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Equilibrium and transient conductivity for gadolium-doped ceria under large perturbations: II. Modeling

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ABSTRACT

A model-based approach is used to interpret equilibrium and transient conductivity measurements for 10% gadolinium-doped ceria: $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$ (GDC10). The measurements were carried out by AC impedance spectroscopy on slender extruded GDC10 rods. Although equilibrium conductivity measurements provide sufficient information from which to derive material properties, it is found that uniquely establishing properties is difficult. Augmenting equilibrium measurements with conductivity relaxation significantly improves the evaluation of needed physical properties. This paper develops and applies the computational implementation of a Nernst–Planck–Poisson (NPP) model to represent and interpret conductivity-relaxation measurements. Defect surface chemistry is represented with both equilibrium and finite-rate kinetic models. The experiments and the models are capable of representing relaxations from strongly reducing to strongly oxidizing gas-phase environments, and vice versa. Compared to alternative models, such as ambipolar models, the NPP approach enables the direct study of large variations in conductivity that are associated with large variations in gas-phase environments.

1. Introduction

This paper is the second of a combined experimental and modeling study to evaluate thermodynamic and transport properties in mixed-conducting ceramics. The companion paper reports the experimental approach and measured results. As illustrated in Fig. 1, the experiments and models are based on slender extruded rods (3.3 mm diameter and 25 mm long) of 10% gadolinium-doped ceria (GDC10, $Ce_{0.9}Gd_{0.1}O_{1.95-\delta}$) with Pt electrodes on the ends. The study considers equilibrium conductivity and conductivity relaxation, using models to interpret the measurements. The operating conditions consider temperatures ranging from 700 °C to 900 °C and the oxygen partial pressures range from 10^{-24} atm to 1 atm. The conductivity relaxations consider rapidly switching the gas phase back and forth between strongly oxidizing and strongly reducing environments. The physical models use a Nernst–Planck–Poisson (NPP) formulation, which is capable of handling large variations in operating environments as well as mixed conductors with three or more charge-carrying defects [1,2]. The objective of the modeling is to interpret the measurements in terms of establishing physical parameters.

In principle, both thermodynamic and transport parameters can be evaluated from equilibrium conductivity measurements. Thermodynamic properties are usually represented as changes in enthalpy and entropy (ΔH° and ΔS°) for assumed defect reactions at the gas–ceramic interfaces. Transport properties of charged-defects are usually represented as activated diffusion coefficients [$D_k = D_k^\circ \exp(-E_k/RT)$]. However, results of the present study show that it can be difficult to unambiguously determine a complete set of properties using equilibrium conductivity measurements alone. Conductivity relaxation provides supporting data that significantly improves the fidelity of property measurements. Additionally, the transient relaxation response provides important information about the effects of surface kinetics.

The experimental configuration and the modeling approach provide significant advantages compared to earlier investigations. The slender rods are designed to produce essentially one-dimensional radial defect transport, which facilitates model-based experimental interpretation. Care is taken to evaluate and minimize any possible end effects that would compromise the one-dimensional interpretation of the results. Previous conductivity relaxation experiments have usually considered only small step changes in the gas-phase environment, which enables interpretation using analytic solutions of ambipolar diffusion models.

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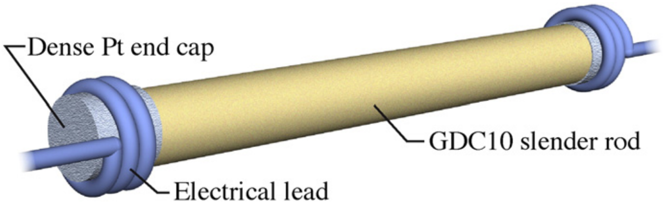

Fig. 1. Illustration of a slender GDC10 rod with Pt end caps and electrical leads on the ends.

The present models using the NPP formulation are not restricted to small gas-phase changes.

Fig. 2 summarizes the conductivity-relaxation measurements reported in the companion paper. The important thing to notice is the great asymmetry between the oxidizing-to-reducing and reducing-to-oxidizing relaxations. The time scale for the oxidizing-to-reducing relaxation is on the order of an hour, whereas the time scale for the reducing-to-oxidizing relaxation is on the order of a few seconds. Fig. 2 also shows that the measured asymmetric conductivity relaxation can be predicted very well by the model. As discussed subsequently, an important objective of the modeling is to interpret and explain the very strong asymmetry.

2. Gadolinia-doped ceria

Gadolinium-doped ceria has a fluorite structure in which Ce^{4+} is partially substituted with Gd^{3+}, generating oxygen vacancies $V_O^{\bullet\bullet}$ as charge-compensating defects. At low oxygen activities, the cerium cations can be reduced from Ce^{4+} to Ce^{3+}, thus further increasing the $V_O^{\bullet\bullet}$ concentration. Transport within the material is understood to be dominated by oxide ions in oxidizing environments and localized electrons (small polarons) in reducing environments [3–7]. A particularly interesting aspect of doped-ceria materials is the cerium redox chemistry. The change in cerium oxidation state (Ce^{4+} to Ce^{3+}) has an important influence on the ion and electron transport as well as in transient responses to changing gas-phase atmospheres.

