ChemPubSoc Europe
DOI: 10.1002/celc.201700629
CHEMELECTROCHEM
Communications

Immittance Data Validation using Fast Fourier Transformation (FFT) Computation – Synthetic and Experimental Examples

T. Malkow,*[a] G. Papakonstantinou,[a, c] A. Pilenga,[a] L. Grahl-Madsen,[b] and G. Tsotridis[a]

Exact data of an electric circuit (EC) model of RLC (resistor, inductor, capacitor) elements representing rational immittance of LTI (linear, time invariant) systems are numerically Fourier transformed to demonstrate within error bounds applicability of the Hilbert integral tranform (HT) and Kramers-Kronig (KK) integral tranform (KKT) method. Immittance spectroscopy (IS) data are validated for their HT (KKT) compliance using non-equispaced fast Fourier transformation (NFFT) computations. Failing of HT (KKT) testing may not only stem from non-compliance with causality, stability and linearity which are readily distinguished using anti HT (KKT) relations. It could also indicate violation of uniform boundedness to be overcome either by using singly or multiply subtracted KK transform (SSKK or MSKK) or by seeking KKT of the same set of data at a complementary immit- tance level. Experimental IS data of a fuel cell (FC) are also numerically HT (KKT) validated by NFFT assessing whether LTI principles are met. Figures of merit are suggested to measure success in numerical validation of IS data.

In a companion communication,[1] we note the usefulness and need for data validation of immittance spectroscopy (IS) measurements and models.[2–12] Immittance (e.g. admittance, Y, impedance, Z, complex capacitance, $C=(j\omega)^{-1}Y$, complex inductance, $L=(j\omega)^{-1}Z$) is known under various other names and appears in modified form too in many other fields of natural sciences and engineering[6–12] where validation of measurements and verification of model data is often likewise required. They basically adhere all to the same principles, comply with the same relations and face the same dilemmas as presented here.

[a] Dr. T. Malkow, Dr. G. Papakonstantinou, A. Pilenga, Dr. G. Tsotridis
European Commission, Directorate-General Joint Research Centre, Westerduinweg 3, 1755 LE Petten (The Netherlands)
E-mail: Thomas.Malkow@ec.europa.eu
[b] L. Grahl-Madsen
EWII Fuel Cells A/S, Emil Neckelmannsvej 15 A&B, 5220 Odense SØ (Denmark)
[c] Dr. G. Papakonstantinou
Present address: Max-Planck-Institut für Dynamik komplexer technischer Systeme, 39106 Magdeburg (Germany)

Supporting information for this article is available on the WWW under https://doi.org/10.1002/celc.201700629

For inertial systems (materials, interfaces or devices) whether oscillatory (dynamic) or at rest, we derived for linear, stable & causal systems[13–17] in the real angular frequency domain (Fourier space), $\Re e\{-js\}=\omega$, $s=\sigma+j\omega$, $0\le\sigma\in\mathbb{R}$, $\omega=2\pi f\in\mathbb{R}$, $(\pm j)^2=-1$ using integral transform properties (theorems)[2,18,19] for continuous, bounded (convergent), **rational** immittance,

$$I(\omega)=\frac{N(\omega)\in\mathbb{C}}{D(\omega)\in\mathbb{C}}=\frac{\sum\limits_{m\in\mathbb{N}\cup\{0\}}a_m\omega^m}{\sum\limits_{n\in\mathbb{N}\cup\{0\}}b_n\omega^n}=\frac{a_0}{b_0}\frac{\prod\limits_{i\in\mathbb{N}}\omega-z_i}{\prod\limits_{j\in\mathbb{N}}\omega-p_j}$$

of finite degree, $\deg N\le\deg D<\infty$ with zeros (roots of N), $z_i\in\mathbb{C}$ and poles (roots of D), $p_j\in\mathbb{C}_-:=\{s\in\mathbb{C}:\Re es<0\}$ Hilbert integral transform (HT) and Kramers-Kronig (KK) integral transform (KKT) relations,[1]

$$\begin{aligned}(I\pm I^*)((-\jmath)^\alpha\omega)&=(-\jmath)^\beta\mathcal{H}(I\mp I^*)((-\jmath)^\alpha\omega),\\&=(-\jmath)^\beta\mathcal{K}(I\mp I^*)((-\jmath)^\alpha\omega),\ \alpha,\beta\in\mathbb{Z}\end{aligned}\tag{1}$$

with $2\alpha^2+\alpha+1=\beta$; * denotes complex conjugation. Taking $\alpha=0$ thus $\beta=1$,

$$\begin{aligned}(I\pm I^*)(\omega)&\ne(-\jmath)^\gamma\mathcal{H}(I\mp I^*)(\omega),\\&\ne(-\jmath)^\gamma\mathcal{K}(I\mp I^*)(\omega).\end{aligned}\tag{2}$$

with $\gamma=0$, $\gamma=-1$ and $\gamma=+2$ are anti HT (KK) relations complementary to (1) when respectively IS linearity (superposition), causality (cause precedes its effect) and stability (dilation, translation & rotation invariance) is violated.[1]

$$\mathcal{H}^\pm I(\omega)=\pm\mathcal{P}\int_{\mathbb{R}}\frac{I(\nu)}{\omega-\nu}\frac{d\nu}{\pi},\ \omega\in\mathbb{R}^+$$

is the linear HT[2,20–23] (forward, $\mathcal{H}^+$ and inverse $\mathcal{H}^-$) on $\mathbb{R}$ where $\mathcal{P}$ signifies the (Cauchy's) principal value taken at $\omega=\nu$ and **all** $I(\omega)$ poles (isolated singularities).

$$\begin{aligned}\mathcal{K}^\pm\Re\mathfrak{e}I(\omega)&=2\,\mathcal{P}\int_{\mathbb{R}^+}\mathcal{H}^\pm\left\{\tfrac{\omega}{\omega^2-\nu^2}\right\}\Im\mathfrak{m}I(\nu)\tfrac{d\nu}{\pi},\ \omega\in\mathbb{R}^+,\\\mathcal{K}^\mp\Im\mathfrak{m}I(\omega)&=2\,\mathcal{P}\int_{\mathbb{R}^+}\mathcal{H}^\mp\left\{\tfrac{\nu}{\omega^2-\nu^2}\right\}\Re\mathfrak{e}I(\nu)\tfrac{d\nu}{\pi}\end{aligned}$$

is the linear KKT (forward, $\mathcal{K}^+$ and inverse $\mathcal{K}^-$) pair on $\mathbb{R}^+:=\{x\in\mathbb{R}:0\le x\}$. It is also known as dispersion relation[13–17,24–26] for the real and imaginary immittance parts, $\Re eI(\omega)=0.5(I+I^*)(\omega)$ and $\Im mI(\omega)=-0.5j(I-I^*)(\omega)$, respectively. Note, HT and KKT are interrelated by the ω domain parity,

$$I(\omega) = I^*(-\omega), \forall\omega \tag{3}$$

stemming from time, t domain reality, $I(t) = I^*(t) \in \mathbb{R}, \forall t \in \mathbb{R}$.

