REVIEWS

Applications of Solid Electrolytes in Heterogeneous Catalysis

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Solid electrolytes are solid-state materials with an electrical conductivity partly or wholly due to ionic displacement. In 1834, Faraday was the first to report the existence of such materials. Faraday observed that, when heated up, PbF_2 could become an excellent electrical conductor. That was due to the mobility of F^- ions in the PbF_2 lattice. Over the last 20 years, research in the area of solid electrolytes has shown considerable growth. In the present review, an attempt is made to summarize recent applications of solid electrolytes in the area of heterogeneous catalysis. The emphasis is on oxygen ion and proton conductors since these are the ones that have been used to some significant extent.

Heterogeneous Catalysis Studies

1. Oxygen Ion Conductors. A large number of solid-state materials that exhibit ionic conductivity are known today, and significant effort has been made in understanding the mechanism of conduction of electricity at the molecular level (*1, 2*). The characterization of a solid electrolyte is usually based on the conduction ion. Apart from the O^{2-} and H^+ conductors, a large number of cations and anions are reported to be the conducting species in various solid electrolytes such as Ag^+, Na^+, Li^+, F^-, Cl^-, etc. (*2, 3*). Oxygen-ion-conducting solid electrolytes are solid solutions of oxides of di- or trivalent cations (Y_2O_3, Yb_2O_3, CaO) in oxides of tetravalent metals such as ZrO_2, ThO_2, and CeO_2. Of particular interest is a solution of 6–10% Y_2O_3 in ZrO_2 (yttria-stabilized zirconia) and a solution of 5–15% CaO in ZrO_2 (calcia-stabilized zirconia).

The above solutions show significantly high oxygen ion conductivity over a wide temperature range. In general, their ionic conductivity increases exponentially with temperature following approximately an Arrhenius expression with activation energy of 10–40 kcal/mol (*2*). In practice, the conductivity of the above solid electrolytes becomes significant and makes them applicable between 400 and 1300 °C. Recently certain fluoride ion conductors have been reported to operate as oxygen sensors from room temperature up to 250 °C (*4*). Nevertheless, the main contribution of solid electrolytes in heterogeneous catalytic research is that, in contrast to aqueous electrolytes, the above materials can operate in a temperature range within which most of the industrially important processes are carried out, i.e., 300–1000 °C. Hence, O^{2-} conductors have been used so far to either study or influence the rates of heterogeneous catalytic oxidations.

1a. Solid Electrolyte Potentiometry. Figure 1 shows the basic principle of solid electrolyte potentiometry (SEP), a continuous and in situ technique used to monitor the thermodynamic activity of oxygen adsorbed on metal surfaces. Two porous metal film electrodes are deposited on the two sides of a thin (50–250-μm) oxygen-ion-conducting solid electrolyte disk. One of the electrodes is exposed to a reacting mixture and serves as a catalyst for the reaction under study. The other side is exposed to a reference gas (e.g., the ambient air), and hence the metal film on that side serves as a reference electrode. Both electrodes have to be porous so that a gas–electrode–electrolyte interline exists in order for this technique to work. The two electrodes are connected to a differential voltmeter. Under open circuit (i.e., zero current conditions), the measured cell voltage, E, satisfies the equation

$$E = \frac{1}{4F}[\mu_{O_2}(\text{catalyst}) - \mu_{O_2}(\text{reference})] \qquad (1)$$

where $\mu_{O_2}(\text{catalyst})$ and $\mu_{O_2}(\text{reference})$ are the chemical potentials of oxygen adsorbed on the reacting side electrode and on the reference side electrode, respectively. The above equation is based on two assumptions:

(a) The solid electrolyte is a pure ionic conductor. In practice, stabilized zirconia is indeed a pure O^{2-} conductor at partial pressures of oxygen as low as 10^{-30} atm and temperatures as high as 1200 °C (*2, 5*).

