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Novel SOFC Anodes for the Direct Electrochemical Oxidation of Hydrocarbons

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Abstract

Recent developments in solid-oxide fuel cells (SOFC) that electrochemically oxidize hydrocarbon fuels to produce electrical power without first reforming them to H_2 are described. First, the operating principles of SOFCs are reviewed, along with a description of state-of-the-art SOFC designs. This is followed by a discussion of the concepts and procedures used in the synthesis of direct-oxidation fuel cells with anodes based on composites of Cu, ceria, and yttria-stabilized zirconia. The discussion focuses on how heterogeneous catalysis has an important role to play in the development of SOFCs that directly oxidize hydrocarbon fuels.

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Key Words: solid-oxide fuel cell, direct oxidation, hydrocarbons, Cu, yttria-stabilized zirconia, ceria.

Introduction

The first solid-oxide fuel cells (SOFCs) were fabricated more than 65 years ago, and slow but steady progress has been made towards their commercialization since that time [1,2]. However, while the electrochemical processes that occur at both electrodes are inherently catalytic, catalytic scientists have not worked extensively on SOFCs and have not had a major impact on the developments that have occurred on these devices. Some excellent catalytic studies have been performed with solid-electrolyte membrane reactors, and this has recently been reviewed by Stoukides [3]; but the influence of this body of work on SOFC development is not large. We believe this is about to change. There is a renewed interest in SOFC technology among catalytic scientists and we believe that the insertion of catalytic concepts could fundamentally change the ways in which SOFCs are fabricated and used.

One of the major differences between SOFCs and most other types of fuel cells is the high operating temperatures, usually between 600 and 1000ºC. Primarily because of this, most effort in SOFC development has focused on large-scale devices, targeting the same market as gas turbines for the production of electricity from natural gas [4]. Compared to low-temperature fuel cells, like proton-exchange-membrane (PEM) fuel cells, much higher efficiencies are possible with SOFCs. In all fuel cells, the fraction of the chemical energy that is not converted to electricity is converted to heat. This waste heat is given up at a useful temperature in SOFCs, so that some of it can be recovered by passing the effluent from the fuel cell through a steam turbine. Furthermore, the operating temperature of an SOFC is similar to that used in steam reforming; therefore, reformation of natural gas to syngas can be performed internally, using the waste heat for the endothermic, steam-reforming reactions. The high operating temperatures nullify the need to use precious metals in electrodes, since oxides and base metals are sufficiently active under these conditions.

Large-scale SOFCs have been successfully demonstrated and have even been operated continuously for years [4]. Indeed, much of the current effort to commercialize large-scale units is focused at lowering their fabrication costs; however, there has recently been significant interest in SOFCs for small-scale operation, including Auxiliary Power Units (APU) [5,6] and even for engine replacement in automobiles [7]. This interest has been sparked by the relatively high fuel flexibility of SOFCs. In low-temperature fuel cells, protons are the ionic specie that migrates

through the electrolyte, requiring that only H_2, or a molecule like methanol that decomposes to hydrogen at low temperatures, can be used for the fuel. There are many problems associated with using H_2 as the fuel: 1) Most H_2 is produced from fossil fuels and there is a significant penalty in the overall efficiency of the process due to the reforming steps [8]; 2) H_2 is difficult to store; and 3) H_2 is potentially dangerous and requires special safety consideration. Furthermore, low-temperature fuel cells tend to be very sensitive to small amounts of CO in the fuel because CO adsorbs strongly on the precious-metal catalysts that are required in the electrode. With SOFCs, any combustible material can, in principle, be used to generate electrons electrochemically. In practice, the choice of fuel is limited by the tendency of some fuels to foul the anodes.

The reactions that occur at the fuel-cell electrodes are obviously at least partially catalytic in nature, so that the choice of electrode materials will affect performance and fuel sensitivity. In this paper, we will provide a brief tutorial on the principles involved in SOFCs and then discuss direct-oxidation fuel cells, an area where catalytic science can greatly influence SOFC development for the future.

