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Perovskite thin films deposited by pulsed laser ablation as model systems for electrochemical applications

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Abstract

Thin films of a bifunctional electrocatalyst with the compositions $La_{0.6}Ca_{0.4}CoO_{3-\delta}$ and $La_{0.7}Ca_{0.3}CoO_{3-\delta}$ have been deposited by a variation of pulsed laser deposition, i.e. pulsed reactive crossed-beam laser ablation. These perovskite phases have been used as catalysts for oxygen reduction and evolution in re-chargeable Zn/air batteries. The utilization of a synchronized reactive gas pulse with N_2O or O_2 allows the preparation of perovskite films with almost ideal oxygen content without additional annealing steps and to control the oxygen content of the films. The films with higher oxygen content reveal a lower resistivity. These compositions have been selected to study the influence of the texture on the electrocatalytical activity for oxygen reduction and evolution of the films. Amorphous films, or films with mixed or single orientation can be obtained by varying the target—substrate distance and substrate temperature without changing the composition of the films. A clear influence of the crystallinity on the catalytic activity, i.e. smaller overpotential for the two oxygen reactions, is observed. The amorphous films reveal the largest overpotential, followed by the polycrystalline films with one or more orientations, and the single crystalline films with (100) orientation.
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Contents

1. Introduction

Perovskite is one of the most important structure classes in material science due to a wide range of exceptional physical and chemical properties. The physical properties of the perovskite-type materials, such as ferroelectric, dielectric, pyroelectric, and piezoelectric behavior, will depend on the cationic ordering, anion vacancies, and changes in the structure. In addition to these physical properties numerous important chemical properties are observed, including catalytic activity and oxygen transport capability. The catalytic activity covers reactions such as CO oxidation, NO reduction, CO and CO_2 hydrogenation, SO_2 reduction and various electro-photocatalytic reactions [1] while other perovskites are used for oxygen transport applications (e.g. in gas diffusion electrodes). The ongoing research explores the magnetic and electronic properties [2], but also includes the development of new materials to optimize renewable energy sources, i.e. solid oxide fuel cells [3], direct methanol fuel cells, and metal/air batteries [4].

The most important topic for the production of metal/air batteries (i.e. Zn/air) is the development of new materials for anodes and cathodes. These materials have to be stable under long-term operation conditions (acidic or alkaline medium with an applied potential), and should be cheaper than the commonly used noble metal materials, i.e. Pt.

The Zn/air battery is the battery that offers one of the highest storage densities, which is due to the fact that one of the components in the reaction comes from outside of the battery, i.e. atmospheric oxygen from the air as cathode reactant. The recent design of a re-chargeable Zn/air battery consists of two electrodes, i.e. Zn paste and a bifunctional oxygen electrode with an integrated electrocatalyst for reduction and evolution of oxygen [5,6].

However, one major problem associated with the development of these secondary batteries is the limited lifetime of the bifunctional electrode (which catalyzes the reduction and the evolution of oxygen). The lifetime of this electrode is controlled by the dissolution of the catalyst in the electrolyte [7] and the corrosion of the support material (carbon). Progress has been made in the development of corrosion resistant carbon, e.g. carbon nanotubes [8] as support material for the electrodes [9]. Nevertheless, the development of a stable catalyst is still a challenging task. Only few catalysts are intrinsically bifunctional to act as catalysts for both oxygen reactions. Most of the catalysts exhibit either a low catalytic activity or they are unstable under operating conditions [10,11]. Various catalysts such as noble metals [12], perovskites, spinel, pyrochlore type oxides [13−15], organometallic compounds [16], and other materials [17]

have been evaluated and various methods have been developed to prepare catalytic powders with high surface areas [18]. In particular, the perovskites containing Co, Fe, Mn and Ni are excellent catalysts for the oxygen evolution (OER) and oxygen reduction reaction (ORR) [19,20].

The origin of the catalytic activity is not yet fully understood, but several hypothesis have been suggested: (i) a relation between the catalytic activity and the density of states at the Fermi level [21]; (ii) the influence of the metal−oxygen binding energy and the π back bonding from the oxygen to the neighboring cations [22]; (iii) the presence of oxygen vacancies [23, 24] and (iv) that electrical conductivity and magnetic properties are important [21].

