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Pattern Electrodes for Studying SOFC Electrochemistry

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Pattern anodes can be used to localize reactions and study individual processes like charge transfer, adsorption, diffusion etc. Ceria and Nickel (Ni) pattern anodes were fabricated with the same dimensions with Triple phase boundary (TPB) lengths of 0.2707 m/cm^2. Electrochemical Impedance Spectroscopy (EIS) of Ni anodes yielded results comparable with the results in literature (0.0001 Scm^{-2} at p_{H2O} = 2.4 kPa and 700^oC). Ceria shows a different value for conductivity compared to the nickel, possibly because of the mixed electronic ionic conductivity of ceria and the spreading of the TPB over the surface of ceria. Identifying rate limiting mechanisms on ceria pattern anodes and comparing them with those of nickel gives a more complete picture about elementary processes at the cermet anode.

Introduction

Solid Oxide Fuel Cells (SOFC's) are highly efficient and potentially sustainable producers of electricity. Commercial anodes are porous cermets generally of Nickel (Ni) - Yttria stabilized Zirconia (YSZ) or Ni - Gadolina doped Ceria (GDC). Because of this porous cermet, the structure is an interpenetrating network of ionic and electronically conducting phases, thus making the triple phase boundaries difficult to quantify. Thus the reactions are difficult to study and localize and rate limiting mechanisms cannot be identified accurately. This also makes it difficult to correlate experimental data with models as the elementary kinetics cannot be extracted with precision from experiments. In order to overcome this problem model 2D electrodes were used (1,2) by depositing nickel on YSZ in a specific geometry so that the triple phase boundary is accurately known. This comes as a very close approximation to the cermet anode and with a known TPB, experimental data obtained can be used for determining the kinetics of the cermet anode.

In previous work (8) model 2D electrodes were fabricated with well defined TPB lengths by depositing Nickel on an YSZ disk in a specific pattern (Figure 1). Impedance results obtained were comparable to previous work on Nickel pattern anodes. In this work a step further is taken to analyze mixed ionic electronic conductors (MIEC) like ceria when used as anode materials. Ceria is a well known catalyst for example in water gas shift reactors where they act as a storage medium for oxygen. Ceria based anodes have

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been shown to be tolerant to fuels with higher hydrocarbon content than YSZ based ones (7, 5). Thus the study of fuel oxidation on ceria is an important step in understanding the behavior of MIECs in the cermet anode. The TPB length in ceria is difficult to quantify as it is expected that because of the mixed ionic electronic conductivity of ceria, the TPB spreads across the surface of ceria. Thus it arguably is now a two phase boundary where the electronic and ionic conductivity come from the ceria phase. However for the sake of comparison with nickel it is still referred to as a triple phase boundary. The triple phase boundary between the YSZ and ceria is unlikely to be determining the rate of electrochemical reactions as the surface area of ceria is much higher. The electronic conductivity of ceria is also essential as electrons have to be transferred across the surface of the ceria to the current collectors. Unlike previous work in metal pattern electrodes (1,2) the ceria surface is expected to act as the oxidizer and the metallic (catalytic) phase is completely eliminated. This implies that ceria will act as a catalyst for electrochemical reactions. In order to have a consistent basis for comparison the ceria is deposited on YSZ as a pattern. The oxidation of hydrogen on ceria has been a subject of many studies but mainly focusing on ceria reduction kinetics. However, the behavior of ceria as an anode material and operating as the fuel oxidation electrode is not very clear. In this work, a comparison of nickel pattern anodes and ceria pattern anodes is performed with respect to their polarization characteristics using impedance spectroscopy. It is expected that this will eventually give us a more complete picture about the behavior and kinetics of an actual cermet fuel cell anode. It must be pointed out here that a symmetrical cell was sputtered with identical patterns on both sides of the YSZ disk. As far as the authors know not many symmetrical cell tests on pattern electrodes are available in open literature and this type of testing is useful in identifying particular effects related to the anode kinetics.

