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Proton transfer reaction mass spectrometry for the gas cleaning using commercial and waste-derived materials: Focus on the siloxane removal for SOFC applications

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ABSTRACT

The research efforts for SOFC plants fed by biogas moved from the prototypal research to the feasibility of pilot plants up to achieve industrial size plants. Siloxanes among the other trace compounds contained in biogas appear to be the most detrimental for the fuel cell performance. Siloxanes are difficult to be detected and monitored continuously in the gas matrix. A direct injection mass spectrometry technique (PTRMS) was adopted for the monitoring of siloxane removal. Commercial and waste derived sorbent materials are experimentally tested for the removal of siloxanes. Waste derived material was selected to implement the circular recovery purposes. A simple parametric investigation study was developed. It was considered the influence of gas velocity and sulphur compounds, as co-vapors. Physical and chemical characteristics were correlated to the adsorption capacity. Results show three separated groups. Group I shows the best performance in terms of siloxane removal. There is a direct and strong relation between active surface area and microporous volume with the adsorption capacity. This direct correlation is not verified for some elements such as Fe and S, while it is respected for Cu and K. Higher performance are registered for not all the commercial carbons. In fact, the physical structure and impregnating agents are crucial for the siloxane removal.

1. Introduction

Solid Oxide Fuel Cells are the most promising energy generators in terms of high efficiency, low level of noise and pollutants emission into the environment [1]. Nowadays, the research efforts moved from the prototypal research to the feasibility of pilot plants up to achieve industrial size plants. The reduction of the long-term operation and the reliability of these systems are strongly affected by the presence of volatile organic compounds in the fuel feeding mixture. As reported in literature, several VOCs are identified and monitored in biogas, from sulphur species to aromatic, chlorine and siloxane compounds [2–5]. The gas cleaning section is mandatory for the direct coupling of biogas production section to the SOFC energy generator systems [6–12]. The performance of a SOFC system are mainly affected by the presence of sulphur, chlorine and siloxane compounds [13–19]. The tolerable levels for these systems concern the reversibility of the performance when trace compounds are contained in the fuel feeding. It was considered also the contemporary presence of trace compounds, the operating temperature and the fuel feeding conditions. For sulphur compounds this level is around 1 ppm(v), while for chlorine compounds ranges around 20–40 ppm(v) and for the siloxanes around hundreds of ppb(v) [18,20].

Siloxanes, among the other appear to be the most detrimental compounds on SOFC performance. In fact, at SOFC operating conditions the silica formation (SiO_2) on the anode compartment is possible already at ppb(v) level [21]. The formation of hard solid silica is very abrasive to generator engine and clogs the anode pores preventing the flow of fuel to reach the three-phase boundary zone. The main siloxanes detected in biogas from sewage sludges, and also from OFMSW in most cases are the less water soluble cyclic compounds, particularly D4 (octamethylcyclotetrasiloxane) and D5 (decamethylcyclopentasiloxane). Particularly landfill gases contain also trimethylsilanol, which condensates readily to siloxane compounds [22]. The importance of measuring and removing siloxanes has increased with the growth of the biogas-to-energy market. To measure these compounds is complicated and difficult

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Nomenclature

C_{in}	Inlet trace compound concentration (ppm(v))
D4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
DFT	Density functional theory
EDS	Energy dispersive X-ray spectrometry
GHSV	Gas hourly space velocity (h^{-1})
M	Mass of sorbent (g)
MW	Molecular weight of the trace compound removed (g/mol)
NLDFT	Non-local density functional theory
OFMSW	Organic fraction of municipal solid waste
PDMS	Polymeric dimethylsiloxane membrane
PFA	PerFluoroAlkoxy alkane polymers
ppb(v)	Parts per billion by volume
ppm(v)	Parts per million by volume
ppq(v)	Parts per quadrillion by volume
PTR-ToF-MS	Proton transfer reaction time of flight mass spectrometry
Q_{tot}	Total gas flow rate (Nl/h)
SEM	Scanning electron microscopy
SOFC	Solid oxide fuel cell
SSA	Specific surface area (m^2/g)
V_m	Molar volume (22.414 nl/mol)
Vmicro	Microporous volume (cm^3/g)
VOCs	Volatile organic compounds

