



Reconstruction of relaxation time distribution from linear electrochemical impedance spectroscopy



Yanxiang Zhang^{a, b, *}, Yu Chen^b, Mufu Yan^a, Fanglin Chen^{b, *}

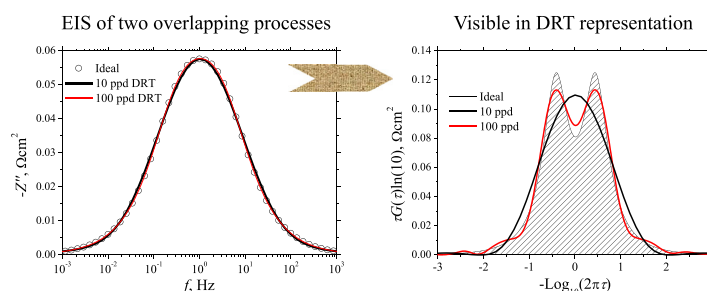
^a National Key Laboratory for Precision Hot Processing of Metals, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, Heilongjiang 150001, China

^b Department of Mechanical Engineering, University of South Carolina, 300 Main Street, Columbia, SC 29208, USA

HIGHLIGHTS

- A method for DRT reconstruction from EIS is presented unambiguously.
- Quality of DRT reconstruction is sensitive to points per frequency decade.
- Resolution of DRT is studied to distinguish overlapping processes of SOFCs.
- This method exhibits high robustness to resist noise embedded in EIS data.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 24 September 2014

Received in revised form

27 November 2014

Accepted 18 February 2015

Available online 26 February 2015

Keywords:

Relaxation time distribution (DRT)

Impedance

Solid oxide fuel cell (SOFC)

Electrochemical process

Resolution

Robustness

ABSTRACT

Linear electrochemical impedance spectroscopy (EIS), and in particular its representation of distribution of relaxation time (DRT), enables the identification of the number of processes and their nature involved in electrochemical cells. With the advantage of high frequency resolution, DRT has recently drawn increasing attention for applications in solid oxide fuel cells (SOFCs). However, the method of DRT reconstruction is not yet presented clearly in terms of what mathematical treatments and theoretical assumptions have been made. Here we present unambiguously a method to reconstruct DRT function of impedance based on Tikhonov regularization. By using the synthetic impedances and analytic DRT functions of RQ element, generalized finite length Warburg element, and Gerischer element with physical quantities representative to those of SOFC processes, we show that the quality of DRT reconstruction is sensitive to the sampling points per decade (*ppd*) of frequency from the impedance measurement. The robustness of the DRT reconstruction to resist noise imbedded in impedance data and numerical calculations can be accomplished by optimizing the weighting factor λ according to well defined criterion.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

Electrochemical impedance spectroscopy (EIS) is widely used to

understand and resolve the reaction kinetics at the functional interfacial layer and bulk of electrochemical cells, such as solid oxide fuel cells (SOFCs), gas separation membranes and lithium batteries over a wide frequency range. Impedance of an electrochemical cell is a complex resistance encountered when an AC current perturbation, $\hat{i}e^{j\omega t}$ flows through the cell, and an AC voltage perturbation, \hat{u} is generated in response [1]. The causality (analytic

* Corresponding authors. Department of Mechanical Engineering, University of South Carolina, 300 Main Street, Columbia, SC 29208, USA.

E-mail addresses: hitzhang@hit.edu.cn (Y. Zhang), chenfa@cec.sc.edu (F. Chen).

relation) between \hat{u} and $\hat{i}e^{j\omega t}$ permits the Taylor expansion of \hat{u} with respect to $\hat{i}e^{j\omega t}$ [2],

$$\hat{u} = \sum_{k=1}^{\infty} \frac{\hat{u}^{(k)}}{k!} (\hat{i}e^{j\omega t})^k = \sum_{k=1}^{\infty} \hat{v}_k e^{jk\omega t} \quad (1)$$

where $\hat{u}^{(k)}$ is the k th derivative, and $\hat{v}_k = \hat{u}^{(k)} \hat{i}^k / k!$ is the k th harmonic of \hat{u} , which can be expressed as a power series [3],

$$\hat{v}_k = \sum_{r=1}^{\infty} \left(\hat{i}/\hat{i}^*\right)^{k+2r-2} \hat{\eta}_{k,k+2r-2} \quad (2)$$

where \hat{i}^* is a real current constant that characterizes the nonlinearity of the cell; the harmonic terms $\hat{\eta}_{k,k+2r-2}$ are univariate functions of angular frequency ω . Therefore, the impedance related to the m th order contribution to the k th harmonic \hat{v}_k through \hat{i}^* is given by Refs. [3],

$$Z_{k,m}(\omega) = \hat{\eta}_{k,m} / \hat{i}^* \quad (3)$$

One can resolve the impedance only when Eq. (1) converges, yielding $|\hat{i}| < \lim_{k \rightarrow \infty} |(k+1)\hat{u}^{(k)} / \hat{u}^{(k+1)}|$. When the module of \hat{i} is sufficiently small, only the first-order Taylor expansion of \hat{u} is pronounced and the higher harmonics in Eq. (1) are negligible. In addition, the harmonic terms $\hat{\eta}_{k,m}$ for $m > 1$ in Eq. (2) are also negligible. Consequently, the impedance becomes [2,3],

$$Z(\omega) = \hat{\eta}_{1,1} / \hat{i}^* = \hat{v}_1 / \hat{i} \quad (4)$$

This treatment is known as linearization. The validity can be tested by Kramers–Kronig transform, which demonstrates that the real component Z' and imaginary component Z'' are interconvertible when $Z(\omega)$ is analytic in the upper half-plane of ω (indicating causal and stable), and $|\omega Z(\omega) - \omega Z'(\infty)|$ approaches zero as ω approaches infinity (indicating no inductive effect at high frequency) [4]. Nowadays, linearization has become the industry standard in EIS instrumentations, and higher harmonics are filtered out during EIS measurements [5].

