Imperial College London

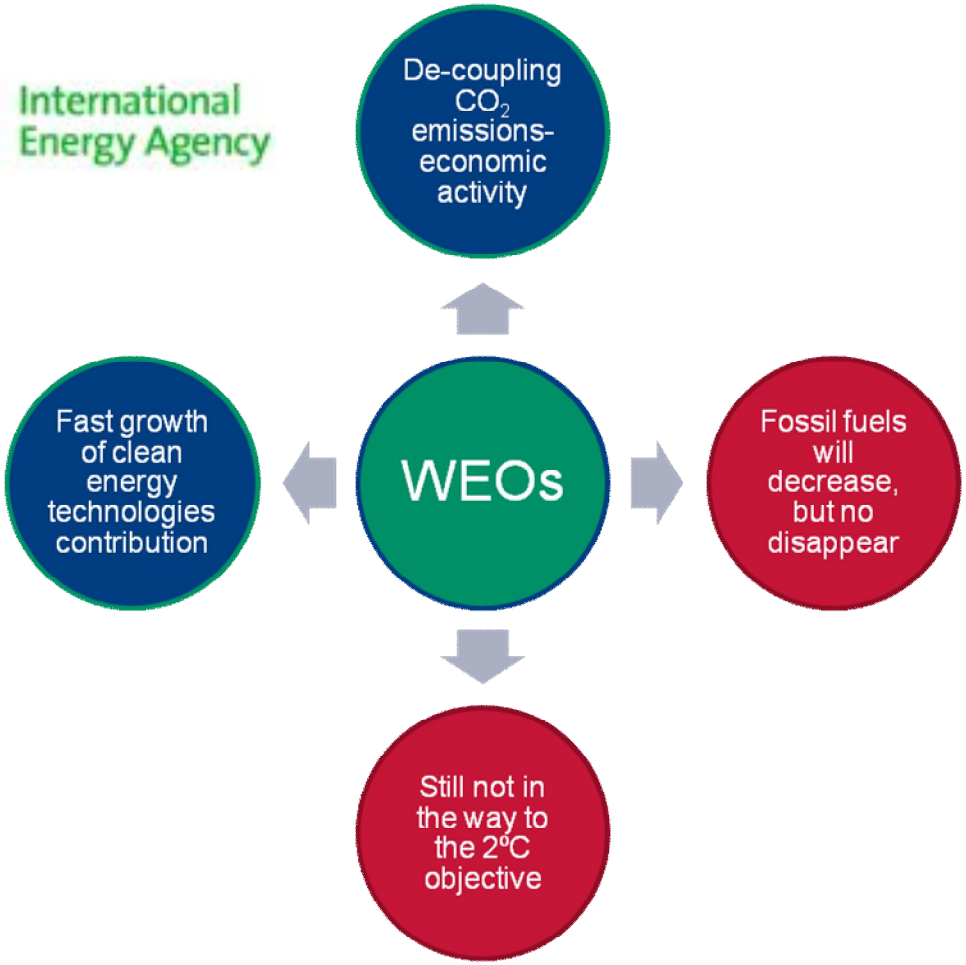
Mixed Ionic-Electronic Conductors for their Application in Oxygen Transport Membranes

Dr. Jose M. Bermudez, Dr. Marcos Millan
Chemical Engineering Department, Imperial College London, UK

