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# Pulsed laser deposition of electrochemically active perovskite films

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## Abstract

$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  (LCCO) thin films were deposited on MgO(0 0 1) and stainless steel substrates by pulsed reactive crossed-beam laser ablation. High resolution X-ray diffraction (XRD) spectra of the films showed that their quality depends on the oxygen background during cooling. Rutherford backscattering spectrometry measurements reveal that under optimal conditions the films have the same stoichiometry as the original target. X-ray photoelectron spectroscopy (XPS) was applied to characterize the surface of the films, which revealed two oxygen and calcium species: the one at lower binding energy, corresponds to oxygen from the perovskite structure and the one at higher binding energy correspond to Ca–O surface species and adsorbed oxygen. The electrochemical activity of the LCCO films is influenced by the crystallinity of the perovskite electrodes. The structural and electrochemical properties depend on the preparation conditions and substrate.

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## 1. Introduction

Pulsed laser deposition (PLD) has been shown to be an attractive method of producing thin films of non-volatile and multicomponent materials [1–7]. Non-stoichiometric material transfer from bulk to film of compound materials can often be circumvented by performing ablation in an ambient atmosphere of the deficient species. This requires high working pressures of any gas between 1 Pa and 1 bar. PLD in conjunction with a synchronized pulsed gas source provides an extra degree of freedom in processing the ablation

plume. This technique is called pulsed reactive crossed-beam laser ablation (PRCLA) [8,9]. The gas pulse crosses the ablation plume close to its origin, allowing an increase of gas phase interaction and the probability of reactive scattering, while letting the resulting species propagate freely away from the localized scattering region. The advantage of PRCLA compared with PLD was demonstrated by Willmott and Antoni [10] in the growth of GaN.

The most reliable way to evaluate different materials for their electrocatalytic activity is the preparation of dense, thin films on a substrate with no electrochemical activity, where the interface electrolyte/oxide is well defined. In this way the catalytic activity can be determined without problems such as reactions of the support and uncertainties about the number of

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active catalytic sites. Electrochemical oxygen evolution and reduction are important reactions in energy storage systems, e.g. fuel cells [11] and metal–air batteries [12]. Various types of electrocatalysts, e.g. Pt and Pt–Ru alloys [13–15] that will operate in a bifunctional mode have been investigated as the key components of these electrodes, but they are expensive. Significant progress has been made in recent years concerning the development of less expensive electrocatalysts such as perovskites (e.g.  $\text{La}_{1-x}\text{Ca}_x\text{CoO}_3$ ), spinels (e.g.  $\text{Co}_3\text{O}_4$ ,  $\text{NiCo}_2\text{O}_4$ ), pyrochlores (e.g.  $\text{Pb}_2\text{Ru}_2\text{Pb}_{1-x}\text{O}_{7-y}$ ,  $\text{Pb}_2\text{Ru}_2\text{O}_{6.5}$ ), other oxides (e.g.  $\text{Na}_{0.8}\text{Pt}_3\text{O}_4$ ), and pyrolyzed macrocycles with Co additives. The state of the art has been reviewed by Swette and Kackley [16], Goodenough and Manoharan [17] and recently by Kinoshita [18]. The application of LCCO for metal–air batteries was proposed first by Shimizu et al. [19] and recently applied in zinc/air batteries by Müller et al. [20]. Pioneering studies concerning the mechanism of the oxygen reduction and evolution reaction at perovskites catalysts were performed by Bockris and Ottagawa [21,22].  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  has been studied in detail, but conflicting results have been published. A first preliminary study of the catalytic activity for oxygen reduction and evolution reaction on some perovskites prepared by PLD was published by Striebel et al. [23]. A deeper understanding of various parameters, which are essential for optimum control of film growth, is necessary. These parameters include, among others, laser fluence, ambient pressure, cooling conditions and distance between substrate and target.

