Degradation mechanisms and advanced characterization and testing (II)

Impact of fuel contaminants on SOFC degradation

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The real-life operation of solid oxide fuel cell (SOFC) systems has to deal with fuel contaminants that might reduce even significantly the lifetime of stack (and also balance of plant) depending on the type and amount of contaminant present.

From a cell-perspective, studying the impact of contaminants on performance and materials allow to understand the interactions occurring with the cell and to identify the current weak points of the technology that can be overcome by improving cell materials and operative configurations. From a system-perspective, detecting and correlating observed stack performance degradation with fuel contamination is fundamental to implement correctional procedures (e.g., change of clean-up vessels catalysts) and/or trigger alarms to prevent a further contamination of the fuel cell.

In the past years, the STEPS group of Politecnico di Torino built up a wide expertise in the study of SOFC degradation induced by contaminants, from system and stack level to cell level. Studies based on experiments with several fuel contaminants allowed to develop empirical degradation models that are able to quantitatively predict the range of degradation rate resulting from known amounts of contaminants in the fuel stream \cite{Lanzini_2017}. A variety of contaminants are related to the use of practical fuels alternative to natural gas and hydrogen. In particular, the studies focused on those typical of biogas applications (H\textsubscript{2}S, HCl, tars, siloxanes). Among them, H\textsubscript{2}S and siloxanes are the most abundant contaminants for sewage biogas.

In this presentation, we reviewed the main degradation mechanisms related to the above-mentioned contaminants and their interaction with SOFCs, providing a quantification of degradation and/or deactivation for each single contaminant on the basis of experiments. Except for HCl, the impact of the contaminant on the SOFC performance was always considerable. Therefore, a deep clean-up of the incoming raw gas feed must be carried out. The design of a contaminant removal system for sewage biogas with two series connected adsorption beds for the removal of H\textsubscript{2}S and siloxane has been also presented. The considered sorbent materials were activated carbons. The presentation finally showed the quite high penalty related to gas cleaning in terms of the overall plant profitability, with an estimated operating cost of the clean-up unit of around 1-2 $\text{cent kWh}^{-1}$ against the values $<0.5$ $\text{cent kWh}^{-1}$ indicated in the long term to make integrated biogas SOFC systems highly competitive \cite{Argonne_2014}.

Acknowledgements
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References
\cite{Argonne_2014} Argonne National Laboratory, "Gas Clean-Up for Fuel Cell Application Workshop," 2014, pp. 1–32.

Degradation Mechanisms in Solid Oxide Cells and Systems Workshop Proceedings
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Energy Department (DENERG) – Politecnico di Torino

Synergies of Thermo-chemical and Electro-chemical Power Systems
- STEPS -
Outline

- Alternative fuels for SOFC systems: contaminants issues
- Main biogas contaminants and degradation mechanisms
- Measuring the degradation: extrapolation from experiments
- DEMOSOFC: design of contaminants removal system
Alternative fuels for SOFCs: issues

Alternative fuels: fuels different from grid NG (biogas, syngas, bio-syngas)

- Fluctuation of fuel supply, daily and seasonally (e.g., biogas)
- Contaminants (sulfur, siloxanes, chlorine, aromatics, also odorants for grid NG, etc.)

GAS STORAGE & PLANT MANAGEMENT

Discontinuous operation, low SOFC capacity factor

main issues

Reduction of SOFC (and system components, e.g. fuel reformer) performance and lifetime

GAS CLEANING
Dealing with contaminants

Solving contaminants issues

Ideal solution

Complete cleaning of feed gas

PROS
Better plant performance and longer lifetime

CONS
Higher investment and operation costs

Realistic solution

Removal of most harmful contaminants from feed gas

Economic trade-off between performance & lifetime (i.e., plant profit) and cleaning costs
Dealing with contaminants

**Study of contaminants impact** on SOFC performance and degradation is needed to identify the most harmful substances and their tolerable limits.

