Electrochemistry Communications 182 (2026) 108100

Contents lists available at ScienceDirect

Electrochemistry Communications

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

A comment on “On the futility of the Fuoss–Kirkwood relation”

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ARTICLE INFO

Dataset link: https://repo.ijs.si/zigag/fuoss-kirkwood-transform

Keywords:
Distribution of relaxation times
Fuoss–Kirkwood relation
Equivalent circuit models
Theory

ABSTRACT

Recently a point was made in this journal, that the well-known relation — the Fuoss–Kirkwood formula — between impedance of a causal, linear device and the pertaining distribution of relaxation times is futile. We point-out the incorrect use of relation and provide evidence that the formula is applicable when used correctly.

1. Introduction

Deconvolution of data gained from electrochemical impedance spectroscopy (EIS) can be performed via the distribution of relaxation times (DRT) after the non-relaxing processes have been accounted for. This allows for an intuitive interpretation of the relaxation processes that govern the behavior of the device. To ensure that the interpretation is valid resulting DRT is often compared to DRTs obtained from equivalent circuit models (ECMs), that are perceived as providing a good fit to the data. Since ECMs are provided in closed-form, they can be transformed to DRT in a straightforward manner [1].

Unfortunately, due to the sometimes vague notation otherwise simple transformation can yield erroneous results. This is what we believe happened in [2], where a claim is made that the transformation is futile. In this paper we seek to correct the record and provide a clear demonstration that the transformation works if used correctly.

Paper is constructed as follows. First we provide a short mathematical introduction to DRT. Then we illuminate the transformation issue and provide a concrete example of a valid transformation.

2. Discussion

DRT, denoted as $g(\log\tilde{\tau})$, is given by [3]

$$\hat{Z}(\mathrm{j}\omega) = \int_{-\infty}^{\infty} \frac{g(\log\tilde{\tau})}{\mathrm{j}\omega\tilde{\tau}+1}\,\mathrm{d}\log\tilde{\tau} = \int_{-\infty}^{\infty} \frac{g(x)}{\mathrm{j}\omega\exp[x]+1}\,\mathrm{d}x, \tag{1}$$

where $\hat{Z}(\mathrm{j}\omega)$ is the impedance of investigated system, ω is the circular frequency, $\log\tilde{\tau}$ is the natural logarithm of relaxation time, also denoted as x and $\mathrm{j} = \sqrt{-1}$. $\hat{Z}(\mathrm{j}\omega)$ and $g(\log\tilde{\tau})$ carry the same amount of information on the investigated device, but DRT is considered easier to interpret, since it describes the system in simple terms of resistors and capacitors.

Without knowing the impedance in closed-form, i.e., only having access to (noisy) measurements, finding DRT is an ill-posed problem. This means specialized procedures are required to obtain a valid solution to (1) [3].

In order to proceed with obtaining DRTs for closed-form $\hat{Z}(\mathrm{j}\omega)$, we make a change of variables

$$Z(x) = \hat{Z}(\mathrm{j}\omega), \tag{2}$$

where $x = \log(1/\omega)$, meaning $Z(x) = \hat{Z}\left(\mathrm{j}\frac{1}{\exp(x)}\right)$. Next, we decompose the impedance into real and imaginary parts

$$Z(x) = \Re\{Z(x)\}(x) - \mathrm{j}\Im\{Z(x)\}(x) = J(x) - \mathrm{j}H(x), \tag{3}$$

where $\Re$ and $\Im$ denote real and imaginary part, respectively. Note that we perform the decomposition with $x \in \mathbb{R}$ in mind, but we will put complex values in it later.

