Validation of Impedance-Data and of Impedance-Based Modeling Approach of Electrochemical Cells by Means of Mathematical System Theory

Jonny Dambrowski[12]

[1]*Faculty of Mathematics & Informatics, OTH Regensburg, Universitaets-Str. 31, 93053 Regensburg-Germany*

[2]*Energy Storage Research Department of Deutronic Elektronik GmbH, Deutronic-Str.5, 84166 Adlkofen-Germany*

***Abstract*—In this paper we present a formulation of system requirements for obtaining valid impedance measurement data, and, which is often blended, for the Kramers-Kronig transformation (KKT), in terms of mathematical system theory. This leads in particular to a formal definition of the impedance of an electrochemical system. Additionally, we introduce mathematical foundations for validity tests of impedance data by characterizing the system properties in time and frequency domain. Finally, we give some new characterizations of the passivity property, which is fundamental for impedance based modeling approach, and which is of practical relevancy and widely used in field.**

***Index Terms*—Electrochemical impedance spectroscopy, EIS, Kramers-Kronig transform, Passivity, Convolution system**

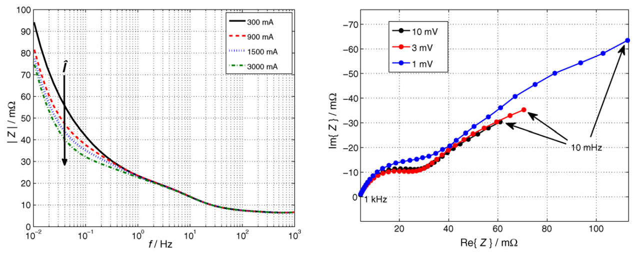
I. Introduction

The electrochemical impedance spectroscopy (EIS) is a prominent technique for characterization [1], [9], modeling [2], [8] and state diagnostic [3], [4], [5], [8] of electrochemical energy storage systems. The object of the EIS is to determine the (complex) impedance $Z(\omega) \in \mathbb{C}$ of an electrochemical system at various frequencies ω. Remember, this function is often visualized by Nyquist- $(Z', -Z'')$ and Bode-plot $|Z|(\omega), \varphi(\omega)$, where Z' is the real part, Z'' the imaginary part, $|Z|$ the modulus and φ the phase of Z. The term *EIS* dissembles twofold: on the one hand a measurement method to extract the impedance itself, on the other hand an analysis tool to extract information about the electrochemical device. In this paper we need both of them. The first one leads to validation of impedance measurement data, whilst the second answers, whether an impedance spectrum (IS) represents in particular a passive system (in the case of valid impedance data).

A. Validation of impedance measurement data

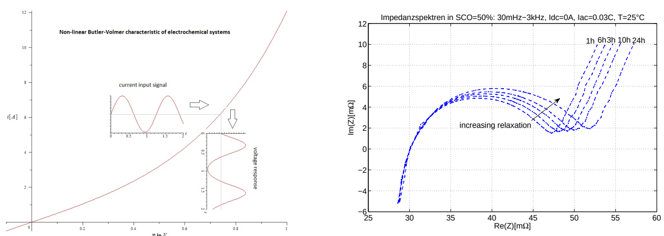
One of the most underestimated problem lies in the validity of measured impedance data. The key ingredient to overcome this is to perform the EIS measurement in such way, that certain a priori technical assumptions are fulfilled. Unfortunately, the design of a valid EIS measurement is non trivial in practise [6], [9], [10]; Fig. 2, 4 shows typical error scources leading to invalid EIS data. For example, an electrochemical device is neither linear (due to Butler-Volmer characteristic or transport phenomena) nor stationary (because the IS is sensitive to short and middle time history). By Fig. 1 it can be seen, that different measurement setup leads to different EIS measurement data. The natural question arising from this is: How can the experimenter decide that measurement data are valid? To ensure the validity and hence the existence of the impedance, several authors in the field mentioned technical assumptions, i.e. linearity, causility, stabilitiy, sometimes finiteness, uniqueness, stationarity and consistency, but a precise definition and how many assumptions are necessary, is still missing. Additionally the terminology is not consistent. For example: in [14], [15] linearity, causality, stability, and in [16], [12], [18] is additionally finitness assumed. However, finitness in the sense of [18], [17] is not same as in [16], [12], because in the last cases *continuity* of $Z(\omega)$ is additionally assumed. Furthermore stability in the sense of [14] is not the same as in [16], [12], [18]; in [17] uniqueness, and in [13] consistency is additionally assumed. In [14], [15] time invariance is concluded from causality, even in [6] the

Manuscript submitted June 05. 2013;



(a) Galvanostatic excitation (b) Pseudo-galvanostatic excitation

Figure 1. EIS measurements at different excitation amplitudes at the same SoC ($I_{\mathrm{DC}} = 0A$) and temperature [10]. Which setup leads to valid EIS measurement data?



