Bio-Methanol fueled Intermediate Temperature Solid Oxide Fuel Cell:
A future solution as component in auxiliary power unit for eco-transportation

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Abstract:

Nickel-SDC anode was experimentally demonstrated for the direct utilization of bio-methanol in solid oxide fuel cells at intermediate temperature (IT) range. Cell performance was determined (350 mW/cm² at 750 °C) in operating conditions propitious to carbon deposition. Cell performance with methanol was slightly higher than with hydrogen. Different reactants distribution adjacent to the double conducting electrolyte may explain the improved cell output. Better performance with methanol could be also consequence of the improved electronic conductivity in the presence of carbon deposits. Results indicated that catalytic decomposition of methanol in the anodic three phase boundaries is dependent of temperature and governed by a complex anodic electrochemical dynamics. Anode gases were analyzed and a process scheme including H₂/CO/CH₃OH has been proposed. An experimental protocol using a switch between hydrogen and methanol feed was elucidated and a series of chemical reactions was proposed inducing the coking removing from anode. For a pre-feasibility assessment of the experimental cell, performance comparison with Delphi Gen 3 cell fed by diesel used as element in an auxiliary power unit was proposed. Obtained results are encouraging to go down the thorny and long-pathway to make the APU-SOFC technology viable for the eco-transportation sector.

Keywords:

Eco-transportation, Bio-methanol, direct utilization, Intermediate temperature Solid oxide fuel cell, Auxiliary power unit.

1. Introduction:

The global energy crisis and greenhouse gas emissions reduction targets are common place across the world and transportation has become one of the most critical areas to be addressed. By 2020, 62% of the global petroleum consumption will be from vehicles causing an increase in the global CO₂ emission by 30 to 50% where 25% of this increase is caused by vehicles [1]. Internal combustion engines (ICE) are nowadays the main power type used by vehicles. Therefore, increasing the use of public transport and promoting the development of low-to-zero-emission vehicles presents two key objectives that researchers must pay attention to.

Fuel cells in transport sector are coming of age and touted as the dominant propulsion technology for the future. Almost every vehicle industry has launched major fuel cell vehicle development programs using a new approach based on the focus of niche markets. One pioneering market is auxiliary power units (APU) [2,3,4].

The use of APUs, particularly fuel cells-based APUs presents a promising solution especially for heavy duty trucks. Conventionally, a certain percentage of these vehicles are used for long-haul driving, which are left idling overnight using its diesel engine in order to ensure that heat and power are available to the driver inside the truck's cabin. The power is needed for lighting, heating, air-conditioning, and comfort-items such as microwave ovens, refrigeration units and coffee makers. While idling, i.e. under low power demand compared to the rated power, the Internal Combustion Engine (ICE) of the truck works inefficiently (<10%) generating emissions and accelerating engine wear. It is estimated by the U.S. Environmental Protection Agency (U.S. EPA) [5] that trucks and locomotive engines idling for long durations consume over 4.55 billion liters of diesel fuel annually and release over 11million metric tons of CO₂ as well as 150,000 metric tons of NO_x, which is equivalent to the greenhouse emission (GHG) coming from 2.3 million passenger vehicles on the road each year [6].

The use of an APU with fuel cells is especially appropriate for this type of vehicles which have high demand of electric power when the ICE is turned off. This engine-independent electricity supplier can significantly improve the quality of the electricity generation, far beyond that achievable by the conventional combination of a generator coupled to the ICE and a battery.

A promising alternative technology is the solid oxide fuel cell auxiliary power unit (SOFC-APU) which demonstrated the ability to provide power in the low power range of 2 to 20 kW for heavy duty trucks during standstill durations. The SOFC system not only possesses high fuel efficiency, low GHG emissions, and quiet operation, but the system can also utilize a wide range of fuel sources, conversion technologies and fuel processing producing anH₂-rich gas delivered to the anode side of the fuel cell stack. Fuel sources used in SOFC-APUs can vary from gasoline, diesel, methanol, ethanol, natural gas, liquid petroleum gas to hydrogen.

SOFC development in the vehicle industry includes AVL, Eberspracher and Elcogen in Europe, as well as Delphi, Protonex and Ultra Electronics AMI in North America [2].

Recently, the goal of the DESTA project [2,7,8] to demonstrate the first Solid Oxide Fuel Cell Auxiliary Power Unit on a heavy duty truck in Europe has been achieved and the world premiere diesel-operated SOFC APU on a long haul truck was successfully presented. The APU system developed and supplied by Eberspächer, was integrated and tested by Volvo on a long haul truck for the North American market. It is able of converting conventional US diesel into a hydrogen and carbon monoxide rich gas and finally into electricity. With the DESTA system, 3 kW of electrical net power can be supplied with an efficiency of 30%, very low NO_x emissions and no diesel particles. Compared to engine idling of a heavy-duty truck the CO₂ emissions could be reduced by 71 %. The diesel consumption is 1.0 l/h at an

electrical net power of 3 kW. The start-up time of the APU system lies between 30 and 70 minutes, depending on the stack temperature (cold and warm start). Recently, SAFARI project was launched aiming to design an SOFC-APU for trucks, using liquefied methane, to provide power, heat and cooling for the cab, in an efficient way. Methane (CH_4) was chosen because it is increasingly used in the Europe as the fuel supply for trucks and because it is economic, cleaner than diesel, and is becoming widely available [2, 9].

