Short Communication

Ceria Electrocatalysis Compared to Nickel Using Pattern Anodes

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Ceria and nickel pattern anodes are prepared and tested in order to gain a fundamental insight into the electrochemical oxidation of hydrogen on either of these surfaces. It is found that ceria is highly active towards electrochemical oxidation of hydrogen with lower polarisation resistance because of the mixed ionic electronic conductivity of ceria. In addition, the activation energy with ceria patterns is much lower indicating that the ceramic catalysed pathway is much faster as well. Thus hydrogen oxidation can proceed on ceria independent of nickel and can indeed be faster than when catalysed by nickel.
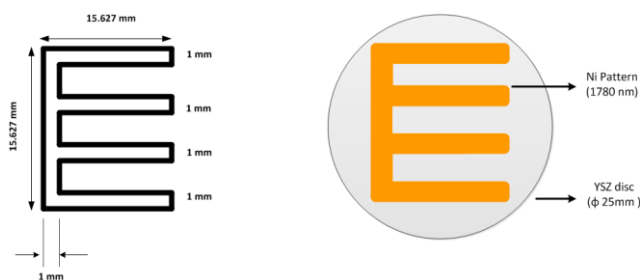
1. INTRODUCTION

While Solid Oxide Fuel Cells (SOFCs) have been known to be highly efficient devices, several challenges exist in the long term use of SOFCs in power generation. The anode electrochemistry has been a subject of a large number of studies especially with 2D model electrodes [1-3]. The need for a model electrode arises from the fact that a commercial cermet anode is a porous interpenetrating network of ionic and metallic phases. This makes the triple phase boundary (TPB) very difficult to determine precisely and hence it is difficult to obtain kinetic data. Previous work on model electrodes has focussed on nickel as the electrode. However in case of cermet anodes of nickel - gadolinia doped ceria (GDC), the GDC also has a finite electronic conductivity. Hence the triple phase boundaries in this anode is possibly not limited to the contact zone between nickel and GDC.

Ceria is an interesting material especially for SOFC anodes because of their high performance with hydrocarbon fuels [4,5]. Mixed electronic ionic conductors (MIEC) like ceria are especially interesting materials for SOFC anodes because the TPB is not limited to the interface between the metal and ceramic but can spread to the ceramic phase. This can lead to enhancement of reactive sites and decrease of polarization resistance. For electrochemical oxidation of hydrogen on ceria, a process similar to ceria reduction occurs where oxygen ions are provided from the bulk to the surface where the bulk of ceria gains oxygen ions from the electrolyte. Samaria doped ceria (SDC) deposited on YSZ has been studied recently with metallic patterns on the surface of SDC [6]. Subsequent experiments were performed with metallic patterns covered with SDC. However, SDC was not in the form of a pattern where the electrochemical reaction proceeds only via the ceramic. While ceria has been studied as a catalyst in the past, most studies have been related to kinetics of ceria reduction [7-9]. The use of ceria as a electrocatalyst is not well understood. In this work ceria is deposited as a pattern on Yttria Stabilised Zirconia (YSZ) and it is expected to act as the electrocatalyst instead of traditional nickel. For this a comparison is made with nickel pattern anode with the same dimensions. In general, very little is known about the electrochemical oxidation of hydrogen on ceria which is significant in case of electrodes with nickel and doped ceria especially with use of contaminated fuels.

2. EXPERIMENTAL

A stainless steel mask was fabricated in-house with a desired pattern that could house the electrolyte (YSZ) discs (25 mm diameter) as shown in Figure 4.

Figure 1. Schematic of pattern anodes [10][14]

Nickel was deposited on YSZ by DC magnetron sputtering under argon at 100 W power, $5*10^{-7}$ mbar basis pressure in chamber and $3*10^{-6}$ bar pressure during sputtering. The film growth rate was 0.12 nm/s. The thickness of the nickel pattern deposited was 1780 nm. Ceria pattern anodes were deposited on YSZ using the same mask as before with a Ce_2O_3 target. The sputtering was carried out at 150 W under argon gas , $5*10^{-7}$ mbar basis pressure in chamber and $3*10^{-6}$ bar pressure during sputtering. The deposition rate was 0.035 nm/s. The thickness of the ceria patterns deposited was 500 nm. There were no visual defects on the deposited patterns (ascertained by light microscopy as well). Scanning Electron Microscopy (SEM) images of the nickel and ceria patterns (Figure 5a and b respectively) showed that the pattern is not porous. Two gold wires are attached to the ends of the pattern which act as current collectors. The prepared cells were then tested between temperatures of

