

# A Novel Biogas-Fueled-SOFC Aided Process for Direct Production of Electricity from Wastewater Treatment: Comparison of the Performances of High and Intermediate Temperature SOFCs

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## Abstract

A novel process for the treatment of municipal and industrial wastewater is developed, which leads to the direct production of electricity, and/or H<sub>2</sub>, with an environmentally friendly way. The electricity production is directly, and in high efficiency, obtained via novel biogas fuelled fuel cells, which are also developed here and concern an important subunit of the overall process. Biogas is generated by the anaerobic treatment of the activated sludge that emanates from the already processed municipal waste, while H<sub>2</sub> is achieved from the electrolytic degradation of the high COD industrial waste. A sort description of the novel process is presented while the performances of two types, i.e. high and intermediate temperatures, solid oxide fuel cells (SOFCs) tested on direct feed of simulated biogas mixtures are comparatively analyzed.

*Keywords:* Biogas, SOFC, Wastewater treatment,

## 1. Introduction

The biological treatment of wastewater is a widely acceptable process that takes place aerobically or anaerobically. The anaerobic treatment is mainly preferred for the treatment of waste of high BOD/COD, since it requires considerably smaller plants-installations, is related to smaller production of sludge and offers the possibility of periodical operation. Moreover, it leads to the generation of biogas, extensively produced today in an indigenous local base, which under some constrains is currently used for the production of heat energy by the use of specialized burners [1, 2]. It is a mixture of gases with main constituents of CH<sub>4</sub> and CO<sub>2</sub>. Because of the different ways of production and the different waste sources, biogas composition varies significantly depending not only on different locations but also over time. Its composition usually lies within the following ranges: CH<sub>4</sub> = (50-70%), CO<sub>2</sub> = (25-50%), H<sub>2</sub> = (1-5%) and N<sub>2</sub> = (0.3-3%) with various minor impurities, notably NH<sub>3</sub>, H<sub>2</sub>S and halides. Combustion of biogas to produce heat, a low quality form of energy, is not the most desirable utilization. Moreover, poor biogases (i.e., with low CH<sub>4</sub>/CO<sub>2</sub> ratio) are practically unusable nowadays because at low methane levels the operation of conventional burners is problematic [2]. In such cases large quantities of poor-quality biogases are currently wasted by detrimental venting to the atmosphere, contributing to its pollution. However, biogas is cheap, widely available and represents a renewable energy reserve; any efficient innovative utilization of biogas for energy production should be greatly desirable.

On the other hand, during the last three decades solid electrolyte galvanic cells have been studied intensively as power-producing devices (Fuel Cells) [3]. They can convert a significant portion of the Gibbs energy change of exothermic reactions into electricity rather than heat, their thermodynamic efficiency comparing favorably to thermal power generation schemes which are limited by Carnot-type constraints [3]. Fuel cells have received increasing development for an extensive range of applications, while the idea of constructing novel fuel cells directly fueled with biogas, capable to operate satisfactorily at any quality of biogas feed, producing electrical energy, is of great practical importance. In this advantageous fuel cell concept the methane dry-reforming reaction

$$\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad (1)$$

should take place internally, without the necessity of an external reformer, onto the anodic electrode of the fuel cell, simultaneously with the charge transfer reactions

$$\text{H}_2 + \text{O}^{2-} \rightarrow \text{H}_2\text{O} + 2\text{e}^- \quad \text{and} \quad \text{CO} + \text{O}^{2-} \rightarrow \text{CO}_2 + 2\text{e}^- \quad (2)$$

that lead to electricity production [4].

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Regarding the technologies of the municipal and industrial wastewater treatment, they are, in general, sufficiently developed. However, depending on the nature of the waste, there are cases (i.e., high COD industrial waste for example olive mill wastewater) where the current treatment technologies are not satisfactory solutions. Several more efficient proposals could be found in the open and patent literature the last decades which are based variously on chemical, biological and advanced oxidation methods. However, their complexities make their application difficult. The electrolytic degradation of waste seems to be sufficiently more simple and promising.

In the present work we describe a novel process which combines the coordinated operation of the anaerobic biological treatment of municipal activated sludge and industrial wastewater and the electrolytic degradation of the high COD industrial waste, with a biogas fueled solid oxide fuel cell. The process produces electrical energy with simultaneous treatment of a wide COD range of municipal and industrial wastewaters. Two types, i.e., intermediate and high temperature SOFCs, operating directly on simulated biogas feeds, are developed and tested. The intermediate temperature SOFC is based on gadolinia doped ceria (GDC) solid electrolyte, while the high temperature SOFC on yttria stabilized zirconia (YSZ) solid electrolyte. A  $\text{La}_{0.54}\text{Sr}_{0.46}\text{MnO}_3$  perovskite was used as cathodic material in both cells, while Ni(Au)-GDC and Ni-YSZ cermet anodes were used for the GDC-SOFC and YSZ-SOFC respectively. The electrical output characteristics of the cells are comparatively analyzed.

