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HIGHLIGHTS

- A new both Co- and Fe-free titanate-based oxygen transport membrane is developed
- The membrane exhibits superior reduction tolerance in 20 vol.% H₂/Ar
- The membrane shows an environment-induced mixed conductivity
- The material is well suited for membrane reactor for coupling two reactions

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Chemical Environment-Induced Mixed Conductivity of Titanate as a Highly Stable Oxygen Transport Membrane

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SUMMARY
Coupling of two oxygen-involved reactions at the opposite sides of an oxygen transport membrane (OTM) has demonstrated great potential for process intensification. However, the current cobalt- or iron-containing OTMs suffer from poor reduction tolerance, which are incompetent for membrane reactor working in low oxygen partial pressure ($p_{O_2}$). Here, we report for the first time a both Co- and Fe-free $\text{SrMg}_{0.15}\text{Zr}_{0.05}\text{Ti}_{0.8}\text{O}_3$ (SMZ-Ti) membrane that exhibits both superior reduction tolerance for 100 h in 20 vol.% $\text{H}_2/\text{Ar}$ and environment-induced mixed conductivity due to the modest reduction of $\text{Ti}^{4+}$ to $\text{Ti}^{3+}$ in low $p_{O_2}$. We further demonstrate that SMZ-Ti is ideally suited for membrane reactor where water splitting is coupled with methane reforming at the opposite sides to simultaneously obtain hydrogen and synthesis gas. These results extend the scope of mixed conducting materials to include titanates and open up new avenues for the design of chemically stable membrane materials for high-performance membrane reactors.

INTRODUCTION
Process intensification based on catalytic membrane reactors (CMRs) combing catalytic reactions and separation processes in one single unit presents one of the most important trends in today’s chemical engineering and process technology (Morejudo et al., 2016; Tou et al., 2017). As one of the typical inorganic membranes for CMRs, dense oxygen transport membranes (OTMs) with mixed ionic-electronic conductivity (Wang et al., 2005a, 2005b) exhibit high oxygen ion permeability and infinite selectivity at elevated temperatures because of mobile oxygen vacancies and electronic defects. These features enable an OTM to simultaneously combine oxygen-related chemical reactions at two opposite sides of the membrane, leading to an integral coupling of reaction-separation-reaction processes and, hence, benefit with regard to energy consumption, capital cost, and catalytic performance. These benefits of OTM reactor have been demonstrated in our previous works (Jiang et al., 2008; Jiang et al., 2009a, 2009b; Jiang et al., 2010a, 2010b). For example, water splitting was coupled with partial oxidation of methane (POM) using a $\text{BaCo}_{0.5}\text{Fe}_{0.5}\text{Zr}_{1-x}\text{Y}_{x}\text{O}_3$ membrane (Jiang et al., 2008). At one side of the membrane, hydrogen is obtained from water splitting; meanwhile, at the other side, POM reaction occurs to produce synthesis gas with a $\text{H}_2/\text{CO}$ ratio of around 2, which is proper for the subsequent Fischer-Tropsch or methanol production. In addition, some other researchers combine two oxygen-involved reactions at the opposite sides of OTM reactors for two synthesis gases (i.e., $\text{H}_2/\text{N}_2$ and $\text{H}_2/\text{CO}$) production for ammonia and liquid fuel (Li et al., 2016), large-scale hydrogen production (Fang et al., 2016; Li et al., 2017), or CO$_2$ capture and utilization (Kathiraser et al., 2013; Zhang et al., 2014), further underscoring the promise of OTM reactors for coupling two reactions on the opposite sides.

In spite of these advantages, distinct skepticism currently remains about the applicability of such reactors owing to the poor reduction tolerance of the existing OTM materials whose two sides are usually subjected to an oxygen-containing species ($\text{H}_2\text{O}, \text{NO}_x$) and a reductive gas ($\text{CH}_4, \text{C}_2\text{H}_4$), respectively. Conventional “first-generation” OTMs are based on cobalt perovskite oxides (e.g., $\text{Ba}_0.5\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$) that exhibit high oxygen permeability and work well for air separation at relatively high oxygen partial pressure ($p_{O_2}$) (Tan et al., 2008; Thursfield and Metcalfe, 2007), but the performance of Co-based membranes drops rapidly owing to the fast and deep reduction of cobalt ions followed by the eventual collapse of perovskite structure under low $p_{O_2}$ environments in which two reactions are coupled at opposite sides of the membranes (Bouwmeester, 2003; Ovenstone et al., 2008). “Second-generation” OTMs, based on...
iron-containing oxides such as $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_3$-$d$, $\text{BaCe}_{1-x}\text{Fe}_x\text{O}_3$-$d$, and dual phase $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$–$\text{NiFe}_2\text{O}_4$, exhibit relatively higher stability in low $p_{\text{O}_2}$ than Co-based membrane (Luo et al., 2011; Wang et al., 2005a, 2005b; Zhu et al., 2006). Regrettably, performance degradation of Fe-based membranes cannot be avoided since the damage of Fe-based material is also inevitable (Neagu et al., 2013) when being used as reactor for coupling two chemical reactions under low $p_{\text{O}_2}$. Hence, there is an urgent need to develop new membrane materials that allow the deployment of OTM reactors exhibiting desirable oxygen permeability as well as high chemical stability under low $p_{\text{O}_2}$ atmospheres such as $\text{H}_2\text{O}$, $\text{CH}_4$, and $\text{H}_2$.

In this regard, titanates (e.g., $\text{SrTiO}_3$) are very intriguing materials because of the following considerations. (1) Titanates have excellent chemical and redox stability at high temperatures (Calle-Vallejo et al., 2010). (2) Under low $p_{\text{O}_2}$ atmospheres, titanates show n-type conduction behaviors because of the reduction of Ti from 4+ to 3+ (Balachandran and Eror, 1981; Singh et al., 2013). Such reduction is compensated by the release of lattice oxygen from titanates to fulfill the electric neutrality and thereby forming oxygen vacancies (Balachandran and Eror, 1981; De Souza, 2015), enabling these titanates to possess mixed oxygen ionic-electronic conductivity for the applications in electrode for solid oxide fuel cells (SOFCs) (Rui-Morales et al., 2006) and electrocatalyst for metal-air batteries (Chen et al., 2015). (3) Furthermore, the ionic radii of $\text{Ti}^{4+}$ and $\text{Ti}^{3+}$ are comparable, which can avoid the large thermal and chemical expansions of titanates and ensure their mechanical and structural integrity under high temperature and reducing atmospheres. (4) The deep reduction of TiO$_x$ to metallic state in $\text{H}_2$ is thermodynamically unfavorable (Neagu et al., 2013), suggesting superior chemical stability of titanates compared with cobalt- or iron-containing oxides (Calle-Vallejo et al., 2010). (5) Finally, B-site doping of Mg acceptor in titanates is helpful in creating more oxygen vacancies and lowering the sintering temperature (Li et al., 2014). Hence, the facts of the mixed ionic-electronic conductivity of titanates induced by low $p_{\text{O}_2}$ environment and their superior chemical stability provide an opportunity to develop a new-generation titanate-based OTM reactor that is very suitable for coupling two oxygen-related reactions in low $p_{\text{O}_2}$ environments.

