Oxidation of dry methane on the surface of oxygen ion-conducting membranes

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The surface exchange limitations of oxygen permeation through dense mixed-conducting membranes enhance membrane stability, enabling the operation of mixed conductors, such as \(\text{La}_{0.5}\text{Sr}_{0.7}\text{Co}_{0.3}\text{Ga}_{0.2}\text{O}_{2-\delta}\) (LSCG) and \(\text{La}_{2}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{2-\delta}\) (LNC), under air/dry CH\(_4\) gradient up to temperatures as high as 1173–1223 K. Testing of these materials in a model disk-shaped membrane reactor at 1023–1223 K showed high CO\(_2\) yields (>75\%). In particular, at 1173 K, the CO selectivity was 17\% for LNC and 2\% for LSCG ceramics, with methane conversion efficiency of 20 and 37\% respectively. Similar tendency was observed for a fuel cell-type reactor with yttria-stabilized zirconia solid electrolyte and cermet \(\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{2-\delta}/\text{Pt}\) anode, where decreasing the molar ratio between methane and electrochemically supplied oxygen from approximately 10 to 2 decreases CO/CO\(_2\) ratio at the outlet down to 0.3. This behavior suggests significant role of the complete methane oxidation on the interface between an oxygen ion-conducting membrane and gas phase, thus making it necessary to incorporate reforming catalysts in the reactors.

KEY WORDS: partial oxidation; synthesis gas; membrane; mixed conductor; solid electrolyte; perovskite; oxygen permeation; fuel cell.

1. Introduction

Synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, is the most important feedstock for commercial Fischer–Tropsch and methanol synthesis [1,2]. The industrial production of synthesis gas is based on steam reforming of methane, the main component of natural gas. This process is, however, energy intensive to the highly endothermic nature of the reaction

\[
\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2, \quad \Delta H_{298}^\circ = 206 \text{kJ/mol}
\]

and yields \(\text{H}_2/\text{CO}\) molar ratio higher than optimum required for further syngas conversion into hydrocarbons or methanol. One alternative route relates to the catalytic partial oxidation of methane, which is mildly exothermic

\[
\text{CH}_4 + 1/2\text{O}_2 = \text{CO} + 2\text{H}_2, \quad \Delta H_{298}^\circ = -36 \text{kJ/mol}
\]

and gives an optimum \(\text{H}_2/\text{CO}\) ratio of 2 [1,2]. The main cost of syngas production by the partial oxidation is associated with cryogenic oxygen plants [1–3].

Contrary to conventional technologies, the use of solid oxide fuel cells (SOFCs) and/or dense mixed-conducting membranes makes it possible to combine oxygen separation, partial oxidation and reforming of methane in a single reactor [3–11]. The development of economically feasible SOFCs is also of great interest for power generation due to high energy-conversion efficiency, fuel flexibility and environmental impact [12,13].

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The use of SOFC-type reactors for the natural gas conversion requires relatively high currents and low electrode polarization; this is only possible when using catalytically active anode components such as \(\text{CeO}_2\), which promote oxidation reactions, suppress carbon deposition and enlarge electrochemical reaction zone [14–18]. The reactors with mixed-conducting membranes can operate without external circuitry and are thus simpler compared to SOFCs. During the last decade, significant attention has been focused on perovskite-type mixed conductors (\(\text{La}_{1-A}\text{Co}_A\text{Fe}_3\text{O}_5\)) (A = Sr or Ba), tested for partial oxidation and oxidative coupling of methane [6–11]. One should mention that thermodynamic stability of cobaltite- and ferrite-based perovskites in highly reducing environments is rather insufficient [19]; the stable operation is only possible in the presence of steady state oxygen permeation flux across the membrane. As shown below, such a kinetic stabilization is achieved when the overall oxygen transport is limited by exchange rate on the membrane permeate-side surface.

The present work is focused on the evaluation of mixed-conducting \(\text{La}_{0.5}\text{Sr}_{0.7}\text{Co}_{0.3}\text{Ga}_{0.2}\text{O}_{3-\delta}\) (LSCG) and \(\text{La}_{2}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{2-\delta}\) (LNC) ceramics in a model reactor for direct oxidation of dry CH\(_4\). \(\text{La}_{2}\text{Ni}_{0.5}\text{Co}_{0.5}\text{O}_{2-\delta}\) with a \(\text{K}_2\text{NiF}_4\)-type structure and perovskite-like \(\text{La}_{0.5}\text{Sr}_{0.7}\text{Co}_{3-\delta}\) are known to exhibit substantially high oxygen permeability [20,21]. In order to suppress chemical expansion induced by the oxygen chemical...
potential variations, the perovskite phase is doped with gallium [22]. The performance of the mixed-conducting membranes is compared with that of a SOFC-type reactor made of yttria-stabilized zirconia (YSZ) electrolyte with cermet Ce$_{0.8}$Gd$_{0.2}$O$_{2-δ}$/Pt anodes.