## 2. Description of the Novel Process and Experimental Methods

Figure 1 shows the flow chart configuration of the novel process. The first stage of the process includes anaerobic treatment either of the activated sludge that emanates from already processed in previous stage municipal waste unit-1A or of the industrial waste (unit-1B). The produced biogas from these units is led to the fuel cell unit-2A for electrical energy production through the internal dry-reforming of methane accompanied by the electro-oxidation of the produced CO and H<sub>2</sub> by O<sup>2-</sup>. The fuel cell outlet stream, containing mainly CO<sub>2</sub>, is led to a subsequent unit where CO<sub>2</sub> is trapped by adsorption in zeolite molecular sieves. Controlled periodical thermal desorption of CO<sub>2</sub> from the CO<sub>2</sub>-trapping unit is then performed and the released CO<sub>2</sub> is stored. Part of this can be recycled to the fuel cell for the adjustment of the quality of the biogas feed to the fuel cell unit. Regulation of the CH<sub>4</sub>/CO<sub>2</sub> ratio at the desirable level for the optimum operation of the cell is thus achieved.

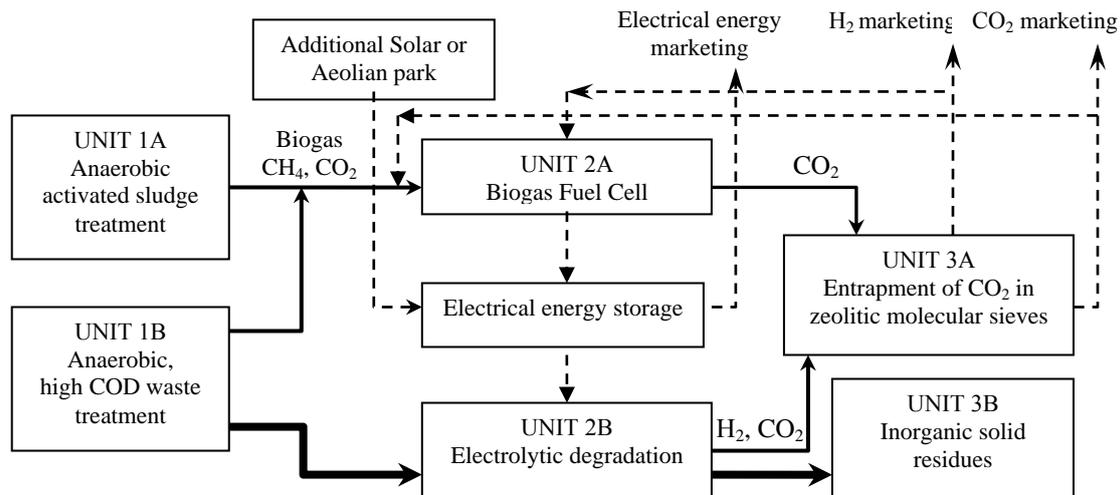


Figure 1: Flow chart of the novel process for the treatment of high COD wastewater and activated sludge for the simultaneous production of electrical energy and H<sub>2</sub>.

On the other hand, the wastewater effluent from the anaerobic biological treatment unit-1B is fed to the electrolytic degradation unit-2B, where deep degradation of organics to H<sub>2</sub> and CO<sub>2</sub> is performed. The produced gas of the degradation unit-2B, after passing through the CO<sub>2</sub>-trapping unit, is pure H<sub>2</sub>. Part of this hydrogen can be supplied to the fuel cell unit-2A for further electricity production, while the rest is stored. The consumption of the electrical energy that is required in the unit of the electrolytic decomposition of waste (unit-2B) is obviously part of the electricity produced by the biogas fuel cell unit-2A. The residue of the electrolytic degradation unit-2B is water with a few, mainly inorganic, components that are precipitated and removed. The whole process satisfies its energy needs by itself and moreover it produces additional electrical energy, which can be fed in the power transmission national grid as a renewable source of energy. Photovoltaic and/or aeolian park units can be installed contributing to the electrical energy production; the collected solar or aeolian power could be supplied to the electrolytic degradation unit-2B or added to the total electrical energy produced by the process.

The described process is designed for the treatment of any type of biomasses and wastewaters even for those of high COD. Its products, electrical energy, H<sub>2</sub> and CO<sub>2</sub>, are highly marketable, while no gas or liquid or solid pollutants are vented to the environment.

