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Additional Information

Catalytic activation of ceramic H₂ membranes for CMR processes

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Abstract

The application of catalytic membrane reactors can overcome some of the disadvantages that reactions for the direct conversion of methane to fuels and petrochemicals present. Hydrogen separation membranes can shift the reaction equilibrium by hydrogen removal, improving the separation, selectivity and yield of the reactions. La_{5.5}WO_{11.25-δ}/La_{0.87}Sr_{0.13}CrO_{3-δ} (LWO/LSC) based membranes present a high H₂ flux within the temperature range where CMR can be applied. However, the catalytic activity of the material is very low and it has to be improved. This work presents the development of different catalytic layers based on LSC material and the study of their influence on the H₂ flux obtained by using 60/40-LWO/LSC membranes. Membranes coated with porous layer made of Ni-infiltrated La_{0.75}Ce_{0.1}Sr_{0.15}CrO_{3-δ} exhibited the best permeation flux but still 20% lower than the one reached using Pt layers. Stability of the catalytic layers is also evaluated under H₂ permeation conditions and under high steam content methane.

1. Introduction

The direct conversion of methane to fuels and petrochemicals represents a major challenge. Steam reforming of light hydrocarbons is an industrially important chemical reaction and a key step for producing hydrogen and syngas for ammonia and methanol production, hydrocracking, Fischer-Tropsch synthesis and other important processes in the oil refining and petrochemical industries [1, 2]. Industrial fixed-bed steam reformers suffer however from several problems which seriously affect their operation and performance [3]. These problems comprise low catalyst effectiveness, low heat transfer rates, large temperature gradients and thermodynamic equilibrium constraints. In the last years, the catalytic conversion of methane to aromatics via non-oxidative routes has attracted significant attention. However, this reaction presents very low equilibrium conversions and benzene yields of only $\sim 7\%$ at the required temperature (950 K) [4].

The integration of this kind of reactions in catalytic membrane reactors (CMR) may allow the process efficiency to be substantially increased. The reaction equilibrium can be shifted by controlled hydrogen removal with the consequent enhancement of separation, selectivity and yield of these reactions [5, 6]. Dense mixed-conducting ceramic membranes are one of the typical inorganic membranes for CMR, specifically, mixed proton electron conducting membranes which present an important hydrogen permeability and catalytic activity at high temperatures [7, 8]. Several ceramic membranes have been tested for water gas shift reaction at high temperature (700-900 °C) and the reported results are promising [9, 10].

Despite the advantages of these membranes, H_2 fluxes obtained up to date are still low for their short-term industrial application. Aiming to improve the H_2 flux, research has been recently focused in the development of dual phase composites, materials formed by two phases, one electron conducting phase and another phase mainly proton conducting. With this strategy, an important improvement of the H_2 flux and stability has been obtained as compared with the single constituent materials. It is noteworthy the significant H_2 fluxes obtained with several cer-mets as Ni-BaCe_{0.9}Y_{0.1}O_{3- δ} [11], Ni-BaZr_{0.1}Ce_{0.7}Y_{0.2}O_{3- δ} [12] and Ni-BaCe_{0.85}Tb_{0.05}Zr_{0.1}O_{3- δ} [13]. As well as the cer-cers based on BaCeO_{3- δ} or BaCe_{1-x}Zr_xO_{3- δ} based materials as protonic phase and doped ceria as electronic phase [14, 15].

Among the reported dual phase composites, La_{5.5}WO_{11.25- δ} /La_{0.87}Sr_{0.13}CrO_{3- δ} (LWO/LSC) based cer-cers present an excellent H_2 flux permeation [16, 17] (which comprises the H_2 flux due to proton transport through the membrane in addition to the H_2 produced by water splitting and concomitant oxide-ion transport) and stability in different atmospheres. Despite the high H_2 flux obtained with this material, it presents a poor catalytic activity toward H_2 exchange [16]. For this reason, a development of a catalytic layer for the improvement of the surface kinetics is mandatory in order to apply this material in CMR.

This strategy has been widely employed for oxygen permeable membranes based on mixed ionic electronic conductors.[18-21] Regarding surface kinetics improvement in H₂ permeable membranes, the use of Pt as catalytic layer is the most reported for different materials as cerates [22], tungstates [23] and dual phase composites [14, 24, 25]. Ni and Pd particles were also employed for the coating of a BaCe_{0.85}Tb_{0.05}Co_{0.1}O_{3-δ} perovskite hollow fibre membrane obtaining a significant H₂ flux improvement [26].