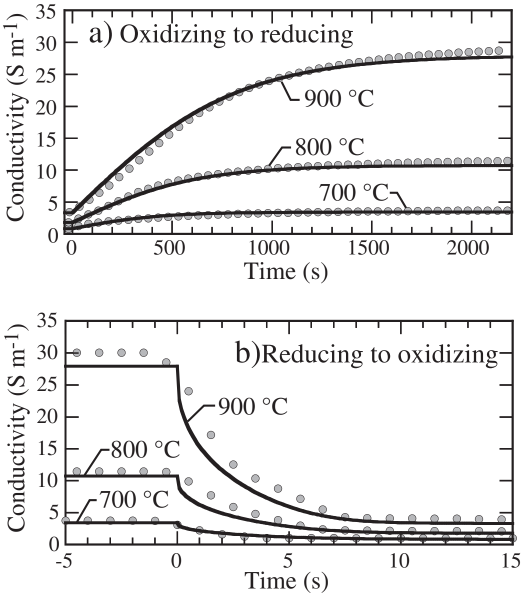

Fig. 2. Comparison of model-predicted conductivity relaxation histories (lines) and the experimental measurement (filled circles) at temperatures of 700, 800, and 900 °C and 1 atm. The reducing gas-phase mixture is 4.0% H_2, 3.0% H_2O and 93% Ar, and the oxidizing gas-phase composition is 97% O_2 and 3% H_2O. a) Relaxation from the oxidizing to reducing conditions; b) relaxation from the reducing to oxidizing environment.

2.1. Defect chemistry

Using Kröger–Vink notation, the overall reaction process at the GDC10 surface can be represented *globally* as

$$O_O^{\times} + 2Ce_{Ce}^{\times} \underset{k_{G,b}}{\overset{k_{G,f}}{\rightleftharpoons}} V_O^{\bullet\bullet} + 2Ce_{Ce}' + \frac{1}{2}O_2(g) \tag{1}$$

where the small polaron is denoted as Ce_{Ce}', and the forward and backward reaction coefficients are denoted as $k_{G,f}$ and $k_{G,b}$. The production rates of defects on the surface can be represented as,

$$\dot{s}_{V_O^{\bullet\bullet}} = \dot{q}_G, \quad \dot{s}_{O_O^{\times}} = -\dot{q}_G, \tag{2}$$

$$\dot{s}_{Ce_{Ce}^{\times}} = -2\dot{q}_G, \quad \dot{s}_{Ce_{Ce}'} = 2\dot{q}_G, \tag{3}$$

where the rate of progress of the global reaction$\dot{q}_G$ is evaluated as

$$\dot{q}_G = k_{G,f}\left[O_O^{\times}\right]\left[Ce_{Ce}^{\times}\right]^2 - k_{G,b}\left[V_O^{\bullet\bullet}\right]\left[Ce_{Ce}'\right]^2\left[O_2\right]^{1/2}. \tag{4}$$

At equilibrium, $\dot{q}_G = 0$. The global reaction (Eq. (1)) is likely the result of multiple elementary steps, in which case the reaction orders may be different from those indicated by Eq. (4). However, as discussed subsequently, an important aspect of the present model is to explore the influence of any surface-kinetic limitations. For this purpose, the approximate global representation is entirely adequate. The equilibrium constant, written in terms of the molar concentrations, can be expressed as

$$K_{c,G} = \frac{k_{G,f}}{k_{G,b}} = \frac{\left[Ce_{Ce}'\right]^2\left[V_O^{\bullet\bullet}\right]}{\left[Ce_{Ce}^{\times}\right]^2\left[O_O^{\times}\right]}\left[O_2\right]^{1/2} = K_{p,G}\left[\frac{P_{atm}}{RT}\right]^{1/2}, \tag{5}$$

where R is the gas constant, T is temperature, and P_{atm} is the standard atmospheric pressure. The constant-pressure equilibrium constant $K_{p,G}$ is defined as

$$K_{p,G} = \frac{\left[Ce_{Ce}'\right]_L^2\left[V_O^{\bullet\bullet}\right]_L}{\left[Ce_{Ce}^{\times}\right]_L^2\left[O_O^{\times}\right]_L}p_{O_2}^{1/2}, \tag{6}$$

where the formula-unit concentrations $[X_k]_L$ are related to the molar concentrations $[X_k]$ via the molar volume V_m as $[X_k]_L = [X_k]V_m$. For GDC10, the lattice molar volume is $V_m = 24.3 \times 10^{-6}$ m^3 mol^{-1}. The value of $K_{p,G}$ can be evaluated in terms of thermodynamic properties as

$$K_{p,G} = \exp\left(-\frac{\Delta G^{\circ}}{RT}\right), \tag{7}$$

where $\Delta G^{\circ} = \Delta H^{\circ} - T\Delta S^{\circ}$ is the Gibbs free-energy change associated with the global defect reaction (Eq. (1)). The corresponding standard-state enthalpy and entropy changes are represented as ΔH° and ΔS°, respectively.

The equilibrium constants can be used in two ways. It is commonly assumed that the defect chemistry at the GDC10–gas interface is equilibrated. In this case, the equilibrium constant is used to evaluate the defect concentrations as functions of temperature and the gas-phase environment. Alternatively, the defect chemistry at the ceramic–gas surface may be kinetically limited. In this case, the equilibrium constant is used to establish the relationship between forward and reverse rates such as to satisfy microscopic reversibility.