A well established method for analyzing electrochemical processes is to fit linearized mechanism models with linear EIS measurements [6]. For example, in the application in SOFCs, the following linearized models are oft-used to characterize the cathodic and anodic processes [7]:

1) RQ element model: It consists of a parallel connection of polarization resistor, R , and a constant phase element, $1/(j\omega)^n Q$. The impedance is accordingly given by [6],

$$Z(\omega) = \frac{R}{1 + (j\omega)^n RQ} \quad (5)$$

where n is a dimensionless constant in the range from 0 to 1, showing non-ideal double-layer capacitor behavior of the constant phase element; Q is the pre-factor of the constant phase element, with unit of $\text{sec}^n/[R]$. For $n = 1$, RQ element degrades into RC element, showing ideal double-layer capacitor behavior. The reciprocal of angular frequency corresponding to the maximum $-Z''$ is known as the characteristic time, given by $\sqrt[n]{RQ}$. This model is usually used to characterize the impedance response of surface exchange (or charge transfer reactions) near electrode/electrolyte interface [8–17].

2) Generalized finite length Warburg (G-FLW) element model: It describes the impedance imparted by mass transport, given by [9],

$$Z(\omega) = R_w \frac{\tanh[(j\omega\tau_w)^{n_w}]}{(j\omega\tau_w)^{n_w}} \quad (6)$$

where R_w is the polarization resistance of mass transport; n_w is a constant approaching but not higher than 0.5; τ_w is defined as l^2/D_{eff} where l is the finite length and D_{eff} is the effective diffusivity. This model is usually used to characterize the impedance response of gas diffusion within porous electrodes [9–12,17,18].

3) Gerischer element model: It describes the coupling of surface exchange of oxygen and transport of oxygen ions within porous mixed ionic electronic conductor cathodes, where the resistance of electron transport is negligible. The impedance is given by [19],

$$Z(\omega) = \frac{R_c}{\sqrt{1 + j\omega\tau_c}} \quad (7)$$

where R_c is the polarization resistance of the coupling process; τ_c is the characteristic time. R_c and τ_c depend on surface exchange coefficient and oxygen diffusion coefficient of the cathode material, electrode microstructure, and the operating conditions. This model is usually used to characterize the impedance response of oxygen surface exchange kinetics and O^{2-} diffusion in the bulk of (La,Sr)(Co,Fe) O_3 (LSCF) based cathode [9–12,17].

Depending on SOFC configuration, fuel cell materials, and working conditions, the mechanism model describing the entire picture of electrochemical processes could be a complicated combination of the above element models or their derivatives [6]. However, it is very challenging to identify the optimal model from many analogs, partially due to the following reasons: 1) Many models fit the EIS data equally well in terms of Nyquist, Real-and-Imaginary and Bode representations [3]; 2) The impedance responses of electrochemical processes might overlap significantly in frequency domain. In other words, the impedance at an angular frequency ω contains remarkable contributions from any process with a characteristic time above and below ω^{-1} [20]. Thus, it is of great importance to develop new analysis method with improved frequency resolution.

By an extension of the Debye relaxation relation with a single relaxation time, the concept of distribution of relaxation time (DRT) with a high frequency resolution (which will be shown in what follows) was proposed and regarded as the origin of constant phase elements [1]. By assuming a linear relaxation process, the principle of superposition allows the impedance to be generalized [1],

$$Z(\omega) - Z'(\infty) = \int_0^{\infty} \frac{G(\tau)}{1 + j\omega\tau} d\tau \quad (8)$$

where $G(\tau)$ is defined as the DRT of impedance Z ; τ is the relaxation time; $Z'(\infty)$ is the limitation of the real part of Z as angular frequency ω approaches infinity. Consequently, the impedance can be represented as series connection of infinite number of circuits made of a parallel connection of polarization resistor $G(\tau)d\tau$ and a capacitor $\tau/G(\tau)d\tau$, such that $G(\tau)d\tau$ specifies the fraction of the total polarization resistance associated with relaxation times in the interval between τ and $\tau + d\tau$. It follows that $G(\tau)$ is subject to,

$$\int_0^{\infty} G(\tau) d\tau = Z'(0) - Z'(\infty) \quad (9)$$

where $Z'(0) - Z'(\infty)$ denotes the total polarization resistance; $Z'(0)$ is the limitation of the real part of impedance Z as ω approaches zero. The unique analytic solution of DRT for a generic impedance spectroscopy was first derived by Fuoss and Kirkwood [21],

Download English Version:

<https://daneshyari.com/en/article/1292845>

Download Persian Version:

<https://daneshyari.com/article/1292845>

[Daneshyari.com](https://daneshyari.com)