Carbon Dioxide Reforming of Methane using an Isothermal Redox Membrane Reactor

Ronald Michalsky,* Dominique Neuhaus, and Aldo Steinfeld

The continuous production of carbon monoxide (CO) and hydrogen (H₂) by dry reforming of methane (CH₄) is demonstrated isothermally using a ceramic redox membrane in absence of additional catalysts. The reactor technology realizes the continuous splitting of CO₂ to CO on the inner side of a tubular membrane and the partial oxidation of CH₄ with the lattice oxygen to form syngas on the outer side. Lax⁰Srₓ₁₋ₓFe₀.₅O₃₋ₓ (LSCF) membranes evaluated at 840–1030 °C yielded up to 1.27 μmol CO g⁻¹ LSCF⁻¹ from CO₂, 3.77 μmol H₂ g⁻¹ s⁻¹ from CH₄, and CO from CH₄ at approximately the same rate as CO from CO₂. We compute the free energy of the oxygen vacancy formation for La₀.₅Srₓ₀.₅MnO₃₋ₓ (B, B’ = Mn, Fe, Co, Cu) using electronic structure theory to understand how CO₂ reduction limits dry reforming of methane using LSCF and to show how the CO₂ conversion can be increased by using advanced redox materials such as La₀.₅Sr₀.₅MnO₃₋ₓ and La₀.₅Sr₀.₅Mn₀.₅Co₀.₅O₁₋ₓ.

Introduction

Thermochemical redox cycles for splitting of CO₂ and H₂O facilitate storage of solar energy in the form of synthetic chemical fuels, such as CO and H₂ (syngas—the building block of liquid hydrocarbon fuels).[¹] Concentrated solar energy supplies high-temperature process heat to the endothermic reduction of a metal oxide[²]—such as ceria,[³,⁴] ferrites,[⁵,⁶] and perovskites[⁷–⁹]—liberating O₂. In a second exothermic step at lower temperatures, the reduced metal oxide splits CO₂ and H₂O into CO and H₂. Alternatively, isothermal redox cycling driven by pressure swing was demonstrated recently.[⁶,¹¹] To advance this concept, we report dry (CO₂) reforming of CH₄ (dry reforming methane, DRM) into syngas using an isothermal redox membrane reactor, according to the net reaction: CH₄ + CO₂ → 2CO + 2H₂. The concept is based on the continuous splitting of CO₂ to CO on one side of the membrane and the partial oxidation of CH₄ using the lattice oxygen to produce syngas on the other side, with oxygen (vacancies) being conducted across the membrane. We have chosen DRM to demonstrate the utility of redox membranes because the reaction proceeds at elevated temperatures and is endothermic by approximately 247 kJ mol⁻¹ CO₂.[¹²] Typically, catalyst deactivation by coke deposition from DRM side reactions is alleviated by the use of rare noble metal catalysts.[¹³,¹⁴] Such expensive materials[¹⁵] are not required at above 900 °C[¹⁴,¹⁶] if the deposited carbon can be oxidized[¹³,¹⁷] for instance with the lattice oxygen of a metal oxide redox material. Membrane reactors have been used previously for DRM to boost gas conversion by separating H₂[¹³,¹⁴,¹⁶] or to supply heat from the partial oxidation of CH₄ using air as reactant.[¹⁴,¹⁹,²⁰] The latter application is similar to chemical looping with metal oxide redox materials as oxygen carriers.[²¹] Research for solar-driven DRM has focused on non-catalytic DRM, reaching up to 65% CO₂ conversion at 1700 °C[²²] and DRM with fixed beds of CeO₂–Fe₂O₃ reaching 30% CO₂ conversion at 600 °C; H₂ is, however, consumed in the formation of H₂O.[¹⁷,²³]

In this study, we develop and demonstrate the feasibility of DRM using an isothermal redox membrane reactor that combines the benefits of continuous isothermal solar fuel production with those of thermochemical DRM. Conceptually, CO₂ is reduced by the oxygen vacancies of a perovskite membrane into CO:

\[ \text{ABO}_{3-x} + (\delta-x)\text{CO}_2(g) \rightarrow \text{ABO}_{3-x} + (\delta-x)\text{CO}(g) \]  