Imperial College London

Introduction

International Energy Agency



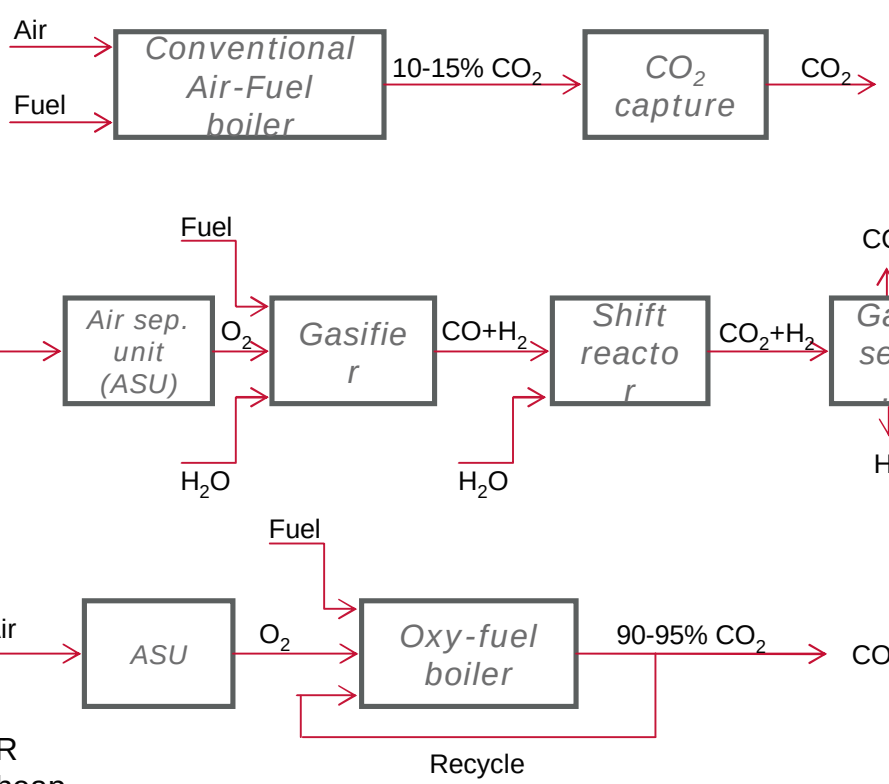
Imperial College London

Introduction

Postcombustion

Precombustion

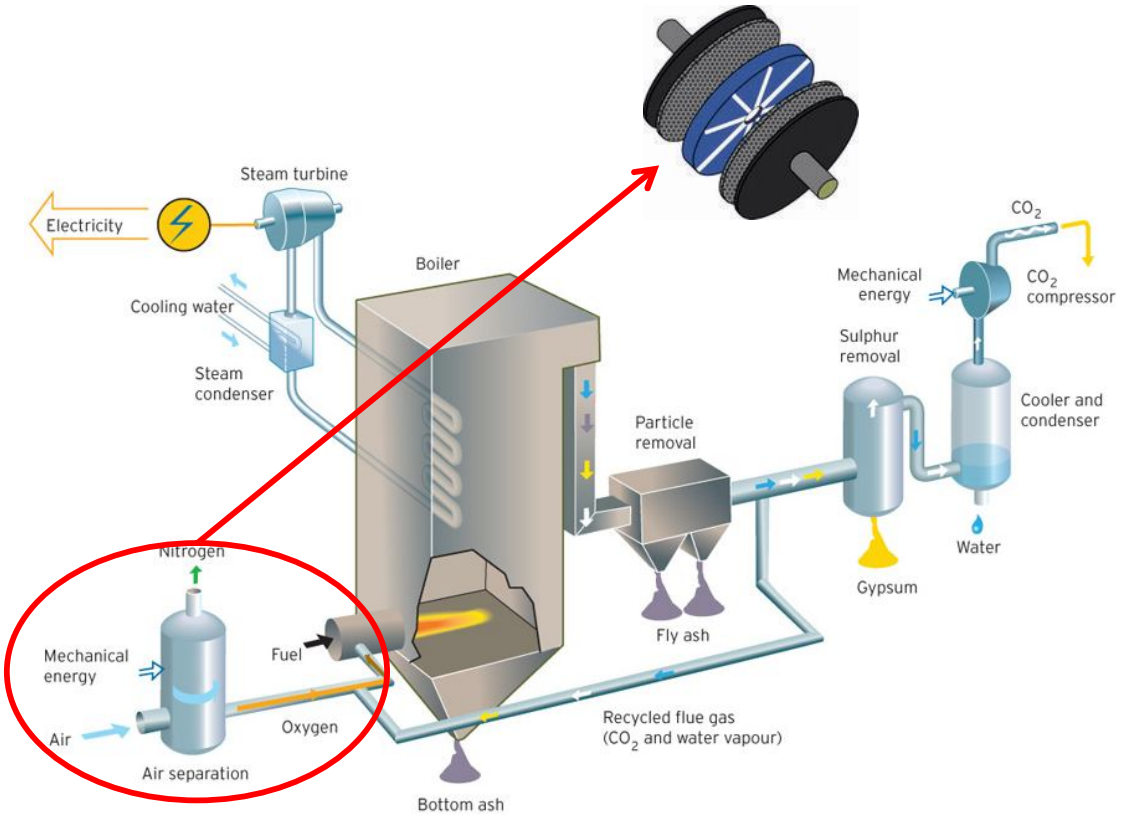
Oxycombustion

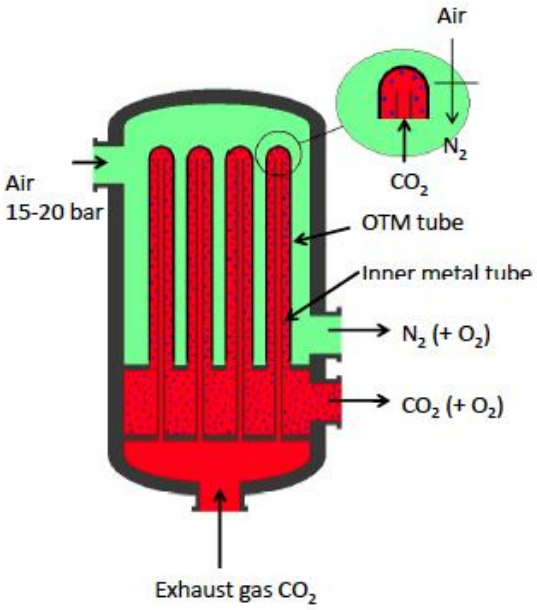


- High development – EOR
