

Mixed conducting materials for partial oxidation of hydrocarbons

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Thermodynamic calculations with additional conditions for the conservation of carbon and hydrogen were used to predict the gas composition obtained by partial oxidation of methane as a function of oxygen partial pressure and temperature; this was used to assess the stability and oxygen permeability requirements of mixed conducting membrane materials proposed for this purpose. A re-examination of known mixed conductors shows that most materials with highest permeability still fail to fulfil the requirements of stability under reducing conditions. Other materials possess sufficient stability but their oxygen permeability is insufficient. Different approaches were thus used to attempt to overcome those limitations, including changes in composition in the A and B site positions of ABO_3 perovskites, and tests of materials with different structure types. Promising results were obtained mainly for some materials with perovskite or related K_2NiF_4 -type structures. Limited stability of the most promising materials shows that one should rely mainly on kinetic limitations in the permeate side to protect the mixed conductor from severe reducing conditions.

Materiales conductores mixtos para la Oxidación Parcial de Hidrocarburos

Se han usado cálculos termodinámicos con condiciones adicionales para la conservación del carbono e hidrógeno para predecir la composición del gas obtenido mediante la oxidación parcial del metano en función de la presión parcial de oxígeno y de la temperatura; esto se ha usado para asegurar los requerimientos de estabilidad y permeabilidad al oxígeno de los materiales conductores mixtos empleados como membrana para este propósito. Un nuevo exámen de los conductores mixtos conocidos muestra que la mayoría de los materiales con la mayor permeabilidad todavía fallan en el cumplimiento de los requerimientos de estabilidad bajo condiciones reductoras. Otros materiales poseen suficiente estabilidad, pero su permeabilidad al oxígeno es insuficiente. Por ello se han empleado diferentes aproximaciones para intentar superar esas limitaciones, incluyendo cambios en la composición en las posiciones A y B de de las perovskitas ABO_3 , y pruebas con materiales con estructuras diferentes. Se han obtenido resultados prometedores principalmente en algunos materiales con estructura perovskita o estructuras relacionadas con K_2NiF_4 . La estabilidad limitada de los materiales más prometedores muestra que los estudios deben hacerse principalmente sobre las limitaciones cinéticas del lado permeable para proteger el conductor mixto en condiciones reductoras severas.

1. INTRODUCTION

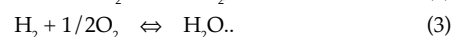
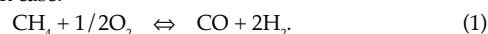
The main methods proposed to convert hydrocarbons to a mixture of hydrogen and carbon monoxide (syngas), have been steam reforming and partial oxidation by means of mesoporous membranes, mixed conductors with high electrochemical oxygen permeability, or ionic conductors working under short circuited conditions or assisted by an external applied field. The mixed conducting membranes possess interesting advantages relative to endothermic steam reforming, or electrically assisted partial oxidation. In addition to high oxygen permeability the mixed conductor must meet other requirements of catalytic activity, stability under wide ranges of chemical potential and in the presence of CO_2 , steam, SO_x , etc., and low thermal and chemical expansion under larger gradients of oxygen chemical potential.

A relatively wide range of mixed conductors has been studied for these membrane reactors [1-17], including single phase and composite materials consisting of a metallic conductor and a good ionic conductor. This concept is widely discarded because these composite materials are either based on noble metals of prohibitive cost, or fail to meet the required stability (e.g. $Ag/Bi(Er)O_{1.5}$) or oxidation resistance conditions. The emphasis has thus been on mixed conducting ceramics, mainly single phase [1-16], and occasionally 2-phase ceramic/ceramic composites [17]. Perovskite materials $Sr_{1-x}La_xCoO_{3-\delta}$ [3-5] and $Sr_{1-x}La_xFeO_{3-\delta}$ possess the highest permeability, limited stability, and excessive thermal and chemical expansion. Other mixed conductors are based on perovskite materials with higher stability (e.g. gallates [6,10] and titanates [7-9]) with mixed valent additives. Some La_2NiO_4 -

based materials combine good permeability and relatively low thermal thermal expansion [12-16].

