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Perspectives on achievements and challenges of oxygen transport dual-functional membrane reactors

Guoxing Chen[1] | **Marc Widenmeyer**[2] | **Xiao Yu**[1] | **Ning Han**[3] | **Xiaoyao Tan**[4] | **Gert Homm**[1] | **Shaomin Liu**[4] | **Anke Weidenkaff**[1,2]

[1]Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS, Alzenau, Germany

[2]Department of Materials and Earth Sciences, Technical University Darmstadt, Darmstadt, Germany

[3]Department of Materials Engineering, KU Leuven, Leuven, Belgium

[4]State Key Laboratory of Separation Membranes and Membrane Processes, School of Chemical Engineering, Tiangong University, Tianjin, China

Correspondence
Guoxing Chen, Fraunhofer Research Institution for Materials Recycling and Resource Strategies IWKS, Brentanostraße 2a, 63755 Alzenau, Germany.
Email: guoxing.chen@iwks.fraunhofer.de

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Abstract

The integration of membrane separation processes with chemical reactions through oxygen transport dual-functional membrane reactors has attracted significant attention due to the potential for process intensification, which also can create a synergy between the two units. This approach holds promise for promoting green chemistry principles by reducing energy consumption and environmental pollution. Despite its potential, a comprehensive review of recent advancements exploring the full potential of oxygen transport dual-functional membrane reactors (coupling two distinct reactions) in enhancing membrane performance is currently lacking. To address this gap, this perspective article presents various concepts and principles of oxygen transport dual-functional membrane reactors and provides an overview of recent advances and applications. Additionally, the challenges and opportunities for future research to enhance the efficiency of the process toward industrialization are discussed and highlighted. These include developing novel oxygen transport membrane materials, optimizing membrane engineering, innovating membrane reactor design, and exploring new applications and reaction mechanisms.

KEYWORDS
membranes, perovskites, thermal decomposition

1 | INTRODUCTION

Membrane separation technology has received increasing attention worldwide due to its energy saving feature. Membrane reactors can integrate reaction and separation processes in a single unit, which can significantly enhance the performance (conversion, selectivity, and yield) of these equilibrium-limited reactions. Such a chemical process intensification technology possesses obvious advantages compared with conventional multistep systems—such as lower energy requirements, reducing system volume, the possibility of heat integration, and safer operation.[1,2] Membrane reactor technology has been the focus of research for many years, but it is still in a developing stage due

to the need for highly stable membrane materials that can withstand the oxidizing or reducing reaction environments at high temperatures. Currently, commercial-scale membrane reactors can be found in biochemical processes that operate at temperatures lower than 60°C, where polymeric membranes are suitable for use.[3] However, for petrochemical industry processes that occur at temperatures higher than 800°C, inorganic or ceramic membranes are required instead of polymeric ones. Coincidently, dense ion conducting perovskite oxide ceramic membranes exhibit high oxygen permeation flux and can be used as membrane reactors for high-temperature oxidations. In comparison to pure ion conducting membranes, mixed ionic and electronic conducting (MIEC) ceramics can simplify the design of the membrane reactor without the need for an external circuit.

The MIEC oxygen transport membrane (OTM) reactors generally can be classified as oxygen distributor- or oxygen extractor-type based on the different roles they serve. As an oxygen distributor, the membrane allows oxygen in the feed gas of air to permeate through and be distributed uniformly for participating in oxidation reactions. The most common applications are partial oxidation of methane (POM) to syngas, selective oxidation of ammonia, oxidative coupling of methane (OCM) to C_2 hydrocarbons, and oxidative dehydrogenation of light alkanes to olefins. In the case of oxygen extractor-type OTM reactor, oxygen can be in situ extracted from a reaction mixture on one membrane side to shift the reaction to the desirable product side. These reactions include CO_2 decomposition, nitric oxide decomposition, and water splitting (WS). There have been numerous reviews that provide in-depth summaries of the applications of these two types of OTM reactors.[1,4–8] In recent years, there has been growing interest in coupling two distinct reactions through an OTM reactor to speed up chemical reactions due to advancements in the stability of membrane materials.[8–11] The coupling reaction can be accomplished by decomposing oxygen-containing gases (e.g., H_2O and CO_2) in combination with another oxidative process for improving the oxygen extraction efficiency such as POM. In order to accelerate the reaction rate of some specific reactions, it is necessary to load additional catalysts on the membrane surface. The optimal amounts of catalyst loading and catalyst interaction mode with the membrane reactors are essential for maximizing OTM reactor performance. The potential of oxygen transport dual-functional membrane reactors (coupling two distinct reactions) as an effective measure of enhancing membrane performance has yet to be fully explored in a comprehensive review of recent advances. This perspective paper aims to bridge this gap by providing a critical analysis of the latest progress in coupling two chemical reactions using an OTM reactor, as well as outlining current limitations and future challenges in the practical application of this technology. To this end, we present an overview of recent developments and discuss various aspects that require further investigation, such as the development of novel OTM materials, optimization of membrane engineering, and innovation in membrane reactor design, as well as exploring new applications and reaction mechanisms.

2 | RECENT ACHIEVEMENTS AND FUTURE CHALLENGES

Combining two distinct reactions through the implementation of an OTM reactor presents an efficient approach to enhance the speed and efficiency of chemical processes. By employing an OTM, oxygen ions can be transported from one reaction site to another, enabling simultaneous reactions and minimizing the reliance on external oxygen supply. The underlying principle involves utilizing the OTM to transfer oxygen ions generated in an oxygen-producing reaction to a separate reaction site where they react with a fuel gas, leading to the production of the desired chemical product. This configuration allows the two reactions to take place on opposite sides of the OTM reactor. An important advantage of coupling these distinct reactions through an OTM reactor is the considerable increase in yield and selectivity of the desired product. Hollow fiber membranes, known for their high oxygen permeability, have been extensively investigated and implemented in oxygen transport dual-functional membrane reactors.[2] The coupling of reactions can be achieved by the dissociation of oxygen-containing gases (e.g., H_2O, CO_2, and NO_x) in combination with other oxidative processes like the POM as shown in Figure 1. The development of suitable OTM materials tailored to specific applications necessitates varying specifications. This section provides an overview of recent advancements and offers insights into several aspects that require further investigation in this field.

