Measurement of Polarization Resistance of LSM + YSZ Electrodes on YSZ using AC and DC Methods

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Abstract

Most of the measurements of electrode polarization resistance are conducted using electrochemical impedance spectroscopy (EIS). The electrochemical devices, however, are typically used in a DC mode. The objective of the present work was to measure electrode polarization resistance using both EIS and DC techniques. A solid cylinder of 8YSZ of diameter ~1.17 cm and length ~5.00 cm was made by powder pressing followed by sintering. LSM + YSZ electrodes were applied on the two end surfaces of the cylinder upon which gold mesh was placed. Four Pt electrodes/probes were painted along the circumference. During DC measurements, DC voltage was applied across the end electrodes and potentials were measured at all four probes. The current was also measured. From these measurements electrode polarizations were estimated separately for the two electrodes as a function of current. EIS was conducted across the two end electrodes as well as across electrode-1 and probe-2, and across probe-2 and electrode-2. This allowed the determination of the polarization resistances of the two electrodes separately. Point by point additions of the electrode-1/probe-2 and probe-2/electrode-2 spectra matched the electrode-1/electrode-2 spectra. There was good agreement between the DC and the EIS measurements.

I. Introduction

In most solid oxide cells (SOC) made using a thin electrolyte, electrode-supported structure, polarization resistance of the oxygen electrode is dominant. In such devices, it is generally not possible to measure the polarization resistances of the two electrodes separately. Thus, typically EIS spectra are obtained on the entire cell and it is necessary to de-convolute the spectra. But de-convolution is an inverse problem and lacks uniqueness. Multiple equivalent circuits can describe the same experimentally obtained spectra. As an example, if an EIS spectra is a simple semi-circle (Figure 1(a)), two different equivalent circuits shown in Figures 1(b) and 1(c) can equally well describe the spectra. Figure 1(b) shows a system in which one electrode is perfect (zero polarization resistance). Figure 1(c) shows an equivalent circuit where both electrodes exhibit identical behavior. Thus, the determination of which of the two equivalent circuits describes the system is not possible from the measured spectra. Also, electrochemical studies are typically done using EIS, an AC technique. But, the devices are used in a DC mode. The objective of the present work was thus to investigate electrode kinetics using both DC and AC methods and compare the results. This was done using a long cylindrical sample of 8YSZ. The present experiments were conducted at one temperature only. Future experiments will be conducted at several temperatures.

II. Experimental Procedure

A cylindrical sample of 8YSZ was fabricated by iso-statically pressing powder in a polyurethane mold in an isostatic press and sintering in air at 1600°C for 4 h. The diameter of the cylinder was ~1 cm and the length was ~ 5 cm. Platinum paste as ~ 2 mm wide strip electrodes (probes) were circumferentially applied along the length of cylinder at four places approximately 1.2 cm apart to which platinum wires were attached and fired at 900°C. LSM + YSZ (each 50 wt.%) electrodes were applied to the circular end surfaces and fired at 1000°C for 2 h. Alumina tubes were used to isolate the wires. A ceramic fixture was fabricated to place the sample with wires attached to the four probes. Gold mesh was adhered to the end electrodes using gold paste. Platinum wires were attached to the gold mesh. The sample and the ceramic fixture assembly were placed in a tubular furnace. The wires protruded out of the furnace. Measurements were conducted in O_2-N_2 gas mixtures containing 100%, 10%, 5% and 1% O_2. All testing was done at 611°C. Electrical testing was done using both DC and AC (EIS) techniques. For DC studies, a DC voltage was applied in the range of 0.05 V to 0.38 V across the sample. At each applied voltage, the corresponding current was measured and potentials at all four probes were measured. A total of eight Keithley 2000 meters were used and automated via Labview. Six meters read potentials, 1 meter read the current and 1 meter read the temperature with a K-type thermocouple. From these measurements both the YSZ ionic resistivity and the electrode polarizations were determined. Figure 2(a) shows the sample geometry. Figure 2(b) shows the DC equivalent circuit for the sample. The polarization resistances at the two end electrodes are denoted by R_{C_1} and R_{C_2}. The overpotentials at the end electrodes 1 and 2 are respectively given by η_{C_1} and η_{C_2}. In principle, R_{E_1}, R_{E_2}, R_{E_3}, and R_{E_4} are polarization resistances for the platinum strip electrodes. However, the input resistance of the measuring meter is much larger (in the several GΩ range). Thus, the very small trickle current that passes through the meters is negligible. Therefore, these resistances do not factor in the measurements. In terms of the measured quantities, the overpotential is given by

