LOW COST (La,Sr)MnO₃ CATHODE MATERIAL WITH EXCELLENT ELECTROCHEMICAL PROPERTIES

Evelyn Proß,¹ Jörg Laube,¹ André Weber,² Axel C. Müller² and Ellen Ivers-Tiffée²

¹H. C. Starck GmbH
Laufenburg, Germany
²Institut für Werkstoffe der Elektrotechnik (IWE)
Universität Karlsruhe (TH)
Adenauerring 20b, D-76131 Karlsruhe, Germany

ABSTRACT

The main objectives of H. C. Starck’s internal development program for powders used in SOFC applications are to meet the cost targets of the customers as well as the performance requirements during cell operation. Optimization of LSM-powder engineering process resulted in very homogenous powders with good crystallographic properties. The morphological properties can be adapted to customer requirements, the primary particle size can be varied in the range of few micrometers down to submicron powders.

Electrochemical performance tests of electrolyte supported single cells with cathodes based on these LSM-powders were conducted at the IWE, Universität Karlsruhe (TH). The single cells were characterized with respect to performance and long term behavior (> 1000 h) including load and thermal cycling. Current densities of 0.18 A/cm² (750°C), 0.43 A/cm² (850°C) and 0.7 A/cm² (950°C) were achieved at a cell voltage of 0.7 V. The long term stability and thermal cycling behavior was acceptable for mono-layer cathodes; and performance and degradation were in good agreement with the standard type cathode compositions and microstructure.

INTRODUCTION

Strontium doped lanthanum manganese (LSM) is a state of the art cathode material for solid oxide fuel cells. An evaluation of the most promising existing powder production processes for LSM was made using the criteria of cost, powder quality, scale-up potential and ecological aspects (Table 1). Further, processes described in the literature such as freeze drying method, emulsion method, self-propagating high temperature synthesis (SHS) and some wet chemical techniques were excluded on the basis of their high costs or because of their elaborate scaling-up for production.

The most promising processes were selected in order to meet the main objectives of H. C. Starck’s internal development program for powders used in SOFC applications. These objectives are to meet the cost targets of the customers as well as the performance requirements during operation.

Electrochemical Society Proceedings Volume 2003-07 391
Table 1. Comparison of powder production processes based on a literature research.

| Process          | Description                                                                 | Advantages                                         | Disadvantages                        |
|------------------|------------------------------------------------------------------------------|----------------------------------------------------|---------------------------------------|
| Solid state      | Grinding, Mixing, Temperature treatment of the mixed precursor               | Easy to scale up, Easy to transfer on other compositions, Low costs, No waste water / gases | Low purity, Low homogeneity, Imprecise stoichiometry |
| reaction         |                                                                              |                                                   |                                       |
| Sol-Gel techniques| Gels from solutions of cations and organic precursors*, Calcination or Self-Combustion / Sintering | Homogeneous fine powdered products                  | High quantities of organic compounds, Nitrous gases, Costly |
| Spray pyrolysis  | Thermal decomposition of aqueous nitrate solution droplets in a hot reaction chamber, Sometimes application of organic chelate complexes for the reduction of the nitrate | Homogeneous fine powdered products                  | Expensive equipment, difficult to scale up |
| Co-precipitation | Co-precipitation of the corresponding cations as carbonates, hydroxides or oxalates, Calcination / Sintering | Homogeneous fine powdered products, Low costs      | Different solubilities of the cations, Waste water problem, Difficult to transfer on other compositions |

*Some commonly used systems are citric acid / ethylene glycol (Pechini process), glycine/nitrate, polyacrylic acid.

EXPERIMENTAL

The applicability of the powders was evaluated by electrochemical tests of single cells exhibiting a screen printed monolayer cathode. A screen printing paste was produced by mixing the LSM-powder with an organic binder. Electrolyte supported single cells were prepared by first screen printing a NiO/YSZ-composite as an anode onto the 150 μm thick 8YSZ-substrate (8YSZ: 8 mol% Y2O3 doped ZrO2). After drying the screen printed anode layer in a hot air cabinet at 80°C for 12 hours, the LSM cathode-layer was screen printed on the opposite site and subsequently dried like the anode layer. The electrodes were co-fired according to an established sintering program with a maximum sintering temperature of 1300°C for 5 hours in air. The single cells exhibiting an active working electrode area of 10 cm² and additional reference electrodes of 0.25 cm² on both sides were tested in a single cell testing bench under realistic cell operating conditions (1). The losses and degradation of the individual electrodes were acquired by means of the reference electrodes. After heating up the cell to the maximum operation temperature of 950°C, the NiO in the anode layer was reduced to metallic Ni by an incremental increase of the hydrogen content in the fuel gas. In the next step the current density was slowly increasing at a rate of 0.2 A/cm² per minute.
increased to 500 mA/cm². C/V-characteristics were acquired at different temperatures (750 - 950°C) at various fuel utilizations. The long term stability was tested under galvanostatic conditions (400 mA/cm²) as well as under cyclic load conditions (each 12 h alternating between 0 and 500 mA/cm²). In addition, the cell was thermally cycled several times to gather information about the adhesion of the cathode layer on the electrolyte substrate.

