Derivation of a Distribution Function of Relaxation Times for the (fractal) Finite Length Warburg.

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An analytic Distribution Function of Relaxation Times (DFRT) is derived for the fractal Finite Length Warburg (f-FWL, also called ‘Generalized FWL’) with impedance expression: \( Z_{f-FWL}(\omega) = Z_0 \tanh \left( \alpha_0 \tau_0 \right)^{\alpha_0} \). \( \tau_0 \) is the characteristic time constant of the f-FWL. Analysis shows that for \( n \to 0.5 \) (i.e. the ideal FWL) the DFRT transforms into an infinite series of \( \delta \)-functions that appear in the \( \tau \)-domain at positions given by \( \tau_n = \tau_0 \left( \pi^2 k^2 - j_0^2 \right) \) with \( k = 1, 2, 3, \ldots \). The mathematical surface areas of these \( \delta \)-functions are proportional to \( \tau_n \). It is found that the FWL impedance can be simulated by an infinite series combination of parallel \( (R_0 C_0) \)-circuits, with \( R_0 = C_0 \tau_0^{-1} \) and \( \tau_n \) as defined above. \( R_0 = 2 \tau_n \tau_0 \) and \( \tau_n = 0.5 \tau_0 \). This is the d-c-resistance value of the FLW.

A full analysis of these DFRT expressions is presented and compared with impedance inversion techniques based on Tikhonov regularization and multi-(RQ) CNLS-fits \( (m)(RQ) \). Transformation of simple \( m(RQ) \)fits provide a reasonably close presentation in \( \tau \)-space of the f-FWL, clearly showing the first two major peaks. Impedance reconstructions from both the Tikhonov and \( m(RQ) \)fit derived DFRT’s show a close match to the original data.

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1. Introduction

Over the last fifty years Electrochemical Impedance Spectroscopy (EIS) has been developed into an important research tool for studying electrochemically active systems [1]. The principles, practises and applications of EIS have now been laid down in a number of important textbooks [2–5]. Impedance spectroscopy has also become a major research method for characterising Solid Oxide Fuel Cells (SOFC) [6] and Solid Oxide Electrolyser Cells (SOEC) [7] at a fundamental level for well-defined half cells, as well as on a systems level for complete cells. Due to the nature of the complex, porous electrodes, where the adsorption, charge transfer and transport processes are distributed over a significant part of the microstructure, the impedance graphs are not easy to model with so-called equivalent circuits using complex nonlinear least squares (CNLS) fitting routines [8–12]. Recently there has been renewed interest into the transformation of the frequency dispersion into a distribution function of relaxation times (DFRT) [13–29]. Especially the group of Ivers-Tiffée has pioneered the use of DFRT analysis in the study of SOFCs [15,17,18] and Li-ion batteries [19,21]. The DFRT provides a model-free representation of essential relaxation times that are directly connected to the physical transport and (charge) transfer processes. For SOFC, SOEC and other fuel cells, the study of the position and the peak height as function of temperature and/or partial pressure of the gas phase components provides insight in the transport processes in the electrodes. In battery research the change of the DFRT with the ‘State of Charge’ provides essential information, while for Solar Cell research the relation between illumination level and the corresponding DFRT could be able to reveal fundamental processes. Furthermore, it can be an interesting approach to use DFRT to study aging in a variety of electrochemical systems.

The transformation to the \( \tau \)-domain is defined by:

\[
Z(\omega) = R_\infty + \frac{1}{Z(\infty)} \int_{-\infty}^{\infty} \frac{G(\tau)}{1 + j0 \omega \tau} d\ln \tau
\]  

(1)

\( Z(\omega) \) is the measured impedance, \( R_\infty \) is the high frequency cut-off resistance, \( R_p \) is the polarization resistance and \( G(\tau) \) is the sought distribution function of relaxation times (DFRT). \( G(\tau) \) is a normalized real function with: \( |G(\tau)| d\ln \tau = 1 \). The \( \tau \)-domain is the inverse of the frequency domain with \( \tau = (2\pi \cdot f)^{-1} \). Unfortunately, Eq. (1) is known as an ill-posed inverse problem for which many solutions are possible. Imposing the (logical) restriction that \( G(\tau) \) must always be positive reduces the number of possibilities. Several methods exist to arrive at a viable DFRT: Fourier Transform (FT) [15,17,28,29], Tikhonov Regularization (TR) [16,18–27],

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Maximum Entropy (ME) [13,14] and multiple-(RQ) CNLS-fit, abbreviated ‘m(RQ)fit’ [28,29]. In the Fourier Transform method a window function must be applied, which will dampen unwanted oscillations [28]. The width and shape of this window has significant influence on the shape of the DFRT. But also the Tikhonov Regularization and the Maximum Entropy require the adjustment of a ‘smoothing’ parameter in order to obtain an acceptable DFRT. Recently a critical comparison between the FT and m(RQ)fit has been published by this author [28]. In a second paper [29] a comparison was made between the FT and TR methods and the m(RQ)fit. For the TR-transformations a publicly available MatLab application was used [30].

A quite different approach is taken by the group of Tsur [31–33]. They use evolutionary programming (dubbed ‘ISGP’, ref [33]) for constructing a distribution function based on a selected set from a large library of plausible functions. In the evolutionary programming the number and types of functions, and their parameters, are automatically adjusted until the impedance conversion of the DFRT matches, within predefined criteria, the original measurement data. The clear advantage is that no smoothing parameter is needed in order to arrive at an optimal result. The drawback could be the lack of a physical interpretation of certain functions that have no clear counterpart in the impedance representation. There are a few impedance functions that do have an exact DFRT: the (RQ) or ZARC [2], which is a parallel combination of a resistance and a constant phase element (symbol: Q), with ZQ(ω) = Z0(jω)^α; the Havriliak-Negami (H-N) response [28,34,35] and the Gerischer [29,36] or chemical impedance [37], which is a special case of the H-N relation. It is important to note that the parallel combination of a resistance with a capacitance, (RC), is represented in the τ-domain by a δ-function.