2.1 | Water splitting coupling with oxidative process

WS for hydrogen production has been an active area of research for many years. Although photocatalysis using solar energy has been extensively investigated, the low efficiency of these semiconductor catalysts has limited their practical applications.[1,2] Alternative methods, such as electrolysis or direct thermal water decomposition, have been explored.[1,2] However, conventional reactors face challenges due to the low equilibrium constant for H_2

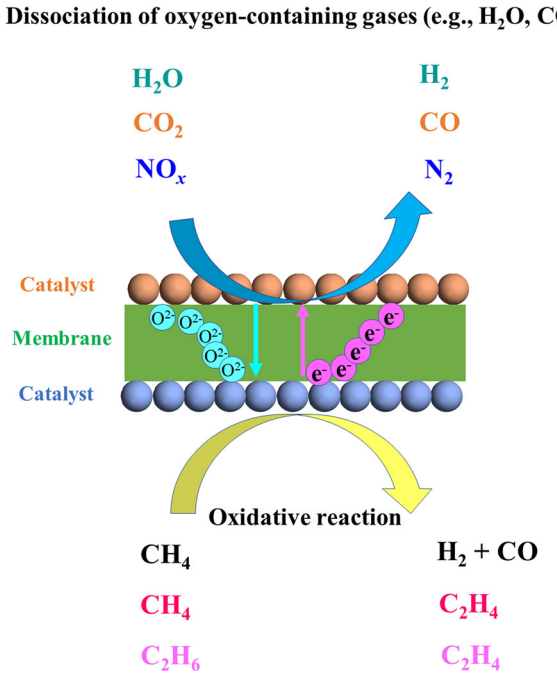

FIGURE 1 Schematic diagram of oxygen transport dual-functional membrane reactor for coupling dissociation of oxygen-containing gases (e.g., H_2O, CO_2, and NO_x) with an oxidative process (e.g., partial oxidation of methane [POM] and oxidative coupling of methane [OCM]).

production from water dissociation. The use of membrane reactors can significantly improve H_2 generation by shifting the equilibrium through the removal of one of the products, namely, oxygen. Caro et al. tested their $BaCo_xFe_yZr_{1-x-y}O_{3-\delta}$ hollow fiber membrane for WS coupling with POM.[12] The observed H_2 production rate at 950°C was 0.7 mL cm^{-2} min^{-1}. It is worth noting that the use of an inert sweep gas (helium) would result in a very low H_2 production rate of less than 0.025 mL cm^{-2} min^{-1} unless highly reducing gases such as CO, H_2, CH_4, or C_2H_6 are added to rapidly consume the oxygen in the permeate side.[13] In solely the viewpoint of H_2 production, CO or H_2 is a better reductant than others as its reaction with oxygen is more exothermic and spontaneous, thus, can efficiently lower the oxygen partial pressure in the permeate side. Some researchers are using waste H_2 to get pure H_2 by condensing unreacted steam.[1,2,7,14] Many other researchers are more interested in coupling with an oxidative process reaction to get more useful products from the membrane reactors.[1,7] The H_2 production rate is strongly associated with the oxygen consumption rate in the permeate side for fast oxygen extraction in the water dissociation side. For a better performance, Jiang et al. modified the $BaCo_xFe_yZr_{1-x-y}O_{3-\delta}$ (BCFZ) membrane surface by coating a catalytically active $BaCo_xFe_yZr_{0.9-x-y}Pd_{0.1}O_{3-\delta}$ (BCFZ-Pd) porous layer for POM.[15] This modification increased the membrane's oxygen extraction capability 3.5 times relative to the original BCFZ membrane, leading to an increase in H_2 production rate from 0.7 to 2.1 mL cm^{-2} min^{-1} at 950°C. Another approach to improve H_2 production is to increase the reaction kinetics of POM, for example, by packing a catalyst. Jiang et al. reported WS in a BCFZ hollow fiber membrane (thickness 0.17 mm) packed with Ni-based catalysts surrounding the hollow fiber for POM reaction.[13] At 950°C, the H_2 forming rate was further improved to 3.1 mL cm^{-2} min^{-1} with a CH_4 conversion of 70% and CO selectivity of 60%. These results are very inspiring, but the most challenging issue is the poor membrane stability of Co/Fe-containing perovskite oxides as the cobalt or iron components are easily reduced to metal phase. The cobalt or iron leaching out from the perovskite lattice would definitely have a negative influence on the oxygen transport but may provide a catalytic effect on WS, details of which have not been reported. To overcome the poor stability issue of Co-containing perovskite oxides, Fang et al. investigated WS coupled with POM using a more robust dual-phase MIEC disk-shaped membrane composed of $Ce_{0.85}Sm_{0.15}O_{1.925}$ (SDC) and $Sm_{0.6}Sr_{0.4}Al_{0.34}Fe_{0.7}O_{3-\delta}$ (SSAF) with a sandwich-like symmetrical structured catalyst on each membrane side to promote both reactions (WS and POM).[16] As anticipated, the H_2 production rate could reach 11.7 mL min^{-1} cm^{-2} due to the improved catalytic efficiency for both reactions. More importantly, the membrane reactor could maintain a stable performance over 100-h-operation, which indicates a good chemical stability under conditions suitable for WS and POM.

Coupling water decomposition in combination with other oxidative processes has also been studied. A novel coupling reaction process for H_2 production is reported by Zhu et al., where WS is combined with ethanol oxidative steam reforming in a tubular $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ (SCFZ) membrane reactor.[17] At 750°C, hydrogen production rates of 6.8 and 1.8 mL min^{-1} cm^{-2} were achieved for ethanol oxidative steam reforming and water decomposition on the two sides of the OTM, respectively. Cao et al. reported their results of WS coupling with OCM in a novel asymmetric $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF) membrane consisting of a dense top layer (70 μm in thickness) and thick porous support layer (830 μm in thickness) with 34% open porosity.[18] Methane oxidative coupling was tested in the dense membrane side with an $Mn–Na_2WO_4$ catalyst deposition, and steam was fed to the porous BSCF side. At 950°C, an H_2 production rate of 3.3 mL cm^{-2} min^{-1} with 26% of CH_4 conversion and 6.5% C_2 selectivity was achieved. There is no doubt that the porous BSCF layer added a catalytic effect to the WS reaction; however, the stability of BSCF membrane is an issue. Jiang et al. studied WS coupling with oxidative dehydrogenation of ethane

(ODE) in a BCFZ hollow fiber membrane to produce hydrogen and ethylene.[19] An H_2 production rate of around 1.0 mL cm^{-2} min^{-1} was achieved in the core side of BCFZ hollow fiber with C_2H_4 yield around 53% in the shell side at 800°C without extra catalyst addition.

