JOURNAL OF APPLIED ELECTROCHEMISTRY 22 (1992) 553–557

The numerical inversion of the Laplace transform applied to impedance spectroscopy

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Received 14 August 1990; revised 11 February 1991

Numerical inversion of the Laplace transform extends the use of results obtained by impedance spectroscopy to evaluation of the time response of electrochemical systems. Based on impedance spectroscopy results the characteristics of the electrical impulses (shape, duration, etc.) can be tailored by computer experiments so that a desired behavior of electrodes is achieved. The technique can also be used for optimization of the preparation parameters with respect to electrode performance.

1. Introduction

Impedance spectroscopy is widely accepted as a method of investigation of charge transport processes [1]. It is used for both solid state and solution electrochemical systems [2, 3]. The impedance values are generally obtained as a function of frequency under a sinusoidal perturbation and are interpreted in terms of equivalent circuits with frequency dependent components. The analysis of the system in terms of equivalent circuits makes impedance spectroscopy a powerful engineering tool. The physical meaning of the components of the equivalent circuit is assigned, however, on the basis of complementary physico-chemical measurements. The interpretation of results assumes a linear response to perturbation. This constraint dictates the limits imposed on the amplitude of the perturbation used for measurement and makes extrapolation of data obtained under small perturbations of limited predictive capability to situations in which the perturbation is large. Complications arise when the response to perturbations with non-sinusoidal time dependence is predicted. Examples of such systems are neural stimulation electrodes to which square current pulses are applied. In these cases it might be desirable to predict, for example, the electrode potential at each moment in order to operate the electrode within physiologically safe limits [4].

Obtaining the time dependence of the response of the system is possible in principle because time and frequency are Laplace conjugates. Therefore the inverse Laplace transform of the equivalent circuit must be found and multiplied by the value of the current at each moment. This is a more difficult task than it appears because of the complexity of the equivalent circuits, which is the rule rather than the exception for most real systems [2, 3]. This latter problem can be addressed numerically as long as the approximations involved in applying impedance spectroscopy are valid. The following approach was selected. A time dependent current perturbation is transposed to the frequency domain by applying the Laplace transform. The result is then multiplied by the frequency dependent impedance of a circuit equivalent to the physical system of interest and the potential response is obtained. This potential waveform is numerically inverted in the Laplace space and the result is the time evolution of the potential excursion of the system. In equation form, this becomes:

$$V(t) = \mathscr{L}^{-1}V(j\omega) = \mathscr{L}^{-1}[Z(j\omega)^{*}\mathscr{L}i(t)] \quad (1)$$

where V is voltage, t is time, $\mathscr{L}$ and $\mathscr{L}^{-1}$ are the Laplace transform and its inverse, respectively, $j = +(-1)^{1/2}$, ω is the angular frequency, Z is impedance and i is current.

2. Results

Since the inversion of the Laplace transform is an ill-conditioned problem, there is no general technique for its numerical implementation [5]. Two recently published algorithms for the numerical Laplace inversion were tested in the present work [6], [7]. The first one is based on Weeks' algorithm and is very efficient, but is not suitable for functions whose derivatives are not continuous, such as square waves [6]. The second algorithm is very robust and performed reasonably well in all the cases tested. It approximates the value of the inverse Laplace transform by the Durbin formula [8]:

