



Proton transfer reaction-mass spectrometry as a rapid inline tool for filter efficiency of activated charcoal in support of the development of Solid Oxide Fuel Cells fueled with biogas

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ABSTRACT

Efficient power technologies such as high temperature fuel cells demand ultra-low concentrations of contaminants in the fuel feed e.g. <1 ppm(v), imposing stringent requirements on fuel clean-up technology. Proton transfer reaction-mass spectrometry (PTR-MS), being fast and suitable to measure ultra-low concentrations can be an optimal tool for the characterization of clean-up methods. It is exploited here for the simultaneous measurement of breakthrough curves of biogas filters loaded with a mix of compounds that simulate biogas pollutants. The sorbent materials are able to efficiently remove propanethiol and butanethiol and to a lesser degree methanethiol and hydrogen sulfide. Carbon disulfide and dimethylsulfide were the compounds that elute from the filters. These results support the development of set-ups for the cleaning of real biogas from the Organic Fraction of Municipal Solid Waste (OFMSW) and its use for Solid Oxide Fuel Cell (SOFC) feeding.

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1. Introduction

Fuel cells are a very interesting technology due to the efficient energy generation through electrochemical fuel conversion instead of fuel combustion [1]. Solid Oxide Fuel Cells (SOFCs) are the most promising fuel cell technology [2,3]. One of the main advantages of SOFCs is their remarkable fuel flexibility [4]. In fact, both, hydrocarbons (e.g., CH₄ [5,6]) and carbon monoxide, or even H₂/CO₂ [7] could be eligible fuels for the energy production from SOFCs. Biogas is one possible fuel for SOFCs [3,8,9], for a review see [10]. Biogas is produced from organic matter digestion with methane and carbon dioxide as principal gas mixture elements. Next to these main biogas constituents, a wide and variable range of trace compounds are contained in biogas [11]. However, SOFCs are sensitive in their performance to certain fuel impurities, mostly to sulfur compounds that may decrease cell efficiency and degrade the fuel cell [3]. Sulfur poisoning and carbon deposition phenomena [12] are two of the main problems that have to be addressed for a number of fuel types for SOFC systems.

Particular interest for SOFCs technology arises for H₂S and sulfur compounds in general, chlorine, siloxanes [13] and higher hydrocarbons [3]. At the typical SOFC operating temperature (600–1200 °C) sulfur compounds are thermodynamically converted to H₂S [14]. H₂S acts as a poisoning compound interacting with the nickel containing anode. The mechanisms observed are reversible [15] and irreversible [16]. Low H₂S concentrations of around 1–5 ppm(v) and below [17] act reversibly, probably by adsorbing to the surface and by blocking the active sites [17]. However, several mechanisms [3,18,19] have been proposed, also in relation to operating conditions [17]. Bao et al. [17] studied the effects of the concentration of H₂S on a Ni-YSZ anode, and they concluded that 1 ppm(v) could be the tolerable limit of H₂S for SOFCs. At such low concentration levels, sulfur molecules are adsorbed reversibly on nickel dispersed grains, thus reducing the three-phase boundary and, consequently, cell performance [3]. In principle, there are two possible approaches to solve the H₂S problem. The first one concerns the material side, namely the development of sulfur tolerant materials, while the second one involves biogas clean up. This work focuses on the latter strategy: VOSC removal from biogas using activated carbons as filters.

There is a general interest in measuring VOSCs in biogas [10]; on the one hand for monitoring and optimizing biogas production and quality

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Nomenclature

CIMS	chemical ionization mass spectrometry
c_{in}	inlet concentration
c_{out}	outlet concentration
cps	counts per second
ΔG	Gibbs free energy
k	overall adsorption rate coefficient (min^{-1})
M	weight of the carbon (g)
MFC	mass flow controller
OFMSW	Organic Fraction of Municipal Solid Waste
ppb(v)	parts per billion (volume)
ppm(v)	parts per million (volume)
ppm(w)	parts per million (weight)
ppq(v)	parts per quadrillion (volume)
ppt(v)	parts per trillion (volume)
PTR-MS	proton transfer reaction-mass spectrometry
Q	volumetric flow rate (scm)
ρ_b	bulk density of the carbon bed (g/cm^3)
scm	standard cubic centimeter per minute (mass flow units)
SOFC	Solid Oxide Fuel Cell
t_b	breakthrough time (min)
ToF	time-of-flight (analyzer type of mass spectrometers)
VOCs	volatile organic compounds
VOSCs	volatile organic sulfur compounds
W_e	static adsorption capacity (g/g)

control and on the other hand for measuring the effects of biogas components on SOFC.

