Methane steam reforming at low temperatures in a BaZr$_{0.7}$Ce$_{0.2}$Y$_{0.1}$O$_{2.9}$ proton conducting membrane reactor

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ABSTRACT

The feasibility of Methane steam reforming (MSR) at low temperatures (450–650 °C) was studied in a Ni-BZCY72/BZCY72/Cu proton conducting membrane reactor, which allowed for the simultaneous separation of hydrogen. The cell reactor was first tested under open-circuit conditions, i.e., with the reactor operating as a catalytic reformer. The impact of several parameters, such as steam to carbon feed ratio, the operating temperature and the total flow rate was evaluated. The Ni-BZCY72 electrode exhibited high catalytic activity with methane conversion close to thermodynamic equilibrium, which was attributed to the high nickel content (45 wt.% after full reduction), as well as to the presence of ceria and zirconia in the support. Carbon dioxide was the main carbonaceous product with a molar ratio to carbon monoxide higher than 9, indicating that the Water Gas Shift reaction was predominant in the process. When hydrogen was electrochemically transported from the Ni-BZCY72 anode to the Cu cathode, a significant increase in methane conversion and hydrogen yield was observed. The methane conversion and hydrogen yield were improved by up to 50% in the temperature range of 550–650 °C over their corresponding open-circuit values. The BZCY72 perovskite exhibited satisfying proton fluxes and transference numbers at all temperatures and applied cell voltages examined. Finally, the Ni-BZCY72 reactor cell showed excellent chemical stability and durability, as well as coke tolerance for 24 h on stream.
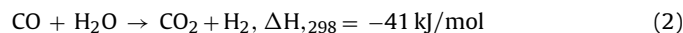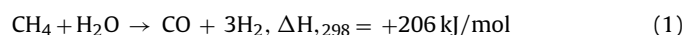
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1. Introduction

In the last few years, hydrogen has gained great interest as a future clean fuel for combustion engines or even fuel cells. The interest has increased significantly at the prospect of an emerging energy net, which will provide clean and viable energy solutions based on hydrogen and renewable sources. Thus, efficient production processes for hydrogen have been proposed and developed. These processes can be divided into three groups: (a) catalytic reforming of fossil fuels (natural gas accounts for more than 50% of the global production) (b) steam gasification of coal and (c) water electrolysis in alkaline solutions [1].

As the major component of natural gas methane is a compound of significant importance. Two factors, however, limit its use as a raw material. The first is that natural gas transportation is not economically advantageous and the second is that

methane is a refractory molecule which complicates its conversion into upgraded products. Methane steam reforming (MSR) is the most efficient industrial technology for upgrading methane to useful products, such as hydrogen. MSR is a highly endothermic process in which Ni-based catalysts are employed to produce syngas, usually around a 1:3 of CO/H$_2$ ratio, at elevated temperatures (800–1000 °C). The dominant reactions are the highly endothermic reforming Reaction (1) and the slightly exothermic water gas shift (WGS) Reaction (2):

$$CH_4 + H_2O \rightarrow CO + 3H_2, \Delta H_{,298} = +206 \, kJ/mol \tag{1}$$

$$CO + H_2O \rightarrow CO_2 + H_2, \Delta H_{,298} = -41 \, kJ/mol \tag{2}$$

Syngas is a key-intermediate in the chemical industry and it is primarily used by ammonia and methanol manufacturers, as well as by refineries for hydrotreating [2]. In particular, the ammonia synthesis process requires high purity hydrogen derived through rather expensive separation procedures [1,3].

In the last few years, methane steam reforming at low temperatures (LT-MSR), i.e., between 400 and 650 °C, has been proposed to reduce the overall cost of the process [4,5]. Low temperatures

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favor WGS and the dominant route of hydrogen production is the following:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2, \Delta H_{,298} = +165 \text{ kJ/mol} \tag{3}$$
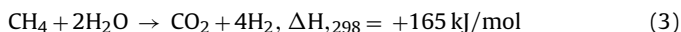
The diminished energy demands and the cheaper reformer construction materials, due to lower operation temperatures, can lead to a significant reduction of the overall cost. Furthermore, the faster start-up and the absence of a WGS reactor are additional reasons that have made this idea attractive to many researchers [4,5]. However, despite the above advantages, at low temperatures methane conversion is suppressed by thermodynamic and kinetic limitations [6]. A possible solution to this problem is the use of catalytic membrane reactors (CMR) which allow continuous hydrogen removal and as a consequence an increase in methane conversion according to Le Chatelier's principle [5,7,8].

The CMR employs a selective Pd membrane with the reforming reactions and hydrogen separation taking place in a single stage [5,9,10]. The difference in hydrogen's chemical potential, which is enhanced by higher pressures in the reaction compartment, constitutes the driving force for hydrogen migration through the Pd membrane [5,9]. Complete methane conversion at 500–600 °C has been reported in these kind of systems, but in order to achieve it, high pressures that do not thermodynamically favor the MSR reaction were employed and the energy consumption increased [6]. Proton-conducting solid electrolytes have also been successfully tested as membranes for shifting the equilibrium of the MSR process, but usually as solid oxide fuel cells (SOFC) internal reformers operating at high temperatures of around 700–1000 °C [11–14]. In most of these cases, however, the primary aim was to generate electrical power and not to produce pure hydrogen [11–14].