The best method to overcome this influence is the study of model systems where the electrodes are prepared on inactive substrates with well-defined electrolyte/oxide interfaces. This will allow studies and comparisons of the mechanisms of the oxygen reduction/evolution reaction of different perovskite oxides without any interference from the carbon support material. These interferences are electrochemical activity and stability of the carbon, and the uncertainty related to the real area of the electrode due to the porous structure. Another advantage of the model system is the possibility to study the influence of the crystallographic orientation on the catalytic activity. The best model system will therefore be dense crystalline films deposited on an inactive substrate, which can be considered as ideal ''two-dimensional'' model electrodes. Thin films can of course be prepared by various techniques that range from chemical solution deposition (CSD) by, e.g., sol-gel processes, chemical vapor deposition (CVD) of, e.g., metal-organic precursors, and physical vapor deposition (PVD) by, e.g., RF sputtering and pulsed laser deposition (PLD). PLD has emerged over the last decade as one of the most promising methods for the deposition of high-quality thin films of materials having a complex stoichiometry, and for the deposition of films that cannot be obtained by other methods (e.g., of metastable phases) [25−27].

PLD allows one to vary a large number of deposition parameters which can be used to obtain a high control over film growth and, thus, to tailor the properties, which normally is not possible to the same extent using other methods. The deposition parameters that can be utilized for this are the laser energy, wavelength, pulse length and repetition rate, the background pressure, the substrate material and temperature, and the target−substrate distance. These parameters can, e.g., be utilized to control the state and kinetic energy of the ablated species, which influences directly the film growth and surface quality of the films. A variation of PLD, i.e. pulsed reactive crossed-beam laser ablation (PRCLA), where a synchronized reactive gas pulse interacts close to the target with the ablation plumes, gives another deposition parameter to optimize the film growth (general scheme shown in Fig. 1) [25].

2. Experimental

Thin films of $La_{0.6}Ca_{0.4}CoO_3$ and $La_{0.7}Ca_{0.3}CoO_3$ (LCCO) were deposited by PRCLA, using a rotating rod target, which was sintered from powders prepared by spray pyrolysis at Praxair Surface Technology. A KrF excimer laser ($\lambda = 248$ nm) with a pulse duration of 17 ns was used as the irradiation source. The target material is located normally at a distance of 4.5 cm from the substrate, but this distance can be varied if necessary. The target was ablated with a laser fluence of 7.6 J cm^{-2} at a repetition rate of 10 Hz with 21 000 pulses for each film.

The films were grown on MgO (100), (110), (111) substrates ($10 \times 10 \times 0.5$ mm^3) with one side polished and at a typical temperature of 650 °C (for some experiments this value was changed). The substrates were rotated during the deposition to obtain uniform film thickness.
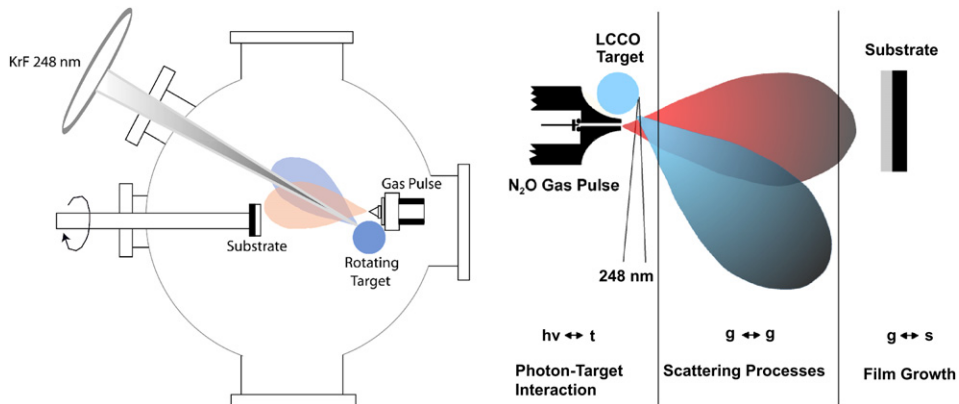
Fig. 1. Scheme of the experimental setup (left) and reactive gas pulse interaction.

