

Special Theme Research Article

Direct utilization of ethanol on ceria-based anodes for solid oxide fuel cells

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ABSTRACT: The direct utilization of ethanol was investigated in Cu–CeO₂, Cu–Zr_{0.35}Ce_{0.65}O₂ (ZDC) and Cu/Ru–Zr_{0.35}Ce_{0.65}O₂ anodes for solid oxide fuel cells (SOFC). The anodes were prepared by impregnation with nitrate precursors on a porous layer of yttria-stabilized zirconia (YSZ) obtained by tape casting, while (La_{0.8}Sr_{0.2}MnO_{3–δ}) LSM cathodes were screen-printed. The cells were tested in both hydrogen and ethanol. The outlet gas composition was monitored with a gas chromatograph, which showed that almost all the ethanol was decomposed, mainly to H₂, CH₄, CO, H₂O and C₂H₄. The maximum power outputs obtained in ethanol were 0.075 and 0.400 W/cm² on Cu–CeO₂|YSZ|LSM and Cu–ZDC|YSZ|LSM, respectively. All cells were more active in alcohol than in hydrogen with the peak performance occurring after approximately 4 h. That is, the power density initially increased, peaked and then decreased. This behavior was likely a consequence of carbon deposition that initially results in an improvement of the electronic conductivity in the anode but later results in the blocking of the active sites. Zirconia doping (in the ZDC anodes) resulted in better stability and, in addition, the initial activity of the ZDC anodes could be recovered after approximately 1 h of exposure to humidified hydrogen, whereas the initial activity of the ceria anodes could not be recovered. The addition of ruthenium (<0.5 wt%) further improved the stability by delaying the onset of carbon formation. © 2008 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: solid oxide fuel cells; ethanol; direct utilization; Cu–CeO₂; Zr_xCe_{1–x}O₂; Ru; carbon formation

INTRODUCTION

Solid oxide fuel cells (SOFC) are electrochemical devices that convert the chemical energy of a fuel directly into electrical power and heat. SOFC typically operate on hydrogen or reformed natural gas and are characterized by high conversion efficiencies and low direct emission of pollutants.^[1] The preferred field of application for SOFC is stationary power generation with a power output larger than 1 kW; however, there is increasing interest in developing SOFC as small auxiliary power units and portable power generation systems.^[2,3] In these types of applications, it is convenient to utilize high energy density liquid fuels rather than natural gas, and to simplify the system as much as possible by eliminating fuel purification and reforming units.

At the high temperatures (973–1273 K) at which SOFC operate, it is possible to internally reform hydrocarbon fuels (such as methane) on the typical nickel

yttria-stabilized zirconia (Ni–YSZ) anodes, provided that a high steam to carbon ratio is used to prevent the deposition of carbon^[4,5] (e.g. S/C >2 for CH₄). The introduction of water with the fuel, however, lowers the power output. In addition, it is still necessary to purify the fuel from impurities containing sulfur to avoid the irreversible poisoning of Ni.^[6] The development of alternative anodes that are simultaneously tolerant to coking and sulfur poisoning, and have performances comparable to Ni–YSZ cermets represents the ideal solution. In the case of portable power applications, a reasonable alternative is the direct utilization of liquid fuels that do not contain sulfur, such as methanol (MeOH) and ethanol (EtOH). The risk of coking is less severe for light alcohols compared to other liquid fuels (e.g. gasoline and diesel). For pure MeOH, carbon deposition is not thermodynamically favorable at high temperatures,^[7] while at lower temperatures carbon formation can be prevented by adding a small amount of steam (<10 mol%) or other additives. Alternatively, commercial EtOH, which typically contains water (>5 wt%), could be blended with MeOH to reduce coking.

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Ni-YSZ is not the ideal anode for the direct utilization of light alcohols because of its inactivity for the electrochemical oxidation of CO^[8] and because nickel catalyzes the formation of carbon nanotubes, with undiluted alcohol feeds, that leads to the destruction of the anodic microstructure.^[9] Consequently, alternative anodic compositions are being developed.^[10–12] In particular, metal/ceria anodes are among the most promising for the direct utilization of hydrocarbons in SOFC.^[13] In Cu/CeO₂ anodes, both the reforming and electrochemical reactions occur on the cerium oxide, while copper enhances the electronic conductivity. For hydrocarbon feeds, Gorte and co-workers showed that direct utilization in SOFC is possible^[14] and identified more active anode compositions and microstructures such as Cu–Co/CeO₂.^[15] The main problems with metal/ceria anodes are the poor thermal stability of ceria, which causes a loss of activity, and the sintering of copper, which results in a decrease in electronic conductivity.^[12]

Thermal stability and compatibility with the electrolyte can be improved by doping the ceria with zirconia (Zr_xCe_{1–x}O₂, ZDC).^[16] In addition, the presence of Zr⁴⁺ ions in the lattice makes the valence change of cerium easier, improving both oxygen storage capacity and ionic conductivity,^[17] and also increases the adsorption capacity for H₂ and CO,^[18] which probably has a positive effect on the electrochemical oxidation of these species. The electronic conductivity can be increased by using a metal or alloy that has a high melting point, and, like copper, has a relatively weak capacity for catalyzing reactions involved in the coking process.^[19] Alternatively, because copper is such a good catalyst for the reforming and catalytic decomposition of MeOH and EtOH,^[20–22] it may be worthwhile to improve the conductivity by increasing the Cu loading rather than replacing the Cu completely.

There is no published work on the direct utilization of ethanol on Cu–CeO₂ anodes. In this context, direct utilization refers to feeding ethanol without any other oxidant (including water) to the anode. Some work has been done on the direct internal reforming of ethanol on Ni–YSZ anodes,^[23] Cu–CeO₂ scandia stabilized zirconia (ScSZ) composite anodes,^[24] La_{0.75}Sr_{0.25}Mn_{0.5}Cr_{0.5}O_{3–δ} (LSCM) anodes,^[25] and Fe–Ni/ScSZ cermets.^[26] In the case of direct internal reforming, steam is added to ethanol to reform the ethanol on the surface of the anode and produce hydrogen (i.e. EtOH reforming: C₂H₅OH + H₂O = 4H₂ + 2CO and water-gas shift reaction: CO + H₂O = H₂ + CO₂). The produced hydrogen is then electrochemically oxidized on the anode functional layer. The steam to ethanol molar ratio used in internal reforming must be greater than 1 to avoid carbon deposition.