Another interesting approach which is schematically represented in Fig. 1 is the use of a Solid Electrolyte Membrane Reactor (SEMR) for pure hydrogen production [15,16]. A gas mixture of methane saturated with steam is fed over the electro-catalyst (anode) where catalytic Reactions (1)–(3) take place. At closed-circuit conditions, with the use of an external power source, the produced hydrogen is converted into protons at the anode which are transported through the solid electrolyte to the cathode. At the cathode protons recombine with electrons and form molecular hydrogen which eventually evolves to the gas phase. This approach has the advantages of the CMR and at the same time, the employment of expensive Pd membranes and higher pressures is avoided. In the present communication, the MSR reaction was studied in a proton (H^+) conducting membrane reactor. The reactor consisted of a $BaZr_{0.7}Ce_{0.2}Y_{0.1}O_{2.9}$ (BZCY72) perovskite, which served as the proton conducting membrane, a tubular Ni-BZCY72 cermet, which served as the anodic electrode and a film of metallic Cu serving as the cathode. The anodic electro-catalyst is considered appropriate for this application because of its high Ni content and the presence of cerium and zirconium mixed oxides. The latter have been reported as very active supports [4,6]. The feasibility of LT-MSR in a SEMR at temperatures between 450 and 650 °C and under atmospheric pressure is examined, both catalytically and when hydrogen is electrochemically removed from the Ni-BZCY72 catalyst.

2. Experimental

2.1. Preparation and characterization of the proton conducting membrane reactor

The experimental apparatus used in the present study has been described in detail in a previous communication [17] and the schematic depiction of the reactor cell can be found therein. It was a slip-cast, electrode-supported tube, 20 cm long, with a diameter of nearly 1 cm and closed at one end, which was fabricated by CoorsTek Inc. (Golden, CO, USA). The cell was supported by its anode which was a porous two phase electrode (60 wt.% NiO–40 wt.% BZCY72) of an approximately 750 μm thickness and served as the working electrode. This high Ni content ensures not only a high conductivity of the cermet electrode but also, after the reduction of NiO to Ni, porosity which will facilitate gas diffusion to and from the three phase boundary (TPB). On the outer surface of this electrode a dense layer of BZCY72 with a thickness of 30 μm formed the electrolyte membrane of the cell [18]. A porous copper film was deposited on the outer surface of the BZCY72 electrolyte and served as the cathode (counter electrode). This electrode was prepared from a copper organometallic paste (Heraeus Precious Metals C7440 conductor paste). The paste was applied uniformly on the external surface of the tube near its closed end, over an area of 20 cm^2 followed by sintering at 1000 °C for 1 h under a 1 l min^{-1} flow of 4% hydrogen to argon.

The microstructure of the tube's surfaces was studied with TEM and SEM analyses. Preparation for the TEM analysis was accomplished with a FEI Helios NanoLab^{TM} 600i DualBeam^{TM} and was cleaned with 2 kV Ga beam. The image of the BZCY72 dense electrolyte was acquired using a 200 kV Philips CM200 transmission electron microscope. A Phenom ProX scanning electron microscope was used to acquire images of the cell cross sections, both polished and "as fractured" (with a diamond saw). X-ray diffractograms were obtained using a Bruker D8 Discover theta–theta diffractometer with a Cu Kα beam operating at 40 kV, 40 mA and a scan-rate o 0.3° in the 2θ range of 20°–80°. The patterns were obtained for both the BZCY72 electrolyte membrane and the Ni-BZCY72 cermet anode.

Temperature Programmed Oxidation (TPO) was used to examine the extent of carbon deposition at the anode. The Ni-BZCY72 anode was first exposed to a helium flow of 50 ml cm^{-3}, then the temperature was raised to 250 °C at a rate of $5 °C \text{ min}^{-1}$ and was kept there for 1 h. This step was conducted to evaporate the adsorbed methane and water on the catalyst. Then, the reactor was heated to 800 °C under a flow of 5% oxygen in helium with a rate of $5 °C \text{ min}^{-1}$. The carbon dioxide and oxygen gasses were monitored continuously using a Binos infrared analyzer.

2.2. Reactant and product analysis

Reactant gas, methane and diluent nitrogen (Air Liquide Hellas) were certified standards of 99.95 or 5.2% and 99.999%, respectively. The steam feed was provided by bubbling the CH_4-N_2 mixture through a saturator. In order to prevent steam condensation the feed and exhaust tubes of the anode chamber were heated to at least 50 °C above the saturator's temperature. In the cathode chamber, a second stream of pure nitrogen was fed and served as a sweep gas for the hydrogen on that side. Analysis of reactants and products was performed by online gas chromatography. A SHIMADZU GC-14B chromatograph, equipped with a Molecular Sieve 5A column and nitrogen as the carrier gas, was used to measure the hydrogen concentration in the exhaust streams of both the outer (cathode) and the inner (anode) chamber. The carbon containing compounds (CH_4, CO, and CO_2) in the anode chamber exhaust stream, as well as methane concentration in the anode feed, were analyzed using a SHIMADZU GC-2014 chromatograph, which was equipped with a Porapak Q column and He as the carrier gas. The deviation in carbon balance did not exceed 3% indicating insignificant formation of carbon or other products.

All catalytic data were based on gas chromatograph measurements. In particular, conversion of reactants, selectivity and yield of products were calculated as follows.

$$CH_4 \text{ Conversion: } X_{CH_4} = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \text{ [\%]} \tag{4}$$