$$\eta_{C_1} = V_{C_1-E_1} - \rho \frac{l_{RYSZ1}}{A} I \tag{1}$$

where $V_{C_1-E_1}$ is the measured voltage between electrode-1 and E_1, $l_{R_{YSZ_1}}$ is the distance between electrode-1 and E_1, A is the cross-sectional area of the YSZ cylinder, ρ is the ionic resistivity of YSZ, and I is the measured current. Similar equation is applicable to electrode-2. Measurements were made over a range of current densities. This allowed a study of overpotential as a function of current density. EIS measurements were made over a frequency range from 1 MHz to 0.1 Hz with a voltage amplitude of 14 mV. EIS spectra were obtained across electrode-1 and electrode-2, across electrode-1 and probe E_2, and across probe E_2 and electrode-2. The objective was to separately determine the polarization resistances of the two electrodes. Also, the objective was to determine if the sum of the spectra across electrode-1 and probe-2 and across probe-2 and electrode-2 match the spectra across electrode-1 and electrode-2.

III. Results and Discussion

Figure 3 shows a photograph of the sample with four platinum wires attached to Pt strip electrodes and also shows one of the end LSM + YSZ electrodes. Figure 4 shows the measured resistance between probes as a function of distance along the length of the cylinder. Voltage applied was 0.36 V. The slope gives the YSZ resistance per unit length, from which the YSZ resistivity can be determined. The measurements were made in various gas mixtures with oxygen concentration ranging between 1% and 100%. The slope was essentially the same, consistent with expectations. That is, the ionic resistivity over this partial pressure of oxygen range is independent of oxygen partial pressure. Also, at this low temperature, the interior stoichiometry of the sample is expected to remain fixed, regardless of the O_2 concentration in the gas.

Figure 5 shows the EIS results on the sample in 1% O_2. The measurements were conducted with no DC bias. In DC measurements, the right electrode was connected to the positive terminal of the voltage source while the left one was connected to the negative terminal. Thus, at the left electrode, oxygen reduction reaction (ORR) occurs and at the right electrode oxygen evolution reaction (OER) occurs. Figure 5(a) shows EIS spectra between the left electrode (electrode-1) and the right electrode (electrode-2) (blue circles), between electrode-1 and probe-2 (orange circles) and between probe-2 and electrode-2 (grey circles). It is seen that the polarization of the left electrode is considerably greater than that of the right electrode, this despite the fact that both electrodes were identical. The high frequency intercepts corresponding to both the left and the right electrodes are approximately the same, about 350 Ω. The high frequency intercept of the entire sample is about 700 Ω. Figure 5(b) shows the EIS spectra across the entire sample (blue circles, the same as in Figure 5) and point by point sum of the EIS spectra between electrode-1 and probe-2 and between probe-2 and electrode-2 (orange circles). As seen in the figure, the sum of the spectra almost exactly overlaps with the spectra across the entire sample. Only at very high frequencies, where inductive contribution from the wires and the instrument is substantial, the spectra differ somewhat. This is expected since in each experiment any slight inadvertent twisting of the wires can lead to different inductance and thus that part of the spectrum is not reproducible. It is also possible that inductive coupling between adjacent wires was present. The virtually perfect match of the spectra shows that the approach used here to isolate the individual electrode spectra is satisfactory. This also shows that it is possible to separately measure polarization resistances of the electrodes.

