

2- Membranes for gas separation (molecular sieves and composites)

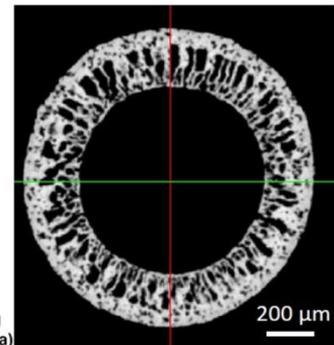
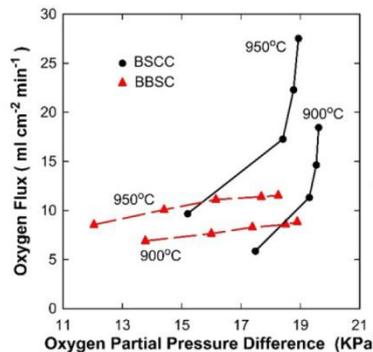
Copper oxide - perovskite mixed matrix membranes delivering very high oxygen fluxes

J. Membr. Sci. 526 (2017) 323-333

Collaborations: The University of Queensland-Australia, Université des Antilles- Guadeloupe-France, Curtin University-Australia ; Universidad Politécnica de Valencia- Spain.

Involved MCP researchers: Anne Julbe

Here we show that copper substitution in perovskite-type barium strontium cobalt copper oxide (BSCC) membranes confers extreme high oxygen fluxes well beyond the state of art, reaching $27.5 \text{ ml cm}^{-2} \text{ min}^{-1}$ at 950°C . A key feature of BSCC is the formation of a mixed matrix catalyst-perovskite membrane caused by the partial segregation of copper, leading to the formation of an intergranular network



of copper-rich oxide between perovskite grains. BSCC membranes delivered pressure normalized oxygen flux (i.e. permeance) of up to 86 times higher, above pressure difference of 18 kPa, as compared to best perovskite membrane, BBSC, due to the catalytic effect of segregated copper oxide. Unlike conventional dual-phase membranes which contains ion and electron conducting phases, this work shows for the first time perovskite-type membranes consisting of a mixed matrix of oxygen ion/electron conducting (perovskite) and catalytic (copper oxide) phases, thus paving the way to the development of high performance membranes for oxygen separation from air for clean energy applications.

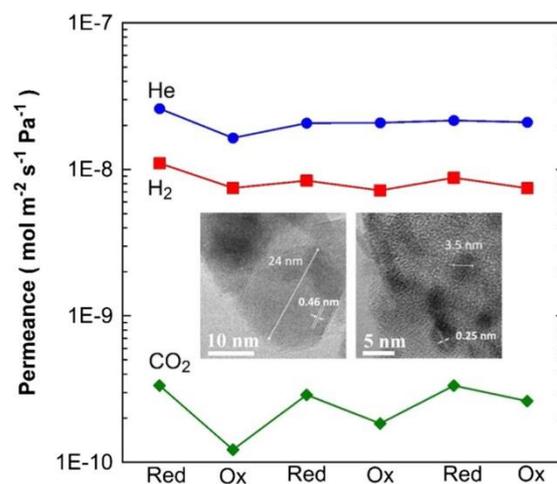
Gas permeation redox effect of binary iron oxide / cobalt oxide silica membranes

Separation and purification Technology 171 (2016) 248–255

Collaboration: The University of Queensland-Australia

Involved MCP researchers: Anne Julbe

This work investigates the redox cycling effect on the physicochemical characteristics and gas permeation behaviour of binary metal oxide (iron/cobalt) silica membranes prepared by sol-gel method from tetraethyl orthosilicate, cobalt and iron nitrates, peroxide and water. A Fe/Co ratio of 10/90 conferred more stable silica microstructure under redox cycling, contrary to Fe/Co ratios P25/75 which led to structural densification after the first redox cycle.



The gas permeance redox effect of Fe/Co = 10/90 silica membranes resulted in a switchable permeance increase and decrease as the membrane was reduced and oxidised, respectively. However, the extent of the switchable changes were not constant and tended to decrease at each cycle, as evidenced by the He/CO₂ permselectivity shift from a higher value of 130 (first oxidation cycle) down to 80 (third oxidation cycle). It was found that a shift in temperature corresponding to the exothermic oxidation peak, attributed to the progressive changes in the formation of Fe_xCo_{1-x}O_y mixed oxide embedded in the silica matrix at each redox cycle. This was further supported by the sequential disappearance of the infrared absorbance peak at 565 cm^{-1} upon redox cycling, thus demonstrating structural re-arrangement of the membrane. The permselectivity of He and H₂ over CO₂ sequentially decreased at a higher ratio for after the oxidation cycle, as a result of the silica matrix

densification at high temperatures (400 °C).

Evaluation of a new supercritical CO₂-assisted deposition method for preparing gas selective polymer/zeolite composite membranes

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Collaborations: Specific Polymers

Involved MCP researchers: Anne Julbe, Martin Drobek

*This work evaluates a new eco-friendly strategy for preparing ultrathin gas selective membranes on top of a microporous support. The method involves the dissolution of small amounts of quantity fluorinated oligomers with alkoxy silanes functional groups in supercritical CO₂ (scCO₂) and their transport to the substrate followed by the subsequent deposition/filtration under high pressure using a MFI zeolite membrane support (silicalite-1 (S-1), channel size ~5.5Å). During the deposition process, the oligomers are compressed on the zeolite surface and potentially forced in the intercrystalline defects of the zeolite membrane, if any. The performance of this new type of polymer/zeolite composite membranes has been evaluated for both single gas permeation and gas mixture separations. Attractive results were obtained applying oligomers with short molecular chains (~1-2nm; ~300-600g.mol⁻¹), easily forming an interpenetrated compact network during the deposition process at 15MPa and 50°C. High permselectivities were obtained at 25°C ($\alpha^*_{He/N_2} = 85-135$ and $\alpha^*_{CO_2/N_2} = 51-81$ with the He and CO₂ permeance up to $2.8 \cdot 10^{-8}$ mol.m⁻².s⁻¹.Pa⁻¹) together with attractive separation factors ($F_{H_2/N_2} = 49$ and $F_{CO_2/N_2} = 18$).*

