The role of cerium in the development of perovskite oxides as electrodes for the direct use of biogas in solid oxide fuel cells

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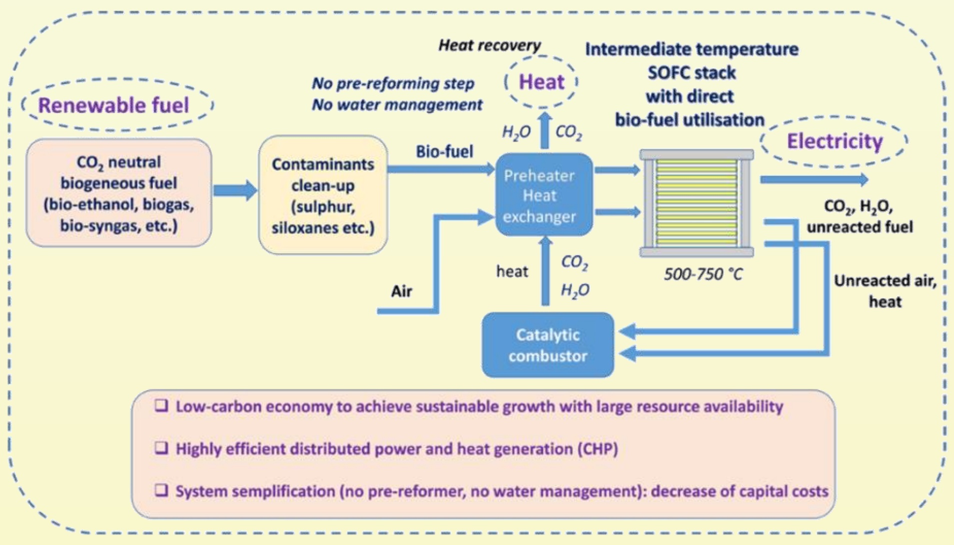
Introduction

Solid Oxide Fuel Cells (SOFCs)

devices able to generate electricity and heat through electrochemical oxidation of different fuels with low greenhouse emissions[1].

SOCF's anode: Yttria stabilized Zirconia (Ni-YSZ)

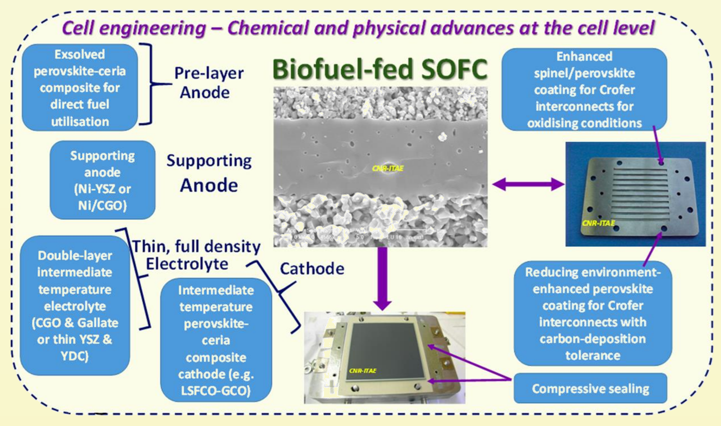
- Best catalytic performance
- High electron conductivity
- Deactivation of active sites due to carbon deposition[1]



DIRECTBIOPOWER project aim

development of new generation SOFC for the direct utilization of biofuels with:

-high sulphur tolerance
-longer life-time
-utilization of bio-fuels



Methodology

Synthesis of La- and Ce-based perovskites → **Characterization of the samples** → **Soot oxidation reaction** → **Methane dry-reforming tests**

Solution Combustion Synthesis (SCS) procedure [2]: $La_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (LSFC), $La_{0.3}Sr_{0.7}Fe_{0.7}Ti_{0.3}O_{3-\delta}$ (LSFT), $La_{0.4}Sr_{0.4}Ba_{0.2}TiO_{3+\delta}$ (LSBT), CeO_2.

Hydrothermal procedure [3]: $Ce_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-\delta}$ (CSFC)

Characterization analyses:
- N_2 physisorption at -196 °C
- FESEM
- XPS

Soot oxidation under *loose contact* conditions in order to simulate the carbon deposition on anode surface.

Methane dry reforming operated by Università di Udine on the samples impregnated with 7 wt.% of Ni.

Physico-chemical Characterizations

Table 1 XPS results.

Catalyst	XPS results		
	O_α/O_β	Fe^{2+}/Fe^{3+}	Ce^{3+}/Ce^{4+}
LSBT	0.34	-	-
LSFT	0.17	0.55	-
LSFC	0.50	0.79	-
CSFC	**17.98**	**1.31**	**0.11**
CeO_2	**0.47**	-	**0.28**