2. Experimental

Powders of LNC and LSCG were prepared by the glycine-nitrate process (GNP), a self-combustion synthesis technique using glycine as a fuel and nitrates of metal components as an oxidant [23]. In the course of GNP, glycine was added into aqueous nitrate solution containing metal cations in stoichiometric proportions (molar glycine/nitrate ratio of 2:1). After drying and firing, the resultant powders were ball-milled and annealed in air at 1073 K for 2 h. Dense ceramic samples were pressed at 300–400 MPa and then sintered in air at 1533–1553 K for 2 h. The X-ray diffraction (XRD) analysis of ceramics showed formation of single phases, with tetragonal K$_2$NiF$_4$-type structure for LNC and cubic perovskite for LSCG, in agreement with [20,21]. The density of the ceramics was 96–97% of their theoretical density calculated from XRD data.

Characterization of ceramic materials included XRD, scanning and transmission electron microscopy (SEM and TEM) coupled with energy dispersive spectroscopy (EDS), measurements of total conductivity and Seebeck coefficient as function of temperature and oxygen partial pressure, and determination of steady state oxygen permeation fluxes. A detailed description of the experimental procedures and equipment used for characterization was published elsewhere ([20–22,24] and references therein). The phase stability boundaries at reduced $p(O_2)$ were estimated from results on the total conductivity ($\sigma$) and Seebeck coefficient ($\alpha$). As an example, figure 1 illustrates the determination of stability limits from the data on total conductivity at 973 K. The oxygen pressure, at which the slope of log-$\sigma$-log $p(O_2)$ and $\alpha$-log $p(O_2)$ dependencies started to change, was considered as a stability boundary at a given temperature. Further reduction of oxygen partial pressure resulted in drastic irreversible degradation in electric properties due to phase decomposition of ceramics.

The experimental setup for the methane oxidation studies comprised a dense disk-shaped membrane, hermetically sealed onto YSZ tube, and an electrochemical oxygen sensor at the outlet of the cell. In all cases, effective geometric area of the membrane surface exposed to methane flow was 0.64 cm$^2$. For LNC and LSCG membranes, catalytically active porous layers were applied onto the permeate-side surface; their composition and fabrication conditions are listed in table 1. The SOFC-type cell consisted of one YSZ disc with Ce$_{0.8}$Gd$_{0.2}$O$_{2-δ}$/Pt cermet anode (50:50 wt%) and porous platinum cathode; platinum wires were used as current collectors. Nanocrystalline powder of Ce$_{0.8}$Gd$_{0.2}$O$_{2-δ}$ (CGO) used for the anode was prepared by the cellulose-precursor technique described elsewhere [16,24]; after anode fabrication at 1273 K (table 1), the size of CGO particles determined by TEM was 20–60 nm. The anode microstructure represents a matrix of large platinum particles (0.2–2 $\mu$m), covered with porous agglomerates of nanocrystalline CGO (figure 2(a)).

In the course of steady state electrocatalytic experiments, dry CH$_4$ (≥99.995% purity) diluted with helium was supplied onto the permeate side of a mixed-conducting membrane or onto the anode of the SOFC-type reactor, with the feed side or cathode being exposed to atmospheric air. The gas-flow composition and rate at the reactor inlet were fixed by Bronkhorst mass-flow

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Table 1

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Thickness $d$ (mm)</th>
<th>Layer</th>
<th>Composition</th>
<th>Annealing</th>
<th>Sheet density (mg/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNC</td>
<td>0.60</td>
<td>Permeate-side surface</td>
<td>LNC/Pt (50:50 wt.%)</td>
<td>1273 K, h</td>
<td>5.6±0.1</td>
</tr>
<tr>
<td>LSCG</td>
<td>0.95</td>
<td>Permeate-side surface</td>
<td>Pt</td>
<td>1223 K, 0.5 h</td>
<td>8.6±0.1</td>
</tr>
<tr>
<td>YSZ</td>
<td>0.90</td>
<td>Anode</td>
<td>CGO/Pt (50:50 wt.%)</td>
<td>1273 K, h</td>
<td>9±1</td>
</tr>
</tbody>
</table>