(b) The dominant charge-transfer reaction at the gas-electrolyte–electrode interline is

$$O^{2-} \rightleftharpoons O_{(a)} + 2e \qquad (2)$$

where O^{2-} and $O_{(a)}$ stand for zirconia lattice oxygen ion and oxygen atomically adsorbed on the electrode surface, respectively. Furthermore the above reaction has to be in thermodynamic equilibrium. This is always true for the reference electrode because there is no reaction taking place on that side and there is no reactant (fuel) to react with lattice oxygen and force the above reaction to deviate from equilibrium. On the catalyst–electrode side, however, the above assumption may not hold since the possibility exists for other adsorbed species to react with O^{2-}:

$$O^{2-} + S_{(a)} \rightleftharpoons T_{(a)} + 2e \qquad (3)$$
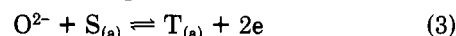
where $S_{(a)}$ and $T_{(a)}$ stand for adsorbed species (e.g., CO and CO_2 for the reaction of CO oxidation). It has been shown experimentally (*6*) that eq 2 is characterized by a relatively much higher exchange current density compared to other charge-transfer reactions on metal electrodes deposited on stabilized zirconia. Therefore, the possibility of appearance of a "mixed" potential is low.

The chemical potential of oxygen adsorbed on either electrode can be written as

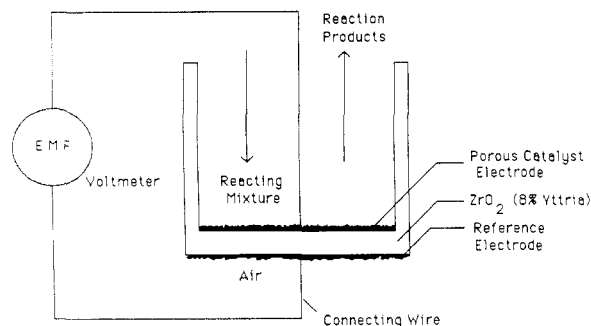$$\mu_{O_2} = \mu_{O_2}{}^\circ + RT \ln a_o{}^2 \qquad (4)$$

Figure 1. Schematic diagram of apparatus for oxygen activity (SEP) measurements.

where $\mu_{O_2}^{\circ}$ is the standard chemical potential of oxygen in the gas phase and a_o^2 is the square of the thermodynamic activity of atomically adsorbed oxygen. From eq 1 and 4, one can get

$$E = \frac{RT}{4F} \ln [a_o^2(\text{catalyst})/a_o^2(\text{reference})] \qquad (5)$$

On the reference side, $a_o^2(\text{reference})$ can be replaced by the partial pressure of oxygen in the gas phase. Therefore, for air as the reference gas, eq 5 can be arranged to give

$$a_o(\text{catalyst}) = (0.21)^{1/2} \exp(2FE/RT) \qquad (6)$$

The above equation allows continuous measurement of the thermodynamic activity of oxygen adsorbed on the catalyst surface during reaction. Physically, $a_o^2(\text{catalyst})$ corresponds to the gas-phase partial pressure of oxygen that would be in equilibrium with the adsorbed oxygen if such equilibrium were established. When the partial pressure of oxygen in the reacting side can be measured independently (analysis by a gas chromatograph or any other analytical tool), it is easy to determine whether thermodynamic equilibrium between adsorbed and gaseous oxygen exists or not. If indeed such an equilibrium exists, then

$$a_o^2(\text{catalyst}) = P_{O_2} \qquad (7)$$

where P_{O_2} is the partial pressure of oxygen in the gas phase. If, on the other hand, the overall catalytic reaction is limited by the adsorption of oxygen, equilibrium is not established between adsorbed and gaseous oxygen and

$$a_o^2(\text{catalyst}) \ll P_{O_2} \qquad (8)$$

The above analysis constitutes the basic principle of the electrochemical technique generally known as solid electrolyte potentiometry (SEP). Two more points should be mentioned about SEP:

(a) Equation 6 gives $a_o(\text{catalyst})$ on the gas–electrode–electrolyte interline. If the whole catalyst–electrode surface is exposed to the same gaseous composition, then $a_o(\text{catalyst})$ reflects the thermodynamic activity of oxygen adsorbed at any point on the surface. Hence, absence of intrapellet diffusion problems is necessary for eq 6 to be valid everywhere on the catalyst surface.