700 and 850 ^{o}C under humidified hydrogen and impedance spectra was obtained at each temperature for both the cells.
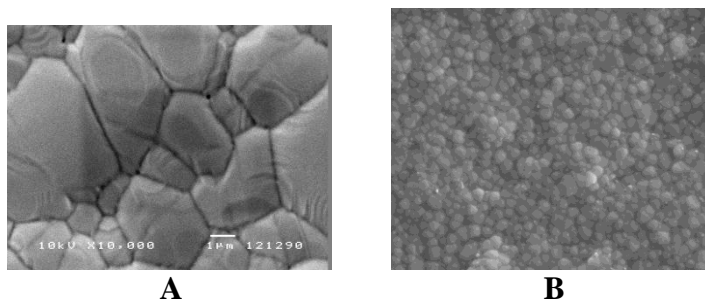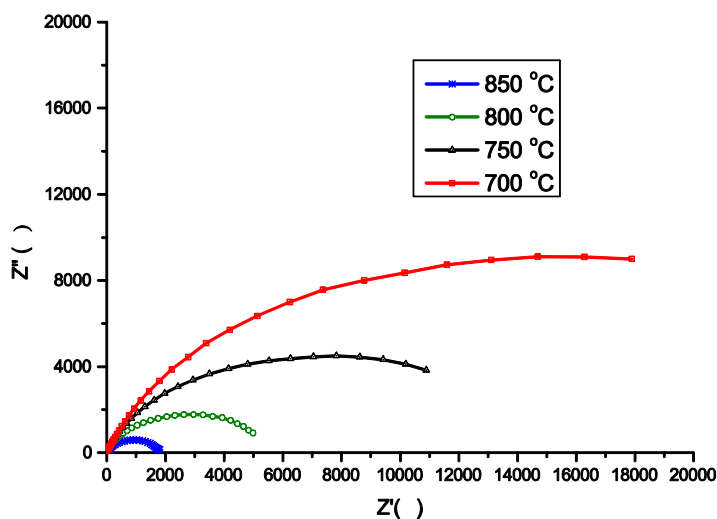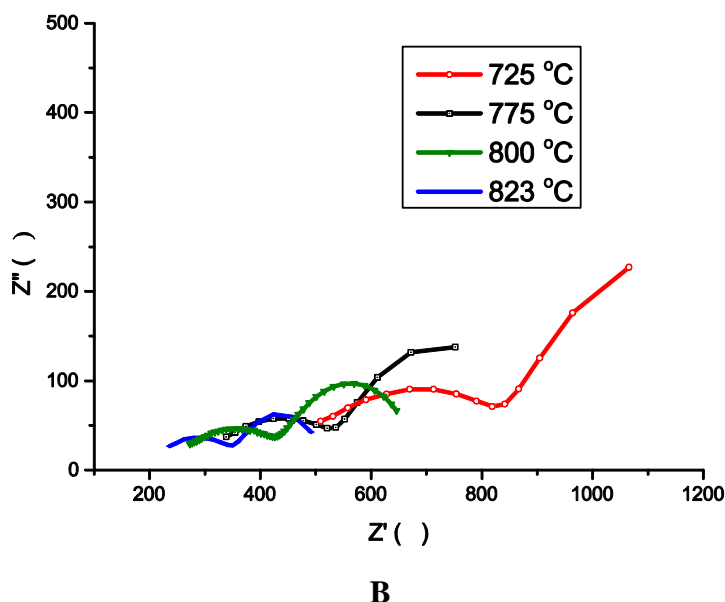

Figure 2. SEM image of a) nickel pattern anodes and b)ceria pattern anodes
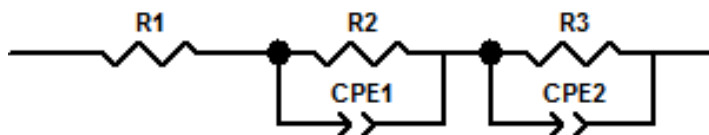
3. RESULTS AND DISCUSSION

Sputtering of nickel and ceria through steel masks on YSZ gave excellent 2D patterns but at the cost of higher line widths of nickel. The line width obtained was 1 mm as compared to micrometer range obtained by other researchers [1-3]. The TPB length obtained was 0.2027 m/cm^2. Comparing with previous work, there is quite a spread in the conductivity obtained by various groups for nickel pattern anodes (Bieberle et al, Mizusaki et al and De Boer at 2.33 kPa partial pressure of water, rest hydrogen, L$_{TPB}$ of 0.2707 m/cm^2 and 700 ^{0}C varies between $10^{-4} – 10^{-5}$ S/cm^2 using appropriate assumptions for calculations (10) (14). However, we can conclude that the total electrode conductivity value obtained in this work for similar experimental conditions is within a reasonable range. This shows that model 2D electrodes prepared in a much simpler way yield relatively good results, which are quite comparable with the expensive fabrication techniques.

