



Research article

Dimethyl sulfide adsorption from natural gas for solid oxide fuel cell applications

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ABSTRACT

The use of solid oxide fuel cell (SOFC) systems in micro-CHP applications is of great interest because of high efficiency, low emissions and absence of noise. However, SOFCs are sensitive to degradation caused by organic sulfur compounds present in natural gas or added as odorants. Among them, dimethyl sulfide (DMS) is one of the sulfur species most resistant to purification treatments and, relative to DMS removal, a lack in literature is highlighted for the investigated application.

Regarding adsorption technology, the present work deals with an organic sensitivity performance analysis of different commercial sorbents. Virgin and impregnated activated carbons and a natural zeolite were tested, varying gas hourly space velocity, reactor geometry and filter assembly. Because of differences in activity towards DMS exhibited by the investigated materials, to exploit their selectivity, also layered sorbents were realized and tested. Starting from resulting data, for the yearly operation of 1 kW_{el} SOFC-based micro-CHP system, an optimization of filter assembly (also considering multi-layered configurations) and operative conditions was performed, leading to a strong reduction in filter volume (up to five times) and cost (more than three times), with overall pressure drops compatible with pipeline gas distribution pressure.

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1. Introduction

Micro-combined heat and power systems using solid oxide fuel cells represent a very attractive opportunity for small scale heat and power production in terms of fuel saving and lower carbon emissions, because of high efficiency and low environmental impact. Natural gas (NG) is an important potential feedstock for the production of hydrogen for SOFC-based CHP systems; moreover NG is a widely applied fuel for final user application, due to its well-developed infrastructure and relatively abundant supply.

In all pipeline gases sulfur compounds are added intentionally as odorants for leak detection and may be composed of thiophenes, mercaptans, sulfides or disulfides, which are highly reactive sulfur-containing species, well known for their disagreeable odors. Before odorant addition, NG contains also other sulfur species naturally present in the mixture, such as hydrogen sulfide (H₂S) and dimethyl sulfide (DMS). The first one is completely removed through absorption using basic solutions (principally MEA and DEA) during the treatments operated immediately after the extraction to prevent pipelines corrosion,

worsen by the high pressure (70 bar) of NG main distribution network. On the contrary, DMS, that is one of the most resistant sulfur species, can be able to move, almost unaltered, from the extraction point to the final user, with concentrations in the order of several ppmv [1]. Moreover, in many countries (not in Italy), DMS is also used as natural gas odorant, mainly in blends with TBM [2].

Sulfur compounds strongly poison reformer and fuel cell catalysts. Within the SOFC, all sulfur compounds are converted into nickel sulfides, which are chemisorbed on nickel catalysts, covering active sites on electrodes surface [3,4]. In some cases, the presence of sulfur compounds causes immediate performance deterioration; more often, a long-term performance degradation occurs, over a long exposition period, due to a continuous deposition on the anode catalyst surface [5]. Therefore, to prevent detrimental effects on SOFC catalysts, sulfur concentration has to be reduced to 1 ppmv [6] or lower [7,8].

In literature, different clean-up technologies are used to remove both inorganic and organic sulfur compounds, but not all can reach the ultra-low sulfur levels required for fuel cell systems [9] or can be selective for the elimination of targeted sulfur species, as the DMS here investigated [10]. Moreover, many desulfurization techniques need complex integration into the plant and therefore they are not suitable for micro-CHP applications [1]. In this case, in fact, the desired requirements for a filtering solution are: high efficiency, reliability, system simplicity, low costs and easy maintenance [8]. Chemical

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Nomenclature

$A_{B.E.T.}$	B.E.T. specific surface area
AC	activated carbon
C_{ads}	adsorption capacity
CHP	combined heat and power
C_{in}	inlet concentration
C_{out}	outlet concentration
DEA	diethanolamine
DMS	dimethyl sulfide
EM	ethyl mercaptan
GHSV	gas hourly space velocity
HDS	hydrodesulphurization
ID	reactor inner diameter
LHV	lower heating value
MEA	monoethanolamine
MM	methyl mercaptan
NG	natural gas
SCO	selective catalytic oxidation
SOFC	solid oxide fuel cell
STP	standard temperature and pressure
TBM	tert-butyl mercaptan
t_{br}	breakthrough time
THT	tetrahydrothiophene
V_{μ}	micropore volume

scrubbers present drawbacks related to outlet sulfur concentration higher than fuel cell tolerance limits and system complexity [11,12]. Biological systems have many disadvantages, because they require a continuous control of the bacteria growth, an accurate conservation of pH values and moisture content [13,14]. Also membrane technologies present the difficulty to obtain high removal capacities in a single treatment cycle and they often have to be coupled with other desulfurization methods [15].