Basic Operating Principles of an SOFC

Fig. 1 is a schematic diagram showing how SOFCs work. Like all fuel cells, SOFCs generate electricity electrochemically and are not limited by the Carnot cycle, so that high chemical-to-electrical efficiencies can be achieved. Starting from the cathode (the air electrode), molecular O_2 is first reduced to oxygen anions, using electrons external from the cell, in a half-cell reaction that can be written as follows:

$$\tfrac{1}{2}O_2 + 2\,e^- = O^{2-}. \qquad (1)$$

In order to accomplish this reaction, the cathode must be able to dissociate O_2 and be electronically conductive. Precious metals, like Pt, were sometimes used in the past but these are not commercially practical for cost reasons. Most recent work has focused on electronically conductive oxides, such as Sr-doped $LaMnO_3$ (LSM) and similar oxides [2]. While this review will not discuss problems with existing cathode materials, the reader should be aware that the search for better cathode materials is continuing, particularly for SOFCs that operate at temperatures below 800ºC [9]. The ideal cathode material should readily dissociate molecular

oxygen, have high electronic and ionic conductivities, and have a coefficient of thermal expansion that matches that of the electrolyte.

The next major component in the SOFC is the ceramic electrolyte. The electrolyte must be dense in order to separate the air and fuel compartments, must possess high ionic conductivity in order to allow easy migration of oxygen anions, and must be an electronic insulator. Furthermore, the electrolyte must maintain these properties over a wide range of $P(O_2)$, since the partial pressure (or, more properly, the fugacity) of O_2 changes from ~1 atm at the cathode to ~10^{-20} atm or lower at the anode. The operating temperature for SOFCs is largely determined by the temperature required to achieve sufficient ionic conductivity in the electrolyte, so that research on electrolytes has dominated the field. The most commonly used electrolyte material is yttria-stabilized zirconia (YSZ). Some other oxides, such as doped ceria, are under consideration because they have higher ionic conductivities [10-12]; however, YSZ continues to be the material of choice because it is stable over a wide range of $P(O_2)$, has reasonable mechanical strength, and is inexpensive. Because decreased operating temperatures simplify the materials requirements in other parts of the SOFC, there is a trend towards using very thin electrolytes supported on one of the electrodes.

In the electrolyte, the oxygen anions migrate from the cathode towards the anode (the fuel electrode) in response to the difference in chemical potentials for O_2. At equilibrium, the voltage across the electrodes (the cell potential) is given by the Nernst Equation, which simply states that the maximum work an electron can perform in going from the anode to the cathode is directly related to the difference in the O_2 chemical potentials on the two electrodes:

$$E = RT/2F^* \ln\{P(O_{2\ anode})^{1/2}/P(O_{2\ cathode})^{1/2}\}. \qquad (2)$$

In this equation, the oxygen fugacity at the cathode, $P(O_{2\ cathode})$, is the partial pressure of O_2 in the air, while the fugacity at the anode, $P(O_{2\ anode})$, is established by an equilibrium reaction. For example, if the fuel is H_2 and equilibrium is established for H_2 oxidation, the partial pressures of H_2 and H_2O in the anode compartment can be used to determine $P(O_{2\ anode})$ from the equilibrium expression for H_2 oxidation. The Nernst Equation then becomes the following:

$$E = E_o + RT/2F^* \ln\{P(H_{2\ anode})^{1/2}*P(H_2O_{\ anode})/P(O_{2\ cathode})^{1/2}\}. \qquad (3)$$

In this equation, E_o is equal to $\Delta G_o/2$, where ΔG_o is the standard Gibbs Free Energy change for the overall reaction at the cell temperature, and the 2 accounts for the number of electrons

transferred in the half-cell reactions. Under load conditions, when current is flowing, the cell potential will be less the theoretical, equilibrium potential in Equation 3 due to various losses, such as the IR drop across the electrolyte. Because the work that can be performed by the electrons is directly proportional to the potential, the efficiency of the cell decreases with increasing current.

