REPORT TITLE:

**ACTIVE CATHODES FOR SUPER-HIGH POWER DENSITY SOLID OXIDE
FUEL CELLS THROUGH SPACE CHARGE EFFECTS**

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ABSTRACT

This report summarizes the work done during the ninth quarter of the project. Effort was devoted towards evaluating the charge transfer characteristics using patterned electrodes. This is an extension of our earlier work on LSM/YSZ system. The work reported here was conducted on platinum (Pt)/YSZ. Even though Pt is expensive, as long as the amount used is very small, cost is not a consideration. The intended use is thus by infiltration of Pt (or other noble metals) using a solution of Pt (or other noble metal) salt into a standard cathode (such as that made with LSM and YSZ). A manuscript based on this work has been accepted for publication in the Journal of the Electrochemical Society. This report includes parts of the manuscript accepted for publication in the Journal of the Electrochemical Society.

Yttria-Stabilized Zirconia (YSZ) electrolyte discs with patterned platinum (Pt) electrodes having different three phase boundary (TPB) lengths (l_{TPB}), but the same electrode-electrolyte interface area, were deposited on one of the two faces using photomicroolithography. Platinum counter electrode was applied on the other face, and a platinum wire reference electrode was positioned along the cylindrical surface. Impedance spectra under zero applied bias were obtained in oxygen partial pressures, (p_{O_2}), ranging between 10^{-3} and 1 atm and over a range of temperatures between 650 and 800°C. Area specific charge transfer resistance, R_{ct} , was found to vary inversely with l_{TPB} . The value of charge transfer resistivity, ρ_{ct} , corresponding to the charge transfer reaction occurring at TPB, was estimated at various temperatures and p_{O_2} . The R_{ct} and ρ_{ct} decrease with increasing p_{O_2} and with increasing temperature. The activation energy for the overall charge transfer reaction was found to vary between 0.75 eV at a p_{O_2} of 0.001 atm and 1.63 eV for a p_{O_2} of 1 atm.

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INTRODUCTION

Electrode transport properties, namely ionic and electronic conductivities, and morphology have a profound effect on electrode polarization and thus on solid oxide fuel cell (SOFC) performance. A large part of the polarization loss is associated with the cathode in the form of activation polarization. In most studies on polarization studies, the microstructure is rarely characterized or analyzed. Important microstructural parameter for composite electrodes is the three phase boundary (TPB) length. Thus, measured polarization resistance using screen-printed electrodes at best is applicable for the particular material used with whatever may be the particle size, loading and the unknown TPB. Thus, most published works on the measurement of polarization resistance offer little information of a fundamental nature. In this work, patterned Pt electrodes were deposited using micro photo lithography on YSZ discs, and polarization resistance was measured using the three-electrode system under zero applied bias. From these measurements, charge transfer resistivity, $\rho_{ct}(T, p_{O_2})$ of Pt/YSZ was measured over a range of temperatures and oxygen partial pressures. As-measured $\rho_{ct}(T, p_{O_2})$ provides fundamental information on charge transfer (activation process), free of microstructural effects. Once such measurements are made, in principle, the activation polarization resistance of a given electrode can be estimated, provided microstructural details are known.

EXECUTIVE SUMMARY

Solid oxide fuel cells (SOFC) can operate over a wide temperature range, from ~600 to 1000°C, and can use a variety of hydrocarbon fuels, once appropriately processed. The current target for SOFC is about 800°C, although efforts are presently underway to lower the operating temperature below 700°C. The largest voltage loss (polarization) in SOFC is known to occur at the cathode, especially at relatively low temperatures (<800°C). There are two types of cathodic polarizations: (1) Concentration polarization – that associated with gas transport. (2) Activation polarization – that associated with the occurrence of the overall electrochemical cathodic reaction of charge transfer. The fundamental parameter governing the activation polarization, free of microstructural effects, is the charge transfer resistivity, $\rho_{ct}(T, p_{O_2})$. This report describes the use of patterned electrodes to measure $\rho_{ct}(T, p_{O_2})$ at a Pt/YSZ TPB. A manuscript based on this work was accepted recently for publication in the Journal of the Electrochemical Society.

