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Multilayer High-Performance Ceramic Anodes

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Abstract

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Comments

Multilayer High-Performance Ceramic Anodes

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A new approach to the design of ceramic anodes that uses a thin catalytically active functional layer that has only modest electronic conductivity sandwiched between the electrolyte and a non-catalytic electronically conducting ceramic layer that is used as the current collector is described. The anode design is flexible and allows various materials to be used in the functional and current-collector layers. Results are presented for anodes with thin functional layers (12 μm) consisting of a porous CeO_2/YSZ composite impregnated with 1 wt% Pd to optimize catalytic activity and a 100 μm thick layer of porous $La_{0.3}Sr_{0.7}TiO_3$ (LST) as the current collector. Low anode impedances and excellent overall performance were obtained with cells with these anodes while operating on both humidified hydrogen and hydrocarbon fuels.

Introduction

While Ni based anodes for SOFCs have many advantages including high performance when operating on H_2 or synthesis gas, they also have the disadvantages of low sulfur tolerance (1), poor redox stability (2), and low fuel flexibility since they are prone to coking when exposed to hydrocarbons (3). Ceramic-based anodes which use an electronically conducting ceramic material as both the current collector and oxidation catalyst have been proposed as an alternative which may be able to overcome some of the limitations of the Ni-based systems (4-10). Unfortunately, to date the performance of most ceramic anode formulations have been modest compared to that of conventional Ni cermets and as a result higher temperatures are required to produce comparable power densities. This is due in large part to the unavailability of electronically conducting oxides that also exhibit high ionic conductivity, catalytic activity for hydrocarbon oxidation, and chemical and thermal expansion compatibility with yttria-stabilized zirconia (YSZ) electrolyte.

In the work reported here we propose a new approach to the design of ceramic anodes in which two separate materials are used for electronic conductivity and catalytic activity. The concept relies on using a thin functional layer composed of Pd-doped ceria in YSZ adjacent to the YSZ electrolyte and a much thicker layer of $La_{0.3}Sr_{0.7}TiO_3$ (LST) which is used as the current collector. While the Pd-doped-CeO_2/YSZ functional layer has only modest electronic conductivity, its resistance can be maintained at acceptable values by making the layer very thin (~10 μm) and cells with this anode design exhibit excellent performance characteristics. LST was chosen as the current collecting ceramic material for this study because it has a similar CTE to that of YSZ and does not react with YSZ,

even after co-firing at 1823 K (11,12). Furthermore, LST has no ionic conductivity and is a poor electrocatalyst and therefore can only act as a current conductor.

Experimental

The general approach for cell fabrication involved synthesis of the electrodes by impregnation of porous YSZ and has been described previously (12,14). A YSZ wafer was prepared by firing laminated YSZ green tapes with and without sacrificial pore formers at 1823 K to produce two porous YSZ layers separated by a dense, 75 μm thick, electrolyte layer. For cells using LST as the anode current collector a glycerol slurry of LST powder was pasted onto the 12 μm porous YSZ layer followed by firing at 1823 K to provide a structure like that shown in Figure 1.
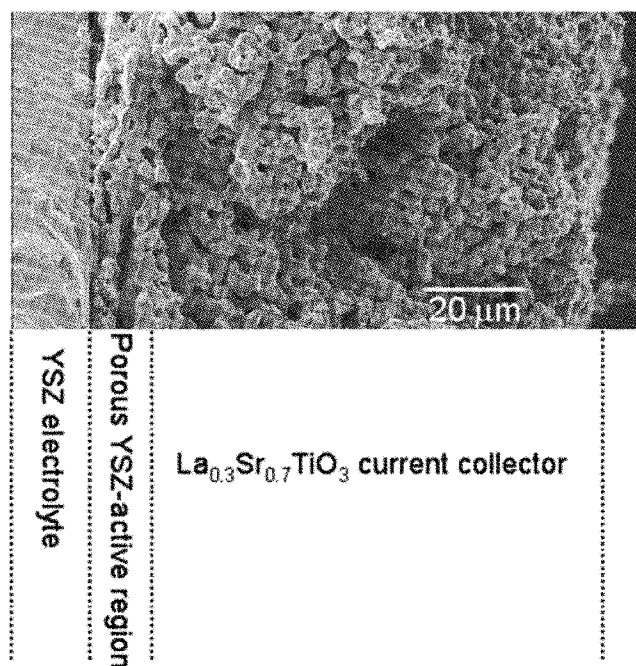

