



Enhanced density of sol–gel derived $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$ thin film with an electric field assisted deposition

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ABSTRACT

A uniform and dense (relative density 89%) $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) thin film (84 nm thick) has been prepared on $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) substrate using a water-based sol–gel method, in order to improve the operating stability of intermediate temperature cathode. An in situ static electric field was applied in the deposition/drying process, and found to obviously affect phase formation and thickness of the final LSM film. It was proposed that the orientation of macromolecules (such as chelating agents and surfactants) and the packing density of metal cations may be influenced by electric field during the deposition process.

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1. Introduction

In recent years, the $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) based cathode for solid oxide fuel cells (SOFCs) has been extensively investigated due to its much higher ionic and electronic conductivities and hence better performance than those of the conventional $(\text{La,Sr})\text{MnO}_{3-\delta}$ (LSM) cathode in the temperature range of 600–800 °C [1]. However, the long-term stability of LSCF cathode is still a concern for practical applications [1–3]. Recently, Liu group proposed new electrode architecture, consisting of an LSCF cathode backbone coated with a dense, thin-film LSM catalyst in order to make effective use of the desirable properties of two different materials: the high ionic and electronic conductivities of an LSCF backbone and the excellent stability of an LSM coating [4].

A lot of methods, such as plasma spraying [5], pulsed laser deposition (PLD) [6], screen printing technique [7], electrostatic spray deposition (ESD) [8], laser molecular beam epitaxy [9] and rf-magnetron sputtering [10], have been used to prepare LSM thin/thick cathode which are, however, more likely to prepare flat film than surface coating especially onto porous cathode. Recently, a continuous $(\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_{3-\delta}$ coating has been prepared by Choi et al. via a sol–gel process [11], in which relevant acetate along with acetic acid and 2-methoxyethanol was used as precursor and solvent, respectively. However, such a water-free-based solution infiltration method seems to have

some drawbacks which would not be preferred in SOFC industry techniques. First of all, all solvents in non-aqueous solution will result in rising costs, compared with those in water-based solution. Secondly, the freezing temperature of the acetic acid is relatively high, i.e., 16.5 °C, and the viscosity of the solution would change a lot near room temperature, which is not the conducive to the deposition of the thin film in porous cathode backbone. Last but not least, based on the environment-benign view, 2-methoxyethanol and acetic acid are not the good choices since the former is poisonous while the latter has a pretty nasty smell. Therefore, it is desirable to develop a simple water-based solution process instead. Theoretically, the thinner and more continuous LSM coating would result in greater activity and stability improvement. For example, a thin LSM coating will lead to a low O^{2-} conductive resistance while a continuous LSM coating will cover surface completely and ensure the stability improvement of the LSCF cathode.

In this study, we report our findings in preparation and characterization of LSM thin films on dense LSCF substrates using a water-based sol–gel process. Further, we observe the effect of an applied electric field on final LSM films.

2. Experimental procedure

The typical $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_{3-\delta}$ (LSM) aqueous solution (0.03 M) was prepared by dissolving appropriate amounts of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (> 99%), $\text{Sr}(\text{NO}_3)_2$ (> 99%) and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.98%) in distilled water. Glycine, polyvinyl pyrrolidone (PVP) and ethanol were used as

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chelating agent and surfactants, respectively. pH value of the final LSM solution was adjusted to 3.

LSM film was prepared on one side (polished down to 1 μm) of LSCF pellet that was prepared by dry-pressing LSCF powders at 250 MPa and then sintering at 1350 $^{\circ}\text{C}$ for 7 h in an oxygen flux. The LSM solution was controlled and dropped onto LSCF surface by a micro-syringe, and then dried under a stable temperature of 25 $^{\circ}\text{C}$ and relative humidity of 75%. During the drying process an external static electric field was applied to assist deposition. Deposited precursor was finally annealed at 800 $^{\circ}\text{C}$ for 1 h to produce LSM film. The perovskite phase was characterized by XRD (X'Pert Pro Alpha-1) using $\text{CuK}\alpha$ radiation. And the microstructure development of the LSM film was detected using thermally assisted FE-SEM (LEO 1530 Gemini, Zeiss).

