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Advanced tubular solid oxide fuel cells with high efficiency for internal reforming of hydrocarbon fuels

Praveen K. Cheekatamarla*, Caine M. Finnerty, Yanhai Du, Juan Jiang, Jian Dong, P.G. Dewald, C.R. Robinson

NanoDynamics Energy Inc., 901 Fuhrmann Blvd, Buffalo, NY 14203, United States

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ABSTRACT

Solid oxide fuel cells (SOFCs) constitute an attractive power-generation technology that converts chemical energy directly into electricity while causing little pollution. NanoDynamics Energy (NDE) Inc. has developed micro-tubular SOFC-based portable power generation systems that run on both gaseous and liquid fuels. In this paper, we present our next generation solid oxide fuel cells that exhibit total efficiencies in excess of 60% running on hydrogen fuel and 40+% running on readily available gaseous hydrocarbon fuels such as propane, butane etc. The advanced fuel cell design enables power generation at very high power densities and efficiencies (lower heating value-based) while reforming different hydrocarbon fuels directly inside the tubular SOFC without the aid of fuel pre-processing/reforming. The integrated catalytic layered SOFC demonstrated stable performance for >1000 h at high efficiency while running on propane fuel at sub-stoichiometric oxygen-to-fuel ratios. This technology will facilitate the introduction of highly efficient, reliable, fuel flexible, and lightweight portable power generation systems.

1. Introduction

There is an increasing demand for power generation systems with high efficiency and low emissions due to depleting energy resources and global warming. Fuel cells are considered to be the enabling clean energy technology because of their ability to convert the chemical energy of the fuel directly in to electrical energy, therefore, they can theoretically achieve a high electrical efficiency.

The solid oxide fuel cell (SOFC) is a solid-state device, which typically operates at temperatures of 600–1000 °C. SOFCs reduce most of the problems encountered in other fuel cell technologies, e.g. corrosion and water management problems in Molten Carbonate Fuel Cell (MCFC) and Polymer Electrolyte Fuel Cell (PEFC), respectively. In addition, the fuel flexibility of the SOFC is a major advantage because of its ability to oxidize both H_2, CO, and some small chain hydrocarbons, decreasing the costs associated with the production of pure hydrogen required by low temperature fuel cells. Also, from a complete system standpoint, the high operating temperature of the system embeds more heat energy, which can be recuperated and properly utilized within the system. Theoretically, such a design can lead to higher overall system efficiency.

Hydrocarbon fuels such as natural gas, propane, gasoline, kerosene and diesel are less expensive, more easily and more safely stored, and more readily available than hydrogen. A common problem when using hydrocarbon fuels directly in a SOFC is the susceptibility of nickel-based anodes to suffer carbon deposition preventing nickel's catalytic activity and electrical conductivity [1–6]. In addition, carbon deposition can form a barrier layer on the anode and prevent gas reactions with fuels [2,6]. It also can disrupt the anode structure by pushing nickel particles apart, damaging the cell [6].

The most common approach to the use of hydrocarbons as the energy source for fuel cells is with the aid of an external reformer device, in which the fuel is catalytically reacted with oxygen (partial oxidation reforming), water (steam reforming), or both (autothermal reforming), to form a mixture of H_2, CO, CO_2, N_2, and H_2O, which increases the cost and complexity of a fuel cell system.

Several studies based on detailed models of transport and chemistry were systematically analyzed for the effect of various parameters on cell performance for internal reforming SOFCs [7–11]. Most of these studies however utilized steam reforming process.

Dry reforming of methane by feeding different biogas compositions directly in to the modified and un-modified Ni-based SOFCs was also investigated and published [12–14]. Other approaches involving the direct internal reforming of different gaseous hydrocarbon fuels using steam was also evaluated on SOFCs doped with

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* Corresponding author. Tel.: +1 716 880 1021; fax: +1 716 853 8996.
E-mail address: praveen_chemi@yahoo.com (P.K. Cheekatamarla).

