

Solid Electrolytes: Applications in Heterogeneous Catalysis and Chemical Cogeneration

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Solid electrolytes have found applications in several areas, including (a) sensors, (b) separators, (c) solid oxide fuel cells, and (d) solid-state batteries. In addition, solid electrolytes have been used in the construction of solid electrolyte cell reactors (SECRs), in which heterogeneous catalytic reactions have been studied. Also, SECRs have been used as chemical cogenerative fuel cells, i.e., for the simultaneous production of electricity and useful compounds. In the present work, a survey of the studies conducted in SECRs is presented. The fundamental operating principles, results in technologically important reactions, and the hurdles that should be overcome to bring SECRs into industrial practice are discussed.

1. Introduction

Solid electrolytes are solid-state materials that exhibit significant ionic conductivity at elevated temperatures. Since any solid, in principle, has nonzero ionic and electronic conductivity, it has been established that the solid electrolytes in which the transference number for ions is two or more orders of magnitude higher than that for electrons are to be called “pure” ionic conductors. If, on the other hand, the ionic and electronic transference numbers are of comparable magnitude, the solid electrolyte is called a “mixed” conductor. The characterization of a solid electrolyte is usually based on the conducting anion or cation. Currently, O^{2-} , F^- , H^+ , K^+ , Na^+ , Cu^+ , Ag^+ , and Li^+ conductors have been discovered, and their properties have been studied in detail.¹ Because of the industrial importance of catalytic oxidations and hydrogenations, oxygen ion (O^{2-}) and proton (H^+) conductors are the most widely used. Solid-state oxygen-ion conductors are solid solutions of oxides of divalent or trivalent cations (Y_2O_3 , CaO , Yb_2O_3) in oxides of tetravalent metals (ZrO_2 , ThO_2 , CeO_2). Their O^{2-} conductivity is based on the oxygen ion vacancies created in the lattice of the tetravalent metal oxide when doped with the oxide of the divalent or trivalent metal. Because of its chemical stability and mechanical strength, the most popular O^{2-} conductor is a 6–10 mol % Y_2O_3 in ZrO_2 (this is called yttria-stabilized zirconia, YSZ). The high-temperature proton conductors are perovskite-type oxides, usually based on $SrCeO_3$ or $BaCeO_3$. Note that the ionic conductivity of solid electrolytes is not due to their porosity. Both purely ionic and mixed conductors are dense materials, and their conductivity is based on ionic displacement through their lattice.

In the last four decades, solid electrolytes have found several applications in (a) sensors, (b) separators, (c) solid oxide fuel cells, and (d) solid-state batteries. Furthermore, solid electrolytes have also been used in the construction of solid electrolyte cell-reactors (SECRs), in which heterogeneous catalytic reactions have been studied. The present work is a survey and review of the studies that have been conducted in SECRs. Studies that could belong in the four basic types of applications previously described are not included. Hence, this paper contains studies in which the primary goal was the production of a compound through a chemical or an electrochemical reaction.

Several review articles that partly or wholly cover this particular field already have been published.^{2–15} Because the topic of SECRs is related to several scientific fields, such as solid-state ionics, electrochemistry, heterogeneous catalysis, and chemical reaction engineering, the scope of this review is not only to provide a survey of relevant studies but also to present in a simple way the characteristic features, methods, and techniques used in this class of reactor. Hence, the next section describes the design and configuration characteristics of SECRs, as well as their differences from the other types of reactors. The goals of the studies performed in SECRs and the methods and techniques used to achieve these goals are then presented. A survey of SECR works is then shown in tables, followed by the most important findings for each reaction system. The final section contains technoeconomic aspects and describes the requirements to be met and the hurdles to be overcome to bring SECRs into industrial practice.

2. Types, Designs, and Configurations of SECRs

Figure 1 shows schematically the configuration of a SECR. In this particular example, the solid electrolyte is an oxygen

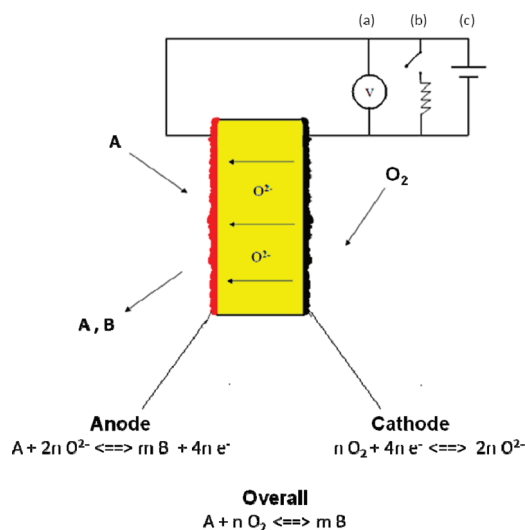
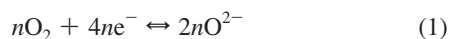


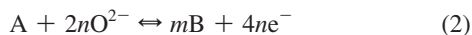
Figure 1. Configuration of an oxygen-ion-conducting solid-electrolyte cell: (a) open-circuit operation, (b) closed-circuit operation in the fuel-cell mode, and (c) closed-circuit operation in the “pumping” mode.

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ion (O^{2-}) conductor. The cell consists of a dense solid electrolyte membrane and two porous electrodes. At least one of the electrodes is exposed to oxygen or to an oxygen-containing gas (in Figure 1, it is the cathode). The other electrode is exposed to the reacting mixture. At the cathode, oxygen is converted to O^{2-} ions:



In the form of O^{2-} , oxygen is electrochemically transferred to the anode, where the reaction



takes place. Hence, the overall chemical reaction that takes place can be written stoichiometrically as



The two electrodes are connected either to a voltmeter (case a), an external resistive load (case b), or an external power source (case c). As long as the chemical potential of oxygen is different at the two sides of the cell, a driving force for oxygen transport across the solid electrolyte exists and the cell may operate in one of the following modes:

Case a: In the open-circuit operation, there is no net current through the electrolyte. The difference in chemical potential is converted to the open-circuit voltage of the cell. Reaction kinetics can be combined with potentiometric data to elucidate the reaction mechanism.

Case b: In the closed-circuit operation, oxygen travels from the cathode to the anode, where it reacts with reactant A to produce B, according to reaction 3. Simultaneously, the electric circuit is closed and if the goal is the production of electricity, chemical energy can be converted directly to electrical energy.

Case c: If the primary goal is not the production of electricity but, instead, the electrochemical production of compound B, the external power source can be used to impose a current (and, equivalently, an oxygen flux) through the cell in the desired direction. This last mode of operation is called electrochemical oxygen "pumping". In fact, the term "pumping" should be used only in cases where the ion is forced to flow in the direction opposite to the thermodynamically expected one. However, it has been also used to show that the flux is driven externally, regardless of the spontaneous direction of the flow.

Depending on whether the two electrodes are gas-tight and separated from each other, two types of reactor designs may exist: the double-chamber reactor and the single-chamber reactor. A schematic diagram of a typical double-chamber SECR is shown in Figure 2. In this design, anode and cathode are exposed to different gaseous mixtures. Figures 2a and 2b are schematic diagrams of double-chamber O^{2-} and H^+ reactors, respectively. Figure 2c is a schematic of a membrane reactor rather than a SECR. The solid material that divides the reactor into two chambers exhibits mixed ($O^{2-}-e^-$) conductivity. Because both electrons and oxygen ions contribute to charge transport, the mixed conductor is internally short-circuited. Therefore, there is no need for electrodes or an external circuit. The ionic flow is counterbalanced by an equivalent electron flow in the opposite direction. This device appears superior to pure ion conductors since no closed electrical circuit is required. In practice, a mixed $O^{2-}-e^-$ conductor operates as a neutrally charged oxygen (O) conductor. On the other hand, in this type of SECR, the driving force for oxygen transport is the difference in chemical potential across the membrane and, therefore, it is

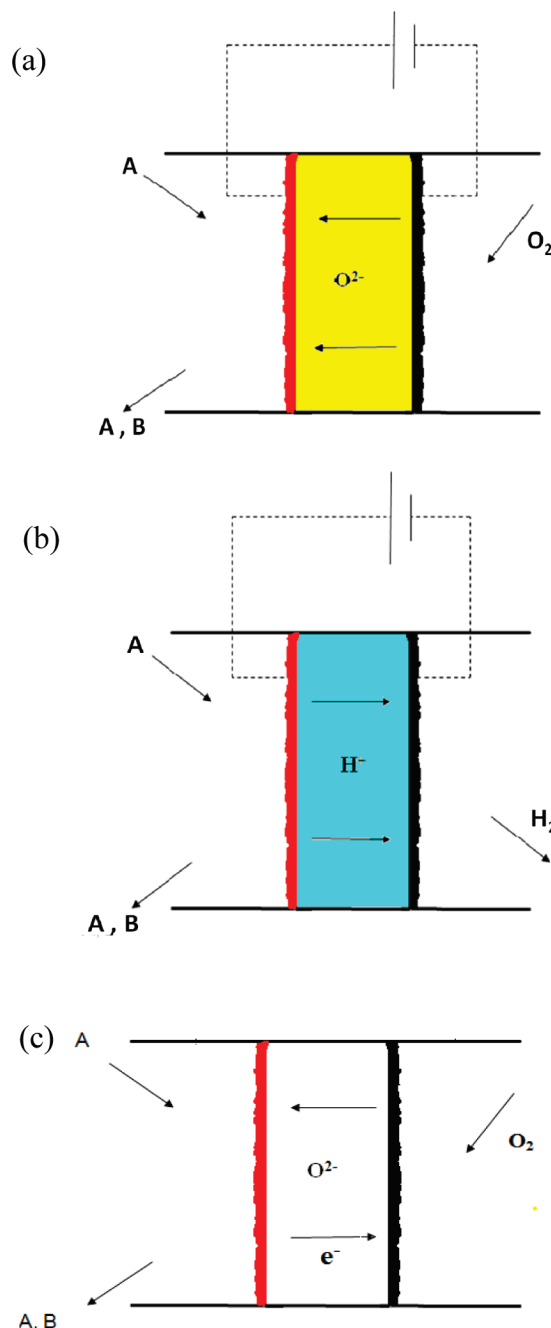


Figure 2. Schematic diagram of a double-chamber cell reactor with (a) an oxygen-ion conductor, (b) a proton conductor, and (c) a mixed ($O^{2-}-e^-$) conductor.

not possible to control the oxygen flux effectively using an electrical power source.

Figures 3a and 3b show the design of single-chamber O^{2-} - and H^+ -conducting SECRs, respectively. Unlike the double-chamber SECR, this cell does not provide for separate feed in two chambers. The solid electrolyte is suspended in a flow of the reacting mixture. The advantage of this design is that it is easier to apply to existing catalytic processes, because it does not require reactants to be separated.

3. Applications of Solid Electrolyte Cell Reactors (SECRs): Methods and Techniques Used

Solid electrolyte cell reactors (SECRs) have been used to study a very large number of catalytic reaction systems, including (1) decomposition and reduction of NO_x compounds,

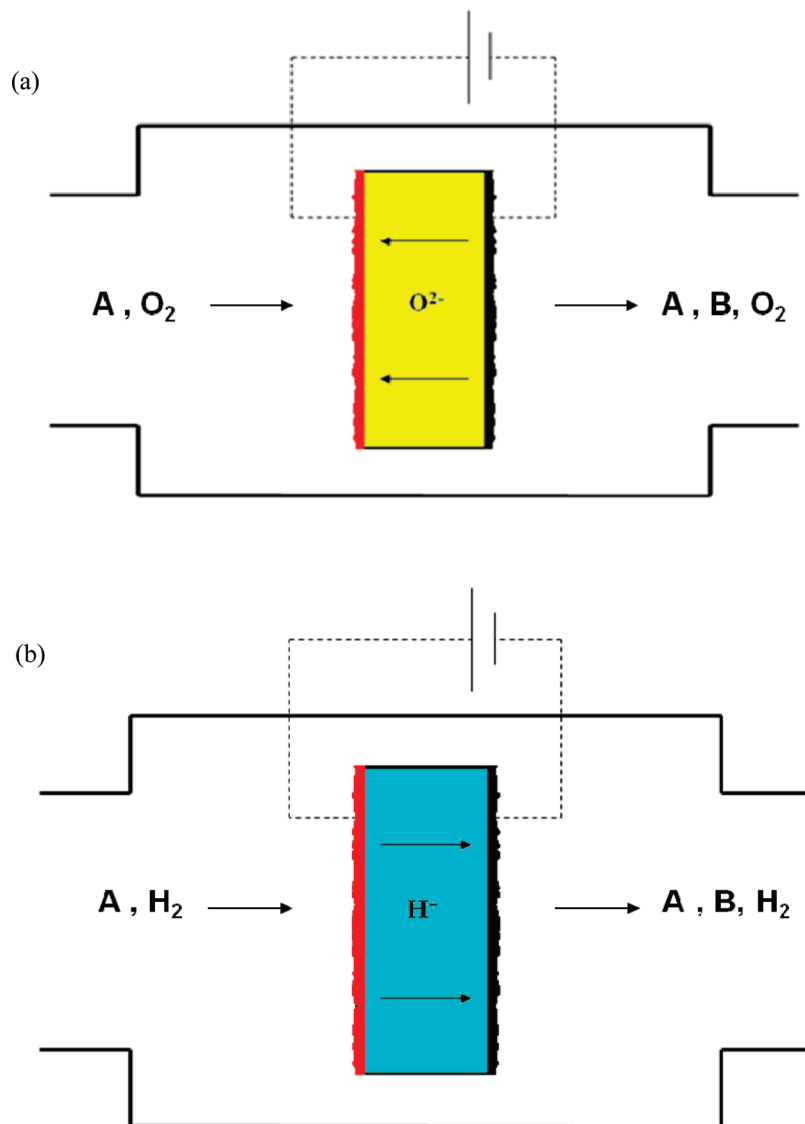


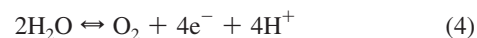
Figure 3. Schematic diagram of a single-chamber cell reactor with (a) a oxygen-ion conductor and (b) a proton conductor.

(2) partial and deep oxidation of alkanes, (3) partial and deep oxidation of alkenes and alkynes, (4) CO oxidation and CO₂ dissociation, (5) H₂ oxidation and steam electrolysis, (6) forward and reverse water-gas shift (WGS) reaction, (7) synthesis and decomposition of ammonia, (9) oxidation or hydrogenation of aromatic compounds, (10) reactions of sulfur compounds, and (11) oxidation and decomposition of alcohols.

Depending on the reaction system, a variety of goals existed in these studies. These goals, which were primarily based on the differences between a SECR and a conventional catalytic reactor, were (i) to take advantage of the selective conduction of ions, (ii) to investigate the mechanism of a catalytic reaction, (iii) to improve the yield to the desired product by operating under a closed circuit, and (iv) to cogenerate electricity and value-added chemical compounds by operating the SECR in the fuel-cell mode. Examples from each category are given below.

3.1. Selective Conduction of Ions. The earlier applications of SECRs in catalytic research focused on the advantageous characteristics of the selective conduction of ions in these systems. In a SECR, the conduction of species can be very specific, e.g., O²⁻ only, as shown in Figure 4. In that cell, the solid electrolyte serves not only as an oxygen-ion conductor but also as a separator of nitrogen and oxygen. Therefore, even

if the cathode is exposed to air or any mixture of oxygen with other gases, only oxygen will be transported through the solid electrolyte. Thus, the SECR serves as a natural separator of the two principle components of the ambient air: nitrogen and oxygen. In conventional systems, separation of nitrogen from the product stream can be costly, depending on the products. Typically, if air is used as the oxidant in a catalytic oxidation reaction, the effluent gases contain ~50% N₂. Hence, if nitrogen is eliminated, the reactor volume will be reduced by half. In addition, reaction kinetics may be affected positively. Figure 5 shows the use of a H⁺ conductor for the reduction of NO by steam.^{16–18} At the anode, steam is electrolyzed, according to the reaction



while, at the cathode, NO reacts with protons to produce molecular nitrogen:



The overall cell reaction is



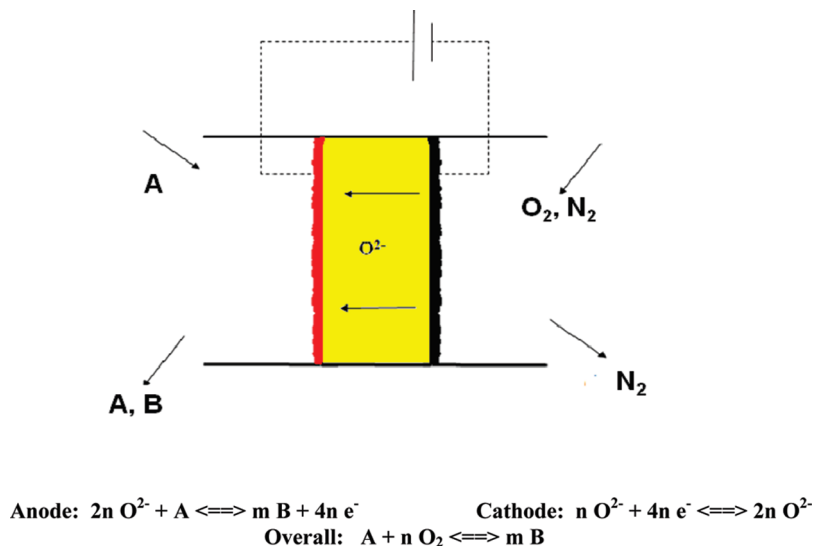


Figure 4. Schematic diagram of a SECR used for separating O_2 from N_2 at the cathode and reaction of N_2 -free O_2 at the anode.

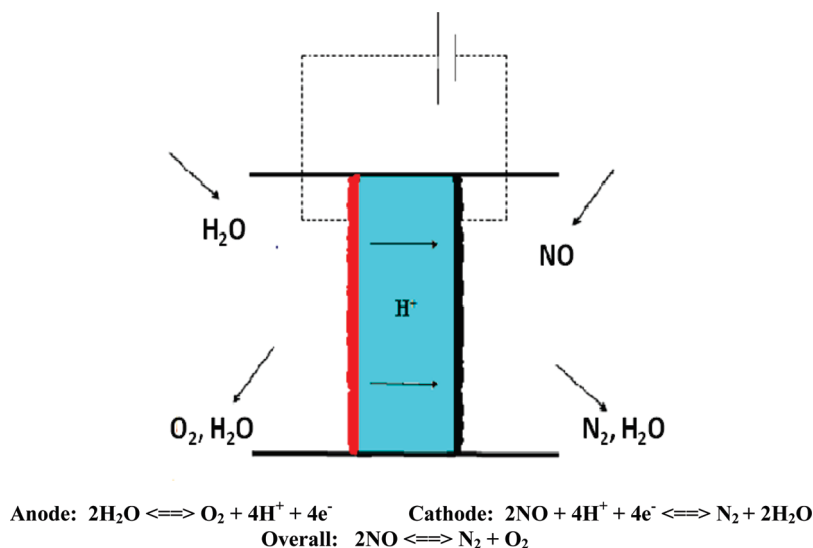
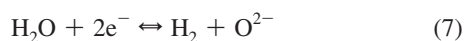


Figure 5. Schematic diagram of a SECR used for the reduction of NO by steam.

It can be seen that steam is regenerated at the cathode and N_2 -clean O_2 is produced at the anode.

The selective conduction of ions offers another advantage: poisonous impurities that may accompany one of the reactants cannot be transferred through the solid electrolyte. For example, in the industrial production of ammonia, a significant fraction of the cost lies in the preparation and purification of the synthesis gas; trace amounts of sulfur or oxygen cause irreversible poisoning of the catalyst. Figures 6a and 6b show how ammonia was synthesized from steam and nitrogen in O^{2-} and H^+ SECRs, respectively.¹⁹ In the H^+ cell of Figure 6a, steam was electrolyzed at the anode to produce protons and oxygen. Protons that were transported to the cathode reacted with nitrogen to produce ammonia. In the O^{2-} cell (Figure 6b), steam and nitrogen were fed into the reactor together at the cathode. Steam was electrolyzed and the hydrogen that was produced reacted with nitrogen.

The mixed ($\text{O}^{2-}-\text{e}^-$) conducting cell of Figure 7 is used for the partial oxidation of methane to synthesis gas.²⁰ At the right-hand side, steam is converted to O^{2-} ions and hydrogen (H_2):



On the left-hand side of the reaction, methane (CH_4) reacts with O^{2-} to produce carbon monoxide (CO) and H_2 :



The overall reaction is the steam reforming of methane:



3.2. Studies of the Mechanism of Catalytic Reactions.

When the SECR of Figure 1 operates under open-circuit (i.e., zero-current) conditions, potentiometric information can be extracted, which can be combined with catalytic measurements to elucidate the mechanism of the reaction under study. Essentially, the cell operates as a regular catalytic reactor with all reactants fed together in the gas phase. In this case, the difference in chemical potential is converted to the open-circuit electromotive force of the cell. If the counterelectrode is exposed to air (with an oxygen partial pressure of $P_{\text{O}_2} = 0.21$ bar), it has been shown^{2,4,6,7,10,21} that the thermodynamic activity of atomic oxygen adsorbed on the catalyst surface is given by the equation

$$a_{\text{O}} = (0.21)^{0.5} \exp\left(\frac{2FE}{RT}\right) \quad (10)$$

where F is the Faraday constant, R the ideal gas constant, T the absolute temperature, E the electromotive force (emf) of the cell, and a_{O} the activity of atomically adsorbed oxygen. This technique, which is called solid electrolyte potentiometry (SEP), has been used in the study of several important catalytic systems, as shown in Table 1.

SEP is very useful in heterogeneous catalysis studies, because (a) it is an “in situ” technique and (b) the emf measurement is continuous. The latter is extremely helpful in examining transient or oscillatory phenomena. Hence, SEP was used in the studies

of CO oxidation on platinum,³² ethylene oxidation on platinum,^{52,54,55} propylene oxide oxidation on silver,^{59,60} hydrogen oxidation on nickel,^{37–39} and propane oxidation on platinum.^{63–65} Also, SEP measurements have been used to study phase changes, such as the decomposition of a metal oxide.^{30–33,41,43,61,62,71,72} Although this technique was originally applied on metal electrodes, it was later shown that, under certain conditions, this technique also can be extended to oxide electrodes.^{34,61,62,68,69}

The validity of eq 10 is based on several assumptions,^{9,10,68–70} which can be summarized as follows:

(a) The solid electrolyte is a pure ionic conductor. In practice, YSZ is a pure O^{2-} conductor. However, this is not true for most

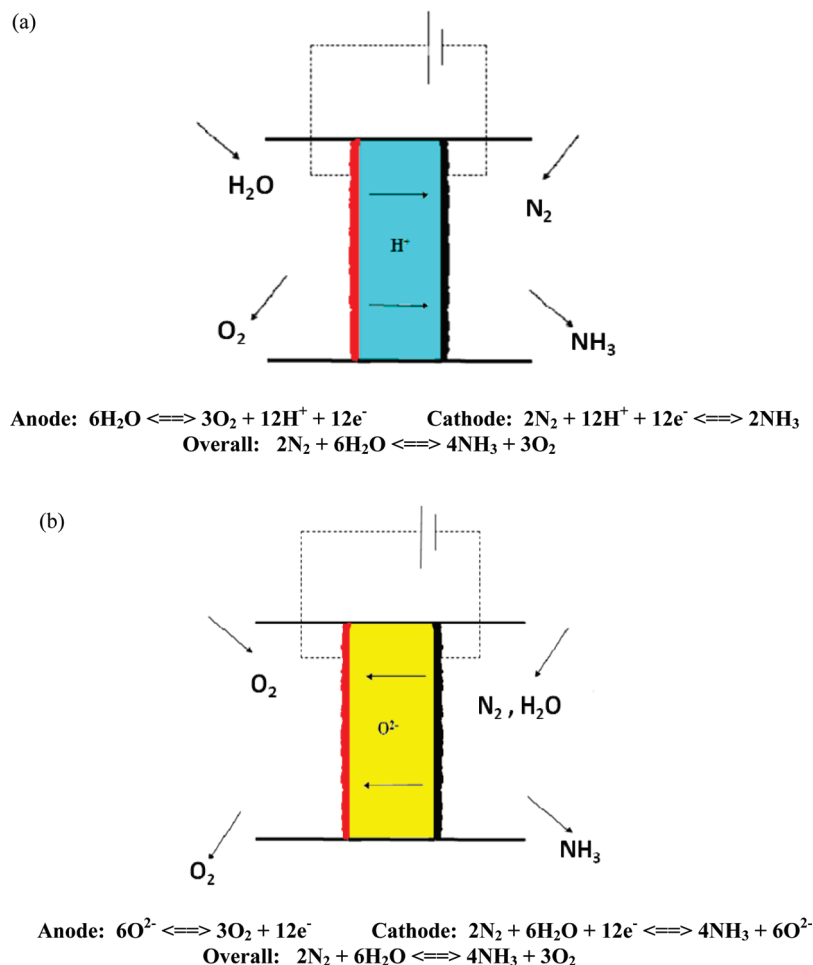


Figure 6. Schematic diagram of a SECR used for NH_3 synthesis from N_2 and H_2O in (a) a proton-conducting cell and (b) an oxygen-ion-conducting cell.

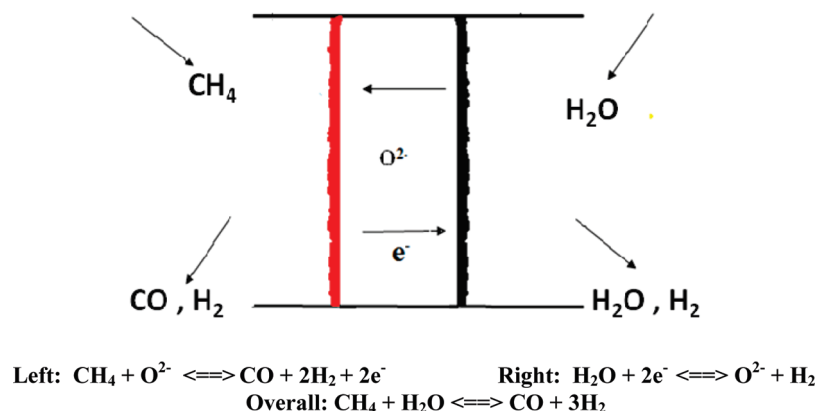


Figure 7. Schematic diagram of a SECR used for steam splitting and methane conversion to carbon monoxide (CO) and hydrogen (H_2).

H⁺ conductors, for which the transference number may deviate considerably from unity.^{8,9} Hence, SEP is essentially limited to O²⁻ conductors. All the SEP works listed in Table 1 report measurements of the thermodynamic activity of adsorbed oxygen.

(b) The dominant charge-transfer reaction at the gas–electrode–electrolyte interline is the conversion of O²⁻ ions to atomically adsorbed oxygen. Furthermore, this reaction must be in thermodynamic equilibrium. The last assumption may not hold on the catalyst–electrode side, since other adsorbed species may react with O²⁻. In that case, a mixed potential is measured and eq 10 cannot be used. Nevertheless, it has been shown that, even when the above assumptions are not met, the measured emf of the cell (*E*) reflects the difference between the working function of the working electrode and the reference electrode.¹⁰ Thus, although in that case, the measured voltage cannot be associated with any entity on the molecular level, SECRs can still operate as work function probes.

3.3. Electrochemical Promotion of Catalytic Reactions. Solid electrolytes can be used to promote catalytic reaction rates electrochemically. As already mentioned, when gaseous O₂ is introduced together with reactant A and the circuit is open, the device described by Figure 1 can operate as a catalytic reactor. When the circuit is closed, the cell can additionally function as an electrochemical oxygen “pump”. A current *I* corresponds to *I*/(4*F*) moles of oxygen per second being transported through the solid electrolyte. If *r*_o and *r* are the open- and closed-circuit reaction rates, respectively (expressed in terms of the number of moles of oxygen/s), one can easily calculate the value of the dimensionless numbers Λ and ρ , which are defined as

$$\Lambda = \frac{\Delta r}{I/(4F)} = \frac{r - r_o}{I/(4F)} \quad (11)$$

and

$$\rho = \frac{r}{r_o} \quad (12)$$

If $\Lambda = 1$, the effect is Faradaic, i.e., the increase in reaction rate equals the rate of ion transport through the electrolyte. In 1981, it was reported⁷³ that the oxidation of ethylene on silver exhibited a strong non-Faradaic effect (i.e., the values of both Λ and ρ could exceed unity). Since then, the phenomenon of non-Faradaic electrochemical modification of catalytic activity (NEMCA), which is also called the electrochemical promotion of catalysis (EPOC), has been observed in numerous catalytic reaction systems.^{10,74} Today, more than 70 catalytic reaction systems have been found to exhibit NEMCA, including oxidations, reductions, hydrogenations, decompositions, and isomerizations. These reactions have been electrochemically promoted on Pt, Ag, Pd, Au, Rh, Ni, Fe, IrO₂, and RuO₂ catalysts deposited on O²⁻, H⁺, Na⁺, K⁺, Pb²⁺, F⁻, and mixed (ionic–electronic) conductors, using either double- or single-chamber SECRs. Λ values as high as 3×10^5 and ρ values as high as 1400 have been reported.⁷⁴ Also, note that the dimensionless parameter ρ is essentially the ratio of two reaction rates, *r* and *r*_o (i.e., the closed- and open-circuit reaction rates, respectively). Thus, if two reactions take place (e.g., R1 and R2), then two ρ values will be observed: ρ_1 and ρ_2 , respectively. Because of the nature of electrochemical promotion, it is highly unlikely that ρ_1 will be equal to ρ_2 . Therefore, the individual

Table 1. Solid Electrolyte Potentiometry (SEP) Studies

| reactants and products | working electrodes | reference(s) |
|--|--|---------------|
| SO ₂ , O ₂ ⇒ SO ₃ | Pt, Au, Ag | 22 |
| CO, O ₂ ⇒ CO ₂ | Pt, Ag, Fe, La-Sr-Mn oxide, Cu–Cu ₂ O–CuO | 23–36 |
| H ₂ , O ₂ ⇒ H ₂ O | Ni, Ag, Au, Pt, Cu–Cu ₂ O–CuO | 37–43 |
| NO ⇒ N ₂ , O ₂ | Pt, Pd | 44, 45 |
| NO, NH ₃ , O ₂ ⇒ N ₂ , H ₂ O | Pt | 46 |
| CH ₄ , O ₂ ⇒ CO, H ₂ , CO ₂ , H ₂ O | Pt, Au, Ag, Pd, Ni | 42, 43, 47–50 |
| C ₂ H ₄ O, O ₂ ⇒ CO ₂ , H ₂ O | Ag | 51 |
| C ₂ H ₄ , O ₂ ⇒ CO ₂ , H ₂ O | Ag, Pt | 38, 52–55 |
| C ₃ H ₆ , O ₂ ⇒ CO ₂ , H ₂ O | Ag, Pt | 56–58 |
| C ₃ H ₆ O, O ₂ ⇒ CO ₂ , H ₂ O | Ag | 59, 60 |
| C ₃ H ₆ , O ₂ ⇒ C ₃ H ₄ O, H ₂ O | Cu–Cu ₂ O–CuO, Fe ₂ O ₃ –Sb ₂ O ₄ | 61, 62 |
| C ₃ H ₈ , O ₂ ⇒ CO ₂ , H ₂ O | Pd, Pt, Ag | 57, 58, 63–65 |
| C ₃ H ₄ O, O ₂ ⇒ C ₃ H ₃ OOH | Mo ₁₂ V ₃ Cu ₂₂ O ₄₄ | 66 |
| C ₃ H ₈ , O ₂ ⇒ C ₃ H ₆ , H ₂ O | Mg ₂ V ₂ O ₇ | 67 |

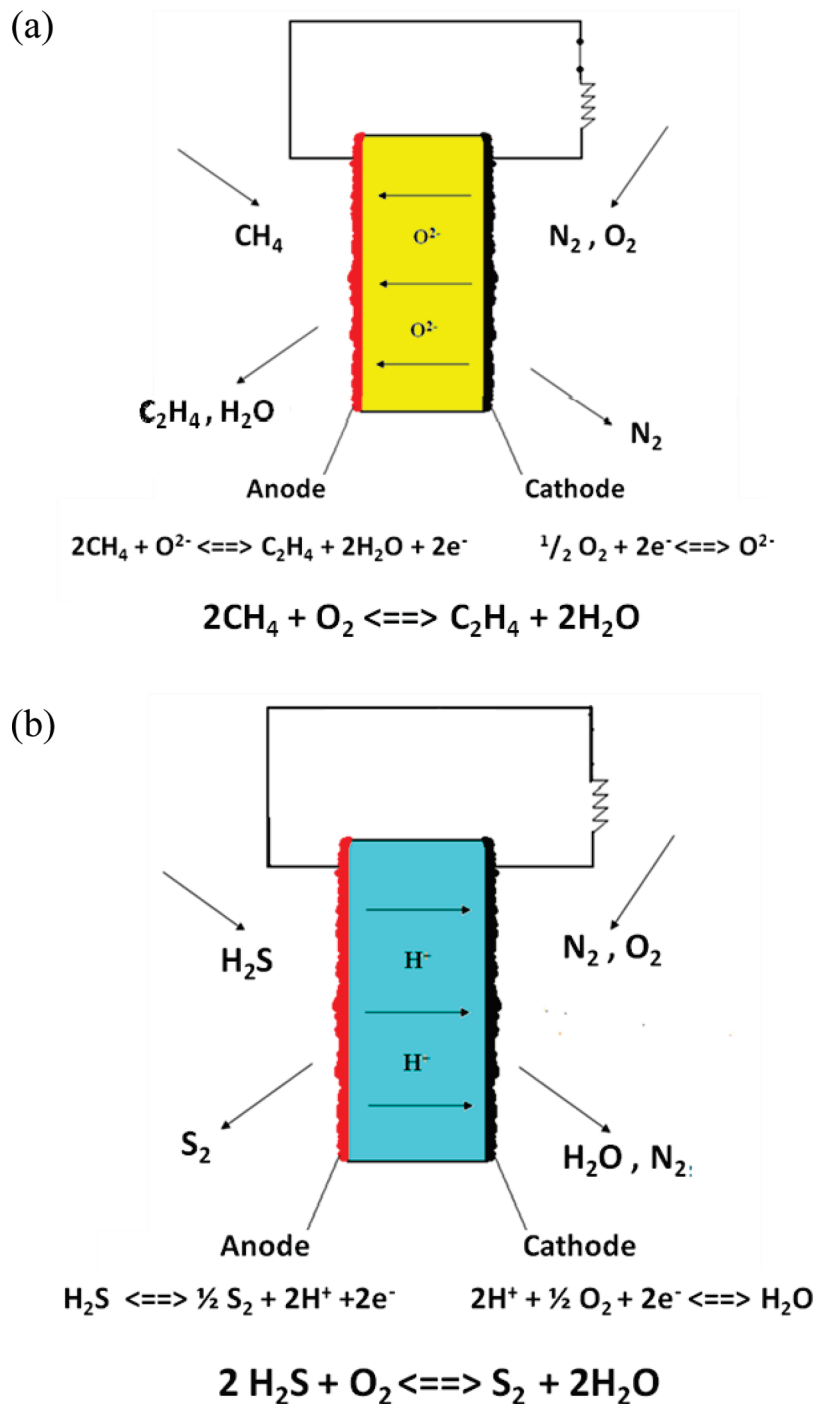


Figure 8. Schematic diagram of SECRs used for chemical cogeneration: (a) conversion of methane to ethylene and (b) conversion of hydrogen sulfide to sulfur.

reaction rates as well as the intrinsic selectivity will be affected by “pumping” ions to or from the catalyst surface.

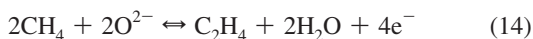
According to the majority of experimental findings and theoretical calculations, this phenomenon is due to the introduction of charged species from the solid electrolyte to the catalyst/gas interface. An overall neutral double layer is thus formed. This double layer, in turn, alters the work function of the catalyst surface and the chemisorptive bond strength of the reacting species, resulting in a reversible alteration of the reaction rate.⁷⁴ Several comprehensive reviews of this subject have already been published;^{6,10,74} the reader can refer to this literature for more details. NEMCA can have a significant impact on catalytic research, because (a) the surface modification can be monitored electrochemically (i.e., unlike gas-phase or solid surface pro-

motors, solid electrolytes offer dynamic manipulation of the catalyst properties); (b) if a strong NEMCA effect is observed, the product yield or selectivity can be altered by imposing an ionic flux orders of magnitude lower than the stoichiometrically required; and (c) the catalytic activity or selectivity can be modified using the single-chamber cell (see Figure 3), which does not require the reactants to be separated.

3.4. Chemical Cogeneration. SECRs offer the advantage of producing both electrical energy and useful chemicals. This is schematically shown in Figures 8a and 8b. In Figure 8a, methane flows over the anode while air flows over the cathode of an O²⁻ cell.^{75–78} At the cathode, oxygen is converted to O²⁻ ions:



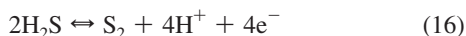
At the anode, methane is converted to ethylene (C_2H_4):



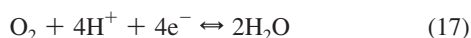
which makes the overall cell reaction



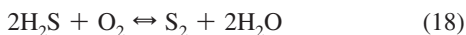
At the same time, the spontaneous flow of O^{2-} from the cathode to the anode closes the electrical circuit and converts chemical energy directly to electrical energy. Similarly, in the H^+ SECR of Figure 8b,⁷⁹ H_2S is converted to S_2 and protons at the anode:



while, at the cathode, protons react with oxygen to produce steam,



resulting in the following overall reaction:



The concept of simultaneous production of useful chemicals and electricity in SECRs, which is known as chemical cogeneration, was first demonstrated in 1980 for the production of NO, using ammonia as the fuel.^{80–82} A list of chemical cogeneration studies is shown in Table 2. The left-hand column shows the type of ion conductor used. The next column shows the material used as the working electrode (catalyst). The last two columns show the reactants and products of each catalytic system studied and the corresponding reference source(s), respectively.

4. Catalytic Studies in SECRs

The catalytic reaction systems that have been studied in SECRs are presented in tables that include works published before the spring of 2009. The most important findings for each reaction are discussed briefly. Each table is divided in two sections. The first contains studies in which ionic conductors (O^{2-} , H^+) were used. The left-hand column shows the type of ion conductor used. The next column shows the material used as working electrode (catalyst). The last two columns show the reactants and products of each catalytic system studied and the corresponding reference source(s), respectively. The second section contains studies with mixed ($\text{O}^{2-}-\text{e}^-$) conductors. Similarly, the left-hand column shows the conducting species. The next column shows the material used as a catalyst for the reaction under study. The last two columns are the same as those in the first section.