3. Results and discussion

Effect of electric field on microstructure of LSM film: The thicknesses of LSM thin films without or with static electric field assisted deposition (SEFAD, field strength 66.7 kV/m) were examined by scanning electron microscopy (SEM) technique, and are compared in Fig. 1a and b. The thickness is 123 nm for LSM film without SEFAD while the thickness is 84 nm for LSM film with SEFAD. The theoretical thickness can be calculated, according to the mass of LSM (2.8E–05 g) and the area of LSM film (0.587 cm^2). It is 75 nm, so the relative densities for the LSM films with and without SEFAD are 89% and 60%, respectively. The relative density was improved by 1.5 times after the introduction of electric field.

It can also be seen from the SEM images that the microstructures of the two films are obviously different. The cross-sectional image of LSM film without SEFAD (Fig. 1a) showed some big particles with an average grain size of 50 nm; but for the film with SEFAD (Fig. 1b), the particles disappeared and it was sintered to a much denser film with sharp angles in the cross-section. This may be explained by a speculation model where the orientation of the macromolecules (PVP or Glycine) is affected by in situ electric field. Without electric field, the macromolecules in solution and deposition layer had random orientation (Fig. 1c) and easily reacted with metal salts to form a complex, which was more likely to form fine particles after sintering [12]. After introduction of a static electric field, the orientation of macromolecules became almost the same due to polarization, as shown in Fig. 1d. So, the packing density of metal cations was improved especially in the vertical direction, which can promote sintering

densification process, resulting in enhanced density of 89% for final LSM film.

Effect of electric field on the LSM crystallization: Fig. 2 plots the XRD patterns of LSM films with/without SEFAD after annealing at 700 or 800 $^{\circ}\text{C}$ for 1 h. Note that the thicknesses of LSM films here were $\sim 5 \mu\text{m}$ in order to weaken the signal from LSCF substrate. After heating to 800 $^{\circ}\text{C}$, the XRD profiles look the same, standard perovskite phase, for the two kinds of LSM film with/without SEFAD. When decreasing the temperature to 700 $^{\circ}\text{C}$, the difference between the two films became obvious. Although the LSM film with SEFAD displays lower peak intensity compared with that at 800 $^{\circ}\text{C}$, the number and position of the peaks are all the same, indicating that the LSM perovskite phase can be achieved also at 700 $^{\circ}\text{C}$. But for the film without SEFAD, the peak intensity was even lower, and showed just some main peaks of (110), (024) and (214). It indicates that the applied electric field can decrease crystallization temperature of LSM thin film by at least 100 $^{\circ}\text{C}$. This may be explained by enhanced packing density of metal cations over LSCF substrate due to the applied electric field. This is favorable for phase formation and expected to increase relative density and thus decrease thickness of the final LSM film.

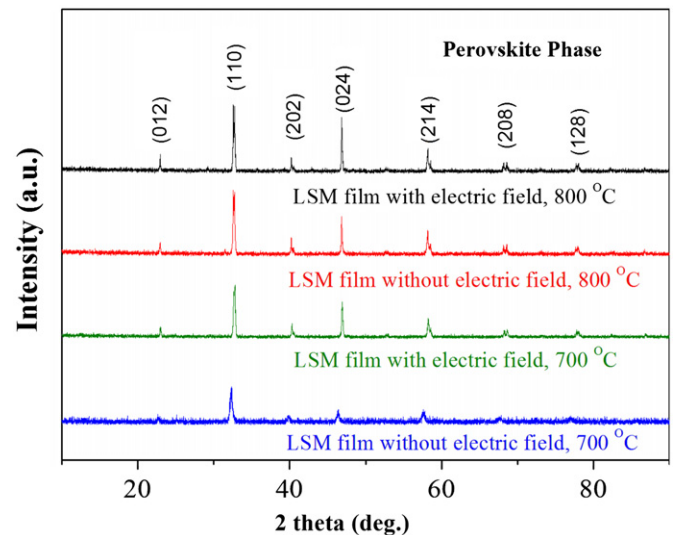


Fig. 2. XRD patterns for the LSM thin films coated on LSCF substrate with/without SEFAD, annealed at 700 $^{\circ}\text{C}$ or 800 $^{\circ}\text{C}$.