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different active metals [15]. Novel Copper-based SOFCs were also developed for direct oxidation of different hydrocarbon fuels via the electrochemical oxidation approach [5]. The application of porous barrier layers and catalytic layers to extend the range of coke-free operation on Ni-YSZ anode structures, with different fuels using either a dry reforming or oxygen assisted dry reforming approach was also successfully demonstrated [2,16].

NanoDynamics Energy Inc. (NDE) is involved in the development of portable power generation systems based on the SOFC technology. In the past [17], we have demonstrated the internal reforming capabilities of our first generation SOFC technology with reliability. Partial oxidation was chosen as the fuel reforming approach because of its numerous advantages over other processes that require steam and/or carbon dioxide. Steam reforming of fuels is more energy efficient than partial oxidation (POX). However, for a portable power generating system, POX is more favorable due to its faster startup, simple design, the lack of water management and steam generation, less balance-of-plant requirements, which make the system lighter, reliable, and faster. These advantages from POX definitely outweigh the higher efficiency of the steam reforming process, particularly for a portable power generating system.

The objective of our present study was to develop a solid oxide fuel cell that is highly efficient in converting the chemical energy directly in to the useful electrical energy without the aid of any fuel pre-processing/reforming. Both single cell and stack testing results will be presented for hydrogen, propane, and butane fuels.

2. Experimental

A tubular SOFC with anode support, electrolyte, and cathode layers was fabricated. A porous catalyst support membrane was coated on the anode surface using a slurry containing active catalytic materials tailored according to the reaction chemistry. The composition of the fabricated SOFC including the catalytic layer cannot be disclosed due to proprietary reasons.

The experiments presented in this study were conducted inside an electric furnace maintained at 800 °C. Fuel along with air was supplied to the anode side of the cell for partial oxidation at oxygen-to-fuel ratios ranging from 1.06 to 1.6. Cathode side of the cell was continuously supplied with air while calibrated unit mass flow controllers (MKS) were used to control the flow rates. The hot product gas leaving the single-cell was analyzed using GC–MS to monitor fuel conversion and catalytic performance during transients. A programmable electronic load (AmRel, model# 150-60-30) was used for applying loads in different modes. All the long-term stability tests were conducted at peak power operation characteristics.

The results presented hereafter were all performed on our advanced 4-layer tubular SOFCs with an integrated catalytic layer designed for handling gaseous hydrocarbons as well as hydrogen. The tests were conducted under flow-in/flow-out conditions (single pass, no recycle of the anode fuel exhaust). Fuel cell efficiencies reported throughout the article were calculated by comparing the electric power generated vs. lower heating value (LHV) of the fuel supplied. LHV of the propane fuel was assumed to be 43.85 MJ kg^{-1} [18,19]. Different generations of SOFC technologies are represented as G1, G2, G3, G4, for example G4 denotes 4th generation SOFC.

3. Results and discussion

3.1. Hydrogen fueled SOFC performance

The efficiency of a series of different generation SOFCs fueled by hydrogen at different flow rates was measured. It was noticed that for similar geometries and hydrogen flow rates on G1 and G4 cells the efficiency increased from 42% to 60%, demonstrating the superior performance of G4 SOFCs fueled by hydrogen.

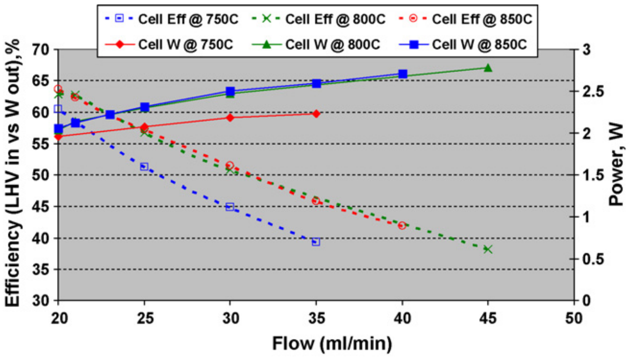

Fig. 1. Cell efficiency and Power as a function of hydrogen flow rate on a G4 cell operated at 800 °C.

More tests were conducted on the G4 cell to evaluate its performance at different hydrogen flow rates and operating temperatures, the results of which are shown in Fig. 1. It is clear that at operating temperatures above 800 °C the cell produces >2 W of electrical power maintaining efficiencies above 60% at lower hydrogen flow rates. Higher hydrogen flow rates however resulted in higher power output but with a loss in efficiency (<50%).