Here, we first report a novel chemical environment-responsive mixed conducting $\text{SrMg}_{0.15}\text{Zr}_{0.05}\text{Ti}_{0.8}\text{O}_3$-$a$ (SMZ-Ti) oxygen transport membrane containing neither cobalt nor iron. With high valency and excellent anti-reduction properties, the Zr doping at the Ti-site of SMZ-Ti was used to dismiss the mismatch between cations for stabilizing the cubic structure. When being exposed to air as shown in Scheme 1, perovskite SMZ-Ti shows very poor mixed conductivity because the change of Ti valence from 4+ to 3+ is highly restricted under high $p_{\text{O}_2}$ environment, and thus the Ti-based membrane shows negligible oxygen permeability under high $p_{\text{O}_2}$ environment. Once both sides of the SMZ-Ti membrane are subjected to steam and
methane, respectively, these low $p_{O2}$ environments induce the release of lattice oxygen (O*) from SMZ-Ti, forming oxygen vacancies in the lattice, which are subsequently compensated by the modest reduction of Ti$^{4+}$ to Ti$^{3+}$ (Ti$^{4+}$ + e$^-$/Ti$^{3+}$). These oxygen vacancies and electronic defects induced by the chemical environment enable the dense SMZ-Ti membrane to show a mixed oxygen ionic-electronic conductivity and oxygen permeability, thus allowing the permeation of oxygen produced from water dissociation (H$_2$O / O* + H$_2$) on the membrane surface to the other side where it is consumed by POM to produce synthesis gas (CH$_4$ + O* / CO + 2 H$_2$). Simultaneously, pure hydrogen as the product of water splitting is obtained. Apart from this chemical environment-induced mixed conductivity, SMZ-Ti also exhibits superior chemical stability under these low $p_{O2}$ atmospheres because the titanium ions (Ti$^{4+}$/Ti$^{3+}$) will not be deeply reduced to metallic state (Ti$^0$), contrasting with the well-known cobalt- or iron-containing membranes. Therefore, these features of SMZ-Ti dovetail exactly with OTM reactors to couple reaction-separation-reaction process, extend the scope of mixed conducting materials to include titanates, and open up new avenues for the design of promising chemically stable membrane materials for use in high-performance membrane reactors under harsh reaction conditions.

RESULTS AND DISCUSSION

Chemical Stability in Low $p_{O2}$ Atmospheres

As mentioned earlier, OTM reactors for practical application must exhibit excellent chemical resistance to reducing gases. When coupling two reactions in an OTM reactor, H$_2$ either is formed at the membrane surface by light hydrocarbon conversion process or exits on both sides of membrane. To evaluate the chemical stability against reducing atmosphere, SMZ-Ti membranes were treated in H$_2$ atmosphere, comparing with five typical Co- or Fe-containing OTMs, including BaFe$_{0.4}$Zr$_{0.2}$Co$_{0.4}$O$_3$-d (BFZ-Co) (Jiang et al., 2010a, 2010b), Ba$_{0.95}$Ce$_{0.05}$Fe$_{0.9}$O$_{3.3}$-d (BC-Fe) (Li et al., 2016), Sm$_{0.13}$Ce$_{0.87}$O$_{1.925}$ – Sm$_{0.05}$Sr$_{0.1}$Al$_{0.3}$Fe$_{0.7}$O$_{3.3}$-d (SDC-SSAFe) (Fang et al., 2016; Li et al., 2017), La$_{0.9}$Ca$_{0.1}$FeO$_3$-d (LC-Fe) (Wu et al., 2015), and SrTi$_{0.75}$Fe$_{0.25}$O$_3$-d (ST-Fe) (Schulze-Küppers et al., 2015). Figures 1 and S1 depict the X-ray diffraction (XRD) patterns of SMZ-Ti, BFZ-Co, BC-Fe, SDC – SSAFe, LC-Fe, and ST-Fe membranes before and after H$_2$ treatment. As shown in Figure 1A, the as-synthesized SMZ-Ti membrane reveals a highly crystalline character, indexed as the cubic perovskite phase with space group Pm-3m. A weak peak at around 43° (2θ) could be assigned to MgO (Tkach et al., 2004). The structural evolution of SmMg$_2$Zr$_{0.03}$Ti$_{0.9}$O$_{3.3}$-d with varying Mg contents was investigated (Figure S2), and SmMg$_{0.1}$Zr$_{0.03}$Ti$_{0.9}$O$_{3.3}$-d was selected for the following studies. After annealing in a 20 vol.% H$_2$/Ar atmosphere at 900°C for 24 h, the peaks in XRD pattern in Figure 1B of SMZ-Ti oxide associated with the cubic perovskite
structures of the conventional BFZ-Co, BC-Fe, LC-Fe, and ST-Fe membrane materials were decomposed seriously after exposure to 20 vol.% H2-Ar atmosphere for 24 h (Figures 1b and S1). Similarly, after the same atmosphere exposure, a few impurity phases corresponding to Sr4Fe6O13 (JCPDS no. 78-2403) and Fe metallic (JCPDS no. 87-0721) were also observed in the XRD pattern of the SDC–SSAFe membrane, indicating that this membrane material is still chemically unstable in the low oxygen partial pressure atmosphere. Thus, these chemical stability tests reveal that SMZ-Ti shows superior reduction-tolerant ability compared with the conventional Co- or Fe-containing membranes, which will assure the long-term operating durability of the SMZ-Ti membrane used as a membrane reactor working in reducing atmospheres.

**Oxygen Permeability of SMZ-Ti under Different Working Conditions**

Besides the superior chemical stability in low pO2, another core requirement for new-generation OTMs is that the membrane should also possess a desirable oxygen permeability in low pO2 environment. Therefore, the oxygen permeation flux of the SMZ-Ti membrane was investigated under four working conditions with different pO2. The order of these working conditions for permeation measurement was Cond. I, Cond. II, Cond. III, and Cond. IV. As shown in Figure 2A, when one side of the membrane was fed with air while helium was swept on the other side (Cond. I), the oxygen permeation flux of the doped perovskite SMZ-Ti was about 0.02 cm3 min−1 cm−2 at 990°C. This value is approximately one order of magnitude higher than that of undoped SrTiO3 membrane exposed to air/argon pO2 gradient at 1000°C (Schulze-Küppers et al., 2015), indicating the positive influence of Mg and/or Zr doping on oxygen permeability of SrTiO3. This observation can be supported by the increased electrical conductivity and reduced activation energy for oxygen transport through Mg-doped SrTiO3 as compared with undoped SrTiO3 (Inoue et al., 1991; McCollm and Irvine, 2001). However, the oxygen permeation flux of such titanate-based membrane is still too low under high pO2 because of the presence of air. Once the helium sweep gas was changed to diluted hydrogen (Cond. II), the flux increased dramatically to over 0.1 cm3 min−1 cm−2; continuously climbed up to 0.21 cm3 min−1 cm−2 when both sides of the SMZ-Ti membrane were subjected to steam and methane, respectively (Cond. III); and even reached a value of 0.56 cm3 min−1 cm−2 after introducing some CO2 into the CH4 stream (Cond. IV) to form much lower pO2 at the methane side owing to the DRM reaction (CH4 + CO2 → 2CO + 2H2). These distinct differences in oxygen permeation flux of the SMZ-Ti membrane exposed to the above-mentioned four conditions show that pO2 is strongly associated with oxygen permeability of SMZ-Ti.

