Preparation of Mixed Ionic Electronic Conducting (MIEC) Membrane Supported on Al₂O₃ Substrate: Effects of Substrate Morphology

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Abstract. Two types of solvents [N-methyl-2-pyrrolidone (NMP) and dimethyl sulfoxide (DMSO)] were used in the preparation of alumina (Al₂O₃) dope suspensions whereby the dope was allowed to experience phase inversion in the coagulation bath. The green body of alumina discs were sintered at 1450 oC and the morphologies of prepared alumina-NMP and alumina-DMSO were studied. To improve the catalytic activity of the oxygen transport membrane for oxygen separation purposes, surface modifications of the membranes were carried out using different mixed ionic electronic conducting (MIEC) oxides catalysts (LCF 91 and LSF 55). The oxide powders and viscous sol were synthesised using sol-gel method and calcined at 950 oC to form pure perovskite structure of MIEC materials and studied using XRD while the specific surface area of the calcined powder was measured using BET (Brunauer-Emmett-Tellet) technique. The honey-like MIEC sols were used for surface modification and conducted via dip-coating method and the morphology of the surface-modified alumina membranes were analysed using SEM with EDS mapping. From the study, it was found that the amount of MIEC oxide deposited onto alumina-DMSO is higher than alumina-NMP.

1. Introduction
Since the start of the industrial revolution in the 18th century, human activities have massively upraised the greenhouse gases concentration in the atmosphere. This unpleasant circumstance has led to the invention of new technologies that can capture and sequestrate CO₂, which is known as carbon capture and storage (CCS) [1,2]. Oxy-fuel combustion using oxygen instead of air is one of the available CCS technologies. By eliminate nitrogen from the combustion process, a pure stream of CO₂ and H₂O can be formed. The uses of MIEC-based ceramic membrane that allow only oxygen to pass through across its membrane wall can be considered as the potential replacement to conventional method like cryogenic distillation and pressure swing adsorption as it can reduce cost, energy and more adapting to green technology and sustainable approach [3]. Surface modification of MIEC materials onto ceramic substrates has been extensively studied recently. In our previous work, La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ was used as surface-modified materials onto the same material hollow fibre substrates and the deposition was carried out via vacuum assisted technique [4]. In this study, alumina, Al₂O₃, was used as the substrates material for the deposition of lanthanum-based MIEC oxides. Alumina membrane shows little oxygen permeation activities. Therefore, to improve the oxygen permeability, mixed ionic electronic conducting (MIEC) materials such as lanthanum cobalt ferrite oxide, LaCo₀.₉Fe₀.₁O₃₋δ (LCF 91) and lanthanum strontium ferrite oxide, La₀.₅Sr₀.₅FeO₃₋δ (LSF 55) were selected in this study as catalyst for surface modification on alumina disc substrates. Based on study by Jin et al. [5], it has been learnt that the viscosity of the catalytic sol plays an important role in deposition properties since
less viscous sol could infiltrate better through the membrane and higher viscosity sol will lead to non-homogenous deposition and micro-cracks on the membrane surface [5]. Thus, the viscosity of the catalytic sol must be properly controlled in order to form a homogenous deposition.

The oxygen permeation rate can also be improved by using porous substrates for the deposition of MIEC oxides [6]. By fabricating ceramic substrates which having huge number of finger-like and sponge-like structures, they could provide a good support for the catalysts deposition. Thus, the objective of this research was to prepared LCF 91 and LSF 55 perovskite MIEC oxides supported on different types of alumina disc substrates fabricated from two different solvent (DMSO or NMP) and the morphological of both MIEC membranes were studied.

2. Experimental

2.1. Preparation of MIEC Oxides

The MIEC oxides were prepared using sol-gel method [7]. Stoichiometric amount of metal nitrates such as La(NO₃)₃.6H₂O, Sr(NO₃)₂, Co(NO₃)₂.6H₂O and Fe(NO₃)₃.9H₂O were used according to the required MIEC oxides formula and dissolved in distilled water. Chelating agent, citric acid (anhydrous, Merck), and polymerization agent, ethylene glycol (> 99.9%, Merck) were then added to the metal nitrates solution with a molar ratio of ethylene glycol to citric acid to metal nitrates of 9:3:1. The solution was stirred and heated at 80°C for 5 h till brownish sol was formed. Then, heated MIEC sol was further evaporated in oven at 80°C for over 40 h to allow polyesterification process and form honey-like viscous of MIEC sol. The calcination of the sol was carried out at 750, 850 and 950°C for 4 h to investigate the development of perovskite structure.