Figure 6(a) shows EIS spectra between the left electrode (electrode-1) and probe-2 (orange circles), between probe-2 and the right electrode (electrode-2) (grey circles), and across the left electrode and the right electrode (blue circles) in 100% O_2. Figure 6(b) shows EIS spectra across the left electrode and the right electrode (blue circles) and the sum of spectra across the left electrode and probe-2 and across probe-2 and the right electrode (orange circles). As can be seen, the sum matches well with the spectra across the entire sample. The polarization resistance in 100% O_2 is much smaller than in 1% O_2.

Figure 7(a) shows a plot of overpotential vs. current density for the left electrode determined using equation (1) in a gas mixture containing 1% O_2. The plot is not linear and the intercept is near zero as expected. The nonlinearity can be described by Tafel type behavior. Fitting the low overpotential regime to a straight line gives a polarization resistance of ~4277 Ωcm^2. Figure 7(b) shows a similar plot for the right electrode. The intercept is nonzero. The width of the Pt strips was about 2 mm. The nonzero intercept is thus believed to be due to too wide Pt strips, which may have prevented an accurate measurement of YSZ resistance needed in equation (1). This probably resulted in over estimation of the ohmic polarization and due to a smaller polarization led to some error in these measurements. For the right electrode, the polarization resistance was estimated as ~443 Ωcm^2.

Figure 8(a) shows a plot of overpotential vs. current density for the left electrode using equation (1) in a gas mixture containing 100% O_2. The plot is not linear and the intercept is near zero as expected. Approximate fitting to a straight line gives a polarization resistance of ~1056 Ωcm^2. Figure 7(b) shows a similar plot for the right electrode. The intercept is nonzero. The width of the Pt strips was about 2 mm. The nonzero intercept is thus believed to be due to too wide Pt strips, which may have prevented accurate measurement of YSZ resistance needed in equation (1). For the right electrode, the polarization resistance is ~136 Ωcm^2. For electrode-1, the intercept is nearly zero since the absolute values of the polarization resistance are much larger than those for electrode-2. The very high polarization resistances measured suggests that the electrodes were not of god quality. Electrode microstructure will be examined to determine if the LSM and YSZ phases were not contiguous or if the porosity was not sufficient. The objective of this work was to determine if electrode polarization resistances can be measured separately. Future work will focus on using highly active electrodes.

IV. Summary

Electrode polarizations were measured on LSM + YSZ electrodes on a YSZ cylinder by both DC and EIS techniques. Four platinum strips were applied circumferentially along the length of the cylinder. In DC measurements, a DC voltage was applied across the sample and potentials were measured at the four probes. From these measurements, the ionic resistivity of YSZ and electrode overpotentials for the two electrodes were separately measured. EIS spectra were obtained across electrode-1 and probe-2 and across probe-2 and electrode-2. From these measurements, electrode polarizations of the two electrodes were separately obtained. EIS spectra were also obtained across electrode-1 and electrode-2. These spectra matched well with the sum of the spectra across electrode-1 and probe-2 and across probe-2 and electrode-2. This shows that electrode polarizations could be obtained separately for the two electrodes.

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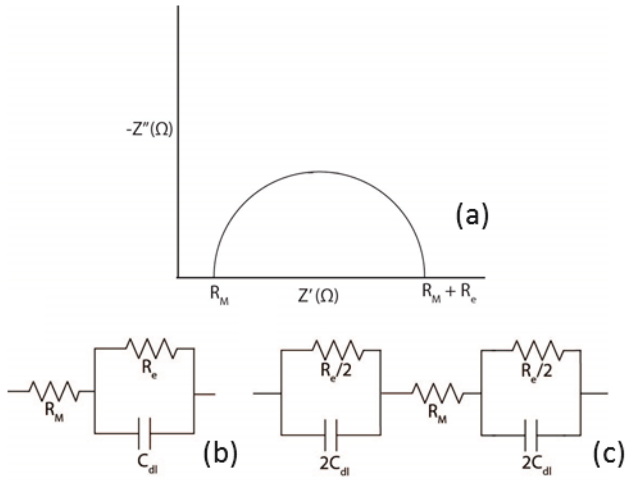

Figure 1: (a) Schematic EIS spectra which is a semicircle. (b) A possible equivalent circuit in which one electrode is perfect (zero polarization resistance). (c) A possible equivalent circuit in which both electrodes are identical. Both circuits give the same EIS spectra shown in (a).