## 2. Experimental

The PRCLA experimental setup has been described previously in detail [8,24,25]. LCCO films were deposited by ablation of a rotating stoichiometric  $\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$  target prepared by spray pyrolysis using a KrF excimer laser ( $\lambda = 248$  nm, 17 ns pulse length). The stoichiometry of the target was confirmed by atomic emission spectroscopy (AES). The laser fluence was  $7.6 \text{ J cm}^{-2}$  with a repetition rate of 10 Hz. The films were grown on  $\text{MgO}(001)$  and stainless steel (Cr–Ni, type SUS 304,  $10 \times 10 \times 0.5 \text{ mm}^3$ ) at a substrate temperature of  $650^\circ\text{C}$ . The oxide substrates were polished on one side. The substrates were heated

by clamping them to Si substrates, where the rough sides of both the Si and oxide substrates were in contact. The Si substrates were ohmically heated by passing a DC current through them. The temperature of the Si substrates was determined by monitoring the resistivity of the Si wafer, which can be compared to reference tables [26]. Two different oxygen sources were used during film growth, from a synchronized pulsed valve operating at a backing pressure of 2 bar  $\text{N}_2\text{O}$  (99.999% purity, pulse length of 400  $\mu\text{s}$ ) and a leak valve to provide an additional background pressure of  $\text{O}_2$  of  $\approx 8 \times 10^{-4}$  mbar. After growth, the films were cooled to room temperature with four procedures: cooling at a rate of  $5^\circ\text{C}/\text{min}$ ; or a faster stepwise cooling, where an initial rapid cooling step ( $\approx 175^\circ\text{C}$ ) is followed by a stepwise reduction in current over 50 min, which corresponds approximately to a half-parabola-like reduction in temperature. Both procedures were carried out with and without  $8 \times 10^{-4}$  mbar oxygen background. After reaching  $300^\circ\text{C}$  (both series) the chamber was vented and the films were removed after 15 min.

During the deposition process, emission spectra were measured using a spectrometer (Acton Research Corporation Spectra Pro-500) with an I-CCD camera (Princeton Instrument) connected via a fiber optic to the PLD chamber. The film thickness and surface roughness were determined with a Profilometer (Dektak 8000). Structure, crystalline quality and texture of the films have been studied by X-ray diffraction (XRD) measurements in Bragg-Brentano geometry using  $\text{Cu K}\alpha$  radiation. The X-ray photoelectron spectroscopy (XPS) data were measured with a VG Escalab 220iXL using monochromatic  $\text{Al K}\alpha$  radiation, RBS measurements were performed using a 2 MeV  $^4\text{He}$  beam and a surface barrier silicon detector. The collected data were then analyzed using the RUMP program [27]. The electrochemical activity of the LCCO film for oxygen generation was measured with a three electrodes arrangement with the LCCO as working electrode, a Pt-wire as counterelectrode, and an  $\text{Hg}/\text{HgO}$  as reference electrode with a potentiostat (Amel instruments, model 2049). The electrodes are submerged in a cell with  $\text{KOH}$  1M. Oxygen is bubbled through the  $\text{KOH}$  solution until saturation, and a potential is applied to the electrode getting a current as an answer, that is normalized for the area of the electrode.

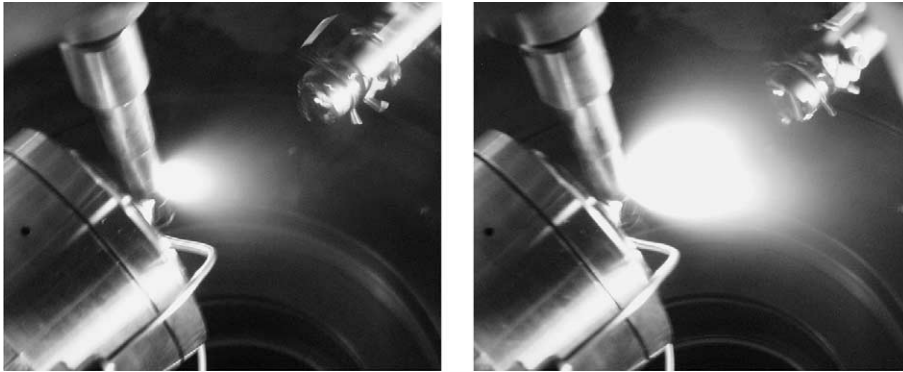


Fig. 1. Photograph of the ablation plume without (left) and with (right)  $\text{N}_2\text{O}$  gas pulse.