Figure 1. SEM micrographs of the anode region, prior to the addition of catalysts, of the cells used in this study.

40-wt%-LSF-YSZ composite cathodes were fabricated by impregnation of the 300-μm porous YSZ with aqueous solutions containing $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, and $Fe(NO_3)_3 \cdot 9H_2O$ at a molar ratio of La:Sr:Fe = 0.8:0.2:1, followed by calcination to 1123 K (15). The porous YSZ in the anode layer was then impregnated with CeO_2 and Pd using the corresponding nitrate salts. Finally, Ag paste and Ag wire were applied to both the anode and cathode sides for external current collection. The fuel cells were tested using both humidified H_2 and CH_4 fuels and impedance spectra were measured at 0.2 A/cm^2 in the galvanostatic mode using a Gamry Instruments impedance spectrometer.

Results and Discussion

Figure 2 displays voltage versus current and power versus current performance data for a fuel cell with a structure similar to that shown in Figure 1 while using humidified H_2 as the fuel. Impedance data are also included in the figure. The 12 μm porous YSZ functional layer in this cell contained 1 wt% Pd and 40 wt% ceria and the LST current

conduction layer was 100 μm thick. The cell was attached to a an alumina tube for testing purposes and the anode was exposed to humidified H_2 while heating the cell up to operating temperature. No special reduction treatments were used to help improve the electronic conductivity of the LST layer. As shown in Figure 2, the maximum power densities for this cell when operating with humidified H_2 at 973 and 1073 K were 339 and 653 mW/cm^2, respectively. For comparison purposes in another set of experiments that are reported elsewhere (16), similar cells were constructed in which the LST conduction layer was omitted and Ag paste was painted directly on the external surface of the anode functional layer and used for current collection. The maximum power densities for this cell using humidified H_2 at 973 and 1073 K were 401 and 865 mW/cm^2. These results show that while the use of LST as the current collector decreases performance somewhat the overall performance with the LST current collector is still acceptable. Comparison of impedance spectra of the two cells at 973 K reveals that the performance difference is due primarily to a slightly higher ohmic resistance in the cell with the LST current collector. This cell with the LST current collector had an ohmic resistance of 0.58 $\Omega \cdot cm^2$ while that for the cell with the Ag current collector was 0.49 $\Omega \cdot cm^2$. The non-ohmic impedances for the two cells at 973 K were similar, 0.27 $\Omega \cdot cm^2$ for the LST cell and 0.22 $\Omega \cdot cm^2$ for the Ag cell.
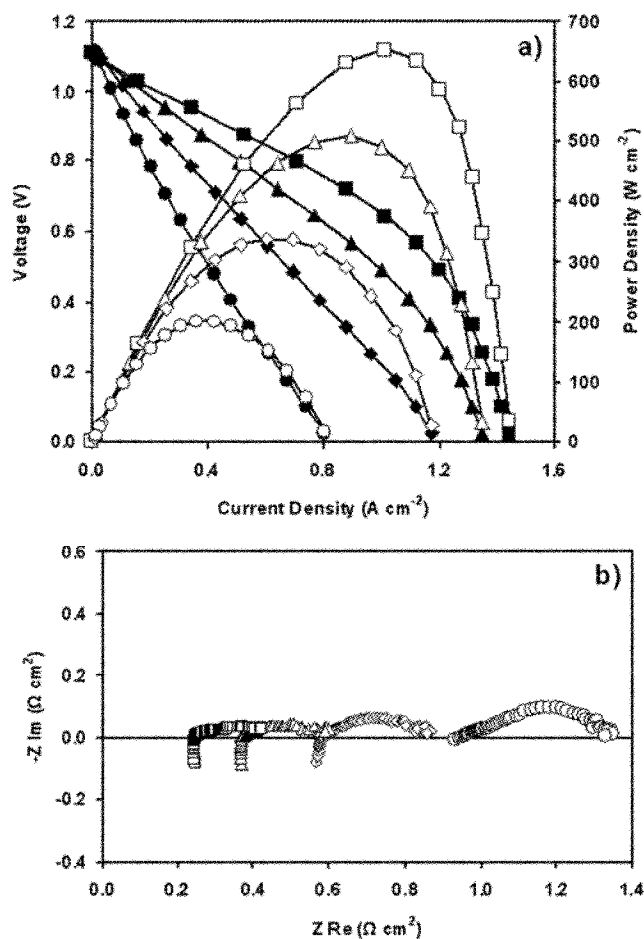

