

CHEMICAL SYNTHESIS OF LSGM POWDERS FOR SOLID OXIDE FUEL CELL (SOFC) ELECTROLYTE

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ABSTRACT

Synthesis of LSGM ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$), LSFM ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$), and LSCM ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$) powders were achieved via organic precursor method. Different organic "carrier" molecules were used for powder synthesis. Citric acid, tartaric acid, Pechini precursors, polyvinyl alcohol, and ethylene diaminetetraacetic acid were selected as organic carriers for their ability to stabilize the metal ions. Each organic carrier material exhibited a different degree of effectiveness in the synthesis of the mixed oxide powders. One of the main factors affecting the phase purity appears to be the interaction of the functional groups with the constituent cations. The effectiveness of the organic carrier with varying number and type of functional groups is evaluated and discussed in terms of the phase distribution in the powders after the calcination step.

INTRODUCTION

Solid oxide fuel cells are regarded as the energy production systems for 21st century due to their high efficiency, utilization of a variety of the fuel resources, and environmental friendliness. Strontium and magnesium-doped lanthanum gallate (LSGM, e.g. $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_{3-(x+y)/2}$) is a perovskite-type oxide and one of the most promising electrolyte materials for Intermediate Temperature-SOFC applications. Its ionic conductivity values are much higher than the one of YSZ electrolyte, and comparable to that of ceria-based electrolytes in the high and intermediate temperature ranges. Ionic conductivities of YSZ, LSGM, and CGO electrolytes at temperatures 600°C, 800°C, and 1000°C are tabulated in Table 1.

Table 1. Ionic conductivities of YSZ, LSGM, and CGO for 600°C, 800°C, and 1000°C.

Electrolyte	600°C	800°C	1000°C
YSZ	0.003 S/cm ⁽¹⁾	0.03 S/cm ⁽¹⁾	0.1 S/cm ⁽¹⁾
LSGM	0.02 S/cm ⁽²⁾	0.12 - 0.17 S/cm ⁽¹⁾	0.25 S/cm ⁽²⁾
CGO	0.025 S/cm ⁽¹⁾	0.1 S/cm ⁽²⁾	0.25 S/cm ⁽¹⁾

Each electrolyte material in SOFC construction is designed to exhibit the best performance under SOFC operating conditions. Small discrepancies in the composition results in a poorer performance of SOFC. For example, excellent ionic conductivity was achieved with Sr and Mg-doped LaGaO_3 electrolyte material of the following composition ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.83}\text{Mg}_{0.17}\text{O}_{3-\delta}$)³. Small deviations from composition resulted in a decrease in the ionic conductivity. Therefore, it is important to produce pure and single-phase SOFC components with the desired compositions.

The organic precursor technique is a method widely used in mixed oxide powder synthesis⁴⁻⁷. The predicted mechanism in organic precursor method for achieving a stable precursor is the

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chelating/complexing of the metal cations by the functional groups of the organic carrier materials in the solution⁸. This stabilization action is believed to be due to columbic attraction forces between the carboxylic or hydroxyl groups of the carrier materials and metal cations. The molecular geometry of the functional groups is also believed to play an important role in the chelating/complexing ability. As a result of this stabilization, metal cations are distributed homogeneously in the solution and are stabilized in the pre-ceramic precursor after solvent removal. During calcination, after the organic burn-out, an amorphous powder is obtained. At higher temperatures, crystallization of the desired phases takes place. Due to the homogeneity in molecular level, lower diffusion distances for the cations are required to obtain the desired crystal phase. This in turn may result in lower temperatures for phase purity compared to the solid-state reaction technique⁹. Moreover, combustion of the organic materials results in local temperature increases, that help diffusion process and final crystallization.

