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Short communication

A high-precision approach to reconstruct distribution of relaxation times from electrochemical impedance spectroscopy

Yanxiang Zhang [a, *], Yu Chen [b], Mei Li [c], Mufu Yan [a], Meng Ni [d], Changrong Xia [c, **]

[a] National Key Laboratory for Precision Hot Processing of Metals, School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China
[b] Center for Innovative Fuel Cell and Battery Technologies, School of Materials Science and Engineering, Georgia Institute of Technology, GA 30332-0245, USA
[c] CAS Key Laboratory of Materials for Energy Conversion, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei 230026, China
[d] Building Energy Research Group, Department of Building and Real Estate, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China

HIGHLIGHTS

- This approach is free of adjusting parameter.
- The DRT does not contain pseudo peaks.
- Discontinuities in DRT can be captured.
- Well-established algorithm is available.

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ABSTRACT

A new Tikhonov regularization approach without adjusting parameters is proposed for reconstructing distribution of relaxation time (DRT). It is capable of eliminating the pseudo peaks and capturing discontinuities in the DRT, making it feasible to resolve the number and the nature of electrochemical processes without making assumptions.

1. Introduction

Electrochemical impedance spectroscopy (EIS) is the most frequently used methodology to study the electrolyte/electrode behaviours in electrochemical devices, for instance fuel cells, electrolyzers, batteries, and capacitors [1]. The electrochemical processes embedded in the EIS are usually characterized using some well-known representations of the EIS, for example the Nyquist plot, the imaginary impedance *vs.* frequency plot, etc. The number and nature of the electrochemical processes are identified by examining the number of arcs in the EIS curve and by curve-fitting with an equivalent circuit model, respectively [2]. However, this approach could underestimate the number of processes and oversimplify their electrochemical nature, as EIS curve is an integration of the responses of all the elementary processes and some elementary processes may not be shown in the curve [3]. In recent years, distribution of relaxation times (DRT) has shown remarkable capability to differentiate the electrochemical processes and thus is a powerful tool for analyzing electrochemical power sources. The DRT is defined implicitly by Refs. [4,5],

* Corresponding author.
** Corresponding author.
E-mail addresses: hitzhang@hit.edu.cn (Y. Zhang), xiacr@ustc.edu.cn (C. Xia).

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$$-Z''(\omega) = \int_0^\infty \frac{\omega F(\tau)/\ln(10)}{1+(\omega\tau)^2} d\tau \quad (1)$$

where $F(\tau)$ is the DRT function at the relaxation time τ, and $Z''(\omega)$ denotes the imaginary part of the impedance at the angular frequency ω. Characterized by individual peaks in the plot of $F(\tau)$ versus $\log_{10}(\tau)$, the electrochemical processes can be differentiated from each other to the most extent. The integral area of a specific peak corresponds to the resistance of a specific elementary process. Although conceptually simple, the DRT function has to be reconstructed numerically from the EIS data by solving Eq. (1), which is very challenging. The Tikhonov regularization is commonly used for reconstructing the DRT function [4–11]. By optimizing the regularization factor, the DRT function can be reconstructed properly. However, pseudo peaks are sometimes created in the reconstructed DRT plot, limiting the accuracy of this method. Very recently, Ciucci et al. proposed a Bayesian approach by considering the regularization factor as a hyper prior function of roughness of the reconstructed DRT function [12]. It was found that the reconstructed DRT functions were identical to the ideally analytical DRT solutions with proper parameters in the hyper prior function. However, as adjusting parameters are used, the accuracy of the results could be uncertain if the parameters were not properly set.

In this work, we propose a new Tikhonov regularization approach without adjusting parameters. The optimal DRT solution without pseudo peaks and the distribution of regularization factor can be obtained simultaneously by using a well-established algorithm. Using this approach, the Gerischer type DRT can be resolved clearly from the impedance of a symmetric $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF)/$Ce_{0.9}Sm_{0.1}O_{1.95}$ (SDC)/LSCF solid oxide cell, and the cathodic and anodic processes for a Ni−$Zr_{0.92}Y_{0.08}O_{1.96}$ (YSZ)/YSZ/$(La_{0.80}Sr_{0.20})_{0.95}MnO_{3-x}$ (LSM)-YSZ solid oxide cell are well separated. Finally, we propose a generic Tikhonov approach with higher orders distributions of regularization factor. The present Tikhonov approach is the first-order approximation of the generic Tikhonov approach.

2. Theory

Theoretically, the DRT function $F(\tau)$ can be reconstructed by Eq. (1) only if the impedance is linear, causal, and stable [13]. In other words, the real part $Z'(\omega)$ and the imaginary part $Z''(\omega)$ should yield Kramers-Kronig relations, which can be validated using ZSimpWin software, or the computer programs developed by B.A. Boukamp or Ivers-Tiffée group. The reconstruction is to calculate the discrete DRT set $\{F(\tau_n)|n = 1, 2, \ldots, N\}$ using the discrete impedance set $\{Z''(\omega_n)|n = 1, 2, \ldots, N\}$, where $\tau_n = 1/\omega_n$ and N denotes the number of the discrete impedance points collected. In the literature, $\{F(\tau_n)|n = 1, 2, \ldots, N\}$ was calculated by using a constant regularization factor. However, the reconstruction quality depends upon the value of regularization factor. In this work, we postulate a distribution of regularization factor (DRF), $\{\lambda_0(\tau_n)|n = 2, 3, \ldots, N-1\}$ across the relaxation timescale. Combining with the discretization of Eq. (1), the optimal DRT and DRF could be obtained by minimizing the objective function *err* using a new Tikhonov regularization, given by the following matrix formulation,