2. SIMULATION OF LIMITING WORKING CONDITIONS IN MEMBRANE REACTORS

The chemical stability requirements of mixed conducting materials can be estimated by predicting the equilibrium gas phase composition expected under typical conditions of methane partial oxidation, in which case:



Methane cracking, $CH_4 \rightarrow C + 2H_2$, is mainly catalysed by metallic surfaces, and one thus assumes that this is entirely suppressed on all ceramic membranes.

Limiting conditions were estimated by combining the equilibrium constants of reactions 1, 2, 3, with additional relations for the conservation of relevant elements (C and H). One thus obtained the following dependence of the fraction of methane converted α , and gas composition on the oxygen partial pressure pO_2 :

$$\alpha(w_0 + 2\alpha)^2 / [(1+z+w_0 + 2\alpha)^2(1-\alpha)] = K_1 \cdot (pO_2)^{1/2} [1 + K_2 \cdot (pO_2)^{1/2}] [1 + K_3 \cdot (pO_2)^{1/2}]^2 \quad (4)$$

$$[H_2] = [(w_o + 2\alpha)/(1+z+w_o+2\alpha)] / \{1 + [K_3 \cdot (pO_2)^{1/2}]\} \quad (5)$$

$$[CO] = [\alpha/(1+z+w_o+2\alpha)] / \{1 + K_2 \cdot (pO_2)^{1/2}\} \quad (6)$$

$$[CO_2] = [\alpha/(1+z+w_o+2\alpha)] / \{1 + [K_2 \cdot (pO_2)^{1/2}]\}^{-1} \quad (7)$$

$$[H_2O] = [(w_o + 2\alpha)/(1+z+w_o+2\alpha)] / \{1 + [K_3 \cdot (pO_2)^{1/2}]\}^{-1} \quad (8)$$

A balance of oxygen is also needed to establish the relevant relations between the permeability of the membrane material, and working conditions. This can be illustrated on assuming an ideal continuous stirred reactor with supply of an oxygen flux density j through mixed conducting walls of area A . Under steady state regime:

$$2Aj = C_i \{Q_v \cdot ([CO] + 2[CO_2] + [H_2O]) - Q_v^o \cdot [H_2O]\} \quad (9)$$

where C_i is the gas concentration and Q_v^o is the volume flow rate at the inlet. The flux density supplied by the mixed conducting wall is a function of the gradient of oxygen chemical potential. If process is controlled by mixed conduction [3,7]:

$$j = JO_2 \ln(pO_{2i}/pO_{2t})/L = \sigma_{amb} \cdot RT \cdot (4F)^{-2} \cdot \ln[(pO_{2i}/pO_{2t})] \cdot L^{-1} \quad (10)$$

where JO_2 is the specific oxygen permeability, σ_{amb} is the ambipolar conductivity of the mixed conducting material, R is the ideal gas constant, T is absolute temperature, F is the Faraday constant, $(pO_2)_i$ and $(pO_2)_t$ are the values of oxygen partial pressure in the feed and permeate sides, and L is the membrane thickness. In this case, JO_2 is independent of thickness. On the contrary, surface exchange control yields values of j independent of the membrane thickness, whereas JO_2 increases with thickness. Changes both in j and JO_2 with membrane thickness indicate mixed control, which occurs when the thickness of the membrane is close to a critical value $L_c = k/D$, k being a surface exchange coefficient and D the diffusion coefficient [4].

A numerical method was used to solve Eqs. 4 through 10, and a typical example is shown in Fig.1, to illustrate the severe stability and permeability requirements to be met by mixed conducting membrane materials. The fractions of hydrogen and CO typically reach maxima at pO_2 close to 10^{-20} atm and then decrease for more oxidising conditions, yielding CO_2 and H_2O . These stability requirements are excessive for mixed conducting materials based on $LaCoO_3$ [3-5], (Fig.2). Other materials (e.g. $(La,Sr)MnO_3$) are stable but possess insufficient permeability.

The permeability requirements can be accounted for by a dimensionless parameter $J^* = JO_2 \cdot A / (L \cdot Q_v^o \cdot C_i)$ which combines the effects of specific permeability, mass flow rate at the inlet, and geometric parameters of the mixed conducting wall, i.e. area and thickness. At 1173 K the highest combined fractions of $H_2 + CO$ are attained for $J^* \approx 0.009$. Under these conditions, a reactor with membrane thickness of about 1 mm should be able to process about 6.4 kg of methane per hour and per square meter if the specific oxygen permeability reaches $10^{-8} \text{ mol} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$; this is comparable to the highest permeability for the most promising materials. Unfortunately, this range was observed only for materials with relatively poor stability, and the results obtained for more stable materials are lower by 1 to 2 orders of magnitude. A change from self-supported thick membranes to thinner membranes with a porous support is thus probably needed to be able to use materials with specific permeability of the order of 10^{-10} to $10^{-9} \text{ mol} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ or even lower. This must be combined with surface modification or application of suitable catalysts when the membrane thickness is smaller than the critical value, i.e. $L < k/D$.

