CERIA REVISITED: 
ELECTROLYTE OR ELECTRODE MATERIAL?

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ABSTRACT

The current literature on ceria based electrodes and electrolytes are full of conflicting data and claims. Reasons for this are not easily explained but some suggestions may be given. The main overall explanation is that ceria in general is a very complicated material, which under SOFC anode conditions is partially reduced inducing electronic conductivity. This complicates the use of doped ceria as an SOFC electrolyte in spite of its high ionic conductivity. The electronic conductivity makes it possible to use pure and doped ceria in SOFC anodes; but in the ceria electrode literature also, a lot of confusion exists. For example, experiments from our own laboratory show that the actual details such as heat treatment or other fabrication (or measurement) details result in extremely different polarization resistances, but even so, our results are well inside the span of values which may be deduced from literature reports.

INTRODUCTION

Ceria based materials - mainly doped with Gd2O3 or Sm2O3 - have been proposed and investigated as SOFC electrolytes as well as the active part of SOFC electrodes (see e.g. 1-4 and refs. therein). Within both types of application, some confusion exists. This may be because doped ceria materials, which are nominally identical, in reality may be very different, due to variations in grain boundary structure and grain size caused by different heat treatments and differences in purity. In case of ceria electrodes, the properties of the electrode/electrolyte interface also may be profoundly affected by the fabrication procedure as well as the presence of traces of foreign materials. For instance, it is believed that ceria is resistant towards reduction at a temperature of 500°C, and this is probably true for Ce1-xGdxO2-x/2 (CGO) with grain size above 1 micron. However, this is not the case for CGO with a grain size of 0.1 μm and below because, at surfaces and near grain boundaries, Ce4+ is much easily reduced to Ce3+ than Ce4+ in a normal CGO lattice.

Another example is that, even though it is agreed that ceria can work as an SOFC anode on yttria stabilized zirconia electrolyte, for conversion of hydrogen as well as carbon and hydrocarbons, there seem to be real disagreements as to the electrode reaction mechanisms and performance. In addition, discrepancies have appeared in the understanding of whether doped or pure ceria is to be preferred as SOFC anode material. The purpose of this paper is to discuss once more some of the aspects of the applicability of ceria as an SOFC material in light of the recently reported experimental results.
DOPED CERIA AS AN ELECTROLYTE

It has often been claimed that $\text{Ce}_{1-x}\text{Gd}_x\text{O}_{2-x/2}$ ($x = 0.1-0.2$) is the best of known oxide ion conductors in the so-called intermediate temperature range around 600°C. This is the reason for choosing doped ceria as an electrolyte, in spite of the obvious problem of electronic internal leaks, especially in the open circuit condition. Fig. 1 shows a comparison of the conductivity of a scandia-stabilized zirconia with that of $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ (CGO10), which is usually claimed to have the highest conductivity. Our results are in good agreement with results published by others for the same compositions (5,6). These results seem to question the claim of CGO10 being a much better ionic conductor than any zirconia, unless the temperature is well below 600°C.

Even though gadolinia and samaria doped ceria are indeed very good oxide ion conductors, all types of ceria-based electrolytes have the disadvantage of being relatively easy to reduce. The reduction of Ce$^{4+}$ to Ce$^{3+}$ gives rise to electronic conductivity, which in turn causes an electronic leakage current through the electrolyte in operating SOFCs. It is often argued that this problem vanishes when the cell is loaded, because the anode condition will become more oxidizing with increasing current density and overpotential. Naturally, the latter is true, but to what extent the electronic leak current density will decrease with increasing external current is dependent on the actual size of both anode and cathode polarizations. When the current density increases, the overpotential of the cathode decreases, and the cathode side of the electrolyte experience a slight reduction, increasing the local n-type conductivity. This may not be important if the doped ceria is in the form of single crystal or coarse grains, but could be important in the case of nano-sized materials.