Two different oxygen sources were used during film growth, i.e. from a synchronized pulsed valve operating at a backing pressure of 1—3 bar of O_2 or N_2O (99.999% purity, pulse length of 400 μs) and a leak valve to provide an additional background pressure of O_2 of $\approx 8 \times 10^{-2}$ Pa during the deposition. The experimental parameters have been described in detail elsewhere [25]. The films were cooled with a vented chamber and a cooling rate of $\approx 40\,^{\circ}$C/min. The film thickness and surface roughness were measured with a profilometer (Dektak 8000). The crystalline structure and texture of the films were determined by a Siemens D5000 X-ray diffractometer with Bragg—Brentano geometry using Cu Kα radiation. The film stoichiometry was obtained from Rutherford backscattering spectroscopy (RBS) measurements using a 2 MeV ^{4}He beam and a surface barrier silicon detector. The collected data were analyzed using the RUMP program [28]. The transmission electron microscopy (TEM) studies were performed on a Phillips CM 30 apparatus with an EDX detector.

The resistivity of the thin films was measured at various temperatures for films with different oxygen contents with a physical property measurement system (PPMS®) from Quantum Design and four contacts in the van-der-Pauw geometry.

The electrochemical activity of the LCCO films and gas diffusion electrodes for the oxygen reactions was measured with a three electrode arrangement with the LCCO as a working electrode, a Pt-wire as counter-electrode, and a Hg/HgO as reference electrode with a potentiostat (Amel instruments, model 2049). The electrodes are submerged in a cell with a 1 M solution of KOH. Oxygen is bubbled for saturation through the KOH solution. A potential is applied to the electrode, while the corresponding current was measured and normalized with respect to the electrode area (i.e. current density).

3. Results and discussion

3.1. Oxygen content of the films

PRCLA gives, as described above, another deposition parameter that can be varied to obtain control over the oxygen content in the growing films without any post-annealing steps. There are two possible approaches to influence the oxygen content using the reactive gas pulse, i.e. varying the gas pulse pressure (number of molecules) or utilizing gases with different

reactivity, i.e. N_2O or O_2. A series of films was deposited at a constant oxygen background pressure, while oxygen or N_2O was used as gas pulse with different pressures. An increase in the oxygen content of the films can be observed for both gas pulses when the pressure of the gas pulse is increased. An increase of the gas pulse pressure corresponds to a larger amount of gas molecules which will collide with the plasma plume, forming excited state species, which can be easily incorporated in the film. The amount of oxygen present in the film is always higher independently of the pressure, when N_2O is used as a gas pulse instead of O_2. Considering that the contribution of the oxygen background is constant in both cases, the only fact which can explain the observed result is the oxidizing nature of the gas pulse. The interaction of the plume with the gas pulse (O_2 or N_2O) plays a crucial role in producing the atomic oxygen required for the growth of the film. The origin of the atomic oxygen, primarily in the vicinity of the target, is due to the dissociation of N_2O or O_2 by collisional fragmentation with the plasma or electron-impact [29]. The effectiveness of O_2 as an oxidizing agent is limited due to its higher dissociation energy (5.11 eV) compared to the lower value for N_2O (1.67 eV) [29]. The difference in the oxygen content in the films using N_2O or O_2 as gas pulse is minimized when the gas pulse pressure is increased, as shown in Fig. 2. This result indicates that the amount of atomic oxygen in the instantaneous flux can be directly controlled by adjusting the pressure of the gas pulse. It is also noteworthy to mention that the presence of an oxygen background during the film growth is also necessary to be able to obtain films with higher oxygen content using PRCLA.

Films grown in the O_2 background are dark and mirror like, independent of the cooling conditions. The film thickness measured by a profilometer is around 250 nm (21 000 pulses) with a roughness in the range of 1–5 nm. The composition of the films, measured by RBS, can be $La_{0.64}Ca_{0.35}Co_{0.95}O_3$ (with 5% error for each element) under optimum deposition conditions, suggesting an almost perfectly congruent material transfer.

3.2. Resistivity of the films

For an application of the films as electrocatalysts it is of course a necessary condition that the films are conductive. The resistivity of the films was therefore tested as function of the
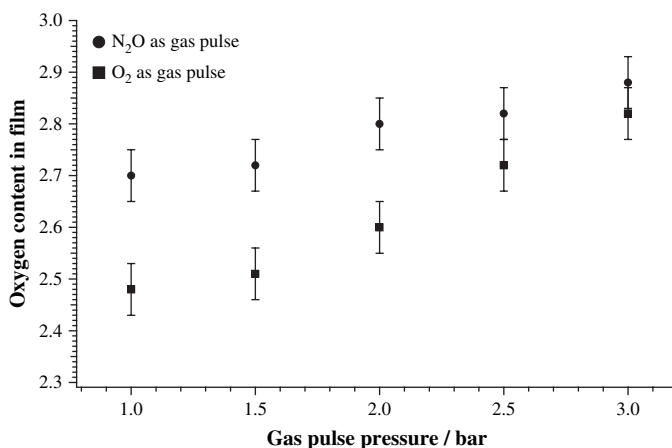