(a) Violation of linearity (b) Violation of stationarity

Figure 2. Error scources for valid EIS measurement

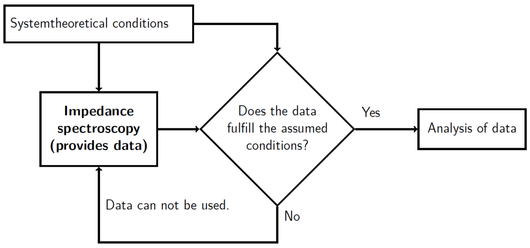


Figure 3. Concept for validating EIS measurement data.

equivalence is claimed. Finally in [10] is claimed that the harmonics are eigenfunctions of linear systems. Unfortunately this not true, as time-invariance is necessary to prove the assertion [23]. Thus, by the above examples, we have to clearify this situation by translating technical assumptions in pure mathematical ones. By characterizing them in time and frequency domain we obtain formal verification methods for merely experimental gained impedance measurement data, see Fig. 3.

A prominent tool for validation of impedance data is the Kramers-Kronig transform (KKT) [12], [18], [14], [13], [16], [20]. Performing KKT requires also assumptions on the impedance-function which are different from the system requirements of EIS. Unfortunately the actual literature situation leads, analogously to the above arguments, to misunderstandings blending the assumptions on EIS and on KKT. The KKT relates real and imaginary part of a complex valued function, that is, the real part can be calculated by KKT from its imaginary part and vice versa. Hence by comparing of calculated real part and measured real part of given impedance measurement data the self-consistency of the EIS data can be tested. In this paper we introduce the KKT by means of the Hilbert transform, extract the assumptions on the complex valued function such that its real and imaginary part are relaeted by KKT and finally we use KKT for characterizing system properties of electrochemical energy storage devices, which can be used for autometed validation testing routines.

B. Validity of impedance based modelling approach

The impedance based modelling approach is widely used for representing electrochemical cells including not only (finite) electric circuits (EC) models [7], [8], [4] but also distributed, possibly an infinity set of ECs, acting as small signal approximation of diffusion elements or constant phase elements (CPE) [2], [12], [14], [13]. All such ECs can be generalized by passivity property of linear systems. In this paper we present a formal validation concept of passive systems in frequency domain, such that it can be used to EIS measurement data; in other words, it can be tested, whether the measured IS represents a passive linear system.

II. MATHEMATICAL SYSTEM THEORY

In this section we review some basic notations of system theory. Beside well known statements, there are also some new results, which will be introduced and proved here.

A system $\mathscr{S}$ is an operator $T : \mathfrak{X} \to \mathfrak{Y}$ between two complex normed (signal) vector spaces $\mathfrak{X}$ and $\mathfrak{Y}$, mapping $x := x(t)$ to $y := y(t) := T\{x(t)\}$. The elements of the signal spaces are often real or complex valued function of time t or frequency ω. In this paper the Lebesgue spaces $L^p := L^p(\mathbb{R}),\ p = 1, 2, \infty$ with p-norm $\|.\|_p$ or subspaces of them are usually considered as signal spaces. Let $a \in \mathbb{R}$. Define translation map $\tau_a : \mathfrak{X} \to \mathfrak{X}$ by $\tau_a x(t) := x(t - a)$.

Definition 1. A system $\mathscr{S}$ is called
(i) real, if $x(t) \in \mathbb{R} \ \Rightarrow\ y(t) := T\{x(t)\} \in \mathbb{R}$.
(ii) linear, if $T\{\lambda x_1(t) + \mu x_2(t)\} = \lambda y_1(t) + \mu y_2(t)$ for all $x_1, x_2 \in \mathfrak{X}$ and all $\lambda, \mu \in \mathbb{R}$.
(iii) time-invariant or stationary, if $T\{\tau_a x(t)\} = \tau_a T\{x(t)\}$ for all $x \in X$ and all $a \in \mathbb{R}$.
(iv) causal, if $\forall_{t\leq t_0} : x_1(t) = x_2(t) \ \Rightarrow\ \forall_{t\leq t_0} : y_1(t) = y_2(t)$.
(v) (bibo-) stable, if there are constants $M, \tilde{M} \in \mathbb{R}$, such that $|x(t)| < M \Rightarrow |y(t)| < \tilde{M}$ for all $t \in \mathbb{R}$.
(vi) L^p-stable, if $x(t) \in L^p \ \Rightarrow\ y(t) \in L^p$ for $p = [1, \infty]$.

A linear and time-invariant system is often called LTI-system. Let $h(t) := T\{\delta(t)\}$ be the impulse response of the Dirac impulse δ (read as limit of regular distribution, and for $p = 1, 2$ use $L^p \hookrightarrow \mathcal{D}'$ in the space of distributions). Then it is well known [19] (Thm.6.33):

$$T\{x(t)\} = (h * x)(t) \ \Leftrightarrow\ T \text{ is bounded and LTI.} \quad (1)$$

whereas $(h*x)(t)$ denotes the convolution product defined by $\int_{\mathbb{R}} x(\tau)h(t - \tau)\mathrm{d}\tau$. A System $\mathscr{S}$ which can be represented by (1) is called convolution system. The Fourier-transform $H(\omega) := \mathcal{F}[h(t)] \overset{(1)}{=} Y(\omega)/X(\omega)$ is called transfer-function of the system $\mathscr{S}$.

A. Stability

A stable system maps a bounded input into a bounded output signal. It is well known that a convolution system $\mathscr{S}$ is (bibo)stable iff its impulse response h is integrable, that is $h(t) \in L^1$. But this ensures the existence of $H(\omega)$ as Fourier transform of $h(t)$ and hence:

Lemma 2. The tranfer function H of a stable convolution system $\mathscr{S}$ is bounded, continuous and $\lim_{|\omega|\to\infty} |H(\omega)| = 0$.