Comparing the right hand side (RHS) of (2) to that of (1) and using (3), we conclude that compared to linear, causal & stable IS data the real part of the immittance becomes imaginary and the imaginary part becomes real and negated for non-linear data ($\gamma = 0$). For acausal data ($\gamma = -1$), the real and imaginary parts both become negated. Instability in IS data ($\gamma = +2$) is exhibited by the real part to become imaginary and negated and the imaginary part to become real.[1] These implications have obviously no consequence for the immittance magnitude (modulus), $|I(\omega)| = \sqrt{\Re e^2 I(\omega) + \Im m^2 I(\omega)}$.

In contrast, acausal data compared to causal data would exhibit a shift of $-\pi$ (counted anti clockwise) in the principal argument (phase) of the immittance, $\arg I(\omega) = \theta(\omega) = \tan^{-1}\left(\frac{\Im m}{\Re e} I(\omega)\right), \ -\pi \leq \operatorname{Arg} I < \pi$ while the loss (dissipation) factor (LF), $\tan\theta(\omega)$ remains unaltered. Non-linear and unstable data would both exhibit a LF change from $\tan\theta(\omega)$ to $-\cot\theta(\omega)$ compared to HT (KKT) compliant data.[1] These implications are the cornerstones of our numerical validation to reveal LTI violation in the IS data.

Further, causality, $I(t < 0) = 0$ implies as outlined elsewhere[1] vanishing (conjugate) instantaneous immittance,

$$\lim_{|\omega| \to \infty} (I \pm I^*)(\omega) = (I \pm I^*)(|\omega| \to \infty) = 0 \tag{4}$$

by the initial value theorem of the Fourier integral transform (FT) (forward, $\mathcal{F}$ and backward or inverse, $\mathcal{F}^{-1}$),[2,18,19]

$$\begin{aligned} I(\jmath^\alpha\omega) = \ & \mathcal{F}I((-\jmath)^\alpha t) = \ (-\jmath)^\alpha \int_{(-\jmath)^\alpha\mathbb{R}} I((-\jmath)^\alpha t) e^{-\jmath\omega t} \mathrm{d}t, \\ I((-\jmath)^\alpha t) = \ & \mathcal{F}^{-1} I(\jmath^\alpha\omega) = \ \frac{\jmath^\alpha}{2\pi} \int_{\jmath^\alpha\mathbb{R}} I(\jmath^\alpha\omega) e^{\jmath\omega t} \mathrm{d}\omega, \ \alpha \in \mathbb{Z}. \end{aligned} \tag{5}$$

Diverging $I(|\omega| \to \infty)$, needs division of $I(\omega)$ by $(j\omega)^n, n \in \mathbb{N}\backslash\{0\}$ to meet (4) and ensure convergence of the RHS of (1). Finite $I(|\omega| \to \infty) \neq 0$ requires its subtraction from the left hand side (LHS) of (1) to meet (4) yielding, noting $\mathcal{P}\int_{\mathbb{R}} |\omega - \nu|^{-1} \mathrm{d}\nu = 0$, singly subtractive (SS) HT (KKT) relations,[4,5,27]

$$\begin{aligned} (I \pm I^*)(\omega) - (I \pm I^*)(|\omega| \to \infty) \ &= -\jmath\mathcal{H}(I \mp I^*)(\omega), \\ &= -\jmath\mathcal{K}(I \mp I^*)(\omega). \end{aligned} \tag{6}$$

Remark, any open right half s plane (RHP) pole, $p_j \in \mathbb{C}_+ := \{s \in \mathbb{C} : \Re e\{s\} > 0\}$ implies by the residue theorem,[28] $|I(|t| \to \infty)| \to \infty$. Thus, unless zero-pole cancellation, $|p_j| = |z_i|$ occurs, I in (1) and (5) would diverge. In this case, multiply subtractive (MS) KK relations,[4,5,27]

$$\begin{aligned} \mathfrak{Re} \sum_i \frac{I(\omega) - I(p_i)}{(\omega - p_i)^{n_{p_i}}} &= \mathcal{K}^+ \mathfrak{Im} \sum_i \frac{I(\omega) - I(p_i)}{(\omega - p_i)^{n_{p_i}}}, \\ \mathfrak{Im} \sum_i \frac{I(\omega) - I(p_i)}{(\omega - p_i)^{n_{p_i}}} &= \mathcal{K}^- \mathfrak{Re} \sum_i \frac{I(\omega) - I(p_i)}{(\omega - p_i)^{n_{p_i}}} \end{aligned}$$

with $n_{p_i} > 0, \forall i$ can be used to yield piecewise (sectionally) continuous I with **all** RHP poles (counting multiplicities) removed to meet (4).

The dilemma is knowing *a priori* all singularities in the measured IS data to be validated or to assume a physically significant model which describes well the yet to be validated raw IS data.

