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Sustainable energy system combined biogas-feed-Solid Oxide Fuel Cell and Microalgae technology

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***Abstract*—*In the new frontier of energy and environmental safety, new efficient and clean safe energy conversion systems are required. In this sense, the present work is framed within the context of Circular Economy and proposes a multidisciplinary study for the development of more efficient, economically viable and non-polluting energy conversion systems, based on the synergetic combination of different technologies: fuel cells, biofuels, CO_2 capture, and the use of solar energy and microalgae. In a first step, a doped cerium oxide (Rh/Cu-CeCa) was evaluated as SOFC anode at 1023 K and using H_2 and biogas from different sources (algal biogas and landfill biogas) as fuel. Achieved maximum power density for the single cell running on algal biogas was 80 % higher than that obtained with landfill biogas. The comparative study shows the benefits of algal biogas as fuel for SOFC and clean energy production.*

Keywords*—*sustainable energy, carbon neutrality, microalgae biogas, solid oxide fuel cell, impurity-tolerant anodes

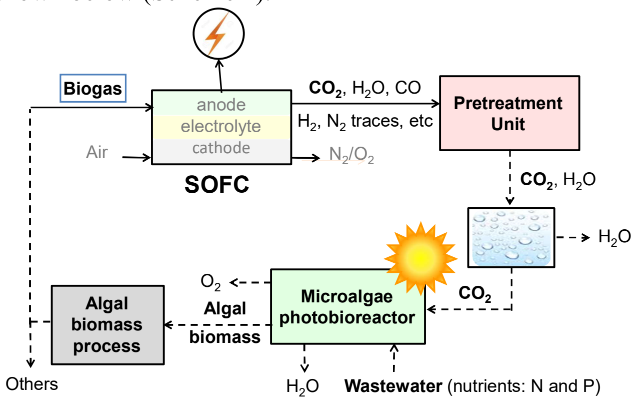
I. Introduction

Climate change, the scarcity of fossil fuels and the sharp increase in energy demand, especially in emerging economies, have led to a growing interest in the search for new and efficient ways to generate clean energy [1]. The world energy strategy for the next decade is a shift towards efficient energy sources with a low carbon footprint and based on renewable energy sources to achieve sustainable development, avoiding greenhouse gas emissions and environmental damage which are leading to disquieting climate change [2].

Solid Oxide Fuel Cells (SOFCs) can be considered as the most flexible energy converter in terms of fuel selection. In contrast with other types of fuel cells, SOFCs can use fossil and biogenic fuels [3]. The use of hydrocarbon fuels entails the formation of CO_2 in the anodic chamber, nevertheless, the use of biofuels more carbon-neutral, such as biogas, minimises the carbon footprint of these devices and reduces the environmental impact [4]. However, this kind of fuels contains a wide range of impurities that can be harmful to the SOFC system operation if not properly removed and monitored, such as H_2S, VOCs, siloxanes, chloride or phosphorus compounds, etc. The gradual accumulation of impurities at the electrode/electrolyte interface reduces the electrochemical activity by blocking the active sites of the cell and is one of the main sources of cell degradation [5]. Different approaches have been proposed for external fuel purification before the SOFC. However, from a scientific point of view, and thinking about the future commercialisation of these devices, the search of new anodic materials less prone to degradation due to the impurities that allow the direct electrochemical conversion, stands out as an appealing strategy for converting biofuels directly into electricity with high efficiency and broad versatility.

On the other hand, biofuels from clean and renewable bioresources have been widely studied as an alternative to fossil fuels. In this context, microalgae appear like an interesting option [6-8]. A microalga is an autotroph microorganism that can use wastewater and even seawater for their culture, can be grown in non-arable land and their cultivation does not compete with food production. Furthermore, these microorganisms can fix CO_2 from the air and convert into biomass, and culture media can be enriched with carbon dioxide from gases exhausted from power plants or other sources, reducing carbon dioxide emissions. Thus, the anaerobic digestion of algal biomass to biogas possesses advantages compared to other biofuel sources and conversion techniques as well as leading to a “cleaner” biogas, containing very low or null concentration levels of impurities such as sulfur, siloxanes, etc.

In this context, the present work aims to comparatively evaluate the performance of a SOFC fueled with algal biogas and landfill biogas. A novel impurity-tolerant ceria-based anode has been tested. The effect of biofuel composition on single-cell performance and long-term stability are investigated. The exhaust gas composition of the biogas fueled SOFCs has been analysed to quantify the CO_2 content and study its capture and recycling processes using microalgae. The proposed energy system is an interesting choice for a cleaner and sustainable energy production, promoting the integration of renewable energies and waste management. A global scheme for this system is shown below (Scheme 1).