For practical applications, liquefied propane gas (or a mixture such as LPG) is an ideal candidate for SOFC-based power generation systems because its energy density is comparable or better than that of gasoline and kerosene fuels. In addition, propane is widely available and easily transportable. A broad range of studies were conducted on the next generation SOFCs using both propane and butane and the results are discussed below.

3.2. Propane and Butane fueled SOFC performance

Fig. 2 shows the power output from 1st generation and different 4th generation SOFCs during the partial oxidation reforming of propane gas via internal reforming inside the tubular cell. All the cells were operated at 800 °C and peak power loads. The amount of propane supplied was the same for G1, G4a and G4b cells, but 2.5 times higher in the G4c cell. It is clear that the total power output from G1 cell is significantly lower than that of G4 series of cells in spite of similar active surface areas and fuel flow rates. It can also be noticed that G4b cell produced higher power than the G4a cell even though the active surface area was shortened by

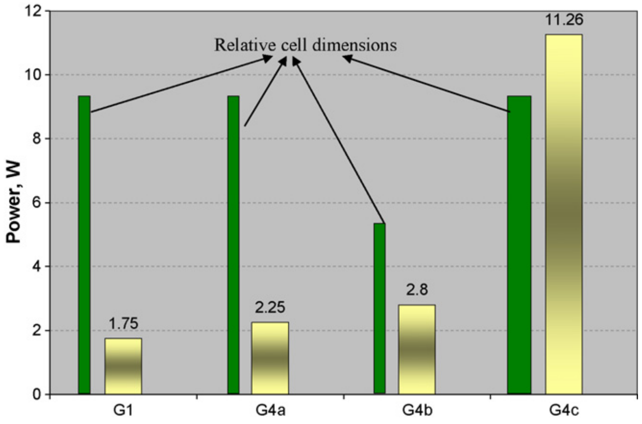

Fig. 2. Power output from different 4th generation SOFCs fueled by propane gas (varied flow rates) during internal reforming via partial oxidation process at cell operating temperature of 800 °C. Relative cell dimensions are also shown (not to scale).

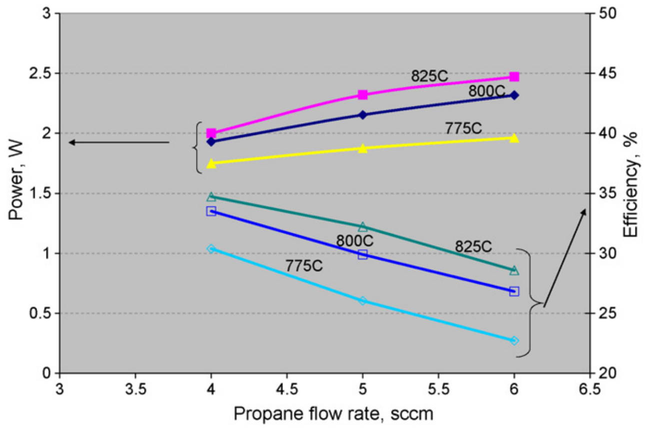

Fig. 3. Power output and fuel cell efficiency as a function of propane flow rate at different operating temperatures during internal partial oxidation reforming at oxygen-to-fuel ratio of 1.54 on G4b SOFC.

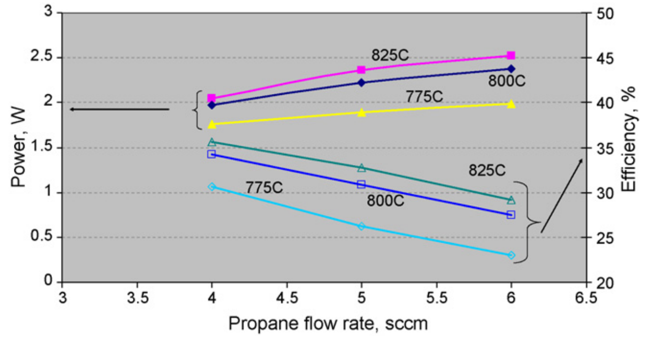

Fig. 4. Power output and fuel cell efficiency as a function of propane flow rate at different operating temperatures during internal partial oxidation reforming at oxygen-to-fuel ratio of 1.30 on G4b SOFC.

