Hydrogen production in solid electrolyte membrane reactors (SEMRs)

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Received 10 November 2005; received in revised form 24 March 2006

Abstract

In the present work, the prospects and trends of solid electrolyte membrane reactors (SEMRs) towards hydrogen production, are discussed. Initially, an overview of the principles, the properties and the techniques related to the usage of the SEMRs, are presented. In the following, a literature survey covering earlier and recent developments of the various methods (e.g. reforming or partial oxidation or dehydrogenation of hydrocarbons, steam electrolysis) employed in the SEMRs for the production of hydrogen, is performed. Finally, the current status of this research field is analyzed and future research topics are proposed.

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Keywords: Hydrogen production; Solid electrolyte membrane reactors; Oxygen ion conductor; Proton conductor; Partial oxidation of hydrocarbons; Reforming of hydrocarbons; Dehydrogenation of hydrocarbons; Steam electrolysis

1. Introduction

In recent years, intensive focus has been given to “hydrogen economy”. The interest has been increased significantly due to the looming prospect of an emerging energy net, which will provide clean and viable energy solutions. The economy which is based on the utilization of hydrogen, as the basic energy carrier, it can resolve permanently all uncertainties, dealing with fossil fuel exhaustion, air pollution and climate change due to greenhouse effect and/or ozone depletion problems. Hydrogen as a fuel, provides the potential of a reliable and renewable energy system, which emits practically zero air pollutants and especially carbon dioxide. The forthcoming “hydrogen economy” era, however, requires intensive research efforts towards various scientific fields such as hydrogen production [1–4].

The worldwide scale up of hydrogen infrastructure, should be accompanied with an equivalent increase of its production from hydrogen containing compounds (e.g. water, fossil fuels, biomass) [1,4–7]. Electrolysis is a method where carbon dioxide emissions are negligible, but it will become economically effective only when the required power will be provided from renewable energy sources (nowadays renewable energy sources are more expensive compared to other energy sources, however it is expected that in the near future advanced-low cost technologies will be developed and they will allow the broadening of renewable energy resources commercial applications) [2,8]. Up to date, electrolysis is a less efficient method compared with the production of hydrogen from fossil fuels (based on the required amounts of energy and therefore high costs), and this reality is not expected to change in the oncoming decades [5–9]. Today’s 96% of the global hydrogen production is derived from the catalytic reforming of fossil fuels (e.g. natural gas (60–90% CH\textsubscript{4}), gasoil) [6,7,9–11]. In parallel, significant research efforts are dedicated to the application of solid electrolyte membrane reactors (SEMRs) in hydrogen production [6,9–21]. The present paper focuses on the corresponding research field and presents the prospects, trends and research developments of the electro-catalytic hydrogen production in SEMRs.
2. Solid electrolyte membrane reactors (SEMRs)

Membranes are materials, which allow the selective permeation of at least one of the species of a mixture to which they are exposed. Membrane reactors consist mainly of a membrane, which plays the role of the reactor wall. At least one of the reactants or the product of the reaction are supplied or removed through the membrane, providing several advantages, such as the simultaneous reaction and separation in the same device [22].

Solid electrolyte ceramic membranes belong to the general category of inorganic dense membranes [22]. These membranes, at high operating temperatures together with the application of two porous electrodes, which are deposited on both sides of the membrane, allow the selective permeation of ionic species e.g. O$_2^-$, H$^+$, Na$^+$, Li$^+$, etc. SEMRs are devices similar to fuel cells and they can exhibit increased yields towards production of useful chemicals or/and electrical energy. In the literature there are various reviews analyzing the application of SEMRs in the promotion of catalytic reactions [23–33].

Fig. 1 presents the main operation principles that describe SEMRs. A SEMR is consisted mainly of a ceramic solid electrolyte membrane (e.g. in the most cases O$_2^-$ or H$^+$ conductor), in which two porous metal or metal oxide electrodes are deposited on both sides of the membrane. Counter and reference electrodes are exposed to a gas mixture which contains oxygen or hydrogen, while working electrode is exposed to the reacting mixture and it functions also as the catalyst of the chemical reaction. If the oxygen or hydrogen chemical potential is different on the two sides of the membrane, a spontaneous driving force is developed which permits the ionic electro-active species (O$_2^-$ or H$^+$) to permeate through the electrolyte lattice structure. This process is accompanied with the development of a potential or an electrical current between the electrodes.

The main applications of the cell, depicted in Fig. 1, are the electrochemical sensors (case a), when the potential of the cell is affected by the concentration of the compound which is needed to be detected [34], the fuel cells (case c), which can convert the free energy of the reaction directly to electrical energy, bypassing the thermodynamic limitations of the conventional thermal engines [35,36] and the SEMRs (case b), where the target is the electrochemical modification of the catalytic activity towards higher reaction rates [30,31]. Other applications of great importance are solid state batteries [37], oxygen separators [38], hydrogen separators [13], dehumidifiers [13], etc.

The electrochemical cell can operate under the following modes:

2.1. Open circuit operation

The spontaneous tendency of the electro-active ionic species (oxygen ion or proton) to move to the low concentration side of the membrane is countbalanced by the huge resistance of a voltmeter (case a, Fig. 1). Consequently, a potential is developed between the electrodes, which is corresponded to the voltage that it can be calculated from Nernst’s equation and can be directly related with the difference in the chemical potentials of the electro-active ionic species on both sides of the solid electrolyte membrane. Therefore, in this particular case, there is no net current through the electrolyte.

From the pioneering research works of the 1970s [39–41], it was clarified that the above behavior of the solid electrolyte cells can be used for the absorbed oxygen or adsorbed hydrogen activity measurement on the working electrode, which also play the role of the catalyst for the oxidation or hydro-dehydrogenation reactions carried out in the membrane reactor. The thermodynamic activity of the atomic oxygen or hydrogen, which is adsorbed on the catalyst’s surface can be calculated by using the following corresponding equations:

$$\ln \frac{a_{O,E}}{a_{O,A}} = \frac{nFE}{RT} \quad \text{and} \quad \ln \frac{a_{H,E}}{a_{H,A}} = \frac{nFE}{RT},$$

where $n$ is the number of electrons, which are interchanged during the basic electrochemical processes, performed in the cell:

Oxygen conductors: O$_{ad}$ + 2e$^- \leftrightarrow$ O$_2^-$,  
Proton conductors: H$_{ad}$ $\leftrightarrow$ H$^+$ + e$^-$.  

$F$ is Faraday’s constant, $R$ is the ideal gas constant, $T$ is the absolute temperature, $E$ is the electromotive force (emf) of the cell and $a_i$ is the activity of the atomically adsorbed oxygen or hydrogen, on the working electrode ($W$) or reference ($R$), respectively [23–27,41–43]. The corresponding technique called solid electrolyte potentiometry (SEP) in combination with kinetic measurements, has been used for the mechanistic study of numerous chemical reactions [39–63] on various electrodes/catalysts (Ni, Ag, Fe, Pd, etc.).

2.2. Closed circuit operation

Whenever an external potential or current is imposed with the aid of a Galvanostat–Potentiostat (case b, Fig. 1) a controlled flux of ionic species are supplied or removed to or from the working electrode/catalyst providing a significant reversed change on the reaction rate [32]. An electrical current, $I$, corresponds to an equivalent flux of $I$/2F atoms of O/s and
In early studies, in which the total amount of oxygen required for the reaction was supplied electrochemically as $O^{2-}$, the maximum attainable rate of oxygen consumption at the anode was equal to the rate of $O^{2-}$ transport through the solid electrolyte. This is the case of Faradaic operation. Specifically, in the case where the electro-active ionic species are supplied both from the gas phase and electrochemically, through the electrolyte, the enhancement of the catalytic reaction rate may exceed the rate of the electrochemical supply of ionic species. Vayenas et al. [32,64–66] defined the enhancement factor $A$ as:

$$A = \frac{\Delta r}{I/nF}$$  \hspace{1cm} \text{(3)}

the ratio of the catalytic rate enhancement, $\Delta r$ ($\Delta r$ is the difference between the electro-catalytic rate at current $I$ and the catalytic rate at open circuit conditions both expressed in gram atoms of oxygen or hydrogen per second) over the imposing electrochemical (ion transport) rate through the electrolyte ($I/nF$). In the case of ethylene oxidation reaction on Pt, $A$ values of the order of $3 \times 10^5$ were observed [32]. This observation means that for every $O^{2-}$ supplied electrochemically to the working electrode, $10^5$ more oxygen atoms from the gas phase participated in the catalytic reaction, enhancing the catalytic rate by at least two orders of magnitude [32]. This phenomenon of the non-Faradaic electrochemical modification of catalytic activity (NEMCA), has been attributed to changes in the catalysts’ work function, which are caused due to the electrochemical ion pumping [32]. This technique has been applied both to $O^{2-}$ SEMRs (e.g. hydrocarbons oxidation) and to $H^+$ SEMRs (e.g. ammonia synthesis), with remarkable success [32,67].

Respectively, (case c, Fig. 1) a reaction which produces or consumes the electro-active ions, on the working electrode surface, maintains the concentration difference of oxygen anions or protons, on the two sides of the electrolyte, and thus as a result an electrical current is developed between the two electrodes (fuel cell operation).