(1)

The perovskite has ABO₃₋ₓ stoichiometry, where A and B are metal cations in twelve- and six-coordinated interstices and δ is the oxygen non-stoichiometry. The oxygen that is absorbed by the membrane on one side travels along an oxygen vacancy gradient to the other membrane side and is abstracted from the solid by reforming of CH₄ into CO and H₂:

\[ \text{ABO}_{3-x} + (\delta-x)\text{CH}_4(g) \rightarrow \text{ABO}_{3-x} + (\delta-x)\text{CO}(g) + 2(\delta-x)\text{H}_2(g) \]

(2)

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As the oxygen is continuously replenished from CO₂, the formation of a thick layer of reduced metal oxide is avoided, which, in turn, augments the oxygen conduction kinetics.[24,25] Overall, CO₂ and CH₄ are reformed into solar syngas, whose energetic value has been solar-upgraded by a factor of 1.31 over that of the methane feedstock.[24] To achieve this, the redox membrane provides variable metal oxidation states accessible through oxidation with CO₂ and reduction with CH₄ at elevated temperatures. This is in contrast to the previously reported thermolysis of H₂O and CO₂ yielding O₂, H₂, and CO, driven by O₂ separation using dense ceramic membranes,[27,28] and an extension of the previously reported membrane-assisted production of H₂ from H₂O using a reducing gas such as CH₄, CO, or H₂.[29,30]

Results and Discussion
Evaluation of LaₓSr₁₋ₓCo₂Fe₄O₁₀₋₃ redox membranes
To demonstrate the feasibility of this concept, we have selected LaₓSr₁₋ₓCo₂Fe₄O₁₀₋₃ (LSCF) as the redox material. This is based on its superior oxygen conductivity and typically high oxygen vacancy concentrations, stability of the nonstoichiometric cubic phase, the redox activity of cobalt and iron, and the relatively low carbonate formation tendency.[2,6,25,31,32] To optimize performance, the following section provides a guide for the rational design of prospective redox materials using optimized reaction thermodynamics. One-end open tubular LSCF redox membranes were fabricated using a phase inversion technique and evaluated for DRM using a tube-in-shell membrane reactor, as described in detail in the Supporting Information. Figure 1A shows the isothermal production rates of CO by CO₂ splitting in the membrane cavity at steady-state. Figure 1B shows the equivalent rates for the production of CO and H₂ from CH₄ reforming in the reactor shell. The formation of CO from CH₄ is relatively stable over the course of 20 min and, as expected from mass balance, approximately equal to CO formation from CO₂. Purgation of the reactor in absence of the redox membrane at these temperatures with CO₂ did not yield CO. This confirms that CO₂ is reduced into CO at the inner membrane surface and that the abstracted oxygen is transported across the membrane to activate CH₄ at the outer membrane surface, yielding CO and H₂.

CO formation rates increase by approximately two orders of magnitude upon increasing reaction temperatures from 841 to 1029°C, whereas H₂ formation is on average 2.8–6.8 times that of the shell-sided CO formation. This suggests that H₂ is formed by several mechanisms, that is, through reforming of CH₄ into H₂ and CO, but also through CH₄ decomposition into H₂ and solid carbon, and, to a smaller extent, through CH₄ reforming into higher hydrocarbons. Carbon deposition was confirmed visually at the cooler reactor outlet. Further, gas chromatographic (GC) analysis of the shell-sided gas showed traces of C₁H₂ and C₂H₆, whereas CO₂ and H₂O were below the detection limit. Thus, we suggest the decomposition of CH₄ as the major side-reaction to DRM. This is also supported by the higher activation energy for H₂ formation, that is, 158.8 kJ mol⁻¹ as estimated from Arrhenius plots given in the Supporting Information, relative to 96.85 and 127.5 kJ mol⁻¹ for cavity- and shell-sided CO formation. As these values for thermochemical DRM are at the upper end of the range of activation energies for catalytic DRM (i.e., 63–99 kJ mol⁻¹ CO₂ and 63–123 kJ mol⁻¹ CH₄),[13] we expect that the formation of oxygen vacancies limits the reaction kinetics, as this is the major difference in the CH₄ activation step to catalytic DRM.