4.1. Decomposition and Reduction of NO_x . A list of studies of the decomposition of NO_x conducted in SECRs is shown in Table 3. Nitrogen oxides appear in the auto exhaust emissions, together with CO and unburned hydrocarbons. Therefore, there has been a great demand for an effective purification of the exhaust gases. In addition to the classical methods of catalytic promotion, SECRs were used to study and enhance the decomposition of NO_x by “pumping” oxygen away from the catalyst. Furthermore, SECRs were used to electrochemically promote the catalytic reduction of NO_x by hydrocarbons (NEMCA).

The decomposition of NO was among the earliest SECR studies (if not the first). In 1975, Pancharatnam, Huggins, and Mason studied the effect of oxygen pumping on the rate of decomposition of NO in an O^{2-} SECR using platinum or gold as the working electrodes.¹²¹ The authors found that, when oxygen was “pumped” away from the catalyst, the rate of NO decomposition could exceed the open-circuit rate by 3 orders of magnitude. Gür and Huggins continued and extended the work and observed even greater rate enhancements upon electrochemical oxygen pumping.^{120,122}

After a period of diminished interest, research in the area (of electrochemical reduction of NO_x) was revived and has remained intensive since the early 1990s. As shown in Table 3, numerous materials have been tested as working electrodes (catalysts). In addition to noble metals such as platinum, gold, palladium, and rhodium, transition-metal oxides, mixed oxides, and mixtures of a metal with an oxide were tested. In the latter case, the metal phase was added to increase the electric conductivity of the catalyst.

The need for an effective control of hazardous auto exhaust emissions led several research groups to use O^{2-} SECRs for the reaction of NO_x with reducing compounds such as CO,^{130,139,142} CH_4 ,^{135–137} C_2H_4 ,^{125,131,146} C_3H_6 ,^{58,127–129,140,141,143–145,171,172,359} and NH_3 .^{46,158} In most of the above works, NO_x was fed at the cathode, together with the reducing compound, and the effect of O^{2-} pumping on the reaction rate was studied. The highest NEMCA effect was observed during the reduction of NO by C_3H_6 on Rh when the rate enhancement factor (ρ) reached values as high as 150.¹⁴³

Hibino and co-workers tested the possibility of simultaneous reduction of NO and oxidation of CH_4 either in a single- or a double-chamber cell.^{135–137} In the single-chamber SECR, the reaction was conducted successfully under closed-circuit conditions at temperatures as low as 400 °C.¹³⁷ In the double-chamber SECR and under closed-circuit conditions, NO was reduced to N_2 at the cathode and CH_4 was oxidized to CO and CO_2 at both the anode and the cathode.¹³⁶ Iwahara and co-workers^{16–18} used H^+ conductors for the reduction of NO, as already shown in Figure 5. Steam is electrolyzed at the anode, and the produced protons reduced NO to N_2 .^{16–18}

In addition to O^{2-} and H^+ , the possibility of NEMCA enhancement of the reaction rate was investigated utilizing $\text{Na}^{+174–185}$ and $\text{K}^{+172,178,186–190}$ conductors. The electrochemical promotion effect varied considerably and depended on the working electrode and on the reducing agent used. During the reaction of NO with H_2 , and upon pumping Na^+ ions to the platinum surface, a strong NEMCA effect was observed with Λ values as large as 10^5 and ρ values as large as 30.¹⁷⁴

Valverde and co-workers¹⁸⁹ proposed and tested a SECR as a NO_x storage/reduction catalyst. The storage device consisted of a platinum electrode deposited on K- β - Al_2O_3 , which is a K^+ conductor. Under negative polarization, NO_x was stored in the form of potassium nitrates. Under positive polarization, the stored nitrates were desorbed and reduced to N_2 and the catalyst was regenerated.

4.2. Methane Conversion to C_2 Hydrocarbons. The conversion of methane to ethane and ethylene (C_2 hydrocarbons) is the reaction that is studied most thoroughly and intensively in SECRs. As shown in Table 4, oxygen ion (O^{2-}), proton (H^+), and mixed ($\text{O}^{2-}-\text{e}^-$, H^+-e^-) conducting cells have been tested to maximize the conversion of methane to C_2 compounds.

In the presence of a variety of catalysts, methane and oxygen react to produce C_2 compounds, with CO and CO_2 being the major carbon-containing byproducts. The C_2 selectivity de-

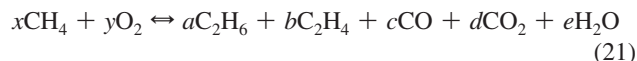
creases with conversion; therefore, the C₂ yield (the product of C₂ selectivity times conversion) remains quite low (<25%). The type and state of oxygen used are crucially important, with regard to achieving high yields. Hence, the motivation for the first SECR studies of methane coupling in the mid-1980s^{191,199,200} was primarily based on the use of O²⁻ ions rather gaseous O₂:

At the cathode:



At the anode:

Overall:



As Table 4 shows, a large variety of catalysts has been tested since then. It was found that, under certain conditions, the use

Table 2. Studies of Chemical Cogeneration

| conducting ions | working electrode | reactants and products | references |
|---------------------------------|--|--|-------------|
| O ²⁻ | Pt | NH ₃ , O ₂ ⇒ NO, H ₂ O | 80–84 |
| O ²⁻ | Pt | CH ₄ , O ₂ ⇒ CO, H ₂ | 85–89 |
| O ²⁻ | Pt | C, O ₂ ⇒ CO, CO ₂ | 90–92 |
| O ²⁻ | Pt | H ₂ S, O ₂ ⇒ S, SO ₂ , H ₂ O | 79, 93–95 |
| O ²⁻ | Pt | ethylbenzene, O ₂ ⇒ styrene, H ₂ O | 96, 97 |
| O ²⁻ | Pt | butene, O ₂ ⇒ butadiene, H ₂ O | 98 |
| O ²⁻ | Pt (Rh) | CH ₄ , NH ₃ ⇒ HCN, H ₂ O, CO, H ₂ | 99–101, 119 |
| O ²⁻ | mixed oxides | NH ₃ , O ₂ ⇒ NO, H ₂ O | 80–84 |
| O ²⁻ | Pd | CH ₄ , O ₂ ⇒ CO, H ₂ | 85–88 |
| O ²⁻ | Fe | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO ₂ | 102 |
| O ²⁻ | Fe–C | C, O ₂ ⇒ CO | 103 |
| O ²⁻ | Ag–Bi ₂ O ₃ | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO ₂ | 102 |
| O ²⁻ | YBa ₂ Cu ₃ O _x | CH ₄ , O ₂ ⇒ CH ₃ OH, CH ₂ O, CO, CO ₂ | 104 |
| O ²⁻ | Ni | CH ₄ , O ₂ ⇒ CO, H ₂ | 105, 106 |
| O ²⁻ | Ni-YSZ | CH ₄ , O ₂ ⇒ CO, H ₂ , (H ₂ O, CO ₂) | 107 |
| O ²⁻ | Au | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO ₂ | 75 |
| O ²⁻ | Au oxides | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO ₂ | 75 |
| O ²⁻ | Ag | CH ₃ OH, O ₂ ⇒ CH ₂ O, CO, CO ₂ | 108 |
| O ²⁻ | Ag/Sr/La ₂ O ₃ –Bi ₂ O ₃ | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO ₂ | 77 |
| O ²⁻ | Ag/Mo–Ni sulfides | H ₂ S, O ₂ ⇒ S ₂ , SO ₂ , H ₂ O | 109 |
| O ²⁻ | transition-metal carbides | C, O ₂ ⇒ CO | 110 |
| O ²⁻ | thiospinels | H ₂ S, O ₂ ⇒ S, SO ₂ , H ₂ O | 79, 93–95 |
| O ²⁻ | La _{0.7} Sr _{0.3} VO ₃ | CH ₄ , H ₂ S, O ₂ ⇒ S, CS ₂ , SO ₂ , CO ₂ , H ₂ O | 111 |
| O ²⁻ | LaAlO | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO _x | 76, 78 |
| O ²⁻ | MoV _{0.3} Te _{0.17} Nb _{0.12} O | C ₃ H ₈ , O ₂ ⇒ acrylic acid, CO ₂ , H ₂ O | 112 |
| H ⁺ | Pt | C ₂ H ₆ , O ₂ ⇒ C ₂ H ₄ , H ₂ O | 113 |
| H ⁺ | Pt | H ₂ S, O ₂ ⇒ S, SO ₂ , H ₂ O | 79, 93–95 |
| H ⁺ | Pt | CH ₄ , H ₂ O, O ₂ ⇒ CO, H ₂ | 114 |
| H ⁺ | Pt | C ₂ –C ₄ , O ₂ ⇒ C ₆ –C ₈ hydrocarbons, CO ₂ , H ₂ O | 116 also |
| H ⁺ | thiospinels | H ₂ S, O ₂ ⇒ S, SO ₂ , H ₂ O | 79, 93–95 |
| H ⁺ | Ag/Li ₂ SO ₄ | H ₂ S, O ₂ ⇒ S ₂ , SO ₂ , H ₂ O | 117 |
| H ⁺ | metal sulfides | H ₂ S, O ₂ ⇒ S ₂ , H ₂ O | 118 |
| O ²⁻ –H ⁺ | Ni | CH ₄ , H ₂ O, O ₂ ⇒ CO, H ₂ | 115 |

Table 3. Decomposition and Reduction of NO_x

| Ionic Conducting SECRs | | | |
|-------------------------|--|---|-------------------|
| conducting ions/species | working electrode | reactants and products | reference(s) |
| O ²⁻ | Pt | NO ⇒ N ₂ , O ₂ | 44, 120–126 |
| O ²⁻ | Pt | NO, NH ₃ ⇒ N ₂ , O ₂ | 46 |
| O ²⁻ | Pt | NO, C ₂ H ₄ ⇒ N ₂ , CO ₂ , H ₂ O | 125 |
| O ²⁻ | Pt | NO, C ₃ H ₆ ⇒ N ₂ , CO ₂ , H ₂ O | 127–129 |
| O ²⁻ | Pt | NO, C ₃ H ₆ , C ₃ H ₈ ⇒ N ₂ , CO ₂ , H ₂ O | 58 |
| O ²⁻ | Pt | N ₂ O, CO ⇒ N ₂ , CO ₂ | 130 |
| O ²⁻ | Pt–Rh | NO, C ₂ H ₄ ⇒ N ₂ , CO ₂ , H ₂ O | 131 |
| O ²⁻ | Pt–Rh | NO, C ₃ H ₆ ⇒ N ₂ , CO ₂ , H ₂ O | 129 |
| O ²⁻ | Au | NO ⇒ N ₂ , O ₂ | 121, 124, 132 |
| O ²⁻ | Pd | NO ⇒ N ₂ , O ₂ | 45, 124, 133, 134 |
| O ²⁻ | Pd | NO, CH ₄ ⇒ N ₂ , CO ₂ , H ₂ O | 135–137 |
| O ²⁻ | Pd | NO, N ₂ O, CO ⇒ N ₂ , CO ₂ | 125, 138 |
| O ²⁻ | Pd | NO, CO ⇒ N ₂ O, N ₂ , CO ₂ | 139 |
| O ²⁻ | Pd | NO, C ₃ H ₆ ⇒ N ₂ , CO ₂ , H ₂ O | 140, 141 |
| O ²⁻ | Rh | NO ⇒ N ₂ , O ₂ | 124 |
| O ²⁻ | Rh | NO, CO ⇒ N ₂ , CO ₂ | 142 |
| O ²⁻ | Rh | NO, C ₂ H ₄ ⇒ N ₂ , CO ₂ , H ₂ O | 129, 143–145 |
| O ²⁻ | Rh | NO, C ₃ H ₆ ⇒ N ₂ , CO ₂ , H ₂ O | 146 |
| O ²⁻ | Rh–Ag | NO, C ₃ H ₆ ⇒ N ₂ , CO ₂ , H ₂ O | 147 |
| O ²⁻ | RuO ₂ –Ag, RuO ₂ –Pd | NO ⇒ N ₂ , O ₂ | 134, 148 |
| O ²⁻ | (NiO–YSZ)/Pt | NO _x ⇒ N ₂ , O ₂ | 149–155 |
| O ²⁻ | (NiO–CeGdO)/Pt | NO ⇒ N ₂ , O ₂ | 156 |
| O ²⁻ | Cu/Cu ₂ O/CuO | NO ⇒ N ₂ , O ₂ | 157 |
| O ²⁻ | V ₂ O ₅ | NO, NH ₃ ⇒ N ₂ , H ₂ O | 158 |
| O ²⁻ | transition-metal oxides | NO ⇒ N ₂ , O ₂ | 159 |
| O ²⁻ | perovskites, mixed oxides | NO ⇒ N ₂ , O ₂ | 153, 160 |
| O ²⁻ | (La _{0.8} Sr _{0.2}) _{0.95} MnO ₃ | NO ⇒ N ₂ , O ₂ | 161 |
| O ²⁻ | La _{0.3} Sr _{0.7} FeO ₃ | NO ₂ ⇒ N ₂ , O ₂ | 162 |
| O ²⁻ | La _{0.6} Sr _{0.4} Fe _{1-x} Mn _x O ₃ | NO ⇒ N ₂ , O ₂ | 163 |
| O ²⁻ | LaCoO ₃ , LaMnO ₃ | NO ⇒ N ₂ , O ₂ | 164, 165 |

Table 3. Continued

| Ionic Conducting SECRs | | | |
|------------------------------------|--|---|------------------|
| conducting ions/species | working electrode | reactants and products | reference(s) |
| O^{2-} | BaCo(Al,Ga) ₁₁ O ₁₉ -Pt | $NO \Rightarrow N_2, O_2$ | 166 |
| O^{2-} | La _{0.6} Sr _{0.4} Co _{0.2} Fe _{0.8} O ₃ | $NO \Rightarrow N_2, O_2$ | 167, 168 |
| O^{2-} | (La ₂ Sn ₂ O ₇ -YSZ)/Pt | $NO \Rightarrow N_2, O_2$ | 169 |
| O^{2-} | Ir | $NO \Rightarrow N_2, O_2$ | 170 |
| O^{2-} | Ir | $NO, C_3H_6 \Rightarrow N_2, CO_2, H_2O$ | 171, 172 |
| Na^+ | Pt | $NO, H_2 \Rightarrow N_2, H_2O$ | 174 |
| Na^+ | Pt | $NO, CO \Rightarrow N_2, CO_2$ | 175, 176 |
| Na^+ | Cu | $NO, CO, C_3H_6 \Rightarrow N_2, CO_2$ | 177–179 |
| Na^+ | Pt | $NO, CO, C_3H_6 \Rightarrow N_2, H_2O, CO_2$ | 178, 180–182 |
| Na^+ | Pd | $NO, C_3H_6 \Rightarrow N_2, H_2O, CO_2$ | 183 |
| Na^+ | Rh | $NO, CO, C_3H_6 \Rightarrow N_2, H_2O, CO_2$ | 178, 184, 185 |
| K^+ | Rh | $NO, CO, C_3H_6 \Rightarrow N_2, H_2O, CO_2$ | 178 |
| K^+ | Pt | $NO, CO, C_3H_6 \Rightarrow N_2, H_2O, CO_2$ | 178, 186–188 |
| K^+ | Pt | $NO, K/Al_2O_3 \Rightarrow N_2, O_2, KNO_3$ | 189 |
| K^+ | Pt | $N_2O, H_2O, C_3H_6 \Rightarrow N_2, H_2O, CO_2$ | 186, 187, 190 |
| K^+ | Ir | $NO, C_3H_6 \Rightarrow N_2, H_2O, CO_2$ | 172 |
| K^+ | Cu | $NO, CO, C_3H_6 \Rightarrow N_2, H_2O, CO_2$ | 178 |
| H^+ | Pt/Ba/Al ₂ O ₃ | $NO, H_2O \Rightarrow N_2, O_2$ | 16, 18 |
| H^+ | Pt-Sr/Al ₂ O ₃ | $NO, H_2O \Rightarrow N_2, O_2$ | 17 |
| Mixed Conducting SECRs | | | |
| conducting species $O^{2-}-e^-$ | catalyst Pt | reactants and products $NO \Rightarrow N_2, O_2$ | reference 173 |

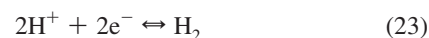
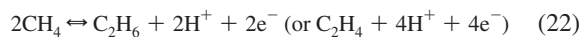
of ionic oxygen improved the catalytic properties of the electrodes but not to an impressive level. Several explanations were given⁹ for this rather moderate effect:

(a) Because most C₂ catalysts are very poor electrical conductors, the usual solution was to prepare an anodic electrode by mixing a metal with a metal oxide. When O²⁻ ions reach the electrode–electrolyte–gas boundary, however, methane can react with oxygen not only on the oxide but also on the metal surface; and metals are poorly selective catalysts.

(b) The NEMCA phenomenon by which either the reaction rate or the selectivity to the desired product could be substantially enhanced was much less pronounced with this particular reaction system. This is partly due to the relatively higher temperatures required to activate methane; the lower the temperature, the better the NEMCA results (higher values of Λ and ρ) that are attained.^{9,10} Another unfortunate peculiarity

with this reaction is that it involves both surface and gas-phase reaction steps. Electrochemical oxygen pumping can modify surface properties, not gas-phase reactions. Hence, it was reasonable to observe a weaker effect, compared to studies where the reaction is entirely catalytic.

The discovery of high-temperature solid-state proton conductors⁸ directed various research groups into a different route, based on methane dimerization via dehydrogenation rather than partial oxidation. The following reactions are assumed to occur in these SECRs:



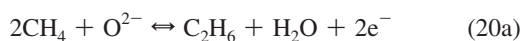
with the overall reaction being

Table 4. Methane Conversion to C₂ Hydrocarbons

| Ionic Conducting SECRs | | | |
|------------------------|--|--|----------------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| O ²⁻ | Ag | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 92, 102, 191–198 |
| O ²⁻ | Bi ₂ O ₃ –Ag | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 102, 199–202 |
| O ²⁻ | Cu | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 102, 195, 201, 202 |
| O ²⁻ | Fe | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 102 |
| O ²⁻ | 0.8 Ag–0.2 Pd | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 195 |
| O ²⁻ | Ni | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 195 |
| O ²⁻ | Pt | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 50, 195–197, 201–203 |
| O ²⁻ | LaCrO ₃ | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 195 |
| O ²⁻ | LaAlO | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 76, 78 |
| O ²⁻ | Li/MgO–Ag | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 191, 201, 202 |
| O ²⁻ | KF/Au, BaCO ₃ /Au, NaCl/Au, YSZ–Au Ho ₂ O ₃ /Au, Sm ₂ O ₃ /Au, Bi ₂ O ₃ /Au | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 75, 206 |
| O ²⁻ | Pt/Sm ₂ O ₃ /La _{0.83} Sr _{0.1} MnO ₃ | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 204 |
| O ²⁻ | Bi ₂ O ₃ –Pr ₆ O ₁₁ | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 205 |
| O ²⁻ | Bi ₂ O ₃ –Pt, Sm ₂ O ₃ –Ag, Mo–Ag | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 201, 202 |
| O ²⁻ | LiCl/NiO–Au | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 207 |
| O ²⁻ | LiNiO ₂ –Au | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 208 |
| O ²⁻ | various perovskites | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 209, 210 |
| O ²⁻ | MnO _x | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 211, 212 |
| O ²⁻ | 80% Ag, 20% Sm ₂ O ₃ (CaO) | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 110, 213 |
| O ²⁻ | Au–SrCeO ₃ | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 214 |
| O ²⁻ | La–Sr–Co–Fe perovskites | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 215, 216 |
| O ²⁻ | Ag(Mn–Na–K) | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 198 |
| O ²⁻ | Ag(Mn/Na ₂ WO ₄ /SiO ₂) | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 198 |
| O ²⁻ | Ag(Mn/K ₂ WO ₄ /SiO ₂) | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 198 |
| O ²⁻ | various perovskites | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 218 |
| O ²⁻ | LSM | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 219 |
| H ⁺ | Ag | CH ₄ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ | 214, 248 |
| H ⁺ | Ag | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, H ₂ | 242, 249, 250 |
| H ⁺ | Pt | CH ₄ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ | 251, 252 |
| H ⁺ | Pt | CH ₄ , H ₂ O, O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO _x | 114 |
| H ⁺ | La _{0.6} Sr _{0.4} MnO ₃ | CH ₄ , H ₂ O, O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO _x | 253 |
| H ⁺ | SrTi _{0.4} Mg _{0.6} O ₃ | CH ₄ , H ₂ O, O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO _x | 254 |
| H ⁺ | | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, H ₂ | 255 |
| H ⁺ | YDC–Ca ₃ (PO ₄) ₂ –K ₃ PO ₄ | CH ₄ ⇒ C ₂ H ₄ , C ₂ H ₆ | 256 |
| Li+ | Au | CH ₄ , O ₂ ⇒ C ₂ H ₄ , C ₂ H ₆ , H ₂ O, CO, CO ₂ | 259, 260 |

Table 4. Continued

| Mixed Conducting SECRs | | | |
|------------------------|--|--|------------------|
| conducting species | catalyst | reactants and products | reference(s) |
| $H^+ - e^-$ | Pt | $CH_4, H_2O, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO_x$ | 258 |
| $H^+ - e^-$ | $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O$ | 257 |
| $H^+ - e^- - O^{2-}$ | Ag | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 248 |
| $O^{2-} - e^-$ | MgO–PbO | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 243 |
| $O^{2-} - e^-$ | $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-\alpha}$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 226, 244–247 |
| $O^{2-} - e^-$ | Pt | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 220 |
| $O^{2-} - e^-$ | Pt/MgO | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 221 |
| $O^{2-} - e^-$ | $Pt/La_2Ni_{0.9}Co_{0.1}O_{4+\delta}$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 220 |
| $O^{2-} - e^-$ | La–Sr–Co–Fe perovskites | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 215–217, 222–227 |
| $O^{2-} - e^-$ | La–Ba–Co–Fe perovskite | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 222, 228 |
| $O^{2-} - e^-$ | $MaNa_dMg_bZr_cO_x$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 229, 230 |
| $O^{2-} - e^-$ | Li/MgO | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 229, 230 |
| $O^{2-} - e^-$ | $LiLaNiO/\gamma-Al_2O_3$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 231 |
| $O^{2-} - e^-$ | $La_{0.8}Sr_{0.2}CoO_3$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 232, 233 |
| $O^{2-} - e^-$ | $SrCo_{0.8}Fe_{0.2}O_3$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 232, 233 |
| $O^{2-} - e^-$ | $SrTi_{0.9}Li_{0.1}O_3$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 234 |
| $O^{2-} - e^-$ | $BaCe_{0.8}Gd_{0.2}O_3$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 235, 236 |
| $O^{2-} - e^-$ | $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 237 |
| $O^{2-} - e^-$ | $Y_2O_3-Bi_2O_3$ | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 238–240 |
| $O^{2-} - e^-$ | La/MgO | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 241 |
| $O^{2-} - e^-$ | La–Sr/CaO | $CH_4, O_2 \Rightarrow C_2H_4, C_2H_6, H_2O, CO, CO_2$ | 237 |



The use of proton conductors did solve the problem of the production of undesirable oxygenates (CO, CO₂); but, again, the C₂ yields were not impressive either. One of the reasons for this is that, without oxygen, the rate of methane pyrolysis ($CH_4 \rightleftharpoons C + 2H_2$) also increases considerably.

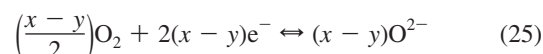
The use of mixed ($O^{2-} - e^-$) conducting SECRs eliminates the need for metal electrodes because there is no requirement for closed electrical circuit. Thus, working with this type of reactor, several groups reported yields exceeding 10%. Remarkably higher yields (i.e., 25%–30%) were reported in the patent literature.^{217,229,230}

Hibino, Masegi, and Iwahara²⁵⁹ used a single-chamber cell with a Li⁺ ion conductor and Au electrodes, and they tested the operation under alternating current (AC) conditions instead of direct current (DC) conditions. At an AC voltage of 3 V, the conversion of methane was twice that obtained under open-circuit conditions, while the corresponding C₂ selectivity was 50% higher. The authors also studied the effect of frequency at a constant AC voltage of 3 V. A volcano diagram was produced with the maximum enhancement ratio (ρ) close to 3.5 at a

frequency of 1 Hz, when ρ was plotted versus the imposed frequency. The proposed interpretation assumed that the rate enhancement is associated with accumulation of Li⁺ cations on the electrode surface. This, in turn, was associated with the increase in the rate of methyl radicals from methane, which is the crucial step for methane conversion to C₂ hydrocarbons. Later, Hibino et al. repeated and extended these experiments in both single-chamber and double-chamber cells.²⁶⁰ The idea to vary the frequency to maximize the formation rate of the desired product adds to the existing electrochemical tools and gives new alternatives to both study and influence catalytic reaction rates.

4.3. Methane Conversion to Synthesis Gas. Table 5 contains studies for the conversion of methane to CO and H₂ in SECRs. Similar to the conversion to C₂ hydrocarbons, the electrochemical production of syngas from methane was first tested in O^{2-} SECRs. To avoid carbon formation, methane–steam mixtures, instead of pure methane, were fed at the anode and were oxidized by electrochemically supplied oxygen, according to the following reactions:

Cathode:



Anode:

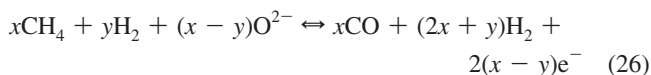
Table 5. Methane Conversion to Synthesis Gas^a

| Ionic Conducting SECRs | | | |
|------------------------|---|---------------------------------------|------------------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| O^{2-} | Pt | $CH_4, O_2 \Rightarrow CO, H_2$ | 85, 88, 251, 261–268 |
| O^{2-} | Pt | $CH_4, O_2, H_2O \Rightarrow CO, H_2$ | 269 |
| O^{2-} | Pt-CeO ₃ | $CH_4, O_2 \Rightarrow CO, H_2$ | 268 |
| O^{2-} | PtBi | $CH_4, O_2 \Rightarrow CO, H_2$ | 262 |
| O^{2-} | PtBi cermets | $CH_4, O_2 \Rightarrow CO, H_2$ | 262 |
| O^{2-} | Ag | $CH_4, O_2 \Rightarrow CO, H_2$ | 268 |
| O^{2-} | C | $CH_4, O_2 \Rightarrow CO, H_2$ | 270, 271 |
| O^{2-} | Ni | $CH_4, O_2 \Rightarrow CO, H_2$ | 263, 265, 268, 272–276 |
| O^{2-} | Ni | $CH_4, O_2, H_2O \Rightarrow CO, H_2$ | 269 |
| O^{2-} | Ni | $CH_4, H_2O \Rightarrow CO, H_2$ | 277 |
| O^{2-} | Ni/YSZ | $CH_4, O_2 \Rightarrow CO, H_2$ | 262 |
| O^{2-} | Ni/YSZ | $CH_4, H_2O \Rightarrow CO, H_2$ | 278, 279 |
| O^{2-} | Ni-YSZ cermet | $CH_4, O_2 \Rightarrow CO, H_2$ | 272, 277, 280–283 |
| O^{2-} | Ni-YSZ cermet | $CH_4, H_2O \Rightarrow CO, H_2$ | 277, 284, 285 |
| O^{2-} | NiAu/YSZ | $CH_4, O_2 \Rightarrow CO, H_2$ | 286 |
| O^{2-} | NiAu/YSZ | $CH_4, O_2, H_2O \Rightarrow CO, H_2$ | 287, 288 |
| O^{2-} | Ni(Pt–Ni/Al ₂ O ₃) | $CH_4, O_2 \Rightarrow CO, H_2$ | 105, 106 |
| O^{2-} | Ni/Al ₂ O ₃ | $CH_4, O_2 \Rightarrow CO, H_2$ | 289, 290 |
| O^{2-} | Ni/ γ -Al ₂ O ₃ | $CH_4, O_2 \Rightarrow CO, H_2$ | 291–293 |
| O^{2-} | Ni-SDC | $CH_4, O_2 \Rightarrow CO, H_2$ | 294 |
| O^{2-} | NiO-YSZ | $CH_4, O_2 \Rightarrow CO, H_2$ | 296, 297 |
| O^{2-} | Ni/Ca _{0.8} Sr _{0.2} TiO ₃ | $CH_4, O_2 \Rightarrow CO, H_2$ | 298 |
| O^{2-} | Ni-ZrO ₂ –CeO ₂ | $CH_4, H_2O \Rightarrow CO, H_2$ | 299 |
| O^{2-} | Fe | $CH_4, O_2 \Rightarrow CO, H_2$ | 263, 300–302 |
| O^{2-} | Fe | $CH_4, O_2, H_2O \Rightarrow CO, H_2$ | 269 |
| O^{2-} | VC | $CH_4, O_2 \Rightarrow CO, H_2$ | 263 |
| O^{2-} | VC | $CH_4, O_2, H_2O \Rightarrow CO, H_2$ | 269 |
| O^{2-} | LaCaCrO ₃ | $CH_4, O_2 \Rightarrow CO, H_2$ | 263, 303 |
| O^{2-} | LaCaCrO ₃ | $CH_4, O_2, H_2O \Rightarrow CO, H_2$ | 269 |
| O^{2-} | La _{1.8} Al _{0.2} O ₃ | $CH_4, O_2 \Rightarrow CO, H_2$ | 304 |

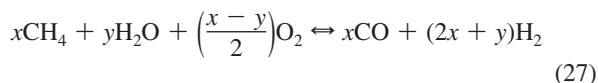
Table 5. Continued

| Ionic Conducting SECRs | | | |
|------------------------|---|---------------------------------------|------------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| O^{2-} | Pd | $CH_4, O_2 \Rightarrow CO, H_2$ | 86, 88, 305, 306 |
| O^{2-} | Bi_2O_3 -GDC | $CH_4, O_2 \Rightarrow CO, H_2$ | 307 |
| O^{2-} | Rh | $CH_4, O_2 \Rightarrow CO, H_2$ | 276, 308–312 |
| O^{2-} | Rh/TiO ₂ /YSZ | $CH_4, O_2 \Rightarrow CO, H_2$ | 313 |
| O^{2-} | Ru-YSZ | $CH_4, O_2 \Rightarrow CO, H_2$ | 314 |
| O^{2-} | RuO_x -YSZ | $CH_4, O_2 \Rightarrow CO, H_2$ | 315 |
| O^{2-} | LiLaNiO/ γ -Al ₂ O ₃ | $CH_4, O_2 \Rightarrow CO, H_2$ | 316, 317 |
| O^{2-} | La-Sr-Fe perovskites | $CH_4, O_2 \Rightarrow CO, H_2$ | 337 |
| H^+ | Pd | $CH_4, O_2 \Rightarrow CO, H_2$ | 86, 88 |
| H^+ | Pt | $CH_4, O_2 \Rightarrow CO, H_2$ | 87 |
| $H^+ - O^{2-}$ | Pt | $CH_4, O_2, H_2O \Rightarrow CO, H_2$ | 115 |
| $H^+ - O^{2-}$ | Ni | $CH_4, O_2, H_2O \Rightarrow CO, H_2$ | 115 |
| Mixed Conducting SECRs | | | |
| conducting species | catalyst | reactants and products | reference(s) |
| $O^{2-} - e^-$ | La-Ca-Fe perovskites | $CH_4, O_2 \Rightarrow CO, H_2$ | 338 |
| $O^{2-} - e^-$ | Pt | $CH_4, O_2 \Rightarrow CO, H_2$ | 217, 318 |
| $O^{2-} - e^-$ | Ni | $CH_4, O_2 \Rightarrow CO, H_2$ | 276, 318 |
| $O^{2-} - e^-$ | oxide-supported Ni | $CH_4, O_2 \Rightarrow CO, H_2$ | 319–323 |
| $O^{2-} - e^-$ | Ni-LDC | $CH_4, O_2 \Rightarrow CO, H_2$ | 295 |
| $O^{2-} - e^-$ | Ni/Ca _{0.8} Sr _{0.2} Ti _{1-x} Fe _x O _{3-a} | $CH_4, O_2 \Rightarrow CO, H_2$ | 324 |
| $O^{2-} - e^-$ | Pd | $CH_4, O_2 \Rightarrow CO, H_2$ | 217, 321 |
| $O^{2-} - e^-$ | Rh | $CH_4, O_2 \Rightarrow CO, H_2$ | 321, 310, 276 |
| $O^{2-} - e^-$ | Rh-based | $CH_4, O_2 \Rightarrow CO, H_2$ | 325–330 |
| $O^{2-} - e^-$ | Ru | $CH_4, O_2 \Rightarrow CO, H_2$ | 321 |
| $O^{2-} - e^-$ | Co | $CH_4, O_2 \Rightarrow CO, H_2$ | 321 |
| $O^{2-} - e^-$ | Fe | $CH_4, O_2 \Rightarrow CO, H_2$ | 321 |
| $O^{2-} - e^-$ | La-Sr-Co-Fe perovskites | $CH_4, O_2 \Rightarrow CO, H_2$ | 331 |
| $O^{2-} - e^-$ | SDC | $CH_4, O_2 \Rightarrow CO, H_2$ | 331 |
| $O^{2-} - e^-$ | LiLaNiO/ γ -Al ₂ O ₃ | $CH_4, O_2 \Rightarrow CO, H_2$ | 231, 332–335 |
| $O^{2-} - e^-$ | BINIVOX | $CH_4, O_2 \Rightarrow CO, H_2$ | 336 |

^a Abbreviations: CGO, cerium–gadolinium oxide; LDC, lanthanum-doped ceria; SDC, samaria-doped ceria; BITAVOX, Bi₂Ta_{0.2}V_{0.8}O_{5.5}; and BINIVOX, Bi₂Ni_{0.1}V_{0.9}O_{5.35}.



Overall:



As shown in Table 5, in addition to the traditional Ni-YSZ cermets, numerous materials were tested as anodic electrodes, including metals (platinum, palladium, rhodium, ruthenium, silver, iron, nickel), conductive oxides (e.g., perovskites), and metal-oxide mixtures.

It is worth mentioning that, although the goal was the production of electricity, one of the earliest SECRs converting methane to syngas was essentially a chemical cogenerative fuel cell.^{270,271} In a YSZ cell, methane decomposed to hydrogen and carbon, with the latter serving as the anodic electrode. Molten silver was the cathodic electrode, through which air was bubbled. Oxygen from the air was electrochemically transported to the anode and oxidized carbon to produce CO. This promising idea of simultaneous generation of electricity and syngas from methane was pursued and evaluated by several research groups, using innovative designs and modifications.^{85–89,105–107}

In the last two decades, mixed-conducting SECRs were also extensively tested for the production of syngas, as shown in Table 5. The advantage of these SECRs is that there is no need for electrodes and wires, while, at the same time, oxygen is transported in the form of ions rather than molecules. Another alternative proposed that eliminates the requirement of wires for current collection was the development of a dual-function material incorporating an ion conducting phase and an electron conducting phase e.g. a Pd-YSZ material. Hence, instead of one mixed conducting phase that should fulfill all requirements, duties were split among the two separate phases.⁹

The conversion of methane to synthesis gas was also examined in H^+ and $\text{H}^+ - \text{O}^{2-}$ SECRs.^{85–88,115} Using a mixed ($\text{H}^+ - \text{O}^{2-}$) conductor and Pt electrodes, Iwahara, Uchida, and Morimoto achieved high conversions to syngas. Protons were pumped away from the methane–steam side and at the cathode H^+ and O_2 reacted to produce H_2O .¹¹⁵ The advantage of this cell is that both conducting ions contribute to the formation of the desired products.

Hibino et al. examined the effect of alternating current on the reaction rate using an O^{2-} SECR with Pd electrodes.³⁰⁵ At an AC voltage of 3 V and a frequency of 60 Hz, the conversion of methane was twice that obtained under open-circuit conditions. It was proposed that the oxygen species formed at the three-phase boundary oxidize methane to CO while the oxygen species transferred to the catalyst (Pd) surface react with CH_4 (or CO) to produce CO_2 and H_2O . Consequently, the application of an AC voltage in the range $10 - 10^3$ Hz enhanced the rate of CO formation, because the oxygen species formed in this frequency regime could not migrate to the Pd surface and most of them remained in the vicinity of the three-phase boundary.³⁰⁵

4.4. Miscellaneous Reactions of Methane. As shown in Tables 4 and 5, most of the studies of methane activation conducted in SECRs focused on the production of either synthesis gas or C_2 hydrocarbons. Table 6 contains SECR works in which several other reactions of methane were studied.

The complete oxidation of CH_4 in O^{2-} SECRs has been studied over the last four decades. The incentive was to operate in the fuel-cell mode with methane first internally reformed to syngas and then completely oxidized to CO_2 and H_2O . Carbon

formation and limited reactivity of methane were problems that had to be solved and, to this end, a large variety of electrodes (catalysts) were tested, including platinum,^{47,50,229,342–344} gold,⁴⁷ silver,^{47,48,342} palladium,^{49,350–352} Cu-based cermets and composites,^{353–356} and various conductive mixed oxides.^{229,357–365}

The production of HCN from $\text{CH}_4 - \text{NH}_3$ mixtures was studied in double-chamber Pt|YSZ|Pt cells.^{99–101,348} High selectivities to HCN were obtained and the SECR could operate adiabatically if the CH_4/NH_3 ratio was kept higher than 1.25.

Methanol or formaldehyde production from methane was not successful on palladium⁴⁸ or silver;⁴⁹ on these materials, only trace amounts of these products were formed. More-promising results were obtained when a Y-Ba-Cu-based mixed-conductor was used as the anodic electrode.^{104,364}

The activation of methane has also been studied in proton-conducting cells. Mori²⁵¹ used a H^+ SECR with Pt electrodes to produce pure hydrogen from methane. At the anode, methane decomposed to carbon and protons, which were then transferred to the cathode, producing pure hydrogen gas (H_2). Belyaev et al. oxidized $\text{CH}_4 - \text{O}_2$ mixtures to CO_2 at the cathode and simultaneously electrolyzed steam at the anode.^{370,371} Hibino et al. passed $\text{CH}_4 - \text{CO}_2$ mixtures over the anode and pumped H^+ away, to accelerate both the reforming of methane and its conversion to C_2 hydrocarbons.³⁶⁸ Using Y-Ba cerates as proton conductors, Coors studied the methane steam reforming reaction with the SECR operating in the fuel-cell mode. Ambipolar steam permeation from the cathode to the anode was observed, and this eliminated the requirement for steam injection.^{372,373} In a recent study, Yamaguchi et al. converted $\text{CH}_4 - \text{O}_2$ mixtures to CO_2 and H^+ at the anode, with the latter transported through the solid electrolyte to produce pure H_2 at the cathode.³⁷⁴

4.5. Hydrogen Oxidation, via the Reaction $\text{H}_2 + 1/2\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$. The reaction of hydrogen oxidation was studied in SECRs in both directions: oxidation of H_2 and decomposition of H_2O . The relevant studies are shown in Table 7.