Figure 2. (a) i-V polarization curves and (b) impedance spectra on a 12 μm Ce-Pd-YSZ anode with a LST current collector in humidified H_2 (3% H_2O). Data are shown for the following temperatures: circles, 923 K; diamonds, 973 K; triangles, 1023 K; and squares, 1073 K.

While the performance data for the cell with the Pd-CeO$_2$-YSZ functional layer and LST current collector are encouraging, the true test of a ceramic anode is its performance while operating with a hydrocarbon-based fuel. We, therefore, also tested the performance of this cell using humidified (3% H$_2$O) CH$_4$ as the fuel. The results of these tests are presented in Figure 3 which displays voltage versus current and power versus current data and impedance spectra as a function of temperature. Note that the maximum power densities were 208 mW/cm^2 at 973 K and 539 mW/cm^2 at 1073 K and approach those obtained with humidified H$_2$ at these temperatures. Since that the fuel utilization in these tests was less than 1%, negligible amounts of water were generated in the anode. It is important to note that for these conditions one would observe carbon deposition on traditional Ni/YSZ cermet anodes. The data in Figure 3 also shows that the open-circuit voltages (OCV) at each temperature are greater than 1.15 V. This value is higher than that which would be achieved using humidified H$_2$ or CO, therefore ruling out the possibility that the cell performance is achieved through a reforming process, suggesting that the hydrocarbon is oxidized directly. Finally, the anode exhibited no evidence for carbon formation during an overnight exposure to CH$_4$.
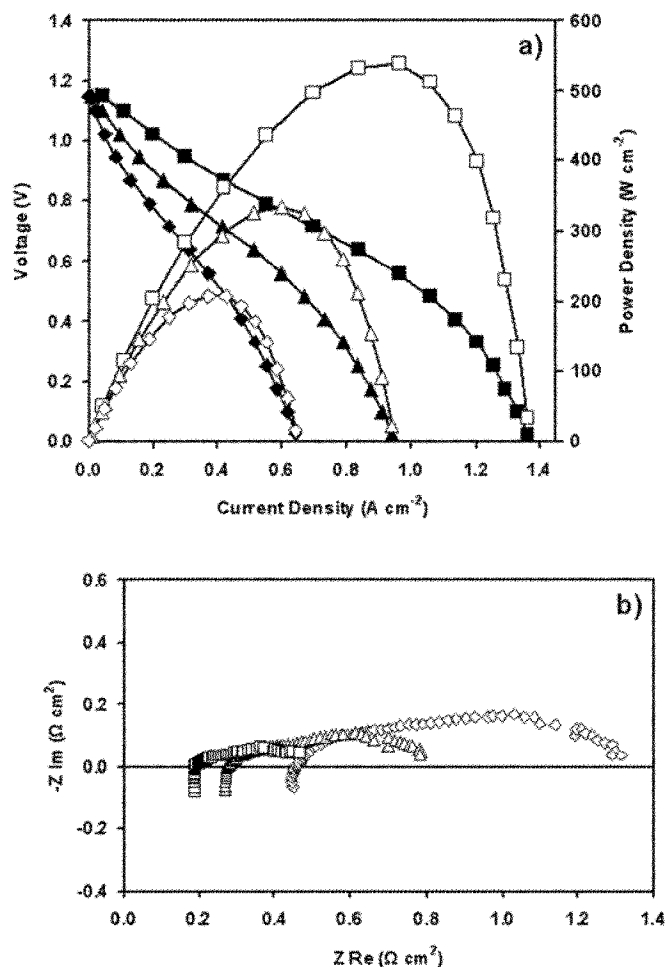