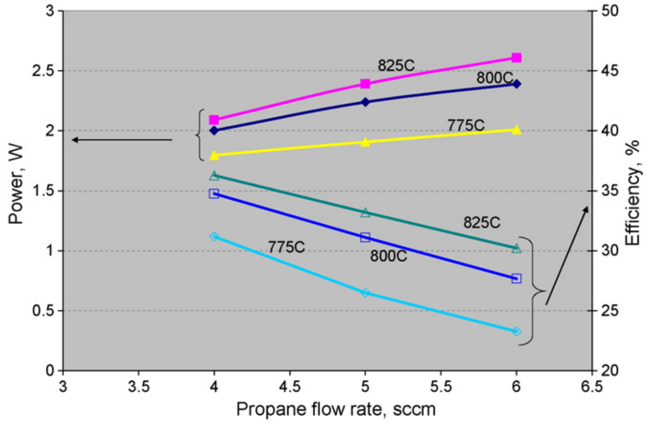

Fig. 5. Power output and fuel cell efficiency as a function of propane flow rate at different operating temperatures during internal partial oxidation reforming at oxygen-to-fuel ratio of 1.30 on G4b SOFC.

approximately 30%. The improvement in power output and power density of these cells was due to the optimization of active cell components including anode, electrolyte and cathode. The major contribution was from significant improvements in the microstructure of the anode and electrolyte, facilitating lower mass transfer resistance (higher porosity) and higher electric conductivity. Further details regarding the cell structure and catalyst composition cannot be divulged as they are considered proprietary to NDE.

In our earlier work [17] we showed the power output from an internal reforming SOFC fuelled by propane gas via partial oxidation reforming at different O_2/C ratios. However, in the current study a slow degradation in power was noticed with time while operating at close to stoichiometric oxygen-to-fuel ratio, even though the short-term stability was good. Also, it has to be noted that the long-term stability was excellent for a period of >1000 h of continuous operation at higher than stoichiometric oxygen-to-fuel ratios [17]. Temperature programmed oxidation tests with mass spectrometer (MS) revealed the formation of carbon on the catalyst's surface (not shown). These results suggest that the lack of oxidant leads to the formation of carbon (filament type, moderately reactive with oxygen) and eventually the degradation in power output.

Due to the promising performance of G4 cells, further studies were conducted by modifying the catalytic layer in order to utilize the available oxygen ions supplied from the cathode side and enhance the partial oxidation process. G4b cells coated with the modified catalytic layer were then tested for their performance during the POX reforming of propane at different oxygen-to-fuel ratios. Fig. 3 shows the power output and fuel cell efficiency as a function of propane flow rate at different operating temperatures. All the tests were conducted at an oxygen-to-fuel ratio of 1.54 while varying the operating temperature. As expected, the total power generated increased with increasing temperature and the amount of fuel supplied. This cell demonstrated a total power output of 2 W at an overall efficiency of 34.72% and 2.47 W at 29% efficiency when operated at 825 °C. The same cell was also subjected to similar tests for evaluating the effect of propane flow rate on power by changing the oxygen-to-fuel ratio from 1.54 to 1.40 and then to 1.30. The results from these tests can be seen in Figs. 4 and 5, respectively. It can be noticed that the total power output increased to >2.5 W with an efficiency of >30% when operated at 825 °C and 6 ccm of propane. Also shown is the data for lower propane flow rates for which the power output was above 2 W at efficiencies above 36%.