RESULTS AND DISCUSSION

Powder Properties

The optimization of the powder engineering procedure-steps resulted in very homogenous products with good crystallographic properties. The primary particle size of LSM can be adapted to customer requirements in the range of few micrometers down to submicron powders by applying appropriate crushing procedures. Additionally, spray dried agglomerates of the fine powders can be offered for better handling.

A lot of work was done for the development of the chemical investigation methods in order to get a high reproducibility and low standard deviations of the compositions. Through the earned know-how, the contents of La, Sr and Mn are adjustable within close limits and can be adapted to customer requirements as well.

As one example, the LSM powder selected for electrochemical characterization is shown in Figures 1 and 2. The powder was understoichiometric with a composition of La₀.₇₅Sr₀.₂₃MnO₃. After temperature treatment the particle size of the powder ranged from approximately 1 to 5 µm (Figure 1). The slightly sintered grains are nearly spherical and homogenous. The crushed powder (Figure 2) had a mean particle size of about 1.5 µm and a specific surface area of 2.4 m²/g. The particle size distribution was monomodal and very narrow (Figure 3).

A finer grained powder with a mean particle size of 0.63 µm and a BET-value of about 6.4 m²/g is presented in Figure 4.

Figure 1. SEM image of the LSM powder used in the cathode after temperature treatment.
Figure 2. SEM image of the LSM powder used in the cathode after final crushing.

Figure 3. Particle size distribution of the LSM powder used in the cathode.

Figure 4. SEM image of a fine powdered LSM ($d_{50} = 0.63 \mu m$, BET: $6.36 m^2/g$).

Electrochemical Society Proceedings Volume 2003-07
As mentioned above the stoichiometry of the LSM powder used in the cathode layer was $\text{La}_{0.75}\text{Sr}_{0.23}\text{MnO}_3$. Contents of La, Sr, Mn and the major impurities are presented in Table 2.

| Metal content | Major impurities |
|---------------|------------------|
| La            | Na 4 ppm         |
| Sr            | K 1 ppm          |
| Mn            | Al 80 ppm        |
| Calculated stoichiometry | $\text{La}_{0.75}\text{Sr}_{0.23}\text{MnO}_3$ |

The XRD showed a LSM single phase (Figure 5). For other target compositions, in some cases a $\text{Mn}_3\text{O}_4$ phase was detected, but the quantity was always less than one percent.

![XRD of the LSM powder used in the cathode.](image)

**Figure 5.** XRD of the LSM powder used in the cathode.

**Electrochemical Properties**

Figure 6 shows a scanning electron micrograph of the screen printed cathode layer, which has been sintered on top of the 8YSZ electrolyte substrate at 1300°C. The layer exhibits a homogeneous microstructure and a sufficient porosity. No larger pores, cracks or delamination were observed. Due to the large number of contact points at the cathode/electrolyte interface, the cathode layer showed a good adhesion to the electrolyte. An acceptable electrochemical performance for this type of cathode is expected.
Figure 6. SEM micrograph of screen printed cathode layer sintered at 1300°C / 5 h.

Figure 7. C/V-characteristics of a single cell at different temperatures.

Figure 7 shows the C/V-characteristics of a single cell operated with air as the oxidant and hydrogen as the fuel. Current densities of 0.18 A/cm² (750°C), 0.43 A/cm² (850°C) and 0.7 A/cm² (950°C) were realized at a cell voltage of 0.7 V. The maximum power density was 350 mW/cm² at 850°C and nearly 500 mW at 950°C. For current densities > 700 mA/cm² an increasing slope of the C/V-characteristics must be attributed to gas diffusion polarization.
In Figure 8, the performance of single cells with the HCST-cathode is compared to the average value of similar cells (i.e. similar electrolyte substrate, anode and sintering procedure) with different types of screen printed monolayer LSM cathodes (cathode powders from other suppliers, powders prepared at IWE varying in morphology, screen printed layers with different thicknesses and microstructures). For all temperatures the HCST-cathode shows an excellent performance.