Experimental

In this work ceria is deposited on a YSZ disk as exactly the same pattern as the nickel. A stainless steel mask was fabricated in-house same as with the nickel pattern anodes. For details about the dimensions of the mask the reader is referred to (8). Ceria was sputtered on the YSZ disk via the mask by DC magnetron sputtering. In this work as well, symmetrical (anode) cells were sputtered with identical patterns on both sides of the YSZ disk. Two gold wires are attached to the ends of the pattern which act as current collectors. Impedance measurements are performed using the setup as described by Aravind et al (3). The impedance measurements are carried out between 700 and 850 ^{o}C under humidified hydrogen.

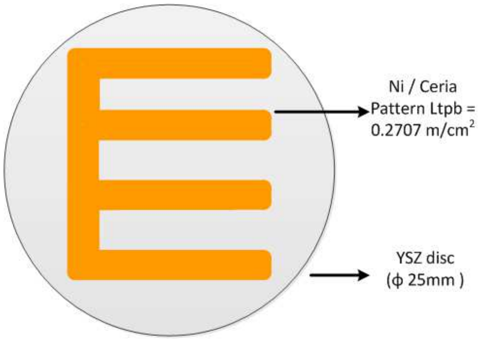

Figure 1. Nickel or ceria pattern as deposited.

Results and Discussion

Figure 2 shows the impedance spectra obtained from nickel pattern anodes. It is clear that the polarization resistance is quite high which can be related to the small TPB length. Figure 3 shows the impedance spectra obtained with ceria pattern anodes. Comparing with Nickel pattern anodes, we can conclude that the overall resistance in case of ceria pattern anodes is much smaller than that of Nickel pattern anodes. Equivalent circuit fitting using the circuit shown in Figure 4 was carried out for both sets of data. In both cases the spectra consists of a high frequency and a low frequency R-CPE element along with the series resistance