The third major component in the SOFC is the anode, or fuel electrode. The anode must catalyze the reaction of the fuel with O^{2-} from the electrolyte and conduct the electrons that are produced in this reaction to the external circuit. If H_2 is the fuel, the half-cell reaction can be written as follows:

$$H_2 + O^{2-} = H_2O + 2\ e^-. \qquad (4)$$

In conventional designs using YSZ as the electrolyte, the anode is a ceramic-metallic composite (usually referred to as a "cermet") of nickel and YSZ. The composition of the Ni cermet is typically at least 30-vol% Ni to achieve the percolation threshold for electronic conduction [13]. The high metal content of the anode prevents the use of precious metals for obvious reasons. The YSZ provides a thermal expansion match with the YSZ electrolyte and ionic conductivity within the anode to extend the reaction zone in the anode, referred to as the three-phase boundary. While other metals can be used in the anode, Ni is almost universally used because it is inexpensive, it has excellent mechanical and electrical properties, and it is a good steam-reforming catalyst. In large-scale applications, the fuel is natural gas that must be steam reformed to a syngas. While the surface area of the Ni anode may not be sufficient to carry the reaction to completion, the Ni anode can certainly assist the reaction.

Traditional, State-of-the-Art SOFC

At the present time, the most advanced SOFCs are clearly those based on YSZ electrolytes, with a Ni- YSZ anode and an LSM cathode. Because of the need to decrease the resistance of the electrolyte, there is a trend to use thin electrolyte films, ~5 to 20 μm, supported on one of the electrodes. Cathode-supported SOFCs are used in the tubular designs being promoted by Siemens-Westinghouse [4]. The manufacturing process for these cathode-supported cells starts with a porous LSM tube, onto which the electrolyte and anode are deposited. The primary problem with this design is that it is difficult to form a dense YSZ layer onto the LSM

tube. To form a dense YSZ film by sintering of powders, it is usually necessary to calcine to at least 1300ºC, at which temperature La can react with ZrO_2 to form an insulating layer of $La_2Zr_2O_7$ [14]. Therefore, the current method of preparing thin films on LSM is by electrochemical vapor deposition, which raises the cost of the cells significantly. The power densities that are reported for cathode-supported cells also tend to be low.

The other major SOFC design is based on a planar configuration, in which the cells are stacked on top of each other [2,15-17]. Unlike tubular designs, planar SOFCs require seals to separate the anode and cathode compartments; but they are otherwise easier to construct and can give higher power densities on a volumetric scale. With planar SOFCs, there is a trend to use anode-supported electrolytes, which are relatively easy to fabricate using methods like tape calendaring or tape casting [2]. In this approach, the initial green body is made up of two layers, one containing pure YSZ and the other NiO and YSZ. Because NiO and YSZ do not form solid solutions, even at high temperatures, the green body can be fired to form a dense YSZ film on a NiO-YSZ composite. After addition of the cathode layer by a method such as screen printing, the NiO-YSZ layer is reduced to form a porous Ni-YSZ composite. The Ni-YSZ layer in these anode-supported cells is typically 0.5 to 1.0 mm thick to provide mechanical strength. Very high power densities, up to 1.8 W/cm^2 (~3.5 A/cm^2 at 0.5 V) have been reported for this type of cell at 800ºC [6,18].

The Anode Three-Phase Boundary

Because the performance of an SOFC depends strongly on the anode structure and because some aspects of electrochemical reactions are quite different from normal heterogeneous reactions, it is useful to consider how the anode works on a microscopic scale [19,20]. The electrochemical reaction can only occur at the three-phase boundary (TPB), which is defined as the collection of sites where the electrolyte, the electron-conducting metal phase, and the gas phase all come together. A cartoon of the region between the electrolyte and the anode where the TPB exists is shown in Fig. 2. If there is a breakdown in connectivity in any one of the three phases, the reaction cannot occur. If ions from the electrolyte cannot reach the reaction site, if gas-phase fuel molecules cannot reach the site, or if electrons cannot be removed from the site, then that site cannot contribute to the performance of the cell. While the structure and

composition clearly affect the size of the TPB, various theoretical and experimental methods have been used to estimate that it extends no more than approximately 10 μm from the electrolyte into the electrode [19,21,22]. Essentially, so long as the diffusion of ions through the electrolyte partially limits the performance, the concentration of excess ions in the oxide phase of the anode will be insignificant.