2.1. Erroneous transformation to DRT

First we investigate an *erroneous* procedure for obtaining DRT given in [2]

$$g(x) = -\frac{1}{\pi}\Im\left\{Z\left(x+\mathrm{j}\frac{\pi}{2}\right) + Z\left(x-\mathrm{j}\frac{\pi}{2}\right)\right\} \tag{4}$$
$$= -\frac{1}{\pi}\Im\left\{Z\left(x+\mathrm{j}\frac{\pi}{2}\right) + Z\left(\left(x+\mathrm{j}\frac{\pi}{2}\right)^{*}\right)\right\}$$

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https://doi.org/10.1016/j.elecom.2025.108100
Received 13 October 2025; Received in revised form 15 December 2025; Accepted 17 December 2025
Available online 18 December 2025

$$\overset{\text{error}}{=} -\frac{1}{\pi}\Im\left\{Z\left(x+\mathrm{j}\frac{\pi}{2}\right)+Z^*\left(x+\mathrm{j}\frac{\pi}{2}\right)\right\}$$
$$= -\frac{1}{\pi}\Im\left\{2\Re Z\left(x+\mathrm{j}\frac{\pi}{2}\right)\right\} = 0,$$

where * denotes complex conjugation, i.e. $y^* = (a + \mathrm{j}b)^* = a - \mathrm{j}b,\ a, b \in \mathbb{R}$. We see that $g(x)$ has a fixed value of zero, bringing us to the same conclusion as in [2] — that this formula is not useful at all.

The problem is assuming that $Z(x^*) = Z^*(x)$, see lines with "error" above the pertaining equality sign in (4). This is in fact not correct, but $\hat{Z}((\mathrm{j}\omega)^*) = \hat{Z}^*(\mathrm{j}\omega)$ is (see Appendix A). This is what has probably caused the confusion.

2.2. Fuoss–Kirkwood's definition

Just like (4) Fuoss–Kirkwood version of the inversion formula is defined via the imaginary part $H(x)$ [1]

$$g(x) = -\frac{1}{\pi}\Im\left\{Z\left(x+\mathrm{j}\frac{\pi}{2}\right)+Z\left(x-\mathrm{j}\frac{\pi}{2}\right)\right\} \quad (5)$$
$$= \frac{1}{\pi}\left(H\left(x+\mathrm{j}\frac{\pi}{2}\right)+H\left(x-\mathrm{j}\frac{\pi}{2}\right)\right),$$

and it does not introduce any simplifications.

2.3. Showcasing Fuoss–Kirkwood's relation

Let us show the transformation on Cole-Cole (RQ) ECM element, given by [4]

$$Z_{\mathrm{RQ}}(\omega) = \frac{R}{(\mathrm{j}\omega\tau_0)^\alpha + 1}, \quad (6)$$

where R is the resistance, τ is the characteristic relaxation time and α is a scalar indicating deviation from the ideal RC circuit. RQ element is commonly used to model batteries [5], fuel cells [6], dielectric properties of biological tissues [7], for corrosion analysis [8], etc. We can decompose this impedance into a real and an imaginary part

$$Z_{\mathrm{RQ}}(\omega) = R\frac{(\omega\tau_0)^\alpha(\cos(\theta) - \mathrm{j}\sin(\theta)) + 1}{(\omega\tau_0)^{2\alpha} + 2(\omega\tau_0)^\alpha\cos(\theta) + 1} \quad (7)$$
$$= R\frac{(\omega\tau_0)^\alpha\cos(\theta) + 1}{(\omega\tau_0)^{2\alpha} + 2(\omega\tau_0)^\alpha\cos(\theta) + 1} - \mathrm{j}R\frac{(\omega\tau_0)^\alpha\sin(\theta)}{(\omega\tau_0)^{2\alpha} + 2(\omega\tau_0)^\alpha\cos(\theta) + 1},$$

where $\theta = \frac{\alpha\pi}{2}$.

This gives us the imaginary part, given by

$$H_{\mathrm{RQ}}(x) = R\frac{\exp[\alpha(\log\tau_0 - x)]\sin(\theta)}{\exp[2\alpha(\log\tau_0 - x)] + 2\exp[\alpha(\log\tau_0 - x)]\cos(\theta) + 1}. \quad (8)$$