The aim of this work is the synthesis and development of different catalytic coatings layers for the mixed protonic-electronic 60/40-LWO/LSC (60:40 in volume) composite with the purpose of performing different catalytic reactions as steam methane reforming (SMR) or methane dehydroaromatization (MDA) in a CMR. Targeted properties of the porous catalytic layers are listed: (a) high electronic conductivity; (b) redox stable under high steam content methane and coking resistant under atmospheres composed of dry methane, ethylene and aromatic vapours; and (c) high catalytic activity towards hydrogen activation. This work presents the development of different catalytic coatings based on LSC materials compatibles with LWO/LSC. H₂ permeation measurements have been performed by using 60/40-LWO/LSC membranes with the developed catalytic coatings. H₂ flux has been studied as a function of the temperature, of the H₂ concentration in the feed and hydration conditions of the membrane. For the best membrane, H₂ permeation measurements under CH₄ containing stream have been accomplished. Finally, stability tests under high steam content methane have been performed and the integrity of the samples has been evaluated by XRD and SEM.

2. Experimental

60/40-LWO/LSC (60:40 vol%) composite was prepared by mixing the corresponding amounts of LWO (provided by Cerprotech (NO) and calcined at 800 °C) and LSC (provided by Praxair (US) and calcined at 900 °C) and both materials were ball-milled together for 24 hours.

LSC based materials (employed as catalytic layers) as powders were synthesized by using the citrate reaction route [27] with a final calcination temperature of 900 and 1000 °C. The following LSC based materials were synthesized: La_{0.87}Sr_{0.13}CrO_{3-δ} (LSC), La_{0.75}Ce_{0.1}Sr_{0.15}CrO_{3-δ} (LCeSC), La_{0.85}Sr_{0.15}Cr_{0.8}Ni_{0.2}O_{3-δ} (LSCN) and La_{0.75}Ce_{0.1}Sr_{0.15}Cr_{0.95}Ru_{0.05}O_{3-δ} (LCeSCR).

Crystalline phases were identified by X-ray diffraction (XRD) performed in a CubiX FAST equipment using CuK α _{1,2} radiation and an X'Celerator detector in Bragg-Brentano geometry in the 2 θ range from 20 to 70°. XRD patterns were analyzed using X'PertHighscore Plus software (PANalytical).

Composite membranes used in H₂ permeation measurements consisted of a gastight disc with 15 mm diameter. Membranes were prepared by uniaxially pressing at 72 MPa of the mixtures before sintering at 1550 °C for 6 h in air.

Catalytic layers made of LSC based materials were obtained by screen-printing the inks on both sides of 60/40-LWO/LSC membranes. Inks were made by mixing the milled powders with a solution of ethylcellulose in terpineol (6%-wt.) and subsequently refined using a three roller mill (Exakt). Pt conducting paste was provided by MaTeck (Germany).

Six different coatings were prepared: (a) Pt (reference), (b) LSC, (c) LCeSC, (d) LSCN, (e) LCeSCR and (f) LCeSC infiltrated with Ni, in order to promote the surface reactions. Ni infiltration was made by following the procedure explained elsewhere [27] and using 5 M water solution of Ni nitrate. Firing temperature of screen-printed membranes was 1150 °C for 2 h.

Permeation measurements were performed on a double chamber quartz reactor following the procedure describe elsewhere [28, 29]. A mixture of H₂-He (100 mL·min⁻¹) was used as feed gas whereas Ar was employed as sweep gas (150 mL·min⁻¹). The H₂ content in the permeate side was analyzed using micro-GC Varian CP-4900 equipped with Molsieve5A and PoraPlot-Q glass capillary modules. Sealing was obtained using silver rings and applying a spring load. Appropriate sealing was confirmed by continuously monitoring the He concentration in the permeate stream. An acceptable sealing was considered when the helium concentration was lower than 5% of the H₂ permeated. Real H₂ permeation was then calculated by subtracting the He to the total H₂ flow observed [30].

Permeation measurements were accomplished under four hydration degree configurations: C1, dry atmosphere in both sides of the membrane (feed and permeate side); C2, feed side humidified (pH₂O=0.03 atm); C3, both membrane sides humidified (pH₂O=0.03 atm) and C4, sweep side humidified (pH₂O=0.03 atm). Permeation was also performed by using 30% CH₄, 50% H₂ and 20% He as feed, in order to check the H₂ flux under CH₄ containing atmospheres.

60-LWO/LSC (without catalytic layer), LCeSCRu and LCeSC-Ni samples were subsequently treated under an atmosphere composed by 50 % CH₄ and 50% H₂O, at 3 bar and 700 °C for 24 hours.