One issue while working with alcohol feeds is the thermal decomposition of the feed. At the typical SOFC

anodic conditions (i.e. >700 °C and pO₂ < 10^{–20} atm), the thermal decomposition (pyrolysis) of ethanol is significant. According to theoretical and experimental studies,^[27,28] the main products of EtOH pyrolysis are H₂, CO, CH₄, C₂H₄ and H₂O. The presence of CH₄ and C₂H₄, in particular, will result in carbon deposition. Therefore, for the direct utilization of ethanol-based fuels in SOFC it is necessary to develop anodes that can oxidize all the species produced by pyrolysis, catalytic decomposition and reforming, and tolerate some carbon formation. It is particularly desirable if the carbon deposits do not alter and/or damage the microstructure of the anodes, so that the initial performance can be recovered by varying the operating conditions (for example, purging the anode occasionally with humidified H₂).

In this study, Cu–CeO₂, Cu–Zr_{0.35}Ce_{0.65}O₂ and Cu/Ru–Zr_{0.35}Ce_{0.65}O₂ SOFC anodes were tested in hydrogen and dehydrated ethanol. Button cells, fabricated using YSZ as electrolyte and La_{0.8}Sr_{0.2}MnO_{3–δ} (LSM) as cathode, were investigated to assess the performance and stability of Cu–CeO₂ based anodes for the direct utilization of ethanol, to analyze the nature of carbon deposits, and to verify if the cell performance was recoverable after severe coking. Electrochemical impedance spectroscopy, Steady-state polarization measurements, direct current (dc) stability measurements and scanning electron microscopy (SEM) were used to characterize the cells.

EXPERIMENTAL

Preparation of the electrolyte, anode support and cathode

A dense electrolyte layer was prepared by tape casting using commercial YSZ powder (TZ-8Y, Tosoh, Japan) with the formulation given in Table 1. This formulation was based on the method of Corbin *et al.*^[29] and modified using corn starch (generic brand, average particle size *ca* 10 μm) and graphite powder (Alfa Aesar-325 mesh) as pore formers to obtain a porous YSZ layer for the anode. The other ingredients were dehydrated ethyl alcohol (Commercial Alcohols, Inc.), toluene (VWR, ACS grade), and fish oil used as supplied (Tape Casting Warehouse, Morrisville, PA, USA). The polymer solution contains 19.5 wt% polyvinyl butyral (Tape Casting Warehouse, B79), 36.5 wt% butylbenzylphthalate (Tape Casting Warehouse, S160), 17.2 wt% dehydrated ethyl alcohol, and 26.9 wt% toluene. The weight and porosity of each layer (dense or porous) were determined individually after sintering such that the mass fraction of each layer in the final cell could be estimated.

Green tapes of both the dense and porous electrolytes were laminated together and punched into disks, 2.6 cm in diameter. A ring-shaped YSZ dense layer was pressed

Table 1. Tape cast formulations.

Component	Mass for dense YSZ (g)	Mass for porous YSZ (g)
Ethyl alcohol	7.67	8.50
Toluene	11.25	11.25
Fish oil	1.10	1.10
Polymer solution	20.50	20.50
YSZ	50.00	28.02
Corn starch	–	15.04
Graphite	–	6.95

on the electrolyte to improve the mechanical strength at the edges of the cell. Cells so obtained were sintered at 1773 K with a heating rate of 2 K/min.^[29] After sintering, the thickness of the dense and porous layers were ~ 45 and $60\ \mu\text{m}$, respectively (Fig. 1(a)), while the apparent porosity of the porous layer was estimated as 60% based on Archimedes' method. The cathode was obtained by screen-printing a paste composed of α -terpineol (Alfa Aesar), LSM (Praxair Specialty Ceramics), YSZ and graphite powder on the electrolyte. The

