

Electrochemical Impedance Spectroscopy of Gadolinia-Doped Ceria: Role of Leads/Instrument Impedance

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Electrochemical Impedance Spectroscopy (EIS) is routinely used for the study of electrochemical systems. In most measurements, low frequency data correspond to electrode effects and high frequency data correspond to grain/grain boundary effects of the electrolyte. It is well known that at high frequencies, effects of leads/instrument impedance arising from inductive effects can be significant. In many studies, the leads/instruments impedance is subtracted before interpreting data. However, in some studies, data below the x-axis in the plots of $-Imz(\omega)$ vs. $Rez(\omega)$ are cutoff and the remainder of the data are fitted using a CPE. The objective of this work was to investigate the effects of leads/instrument on the measured EIS spectra on gadolinia-doped ceria (GDC) samples with focus on the high frequency regime.

In the simplest description of a typical solid electrolyte sample with electrodes, the equivalent circuit may be described by parallel R-C circuit elements (Fig. 1) in which the leads/instrument impedance is represented by a series R-L circuit element [1, 2]. At low temperatures, on a typical sample such as yttria-stabilized zirconia (YSZ), three distinct arcs are observed (as in Fig. 1). However, typical EIS data always show inductive spectra at very high frequencies, which are caused by the leads/instrument. As the testing temperature is increased, the sample impedance decreases and relative contribution of the leads/instrument impedance increases [3].

Real and imaginary parts of the impedance corresponding to the equivalent circuit in Fig. 1 are given by equation (1) below

$$Re z(\omega) = R_l + \frac{R_g}{(1 + R_g^2 \omega^2 C_g^2)} + \frac{R_{gb}}{(1 + R_{gb}^2 \omega^2 C_{gb}^2)} + \frac{R_E}{(1 + R_E^2 \omega^2 C_E^2)} \quad (1a)$$

$$Im z(\omega) = \omega \left[L - \frac{R_g^2 C_g}{(1 + R_g^2 \omega^2 C_g^2)} - \frac{R_{gb}^2 C_{gb}}{(1 + R_{gb}^2 \omega^2 C_{gb}^2)} - \frac{R_E^2 C_E}{(1 + R_E^2 \omega^2 C_E^2)} \right] \quad (1b)$$

From the analysis of the equivalent circuit, it can be shown that only one intercept exists, at which the corresponding frequency is denoted as ω^* , and the value of this intercept depends upon the temperature (relative values of the various contributions to the impedance). Fig. 2 shows the expected shapes of the impedance plots at various temperatures. The various regimes are characterized by maxima, minima and inflexion points observed in the $-Imz(\omega)$ vs. $Rez(\omega)$ plots. At low temperatures, three distinct arcs are expected. At very high temperatures, no arc may be observed and the entire spectra may lie below the x-axis. Still, the $\omega \rightarrow 0$ intercept gives the total ohmic contribution.

Fig. 3 shows the measured spectra on a GDC sample over a range of temperatures. At low temperatures (400°C), the grain boundary arc is clearly visible and no data points lie below the x-axis. At higher temperatures (650°C), two arcs can be observed with much of the data lying below the x-axis (inductive effects). At even higher temperatures (750°C), the high frequency arc is not observed. The present work shows that the high frequency data

corresponding to grain boundary effects, can be adequately represented by a parallel R-C circuit.

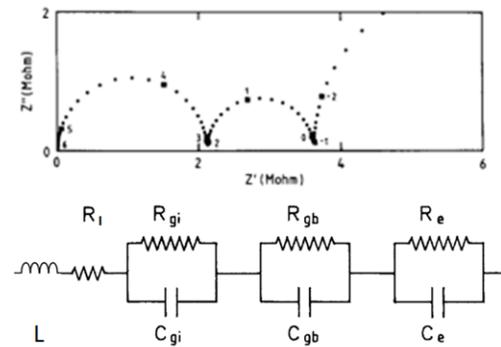


Fig. 1 Electrochemical Impedance Spectroscopy of yttria-stabilized zirconia at low temperatures [1]. The corresponding equivalent circuit is shown including the leads/instrument impedance.

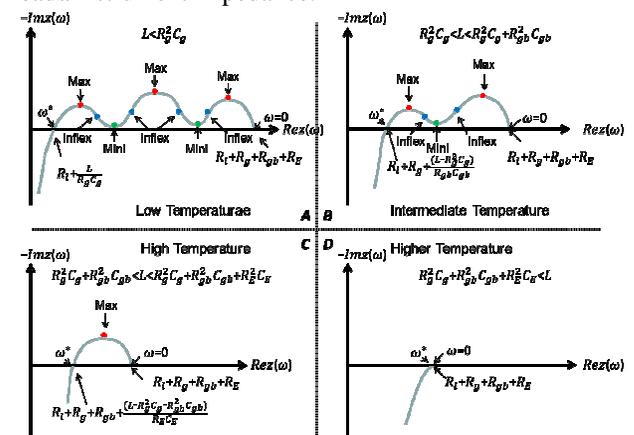


Fig. 2 Expected spectra as a function of temperature.

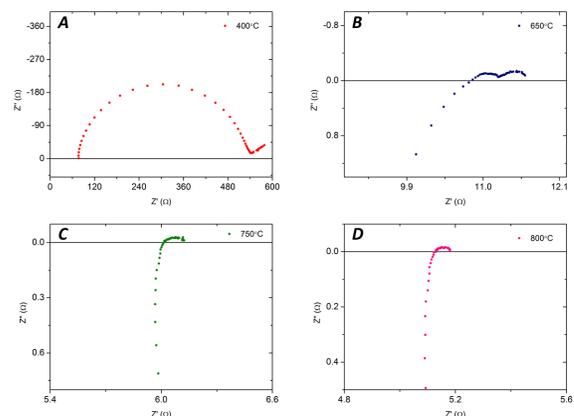


Fig. 3 EIS measurements on a GDC sample at different temperatures. These results correspond to the various cases shown in Fig. 2. A shows the full grain boundary arc. The grain arc is missing because the highest frequency was not high enough. The electrode arc is only partly formed because the lowest frequency was not low enough. B coincides with Fig. 2B. C and D correspond to Fig. 2C.

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