In the sequel, we briefly outline our quantitative approach on the validation of IS data by fast FT (FFT) computation[29,30] using (1) demonstrated on two examples namely exact data of an electric circuit (EC) model (Figure 1) and of experimental fuel cell (FC) data. First, we use (1) to analytically integrate

$$\begin{aligned} Z(\omega) = \frac{1}{Y(\omega)} = \ & R_1 \frac{(1+\jmath\omega\tau_1)(1+\jmath\omega\tau_2) + \tau_{12}^{-1}\tau_2}{1+\jmath\omega\tau_2} \\ = \ & R_1 \frac{(\omega - z_1^Z)(\omega - z_2^Z)}{\omega - p^Z}, \end{aligned} \tag{7}$$

the impedance and admittance of the EC model displayed in Figure 1 which represents an inherent LTI (linear, time invariant)

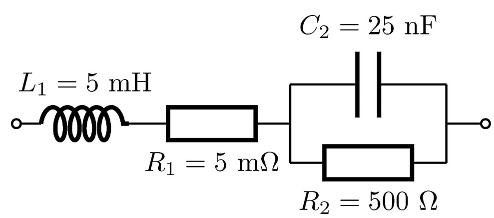

Figure 1. Example of an EC model with time constants, $\tau_1 = L_1/R_1 = 1$ *s*, $\tau_2 = R_2C_2 = 12.5$ *μs* & $\tau_{12} = R_1C_2 = 0.125$ *ns*; $Y_{(7)}$ poles ($Z_{(7)}$ zeros), $p_{1,2}^{Y_{(7)}} = z_{1,2}^{Z_{(7)}} = j/2(\tau_1^{-1} + \tau_2^{-1})\ (1 \pm \sqrt{1 - 4\tau_1^{-1}(\tau_2^{-1} + \tau_{12}^{-1})/(\tau_1^{-1} + \tau_2^{-1})^2} \approx (\pm 80 + 40j)$ *kHz* and $Z_{(7)}$ pole ($Y_{(7)}$ zero), $p^{Z_{(7)}} = z^{Y_{(7)}} = j\tau_2^{-1} = 80j$ kHz.

system with passive elements such as resistors, R_1 & R_2, inductor, L_1, and capacitor, C_2 (RLC network).

What follows is the numerical validation of exact data of $Z_{(7)}$ & $Y_{(7)}$ to check for linearity, causality and stability violations with figures of merit (Table 1) before performing the same for the experimental data (Table 2). We conclude with some general suggestions to enhance IS data analysis.

Note, the numerical validation makes use of the FT convolution theorem[18] to apply FFT forth and back to the LHS of (1) to obtain ${}^{\pm}\Delta(\omega) = \mathcal{F}^{\mp}\mathcal{F}^{\pm}I(\omega)$ and to its RHS to obtain for HT[31–36] $\Delta_{HT}^{\pm}(\omega) = (2\pi)^{-1}\mathcal{F}^{\mp}\left\{\operatorname{sgn}(\mp t)\mathcal{F}^{\pm}I(\omega)\right\}$ and for KKT, $\Delta_{KKT}^{\pm}(\omega) = (2\pi)^{-1}\mathcal{F}^{\mp}\ \left\{0.25\operatorname{sgn}(\mp t)\mathcal{F}^{\pm}I(\omega)\right\}$ employing the Fubini-Tonelli theorem;[2,37,38] $\operatorname{sgn}(t \neq 0) = t/|t|$ & $\operatorname{sgn}(0) = 0$ is the signum function.[19] The mismatch,

$$\Delta(\omega) = (I - \Delta_{\pm})(\omega) \tag{8}$$

with $\Delta_{\pm}(\omega) = 0.5[\Delta^{\pm} + \Delta^{\mp}](\omega)$ is a measure of validation of numerical error,

$$\varepsilon(\omega) = (I - {}_{\pm}\Delta)\ (\omega) \tag{9}$$

where ${}_{\pm}\Delta(\omega) = 0.5[{}^{\pm}\Delta + {}^{\mp}\Delta](\omega)$. These quantities are computed by the non-equispaced FFT (NFFT) C subroutine library[39]

Table 1. Comparison of figures of merit for the HT (KKT) validation by NFFT computation of synthetic data of $Z_{(7)}$ and $Y_{(7)}$ using (1) to those of $C_{(12)}$.

		–		2% additive white noise	
		$\Delta(\pm\sigma_\Delta)$	$\varepsilon(\pm\sigma_\varepsilon)$	$\Delta(\pm\sigma_\Delta)$	$\varepsilon(\pm\sigma_\varepsilon)$
			HT validation		
$Z_{(7)}$	$\overline{\langle\cdot_{\mathrm{abs}}\rangle}$	$1.28(\pm 0.912)\cdot 10^{+10}$	$3.15(\pm 3.849)\cdot 10^{+08}$		
$Y_{(7)}$		$1.52(\pm 0.748)\cdot 10^{+02}$	$2.58(\pm 2.996)\cdot 10^{+01}$		
$C_{(12)}$		$1.46(\pm 0.744)\cdot 10^{-10}$	$2.23(\pm 2.902)\cdot 10^{-11}$	$1.47(\pm 0.752)\cdot 10^{-10}$	$2.26(\pm 2.936)\cdot 10^{-11}$
$Z_{(7)}$	$\overline{\langle\cdot_{\mathrm{arg}}\rangle}$	$0.005(\pm 1.5706)$	$5\cdot 10^{-07}(\pm 1.4789)$		
$Y_{(7)}$		$0.002(\pm 0.8928)$	$2\cdot 10^{-09}(\pm 1.5361)$		
$C_{(12)}$		$0.062(\pm 0.5803)$	$-2\cdot 10^{-10}(\pm 1.5055)$	$0.062(\pm 0.5800)$	$4\cdot 10^{-08}(\pm 1.5056)$
			KKT validation		
$Z_{(7)}$	$\overline{\langle\cdot_{\mathrm{abs}}\rangle}$	$6.17(\pm 2.508)\cdot 10^{+08}$	$8.65(\pm 4.790)\cdot 10^{+07}$		
$Y_{(7)}$		$3.61(\pm 1.700)\cdot 10^{+01}$	$5.00(\pm 2.869)\cdot 10^{+00}$		
$C_{(12)}$		$3.64(\pm 1.671)\cdot 10^{-11}$	$4.87(\pm 2.809)\cdot 10^{-12}$	$3.68(\pm 1.691)\cdot 10^{-11}$	$4.93(\pm 2.842)\cdot 10^{-12}$
$Z_{(7)}$	$\overline{\langle\cdot_{\mathrm{arg}}\rangle}$	$1.138(\pm 1.5377)$	$0.894(\pm 1.5640)$		
$Y_{(7)}$		$-1.367(\pm 1.5196)$	$-1.442(\pm 1.5109)$		
$C_{(12)}$		$1.765(\pm 1.4657)$	$1.877(\pm 1.5002)$	$1.766(\pm 1.4628)$	$1.877(\pm 1.5026)$

Table 2. Figures of merit for the HT (KKT) validation of experimental *Z, Y, L* & *C* data and their respective MS pendants (13) by NFFT computation of (1).