The maximum fuel production rates at 1029°C were 1.27 ± 0.05 mmol CO LSCF⁻¹ s⁻¹ from CO₂ and 3.77 ± 0.08 mmol H₂ g⁻¹ s⁻¹ from CH₄, as shown with Figure 1A. Figure 2A shows the conversion of CH₄ and CO₂ at various temperatures, reaching at 1029°C 17.0 ± 0.7% and 8.0 ± 0.7%, respectively. This can be understood due to DRM with concurrent CH₄ decomposition. As expected, the yield of CO from CH₄ matches the yield of CO from CO₂, closing the mass balance and confirming total selectivity, as well as indicating the continuous formation, conduction, and consumption of oxygen vacancies. Equilibrium CO₂ conversion for catalytic
DRM at 750–850 °C is above 90%,[33] experimentally reported are 23–96%, dependent on catalyst material and support.[34] Solar-driven catalytic steam reforming of CH₄ at 500 °C has been reported with 14.8% CH₄ conversion, yielding CO₂ and up to 58.2 μmol/g catalyst s⁻¹.[34] Thermochemical conversion of CO₂ and CH₄ into CO and H₂O may yield 150 μmol CO₂·g⁻¹·s⁻¹ (through metal oxide reduction with CH₄) and 10 μmol CO₂·g⁻¹·s⁻¹ (through metal oxide oxidation with CO₂) using a packed bed of 5% Ni/Co₃O₄–Fe₂O₃ at 600 °C[37] and 32 μmol CO₂·g⁻¹·s⁻¹ (through metal oxide oxidation with CO₂) using CeO₂–Fe₂O₃ without a catalyst.[33] The CO and H₂ production rates as well as the conversion of CH₄ and CO₂ reported here are below those reported previously, but there has not been any attempt to optimize the reactor yet. Means to improve CH₄ and CO₂ conversion include increasing the reaction temperature to facilitate a more exergonic CH₄ activation and optimization of the redox material for certain selected operating conditions, as discussed in the following section. Reaction rates may be increased by optimizing the reactor and membrane geometries to minimize the conceivable surface limitations and mass transport limitations. The goal of this work is to demonstrate experimentally, to the best of our knowledge for the first time, the feasibility of continuous syngas production by DRM with an isothermal redox membrane reactor. The process circumvents the use of noble metal catalysts, avoids the formation of CO₂ (from CH₄ or CO oxidation) or H₂O (from CH₄ or H₂ oxidation), and may facilitate an energetically efficient continuous solar fuel production.

Continuous production of solar syngas using the redox membrane reactor concept is in contrast to the cyclic evolution using previous solar reactors.[3,4] This is demonstrated in Figure 2B showing the continuous production of CO from CO₂ in the cavity of the redox membrane at 1029 °C. Integration of the CO production rate at above 1000 °C gives a net CO production of 4.82 mmol CO/LSCF from CO₂ after 85 min.

Decreasing CO production, as shown in Figure 2B after approximately two hours, can be understood due to minor but gradual deposition of carbon at the membrane exterior. This can be avoided by using higher reaction temperatures and by co-feeding H₂O.

Figure 3 shows scanning electron microscopy (SEM) and X-ray diffraction (XRD) analyses of the membranes before and after DRM. The membranes have a dense gas-tight surface, as shown in Figure 3A, and an asymmetric bulk structure derived from the synthesis[18,33] as shown in Figure 3B. The asymmetric structure was preserved after several hours of DRM (Figure 3D). Carbon deposited at the surface (Figure 3C) due to CH₄ decomposition.[14,16,36] Amorphous carbon was detected as well by XRD, shown in Figure 3E.

The sharpening of the diffraction signals indicates the desirable sintering of the metal oxide particles upon fabricating dense membranes, but detrimental carbonate formation[13,37] was not observed. The asymmetric structure indicates that the gas conversion may be increased[38] by using membranes featuring a high specific surface area[39] on the side that limits fuel yields.