(b) If more than one type of oxygen exists on the catalyst surface and these species are in thermodynamic equilibrium with each other, then SEP can still be used. In that case, the measured open-circuit voltage, E, will reflect the common chemical potential of these species. It will not be possible, however, to determine the nature of these adsorbed oxygen species with the aid of SEP only. If more than one type of oxygen exists and they are not in equilibrium with each other, SEP will reflect the activity of those oxygen species that will equilibrate faster with O^{2-} at the three-phase interline. In most cases, atomically adsorbed oxygen is the oxygen species most likely to

Table I. Solid Electrolyte Aided Open-Circuit Studies

| catalyst (electrode) used	catalytic reaction studied	ref
Pt, Au, Ag	$SO_2 + {}^1/_2O_2 \rightarrow SO_3$	10
Pt, Pt (Pb)	$CO + {}^1/_2O_2 \rightarrow CO_2$	91
Ag	$CH_2\text{-}CH_2 \diagdown_O\diagup + {}^5/_2O_2 \longrightarrow 2CO_2 + 2H_2O$	7
Ag	$CH_2 = CH_2 + O_2 \rightarrow$ $CH_2\text{---}CH_2 \diagdown_O\diagup + CO_2 + H_2O$	13, 14
Pt	$CH_2{=}CH_2 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	8, 11, 12
Ag	$CH_3CH\text{---}CH_2 \diagdown_O\diagup + 4O_2 \longrightarrow 3CO_2 + 3H_2O$	15, 16
Ag	$CH_3CH{=}CH_2 + O_2 \rightarrow$ $CH_3CH\text{---}CH_2 \diagdown_O\diagup + CO_2 + H_2O$	17
Ni	$H_2 + {}^1/_2O_2 \rightarrow H_2O$	18, 19, 20
Ag	$H_2 + {}^1/_2O_2 \rightarrow H_2O$	30
Pt	$CO + {}^1/_2O_2 \rightarrow CO_2$	21, 28
Pt	$NO \text{ (or } NO_2) \rightarrow N_2 + O_2$	92
Pd, Ni	$CO + {}^1/_2O_2 \rightarrow CO_2$	24
VPO	$C_4H_8 + O_2 \rightarrow C_4H_6 + CO + CO_2 + H_2O$	31
Ag, Pd	$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	29, 32
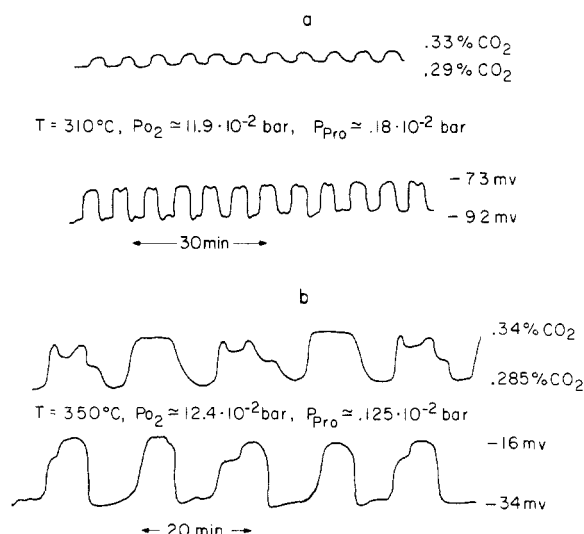
Figure 2. Typical rate and oxygen activity oscillations during the oxidation of propylene oxide over polycrystalline silver. Reprinted with permission from ref 15. Copyright 1982 Academic Press.

equilibrate faster with the zirconia lattice O^{2-} (7, 8).

