

# Physicochemical compatibility of CGO fluorite, LSM and LSCF perovskite electrode materials with $\text{La}_2\text{Mo}_2\text{O}_9$ fast oxide-ion conductor

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## Abstract

The reactivity of typical electrode materials for solid oxide fuel cells, namely  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF),  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  (LSM) and  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (CGO), with fast oxide-ion conductor  $\text{La}_2\text{Mo}_2\text{O}_9$  is thoroughly studied using X-ray diffractometry. Modifications in the materials diffraction patterns and occurrence of impurity diffraction peaks are evidenced in LSCF and LSM above 700–800 °C. They are interpreted in terms of cationic migrations from one material phase to the other (typically strontium depletion/substitution), and subsequent formation of subsidiary phases (for instance strontium molybdate). With CGO no reactivity is observed up to 1000 °C. For all three electrode materials the thermal expansion coefficient (TEC) is measured from X-ray thermodiffractiongrams and compared to that of  $\text{La}_2\text{Mo}_2\text{O}_9$ .

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## 0. Introduction

Fast oxide-ion conductors attract considerable interest because of their potential application as electrolyte for solid oxide fuel cell. The most widely used electrolyte is yttria stabilized zirconia (YSZ) but it has a relatively high working temperature, around 1000 °C, necessary to reach high oxide ion mobility. Active research focus on looking for better oxide-ion conductors at lower operating temperature, namely in the range 700–800 °C. Due to their high ionic conductivity at 600–800 °C, doped ceria have been proposed as intermediate temperature electrolyte [1–3]. However, at low oxygen partial pressure, un-

doped and doped ceria exhibit mixed ionic and electronic conduction, making them more suitable as SOFC anode materials [4–6]. The doped lanthanum gallate perovskite  $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{2.85}$  (LSGM) which exhibits an excellent conductivity over a broad range of oxygen partial pressures  $10^{-22} \leq \text{PO}_2 \leq 1$  atm [7–9] (larger than 0.1 S/cm at 800 °C) can be considered as a good electrolyte candidate.

Recently, we have discovered a new family of fast oxide-ion conductors, whose parent compound is the lanthanum molybdate  $\text{La}_2\text{Mo}_2\text{O}_9$  which exhibits, around 580 °C, a transition from a slightly distorted low temperature  $\alpha$  form, to a cubic high temperature  $\beta$  form [10,11]. Above this transition temperature, the oxide-ion conductivity is higher than that of YSZ. The drawbacks of pure lanthanum molybdate are the degradation in reducing atmosphere, related to known high reducibility of hexavalent molybdenum cation, and the first order phase transition. Improvement of the stability against reduction was achieved through isovalent tungsten substitution [12], while all cationic site substitution (LAMOx

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family)—except with neodymium—stabilize above a certain rate the cubic  $\beta$  form at room temperature [11,13].

The chemical and mechanical compatibilities between electrode materials and electrolyte are a prerequisite to any further cell testing. Indeed, the formation of reaction products at the electrode/electrolyte interface could be detrimental to the cell efficiency. The cationic inter-diffusion has to be limited in order to prevent the degradation of electrode and electrolyte materials properties. Finally, the determination and comparison of thermal expansion coefficients is needed to select the mechanically compatible electrode/electrolyte materials.

Concerning electrode materials, strontium-doped lanthanum manganites  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_{3-\delta}$  (LSM) have been used extensively as the cathode material in YSZ-based SOFC due to their close thermal expansion match. In spite of their very poor oxide ion conduction in oxidizing atmospheres, the interest in LSM lies in the high electronic conductivity arising from the mixed valence state of manganese. Strontium lanthanum cobaltites  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  (LSC) have also been proposed as possible cathode materials. Indeed, these perovskites are known to have high catalytic activity towards the reduction of oxygen, to retain their oxygen deficiency and high oxygen-self-diffusion coefficients even in an oxidizing atmosphere, and to exhibit high electronic conductivity [14]. To decrease the large thermal expansion coefficient associated with  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  cathodes, substantial studies have been performed on iron substituted samples [15,16]. The optimal conductivity/expansion properties were found in the composition  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ . The addition of an ionic conductor (yttria stabilized zirconia (YSZ) or gadolinium doped ceria (CGO)) to mixed electronic and ionic conductors as  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  (LSM) [17,18],  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) [19] is actually considered to improve the cathode performance in intermediate temperature solid oxide fuel cells.

