Synthesis and characterization of $La_2NiO_{4-\delta}$ coatings deposited by reactive magnetron sputtering using plasma emission monitoring

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Introduction :

It is well known that the short life time and the high cost of each component of nowadays Solid Oxide Fuel Cells (SOFC) are induced by their high operating temperature. Many researches focus on the decrease of this operating temperature without reduction of the fuel cell performances (IT-SOFC). Regarding the cathode, one solution is to increase the electrocatalytic properties. Purely electronic conductor perovskite materials (for example LSM : $La_{1-x}Sr_xMnO_3$) are used in standard SOFC devices. $A_2MO_{4+\delta}$ compounds, with K_2NiF_4 structure have recently been investigated as substitutes to LSM. Indeed, these materials are mixed ionic and electronic conductors (MIECs) that moreover exhibit rather high electrocatalytic properties. It is then possible to synthesize them as dense materials for SOFC cathodes. Among these materials, lanthanum nickelates $La_2NiO_{4+\delta}$ exhibits convenient electrochemical characteristics [1- 4]. Its thermal expansion coefficient (TEC) is very close to that of the most commonly used electrolyte materials (13 10^{-6} K^{-1}, 11.9 10^{-6} K^{-1} and 11.6 10^{-6} K^{-1} for $La_2NiO_{4+\delta}$, CeO_2-Gd_2O_3 (CGO) and ZrO_2-Y_2O_3 (YSZ) respectively). Its oxygen ionic conductivity and surface exchange coefficient are interesting and seem much better than those of $La_{1-x}Sr_xMnO_3$ (LSM) and $La_{1-x}Sr_xCo_{1-y}Fe_yO_3$ (LSCF), the most commonly used cathodes [2, 5-6].

The deposition of La_2NiO_4 coatings by reactive magnetron sputtering has already successfully been performed under so called stable conditions in a laboratory vessel [7]. In this study, we investigate the feasibility of $La_2NiO_{4+\delta}$ coatings deposited by reactive magnetron sputtering under unstable conditions using Plasma Emission Monitoring (PEM) [8, 9].

The chemical composition of the coatings was measured by Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy. The influence of the La/Ni ratio on the structure was checked by X-Ray Diffraction analyses.

Experimental details

- Sputtering device:

The experimental device is a 100-litre Alcatel SCM 650 sputtering chamber pumped down via a system combining XDS35i Dry Pump and a 5401CP turbo-molecular pump. The sputtering chamber is equipped with three 200 mm diameter magnetron targets and with a 620 mm diameter rotating substrate holder parallel to the targets at a distance of about 110 mm. The distance between the targets axis and that of the substrate holder is 170 mm. The La and Ni targets are supplied thanks to a pulsed DC Advanced Energy dual generator allowing the control of the discharge current, power or voltage. The discharge current is fixed at 2.5 A on the La target and modified on the Ni target from 0.25 to 0.45 A to obtain the convenient composition of K_2NiF_4 structure. The substrates are alumina and YSZ pellets as well as glass slides positioned next to the target at 170 mm from the axis of the substrate holder. Argon and oxygen flow rates are controlled with Brooks flowmeters and the pressure is measured using a MKS Baratron gauge.
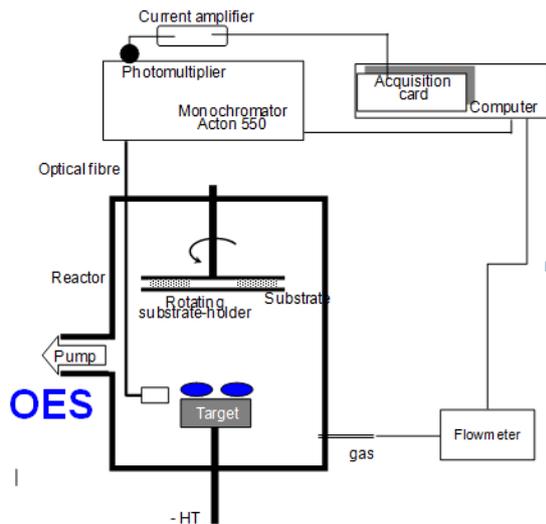
Figure 1 : Scheme of the principle of PEM

The deposition stage is monitored using a closed loop control PEM (Plasma Emission Monitoring) system (Figure 1) using optical emission spectroscopy (OES) [10]. The technique is based on the measurement of the optical intensity of the 395 nm La emission line (I^*_{La}) measured in a volume near the target. The signal is sent via an optical fiber to a Ropper Scientific SpectraPro 500i spectrometer, with a 1200 groove mm^{-2} grating and a photomultiplier tube (Hamamatsu R 636). Then, the information is transferred to a computer where a program developed under Labview® monitors the oxygen flow rate to maintain the selected intensity of the optical signal I^*_{La}.