Among the dry processes, hydrodesulphurization (HDS) requires hydrogen supply at high temperature and pressure; moreover, system operation is complex and not suitable to be implemented in small scale applications [16]. Also selective catalytic oxidation (SCO) needs high temperature to perform sulfur compounds oxidation [10].

On the contrary, adsorption technology on porous materials can be performed using simple systems also operating at room conditions [1, 8]. Moreover, it can guarantee sub-ppm level of outlet sulfur concentration, with 100% efficiency [11], representing an attractive option for desulfurization finalized to micro-CHP fuel cell applications.

Commercial sorbents, like activated carbons (ACs), zeolites, sepiolite or metal oxides have been extensively used for sulfur compounds adsorption [17–21]. Moreover, the influence of pore size distribution, typology of raw materials, particles size and surface modification on filter efficiency and selectivity has been investigated [7,10,22–25,29–32]. Regarding DMS uptake, specifically for natural gas purification, only some studies have been done [10,33–35], evidencing the difficulty in DMS removal [36] and the need of more experimentation in this direction.

Sorbent removal capability strongly depends on many parameters related to the operative conditions of the system [26,27], such as gas hourly space velocity, filter geometry and filter assembly, which have to be optimized in order to obtain a compact filter with high removal activity. Furthermore, sorbents display differences in adsorptive capacity towards single sulfur compounds simultaneously present in a gas mixture and therefore a composite sorbent could be optimized for this purpose [11,28].

A systematic and complete analysis of the effects of the cited functional parameters has not been performed yet. It is instead of fundamental importance for the evaluation of filter overall performance, needed for the design and optimization of the clean-up section. In this

context and in order to fill the literature gap, a sensitivity analysis on the considered functional parameters was provided. All adsorption tests, aiming to DMS removal, were carried out in a fixed bed flow reactor, suitably designed and realized for the scopes of this work. For the experimentation, three sorbent materials with different characteristics were used, in particular a non-impregnated activated carbon, an impregnated AC and a natural zeolite. All investigated materials were characterized before and after the sorption tests using nitrogen adsorption-desorption measurements (B.E.T. method), to highlight changes in specific surface area and micropore volume correlated with the outcomes of the adsorption tests.

DMS removal experiments were realized using a pipeline natural gas mixture collected before the odorization point, to evaluate the effect on adsorption capacity of sorbent typology, gas hourly space velocity, geometric reactor properties (in terms of filter height/diameter ratio) and filter assembly (using a mesh or layers of rock wool). Complementary runs were performed on the same materials using H₂S in concentration equivalent to the average amount of odorants present in natural gas pipelines, in order to have information about sorbents selectivity. Furthermore, a layered filter solution was investigated, on the basis of sulfur removal capability of single materials.

Basing on all the experimental resulting data, the optimized filter assembly was determined, aiming to material requirement minimization and pressure drop limitation compatibly to the final user (e.g. domestic) grid, characterized by only several mbar of pressure. As discussed in Section 3.2.2, for the yearly operation of 1 kW_{el} SOFC stack, a diminution in cartridge volume up to five times, with significant decrease in related material cost and reduced pressure drop, was obtained for the optimized filter.

2. Experimental

2.1. Sorbent selection and surface characterization

Three commercial sorbents were selected, in particular two steam activated carbons supplied by Norit (AC RB1 and AC RGM1) and a natural zeolite supplied by ATZ (Apostolico & Tanagro Zeoliti).

Norit RB1 is a non-impregnated steam activated carbon, with a particle diameter of 1 mm, characterized by high adsorption capacity and removal efficiency for contaminants present in gas flows at moderate concentrations.

Norit RGM1 is a steam activated carbon impregnated with Cu (II) and Cr (IV) salts, with a particle diameter of 1 mm, targeted for the removal of low concentrations of sulfur compounds especially from dry gases.

Zeolite ATZ is a natural zeolite, mainly composed of cabasite and phillipsite, with a particle size in the range of 0.2–1.5 mm, commonly used as adsorbent material for gas purification.

Table 1

Main characteristics of selected materials used for adsorption tests.

Adsorbent	Particles shape	Particles size (mm)	Bulk density (kg/m ³)
AC RB1	Pellets	1.0	480
AC RGM1	Pellets	1.0	485
Zeolite ATZ	Granular	0.2–1.5	875

Table 2

B.E.T. surface area ($A_{B.E.T.}$) and micropore volume (V_{μ}) of the selected adsorbent materials.

Sample	$A_{B.E.T.}$ (m ² /g)	V_{μ} (cm ³ /g)
AC RGM1	1599	0.66
AC RB1	1101	0.44
Zeolite ATZ	111	0.04

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