The proof of this lemma is standard and can be found in [19] (Thm.7.5). It provides an imagination of the tranfer function H. In the next section III this result will be related to a certain technical assumption on the electrochenical device yielding valid EIS-data.

Remark 3. Let $\mathscr{S}$ be a LTI system and $h \in L^1$, then the corresponding system operator $T := h*\_ : L^p \to L^p,\ x(t) \mapsto (h * x)(t)$ of $\mathscr{S}$ is bounded for all $p \in [1, \infty]$ and hence $\mathscr{S}$ is a convolution system. In particular: A stable convolution system is also L^p-stable.

B. Real Systems

It seems to be natural that a real system maps real input in to real output signals. But, from a formal point of view there will be some important consequenses.

Lemma 4. Let $\mathscr{S}$ be a convolution system, $h(t)$ the impulse response, and $H(\omega) = F(\omega) + iG(\omega)$ the tranfer function of

$\mathscr{S}$. Then the following are equivalent:
(i) $\mathscr{S}$ is real
(ii) $h(t) \in \mathbb{R}$ for all t's
(iii) $\overline{H(\omega)} = H(-\omega)$ for all ω's (conjugate symmetry)
(iv) ($F(-\omega) = F(\omega)$ and $G(-\omega) = -G(\omega)$ for alle ω's

Proof. $(i) \Leftrightarrow (ii)$: As convolution system $\mathscr{S}$ is represented by $y(t) = T\{x(t)\} = (h * x)(t)$. $(ii) \Leftrightarrow (iii)$ is a trivial consequence of Fourier tranform of real $h(t)$ and last equivalence is abvious. □

Note: (a) the existence of Fourier transform is implicitly assumed, e.g. $h \in L^1$; (b) of course, for the last equivalence none of the assumptions are necessary.

C. Kramers-Kronig Transformation and Causality

In causal systems the response on the output cannot be present befor the input has been excited. We review some well known results in the following

Proposition 5. *(i) A linear system $\mathscr{S}$ is causal, iff*

$$\forall\, x \in \mathfrak{X} \text{ s.t. } x(t < t_0) = 0 \implies y(t < t_0) = 0$$

(ii) A convolution system $\mathscr{S}$ is causal, iff $h(t < 0) = 0$ holds.

In consequence: A convolution system $\mathscr{S}$ is causal, if for all $x \in \mathfrak{X}$ such that $x(t < 0) = 0$ implies $y(t < 0) = 0$.

We start with the origin of the KKT, the Hilbert transform.

Definition 6. The Hilbert-transform (HT) of a real function $X : \mathbb{R} \to \mathbb{R}$ in $\mathfrak{X}$ is the linear operator $\mathscr{H} : \mathfrak{X} \to \mathfrak{X}$, defined by:

$$\mathscr{H}[X](\omega_0) = \frac{1}{\pi} \fint_{\mathbb{R}} \frac{X(\omega)}{\omega - \omega_0} d\omega \tag{2}$$

Thereby $\fint$ denotes the Cauchy principal value.

The following theorem by Titchmarsh provides a connection between the HT of real and imaginary part of a given complex function $H(\omega)$ in the frequency domain and a certain property of the corresponding function $h(t)$ in the time domain.

Theorem 7 (Titchmarsh)**.** *Let $s = \sigma + i\omega \in \mathbb{C}$ and $H(\omega) = F(\omega) + iG(\omega) \in L^2$. Then the following statements are equivalent:*

1) *$H(\omega)$ is the limit of a function $H(\sigma + i\omega)\big|_{\sigma \to 0+} \to H(\omega)$ which is holomorph in the right halfplane and satisfies*
$$\sup_{\sigma > 0} \left\{ \int_{-\infty}^{\infty} |H(\sigma + i\omega)|^2 \mathrm{d}\omega \right\} = K < \infty \tag{3}$$
2) *$F(\omega)$ is related to $G(\omega)$ by the Hilbert transform, i.e. $F(\omega_0) = -\mathscr{H}[G](\omega_0)$*
3) *$G(\omega)$ is related to $F(\omega)$ by the Hilbert transform, i.e. $G(\omega_0) = \mathscr{H}[F](\omega_0)$*
4) *The time domain function $h(t) = \mathcal{F}^{-1}\{H(\omega)\} \in L^2$ satisfies $h(t < 0) = 0$*

Proof. The non trival proof can be found in [21]. □

Remark 8. (i) A time function with $h(t) = 0$ for all $t < 0$ is also called a *causal* signal, and hence Titchmarsh's theorem characerizes the causal signals of finite energy, i.e. $h \in L^2$, in time and frequency domain. (ii) The equivalence of 1) and 4) is just the classical Paley-Wiener theorem [19] (Ch.7).

$$F(\omega_0) = -\frac{1}{\pi} \fint_{\mathbb{R}} \frac{G(\omega)}{\omega - \omega_0} d\omega \overset{\text{HT}}{\underset{\text{pair}}{\longleftrightarrow}} \frac{1}{\pi} \fint_{\mathbb{R}} \frac{F(\omega)}{\omega - \omega_0} d\omega = G(\omega_0)$$

Whenever the complex function $H(\omega) = F(\omega) + iG(\omega)$ fulfills one of conditions in Titchmarsh's theorem, that is the real F and imaginary part G are related by HT, then F, G are called a *Hilbert pair* (HT-pair). It is important to note, that $H(\omega)$ does not need to be a transfer function of a convolution system, but if it is, Titchmarsh provides a characterization of the system property *causality* in the time and frequency domain. Thus:

Corollary 9. Let $\mathscr{S}$ be a convolution system, and $H(\omega) = F(\omega) + iG(\omega) \in L^2$ the tranfer function of $\mathscr{S}$. Then $\mathscr{S}$ is causal iff F and G are a HT-pair.