Different types of the organic carrier materials can be used in oxide synthesis. One of the successful techniques for single phase mixed oxide powders is Pechini process¹⁰. Pechini process operates through polyesterification between hydrocarboxylic acids such as citric acid, and polyhydroxy alcohols such as ethylene glycol¹⁰. According to the ester reaction shown below, carboxyl end of citric acid and hydroxyl end of ethylene glycol react and a water molecule is released. The acid acts as a chelating agent that stabilizes the cations dissolved in the solution.

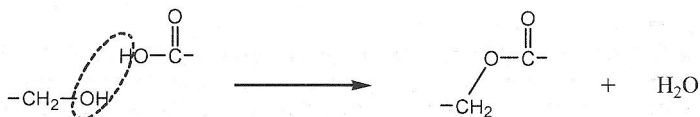


Figure 1. Ester reaction.

The polymerization is based on the polyesterification between the metal-chelate complexes and polyhydroxyl alcohols. By the polyesterification process, randomly coiled macromolecular chains are obtained. These chains may chelate cations uniformly and form very stable metal-organic complexes. Moreover, due to chelating action and high viscosity polymeric network, cation segregation during solvent evaporation is hindered. The resultant ceramic powders possess better chemical homogeneity and smaller particle size. Organic precursor methods with different organic carrier materials, such as citrate synthesis, polymeric precursor synthesis, and urea method have been employed in various oxide syntheses. However there are few studies on the chemical synthesis of SOFC components via different carrier materials^{11,12}. In this study LSGM synthesis was conducted via the organic precursor method. Also the effects of different carrier materials on phase purity and crystallization behavior were investigated. Additionally, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSFM) and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSCM) powders were synthesized with the same synthesis route and organic carrier materials. In the synthesis of LSFM and LSCM powders, the stoichiometry used in LSGM synthesis was kept to investigate the effects of different cations (Fe^{3+} or Cr^{3+} in place of Ga^{3+}). Iron and chromium were chosen to replace gallium such that the new materials can be evaluated as candidates for SOFC interconnect and cathode materials.

EXPERIMENTAL PROCEDURE

Cation sources were nitrate salts of the desired cations selected for their high solubility in cold water. Lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, >99%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), gallium nitrate nanohydrate ($\text{Ga}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 99.9%, ChemPur Feinchemikalien und Forschungsbedarf GmbH, Karlsruhe, Germany), strontium nitrate ($\text{Sr}(\text{NO}_3)_2$, >99%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), magnesium nitrate hexahydrate ($\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), iron nitrate nanohydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), chromium nitrate nanohydrate ($\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, all three salts >99%, Merck KgaA, Darmstadt, Germany) were the sources of lanthanum, gallium, strontium, magnesium, iron, and chromium, respectively.

Polyvinyl alcohol, PVA ($n \cdot \text{C}_2\text{H}_4\text{O}$, MW = 72000, >98%, Merck KgaA, Darmstadt, Germany), citric acid ($\text{C}_6\text{H}_8\text{O}_7$, >99.5%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), ethylenediaminetetraacetic acid, EDTA ($\text{C}_{10}\text{H}_{16}\text{N}_2\text{O}_8$, 98%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany), tartaric acid ($\text{C}_4\text{H}_6\text{O}_6$, 99.7%, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany) and ethylene glycol, EG ($\text{C}_2\text{H}_4\text{O}_2$, 99.5%, Carlo Erba Reagenti, Mendetison Group) were the organic/polymeric materials used as "carriers" for the cations. Distilled water and nitric acid (HNO_3 , 65% solution, Sigma Aldrich Chemie GmbH, Taufkirchen, Germany) were utilized as solvents in the experiments where indicated.