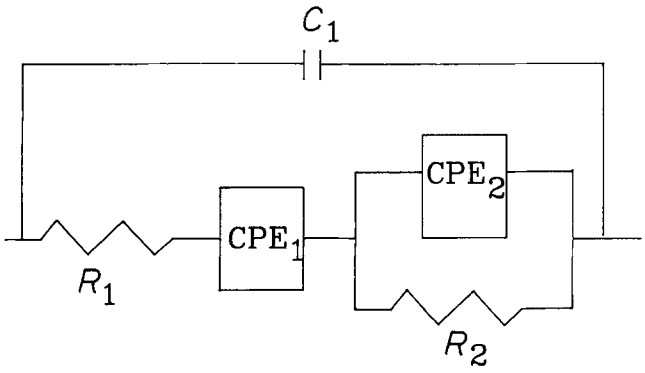
$$\bar{f}(t) = \frac{e^{\alpha t}}{T}\left[\frac{\mathrm{Re}\{F(\alpha)\}}{2} + \sum_{k=1}^{\infty}\mathrm{Re}\left\{F\left(\alpha + \frac{ikn}{T}\right)\right\} \times \cos\left(\frac{knt}{T}\right) - \sum_{k=1}^{\infty}\mathrm{Im}\left\{F\left(\alpha + \frac{ikn}{T}\right)\right\} \times \sin\left(\frac{knt}{T}\right)\right] \quad (2)$$

where $F(x)$ is the direct Laplace transform given by

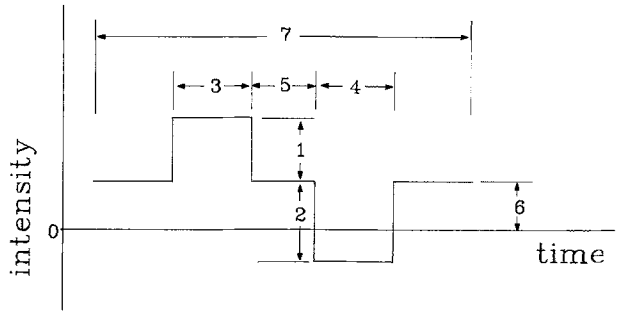
$$F(x) = \int_0^{\infty}\exp(-xt)f(t)\mathrm{d}t \quad (3)$$

The truncation error, expressed by

$$E = f(t) - \bar{f}(t) = \sum_{n=1}^{\infty}\exp(-2n\alpha T)f(2nT + t), \quad (4)$$



SCHEME I



SCHEME II

is adjusted by the choice of the parameters T and α.

Considerable effort was spent testing the algorithms and their implementation. The tests were meant to confirm the validity of the computer implementation of the algorithm by transferring functions with known Laplace transform, including square pulses, from frequency domain to time domain functions. For the present specific application several combinations of passive elements common in equivalent circuits, such as resistors, capacitors and inductances were tested as well. All the results were satisfactory, except for cases in which a large number of periods were considered; in these cases some "ringing" occurred (e.g. see Fig. 3).

In the following, several applications are presented in order to illustrate the utility of the method and the type of information that can be obtained. An immediate application of the method outlined above is for tailoring pulse shapes optimal for electrodes characterized by impedance spectroscopy. A second important application is identifying the most important parameters in the equivalent circuit that affect the time response, and attempting to control them. The latter can be achieved, for example, by optimization of the parameters for electrode preparation or pretreatment.

Once the validity of the procedure was established, two types of experiments were performed: changing the perturbation pulse shape and changing the values of parameters in the equivalent circuit. The aim of experiments in the first category was to examine the potential excursion of electrodes under current perturbations with different pulse shapes and duration. In the latter category of experiments the importance of various parameters is assessed. Changing the numeric value of the circuit components corresponds to altering the electrode characteristics by changing the conditions of preparation or pretreatment. Thus emphasis can later be placed on preparation methods that affect the most significant parameters.

For illustration, the method of numerical inversion of the Laplace transform was applied to equivalent circuits previously derived for iridium oxide electrodes prepared by electrochemical growth and by sputtering [9, 10]. The most general equivalent circuit derived from impedance spectroscopy data for these and other iridium oxide electrodes is shown in Scheme I.

