Electrochimica Acta 154 (2015) 35–46

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Fourier transform distribution function of relaxation times; application and limitations

Bernard A. Boukamp

University of Twente, Faculty of Science and Technology & MESA+ Institute for Nanotechnology, P.O.Box 217, 7500AE Enschede, The Netherlands

ARTICLE INFO

Article history:
Received 16 October 2014
Received in revised form 2 December 2014
Accepted 9 December 2014
Available online 12 December 2014

Keywords:
Distribution function of relaxation times (DFRT)
Fourier transform
electrochemical impedance spectroscopy (EIS)
Solid state electrochemistry

ABSTRACT

A simple Fourier transform (FT) method is presented for obtaining a Distribution Function of Relaxation Times (DFRT) for electrochemical impedance spectroscopy (EIS) data. By using a special data extension procedure the FT is performed over the range from $-\infty \leq \ln\omega \leq +\infty$. The integration procedure is analytic in the end regions, otherwise a quadratic interpolation is used. For the necessary windowing of the first FT result, a special Tanh window function is used, which shows better results than the well-known Hann window function. An alternative approach, based on a complex nonlinear least squares (CNLS) fit of a linear sequence of (RQ)'s, provides the DFRT directly, but often significantly deviating from the FT-DFRT. With several examples the usefulness of a DFRT in impedance analysis is tested. The main conclusion is that the visibility in the DFRT of separate dispersive contributions strongly depends on the associated resistance and the width of the distribution. 'Near equal strength' dispersive contributions show up in the DFRT, where the area under the DFRT-peak represents the 'strength' or resistance. But small peaks with a large FWHM are lost, although these can easily be identified in a CNLS-fit.

A comparison between the finite length Warburg (FLW) and the almost identical Gerischer impedance shows a clear difference in the DFRT. Indications are found that the characteristic Gerischer DFRT might be distinguishable in real measurement DFRT's.

In cooperation with an external group a brief test with an adaptive genetic evolution method showed promising results for a direct definition of a DFRT. In this process the reconstructed impedance is matched to the actual measurement.

1. Introduction

Electrochemical Impedance Spectroscopy (EIS) has come a long way since its introduction in wet-electrochemical research by Sluyters and Sluyters-Rehbach in the sixties of the last century [1,2]. In the seventies it was recognized by the solid state research community as an important tool for studying ionic conductivity and electrode effects. It proved to be far superior to the, then standard, practice of single frequency measurements. In that time it moved from manual graphical analysis of simple systems to computer aided analysis for progressively more complex systems. Notably Macdonald [3,4], Boukamp [5,6] and others [7,8] have contributed to this rapid expansion with the development of complex nonlinear least squares (CNLS) analysis programs.

A recent overview of the status of impedance data analysis, based on the concept of 'Equivalent Circuits' (abbreviated 'EqC'), has been presented in ref. [9]. New directions that did not involve electrical analogs were also receiving some attention [10], but most publications relied on an equivalent circuit interpretation which was based on a limited set of direct electrical relations (*R, C, L*) and more complex transfer functions derived from the Laplace transform of (bounded) diffusion equations (Warburg types [11–13] and Gerischer [14,15] or chemical impedance [16]) as well as empirical relations, e.g. the constant phase element, or CPE [17], and the Havriliak-Negami response function [18]. Since then several books on impedance spectroscopy have become available, notably by Barsoukov and Macdonald [19], Orazem and Tribollet [20] and Lvovich [21]. The most recent book by Lasia [22] presents an excellent introduction into EIS, its mathematics and data analysis.

In solid oxide fuel cell (SOFC) research EIS has played an important role in characterizing ionic transport processes in separate anode, cathode or electrolyte studies. Its application to complete cells, however, has created significant challenges as it becomes difficult to breakdown the frequency dispersion of the impedance in the separate anode and cathode processes. This is caused by closely spaced time constants for the various electrochemical processes in both electrodes.

http://dx.doi.org/10.1016/j.electacta.2014.12.059
0013-4686/

In this area of research the definition of a distribution function of relaxation times (DFRT) has been found to be useful for analyzing the measured impedance response. This DFRT, i.e. $R_p \cdot G(\tau)$, is found from the inversion of the following well-known equation:

$$Z(\omega_i) = R_\infty + R_{pol}\int_0^\infty \frac{\gamma(\tau)}{1+j\omega_i\tau}d\tau = R_\infty + R_{pol}\int_{-\infty}^{\infty} \frac{G(\tau)}{1+j\omega_i\tau}d\ln\tau \quad (1)$$

with: $G(\tau) = \tau \cdot \gamma(\tau)$ and: $\int_{-\infty}^{\infty} G(\tau)d\ln\tau = 1$. R_∞ is the high frequency cut-off resistance and R_{pol} is the polarization resistance, $R_{pol} = R_{dc} - R_\infty$, with R_{dc} the impedance value for $\omega \to 0$. Solving Eq. (1) for $G(\tau)$ is known as an ill-posed inverse problem. Various methods have been devised to obtain a useful representation of $G(\tau)$. In a recent publication [23] the research group of Prof. Ivers-Tiffée presented a Fourier transform method which derived the $G(\tau)$-DFRT from the imaginary part of the impedance. This method has been taken as the basis for this study.

Hörlin has proposed and demonstrated the usefulness of the maximum entropy method [24,25] for solving Eq. (1). Apparently this method has received very little attention in the solid state community. Another mathematical procedure is known as the 'Tikhonov regularization' [26]. Both methods require adjustment of the procedure with a 'smoothing parameter'. Too little smoothing yields unrealistic oscillations and superfluous small peaks, too much results in a rather smooth curve, suppressing the essential details. Saccoccio et al. [27] have recently presented an automated optimization method for the Tikhonov regularization.

