



April 2002

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Recommended Citation

Gorte, R. J., Kim, H., & Vohs, J. M. (2002). Novel SOFC Anodes for the Direct Electrochemical Oxidation of Hydrocarbon. Retrieved from http://repository.upenn.edu/cbe_papers/36

Postprint version. Published in *Journal of Power Sources*, Volume 106, Issues 1-2, 1 April 2002, pages 10-15.
Publisher URL: [http://dx.doi.org/10.1016/S0378-7753\(01\)01021-7](http://dx.doi.org/10.1016/S0378-7753(01)01021-7)

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Abstract

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Comments

Postprint version. Published in *Journal of Power Sources*, Volume 106, Issues 1-2, 1 April 2002, pages 10-15.

Publisher URL: [http://dx.doi.org/10.1016/S0378-7753\(01\)01021-7](http://dx.doi.org/10.1016/S0378-7753(01)01021-7)

Novel SOFC Anodes for the Direct Electrochemical Oxidation of Hydrocarbon

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Abstract

This paper describes recent developments in solid-oxide fuel cells (SOFC) that use Cu-based cermets as the anode for direct oxidation of hydrocarbon fuels, including liquids such as gasoline, to generate electrical power without the need for first reforming that fuel to H₂. Cu-YSZ cermets were found to be stable in hydrocarbon environments, but exhibited low performance for direct oxidation. Reasonable power densities could only be achieved with the addition of a catalytic oxide, like ceria, with the Cu cermet. Electrochemical oxidation studies demonstrated that the initial products for reaction depend on the catalytic oxide. Finally, the effect of sulfur impurities in the fuel is discussed.

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Introduction

The vast majority of H₂ produced today is generated by steam reforming of hydrocarbons [1,2]. Whether or not we move towards a hydrogen-based economy, it seems inevitable that hydrocarbons will remain the major energy source for the foreseeable future. Therefore, the fact that most fuel cells currently under development require the fuel to be H₂ represents a major hurdle for wide-spread adoption of fuel cells. If hydrocarbon reforming is performed at the site of the fuel cell, the system becomes more complex, expensive, and difficult to control. If reforming is performed at a central location, storage and distribution-infrastructure issues need to be solved. Furthermore, reforming almost inevitably leads to a significant loss in the “well-to-wheels” efficiency. Some calculations even suggest that the overall efficiency of fuel-cell systems after reforming may not exceed that of advanced systems based on heat engines [3]. Since the primary attraction of fuel cells in many applications is their high efficiency, the reforming step could prevent implementation of fuel cells in those cases.

The development of direct-oxidation fuel cells, ones that use hydrocarbons directly *without* reforming, could have important consequences for the commercialization of fuel cells. Direct oxidation of hydrocarbon fuels is theoretically possible in solid-oxide fuel cells (SOFC) because O²⁻ anions, not protons, are the species transported through the electrolyte membrane. Briefly, an SOFC generates electricity through the reduction of O₂ to O²⁻ anions at the cathode, transfer of the anions through an electrolyte that is an electronic insulator (usually yttria-stabilized zirconia, YSZ), and finally by the oxidation of the fuel with O²⁻ anions at the anode. Effectively, the chemical energy produced when the fuel is oxidized is given up to the electrons produced at the anode. The anode must be an electronic conductor and also a catalyst for oxidation of the fuel by O²⁻ anions.

The problem that prevents direct oxidation in SOFCs is the tendency of anodes to catalyze carbon formation. Indeed, carbon formation is usually thermodynamically favored with hydrocarbon fuels at the low O₂ fugacities that exist in the anode compartment, unless there is also a large quantity of steam [4]. Therefore, the conventional approach to avoiding carbon formation is to simply add steam or oxygen with the fuel. The anode, almost always made with Ni, helps catalyze the approach to equilibrium, which in the presence of excess steam favors production of H₂. In addition to the added complexity of a system in which steam is added with

the hydrocarbon, the added steam is effectively a diluent that reduces the anode fuel concentration. A less conventional approach has been used by Barnett and coworkers, who showed that direct, electrochemical oxidation of methane is possible for a narrow range of operating temperatures where carbon formation is not favored [5]. Unfortunately, there is no thermodynamic window of stability at practical temperatures for hydrocarbons other than methane [6]. Therefore, direct oxidation is not in general possible for anodes which contain Ni or other materials that catalyze the approach to equilibrium.

