



Influence of co-vapors on biogas filtration for fuel cells monitored with PTR-MS (Proton Transfer Reaction-Mass Spectrometry)



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ABSTRACT

Solid Oxide Fuel Cells (SOFCs) fed by biogenic fuels are a key renewable energy technology. Fuel contaminants, and sulfur compounds in particular, can strongly decrease SOFC performance. For this reason, their accurate, high sensitivity, and rapid monitoring and the development of successful removal strategies are major challenges in SOFC research.

In this work the removal efficiency of commercial activated carbon filters for biogas filtering upstream of an SOFC was investigated using a Proton Transfer Reaction-Mass Spectrometry instrument (PTR-MS). In particular, we tested sulfur compounds by focusing on the effect of co-vapor adsorption (aromatic, carbonyl and chloro-compounds which are biogas pollutants) on filter performance. The results demonstrate the applicability of PTR-MS for investigating covapor effects which are of practical relevance for SOFC development.

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1. Introduction

Greenhouse gas (GHG) emission to the atmosphere is recognized as a huge environmental problem affecting a wide range of fields ranging from the agricultural to the industrial sectors [1]. Possible solutions are the reduction of fossil fuel usage through substitution with renewable energy sources and the development of advanced technologies that allow for an efficient and cleaner exploitation of fuels. The European climate and energy change protocol EU 20–20–20 focuses on reducing the energy demand from fossil fuels and on increasing the exploitation of alternative resources [1–3], such as biogas [4]. The generation and commercial exploitation of biogas is still under development, and several approaches exist [2,5]. One of them is biogas production from

the Organic Fraction of Municipal Solid Waste (OFMSW) in a dry anaerobic digester and its use in fuel cells [6]. Fuel cells directly transform fuel into electrical energy by electro-chemical reactions and thus avoid the energy loss related to heat generation. Amongst fuel cells, Solid Oxide Fuel Cells (SOFCs) achieve the highest electrical conversion efficiencies [5]. Extensive research has been performed on fuel cells [7], and some real world applications exist but they are too expensive to become a widespread commodity. We investigate usage of biogas combined with the efficient exploitation of fuel with SOFCs [8–10]. One of the challenges is that SOFCs have a low tolerability for contaminant Volatile Organic Compounds (VOCs): cell voltage decrease, cell power drop and fuel cell degradation are the main consequences of fuel impurities for the anode compartment [11] as well as carbon deposition phenomena [12,13]. The problem of VOC tolerability is addressed by making fuel cells more tolerant against VOCs [14,15], or by reducing the amount of VOCs in the fuels [16–18]. The most relevant volatile contaminants are sulfur [6], aromatic [19] and carbonyl [20] chloro-compounds [6,13,20,21] and siloxanes, the latter two groups are derived from the starting biomass loaded into the digester [6]. Hence, it is necessary to implement a cleaning section which effectively removes the VOCs from the biogas in order to fuel SOFCs. However, studies on the effective removal of all VOCs in order to produce highly pure, fuel cell-grade biogas are rare, as the main focus is on H₂S or sulfur compound removal only [22,23]. Typically the effect

Abbreviations: DMS, dimethylsulfide; *E/N*, ratio of the electric field to the number density; GHG, Greenhouse gas; GHSV, Gas Hourly Space Velocity; i-PM, isopropyl mercaptan; μ -CHP, micro Cogeneration Heat and Power plants; *m/z*, mass to charge ratio; OFMSW, Organic Fraction of Municipal Solid Waste; PDMS, polymeric dimethylsiloxane membrane; ppbv, parts-per-billion volume; ppmv, parts-per-million volume; ppqv, parts-per-quadrillion volume; pptv, parts-per-trillion volume; sccm, standard cubic centimeters; SOFCs, Solid Oxide Fuel Cells; Td, Townsend (1 Td = 10⁻¹⁷ Vcm²); ToF, Time of Flight (mass analyzer type); VOCs, Volatile Organic Compounds.

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that different VOCs have on each other's removal rate is overlooked. Part of the problem is related to the detection of VOCs, as a fast method with low limit of detection has to be used. Hence, here we focus on the co-vapor effects, as this allows selecting cleanup strategies optimized for biogas.

1.1. Fuel processing: gas cleaning unit

VOCs removal by activated carbon adsorption represents a valid and economic option [24]. The main properties of activated carbon filters for the effective removal of VOCs are the pore volume ($0.3\text{--}0.6\text{ ml g}^{-1}$) [25] and their distribution [26], the large surface area ($900\text{--}1500\text{ m}^2\text{g}^{-1}$) [27] and the impregnation with metal particles due to their redox properties [27]. Physisorption and chemisorption are the two underlying physical phenomena by which determine adsorption. The first one deploys weak Van der Waals forces whereas the second one involves the stronger covalent and ionic bonds. Van der Waals forces require polar or polarizable compounds. Typically, compounds with no dipole moment are attracted to non-polar molecules, as is the case for carbon particles and e.g. nitrogen. Vice versa compounds with higher dipole moment ($>0\text{ D}$), see Table 1, are attracted to polar molecules, such as metal ions and sulfur, aromatic and carbonyl compounds [25,28]. Typical metals adopted are iron, copper, silver and chromium.

