Electricity production from wastewater treatment via a novel biogas-SOFC aided process

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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_2, by an environmentally friendly way. Through this process, production of electricity is obtained by a novel direct-biogas-fuelled fuel cell, which is also developed here, that concerns a major subunit of the overall process. Both intermediate and high temperature solid oxide fuel cells (IT- and HT-SOFCs) based on 10mol% Gd_2O_3 doped CeO_2 (gadolinia doped ceria, GDC) and 8mol% Y_2O_3 stabilized ZrO_2 (yttria stabilized zirconia, YSZ) solid electrolytes, respectively, have been constructed and tested, while three different Ni-based cermets were used as anodic materials. The operation performances of these cells under direct feed of simulated biogas mixtures are comparatively discussed.
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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 biological oxygen demand (BOC) or chemical oxygen demand (COD), since it requires considerably smaller plants-installations, is related to less production of sludge and offers the possibility of periodical operation. Moreover, it leads to the generation of biogas; its composition usually lies within the following ranges: $CH_4 = (50–70\%)$, $CO_2 = (25–50\%)$, $H_2 = (1–5\%)$ and $N_2 = (0.3–3\%)$ with various minor impurities, notably NH_3, H_2S and halides. Biogas is extensively produced today in an indigenous local base and, under some constrains, it is currently used for the production of heat energy by the use of specialized burners [1]. However, combustion of biogas to produce heat, a low quality form of energy, may not be considered as its most desirable utilization. Moreover, poor bio-gases (i.e., low CH_4/CO_2 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 unfortunately 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, solid electrolyte galvanic cells are currently studied intensively as power-producing devices (i.e., fuel cells). FCs can convert a significant portion of the Gibbs energy change of exothermic reactions into electricity rather than heat. Their thermodynamic efficiency is favorably compared 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, is of great practical importance. In this advantageous fuel cell concept the methane dry-reforming reaction:

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \tag{1}$$
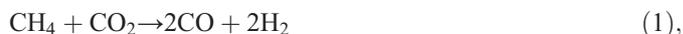
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should take place internally, without the necessity of an external reformer, on the fuel cell anode, simultaneously with the electricity production related charge transfer reactions:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^-, CO + O^{2-} \rightarrow CO_2 + 2e^-$$
$$\text{and } C(s) + 2O^{2-} \rightarrow CO_2 + 4e^- \qquad (2).$$
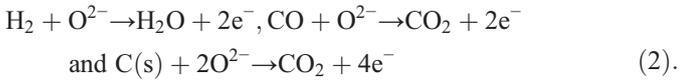
Regarding the technologies of the municipal and industrial wastewater treatment, they are, in general, sufficiently developed. However, depending on the nature of the waste, there are cases (i.e. high COD industrial waste; e.g. olive mill wastewater), where the current treatment technologies are not satisfactory solutions. Several more efficient proposals could be found in the literature nowadays, which are based variously on chemical, biological and advanced oxidation methods [4]. However, their complexities make their application difficult. The electrolytic degradation of waste seems to be relatively 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. Intermediate, as well as high temperature SOFCs, based respectively on GDC and YSZ solid electrolytes and operating directly on simulated biogas feeds, are developed and tested. $La_{0.54}Sr_{0.46}MnO_3$ perovskite was used as cathodic material in both cell types, while Ni-GDC, Ni(Au)-GDC and Ni-YSZ cermet anodes were used for the GDC-SOFC and YSZ-SOFC respectively. The operation output characteristics of these cells are comparatively analyzed.