MS was used in situ to monitor the exhaust gas composition after the propane–air feed mixture underwent reforming in the catalyst membrane and electrochemical oxidation in the anode. Fig. 6 shows the power output as a function of G4b cell operating temperature during the internal reforming of propane fuel. Also shown are the MS signal intensities of different gas streams measured at the anode exhaust. Oxygen-to-fuel ratio was maintained at a stoichiometric value (partial oxidation) of 1.50 while the cell temperature was ramped from ambient to 600 °C and it was lowered to 1.30 from 600 to 800 °C. It has to be noted that the cell was loaded in constant voltage mode through out the operation. The propane and oxygen signal intensities start to decrease at temperatures above 450 °C

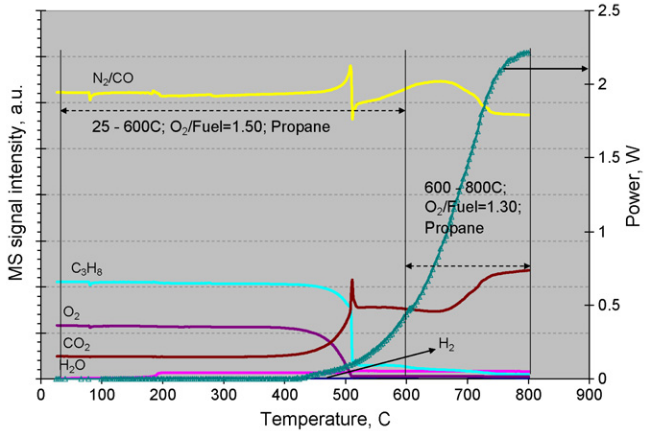

Fig. 6. Power output as a function of G4b operating temperature during the internal reforming of propane gas at different oxygen-to-fuel ratios during the startup from ambient temperature. Also shown are the mass spectrometer signal intensities of different gas streams measured at the anode exhaust.

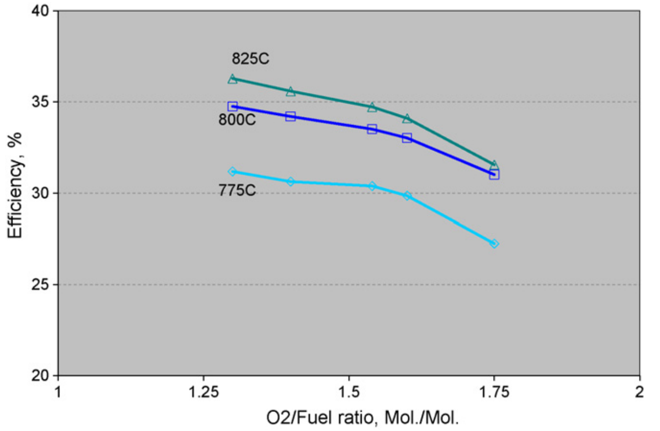

Fig. 7. Fuel cell efficiency as a function of oxygen-to-fuel ratio at different operating temperatures during internal partial oxidation reforming on G4b SOFC at a propane flow rate of 4 sccm.

and completely consumed at temperatures above 700 °C. The oxidation reactions are initiated at approximately 500 °C resulting in the formation of H_2, CO, CO_2 and H_2O due to both chemical and electrochemical reactions. The light-off temperature for propane was higher compared to our previous results [17] because of the lower oxygen-to-fuel ratio utilized in the current study. The G4b cell performance compared with the baseline technology [20] indicates that the power density from the 4th generation SOFC with optimized microstructure increased by 50%.

Fig. 7 shows the G4b cell efficiency as a function of oxygen-to-fuel ratio at different operating temperatures while supplying the propane fuel at a flow rate of 4 sccm. The total power output was between 1.5 and 2.07 W depending on the ratio and operating temperature. As expected, the effect of ratio was more pronounced at values above 1.6. The higher ratios (above POX stoichiometry) lead to the formation of undesired CO_2 and H_2O products from the catalytic reaction resulting in the loss of fuel (H_2 and CO) that can be electrochemically oxidized.

MS analysis of the composition of anode exhaust from the internal reforming G4b cell operated on propane–air mixtures at different oxygen-to-fuel ratios at 800 °C and fixed electronic load showed higher concentrations of CO_2 and H_2O as the ratio increased from 1.3 to 1.75 suggesting total oxidation of some of the fuel resulting in higher amounts of combustion products in the exhaust.