AVL has developed SOFC-APUs since 2002. The system is operated with conventional diesel fuel and reaches a net electrical power of 3kW at an electrical efficiency of 35%. The system can also provide heat independent of fuel cell operation up to 10kW. The system is intended for truck anti-idling, maritime and other mobile power generator applications [2].

Delphi Automotive Systems is developing Solid Oxide Fuel Cell (SOFC) technology for automotive applications - primarily as an on-board APU. In 2008, Delphi corp. successively tested an SOFC-APU system to function the electric system and air-conditioning of a Peterbilt model 386 truck cabin and sleeper under idling conditions for 10 h. Delphi claims its system runs quietly and more efficiently than APUs with traditional combustion engines. The APU provided an average of 800 W of electricity to the truck. The Delphi SOFC- APU uses low-sulfur diesel as fuels, and yttria-stabilized zirconia ceramic electrolyte. Delphi had developed the fourth-generation SOFC stack. The A-Level design APU, currently operating, contains the Gen 3 stack (1.5 kW output), while the latest B-Level design APU, which contains the Gen 4 stack (3 kW output), was being assembled in May 2011. Delphi is trying to move the SOFC-APU out of the laboratory and is now focused on its commercial viability [2, 10, 11].

Energy conversion technologies nowadays have as a target the reduction of their greenhouse gases emissions and research of alternative renewable sources of energy is needed. In this sense, several investigations in the transport sector have paid great attention on using non-petroleum, renewable, sustainable and non-polluting bio-fuels [12]. Bio-fuels derived from biomass appear attractive from both environmental and economic standpoints. Thus, switching from fossil fuels to renewable bio-fuels could be accordingly considered as a powerful way to reduce anthropogenic CO_2 emissions.

Bio-methanol as fuel is CO_2 neutral, clean, renewable and sustainable since produced from agricultural and/or animal byproducts and biomass. Presently, it can be obtained from biomass fermentation at 66% efficiency [13]. It can be also produced from biomass via gasification and subsequent methanol synthesis over a catalyst from the synthesis gas (syngas). Prior to methanol synthesis, the syngas must generally undergo cleaning, shift reaction and compression [14]. In a liquid state at ambient conditions, bio-methanol has a relatively high energy density (15.8 MJ m^{-3}) which eases the problem of handling, transport, distribution and storage if compared to gaseous hydrogen making its use beneficial from an infrastructure perspective [15]. Bio-methanol can be among the various possible fuels for SOFC systems making it a promising technology for electrochemical power generation [14].

Methanol has been extensively tested in lab-scale SOFC [16-20]. Methanol could be also easily reformed back to a mixture of CO and H_2 at relatively low temperatures compared with ethanol where decomposition reaction ($\text{C}_2\text{H}_5\text{OH} \leftrightarrow 3 \text{ H}_2 + \text{CO} + \text{C}$) dictates the equilibrium products only above 850°C giving rise of coking [21-24]. It has been shown that although feasible the direct utilization of methanol can lead to cumulative carbon deposits which may modify the anode microstructure and reduce subsequently the SOFC performance. Many efforts have been made to investigate the effect of carbon deposition on SOFC performance. Saunders et al. [18] found that carbon formed on Ni anodes when operated on methanol and the amount of carbon deposition was increased with decreasing temperature over the range of $700\text{--}850^\circ\text{C}$. In contrast, Jiang and Virkar [16] reported that there was no carbon deposition when SOFC operated on direct methanol at temperatures as low as 550°C . Another

investigation, reported by Bi et al. [19], has also achieved good results when using Ni-GDC anodes without elucidating the carbon deposition problem that appears on the anode.

Bio-methanol is much different from other hydrocarbon fuels. It carries sufficient oxygen to avoid entering into the thermodynamically unstable, carbon-forming regime [25, 26]. So, anode coking and deactivation and structure instability seems to be reduced using bio-methanol.

Recently, Li et al. [27] reported an improvement of the SOFC performance using a reduced $\text{La}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$ (LNF) as anode under methanol feed. They proved that the carbon deposited shows a reasonable stability and has high degree of graphitization bringing a higher electrical conductivity which provides more conductive paths for electrons. Hence, methanol could be considered as a promising candidate fuel for SOFC.

Therefore, the suitability to run SOFC on methanol makes it a possible choice for APUs used in several transportation applications [2]. Indeed, an EU-funded METHAPU project started at 2006 and reached a significant milestone in 2010 when consortium proved for the first time the trials on a prototype of a methanol-based SOFC-APU. The prototype is tried and tested for performance and emissions under real-life conditions onboard a vessel (the MV Undine, a pure car truck carrier (PCTC)) involved in trading between Asia, Europe and the USA. The fuel cell unit, which has a nominal output of 20 kW, is based on planar SOFC technology fueled by methanol. Methanol is particularly suited for fuelling the Wärtsilä's WFC20 fuel cell unit since it can be easily reformed to a composition suitable for the unit. Methanol is available in all major harbours. This 20kW SOFC-APU unit has been demonstrated, with a longer term target of 250 kW [28, 29].