The objective of the present work was to investigate the cathode reaction mechanism at a platinum electrode using patterned electrodes. Many studies have been reported on the oxygen reduction kinetics at platinum electrodes, but there appear to be no reported studies using platinum electrodes of well-defined geometry as used in this study [1-8]. In addition, there is no unanimity on the exact details of the cathodic reaction process though it is generally believed that the reaction steps include adsorption of oxygen, dissociation of molecular species into atomic species, migration of molecular or atomic species to the TPB region, the occurrence of electron transfer reaction and the transfer of ions across the TPB region into the solid electrolyte. Often for simplicity it is assumed that one of the above is the rate-limiting step with the rest of the steps being close to equilibrium, although this is often an oversimplification. Several rate-limiting steps in the charge transfer mechanism have been reported and the variation of the polarization resistance on p_{O_2} has been reported to follow either $p_{O_2}^{-1/2}$ or $p_{O_2}^{-1}$ dependence [1-10]. The reported literature thus shows that while the p_{O_2} dependence of the charge transfer resistance is reasonable, the details of the overall reaction mechanisms are not well understood.

The present work was undertaken to investigate charge transfer characteristics at the Pt/YSZ/gas phase TPB using patterned electrodes and compare the results with those obtained on the LSM/YSZ/gas phase system [11]. Patterned platinum electrodes of well-defined TPBs were sputter-deposited on sintered YSZ discs and impedance spectroscopy under zero applied bias was used to obtain the polarization resistance over a range of temperatures between 650 and 800°C and a p_{O_2} range between 10^{-3} and 1 atm.

EXPERIMENTAL

Discs of YSZ (Tosoh Corporation, Japan) were fabricated using conventional ceramic processing methods involving die-pressing of powder compacts followed by sintering in air. The powder was pressed in a circular die using a uni-axial press under a load of 4,500 kg. The discs obtained were then sintered at 1500°C for 5 hours in air. One surface of each disc was polished to a 1 micron finish. After polishing, a groove was machined along the cylindrical surface of the disc at a distance of nearly 1.5 mm from the polished surface. The discs were then cleaned in soap solution followed by rinsing in acetone, in de-ionized water and dried at 500°C for 2 hours.

Patterned (line patterns with electrode-electrolyte contact area fraction $A_A = 0.5$) platinum electrodes corresponding to a wide range of l_{TPBP} were fabricated on the polished surfaces in a circular area of 1 cm diameter (area = 0.785 cm²) at the center of each disc using photomicro lithography and sputtering techniques. In order to obtain the line pattern of the electrode, the disc was initially coated with positive photoresist Shipley 1818 and was baked at 100°C for 5 minutes. The sample was then exposed to UV light for 20 seconds using previously prepared dark field masks with appropriate line patterns. The exposed samples were developed using MF 321 developer for nearly 30 seconds, rinsed in DI water and dried. Samples with various patterns were prepared using different masks, each having the same A_A but different l_{TPBP} . The patterned samples were then loaded into a sputtering chamber. Platinum electrodes of nearly 1 µm thickness were sputter deposited using a platinum target by DC sputtering using argon plasma. The YSZ discs were held at a distance of ~15 cm from the target and were at room temperature during sputtering. The chamber pressure was kept at a low pressure (1 mTorr) to obtain a dense thin film of platinum. After sputtering the discs were washed in acetone to lift off the photoresist and the platinum film on top of the photoresist, giving rise to the desired platinum line pattern. The discs with platinum patterned electrodes were later annealed at 900°C for 2 hours. The electrode morphology was examined before and after annealing, and after electrochemical testing using an optical profilometer and a scanning electron microscope (SEM).

A counter electrode of platinum was applied using platinum resinate, again in a circular area of 1 cm diameter, at the center of the opposite face of the disc so that it is symmetric with respect to the patterned platinum working electrode. The discs were again annealed at 900°C for 2 hours to remove organic components from platinum resinate and to obtain a well-bonded, porous platinum counter electrode. A platinum reference electrode in the form of a ring was positioned along the groove on the cylindrical surface of the disc.