The TPB concept has important implications for optimization of anodes. First, YSZ particles like that marked a) in Fig. 2 will not contribute to the electrochemical performance because ions from the electrolyte cannot reach the metal-oxide interface at that position. In normal heterogeneous catalysis, optimization of the surface area by decreasing the particle size usually increases the reactivity. For the electrochemical oxidation in the anode, increasing surface area will only help if one can ensure that there is good ionic connectivity between the electrolyte and the active site. Another way of stating this is that the “fingers” of electrolyte material extending into the anode region in Fig. 2 should have a length and thickness comparable to the size of the region where the TPB exists, on the order of several microns [22,23]. Compared to catalytic materials, this is very large and corresponds to materials with very low specific surface areas. Similarly, metal particles like that marked b) in Fig. 2 will also be ineffective, even though there is good ionic connectivity to the electrolyte. In this case, electrons formed by the electrochemical reaction cannot be removed to the external circuit.

The schematic in Fig. 2 has important implications for anode synthesis. Obtaining electrolyte “fingers” that extend far into the anode requires high requires high-temperature sintering. When oxide particles are simply pressed together at low temperatures, there will be large grain-boundary resistances that will prevent the free flow of oxygen anions. Removing the grain-boundary resistance between YSZ particles typically requires a sintering temperature of at least 1300ºC; however, some materials within the anode and cathode may not be compatible with high temperatures, due to either solid-state reactions between materials or melting of some components. For example, the problem of having solid-state reactions between the LSM cathode and the YSZ electrolyte was discussed in the previous section. Some other implications of high-temperature compatibility will become apparent later when we discuss fabrication of Cu cermets.

Finally, it is clear that significant electric-field gradients can only occur near the TPB. Far from the TPB, the oxide phase will be completely inert, other than providing structural support of

the anode. The metal phase in the anode far from the TPB is needed to provide electronic conductivity and may also assist in reforming catalysis if the metal is catalytically active. It is not, however, possible for there to be significant electric-field gradients in the metal phase in the absence of enormous current flows, so that the catalytic properties of the metal phase will be affected in exactly the same manner as when one raises the potential of a metal by contact with a battery. The catalytic properties of the oxide and metal beyond the electrode-electrolyte interfacial region will be those of the materials in the absence of an electrochemical cell. In other words, the catalytic enhancements observed for some reactions using anode catalysts, described by Vayenas and coworkers and labeled Non-Faradaic Modification of Catalytic Activity (NEMCA) [24], can only be important in the TPB region.

Direct-Oxidation of Hydrocarbons

It is common in the fuel cell literature to refer to fuel cells that reform hydrocarbons to syngas internally as “direct-oxidation” fuel cells [25,26]; however, we will only use the term “direct-oxidation” to refer to fuel cells in which the hydrocarbon fuel is oxidized electrochemically without first producing H_2 and CO. Direct oxidation, without reforming, is theoretically possible with SOFCs. Given that reforming adds significant cost and complexity to the fuel-cell system, direct oxidation would have significant advantages over fuel cells that require the fuel to be H_2 for reasons discussed earlier. Since the development of direct-oxidation fuel cells has been the primary goal of our work at Penn, the remainder of this article will focus on issues involving direct oxidation.

Stability Towards Carbon Formation

The main problem preventing direct oxidation is that the presence of hydrocarbons at high temperatures can lead to coke formation. For example, with methane as fuel, thermodynamic calculations predict that carbon should form at 800ºC and 1 atm unless steam is co-fed with the methane at a H_2O:CH_4 ratio greater than one [27]. Of course, thermodynamics also predicts that n-octane should form carbon at room temperature unless the H_2O:C ratio is greater than 4 [27]. Clearly, kinetics plays a role in the formation of carbon that is at least as important as that played by thermodynamics.

State-of-the-art anodes all use Ni-based anodes. While Ni is an excellent steam-reforming catalyst, it is also an excellent catalyst for synthesizing carbon. Indeed, Ni tends to form carbon even under conditions where carbon formation is not thermodynamically predicted. For example, thermodynamic equilibrium calculations suggest that it should be possible to steam reform n-octane at 800ºC with a H_2O:C ratio of less than 1.5. Experimentally, these conditions would certainly lead to carbon formation. The problem with carbon formation is graphically demonstrated by the results in Fig. 3, which shows a picture of a Ni-YSZ cermet after heating in H_2 at 800ºC, after heating in 100% CH_4 at 800ºC for 1.5 hrs, and after heating in 40% toluene at 700ºC for 1.5 hrs [28,29]. The amount of carbon formed on the Ni cermet by exposure to CH_4 and toluene are clearly unacceptable. Furthermore, the Ni cermet fractured after exposure to toluene, probably due to expansion of the Ni phase upon formation of Ni carbide.