The use of oxygen-ion-conducting solid electrolytes in elucidating the mechanism of heterogeneous catalytic oxidations was first suggested by Wagner in 1970 (9). Since then, a number of studies have been carried out, with—to our knowledge—Vayenas and Saltsburg being the first in 1976 (10). Table I summarizes the various SEP studies conducted thus far. The technique of SEP has been shown to be particularly helpful when oscillatory or periodic phenomena in the reaction rate are observed. Such SEP studies reported up to date are the oxidation of ethylene on platinum (10–12), propylene oxide on silver (15, 16), carbon monoxide on platinum (21–28), and hydrogen on nickel (18–20). Figure 2 contains reaction rate and SEP measurements during the catalytic oxidation of propylene oxide over polycrystalline silver (15). The reaction was studied in a well-mixed reactor (CSTR), and the period and amplitude of the oscillations were found to depend on temperature and residence time, as well as on gas composition. The rate of CO_2 production and the surface oxygen activity oscillated simultaneously, with increasing

oxygen activity (decreasing cell voltage) generally corresponding to increasing reaction rate (increase in outlet CO_2). As shown in part b of Figure 2, the oscillations were often quite complex, and in such a case the details of the rate oscillation waveform frequently differed from those of the oxygen activity oscillation. It was generally found that the observed fluctuations in the reaction rate corresponded to in-phase fluctuations in the measured cell voltage. In the case of CO oxidation on Pt, Okamoto et al. (21, 22) suggested that a mixed cell potential appears. A different interpretation of their results was offered by Vayenas (23). Recently, Metcalfe and Sundaresan (24, 26) combined SEP with exchange current density measurements during the above reaction. Although such experiments are difficult and time consuming, it is certain that much more information about the electrode–electrolyte interaction can be thus extracted. Similar exchange current density studies have been carried out recently on different reaction systems (33, 34). Vayenas and co-workers have recently studied in detail the oxidation of CO on Pt with the aid of SEP and concluded that the rate and emf oscillations observed are due to periodic formation and decomposition of surface PtO_2 (25).

The advantages of SEP can be summarized as follows:

(a) It is an in situ technique. The surface oxygen activity can be measured under reaction conditions. Ultrahigh vacuum or low temperature is not required. It is also important that the technique is applicable in a temperature range within which most of the industrially important catalytic oxidations take place.

(b) The cell voltage measurement is continuous. As mentioned above, this is extremely helpful in examining transient and/or periodic phenomena on catalytic surfaces.

Needless to say, information obtained by SEP measurements alone cannot provide a conclusive interpretation of the reaction mechanism. In the studies that have been conducted to date, SEP was used in conjunction with kinetic measurements in order to distinguish among rival kinetic models. Combination of SEP with other in situ spectroscopic techniques could be very useful in studies that will be performed in the future.

Electrochemical Oxygen Pumping (EOP). Oxygen-ion-conducting solid electrolytes can be used as oxygen "pumps". The apparatus used for the above purpose can be the same as that used for SEP studies. The difference lies in the closed-circuit operation as opposed to SEP, which requires open-circuit conditions. Hence, a galvanostat–potentiostat or another external power source can be used to impose a current through the solid electrolyte cell. For O^{2-} conductors, electrical current is equivalent to oxygen ion transport through the electrolyte. Depending on the voltage polarity, oxygen can be pumped electrochemically to or from the catalyst–electrode during reaction. In 1975, Pancharatnam et al. were the first to apply this technique of electrochemical oxygen pumping (EOP) during the decomposition of nitric oxide (35). The above workers found that the rate of NO decomposition on Pt and Au electrodes could be increased by 2 orders of magnitude by using EOP to pump oxygen away from the catalyst. The phenomenon was then studied in more detail by Gür and Huggins' (36). Table II summarizes the catalytic studies that have been carried out thus far with the aid of EOP.

It is worth mentioning that by this technique not only the reactant conversion but also the selectivity to the desired product can be significantly altered. Stoukides and Vayenas (37, 38) showed that the yield and selectivity to ethylene oxide could be altered dramatically by using EOP