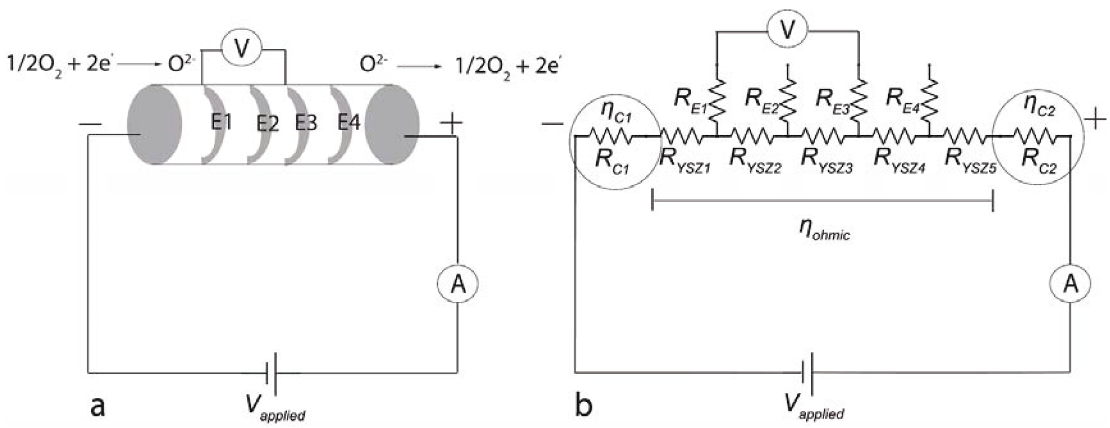

Figure 2: (a) A schematic of the sample. (b) The corresponding equivalent circuit.

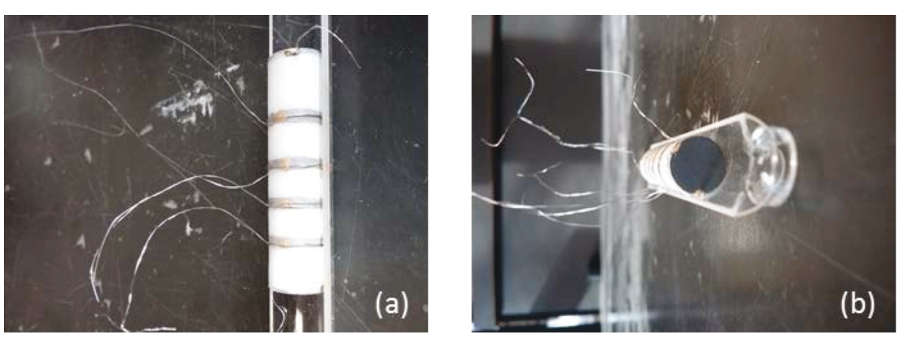

Figure 3: (a) A photograph of the YSZ sample with four Pt wires attached to the Pt strip electrodes. (b) A photograph showing the circular LSM + YSZ electrode.