To gain insight into the relationship between the pO2 and oxygen permeability of SMZ-Ti, we performed equilibrium pO2 calculation based on the gas components on the opposite sites of the SMZ-Ti membrane at 1 atm and 990°C using Gibbs free energy minimization algorithm on HSC Chemistry 5.0 software (Table S1), the same method as previous studies on the thermodynamic equilibrium for H2O splitting and DRM (Furler et al., 2012; Gardner et al., 2013). As shown in Figure 2B, the pO2 at the two sides of the SMZ-Ti membrane decreases from 10−2.7/10−3.2 atm at Cond. I to 10−9.5/10−15.4 atm at Cond. IV, corresponding to the gradual increase in oxygen permeation flux presented in Figure 2A. Compared with the pO2 at permeate side under Cond. I, a much lower pO2 of 10−15.7 atm under Cond. II is obtained because of the hydrogen gas, which facilitates the formation of electronic defects and oxygen vacancies in SMZ-Ti due to the reduction of Ti4+ to Ti3+, as well as a larger gradient of pO2 across the membrane as driving force, and thereby yields a higher permeation flux of 0.13 cm3 min−1 cm−2. This environment-responsive mixed conductivity of SMZ-Ti is further verified by the increase of oxygen permeation flux of the SMZ-Ti membrane when both sides of the membrane are exposed to H2O and CH4 or H2O and CH4–CO2 atmospheres with lower pO2 (Cond. III and Cond. IV), respectively, even though the pO2 gradient across the membrane in either cases is slightly smaller than that for air/He–H2 gradient (Cond. II). Basically, the pO2 calculated by HSC Chemistry represents an overall average equilibrium amount of oxygen in a whole system. However, if a series of chemical reactions takes place sequentially in the system, the involved components will be unevenly distributed and thus lead to a pO2 gradient throughout the catalyst bed (Chen et al., 2018). In the case of Cond. IV in the present work, a series of catalytic reforming and syngas oxidation reactions occurs at the permeate side of the SMZ-Ti membrane (Figure S3). The CO and H2 produced from dry reforming of CH4 with CO2 at the top zone of catalyst bed can reach the near SMZ-Ti surface and further consume the permeated oxygen species, thus obtaining the highest environment-induced mixed conductivity and oxygen permeation flux. It is necessary to point out that the thickness of the SMZ-Ti membrane used here is 0.7 mm, which means that the permeation flux can be improved by shaping the material into hollow fiber configuration membrane with thin dense layer and larger effective area. Also, the rate-controlling step
in this H2O splitting-oxygen separation-catalytic reforming process will be determined in the future, and further enhanced oxygen permeation flux can be expected. Obviously, the oxygen permeation flux of the SMZ-Ti membrane is obviously increasing with decreasing $p_{O2}$, even though the driving force between feed and permeate sides decreases in particular from Cond. II to Cond. III, which likely results from the chemical environment-induced mixed conductivity of SMZ-Ti. This feature finely matches the working environment of OTM reactor for coupling two reactions.

**Electrical Conductivity of SMZ-Ti under Low $p_{O2}$ Atmospheres**

The environment-induced mixed conductivity of the SMZ-Ti membrane can be also validated from the point of the electrical conductivity under different $p_{O2}$ atmospheres. For this purpose, electrochemical impedance spectra measurements were performed to investigate the electrical conduction behavior of SMZ-Ti. The Nyquist plots of AC impedance measurements of SMZ-Ti under different $p_{O2}$ at 900°C are shown in Figure 3A. The oxygen partial pressure was controlled by means of Ar-H2-H2O gas mixtures, which are similar to water splitting.

**Figure 2. Oxygen Permeability of SMZ-Ti Membrane**

Oxygen permeation flux (A) and $p_{O2}$ at the two sides (B) of SMZ-Ti membranes at 990°C under four different operating conditions (see also Figure S3 and Table S1).

(Cond. I) $F_{Air} = 60 \text{ cm}^3 \text{ min}^{-1}$; $F_{H2} = 20 \text{ cm}^3 \text{ min}^{-1}$.

(Cond. II) $F_{Air} = 15 \text{ cm}^3 \text{ min}^{-1}$; $F_{H2} = 5 \text{ cm}^3 \text{ min}^{-1}$ diluted by 15 cm$^3$ min$^{-1}$ of helium.

(Cond. III) $F_{H2O} = 30 \text{ cm}^3 \text{ min}^{-1}$ carried by 10 cm$^3$ min$^{-1}$ of helium; $F_{CH4} = 3 \text{ cm}^3 \text{ min}^{-1}$ diluted by 13 cm$^3$ min$^{-1}$ of helium, 4 cm$^3$ min$^{-1}$ of N2 as internal standard gas.

(Cond. IV) $F_{H2O} = 30 \text{ cm}^3 \text{ min}^{-1}$ carried by 10 cm$^3$ min$^{-1}$ of helium; $F_{CH4} = 3 \text{ cm}^3 \text{ min}^{-1}$, $F_{CO2} = 1.5 \text{ cm}^3 \text{ min}^{-1}$ diluted by 11.5 cm$^3$ min$^{-1}$ of helium, 4 cm$^3$ min$^{-1}$ of N2 as internal standard gas.
condition as shown in Figure 1. The typical stabilization time for each impedance measurement condition was over 50 h. A model circuit was used for simulating the impedance data as shown in the inset of Figure 3A, where $R$ is a resistance, $L$ is an inductance, and CPE is a constant phase element. From the simulation results, $R_1$ can be assigned as total resistance across the measured sample, $L_1$ is the inductance from the system setup, $R_2$/CPE2 represents the contact resistance in between sample and electrode and $R_3$/CPE3 is the electrochemical reaction for gas exchange in between sample and atmosphere (Irvine et al., 1990). Based on the Nyquist plots and the model circuit, the electrical conductivity of SMZ-Ti increases gradually with decreasing $p_{O_2}$ according to the $H_2/H_2O$ mole ratio, showing an n-type conduction behavior. In particular, the resistance of SMZ-Ti under dry 3 vol.% $H_2/Ar$ atmosphere was approximately 10 $\Omega$ and thereby the electrical conductivity in this case was $\sim 0.1$ S/cm. This value is basically in agreement with the conductivity of SrTiO3 in previous studies (Balachandran and Eror, 1981; Inoue et al., 1991).

After nearly 300 h of the impedance measurement at low $p_{O_2}$ atmospheres, the chemical state of Ti ions in the spent SMZ-Ti sample was studied by X-ray photoelectron spectroscopy (XPS) analysis to
compare with the results of the sample before impedance measurement. As shown in Figure 3B, the peaks of the fresh SMZ-Ti sample located at binding energies 458.7 eV (Ti 2p3/2) and 464.4 eV (Ti 2p1/2) are ascribed to Ti4+ in perovskite lattice (Bharti et al., 2016). The Ti 2p shoulder peaks at binding energy 457.7 eV (Ti 2p3/2) and 463.4 eV (Ti 2p1/2) are corresponding to Ti3+ (Wang et al., 2011), which is related to the intrinsic excitation of electrons from the valence bands of Ti4+ to the conduction bands by Mg2+ acceptor doping and thereby resulting in the reduction to Ti3+ to fulfill the electric neutrality criteria (Singh et al., 2013). After impedance measurement, the percentage of Ti3+ in Ti cations for the used SMZ-Ti sample increased significantly compared with the as-prepared sample, revealing the chemical reduction of Ti4+ ions in 3% H2-Ar at 900°C. Also, it can be inferred that such environment-induced Ti4+ reduction will be further enhanced by decreasing the pO2 (e.g. 50 vol.% H2). In addition, no XPS peaks of Ti2+, Ti+, and metallic Ti0 species were observed in the used sample after this long-term exposure to low pO2 atmospheres, indicating that no deep reduction occurred for Ti4+/Ti3+ ions to cause cubic structure distortion. Accordingly, SMZ-Ti has superior reduction tolerance, which is again confirmed by the XRD patterns of the SMZ-Ti sample before and after impedance measurement (Figure S4).