Hydrogen is considered the energy currency of the future; therefore, the mechanism of its catalytic oxidation is of practical interest. SEP studies were conducted in O^{2-} SECRs, on Ni, Ag, and Cu–CuO electrodes.^{37,40,41} The reaction on nickel exhibited oscillatory behavior and, hence, kinetic and SEP measurements were combined to interpret these interesting phenomena.^{38,39} Similarly, SEP and kinetic information was combined to elucidate the mechanism of hydrogen oxidation on copper and determine the oxidation state of the catalyst during reaction.⁴¹ The highest rates were attained on the reduced surface (copper), but the reaction usually occurred on Cu_2O and CuO surfaces.

Steam electrolysis at high temperatures has certain advantages: (a) electrode overpotentials are reduced, (b) the free-energy change for the decomposition of H_2O is reduced, and (c) ceramic solid oxide materials are almost corrosion-free, as opposed to low-temperature electrolysis cells.³⁹² Thus, steam electrolysis has been studied in SECRs by quite a few research groups for all types of conductors, i.e., O^{2-} ion,^{375–377} proton,^{383–392} and mixed^{380,381,390,393,427} conductors. Calés and Baumard^{375,377} used an O^{2-} SECR as an oxygen separator and produced hydrogen by thermally decomposing water at high temperatures. Guan et al.³⁹⁰ used doped barium cerates (mixed, $\text{H}^+ - \text{e}^-$ conductors) and examined the performance of the SECR as a hydrogen separator operating at much lower temperatures (500–800 °C). Iwahara and co-workers discussed the advantages of using either a purely H^+ , a purely O^{2-} , or a mixed conductor, for high-temperature electrolysis.^{383,387} Also, Iwahara, Hibino, and Sunano tested the operation of a SECR as an electrochemical steam pump.³⁸⁶ Water decomposed at the anode,

Table 6. Miscellaneous Reactions of Methane

| conducting ions | working electrode | reactants and products | reference(s) |
|-----------------|--|---|----------------------|
| O^{2-} | Pt | $CH_4, O_2 \Rightarrow CO, CO_2, H_2, H_2O$ | 339–341 |
| O^{2-} | Pt, | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 47, 50, 229, 342–344 |
| O^{2-} | Pt | $CH_4, O_2 \Rightarrow CO_2, H_2O, CO$ | 345, 366 |
| O^{2-} | Pt | $CH_4, O_2 \Rightarrow H_2, H_2O, CO_x, C_2H_4, C_2H_6$ | 347 |
| O^{2-} | Pt | $CH_4, O_2, NH_3 \Rightarrow HCN, CO, H_2, H_2O$ | 99–101, 348 |
| O^{2-} | Au | $CH_4, O_2 \Rightarrow CO, CO_2, H_2, H_2O$ | 339–341, 345 |
| O^{2-} | Au | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 47 |
| O^{2-} | Ag | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 47, 48, 342 |
| O^{2-} | Ag | $CH_4, O_2 \Rightarrow CO_2, H_2O, CO$ | 345 |
| O^{2-} | Ag | $CH_4, O_2 \Rightarrow H_2, H_2O, CO_x, C_2H_4, C_2H_6$ | 347 |
| O^{2-} | Pd, Pd/CeO ₂ | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 49, 350–352 |
| O^{2-} | Cu-Ni cermets, Cu-Ce-YSZ composites | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 353–355 |
| O^{2-} | Ba-Cu-Ni-CGO | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 356 |
| O^{2-} | LaMnO ₃ oxides, LaSrCrFeO ₃ | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 229, 357–359 |
| O^{2-} | Ce–Gd oxides | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 360, 361 |
| O^{2-} | LiFeO ₂ , LaCaCrO ₃ , Nb-Ce oxides | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 362–364 |
| O^{2-} | Sr _{2-x} La _x MgMoO ₆ | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 365 |
| O^{2-} | YBa ₂ Cu ₃ O _x | $CH_4, O_2 \Rightarrow CO, CH_3OH, HCHO, CO_2$ | 104, 364 |
| O^{2-} | Ni-YSZ | $CH_4, O_2 \Rightarrow H_2, H_2O, CO_x, C_2H_4, C_2H_6$ | 347 |
| O^{2-} | Ni-YSZ | $CH_4, CO_2 \Rightarrow CO, H_2, H_2O, CO_2$ | 346 |
| O^{2-} | Ni(Au)-YSZ | $CH_4, CO_2 \Rightarrow CO, H_2, H_2O, CO_2$ | 349 |
| O^{2-} | CeO ₂ - Ni/YSZ | $CH_4, H_2O, O_2 \Rightarrow CO, H_2, H_2O, CO_2$ | 367 |
| H^+ | Pt | $CH_4, H_2O \Rightarrow CO, CO_2, H_2, C_2H_4, C_2H_6$ | 114 |
| H^+ | Pt | $CH_4 \Rightarrow C, H_2$ | 252 |
| H^+ | Ag | $CH_4, CO_2 \Rightarrow CO, CO_2, H_2, C_2H_4, C_2H_6$ | 368 |
| H^+ | Ni | $CH_4, CO_2 \Rightarrow CO, H_2$ | 368 |
| H^+ | Ni | $CH_4, CO_2 \Rightarrow CO, H_2O$ | 368 |
| H^+ | MoO ₃ | $CH_4 \Rightarrow C_2 + \text{hydrocarbons}$ | 369 |
| H^+ | Pt | $CH_4, O_2 \Rightarrow CO_2, H_2O$ | 370, 371 |
| H^+ | Pt | $CH_4, H_2O, O_2 \Rightarrow CO_2, H_2O$ | 372, 373 |
| H^+ | Ag | $CH_4, O_2 \Rightarrow CO_2, H_2$ | 374 |

H^+ cations were transported through the electrolyte and reacted with oxygen at the cathode to produce H_2O again. This device was used to extract traces of water vapor from gaseous

streams.³⁸⁶ Recently, Kobayashi et al.³⁹¹ and Matsumoto et al.³⁸⁹ tested new proton-conducting materials in an effort to increase the current efficiency of steam electrolysis.

Table 7. Hydrogen Oxidation, via the Reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O}$

| Ionic Conducting SECRs | | | |
|----------------------------|--------------------------|---|----------------------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| O^{2-} | Ni | $\text{H}_2, \text{O}_2 \Rightarrow \text{H}_2\text{O}$ | 37–39, 378, 379 |
| O^{2-} | Ag | $\text{H}_2, \text{O}_2 \Rightarrow \text{H}_2\text{O}$ | 40 |
| O^{2-} | Cu–Cu ₂ O–CuO | $\text{H}_2, \text{O}_2 \Rightarrow \text{H}_2\text{O}$ | 41 |
| H^+ | Pt | $\text{H}_2\text{O} \Rightarrow \text{H}_2, \text{O}_2$ | 383–392 |
| H^+ | Ag | $\text{H}_2\text{O} \Rightarrow \text{H}_2, \text{O}_2$ | 390 |
| Mixed Conducting SECRs | | | |
| conducting species | catalyst | reactants and products | reference(s) |
| $\text{O}^{2-}-\text{e}^-$ | | $\text{H}_2\text{O} \Rightarrow \text{H}_2, \text{O}_2$ | 375–377, 380–382, 390, 393 |

4.6. Oxidation of Carbon Monoxide, via the Reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$. Similar to hydrogen oxidation, the oxidation of CO was studied in SECRs in both directions. Table 8 contains the relevant studies.

Because carbon monoxide (CO) is one of the main pollutants of auto exhaust emissions, the oxidation of CO on platinum has become one of the most extensively studied catalytic reactions. Furthermore, the catalytic oxidation of CO on platinum has attracted the interest of numerous researchers because of the sustained oscillatory phenomena observed in the reaction rate under certain conditions. Hence, several research groups combined kinetic and SEP data to interpret this unsteady-state behavior of the reaction rate.^{23–33} In addition to platinum, the technique of SEP was employed in the studies of CO oxidation on metals such as silver⁴⁰⁴ and iron,³⁶ as well as on oxides (i.e., mixed La–Sr–Mn oxides³⁵ and Cu–Cu₂O–CuO.³⁴ In the latter study, it was possible to show that phase changes of the catalyst were dictated not only by thermodynamics but also by kinetics.

The primary goal for studying the reverse reaction of CO₂ decomposition was the production of oxygen. SECRs can operate at high temperatures at which the oxidation of CO is no longer an irreversible reaction. Consequently, in an O^{2-} cell, oxygen can be “pumped” away from the reacting mixture, resulting in an increase in the equilibrium concentration of O₂. This idea was tested both in O^{2-} conducting^{408,411} and mixed ($\text{O}^{2-}-\text{e}^-$) conducting SECRs.

The forward reaction of CO oxidation was investigated for NEMCA effects by quite a few researchers. It was found that the reaction was electrochemically promoted on platinum,^{395,396,398–402,418–420} palladium,⁵ gold,^{401,403} silver,⁴⁰⁴ and Ag–Pd,^{401,405} in O^{2-} cells. Furthermore, NEMCA was also observed when, instead of O^{2-} conductors, F[−] and Na⁺ conductors were used.^{418–420} Values as high as 10⁵ (Na⁺ conductor/Pt electrode⁴²⁰) and 15 (O^{2-} conductor/Ag electrode⁴⁰⁴) were reported for Λ and ρ , respectively.

4.7. Reactions of Ethane and Higher Alkanes. The catalytic oxidation of ethane and higher alkanes was studied, primarily in O^{2-} SECRs, in an effort to (1) increase the rate of complete oxidation by operating under closed-circuit conditions and (2) increase the selectivity to the desired product of partial oxidation by appropriate polarization of the electrode (catalyst) surface. Similarly, dehydrogenation reactions resulting in the production of alkenes and hydrogen have been studied in H^+ SECRs.

Studies of oxidation of alkanes, other than methane, are listed in Table 9. It can be seen that the majority of these works focused in the conversion of alkanes to the corresponding alkenes, via either a partial oxidation or a dehydrogenation reaction. Recently, the use of pure hydrogen as a fuel (e.g., in fuel cells) has added to the importance of such processes. Alkanes can be converted to alkenes and hydrogen, with the latter simultaneously separated from the reaction mixture.

The conversion of ethane to ethene was first studied in a H^+ SECR by Iwahara et al.¹¹³ Ethane was converted to ethylene with a cogeneration of electrical energy. The same reaction was then studied in both O^{2-} (see refs 427, 428, 452–454) or mixed conducting^{217,336,456,459,461} SECRs. The effect of electrochemical promotion for ethane oxidation was studied in a single-chamber cell of the type Au/YSZ/Pt by Kaloyannis and Vayenas.^{427,428} When O^{2-} ions were pumped to the Pt electrode, a rate enhancement (ρ) of 20 was observed with corresponding Λ values on the order of 200. The NEMCA effect was less profound when O^{2-} ions were pumped toward the Au electrode.

The selective oxidation of ethane to acetaldehyde was studied by Hamakawa et al. in a double-chamber cell of the type Au/YSZ/Ag. When O^{2-} ions were pumped to the Au electrode, acetaldehyde at a selectivity of 45% was formed, while the use of gaseous oxygen did not produce acetaldehyde.⁴³⁶ Using a similar double-chamber cell, York et al. studied the partial oxidation of ethane, propane, and butane.^{437,438} By pumping O^{2-} ions to the Au electrode, ethane was converted to acetaldehyde, propane was converted to acetone and acrylaldehyde, butane was converted to methy-ethyl and methyl-vinyl ketones, and isobutane was converted to methacrolein. When gaseous O₂ replaced O^{2-} , only CO and CO₂ were produced.

The partial and complete oxidation of propane has been studied extensively in several types (O^{2-} , H^+ , K^+ , Na^+ , $\text{O}^{2-}-\text{e}^-$, $\text{O}^{2-}-\text{H}^+$) of cells. As seen in Table 9, the goal in most of these studies was the production of propylene. The complete oxidation of propane was also studied in various types of SECRs in a search for strong NEMCA effects. It is worth mentioning that, during the oxidation of propane on platinum, rate enhancements (ρ) up to 1400 were observed.^{63,431} This is the highest electrochemical rate enhancement ever observed with any catalytic reaction system studied in a SECR. Recently, it was reported¹¹² that acrylic acid and electric power were produced in a cogenerative fuel cell that used propane as fuel and operated at intermediate temperatures (i.e., 400–450 °C).

Table 8. Oxidation of Carbon Monoxide, via the Reaction $\text{CO} + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO}_2$ ^a

| Ionic Conducting SECRs | | | |
|----------------------------|------------------------------------|--|---------------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| O^{2-} | Pt | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 24–33, 342, 394–402 |
| O^{2-} | Au | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 401, 403 |
| O^{2-} | Ag | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 404 |
| O^{2-} | La–Sr–Mn oxide | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 35 |
| O^{2-} | Ag–Pd | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 401, 405 |
| O^{2-} | Cu–Cu ₂ O–CuO | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 34 |
| O^{2-} | Sr–Fe–Co oxide | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 406 |
| O^{2-} | Fe | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 36 |
| O^{2-} | Ni–YSZ | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 378, 407 |
| O^{2-} | Pt | $\text{CO}_2 \Rightarrow \text{CO}, \text{O}_2$ | 411, 412 |
| O^{2-} | Pd/SCFZ | $\text{CO}_2 \Rightarrow \text{CO}, \text{O}_2$ | 413 |
| O^{2-} | LSCM/Pd/CZY | $\text{CO}_2 \Rightarrow \text{CO}, \text{O}_2$ | 414 |
| O^{2-} | SCFZ | $\text{CO}_2 \Rightarrow \text{CO}, \text{O}_2$ | 415 |
| F^- | Pt | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 418 |
| Na^+ | Pt | $\text{CO}, \text{O}_2 \Rightarrow \text{CO}_2$ | 419, 420 |
| Mixed Conducting SECRs | | | |
| conducting species | catalyst | reactants and products | reference(s) |
| $\text{O}^{2-}-\text{e}^-$ | | $\text{CO}_2 \Rightarrow \text{CO}, \text{O}_2$ | 408–410 |
| $\text{O}^{2-}-\text{e}^-$ | | $\text{CO}_2 \Rightarrow \text{CO}, \text{O}_2$ | 416 |
| $\text{O}^{2-}-\text{e}^-$ | NiO/Al ₂ O ₃ | $\text{CO}_2, \text{CH}_4 \Rightarrow \text{CO}, \text{H}_2, \text{O}_2$ | 417 |

^a Abbreviations: SCFZ, SrCo_{0.4}Fe_{0.5}Zr_{0.1}O_{3-δ}; LSCM, La_{0.8}Sr_{0.2}Cr_{0.5}Mn_{0.5}O₃; and CZY, Ce_{0.48}Zr_{0.48}Y_{0.04}O₂.

Similar to propane, the oxidation of butane was studied in SECRs in an effort to (a) attain high selectivities to butene^{428,440–442} and (b) achieve higher combustion rates.^{355,424,454} Moreover, the production of maleic anhydride from the partial oxidation of butane was tested in the last five years using various SECRs with different design and reactant feed modes.^{443–449,455} Generally, electrochemically supplied oxygen was more reactive, but less selective, to maleic anhydride than gaseous oxygen.⁴⁴³

4.8. Reactions of Unsaturated Hydrocarbons. The oxidation of alkenes, primarily ethylene and propylene, has been studied in SECRs by a large number of research groups, as shown in Table 10. The goal in these studies was to enhance the yield to the desired product via appropriate control of the cell voltage.

Among the first SECR studies was the partial oxidation of ethylene to ethylene oxide on Ag catalysts.^{51,53} Also, this reaction system is the first in which a NEMCA effect was reported.⁷³ Since then, many SECR studies of this reaction have been reported in which O^{2-} , H^+ , Na^+ , and mixed $\text{O}^{2-}-\text{e}^-$

conductors were utilized.^{230,469,474,475,482,483} Table 10 shows that, in addition to the partial oxidation on silver, the deep oxidation of ethylene (to CO_2 and H_2O) has also been studied in O^{2-} , H^+ , Na^+ , and $\text{O}^{2-}-\text{e}^-$ SECRs using palladium, platinum, rhodium, IrO₂, RuO₂, and various perovskites as working electrodes. Most of these works report on a significant electrochemical promotion effect. Note that the highest Λ values (up to 3×10^5) ever reported were for this reaction on a Pt catalyst deposited on an oxygen-ion conductor.^{10,496}

Similar to ethylene, both the partial oxidation and complete oxidation of propylene have been studied extensively. The deep oxidation to CO_2 and H_2O was found to be electrochemically promoted on platinum,^{57,58,70,435,452,500,504,505} rhodium,⁵¹⁸ and La–Sr–Co–Fe perovskites.⁴⁶⁷ Electrochemical promotion was also observed on platinum when, instead of O^{2-} conductors, Na^+ or K^+ conductors were used.^{57,472,473,481} Although not as strong as that observed with ethylene oxidation, the NEMCA effect was considerably strong, with values up to $\Lambda = 3000$ and $\rho = 10$.

Table 9. The Oxidation of Ethane and Higher Alkanes (C₂, C₃, C₄, etc.)^a

| Ionic Conducting SECRs | | | |
|------------------------|--|---|----------------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| H ⁺ | Pt | C ₂ H ₆ , O ₂ ⇒ C ₂ H ₄ , CO ₂ , H ₂ O | 113 |
| H ⁺ | Pt | C ₃ H ₈ ⇒ C ₃ H ₆ , H ₂ | 421, 422 |
| H ⁺ | Pt | C ₁ – C ₄ , O ₂ ⇒ CO ₂ , H ₂ O | 423, 424 |
| H ⁺ | Ni | C ₂ H ₆ , O ₂ ⇒ C ₂ H ₄ , H ₂ O | 113 |
| H ⁺ | Pd | C ₃ H ₈ ⇒ C ₃ H ₆ , H ₂ | 421 |
| H ⁺ | Pd | C ₃ H ₈ , H ₂ O ⇒ C ₃ H ₆ , H ₂ | 424 |
| H ⁺ | Ag/Cr ₂ O ₃ | C ₃ H ₈ , O ₂ ⇒ C ₃ H ₆ , H ₂ O | 425 |
| H ⁺ | Ag/Cr ₂ O ₃ -0.5%K | C ₃ H ₈ , O ₂ ⇒ C ₃ H ₆ , H ₂ O | 425 |
| K ⁺ | Pt/C | C ₃ H ₈ , CO, O ₂ ⇒ CO ₂ , H ₂ O | 402, 426 |
| O ²⁻ | Pt | C ₂ H ₆ , O ₂ ⇒ C ₂ H ₄ , CO ₂ , H ₂ O | 427 |
| O ²⁻ | Pt | C ₃ H ₈ , O ₂ ⇒ C ₃ H ₆ , CO ₂ , H ₂ O | 63–65, 429 |
| O ²⁻ | Pt | C ₃ H ₈ , O ₂ ⇒ CO ₂ , H ₂ O | 57, 58, 424, 430–435 |
| O ²⁻ | Au | C ₂ H ₆ , O ₂ ⇒ CH ₃ CHO, CO _x , H ₂ O | 436, 437 |
| O ²⁻ | Au | <i>i</i> -butane, O ₂ ⇒ methacrolein, acetone | 437, 438 |
| O ²⁻ | Au | butane, O ₂ ⇒ methyl ethyl ketone | 437 |
| O ²⁻ | Au/MoO ₃ -V ₂ O ₅ | C ₂ -C ₄ , O ₂ ⇒ C ₂ -C ₄ alkenes and oxygenates | 439–442 |
| O ²⁻ | Au/VPO | C ₄ H ₁₀ , O ₂ ⇒ C ₂ H ₂ (CO) ₂ O, CO _x , H ₂ O | 443–449 |
| O ²⁻ | Au (Ag)/V-Mg-O ¹ | C ₃ H ₈ , O ₂ ⇒ C ₃ H ₆ , CO ₂ , H ₂ O | 450, 451 |
| O ²⁻ | Ag | C ₃ H ₈ , O ₂ ⇒ C ₃ H ₆ , CO ₂ , H ₂ O | 65 |
| O ²⁻ | perovskites | C ₂ H ₆ , O ₂ ⇒ C ₂ H ₄ , CO ₂ , H ₂ O | 452 |
| O ²⁻ | Cu | C ₂ H ₆ , O ₂ ⇒ C ₂ H ₄ , CO ₂ , H ₂ O | 453 |
| O ²⁻ | Cu _{0.7} Co _{0.3} -CeO ₂ | C ₄ H ₁₀ , O ₂ ⇒ CO ₂ , H ₂ O | 454 |
| O ²⁻ | Cu cermet | C ₄ H ₁₀ , O ₂ ⇒ CO ₂ , H ₂ O | 355 |
| O ²⁻ | Pd | C ₃ H ₈ , O ₂ ⇒ C ₃ H ₆ , CO ₂ , H ₂ O | 65 |
| O ²⁻ | Pd | C ₂ H ₆ , O ₂ ⇒ C ₂ H ₄ , H ₂ O | 455 |
| O ²⁻ | LSM-based | C ₃ H ₈ , O ₂ ⇒ CO ₂ , H ₂ O | 456 |
| O ²⁻ | Co-VPO | C ₄ H ₁₀ , O ₂ ⇒ C ₂ H ₂ (CO) ₂ O, CO ₂ , H ₂ O | 455 |
| O ²⁻ | VMgO | C ₃ H ₈ , O ₂ ⇒ C ₃ H ₆ , CO ₂ , H ₂ O | 67, 455 |
| O ²⁻ | VMgO | C ₂ H ₆ , O ₂ ⇒ C ₂ H ₄ , H ₂ O | 455 |
| O ²⁻ | Sr _{1.2} La _{0.8} MgMoO _{6-δ} | C ₃ H ₈ (H ₂ O), O ₂ ⇒ CO ₂ , H ₂ O | 365 |

Table 9. Continued

| Ionic Conducting SECRs | | | |
|------------------------|---|--|--------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| O^{2-} | $Sr_{1.2}La_{0.8}MgMoO_{6-\delta}$ | $C_2H_6(H_2O), O_2 \Rightarrow CO_2, H_2O$ | 365 |
| O^{2-} | Rh | $C_3H_8, O_2 \Rightarrow CO_2, H_2O$ | 430, 431 |
| O^{2-} | Ni-CGO | $C_3H_8, O_2 \Rightarrow C_3H_6, CO_2, H_2O$ | 457 |
| O^{2-} | Ni-LSCF | $C_3H_8, O_2 \Rightarrow CO, CO_2, H_2, H_2O$ | 458 |
| O^{2-} | MoVTeNbO | $C_3H_8, O_2 \Rightarrow$ acrylic acid, CO, CO_2, H_2O | 112 |
| O^{2-} | Au/LSM | $C_3H_8, O_2 \Rightarrow C_3H_6, CO, CO_2, H_2O$ | 456 |
| Na^+ | Pt | $C_3H_8, O_2 \Rightarrow CO_2, H_2O$ | 57, 462 |
| Mixed Conducting SECRs | | | |
| conducting species | catalyst | reactants and products | reference(s) |
| $O^{2-}-e^-$ | VPO/Ce-Fe | $C_4H_{10}, O_2 \Rightarrow C_2H_2(CO)_2O, CO_2, H_2O$ | 445 |
| $O^{2-}-e^-$ | $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ | $C_2H_6, O_2 \Rightarrow C_2H_4, CO_2, H_2O$ | 459 |
| $O^{2-}-e^-$ | $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ | $C_3H_8, O_2 \Rightarrow C_3H_6, CO_2, H_2O$ | 459 |
| $O^{2-}-e^-$ | Pd | $C_2H_6, O_2 \Rightarrow C_2H_4, C_2H_2, CO_2, H_2O$ | 217 |
| $O^{2-}-e^-$ | Pd | $C_3H_8, O_2 \Rightarrow C_3H_6, CO_2, H_2O$ | 217 |
| $O^{2-}-e^-$ | Pt | $C_2H_6, O_2 \Rightarrow C_2H_4, C_2H_2, CO_2, H_2O$ | 217 |
| $O^{2-}-e^-$ | Pt | $C_3H_8, O_2 \Rightarrow C_3H_6, CO_2, H_2O$ | 217 |
| $O^{2-}-e^-$ | LiLaNiO | $C_2H_6, O_2 \Rightarrow CO, H_2$ | 461 |
| $O^{2-}-e^-$ | $Bi_4V_2O_{11}$ | $C_3H_8, O_2 \Rightarrow C_3H_6, CO, CO_2, H_2O$ | 336 |
| $O^{2-}-e^-$ | $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ | $C_3H_8, O_2 \Rightarrow C_3H_6, CO, CO_2, H_2O$ | 336 |
| $O^{2-}-e^-$ | $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$ | $C_2H_6, O_2 \Rightarrow C_2H_4, CO, CO_2, H_2O$ | 336 |
| $O^{2-}-e^-$ | $Bi_2Ni_{0.1}V_{0.9}O_{5.35}$ | $C_3H_8, O_2 \Rightarrow C_3H_6, CO, CO_2, H_2O$ | 336 |
| $O^{2-}-e^-$ | $Bi_2Ni_{0.1}V_{0.9}O_{5.35}$ | $C_2H_6, O_2 \Rightarrow C_2H_4, CO, CO_2, H_2O$ | 336 |
| $O^{2-}-e^-$ | $Bi_2V_{0.9}Co_{0.1}O_{5.35+\delta}$ | $C_3H_8, O_2 \Rightarrow C_3H_6, CO, CO_2, H_2O$ | 428 |
| $O^{2-}-e^-$ | Au- $Bi_2V_{0.9}Co_{0.1}O_{5.35+\delta}$ cermet | $C_3H_8, O_2 \Rightarrow C_3H_6, CO, CO_2, H_2O$ | 428 |
| $O^{2-}-e^-$ | $Bi_{1.5}Y_{0.3}Sm_{0.2}O_3$ | $C_2H_6, O_2 \Rightarrow C_2H_4, CO_2, H_2O$ | 460 |

^a Abbreviations: VPO, vanadium phosphorous oxide; VMgO, $Mg_2V_2O_7$; CGO, cerium-gadolinium oxide; LSCF, $La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O_3$; BITAVOX, $Bi_2Ta_{0.2}V_{0.8}O_{5.5}$; BINIVOX, $Bi_2Ni_{0.1}V_{0.9}O_{5.35}$; and BICOVOX, $Bi_2V_{0.9}Co_{0.1}O_{5.35+\delta}$.

Several research groups examined the formation of products of the partial oxidation of propylene and compared the yields obtained in SECRs to those obtained in conventional catalytic reactors. Most of the works focused on the production of acrolein,^{61,62,67,70,466,487-495,514} followed by propylene oxide,^{56,59,60,230,487} hexadiene and benzene,^{507,508,529} and acrylic acid.⁴⁶

The conversion of butene to butadiene was among the earliest SECR studies.^{98,230} Because of its industrial importance, the

interest in this reaction continued.^{488,491,492} Using an O^{2-} SECR, Takehira et al. converted isobutene to methacrolein over MoO_3 and V_2O_5 catalysts.^{441,442} The selectivity to methacrolein was higher when oxygen was supplied electrochemically (as O^{2-}) than when it was supplied as gaseous O_2 .⁴⁴¹

4.9. Synthesis and Decomposition of Ammonia. SECR studies of ammonia synthesis and decomposition are shown in Table 11. As expected, proton rather than oxygen-ion conductors were employed in most of these works.

Table 10. Reactions of Unsaturated Hydrocarbons^a

| Ionic Conducting SECRs | | | |
|------------------------|---|--|------------------------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| H ⁺ | Pt | C ₂ H ₄ , O ₂ ⇒ CO ₂ , H ₂ O | 463–465 |
| H ⁺ | Pd | C ₂ H ₄ , O ₂ ⇒ CO ₂ , H ₂ O | 428 |
| H ⁺ | Pd | C ₂ H ₄ , H ₂ O, O ₂ ⇒ CH ₃ CHO, H ₂ O | 466 |
| H ⁺ | Pd | C ₃ H ₆ , H ₂ O, O ₂ ⇒ acrolein, acrylic acid, acetone, CO ₂ , H ₂ O | 466 |
| K ⁺ | Ag | C ₂ H ₄ , O ₂ ⇒ ethylene oxide, CO ₂ , H ₂ O | 523 |
| K ⁺ | Pt | C ₃ H ₆ , O ₂ ⇒ CO ₂ , H ₂ O | 481 |
| Na ⁺ | Pt | C ₂ H ₄ , O ₂ ⇒ CO ₂ , H ₂ O | 468–470 |
| Na ⁺ | Pt | C ₂ H ₂ , H ₂ ⇒ C ₂ H ₄ | 471 |
| Na ⁺ | Pt | C ₃ H ₆ , O ₂ ⇒ CO ₂ , H ₂ O | 57, 472, 473 |
| Na ⁺ | Pt | C ₃ H ₆ , NO, O ₂ ⇒ N ₂ , CO ₂ , H ₂ O | 180 |
| Na ⁺ | Pd | C ₂ H ₄ , O ₂ ⇒ CO ₂ , H ₂ O | 428 |
| Na ⁺ | Ag | C ₂ H ₄ , O ₂ ⇒ ethylene oxide, CO ₂ , H ₂ O | 469, 474, 475 |
| Pd ⁺ | Pt(-Pd) | C ₂ H ₂ , H ₂ ⇒ C ₂ H ₄ | 476, 477 |
| O ²⁻ | Ag | ethylene oxide, O ₂ ⇒ CO ₂ , H ₂ O | 51 |
| O ²⁻ | Ag | C ₂ H ₄ , O ₂ ⇒ ethylene oxide, CO ₂ , H ₂ O | 53, 73, 478–480, 482, 483 |
| O ²⁻ | Ag | propylene oxide, O ₂ ⇒ CO ₂ , H ₂ O | 59, 60 |
| O ²⁻ | Ag | C ₃ H ₆ , O ₂ ⇒ propylene oxide, CO ₂ , H ₂ O | 56, 484 |
| O ²⁻ | Ag | C ₃ H ₆ , O ₂ ⇒ acrolein, 1,5-hexadiene, CO ₂ , H ₂ O | 485, 486 |
| O ²⁻ | Au | CH ₂ =CHCH ₃ , O ₂ ⇒ acrolein, CO, CO ₂ , H ₂ O | 487–490 |
| O ²⁻ | Au | 1-butene, O ₂ ⇒ 1,3-butadiene, CO, CO ₂ , H ₂ O | 98, 488, 491, 492 |
| O ²⁻ | Au–Ag | C ₃ H ₆ , O ₂ ⇒ acrolein, 1,5-hexadiene, CO ₂ , H ₂ O | 486 |
| O ²⁻ | Au–MoO ₃ | C ₃ H ₆ , O ₂ ⇒ acrolein, CO, CO ₂ , H ₂ O | 493 |
| O ²⁻ | Au/MoO ₃ –Bi ₂ O ₃ | C ₃ H ₆ , O ₂ ⇒ acrolein, CO, CO ₂ , H ₂ | 491 |
| O ²⁻ | Au/MoO ₃ –Bi ₂ O ₃ | 1-butene, O ₂ ⇒ 1,3-butadiene, CO, CO ₂ , H ₂ O | 98, 488, 491, 492 |
| O ²⁻ | Au/MoO ₃ | C ₂ –C ₄ alkenes, O ₂ ⇒ C ₂ –C ₄ aldehydes, CO ₂ , H ₂ O | 441, 442 |
| O ²⁻ | Au/V ₂ O ₅ | C ₂ –C ₄ alkenes, O ₂ ⇒ C ₂ –C ₄ aldehydes, CO ₂ , H ₂ O | 441, 442 |
| O ²⁻ | Au/(Pb, Bi)MoO ₄ | C ₃ H ₆ , O ₂ ⇒ acrolein, CO, CO ₂ , H ₂ O | 492 |
| O ²⁻ | Au/YSZ | C ₃ H ₆ , O ₂ ⇒ acrolein, CO, CO ₂ , H ₂ O | 494 |
| O ²⁻ | Dispersed Pt on Au | C ₂ H ₄ , O ₂ ⇒ CO ₂ , H ₂ O | 495 |
| O ²⁻ | Pt | C ₂ H ₄ , O ₂ ⇒ CO ₂ , H ₂ O | 5, 52, 55, 428, 496–503, 521 |

Table 10. Continued

| Ionic Conducting SECRs | | | |
|------------------------|---------------------------------------|---|-------------------------------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| O^{2-} | Pt | $C_3H_6, O_2 \Rightarrow CO_2, H_2O$ | 57, 58, 70, 435, 452, 500, 504, 505 |
| O^{2-} | Pt | 1-butene, $O_2 \Rightarrow$ 1,3-butadiene, CO, CO_2, H_2O | 98, 488, 491, 492 |
| O^{2-} | Pd | $C_2H_4, O_2 \Rightarrow CO_2, H_2O$ | 350, 506 |
| O^{2-} | Cu, Cu_2O , CuO | $C_3H_6, O_2 \Rightarrow$ acrolein, CO, CO_2, H_2O | 61, 62, 67 |
| O^{2-} | $(Bi_2O_3)_{0.85}(La_2O_3)_{0.15}$ | $C_3H_6, O_2 \Rightarrow$ benzene, hexadiene | 507, 508 |
| O^{2-} | $Fe_2O_3-Sb_2O_4$ | $C_3H_6, O_2 \Rightarrow$ acrolein, CO, CO_2, H_2O | 70 |
| O^{2-} | IrO_2 | $C_2H_4, O_2 \Rightarrow CO_2, H_2O$ | 6, 499, 509–512 |
| O^{2-} | $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ | $C_2H_4, O_2 \Rightarrow CO_2, H_2O$ | 513 |
| O^{2-} | $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_3$ | $C_3H_6, O_2 \Rightarrow CO_2, H_2O$ | 467 |
| O^{2-} | $MoO_3-Bi_2O_3$ | $C_3H_6, O_2 \Rightarrow$ acrolein, CO, CO_2, H_2O | 514 |
| O^{2-} | Rh | $C_2H_4, O_2 \Rightarrow CO_2, H_2O$ | 6, 497, 499, 515–517 |
| O^{2-} | Rh | $C_3H_6, O_2 \Rightarrow CO_2, H_2O$ | 518 |
| O^{2-} | RuO_2 | $C_2H_4, O_2 \Rightarrow CO_2, H_2O$ | 519, 520 |
| O^{2-} | YSZ | $C_3H_6, O_2 \Rightarrow$ acrolein, CO, CO_2, H_2O | 495 |
| Mixed Conducting SECRs | | | |
| conducting species | working electrode | reactants and products | reference(s) |
| $O^{2-}-e^-$ | Ag | $C_2H_4, O_2 \Rightarrow$ ethylene oxide, CO_2, H_2O | 230 |
| $O^{2-}-e^-$ | Ag | $C_3H_6, O_2 \Rightarrow$ propylene oxide, CO_2, H_2O | 230 |
| $O^{2-}-e^-$ | Pt | $C_2H_4, O_2 \Rightarrow CO_2, H_2O$ | 522 |
| $O^{2-}-e^-$ | $W_3Sb_2O_3$ | butene, $O_2 \Rightarrow$ butadiene | 230 |
| $O^{2-}-e^-$ | BITAVOX | $C_3H_6, O_2 \Rightarrow$ mild oxidation products, CO, CO_2, H_2O | 524–526 |
| $O^{2-}-e^-$ | BICOVOX | $C_3H_6, O_2 \Rightarrow$ mild oxidation products, CO, CO_2, H_2O | 524, 526–528 |
| $O^{2-}-e^-$ | BICUVOX | $C_3H_6, O_2 \Rightarrow$ mild oxidation products, CO, CO_2, H_2O | 524, 526, 527 |
| $O^{2-}-e^-$ | mixed Bi oxides | $C_3H_6, O_2 \Rightarrow$ benzene, 1,5-hexadiene, CO, CO_2, H_2O | 529 |
| $O^{2-}-e^-$ | $Bi_2O_3Er_2O_3$ | $C_3H_6, O_2 \Rightarrow$ mild oxidation products, CO, CO_2, H_2O | 528 |
| $O^{2-}-e^-$ | $Bi_2O_3Er_2O_3-Ag$ cermet | $C_3H_6, O_2 \Rightarrow$ mild oxidation products, CO, CO_2, H_2O | 528 |

^a Abbreviations: BITAVOX, $Bi_2V_{0.8}Ta_{0.2}O_{5.5}$; BICOVOX, $Bi_2V_{0.9}Co_{0.12}O_{5.35}$; and BICUVOX, $Bi_2V_{0.9}Cu_{0.1}O_{5.35}$.

The dominant process for NH_3 synthesis is the Haber process, which involves the reaction of gaseous N_2 and H_2 on an Fe-based catalyst at high pressures. The search for more-active catalysts made it possible to operate at lower temperatures and pressures. Also, parallel to the catalyst optimization, several alternative processes have been proposed including the electrochemical synthesis in

SECRs.^{19,531–535,537,539–546,551} The reaction was first studied by Marnellos et al.^{534,535} in a H^+ SECR on Pd electrodes. Yokari et al.⁵³⁷ used a single-chamber reactor and studied the reaction on a commercial Fe catalyst. Upon “pumping” H^+ cations to the catalyst surface, the reaction rate could increase by as much as 1300%. Wang et al.^{539–542} tested a large number of protonic conductors and concluded that the

Table 11. Synthesis and Decomposition of Ammonia

| conducting ions | working electrode | reactants and products | reference(s) |
|-----------------|---|--|----------------|
| O ²⁻ | Pt | NH ₃ , O ₂ ⇒ N ₂ , NO, H ₂ O | 80–82, 84, 530 |
| O ²⁻ | La–Co–Sr based oxides | NH ₃ , O ₂ ⇒ N ₂ , NO, H ₂ O | 83 |
| O ²⁻ | Fe–Ag | NH ₃ , O ₂ ⇒ N ₂ , H ₂ O | 530 |
| O ²⁻ | Fe–Pt | NH ₃ , O ₂ ⇒ N ₂ , NO, H ₂ O | 530 |
| O ²⁻ | Ru | N ₂ , H ₂ O ⇒ NH ₃ | 19 |
| H ⁺ | Pd | N ₂ , H ₂ ⇒ NH ₃ | 531–535 |
| H ⁺ | Fe | NH ₃ ⇒ N ₂ , H ₂ | 536 |
| H ⁺ | Fe | N ₂ , H ₂ ⇒ NH ₃ | 537, 538 |
| H ⁺ | Ag–Pd | N ₂ , H ₂ ⇒ NH ₃ | 539–546 |
| H ⁺ | Ru | NH ₃ ⇒ N ₂ , H ₂ | 547 |
| H ⁺ | Ni–Ce _{0.8} Ga _{1.2} O _{1.9} | NH ₃ , O ₂ ⇒ N ₂ , H ₂ O | 546 |
| H ⁺ | Pt | NH ₃ , O ₂ ⇒ N ₂ , H ₂ O | 549 |
| H ⁺ | Pt | NH ₃ , O ₂ ⇒ N ₂ , H ₂ O | 550 |
| H ⁺ | Pt | N ₂ , H ₂ ⇒ NH ₃ | 551 |
| H ⁺ | Ag | NH ₃ ⇒ N ₂ , H ₂ | 552 |
| H ⁺ | Ru | N ₂ , H ₂ O ⇒ NH ₃ | 19 |
| K ⁺ | Fe | NH ₃ ⇒ N ₂ , H ₂ | 536 |

rate of NH₃ synthesis is limited by the conductivity of the solid electrolyte. A Pd–Ag alloy served as the working electrode in their studies. A similar approach was followed by Chen et al.^{545,546} In a recent study,¹⁹ ammonia was synthesized via the reaction of gaseous nitrogen with steam rather than molecular H₂, using not only H⁺, but also O²⁻ conductors.