Ceria powder with particle size in the near 1 μm range is relatively difficult to sinter, and a temperature of 1500°C is normally required. Therefore, a lot of R&D has been carried out in order to lower this sintering temperature. This work has been very successful. It has been revealed that nano-sized ceria powder may be sintered dense at temperatures below 1000°C (7-9). However, ceria nano-particles as well as the grain boundary zones in doped ceria electrolytes are much easily reduced than single crystal ceria. The free enthalpy of reaction for reduction of 10 nm ceria particles is less than half of that for large crystals (10,11). As the ceria sintered at 1000°C and below has submicron grains, it is to be expected that the electronic leakage problem will be significantly larger for such electrolytes than for high temperature sintered large grained CGO. For example, this is reflected in the fact that the open circuit voltage for SOFCs with low temperature sintered thin CGO electrolytes is only 950 mV at 570°C (12), in contrast to model calculations based on data for ordinary CGO (1), which predict an OCV near the theoretical value of 1140 mV using H$_2$ with 3% H$_2$O as anode gas and air as cathode gas. With an area specific internal resistance (ASR) of 0.6 Ωcm$^2$ this situation corresponds to a leak current density of (1.14 - 0.95) mV/0.6 Ωcm$^2 = 0.32$ Acm$^-2$. Higher leak current densities may be deduced from other reports on SOFC with ceria based electrolyte (13,14,15), in which OCV values below 900 mV were observed at temperatures as low as 450°C. Even though the leak current density may be smaller when the cell is polarized, the question is if such leak current densities will be acceptable in commercial SOFC stacks.
CGO becomes relatively more stable in H₂-H₂O with decreasing temperatures (1,2). Thus it may be argued that by lowering the temperature further below 500°C, it should be possible to avoid the electronic leak though the electrolyte. This is, however, not necessarily so, because in order to decrease the temperature, the electrolyte thickness also has to be reduced in order to avoid a too large an ionic resistance across the electrolyte, but the electronic resistance of the electrolyte will also in first approximation be proportional to the thickness of the electrolyte. Furthermore, the activation energy of the electron mobility in CGO is in the range of 0.2 - 0.4 eV, much lower than the activation energy of around 0.7 eV for the oxide ion mobility in CGO. This means that, even though the electron carrier density decreases with temperature, the ratio between electronic and ionic conductivity will not decrease to the same extent.

Finally, it should be mentioned that the leak current density is also a function of cell polarization. It is usually assumed that the current leakage will be much smaller when the cell is polarized. The argument is that then the oxygen potential on the anode side of the CGO electrolyte will become higher and little Ce⁴⁺ will be reduced. However, there is not necessarily a big difference. If the cathode polarization is large and the anode polarization is small, then the redox potential will not change much at the anode, but the cathode side will experience a significantly reduced potential. Both more experiments and a detailed cell modeling are necessary in order to quantify these effects.
There is not much doubt that ceria can work as an SOFC anode on yttria stabilized zirconia electrolytes for conversion of hydrogen as well as carbon and hydrocarbons, but there are conflicting reports regarding electrode reaction mechanisms and performance. One of the issues under debate is whether the conversion of almost dry hydrocarbons can take place through a direct electrochemical oxidation, or if it is cracking followed by oxidation of the cracking product, hydrogen, (and thereafter also steam reforming using the water formed by the oxidation of the hydrogen, called secondary reforming). This has been discussed previously (16,17). There is now a tendency towards an agreement that the conversion is oxidation of cracking products or reformed hydrocarbons and not direct electrochemical oxidation.

Other discrepancies have appeared in the literature. One is about the materials and the condition at which carbon deposition may be a problem. Another is on the understanding of whether doped or pure ceria is to be preferred as an SOFC anode material. A third is about the actual performance (rate of hydrocarbon oxidation) of ceria-containing anodes.

First, regarding the carbon deposition, we think that the extensive literature on pyrolysis, cracking and reforming of hydrocarbons should be consulted much more by the researchers working with anodes for hydrocarbon conversion, see e.g. (18,19,20). From such literature, we conclude that stagnant methane will crack at temperatures as low as 700°C, and that higher hydrocarbons such as propane and butane will crack in the gas phase at temperatures as low as 600°C. On transition metals like Ni, the cracking of methane may take place already at 450°C. The high-temperature chemistry of hydrocarbons is quite complex and, therefore, at specific conditions carbon precipitation may be avoided and, at other slightly different conditions, the whole system will be smothered in carbon. Two aspects here are of special importance: 1) the space velocity, as this will be important for the concentration of radicals, and 2) the autocatalytic nature of carbon precipitation.