- CO_2 capture easy and cheap
- Near-zero emission technology
- Reduction in NO_x and SO_x emissions

Imperial College London

Introduction



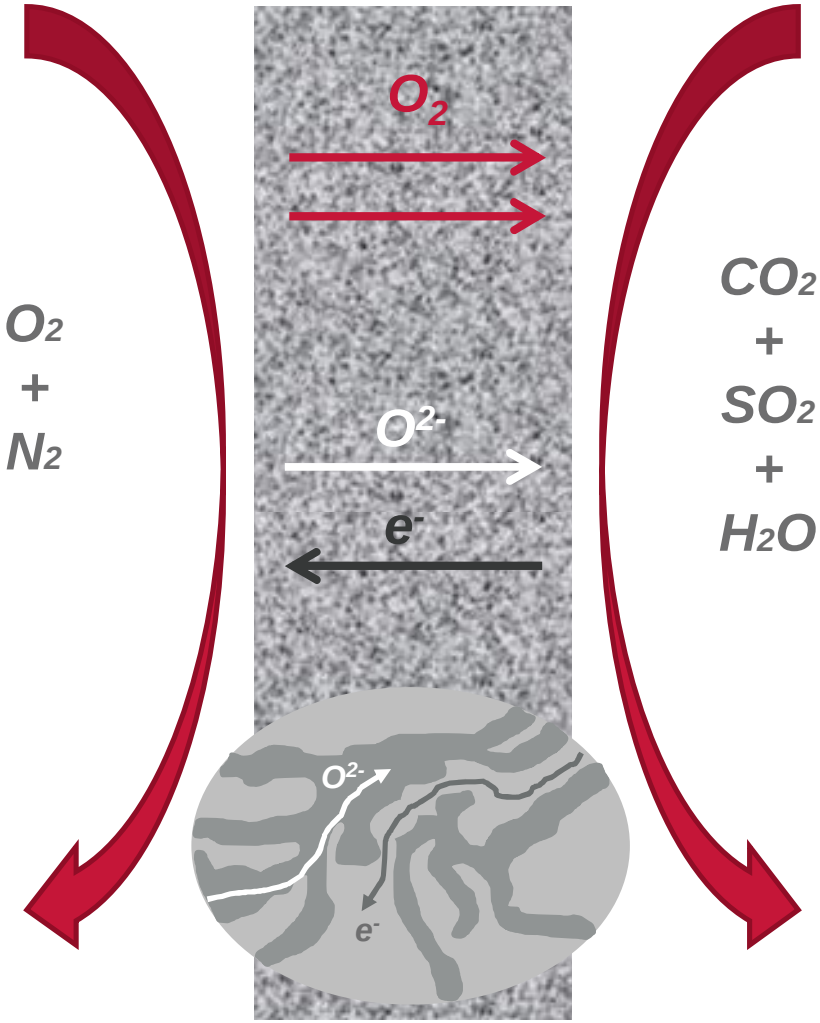


- High energy penalty

→ **OXYGEN TRANSPORT MEMBRANES (OTM)**

Imperial College London

Introduction



Mixed Ionic Electronic Conductors (MIEC)