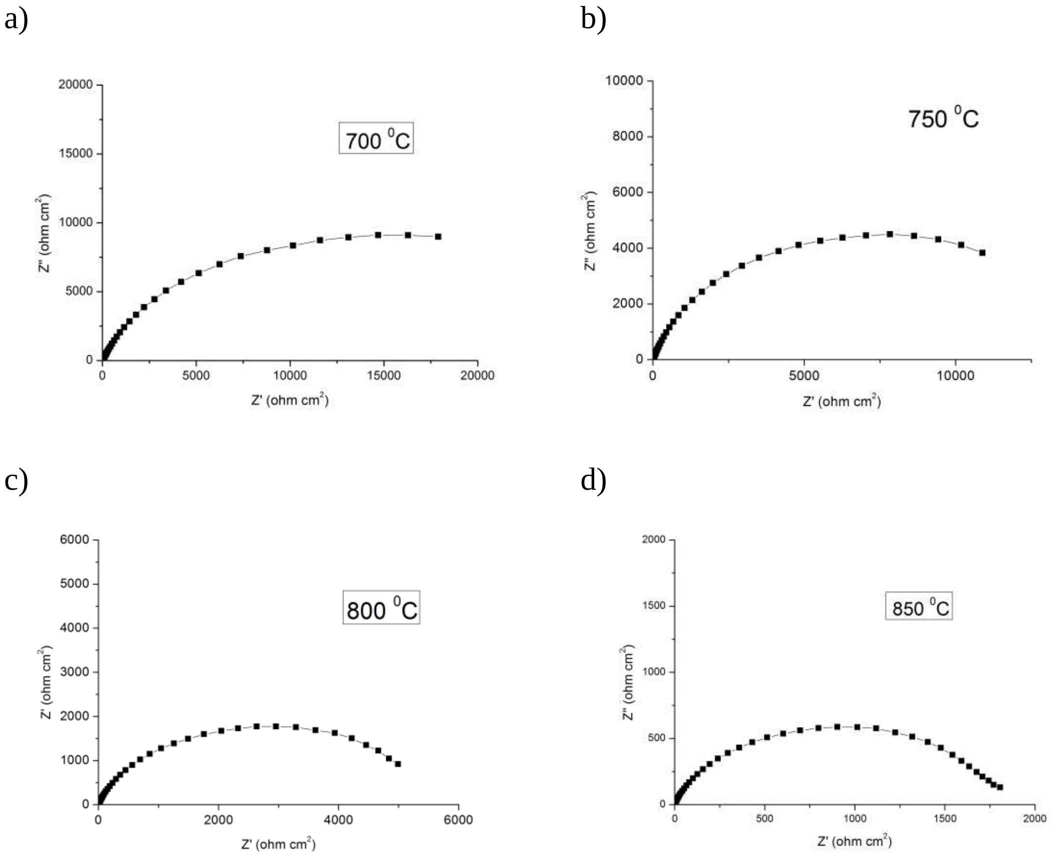

Figure 2. Impedance spectra with Nickel pattern anodes at different temperatures a) 700 °C b) 750 °C c) 800 °C d) 850 °C.

It is interesting to note that the series resistance (R1 in equivalent circuit) is much higher in case of ceria. In case of nickel at 800 °C it is around 0.87 ohm cm^2 (not visible in the graph because of scale) while in case of ceria pattern the resistance is as high as 250 ohm cm^2. This is interesting as it can be related to the lack of long range electronic conductivity on the surface of ceria. In case of Nickel the metallic surface is highly conductive and there is no limitation with respect to current collection. This is however not true in case of ceria where in spite of the MIEC nature of ceria there will be a limitation to current carrying. Since the pattern is connected to gold wires at 2 diametrical ends, in general the electrons have to travel at least a few mm before they reach the wire.

While the oxidation of hydrogen on the surface of ceria is well known in case of reduction of ceria (4, 6, 9), the use of reduced ceria as an oxidation electrode is not well explored. Ceria demonstrates two stable oxidation states Ce^{3+} and Ce^{4+} thus making removal of oxygen in non- stoichiometric quantities possible. Thus after reduction, a stoichiometry of $CeO_{(2-x)}$ is stable as well (11). In the present study, because of the long exposure to a reducing atmosphere, the surface of ceria should be entirely reduced and any further removal of oxygen would not take place without electrochemically driving the reaction where the oxygen is supplied via the electrolyte.

From the small polarization resistance of ceria pattern anodes, it is clear that the surface of ceria is active for hydrogen oxidation. The oxidation of hydrogen on the surface of reduced ceria makes the triple phase boundary of the pattern very difficult to determine as it would seem the reaction is not limited only to the border between YSZ and ceria but it spreads over the surface of ceria.

