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13. ABSTRACT (MAX 200 WORDS): AN ASYST PROGRAM TO AUTOMATE A.C. IMPEDANCE ANALYSIS OF AN ELECTROCHEMICAL CELL IS DESCRIBED. THE PROGRAM CONDUCTS THE EXPERIMENT AND ALLOWS VARIOUS ANALYSIS SCHEMES, SUCH AS KRAMERS-KRONIG R TRANSFORMS AND NONLINEAR LEAST-SQUARES DATA FITTING, TO BE APPLIED TO THE EXPERIMENTAL DATA. A PURPOSE-BUILT INTERFACE IS ALSO DESCRIBED THAT ALLOWS THE ACCUMULATION OF HIGH QUALITY DATA IN A MINIMUM PERIOD OF TIME.					
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Computer Aided Electrochemistry Using ASYST. II—A.C. Impedance Analysis

An ASYST program to automate a.c. impedance analysis of an electrochemical cell is described. The program conducts the experiment and allows various analysis schemes, such as Kramers-Kronig transforms and nonlinear least-squares data fitting, to be applied to the experimental data. A purpose-built interface is also described that allows the accumulation of high quality data in a minimum period of time.

Previously, the use of the ASYST language in instantaneous corrosion rate analysis and surface potential mapping was reported.¹ The present paper extends these principles to the automation of a.c. impedance measurements of electrochemical systems. Prior to the introduction of laboratory computers and modern instrumentation, a.c. impedance analysis (or impedance spectroscopy) was not a routinely used technique. Most equipment was purpose-built and did not possess a sufficiently wide frequency range, and the data were generally collected on a frequency by frequency basis. This resulted in long measurement times and the possibility that the system was not at equilibrium during all measurements. Once data collection was completed it was then necessary to convert the raw experimental data into impedances before any analysis could be attempted. This generally entailed fitting the experimentally obtained impedances to a circuit model² of the electrochemical system under study.

Data conversion and analysis were laborious and, in some instances, the circuit model was too complicated to be analyzed by hand.

However, the introduction of frequency response analyzers (for example, the Solartron 1250, and the Voltech TFA2001) has simplified data collection, although ensuring system equilibrium over long experimental periods is still a problem (which can be eliminated using white noise measurements³). Laboratory or personal computers can then be used to quickly convert the raw data to impedances and to carry out the analysis using circuit models. Because some circuit models are quite complicated, separate collection and analysis programs may be required.

Modern computerized instrumentation usually has an IEEE-488 (also known as HP-IB or GPIB) interface fitted, or available as an option, whereas ASYST version 3.1 supports 23 different IEEE-488 interface cards and has a wide range of words available to control IEEE-488 devices. Thus, an ASYST program can control various instru-

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ments during an experiment, and may even change the experimental parameters during data collection, depending on the level of intelligence built into the program. Allowing variation of experimental parameters is necessary in impedance spectroscopy to obtain the best signal-to-noise ratio because the measured signal (that is, a.c. current) varies over several orders of magnitude as the frequency is varied. In a typical experiment the frequency may range from 10 mHz to 100 kHz. The program and hardware used to study the a.c. impedance response of corroding systems is described. Such a program and hardware can also be applied to measure the response of most electrochemical systems.

Experimental

A conventional three-electrode cell, that is, one containing a metallic sample—the working electrode, a large area platinum gauze electrode—the auxiliary electrode, and reference electrode, was used in this work. In some instances, a platinum wire coupled to the reference electrode through a small capacitor was also inserted into the cell to eliminate high frequency phase shifts introduced by the reference electrode.⁴ A steady d.c. bias plus an a.c. signal, typically 10 mV or less in amplitude and constant frequency, was applied to the cell and the a.c. current flowing through the cell was measured. The a.c. current was measured at different frequencies over the frequency range of interest.

Hardware

A Princeton Applied Research (PAR) model 273 potentiostat, a Solartron 1250 frequency response analyzer (FRA), and a Gould 1602 digital storage oscilloscope were used in this work. Communication between the IBM PC compatible computer and the potentiostat or FRA was through a National GPIB-PC2A IEEE-488 interface card.