2. Description of the novel process and experimental

Fig. 1 (top) shows the flow chart configuration of the novel process. The first stage of the process involves 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 internally (on the anode) produced CO and H_2 by O^{2-}. The fuel cell outlet stream
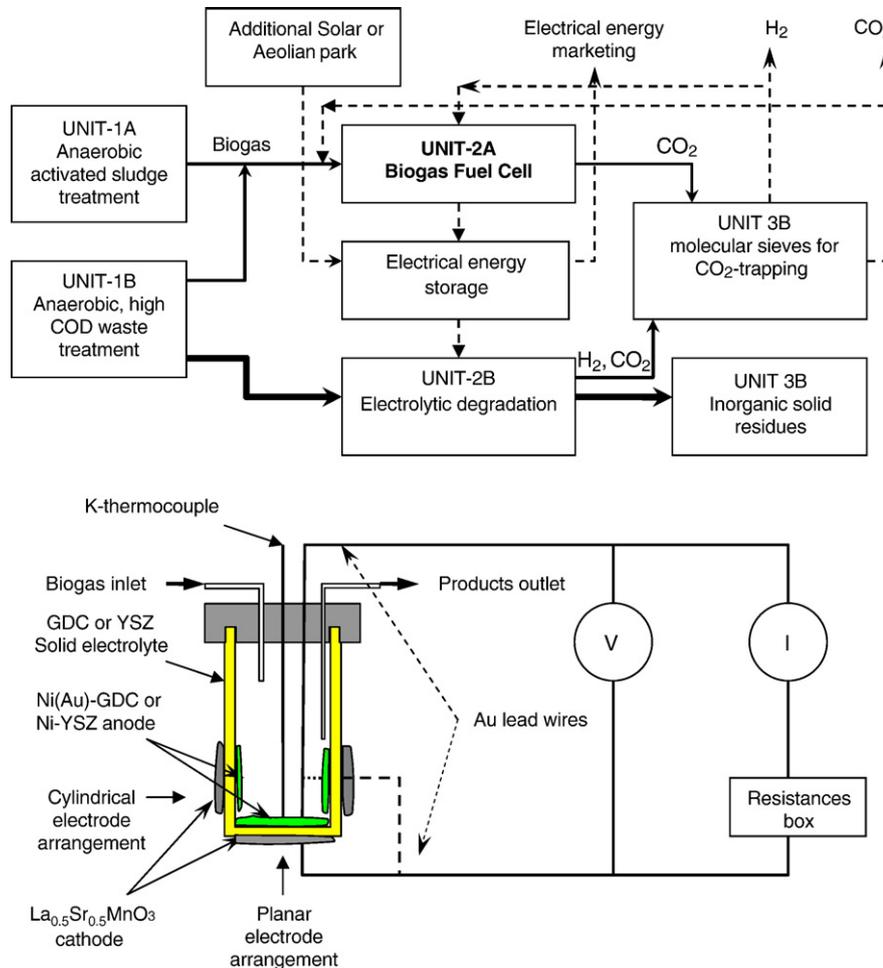
Fig. 1. (Top): Flow chart of the novel process for the municipal and industrial wastewater treatment and the simultaneous production of electrical power. (Bottom): Electrodes and electrical circuit configurations of the experimental biogas fueled SOFCs.

is led to a subsequent unit, where CO_2 is trapped by adsorption at low temperatures (typically $< \sim 100$ °C) in zeolite molecular sieves. Molecular sieve 5A (Linde), for example, selectively and very efficiently ($\sim 100\%$) traps carbon dioxide, while other entities, e.g. CH_4, H_2, O_2 or CO that can be found in small quantities at the effluent stream are practically untrapped [5,6]. Controlled periodical thermal desorption of CO_2 from the CO_2-trapping unit (at $T > \sim 250$ °C) is then performed and a portion of the released CO_2 can be recycled to the fuel cell for the adjustment of the "quality" (i.e., CH_4/CO_2 ratio) of the biogas fed to the fuel cell unit. Adjustment of the CH_4/CO_2 ratio at the desirable level for the optimal cell operation is thus achieved. Equimolar or low-CH_4 biogas feed compositions are expected to prevent carbon deposition on the anode; the former also optimizes cell power output (see results section). The rest CO_2 can be supplied to CO_2-consumer industries such as agrichem-ical-fertilizer manufactories, carbonated refreshment and beer manufacturing plants, etc.