The decomposition of NH₃ is a potential method to produce very pure hydrogen for fuel-cell applications. Thus, the reaction was studied in SECRs using Fe,^{536–538} Ag,⁵⁵² and Ru⁵⁴⁷ electrodes. The use of ammonia directly as a fuel in high-temperature fuel cells was also investigated. In the early 1980s, Vayenas et al.^{80–82,84} studied the cogeneration of electricity and NO from the partial oxidation of NH₃ in the Pt/YSZ/Pt cell. High NO selectivities (>90%) and reasonable power output were attained at 700–800 °C.⁸⁴ Using the same concept, Sammes and Steele⁸³ tested various Co-based mixed oxides as electrodes. Recently, the idea to use ammonia as a source of hydrogen for fuel cells was investigated in both proton and O²⁻ SECRs with promising results.^{530,548–550}

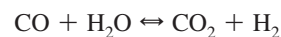
4.10. Reactions of Carbon, Carbon Oxides, and Hydrogen. Table 12 contains SECR works in which carbon, carbon monoxide (CO), or hydrogen (H₂) was one of the reactants.

The conversion of CO–H₂ or CO₂–H₂ mixtures into hydrocarbons, primarily methane, was among the first SECR studies.

Gür and Huggins⁵⁶⁰ showed that, upon electrochemical oxygen pumping away from Ni or Pt electrodes, the rate of conversion to methane can be up to 2 orders of magnitude higher than those attained under open-circuit conditions.^{560,561} In the last two decades, this reaction has been studied on iron,⁵⁶⁵ silver,⁵⁵⁸ rhodium,^{557,569,570} cobalt,⁵⁶⁵ and ruthenium,⁵⁵⁶ as well as on oxide electrodes.^{570,571}

Several researchers examined the feasibility of a process in which coal is converted to CO with a simultaneous production of electrical energy.^{90–92,103,269} Nakagawa and Ishida⁹² used charcoal as raw fuel and pumped O²⁻ ions to convert 95% of C to CO. Yentekakis et al.¹⁰³ used fused iron, both as an anode and as a carbon reservoir, and achieved appreciably high power densities. Horita et al. proposed the use of carbides as anodic electrodes, so that carbon could be activated by the reaction of carbide formation.²⁶⁹ Gür and Huggins succeeded in the conversion of carbon directly to CO₂, using a design that provided for two different temperature zones.^{90,91}

The water-gas shift (WGS) reaction, which is described as



was studied primarily in H⁺ SECRs.^{113,373,388,553,554} By removing hydrogen from the reacting mixture, the reaction equilibrium is shifted to the right and higher conversions to H₂ can be obtained. Moreover, the reaction rate could be further enhanced

Table 12. Reactions of Carbon, Carbon Monoxide, and Hydrogen^a

| Ionic Conducting SECRs | | | |
|------------------------|---------------------|--|--------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| H ⁺ | Pt | CO, H ₂ O, O ₂ ⇒ CO ₂ , H ₂ , H ₂ O | 113, 373 |
| H ⁺ | Pt | CO, H ₂ O, H ₂ ⇒ CO ₂ , H ₂ | 388 |
| H ⁺ | Pd | CO, H ₂ O ⇒ CO ₂ , H ₂ | 553 |
| H ⁺ | Cu | CO ₂ , H ₂ ⇒ CO, H ₂ O | 554 |
| Na ⁺ | Pd | H ₂ , CO ₂ ⇒ CO, H ₂ O | 555 |
| Na ⁺ | Ru | H ₂ , CO ₂ , CO ⇒ CH ₄ , H ₂ O | 556 |
| K ⁺ | Rh | H ₂ , CO ⇒ C ₁ –C ₄ hydrocarbons, H ₂ O | 557 |
| O ²⁻ | Ag | CO ₂ , H ₂ ⇒ CH ₄ , H ₂ O, O ₂ | 558 |
| O ²⁻ | Ag | CO ₂ , H ₂ O, C ₂ H ₄ , O ₂ ⇒ H ₂ , CO ₂ , H ₂ O | 559 |
| O ²⁻ | Pt | H ₂ , CO ₂ , CO ⇒ CH ₄ , H ₂ O | 560, 561 |
| O ²⁻ | Pt | H ₂ , CO ₂ ⇒ CH ₄ , H ₂ O | 562, 563 |
| O ²⁻ | Pt | CO ₂ , H ₂ O, C ₂ H ₄ , O ₂ ⇒ H ₂ , CO ₂ , H ₂ O | 559 |
| O ²⁻ | Pt | C, O ₂ ⇒ CO, CO ₂ , | 90–92, 564 |
| O ²⁻ | Pt-YSZ | C, O ₂ ⇒ CO, CO ₂ | 564 |
| O ²⁻ | Fe | H ₂ , CO ⇒ CH ₄ , H ₂ O | 565 |
| O ²⁻ | Co | H ₂ , CO ⇒ CH ₄ , H ₂ O | 565 |
| O ²⁻ | Pd | H ₂ , CO ₂ ⇒ CO, H ₂ O | 555 |
| O ²⁻ | Pd | CO ₂ , H ₂ O, C ₂ H ₄ , O ₂ ⇒ H ₂ , CO ₂ , H ₂ O | 559 |
| O ²⁻ | Ni | C, O ₂ ⇒ CO, CO ₂ | 564 |
| O ²⁻ | Ni | H ₂ , CO ⇒ CH ₄ , H ₂ O | 565 |
| O ²⁻ | Ni | H ₂ , CO ₂ , CO ⇒ CH ₄ , H ₂ O | 560, 561 |
| O ²⁻ | Ni | CO ₂ , H ₂ O, C ₂ H ₄ , O ₂ ⇒ H ₂ , CO ₂ , H ₂ O | 559 |
| O ²⁻ | Ni/GDC | C, O ₂ ⇒ CO, CO ₂ | 566 |
| O ²⁻ | Ni-CeO ₂ | C, O ₂ ⇒ CO, CO ₂ | 564, 567 |
| O ²⁻ | Ni-YSZ | CO, H ₂ , O ₂ ⇒ CO ₂ , H ₂ O | 568 |
| O ²⁻ | Ni-YSZ | CH ₄ , H ₂ O, O ₂ ⇒ CO ₂ , CO, H ₂ O | 568 |
| O ²⁻ | Rh | H ₂ , CO ₂ ⇒ CH ₄ , CO | 569, 570 |
| O ²⁻ | FeC | C, O ₂ ⇒ CO | 103 |
| O ²⁻ | TiC, VC, WC, ZrC | C, O ₂ ⇒ CO | 269 |
| O ²⁻ | CuMoO ₄ | H ₂ , CO ₂ , CO ⇒ CH ₄ , H ₂ O | 571 |

Table 12. Continued

| Ionic Conducting SECRs | | | |
|------------------------|--------------------|--|--------------|
| conducting ions | working electrode | reactants and products | reference(s) |
| O^{2-} | CuTiO ₂ | $H_2, CO_2 \Rightarrow CO, CH_4, C_2H_4, H_2O$ | 570 |
| O^{2-} | MoVO ₆ | $H_2, CO_2, CO \Rightarrow CH_4, H_2O$ | 571 |
| O^{2-} | GDC/LSCM | $H_2, CH_4, H_2O \Rightarrow CO_2, CO, H_2O$ | 572 |
| Mixed Conducting SECRs | | | |
| conducting species | working electrode | reactants and products | reference(s) |
| $O^{2-}-e^-$ | | $H_2O, CO \Rightarrow CO_2, H_2$ | 573 |
| $O^{2-}-e^-$ | | $CO, H_2, O_2 \Rightarrow CO_2, H_2O$ | 574 |
| $O^{2-}-e^-$ | C | $C, O_2 \Rightarrow CO$ | 575 |
| $O^{2-}-e^-$ | Pt | $H_2O, CO \Rightarrow CO_2, H_2$ | 384 |
| $O^{2-}-e^-$ | Pt | $CO, H_2, O_2 \Rightarrow CO_2, H_2O$ | 576 |
| $O^{2-}-e^-$ | Mo-YSZ cermet | $CO, H_2, O_2 \Rightarrow CO_2, H_2O$ | 577 |

^a Abbreviations: LSCM, La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O₃; and GDC, Gd_{0.2}Ce_{0.8}O_{1.9}.

by NEMCA. On Pd electrodes, a moderate NEMCA effect was observed⁵⁵³ (ρ and Λ values up to 2.0 and 8.0, respectively). The reverse WGS reaction was also found to exhibit NEMCA. On a Cu electrode and upon pumping protons to the Cu surface, the intrinsic catalytic activity was increased by up to a factor of 10.⁵⁵⁴ On a Pd catalyst-electrode interfaced to an O^{2-} conductor, the rate of CO formation was enhanced by a factor of up to ~ 6 by applying either negative or positive overpotentials.⁵⁵⁵ When instead of an O^{2-} conductor, a Na^+ conductor was used, the CO formation rate increased by a factor of up to 7 when sodium was supplied to the catalyst.⁵⁵⁵ Pekridis et al.⁵⁶³ studied the reverse WGS reaction in a Pt|YSZ|Pt cell and observed a moderate NEMCA effect ($\Lambda < 10$). The authors also examined the conditions under which the electrical power output of the cell is optimized when the SECR operates in the fuel-cell mode.⁵⁶³

4.11. Reactions of Sulfur Compounds. Reactions of sulfur compounds studied in SECRs include SO₂ oxidation, SO₂ decomposition, SO₃ decomposition, H₂S oxidation, and H₂S decomposition. A list of them is given in Table 13.

The oxidation of SO₂ to SO₃ on Au, Ag, and Pt electrodes was the first SEP study; the reaction kinetics was combined with SEP to investigate the reaction mechanism.²² The same reaction was studied on Pt and V₂O₅ under closed-circuit conditions. It was found that, by pumping oxygen to the catalyst surface, the yields to SO₃ could exceed those predicted by thermodynamics in a conventional catalytic reactor.⁵⁸²

The reaction of SO₂ decomposition was studied by Cicero and Jarr, who tested various transition-metal oxides as cathodic electrode-catalysts. By pumping oxygen away from the cathode surface, sulfur dioxide decomposed to its elements.¹⁵⁹ Similarly, the decomposition of SO₃ (electrolysis), and its conversion to SO₂ and O₂, was studied in a Pt|YSZ|Pt cell at 500–600 °C. It was found that, depending on the temperature of operation, the rate-determining process may involve adsorption and dissociation of SO₃ or surface diffusion on the electrode.⁵⁸³

The reactions of H₂S oxidation and decomposition were studied in both O^{2-} and H^+ SECRs, as shown in Table 13. The

goal in these studies was to increase the rate of H₂S decomposition by “pumping” O^{2-} or H^+ ions to or from the catalyst surface, respectively. In 1987, Pujare et al. first tested the performance of O^{2-} cells with thiospinel anodes.⁹³ Following this pioneering work, several research groups searched for effective and durable anodic electrodes and reported on the performance of metals, metal sulfides, and mixed compounds.^{94,95,480,483,484,492,493,496,510,514,580,586}

The operating characteristics of a chemical cogenerative H₂S fuel cell were examined by several research groups. Yentekakis and Vayenas first studied the cogeneration of SO₂ and electricity in a Pt|YSZ|Pt cell.⁹⁴ Although the current densities generated by the cell were not very high, the selectivity to SO₂ was $\sim 100\%$ at low H₂S/ O^{2-} ratios. Kirk and Winnick tested the performance of both O^{2-} and H^+ H₂S fuel cells.⁹⁵ Higher current densities were obtained with the O^{2-} fuel cell, while the use of the proton conductors eliminated the possibility of SO₂ production. Side reactions occurred (formation of sulphates) and caused gradual degradation in both cells. To this end, Peterson and Winnick tested Li₂SO₄ electrolytes which could operate stably with reasonable power output.⁷⁹ Generally, cell degradation and side reactions on the working electrode have been problematic with H₂S. As seen in Table 13, research in this area is continuing. In the past decade, the groups of Chuang, Luo, and Sanger proposed and tested several innovative solutions.^{109,117,587–589,593–598,600}

4.12. Oxidation and Decomposition of Alcohols and Aldehydes. In the 1980s, Mason et al.,^{340,341,603} studied the oxidation of methanol and ethanol in O^{2-} SECRs on Pt and Au electrode-catalysts. Because of the similarities of the reaction rates on the two catalysts, the authors concluded that the reaction takes place on the electrolyte rather than on the electrode surface. A few years later, Neophytides and Vayenas studied the cogeneration of electricity and formaldehyde from methanol in the Ag|YSZ|Ag cell. Electricity was produced, with an up to 30% conversion of methanol and with up to 90% selectivity to formaldehyde.¹⁰⁸

The electrochemical promotion of methanol oxidation and methanol decomposition was studied on Ag and Pt electrodes.^{601,602,606,607} It was found that both methanol conversion

Table 13. Reactions of Sulfur Compounds

| conducting ions | working electrode | reactants and products | reference(s) |
|-----------------|-------------------------|--|------------------|
| O^{2-} | Pt | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 94, 95, 578, 579 |
| O^{2-} | Pt | $H_2S \Rightarrow S_2, H_2$ | 580, 581 |
| O^{2-} | Pt | $SO_2, O_2 \Rightarrow SO_3$ | 22, 582, 583 |
| O^{2-} | Au | $SO_2, O_2 \Rightarrow SO_3$ | 22 |
| O^{2-} | Ag | $SO_2, O_2 \Rightarrow SO_3$ | 22 |
| O^{2-} | V_2O_5 | $SO_2, O_2 \Rightarrow SO_3$ | 582 |
| O^{2-} | transition-metal oxides | $SO_2 \Rightarrow S_8, O_2$ | 259 |
| O^{2-} | MoS_2 | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 584 |
| O^{2-} | $CuFeS_2$ | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 93 |
| O^{2-} | $CuFe_2S_4$ | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 585 |
| O^{2-} | WS_2 | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 586 |
| O^{2-} | Mo-Ni-S | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 587, 588 |
| O^{2-} | MoS_2 -NiS-Ag | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 109 |
| O^{2-} | metal sulfides | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 589, 590 |
| O^{2-} | Cu-Ni-Co-Fe thiospinels | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 584, 586 |
| O^{2-} | NiO-based | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 591 |
| O^{2-} | $La_{0.7}Sr_{0.3}VO_3$ | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 592 |
| H^+ | Pt | $H_2S \Rightarrow S_2, H_2$ | 79, 95 |
| H^+ | Pt/C | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 118, 593–595 |
| H^+ | Pd-C | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 593–595 |
| H^+ | MoS_2 | $H_2S \Rightarrow S_2, H_2$ | 595, 596 |
| H^+ | MoS_2, CoS_2, WS_2 | $H_2S, CH_4, C_2H_6, CO_2, O_2 \Rightarrow S_2, SO_2, CO_2, H_2, H_2O$ | 593 |
| H^+ | MoS_2 -C | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 594, 595 |
| H^+ | Li_2SO_4 -based | $H_2S \Rightarrow S_2, H_2$ | 117 |
| H^+ | Li_2SO_4 -based | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 597–599 |
| H^+ | various catalysts | $H_2S, O_2 \Rightarrow S_2, SO_2, H_2, H_2O$ | 600 |

and selectivity to formaldehyde were markedly affected by oxygen pumping. On silver, values as high as $\Lambda = 25$ and $\rho = 6$ were reported,⁶⁰⁶ whereas on platinum, the corresponding values were of the order of 10^4 and 5, respectively.^{601,602}

The oxidation of ethanol has been studied on metal oxide as well as metal electrodes.^{604,605,608–610} On platinum, a strong NEMCA effect was observed and the rate of acetaldehyde formation being enhanced (Λ values on the order of 100, and ρ values up to 7) upon supplying O^{2-} ions electrochemically.^{604,605} Iwahara and co-workers examined the operation of H^+ SECRs

in the fuel-cell mode with methanol–steam or ethanol–steam mixtures decomposing at the anode and protons reacting with O_2 at the cathode to produce H_2O .^{113,114} Strontium- and barium-doped cerates were tested as solid electrolytes. The use of barium cerates resulted in higher cell conductivity but, at the same time, these materials exhibited mixed ($H^+ - O^{2-}$) conductivity.

The partial oxidation of acrolein to acrylic acid was studied over an oxidic (Mo-V-Cu) catalyst. Kinetic measurements were combined with SEP data to determine the oxidation state of the catalyst under working conditions.⁶⁶

Table 14. SECR Studies of Miscellaneous Reactions

| conducting ions | working electrode | reactants and products | reference(s) |
|--|---|---|---------------|
| (i) Oxidation and Decomposition of Alcohols and Aldehydes | | | |
| H ⁺ | Pt | CH ₃ CH ₂ OH, O ₂ ⇒ CO, H ₂ , H ₂ O | 113 |
| H ⁺ | Pt | CH ₃ OH, O ₂ ⇒ CO, H ₂ , H ₂ O | 114 |
| O ²⁻ | Pt | CH ₃ OH, O ₂ ⇒ CH ₂ O, CO ₂ , H ₂ O | 601, 602 |
| O ²⁻ | Pt | CH ₃ OH, CH ₃ CH ₂ OH, O ₂ ⇒ H ₂ , CO ₂ , H ₂ O | 340, 341, 603 |
| O ²⁻ | Pt | CH ₃ CH ₂ OH, O ₂ ⇒ CH ₃ CHO, CO ₂ , H ₂ O | 604, 605 |
| O ²⁻ | Au | CH ₃ OH, CH ₃ CH ₂ OH, O ₂ ⇒ H ₂ , CO ₂ , H ₂ O | 340, 341, 603 |
| O ²⁻ | Ag | CH ₃ OH, O ₂ ⇒ CH ₂ O, CO, CH ₄ , H ₂ O | 108, 606, 607 |
| O ²⁻ | LSCF ^a | CH ₃ CH ₂ OH, O ₂ ⇒ CH ₂ O, CH ₃ CHO, CO _x , H ₂ O | 608, 609 |
| O ²⁻ | Fe–Ni–ScSZ cermet | CH ₃ CH ₂ OH, O ₂ ⇒ CO ₂ , H ₂ O | 610 |
| O ²⁻ | Mo ₁₂ V ₃ Cu _{2.2} O ₄₄ | acrolein, O ₂ ⇒ acrylic acid | 66 |
| (ii) Hydrogenation and Oxidation of Aromatics | | | |
| O ²⁻ | V ₂ O ₅ | C ₆ H ₆ , O ₂ ⇒ maleic anhydride, CO | 611, 612 |
| O ²⁻ | Pt | ethylbenzene ⇒ styrene | 96, 97 |
| O ²⁻ | Ag | toluene ⇒ CO ₂ , H ₂ O | 613–615 |
| Na ⁺ | Pt | C ₆ H ₆ ⇒ C ₆ H ₁₂ | 616, 617 |

^a LSCF = La_{0.6}Sr_{0.4}Fe_{0.8}Co_{0.2}O₃.

4.13. Oxidation and Hydrogenation of Aromatic Compounds. Pizzini et al.^{611,612} studied the oxidation of benzene to maleic anhydride under both open- and closed-circuit conditions, using either Pt or Pt/V₂O₅ catalysts. With Pt/V₂O₅, more than 70% of the electrochemically supplied oxygen was consumed, whereas, with platinum, oxygen consumption was ~100%.⁶¹¹

The oxidative dehydrogenation of ethylbenzene to styrene was studied by Michaels and Vayenas in a Pt/YSZ/Pt SECR.^{96,97} The rates of both styrene formation and ethylbenzene oxidation to CO₂ were enhanced upon electrochemical supply of O²⁻ to the catalyst.

Using a Na⁺ SECR, Haller et al. studied the hydrogenation of benzene to cyclohexane on Pt electrodes.^{616,617} A dramatic increase in the reaction rate was observed when Na⁺ was pumped to the Pt surface.

Recently, the catalytic oxidation of toluene was studied on a Ag electrode deposited on YSZ. It was found that the reaction rate can be significantly promoted upon cathodic polarization (i.e., the removal of O²⁻ from the catalyst surface).^{613–615}

5. Current Experience, Economic Considerations and Future Directions

Tables 3–14 show that a large number of industrially important reactions have been studied in SECRs and several promising results have been obtained. Clearly, there is a growing interest in the development of these systems. In a review article from the year 2000, about 300 works related to SECRs were

reported.⁹ As seen in the tables and list of references given in the present work, this number has doubled in the past decade. The increased need for energy conservation and cleaner technologies motivated many research groups to exploit the advantageous characteristics of SECRs. From the viewpoint of practical applications, these advantages are summarized as follows:

(1) The SECR can operate as a catalytic membrane reactor (i.e., produce the desired compound and simultaneously separate it from the reacting mixture). Also, because of the selective conduction of a specific ion, impurities and poisons are avoided. Hence, the need for extensive purification is eliminated.

(2) The desired product and electrical power can be cogenerated.

(3) The intrinsic catalytic activity can be dynamically modified (NEMCA).

Given the above advantages, it is perhaps puzzling that SECRs have not yet been scaled up and used in industrial processes. The answer is not straightforward. On one hand, as already discussed in previous reviews,^{9,10,618} there are several hurdles that these reactors must overcome on their way to commercialization:

(1) High cost of capital investment: The major portion of the capital cost lies in the cost of the reactor (electrolyte, electrodes, sealing materials).

(2) New technology and long-term testing: The introduction of a new technology requires major changes in the reactor design. Industries are reluctant to adopt a completely new process, especially with the risk of introducing a relatively immature technology. Very few of the SECR processes have been tested for durability and sustained performance for longer than 1000 h.

(3) Low ionic fluxes: In most of the processes in which the SECR is used, at least one of the reactants (usually oxygen) must be supplied through the solid electrolyte membrane. Although, in the last two decades, new materials with high ionic conductivity have been discovered and tested, research is still needed in this direction. Along these lines, if a process does not require the entire amount of the reactant to be supplied through the membrane (e.g., when the SECR is used as an electrochemical promoter of the working electrode (NEMCA)), chances for scaling up into a pilot plant level are considerably higher.

(4) Limited diversity of the industrial sector: Even when a technoeconomic analysis shows that chemical cogeneration is advantageous for a certain chemical product, both chemical companies and electric power industries will be reluctant to enter two worlds, i.e., chemicals and electrical power generation; additional expertise and significant modifications in their production process will be needed.

(5) High temperatures and inexpensive products: For chemical cogenerative SECRs, the operating temperature must be $\sim 800^\circ\text{C}$ or higher to attain acceptably high ionic fluxes. At such high temperatures, however, large molecules decompose and only small-size molecules survive. Small molecules are generally inexpensive compounds. This is the reason why membrane reactor-based processes that are related to low-temperature applications, such as the bioproduction of fine chemicals, have already proven their economic worth.⁶¹⁸

Although the possibilities offered by SECRs have been discussed in the past in various reviews,^{1–15,619–622} very few detailed technoeconomic studies can be found in the literature.^{618,623–631} Of the latter, the earlier works considered that, from the economic point of view, the chemical cogenerative is the most attractive SECR, because useful chemicals are produced with a simultaneous generation of electricity. Spillman et al.⁶²³ compared the economics of three SECRs: a regular fuel cell that produced electricity only, an electrolytic cell that produced a chemical reaction by consuming electrical energy, and a cogenerative cell. Their analysis showed that, for chemical cogeneration to be preferable, the difference in the values of the reactants and products should be low, the reaction free energy change should be high, and the molecular weight of the product should be low. Vayenas et al.^{624,625} showed that, for a chemical reaction to be a good candidate for chemical cogeneration, it must be highly exothermic, the reactants and products must be inexpensive, and the operating temperature must be high.

Note that the above-mentioned inhibiting reasons are quite general and the effects on each candidate process may vary considerably. A detailed analysis is needed to determine the economic feasibility of each particular process.^{9,625} Furthermore, in addition to the traditional technoeconomic criteria, new parameters, such as the environmental cost (e.g., from the CO_2 emissions⁶²⁹), should be included in the economic evaluation. A good example of the importance of new criteria can be found in cogenerative fuel cells in which methane is the fuel. In two studies that were reported in 1995,^{626,627} the economics of three different methane SECRs were compared. The first was a cogenerative cell that produced C_2 hydrocarbons and electricity,

the second was another cogenerative cell that produced synthesis gas and electricity, and the third was a regular fuel cell that oxidized methane completely to CO_2 and H_2O . The results showed that, opposite to intuition, the regular fuel cell was the one with the greatest profit. The main reason for this unexpected result was the much higher fixed investment required in the chemical cogeneration cases. A few years later, Liu et al, concluded that, among the various membrane processes considered for methane coupling, those using mixed ($\text{H}^+ - \text{e}^-$) conductors were the most promising.⁶³¹ In 2005, a new study re-examined the economics of ethylene production via the oxidative coupling of methane, which is a process that was not considered to be feasible.⁶²⁸ To this end, two schemes were compared: one in which ethylene and electricity were cogenerated in a SECR, and one in which ethylene and electricity were produced separately by conventional processes at the exact same amounts. The comparison indicated that a plant cogenerating ethylene and electricity indeed has rather low profitability. If, however, the significant reduction in the CO_2 emissions is taken into account, the economics may improve considerably. Furthermore, a more promising alternative for the oxidative coupling of methane was a mixed ($\text{O}^{2-} - \text{e}^-$) conducting SECR that not only reduces the CO_2 emissions, but also eliminates the oxygen plant.⁶²⁸

Hence, in the past decade, many applications that were disregarded in the past have been revisited and the possibility for further development has been re-examined. An example of such a process is the conversion of methane to C_2 hydrocarbons or to synthesis gas with the use of O^{2-} , H^+ , or mixed conductors. Other examples are processes related to hydrogen production. Hydrogen is considered the energy currency of the future; therefore, its production technology is going to have a considerable impact on energy economy. Therefore, processes that involve hydrogen production–separation, together with the production of an industrially important compound (e.g., conversion of C_3H_8 into C_3H_6 with simultaneous separation and production of pure H_2 in H^+ SECRs) may be brought closer to commercialization in the near future.

Also, processes that do not require a high ionic flux have a better chance for industrial application. The SECR can also be used as a catalytic “promoter”, rather than as a membrane reactor. If a reaction exhibits NEMCA with high Λ values, both reactants can be fed in together in the gas phase and the single-chamber cells of Figure 3a or 3b can be used. Moreover, with recent advances such as the novel monolithic electropromoted reactor,^{632–634} NEMCA has been brought much closer to utilization.

6. Conclusions

In the last four decades, solid electrolyte cell reactors (SECRs) have been used to both study and influence the rates of heterogeneous catalytic reactions. For several reactions, notable advantages of a SECR versus a conventional catalytic reactor have been identified. However, this advantageous performance has not yet been sufficient enough to promote these processes to a larger scale.

However, all this research work has not been done without benefits. First, with either the open-circuit or closed-circuit operation, SECR studies provided information very useful in elucidating the reaction mechanism, information that could not have been obtained otherwise. Second, research in this particular field has provided the industrial world with several potential alternatives to existing catalytic routes. Third, with the continuous progress in materials science and solid-state ionics, one

should expect that, in the near future, economic factors that currently inhibit the scaleup of these processes will be substantially decreased, to allow large-scale applications.

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Literature Cited

- (1) Gellings, P. J.; Bouwmeester, H. J. M., Eds.; *The CRC Handbook of Solid State Electrochemistry*; CRC Press: Boca Raton, FL, 1997.
- (2) Vayenas, C. G. Catalytic and Electrocatalytic Reactions in Solid Oxide Fuel Cells. *Solid State Ionics* **1988**, 28–30, 1521.
- (3) Gellings, P. J.; Koopmans, H. J. A.; Burggraaf, A. J. Electrocatalytic Phenomena in Gas Phase Reactions in Solid Electrolyte Electrochemical Cells. *Appl. Catal.* **1988**, 39, 1.
- (4) Stoukides, M. Applications of Solid Electrolytes in Heterogeneous Catalysis. *Ind. Eng. Chem. Res.* **1988**, 27, 1745.
- (5) Vayenas, C. G.; Bebelis, S. I.; Yentekakis, I. V.; Lintz, H.-G. Non-Faradaic Electrochemical Modification of Catalytic Activity. A Status Report. *Catal. Today* **1992**, 11, 303.
- (6) Vayenas, C. G.; Jaksic, M. M.; Bebelis, S. I.; Neophytides, S. G. *The Electrochemical Activation of Catalytic Reactions Modern Aspects in Electrochemistry*; Bockris, J. O'M., Conway, B. E., White, R. E., Eds.; Plenum: New York, 1996.
- (7) Metcalfe, I. Stabilized-Zirconia Solid Electrolyte Membranes in Catalysis. *Catal. Today* **1994**, 20, 283.
- (8) Iwahara, H.; Shimura, T.; Matsumoto, H. Protonic Conduction in Oxides at Elevated Temperatures and Their Possible Applications. *Electrochemistry* **2000**, 68, 154.
- (9) Stoukides, M. Solid-Electrolyte Membrane Reactors: Current Experience and Future Outlook. *Catal. Rev.—Sci. Eng.* **2000**, 42, 1.
- (10) Vayenas, C. G.; Bebelis, S.; Pliangos, C.; Brosda, S.; Tsiplakides, D. *Electrochemical Activation of Catalysts: Promotion, Electrochemical Promotion and Metal-Support Interactions*; Kluwer Academic/Plenum Publishers: New York, 2001.
- (11) Sundmacher, K.; Rihko-Struckmann, L. K.; Galvita, V. Solid Electrolyte Membrane Reactors: Status and Trends. *Catal. Today* **2005**, 104 (2–4), 185.
- (12) Marnellos, G.; Stoukides, M. Catalytic Studies in Electrochemical Membrane Reactors. *Solid State Ionics* **2004**, 175, 597.
- (13) Kokkofitis, C.; Ouzounidou, M.; Skodra, A.; Stoukides, M. High Temperature Proton Conductors: Applications in Catalytic Process. *Solid State Ionics* **2007**, 178, 507.
- (14) Athanassiou, C.; Pekridis, G.; Kaklidis, N.; Kalimeri, K.; Vartzoka, S.; Marnellos, G. Hydrogen Production in Solid Electrolyte Membrane Reactors (SEMRs). *Int. J. Hydrogen Energy* **2007**, 32 (1), 38.
- (15) Liu, Y. Y.; Tan, X. Y.; Li, K. Mixed Conducting Ceramics For Catalytic Membrane Processing. *Catal. Rev.—Sci. Eng.* **2006**, 48 (2), 145.
- (16) Kobayashi, T.; Abe, K.; Ukyo, Y.; Iwahara, H. Performance of Electrolysis with Proton and Oxide-Ion Conducting Electrolyte for Reducing Nitrogen Oxide. *Solid State Ionics* **2002**, 154–155, 699.
- (17) Kobayashi, T.; Abe, K.; Ukyo, Y.; Iwahara, H. Reduction of Nitrogen Oxide by Steam Electrolysis Cell using a Protonic Conductor $\text{SrZr}_{0.9}\text{Yb}_{0.1}\text{O}_{3-\alpha}$. *Solid State Ionics* **2000**, 134, 241.
- (18) Kobayashi, T.; Yamazaki, K.; Abe, K.; Ukyo, Y.; Iwahara, H. Removal of Nitrogen Oxide by Steam Electrolysis Cell with Proton Conducting Ceramics and a $\text{Co/Al}_2\text{O}_3$ Catalyst. *J. Ceram. Soc. Jpn.* **2000**, 108, 554.
- (19) Skodra, A.; Stoukides, M. Electrocatalytic Synthesis of Ammonia From Steam and Nitrogen at Atmospheric Pressure. *Solid State Ionics* **2009**, 180, 1332.
- (20) Jiang, H.; Wang, H.; Werth, S.; Schiestel, T.; Caro, J. Simultaneous Production of Hydrogen and Synthesis Gas by Combining Water Splitting with Partial Oxidation of Methane in a Hollow-fiber Membrane Reactor. *Angew. Chem.—Int. Ed.* **2008**, 47 (48), 9341.
- (21) Lintz, H.-G.; Vayenas, C. G. Solid Ion Conductors in Heterogeneous Catalysis. *Angew. Chem.* **1989**, 28, 708.
- (22) Vayenas, C. G.; Saltsburg, H. M. Chemistry at Catalytic Surfaces. The SO_2 Oxidation on Noble Metals. *J. Catal.* **1979**, 57, 296.
- (23) Hetrick, R. E.; Logothetis, E. M. Oscillations in the EMF of Solid-State Electrochemical Oxygen Sensors. *Appl. Phys. Lett.* **1979**, 34, 117.
- (24) Okamoto, H.; Kawamura, G.; Kudo, T. Non-Ideal Emf Behavior of Zirconia Oxygen Sensors. *Solid State Ionics* **1981**, 3/4, 453.
- (25) Okamoto, H.; Kawamura, G.; Kudo, T. Relation between Surface Adsorption States and EMF in a Solid Electrolyte Concentration Cell During Carbon Monoxide Oxidation on Platinum Studied by Local Current Measurement. *J. Catal.* **1984**, 86, 437.
- (26) Okamoto, H.; Kawamura, G.; Kudo, T. Carbon Monoxide Oxidation on Platinum Studied by Local Current and EMF in a Solid Electrolyte Concentration Cell. *J. Catal.* **1984**, 87, 1.
- (27) Vayenas, C. G. Comment on the “Interpretation of the Electromotive Forces of Solid Electrolyte Concentration Cells During CO Oxidation on Platinum” and on “Electromotive Forces Studies of CO Oxidation on Platinum”. *J. Catal.* **1984**, 90, 371.
- (28) Ehrhardt, J. J.; Häfele, E.; Lintz, H.-G.; Martins, A. F. Surface Preparations for Solid Electrolyte Aided Studies in Heterogeneous Catalysis. *Ber. Bunsen. Phys. Chem.* **1985**, 89, 894.
- (29) Metcalfe, I. S.; Sundaresan, S. Oxygen Storage in Automobile Exhaust Catalyst. *Chem. Eng. Sci.* **1986**, 41, 1109.
- (30) Häfele, E.; Lintz, H.-G. Elektrodencharakterisierung und Grenztemperatur bei der Elektrochemischen Messung der Sauerstoffaktivität an Platin. *Solid State Ionics* **1987**, 23, 235.
- (31) Häfele, E.; Lintz, H.-G. Investigation of the Oxidation of Carbon Monoxide on Polycrystalline Platinum with Simultaneous Measurement of the Oxygen Activity at the Catalyst Surface. *Ber. Bunsen. Phys. Chem.* **1988**, 92, 188.
- (32) Yentekakis, I. V.; Neophytides, S.; Vayenas, C. G. Solid Electrolyte Aided Study of the Mechanism of CO Oxidation on Polycrystalline Platinum. *J. Catal.* **1988**, 111, 152.
- (33) Metcalfe, I. S.; Sundaresan, S. Oxygen Transfer Between Metals and Oxygen-Ion Conductiong Supports. *AIChE J.* **1988**, 34, 195.
- (34) Hildenbrand, H.-H.; Lintz, H.-G. Solid Electrolyte Potentiometric at an Oxide Electrode. *Appl. Catal.* **1989**, 49, L1.
- (35) Petrolekas, P.; Metcalfe, I. S. Solid Electrolyte Potentiometric Study of $\text{La}(\text{Sr})\text{MnO}_3$ Catalyst during Carbon Monoxide Oxidation. In *Proceedings of the International Chemical Engineering Research Event*, Birmingham, U.K., January 1993.
- (36) Marnellos, G. E.; Zisekas, S. T.; Kungolos, A. G. Catalytic and Electrocatalytic Oxidation of Carbon Monoxide On a Fe Electrode in a Solid Electrolyte Cell. *Appl. Catal., B* **2003**, 42 (3), 225.
- (37) Saranteas, C.; Stoukides, M. Kinetics and Rate Oscillations During Hydrogen Oxidation on Nickel. *J. Catal.* **1985**, 93, 417.
- (38) Arif, H.; Stoukides, M. Rate and Oxygen Activity Oscillations During Hydrogen Oxidation on Nickel Films in a CSTR. *Chem. Eng. Sci.* **1986**, 41, 945.
- (39) Eng, D.; Stoukides, M.; McNally, T. Rate and Oxygen Activity Oscillations During Hydrogen Oxidation on Polycrystalline Nickel. *J. Catal.* **1987**, 106, 342.
- (40) Hillary, A.; Stoukides, M. Solid Electrolyte Aided Study of Hydrogen Oxidation on Polycrystalline Silver. *J. Catal.* **1988**, 113, 295.
- (41) Balian, A.; Hatzigiannis, G.; Eng, D.; Stoukides, M. Solid Electrolyte Aided Study of the Oxidation of Hydrogen on Copper and Copper Oxide Catalysis. *J. Catal.* **1994**, 145, 526.
- (42) Mordarski, G.; Suski, L.; Ruggiero, A.; Kolacz, J.; Wyrwa, J. Open-Circuit-Potentials of Gas/Electrode/YSZ Boundary versus Molten Carbonate Reference Electrode at Medium Temperatures—II. Potential Response of Au, Pt and Ni-Cermet Electrodes in $\text{CH}_4 + \text{O}_2$ and $\text{H}_2 + \text{O}_2$ Gas Mixtures. *Electrochim. Acta* **2005**, 50 (14), 2781.
- (43) Suski, L.; Kolacz, J.; Mordarski, G.; Ruggiero, M. Determination of Open-Circuit Potentials at Gas/Electrode/YSZ Boundary versus Molten Carbonate Reference Electrode at Medium Temperatures—I. Potentials of Au and Pt in O_2 and $\text{H}_2 + \text{H}_2\text{O}$ Atmospheres. *Electrochim. Acta* **2005**, 50 (14), 2771.
- (44) Gessner, M. A.; Nagy, S. G.; Michaels, J. N. Multiple Charge-Transfer Reactions in Zirconia Electrolysis Cells: NO_x Reduction on Platinum. *J. Electrochem. Soc.* **1988**, 135, 1294.
- (45) Hibino, T.; Ushiki, K.; Kuwahara, Y. Mechanism of NO Decomposition in a Solid Electrolyte Reactor by SEP Method. *Solid State Ionics* **1997**, 98, 185.
- (46) Brück, J.; Lintz, H.-G.; Oerter, M. Solid Electrolyte Potentiometry Aided Study of the Selective Catalytic Reduction of Nitric Oxide on Platinum Catalysis. *Catal. Today* **1993**, 17, 95.
- (47) Haaland, D. M. Non-Catalytic Electrodes for Solid-Electrolyte Oxygen Sensors. *J. Electrochem. Soc.* **1980**, 127, 796.
- (48) Seimanides, S.; Stoukides, M. Solid Electrolyte Aided Study of Methane Oxidation on Polycrystalline Silver. *J. Catal.* **1984**, 88, 490.
- (49) Seimanides, S.; Stoukides, M. Catalytic Oxidation of Methane on Polycrystalline Palladium Supported on Stabilized Zirconia. *J. Catal.* **1986**, 98, 540.
- (50) Eng, D.; Stoukides, M. Catalytic and Electrochemical Oxidation of Methane on Platinum. *J. Catal.* **1991**, 130, 306.