Single phase perovskites

$A_xA'_{1-x}B_yB'_{1-y}O_{3-\delta}$

High performance

$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Low stability

High stability

$BaCe_xFe_{1-x}O_{3-\delta}$

$Ba_{0.5}Sr_{0.5}Zn_{0.2}Fe_{0.8}O_{3-\delta}$

Low permeability

Dual-phase membranes

Ionic cond.	Electronic cond.
Fluorites	Perovskites
Doped ZrO_2	Spinels
Doped CeO_2	

Imperial College
London

Objective

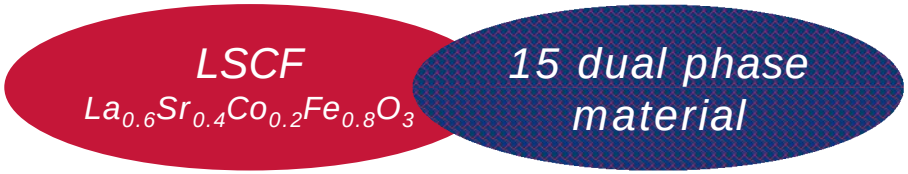
Study the thermochemical stability under close to real operation conditions of a series of MIECs with high potential for being used in 4-end modules of OTM for oxy-fuel combustion processes

Imperial College London

Experimental

Single phase - reference

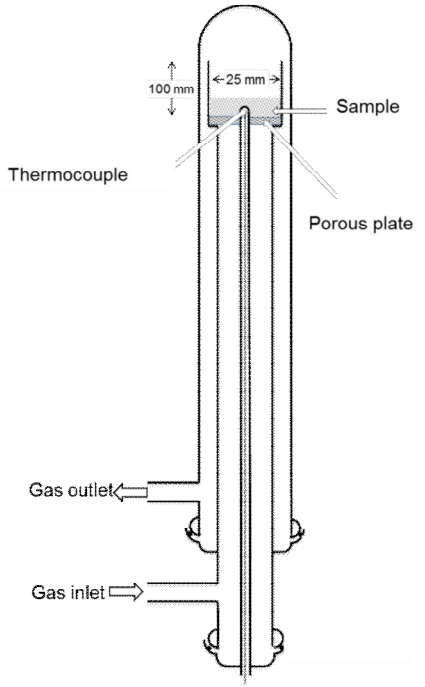
Dual phase



CGO-FCO 60/40 and 85/15 – $Ce_{0.8}Gd_{0.2}O_2$-$FeCo_2O_4$
YSZ-MCO – *Sc/Y-doped* ZrO_2-$MnCo_2O_4$
YSZ-AZO – *Sc/Y-doped* ZrO_2-$Zn_{0.98}Al_{0.02}O_{1.01}$
YSZ-LCM – *Sc/Y-doped* ZrO_2-$La_{1.0}Cr_{0.9}Mg_{0.1}O_3$
YSZ-LCCN – *Sc/Y-doped* ZrO_2-$LaCr_{0.85}Cu_{0.01}Ni_{0.05}O_3$
NFO-CTO – $Ce_{0.8}Tb_{0.2}O_2$–Ni_2FeO_4
NFO-CTO + Catalysts

