CHARACTERIZATION OF NEW CERAMIC ANODE MATERIALS FOR DIRECT METHANE OXIDATION IN SOFC

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ABSTRACT

Various perovskite materials, based on lanthanum chromite or strontium titanate, were synthesized and studied considering their use as ceramic anodes in SOFC. The powders were characterized by TG/DTA and XRD. Conductivity data between room temperature and 900°C both in oxidizing and reducing atmosphere were collected. The expansion behavior in both atmospheres was investigated and the thermal expansion coefficient up to 1200°C determined. Some materials showed electrical conductivities up to 100 S/cm, others had promising thermomechanical properties. So far a combination of the advantageous properties has not been found for the materials under consideration.

INTRODUCTION

The state-of-the-art anode in SOFC consists of a Ni/YSZ cermet (YSZ: Yttria Stabilized Zirconia) optimized for the oxidation of hydrogen. Because hydrocarbon fuels will be used in the near future, external or internal reforming of the fuel is necessary. However, the use of humidified natural gas may cause carbon deposition during internal reforming leading to performance losses. In the case of the presence of sulfur, poisoning also occurs. The nickel metal in the cermet tends to agglomerate with time, which leads to reduced three-phase-boundaries and decreasing electrochemical conversion of the fuel. Additional components in the power plant for both reforming and gas cleaning to obtain pure hydrogen increase the investment costs. Therefore, avoiding the problems of the Ni/YSZ cermet would be a step forward in achieving long-term stable anodes. A search for appropriate mixed-conducting ceramic materials with required anode properties was carried out in the field of perovskites. These requirements for anodes in SOFCs are:

- chemical stability in anodic atmospheres
- appropriate catalytic activity
- high electronic and ionic conductivity to avoid losses due to electrical resistance
- compatibility with respect to the thermal expansion coefficient (TEC) of the other cell components
- no chemical reaction with the electrolyte or the interconnect, even after long operation time at elevated temperatures
Nickel, although highly conductive and catalytically active, shows several disadvantages compared to ceramic materials. It tends to promote coking and suffers from sulfur poisoning (1). The use of a ceramic anode seems to be a conceivable solution for the present problems. Some work has already been performed in this field by various groups (2-5). For selecting the desired materials we have to consider the specifications within Jülich's planar concept for SOFC (6), particularly the support function of the anode for the mechanical stability of the whole cell and the chemical stability at high temperatures because of the co-firing with the electrolyte.

EXPERIMENTAL

Materials, based on lanthanum chromite or strontium titanate, were synthesized using the Pechini method (7). Nitrates and oxides of the metals were complexed in an aqueous solution with citric acid over several hours, then heated with ethylene glycol to get a polyesterification of the mixture. Finally, after removal of the excess liquid through drying, a resin was formed, which was heated (200 to 300°C) to decompose the organic constituents, ground and calcined at 900°C to get the powder. Main advantage of this method is the ability to achieve very good chemical homogeneity.

Before calcination the obtained powders were examined with thermogravimetry and differential thermal analysis up to 1400°C. The calcined powders were pressed uniaxially into bars with dimensions of about 2x5x40 mm. The specimens were sintered in air at 1400°C for 10 hours. The bars were used for conductivity measurements up to 900°C and for dilatometric measurements up to 1400°C. Both dilatometry and conductivity measurements were performed in oxidizing (air) and reducing atmosphere (argon with 4% hydrogen). X-ray diffraction was carried out on calcined powders as well as on sintered and reground pellets to check the homogeneity and purity.

RESULTS AND DISCUSSION

The particle size distribution of several perovskites is shown in Figure 1. A typical mean diameter of 0.3 to 3 μm is obtained. After calcination the powders are fine enough for further processing. Nevertheless, the coarser powders were milled in a ball mill but without significant particle size reduction. Variations of the mean particle size can be explained by different chemical compositions. The titanium-rich powders revealed a very broad particle size distribution with a mean diameter of 1 - 1.5 μm, whereas the chromium-rich samples gave a narrow distribution and a mean diameter of 0.4 μm.

The XRD patterns of the calcined powders showed usually broad peaks and sometimes small amounts of binary oxides, but most of them were single phase. Sintered powders showed sharper peaks, typically two to three times higher intensities than in the case of calcined powders indicating a much better crystallization.

Thermogravimetry revealed the disappearance of the organic residuals at temperatures between 400 and 600°C. DTA measurements showed no phase transitions or melting below 1400°C.
The observed values of the specific conductivity varied between 0.02 and 100 S/cm at 900°C (Figure 2). For the compositions shown, conductivity in argon/4% hydrogen was generally better than in air, in the case of chromium-rich samples this was the opposite (see Figure 3). In the case of p-type conductors conductivity decreases in reducing atmosphere because of the decrease of charge carriers (holes) in combination with an increase of oxygen vacancies \([7,8]\). In the case of n-type conductors charge carriers (electrons) are formed during reduction.