The microstructure of the catalytic layers and membranes was investigated using field emission scanning electron microscopy (FE-SEM) (Zeiss Ultra 55) and elemental analysis was carried out with energy-dispersive X-ray spectroscopy (EDS) (INCA, Oxford). The integrity of the samples was also checked by XRD.

3. Results

3.1. Synthesis of LSC based materials

Formula of the synthesized compounds based on LSC, their abbreviation and the corresponding calcination temperature are listed in Table 1. Room temperature XRD patterns of the developed LSC based materials as powders listed in Table 1 are shown in Figure 1. The predominant crystalline phase corresponds to the orthorhombic perovskite [31], however some minor peaks ascribed to SrCrO₄ and CeO₂ impurities can be also observed. Nevertheless, these impurities

disappear at higher calcination temperatures, $T > 1050$ °C [32], where no secondary phases are detected as can be observed in Figure 7.

Compounds	Nomenclature	Calcination temperature of the powder (°C)
$\text{La}_{0.87}\text{Sr}_{0.13}\text{CrO}_{3-\delta}$	LSC	900
$\text{La}_{0.75}\text{Ce}_{0.1}\text{Sr}_{0.15}\text{CrO}_{3-\delta}$	LCeSC	900
$\text{La}_{0.75}\text{Ce}_{0.1}\text{Sr}_{0.15}\text{Cr}_{0.95}\text{Ru}_{0.05}\text{O}_{3-\delta}$	LCeSCR	1000
$\text{La}_{0.85}\text{Sr}_{0.15}\text{Cr}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$	LSCN	900

Table 1: Stoichiometry, nomenclature and calcination temperature of LSC based compounds developed for catalytic coatings.

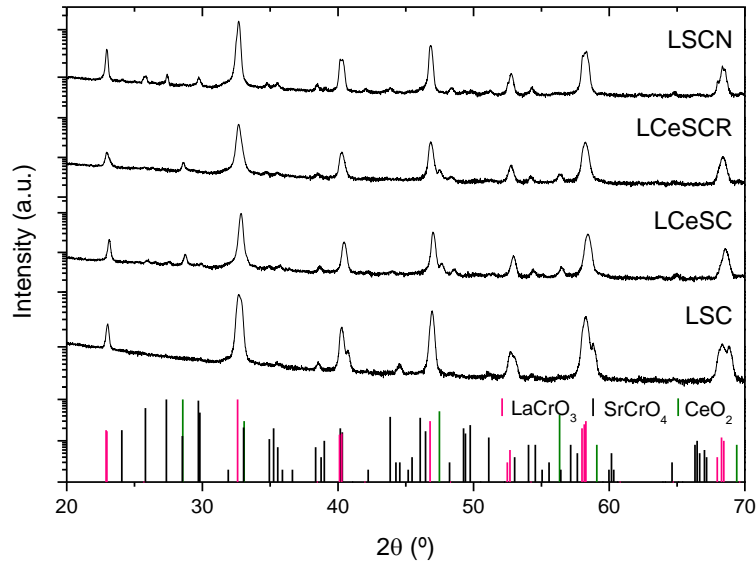


Figure 1: XRD patterns (y axis in \log scale) of the LSC calcined powders. Reference patterns of SrCrO_4 , LaCrO_3 and CeO_2 have been depicted for comparison (bottom).

3.2. Hydrogen permeation

3.2.1. Pt catalytic coating

The 60/40-LWO/LSC composition was selected due to the significant H_2 permeation that presents, higher than the reported for 20/80-LWO/LSC and 50/50-LWO/LSC [16]. H_2 fluxes for the three composites (expressed as $\text{mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-1}$ in order to disregard the effect of the thickness) are plotted in Figure 2a as a function of temperature under C3 conditions. Note that the three membranes were coated with Pt ink on both sides of the membrane. H_2 flux obtained for 60/40-LWO/LSC is 1.1 and 3.9 times higher than 50/50-LWO/LSC and 20/80-LWO/LSC, respectively.

