Data acquisition system for electrochemical applications*

U. v. ALPEN, K. GRAF, M. HAFENDÖRFER

Max-Planck-Institut für Festkörperforschung, 7000 Stuttgart 80, Federal Republic of Germany

A low cost data acquisition system for electrochemical cells has been devised on the basis of the new microprocessor computer generation with IEC–BUS interface connections. This modular structure allows the application and extension of the proposed system to all IEC–BUS[†] compatible measuring apparatus. Our special interest was focused on the control of experiments with a large data flow like impedance spectroscopy as well as long time experiments like the temperature dependence of a cell e.m.f. Beside this, experiments like d.c.-conductivity, discharge characteristics and current–voltage curves can easily be carried out. The programs have been developed in a way which allows an application of the system in scientific laboratories as well as in the routine quality control of electrochemical device production.

1. Introduction

In recent years there has been rapidly increasing interest in automatic acquisition systems for electro-chemical applications because of the following reasons:

(a) Conventional electrochemical experiments take a long time because the data have to be measured under the steady-state conditions. Diffusion of the mobile ionic or electronic species is the rate-determining process and therefore it takes a long time in most cases for equilibrium to be reached. A computer controlled system has the advantage of performing these long-time experiments continuously without any assistance. As an example we will describe the data processing of the temperature dependence of a cell e.m.f. with the calculation of the resulting thermodynamic data.

(b) The impedance method has been increasingly used in recent years to study electrochemical cells. This method is extremely time consuming because a high flux rate of data has to be measured in order to calculate an impedance diagram of an electrochemical cell. A simple computer-based set-up is able to collect all impedance data during a frequency sweep of an electrochemical cell and to analyse and plot the data simultaneously in a rather short time. In addition the data acquisition system is able to scan the impedance spectra in a given temperature range to analyse, for example, the temperature dependence of the electrolyte resistance and the double-layer capacity.

(c) The new microprocessor computers with large memory and advanced programming facilities like the HP 9825 used in this system, allow data acquisition systems for electrochemical applications to be built up at low cost. The IEC–BUS system leads to the use of standardized components which are independent of a special calculator. The IEC interface connections make it feasible to control nearly all electrochemical measuring apparatus, so an extension of such a system to all kinds of applications is possible. The stand-alone version of such a computer system is extremely reliable, versatile and independent. In addition its total installation costs are small compared to the cost of a conventional processor computer with time sharing including the data transfer

---

units. The software can easily be fitted to every individual problem without entering into the operational system. The software is characterized by the implementation of a high level programming language with an interpretative operational system.

2. Experimental

An electrochemical data acquisition system generally needs temperature control and temperature sweep facilities. An IEC–BUS programmable temperature controller has been built. The temperature is set by the computer via a DA-converter and controlled by a PID-regulator; a NiCr–Ni thermoelement with a $0°$ C reference is used as the temperature sensor. Temperatures can be set by the computer in the range of ambient to $1300°$ C with an accuracy better than 0.1 percent. The temperature is read out by a digital thermometer (in this apparatus a Fluke 2100 A) also working with a NiCr–Ni thermoelement.

For the direct measurement of the electrochemical impedance we used a system proposed by Armstrong et al. [1] using a Solartron Frequency Response Analyser. The frequency of a programmable generator is set in a certain frequency range with defined steps by the computer. A correlator analyses the response of the electrochemical system to the sinusoidal perturbation, and compares the signal X over a current-measuring resistor with the signal Y over the electrochemical cell. The phase and amplitude of the real and imaginary part of the impedance are displayed in the computer and printed out. It is possible to work in the frequency range 10^{-4}–10^6 Hz (with the 1174 Solartron Frequency Response Analyser) with a frequency resolution of 10^{-4} Hz and amplitudes of 10 mV to 10 V r.m.s. It should be emphasized that measurements below 1 Hz take a considerable amount of time because the period of the signal becomes the major contribution to the total experimental time at these low frequencies. Because of the high noise level at low frequencies one has to integrate over some periods for the detection of a true signal. This leads to extremely long total experimental times. In the frequency range 10^4–10^{-2} Hz, ten periods of integration lead to a total measuring time of about 2·5 h.

