Comparison between the impedance spectra of Li/SOCl₂ batteries obtained using the time and the frequency domain measurement techniques

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A comparison between the impedance spectra of Li/SOCl₂ batteries obtained in the time and frequency domains is reported. It is demonstrated that by averaging over several responses the accuracy in the time domain is greatly improved. On the other hand, it was found that the time domain technique caused nonlinearity in the system response even at very small amplitudes of excitation (for example corresponding to a potential drop of 30 mV). The method is useful for routine characterization of the quality of galvanic cells in industrial production. The accuracy compared with market-available impedance spectrometers operating in the frequency domain is satisfactory ($\pm 10\%$), the price being much lower.

Nomenclature

g_i	parameters of model fequency response
g_{id}	parameters g_i obtained by deconvolution
g_{ir}	parameters g_i obtained by frequency domain method
H	frequency response
H_m	model frequency response
H_r	reference frequency response
$i(t)$	excitation current
$I(\omega)$	Fourier transform of the $i(t)$
Im	imaginary part
j	imaginary unit ($\sqrt{-1}$)
M	Number of independent measurements
N	number of samples

Re	real part
R	resistance
R_0	ohmic resistance
T	sampling time
$u(t)$	response voltage
$U(\omega)$	Fourier transform of $u(t)$
α	dispersion factor
ω	angular frequency
$\Phi(\omega)$	phase spectrum
ε_a	relative amplitude error
ε_{gi}	relative error of g_i
$\bar{\varepsilon}_a$	average relative amplitude error
ε_p	relative phase error
$\bar{\varepsilon}_p$	average relative phase error
τ_0	mean relaxation time

1. Introduction

The frequency response of an element can be determined in the frequency or in the time domain. The former technique has become a standard procedure while the latter is rarely used, although, at least from the theoretical point of view, it should give the same results, since the independent variables (frequency and time) are uniformly interrelated by the Fourier transform (FT) [1]. Applications of the time domain techniques began in the fifties and sixties when different authors tried to determine the internal resistance of electrochemical cells by applying an excitation signal in the pulse form and measuring the response [2–6]. A common feature of the above approaches is that the parameters of the corresponding equivalent circuit were determined directly from the response in the time domain.

Intensive development of pulse techniques was made by several workers [7–10], who transformed the time response into the frequency domain to obtain the frequency response. They used different shapes of excitation. To reduce noise they applied several independent pulses and averaged the response. Unfortunately, they could not compare the results obtained by the frequency domain technique because at that time appropriate devices for such measurements were not available.

The present purpose was to build a simple device working in the time domain using the FT technique, which would enable comparison of the time domain technique with frequency domain measurements.

2. Theoretical considerations

In practice a cell is excited by a pulse $i(t)$ of finite width which is sampled in the discrete time points nT, to yield a response $u(t)$, both signals being sampled in N discrete points at time intervals T. Thus, N points at times nT ($0 \leqslant n < N$) are obtained. In this case, the frequency response $H(\omega)$ is given in the discrete form and can be determined by a deconvolution equation
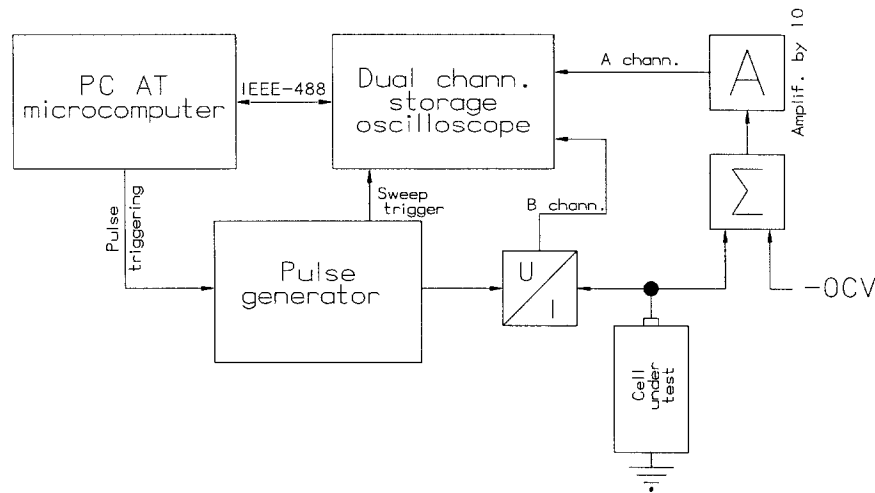
Fig. 1. Schematic diagram of the measuring system for determining the pulse response.