The generator of the FRA was connected to the external input of the potentiostat via a $\times 10$ attenuator. This attenuator was introduced between the two instruments so as to allow application of excitation signals with amplitudes smaller than 10 mV (without the attenuator the smallest amplitude possible was 10 mV RMS).

Although it is possible to obtain measurements by directly connecting the I- and E-monitor outputs of the poten-

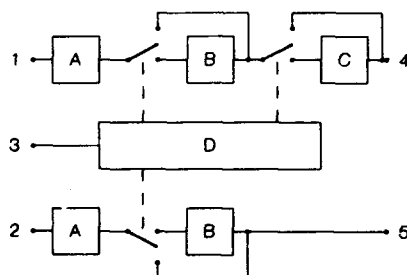
tioostat directly to channels 1 and 2, respectively, of the FRA, in the present work a purpose-built interface was inserted between the two instruments. Figure 1 shows a block diagram for this interface. Control of the various interface functions was achieved through the opto-isolated control block (D), which was connected to the auxiliary interface of the PAR 273 potentiostat. Hence the external interface settings were made by issuing appropriate IEEE-488 commands that manipulated the control lines of the PAR 273 auxiliary interface.

Incoming current (I) and potential (E) signals entering the external interface first passed through auto-zeroing blocks (A) that eliminated any d.c. bias in the two signals. Therefore, the input sensitivity of the two input channels of the FRA could be increased without overloading the input amplifiers due to extraneous d.c. voltages. Increased input sensitivity resulted in a higher signal-to-noise ratio. Elimination of d.c. bias could also be obtained at high frequencies by using a.c. coupling on the FRA input channels. A.c. coupling, however, would be impractical at low frequencies because the corner frequency of the high-pass filter is ca. 1 Hz.

The 40 Hz low-pass filters (B), which were only switched into the circuit when the measurement frequency was less than or equal to 1 Hz, were used to reduce the noise present in both the I and E signals; 40 Hz filters were placed in both channels to minimize any phase shifts between the two channels. Without these filters, measurements at low frequencies were prevented unless the signals were integrated for several (ca. >5) cycles to remove the errors arising from the high frequency noise (particularly in the I signal). Such signal integration over many cycles significantly increased the time of the experiment and the probability that the system was not continuously in equilibrium. Thus, introduction of the external 40 Hz filters reduced the experimental time and equilibrium constraints by allowing accumulation of high quality data from signals that were only integrated over one cycle. Filtering of the I signal has previously been recommended by Kendig et al.⁵

In addition, the I signal could be amplified using the $\times 10$ amplifier (C), which was used only at the lower frequencies as it introduced phase shifts in the signal when the frequency exceeded

FIGURE 1 Block diagram of external interface. (A) Auto-zeroing amplifier; (B) 40 Hz low-pass filter; (C) $\times 10$ amplifier; (D) opto-isolated control interface. (1) PAR 273 I-monitor output; (2) PAR 273 E-monitor output; (3) PAR 273 auxiliary interface output; (4) FRA channel 1 input; (5) FRA channel 2 input.



ca. 150 Hz. Two criteria had to be met before the amplifier was used: low current sensitivity in the PAR 273 coupled with the highest FRA input sensitivity (i.e., 30 mV range). Under these conditions, some increase in the data quality was obtained when the $\times 10$ amplifier was used.

Software

The program was written using ASYST version 2.1 but could also be compiled under version 3.1. Minimum computer (IBM compatible) requirements are a hard disk, 640 Kbytes of memory (no expanded memory required), an EGA color card and compatible monitor, optional Hewlett-Packard compatible plotter (models HP7470A, HP7550A, HP7475A, or HP7440A), and optional dot-matrix printer. This program is similar in design to the previous programs¹ in that: (1) the program is menu driven, (2) full error trapping is implemented, and (3) the program was written so that "bugs" in ASYST version 2.1 did not abort the program. An install program is used to set up various default parameters before the program proper is executed.

