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# Electrochemical studies of methane activation

M. STOUKIDES

*Department of Chemical Engineering, Aristotle University of Thessaloniki, Thessaloniki, 54006, Greece*

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The direct conversion of methane into useful and more versatile chemicals is a subject that has attracted the interest of numerous researchers. Methane is a refractory molecule and therefore very difficult to convert to upgraded products. In the last thirty years, the electrochemical studies of methane activation have contributed significantly by adding various alternative solutions to this very challenging research problem. In the present communication, the most important findings of low, moderate and high temperature electrochemical studies are reviewed. Since methane activation is easier at elevated temperatures, solid electrolyte cells have been used more extensively. Most of these high-temperature works focused on the production of either synthesis gas or of $C_2$ compounds. A third vital alternative is the development of the internally reformed methane fuel cell. Results are discussed and compared with those of conventional catalytic processes.

## 1. Introduction

Methane is a raw material of great synthetic importance and an abundant natural resource as the main constituent of natural gas. Nevertheless, it is primarily used only as fuel because two factors limit its use as a raw chemical. The first is that transporting methane gas or even liquified natural gas is not economical. Therefore, it is highly desirable to transform methane into transportable raw materials or products. The second factor is that methane is a very stable molecule and its direct conversion to useful chemicals is very difficult [1, 2]. Today, over 90% of methane is consumed as heating fuel. Because transportation of natural gas from remote sites is costly, it has often been suggested that natural gas, namely methane, should be converted to more easily transported liquid fuel [1, 3]

As a raw material for chemical industries, the two leading uses of methane are in the production of methanol and ammonia. Ammonia and methanol rank in the top twenty commercial chemicals produced in USA [4]. Methane must be first transformed into synthesis gas before usage in either ammonia or methanol synthesis. Clearly, this process makes conversion into synthesis gas the dominant process of methane upgrading. The term synthesis gas is generally used for a mixture of carbon monoxide and hydrogen, preferably at a 1:2 or 1:3 ratio [5]. The dominant route to the production of synthesis gas today, is the methane steam reforming process. The reaction can be stoichiometrically expressed as

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \qquad (1)$$

A considerable disadvantage of the steam reforming process is the reaction endothermicity. The endothermicity results from the addition of steam in which a significant amount of energy is required to decompose water into its elements. The presence of steam, however, reduces the problem of carbon deposition [6]. Recently, the partial oxidation of methane to CO and $H_2$ without the addition of steam has been reexamined and promising results were found [7]. The reaction in this case is

$$CH_4 + 1/2O_2 \longrightarrow CO + 2H_2 \qquad (2)$$

Combinations of Reactions 1 and 2 have been examined in an effort to simultaneously reduce both carbon deposition and heat requirement.

In addition to syngas formation, there are several lesser routes to upgrade methane such as ammoxidation to HCN, chlorination to chloromethanes, carbon disulfide production and acetylene synthesis. Of great importance is the direct oxidation of methane to produce methanol, formaldehyde, or dimerized products, ethane and ethylene. None of these reactions, however, has yet found large-scale commercial application due to either limited catalytic activity, short catalytic life or low product selectivity [2]. Despite the limited selectivities and yields, numerous studies have been reported on the direct partial or complete oxidation of methane. Several reviews of these research efforts to upgrade methane have already been published [1, 3, 8–13] and a lot of experimental details of the above studies can be found therein.

Only one aspect of this challenging research area, namely the electrochemical studies of methane activation, are presented in this work. Several comprehensive reviews of the rather large amount of literature on the subject of electrochemical activation of methane have been published. Cairns [14] reviewed earlier work up to late 1960s and, more recently, Amenomiya *et al.* included in their review a chapter on electrochemical oxidative coupling [3]. Studies of electrochemical conversion of methane to methanol and formaldehyde

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were summarized by Gesser and Hunter [1]. Catalytic and electrocatalytic studies of methane oxidation using solid oxide membranes, were also reviewed [2, 15].

The present communication is an updated and generalized version of the work published four years ago [2]. An effort was made to focus on material not covered in the previous reviews although some overlapping became inevitable. First, the electrochemical studies performed at low and moderate temperatures are presented. The work performed at high temperatures (600–1000 °C) using solid electrolyte cells, follows. The economic feasibility of some of the projected processes and the problems needed to be overcome in order to make scaling-up practical are also briefly discussed.

## 2. Electrochemical studies at low and moderate temperatures

Aqueous, low-temperature electrochemical cells were first tested for methane conversion. The motivation for the electrochemical approach is based on the ability of electrochemical cells to modify the rates of charge transfer reactions by appropriate control of the cell potential. A successful selection of electrode material and operating potential may stabilize the desired intermediates or reduce the activation energy of the reaction. Also, it is known that under the same conditions, electrochemical reactions are generally faster than the corresponding chemical reactions and therefore a significant effect on slow reactions, such as the partial or complete oxidation of methane, may be expected. Furthermore, it was soon [16, 17] realized that the activation of methane is connected to the presence of charged species which serve either as initiators or as catalytically active centres. Hence, it was reasonable to expect that an electrochemical route would more easily result in the formation and control of these ionic species. Finally, operation in the fuel cell mode could result in the direct conversion of chemical into electrical energy.

Table 1 contains experimental studies of methane partial or complete oxidation performed at either

*Table 1. Studies of electrochemical activation of methane at low and moderate temperatures*

| *Electrolyte** | *Electrode (anode)* | *Products* | *Study type*† | *T*/°C | *Reference* |
|---|---|---|---|---|---|
| Slf. Ph–For | Pt, Pd | $CO_2$ | 1 | 27–85 | 18 |
| 85% PA | Pt-black | $CO_2$ + residues | 1 | 150 | 19 |
| 85% PA | Pt | $CO_2$ | 1 | 150 | 20 |
| SA–KOH | Pt-black | $CO_2$ | 0 | 25–65 | 21 |
| Sa–PA | Pt-Raney/Au | $CO_2$ | 0, 1 | 90–110 | 22 |
| 80–95% PA | Pt | $CO_2$ | 1 | 130 | 23 |
| SA | Pt-Raney | $CO_2$ | 1 | 100 | 24 |
| SA–KOH | Pt-Raney | $CH_x \longrightarrow CO_2$ | 0 | 40–100 | 25 |
| HF–CsF | Pt | $CO_2$ | 1 | 105–150 | 26 |
| $HClO_4$ | Pt-black | $CO_2$ | 0 | 65 | 27 |
| 75% PA | Pt-black | $CO_2$ | 0 | 60–120 | 28 |
| 85% PA | Pt | $CO_2$ | 1 | 150 | 29 |
| 80% PA | Pt | $CO_2$ | 0 | 130 | 30 |
| PA–SA | Pt | $CO_2$ | 0 | 80–90 | 31 |
| 80% PA | Pt | $(=C–OH) \longrightarrow CO_2$ | 0 | 130 | 32 |
| 80% PA | Pt/Cu | $(=C–OH) \longrightarrow CO_2$ | 0 | 130 | 33 |
| 80% PA | Pt | $CO_2$ | 0 | 130 | 34 |
| $FSO_3H$ | Pt | – | 0 | 25 | 35 |
| 80–90% PA | Pt | $CO_2$? | 0 | 130 | 36 |
| KF | Pt | $(HCO)_{ad}$ | 0 | 80 | 37 |
| SA | Pt/Pt | $(CH_3)_{ads} \longrightarrow CO_2$ | 0 | 80 | 38 |
| SA | Pt/Pt | $(COH)_{ads}, (CO)_{ads)}$? | 0 | 26 | 39 |
| $CF_3SO_3H$ | Pt | $CO_2$ | 0, 1 | 95–130 | 40 |
| $CF_3SO_3H$ | Pt/Pt | $CO_2$? | 0 | 80–100 | 41 |
| SA | Pt/Pt | $(COH)_{ads}, (CO)_{ads} \longrightarrow CO_2$ | 0 | 80–100 | 42, 43 |
| HF–$SbF_5$ | Pt | $(CH_3\cdot)$, $C_2H_6$ | 0 | 0 | 44 |
| $NaClO_4$ | Pt-black | $CO_2$ | 0 | 23 | 45 |
| $CH_3CN$ | Pt | $CH_3N^+CCH_3$ | 0 | 25? | 46 |
| KCl | Pt | $CH_3OH$, $CH_xCl_{4-x}$ | 0 | 25 | 47, 50 |
| $CF_3SO_3H$ | n-$TiO_2$ | $CH_3. \longrightarrow$ ? | 0 | 100 | 48 |
| 85% PA | Pt, Ir, Rh, Ru | $CO_2$ | 0 | 140 | 49 |
| SA–$FeSO_4$ | CoPc/C | $CH_2O$, HCOOH | 0 | 25 | 51 |
| Nafion®–H | Teflon® ($H_2O_2$) | $CH_3OH$ | 0 | 60–120 | 52 |
| KOH, NaOH | C, Hg, Au | $CH_2O$, HCOOH | 0 | 25 | 53 |
| SA | Ni–Pt | $CO_2$? | 0 | 25 | 54 |
| MC | Ni | $CO_2$ | 1 | 600–700 | 55 |
| MC | Ni/Al | $CO_2$ | 1 | 650 | 56 |
| MC | Ni? | $CO_2$ | 1 | 650 | 57 |