Table II. Electrochemical Oxygen Pumping Studies

| anodic electrode (catalyst)	reaction studied	ref
Pt	$CO + {}^1/_2O_2 \rightarrow CO_2$, $H_2 + {}^1/_2O_2 \rightarrow H_2O$	6
Pt, Au	CO, H_2, CH_4CH_3OH, C_2H_5OH oxidations	47–50
Pt	$CO + {}^1/_2O_2 \rightarrow CO_2$	51
Pt, Au	$2NO \rightarrow N_2 + O_2$	35, 36
Fe, Ni, Pt	$CO + 3H_2 \rightarrow CH_4$	41
Ag	$C_2H_4 + O_2 \rightarrow C_2H_4O + CO_2 + H_2O$	37, 38
Ag	$C_3H_6 + O_2 \rightarrow C_3H_6O + CO_2 + H_2O$	39, 40
Ag, Ag–MgO, Fe, Au	$CH_4 + O_2 \rightarrow C_2H_4 + C_2H_6 + CO + CO_2 + H_2O$	44, 45
Ag–Bi$_2$O$_3$	$CH_4 + O_2 \rightarrow C_2H_4 + C_2H_6 + CO_2 + H_2O$	42
MoO$_3$–Bi$_2$O$_3$	propylene $\xrightarrow{O_2}$ acrylaldehyde, carbon oxides	52
Bi$_2$O$_3$–La$_2$O$_3$	propylene $\xrightarrow{O_2}$ C$_3$ dimers	46
Ag, Ni, Pd, Pt	$CH_4 + H_2O \rightarrow CO + 3H_2$	53
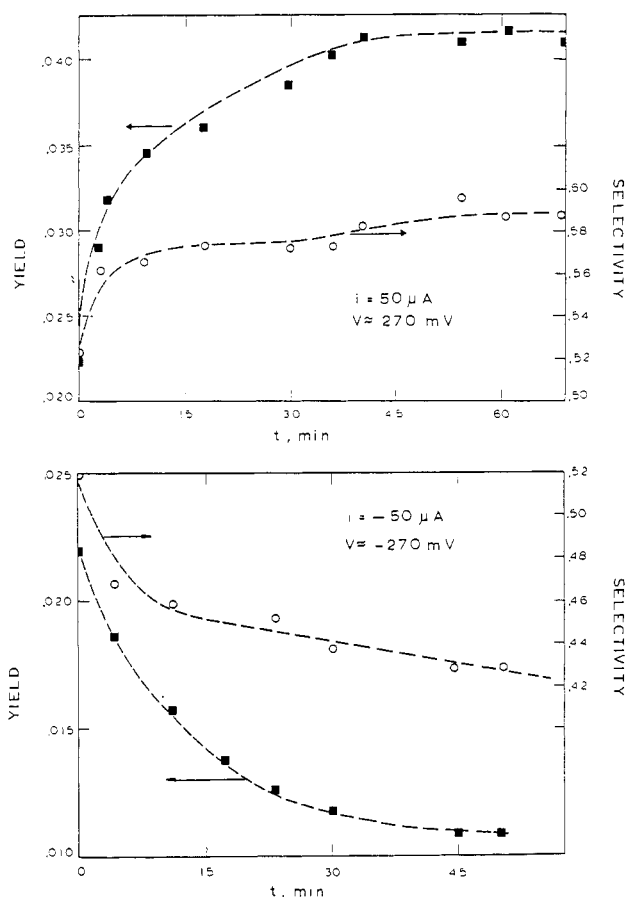
Figure 3. Effect of oxygen pumping on yield and selectivity to ethylene oxide during ethylene oxidation. Top: oxygen pumped to the catalyst, $T = 400$ °C, $i = 50$ μA. Bottom: oxygen pumped from the catalyst, $T = 400$ °C, $i = -50$ μA. Reprinted with permission from ref 37. Copyright 1981 Academic Press.

during ethylene oxidation on polycrystalline Ag electrodes. Figure 3 shows the effect of applying a constant current $i = \pm 50$ μA to the reactor cell, while monitoring the rates of ethylene epoxidation and deep oxidation. With the cell open-circuited, the electrode exposed to the reactive ethylene–oxygen mixture acts as a normal catalyst for parallel olefin epoxidation and deep oxidation. Under typical operating conditions, the catalyst exhibits at $t < 0$ (open-circuited cell) an intrinsic selectivity of 52% and a corresponding ethylene oxide yield of 2.3%. At $t > 0$, a constant current of 50 μA is imposed across the cell and O^{2-} ions are pumped to the catalyst (top part of Figure 3). When the system reaches steady state, the selectivity has