The area under a DFRT curve, defined as R · G(τ) d ln(τ), is equal to the dc-resistance of the impedance counterpart (i.e. R for the ‘(RQ)’ or ZARC), which follows from the normalization of G(τ) and Eq. (1). For a (RC) circuit, however, the resistance information is inaccessible in the τ-domain as the DFRT becomes a δ-function, although the mathematical surface area is equal to R_0 · π. Hence, a pure capacitance in parallel with a resistance in the impedance complicates the construction of a DFRT. A simple approach is to approximate the δ-function by a sharp Gauss function [28,29]:

\[ R \cdot G_{RC}(\tau) \approx \frac{R}{W\sqrt{\pi}} e^{-\left(\frac{\tau_0}{\tau}\right)^2} \]  

(2)

where \( \tau_0 = R \cdot C \cdot W \) was set at 0.15 as a good compromise for visibility (width) and peak height (not too large with respect to other peaks) and small error with respect to the impedance reconstruction from the DFRT [28]. A smaller value for W will decrease the width and increase the peak height, while the area under the curve remains equal to R.

Besides the Gerischer impedance, the Finite Length Warburg (FLW, [38]) is also a common diffusion based impedance function. It presents the frequency dispersion for one-dimensional diffusion through a layer with a fixed activity for the mobile ion at one interface. Stoyanov [39] has, based on a bounded constant phase element (BCP), derived a fractal form for the finite length Warburg, indicated here by f-FLW (see the next section). It seems that for these two bounded diffusion dispersions no exact DFRT has been published so far. In this publication a general DFRT for the f-FLW is derived using a special transformation method [40]. For this a new frequency dependent variable is introduced:

\[ z = \ln(\omega - \tau_0) = \ln\left(\frac{\tau_0}{\tau}\right) \]  

(3)

with \( \tau_0 \) the characteristic time constant for the dispersion relation that is to be transformed. The DFRT, G(τ), is then obtained from the imaginary part of the impedance expression by the following transform process:

\[ Z_0 \cdot G(\tau) = \frac{1}{\pi} \left[ Z_{\text{mag}}\left(z + j\frac{\pi}{2}\right) + Z_{\text{mag}}\left(z - j\frac{\pi}{2}\right) \right] \]  

(4)

\[ Z_0 \] represents the dc-resistance of the impedance function. Using this approach it is quite simple to derive the well-known DFRT for a (RQ) circuit [41] from the imaginary part

\[ \text{Z}_{\text{mag}}(\omega) = Z_0 \cdot \omega^{-\alpha}\sin(\pi\alpha/2); \]

\[ R \cdot G_{RQ}(\tau) = \frac{R}{2\pi} \frac{\sin(\pi\tau)}{\tau} + \cos(\pi\tau) \]  

(5)

The characteristic time constant is given by: \( \tau_0 = (R/Z_0)^{1/\alpha} \), Z_0 is the CPE constant defined above. Eq. (5) represents a symmetric peak centred around \( \tau_0 \) on a log(τ) scale. For \( n = 1 \), i.e. the CPE becomes a pure capacitance, a δ-function is obtained. For lower values of n the spread of the peak increases rapidly [28].

In the following section the impedance expression for one-dimensional diffusion through a mixed conducting layer is presented. From this the fractal FLW, also known as ‘generalized FLW’, is derived. The compact impedance expression is divided into a separate real and imaginary part, needed for the transform to a DFRT using Eq. (4). It is not possible to directly derive the DFRT for the ideal FLW using the transform method of Eq. (4), as is indicated in Section 4. Therefore first the general DFRT of a f-FLW is developed and the limiting cases for τ → 0 and τ → ∞ are explored. The DFRT for the ideal FLW is then obtained using a special approach for \( n < 0.5 \). Finally the DFRT’s obtained from Tikhonov Regularization and multi-(RQ) CNLS-fits (i.e. ‘m(RQ)fit’) are compared to the exact DFRT representations.

2. FLW dispersion relation

The Finite Length Warburg is derived for a linear diffusion problem with a special boundary condition, see Fig. 1. The electrode is a mixed ionic and electronic conductor (MIEC). It is assumed that the electronic conductivity is sufficiently large, so that it can be ignored in the derivation. In the presented 3-electrode set up the activity of the mobile ion is measured at the electrode/electrolyte interface with respect to the (standard) activity of the reference electrode. The current through the

![Fig. 1](image-url)
working electrode is provided by the counter electrode. The
electrode area is $A$, the thickness is $l$ and $D$ is the chemical diffusion
coefficient. At the backplane at $x = l$, the concentration (or activity)
of the mobile ion is fixed to the equilibrium concentration, $C_0$ (or
fixed activity, $a_0$). This presents an ideally fast transfer of mobile
ions at the back plane. For the electrode/electrolyte interface the
particle flux is described by Fick’s first law:

$$ j = -D \frac{dC(x,t)}{dx} |_{x=0} $$

(6)

The time dependent concentration in the electrode is given by
Fick’s second law:

$$ \frac{dC(x,t)}{dt} = \frac{D}{l^2} \frac{d^2C(x,t)}{dx^2} $$

(7)

The boundary condition for $x = l$ is expressed by:

$$ C(x,t)|_{x=l} = C_0 $$

(8)

Applying a small potential perturbation, $\Delta E$, will cause a small
change in the concentration, with $C(x,t) = C_0 + \Delta C(x,t)$. The change
in activity, $\Delta t$, at the electrode/electrolyte interface is given by the
Nernst relation, which becomes linear for a small perturbation, with $z$
the charge of the mobile ion:

$$ \Delta E = \frac{RT}{zF} \ln \left( \frac{a(t)}{a_0} \right) = \frac{RT}{2F} \ln \left( \frac{a(t)}{a_0} \right) = \frac{RT}{2F} \Delta a(t) $$

(9)

The relation between activity and concentration is given by the
Thermodynamic Factor, $\Gamma$:

$$ \Delta a \approx \frac{d\Gamma}{dE} = \frac{a}{C} \frac{d\ln a}{d\ln C} = \frac{a}{C} \Gamma $$

(10)

