeds about 150 mV, with a maximum current of 1 A, when the voltage drop will be about 800 mV. Thus the maximum total voltage drop across the shunt will be 3.4 V at a current of 1 A. In order to limit the voltage drop for measurements which do not require the low current capability, the unit gives access to all points of the shunt, so that selected resistors can be by- passed. A subsidiary advantage of this scheme, compared to common alternatives which rely on switching of resistors, is that the impedance of the current shunt does not change suddenly.

The low current resolution of the current measurement is controlled by the input bias current of the instrumentation amplifier. This is specified as 50 nA, but in practice the uncertainty in current measurement appears to be around 10 nA.

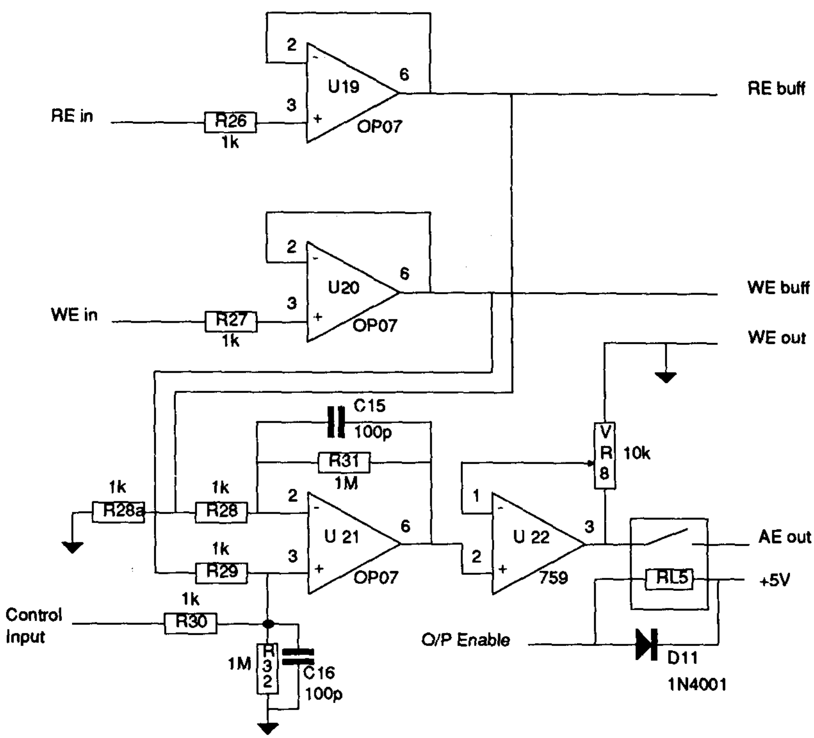

Figure 6 Potentiostat

Potentiostat

As the unit was intended for an educational situation, it was considered important that a full four terminal potentiostat should be provided, with separate voltage sensing and current sourcing terminals for the working electrode. This meant that the common single amplifier circuit could not easily be used, and the three-amplifier circuit of figure 6 was used, with a fourth amplifier (U22) being added to increase the current output capability. Amplifiers U19 and U20 are configured as unity-gain, non-inverting buffers for the working and reference electrode potentials. The outputs of these amplifiers are combined with the reference voltage (normally supplied by the DAC) in the summing amplifier, U21. This amplifier determines the gain and frequency response of the potentiostat. As drawn the gain has been kept relatively low at 1000 (i.e. a change of 1 mV in the potential difference between the working and reference electrodes will result in a change of 1V at the auxiliary electrode output). This helps to prevent high frequency instability, at the expense of reducing the precision of control of the potential. If required the gain may be made adjustable by use of VR8, although for normal units this is omitted, and the output of U22 connected directly to its inverting input. The frequency response is limited to about 10 kHz (depending on the cell and reference electrode characteristics) in order to match the maximum