Proof. By Prop.5 (ii) a convolution system $\mathscr{S}$ is causal, iff $h(t < 0) = 0$. Due $h(t) = \mathcal{F}^{-1}\{H(\omega)\}$ and the Fourier transform is an unitary operator on the Hilbert space L^2 the assumption $H \in L^2$ implies $h \in L^2$. Applying Titchmarsh's theorem the assertion follows. □

This corollary and the following are only slightly new results. However, the consequences are fundamental for the object of this paper, as will be seen in the next section III.

Theorem 10. *Let $H(\omega) = F(\omega) + iG(\omega)$ be a complex valued function in L^2, s.t. real and imaginary part F, G is a conjugate symmetrical Hilbert pair. Then the following relations holds*

$$F(\omega_0) = -\frac{2}{\pi} \fint_0^\infty \frac{\omega G(\omega)}{\omega^2 - \omega_0^2} d\omega \overset{\text{KKT}}{\underset{\text{pair}}{\longleftrightarrow}} \frac{2}{\pi} \fint_0^\infty \frac{\omega_0 F(\omega)}{\omega^2 - \omega_0^2} d\omega = G(\omega_0)$$

which are called Kramers-Kronig relations or (KKT pair).

Proof. Starting from Hilbert pair relations and using the property of real systems satisfying the conjugate symmetry of the transfer function (Lemma 4 (iv)), the assertion follows. A detailed proof will be found in a separate publication. □

Corollary 11. For real (and *not* necessary linear) systems the Kramers-Kronig and the Hilbert pair relations are equivalent.

This give rise to reformulate the theorem of Titchmarsh and the corollary in terms of KKT by using the properties of real systems. It seems to be superfluous to do that, but there are practical reasons justifying this consideration: (1) all physical systems are real systems; (2) the symmetry properties of real systems lead to conditions which are more simpler to check by practical algorithms, and furthermore (3) the results give rise to a partially insight to relevent physical or technical properties of the considered systems in pure formal way.

D. Passivity

Passive systems are largely studied in electrical network theory. Such systems are unable to generate energy. We start with a weaker form of passivity.

Definition 12. A system $\mathscr{S}$ is called weak-passive, if for all $x(t) \in \mathfrak{X}$ and $y(t) := T\{x(t)\} \in \mathfrak{Y}$ the condition holds:

$$\Re\left\{\int_{\mathbb{R}} \overline{x(t)} y(t) \mathrm{d}t\right\} \in \mathbb{R}_0^+$$

Such a system is called passive, if furthermore for all $\tau > -\infty$ the condition holds

$$\Re\left\{\int_{-\infty}^{\tau} \overline{x(t)} y(t) \mathrm{d}t\right\} \in \mathbb{R}_0^+$$

In both cases the existence of the integrals is implicitly assumed. A passive system is obviously also weak-passive, but not vice versa.

Lemma 13. Let $\mathscr{S}$ be a convolution system, and let $h(t) = \mathcal{F}^{-1}\{H(\omega)\}$ the impulse response and $H(\omega)$ the tranfer function. Then $\mathscr{S}$ is weak-passive, iff $\Re\{H(\omega)\} =: F(\omega) \geq 0$ for a.e. (almost everywhere) ω's.

Proof. Let $x \in \mathfrak{X}$. By definition we conclude

$$y(t) = \int_{\mathbb{R}} x(\tau) h(t-\tau) \mathrm{d}t = \frac{1}{\sqrt{2\pi}} \int_{\tau=-\infty}^{+\infty} x(\tau) \int_{\omega=-\infty}^{+\infty} H(\omega) e^{i\omega t} e^{-i\omega\tau} \mathrm{d}\omega \mathrm{d}\tau$$

and hence

$$\int_{\mathbb{R}} \overline{x(t)} y(t) \mathrm{d}t = \frac{1}{\sqrt{2\pi}} \int_{\mathbb{R}} H(\omega) \overline{\int_{\mathbb{R}} x(t) e^{-i\omega t} \mathrm{d}t} \int_{\mathbb{R}} x(\tau) e^{-i\omega\tau} \mathrm{d}\tau \mathrm{d}\omega$$
$$\overset{(*)}{=} \sqrt{2\pi} \int_{\mathbb{R}} H(\omega) |X(\omega)|^2 \mathrm{d}\omega.$$

For $F(\omega) = \Re\{H(\omega)\}$ this implies

$$\Re\left\{\int_{\mathbb{R}} \overline{x(t)} y(t) \mathrm{d}t\right\} = \sqrt{2\pi} \int_{\mathbb{R}} F(\omega) |X(\omega)|^2 \mathrm{d}\omega. \tag{4}$$

If $F \geq 0$ a.e. then obviously (4) ≥ 0. Conversely, if $\mathscr{S}$ is weak-passive, then this is true for all possible $X(\omega)$, in particular for all continuous function X with compact support. Thus, by density argument, $F \geq 0$ a.e. □

Note, if e.g. $h \in L^1 \cap L^2$, then $\mathcal{F}$ and $\mathcal{F}^{-1}$ exist and by Lemma 2 H is continuous, which implies $F(\omega) \geq 0$ for all ω's.