### 3. Results and discussion

The difference between PRCLA and PLD is shown in Fig. 1. The ablation plume of PRCLA is, due to its interaction with the  $\text{N}_2\text{O}$  gas pulse, much brighter and extends further from the target. The film quality is independent of the number of laser pulses delivered to the target, but is strongly affected by two other parameters. For laser fluences above  $12 \text{ J cm}^{-2}$ , droplets were ejected from the target and incorporated in the film. Below this energy density, no droplet formation was observed. Most important is the presence of the oxygen background to avoid oxygen deficient films. It has been suggested by Craciun et al. [28] that prolonged laser ablation of  $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$  (LSCO) causes preferential oxygen evaporation, which results in volume absorption and explosive volume boiling, causing the laser droplets to be ejected [28]. This is not the case of the very similar LCCO compound, where even after  $2 \times 10^6$  pulses to the target no changes in the film quality was observed. Gupta and Hussey [29], on the other hand, produced  $\text{YBa}_2\text{Cu}_3\text{O}_{(7-x)}$  films by PLD in conjunction with a pulsed oxidizing source. They found, that although higher film quality could be obtained by using  $\text{N}_2\text{O}$  instead of  $\text{O}_2$  for the gas pulse, it was still necessary to use a background of  $\text{O}_2$  to force the equilibrium stoichiometry of the film to more complete oxidation. Our results with LCCO appear to be more consistent with this interpretation.

Films grown with the background  $\text{O}_2$  are dark and mirror-like, independent of the cooling conditions. The film thickness measured by a profilometer is around

500 nm with a roughness in the range 4–5 nm. The compositions of the films were measured by RBS as being  $\text{La}_{0.64 \pm 0.04}\text{Ca}_{0.35 \pm 0.02}\text{Co}_{0.95 \pm 0.05}\text{O}_{3 \pm 0.21}$ , hence material transfer by ns ablation is almost perfectly congruent.

In situ emission spectroscopy of the ablation plume over a wide spectral range is shown, with and without the  $\text{N}_2\text{O}$  gas pulse, in Fig. 2. Higher intensities are obtained with the gas pulse, but no new peaks are observed under these two conditions. However, much higher intensities are observed in the range between 300 and 500 nm (see insert in Fig. 2) and 630–800 nm, which are mainly, associated with high ionization states of Ca and La. A detailed analysis of these data will be published elsewhere.

The XRD spectra of LCCO, after applying different cooling conditions, reveal only the formation of the crystalline perovskite (shown in Fig. 3). The LCCO(1 1 0) and the LCCO(2 0 0) peaks at  $33.18^\circ$  and  $47.97^\circ$ , respectively, were the only non-substrate peaks appearing in the XRD  $\theta$ - $2\theta$  scan at  $\chi = 0$ . The higher intensity of the LCCO(2 0 0) peak indicates that the LCCO is preferentially orientated in the (2 0 0) direction of the MgO. A better film quality is obtained when the films are cooled without oxygen. This is independent of the cooling rate, indicating that in the presence of oxygen the film structure is maybe altered by influencing the oxygen out/in diffusion equilibrium which is significant at temperatures above  $300^\circ\text{C}$ . Films grown under the same experimental conditions, but using the fast cooling procedure without oxygen background, were completely epitaxial

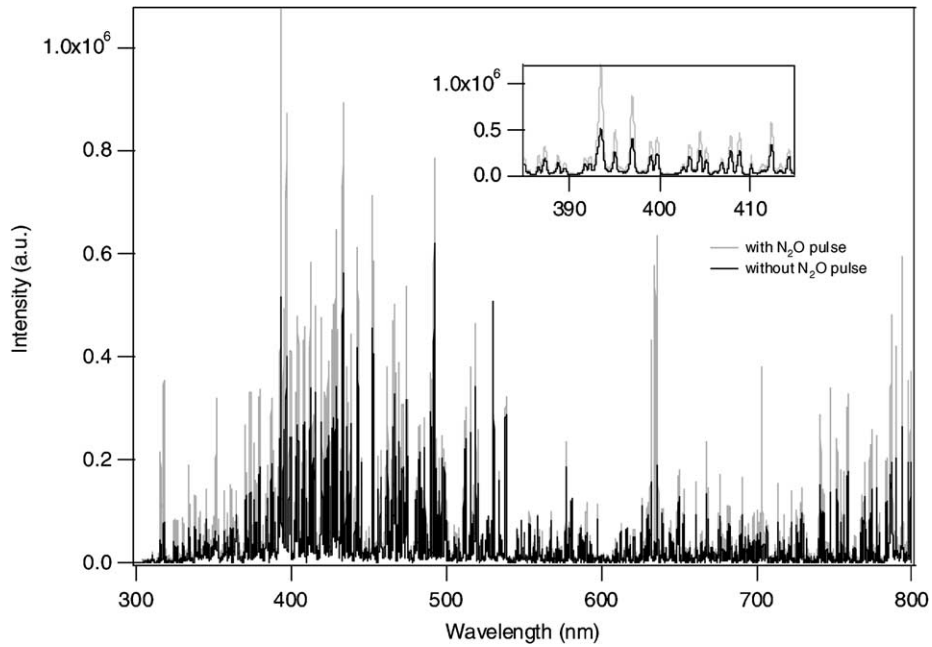


Fig. 2. Emission spectra of LCCO with and without gas pulse from 300 to 800 nm. The insert shows the pronounced increase of the band intensities in the lower wavelength range.