* PA = $H_3PO_4$, SA = $H_2SO_4$, MC = molten carbonate

† 1 = fuel cell, 0 = other (Electrolysis, cyclic voltammetry, galvanostatic, etc.).

low temperatures (up to 150 °C, mostly in aqueous electrolyte cells) or at moderately high temperatures (500–650 °C, in molten carbonate cells). The first and the second column of the table show the electrolyte and the anodic electrode, respectively. The next column shows the principal reaction products. The fourth column shows the type of experiments performed. Number 1 refers to fuel cell operation and number 0 refers to all other (electrolysis, cyclic voltammetry, galvanostatic etc.). It can be seen that noble metals (Pt, Pd) were mostly used as electrodes. When the electrolyte was aqueous, acidic solutions were used because in alkaline solutions methane was neither adsorbed nor oxidized [3]. In acidic solutions, adsorption of $CH_4$ on the anode was the usual rate determining step.

Ogura *et al.* combined electrochemical and photochemical oxidation of methane using a KCl solution as electrolyte [47, 50]. A low-pressure mercury lamp was used for the illumination of the anode surface which was exposed to the gas phase. Methanol and chloromethanes were formed and the product composition depended strongly on the cell potential [47]. In an effort to mimic the microbial process by which methane is converted to methanol, Cook and Sammels [51] constructed an aqueous electrolyte ($H_2SO_4$–$FeSO_4$) cell in which formaldehyde and formic acid were the main products followed by methanol and higher alcohols. Unusually high methanol and formaldehyde yields were reported by Frese [53] who used an alkaline electrolyte containing dissolved oxygen. Carbon monoxide and dioxide were produced in minor quantities only. As with the catalytic activation of methane, it was found that the overall reaction scheme includes homogeneous and heterogeneous steps in addition to the charge transfer reactions [53].

As seen in Table 1, with very few promising exceptions, $CO_2$ and $H_2O$ were the products regardless of which mode of operation was chosen. In general, reaction rates although higher than the corresponding catalytic rates at these temperatures, were still too low to attract industrial interest.

The moderate temperature studies listed in Table 1 refer to molten carbonate fuel cells (MCFCs). From the many research works in that area (see, for example, [58]) only those in which methane was the fuel, are listed. In these studies, methane was *internally* reformed (converted to $CO + H_2$) by using the appropriate catalyst (usually Ni-based) at the anode. Clearly, the goal in all the MCFC studies is to maximize the electrical power output via the complete conversion of $CH_4$ to $CO_2$ and $H_2O$. Since these cells operate at relatively elevated temperatures where it is easier to activate methane, promising results have been reported so far for the MCFC. Nevertheless, several problems such as the reaction (and subsequent deactivation) of the reforming catalyst with the molten electrolyte, as well as corrosion that tends to decrease cell performance and life [55], need to be solved.

In summary, there were only a few low or moderate temperature studies in which methane was successfully converted to $C_1$ (containing only one carbon atom, e.g. $CH_3OH$, CO) or $C_2$($C_2H_4$, $C_2H_6$) compounds. The case where the electrochemical approach provided interesting results from the viewpoint of converting methane to more versatile chemicals was with the use of solid electrolyte cells, as explained in the following.

## 3. Electrochemical studies at high temperatures. Solid electrolyte cells

### 3.1. *Applications of solid electrolytes in catalytic studies and processes*

Several cations and anions are reported [2, 59–61] to be conducting species in solid state electrolytes, including $H^+$, and $O^{2-}$. Oxygen-ion conducting solid electrolytes are solid solutions of oxides of di- or trivalent cations in oxides of tetravalent metals with a solution of 6–10% $Y_2O_3$ in $ZrO_2$ (yttria-stabilized zirconia, YSZ) being most frequently used [59–62]. An important advantage of solid electrolytes is that, in contrast to other electrolytes, they can operate at temperatures where most industrially important catalytic processes are effective, i.e. 250–1000 °C.

To construct a solid electrolyte cell, two porous (thickness ~ 5–100 $\mu$m) electrodes are deposited on the two sides of a solid electrolyte. One side is exposed to an oxygen-containing gas (e.g., air or pure oxygen) and the other side is exposed to the reacting mixture. There are three basic applications of $O^{2-}$ conductors in catalytic research. The first application involves open-circuit measurements. For air as cathode gas and if certain assumptions are met [61], the measured open circuit cell voltage, $E$, satisfies the equation:

$$a_{\mathrm{o,c}} = (0.21)^{1/2} \exp\left(\frac{2FE}{RT}\right) \quad (3)$$

where $a_{\mathrm{o,c}}$ is the thermodynamic activity of oxygen adsorbed on the catalyst surface, $F$ is the Faraday constant and $R$ is the ideal gas constant. Equation 3 constitutes the basis of solid electrolyte potentiometry (SEP), a technique that has been used in conjunction with kinetic measurements to elucidate the mechanisms of heterogeneous catalytic oxidations [60–62].

The second application refers to the operation of $O^{2-}$ conducting solid electrolytes in the fuel cell mode. The anode is exposed to a fuel and the cathode is exposed to oxygen or ambient air. Chemical energy is thus directly converted to electrical energy [61]. There are several important characteristics of solid oxide fuel cells (SOFCs). The most important advantage is that they can operate at temperatures at which reaction rates attain values of practical interest. Near room temperature where aqueous electrolytes are useful, industrial reactions are frequently too slow. Today, most chemicals are produced via exothermic catalytic pathways. In a conventional reactor, the enthalpy of an exothermic reaction is converted into heat. If the useful products of such reactions are achieved with cogeneration of electrical energy instead of thermal energy, such a process would be much more attractive [60, 61].

The third application of $O^{2-}$ conductors refers to the operation of the cell as an electrochemical oxygen pump (EOP) [60–62]. If the spontaneously generated current is either very low or in an undesirable direction, an external power source can be used to direct and control the current. A current $I$ corresponds to $I/4F$ moles of oxygen per second transported through the solid electrolyte. Electrochemical oxygen pumps have been used to study several industrial oxidative reactions [60–65]. In early studies, the change in the rate of oxygen consumption was found to be equal to the rate of $O^{2-}$ transport through the solid electrolyte. Vayenas and coworkers [65] defined the dimensionless rate enhancement factor Λ as

$$\Lambda = \frac{\Delta r}{I/2F} \tag{4}$$

where $\Delta r$ is the increase in the catalytic rate of oxygen consumption and $I/2F$ is the imposed flux of $O^{2-}$ through the electrolyte, both in gram-atoms of oxygen per second. In the case of a faradaic effect, all oxygen electrochemically transported through the electrolyte reacts at the anode; i.e., $\Lambda = 1$. When $\Lambda = 10^{-2}$, only 1% of the pumped oxygen reacts at the anode; the remaining oxygen combines at the anode to give molecular gaseous oxygen which can be found in the off-gas stream. Inversely, a value of Λ equal to $10^2$ means that for each gram-atom of oxygen pumped through the electrolyte, 100 gram-atoms of additional gaseous oxygen react to form oxidation products which would not form otherwise. In this last case, the presence of excess gas-phase oxygen at the anode is necessary to permit Λ to exceed unity. Recently, Λ values of the order of $10^2$–$10^5$ were observed during CO, $CH_3OH$, and $C_2H_4$ oxidation [65–67]. This dramatic nonfaradaic electrochemical modification of catalytic activity (NEMCA) was attributed to changes in the catalyst work function caused by oxygen pumping [65]. Electrochemical oxygen pumping effects can have a tremendous impact on catalytic research for two reasons: (i) the surface modification can be monitored electrochemically; unlike gas phase or solid surface promoters, solid electrolytes offer dynamic manipulation of the catalyst properties; and (ii) in cases where a strong NEMCA effect is observed, the product yield or selectivity can be dramatically altered by imposing a current orders of magnitude less than stoichiometrically required. This last fact may counterbalance the cost of supplied electric energy or required changes in the reactor design. Also the appearance of NEMCA effects permits the modification of the catalytic activity or selectivity by using a *single-chamber* cell as shown in Fig. 1. Both electrodes are exposed to the same reactant gas. The design shown in Fig. 1 is easy to apply to existing catalytic processes since it does not require reactants to be separated. The solid electrolyte simply replaces the catalyst support.