- (51) Stoukides, M.; Vayenas, C. G. Solid Electrolyte Aided Study of the Ethylene Oxide Oxidation on Platinum. *J. Catal.* **1980**, *64*, 18.
- (52) Vayenas, C. G.; Georgakis, C.; Michaels, J. N.; Tormo, J. The Role of PtO_x in the Isothermal Rate Oscillations of Ethylene Oxidation on Platinum. *J. Catal.* **1981**, *67*, 348.
- (53) Stoukides, M.; Vayenas, C. G. Solid-Electrolyte Aided Study of the Ethylene Oxidation on Polycrystalline Silver. *J. Catal.* **1981**, *69*, 18.
- (54) Vayenas, C. G.; Michaels, J. N. On the Stability Limit of Surface Platinum Oxide and its Role in Oscillation Phenomena of Platinum Catalyzed Oxidations. *Surf. Sci.* **1982**, *120*, L405.
- (55) Vayenas, C. G.; Lee, B.; Michaels, J. N. Kinetics Limit Cycles and Mechanism of the Ethylene Oxidation on Silver. *J. Catal.* **1980**, *66*, 36.
- (56) Stoukides, M.; Vayenas, C. G. Solid Electrolyte Aided Study of Propylene Oxidation on Silver. *J. Catal.* **1983**, *82*, 45.
- (57) Billard, A.; Vernoux, P. Electrochemical Catalysts for Hydrocarbon Combustion. *Top. Catal.* **2007**, *44* (3), 369.
- (58) Li, X.; Gaillard, F.; Vernoux, P. The Relationship of the Catalytic Activity and the Open-Circuit Potential of Pt Interfaced with YSZ. *Ionics* **2005**, *11* (1–2), 103.
- (59) Stoukides, M.; Vayenas, C. G. Kinetics and Rate Oscillations of the Oxidation of Propylene Oxide on Polycrystalline Silver. *J. Catal.* **1982**, *74*, 266.
- (60) Stoukides, M.; Seimanides, S.; Vayenas, C. G. Rate Oscillations During Propylene Oxide Oxidation in a CSTR. *ACS Symp. Ser.* **1982**, *196*, 165.
- (61) Hildenbrand, H.-H.; Lintz, H.-G. Phase-Composition and Selectivity: Solid Electrolyte Potentiometry Aided Study of the Oxidation of Propane on Copper oxides. *Appl. Catal.* **1990**, *65*, 241.
- (62) Hildenbrand, H.-H.; Lintz, H.-G. Solid Electrolyte Potentiometry Aided of the Influence of Promoters on the Phase Transitions in Copper-Oxide Catalysts under Working Conditions. *Catal. Today* **1991**, *9*, 153.
- (63) Kokkofitis, C.; Karagiannakis, G.; Zisekas, S.; Stoukides, M. Catalytic Study and Electrochemical Promotion of Propane Oxidation on Pt/YSZ. *J. Catal.* **2005**, *234*, 476.
- (64) Kokkofitis, C.; Stoukides, M. Rate and Oxygen Activity Oscillations During Propane Oxidation on Pt/YSZ. *J. Catal.* **2006**, *243*, 428.
- (65) Kokkofitis, C.; Karagiannakis, G.; Stoukides, M. Electrochemical Promotion in O₂-Cells During Propane Oxidation. *Top. Catal.* **2007**, *44*, 361.
- (66) Estenfelder, M.; Lintz, H.-G. Simultaneous Determination of Reaction Kinetics and Oxygen Activity in an Oxidic Multicomponent Catalyst During Partial Oxidations. *J. Catal.* **2000**, *195* (1), 38.
- (67) Ji, B.; Wang, J.; Chu, W.; Zhu, X.; Yang, W.; Lin, L. In Situ Monitoring of the Oxygen Activity on a $\text{Mg}_2\text{V}_2\text{O}_7$ Catalyst During the Oxidative Dehydrogenation of Propane. *Chin. J. Catal.* **2009**, *30* (5), 375.
- (68) Lintz, H.-G. Solid Electrolyte Potentiometry Aided Study of Reactions on Oxidic Catalysts—Results and Perspectives. *Solid State Ionics* **2000**, *136–137*, 727.
- (69) Brück, J.; Lintz, H.-G.; Valentin, G. The Low Temperature Limit of the Application of Solid Electrolyte Potentiometry in Heterogeneous Catalysis. *Solid State Ionics* **1998**, *112* (1–2), 75.
- (70) Mallika, C.; Sreedharan, O. M.; Subasri, R. Use on Air/Platinum as the Reference Electrode in Solid Oxide Electrolyte EMF Measurements. *J. Eur. Ceram. Soc.* **2000**, *20* (13), 2297.
- (71) Metcalfe, I. S. Oxygen-ion Conductivity and Catalysis. *Solid State Ionics* **2000**, *134* (1–2), 51.
- (72) Athanassiou, C.; Pekridis, G.; Kalimeri, K.; Vartzoka, S.; Marnellos, G. Effect of Palladium Oxidation State on the Kinetics and Mechanism of the Charge Transfer Reaction Taking Place at the Pt/YSZ Interface. *Solid State Ionics* **2006**, *177* (11–12), 979.
- (73) Stoukides, M.; Vayenas, C. G. The Effect of Oxygen Pumping on the Rate and Selectivity of Ethylene Oxidation on Ag. *J. Catal.* **1981**, *70*, 137.
- (74) Vayenas, C. G.; Koutsodontis, C. G. Non-Faradaic Electrochemical Activation of Catalysis. *J. Chem. Phys.* **2008**, *128* (18), 182506.
- (75) Otsuka, K.; Suga, K.; Yamanaka, Y. Oxidative Coupling of Methane Applying a Solid Oxide Fuel Cell System. *Catal. Today* **1990**, *6*, 587.
- (76) Tagawa, T.; Moe, K. K.; Ito, M.; Goto, S. Fuel Cell Type Reactor for Chemicals-Energy co-Generation. *Chem. Eng. Sci.* **1999**, *54* (10), 1553.
- (77) Xui-Mei, G.; Hidajat, K.; Ching, C. B. Simulation of a Solid Oxide Fuel Cell for Oxidative Coupling of Methane. *Catal. Today* **1999**, *50* (1), 109.
- (78) Tagawa, T.; Moe, K. K.; Hiramatsu, T.; Goto, S. Design of Electrode for Solid Oxide Fuel Cells Reactor. *Solid State Ionics* **1998**, *106* (3–4), 227.
- (79) Peterson, D.; Winnick, J. A Hydrogen Sulfide Fuel Cell Using a Proton Conducting Solid Electrolyte. *J. Electrochem. Soc.* **1996**, *143*, L55.
- (80) Farr, R. D.; Vayenas, C. G. Ammonia High Temperature Solid Electrolyte Fuel Cell. *J. Electrochem. Soc.* **1980**, *127*, 1478.
- (81) Vayenas, C. G.; Farr, R. D. Cogeneration of Electric Energy and Nitric Oxide. *Science* **1980**, *208*, 593.
- (82) Sigal, C. T.; Vayenas, C. G. Ammonia Oxidation to Nitric Oxide in a Solid Electrolyte Fuel Cell. *Solid State Ionics* **1981**, *5*, 567.
- (83) Sammes, N. M.; Steele, B. C. H. The Catalytic Oxidation of Ammonia in a Ceramic Electrochemical Reactor Using Metal Oxide Electrodes. *J. Catal.* **1994**, *145*, 187.
- (84) Manton, M. R. S.; Sawin, H.; Scharfman, R. M.; Sigal, C. T.; Vayenas, C. G.; Wei, J. Cogeneration of Electrical Power and Nitric Oxide in a Solid-Electrolyte Fuel Cell. *Energy Technol.* **1984**, *11*, 794.
- (85) Asano, K.; Iwahara, H. Performance of a One-Chamber Solid Oxide Fuel Cell with a Surface-Modified Zirconia Electrolyte. *J. Electrochem. Soc.* **1997**, *144*, 3125.
- (86) Hibino, T.; Ushiki, K.; Kuwahara, Y. New Concept for Simplifying SOFC System. *Solid State Ionics* **1996**, *91*, 69.
- (87) Asano, K.; Hibino, T.; Iwahara, H. A New Solid Oxide Fuel Cell System Using the Partial Oxidation of Membrane. *J. Electrochem. Soc.* **1995**, *142*, 3241.
- (88) Hibino, T.; Ushiki, K.; Sato, T.; Kuwahara, Y. A Novel Cell Design for Simplifying SOFC System. *Solid State Ionics* **1995**, *81*, 1.
- (89) Semin, G. L.; Belyaev, V. D.; Demin, A. K.; Sobyenin, V. A. Methane Conversion to Syngas over Pt-Based Electrode in a Solid Oxide Fuel Cell Reactor. *Appl. Catal., A* **1999**, *181* (1), 131.
- (90) Gür, T. M.; Huggins, R. A. Direct Electrochemical Conversion of Carbon to Electrical Energy in a High Temperature Fuel Cell. *J. Electrochem. Soc.* **1992**, *139*, L95.
- (91) Gür, T. M.; Huggins, R. A. Direct Electrochemical Conversion of Carbon to Electrical Energy in a High Temperature Fuel Cell, U.S. Patent 5,376,469, 1994.
- (92) Nakagawa, N.; Ishida, M. Performance of an Internal Direct-Oxidation Carbon Fuel Cell and Its Evaluation by Graphic Exergy Analysis. *Ind. Eng. Chem. Res.* **1988**, *27*, 1181.
- (93) Pujare, N.; Semkow, K.; Samuels, A. Direct H₂S/Air Solid Oxide Fuel Cell. *J. Electrochem. Soc.* **1987**, *134*, 2639.
- (94) Yentekakis, I. V.; Vayenas, C. G. Chemical Cogeneration in Solid Electrolyte Cells. The Oxidation of H₂S to SO₂. *J. Electrochem. Soc.* **1989**, *136*, 996.
- (95) Kirk, T. J.; Winnick, J. A Hydrogen Sulfide Solid-Oxide Fuel Cell Using Ceria-Based Electrolytes. *J. Electrochem. Soc.* **1993**, *140*, 3494.
- (96) Michaels, J. N.; Vayenas, C. G. Styrene Production from Ethylbenzene on Platinum in a Zirconia Electrochemical Reactor. *J. Electrochem. Soc.* **1984**, *131*, 2544.
- (97) Michaels, J. N.; Vayenas, C. G. Kinetics of Vapor-Phase Electrochemical Oxidative Dehydrogenation of Ethylbenzene. *J. Catal.* **1984**, *85*, 477.
- (98) Manton, M. R. S. Oxidation of Butone Over Platinum Catalysts in a Zirconia–Yttria Electrochemical Reactor, Ph.D. Thesis, Massachusetts Institute of Technology, Cambridge, MA, 1986.
- (99) McKenna, E.; Stoukides, M. Modeling of HCN Synthesis in a Solid Electrolyte Fuel Cells. *Chem. Eng. Sci.* **1992**, *47*, 2951.
- (100) Kiratzis, N.; Stoukides, M. The synthesis of Hydrogen Cyanide in a Solid Electrolyte Fuel Cell. *J. Electrochem. Soc.* **1987**, *134*, 1925.
- (101) Othoneos, A.; Kiratzis, N.; Stoukides, M. Modeling of HCN Synthesis in a Solid Electrolyte Fuel Cell. In *Proceedings of the 2nd International Symposium on SOFC*, Athens, Greece; EC Publications, Luxemburg, 1991; p 369.
- (102) Eng, D.; Stoukides, M. Partial Oxidation of Methane in a Solid Electrolyte Cell. In *Proceedings of the 9th International Congress on Catalysis*; Phillips, M. J., Ternan, M., Eds.; The Chemical Institute of Canada: Ontario, Canada, 1988; Vol. 2, p 974.
- (103) Yentekakis, I. V.; Debenedetti, P. G.; Costa, B. A Novel Fused Metal Anode Solid Electrolyte Fuel Cell for Direct Coal Gasification: A Steady-State Model. *Ind. Eng. Chem. Res.* **1989**, *28*, 1414.
- (104) Gür, T. M.; Wise, H.; Huggins, R. A. Method and Apparatus for Partial Oxidation of Methane and Cogeneration of Electrical Energy, U.S. Patent 5,364,506, 1994.
- (105) Ishihara, T.; Hiei, Y.; Takita, Y. Oxidative Reforming of Membrane Using SOFC with LaGaO₃ Based Electrolyte. *Solid State Ionics* **1995**, *79*, 371.
- (106) Hiei, Y.; Ishihara, T.; Takita, Y. Partial Oxidation of Methane for Internally Reformed SOFC. *Solid State Ionics* **1996**, *86–88*, 1267.
- (107) Zhu, H.; Kee, R. J.; Pillai, M. R.; Barnett, S. A. Modeling Electrochemical Partial Oxidation of Methane for Cogeneration of Electricity and Syngas in Solid-Oxide Fuel Cells. *J. Power Sources* **2008**, *183*, 143.
- (108) Neophytides, S.; Vayenas, C. G. Chemical Cogeneration in Solid Electrolyte Cells. The Oxidation of CH₃OH to H₂CO. *J. Electrochem. Soc.* **1990**, *137*, 839.

- (109) Wei, G. L.; Liu, M.; Luo, J. L.; Sanger, A. R.; Chuang, K. T. Influence of Gas Flow Rate on Performance of $\text{H}_2\text{S}/\text{Air}$ Solid Oxide Fuel Cells with $\text{MoS}_2\text{-NiS-Ag}$ Anode. *J. Electrochem. Soc.* **2003**, *150* (4), A463.
- (110) Horita, T.; Sakai, N.; Kawada, T.; Yokokawa, H.; Dokiya, M. Electrochemical Oxidation of Membrane by Alternating Current Electrolysis Using YSZ. *J. Electrochem. Soc.* **1995**, *142*, 2621.
- (111) Cheng, Z.; Zha, S. W.; Aguilar, L.; Wang, D.; Winnick, J.; Liu, M. A Solid Oxide Fuel Cell Running on $\text{H}_2\text{S}/\text{CH}_4$ Fuel Mixtures. *Electrochem. Solid State Lett.* **2006**, *9* (1), A31.
- (112) Ji, B.; Wang, J.; Chu, W.; Yang, W.; Lin, L. Acrylic Acid and Electric Power Cogeneration in an SOFC Reactor. *Chem. Commun.* **2009**, *15*, 2038.
- (113) Iwahara, H.; Uchida, H.; Tanaka, S. High-Temperature Type Proton Conductive Solid Oxide Fuel Cells Using Various Fuels. *J. Appl. Electrochem.* **1986**, *16*, 663.
- (114) Iwahara, H.; Uchida, H.; Morimoto, K.; Hosogi, S. High-temperature C_1 -gas fuel cells using proton-conducting solid electrolytes. *J. Appl. Electrochem.* **1989**, *19*, 448.
- (115) Iwahara, H.; Uchida, H.; Morimoto, K. High Temperature Solid Electrolyte Fuel Cells using Perovskite-Type Oxide Based on BaCeO_3 . *J. Electrochem. Soc.* **1990**, *137*, 462.
- (116) Li, W. S.; Lu, D. S.; Luo, J. L.; Chuang, K. T. Chemicals and Energy Co-Generation from Direct Hydrocarbons/Oxygen Proton Exchange Membrane Fuel Cell. *J. Power Sources* **2008**, *145* (2), 376.
- (117) Zhong, L.; Qi, M.; Wei, G.; Luo, J.; Chuang, K. Intermediate-Temperature H_2S Fuel Cell with a Li_2SO_4 -Based Proton-Conducting Membrane. *Chin. J. Chem. Eng.* **2006**, *14* (1), 51.
- (118) Zhu, B. Advanced Environmental/Energy Technology: Desulfurization and Fuel Cell Cogeneration. *Fuel Cells Bull.* **1999**, *2* (4), 9.
- (119) Seimaniades, S.; Eng, D.; Stoukides, M. In *Proceedings of the World Congress III of Chemical Engineering*, Tokyo, Japan, September 21–25, 1986; Vol. IV, p 399.
- (120) Gür, T. M.; Huggins, R. A. Decomposition of Nitric Oxide on Zirconia in a Solid-State Electrochemical Cell. *J. Electrochem. Soc.* **1979**, *126*, 1067.
- (121) Pancharatnam, S.; Huggins, R. A.; Mason, D. M. Catalytic Decomposition of Nitric Oxide on Zirconia by Electrolytic Removal of Oxygen. *J. Electrochem. Soc.* **1975**, *122*, 869.
- (122) Gür, T. M.; Huggins, R. A. Decomposition of Nitric Oxide Using Solid State Electrolyte. in *Fast Ion Transport in Solids*; Vashishta, P., Mundy, J. N., Shenoy, G. K., Eds.; Elsevier: Amsterdam, 1979; pp 109–112.
- (123) Walsh, K. J.; Fedkiw, P. S. Nitric Oxide Reduction Using Platinum Electrodes on YSZ. *Solid State Ionics* **1997**, *93*, 17.
- (124) Hibino, T.; Inoue, T.; Sano, M. Electrochemical Reduction of NO by Alternating Current Electrolysis Using YSZ as the Solid Electrolyte. Part I. *Solid State Ionics* **2000**, *130*, 19.
- (125) Marwood, M.; Kaloyiannis, A. C.; Vayenas, C. G. Electrochemical Promotion of the NO Reduction by C_2H_4 on Pt/YSZ and by CO on Pd/YSZ. *Ionics* **1996**, *2*, 302.
- (126) Kaneko, H.; Taimatsu, H.; Isaji, H.; Sugano, K. Reduction of Pulse-Injected Nitric Monoxide Using a Zirconia Oxygen Pump-Gauge. *Solid State Ionics* **2000**, *136–137*, 607.
- (127) Lintanf, A.; Djurado, E.; Vernoux, P. Pt/YSZ Electrochemical Catalysts Prepared by Electrostatic Spray Deposition for Selective Catalytic Reduction of NO by C_3H_6 . *Solid State Ionics* **2008**, *178* (39–40), 1998.
- (128) Dorado, F.; de Lucas-Consuegra, A.; Jiménez, C.; Valverde, J. L. Influence of the Reaction Temperature on the Electrochemical Promoted Catalytic Behaviour of Platinum Impregnated Catalysts for the Reduction of Nitrogen Oxides under Lean Burn Conditions. *Appl. Catal., A* **2007**, *321* (1), 86.
- (129) Sakamoto, Y.; Okumura, K.; Shinjoh, H.; Lepage, M.; Brosda, S. Temperature Dependence of Electrochemically Promoted NO Reduction by C_3H_6 Under Stoichiometric Conditions Using Me/YSZ/Au (Me = Rh, RhPt, Pt) Electrochemical Catalysts. *Catal. Today* **2009**, *146*, 229.
- (130) Belyaev, V. D.; Politova, T. I.; Sobyanyan, V. A. N_2O Reduction by CO over Pt Electrode in a Solid Oxide Electrolyte Cell. *Catal. Lett.* **1999**, *57* (1–2), 43.
- (131) Koutsodontis, C.; Hammad, A.; Lepage, M.; Sakamoto, Y.; Fóti, G.; Vayenas, C. G. Electrochemical Promotion of NO Reduction by C_2H_4 in Excess O_2 Using a Monolithic Electropromoted Reactor and Pt-Rh Sputtered Electrodes. *Top. Catal.* **2008**, *50* (1–4), 192.
- (132) Hibino, T.; Ushiki, K.; Kuwahara, Y. Electrochemical Oxygen Pump Using CeO_2 -based Solid Electrolyte for NO_x Detection Independent of O_2 Concentration. *Solid State Ionics* **1997**, *93*, 309.
- (133) Hibino, T.; Ushiki, K.; Kuwahara, Y.; Mizuno, M. Electrochemical Removal of NO in the Presence of Excess O_2 , H_2O and CO_2 Using Sm_2O_3 -Doped CeO_2 as a Solid Electrolyte. *Solid State Ionics* **1996**, *89*, 13.
- (134) Wang, X.; Zhao, Q.; Cai, T. Selective Decomposition of NO in the Presence of Excess O_2 in Electrochemical Cells. *J. Appl. Electrochem.* **2004**, *34* (9), 945.
- (135) Hibino, T. Electrochemical Removal of NO and CH_4 from Oxidizing Atmosphere. *Chem. Lett.* **1994**, *23* (5), 927.
- (136) Hibino, T. Electrochemical Removal of both NO and CH_4 under Lean-Burn Conditions. *J. Appl. Electrochem.* **1995**, *25*, 203.
- (137) Hibino, T.; Ushiki, K.; Kuwahara, Y.; Mizuno, M. Electrochemical Removal of NO and CH_4 in the Presence of Excess O_2 , H_2O and CO_2 Using Sm_2O_3 -Doped CeO_2 as a Solid Electrolyte. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 4297.
- (138) Marwood, M.; Vayenas, C. G. Electrochemical Promotion of the Catalytic Reduction of NO by CO on Palladium. *J. Catal.* **1997**, *170*, 275.
- (139) Kim, S.; Haller, G. L. Solid Electrolyte Aided Studies of NO-CO Reaction on Pd. *Solid State Ionics* **2000**, *136–137*, 693.
- (140) Yentekakis, I. V.; Lambert, R. M.; Tikhov, M. S.; Konsolakis, M.; Kioussis, V. Promotion of Sodium in Emission Control: A Kinetic and Spectroscopic Study of the Pd-catalyzed Reduction of NO by Propene. *J. Catal.* **1998**, *176* (1), 82.
- (141) Yentekakis, I.; Palermo, A.; Filkin, N. C.; Tikhov, M. S.; Lambert, R. M. In Situ Electrochemical Promotion by Sodium of the Platinum-Catalyzed Reduction of NO by Propene. *J. Phys. Chem. B* **1997**, *101*, 3759.
- (142) Pliangos, C.; Raptis, C.; Badas, T.; Tsiplakides, D.; Vayenas, C. G. Electrochemical Promotion of a Classically Promoted Rh Catalyst for the Reduction of NO. *Electrochim. Acta* **2000**, *46* (2–3), 331.
- (143) Pliangos, C.; Raptis, C.; Badas, T.; Vayenas, C. G. Electrochemical Promotion of NO Reduction by C_3H_6 on Rh/YSZ Catalyst-Electrodes. *Solid State Ionics* **2000**, *136–137*, 767.
- (144) Fóti, G.; Lavanchy, O.; Comninellis, C. Electrochemical Promotion of Rh Catalyst in Gas-phase Reduction of NO by Propylene. *J. Appl. Electrochem.* **2000**, *30* (11), 1223.
- (145) Constantinou, I.; Archonta, D.; Brosda, S.; Lepage, M.; Sakamoto, Y.; Vayenas, C. G. Electrochemical Promotion of NO Reduction by C_3H_6 on Rh Catalyst—Electrode Films Supported on YSZ and on Dispersed Rh/YSZ Catalysts. *J. Catal.* **2007**, *251* (2), 400.
- (146) Souentie, S.; Hammad, A.; Brosda, S.; Foti, G.; Vayenas, C. G. Electrochemical Promotion of NO Reduction by C_2H_4 in 10% O_2 Using a Monolithic Electropromoted Reactor with Rh/YSZ/Pt Elements. *J. Appl. Electrochem.* **2008**, *38* (8), 1159.
- (147) Williams, F. J.; Mcleod, N.; Tikhov, M. S.; Lambert, R. M. Electrochemical Promotion of Bimetallic Rh-Ag/YSZ Catalysts for the Reduction of NO under Lean Burn Conditions. *Electrochim. Acta* **2002**, *47* (8), 1259.
- (148) Iwayama, K.; Wang, X.; Sano, M. Selective Decomposition of Nitrogen Monoxide to Nitrogen in the Presence of Oxygen on RnO_3/Ag (cathode)/Yttria-Stabilized Zirconia/Pb (anode). *Appl. Catal., B* **1998**, *19*, 137.
- (149) Awano, M.; Bredikhin, S.; Aronin, A.; Abrosimova, G.; Katayama, S.; Hiramatsu, T. NO_x Decomposition by Electrochemical Reactor with Electrochemically Assembled Multilayer Electrode. *Solid State Ionics* **2004**, *175* (1–4), 605.
- (150) Matsuda, K.; Bredikhin, S.; Maeda, K.; Awano, M. Optimization of an Electrochemical Cell for NO Decomposition by Compositional Control of the Electro-catalytic Electrode. *Solid State Ionics* **2003**, *156* (1–2), 223.
- (151) Matsuda, K.; Bredikhin, S.; Maeda, K.; Awano, M. Optimization of a Composite Working Electrode for a New Family of Electrochemical Cell for NO Decomposition. *J. Am. Ceram. Soc.* **2003**, *86* (7), 1155.
- (152) Matsuda, K.; Bredikhin, S.; Maeda, K.; Awano, M. Novel Low Voltage Electrochemical Cell for NO Decomposition. *Solid State Ionics* **2002**, *149* (3–4), 237.
- (153) Bredikhin, S.; Maeda, K.; Awano, M. Low Current Density Electrochemical Cell for NO Decomposition. *Solid State Ionics* **2002**, *152–153*, 727.
- (154) Bredikhin, S.; Maeda, K.; Awano, M. NO Decomposition by an Electrochemical Cell with Mixed Oxide Working Electrode. *Solid State Ionics* **2001**, *144* (1–2), 1.
- (155) Bredikhin, S.; Maeda, K.; Awano, M. Peculiarity of NO Decomposition by Electrochemical Cell with a Mixed Oxide Working Electrode. *J. Electrochem. Soc.* **2001**, *148* (10), D133.
- (156) Wang, S.; Awano, M.; Maeda, K. Synthesis and Characterization of Dense NiO -(CGO) Cathode Interlayer for Electrocatalytic Reduction of NO. *J. Electrochem. Soc.* **2003**, *150* (12), D209.
- (157) Hansen, K. K.; Christensen, H.; Skou, E. M.; Skaarup, S. V. Electrochemical Reduction of NO and O_2 on Cu/CuO. *J. Appl. Electrochem.* **2000**, *30*, 193.
- (158) Brück, J.; Lintz, H.-G. Combined Kinetic and Potentiometric Measurements of the Reduction of Nitrogen Monoxide on Vanadia Titania Catalysts. *Chem. Eng. Proc.* **1999**, *38*, 571.

- (159) Cicero, D. C.; Jarr, L. A. Application of Ceramic Membranes in Advanced Coal-Based Power Generation Systems. *Sep. Sci. Technol.* **1990**, 25, 1455.
- (160) Wachsmann, E. D.; Jayaweera, P.; Krishnan, K.; Sanjurjo, A. Electrocatalytic Reduction of NO_x on La_{1-x}A_xB_yO_{3-δ} Evidence of Electrically Enhanced Activity. *Solid State Ionics* **2000**, 136–137, 775.
- (161) Hwang, H. J.; Moon, J.-W.; Awano, M. Microstructure and NO Decomposition Behavior of Sol–Gel Derived (La_{0.8}Sr_{0.2})_{0.95}MnO₃/yttria-Stabilized Zirconia Nanocomposite Thin Film. *Mater. Res. Bul.* **2003**, 38 (2), 311.
- (162) Hansen, K. K. Electrochemical Reduction of NO₂ Studied by the Use of Cone-Shaped Electrodes. *Electrochem. Commun.* **2007**, 9 (11), 2721.
- (163) Kammer, K.; Skou, E. M. LSFM Perovskites as Cathodes as the Electrochemical Reduction of NO. *Solid State Ionics* **2005**, 176 (9–10), 915.
- (164) Hwang, H. J.; Awano, M. Preparation of LaCoO₃ Catalytic Thin Film by the Sol–Gel Process and Its NO Decomposition Characteristics. *J. Eur. Ceram. Soc.* **2001**, 21 (10–11), 2103.
- (165) Hansen, K.; Skou, E. M.; Christensen, H. Perovskites as Cathodes for Nitric Oxide Reduction. *J. Electrochem. Soc.* **2000**, 147 (5), 2007.
- (166) Yamaguchi, T.; Sakamoto, W.; Yogo, T.; Hirano, S. I.; Kikuta, K. Synthesis and Catalytic Properties of the Electrochemical NO_x Reduction System. *Catal. Lett.* **2005**, 103 (3–4), 271.
- (167) Hwang, H. J.; Moon, J. W.; Awano, M. Fabrication of Novel Type Solid Electrolyte Membrane Reactors for Exhaust Gas Purification. *J. Eur. Ceram. Soc.* **2004**, 24 (6), 1325.
- (168) Hwang, H. J.; Moon, J. W.; Awano, M. Electrochemical Removal of NO_x by Scandium Doped Zirconia Membrane Reactor with Ceria Buffer Layer. *J. Electroceram.* **2004**, 13 (1–3), 727.
- (169) Park, S.; Song, H. S.; Choi, H.-J.; Moon, J. NO Decomposition Over the Electrochemical Cell of Lanthanum Stannate Pyrochlore and YSZ Composite Electrode. *Solid State Ionics* **2004**, 175 (1–4), 625.
- (170) Walsh, K. J.; Fedkiw, P. S. Nitric Oxide Reduction Using Iridium Electrodes in YSZ. *Solid State Ionics* **1997**, 104, 97.
- (171) Vernoux, P.; Gaillard, F.; Karoum, R.; Billard, A. Reduction of Nitrogen Oxides Over Ir/YSZ Electrochemical Catalysts. *Appl. Catal., B* **2007**, 73 (1–2), 73.
- (172) Goula, G.; Katzourakis, P.; Vakakis, N.; Papadam, T.; Konsolakis, M.; Tikhov, M.; Yentekakis, I. V. The Effect of Potassium on the Ir/C₃H₆ + NO + O₂ Catalytic System. *Catal. Today* **2007**, 127 (1–4), 199.
- (173) Dixon, A. G.; Moser, W. R.; Ma, Y. H. Waste Reduction and Recovery Using O₂-Permeable Membrane Reactors. *Ind. Eng. Chem. Res.* **1994**, 33, 3015.
- (174) Mar'ina, O. A.; Yentekakis, I. V.; Vayenas, C. G.; Palermo, A.; Lambert, R. M. In Situ Controlled Promotion of Catalyst Surfaces via NEMCA: The Effect of Na on the Pt-Catalyzed NO Reduction by H₂. *J. Catal.* **1997**, 166, 218.
- (175) Lambert, R. M.; Harkness, I. R.; Yentekakis, I. V.; Vayenas, C. G. Electrochemical Promotion in Emission Control Catalysis. *Ionics* **1995**, 1, 29.
- (176) Palermo, A.; Tikhov, M. S.; Filkin, N. C.; Lambert, R. M.; Yentekakis, I. V.; Vayenas, C. G. Electrochemical Promotion of NO Reduction by CO and by Propene. *Stud. Surf. Sci. Catal.* **1996**, 101, 513.
- (177) Lambert, R. M.; Williams, F.; Palermo, A.; Tikhov, M. S. Modelling Alkali Promotion in Heterogeneous Catalysis: In Situ Electrochemical Control of Catalytic Reactions. *Top. Catal.* **2000**, 13 (1–2), 91.
- (178) Lambert, R. M.; Palermo, A.; Williams, F. J.; Tikhov, M. S. Electrochemical Promotion of Catalytic Reactions Using Alkali Ion Conductors. *Solid State Ionics* **2000**, 136–137, 677.
- (179) Williams, F.; Palermo, A.; Tikhov, M. S.; Lambert, R. M. First Demonstration of In Situ Electrochemical Control of a Base Metal Catalyst: Spectroscopic and Kinetic Study of the CO + NO Reaction Over Na-Promoted Cu. *J. Phys. Chem. B* **1999**, 103 (45), 9960.
- (180) Vernoux, P.; Gaillard, F.; Lopez, C.; Siebert, E. Coupling Catalysis to Electrochemistry: A Solution to Selective Reduction of Nitrogen Oxides in Lean-burn Engine Exhausts. *J. Catal.* **2003**, 217, 203.
- (181) De Lucas-Consuegra, A.; Dorado, F.; Valverde, J. L.; Vernoux, P. Electrochemical Promotion of Platinum Impregnated Catalyst for the Selective Catalytic Reduction of NO by Propene in Presence of Oxygen. *Appl. Catal., B* **2007**, 73 (1–2), 42.
- (182) Yentekakis, I. V.; Konsolakis, M.; Lambert, R. M.; Palermo, A.; Tikhov, M. Successful Application of Electrochemical Promotion to the Design of Effective Conventional Catalyst Formulations. *Solid State Ionics* **2000**, 136, 783.
- (183) Yentekakis, I. V.; Lambert, R. M.; Tikhov, M. S.; Konsolakis, M.; Kiouisis, V. The Effect of Sodium on the Pd-catalyzed Reduction of NO by Methane. *Appl. Catal., B* **1998**, 18 (3–4), 293.
- (184) Williams, F. J.; Palermo, A.; Tikhov, M. S.; Lambert, R. M. Electrochemical Promotion of the Rhodium-Catalyzed Reduction of NO by Propene: Kinetics and Spectroscopy. *J. Phys. Chem. B* **2001**, 105, 1381.
- (185) Williams, F. J.; Palermo, A.; Tikhov, M. S.; Lambert, R. M. Electrochemical Promotion by Sodium of the Rhodium-catalyzed NO + CO Reaction. *J. Phys. Chem.* **2000**, B 104 (60), 11883.
- (186) De Lucas-Consuegra, A.; Dorado, F.; Jiménez-Borja, C.; Valverde, J. L. Electrochemical Promotion of Pt Impregnated Catalyst for the Treatment of Automotive Exhaust Emissions. *J. Appl. Electrochem.* **2008**, 38 (8), 1151.
- (187) De Lucas-Consuegra, A.; Dorado, F.; Jiménez-Borja, C.; Valverde, J. L. Influence of the Reaction Conditions on the Electrochemical Promotion by Potassium for the Selective Catalytic Reduction of N₂O by C₃H₆ on Platinum. *Appl. Catal., B* **2008**, 78 (3–4), 222.
- (188) De Lucas-Consuegra, A.; Dorado, F.; Jiménez-Borja, C.; Caravaca, Á.; Vernoux, P.; Valverde, J. L. Use of Potassium Conductors in the Electrochemical Promotion of Environmental Catalysis. *Catal. Today* **2009**, 146, 293.
- (189) De Lucas-Consuegra, A.; Caravaca, Á.; Sánchez, P.; Dorado, F.; Valverde, J. L. A New Improvement of Catalysis by Solid-State Electrochemistry: An Electrochemically Assisted NO_x Storage/Reduction Catalyst. *J. Catal.* **2008**, 259 (1), 54.
- (190) De Lucas-Consuegra, A.; Caravaca, Á.; Dorado, F.; Valverde, J. L. Pt/K-β-Al₂O₃ Solid Electrolyte Cell as a “Smart Electrochemical Catalyst” for the Effective Removal of NO_x Under Wet Reaction Conditions. *Catal. Today* **2009**, 146 (1), 330.
- (191) Seimanides, S.; Stoukides, M. Electrochemical Modification of Ag-MgO Catalyst Electrodes During Methane Oxidation. *J. Electrochem. Soc.* **1986**, 133, 1535.
- (192) Belyaev, V. D.; Sobyenin, V. A.; Arzhannikov, V. A.; Neuimin, A. D. *Dokl. Akad. Nauk. SSSR* **1989**, 305, 1389.
- (193) Nagamoto, H.; Hayashi, K.; Inoue, H. Methane Oxidation by Oxygen Transported Through Solid Electrolyte. *J. Catal.* **1990**, 26, 671.
- (194) Belyaev, V. D.; Sobyenin, V. A.; Mar'ina, O. A. Oxidative Dimerisation of Methane on Silver–Palladium Alloy Electrode, Connected with a Solid Oxide Electrolyte. *Izv. Sib. Otd. Akad. Nauk. SSSR, Ser. Ser. Khim.* **1990**, 1, 27.
- (195) Belyaev, V. D.; Bazhan, O. V.; Sobyenin, V. A.; Parmon, V. N. Oxidative Dimerization of Nitric Oxide on Zirconia in a Solid-State Electrochemical Cell. In *New Developments in Selective Oxidation*; Centi, G., Trifiro, F., Eds.; Elsevier: Amsterdam, 1990.
- (196) Tsiakaras, P.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity: 7. The Oxidation of CH₄ on Pt. *J. Catal.* **1993**, 140, 53.
- (197) Tsiakaras, P.; Vayenas, C. G. Oxidative Coupling of CH₄ on Ag Catalyst Electrodes Deposited on ZrO₂ (8 mol % Y₂O₃). *J. Catal.* **1993**, 144, 333.
- (198) Lapena-Rey, N.; Middleton, P. H. The Selective Oxidation of Methane to Ethane and Ethylene in a Solid Oxide Electrolyte Reactor. *Appl. Catal., A* **2003**, 240 (1–2), 207.
- (199) Otsuka, K.; Yokoyama, S.; Morikawa, A. Catalytic Activity and Selectivity Control for Oxidative Coupling of Methane by Oxygen-Pumping Through Yttria-Stabilized Zirconia. *Chem. Lett.* **1985**, 15 (3), 319.
- (200) Otsuka, K.; Morikawa, A. Hydrocarbons, Jpn. Patent 61-30688, 1986.
- (201) Mazanec, T. J. Process for the Electrocatalytic Conversion of Light Hydrocarbons to Synthesis Gas, U.S. Patent 4,793,904, 1988.
- (202) Mazanec, T. J. Process for the Electrocatalytic Oxidation of Low Molecular Weight Hydrocarbons to Higher Weight Hydrocarbons, U.S. Patent 4,802,958, 1989.
- (203) Vayenas, C. G.; Bebelis, S.; Tsiakaras, P.; Yentekakis, Y.; Karasali, H. Non-Faradaic Electrochemical Modification of the Catalytic Activity of Platinum Metals: Reversible Promotion of Platinum Metal Catalysts. *Plat. Met. Rev.* **1990**, 34 (3), 122.
- (204) Pujare, N. U.; Sammells, A. F. Methane Activation to C₂ Hydrocarbon Species in Solid Oxide Fuel Cell. *J. Electrochem. Soc.* **1988**, 135, 2544.
- (205) Steele, B. C. H.; Kelly, I.; Middleton, H.; Rudkin, R. Oxidation of Methane in Solid State Electrochemical Reactors. *Solid State Ionics* **1988**, 28/30, 1547.
- (206) Eng, D.; Stoukides, M. The Catalytic and Electrocatalytic Coupling of Methane Over Yttria-Stabilized Zirconia. *Catal. Lett.* **1991**, 9, 47.
- (207) Otsuka, K.; Suga, K.; Yamanaka, I. Electrochemical Enhancement of Oxidative Coupling of Methane over LiCe-Doped NiO Using Stabilized Zirconia Electrolyte. *Catal. Lett.* **1988**, 1, 423.
- (208) Otsuka, K.; Suga, K.; Yamanaka, I. Electrochemical Control for Oxidative Coupling of Methane Over LiNiO₂ Using Solid Electrolytes. *Chem. Lett.* **1988**, 17 (2), 317.