The thermodynamic factor, $\Gamma$, can be obtained from a so-called
titration experiment where the Nernst potential (or oxygen partial
pressure) is measured as function of added concentration of the
mobile ion. The solution of the set of diffusion and boundary
equations is easily obtained by Laplace transform, see Appendix A.
The Laplace transform leads directly to the impedance expression
for the FLW (Eq. (A7)):

$$ Z_{FLW}(\omega) = \frac{Z_0}{\sqrt{\omega \tau_0}} \tanh \left( \sqrt{\omega \tau_0} \right) $$

with $Z_0 = \frac{RT}{2F} a_0 \frac{d\ln a}{d\ln C}$ and $\tau_0 = \frac{l^2}{D}$

(11)

where $z$ is the charge of the mobile ion. $F$, $R$ and $T$ have their usual
meaning. An example of the dispersion in the impedance representation, for $Z_0 = 1 \Omega$ and $\tau_0 = 1 s$, is given in Fig. 2. For high
frequencies a semi-infinite diffusion (or Warburg) $Z(\omega) =
Z_0(j\omega \tau_0)^{-0.5}$ is obtained, i.e. the perturbation does not reach
the backplane at $x = l$. At low frequencies the dispersion becomes
very close to a semi-circle, i.e. a R(\|C) circuit. Here the ‘Circuit
Description Code’ is used (CDC, [42]). It is important to note that in
this derivation it is assumed that the electronic conductivity of the
electrode is significantly larger than the ionic conductivity and hence
can be ignored. When the electronic conductivity is relatively low
then the special derivation by Jamnik and Maier [43,44] must be used,
which leads to a more complex dispersion relation.

3. Fractal Finite Length Warburg

The fractal-FLW is a phenomenological expression, in analogy
with the parallel combination of a resistance and a constant phase
element (CPE) or ‘ZARC’ element [39]. Eq. (11) is then rephrased by:

$$ Z_{fFLW}(\omega) = \frac{Z_0}{(j\omega \tau_0)^n} \tanh(j \omega \tau_0)^n, \ n \leq 0.5 $$

(12)

In Appendix B the separation into a real and imaginary part is
presented, which results in (Eq. (B4)):

$$ Z_{fFLW}(\omega) = \frac{Z_0}{(j\omega \tau_0)^n} $$

$$ C \cdot \sinh 2\alpha + S \cdot \sin 2\beta - j(S \cdot \sinh 2\alpha - C \cdot \sin 2\beta) $$

$$ \cosh 2\alpha + \cosh 2\beta $$

(13)

With $C = \cos(n\pi/2)$, $S = \sin(n\pi/2)$, $\alpha = (\omega \tau_0)^n C$ and $\beta = (\omega \tau_0)^n S$

Fig. 2 also shows the dispersions for a f-FLW with $n = 0.45$ and
$n = 0.4$.

4. Derivation of the DFRT

The transformation procedure presented by Eqs. (3) and (4) in
the introduction, will be used for deriving the DFRT for the f-FLW.
Inserting the variable $z = j\pi / \Omega$, with $z = \ln(\tau_0 / \pi)$, in the imaginary part
of Eq. (13) results in:

$$ Z_0 \cdot G_{fFLW}(z) = \frac{Z_0}{\pi} \left[ Z_{fFLW, \text{lm}}(z + j\pi/2) + Z_{fFLW, \text{lm}}(z - j\pi/2) \right] $$

$$ = Z_0 \left[ G_{fFLW}(\tau) + G_{fFLW}(\tau) \right] $$

(14)

From the complete analysis of Eq. (14) it was found that only the
$G_{fFLW}(r)$ term needs to be calculated. The transform to $G_{fFLW}(r)$
yields exactly the same real part with an opposite sign for the
imaginary part. This is not surprising as the DFRT should be a real
function. Hence only the real part of $G_{fFLW}(r)$ needs to be
considered with $G_{fFLW}(r) = 2\mathfrak{R}(G_{fFLW}(r))$.

Replacing $\omega$ by $(z + j\pi/2)$ in the first part of Eq. (13) leads to the following transformation:

$$ \frac{Z_0}{(j\omega \tau_0)^n} = Z_0 \left[ e^{j\pi/2} \right] $$

$$ = Z_0 \cdot e^{-nz} \left[ \cos \left( \frac{n\pi}{2} \right) - j \sin \left( \frac{n\pi}{2} \right) \right] $$

(15)

where $Q^2 = (\tau_0 / \pi)^2$. Here ‘$\tau$’ signifies the transformation step. The transform of the denominator of Eq. (13) yields, see Appendix C for
the derivation, Eq. (C3):

$$ \cosh 2\alpha + \cosh 2\beta = \left[ \cosh 2QC^2 + \cosh 2QS^2 \right] $$

$$ + j \left( \sinh 2QC^2 - \sinh 2QS^2 \right) \cdot \sin \beta $$

(16)
with \( B = 2Q \cos \frac{\pi n}{\tau_0} \). The transform of the imaginary part of the numerator of Eq. (13) is derived in the same manner, see Appendix D, Eq. (D3):

\[
S \sinh 2\alpha - C \sin2\beta \rightarrow S \cdot \sinh 2QC^2 \cdot \cos B - C \cdot \cosh 2QS^2 \cdot \sin B + j\left( S \cdot \cosh 2QC^2 \cdot \sin B - C \cdot \sinh 2QS^2 \cdot \cos B \right)
\]

(17)

In the following sections the terms numerator and denominator will be abbreviated in equations by \( \text{Num.} \) and \( \text{Denom.} \) respectively. Multiplying this result with \( Z_0 \cdot Q^{-1} \cdot (C - JS) \) from Eq. (15) gives:

\[
\text{Num.} = Z_0 \left\{ \frac{C}{\sinh 2QC^2} - \sinh 2QS^2 \right\} \cos B + \left( S^2 \cosh 2QC^2 - C^2 \cosh 2QS^2 \right) \sin B + j\left( -S^2 \sinh 2QC^2 + C^2 \sinh 2QS^2 \right) \cos B + CS \left( \cosh 2QC^2 + \cosh 2QS^2 \right) \sin B
\]

(18)

It is interesting to note that for \( n = 0.5 \), i.e. \( C = S = \sqrt{1} \), the denominator changes to: \( 2Q \cdot \cosh(Q) \cos(Q) \), while the real part of the numerator becomes zero! Eqs. (16) and (18) can easily be combined in a spreadsheet to calculate the distribution function for a limited range of \( \tau \)-values. The DFRT’s for \( n = 0.45, 0.48 \) and 0.49 are presented in Fig. 3. It shows for each DFRT one major peak, situated at a lower value than the characteristic time constant, \( \tau_0 \), followed by smaller peaks for decreasing \( \tau \). The appearance of the DFRT’s are similar to those presented by Leondie et al. [17], although no mathematical expression is presented in that publication. For too small values of \( \tau \), the arguments of the hyperbolic functions become too large to be evaluated in a spreadsheet. Hence a different approach is needed for small \( \tau \).