Platinum mesh was used as contact on both working and counter electrodes. The sample was then assembled between two alumina rings with the help of two honeycomb alumina discs, two threaded rods, springs and wing nuts. Care was taken to ensure that both the working and the counter electrodes were completely exposed to the external atmosphere, while firmly holding the platinum contact mesh onto the electrodes. Electrical connections were made to the platinum meshes by connecting platinum wires to them. The sample assembly was then placed

inside an alumina tube such that the disc was near the closed end of the tube, with the working electrode always facing the closed end of the tube. The tube was tightly sealed using a rubber cork. Holes were drilled in the cork through which the platinum leads for electrical connection and the rods to hold the disc were inserted. Gas inlet and outlet tubes were also inserted through the rubber cork. The inlet tube was long enough to ensure the release of gas very close to the working electrode. The alumina tube containing the disc assembly was then placed in a horizontal tube furnace such that the disc was positioned near the center of the furnace. The tip of a thermocouple was placed very near the disc to measure the temperature. The inlet tube was connected to compressed gas cylinders containing premixed gases of desired compositions. A flow rate of nearly 200 ml/minute was used to continuously circulate the desired premixed gas of a given oxygen partial pressure. The system was allowed to equilibrate at each condition of temperature and oxygen partial pressure before making measurements. Impedance spectra were obtained using Solartron Impedance/gain-phase analyzer (SI-1260) in combination with Solartron Electrochemical Interface (SI-1287), over a range of temperatures between 650 and 800°C, and in gas mixtures with oxygen partial pressure ranging between 10^{-3} and 1 atm.

RESULTS AND DISCUSSION

Morphology of the Platinum electrode:

Figure 1 shows a schematic of a TPB at which charge transfer occurs. An optical profilometric trace of the as-sputtered platinum electrode is shown in Figure 2 and an SEM image of the same is shown in Figure 3(a), both of which clearly show a well-defined line pattern. The l_{TPBp} of this sample was 250 cm^{-1} . The images show that the as-prepared electrode edges are smooth and continuous. This allows precise determination of the l_{TPBp} , which was varied from sample to sample by varying the width of the line and the space between the lines, while keeping the A_A constant. The l_{TPBp} for the various patterns, as-calculated from the geometry of the as-sputtered electrodes, were 500, 250, 100 and 50 cm^{-1} (corresponding to platinum line widths of 20, 40, 100 and 200 microns, respectively). An SEM image of the sample with $l_{TPBp} = 250 \text{ cm}^{-1}$ after testing is shown in Figure 3(b). After annealing and testing, the electrode morphology changed substantially. The edges of the electrode appeared wavy and the electrode developed pits. The waviness of the edges (α) increases the TPB length from l_{TPBp} to $l_{TPBp}(1 + \alpha)$. The pits inside the electrode area, which appear to form due to some de-wetting and coalescence, introduce additional three-phase boundary length (TPB), namely l_{TPB_0} . Hence the actual three-phase boundary length is higher by l_{TPB_0} . It was assumed that most of the morphological change occurred during annealing and the first few hours in the test setup, and thereafter the morphology did not change with time. Thus, for the calculations of charge transfer resistance from a given sample, the final morphology was assumed for all measurements. The $l_{TPBp}(1 + \alpha)$ was estimated from SEM pictures by using a very thin thread. The thread was initially placed carefully along the jagged edges of the platinum electrode on high magnification SEM images, so that it follows the shape of the electrode edge as closely as possible. The thread was then straightened and its length was measured. The ratio of the thread length to the edge length gives $(1 + \alpha)$. The estimated value of α was found to be ~ 0.26 . The

l_{TPB_0} was estimated using techniques in quantitative stereology [12]. For this measurement, all tested samples were examined under SEM and several micrographs were obtained randomly on the patterned electrode area of each sample. Horizontal and vertical test lines were drawn on the images of the platinum-covered surfaces and the point intersections per unit length (p_L) where the pits in the film intercept the test line, were measured. The length of the perimeter of the pores in the film per unit area (L_A) was estimated using the equation $L_A = \frac{\pi}{2} p_L$ [12]. The average value of L_A was found to be $1588 \pm 28 \text{ cm}^{-1}$. The area fraction of platinum in the patterned electrode, A_A , is 0.50. Therefore, we have $l_{TPB_0} = A_A \times L_A = 0.50 \times 1588 = 794 \text{ cm}^{-1}$. Using the estimated values of α and l_{TPB_0} , the total l_{TPB} calculated for the four samples were ~ 1430 , ~ 1110 , ~ 920 , and $\sim 860 \text{ cm}^{-1}$, respectively, corresponding to l_{TPBp} of 500, 250, 100 and 50 cm^{-1} .