Permeation of 60/40-LWO/LSC coated with Pt was evaluated as a function of the temperature under four different hydration conditions: (C1) both sides of the membrane dry, (C2) feed side humidified, (C3) both sides of the membrane humidified and (C4) only sweep side humidified. Humidified gas streams contains 3% of water ($p_{\text{H}_2\text{O}}=0.03$ atm). The H_2 fluxes obtained are depicted in Figure 2b. Different behaviours can be distinguished depending on the gas hydration configuration, as it was previously observed for 50/50-LWO/LSC. H_2 flux is very low under C1 as corresponds to the deficiency of protonic charge carriers in the oxide under dry conditions. H_2 permeation increases when H_2 feed side is humidified (C2) due to the hydration of the membrane and the subsequently increase of proton incorporation. Under C3 and C4, water splitting in the sweep side originated from the oxygen ion transport from the sweep side to the feed side contributes to the total H_2 flux. In fact, when both sides are humidified, C3, the H_2 flux increases reaching values up to $0.22 \text{ mL}\cdot\text{min}^{-1}\cdot\text{cm}^{-2}$. This rise is related to the higher proton transport and stems from the enhanced hydration degree of the oxide which provokes an increase in the proton concentration and thus in the proton. A contribution of 50% proton transport-50% water splitting has been reported for 50/50-LWO/LSC at 700°C under similar conditions using deuterium-labelled tracers [24]. For that reason together with the prevailing proton conductivity of LWO [33] in this range of temperature, at least a contribution of 50% proton transport is expected for the studied composite material.

On the other hand, when only the sweep side is humidified, H_2 flux decreases as compared with the previous condition. This drop is related to the lower degree of hydration of the membrane which causes the decrease of the proton transport. Conversely, in this configuration, the p_{O_2} gradient is slightly higher than in the previous one, resulting in an increase in the H_2 flux produced via water splitting. The point that H_2 flux in C4 is lower than in C3 indicates a prevailing proton transport in the material within the studied temperature range. This behaviour is in line with the transference number of LWO [33], i.e., this effect becomes progressively more important with decreasing temperatures and protons become the prevailing carriers at temperatures below 700°C .

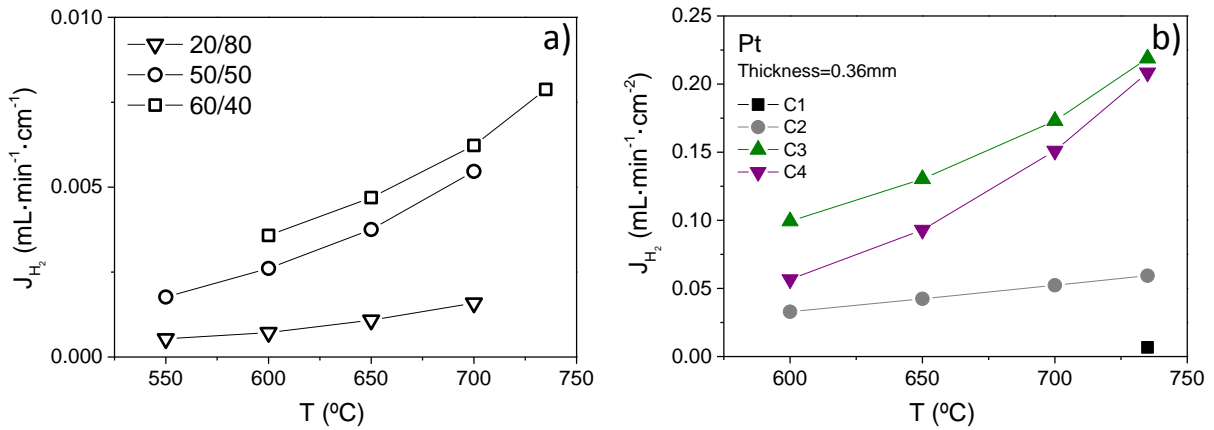


Figure 2: H₂ flux (permeability) as a function of temperature for 20/80, 50/50 and 60/40-LWO/LSC with a Pt coating under C3 configuration expressed as mL·min⁻¹·cm⁻¹ (b) H₂ flux (expressed as mL·min⁻¹·cm⁻²) as a function of temperature for 60/40-LWO/LSC under C1, C2, C3 and C4 configurations.

3.2.2. LSC based catalytic coatings

The H₂ permeation was studied for different 60/40-LWO/LSC membranes activated using five different porous catalytic coatings on both sides of the membrane: (i) 20 μm layer of LSC, (ii) 20 μm layer of LCeSC, (iii) 20 μm layer of LCeSCR, (iv) 20 μm layer of LSCN and (v) 20 μm layer of LCeSC infiltrated with Ni (LCeSC-Ni). All deposited LSC layers were sintered in air at 1150 °C. This sintering temperature was previously optimized to reach proper electrochemical performance for LSCN when tested as proton conducting fuel cell anode on LWO electrolytes [32].