In solid oxide fuel cells, methanol (CH_3OH) is directly fed to the anode chamber of the fuel cell, and air is supplied to the cathode chamber of the cell. When methanol reaches the anode/electrolyte functional layer, pyrolysis and catalytic decomposition reactions of methanol can take place leading to a gas-phase composition rich on H_2 and CO . These species will react electrochemically following Eq. (1) and (2) to produce current.

Oxygen in air available at the cathode/electrolyte interface reacts with electrons to form oxygen ions. The oxygen ions are transported through the ceramic electrolyte and electrons flow through the external electric circuit (load).

Direct utilization of methanol seems to be dependent on several operating conditions particularly the temperature. Cimenti and Hill [30] proved experimentally that only at 850 °C, all the methanol decomposes to syngas H_2/CO mixture and they also reported that the methanol decomposition did not start until 700 °C. Lo Faro et al. [13] have also concluded that under OCV, part of methanol is not converted to syngas as also confirmed by the conducted ex-situ catalytic test giving rise to its direct oxidation reaction:

Other authors [15, 26] have reported also the possibility of total (Eq.3) and partial (Eq.4) methanol direct electrochemical oxidation in SOFC anode.

Thus, electrochemical oxidation of unconverted fraction of methanol could be considered through the mixed reaction dynamics of the anode fed directly by methanol.

On the light of the previous analysis, direct utilization of methanol in SOFC leads to a complex reactions mechanisms within the anode side which needs a deep experimental investigation based on gas analysis in the different SOFC operating conditions. The SOFC anodic process will be investigated here using gas chromatography analysis (GC) carried in-situ and ex-situ the anode by analyzing the effluent stream from methanol catalytic thermal decomposition test. Carbon deposition removing reactions will be also discussed based on a

new proposed experimental protocol using a switch between pure hydrogen and methanol feed to the SOFC. The studied bio-methanol IT- SOFC will be therefore assessed as a possible éco-component in an SOFC-APU compared to Delphi SOFC Gen 3 (105 cm²) used in diesel APU.

2. Materials and Methods

2.1. Preparation of electrolyte-supported SOFC single cell

An electrolyte-supported single cell was prepared using the cold pressing technique at 500 MPa (30 kpsi) following the subsequent adding of the composite electrolyte and cathode powders.

The composite electrolyte material was made by mixing Ceria-doped Samarium (SDC) with molten carbonate (MC) which consisted of Li₂CO₃/Na₂CO₃ eutectic mixture in a mole ratio of 2:1. The SDC powder was prepared via Oxalate co-precipitation process. The SDC preparation procedure has been described elsewhere [31]. It has been proved experimentally by our co-workers [32] that in such composite electrolyte materials, O²⁻/H⁺ conduction takes place when H₂ and O₂ are used as the SOFC reactants via a quantitative measurement of the reaction products, i.e. H₂O and CO₂ evolved from the cell submitted to a current-interruption technique.

The cathode materials consisted of 30 wt% composite electrolyte and 70 wt% Li_xNi_{1-x}O powders. The formed single cell discs were then sintered at 700 °C for 1 h in air. The electrolyte thickness was about 650 µm whereas the cathode thickness was about 350 µm.

Fine NiO powder was prepared through heating of proper amount of Ni(NO₃)₂·6H₂O powder (99%, Chemical Reagent, China) at 700 °C for 2 h until it combusted. A mixture of NiO and Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) powders in a weight ratio of 6:4 was screen printed to the formed cell discs of 13 mm diameter and subsequently calcined at 700 °C for 1 h to form the anode layer of about 4 µm thick. The porosity of the anode was found by the use of the software image treatment (FiJ). It is about 35%. Ag paste was applied on both sides of the cell as current collectors. A thin silver ring of 10 mm diameter was introduced in the cell holder just below the cathode side in order to ensure efficient current collection. The effective area of the electrodes was 0.5 cm².

2.2. Description of the SOFC test rig

The SOFC test rig along with the furnace used for the evaluation of the cell performance is represented in Fig. 1. The test rig consisted of a furnace and a gas supplying system.

The cell holder furnace (Fig. 1(b)) used in the testing was built using Thermal Ceramics insulating fire bricks and nichrome ribbon resistance elements, and could accommodate the fuel cell holder. Power was supplied to the furnace by a controller. All gases were delivered via mass flow controllers to the SOFC test rig.

Gases were not preheated, whereas liquid methanol was pumped to the SOFC test rig using a peristaltic pump (2ZB -1L10, china) as shown in Fig. 1(a) then passed through a heated evaporation chamber using an evaporator maintained at 150 °C (Fig. 1(b)). This evaporation step is required to facilitate the flowing of methanol as it expands during the evaporation and this expansion moves the methanol gas through the evaporator during cell operation. A heated line downstream of the evaporator was also adopted ensuring that no condensation occurred before entering directly the cell holder, situated within the horizontal furnace. Argon was used as a carrier gas for the methanol. The evaporated mixture was then fed to the fuel cell maintained at 650 °C. The exhaust gases from the fuel cell could be sent to analytical tools such as a gas chromatograph for analysis, or vented if analysis was not required. The gas piping arrangement was detailed in Fig.1 (c). The electrical performance of the SOFC was

measured with a Versastat 3 Potentiostat-Galvanostat capable of varying the electrical load as required. Current and voltage values were varied and logged using the Versastudio software.