reached 59%, while the yield of ethylene oxide almost doubles. Repeating the same experiment with a current of -50 μA decreases the selectivity to 42% and the ethylene oxide yield to 1.1 (bottom part of Figure 3). Thus, the selectivity changes from 42% to 59% and the yield from 1.1% to 4.4% by simply applying a current of ± 50 μA to the cell. Similar results were obtained during the oxidation of propylene on silver (39, 40). Gür and Huggins used EOP to increase the rate of CH_4 formation from CO and H_2 on Fe, Ni, and Pt surfaces (41). In 1985, Otsuka and his co-workers were the first to use a metal–metal oxide mixture as electrode–catalyst and apply the EOP technique during the partial oxidation of methane (42). The above research group used a $Ag–Bi_2O_3$ catalyst to increase the rate of methane dimerization to C_2 hydrocarbons (ethane and ethylene). The same reaction was studied by Seimanides et al. on a number of metal and metal oxide electrodes (43–45). Recently, DiCosimo et al. studied the oxidative dehydrodimerization of propylene to C_3 dimers (1,5-hexadiene and benzene) using $Bi_2O_3–La_2O_3$ which served both as a catalyst and as an oxygen ion conductor (46). Using various anodic and cathodic electrodes (see Table II) Otsuka and his co-workers passed a H_2O stream over the cathode and a hydrocarbon stream (CH_4 or C_2H_6) over the anode. By EOP, hydrogen and oxygen were produced at the cathode and oxygen was transported through the zirconia wall to oxidize CH_4 or C_2H_4 to CO and CO_2 (53). Yentekakis and Vayenas studied the effect of EOP on the rate of CO oxidation on polycrystalline platinum. Under certain conditions, a 5-fold increase in the reaction rate was observed. Furthermore, the imposed current could affect the frequency of the rate oscillations and even stop them completely or induce them by adjusting the rate of O^{2-} transfer (51).

It is clear from the above that EOP is a very effective tool to modify electrochemically catalytic surfaces. In most cases, the nature of the catalyst–electrode is altered in a reversible fashion; i.e., the catalyst reactivity and selectivity return to their intrinsic value upon interruption of the electrical current. It may be too early to risk a general mechanism explaining the EOP results. Most probably, the pumping effect is complicated, and in addition to the cell voltage applied, other parameters are important, such as the nature of the catalyst–electrode and of the electrolyte, the composition of the reacting mixture, the ratio of catalyst surface area to the superficial area of ion transport, and the operating temperature (38, 54). In studies performed at relatively low temperatures (400 °C), a significant electrocatalytic effect was observed. For example, in the cases of ethylene and propylene oxidation (37, 40), the reaction rate enhancement (measured as an increase in moles of O_2 consumed) could be as much as 500 times the rate of oxygen transport through the electrolyte. At higher temperatures, however, a "Faradaic" effect is observed; i.e., the amount of oxygen consumed at the anode is equal to the rate of electrochemical oxygen transport (44, 45). It is not clear at this point that the operating temperature is the only parameter determining the Faradaic or non-Faradaic behavior of the cells.

High-Temperature Fuel Cells: Simultaneous Generation of Electrical Energy and Useful Chemicals. Fuel cells are devices that convert chemical energy directly to electrical energy. In such a device, the anode is exposed to a fuel, the cathode is exposed to oxygen or air (Figure 4), and electrical energy is produced in nearly a reversible fashion. When a solid electrolyte is used in a fuel cell, high temperature of operation can be employed. Such high-temperature cells working at between 700 and 1200 °C
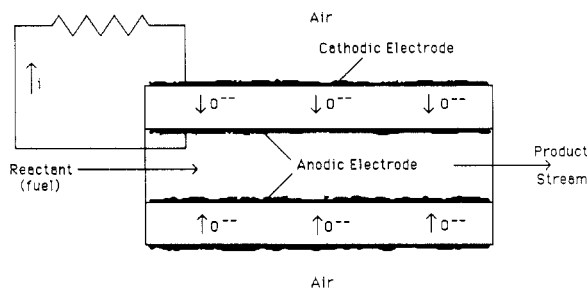

Figure 4. Schematic diagram of an O^{2-}-conducting solid electrolyte fuel cell.