Figure 2 displays the general menu arrangement of the impedance analysis program. Because it was impossible to fit all the code into 640 Kbytes of memory, the program was subdivided into several overlays. The main program defines all common variables, displays the main menu, and accesses the overlays. It also includes the subroutines for error message output, user input, disk input/output, and other common subroutines. Submenus and subroutines associated with each box in Figure 2 were combined into separate overlays of which there are currently ten, including three

"analyse data" and two "do experiment" overlays. Users can directly access seven submenus from the main menu, namely "initialise," "do experiment," "save data," "analyse data," "plot data," "transfer data," and "quit."

From the "initialise" submenu the user can enter the value for the electrode area, inform the program what devices are attached (e.g., printer, plotter, and purpose built interface), initialize the IEEE-488 bus, and specify which analysis overlay to use when the "analyse data" option is selected from the main menu.

Various experimental options and parameters are set in the first two submenus in the "do experiment" overlay. The first submenu sets the potentiostat parameters such as current ranges, potentiostat bandwidth, applied potential, and so forth, whereas the second submenu allows the user to set FRA and interface parameters, for example, signal amplitude, frequency range, and interface gain, as well as several others. Since the frequency of the excitation signal varies over a wide range during a typical experiment, the program allows up to three changes in various potentiostat, FRA, and interface parameters during data collection. By allowing various instrumental parameters to change, a significant decrease in noise level results, provided the frequencies at which the parameters change and the values of the parameters are chosen carefully. Parameters subject to change during an experiment are the current range and bandwidth of the potentiostat, the integration period and input sensitivity of the FRA, and the gain of the interface.

Collection of the impedance data is conducted via the third submenu in the "do experiment" overlay. Prior to data

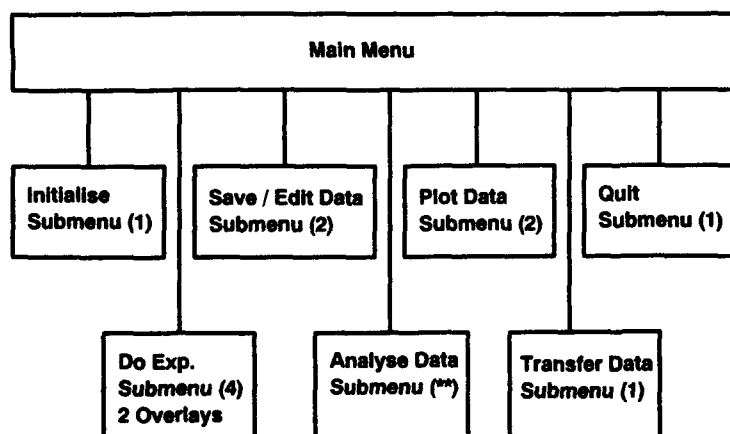


FIGURE 2 Submenu/overlay configuration for the impedance analysis program. (×) = number of submenus in the overlay; ** = number of submenus dependent upon the chosen analysis overlay.

collection, the working electrode may be conditioned at a present potential for a set period followed by a rest period at open circuit (these times and potentials are set in the first submenu). During data collection, the frequency is set to the required value, the reading cycle of the FRA is initiated, and the data read from the FRA prior to a new cycle commencing. If the data from the FRA are invalid due to an overload error, the program repeats the measurement at the same frequency using a less sensitive current range in an attempt to obtain data that are valid.

A further selection from the third submenu allows so-called "automatic" data collection (activation of the fourth submenu in the "do experiment" overlay). Automatic data collection routines are contained in a separate overlay from the other "do experiment" routines, and consist of a selection of routines from those associated with the third submenu and the first submenu in the "save data" overlay. Thus automatic data collection not only collects the data but also stores it in a disk file.