A second approach to direct oxidation without carbon formation involves choosing anode materials that do not catalyze the approach to equilibrium and the carbon formation that occurs at equilibrium. For example, Steele and coworkers used this approach when they examined electronically conductive oxides as anodes [7]. Oxides do not tend to catalyze C-C bond formation and are therefore resistant to coke formation. While direct, electrochemical oxidation of methane was achieved on these ceramic anodes, the electronic conductivities of oxides appear to be insufficient to give reasonable performance. Our group has chosen to examine ceramic-metallic (“cermet”), composite anodes, similar to conventional Ni-YSZ anodes, but to replace catalytically active Ni with catalytically inert Cu to allow for direct oxidation [8-10]. Obviously, Cu has a much higher electronic conductivity than any oxide at fuel-cell operating conditions; and, unlike Ni, Cu is a poor catalyst for C-C bond formation. By incorporating Cu with ceria, an excellent catalyst for hydrocarbon oxidation [11], we were able to achieve reasonable performance for direct oxidation of various hydrocarbon fuels.

In this paper, we discuss methods for synthesizing Cu-based anodes in SOFCs and some of the performance characteristics of these materials. In principle, the discussion could be applied to SOFCs with any electrolyte; however, we will restrict ourselves to zirconia-based electrolytes, such as YSZ.

Fabrication Methods

In addition to providing electronic conductivity and catalytic activity, the anode in an SOFC must be porous to allow reactant gases to diffuse to the electrolyte interface, since the oxidation reactions occur only in the three-phase boundary, where the gas phase, the metallic phase, and the electrolyte are all in contact. This region is known to extend on the order of 10 μm

into the anode from the electrolyte interface [12,13]. As a final requirement, the thermal coefficient of expansion of the anode must match that of the electrolyte in order to avoid cracking. As mentioned in the previous section, most anodes are prepared from a cermet composite made from Ni and YSZ in order to meet these requirements. Typically, these cermets are approximately 50% Ni so as to ensure electronic connectivity between all the Ni particles in the composite. Fabrication of Ni cermets is usually accomplished by high-temperature calcination of NiO and YSZ powders, followed by reduction of the Ni [14]. The calcination temperature in most synthesis methods must be above 1600 K in order to sinter the YSZ component in the anode and provide ionic connectivity between the YSZ in the anode and the electrolyte.

Because oxides of Cu melt at relatively low temperatures, it is not possible to prepare Cu-cermet anodes in the manner described above. Therefore, 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. In early work, the porous YSZ was prepared from zircon fibers, supported on relatively thick YSZ electrolyte plates [15]. A glycerol slurry of zircon fibers and YSZ powder was applied to the YSZ electrolyte and then calcined to 1800 K, with the YSZ powder binding the zircon fibers onto the electrolyte and the zircon maintaining porosity to high temperatures. This method does not allow for the fabrication of anode-supported, thin electrolytes, which are required in order to achieve high performance. The second method for establishing a porous support for Cu involved introducing pore formers into YSZ ceramic tapes, as shown in the schematic of Fig. 1 [16,17]. Since the porous layer can be thick and mechanically strong, thin electrolytes can be prepared by dual tape casting, in which the thick tape with pore formers is cast onto a thin tape without pore formers. A third 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 [18]. 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. In all of these cases, Cu and other catalytic components are subsequently added to the porous layer by wet impregnation of aqueous salts. After heating to ~ 750 K to decompose the nitrate ions, the copper oxides can be reduced in the normal manner.

Obviously, other methods for making Cu-based cermets can be devised. Assuming Cu cermets do indeed find applications in SOFCs, one should expect intense efforts to develop materials with better mechanical properties and microstructures, in the same manner that has been applied to Ni-based anodes [14].

Evidence for Direct Oxidation of Hydrocarbons

The reason one can use Cu-based cermets for direct-oxidation anodes, while Ni-based cermets are unsuccessful, is graphically demonstrated in Fig. 2, which shows pictures of Cu-YSZ and Ni-YSZ cermets that have been heated in flowing methane for 1.5 hrs at 1073 K. While the Cu cermet was essentially unaffected by this treatment, the Ni cermet was covered with carbon and had fractured, probably due to expansion of the Ni after forming NiC. Obviously, the Ni cermet would not be stable for operation in a dry methane environment. Carbon formation is usually more severe with hydrocarbons other than methane [1]. For example, exposure of a Ni cermet to toluene at 973 K resulted in carbon deposition and fracture of the cermet [10], similar to what is seen in Fig. 2. Finally, while Ni is stable for steam reforming of methane at $H_2O:C$ ratios less than 2, a recent study of n-butane steam reforming over Ni catalysts showed that carbon deposition was severe between 620 and 820 K at $H_2O:C$ ratio of 2 [19], showing carbon formation would be difficult to avoid with hydrocarbons larger than methane on Ni-based anodes.

