MOCVD OF THIN MIXED-CONDUCTING FILMS ON POROUS CERAMIC SUBSTRATES

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Mixed electron and oxygen-ion conducting perovskites have received much attention because of their potential application in oxygen separation or catalytic oxidation processes. The use of ultra-thin membranes would allow operation at considerably lower temperatures compared to conventional thick ceramic membranes. K_2NiF_4-type lanthanum nickelates possess relatively high values of both ionic and electronic conductivity, as well as relatively low thermal expansion coefficients (13×10^{-6} K^{-1}).[1]

Thin iron-doped lanthanum nickelate (LNF) films have been deposited on porous ceramic tubes by metal organic vapor deposition (MOCVD). A new MOCVD system has been constructed and used for the deposition (figure 1). As substrates commercial tubular ultrafiltration membranes with ZrO_2 top layer (100 mm length, 10 mm outer diam., 110 nm pore size) were used. The layers have been analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD). For assessment of the gas tightness of the layers leak rates to nitrogen at room temperature were measured.

2,2,6,6-tetramethyl-3,5-heptadionates of lanthanum, nickel and iron have been used as precursors. The conditions of deposition of the LNF films are summarized in table 1. Dense layers have been obtained with good uniformity of film thickness and composition over the entire substrate as shown in Figure 2. Films deposited under experimental conditions A were deficient in lanthanum (La:Ni = 1,3-1,6), while a La:Ni – ratio >2 was found using conditions B. XRD analysis showed that the material deposited at 480 °C is amorphous. Annealing at 800 °C lead to formation of La_2NiO_4 and $LaNiO_3$ phases.

The leak rates to nitrogen at room temperature vary considerably among individual samples that were deposited under identical conditions. Average values are $3{,}4 \times 10^{-6}$ mol s^{-1} cm^{-2} at $\Delta p = 0{,}5$ bar for LNF (A) samples and $7{,}4 \times 10^{-8}$ mol s^{-1} cm^{-2} for samples B. The permeance of the substrate is 4×10^{-4} mol s^{-1} cm^{-2}. Further studies on the effects of annealing and long-term stability will be made, and gas tightness needs to be further increased. Deposition of other mixed-conducting perovskites will be undertaken.

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References:

[1] V. V. Kharton *et al.*, *J. Mater. Chem.*, **9**, 2623-2629 (1999)

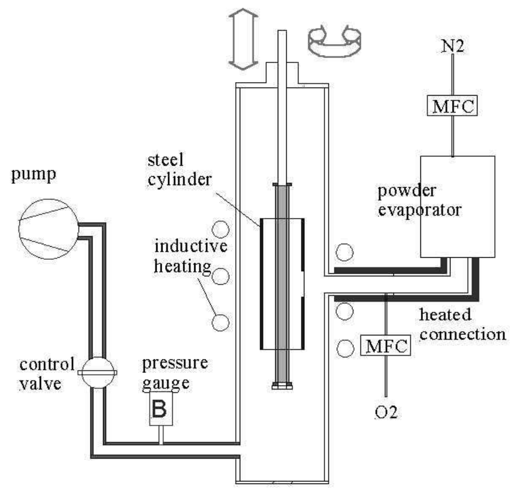

Figure 1: Schematic view of the deposition equipment

Table 1. Deposition conditions for LNF layers

Deposition runs	A	B
Evaporation temp. (°C)	260	260
Deposition temp. (°C)	480	480
Total pressure (mbar)	2	2
O_2 partial pressure (mbar)	1	1
Total gas flow (l/h)	10	10
Precursor molar fraction	0,001	0,001
Growth rate (μm/h)	18	
Precursors	$La(thd)_3$, $Ni(thd)_2$, $Fe(thd)_3$	
Precursor composition	$La_2Ni_{0,98}Fe_{0,02}$	$La_{2,67}Ni_{0,98}Fe_{0,02}$
Total prec. amount (mg)	705	830

thd – tetramethylheptadionate

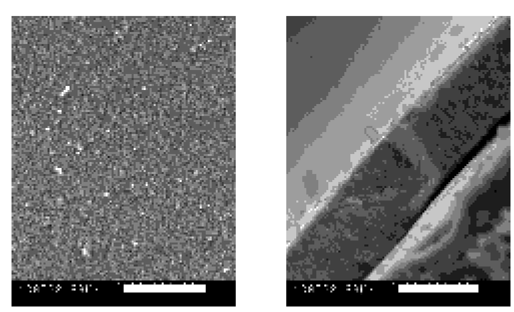

Figure 2: SEM pictures of LNF sample deposited under conditions A: a) top view; c) cross-section. Length of the white bar is 15 μm.