CSFC sample
- O_α/O_β ↑↑
- Fe^{2+}/Fe^{3+} ↑
- Ce^{3+}/Ce^{4+} ↑

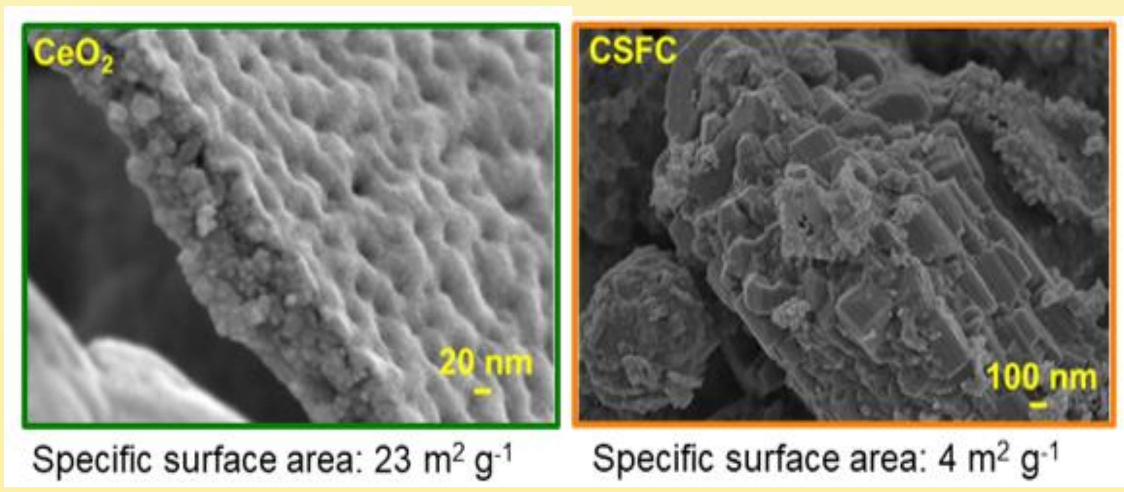


Fig. 1 FESEM images of the most performing catalysts along with their Specific surface area (SSA).

Catalytic tests

Table 2 Results of the methane dry reforming tests over the studied samples.

Catalyst	Methane dry reforming (800 °C)	
	CH_4 conversion (%)	CO_2 conversion (%)
LSBT	1	3
Ni-LSBT	1	4
LSFT	0	2
Ni-LSFT	6	17
LSFC	6	5
Ni-LSFC	6	20
CSFC	0	5
Ni-CSFC	4	3
CeO_2	3	12
Ni-CeO_2	**48**	**75**

Table 2 shows the results of methane dry reforming tests performed feeding a mixture with 44 vol.% CH_4, 23 vol.%CO_2, 22 vol.% He and 5 vol.% N_2.

The most interesting sample is **Ni-CeO_2**: CH_4 conversion 48%, CO_2 conversion 75%

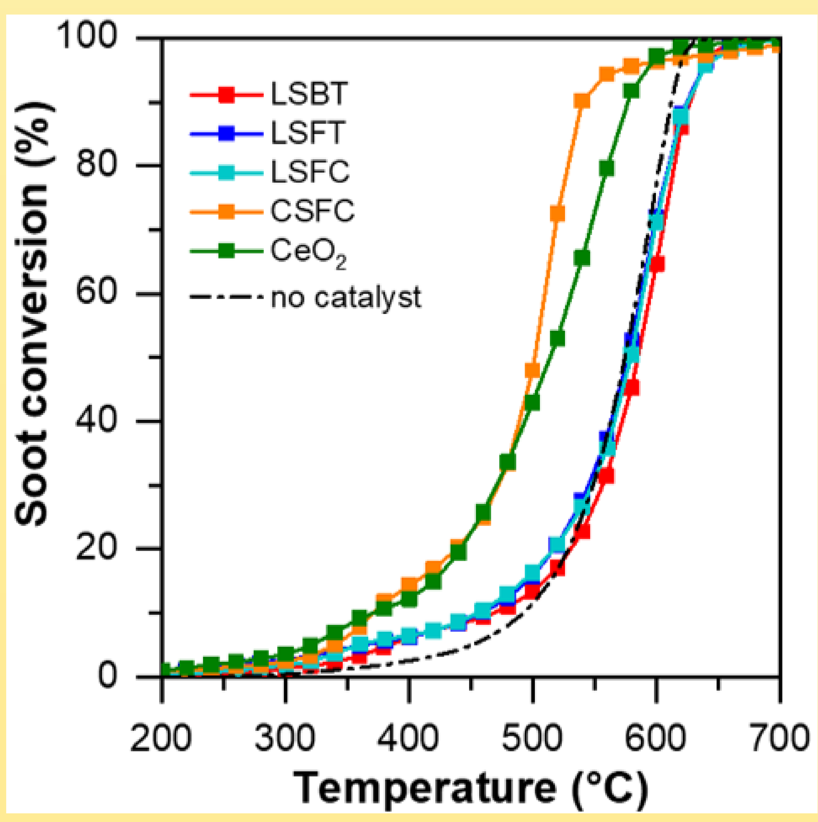


Fig. 2 Soot conversion as a function of the temperature

Soot oxidation results are reported in Figure 2.
The La-based samples do not exhibit outstanding performances. Conversely, the CeO_2 and CSFC show good catalytic performances due to the presence of Ce cation inside the perovskite structure [2,3].

Conclusions

In order to simulate the carbon deposition on SOFC's anode, loose contact conditions were chosen to perform soot oxidation reaction. The CSFC is the most performing catalyst thanks to high amount of surface oxygen and reductant species (Fe^{2+} and Ce^{3+}) that could play a key role in the oxygen spillover mechanism, which significantly increase the catalyst's reactivity towards the soot oxidation reaction.
The Ce-based samples exhibit good methane dry reforming performances, and they could be proposed as alternative to the actual Ni-YSZ.

Acknowledgment

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Bibliography

[1]Song, B., Ruiz-Trejo, E., Bertei, A., & Brandon, N. P. (2018). Quantification of the degradation of Ni-YSZ anodes upon redox cycling. Journal of Power Sources, 374, 61-68.
[2]Rahman, I. Z., Raza, M. A., & Rahman, M. A. (2012). Perovskite based anode materials for solid oxide fuel cell application: A review. Advanced Materials Research, 445, 497-502.
[3]Piumetti, M., Bensaid, S., Andana, T., Dosa, M., Novara, C., Giorgis, F., Russo, N. & Fino, D. (2017). Nanostructured ceria-based materials: effect of the hydrothermal synthesis conditions on the structural properties and catalytic activity. Catalysts, 7(6), 174.