2.2. Preparation of Al₂O₃ Substrates

Alumina disc substrates were prepared using phase inversion-sintering technique [8]. 0.36 wt% of dispersant, Arlacel (Uniqema, USA) was first dissolved in 42.19 wt% solvent prior to the addition of 52.23 wt% alumina powder (Al₂O₃) (< 1 μm alumina, Alfa Aesar). Dimethyl sulfoxide (DMSO) or N-methyl-2-pyrrolidone (NMP) (≥ 99.9%, Merck) were chosen as the solvent to be used in this work. The suspension was roll-milled for 48 hours using tri-roller mill to obtain homogeneous suspension. Then, 5.22 wt% of polymer binder, polyethersulfone (PESf) (Veradel A-301, Solvay Advanced Polymer) was added to the suspension. The added polymer-suspension mixture is further roll-milled for 48 hours. In order to fabricate alumina disc to be used as the substrate for the preparation of MIEC-based membrane, the suspension was poured into the steel plate disc mold. The mold was immediately immersed into the coagulation bath contained tap water to allow the phase inversion process to take place. The prepared alumina discs were then dried at room temperature least for 24 hours prior to sintering process at 1450°C. Two steps sintering process where first the temperature of furnace was increased from room temperature to 600°C at rate of 2°C/min and held for 2 h followed by an increment to 1450°C at rate of 5°C/min and held for 4 h was used in this work.

2.3. Preparation of MIEC Membrane Supported on Al₂O₃ Substrates

In order to deposit the MIEC oxide membrane onto the porous alumina disc substrates, a dip coating technique was used. The alumina discs were dip-coated into the prepared MIEC sol before being calcined in a furnace at 950°C for 4 hours. The amount of MIEC oxide deposited onto the membrane was then calculated using the equation below;

\[
\text{Percentage of weight gain, } \% = \frac{W_2 - W_1}{W_1} \times 100
\]

Whereby, W₁ is the initial weight of disc substrate and W₂ is the surface-modified alumina disc substrate.

2.4. Characterizations

The crystallite structure of MIEC oxides were first analysed using X-ray diffractometer (XRD) (D/Max 2200/PC, Rigaku, Japan) with scanning rate of 5°/min from 20 range from 10° to 80°. Then the rotary viscometer (LVDV-II, Brookfield, USA) was used to measure the viscosity of the MIEC sol, conducted at room temperature (20°C) with rotary speed of 70 rpm. After the calcination of the MIEC
oxides, the surface area of the powder was measured using (3Flex Surface Characterization, Micromeritics, USA) using nitrogen gas with degas temperature of 120°C for 2 h. In order to observe the morphology of the alumina disc substrates prepared using different solvents and the homogeneity of the MIEC deposition onto the disc, SEM (S-3400N, Hitachi, Japan) with EDS analysis (XFlash 6/10, Bruker, USA) was used.

3. Results and Discussion

3.1. Mixed ionic electronic conducting (MIEC) oxides powders

Figure 1 shows the XRD patterns for LCF91 and LSF55 oxides calcined at different temperatures; 750°C, 850°C and 950°C. At 750°C and 850°C, the perovskite structure did not fully develop and the secondary phases can still be observed. However, as the calcination temperature increases, the secondary phases of strontium carbonate in the MIEC were disappeared as they were decomposed during the calcination process. Besides that, higher calcination temperature was found to produce higher and intense peaks, which indicates the increases of particles size, as the grain particles fused to form larger size of particles or oxides. In addition, the peaks are slightly shifted to the right (in the oval-highlighted areas) for both of MIEC oxides, which indicates that the crystal lattices were decreases as the temperature goes up [5].

![Figure 1. XRD patterns of (a) LCF 91 and (b) LSF 55 calcined at different temperature.](image)

For the preparation of MIEC membrane supported on alumina disc substrates, 950°C was chosen as the calcination temperature. The BET surface area for LCF and LSF are found to be around 1.57 and 2.86 m²/g respectively. The BET surface area for both oxides are considered low and it is consistent with the work done by Roseno et al. [9]. Dense structure with low surface area is normally possess by MIEC perovskite-type oxides. The adsorption and desorption process of this materials are normally controlled by the surface oxygen exchange rates and this will allow the oxygen ions and electrons transported into or out of those dense structure aggregated grains [10].Therefore, there is a need to deposit the MIEC oxides onto the porous substrates to increase the active surface area and simultaneously the oxygen flux for membrane.

