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Application of the Kramers Kronig relations to locally resolved impedance data of polymer electrolyte fuel cells

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ABSTRACT

The Kramers Kronig (KK) relations are applied to locally resolved impedance data as obtained from a simple, analytic ‘down the channel’ impedance model of a polymer electrolyte fuel cell (PEFC) air cathode. It is shown that the transport and superposition of oxygen concentration oscillations in gas flow direction can lead to non-causal local cell impedance spectra, while the calculated local cell admittance always fulfills the KK relations. This is explained by the homogeneous distribution of the ac perturbation voltage over the electrode area due to the high electrical conductivity of the bipolar plates. Hence, the KK relations must be applied to the locally resolved admittance data of PEFCs to check if the measured spectra can be a physical response of the system.

1. Introduction

The Kramers Kronig (KK) relations are a widely used tool in natural sciences [1]. The KK relations state, that the imaginary part and the real part of frequency response functions are connected by a special form of the Hilbert Transform, if the underlying response function is linear, causal, stable and finite at all frequencies [2]. It was first applied to electrochemical systems by Tyagay and Kolbasov [3] and since then has been used in electrochemical impedance spectroscopy (EIS) to verify experimental data [2,4]. However, one has to be careful if the KK relations are applied to localized electrochemical impedance spectroscopy (LEIS) data. In LEIS measurements, the applied perturbation signal generally results in a modulation of the cell polarization $\Delta\eta(\omega)$ over the entire electrode area. The local ac current response $\Delta j(x,\omega)$ is measured. The local cell impedance is per definition the ratio $Z_{\mathrm{loc}}(x,\omega) = \Delta\eta(\omega)/\Delta j(x,\omega)$.

The first application of LEIS to PEFCs was reported by Brett et al. [5]. At higher cell polarization the local spectra of a single channel H_2/air PEFC showed a negative value for the low frequency real axis intercept near the air outlet. They showed the correlation of the negative local polarization resistance and the slope of the respective local i/E curve. The work of Schneider et al. [6,7] has demonstrated that the formation and the convective transport of ac oxygen concentration oscillations along the gas channels of H_2/air PEFCs during LEIS measurements can result in the appearance of a low frequency capacitive loop in both integral and local spectra. The loop appears at lower air flow rate and it is indicative for a mass transport limitation along the gas channels [7,8]. In the local spectra either a positive or a negative polarization resistance is observed depending on the air flow rate and the rate of oxygen depletion along the gas flow channels [6–8]. This work has clearly demonstrated that the local ‘impedance’ response of a PEFC in flow configuration is not only related to the local electrical cell perturbation, but also to the ac concentration polarization, which is caused locally by the build-up of oxygen concentration oscillations due to ac current in electrode areas upstream the flow field. Recently, we have demonstrated this effect more generally, as a result of fuel, oxidant or water depletion in PEFCs [8]. In all cases negative polarization resistance values are observed in the local spectra at lower reactant flow rates.

Such negative polarization resistances have also been reported in other fields of electrochemistry. They are most commonly related to systems, which form a passivation layer, and hence, can exhibit a decreasing current despite an increasing overpotential. In a discussion, based on the work of Keddam et al. [9], Cahan and Chen [10] noticed that the impedance spectra of such systems do not fulfill the KK relations. Based on their argument, that such data should not be interpreted as impedance, a discussion began, in which Gabrielli and Keddam [11] showed that the admittance is KK consistent, but the logarithmic form, as used in [10] is inconsistent. They also justified the choice to show the data from [9] in impedance representation as it is an almost general use to plot ac-

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Nomenclature

b	Tafel slope (V)
c	local oxygen concentration (mol/m^3)
c_0	inlet oxygen concentration (mol/m^3)
j	local current density (A/m^2)
j_{mean}	mean current density over the whole cell (A/cm^2)
j_{n}	mean current density in segment n (A/cm^2)
j_0	exchange current density (A/m^2)
k	$-\ln(1-1/\lambda)$ (–)
l	channel length (m)
t	time (s)
t_{c}	channel depth (m)
v	channel flow velocity (m/s)
x	position along the channel (m)
Y_{loc}	local admittance (S/cm^2)
Y_{int}	integral cell admittance over the whole cell (S/cm^2)
Y_{n}	mean admittance in segment n (S/cm^2)
Y_{mn}	admittance matrix element (S/cm^2)
Z_{loc}	local impedance (Ω cm^2)
Z_{n}	mean impedance in segment n (Ω cm^2)
Z_{mn}	impedance matrix element (Ω cm^2)
η	overpotential defined as the difference between the reversible potential with inlet concentration and the cell voltage (V)
η_{n}	overpotential in segment n (A/cm^2)
λ	oxygen stoichiometry (–)
ξ	reduced length (x/l) (–)
ω	angular frequency (l/s)
ω_{c}	$2v/l$ (1/s)
F	Faraday constant (96,485 As/mol)

data in impedance form [11]. All this discussion was based on the Nyquist criterion for stability, which is not fulfilled for systems exhibiting passivation under galvanostatic control.

