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Synthesis and characterization of 40 wt% $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ – 60 wt% $Nd_xSr_{1-x}Fe_{0.9}Cu_{0.1}O_{3-\delta}$ dual-phase membranes for efficient oxygen separation

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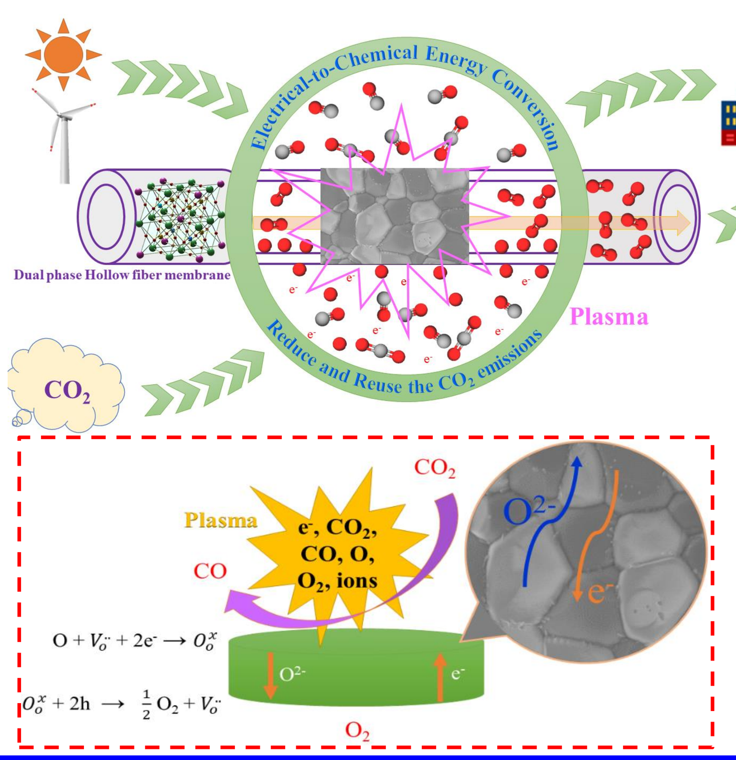
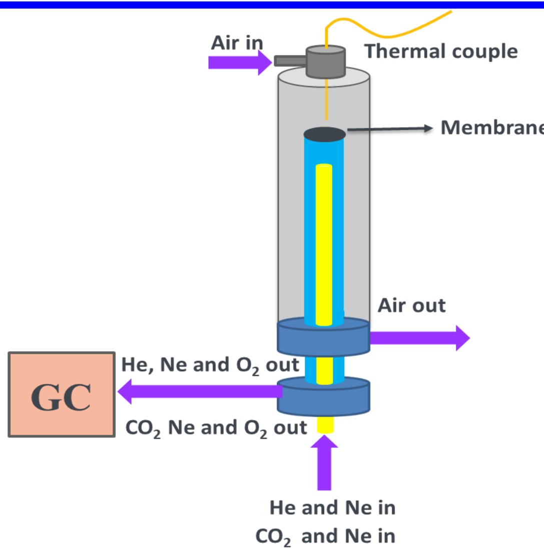
Abstract: Mixed ionic-electronic conducting (MIEC) oxygen transport materials have attracted considerable attention of the scientific community because of their great potential for generating pure oxygen [1-7]. In this study, dense, H_2- and CO_2-resistant, oxygen permeable 40 wt% $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ – 60 wt% $Nd_xSr_{1-x}Fe_{0.9}Cu_{0.1}O_{3-\delta}$ (CPO-N_xS_{1-x}FCO**)** dual-phase membranes were prepared in a one-pot process. These Nd-containing dual-phase membranes have up to 60 % lower material costs than many classically used dual-phase materials. The $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ – $Nd_{0.5}Sr_{0.5}Fe_{0.9}Cu_{0.1}O_{3-\delta}$ sample demonstrates outstanding activity and regenerative ability in presence of different atmospheres especially in reducing atmosphere and pure CO_2 atmosphere in comparison with all investigated samples. In addition, a $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ – $Nd_{0.5}Sr_{0.5}Fe_{0.9}Cu_{0.1}O_{3-\delta}$ membrane (0.65 mm thickness) shows excellent long-term self-healing stability for 125 h. This work demonstrates that dual-phase $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ – $Nd_{0.5}Sr_{0.5}Fe_{0.9}Cu_{0.1}O_{3-\delta}$ membrane is a promising, chemically stable candidate as oxygen suppliers or oxygen distributors for industrial applications such as plasma-based CO_2 conversion and unitization [8, 9].