Li et al. made a breakthrough for coproduced ammonia synthesis gas and liquid-fuel synthesis gas in the membrane reactor ($Ba_{0.98}Ce_{0.05}Fe_{0.95}O_{3-\delta}$) with Ru-based catalyst (1 wt% $Ru/Ce_{0.85}Sm_{0.15}O_{2-\delta}$), integrating nine conventional steps into one unit.[20] The energy consumption for producing two types of synthesis gases can be reduced by 63% via this innovated membrane reactor. It is worthy to note that commercializing these interesting membrane concepts requires robust membranes to withstand the reacting conditions. Creating novel membrane materials with long-term chemical and thermal stabilities and developing a highly efficient catalyst are highly needed.

2.2 | Thermal decomposition of carbon dioxide by coupling with an oxidative process

CO_2 thermal decomposition is highly endothermic, occurring only at high temperature and limited by the thermodynamic equilibrium. Similar to water decomposition, this reaction can be coupled with an oxidative process to boost the CO_2 conversion using MIEC membrane reactors. In this process, CO_2 can be fed to one side of the membrane, and the produced O_2 is extracted to other membrane side to provide oxygen source for oxidative processes.

Fan et al. investigated the CO_2 decomposition coupled with POM in $SrCo_{0.5}FeO_x$ disk membrane (thickness: 1 mm) reactor without loading extra catalyst,[21] and CO_2 conversion of 10% was achieved at 940°C. Later, more promising results were reported by Jin's group at 900°C using an $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ disk membrane (thickness: 1.5 mm) reactor packed with Ni/Al_2O_3 catalyst for POM.[22] The CO_2 conversion, CH_4 conversion, CO selectivity, and H_2/CO ratio are 11.1%, 84.5%, 93%, and 1.8, respectively. The low CO_2 conversion was caused not only by the limited thermodynamic equilibrium but also the kinetic barrier. Realizing this bottleneck, Jin et al. further improved the process by incorporating the catalysts for both reactions in the similar $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ membrane reactor packed with a perovskite oxide supported noble metal catalyst ($Pt/SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$) for CO_2 decomposition and Ni/Al_2O_3 for POM.[23] At 900°C, the achieved CO_2 conversion and selectivity were 15.8% and 100%, respectively. However, it was surprising to see that the improved kinetics on CO_2 conversion did not enhance the POM reactions in the other membrane side.

Zhang et al. applied a dense Al_2O_3-doped $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$ tubular membrane (with Ni/Al_2O_3 catalyst) for coupling the POM reaction with CO_2 decomposition.[24] The CO_2 conversion reached approximately 12.4% at 900°C, whereas the CO selectivity and CH_4 conversion were 93% and 86%, respectively. It is also worth noting that the CO_2 conversion in the tubular membrane is higher than that of using disk-shape membrane at the same reaction temperature, which is mainly resulting from the increasing the oxygen permeation rate by reducing membrane thickness. Recently, Liang et al. demonstrated the simultaneous decomposition of water and carbon dioxide coupled with POM reaction in a dual-phase $Ce_{0.9}Pr_{0.1}O_{2-\delta}$–$Pr_{0.6}Sr_{0.4}FeO_{3-\delta}$ disk membrane reactor (thickness: 0.6 mm).[25] At 930°C, synthesis gas production rates achieved on the H_2O/CO_2 feed and methane sweep sides are 1.3 and 3.9 mL cm^{-2} min^{-1}, respectively. In contrast to typical thermochemical decomposition, effective CO_2 and WS were accomplished at lower temperatures, which was attributed to the in situ rapid removal of the produced oxygen through the dual-phase membranes. Their work proposes a novel perspective and an alternate approach to transform water and CO_2 into synthesis gas by combining solar energy, OTM reactor, and catalytic thermolysis. To improve the CO_2 conversion, coupling of CO_2 decomposition with POM has also been demonstrated in a porous–dense–porous triple-layered composite membrane reactor.[26] It is interesting that this designed membrane reactor can be operating for over 500 h without any decrease of reaction performance. This design is an excellent candidate for combining the membrane reactor stability with high oxygen separation capability for potential industrial applications.

2.3 | Decomposition of NO_x by coupling with an oxidative process

By coupling with an oxidative reaction, thermal degradation of environment-polluting nitrogen oxides (NO_x, i.e., NO, NO_2, and N_2O) to N_2 and O_2 can also be accomplished in oxygen permeable dual-functional membrane reactors as shown in Figure 1. In contrast to the traditional direct catalytic decomposition procedure,[27] the negative restriction of the produced oxygen on NO_x conversion can be prevented by in situ removal of the surface oxygen employing the dual-functional membrane reactor. Caro's group had demonstrated this new concept employing a $BaCo_xFe_yZr_{1-x-y}O_{3-\delta}$ hollow fiber membrane coupled with POM for the first time and their results revealed that NO or N_2O conversion can reach almost 100% at 875°C.[28,29] The rapid consumption of permeated surface oxygen through using CH_4 results in a larger gradient of oxygen

partial pressure, allowing NO_x decomposition to continue. On the other side of the membrane, 90% selectivity of CO and 90% of methane conversion were obtained simultaneously. In their later work, coupling of N_2O decomposition with CO_2 reforming of CH_4 has been successfully demonstrated in a cobalt-free perovskite $BaFe_{0.9}Zr_{0.05}Al_{0.05}O_{3-\delta}$ (BFZ-Al) membrane reactor.[30] Due to efficient in situ removal of the surface oxygen across the BFZ-Al membrane, almost 100% N_2O conversion was obtained with 94% selectivity of CO and 97% of methane conversion at 900°C on the other side of the membrane. It is also worth noting that even after 100 h of operation, no noticeable decrease in selectivity and activity was discovered, illustrating the outstanding performance of their developed BFZ-Al membrane reactor.

Recently, a novel dual-functional catalytic membrane reactor was developed for simultaneous POM and NO decomposition, where a $BaBi_{0.05}Co_{0.8}Nb_{0.15}O_{3-\delta}$ (BBCN) hollow fiber membrane integrated with Ni-phyllosilicate hollow sphere catalysts was employed.[31] In comparison to previous reported studies,[28,29] the operating temperature required for attaining 100% NO conversion with this dual-functional catalytic membrane reactor was dramatically reduced to 675°C. This excellent performance is primarily attributed to the very high catalytic activity of the employed catalysts and high oxygen permeability of the developed BBCN hollow fiber membrane. Significantly reducing the operating temperature is critical for lowering capital costs and energy consumption to improve the dual-functional membrane reactor's energy efficiency.

