ABSTRACT

Polycrystalline thin films of La$_2$NiO$_{4+δ}$ have been synthesized on YSZ substrates by dip-coating using a polymeric sol. Crack-free films were obtained after sintering in air at temperatures ranging from 800°C to 1000°C. The microstructure, characterized by SEM, shows the formation of dense polycrystalline films with smooth surface and mean grains size of 50 nm, for films sintered at 1000°C. The thickness, evaluated from rugosimetry measurements, is weak (100 nm) and is a function of the viscosity of the sol. The higher the thickness, the higher the viscosity. Then, it is possible by modifying processing parameters to synthesize thin films with a controlled microstructure (thickness and porosity).

INTRODUCTION

The development of solid oxide fuel cells (SOFCs) operating at reduced temperatures (600°C to 800°C) has recently received much attention (1). The operation of SOFCs at a reduced temperature provides several important advantages, including a wider choice of cell and ancillary materials such as use of non-ceramic electrodes and interconnect. It also allows longer cell life due to decreased interdiffusion between cell components and a lower electrode sintering. Finally, it increases SOFC reliability because of a reduced thermal stress, and it reduces cost due to the use of lower cost materials.

Manganite-based SOFCs currently use supported or self-supported LSM cathodes with a typical thickness of 50 μm to 300 μm. This requires SOFCs to operate at about 1000°C to limit cell internal resistances. Thus, one approach to achieve an efficient operation at reduced temperatures is to control the microstructure of the cathode in order to minimize the ohmic losses by increasing the line of the triple boundary point (2,3). This approach requires a suitable process for the elaboration of thin films. Some recent studies have shown that the fabrication of thin layers of LSM with a porosity around 30% via a polymeric method is possible by modifying the processing parameters (4).

Another approach is to improve the properties of the perovskite-type materials based on lanthanum manganites to increase the number of the triple phase boundary points. This requires materials exhibiting both good electrical and ionic conductivities. Among the different classes of oxides, the Ruddlesden Popper materials present the most interesting properties because the ion diffusion in this oxide is some orders of magnitude higher than in perovskite material (5). Indeed, this structure can incorporate additional oxygen on the
interstitial sites which induces ionic and electronic conductivities (6,7). This incorporation is often related to the preparation technique (temperature, atmosphere, etc.).

Thus, this paper presents the development of a reduced-temperature SOFC cathode based on thin films of new materials such as La2NiO4+δ fabricated via a polymeric method. A simple and cost-effective process based on the dip-coating method using a polymeric sol is developed for the fabrication of La2NiO4+δ thin cathode. The effects of several processing parameters such as viscosity, salt concentration and heating temperature on the structure and microstructure of both powders and thin films are also studied.

**EXPERIMENTAL PROCEDURE**

**Sample Preparation**

The polymeric precursors for synthesizing La2NiO4 powders and depositing La2NiO4 thin films are prepared using solutions similar to the ones outlined by the Pechini (8). Controlling the organic content in the organic precursor and the viscosity is critical to obtain dense, crack-free films. Indeed, when the organic content in the precursor is too high, a very large amount of shrinkage appears in the film during pyrolization, inducing film cracking. Similarly when the viscosity of the precursor is too high, the process results in a very thick organic film and, again, cracking appears during pyrolization of the film. Several series of experiments are conduced to reduce the overall organic content of the precursor while keeping an appropriate number of chelation sites - sols with different viscosities and ionic concentrations are used.

Reagent grade La(NO3)3·6H2O and Ni(NO3)2·6H2O were used as starting salts and dissolved in deionised water in stoichiometric amounts. Since the cation concentration in the precursor influences the thickness of the resulting film, a variety of molar concentrations was investigated. HMTA resins were added to the mixture as organic carrier. This resin was made from different chelating and polymeric agents such as hexamethylenetetramine, acetic acid and acetylacetone. The ratio of chelating agent to cation sources in the solution was kept at a constant value of 2. The resulting sols were homogenous and precipitate free. They were heated and stirred until the solution reached viscosities ranging from 25 cP to 60 cP. To produce powders, the sol was then dehydrated and calcined at 400°C in air for 4 hours. Then, the obtained precursor was ground and calcined at a heating rate of 100°C/h, under air for 2 hours for temperatures ranging from 800°C to 1000°C.