- Stuctural Characterisation

The morphology of the coatings is characterized by Scanning Electron Microscopy (SEM) using a JEOL JSM 5800 LV equipped with Energy Dispersive Spectroscopy (EDS) for chemical measurements. The structural features of the coatings were performed in Bragg Brentano configuration X-ray diffraction using a BRUKER D8 focus diffractometer ($CoK_{\alpha1+\alpha2}$ radiations) equipped with the LynxEye linear detector. XRD patterns were collected at room temperature during 10 min in the [20°-80°] scattering angle range by steps of 0.019°. Coating thickness was also determined using the step method with an Altysurf profilometer from Altimet allowing an accuracy of about 20 nm. Before each measurement, the calibration of the experimental device was realised with a reference sample number 787569 accredited by CETIM organisation.

Results and discussion

- **Optimization of the regulation setpoint**

In DC mode, the optical signal of sputtered metal atoms in a pure Ar atmosphere is proportional to the square of the discharge current [11]. By fixing the discharge current of a metallic target, its physicochemical state is usually a monotonic and quite proportional function of the optical signal I^*_M measured by OES [12]. In so called unstable sputtering conditions, i.e. when the oxygen partial pressure-oxygen flow rate curve presents a hysteresis, PEM is a very suitable technique to allow high rate growth of oxide coatings [8].

In this study, the PEM setpoint of I^*_{La} was varied from 40 to 70% of the signal obtained while depositing in pure argon atmosphere. All those deposition conditions take place in the unstable sputtering domain, i.e. where a setpoint cannot be maintained without using a closed loop control system. In previous work, we have shown that increasing the setpoint decreases the coating transparency, and then the oxidation rate of the coating. Indeed, the higher is the setpoint, the higher is the sputtered flow of metal atoms and the lower is the oxygen partial pressure in the reactor. Note that coatings deposited with a setpoint of 5V, i.e. I*La of 50% allows obtaining a transparent La_2O_3 coating with the highest deposition rate.

- **Chemical and structural analyses**

The experimental parameters for the synthesis of the films are summarized in **Table 1**

Deposition parameters	values
Total pressure (Pa)	0.3
Ar flow rate (sccm)	30
Regulation voltage (V)	5
oxygen flow rate (sccm)	5.5 – 6.2
Run duration (h)	1h30 – 2h
Discharge current for La(A) Frequency (Hz) – toff (µs)	2.5 50 - 5
Discharge current for Ni (A) Frequency (Hz) – toff (µs)	0.25 – 0.45 50 - 5

Table 1: Main deposition conditions of the study

Figure 2 presents the evolution of the La/Ni atomic composition ratio measured by EDS as a function of current dissipated on the Ni target. When the current dissipated on the Ni target is 0.3 A, the metallic ratio is about 1.94. This value is close to the expected value of 2 for the La_2NiO_4 compound.
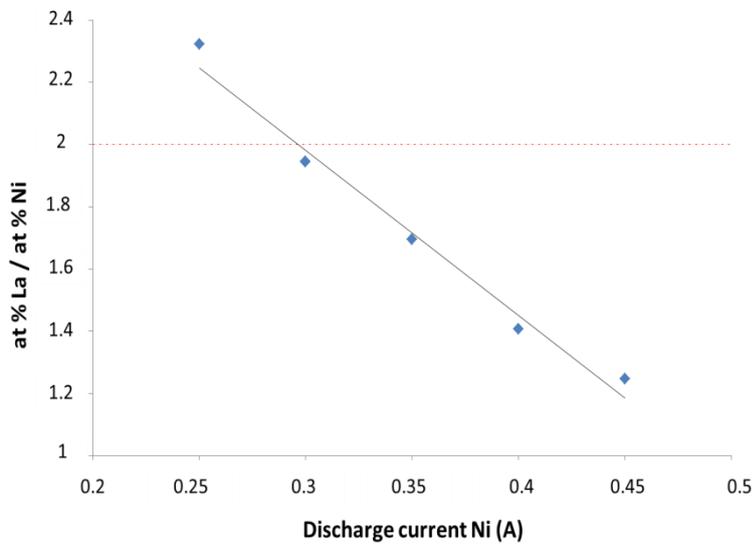