Similar to CO_2 and water decomposition as discussed above, it should be also possible to couple NO_x decomposition with other oxidative processes like ethanol oxidative steam reforming and OCM to simultaneously maximize the reaction efficiency in both sides of the oxygen transport dual-functional membrane reactors, which has not reported in the literature.

3 | OPPORTUNITIES AND FUTURE RESEARCH DIRECTIONS

Despite the considerable advancements in the field of dual-functional membrane reactors as summarized in Table 1, there remain several hurdles that must be overcome before ceramic OTM reactors can be utilized in industrial applications for pollution control and chemical upgrading. To expedite the commercialization of dense ceramic membrane reactors, forthcoming research endeavors concerning new material development, economic feasibility, long-term stability, and fundamental understanding could concentrate on the following four aspects.

3.1 | Oxygen transport membrane material development

The development of suitable membrane materials is of utmost importance for the successful implementation of dual-functional membrane reactors, which are inherently complex due to their integration of multiple processes and different materials, such as membranes and catalysts, into a single unit. Given that the membrane material serves as the core of these reactors, it is essential to prioritize the development of such materials to ensure optimal performance and stability. The development of oxygen permeable membrane materials for various applications requires different specifications. Specifically, CO_2-resistant alkaline earth-metal-free membranes, such as dual-phase or K_2NiF_4-type (Ruddlesden–Popper phase) membranes, are recommended if a CO_2-rich feed or sweep gas was involved.[2,35–40] Coating the membrane surfaces with a CO_2-resistant layer is an effective approach to enhance CO_2 resistance of the membranes with high oxygen permeation fluxes such as Sr- or Ba-containing single-phase perovskite-type OTMs.[2,35,41] An ideal protective layer material requires good ionic conductivity, high chemical and mechanical stability in CO_2 atmosphere at high temperature, and good compatibility with the protected membrane. However, there is a trade-off between the stability (chemical resistance) and the oxygen permeability. Complete substitution of alkaline-earth cations Sr or Ba by rare-earth cations and reduction of cobalt content in single-phase perovskite-type membranes can effectively improve CO_2 resistance[2,35,42,43] but generally reduce the oxygen permeation flux. Table 2 shows the performance comparison of various OTMs recently reported in literature, which can be potential new materials for dual-functional membrane reactors.

When the membrane reactor was used in reducing atmospheres, such as POM for syngas production, the membrane materials need to be stable in the presence of H_2, CO, and CH_4. Cobalt-rich perovskite membranes are unsuitable for this application due to their instability in reducing atmospheres, making cobalt-less or cobalt-free perovskite membranes or dual-phase membranes more favorable. Additionally, increasing the oxygen permeation flux through the membrane is crucial, especially at low temperatures ($T < 600$°C), to satisfy important catalytic reactions that operate at lower temperatures. The development of submicron membranes with modified surface chemistry and/or microstructures can significantly improve oxygen permeation flux by altering surface exchange kinetics.[1,2,7,35,44]

The dual-functional membranes require high stability as the membranes are exposed to two different reaction

TABLE 1 Summary of performance and process parameters of coupling of two chemical reactions through an oxygen transport membrane (OTM) reactor.

Reaction	Membrane composition	Reactor configuration	T (°C)	Catalyst	Performance	Stability (h)	Reference
WS coupling with POM	$La_{0.8}Ca_{0.2}Fe_{0.94}O_{3-\delta}$–Ag	Hollow fiber (wall thickness: 0.25 mm)	950	$Ni/LaNiO_3/\gamma$-Al_2O_3 (POM reaction side)	r_{H2} = 7.9 mL cm^{-2} min^{-1}; $X(CH_4)$ = 58%; $S(CO)$ = 89%	20	32
WS coupling with DRM	$BaMg_{0.1}Zr_{0.05}Ti_{0.85}O_3$	Disk (thickness: 0.7 mm)	990	Ni-based catalyst (Süd-Chemie AG) (DRM reaction side)	r_{H2} = 0.8 mL cm^{-2} min^{-1}; $X(CH_4)$ = 25%; $S(CO)$ = 98%	100	33
Decomposition of H_2O and CO_2 coupling with POM	$Ce_{0.9}Pr_{0.1}O_{2-\delta}$–$Pr_{0.6}Sr_{0.4}FeO_{3-\delta}$	Disk (thickness: 0.6 mm)	930	Ni/Al_2O_3 (POM reaction side)	r_{H2} = 0.6 mL cm^{-2} min^{-1}; $S(CO)$ = 98%	100	25
Decomposition of CO_2 coupling with POM	$La_{0.8}Ca_{0.2}FeO_{3-\delta}$–$Ce_{0.9}Gd_{0.1}O_{2-\delta}$	Disk (thickness: 0.11 mm)	900	NiO–$Ce_{0.9}Gd_{0.1}O_{2-\delta}$–$La_{0.3}Sr_{0.7}TiO_{3-\delta}$ (POM reaction side); $La_{0.8}Ca_{0.2}FeO_{3-\delta}$–$Ce_{0.9}Gd_{0.1}O_{2-\delta}$ (CO_2 decomposition reaction side)	$X(CO_2)$ = 40%; $X(CH_4)$ = 80%; $S(CO)$ = 100%	100	34
Decomposition of CO_2 coupling with POM	Al_2O_3-doped $SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-\delta}$	Tube (thickness: 0.45 mm)	900	Ni/Al_2O_3 (POM reaction side)	$X(CO_2)$ = 12.4%; $X(CH_4)$ = 86%; $S(CO)$ = 93%; H_2/CO = 1.8	–	24
Decomposition of N_xO coupling with POM	$BaFe_{0.9}Zr_{0.05}Al_{0.05}O_3$	Disk (thickness: 1 mm)	900	–	$X(CH_4)$ = 97%; $X(N_2O)$ = 100%; $S(CO)$ = 94%	100	30
Decomposition of NO coupling with POM	$BaBi_{0.05}Co_{0.8}Nb_{0.15}O_{3-\delta}$	Hollow fiber (wall thickness: 0.2 mm)	750	Ni-phyllosilicate hollow sphere (POM reaction side)	$X(CH_4)$ = 95%; $X(NO)$ = 100%; $S(CO)$ = 94%	–	31
Decomposition of N_2O coupling with ODE	$BaCo_xFe_yZr_{1-x-y}O_{3-}$	Hollow fiber (wall thickness: 0.17 mm)	850	Ni/Al_2O_3 (ODE reaction side)	$X(C_2H_6)$ = 85%; $S(C_2H_4)$ = 86%; $X(N_2O)$ = 100%	–	12

Note: The stability (h) value represents the maximum duration of the measurements conducted in the respective studies cited without breakdown; T: temperature (°C).