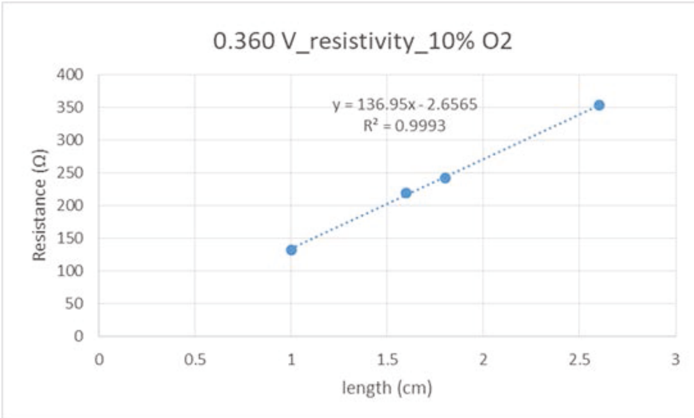

Figure 4: Resistance as a function of distance, measured at the four probes in 10% O_2. The slope gives the resistance per unit length.

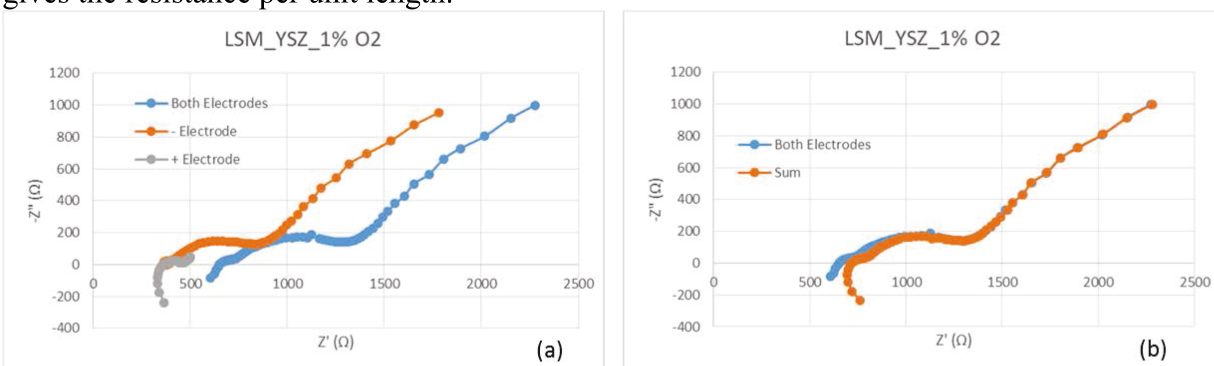

Figure 5: (a) EIS spectra across electrode-1 and electrode-2 (blue), electrode-1 and probe-2 (orange) and probe-2 and electrode-2 (grey) in 1% O_2. (b) EIS spectra across electrode-1 and electrode-2 (blue), and point by point sum of spectra across electrode-1 and probe-2 and probe-2 and electrode-2 (orange) in 1% O_2.

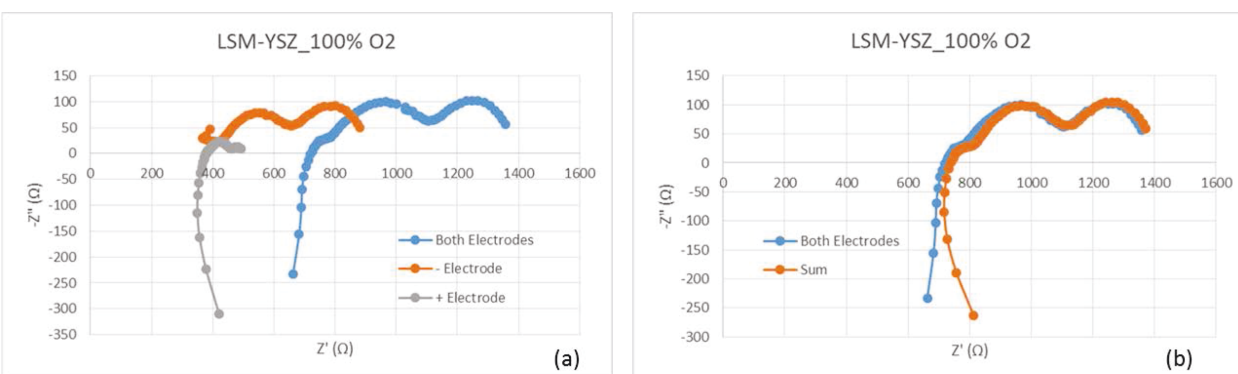

Figure 6: (a) EIS spectra across electrode-1 and probe-2 (grey), probe-2 and electrode-2 (orange), and across electrode-1 and electrode 2 (blue) in 100% O_2. (b) EIS spectra across electrode-1 and electrode-2 (blue), and point by point sum of spectra across electrode-1 and probe-2 and probe-2 and electrode-2 (blue) in 100% O_2.