A

Figure 3. Impedance spectra with a) nickel pattern anodes and b)ceria pattern anodes [10] [14]

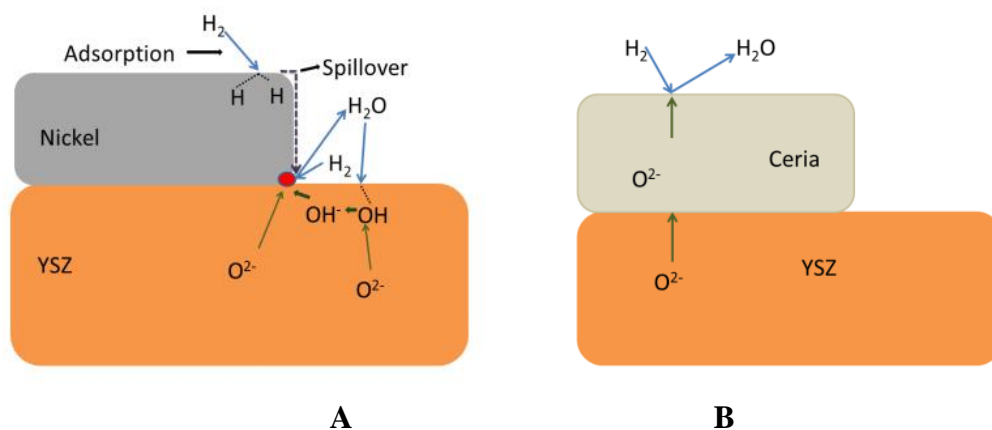**Figure 4.** Equivalent circuit model

Figure 2 a) and b) show the impedance spectra obtained with nickel and ceria pattern anodes respectively at different temperatures. The higher polarization resistance of the nickel pattern anode could be related to the small reaction zone along the TPB. However in case of ceria, because of the electronic conductivity, the TPB spreads over the surface of ceria. So, this is arguably a two phase boundary because of which the polarization resistance is much smaller. Equivalent circuit fitting using the circuit shown in Figure 3 was carried out using 2 R CPE in series with a resistance in both cases. The series resistance in case of ceria is much higher than that of nickel. This can be because of the lack of long range electronic conductivity on the ceria since the current collector is connected only at the two diametrical ends of the pattern. There are indications that the active region in doped ceria can extend to 150 μm [6,11] from the current collector, while the distance from the current collector in our patterns is of the order of mm. This limit may limit the active area to a smaller region near the current collector. However, from the polarization it is clear that the ceria is active for electrochemical hydrogen oxidation, even more so than nickel.

Table 1. Activation energies for ceria and nickel pattern anodes

	High frequency(kJ/mol)	Low frequency(kJ/mol)
Nickel Pattern	191	163
Ceria Pattern	94	89

The activation energy obtained for nickel at high frequency is typical for a spillover kind of charge transfer mechanism [12,13]. The high frequency activation energy for ceria is around 90 kJ/mol which makes a spillover kind of pathway is unlikely on ceria and the oxidation reaction is likely to proceed on the surface of ceria (Figure 3 a) and b)). The smaller polarisation resistance also indicates that the oxidation reaction is not limited to the interface of electrode/ electrolyte as in case of nickel but the active zone spreads on the surface

In addition to the polarization being smaller in case of ceria pattern anodes, the activation energy is lower as well at both high and low frequencies. This implies that the reactions can proceed faster on the surface of ceria. Previous work [6] has described higher activity of ceria on the basis of polarization resistance as measurements were carried out at a single temperature. The polarization resistance obtained in [6] is much smaller possibly because of the metallic pattern being embedded in the ceria leading to better electronic conductivity. In addition, undoped ceria is in the shape of a pattern in this work. However, the polarization resistance can be affected by the geometry of the pattern, its proximity to the current collector etc. The activation energy for a process can be taken as a measure of difficulty for the process to occur. In general, for the same overall reaction, a lower activation barrier implies better catalysis. Comparing the activation energies for nickel and ceria pattern anodes, it would seem ceria is a better electrocatalyst than nickel as the overall reactions are same for both the anodes. Thus, there is kinetic evidence that hydrogen oxidation is actually faster on the ceramic than when catalyzed by the metal.

Figure 5. Hydrogen oxidation on a) nickel pattern anodes and b)ceria pattern anodes

4. CONCLUSIONS

Symmetrical cell nickel and ceria pattern anodes were made using a metallic mask. Nickel pattern anodes show reasonable conductivity when compared with previous work. It is clear that ceria can act as an electrode for hydrogen oxidation. The activation energies obtained for ceria are much lower than those obtained for nickel pattern anodes. This indicates that ceria is even better than nickel at electrocatalysis irrespective of geometry effects which can affect the polarization resistance. This needs to be further refined using detailed modeling in order to predict a pathway for hydrogen oxidation on ceria pattern anodes which is ongoing work.

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