SYNTHESIS AND CHARACTERIZATION OF
A NEW PEROVSKITE MATERIAL FOR SOFC APPLICATIONS

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ABSTRACT

A new compound La$_{0.70}$Ca$_{0.30}$Cr$_{0.85}$Co$_{0.05}$Fe$_{0.05}$Ni$_{0.05}$O$_3$ has been synthesized via a drip pyrolysis method involving glucose as a combustion fuel. Using a large spectrum of characterization methods the material has been investigated with respect to SOFC requirements. The compound exhibited promising possibilities as an interconnect material.

1. INTRODUCTION

Calcium-doped lanthanum chromite with Cr deficiency exposes good sinterability properties in air at temperatures as low as 1300°C (1, 2).

Nasrallah et al. (3) prepared calcium-doped LaCrO$_3$ perovskites in stoichiometric compositions. But they partially substituted chromium with cobalt up to 20%. It seems that too high cobalt doping is not advantageous because of unacceptably high thermal expansion coefficient and possibly some chemical instability at low partial oxygen pressure.

Recently, we prepared and investigated the similar compositions with lower cobalt doping (4). In order to diminish the thermal expansion coefficient, alternative cation dopings on B site (in perovskite ABO$_3$) has been chosen in the present work. Until now, other perovskites, as LaFeO$_3$, LaCoO$_3$ and LaNiO$_3$ have been used in SOFC (5, 6). Therefore, doping with Co, Fe and Ni on B site is proposed.
2. EXPERIMENTAL

The perovskite type powder $\text{La}_{0.7}\text{Ca}_{0.3}\text{Cr}_{0.85}\text{Co}_{0.05}\text{Fe}_{0.05}\text{Ni}_{0.05}\text{O}_3$ has been prepared by a drip pyrolysis method (7). A 1.5 M aqueous solution, starting from nitrates of La, Ca, Cr, Co and Ni and ferrous acetate, was prepared. The glucose in the molar ratio 1:1 with respect to the total metal was added. The stock solution fed by a membrane pump was dripped into a rotary furnace at a rate of about 10 cm³/min. The inner furnace wall temperature was approx. 550°C.

The as synthesized powder was examined by the following methods: XRD, carbon content, surface area and SEM. The powder was ground with polyethylene glycol (molecular weight 4000 g/mol) and pressed in pellets at about 32 MPa.

The pellets were sintered at temperatures between 1200 and 1400°C in air for 2 hours. Furthermore, a shrinkage determination was carried out by dilatometry.

Thermal expansion coefficients and electrical conductivity were measured on the pellets sintered at 1300°C in air for 2 hours. The conductivity was determined both in air and reducing atmosphere at 1000°C.

The stability in reducing atmosphere was investigated on pellets sintered at 1300°C by varying the atmosphere during thermogravimetric measurements at 1000°C.

3. RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern for the as synthesized powder (a), sintered pellets at 1300°C in air for 2 hours (b), and the pellet on which the electrical conductivity was measured (in reducing atmosphere) (c). As seen in the pattern, all samples have a perovskite type structure, space group PNMA with orthorhombic structure. Crystallite size of as synthesized powder is about 26 nm. Possibly, the powder contains some very small traces of $\text{La}_2\text{CrO}_6$ (the peak around 28.30 2θ angle). The pseudocubic parameter is evaluated to $a_0 = 0.386$ nm. The BET specific area is found to be 22.5 m²/g. The orthorhombic structure becomes more evident after sintering at 1200°C, and the crystalline parameters were calculated as: $a = 0.544$ nm, $b = 0.770$ nm, $c = 0.546$ nm, whereas the unit cell volume is 0.229 nm³ and theoretical density 6.10 g/cm³.
Thermal expansion coefficient carried out in dilatometry equals to $10.78 \times 10^{-6}$/K in the temperature range from room temperature to 1000°C in air, and Fig. 2 (a) presents the variation of $(\Delta L/L_0)$ on a sintered pellet.

Fig. 2 (b) presents furthermore the shrinkage curve by sintering in air up to 1200°C. The sintering process already begins at 800°C and the sintering rate has a maximum between 950 and 1050°C. The total shrinkage has been calculated to 33%, whereas the green density has been determined to about 28% TD which can be considered too low for optimal densification. Sintering at 1400°C increases the density to above 90% of the theoretical density. This sintering behaviour is believed to be due to a "transient liquid phase". A similar argument has been used in the case of lanthanum chromite doped with calcium published by several authors (1, 3).

As synthesized powders contain minute amounts of $\text{La}_2\text{CrO}_6$ (at most 1 wt%).

The carbon content in as synthesized powder is about 1.3 wt%. This is removed after a calcination at 700°C for 2 hours.

The electrical conductivity measured in air on the pellet sintered at 1400°C results in a value of $\sigma = 42$ S/cm at 1000°C without correlation for the actual theoretical density of the pellet. The temperature dependence on conductivity between 500 and 1000°C, in air obeys the small polaron mechanism and the activation energy is calculated to $E_a = 0.17$ eV, and the pre-exponential factor to $\log \sigma_0$ (S/cm) = 5.4.

The conductivity measured in moist 3% H$_2$ (partial oxygen pressure $p_{O_2} \approx 10^{-18}$ atm.), and T = 1000°C, has been determined to 1.3 S/cm, while the conductivity after reoxidation of the same specimen changed to a value of 26 S/cm at 1000°C. Obviously, electrical conductivity is not a fully reversible property during reduction/oxidation cycles for this compound.

Thermogravimetric investigation in reducing atmosphere at 1000°C results in weight loss which was not totally recuperated in the reoxidation process after several hours. But the XRD examination of the sample exposed only perovskite structure (Fig. 1(c)) which might be in a substoichiometric state ($\text{ABO}_{3.5}$).
Based on experiences presented in another work (4) it can be expected that higher sintering densities of this material can be obtained by using an optimal powder preparation technique.

4. CONCLUSION

- The work demonstrates that it is possible to synthesize a single phase perovskite based on lanthanum chromites doped with calcium (on A site) and cobalt, iron and nickel (on B site).

- The powder pressed in pellets (or eventually tape cast) shows high sinterability in air. More than 90% of theoretical density can be reached at 1400°C for 2 hours.

- The electrical conductivity in air follows small polaron theory and has a value of 42 S/cm which is comparable with that of La(Sr)CrO₃ (8, 9).

- The thermal expansion coefficient of the synthesized compound is $-10.78 \times 10^{-6}/°K$, which is very near to that of zirconia (10).

- The compound might be considered as candidate for SOFC interconnect.

5. ACKNOWLEDGMENTS

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Fig. 1  XRD patterns of $\text{La}_{0.70}\text{Ca}_{0.30}\text{Cr}_{0.85}\text{Co}_{0.05}\text{Fe}_{0.05}\text{Ni}_{0.05}\text{O}_3$. As synthesized (a); sintered at 1300°C, 2 h (b); treated in moist 3% H$_2$ (c).
Fig. 2 Thermal expansion of La$_{0.70}$Ca$_{0.30}$Cr$_{0.85}$Co$_{0.05}$Fe$_{0.05}$Ni$_{0.05}$O$_3$ (a) and linear shrinkage during sintering (b).