Corollary 14. A real convolution system $\mathscr{S}$ is weak-passive, iff for all real valued $x(t) \in \mathfrak{X}$ the following holds:

$$\int_{\mathbb{R}} x(t) y(t) \mathrm{d}t = \sqrt{2\pi} \int_{\mathbb{R}} F(\omega) |X(\omega)|^2 \mathrm{d}\omega \in \mathbb{R}_0^+ \tag{5}$$

Proof. $\Rightarrow$: Using Lemma 4 it follows, that for real systems the impulse response h is a real valued function, i.e. $h(t) \in \mathbb{R}$. This is by the same Lemma equivalent to the conjugate symmetry of the tranfer function $H = F + iG$, which is equivalent to the fact that F is even and G is odd as function. Apply the analogous argumemts to $x(t) \in \mathbb{R}$. Thus, integrating $H|X|^2$ as in (*) the odd part vanishes and hence (5) is established.
$\Leftarrow$: Let $x \in \mathfrak{X}$. By definition of weak-passivity, all and thus complex valued functions $x(t) \in \mathbb{C}$ has to be take into account. Thus $x = x_1 + ix_2$ whereas $x_1(t), x_2(t) \in \mathbb{R}$ are the real and the imaginary part of $x(t)$. Due $\mathscr{S}$ is real it follows that $y(t) = y_1(t) + iy_2(t)$ with $y_k(t) := T\{x_k(t)\} \in \mathbb{R}$, $k = 1, 2$. Then:

$$\Re\left\{\int_{\mathbb{R}} \overline{x(t)} y(t) \mathrm{d}t\right\} = \int_{\mathbb{R}} x_1(t) y_1(t) \mathrm{d}t + \int_{\mathbb{R}} x_2(t) y_2(t) \mathrm{d}t$$

By assumption (5) the integrals on the right side are separately ≥ 0 and hence also the left side, which proves the assertion. □

Proposition 15. *Let $\mathscr{S}$ be a real convolution system and H the tranfer function of $\mathscr{S}$. Then $\Re\{H(\omega)\} =: F(\omega) \in L^1$.*

Proof. Set $x(t) := \delta(t)$. Then $y(t) = h(t)$ and due $\mathcal{F}[\delta] = 1$ we conclude

$$\int_{\mathbb{R}} x(t) y(t) \mathrm{d}t \overset{\text{Cor.14}}{=} \sqrt{2\pi} \int_{\mathbb{R}} F(\omega) |X(\omega)|^2 \mathrm{d}\omega$$
$$= \sqrt{2\pi} \int_{\mathbb{R}} F(\omega) |1|^2 \mathrm{d}\omega$$
$$\overset{\text{Lemma 13}}{=} \sqrt{2\pi} \int_{\mathbb{R}} |F(\omega)| \mathrm{d}\omega$$

By assumption the left integral exists and is ≥ 0 and thus the right side is equal to $\sqrt{2\pi}\|F\|_1 < \infty$ and also existent. □

Note, this result is valuable, because the Fourier transform H of an element $h \in L^1$ need not be in L^1.

A well known fact is: every passive system is causal [22] (Ch.10.3). But here we state also a reverse direction which leads to a new characterization of passivity.

Theorem 16. *Let $\mathscr{S}$ be a linear system. Then $\mathscr{S}$ is passive, iff it is weak-passive and causal.*

Proof. $\Rightarrow$: Let $x(t) \in \mathfrak{X}$ with $x(t < t_0) = 0$ for a $t_0 \in \mathbb{R}$. We have to show $y(t) := T\{x(t)\} = 0$ for all $t < t_0$. For that choose an arbitrary $x_1(t) \in \mathfrak{X}$ and a $\lambda := \chi + i\gamma \in \mathbb{C}$. Set $x_2 := x_1 + \lambda x$. Then

$$x_1 = x_2 \qquad \text{for } t < t_0 \tag{6}$$

By linearity of T we have $y_2 := T\{x_2\} = T\{x_1 + \lambda x\} = y_1 + \lambda y$ whereas $y_1 := T\{x_1\}$. Use the passivity, then it follows for every $\tau > -\infty$:

$$0 \leq \Re\left\{\int_{-\infty}^{\tau} \overline{x_2(t)} y_2(t) \mathrm{d}t\right\}$$
$$= \Re\left\{\int_{-\infty}^{\tau} \overline{x_1(t)} y_1(t) \mathrm{d}t\right\} + \chi \Re\left\{\int_{-\infty}^{\tau} \overline{x(t)} y_1(t) \mathrm{d}t + \dots\right\}$$

