Influence of SO₂ on the phase structure, oxygen permeation and microstructure of K₂NiF₄-type hollow fiber membranes

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HIGHLIGHTS

- SO₂ concentration, temperature and exposure time affect sulfate formation.
- The sulfation equation can reach a dynamic equilibrium.
- Sulfate forms on the membrane surface after SO₂ treatment.
- The spent membrane shows a porous structure after SO₂ treatment.
- PLNCG hollow fiber membrane is sensitive to SO₂.

Abstract

The effect of SO₂ on the phase structure, microstructure and the oxygen permeation of a K₂NiF₄-type membrane based on (Pr₀.₉La₀.₁)₂(Ni₀.₇₄Cu₀.₂₁Ga₀.₀₅)O₄⁺δ (PLNCG) are investigated. The phase structures of the PLNCG powder samples exposed to SO₂-containing atmosphere for different exposure time with different SO₂ concentrations at different temperatures are characterized by XRD. The SO₂ erosion on the oxygen permeation flux through PLNCG hollow fiber membrane and its recovery are also studied. After the SO₂ 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. K₂NiF₄-structure of the PLNCG membrane has been destroyed by SO₂ and Pr₂O₂SO₄, La₂O₂SO₄, NiO are formed in the spent membrane, which indicate PLNCG is sensitive to SO₂.

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1. Introduction

Fossil-fuel fired power plants are responsible for more than one third of the total global CO₂ 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 consisting of highly concentrated CO₂ with some steam, O₂ and ppm-concentrated SO₂ [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 CO₂ 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.% CO₂, 1–3 vol.% O₂ and 400 ppm SO₂ [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 CO₂ can be obtained above 70 vol.% [3–5]. Therefore, intensive efforts have been made to develop CO₂-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 CO₂ due to the formation of carbonates [25–32], the alkaline-earth metal-free K₂NiF₄-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 K₂NiF₄-type MIEC membrane materials become more and