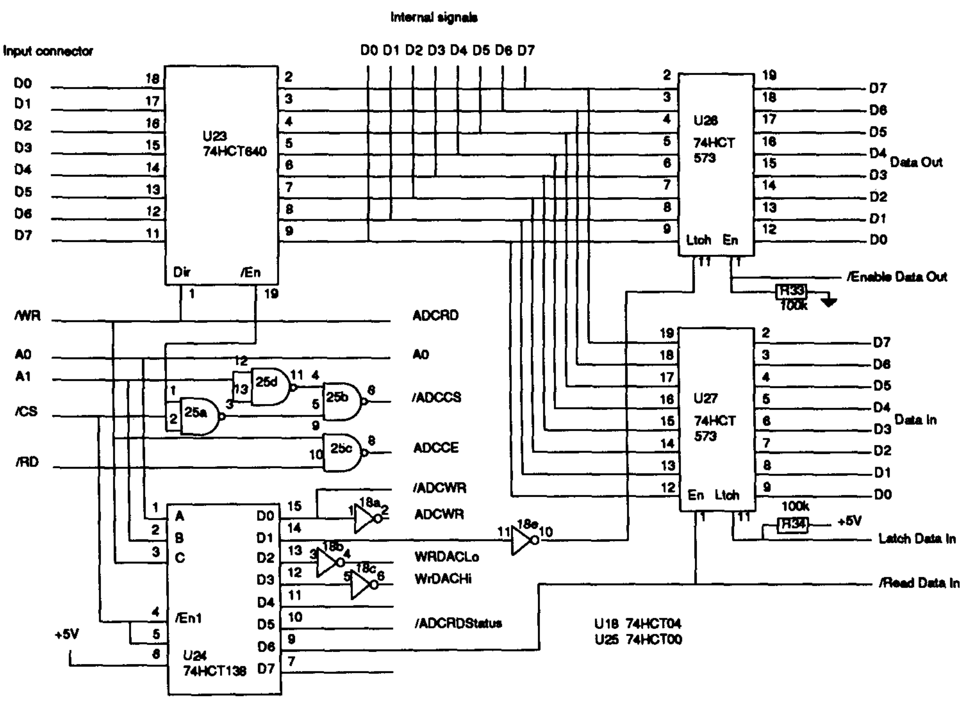

Figure 7 Control Circuitry and Digital Input and Output

capabilities of other parts of the circuit in terms of speed of measurement. This does result in a rather high susceptibility to high frequency instability and to mains frequency noise pick-up at the reference electrode input. A much more stable (though necessarily much slower) response can be obtained by using 100 nF capacitors for C15 and C16. A similar effect can also be achieved by the use of a capacitor of about 1 µF connected between the auxiliary and reference terminals, although this approach is somewhat more dependent on the characteristics of the cell.

Digital Input And Output

Largely because spare control lines and a small amount of spare space on the circuit board were available, eight bits of digital input and output are provided (figure 7). By default the input is unlatched and the tri-state output is permanently enabled, but either of these can be over-ridden if desired.

Control Circuitry

The control circuitry (figure 7) provides buffering of the data bus (U23), and generation of read and write control signals. Currently the only CMOS buffer

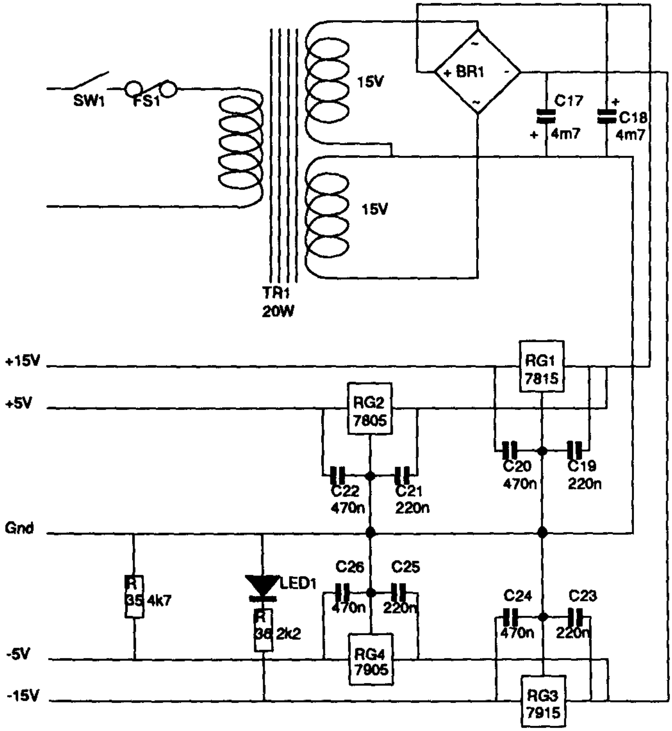

Figure 8 Power Supply

suitable for use for buffering the data bus is the inverting 74HCT640, but the 74HCT645 can be used to give a non-inverting input when and if it becomes available.

Power Supply

Figure 8 shows the simple regulated power supply for the unit. Low noise ground and power distribution is essential for satisfactory performance. The power supplies should also be heavily decoupled with 0.1 μF capacitors distributed over the circuit.

The ground configuration is particularly important for satisfactory operation, and care in the layout of the circuit is required to avoid ground loops. The analogue and digital grounds should be kept separate, in order to minimize the coupling of digital switching noise into the analogue circuitry.