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_2 and CO_2 is performed. The produced gas of the degradation unit-2B, after passing through the CO_2-trapping unit, is pure H_2. Part of this H_2 can be supplied to the fuel cell unit-2A for further power production. The consumption of the electrical energy that is required in the unit of the electrolytic degradation of waste (unit-2B) is obviously part of the electricity produced by the biogas fuel cell. The residue of the electrolytic degradation unit-2B is water with a few, mainly inorganic, components that are precipitated and can be supplied as fertilizer for agricultural use. 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. 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_2 and CO_2, are highly marketable, while all gas, liquid or solid effluents are well controlled and not vented to the environment.

Fig. 1 (bottom) shows the schematic of the fuel cell reactor configuration. It consists of a solid electrolyte (GDC or YSZ) tube closed at one end. A $La_{0.5}Sr_{0.5}MnO_3$ perovskite thin film coated at the outside bottom (planar type SOFC) or peripheral (tubular type SOFC) wall of the tube plays the role of the cathode. A porous Ni-GDC, Ni(Au)-GDC or Ni-YSZ cermet film deposited on the opposite inside 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 [7,8]. 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 α-Al_2O_3 tubing (Fig. 1 bot-tom); the external electrical circuit arrangement is also shown in figure. The reason of using Au in one of our Ni-cermet composites (i.e. Ni(Au)-GDC) was dictated by recent studies, which show that the incorporation of Au into Ni-cermet composites inhibit graphitic carbon deposition, promoting other, reactive with O_{ads} or O^{2-}, forms of carbon (carbidic and adsorbed carbon) [9,10].

The composition of simulated biogas mixture was controlled by mass flow meters (MKS-247) and fed to the cell at 1 bar. Reactants (Messer Hellas certified CO_2 and CH_4) and products (CO and H_2) analysis were performed by on-line gas chromatography (Shimadzu 14B) and mass spectroscopy (Pfeiffer-Vacuum, Omnistar Prisma).

Before acquisition of fuel cell operation data, the anode was *in situ* reduced by a 60 cm^3/min flow of 10% H_2/He (30 min at 650 °C and 850 °C for Ni- or Ni(Au)-GDC and Ni-YSZ cermets, respectively). This activated the electrode for catalytic dry-reforming and also rendered it electrically conducting.

3. Results and discussion

Fig. 2a shows voltage–current performance characteristics of the cells studied: two GDC-based intermediate temperature and one YSZ-based high temperature SOFCs. The corresponding power output densities of the cells are shown in Fig. 2b. For the intermediate temperature GDC-SOFCs, one was of cylindrical electrodes arrangement (the electrodes were deposited at the opposite sides of the cylindrical wall of the tube, which has a thickness of ~ 1.6 mm) and the other of planar electrodes arrangement (electrodes were deposited at the opposite sides of
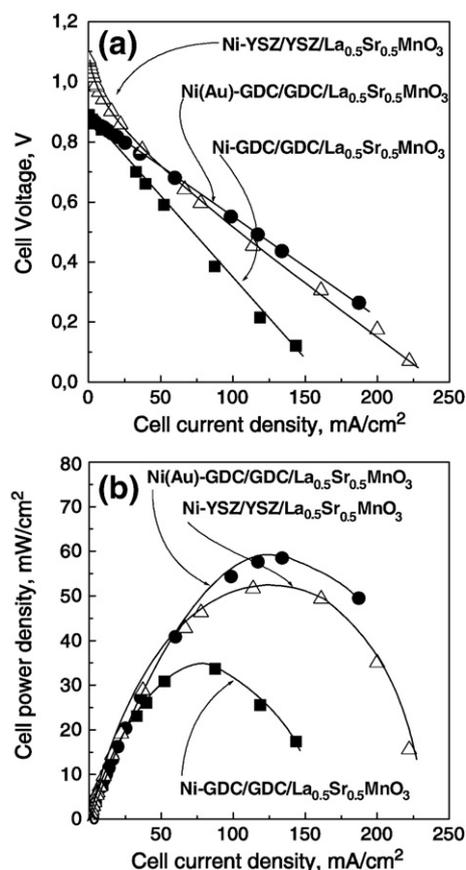
Fig. 2. Voltage–current (a) and power density–current (b) behavior of the biogas fueled fuel cells under equimolar 50%CH_4/50%CO_2 feed. Other conditions: $T = 875$ °C, $F = 60$ cm^3/min for the Ni-YSZ/YSZ/$La_{0.5}Sr_{0.5}MnO_3$ cell; $T = 640$ °C, $F = 20$ cm^3/min for the Ni(Au)-GDC/GDC/$La_{0.5}Sr_{0.5}MnO_3$ cell; $T = 630$ °C, $F = 60$ cm^3/min for the Ni-GDC/GDC/$La_{0.5}Sr_{0.5}MnO_3$ cell.