3.2. MIEC solutions

The viscosity of LCF91 sol was observed to be higher than LSF 55, in which 78.09 cp in compared to 63.34. This value is consistent in a range of suitable viscosity for deposition as suggested by Jin et al. [5].This is because if the MIEC sol viscosity is below 5 cp, it could lead to formation of holes and
non-homogenous coating due to discontinuities in the membrane. Meanwhile, if the catalytic sol is too viscous (higher than 80 cp), formation of cracks due to non-homogeneity of MIEC deposition onto the support [5]. Thus, MIEC sols with honey-like texture were chosen to be deposited onto alumina disc substrate. The dip-coating technique allow the deposition of 3.4 wt% LCF & 2.94 wt% LSF onto the disc substrates (refer Figure 3).

3.3. Effect of solvents on the morphology of alumina substrates

Figure 2 shows the SEM images of LCF membrane supported on alumina substrates, which was prepared using (a) DMSO and (b) NMP solvents. It was found that the alumina disc prepared using DMSO (1.46 mm) was thicker in compared to NMP (1.14 mm). Interestingly, the morphology of DMSO was better in compared to NMP, in which an asymmetric structure consists of straight finger-like structure was observed with longest finger-like pore of 1.34 mm (approx. length). Meanwhile, asymmetric structure with sponge-like layer across the entire cross-section was observed for NMP substrates. As the compositions of suspensions used to prepare the discs were fixed in this study, it was believed that the solvent power plays a very important role in determining the final morphology of the substrates.

![Figure 2](image.png)

*Figure 2.* SEM images of LCF membrane supported on different alumina substrates prepared using solvent DMSO (a and c) and NMP (b and d).

The dope prepared using NMP was in compared to DMSO and therefore, during the phase inversion process (the convection of solvent and coagulant), the dope experienced faster water influx in compared to the solvent outflow due to the high concentration of coagulant at the interface, resulting the formation of short pore channels at the top (approx. length of 114 µm) and dense sponge-like structure at the bottom of the substrates [11]. Figure 3 compares the amount of MIEC (LCF 91 and LSF 55) deposited onto the disc substrates. Generally, both type of discs can act as good substrates for the deposition of MIEC. It was found that the amount of MIEC oxides deposited on alumina-DMSO substrates was higher than alumina-NMP. This might be due to the existence of finger-like structures that can entrapped more catalytic sol. Based on the study conducted, alumina-DMSO disc were chosen as the substrates for the deposition of MIEC oxides due to its feature which consisting opened finger-like structure.
Figure 3. Percentage of MIEC oxides weight gain after calcination.

3.4. Surface modification of alumina substrates using LCF and LSF oxides
Figure 4 compares the dispersion of LCF 91 and LSF 55 oxides on alumina-DMSO disc substrate.

The SEM images show that the MIEC oxides were well-deposited across alumina cross-section. In general, both MIEC were homogenously deposited into the finger- and sponge-like structure of the substrates, covering the Al₂O₃ particles. As the alumina was used as the substrates, the EDS mapping shows a high amount of Al and O element. In compared to the work done by Abdullah et al. [12], the deposition of MIEC membrane in this work was more uniformed.

4. Conclusion
Two types of MIEC oxides (LCF 91 and LSF 55), were successfully prepared using sol-gel method and calcined at 950°C to obtain pure perovskite structure. However, as the MIEC oxides possess low surface area due to high calcination temperature, the MIEC oxides need to be deposited onto the porous alumina disc membrane to obtain higher oxygen permeation. The amount of MIEC oxides deposited was in a range of 1.1 – 3.4 %, in which the use of alumina substrates allows higher amount of MIEC oxides to be deposited. This might be due to the long and uniform finger-like. From the EDS mapping, all the respective elements for both MIEC oxides shows a uniform and well dispersed across...
the alumina-DMSO disc substrates thickness. Therefore, this membrane can be tested for oxygen permeation in the future study to evaluate its performance as oxygen transport membrane.

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