In the past, oxygen-ion conducting solid electrolytes were the only electrolytes used in heterogeneous catalysis to an appreciable extent [60–62]. Recently, however, several promising developments have been made with other types of electrolytes. Certain perovskite-type oxides doped with rare earth oxides (e.g. $SrCe_{0.95}Yb_{0.05}O_3$), have been shown to exhibit high $H^+$ conductivity at temperatures as high as 1000 °C [68]. Hence, these electrolytes can operate at conditions at which industrial hydro- and dehydrogenation reactions take place [61]. Furthermore, several solid oxide membranes have been developed that exhibit mixed electron and $O^{2-}$ conductivity [69] or mixed $H^+$ and $O^{2-}$ conductivity [70]. These novel developments may aid current and future efforts to either study or influence the rates of catalytic reactions.

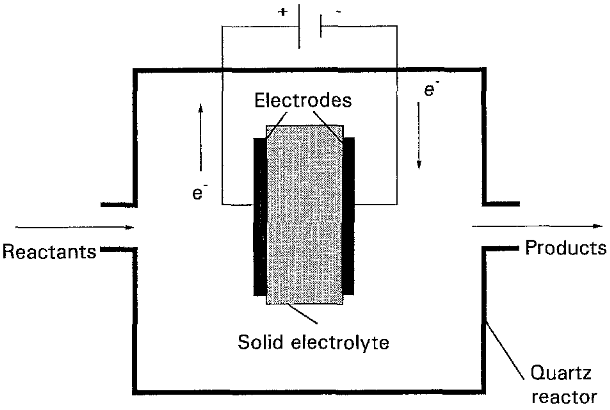

Fig. 1. Schematic diagram of solid electrolyte *single-chamber* cell.

### 3.2. *Comparison of conventional catalytic processes with the solid electrolyte-aided approach*

Figure 2 shows, in simple form, the differences between a conventional catalytic reactor and a solid electrolyte cell-reactor. It is assumed that a reaction of methane and oxygen occurs in both reactors. Oxygen, usually in the form of air, is fed together with the reactant into the conventional reactor (Fig. 2(a)) filled with catalyst particles. The reactor walls can be any material that satisfies basic requirements regarding mechanical strength, stability at high temperatures, and catalytic inactivity so that undesired side-products are formed to a negligible extent.

A solid electrolyte cell-reactor is similar to a typical aqueous electrolyte cell. The difference is that the electrolyte is in the solid state. For an oxidative reaction, it is considered that the conducting species of the solid electrolyte is $O^{2-}$. Hence, YSZ is used as the electrolyte and at the same time, as a wall for the reactor of Fig. 2(b). The YSZ wall is covered from both sides by two porous metal films that serve as electrodes. The reactant or fuel enters without oxygen which instead is supplied through the wall as $O^{2-}$. The oxidative reaction occurs on the inside electrode surface.

Given this configuration, a number of differences can be identified:

(i) In the electrochemical reactor, the YSZ wall serves not only as an electrolyte but also as a separator of nitrogen from oxygen of the air. Therefore, even if the cathode is exposed to air (Fig. 2(b)) or any mixture of oxygen with other gases, it is only oxygen that can be transported through the solid electrolyte. In many catalytic oxidations, the cost of separating pure oxygen from air is such that it is preferable to utilize air ($N_2 + O_2$) as feed to the reactor. Utilizing air means, of course, that the reactor volume must be larger. Typically, in a catalytic oxidation reaction, the effluent gases contain about 50% $N_2$ if air is used as the oxidant.

(ii) It is likely that when oxygen is supplied electrochemically as $O^{2-}$, the catalytic activity or selectivity to the desired products is different from the case when supplying gaseous $O_2$. Noteworthy is the fact that the cell of Fig. 2(b) can also operate, if desired, as a conventional catalytic reactor. To do that, open-circuit conditions are used and oxygen is co-fed as gaseous $O_2$ with the fuel gas. In general, the reactivity of gaseous $O_2$ and ionic $O^{2-}$ has been experimentally found to be different. But even if the behaviour of these two oxygen species is similar, the electrochemical reactor of Fig. 2(b) offers the possibility of dynamic modification of the catalyst activity. Modification of the catalytic activity occurs when the reacting system exhibits the NEMCA effect, as described earlier.

(iii) The concentration profile of oxygen is different in the two reactors shown in Fig. 2(a) and (b). In the catalytic reactor, oxygen diffuses to and reacts on the catalyst surface. The $O_2$ concentration in the bulk gas volume of the reactor is higher than at the surface. In the reactor of Fig. 2(b), however, oxygen is supplied through the YSZ electrolyte wall. Therefore, the $O_2$ concentration profile inside the reactor is the inverse of the profile of the conventional reactor. Ionic oxygen is also consumed on the electrode surface and unreacted oxygen diffuses to the gas phase, but forms a profile with decreasing $O_2$ concentration from the surface to the bulk. In practice, with a highly active electrode, the gas-phase concentration of oxygen remains insignificant. This is important in cases where gas-phase reactions must be avoided. Also, in all the oxidation reactions, the fuel to oxygen ratio must stay outside the explosion limits, and this adds another parameter in the design and in the cost of the reactor [1]. Clearly, this concern is minimized in the reactor of Fig. 2(b) since the oxygen concentration over the anode is kept at very low levels.

(iv) The reactor of Fig. 2(b) can operate as a conventional fuel cell in which reaction products (of complete oxidation of fuels such as $H_2O$ and $CO_2$) need not be collected, but only electrical energy is generated. This reactor can also operate as a chemical cogenerator, in which valuable chemicals are produced simultaneously with electrical energy. In this case, the cooling requirements are moderate compared to a catalytic reactor producing the same compounds because a major portion of the reaction exothermicity is directly converted into electricity.

Given all these advantages, it is perhaps puzzling that solid electrolyte cells have not been used extensively, especially for the activation of methane where the conventional approaches involve many difficulties. This is partially answered in the following where results of lab-scale studies are briefly discussed.