Scheme 1 Proposed system for cleaner and sustainable energy production. Included in this work (straight line), future research (dashed line)

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II. EXPERIMENTAL

A. *Synthesis and characterization of SOFC anode*

The Rh/Cu-CeCa (0.4 wt.% Rh) was prepared by incipient wetness impregnation of the Cu-CeCa (40 at.% Cu combined with $Ca_{0.1}Ce_{0.9}O_{2-\delta}$) previously synthesized by inverse microemulsion method [9], with an aqueous $Rh(NO_3)_3$ solution. After impregnation, the sample was dried at 373 K and calcined under air at 1023 K for 2 h. The material was characterized by a multi-technique approach including XRD, XPS, Raman, ICP-AES and electrical conductivity measurements along with analysis of its chemical compatibility with SDC electrolyte and sulfur tolerance tests in H_2 fuel. Main results of this characterization have been previously reported [10].

B. *Single cell performance*

For its evaluation using different biogas a single cell, with an active area of 0.3 cm^2, was prepared using SDC electrolyte and LSM cathode. Details of the preparation method can be found elsewhere [11].

Biogas composition fluctuates significantly during its production process and it is highly dependent on the substrate used for that. For this study, we prepare different gas mixtures simulated biogas. We selected algal biogas (mainly constituted by methane and CO_2 60/40 vol. and sulfur-free) produced by anaerobic digestion of algal biomass in the presence of microalgae Spirulina [12]. For landfill biogas, similar methane content (60 vol. %) was used and 500 ppm of H_2S, a common biogas impurity, were incorporated into the composition.

Single cell was galvanostatically operated at 1023 K for 862 h under humidified hydrogen and biogas mixtures. Impedance spectra and current-voltage curves were regularly collected.

To quantify the concentration of carbon dioxide in the exhaust gas of the SOFCs, and study its capture and recycling processes using microalgae, the catalytic activity of anode material for biogas reforming were tested in a continuous-flow quartz reactor. Reactants and products were analysed on-line by gas chromatography using two packed columns filled with molecular sieve and Porapak Q.

III. RESULTS AND DISCUSSION

Rh/Cu-CeCa is mainly constituted by a fluorite phase of $Cu_xCa_yCe_{1-x-y}O_{2-\delta}$ mixed oxide and additional phases of metal oxides that, under working conditions, are reduced to the corresponding metallic phases (Cu^0 and Rh^0) which coexist with the mixed oxide. It presents optimal electrical characteristics, excellent thermal compatibility, based on the TEC values that are closed to those for common SOFC electrolytes as well as good chemical compatibility with SDC electrolyte [10].

Fig. 1 shows the power densities of single cell at 1023 K as a function of the fuel composition. For their comparison, in this figure values obtained with the same single cell running on hydrogen, sulfur-containing H_2, simulated algal biogas and landfill biogas are shown. Cell voltage remained stable during all process under current demand and different fuel composition. The I–V curves together with the power density of the fuel operating with H_2 and two different biogas are shown in Fig. 2. The main results of the single cell evaluation are collected in Table 1