Low temperature chemical synthesis of three different mixed oxides with four-cations, $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSGM), $\text{La}_{0.9}\text{Sr}_{0.1}\text{Cr}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSCM), and $\text{La}_{0.9}\text{Sr}_{0.1}\text{Fe}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$ (LSFM) was investigated to produce these mixed-oxides as single phase, fine powders. For the synthesis, desired amounts of cation salts were dissolved in distilled water/organic carrier solutions to obtain exact stoichiometry. In the organic precursor route with organic/polymeric carrier materials, the amounts of carrier materials were determined to obtain 1:1 cation to organic molecule ratio in the solution. For the synthesis of LSGM, two different synthesis concepts were applied. In both routes, nitrate salts of each constituent cation were selected as the cation source. Polyvinyl alcohol (PVA, Steric entrapment method¹³), citric acid (CA), tartaric acid (TA), ethylene diaminetetraacetic acid (EDTA), or Pechini precursors (with 60% citric acid – 40% and ethylene glycol, or 90% citric acid – 10% ethylene glycol mixtures) were used as the organic carrier materials in solution. In the synthesis of LSGM with EDTA as the carrier material, nitric acid was the solvent. In the second production route, the nitrate salt of each constituent cation was dissolved in distilled water without any organic molecule. Solutions were mixed with a magnetic stirrer and heated up to 300°C to evaporate the solvents and to obtain a crisp powder. These organo-metallic precursors were ground and calcined in pure alumina crucibles at 700°C, 800°C, 900°C, 1000°C, 1050°C, 1100°C, 1150°C, or 1200°C in a box furnace (in air) with 10°C/min heating rate. After reaching the final temperature the furnace was turned off immediately and the powders were allowed to cool in the furnace.

In LSFM and LSCM synthesis, calcination temperatures, 500°C, 550°C, 600°C, 650°C, 700°C, 750°C, 800°C, and 850°C were used. Crystal structure and phase distribution of the powders at room temperature were studied with an x-ray powder diffractometer (Bruker AXS-D8, Karlsruhe, Germany). The measurements were performed in the 2 θ range of 10° - 90° at 40 kV and 40 mA, using Cu-K α radiation. In all measurements, the step size was 0.03°, and data collection period was 2 seconds in each step. K α_2 peaks were suppressed in the x-ray diffraction measurements. In x-ray diffraction plots, the percentages of each phase were calculated by taking the ratio of the height in the intensity axis of the main peak (100% peak) of each phase, to the sum of the height of the main peaks of all phases. Prior to the peak-height measurements, background subtraction was performed. For phase identification, the experimental spectra were

compared to the characteristic x-ray card files in the JCPDS database. For phases that were synthesized in this work for the first time, the experimental spectra were compared to the JCPDS file for the compound from which the new mixed cation oxide was derived, i.e. the LSGM x-ray spectrum was compared to the JCPDS file for LaFeO_3 and $\text{La}_{0.9}\text{Sr}_{0.1}\text{FeO}_{2.95}$; while the LSCM x-ray spectrum was compared to the JCPDS file for LaCrO_3 .

RESULTS and DISCUSSION

LSGM Synthesis

Tables 2-4 list the percent amounts of phases in the powders obtained with a different organic carrier molecule and calcined at the specified temperatures. The amounts are determined from the XRD intensities. Figure 2 illustrates the effectiveness of the carrier molecules in terms of LSGM phase amount in the powders as a function of calcination temperature.

Table 2. Phase percentages of powders for two different Pechini precursors.

<i>Pechini (60-40)</i>	<i>LSGM</i>	<i>LaSrGaO₄</i>	<i>SrLaGa₃O₇</i>	<i>La₄Ga₂O₉</i>	<i>Pechini (90-10)</i>	<i>LSGM</i>	<i>LaSrGaO₄</i>	<i>SrLaGa₃O₇</i>	<i>La₄Ga₂O₉</i>
800°C	0.0%	0.0%	60.0%	40.0%	800°C	5.0%	3.4%	62.8%	28.8%
900°C	12.8%	0.6%	39.2%	47.4%	900°C	76.5%	4.5%	7.5%	11.5%
1000°C	53.0%	1.2%	19.7%	26.0%	1000°C	89.4%	2.8%	3.4%	4.4%
1050°C	67.4%	1.3%	11.2%	20.1%	1050°C	92.8%	5.2%	1.1%	0.9%
1100°C	85.0%	1.8%	4.4%	8.7%	1100°C	89.9%	7.4%	2.2%	0.5%
1150°C	95.8%	4.2%	0.0%	0.0%	1150°C	95.2%	4.1%	0.7%	0.0%
1200°C	94.9%	5.1%	0.0%	0.0%	1200°C	92.2%	6.6%	1.2%	0.0%

