



A study of gadolinia-doped ceria electrolyte by electrochemical impedance spectroscopy



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HIGHLIGHTS

- Measured conductivity of gadolinia-doped ceria by impedance spectroscopy.
- Described transport using an equivalent circuit including leads impedance.
- Determined parameters from maxima and minima of impedance spectra.
- Grain boundary arc can be described accurately by a resistor-capacitor element.

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ABSTRACT

Samples of Gd₂O₃-doped CeO₂ (GDC) were fabricated by sintering of powder compacts. Impedance spectra were measured from 400 °C to 675 °C in air by electrochemical impedance spectroscopy (EIS). Above ~500 °C, high frequency arc was not semicircular but could be fitted with a constant phase element (CPE). Above ~625 °C, high frequency arc could not be resolved due to a significant contribution from the inductive load. The impedance spectra were described using a simple equivalent circuit which included the leads/instrument impedance. The leads/instrument impedance was measured over a range of frequencies and temperatures. The high frequency part of the impedance after subtracting leads/instrument impedance could be resolved even at the highest measurement temperature and was described by a semicircle representative of transport across grain boundaries. From these measurements, grain and grain boundary resistivities were determined. The corresponding activation energies were 0.69 eV and 1.11 eV, respectively. The grain boundary capacitance was nearly independent of temperature. The present results show that grain boundary effects can be described by a resistor and a capacitor. Relevant equivalent circuit parameters were obtained from intercepts, maxima and minima in impedance diagrams.

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1. Introduction

Electrochemical Impedance Spectroscopy (EIS) is a technique which measures the response of a sample under an AC stimulus in which the frequency is varied over a wide range. EIS has wide applicability, and has been used for the study of ionic conductors, dielectric materials, semiconductors, solar cells, fuel cells, batteries and corrosion. With improvements in equipment over the years, four types of techniques are typically used to measure and interpret the impedance. They are: AC bridge, Lissajous analysis, phase-

sensitive detection and Fourier analysis. The general approach involves the application of a single frequency input and the measurement of the corresponding current (I) flowing through and the potential drop (V) across the sample. From the measurement of I and V as well as the phase difference over a wide range of frequencies, the real and the imaginary parts of the impedance as a function of frequency can be determined. In 1969, Bauerle in a landmark paper in solid state ionics investigated transport through yttria-stabilized zirconia (YSZ) samples with various applied electrodes and in several atmospheres using electrochemical admittance spectroscopy [1]. Bauerle showed that the measured admittance data could be fitted to semicircles or depressed semicircles in the admittance plane. These semicircles at high frequencies correspond to transport properties through the grain

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interiors and across the grain boundaries, and at low frequencies correspond to electrode effects [1]. Bauerle used an equivalent circuit comprising a pure resistor and a pure capacitor in parallel to describe the sample behavior at high frequencies which accurately reproduced the measured spectra. Electrode effects were in part represented using Warburg impedance. Since this original paper, the use of EIS has become commonplace in the study of solid state ionics [2].

The resolution of grain and grain-boundary effects usually requires a high frequency input, often exceeding 100 kHz. It is well known that at high frequencies, there can be a significant contribution from an inductive load, the origin of which lies in the lead wires used to connect to the sample as well as parts of the instrumentation. The effect of the inductive load reflects as an imaginary part of the impedance below the x -axis when the real part is plotted on the positive x -axis and negative of the imaginary part is plotted on the positive y -axis. Thus, in a typical plotting scheme, the capacitive effects appear above the x -axis and the inductive effects appear below the x -axis. When both capacitive and inductive contributions are present to a significant extent, their effects are reflected in the spectra regardless of whether the actual spectra lie above or below the x -axis. Many studies have shown that it is essential to subtract the effects of the leads/instrument before data can be adequately interpreted [2–4]. In a study of $(\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta})$ LSCF cathodes using EIS, Esquirol et al. measured the leads/instrument inductance as ~ 125 nH, and the corresponding leads/instrument impedance was subtracted from the raw EIS data [3]. Samson et al. [4] also measured the impedance of an empty cell and subtracted it from the raw data in their study of Sr-doped LaCoO_3 (LSC) cathodes [4]. In many recent studies, however, the approach used has been to ignore that part of the impedance which lies below the x -axis and fit the remaining portion above the x -axis (which is generally not semicircular) using a CPE [5–8]. However, such a procedure does not account for the impedance of the leads/instrument and as such may not represent an accurate measurement of the sample impedance. For example, in a study of electrolyte resistivity, Suzuki et al. did not remove the leads/instrument impedance [5]. They noted that there was a large difference in the measured electrolyte resistance and that expected from separate measurements on bulk samples [5]. They attributed the observed large difference in the electrolyte resistance between the expected value and the measured value to the multilayer structure of their sample [5]. However, the leads/instrument impedance is expected to contain both resistive and inductive contributions, which right-shift the arc leading to an intercept at a larger value (than the sample resistance) on the real axis unless the leads/instrument impedance has been subtracted out. Wang et al. [6] investigated $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}/\text{Zr}_{0.92}\text{Y}_{0.08}\text{O}_2$ porous electrodes by EIS. In their work the high frequency intercept was equated to the electrolyte and the lead resistance. However, inductive effects of the leads were neglected. Similarly, Zajac et al. investigated the resistivity of doped ceria by EIS [7,8]. In their study, the data below the x -axis were cutoff and the remaining data were analyzed by a CPE as the arcs clearly were not semicircular [7,8].