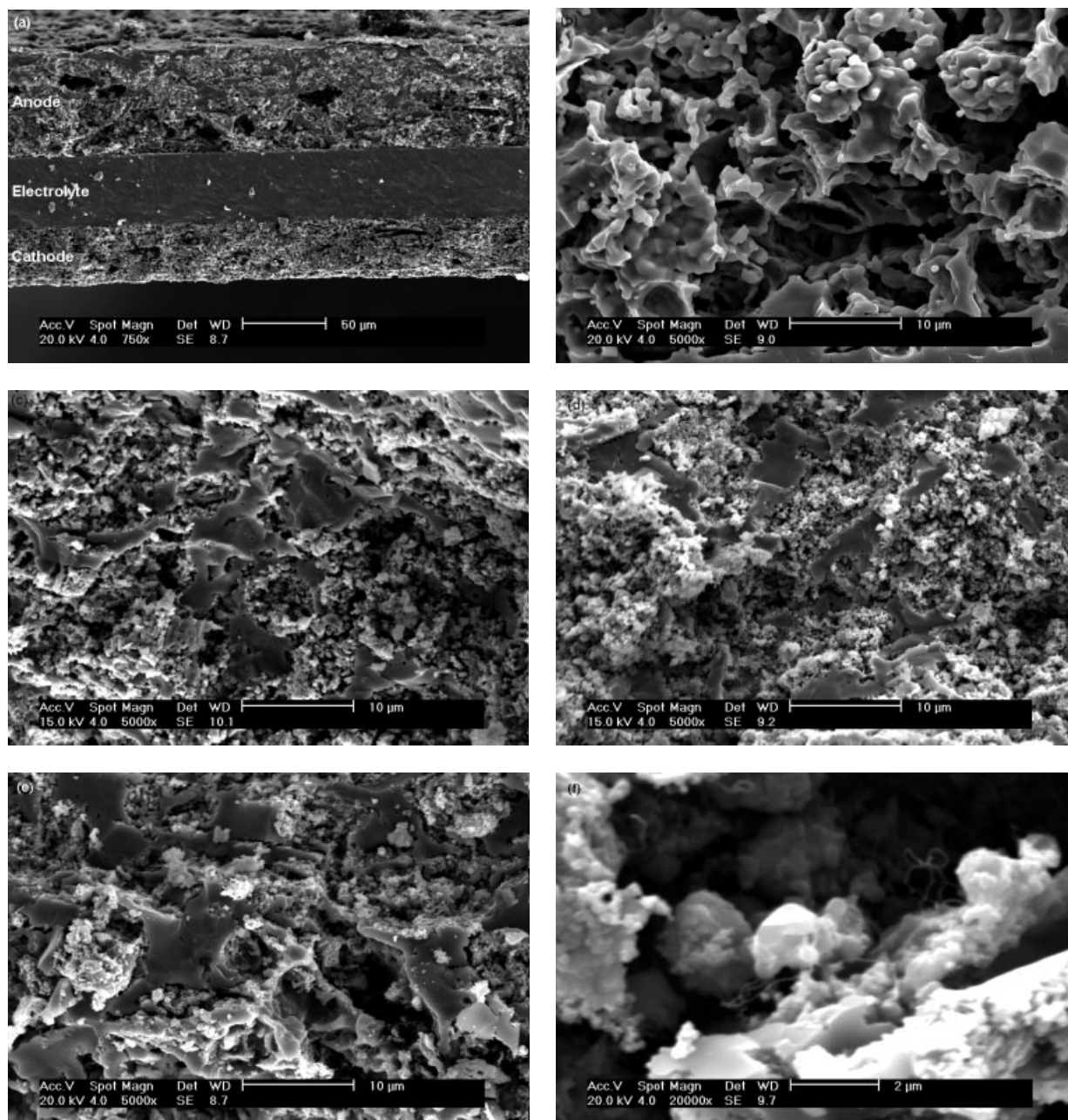


Figure 1. SEM micrographs of (a) Cu-ZDC|YSZ|LSM cell before reduction; (b) Porous YSZ layer before impregnation; (c) Morphology of the YSZ layer impregnated with Cu-ZDC (Cell 3) after reduction; (d) Morphology of the Cu-ZDC anode (Cell 4) after 16 h exposure to EtOH; (e) and (f) Cu(Ru)-ZDC anode (Cell 7) exposed to EtOH for 22 h and humidified H_2 for 48 h at different magnifications.

powder used to obtain the cathode was composed of 47.7 wt% LSM, 43.2 wt% YSZ and 9.1 wt% graphite. After firing at 1523 K for 2 h, the average thickness of the LSM cathodes was $\sim 25 \mu\text{m}$ and the area was 0.21 cm^2 .

Anode preparation and characterization

Cu–CeO₂ anodes were obtained by impregnation of the YSZ porous layer with a solution of Ce(NO₃)₃ · 6H₂O (Alfa Aesar) in isopropyl alcohol similar to the procedure of Gorte *et al.*^[19] The impregnated cells were dried at 343 K under vacuum for 15 min and then fired at 723 K for 60 min using heating and cooling rates of 2 and 5 K/min, respectively. This procedure was repeated until the weight of the ceria layer was equivalent to 10 wt% of the porous layer. Copper was added to the anodes by impregnation with a solution of Cu(NO₃)₂ · 3H₂O (Alfa Aesar) in isopropyl alcohol. The same procedure described above was repeated until a Cu content of 20 wt% (with respect to the porous layer) was obtained. The CuO₂ was reduced *in situ* using H₂.

Cu–Zr_{0.35}Ce_{0.65}O₂ (Cu–ZDC) and Cu/Ru–Zr_{0.35}Ce_{0.65}O₂ (Cu/Ru–ZDC) were prepared in a similar manner. Zr_{0.35}Ce_{0.65}O₂ (ZDC) was deposited on the porous layer using an aqueous solution containing ZrO(NO₃)₂ · xH₂O and (NH₄)₂Ce(NO₃)₆ (Alfa Aesar) at the desired molar ratio. Cerium–ammonium nitrate precursor was selected rather than cerium nitrate because this precursor produces a ZDC solid solution (single phase) at lower firing temperatures.^[30] The final ZDC content was 30 wt%. Cu was added as described above to reach a loading of 40 wt%. Both mass percents are with respect to the porous layer.

Ruthenium supported on ceria is an excellent catalyst for the reforming of ethanol.^[31,32] For this reason Ru was selected to verify its effect on Cu–ZDC anodes. Cu–ZDC anodes were impregnated with a solution of RuCl₃ (40 g/l) in isopropyl alcohol and calcined at 1073 K for 1 h. The Ru content was estimated to be <0.5 wt% with respect to the Cu loading.

Eight cells were prepared. Cu–CeO₂ anodes (Cells 1 and 2) were tested for 100 h in diluted EtOH (EtOH 8 vol% in He), while Cu–ZDC anodes (Cells 3, 4 and 5) and Cu/Ru–ZDC anodes (Cells 6, 7 and 8) were tested in EtOH injected directly into the cell (as described below). The morphology of the anodes was analyzed before and after testing by SEM using a Philips ESEM-XL30, equipped with an analyzer for energy-dispersive X-ray spectroscopy (EDAX). All SEM images are cross-sections of the cells or anodes. The samples were gold-coated before imaging.

Experimental cell and setup

On the cathode side, the current collectors were made of Pt wire (Omega Eng. Inc.) attached using Pt paste

(Engelhard). On the anode side, Ag wire (Alfa Aesar) and ink (Alfa Aesar) were used. The cell was attached to an alumina tube (13 mm in diameter, Vesuvius Ceramics) using glass sealing paste (4460, ESL Electro-Science), cured with a ceramic cement (Ultra-Temp 516 Aremco) on the air side. Ag wires (Alfa Aesar) inserted in Nextel sleeving (Omega) were used as lead wires. The lead wires were twisted to reduce stray inductance in impedance measurements. Quartz tubes were used as fuel and air inlets in the cell arrangement shown in Fig. 2(a). The H₂ flow rate was 50 ml(standard temperature and pressure)/min, while the air flow rate on the cathode side was 150 ml(STP)/min (note all flow rates are at STP unless otherwise stated).