Temperature: 850-900 ºC
TOS: 8 h

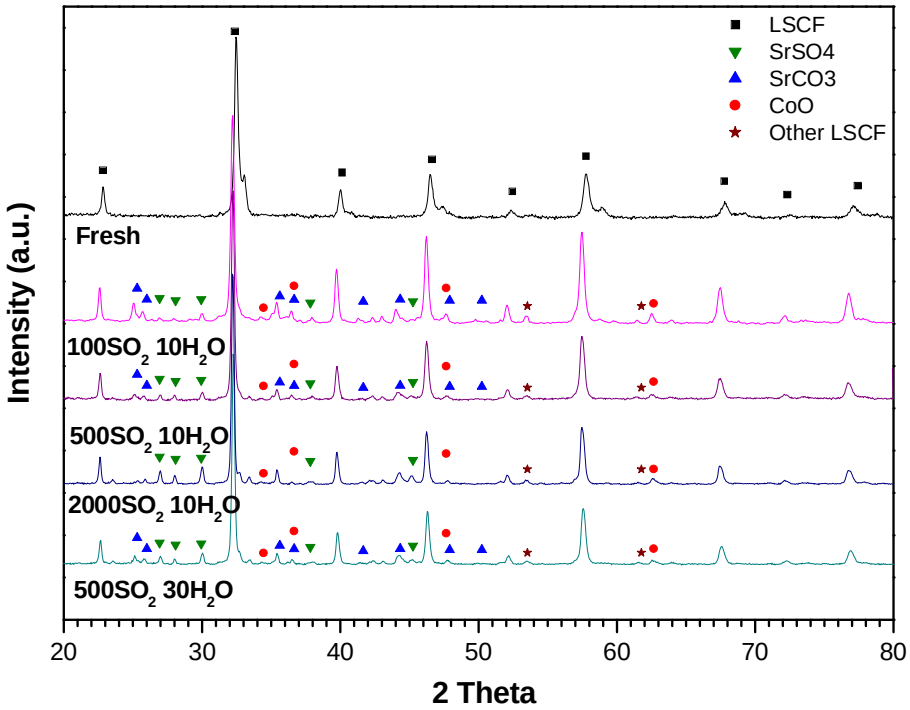
Simulated gas stream
- 98-100% CO_2 d.b.
- 0-2000 ppm SO_2 d.b.
- 0-30% H_2O



Imperial College London

Results

LSCF
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$



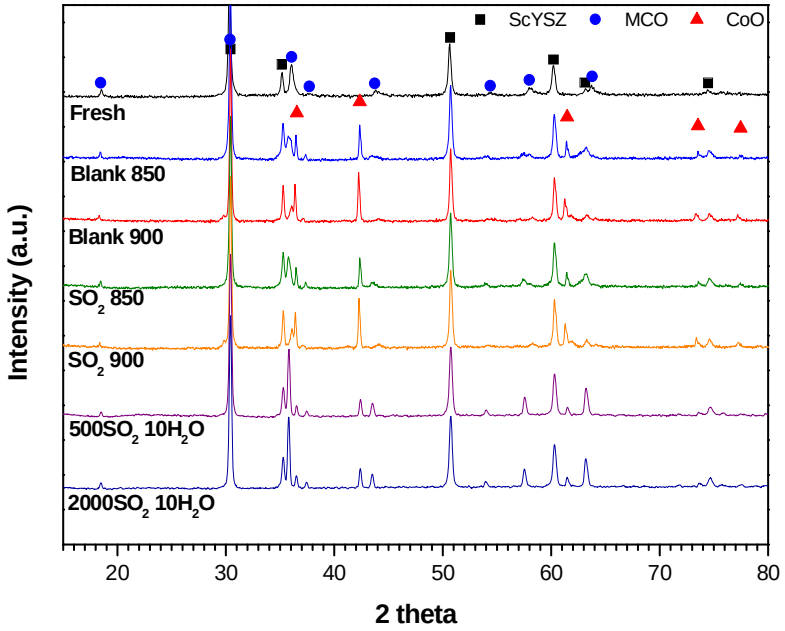
- LSCF is unstable in all conditions
- CO_2 gives rise to $SrCO_3$ and SO_2 gives rise to $SrSO_4$
- Co and Fe were segregated as oxides
- Competitive reactions between LSCF and CO_2/SO_2, with SO_2 been stronger