The R's and the C's stand for resistors and capacitors, respectively. The CPE's are the so-called constant phase elements. These are components whose impedance can be expressed, over a specified frequency range, as

$$Z_{\mathrm{CPE}} = (1/A)(j\omega)^{-\beta} \tag{5}$$

where A is a real number whose dimensions are related to the exponent β such as to get the correct impedance units. The exponent β has values between 0 and 1. A value of 0 is characteristic for a resistor, a value of 1 corresponds to a capacitor, and a value of 1/2 can be assigned to diffusion phenomena [11], or to porous electrodes with cylindrical pores [12]. Values different from those have been attributed, among others, to fractal dimension of the interface [13], or self-similar mixtures of conductors and dielectrics [14]. The total impedance of the circuit in Scheme I is

$$Z = \left\{ \left[R_1 + A_1(i\omega)^{-\beta_1} + \frac{R_2 A_2}{A_2 + R_2(i\omega)^{\beta_2}} \right]^{-1} + i\omega C_1 \right\}^{-1} \tag{6}$$

The physical meaning of the components in the equivalent circuit was assigned as follows [9]: C_1 is the cell capacitance, R_1 is the resistance of the bulk solution, CPE_1 is associated with the electrolyte inside the pores, R_2 is the electronic conductivity of the iridium oxide layer, and CPE_2 represents the charge movement between discrete sites in the iridium oxide. The exponents involved in the CPE are associated with morphological effects, for example, movement of charge along tortuous paths. The actual values of the parameters can be obtained by means of nonlinear least squares fitting as described in [1]. In some cases the best fit value of β_2 was unity, thus the CPE element being a pure capacitor [9].

The importance of the pulse shape has been stressed many times [4]. In the present work, square waves were selected. The square pulse perturbation is one of the most widely used perturbations for neural prostheses and is characterized by several parameters as shown in Scheme II: the maximum and minimum value of the signal (2 parameters: *1* and *2*); duration of the perturbation at minimum and maximum value (2 parameters: *3* and *4*); time interval between the polarity change (1 parameter: *5*); offset (1 parameter: *6*); and period (1 parameter: *7*). The large number of parameters is a mixed blessing for the experimenter:

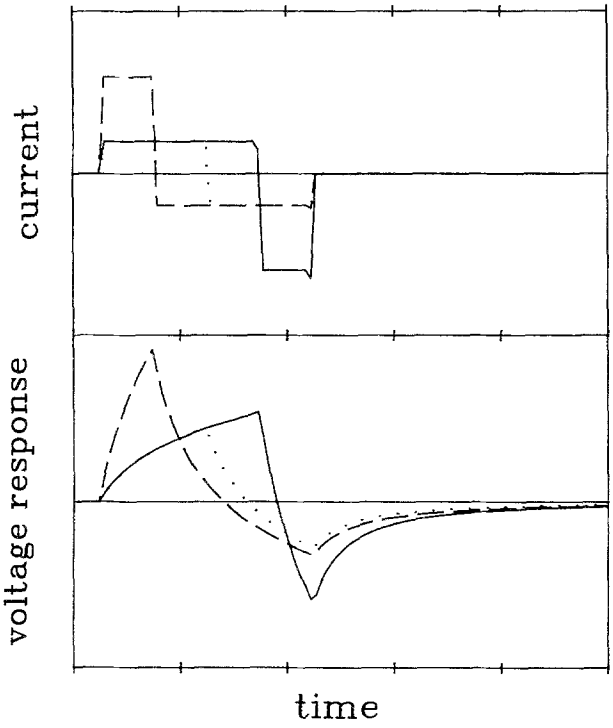


Fig. 1. Influence of the shape of the perturbation on the potential excursion of the electrode. Two asymmetric, balanced pulses have been applied: one in which the first half is more intense (dashed line), and the other in which the second half excursion is more intense (continuous line). A symmetrical pulse (dotted trace) is also shown to illustrate the asymmetry of the potential excursion under symmetrical pulses.

on the one hand it gives a great flexibility, on the other hand a huge number of experiments is necessary to find an absolute optimum.