Applying (6) for $-\infty < \tau \leq t_0$, then it remains

$$\Re\left\{\int_{-\infty}^{\tau} \overline{x_1(t)} y_1(t) \mathrm{d}t\right\} + \chi \Re\left\{\int_{-\infty}^{\tau} \overline{x(t)} y(t) \mathrm{d}t\right\} \in \mathbb{R}_0^+$$

for all $\chi \in \mathbb{R}$. This can be only true, if the 2nd integrand vanishes, and hence $x_1(t) y(t) = 0$ for a.e. $t < t_0$. Due x_1 is arbitrary chosen, by ordinary density argument, it suffices to consider those with compact support, it follows $y(t) = 0$ for all $t < t_0$.
$\Leftarrow$: Let $x(t) \in \mathfrak{X}$ and $y := Tx$ as usually. Let $\tau \in \mathbb{R}_0^+$. (Note, this is no restriction of generality.) Define $\tilde{x}(t) := x(t)$ for $t > \tau$ and 0 otherwise. Hence, by causality $\tilde{y}(t) := T\{\tilde{x}(t)\} = y(t)$ for $t > \tau$ and 0 otherwise. Thus

$$\begin{aligned}\Re\left\{\int_{-\infty}^{\tau}\overline{x(t)}y(t)\mathrm{d}t\right\} &= \Re\left\{\int_{-\tau}^{\infty}\overline{\tilde{x}(-t)}\tilde{y}(-t)\mathrm{d}t\right\}\\ &= \Re\left\{\int_{\mathbb{R}}\overline{\tilde{x}(-t)}\tilde{y}(-t)\mathrm{d}t\right\}\in\mathbb{R}_0^+\end{aligned}$$

and also the passivity property is established. □

Now we can formulate the main result of this section:

Theorem 17. *Let $\mathscr{S}$ be a real convolution system with $H(\omega) = F(\omega) + iG(\omega) \in L^2$. Then the following holds: $\mathscr{S}$ is passive, iff $F(\omega) \geq 0$ for a.e. ω's and F, G are a KKT-pair.*

Proof. If $\mathscr{S}$ is passive, then obviously weak-passive and by Thm.16 causal. For the converse direction use Lemma 13 and obtain the property weak-passive from $F \geq 0$ a.e. The causality is deduced by Cor. 9 and Cor. 11. Again applying theorem 16 the assertion of the reverse direction is also proved. □

III. Application to electrochemical Systems

The object of this section is to apply the mathematical approach, developed in the last section II, to: (1) define the classical impedance as well as state sufficient and necessary conditions for its existence; (2) correlate the mathematical system properties to technical assumptions discussed in literature (see Sec.I). Finally we state, which of the results from Sec.II can be used for an automatism of test procedure for validating EIS data.

The main purpose of this paper is to understand the electrochemical device as a *system* in the sense of previous section II. Of course eletrochemical systems are non-linear and also time-variant. However, as usually in science and technology, non-linear systems will be approximated by linear systems, local at a certain working point of the system. This is consistent to EIS measurement, because by this method the energy storage system is operated in small-signal range. In consquense linear system theory is an appropriate tool for validation of impedance measurement data.

A. Definition of the impedance for convolution systems

The impedance is only defined for real convolution systems.

Definition 18. Let $i(t)$ the current input and $u(t)$ the voltage respond signal. Then the *impedance* of a real convolution system (1) is a complex valued function $Z : I \to \mathbb{C}$ whereas $I \subset \mathbb{R}_0^+$ is an interval, defined by

$$Z(\omega) := H(\omega) = \frac{\mathcal{F}[u](\omega)}{\mathcal{F}[i](\omega)} = \frac{U(\omega)}{I(\omega)}. \qquad (7)$$

Thus the classical impedance $Z(\omega)$ is the tranfer function of the considered electrochemical system, if the current is applied as input and voltage response as output signal is measured. Obviously, this definition is not sufficient to ensure the existence of $Z(\omega)$, in particular, if the existence of the Fourier transform of current and voltage signal is implicitly assumed. From Def.18 follows, that the electrochemical system has to be a LTI system. But LTI is not sufficient for convolution representation of the system. Because $y(t) = T\{x(t)\} = (h * x)(t)$ uses the fact, that T must be bounded, or equivalent T must be continuous, this has also to be taken into account.

Proposition 19. *The existence of the impedance $Z(\omega)$ of an electrochemical system $\mathscr{S}$ is guaranteed, if it is a real LTI system, whose impulse response $h(t)$ is in L^1.*

Proof. For $h \in L^1$ set $T_h := h * \_$, which is bounded by Rem.3. Thus $\mathscr{S}$ is a convolution system. By Lemma 2 the tranfer function $Z(\omega)$ is countinuous, bounded for all ω's. □

Corollary 20. For all real (bibo)stable convolution systems the existence of the impedance is guaranteed.

In various practical situations these conditions are applicable. Note, in small-signal modeling of electrochemical energy storage systems there are also unbounded diffusion elements [12] (Fig.2.1.13(a)), which implies, that above statements can only be sufficient but not necessary conditions for the existence of $Z(\omega)$. Note, the Def.18 includes the general cases also.