Imperial College London

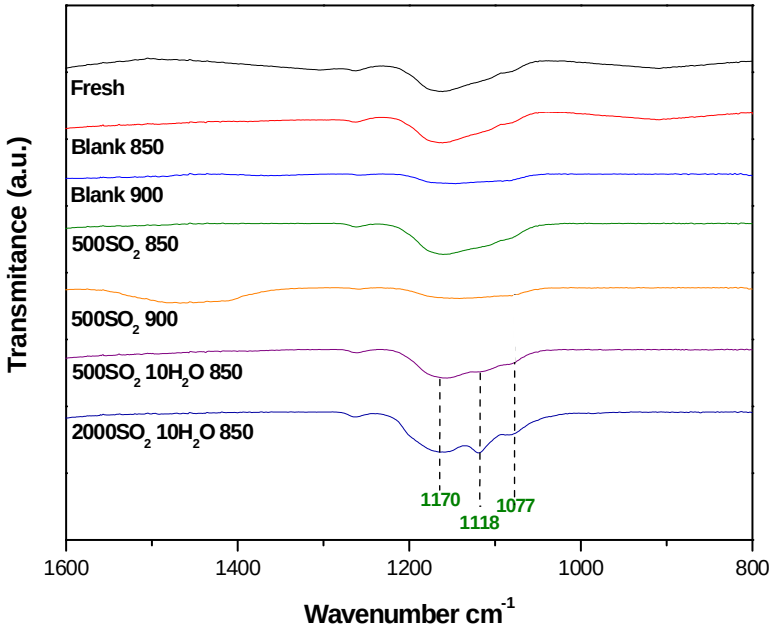
Results

YSZ-MCO 70-30

$Sc_2O_3/Y_2O_3/ZrO_2$-$MnCo_2O_4$



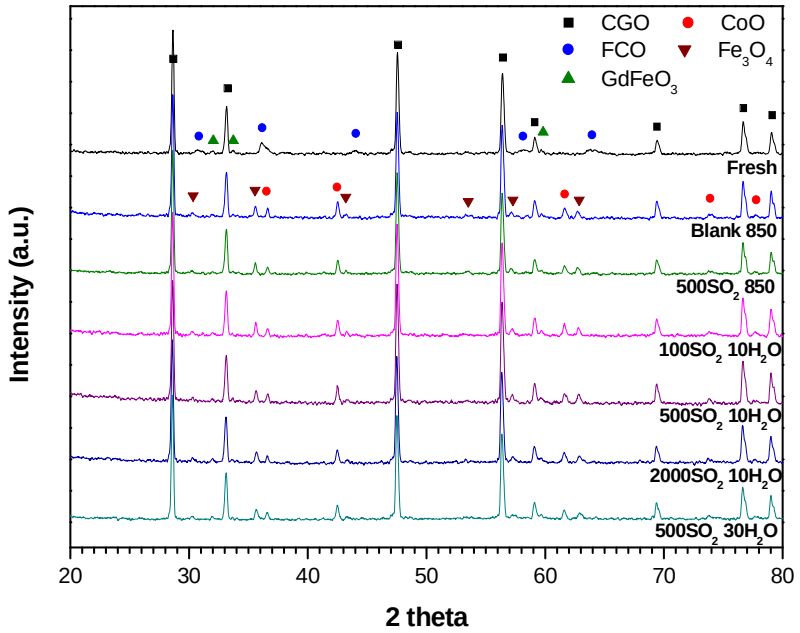
- Electronic conductor (MCO spinel) unstable against CO_2 and high concentrations of SO_2
- CO_2 promotes segregation of Co
- SO_2 gives rise to the formation of sulphates