As the ethylene glycol amount in the Pechini precursor was decreased to 90:10 CA:EG, the amount of LSGM appeared to increase at a given calcination temperature (see Table 2). This may be due to an increased number of active carboxylic ends of citric acid compared to the 60:40 CA:EG precursor. To this end, the use of citric acid alone could give better phase distribution due to a more effective chelating action. When citric acid alone was used as the organic carrier, a strong increase in the percentage of LSGM phase was observed in powders calcined between 800°C and 900°C (Table 3). The better LSGM yield of the citric acid as the carrier material, compared to Pechini process may be explained by the large number of free active carboxylic groups of the citric acid, without the ethylene glycol to esterify with. The effectiveness of the citric acid in stabilizing cations stems from the "claw" shape arrangement of carboxylic groups of the citric acid, which is suitable to chelate cations. In Pechini process, ethylene glycol molecules attach to the carboxylic ends of citric acid molecules according to the reaction in Figure 1 and thereby decrease the number of active carboxylic ends. This in turn decreased the effectiveness of citric acid molecules for chelating La^{+3} , Sr^{+2} , Ga^{+3} , and Mg^{+2} ions in the Pechini solution.

Table 3. Phase percentages of powders for precursors with CA and TA.

CA	LSGM	LaSrGaO ₄	SrLaGa ₃ O ₇	La ₂ Ga ₂ O ₉	TA	LSGM	LaSrGaO ₄	SrLaGa ₃ O ₇	La ₂ Ga ₂ O ₉
800°C	10,1%	1,9%	61,4%	26,7%	800°C	27,1%	0,0%	55,5%	17,5%
900°C	94,2%	0,8%	2,3%	2,8%	900°C	28,8%	0,0%	39,3%	31,8%
1000°C	96,4%	1,6%	0,5%	1,5%	1000°C	62,7%	0,0%	16,5%	20,8%
1050°C	96,0%	4,0%	0,0%	0,0%	1050°C	96,4%	0,5%	1,6%	1,5%
1100°C	92,8%	7,2%	0,0%	0,0%	1100°C	98,7%	1,3%	0,0%	0,0%
1150°C	95,7%	4,3%	0,0%	0,0%	1150°C	99,0%	1,0%	0,0%	0,0%
1200°C	95,0%	5,0%	0,0%	0,0%	1200°C	97,9%	2,1%	0,0%	0,0%

To see the effect of the number of carboxylic ends in the chelating cations, different acids with two or four carboxylic ends (tartaric acid and EDTA) were used as the carrier material. Tartaric acid has two carboxylic groups in its molecular structure. As mentioned before, the chelating ability of citric acid is due to its three carboxylic ends. Therefore tartaric acid with two carboxylic groups may be less effective, resulting in a lower LSGM phase amount for the same temperatures. Also the geometry of these molecules may play an important role in the chelating action. Experiments with tartaric acid confirmed the expected relationship between the number of carboxylic ends, geometry of the carrier molecule and the chelating ability. In LSGM powder synthesis with tartaric acid as the carrier material, lower amounts of LSGM phase were obtained (28.8% and 62.7% at 900°C and 1000°C, respectively) in comparison to the LSGM powder synthesized with citric acid (94.2% and 96.4% at 900°C and 1000°C, respectively) as the carrier material at low temperatures (see Table 3). However, the amount of LSGM phase calcined from TA-acid precursors at temperatures above 1050°C was larger than those prepared with citric acid based precursors.

Table 4. Phase percentages of powders for precursors with EDTA and PVA.