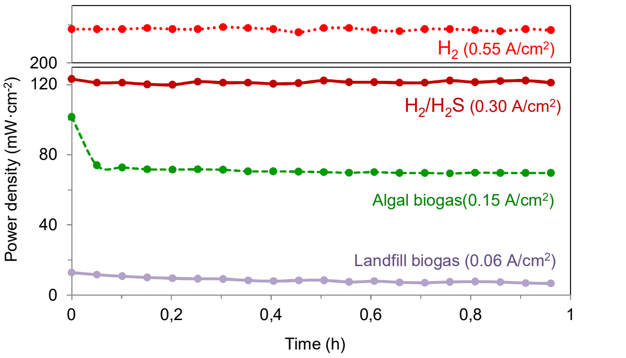

Fig. 1 Power densities of single cell at 1023 K as function of fuel composition

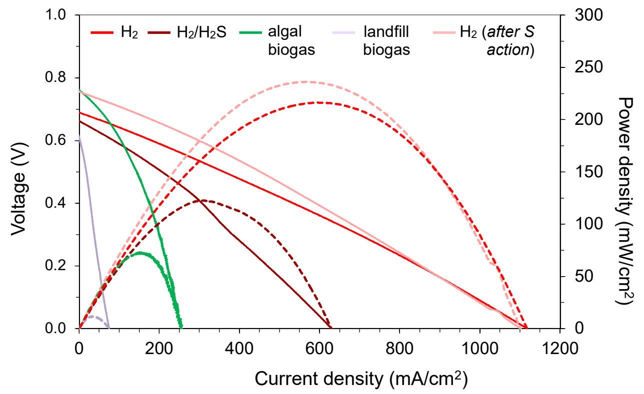

Fig. 2 I–V (solid line) and I–P (dashed line) curves of the single cell at 1023 K as a function of fuel composition

TABLE I
MAIN RESULTS OF Rh/Cu-CaCe /SDC / LSM SINGLE CELL EVALUATION

H_2S containing fuel*	I_{max} (mA/cm^2)	P_{max} (mW/cm^2)	Resistances ($\Omega\cdot cm^2$)	
			R_Ω	R_p
H_2 (*before S action*)	1116	216	0.26	022
H_2/H_2S	628	122	0.33	0.47
Algal biogas	258	74	0.46	0,62
Landfill biogas	77	12	0.70	4.40
H_2 (*after S action*)	1100	236	0.28	0.20

* H_2S content= 500 ppm (v)

The maximum current density (I_{max}), at 0 V, and the maximum power density significantly decrease when simulated biogas, algal biogas and landfill biogas, are used instead of pure humidified hydrogen. Values achieved for maximum power density were 74, 12 and 216 mW/cm^2, respectively. This electrical efficiency decrease, more than 50 %, running on simulated biogas, is attributed to chemical limitations; internal biogas reforming can involves several reactions, including the formation of carbon deposits.

On the other hand, in the cases of singe cell running on biogas, algal and landfill biogas, it can be observed a significant worsening of single cell performance running on landfill biogas. The presence of sulfur compounds in the fuel composition of landfill biogas implies a significant decrease in the maximum values of current density and power density, more than 70 % and 80 %, respectively. Based on results from XRD characterisation (data not shown) it can be concluded that it is mainly due to the sulfurization of the anode material, several sulfides (CaS, Cu_2S, CuS, RhS_2) and cerium oxisulfide ($Ce_2O_2S_2$) are formed under working conditions. However, upon removing H_2S from the fuel gas, cell voltage started to recover toward the initial cell voltage and no sulfur compounds were detected in the anode side, indicating that such H_2S poisoning is almost reversible under these operating conditions. It should be noted that the presence of sulfur in the biogas compositions negatively affects to a greater extent the single cell performance, in comparison with pure hydrogen (Fig.2).

A similar study was carried out on single cell using H_2 as fuel, 500 ppm of H_2S were added to fuel composition (Fig. 1 and Fig. 2). In this case, as it was expected, the negative effect on single cell performance of sulfur presence is similar than in biogas and anode sulfurization occurs, the maximum power density was reduced almost 50 % (Table 1).

Impedance spectroscopy measurements were recorded after each IV curve. As seen in Table 1 and Fig. 3, the ohmic resistance (R_Ω) of the single is much lower in hydrogen (0.26 $\Omega \cdot cm^2$) than that running on biogas mixtures (0.46 and 0.70 $\Omega \cdot cm^2$ for algal and landfill biogas, respectively) due to lower pO_2 in the anode.

On the other hand, more significant is the effect of different fuels on the polarization resistances (Rp). In H_2S-containing fuels (500 ppm H_2S-H_2 and -biogas), the polarization resistance highly increases due to anode sulfurization and chemical limitations; in the case of H_2 fuel (Fig. 3a) Rp is duplicated whereas in biogas fuel (landfill biogas vs algal biogas, Fig. 3b) it is increased by a factor of 7. It should be noted, that although single cell performance is limited running on H_2S-containing fuels, it is recovered after running on humidified hydrogen. This fact gives evidence of the reversible sulfur poisoning of the anode catalyst.

Finally, the catalytic activity test of the anode material (Rh/Cu-CeCa) for biogas reforming, using a methane-carbon dioxide mixture (60/40 vol. %) shown a methane conversion of 58 % at 1023 K, the operating temperature of the single cell (Fig. 4a). The exhaust gas was analysed by gas chromatography and it was composed by a mixture of CH_4, CO_2, H_2 and CO (Fig. 4b), being the CO_2 content 10.7 mol. %. When the temperature was increased to 1073 K the selectivity to CO and H_2 was practically 100 % and less than 2 mol. % of CO_2 was detected.