[11]:

$$H(\omega) = \frac{U(\omega)}{I(\omega)} \qquad (1)$$

where $U(\omega)$ and $I(\omega)$ represent the discrete Fourier transform (DFT) of the excitation and response signal, respectively. Thus DFT 'calculates' the frequency spectrum of a time signal and maps the discretely given samples from the time into the frequency domain [1].

The frequency response given by Equation 1 is a complex function with a corresponding amplitude and phase. The amplitude is equal to the absolute value of the frequency response ($|H(\omega)|$), whereas the phase can be defined as:

$$\Phi(\omega) = \tan^{-1}\left(\frac{\text{Im } [H(\omega)]}{\text{Re } [H(\omega)]}\right) \qquad (2)$$

In reality, during sampling there is always some noise which is added to the excitation and response signal and which influences the spectrum shape. Distortions due to noise can be successfully decreased by M-times independent excitation and by averaging the sampled signals according to Equation 3, which must be done

before DFT and the deconvolution are performed:

$$u(t) = \frac{1}{M} \sum_{i=1}^{M} u_i(t) \qquad 0 \leqslant t \leqslant nT \qquad (3)$$

In accordance with a standard theorem [12], the standard deviation of results caused by noise decreases proportionally to the square root of the number of measurements.

3. Definition of the error of the measurements

The accuracy of the measurement technique can be estimated by the following procedure. The relative error of the calculated discrete amplitude and the phase part of the frequency response $H(\omega)$ is defined according to the frequency domain measurement $H_r(\omega)$ for a particular frequency ω:

$$\varepsilon(\omega)_a = \frac{|H_r(\omega)| - |H(\omega)|}{|H_r(\omega)|} \times 100\% \qquad (4)$$

$$\varepsilon(\omega)_p = \frac{\Phi_r(\omega) - \Phi(\omega)}{\Phi_r(\omega)} \times 100\% \qquad (5)$$

If the method described is to be used for characterization of the quality of galvanic cells, then a model
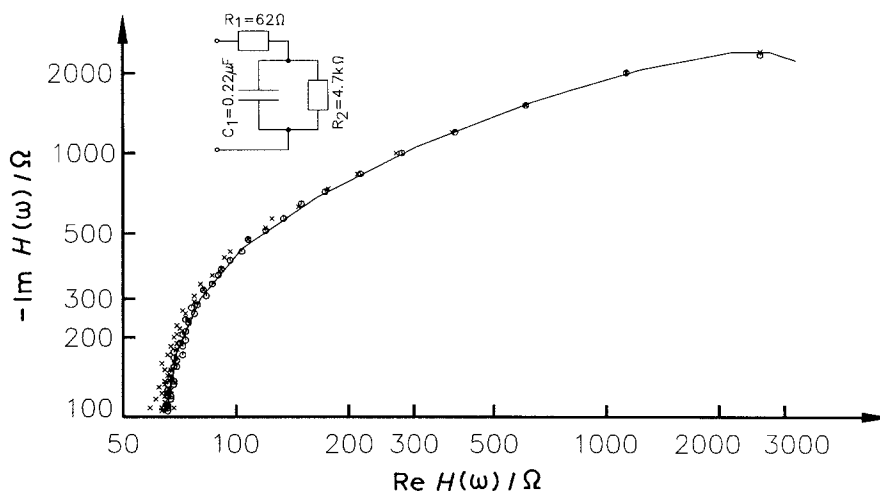

Fig. 2. Comparison between the frequency response of a standard RC term determined by deconvolution after 1 and 16 excitations and frequency domain measurement. Key: (———) frequency domain, (x) single pulse time domain, and (O) 16 pulses time domain.