		–		a = 1		a = 2	
		$\Delta(\pm\sigma_\Delta)$	$\varepsilon(\pm\sigma_\varepsilon)$	$\Delta(\pm\sigma_\Delta)$	$\varepsilon(\pm\sigma_\varepsilon)$	$\Delta(\pm\sigma_\Delta)$	$\varepsilon(\pm\sigma_\varepsilon)$
				HT validation			
Z	$\overline{\langle\cdot_{\mathrm{abs}}\rangle}$	$6.39(\pm 3.251)\cdot 10^{+01}$	$1.16(\pm 0.367)\cdot 10^{+03}$	$1.90(\pm 1.001)\cdot 10^{+01}$	$2.97(\pm 1.186)\cdot 10^{+01}$	$7.03(\pm 3.125)\cdot 10^{-02}$	$1.96(\pm 0.973)\cdot 10^{-01}$
Y		$3.90(\pm 1.929)\cdot 10^{+04}$	$7.89(\pm 2.085)\cdot 10^{+01}$	$1.14(\pm 0.598)\cdot 10^{+04}$	$1.78(\pm 0.708)\cdot 10^{+04}$	$4.20(\pm 1.862)\cdot 10^{+01}$	$1.05(\pm 0.526)\cdot 10^{+02}$
L		$4.82(\pm 0.252)\cdot 10^{-01}$	$1.18(\pm 0.510)\cdot 10^{+00}$	$3.32(\pm 1.642)\cdot 10^{-01}$	$5.17(\pm 2.006)\cdot 10^{-01}$	$2.97(\pm 6.235)\cdot 10^{-02}$	$1.52(\pm 1.124)\cdot 10^{+00}$
C		$2.51(\pm 1.297)\cdot 10^{+02}$	$6.13(\pm 2.628)\cdot 10^{+02}$	$1.59(\pm 0.777)\cdot 10^{+02}$	$2.46(\pm 0.951)\cdot 10^{+02}$	$1.53(\pm 3.323)\cdot 10^{+01}$	$7.89(\pm 5.743)\cdot 10^{+02}$
Z	$\overline{\langle\cdot_{\mathrm{arg}}\rangle}$	$-0.020(\pm 1.5245)$	$9\cdot 10^{-18}(\pm 0.0673)$	$0.246(\pm 0.7704)$	$0.331(\pm 1.5149)$	$1.631(\pm 1.5254)$	$-8\cdot 10^{-16}(\pm 1.3437)$
Y		$0.016(\pm 1.4883)$	$4\cdot 10^{-18}(\pm 0.0638)$	$-0.421(\pm 0.7857)$	$-0.331(\pm 1.4347)$	$-1.412(\pm 1.5289)$	$-2\cdot 10^{-15}(\pm 1.3590)$
L		$-0.233(\pm 0.8910)$	$2\cdot 10^{-15}(\pm 1.4349)$	$-0.303(\pm 0.9382)$	$-8\cdot 10^{-15}(\pm 1.1504)$	$-1.269(\pm 1.5341)$	$1\cdot 10^{-14}(\pm 1.5674)$
C		$-0.200(\pm 1.0352)$	$-3\cdot 10^{-15}(\pm 1.5120)$	$-0.322(\pm 1.3910)$	$-1\cdot 10^{-15}(\pm 1.1375)$	$1.542(\pm 1.5597)$	$-4\cdot 10^{-15}(\pm 1.5678)$
				KKT validation			
Z	$\overline{\langle\cdot_{\mathrm{abs}}\rangle}$	$1.89(\pm 0.496)\cdot 10^{+01}$	$2.31(\pm 1.014)\cdot 10^{+01}$	$6.64(\pm 1.627)\cdot 10^{+00}$	$8.01(\pm 3.616)\cdot 10^{+00}$	$4.45(\pm 1.132)\cdot 10^{-02}$	$1.12(\pm 0.481)\cdot 10^{-01}$
Y		$1.11(\pm 0.309)\cdot 10^{+04}$	$1.37(\pm 0.574)\cdot 10^{+04}$	$3.79(\pm 0.942)\cdot 10^{+03}$	$4.59(\pm 2.074)\cdot 10^{+03}$	$2.59(\pm 0.640)\cdot 10^{+01}$	$6.50(\pm 2.579)\cdot 10^{+01}$
L		$1.06(\pm 0.240)\cdot 10^{+01}$	$1.25(\pm 0.551)\cdot 10^{+01}$	$1.03(\pm 0.241)\cdot 10^{+02}$	$1.22(\pm 1.546)\cdot 10^{+02}$	$6.51(\pm 1.985)\cdot 10^{-01}$	$3.77(\pm 1.342)\cdot 10^{+00}$
C		$5.47(\pm 1.240)\cdot 10^{+03}$	$6.48(\pm 2.847)\cdot 10^{+03}$	$5.30(\pm 1.239)\cdot 10^{+04}$	$6.271(\pm 2.814)\cdot 10^{+04}$	$3.35(\pm 1.022)\cdot 10^{+02}$	$1.94(\pm 0.691)\cdot 10^{+03}$
Z	$\overline{\langle\cdot_{\mathrm{arg}}\rangle}$	$-0.451(\pm 0.5241)$	$-0.394(\pm 1.4505)$	$0.172(\pm 0.8709)$	$0.191(\pm 1.5186)$	$0.045(\pm 0.0113)$	$0.120(\pm 0.0481)$
Y		$-0.081(\pm 0.3395)$	$-0.427(\pm 1.3555)$	$1.165(\pm 1.2954)$	$-0.470(\pm 1.5191)$	$-0.156(\pm 1.5415)$	$-0.973(\pm 1.5332)$
L		$-1.628(\pm 1.5138)$	$-0.984(\pm 1.5177)$	$1.560(\pm 1.5597)$	$0.251(\pm 1.2707)$	$-1.502(\pm 1.4964)$	$-1.098(\pm 1.5019)$
C		$-1.570(\pm 1.5693)$	$-0.844(\pm 1.3514)$	$1.563(\pm 1.5627)$	$0.253(\pm 1.2920)$	$-1.499(\pm 1.4936)$	$-1.014(\pm 1.5220)$

which contains routines for the fast summation of complex valued trigonometric series of discrete, irregularly sampled data on the half open interval $\left[-\frac{1}{2},\frac{1}{2}\right[$.