EDTA	LSGM	LaSrGaO ₄	SrLaGa ₃ O ₇	La ₂ Ga ₂ O ₉	PVA	LSGM	LaSrGaO ₄	SrLaGa ₃ O ₇	La ₂ Ga ₂ O ₉
800°C	6,6%	0,0%	56,4%	37,0%	800°C	0,0%	0,0%	33,8%	66,2%
900°C	42,5%	3,7%	29,7%	24,1%	900°C	0,0%	0,0%	38,2%	61,8%
1000°C	87,2%	2,5%	5,1%	5,2%	1000°C	4,3%	0,0%	39,5%	56,2%
1050°C	84,4%	4,5%	7,1%	4,0%	1050°C	35,2%	1,5%	26,4%	36,9%
1100°C	88,2%	3,5%	5,0%	3,3%	1100°C	36,7%	0,6%	25,6%	37,1%
1150°C	91,9%	3,6%	3,0%	1,5%	1150°C	85,8%	2,7%	4,4%	7,0%
1200°C	94,6%	3,2%	2,2%	0,0%	1200°C	96,5%	3,5%	0,0%	0,0%

EDTA was also used as the carrier material in the LSGM synthesis. EDTA appears to be more efficient than TA but still less effective than CA (see Tables 3 and 4). If a simple relationship between the number of carboxylic acid ends of a molecule and its effectiveness in chelating various cations were to be expected, EDTA should have been a more effective carrier molecule for mixed cations.

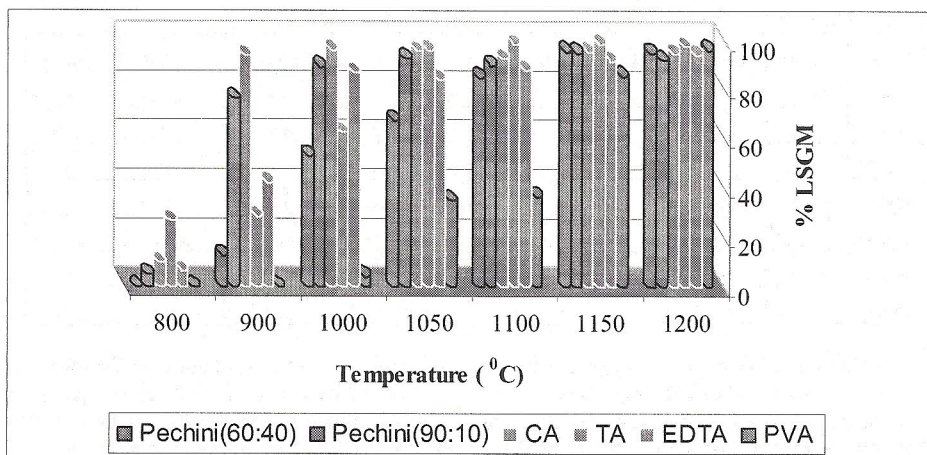


Figure 2. LSGM percentages of the powders calcined with different carriers at different temperatures.

In the experiments conducted with the carrier materials that have carboxylic ends, such as Pechini precursors, CA, TA, and EDTA; the percentage of $\text{LaSrGa}_3\text{O}_7$ phase was higher than $\text{La}_4\text{Ga}_2\text{O}_9$ phase below 1000°C (see Tables 2-4). However, in LSGM synthesis with PVA, the percentage of $\text{La}_4\text{Ga}_2\text{O}_9$ phase was higher than the $\text{LaSrGa}_3\text{O}_7$ phase (see Table 4). $\text{La}_4\text{Ga}_2\text{O}_9$ phase is lanthanum-rich, $\text{LaSrGa}_3\text{O}_7$ phase is gallium-rich. Therefore, it appears that an interaction (complexing) of PVA with lanthanum ions may be less favored compared to gallium ions in a system composed of these four cations. Thus, an early crystallization of $\text{La}_4\text{Ga}_2\text{O}_9$ phase is more favorable than the other phases because of the loosely held La^{3+} ions in PVA-cation polymeric network at low temperatures (below 800°C). Also, LSGM percentage in the resulting powders calcined up to 1100°C was considerably small compared to the LSGM percentage in the powders synthesized with Pechini precursors, CA, TA, or EDTA (see Tables 2-4). LSGM powders synthesized using nitrate sources of all cations without using any complexing or chelating agent yielded much lower amounts of LSGM at any calcinations temperature. The results once more confirmed the effectiveness of carrier material in mixed oxide synthesis. The highest amount of LSGM phase obtained without any organic carrier in the process was 58.6% at 1200°C .