The use of a CPE generally leads to a better fit to the data than using a capacitor. This of course is not surprising as fitting with a CPE requires two parameters unlike a capacitor, which only needs one parameter. However, the use of a CPE often makes it difficult to offer a unique physical interpretation of the data as the fitting itself may lack uniqueness. In this work, we investigated the conductivity of GDC samples with the objective being the determination of grain and grain boundary ion transport properties. The leads/instrument impedance was separately measured and was subtracted from the data before fitting. The measurements were conducted using the two terminal method. While many studies in the past have

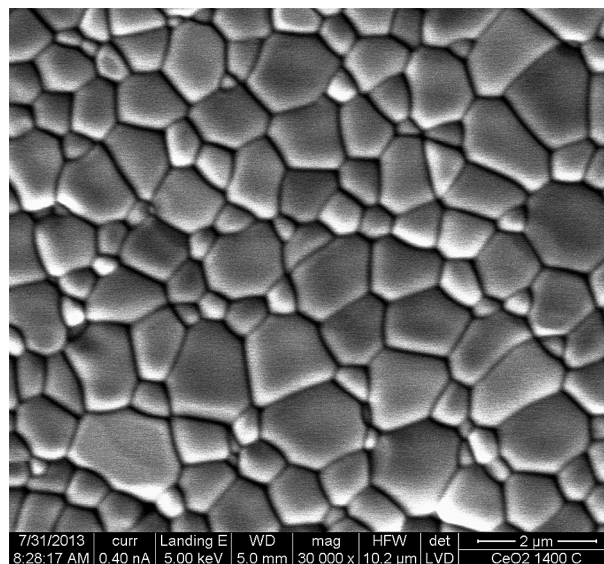


Fig. 1. An SEM image of the GDC sample showing an equiaxed microstructure. The average grain size is ~ 1.1 μm .

emphasized the need to subtract the leads/instrument contribution [2–4], the continual use of procedures in which the inductive part is cutoff and the remainder of the data are fitted using a CPE suggests that revisiting this issue may be of value. The present study also analyzes the data in light of simple equivalent circuits but with the inclusion of the leads/instrument impedance. The present work also attempts to extract relevant parameters of the equivalent circuit from intercepts, maxima and minima in the impedance diagrams.

2. Experimental procedure

Pellets of Gd_2O_3 -doped ceria (GDC) powder of composition 80 mol.% CeO_2 –20 mol.% $\text{GdO}_{1.5}$ were die-pressed and sintered in air at 1400 °C for 2 h. The typical thickness of the pellets was ~ 1.4 mm. Pt paste was applied on both sides of the pellets and they were fired at 800 °C in air for 1 h. Samples of two different electrode geometries (sizes) were used in this study; one set of samples with electrodes 15.8 mm in diameter and the other with electrodes 4.8 mm in diameter.

Impedance spectra were obtained on the samples in air over a range of temperatures between 400 °C and 675 °C in 25° intervals using the two terminal method. The impedance measurements were conducted using Solartron 1260 Frequency Response Analyzer over a frequency (f) range between 0.1 Hz and 1 MHz. Impedance spectra over the same range of temperatures and frequencies were also obtained without the sample (the empty cell) by shorting the two lead wires. This corresponds to the inductive-resistive contribution of the lead wires and the testing setup.

3. Results and discussion

The density of the sintered samples was measured to be 7.0426 g ml^{-1} , which is about 97.37% of theoretical. Fig. 1 shows a scanning electron micrograph (SEM) of a polished and thermally etched sample of a GDC sample. The microstructure is equiaxed and the average grain size is ~ 1.1 μm . Fig. 2 shows an example of how the impedance was measured and interpreted. The corresponding equivalent circuits are shown as insets. Also, an inset in Fig. 2 shows schematics of the two samples used with different electrode areas. For simplicity, the electrodes were also modeled using a parallel R –

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