Since

$$\exp\left[\alpha\left(\log\tau_0 - x \pm \mathrm{j}\frac{\pi}{2}\right)\right] = \exp[\alpha(\log\tau_0 - x)]\exp\left[\pm\mathrm{j}\theta\right], \quad (9)$$

and denoting $A = \exp[\alpha(\log\tau_0 - x)]$, we can write

$$\frac{\pi g(x)}{RA\sin(\theta)} = \frac{\exp\left[-\mathrm{j}\theta\right]}{A^2\exp\left[-2\mathrm{j}\theta\right] + 2A\exp\left[-\mathrm{j}\theta\right]\cos(\theta) + 1} \quad (10)$$
$$+ \frac{\exp\left[\mathrm{j}\theta\right]}{A^2\exp\left[2\mathrm{j}\theta\right] + 2A\exp\left[\mathrm{j}\theta\right]\cos(\theta) + 1}$$
$$= \frac{2\cos(\theta)}{A^2 + 2A\cos(2\theta) + 1}.$$

This gives then

$$g_{\mathrm{RQ}}(x) = \frac{1}{\pi}\frac{RA\sin(2\theta)}{A^2 + 2A\cos(2\theta) + 1} \quad (11)$$
$$= \frac{1}{\pi}\frac{R\exp[\alpha(\log\tau_0 - x)]\sin(\alpha\pi)}{\exp[2\alpha(\log\tau_0 - x)] + 2\exp[\alpha(\log\tau_0 - x)]\cos(\alpha\pi) + 1},$$

which is in line with other results for $g_{\mathrm{RQ}}(x)$ [9].

2.4. Proving transformation via simulation

Fig. 1 shows that if we take computer and simulate an RQ element (where $R = 0.5$, $\alpha = 0.8$ and $\tau_0 = 1$; the units are dimensionless), transform its impedance into DRT using (5) and back via (1), everything is consistent, as we reproduce the original impedance.

2.5. Other ECM elements

Direct inversion formula (5) can be applied to obtain not just DRT of an RQ element, but also of Havriliak-Negami and Gerischer elements [9].

Interestingly enough, direct inversion of the simple RC element, whose impedance is given by (6) with $\alpha = 1$, fails. This is due to the actual solution of (1) for Z_{RC} being a Dirac delta function, which is actually not a function at all [10] and cannot be described by (5). For additional insight, see Appendix B.

Similarly, finite-length Warburg (FLW) cannot be directly inverted by the Fuoss–Kirkwood's equation. Since FLW can be rewritten as a sum of RC elements [11], it suffers from the same problem with inversion.

Still, with additional care DRTs of both RC and FLW can be approximated as functions using Fuoss–Kirkwood inversion, see [9] for discussion.

3. Conclusion

We have provided evidence that Fuoss–Kirkwood relation is valid and have clarified the cause of the issue reported in [2]. We suggest that the work undertaken to address this now-resolved issue be reframed in a different context.

CRediT authorship contribution statement

Žiga Gradišar: Writing – review & editing, Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Conceptualization. **Pavle Boškoski:** Writing – review & editing, Writing – original draft, Validation, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Funding acknowledgments

The authors express sincere gratitude for the support received for the project "Probabilistic and explainable data-driven modeling of solid-oxide systems" jointly financed by the Slovenian Research and Innovation Agency (ARIS) (project number J2-4452), and the Austrian Science Fund (FWF) (project number I 6251-N). The authors also acknowledge the research core funding No. P2-0001, which is financially supported by the Slovenian Research and Innovation Agency (ARIS).

Declaration of competing interest

None.

Appendix A. Proof $\hat{Z}((\mathrm{j}\omega)^*) = \hat{Z}^*(\mathrm{j}\omega)$

To obtain impedance from time-domain impulse response $z(t)$ of a casual, time-invariant linear system, we just take its Laplace transform [12, Chapter 13, p. 564, Property 4]. Furthermore, if we complex-conjugate it, we obtain

$$\hat{Z}^*(s) = \left(\int_0^\infty z(t)\exp(-st)\,\mathrm{d}t\right)^* = \int_0^\infty z(t)\exp(-s^*t)\,\mathrm{d}t = \hat{Z}(s^*). \quad (A.1)$$

where $s = \sigma + \mathrm{j}\omega, \sigma, \omega \in \mathbb{R}$.