The second discrepancy is that it has, on one side, been claimed that undoped ceria is a better anode material than CSO or CGO (21). The experimental evidence behind the claim is a relatively small difference in current density - voltage (i-V) curves for two cells, one with pure ceria and the other with CSO in the anode. However, a main part of the difference in the i-V curves is due to differences in OCV of the two cells. The explanation given was that pure ceria has a much bigger oxygen capacity than doped ceria, as proven for ceria used in heterogeneous catalysis. However, this explanation is problematic in case of SOFC anodes, because pure ceria will be in a reduced state when it operates in a hydrocarbon or hydrogen environment. Our contradicting claim, on the other hand, is that doped is better than pure ceria. Measurements on cone electrodes of CGO in CH₄ with 3% H₂O show that CGO is considerably better than undoped ceria, Fig. 2 (22). The explanation for this is, at least in part, that the higher ionic conductivity of CGO, compared to pure ceria, supports a larger electrochemical active area on the doped ceria.

The third discrepancy is about the actual performance (rate of hydrocarbon oxidation) of ceria-containing anodes and it is two-fold:
a) Ceria-containing electrodes on ceria-based electrolytes seem much better than similar electrodes on YSZ. The reason for this is probably that a partial oxidation of hydrocarbon will take place even at OCV if the electrolyte is ceria based, due to electronic leakage in parallel to oxide ion conduction, which is the equivalent to oxygen diffusion through the electrolyte. Then the electrochemical reaction will be oxidation of H₂ and CO, the reaction products of the partial oxidation.

b) There is an apparent discrepancy in the data obtained even within the laboratory of the present authors. On one hand, the results in Figure 2 show that the area specific polarization resistance (ASR) is of the same order as those reported for other low temperature measurements on cells with porous electrodes (23), but, on the other hand, these are extremely low polarization resistances (i.e. very high exchange current densities – very high reaction rates) compared to the low reaction rates found at much higher temperatures, as shown in Fig. 3 (24). However, the results of Fig. 3 are consistent with results from our group on porous CGO electrodes sintered onto YSZ and tested at 1000°C as discussed previously (16).

A characteristic current density of 1 μAcm⁻² at 700°C is equivalent to a polarization resistance of ca 40 kΩcm⁻². The reason for this discrepancy is not entirely clear to us, but it is speculated that it may be due to the differences in preparation procedure and heat treatment, which in turn will be reflected in the surface/interface structures. There may also be a large difference in the outermost composition of a cone tip, which has been ground just before the measurement, and the surface of a material sintered at 1300°C at which temperature significant segregations of components and impurities may take place. Finally, the active area of the cone electrodes is determined using the so-called Newman’s formula using the serial resistance as determined by impedance spectroscopy, and this may introduce errors at relative oxidizing anode conditions as especially the doped ceria has a relative low electronic conductivity. The apparent disagreement between the

Figure 2. ASR values of CGO cone electrodes as a function of x in Ce₁₋ₓGdₓO₂₋d at OCV at 650°C in methane with 3% H₂O (22).
different experiment types certainly requires and deserves more experimental as well as theoretical work.

![Graph showing turnover frequencies for reaction of dry methane with CGO and for steam reforming with 5% methane / 5.5% steam over gadolinia doped ceria.](image)

Figure 3. Turnover frequencies for reaction of dry methane with CGO and for steam reforming with 5% methane / 5.5% steam over gadolinia doped ceria. After Aguiar et al. (24) with our addition of the current densities based on the assumption of 8 electrons per turnover.

CONCLUSIONS

Ceria may be used as an SOFC electrolyte if the loss in fuel utilization at open circuit voltage and on part load is commercially acceptable. However, the arguments for using doped ceria as an electrolyte for SOFC operation in the temperature regime around 600°C are weak. The available facts seem to favor the view that doped ceria is a helpful constituent in SOFC anodes, but much work is still needed to reveal the mechanisms of the interactions between ceria, zirconia and electron conducting constituents.

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