2.3. Types of SEMRs

In Fig. 2 the three most used configurations of SEMRs are schematically presented. In case (a) a solid electrolyte ceramic tube closed at one end, is enclosed to another tube (usually quartz). The two electrodes are deposited at the inside and outside bottom of the inner tube. The definition of which electrode is the anode and which is the cathode depends on the reaction and the conductive ion. When is needed to measure the potential of the working electrode excluding the ohmic losses, a third electrode (reference), must be added. When the reaction is taking place in the inner chamber of the SEMR, supply or removal of the produced hydrogen is carried out in the outer chamber. In the case of $O^{2-}$ conductors, the second tube can be dispensed with the solid electrolyte, which can be exposed directly to the atmospheric air. The turbulent supply of the reactants through a nozzle simulates SEMR (Fig. 2a) operation to a continuous stirred tank reactor (CSTR).

The SEMR presented in Fig. 2b, is also a CSTR, however both electrodes are exposed to the same reacting mixture, while in the SEMR of Fig. 2c reactants and products are separated by the solid electrolyte wall and the composition of each stream changes along the reactor length (plug flow reactor operation).

SEMRs are somehow particular cases of catalytic reactors and some additional requirements should be fulfilled. Therefore, working electrode/catalyst should be porous enough in order to achieve an effective three phase boundary between the gas phase, the electrode and the solid electrolyte, where the basic electrochemical reactions (2) are taking place, in the opposite direction. The layer should be very thin in order to avoid concentration gradients inside the pores. In general, all electrodes (working, counter and reference) should be porous and exhibit high conductivity (electronic and ionic) and high electro-catalytic activity towards the electrochemical reactions, which are carried out in both the anode and cathode compartments of the SEMRs.

In a conventional catalytic reactor, two of the most important design parameters are the molecular flow rate and the ratio of catalytic surface to the reactor volume. In SEMRs, reactants are introduced either from the gas phase or electrochemically (ionic flux) through the solid electrolyte, which is depending only to the three phase boundary between gas phase/electrode/electrolyte and not to the catalyst surface [30].

2.4. Advantages of SEMRs

The selective conductivity of one and only ion, in the majority of SEMRs, gives them the significant advantage to function as separators of the reacting oxygen from the nitrogen of the air or of the produced hydrogen. Therefore, in the first case if the cathode is exposed to the air or any gas mixture containing oxygen, only oxygen is transferred through the solid electrolyte. This is a very important advantage since on the one hand it reduces the volumetric flow rate of the reactants (decreasing reactor’s volume, thermal demands, etc.), and on the other hand any harmful impurities that could present with the reactants and could deactivate the electrode/catalyst (e.g. sulfur compounds) are avoided [30].

Also, it has been experimentally proven, that the electrochemical supply of oxygen anions to the electrode/catalyst can enhance the reaction rate [32], modify the selectivity, and eliminate undesired processes such as coke deposition [68,69]. Accordingly, in the case of electrochemical supply of protons at the electrode/catalyst, a shift on the chemical equilibrium of hydrogenation reactions, was observed [67].

Finally, SEMRs can operate as devices where the production of useful chemical products is combined with the simultaneous power generation. Therefore, under closed circuit operation, the maintenance of the difference in concentrations between the electro-active species on the two sides of the membrane, due to the chemical reaction (consumption or generation of electro-active species on the working electrode), can produce electrical energy (fuel cell operation) combined with the electrochemical enhancement of the chemical reaction (membrane
3. Hydrogen production in SEMRs

Hydrogen can be produced from water by steam (or water) electrolysis and from the hydrocarbons by one of the following processes: steam reforming, partial oxidation, auto-thermal reforming, dehydrogenation.

In all SEMR’s studies dealing with the production of hydrogen the solid electrolyte was either O$_2^-$ (e.g. mainly Yttria Stabilized Zirconia, YSZ) or H$^+$ (e.g. mainly SrCe$_{0.95}$Yb$_{0.05}$O$_3$, SCY) conductor. This can be attributed to two significant reasons:

1. O$_2^-$ SEMRs are by far the most widely used in all studies. For nearly two decades, only O$_2^-$ SEMRs were used [30]. In the early 1980s, Iwahara and co-workers discovered materials exhibiting protonic conductivity at elevated temperatures ($T > 600^\circ$C) and since then many studies deals with H$^+$ SEMRs [13]. Following O$_2^-$ and H$^+$, several cationic (Na$^+$, K$^+$, Li$^+$), anionic (F$^-$) as well as mixed conductors (O$_2^-$e$^-$, H$^+$e$^-$, O$_2^-$H$^+$) have been used in several occasions [31].

2. As it was analyzed before the advantages of SEMRs are enhanced in cases when a reactant (e.g. O$_2$) or a product (e.g. H$_2$) of the chemical reaction is the electro-active species that can be transferred through the solid electrolyte. Therefore, it is clear that O$^{2-}$ or H$^+$ SEMRs are the most appropriate reactors for the production of hydrogen.

Fig. 2. Schematic presentation of SEMRs designs: (a) double chamber continuous stirred tank reactor cell; (b) single chamber continuous stirred tank reactor cell; and (c) double chamber plug flow reactor cell.
Table 1
Hydrogen production in O$_2$−SEM Rs

<table>
<thead>
<tr>
<th>Reaction</th>
<th>MO</th>
<th>Solid electrolyte</th>
<th>Working electrode</th>
<th>Temperature (°C)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Partial oxidation of hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Partial oxidation of CH$_4$</td>
<td>1, 2</td>
<td>YSZ</td>
<td>Ni</td>
<td>750–1000</td>
<td>[72,76,78,80,82,90–93]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CSZ</td>
<td>Ni-SDC</td>
<td>700–800</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>SDC</td>
<td>Ni-ZrO$_2$-CeO$_2$</td>
<td>800–850</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ni(Pr-Ni/Al$_2$O$_3$)</td>
<td>1000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1, 2</td>
<td>YSZ</td>
<td>Ni-Au</td>
<td>750–850</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ni-Ca$<em>{0.8}$Sr$</em>{0.2}$Ti$<em>{0.9}$Fe$</em>{0.1}$O$_{3-a}$</td>
<td>900</td>
<td>[68,69,71,72,80,90]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>YSZ</td>
<td>Fe</td>
<td>800–1000</td>
<td>[75,80,90]</td>
</tr>
<tr>
<td></td>
<td>1, 2</td>
<td>YSZ</td>
<td>Pt</td>
<td>700–1000</td>
<td>[72,76,79–81,90,93,131]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt-CeO$_2$</td>
<td>800</td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>PbBi</td>
<td>800–1000</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1, 2</td>
<td>YSZ</td>
<td>Rh</td>
<td>500–850</td>
<td>[73,74,87–89]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rh-TiO$_2$</td>
<td>550</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1, 2</td>
<td>YSZ</td>
<td>Ru-YSZ</td>
<td>700–800</td>
<td>[77]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>YSZ</td>
<td>La$<em>1$$</em>{4}$Al$<em>{0.7}$O$</em>{3-a}$</td>
<td>950</td>
<td>[94,95]</td>
</tr>
<tr>
<td></td>
<td>1, 2</td>
<td>YSZ</td>
<td>La$<em>{0.8}$Sr$</em>{0.4}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-a}$</td>
<td>700–850</td>
<td>[96]</td>
</tr>
<tr>
<td>Partial oxidation of higher hydrocarbons</td>
<td>1</td>
<td>YSZ</td>
<td>MoO$_3$-Au</td>
<td>500</td>
<td>[97,98]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>V$_2$O$_5$-Au</td>
<td>500</td>
<td></td>
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<tr>
<td></td>
<td></td>
<td></td>
<td>MoO$_3$-V$_2$O$_5$-Au</td>
<td>500</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>CaSZ</td>
<td>Ag</td>
<td>450–500</td>
<td>[99]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>YSZ</td>
<td>VPO-Au</td>
<td>447–517</td>
<td>[100]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>YSZ</td>
<td>La$<em>{0.8}$Sr$</em>{0.4}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-a}$</td>
<td>300–750</td>
<td>[101]</td>
</tr>
<tr>
<td>Reforming of hydrocarbons</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Steam reforming of CH$_4$</td>
<td>1</td>
<td>YSZ</td>
<td>Ni</td>
<td>750–950</td>
<td>[107–109]</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>YSZ</td>
<td>Ni-YSZ</td>
<td>850–950</td>
<td>[69]</td>
</tr>
<tr>
<td>Internal steam reforming of CH$_4$ in SOFCs</td>
<td>1, 2</td>
<td>YSZ</td>
<td>Fe</td>
<td>800–1000</td>
<td>[110,111]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ni-YSZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1, 2</td>
<td>YSZ</td>
<td>Ni-YSZ</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1, 2</td>
<td>YSZ</td>
<td>Ni-YSZ-FeO$_2$</td>
<td>800–1000</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ce$<em>{0.6}$Gd$</em>{0.4}$O$_{1.8}$</td>
<td>800–1000</td>
<td>[113]</td>
</tr>
<tr>
<td>Internal dry reforming of CH$_4$ in SOFCs</td>
<td>1, 2</td>
<td>YSZ</td>
<td>Pt</td>
<td>600–900</td>
<td>[114,115]</td>
</tr>
<tr>
<td></td>
<td>1, 2</td>
<td>YSZ</td>
<td>Ni-YSZ-FeO$_2$</td>
<td>700–800</td>
<td>[114,115]</td>
</tr>
<tr>
<td>Steam electrolysis</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>CSZ</td>
<td>NiO</td>
<td>700–800</td>
<td>[116–120]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>ZrO$_2$-TiO$_2$-Y$_2$O$_3$</td>
<td>—</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

MO, Mode of operation; 1, Galvanostatic/potentiostatic mode; 2, Fuel cell mode.