- (209) Kuchynka, D. J.; Cook, R. L.; Sammells, A. F. Electrochemical Natural Gas Conversion to More Valuable Species. *J. Electrochem. Soc.* **1991**, *138*, 1284.
- (210) White, J. H.; Needham, E. A.; Cook, R. L.; Sammells, A. F. The Electrochemical Oxidative Dimerization of Methane. *Solid State Ionics* **1992**, *53–56*, 149.
- (211) Bebelis, S.; Yentekakis, Y.; Neophytides, S.; Tsiakaras, P.; Karasali, H.; Vayenas, C. G. *Proceedings of the 3rd International Symposium SOFC*; Singhal, S.; Iwahara, H., Eds.; The Electrochemical Society: Pennington, NJ, 1993; p 926.
- (212) Dimoulas, G.; Markos, S.; Tsiakaras, P. Catalytic and Electro-catalytic Activation of Methane Over Manganese Oxide Deposited on YSZ. *Ionics* **1997**, *3*, 453.
- (213) Yentekakis, I. V.; Jiang, Y.; Makri, M.; Vayenas, C. G. Ethylene Production from Methane in a Gas Recycle Electrocatalytic Reactor Separator. *Ionics* **1995**, *1*, 286.
- (214) Bonanos, N. Electrochemical Aspects of Perovskite Proton Conductors. In *Proceedings of the 14th Riso International Symposium on Materials Science*, Roskilde, Denmark, 1993.
- (215) Athanasiou, C.; Marnellos, G.; ten Elshof, J. E.; Tsiakaras, P.; Bouwmeester, H. J. M.; Stoukides, M. Methane Activation on a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ Perovskite: Catalytic and Electrocatalytic Results. *Ionics* **1997**, *3*, 128.
- (216) Tsiakaras, P.; Marnellos, G.; Athanasiou, C.; Stoukides, M.; ten Elshof, J. E.; Bouwmeester, H. J. M. Methane Activation on a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ Perovskite Catalytic and Electrocatalytic Results. *Appl. Catal.* **1998**, *169*, 249.
- (217) Mazanec, T. J.; Cable, T. L.; Frye, J. G.; Kliewer, W. R. Solid-Component Membranes Electrochemical Reactor Components Electrochemical Reactors Use of Membranes Reactor Components and Reactor for Oxidation Reactions, U.S. Patent 5,591,315, 1997.
- (218) Jun, L.; Ling, Z.; Guanzhong, L. Activation of Methane Over Perovskite Catalysts. *Ind. Eng. Chem. Res.* **2009**, *48* (2), 641.
- (219) Kiatkittipong, W.; Tagawa, T.; Goto, S.; Assabumrungrat, S.; Praserttham, P. TPD Study in LSM/YSZ/LaAlO System for the Use of Fuel Cell Type Reactor. *Solid State Ionics* **2004**, *166*, 127.
- (220) Kharton, V. V.; Yaremchenko, A. A.; Valente, A. A.; Sobyamin, V. A.; Belyaev, V. D.; Semin, G. L.; Veniaminov, S. A.; Tsipis, E. V.; Shaula, A. L.; Frade, J. R.; Rocha, J. Methane Oxidation Over Fe-, Co-, Ni- and V-Containing Mixed Conductors. *Solid State Ionics* **2005**, *176* (7–8), 781.
- (221) Haag, S.; van Veen, A. C.; Mirodatos, C. Influence of Oxygen Supply Rates on Performances of Catalytic Membrane Reactors. Application to the Oxidative Coupling of Methane. *Catal. Today* **2007**, *127* (1–4), 157.
- (222) Ten Elshof, J. E.; van Hassel, B. A.; Bouwmeester, H. J. M. Activation of Methane Using Solid Oxide Membranes. *Catal. Today* **1995**, *25*, 397.
- (223) Ten Elshof, J. E.; Bouwmeester, H. J. M.; Verweij, H. Oxidative Coupling of Methane in a Mixed-Conducting Perovskite Membrane Reactor. *Appl. Catal.* **1995**, *130*, 195.
- (224) Taheri, Z.; Nazari, K.; Safekordi, A. A.; Seyed-Matin, N.; Ahmadi, R.; Esmaeili, N.; Tofigh, A. Oxygen Permeation and Oxidative Coupling of methane in Membrane Reactor: A New Facile Synthesis Method for Selective Perovskite Catalyst. *J. Mol. Catal. A—Chem.* **2008**, *286* (1–2), 79.
- (225) Tan, X.; Li, K. Oxidative Coupling of Methane in a Perovskite Hollow Fiber Membrane Reactor. *Ind. Eng. Chem. Res.* **2006**, *45* (1), 142.
- (226) Platon, C. E.; Thomson, W. J. A Comparison of LSCF-6428 and Bys for the Oxidative Conversion of Methane and Ethane. *Ind. Eng. Chem. Res.* **2002**, *41* (26), 6637.
- (227) Zeng, Y.; Lin, Y. S.; Swartz, S. L. Perovskite-Type Ceramic Membrane: Synthesis, Oxygen Permeation and Membrane Reactor Performance for Oxidative Coupling of Methane. *J. Membr. Sci.* **1998**, *150* (1), 87.
- (228) Lu, Y.; Dixon, A. G.; Moser, W. R.; Ma, Y. H.; Balachandram, U. Oxygen-Permeable Dense Membrane Reactor for the Oxidative Coupling of Methane. *J. Membr. Sci.* **2000**, *170* (1), 27.
- (229) Hazbun, E. A. Ceramic Membrane for Hydrocarbon Conversion, U.S. Patent 4,791,079, 1988.
- (230) Hazbun, E. A. Ceramic Membrane and Use Thereof for Hydrocarbon Conversion, U.S. Patent 4,827,071, 1989.
- (231) Shao, Z.; Dong, H.; Xiong, G.; Cong, Y.; Yang, W. Performance of a Mixed-Conducting Ceramic Membrane Reactor with High Oxygen Permeability for Methane Conversion. *J. Membr. Sci.* **2001**, *183* (2), 181.
- (232) Wang, W.; Lin, Y. S. Analysis of Oxidative Coupling of Methane in Dense Oxide Membrane Reactors. *J. Membr. Sci.* **1995**, *103*, 219.
- (233) Lin, Y. S.; Zeng, Y. Catalytic Properties of Oxygen Semipermeable Perovskite-Type Ceramic Membrane Materials for Oxidative Coupling of Methane. *J. Catal.* **1996**, *164*, 220.
- (234) Tan, X.; Pang, Z.; Gu, Z.; Liu, S. Catalytic Perovskite Hollow Fibre Membrane Reactors for Methane Oxidative Coupling. *J. Membr. Sci.* **2007**, *302* (1–2), 109.
- (235) Hibino, T.; Sato, T.; Ushiki, K.; Kuwahara, Y. Membrane Reactor for Oxidative Coupling of CH_4 with an Oxide Ion-Electron Hole Mixed Conductor. *J. Chem. Soc. Faraday Trans.* **1995**, *41*, 4419.
- (236) Hibino, T.; Ushiki, K.; Kuwahara, Y. Oxidative Coupling Reaction of CH_4 Using Oxide Ion and Electron Hole Mixed Conductive $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_3$ Ceramic as a Membrane Reactor. *J. Chem. Soc. Chem. Commun.* **1995**, 1001.
- (237) Wang, H.; Cong, Y.; Yang, W. Oxidative Coupling of Methane in $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ Tubular Membrane Reactors. *Catal. Today* **2005**, *104*, 160.
- (238) Zeng, Y.; Lin, Y. S. Oxidative Coupling of Methane on Oxygen-Semipermeable Yttria-Doped Bismuth Oxide Ceramics in a Reducing Atmosphere. *Ind. Eng. Chem. Res.* **1997**, *36*, 277.
- (239) Zeng, Y.; Lin, Y. S. Catalytic Properties of Yttria Doped Bismuth Oxide Ceramics for Oxidative Coupling of Methane. *Appl. Catal.* **1997**, *159*, 101.
- (240) Zheng, Y.; Lin, Y. S. Oxygen Permeation and Oxidative Coupling of Methane in Yttria Doped Bismuth Oxide Membrane Reactor. *J. Catal.* **2000**, *193*, 58.
- (241) Lu, Y.; Dixon, A. G.; Moser, W. R.; Ma, Y. H.; Balachandran, U. Oxidative coupling of methane using oxygen-permeable dense membrane reactors. *Catal. Today* **2000**, *56*, 297.
- (242) Hamakawa, S.; Hibino, T.; Iwahara, H. Electrochemical Methane Coupling Using Protonic Conductors. *J. Electrochem. Soc.* **1993**, *140*, 459.
- (243) Omata, K.; Yamazaki, O.; Tomita, K.; Fujimoto, K. Oxidative Coupling of Methane on an ABO_3 Type Oxide with Mixed Conductivity. *J. Chem. Soc. Chem. Commun.* **1994**, 1647.
- (244) Akin, F. T.; Lin, Y. S. Controlled Oxidative Coupling of Methane by Ionic Conducting Ceramic Membrane. *Catal. Lett.* **2002**, *78* (1–4), 239.
- (245) Zeng, Y.; Lin, Y. S. Oxidative Coupling of Methane on Improved Bismuth Oxide Membrane Reactors. *AIChE J.* **2001**, *47* (2), 436.
- (246) Akin, F. T.; Lin, Y. S.; Zeng, Y. Comparative Study on Oxygen Permeation and Oxidative Coupling of Methane on Disk-Shaped and Tubular Dense Ceramic Membrane Reactors. *Ind. Eng. Chem. Res.* **2001**, *40* (25), 5908.
- (247) Zeng, Y.; Akin, F. T.; Lin, Y. S. Oxidative Coupling of Methane on Fluorite-Structured Samarium-Yttrium-Bismuth Oxide. *Appl. Catal., A* **2001**, *213* (1), 33.
- (248) Langguth, J.; Dittmeyer, R.; Hofmann, H.; Tomandl, G. Studies on Oxidative Coupling of Methane Using High-Temperature Proton-Conducting Membranes. *Appl. Catal.* **1997**, *158*, 287.
- (249) Chiang, P.-H.; Eng, D.; Stoukides, M. Electrocatalytic Methane Dimerization with a Yb-Doped SrCeO_3 Solid Electrolyte. *J. Electrochem. Soc.* **1991**, *138*, L11.
- (250) Chiang, P.-H.; Eng, D.; Alqahtany, H.; Stoukides, M. Nonoxidative Methane Coupling with the Aid of Solid Electrolytes. *Solid State Ionics* **1992**, *53–56*, 135.
- (251) Mori, K.; Imai, T. Methane Reforming, Jpn. Patent 62-128901, 1987.
- (252) Mori, K.; Iida, K. Decomposition of Methane, Jpn. Patent 62-139889, 1987.
- (253) Woldman, L. S.; Sokolovskii, V. D. Electrocatalytic Methane Coupling in the Absence of Oxygen on a High-Temperature Proton-Conducting Electrolyte. *Catal. Lett.* **1991**, *8*, 61.
- (254) Terai, T.; Li, X.; Tomishige, K.; Fujimoto, K. Development of Catalyst-Membrane System for Oxidative Coupling of Methane by Water. *Chem. Lett.* **1999**, *28* (4), 323.
- (255) White, J. H.; Schwartz, M.; Sammells, A. F. Solid state proton and electron mediating membrane and use in catalytic membrane reactors, U.S. Patent 5,821,185, 1998.
- (256) Wang, B. H.; Wang, J. D.; Liu, R. Q.; Xie, Y. H.; Li, Z. J. Synthesis of Ammonia from Natural Gas at Atmospheric Pressure with Doped Ceria- $\text{Ca}_3(\text{PO}_4)_2$ - K_3PO_4 Composite Electrolyte and Its Proton Conductivity at Intermediate Temperature. *J. Solid State Electrochem.* **2006**, *11* (1), 27.
- (257) Liu, Y. T.; Tan, X. Y.; Li, K. Nonoxidative Methane Coupling in a $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ (SCYb) Hollow Fiber Membrane Reactor. *Ind. Eng. Chem. Res.* **2006**, *45* (11), 3782.
- (258) Hamakawa, S.; Hibino, T.; Iwahara, H. Electrochemical Hydrogen Permeation in a Proton-Hole Mixed Conductor and Its Application to a Membrane Reactor. *J. Electrochem. Soc.* **1994**, *141*, 1720.
- (259) Hibino, T.; Masegi, A.; Iwahara, H. Electrocatalytic Oxidation of Methane by Alternating Current Electrolysis Using YSZ. *J. Electrochem. Soc.* **1995**, *142*, L72.

- (260) Hibino, T.; Ushiki, K.; Kuwahara, Y.; Masegi, A.; Iwahara, H. Oxidative Coupling of CH₄ Using Alkali-Metal Ion Conductors as a Solid Electrolyte. *J. Chem. Soc. Faraday Trans.* **1996**, 92, 2393.
- (261) Weissbart, J.; Ruka, R. A Solid Electrolyte Fuel Cell. *J. Electrochem. Soc.* **1962**, 109, 723.
- (262) Mazanec, T. J.; Cable, T. L.; Frye, J. G., Jr. Electrocatalytic Cells for Chemical Reaction. *Solid State Ionics* **1992**, 53/56, 111.
- (263) Jiang, Y.; Yentekakis, I. V.; Vayenas, C. G. Methane to Ethylene with 85% Yield in a Gas Recycle Electrocatalytic Reactor—Separator. *Science* **1994**, 264, 1563.
- (264) Gal'vita, V. V.; Belyaev, V. D.; Parmon, V. N.; Sobyannin, V. A. Conversion of Methane to Synthesis Gas over Pt Electrode in a Cell with Oxide Electrolyte. *Catal. Lett.* **1996**, 39, 209.
- (265) Sobyannin, V. A.; Belyaev, V. D. Gas-Phase Electrolysis: Methane Oxidation to Syngas in a Solid Oxide Fuel Cell Reactor. *Solid State Ionics* **2000**, 136–137, 747.
- (266) Onuma, S.; Kaimai, A.; Kawamura, K.; Nigara, Y.; Kawada, T.; Misusaki, J.; Tagawa, H. Influence of the Coexisting Gases on the Electrochemical Reaction Rates between 873 and 1173 K in a CH₄–H₂O/Pt/YSZ System. *Solid State Ionics* **2000**, 132, 309.
- (267) Zurek, S.; Mosialek, M.; Tomczyk, P.; Oblakowska, D. Investigation of the Partial Oxidation of Methane at the Interface Metal (Pt, Au) Vertical Bar [YSZ]. *J. Electrocer.* **2005**, 15 (1), 83.
- (268) Sobyannin, V. A.; Belyaev, V. D.; Gal'vita, V. V. Syngas Production from Methane in an Electrochemical Membrane Reactor. *Catal. Today* **1998**, 42 (3), 337.
- (269) Horita, T.; Sakai, N.; Kawada, T.; Yokokawa, H.; Dokiya, M. Oxidation and Steam Reforming of CH₄ on Ni and Fe Anodes Under Low Humidity Conditions in Solid Oxide Fuel Cells. *J. Electrochem. Soc.* **1996**, 143, 1161.
- (270) Tragert, W. E.; Fullman, R. L.; Carter, R. E. Fuel Cell, U. S. Patent 3,138,490, 1964.
- (271) White, D. W. A Zirconia Electrolyte Fuel Cell. *Rev. Energ. Primaire* **1966**, 2, 10.
- (272) Yentekakis, I. V.; Neophytides, S.; Kaloyiannis, A. C.; Vayenas, C. G. Kinetics of Internal Steam Reforming of CH₄ and Their Effect on SOFC Performance. In *Proceedings of the 3rd International Symposium on SOFC*; Singhal, S., Iwahara, H., Eds.; The Electrochemical Society: Pennington, NJ, 1993; p 904.
- (273) Yamada, T.; Hiei, Y.; Akbay, T.; Ishihara, T.; Takita, Y. Simultaneous Generation of Synthesis Gas and Electric Power by Internal Reforming Fuel Cells Utilizing LaGaO₃ Based Electrolytes. *Solid State Ionics* **1998**, 113–115, 253.
- (274) Hamakawa, S.; Hayakawa, T.; Suzuki, K.; Murata, K.; Takehira, K.; Yoshino, S.; Nakamura, J.; Uchijima, T. Methane conversion into synthesis gas using an electrochemical membrane reactor. *Solid State Ionics* **2000**, 136–137, 761.
- (275) Ishihara, T.; Yamada, T.; Akbay, T.; Takita, Y. Partial Oxidation of Methane over Fuel Cell Type Reactor for Simultaneous Generation of Synthesis Gas and Electric Power. *Chem. Eng. Sci.* **1999**, 54, 1535.
- (276) Ishihara, T.; Takita, Y. Partial Oxidation of Methane into Syngas with Oxygen Permeating Ceramic Membrane Reactors. *Catal. Surv. Jpn.* **2000**, 4 (2), 125.
- (277) Yentekakis, I. V.; Jiang, Y.; Neophytides, S.; Bebelis, S.; Vayenas, C. G. Catalysis, Electrocatalysis and Electrochemical Promotion of the Steam Reforming of Methane over Ni Film Ni-YSZ Cermet Anodes. *Ionics* **1995**, 1, 491.
- (278) Lee, A. L.; Zabransky, R. F.; Huber, W. J. Internal Reforming Development for Solid Oxide Fuel Cells. *Ind. Eng. Chem. Res.* **1990**, 29, 766.
- (279) Ahmed, K.; Foger, K. Kinetics of Internal Steam Reforming of Methane on Ni/YSZ-Based Anodes for Solid Oxide Fuel Cells. *Catal. Today* **2000**, 63 (2–4), 479.
- (280) Ledjeff, K.; Rohrbach, T.; Schaumberg, G. Internal Reforming for Solid Oxide Fuel Cells. In *Proceedings of the 2nd International Symposium on SOFC*; Grosz, F. et al., Eds.; Commission of the European Communities: Luxembourg, 1991; p 323.
- (281) Zanibelli, L.; Flego, C.; Perego, C.; Rizzo, C. A Catalytic Study of Ni/YSZ Cermets for Internal Reforming SOFC. *Proceedings of the 1st European SOFC Forum*, Lucerne, Switzerland, 1994; Vol. 1, p 207.
- (282) Hsiao, H. C.; Selman, J. R. New Developments in Fuel Cells. *Proceedings of the 3rd International Symposium on SOFC*; Singhal, S., Iwahara, H., Eds.; The Electrochemical Society: Pennington, NJ, 1993; p 895.
- (283) Triantafyllopoulos, N. C.; Neophytides, S. G. The Nature and Binding Strength of Carbon Adspecies Formed During the Equilibrium Dissociative Adsorption of CH₄ on Ni-YSZ Cermet Catalysts. *J. Catal.* **2003**, 217 (2), 324.
- (284) Bebelis, S.; Zeritis, A.; Tiropiani, C.; Neophytides, S. G. Intrinsic Kinetics of Internal Steam Reforming of CH₄ over a Ni-YSZ-Cermet Catalyst-Electrode. *Ind. Eng. Chem. Res.* **2000**, 39 (12), 4920.
- (285) Bebelis, S.; Neophytides, S. AC Impedance Study of Ni-YSZ Cermet Anodes in Methane-Fueled Internal Reforming YSZ Fuel Cells. *Solid State Ionics* **2002**, 152–153, 447.
- (286) Triantafyllopoulos, N. C.; Neophytides, S. G. Dissociative Adsorption of CH₄ on NiAu/YSZ: The Nature of Adsorbed Carbonaceous Species and the Inhibition of Graphitic C Formation. *J. Catal.* **2006**, 239 (1), 187.
- (287) Gavrielatos, I.; Drakopoulos, V.; Neophytides, S. G. Carbon Tolerant Ni-Au SOFC Electrodes Operating under Internal Steam Reforming Conditions. *J. Catal.* **2008**, 259 (1), 75.
- (288) Gavrielatos, I.; Neophytides, S. High Tolerant to Carbon Deposition Ni-based Electrodes under Internal Steam Reforming Conditions. *ECS Trans.* **2007**, 7, 1483.
- (289) Jin, W.; Gu, X.; Li, S.; Huang, P.; Xu, N.; Shi, J. Experimental and Simulation Study on a Catalyst Packed Tubular Dense Membrane Reactor for Partial Oxidation of Methane to Syngas. *J. Chem. Eng. Sci.* **2000**, 55 (14), 2617.
- (290) Gu, X.; Jin, W.; Chen, C.; Xu, N.; Shi, J.; Ma, Y. H. YSZ–SrCo_{0.4}Fe_{0.6}O_{3–δ} Membranes for the Partial Oxidation of Methane to Syngas. *AIChE J.* **2002**, 48 (9), 2051.
- (291) Zhang, C.; Chang, X. F.; Dong, X. F.; Jin, W.; Xu, N. The Oxidative Steam Reforming of Methane to Syngas in a Thin Tubular Mixed-Conducting Membrane Reactor. *J. Membr. Sci.* **2008**, 320 (1–2), 401.
- (292) Feng, S. J.; Ran, S.; Zhu, D. C.; Liu, W.; Chen, C. S. Synthesis Gas Production from Methane with SrFeCo_{0.5}O₅ Membrane Reactor. *Energy Fuels* **2004**, 18 (2), 385.
- (293) Chen, C.-S.; Feng, S.-J.; Ran, S.; Zhu, D.-C.; Liu, W.; Bouwmeester, H. J. M. Conversion of Methane to Syngas by a Membrane-Based Oxidation-Reforming Process. *Angew. Chem.—Int. Ed.* **2003**, 42 (42), 5196.
- (294) Zhang, X.; Ohara, S.; Chen, H.; Fukui, T. Conversion of Methane to Syngas in a Solid Oxide Fuel Cell with Ni-SDC Anode and LSGM Electrolyte. *Fuel* **2002**, 81, 989.
- (295) Lin, Y.; Pillai, M. R.; Bierschenk, D. M.; Stevens, B. L.; Barnett, S. A. Methane Partial Oxidation Using a (La_{0.6}Sr_{0.4})(Ga_{0.8}Mg_{0.05}Co_{0.15})O_{3–δ} Membrane. *Catal. Lett.* **2008**, 124 (1–2), 1.
- (296) Yin, X.; Hong, L.; Liu, Z. L. Asymmetric Tubular Oxygen-Permeable Ceramic Membrane Reactor for Partial Oxidation of Methane. *J. Phys. Chem. C* **2007**, 111 (26), 9194.
- (297) Yin, X.; Hong, L.; Liu, Z. J. Integrating Air Separation with Partial Oxidation of Methane—A Novel Configuration of Asymmetric Tubular Ceramic Membrane Reactor. *Membr. Sci.* **2008**, 311 (1–2), 89.
- (298) Hamakawa, S.; Shiozaki, R.; Hayakawa, T.; Suzuki, K.; Murata, K.; Takehira, K.; Koizumi, M.; Nakamura, J.; Uchijima, T. Partial Oxidation of Methane to Synthesis Gas Using Ni/Ca_{0.8}Sr_{0.2}TiO₃ Anode Catalyst. *J. Electrochem. Soc.* **2000**, 147 (3), 839.
- (299) Belyaev, V. D.; Politova, T. I.; Mar'ina, O. A.; Sobyannin, V. A. Internal Steam Reforming of Methane over Ni-Based Electrode in Solid Oxide Fuel Cell. *Appl. Catal.* **1995**, 133, 47.
- (300) Alqahtany, H.; Eng, D.; Stoukides, M. Synthesis Gas Production from Methane Over an Ion Electrode in a Solid Electrolyte Cell. *J. Electrochem. Soc.* **1993**, 140, 1677.
- (301) Alqahtany, H.; Eng, D.; Stoukides, M. Methane Steam Reforming Over Fe Electrodes in a Solid Electrolyte Cell. *Energy Fuels* **1993**, 7, 495.
- (302) Kungolos, A.; Tsiakaras, P.; Stoukides, M. Production of Synthesis Gas in a Solid Electrolyte Cell. *Ionics* **1995**, 1, 214.
- (303) Norby, T.; Osborg, P. A.; Dyrbye, O.; Hildrum, R.; Seiersten, M.; Glénne, R. XPS and SEM Studies of Ca- and Ni-substituted LaCrO₃ after quenching from reducing and oxidizing atmospheres at 800 °C. *Proceedings of the 1st European SOFC Forum*, Lucerne, Switzerland, 1994; Vol. 1, p 217.
- (304) Tagawa, T.; Kuroyanagi, K.; Goto, S.; Assabumrungrat, S.; Praserttham, P. Selective Oxidation of Methane in a SOFC-Type Reactor: Effect of Applied Potential. *Chem. Eng. J.* **2003**, 93 (1), 3.
- (305) Hibino, T.; Masegi, A.; Iwahara, H. Electrocatalytic Oxidation of Methane by Alternating Current Electrolysis Using Yttria Stabilized Zirconia. *J. Electrochem. Soc.* **1995**, 142, 3262.
- (306) Hamakawa, S.; Koizumi, M.; Sato, K.; Nakamura, J.; Uchijima, T.; Murata, K.; Hayakawa, T.; Takehira, K. Synthesis Gas Production in Methane Conversion using the Pd/Yttria-Stabilized Zirconia/Ag Electrochemical Membrane System. *Catal. Lett.* **1998**, 52, 191.
- (307) Huang, T.-J.; Li, J.-F. Direct Methane Oxidation Over a Bi₂O₃–GDC System. *J. Power Sources* **2007**, 173 (2 SI), 959.
- (308) Sato, K.; Nakamura, J.; Uchijima, T.; Hayakawa, T.; Hamakawa, S.; Tsunoda, T.; Takehira, K. Partial Oxidation of CH₄ to Synthesis Gas Using an Rh/YSZ/Ag Electrochemical Membrane Reactor. *J. Chem. Soc. Faraday Trans.* **1995**, 91, 1655.

- (309) Takehira, K.; Hayakawa, T.; Hamakawa, S.; Tsunoda, T.; Sato, K.; Nakamura, J.; Uchijima, T. Direct Partial Oxidation of Methane into Synthesis Gas Over Rh/YSZ/Ag. *Catal. Today* **1996**, *29*, 39.
- (310) Ritchie, J. T.; Richardson, J. T.; Luss, D. Ceramic Membrane Reactor for Synthesis Gas Production. *AIChE J.* **2001**, *47* (9), 2092.
- (311) Maiya, P. S.; Anderson, T. J.; Mieville, R. L.; Dusek, J. T. Maximizing H₂ Production by Combined Partial Oxidation of CH₄ and Water Gas Shift Reaction. *Appl. Catal., A* **2000**, *196*, 65.
- (312) Sato, K.; Nakamura, J.; Uchijima, T.; Hayakawa, T.; Hamakawa, S.; Tsunoda, T.; Shishido, T.; Takehira, K. Role of Rhodium Anode in the YSZ-Aided CH₄ Oxidation into Syngas. *Solid State Ionics* **2000**, *136–137*, 753.
- (313) Baranova, E. A.; Fóti, G.; Comninellis, C. Current-assisted Activation of Rh/TiO₂/YSZ Catalyst. *Electrochem. Commun.* **2004**, *6* (4), 389.
- (314) Vernoux, P.; Guindet, J.; Gehain, E.; Kleitz, M. Catalysts for Continuous Methane Reforming in Medium Temperature SOFC. In *Proceedings of the 5th Symposium on SOFC*, Aachen, Germany, 1997.
- (315) Bebelis, S.; Neophytides, S.; Kotsionopoulos, N.; Triantafyllopoulos, N.; Colomer, M. T.; Jurado, J. Methane Oxidation on Composite Ruthenium Electrodes in YSZ Cells. *Solid State Ionics* **2006**, *177* (19–25), 2087.
- (316) Wang, H. H.; Cong, Y.; Yang, W. S. Partial Oxidation of Methane to Syngas in Tubular Oxygen-Permeable Reactor. *Chin. Sci. Bul.* **2002**, *47* (7), 534.
- (317) Tong, J.; Yang, W.; Suda, H.; Haraya, K. Initiation of Oxygen Permeation and POM Reaction in Different Mixed Conducting Ceramic Membrane Reactors. *Catal. Today* **2006**, *118* (1–2), 144.
- (318) Murphy, S. M.; Slade, D. A.; Nordheden, K. J.; Stagg-Williams, S. M. Synthesis Gas Generation Using Ionic/Electronic Oxygen Permeable Membranes. In *2005 AIChE Annual Meeting, Conference Proceedings*; American Chemical Society: Washington, DC, 2005; p 2177.
- (319) Jin, W.; Li, S.; Huang, P.; Xu, N.; Shi, J.; Lin, Y. S. Tubular Lanthanum Cobaltite Perovskite Type Membrane Reactors for Partial Oxidation of Methane to Syngas. *J. Membr. Sci.* **2000**, *166*, 13.
- (320) Lu, X.; Liu, M. Effect of Surface Modification on Catalytic Properties of Sr_{0.25}Bi_{0.3}FeO_{3-δ} Membranes. *Electrochem. Solid State Lett.* **1999**, *2* (9), 452.
- (321) Ishihara, T.; Tsuruta, Y.; Todaka, T.; Nishiguchi, H.; Takita, Y. Fe Doped LaGaO₃ Perovskite Oxide as an Oxygen Separating Membrane for CH₄ Partial Oxidation. *Solid State Ionics* **2002**, *152–153*, 709.
- (322) Hamakawa, S.; Sato, K.; Inoue, T.; Nishioka, M.; Kobayashi, K.; Mizukami, F. Design of One-Component Ceramic Membrane-Reactor for Natural Gas Conversion. *Catal. Today* **2006**, *117* (1–3), 297.
- (323) Hamakawa, S.; Yoshino, S.; Nakamura, J.; Liu, Y.; Tsyganok, A.; Suzuki, K.; Murata, K.; Hayakawa, T. Role for Lattice Oxygen Migration in Ni-Based Catalyst for Natural Gas Conversion. *Electrochem. Solid State Lett.* **2001**, *4* (10), D9.
- (324) Hamakawa, S.; Hayakawa, T.; Mizukami, F. Research on a Ceramics Membrane Reactor for Natural Gas Conversion. *Catal. Surv. Asia* **2005**, *9* (2), 95.
- (325) Balachandran, U.; Dusek, J. T.; Mieville, R. L.; Poeppel, R. B.; Kleefisch, M. S.; Pei, S.; Kobylinski, T. P.; Udovich, C. A.; Bose, A. C. Dense Ceramic Membranes for Partial Oxidation of Methane to Syngas. *Appl. Catal.* **1995**, *133*, 19.
- (326) Balachandran, U.; Dusek, J. T.; Sweeney, S. M.; Mieville, R. L.; Poeppel, R. B.; Maiya, P. S.; Kleefisch, M. S.; Kobylinski, T. P.; Udovich, C. A.; Bose, A. C. Methane to Syngas via Ceramic Membranes. *Am. Ceram. Soc. Bull.* **1995**, *74*, 71.
- (327) Pei, S.; Kleefisch, M. S.; Kobylinski, T. P.; Faber, J.; Udovich, C. A.; Zhang-McCoy, V.; Dabrowski, B.; Balachandran, U.; Mieville, R. L.; Poeppel, R. B. Failure Mechanisms of Ceramic Membrane Reactors in Partial Oxidation of Methane to Syngas. *Catal. Lett.* **1995**, *30*, 201.
- (328) Balachandran, U.; Dusek, J. T.; Maiya, P. S.; Ma, B.; Mieville, R. L.; Kleefisch, M. S.; Udovich, C. A. Ceramic Membrane Reactor for Converting Methane to Syngas. *Catal. Today* **1997**, *36*, 265.
- (329) Balachandran, U.; Ma, B. Mixed-Conducting Dense Ceramic Membranes for Air Separation and Natural Gas Conversion. *J. Solid State Electrochem.* **2006**, *10* (8), 617.
- (330) Ikeguchi, M.; Mimura, T.; Sekine, Y.; Kikuchi, E.; Matsukata, M. Reaction and Oxygen Permeation Studies in Sm_{0.4}Ba_{0.6}Fe_{0.8}Co_{0.2}O_{3-δ} Membrane Reactor for Partial Oxidation of Methane to Syngas. *Appl. Catal., A* **2005**, *290* (1–2), 212.
- (331) Wachsmann, E. D.; Clites, T. L. Stable Mixed-Conducting Bilayer Membranes for Direct Conversion of Methane to Syngas. *J. Electrochem. Soc.* **2002**, *149* (3), A242.
- (332) Lu, H.; Tong, J.; Cong, Y.; Yang, W. Partial Oxidation of Methane in Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} Membrane Reactor at High Pressures. *Catal. Today* **2005**, *104* (2–4), 154.
- (333) Shao, Z.; Xiong, G.; Dong, H.; Yang, W.; Lin, L. Synthesis, Oxygen Permeation Study and Membrane Performance of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} Oxygen-Permeable Dense Ceramic Reactor for Partial Oxidation of Methane to Syngas. *Sep. Purif. Technol.* **2001**, *25* (1–3), 97.
- (334) Dong, H.; Shao, Z. P.; Xiong, G. X.; Tong, J.; Sheng, S.; Yang, W. Investigation on POM Reaction in a New Perovskite Membrane Reactor. *Catal. Today* **2001**, *67* (1–3), 3.
- (335) Tong, J.; Yang, W.; Cai, R.; Zhu, B.; Lin, L. Novel and Ideal Zirconium-Based Dense Membrane Reactors for Partial Oxidation of Methane to Syngas. *Catal. Lett.* **2002**, *78* (1–4), 129.
- (336) Löfberg, A.; Bodet, H.; Pirovano, C.; Steil, M. C.; Vannier, R.-N.; Bordes-Richard, E. Bi₂V_{1-x}Me₂O_{5.5-δ} (Me = Ta, Ni) Membranes for Selective Oxidation of C₁–C₃ Alkanes in a Catalytic Dense Membrane Reactor. *Catal. Today* **2006**, *117* (1–3), 168.
- (337) Li, R.; Yu, C.; Shen, S. Partial Oxidation of Methane To Syngas Using Lattice Oxygen of La_{1-x}Sr_xFeO₃ Perovskite Oxide Catalysts Instead of Molecular Oxygen. *J. Nat. Gas Chem.* **2002**, *11*, 137.
- (338) Boivin, J. C.; Mairesse, G. Reactivity of Surface and Bulk Oxygen in La_{1-x}Ca_xFeO_{3-y} System with Respect to Methane Oxidation. *Chem. Mater.* **1998**, *10* (10), 2870.
- (339) Goffe, R. A.; Mason, D. M. Electrocatalytic Oxidation of Hydrocarbons on a Stabilized-Zirconia Electrolyte Employing Gold or Platinum Electrodes. *J. Electrochem. Soc.* **1981**, *11*, 447.
- (340) Ong, B. G.; Chiang, C. G.; Mason, D. M. Electrocatalytic Role of Stabilized Zirconia on the Anodic Current-Over Potential Behavior in Hydrocarbon Fuel Cells. *Solid State Ionics* **1981**, *3/4*, 447.
- (341) Nguyen, B. C.; Lin, T. A.; Mason, D. M. Electrocatalytic Reactivity of Hydrocarbons on a Zirconia Electrolyte Surface. *J. Electrochem. Soc.* **1986**, *133*, 1807.
- (342) Sandler, Y. L. The Response of the Stabilized Zirconia Galvanic Cell to Membrane–Oxygen Mixtures. *J. Electrochem. Soc.* **1971**, *118*, 1378.
- (343) Christ, H. J.; Sockel, H. G. Determination of Oxygen Activities in Highly Diluted Gas Mixtures Using a Solid-State Electrolyte Cell. *High Temp. Technol.* **1987**, *5*, 123.
- (344) Belyaev, V. D.; Sobyanin, V. A.; Demin, A. K.; Lipilin, A. S.; Zapesotskii, V. E. The Influence of Electrochemical Pumping of Oxygen Through a Solid Oxide Electrolyte on the Catalytic Properties of Platinum in Methane Oxidation. *Mendeleev Commun.* **1991**, 53.
- (345) Mar'ina, O. A.; Sobyanin, V. A.; Belyaev, V. D.; Parmon, V. N. The Effect of Electrochemical Oxygen Pumping on Catalytic Properties of Ag and Au Electrodes at Gas-Phase Oxidation of CH₄. *Catal. Today* **1992**, *13*, 567.
- (346) Goula, G.; Kioussis, V.; Nalbandian, L.; Yentekakis, I. V. Catalytic and Electrocatalytic Behavior of Ni-Based Cermet Anodes Under Internal Dry Reforming of CH₄+CO₂ Mixtures in SOFCS. *Solid State Ionics* **2006**, *177*, 2119.
- (347) Bonanos, N. Electrochemical Studies of Methane Oxidation on Silver, Platinum and Nickel/Zirconia. In *Proceedings of the 2nd Nordic Symposium on High Temperature Fuel Cells*, Geilo, Norway, 1994.
- (348) Kiratzis, N.; Stoukides, M. The Synthesis of HCN in a Solid Electrolyte Cell. *J. Catal.* **1991**, *132*, 257.
- (349) Yentekakis, I. V. Open and Closed-Circuit Study of an Intermediate Temperature SOFC Directly Fueled with Simulated Biogas Mixtures. *J. Power Sources* **2006**, *160*, 422.
- (350) Frantzis, A. D.; Bebelis, S.; Vayenas, C. G. Electrochemical Promotion (NEMCA) of CH₄ and C₂H₄ Oxidation on Pd/YSZ and Investigation of the Origin of NEMCA via AC Impedance Spectroscopy. *Solid State Ionics* **2000**, *136–137*, 863.
- (351) Roche, V.; Karoum, R.; Billard, A.; Revel, R.; Vernoux, P. J. Electrochemical Promotion of Deep Oxidation of Methane on Pd/YSZ. *Appl. Electrochem.* **2008**, *38* (8), 1111.
- (352) Jiménez-Borja, C.; Dorado, F.; de Lucas-Consuegra, A.; García-Vargas, J. M.; Valverde, J. L. Complete Oxidation of Methane on Pd/YSZ and Pd/CeO₂/YSZ by Electrochemical Promotion. *Catal. Today* **2009**, *146*, 326.
- (353) Gorte, R. J.; Vohs, J. M. Novel SOFC Anodes for the Direct Electrochemical Oxidation of Hydrocarbons. *J. Catal.* **2003**, *216* (1–2), 477.
- (354) Kim, H.; Lu, C.; Worrell, W. L.; Vohs, J. M.; Gorte, R. J. Cu-Ni Cermet Anodes for Direct Oxidation of Methane in Solid-Oxide Fuel Cells. *J. Electrochem. Soc.* **2002**, *149* (3), A247.
- (355) Gorte, R. J.; Park, S.; Vohs, J. M.; Wang, C. Anodes for Direct Oxidation of Dry Hydrocarbons in a Solid-Oxide Fuel Cell. *Adv. Mater.* **2000**, *12* (19), 1465.
- (356) La Rosa, D.; Sin, A.; Lo Faro, M.; Monforte, G.; Antonucci, V.; Arico, A. S. Mitigation of Carbon Deposits Formation in Intermediate Temperature Solid Oxide Fuel Cells Fed with Dry Methane by Anode Doping with Barium. *J. Power Sources* **2009**, *193*, 160.