Abbreviations: DRM, dry reforming of methane; ODE, oxidative dehydrogenation of ethane; POM, partial oxidation of methane; S, selectivity; WS, water splitting; X, conversion.

TABLE 2 An overview of the oxygen permeation flux data from several potential oxygen transport membranes (OTMs) recently reported in literature.

Membrane composition	Configurations	d (mm)	$J(O_2)$[a] (mL cm^{-2} min^{-1})	$J(O_2)$[b] (mL cm^{-2} min^{-1})	T (°C)	$J(O_2)$[b] stability (h)	Reference
30 wt% $La_{0.15}Sr_{0.85}FeO_{3-\delta}$–70 wt% $La_{0.15}Ce_{0.8}Cu_{0.05}O_{2-\delta}$	Disk	0.6	0.45	0.27	900	100	45
60 wt% $Ce_{0.9}Nd_{0.1}O_{2-\delta}$–40 wt% $Nd_{0.6}Sr_{0.4}CoO_{3-\delta}$	Disk	0.6	0.65	0.55	950	150	46
40 wt% $Ce_{0.9}Pr_{0.1}O_{2-\delta}$–60 wt% $Nd0_{0.5}Sr_{0.5}Fe_{0.9}Cu_{0.1}O_{3-\delta}$	Disk	0.6	0.97	0.32	1223	70	47
60 wt% $Ce_{0.8}Sm_{0.2}O_{2-\delta}$–40 wt% $Sm_{0.3}Sr_{0.7}Cu_{0.2}Fe_{0.8}O_{3-\delta}$	Disk	0.6	0.84	0.7	950	400	48
25 wt% $Sm_{0.2}Ce_{0.8}O_{1.925}$–75 wt% $SrCo_{0.4}Fe_{0.55}Zr_{0.05}O_{3-\delta}$ (SDC–SCFZ)	Disk	0.6	1.26	–	950	72	49
75 wt% $Ce_{0.85}Sm_{0.15}O_{1.925}$–25 wt% $Sm_{0.6}Sr_{0.4}Al_{0.3}Fe_{0.7}O_{3-\delta}$	Hollow fiber	~0.32	1.03	0.915	950	56	50
$La_2Ni_{0.95}Mo_{0.05}O_{4+\delta}$	Hollow fiber	–	2.88	2.75	950	185	51
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	Six-channel hollow fiber	0.052	1.87	–	950	–	52
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$–$(La_{0.5}Sr_{0.5})_2CoO_{4+\delta}$	Hollow fiber	–	3.2	2.6	900	100	53
$La_2Ni_{0.95}Mo_{0.05}O_{4+\delta}$	Hollow fiber	–	2.88	2.75	950	185	51
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	19-channel hollow fiber	–	8.85	–	900	–	54

Note: d is the membrane thickness (mm).

[a]Oxygen permeation flux under air/He or air/Ar gradient.

[b]Oxygen permeation flux under air/CO_2 gradient. The stability (h) value represents the maximum duration of the measurements conducted in the respective studies cited without breakdown. T: temperature (°C).

conditions, in most cases, to withstand the erosion of reducing gases (i.e., hydrogen or methane) and acidic gases (i.e., CO_2) at high temperatures. The mixed ionic-electronic conducting membranes with such high chemical resistance in single phase are rarely reported; thus, dual-phase membranes may have their niche for such applications. The oxygen ionic conducting phase and electronic phase can be individually chosen from these robust components like a fluorite-type conductor (yttria-stabilized zirconia, Sm-doped ceria (SDC), or Gd-doped ceria). In particular, a novel design consisting of a robust ion conductor with an external metal coating as the short circuit was put forward to enhance the CO_2 and H_2 resistance.[55,56] These new designs may have potentials for dual-functional membrane reactors, despite that no literature has been reported.

3.2 | Engineering of the membrane

Enhancing the performance of membrane reactors through engineering of the membranes can be achieved by various strategies. One of the effective strategies is to modify the membrane configurations by preparing an asymmetric or hollow fiber membrane, which reduces the membrane thickness and decreases oxygen ion diffusion resistance.[2,35,57] Membrane reactors generally require to load an extra catalyst. Thus, catalyst development for membrane reactors is crucial to enhance performance. However, limited research has been conducted in this area. Most catalysts are supported by alumina, silica, or zeolites with limited oxygen ionic conductivities, which can react with membrane materials at high temperatures, thereby reducing the membrane's oxygen permeability.[2] To address this issue, in situ precipitating of nanoparticle catalysts in membrane materials is a more suitable approach for membrane reactors, as it can provide catalytic activities for reactions and weaken the negative effects of the reaction between the membrane and the catalyst. Recently, Jin et al.[58] demonstrated an "in situ growth" strategy to design homologous perovskite catalysts applied within a perovskite membrane reactor for the POM as shown in Figure 2. FeNi ($FeNi_3$) bimetallic nanoparticles exsolved from $Sr_{0.9}(Fe_{0.81}Ta_{0.09}Ni_{0.1})O_{3-\delta}$ (STFN) parent oxide to form the FeNi/STFN exsolution-based catalyst, which was used to construct a catalytic membrane reactor based on a $Ba_{0.5}Co_{0.5}Fe_{0.22}Nb_{0.08}O_{3-\delta}$ hollow fiber membrane (four-channel). The performance of the catalytic membrane reactor was dramatically improved with FeNi/SFTN0.9 over the fresh STFN catalyst, demonstrating the advantages of using an exsolution-based perovskite catalyst and effectively suppressing its excessive exsolution/dissolution. The CH_4 conversion, CO selectivity, H_2 selectivity, and H_2/CO ratio were 98%, 97%, 98%, and 2.2, respectively. This study provides valuable insights into the development of customized catalysts for dual-functional membrane reactors.