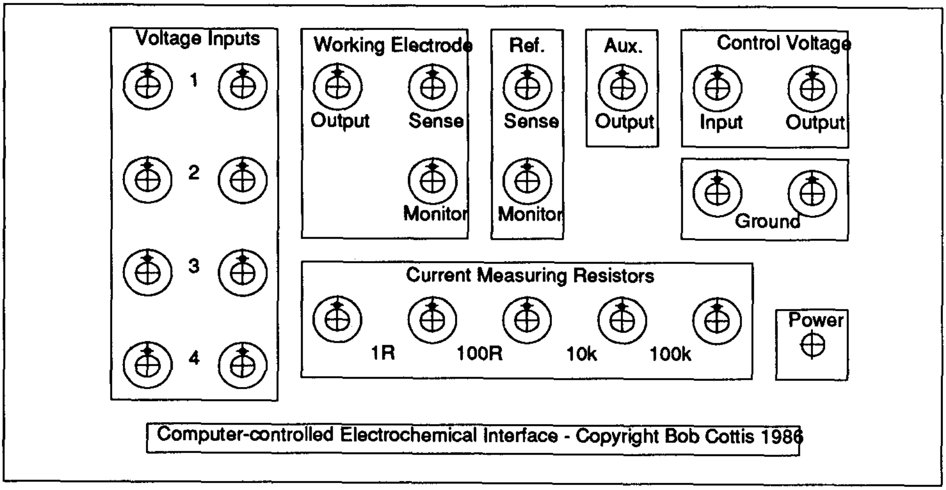

Figure 9 Suggested Front Panel Layout

External Connections

For use in its intended training role it is suggested that the various internal functions should be made independently available to the user. The front panel used in the unit at UMIST is shown in figure 9. With this design the connection from the DAC output to the potentiostat control input must be made by the user, and the control voltage can be checked prior to the connecting the cell. Similarly the current shunt must be connected at a suitable point in the circuit, and the voltage across the various measuring resistors may be checked. This approach also has benefits in the flexibility of the unit. For example the four voltage inputs can be used for potential-time monitoring, while the potentiostat can be combined with the current shunt to produce a wide range zero resistance ammeter. For more dedicated application, many of these connections could be wired internally.

Computer Interface

The interface for the Amstrad CPC 6128 is shown in figure 10. This is a Z80-based computer, the only unusual feature being the use of 16-bit addressing for I/O devices and the on-board use of much of the available I/O space. In order to minimize the interface components the interface maps the registers of the electrochemical interface to fixed locations in the I/O space. Should these addresses conflict with other devices it would be possible to use other I/O addresses by reconfiguration of the address lines to U28 and U29.