Other electrochemical experiments may also be conducted from the "do experiment" submenus. The first submenu permits the user to monitor the open-circuit potential of the working electrode with time, and conduct small-amplitude pulse experiments which are useful for determining the minimum a.c. frequency that needs to be applied during an impedance data collection. One further experiment, initiated from the second submenu, monitors the impedance response of the electrochemical cell at the lowest a.c. frequency chosen by the user as a function of the amplitude of the excitation signal. Such an experiment can be used to determine the maximum a.c. signal amplitude that can be applied to the cell while still retaining a linear relationship between the applied a.c. voltage and the measured a.c. current.²

The first submenu in the "save data" overlay permits the specification of file parameters (directory and file name) under which the experimental data can be saved, and three comments which are saved with the data (all these parameters can also be specified in the fourth submenu of the "do experiment" overlay). Tasks that can be selected at this menu include saving the data to disk and displaying the impedance data on the printer. The second submenu in this

overlay allows the user to edit or delete the occasional error that may appear in the impedance data.

There are several different "analyse data" overlays that can be accessed from the main menu, although only one such overlay can be loaded at any one time (as specified in the "initialise" submenu). One overlay contains simple, linear least-squares routines used to analyze straight lines observed in data plots such as $-Z''$ versus Z' , Z' versus $\omega^{-1/2}$, or Z' versus $\omega Z''$; where Z' is the real part of the impedance, Z'' is the imaginary part of the impedance, and ω is the angular frequency. Also included in this overlay is a nonlinear least-squares routine for analysis of semicircular plots of $-Z''$ versus Z' based upon the method of Kendig et al.⁶ The second analysis overlay allows the user to pass a cubic spline through the experimental data. This cubic spline is suitable for drawing a smooth curve through a plot of the experimental data, or it can be used to calculate the Kramers-Kronig (KK) transforms,^{7,8} routines which are also contained in the second analysis overlay. A third overlay allows analysis of impedance data collected from systems with very slow corrosion rates, using a procedure similar to that proposed by Shih and Mansfeld.⁹ Most analysis overlays permit the user to specify the analysis frequency range, save and plot the generated data, as well as list the data on the printer. Users familiar with the ASYST language can easily write other analysis overlays and access them through the main program.

Plotting of the experimental and analyzed data is carried out in the "plot data" overlay. The first submenu in this overlay sets various plot parameters and options including the frequency range of the data to plot, the plot type, a color and symbol for the plotted data, x- and y-axis ranges, single or multiple plots on one page, and the plotting device. Presently, users can select from 14 plot types such as Nyquist (both Z'' versus Z' and Y'' versus Y'), Bode ($\log(|Z|)$ and ϕ both versus $\log(\omega)$ on the same plot or on different plots), and Z' versus $\omega^{-1/2}$, where Y' and Y'' are the real and imaginary components of the admittance and $|Z|$ and ϕ are the magnitude and phase angle of the impedance. The second submenu permits users to alter rarely changed options or parameters such as grids and zero axes on the plots as well as the plotter pen speed.