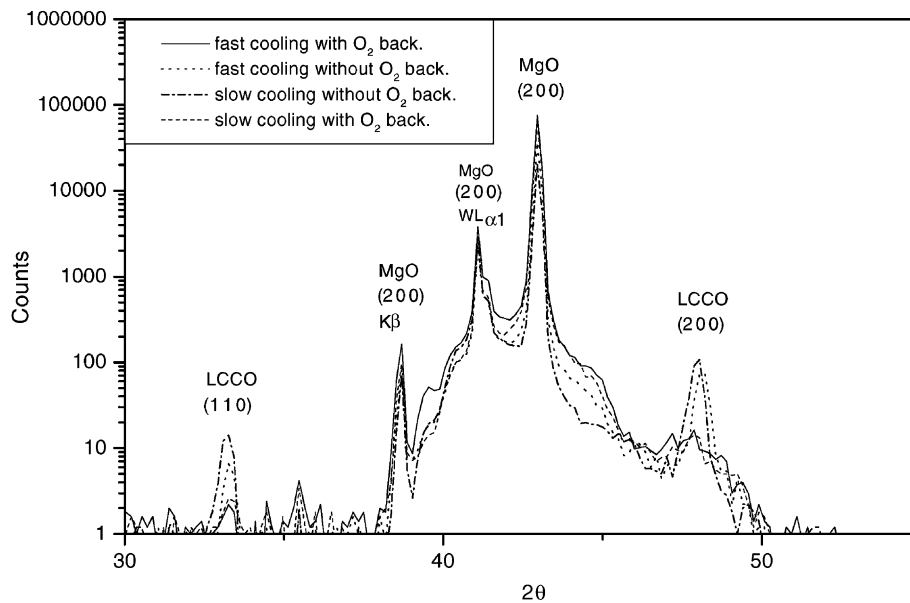


Fig. 3.  $\theta$ - $2\theta$  XRD spectra of LCCO obtained from different cooling conditions.

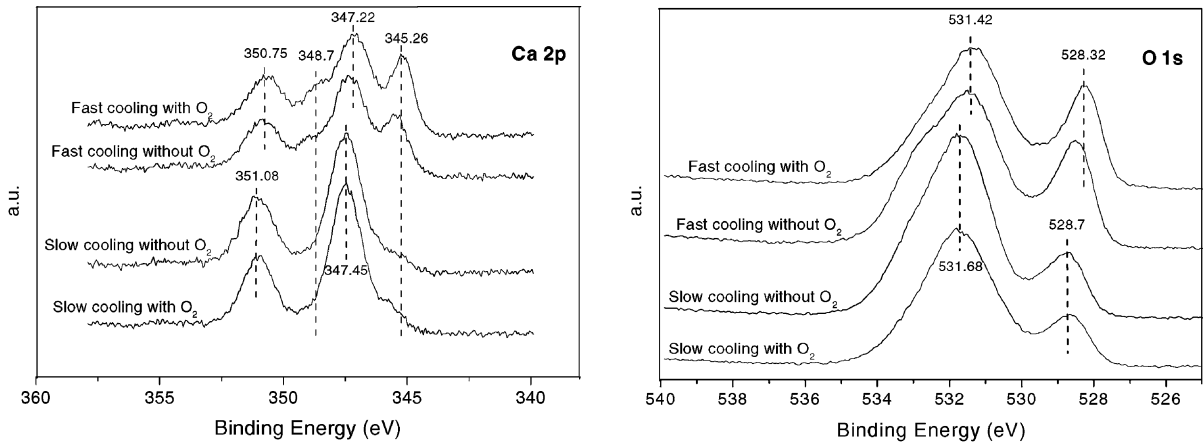


Fig. 4. XPS spectra of Ca 2p (left) and O 1s (right) peaks of LCCO films prepared with different cooling conditions.

(confirmed by high resolution TEM measurements, not shown).