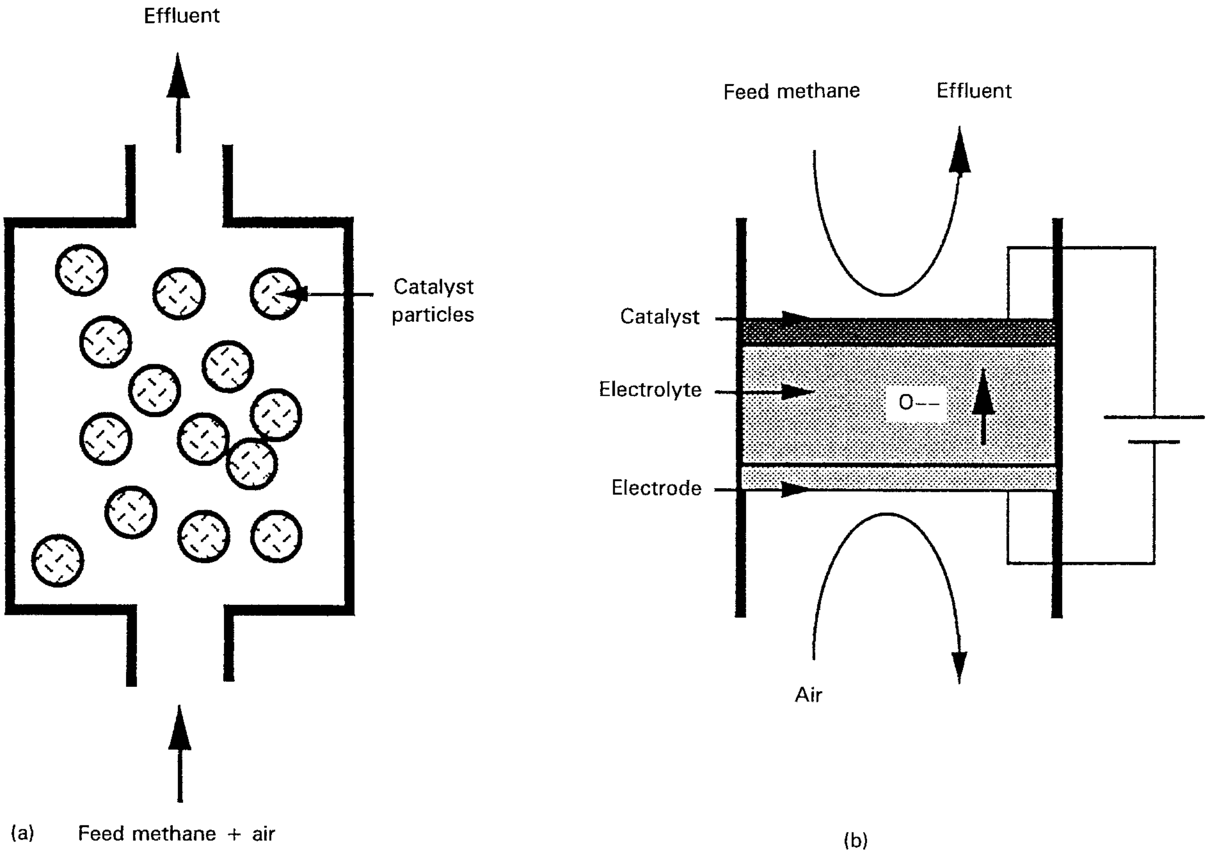

Fig. 2. (a) Conventional catalytic reactors and (b) electrochemical reactors.

### 3.3. *Methane conversion to $C_1$ products*

Table 2 lists solid electrolyte-aided studies of $CH_4$ conversion to $C_1$ compounds. The fourth column shows the type of experiments performed. Numbers 1, 2, and 3 refer to open circuit, oxygen pumping, and fuel cell studies, respectively. In most of the works, the reaction products were $CO_2$ and $H_2O$. This does not mean that all these studies were unsuccessful attempts to convert methane to more versatile and useful products. Indeed, this was the case in only a few of them as, for example, in [77] and [81] in which the goal was the direct conversion of methane to formaldehyde and methanol. Results were not encouraging, however, since only trace amounts of these compounds were produced [78]. Reaction kinetics and mechanistic investigation was also the goal in quite a few studies of Table 2 [72, 75, 82, 100], in which $CO_2$ and $H_2O$ were the reaction products.

The original incentive for using methane-fuelled solid electrolyte cells was to operate in the fuel cell mode. The complete oxidation of methane is a very exothermic reaction ($\Delta H^0_{298\,K} = -802\,kJ\,mol^{-1}$) with a comparably large free energy change ($\Delta H^0_{298\,K} = -800\,kJ\,mol^{-1}$). As fuel, methane is quite inexpensive and hydrogen is primarily produced from natural gas. Therefore, $CH_4$ should be a better candidate fuel for high-temperature cells. This explains the pioneering work of the 1960s in which methane was either externally or internally reformed in stabilized zirconia fuel cells [2, 71, 73]. Later, however, hydrogen was almost exclusively used in laboratory scale and pilot plant fuel cells. Carbon formation and limited reactivity of methane were difficulties identified with most of the anodic electrodes that were tested. These were added to the many other design and material selection problems and made the hydrogen choice more preferable. Nevertheless, the interest for methane-fuelled cells has recently reappeared with a variety of metals and metal oxides (perovskites) tested for anodic performance [88, 89, 93, 97, 108] and with a lot of promising features identified.

Table 2 shows that, in addition to the complete oxidation ($CO_2$ and $H_2O$) studies, research on electro-

*Table 2. Electrochemical studies of methane conversion to $C_1$ products in solid electrolyte cells*

| *Electrolyte** | *Electrode (anode)* | *Overall reaction* | *Type of study*† | $T/°C$ | *Reference* |
|---|---|---|---|---|---|
| CSZ | Pt | § | 3 | 1015 | 71 |
| CSZ, YSZ | C | $CH_4 + 1/2O_2 \longrightarrow CO + 2H_2$ | 3 | 1000–1200 | 72, 73 |
| CSZ | Ag, Pt | $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ | 1 | 550–850 | 74 |
| CSZ, YSZ | Ag, Pt, Au | $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ | 1 | 500–800 | 75 |
| SSZ | Pt, Au | § | 2 | 700–850 | 76 |
| YSZ | Ag | $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ | 1, 2 | 400–600 | 77, 78 |
| CSZ, YSZ | Ag, Pt, Ni, $In_2O_3$–$SnO_3$ | § | 2 | 600–1000 | 79 |
| SSZ | Pt, Au | § | 2 | 700–850 | 80 |
| YSZ | Pd | $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ | 1, 2 | 400–600 | 78, 81 |
| CSZ | Pt | $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ | 1 | 650–1000 | 82 |
| YSZ | Pt, Pt(Rh) | $CH_4 + NH_3 + O_2 \longrightarrow HCN + H_2O\,(+CO, H_2, N_2)$ | 1, 2, 3 | 750–1000 | 83, 84, 94 |
| $SrCeYbO_3$ | Pt | $CH_4 \longrightarrow H_2 + C$ | 2 | 900 | 85 |
| CSZ, YSZ | Pt | $CH_4 + 1/2O_2 \longrightarrow CO + 2H_2$ | 2 | > 700 | 86 |
| YSZ | Fe | $CH_4 + 1/2O_2 \longrightarrow CO + 2H_2$ | 2, 3 | 700–900 | 87 |
| YSZ | Pt, $LaMnO_3$ series | $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ | 2, 3 | 800 | 88, 89 |
| YSZ | Ag, Pt | $CH_4 \longrightarrow CO_2\,(+C_2's)$ | 1, 2 | 650–750 | 66, 93 |
| – | $Ni/ZrO_2$ | $CH_4 + H_2O \longrightarrow CO + 3H_2$ | 1 | 800–1000 | 92 |
| YSZ | Pt | $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ | 1, 2 | 600–900 | 90 |
| YSZ | Ag, Pt | $CH_4 \longrightarrow CO_2\,(+C_2's)$ | 1, 2 | 650–750 | 66, 93 |
| Nd-$BaCeO_3$ | Pt, Ni | $CH_4 + H_2O \longrightarrow CO + 3H_2$ | 3 | 900–1000 | 70 |
| YSZ | Ce–Cd oxide | $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$ | 2, 3 | 800–1000 | 91 |
| YSZ | Fe | $CH_4 + O_2(O^{2-}) \longrightarrow CO + H_2$ | 1, 2 | 850–950 | 95, 113 |
| YSZ | Fe, Ni, Pt, $LaCaCrO_3$ | $CH_4 + O_2(O^{2-}) \longrightarrow CO + H_2$ | 3 | 1000 | 112 |
| YSZ | Fe | $CH_4 + H_2O + O^{2-} \longrightarrow CO + H_2$ | 1, 2 | 850–950 | 102, 107 |
| YSZ | Ni/YSZ cermet | $CH_4 + H_2O + O^{2-} \longrightarrow CO + H_2$ | 3 | 800–930 | 96, 114 |
| – | $Sm_2O_3$, $LaCaCrO_3$ | $CH_4 + O_2 \longrightarrow CO, CO_2 + C_2$ | 1 | 500–800 | 97 |
| YSZ | Ag, Au | $CH_4 + O_2(O^{2-}) \longrightarrow CO, CO_2, C_2$ | 1, 2 | 700–800 | 98 |
| YSZ | Au | $CH_4 + O_2(O^{2-}) \longrightarrow CO, CO_2$ | 1, 2 | 700–750 | 99 |
| YSZ | Pt | $CH_4 + O_2(O^{2-}) \longrightarrow CO_2 + H_2O$ | 1, 2 | 700–750 | 100 |
| YSZ | Ni/YSZ cermet | $CH_4 + O_2(O^{2-}) \longrightarrow CO + H_2$ | 3 | 600–1200 | 101 |
| YSZ | Ni/YSZ cermet<br>Pt, PtBi, PtBi-cermet | $CH_4 + O^{2-} \longrightarrow CO + H_2$ | 2, 3 | 800–1100 | 103 |
| YSZ | Ag, Ni | $CH_4 + O_2(O^{2-}) \longrightarrow CO_x, C_2$ | 1, 2 | 600–800 | 105 |
| YSZ | Ni/YSZ cermet | $CH_4 + H_2O + O^{2-} \longrightarrow CO_2 + H_2$ | 3 | 500–1150 | 109 |
| YSZ | Ni/YSZ cermet | $CH_4 + O_2(O^{2-}) \longrightarrow CO + H_2$ | 2, 3 | 700–1000 | 115 |
| YSZ | $La_{0.7}Ca_{0.3}CrO_3$ | $CH_4 + O_2(O^{2-}) \longrightarrow CO + H_2$ | 1, 3 | 900 | 116 |

* CSZ = ceria-stabilized zirconia, SSZ = scandia-stabilized zirconia, YSZ = yttria-stabilized zirconia.