It must be mentioned here that the majority of the SEMRs’ studies corresponded to bench-scale experiments. Therefore, reactor volumes were ranged between 50 and 70 cm$^3$, while typical flow rates of 50–150 ml/min, were used.

In the following, a literature review concerning hydrogen production in SEMRs, will be presented. The presentation will be separated into two main sections, the O$_2$− and the H$^+$ SEMR studies. Each section will be consisted of different parts depending on the reactions that have been studied in each SEMR.

3.1. Hydrogen production in O$_2$−SEM Rs

The main chemical reactions that have been used for hydrogen production in O$_2$−SEM Rs are presented in Table 1. The majority of the works is dealing with the partial oxidation of hydrocarbons (mainly methane and more recently higher hydrocarbons) to synthesis gas, while reforming (either steam or dry) of hydrocarbons in the most cases has been combined with fuel cell operation (internal reforming).

3.1.1. Partial oxidation of hydrocarbons

Methane and other hydrocarbons can be converted to hydrogen via partial oxidation which may be catalysed or uncatalysed or a combination of both. Partial oxidation is a reforming process in which the fuel is partially combusted in an exothermic reaction which provides heat for other reactions in the reforming system. The oxygen fed to the system is sub-stoichiometric so that both CO and CO$_2$ are formed in the system. A water–gas shift reaction can transform the CO from the first reaction further into CO$_2$. Reactions are:

$$\text{CH}_4 + \frac{1}{2}\text{O}_2 \leftrightarrow \text{CO} + \text{2H}_2,$$  (4)
CH₄ + O₂ ↔ CO₂ + 2H₂. (5)

Methane partial oxidation occurs on heterogeneous selective catalysts exhibiting high selectivity towards CO/H₂ at temperature of 850 °C [70]. Partial oxidation even though produces lower ratios of H₂/CO, it is a very important reaction since, in contrary with hydrocarbon reforming, is an exothermic reaction with high reaction rate.

The most common studies in O²⁻ SEMRs are partial or selective oxidation of hydrocarbons. The majority of the works deals with the partial oxidation of methane either in SEMRs or internally in SOFCs. Recently emphasis has been given to the selective oxidation of higher hydrocarbons and ethanol.

3.1.1.1. Partial oxidation of CH₄. The electro-catalytic partial oxidation of methane to synthesis gas has been studied on various electrodes, but mainly on Fe [68,69,71,72,80,90], Rh [73,74,87–89], Ag [75,80,90], Pt [72,76,79–81,90,93,131], Ru [77] and Ni [72,76,78,80,82,90–93,102–106,108–110], based catalysts. As far as the catalytic behavior of the reaction concerns, Hickman and Schmidt [83,84] reported the production of hydrogen on Pt and Rh surfaces and at a temperature range between 927–1127 °C, while Tsang et al. [85] found that transition or noble metals, such as Ni, Ru, Rh, Pd, Ir and Pt deposited over alumina are active even at temperatures lower than 800 °C, due to the combustion/reforming mechanism. On rhodium, the reaction is taking place via the decomposition of CH₄ to CHₓ, which is followed by the reaction between CHₓ and O(ads) [83,84]. On nickel surfaces, carbon formation is carried out through the decomposition of the adsorbed CHₓ to adsorbed atoms of C, with the simultaneous production of H₂ [85].

Alqahtany et al. studied the effect of two oxygen sources, gaseous molecular oxygen and ionically transported oxygen, on methane conversion and selectivity to synthesis gas, on Fe electrodes in an O²⁻ (YSZ) SEMR at a temperature range between 800 and 950 °C [68]. In the second case (electrochemical oxygen), the CO selectivity and yield were increased compared with the gas phase oxygen and were nearly 100% and 73%, respectively. However, these two kinds of oxygen did not differ significantly in H₂ formation (produced H₂ was not oxidized by the electrochemical oxygen), while carbon deposition was reduced. By implementing the SEP technique, reduced Fe was found to be more active than the oxidized one. At high CH₄/O₂ ratios, the rate of carbon formation was comparable with the rate of CO formation and it was enhanced by increasing the temperature. By assuming that carbon formation is taking place via the decomposition of methyl radicals [86], they assumed that even though the electrochemical pumping favors the production of CO it did not affect the production of H₂ [68,71].

Takehira et al. studied the methane partial oxidation reaction on Rh at 500 °C, and they focused on the O²⁻ diffusion on the anode surface, a process which seemed to favor the direct partial oxidation mechanism [73,74,87]. The product distribution was different to that predicted by thermodynamics, therefore reforming reactions were not taken into account, while the excess H₂ was attributed to carbon deposition. The morphology as well as the oxidative state of the anode affected the direct partial oxidation of CH₄ [73,74]. The oxidized catalytic surface or the high surface oxygen concentration favored total combustion, while the reduced catalyst promoted the partial oxidation reaction [74,87]. Direct partial oxidation mechanism involved the dissociative adsorption of CH₄, which is not favored by the presence of Rh₂O₃. XRD analysis showed that during electro-chemical oxygen pumping, Rh₂O₃ was formed on the external surface of the electrode, while Rh was prevailed on the bulk phase of the electrode [87]. According to previous works [88], it was suggested the mechanistic model depicted in Fig. 3, which involves two types of active sites, one on the surface of the gas phase/Rh/YSZ three phase boundary, where complete combustion is favored and the second on the gas phase/Rh interface, where O²⁻ anions are transformed to adsorbed surface oxygen and reacted with CH₄ to produce CO and H₂ [87]. During the electrochemical oxygen pumping, the oxidation state of Rh was controlled by the competitive consumption of oxygen by Rh or CH₄ [74]. When the O²⁻ supply was increased, Rh surface was oxidized, becoming more active for complete oxidation [88]. Electrochemical O²⁻ pumping affected substantially the morphology of Rh surface anode and as a consequence the production of hydrogen was increased dramatically.

Baranova et al. [89] examined the catalytic activity of the dispersed Rh–TiO₂ interlayer deposited on YSZ for the partial oxidation of methane to synthesis gas. High CO selectivity (97%) was achieved in a wide range of different CH₄/O₂ ratios at 550 °C. Under working conditions Rhodium catalyst had two distinguished surface states: active and inactive (Fig. 4). According to the catalyst potential the above states correspond to rhodium metal (active state) and rhodium oxide (inactive state). The remarkable results in terms of catalytic activity and selectivity when Rh is interfaced with TiO₂ are related to the lowered stability of surface Rh oxide against reduction to:

![Fig. 3. Schematic presentation of the direct partial oxidation mechanism.](image)

![Fig. 4. “Wireless” electrochemical promotion of CH₄ partial oxidation on Rh interfaced with TiO₂ with internal short circuiting.](image)
metallic Rh. This phenomenon was attributed to the difference of work functions between the catalyst and the support [89].

Galvita et al. [78,79], used Ni electrodes at a temperature range between 750 and 850°C, where the mechanism of direct partial oxidation is prevailing and is close to thermodynamic equilibrium. In contrary with previous catalytic works [85], the increase of reactants’ flow rate at constant reactants’ concentration, did not affect the selectivity, excluding the combustion/reforming mechanism. Sobyanin et al. studied the electrocatalytic partial oxidation of methane on Pt, Ni, Ag, Fe and Pt/CoOx electrodes [80,90] at 660–850°C and CH4/O2 ratio equal to 0.8–2.0, and they achieved high conversion rates. The optimum reaction conditions were achieved at temperatures 800–850°C and at CH4/O2 ratios equal to 1–2. Under these reaction conditions a complete conversion of the electrochemical O2− was obtained towards a mixture of H2/CO ratio equal to 2. This high conversion was attributed to carbon oxidation by the electrochemical oxygen, which especially in the case of Pt electrodes and at low temperatures (> 660°C) led to higher yields.

Semin et al. [81] studied the reaction on Pt electrodes at 800°C, and they reported methane conversion and CO selectivity of the order of 97% and 95%, respectively. The reactor operated as a fuel cell and the electrode was stable and durable against carbon deposition. In contrary to previous works on Fe, Pt, and Ni, where electrodes with smaller apparent surface area were used and methane was diluted in inert gas, Semin et al. used electrodes with higher apparent surface area and pure methane as a feed. By increasing the volumetric flow rate or by reducing the CH4/O2 ratio, the selectivity of partial oxidation was decreased while on the other hand methane conversion was enhanced. The product distribution was close to that expected for thermodynamic equilibrium, assuming the combustion/reforming mechanism (Fig. 5) and the rate was increasing linearly with methane.