The experiments presented here for illustration were performed with pulses with zero offset, without delay between the change in polarity and "charge balanced", i.e. the areas above and under the zero line are equal. These constraints reduce the number of parameters, because the time between the polarity change and the offset are fixed to zero and the product current times duration must be equal in the two directions.

A first set of experiments involved pulses the amplitude of which was different in the two directions (parameters *1* and *2* in Scheme II). Figure 1 shows the current pulse shape reconstructed by inverse Laplace transform (upper) and the potential response of the circuit in Scheme I. Reconstructed square waves mean that square pulses in time domain were transformed by the Laplace transform in frequency domain and then transformed back in time domain by numerical inversion. Although asymmetric, the pulses are balanced and both pass the same amount of charge. The *voltage* excursion of the system (the difference between the most cathodic potential and the most anodic potential) is about the same for the two asymmetric pulses, but the *potential* excursion, i.e. the cathodic and anodic values of the potential, is very different. This result agrees with the experimental observation that charged balanced pulses in which the amplitude of the first pulse and that of the balancing one are different can give superior results with respect to charge injection [15]. Another immediate observation is that, even for widely spaced (the period was 100 times longer than the pulse duration), perfectly symmetrical pulses, the potential excursion is asymmetric with respect to the open circuit potential (dotted trace in Fig. 1). The observation that the potential of the unwanted redox reactions can be avoided, even with "Lilly pulses", by simply applying pulses having the appropriate polarity agrees well with experimental data in the literature [4]. The effect of changing the duration of the pulse in one of the directions (i.e. parameter *4* in Scheme II) is illustrated in Fig. 2. The potential excursion became equal in both directions by making the balancing current pulse half as short as the initial pulse, while preserving the charge balance. While the effect is general, the equality was fortuitous and specific to the set of parameters chosen for simulation (see below).

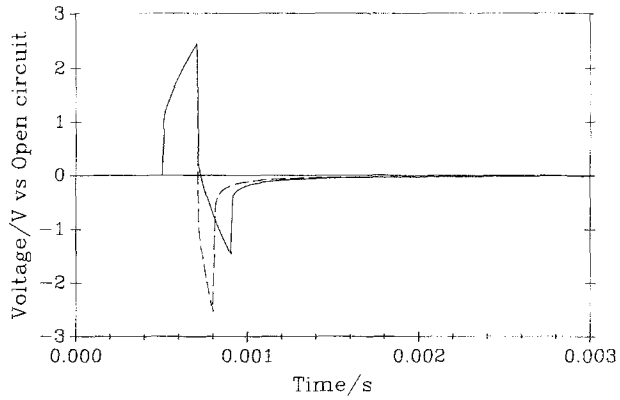


Fig. 2. Change in the potential excursion by tailoring the pulse shape. The duration of the balancing pulse is half that of the initial pulse.

Figure 3 shows the effect of applying pulse trains of different shape. Besides the asymmetry noted for the widely spaced pulses, it is observed that the values of the potential extrema shift due to lack of time to relax between pulses. This effect has been observed for Pt–Ir electrodes used for square wave "packet" simulation of the striate cortex [16].

For experiments involving the characteristics of the electrode a simpler equivalent circuit, previously derived for iridium oxide electrodes prepared by sputtering, was used [10]. This circuit lacks the parallel capacitor C_1 (see Scheme I) and its impedance is

$$Z = R_1 + A_1(i\omega)^{-\beta_1} + \frac{R_2 A_2}{A_2 + R_2(i\omega)^{\beta_2}} \qquad (7)$$

The starting values for the parameters in the circuit were: $R_1 = 6\,\Omega$, $A_1 = 33.5 \times 10^{-5}$, $\beta_1 = 0.673$, $A_2 = 6.7 \times 10^{-5}$, $\beta_2 = 0.459$, $R_2 = 188\,\Omega$. All the experiments involving changes in the circuit parameters were based on the response of the electrode to a charge balanced, anodic first, symmetrical current pulse without any delay between the polarity change. The initial values of the parameters were changed for checking their influence on the excursion of the potential under short square pulses.