The impedance spectra indicate that the electrical conductivity of SMZ-Ti increases by decreasing the pO2, showing an n-type conduction behavior. Such behavior is related to the modest reduction of Ti4+ to Ti3+ in low pO2 according to the XPS studies of SMZ-Ti sample before and after impedance measurement. Furthermore, this n-type conduction behavior of SMZ-Ti is in accordance with the observed oxygen permeation fluxes of the SMZ-Ti membrane under different working conditions as shown in Figure 2, which again confirms that lower pO2 environment can induce the modest reduction of Ti4+ to Ti3+ in SMZ-Ti, allowing the SMZ-Ti membrane to possess higher mixed conductivity and better oxygen permeability.

Membrane Performance under Reaction Condition

After confirming that the SMZ-Ti membrane possesses superior chemical stability and good oxygen permeation flux under low pO2, we then proceeded to evaluate SMZ-Ti membrane performance under harsh chemical reaction conditions. For this purpose, coupling of water splitting with dry reforming of methane is an ideal model process because it provides a good platform to investigate the tolerance of the SMZ-Ti membrane to harsh chemical environment, including CH4, H2, CO2, and CO, especially CO2, which is another main problem of many perovskite-type OTMs suffering from CO2 erosion via carbonate formation (Yi et al., 2010; Zhang et al., 2017).

Following a 100-h operation at varying conditions, two sides of the SMZ-Ti membrane was then subjected to H2O splitting and dry reforming of CH4 (mole ratio of CH4/CO2 = 2), respectively, and continuously operated at constant condition for another 100 h, as shown in Figure 4A. Throughout this period, CH4 conversion remained at about 72% without any fluctuations, CO selectivity was high (96%–97%), and at the opposite side the H2 production rate stayed roughly at 1.1 cm3 min−1 cm−2. These results indicate that SMZ-Ti was operated steadily when its two sides were subjected to the reaction conditions of water splitting coupled with dry reforming of methane. Noted that the CH4 conversion in this case exceeds the equilibrium value of CH4 conversion according to DRM reaction (CH4 + CO2 → 2CO + 2H2) calculated by HSC Chemistry 5.0 (Figure S5), suggesting that POM also takes place with DRM. The composition of the effluent stream at the permeate side as function of time was provided in Table S2. A typical gas composition of ~48% He, ~16.3% N2, ~3.6% CH4, ~17.2% H2, ~14.9% CO, and a small amount of CO2 implies that the possible H2O and/or CO2 formed at the membrane surface were finally converted with unreacted methane to syngas via reforming processes. The carbon balance at this side of the membrane maintained at over 96% within the investigation period. However, it is clear that the mole balance of carbon increased slowly with operating time, suggesting that slight carbon deposition may take place in the catalyst bed. This is confirmed by the thermogravimetric analysis of the Ni/Al2O3 catalyst after an approximately 200-h operation (Figure S6).

Both sides of the spent SMZ-Ti membrane were studied by scanning electron microscope (SEM)-energy-dispersive X-ray spectroscopy (EDXS). The same as the as-prepared SMZ-Ti membrane (Figure S7), the spent membrane was still intact and did not show any physical damage (Figures 4B and 4D). What is more, the Ti element (small white spots) at the two sides of the spent membrane was evenly distributed (Figures 4C and 4E). In contrast to the conventional cobalt-containing Ba0.5Sr0.5Co0.8Fe0.2O3−δ (BSCF)
membrane treated under simulated H₂O splitting condition for only 0.5 h, many small particles of 2–5 μm were observed on the cross section of the membrane (Figure 4F). EDXS results reveal that these particles mainly consisted of cobalt (Figure 4G), indicating that the cobalt ions in BSCF were reduced and exsolved from the perovskite lattice under such low pO₂ atmosphere. This is similar to the previous observations of the cobalt-based oxygen transport membrane (Jiang et al., 2010a, 2010b). The slight carbon enrichment at the CH₄-CO₂ side of the spent membrane (Figure S8) is probably due to a small amount of coke deposition and/or carbonate formation on the membrane surface. To examine the CO₂ tolerance of SMZ-Ti, the SMZ-Ti sample was subjected to annealing in 7.5 vol.% CO₂/He at 990°C for 24 h. The cubic structure of
CO₂-annealed SMZ-Ti remained unchanged, and no obvious carbonate formation was observed (Figure S9). This observation is in contrast with that for BSCF after exposure to CO₂ under the same condition. These results clearly demonstrate that SMZ-Ti had better CO₂ tolerance than BSCF. Compared with the as-prepared SMZ-Ti membrane, no obvious difference in the XRD patterns of the spent membrane except the strontium silicate diffraction peaks (due to commercial glass sealant used in this work) was found (Figure S10). Thus, all these results confirm that SMZ-Ti is a reduction-tolerant, CO₂-stable and high-permeability oxygen transport membrane, holding great promise for a new-generation membrane used as membrane reactors.

**Conclusions**

We report the first novel chemical environment-induced mixed conducting SMZ-Ti oxygen transport membrane (OTM) containing neither cobalt nor iron. Contrary to the well-known cobalt- or iron-containing membrane suffering from poor reduction tolerance, our results demonstrate that the novel SMZ-Ti membrane exhibits both excellent chemical stability for 100 h in 20 vol.% H₂/Ar and environment-induced mixed ionic-electronic conductivity due to the modest reduction of Ti⁴⁺ to Ti³⁺ in low pO₂. These features dovetail exactly with OTM reactors to couple two reactions under low pO₂, which was also highlighted by coupling water splitting with methane reforming at the opposite sides to simultaneously obtain pure hydrogen and synthesis gas. Our findings of a new class of mixed ionic-electronic conductor can extend the limited choice of OTM materials to include titanates and open up new avenues for the design of promising chemically stable membrane materials for use in high-performance membrane reactors toward green and sustainable chemistry.

**Limitations of the Study**

In this study, the thickness of the SMZ-Ti membrane used is 700 μm. So, hollow fiber configuration SMZ-Ti membranes with thin dense layer and larger effective area will be developed for further improving the permeation flux.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**SUPPLEMENTAL INFORMATION**

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.08.032.

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**AUTHOR CONTRIBUTIONS**

H.J. and G.H. conceived and designed the experiments. G.H. conducted the experiments and summarized the data. W.L. conducted the sample preparation. C.-L.T. performed the modeling of impedance spectra. X.X. undertook the treatment of BSCF sample. S.B. and W.A.M. assisted with the impedance measurement and sample annealing. H.J. supervised the whole work. H.J. and G.H. wrote the manuscript.

**DECLARATION OF INTERESTS**

The authors declare that they have no competing interests.

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REFERENCES

Balachandran, U., and Eror, N.G. (1981). Electrical conductivity in strontium titanate. J. Solid State Chem. 39, 351–359.

Bharti, B., Kumar, S., Lee, H.N., and Kumar, R. (2016). Formation of oxygen vacancies and 73rd state in TiO2 thin film and enhanced optical properties by air plasma treatment. Sci. Rep. 6, 32355.

Bouwmeester, H.J.M. (2003). Dense ceramic membranes for methane conversion. Catal. Today 82, 141–150.

Calle-Vallejo, F., Martínez, J.I., García-Lastra, J.M., Mengesen, M., and Rosmeisld, J. (2010). Trends in stability of perovskite oxides. Angew. Chem. Int. Ed. 49, 7669–7701.

Chen, C.-F., King, G., Dickerson, R.M., Papin, P.A., Gupta, S., Kellogg, W.R., and Wu, G. (2015). Oxygen-deficient BaTiO3 perovskite as an efficient bifunctional oxygen electrocatalyst. Nano Energy 13, 423–432.

Chen, Y., de Glee, B., Tang, Y., Wang, Z., Zhao, B., Wei, Y., Zhang, L., Yoo, S., Pei, K., Kim, J.H., et al. (2018). A robust fuel cell operated on nearly dry methane at 500 °C enabled by synergetic thermal catalysis and electrocatalysis. Nat. Energy 3, 1042–1050.