Fig. 2. Oxygen stoichiometry index of LCCO films as a function of pressure for O_2 and N_2O gas pulses, respectively, with a constant oxygen background of 8×10^{-2} Pa.

temperature and oxygen content of the films. A much higher resistivity is obtained for perovskite films with lower oxygen content (shown in Fig. 3). This result can be rationalized by a quite simple approach: if we consider only the stoichiometry of the films and the possibility of Co to exist in two different oxidation states (III and IV), the films would then have a nominal composition of

$$La_{1-x}^{3+}Ca_x^{2+}Co_{1-x+2\delta}^{III}Co_{x-2\delta}^{IV}O_{3-\delta}$$
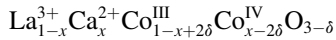
where an increase of δ results in a decrease of Co^{IV} and therefore a decrease of the electron mobility and an increased resistivity. It is noteworthy to mention that the oxygen vacancies normally act as electron donors in transition metal oxides [30], such as $SrTiO_3$ and increase the charge carrier concentration in n-type semiconductors. The films with the lowest resistivity, i.e. the films with the highest oxygen content were chosen for the electrochemical characterization of the films.

3.3. Crystallinity of the films

One important aspect of the electrocatalytic reactivity of a material that can only be determined for thin films and not for gas diffusion electrodes (which consist of several components) is the influence of the crystallinity on the catalytic activity. PLD and PRCLA allow a unique control over the crystallinity of a given material without changing the chemical composition. Single crystalline MgO substrates were applied to ensure that no electrocatalytical activity is due to the substrate. The selection of this non-conducting substrate material is the other reason why the films with higher conductivity were selected. The disadvantage of using MgO as a substrate is the pronounced lattice mismatch to the LCCO films (Mg) with $a = 0.421$ nm and LCCO with $a = 0.3879$ nm [31–37]. This mismatch is clearly visible in the high resolution TEM image (Fig. 4, left), where the interface between the two materials is clearly visible which
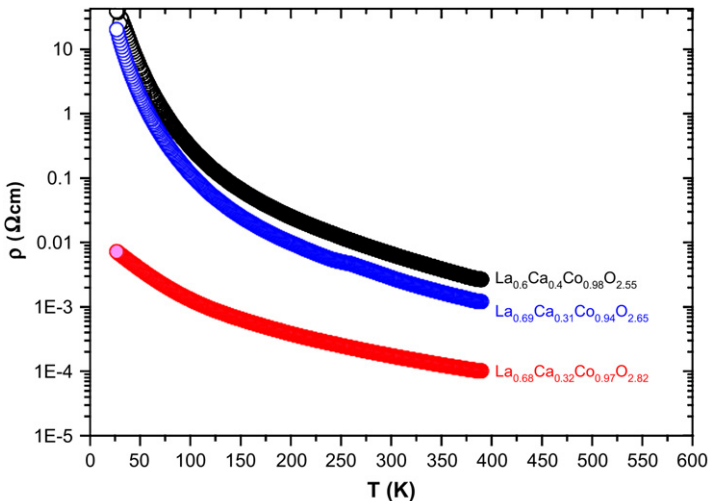

Fig. 3. Resistivity as a function of the temperature for perovskite films with different oxygen contents (from RBS measurements).
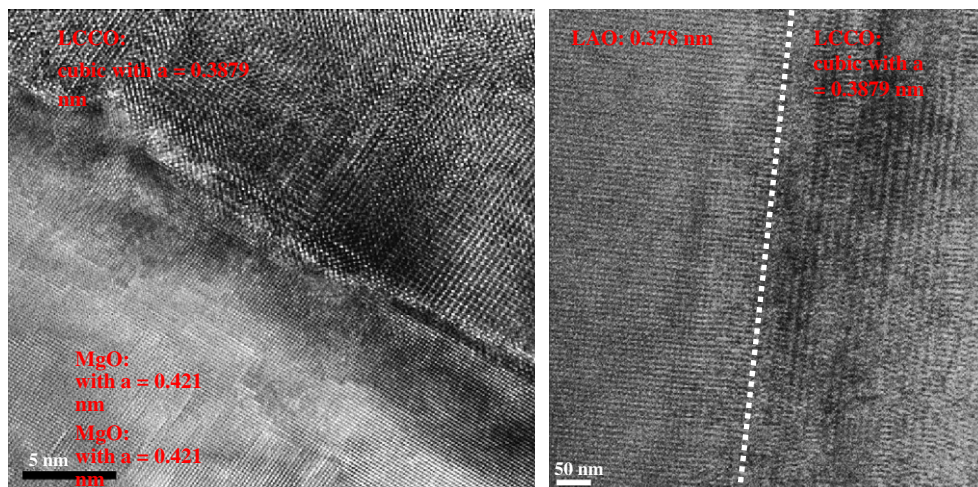
Fig. 4. TEM cross-section of thin films of $La_{0.6}Ca_{0.4}CoO_3$ deposited on MgO (left) and $LaAlO_3$ (right). The interface with defects (stress) is clearly visible in the case of the MgO substrates, but also the epitaxial growth for both materials. The dotted line in the right image indicates the interface between the film and substrate.

