

Oxygen Permeation Studies of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_x$ Asymmetric Membranes

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Due to their infinite theoretical oxygen separation factor and staged addition of oxygen at higher temperature, mixed ionic-electronic conductive (O-MIEC) membranes not only show great potential applications in the pure oxygen production, but also be expected to be desirable catalytic reactor materials for many chemical reactions of the industry interest. Preparing asymmetric O-MIEC membranes, which contain one thin film and one porous substrate, is considered to be practically efficient means to improve the oxygen permeation performance of O-MIEC membranes due to two facts:(i) it can reduce the diffusion resistance of oxygen permeation through membranes;(ii) it also can maintain the necessary mechanical strength of such membranes. $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_x$ (BSCF) is the new O-MIEC material, which has been demonstrated to have the promising potentials in oxygen permeation reactors [1]. Our previous studies showed for the dense thick BSCF, the bulk diffusion is dominating factor for the oxygen permeation through it [2]. Therefore, the objective of this study is to investigate the performance of BSCF asymmetric membranes fabricated by the dry-pressing method. Furthermore, the important factors affecting the oxygen permeation performance of those membranes including the thickness of thin film and the porosity of the substrates were examined carefully.

BSCF powders were prepared by Citrate-EDTA method [3,4]. The asymmetric BSCF membranes were prepared by the dry-pressing method [5]. The weighed amounts of BSCF green powders were first added into a stainless die with 2mm diameter. The surface of BSCF powders was softly leveled off by the isostatical press. Then, the mixture of BSCF green powders with ethyl-cellulose (EC) and carbon fiber (CF) was added into the die. The die was pressed under 250 MPa for 5-7 minutes to form the green BSCF asymmetric membranes. Finally, the membranes were sintered at 1150°C for 5 hours with ramping and cooling rate of 1°Cmin⁻¹ in the muffle furnace. The burning-out of ethyl-cellulose and carbon fiber resulted in the formation of the porous support. No binder was added during the preparation process to avoid the possible effect on the performance of membranes. Oxygen flux tests were performed in the two-sided concentric quartz tube reactor. To avoid the gas leakage from the ambient air atmosphere, the reactor was sealed at 1073K using gold ring gaskets between the outer quartz tubes and the membrane surfaces. Pressure against the gold seal was maintained by an external nitrogen pneumatic press. The whole reactor was installed in a tubular furnace. The K-type thermocouple was used to control the temperature of the furnace. Air was introduced into the bottom side of reactor (oxygen supply side of the membrane), and 20 mlmin⁻¹ Ar was used to sweep the topside of reactor (oxygen permeate side of the membrane). The effluent gases from the oxygen-lean side of the membrane were analyzed simultaneously with the Balzers Omnistar mass spectrometer and oxygen sensor.

The typical morphology of the asymmetric membranes is shown in Figure 1. A clear interface between the thin film and porous support was observed. To ensure the mechanical integrity of the membranes, helium was used on the air side of the membrane and the permeate side was monitored for helium leaks. No helium was observed on the permeate side which indicates that no defects or leaks are present at 1073K.

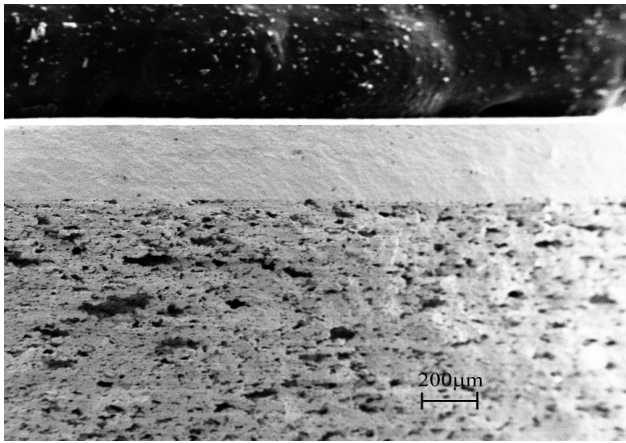


Figure.1 SEM micrographs of BSCF asymmetric membranes (cross-section view)