Motivation & Oxygen permeation setup



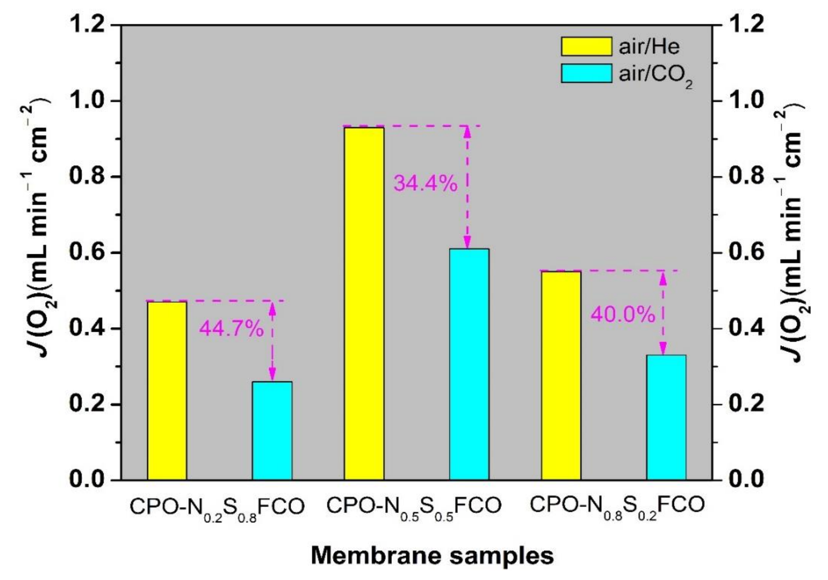


Schematic diagram of the experimental set-up

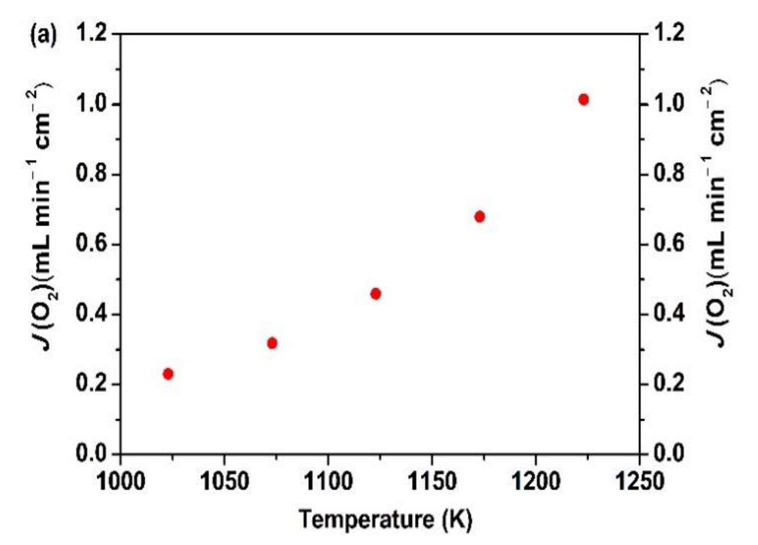
Experimental conditions:

- Temperature: 1023K-1173 K
- Thickness: 0.6 and 0.65 mm
- Feed side flow rate: 150 mL min^{-1}
- Sweep side flow rate : 30 mL min^{-1}

Oxygen permeation tests



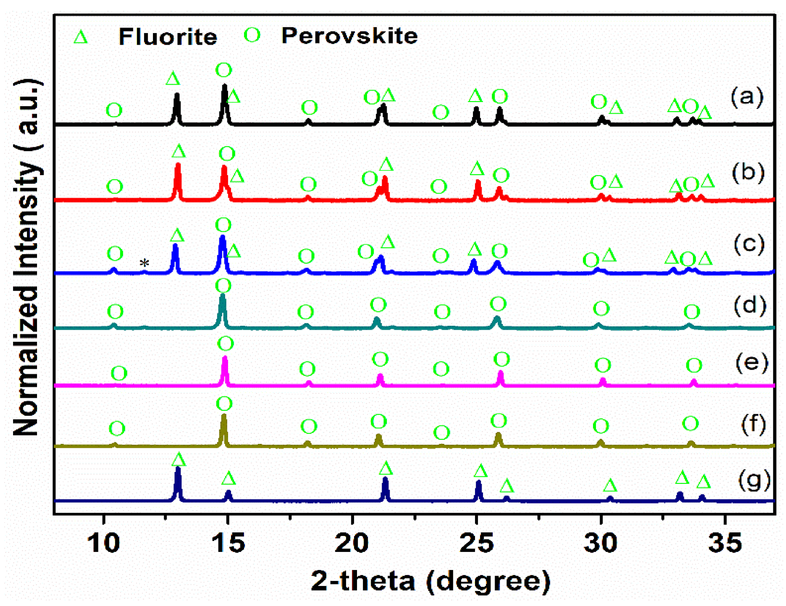
Oxygen permeation fluxes of CPO-NSFCO membranes (0.6 mm) of different compositions in Air/He and Air/CO_2



