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Editorial

CO_2 Resistance Ceramic Oxygen Permeable Membrane: Understanding for Designing, and Designing for Applications

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Editorial

Clean energy delivery is a global goal to avert the climate change impacts arising from greenhouse gas emissions. Oxygen transport membranes (OTMs) with mixed ionic-electronic conductivity (MIEC) are attractive as environment-friendly, economical, and efficient means of producing oxygen from air. Especially, CO_2 resistance is an enabling property for the wide-scale implementation of oxygen-selective mixed ionic-electronic conducting membranes in clean energy technologies, i.e., oxy-fuel combustion, clean coal energy delivery, and catalytic membrane reactors for greener chemical synthesis. Therefore, the significant rise in the number of studies over the past decade and the major progress in CO_2-resistant MIEC materials warrant systematic guidelines on this topic.

The main subfields of MIEC are single-type perovskite oxygen permeable membrane and dual phase-type oxygen permeable membrane. Single perovskite-type oxide membranes with the general formula ABO3 (A=alkaline earth metals or lanthanide element; B=transition metal). Typically, alkaline earth cobaltites such as $Ba_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$, $BaCo_{1-y}Fe_yO_{3-\delta}$, and $SrCo_{1-y}Fe_yO_{3-\delta}$ were fabricated as high oxygen permeation membranes. However, their wide spread applications of the above oxygen permeation membranes are hampered owing to the poor phase stability and chemical stability under a large oxygen concentration gradient, with one side of the membrane exposed to air as oxidizing atmosphere and the other side to a reducing or CO_2 containing atmosphere. In order to improve the CO_2 stability of single perovskite-type oxygen permeable membrane, researchers reduce the basicity of the perovskite oxide is by decreasing the electron density of oxide ions. On the other hand, from the perspective of the Lewis acid–base concept, partial substitution of B-site elements with fixed valence cat-ions serves as an alternative option to improve the stability of perovskite membranes (e.g. $BaCo_xFe_yZr_zO_{3-\delta}$). However, for most of the perovskite materials, a trade-off generally exists between CO_2 resistance and O_2 permeability.

Another type of MIEC membranes is called "dual phase membranes", which consist of a micro-scale mixture of well-separated grains of an oxygen ion conductor (OIC) and an electron conductor (EC). Most of the transitional dual phase membranes are used noble metals as EC. However, if noble metals are used as EC, their high price turns out as drawback. Further, often reactions between the OIC and EC at the high operational temperatures take place; new phases of lower ionic and electronic conductivity are formed and stability problems are reported. For reducing the price and enhancing the CO2 stability, Caro group first proposed a novel CO2-stable dual-phase membrane without noble metals and alkaline-earth metals, E.g. $NiFe_2O_4$-$Ce_{0.9}Gd_{0.1}O_2$–δ(NFO-CGO), Fe_2O_3-$Ce_{0.9}Gd_{0.1}O_{2-\delta}$(FO-CGO) and $Mn_{1.5}Co_{1.5}O_{4-\delta}$-$Ce_{0.9}Pr_{0.1}O_{2-\delta}$(MCO-CPO). Ever since this novel dual phase proposed, more and more novel CO_2-stable dual phase membranes have been reported. Dual-phase membranes generally have better stability than perovskite membranes. However, most of the dual phase membranes have low oxygen permeability. The main reason for the low O_2 flux is the large amount of fluorite phase such as $Ce_{0.8}Tb_{0.2}O_{2-\delta}$, $Ce_{0.9}Pr_{0.1}O_{2-\delta}$, $Ce_{0.8}Sm_{0.2}O_{2-\delta}$, $Ce_{0.9}Gd_{0.1}O_{2-\delta}$, $Y_{0.08}Zr_{0.92}O_{2-\delta}$ and $Ce_{0.9}Nd_{0.1}O_{2-\delta}$; all of which have very low O_2 permeability due to the limited electronic conductivity. In order to improve the oxygen permeability, recently, Armin group proposed to use mixed ionic and electronic conductivity to instead of pure electronic and pure ionic phases. The oxygen permeability has been enhanced remarkably. However, these dual-phase membranes still displayed less than 1 mL min-1 cm-2 at 950 ^{O}C when CO_2 was used as the sweep gas.

In retrospect, there is an obvious trade-off between CO_2 resistance and O_2 permeation flux which makes it difficult to achieve simultaneously high CO_2 resistance and high O_2 permeation flux within a single-phase material. The two most promising major directions can be delineated as follows: (1) New membrane materials and configurations with high CO_2 resistance and high O_2 permeation flux; (2) Beneficial phase reactions and conductive phase generation along grain boundaries in dual-phase membranes.