to realize due to their higher molecular weight and ultra-low concentration detected in biogas. Nowadays, standard methods for analysing siloxanes in the gas matrix are not present. Based on the literature, several different methods are available for analysis [22–25]. PTR-MS is one of the most promising direct injection mass spectrometry technique adopted [26]. This technique is based on an efficient implementation of chemical ionization based on proton transfer from hydronium ions and allows the rapid and on-line monitoring of most volatile compounds. Among the major removal techniques, the adsorption removal covers an important role due to its simplicity and low costs [27,28]. Non-regenerative adsorption on fixed beds of activated carbon is the most common solution for industrial plants. Generally, the most common configuration is referred to as lead and lag arrangement. When the first bed experience breakthrough it is replaced by a fresh adsorber, the sequence is reversed, i.e., the former second adsorber becomes the first adsorber. The most common sorbent material for the gas cleaning is activated carbon, as reported in literature [6,7,29,30]. The circular way of thinking applied to wastes from energy plants could be an interesting way for the material recovery. In this study a waste-derived material from a pyrolysis plant was adopted as sorbent material for the gas cleaning for SOFC feeding requirements. This paper also focuses on the proton transfer reaction mass spectrometry detection technique for the siloxanes removal adopting commercial and waste derived sorbent materials. The removal performance of single siloxane and contemporary presence with sulphur compounds were also reported.

2. Experimental methods

2.1. Anaerobic digestion pilot plant

The biogas production was achieved using as a substrate the organic fraction of municipal solid waste. These wastes are collected from the local municipality and treated in a pilot plant. The dry anaerobic digestion pilot plant is located at Foundation Edmund Mach – S. Michele a/A, Italy (TN). The first process applied to biogas is the removal of undesired components, such as stones, papers, plastics and glasses. The working volume of the digester is 16 m^3 with frontal load. The rectangular reinforced concrete module is loaded frontally and the sealing is ensured by resins. Chipped wood was mixed with OFMSW before the digester loading. The suitable porosity was achieved at a volume ratio from 0.62 to 0.72. To rapidly start the methanogenic process the biomass was subjected to a four day pre-oxidation process. In such manner the initial lag phase was reduced with the CO_2 production. After the aerobic phase, the digester was sealed for the aerobic to anaerobic transition. The biomass temperature was thermostatically controlled by fixed floor and wall coils and by leachate sprinkling. In approximately 30 days the anaerobic digestion was accomplished. To use the biomass as fertilizer, the exploited biomass was subjected to a further aerobic composting treatment for 22 days. The composition and physico-chemical characteristics of the OFMSW batch adopted are reported in Table 1.

2.2. Description of the experimental setup

Fig. 1 shows the test rig. Mass flow controllers (MKS instruments Inc., USA) are adopted with an exploitable range from 100 to 200 sccm. The simulated biogas mixture with pollutants is regulated with two electronic mass flow controllers to feed carbon cartridges, whereas the remaining one is used for measuring a blank condition. This blank condition represents the biogas mixture with pollutants that need to be removed from the filter. A double line for the gas cleaning is implemented to reduce the experimental testing time. Three other mass flow controllers are adopted for the second part of the experiment: the co-vapors removal influence on D4 removal using sulphur compounds. Sulphur compounds are the most common pollutants contained in the biogas and, with siloxanes the most detrimental compounds for SOFC applications. Single filter bed configuration is tested using different commercial and waste derived sorbents.

According to the scheme reported in Fig. 1 were adopted PFA tubes (1/4 in. diameter, length ~3 m) and fittings (Swagelok Ltd., USA). Carbon cartridges were made with teflon tubes (4 cm length and 6 mm diameter), and the mass loaded in the middle of the car-

Table 1
Physicochemical characteristics and composition of the OFMSW batch.

	Volume (m^3)	Mass (t)	Water content (%)	Volatile Solids (%)	pH in	pH out
Digestate from previous batch	7.23 [±0.22]	6.86 [±0.47]	61.5 [±0.9]	55.8 [±3.1]	8.5 [±0.2]	
OFMSW + Wood	9.2 [±0.38]	5.3 [±0.46]	59.1 [±0.76]	82 [±3.2]	5.7 [±0.2]	
Final mix	14.95 [±0.38]	11.80 [±0.44]	58.5 [±1.05]	56.7 [±3.0]	7.9 [±0.2]	8.3 [±0.2]

Where:
- pH in: pH at the anaerobic digestion starting.
- pH out: value of pH at end of anaerobic digestion process.
- Final mix: total matter loaded into the digester.
- the standard deviation of measurements are indicated in square brackets.