3. EXPERIMENTAL METHODS

Standard powder reactions and the glycine-nitrate method have been used to prepare powders of a variety of materials with perovskite, K_2NiF_4 , and other structure types, as described in detail elsewhere

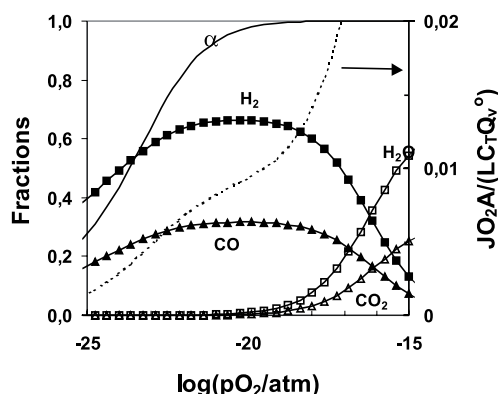


Fig1 Predictions of fraction of methane converted, gas composition and permeability requirements versus oxygen partial pressure, assuming equilibrium conditions.

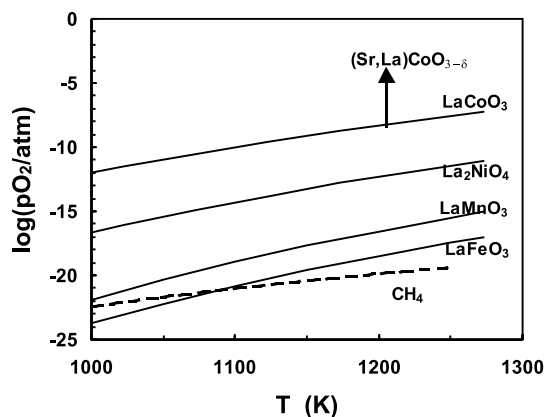


Fig.2 Stability limits of representative mixed conducting materials at 1173K, under reducing conditions predicted with data reported in references [19] and [20]. The dashed line represents conditions required to attain the highest fractions of CO and H_2 by partial oxidation of methane.

[6-10,13-17], with intermediate calcination and regrinding steps to ensure complete conversion of reactants and homogeneity. XRD was used for phase identification, and to evaluate the unit cell parameters. Neutron diffraction and Mossbauer spectroscopy were occasionally used for complementary analysis. SEM/EDS analysis was used for microstructural characterisation and standard picnometry was used to evaluate the actual density. The transport properties and defect chemistry were characterised by conductivity and Seebeck coefficient measurements versus pO_2 and T , oxygen permeability, faradaic efficiency, and coulometric titration, as described in references [6-10,13-17]. Stability limits were estimated from sudden changes in the dependence of oxygen stoichiometry, conductivity, and/or Seebeck coefficient versus pO_2 . Studies of partial oxidation of methane with mixed conducting ceramics were performed as described in [18].

4. PERMEABILITY AND CHEMICAL STABILITY REQUIREMENTS

The most promising mixed conducting materials possess perovskite or K_2NiF_4 structure types, and contain one or a combination of transition elements Fe, Co, Ni or Cu. $Sr(Co,Fe)O_3$ materials possess the highest specific permeability (about $10^{-7} \text{ mol} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$) but are unstable [21], due to a perovskite to brownmillerite phase change. The stability of $LaCoO_3$ is also insufficient, as reported in [19,20], and shown in Fig.2. The stability limits of $LaFeO_3$ and $LaMnO_3$ [19] are suitable (Fig.2). Suitable compositions changes enhance the permeability, especially for $(La,Sr)FeO_{3-\delta}$ (from about $10^{-10} \text{ mol} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$ to $10^{-8} \text{ mol} \cdot \text{cm}^{-1} \cdot \text{s}^{-1}$).

cm⁻¹.s⁻¹). However, this lowers the stability (Fig.3). One must thus seek a compromise between sufficient permeability and stability, as suggested in Fig.3 for (Sr,La)FeO₃ and (La,Sr)(Ga,M)O₃, M=Fe,Co,Ni.