B. Discussion of mathematical results in technical context

1) Real systems: The impedance function $Z(\omega)$ is defined on an intervall containing in $\mathbb{R}_0^+$. The mathematical meaning comes from the assumption of *real* system in Def.18. By Lemma 4 (iv) the real part Z' of the tranfer function $Z = Z' + iZ''$ is even, and the imginary part Z'' is odd in ω. Thus Z is unique determined by $Z_{|\mathbb{R}_0^+}$. This is congruent to technical assumption that there is no negative frequency.

Remark 21. Let $\mathscr{S}$ be a real convolution system, and assume the existence of the Fourier transform $H(\omega) = F(\omega) + iG(\omega)$ of the impulse response $h(t)$. Then $G(0) = 0$ and if e.g. $h \in L^1$ then additionally $F(0) < \infty$.

Note, this formal conclusion reflects also a common small-signal model of diffusion process widely used for electrochemical cells, more exactly, the Warburg diffusion element of finite length with unbounded reservoir [12] (Fig. 2.1.13 (b)).

2) Real systems and Kramers-Kronig transform: For real systems HT and KKT are equivalent, as seen in Cor. 11. Thus, Titchmarsh's theorem and the Cor. 9 can be reformulated for real systems and hence in terms of KKT-pair instaed of HT-pair. The advantages of KKT are: (1) to evaluate an integral from 0 to ∞ is easier then from $-\infty$ to $+\infty$; note, practical EIS measurements will be done on discrete ω's and of course finite frequency range (for batteries 1mHz-10kHz), but calculating, e.g. imaginary part at ω_0 from the real part of Z needs an integration over the whole frequency range, i.e. $\omega = 0$ to $\omega = +\infty$. Thus the problem for appropriate numerical extrapolation, which is non trivial, is only the half in the case of KKT. (2) Technically, for $\omega \to \infty$ we expect that the impedance converges to the real ohmic resistance of the electrochemical system, i.e. $Z(\omega \to \infty) = Z_\infty \in \mathbb{R}^+$. Thus, the tranfere function Z does not converge to 0. Thus, Z can not be in L^2 and hence assumption on KKT fails. But subtracting F_∞ from real part of Z preserves the L^2 property. This is implicitly done without changing the notation of the tranfer function $Z(\omega) = Z'(\omega) + iZ''(\omega) \in L^2$. (3) Under

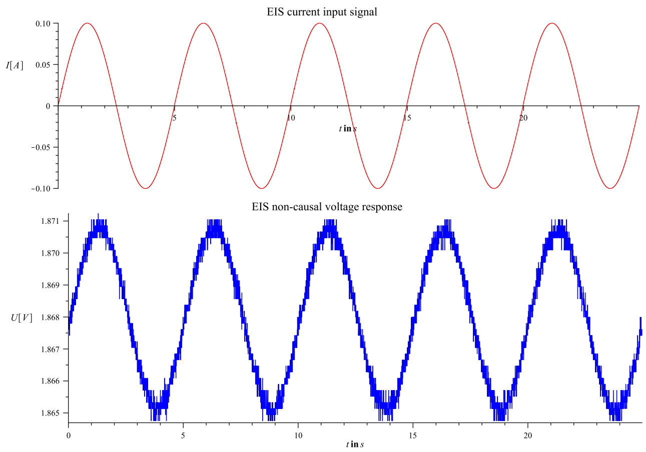


Figure 4. Violation of causality during EIS measurement from noisy disturbance at a lithium-ion cell.

the assumption of differentiability of Z', Z'' the poles $\pm\omega_0$ in the KKT can be removed, and thus the KKT relations in Thm. 10 are usually integrals. In [18] this was used for numerical implementation of KKT.

3) Causality: All of the authors known publications in the field of electrochemical energy storage systems assume causality, e.g. "the response of the system is due only to the perturbation applied, and does not contain significant contributions from spurious source" in [16]. The last one means, inspite of the fact that every technical realizable system must be causal, the measurement environment may be generate noises on the output, which are uncaused by input excitation, as shown in Fig. 4. Causality is thus a valuable requirement for valide impedance data. In consequence, the existence of the impedance does not imply its validity. What can not be found in the literature is a second (potential) application of causality, arising from *automatic countinuity theory* and states [24]:

Theorem 22. *A causal LTI operator $T : \mathfrak{X} \to \mathfrak{Y}$ is bounded and hence it defines a convolution system in the sense of (1).*

Thus, concerning system assumptions for the existence of Z, as in (1), *bounded* can be replaced in principle by *causal*.

Proposition 23. *The existence of the impedance $Z(\omega)$ of an electrochemical system $\mathscr{S}$ is guaranteed, if it is real, LTI, causal and $Z \in L^2$.*

Unfortunately, to apply Titchmarsh's theorem the system already must be a convolution system. This assumption is actual necessary and used in Prop. 5 (ii) for the equivalence: $\mathscr{S}$ is causal iff $h(t < 0) = 0$. For real systems Cor. 9 can be stated in terms of KKT:

Theorem 24 (Causality)**.** *Let $\mathscr{S}$ be a real convolution system and $Z = Z' + iZ'' \in L^2$. Then $\mathscr{S}$ is causal iff Z' and Z'' are a KKT-pair.*

Thus, if KKT fails on EIS data of a real convolution system, then $\mathscr{S}$ is non causal or of infinite energy. If the convolution property of a considered electrochemical system is not known, and (1) Z', Z'' are KKT-pair, there is nothing to conclude; (2) for Z', Z'' the KKT fails, then the EIS data do not represent a valid impedance.