The precursor solutions were dip-coated onto YSZ substrates. Prior to coating, the substrates were polished to a roughness of 10 nm, cleaned by immersion in deionized water and dried in air. The precursor coated films were heated in air at temperatures ranging from 650°C to 1000°C.

**Viscosity**

The sol viscosity was measured with a rotating-spindle viscometer. Sets of measurements were taken at all rotational speeds where a reading of the viscosity value could be obtained.

Electrochemical Society Proceedings Volume 2003-07
Thermal Analysis

The pyrolysis and decomposition behavior of the crushed precursors were monitored by simultaneous differential thermal and thermogravimetric analyses (DTA/TGA) (Setaram TG-DTA 92) up to 1000°C at a heating rate of 5°C/min under air. The oxygen content in La2NiO4 powder was evaluated from a thermogravimetric analysis under a mixture of 10% of hydrogen in argon.

X-Ray Diffraction Analysis

X-ray diffraction powders measurements were done using a Seifert XRD 3003 TT diffractometer (Cu-Kα radiation). The structural investigations of the thin films were carried out with a Siemens D500 diffractometer.

Chemical Analysis

To determine the lanthanum to nickel ratio in the calcined powder, the chemical composition was analysed by atomic absorption spectroscopy. The La: Ni ratio was found to be slightly higher than 2.

To confirm the non-stoichiometry levels evaluated from TG analyses, titrations were done according to chemical method (9).

Electron Microscopy

The morphology and the microstructure of thin films were examined by scanning electron microscopy, SEM (JEOL- JSM – 35CF).

Rugosimetry

The thickness of thin film was evaluated with an optical profilometer.

RESULTS

The precursor solution is heated at 70°C until it reaches an appropriate viscosity. Then, it is dehydrated at 200°C overnight. The obtained precursor is thermogravimetrically characterized to determine the temperature at which the organics fully pyrolyze. Figure 1 shows the TGA and DTA results for the La2NiO4 precursor obtained from HMTA resin process. The thermal analysis of the process turns out to be complex. The thermal analysis of HMTA process reveals a three-step weight loss with corresponding DTA curves. The first weight loss which occurs at around 90°C corresponds to the elimination of water compounds that were not removed during the initial solution drying process. The second major weight loss in TGA occurs between 200 and 500°C, and is caused by the burnout of pyrolyzed organics. The third peak, around 700°C, may be attributed to the decomposition of amorphous oxycarbonates formed during the previous step (10). There is no more weight loss above 700°C. These results are confirmed by DTA experiments. Indeed, the DTA results show an endothermic reaction starting at 90°C related to water
loss and exothermic reactions starting at 300°C related to the pyrolysis of the organic precursor and La$_2$NiO$_4$ formation. No reaction is observed above 700°C.

Studies on LaSrMnO$_3$ films show that the thickness of the film is related to the ionic concentration. Accordingly, the first step is to determine the limit concentration which will allow us to prepare thick films by keeping the Ruddlesden Popper phase. For this study, different polymeric sols with various ionic concentrations ranging from 0.15 to 0.60 mol.L$^{-1}$ are synthesized. Only the concentration of 0.15 mol.L$^{-1}$ leads to the formation of the pure phase. For concentrations larger than 0.15 mol.L$^{-1}$, La$_3$Ni$_2$O$_7$ and La$_2$O$_3$ oxides appear. Thus, the limit concentration allowing the synthesis of thick film with the Ruddlesden Popper phase is 0.15 mol.L$^{-1}$.

![Figure 1. TGA curve (a) and DTA (b) curve of La$_2$NiO$_4$+5 gel under air.](image)

Figure 2 shows the phase evolution in La$_2$NiO$_{4+5}$ powders characterized by XRD analyses. A diffuse XRD pattern is obtained for the powder heat treated at 650°C, indicating that the precursor is amorphous (not reported in this figure). For temperatures above 700°C, the La$_2$NiO$_4$ forms, as shown by the XRD patterns. Since no weight loss is observed for temperatures above 800°C, La$_2$NiO$_{4+5}$ is likely to nucleate from an inorganic amorphous matrix. No intermediate phase is observed; however, the weight loss at 700°C corresponds to the formation of an intermediate phase according to Gaudon's works on LSM (10). In this work, we do not detect this mixed carbonate by XRD; this could be associated with the low level of crystallinity of the phase.