the flat bottom of the tube, which has a thickness of ~ 1.1 mm) (Fig. 1 bottom). The anode of the former cell was 65wt.% Ni-GDC cermet, while the anode of the latter was 65wt.% Ni (0.45wt.% Au)-GDC. The anode of the YSZ-SOFC was 65wt.% Ni-YSZ cermet and the thickness of the YSZ solid electrolyte ~ 1 mm (planar electrodes arrangement).

The results in Fig. 2a show a clear linear dependence of cell voltage on current density for both intermediate temperature GDC-SOFCs: *this demonstrates that ohmic polarization is the only source of polarization for these cells.* It is worth emphasizing, the absence of activation and concentration polarizations in the GDC-SOFCs under biogas fuelling. On the contrary, the voltage–current output of the high temperature YSZ-SOFC is rather complex (Fig. 2a). The initial exponential-like decline of the cell voltage versus increasing current implies the appearance of activation polarization.

The absence of exponential-like declination at low currents ($i \rightarrow 0$) in the case of GDC-SOFCs indicates that the activation overpotential component of the overall cell polarization is very low compared to the ohmic overpotential component, implying that under these conditions anodic and cathodic charge transfer reactions are fast on the anodic and cathodic materials employed. For practical issues this appears promising, since substantial improvements in power output of the GDC-based SOFCs could be simply obtained by using thinner GDC components or by increasing operation temperature: both would lead to a reduction in ohmic overpotential. On the other hand, the V–i performance (and thus cell power, Fig. 2b) of the high temperature YSZ-based 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 fuelled cell on the Ni-YSZ anode under the conditions used, indicating the necessity of improvements in its electrocatalytic properties by evaluating its composition or by supplying appropriate promoters. The different behaviour of the Ni-GDC and Ni-YSZ cermets regarding to activation polarization phenomena is most likely related to the participation or not of their different substrate components (i.e., GDC or YSZ) on the chemical/electrochemical reactions related to the methane dry-reforming process; indeed, it has been shown that ceria-containing Ni-cermet composites offer significantly enhanced chemical [11] or electrochemical [12] activities during this process.

The power efficiency of the cells was studied under several CH_4/CO_2 biogas feed compositions including poor, equimolar and rich CH_4/CO_2 compositions. All three cells tested were found to operate satisfactorily at any of these feeds. However, as Fig. 3 shows, they offered superior power outputs in the case of equimolar CH_4/CO_2 feed. This is most probably related to the fact that at this composition the rate of the internal dry(CO_2)-reforming of methane (reaction 1) is maximized over Ni-catalysts [7,8]. Fig. 3 also shows that rich biogas feeds do not cause significant attenuation in cell power output from its optimal value; power inhibition appears to be relatively more substantial with poor biogas feeds.