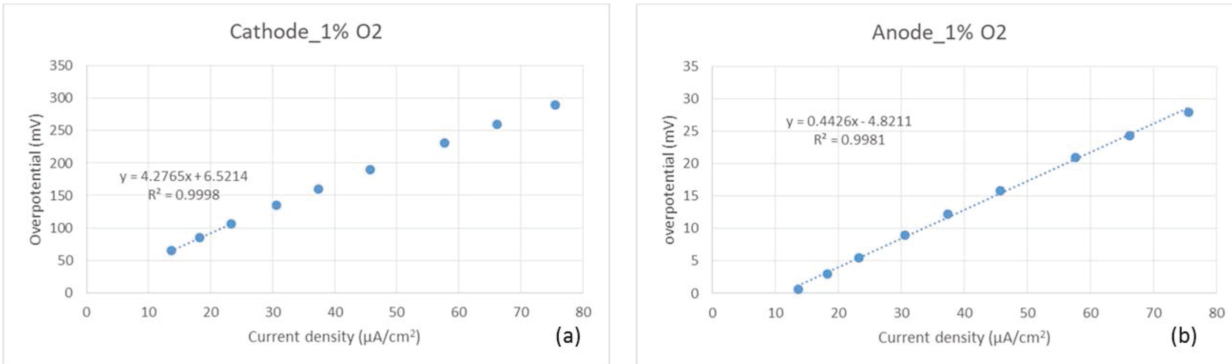

Figure 7: (a) Overpotential vs. current density for electrode-1 (cathode) in 1% O_2. (b) Overpotential vs. current density for electrode-2 (anode) in 1% O_2.

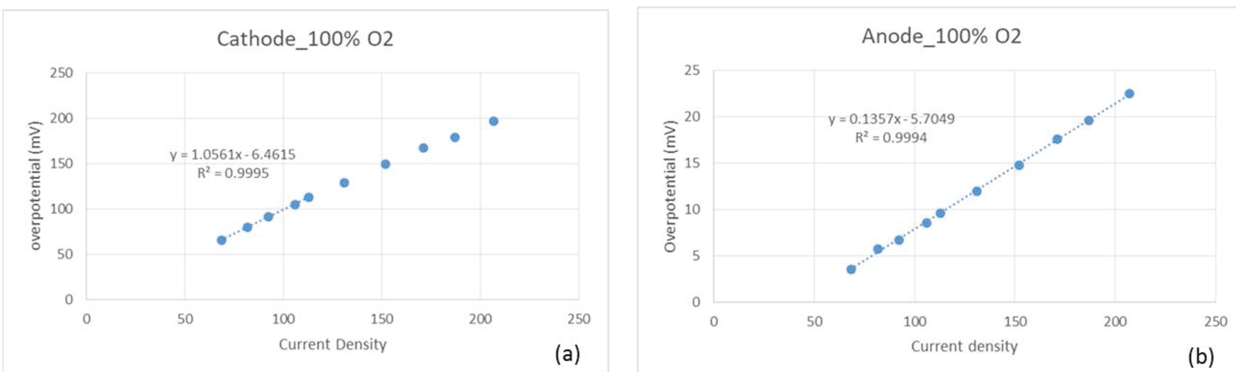

Figure 8: (a) Overpotential vs. current density for electrode-1 (cathode) in 100% O_2. (b) Overpotential vs. current density for electrode-2 (anode) in 100% O_2.