- (357) Lu, X. C.; Zhu, J. H. Cu(Pd)-Impregnated $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ Anodes for Direct Utilization of Methane in SOFC. *Solid State Ionics* **2007**, *178* (25–26), 1467.
- (358) Jiang, S. P.; Chen, X. J.; Chan, S. H.; Kwok, J. T. GDC-Impregnated ($\text{La}_{0.75}\text{Sr}_{0.25}$) ($\text{Cr}_{0.5}\text{Mn}_{0.5}$) O_3 Anodes for Direct Utilization of Methane in Solid Oxide Fuel Cells. *J. Electrochem. Soc.* **2006**, *153* (5), A850.
- (359) Tao, S.; Irvine, J. T. S. Catalytic Properties of the Perovskite Oxide $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Fe}_{0.5}\text{O}_{3-\delta}$ in Relation to Its Potential as a Solid Oxide Fuel Cell Anode Material. *Chem. Mater.* **2004**, *16* (21), 4116.
- (360) Metcalfe, I. S.; Baker, R. T. Temperature Programmed Investigation of La(Ca)CrO₃ Anode for the Oxidation of Methane in Solid Oxide Fuel Cells. *Catal. Today* **1996**, *27*, 285.
- (361) Marina, O. A.; Mogensén, M. High Temperature Conversion of Methane on a Composite Gadolinia Based Ceria Gold Anode. *Appl. Catal., A* **1999**, *189*, 117.
- (362) Metcalfe, I. S.; Middleton, P. H.; Petrolekas, P.; Steele, B. C. H. Hydrocarbon Activation in Solid-State Electrochemical Cells. *Solid State Ionics* **1992**, *57*, 259.
- (363) Baker, R. T.; Metcalfe, I. S.; Middleton, P. H.; Steele, B. C. H. Evaluation of Perovskite Anodes for the Complete Oxidation of Dry Methane in Solid Oxide Fuel Cells. *Solid State Ionics* **1994**, *72*, 328.
- (364) Gür, T. M.; Wise, H.; Huggins, R. A. Partial Oxidation of Methane Catalysed by $\text{YBa}_2\text{Cu}_3\text{O}_x$ in a Solid State Electrochemical Reactor. *Catal. Lett.* **1994**, *23*, 387.
- (365) Ji, Y.; Huang, Y.-H.; Ying, J.-R.; Goodenough, J. B. Electrochemical Performance of La-Doped $\text{Sr}_2\text{MgMoO}_{6-\delta}$ in Natural Gas. *Electrochem. Commun.* **2007**, *9* (8), 1881.
- (366) Gur, T. M.; Raistrick, I. D.; Huggins, R. A. Steady State D-C Polarization Characteristics of the O₂/Pt/Stabilized Zirconia Interface. *J. Electrochem. Soc.* **1980**, *127* (12), 2620.
- (367) Chen, X. J.; Khor, K. A.; Chan, S. H. Suppression of carbon deposition at CeO₂-modified Ni/YSZ anodes in weakly humidified CH₄ at 850°C. *Electrochem. Solid State Lett.* **2005**, *8* (2), A79.
- (368) Hibino, T.; Hamakawa, S.; Suzuki, T.; Iwahara, H. Recycling of carbon dioxide using a proton conductor as a solid electrolyte. *J. Appl. Electrochem.* **1994**, *24*, 126.
- (369) Borry, R. W., III.; Lu, E. C.; Kim, Y.-H.; Iglesia, E. Non-Oxidative Catalytic Conversion of Methane with Continuous Hydrogen Removal. *Stud. Surf. Sci. Catal.* **1998**, *119*, 403.
- (370) Belyaev, V. D.; Gal'vita, V. V.; Gorelov, V. P.; Sobyenin, V. A. Oxidation of Methane Over Platinum in a Solid Proton-Conducting Electrolyte Cell. *Catal. Lett.* **1995**, *30*, 151.
- (371) Belyaev, V. D.; Sobyenin, V. A.; Gorelov, V. P.; Gal'vita, V. V. Effect of Hydrogen Pumping on the Rate of Methane Oxidation over Pt Electrode. *Catal. Today* **1995**, *24*, 301.
- (372) Coors, W. G. Protonic Ceramic Fuel Cells for High-Efficiency Operation with Methane. *J. Power Sources* **2003**, *118*, 150.
- (373) Coors, W. G. Steam Reforming and Water-Gas Shift by Steam Permeation in a Protonic Ceramic Fuel-Cell. *J. Electrochem. Soc.* **2004**, *151*, A994.
- (374) Yamaguchi, S.; Yamamoto, S.; Tsuchiya, B.; Nagata, S.; Shishido, T. Construction of Fuel Reformer Using Proton Conducting Oxides Electrolyte and Hydrogen-Permeable Metal Membrane Cathode. *J. Power Sources* **2005**, *45*, 712.
- (375) Cales, B.; Baumard, J. F. Production of Hydrogen by Direct Thermal-Decomposition of Water. *High Temp.–High Pressure* **1982**, *14*, 681.
- (376) Lede, J.; Lapique, F.; Villermaux, J.; Cales, B.; Ounalli, A.; Baumard, J. F.; Antony, A. M. Production of Hydrogen by Direct Thermal Decomposition of Water: Preliminary Investigations. *Int. J. Hydrogen Energy* **1982**, *7*, 939.
- (377) Cales, B.; Baumard, J. F. Oxygen Semipermeability and Electronic Conductivity in Calcia-Stabilized Zirconia. *J. Mater. Sci.* **1982**, *17*, 3243.
- (378) Matuzaki, Y.; Yasuda, I. Electrochemical Oxidation of H₂ and CO in a H₂–H₂O–CO–CO₂ System at the Interface of a Ni-YSZ Cermet Electrode and YSZ Electrolyte. *J. Electrochem. Soc.* **2000**, *147*, 1630.
- (379) Ihara, M.; Kusano, T.; Yokoyama, C. Competitive Adsorption Reaction Mechanism of Ni/Yttria-Stabilized Zirconia Cermet Anodes in H₂–H₂O Solid Oxide Fuel Cells. *J. Electrochem. Soc.* **2001**, *148*, A209.
- (380) Naito, H.; Arashi, H. Hydrogen Production from Direct Water Splitting at High Temperatures using a ZrO₂–TiO₂–Y₂O₃ Membrane. *Solid State Ionics* **1995**, *79*, 366.
- (381) Nigara, Y.; Watanabe, K.; Kawamura, K.; Mizusaki, J.; Ishigame, M. Oxygen Permeation in ZrO₂–CeO₂–CaO for Application to Oxygen Separation from Thermally Decomposed H₂O. *J. Electrochem. Soc.* **1997**, *144*, 1050.
- (382) Balachandran, U.; Lee, T. H.; Wang, S.; Dorris, S. E. Use of a Mixed Conducting Membranes to Produce Hydrogen by Water Dissociation. *Int. J. Hydrogen Energy* **2004**, *29* (3), 291.
- (383) Iwahara, H. High-Temperature Proton Conducting Oxides and their Applications to Solid Electrolyte Fuel Cells and Steam Electrolyzer for Hydrogen Production. *Solid State Ionics* **1988**, *28–30*, 573.
- (384) Iwahara, H. Hydrogen Production Using Oxide Ionic or Protonic Conductor. In *Recent Advances in Fast Ion Conducting Materials and Devices*; Chowdari, B. V. R., Liu, Q.-G., Chen, L.-Q., Eds.; World Scientific: Singapore, 1990; pp147–154.
- (385) Nagata, M.; Iwahara, H. The Measurement of Water Vapour Pressure in an SOFC Anode During Discharge. *J. Appl. Electrochem.* **1993**, *23*, 275.
- (386) Iwahara, H.; Hibino, T.; Sunano, T. An Electrochemical Steam Pump Using a Proton Conducting Ceramic. *J. Appl. Electrochem.* **1996**, *26*, 829.
- (387) Iwahara, H.; Matsumoto, H.; Takeuchi, K. Electrochemical Dehumidification Using Proton Conducting Ceramics. *Solid State Ionics* **2000**, *136–137*, 133.
- (388) Matsumoto, H.; Okubo, M.; Hamajima, S.; Katahira, K.; Iwahara, H. Extraction and Production of Hydrogen Using High-Temperature Proton Conductor. *Solid State Ionics* **2002**, *152–153*, 715.
- (389) Matsumoto, H.; Shimura, T.; Iwahara, H.; Higuchi, T.; Yashiro, K.; Kaimai, A.; Kawada, T.; Misusaki, J. Hydrogen Separation Using Proton-Conducting Perovskites. *J. Alloys Compd.* **2006**, *408–412*, 456.
- (390) Guan, J.; Dorris, S. E.; Balachandran, U.; Liu, M. Transport Properties of Ce_{0.95}Y_{0.05}O_{5-α} Mixed Conductor for Hydrogen Separation. *Solid State Ionics* **1997**, *100*, 45.
- (391) Kobayashi, T.; Abe, K.; Ukyo, Y.; Matsumoto, H. Study on Current Efficiency of Steam Electrolysis Using a Partial Protonic Conductor SrZr_{0.9}Yb_{0.1}O_{3-α}. *Solid State Ionics* **2001**, *138*, 243.
- (392) Stuart, P. A.; Unno, T.; Kilner, J. A.; Skinner, S. J. Solid Oxide Proton Conducting Steam Electrolysers. *Solid State Ionics* **2008**, *179* (21–26), 1120.
- (393) Balachandran, U.; Lee, T. H.; Dorris, S. E. Hydrogen Production by Water Dissociation using Mixed Conducting Dense Ceramic Membranes. *Int. J. Hydrogen Energy* **2007**, *32* (4), 451.
- (394) Okamoto, H.; Kawamura, G.; Kudo, T. Carbon Monoxide Gas Sensor Made of Stabilized Zirconia. *Solid State Ionics* **1980**, *1*, 319.
- (395) Yentekakis, I. V.; Vayenas, C. G. The Effect of Electrochemical Oxygen Pumping on the Steady State and Oscillatory Behavior of CO Oxidation on Polycrystalline Pt. *J. Catal.* **1988**, *111*, 170.
- (396) Marwood, M.; Vayenas, C. G. Electrochemical Promotion of Electronically Isolated Pt Catalysts on Stabilized Zirconia. *J. Catal.* **1997**, *168*, 538.
- (397) Etsell, T. H.; Flengas, S. N. The Electrical Properties of Solid Oxide Electrolytes. *Chem. Rev.* **1970**, *70*, 339.
- (398) Emery, D. A.; Luke, R. J. C.; Middleton, P. H.; Metcalfe, I. S. Electrochemical Enhancement of Carbon Monoxide Oxidation over Yttria Stabilized Zirconia Supported Platinum Catalysts. *J. Electrochem. Soc.* **1999**, *146*, 2188.
- (399) Poppe, J.; Völkening, S.; Schaak, A.; Schütz, E.; Janek, J.; Imbihl, R. Electrochemical Promotion of Catalytic CO Oxidation on Pt/YSZ Catalysts Under Low Pressure Conditions. *Phys. Chem. Chem. Phys.* **1999**, *1* (22), 5241.
- (400) Katsaounis, A.; Nikopoulou, Z.; Verykios, X. E.; Vayenas, C. G. Comparative Isotope-aided Investigation of Electrochemical Promotion and Metal-support Interactions: 2. CO Oxidation by ¹⁸O₂ on Electropromoted Pt Films Deposited on YSZ and on Nanodispersed Pt/YSZ Catalysts. *J. Catal.* **2004**, *226* (1), 197.
- (401) Belyaev, V. D.; Politova, T. I.; Sobyenin, V. A. Effect of Non-Faradaic Electrochemical Modification of Catalytic Activity. *Solid State Ionics* **2000**, *136–137*, 721.
- (402) Tsampas, M. N.; Sapountzi, F. M.; Vayenas, C. G. Electrochemical promotion of CO oxidation on Pt/YSZ: The effect of catalyst potential on the induction of highly active stationary and oscillatory states. *Catal. Today* **2009**, *146*, 351.
- (403) Mar'ina, O. A.; Sobyenin, V. A. The Effect of Electrochemical Oxygen Pumping on the Rate of CO Oxidation on Au Electrode-Catalyst. *Catal. Lett.* **1992**, *13*, 61.
- (404) Karavasilis, C.; Bebelis, S.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity in Stabilized Zirconia Cells: The Oxidation of CO on Polycrystalline Ag. *Mater. Sci. Forum* **1991**, *76*, 171.
- (405) Politova, T. I.; Gal'vita, V. V.; Belyaev, V. D.; Sobyenin, V. A. Non-Faradaic Catalysis: The Case of CO Oxidation over Ag-Pd Alloy Electrode in a Solid Oxide Electrolyte Cell. *Catal. Lett.* **1997**, *44*, 75.

- (406) Ran, S.; Zhang, X.; Yang, P. H.; Jiang, M.; Peng, D. K.; Chen, C. S. Oxygen Transport Through $\text{SrFe}_{1.125}\text{Co}_{0.375}\text{O}_3$ Coupled with Oxidation of Carbon Monoxide. *Solid State Ionics* **2000**, *135* (1–4), 1.
- (407) Holtappels, P.; De Haart, L. G. J.; Stimming, U.; Vinke, I. C.; Mogensen, M. Reaction of CO/CO_2 Gas Mixtures on Ni-YSZ Cermet Electrodes. *J. Appl. Electrochem.* **1999**, *29*, 561.
- (408) Itoh, N.; Sanchez, C. M. A.; Xu, W.-C.; Haraya, K.; Hongo, M. Application of a Membrane Reactor System to Thermal Decomposition of CO_2 . *J. Membr. Sci.* **1993**, *77*, 245.
- (409) Fan, Y.; Ren, J.-Y.; Onstot, W.; Pasale, J.; Tsotsis, T. T.; Egolfopoulos, F. N. Reactor and Technical Feasibility Aspects of a CO_2 Decomposition-based Power Generation Cycle, Utilizing a High-temperature Membrane Reactor. *Ind. Eng. Chem. Res.* **2003**, *42* (12), 2618.
- (410) Ren, J.-Y.; Tsotsis, T. T.; Egolfopoulos, F. N. Basic Aspects of Combustion Stability and Pollutant Emissions of a CO_2 Decomposition-based Power-generation Cycle. *Ind. Eng. Chem. Res.* **2002**, *41* (18), 4543.
- (411) Sridhar, K. R.; Vaniman, B. T. Oxygen Production on Mars using Solid Oxide Electrolysis. *Solid State Ionics* **1997**, *93*, 321.
- (412) Tao, G.; Sridhar, K. R.; Chan, C. L. Study of Carbon Dioxide Electrolysis at Electrode/Electrolyte Interface: Part 1. Pt/YSZ Interface. *Solid State Ionics* **2004**, *175* (1–4), 615.
- (413) Jin, W.; Zhang, C.; Chang, X.; Fan, Y.; Xing, W.; Xu, N. Efficient Catalytic Decomposition of CO_2 to CO and O_2 Over Pd/Mixed-conducting Oxide Catalyst in an Oxygen-permeable Membrane Reactor. *Environ. Sci. Technol.* **2008**, *42* (8), 3064.
- (414) Bidrawn, F.; Kim, G.; Corre, G.; Irvine, J. T. S. Efficient Reduction of CO_2 in a Solid Oxide Electrolyzer. *Electrochem. Solid State Lett.* **2008**, *11* (9), B167.
- (415) Jin, W.; Zhang, C.; Chang, X.; Fan, Y.; Xu, N. Improving Performance of a Dense Membrane Reactor for Thermal Decomposition of CO_2 via Surface Modification. *Ind. Eng. Chem. Res.* **2007**, *46* (7), 2000.
- (416) Nigara, Y.; Cales, B. Production of Carbon Monoxide by Direct Thermal Splitting of Carbon Dioxide at High Temperature. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 1997.
- (417) Jin, W.; Zhang, C.; Zhang, P.; Fan, Y.; Xu, N. Thermal Decomposition of Carbon Dioxide Coupled with POM in a Membrane Reactor. *AIChE J.* **2006**, *52* (7), 2545.
- (418) Yentekakis, I. V.; Vayenas, C. G. In Situ Controlled Promotion of Pt for CO Oxidation via NEMCA Using CaF_2 as the Solid Electrolyte. *J. Catal.* **1994**, *149*, 238.
- (419) Vayenas, C. G.; Bebelis, S.; Yentekakis, I. V.; Karavasilis, C.; Jiang, Y. Non-Faradaic Electrochemical Modification of Catalytic Activity: Solid Electrolytes as Active Catalyst Supports. *Solid State Ionics* **1994**, *72*, 321.
- (420) Yentekakis, I. V.; Moggridge, G.; Vayenas, C. G.; Lambert, R. M. In Situ Controlled Promotion of Catalyst Surfaces via NEMCA: The Effect of Na on the Pt-Catalyzed CO Oxidation. *J. Catal.* **1994**, *146*, 292.
- (421) Karagiannakis, G.; Kokkofitis, C.; Zisekas, S.; Stoukides, M. Catalytic and Electrocatalytic Production of H_2 from Propane Decomposition over Pt and Pd in a H^+ Conducting Membrane-Reactor. *Catal. Today* **2005**, *104*, 219.
- (422) Feng, Y.; Luo, J.; Chuang, K. T. Propane Dehydrogenation in a Proton-conducting Fuel Cell. *J. Phys. Chem. C* **2008**, *112* (26), 9943.
- (423) Hibino, T.; Hashimoto, A.; Mori, K.; Sano, M. Mixed Potentials at Metal-Electrode and Proton-Conducting Electrolyte Interfaces in Hydrocarbon–Oxygen Mixtures. *J. Phys. Chem. B* **2001**, *105* (43), 10648.
- (424) Karagiannakis, G.; Zisekas, S.; Kokkofitis, C.; Stoukides, M. Effect of H_2O Presence on the Propane Decomposition Reaction over Pd in a Proton Conducting Membrane Reactor. *Appl. Catal., A* **2006**, *301*, 265.
- (425) Feng, Y.; Luo, J. L.; Chuang, K. T. Carbon Deposition During Propane Dehydrogenation in a Fuel Cell. *J. Power Sources* **2007**, *167* (2), 486.
- (426) De Lucas-Consuegra, A.; Princivalle, A.; Caravaca, A.; Dorado, F.; Marouf, A.; Guizard, C.; Valverde, J. L.; Vernoux, P. Preparation and Characterization of a Low Particle Size Pt/C Catalyst Electrode for the Simultaneous Electrochemical Promotion of CO and C_3H_8 Oxidation. *Appl. Catal., A* **2009**, *365*, 274.
- (427) Kaloyiannis, A.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity. *J. Catal.* **1997**, *171*, 148.
- (428) Bodet, H.; Löfberg, A.; Pirovano, C.; Steil, M. C.; Vannier, R. N.; Bordes-Richard, E. Electrochemical Modification of the Catalytic Properties of Composite Membranes of Substituted $\text{Bi}_4\text{V}_2\text{O}_{11}$ (BIMEVOX) for Propane Oxidation in a Catalytic Dense Membrane Reactor. *Catal. Today* **2009**, *141*, 260.
- (429) Vernoux, P.; Guth, M.; Li, X. Ionically Conducting Ceramics as Alternative Catalyst Supports. *Electrochem. Solid State Lett.* **2009**, *12* (7), E9.
- (430) Bebelis, S.; Kotsionopoulos, N. Non-Faradaic Electrochemical Modification of the Catalytic Activity for Propane Combustion of Pt/YSZ And Rh/YSZ Catalyst-Electrodes. *Solid State Ionics* **2006**, *177* (26–32), 2205.
- (431) Kotsionopoulos, N.; Bebelis, S. Electrochemical Promotion of the Oxidation of Propane on Pt/YSZ and Rh/YSZ Catalyst-electrodes. *J. Appl. Electrochem.* **2005**, *35* (12), 1253.
- (432) Billiard, A.; Vernoux, P. Influence of the Thickness of Sputter-Deposited Platinum Films on the Electrochemical Promotion of Propane Combustion. *Ionics* **2005**, *11* (1–2), 126.
- (433) Bultel, L.; Vernoux, P.; Gaillard, F.; Roux, C.; Siebert, E. Electrochemical and Catalytic Properties of Porous Pt-YSZ Composites. *Solid State Ionics* **2005**, *176* (7–8), 793.
- (434) Piram, A.; Li, X.; Gaillard, F.; Lopez, C.; Billard, A.; Vernoux, P. Electrochemical Promotion of Environmental Catalysis. *Ionics* **2005**, *11* (5–6), 327.
- (435) Vernoux, P.; Gaillard, F.; Bultel, L.; Siebert, E.; Primet, M. Electrochemical Promotion on Propane and Propene Oxidation on Pt/YSZ. *J. Catal.* **2002**, *208*, 412.
- (436) Hamakawa, S.; Sato, K.; Hayakawa, T.; York, A. P. E.; Tsunoda, T.; Suzuki, K.; Shimizu, M.; Takehira, K. Selective Oxidation of Ethane Using the Au/YSZ/Ag Electrochemical Membrane System. *J. Electrochem. Soc.* **1997**, *144*, 1.
- (437) York, A. P. E.; Hamakawa, S.; Hayakawa, T.; Sato, K.; Tsunoda, T.; Takehira, K. Partial Oxidation of C_2 – C_4 Alkanes into Oxygenates Using an Au/YSZ/Ag Electrochemical Reaction Cell. *J. Chem. Soc. Faraday Trans.* **1996**, *92*, 3579.
- (438) York, A. P. E.; Hamakawa, S.; Hayakawa, T.; Tsunoda, T.; Takehira, K. Methacrolein production from isobutane using an Au/YSZ/Ag electrochemical reaction cell. *J. Electrochem. Soc.* **1996**, *143*, L249.
- (439) Takehira, K.; Sakai, N.; Shimomura, J.; Kajioka, H.; Hamakawa, S.; Shishido, T.; Kawabata, T.; Takaki, K. Oxidation of C_2 – C_4 alkanes over MoO_3 – V_2O_5 Supported on a YSZ-Aided Membrane Reactor. *Appl. Catal., A* **2004**, *277* (1–2), 209.
- (440) Takehira, K.; Shishido, T.; Sakai, N.; Shimomura, J.; Hamakawa, S.; Kajioka, H. Oxidation of Lower Alkanes over MoO_3 – V_2O_5 Supported on YSZ-Aided Membrane Reactor. *Desalination* **2002**, *144*, 425.
- (441) Takehira, K.; Komatsu, T.; Sakai, N.; Kajioka, H.; Hamakawa, S.; Shishido, T.; Kawabata, T.; Takaki, K. Oxidation of C_2 – C_4 Hydrocarbons into Oxygenates over MoO_3 or V_2O_5 on a YSZ-aided membrane reactor. *Appl. Catal., A* **2004**, *273* (1–2), 133.
- (442) Takehira, K.; Shishido, T.; Komatsu, T.; Hamakawa, S.; Kajioka, H. YSZ Aided Oxidation of C_2 – C_4 Hydrocarbons into Oxygenates over MoO_3 or V_2O_5 . *Solid State Ionics* **2002**, *152*–153, 641.
- (443) Ye, Y. M.; Rihko-Struckmann, L.; Munder, B.; Sundmacher, K. Partial Oxidation of *n*-Butane in a Solid Electrolyte Membrane Reactor. *J. Electrochem. Soc.* **2006**, *153* (2), D21.
- (444) Ye, Y. M.; Rihko-Struckmann, L.; Munder, B.; Sundmacher, K. Partial Oxidation of *n*-Butane in a Solid Electrolyte Membrane Reactor: Periodic and Steady-State Operations. *Appl. Catal., A* **2005**, *285* (1–2), 86.
- (445) Shen, S. K.; Li, R. J.; Zhou, J. P.; Yu, C. C. Selective Oxidation Of Light Hydrocarbons Using Lattice Oxygen Instead of Molecular Oxygen. *Chin. J. Chem. Eng.* **2003**, *11* (6), 649.
- (446) Chalakov, L.; Rihko-Struckmann, L. K.; Munder, B.; Rau, H.; Sundmacher, K. Reaction Induced Current Generation by Butane Oxidation in High Temperature Electrochemical Membrane Reactor. *Chem. Eng. J.* **2007**, *131* (1–3), 15.
- (447) Munder, B.; Ye, Y.; Rihko-Struckmann, L.; Sundmacher, K. Solid Electrolyte Membrane Reactor for Controlled Partial Oxidation of Hydrocarbons: Model and Experimental Validation. *Catal. Today* **2005**, *104* (2–4), 138.
- (448) Ye, Y.-M.; Rihko-Struckmann, L.; Munder, B.; Rau, H.; Sundmacher, K. Feasibility of an Electrochemical Membrane Reactor for the Partial Oxidation of *n*-Butane to Maleic Anhydride. *Ind. Eng. Chem. Res.* **2004**, *43* (16), 4551.
- (449) Munder, B.; Rihko-Struckmann, L.; Sundmacher, K. Steady-State and Forced-Periodic Operation of Solid Electrolyte Membrane Reactors for Selective Oxidation of *n*-Butane to Maleic Anhydride. *Chem. Eng. Sci.* **2007**, *62*, 5663.
- (450) Wang, R.; Xie, M.; Li, P.; Ng, C. Catalytic and Electrocatalytic Oxidation of Propane on V-Mg-O and V-Mg-O(Ag) Catalysts. *Catal. Lett.* **1994**, *24*, 67.
- (451) Ji, B.; Wang, J.; Chu, W.; Zhu, X.; Yang, W.; Lin, L. In Situ Monitoring of the Oxygen Activity on a $\text{Mg}_2\text{V}_2\text{O}_7$ Catalyst During the Oxidative Dehydrogenation of Propane. *Chin. J. Catal.* **2009**, *30* (5), 375.

- (452) Hibino, T.; Hashimoto, A.; Inoue, T.; Tokuno, J.; Yoshida, S.; Sano, M. Single Chamber Solid Oxide Fuel Cells at Intermediate Temperatures with Various Hydrocarbon Air Mixtures. *J. Electrochem. Soc.* **2000**, *147*, 2888.
- (453) McIntosh, S.; Vohs, J. M.; Gorte, R. J. An Examination of Lanthanide Additives on the Performance of Cu-YSZ Cermet Anodes. *Electrochim. Acta* **2002**, *47*, 3815.
- (454) Ahn, K.; Lee, S.-I.; Huang, Y.; Vohs, J. M.; Gorte, R. J. Solid Oxide Fuel Cells for Direct Utilization of Hydrocarbons Prepared by Lamination Methods. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **2004**, *49* (2), 755.
- (455) Dalmon, J. A.; Cruz-Lopez, A.; Farrusseng, D.; Guilhaume, N.; Iojoiu, E.; Jalibert, J. C.; Miachon, S.; Mirodatos, C.; Pantazidis, A.; Rebeilleau-Dassonneville, M.; Schuurman, Y.; van Veen, A. C. Oxidation in Catalytic Membrane Reactors. *Appl. Catal., A* **2007**, *325* (2), 198.
- (456) Roche, V.; Siebert, E.; Steil, M. C.; Deloume, J. P.; Roux, C.; Pagnier, T.; Revel, R.; Vernoux, P. Electrochemical Promotion of Propane Deep Oxidation on Doped Lanthanum Manganites. *Ionics* **2008**, *14* (3), 235.
- (457) Lo Faro, M.; La Rosa, D.; Nicotera, I.; Antonucci, V.; Aricò, A. S. Electrochemical Behaviour of Propane-fed Solid Oxide Fuel Cells Based on Low Ni Content Anode Catalysts. *Electrochim. Acta* **2009**, *54*, 5280.
- (458) Lo Faro, M.; La Rosa, D.; Nicotera, I.; Antonucci, V.; Aricò, A. S. Electrochemical Investigation of a Propane-fed Solid Oxide Fuel Cell Based on a Composite Ni-Perovskite Anode Catalyst. *Appl. Catal., B* **2009**, *89*, 49.
- (459) Yang, W.; Wang, H.; Zhu, X.; Lin, L. Development and Application of Oxygen Permeable Membrane in Selective Oxidation of Light Alkanes. *Top. Catal.* **2005**, *35* (1–2), 155.
- (460) Akin, F. T.; Lin, Y. S. Selective Oxidation of Ethane to Ethylene in a Dense Tubular Membrane Reactor. *J. Membr. Sci.* **2002**, *209*, 457.
- (461) Wang, H.; Cong, Y.; Yang, W. Partial Oxidation of Ethane to Syngas in an Oxygen-permeable Membrane Reactor. *J. Membr. Sci.* **2002**, *209* (1), 143.
- (462) Kotsionopoulos, N.; Bebelis, S. In Situ Electrochemical Modification of Catalytic Activity for Propane Combustion of Pt/ β -Al₂O₃ Catalyst-Electrodes. *Top. Catal.* **2007**, *44* (3), 379.
- (463) Makri, M.; Buekenhoudt, A.; Luyten, J.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of the Catalytic Activity of Pt using a CaZr_{0.9}In_{0.1}O_{3- α} Proton Conductor. *Ionics* **1996**, *2*, 282.
- (464) Poulidi, D.; Castillo-del-Rio, M. A.; Salar, R.; Thurstfield, A.; Metcalfe, I. S. Electrochemical Promotion of Catalysis Using Solid-State Proton-Conducting Membranes. *Solid State Ionics* **2003**, *162–163*, 305.
- (465) Thurstfield, A.; Brosda, S.; Pliangos, C.; Schober, T.; Vayenas, C. G. Electrochemical Promotion of an Oxidation Reaction Using a Proton Conductor. *Electrochim. Acta* **2003**, *48*, 3779.
- (466) Otsuka, K.; Yamanaka, I. Electrochemical Cells as Reactors for Selective Oxygenation of Hydrocarbons at Low Temperature. *Catal. Today* **1998**, *41* (4), 311.
- (467) Gaillard, F.; Li, X.; Uray, M.; Vernoux, P. Electrochemical Promotion of Propene Combustion in Air Excess on Perovskite Catalyst. *Catal. Lett.* **2004**, *96* (3–4), 177.
- (468) Vayenas, C. G.; Bebelis, S.; Despotopoulou, M. Non-Faradaic Electrochemical Modification of Catalytic Activity. The use of β'' -Al₂O₃ as the Solid Electrolyte. *J. Catal.* **1991**, *128*, 415.
- (469) Harkness, I. R.; Hardacre, C.; Lambert, R. M.; Yentekakis, I. V.; Vayenas, C. G. Ethylene Oxidation and Studies with a Pt(111)/Na Model Catalyst. *J. Catal.* **1996**, *160*, 19.
- (470) Petrolekas, P. D.; Brosda, S.; Vayenas, C. G. Electrochemical Promotion of Pt Catalyst Electrodes Deposited on Na₂Zr₂Si₂PO₁₂ During Ethylene Oxidation. *J. Electrochem. Soc.* **1998**, *145* (5), 1469.
- (471) Tracey, S.; Palermo, A.; Vazquez, J. P. H.; Lambert, R. M. In Situ Electrochemical Promotion by Sodium of the Selective Hydrogenation of Acetylene Over Platinum. *J. Catal.* **1998**, *179* (1), 231.
- (472) Vernoux, P.; Gaillard, F.; Lopez, C.; Siebert, E. In Situ Electrochemical Control of the Catalytic Activity of Platinum for the Propene Oxidation. *Solid State Ionics* **2004**, *175* (1–4), 609.
- (473) Filkin, N. C.; Tikhov, M. S.; Palermo, A.; Lambert, R. M. A Kinetic and Spectroscopic Study of the In Situ Electrochemical Promotion by Sodium of the Platinum Catalyzed Combustion of Propene. *J. Phys. Chem. A* **1999**, *103*, 2680.
- (474) Karavasilis, C.; Bebelis, S.; Vayenas, C. G. Selectivity Maximization of Ethylene Epoxidation via NEMCA with Zirconia and β'' -Al₂O₃ solid Electrolytes. *Ionics* **1995**, *1*, 85.
- (475) Karavasilis, C.; Bebelis, S.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity: X. Ethylene Epoxidation on Ag Deposited on Stabilized ZrO₂ in the Presence of Chlorine Moderators. *J. Catal.* **1996**, *160*, 190.
- (476) Williams, F. J.; Palermo, A.; Holgado, J. P.; Lambert, R. M. First Demonstration of In Situ Electrochemical Control of the Composition and Performance of an Alloy Catalyst During Reaction. *J. Catal.* **2002**, *210*, 237.
- (477) Palermo, A.; Williams, F. J.; Lambert, R. M. In Situ Control of the Composition and Performance of a Bimetallic Alloy Catalyst: The Selective Hydrogenation of Acetylene over Pt/Pb. *J. Phys. Chem. B* **2002**, *106* (39), 10215.
- (478) Stoukides, M.; Pavlou, S. Ethylene Oxidation on Ag—Effects of Ethylene Oxide and of External Transfer Limitations. *Chem. Eng. Commun.* **1986**, *44*, 53.
- (479) Stoukides, M.; Vayenas, C. G. Transient and Steady-State Vapor Phase Electrocatalytic Ethylene Epoxidation. *ACS Symp. Ser.* **1982**, *178*, 181.
- (480) Stoukides, M.; Vayenas, C. G. Methods and Apparatus for Oxidizing Ethylene to Ethylene Oxide, U.S. Patent 4,329,208, 1982.
- (481) De Lucas-Consuegra, A.; Dorado, F.; Valverde, J. L.; Karoum, R.; Vernoux, P. Low-Temperature Propene Combustion over Pt/K- β -Al₂O₃ Electrochemical Catalyst: Characterization, Catalytic Activity Measurements, and Investigation of the NEMCA Effect. *J. Catal.* **2007**, *251* (2), 474.
- (482) Bebelis, S.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity. 5. Oxygen Chemisorption on Silver. *J. Catal.* **1992**, *138*, 570.
- (483) Vayenas, C. G.; Ladas, S.; Bebelis, S.; Yentekakis, I. V.; Neophytides, S.; Jiang, Y.; Karavasilis, C.; Pliangos, C. Electrochemical Promotion in Catalysis: Non-Faradaic Electrochemical Modification of Catalytic Activity. *Electrochim. Acta* **1994**, *39*, 1849.
- (484) Stoukides, M.; Vayenas, C. G. Electrocatalytic Rate Enhancement of Propylene Epoxidation on Porous Silver Electrodes Using a Zirconia Oxygen Pump. *J. Electrochem. Soc.* **1984**, *131*, 839.
- (485) Hellgardt, K.; Cumming, I. W.; Al-Musa, A. The Effect of Electrochemical Oxygen on the Selectivity of the Partial Oxidation of Propene Over Silver Catalysts. *Solid State Ionics* **2005**, *176* (7–8), 831.
- (486) Zemichael, F. W.; Al-Musa, A.; Cumming, I. W.; Hellgardt, K. Propene Partial Oxidation Over Au-Ag Alloy and Ag Catalysts Using Electrochemical Oxygen. *Solid State Ionics* **2008**, *179* (27–32), 1401.
- (487) Hayakawa, T.; Tsunoda, T.; Orita, H.; Kameyama, T.; Takahashi, H.; Takehira, K.; Fukuda, K. Partial Oxidation of Propene by Active Oxygen Generated Electrochemically on Gold Through Yttria-Stabilized Zirconia. *J. Chem. Soc., Chem. Commun.* **1986**, 961.
- (488) Tsunoda, T.; Hayakawa, T.; Imai, Y.; Kameyama, T.; Fukuda, K.; Takehira, K. Alkene Oxidation Over the Au/Yttria Stabilized Zirconia/Ag System. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1111.
- (489) Hamakawa, S.; Hayakawa, T.; York, A. P. E.; Tsunoda, T.; Yoon, Y. S.; Suzuki, K.; Shimizu, M.; Takehira, K. Selective Oxidation of Propene Using an Electrochemical Membrane Reactor with CeO₂-Based Solid Electrolyte. *J. Electrochem. Soc.* **1996**, *143*, 1264.
- (490) Hamakawa, S.; Hayakawa, T.; Yasuda, H.; Suzuki, K.; Shimizu, M.; Takehira, K. Acrylaldehyde Production from Propane on Inert Gold Electrode Using an Electrochemical Membrane Reactor with (CeO₂)_{0.8}(SmO_{1.5})_{0.2} Electrolyte. *J. Electrochem. Soc.* **1995**, *142*, L159.
- (491) Tsunoda, T.; Hayakawa, T.; Sato, K.; Kameyama, T.; Fukuda, K.; Takehira, K. Alkene Oxidation over the Au/YSZ/Ag System. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1117.
- (492) Tsunoda, T.; Hayakawa, T.; Kameyama, T.; Fukuda, K.; Takehira, K. Alkene Oxidation over the (Pb, Bi)MoO₄/Au/YSZ/Ag System. *J. Chem. Soc. Faraday Trans.* **1995**, *91*, 1125.
- (493) Tsunoda, T.; Hayakawa, T.; Imai, Y.; Kameyama, T.; Takehira, K.; Fukuda, K. Propene Oxidation over MoO₃ Film Deposited on an Au/YSZ/Ag Electrochemical Membrane Reactor. *Catal. Today* **1995**, *25*, 371.
- (494) Hamakawa, S.; Hayakawa, T.; Tsunoda, T.; Suzuki, K.; Murata, K.; Takehira, K. Partial Oxidation of Propene to Acrylaldehyde with an Electrochemical Membrane Reactor Coated with Yttria-Stabilized Zirconia. *Electrochem. Solid State Lett.* **1998**, *1*, 220.
- (495) Marwood, M.; Vayenas, C. G. Electrochemical Promotion of a Dispersed Platinum Catalyst. *J. Catal.* **1998**, *178* (2), 429.
- (496) Bebelis, S.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity. *J. Catal.* **1989**, *118*, 125.
- (497) Pliangos, C.; Yentekakis, I. V.; Verykios, X. E.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity. Rh-Catalysed C₂H₄ Oxidation. *J. Catal.* **1995**, *154*, 124.
- (498) Petrolekas, P. D.; Balomenou, S.; Vayenas, C. G. Electrochemical Promotion of Ethylene Oxidation on Pt Catalyst Films Deposited on CeO₂. *J. Electrochem. Soc.* **1998**, *145* (4), 1202.
- (499) Nicole, J.; Comminellis, Ch.; Pliangos, C.; Verykios, X. E. Electrochemical Promotion and Metal-Support Interactions. *J. Catal.* **2001**, *204* (1), 23.