De Souza, R.A. (2015). Oxygen diffusion in SrTiO3 and related perovskite oxides. Adv. Funct. Mater. 25, 6326–6342.

Fang, W., Steinbach, F., Cao, Z., Zhu, X., and Lai, D. (2016). A highly efficient sandwich-like symmetrical dual-phase oxygen-transporting membrane reactor for hydrogen production by water splitting. Angew. Chem. Int. Ed. 128, 8790–8793.

Furler, P., Scheffe, J.R., and Steinfeld, A. (2012). Syngas production by simultaneous splitting of H2O and CO2 via ceria redox reactions in a high-temperature solar reactor. Energy Environ. Sci. 5, 353–360.

Gardner, T.H., Spivey, J.J., Kugler, E.L., and Pakhare, D. (2013). CH3CO2–forming over Ni-substituted barium hexaaluminate catalysts. Appl. Catal. A Gen. 455, 129–136.

Inoue, T., Seki, N., Kamimura, J.-i., Eguchi, K., and Arai, H. (1991). The conduction mechanism and defect structure of acceptor- and donor-doped SrTiO3. Solid State Ionics 48, 283–293.

Irvine, J.T.S., Sinclair, D.C., and West, A.R. (1990). Electroceramics: characterization by impedance spectroscopy. Adv. Mater. 2, 132–138.

Jiang, H., Cao, Z., Schirmeister, S., Schiestel, T., and Caro, J. (2010a). A coupling strategy to produce hydrogen and ethylene in a membrane reactor. Angew. Chem. Int. Ed. 49, 5656–5660.

Jiang, H., Liang, F., Czuprát, O., Efimov, K., Feldhoff, A., Schirmeister, S., Schiestel, T., Wang, H., and Caro, J. (2010b). Hydrogen production by water dissociation in surface-modified BaCo2Fe2Zr1−xO7−x hollow-fiber membrane reactor with improved oxygen permeation. Chem. Eur. J. 16, 7898–7903.

Jiang, H., Wang, H., Liang, F., Werth, S., Schiestel, T., and Caro, J. (2009a). Direct decomposition of nitrous oxide to nitrogen by in situ oxygen removal with a perovskite membrane. Angew. Chem. Int. Ed. 48, 2983–2986.

Jiang, H., Xing, L., Czuprát, O., Wang, H., Schirmeister, S., Schiestel, T., and Caro, J. (2009b). Highly effective NO decomposition by in situ removal of inhibitor oxygen using an oxygen transporting membrane. Chem. Commun. 6738–6740.

Jiang, H., Wang, H., Werth, S., Schiestel, T., and Caro, J. (2008). Simultaneous production of hydrogen and synthesis gas by combining water splitting with partial oxidation of methane in a hollow-fiber membrane reactor. Angew. Chem. Int. Ed. 47, 9361–9364.

Kathiraser, Y., Wang, Z., and Kawi, S. (2013). Oxidative CO2 reforming of methane in La2−xSrxCuO4−δ (LSCO) hollow fiber membrane reactor. Environ. Sci. Technol. 47, 14510–14517.

Li, M., Pietrowski, M.J., De Souza, R.A., Zhang, H., Reaney, I.M., Cook, S.N., Kilter, J.A., and Sinclair, D.C. (2014). A family of oxide ion conductors based on the ferroelectric perovskite Na0.5Bi0.5TiO3. Nat. Mater. 13, 31–35.

Li, W., Cao, Z., Cai, L., Zhang, L., Zhu, X., and Yang, W. (2017). H2O-tolerant oxygen-permeable ceramic membranes for hydrogen separation with a performance comparable to those of palladium-based membranes. Energy Environ. Sci. 10, 101–106.

Li, W., Zhu, X., Chen, S., and Yang, W. (2016). Integration of nine steps into one membrane reactor to produce synthesis gases for ammonia and liquid fuel. Angew. Chem. Int. Ed. 55, 8566–8570.

Luo, H., Efimov, K., Jiang, H., Feldhoff, A., Wang, H., and Caro, J. (2013). CO2-stable and cobalt-free dual-phase membrane for oxygen separation. Angew. Chem. Int. Ed. 50, 759–763.

McCom, T.D., and Irvine, J.T.S. (2001). B site doped strontium titanate as a potential SOFC substrate. Ionics 7, 116–121.

Morejoud, S.H., Zanón, R., Escalés, S., Yuste, C., Tizad, I., Malero-Fejdi, H., Vestre, P.K., Coors, W.G., Martínez, A., Norby, T., Serra, J.M., and Kjølseth, C. (2016). Direct conversion of methane to aromatics in a catalytic co-ionic membrane reactor. Science 353, 563–566.

Neagu, D., Tsekouras, G., Miller, D.N., Me´ nard, J.P., and Ghoniem, A.F. (2015). Toward enhanced hydrogen generation from water using oxygen permeating LFC membranes. Phys. Chem. Chem. Phys. 17, 10093–10107.

Ni, J.X., Schroeder, M., Weirich, T., and Mayer, J. (2010). Behavior of BaCo2Fe2O7, Fe, NbO1−δ, and SrBi1−δTiO3 perovskite in CO2-containing atmospheres: degradation mechanism and materials design. Chem. Mater. 22, 6246–6253.

Zhang, C., Sunarso, J., and Liu, S. (2017). Designing CO2-resistant oxygen-selective mixed ionic-electronic conducting membranes: guidelines, recent advances, and forward directions. Chem. Soc. Rev. 46, 2941–3005.

Zhang, K., Zhang, G., Liu, Z., Zhu, J., Zhu, N., and Jin, W. (2014). Enhanced stability of membrane reactor for thermal decomposition of CO2 via porous-dense-porous triple-layer composite membrane. J. Membr. Sci. 471, 9–15.

Zhu, X., Wang, H., and Yang, W. (2006). Structural stability and oxygen permeability of cerium lightly doped BaFe12O19 ceramic membranes. Solid State Ionics 177, 2917–2921.
Supplemental Information

Chemical Environment-Induced Mixed Conductivity of Titanate as a Highly Stable Oxygen Transport Membrane

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Supplemental Information

Supporting Figures

Figure S1. XRD patterns of LC-Fe and ST-Fe membrane materials before and after annealing in 20 vol.% H₂/Ar at 900 °C for 24 h. (Related to Figure 1b)

As shown in Figure S1, the cubic perovskite structures of the conventional LC-Fe and ST-Fe membrane materials were decomposed seriously after exposure to 20 vol.% H₂/Ar atmosphere for 24 h, indicating the poor chemical stability under reducing atmospheres relative to SMZ-Ti.
Figure S2. XRD patterns of SMZ-Ti oxides with different Mg content: SrMg$_x$Zr$_{0.05}$Ti$_{0.95-x}$O$_{3-\delta}$ (SMZ-Ti, x= 0.05; 0.08, 0.1, 0.15) after calcinations at 950 °C for 10 h. (Related to Figure 1a)