We improved the signal-to-noise ratio of the Frequency Response Analyser in the whole frequency range by measuring with computer-controlled passive filters. The calculator adjusts a pair of passive filters in the signal and reference path of the analyser for every frequency decade via a digital universal input–output interface which is controlled by a multiprogrammer. This can easily be performed with pairs of absolutely equally designed filters because the phase shift at each filter forming the ratio of voltage (signal Y) to current (reference X) is neglected.

Including the passive filters the detected signal is large enough also at very low frequencies to perform the measurements. Integrating one period of the signal only in the whole frequency range, this leads to the minimum total experimental time. The frequency swept direct impedance measurement with a Frequency Response Analyser is not a null method and therefore a finite a.c. current is drawn from the system under investigation.

The impedance analysis thus can be effected by the construction of the cell assembly, the input impedance of the Analyser and the current-measuring resistor [2]. The cell assembly and geometry can be easily optimized by the use of an ideal geometrical configuration and by using highly insulating material for the sample holder.

The input impedance of the Frequency Analyser may affect the impedance analysis also in highly conducting electrochemical systems at low frequencies [2]. Therefore one should apply an impedance converter in most cases to obtain correct impedance results. We transformed the input impedance of 10^6 Ω, 40 pF of the Solartron 1172 to values of 10^{10} Ω, 10 pF. This impedance converter is directly coupled to the sample holder, so one need not take into account the impedance of the cables connecting the Analyser and measuring assembly.

The current standard is extremely important for a correct evaluation of the impedance data [2]. In our system a programmable current resistor is included that enables a fast standard resistor selection by the computer. Before the impedance run is started the current resistor is selected by measuring the imaginary part of the impedance as a function of the current-measuring resistance in the high frequency range 1 Hz–1 MHz. The smallest current standard which does not give a negative imaginary part of the impedance is chosen.
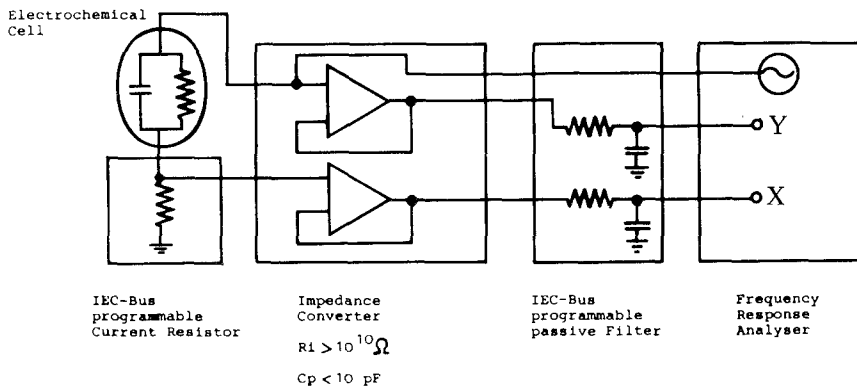
Fig. 1. Schematic diagram of the measuring circuit of the impedance with the Frequency Response Analyser.

In Fig. 1 the schematic set-up of the impedance measurement assembly is shown. This consists of the programmable current standard, the impedance converter and the programmable passive filter all coupled in a box which is directly connected to the electrochemical cell. As an example the impedance diagram of the superionic conductor Li_3N [3, 4] with ionically blocking Au-electrodes is shown in Fig. 2. A semicircle, attributed to the electrolyte resistance R_E in parallel with the geometrical capacity C_g, is followed by a steep increase of the imaginary part of the impedance due to the series connection of the double-layer capacity C_{dl}. Computer analysis can be performed with the obtained impedance data to get the values at R_E, C_g and C_{dl}. As described in [1] the exact shape of the semicircle can be analysed by the plot of the real part of the impedance Z' as a function of the imaginary part Z'', times the frequency ω, $\omega Z''$, the shape of the line giving directly the product of $R_E C_g$. R_E is either given by the intercept of the impedance with the real axis or in the analysis by the intersection of $\omega Z''$ with the real axis. The influence of the series double-layer capacity can be analysed by plotting $1/\omega Z''$ as a function of ω.