The effect of "changing the electrolyte" to a less

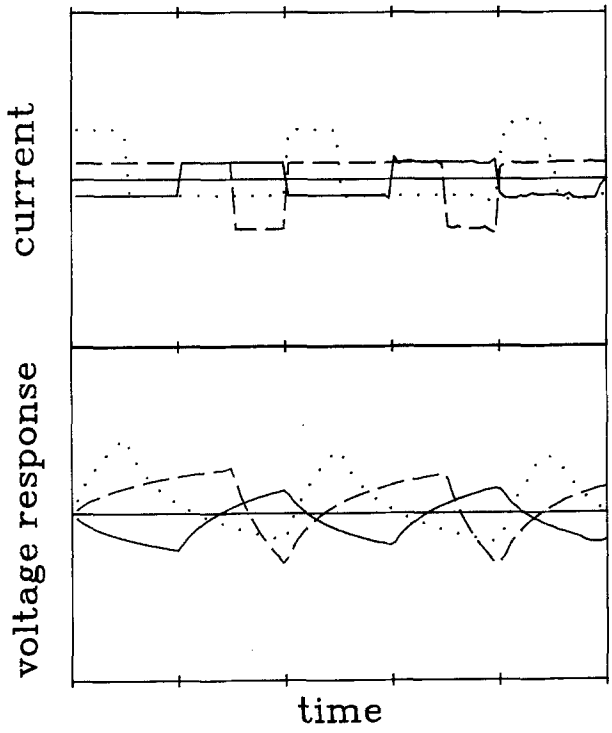


Fig. 3. Change in electrode potential under current pulses in close succession. In the third cycle some "ringing" was observed and the effect became severe after the third cycle. Two asymmetric, balanced pulse trains have been applied: one in which the first half is more intense (dashed line), and the other in which the second half excursion is more intense (continuous line). A symmetrical pulse train (dotted trace) is also shown to illustrate the asymmetry of the potential excursion under symmetrical pulses.

conducting one was modelled by increasing the value of R_1 by one order of magnitude and decreasing the value of A_1 by one order of magnitude, while keeping constant the rest of the parameters. The result, compared with the response of the original electrode is shown in Fig. 4. it is worth noting that taking into consideration the changes in both R_1 and CPE_1 results in a complete change in the pulse behavior of the system, while an increase solely in the resistance of the bulk solution, R_1, brings about only an increase of the "access potential" (dotted line in Fig. 4).

Changing the value of the exponent β_1 corresponds in our interpretation to changing the morphology of

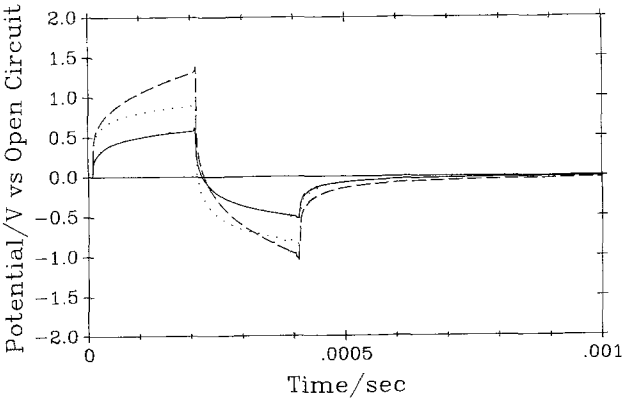


Fig. 4. Influence of changing the parameters associated with the conductivity of the solution, R_1 and A_1, by one order of magnitude, on the potential excursion of the electrode (dashed trace). The dotted trace shows the effect of changing R_1 alone.