Compared to SrMg$_{0.15}$Zr$_{0.05}$Ti$_{0.8}$O$_{3-\delta}$ consisted of a mixed dual phases (i.e. perovskite and MgO), all the other three titanates with lower Mg doping content, x = 0.05, 0.08 and 0.1, can be well crystallized with cubic perovskite structure without any additional phases. In addition, for low Mg contents (x ≤ 0.1), the XRD peak shifts gradually towards smaller angles with increasing Mg content from x = 0.05 to 0.1, indicating the expansion of the unit cell since the ionic radius of Mg$^{2+}$(VI) (0.72 Å) is larger than those of Ti$^{4+}$. These results indicate that the solubility limit of Mg cation in SrMg$_x$Zr$_{0.05}$Ti$_{0.95-x}$O$_{3-\delta}$ is higher than 0.1. These observations are in agreement with the results for SrTi$_1$$_{1-y}$Mg$_y$O$_3$ systems (Tkach et al., 2004). In the meanwhile, considering the benefits of Mg$^{2+}$ ions doping for oxygen vacancy formation in SMZ-Ti, we selected SrMg$_{0.15}$Zr$_{0.05}$Ti$_{0.8}$O$_{3-\delta}$ to demonstrate its environment-induced mixed conductivity for coupling H$_2$O splitting with CH$_4$ reforming under low pO$_2$ atmospheres.
As shown in Figure S3, before CH$_4$ and CO$_2$ reaching the membrane surface, dry reforming of methane with carbon dioxide (\(\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2\)) first takes place in the top zone of the catalyst, i.e. Ni/Al$_2$O$_3$. The generated syngas will further move to the membrane surface and be oxidized by the permeated oxygen on the membrane surface (\(\text{CO} + \text{H}_2 + 2\text{O}^* \rightarrow \text{H}_2\text{O} + \text{CO}_2\)). At the same time, part of the permeated oxygen may also be consumed by methane combustion according to POM reaction (\(\text{CH}_4 + \text{O}^* \rightarrow \text{CO} + 2\text{H}_2\)). The formed H$_2$O and CO$_2$ will leave from the membrane surface and react with the excess methane to produce syngas (CO$_2$ reforming and H$_2$O reforming) before leaving the catalyst bed.
Compared with the fresh membrane, no additional peaks of SMZ-Ti after electrical impedance spectroscopy (EIS) measurement was observed, which indicates the excellent redox stability of SMZ-Ti material in humidified H₂ and dry H₂ at high temperatures.

Figure S4. XRD pattern of SMZ-Ti membrane before and after electrical impedance spectroscopy (EIS) measurement for nearly 300 h. (Related to Figure 3)
These plots were created by using Gibbs free energy minimization algorithm on HSC Chemistry 5.0 software. This calculation shows that the methane conversion at all temperature after 800 °C is constant for each case. Formation of H₂O by reverse water gas shift (RWGS) is not significant between 400 – 800 °C, which is in agreement with the free energy calculations by Wang et al. (Wang et al., 1996). According to Figure S5, the equilibrium compositions of helium and methane (C₅He and C₅CH₄) at 990 °C are 67.4% and 6.52% respectively. So, the equilibrium methane conversion (XCH₄, 990 °C) is 50.02%.

\[
X_{\text{CH}_4, \ 990 {^\circ}C} = \frac{F_{\text{He, feed}} \times C_{\text{He}}}{F_{\text{CH}_4, \text{ feed}}} \times 100\% = \frac{3 \times 15.5 \times 0.0652}{0.674} \times 100\% = 50.02\%
\]

This methane conversion is lower than that using SMZ-Ti membrane reactor coupling water splitting with dry reforming of methane, suggesting that partial oxidation of methane (POM) may occur simultaneously with DRM in the SMZ-Ti membrane reactor.
Figure S6. TGA behavior of the Ni/Al₂O₃ catalyst after the long-term methane reforming test. (Related to Figure 4a)

Similar to previous reports about TGA behaviors of spent Ni/Al₂O₃ catalyst (Zhou et al., 2015), an increase in the sample weight for the catalyst in the present work was observed at temperatures of 100 – 600 °C that could be due to the oxidation of Ni to nickel oxides. Higher than 600 °C, the weight of the catalyst decreased quickly and became stable at approximately 98% at 800 °C. Based on the TGA curve, the amount of deposited coke on the spent Ni/Al₂O₃ catalyst was only approximately 3.05 wt.%. 
Figure S7 SEM images of as-prepared SMZ-Ti, where (a) and (b) are from surface view and (c) and (d) are from cross sectional views. (Related to Figure 4)

As shown in Figure S7, SMZ-Ti membrane is well sintered with large grains of 1 – 5 μm according to the surface morphology. From the cross-sectional view, the SMZ-Ti membrane was dense without pores.
As shown in Figure S8, no obvious enrichment of strontium and carbon along the fractured cross-section of the spent SMZ-Ti membrane was observed, indicating the SMZ-Ti membrane was not eroded by CO$_2$ during long-term exposure of methane and carbon dioxide at high temperature. In contrast, the performance of the cobalt and iron containing SrCo$_{0.4}$Fe$_{0.5}$Zr$_{0.1}$O$_{3-\delta}$ membrane reactor for coupling of POM with carbon dioxide decomposition was degraded seriously within 60 hours and the membrane broke significantly due to the erosion by the CO$_2$ and reducing atmospheres (Jin et al., 2008).
According to the XRD results, the cubic structure of SMZ-Ti remained unchanged, and no carbonate formation was observed after the annealing. This observation is in contrast with that for Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF), for which the perovskite structure has been partially or almost completely decomposed after exposure to CO$_2$ under the same condition. These results clearly demonstrate excellent CO$_2$ tolerance of SMZ-Ti.
Figure S10 XRD patterns on the steam side (a) and the methane side (b) of spent SMZ-Ti membrane after coupling of water splitting and methane reforming. (Related to Figure 1a and Figure 4)

Figure S10 shows the XRD patterns of both side of the SMZ-Ti membrane after coupling process. Except the additional peaks of strontium silicate resulted from ceramic sealant at high temperature, the patterns either for steam side or methane side of spent SMZ-Ti membrane show no difference, which prove that SMZ-Ti membrane reactor are stable under reactions conditions.
### Supporting Tables

Table S1. The equilibrium $pO_2$ at the two sides of SMZ-Ti membrane under four conditions. (Related to Figure 2)

| Condition | Feed side | Permeate side | Gas composition for calculation | Equilibrium $pO_2$ at 990 °C / atm |
|-----------|-----------|---------------|---------------------------------|-----------------------------------|
| I         | N$_2$ (47.4 cm$^3$ min$^{-1}$) | He (20 cm$^3$ min$^{-1}$), O$_2$ (0.012 cm$^3$ min$^{-1}$) | 0.21                             |
| II        | N$_2$ (11.85 cm$^3$ min$^{-1}$) | He (15 cm$^3$ min$^{-1}$), H$_2$ (5 cm$^3$ min$^{-1}$), O$_2$ (0.081 cm$^3$ min$^{-1}$) | 0.204                            |
| III       | He (10 cm$^3$ min$^{-1}$) | N$_2$ (4 cm$^3$ min$^{-1}$), CH$_4$ (3 cm$^3$ min$^{-1}$), O$_2$ (0.13 cm$^3$ min$^{-1}$) | 2.45 x 10$^{-9}$                  |
| IV         | He (10 cm$^3$ min$^{-1}$) | N$_2$ (4 cm$^3$ min$^{-1}$), CH$_4$ (3 cm$^3$ min$^{-1}$) | 3.87 x 10$^{-21}$                  |