![Graph showing performance comparison](image)

**Figure 8. Performance of the tested single cells with HCST-cathode in comparison with other cells with different types of LSM-cathodes.**

Figure 9 shows the long term behavior of the single cell operated under cyclic load conditions. The current density was alternated between 0 and 500 mA/cm² each 12 h.

![Graph showing long term operation](image)

**Figure 9. Long term operation under cyclic load conditions (each 12 h alternating between 0 and 500 mA/cm²).**

Electrochemical Society Proceedings Volume 2003-07 397
Each time the current was increased from 0 to 500 mA/cm² (0.01 A/sec), the cell voltage decreased significantly and then recovered within about one hour. The overall voltage degradation of the cell, i.e. the degradation of cathode, anode and electrolyte during 800 h of operation under cyclic load was 48 mV. The main part of this degradation took place during the first 400 h (39 mV) and decreased significantly with time. Galvanostatic operation (400 mA/cm²) resulted in an initial degradation rate of 44 μV/h.

In addition to galvanostatic and load cycling, the cells were also thermally cycled several times. In Figure 10 the sequence of a thermal cycle is shown. After each thermal cycle the performance of the cell was evaluated by C/V-characteristics.

![Figure 10. Sequence of a thermal cycle. After switching of the current, the cell is cooled down to room temperature applying a H₂/N₂-mixture at the anode and then heated up to an operating temperature of 950°C again.](image)

![Figure 11. Performance of a single cell as a function of thermal cycles.](image)
Figure 11 shows the performance, i.e. the current density at 0.7 V cell voltage as a function of thermal cycles. Thermal cycle 0 is related to the initial performance of the cell, the operation time of the cell during the following thermal cycles is given in brackets. Compared to other cells with a monolayer LSM cathode, the thermal cycling stability of the HCST-cathode was significantly better, no large area delamination of the cathode layer was observed (2). The microstructural changes of the cathode layer during operation for 1300 h including load and thermal cycling were investigated by SEM. No significant microstructural changes or densification of the cathode layer was observed. Only at the cathode/electrolyte interface, slight changes, which are typical for monolayer LSM cathodes and must be attributed to the operating conditions (3, 4), appeared.

CONCLUSIONS AND OUTLOOK

The optimization of a low cost LSM-powder engineering process resulted in very homogenous powders with good crystallographic properties. Powder characteristics like composition and grain size distribution can be adapted to customer requirements.

Single cells with a monolayer cathode based on H. C. Starck powder show excellent electrochemical behavior. In comparison with other cathode materials prepared by solid state reaction as well as costly processing methods, cell performance observed for the investigated type of single cell was comparable or even better. In case of more complex cathode structures, the application of powders produced by low cost technologies with an adapted composition and morphology appears to be feasible.

REFERENCES

1. A. Weber, A. Müller, D. Herbstritt, E. Ivers-Tiffée, Characterization of SOFC Single Cells, *Proceedings 7th Int. Symp. on SOFC*, Eds. H. Yokokawa and S. C. Singhal, The Electrochemical Society, PV 2001-16, 952-962, (2001).

2. D. Herbstritt, A. Krügel, A. Weber, E. Ivers-Tiffée, Thermocyclic Load: Delamination Defects and Electrical Performance of Single Cells, *Proceedings 7th Int. Symp. on SOFC*, Eds. H. Yokokawa and S. C. Singhal, The Electrochemical Society, PV 2001-16, 942-951, (2001).

3. A. Weber, R. Männer, R. Waser, E. Ivers-Tiffée, Interaction between microstructure and electrical properties of screen printed cathodes in SOFC single cells, Denki Kagaku, *J. of the Electrochemical Society of Japan*, Vol. 64, No. 6, 582-589 (1996).

4. A. Weber, R. Männner, B. Jobst, M. Schiele, H. Cerva, R. Waser, E. Ivers-Tiffée, The Influence of A-Site-Deficiency to the Reaction Kinetics of Strontium Doped Lanthanum-Manganite Perovskite Type SOFC-Cathodes, *High Temperature Electrochemistry: Ceramics and Metals*, Ed. F. W. Poulsen, Risoe National Laboratory, 473-478, (1996).