Table III. Solid Electrolyte Fuel Cells Cogenerating Electrical Power and Useful Chemicals

anodic electrode	chemical reaction	ref
Pt	$NH_3 \xrightarrow{O_2} NO + H_2O$	60–63
Pt(Rh)	$NH_3 + CH_4 \xrightarrow{O_2} HCN$	64
Pt	$C_4H_8 \xrightarrow{O_2} C_4H_6$	65
Fe, $Ag–Bi_2O_3$	$CH_4 \xrightarrow{O_2} C_2H_4, C_2H_6$	45
Pt	ethylbenzene $\xrightarrow{O_2}$ styrene	66, 67
Ag	$CH_3OH \xrightarrow{O_2} CH_2O$	54, 68
Pt	$H_2S \xrightarrow{O_2} SO_2, SO_3$	54, 69

offer the advantage of combusting conventional carbonaceous fuels with air, without significant overpotential due to internal reforming (55). In comparison with molten salt fuel cells, solid electrolyte cells support temperature cycling more easily because no phase transformation occurs between room temperature and working temperature. Furthermore, solid electrolyte cells are expected to be lighter for a given power output. Taken as a whole, an entirely solid system looks attractive from an engineering point of view (55, 56).

Several investigators have examined the operation of solid electrolyte fuel cells using H_2, CO, or CH_4 as a fuel and converting them into products of complete oxidation, i.e., CO_2 and H_2O (57–59). It is extremely desirable to partially oxidize fuels where the fuel cell products are as economically valuable or more valuable than the fuel itself. Solid electrolytes are a useful tool since they can operate at temperatures of industrial interest. Today a large number of chemicals are produced via an exothermic heterogeneous catalytic reaction pathway. In a conventional reactor, the enthalpy of an exothermic reaction is converted into heat, a "low-quality" type of energy. Obviously if the production of such useful chemicals were achieved with cogeneration of electric energy instead of thermal energy, such a process would be much more attractive. On the basis of this idea, in 1980, Vayenas and his co-workers succeeded in oxidizing quantitatively ammonia to nitric oxide with simultaneous generation of electrical power in a stabilized zirconia cell operating at 800–900 °C (60–62). The same reaction was studied later in a similar fuel cell but with a 100-fold increase in the power output, while the selectivity to NO remained as high as 90% (63). Table III contains the fuel cell studies that have been reported so far and focus on the cogeneration of electricity and industrially useful chemicals. We have not included in this table fuel cell studies in which fuels such as CO or H_2 were combusted to complete oxidation products, i.e., CO_2 and H_2O.

In addition to the production of electricity instead of thermal energy, stabilized zirconia fuel cells offer another advantage: the O^{2-} conductor serves as an O_2–N_2 separator at the same time. Only pure oxygen is supplied to the anode even if the cathode is exposed to ambient air (Figure 4). This can decrease significantly the amount of gases pumped out from the reactor. For example, in the case of the Andrussow process, a mixture of air, methane, and ammonia is converted to hydrogen cyanide (64, 70). If a stabilized zirconia cell is used and the cathode is exposed to ambient air, the same amount of HCN can be produced with a 2-fold decrease in the off-gas stream.

Although the feasibility of chemical cogeneration has been demonstrated in the laboratory for a number of important exothermic industrial reactions, there are still numerous technical problems to be investigated (54). In all studies shown in Table III, the primary concern was to determine the optimum conditions for maximum yield of the desired products. To that end, a fuel cell configuration such as that shown in Figure 4 (cylindrical tube) was sufficient enough to obtain a good and reproducible set of kinetic data. Nevertheless, it is certain that a different geometry and design may lead to remarkable increases in either the power output or the charge-transfer area per unit volume of the cell (58, 71, 72). It will be necessary to combine state-of-the-art technology for producing thin (50-μm) zirconia films with the anode materials shown in Table III, to make chemical cogeneration in solid electrolyte fuel cells commercially attractive (54).