Materials with different structure types were also studied in attempts to enhance the permeability without spoiling the stability or to improve the stability while retaining high permeability. Perovskites often possess the highest permeability, as shown for materials containing Fe (Table I), except possibly for some materials with K₂NiF₄ structure (Fig. 4). The stability of La₂NiO₄ is clearly superior to those of LaNiO₃ and LaCoO₃ (Fig.2), and permeability results obtained for La₂NiO₄-based materials are similar to those obtained for promising (La,Sr)FeO₃ materials at about 1073 K (10⁻⁹ to 2x10⁻⁹ mol.cm⁻¹.s⁻¹).

TABLE I: SPECIFIC OXYGEN PERMEABILITY OF REPRESENTATIVE MIXED CONDUCTORS CONTAINING FE, OBTAINED WITH MEMBRANE THICKNESS L=1mm, AND OXYGEN PARTIAL PRESSURES P₁=2.1 kPa, P₂=21 kPa.

Materials	J _{O₂} (mol.cm ⁻¹ .s ⁻¹)	
	T=1173 K	T=1223 K
La _{0.7} Sr _{0.3} Fe _{0.6} Ga _{0.4} O _{3-δ}	9.1x10 ⁹	1.4x10 ⁸
La _{0.3} Sr _{0.7} FeO ₃	7.5x10 ⁹	1.3x10 ⁸
La ₂ Ni _{0.9} Fe _{0.1} O _{4-δ}	3.1x10 ⁹	
La _{0.8} Sr _{0.2} Ga _{0.6} Mg _{0.2} Fe _{0.2} O _{3-δ}	2.9x10 ⁹	4.3x10 ⁹
LaFe _{0.7} Ni _{0.3} O _{3-δ}		3.7x10 ¹⁰
Sr ₂ FeO ₁₃	2.3x10 ¹¹	
Y _{2.5} Ca _{0.5} Fe ₄ NiO _{12.8}	0.77x10 ¹¹	2.2x10 ¹¹
LaFe _{0.8} Ni _{0.2} O _{3-δ}		1.9x10 ¹¹
Y _{2.5} Ca _{0.5} Fe ₄ O _{12.8}	3.4x10 ¹²	7.8x10 ¹²
Gd ₃ Fe ₅ O ₁₂	2.00x10 ¹²	5.2x10 ¹²

Permeability changes can be attained by partial substitution in the A and/or B-site of perovskites and K₂NiF₄ compounds (see Fig.3 and Table II). A possible interpretation for those effects on permeability might be based on the values of tolerance factor $t = 0.7071(r_{Ln} + r_O) / (r_{Cu} + r_O)$, as found for Ln₂CuO_{4+δ} Ln=La,Pr,Nd. Similar arguments and/or the similarity between the radii of Ln and Sr might explain differences in permeability results for Sr_{0.7}Ln_{0.3}CoO_{3-δ} (Table II).

TABLE II: SPECIFIC PERMEABILITY RESULTS FOR Ln₂CuO_{4+δ}-BASED MATERIALS OBTAINED AT 1173K (Ln=Pr and Nd) OR 1123 K (La), WITH MEMBRANE THICKNESS L=1 mm, AND FOR Sr_{0.7}Ln_{0.3}CoO_{3-δ} AT 1153K, WITH L=1.4 mm. THE VALUES OF TOLERANCE FACTORS FOR K₂MO₄ COMPOUNDS WERE CALCULATED AS $t = 0.7071(r_{Ln} + r_O) / (r_M + r_O)$, USING IONIC RADII REPORTED BY SHANNON [22] FOR M²⁺ WITH COORDINATION 6 AND Ln³⁺ WITH COORDINATION 9. $\Delta t = 0.7071\{(r_{Ln} + r_O) - (r_{Sr} + r_O)\} / (r_{Co} + r_O)$ REPRESENTS THE DIFFERENCE BETWEEN TOLERANCE FACTORS CALCULATED FOR THE CO-EXISTING SPECIES IN THE A-SITE POSITION OF Sr_{0.7}Ln_{0.3}CoO_{3-δ} WITH COORDINATION 12 FOR Ln³⁺ OR Sr²⁺ AND COORDINATION 6 FOR Co³⁺ (HIGH SPIN).