Hamakawa et al. [91,92], used Ni on Ca0.8Sr0.2Ti1−xFexO3−δ as an electrode/catalyst. Electrochemical O2− pumping enhanced the yield and selectivity of CO. Ni–Ca0.8Sr0.2Ti1−xFe4O3−δ electrode was stable against carbon deposition compared with conventional catalysts Ni1.0/a-Al2O3 and Ni/Ca0.8Sr0.2TiO3, where carbon deposition is carried out at the interface between metal/support. This phenomenon was attributed to methane oxidation by lattice oxygen on the Ni/Ca0.8Sr0.2Ti1−xFe4O3−δ interface due to the high O2− conductivity exhibited by the latter. In general, Ni electrodes/perovskites (e.g. Ni/(Ca,Sr)TiO3 or Ni/BaTiO3) exhibited high activity towards methane oxidation and low carbon formation, with the only disadvantage of low electronic conductivity. Iwahara et al. [93] reported that CaTiO3 substituted by Fe3+ achieved an appreciable electronic conductivity. The electrode that was used showed mixed (ionic/electronic) conductivity, with oxygen transport number equal to 0.27. The formation rates of CO and H2 increased linearly with the imposed current while no formation of CO2 was observed. When the electrochemical supply of O2− exceeded the reaction rate, the rate was decreased dramatically due to the oxidation of Ni to NiO.

Tagawa et al. [94], have tested the effect of the imposed potential in the selective oxidation of methane on La1.8Al0.2O3 electrodes. Their work focused both on the partial oxidation and on the oxidative coupling of methane. Temperature programmed desorption measurements showed that the quantity of the adsorbed oxygen in the anode was enhanced by the increase of the potential. During the electrochemical oxygen supply, positive potentials increased the CO and CO2 formation rates, while the application of negative potentials decreased the corresponding formation rates. During the simultaneous supply of gas phase and electrochemical oxygen the catalytic activity of the anode was enhanced in a non-Faradaic way. The surface oxygen species favored the CO, CO2 formation, while the participation of lattice oxygen at higher temperatures led to oxidative coupling products, according to previous works [95]. During the application of positive potentials, the quantity of the adsorbed oxygen was increased, while desorption of lattice oxygen was not enhanced.

Under open circuit conditions, C2 hydrocarbons were selectively produced, while by imposing positive potentials CO formation was increased, without affecting the formation of C3’s, as it was expected since positive potentials increased the amount of adsorbed oxygen without affecting the participation of the lattice oxygen. Respectively, by imposing negative potentials, the CO, CO2 formation rates were decreased, while the formation rate of C2 remained unchanged.

Tsiakaras et al. [96], employed the La0.6Sr0.4Co0.8Fe0.2O3 (LSCF) perovskite type oxide as a catalyst/electrode in order to study the partial oxidation of methane. The observed product distribution was explained by taking into account the combustion/reforming mechanism. In the case of the gas phase O2, two species of oxygen participated in the proposed mechanism. The weakly bonded electrophilic oxygen, led to the initial formation of CO2 and H2O, while the formation of strongly bonded CO was attributed to perovskite lattice oxygen. Subsequently, CO reacted with the produced H2O.

In the case of electrochemical oxygen supply, the strongly bonded lattice oxygen, O2−, was participated in the reaction. It was reported that the electrochemical O2− led to the oxidation of the deposited carbon, selectively to CO [96], when the perovskite lattice oxygen seemed to favor the partial oxidation of methane. At higher electrochemical pumping rates, the produced CO was oxidized to CO2 or reacted with the produced water to CO2 and H2 (water–gas shift reaction). At lower electrochemical oxygen pumping rates, carbon deposition was observed, which did not seem to be catalyzed when similar
quantities of oxygen and methane are supplied from gas phase. This behavior can be attributed to the presence of adsorbed $O^{−3}$ species, which were located on the catalytic surface, during the electrochemical oxygen anions supply and promoted the acidity of the perovskite active sites. The acid active sites were effective to catalyze the reaction of hydrocarbons and methane pyrolysis. When the oxygen was supplied electrochemically, significant changes in the methane conversion and hydrogen production were observed, which can be attributed to the faster replacement of surface lattice oxygen of the perovskite active sites by the $O^{−2}$ through the bulk phase of the electrode towards its surface.

LSCF is known for its $O^{2−}$ conductivity, which permits the solid state diffusion of oxygen through its bulk phase [38]. Solid state diffusion permitted high fluxes of $O^{2−}$ from the electrolyte/electrode interface to the electrode/gaseous phase interface, which was taking place in parallel with the usual spillover of $O^{2−}$ at the gas phase/electrode/electrolyte three phase boundary and the consecutive surface diffusion of oxygen species to the active sites of the electrodes [32].

The fuel cell-type reactor is the result of the application of fuel cell technology to catalytic-SEM reactors. Reactions which occur on the same catalyst surface in a conventional catalytic reactor are proceeded separately upon the electrodes/catalysts used (e.g. 16 mol% Y2O3-stabilized ZrO2 (YSZ), 15 mol% CaO-stabilized ZrO2 (CSZ), Ce0.8Sm0.2O2 (SDC) and La0.9Sr0.1Ga0.8Mg0.2O3 (LSGM)) [102,103]. Simultaneous production of thermal energy, electric power and CO/H2 gas mixtures was achieved in all cases.

The open circuit voltage (OCV) as well as the maximum power density were strongly dependent on the used solid electrolyte and especially on their oxide ionic conductivity, while CO/H2 gas mixture was slightly affected. Since higher power density gave a higher yield of CO2, the permeated oxygen seemed to be mainly consumed by the oxidation of H2 and/or CO which was formed by the selective oxidation of CH4 by O2. Among the solid electrolytes examined, the highest power density as well as the highest yield for synthesis gas production were obtained on the fuel cell reactor where LSGM-based perovskite type oxide was used as the solid electrolyte. The conversions of O2 and CH4 were hardly dependent upon the current density across the cell, while yield of CO and H2 decreased and that of CO2 increased with increasing current density. Therefore, it seemed likely that the amount of CO and H2 oxidized by the permeated oxygen increased with increasing current density. Conversion of CH4, drastically decreased with decreasing the amount of oxygen and CH4 conversion was as low as 25% when only CH4 was supplied to the anode side [102,103].

Takita et al. found also that doping of small amounts of Fe or Co to LSGM solid electrolyte was highly effective for increasing oxide ion conductivity. Consequently, applications of Fe or Co doped on LSGM electrolytes for fuel cells in which CH4 partial oxidation was taking place, increased the power density and the yield of synthesis gas. This observation was attributed to the enhancement of hole conduction due to Fe or Co doping.

Zhang et al. [106] used Ni-SDC as an anodic electrode in a fuel cell system with a LSGM perovskite as the electrolyte, at 700–800°C. The H2/CO ratio was increased from 1.4 to 2.0 with the increase of the electrical current, while CO/CO2 ratio was decreased. Anodic potentials affected products selectivity and low polarization favored the production of synthesis gas with high H2/CO ratio. The decrease of methane flux increased the H2 and CO concentrations indicating a combustion/reforming mechanism. Fully oxidized Ni catalyst led to complete combustion products, while reforming reactions were enhanced on reduced surface. By imposing an electrical current to the cell, electrochemical oxygen regenerated the electroactive sites of Ni, shifting reaction equilibrium to the products and increasing the efficiency of the cell.

3.1.1.2. Partial oxidation of higher hydrocarbons. Recently, attention has been given on the partial oxidation of higher hydrocarbons (C2–C4) in SEMRs [97–100]. The truth is that the main target of these works is the formation of petrochemical intermediates and not hydrogen production. However, partial oxidation product streams always contain hydrogen at high concentrations, that is why many petrochemical industries are interested in the development of selective hydrogen separation membranes.

Takehira et al. [97,98] studied the selective partial oxidation of C2–C4 hydrocarbons on MoO3, V2O5 and MoO3–V2O5 at 500°C, in a SEMR consisted of YSZ as the solid electrolyte and gold and silver as the anode and cathode, respectively. Au was used in order to ensure electronic conductivity. Two types of oxygen source were used, the gaseous and the electrochemical oxygen.

Propane and isobutene were oxidized to propylene and methacrolein, respectively, on V2O5, while neither alkane was oxidized on MoO3, under oxygen pumping. Ethane was not remarkably oxidized even on V2O5 due to the strong C–H bond [98]. It was concluded that H abstraction is the rate determining step (rds) of the alkane oxidation on V2O5, where reduction–oxidation of vanadium sites produced acid/base properties on the catalyst surface, affecting the catalytic behavior. Alkenes were partially oxidized on both MoO3 and V2O5. The selectivity to acetaldehyde, acrolein and methacrolein from ethylene, propylene, and isobutylene, respectively, were higher on the former than on the latter. Alkenes were oxidized more efficiently under oxygen pumping than by gaseous oxygen on MoO3, while on the other hand, alkenes were far more rapidly oxidized by gaseous oxygen compared to electrochemical oxygen, on V2O5.

Similar reactions were studied in the MoO3–V2O5 system, where it was expected that the use of MoO3 coupled with V2O5 under oxygen pumping would enhance the activity [98]. MoV2O8 formed as the active phase in the MoO3–V2O5 mixed oxide catalyst. Ethane and propene were oxidatively dehydrogenated to ethene and propene, respectively, while isobutane
The (0 0 1) and (1 1 0) planes of MoV$_2$O$_8$ appeared most intensively for the V content of 43.7 and 53.4%, and the formations of propene and ethene were most efficiently accelerated on the former and the latter, respectively. (1 1 0) plane was more active than the (0 0 1) plane and the primary C–H bond in ethane required higher activity for the dehydrogenation than did the secondary C–H bond in propane.