2.3. Evaluation of the cell Performance

In order to avoid the possible catalytic decomposition of methanol to form carbon in the gas tubing blocking the anode outlet gas, a fine alumina tube was inserted in the gas tubing of our home-made cell holder. Liquid methanol was directly injected into the anode compartment at a feeding rate of 2 ml/h by a peristaltic pump and then vaporized into gas at the anode side. NiO in the anode was directly reduced to form metal Ni in situ by methanol gas at 600 °C before carrying out the electrochemical measurement. Pure Oxygen fed the cathode side with a flow rate of 50 ml min⁻¹. The cell voltages and output currents of the SOFC were measured and recorded using an electrochemical working station.

3. Results and Discussion

3.1. Feasibility of direct utilization of methanol in SOFC

Fig. 2(a) shows the performances for the methanol fueled IT-SOFCs with 13 mm in diameter at 750 °C compared to the hydrogen fueled one using the Ni-SDC anode material vs. the Li_xNi_{1-x}O with LN-SDC cathode. The OCV values are 0.967 V in hydrogen and 1.038 V in methanol. Cimenti and Hill [22] claimed that the equilibrium potential calculated by the Nernst equation is typically close to the OCV for SOFC powered by hydrogen. According to their results, at 750 °C, the equilibrium potential is about 0.98 V which is quite similar to the reported OCV in Fig.2 (a). However using alcohols, the equilibrium potential value exhibits always an overestimated value and may also vary with time as possible change in the anodic species composition is possible. At 750 °C, SOFC fed by methanol delivers an equilibrium potential of about 1.26 V [22] which is higher by 220 mV from the obtained OCV (1.038 V). This difference could be explained by the equilibrium composition yielded from decomposed methanol under Ni-SDC anode. In addition, the OCV will be improved by using a partial pressure of one for pure O₂.

The maximum power density of 350 mW.cm⁻² is obtained at 750 °C, which is slightly higher than that of pure hydrogen and appears promising for SOFC applications.

This good performance can be related to several reasons. First, in the Ni/SDC anode, Ni particles are surrounded by the oxygen ion conductor SDC, which can supply sufficient oxygen species for the direct electrochemical oxidation of H₂, CO and methanol (Eq. 1,2,3) and the partial electrochemical oxidation of methanol (Eq. 4), and thereby can suppress the carbon deposition on Ni particles [13,15].

Noting that the oxidation reactions mechanisms are exothermic thus they will provide heat required for the methanol decomposition reaction (Eq. 5) [22, 33].

And even if some carbon deposits would occur, the oxygen species from SDC can promote their removal, similarly to the effects of ceria related materials mentioned in the reforming literature [34-36].

Second, the obtained better performance with methanol could be thanks to the improvement of electronic conductivity by the presence of carbon deposits [27].

It is noticed also that formation of carbon species from pyrolysis of methanol is more favorable at higher temperatures while our operating temperature is much lower than that used in SOFCs with conventional electrolytes (YSZ and LSGM) that typically needs an operating temperatures higher than 800 °C to conduct.

The total polarization of an SOFC is composed of ohmic, anode and cathode losses. Fig.2 (b) illustrates the SOFC equilibrium impedance curves measured under pure hydrogen and pure methanol at 750 °C and helps to analyze the I-V curves (Fig 2.a). The complex plot measured

in H_2 contains one depressed arc followed by a tail whereas that obtained in methanol contains two arcs. In one side, the ohmic resistance (high frequency intercept with real axis) was slightly the same in H_2 and in methanol (0.449 and 0.459 $\Omega.cm^2$, respectively). In the other side, the polarization resistance (anode and cathode) in methanol was $\sim 0.5 \Omega.cm^2$, while in pure hydrogen; the spectrum was not closed at low frequencies. Using methanol, the presence of two arcs implied that there were two-rate-limiting processes for the electrode reaction and diffusion mechanisms [37]. The electrolyte/electrode interfacial resistance which could be determined by subtracting ohmic resistance from overall resistance was about 0.05 $\Omega.cm^2$ for methanol fed cell [38].

Using pure H_2 as fuel, the impedance spectrum increased linearly with decreasing frequency, similar to infinite-length Warburg impedance [39]. It should be pointed out that both cells were fabricated by the same technical procedure, same electrolyte and electrode materials, expect that the fuel was modified. So, the difference in the complex plots should be related to the characteristic relaxation times associated to the anodic reactant oxidation reactions (pure H_2 , or a gas-phase mixture of $H_2/CO/CH_3OH$) [13, 15].

From the characteristic curve of cell voltage and current density of SOFC fueled by dry methanol (Fig.2 a), at 0.557 V, the maximum power density is about 350 $mW.cm^{-2}$ and the corresponding current density is 628 $mA.cm^{-2}$. Regarding the performance comparison study shown in Fig. 2(c), the tested cell appears promising as a possible eco-component in SOFC-APU as output seems to be comparable with a typical Gen3 optimized cell size (105 cm^2) designed by Delphi for a range of packaging requirements [10,11]. The difference in the $I-V$ and $I-P$ profiles is related to the ohmic losses of the experimental cell which requires design optimization and further R&D up-scaling investigation.