is not the case for a lattice matched $LaAlO_3$ substrate (Fig. 4, right). It was, however, possible to grow single crystalline films of LCCO with cubic structure on the MgO substrates.

A variation of two deposition parameters, i.e. substrate temperature and target−substrate distance, yielded films on MgO (100) substrates with the same chemical composition, but with crystallographic structures that ranged from amorphous to polycrystalline ((100) and (110) orientations) and single crystalline films with (100) orientation. Polycrystalline films with a large number of orientations are obtained on polycrystalline substrates, such as stainless steel, while single crystalline films with other orientation could be prepared when MgO substrates with other orientations are applied. In the case of MgO (110) it was only possible to grow films with mixed orientations (100) and (110) using the same deposition conditions as for the growth of single crystalline LCCO films on MgO (100). For MgO (111) substrates it was possible to obtain LCCO films with (110) orientation.

3.4. Electrocatalytical characterization of the films

To evaluate whether the measurements of the thin films are comparable to data obtained for gas diffusion electrodes it is necessary to consider the fundamental processes. 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 can be assumed to be the same for both electrode types. For the last two steps a pronounced difference exists between the gas diffusion and the thin film electrodes. In the gas diffusion electrode the surface is porous and the real area of the electrode is very difficult 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. The surface area is very similar to the geometrical area and only the catalyst is present on the surface. These differences suggest that different adsorption mechanisms are present 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 the quantification of carriers in the crystal lattice during the electrochemical measurements is nearly impossible. 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 should therefore be associated with a large systematic error. To evaluate this error, polarization curves under steady state conditions were measured to study the electrochemical activity of the LCCO materials as gas diffusion and thin film electrodes. For these measurements two electrodes were selected: (i) an optimized gas diffusion electrode as a reference and (ii) an LCCO single crystalline film deposited on MgO (100). The model system presents a slightly smaller overpotential for the two oxygen reactions than the optimized gas diffusion electrode. The model system is more active for the oxygen evolution reaction while the gas diffusion electrode is more active for the oxygen reduction reaction. An important factor is that the 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 [37]. Therefore LCCO films with different crystallinity were studied allowing a direct comparison of the catalytic activity as function of the texture. The polarization curves for thin amorphous, mixed, and single crystalline LCCO films are compared in Fig. 5. The polarization curves show that the crystallinity directly influences the catalytic activity for oxygen reduction and evolution reactions (measured by the overpotential). The overpotential is the difference between the values indicated with the arrows in Fig. 5. The film with the smallest overpotential (597 mV) is the (100) oriented sample followed by the film with mixed (110) and (100) orientations (679 mV) and the amorphous film (738 mV). An electrochemical process, as discussed previously, involves several steps, i.e. mass transfer, chemical reaction, adsorption/desorption, and electron transfer. The result indicates that the only step that can influence
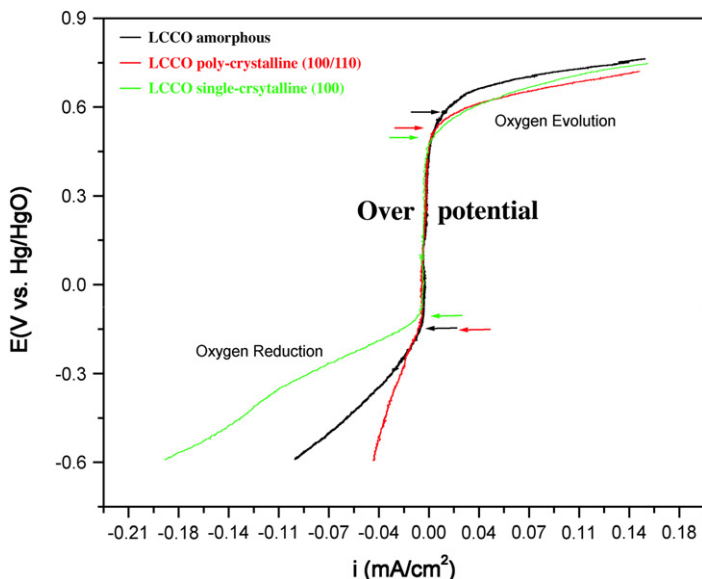

