



Can thin perovskite film materials be applied as model systems for battery applications?

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Abstract

The catalytic performance of carbon-based perovskite gas diffusion electrodes and thin films of identical perovskite catalyst phases ($\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ (LCCO), $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ (LCMO) and $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (LCMNO)) has been compared. The thin films were deposited on $\text{MgO}(1\ 0\ 0)$, $\text{MgO}(1\ 1\ 0)$, and $\text{MgO}(1\ 1\ 1)$ by pulsed reactive crossed-beam laser ablation (PRCLA). The quality of the films was determined by analyzing the composition as well as the crystallographic phase structure and texture of the electrodes. The catalytic activity for both the oxygen reduction and oxygen evolution reactions is evaluated from polarization curves for the selected electrodes. The compositional analysis of the films indicates that the ablation is congruent mainly for the LCCO, and that the films are nearly stoichiometric in their composition. The crystallographic orientation of the grown films is affected by the substrate. Under the selected deposition conditions it was not possible to grow parallel epitaxial films on $\text{MgO}(1\ 1\ 0)$ and $\text{MgO}(1\ 1\ 1)$. The key factors for epitaxy are besides the lattice misfit, also chemical/electronic interactions between film and substrate. The predominant crystallographic orientation is the one corresponding to the next lower surface/interfacial energy. The prepared films act as bifunctional catalysts, and the electrochemical experiments indicate that different exposed surfaces affect the performance of the electrode. The most active electrode was found to be the $(1\ 0\ 0)$ textured film.

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1. Introduction

Perovskite type metal oxides, particularly $\text{La}_{1-x}\text{Ca}_x\text{CoO}_{3-\delta}$, have been recently applied as catalysts in electrodes of rechargeable Zn–air batteries

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[1,2]. The optimization of the best catalyst is difficult, due to the strong interaction with various electrode components, such as the carbon support. The best method to overcome this interaction is the preparation of electrodes on inactive substrates with well-defined electrolyte/oxide interfaces, as “materials screening” or model systems. The model systems consist of thin films of the perovskite material deposited by pulsed reactive crossed-beam laser ablation (PRCLA) on inactive substrates [3]. This allows us to study and compare the catalytic activity of different perovskite oxides for the oxygen reduction/evolution reaction without any interference from the support material (such as electrochemical activity and stability of the carbon, or the uncertainty about the real area of the electrode due to the changing porous structure). Various parameters can be changed for the described deposition process so that the composition, morphology, and crystallographic structure of the resulting films can be controlled [4]. The latter allow us to study the influence of a specific exposed crystallographic orientation of the catalyst, which is impossible to test with the applied catalyst powders. A great advantage of PRCLA, compared to conventional PLD, is the possibility to produce films with a defined oxygen content. An additional processing step, i.e. annealing in an oxygen atmosphere can therefore be avoided [5].

A better catalyst is defined here as a material which increases the rate of a specific reaction. A suitable way to compare the electrochemical catalytic activity of different electrodes is by measuring the polarization curves, in which the current is determined as a function of the potential under steady-state conditions. The area of the electrodes is then normalized to the geometrical area to allow a direct comparison of different electrodes.

In this study, polarization curves of carbon-based perovskite gas diffusion electrodes and thin films of the same perovskite type electrocatalysts, i.e. $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ (LCCO), $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$ (LCMO) and $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ (LCMNO), deposited on $\text{MgO}(1\ 0\ 0)$, were measured and compared for the oxygen evolution/reduction reactions. Additionally, the influence of the crystallographic orientation on the catalytic activity was studied for $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ films. Additionally, the influence of the crystallographic orientation on the catalytic activity of the $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ films deposited on

$\text{MgO}(1\ 0\ 0)$, $\text{MgO}(1\ 1\ 0)$, and $\text{MgO}(1\ 1\ 1)$ was studied.