The relative size of different 4th generation SOFCs is shown in Fig. 2. G4c cells were built by scaling up of G4b SOFCs after modifying the cathode material to further enhance the overall performance. These cells were also subjected to similar tests that were conducted on G4b. Power output along with efficiency during the internal POX reforming of propane gas at different oxygen-to-fuel ratios and propane flow rates for these cells is shown in Fig. 8. This cell demonstrated 11.3 W at an efficiency of 25% and 10.6 watts at an efficiency of 30%. The cell did not show severe drop in power even though the fuel flow rate was decreased from 32 to 15 sccm, demonstrating 8.65 W at an efficiency of 40.5%. One of the primary reasons for these higher efficiencies with G4 technology is due to lower mass transfer resistance resulting in better access to the triple phase boundaries and hence higher electrochemical reforming activity of propane fuel.

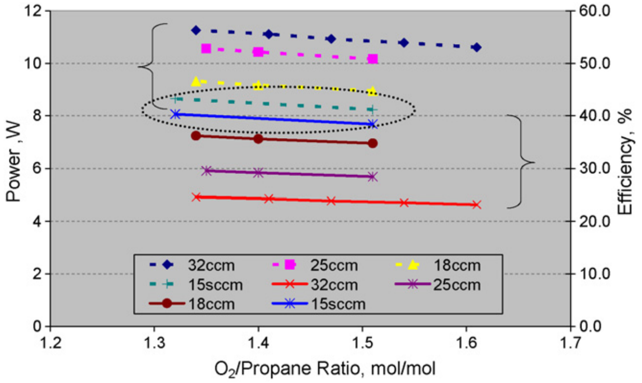

Fig. 8. G4c SOFC power output and efficiency vs. O_2/propane ratio at different flow rates and an operating temperature of 800 °C.

As mentioned before, all the internal reforming tests were conducted by feeding the fuel/air mixture in a single pass. The overall efficiency can definitely be improved by recycling some of the anode exhaust back in to the feed stream. Theoretical calculations with exhaust recycle showed that 50–60% efficiencies on propane fuel are practically possible for a portable power generating system which is the subject of our future research work. For comparison, Fig. 9 shows the calculated overall efficiency (electric power generated/LHV of fuel in to the system) as a function of different fuel cell efficiencies (selectivity towards generating electric power rather than heat) at various fuel utilization values. An 85% reforming efficiency was assumed for these calculations. It can be noticed that the maximum overall efficiency for the best case approaches only 40.8%, in spite of 60% fuel cell efficiency and 80% fuel utilization. Practical systems, however, operate at 70–75% fuel utilization and 50% cell efficiency for long-term durability in which case the overall efficiency will be approximately 33%. The assumed efficiency for fuel reforming is usually possible with steam reforming technique which requires water and heat to generate the steam making the system bulky.

Considering the reforming technique which was utilized in all our studies was partial oxidation and that there was no recycle of the exhaust stream we feel that a 40+% efficiency is quite remarkable. We would also like to reiterate the fact that the efficiency values reported through out this study are calculated by comparing the power in (LHV of the fuel) vs. electric power out. These numbers are quite significant for a portable system utilizing tubular SOFC technology given its inherent advantages which solve the problems related to cracking, thermal-cycling, start-up time and sealing encountered by the planar SOFC technology. This advanced technology will thus provide energy, environmental, and economic benefits. For example, an 85% savings in total energy consumption can be achieved by running a 1000 W SOFC generator (with an efficiency of approximately 40%) on propane rather than running a 7% efficient conventional diesel generator. And given that

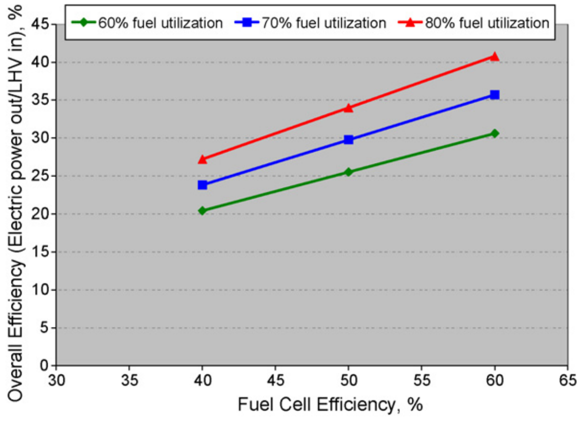

Fig. 9. Overall efficiency (electric power out/LHV fuel in) as a function of fuel cell efficiency on general fuel cell technologies calculated at different fuel utilization values assuming 85% reforming efficiency.