Table 1. Comparison of the accuracy of fitted values of RC circuit elements determined by frequency and time domain method

Element	Nominal value	Fitted value and relative error	
		Frequency domain	Time domain
R_1	61.8 Ω (±0.5%)	62.3 Ω (−0.8%)	67.2 Ω (−8.7%)
R_2	4710 Ω (±0.5%)	4743 Ω (−0.7%)	4855 Ω (−3.1%)
C_1	0.22 μF (±2%)	0.222μF (−0.9%)	0.221 μF (−0.5%)

frequency response $H_m(\omega, g_i)$ with as few parameters g_i as possible should be ascribed to the frequency response of the cell, so that characterization is quick and easy, and as such is suitable for routine tests. Now, if the frequency response obtained using the method described is fitted to the model function, characteristic values of parameters g_i are obtained and can be used for a quick characterization of cell properties. However, in analysing the accuracy of the method, the parameters obtained should be compared to those obtained in fitting a frequency domain method. The relative error of parameters g_i for a certain measurement is defined thus

$$\varepsilon_{gi} = \frac{g_{ir} - g_{id}}{g_{ir}} \times 100\% \qquad (6)$$

which gives the approximate accuracy of the measurement method.

The frequency response of $Li/SOCl_2$ batteries can be satisfactorily approximated by the Cole-Cole equation [13]:

$$H(\omega) = R_0 + \frac{R}{1 + (j\omega\tau_0)^\alpha} \qquad (7)$$

R_0 being the ohmic resistance, R the resistance, τ_0 the mean relaxation time and α the dispersion factor. For the present purpose the Cole-Cole equation served as the model function.

4. Measurement system

The measurement system for determining the frequency response by the pulse method is shown schematically in Fig. 1. A personal computer triggers the voltage pulse

generator (HP 9011A), while the voltage-to-current converter (laboratory made) generates a current pulse by which the battery is excited. The measurement system was adapted for testing of $Li/SOCl_2$ batteries which have an open circuit voltage (o.c.v.) of 3.67 V. For this purpose a differential amplifier was made and used to subtract the o.c.v. from the measured voltage and to amplify the signal by a factor of 10. The output of this was connected to a Nicolet NIC 320 oscilloscope, and this via an IEC bus to a microcomputer which served for data acquisition.

The PC software was written in Pascal and comprised the control of the oscilloscope, DFT and deconvolution, as well as graphical representation of the results.

The measured results were compared to measurements obtained using a reference measurement system operating in the frequency domain, i.e. a Solartron 1250 frequency response analyser (FRA) a Solartron 1286 Electrochemical Interface (ECI) and an HP9816 microcomputer.

5. Results and discussion

Using the pulse measurement system described above, preliminary tests were first made on a standard RC circuit (Fig. 2). As the o.c.v. of such a circuit is zero and the response is linear even at relatively high voltages over (1 V), the differential amplifier unit could be omitted in these measurements. Results were compared to those obtained by the frequency domain method. Here two characteristic measurements differing only in the number of applied pulses are reported. Thus 1 and 16 pulses were applied in the first
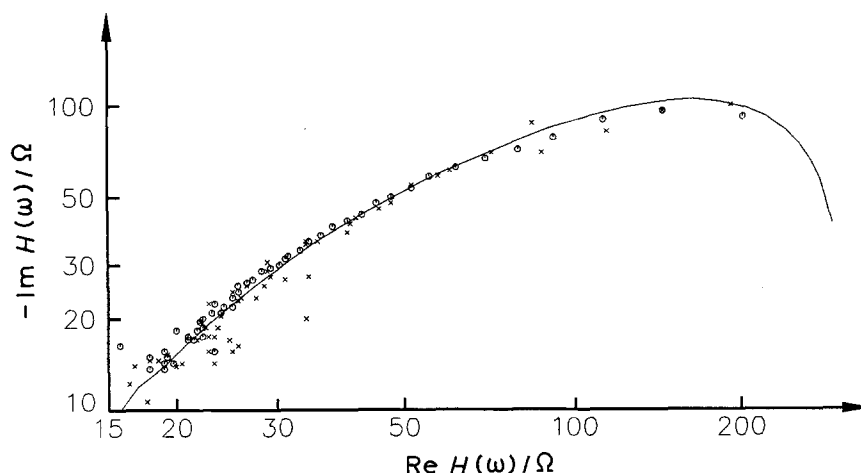
Fig. 3. Frequency response of a Li–SOCl$_2$ cell determined by deconvolution after 1 and 16 pulses in comparison with the response of the frequency domain method before excitation. Key: (——) frequency domain, (×) pulse time domain, and (O) 16 pulses time domain.
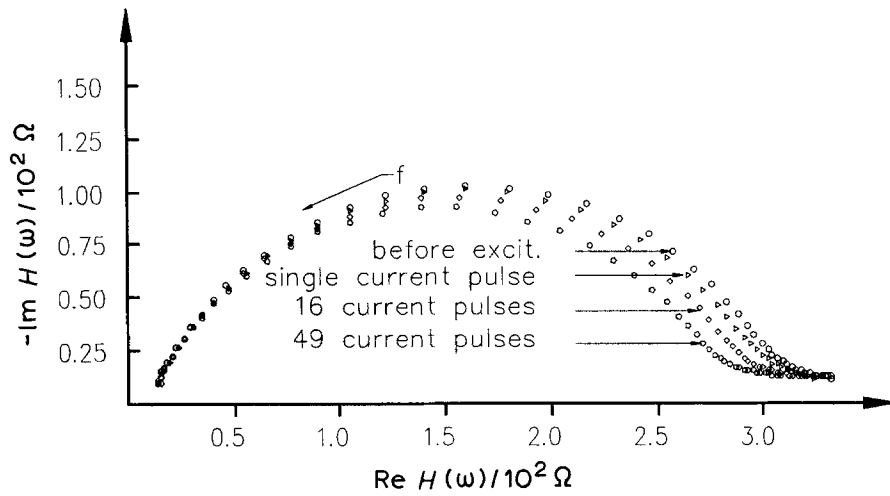
Fig. 4. Frequency response of a Li-SOCl₂ cell before excitation and after excitation using a different number of excitation pulses.