In addition to the development of efficient catalysts, understanding the influence of different catalyst loading methods on membrane reactor performance is crucial for efficiently integrating the catalyst within the reactor. To this end, the working principles for four types of catalyst contact modes (I–IV), as illustrated in Figure 2, can provide a simple guideline for designing membrane reactors for different oxidative reactions. For the OCM reaction, mode-III, where the catalysts possess ion conducting properties and are intimately contacted with the membrane, is considered the best situation. In this mode, the triple-phase-boundary (TPB) area is significantly expanded to the whole exposed particle surface. The entire membrane surface may act as a catalyst, allowing the utilization of ionized oxygen only without gas-phase oxygen if the reaction and permeation rates are well-controlled and matched. However, for some oxidations, such as those that do not benefit from catalysts of mode-III, a better design is mode-IV, which combines modes-II and -III by integrating normal catalyst and membrane material particles together to promote the reaction by expanding the TPB area. In mode-I, mainly gaseous oxygen reaches the catalyst surface to participate in reactions, but for POM, the oxygen partial pressure at the membrane interface facing the catalyst can protect the membrane in a strongly reducing atmosphere. To achieve better performance, the design must take into account the specific reaction mechanism requiring either controlled gaseous oxygen or lattice oxygen. Understanding the fundamentals of catalyst contact mode and their combination will aid in improving membrane reactor performance. A more comprehensive discussion of catalyst contact mode and their combination can be found in Refs. [2, 59].

Incorporating catalysts in membrane reactors while ensuring their retention on the membrane surface is a critical concern as loosely attached catalysts are prone to detachment under high-temperature fluid flow or by aggregation driven by a reduction in surface free energy. Recently, Han and Liu et al.[60] demonstrated the development of a wrinkled outer surface morphology for $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) hollow fiber membrane, as depicted in Figure 2c, which represents a novel strategy for catalytic carrier design. The Ag-coated wrinkled LSCF membrane exhibited an O_2 flux of 1.27 mL cm^{-2} min^{-1} at 900°C, which was two times higher than that of the conventional membrane with Ag-coating under the same conditions. This study presents a valuable approach toward membrane engineering for anchoring catalysts in membrane reactors. Ideally, the honeycomb structure's microchannels should be located on the outer surface,

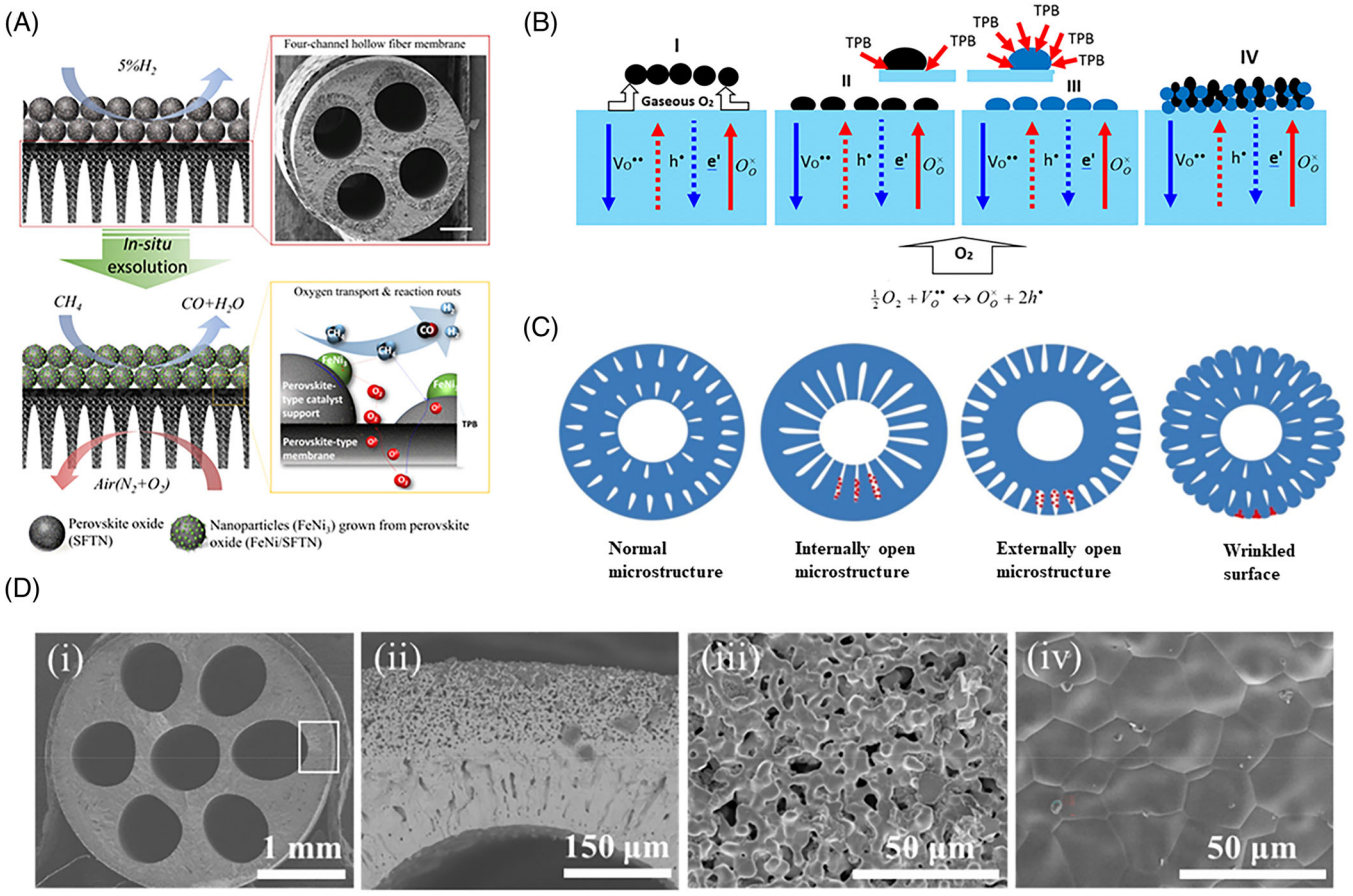

FIGURE 2 (a) Schematic diagrams of a new catalytic membrane reactor with exsolution-based catalysts designed by a "in situ growth" strategy. (b) Reaction pathways and oxygen permeation for oxidative reactions by oxygen transport membranes (OTMs) with various catalyst contact modes. (c) A schematic representation of the different cross-sectional microstructures of hollow fiber membranes. (d) Scanning electron microscope [SEM] images of the SFN/SCN dual-layered hollow fiber: (i) cross section; (ii) zoomed-in area marked on (i); (iii) outer porous surface; (iv) inner dense surface. *Source*: (a) Reprinted with permission from Ref. [58]. Copyright 2020 Elsevier; (b) reprinted with permission from Ref. [2]. Copyright 2022 John Wiley and Sons; (c) reprinted with permission from Ref. [60]. Copyright 2021 Elsevier; (d) reprinted with permission from Ref. [65]. Copyright 2023 Elsevier.

as illustrated in Figure 2c. However, creating externally open pores is challenging without the inclusion of an extra acid etching step.[61] In this regard, engineering a membrane that offers high mechanical strength and excellent oxygen permeability is crucial for practical industrial applications, which is highly needed to be explored in future.