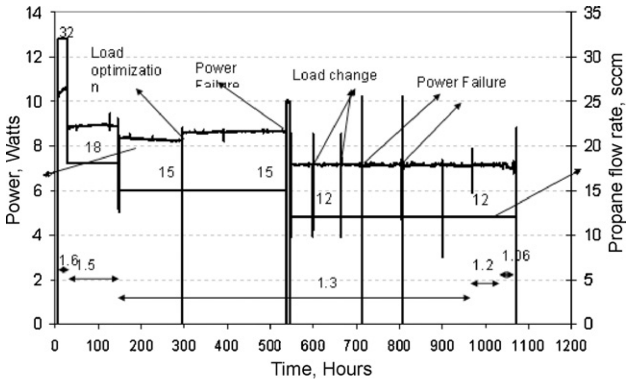

Fig. 10. Power output, efficiency, and propane flow rate as a function of time during the long-term stability test performed on a G4c cell at 800 °C.

a more efficient device will consume less fuel, the environmental and economic benefits can also be realized, such as 90% savings in fuel cost can be achieved by operating a 1 kW portable propane power generator on a 40% efficient SOFC technology rather than the conventional 7% efficient diesel generator.

A drawback of using gaseous hydrocarbon-powered SOFC generators is the production of carbon dioxide, a greenhouse gas that is the major cause of global warming, even though the emission of carbon dioxide from an SOFC generator is 85% less than that of a diesel generator. The greenhouse effect of carbon dioxide emissions, however, can be completely eliminated by switching to renewable fuels, which have been successfully demonstrated [17].

Based on the results discussed so far G4c cells seem to show the best efficiencies using propane internal partial oxidation reforming process. It is important that these cells demonstrate stable performance with time especially under the conditions of direct internal reforming of the hydrocarbon fuel at sub-stoichiometric oxygen-to-fuel ratios. For this purpose, a long-term test was conducted to find out the stability and the results are shown in Fig. 10. The test was started with a propane flow rate of 32 sccm at an oxygen-to-fuel ratio of 1.60 followed by a lower propane flow rate of 18 sccm at a ratio of 1.5 until 135 h of continuous operation. The flow rate was further lowered to 15 sccm and maintained at a ratio of 1.30 until 550 h of continuous operation. The flow rate was later adjusted to 13 sccm at the same ratio and operated until 965 h. Lower ratios were also tested by operating the cell at 1.20 ratio until 1070 h. A ratio of 1.06 however resulted in slow degradation of power output which was restored after switching back to 1.20 and the test was stopped to examine the cell. The LHV efficiency of the cell through out the operation was calculated. It is clear that the cell maintains an overall efficiency of >40% after optimizing the electronic load at 295 h. These results clearly show that the next generation advanced 4-layer SOFCs with integrated catalytic layer can demonstrate stable performance on hydrocarbon fuels via partial oxidation (internal reforming) at sub-stoichiometric air-to-fuel ratios with LHV efficiencies above 40%. The anode of the spent cell was then subjected to TPO tests and no presence of coke was observed suggesting a good equilibrium between carbon deposition and its removal by the oxidation reactions on the catalytic surface. Detailed mechanistic studies are under investigation to further improve the performance of catalytic and anode materials.