3.2. Effect of temperature on SOFC fueled by dry methanol

The effect of temperature on the IT-SOFC performance running with dry methanol is showed in Fig. 3. The maximum power density increased from 123 $mW cm^{-2}$ at 650 $^{\circ}C$ to 205 $mW.cm^{-2}$ at 700 $^{\circ}C$ and 350 $mW.cm^{-2}$ at 750 $^{\circ}C$. Because the majority of the losses in this cell were associated with the electrolyte, most of this improvement is due to a decrease in the ohmic losses. EIS complex plots given in Fig. 3 show that the ohmic loss of the composite electrolyte is the major contributor to the SOFC polarization loss. This is expected for the 650 μm thick electrolyte based SOFC. This loss is dependent on operating temperatures under methanol fed SOFC. The ohmic resistance (deduced from the high frequency intercept with real axis) decreases with temperature rise from 0.55, 0.49 to 0.44 $\Omega.cm^2$ at 650, 700 and 750 $^{\circ}C$, respectively. This loss is higher compared to electrode polarization resistance. For SOFC operating at 750 $^{\circ}C$, the electrode resistance was about 0.05 $\Omega.cm^2$ which represents only 10% of the total cell impedance (measured at low frequency). Even at 650 $^{\circ}C$, the ohmic resistance represents about 67% from the total cell resistance ($\sim 0.84 \Omega.cm^2$).

Furthermore, using pure oxygen as cathode gas permits to minimize the polarization resistance including both diffusion and activation contributions of the tested SOFC cells [40]. The diffusion losses were removed compared to the possible diffusion limitation caused by O_2 in N_2 when using air as cathode gas. In addition, the cathode reaction rate will be improved by using a partial pressure of one for oxygen. The EIS plots behavior was in good agreement with reported SOFC complex curves by DiGiuseppe and Sun [40] indicating that the diffusion resistance was removed as the switch from air to pure O_2 gas was done to the LSCF cathode inlet.

The maximum fuel utilization ($U_{f,max}$) with respect to SOFC temperature was calculated according to Eq.(8) [21] and obtained value are summarized in Table 1. Where i_{lim} is the limiting current density of the SOFC, n is the number of electrons produced by one methanol molecule oxidation (i.e. 6 electrons as given by Eq. (3)) and F is the faraday constant (96485

As.mol⁻¹). The methanol molar flow rate at the inlet of the anode ($Q_{Methanol}$) was estimated to be $1.37 \cdot 10^{-5}$ mol/s.

$$U_{f,max} = \frac{i_{lim} \cdot area}{n \cdot F \cdot Q_{Methanol}} \quad (6)$$

It is known that the carbon deposition boundary (CDB) in SOFC anodes is directly related to the fuel utilization and the operating temperatures. The CDB shifts towards lower fuel utilization as the temperatures increases [21]. Obtained real values are compared to theoretical calculations presented elsewhere [21]. They showed that carbon deposition was favorable on SOFC anodes working at 650 and 700 °C which is firstly caused by some oxygen leak through the not well densified electrolyte layer inducing the occurrence of the methanol partial oxidation reaction (Eq.7) reducing thus the $U_{f,max}$ [33,41].

However, SOFC fueled directly by methanol was just outside the carbon formation region at 750 °C which indicates enhanced electrolyte impermeability to oxygen gas leak. Dust-like carbon deposits were present on the internal surface of the alumina tube inserted in the gas piping up to 1 to 2 cm from the anode and as shown in Fig. 4 in the anode surface.

These performances in methanol are remarkably good and even higher than those previously reported in the absence of steam at 1000 °C [42].

A short-term durability of the SOFC fed by pure methanol at open circuit conditions and under constant current was performed in order to evaluate the reproducibility of the cell performance and the compatibility between electrodes and electrolyte materials.

Fig.5 shows a short-term durability analysis of a SOFC based on Ni-SDC anode and fed continuously with pure methanol at 750 °C. The cell was heated to 750 °C at 5 °C/min under open circuit conditions. The anode was fuelled by pure methanol starting from 600 °C. The cathode gas was introduced subsequently when the temperature reaches 750 °C and a rapid rise in cell voltage was observed. The measured OCV was nearly constant during almost 90 min testing period ranging from 1.12 V to 1.04 V. This voltage is in good agreement with reported methanol fed SOFC voltage [43]. This experimental durability test approves the previously reported OCV value of the SOFC fed by methanol at 750 °C (Fig.2 (a)). The same cell was held at a constant current of about 20 mA at constant temperature (750 °C) to test the cell stability and to analyze the reproducibility of the electrochemical cell behavior. As expected, the voltage decreases slightly to 0.94 V and maintained thereafter for 150 min between 0.94 and 1.0 V. This voltage is also in good agreement with the reported SOFC voltage at around 40 mA.cm⁻² given in Fig. 2(a). The SOFC voltage declines subsequently as possible carbon deposits seems to deactivate the Ni-SDC anode with the continuously anode running under pure methanol as given in Fig.4.

3.3. Catalytic decomposition test of methanol over Ni-SDC

Methanol decomposition to CO and H₂ is an endothermic ($\Delta H_{298} = +90.7$ kJ/mol) reaction [44]. In practical application, methanol decomposition is an on-site source of hydrogen and/or carbon monoxide for chemical processes and also for fuel cells. Catalysts containing nickel are generally active in methanol decomposition. In this sense, this part will be devoted to study the methanol catalytic decomposition over a cermet material (Ni-SDC) in order to elucidate the mechanisms occurring chemically and electrochemically on the TPB of the anode.