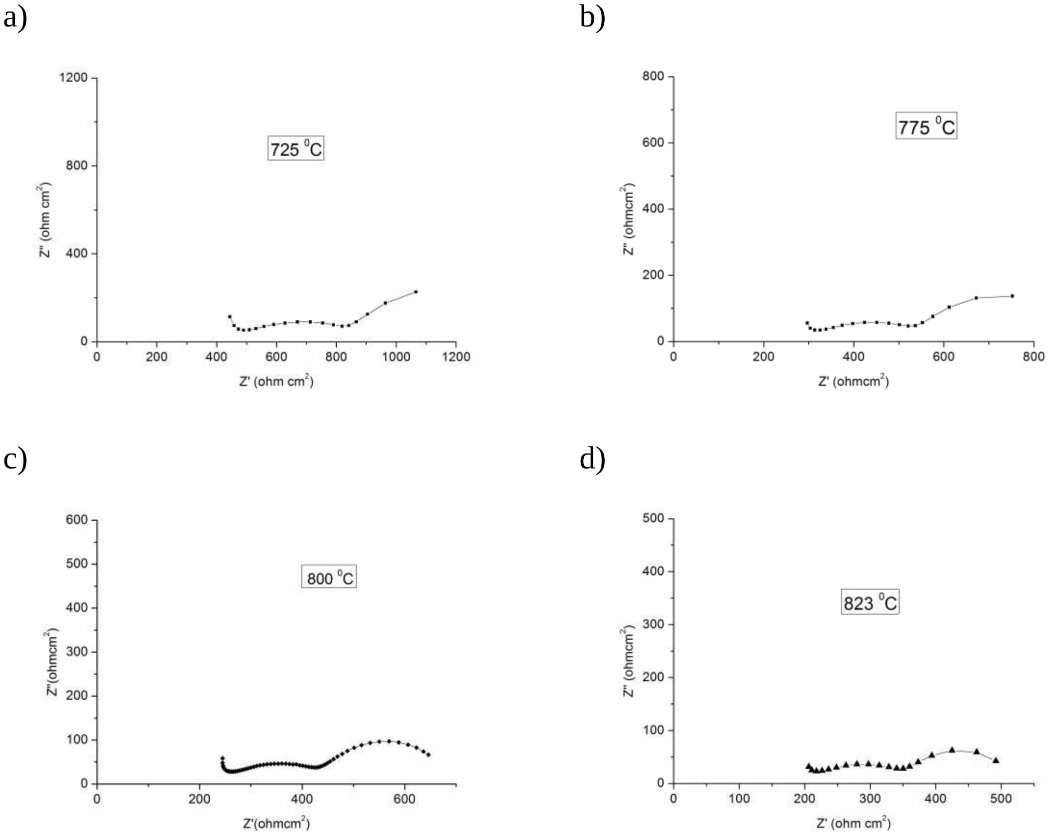

Figure 3. Impedance spectra with ceria pattern anodes at different temperatures a) 725 °C b) 775 °C c) 800 °C d) 823 °C,

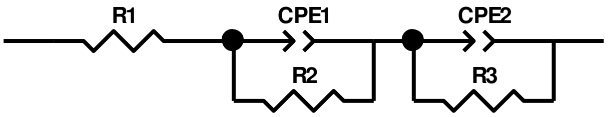

Figure 4. Equivalent circuit model for ceria and nickel pattern anodes impedace spectra.

Previous work (1,2) has mostly been limited to studying kinetics related to metallic electrodes and corresponding mechanisms. Also very high TPB lengths have made it difficult to study faster processes like charge transfer which would be possible in this case because of the very small TPB length where the limitation may occur in charge transfer. Metallic patterns on ceria surface have been studied recently (10) where samaria doped ceria (SDC) was deposited on YSZ and subsequently metal patterns were deposited on SDC. Additionally the entire surface of ceria is exposed for fuel oxidation with the metal patterns embedded in the surface of ceria. It was concluded that ceria surface is highly active for hydrogen oxidation which is consistent with the findings in this work. The polarization resistance obtained was lower compared to that in this study. This may be because of the current collection occurs through the metal patterns which are under the ceria surface thus decreasing the diffusion lengths. Also the surface area of ceria is lower. In addition SDC is used as opposed to undoped ceria in this study and as such the ionic conductivity would be lower. Also, the ceria itself is not in the shape of a pattern, but rather is the entire surface exposed to the fuel. Patterned ceria is useful to compare the oxidation kinetics of ceria with nickel and the possible contribution that can be obtained in real cell conditions.

Conclusions

Pattern anodes of ceria were fabricated and impedance spectra were recorded for these with hydrogen as fuel. The TPBs in case of ceria are spread over the surface of ceria and hydrogen oxidation can take place all over the surface of ceria while it is limited only to the TPBs in case of nickel patterns. Thus the polarization for ceria pattern is much lower as compared to nickel pattern anodes.

The kinetic parameters obtained from impedance data of the nickel and ceria pattern anodes can be used to identify rate limiting mechanisms and provide a basis for modeling the fundamental electrochemistry in macro scale models. Future work will focus on obtaining kinetic parameters for the processes from curve fitting and identifying rate limiting mechanisms. Additionally with changes the gas atmosphere, the behavior of ceria as a catalyst may be different and this is considered as future work using ceria pattern anodes. Combining the mechanistic details from nickel and ceria pattern anodes, more clarity can be obtained about the overall fuel oxidation kinetics at the cermet anode.

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