Fig. 3 demonstrates that stable power generation can be achieved through direct oxidation of methane on Cu-cermet anodes [8]. In this experiment, the cell potential was held at 0.5 V and the current density was measured as a function of time as the fuel was changed from H_2 to CH_4 and back to H_2 for cells with a Cu-cermet anode and a Ni-cermet anode. Although the measurements were performed at 1073 K, the power densities were low, primarily due to the use of thick, 230- μm electrolytes. With the Ni cermet, performance was stable in H_2 , but rapidly dropped in CH_4 . Changing the fuel back to H_2 did not restore the performance of the Ni cermet. While the power density on the Cu cermet was found to drop when the fuel was switched from H_2 to CH_4 , the performance in CH_4 was stable and the power density returned to its initial value when the fuel was switched back to H_2 .

It is important to establish that the data in Fig. 3 results from direct oxidation of CH₄ and not some kind of reforming process. Because the cell used for the data in Fig. 3 was small and the flow rate was large, the conversion of CH₄ was always less than ~6%. In principle, the production of electrons could be explained by reforming reactions like 2CH₄ reacting to C₂H₆ and H₂, with only H₂ being electrochemically oxidized. However, Fig. 4 demonstrates that reforming is not responsible for the power generation with methane on the Cu-cermet anode and that the electrons were indeed produced by direct oxidation [8]. Here, the concentration of the outlet from the anode was measured as a function of the current density using gas chromatography. The data demonstrate that there were no leaks in our cell, since the production of CO₂ was undetectable under open-circuit conditions. Furthermore, the production of CO₂ and the conversion of CH₄ increased linearly with the current density, as should be expected for direct oxidation by a simple Faradaic process. Finally, additional proof that reaction occurs by direct oxidation of methane on the Cu-cermet anode comes from the agreement between the data points and the solid line. The solid line corresponds to the *calculated* production of CO₂, assuming that the only reaction is the total oxidation of CH₄ according to reaction (1):



The agreement between the CO₂ production determined from GC analysis and from electronic measurements is strong evidence that reforming was inconsequential in this experiment.

The direct oxidation of hydrocarbon fuels is not limited to CH₄. In previous papers, we have demonstrated that stable power generation can be achieved with anodes made from Cu cermets using a wide variety of hydrocarbon fuels, including n-butane [9], toluene, decane, and synthetic diesel fuel [10]. In the case of the fuels that are liquids at room temperature, it was even possible to inject the liquids directly into the anode compartment [10]. Again, analysis of the effluent from the anode indicated that CO₂ and water were formed in amounts that agreed with the electronic current [9]. Fig. 5 shows results from an experiment in which pure gasoline (unleaded regular, purchased from a Mobil station in Philadelphia) was fed directly into the cell at 973 K. The model fuel cell and experimental conditions used in this measurement were similar to those in Reference [10]. The data demonstrates relatively stable performance, even with this complex fuel. The noise in the data of Fig. 5 results from condensation of liquids in the exit lines

from the model fuel cell, but we did not observe evidence of coke formation during the period of the experiment.

Role of Ceria

We have alluded to the fact that fuel cells prepared from Cu-YSZ cermets that did not contain ceria showed very poor performance, especially with hydrocarbon fuels. This is shown in Fig. 6, where the cell potentials are shown as a function of current densities for CH₄, n-butane, and H₂ for two fuel cells that were identical, except that ceria was added to the cell in Fig. 6b), but not to the cell in Fig. 6a). In the absence of ceria, even the open-circuit voltage (OCV) for CH₄ at 973 K is poor [16]. OCVs for n-butane and H₂ on the Cu-YSZ anode were 1.05 and 1.1 V, respectively; however, the power densities were still much lower than were found with the Cu/ceria-YSZ anode.

Evidence has been presented that ceria assists in charge transfer at the three-phase boundary [20]; however, ceria may well play multiple roles in this system and we suggest that the primary role of ceria is as an oxidation catalyst. As a demonstration of this, cells were prepared in which molybdena was substituted for ceria at the anode; and the products of the electrochemical reaction at 720 K were then monitored while using propylene as the fuel. The low operating temperature made it necessary to apply a potential across the cell to electrochemically pump oxygen to the anode, but it also made it possible to observe the selectivity of the oxide catalysts. For both Cu/ceria-YSZ and Cu/molybdena-YSZ anodes, reaction was negligible at open circuit, indicating that reaction due to leaks was insignificant. Reaction rates increased linearly with the current density, demonstrating the oxidation of the propylene by the oxygen anions coming through the electrolyte. For cells containing ceria, essentially all of the propylene which reacted formed CO₂ and water. However, for cells containing molybdena in place of ceria, the primary product at low current densities was acrolein. Even at 0.5 A/cm², the selectivity of propylene to acrolein was greater than 50%.