On the other hand, with $Z(x) = \hat{Z}(\mathrm{j}\omega)$ and $x = \log(1/\omega)$, we have

$$Z(x^*) = \hat{Z}\left(\mathrm{j}\frac{1}{\exp(x^*)}\right) = \hat{Z}\left(\mathrm{j}\left(\frac{1}{\exp(x)}\right)^*\right) \quad (A.2)$$

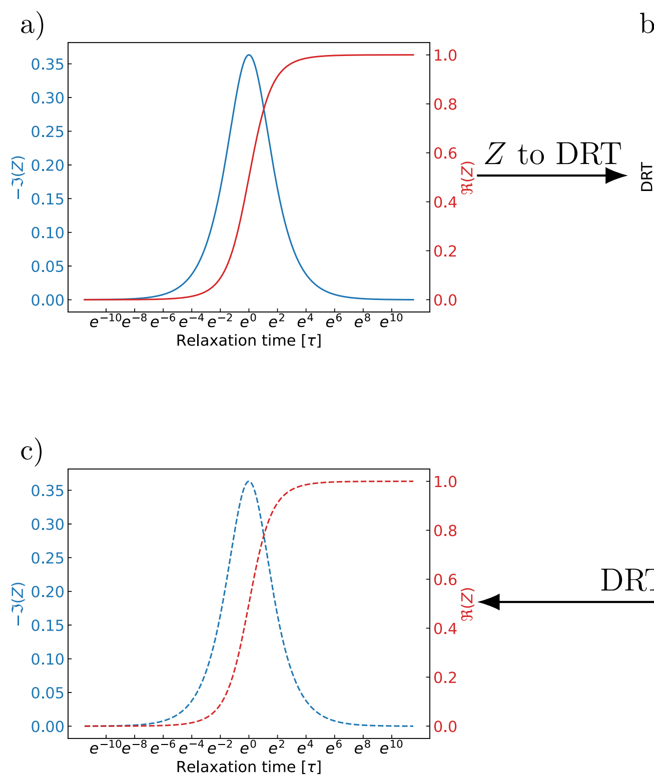

Fig. 1. Workflow for the validation of (5). (a) Impedance of a simulated RQ element ($R = 0.5$, $\alpha = 0.8$ and $\tau_0 = 1$) is converted to (b) the corresponding DRT directly (5) and using closed-form (11). (c) The DRT is then integrated to reconstruct the original impedance. Impedance is denoted by Z, where $\Re(Z)$ is its real and $\Im(Z)$ its imaginary part. All units are dimensionless.

$$= \hat{Z}\left(\left(\left(-\mathrm{j}\frac{1}{\exp(x)}\right)\right)^*\right) = \hat{Z}^*\left(-\mathrm{j}\frac{1}{\exp(x)}\right) \neq \hat{Z}^*\left(\mathrm{j}\frac{1}{\exp(x)}\right) = Z^*(x).$$

We see that a transformation of variables can introduce different properties to what we perceive as impedance.

Appendix B. DRT of RC element

Since RC is a special case of an RQ element with $\alpha = 1$, we can carefully (using a limit) start from (11)

$$g_{\mathrm{RC}}(x) = \lim_{\alpha\to 1^-} \frac{1}{\pi} \frac{R\exp[\alpha(\log\tau_0 - x)]\sin(\alpha\pi)}{\exp[2\alpha(\log\tau_0 - x)] + 2\exp[\alpha(\log\tau_0 - x)]\cos(\alpha\pi) + 1}. \tag{B.1}$$

The limit was taken from the left as $\alpha \in (0, 1]$. Since $\lim_{\alpha\to 1^-}\sin(\alpha\pi) = 0$, $g_{\mathrm{RC}}(x)$ is equal to zero expect perhaps for zeros in the denominator. Denoting $A = \alpha(\log\tau_0 - x)$, we find zeros in the denominator as

$$\exp[2A] - 2\exp[A] + 1 = (\exp[A] - 1)^2 = 0. \tag{B.2}$$

Since $A \in \mathbb{R}$, there is only one solution, $A = 0$, which in turn gives $x = \log\tau$. For the special case of zero in the denominator (B.1) results in

$$g_{\mathrm{RC}}(x = \log\tau_0) = \lim_{\alpha\to 1^-}\frac{R}{2\pi}\frac{\sin(\alpha\pi)}{1+\cos(\alpha\pi)} = \lim_{\alpha\to 1^-}\frac{R}{2\pi}\tan\left(\frac{\alpha\pi}{2}\right) = \infty, \tag{B.3}$$

which defines the DRT as

$$g_{\mathrm{RC}}(x) = \begin{cases} 0, & \text{if } x = \log\tau_0, \\ \infty, & \text{else }. \end{cases} \tag{B.4}$$

Together with the fact that $\lim_{\alpha\to 1^-}\int_{-\infty}^{\infty} g_{\mathrm{RQ}}(x)\,dx = \lim_{\alpha\to 1^-} R = R$, $g_{\mathrm{RC}}(x)$ is a member of heuristically defined Dirac delta functions [10].

