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Generalized electrical conductivity relaxation approach to determine electrochemical kinetic properties for MIECs

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ABSTRACT

Electrical conductivity relaxation (ECR) technique has been widely used to determine kinetic properties of mixed ionic and electronic conductors (MIECs). However, this technique is only applicable for reliable determination of kinetic parameters within a confined range of chemical Biot numbers. Since the kinetic properties of the materials are not known a priori, this imposes great difficulties on how to verify the obtained kinetic parameters from obtained ECR data. Further due to the ill-posed nature of ECR problem, the measurement noise could lead to significant uncertainties in the determined kinetic parameters. Herein a generalized ECR (g-ECR) approach is developed by coherently incorporating multiple ECR measurements simultaneously into an inverse algorithm. This new approach is able to improve the accuracy of calculated kinetic parameters and attenuate uncertainties induced by measurement noise over a wider range of chemical Biot numbers than the ECR approach with a single measurement. The capability of both reducing uncertainties and increasing the range of chemical Biot numbers for accurate parameter determination can be achieved by increasing the number of employed ECR measurement responses. A case study of ECR measurement for $PrBa(Co_{0.75}Fe_{0.25})_2O_{5+\delta}$ is performed in a mixture gas of N_2/Air at 600 °C. The kinetic parameters are determined and evaluated using this g-ECR approach. The rationality of using g-ECR approach instead of ECR approach is verified.

1. Introduction

Mixed ionic and electronic conductors (MIECs) have wide applications for energy conversion and storage such as solid oxide electrochemical cells [1–3], high temperature oxygen sensors [4], and electrochemical gas separation membranes [5]. Quantitative characterization is a critical step toward developing high performance MIECs. In the past two decades, a few experimental techniques have been studied to determine kinetic properties of MIECs. These include isotope exchange technique [6–9], electrical conductivity relaxation (ECR) [10], thermogravimetry relaxation [11], and impedance spectroscopy [12]. Typically, kinetic properties of an MIEC include surface exchange coefficient and bulk diffusivity. And the determination of such properties is usually obtained by combining experimental data with appropriate analysis methods. Depending on the specific experimental design and assumptions, some of these approaches can only obtain surface exchange coefficient such as the impedance method for thin film cathodes [13], impulse isotope exchange for powder materials [14], and simplified ECR with the assumption that relaxation kinetics is controlled by the surface exchange process [15]. To obtain both surface exchange coefficient and bulk diffusivity parameters, the isotope exchange and ECR approaches are usually resorted to in the literature [16–24]. The isotope exchange approach involves an oxygen isotope ^{18}O exchange experiment and the measurement of ^{18}O diffusion profiles in the bulk sample. The surface exchange coefficient and bulk diffusivity are then determined by fitting the diffusion equation with isotope exchange depth profiles [16,17]. Due to expensive equipment and complicated operations, the wide application of isotope exchange approach is limited. The ECR approach is relative convenient and cost-effective, thus widely employed in literature [18–24].

Two steps are needed in order to obtain electrochemical kinetic properties of MIECs using the ECR approach. The first step is to generate transient conductivity responses of a bulk sample by step-changing the surrounding oxygen partial pressure from one value to another. The second step is to determine surface exchange coefficient and bulk diffusivity so that the model predictions can match with experimental data under identical operating conditions. The determination of kinetic properties from ECR measurement is a typical ill-posed problem, where a small deviation in model predictions may lead to large errors in calculated kinetic parameters. In the above referenced work, the conductivity of the bulk sample is predicted using analytical solutions of the diffusion equation. The analytical solutions are generally represented in the form of infinite series for the bulk samples of either cylindrical bar

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Nomenclature

k	surface exchange coefficient, cm/s
D	oxygen diffusivity, cm^2/s
c	concentration, mol/cm^3
t	time, s
x, y, z	Cartesian coordinate, m
J	Matching error function
$\mathbf{u}$	parameter vector
$\mathbf{X}$	sensitivity matrix
S	standard deviation
Bi	Biot number
l	characteristic length, m
L	length, m
a	height, m
b	width, m
Y	measured conductivity
$\mathbf{Y}$	vector of measured conductivity

Greek symbols

σ	conductivity
$\boldsymbol{\sigma}$	conductivity vector
ε	Tolerance for convergence
α, β	convergence parameters
τ	dimensionless time
μ	damping factor

Superscripts/subscripts

0	the initial state
∞	the final state
O	oxygen vacancy
h	electron hole
n	normalized
T	Transpose (of a matrix)
meas	measurement
s, i	iterative number
*	average value