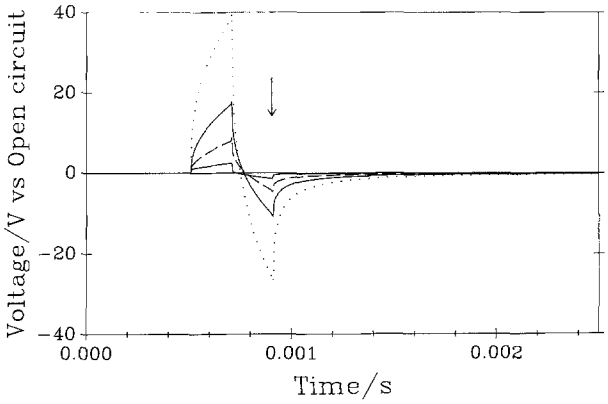


Fig. 5. Influence of changing the parameter β_1 associated with morphology, on the potential excursion of the electrode. The arrow shows the direction of the change from 0.4 (dotted line) to 0.5 (solid line) to 0.6 (dashed line) to 0.8 (continuous line).

the path followed by charge in the pore solution. The result of such changes around the "diffusion" value, 1/2, is shown in Fig. 5. Figure 5 illustrates the large effect of morphology on performance of electrodes with similar characteristics of the constituent material. An increase of more than an order of magnitude in the voltage response is observed when the exponent β_1 doubles its value. This behaviour contrasts with the negligible influence of similar changes in the parameter β_2 (not shown). The weak dependence of β_2 reflects the fact that charge has an alternate route to hopping, that of electronic conduction. Therefore if one wants to increase the efficiency of charge injection, the efforts should be focussed on changing the parameter β_1, which would correspond to the porosity of the oxide layer on the electrode. It has been shown in the past that there exists a quantitative correlation between charge storage capacity and morphology, but no physical assignment has been given [17]. The present analysis attempts to pinpoint the most influential factor with respect to fast discharge and this seems to be the porosity of the electrode.

In real life applications it is essential to be sure that the results obtained by impedance spectroscopy can be reliably converted from the time domain to frequency domain under a specific perturbation. Two methods can be used for checking the convertibility, depending of the experimental conditions and of the chemistry involved. One valid test is to increase gradually the amplitude of the perturbation used for the impedance spectroscopy measurement. Up to a certain value of the amplitude the measured impedance will remain unchanged, meaning that the linearity of the response as a function of perturbation is preserved. When a critical value of the amplitude is reached, the measured impedance will start changing, meaning that the response is no longer a linear function of the perturbation. This method is however subject to limitations in the electronic hardware and constraints imposed by the chemistry involved. A second test, performed in the time domain, relies on the comparison of the shape of the potential response to pulses of different polarity. If the response to the

two perturbations are mirror images of each other, then the assumptions involved in the use of transfer functions are valid for that particular set of experimental conditions. In other words, no changes occur in the values of the components of the equivalent circuit on the time scale of the perturbation. For example, it is known that the electronic conductivity of iridium oxide changes with potential, but the change occurs on a much longer time scale than the perturbations involved in impedance spectroscopy [18]. The latter method involves changing the electrode potential and possibly the chemistry of the system.

A final caveat is in order at this point. Although the result of these experiments is free of experimental artifacts and not more expensive than the computer resources, it is subject to floating point calculation errors and truncation errors.

3. Conclusions

In the conclusion, the present work shows that:
(i) numerical methods can be used to extend the use of results obtained by impedance spectroscopy for evaluating the time response of various systems.
(ii) the characteristics of the perturbation (shape, duration, etc.) can be tailored by computer experiments for various materials characterized by impedance spectroscopy, in order to operate them within desired limits (e.g. physiologically safe); in other words that the electrical pulse shape, e.g. for neural stimulation, should be changed when using electrodes made from different materials, or even prepared by different routes.
(iii) it is possible to assess the importance of the different components in an equivalent circuit for the optimization of time dependent processes.

Acknowledgements

Useful comments from Dr J. R. Macdonald, Professor R. P. Buck, Dr L. S. Robblee, and Ms A. G. Kimball are gratefully acknowledged.

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