Direct-oxidation SOFCs are only possible if the anodes are inert for carbon formation. For example, most oxides do not catalyze carbon formation in the same way that Ni does and several groups have demonstrated direct oxidation of methane with electronically conductive oxides as the SOFC anode [30,31]. Unfortunately, the power densities for these cells were very low. This was probably due to the fact that the oxides anodes had insufficient electronic conductivity. At Penn, we chose to examine Cu cermets as anodes because Cu is an excellent electronic conductor but a poor catalyst for C-C bond formation, a reaction that is likely related to coke formation. Fig. 4 shows pictures of a Cu-YSZ cermet after heating in CH_4 at 800ºC for 1.5 hrs, and after heating in toluene at 700ºC for 1.5 hrs. (The white ring on the outside of the sample in Fig. 4a) is a YSZ support ring used to mount the cells.) Unlike the results obtained for the Ni cermets following the same treatments, only negligible amounts of carbon were formed on the Cu cermets.

While carbon can and does form on Cu when it is exposed to hydrocarbons at high temperatures, it is important to notice that there is a fundamental difference in the mechanism for carbon formation on Cu compared to metals like Ni, Co, or Fe. The mechanism for carbon formation with these latter metals has been studied extensively because of its importance in steam reforming [32]. The mechanism involves cracking of the hydrocarbon on the Ni surface, dissolution of the carbon into the bulk metal, and the precipitation of carbon at a surface on the Ni, often as graphite. The carbon evolving from the bulk metal can produce very high pressures,

which can cause materials to fracture, as Fig. 4 demonstrates. On Cu, carbon appears to form by simple deposition of carbon compounds on the surface. For example, when a Cu-YSZ sample was exposed to 100% toluene at 800ºC for several hours [28], we observed a shiny, graphite layer form on the Cu cermet; however, the Cu cermet remained undamaged and physical removal of the graphite layer by scraping revealed the unchanged, Cu-colored cermet. The importance of this observation is that the physical damage caused by carbon formation on Ni does not appear to be a problem on Cu.

While Cu cermets are very promising for application to direct-oxidation fuel cells, Cu does have several limitations. First, the low melting temperature of CuO_x makes it more difficult to fabricate Cu cermets [33-36]. Similarly, the relatively low melting temperature of Cu metal limits the operation of SOFCs based on Cu to the intermediate temperature range. Second, Cu is a very poor catalyst for activation of hydrocarbons. The same property that allows Cu to be used for direct-oxidation anodes causes anodes made from Cu to exhibit very poor performance in hydrocarbon fuels [34]. In the next sections, we will discuss possible solutions for dealing with each of these issues.

Fabrication of Cu Cermets

The most common method for fabricating Ni-YSZ cermets is to simply “press” a mixture of NiO and YSZ powders, calcine the mixture to high temperatures, and then reduce the NiO to Ni. Tape casting, tape calendaring, and similar ceramics-processing methods can obviously replace the initial pressing step for the NiO-YSZ mixture [2]. Typically, the calcination step must be carried out above 1300ºC in order to sinter the YSZ component of the cermet and achieve good ionic connectivity in the oxide phase. Fortunately, NiO and YSZ have little tendency to form solid solutions, so that the two phases remain separate even at high temperatures [36]. While the structure of the anode strongly influences the final properties of the fuel cell, the structure can be controlled through the size of the NiO and YSZ particles and through the addition of sacrificial pore formers [37].

Unfortunately, Cu-YSZ cermets cannot be produced in this manner. First, Cu_2O melts at 1235ºC and CuO at 1326ºC, temperatures that are too low to ensure sintering of the YSZ component. Equally serious, we have observed migration of Cu ions into YSZ following high-

temperature calcination. To avoid these problems, we developed several novel fabrication methods in which the porous YSZ part of the cermet is prepared first and the Cu is added in a separate step that does not require high-temperature processing. In our early work, the porous YSZ was prepared from YSZ fibers, stabilized with a zircon coating, supported on relatively thick YSZ electrolyte plates [33]. A glycerol slurry of the fibers and normal YSZ powder was applied to the YSZ electrolyte and then calcined to high temperatures to form a porous matrix. The matrix was then impregnated with aqueous solutions of $Cu(NO_3)_2$, heated to 450ºC to decompose the nitrate, and finally reduced in H_2 at the operating conditions to form the Cu-YSZ composite. This method does not allow for the fabrication of anode-supported, thin electrolytes, which are required in order to achieve high performance.