Figure 2: Evolution of atomic composition ratio La/Ni measured by EDS as a function of current dissipated on the Ni target

XRD performed on as-deposited samples shows the presence of an amorphous structure whatever the composition. In a previous study [7], we have shown that the La_2NiO_4 phase crystallization begins from 973 K and increases with the annealing temperature. At 1073 K, it was identified that most of the coating crystallized in the La_2NiO_4 structure. Hence, it was decided to perform annealing treatments for 2 h at 1173 K in order to crystallize La_2NiO_4 structure.

Figure 3 presents the evolution of the sample structure as a function of the La/Ni atomic ratio after annealing at 1173 K. When the Ni content is higher (i.e La/Ni < 2), the coating crystallizes under $LaNiO_3$ perovskite structure. The La_2NiO_4 structure appears for a La/Ni ratio around 1.7 and this structure is well defined when the ratio is close to 2. A mixture of La_2O_3 and La_2NiO_4 phases is identified when the La/Ni ratio is over 2.
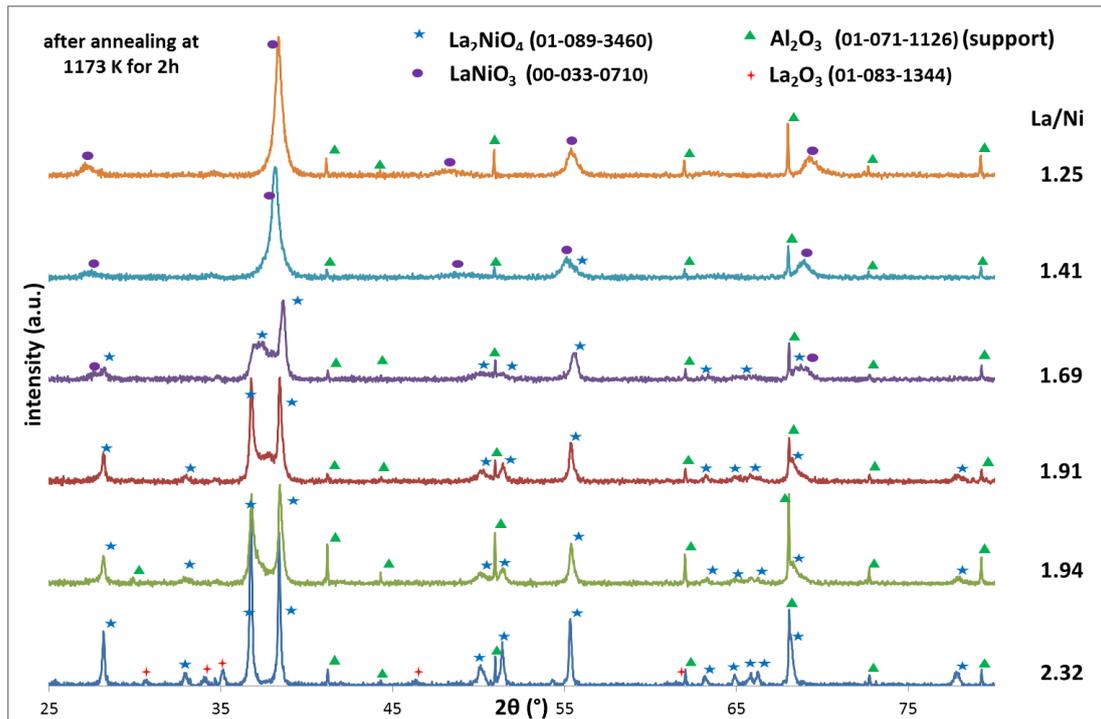
Figure 3: XRD pattern after annealing at 1173K for 2h under air as function of La/Ni atomic content ratio

Conclusion :

La-Ni-O coatings were deposited on different substrates by co-sputtering from Ni and La metallic targets in a presence of a reactive argon-oxygen mixture using plasma emission monitoring process. This technique allows the control of oxygen flow rate under unstable conditions and permits the deposition of stoichiometric coatings with high sputtering rate. The as-deposited coatings are amorphous and need an annealing treatment to crystallize on the targeted structure. At 1173 K, the different phase crystallization is completed. For 0.3 A, La_2NiO_4 phase is crystallized without phase pollution.

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