† 1 = open-circuit, 2 = oxygen pump, 3 = fuel cell.

§ Exact product distribution was not given.

chemical conversion of methane to $C_1$ compounds includes the production of hydrogen [79, 85], the synthesis of hydrogen cyanide [83, 84, 94] and the production of synthesis gas [70, 86, 87, 95, 96, 110–116]. Mori used a proton conductor and platinum electrodes and decomposed $CH_4$ to C and $H_2$ at the anode. Hydrogen was transported as $H^+$ through the electrolyte and formed high purity molecular $H_2$ at the cathode [86]. Otsuka, Yokoyama and Morikawa used a stabilized zirconia cell in which steam was passing over the cathode and methane over the anode. Hydrogen and oxygen were formed at the cathode and oxygen was transferred at the anode to oxidize methane [79]. A stabilized zirconia cell with platinum electrodes was used to produce HCN by oxidizing methane-ammonia mixtures at the anode [83, 84, 94]. High selectivities to HCN were achieved and the main oxygen-containing compound was CO [84]. Mahmood and Bonanos [105] studied the oxidation of methane on silver and on nickel-zirconia electrodes at 600–800 °C. The reaction kinetics were first measured in a conventional microreactor and then each half-cell reaction was measured separately in a three-electrode electrochemical reactor. It was found that the mixed potential model predicted the behaviour of the $CH_4$–$O_2$ system in a satisfactory manner under both, open circuit and under cathodic polarization. Their work showed the usefulness of the mixed potential approach in the analysis of the mechanism of catalytic oxidations [105].

Parallel to recent catalytic studies [7], several research groups have shown considerable interest in studying and optimizing the formation of syngas from methane [90, 95, 96, 101, 102]. Steam reforming (Reaction 1) is the major industrial route to upgrade methane. The reaction is strongly endothermic ($\Delta H^0_{298\,K} = +206\,kJ\,mol^{-1}$) as opposed to the partial oxidation reaction (Reaction 2) which is slightly exothermic ($\Delta H^0_{298\,K} = -35.7\,kJ\,mol^{-1}$). Despite its energy efficiency, Reaction 1 compares favourably with Reaction 2 because the addition of steam diminishes the problem of carbon formation. The electrochemical production of syngas from methane seems to be advantageous compared to the conventional catalytic approach since reactions 1 and 2 could be combined in an elegant way. If, for example, an oxygen ion conducting cell is used and methane-steam mixtures are fed at the anode with the cathode exposed to oxygen (air), the following reactions would take place:

at the cathode:

$$(x-y)/2\,O_2 + 2(x-y)\,e^- \longrightarrow (x-y)O^{2-} \qquad (5)$$

at the anode:

$$xCH_4 + yH_2O + (x-y)O^{2-} \longrightarrow xCO + (2x+y)H_2 + 2(x-y)\,e^- \qquad (6)$$

and overall:

$$xCH_4 + yH_2O + (x-y)/2\,O_2 \longrightarrow xCO + (2x+y)H_2 \qquad (7)$$

In such a cell the endothermicity problem is reduced because oxygen is partially replacing steam. Furthermore, if the goal is to produce electrical energy rather than synthesis gas, methane can be internally reformed and then completely oxidized in the same type of cell:

Cathode:

$$2xO_2 + 4x\,e^- \longrightarrow 2xO^{2-} \qquad (8)$$

Anode:

$$xCH_4 + yH_2O \longrightarrow xCO + (2x+y)H_2 \qquad (9)$$

$$xCO + x/2\,O^{2-} \longrightarrow xCO_2 + x\,e^- \qquad (10)$$

$$(2x+y)H_2 + (2x+y)/2O^{2-} \longrightarrow (2x+y)H_2O + (2x+y)\,e^- \qquad (11)$$

Overall:

$$CH_4 + 2\,O_2 \longrightarrow CO_2 + 2H_2O \qquad (12)$$

It is clear that the selection of the appropriate anodic electrode would strongly affect both, reaction conversion and product composition. Nickel is the traditional catalyst for methane steam reforming and a cermet is the traditional anodic structure for solid oxide fuel cells. Lee *et al.*, studied the kinetics of the $CH_4$–$H_2O$ reaction in the absence of $O_2$ on nickel-zirconia cermets [92]. Most of their results, however, are equilibrium limited and do not represent intrinsic kinetics.

Yentekakis *et al.* [96] used a Ni–YSZ cermet |YSZ|$La_{0.75}Sr_{0.25}MnO_3$ cell to study the kinetics of reaction 1 at 800–930 °C. Under open circuit, the optimal $S/C$ ratio for maximization of the reaction rate was 0.25–0.5. Under closed circuit, the cell power output reached a maximum for much higher $S/C$ (about 1.7). This difference was attributed to the effect of the cell current on the reforming kinetics and on the different reactivities of $H_2$ and CO on the anode surface [96]. The kinetics of carbon deposition and syngas generation on Ni–YSZ-cermet were studied by Bebelis *et al.* at 825–950 °C. It was found that carbon formation is independent of the methane partial pressure while under porarization conditions, carbon deposition is substantially reduced [114]. The effect of nickel content of Ni–YSZ cermets on the catalytic activity for internal reforming was studied by Zanibelli *et al.* It was found that the nickel characteristics were improved by thermal treatment in a steam-hydrogen atmosphere. The authors also searched for the optimum nickel content that results in both good catalytic performance and high electrical conductivity [115]. Norby *et al.* [116], studied the electrochemical oxidation of methane using $La_{0.7}Ca_{0.3}CrO_3$–YSZ as anodic electrode. Interesting results from the methane conversion viewpoint were obtained although operation under reducing conditions caused gradual degradation of the electrode.

Alqahtany *et al.* studied the partial oxidation of methane to syngas in the presence [102] and in the absence [95] of steam at 800–950 °C, using iron instead of nickel as anodic electrode. It was found that Fe was very effective and in the presence of steam, the CO yield (moles of CO formed per mole of $CH_4$

fed in) could exceed 85% [102]. Electrochemically supplied $O^{2-}$ was more active than gaseous $O_2$ in producing CO while there was no difference between the two oxygen sources in the $H_2$ formation rates. Ionic oxygen was also more effective in eliminating carbon formation [95, 102]. Under open circuit, the surface oxygen activity was monitored by SEP and it was found that high selectivity and yield to syngas is achieved as long as the Fe electrode is maintained in its reduced state [95, 113]. Horita *et al.*, tested various materials for anodic performance including Fe, Ni, Pt and calcium-doped lanthanum chromite [112]. In agreement with the results of Alqahtany *et al.* [95, 102], their results showed that Fe is very active in producing synthesis gas and that electrochemical oxygen is effectively oxidizing carbon deposited on the electrode.

Ledjeff *et al.* [109], compared the performance of fuel cells in which the reforming was either internal, indirectly internal, or external. The latter seems to be less favourable because with internal reforming, the waste heat of the fuel cell is more efficiently utilized. The above authors also examined and discussed the thermodynamics of carbon deposition at various temperatures and steam to methane ratios and the problem of sulphur contamination of the nickel surface [109]. Gubner and Landes [110], studied the effect of the reactions of steam reforming and partial oxidation on the work that can be delivered by a methane SOFC. The above authors examined how the temperature and the methane/steam ratio affect the amount of work that can be produced per mol of methane. Hsiao and Selman [101] developed a mathematical model in order to determine the steam to methane ratios ($S/C$) within which the cell can operate safely, i.e. without carbon formation. The model predictions were mostly based on thermodynamic equilibrium calculations due to the lack of reliable experimental data. Theoretically, the cell could operate at $S/C$ of about 1.0 without carbon deposition but in practice, local variations of temperature and composition require a higher $S/C$ ratio (about 3.0) for safe operation [101]. The economics of syngas generation in small SOFC units are discussed in a recent paper by Antonucci [111].

Iwahara, Uchida and Morimoto [70] used a Nd-doped barium cerate as electrolyte and platinum electrodes to construct a mixed-conducting ($H^+$ and $O^{2-}$) cell. Mixtures of methane with steam were fed in at 900–1000 °C and high conversion to syngas was observed. Under closed circuit, current densities exceeding $0.5\,A\,cm^{-2}$ were attained. The advantage of this cell is that both conducting ions contribute to the formation of the desired products.