The simplest interpretation of these results is that ceria and molybdena act as catalysts in the three-phase-boundary region, where the gas-phase fuel, the electrolyte, and the electronic conductor all come together. Either molybdena or ceria are oxidized by O²⁻ coming through the electrolyte and then subsequently reduced by the fuel. 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. In this picture, Cu is only an electronic conductor required for charge neutralization and not a catalyst for direct oxidation.

Sulfur Tolerance

Most commercially available fuels contain sulfur. In the case of natural gas, sulfur-containing compounds are added as odorants. While the allowable sulfur levels are being continuously reduced for gasoline and diesel fuel, these fuels will contain significant quantities of sulfur for the foreseeable future. Fortunately, the Cu-based cermets are significantly more tolerant of sulfur than the conventional, Ni-based cermets [21].

First, copper sulfides are less stable than NiS [22]. Furthermore, because Cu does not appear to play a catalytic role in the anode, surface sulfides will probably not affect performance. In agreement with this, we found that it was possible to operate a cell made with a Cu-YSZ anode in n-decane containing 5000 ppm sulfur, added as thiophene, without deactivation for 24 hrs. As discussed in the previous section, the performance of a Cu-YSZ cermet, without added ceria, is poor. When ceria was added to the anode to make a Cu/ceria-YSZ cermet, we observed severe deactivation with 5000 ppm [23]. Based on thermodynamic arguments, it appears that deactivation is due to formation of Ce_2O_2S . In agreement with this picture, the cell made with a Cu/ceria-YSZ cermet anode could be restored by simply exposing the anode to steam at the operating temperature, 973 K. Furthermore, by choosing the operating conditions so as to avoid formation of Ce_2O_2S , the cell could be operated for long times in the presence of sulfur. For example, we have shown that the Cu-based anodes can perform without difficulty in fuels containing at least 100 ppm of sulfur, a level sufficiently high to allow direct oxidation of some modern fuels.

Conclusions

We have demonstrated that electrical power generation can be achieved through the direct electrochemical oxidation of a wide variety of hydrocarbon fuels, including liquid fuels, in an SOFC. By careful consideration of the materials used in SOFC anodes, it is possible to make fuel cells that are resistant to coke formation and reasonably sulfur tolerant. Because only few

attempts have been made to fabricate direct-oxidation SOFCs, additional discoveries are almost certain to occur in the next few years. New materials with improved catalytic properties may still be discovered. Significant improvements in the performance can be expected when fuel cells are synthesized with thinner electrolytes, with improved anode structures, and with enhanced anode oxidation activities. Because the direct oxidation of hydrocarbon fuels provides so many advantages, we expect to see rapid advances in the development of these cells in the years to come.

Acknowledgment

This work was supported by the United States Office of Naval Research.

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Figure Captions

Fig. 1 A diagram of the dual, tape-cast procedure used in preparing anode-supported fuel cell. (Taken from Reference 16.)

Fig. 2 Photographs of metal-YSZ cermets after heating to 1073 K in flowing methane for 1.5 hrs. a) Cu-YSZ and b) Ni-YSZ.

Fig. 3 Current densities as a function of time for changes in the fuel at 1073 K. The cell potential was maintained at 0.5 volts. (○) Ni/CeO₂/YSZ; (●) Cu/CeO₂/YSZ. (Taken from Reference 8.)

Fig. 4 The conversion of methane at 1073 K using cell with a Cu/CeO₂/YSZ anode and an electrolyte thickness of 130 μm. The points (○) were determined from gas analysis and the line was calculated from the electrical current and the reaction $\text{CH}_4 + \text{O}^{2-} = \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^-$. (Taken from Reference 8.)

Fig. 5 Plot of cell potential and current density as a function of time for gasoline. The fuel was fed to the cell with N₂ at a concentration of 40 wt% hydrocarbon. The measurements were performed in a similar manner to that described in Reference 10.

Fig. 6 a) Power densities and current density-voltage relationships for an SOFC using a Cu-YSZ cermet as the anode at 973 K. The cell had a 60-μm electrolyte, and data are shown for the following fuels: H₂(○), C₄H₁₀(△), and CH₄(□). (Taken from Reference 16.)
b) Power densities and current density-voltage relationships for an SOFC using a Cu-ceria-YSZ cermet as the anode at 973 K. The cell had a 60-μm electrolyte, and data are shown for the following fuels: H₂(○), C₄H₁₀(△), and CH₄(□). (Taken from Reference 16.)