2. Experimental

The catalysts obtained from Praxair Surface Technology, were produced by spray pyrolysis. The preparation of the gas diffusion electrode is described in detail elsewhere [1]. $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$, and $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ films were deposited on $\text{MgO}(1\ 0\ 0)$, and $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ was deposited on $\text{MgO}(1\ 0\ 0)$, $\text{MgO}(1\ 1\ 0)$ and $\text{MgO}(1\ 1\ 1)$ oriented single crystals. All the films were grown at $650\ ^\circ\text{C}$. A KrF excimer laser ($\lambda = 248\ \text{nm}$, $17\ \text{ns}$ pulse length, $21,000$ pulses), with a laser fluence of $7.6\ \text{J cm}^{-2}$ and a repetition rate of $10\ \text{Hz}$ was used for the ablation process. The target material (i.e. rod) was located at $4.5\ \text{cm}$ from the substrate. Two oxidizing sources were used during the experiments: a synchronized N_2O pulse (99.999% purity, pulse length of $400\ \mu\text{s}$, backing pressure = $2\ \text{bar}$) and oxygen from a leak valve to provide an additional background pressure of $\approx 8 \times 10^{-4}\ \text{mbar}$ during the deposition. The time delay between the gas pulse and the laser pulse was optimized, for the maximum interaction between the ablation plasma and the gas pulse. More details about the procedure have been described elsewhere [6]. The film thickness and surface roughness were determined with a profilometer (Dektak 8000). The crystalline structure and texture of the films have been studied by X-ray diffraction measurements in Bragg-Brentano geometry using $\text{Cu K}\alpha$ radiation. The film composition was determined by Rutherford backscattering spectroscopy (RBS) measurements using a $2\ \text{MeV } ^4\text{He}$ beam and a surface barrier silicon detector. Prior to the electrochemical measurements, the data were analyzed using the RUMP program [7]. The electrochemical measurements were performed in a three-compartment cell, at room temperature, in $1\ \text{M KOH}$. A large-area platinum wire was used as a secondary electrode and Hg/HgO as the reference electrode. The electrochemical measurements were carried out with a bipotentiostat Pine model AFCBP1. Steady-state measurements were performed on oxygen-saturated solution for the gas diffusion electrode and the thin films. The steady-state measurements were carried out with a sweep rate of $2\ \text{mV/s}$ in the static mode. The

sweep range was from -600 to 700 mV (cobaltates), and from -400 to 1000 mV (manganates). The starting and final point for the scan was always set to 200 mV (range of the double layer capacity) to avoid the decomposition of the electrode. The steady-state curves presented for the gas diffusion and the thin film electrodes are not corrected for an ohmic drop. Nevertheless, the magnitude of the resistance should be small considering the luggin capilar that is used to connect the reference electrode with the work electrode. It was also ensured that no oxygen bubbles were formed between the capilar and the work electrode which would interfere with the measurements. We plan in the near future to correct the measurements for the uncompensated resistance point by point for each measured potential.

3. Results and discussion

3.1. Film deposition

The application of the reactive gas pulse results in a brighter and larger ablation plume, for all the applied perovskites. All deposited films are black and mirrorlike. The film thickness and roughness, measured by the profilometer, can be controlled by the number of laser pulses during the deposition. In general, the films were deposited using 21,000 pulses which results in a film thickness of around 200 nm with a roughness in the range of $2-4$ nm. The film composition was measured by RBS (Table 1). No nitrogen incorporation into the films was observed. The film composition indicates that the ablation is congruent for LCCO whereas a small loss of Mn ions is observed for LCMO [8]. It has been suggested by Choi et al. [9], that the structural difference and lattice mismatch between LCMO and MgO, induce disloca-

tion of Mn ions along grain boundaries, facilitating the loss of Mn ions during oxygen annealing. Boyd and Zhang [8] has also observed loss of Mn when the substrate temperature is higher than 700 °C.