and the second case, respectively. Deconvolution of both measurements were compared with the results obtained by the frequency domain method (Fig. 2). It can be seen that averaging 16 independent pulse responses successfully reduces noise in comparison with a single pulse measurement.

Table 1 shows nominal values of the RC term used, and values determined by frequency and time domain methods (average of 16 pulse responses). It is evident that the serial resistance (R_1) was determined least accurately. This can be explained by the shape of excitation pulse in frequency domain $(\sin(\omega)/\omega)$.

Such a spectrum has its lowest amplitude at highest frequencies, which is exactly the part containing the information about serial resistance. Because the accuracy of measurement depends on the amplitude of the excitation signal, the relative error of the determination of R_1 is largest. When using frequency domain, the amplitude of the excitation signal is frequency independent, therefore the relative errors of values of all equivalent circuit elements are similar.

From Table 1 it also follows that the values obtained by frequency domain technique are closer to nominal
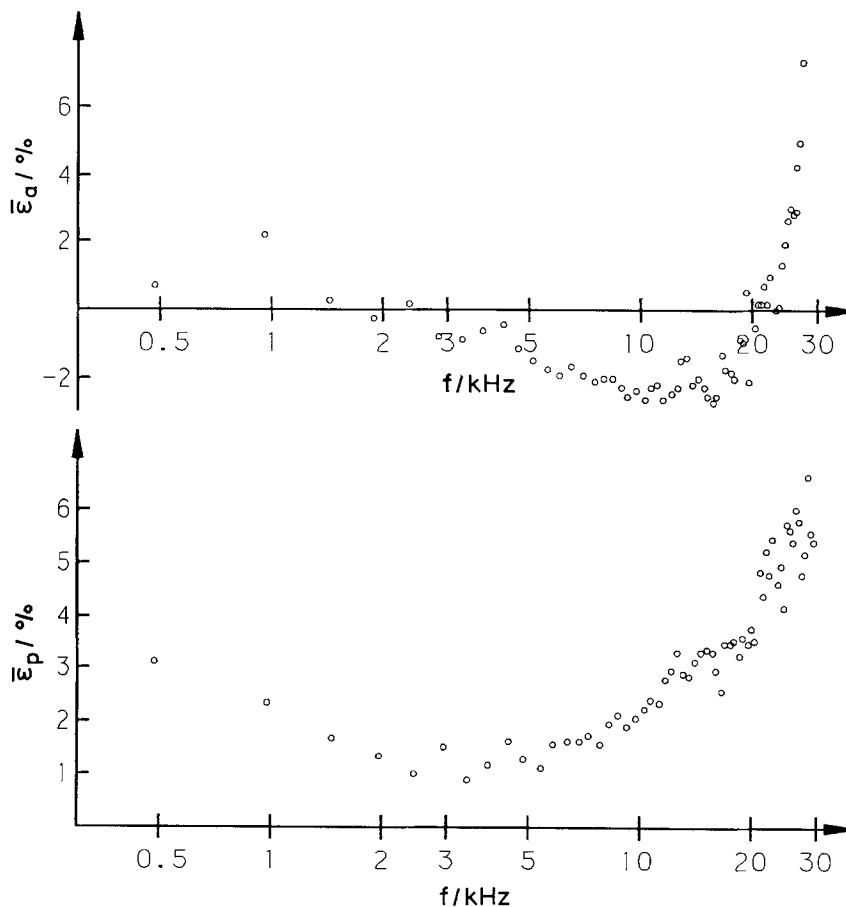

Fig. 5. Average relative error of the frequency response calculated as an arithmetic average of errors of 12 different Li-SOCl₂ cells.