Hence we select activated carbon filters as purification method and compare the performance of different filters in VOC removal, which use different metals for activation.

1.2. Effect of co-vapors on filter performance

Of particular interest in this study is the effect of co-vapors on the removal efficiency of sulfur compounds and VOCs. Literature on active carbons generally concerns the removal of halogens, sulfur and siloxane from gas [29]. Only few studies focus on the competitive adsorption of organic compounds on carbon beds and Hernandez et al. [23] studied the natural gas desulfurization process with different activated carbons, deploying commercial (RGM3 from Norit) and synthesized (from Ni/SiO₂-Al₂O₃) activated carbons. They reported breakthrough time results using a gas chromatograph instrument. Hernandez et al. [22,23] related co-adsorption results for several compounds contained in natural gas, such as dimethylsulfide (DMS), carbon disulfide, methyl mercaptan, ethyl mercaptan, isopropyl mercaptan (i-PM) and tetrahydrothiophene (THT). They observed that the outlet sulfur concentration was dictated by adsorption of alkyl-substituted dibenzothiophene compounds, which showed lower breakthrough times. Hence, the effect of multi components (co-vapors) with different organic compound concentrations on the removal efficiency of filters needs a detailed study due to the stringent requirements for SOFCs.

1.3. VOC detection method

As already mentioned, part of the problem of monitoring VOCs is that a time-resolved method with a low limit of detection is required

for investigating co-vapor effects. We choose the technique of Proton Transfer Reaction-Mass Spectrometry (PTR-MS). Gas chromatography is not suited for real time monitoring, because it necessitates sample preparation and requires longer analysis time, even if it is preferable for compound identification [30]. For instance, in a literature study [23], instead of a continuous trend only one data point after 2.3 h of test was exhibited. Besides this problem, the separation column used didn't allow for a clear distinction between compounds such as DMS and i-PM due to overlapping signals. On the other hand, PTR-MS equipped with a Time of Flight detector allows for online monitoring and for the distinction between DMS and i-PM. In our previous work [31], a PTR-ToF-MS was already used to characterize two different commercial activated carbons for their removal efficiency of sulfur compounds only. Therein we displayed a real time trend and we measured the breakthrough times in a single and double filter bed configuration in order to identify the best solution for sulfur removal. The aim of the present study is to investigate the competitive adsorption of sulfur, aromatic, chloro- and carbonyl compounds, on line and in real time, with different filter configurations and with various GHSV values for two commercial activated carbons in view of SOFC related applications.

2. Materials and methods

Herein we describe the materials used, the experimental setup, a description of the system used for detecting VOCs (the PTR-MS), and the mathematical method used for obtaining quantitatively comparable results.

2.1. Materials

The experimental set-up for the removal capacity of several VOCs contained in biogas comprises two different commercial activated carbons, Sulfatrap R8 (TDA Research Inc., USA) and Norit RGM3 (Norit, USA). Only activated carbon samples were selected which are commercially available, and they had to be capable of removing in particular sulfur compounds. In Table 2 the principal properties of the activated carbon filters are given. Note that for our tests the two carbon samples were ground in order to reach a grain dimension of about 0.5–1 mm. For the purpose of comparable measurement results, humidity conditions and starting VOC concentrations were kept constant. This allows us to avoid additional calibration measurements that would otherwise be necessary, due to the influence of water on absolute VOC quantification [6,32]. The relative humidity of the carbon filter samples was 19.5% taking temperature and pressure conditions into account. The biogas pollutants are simulated by using two prepared gas cylinders mixtures, (Rivoira S.p.A., Italy). The biogas pollutants were obtained as a ready mix in a gas cylinder (named B1) for sulfur compounds, and in a second gas cylinder (named B2), for aromatic, chlorinated and carbonyl compounds (Rivoira S.p.A, Italy), see Table 3 for the compound

Table 1
Dipole moments for different compounds of interest.

Compound	Dipole moment (Debye)	Reference
Hydrogen sulfide	0.95	[28]
Methanethiol	1.52	[28]
Dimethylsulfide	1.58	[28]
Propanethiol	1.55	[21]
Butanethiol	1.54	[21]
Chloroethane	6.7	[28]
2-Butanone	2.76	[28]
Toluene	1.3	[28]
Styrene	0.3	[28]

Table 2
Characterization of the activated carbon filters R8 and RGM3.

Component	CAS #	Weight (%)	Surface area (m ² /g)	Differential pore volume (cm ³ /g)
<i>Sulfatrap R8</i>				
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%		
<i>Norit RGM3</i>				
Carbon	7440-44-0	>90%	978	0.3
Cu salts (II)	1317-38-0	<8%		
Cr salts (VI)	7740-47-3	<4%		

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