**Most common contaminants** of alternative SOFC fuels

<table>
<thead>
<tr>
<th>Sulfur (H₂S)</th>
<th>Chlorine (HCl)</th>
<th>Siloxanes (D₄, D₅)</th>
<th>Tars (benzene, toluene, naphthalene)</th>
<th>NG odorants (TBM - (CH₃)₃CSH, THT - (CH₂)₄S)</th>
</tr>
</thead>
</table>

Contaminants **type** and **concentration** depend on the specific application.
Example: biogas from WWTP

PoliTo is the coordinator of SOFCOM and DEMOSOF projects, aimed at demonstrating the technical and economic feasibility of operating a SOFC (2 kW – 174 kW) running on anaerobic digestion (AD) biogas from waste water treatment plants (SMAT).

In both projects, the contaminants characterization of the biogas from the specific WWTP is the first step for the selection of proper removal systems and its sizing.
Contaminant in biogas from WWTP Castiglione

<table>
<thead>
<tr>
<th>Type</th>
<th>Sulfur</th>
<th>Chlorine</th>
<th>Siloxanes</th>
<th>Tars</th>
</tr>
</thead>
<tbody>
<tr>
<td>Range in biogas (ppm_v)</td>
<td>50-100</td>
<td>~1</td>
<td>~1 (max. 1.14)</td>
<td>low</td>
</tr>
</tbody>
</table>
Example: biogas from WWTP

DEMOSOFC project – WWTP in Collegno

Contaminants in biogas from WWTP Collegno

- H2S
- Silicon

Degradation Mechanisms in Solid Oxide Cells and Systems – Barcelona, February 17th 2017
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Degradation mechanism: in Ni-anode SOFCs, adsorption (chemisorption) of S on Ni surface (fast mechanism) takes place until the equilibrium coverage of Ni is reached; anode micro-structural modifications are reported on the long term.

Chemisorption:

\[
H_2S(g) \leftrightarrow HS_{(ads)} + H_{(g/ads)} \leftrightarrow S_{(ads)} + H_2(g/ads)
\]

SOFC degradation by sulfur (H\(_2\)S)

**Degradation effects:** short-term and long-term effects.

**Short-term degradation**
Fast coverage of Ni surface due to S adsorption. The entire available Ni surface is affected by sulfur contamination, including TPB.

**Long-term degradation**
Micro-structural changes (Ni particle coarsening or nickel migration) for long-term exposure at high overpotential. Increased porosity and lack of percolating Ni at the anode/electrolyte interface.

SOFC degradation by sulfur (H₂S)

Impact on SOFC performance: fast deactivation, followed by a quasi-stable cell voltage profile. Fast voltage drop due to Ni surface coverage until equilibrium reached, the performance drop is linearly dependent with sulfur coverage ($\theta_s$). Ni deactivation is partially reversible, full performance recovery measured for H₂S concentrations below 2 ppm(v).

Sulfur adsorption described by Temkin isotherm

$$\frac{p_{H_2S}}{p_{H_2}} = e^{[\Delta H^0/(1-a\theta_s)RT-\Delta S^0/R]}$$

Performance drop is lower for higher current density due to higher sulfur desorption rate.

$$S_{(ads)} + 2O^{2-} = SO_2_{(g)} + 4e^-$$

Degradation mechanism: siloxanes – organic silicon compounds \([(\text{CH}_3)_2\text{SiO}]_{4/5}\) – are thermally decomposed to form \(\text{SiO}_2\) (silica) that condensates on anode surfaces (also interconnects). Irreversible degradation mechanism.

\[
\begin{align*}
\text{Si(OH)}_4 & \rightleftharpoons \text{SiO}_2(s) + 2\text{H}_2\text{O} \\
(\text{CH}_3)_2\text{SiO})_{4/5} \text{(g)} + 20\text{H}_2\text{O} & \rightleftharpoons 4\text{Si(OH)}_4\text{(g)} + 8\text{CO} + 24\text{H}_2
\end{align*}
\]

\(\bullet\) = \(\text{SiO}_2\) deposit

SOFC degradation by siloxanes

**Impact on SOFC performance**: constant voltage drop due to silica accumulation on active surface. Very high degradation rates for ppb(v) levels.