Mapping $\omega:\mathbb{R}\rightarrow\left[-\frac{1}{2},\frac{1}{2}\right[$ for HT validation through $\frac{\omega-\min\{\omega\}}{\max\{\omega\}-\min\{\omega\}}-\frac{1}{2}$ and $\omega:\mathbb{R}^{+}\rightarrow\left[0,\frac{1}{2}\right[$ for KKT validation through $\frac{\omega-\min\{\omega\}}{2(\max\{\omega\}-\min\{\omega\})}$,[40] the immittances of (5) are evaluated as approximations to the Fourier coefficients of the respective discrete version of the FT integrals (5). It neglects at the expense to introduce an unknown error in the computation of (8) & (9) any existent but unmeasured $I(\omega)$ at $|\omega|\in]\min\{\omega\},\max\{\omega\}[$ to avoid immittance extrapolation to frequencies outside the measured range which is likewise vulnerable to errors.

NFFT rather than FFT is used since the latter requires uniformly spaced data, not always feasible particularly in the presence of apparent outliers in the data and incomplete measurement records.

Note, interpolation to obtain uniformally spaced frequency data is already implemented in NFFT[39] using the Kaiser-Bessel window function[41–43] by default. For this reason we are not attempting to employ any additional window (weighting) function to improve data validation.[30]

Ideally, $\cdot_n := \cdot(\omega_n), n\in\{1,\ldots,N\}$ where $\cdot$ is a placeholder for Δ and ε, yield the inevitable measurement noise in the IS data presumably randomly distributed over all *N* frequencies measured. Practically, numerical errors blend in too besides the errors due to spectrum truncation within the measured frequency range.[30]

Note, invalid data would far beyond reasonably expected errors in the spectra be characterised by too great a magnitude in Δ_n,

$$\Delta_{\mathrm{abs},n}=\sqrt{\mathfrak{Re}^2\Delta_n+\mathfrak{Im}^2\Delta_n}. \tag{10}$$

More accurate implications are deduced by quantifying the validation through figures of merit such as the normalised absolute mean,

$$\overline{\langle \cdot_{\mathrm{abs}} \rangle} := \frac{1}{N} \sum_n \cdot_{\mathrm{abs},n} \tag{11}$$

with unbiased standard deviation, $\sigma_{\overline{\langle \cdot_{abs} \rangle}} := \sqrt{\frac{1}{N-1} \sum_n \left(\cdot_{abs,n} - \overline{\langle \cdot \rangle} \right)^2}$. Then, principally the smaller $\overline{\langle \Delta_{abs} \rangle}$, the greater in extent is the validation success.

But, the mean (11) is essentially the same given the very definition of the modulus (10) when HT (KKT) validating raw IS data using the RHS of either (1) or (2). In fact, their validation differs in the computed I for the very same data only by the factor, $(-j)^{\gamma}$ with $\gamma = +1$ for linear, causal & stable data compliant with HT (KKT) relation (1) and with $\gamma = 0$ for non-linear data, $\gamma = -1$ for acausal data and $\gamma = +2$ for unstable data.

Since the latter three cases of LTI violations result as said before in phase changes, we define two argument (phase) deviations,

$$\Delta_{\arg,n} := \arg I_n - \arg \Delta_{\pm,n}, \; \varepsilon_{\arg,n} := \arg I_n - \arg {}_{\pm}\Delta_n.$$

Then, for (almost) vanishing $\overline{\langle \Delta_{\arg} \rangle}$, the underlying data are least likely to be non-linear, unstable or acausal. Thus, HT (KKT) compliant raw IS data have both small $\overline{\langle \Delta_{abs} \rangle}$ and small $\overline{\langle \Delta_{\arg} \rangle}$ virtually vanishing.

Note, the underlying raw IS data are likely to be acausal where $\overline{\langle \Delta_{\arg} \rangle}$ is similar to $-\pi$. Non-linear and unstable data may be revealed by appropriately defining $\overline{\langle \Delta_{\tan} \rangle}$ & $\overline{\langle \Delta_{\cot} \rangle}$ when indeed interested in the cause of non-compliance.

Caution is advised when applying the polar form, $I(\omega) = |I(\omega)| e^{j \arg I(\omega)}$ to (1) or (6). Their corresponding HT (KK) relations for $\ln|I(\omega)|$ and $\theta(\omega)$ known as Bode's gain-phase relations are strictly valid only for minimum phase (MP) systems[27] where the absolute difference in upper half s plane (UHP) zeros and RHP poles is at most unity; thus, $|\max\{\theta(\omega)\}| \leq \pi, \forall \omega$ by the Principle Argument theorem.[44] They inevitably fail for non-minimum phase (NMP) systems particular active systems with $|\max\{\theta(\omega)\}| > \pi$. This is unless **all** their RHP poles and UHP zeros are known *a priori* to resolve the ambiguity in the determination of $\theta(\omega)$ from $\ln|I(\omega)|$ and *vice versa*.

Thus, numerical validation of IS data by Bode relations along with the estimation of **all** RHP poles and UHP zeros is preposterous.

Turning to our synthetic example, we note the use of the impedance (7) in (1) is not possible as its imaginary part diverges at $|\omega| \to \infty$. Also, $(Z(\omega) - Z(\infty))/(\omega - \infty) = 1$ vanishes when applying HT (KKT).