4.1. Analysis for small \( \tau \)

For small \( \tau \)-values the argument \( Q \) becomes large, hence the \( \sinh() \) and the \( \cosh() \) functions can be approximated by the positive exponentials, e.g.:

\[
\sinh 2QC^2 \approx \cosh 2QC^2 \approx \frac{1}{2} e^{2QC^2}
\]

(19)

Thus Eqs. (16), (18) can be reduced by replacing the hyperbolic functions by their respective exponential functions. Furthermore, both the numerator and denominator can be divided by the right hand side of Eq. (19). Now a relatively simple function for the DFRT is found (in which the factor 2 has been taken care of):

\[
Z_0 \cdot G(\tau) = \frac{Z_0}{\pi} \left( \frac{\tau}{\tau_0} \right)^n \frac{\sin(n\pi/2) - 2\cos(n\pi/2) \cdot \tau \cdot \sin(2Q\sin(n\pi/2))}{1 + 2Y \cdot \cos(2Q\sin(n\pi/2)) + Y^2}
\]

(20)

with \( Y = \exp(-2Q\cos(n\pi/2)) \). Written out in full, Eq. (20) becomes:

\[
Z_0 \cdot G(\tau) = \frac{Z_0}{\pi} \left( \frac{\tau}{\tau_0} \right)^n \frac{\sin(n\pi) \left( 1 - \frac{Y^2}{1 + 2Y \cdot \cos(2Q\sin(n\pi/2)) + Y^2} \right) - 2\cos(n\pi) \cdot \tau \cdot \sin(2Q\sin(n\pi/2))}{1 + 2e^{-4Q^2\sin(n\pi/2)} \cdot \cos(2Q\sin(n\pi/2)) + e^{-4Q^2\sin(n\pi/2)}}
\]

(21)

In Fig. 4 the DFRT of the simplified function of Eq. (21) is compared to the DFRT obtained from a simulation using the full expressions defined by the combination of Eqs. (16), (18). It is surprising that, within the accuracy of Excel, the results are exactly identical over the entire \( \tau \)-range for which Eqs. (16), (18) can be evaluated. Hence Eq. (21) can be taken as a simplified expression that exactly represents the DFRT of a flat-LFW. For very small values of \( \tau \) (e.g. \( \tau < \tau_0 \cdot 10^{-3} \) for \( n = 0.45 \) Eq. (21) can be further reduced to a simple power relation, presented as the dashed lines in Fig. 5:

\[
Z_0 \cdot G(\tau) = \frac{Z_0}{\pi} \left( \frac{\tau}{\tau_0} \right)^n \cdot \sin(n\pi)
\]

(22)

Whereas the DFRT shows for \( n = 0.45 \) a few decreasing peaks for \( \tau < \tau_0 \), the number of peaks increase rapidly for \( n \) approaching 0.5. This is clearly demonstrated by the DFRT for \( n = 0.48 \) in Fig. 5. The limiting \( \tau \)-value below which Eq. (22) can be applied shifts rapidly for \( n \to 0.5 \) to \( \tau = 0 \), or \( \ln(\tau) \to -\infty \). Although it seems that Eq. (22) gives a finite result for \( n \to 0.5 \), the upper limit in \( \tau \) for which this equation can be used goes to zero.

4.2. Analysis for large \( \tau \)

For large \( \tau \) (i.e. \( \tau >> \tau_0 \)) the arguments of the exponential and goniometric functions of \( Q \) approach zero, hence these functions must be expanded in their series. It is essential to include higher order terms containing \( Q^3 \). With writing Eq. (21) as:

\[
Z_0 \cdot G(\tau) = \frac{Z_0}{\pi} \frac{\text{Num.} - \text{Num.} \cdot B}{\text{Denom.}}
\]

(23)

![Fig. 3](image1.png) Calculated DFRT's for \( n = 0.45, n = 0.48 \) and \( n = 0.49 \). The major peaks fall below the characteristic time constant \( \tau_0 \).

![Fig. 4](image2.png) Comparison between the exact DFRT, eqs (23,25) and the simplified solution, eq. (28) for \( n = 0.45 \).
the separate contributions can be evaluated:

\[ \text{Num}_{A} = 2CS(1 - e^{-4Qcos(n\pi)}) \approx 
= 4Q\cos(n\pi)\sin(n\pi) - 8Q^2\cos^2(n\pi)\sin(n\pi) + \frac{32}{3}Q^3\cos^3(n\pi)\sin(n\pi) \]

(24)

and:

\[ \text{Num}_{B} = 2\cos(n\pi) \cdot e^{-2Qcos(n\pi)} \cdot \sin(2Q\sin(n\pi)) \approx 
= 4Q\cos(n\pi)\sin(n\pi) - 8Q^2\cos^2(n\pi)\sin(n\pi) + 
+8Q^3\cos^3(n\pi)\sin(n\pi) - \frac{8}{3}Q^3\cos(n\pi)\sin^3(n\pi) \]

(25)

The denominator of Eq. (21) can be expanded to:

\[ \text{Denom.} = Q\left[1 + 2e^{-2Qcos(n\pi)} \cdot \cos(2Q\sin(n\pi)) + e^{-4Qcos(n\pi)}\right] \approx 4Q \]

(26)

Combination of Eqs. (24)–(26) leads to the limiting expression for \( \tau >> \tau_0 \):

\[ Z_0 \cdot G(\tau) = \frac{Z_0}{\pi} \frac{\frac{8Q^3\cos(n\pi)\sin(n\pi)}{\cos^2(n\pi) + \sin^2(n\pi)}}{4Q} 
= \frac{Z_0}{\pi} \frac{\tau_0^{2\delta}}{\sin(2n\pi)} \]

(27)

For \( n = 0.5 \) Eq. (27) becomes zero.