The catalytic experiments were performed in a fixed-bed continuous flow reactor operated at atmospheric pressure. The catalyst NiO-SDC (0.05-0.10 g) is introduced in a tube reactor made of silica glass tube (id 50 mm). After reducing the sample in a flow of hydrogen (40 ml.min⁻¹) for 4 h at 600 °C, methanol was fed with an argon gas carrier at 600 °C. The total flow rate of the reaction gas was around 100 ml.min⁻¹. The temperature was raised with a rate

of 5 °C. min⁻¹ in the range of 600–750 °C. The reactant and products were analyzed with an on-stream Perkin Elmer Clarus 500 gas chromatograph equipped with a thermal conductivity detector (TCD). The GC contained two capillary columns: Porapac N for CO₂, CO and CH₄ detection and Molecular Sieve column 13X for H₂, O₂ and N₂ detection.

Fig. 6(a) shows that methanol was stoichiometrically decomposed to carbon monoxide and hydrogen over the Ni-SDC catalyst under the chosen reaction conditions. Negligible amounts of methane, CO₂ and water were detected as by-products showing distribution values lower than 10% at T>600 °C. H₂ dominates the proportion of the mixture during the catalytic test followed by CO up to 650 °C. Thus, we can notice that methanol can be converted into H₂/CO gas mixtures via the decomposition reaction (Eq.5)

Yasumori et al. [45] proposed the following reaction mechanism for methanol decomposition (Eq.5) over a nickel surface. The reaction steps consists of: (1) a dissociative adsorption of methanol to methoxy groups and hydrogen adsorbed on nickel sites (Eq .8), (2) a decomposition of the methoxy groups promoted by the adsorbed hydrogen (Eqs. 9-10), and (3) a desorption of the surface carbon monoxide and hydrogen species (Eqs. 11-12).

At a temperature range between 650 °C and 700 °C, an increase in CO is observed simultaneously with a decrease in CO₂ concentration. This can be explained by the Boudouard reaction ($\text{C} + \text{CO}_2 \leftrightarrow 2\text{CO}$) taking place at this range of temperature. The carbon deposits may have as origin the probable following reactions:

Regarding the low methane fraction, the H₂ formed by reaction (14) seems to be limited compared to the H₂ consumed by Eq. (13) explaining thus the slight decrease in H₂.

Above 700 °C, the more probable reaction to occur was (Eq. 14) and thus an equal share of the two components (CO/H₂) in the gas phase was observed.

Thus, we can notice that methanol can be converted into H₂/CO gas mixtures via the previously cited chemical reactions depending of the operating temperature. This trend leads to a different electrochemical behavior if methanol was used in SOFC.

The selectivity is calculated via the formula ($S_i = C_i / \sum C_i$) where C_i is the molar flow of product i in the outlet stream. Results are plotted in Fig. 6(b) and show that the selectivity of H₂ is nearly the double of that of CO up to 650 °C but it became nearly equilibrated between CO and H₂ above 700 °C. According to this result, the presence of H₂ and CO gas mixtures in the anode chamber should be considered when establishing the anode reaction mechanisms of an IT-SOFC fueled directly by pure methanol.

3.4. Electrochemistry investigation of an SOFC fueled by methanol

As demonstrated previously, the Ni/SDC anode mechanism of the SOFC seems to be very complicated in term of fuel composition and composite electrolyte double conductions. As well known in the O²⁻ conduction pathway, when methanol is used as fuel, it decomposes at the anode to CO and H₂ (Fig.6) which react with oxygen ions transported through the LN-SDC electrolyte, thereby generating useful power according to Eqs.1 and 2 [23, 33]. It has been also shown that total and partial electrochemical oxidation of unconverted fraction of methanol (Eq.3, 4) may take place.

The only reaction occurring in the cathode side of the SOFC is that given by Eq. 15 and no exhaust gas was noted.

In this work, water droplets after SOFC cell operation in both the anode and cathode sides at 700 and 750 °C were observed. The H₂O produced in the anode comes from the pre-cited electrochemical reactions (Eq. 1 and 3). Whereas, when pure H₂ is used as fuel, the H₂O found at the cathode side couldn't be explained only by the presence of H⁺ protons conduction coming from the anode to the cathode side through the LN-SDC composite electrolyte (Eq.16) which leads to steam production via reaction (Eq.17):

In SOFC fed by methanol, in addition to the steam produced by Eq. 17, probable additional H₂O is produced by the following reactions mechanism:

In order to more understand the electrochemical mechanisms taking place in the IT-SOFC fed directly by methanol, an experimental measurement of gas analysis was carried demonstrating a variation in H₂ and CO₂ quantities before and after SOFC cell operation at 700 and 750 °C. Results are plotted in Fig. 7 (a) and (b) showing that the H₂ decreases after cell operation by 15% at 700 °C and 5% at 750 °C which indicates its consumption according to the hydrogen oxidation reactions (Eqs. 1 and 16) more kinetically rapid than the partial methanol electrochemical oxidation reaction (Eq.4) normally should produce few amount of H₂ in the anode.