The XRD pattern of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$, $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$, and $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{0.9}\text{Ni}_{0.1}\text{O}_{3-\delta}$ deposited on MgO(1 0 0) (not shown here), present in all cases only the formation of crystalline LCCO, LCMO and LCMNO phases. For the LCCO film an intense LCCO(2 0 0) reflection at 47.87° is observed, indicating an orientation of the film in the (2 0 0) direction. In the case of LCMO, several small reflexes of the phase are present and an intense LCMO(2 0 0) reflection at 32.7° is observed, which indicates that the film is preferentially oriented in the (2 0 0) direction. This result can be explained by the lower deposition temperature (i.e. 650 °C), which in the case of manganese is reported to be superior to 750 °C [10–12]. Another reason is the higher lattice mismatch with respect to MgO, which can produce strain and defects, affecting the epitaxial growth of the film [13]. For the LCMNO, similar results to those for LCMO should be expected, due to the partial (10%) substitution of Manganese-ion by the similarly sized Nickel-ions. In this case the same PDF-file (i.e. LCMO, JCPDS 46-0513) was used to index the observed peaks. Similar results have been published for manganite perovskite powders substituted by Co, Fe or Ni [14]. The X ray diffractogram shows an intense LCMNO(2 0 0) reflex at 32.7° and a small reflex at 58.43° indexed as LCMNO(0 4 2). No reflexes due to nickel calcium or lanthanum oxides or other impurity phases are observed. These data strongly suggest that the highly textured growth of the film on a substrate, depends on the chosen substrate (lattice mismatch) and on the selected deposition temperature.

Fig. 1 shows the XRD pattern of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_{3-\delta}$ deposited on MgO(1 0 0), MgO(1 1 0) and MgO(1 1 1). In all cases only the formation of a crystalline LCCO phase is observed. The XRD of the LCCO film deposited on MgO(1 0 0) shows only the (2 0 0) reflection, indicating that the film grows epitaxially to the substrate. When the film is deposited on the (1 1 0) substrate surface only a small LCCO(1 1 0) peak at 33.3° is observed, but the predominant orientation corresponds to LCCO(2 0 0). When the substrate is cut along the (1 1 1) orientation the XRD pattern of the grown film show only a LCCO(1 1 0) reflex at 33.3° and

Table 1
Composition of perovskite oxides thin films, deposited on different MgO substrates determined by RBS

Film Name	Stoichiometry
LCCO, MgO(1 0 0)	$\text{La}_{0.68}\text{Ca}_{0.32}\text{Co}_{0.93}\text{O}_{2.75}$
LCCO, MgO(1 1 0)	$\text{La}_{0.65}\text{Ca}_{0.35}\text{Co}_{0.94}\text{O}_{2.75}$
LCCO, MgO(1 1 1)	$\text{La}_{0.68}\text{Ca}_{0.32}\text{Co}_{0.97}\text{O}_{2.7}$
LCMO, MgO(1 0 0)	$\text{La}_{0.71}\text{Ca}_{0.29}\text{Mn}_{0.9}\text{O}_{2.8}$
LCMNO, MgO(1 0 0)	$\text{La}_{0.71}\text{Ca}_{0.29}\text{Mn}_{0.82}\text{Ni}_{0.1}\text{O}_{2.8}$

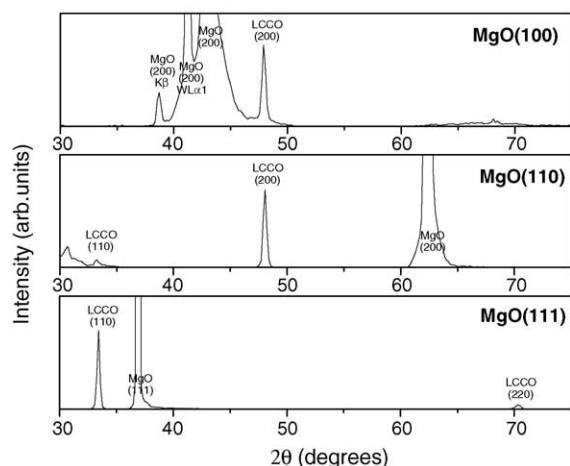


Fig. 1. X ray diffractogram of $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$ deposited on $\text{MgO}(1\ 0\ 0)$, $\text{MgO}(1\ 1\ 0)$ and $\text{MgO}(1\ 1\ 1)$.