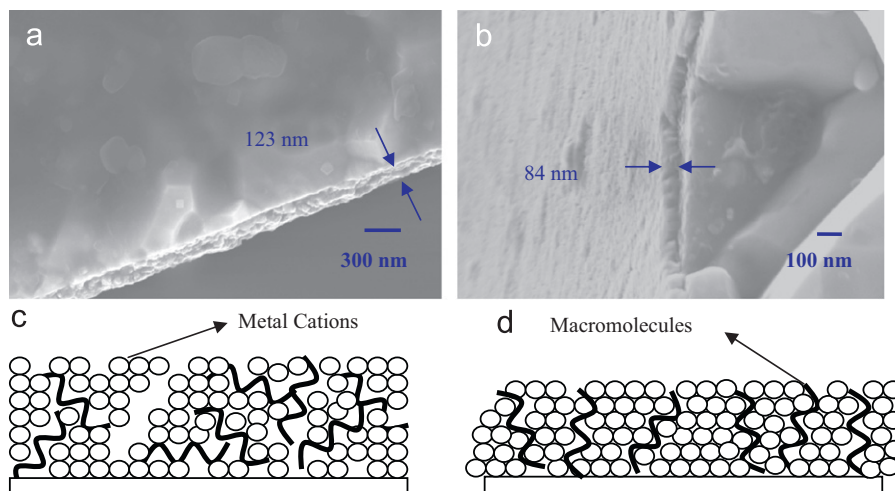


Fig. 1. Cross-sectional images of LSM films coated on LSCF substrate (a) without or (b) with SEFAD; schematic diagram to show the orientation of macromolecules and packing density of metal cations in deposition layer over LSCF substrate (c) without or (d) with SEFAD prior to sintering.

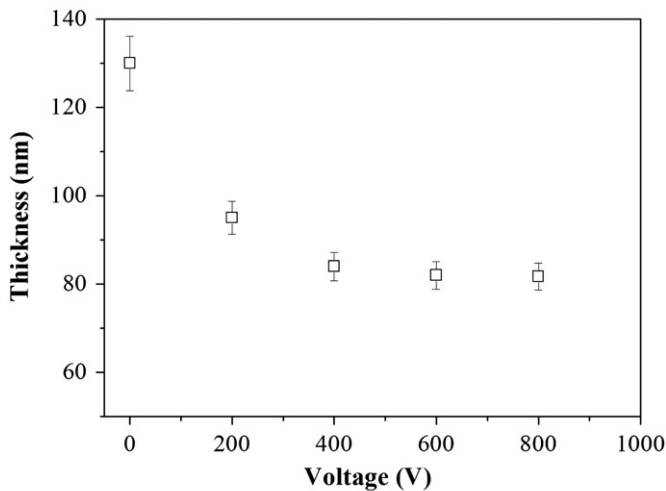


Fig. 3. Change of thickness for final LSM film with increasing external electric voltage.

Table 1

Relative densities of LSM films derived from different volumes of LSM solutions with (RD_1) or without (RD_2) an external voltage of 400 V.

	4 μ L	6 μ L	8 μ L	10 μ L
RD_1 (%)	89	87	84	84
RD_2 (%)	60	59	55	49

Effect of electric field strength on the thickness of LSM film: 4 μ L of LSM solution was deposited and dried at different voltages of 0, 200, 400, 600, 800 and 1000 V. The corresponding electric field strengths were 0, 33.3, 66.7, 100, 133.3 and 166.7 kV/m. The thicknesses of final LSM films were characterized by a SEM technique, and the test results are shown in Fig. 3. It can be seen that the thickness decreased with increasing external voltage obviously until 400 V or 66.7 kV/m. From 400 to 1000 V, the change of thickness was not obvious, demonstrating that the voltage of 400 V was a threshold value. Above 1000 V, the film surface was uneven.

Different volumes (4, 6, 8 or 10 μ L) of LSM solutions were deposited and dried in the same conditions (25 $^{\circ}$ C, relative humidity 75% and electric field strength 66.7 kV/m). The thicknesses of final LSM films were characterized by a SEM technique. And the relative density can be calculated. It was increased from \sim 50% to \sim 90% after the introduction of in situ electric field (66.7 kV/m), as shown in Table 1.

4. Conclusions

An in situ electric field was found to have a large influence on properties of sol-gel derived LSM film. The crystallization temperature was reduced by \sim 100 $^{\circ}$ C; the microstructure was changed a lot; and the relative density was improved by 30–40%.

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