Oxygen permeation fluxes of CPO-$N_{0.5}S_{0.5}$FCO membrane (0.6 mm) at different temperatures in Air/He

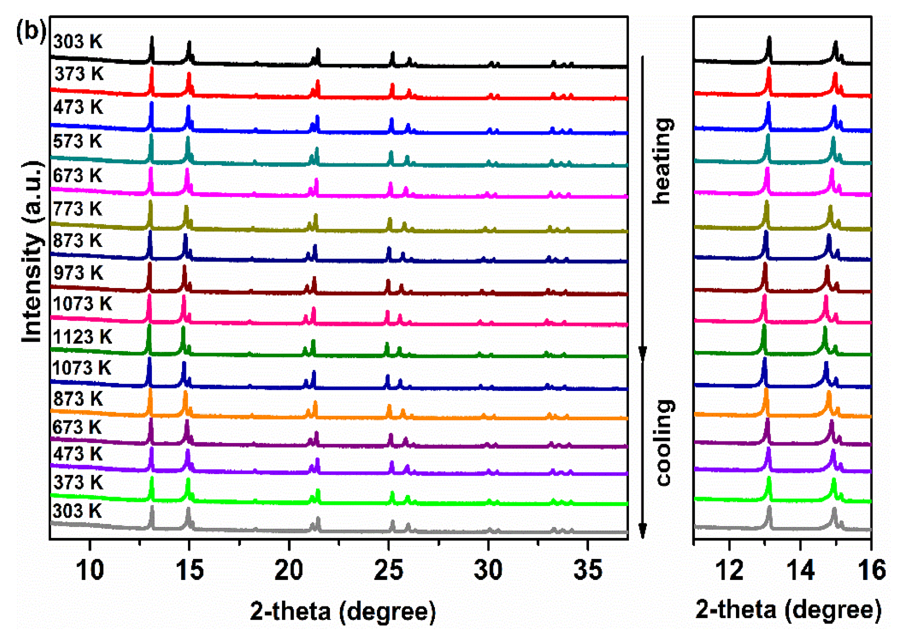
- The oxygen permeation flux of the CPO – $N_{0.5}S_{0.5}$FCO dual-phase membrane reaches 0.95 ml cm^{-2} min^{-1} at 1223 K, being the highest oxygen permeation flux among the investigated membranes.