EtOH was supplied by two methods. In the first method, He was passed at 50 ml/min through a thermostatic bubbler, at 303 K, containing dehydrated alcohol (Commercial Alcohols, Inc.). This method resulted in a stable EtOH concentration (*ca* 10 vol%) at the inlet and allowed for tests over 100 h to be performed without interruption. For shorter experiments (<25 h), dehydrated EtOH was injected directly to the anode compartment, using a syringe pump (PHD 2000 Harvard), at 2 ml/h through a capillary inlet tube (Lexsis 0.43/0.32). This method was used for the remainder of the experiments in order to obtain a higher partial pressure of EtOH. The outlet gases were directed into a micro-gas chromatograph (GC) (Agilent Technologies 3000 mGC) and into a cold trap kept at 200 K before being vented. The micro-GC has three channels (Molecular Sieve, Plot U, OV1) and was calibrated for the quantification of H₂, CH₄, CO, C₂H₄, C₂H₆, HCHO, CH₃CHO, CH₃OH and CH₃CH₂OH. The quality of the liquid EtOH and the composition of the condensate from the cold trap were analyzed using a Gas chromatography-mass spectrometry (Agilent Technologies 5975B-6890N). A schematic of the experimental set-up is shown in Fig. 2(b).

Electrochemical testing

Steady-state voltage *vs* current curves (*i*–*V*) and electrochemical impedance spectra (EIS) were measured using a potentiostat (1287, Solartron Analytical) interfaced to a frequency response analyzer (1260A, Solartron Analytical). Current–voltage curves were obtained from potentiostatic steps of 3 min taken every 50 mV. EIS were determined at open circuit potential (OCP) with an amplitude of 20 mV for the frequency range 0.01–10⁶ Hz. Stability of the cells was determined either at constant potential (potentiostatic) over a period of 10 or 20 h, or at constant load (using an in-house made variable-load circuit interfaced to Lab-View, module FP AI110, National Instruments) over a period of 100 h. The typical testing procedure was as follows. First, cells were heated to 1073 K and tested

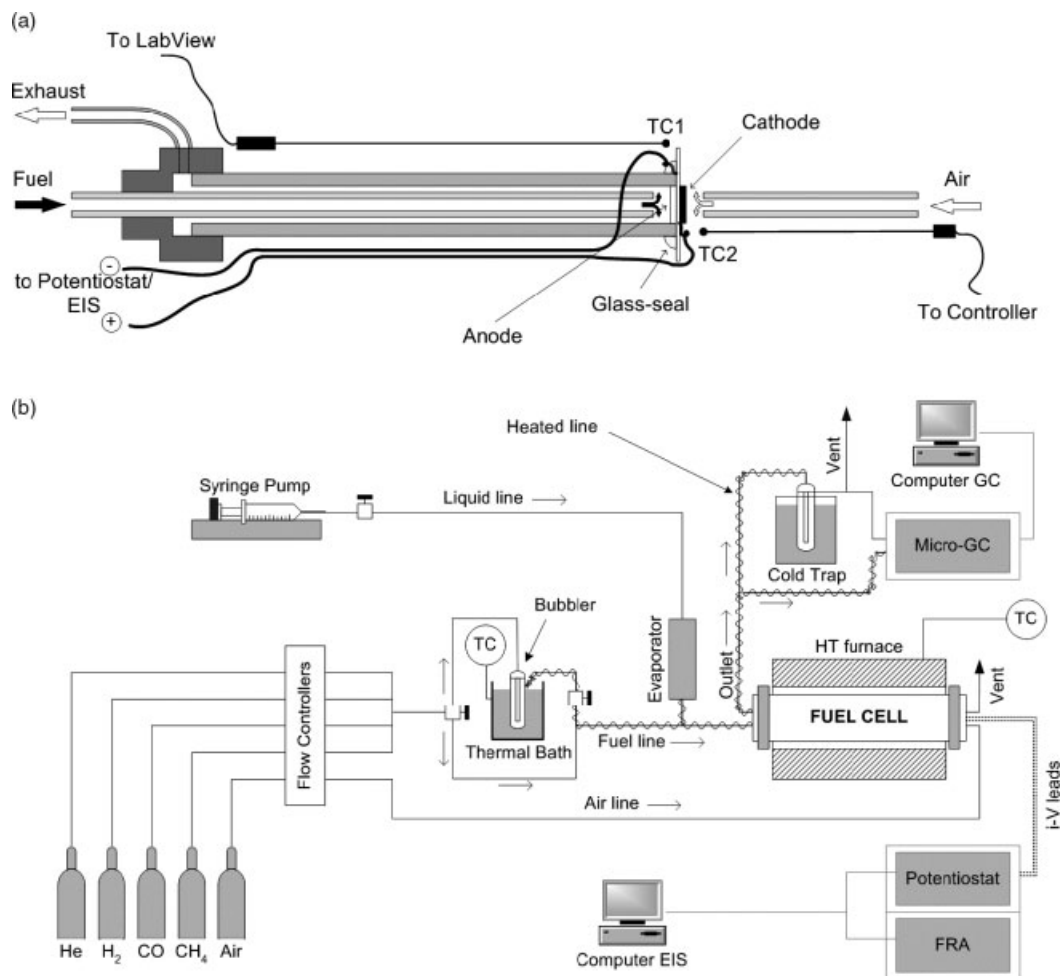


Figure 2. Schematic of the two-terminal cell (a) and experimental setup (b).

in dry H₂ to verify the sealing was sufficient. The cells producing a stable voltage larger than 1.15 V (in dry H₂) were exposed to humidified H₂ (*ca* 4 vol%, bubbler temperature 301 K) and stabilized for at least 12 h before further measurements. After testing in humidified H₂ at 1073, 1023 and 973 K, the cells were returned to 1073 K and tested in EtOH. Some of the cells were tested again with humidified H₂ to verify if the exposure to EtOH caused irreversible changes to the anode microstructure. All cells were cooled to room temperature in dry He at the end of the measurements.