5. Derivation of the DFRT for the ideal FLW

Analysis for limit \( n \rightarrow 0.5 \)

Inserting \( n = 0.5 \) directly into Eq. (18) does not yield a result as the hyperbolic functions will reduce to cosh(Q) and sinh(Q), which will cancel out in the numerator of Eq. (18). In order to analyse the DFRT for \( n = 0.5 \), one should approach this value by replacing \( n \) by:

\[ n = 0.5 - \frac{\delta}{\pi} \]

(28)

As a result for \( \delta \rightarrow 0 \) the following relations simplify to:

\[ \sin(n\pi) = \sin\left(\frac{\pi}{2} - \delta\right) = \cos(\delta) \approx 1 \]

\[ \cos(n\pi) = \cos\left(\frac{\pi}{2} - \delta\right) = \sin(\delta) \approx \delta \]

(29)

Using the first terms of the goniometric and exponential series expansions, Eq. (21) can be rewritten as:

\[ Z_0G(\tau) = \frac{Z_0}{\pi} \frac{2\delta + (2\delta^2 - Q^{-1}) \cdot \sin(2Q\delta)}{1 + (1 - 2Q\delta) \cdot \cos(2Q\delta) - 2Q\delta} \]

(30)

For \( n = 0.5 \), i.e. \( \delta = 0 \), the denominator of Eq. (30) reduces to:

\[ \text{Denom.} = 1 + \cos(2Q) \]

(31)

For \( Q = \pi \cdot (k-0.5) \), with \( k = 1, 2, \ldots \), the denominator becomes zero, which results in a \( \delta \)-function for the DFRT. Hence \( G(\tau) \) will become a sum of \( \delta \)-functions. The \( \tau_k \) positions are given by:

\[ \tau_k = \frac{\tau_0}{\pi^2 \cdot (k - 0.5)^2}, \; k = 1, 2, \ldots \]

(32)

The first \( \delta \)-function occurs at \( 0.4053 \times \tau_0 \). For small values of \( \delta \) (i.e. \( \delta < 10^{-3} \)) it is possible to calculate the maximum values for \( G(\tau_k) \). Fig. 6 shows the results for the first 10 maxima in \( G(\tau) \) for decreasing values of \( \delta \). From this a clear relation between the maxima, \( \tau \) and \( \delta \) is obtained:

\[ \text{(33)} \]

The surface area under the peak represents the corresponding dc-resistance value of the related impedance expression. The problem here is that there is no clear way to separate the areas under the consecutive peaks (see Fig. 5 for the case \( n = 0.48 \)) and to relate these to corresponding resistance values. When \( \delta \rightarrow 0 \), the peaks collapse to \( \delta \)-functions with no observable surface area. In the impedance representation, however, a \( \delta \)-function is represented by a capacitance and resistance in parallel, e.g.: (RC). Hence it seems plausible to simulate the DFRT for a FLW with an infinite series of \( \delta \)-functions that are represented in the frequency domain by an infinite series of (RC) circuits with time constants defined by Eq. (32). In a simulation effort in a spreadsheet it was observed that the following relation leads to the Finite Length Warburg dispersion:

\[ Z_{FLW}(\omega) = \sum_{k=1}^{\infty} 2\tau_k \frac{1 - j\omega\tau_k}{1 + \omega^2\tau_k^2} \]

(34)

Fig. 7 shows the simulation of a FLW with \( Z_0 = 1 \Omega \) and \( \tau_0 = 1 \text{s} \), together with the approximation using Eq. (34) for the first ten \( \tau_k \) values. Up to a frequency of \( f \approx 20 \times \tau_0^{-1} \text{Hz} \) the error is less than 1% for a 10-(RC) simulation. For a 100-(RC) simulation the 1% error lies above \( f \approx 2 \times 10^3 \times \tau_0^{-1} \text{Hz} \).

6. Discussion

A remarkable result is the identity between the complex DFRT, formed by the quotient of Eq. (18) and Eq. (16), and the simplified Eq. (21), which is obtained through an approximation for small \( \tau \)-values. No effort has been undertaken to provide a rigorous proof...
for this identity, as this would be outside the scope of this contribution.

The derived DFRT equations provide a useful addition to the library of functions used in the evolutionary algorithm method. This reversed transform method, developed by the group of Tsur [31–33], has been described briefly in the introduction. But these equations are also useful for the comparison of regular inversions of impedance data to the τ-domain. The order of mismatch shows how reliable the DFRT transform methods are. First we will consider the f-FLW with \( n = 0.45 \). The simulation, with \( Z_0 = 1 \ \Omega \) and \( \tau_0 = 1 \ \text{s} \), is performed over the frequency range 0.1 mHz – 1 MHz. For the DFRT analysis with Tikhonov regularization the publically available MatLab application ‘DRTTools’ [30] is used. This program has many adjustable parameters, but here the default setting is used except for the regularization parameter, \( R_P \). In a previous study [29] it was observed that an increase in \( R_P \) diminished the (unwanted) oscillations in the DFRT, but also widened and lowered the peaks significantly.

The \( m(RQ) \) fit was performed with the CNLS-fit program ‘EqCWin’ [46]. In this procedure first a part of the low frequency end is fitted to a \( R(RQ) \) circuit. Next the \( (RQ) \) dispersion is subtracted from the overall dispersion. Again a \( R(RQ) \) circuit is fitted to an appropriate low frequency part of the altered dispersion. Next the combination of a \( R(RQ) \) is fitted to a low frequency section of the original data, resulting in a new, improved set of circuit parameters. The \( (RQ) \) of \( (RQ) \) part of the fitted \( R(RQ) \) circuit is again subtracted from the original dispersion and a new \( R(RQ) \) circuit is fitted to an appropriate section of the remainder of the frequency dispersion. This process of iterative adding of \( R(RQ) \) to the subtracted \( (RQ) \) is continued until an acceptable match between data and model is obtained. Each \( (RQ) \) circuit has a counterpart in the \( \tau \)-domain according to Eq. (5), hence adding the separate \( R_i \; G_i(\tau) \) functions yields a (close) approximation of the DFRT. In some instances the CNLS procedure resulted in the shift of a \( (RQ) \) into a \( (RC) \) combination (i.e.: \( n = 1 \)). In those cases the corresponding \( R_i \); \( G_i(\tau) \) was calculated using the Gauss approximation of Eq. (2). The number of \( (RQ) \) and \( (RC) \) combinations in the \( m(RQ) \) fit are indicated as \( x \) \((RQ)\)-\( y \)(RC), with \( x \) and \( y \) the number of respective \( (RQ) \) and \( (RC) \) sub-circuits. The high frequency cut-off resistance, \( R_c \), which is part of the CNLS-fit, has been omitted from the description of the circuits used for the transformation.