The XPS spectra in the range of the Ca 2p and O 1s peaks of an LCCO films, obtained from different cooling conditions, are shown in Fig. 4. Two doublets with peak energies around 345 (+348) and 347 (+350) eV for the Ca 2p<sub>3/2</sub> and Ca 2p<sub>1/2</sub> signal are detected. This suggests that two calcium species are present on the film surface. In the O 1s spectra two

peaks are observed around 528 and 531 eV, indicating the presence of two oxygen species. The amplitude of the second peak (lower binding energy) follows the same trend for Ca and O, suggesting that both peaks originate from the same species.

To clarify the origin of this two species sputtering and angle resolved XPS experiments were performed. Upon sputtering the peaks at higher binding energy (Ca and O) disappear almost immediately,

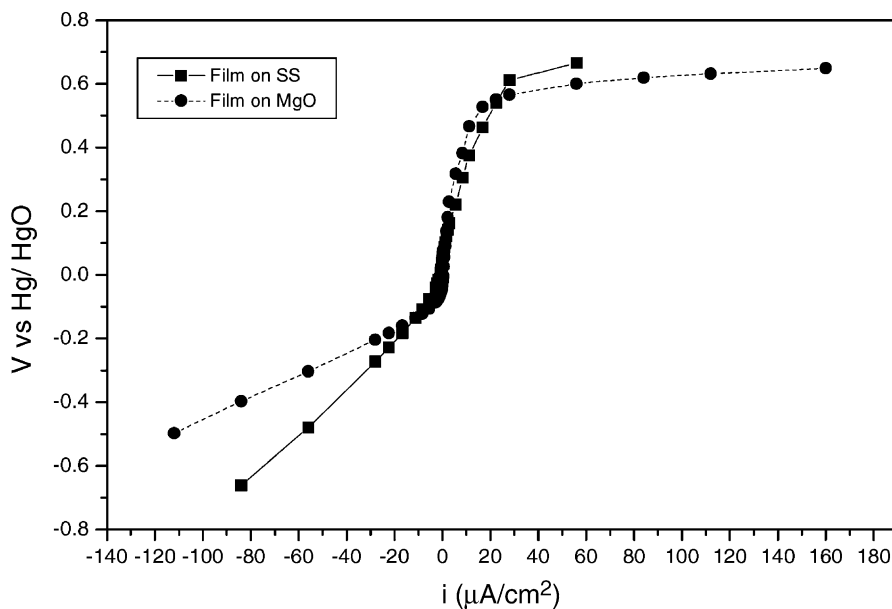


Fig. 5. Current density versus potential curve for LCCO electrodes in 1 M KOH.

while the peaks at lower binding energy remain; and become even more intense upon further sputtering. Therefore, we assign the peaks at higher binding energy to surface species and the peaks at lower binding energy to the perovskite structure. The surface species could correspond to  $\text{CaCO}_3$ ,  $\text{CaO}$  [30] and/or oxygen physisorbed on the surface [31]. The ratios of the peaks (lower binding energy/higher binding energy) from the different cooling conditions suggest that for a fast cooling process, less surface species are formed. This suggests that the generation of the Ca–O surface species is strongly influenced by the surface reaction rate which is zero-order with respect to the oxygen partial pressure in the investigate range.

Two films were selected to test the influence of the crystallinity on the electrochemical activity. One film was grown on  $\text{MgO}$  (single crystalline), the other on stainless steel (polycrystalline). For the electrochemical reaction only the surface of the LCCO is in contact with the solution and the reaction occurs just at the interface between electrolyte/electrode. The electrochemical activity of the films for oxygen reactions is shown in Fig. 5. The film on  $\text{MgO}$  presents higher current densities at the same voltage than the polycrystalline film on stainless steel. This effect is more pronounced for the oxygen reduction reaction (negative current range) than for the oxygen evolution reaction. This difference is due to a different activity of the catalyst for the two oxygen reactions and not to an ohmic drop in the electrodes.

#### 4. Conclusions

PRCLA was used as deposition technique to grow LCCO films on  $\text{MgO}(0\ 0\ 1)$  substrates under various cooling conditions. Multicomponent films grown with PRCLA have the correct oxygen stoichiometry. The XRD and XPS analysis reveal that the crystallinity and surface quality of the film is strongly affected by the cooling procedure. The preliminary electrochemistry analysis proves that the crystallinity of the film plays an important role in the catalytic activity of these electrocatalysts. The influence of the deposition parameter shows that it is necessary to optimize the PRCLA conditions for this material to ensure high quality films. This allows a correlation of

the crystallographic structure with the electrochemical activity.

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