Table 2. Relative errors in determining parameters R_0, α and τ_0 by the pulse method as compared to the frequency domain method

Battery no.	Relative error/%			
	R_0	R	τ_0	α
17	2.3	1.6	0.8	0.1
18	38.8	−2.2	−5.8	3.8
19	7.0	5.8	1.6	−3.2
22	−8.8	7.7	5.7	5.2
33	4.8	1.0	0.6	1.5
34	6.5	−1.3	−7.8	3.2
36	−3.4	0.7	0.9	0.1
37	9.2	0.1	0.5	0.4
38	8.1	2.8	1.2	0.8
49	11.4	1.6	−0.4	−0.4
50	9.5	2.6	4.4	−0.9
54	45.0	−1.9	−0.8	3.7

ones. Hence, the frequency domain technique was used as the reference measurement method.

The same experimental procedure was applied in the second set of measurements to industrial (25 × 25) Li-SOCl$_2$ batteries at room temperature. Here the differential amplifier was included in the measurement equipment so that the full-scale range at the maximum sensitivity of the oscilloscope was ± 15 mV. Batteries were excited by current pulses of 20 μs duration and of such amplitude that the resulting potential drop was about 30 mV. These experimental conditions were designed to satisfy the linearity of response of the measured cell. The results obtained by one and 16 pulses in comparison with the frequency domain measurement are shown in Fig. 3. It can be seen that the level of noise was again reduced by averaging 16 independent pulse measurements.

Using the time-domain technique it was found that the frequency response of the galvanic cell was temporarily changed by the applied excitation. Therefore the influence of the time domain technique on the frequency response of a battery was checked using the frequency domain method. The results shown in Fig. 4 demonstrate the changes with increasing number of pulses. It was found that the frequency response, is decreased in comparison with the initial state (Fig. 4). After several hours, or even days, the initial state of the response is reestablished. It may be concluded that by the application of pulses the Li-SOCl$_2$ cells were slightly depassivated. However, the same effect was observed in preliminary tests made on Lechlanché cells, which leads to the conclusion that the observed phenomenon is of more fundamental character.

The results in Figs. 3 and 4 show that the increase in the number of pulses improves the signal-to-noise ratio, while, on the other hand, it changes the frequency response more intensively. On the basis of the above results, the compromize of using 16 pulses to calculate the frequency response from time-domian measurements was adopted. In total, 12 batteries were analysed. Fig. 5 shows the average value of the amplitude and phase error averaged over 12 tested batteries.

All frequency domain measurements and calculated frequency responses were fitted by the Cole–Cole equation (7) from which parameters R, τ_0 and α were determined. Typical values were $R_0 = 10\,\Omega$, $R = 200\,\Omega$, $\tau_0 = 100\,\mu$s, $\alpha = 0.75$. Relative errors obtained by the pulse method compared to the results of the frequency domain method are given in Table 2.

6. Conclusions

The deconvolution procedure has rarely found application in impedance spectroscopy. The reason perhaps lies in the high noise-to-signal ratio appearing during measurements in the time domain and consequently, the relatively narrow frequency range in which the transfer function can be accurately obtained. In this paper it is confirmed that the noise can be effectively reduced by averaging the reponses of several individual pulses. In this case the deconvolution procedure is possible and successful. On the other hand, it was found that the described excitation in the time domain, in contrast to the frequency domain methods, leads to an additional relaxation of a galvanic cell which occurs on a time scale several orders of magnitude larger than that exploited by the technique.

It was shown by the example of the Li-SOCl$_2$ system that using relatively simple and cheap pulse techniques, useful results can be obtained. For industrial applications the accuracy obtained (± 10% according to the frequency domain measurements), as well as the relative narrow frequency range of the described technique (2–3 decades), is usually satisfactory.

Further progress in the field can be achieved by changing the method of excitation, i.e. using an alternating instead of a unidirectional sequence of pulses.

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