Impedance spectroscopy of Gd-doped ceria analyzed by genetic programming (ISGP) method

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ABSTRACT

This work presents the distribution function of relaxation time (DFRT) analysis of Gd doped ceria (GDC) and cobalt co-doped GDC prepared by precipitation method. Ionic transport properties and grain-boundary phenomena are discussed thoroughly based on the DFRT. The impedance results, especially the bulk and grain-boundary conductivities ($\sigma_b$ and $\sigma_{gb}$) and activation energies ($E_b$ and $E_{gb}$) obtained from the ISGP, are compared with the values obtained from the Equivalent Circuit Model. Grain boundary space charge (SC) effects discussed so far in the literature, generally do not consider the defect interaction between the oxygen vacancies and acceptor dopants in ceria and other oxide ion conductors. However, ISGP study clearly evidence the co-existence of SC effect and defect association in grain boundary regions, and both contribute to the grain boundary resistance ($R_{gb}$) at lower temperatures. The effect of sintering aid (Co) on the grain boundary activity is discussed considering both phenomena. Lower sintering temperature of the samples results in a relatively smaller grain boundary potential ($\Phi(0)$) i.e., 0.15, 0.17 and 0.19 V at 300 °C in 0, 1 and 3 mol% Co co-doped GDC, respectively.

1. Introduction

Impedance spectroscopy (IS) is one of the key characterization tools in the fields of electrochemical energy technology and electro-ceramics. Equivalent circuit models have been widely used for the analysis of IS. In the case where the relaxation time constant ($\tau$) of two different phenomena are very close, their responses to applied AC field appear as overlapping semicircles or a single semicircle in the impedance spectra. In that case, it is difficult to distinguish between two different processes accurately by using an equivalent circuit model, and in general, many different configurations of equivalent circuits can provide very similar impedance spectra.

Our group has developed an evolutionary programming technique for the analysis of IS. The details of this so-called impedance spectroscopy by genetic programming (ISGP) are discussed in previous reports [1–3]. This method provides an analytic form of the underlying distribution function of relaxation times (DFRT, a.k.a. $\Gamma$) without the need to employ any filtering. In this work we have studied the relaxation time distribution in nanocrystalline 10 mol% Gd doped ceria (GDC) and CoO (1–3 mol%) co-doped GDC prepared by precipitation method, to understand the ionic transport processes through DFRT using ISGP analysis. A comparative study is performed based on ISGP results and that of equivalent circuit model.

2. Experimental

The nanocrystalline GDC powder was prepared by co-precipitation method. For the co-doped samples, 1 & 3 mol% CoO was added to the GDC powder by deposition precipitation method (abbreviated here as GDCCo1 and GDCCo3, respectively) [4,5]. Details of the sample preparation are described in a previous report [6]. Surface area of nanoparticles (obtained by BET) was about 78.9, 119.6, and 124.5 m²/g for GDC, GDCCo1 and GDCCo3, respectively. The powders were pressed into pellets by applying a pressure of 50 MPa uniaxially followed by 200 MPa in cold isostatic pressing (CIP). Pellets were sintered at 900 °C for 2 h and their densities were measured by the Archimedes method. The relative densities of sintered pellets were about 90 and 97% for GDC and co-doped GDC, respectively. The average grain sizes in the sintered pellets were 62, 86 and 81 nm for GDC, GDCCo1 and GDCCo3 respectively [6]. Impedance measurements were carried out in air by 2-probe method using Solartron 1260 gain/phase analyzer, in the frequency range of 1 Hz to 10 MHz. Impedance data for the temperature range of 200–500 °C were analyzed by ISGP to obtain the DFRT. Conductivities ($\sigma$) at the grain boundaries and bulk of the samples were obtained using the relation; $\sigma = L / (RA)$, where L and A are the thickness and cross-sectional area of the pellet, and R is the relevant resistance calculated from the DFRT.
3. Results and discussion

Typical Nyquist plots for GDC, GDCCo1 and GDCCo3 at various temperatures are shown in Fig. 1(a–f), which appear to consist of two semicircles at higher and intermediate frequencies and a spike at the lower frequency range. In a previous work, an equivalent circuit model was used to fit the impedance spectra. The semicircles at higher and intermediate frequencies with capacitance values in the range of $10^{-12}$–$10^{-11}$ and $10^{-10}$–$10^{-8}$ F, were attributed to the bulk and grain boundary conductivity, respectively. The spike at lower frequency region (with capacitance $10^{-6}$ F) is generally attributed to the electrode effect [6–9]. Note that the latter cannot be determined with high certainty since the corresponding central time constant is completely out of the measured frequency range. Only the bulk and grain boundary semicircles were considered for the analysis and the electrode part was ignored [6].

In this work impedance plots were fitted with ISGP, Fig. 1(a–f). DFRT plots for all the samples at various temperatures are shown in Fig. 2 (a–c). At temperatures below 300 °C, $r$ vs. log $\tau$ plots exhibit the presence of a peak (P1) at higher frequencies (i.e., at lower $\tau$), two peaks (P2 and P3) at the intermediate region and two closely overlapping peaks (P4 and P5) at lower frequencies. The additional peak at intermediate region (P3) is more apparent in GDCCo3, see Fig. 2(c).

The area under a peak is used to calculate the corresponding resistance ($R$) [2]. In a simple lumped elements circuit, $RC = \tau$ and the DFRT has the form of a delta function. At a more general case, the reactance/capacitance (still abbreviated here as C) is calculated using the same relation, where $\tau$ is obtained from the central peak position. Values of $R$, $\tau$, and C for all the peaks are given in Table-1. The values of reactance/capacitance (C) are in the order of $10^{-11}$, $10^{-10}$ and $10^{-9}$ F, for the peaks P1, P2 and P3, respectively, and they match well with the capacitance obtained from equivalent circuit model when the CPE are corrected for the power factor [6]. Hence the peak P1 can be attributed to the bulk conductivity, and peaks P2 and P3 at the intermediate frequencies are attributed to grain-boundary activities. Peaks P4 & P5 at lower frequencies (i.e., at higher log $\tau$) correspond to the spike in the Nyquist plots due to the electrode processes.

Fig. 2 (a–c) shows that, for all the samples, two relaxation phenomena contribute to the grain-boundary resistance at lower temperatures. As the temperature increases, the peak positions shift towards lower $\tau$, indicating the relaxation phenomena at the bulk and grain boundaries are thermally activated processes. Peak P1 disappears at temperatures above 340 °C in GDC, and above 300 °C in both GDCCo1 and GDCCo3. Peak P2 appears throughout the temperature range of study. Peak P3 disappears above 240 °C in GDC, whereas it appears up to 300 and 440 °C in GDCCo1 and GDCCo3, respectively.
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