Figure 3 shows the H₂ permeation fluxes as a function of the temperature for the membranes coated with LSC (a), LCeSC (b), LCeSCR (c), LSCN (d) and LCeSC-Ni (e). Only the membranes coated with LSC and LCeSC-Ni present similar behavior depending on the hydration configuration as Pt coated membrane, i.e. H₂ flux in C3 is higher than in C4. This indicates that the degree of hydrogen flux vs hydrogen produced by water splitting is influenced by the catalytic layer. Both LCeSCR and LCeSC present an increased catalytic activity toward O₂ exchange that gives rise to a higher contribution of the H₂ produced by water splitting as compared to H₂ permeation. LSCN presents an unexpected behaviour; one would expect the same behaviour as LCeSC-Ni, maybe with lower catalytic activity due to the lower Ni concentration.

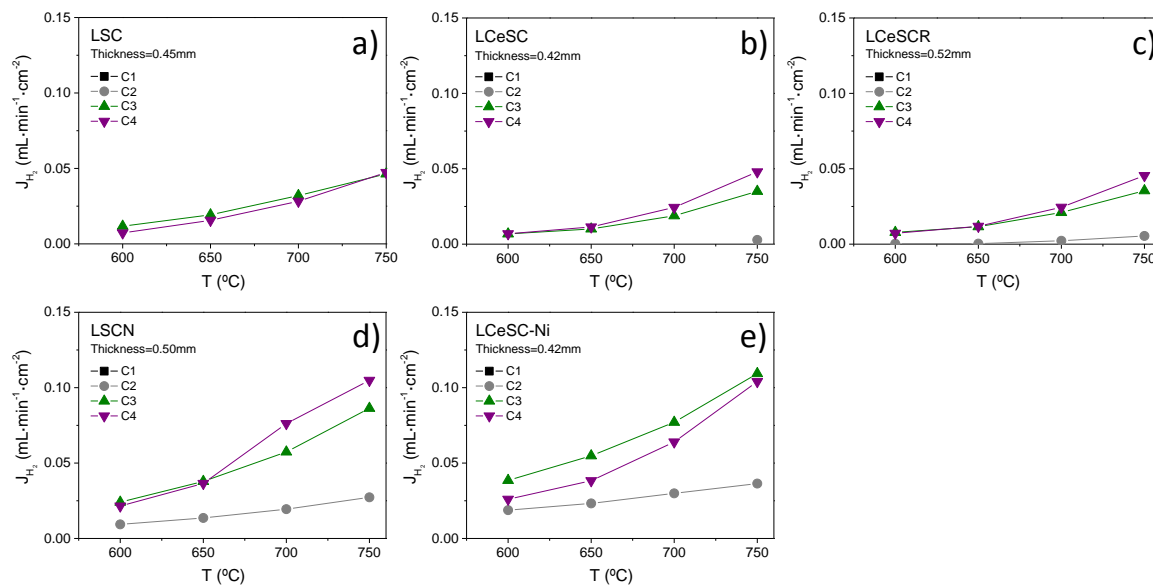


Figure 3: H₂ flux as function of temperature for 60/40-LWO/LSC with different activation catalytic layers: LSC (a), LSCN (b), LCeSCR (c), LCeSC (d) and LCeSC-Ni (e) in four different hydration degree configurations: C2, C3 and C4.

A comparison of the H₂ fluxes (expressed as mL·min⁻¹·cm⁻¹, in order to neglect the thickness influence) obtained for the five membranes with different catalytic layers and Pt coated membrane is depicted in Figure 4 for C2 (a), C3 (b) and C4 (c) conditions. Pt activated membrane presents the highest H₂ fluxes in the three evaluated conditions, followed by the LCeSC-Ni and LSCN coated membranes. Ni nanoparticles are formed on the LCeSC-Ni grain surface due to the reduction of the infiltrated Ni [34] whereas on LSCN they are formed from Ni reduction with subsequently precipitation on the grain surface [35]. The higher H₂ flux obtained with the Ni containing layers is ascribed to the active catalytic activity of Ni nanoparticles for the H₂/O₂ bond breaking in addition with the high electronic conductivity of these compounds which allows the three-phase boundary area to be increased. In fact, the addition of Ni to LSC anodes has been reported to boost surface reaction processes, appearing at low frequencies in impedance spectra [27]. This improvement was higher (as in this work) when the Ni was infiltrated, ascribed to a better dispersion and higher surface coverage of Ni nanoparticles [27, 34]. However, under C4 condition, the values obtained with LSCN are slightly higher at the highest tested temperature and the cause of this effect remains unknown. At this point, one may speculate about the distinct activity of the Ni reaction sites in LSCN and Ni-infiltrated electrodes towards H₂ activation and water splitting. Specifically, the results for C4 (dry feed side) may suggest that the infiltrated Ni particles are more active towards water splitting than the particles from the LSCN.