Understanding the redox capacity of metal oxides for DRM

To describe thermodynamic limits[7] and trends[38] in the performance of metal oxide redox materials and to guide the optimization of redox materials for DRM, Figure 4A plots the Gibbs free energy (ΔG) of the metal oxide oxidation with CO₂ [Eq. (1)] and the metal oxide reduction with CH₄ [Eq. (2)] for binary metal oxides vs. the enthalpy of the oxide reduction. The analysis displays a trade-off inherent to redox materials:[10,39,40] materials that facilitate high CO₂ conversion bind lattice oxygen strongly, whereas materials that facilitate high CH₄ conversion bind lattice oxygen weakly. The ideal materials compositions are where these effects balance, located at the intersection of both curves. Ideally, both reac-
The redox cycle is and the reforming of CH$_2$08. We employ electrochemical activation with increasing temperature. The DFT models of the perovskites surfaces are shown with panel D representatively shown with Figure 4D. Plotting of density functional theory calculations with increasing temperature. Perovskites circumvent changes of the crystal class and phase of stoichiometric metal oxide redox materials\cite{2,8–10} and have attracted much attention for fuel cells and oxygen separation due to their tunable oxygen vacancy concentrations and high oxygen vacancy conductivities.\cite{25,31} We employ electronic structure theory to quantify the thermodynamic limitations of LSCF redox membranes and to identify advanced perovskite compositions for solar-driven DRM. The thermochemical stability and the reaction energetics for perovskites are calculated from the scaling relation of density functional theory (DFT)-computed free energies of oxygen vacancy formation, $\Delta G[O]$, for La$_{1-x}$Sr$_x$B$_{1/2}$O$_{3-\delta}$ and the redox energetics of bulk metal oxides. To establish trends in $\Delta G[O]$ we have chosen B, B’ = Mn, Fe, Co, Cu and computed $\Delta G[O]$ for all possible terminations of the thermodynamically stable (010) facet\cite{39} shown with Figure 4D. Plotting the data for perovskites together with those for binary metal oxides shows, in Figure 4A, that perovskites can reproduce the redox energetics of expensive or toxic materials\cite{39}—such as LaCuO$_2$-terminated La$_{1/2}$Sr$_{1/2}$Fe$_{0.5}$Cu$_{0.5}$O$_{3-\delta}(010)$ with a stability comparable to that of RhO/Rh$_2$O, as shown in the Supporting Information. Furthermore, perovskites may fill stability gaps where no simple metal oxides are available—for example, SrCuO$_2$-terminated La$_{1/2}$Sr$_{1/2}$Fe$_{0.5}$Cu$_{0.5}$O$_{3-\delta}(010)$ has a stability that is intermediate to Auo$_2$/Au and Ag$_2$O/Ag. Figure 4B,C indicates that DRM with LSCF redox membranes is limited thermodynamically by CO$_2$ reduction. We suggest that better materials choices are La$_{1/2}$Sr$_{1/2}$Mn$_{1/2}$O$_{3-\delta}$ and La$_{1/2}$Sr$_{1/2}$MnO$_{3-\delta}$, which approach free energy values of zero for both reactions at 627°C. At higher temperatures, higher conversions may be achieved with thermochemically more stable perovskites.