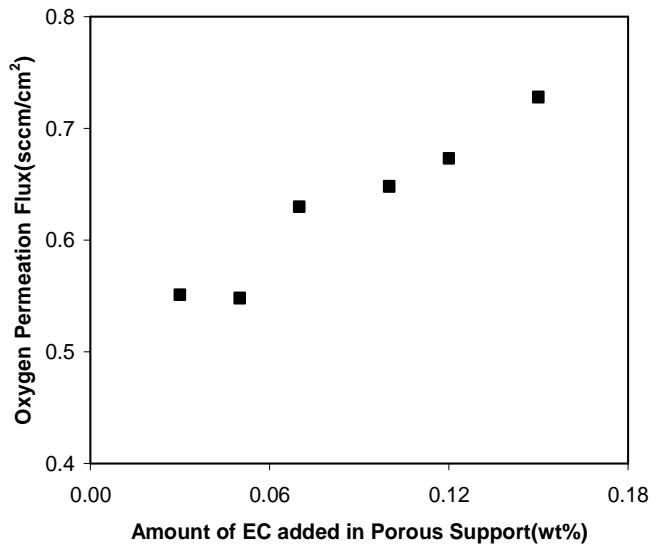


Figure.2 Effect of EC on oxygen fluxes of BSCF asymmetric membranes (1073K)

To investigate the contribution of EC to oxygen fluxes of asymmetric BSCF membranes, different amounts of EC were mixed during the porous support preparation, while keeping the thickness of thin film same. When the EC is burned off, the resultant porous supports will have different void fractions. The results presented in Figure 2 show the oxygen fluxes increase with the increase of the amount of added EC. However, the flux increase is not linear. We believe although the removal of EC results in the formation of void, however parts of those voids (pores or holes) are discrete and not connected, especially when only small amount of EC was added. Those unconnected pores or holes cannot facilitate the diffusion of oxygen, therefore cannot lead to the increase of the oxygen flux. To demonstrate this explanation, small amounts of CF were added into BSCF powder mixture during porous supports preparation while keeping the EC content at 10wt% and the thickness of thin film same. The corresponding fluxes show that the addition of CF to the porous support increases the oxygen flux dramatically. This increase is attributed to the ability of the CF to connect some of the discrete voids that were isolated in the supports without CF.

To understand the oxygen permeation through the asymmetric membrane, the oxygen fluxes of asymmetric membranes with different thin film thicknesses were investigated and the results are shown in Figure 3. Our previous studies showed for the thick symmetric BSCF membranes, the bulk diffusion is the dominating step for the oxygen permeation through it [2]. According to the Wagner equation under the bulk diffusion control, the oxygen flux is inversely proportional to the thickness of the membrane [6]. This inversely proportional relation is also presented in Figure 3 (shown as the solid line). The oxygen flux of asymmetric membranes increases with the decrease of the thin-film

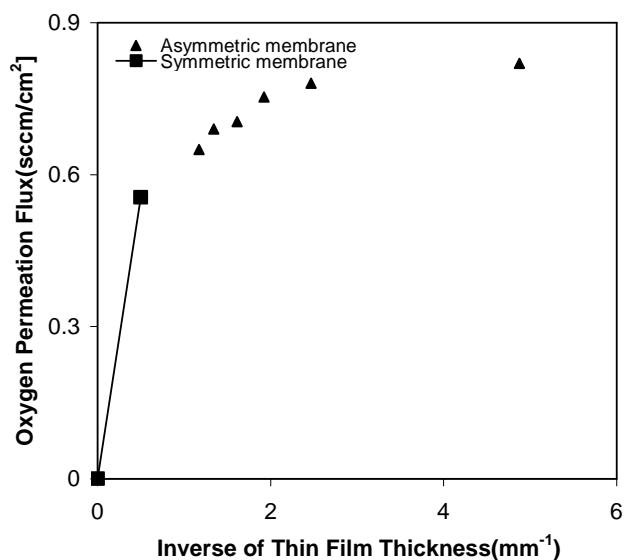


Figure.3 Dependence of oxygen fluxes of BSCF asymmetric membranes on the thickness of thin film (1073K)

thickness as expected. That indicates the bulk diffusion plays the role in the oxygen permeation through the membranes. However, those oxygen fluxes are lower than the corresponding theoretical values, and the increasing trend diminishes. The first explanation is the porous support still exerts the resistance to the oxygen permeation. Though the addition of CF connected parts of originally close-ended pores, but it isn't guaranteed that the fully connected pores network is formed in the whole porous support. Therefore, the resistance exerted by the porous support is inevitable. Another possible explanation is that as the thin-film thickness decreases, the influence of the surface exchange increases, and the oxygen permeation shifts to the transitional stage, in which the bulk diffusion and surface exchange all play the roles. As the thickness then approaches the characteristic thickness, surface exchange becomes dominating. During the transfer of the rate-limiting step, the relation of the oxygen flux to thickness is not inversely proportional, which also results in the deviation of the oxygen flux from the theoretical values calculated according to Wagner's equation.

Reference

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