The electrochemical oxygen pumping system supplied continuously dissociated oxygen species onto the active sites on MoV$_2$O$_8$ catalyst film and therefore drastically enhanced the oxidative dehydrogenation of ethane and propane at the active sites compared to the conventional fixed-bed reactor.

Hellgardt et al. [99] examined the partial oxidation of propene on silver at two temperatures (450 and 500°C) under highly reducing conditions (small oxygen/propane ratio). Two partial oxidation products were detected, namely, acrolein and 1,5-hexadiene, in addition to the total oxidation products. Electrochemical oxygen supply to the catalyst through a solid electrolyte membrane induced the formation of 1,5-hexadiene, whilst gas-phase oxygen provision yielded mainly acrolein. Total oxidation product selectivity was not affected. It was suggested that different surface oxygen species (dependent on the means of oxygen supply) may be responsible for the observed behavior.

Ye et al. [100] used a SEMR to study the selective partial oxidation of n-butane to maleic anhydride (MA) on a vanadium phosphorus oxide (VPO) catalyst. Periodic redox experiments, in which electrical oxygen pumping and butane oxidation were carried out sequentially, confirmed that the reduced activity of the VPO catalyst in the butane oxidation could be regenerated by electrical oxygen pumping. Two possible oxidation mechanisms were proposed: direct electrochemical oxidation in the first VPO layer and non-direct electrochemical oxidation in the second VPO layer. The results of steady-state experiments demonstrated the influences of operating conditions such as imposing current, reaction temperature, butane concentration and flow rate on the conversion of reactants and selectivity to products and MA yield. The selectivity to MA was 50–53% and butane conversion was 15–18% with MA yield of 8–10%.

Ethanol has been recognized as a quality motor fuel since the design of the first combustion engines because of its high octane and thermal content. Despite the fact that it is currently used only as a component of light-duty vehicle fuels, it is also possible to use it in fuel cells for the production of electrical power with efficiencies attaining 50–65%. Douvatzides and Tsiakaras [101] studied the ethanol oxidation reaction on the perovskite-type La$_{0.4}$Sr$_{0.4}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$ catalyst deposited in a YSZ solid electrolyte reactor, at a temperature range of 300–750°C and fuel rich reactant mixtures. Total ethanol conversion was attained at the highest temperature leading mainly to acetaldehyde. The electrochemical supply of oxygen anions mainly affected the formation rates of CO and CO$_2$.

3.1.2. Reforming of hydrocarbons

In the term “reforming of hydrocarbons” are included the steam and dry (with CO$_2$) reforming of hydrocarbons (mainly methane). Both reactions are strongly endothermic and thus high operating temperatures are required, in order to overcome the thermodynamic limitations. On the other hand, solid oxide fuel cells (SOFCs) are also operating at these high temperatures and therefore reforming reactions can be performed “in situ” (internal reforming), in the SOFC system.

3.1.2.1. Steam reforming of CH$_4$

Nowadays steam reforming is one of the main methods for the production of H$_2$. Although partial oxidation and coal gasification also play a vital role in hydrogen production, steam reforming is cheaper and more energy efficient than the former two methods [6,70].

In general, the reaction for steam reforming of a hydrocarbon into a mixture of hydrogen and carbon monoxide (synthesis gas) is as follows:

$$C_nH_m + nH_2O \leftrightarrow nCO + (n + m/2)H_2.$$  (6)

This reaction is endothermic ($\Delta H_0 > 0$) which leads to the need of heat transfer [30]. Reactor designs are typically limited by heat transfer rather than the reaction kinetics. A further process is normally the conversion of CO in the water–gas shift reaction to CO$_2$ by utilizing the excess steam:

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (\Delta H_0 = -41.2 \text{kJ/mol}).$$  (7)

Steam reforming of most hydrocarbons occurs only on appropriate catalysts and at elevated temperatures (> 800°C). Catalysts for steam reforming are usually group VIII metals (Rh, Ni, Ru, Pt, Ir, and Pd) [70] whereby Ni seems to be the most effective of this group. Depending on the catalyst’s selectivity and on the saturation of the used hydrocarbons, the decomposition of the hydrocarbon may be favored over the reaction with steam. This process, called coke formation, can deactivate the catalyst in different ways [70]. To avoid coke formation an optimum fuel to steam ratio must be maintained throughout the entire system.

Bebelis et al. [107] studied the kinetics of methane steam reforming on Ni–YSZ cermet electrodes. Under open circuit conditions and at a temperature range of 800–900°C, the reaction exhibited Langmuir–Hinselwood kinetics, due to the competitive adsorption of CH$_4$ and H$_2$O molecules. Kinetic results were interpreted by a mechanistic scheme (Fig. 6), which involved two rdss, the adsorption of methane and the surface reaction.

![Fig. 6. Schematic presentation of the steam reforming mechanism.](afii9797)
between C_{ad} with O_{ad} species, which were originated by H_{2}O absorption. The relative reaction rates of these steps affected both the apparent activation energy and carbon deposition. As far as the CO_{2} formation rate concerns, kinetic results were explained by considering as rds the surface reaction of absorbed CO with O_{ad}. At anodic polarization conditions, carbon deposition rate was decreased at about 33%, while the electrochemical supply of O^{2−}− favored either the production of CO/H_{2} or CO_{2}/H_{2}O mixtures, depending on the P_{CH_{4}}/P_{H_{2}O} ratio.

In addition, at Ni–YSZ cermet electrodes, Yentekakis et al. [108,109] studied the kinetics of methane steam reforming, at 750–950°C and it was also found that reaction followed Langmuir–Hinselwood behavior due to the competitive adsorption of methyl radicals and O or OH− species. Maximum reaction rates were observed at CH_{4}/H_{2}O average ratios of 0.25−0.5. Under a critical H_{2}O concentration, where Boudouard reaction (2CO → CO_{2} + C) was thermodynamically favored, CH_{4} conversion was eliminated and strong carbon deposition was taken place. At higher P_{H_{2}O}, methane consumption rate was increased linearly in respect to P_{H_{2}O} to a maximum value, which was shifted to higher temperatures as temperature was increased. At higher P_{H_{2}O} the rate was decreased. Under electrochemical pumping the critical H_{2}O partial pressure decreased, while the CO rate increased at about 5700%. Carbon formation decreased during the application of positive currents, indicating that it was an electropheric reaction.

Using Fe [69] electrodes, the electrochemical supply of O^{2−} promoted the CO formation rate without affecting H_{2} yield. Therefore, H_{2}/CO ratio decreased with current application, while H_{2} formation increased with increasing CH_{4} partial pressure. Carbon formation occurred in both cases, but it was lower in the former case, while methane and steam conversions were lower than those predicted by thermodynamics. In the absence of oxygen, carbon formation rate was comparable to the corresponding CO formation rate. Electrochemical O^{2−}− activated the deposited carbon more easily than gas phase O_{2}, which is difficult to diffuse to Fe electrode, especially when it is covered by carbon. CO_{2} formation rate was enhanced by gas phase O_{2} rather than electrochemical oxygen, O^{2−}. Reforming activation energy was higher in the case of O^{2−} (21.3 kcal/mol) compared to the corresponding activation energy in the case of gas phase O_{2} (9.3 kcal/mol). Hydrogen formation rate exhibited the same behavior at systems containing H_{2}O and H_{2}O + O^{2−}− and it was decreased in the case of H_{2}O + O_{2} systems.

3.1.2.3. Internal steam reforming of CH_{4} SOFCs. Belyaev et al. [110] used Ni–YSZ–CeO_{2} as anode at 800–850°C and steam/methane ratios equal to 2−4. The rate was first order in respect to methane and the apparent activation energy was equal to 39 kcal/mol. Anodic and cathodic electrode polarization did not cause any noticeable changes. The reaction order of H_{2}O was close to zero. Addition of CeO_{2} promoted both the catalytic and electro-catalytic activity of the electrodes and decreased the carbon formation. At anodic polarization, O^{2−}− ions oxidized reforming products, while during cathodic polarization steam electrolysis rate was increased. Under close circuit conditions, Ni–ZrO_{2}–CeO_{2} electrode exhibited high electrochemical activation towards both hydrogen oxidation and steam electrolysis. At anodic polarization, the electrochemical activation in the presence of CH_{4}/H_{2}O was lower compared to that of H_{2}−H_{2}O mixture, because in the former case electrochemical H_{2} oxidation reaction is controlled by H_{2} formation during CH_{4} reforming. The imposition of anodic currents resulted in the reversible increase of methane conversion. Electrochemical oxygen consumed the produced hydrogen without affecting the rates of CO and CO_{2}. In contrary, the application of cathodic currents decreased the CO and CO_{2} formation rates and consequently CH_{4} conversion.

Nakagawa et al. [111] studied the same system, but moreover they measured the effect of hydrogen partial pressure. It was found that the catalytic activity of the Ni–YSZ–CeO_{2} anode was higher compared to that of Ni–YSZ especially at lower temperatures as long as the reaction gas mixture contained hydrogen. A gradual deterioration of the catalytic activity of the anode was observed at low P_{H_{2}} and high P_{H_{2}O} atmospheres and also at high current densities, which was attributed to the oxidation of Ni surface by steam at high P_{H_{2}O} (either presented in the reacting mixture or water that is produced via the electrochemical oxidation).