Using instead the admittance (7) requires accounting for its two RHP poles, $p_1^{Y_{(7)}}$ & $p_2^{Y_{(7)}}$ (see Supporting Information, SI) and for vanishing at $|\omega| \to \infty$ of the resultant admittance to be also non-singular at $\omega \to 0$; hence, we arrive at the complex capacitance,

$$\begin{aligned} C(\omega) &= \jmath \tfrac{2}{R_1} + (\jmath\omega)^{-1} \sum_{i=1}^{2} \left(\omega - p_1^{Y_{(7)}}\right)\left(\omega - p_2^{Y_{(7)}}\right) Y_{(7)}(\omega) \\ &- \left(p_i^{Y_{(7)}} - p_1^{Y_{(7)}}\right)\left(p_i^{Y_{(7)}} - p_2^{Y_{(7)}}\right) Y_{(7)}\left(p_i^{Y_{(7)}}\right) \\ &= \tfrac{2}{\jmath\omega R_1}\left(\left(\omega - z^{Y_{(7)}}\right) - \left(\tfrac{p_1^{Y_{(7)}} + p_2^{Y_{(7)}}}{2} - z^{Y_{(7)}}\right)\right) + \jmath \tfrac{2}{R_1} \end{aligned} \tag{12}$$

Using (12) in (7) with $\alpha = 0$ hence $\beta = 1$, we obtain analytically by integration

$$\mathcal{P}\int_{-\infty}^{+\infty} \jmath \tfrac{R_1}{2} \tfrac{C_{(12)}(\nu)}{\omega - \nu} \tfrac{\mathrm{d}\nu}{\pi\jmath} = -\mathcal{P}\int_{-\infty}^{+\infty} \tfrac{p_1^{Y_{(7)}} + p_2^{Y_{(7)}}}{2\nu(\omega-\nu)} \tfrac{\mathrm{d}\nu}{\pi\jmath} = \\ -\tfrac{p_1^{Y_{(7)}} + p_2^{Y_{(7)}}}{2\pi\jmath\omega}(\ln(\nu) - \ln(\nu - \omega))\Big|_{\nu\to-\infty}^{\nu\to+\infty} = -k\tfrac{p_1^{Y_{(7)}} + p_2^{Y_{(7)}}}{2\omega} = -\jmath\tfrac{R_1}{2} k C_{(12)}(\omega)$$

$$-\mathcal{P}\int_0^{\infty} R_1 \tfrac{(\omega\mathfrak{Re} - \jmath\nu\mathfrak{Im}) C_{(12)}(\nu)}{\omega^2 - \nu^2} \tfrac{\mathrm{d}\nu}{\pi\jmath} = \mathcal{P}\int_0^{\infty} R_1 \tfrac{(\omega\mathfrak{Re} - \jmath\nu\mathfrak{Im})(p_1^{Y_{(7)}} + p_2^{Y_{(7)}})}{\nu(\nu^2 - \omega^2)} \tfrac{\mathrm{d}\nu}{\pi\jmath} = \\ -\tfrac{p_1^{Y_{(7)}} + p_2^{Y_{(7)}}}{2\pi\jmath\omega}(2\ln(\nu) - \ln(\nu^2 - \omega^2))\Big|_{\nu=0}^{\nu\to\infty} = -k\tfrac{p_1^{Y_{(7)}} + p_2^{Y_{(7)}}}{2\omega} = -\jmath\tfrac{R_1}{2} k C_{(12)}(\omega)$$

to conclude with $\ln(-1) = (1+2k)\pi j, k \in \mathbb{Z}$ that $j\frac{R_1}{2} C_{(12)}$ is HT (KKT) compliant. By the Principle Argument, the winding number, $k = 1$ is the difference in the number of UHP zeros and RHP poles of $j\frac{R_1}{2} C_{(12)}$ namely $z^{j\frac{R_1}{2} C_{(12)}} = z^{Y_{(7)}}$ and none, respectively.

Numerically, the HT (KKT) validation of $Z_{(7)}$ & $Y_{(7)}$ by NFFT computation (see SI) reveals through too great means (Table 1) their non-compliance with (1). In contrast, the means of the NFFT computed $C_{(12)}$ data (see SI) are well below unity indicating as expected compliance with (1) inherently owed to finiteness and continuity (convergence) of $C_{(12)}$ absent for $Z_{(7)}$ and $Y_{(7)}$. From the synthetic nature of the $Z_{(7)}$ & $Y_{(7)}$ data consisting in our example of logarithmically spaced data points per decade of frequency, $f \in [10^{-3}, 10^{6}]$Hz (see SI), we know that failing numerical validation is attributable to unboundedness, $|\Im m Z_{(7)}(|\infty|)| \to \infty$ and the discontinuity at $p_1^{Y_{(7)}} \approx (80 + 40j)$ kHz rather than to violated linearity, causality or stability. In this respect, we remind that convergence is prerequisite for the existence of the principal value integrals (1).

Further, we note for all computed Δ and ε rather marginal differences in the HT and KKT validation approaches. Essentially, the very same set of data are used in the two approaches with the only distinction of the data duplicated in the HT case using (3) and simply duplicated in the KKT case.

Owing to parity (3) linking HT and KKT, a disparity beyond numerical error between both validations could suggest anti-symmetry, $I(0^{\pm}) + I(0^{\mp}) = 0$ compared to symmetry, $I(0^{\pm}) - I(0^{\mp}) = 0$.

Also, against additive random noise of 2% in magnitude representative of measurement error in the IS data, the method of NFFT computation is evidently robust for both approaches (cf $C_{(12)}$ the last two columns in Table 1).

Another example demonstrating HT (KKT) validation are experimental fuel cell (FC) impedance data measured in logarithmic spacing in the frequency range, $f \in [5 \cdot 10^{-2}, 10^{4}]$Hz (see SI). For the NFFT computation, we derive from these data their corresponding data of admittance, inductance and capacitance (see SI). We also use exemplary for $a = 1$ and $a = 2$

their MS pendants,

$$I(\omega_n) = \sum_{i \neq n} \frac{I(\omega_n) - I(\omega_i)}{(\omega_n - \omega_i)^a},\ n \in \{0, \ldots, N-1\}. \tag{13}$$

to verify improved convergence of (1)[4,5,27] in the NFFT computations (see SI).

Notably, among the immittance data only those at the inductance level are with certainty LTI compliant as the magnitude mean is below unity and the argument mean almost vanishes for HT validation (Table 2). Also, the convergence at this level is evidently improved using subtracted HT (KKT) relations (13) as the magnitude mean further reduces with $a=1$ and more so with $a=2$. This is also true for the impedance level of the measured data. But, the picture is not that conclusive when comparing the computed argument mean of these data.