- (500) Beatrice, P.; Pliangos, C.; Worrell, W. L.; Vayenas, C. G. Electrochemical Promotion of Ethylene and Propylene Oxidation on Pt Deposited on Ytria-Titania-Zirconia. *Solid State Ionics* **2000**, 136–137, 833.
- (501) Balomenou, S.; Pitselis, G.; Polydoros, D.; Giannikos, A.; Vradis, A.; Frenzel, A.; Pliangos, C.; Pütter, H.; Vayenas, C. G. Electrochemical Promotion of Pd, Fe and Distributed Pt Catalyst-Electrodes. *Solid State Ionics* **2000**, 136–137, 857.
- (502) Tsiplakides, D.; Neophytides, S.; Vayenas, C. G. Investigation of Electrochemical Promotion Using Temperature-Programmed Desorption and Work Function Measurements. *Solid State Ionics* **2000**, 136–137, 839.
- (503) Wodiunig, S.; Bokeloh, F.; Comninellis, C. Electrochemical Promotion of Bipolar Electrodes: An Estimation of the Current Bypass. *Electrochim. Acta* **2000**, 46 (2–3), 357.
- (504) Karoum, R.; de Lucas-Consuegra, A.; Dorado, F.; Valverde, J. L.; Billard, A.; Vernoux, P. Towards a New Definition of EPOC Parameters for Anionic Electrochemical Catalysts: Case of Propene Combustion. *J. Appl. Electrochem.* **2008**, 38 (8), 1083.
- (505) Kaloyannis, A.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity. 12. Propylene Oxidation on Pt. *J. Catal.* **1999**, 182 (1), 37.
- (506) Yiokari, K.; Bebelis, S. In Situ Controlled Electrochemical Promotion of Catalyst Surfaces: Pd-Catalysed Ethylene Oxidation. *J. Appl. Electrochem.* **2000**, 30 (11), 1277.
- (507) Di Cosimo, R. D.; Burrington, J. D.; Grasselli, R. K. Oxidative Dehydrodimerization of Propylene over a $\text{Bi}_2\text{O}_3\text{--La}_2\text{O}_3$ Oxide Ion-Conductive Catalyst. *J. Catal.* **1986**, 102, 234.
- (508) Di Cosimo, R. D.; Burrington, J. D.; Grasselli, R. K. Process for Effecting Oxidative Dehydrodimerization, U.S. Patent 4,571,443, 1986.
- (509) Varkarakis, E.; Nicole, J.; Plattner, E.; Comninellis, Ch.; Vayenas, C. G. Electrochemical Promotion of IrO_2 Catalyst for the Gas Phase Combustion of Ethylene. *J. Appl. Electrochem.* **1995**, 25, 978.
- (510) Nicole, J.; Comninellis, C. Electrochemical Promotion of IrO_2 Catalyst Activity for the Gas Phase Combustion of Ethylene. *J. Appl. Electrochem.* **1998**, 28, 223.
- (511) Foti, G.; Stankovic, V.; Bolzonella, I.; Comninellis, C. Transient Behavior of Electrochemical Promotion of Gas-Phase Catalytic Reactions. *J. Electroanal. Chem.* **2002**, 532, 191.
- (512) Tsiplakides, D.; Nicole, J.; Vayenas, C. G.; Comninellis, Ch. Work Function and Catalytic Activity Measurements of an IrO_2 Film Deposited on YSZ Subjected to in Situ Electrochemical Promotion. *J. Electrochem. Soc.* **1998**, 145 (3), 905.
- (513) Marnellos, G.; Athanasiou, C.; Angelidis, T.; Stoukides, M. Catalytic and Electrocatalytic Oxidation of Ethylene on a Perovskite Electrode in a Solid Electrolyte Cell. *Ionics* **1997**, 3, 96.
- (514) Hayakawa, T.; Tsunoda, T.; Orita, H.; Kameyama, T.; Takahashi, H.; Fukuda, K.; Takehira, K. A Solid Electrolyte-Aided Study of Propene Oxidation on an $\text{MoO}_3\text{--Bi}_2\text{O}_3$ Catalyst. *J. Chem. Soc., Chem. Commun.* **1987**, 780.
- (515) Baranova, E. A.; Fóti, G.; Jotterand, H.; Comninellis, Ch. Electrochemical Modification of the Catalytic Activity of TiO_2/YSZ Supported Rhodium Films. *Top. Catal.* **2007**, 44 (3), 355.
- (516) Baranova, E. A.; Thursfield, A.; Brosda, S.; Fóti, G.; Comninellis, Ch.; Vayenas, C. G. Electrochemical Promotion of Ethylene Oxidation Over Rh Catalyst Thin Films Sputtered on YSZ and TiO_2/YSZ Supports. *J. Electrochem. Soc.* **2005**, 152 (2), E40.
- (517) Baranova, E. A.; Thursfield, A.; Brosda, S.; Fóti, G.; Comninellis, Ch.; Vayenas, C. G. Electrochemically Induced Oscillations of C_2H_4 Oxidation Over Thin Sputtered Rh Catalyst Films. *Catal. Lett.* **2005**, 105 (1–2), 15.
- (518) Fóti, G.; Bolzonella, I.; Bachelin, D.; Comninellis, Ch. Relation Between Potential and Catalytic Activity of Rhodium in Propylene Combustion. *J. Appl. Electrochem.* **2004**, 34 (1), 9.
- (519) Constantinou, I.; Bolzonella, I.; Pliangos, C.; Comninellis, Ch.; Vayenas, C. G. Electrochemical Promotion of RuO_2 Catalysts for the Combustion of Toluene and Ethylene. *Catal. Lett.* **2005**, 100 (3–4), 125.
- (520) Wodiunig, S.; Bokeloh, F.; Nicole, J.; Comninellis, C. Electrochemical Promotion of RuO_2 Catalyst Dispersed on an Ytria-stabilized Zirconia Monolith. *Electrochem. Solid State Lett.* **1999**, 2 (6), 281.
- (521) Pliangos, C.; Yentekakis, I. V.; Ladas, S.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of the Catalytic Activity of Pt Deposited on TiO_2 . *J. Catal.* **1996**, 159, 189.
- (522) Poulidi, D.; Thursfield, A.; Metcalfe, I. S. Electrochemical Promotion of Catalysis Controlled by Chemical Potential Difference across a Mixed Ionic–Electronic Conducting Ceramic Membrane—An Example of Wireless NEMCA. *Top. Catal.* **2007**, 44 (3), 435.
- (523) Palermo, A.; Husain, A.; Lambert, R. M. Triply-promoted Ethene Epoxidation: NO_x Promotion of the Ag-catalysed Reaction in the Presence of Alkali and Chlorine under Electrochemical Control. *Catal. Lett.* **2000**, 69 (3–4), 175.
- (524) Pirovano, C.; Löfberg, A.; Bodet, H.; Bordes-Richard, E.; Steil, M. C.; Vannier, R. N. BIMEVOX as Dense Membrane in Catalytic Reactor ($\text{ME} = \text{Co}, \text{Cu}, \text{Ta}$). *Solid State Ionics* **2006**, 177 (26–32), 2241 (Special Issue).
- (525) Löfberg, A.; Bodet, H.; Pirovano, C.; Steil, M. C.; Vannier, R. N.; Bordes-Richard, E. Selective Oxidation of Hydrocarbons in a Catalytic Dense Membrane Reactor: Catalytic Properties of BIMEVOX ($\text{Me} = \text{Ta}$). *Catal. Today* **2006**, 118 (1–2), 223.
- (526) Löfberg, A.; Bodet, H.; Pirovano, C.; Steil, M. C.; Vannier, R. N.; Bordes-Richard, E. Catalytic Dense Membranes of Doped $\text{Bi}_4\text{V}_3\text{O}_{11}$ (BIMEVOX) for Selective Partial Oxidation: Chemistry of Defects Versus Catalysis. *Top. Catal.* **2006**, 38 (1–3), 169.
- (527) Löfberg, A.; Pirovano, C.; Steil, M. C.; Vannier, R. N.; Bordes-Richard, E. Transient Behaviour of Dense Catalytic Membranes Based on Cu- and Co-Doped $\text{Bi}_4\text{V}_3\text{O}_{11}$ (BIMEVOX) in the Oxidation of Propene and Propane. *Catal. Today* **2006**, 112 (1–4), 8.
- (528) Löfberg, A.; Boujmaï, S.; Capoen, E.; Steil, M. C.; Pirovano, C.; Vannier, R. N.; Mairesse, G.; Bordes-Richard, E. Oxygen Permeation Versus Catalytic Properties of Bismuth-Based Oxide Ion Conductors Used for Propene Oxidation in a Catalytic Dense Membrane Reactor. *Catal. Today* **2004**, 91–92, 79.
- (529) Courson, C.; Taouk, B.; Bordes, E. Ion Oxide Conductor as a Catalytic Membrane for Selective Oxidation of Hydrocarbons. *Catal. Lett.* **2000**, 66 (3), 129.
- (530) Wojcik, A.; Middleton, H.; Damopoulos, I.; Van Herle, J. Ammonia as a Fuel in Solid Oxide Fuel Cells. *J. Power Sources* **2003**, 118 (1–2), 342.
- (531) Panagos, E.; Voudouris, I.; Stoukides, M. Modelling of Equilibrium Limited Hydrogenation Reaction Carried out in H^+ Conducting Solid Oxide Membrane Reactors. *Chem. Eng. Sci.* **1996**, 51, 3175.
- (532) Marnellos, G.; Athanasiou, C.; Tsiakaras, P.; Stoukides, M. Modeling of Solid H^+ Conducting Cells: Thermodynamics and Kinetics. *Ionics* **1996**, 2, 412.
- (533) Marnellos, G.; Sanopoulou, O.; Rizou, A.; Stoukides, M. The Use of Proton Conducting Solid Electrolytes for Improved Performance of Hydro- and Dehydrogenation Reactors. *Solid State Ionics* **1997**, 97, 375.
- (534) Marnellos, G.; Stoukides, M. Ammonia Synthesis at Atmospheric Pressure. *Science* **1998**, 282, 95.
- (535) Marnellos, G.; Zisekas, S.; Stoukides, M. Synthesis of Ammonia at Atmospheric Pressure with the Use of Solid State Proton Conductors. *J. Catal.* **2000**, 193, 80.
- (536) Pitselis, G. E.; Petrolekas, P. D.; Vayenas, C. G. Electrochemical Promotion of Ammonia Decomposition over Fe Catalyst Films Interfaced with K^+ and H^+ Conductors. *Ionics* **1997**, 3, 110.
- (537) Yokari, C. G.; Pitselis, G. E.; Polydoros, D. G.; Katsaounis, A. D.; Vayenas, C. G. High-Pressure Electrochemical Promotion of Ammonia Synthesis over an Industrial Iron Catalyst. *J. Phys. Chem. A* **2000**, 104, 10600.
- (538) Ouzounidou, M.; Skodra, A.; Kokkofitis, C.; Stoukides, M. Catalytic and Electrocatalytic Synthesis of NH_3 in a H^+ Conducting Cell by Using an Industrial Fe Catalyst. *Solid State Ionics* **2007**, 178, 153.
- (539) Xie, Y. H.; Wang, J. D.; Liu, R. Q.; Su, X. T. Preparation of $\text{La}_{1.9}\text{Ca}_{0.1}\text{Zr}_{0.95}\text{O}_{6.95}$ with Pyrochlore Structure and Its Application in Synthesis of Ammonia at Atmospheric Pressure. *Solid State Ionics* **2004**, 168, 117.
- (540) Li, S. Z.; Liu, R. Q.; Xie, Y. H.; Feng, S.; Wang, J. D. A Novel Method for Preparation of Doped $\text{Ba}_3(\text{Ca}_{1.18}\text{Nb}_{1.82})\text{O}_{9.5}$: Application to Ammonia Synthesis at Atmospheric Pressure. *Solid State Ionics* **2005**, 176, 1063.
- (541) Li, S. Z.; Liu, R. Q.; Wang, J. D.; Xie, Y. H.; Yue, F. J. Preparation $\text{BaCe}_{0.8}\text{Gd}_{0.2}\text{O}_{3-\delta}$ by the Citrate Method and Its Application in the Synthesis of Ammonia at Atmospheric Pressure. *Solid State Electrochem.* **2005**, 9, 201.
- (542) Liu, R. Q.; Xie, Y. H.; Wang, J. D.; Li, S. Z.; Wang, B. H. Synthesis of Ammonia at Atmospheric Pressure With $\text{Ce}_{0.8}\text{M}_{0.2}\text{O}_{2-\delta}$ ($\text{M} = \text{La}, \text{Y}, \text{Gd}, \text{Sm}$) and Their Proton Conduction at Intermediate Temperature. *Solid State Ionics* **2006**, 177, 73.
- (543) Li, Z.; Liu, R. Q.; Wang, J. D.; Xu, Z.; Xie, Y. H.; Wang, B. H. Preparation of Double-Doped BaCeO_3 and Its Application in the Synthesis of Ammonia at Atmospheric Pressure. *Sci. Technol. Adv. Mater.* **2007**, 8 (7–8), 566.
- (544) Chen, C.; Ma, G. Preparation, Proton Conduction, and Application in Ammonia Synthesis at Atmospheric Pressure of $\text{La}_{0.9}\text{Ba}_{0.1}\text{Ga}_{1-x}\text{Mg}_x\text{O}_{3-\alpha}$. *J. Mater. Sci.* **2008**, 43 (15), 5109.
- (545) Xu, G.; Liu, R. $\text{Sm}_{1.5}\text{Sr}_{0.5}\text{MO}_4$ ($\text{M} = \text{Ni}, \text{Co}, \text{Fe}$) Cathode Catalysts for Ammonia Synthesis at Atmospheric Pressure and Low Temperature. *Chin. J. Chem.* **2009**, 27 (4), 677.

- (546) Chen, C.; Wang, W.; Ma, G. Proton Conduction in $\text{La}_{0.9}\text{M}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\alpha}$ at Intermediate Temperature and Its Application to Synthesis of Ammonia at Atmospheric Pressure. *Acta Chim. Sin.* **2009**, 67 (7), 623.
- (547) Skodra, A.; Ouzounidou, M.; Stoukides, M. NH_3 Decomposition in a Single Chamber Proton-Conducting Cell. *Solid State Ionics* **2006**, 177, 2217.
- (548) Zhang, L.; Yang, W. Direct Ammonia Solid Oxide Fuel Cell Based on thin Proton-conducting Electrolyte. *J. Power Sources* **2008**, 179 (1), 92.
- (549) Pelletier, L.; McFarlan, A.; Maffei, N. Ammonia Fuel Cell using Doped Barium Cerate Proton Conducting Solid Electrolytes. *J. Power Sources* **2005**, 145 (2), 262.
- (550) McFarlan, A.; Pelletier, L.; Maffei, N. An Intermediate-temperature Ammonia Fuel Cell Using Gd-doped Barium Cerate Electrolyte. *J. Electrochem. Soc.* **2004**, 151 (6), A930.
- (551) Li, Z.-J.; Wang, J.-D.; Liu, R.-Q.; Xu, Z.; Xie, Y.-H. Preparation and Application of Perovskite-type Oxides to Atmospheric Pressure Ammonia Synthesis. *Am. Ceram. Soc. Bull.* **2006**, 85 (12), 9501.
- (552) Zisekas, S.; Karagiannakis, G.; Kokkofitis, C.; Stoukides, M. NH_3 Decomposition in a Proton Conducting Solid Electrolyte Cell. *J. Appl. Electrochem.* **2008**, 38, 1143.
- (553) Kokkofitis, C.; Ouzounidou, M.; Skodra, A.; Stoukides, M. Catalytic and Electrocatalytic Production of H_2 from the Water Gas Shift Reaction over Pd in a High Temperature Proton Conducting Cell-Reactor. *Solid State Ionics* **2006**, 178, 475.
- (554) Karagiannakis, G.; Zisekas, S.; Stoukides, M. Hydrogeneration of Carbon Dioxide on Cu in a H^+ Conducting Membrane Reactor. *Solid State Ionics* **2003**, 162–163, 313.
- (555) Bebelis, S.; Karasali, H.; Vayenas, C. G. Electrochemical Promotion of the CO_2 Hydrogenation on Pd/YSZ and Pd/ β'' - Al_2O_3 Catalyst-Electrodes. *Solid State Ionics* **2008**, 179 (27–32), 1391.
- (556) Williams, F. J.; Lambert, R. M. A Study of Sodium Promotion in Fischer–Tropsch Synthesis: Electrochemical Control of a Ruthenium Model Catalyst. *Catal. Lett.* **2000**, 70, 9.
- (557) Urquhart, A. J.; Keel, J. M.; Williams, F. J.; Lambert, R. M. Electrochemical Promotion by Potassium of Rhodium-Catalyzed Fischer–Tropsch Synthesis: XP Spectroscopy and Reaction Studies. *J. Phys. Chem. B* **2003**, 107 (38), 10591.
- (558) Furukawa, S.; Okada, M.; Suzuki, Y. Isolation of Oxygen Formed During Catalytic Reduction of Carbon Dioxide Using a Solid Electrolyte Membrane. *Energy Fuels* **1999**, 13 (5), 1074.
- (559) Otsuka, K.; Yokoyama, S.; Morikawa, A. Steam Reforming of Hydrocarbons and Water Gas Shift Reaction Through a Wall of Stabilized Zirconia Used as Hydrogen Separator. *Bull. Chem. Soc. Jpn.* **1984**, 57, 3286.
- (560) Gür, T. M.; Huggins, R. A. Electrocatalytic Synthesis of Methane Stabilized Zirconia from H_2/CO_2 Mixtures. *Solid State Ionics* **1981**, 5, 563.
- (561) Gür, T. M.; Huggins, R. A. Methane Synthesis on Nickel by Solid-State Ionic Method. *Science* **1983**, 219, 967.
- (562) Gür, T. M.; Wise, H.; Huggins, R. A. Electrocatalytic Conversion of Carbon Dioxide to Methane and Oxygen with an Oxygen Ion-Conducting electrolyte. *J. Catal.* **1991**, 129, 216.
- (563) Pekridis, G.; Kalimeri, K.; Kakiadis, N.; Vakouftis, E.; Iliopoulou, E. F.; Athanasiou, C.; Marnellos, G. E. Electro-kinetic Study of the Reverse Water Gas Shift Reaction (RWGS) Reaction and its Potential Role in the Production of Power in a Solid Oxide Fuel Cell (SOFC). *Catal. Today* **2007**, 127, 337.
- (564) Li, S.; Lee, A. C.; Mitchell, R. E.; Gür, T. M. Direct Carbon Conversion in a Helium Fluidized Bed Fuel Cell. *Solid State Ionics* **2008**, 179 (27–32), 1549.
- (565) Gür, T. M.; Huggins, R. A. Methane Synthesis over Transition Metal Electrodes in a Solid Ionic Cell. *J. Catal.* **1986**, 102, 443.
- (566) Saito, H.; Hasegawa, S.; Ihara, M. Effective Anode Thickness in Rechargeable Direct Carbon Fuel Cells Using Fuel Charged by Methane. *J. Electrochem. Soc.* **2008**, 155 (4), B443.
- (567) Lee, A. C.; Li, S.; Mitchell, R. E.; Gür, T. M. Conversion of Solid Carbonaceous Fuels in a Fluidized Bed Fuel Cell. *Electrochem. Solid State Lett.* **2008**, 11 (2), B20.
- (568) Weber, A.; Sauer, B.; Müller, A. C.; Herbstritt, D.; Ivers-Tiffée, E. Oxidation of H_2 , CO and Methane in SOFCs with Ni/YSZ–Cermet Anodes. *Solid State Ionics* **2002**, 152–153, 543.
- (569) Bebelis, S.; Karasali, H.; Vayenas, C. G. Electrochemical Promotion of CO_2 Hydrogenation on Rh/YSZ Electrodes. *J. Appl. Electrochem.* **2008**, 38 (8), 1127.
- (570) Papaioannou, E. I.; Souentie, S.; Hammad, A.; Vayenas, C. G. Electrochemical Promotion of the CO_2 Hydrogenation Reaction Using Thin Rh, Pt and Cu Films in a Monolithic Reactor at Atmospheric Pressure. *Catal. Today* **2009**, 146, 336.
- (571) Estenfelder, M.; Lintz, H.-G. The use of Solid Electrolyte Potentiometry in the Study of Oxygen Transfer in Oxidic Catalysts. *Appl. Catal., A* **2000**, 202, 223.
- (572) Chen, X. J.; Liu, Q. L.; Chan, S. H.; Brandon, N. P.; Khor, K. A. High Performance Cathode-Supported SOFC with Perovskite Anode Operating in Weakly Humidified Hydrogen and Methane. *Electrochem. Commun.* **2007**, 9 (4), 767.
- (573) Esaka, T.; Fujii, T.; Suwa, K.; Iwahara, H. Electrical Conduction in $\text{CaTi}_{1-x}\text{Fe}_x\text{O}_{3-\delta}$ Under Low Oxygen Pressure and Its Application for Hydrogen Production. *Solid State Ionics* **1990**, 40, 544.
- (574) Iwase, M.; Tanida, M.; Mclean, A.; Tori, T. Electronically Driven Transport of Oxygen From Liquid Iron to $\text{CO} + \text{CO}_2$ Gas Mixtures Through Stabilized Zirconia. *Metall. Trans.* **1981**, 12B, 517.
- (575) Shimura, T.; Itoh, M.; Iwahara, H. A Novel Approach for Gasification of Carbon Using a Mixed Conductor. *J. Appl. Electrochem.* **1998**, 28 (7), 683.
- (576) Oberg, K. E.; Friedman, L. M.; Boorstein, W. M.; Rapp, R. A. The Diffusivity and Solubility of Oxygen in Liquid Copper and Liquid Silver from Electrochemical Measurements. *Metall. Trans.* **1973**, 4B, 75.
- (577) Hasham, Z.; Pal, U.; Chou, K. C.; Worrell, W. L. Deoxidation of Molten Steel Using a Short Circuited Solid Oxide Electrochemical Cell. *J. Electrochem. Soc.* **1995**, 142, 469.
- (578) Liu, M.; He, P.; Luo, J. L.; Sanger, A. R.; Chuang, K. T. Performance of a Solid Oxide Fuel Cell Utilizing Hydrogen Sulfide as Fuel. *J. Power Sources* **2001**, 94 (1), 20.
- (579) Yates, C.; Winnick, J. Anode Materials for a Hydrogen Sulfide Solid Oxide Fuel Cell. *J. Electrochem. Soc.* **1999**, 146 (8), 2841.
- (580) Alqahtany, H.; Chiang, P.-H.; Eng, D.; Robbat, A.; Stoukides, M. Electrocatalytic Decomposition of Hydrogen Sulfide. *Catal. Lett.* **1992**, 13, 289.
- (581) Peterson, D. R.; Winnick, J. Utilization of Hydrogen Sulfide in an Intermediate-Temperature Ceria-Based Solid Oxide Fuel Cell. *J. Electrochem. Soc.* **1998**, 145 (5), 1449.
- (582) Mari, C. M.; Molteni, A.; Pizzini, S. Gas Phase Electrocatalytic Oxidation of SO_2 by Solid State Electrochemical Technique. *Electrochim. Acta* **1979**, 24, 745.
- (583) Suzuki, C.; Nakagiri, T.; Aoto, K. The Refinement of the Rate Determining Process in Sulfur Trioxide Electrolysis Using the Electrolysis Cell. *Int. J. Hydrogen Energy* **2007**, 32 (12), 1771.
- (584) Liu, M.; Wei, G.; Luo, J.; Sanger, A. R.; Chuang, K. T. Use of Metal Sulfides as Anode Catalysts in H_2S –Air SOFCs. *J. Electrochem. Soc.* **2003**, 150 (8), A1025.
- (585) Tremblay, J. P.; Marquez, A. I.; Ohn, T. R.; Bayless, D. J. Effect of Coal Syngas and H_2S on the Performance of Solid Oxide Fuel Cells: Single-Cell Tests. *J. Power Sources* **2006**, 158 (1), 263.
- (586) Pujare, N. U.; Tsai, K. J.; Samuels, A. F. An Electrochemical Claus Process for Sulfur Recovery. *J. Electrochem. Soc.* **1989**, 136, 3662.
- (587) Wei, G. L.; Luo, J. L.; Sanger, A. R.; Chuang, K. T. High-Activity Mo–Ni–S Anode Catalysts for H_2S –Air Solid Oxide Fuel Cells. *J. New Mater. Electrochem. Syst.* **2005**, 8 (1), 59.
- (588) Wei, G. L.; Luo, J. L.; Sanger, A. R.; Chuang, K. T. High-Performance Anode for H_2S –Air SOFCs. *J. Electrochem. Soc.* **2004**, 151 (2), A232.
- (589) Vorontsov, V.; Luo, J. L.; Sanger, A. R.; Chuang, K. T. Synthesis and Characterization of New Ternary Transition Metal Sulfide Anodes for H_2S -Powered Solid Oxide Fuel Cell. *J. Power Sources* **2008**, 183 (1), 76.
- (590) Monder, D. S.; Nandakumar, K.; Chuang, K. T. Model Development for a SOFC Button Cell Using H_2S as Fuel. *J. Power Sources* **2006**, 162 (1), 400.
- (591) Zhong, L.; Luo, J.; Karl, C. Investigation of Cathode Catalysts for Intermediate-Temperature H_2S –Air Fuel Cells. *Chin. J. Chem. Eng.* **2007**, 15 (3), 305.
- (592) Aguilar, L.; Zha, S. W.; Li, S. W.; Winnick, J.; Liu, M. Sulfur-Tolerant Materials for the Hydrogen Sulfide SOFC. *Electrochem. Solid State Lett.* **2004**, 7 (10), A324.
- (593) Chuang, K. T.; Sanger, A. R.; Slavov, S. V.; Donini, J. C. Proton-Conducting Solid State H_2S – O_2 Fuel Cell. 3. Operation Using H_2S –Hydrocarbon Mixtures as Anode Feed. *Int. J. Hydrogen Energy* **2001**, 26 (1), 103.
- (594) Chuang, K. T.; Donini, J. C.; Sanger, A. R.; Slavov, S. V. Proton-Conducting Solid State H_2S – O_2 Fuel Cell. 2. Production of Liquid Sulfur at 120–145 °C. *Int. J. Hydrogen Energy* **2000**, 25 (9), 887.
- (595) Slavov, S. V.; Chuang, K. T.; Sanger, A. R.; Donini, J. C.; Kot, J.; Petrovic, S. A Proton Conduction Solid State H_2S – O_2 Fuel Cell. 1. Anode Catalysts and Operation at Atmospheric Pressure and 20–90 °C. *Int. J. Hydrogen Energy* **1998**, 23 (12), 1203.
- (596) Vorontsov, V.; An, W.; Luo, J. L.; Sanger, A. R.; Chuang, K. T. Performance and Stability of Composite Nickel and Molybdenum Sulfide-Based Anodes for SOFC Utilizing H_2S . *J. Power Sources* **2008**, 179 (1), 9.

- (597) Li, J.; Luo, J. L.; Chuang, K. T.; Sanger, A. R. Proton Conductivity and Chemical Stability of Li_2SO_4 Based Electrolyte in a H_2S -Air Fuel Cell. *J. Power Sources* **2006**, *160*, 909.
- (598) Wei, G.-L.; Luo, J.-L.; Sanger, A. R.; Chuang, K. T.; Zhong, L. Li_2SO_4 -Based Proton-Conducting Membrane for H_2S -Air Fuel Cell. *J. Power Sources* **2005**, *145* (1), 1.
- (599) Zhu, B.; Tao, S. Chemical Stability Study of Li_2SO_4 in a $\text{H}_2\text{S}/\text{O}_2$ Fuel Cell. *Solid State Ionics* **2000**, *127* (1–2), 83.
- (600) Chuang, K. T.; Luo, J. L.; Sanger, A. R. Evolution of Fuel Cells Powered by H_2S -Containing Gases. *Chem. Ind. Chem. Eng. Q.* **2008**, *14* (2), 69.
- (601) Vayenas, C. G.; Neophytides, S. Non-Faradaic Electrochemical Modification of Catalytic Activity. The Case of Methanol Oxidation on Pt. *J. Catal.* **1991**, *127*, 645.
- (602) Cavalca, C. A.; Larsen, G.; Vayenas, C. G.; Haller, G. L. Electrochemical Modification of CH_3OH Oxidation Selectivity and Activity on a Pt Single-Pellet Catalytic Reactor. *J. Phys. Chem.* **1993**, *97*, 6115.
- (603) Rincon-Rubio, L. M.; Nguyen, B. C.; Mason, D. M. Coupled Electrocatalysis and Gas Phase Diffusion in a Stabilized-Zirconia Tubular Flow Oxygen Pump. *J. Electrochem. Soc.* **1985**, *132*, 2919.
- (604) Tsiakaras, P.; Douvartzides, S.; Demin, A. K.; Sobyannin, V. A. The Oxidation of Ethanol over Pt Catalyst-Electrodes Deposited on ZrO_2 (8% mol ZrO_3). *Solid State Ionics* **2002**, *152–153*, 721.
- (605) Tsiakaras, P. E.; Douvartzides, S. L. Electrochemically Promoted Catalysis: The Case of Ethanol Oxidation over Pt. *J. Catal.* **2002**, *211* (2), 521.
- (606) Neophytides, S.; Vayenas, C. G. Non-Faradaic Electrochemical Modification of Catalytic Activity. The Case of Methanol Dehydrogenation and Decomposition on Ag. *J. Catal.* **1989**, *118*, 147.
- (607) Hong, J. K.; Oh, I.-H.; Hong, S.-A.; Lee, W. Y. Electrochemical Oxidation of Methanol over a Silver Electrode Deposited on Yttria-Stabilized Zirconia Electrolyte. *J. Catal.* **1996**, *163*, 95.
- (608) Douvartzides, S. L.; Tsiakaras, P. E. Catalytic and Electrocatalytic Oxidation of Ethanol over a $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ Perovskite-Type Catalyst. *Solid State Ionics* **2000**, *136–137*, 849.
- (609) Tsiakaras, P.; Douvartzides, S.; Athanasiou, C.; Georgakakis, N. High Temperature Electrochemical Oxidation of Ethanol Over Perovskite-Type Oxides. *React. Kinet. Catal. Lett.* **2000**, *71* (1), 19.
- (610) Huang, B.; Wang, S. R.; Liu, R. Z.; Wen, T. L. Preparation and Performance Characterization of the Fe-Ni/ScSZ Cermet Anode for Oxidation of Ethanol Fuel in SOFCs. *J. Power Sources* **2007**, *167* (2), 288.
- (611) Pizzini, S.; Mari, C. M.; Hadjicostantis, D. C. The Use of Non-stoichiometric CeO_2 as Oxygen Sensitive Electrode in an Electrochemical Solid State Oxygen Meter. In *Reactivity of Solids*; Wood, J. et al., Eds.; Plenum: New York, 1977; p 161.
- (612) Pizzini, S.; Mari, C. M.; Zanderighi, L. Gas-phase Electrocatalytic Oxidation of Benzene Using a Solid State Electrochemical Reactor. *Gazz. Chim. Ital.* **1980**, *110*, 389.
- (613) Li, N.; Gaillard, F.; Boréave, A. Electrochemical Promotion of Ag Catalyst for the Low Temperature Combustion of Toluene. *Catal. Commun.* **2008**, *9* (6), 1439.
- (614) Li, N.; Gaillard, F. Catalytic Combustion of Toluene over Electrochemically Promoted Ag Catalyst. *Appl. Catal., B* **2009**, *88*, 152.
- (615) Gaillard, F.; Li, N. Electrochemical Promotion of Toluene Combustion on an Inexpensive Metallic Catalyst. *Catal. Today* **2009**, *146*, 345.
- (616) Basini, L.; Cavalca, C. A.; Haller, G. L. Electrochemical Promotion of Oxygen Atom Back-Spillover from Yttria-Stabilized Zirconia onto a Porous Platinum Electrode: Detection of SERS Signals. *J. Phys. Chem.* **1994**, *98*, 10853.
- (617) Cavalca, C. A.; Haller, G. L. Solid Electrolytes as Active Catalyst Supports: Electrochemical Modification of Benzene Hydrogenation Activity on $\text{Pt}/\beta''\text{-(Na)Al}_2\text{O}_3$. *J. Catal.* **1998**, *177* (2), 389.
- (618) Sanchez Marcano, J. G.; Tsotsis, T. T. *Catalytic Membranes and Membrane Reactors*; Wiley-VCH: Weinheim, Germany, 2002, 223.
- (619) Li, L.; Borry, R. W.; Iglesia, E. Design and Optimization of Catalysts and Membrane Reactors for the Non-Oxidative Conversion of Methane. *Chem. Eng. Sci.* **2002**, *57*, 4595.
- (620) Estenfelder, M.; Hahn, T.; Lintz, H. G. Solid Electrolyte Potentiometry Aided Studies of Oxidic Catalysts. *Catal. Rev.-Sci. Eng.* **2004**, *46* (1), 1.
- (621) Hemmes, K.; Dijkema, G. P. J.; Van Der Kooi, H. J. From Chemical Processes to Electrochemical Processes: The Key to Minimal Entropy Production. *Russ. J. Electrochem.* **2004**, *40*, 1100.
- (622) Lintz, H.-G.; Reitzmann, A. Alternative Reaction Engineering Concepts in Partial Oxidations on Oxidic Catalysts. *Catal. Rev.-Sci. Eng.* **2007**, *49* (1), 1.
- (623) Spillman, R. W.; Spotnitz, R. M.; Lundquist, J. T., Jr. Why Not Make Chemicals in Fuel Cells. *CHEMTECH* **1984**, *14*, 176.
- (624) Vayenas, C. G.; Bebelis, S. I.; Kyriazis, C. C. Cogeneration: Electricity + Chemicals, Part 1: Solid Electrolytes. *CHEMTECH* **1991**, *21*, 422.
- (625) Vayenas, C. G.; Bebelis, S. I.; Kyriazis, C. C. Cogeneration: Electricity + Chemicals, Part 2: Nonfaradaic Catalysis. *CHEMTECH* **1991**, *21*, 500.
- (626) Brouzas, T.; Chiang, P.-H.; Eng, D.; Stoukides, M. Economic Evaluation of a Methane Solid Oxide Fuel Cell. *Ionics* **1995**, *1*, 328.
- (627) Chiang, P.-H.; Eng, D.; Stoukides, M. Methane Oxidative Coupling: Technical and Economic Evaluation of a Chemical Cogenerative Fuel Cell. *Energy Fuels* **1995**, *9*, 794.
- (628) Hugill, J. A.; Tillemans, F. W. A.; Dijkstra, J. W.; Spoelstra, S. Feasibility Study on the Co-Generation of Ethylene and Electricity Through Oxidative Coupling of Methane. *Appl. Therm. Eng.* **2005**, *25*, 1259.
- (629) Bredesen, R.; Jordal, K.; Bolland, O. High-Temperature Membranes in Power Generation with CO_2 Capture. *Chem. Eng. Process.* **2004**, *43* (9), 1129.
- (630) Alcaide, F.; Cabot, P.-L.; Brillas, E. Fuel Cells for Chemicals and Energy Cogeneration. *J. Power Sources* **2006**, *153* (1), 47.
- (631) Liu, Y. Y.; Tan, X. Y.; Li, K.; Hughes, R. Methane Coupling Using Catalytic Membrane Reactors. *Catal. Rev.-Sci. Eng.* **2001**, *43*, 147.
- (632) Balomenou, S.; Tsiplakides, D.; Katsaounis, A.; Thiemann-Handler, S.; Cramer, B.; Foti, G.; Comninellis, Ch.; Vayenas, C. G. Novel Monolithic Electrochemically Promoted Catalytic Reactor for Environmentally Important Reactions. *Appl. Catal., B* **2004**, *52*, 181.
- (633) Balomenou, S.; Tsiplakides, D.; Vayenas, C. G.; Poulston, S.; Houel, V.; Collier, P.; Constandopoulos, A. G.; Agraftiotis, C. Electrochemical Promotion in a Monolith Electrochemical Plate Reactor Applied to Simulated and Real Automotive Pollution Control. *Top. Catal.* **2007**, *44*, 481.
- (634) Tsiplakides, D.; Balomenou, S. Electrochemical Promoted Catalysis: Towards Practical Utilization. *Chem. Ind. Chem. Eng. Q.* **2008**, *14* (2), 97.

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