RESULTS AND DISCUSSION

Cu–CeO₂ anodes (Cells 1 and 2)

The performance of Cell 1 is shown in Fig. 3. The OCP in humidified H₂ was 1.072 V, while in ~ 10 vol% EtOH (inlet gas composition) the OCP was initially 1.038 V. The maximum initial power outputs in H₂ and EtOH were 0.070 W/cm² at 0.550 V, and 0.075 W/cm² at 0.425 V, respectively. The variation of power density

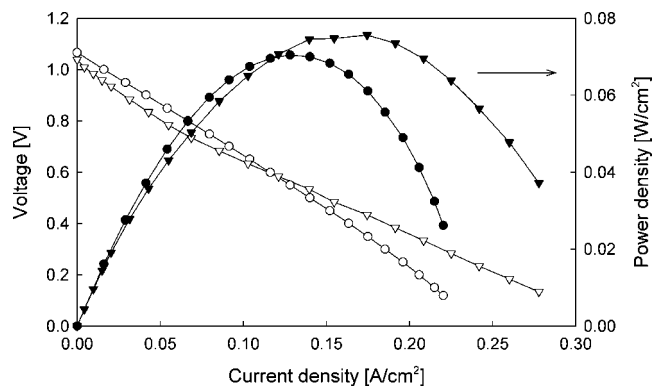


Figure 3. *i*–*V* curves (open symbols) and power density (filled symbols) for Cu–CeO₂ (Cell 1) at 1073 K in (○, ●) humidified H₂ and (▽, ▼) EtOH. The inlet EtOH concentration was 10 vol% in He.

in EtOH at constant load over a period of 100 h is shown in Fig. 4. The initial potential drop (ΔV) was ~ 0.5 V vs OCP. In the first 4 h, the power increased from 0.065 to 0.072 W/cm², and the voltage increased to 0.61 V. In the following 60 h, the power decreased

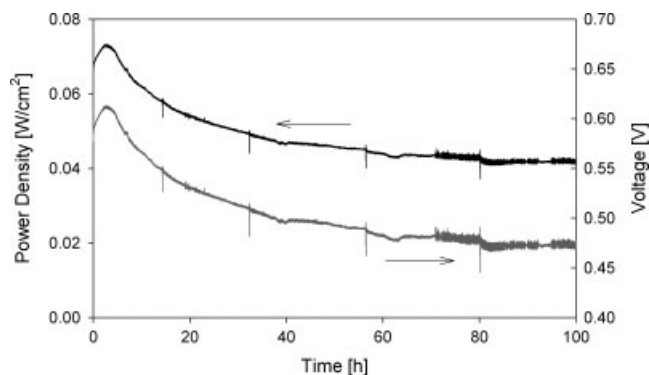


Figure 4. Stability at constant load for Cu–CeO₂ (Cell 1) at 1073 K in EtOH (inlet concentration of 10 vol% in He).

to a final steady-state value of 0.045 W/cm² with a voltage of 0.475 V. A possible explanation of the behavior observed in Fig. 4 has been given by McIntosh *et al.*^[33] namely, carbon deposits initially cause an improvement in the electrode conductivity, favoring higher cell performance, but eventually, these deposits cover active sites and plug pores resulting in decreased cell performance.

As mentioned previously, ethanol decomposes in the gas phase at 1073 K. The outlet gas composition from Cell 1 after exposure to EtOH for 50 h is given in Table 2. EtOH was almost completely decomposed to mainly H₂, CO and CH₄. Note that the maximum fuel utilization in these experiments was less than 5%. Because the cell was operated at OCP, the water present was produced by the pyrolysis of EtOH, and possibly by the direct oxidation of hydrogen with oxygen if small air leaks were present, and not by electrochemical oxidation. The calculated potential based on the outlet gas composition is slightly higher than the measured OCP (1.105 vs 1.038 V). Ethylene (C₂H₄) was present at 2.4 vol% and this species is an important precursor of carbon formation via pyrolysis. Indeed, SEM analysis of Cell 1 after testing for 100 h revealed the presence of carbon deposits on the external surface of the electrode (visible also on the alumina tube), but the cross-section of the electrode appeared to be free of carbon. EDAX analysis, however, revealed the presence of small amounts of carbon (<5 wt%) inside the pores. No carbon was present on the as-prepared anodes and no Ag (from the lead wires) was detected by EDAX on any of the spent anodes in this study. The compositions obtained by EDAX are only semiquantitative and are reported only to give a rough estimate of the amount of carbon deposited on the anodes.

A second cell (Cell 2) was tested in H₂ and EtOH and similar results in terms of power density and stability were obtained. After 24 h in EtOH, the cell was re-exposed to humidified H₂ but a significant decrease in performance was observed (maximum power in H₂ dropped from 0.080 to 0.040 W/cm²). The SEM images

Table 2. Outlet gas compositions (vol%) after reaction of ethanol over various anodes for different times.

Species	Cu–CeO ₂ (Cell 1) at time 48–52 h ^a	Cu–Ru/ZDC (Cell 7) at time 0 h	Cu–Ru/ZDC (Cell 7) after 22 h
H ₂	8.5	34.5	21.7
CO	7.2	29.9	25.0
CH ₄	6.6	15.2	24.7
CO ₂	0.1	0.4	3.1
C ₂ H ₄	2.4	1.7	5.5
C ₂ H ₆	0.0	0.8	1.7
HCHO	0.0	0.0	0.2
CH ₃ CHO	0.7	0.0	0.3
H ₂ O	3.5	0.91	16.4
CH ₃ CH ₂ OH	0.1	0.0	0.0
N ₂	0.9	3.8	3.2
He	63.9	–	–
Potentials			
OCP (V)	1.038	1.097	1.095
E _{ideal} ^b (V)	1.105	1.199	1.123

The measured OCP values and calculated ideal potentials are also included. Ethanol was supplied to Cell 1 through the bubbler and to Cell 7 by direct injection.

^a Values have been averaged over this period; the standard deviation of the concentration is less than 0.4 and typically equal to 0.1.

^b Ideal potential calculated using the Nernst equation including all the species detected by GC plus graphite.

of this electrode (not shown here) revealed agglomeration of CeO₂, as already observed by Kim *et al.*,^[34] which causes a reduction of electronic conductivity. Thus, it is likely that the decrease in performance of the cell (Fig. 4) was caused by both the thermal instability of ceria and Cu, since the Cu and ceria loading of the electrodes was low, and the carbon formation. To address the first issue, the Cu loading was increased and the ceria was doped with zirconia in the other cells.