We are nevertheless prompted to regard the experimental data at least at the impedance and inductance level as LTI compliant. At the other two levels, these data may contain singularities or may prove unbounded.

This could be of value when simulating the measured IS data by an equivalent electric circuit (EEC) model for further analysis.

Also, comparing HT validation to KKT validation for both our synthetic data and experimental data we are with regard to the computed magnitude mean and the computed argument inclined to prefer the former by the latter validation method to give credit to parity (3) over plainly duplicating the measured data.

In summary, we exemplary show applicability of numerical validation using the convolution theorem to NFFT compute synthetic and experimental IS data for their HT (KKT) compliance to quantitatively check by figures of merit for linearity, causality and stability violations.

Furthermore, we demonstrate on a simple RLC network analytically and numerically that IS data are only HT (KKT) transformable when convergence (continuity & finiteness) is also accounted for, e.g. by excluding removable singularities in the data.

We remind that the relations (1), (6) and (13) apply to rational, irreducible immittances (of RLC networks) corresponding in the time domain to ordinary differential equations of integer order with constant coefficients rather than to irrational immittances (i.e. Warburg and Gerischer like) constituting partial differential equations with or without memory (delay) of integer, fractional and/or fractal order in the time domain.[45–60]

But truncated series expansions[61] could most often assist in approximating irrational by rational immittances to seek the validation of the latter instead.

Given the invariance of the dispersion relations by dilation, translation and rotation, we suggest to also include imaginary frequencies by letting $\omega \rightarrow \pm j\omega$ in (1) with $\alpha=-1$, $\beta=2$ or $\alpha=1$, $\beta=4$ in data validation (see SI). The same may be applied in parameter identification of equivalent EC models, pole-zero estimation and determination of relaxation (retardation) time constants.

FT of (1) may even be used by letting $\omega \rightarrow s \in \mathbb{C}$ to obtain spectra of complex frequency from real frequency data.

The first principle derivation of linear dispersion relations truly applicable to irrational immittances (transfer functions) occurring in many other fields of natural sciences and engineering[2–9,13–17] is a future challenge. Note, spatial coordinate, wave number, momentum and energy could readily replace ω and ν as variables in the relations (1), (6) and (13) when applied to complex valued quantities other than immittances. Also a non-integer α in (1) merits future consideration.

Acknowledgment

Funding was received from the EU's Seventh Framework Programme for the Fuel Cells and Hydrogen Joint Technology Initiative under grant agreement number 245113. Special thanks to its developers making NFFT[39] freely available. Also, the authors acknowledge valuable comments and suggestions by two anonymous reviewers.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Boundedness · causality · continuity · linearity · stability

[1] T. Malkow, *ChemElectroChem* **2017**, doi:10.1002/celc.201700630.
[2] F. W. King, *Hilbert Transforms, Volumes 1 & 2, Nos. 124–125 of Encyclopedia of Mathematics and its Applications*, Cambridge Univ. Press, Cambridge, **2008** & **2009**.
[3] N. I. Muskhelishvili, *Singular integral equations: boundary problems of functions theory and their application to mathematical physics*, Dover Publications, Inc., Mineola, NY, **2008**.
[4] H. M. Nussenzveig, *Causality and dispersion relations*, Vol. 95 of Mathematics in science and engineering, Academ. Press, Inc., New York, London, **1972**.
[5] V. Lucarini, K.-E. Peiponen, J. J. Saarinen, E. M. Vartiainen, *Kramers-Kronig Relations in Optical Materials Research*, Vol. 110 of Springer Series in Optical Sciences, Springer-Verlag, Berlin, Heidelberg, **2005**.
[6] J. Singh (Ed.), *Optical Properties of Condensed Matter and Applications, of Materials for Electronic and Optoelectronic Applications*, J. Wiley & Sons, Ltd, Chichester, **2006**.
[7] E. M. Lifshitz, L. P. Pitaevskii (Eds.), *Electrodynamics of Continuous Media 2nd ed.*, Vol. 8 of Course of Theoretical Physics, Pergamon Press, New York, Oxford, Toronto, Sydney, Frankfurt, Paris, **1984**.
[8] Y. Yan, R. Xu, *Ann. Rev. Phys. Chem.* **2005**, *56*, 187–219.
[9] K. C. Meza-Fajardo, C. G. Lai, *Geophys. J. Int.* **2007**, *171*, 1247–1257.
[10] M. Feldman, *Hilbert Transform Applications in Mechanical Vibration*, J. Wiley & Sons, Ltd, Chichester, **2011**.
[11] M. Feldman, *Mech. Syst. Signal Process.* **2011**, *25*, 735–802.
[12] K.-T. Chau, *Analytic Methods in Geomechanics*, CRC Press LLC, Boca Raton, London, New York, **2013**.
[13] E. Barsoukov, J. R. Macdonald (Eds.), *Impedance Spectroscopy: Theory, Experiment, and Applications 2nd ed.*, Wiley-Intersci., Chichester, **2005**.
[14] M. E. Orazem, B. Tribollet (Eds.), *Electrochemical Impedance Spectroscopy 1st ed.*, J. Wiley & Sons, Inc., Hoboken, NJ, **2008**.
[15] V. F. Lvovich, *Impedance Spectroscopy: Applications to Electrochemical and Dielectric Phenomena*, J. Wiley & Son, Hoboken, NJ, **2012**.