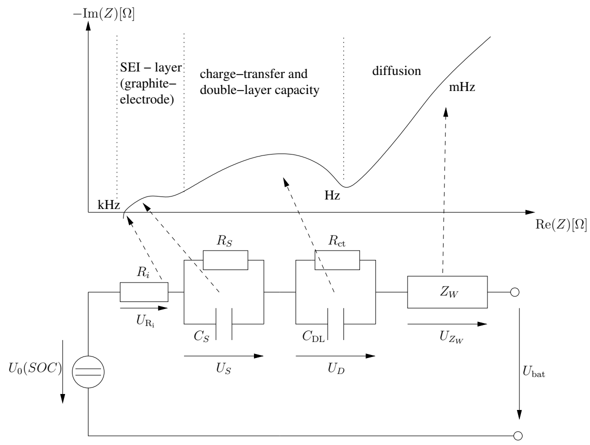


Figure 5. Schematic view of an impedance-spectrum (Nyquist plot) of a lithium-ion battery on the top, and the relations to electric-circuit (EC) model at the bottom, consisting an SoC dependent ideal voltage scource $U_0(SOC)$, the ohmic resistance R_i, two parallel RC-devices, the first R_sC_s comprises the passivation property of the graphite-electrode by the solid-electrolyte-interface (SEI), the second the charge-transfer R_{ct} and the double-layer capacity C_{DL}, and finally the Warburg element Z_W for diffusion processes.

For derivation of the KKT relations, the system need neither to be linear nor time invariant. This fact is fully in contrast to publication situation in electrochemical energy storage systems [18], [16], [12] (Ch.4.4.5), [14] (Ch.22), [20]. A conrete non-linear system that fulfill KKT relations is given in [11]. By Titchmarsh's theorem the ability to fulfill the KKT relations is a question on a complex valued function $H(\omega)$ on the reals, and hence a pure mathematical question. H need not to be a tranfer function of a convolution system. Thus the assumption on KKT can be states as follows:

Proposition 25. *Let $H(\omega) := F(\omega) + iG(\omega) \in L^2$ and $\overline{H(\omega)} = H(-\omega)$. Then F, G are a KKT - pair, iff $h(t) := \mathcal{F}^{-1}\{H(\omega)\}$ is a causal signal, i.e. $h(t < 0) = 0$.*

C. Passivity

A common method for modeling electrochemical energy storage systems is by lumped (or distributed) passive (constant) electrical circuit (EC) elements, e.g. resistors, capacitators and inductors (or constant phase, Warburg elements) [2], [3], [4]. Fig. 5 illustrates such EC based modeling approach. As electrochemical devices are non-linear systems such EC-models can only be valid if the system is operated in the small-signal range. Thus EIS is a valuable tool for model building of electrochemical cells by EC-models. Indeed, at a given working point, the electrical, electrochemical and chemical processes wihtin energy storage system can be approximated by ECs and thus it is possible to simulate the dynamic behavior in terms of the voltage response by stimulating current input signal. The object of this section is to decide on experimental EIS data, whether the convolution system is passive and hence the impedance spectrum can be modeled by (possible infinite) ECs.

Theorem 26. *Suppose EIS measurement data are given $Z(\omega) = Z'(\omega) + iZ''(\omega) \in L^2$, s.t. they represent a real* *convolution system $\mathscr{S}$. Then $\mathscr{S}$ is passive iff $Z'(\omega) \geq 0$ for a.e. ω's and Z', Z'' are a KKT-pair.*

Note: (1) This theorem has the potential for an automatic test procedure by applying KKT and check $Z' \geq 0$ on the concrete given EIS data. (2) Suppose the test procedure says the system is passive. Then by Thm. 16 the system is causal and hence the measured EIS data are valid. (3) A general passive convolution system is not the same as a system descibed by a finite set of ordinary linear differential equations with constant coefficients. (4) Of course, a numerical implementation of distributed elements considers only a finite set of ECs upto an error tolerance smaller then a given $\varepsilon > 0$, but our object is to extract condition in most of generality.

IV. Conclusion and Outlook

The object of this paper was to extract conditons for validating measured EIS data by using mathematical system theory. To solve such type of problems, the system-theoretical point of view of electrochemical devices was necessary and also the role of EIS in this consideration. The next step was to define impedance of an electrochemical system, and find necessary and sufficient conditions for the existence. Inspite of the fact, that the idea of system description of electrochemical devices goes back to 1980s, a rigorous treatment is unfortunately missing til this day. In literature inconsistencies can be found regarding the precise number of assumptions, the terminology used and the definitions adopted when considering the validation of EIS data and in addition the conditions for the existence of KKT-relations. We overcome this inconsistencies by using the language of mathematical system theory. This notion leads in canonical way to a separation of the existence and of the validity property of the impedance, and furthermore of existence of KKT-relations. By characterizing several system properties in time and frequency domain we found also new mathematical results. This paper is only a starting point for a rigorous mathematical treatment of electrochemical devices. There are still many open questions for future research activity.

Acknowledgment

I want to speak out my gratitude to my student Boris Dotz.

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