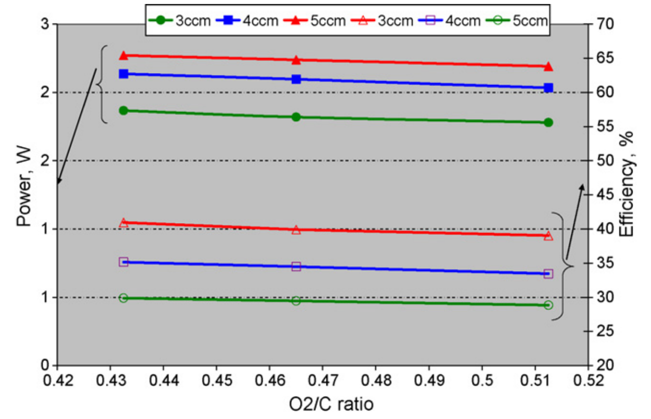

Fig. 11. Power output and efficiency as a function of oxygen-to-carbon ratio and different butane fuel flow rates during the internal partial oxidation reforming in G4b cell operated at 800 °C.

Our earlier work has shown the fuel flexibility of the internal reforming SOFC [17] where the range of fuels included methane, biogas, propane, butane, gas mixtures of propane and butane, ethanol. The G4b cell was hence tested for its performance on butane fuel and the results are shown in Fig. 11. It can be noticed that the cell demonstrated >2.25 W at efficiencies of approximately 30% and >1.9 W at efficiencies of approximately 40%. The G4c cell was also tested for its performance on butane fuel and the results demonstrated a total power output of 8.9 W at an efficiency of 40.1%. The lower efficiency on butane fuel (compared with propane) is due to the lower hydrogen-to-carbon ratio (2.5) compared to propane (2.67) leading to slightly lower concentration of hydrogen which has higher electrochemical activity compared to carbon monoxide generated from the internal reforming process [21,22]. The new 4th generation SOFCs with integrated catalytic layer developed for sub-stoichiometric air-to-fuel operating conditions definitely show a great promise for handling multiple fuels at very high efficiencies.

Due to the promising results noticed on single cells, a stack containing more than 10 G4b SOFCs was constructed and tested on both hydrogen fuel and propane fuel, the results of which can be seen in Fig. 12. This stack demonstrated ~28 W on hydrogen fuel and ~25.5 W on propane fuel at efficiencies of 55% and 38%, respectively. A thermal image of the stack taken by an infra red camera while operating is also shown in the figure. It can be seen that the outside temperature of the stack while operating at optimal conditions was approximately 65–80 °C.

A portable power generating system based on this innovative stack design was recently constructed and demonstrated in house producing more than 25 W of power with ~35% efficiency in converting the fuel's energy to electricity with a gravimetric system energy density of ~800 Wh kg^{-1} [23] over the time period tested.

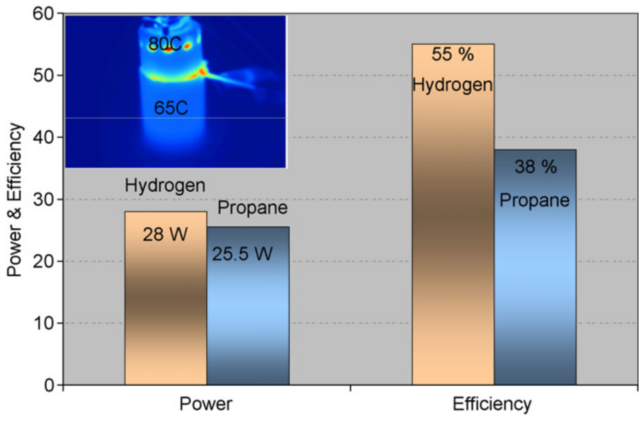

Fig. 12. Power output and efficiency of a stack consisting of >10 G4b cells operating at optimum conditions on hydrogen and propane fuels. Thermal image of a stack in operation can also be seen.

4. Summary

Novel 4-layer tubular solid oxide fuel cells with integrated catalytic layer were demonstrated on hydrogen and hydrocarbons (propane, butane) with efficiencies approaching 60% and 40%, respectively. Electrochemical and catalytic materials, along with the cell microstructure were engineered to demonstrate stable operation of SOFCs in sub-stoichiometric oxygen-to-fuel atmospheres at high efficiencies without the aid of fuel preprocessing or external reforming. Partial oxidation reforming was conducted internal to the cell with different fuels. A stack was constructed based on these next generation SOFCs and tested on both hydrogen and propane. All these factors will facilitate the introduction of highly efficient, reliable, fuel flexible, and lightweight portable power generation systems.

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