On the other hand, H₂ fluxes obtained for the LSC, LCeSC and LCeSCR activated membranes present practically the same values, indicating a relatively low catalytic activity for H₂ and O₂ evolution/oxidation reactions [36]. Despite the higher total and *p*-type electronic conductivity that LCeSC possesses [34] and the relatively high catalytic activity of Ru [37] for hydrocarbon reforming and syngas conversion, these membranes exhibit a similar magnitude of the H₂ flux as the obtained using the LSC activated membrane. The low catalytic activity of LCeSCR could be related with the Ru concentration in the perovskite lattice, which turns out to be insufficient to form enough Ru⁰ nanoparticles by precipitation on the grain surface and to reach a proper surface coverage of the LCeSCR backbone structure.

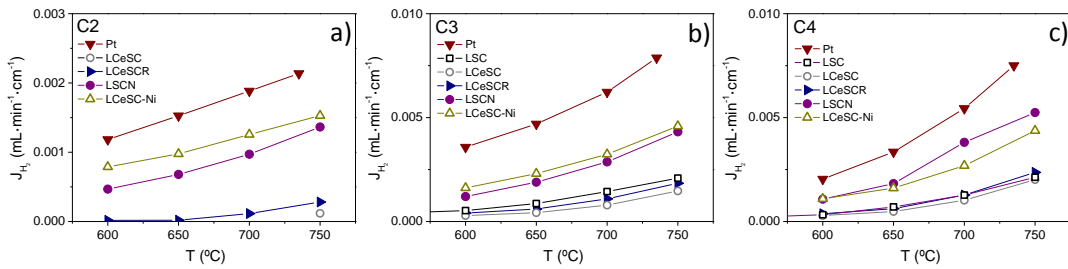


Figure 4: Comparison of the H₂ flux obtained for 60/40-LWO/LSC with the different activation catalytic layers under C2 (a), C3 (b) and C4 (c) hydration configurations. Note the distinct y-axis for (a)

3.3. Stability study

The stability and proton transport under CH₄ atmospheres was evaluated for LCeSC-Ni coated membrane. With this purpose, H₂ permeation measurements were performed at 750 °C during 5 hours feeding 30% CH₄, 50% H₂ and 20% He and humidifying both sides of the membrane (C3) (note that the same specimen was used in all the measurements, without and with CH₄ in the feed). H₂ fluxes obtained by using 50% H₂-50% He and 30% CH₄-50% H₂-20% He as feed gas are compared in Figure 5. H₂ flux obtained under CH₄ containing atmosphere remained unchanged for 6 hours which demonstrates the stability of the compound in these conditions. In addition, permeation values were higher than those obtained employing 50% H₂-50% He as expected from the higher *p*H₂ gradient under CH₄-containing stream, i.e., larger driving force for the separation.

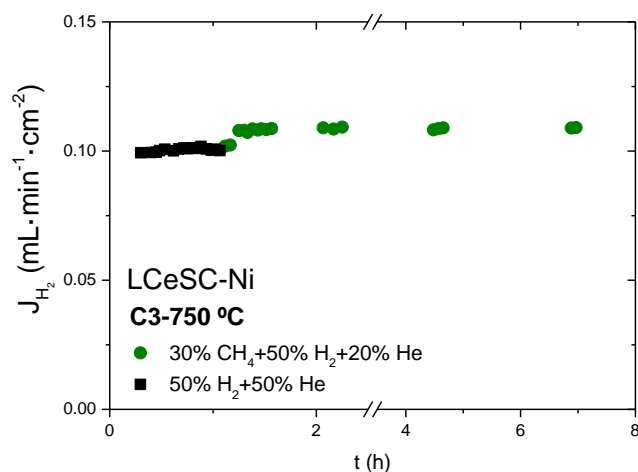


Figure 5: H₂ flux as a function of time for 60/40-LWO/LSC coated with LCeSC-Ni feeding 50% H₂ in He and a mixture composed by 30% CH₄, 50% H₂ and 20% He at 750 °C.

The microstructure of the catalytic layers after the permeation measurements was checked by FE-SEM analysis. Images of the LCeSC (a), LCeSC-Ni (b) and LCeSCR (c) coated membranes (Figure 6) reveal that the integrity of the interface between catalytic layer and membrane is well-preserved. Figure 6 d-i shows the morphology of the catalytic layers. LCeSC presents a heterogeneous distribution of the particle size, ranging from 0.2 to 1 μm (Figure 6d,g). Ni nanoparticles fully cover the LCeSC-Ni grain surface as can be observed in Figure 6e,h. Higher magnification images of them could not be obtained due to the organic remains after permeation measurements that could be ascribed to the coke formation when CH₄ was used as feed. Finally, Ru nanoparticles were not detected in LCeSCR (Figure 6f,i), fact that can explain its lower catalytic activity.