In addition, an increase from 2 to 6 hours in the time at the annealing temperature (900°C, 1000°C) does not change the symmetry of the structure which indicates the formation of a stable phase.
The X-ray diffraction patterns of La$_2$NiO$_{4+x}$ calcined at 1000°C in air for 2 hours were studied by the Rietveld method. The Rietveld refinement profile is shown in Figure 3. From this result, one observes an orthorhombic unit of La$_2$NiO$_4$ (Fmmm space group) with $a = 5.4584$ Å and $b = 5.4659$ Å, $c = 12.6974$ Å (9).

This result is confirmed by the reconstitution of the reciprocal lattice from different electron diffraction patterns (11).

The average of the crystallites is calculated from the Rietveld refinement results and the average of the grains size from the MET micrographies. The average size is 110-150 nm for crystallites and is 130 -160 nm for the grains.
Grazing angle X-ray diffraction patterns of the La$_2$NiO$_{4+\delta}$ thin films synthesized were obtained for films synthesized with a viscosity of 53 cP and calcinated at 1000°C in air during 2 hours. Figure 4 shows the result obtained for a 100 nm thick sample using a grazing angle of 1°. Under these conditions, no peak corresponding to the YSZ substrate can be observed, which indicates that the X-ray beam does not penetrate the La$_2$NiO$_{4+\delta}$ film. These results are representative of a layer of the film close to the surface. Only La$_2$NiO$_{4+\delta}$ phase peaks with the K$_2$NiF$_4$ structure are observed. It is difficult to determine the phase symmetry of the film due to the symmetry of the grazing incidence apparatus.

![Figure 4. Grazing angle X-ray diffraction patterns of film deposited on YSZ substrate and annealed at 1000°C in air for 2 hours.](image)

However, a comparison of the X-ray diffraction patterns obtained on powders and thin films shows that the position of the peak is the same. It implies that the symmetry of the film is orthorhombic. In this phase, the orthorhombic symmetry is obtained for high non stoichiometry levels (12). Accordingly, the non stoichiometry level in the film can be estimated at 0.20. In addition, a study of peaks intensity of XRD films shows that our films are polycrystalline with a random orientation.

In order to confirm that the orthorhombic symmetry corresponds to high non stoichiometry levels in the La$_2$NiO$_{4+\delta}$, the non stoichiometry of powders obtained in the same conditions is determined from both TG analyses under a reductive gas (11) and chemical titrations (9). The results are similar. The non stoichiometry level depends on the heat treatment and the value of 0.20 is obtained for powders calcined at 1000°C. This
The effects of the viscosity and of the heating temperature on the microstructure of the thin films are then studied. Figure 5 reports the Scanning Electron Microscopy micrographs of La$_2$NiO$_{4+y}$ thin films deposited on YSZ substrates for different heating temperatures and viscosities. The microstructure of the film depends on the processing parameters. However, whatever the conditions used, one obtains a crack-free film with a smooth surface. The roughness of the film is small and lower than 10 nm (11). For a heating temperature of 800°C, the viscosity of the polymeric sols influences the surface morphology of the film. When the viscosity is low, films have no definite grain size, indicating poor crystallinity of the film. However, an increase in viscosity allows synthesizing a denser film. This result can be correlated to the concentration of water in the polymeric sol. Indeed, the higher the viscosity, the lower the water concentration in the sol, and thus denser the microstructure.

Another way to densify films is to increase the heating temperature. Figures 5b and 5c show the SEM of the La$_2$NiO$_{4+y}$ thin films annealed at 800°C and 1000°C for 2 hours. A crack-free film with a smooth surface and with a well-defined grain structure is obtained for T = 1000°C. This well-defined grain structure for the films indicates that the film has a fine microstructure. The micrographs in Figure 5 show that the microstructure evolves as a function of the heat treatment. Small grain domains are observed for films calcined at 1000°C. Compared to Figure 5b, one observes a rearrangement of crystalline domains.