Nickel is a well established catalyst for reforming reactions and an effective electro-catalyst for the electrochemical oxidation of hydrogen. However, carbon deposition remains a significant problem, specifically at high P_{CH_{4}}, and thus high steam/carbon ratios (> 2) are needed, which decreased the yield to synthesis gas production. Ce_{1−x}Gd_{x}O_{3−α} anodes, have been reported to effectively catalyze methane oxidation [112], however at reduced conditions become a mixed ionic and electronic conductors. The ability of Ce to decrease carbon deposition, allow the cell to operate at low steam/carbon ratios. Marina and Mogensen [112] tested the direct electrochemical methane oxidation on Ce_{0.6}Gd_{0.4}O_{1.8} (CGO) electrode. The electrode exhibited low electro-catalytic activity towards either oxidation or reforming reactions, implying that methane conversion, under open circuit conditions and low anodic overpotentials was
attributed to homogeneous methane pyrolysis. No carbon deposition was observed even after 350 h of operation at 1000°C and steam/carbon ratio up to 0.1. The apparent activation energy was equal to 150 kJ/mol and it was not affected by water concentration, while it was increased under current application to 158 kJ/mol. These values are indicating that methane pyrolysis was the rds of a chain reaction, which included the formation of methyl radicals [112]. Positive overpotentials enhanced both the rates of H2 and CO combustion, complete and partial oxidation of methane and carbon oxidation. Anodic polarization increased methane conversion and CO2 selectivity, while decreased CO selectivity. Negative currents led to the electro-catalytic steam reduction, decreasing methane conversion and increasing hydrogen production, while CO formation was remained unchanged. The dependence of the rate from the reaction 1/2 H2 → CO2 increased with time on stream because it was impossible to avoid carbon deposition. By increasing anodic currents, CO formation rate was increased and carbon formation rate decreased. The equilibrium constant increased with temperature. Therefore, carbon deposition decreased while the total reaction rate was increased with time on stream at low anodic currents because resistance to carbon deposition. Under open circuit conditions, the reaction rate increased linearly in respect to temperature and carbon formation rate decreased. The equilibrium constant of Boudouard reaction decreased by increasing temperature, while on the other hand methane decomposition equilibrium constant increased with temperature. Therefore, carbon deposition was avoided at high temperatures and at high CO2/CH4 ratios. Under closed circuit operation the reaction rate decreased with time on stream at low anodic currents because it was impossible to avoid carbon deposition. By increasing anodic currents, CO formation rate was increased and carbon formation decreased while the total reaction rate was not affected due to oxygen ions reacting with the deposited carbon to form CO. In Nickel particles CH4 and CO2 are decomposed to CH3 and CO + O, respectively. In the following surface, carbon was oxidized either by the atomic oxygen derived from CO2 decomposition or by the electrochemical oxygen, O2−, taking place at the three phase boundary.

Moon and Ryu [115] examined methane dry reforming on NiO–MgO electrode/catalyst. The reaction rate under closed circuit operation was stable and higher compared with the corresponding reaction rate under open circuit conditions, due to the reaction between electrochemical oxygen and surface carbon. NiO–MgO exhibited higher reaction rates and greater stability than NiO electrodes.

3.1.3. Steam electrolysis

The electrolysis of water is also a major process in hydrogen production

\[ \text{H}_2\text{O} \leftrightarrow \text{H}_2 + \frac{1}{2}\text{O}_2. \]  

(8)
Hydrogen produced by steam electrolysis is pure and most of all the processes can be completely zero-emission if the electricity used to electrolyse the water is provided from a renewable source such as water or wind or solar energy. Hydro-electric power plants could enhance the energy storage by using the electricity to produce hydrogen. Solar energy is also a clean source such as water or wind or solar energy. Hydro-electric power plants could enhance the energy storage by using the electricity to produce hydrogen. Solar energy is also a clean technique for electrolysis of water [70].

Water decomposition has also been studied in O$_2^-$ SEMRs [116–120], by exploiting the unique advantage of SEMRs, that is the simultaneous reaction/separation process in the same device. Elements produced by water dissociation consist of six species: H$_2$O, HO, H, O, H$_2$ and O$_2$. The dissociation of water occurs by the following chemical reactions:

\[ \text{H}_2\text{O} \rightarrow \text{HO} + \text{H}, \]  
\[ \text{HO} \rightarrow \text{H} + \text{O}, \]  
\[ 2\text{H} \rightarrow \text{H}_2, \]  
\[ 2\text{O} \rightarrow \text{O}_2. \]  

Cales and Baumard [116–118] used an O$_2^-$ SEMR (calcia-stabilized zirconia) as an oxygen conductor and produced hydrogen by thermally (without an electrode/catalyst) decomposing water at very high temperatures (> 1400 °C). Naito and Arashi [119] and Nigara et al. [120] used mixed (ionic and electronic) conductors (ZrO$_2$–TiO$_2$–Y$_2$O$_3$) in order to obtain higher oxygen fluxes. Water vapor was introduced at the one side of the membrane and started to dissociate into species (H$_2$ and O$_2$). By keeping the oxygen partial pressure in the other side of the membrane low (sweeping with a carrier gas) the dissociated oxygen permeated the membrane and oxygen and produced hydrogen are separated.

### 3.2. Hydrogen production in $H^+$ SEMRs

A typical proton-conducting ceramic membrane, SrCe$_{0.95}$Yb$_{0.05}$O$_{3-x}$, is a solid solution based on the perovskite-type oxide SrCeO$_3$, in which 5% of Ce is replaced by Yb. Other perovskite-type oxides based on SrCeO$_3$ or BaCeO$_3$, in which some trivalent cations are partially substituted for cerium, also exhibit protonic conductivity [13,121,122]. The general formula is written as SrCe$_{1-x}$MX$_{3−x}$O$_{3−x}$ or BaCe$_{1-x}$MX$_{3−x}$O$_{3−x}$ where M is some rare earth element, x is less than its upper limit of solid solution formation range (usually less than 0.2) and a is the number of oxygen deficiencies per unit formula of the perovskite-type oxide.

The ceramics of these perovskite-type oxide solid solutions exhibit p-type electronic (hole) conduction under oxidizing atmosphere free from hydrogen or water vapour at high temperature. However, when they are exposed to hydrogen or water vapour-containing atmospheres at elevated temperatures, the electronic conductivity decreases and protonic conduction appears. Their conductivities in hydrogen atmosphere are of the order of $10^{-2}−10^{-3}$ S cm$^{-1}$ at 600–1000 °C [13].

Proton-conducting ceramic membranes have two fundamental characteristics that can be utilized for protonic devices. When the EMF of a galvanic cell is utilized as a signal that depends on the chemical potential of hydrogen in a specified chemical compound, this device is called a hydrogen activity sensor [122]. When the electric power of a proton conducting cell is utilized, this device is a kind of fuel cell. Another significant function of protonic conductors is the selective electrochemical hydrogen transport that is based on the preferential migration of protons in solids. This function can be applied to hydrogen separation or extraction from gas mixtures, and the devices are called hydrogen pumps [123]. None of the above applications, except hydrogen sensors has been commercialized, due to inadequate (for commercial applications) achieved proton transport numbers$^1$ of the developed proton conducting ceramic membranes.

All reactions and methods that have been employed to produce hydrogen in $H^+$ SEMRs are listed in Table 2.

---

Table 2

<table>
<thead>
<tr>
<th>Reaction</th>
<th>MO</th>
<th>Solid electrolyte</th>
<th>Working electrode</th>
<th>Temperature (°C)</th>
<th>References</th>
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</thead>
<tbody>
<tr>
<td>Hydrocarbons pumps</td>
<td>1</td>
<td>SCY</td>
<td>Pt</td>
<td>900</td>
<td>[124,125]</td>
</tr>
<tr>
<td>Hydrogen production from CH$_4$</td>
<td>1</td>
<td>SCY</td>
<td>Pt</td>
<td>600–750</td>
<td>[128]</td>
</tr>
<tr>
<td>CH$_4$ non-oxidative dimerization</td>
<td>1</td>
<td>SCY</td>
<td>Ag</td>
<td>600–750</td>
<td>[130]</td>
</tr>
<tr>
<td>CH$_4$ cracking</td>
<td>1</td>
<td>SCY</td>
<td>Pt</td>
<td>900</td>
<td>[131]</td>
</tr>
<tr>
<td>CH$_4$ dry reforming</td>
<td>1</td>
<td>SCY</td>
<td>Pt</td>
<td>700–900</td>
<td>[132]</td>
</tr>
<tr>
<td>Higher hydrocarbons dehydrogenation</td>
<td>1</td>
<td>SCY</td>
<td>Pt</td>
<td>700</td>
<td>[125,133]</td>
</tr>
<tr>
<td>Steam electrolysis</td>
<td>1</td>
<td>SCY</td>
<td>Pt</td>
<td>650–750</td>
<td>[134]</td>
</tr>
<tr>
<td>Steam electrolysis</td>
<td>1</td>
<td>SCY</td>
<td>Pd</td>
<td>650–750</td>
<td>[134]</td>
</tr>
<tr>
<td>Hydrocarbons pumps</td>
<td>1</td>
<td>SCY</td>
<td>Pt</td>
<td>600–750</td>
<td>[135]</td>
</tr>
<tr>
<td>Hydrogen production in H$_2$O</td>
<td>1</td>
<td>SCY</td>
<td>Pt</td>
<td>460–700</td>
<td>[125,136]</td>
</tr>
</tbody>
</table>

MO, Mode of operation; 1, Galvanostatic/potentiostatic mode; 2, fuel cell mode.