After the permeation measurements, the stability under high steam content methane of the LCeSCRu and LCeSC-Ni coated membranes was evaluated by annealing under an atmosphere composed by 50% CH₄ and 50% H₂O at 700 °C and 3 bars for 24 hours. These conditions are mimicking those encountered in steam methane reforming (SMR) reactors, which is an appealing application for high temperature hydrogen membrane. The integrity of the samples was checked by XRD before and after the treatment. The samples treated under the abovementioned conditions were the previous used membranes in permeation measurements. XRD patterns of these membranes before and after the treatment are displayed in Figure 7 where no secondary phases can be detected after the annealing. Furthermore, no reaction or interaction between metallic Ni nanoparticles and LWO can be observed, proving the compatibility between Ni/LWO under permeation conditions [38, 39]. This is indeed a crucial aspect since NiO and LWO are prone to react at temperatures above 900 °C under oxidizing conditions.

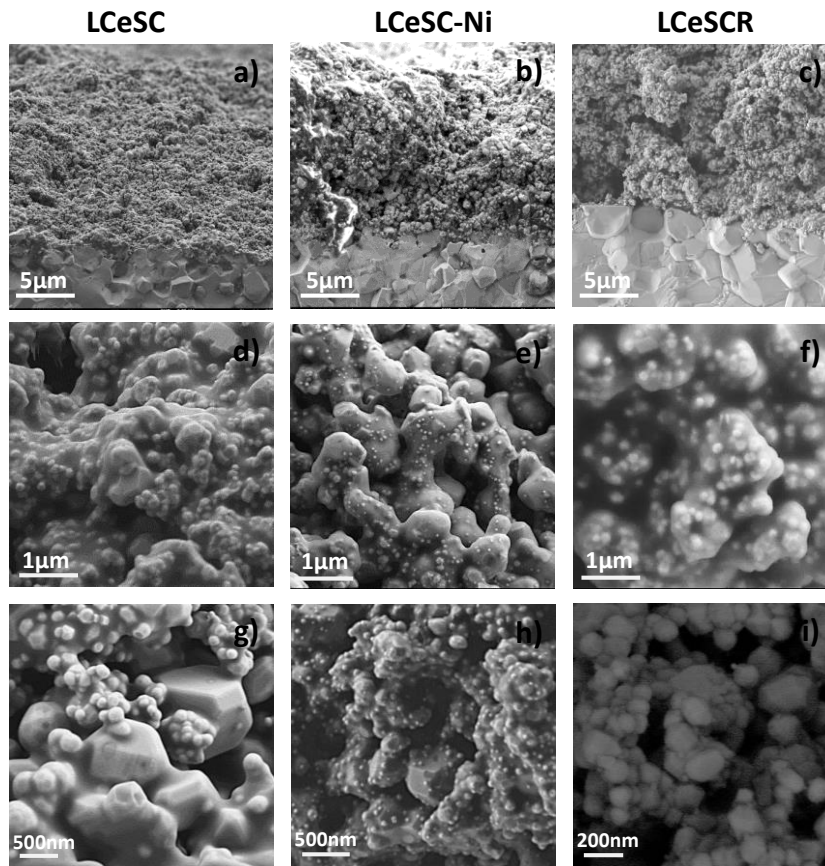


Figure 6: SEM analysis of the fractured cross-section of the studied membranes (a,b,c) and catalytic surface (d-i).

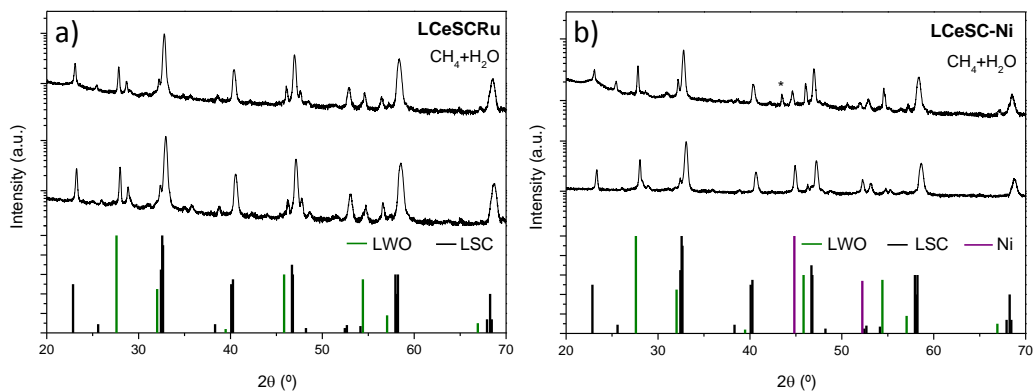


Figure 7: XRD patterns of the membranes coated with LCeSCRu (a) and LCeSC-Ni (b) after stability treatment (50% CH₄ and 50% H₂O at 700 °C and 3 bars for 24 hours). * corresponds to sample holder.