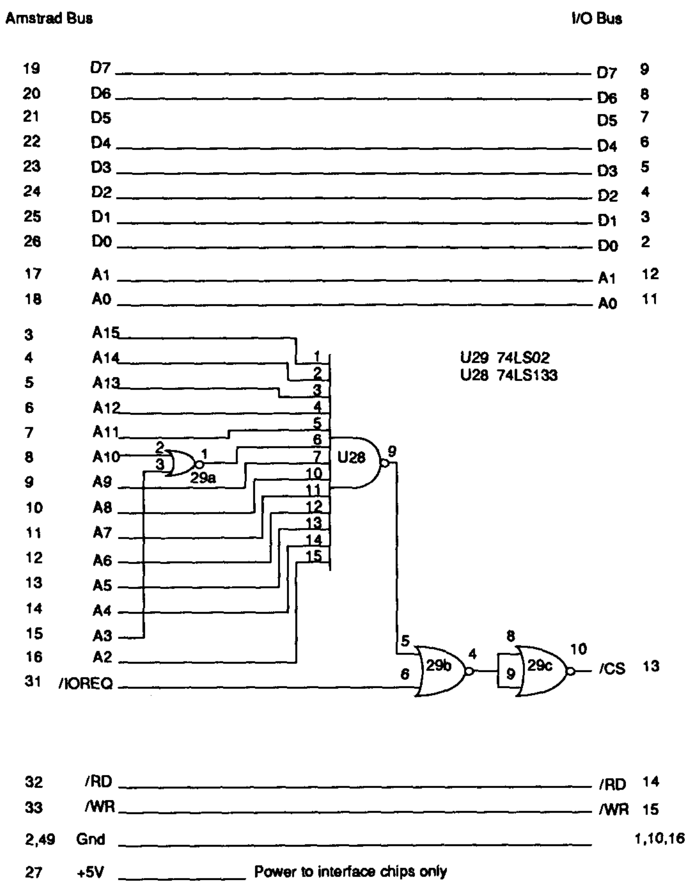

Figure 10 Computer Interface Circuit for Amstrad CPC 6128

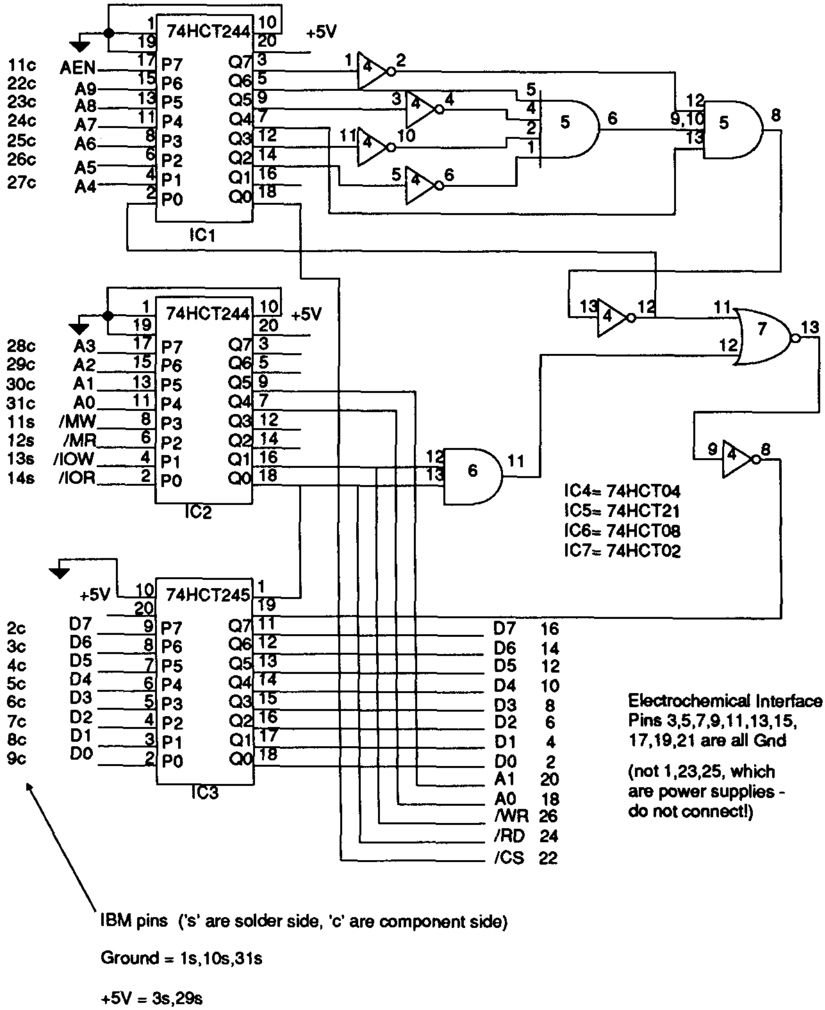

Figure 11 Computer Interface Circuit for IBM PC

An interface for the IBM PC and compatible computers is shown in figure 11. This is based on the Vero prototyping board, and also uses fixed locations for the I/O port.

Applications

With suitable programming this unit can perform a range of experiments. The most obvious of these is the performance of a potentiodynamic sweep, with the current being recorded as a function of the controlled potential. The method by which this is achieved will vary according to the computer being used, but at a minimum it will involve updating the output voltage from the DAC and measuring the current flowing at regular intervals. For the Amstrad CPC 6128 this was achieved using a relatively simple BASIC program. This used the EVERY timer interrupt function to update the control voltage and to read the current flowing once every second. Because the measurement of low currents tends to be very sensitive to mains frequency interference, it was found that much less 'noisy' current readings were obtained by using a short machine code subroutine to sum 256 readings over the period of one mains cycle (20 ms in the UK). Because the Amstrad timer is stopped during disk accesses, the data collected was stored in an array during an experiment, and only stored on disc when the experiment was complete. More recently low cost IBM PC clones have become available, and these have been used for recent work. A considerably more sophisticated program has been developed for these computers, using the GEM environment to produce a flexible yet easy to use system. Despite the rather more complex programming required in this case, in essence the program still involves the updating of the DAC output and the measurement and recording of input currents and voltages at regular intervals.

For a second application a transient-recorder mode of operation was required, with relatively infrequent recording of potential over long periods, with occasional high frequency recording when a transient event was detected. For this application it is impossible to entirely avoid the problems associated with disc accesses on the Amstrad CPC series of computers. However, with IBM compatible computers it it possible to use the system clock interrupt to give regular readings, even during disk accesses. The normal system clock interrupt occurs approximately every 54 msec, but this frequency can be increased if necessary (the details of this operation are beyond the scope of this paper but details may be obtained from the author).

Other applications for which the unit is being used or considered are the recording of load-time and potential records for slow strain-rate stress corrosion testing; the generation of control signals for low frequency corrosion fatigue tests and the control of electrochemical hydrogen permeation measurements.

Acknowledgements

The development of this unit has been assisted by several members of the staff of the Corrosion and Protection Centre, particularly Dr. S. Turgoose and Mr. R. Brighouse. The author also acknowledges the provision of laboratory facilities by the Head of the Corrosion and Protection Centre.