A common problem of the hydrocarbons fueled SOFCs is their progressive deactivation due to graphitic carbon deposition
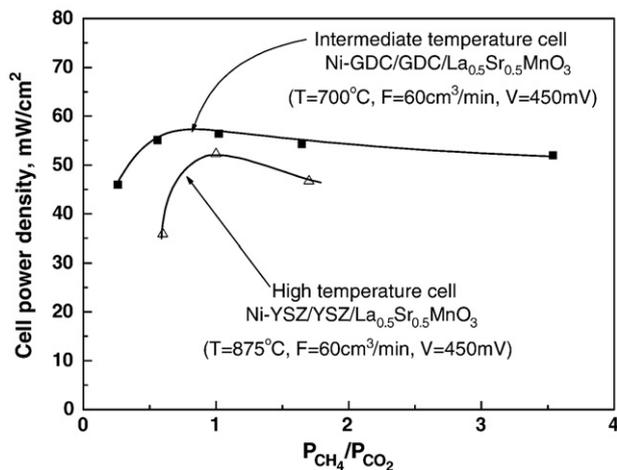
Fig. 3. The dependence of cell power density output on CH_4/CO_2 feed composition at a constant temperature and cell voltage. Conditions: $T = 875$ °C, $V = 450$ mV, $F = 60$ cm³/min for the Ni-YSZ/YSZ/La$_{0.5}$Sr$_{0.5}$MnO$_3$ cell; $T = 700$ °C, $V = 450$ mV, $F = 60$ cm³/min for the Ni-GDC/GDC/La$_{0.5}$Sr$_{0.5}$MnO$_3$ cell.

and accumulation on the anode. Ni-based catalysts or electro-catalysts' deactivation under steam- or CO_2-reforming of methane reactions have been often reported in the literature [13–15]. As a consequence, long-term experiments are required in order to assess the practical potential of the constructed anodes under the use of interest. Some preliminary experiments with this purpose have been performed up to now: the high temperature (Ni-YSZ/YSZ/La$_{0.5}$Sr$_{0.5}$MnO$_3$) cell was operated for more than 200h at constant temperature ($T = 875$ °C) and cell potential ($V = 450$mV) under equimolar biogas feed composition, showing very good power output stability. Similarly, the Ni(Au)-GDC/GDC/La$_{0.5}$Sr$_{0.5}$MnO$_3$ intermediate temperature cell was found to operate very stably for more than 120h tested at $T = 640$ °C and equimolar feed composition. However, it is expected that the tendency of the system for graphitic carbon deposition or Ni oxidation to the less active form of NiO – both factors can significantly influence cell performance – may depend on the CH_4/CO_2 ratio of the feed; rich biogases are expected to favor carbon deposition, while poor biogases probably favor Ni catalyst oxidation. Due to the potential practical importance of these aspects, cell stability experiments under these conditions are currently in progress.

4. Conclusions

Intermediate temperature GDC-SOFC with Ni-GDC and Ni (Au)-GDC cermet anodes and high temperature YSZ-SOFC with Ni-YSZ cermet anode operated with biogas feeds appear to be promising for electrical energy production. Although cells operate satisfactorily in a variety of biogas compositions, including poor-, equimolar- and rich-quality biogases, equimolar CH_4/CO_2 feed maximizes the electrical power output characteristics of the cells. For the intermediate temperature GDC-SOFC, ohmic polarization is the only source of polarization, indicating the way for improving the cell performance. Activation polarization found to participate in the voltage

attenuation of the high temperature YSZ-based biogas fuel cell implies that improvements of the electrocatalytic behavior of the anodic materials (e.g., via promoters) may be considered for the enhancement of cell performance. These novel, direct-biogas fuelled SOFCs can compose a central unit of a process for the treatment of municipal and industrial wastewater with simultaneous production of electrical energy by an environmentally friendly way.

Acknowledgments

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