The grain size exhibits substantial modifications with heat treatment temperature. At 800°C, one observes a fine grain structure with grains on the order of 20 nm. An additional increase in the heat treatment temperature to 1000°C results in an increase in the grain size to approximately 50 nm.

The thickness of the La$_2$NiO$_{4+y}$ thin films evaluated by rugosimetry measurements is reported in Figure 6 as a function of the viscosity. The film thickness increases with the viscosity. This evolution follows the Landau Levich law. The higher the thickness, the higher the viscosity.
DISCUSSION

The thermal analysis results as well as the XRD and SEM results show that La$_2$NiO$_{4.8}$ thin films are obtained after the deposition of a polymeric solution of precursor on YSZ substrate and heat treatment at temperatures above 800°C. No intermediate phase is observed before the phase formation and a very high level of crystallinity can be observed after heat treatment at 1000°C. SEM observations indicate that clusters of small crystals form during the crystallization. A microstructure formed by aggregates of nanometric grains is observed after heat treatment at 1000°C. While increasing the heat treatment, these clusters or domains of small grains sinter to form a dense and crack-free granular microstructure. This type of microstructure leads to the formation of smooth surfaces as shown in Figure 5c micrograph.

According to these results, the following microstructural evolution for the La$_2$NiO$_{4.8}$ thin films, prepared from polymeric precursors, can be proposed: (a) formation of clusters of nanometric crystals from an amorphous matrix; (b) densification of clusters resulting in a microstructure consisting of small grains domains, (c) densification or grain growth of the small grain domains forming a polycrystalline microstructure with granular texture, low porosity and a smooth surface.

The thickness of the film is evaluated from rugosimetry experiments. The thickness is small and depends on the viscosity of the polymeric sols. The higher the thickness, the higher the viscosity. However, the thickness reached for one coating for the highest viscosity (60 cP) is 100 nm, which is too small for the application of these materials in SOFC devices. One of the ways to make thick layer is to increase the number of coatings during the synthesis of the film. In addition, these results show that despite the small thickness of the layer, it is possible to fabricate films with different porosities by controlling the viscosity of the polymeric sols. The control of the microstructure is

Electrochemical Society Proceedings Volume 2003-07
critical for a good performance of SOFCs. Indeed, the reduction of the oxygen depends both on the cathode composition and on the microstructure (12,13). When the cathode material is a mixed conductor, the microstructure has to be dense in order to minimize ohmic losses. Thus, the fabrication of dense La$_2$NiO$_{4+x}$ materials via a polymeric method is important for SOFCs.

The development of new mixed ionic-electronic conductors, La$_2$NiO$_{4+x}$, is important for solid oxide fuel cell cathode materials because they may provide a significant decrease in polarization losses due to an enlargement of the electrochemical reaction zone (6). Both the electrical conductivity and the ionic conductivity of these materials depend on the non stoichiometric level. Good electrical conductivity is obtained for materials exhibiting high non stoichiometry although good ionic conductivity for materials having low non stoichiometry level. Thus, a compromise in terms of non stoichiometry should be found in order to have both a good electrical and a good ionic conductivity. In this study, the synthesis process allows a control of the non stoichiometry level by modifying the heating temperature. In addition, the non stoichiometry level can be adjusted by modifying the nature of the chelating and polymeric agents used during the synthesis of the polymeric solution (11). A value as small as 0.15 can be reached.

**CONCLUSIONS**

Homogeneous, crack-free, dense thin films with Ruddlesden Popper structure are prepared on YSZ substrates using a polymeric precursor synthesized via a chemically modified Pechini process. The XRD results show that the film is polycrystalline with a random orientation. Correlations between XRD results on powders and thin films allow an estimation of the film non stoichiometry level of 0.20.

Correlations between the sol viscosity, the calcination temperature and the microstructure of the film are observed. Indeed, the thickness of the films depends on the viscosity. An increase in the viscosity leads to an increase of the thickness of the films up to 100 nm. However, the heating temperature does not affect the thickness of the film for films heat-treated at 800°C and 1000°C. The heat treatment only modifies the microstructure. A denser structure is obtained for a higher temperature, 1000°C. Thus, using a polymeric method, the microstructure of the films can be adjusted by controlling the processing parameters.

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