Cu–ZDC anodes (Cells 3, 4 and 5)

The ZDC and Cu loadings were 30 and 40%, respectively, in the three cells with Cu–ZDC anodes. Figure 1(b) is an SEM image of the YSZ porous layer before impregnation, while Fig. 1(c) is an image after impregnation and reduction. These images verify that the Cu and ZDC have been well dispersed and, thus, should provide good conductivity and numerous active sites.

Cell 3 was tested only in humidified H₂; the OCP was 1.080 V and the maximum power was 0.250 W/cm² at 0.510 V, which is a significant improvement in performance over the Cu–CeO₂ anode. The stability of this cell in H₂ was tested for 24 h (potentiostatic) and over this time period the maximum power density decreased by 3% before reaching a steady state, indicating relatively good stability.

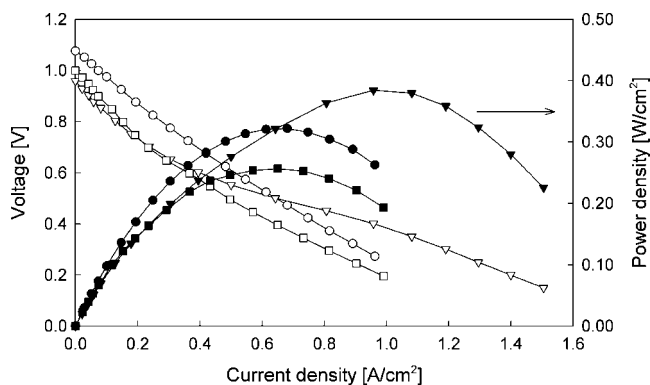


Figure 5. i - V curves (open symbols) and power density (filled symbols) for Cu-ZDC (Cell 4) at 1073 K in ($\circ$, $\bullet$) humidified H_2 , and EtOH (direct injection) after (∇ , $\blacktriangledown$) 1 h, and ($\square$, $\blacksquare$) 24 h.

Cell 4 was tested initially in humidified H_2 and then in EtOH (directly injected using the syringe pump). As shown in Fig. 5, in H_2 the OCP was 1.080 V and the maximum power was 0.320 W/cm^2 at 0.530 V, while in EtOH the OCP was initially 0.970 V and the maximum power was 0.385 W/cm^2 at 0.405 V. The stability in direct EtOH is shown in Fig. 6, and the trend is similar to the Cu-CeO₂ cells but the power density is significantly higher for the Cu-ZDC cell. The degradation rate for Cell 4 after reaching peak power (i.e. after 4 h) was $\sim 5\%$ per hour. After a total of 16 h in EtOH the cell was quenched in dry He and the anode was examined with SEM. Although a considerable amount of soot was deposited on the cell walls and on the anode surface, the microstructure of the Cu-ZDC anode, shown in Fig. 1(d), appeared similar to that of the anode before exposure to EtOH (Fig. 1(c)). EDAX analysis revealed, however, the presence of an average of 20 wt% carbon on the porous surface, which is likely responsible for the increase and decrease in performance over time (Fig. 6). No Cu or ZDC sintering was evident in the SEM analysis. The experiments performed with Cell 4 were repeated using Cell 5 to ensure reproducibility. Overall the results were very similar: OCP and maximum power of 1.069 V and 0.190 W/cm^2 at 0.530 V in H_2 , and 0.999 V and 0.220 W/cm^2 at 0.420 V in EtOH (see Table 3 for summary of results). The reduced performance of Cell 5 relative to Cell 4 is likely a consequence of the difficulty of exactly reproducing handmade cells. The stability behavior of this cell was similar to Cell 4, with a power decrease of $\sim 45\%$ after 20 h in EtOH (degradation rate after the power peak (i.e. last 15 h) was $\sim 3\%$ per hour).

Cu/Ru-ZDC anodes (Cells 6, 7 and 8)

The last set of experiments was performed on three cells with Cu-ZDC anodes impregnated with Ru. Cells

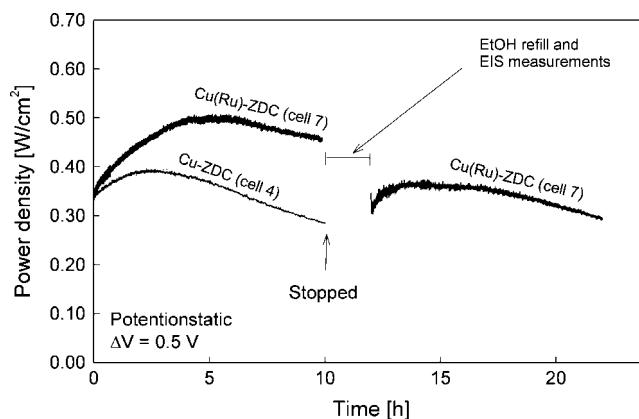


Figure 6. Stability in EtOH (direct injection) at 1073 K for Cu-ZDC (Cell 4) and Cu/Ru-ZDC (Cell 7).

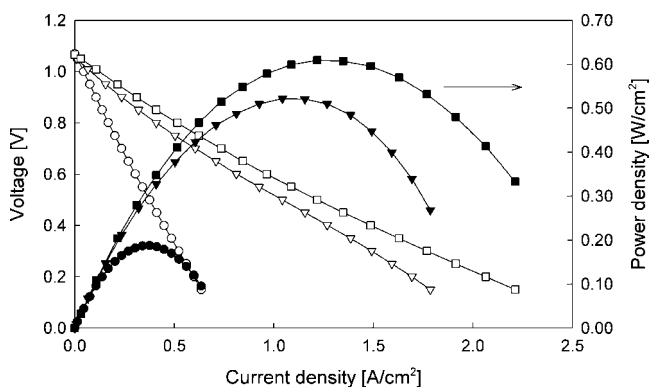


Figure 7. i - V curves (open symbols) and power density (filled symbols) for Cu/Ru-ZDC (Cell 7) at 1073 K in humidified H_2 ($\circ$, $\bullet$) before exposure to EtOH, and after exposure to EtOH for (∇ , $\blacktriangledown$) 24 h and ($\square$, $\blacksquare$) 48 h.