A second method for establishing a porous YSZ matrix into which Cu can be impregnated involves dual tape casting, as shown schematically in Fig. 5 [34,35]. In tape casting, oxide powders are mixed together with binders and surfactants, then spread into a film over a carrier such as mylar [38]. Upon calcination, the binders are burned out and the oxide particles sintered to form dense structures. Pore formers, such as graphite or cellulose, can be added to the green tape to introduce a controlled level of porosity. For example, with the appropriate choice of conditions, we have observed porosities as high as 80% in YSZ after calcination to 1550ºC [39]. In dual tape casting, a second layer, which could have a different composition, is spread onto the first green layer. In the case shown in Fig. 5, graphite pore formers are added to the second layer to achieve porosity after calcination, but not to the first. Since the porous layer can be thick and mechanically strong, the dense electrolyte layer can be very thin.

A variation on this dual-tape-casting method involves making a NiO-YSZ composite with a thin YSZ electrolyte in the same manner that is used to make a normal, anode-supported electrolyte with Ni-YSZ cermets [36]. After reduction of NiO, the Ni can be leached out of the YSZ using boiling nitric acid, leaving a dense YSZ layer supported on the porous YSZ substrate. An SEM picture of a porous YSZ prepared by leaching Ni from a Ni-YSZ cermet is shown in Fig. 6. The porosity of this particular sample was estimated to be 77% by Hg porosimetry, with a fairly narrow pore-size distribution between 2 and 4 μm; but we have demonstrated that the pore sizes can be controlled to a significant extent.

While it is likely that other methods for preparing Cu-YSZ cermets will be devised, the materials prepared by dual tape casting have some very attractive features. Obviously, the YSZ components are very well connected because they have been sintered at such high temperatures. Because the Cu is added after the YSZ matrix has been established, the structure of the composite is clearly not random; therefore, less metal should be necessary for achieving high electronic conductivities. Furthermore, all processing steps for adding the Cu phase are accomplished at relatively low temperatures, avoiding constraints due to solid-state reactions between Cu and YSZ. Obviously, components other than Cu can be added using similar procedures. This ability to add additional, catalytic components will be shown to be very important in the next section.

Catalytic Requirements

It is well known from the literature that Cu is a poor catalyst for hydrocarbon hydrogenolysis [40], and it is likely this property that gives Cu cermets their superior stability towards coking. However, in order to catalyze the reaction of hydrocarbon fuels, it is necessary to have a good oxidation catalyst, preferably one that is also an ionic conductor capable of transferring oxygen ions from the electrolyte to catalyst surface. Obviously, the catalyst cannot promote carbon formation. The best way to achieve both high electronic conductivity and catalytic activity, without compromising other materials properties, is to use a composite in which the catalytic and electron-conduction properties are handled by different materials. In this way, Cu does not need to fulfill a catalytic role. The synthesis procedure from the previous section allows a wide range of catalysts to be incorporated into the anode structure.

Excluding metal catalysts from consideration, ceria is known to be one of the best oxidation catalysts [41]. Along with its catalytic properties, reduced ceria is both an ionic and electronic conductor and should assist in charge transfer at the TPB [42]. In agreement with those expectations, it has been shown that the addition of ceria to a Cu-YSZ composite anode significantly increased the performance of an SOFC for direct oxidation of hydrocarbons [34,43,44].

There is ample evidence that the role of ceria is at least partially catalytic. One important demonstration of this comes from experiments with Cu-YSZ cells that were prepared with

molybdena substituted for ceria in the anode [45]. The Cu-ceria-YSZ or the Cu-molybdena-YSZ cells were heated to 450ºC with flowing propylene fed to the anode. The products leaving the cell were then monitored with a gas chromatograph while applying an electrical potential across the cell to pump oxygen ions through the electrolyte. With the Cu-ceria-YSZ cell, the products were CO_2 and water, with traces of CO. The rate of CO_2 formation increased linearly with the current and agreed well with the Faradaic prediction:

$$C_3H_6 + 9O^{2-} = 3CO_2 + 3H_2O + 18e^-. \quad (5)$$

For the Cu-molybdena-YSZ cell, the rate of product formation again increased linearly with current; but the primary product at low current densities was acrolein.