### 3.4. *Methane conversion to $C_2$ products*

Over the last ten years, the one-step conversion of methane to $C_2$ compounds, i.e. ethane and ethylene, also termed oxidative coupling, has become one of the most challenging problems in catalysis research. In the presence of a variety of catalysts and at 600–850 °C, methane and oxygen react to produce $C_2$ hydrocarbons with CO and $CO_2$ being the major carbon-containing byproducts. What makes this system very interesting is that the $C_2$ selectivity ($S$) decreases as the overall conversion of methane ($X$) increases. Thus, the $C_2$ yield ($Y$) which is the product of $S$ and $X$ and is the parameter to be maximized, is usually limited [3]. Recently, several innovative reactor design approaches have been proposed [117, 118] in which yields well in excess of 50% have been achieved. Nevertheless, the problem of low *per pass* yields remains unsolved.

As with most of the catalytic partial oxidation reactions, it was realized that a key in achieving industrially acceptable $C_2$ yields was the type and state of oxygen used [119, 122]. Several researchers tested a number of alternatives including: (i) using a sequential feed of oxygen and methane so that the reactant oxygen was either adsorbed on the catalyst surface or became incorporated into the oxygen lattice of an oxide catalyst; and (ii) using a metal oxide in which one metal had two accessible positive oxidation states so that lattice oxygen was the reactant instead of gaseous dioxygen [1]. Along these lines, solid electrolyte cells were tested for methane oxidative coupling in the last ten years.

Table 3 summarises these studies. In addition to the type of electrolyte used, the electrode in contact with the $CH_4$ stream, the operating temperature, and the mode of operation, the table also includes the $\Lambda$ values and the maximum $C_2$ yield, $Y$, (whenever it was possible to calculate them from the presented data), achieved in each study.

The first solid electrolyte-aided studies of methane coupling appeared about ten years ago [125, 127, 128]. Since then, a large number of studies with YSZ cells has been reported with a variety of metal and metal–metal oxide mixtures used as anodic electrodes [123–132, 145–148]. The motivation for these works was primarily based on the expected different reactivity between $O^{2-}$and gaseous dioxygen $O_2$. Indeed, it was found that under certain conditions, ionic oxygen did give better $C_2$ selectivities and yields [2]. Nevertheless, it was a moderately, and not dramatically better performance [2].

In 1988, Otsuka and coworkers used the single chamber cell (Fig. 1) to study the effect of oxygen pumping on methane oxidation [133, 134]. To the best of our knowledge, this was the first time that a solid electrolyte cell of that configuration was used. Otsuka *et al.* suspended the YSZ disc in a methane-oxygen stream. A gold electrode was used on one side and a LiCl/NiO powder spread on a gold film was used on the other side. Passing current in either direction caused a change in both, methane coupling and $CO_2$ formation rates with a selectivity increase from 60 to 92% [133]. The structure of the LiCl/NiO–Au electrode was crucial for the reaction rate enhancement [133, 134].

Very recently, Jiang *et al.* [118] obtained $C_2$ yields exceeding 88% either by the electrochemical supply of $O^{2-}$ on an 80% Ag/20% $Sm_2O_3$–CaO anode or by using gaseous $O_2$ and a Ag–$Sm_2O_3$ catalyst. These

*Table 3. Electrochemical studies of methane conversion to $C_2$ products in solid electrolyte cells*

| *Electrolyte** | *Electrode (anode)* | *T/°C* | *Type of study*[†] | $\Lambda$ | $Y_{max}$ | *Reference* |
|---|---|---|---|---|---|---|
| YSZ | Ag | 750–840 | 3 | INS | 2.5 | 123 |
| YSZ | Ag | 735–750 | 2 | INS | $< 0.1$ | 124 |
| YSZ | Ag, $Bi_2O_3$–Ag | 700 | 1, 2 | 0.5–1.0 | 2.0–3.0 | 125 |
| YSZ | Ag, $Bi_2O_3$–Ag, Cu, Fe | 750–900 | 1, 2, 3 | $\sim 1.0$ | 3.0 | 87 |
| YSZ | 0.8 Ag–0.2 Pd | 840 | 3 | $\sim 1.0$ | 10 | 126 |
| YSZ | Ag, Cu, Ni, Pt, $LaCrO_3$ oxides | 700–840 | 3 | $\sim 1.0$ | 10 | 126 |
| YSZ | Li/MgO–Ag | 700 | 1, 2 | 0.9–1.0 | 0.2 | 78, 127 |
| YSZ | $Bi_2O_3$–Ag | 700 | 2 | INS | 1.8 | 128 |
| YSZ | Pt | 600–900 | 1, 2 | 0.1–5.0 | 4.0 | 90 |
| YSZ | KF, $BaCO_3$, NaCl, $Bi_2O_3$, $Ho_2O_3$, $Sm_2O_3$ (on a Au electrode) | 800 | 3 | $\sim 1.0$ | 1.6 | 129 |
| YSZ | $Pt/Sm_2O_3/La_{0.83}Sr_{0.1}MnO_3$ | 760 | 2 | $\sim 1.0$ | $< 0.2$ | 130 |
| YSZ | $Bi_2O_3$–$Pr_6O_{11}$ | 700 | 2, 3 | INS | 1.6 | 89 |
| YSZ | YSZ–Au | 900 | 1, 2 | $< 1.0$ | 8.0 | 104 |
| YSZ, CSZ | Li/MgO–Ag, $Bi_2O_3$–Ag, $Bi_2O_3$–Pt, Mo–Ag, Cu, Pt, $Sm_2O_3$–Ag | 700–900 | 2 | INS | 3.1 | 131, 132 |
| YSZ | LiCl/NiO–Au | 700 | 1, 2 | $< 1.0$ | 4.5 | 133 |
| YSZ | $LiNiO_2$–Au | 700 | 1, 2 | 1.0–3.0 | 1.0 | 134 |
| $Y_2O_3$–$TiO_2ZrO_2$ | Li/MgO, $MaNa_aMg_bZr_cO_x$ | 700–850 |  | INS | 20–25 | 135, 136 |
| $SrCe_{0.95}Yb_{0.05}O_3$ | Pt | 800–1000 | 2 | INS | $< 1.0$ | 137, 149 |
| $SrCe_{0.95}Yb_{0.05}O_3$ | Ag | 750 | 2 | $< 1.0$ | $< 0.1$ | 138, 106 |
| $SrCe_{0.95}Yb_{0.05}O_3$ | Ag | 600–750 | 2 | $< 1.0$ | $< 0.1$ | 138–141, 150 |
| $SrCeYbO_3$ | Ag | 900 | 2 | INS | $< 1.0$ | 142, 149 |
| YSZ | PFKs | 900 | 2 | INS | $< 1.0$ | 143 |
| $SrCe_{0.95}Yb_{0.05}O_3$ | $La_{0.6}Sr_{0.4}MnO_3$ | 800–820 | 2 | $< 1.0$ | $< 2.0$ | 144 |
| YSZ | Pt | 720–850 | 1, 2 | 3.0 | 8 | 145, 148 |
| YSZ | Ag | 720–850 | 1, 2 | $< 1.0$ | 8 | 146 |
| YSZ | $MnO_x$ | 750–830 | 1, 2 | 7.0 | 1 | 147 |
| YSZ | 80% Ag, 20% $Sm_2O_3$(CaO) | 800 | 2 | INS | 88 | 118 |

* CSZ = ceria-stabilized zirconia, SSZ = scandia-stabilized zirconia, YSZ = yttria-stabilized zirconia, PFKs = perofskites

[†] 1 = open-circuit, 2 = ionic pump, 3 = fuel cell.

INS: Insufficient information to extract the $\Lambda$ values.

outstandingly high conversions and yields (more than four times those achieved with the best catalysts) were achieved by using a novel design in which ethane and ethylene were trapped in a molecular sieve so that their subsequent oxidation was avoided. Gaseous and electrochemical oxygen were essentially equally active and selective in the production of $C_2$ hydrocarbons [118].

As mentioned earlier, the use of $O^{2-}$ cells as electrochemical oxygen pumps improved the catalytic properties of the electrodes used but not to an impressive level. Table 3 shows that the $C_2$ yields were mostly between 1 and 10%. Several explanations for this rather moderate effect can be given:

(i) For a given methane feed rate, a high yield requires a high $O^{2-}$ flux or equivalently, a high current density. In certain cases (low temperatures, thick solid oxide membrane) the imposed current density cannot exceed an upper limit. This problem can be partly overcome if a very low methane feed flow rate is employed. A low feed rate, however, increases the residence time of the gases over the anode resulting in a decrease in selectivity.

