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# Influence of $SO_2$ on the phase structure, oxygen permeation and microstructure of $K_2NiF_4$-type hollow fiber membranes

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## HIGHLIGHTS

- ▶ $SO_2$ concentration, temperature and exposure time affect sulfate formation.
- ▶ The sulfation equation can reach a dynamic equilibrium.
- ▶ Sulfate forms on the membrane surface after $SO_2$ treatment.
- ▶ The spent membrane shows a porous structure after $SO_2$ treatment.
- ▶ PLNCG hollow fiber membrane is sensitive to $SO_2$.

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## ABSTRACT

The effect of $SO_2$ on the phase structure, microstructure and the oxygen permeation of a $K_2NiF_4$-type membrane based on $(Pr_{0.9}La_{0.1})_2(Ni_{0.74}Cu_{0.21}Ga_{0.05})O_{4+\delta}$ (PLNCG) are investigated. The phase structures of the PLNCG powder samples exposed to $SO_2$-containing atmosphere for different exposure time with different $SO_2$ concentrations at different temperatures are characterized by XRD. The $SO_2$ erosion on the oxygen permeation flux through PLNCG hollow fiber membrane and its recovery are also studied. After the $SO_2$ treatment, the microstructure and phase structure of the spent PLNCG hollow fiber membrane are characterized by SEM, EDS and XRD. The spent membrane shows a porous structure on the sweep side which is rich in sulfur. $K_2NiF_4$-structure of the PLNCG membrane has been destroyed by $SO_2$ and $Pr_2O_2SO_4$, $La_2O_2SO_4$, NiO are formed in the spent membrane, which indicate PLNCG is sensitive to $SO_2$.



## 1. Introduction

Fossil-fuel fired power plants are responsible for more than one third of the total global $CO_2$ emissions [1,2], which should be controlled. One solution might be provided by the oxyfuel process, which involves a de-nitrogenation of the combustion gas and consists in the burning of fossil fuel in an oxygen-enriched atmosphere to produce a flue gas consists of highly concentrated $CO_2$ with some steam, $O_2$ and ppm-concentrated $SO_2$ [3–5]. Recently, ceramic membranes with mixed oxygen-ionic and electronic conductivity (MIEC membranes) [6–9] have attracted increasing attention due to their potential application in oxygen supply for power stations with $CO_2$ sequestration according to the oxyfuel concept [10–15]. For energy saving, the flue gas after the oxyfuel combustion consisted of 25–30 vol.% water vapor, 70–75 vol.% $CO_2$, 1–3 vol.% $O_2$ and 400 ppm $SO_2$ [3–5] will be recycled to the membrane as sweep gas to sweep the permeated oxygen. Therefore, the stability of membrane is very important in the oxyfuel process due to the harsh operation conditions of the MIEC membrane used in the oxyfuel process.

As the main component in the flue gas of the oxyfuel combustion, the concentration of $CO_2$ can be obtained above 70 vol.% [3–5]. Therefore, intensive efforts have been made to develop $CO_2$-tolerant MIEC membrane materials in recent years [16–24]. In order to avoid the alkaline-earth elements such as Ba and Sr which are quite sensitive to $CO_2$ due to the formation of carbonates [25–32], the alkaline-earth metal-free $K_2NiF_4$-type MIEC membrane materials [16–19] and the dual-phase membrane materials made of oxygen-ionic conductor and electronic conductor [20–23], are proposed as alternatives to single-phase perovskites. Due to the different properties between the two phases in the dual-phase membrane material, it is still a challenge to design an excellent dual-phase membrane material with a good chemical compatibility. Therefore, the single-phase alkaline-earth metal-free $K_2NiF_4$-type MIEC membrane materials become more and

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