Material	P ₂ /P ₁	t	Δt	J _{O₂} (mol.cm ⁻¹ .s ⁻¹)
La ₂ CuO _{4+δ}	2.01	0.868		2.3x10 ⁹
	3.37			2.9x10 ⁹
Pr ₂ CuO _{4+δ}	2.58	0.858		8.7x10 ¹¹
Nd ₂ CuO _{4+δ}	2.53	0.851		2.6x10 ¹¹
Sr _{0.7} La _{0.3} CoO _{3-δ}	1.81		0.028	3.6x10 ⁸
"	2.80			2.9x10 ⁸
Sr _{0.7} Nd _{0.3} CoO _{3-δ}	1.96		0.060	2.6x10 ⁸
"	2.67			2.5x10 ⁸
Sr _{0.7} Sm _{0.3} CoO _{3-δ}	2.04		0.070	1.76x10 ⁸
Sr _{0.7} Gd _{0.3} CoO _{3-δ}	2.07		0.081	0.69x10 ⁸

5. ROLE OF SURFACE EXCHANGE KINETICS

One may also seek changes in design to obtain less harmful conditions for the mixed conducting materials. For example, a porous inert layer may provide both the required mechanical strength for relatively thin membranes, and also a diffusion barrier, thus rendering the stability requirements much less demanding. Kinetics may also contribute to bridge the gap between the reducing conditions inside

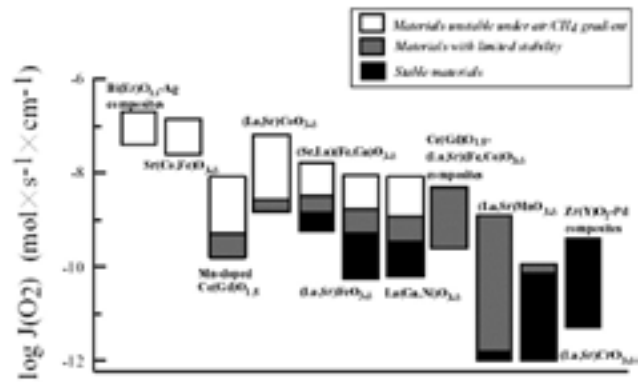


Fig.3 Comparison of specific permeability and stability of several types of mixed conductors.

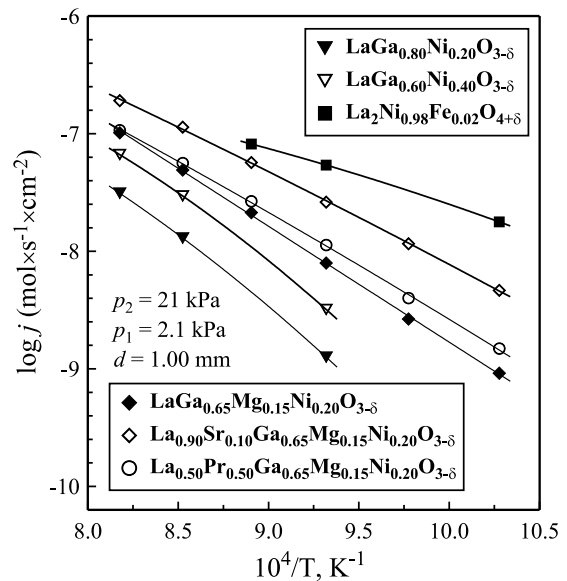


Fig.4 Permeability results obtained for representative mixed conductors containing Ni.

the membrane reactor and the stability range of mixed conductors. The required changes might be related to surface processes at the permeate side of the mixed conducting membrane, and/or deviations from equilibrium in the gas phase, when partial oxidation (Eq.1) becomes somewhat sluggish. Significantly higher oxygen chemical potential is then needed to attain high values of methane conversion. Unfortunately, this is likely to yield further oxidation of CO to CO₂ and/or H₂ to H₂O.

Results obtained for La₂NiO_{4+δ}-based materials indicate that their permeability is controlled by surface exchange at temperatures below about 1073 K, with mixed control at higher temperatures. Mixed control was also often found for perovskite materials. In these cases, one may not attain the required results by lowering the membrane thickness below its critical value, and should instead focus on surface modifications, either by adding catalysts, or depositing a porous layer of the same material with high specific surface area (Fig.5).