LSFM and LSCM Synthesis

Since ionic radii and valences of iron and chromium ions are similar to gallium ion, substitution of these cations with gallium ion may result in powders with similar crystal structure and properties to LSGM. Moreover, LaFeO_3 and LaCrO_3 based oxides are candidate cathode and anode materials for SOFC, respectively. X-ray diffraction results of the calcined powders at different temperatures showed that, single phase LSFM powders were obtained at 550°C with PVA, CA, or EDTA as the carrier materials. This result indicated that organic precursor method is an efficient technique to synthesize multi-cation oxides. According to the author's best knowledge, Sr-doped LaFeO_3 , a three-cation oxide material, could be synthesized at 1200°C with

some amount of undesired phases¹⁴. However, synthesis of LSFM is reported in our work for the first time. In LSCM synthesis, 96.9% LSCM powders were obtained at 850⁰C with PVA as the organic carrier material. Sauvet et al. synthesized Sr-doped LaCrO₃ at 1000⁰C as single phase powder¹⁵. The result in this study may still seem to be promising in light of the difficulty of synthesizing a four-cation oxide rather than a three-cation oxide.

The most intriguing result of this study is the inconsistency of the effectiveness of the organic carrier materials for different powders. In LSGM synthesis CA seems to be the best and PVA seems to be the worst carrier material for low temperature synthesis. A similar tendency was also observed in LSFM synthesis. However, in LSCM synthesis, PVA was the most effective organic carrier among all the others. Moreover, CA was the one of the worst carrier material. These results emphasize the need for studying the effectiveness of “chelating” action to obtain single phase oxide powders. If a strong chelating was the only necessary criterium for desired phase formation, CA should be also effective in LSCM synthesis.

Functional group – ion (or ion group) interaction appears to be also important in desired phase formation. As underlined before, interactions of PVA with lanthanum and gallium ions were different than the other carrier materials. This is an indication of the effect of functional group – ion interaction for different carrier materials. In order to understand cation functional group interaction, Fourier Transform Infrared Spectrometry (FTIR) and Nuclear Magnetic Resonance (NMR) Spectroscopy studies will be conducted on different organo-metallic precursors. FTIR may be useful to determine compositions and relative amounts of functional groups at different calcination temperatures. NMR spectroscopy may be useful to determine chemical structure of the powders at each calcination temperature.

CONCLUSION

In this study, synthesis of LSGM, LSFM, and LSCM powders were performed via organic precursor method by using different organic carrier materials. When calcined at a low temperature (< 1000⁰C), precursors synthesized using citric acid (CA) as the organic carrier material yielded 94,2% LSGM phase in the powders. Maximum LSGM concentration (99%) in the synthesized powders was obtained at 1150⁰C using tartaric acid (TA) as the organic carrier material. In contrast to LSGM, single-phase LSFM was obtained with relative ease from the precursors calcined at 550⁰C. CA appeared to be most effective precursor for low temperature synthesis of LSFM. The best concentration of LSCM phase in the synthesized powders was 96.9%, when polyvinyl alcohol (PVA) was used as the organic carrier material.