Crystal Structure



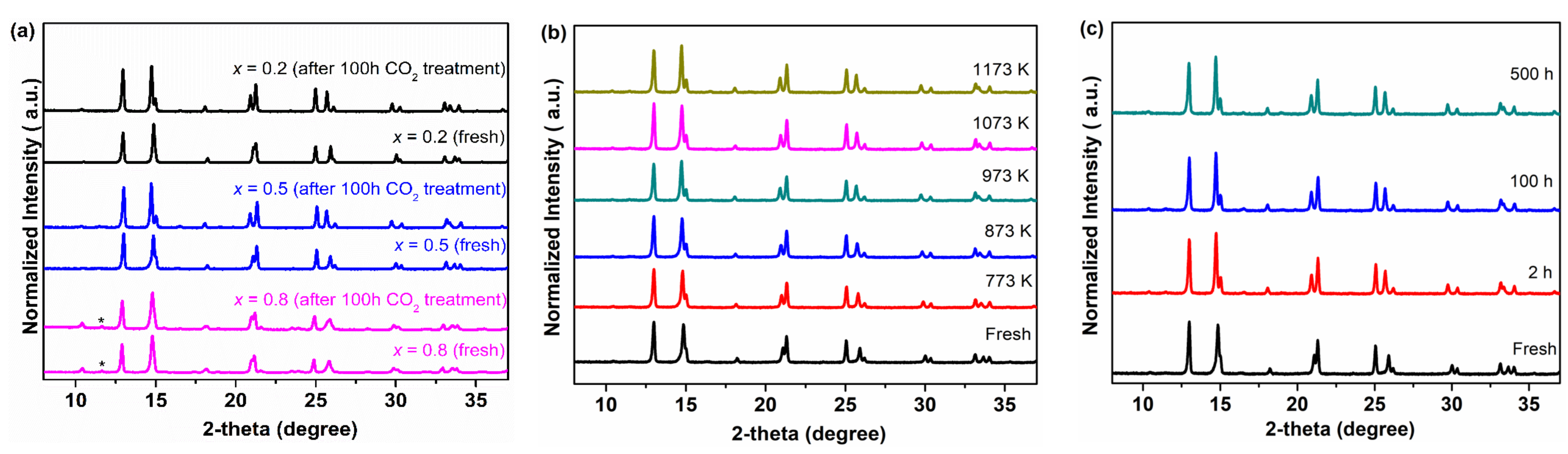
- The characteristic reflections are composed of the fluorite phase and perovskite phase without any impurity phases being generated.
- Good chemical compatibility between the two phases.

Phase stability



- In-situ XRD patterns of CPO – $N_{0.5}S_{0.5}$CFO dual-phase powder in air with different temperature.
- No additional reflections were found that would indicate the presence or formation of other phases
- The membrane exhibits good phase reversibility in air at high temperature

CO_2-tolerance of CPO-N_xS_{1-x}FCO membranes



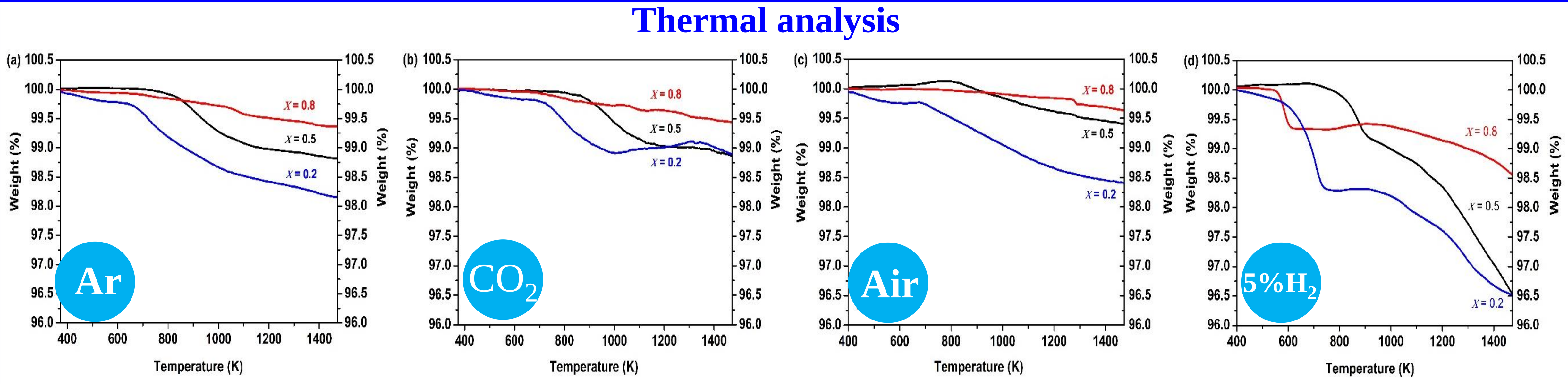
CPO-N_xS_{1-x}FCO (x = 0.2, 0.5, 0.8) samples at 1173 K for 100 h