(ii) The best catalysts for $C_2$ coupling are oxides, not metals. The electrodes, however, must be electron conductors (e.g., metals). The usual solution was to prepare an anodic electrode by mixing a metal (preferably inactive like gold) with a metal oxide. Nevertheless, when oxygen is transferred as $O^{2-}$ through, oxygen ions reach the metal–electrolyte–gas boundary of the anode. Consequently, methane can react with oxygen on the metal as well as on the oxide surface; and metals are poorly selective catalysts. Also if the $O^{2-}$ flux is high and the metal electrode is relatively inactive, a fraction of the transported $O^{2-}$ may combine to form gaseous dioxygen. Hence another solution was tested, i.e. to use conducting oxides as electrodes with the hope that they would serve both purposes (methane coupling and electrical conduction) equally well. Along these lines, a number of perovskite materials had already been tested with promising results [89, 97, 108, 143]. Finally, a clever alternative was tested by Hazbun who used a mixed conductor ($O^{2-}$ and $e^-$) as electrolyte and succeeded in obtaining $C_2$ yields as high as 25% [135, 136]. The $O^{2-}$ flux through the ceramic membrane was counterbalanced by an equivalent electron flux so that there was no need for electrodes to close the circuit. The only disadvantage of this device was that the oxygen flux was based on the oxygen gradient across the membrane and was not electrochemically controlled [2].

(iii) It was mentioned that solid electrolyte cells offer the opportunity of electrochemical modification of the catalytic properties. The NEMCA effect could be very useful in methane coupling because with a very low current, the reaction rate could be strongly enhanced. It can be seen in Table 3, however, that the maximum values of $\Lambda$ obtained were between 5 and 8. Actually, in most of the studies, Λ did not exceed unity. Of course, care should be exercised when comparing the Λ values obtained in $CH_4$ oxidation studies with those previously reported [65]. To obtain a Λ value higher than 1, gaseous oxygen must be introduced with methane over the anodic electrode. If the only oxygen supplied is in the form of $O^{2-}$, it is physically impossible to obtain values greater than 1. In most studies listed in Table 3, gaseous oxygen was not introduced. Unfortunately, even in the few studies where there was a finite gaseous $O_2$ content over the anode, the Λ values obtained were not large [2, 65, 145, 146]. Methane coupling is a peculiar catalytic reaction in that it involves both surface and gas-phase reaction steps. Electrochemical oxygen pumping can modify surface properties, not gas-phase reactions. Even if C–H activation or $CH_3\cdot$ radical formation is enhanced, surface oxidation to $CO_x$ [1] may limit gas-phase coupling over metals such as Ag or Pt. Therefore, it is reasonable to observe a less strong effect compared to studies where the reaction is entirely catalytic.

The moderate success with the $O^{2-}$ cells directed several research groups into a totally different route based on methane conversion to $C_2$ compounds via dehydrogenation rather than partial oxidation [86, 137–142, 144, 149]. Figure 3 shows the reactor-cell configuration used in these studies. The proton conductor was a $SrCe_{0.95}Yb_{0.05}O_3$ perovskite (SCY). The reactions that are assumed to occur in these cells are:

$$2CH_4 \longleftrightarrow C_2H_6 + H_2 \qquad (13)$$

and

$$2CH_4 \longleftrightarrow C_2H_4 + 2H_2 \qquad (14)$$

In the absence of oxygen, the conversion of methane to $C_2$ compounds via Reactions 13 and 14 is thermodynamically limited. At 900 °C, for example, the equilibrium constant for Reaction 13 is about $6 \times 10^{-4}$, which gives a maximum mole fraction of ethane equal to 0.023 only. Continually drawing hydrogen from methane, however, it is possible to upset the thermodynamic equilibrium and increase methane conversion to ethane and ethylene (Fig. 3).

Chiang *et al.* [106, 107, 138–141, 150] used both single and double-chamber SCY cells with Ag electrodes to study the dehydrogenation of methane at 600–750 °C. Upon passing a current, the $C_2$ production rate was increased by as much as 15 times the open circuit rate [139, 150]. Exchange and limiting currents were measured and it was found that even with 100% hydrogen at the anode, surface diffusion of atomically adsorbed hydrogen was rate limiting [141]. When the anode was exposed to 100% methane, an activation energy of about 210 kJ mol$^{-1}$ was found for limiting currents which implied that the overall process was limited by the abstraction of a H atom from $CH_4$ to form a methyl radical [150].

Hamakawa *et al.* [142], studied the dehydrogenation reaction at 900 °C on Ag electrodes using the same SCY electrolyte. Upon introducing $CH_4$ and Ar into the anode and cathode respectively and under galvanostatic operation, hydrogen evolved at the cathode and $C_2$'s were formed at the anode. The conversion of methane was low (about 1%). When argon was replaced by air, a drastic increase in the $C_2$ formation rate was observed. This was explained by the appearance of p-type conduction so that the electrolyte was converted to a mixed conductor ($H^+$ and $e^-$) and the cell was self-short circuited [142].

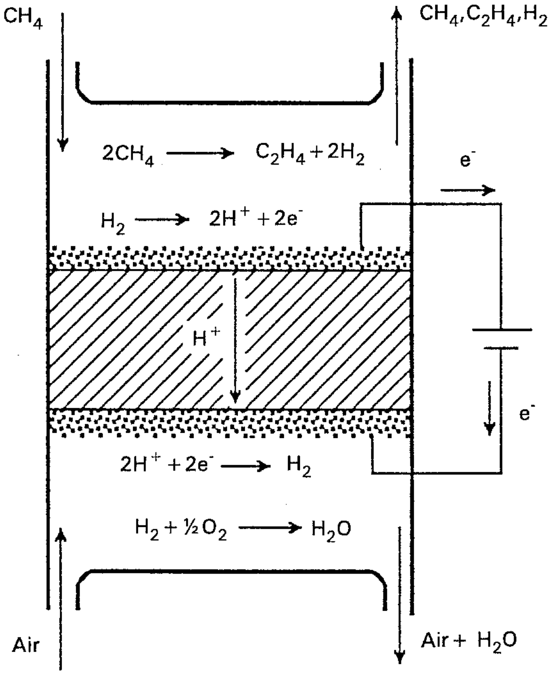

Fig. 3. Solid electrolyte $H^+$ cell for methane dimerization.

In general, the use of $H^+$ cells did solve the problem of the production of undesirable oxygenates (CO, $CO_2$) but, as Table 3 shows, the $C_2$ yields were not impressive either. One of the reasons for this is that without oxygen, methane pyrolysis:

$$CH_4 \longleftrightarrow C + 2H_2 \qquad (15)$$

starts to dominate. The conversion of Reaction 13 increases with increasing temperature which makes operation at high temperatures preferable but Reaction 15 is also favoured at elevated temperatures. A search for new anodic materials or the introduction of $CH_4$–$H_2O$ mixtures instead of $CH_4$ alone, are possible directions for further study of this interesting reaction system.

## 4. Technoeconomic considerations

To our knowledge, none of the above described electrochemical processes has yet found commercial application. A safe explanation is that none of these alternatives compares favourably with the corresponding conventional approaches currently in use. It would be interesting, however, to identify the key factors that affect the economic evaluation of each process. In scaling up of a solid electrolyte aided process of methane activation, several parameters have to be considered: (i) identification of the chemical reaction, (ii) identification of the type of electrochemical operation (ionic pumping, regular fuel cell, cogenerative fuel cell etc.) and (iii) identification of the sizing and location of the plant.

The economics of chemical cogeneration in solid electrolyte cells have been modelled in the past. Spillman *et al.* presented a model by which one could decide which of the three modes of operation of a solid electrolyte cell, fuel cell (producing electricity only), electrolytic cell, or cogenerative cell is economically preferable [151]. Their analysis showed that for chemical cogeneration to be preferable, the difference in values of reactants and products should be low, the reaction $\Delta G$ should be high and the molecular weight of the product should be low [151]. Vayenas *et al.* developed a simple model in which capital costs were also included and tested for the economic feasibility of various candidate cogeneration processes [151, 153]. Results were promising for $H_2SO_4$ and possibly for $HNO_3$ production [152]. The above authors found that good candidate reactions are those that are exothermic, with inexpensive raw materials and products and are carried out at temperatures of 800 °C or higher.