Fig. 8 shows the exact DFRT (Eq. (21)) and two TR-DFRT’s with regularization parameters, \( R_P = 10^{-6} \) and \( R_P = 10^{-4} \). Also a DFRT derived from a \( m(RQ) \) fit with a 6\((RQ)\) circuit (CNLS-\( \chi^2 = 3.4 \times 10^{-5} \)) is presented. The \( m(RQ) \) fit follows the two major peaks quite closely in shape and position. Both TR results show lower peak height and a somewhat increased FWHM (full width at half maximum) for the main peak. With \( R_P = 10^{-6} \) the second peak is poorly reproduced while \( R_P = 10^{-4} \) gives a better result, but with lower peak heights. A good check of the validity of the DFRT is the comparison between the reversed transform, i.e. application of Eq. (1) to obtain the impedance from \( G(\tau) \), and the original impedance data [28,29]. The reconstruction procedure has been described in ref. [28]. Both the TR-DFRT, with \( R_P = 10^{-6} \), and the \( m(RQ) \) fit-DFRT with a 6\((RQ)\) circuit show a very good match with the simulated f-FLW impedance data. This can clearly be seen from the so-called differences graphs of Fig. 9A. Here the relative real and imaginary

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**Fig. 7.** Dispersion of the FLW and the simulation with a series of 10\((RC)\) circuits. In the inset the first 7\((RC)\) are shown. The blue line is the envelope of the separate 10\((RC)\) contributions.

**Fig. 8.** Comparison of DFRT’s for a f-FLW with \( n = 0.45 \). Red line is the exact DFRT. Green and purple lines are for the Tikhonov regularizations with resp. \( R_P = 10^{-6} \) and \( 10^{-4} \). Blue line is derived from the \( m(RQ) \) fit with a 6\((RQ)\) circuit. Dashed lines are scaled with a factor 5 for better visibility.
differences, $\Delta_{\text{real}}$ and $\Delta_{\text{imag}}$ are plotted against $\log f$. The differences are defined as [1]:

$$\Delta_{\text{real},i} = \frac{Z_{\text{real},i} - Z^{\text{recon}}_{\text{real},i}}{|Z_i|}, \quad \Delta_{\text{imag},i} = \frac{Z_{\text{imag},i} - Z^{\text{recon}}_{\text{imag},i}}{|Z_i|}$$

$Z^{\text{recon}}$ represents the reconstructed impedance. The reconstructed $m$[RQ]fit data show a significant deviation in $\Delta_{\text{real}}$ above 1 kHz. This is due to the ‘limited’ range of the calculated DFRT in the $\tau$-domain (from $10^{-7}$ to $10^3$ s). The area under the DFRT curve represents the total dc-resistance (polarisation), which falls just short of 1 $\Omega$, i.e. $Z_0$. Adding a correction of 0.176 m$\Omega$ to the real part of the reconstructed data shows a significant improvement in the residuals plot, see Fig. 9B. But one should also realize that above 2 kHz (i.e. $2 \cdot 10^7 \tau_0$) the impedance magnitude is less than 1% of $Z_0$. The fitted 6[RQ] impedance shows an excellent fit to the simulated data with a $\chi^2 = 3.4 \cdot 10^{-9}$, well below the general noise level. The high frequency deviation (Fig. 9A) of the reconstructed impedance shows that the $\tau$-range of the DFRT should be extended further in order to cover the total polarization resistance (or $Z_0$).

The case of the exact FLW ($n = 0.5$) is more complicated as the frequency dispersion involves capacitive behaviour, see Eq. (34). The Tikhonov regularization shows rather broad peaks, see Fig. 10. The positions of the first ten $\delta$-functions, i.e. the roots of Eq. (32), are presented by the vertical grey lines. The heights represent the relative differences in ‘strength’, which are proportional to $\tau$. The $m$[RQ]fit yielded a 4[RQ]-2[RC] circuit (CNLS-$\chi^2 = 1.8 \cdot 10^{-9}$). In the transform to the $\tau$-domain the two (RC) circuits were approximated with Gauss functions, Eq. (2), with width parameter $W = 0.15$. These two major peaks coincide quite well with the positions of the first two $\delta$-functions, as can be seen in Fig. 10. The relative heights also correspond quite well to the ratio $\tau_1/\tau_2$. The TR and the $m$[RQ] fit transforms show quite some differences, however, the reconstructed impedances agree remarkably well with the simulated impedances. The $m$[RQ]fits for the FLW show a good approximation of the position and height ratio for the first two peaks. But for the Gerischer a poor approximation of its analytical DFRT is obtained with two peaks that lie closer together than for the FLW DFRT [28,29]. This could be used as a discrimination between a FLW and a Gerischer, but interference of other relaxation processes could obscure this observation.

For the Gerischer impedance the asymptote in the DFRT coincides with the characteristic time constant, $\tau_0$. For the FLW it is found from Eq. (32) that the position of the first $\delta$-function at $\tau_1$ is a factor 2.47 smaller than the characteristic time constant, $\tau_0$. The time constant associated with the minimum in the imaginary part of the $m$[RQ]fit resembles $\tau_0$ better than the $\tau$ of $Z^{\text{recon}}$. The difference is due to the fact that $Z^{\text{recon}}$ also includes the capacitive component which is not present in $Z_i$. This effect is also evident in the case of the $Z$-real reconstruction. For the Fig. 11 shows the residuals graph for the TR with $R_P = 10^{-6}$ and the $m$[RQ]fit with a 4[RQ]-2[RC] circuit. This once again shows that it is difficult to define a unique DFRT from inverted impedance data.