*a* Refer to Figure 2.
Table S1 shows the thermodynamic equilibrium $pO_2$ at 990 °C on the feed and permeate of SMZ-Ti membrane subjected to four different conditions at 1 atm. All the equilibrium composition on the two sides are calculated using Gibbs free energy minimization simulations using HSC Chemistry 5.0. Particularly in the case of condition III and condition IV, carbon formation at the permeate side even though not obvious, was taken into account due to the high CH$_4$/O$_2$ ratio of ~25 and CH$_4$/CO$_2$ feed ratio of 2 at high temperature,(Mette et al., 2016; York et al., 2003) respectively.
Table S2. Exit gas composition and carbon balance as function of time of methane reforming into syngas via SMZ-Ti membrane reactor. (Related to Figure 4a)

| Operating time / h | Composition (%) | Carbon balance (X<sub>in</sub>-X<sub>out</sub>/X<sub>in</sub>)*100 |
|--------------------|-----------------|----------------------------------|
|                    | CH<sub>4</sub> | CO<sub>2</sub> | CO  | H<sub>2</sub> | He  | N<sub>2</sub> |                    |
| 1                  | 3.71           | 0.09               | 14.90 | 17.34   | 47.69 | 16.27       | 0.71               |
| 10                 | 3.69           | 0.08               | 14.88 | 17.27   | 47.77 | 16.31       | 1.16               |
| 20                 | 3.57           | 0.08               | 14.92 | 17.13   | 47.93 | 16.37       | 1.87               |
| 35                 | 3.65           | 0.08               | 14.81 | 17.16   | 47.93 | 16.37       | 2.06               |
| 45                 | 3.61           | 0.07               | 14.80 | 17.23   | 47.92 | 16.37       | 2.33               |
| 75                 | 3.50           | 0.06               | 14.80 | 17.23   | 48.02 | 16.39       | 3.21               |

As shown in Table S2, the mole composition of the effluent stream at the permeate side of SMZ-Ti membrane reactor typically contains ~48 % He (carrier gas), ~16.3 % N<sub>2</sub> (internal standard gas in GC), ~3.6 % CH<sub>4</sub>, ~17.2% H<sub>2</sub>, ~14.9% CO and a small amount of CO<sub>2</sub> under H<sub>2</sub>O / (CH<sub>4</sub>-CO<sub>2</sub>) partial pressure gradient at 990 °C, revealing that the deep oxidation products H<sub>2</sub>O and/or CO<sub>2</sub> are finally converted with unreacted CH<sub>4</sub> to syngas via reforming process. The carbon balances maintain over 96% within the investigation period. However, it is clear that the mole balance of carbon increased slowly with operating time, suggesting that slight carbon deposition may take place in the catalyst bed.
**Transparent Methods**

**Synthesis**

The SrMg$_{0.15}$Zr$_{0.05}$Ti$_{0.8}$O$_{3-\delta}$ (SMZ-Ti) membrane powders were synthesized by a combined citric acid and ethylenediaminetetraacetic acid (EDTA) method, as described in detail elsewhere. (Tong et al., 2003) Briefly speaking, stoichiometric amounts of Sr(NO$_3$)$_2$, Mg(NO$_3$)$_2$, and ZrO(NO$_3$)$_3$ powder were dissolved in de-ionized water, followed by the addition of EDTA and citric acid with EDTA: citric acid: total of metal cations molar ratio controlled at around 1: 1.5: 1. After agitation for a certain time, the pH value of the solution was adjusted to round 9 using ammonia solution to form solution A. Then, the stabilized titanium solution B consisting of proper amounts of tetrabutyl titanate (Ti(OC$_4$H$_9$)$_4$), ethanol (CH$_3$CH$_2$OH), acetic acid (CH$_3$COOH) and lactic acid (CH$_3$CHOHCOOH) was introduced into the solution A. The mixed solution was then heated at 120-150 °C for several hours under constant stirring to obtain a gel, which was calcined at 950 °C for 10 h to obtain SMZ-Ti powder with final composition. The resulting powders were uniaxially pressed at 10 MPa into disk membranes. Followed by the sintering of the green disks at 1450 °C in air for 10 h, dense SMZ-Ti membrane disks with thickness of 0.7 mm were obtained.

Similarly, the SrMg$_{0.05}$Zr$_{0.05}$Ti$_{0.9}$O$_{3-\delta}$, SrMg$_{0.08}$Zr$_{0.05}$Ti$_{0.87}$O$_{3-\delta}$, SrMg$_{0.1}$Zr$_{0.05}$Ti$_{0.85}$O$_{3-\delta}$, La$_{0.9}$Ca$_{0.1}$FeO$_{3-\delta}$ (LC-Fe), SrTi$_{0.75}$Fe$_{0.25}$O$_{3-\delta}$ (ST-Fe), BaFe$_{0.4}$Zr$_{0.2}$Co$_{0.4}$O$_{3-\delta}$ (BFZ-Co), Ba$_{0.98}$Ce$_{0.05}$Fe$_{0.95}$O$_{3-\delta}$ (BC-Fe), Ce$_{0.85}$Sm$_{0.15}$O$_{1.925}$ (75 wt.% – Sm$_{0.6}$Sr$_{0.4}$Al$_{0.3}$Fe$_{0.7}$O$_{3-\delta}$ (25 wt.%)) (SDC-SSAFe) and Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ (BSCF) membrane powders were also synthesized by the combined citric acid –EDTA method. All the powders were calcined at 950 °C for 10 h to crystallize well in cubic perovskite structures or cubic perovskite-fluorite structure.
For the deposition of SMZ-Ti porous layer onto the dense SMZ-Ti membrane, SMZ-Ti powders were first crushed well in a mortar, then several drops of distilled water were added to obtain SMZ-Ti paste. The paste was coated on one side of a SMZ-Ti membrane using a fine brush. The coated membranes were sintered at 1300 °C for 2 h in air with a heating and cooling rate of 3 °C/min.

**Electrical impedance measurement**

The dense SMZ-Ti sample for impedance measurement was 1.03 mm thick with a diameter of 15.5 mm. Pt ink was sputtered onto both faces of the sample, and then fired at 1000 °C for 2 h. Two-probe AC impedance spectroscopy of SMZ-Ti at 900 °C was performed using an Alpha-A high performance frequency analyzer (Novocontrol Technologies, Germany) with a voltage amplitude of 40 mV and a frequency range spanning from 0.05 to 1 M Hz. The impedance was measured at 900 °C under atmospheres ranging from wet to dry H₂. Similar to previous studies, (Benisek et al., 2005; Lai et al., 2005) oxygen partial pressures lower than 0.21 atm were obtained using mixtures of Ar, H₂O and H₂, assuming a thermodynamic equilibrium between O₂, H₂ and H₂O. The oxygen partial pressure with H₂/H₂O ratio of 1, 10 and 30 at 900 °C calculated by HSC chemistry 5.0 are $4.9 \times 10^{-15}$, $4.9 \times 10^{-17}$ and $5.5 \times 10^{-18}$ atm, respectively. The total gas flow rates were fixed at 60 cm$^3$ min$^{-1}$ using mass flow controllers. The whole system was allowed to stabilized under each condition before starting measurement. The typical stabilization time was over 50 h under low oxygen partial pressures atmospheres.
Membrane permeation performance

SMZ-Ti membrane pellet was sealed onto the alumina tube using commercial glass powders (Schott AG, Germany) and kept in the middle of an oven for isothermal conditions. The effective membrane area was 0.62 cm$^2$. The membrane reactor configuration was described elsewhere. (Cao et al., 2013) A Ni-based catalyst (0.3 g, Süd Chemie AG) was loaded on the SMZ-Ti porous layer of the membrane disk. The gas leakage of SMZ-Ti membrane at operating temperature was evaluated on the basis of our previous work (Liang et al., 2016). Basically, synthesized air and helium were introduced to the opposite sides of SMZ-Ti membrane. The concentrations of the effluent gas at helium side were measured online by a gas chromatograph (GC, Agilent 7890B). It is acceptable for permeation measurement when the amount of leakage oxygen is typically less than 5% of the total oxygen flux. Also, the gas leakage during the permeation measurement was on-line assessed by the leakage nitrogen from CH$_4$-CO$_2$ side to H$_2$O side of SMZ-Ti membrane.