The reaction of methane oxidative coupling seems to be a good candidate for chemical cogeneration since it fulfills the requirements set by the two previously mentioned research groups, that is, (i) reactants and products are quite cheap, (ii) the reaction is highly exothermic and (iii) the optimum operating temperature is about 800–850 °C [1–3]. Vayenas *et al.* suggested that a more detailed economic analysis is needed in case a reaction satisfies the promising characteristics of their model [152]. Recently, a technoeconomic evaluation and assessment of economic feasibility of two of these processes, oxidative coupling and syngas production, was reported [154]. Each of these products was assumed to form in a solid electrolyte fuel cell which cogenerated electrical energy. Both processes were compared to a third one, an internally reformed methane fuel cell that generated electricity only (complete oxidation to $CO_2$ and $H_2O$). Table 4 summarizes the technoeconomic findings for the three processes. In all three cases, it was assumed that 100 MW of electrical power were produced. In addition, $0.96 \times 10^8$ kg of ethylene and $3 \times 10^8$ kg of syngas ($H_2$/CO ratio of about 2.4/1) were coproduced annually in cases 1 and 2, respectively. In case 1, a 25% $C_2$ yield per pass was considered while in case 2, the assumed CO yield was 63%. For two reasons, the 85% + $C_2$ yields that were recently reported [118], were not used in the technoeconomic analysis. First, these were not per pass yields and therefore the whole economic analysis for a reactor design like that of [118], will be different. Second, these high yields were also achieved with gaseous oxygen in a catalytic reactor which will make the catalytic choice economically preferable. In case 3, a 90% per pass conversion of methane to $CO_2$ and $H_2O$ was assumed. The detailed calculations and the various assumptions on material performance and their prices can be found elsewhere [154] and are not presented in this communication. Table 4 shows that the capital investment and production costs for the typical fuel cell (case 3) are significantly lower than for the two cogenerating cells. On the other hand, there is no chemical credit in case 3 (zero price assumed for $CO_2$ and $H_2O$). It is interesting to see in Table 4 that the numbers for the return on investment (ROI), are appreciably high. To be sound, the minimum rate of return before tax should be 20% or higher. Furthermore, to be highly attractive to industry, the ROI should be near 35% [155]. Only the noncogenerative fuel cell approaches this value. It turns out that the methane coupling fuel cell plant is an economically attractive idea which can be highly profitable for an ethylene price of $0.70 kg$^{-1}$ [154]. This high price has been recently reached in the last few years but has stabilized to much lower values. Even at the current price of $0.46 kg$^{-1}$, ethylene production may be made feasible with government subsidies and tax breaks.

From the technoeconomic analysis of the $C_2$ and the syngas processes, it becomes clear that under certain conditions, the chemical cogeneration approach can be industrially attractive. Why then has industry

*Table 4. Economic Summary for $C_2$, syngas and noncogenerating methane fuel cell plants*

| *Items* | *Cost*/$millions | | |
|---|---|---|---|
| | *Case 1 | †Case 2 | ‡Case 3 |
| Total fixed investment | 251.59 | 180.92 | 162.13 |
| Working capital (15% of fixed capital) | 37.74 | 27.14 | 24.32 |
| **Total capital investment** | 289.33 | 208.06 | 186.45 |
| **Total production cost** | 90.41 | 87.34 | 56.13 |
| Chemical credit | 44.73 | 40.20 | – |
| Steam credit | 21.13 | – | 28.45 |
| Operation cost for electricity | 24.55 | 47.14 | 27.86 |
| Income from electricity | 86.69 | 84.00 | 84.00 |
| **Income before taxes** | 62.14 | 36.86 | 56.14 |
| **Rate of return on investment (ROI) before taxes** | 21.48% | 17.71% | 30.11% |

* Case 1: Fuel cell with cogeneration of ethane and ethylene.
† Case 2: Fuel cell with cogeneration of synthesis gas.
‡ Case 3: Noncogenerative fuel cell ($CO_2 + H_2O$).

not yet adopted the chemical cogeneration approach for any chemical process? Several reasons are as follows:

(a) *Immature testing of SOFC pilot plants.* In the analysis of the syngas and $C_2$ plants, it was assumed that the solid electrolyte reactor would depreciate at a 6.7 year replacement rate [154]. This assumption was based on a reasonable extrapolation of continuous operation of scaled-up state-of-the-art pilot SOFCs which run for up to 25 000 straight hours [156–158]. After an initial burst of optimism of the 1960s and until 1988, there was a declining interest in SOFCs due in part to the fabrication limits and material compatibility of the interconnective and cell parts. Recently, however, the interest has grown again as manifested, among other things, by the International SOFC Symposia [157, 158], each attended by more than 500 participants. Thus, test pilot results showing promise nearing industrial practicality are currently reported. In our estimate, researchers are still 5–10 years from demonstrating that scaled-up SOFCs can run in the 50 000–100 000 hour range.

(b) *Expensive SOFC technology.* The capital investment cost analysis showed that the cost of the zirconia materials is appreciable. The process would be much more attractive if that cost were significantly reduced. Further development in material science and ceramics technology is required to advance the electrolyte and electrode material to a state where they are demonstrably practical.

(c) *Lack of incentives for industry.* Industry is understandably reluctant to adopt a completely new reactor design to replace current designs. A simple addition to existing designs would not be a problem for industry. For example, in Europe, it has been proposed that SOFCs operate not to replace the fossil fuel power plants but to be incorporated into existing plant designs to increase the thermodynamic efficiency and to reduce the environmental pollutants. In such designs, the SOFCs are used to ensure more complete combustion of fuel. For industry, this concept is easier to adopt financially with less risk.

(d) *Limited diversity in industry.* Few companies are diversified as to actually considering investment into electrical power generation and chemical production. Utility companies produce electric power, petrochemical companies produce hydrocarbon compounds, and pharmaceutical companies produce drugs or medicines. For a corporation to enter two worlds, that is, chemicals and electrical power generation, it would need additional expertise. It is simpler to sell the idea of producing several new chemicals to a petrochemical corporation than to a utilities company. There are corporate risks in entering new fields and diversifying on a macroscopic level. A public utilities corporation may not risk venturing into the more privatised chemical industry.

## 5. Summary and conclusions

A large number of research studies regarding the electrochemical activation of methane has been reported in the last thirty years. This electrochemical approach concerns either conversion to more versatile and more useful raw materials or to the direct conversion into electrical energy by using methane as the fuel in fuel cells. At low and moderately high temperatures, most of the studies aiming at the conversion of methane to other chemicals were not very successful. The aqueous or the molten carbonate methane fuel cells gave more promising results. Still, however, the rates attained at these temperatures, although higher than the corresponding chemical reaction rates, are not high enough for industrial applications. Today, most of the fuel cells use hydrogen or hydrogen-carbon monoxide mixtures which have resulted from previous external reforming of methane.

Solid electrolyte cells offer more possibilities of electrochemical production of useful chemicals from methane. Among the various processes tested, the conversion to synthesis gas and the dimerization to $C_2$ products were most extensively investigated. In addition, the direct use of methane (without previous external reforming) as fuel in solid electrolyte fuel cells, appears to be a valid alternative.

Studies of methane coupling have not been done systematically but only in the direction of improving existing catalysts. It has already been found that under certain conditions, it is advantageous to use ionic $O^{2-}$ instead of gaseous $O_2$. Hence, the potential is there and several very promising features have been identified. Currently, the problems of limited yield and of low reactivity and selectivity of metal-based electrodes are dominating. The first problem is bypassed when the reaction is carried out in proton conducting cells with dehydrogenation of methane although, in that case, another problem must be solved, that of methane pyrolysis and carbon deposition. The problem of low selectivities of metal electrodes can be solved by searching for conductive oxides that are catalytically active at the same time.

The conversion of $CH_4$ to synthesis gas via an overall exothermic process is probably the best approach for electrochemical methane utilization. In a cogenerative $O^{2-}$ solid electrolyte cell, methane or methane-steam mixtures will be used as fuel and the overall reaction will be the conversion to syngas with simultaneous generation of electrical energy. Scaling up to an industrial level, however, will still require a lot of work and also the incorporation of material science, reactor design, and heterogeneous catalysis.

Finally, it should be pointed out that all the above processes involve energy production. Energy-related matters are a subject of government concern in which political issues are inevitably involved. Along these lines, future government support (e.g., in the form of subsidising companies that test and promote fuel cell technology) to the industrial sector for 'cleaner' energy production, could modify the above cost analysis and make the electrochemical approach a more attractive alternative.

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