Synthesis and Characterization of Dense Ceramic Membranes for Methane Conversion – Part II

A. Santos[1a], V. A. Fontes[2a], F. A. Oliveira Fontes[2b], J. F. de Sousa[1b], C. P. de Souza[1c]

[1]Departamento de Engenharia Química
[2]Departamento de Engenharia Mecânica
Universidade Federal do Rio Grande do Norte - UFRN /Programa de pós-graduação em Engenharia Química - PPGEQ / Centro de Tecnologia - Av. Sen. Salgado Filho s/n
Campus Universitário, Natal/RN – Brasil, Cep 59.072-970
[a]andaraireq@yahoo.com.br,[b]franciscofontes@uol.com.br, [c]carlson@ufrnet.br

Abstract

The perovskite- type oxide (ABO_3) containing transition metals on the B-site show mixed (electronic/ionic) conductivity. These mixed-conductivity oxides are promising materials for oxygen permeating membranes. The main objective of this research work is to synthesize and characterization ceramic powders of the Sr-Co-Fe-O system for methane conversion using membrane reactor. SCFO powders were synthesized from the route was based on the complex method of combination of acid EDTA and citrate and shown be available by control efficient of synthesis to performed $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, moreover, it presented easy implementation, reproducibility and operation. Powder ceramic was characterized by XRD, microscopic optic, SEM and TG-DTA.

Keywords : Ceramic membrane, Perovskite oxides, synthesis, $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$

1. Introduction

Recently, mixed oxygen-ion and electronic conducting oxides have attracted considerable and increasing attention for use as oxygen separation membranes and membrane reactors for light hydrocarbon conversion (1).

Synthesized from ceramic powders by reaction of solid state oxide (perovskite) with structure on based (ABO_3), where A and B they are transition metals and present high capacity of ionic and electric conductivity. This type of membrane is promising for use in many industrial processes that require a continuous supply of pure oxygen (1, 2).

Since the initial systematic oxygen permeation study of acceptor-doped perovskite oxide membranes of $La_{1-x}A_xFe_yB_{1-y}O_{3-\delta}$ (A: Ca, Sr, Ba; B: Co, Fe, Ni, Cu) were performed by Teraoka et al. (3), many researchers have conducted or are conducting studies on dense ceramic membranes for oxygen separation and membrane reactors. It was reported that $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (1) and $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ (4) possess the highest oxygen permeation fluxes among all the membrane materials developed up to now.

The main objective of this research work is the synthesis and characterization of ceramic powders of SCFO synthesized from a route based in a complex method of combination of EDTA acid and citrate (8).

The next step of this work is the characterization tests of permeability of the oxygen using a projected membrane reactor.

2. Experimental and Results

SCFO powders were synthesized from the route was based on the complex method of combination of acid EDTA and citrate (8). In brief, the calculated amount of nitrates were dissolved in de-ionized water and mixed. The mole ratio of EDTA acid ($C_{10}H_{16}N_2O_8$): citric acid ($C_6H_8O_7$): total metal ions was controlled to be around 1:1.5:1. EDTA acid and $NH_3.H_2O$ solution was prepared, under heating and stirring during a time enough to become a limpid solution. The following step was to mix the solutions: nitrate solution and solution of EDTA acid and $NH_3.H_2O$. The appropriate amount of citric acid was introduced in solution and submitted the heating and stirring, then $NH_3.H_2O$ was added to adjust the pH in 6. Later, final solution was submitted the heating (80°C) and stirring simultaneous. By evaporation the water, a dark purple gel was obtained. The gel was then at 120°C for 15h to get primary powder, which were calcined at 950°C for 5 h to obtain powder with the final composition.

Disc samples with approximate dimensions of 17 mm in diameter and 1 mm in thickness were fabricated from $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ powders (8), and then used for the oxygen permeation measurements in membrane reactor.

Figure 1 shows the result obtained from X-ray Diffraction (XRD) referring to the $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membrane synthesized from route proposed in (8).

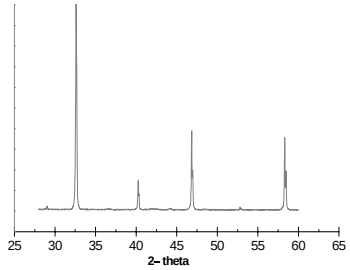

Fig. 1. XRD of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ sample obtained by proposed route on based in the combination EDTA and citrates method.

Figures 2 and 3 shows the results gotten for microscopic optic and SEM, respectively, referring to the membrane of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$.

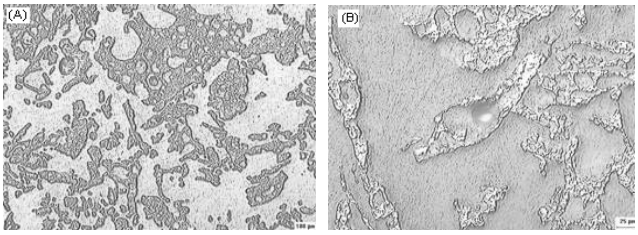

Fig. 2. Microscopic optic of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ sample obtained by proposed route on based in the combination EDTA and citrates method. Zoom: (A) 100X (B) 500X.

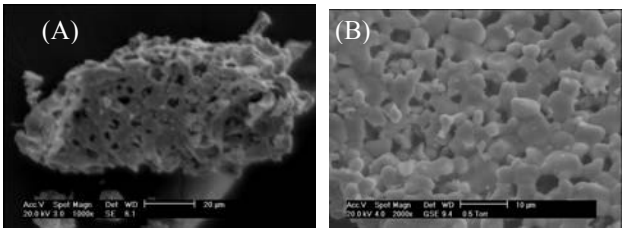

Fig. 3. MEV of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ sample obtained by proposed route on based in the combination EDTA and citrates method. Zoom: (A) 1000x, (B) 2000x.

The microscopic were obtained from an initial mixture of resin polyester and powder $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. From Figure 2 can be observed that the powder $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ probably tends crowding in cellular format.

$SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ morphology was verified from microstructure in according to Figure 3. This result is consistent with Figure 2. The results had presented good agreement with the ones of literature (3, 5-7).

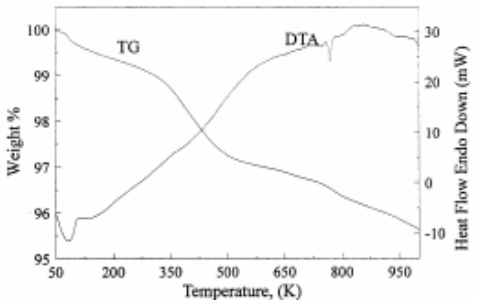

Fig. 4. TG-DTA of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ under N_2 (99.999%) atmosphere.

The TG-DTA results of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ recorded in nitrogen (99.999%) are shown in Figure 4.

It can be seen from Figure 4 shows that the weight of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ sample decreases quickly with the increase of the temperatures and the DTA profile of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ shows a first-order transition with a high endothermic heat effect upon heating about 790°C, which is corresponding to the oxygen vacancy order-disorder transition of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$, good agreement with the literature (3, 7).

3. Conclusions

The proposed route in this work, revealed sufficiently satisfactory for synthesis of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$. The results had presented good agreement with the ones of literature. The same one showed be a trustable procedure and raised reproducibility.

4. References

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