The simplest interpretation of these results is that ceria and molybdena act as catalysts in the TPB region, as shown in Fig. 7. Either molybdena or ceria are oxidized by O^{2-} coming through the electrolyte and then subsequently reduced by the fuel. According to this picture, reaction at the TPB is a simple redox process with a non-conventional oxygen source. Because molybdena is selective for the oxidation of propylene to acrolein, while ceria is nonselective, the products formed in cells with these two catalysts are different.

Another result suggesting ceria is a primarily a catalyst comes from varying the method of synthesizing the Cu-ceria-YSZ anode [35]. Based on the picture in Fig. 7, the relative position of Cu and ceria should be very important, since the ceria must receive oxygen from the electrolyte. In agreement with this, we found that the performance of cells in which aqueous $Ce(NO_3)_3$ is added first and then decomposed to form a ceria layer on the YSZ, followed by Cu addition in a subsequent step, is superior to cells in which the Cu is added first. Third, the performance of a series of cells made with various catalytic oxides followed closely with the relative rates of these oxides in normal, heterogeneous rate measurements for butane oxidation.

The fact that an important step in the electrochemical oxidation within the fuel cell is the reduction of ceria by hydrocarbons places some temperature restrictions on the fuel cell. Since it is necessary for the redox reaction to be rapid in order to achieve reasonable power densities, it is not possible to work at very low temperatures. With Cu-ceria based anodes, we have found that the temperature dependence for fuel cells operating with hydrocarbons is considerably stronger than that for H_2. Furthermore, the temperature dependence for operating with CH_4 is much

stronger than that for other hydrocarbons, in agreement with the well-known fact that CH_4 is less reactive than other hydrocarbons.

Given that the catalytic properties of the anode appear to be very important, the addition of precious-metal catalysts should greatly improve fuel-cell performance for hydrocarbon fuels. While the addition of Pt-group metals to the Cu-based anodes is difficult due to the strong tendency for alloy formation, there is indeed evidence that the addition of metals to a ceria-based anode significantly improves the performance of an SOFC for methane fuels [30]. It was found that the addition of 1 wt% Rh to an anode made of Sm-doped ceria had no effect on power densities measured with H_2 fuels, but greatly increased the electrochemical reaction rate when CH_4 was used as the fuel. The logical conclusion is that the precious metal was needed to oxidize CH_4 and reduce the ceria in the TPB of the anode, but that H_2 was reactive enough so that catalytic properties did not limit the overall cell performance.

Fuel Dependences

The performance of SOFCs with Cu-ceria-YSZ anodes has been tested on a wide variety of hydrocarbon fuels and this has been documented elsewhere [28,44]. With the exception of methane, which is known to be relatively unreactive in normal heterogeneous reactions as well, all of the hydrocarbons we examined appear to give similar performance characteristics. The fuels that were tested include n-butane [44], n-decane, toluene, and a synthetic diesel [28]. The main difference observed between the various fuels is that some fuels tend to form tars via gas-phase free-radical chemistry. Otherwise, with the exception of CH_4, all hydrocarbons that were investigated showed similar power densities. This is shown in Fig. 8, which displays the voltage and current densities for n-decane, toluene, and synthetic diesel as a function of time. In this case, the hydrocarbon fuels were diluted in dry N_2 to a concentration of 40-wt% hydrocarbon to prevent condensation of unreacted fuels that leave the cell. (In our studies, the active area for the fuel cell is ~0.5 cm^2 and a current density of 1 A/cm^2 would require a flow rate of only ~0.1 g/hr of n-decane at 100 % fuel conversion; therefore, the conversions are usually quite low.)