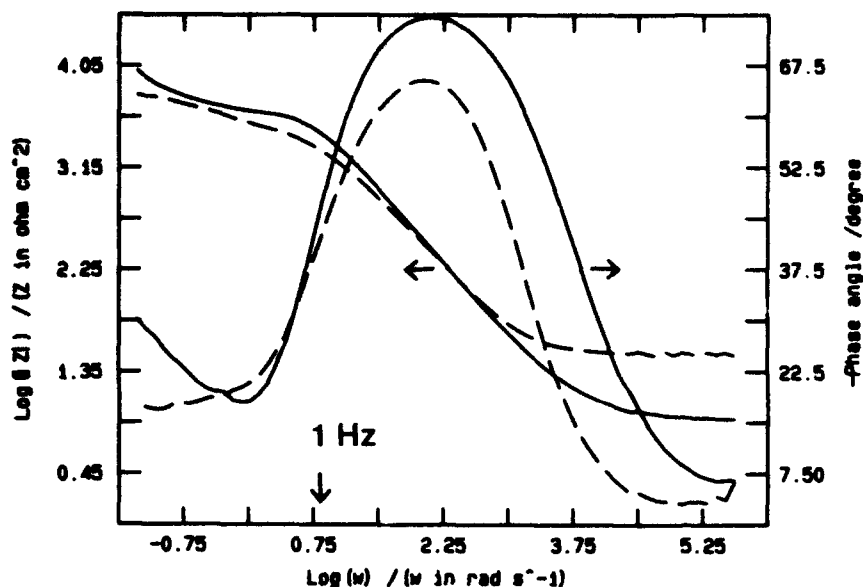


FIGURE 3 Bode plot of the impedance data obtained from (—) 2090 T8E41 (2.25 cm²) and (---) 7075 T6 (2.25 cm²) specimens at their open-circuit corrosion potentials after four days immersion in aerated 3.5% NaCl.

Overlay "transfer data," Figure 2, allows the user to output or input impedance data in ASCII format. This is most useful when the experimental data is to be analyzed by an external nonlinear least-squares analysis program such as LEVM¹⁰ or EQUIVALENT CIRCUIT.¹¹ Finally, the "quit" overlay allows the user to exit the program and return to DOS.

Results and Discussion

Figure 3 displays Bode plots obtained for 2090 T8E41 lithium-aluminum and 7075 T6 aluminum alloys immersed in aerated 3.5% sodium chloride solution.¹² Of particular interest are the measurements below 1 Hz that demonstrate the ability of the experimental equipment to obtain good quality data by integration over only one period of the excitation signal. Both plots display two time constants as indicated by the maxima in the phase plots, that can be attributed to uniform corrosion (low frequency, partially developed time constant) and pitting corrosion (high frequency) as described by Shih and Mansfeld.¹³ An ASYST overlay to implement the analysis procedure recommended by Shih and Mansfeld is currently being developed.

KK transforms are useful in impedance spectroscopy as they can be used to ensure that the experimental data are self-consistent, provided the data fulfill certain conditions.⁷ Three of the KK transforms may be stated as follows:

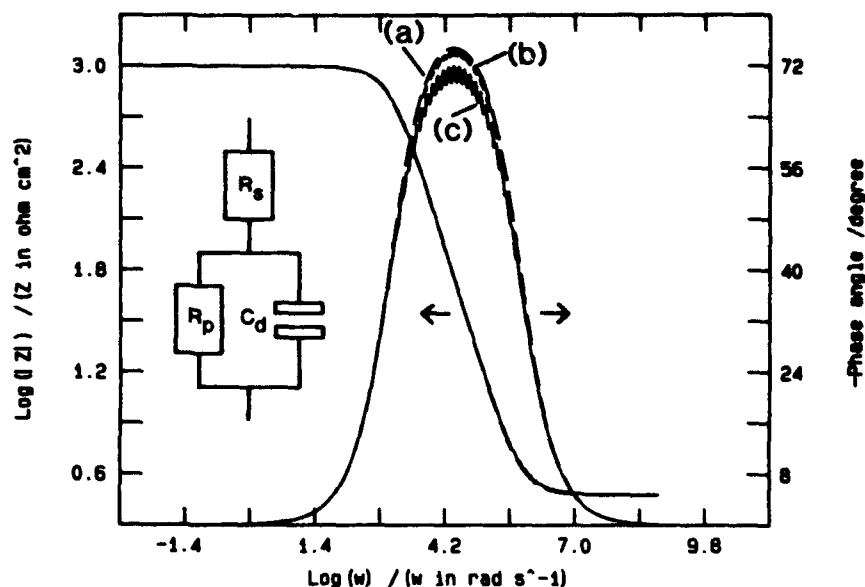
$$Z'(\omega) - Z'(\infty) = \left(\frac{2}{\pi}\right) \int_0^{\infty} \frac{xZ''(x) - \omega Z''(\omega)}{x^2 - \omega^2} dx, \quad (1)$$

$$Z'(\omega) - Z'(0) = \left(\frac{2\omega}{\pi}\right) \int_0^{\infty} \frac{\left(\frac{\omega}{x}\right)Z''(x) - Z''(\omega)}{x^2 - \omega^2} dx, \quad (2)$$

$$Z''(\omega) = -\left(\frac{2\omega}{\pi}\right) \int_0^{\infty} \frac{Z'(x) - Z'(\omega)}{x^2 - \omega^2} dx. \quad (3)$$