The enhancement of mechanical strength in hollow fibers can be achieved by increasing their cross-sectional area through a multichannel configuration.[62–65] This design can provide a larger permeation area and higher membrane-packing density within a given volume. Notably, multichannel hollow fibers utilizing perovskite oxides were first developed by Jin's group for efficient production of pure oxygen.[62] These multichannel fibers have demonstrated significant improvements in both mechanical strength and oxygen permeation flux compared to a single-channel hollow fiber membrane.[63,66] Similar results have been reported in Li's group via investigating three-, four-, seven-channel, and bio-inspired six-channel $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ hollow fibers.[52,67] Additionally, a recent advancement in the field includes the development of $SrFe_{0.8}Nb_{0.2}O_{3-\delta}$ (SFN)/$SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ (SCN) dual-layered seven-channel hollow fiber membranes, fabricated through a co-spinning process and one-step thermal processing (see Figure 2d).[65] These dual-layered seven-channel hollow fiber membranes exhibit superior mechanical strength and high oxygen permeability, with the porous SFN outer layer effectively preventing performance degradation under a CO_2-containing sweep gas in comparison to SCN membranes. Moreover, the SFN/SCN dual-layered membranes exhibit a stable operation for over 200 h in the 20% CO_2–80% He sweep gas, maintaining the high oxygen permeation flux.[65] The advantageous properties of multichannel hollow fiber membranes, including enhanced mechanical strength, permeation flux, and

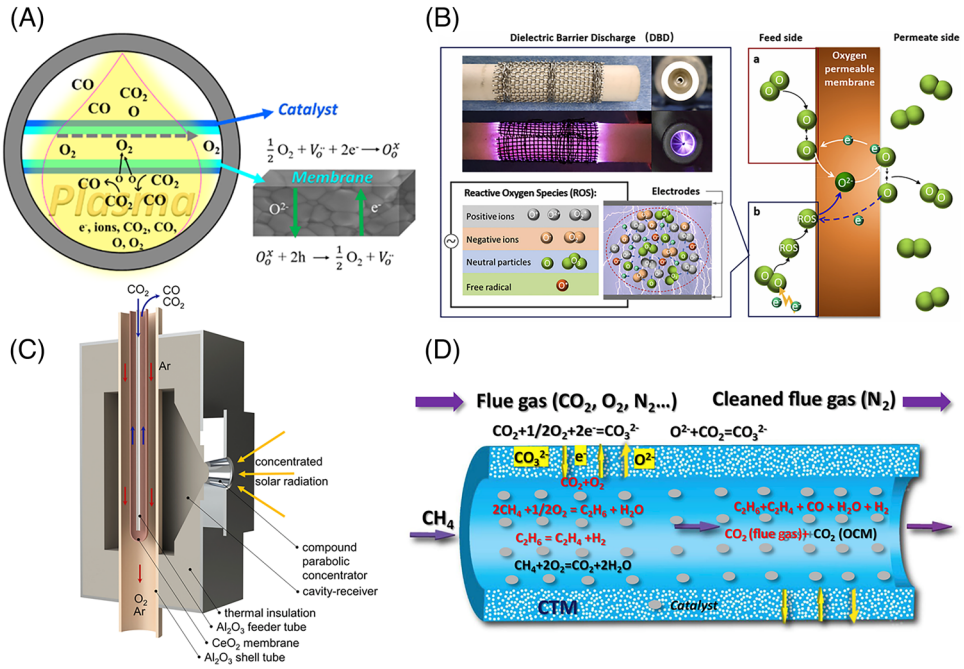

FIGURE 3 (a) Plasma assisted hollow fiber membrane system for CO_2 decomposition and gas separation. (b) A novel dielectric barrier discharge plasma (DBD)-membrane design for efficient oxygen permeation. (c) A schematic representation of the solar-driven thermochemical CO_2 splitting across a CeO_2 membrane reactor. (d) The configurations of CO_2/O_2 cotransport membrane reactor for oxidative coupling of methane (OCM). *Source*: (a) Reprinted with permission from Ref. [68]. Copyright 2020 Elsevier; (b) reprinted with permission from Ref. [74]. Copyright 2022 Elsevier; (c) reprinted with permission from Ref. [75]. Copyright 2017 Elsevier; (d) reprinted with permission from Ref. [78]. Copyright 2022 Elsevier.

packing density, establish them as reliable and economically viable options. Consequently, these membranes represent a significant advancement and a promising future direction in membrane technology, holding potential for scalability and broader applications.

3.3 | Innovation in the OTM reactors

Recently, there have been proposals for innovation concepts on the OTM reactor, which could serve as a promising strategy for future research to enhance the performance of dual-functional membrane reactors. Among the emerging technologies for CO_2 conversion, plasma-based approaches have gained considerable interest due to their flexibility and efficiency.[68–70] Chen et al.[71] first proposed a plasma-assisted $La_{0.6}Ca_{0.4}Co_{0.5}Fe_{0.5}O_{3-\delta}$ (LCCF) hollow fiber membrane concept that simultaneously improved gas separation and CO_2 conversion as depicted in Figure 3a. The oxygen permeation flux was significantly enhanced by almost a factor of 3 in a CO_2 plasma compared to the same LCCF hollow fiber membrane studied under conventional conditions. This improvement was attributed to the unique atmosphere in the CO_2 plasma, which comprises excited species, electrons, radicals, photons, molecules, and ions. The constant high oxygen permeation flux was maintained during long-term operation, which is of particular importance for commercial application. Furthermore, the rapid switching between operation and stand-by demonstrated the additional strength of the developed system to cope with potential unstable energy supply when using renewable energies. Buck et al.[72,73] have conducted further improvements based on this concept, and Zheng et al.[74] confirmed the benefit of the unique atmosphere provided by plasma to enhance oxygen permeability. They proposed a novel dielectric barrier discharge plasma–membrane design for efficient oxygen permeation at low temperatures (Figure 3b). At 600°C with a plasma power of 15 W, the oxygen permeation flux of the $La_{0.6}$ $Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane (disk) increased remarkably by almost 30 times. These newly developed plasma-membrane reactor designs hold particular promise for improving the performance of membrane reactors, especially for important catalytic reactions that operate at lower temperatures, such as OCM.