[16] L. Callegaro, *Electrical Impedance: Principles, Measurement, and Applications, of Series in Sensors*, CRC Press LLC, Boca Raton, London, New York, **2013**.
[17] A. Lasia, *Electrochemical Impedance Spectroscopy and its Applications*, Springer-Verlag, Berlin, Heidelberg, **2014**.
[18] R. N. Bracewell, *The Fourier Transform and Its Applications 3rd ed.*, McGraw Hill, Inc., Boston, **1999**.
[19] M. Abramowitz, I. A. Stegun (Eds.), *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables, No. 55 of NBS Applied Mathematics Series*, Dover Publications, Inc., Mineola, NY, **1972**.
[20] D. Hilbert, *Nachr. Kgl. Ges. Wiss. Gött. Math.-Phys. Kl.* **1904**, *1*, 49–91.
[21] D. Hilbert, *Nachr. Kgl. Ges. Wiss. Gött. Math.-Phys. Kl.* **1906**, *2*, 157–227.
[22] D. Hilbert, *Nachr. Kgl. Ges. Wiss. Gött. Math.-Phys. Kl.* **1906**, *4*, 439–480.
[23] D. Hilbert, *Grundzüge einer allgemeinen Theorie der linearen Integralgleichungen, Fortschritte der mathematischen Wissenschaften in Monographien*, B. G. Teubner, Leipzig, Berlin, **1912**.
[24] H. A. Kramers, *Atti. Cong. Intern. Fisici, (Trans. Volta Centenary Cong.) Como* **1927**, *2*, 545–557
[25] R. (de Lear) Kronig, *J. Opt. Soc. Am.* **1926**, *12*, 547–556.
[26] C. F. Bohren, *Eur. J. Phys.* **2010**, *31*, 573–577.
[27] J. S. Toll, *Phys. Rev.* **1956**, *104*, 1760–1770.
[28] L. V. Ahlfors, *Complex Analysis: an introduction to the theory of analytic functions of one complex variable 3rd ed., of International Series in Pure and Applied Mathematics*, McGraw-Hill, Inc., New York, St. Louis, San Francisco, Auckland, Bogotá, Caracas, Lisbon, London, Madrid, Mexico City, Milan, Montreal, New Dehli, San Juan, Singapore, Sydney, Tokyo, Toronto, **1979**.
[29] J. W. Cooley, J. W. Tukey, *Math. Comp.* **1965**, *19*.
[30] W. H. Press, S. A. Teukolsky, W. T. Vetterling, B. P. Flannery (Eds.), *Numerical Recipes in C The Art of Scientific Computing 2nd ed.*, Cambridge Univ. Press, Cambridge, **1992**, chapter 12, pp. 496–536.
[31] T. J. VanderNoot, *J. Electroanal. Chem.* **1992**, *322*, 9–24.
[32] F. Castro, B. Nabet, *J. Franklin Inst.* **1999**, *336B*, 53–64.
[33] P. Bruzzoni, R. M. Carranza, J. R. Collet Lacoste, E. A. Crespo, *Electrochim. Acta* **2002**, *48*, 341–347.
[34] N. Axelrod, E. Axelrod, A. Gutina, A. Puzenko, P. B. Ishai, Y. Feldman, *Meas. Sci. Technol.* **2004**, *15*, 755.
[35] J. Lucas, E. Géron, T. Ditchi, S. Holé, *AIP Adv.* **2012**, *2*, 032144.
[36] S. Cruz-Manzo, R. Chen, P. Greenwood, *Insights Anal.l Electrochem.* **2015**, *1*, 1–13.
[37] G. Fubini, *Rom. Acc. L. Rend. V* **1907**, *16*, 608–614.
[38] L. Tonelli, *Atti. Accad. Naz. Lincei, Ser. V* **1909**, *18*, 246–253.
[39] J. Keiner, S. Kunis, D. Potts, *ACM Trans. Math. Softw.* **2009**, *36*, 19:1–19:30.
[40] B. Leroy, *Astron. & Astrophys.* **2012**, *515*, A50.
[41] F. J. Harris, *Proc. IEEE* **1978**, *66*, 51–83.
[42] S. Gade, H. Herlufsen, *Brüel & Kjær Techn. Rev.* **1987**, *3*, 1–28.
[43] S. Gade, H. Herlufsen, *Brüel & Kjær Techn. Rev.* **1987**, *4*, 1–35.
[44] A. Cotton-Cla, *Complex Analysis*, Vol. Mathematics 113 of Analysis I: Complex Function Theory, Harvard Univ., Cambridge, MA, **2013**.
[45] E. Warburg, *Ann. Phys. Chem.* **1899**, *67*, 493–499.
[46] H. Gerischer, *Z. Phys. Chem.* **1951**, *198*, 286–314.
[47] J. R. Macdonald, *Phys. Rev.* **1953**, *92*, 4–17.
[48] D. R. Franceschetti, J. R. Macdonald, R. P. Buck, *J. Electrochem. Soc.* **1991**, *138*, 1368–1371.
[49] T. Jacobsen, K. West, *Electrochim. Acta* **1995**, *40*, 255–262.
[50] J. R. Ramos-Barrado, P. G. Montenegro, C. Criado Gab'on, *J. Phys. Chem.* **1996**, *105*, 2813–2815.
[51] J. Bisquert, G. Garcia-Belmonte, P. Bueno, E. Longo, L. O. de Sousa Bulhões, *J. Electroanal. Chem.* **1998**, *452*, 229–234.
[52] J. Bisquert, G. Garcia-Belmonte, F. Fabregat-Santiago, P. R. Bueno, *J. Electroanal. Chem.* **1999**, *475*, 152–163.
[53] C. Criado, P. Galán-Montenegro, P. Velásquez, J. R. Ramos-Barrado, *J. Electroanal. Chem.* **2000**, *488*, 59–63.
[54] J. Jamnik, J. Maier, *Phys. Chem. Chem. Phys.* **2001**, *3*, 1668–1678.
[55] J. Bisquert, A. Compte, *J. Electroanal. Chem.* **2001**, *499*, 112–120.
[56] J. Bisquert, *J. Phys. Chem. B* **2002**, *106*, 325–333.
[57] J. R. Macdonald, L. R. Evangelista, E. K. Lenzi, G. Barbero, *J. Phys. Chem. C* **2011**, *115*, 7648–7655.
[58] P. A. Santoro, J. L. de Paula, E. K. Lenzi, L. R. Evangelista, *J. Chem. Phys.* **2011**, *135*, 114704.
[59] L. R. Evangelista, E. K. Lenzi, G. Barbero, J. R. Macdonald, *J. Phys.: Condens. Matter* **2011**, *23*, 485–005.
[60] E. K. Lenzi, M. K. Lenzi, F. R. G. B. Silva, G. Gonçalves, R. Rossato, R. S. Zola, L. R. Evangelist, *J. Electroanal. Chem.* **2014**, *712*, 82–88.
[61] A. Sadkowski, *Solid State Ionics* **2005**, *175*, 1987–1996.

Manuscript received: June 26, 2017
Accepted Article published: August 8, 2017
Version of record online: September 27, 2017