Surface exchange limitations are not restricted to the feed side of the membrane, and have been reported also for the permeate side. In this case, surface exchange limitations in the permeate side might even play a useful role, by providing kinetic protection from very reducing atmospheres. This possibility was demonstrated by testing La₂Ni_{0.9}Co_{0.1}O_{4+δ} under air/10% H₂-90% N₂, for 250 hours, at 973 K. and La₃Sr_{0.7}Co_{0.8}Ga_{0.2}O_{3-δ} under air/50% CH₄-50% He gradient, at 1123-1223 K, for 200 hours (Fig.6). The kinetic stabilisation was confirmed by

post-mortem SEM analysis. Though these preliminary tests confirmed the potential applicability of mixed conducting membranes, suitable catalysts may be needed to increase the conversion of methane and the selectivity of CO and H₂.

6. CONCLUSIONS

The characteristics of known mixed conductors are still somewhat insufficient to be used as membranes for partial oxidation of hydrocarbons, mainly due to either poor stability or insufficient permeability. However, the present understanding of the effects of composition on transport properties and stability of candidate materials still allows one to expect further improvements. In addition, one may select operation conditions or optimised membrane designs providing kinetic stabilisation, thus bridging the gap between the stability of mixed conducting membrane materials and the actual conditions inside the membrane reactor. Suitable models for the reactor operation conditions must be revised to take into account that kinetic limitations cause significant shifts from predicted equilibrium conditions.

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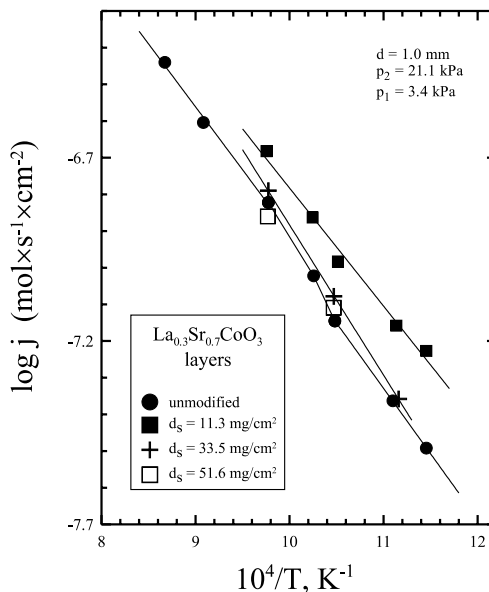


Fig.5 Effects of a porous surface layer on permeability of La_{0.3}Co_{0.7}CoO₃.

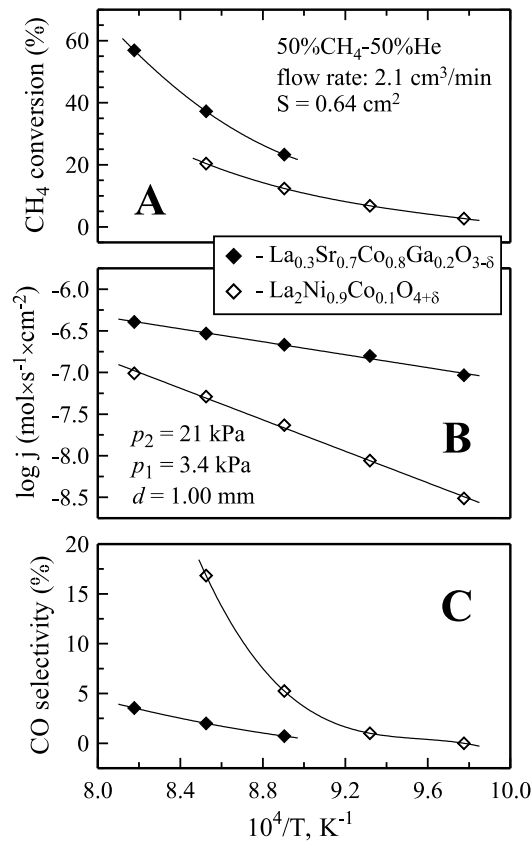


Fig.6 Temperature dependence of methane conversion, CO selectivity obtained by partial oxidation with representative mixed conductors, and the corresponding permeability results.

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