The impedance diagram can be obtained by the computer at a given temperature. The data are printed on a Printer (e.g. HP 9871 A) and stored on a floppy disc (e.g. HP 9885 M). This procedure can be repeated in a given temperature range with certain intervals thus obtaining the temperature dependence of the impedance diagrams. After such a run the temperature dependence of the import-

ant electrochemical parameters like R_E, C_g and C_{dl} is calculated, all data are stored on the floppy disc and diagrams of special interest can be plotted and printed out for further analysis.
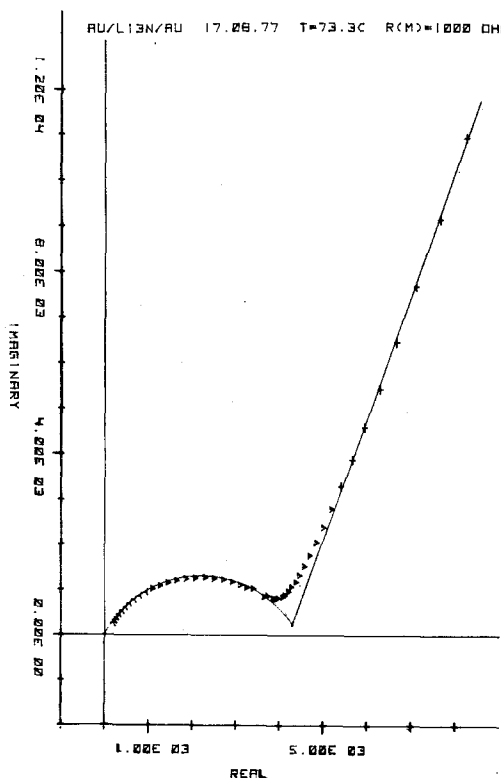
Fig. 2. Impedance diagram for Li_3N with Au electrodes at a temperature of 73·3° C.
Y frequency points from 9999–1259 Hz
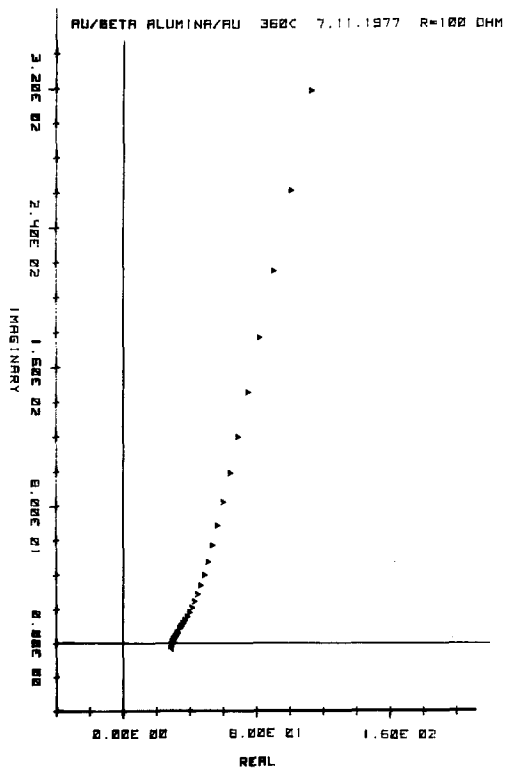△ frequency points from 999–1·259 Hz
+ frequency points from 0·999–0·199 Hz

Fig. 3. Impedance diagram for $\beta''Na_2O \cdot 11\ Al_2O_3$ with Au electrodes at a temperature of 340° C. The high frequency semicircle due to the electrolyte resistance in parallel with the geometrical capacity is not measured. The frequency points are indicated as in Fig. 2.

Fig. 4. Temperature dependence of the e.m.f. of the electrochemical cell $Ag/\beta\text{-}AgI/I$, C.

Quality control of electrochemical devices can be performed by scanning the impedance of the samples under examination and storing all data on the floppy disc. The impedance spectra can be monitored on a television screen and material of insufficient quality can be extracted. Fig. 3 shows the impedance diagram of a $\beta''\text{-}Na_2O \cdot 11\ Al_2O_3$* ceramic with ionically blocking Au electrodes at 360° C. The electrolyte resistance of about 22 Ω is obvious; the intergranular impedance semicircle and the increase of the imaginary part of the impedance due to the double-layer capacity superimpose in the given diagram.

For cell e.m.f. and d.c.-conductivity measurements the data acquisition system is equipped with a digital IEC compatible multimeter (DVM HP 3455 A or Solartron 7065).

* samples of this beta-alumina ceramic were used in sintering experiments and contain 80–90% $\beta''Na_2O \cdot 11\ Al_2O_3$. The remaining part is $\beta\text{-}Na_2O \cdot 11\ Al_2O_3$.