An important issue in direct-oxidation fuel cells is the fuel dilution that occurs with large molecules at high conversions. With n-decane for example, each oxidized molecule forms 21 product molecules. Assuming the only reaction that occurs is the oxidation to CO_2 and H_2O, the

concentration of n-decane at 50% conversion is less than 5 vol%. The effect of dilution will be to cause diffusion limitations within the anode. An obvious solution to this problem is to use the steam produced by oxidation at the entrance to the fuel cell to reform the hydrocarbon farther down the stack. Internal reforming, with the catalyst placed above the anode within the interconnect region, is common practice for molten-carbonate fuel cells operating on CH_4 [25] and the same idea could be used in direct-oxidation SOFCs. However, steam reforming of larger hydrocarbons is difficult and will require nonconventional reforming catalysts [46]. This will be an important challenge for the catalysis community should direct-oxidation fuel cells be commercialized.

Sulfur Tolerance

Essentially all real hydrocarbon fuels contain sulfur and fuel cells can be very sensitive to small amounts of sulfur. For example, Ni is used as a getter for H_2S in automotive, emissions-control catalysis [47] and problems of NiS formation can also occur in SOFCs. Indeed, the sensitivity of SOFC anodes to sulfur impurities appears to be related to the stability of sulfur compounds that can be formed by the materials in the anodes. In the case of Cu-ceria-YSZ anodes, the component most sensitive to sulfur is ceria. Conditions that lead to performance degradation match well with the thermodynamic regime where Ce_2O_2S is predicted to be stable [48]. It is fortunate that reasonably high sulfur concentrations can be used with the Cu-ceria-YSZ anodes; however, the issue of sulfur sensitivity must be evaluated for any additives that are incorporated in the anode.

Future Directions

Direct-oxidation anodes are a relatively new discovery that grew directly from the application of concepts in heterogeneous catalysis to SOFCs. There is much research to do to make these, and all other SOFCs, a commercial reality. Many of the problems that need to be solved are materials problems. The materials that make up the fuel cell need to be robust and resistant to oxidation or reduction. What we have argued here is that catalytic chemistry is also

critical. The ability to oxidize fuels electrochemically requires insights into the surface reactions that occur on the anode.

The major difference between heterogeneous catalysis and SOFC anodes is due to the requirement that, in the SOFC anode, three phases - the gas phase, the electron-conductor phase, and the ionic-conductor phase – must all come together at the site where reaction occurs. This connectivity requirement adds an additional level of complexity not found in normal heterogeneous catalysis. First, compared to catalysts in which only the gas phase and the surface need to be in contact, there is an additional requirement that must be met in the synthesis of anodes with optimal structure. Second, because the electric fields in the TPB region could be substantial, the chemistry in that region may be affected in ways that are difficult to predict [24]. Both of these issues offer exciting research challenges for researchers interested in materials synthesis and characterization of catalytic reactions.

The enormous efficiency advantages inherent with fuel cells compared to other power-generation methods suggest that fuel cells must be part of our energy future. We believe heterogeneous catalysis has an important role to play in the commercialization of SOFCs because of the unique understanding of surface chemistry that practitioners of this science bring to the problem.

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Figure Captions

1) A diagram showing the operating principles for a solid-oxide fuel cell.
2) A schematic of the three-phase-boundary (TPB) region in an SOFC anode. The YSZ particle marked a) is not active because ions from the YSZ electrolyte cannot diffuse to it. The Ni particle marked b) is not active because electrons cannot be removed
3) Photographs of a Ni-YSZ cermet after (a) heating in H_2 at 800ºC, (b) after heating in 100% CH_4 at 800ºC for 1.5 hrs, and (c) after heating in 40% toluene at 700ºC for 1.5 hrs.
4) Photographs of a Cu-YSZ cermet after (a) heating in CH_4 at 800ºC for 1.5 hrs and (b) after heating in 40% toluene at 700ºC for 1.5 hrs
5) A diagram of the dual, tape-cast procedure used in preparing anode-supported fuel cell.
6) Scanning electron micrographs of the 50:50 NiO/YSZ composite after acid leaching.
7) A schematic of the TPB region of the SOFC anode, showing the location of ceria, the catalytically active component for hydrocarbon oxidation.
8) Plots of cell potential and current density as a function of time for n-decane, toluene, and the diesel fuel. Each of the fuels was fed to the cell with N_2 at a concentration of 40 wt% hydrocarbon.