In ref. [28] it has been argued that the DFRT is only capable of showing major relaxation peaks. It is not a procedure that allows to detect minor contributions to the frequency dispersion. The main power of the DFRT is showing the shift in $\tau$-position and/or change in height of the major peaks with temperature or partial pressure of one of the gas components [15].

Diffusion is an important process in fuel cell electrodes and can be part of the rate controlling process. The finite length diffusion or FLW impedance has some similarity in shape with the Gerischer impedance, see inset in Fig. 12. The latter is a semi-infinite diffusion with a coupled side reaction, which results in a finite dc-resistance. The exact DFRT’s are, however, quite different. The Gerischer DFRT is characterized by an asymptotic function for $\tau \rightarrow \tau_0$ and is non-existing (zero) for $\tau > \tau_0$ [29], while the DFRT for a FLW is an infinite series of $\delta$-functions, as shown in Fig. 12. The Tikhonov regularizations rather poorly reproduce the exact DFRT’s, although the reconstructed impedances closely match the simulated impedances. The $m$[RQ]fits for the FLW show a good approximation of the position and height ratio for the first two peaks. But for the Gerischer a poor approximation of its analytical DFRT is obtained with two peaks that lie closer together than for the FLW DFRT [28,29]. This could be used as a discrimination between a FLW and a Gerischer, but interference of other relaxation processes could obscure this observation.
of the FLW, $\tau_{\text{min}}$ is a factor 2.53 smaller than $\tau_0$. This $\tau_{\text{min}}$ is found from the derivative of $Z_{\text{FLW}, \text{im}}$ with respect to $\omega$. The root for $d Z_{\text{FLW}, \text{im}} / d \omega = 0$ can be found through a Newton-Raphson iteration [47]. The difference between $\tau_{\text{min}}$ and $\tau_1$ is due to the higher order ($RC$)-circuits (see Fig. 7) that are included in $\tau_{\text{min}}$. The position of $\tau_{\text{min}}$ for the Gerischer impedance can be obtained directly from the derivative: $\tau_0 / \tau_{\text{min}} = \sqrt{3}$ [47].

It appears that the Tikhonov regularization, TR, always shows a very rapid decay outside the inverse frequency range. This limited $\tau$-range eases the reconstruction of the impedance from the DFRT. In the $m$(RQ)fit method, $n$-values for the CPE can be obtained that are significantly less than 0.7. Fig. 16 in ref. [28] clearly shows that the significant $\tau$-range of the DFRT of such a (RQ) rapidly increases with decreasing $n$. For $n = 0.5$ (Warburg diffusion) the FWHM of the curve extends already over 2.3 decades, while the 10% peak height values of the DFRT curve span more than 5 decades. Hence the reconstruction requires the integration over a significant larger $\tau$-range, or the application of a resistance correction for the incomplete coverage of the area under the DFRT curve, as has been demonstrated above.

7. Conclusions

For the fractal Finite Length Warburg (bounded one-dimensional diffusion) a relatively complex analytic DFRT expression is derived using the transform procedure introduced by Fuoss and Kirkwood [40]. A remarkable point is the position of the major peak at $\tau_0$, which lies well below the characteristic time constant $\tau_0$. From Eq. (32) a ratio of 2.47 is obtained, slightly below the ratio of 2.53 obtained from the frequency of the minimum in $Z_{\text{FLW, im}}$, $\tau_{\text{min}} = (2\pi \cdot f_{\text{min}})^{-1}$ and the characteristic time constant $\tau_0$. The DFRT of the $f$-FLW is characterized by a major peak followed by a series of minor peaks, the number and sharpness strongly depends on the value of $n$. For $n = 0.5$ the ideal FLW is obtained, but a direct derivation of the DFRT is not possible. Thorough analysis of the case where $n$ approaches 0.5 shows that the DFRT of an ideal FLW exists of an infinite series of $\delta$-functions. As a result the ideal FLW can be described as an infinite sum of (RC)'s with $R = 2Z_0 \sigma_0 \pi^2(k - \frac{1}{2})^2$, $k = 1, 2, \ldots, \infty$, and $\sigma_0 = (2Z_0)^{-1}$. Although the Tikhonov regularization presents a DFRT with rather broad peaks in the $\tau$-domain, the reconstructed impedance shows a close match with the original data. Using the $m$(RQ)fit approach a good approximation of the DFRT can be obtained.

As stated before in ref. [29], scientists should be aware of the inherent limits of the Distribution Function of Relaxation Times analysis method, although with prudent use it can help in understanding the essential electrochemical processes in complex systems like fuel- and electrolyser cells, complex electrodes, batteries and solar cells.

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Appendix A. Laplace transform of Finite Length Diffusion Model

The Laplace transforms of Eqs. (6)–(9), with $p$ as Laplace variable, lead to:

\[ J = -D \frac{d \Delta c(x, p)}{dx} \bigg|_{x=0} \]
\[ p \cdot \Delta c(x, p) = D \frac{d^2 \Delta c(x, p)}{dx^2} \bigg|_{x=0} = 0 \quad \text{(A1)} \]

The general solution for the Laplace transform of Fick-2 is given by:

\[ \Delta c(x, p) = \xi \sinh \left( x \sqrt{p / D} \right) + \zeta \cosh \left( x \sqrt{p / D} \right) \quad \text{(A2)} \]

From the boundary condition at $x = l$ (Eq. (A1)) it follows that:

\[ \xi = -\xi \tanh \left( l \sqrt{p / D} \right) \quad \text{(A3)} \]

This leads to a new expression for Fick-1 in Laplace space:

\[ J = -D \left[ \xi \sqrt{p / D} \cosh \left( x \sqrt{p / D} \right) + \zeta \sqrt{p / D} \sinh \left( x \sqrt{p / D} \right) \right]_{x=0} \]
\[ = -D \xi \sqrt{p / D} \quad \text{(A4)} \]
The potential at the electrode/electrolyte interface can then be expressed by (with z the charge of the mobile ion and $\Gamma$ the thermodynamic factor):

$$\Delta E(p) = \frac{RT}{2FC_{eq}} \ln \frac{a_{eq} \sinh a}{C_{eq}} - \frac{RT}{2FC_{eq}} \Delta c(x, p)|_{x=0}$$  