a small reflexion at 70.25° for $\text{LCCO}(2\ 2\ 0)$. The results indicate that the grown film is adopting mainly the orientation with preferable energy and lattice match. A weak reflexion is observed in the substrate orientation. This result suggests that at the initial stage of the growth assumes the orientation of the substrate, and then changes after a critical thickness to obtain an energetically more stable orientation. This effect has been observed by Kief and Egelhoff for Fe and Co [15] and by Lu et al. for LCMO [16]. However, the understanding of the underlying mechanisms, such as preferential formation of a particular kind of phase orientation needs further detailed TEM and XRD studies with thinner films.

3.2. Electrochemistry measurements

Polarization curves for pure carbon (Vulcan XC 72) and a carbon-based gas diffusion electrode that contains the perovskite catalyst for oxygen evolution and reduction were measured and compared (Fig. 2). The activity of the pure carbon is clearly visible, emphasizing the need of model systems to study the activity of the catalyst. The sum of the overpotential for the two oxygen reaction, i.e. evolution and reduction is $\approx 1.5\text{ V}$ for the pure carbon electrode, but is significantly reduced to approximately 800 mV when the catalyst (LCCO) is added to the carbon (especially effective for the oxygen evolution reac-

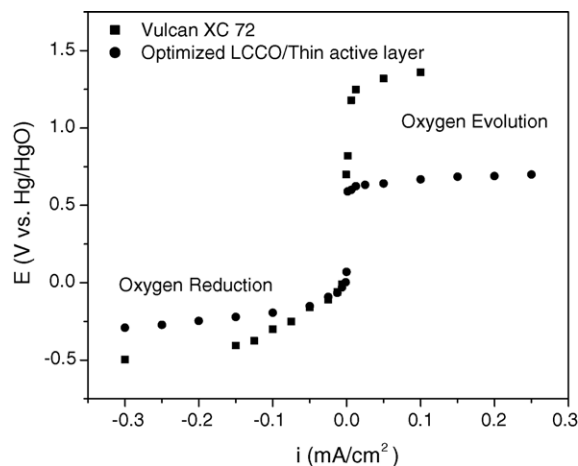


Fig. 2. Polarization curves for carbon and carbon-based perovskite gas diffusion electrode.

tion). Carbon-based electrodes of LCCO, LCMO and LCMNO (Fig. 3A) were produced as reference to be compared with the thin film model systems (Fig. 3B). The polarization curves show that in general the thin films present a slightly smaller overpotential for the two oxygen reactions than the respectively optimized carbon-based perovskite gas diffusion electrode. This is shown in the insert of Fig. 3A where the performance of a gas diffusion and a thin film LCCO electrode are compared. An important factor is that current density values are comparable to the ones obtained for the carbon-based perovskite gas diffusion electrodes, indicating that thin films can be used as model system to screen different perovskite electrodes. A different overpotential is observed for the three perovskite phases in the gas diffusion electrodes. The overpotential was the lowest for cobaltate containing electrodes and slightly higher but quite similar for the two manganate containing electrodes. This suggests that the LCCO electrode has a better performance than the LCMO and LCMNO electrode. In contrast, no difference in the overpotential is observed for different perovskite thin films electrodes. The comparison of the thin films electrodes has to be considered carefully due to the crystallographic differences of the electrodes. The manganate electrodes present several crystal faces with one main orientation compared to the cobaltate electrode where only a single orientation is observed. These different crystal faces exhibit