In the case of LSM patterned electrodes examined in an earlier study, the electrode morphology did not change during annealing or testing [11]. The edges of LSM patterned electrodes appeared very smooth even under high magnification SEM. Hence, in the case of LSM patterned electrodes, the α was taken to be zero in the analysis. Also l_{TPB_0} was mainly due to the defects (pores) in the substrate and no pits developed in the electrode area, unlike the case of platinum electrodes of this study. This could be due to possible better wetting between LSM and YSZ and/or slow transport (of cations) in LSM, which prevents shape changes at the low testing temperatures ($< 800^\circ\text{C}$).

Impedance Analysis:

The impedance spectra obtained on patterned platinum electrodes deposited on YSZ with different l_{TPBp} in air at 800°C , and those obtained on a sample with $l_{TPBp} = 250 \text{ cm}^{-1}$ at various temperatures and in oxygen partial pressures, are given in Figures 4 through 6. The impedance spectra typically consisted of suppressed semicircular arcs. The high frequency intercept of the arc on the real axis (R_1) corresponds to the ohmic resistance and the low frequency intercept (R_2) corresponds to the total resistance of the half cell (between the working and the reference electrodes). In Figures 4 and 5, which correspond to measurements at 800°C , the ohmic part (R_1) is essentially the same. The R_1 for all samples with different l_{TPBp} in Figure 4 is expected to be the same, since it is mainly due to the resistance of the YSZ disc between the working and the reference electrodes. The R_1 does not change with change in p_{O_2} (Figure 5), since over this p_{O_2} range, the ionic conductivity of YSZ is essentially independent of p_{O_2} . In addition, over the short duration of the experiment, the stoichiometry of the interior of the YSZ disc is not expected to change. In Figure 6, in which measurements are given over a range of temperatures between 650°C and 800°C , it can be seen that R_1 decreases with increasing temperature due to the temperature dependence of the ionic conductivity of YSZ. Polarization resistance of the electrode was obtained by subtracting R_1 from R_2 . From the impedance spectra (Figures 4 through 6) it is seen that the polarization resistance depends on l_{TPB} , the oxygen partial pressure, p_{O_2} , and the temperature. The R_{ct}

was calculated by multiplying the polarization resistance with the total electrode area (0.785 cm²).

Dependence of R_{ct} on the three phase boundary length (l_{TPB}):

Figure 7(a) shows plots of $1/R_{ct}$ vs. l_{TPBp} at 800°C in atmospheres with different p_{O_2} and Figure 8(a) shows similar plots in air at different temperatures. It is seen that the $1/R_{ct}$ increases linearly with l_{TPBp} . The inverse of slope gives the charge transfer resistivity divided

by $(1 + \alpha)$, namely $\frac{\rho_{ct}}{(1 + \alpha)}$. It can be seen that a value of zero for l_{TPBp} gives a finite R_{ct} value, i.e., a finite y-intercept. This intercept is given by $\frac{l_{TPB0}}{\rho_{ct}}$. Similar non-zero intercepts for

$1/R_{ct}$ have been reported for microfabricated Ni anodes and LSM cathodes [11,13,14]. The ratio of the y-intercept to the slope of these plots (or the magnitude of the intercept on the negative x-axis) gives $\frac{l_{TPB0}}{(1 + \alpha)}$. Figure 7(b) shows plots of $1/R_{ct}$ vs.

$l_{TPB} = l_{TPBp}(1 + \alpha) + l_{TPB0}$ at 800°C in atmospheres with different p_{O_2} and Figure 8(b) shows similar plots in air at different temperatures. The inverse of slope of these plots gives the charge transfer resistivity, ρ_{ct} , which is a function of temperature and p_{O_2} . It can also be seen that now the linear extrapolation essentially goes through the origin, which is consistent with the assumption that negligible oxygen transport occurs through platinum under the experimental conditions investigated, and virtually all of the charge transfer occurs at the three phase boundaries (TPB). While varying the l_{TPBp} from 50 to 500 (10 fold), the actual l_{TPB} varied only from 860 to 1430 (1.67 fold), due to the significant contribution of l_{TPB0} . Hence, if the charge transfer reaction were to take place only at the TPB, it is expected that R_{ct} should also vary by a factor of 1.67 for the range of l_{TPBp} studied. It was found that R_{ct} varied by nearly the same factor for the range of temperatures and pressures studied, indicating that the charge transfer reaction predominantly occurs at the TPB. The values of ρ_{ct} at different temperatures and p_{O_2} were estimated from the plots of $1/R_{ct}$ vs. l_{TPB} and are summarized in Table 1.