(A5)

The impedance in Laplace space can be defined by dividing the voltage by the current, $I(p) = zFAJ(p)$, where A is the surface area:

$$Z(p) = \frac{\Delta E(p)}{zF \cdot A \cdot J(p)} = \frac{RT \Gamma}{z^{2}F^{2}A_{eq}} \left[ \frac{\xi \sinh \left( \frac{x}{\sqrt{D}} \right) - \xi \cosh \left( \frac{x}{\sqrt{D}} \right) \tan \left( \frac{1}{\sqrt{D}} \right)}{\sqrt{D_x} \tan \left( \frac{1}{\sqrt{D}} \right)} \right]_{x=0}$$

(A6)

The advantage of the Laplace space is that the variable $p$ can be written as $p = s + j\omega$, where $s$ represents the transient to a steady state situation and $\omega$ represents the frequency dependent part (with $\omega = 2\pi f$). Hence, the FLW transfer function follows from Eq. (A6):

$$Z_{FLW}(p) = \frac{RT \Gamma}{z^{2}F^{2}A_{eq}} \left[ \frac{\xi \sinh \left( \frac{x}{\sqrt{D}} \right) - \xi \cosh \left( \frac{x}{\sqrt{D}} \right) \tan \left( \frac{1}{\sqrt{D}} \right)}{\sqrt{D_x} \tan \left( \frac{1}{\sqrt{D}} \right)} \right]_{x=0}$$

(A7)

Appendix B. Derivation of the full impedance expression for a $f$-FLW

The term $(j\omega \tau_0)^n$ in Eq. (12) can be written as:

$$(j\omega \tau_0)^n = (\omega \tau_0)^n \cos \frac{n\pi}{2} + j(\omega \tau_0)^n \sin \frac{n\pi}{2} = \alpha + j\beta$$

(B1)

Substitution of Eq. (B1) in Eq. (12) and expanding the tanh() function yields:

$$Z_{FLW}(\omega) = \frac{Z_0}{(j\omega \tau_0)^n} \tanh((j\omega \tau_0)^n) = \frac{Z_0}{\alpha + j\beta} \tanh(\alpha + j\beta) = \frac{Z_0}{\alpha + j\beta} \left[ e^{\alpha-j\beta} - e^{-\alpha+j\beta} \right]$$

(B2)

Application of the Euler formula, $e^{ix} = \cos x + j\sin x$, leads to the following expression:

$$Z_{FLW}(\omega) = \frac{Z_0(\alpha - j\beta)}{(\omega \tau_0)^n} e^{\alpha \cos \beta - \alpha \sin \beta} + j(\omega \tau_0)^n \sin \frac{n\pi}{2} = \frac{Z_0}{(\omega \tau_0)^n} e^{\alpha \cos \beta + \alpha \sin \beta} + j(\omega \tau_0)^n \sin \frac{n\pi}{2}$$

(B3)

Multiplying by the complex conjugate of the denominator results in a separate real and imaginary part:

$$Z_{FLW}(\omega) = \frac{Z_0(\alpha - j\beta)}{(\omega \tau_0)^n} \left[ \frac{\sinh 2\alpha + j\sin 2\beta}{\cosh 2\alpha + \cosh 2\beta} \right] = \frac{Z_0}{(\omega \tau_0)^n} \left[ \frac{\cos \frac{n\pi}{2} \sinh 2\alpha + \sin \frac{n\pi}{2} \sin 2\beta}{\cosh 2\alpha + \cosh 2\beta} \right]$$

(B4)

For $n = 0.5$ this equation reduces to the well-known FLW-function:

$$Z_{FLW}(\omega) = \frac{Z_0}{\sqrt{2\omega \tau_0}} \left[ \sinh \sqrt{2\omega \tau_0} + \sin \sqrt{2\omega \tau_0} - j \sin \sqrt{2\omega \tau_0} - \sin \sqrt{2\omega \tau_0} \right]$$

(B5)

Appendix C. Transformation of the denominator, Eq. (16)

The transform of the denominator of Eq. (B4) will be done in two parts. First the cosh() function is transformed, followed by the transform of the cosine:

$$\cosh 2\alpha = \frac{1}{2} \left[ e^{\frac{\tau_0}{T}} \cosh \frac{\tau_0}{T} + e^{-\frac{\tau_0}{T}} \cosh \frac{\tau_0}{T} \right] = \frac{1}{2} \left[ e^{2\tau_0} \cos 2\tau_0 + 2\sin 2\tau_0 \right]$$

(C1)

$$\sinh 2\beta = \frac{1}{2} \left[ e^{\frac{\tau_0}{T}} \sinh \frac{\tau_0}{T} + e^{-\frac{\tau_0}{T}} \sinh \frac{\tau_0}{T} \right]$$

(C2)

Combining Eqs. (C1), (C2) yields the following expression for the denominator:

$$\text{Denom.} = (\cosh 2\tau_0^2 + \cosh 2\tau_0^2) \cdot \text{cos} B + j(\sinh 2\tau_0^2 + \sin 2\tau_0^2) \cdot \sin B$$

(C3)

Appendix D. Transformation of the numerator, Eq. (18)

Development of the numerator of the imaginary part, excluding the term before the brackets in Eq. (B4), is also done in two parts:

$$\text{Sin} 2\alpha = \frac{S}{2} \left[ e^{\frac{\tau_0}{T}} \frac{\tau_0}{T} \sinh \frac{\tau_0}{T} - e^{-\frac{\tau_0}{T}} \frac{\tau_0}{T} \sinh \frac{\tau_0}{T} \right]$$

(D1)

And:

$$\text{Csin} 2\beta = \frac{C}{2} \left[ e^{2\tau_0} \cos 2\tau_0 - e^{-2\tau_0} \cos 2\tau_0 \right]$$

(D2)
Combination of Eqs. (D1), (D2) yields:
\[
S\sin 2\alpha + C\sin 2\beta = \frac{S\sin h 2QC^2 - \cos B}{C\cosh 2QS^2 - \sin \beta} + \frac{S\cosh 2QS^2 - \sin \beta}{C\cosh 2QS^2 - \cos B}
\]
(D3)

References

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