CPO-$N_{0.5}S_{0.5}$FCO sample at different temperatures for 2 h

CPO-$N_{0.5}S_{0.5}$FCO sample for different times at 1173 K

- High CO_2 resistance and structural stability
- No carbonate formation

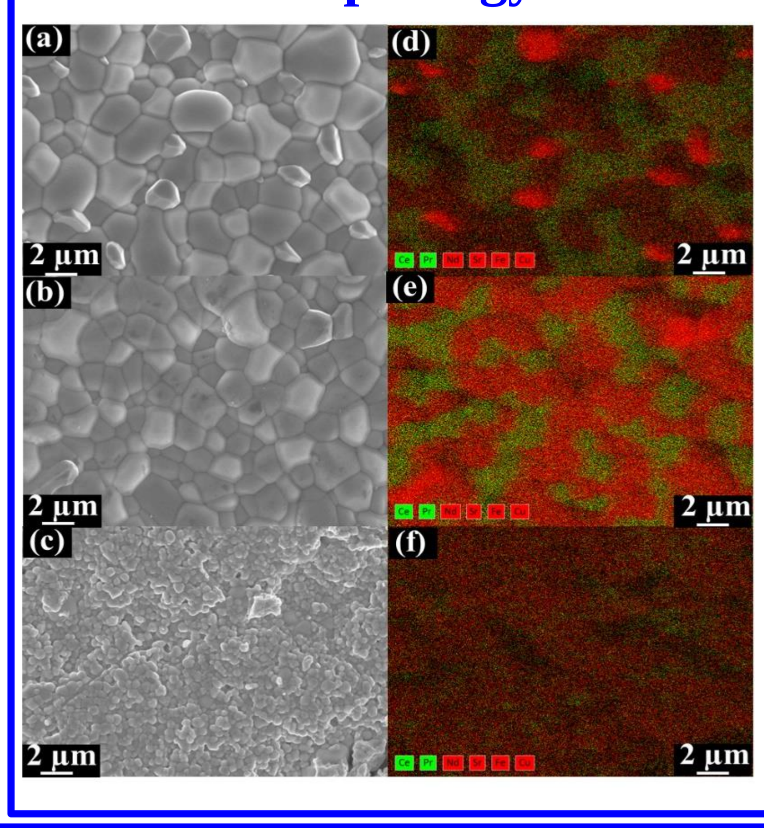
Thermal analysis



TG-curves of $Ce_{0.9}Pr_{0.1}O_{2-\delta}$ – $Nd_xSr_{1-x}Fe_{0.9}Cu_{0.1}O_{3-\delta}$ (x = 0.2, 0.5, 0.8) dual-phase membranes under flowing (a) Ar, (b) CO_2, (c) Air and (d) 5 vol.% H_2-95 vol.% Ar atmospheres (heating rate: 10 K min^{-1}).

- Good thermal and chemical stability under CO_2 atmosphere achieved with suitable Nd content in the dual-phase membranes
- The different mass loss rates at high temperatures, indicating varying amounts of oxygen vacancies

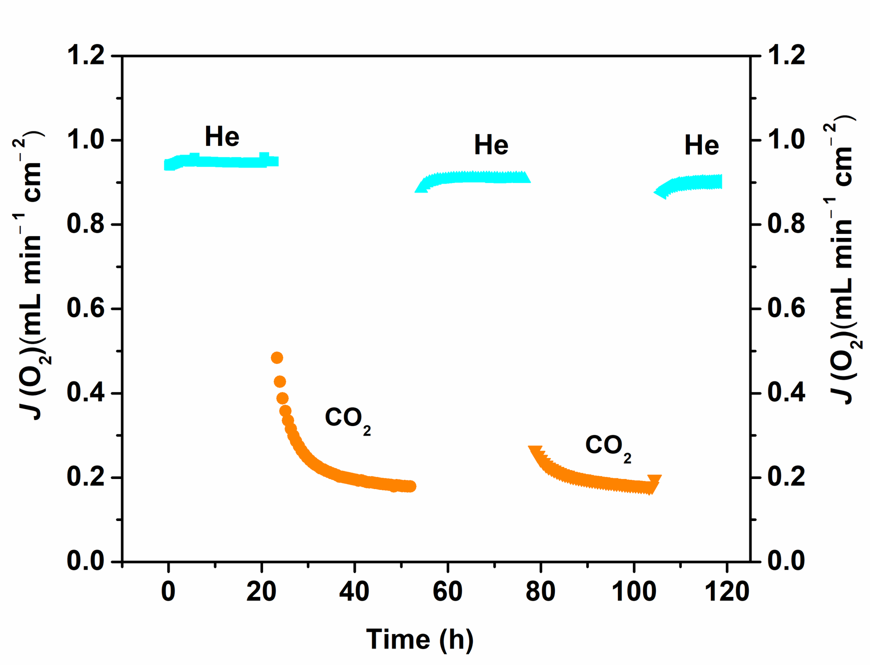
Surface morphology and elemental distribution