For LSM electrodes also, a linear relation between $1/R_{ct}$ and l_{TPBp} was observed consistent with the occurrence of charge transfer reaction at TPB, but with a nonzero, finite value of $1/R_{ct}$ for zero l_{TPBp} [11]. The finite, nonzero value of $1/R_{ct}$ for zero l_{TPBp} in the case of LSM electrodes, however, could not be accounted for exclusively by l_{TPB0} , especially at higher temperatures. The difference was attributed to the occurrence of some mixed conduction through LSM. The contribution of transport through LSM, however, was judged to be rather small at temperatures equal to or lower than 800°C. In the case of platinum electrodes, it appears that transport of oxygen through platinum is even smaller. Thus, it can be concluded that at temperatures lower than 800°C, the charge transfer reaction in the case of platinum-YSZ

system occurs almost exclusively at TPB. The estimated value of ρ_{ct} for platinum on YSZ at 800°C in air was nearly 20 times lower than that of LSM on YSZ, indicating that platinum is a better electrocatalyst for oxygen reduction on YSZ than LSM.

Dependence of R_{ct} and ρ_{ct} on oxygen partial pressure (p_{O_2}):

The measured R_{ct} was found to increase with decreasing p_{O_2} . Plots of ρ_{ct} vs. $\frac{1}{p_{O_2}}$ and

$\rho_{ct} p_{O_2}$ vs. p_{O_2} (associative adsorption) and ρ_{ct} vs. $\frac{1}{\sqrt{p_{O_2}}}$ and $\rho_{ct} \sqrt{p_{O_2}}$ vs. $\sqrt{p_{O_2}}$

(dissociative adsorption) are given respectively in Figures 9 and 10. It can be seen that in the two plots for associative adsorption (Figures 9(a) and 9(b)) and those for dissociative adsorption (Figures 10(a), and 10(b)) the slope in one plot (a) should be the intercept in the other (b) and vice-a-versa. The value of b' and b^* (Table 2) and ρ_{ct}'' (Table 3) were estimated from the slopes and intercepts of the respective plots. These values estimated from Figures 9(a) and 9(b) corresponding to the associative adsorption model do not agree very well with each other, but those estimated from Figures 10(a) and 10(b) corresponding to dissociative adsorption are in better agreement. This suggests that the adsorption mechanism is most likely dissociative, and not associative. But it should also be noted that while using the associative adsorption model it is not necessary to assume that adsorption of nitrogen is negligible, although in that case it will not be possible to estimate b' or ρ_{ct}'' . The estimated values of both b' and b^* were found to decrease with increasing temperature. The temperature dependence of adsorption coefficient can be given by $b(T) = b_0 \exp\left(-\frac{E_{ads}}{k_B T}\right)$, (in which b represents b' or b^*) where E_{ads} is negative. The magnitude of E_{ads} calculated from the slope of the Arrhenius plots of the estimated value of b^* , is given in Figure 11 and is between ~1.16 and ~1.3 eV.

For LSM electrodes of [11] also, the measured R_{ct} was found to increase with decrease in p_{O_2} and the p_{O_2} dependence of R_{ct} was also found to be in better agreement with the dissociative adsorption model. But in that case b^* did not vary much with temperature indicating that the magnitude of E_{ads} is rather small in the case of LSM cathode on YSZ.

Dependence of R_{ct} and ρ_{ct} on temperature:

It was found that R_{ct} and ρ_{ct} increase exponentially with decreasing temperature. All samples with different TPB exhibited the same dependence of R_{ct} on temperature. In Figure 12(a), $\ln(\rho_{ct})$ is plotted vs. inverse of absolute temperature for various p_{O_2} . From the slopes of the plots, the activation energy (E_a) for the overall charge transfer process was estimated. It was observed that the activation energy varied over the p_{O_2} range investigated and was found to

increase with increasing p_{O_2} , ranging between 0.75 eV at 0.001 atm and 1.63 at 1 atm. It was further noted that the activation energy for ρ_{ct}'' (the charge transfer resistance at a surface coverage equal to 1) from dissociative adsorption model estimated from the Arrhenius plot in Figure 12(b) is between ~1.65 and ~1.88 eV.