The CO₂ fraction increases after cell operation by 50% at 700 °C and 28% at 750° C (Fig.7 (b)). This could be assigned to the occurrence of the CO oxidation reaction (Eq. 2) and methanol electrochemical oxidation in both H⁺/O²⁻ conductions (Eqs. 3, 4, 18). The ratio between increase in CO₂ and decrease in H₂ content is affected by the temperature rise. This could be explained by the subsequent reactions sequence between reactions (Eqs. (1) and (18)) more probable to take place at 700 °C than at 750 °C regarding the presence of an unconverted fraction of methanol leading to more CO₂ generation. At 700 °C, a competitive adsorption among CH₃OH, H₂ and CO seems to occur giving a complex reaction mechanisms scheme which is unfortunately not easy to describe accurately. However, at 750 °C the CO oxidation reaction seems to dominate the Ni-SDC anode electrochemistry rather than that of H₂.

3.5. Investigation of the carbon deposition removing

The direct utilization of methanol in SOFC involves many reaction processes in both the gas phase and at the Ni/SDC anode including: (1) Pyrolysis in the anode gas channel and pores forming fragments, (2) catalytic decomposition on the anode surface, (3) electrochemical oxidation in the TPB, (4) dry reforming on the anode TPB and/or oxidation of the methanol, (5) water gas shift reaction on the anode surface, and (6) carbon deposition and suppression [21].

The gas chromatography analysis carried to the SOFC during the phases 2, 4 and 6 of methanol feed are not significant may be due to the coking previously signaled. Apart from the coverage of the anode cell surface by carbon (Fig. 4), a visual examination revealed that carbon particulate was seen mostly in the outlet gas tube which disturbs the inlet steam of gas to the GC. The carbon particulate was also seen in the anode gas entrance region to the cell,

and there was certainly clogging by those. We believe the clogging of carbon at the anode entrance was the major reason for the cell performance deterioration observed after few hours. The proposed testing procedure presented in Fig. 8(a) was as follows. First, the SOFC cell was heated to 600 °C under pure hydrogen atmosphere (40 ml.min⁻¹) to ensure NiO reduction at the anode and remained at this temperature for 4 hours, then tested in dry H₂ (100 ml/min) to verify if the sealing was sufficient. The cell demonstrated the deliverance of a stable voltage larger than 1.12 V when exposed to dry H₂ and stabilized for at least 1 hour before further measurements. After testing in dry H₂ at this temperature, the cell temperature increased to 650 °C without fuel. Thereafter, the cell was tested again in dry hydrogen (100 ml/min) giving a relatively high OCV (1.09 V). After switching off the H₂ and when the OCV decreases to near 0.05 V (10 min), the cell was tested with methanol at this temperature after a stability time of about 30 min at around 0.96 V. The same experimental procedure is followed to test the cell at 700 °C and 750 °C with both H₂ and methanol in order to understand the chemical processes avoiding coking from the anode. GC analysis is carried in order to investigate the chemical process that took place aiming to suppress the carbon deposition problem for the Ni/SDC anode surface. A phenomenon that can induce both cell performance and morphology degradation. Results are plotted in Fig. 8(b).

During the phase of temperature rise, no fuel is powering the anode thus the OCV is almost nil. The cell was cooled to room temperature in argon at the end of the measurements.

Similar IT-SOFC performances were reported in good agreement with previously reported results in Fig. 3 at different temperatures using the proposed hydrogen/methanol switch testing procedure but with suppressed carbon deposition problem on the anode surface. Fig.9 shows the SEM/EDS graphs of the IT-SOFC anode surface after being exposed to both H₂ and methanol according to the mentioned testing procedure. The anode surface analysis indicates that no carbon traces are detected for the cell tested under both H₂ and methanol feed.

If we compare the anode gas effluent when the SOFC is powered by H₂ at different temperatures (Fig. 8(b)) we can confirm the occurrence of several chemical reactions that compete at the anode of a direct methanol-SOFC where the methanol was previously proved to decompose into a mixture of CO/H₂.

During the phase of hydrogen fueled SOFC test at 650 °C (phase1), the amount of hydrogen is majoring the anode gas effluent at about 100 %. Thereafter, the H₂ amount decreases to 52% (phase 3) and 62% (phase 5) at 700 and 750 °C respectively when the cell was fed with pure hydrogen after being substituted by methanol. This could be related to possible remove of some carbon particulate appearing during the methanol feeding phases. This is evidenced via the increase of the CH₄ amount at 700 and 750 °C according to the methanation reaction (Eq. 21):

This reaction is highly exothermic ($\Delta G = -281.26 \text{ kJ/mol}$ at 700 °C) and its equilibrium coefficient (in the order of 10¹⁵) is dependent on temperatures. It decreased slightly among the temperature range 650 °C-750 °C.

When the SOFC was fed with pure hydrogen, the cell was discharged at several temperatures and the water droplets appear abruptly after the threshold current density because of higher electrochemical oxidation of hydrogen and methanol to water (Eqs. 1 and 3).

The amount of carbon monoxide increases significantly from 650 to 700 °C as a product of the methanol decomposition reaction (Eq.5). Elimination of coking could be also explained by the water gas shift reaction (Eq. 22):

At low temperatures, Eq. 22 which represents an endothermic reaction is thermodynamically unlikely. Its equilibrium coefficient ($\sim 10^{-6}$) increases as the temperature rises.