A comprehensive study on the application of the KK relations on unstable systems was provided recently by Sadkowski et al. [12]. They illustrated this problem using both a Voigt circuit [13] with a negative resistance and metal electrodes in a transpassive state, one of which they already investigated in an earlier work [14]. The authors concluded that also the EIS spectra of such electrodes recorded in stable state are KK transformable, provided that proper immittance form is chosen for the KK transformation [14]. In this work we demonstrate that similar considerations hold for the applicability of the KK relations to LEIS data as obtained in PEFCs.

2. Application of the KK relations to PEFC LEIS data

In this work the Fourier transform is defined according to (1).

$$FT\{f(t)\}(\omega) = \int (f(t)\cdot \exp(-i\cdot\omega\cdot t))\,dt \tag{1}$$

This leads to Kramers–Kronig relations of the form (2).

$$\mathrm{Im}[H(\omega_0)] = \frac{2\omega_0}{\pi}\int_0^{\infty}\frac{\mathrm{Re}[H(\omega)]}{\omega^2-\omega_0^2}\,\mathrm{d}\omega \tag{2a}$$

$$\mathrm{Re}[H(\omega_0)] = -\frac{2}{\pi}\int_0^{\infty}\frac{\omega\mathrm{Im}[H(\omega)]}{\omega^2-\omega_0^2}\,\mathrm{d}\omega + \mathrm{const.} \tag{2b}$$

The KK relations are fulfilled, if the response function $H(\omega)$, which is defined over the complex numbers, is holomorphic in the lower half plane, i.e. if any pole has a positive imaginary part.

The KK relations are applied here to local immittance data as obtained from a simple, one-dimensional, 'down the channel' impedance model. The model can be regarded as the 'ac analogue' to that of Kulikovsky et al. [15,16]. It takes into account only the experimentally proven key phenomenon for the appearance of negative polarization resistance values in the local spectra, namely the oxygen mass transport limitation in flow direction [6–8]. Here, the oxygen reduction reaction is assumed to obey a Tafel-law and to be linearly dependent on the oxygen concentration $c(x)$. Ohmic resistances, anode overpotential, and diffusion losses are neglected. The governing equations are given in equation system (3).

$$j(x) = j_0\cdot\frac{c(x)}{c_0}\cdot\exp\left(\frac{\eta}{b}\right) \tag{3a}$$

$$\frac{dc(x)}{dt} = -\frac{j(x)}{4\cdot F\cdot t_{\mathrm{c}}} - v\frac{dc(x)}{dx} \tag{3b}$$

The flow velocity v is assumed to be constant along the flow field, in order to get an analytical solution. In the steady state calculation the time derivatives are set to zero. Inlet conditions are defined through the given inlet concentration $c(0) = c_0$. Using these constraints the steady state solution for the current is given by Eq. (4), with $k = -\ln(1-1/\lambda)$ and $\xi = x/l$, where l represents the channel length, λ the stoichiometry, and j_{mean} the mean current density.

$$j(\xi) = j_{\mathrm{mean}}\cdot\lambda\cdot\exp(-k\cdot\xi)\cdot k \tag{4}$$

The result is identical to the one of Kulikovsky [15,16] for a linear dependence of the current density on oxygen concentration. The stoichiometry λ is connected to the velocity v by:

$$v = \frac{\lambda\cdot j_{\mathrm{mean}}\cdot l}{4\cdot F\cdot t_{\mathrm{c}}\cdot c_0} \tag{5}$$

The slope of the polarization curve in constant flow mode at the operating point is calculated using the following equation:

$$\frac{dj(\xi)}{d\eta} = \frac{j_{\mathrm{mean}}}{b}\cdot\lambda\cdot exp(-k\cdot\xi)\cdot k\cdot(1-\xi\cdot k) \tag{6}$$

In Eq. (6), the slope of the local j/η curve changes sign at $\xi_{\mathrm{t}} = 1/k$. The steady state current distribution is a function of λ only. The local immittance is calculated from Eq. (7), which result from linearization of Eq. (3) and the fact that a time derivative can be expressed as the product of the Fourier transformed function and $i\omega$.

$$\delta j(x,\omega) = \frac{j(x)}{b}\delta\eta + \frac{j(x)}{c(x)}\delta c(x,\omega) \tag{7a}$$

$$\frac{d}{dx}\delta c(x,\omega) = -\frac{\delta j(x,\omega)}{4\cdot F\cdot t_{\mathrm{c}}\cdot v} - i\cdot\frac{\omega}{v}\cdot\delta c(x,\omega),\quad \delta c(0,\omega) = 0 \tag{7b}$$

A serial Ohmic resistance cannot be included into the model without sacrificing the analytic solution. Since no serial Ohmic resistance is included, inclusion of the double layer capacity would lead to a divergence of the admittance for high frequencies. This divergence disturbs the Kramers Kronig relations, as they are based on integration over the whole positive real frequency axis. Consequently, the model does not account for the electrochemical double layer capacity. Note that inclusion of the double layer capacity would only add an additional term to the current, but would neither affect the faradaic current nor the ac-concentration profile. In any case the double layer capacity is of minor importance in the frequency range relevant for the 'down the channel'