$$err = (\mathbf{\Gamma F} - \mathbf{Z})^{\mathrm{T}}(\mathbf{\Gamma F} - \mathbf{Z}) + (\mathbf{D_0 F})^{\mathrm{T}} diag(\boldsymbol{\lambda}_0)^2 (\mathbf{D_0 F}) + \mathbf{F}^{\mathrm{T}}\mathbf{F}(\mathbf{D_1}\boldsymbol{\lambda}_0)^{\mathrm{T}}(\mathbf{D_1}\boldsymbol{\lambda}_0) \quad (2)$$

where $\mathbf{F}$ is a non-negative column vector of N components, with $\mathbf{F}_n = F(\tau_n)$; $\boldsymbol{\lambda}_0$ is a column vector of $(N-2)$ components, with $\boldsymbol{\lambda}_{0n} = \lambda_0(\tau_n)$ for $n = 2, 3, \ldots, N-1$; $\mathbf{\Gamma}$ is a $(N+1) \times N$ matrix, with $\mathbf{\Gamma}_{i,j} = (\omega_i/\omega_j)/[ppd(1+\omega_i^2/\omega_j^2)]$ for $i = 1, 2, \ldots, N$ and $j = 1, 2, \ldots, N$, and $\mathbf{\Gamma}_{N+1,j} = 1/ppd$ for $j = 1, 2, \ldots, N$; *ppd* denotes the number of impedance points per frequency decade; $\mathbf{Z}$ is a column vector of $(N+1)$ components, with $\mathbf{Z}_n = -Z''(\omega_n)$ for $n = 1, 2, \ldots, N$, and $\mathbf{Z}_{N+1}$ is the entire polarization resistance of the impedance (R_p). When the absolute values of $Z''(\omega_1)$ and $Z''(\omega_N)$ are close to zero, say smaller than 1% of $|Z'(\omega_1) - Z'(\omega_N)|$, $\mathbf{Z}_{N+1}$ can be represented by $|Z'(\omega_1) - Z'(\omega_N)|$. Otherwise, R_p may be estimated by extrapolation, such as the method proposed by J. Matthew Esteban and Mark E. Orazem [14]; $\mathbf{D}_0$ is a $(N-2) \times N$ matrix, with $\mathbf{D}_{0n,[n,n+1,n+2]} = [-1\ 2\ -1]$ and the other components of $\mathbf{D}_0$ are zeros; $\mathbf{D}_1$ is a $(N-4) \times (N-2)$ matrix, with $\mathbf{D}_{1n,[n,n+1,n+2]} = [-1\ 2\ -1]$ and the other components of $\mathbf{D}_1$ are zeros; the superscript $^{\mathrm{T}}$ is short for transposition of matrix. It is noted that the objective function degrades into the one of the conventional Tikhonov approach when the DRF is a constant (say λ) throughout the timescale. In this case, λ^2 corresponds to the regularization factor of the conventional Tikhonov approach. The objective function *err* contains three terms. The first term represents the deviation between the original impedance $\mathbf{Z}$ and the one back-calculated by the DRT function $\mathbf{\Gamma F}$. The second term represents the roughness of the DRT function, weighted by the DRF function. This term is the core of the new regularization. The interplay between DRT and DRF across the relaxation timescale can be captured. For example, minimizing *err* permits the roughness around the discontinuities of DRT (if any) being significant by decreasing the corresponding DRF values. Thus, the discontinuities of DRT could be captured, which will be verified in what follows. The discontinuities in the DRT function are common for electrochemical cells, especially those containing mixed ionic-electronic catalysts, for example LSCF [15]. In addition, this regularization is also capable of capturing the continuities in the DRT function by increasing the corresponding DRF values. Thus, pseudo peaks can be avoided, which will also be verified in what follows. The third term represents the roughness of the DRF function. That is, we expect the DRF is a continuous function of relaxation time. Essentially, a continuous DRF means the strength of the regularization at neighboring relaxation times does not vary apparently. This term is crucial to preventing over-fitting of the DRT function. Well-established algorithms are available to minimize Eq. (2). One recommendation is the 'fmincon' function with the trust-region-reflective algorithm built in Matlab package, as used in this work. The trust-region-reflective algorithm is simple yet powerful in optimization, especially in minimizing the objective functions like Eq. (2), which have constrains of only bonds ($\mathbf{F} \geq 0$) and analytic formulas for gradient and Hessian matrix [16]. The initial value of DRF should be sufficiently high, so that the regularization during the iteration is strong enough to prevent over-fitting of DRT. We use an uniform DRT ($\mathbf{F}_i = R_p \times ppd/N$) and an uniform DRF ($\boldsymbol{\lambda}_{0i} = ppd/N$) as the initial values. One can also use the optimized solutions by the conventional Tikhonov regularization as the initial values. The two choices of initial values eventually converge to nearly identical solutions.

3. Results and discussion

We test this approach by using three case studies. The first case uses the synthetic impedances of typical elemental circuits and an integrated circuit model to validate the accuracy of the new approach and to show the robustness against noise. The second case uses the impedance of a symmetric LSCF/SDC/LSCF solid oxide cell to show the capability of capturing the discontinuity in DRT function and the capability of eliminating pseudo peaks for use in realistic impedance. The third case uses the impedances of a Ni-YSZ/YSZ/LSM-YSZ solid oxide cell to show the merits of resolving