The amount of carbon monoxide decreases at 750 °C to 23% (phase 5) when the SOFC was fed by hydrogen as the CO was used as a source for C and CO₂ via Boudouard reaction (Eq. 23) which is really evidenced by the increases of CO₂ amount in the anode gas effluent.

The Boudouard reaction is characterized by a negative Gibbs free energy ($\Delta G = -208.5 \text{ kJ/mol}$ at 750 °C) which promotes the formation of CO₂. The equilibrium coefficient ($\sim 10^{11}$) appropriate for this exothermic reaction depends on temperature and decrease rapidly to ($\sim 10^{10}$) as the temperature increase from 650 °C to 700 °C then slowly by increasing the temperature to 750 °C.

At 750 °C, the amount of CH₄ increases slightly which means that the methanation reaction kinetics (Eq. 21) is still activated. The amount of CO decreases whereas the amount of H₂ increases may be due to the possible competition between Boudouard and the WGSR reactions. Based on the equilibrium thermodynamic calculation, it appears that the methanation reaction (Eq.21) and the Boudouard reaction (Eq. 23) are the major pathways responsible for the carbon removing under these operating conditions and especially at 750 °C as they show the largest change in the free Gibbs Energy at higher temperatures.

4. Conclusions

A bio-methanol fueled IT-Solid oxide fuel cell was investigated in this study. Power density of about 350 mW/cm² was achieved when IT-SOFC is fed with dry methanol at 750 °C. Carbon formation was observed on the Ni/SDC anode surface when fueled with pure methanol and then removed when a switch of H₂/methanol testing procedure was proposed. The occurrence of several chemical reactions mechanisms including the methanation, WGSR and Boudouard reactions could be at the origin of the coking removing.

The catalytic decomposition of methanol in an environment similar to that of an SOFC anode compartment has been studied. This reaction is kinetically active in the operating temperature between 600 and 750 °C yielding a mixture of H₂ and CO with a proportion dependent on the temperature. The GC measurements clearly confirmed that H₂/CO/CH₃OH reactions may contribute to the electrochemistry the IT-SOFC anode fed directly by methanol at 700 °C. A series of probable reactions process taking into account the double (H⁺/O²⁻) conducting LN-SDC electrolyte is thus proposed. However, H₂ and CO electrochemical oxidation reactions seem to govern the anode process at 750 °C. This system has a great potential and several advantages to be used as an APU component in a specific eco-transportation sector. Indeed, tested cell is shown promising to be employed as a component in an APU-SOFC system in comparison to Gen 3 commercial cell developed by Delphi but still requires design optimization to limit ohmic losses and coking. Overall, the successful bio-methanol fed IT-SOFC has a great potential and impact on energy and environment whereas more research is required to achieve this technology up-scaling.

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Table captions

Table 1: Maximum fuel utilization with respect to temperatures of SOFC systems fueled directly by methanol.

Figure captions

Fig. 1: (a) SOFC test rig, (b) testing furnace and evaporator, and (c) schematic of gas piping diagram.

Fig. 2: (a) Voltage and power density as function of current density, (b) EIS complex plots for Ni/SDC|LN-SDC|LiNiO₂-SDC SOFCs fuelled by dry H₂ (■) and dry methanol (●), and (c) comparison of cell performance with Gen3 cell designed by Delphi (■) at 750 °C.

Fig. 3: Voltage and power density as function of current density for SOFCs fuelled by dry methanol at different temperatures. The inset figure shows the EIS complex plots of the SOFCs fed by methanol at different temperatures.

Fig. 4: Image of Ni/SDC anode after testing with methanol.

Fig. 5: Measured voltage versus time for SOFC cell based Ni-SDC anode at 750 °C under open circuit conditions and then at applied constant current.

Fig. 6: (a) Product composition and (b) H₂ and CO selectivity results under methanol catalytic decomposition at different temperatures.

Fig. 7: (a) H₂ and (b) CO₂ quantity yield before and after SOFC cell discharging at 700 and 750 °C.

Fig. 8: (a) The SOFC testing procedure, (b) resulting anode gas effluent of the SOFC fed by hydrogen in phase 1 (650 °C), phase 3 (700 °C) and phase 5 (750 °C).

Fig. 9: SEM/EDS analysis of the anode surface after the proposed hydrogen/methanol testing procedure.

Table 1: Maximum fuel utilization with respect to temperatures of SOFC systems fuelled directly by **m**ethanol.

SOFC Temperature (°C)	i_{lim} (mA/cm ²)	$U_{f,max}$
650	556	3.5
700	753	4.7
750	1051	6.6

2-column fitting image

Fig.1:(a)SOFC test rig, (b) testing furnace and evaporator, and (c) schematic of gas piping diagram.

Single fitting image

Fig. 2: (a) Voltage and power density as function of current density , (b) EIS complex plots for Ni/SDC|LN-SDC| LiNiO₂-SDC SOFCs fuelled by dry H₂ (■) and dry methanol (●), and (c) comparison of cell performance with Gen3 cell designed by Delphi (■) at 750 °C.

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Graphical Abstract