But the Fourier de-convolution method also needs a separate, adjustable windowing function, as will be demonstrated below. Despite these complications, it seems that transforming impedance measurements to DFRT's is becoming a new trend in EIS-analysis. In this publication we will take a closer look at the possibilities and limitations of DFRT analysis. This will be based on four simple questions, each illustrated with a specific impedance problem:

1. How accurately or uniquely does a DFRT describe the impedance measurement?
2. Can a DFRT indicate the presence of special transfer functions, e.g. the finite length Warburg (FLW, [11]) or the Gerischer [14].
3. Can it accurately predict the number of circuit parameters, based on observed time constants?
4. Can it be a substitute analysis method for EIS-data for which no simple EqC exists?

The first question will be illustrated with the simulated data presented by Schichlein et al. [23]. This will allow for a validation of our Fourier de-convolution method, which is based on the principles described in that publication. The difference in appearance of DFRT's for comparable FLW and Gerischer functions will be used for inspection of the second question.

An already published complex EIS analysis on $PbZr_{0.53}Ti_{0.47}O_3$ (PZT, a mixed conducting piezoelectric Perovskite [28,29]) is used to investigate the third question. Temperature and pO_2 dependent measurements could be resolved with one equivalent circuit with up to 12 independent parameters. But arriving at this EqC was not a trivial task, as detailed in ref. [29].

The final question is tested with the impedance of a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathode (LSCF). It was observed that the sintering temperature of the screen-printed cathode had a strong effect on the area specific resistance (ASR) [30]. A sintering temperature of 1200 °C resulted in an optimal ASR, while after sintering at 1300 °C, a significantly larger ASR was obtained. The electrode microstructure showed a large number of closed pores with a distribution in pore size. These electrode impedances could not be resolved with a simple EqC; hence the question 'what can we learn from the DFRT'? In this case the analysis was also carried out by an adaptive genetic evolution algorithm method developed by the group of Tsur [31,32].

Actually measured EIS data have been validated with a Kramers-Kronig test [33]. The results are presented in a so-called residuals graph, a plot of relative differences between the real values and the imaginary values of the data and KK-transform versus log(f), with $\omega = 2\pi f$:

$$\Delta_{re}(\omega_i) = \frac{Z_{dat,re}(\omega_i) - Z_{KK,re}(\omega_i)}{|Z_{dat}(\omega_i)|}, \Delta_{im}(\omega_i) = \frac{Z_{dat,im}(\omega_i) - Z_{KK,im}(\omega_i)}{|Z_{dat}(\omega_i)|} \quad (2)$$

An important check of the validity of a DFRT is its conversion to the impedance representation and comparing it with the measured or originally simulated data in such a residuals graph. Another quality check for fitted data is the *pseudo* χ^2-value (*pseudo*, as χ^2 has not been normalized for the parent distribution of variances). For a CNLS-fit this has been defined as [5]:

$$\chi^2_{CNLS} = \frac{1}{N-M-1} \times \sum_N \frac{\left(Z_{dat,re}(\omega_i) - Z_{mod,re}(\omega_i)\right)^2 + \left(Z_{dat,im}(\omega_i) - Z_{mod,im}(\omega_i)\right)^2}{|Z_{mod}(\omega_i)|^2} \quad (3)$$

Where N is the number of data sets and M the number of adjustable parameters. $Z_{mod}(\omega)$ represents the model function derived from the EqC. For the Kramers-Kronig test a similar pseudo χ^2 has been defined [33]:

$$\chi^2_{KK} = \frac{1}{N}\sum_N \frac{\left(Z_{dat,re}(\omega_i) - Z_{KK,re}(\omega_i)\right)^2 + \left(Z_{dat,im}(\omega_i) - Z_{KK,im}(\omega_i)\right)^2}{|Z_{dat}(\omega_i)|^2} \quad (4)$$

An optimal CNLS-fit has been obtained when the χ^2_{CNLS} -value is close to χ^2_{KK}, i.e. the residuals graph shows mostly the statistical noise. A low value of $\sim 10^{-6}$ generally indicates a very good fit, although for some data sets χ^2-values down to 10^{-8} have been observed. For the comparison of the impedance reconstructed from the DFRT with the original data a χ^2_{diff} is defined. Its definition is analogue to Eq. (4), with $Z_{KK}(\omega)$ replaced by the reconstructed impedance data.

Although the main aim of this contribution is to investigate the possibilities and limits of the Fourier transform DFRT, an alternative method based on a CNLS-fit with a linear series of (RQ) circuits will be used for comparison. Q represents the constant phase element (or CPE) with $Z_Q(\omega) = Y_Q(\omega)^{-1} = [Y_0(j\omega)^n]^{-1}$. Here the circuit description code, as developed by the author, is used [5,9]. The impedance is then fitted to an optimum number of (RQ)'s and (RC)'s so that the residuals graph shows more or less the noise in the data set. Each (RQ) circuit can be directly transformed to a DFRT according to [34,35]:

$$R \cdot G(\tau)_{(RQ)} = \frac{R}{2\pi} \cdot \frac{\sin((1-n)\pi)}{\cosh(nln(\tau/\tau_0)) - \cos((1-n)\pi)} \quad (5)$$

with: $\tau_0 = \omega_0^{-1} = \sqrt[n]{RY_0}$. In the case of a pure capacitance, i.e. $n = 1$ for a (RC)-circuit, Eq. (5) transforms into a δ-function. It will be shown, however, that this δ-function can be approximated by a narrow Gaussian distribution:

$$R \cdot G(\tau)_{Gauss} = \frac{R}{W\sqrt{\pi}} e^{-\left(\frac{\ln(\tau/\tau_0)}{W}\right)^2} \quad (6)$$