Figure 3. (a) i-V polarization curves and (b) impedance spectra on a 12 μm Ce-Pd-YSZ anode with a LST current collector in humidified CH$_4$ (3% H$_2$O). Data are shown for the following temperatures: diamonds, 973 K; triangles, 1023 K; and squares, 1073 K.

As pointed out in the Introduction, it is difficult to design ceramic-based electrodes that have acceptable electronic and ionic conductivity, high catalytic activity, and are chemically and mechanically compatibility with YSZ. In this study we have demonstrated that it is possible to decouple the requirements for catalytic properties from the conduction properties by using two functional layers which are optimized for each purpose. While the idea of separating the electrode into functional and conduction layers is not new, the demonstration that by minimizing its thickness the catalytic activity in the functional layer can be optimized without regard for electronic conductivity is a novel result. Obviously, some conductivity is required in the functional layer; but, as shown in this study, the conductivity can be quite low.

Because dopant levels of Pd were used in the anode in this study, the anode was not entirely ceramic. It should be stressed, however, that the volume percent of metal that was added was too low for it to have significantly influenced the electronic conductivity of the functional layer and its role was only to enhance catalytic activity. Furthermore, the metal content in the electrode is small enough that the electrode would not be damaged by oxidation of the metal, making the electrodes redox stable. While Pd was used because of its high catalytic activity for hydrocarbon oxidation and its tolerance against carbon formation, other metals could also be used. For example, when using syngas or H_2 as the fuel, dopant levels of Ni would likely be adequate for enhancing catalytic activity. Different metal catalysts may also be chosen for applications where sulfur tolerance is required, since ceria itself is quite sulfur tolerant (3).

While ceria is known to be a good oxidation catalyst (17,18), it too could be substituted for other materials in the anode design used in this study. For example ceria-zirconia solutions are known to exhibit higher catalytic activity compared to ceria alone (19) and are also ionically conductive and therefore may further enhance performance of the thin functional layer. Other ceramic materials that have been proposed for use in anodes, such as the perovskite, $Sr_2Mg_{1-x}Mn_xMoO_{6-\delta}$, recently investigated by Huang, et al (8,9) could also be used in this anode design.

Finally, it is significant that the results obtained with the Ag and LST current collectors were similar. This suggests that essentially any material with sufficient electronic conductivity can be used for the conduction layer as long as it is mechanically and chemically compatible with the functional layer. Again, the results of this study suggest a high degree of flexibility in the choice of materials for the conduction layer.

Conclusions

To conclude, the most important finding in this study is that one can obtain excellent performance using ceramic anodes that contain a thin functional layer and a separate conduction layer, even if the conductivity of the functional layer is low. The part of the anode responsible for current collection can be treated separately, allowing materials in each layer to be optimized independently. This strategy of designing each layer in the anode independently allows much greater flexibility in electrode design. While we have identified a set of materials capable of achieving outstanding performance, it seems likely that other materials can be identified with even better catalytic and conduction properties.

Acknowledgments

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