Very little Si is visible in the freshly reduced sample, could be sample preparation.

Measurement of silicon deposition: WDS mapping of anode contact layer (channel boundary) of a freshly reduced sample (before siloxane exposure).

Silicon mapping on Ni-anode

Measurement of silicon deposition: WDS mapping of anode contact layer (channel boundary) after siloxane exposure.

Preferential Si deposition at the anode contact layer (channel boundary of the anode), but large amounts of Si also present in the anode support.

Quantitative chemical analysis (ICP-OES)

**ICP-OES**: Inductively Coupled Plasma Optical Emission Spectroscopy

<table>
<thead>
<tr>
<th></th>
<th>Silicon (wt. ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stack 'A'</td>
<td>150</td>
</tr>
<tr>
<td>Stack 'B'</td>
<td>80</td>
</tr>
<tr>
<td>Stack 'C' - fuel inlet</td>
<td>1990</td>
</tr>
<tr>
<td>Stack 'C' - fuel outlet</td>
<td>370</td>
</tr>
</tbody>
</table>

'A' and 'B' refer to stack cells tested in biogas reformate without contamination. 'C' refer the stack tested with D4-siloxane in the anode feed.

**Post-mortem stack analysis results**

Higher Si concentration near the anode-channel boundary (WDS mapping)

Higher Si concentration at the stack inlet (ICP-OES).
SOFC degradation by chlorine

**Interaction mechanism:** in Ni-anode SOFCs, two interactions mechanisms are reported: 1) adsorption of Chlorine on Ni sites, 2) micro-structural changes due to the formation and sublimation of NiCl$_2$(g). Stronger interactions with stack and system components (corrosion) are expected.

Adsorption of Cl on Ni (fast process) is a reversible process. Lower melting point (higher volatility) of adsorbed Ni-Cl species compared to Ni, possible sublimation and redistribution of Ni particles (irreversible).

\[
\text{HCl(g)} \leftrightarrow \text{Cl(ad)} + 0.5\text{H}_2(\text{g})
\]

Sublimation of NiCl$_2$(g) is an irreversible process. The formation of NiCl$_2$(g) is thermodynamically possible only at very high HCl concentrations (>500 ppmv).

\[
\text{Ni(s)} + 2\text{HCl(g)} \leftrightarrow \text{NiCl}_2(\text{g}) + \text{H}_2(\text{g})
\]


SOFC degradation by chlorine

**Degradation mechanism:** reduced active Ni surface due to Cl coverage. Tests show only partial recovery of initial cell performance after HCl exposure due to irreversible TPB reconstruction.

Performance recovery occurs for low frequency processes (gas conversion), impedance response does not recover for processes related to the TPB (high frequency). Probably micro-structural changes with Ni redistribution.

SEM/EDX shows traces of Cl at the peripheries of Ni grains, suggesting the presence of absorbed chlorine on Ni surface.

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SOFC degradation by chlorine

**Impact on SOFC performance:** the adsorption of chlorine onto Ni surfaces blocks possible reaction sites at the TPB, preventing the electrochemical reactions and leading to an increase in anode overpotential. Lower surface coverage than S.

Single cell tests show reduced impact of Cl poisoning on cells operated with syngas compared to H₂. This is due to CO competing with Cl absorption on Ni atoms. CO is electrochemically oxidized and the adsorbed CO provides protection towards Cl contamination.