Some selected compounds were investigated by dilatometry. Figure 4 shows the behavior of La\(_{0.7}\)Ca\(_{0.3}\)Cr\(_{0.5}\)Ti\(_{0.5}\)O\(_3\) depending on temperature and atmosphere. A sintered bar was heated up to 1200 or 1000°C in air with a rate of 3 K/min to get the thermal expansion coefficient, cooled down by 200°C and kept at this temperature for several hours to see possible changes in time at the particular temperature. Then the atmosphere was switched from air to argon/4% hydrogen and kept for some hours before switching back to air. In this case the TEC is 10.1×10\(^{-6}\) K\(^{-1}\), which fits quite well with the TEC of the solid electrolyte (8). Switching between oxidizing and reducing atmosphere causes only a very small size alteration, visible only in the enlarged picture at the bottom (note the scale of the y-axis) and therefore no mechanical strain is induced.

The expansion behavior of other materials was worse, e.g. in the case of iron-containing sample La\(_{0.7}\)Ca\(_{0.3}\)Cr\(_{0.5}\)Fe\(_{0.2}\) the TEC is of the same order, but switching between atmospheres caused a detrimental length change. Interestingly this increase in length decreases with time, a yet not understood behavior. The TECs of all the investigated materials were between 10 and 12×10\(^{-6}\) K\(^{-1}\), and are – concerning only this property – useful for SOFCs.

![Cumulative particle size distribution of various perovskites.](image)

**Figure 1.** Cumulative particle size distribution of various perovskites.
**Figure 2.** Conductivity of some materials in reducing atmosphere (argon with 4% hydrogen)

**Figure 3.** Comparison of conductivity in air and an argon/4% hydrogen atmosphere for the two materials \( \text{La}_{0.4}\text{Sr}_{0.6}\text{TiO}_3 \) and \( \text{La}_{0.5}\text{Sr}_{0.5}\text{Cr}_{0.5}\text{Ti}_{0.5}\text{O}_3 \). Usually the conductivity of Ti-rich compounds dropped considerably in air (left), about 1 to 5 orders of magnitude, depending on the composition. Chromium-rich samples showed the opposite behavior (right).
Figure 4. Expansion behavior of $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.5}\text{Ti}_{0.5}\text{O}_3$ depending on temperature and atmosphere (top: overview of the experiment; bottom: enlarged scaling to see the small changes)
CONCLUSIONS

Synthesis via the Pechini method is a successful and comfortable way of obtaining powders of high purity and small particle diameters. The TEC of the examined materials fits to the TEC of the other cell components and are in the order of $1 \times 10^{-6}$ K$^{-1}$. In some cases switching between reducing and oxidizing atmosphere leads to negligible length changes which make such compounds attractive for application. However, conductivity of all materials is much lower than of Ni/YSZ anodes, but should be sufficient, if at least 10 to 100 S/cm are achieved. Conductivity under reducing conditions should be larger than under oxidizing conditions. Therefore chromium-rich compositions should be avoided. Long-term stability and catalytic properties are, though not yet investigated, however of great importance and have to be studied in the future.

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REFERENCES

1. P. R. Slater and J. T. S. Irvine, in Proc. 3rd European SOFC Forum, Editor Ph. Stevens, Nantes, France, p. 417 (1998)
2. P. Vernoux, J. Guindet, E. Gehain and M. Kleitz, in Solid Oxide Fuel Cells V, U. Stimming, S. C. Singhal, H. Tagawa and W. Lehnert, Editors, PV 97-40, p. 219, The Electrochemical Society Proceedings Series, Pennington, NJ (1997)
3. J. T. S. Irvine, D. P. Fagg, J. Labrincha and F. M. B. Marques, Catalysis Today, 38, 467 (1997)
4. R. Moos and K. H. Härdtl, J. Appl. Phys., 80[1], 393 (1995)
5. D. P. Fagg, S. M. Fray and J. T. S. Irvine, Solid State Ionics, 72, 235 (1994)
6. H. P. Buchkremer, U. Diekmann, L. G. J. de Haart, H. Kabs, U. Stimming, D. Stöver, in Solid Oxide Fuel Cells V, U. Stimming, S. C. Singhal, H. Tagawa, W. Lehnert, Editors, PV 97-40, p. 160, The Electrochemical Society Proceedings Series, Pennington, NJ (1997).
7. M. P. Pechini, US Patent 3,330,697 (1967)
8. F. Tietz, in: Proc. 9th Int. Conf. Modern Materials & Technologies (CIMTEC '98), Vol. 24, Symp. "Innovative Materials in Advanced Energy Technologies", June 1998, Florence, Italy, Editor P. Vincenzini, Techna Srl., Faenza, Italy, p. 61-70 (1999)