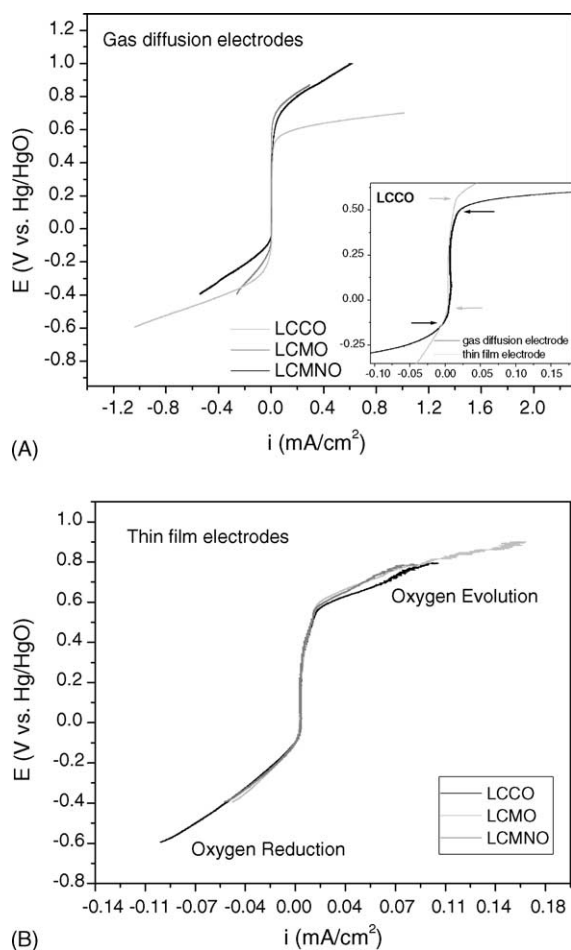


Fig. 3. (A) Polarization curves for LCCO, LCMO and LCMNO gas diffusion electrode. Inset: comparison between LCCO gas diffusion and thin films. (B) polarization curves of LCCO, LCMO and LCMNO thin films deposited MgO(1 0 0).

different properties (i.e. work function) so that the electrochemical behaviour represents an average of the different crystal planes present in the electrode. The observed result, i.e. that different materials behave in the same way, cannot be conclusive because this effect can be due to the different crystallographic quality and not exclusively due to the different materials. For this reason new studies with single crystalline manganate electrodes are planned. Another property which can be considered to influence the catalytic activity is the surface. Two aspects were analyzed to allow a more precise comparison between the different electrodes. The morphology was studied

by AFM, but no significant differences in the structure and in the surface area were found, and the chemical composition of the surface was studied by XPS [17] where no pronounced differences were detected. The only variation of the surface composition is the amount of adventitious carbon absorbed which is removed prior the steady-state measurements by consecutive electrochemical scans. Another result is the difference in the slopes for oxygen reduction and evolution between the different materials on the gas diffusion and thin films electrodes. The different perovskite-gas diffusion electrodes show different slopes for both oxygen reactions. Nevertheless, the different thin films show no difference for the oxygen reduction and a slight difference on the oxygen evolution. This result can be explained due to the different mechanisms present for the oxygen reaction. The oxygen reduction proceeds through a sequential mechanism [18], where the oxygen is reduced on the carbon to form peroxide, followed by peroxide decomposition on the oxide. This can be observed for the gas diffusion electrode where probably the combination of the carbon and the perovskite activity produce different slopes, which cannot be observed on the thin films electrodes where no carbon is present. For the oxygen evolution the perovskite acts directly as catalysts. This can be observed in both kind of electrodes, but more pronounced for the gas diffusion electrode which can be related to the real area of the electrode that is larger for a porous structure.