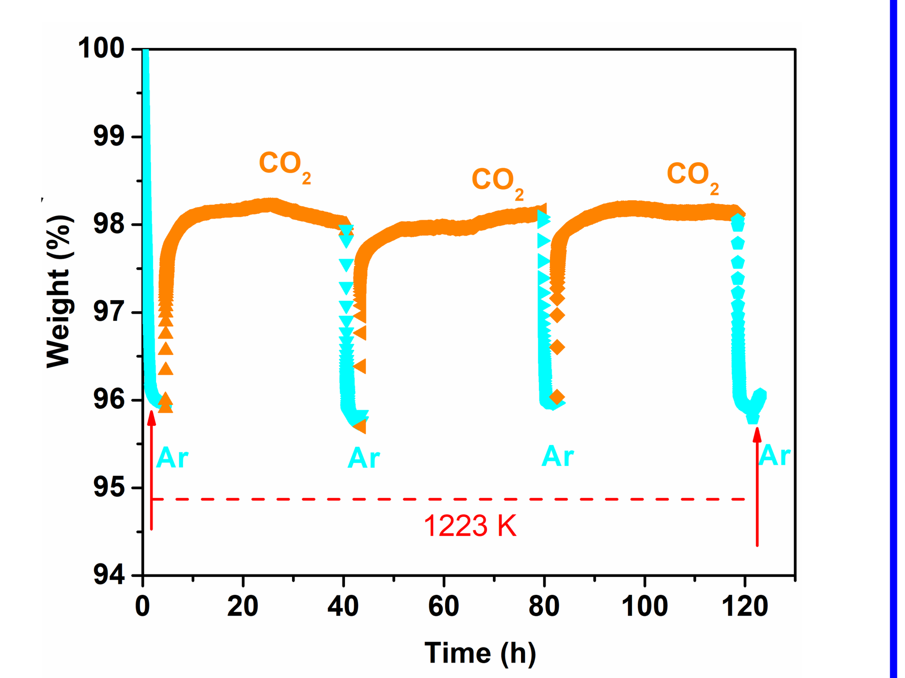
- The ionic-conducting phase and the electronic conducting phase distribute relatively uniformly with suitable Nd content in the dual-phase membrane.

Signals of La *Lα*, Sr *Lα*, Fe *Kα* and Cu *Lα* marked in red, Ce *Lα* and Pr *Lα* signals marked in green.

Long-term oxygen permeation and TGA measurements



Long-term oxygen permeation flux through CPO-$N_{0.5}S_{0.5}$FCO membrane (0.65 mm) at 1223 K under air/He or air/CO_2 gradient



TG-curve of CPO-$N_{0.5}S_{0.5}$FCO dual-phase powder material while periodically changing the gas atmosphere between Ar and CO_2 at 1223 K

- CPO-$N_{0.5}S_{0.5}$FCO membrane shows excellent recover ability with stable oxygen permeation flux of ~ 0.93 mL min^{-1} cm^{-2} under an air/He gradient at 1223 K
- The strong chemical adsorption of CO_2 was experimentally verified by the TGA measurements with periodically changing the gas atmosphere

Conclusions

- ✓ Novel dual-phase membranes were synthesized by an one-pot method.
- ✓ Low-cost and high oxygen permeation flux of Nd containing dual-phase membranes
- ✓ Excellent chemical resistance of the membranes towards different gas atmospheres
- ✓ Strong but reversible adsorption of CO_2 experimentally verified
- ✓ Membrane with adjusted composition demonstrates outstanding regenerative ability
- ✓ O_2 permeable membranes have great potential in plasma-based CO_2 conversion

References

[1] G. Chen, *et al.*, *J. Membr. Sci.*, 590 (2019) 117082.

[2] C. Zhang, *et al.*, *Chem Soc Rev*, 46 (2017) 2941.

[3] G. Chen, *et al.*, *J. Membr. Sci.*, 595 (2020) 117530.

[4] G. Chen, *et al.*, *Front. Chem. Sci. Eng.* 14 (2020) 405.

[5] G. Chen, *et al.*, *Membranes.* 10 (2020) 183.

[6] G. Chen, *et al.*, *Chem. Eng. J.* 392 (2020) 123699.

[7] M. Widenmeyer, *et al.*, *J. Membr. Sci.*, 595 (2020) 117558.

[8] G. Chen, *et al.*, *Appl. Catal. B: Environ*, 190 (2016) 115.

[9] G. Chen, *et al.*, *Appl. Catal. B: Environ*, 214 (2017) 114.

Acknowledgments

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