6 and 7 were tested in H_2 and then in EtOH (direct injection) for a total of 10 and 24 h, respectively. Cell 7 was also tested in H_2 after exposure to EtOH. The results for these cells were very similar, as summarized in Table 3 and shown in Fig. 6 (stability) and Fig. 7 (i - V and power density curves in H_2) for Cell 7. As with the other anodes, the better performance in EtOH relative to H_2 , and the increase in performance over the first 5 h (Fig. 6) are likely a result of the carbon deposition that enhanced the electrical conductivity of the electrode. Continued exposure to EtOH, however, resulted in the deposition of sufficient carbon to block active sites and decrease the performance of the cell at a rate of $\sim 3\%$ per hour for Cell 6 and $\sim 2\%$ per hour for Cell 7, after the peak power. SEM analysis of Cells 6 and 7 revealed that their morphologies were similar to that of Cell 4 as shown in Fig. 1(d), and that there were no visible carbon deposits. EDAX analysis, however, indicated that carbon was present ($<25 \text{ wt\%}$ on Cells 6 and 7; note that the wt% carbon obtained by EDAX is only an approximation).

Table 3. Summary of the performance of the cells in hydrogen and ethanol.

Cell number	H ₂ (before EtOH)		EtOH (initial)	
	OCP (V)	Power density (W/cm ²)	OCP (V)	Power density (W/cm ²)
Cell 1 (Cu–CeO ₂)	1.072	0.070	1.038	0.075
Cell 2 (Cu–CeO ₂)	1.069	0.080	1.023	0.087
Cell 3 (Cu–ZDC)	1.080	0.250	–	–
Cell 4 (Cu–ZDC)	1.080	0.320	0.970	0.385
Cell 5 (Cu–ZDC)	1.069	0.190	0.999	0.220
Cell 6 (Cu/Ru–ZDC)	1.020	0.145	1.020	0.260
Cell 7 (Cu/Ru–ZDC)	1.069	0.187	1.097	0.345
Cell 8 (Cu/Ru–ZDC)	1.076	0.195	1.169	0.251

The composition of the gas phase changed over the 22 h period in which Cell 7 was exposed to EtOH as shown in Table 2 and Fig. 8. For the direct utilization of EtOH, the processes generating the gas mixture in the anodic compartment are the thermal and catalytic decomposition of the alcohol. The former process depends on the flow regime and temperature profile of the cell, whereas the latter is influenced also by the conditions of the electrode surface, which acts as a catalyst. The surface of the anode can be partly deactivated by coking, causing a change in selectivity. Initially, EtOH was decomposed almost entirely to H₂, CO, CH₄ and carbon. Over time, the concentration of CH₄ increased as did the concentrations of C₂H₄, H₂O and CO₂. The OCP, reported in Table 3, varied in accordance with the change in gas composition in proximity of the electrode. The presence of Ru in the anode changed the gas phase composition.

Impedance measurements were taken for all experiments, but only the results for Cell 7 will be presented and discussed since they are representative of all the other cells. The two-terminal cell impedance spectra in humidified H₂ and in EtOH (direct injection) for

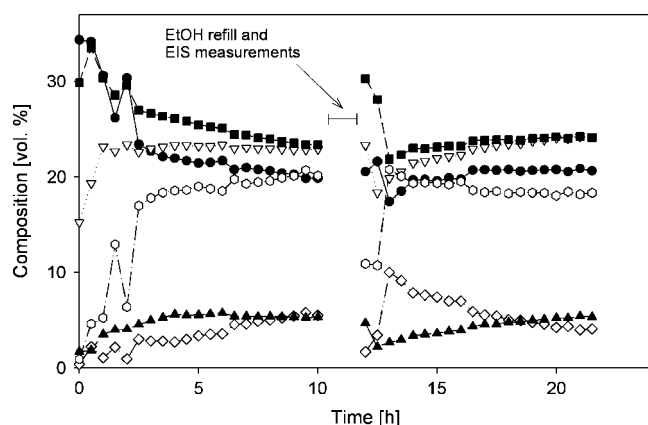


Figure 8. Composition of the outlet gas from Cell 7 during the stability test in EtOH (direct injection) at 1073 K. The species are: (●) H₂, (▽) CH₄, (■) CO, (◇) CO₂, (▲) C₂H₄, and (○) H₂O.

Cell 7 are shown in Fig. 9(a). The high-frequency intercept was always smaller in EtOH than in H₂, which is consistent with increased conductivity of the electrode after exposure to EtOH because of carbon deposition. A low-frequency tail in the impedance spectra has been consistently observed with the direct utilization of EtOH in our work, and resembles Warburg-type impedance (i.e. diffusion impedance). This tail does not touch the real axis even at 0.01 Hz.

To understand what caused this impedance result, Cell 7 was exposed to humidified H₂ after EtOH exposure and the *i*–*V* curves were collected as shown in Fig. 7. In contrast to Cu–CeO₂, the performance of Cu/Ru–ZDC cells increased significantly after exposure to EtOH, and this improvement continued until the maximum power stabilized at 0.610 W/cm² at 0.5 V. This result indicates that the electronic conductivity was not initially maximized and that improvement can be achieved, provided that a high rate of gas diffusion is maintained. The improvement after exposure to EtOH is consistent with the change in the impedance plots of Fig. 9(b). In the impedance spectrum taken 1 h after switching to humidified H₂ a low-frequency tail is still present, while after 12 h this tail is reduced to a semicircle 0.2 Ω cm² in diameter with a peak frequency at 0.16 Hz. Possibly this behavior is a result of gas-diffusion impedance in a stagnant layer external to the anode surface, as explained for the hydrogen oxidation in Ni–YSZ anode by Primdahl *et al.*^[35] However, for EtOH it is possible that the diffusion in the porous layer becomes significant. A smaller low-frequency semicircle (0.1 Ω cm² with peak frequency at 0.20 Hz) was present in the impedance spectrum obtained initially in both dry H₂ (not shown) and humidified H₂ (Fig. 9(a)).