The comparison between the gas diffusion and the thin films will be considered in this study just in a qualitative way. An electrochemical process involves several steps, i.e. mass transfer, chemical reaction, adsorption/desorption, and electron transfer. The mass transfer of oxygen from the solution to the electrode surface is assumed to be the same for both electrode types. For the last two steps a big difference exists between the gas diffusion and the thin film electrode. In the gas diffusion electrode the surface is porous and the real area of the electrode is impossible to determine. Additionally the reactive area consists of carbon and catalyst. Contrary to this, the thin film electrode consists of a compact structure with very few small pores so that the surface area can be assumed to have a similar value as the geometrical area and only the catalyst is present on the surface. These differences will implicate a different adsorption mechanism on

both surfaces. If we consider the electron transfer as well, the situation becomes even more complicated due to the fact that for thin films the electron transfer will be possible only through electron holes or oxygen vacancies and determination of their presence in the crystal lattice is not possible. For the gas diffusion electrode the electron transfer will take place on different surfaces, i.e. on the perovskite (oxygen evolution) and on the carbon followed by the perovskite (oxygen reduction). Any attempt at a quantitative comparison between the systems will therefore be associated with a large systematic error. Therefore, a more quantitative approach in each of the described systems with different perovskite phases is under investigation and will be published in the future.

Fig. 4 presents the polarization curves for LCCO films deposited on MgO(1 0 0), MgO(1 1 0) and MgO(1 1 1). The overpotential between both oxygen reactions is affected by epitaxy, crystallinity, and orientation of the films. The film with the smallest overpotential is the one grown on the MgO(1 0 0) showing an orientation in (2 0 0) direction followed by the film with mixed 1 1 0 and 2 0 0 orientation on the MgO(1 1 0) and the film with preferential (1 1 0) orientation on the MgO(1 1 1) substrate. As explained above we can assume that the only step that can influence the electrochemical behaviour of these three electrodes is that the adsorption of the oxygen molecules is affected by the surface energy of the electrode surface, which depends on the exposed

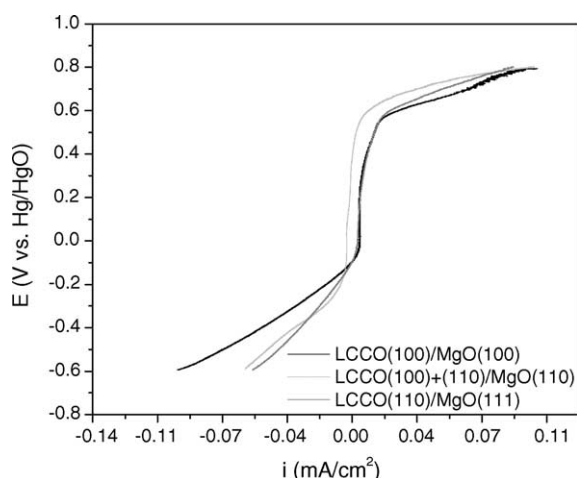


Fig. 4. Polarization curves for LCCO thin films deposited on MgO substrates cut in different orientations.

crystallographic orientation and grain boundaries. The result indicates that the electrode with the more stable surface energy will be the one that will have a better performance.

4. Conclusions

The data reveal that thin films allow a direct comparison of the ‘pure’ catalytic activity of various perovskite oxides. The results show also clearly that the crystallographic orientation of the material has a pronounced influence on the catalytic activity. It is therefore very important to test and compare materials of identical quality and different crystallographic orientations to allow a quantitative comparison of the different materials.

The comparison and correlation of thin film data with gas diffusion electrode data is more complicated, as pronounced differences, such as catalytic mechanism and interplay with the carbon, exist. Future studies will show whether and how the information from both systems can be merged to develop better electrochemical systems, such as bifunctional gas diffusion electrodes.

The question if these films can be applied as model systems for battery applications can be answered in the following way. The preliminary experiments suggest that a first approximation of a material behaviour can be obtained and that it is impossible to directly compare gas diffusion electrodes with thin films without considering the fundamental differences between both electrodes, such as surface area, and crystallinity of the material. Nevertheless, further detailed studies are necessary to ensure the validity of our concept to use thin films as model systems in electrochemical studies.

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