---

$^1$The ratio of proton flux over the other ionic species (e.g. O$_2^-$) or charges (e.g. $e^−$) fluxes that are transported through the membrane. In the case of pure protonic conductivity, proton transport number is equal to unity.
3.2.2. Hydrogen production from CH$_4$

Since only proton species can be transported in these oxides, electrochemical hydrogen separation from various gas mixtures is possible (hydrogen pump). When a hydrogen containing gas mixture is supplied to the anode chamber of a proton-conducting solid electrolyte electrochemical cell and current is applied through it, hydrogen is ionized to form protons, which are transported through the electrolyte to the porous cathode, where they are discharged to form gaseous hydrogen. In this case, in contrast to the conventional fine porous ceramic separator, one can obtain pure hydrogen in an one-step operation without pressurizing or evacuating the gas. Hydrogen gas can be separated at elevated temperatures and the separation rate can be easily controlled by the applied current.

Iwahara et al. [124] have examined the extraction of hydrogen gas using a thin disk of SrCe$_{0.95}$Yb$_{0.05}$O$_{1.9}$ (SCY) or BaCe$_{0.9}$Nd$_{0.1}$O$_{3}$ (BCN) as an electrolyte and porous platinum as an electrode material. They were able to extract hydrogen from the gas mixture of the water–gas shift reaction at 900°C using SCY as a solid electrolyte [125], pyrolized hydrocarbon gases at 650°C using BCN as solid electrolyte [124], and pyrolized hydrogen disulfide [124].

In these experiments, the evolution rate obeyed Faraday’s law when the current density was lower than some critical value which depended on the electrode condition. Above the critical current density, the hydrogen evolution rate began to deviate from the theoretical value calculated from Faraday’s law. Unfortunately, at present, separation rate is still insufficient for coming hydrogen energy system since the conductivity of the existing proton-conducting solids is rather low.

3.2.2. Hydrogen production from CH$_4$

Many methods have been used for hydrogen production from methane in H$^+$ SEMRs, including methane dimerization, pyrolysis, oxidation and reforming, and are depicted in Fig. 8. It must be mentioned here that the majority of the studies were targeted to different goals than hydrogen production (e.g. C$_2$ production, testing of proton conducting materials, etc.).

3.2.2.1. Non-oxidative dimerization of CH$_4$. The non-oxidative dimerization reaction of methane in H$^+$ SEMRs, has been studied by several groups [126–130]. The reactions that are assumed to occur in these cells are:

$$2\text{CH}_4 \leftrightarrow \text{C}_2\text{H}_6 + \text{H}_2 \quad (13)$$

and

$$2\text{CH}_4 \leftrightarrow \text{C}_2\text{H}_2 + 2\text{H}_2 \quad (14)$$

Chiang et al. [128,130] studied the electrocatalytic non-oxidative dimerization of methane to C$_2$ hydrocarbons (ethane and ethylene) and hydrogen on silver electrodes at 600–750°C and atmospheric total pressure. Under open circuit, a steady-state rate of methane consumption, $r_0$, was achieved. By applying current to the cell, the reaction rate of CH$_4$ dehydrogenation was enhanced to as much as 8 times the open circuit rate. The C$_2$ selectivity was always 100%, while no carbon formation was observed.

3.2.2.2. CH$_4$ cracking. The use of H$^+$ SEMRs did solve the problems of the production of undesirable CO and CO$_2$, however C$_2$ yields were not impressive. One of the reasons for this is that without oxygen, methane cracking:

$$\text{CH}_4 \leftrightarrow \text{C} + 2\text{H}_2 \quad (15)$$

starts to dominate. Methane conversion due to reactions (13) and (14) increased with increasing temperature, which makes operation at high temperatures preferable, but reaction (15) is also favored at elevated temperatures.

Mori [131] used a proton conductor and platinum electrodes and decomposed methane to C and H$_2$ at the anode of a H$^+$ SEMR at elevated temperatures ($T = 900\degree$C). Hydrogen was transported in the form of protons through the electrolyte to form molecular hydrogen at the cathode.

3.2.2.3. Dry reforming of CH$_4$. Hibino et al. [132] tested the methane dry reforming (CH$_4$–CO$_2$) reaction on Pt anode in a H$^+$ SEMR at 700–900°C. Hydrogen pumping promoted both synthesis gas and C$_2$ hydrocarbons production rates.

3.2.3. Dehydrogenation of higher hydrocarbons

The dehydrogenation–decomposition of hydrocarbons is an endothermic reaction but provides some advantages to the reactor design. A simple design can be chosen as no shift converter or steam generator, are necessary. The reaction for propane decomposition is [70]:

$$\text{C}_3\text{H}_8 \leftrightarrow 3\text{C} + 4\text{H}_2 \quad (\Delta H_0 = 103.8 \text{kJ/mol}). \quad (16)$$

This reaction, due to its strong endothermicity, occurs at temperatures above 800°C. The carbon by-product accumulates on the surface of the catalysts thus eventually blocking the whole surface area. The catalyst can be regenerated, however, by passing air over the surface to burn off the carbon. Dehydrogenation of higher hydrocarbons (Fig. 8) are, in principle, possible using a proton conducting solid. Distinctive features of this method compared to conventional chemical reactors are as follows:

(1) The compounds to be dehydrogenated are separated from the hydrogen gas to react or to be formed.

![Fig. 8. Hydrogen production from the dehydrogenation of hydrocarbons and steam electrolysis in H$^+$ SEMRs.](image-url)
(2) The chemical potential of hydrogen in the reaction sites at the electrode can be controlled by electrode potential and the reaction rate can be controlled by electric current.

(3) Catalytic activity and selectivity may be controlled by the electrode potential.

Dehydrogenation of ethane has been tried by this method and has been verified to produce ethylene [125,133]. The formation rate of ethylene at the anode increased with increasing current density whereas that of hydrogen decreased when SCY was used as an electrolyte and porous silver as an anode material at 700°C.

Karagiannakis et al. [134], studied C_3H_8 decomposition reaction in a double-chamber proton-conducting cell-reactor (SCY) on both Pt and Pd at a temperature range between 650 and 750°C. The hydrogen produced by the reaction was electrochemically transported through the walls of the proton-conducting disk, to the outer reactor-chamber.

Comparing the two catalysts/electrodes in terms of their catalytic activity, it was found that platinum was superior to palladium, yielding to higher rates of propane decomposition. As far as the products selectivity is concerned, Pt shows a slightly higher selectivity to propylene while shift reactions (CO_X formation) were more favored on Pd. Palladium exhibited severe deactivation after remaining for approximately 24 h on stream, at T = 650°C. The only products observed in this case were carbon, methane and hydrogen [134].

On the other hand, when electrical current was imposed through the reactor cell—so that hydrogen was being transferred from the inner to the outer chamber—the only reaction rates affected were those of H_2, CO and CO_2 formation. These three rates, generally, increased with the imposed current. The increase was much stronger on Pt electrodes, implying that only the side-reactions, due to the water-gas presence in the system, are affected by the electro-catalytic operation of the cell. When severe deactivation of Pd occurred, “proton pumping” away from the catalyst resulted in partial recovery of its previous activity. This recovery stopped as soon as the imposed current was interrupted [134].

3.2.4. Steam reforming of higher hydrocarbons

Although there are many works concerning the dehydrogenation of higher hydrocarbons, those studies mainly targeted to the test of new ceramic materials and their ability to separate the produced hydrogen from the reacting mixture. Recently, Karagiannakis et al. [135] examined the C_3H_8 steam reforming reaction in a double-chamber proton-conducting cell-reactor. The proton conductor was an ytterbium-substituted strontium cerate perovskite disk of the form: SrCe_0.95Yb_0.05O_3−α. The reaction temperature was varied between 600 and 750°C and a polycrystalline palladium film was used as the working electrode-catalyst. Hydrogen produced by the reaction was electrochemically transported through the walls of the proton conducting disk, to the outer reactor-chamber. Upon increasing the H_2O partial pressure from 0.3 to 2.8 kPa, a four-fold increase on the reaction rate was observed. Upon proton “pumping” to the outer chamber, an up to 90% of the produced hydrogen was electrochemically separated from the reaction mixture.

3.2.5. Steam electrolysis

Using a proton-conducting solid electrolyte, one can electrolyze water vapour to produce hydrogen gas at elevated temperatures, as it is depicted in Fig. 8. In contrast to the case of O^2− SEMRs, this type of a steam electrolyzer has, in principle, the advantage that pure hydrogen can be obtained since only protons migrate across the conductor to the cathode.

A bench-scale steam electrolyzer was fabricated by the research group of Iwahara [125] using an one-end closed ceramic tube made of SCY and pure hydrogen gas was extracted at 700°C and at a rate of a few lt/h. This method was verified to produce very pure and dry hydrogen (dew point < −30°C).