Every organic carrier material has exhibited a different performance for the synthesis of mixed oxide powders. Moreover, the performance of one organic carrier material varied for each type of mixed oxide powder synthesis. TA was the best organic carrier material for LSGM synthesis at calcination temperatures larger than 1000⁰C, but it performed poorly in LSCM synthesis when compared to PVA at all calcination temperatures. Cation chelating and/or stabilizing ability of the functional groups of the organic carrier materials does not appear to be scaling just with the number of functional groups of the carrier molecule. A more complex interaction of the organic carrier with different cations may play an important role in synthesis of single phase mixed oxide powders at relatively low temperatures.

REFERENCES

- ¹ J. Fleig, K.D. Kreuer, J. Maier, "Handbook of Advanced Ceramics", *Materials, Applications, and Processing*, Academic Press, 1-60 (2001).
- ² Helmut Ullmann, Nikolai Trofimenko, "Composition, structure and transport properties of perovskite-type oxides", *Solid State Ionics* **119**, 1-8 (1999).
- ³ S.P.S. Badwal, "Stability of solid oxide fuel cell components", *Solid State Ionics* **143**, 39-46 (2001).
- ⁴ G.Ch. Kostogloudis, Ch. Ftikos, A. Ahmad-Khanlou, A. Naoumidis, D. Stöver, "Chemical compatibility of alternative perovskite oxide SOFC cathodes with doped lanthanum gallate solid electrolyte", *Solid State Ionics* **134**, 127-138 (2000).
- ⁵ A. Cüneyt Taş, Peter J. Majewski, Fritz Aldinger, "Chemical preparation of pure and strontium- and/or magnesium-doped lanthanum gallate powders", *J. Am. Ceram. Soc.* **83**[12], 2954-2960 (2000).
- ⁶ F. Riza, Ch. Ftikos, F. Tietz, W. Fischer, "Preparation and characterization of $\text{Ln}_{0.8}\text{Sr}_{0.2}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (Ln=La, Pr, Nd, Sm, Eu, Gd)", *Journal of the European Ceramic Society* **21**, 1769-1773 (2001).
- ⁷ Marko Hrovat, Ariane Ahmad-Khanlou, Zoran Samadzija, Janez Holc, "Interactions between lanthanum gallate based solid electrolyte and ceria", *Materials Research Bulletin*, Vol. **34**, Nos. 12/13, 2027-2034 (1999).
- ⁸ Mehmet A. Gülgün, My H. Nguyen, Waltraud M. Kriven, "Polymerized organic-inorganic synthesis of mixed oxides", *J. Am. Ceram. Soc.* **82**[3], 556-560 (1999).
- ⁹ Mehmet A. Gülgün, Oludele O. Popoola, Waltraud M. Kriven, "Chemical synthesis and characterization of calcium aluminate powders", *J. Am. Ceram. Soc.* **77**[2], 531-539 (1994).
- ¹⁰ M.P. Pechini, U.S. Patent No.3, 330, 697, July (1967).
- ¹¹ M. Marinsek, K. Zupan, J. Maeek, "Ni-YSZ cermet anodes prepared by citrate/nitrate combustion synthesis", *J. Power Sources* **106**, 178-188 (2002).
- ¹² K. Zupan, S. Pejovnik, J. Maeek, "Synthesis of nanometer crystalline lanthanum chromite powders by the citrate-nitrate autoignition reaction", *Acta Chim. Slov.* **48**(1), 137-145 (2001).
- ¹³ Mehmet.A. Gülgün, W.M. Kriven, "Polymerized Organic-Inorganic Complex Route for Mixed-Oxide Synthesis", US patent# 6,482,387.
- ¹⁴ S.P. Simner, J.R. Bonnett, N.L. Canfield, K.D. Meinhardt, V.L. Sprenkle, J.W. Stevenson, "Development of lanthanum ferrite SOFC cathodes", *Journal of Power Sources* **113**(1), 1-10 (2003).
- ¹⁵ A.-L. Sauvet, J. Fouletier, F. Gaillard, M. Primet, "Doped lanthanum chromites as SOFC anode materials", *J. of Catalysis* **209**(1), 25-34 (2002).