Figure 2 shows the schematic of the fuel cell reactor configuration. It consists of a solid electrolyte (GDC or YSZ) tube closed at one end. A  $\text{La}_{0.54}\text{Sr}_{0.46}\text{MnO}_3$  perovskite thin film coated at the outside bottom wall

of the tube plays the role of the cathode. A porous Ni(Au)-GDC or Ni-YSZ cermet film deposited onto the inside bottom wall of the GDC or YSZ solid electrolyte tube plays the role of the anode. The procedures and temperature protocols for the preparation of the cathodic and anodic materials are described in detail elsewhere [5, 6]. The open end of the solid electrolyte tube was clamped to a stainless-steel cap which had provisions for inlet and outlet gas lines and a K-thermocouple with electrical isolation by means of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> tubing (Fig. 2). A gold lead wire was used to establish electrical contact with the inner anodic electrode *via* a spirally shaped end. The electrical circuit was achieved by a second Au lead connected to the perovskite electrode *via* a Pt-mesh pressed onto the cathode.

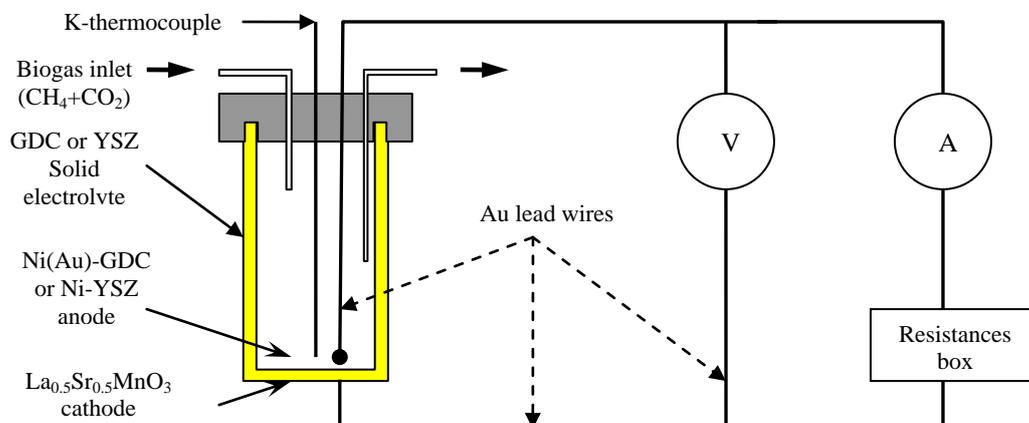


Figure 2. Schematic diagram of the fuel cell reactor

Reactant gases were delivered by mass flow meters (MKS-247). Reactants and products analysis were performed by on-line gas chromatography (Shimadzu 14B; MS-5A and PN columns operated at 80°C) and mass spectroscopy (Pfeiffer-Vacuum, Omnistar Prisma). The reactants were Messer Hellas certified standard CO<sub>2</sub> (99.6%) and CH<sub>4</sub> (99.5%); ultra pure He, H<sub>2</sub> and 20% O<sub>2</sub> in He were used for *in situ* treatment of the anodic electrode when necessary. Before acquisition of fuel cell operation data, the anode was reduced in H<sub>2</sub> flow. This activated the electrode for catalytic dry-reforming and also rendered it electrically conducting.

### 3. Results and Discussion

The electrical efficiency of the cells was tested under three different CH<sub>4</sub>/CO<sub>2</sub> biogas feed compositions: poor, equimolar and rich CH<sub>4</sub>/CO<sub>2</sub> compositions. Both cells were found to operate stably for all these feeds, and both offered superior power outputs in the case of equimolar CH<sub>4</sub>/CO<sub>2</sub> feed. As a reflex we compare cells' operation characteristics under this feed.

Figs. 3a and b show the cells' voltage-current and power-current data, respectively. In the case of the intermediate temperature GDC-SOFC the results in Fig. 3a show a clear linear dependence of cell voltage on current density: *this demonstrates that ohmic polarization is the only source of polarization*. The slope of the voltage-current curve is the ohmic resistance of the cell, a significant part of which is due to the O<sup>2-</sup> transport resistance of the thick (1.1 mm) solid electrolyte. It is worth emphasizing, the absence of activation and concentration polarizations in the GDC-SOFC under biogas fuelling. The power density, of ~60 mW/cm<sup>2</sup>, achieved (Fig. 3b) is also very encouraging regarding of the thickness of the electrolyte (1.1 mm). This value is favorably compared to that of ~90mW/cm<sup>2</sup> reported for GDC-SOFCs with electrolyte thickness of 0.280 mm, operating at similar temperatures and with wet 10% H<sub>2</sub>/N<sub>2</sub> feed [7].

On the contrary, the voltage-current output of the high temperature YSZ-SOFC is rather complex (Fig. 3a). The initial exponential-like decline of the cell voltage versus increasing current implies the appearance of activation overpotential. The slope of the subsequent linear part of the V-I curve is the ohmic resistance of the cell, which seems to be similar or slightly worse than that of the GDC-SOFC with the same solid electrolyte wall thickness. As a result the maximum electrical power output offered by the high temperature SOFC is slightly lower (~52 mW/cm<sup>2</sup>) than that of the intermediate temperature GDC-SOFC (Fig. 3b).