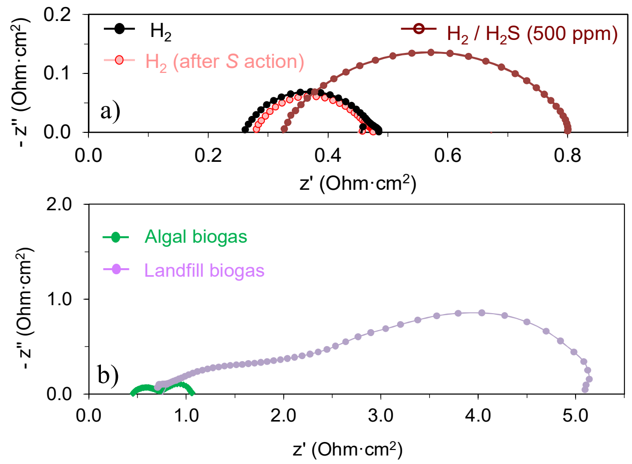

Fig. 3 Impedance spectra for the single cell at 1023 K as a function of fuel composition

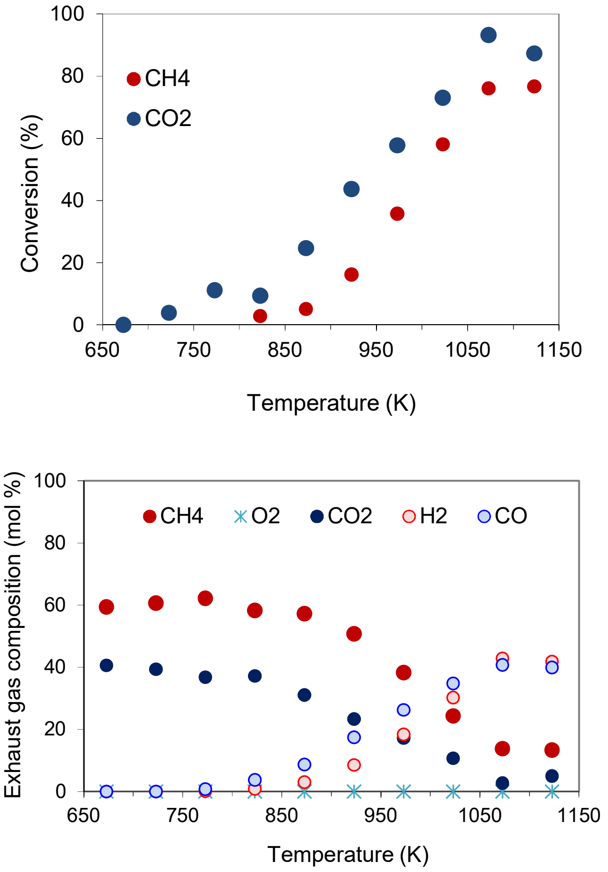

Fig. 4 Biogas reforming on Rh/Cu-CeCa sample: (a) CH_4 and CO_2 conversion; (b) exhaust gas composition as a function of reaction temperature. W/F = 13 g_{cat} h/mol.

IV. Conclusions

The capability of Rh/Cu-CeCa to operate in humidified simulated biogas at relatively low temperature (1023 K) has been demonstrated. The best single cell performance running on simulated biogas was obtained with algal biogas. The maximum power density at 1023 K was 74 mW/cm^2 whereas much lower value (< 80 %) was achieved running on landfill biogas (12 mW/cm^2) due to anode sulfur poisoing.

Although maximum power density of the single cell was lower running on biogas or H_2S-containing fuels comparing with operation using hydrogen, mainly due to the adsorption of sulfur and carbon species, voltage remained stable and cell performance was recovered after exposition to humidified hydrogen.

It has been demonstrated that biogas from anaerobic digestion of algae biomass is a good alternative fuel for SOFCs, based on the absence of poisoning impurities as H_2S. Furthermore, the possibility to capture the CO_2, emitted by the operation of the direct algal biogas SOFC, by biofixation using microalgae opens the opportunities to obtain an effective and non-polluting energy conversion system, in the context of a circular economy.

In the near future, the optimization of a specific treatment of exhaust fuel cell gas running on algal biogas will be studied to capture the CO_2 by microalgae biofixation.

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