[10] or cuboid bar [25]. Numerically, only a limit number of terms in infinite series solution can be used in this conductivity calculation. It is usually difficult to find a general criterion for effective truncation of such infinite series solutions without losing prediction accuracy, because the kinetic properties of the concerned MIEC are not known a priori and the ECR behavior could significantly differ from one material to another. Recently we have developed a new strategy to overcome these issues by coherently combining a direct numerical method with an inverse algorithm solution [26]. The results of similarity study also revealed that ECR approach has intrinsic limitations, in which kinetic parameters can be determined with high reliability only within the mid-range of chemical Biot numbers. When the chemical Biot number is very low or too high, only surface exchange coefficient or bulk diffusivity can be accurately determined respectively. It is worth mentioning that experimental ECR responses usually contain considerable measurement noise. Due to the ill-posed nature of ECR problem, the measurement noise could have significant effects on uncertainties of the calculated kinetic parameters. It is important to develop new strategies that are able to determine kinetic parameters with a high fidelity over a wider range of chemical Biot numbers, while effectively attenuating uncertainties of the calculated kinetic parameters induced by measurement noise.

In this research effort, a generalized ECR (g-ECR) approach is developed using multiple ECR measurements. The ECR measurements can be obtained through either one bulk sample with multiple probes (>4 probes) or multiple bulk samples with four probes for each sample. In the latter case, it is suggested that the relative locations of four probes along the samples are set up differently from one measurement to another. As a result, correlations among multiple ECR responses can be avoided and the kinetic parameters can be obtained in the best unbiased least square sense. The inverse algorithm is designed to determine kinetic parameters and associated uncertainties using multiple ECR responses simultaneously. Comprehensive analyses indicate that the g-ECR approach is able to expand the range of chemical Biot numbers for accurate determination of both surface exchange coefficient and bulk diffusivity. Compared to the existing ECR approach, the g-ECR approach is also able to effectively attenuate uncertainties of kinetic parameters induced by measurement noise. The computed parameter values from g-ECR approach can be uniformly improved by utilizing additional more ECR measurements. The bulk samples of the SOFC cathode material $PrBa(Co_{0.75}Fe_{0.25})_2O_{5+\delta}$ were prepared. Several sets of ECR measurements were made on these prepared samples. The kinetic parameters of $PrBa(Co_{0.75}Fe_{0.25})_2O_{5+\delta}$ were determined and evaluated using the developed g-ECR approach. The rationality of using g-ECR approach instead of ECR approach was verified.

2. Transport modeling and inverse algorithm

2.1. Modeling of surface exchange and bulk diffusion in bulk materials

The measurement principle of g-ECR technique with one bulk sample is schematically illustrated in Fig. 1. A pair of silver wires (in blue) is attached to either end of the cuboid bulk sample with silver paste, through which a constant current is provided to the sample. Additional pairs of silver wires (in red) are also attached to the sample at several points along the sample length and the voltage is measured simultaneously at each location. The sample is mounted inside an alumina tube gas chamber that is installed in a tube furnace to obtain desired operating temperatures while gases with desired compositions are supplied to the gas chamber. Assume that the sample is at equilibrium at an elevated temperature under an initial gas atmosphere (with known oxygen partial pressure). When the oxygen partial pressure is subject to a step change (by changing the gas composition), oxygen surface exchange takes place at the gas/solid interface. The non-equilibrium state at the gas/solid interface then propagates toward the interior of the bulk until the sample reaches a new equilibrium. Under the constant current condition, the state change of the sample is reflected in the change in conductivity, determined by measuring the change in voltage. This change in conductivity, determined from the voltage and current measurements during the sample relaxation process, can be utilized to determine the sample material's surface exchange coefficient and bulk diffusivity properties.

The bulk diffusion and surface exchange processes of a bulk material sample can be described using Fick's second law and a linear kinetic boundary condition respectively. Assuming the sample is isothermal,

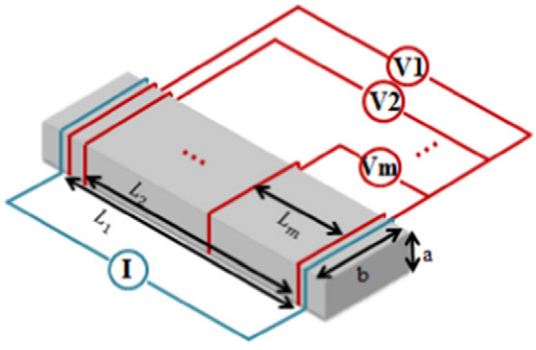

Fig. 1. Schematic illustration of sample assembly for g-ECR measurement.