After exposure to EtOH, there was evidence of carbon formation (SEM images were very similar to that for Cu/ZDC shown in Fig. 1(d)) on the Cu/Ru–ZDC cells but the pores were not completely plugged. Even partial blocking of the pores would increase diffusion resistance and result in the low-frequency tail seen in the impedance spectra (Fig. 9(a)). The average carbon

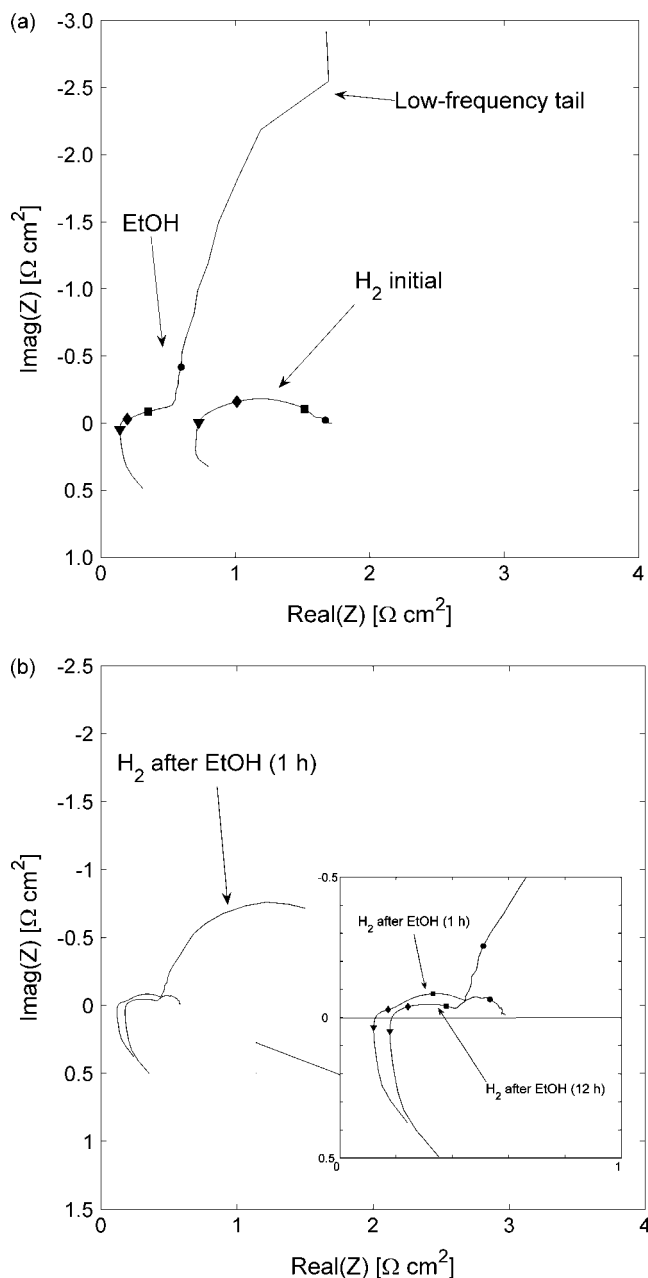


Figure 9. Area-specific impedance spectra of Cu/Ru-ZDC (Cell 7) at 1073 K in (a) humidified H₂ and EtOH (direct injection), and (b) in humidified H₂ after exposure to EtOH at 1073 K. The inset in (b) shows an enlargement of the spectra and the symbols on the spectra represent frequencies at (▼) 10⁵ Hz, (◆) 10³ Hz, (■) 10 Hz, and (●) 0.1 Hz.

content on the anode surface was 25 wt% measured by EDAX but there was no significant visible change in the electrode morphology after exposure to EtOH and re-exposure to humidified H₂. Carbon nanotubes, most likely catalyzed by dispersed Ru,^[36] were visible in some of the pores (Fig. 1(f)) and were not oxidized even after 48 h in humidified H₂. At the end of the experiments with Cell 7 (22 h in EtOH, 48 h in H₂) the ohmic resistance was 0.2 Ω cm² and the polarization resistance (cathode + anode) was only 0.4 Ω cm² at

1073 K (similar EIS as after 12 h in Fig. 9(b)), which indicates that the cell was not significantly damaged by the direct utilization of EtOH.

CONCLUSIONS

In this study, the direct utilization of EtOH at 1073 K in fuel cells with Cu-CeO₂, Cu-ZDC, and Cu/Ru-ZDC anodes has been investigated. The anodes were characterized with *i*-V measurements, dc stability measurements, electron impedance spectroscopy and SEM. The main conclusions are as follows:

- After 60 h in EtOH/He, stable but low (0.045 W/cm²) performance was obtained on Cu-CeO₂ anodes; re-exposure to H₂ and SEM analysis indicated that the microstructure of the anode was irreversibly and negatively changed after exposure to EtOH.
- Zirconia doping of the ceria and increasing the Cu loading from 20 to 40% resulted in better performance (maximum power of 0.400 W/cm²) and stability.
- The addition of dispersed Ru (<0.5%) was effective in delaying anode deactivation by coking and increased the maximum power to greater than 0.500 W/cm² in EtOH.
- With all the anodes tested, the performance peaked within 4–5 h of operation when directly fueled in EtOH. The results suggest that there was an optimal amount of carbon formation. That is, carbon deposits initially increased the electrical conductivity but later deactivated the anode by blocking active sites. Provided that the microstructure did not change during operation, the performance in H₂ after exposure to EtOH was enhanced by carbon formation.
- Both thermal and catalytic decomposition of EtOH have important consequences for the direct utilization of EtOH in SOFC. In EtOH the OCP measured in Cu-ZDC was different from that obtained in Cu/Ru-ZDC cells; furthermore, the OCP varied with the degree of deactivation (related to carbon formation) indicating that the gas composition at the electrochemically active sites is different from the bulk composition and depends on the degree of catalytic decomposition within the conducting, but not electrochemically active, portion of the anode. Possibly, the gas microenvironment surrounding the active sites dictates the actual performance and stability of these anodes.
- The anode microstructure was not destroyed by the direct utilization of EtOH, even though there was carbon formation over 20 h of operation. In agreement with the result obtained by others,^[13] it has been shown that Cu-ZDC anodes can withstand severe coking conditions caused by the direct utilization of EtOH.

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