The computer-controlled temperature sweep of a cell e.m.f. has the advantage that the calculator program takes the steady-state values of the e.m.f. automatically. This is easily realized in a program which sets a certain temperature value, waits for the temperature equilibrium of the whole cell and then measures the e.m.f. as a function of time. The steady-state value of the cell e.m.f. is reached when the e.m.f. is constant within a variable interval of 0·1–0·5 mV for a variable time interval of 5 min to 5 h. This procedure guarantees that only the steady-state value of the cell e.m.f. is measured. The total measuring time is minimized in that the data acquisition system automatically takes only the steady-state values of the system under investigation. In Fig. 4 an example is shown; the e.m.f. of a cell containing $\beta\text{-}AgI$ as electrolyte in the arrangement $Ag/\beta\text{-}AgI/I$, C is measured. From these e.m.f. data the free enthalpy of formation of $\beta\text{-}AgI$ can be calculated.

The d.c.-conductivity can also easily be determined applying a constant current to an electrochemical cell and measuring the voltage across the
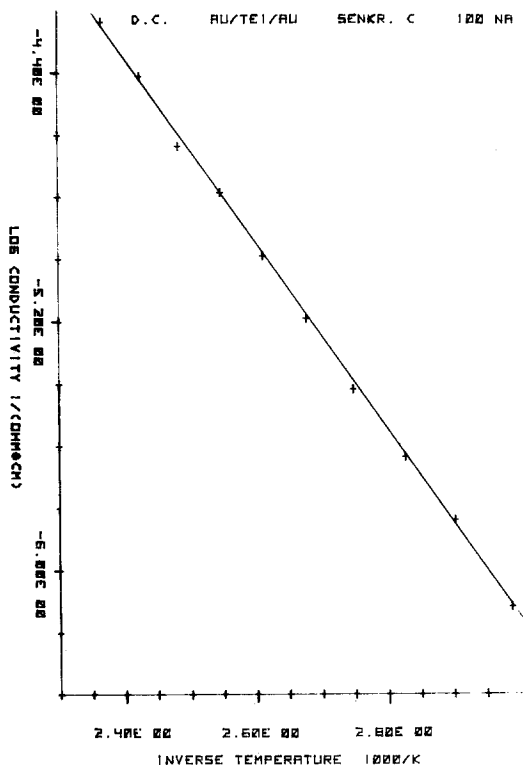
Fig. 5. d.c.-conductivity α-TeI with Au-electrodes as a function of the inverse absolute temperature. Applied constant current was 0·1 μA.
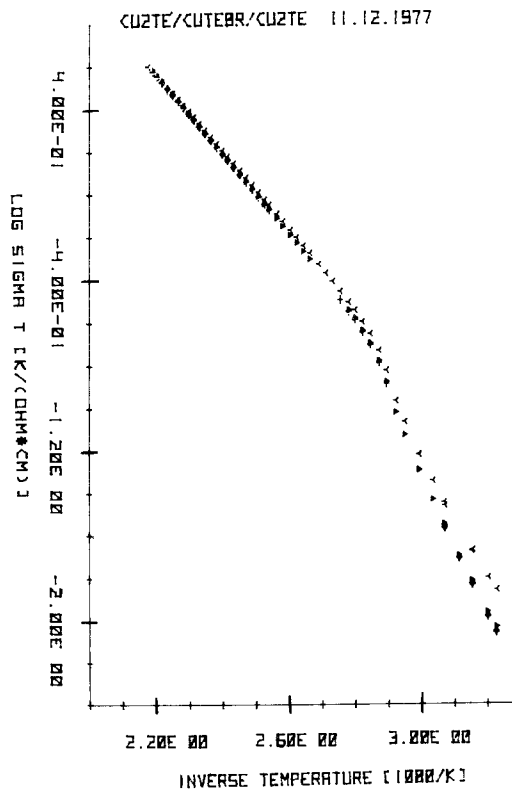
Fig. 6. Semilogarithmic presentation of the product of total bulk conductivity times and absolute temperature as a function of the inverse absolute temperature of a pressed CuTeBr pellet.
+ frequency points of 1 kHz
◊ frequency points of 10 kHz
△ frequency points of 100 kHz.
Y frequency points of 1 MHz

cell with a DVM. This voltage can be measured with a two- or four-probe method. A temperature sweep can be performed as in the e.m.f. program. The calculator also checks the steady-state value of the voltage and directly plots the d.c.-conductivity as a function of the inverse absolute temperature as shown in Fig. 5 for the total conductivity of TeI [5], which is a mixed ionic conductor for iodine.