Fig. 5. Polarization curves of amorphous, single- and polycrystalline LCCO thin films deposited on MgO (100) substrates.

the electrochemical behavior of these three electrodes, i.e. the adsorption of the oxygen molecules, is affected by the surface energy of the electrode surface, which depends on the exposed crystallographic orientation and grain boundaries. It can therefore be concluded that the phase with (100) orientation presents the best performance which was confirmed by depositing LCCO films on MgO substrates with different orientations (e.g. (100), (110), and (111)).

The polarization curves for LCCO films deposited on MgO (100), MgO (110) and MgO (111) are shown in Fig. 6. 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 MgO (100) showing an orientation in (100) direction followed by the film with mixed (110) and (100) orientations on the MgO (110) substrates and the film with preferential (110) orientation on the MgO (111) substrate. As explained above, we can assume that the adsorption of the oxygen molecules is affected by the surface energy of the electrode surface, which depends on the exposed crystallographic orientation and grain boundaries. The result indicates that in the case of the $La_{0.6}Ca_{0.4}CoO_3$ electrodes the best performance is obtained for the (100) orientation, which should have the lowest surface energy.

Similar effects, i.e. that catalytic and adsorptive properties of solid surfaces can depend upon the crystal face, have been reported previously for cyclic voltammograms of the adsorption/desorption of hydrogen on the different surfaces of platinum [38].

4. Conclusions

The utilization of the synchronized reactive gas pulse in PRCLA with N_2O or O_2 facilitates to control the oxygen content of the films without additional annealing steps. The oxygen content has a pronounced influence on the resistivity which is an important parameter for an electrocatalyst. The film composition with the lowest resistivity, i.e. with the higher oxygen content, was characterized as an electrocatalyst for oxygen reduction and evolution reactions.
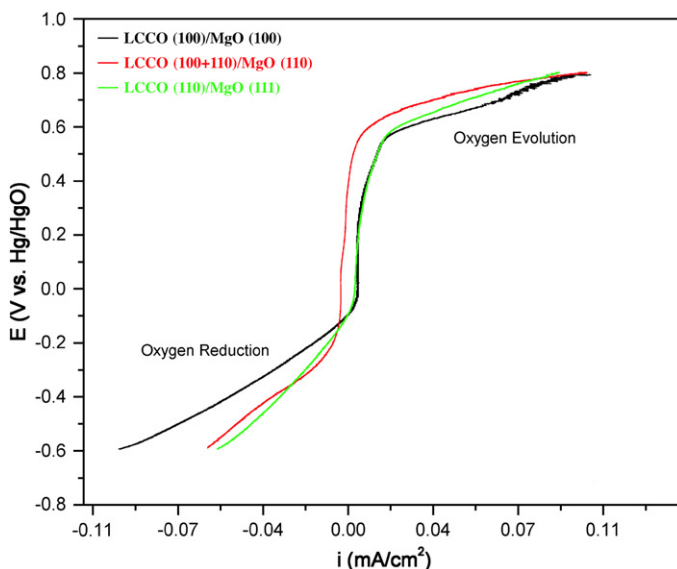

Fig. 6. Polarization curves for LCCO thin films deposited on MgO substrates cut in different orientations.

Amorphous films, films with mixed or single orientation were obtained by varying the target—substrate distance and substrate temperature. A clear influence of the crystallinity on the catalytic activity, i.e. smaller overpotential for the two oxygen reactions, is observed. The single crystalline films reveal a higher activity than the polycrystalline films or amorphous films, while the (100) orientation seems to have a higher activity than the (110) orientation. This shows clearly that thin films with a high degree of control over the texture and composition can be used as model systems to study electrocatalysts. The thin films will also be perfect model systems to study the fundamental chemical reaction steps and rate constants for the oxygen reactions which are still controversial.

Acknowledgements

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