In recent years, there has been significant progress in solar capture and storage technologies, and integrating solar-driven processes into membrane reactors offers a promising approach to convert solar energy into different forms of energy.[2,75,76] Tou et al.[75] conducted an experimental study on the continuous CO_2 splitting under steady-state isothermal/isobaric conditions in a CeO_2

membrane reactor driven by concentrated radiation for the first time (see Figure 3c). A similar concept has also been investigated by Abanades et al.,[76] focusing on the design and development of a new membrane solar reactor for continuous CO_2 splitting. Tou et al. also tested the feasibility of splitting both H_2O and CO_2 in a tubular CeO_2 membrane reactor heated by simulated concentrated solar radiation into separate streams of oxygen and syngas, respectively.[77] This simple solar membrane reactor technology demonstrates its potential for co-splitting CO_2 and H_2O to fuels under high flux conditions. However, heat and mass transfer were impractically slow, restricting the reaction rates. Moreover, these solar-driven processes have not yet been investigated or demonstrated as dual-functional membrane reactors, representing a promising research direction to enhance overall efficiency.

A recent study by Huang et al.[78] has proposed an intriguing CO_2/O_2 cotransport membrane reactor for the OCM conversion, as depicted in Figure 3d. Their results demonstrate that the co-captured CO_2/O_2 mixture converts methane into C_2H_6 in the presence of a catalyst (2% Mn–5% Na_2WO_4/SiO_2). Then C_2H_6 was thermally cracked into H_2 and C_2H_4. The presence of CO_2 leads to a reduction in the local partial pressure of O_2, resulting in a higher C_2 selectivity by reducing the propensity of C_2-products reoxidation. These innovative concepts may provide a new avenue for designing suitable CO_2/O_2 cotransport membrane materials for dual-functional membrane reactors.

However, it should be noted that all the abovementioned innovative concepts are still in the early stages of development, and significant advancements are necessary in the future to improve the efficiency and economics of the process before industrial implementation can be realized.

3.4 | Reaction mechanisms in the dual-functional membrane reactors

Comprehending the relationship between the reconstruction of membranes and catalysts and their activation or deactivation in membrane reactors is crucial to achieve the rational design of high-performance materials that can withstand harsh operating conditions for a long-term operation. Significant progress has been made by the scientific community to improve the understanding of the oxygen transport mechanism.[35,57,79] Spectroscopic techniques have been employed to investigate the degradation processes that occur during membrane exposure to CO_2,[35] but these investigations have not been conducted during the actual application process. In situ characterization analysis has not been carried out for membrane reactors that couple two reactions as well so far. Advanced scientific research methods, such as in situ Fourier-transform infrared spectroscopy being particularly useful for monitoring the creation of the intermediates,[80,81] are highly recommended to investigate the reaction mechanism during the actual reaction processes in dual-functional membrane reactors. The morphological change can be evaluated using in situ transmission electron microscopy, whereas in situ X-ray powder diffraction can provide information on the crystalline structure for a long-term operation.

Computational simulations and modeling have emerged as indispensable tools for advancing the field of membrane reactors. The progress in developing oxygen permeation models has led to the introduction of more sophisticated models that incorporate bulk diffusion and surface exchange reactions, resulting in more accurate predictions of oxygen permeation fluxes. Existing models for oxygen permeation flux include the Wagner, Bouwmeester, Xu–Thomson, Li, Tan and Li, Ghadimi, Kim, Zhu, Van Hassel, and Dimitrakopoulos and Ghoniem models, each based on specific transport mechanisms and underlying assumptions.[2,82] The application prospects of these oxygen permeation models extend beyond their use in membrane reactors, encompassing other reaction-based applications and more extensive modeling studies, such as computational fluid dynamics (CFD).[2,83] For instance, Feng et al. developed a 3D CFD model to investigate the behavior of perovskite hollow fiber membrane modules ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF)) for oxygen separation.[84] Similarly, Sommer et al. explored CFD and continuously stirred tank reactor (CSTR) models to enhance the yield of partial oxidation products in mixed ionic electronic membrane reactors utilizing an LSCF disk membrane reactor for OCM.[85] Their studies shed light on the selectivity of carbon products for different reactor configurations and compared the results of the CFD model with a less complex two-chamber CSTR model. The modeling tools can be used to identify optimal operating conditions and the results demonstrated the importance of gas phase chemistry and flow configuration. It is crucial to note that incorporating oxygen permeation models into reactive membrane technology necessitates additional considerations, such as the impact of pressure drop from combustion and its effects on the driving force of oxygen partial pressure or membrane permeability. Furthermore, the catalytic nature of MIECs should be taken into account to enhance the product yield in future studies.[85] The continuous development of computational simulations and modeling is vital for supporting the rapid progress in experimental-based membrane materials and technology, particularly in simulating the complex behavior of oxygen permeation in dual-functional membrane reactors.[2,82,86]

Nevertheless, there remains a gap in understanding both the stability control of chemical reactions and their

influence on membrane performance. CFD can be a promising approach to investigate local heat transfer behavior, which directly influences the chemical reactions within a membrane reactor. Investigating these fundamental issues will undoubtedly provide valuable insights into the development of next-generation membrane materials and catalysts.

4 | CONCLUSIONS

The utilization of oxygen transport dual-functional membrane reactors for coupling various reactions provides numerous opportunities for energy conversion and storage. Despite recent advancements, the successful application of these oxygen transport dual-functional membrane reactors on a large industrial scale requires overcoming research and technological challenges. The integration of these membrane materials into engineering concepts and devices has been discussed, and innovative concepts offer significant potentials to improve energy efficiency and identify new possibilities for future commercial applications. The development of more robust membranes capable of withstanding the respective reacting conditions on each side of the membrane reactor is crucial. Thus, interdisciplinary approaches must be used to attain the optimal balance between performance and stability for high-performance membrane reactors that promote energy-efficient and sustainable chemistry. As such, more joint efforts from multidisciplinary teams are needed to tackle these challenges.

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CONFLICT OF INTEREST STATEMENT

All the authors declare no conflicts of interest.

ORCID

Guoxing Chen https://orcid.org/0000-0002-1570-4639

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