A possible but not necessary extension of the data acquisition system is, for instance, the application of an IEC compatible automatic capacity, conductivity bridge (like the HP 4270). This bridge enables a direct determination of the conductivities and capacities of an electrochemical system at four frequencies 1 kHz, 10 kHz, 100 kHz and 1 MHz. In some cases the applied amplitude of 100 mV r.m.s. should be decreased by a voltage divider. This bridge allows a fast temperature sweep to obtain the conductivity mechanism. Fig. 6 shows the Arrhenius plot of the total conductivity of CuTeBr as a function of the inverse

absolute temperature; CuTeBr is a copper ionic conductor [6] with a first-order phase transition at 345 K. Such an Arrhenius plot in the temperature range from ambient temperature to 300° C can be obtained in 12 hours sweeping the temperature up to 300° C and back to 25° C.

The data acquisition system proposed is schematically shown in Fig. 7. The floppy disc, line printer as well as the scanner and automatic capacitance bridge are options which are not necessary for a laboratory application. But the great advantage of this data system is the possibility of extending it in such a way that it can be used for routine quality control in industrial applications as well as for non-electrochemical applications during laboratory use. We use, for instance, the automatic capacitance bridge combined with a d.c.-power source and the DVM to measure
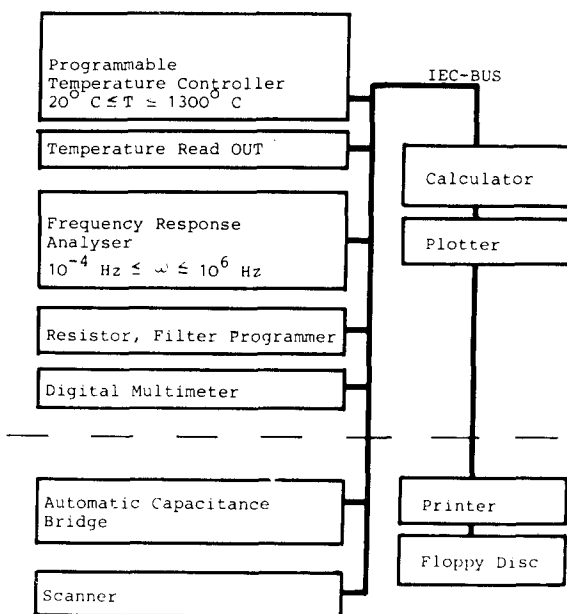
Fig. 7. Schematic diagram of the set-up of the data acquisition system for electrochemical application.

current–voltage characteristics of Schottky barriers on epitaxially-grown GaAs and additionally the capacity versus potential characteristics of the barrier. Within some minutes the free carrier profile of the epitaxially-grown layer can be obtained [7].

3. Conclusions

An electrochemical data acquisition system has been presented, built up partially of commercially available systems such as computers, printers, plotters, floppy discs, scanners, multimeters, and frequency response analysers, partially of specially designed systems such as temperature controllers, filters and current standard programmers and impedance changers.

The programs have been developed in a convenient way so that the processing of the experimental parameters can proceed at nights *or* during weekends.

It has been shown that this system can be applied to a large variety of electrochemical experiments spanning basic research as well as quality control in industrial device production and computer simulation of device applications such as the temperature change behaviour of ZrO_2 oxygen probes (λ-probes) in combustion engines during simulated driving cycles.

References

[1]   R. D. Armstrong, M. F. Bell and A. A. Metcalfe, *J. Electroanalyt. Chem.* 77 (1977) 287.
[2]   T. Dickinson and R. Whitfield, *Electrochim. Acta* 22 (1977) 385.
[3]   U. v. Alpen, A. Rabenau and G. H. Talat, *Appl. Phys. Lett.* 30 (1977) 621.
[4]   U. v. Alpen and M. F. Bell, *J. Electroanalyt Chem.* to be published.
[5]   U. v. Alpen, J. Haag and A. Rabenau, *Mat. Res. Bull.* 1 (1976) 193.
[6]   U. v. Alpen, J. Fenner, J. D. Marcoll and A. Rabenau, *Electrochim. Acta* 22 (1977) 801.
[7]   D. P. Kennedy, P. C. Murley and W. Kleinfelder, *IBM J. Res. Develop.* 12 (1968) 399.