Although extensive studies have been devoted to the reactivity between zirconia and the above electrode materials [20–27], no such work has been carried out yet on  $\text{La}_2\text{Mo}_2\text{O}_9$ . As a side effect of a milling/sintering process, it has been demonstrated that the attrition milling with zirconia balls introduces a pollution detected by EDX spectroscopy [28]. After long-term annealing of the attrited powders, an insulating impurity, most probably  $\text{La}_2\text{Zr}_2\text{O}_7$ , is formed progressively. This is the same phase as that formed at the interface between zirconia and La-based perovskite materials in conventional SOFC devices [20–27].

Concerning the thermal expansion coefficients (TEC), some of the  $\text{La}_2\text{Mo}_2\text{O}_9$ -based materials have been determined by dilatometry or thermodiffraction measurements. It has been shown that the  $\text{La}_2\text{Mo}_2\text{O}_9$  TEC ( $14\text{--}18 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  [29]) can be drastically reduced by Er or W substitutes to La or Mo respectively:  $10.6 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  for  $\text{La}_{1.8}\text{Er}_{0.2}\text{Mo}_2\text{O}_9$  [29] and  $9.7 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$  for  $\text{La}_2\text{Mo}_{0.8}\text{W}_{1.2}\text{O}_9$  [30].

In the present paper, the mechanico-chemical compatibility of likely oxide electrode materials (namely the perovskites  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) and  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$  (LSM), and fluorite  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  (CGO)) with  $\text{La}_2\text{Mo}_2\text{O}_9$  solid oxide ion conductor (as a prelude to more complex LAMOX members) is investigated using X-ray powder diffraction. The paper is structured as follows. Section 1 is devoted to experimental details, whereas Sections 2 and 3 present the results related to the chemical and mechanical compatibility respectively, before a conclusion as Section 4.

## 1. Experimental details

Polycrystalline  $\alpha\text{-La}_2\text{Mo}_2\text{O}_9$  was prepared by conventional solid state reaction. The stoichiometric mixture of  $\text{La}_2\text{O}_3$  and  $\text{MoO}_3$  was first heated at  $500 \text{ }^\circ\text{C}$  for 12 h, and then at  $900 \text{ }^\circ\text{C}$  with several regrindings and heatings. Finely divided powders of electrode materials  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ ,  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  and  $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$  were provided by Rhodia Electronics and Catalysis.

For the reactivity studies, equimolar amount of electrode materials and  $\alpha\text{-La}_2\text{Mo}_2\text{O}_9$ , thoroughly ground in an agate mortar, were spread in a mullite boat. To follow the reactivity evolution, the mixtures were fired in air for 72 h at six arbitrary temperatures 500, 600, 700, 800, 900 and  $1000 \text{ }^\circ\text{C}$  (heating and cooling rates  $2 \text{ }^\circ\text{C}/\text{min}$ ). After completion, X-ray powder diffraction patterns were recorded at room temperature on a  $\theta/2\theta$  Bragg–Brentano Bruker-AXS D8 diffractometer ( $\text{CuK}\alpha_{1+2}$  radiations, room temperature,  $V6/V6$  mode, receiving slit 0.2 mm) equipped with a back graphite monochromator. The annealed powder was dusted through a  $63 \text{ }\mu\text{m}$  sieve on a glass holder. Data collection conditions were 25 s/step of  $0.02^\circ$  in the  $[9^\circ\text{--}130^\circ]$  range. The Rietveld program FullProf [31] was used for full-pattern matching refinements.

Thermal expansion coefficients were estimated from the temperature dependence of unit cell parameters obtained by full-pattern matching refinements. Thermodiffraction patterns were recorded on a  $\theta/\theta$  Bragg–Brentano Philips X'pert MPD PRO diffractometer ( $\text{CuK}\alpha_{1+2}$  radiations) equipped with the X'celerator detector and a HTK 1200 Anton Paar chamber. Diffraction patterns were collected under air flow during 200 min in the  $[5^\circ\text{--}130^\circ]$  scattering angle range, with a  $0.0167^\circ$  step from 25 to  $1000 \text{ }^\circ\text{C}$  (heating and cooling rates  $10 \text{ }^\circ\text{C}/\text{min}$ , temperature stabilisation for 20 min). A temperature calibration of the chamber was carried out using the structural transitions  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$  of  $\text{Bi}_4\text{V}_2\text{O}_{11}$  [32] and the brownmillerite to perovskite transition of  $\text{Ba}_2\text{In}_2\text{O}_5$  [33]. These reference materials were prepared by solid state reaction from elementary oxides. All transition temperatures were previously determined by thermal analysis performed on a coupled TGA-DTA apparatus under air flow (TA Instruments SDT 2960, heating rate  $10 \text{ }^\circ\text{C}/\text{min}$ , temperature range  $30\text{--}1000 \text{ }^\circ\text{C}$ ).

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