Also for LSM electrodes, it was found that R_{ct} and ρ_{ct} increase exponentially with decrease in temperature [11]. The E_a for the overall charge transfer process in the case of LSM on YSZ was ~1.5 eV and was more or less the same for the entire p_{O_2} range studied.

Implications of the Temperature and p_{O_2} dependence of ρ_{ct} :

It was show that (described in detail in the manuscript accepted for publication in the Journal of the Electrochemical Society) that a relationship between ρ_{ct} , ρ_{ct}'' and p_{O_2} for the dissociative adsorption model can be given as follows

$$\rho_{ct} = \rho_{ct}'' \left(\frac{1 + b^* \sqrt{p_{O_2}}}{b^* \sqrt{p_{O_2}}} \right) \quad (1)$$

in which ρ_{ct}'' and b^* are not functions of p_{O_2} . At high values of p_{O_2} , that is for $b^* \sqrt{p_{O_2}} \gg 1$, the above equation can be approximated by

$$\rho_{ct} \approx \rho_{ct}'' \quad (2)$$

and the temperature dependencies of ρ_{ct} and ρ_{ct}'' are essentially the same. The temperature dependence of ρ_{ct}'' may be given as

$$\rho_{ct}'' \approx \rho_{ct(0)}'' \exp \left[\frac{E_a}{k_B T} \right] \quad (3)$$

where $E_a > 0$. Note that as the temperature increases, ρ_{ct}'' decreases. At low values of p_{O_2} , $b^* \sqrt{p_{O_2}} \ll 1$, and equation (1) can be approximated by

$$\rho_{ct} \approx \frac{\rho_{ct}''}{b^* \sqrt{p_{O_2}}} \quad (4)$$

The temperature dependence of b^* may be given by

$$b^* = b_0^* \exp \left[- \frac{E_{ads}}{k_B T} \right] \quad (5)$$

where $E_{ads} < 0$. Note that as the temperature increases, b^* decreases. Thus, the temperature dependence of ρ_{ct} may be given by

$$\rho_{ct} \approx \frac{\rho_{ct(0)}''}{b_0^* \sqrt{p_{O_2}}} \exp \left[\frac{(E_a + E_{ads})}{k_B T} \right] \quad (6)$$

where note that $E_a > E_a + E_{ads}$. Thus, we expect effective higher activation energy at higher p_{O_2} . That is, as the temperature decreases, both ρ_{ct}'' and b^* increase such that the temperature dependence of ρ_{ct} in that case should be weaker. Indeed, as seen in Figure 12(a), the activation energy is higher at higher values of p_{O_2} . As stated earlier, in the case of LSM on YSZ [11], the activation energy was essentially independent of p_{O_2} over the range investigated, which suggests a weaker adsorption of oxygen on LSM as compared that on platinum.

CONCLUSION

Electrochemical reaction of oxygen reduction was investigated at platinum/YSZ electrodes using patterned electrodes deposited by photomicroolithography. A linear relation between $1/R_{ct}$, where R_{ct} is the area specific charge transfer resistance, and l_{TPB} , where l_{TPB} is the TPB line length (cm^{-1}) consistent with the occurrence of charge transfer at TPB was observed over the range of temperatures and oxygen partial pressures, p_{O_2} , examined. Similar results were previously observed on LSM/YSZ system [11]. In addition, the plots essentially went through the origin, indicating that the charge transfer reaction almost exclusively occurred at TPB, with negligible transport through platinum. By contrast, in the case of LSM/YSZ at high temperatures (800°C), small contribution due to transport through LSM was noted [11]. The slope of the plot of $1/R_{ct}$ vs. l_{TPB} , gives the charge transfer resistivity, ρ_{ct} . The estimated value of ρ_{ct} is nearly 20 times lower for platinum on YSZ than that for LSM on YSZ, indicating a higher catalytic activity of platinum than LSM for the oxygen reduction reaction. R_{ct} and ρ_{ct} decrease with increase in p_{O_2} and increase in temperature. Assuming the adsorption of nitrogen is negligible, the variation of measured R_{ct} with p_{O_2} agrees better with the dissociative adsorption model rather than associative adsorption model. The adsorption coefficients were found to vary exponentially with temperature with an activation energy between ~ 1.16 and ~ 1.3 eV. The estimated activation energy for the charge transfer resistivity, ρ_{ct} , varied from 0.75 eV for p_{O_2} of 0.001 atm and 1.65 eV for $p_{O_2} \sim 1$ atm. The activation energy for charge transfer resistivity corresponding to an oxygen surface coverage of 1, namely ρ_{ct}'' , was estimated to be between ~ 1.65 and ~ 1.88 eV.