Kobayashi et al. [136] studied the effect of current to steam electrolysis at temperatures 460–600°C using an electrochemical cell, which was consisted of a proton conductor of the type, SrZr_0.9Yb_0.1O_3−α, as a solid electrolyte and Pt as electrodes. Conversion increased by increasing steam partial pressure and temperature. At closed circuit conditions, H_2 production rate from protons that were transferred to cathode was higher than the corresponding steam oxidation rate to protons and O_2 on the anode. Therefore, during electrolysis, average protons concentration was decreased, while holes concentration was increased in the ceramic lattice. The above observation was considered as the reason of decreased steam electrolysis yield. Generally, the yield was increased with steam partial pressure and temperature and it was decreased by increasing the current density. Although H_2 production rate was almost equal to the theoretical (Faradaic) rate, when electrolysis was started, it was decreased with time and stabilized after 100 min. In the first 100 min the amount of O_2 was lower compared to that of H_2. After 100 min, the produced H_2/O_2 ratio was almost 2/1. Thus, a different mechanism prevails during the start-up of the electrolyzer. This excess hydrogen was attributed to the dissolved protons in the SrZr_0.9Yb_0.1O_3−α lattice.

4. Discussion and conclusions

The transition to a hydrogen-based energy economy, where the main chemical energy carrier is hydrogen and the main non-chemical energy form is electricity, is being developed gradually, and is likely to continue to the middle or end of the 21st century. In the near term, hydrogen will be produced primarily by advanced steam reforming or partial oxidation of natural gas, either at central or distributed facilities.

In the last 40 years, SEMRs have been used to both study and influence the rates of catalytic reactions. Most of the industrially important catalytic oxidations and hydrogenations have been investigated. Specifically, hydrogen production has been studied in both O^2− and H^+ SEMRs by using various methods (e.g. partial oxidation, reforming, dehydrogenation of hydrocarbons and steam electrolysis).

Partial oxidation of methane to hydrogen has been extensively examined in O^2− SEMRs on numerous catalysts/electrodes (Fe, Ni, Rh, Ru, Pt, perovskites etc.), which
their effectiveness towards synthesis gas formation had been proven in previous catalytic studies. The electrochemical oxygen, O$_{2^-}$, showed in most cases higher activity and selectivity to synthesis gas production, compared to gas phase oxygen.

Two basic mechanistic schemes were proposed for the selective oxidation of methane under oxygen pumping: the direct partial oxidation and the combustion/reforming mechanisms. In the direct partial oxidation mechanism, CH$_4$ is directly dissociated to surface carbon and hydrogen, followed by CO formation through oxidation of carbon on the catalyst surface without the pre-formation of CO$_2$, while in the combustion/reforming mechanism a fraction of CH$_4$ is initially oxidized to CO$_2$ and H$_2$O, followed by endothermic steam reforming, CO$_2$ reforming, and water–gas shift reactions.

In the majority of the studies, SEP technique was combined with kinetic measurements in order to both distinguish the active sites (e.g. reduced of oxidized surfaces) and to investigate the reaction mechanism. The former mechanism was prevailed on “partial oxidation” catalysts (e.g. Ni, Fe, Rh), while the combustion/reforming mechanism was prevailed in the case of “combustion” catalysts (e.g. Pt, Pd). Various combinations (bimetallic catalysts, mixed oxides, etc.) of active metals have been also studied leading to remarkable results. In all cases, electrochemical oxygen pumping retarded or eliminated carbon deposition, which is an unsolved problem until now in both the industrial production of hydrogen and in SOFCs.

By taking into account that catalytic steam reforming reaction is the main method employed for hydrogen production in industrial scale and that SOFCs can be combined with reforming reactions to enhance their performance, methane electrocatalytic steam or dry internal reforming reactions are gaining research interest. The majority of the studies are referred to internal reforming (mainly with steam), where simultaneous production of synthesis gas, power and thermal energy can be achieved.

Ni-based electrodes were mainly used to study reforming reactions. The addition of various materials in the catalyst structure was targeted to increase catalytic-electrocatalytic activity, increase conductivity (YSZ) and finally increase carbon resistance (CeO$_2$). Fe, Pt and Ce$_{0.6}$Gd$_{0.6}$O$_{1.8}$, were also used as catalysts/electrodes for the steam reforming reaction. CGO exhibited a different behavior since under anodic polarization enhanced CO$_2$ production, which was attributed to the methane oxidative coupling.

Steam reforming reaction followed in all cases a typical Langmuir–Hinselwood mechanism, where competitive adsorption of methane and H$_2$O governed reaction mechanism. Methane adsorption and dehydrogenation formed chemisorbed surface species, such as CH$_3$(s), CH$_2$(s), CH(s), and C(s), while H$_2$O adsorption and dissociation formed OH(s), H(s), and O(s), respectively. Kinetic results showed that at certain operation conditions, the reaction rate was independent of H$_2$O partial pressure, while methane reaction order was equal to 1. Under anodic polarization conditions only CO formation was enhanced, while hydrogen production remained unchanged. Reaction mechanism was affected by both water–gas shift and Boudouard reactions, according to thermodynamics. In all cases, the electrochemical oxygen supply enhanced both the activity and decreased effectively carbon deposition.

Carbon deposition is a significant obstacle towards the stability and durability of catalysts/electrodes. Numerous investigations have concentrated on the reaction kinetics of carbon formation, seeking to identify new anodic materials and alternative operating conditions. For steam and CO$_2$ reforming of methane two major carbon-formation routes have been identified. In global terms, these are CH$_4$ thermal cracking and the CO disproportionation (i.e., the Boudouard reaction). There are two kinds of carbon deposition the reversible and irreversible carbon formation processes. The reversible carbon deposition, which can be attributed to adsorbed or carbide carbon, is primarily occurred at or near three-phase boundaries and can be oxidized by electrochemical reactions with oxygen ions (O$_{2^-}$). On the contrary, the irreversible carbon formation is taken place on the electrode bulk surfaces where there is excess of CH$_4$ and little oxygen. Therefore, this graphitic carbon formation constitutes a serious problem for cell performance.

Although O$_{2^-}$ SEMRs are undoubtedly the most important field of research and application, however, high temperature proton conducting membranes offer new possibilities for designing electrochemical reactors. An electrochemical hydrogen pump using a proton-conducting solid electrolyte can be conveniently applied, in principle, to the separation or the extraction of pure hydrogen from a gas mixture or from molecules having hydrogen as a component, due to their high protonic conductivity. Until now emphasis has been given more to the development of new proton conducting ceramic membranes with improved properties (chemical and thermal stability, high ionic conductivity) than to the process itself. In other words few studies are referred to traditional methods of producing hydrogen (e.g. reforming reactions), and therefore there are no information concerning reaction mechanisms or electrodes/catalysts characteristics (mainly Pt has been used in the majority of the works performed in H$^+$ SEMRs).

Although there are many advantages concerning H$^+$ SEMRs, several problems need to be solved in order to become competitive in respect to O$_{2^-}$ SEMRs. Due to the requirements of the electrodes and current connectors, the construction of the devices is somewhat more complex in the case of the hydrogen separator compared to conventional separators such as porous ceramic ones or palladium alloy membrane separators. Furthermore, protonic conductivity of the ceramics is not sufficiently high and, in many cases, considerably high temperatures are required to raise it. Moreover, to reduce the electrical resistance of the pump, it is necessary to make a thin film of proton-conducting solid electrolyte. However, to prepare a thin and nonporous film on a porous electrode is technologically difficult. Finally, regarding the chemical reactor using proton conducting ceramics, organic reactions applicable to this method are limited due to the high temperature of operation. Therefore, there is need for research on stable protonic electrolytes exhibiting high conductivity, and active electrodes working in atmospheres with low level of humidity, both in hydrogen (anodes) and in air (cathodes).
The interest in the development of SEMRs has been constantly growing in the last 25 years. The question then is will SEMRs be widely used in industrial applications? There are not enough technoeconomic assessments of SEMRs processes and these are referred only to units that co-generate electricity and chemicals [31]. The outcome of these studies was negative. In general, industry has been reluctant to adopt SEMRs processes. High cost for capital investment, immature technology, limited ionic fluxes are the main reasons for this reality [31].

Nevertheless, in the last decade, quite a few promising efforts have been put into the development of certain SEMRs processes. One such process utilizes mixed (O$^2-$–e$^-$) conductors for the separation of oxygen and nitrogen of the air and further use of oxygen for the partial oxidation of methane to synthesis gas [30]. Another similar reaction–separation process is the removal of hydrogen from hydrocarbon streams (with simultaneous hydrocarbon dehydrogenation) by using H$^+$ SEMRs.

Finally, by taking into account that SOFCs are currently in the pre-commercial phase and that all reactions, in which hydrogen is produced, can be combined in a SOFC system (internal reforming), it is inevitable that hydrogen production in SEMRs will gain increased interest in the following years. In the near future, “hot” topics, such as partial oxidation of higher hydrocarbons, steam or dry reforming of commercially available fuels (e.g. natural gas, gasoline, diesel) and internal reforming in both O$^2-$ and H$^+$ SOFCs, will be extensively examined in order to bridge the gap between SEMRs and market applications.

Acknowledgments

The financial support for the preparation of this article from the Greek Ministry of Education and Religious Affairs (PYTHAGORAS I) is gratefully acknowledged.

References