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Degradation indicators

Different indicators for different degradation types

An **intrinsic degradation** rate is meaningful for **time-progressive degradation processes** (i.e., long-term sulfur degradation, silicon poisoning)

\[
d = - \frac{dASR(t)}{dt} = - \frac{dV(t)}{dt}
\]

**Fast deactivation processes** due to surface coverage up to an equilibrium value (i.e., \(H_2S, HCl\) adsorption) are better described by **voltage drop over initial voltage** (overall degradation).

\[
\Delta d = - \frac{\Delta V}{V^0}
\]
Intrinsic degradation by siloxanes

Intrinsic degradation rate of Ni-anode fuel cell in the presence of siloxanes (D4) derived from experiments. Constant degradation rate $d$ with time.

\[ y = -0.0474x^2 + 0.5491x \]

\[ R^2 = 0.9873 \]

**Intrinsic degradation** with typical siloxane concentration of raw biogas from WWTP (5 mg Si Nm$^{-3}$ equivalent to 1 ppm(v) D4): 1.56 mΩ cm$^2$ hr$^{-1}$

Estimated voltage degradation per 1000 h: > 50%

Complete removal of siloxanes needed!

Overall degradation rate of Ni-anode fuel cell in the presence of H$_2$S, HCl, tars (toluene C$_7$H$_8$, naphthalene C$_{10}$H$_8$) derived from experiments$^{(1-2)}$.

H$_2$S in raw biogas: 30 mg Nm$^{-3}$

Severe SOFC performance drop
High cleaning required!

HCl in raw biogas: 2 mg Nm$^{-3}$

Tar in raw biogas: traces

Mild effect on SOFC
Limited cleaning required


(2) SOFCOM project (www.sofcom.eu)
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Design of biogas cleaning

Contaminants analysis showed the need for removal of siloxanes and H₂S from sewage biogas. It is necessary to properly dimensionate cleaning section to estimate the cost of contaminant removal (fixed bed activated carbon).

**Biogas characterization:**
contaminant concentration ($C_0$)

Contaminant removal by sorbent materials:
adsorption kinetics modeled (Langmuir isotherm) and validated over experiments to calculate adsorption capacity ($mg_{cont}/g_{sorbent}$)

**Contaminant trap dimensioning:**
vessel size ($kg_{sorbent}$)

Breakthrough time
(i.e., refill frequency)

Cost of cleaning per unit of SOFC product
1-2* $cent/kWh_{el}$

Cleaning OPEX
($$/yr)

*cost estimation for DEMOSOFC cleanup system

Adsorption of contaminants on **activated carbons (AC)** in fixed bed reactors. Need for H$_2$S and siloxanes removal. **Experimental campaign for AC selection.**
AC characterization

Adsorption capacity from tests on AC cartridges.

\[ \text{Adsorption capacity, } \text{Ads}_S = \frac{m_{\text{biogas}} \cdot c_S \cdot t_{BT}}{m_{AC}} \]

- Adsorption capacity, \( \text{Ads}_S \)
- Biogas flow rate, \( m_{\text{biogas}} \)
- Sulphur concentration in biogas, \( c_S \)
- Mass of AC in the reactor, \( m_{AC} \)

Raw AC

AC cartridges (id 4/10 mm)

Gas analysis

Breakthrough time \( t_{BT} \)

Gas analysis graph with H2S concentration (ppm) vs. Time (h)
Adsorption modeling

Adsorption capacity from tests influenced by samples geometry (L/D ratio, gas velocity). Models including adsorption (Langmuir) and gas advection-diffusion developed and validated to extend the results to the operating conditions of the cleanup system in the final plant.

Prediction of fixed-bed breakthrough curves for H₂S/siloxanes adsorption from biogas (1D time-dependent model adsorption-advection/diffusion model).
Conclusions

Impact of fuel contaminants: a techno-economic issue

- Contaminants characterization of the alternative fuel (syngas, bio-syngas, biogas)
- Selection of proper degradation indicators for the evaluation of performance loss
- Study of contaminants effect on SOFC (and plant components) for the selection of most harmful contaminants
- Economic evaluation of performance degradation (loss of production and components replacement)
- Design of cleaning for selected contaminants and cleaning cost estimation

Final goal: find the contaminant-induced degradation threshold beyond which the economic effectiveness of the system is compromised
Thank you for your attention!