

ELECTRODE MATERIALS FOR INTERMEDIATE TEMPERATURE SOLID OXIDE FUEL CELLS

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Abstract: Solid oxide fuel cells (SOFCs) are electrochemical ceramic devices operating at high temperature (1000⁰C) as power generators for the future with high efficiency and low emissions. Recently, alternative electrode and electrolyte ceramic materials, notably for lower working temperature, below 800⁰C (IT-SOFCs materials) have been proposed. The paper presents our studies for synthesis and characterization of new electrode ceramic materials for IT-SOFC devices selected for cathodes from the La_{1-x} M_x (Mn,Co)O₃ perovskite-type compositions with M=Sr, Ca and x=0.2-0.6 and for anodes in the Ni-cermets compositions. The influence of Sr, Ca doping on the phase structure development and on sintering behaviour was investigated. The results were correlated with electric conductivity data up to 800⁰C. The role of a stable monophase perovskite structure for the best electrode performances was confirmed.

Key words: ceramic electrodes, cathode, anode, fuel cells, perovskite compounds, electric conductivity

Electrode Materials for IT-SOFC

INTRODUCTION

Lately, a large interest has been shown mainly on synthesis and characterization of modified perovskite cathode materials and Ni-cermets anode materials with good characteristics at temperatures below 800⁰C [1,2,3].

The aim of this work is to investigate the correlation sintering behaviour with phase structure-electric characteristics of some La_{1-x} M_x (Mn,Co)O₃, (M=Sr, Ca and x=0.2-0.6) compositions and of Ni-ytria stabilized zirconia ceremets for the most favorable electrode material characteristics.

EXPERIMENTAL DATA

The considered solid solutions were prepared by standard ceramic technology, using as raw materials high purity oxides and carbonates.

As cathode materials, some of perovskite compounds in the $\text{La}_{1-x}\text{Sr}_x(\text{Mn},\text{Co})\text{O}_3$ system, where $x=0.2-0.6$ referred as S5M, S3M, S2M, SM9, S4C and from $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ where $x=0.2-0.4$ referred as C2M, C3M, C4M, were studied.

For anodes, the cermet-type compositions have been prepared of Ni (30-40% vol) in a yttria stabilized zirconia matrix A3, A4 symbolized have been prepared. Comparatively, the S5M composition ($x=0.55$) was prepared by citrate pyrolysis synthesis at $400-750^\circ\text{C}$ (LS5M symbol).

The starting powders were weighed, ball milled with isopropilic alcohol, dried, calcined in air at $900-1200^\circ\text{C}$ for the synthesis process and pressed into samples. Sintering was carried out at 1250°C for cathodes and at 1100°C for anodes.

For structural characterization, the bulk density measurements and the X-ray diffraction analysis were performed. There were also determined the thermal dilatation coefficient at $20-800^\circ\text{C}$ and the electrical conductivity using the two probe method up to 800°C .

RESULTS AND DISCUSSION

Table 1

The phase structural and sintering results are presented in Table 1.

| Material symbol | Sintered density [g/cm^3] | Open Porosity [%] | Thermal expansion coefficient at $20-800^\circ\text{C}$ $\times [10^{-6}/^\circ\text{C}]$ | Structure type |
|--------------------|---|-------------------|---|--|
| S2M ($x=0.2$) | 5,3 | 9,7 | 10,9 | Orthorhombic |
| S3M ($x=0.3$) | 4,4 | 25,6 | 11,4 | Orthorhombic to hexagonal |
| S5M ($x=0.5$) | 5,4 | 50,6 | 9,1 | Hexagonal and MnO phases traces orthorhombic |
| SM9 ($x=0.2$) | 5,6 | 10,1 | 11,3 | Orthorhombic |
| S4C ($x=0.4$) | 4,1 | 36,6 | 22,5 | Hexagonal |
| S3C ($x=0.3$) | 3,3 | 32,4 | 16,9 | Orthorhombic and the phase traces |
| C2M ($x=0.4$) | 3,7 | 36,7 | 10,6 | Hexagonal and other phases |
| C3M($x=0.45$) | 3,8 | 31,9 | 10,7 | Hexagonal and other phases |
| C4M ($x=0.2$) | 2,8 | 40,4 | 11,1 | Hexagonal |
| LS5M($x=0.55$) | 3,5 | 44,0 | 10,1 | Hexagonal |

| Material symbol | Sintered density [g/cm ³] | Open Porosity [%] | Thermal expansion coefficient at 20-800 ^o C x[10 ⁻⁶ / ^o C] | Structure type |
|-----------------|---------------------------------------|-------------------|---|---------------------------------------|
| 5) | | | | |
| A3 | 4,3 | 32,5 | 10,8 | Monoclinic and cubic ZrO ₂ |
| A4 | 4,2 | 30,8 | 10,3 | Monoclinic and cubic ZrO ₂ |