FIGURE CAPTIONS

Figure 1: Model for charge transfer at a three phase boundary (TPB). In this figure the dimensions are not to scale. While the electrode thickness, width, and electrolyte dimension are on the order of microns, the region through which the actual charge transfer occurs (ε and δ) are on the order of Angstroms.

Figure 2: An optical profilometric trace of platinum patterned electrode on YSZ with $l_{TPBp} = 250 \text{ cm}^{-1}$.

Figure 3: SEM images of a platinum patterned electrode on YSZ with $l_{TPBp} = 250 \text{ cm}^{-1}$ (a) as sputtered, and (b) after testing.

Figure 4: Impedance spectra obtained on YSZ discs with different l_{TPBp} in air at 800°C. The frequency ranges from $f_i = 1 \text{ MHz}$ to $f_f = 0.01 \text{ Hz}$. The frequency at which each spectrum initially crosses the real axis of the impedance, f_{R1} , and the frequency at which the imaginary part reaches its highest value (magnitude), $f_{\max}$, are marked on the spectra.

Figure 5: Impedance spectra obtained on a YSZ disc with $l_{TPBp} = 250 \text{ cm}^{-1}$ at 800°C at various p_{O_2} . The frequency ranges from $f_i = 1 \text{ MHz}$ to $f_f = 0.01 \text{ Hz}$. The frequency at which each spectrum initially crosses the real axis of the impedance, f_{R1} , and the frequency at which the imaginary part reaches its highest value (magnitude), $f_{\max}$, are marked on the spectra.

Figure 6: Impedance spectra obtained on a YSZ disc with $l_{TPBp} = 250 \text{ cm}^{-1}$ in air at various temperatures. The frequency ranges from $f_i = 1 \text{ MHz}$ to $f_f = 0.01 \text{ Hz}$. The frequency at which each spectrum initially crosses the real axis of the impedance, f_{R1} , and the frequency at which the imaginary part reaches its highest value (magnitude), $f_{\max}$, are marked on the spectra.

Figure 7(a): Plots of $1/R_{ct}$ vs. l_{TPBp} at 800°C at various p_{O_2} .

Figure 7(b): Plots of $1/R_{ct}$ vs. l_{TPB} at 800°C at various p_{O_2} .

Figure 8(a): Plots of $1/R_{ct}$ vs. l_{TPBp} in air at various temperatures.

Figure 8(b): Plots of $1/R_{ct}$ vs. l_{TPB} in air at various temperatures.

Figure 9(a): Plots of ρ_{ct} vs. $1/p_{O_2}$ at various temperatures (associative adsorption model).

Figure 9(b): Plots of $\rho_{ct} p_{O_2}$ vs. p_{O_2} at various temperatures (associative adsorption model).

Figure 10(a): Plots of ρ_{ct} vs. $1/\sqrt{p_{O_2}}$ at various temperatures (dissociative adsorption model).

Figure 10(b): Plots of $\rho_{ct} \sqrt{p_{O_2}}$ vs. $\sqrt{p_{O_2}}$ at various temperatures (dissociative adsorption model).

Figure 11: Arrhenius plots of b^* (dissociative adsorption model).

Figure 12(a): Arrhenius plots of ρ_{ct} at various oxygen partial pressures.

Figure 12 (b): Arrhenius plots of ρ_{ct}'' estimated from the dissociative adsorption model.

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Figure 3: SEM images of a platinum patterned electrode on YSZ with $l_{TPBp} = 250 \text{ cm}^{-1}$ (a) as sputtered, and (b) after testing.