In order to check the integrity of the microstructure after the treatment under SMR conditions (50% CH₄ and 50% H₂O at 700 °C), the samples were analyzed by FE-SEM and EDS analysis.

In Figure 8 the fracture cross-sections of LCeSC-Ni and LCeSCRu coated membranes are depicted. To the limit of the technique, the formation of secondary phases during the annealing is not detected. In addition, the membranes are totally dense after the treatment and the layers present good adhesion to the underneath membrane. Well dispersed Ni nanoparticles are detected in the layer LCeSC-Ni. On the other hand, no Ru was detected in the sample LCeSCRu and this fact is ascribed to the initial low concentration of Ru in the sample, which appears to be responsible for the low catalytic activity observed for this sample in the H₂ permeation measurements.

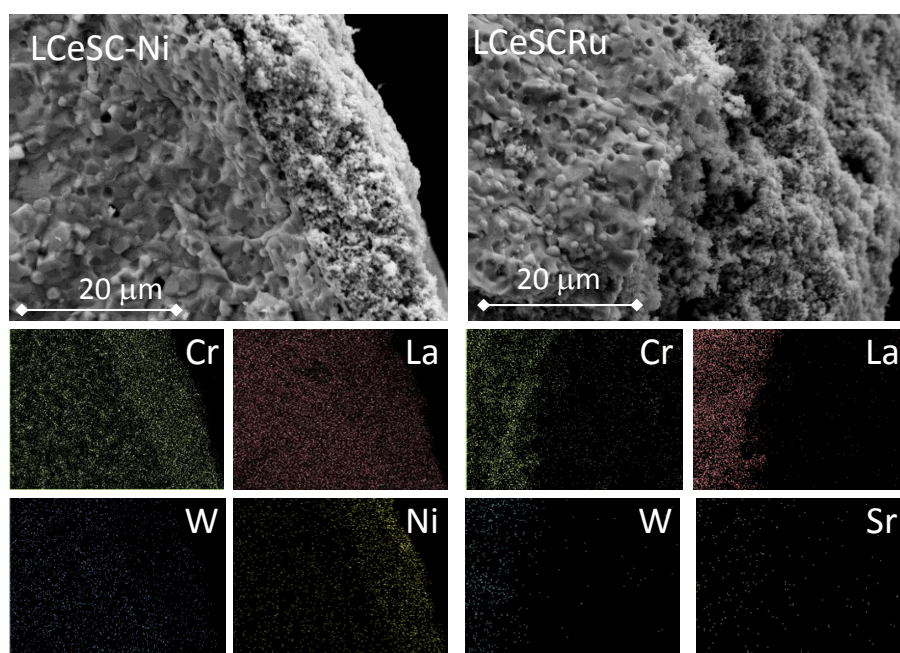


Figure 8: SEM analysis of the fractured cross-section of the LCeSC-Ni and LCeSCRu coated membranes after stability treatment (50% CH₄ and 50% H₂O at 700 °C and 3 bars for 24 hours) and EDS analysis.

4. Conclusions

Different catalytic layers for H₂ evolution have been developed for the surface functionalization of ceramic hydrogen-separation membranes based on LWO/LSC composites, specifically for application in steam methane reforming and MDA using catalytic membrane reactors.

LSC based materials were selected with this purpose for the compatibility with the membrane materials and the promising electrochemical properties as fuel cell anodes. Five layers were deposited and the highest H₂ flux was obtained by using LCeSC-Ni coated membrane due to the important catalytic activity of the Ni nanoparticles to H₂ dissociation, oxidation and surface diffusion of H species. Furthermore, stability of the H₂ permeation by feeding CH₄ was confirmed. In addition, stability under an atmosphere composed by 50% CH₄ and 50% H₂O at

700 °C and 3 bars for LCeSCR and LCeSC-Ni coated membranes was demonstrated at least for 24 hours. Due to the high H₂ flux obtained and the stability under CH₄ and high steam concentration, LWO/LSC composites and LSC based materials are presented as promising membranes and catalytic layers for their application in catalytic membrane reactors.

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