However, even when the conditions are met the calculated KK transforms may indicate that the data are inconsistent. This is shown in Figure 4 where the simulated Bode plot for the circuit displayed in the figure is compared with the Bode plots obtained by transforming the imaginary component of the simulated impedance using transform (2). The transforms were achieved by (i) passing a cubic spline through the simulated impedance data, (ii) generation of a number of evenly distributed (over frequency) data points from the cubic spline coefficients, and (iii) integration using the 1/3 Simpson's rule contained in the ASYST language. As can be seen, when only 200 points are used in step (ii) significant noise is introduced into the transformed data (Fig. 4c), particularly in the capacitive region (i.e., region of maximum phase angle). Increasing the number of points to 900 (current maximum value for the program) reduced the noise significantly

FIGURE 4 Bode plot for the circuit shown: circuit parameters $R_s = 3 \Omega$; $R_p = 1000 \Omega$; $C_d = 100 \mu F$; α (defined in reference 9) = 0.9. (a) (—) Simulated data with no noise added; (b) (---) transform (2) data using 900 points; (c) (—) as in (b) using 200 points.



(Fig. 4b), but the transformed and simulated data are still not in agreement. Transformations using transform (1) provided data that were identical with the simulated data even when only 200 points were used. The converse is true when the capacitor is replaced with an inductor, that is, transform (1) requires significantly more points than transform (2) to ensure good agreement between the theoretical and transformed data. Data obtained from transform (3) were not influenced by the number of data points (>200). Thus, when using the KK transforms it is important to examine what effect varying the number of data points has on the transformed data be-

fore assuming that the experimental data are not consistent.

Figure 5 displays the effect of noise in the impedance data on the KK transforms. The noise introduced into the data was Gaussian noise with a standard deviation set to some percentage of the value of each datum point. Furthermore, it was assumed that there was no correlation between the noise in the imaginary and real components of the impedance. This is a worst case condition as the noise in experimental data lies somewhere between fully correlated and fully uncorrelated noise. Simulated, noisy data transformed using transform (1) result in impedance data that have

FIGURE 5 Bode plot for the circuit shown in Figure 4: circuit parameters the same as Figure 4 except $R_p = 1.0 \times 10^5 \Omega$. (a) Simulated data with 5% added noise; (b) transform (3) data using 300 points; (c) as in (b) using transform (1).

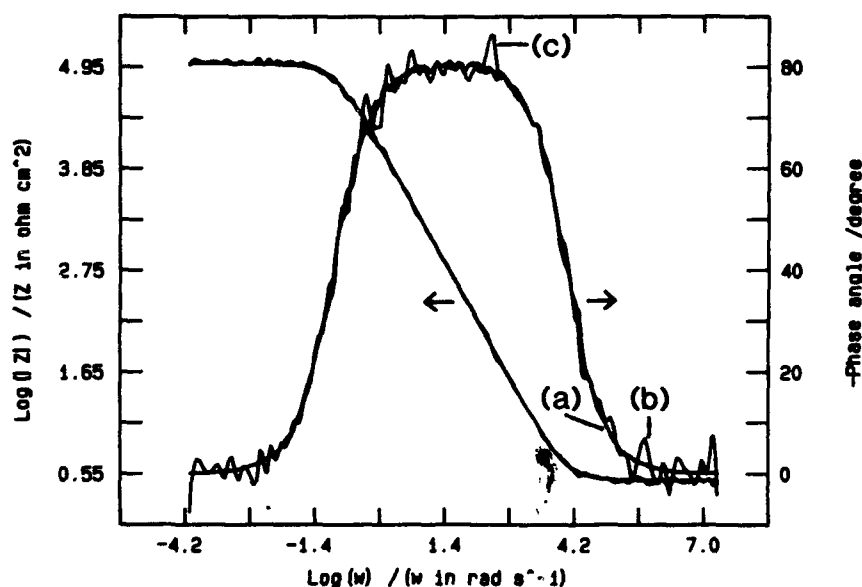


TABLE 1 Circuit parameters obtained by applying the procedure of Shih and Mansfield⁴ to simulated data^a