The absence of activation and concentration polarizations in the case of GDC-SOFC appears very promising and implies that anodic and cathodic charge transfer reactions are fast on the anodic and cathodic materials employed. Equally, mass transfer or diffusion limitations involving the electrode pores, which would cause concentration overpotential, are insignificant. Clearly, substantial improvements in power output of the GDC-SOFC could be obtained by using thinner GDC components or by increasing operation temperature: both would lead to a reduction in ohmic resistance and thus ohmic overpotential. On the other hand, the current-potential output (and thus the power production) of the high temperature YSZ-SOFC appears to be significantly inhibited by the existence of activation polarization as well. This implies that anodic charge transfer reactions are not satisfactorily fast in this biogas fuel cell on the Ni-YSZ cermet anode and under the conditions used. Therefore, in order to enhance cell performance it is necessary to deal with the improvement of the electrocatalytic properties of the anode by evaluating its composition and/or structure or by supplying appropriate promoters.

It is also obvious that despite of the same wall thickness of the GDC and YSZ solid electrolytes used in both intermediate and high temperature biogas fuel cells, the former offers higher power generation at significantly lower temperature, due to its lower ohmic resistance. The worse ionic conductivity of YSZ in comparison to GDC is well known [8]. However, the present results demonstrate that among others (in particular the disadvantage of operating cells at high temperatures), thinner solid electrolyte films are necessary for the design of high temperature YSZ cells, a factor which is harmful to its mechanical robustness.

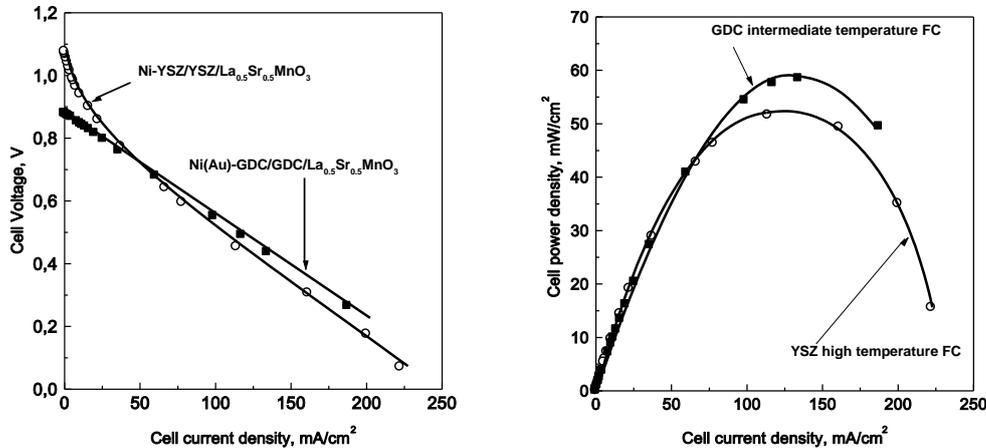


Figure 3: Voltage (a) and power density (b) dependence on current density for the high and intermediate temperature fuel cells of the types  $Ni-YSZ/YSZ/La_{0.5}Sr_{0.5}MnO_3$  and  $Ni(Au)-GDC/GDC/La_{0.5}Sr_{0.5}MnO_3$ , respectively. Equimolar, 50%  $CH_4/50\% CO_2$ , biogas feed.  $T=875^\circ C$ , total flow rate  $F=60\text{ cm}^3/\text{min}$  for the high temperature SOFC;  $T=640^\circ C$  and  $F=20\text{ cm}^3/\text{min}$  for the intermediate temperature SOFC.

#### 4. Conclusions

Intermediate temperature GDC-SOFC with Ni(Au)-GDC cermet anode and high temperature YSZ-SOFC with Ni-YSZ cermet anode operated with biogas feeds both appear to be promising for electrical energy production. An equimolar  $CH_4/CO_2$  feed ratio maximizes the rate of the dry internal reforming reaction of methane and consequently the electrical energy output characteristics of both cells, although both cells operate satisfactorily in a variety of biogas compositions including poor-quality biogases. For the intermediate temperature GDC-SOFC ohmic polarization is the only source of polarization. This demonstrates that, among the other advantages emerging from the lower temperatures of operation of the GDC fuel cells, simpler actions (e.g., lowering the solid electrolyte thickness) could lead to better cell performances. In contrast the appearance of significant activation polarization in the high temperature YSZ biogas fuel cell implies that more difficult actions, including improvements of the electrocatalytic behavior of the anode, are necessary for the enhancement of cell performance.

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