Proton transfer reaction-mass spectrometry (PTR-MS) is an analytical mass spectrometry technique [20–23]. PTR-MS is a high sensitivity mass analytical instrument deploying a proton transfer reaction (chemical ionization with H_3O^+ ions). It is a direct injection instrument with a high time resolution (split seconds) which allows for inline and real-time detection of many VOCs without sample preparation [20–23], even down to particularly low concentrations (ppt(v) range) [24,25]. In addition, PTR-MS has already been used successfully in some filter studies [26–33]. The PTR-MS is used in this work to detect compounds contained in the gas matrix.

In previous work we measured sulfur compounds with PTR-MS, e.g. it was applied to the practical measurements of sulfides and sulfur compounds [24], and including fragmentation pattern determination [34]. Recently, the usefulness of PTR-MS was demonstrated for measurements of biogas produced from an anaerobic digestion of Organic Fraction of Municipal Solid Waste (OFMSW) [11]. The main VOSC compounds identified in biogas using a PTR-ToF-MS were hydrogen sulfide, methanethiol, dimethylsulfide and propanethiol. Due to their high

Table 2

VOCs and their concentrations as contained in the cylinder, MW (MH^+) molecular weight of the protonated parent mass as detected with PTR-MS.

Compound in N_2	Chemical formula	ppm(v)	MW (MH^+ – g/mol)
Butanethiol	$\text{C}_4\text{H}_9\text{SH}$	5.98	91.0582
Propanethiol	$\text{C}_3\text{H}_7\text{SH}$	6.01	77.0425
Carbon disulfide	CS_2	5.98	76.9520
Dimethylsulfide	CH_3SCH_3	5.84	63.0269
Methanethiol	CH_3SH	4.75	49.0112
Hydrogen sulfide	H_2S	5.51	34.9956

concentrations, a gas cleaning section must be provided before feeding the biogas to a SOFC stack.

Typically, filter efficiency tests are performed with a single compound only, in order to keep the results simple and also to avoid covapor effects such as rollover, which is a change in the kinetic behavior of the primary compound of interest. In this work, we explicitly account for a mix of sulfur compounds (pollutants).

Summing up, in this study the PTR-MS instrument was exploited to the simultaneous inline measurement of filters during gas clean-up and the VOSCs adsorption efficiency is investigated. We focus on the removal performance of sulfur compounds from the biogas stream to feed a SOFC system. Previously, we investigated the effect of covapors on the filters removal performance [35]. Our main goal is to investigate the adsorption performance of different commercial activated carbons in order to provide the best choice for real-world cleaning of biogas for SOFCs. Our results allow the optimum design of a biogas cleaning section to feed SOFC stack systems. Moreover, we aim at further exploiting PTR-MS as a fast and inline, multi-sensor and multi-test kinetic measurement tool for filters and VOSCs.

2. Material and methods

2.1. Materials

The experimental set-up for determining the removal capacity for VOCs typically present in biogas, comprises two commercial activated carbons, Sulfatrap R8 (TDA Research Inc., USA) and Norit RGM3 (Norit, USA). In Table 1 the principal properties of the activated carbon filters are reported. The two carbon samples are ground in order to reach a grain dimension of around 0.5–1 mm.

The relative humidity of the carbon filter samples was 19.5%, and humidity was set constant for all experiments. This allows to avoid additional calibration measurements which else would be necessary [11,36]. The biogas pollutant mix was obtained as a ready mix in a gas cylinder (named B1) from Rivoira spa, (Italy). See Table 2 for the compound concentrations. Dilutions of the gas cylinder mix were performed with pure N_2 .

Table 1

Activated carbon filter properties as given by the manufacturer for R8 and RGM3.

Sulfatrap R8				
Component	CAS #	Weight (%)	Surface area (m^2/g)	Differential pore volume (cm^3/g)
Carbon	7440-44-0	<85%	455	0.22
Copper (I) oxide	1317-39-1	<10%		
Copper (II) oxide	1317-38-0	<10%		
Iron (III) oxide	1309-37-1	<10%		
Norit RGM3				
Component	CAS #	Weight (%)	Surface area (m^2/g)	Differential pore volume (cm^3/g)
Carbon	7440-44-0	>90%	978	0.3
Copper salts (II)	1317-38-0	<8%		
Chromium salts (VI)	7740-47-3	<4%		

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