So, naively putting numbers into (5) in case of a RC circuit does not produce a viable result. One must take a more subtle approach to recognize a Dirac delta function and use that as the result.

Appendix C. Acronyms

DRT distribution of relaxation times.
ECM equivalent circuit model.
EIS electrochemical impedance spectroscopy.
FLW finite-length Warburg.

Data availability

The data was generated artificially. The code is available at https://repo.ijs.si/zigag/fuoss-kirkwood-transform.

References

[1] R.M. Fuoss, J.G. Kirkwood, Electrical properties of solids. VIII. Dipole moments in polyvinyl chloride-diphenyl systems*, J. Am. Chem. Soc. 63 (2) (1941) 385–394.

[2] K. Malkow, On the futility of the Fuoss–Kirkwood relation, Electrochem. Commun. 164 (2024) 107731.

[3] A. Maradesa, B. Py, J. Huang, Y. Lu, P. Iurilli, A. Mrozinski, H.M. Law, Y. Wang, Z. Wang, J. Li, S. Xu, Q. Meyer, J. Liu, C. Brivio, A. Gavrilyuk, K. Kobayashi, A. Bertei, N.J. Williams, C. Zhao, M. Danzer, M. Zic, P. Wu, V. Yrjänä, S. Pereverzyev, Y. Chen, A. Weber, S.V. Kalinin, J.P. Schmidt, Y. Tsur, B.A. Boukamp, Q. Zhang, M. Gaberšček, R. O'Hayre, F. Ciucci, Advancing electrochemical impedance analysis through innovations in the distribution of relaxation times method, Joule 8 (7) (2024) 1958–1981.

[4] M.E. Orazem, B. Tribollet, A tutorial on electrochemical impedance spectroscopy, ChemTexts (2020).

[5] C. Fleischer, W. Waag, H.-M. Heyn, D.U. Sauer, On-line adaptive battery impedance parameter and state estimation considering physical principles in reduced order equivalent circuit battery models: Part 1. Requirements, critical review of methods and modeling, J. Power Sources 260 (2014) 276–291.

[6] L. Žnidarič, G. Nusev, B. Morel, J. Mougin, Đ. ani Juričić, P. Boškoski, Evaluating uncertainties in electrochemical impedance spectra of solid oxide fuel cells, Appl. Energy 298 (2021) 117101.

[7] S. Gabriel, R.W. Lau, C. Gabriel, The dielectric properties of biological tissues: III. Parametric models for the dielectric spectrum of tissues, Phys. Med. Biol. 41 (11) (1996) 2271.

[8] R. Zhang, D. Sur, K. Li, J. Witt, R. Black, A. Whittingham, J.R. Scully, J. Hattrick-Simpers, Bayesian assessment of commonly used equivalent circuit models for corrosion analysis in electrochemical impedance spectroscopy, Npj Mater. Degrad. 8 (1) (2024) 120.
[9] B.A. Boukamp, Distribution (function) of relaxation times, successor to complex nonlinear least squares analysis of electrochemical impedance spectroscopy? J. Phys.: Energy 2 (4) (2020) 042001.
[10] Wikipedia contributors, Dirac delta function — Wikipedia, the free encyclopedia, 2025, Online; (Accessed 2 December 2025).
[11] B.A. Boukamp, Derivation of a distribution function of relaxation times for the (fractal) finite length warburg, Electrochim. Acta 252 (2017) 154–163.
[12] C.A. Desoer, E.S. Kuh, Basic Circuit Theory, McGraw-Hill, 1969, See Chapter 13, p. 563, Property 4.