**Figure 4.** Volcano-type plots for solar-driven isothermal CO$_2$ reforming of CH$_4$ at 1 bar and (A) 25°C, (B) 627°C, and (C) 1027°C. Ideal redox materials are located at the intersections of the linear correlations of the free energy of CO$_2$ reduction [Eq. (1), light blue symbols] and CH$_4$ activation [Eq. (2), dark blue symbols] with the enthalpy of reducing a metal oxide into the reduced phase and O$_2$. Negative free energy differences mark exergonic reactions (shaded). Solid symbols are for binary metal oxides (i.e., Ag$_2$O/Ag, Au$_2$O$_3$/Au, BaO/BO, CeO$_2$/CeO, CoO/CoO, CuO/CuO, Cu$_2$O/CuO, Fe$_2$O$_3$/Fe$_2$O$_3$, Fe$_3$O$_4$/Fe$_3$O$_4$, FeOOH/FeOOH, Mn$_2$O$_3$/MnO$_2$, MnO$_2$/MnO, MoO$_2$/MoO, Na$_2$O$_2$/Na$_2$O, Nb$_2$O$_5$/NbO, NiO/NiCO, O$_x$/O$_x$, O$_2$/O$_2$, PrO$_2$/PrO, PbO$_2$/PbO, Pb(OH)$_2$/PbO, RhO$_2$/RhO, RuO$_2$/Ru, SnO$_2$/SnO, TiO$_2$/TiO, TiO$_2$/TiO, TiO$_2$/TiO, TiO$_2$/TiO, TiO$_2$/TiO, TiO$_2$/TiO, TiO$_2$/TiO, V$_2$O$_5$/V$_2$O$_5$, V$_2$O$_5$/V$_2$O$_5$, V$_2$O$_5$/V$_2$O$_5$, V$_2$O$_5$/V$_2$O$_5$, WO$_3$/WO$_3$, WO$_3$/WO$_3$, WO$_3$/WO$_3$, WO$_3$/WO$_3$, ZnO/ZnO, and ZrO$_2/ZrO$); empty symbols are for La$_{2-x}$Sr$_x$B$_{1/2}$O$_{3-\delta}$/La$_{2-x}$Sr$_x$B$_{1/2}$B$_{1/2}$O$_{3-\delta}$ redox pairs (B, B’ = Mn, Fe, Co, Cu) computed using DFT. Selected redox materials are marked with the oxidized metal oxide stoichiometry. The complete data are given in the Supporting Information. Arrows mark the increasingly exergonic CH$_4$ activation with increasing temperature. The DFT models of the perovskite surfaces are shown with panel D, for example, SrCuO$_2$-terminated La$_{1/2}$Sr$_{1/2}$Fe$_{0.5}$Cu$_{0.5}$O$_{3-\delta}(010)$ has a stability that is intermediate to Au$_2$O$_3$/Au and Ag$_2$O/Ag. Figure 4B,C indicates that DRM with LSCF redox membranes is limited thermodynamically by CO$_2$ reduction.
Conclusions

We have demonstrated the CO$_2$ reforming of CH$_4$ (dry reforming methane, DRM) at 840–1030°C into syngas using an isothermal membrane reactor equipped with a La$_{0.8}$Sr$_{0.2}$CoO$_x$Fe$_{0.8}$O$_{1.5}$ (LSCF) redox membrane. This reactor technology realizes the continuous splitting of CO$_2$ to CO on the inner side of a tubular membrane and the partial oxidation of CH$_4$ with the lattice oxygen on syngas on the outer side, producing at 1030°C 1.27 mol CH$_4$/s from CO$_2$, 3.77 mol H$_2$O/s, and CO from CH$_4$ at about the same rate as CO from CO$_2$. CH$_4$ conversion reaches 17%, whereas the CO$_2$ conversion is at maximum 8.0% due to CH$_4$ decomposition. Electronic structure calculations show how CO$_2$ reduction limits the dry reforming of methane with LSCF redox membranes. CO$_2$ conversion may be increased by using La$_{0.8}$Sr$_{0.2}$MnO$_3$ and La$_{0.8}$Sr$_{0.2}$NiO$_3$ with lower oxygen vacancy stabilities. The developed principles may be useful for the rational design of advanced redox materials for solar-driven processes.

Experimental Section

Materials: La$_{0.8}$Sr$_{0.2}$CoO$_x$Fe$_{0.8}$O$_{1.5}$ (LSCF, < 0.5 μm particle size, 10–14 m$^2$/g-surface area), poly(oxo-1,4-phenylenesulfonyl-1,4-phenylene) [PES, (C$_6$H$_4$O$_3$)$_n$], pellets, average mol wt. 60,000], 1-methyl-2-pyrrolidinone (NMP, C$_6$H$_9$NO, liquid, 99%), and polyvinylpyrrolidone (PVP, (C$_6$H$_9$NO)$_n$, powder, average mol wt. 40,000) were from Sigma Aldrich. Coltong high-temperature adhesive (1500°C maximum temperature) was from SFS unimarket AG, DistributionsService. CO$_2$ (99.998%), CH$_4$ (99.5%), Ar (99.999%), and He (99.999%) were from Messer Schweiz AG.