% Noise	0	5	10	20	40
Lower Frequency Limit = 1.2×10^{-2} Hz					
R_s/Ω	$3.00 \pm 1.0 \times 10^{-4}$	2.96 ± 34.81	2.87 ± 70.67	2.57 ± 148.99	0.56 ± 410.15
$R_p/k\Omega$	$100.00 \pm 1.6 \times 10^{-7}$	97.95 ± 0.21	95.40 ± 0.42	88.25 ± 0.89	55.53 ± 2.46
$C_d/\mu F$	100.00 ± 2.92	99.43 ± 4.80	99.80 ± 8.68	104.43 ± 18.06	190.27 ± 77.00
α	0.900 ± 0.001	0.900 ± 0.002	0.899 ± 0.003	0.893 ± 0.006	0.802 ± 0.013
Lower Frequency Limit = 1.2×10^{-3} Hz					
R_s/Ω	$3.00 \pm 1.0 \times 10^{-4}$	2.96 ± 44.66	2.90 ± 90.97	2.75 ± 192.41	2.28 ± 546.92
$R_p/k\Omega$	$100.00 \pm 4.2 \times 10^{-7}$	100.88 ± 0.27	101.38 ± 0.55	100.94 ± 1.15	84.98 ± 3.28
$C_d/\mu F$	100.00 ± 2.91	98.62 ± 4.77	97.93 ± 8.53	99.26 ± 17.13	144.91 ± 53.71
α	0.900 ± 0.001	0.901 ± 0.002	0.901 ± 0.003	0.901 ± 0.006	0.888 ± 0.013

^aCircuit as per Figure 4 with parameters: $R_s = 3.0 \Omega$; $R_p = 1 \times 10^5 \Omega$; $C_d = 100 \mu F$; $\alpha = 0.9$.

accentuated errors towards the center of the capacitive region in the Bode plot (Fig. 5c). On the other hand, transform (3) results in data that contains significantly more noise in the frequency regions on either side of the capacitive region (Fig. 5b). Better agreement between simulated and transformed data was obtained as the noise level was decreased, but differences between the two sets of data could be detected even when the introduced noise was reduced to 2%. Thus, experimental data with a very low noise level (<1% uncorrelated noise) are a prerequisite if the present method is used for calculating the KK transforms. For this reason, the use of smoothing splines or least-squares analysis to eliminate the restriction on the noise level in the experimental data is currently being evaluated.

The other main analysis overlay is concerned with extracting circuit parameters from impedance data obtained from very slowly corroding specimens.⁹ Table 1 displays the results obtained with this procedure using data generated using the component values $R_s = 3.0 \Omega$, $R_p = 1.0 \times 10^5 \Omega$, $C_d = 100 \mu F$, and $\alpha = 0.9$ for the circuit displayed in Figure 4. Inspection of the upper half of the table shows that the calculated values agree well with the actual values, provided the noise in the simulated data does not exceed 20%. Even better agreement between calculated and actual values is obtained when the minimum frequency at which the simulated data were calculated is reduced. The parameter values in the lower half of the table were obtained from simulated data with a lower frequency one order of magnitude below that for the data used in the upper part of the table. Typically, the noise associated with a.c. impedance

data would not exceed 10%, therefore the method of Shih and Mansfield⁹ provides an excellent procedure for determining the circuit parameters for a slowly corroding system.

Program listings and manuals and further information concerning the purpose-built interface are available on request.

Conclusions

ASYST is a powerful language that permits users to control experiments and analyze experimental results. The present program allows collection of electrochemical impedance data and the analysis and displaying of such data. A purpose-built interface ensures that accurate data are collected in a minimum period of time. The program provides simple data analysis functions as well as quite complex ones, including KK transforms and nonlinear least-squares analyses.

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