After leakage test, two sides of SMZ-Ti membrane were successively exposed to four different conditions at 990 °C (i.e.: Air/He, Air/He-H$_2$, He-H$_2$O/CH$_4$-N$_2$-He, He-H$_2$O/CH$_4$-CO$_2$-N$_2$-He,) for oxygen permeation flux measurement. All the gas flow rates were controlled by gas mass-flow controllers (Bronkhorst). The H$_2$O flow was controlled by a liquid mass-flow controller (Bronkhorst) and completely evaporated at 160 °C before it was fed to the reactor. Also the lines from the outlets of products to the gas chromatograph were heated to 160 °C. Gas composition was analyzed by an online gas chromatograph (GC, Agilent 7890B). The oxygen permeation fluxes were calculated from the amount of oxygen in the inlet and outlet streams on the air side.
(Cond. I and Cond. II) or from the amount of generated hydrogen in the outlet streams on the steam side (Cond. III and Cond. IV).

Assuming that the oxygen from water splitting on the steam side under Cond. IV was totally removed and the total flow rate is constant, the hydrogen production rate on the steam side was calculated from the total flow rate $F_{\text{steam}}$ (cm$^3$ min$^{-1}$), the hydrogen concentration $c(H_2)$, and the effective membrane area $S$(cm$^2$) according to Equation (1). The $\text{CH}_4$ conversion $X(\text{CH}_4)$ and the CO selectivity $S$(CO) on the methane-carbon dioxide side were calculated as Equations (2) and (3), where $F(i)$ is the flow rate of species $i$ on the methane-carbon dioxide side of the membrane.

$$ J(H_2) = \frac{F_{\text{steam}} c(H_2)}{S} $$

$$ X(\text{CH}_4) = \left(1 - \frac{F(\text{CH}_4,\text{out})}{F(\text{CH}_4,\text{in})}\right) \times 100\% $$

$$ S$(CO) = \left(\frac{F$(CO$)}{F(\text{CH}_4,\text{in}) + F$(CO$_2$,in$) - F(\text{CH}_4,\text{out}) - F$(CO$_2$,out$)}\right) \times 100\% $$

**Thermal treatment**

The pure SMZ-Ti, BFZ-Co, BC-Fe, SDC-SSAFe, LC-Fe and ST-Fe powders were treated in 20% H$_2$/Ar at 900 °C to prepare the H$_2$-exposed samples. Also, SMZ-Ti and synthesized BSCF powders were annealed in 7.5 vol. % CO$_2$ in helium at 990 °C for 24 h. 1.0 gram of BSCF powder was uniaxial pressed into green disk under 8 MPa. The green pellet was then sintered in air at 1130 °C for 10 h in muffle furnace. Afterwards, the BSCF membrane was treated under H$_2$/H$_2$O atmosphere (1 bar, 2.5 vol.% H$_2$, 75 vol.% H$_2$O, 22.5 vol. % He, total flow is 40 cm$^3$ min$^{-1}$) at 900 °C for 0.5 h.
Characterization

The crystal structures of SMZ-Ti, BFZ-Co, BC-Fe and SDC-SSAFe membrane powders were investigated by using a Bruker D8 ADVANCE diffractometer with a monochromator using Cu Kα radiation. Scanning electron microscopy (SEM) of SMZ-Ti and BSCF membranes was performed using a JEOL JSM-6700F field emission scanning electron microscope equipped with an ultrathin window Energy Dispersive X-ray detector to allow for elemental analysis. X-ray photoelectron spectroscopy (XPS) of SMZ-Ti membrane was performed on a PHI 5000 Versa Probe II (ULVAC-PHI, Inc) model X-ray photoelectron spectrometer instrument (AlKα radiation, \( hν = 1.486 \text{ keV}, \ 50 \text{ W} \)) to analyze the surface of the sample before and after AC electrical impedance measurement. The binding energies (BE) were calibrated by setting the Ti 2p3 peak with the highest BE to 458.7 eV (Naumkin et al., 2012). The amount of carbon deposited on the catalyst was analyzed with TGA. The spent catalyst powder (10.288 mg) was placed in an alumina crucible and heated in flowing Air (rate: 50 cm\(^3\) min\(^{-1}\)) at a heating rate of 5 K min\(^{-1}\) to 800 ºC, followed by cooling to room temperature.
Supplemental References

Benisek, A., Sitte, W. (2005). Control of oxygen partial pressure by means of H₂–H₂O–O₂ or CO–CO₂–O₂ gas mixtures, J. Electrochem. Soc. 152, H157-H160.

Cao, Z., Jiang, H., Luo, H., Baumann, S., Meulenberg, W.A., Assmann, J., Mleczko, L., Liu, Y., Caro, J. (2013). Natural gas to fuels and chemicals: Improved methane aromatization in an oxygen-permeable membrane reactor, Angew. Chem. Int. Ed. 52, 13794-13797.

Jin, W., Zhang, C., Chang, X., Fan, Y., Xing, W., Xu, N. (2008). Efficient catalytic decomposition of CO₂ to CO and O₂ over Pd/mixed-conducting oxide catalyst in an oxygen-permeable membrane reactor, Environm. Sci. Tech. 42, 3064-3068.

Lai, W., Haile, S.M. (2005). Impedance spectroscopy as a tool for chemical and electrochemical analysis of mixed conductors: A case study of ceria, J. Am. Ceram. Soc. 88, 2979-2997.

Liang, W., Megarajan, S.K., Liang, F., Zhang, Y., He, G., Liu, Z., Jiang, H. (2016). Coupling of N₂O decomposition with CO₂ reforming of CH₄ in novel cobalt-free BaFe₀.₉Zr₀.₀₅Al₀.₀₅O₃₋δ oxygen transport membrane reactor, Chem. Eng. J. 305, 176-181.

Mette, K., Kühl, S., Tarasov, A., Willinger, M.G., Kröhnert, J., Wrabetz, S., Trunschke, A., Scherer, M., Gergsdies, F., Düdder, H., Kähler, K., Ortega, K.F., Muhler, M., Schlögl, R., Behrens, M., Lunkenbein, T. (2016). High-temperature stable Ni nanoparticles for the dry reforming of methane, ACS Catal. 6, 7238-7248.

Naumkin, A.V., Kraut-Vass, A., Gaarenstroom, S.W., Powell, C.J., NIST Standard Reference Database 20, Version 4.1. 2012.

Tkach, A., Vilarinho, P.M., Kholkin, A. (2004). Effect of Mg doping on the structural and dielectric properties of strontium titanate ceramics, Appl. Phys. A 79, 2013-2020.

Tong, J., Yang, W., Cai, R., Zhu, B., Xiong, G., Lin, L. (2003). Investigation on the structure stability and oxygen permeability of titanium-doped perovskite-type oxides of BaTi₀.₂CoₓFe₀.₈₋ₓO₃₋δ (x=0.2–0.6), Sep. Purif. Tech. 32, 289-299.

Wang, S., Lu, G.Q., Millar, G.J. (1996). Carbon dioxide reforming of methane to produce synthesis gas over metal-supported catalysts: State of the art, Energy & Fuels 10, 896-904.

York, A.P.E., Xiao, T., Green, M.L.H. (2003). Brief overview of the partial oxidation of methane to synthesis gas, Top. Catal. 22, 345-358.

Zhou, L., Li, L., Wei, N., Li, J., Basset, J.-M. (2015). Effect of NiAl₂O₄ formation on Ni/Al₂O₃ stability during dry reforming of methane, ChemCatChem 7, 2508-2516.