Redox membrane fabrication: Full details of the experimental methods are given in the Supporting Information. One-end open tubular redox membranes (6.0 mm outer diameter, OD, 4.8 mm inner diameter, ID) were fabricated by phase inversion, following procedures similar to those described previously. To prepare a perovskite solution, 5.8 wt% PES and 0.4 wt% PVP were soluted in 23.3 wt.% NMP stirred at approximately 20°C. 250 rpm, C-MAG HS 4 magnetic stirrer, IKA). Gradually, 70.5 wt% LSCF was added to the solution stirred in a closed beaker for at least 24 hrs. To prepare membrane precursors, siliccone templates (High-Flexible tubing, 3 mm ID, 7 mm OD, RCT Reichelt Chemietechnik GmbH & Co.) were coated with perovskite solution that was thereafter solidified by phase inversion in a water bath for 1 h (unfiltered tap water was used as coagulant). The precursors were dried in air at 20°C for 5 min, separated from the templates by lateral elastic deformation of the template, placed into the water bath for 10 min, dried overnight, and sintered on fractions of recitulated porous ceria[11] support for 2 hrs at 1300°C (oven model HT 64/16, Nabertherm).

CO$_2$ splitting: A tube-in-shell isothermal redox membrane reactor (Figure S1, Supporting Information) was constructed using a LSCF redox membrane enclosed in a quartz tube (21 mm ID, 25 mm OD, 300 mm length, UV-Technik Speziallampen GmbH). Compressed CO$_2$ and CH$_4$ were connected using Inconel tubing (Alloy 600, Bibus Metals AG) to the membrane cavity and the reactor shell, respectively. The reactor was equipped with an electric furnace (MTF 10/25/130, 0.375 kW, Carbolite), electronic mass flow meters (F-201CV, Bronkhorst), and a K-type thermocouple to measure the temperature (±5°C) between the membrane and the reactor shell. The permeability of the membranes to CH$_4$, CO$_2$, and H$_2$ and the presence of O$_2$ in the reactor were evaluated. Membranes were deemed dense if the permeability at 20°C was < 5 × 10$^{-8}$ mol m$^{-2}$ Pa$^{-1}$ s$^{-1}$. DRM with LSCF redox membranes was evaluated at 841–1029°C by supplying 28.3 mL CO$_2$/min and 19.9 mL CH$_4$/min at ambient pressure. Gas compositions were analyzed using an inline gas chromatograph (490 Micro GC, Agilent Technologies).

Solid-state analysis: Membranes were characterized by using XRD (Cu Kα radiation, 20–80° 2θ, 0.06° min$^{-1}$ scan rate, 45 kV/ 20 mA output, PANalytical/X’Pert MPD/DY636, Philips) and SEM using a Zeiss Supra 50VP microscope.

Thermodynamic equilibrium calculations: To rationally design metal-oxide redox materials for DRM, we computed a volcano-type ploq[40,41] from the thermochemical equilibrium of 38 redox pairs as a function of temperature and pressure by employing tabulated free energy data.[42]

Electronic structure computations: Computational details are given in-depth elsewhere and in the Supporting Information. Briefly, the thermochemical stability of 10 La$_{0.8}$Sr$_{0.2}$B$_2$O$_7$ (LSCF, B = Mn, Fe, Co, Cu) perovskites and the free energy of forming oxygen vacancies at the (010) facet were computed using DFT with the Grid-based projector-augmented wave (GPW) code[43] in the atomic simulation environment (ASE).[44] Exchange-correlation interactions were treated by the revised Perdew–Burke–Ernzerhof (RPBE) functional.[45] Similar to previous DFT studies of perovskites, all DFT calculations use the generalized gradient approximation (GGA) without a Hubbard U correction, as we have reported previously that this addition does not improve the description of surface reactivity with the employed models of Perovskites containing Mn, Fe, and Co were modeled using spin-polarized calculations.

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