2. Solid-State Proton Conductors.

The importance of H^+ solid-state conductors has been pointed out recently through a number of international conferences in which the results of both experimental and theoretical work in the above field were presented (73, 74). Possibly, at least 1000 materials are reported to show some degree of proton conduction (75). From the engineering viewpoint, however, only a few of them are of potential interest because they have considerably high electrical conductivity and mechanical strength. Well-known solid electrolytes with high proton conductivity include H_3OClO_4 (76), $HUO_2PO_4 \cdot 4H_2O$ (73, 77), perfluorinated membranes with the commercial name Nafion (78), and several protonic β' and β''-aluminas (79–82). The above materials exhibit high H^+ conductivity at low temperatures (10^{-3} Ω^{-1} cm^{-1} at 25 °C) but fail to operate properly at temperatures above 250–300 °C. Recently, Iwahara and his co-workers reported that some sintered oxides based on $SrCeO_3$ show very high H^+ conductivity at temperatures as high as 1000 °C (83).

$SrCe_{0.95}$ $Y_{0.05}O_{3-a}$, $SrCe_{0.95}$ $Yb_{0.05}O_{3-a}$, and $SrCe_{0.95}Sc_{0.05}O_{3-a}$, with a being the number of deficiencies per perovskite-type unit cell, belong to this class of conductors (83, 84). The above materials may be found very useful in heterogeneous catalysis in the future because their proton conductivity is high at temperatures at which industrial hydrogenation and dehydrogenation reactions take place.

Despite their potential application, only a few catalytic studies have been reported thus far using H^+ conductors (85–90). The techniques of SEP, electrochemical pumping (EHP in the case of H^+ cells), and fuel cell operation can be applied to proton-conducting solid electrolytes in exactly the same way as that described in the previous section and shown in Figures 1–3. The only differences will be in the solid electrolyte material to be used and in the reference gas which should contain hydrogen or a hydrogen source compound (e.g., a hydrocarbon or H_2O).

In 1982 Mullins and Saltsburg studied the Pt-catalyzed ethylene hydrogenation in a β''-alumina solid electrolyte

cell (85, 86). Using the SEP principle, the above workers measured in situ the thermodynamic activity of hydrogen chemisorbed on the platinum electrode. Since the cell was operated under open circuit only, it was possible to report EMF measurements at temperatures up to 450 °C (85). Iwahara and his co-workers used the $SrCeO_3$-based conductors in order to study steam electrolysis for hydrogen production at 600–1000 °C (87) and operation of humidity sensors at elevated temperatures (89).

Recently, Iwahara et al. succeeded in cogenerating electrical power and ethylene in a fuel cell operating at 800–1000 °C (90). The anodic electrode (porous platinum) was exposed to an ethane stream while air was passed over the anode. Ethane was decomposed to ethylene and hydrogen, and hydrogen was spontaneously transported as H^+ through the electrolyte. At the cathode, oxygen of the air reacted with H^+ to produce H_2O. The net reaction could be written as

$$C_2H_6 + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + H_2O$$
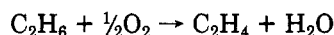
Hence, the above fuel cell could produce electricity and at the same time convert ethane to ethylene. Similar studies were performed by the above research group using CH_3CH_2OH or mixtures of $CO + H_2O$ instead of C_2H_6 (90). The major limitation of all these fuel cells was the resistance of the solid electrolyte followed by the cathodic polarization while polarization was negligibly small at the anodic electrode (84, 90).

Conclusions

Over the last 15 years, numerous applications of solid electrolytes in heterogeneous catalysis have been investigated. Emphasis so far has been on using oxygen or proton-conducting materials to study and to influence the rates of catalytic oxidations and hydrogenations, respectively. Results look very promising, especially in the fuel cell area which may become a potential alternative to conventional energy production pathways in the future. Solid electrolyte materials with improved properties are constantly reported. Promoting the already gained laboratory knowledge and background into applications of the industrial level will require intense collaboration between workers in the fields of materials science and heterogeneous catalysis.

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