The XRD patterns obtained pointed out the achievement of a phase structure with orthorhombic or hexagonal - rhombohedral symmetry, La_{1-x} M_x(Mn,Co)O₃ compound (M=Sr,Ca) and with a corresponding distortion from orthorhombic to hexagonal due to the doping quantity (Sr,Ca) by cationic substitution on La site in their crystalline lattice. Thus, at a lower Sr (S2M, S3M SM9) or Ca (C2M, C3M) content have been noticed the achievement of an orthorhombic symmetry. At a x(Sr, Ca) content ≥ 0.4 is formed the most stable structure with a monophasic hexagonal-rhombohedral symmetry. This result is the most concluding for the composition with x(Sr)=0.55, prepared by citrate-pyrolisis synthesis, which shown the total development of the monophasic symmetry, and the best crystallization.

Also, it has been noticed a variable sintering process, as an effect of the cathode composition doping.

The influence of the Sr doping at $x \geq 0.2$ and with Ca at $0.25 \leq x \leq 0.55$ in the manganite and cobaltite investigated systems, takes place by a sintering adequate behaviour, with increasing of porosity up to 50.6 %.

At the Sr doping is delimited the composition with $x = 0.55$, having a densification corresponding of a IT-SOFC electrode material [4,5]. From the samples with Ca doping, C4M shown the most favorable densification.

The X-ray diffraction structural analysis carried out on A3, A4 anode materials show the development of the phase structure specific of a cermet-type material, containing two different phases of the two components: a majority phase formed in the ZrO₂-Y₂O₃ solid solution, and a NiO cubic phase.

The electric conductivity data from the fig.1 show the same influence of the doping and of the phase structure upon the conductivity values. So, the S4C, C4M, LS5M cathodes and A4 anode show the best electrical conductivity behaviour in the elevated temperature range (600-800^oC) required for a good electrode function in a IT-SOFC device.

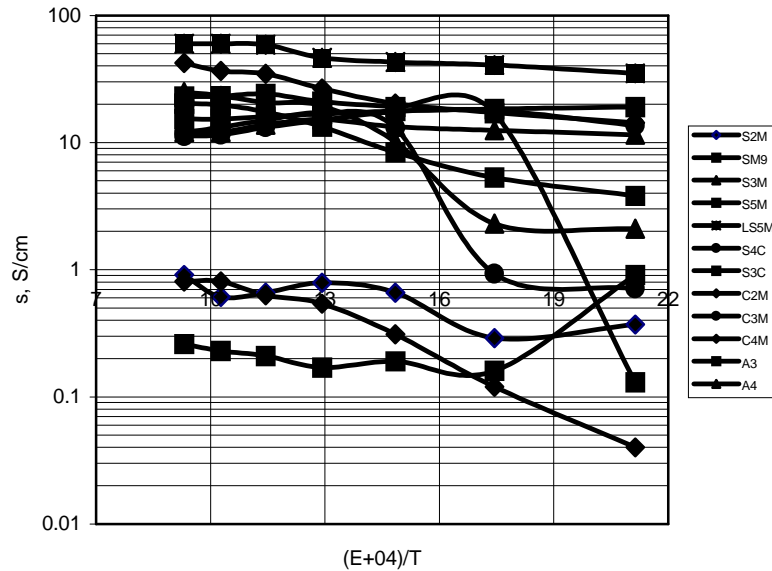


Fig.1- The electric conductivity variation function of temperature

CONCLUSIONS

From the results shown above it can be concluded that the studied perovskite compounds $\text{La}_{1-x}\text{M}_x(\text{Mn,Co})\text{O}_3$ systems ($\text{M}=\text{Sr,Ca}$) synthesized by classic technology and chemical synthesis can be recommended of electrode materials only if they are formed with a hexagonal-rhombohedral monophase perovskite structure and if they show a suitable sintering behaviour.

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