Figure 4: Impedance spectra obtained on YSZ discs with different l_{TPBP} in air at 800°C. The frequency ranges from $f_i = 1 \text{ MHz}$ to $f_f = 0.01 \text{ Hz}$. The frequency at which each spectrum initially crosses the real axis of the impedance, f_{R1} , and the frequency at which the imaginary part reaches its highest value (magnitude), f_{max} , are marked on the spectra.

Figure 5: Impedance spectra obtained on a YSZ disc with $l_{TPBp} = 250 \text{ cm}^{-1}$ at 800°C at various p_{O_2} . The frequency ranges from $f_i = 1 \text{ MHz}$ to $f_f = 0.01 \text{ Hz}$. The frequency at which each spectrum initially crosses the real axis of the impedance, f_{R1} , and the frequency at which the imaginary part reaches its highest value (magnitude), f_{max} , are marked on the spectra.

Figure 6: Impedance spectra obtained on a YSZ disc with $l_{TPBP} = 250 \text{ cm}^{-1}$ in air at various temperatures. The frequency ranges from $f_i = 1 \text{ MHz}$ to $f_f = 0.01 \text{ Hz}$. The frequency at which each spectrum initially crosses the real axis of the impedance, f_{R1} , and the frequency at which the imaginary part reaches its highest value (magnitude), f_{max} , are marked on the spectra.

Figure 7(a): Plots of $1/R_{ct}$ vs. l_{TPBP} at 800°C at various p_{O_2} .

Figure 7(b): Plots of $1/R_{ct}$ vs. l_{TPB} at 800°C at various p_{O_2} .

Figure 8(a): Plots of $1/R_{ct}$ vs. l_{TPBp} in air at various temperatures.

Figure 8(b): Plots of $1/R_{ct}$ vs. l_{TPB} in air at various temperatures.

Figure 9(a): Plots of ρ_{ct} vs. $1/p_{O_2}$ at various temperatures (associative adsorption model).

Figure 9(b): Plots of $\rho_{ct} p_{O_2}$ vs. p_{O_2} at various temperatures (associative adsorption model).

Figure 10(a): Plots of ρ_{ct} vs. $1/\sqrt{p_{O_2}}$ at various temperatures (dissociative adsorption model).

Figure 10(b): Plots of $\rho_{ct}\sqrt{p_{O_2}}$ vs. $\sqrt{p_{O_2}}$ at various temperatures (dissociative adsorption model).

Figure 11: Arrhenius plots of b^* (dissociative adsorption model).

Figure 12(a): Arrhenius plots of ρ_{ct} at various oxygen partial pressures.

Figure 12 (b): Arrhenius plots of ρ_{ct}'' estimated from the dissociative adsorption model.

TABLES

Table 1: Values of ρ_{ct} ($\Omega\text{-cm}$) estimated from $1/R_{ct}$ vs. l_{TPB} plots at various temperatures and oxygen partial pressures

Temp \ p_{O_2}	1 atm	0.21 atm	0.1 atm	0.05 atm	0.01 atm	0.001 atm
800°C	2900	5200	7300	8700	13700	39200
750°C	6700	9500	11400	14100	22700	41100
700°C	19900	26100	27600	30600	42400	69400
650°C	48200	52900	59000	67300	84400	137500

Table 2: Estimated values of adsorption coefficients from Figures 9 and 10.

	Estimated from	800°C	750°C	700°C	650°C
Associative b'	Figure 9a	199.35	397.27	658.4	753.9
	Figure 9b	9.9	19.8	34.5	67.07
Dissociative b^*	Figure 10a	2.4	7.55	14.9	17.71
	Figure 10b	1.16	3.07	6.89	10.99

Table 3: Estimated values ρ_{ct}'' (Ω -cm) from Figures 9 and 10.

	Estimated from	800°C	750°C	700°C	650°C
Associative	Figure 9a	6600	11900	28000	59900
	Figure 9b	2700	6500	19500	47600
Dissociative	Figure 10a	2800	8200	22700	50200
	Figure 10b	1700	5200	18000	44400

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LIST OF ACRONYMS AND ABBREVIATIONS

DC:	Direct Current
DI:	De-Ionized
LSM:	Sr-doped LaMnO ₃
SEM:	Scanning Electron Microscope
SOFC:	Solid oxide fuel cell
TPB:	Three Phase Boundary
UV:	Ultra-Violet
YSZ:	Yttria-stabilized zirconia