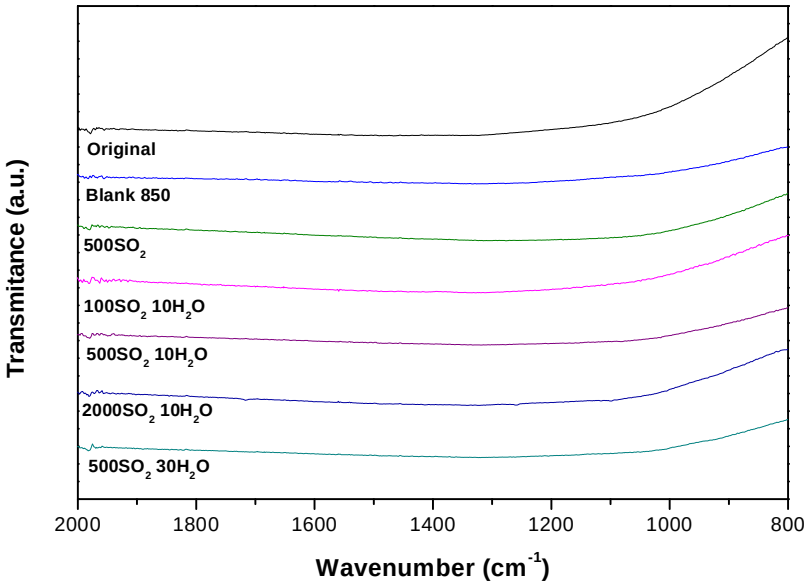
Imperial College London

Results

CGO-FCO 60-40
$Ce_{0.8}Gd_{0.2}O_2$-$FeCo_2O_4$



- Electronic conductor (FCO spinel) unstable against CO_2
- CO_2 promotes segregation of Co and Fe
- Low impact on the O_2 transport: ionic conductivity is the limiting factor

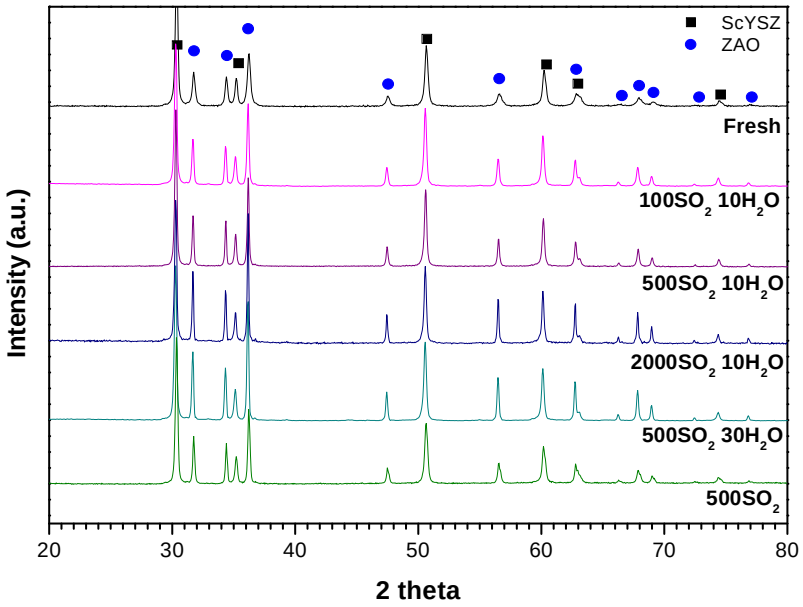


Imperial College London

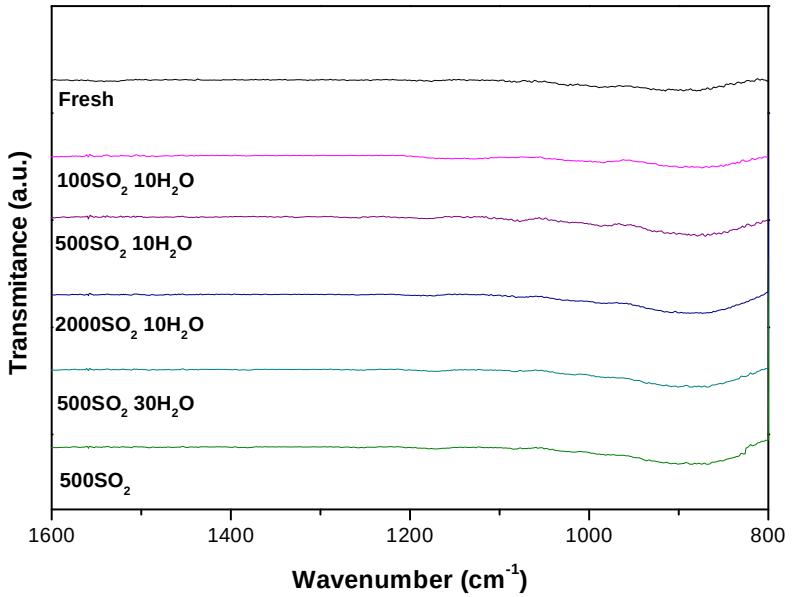
Results

YSZ-AZO 50-50

$Sc_2O_3/Y_2O_3/ZrO_2\text{-}Zn_{0.98}Al_{0.02}O$



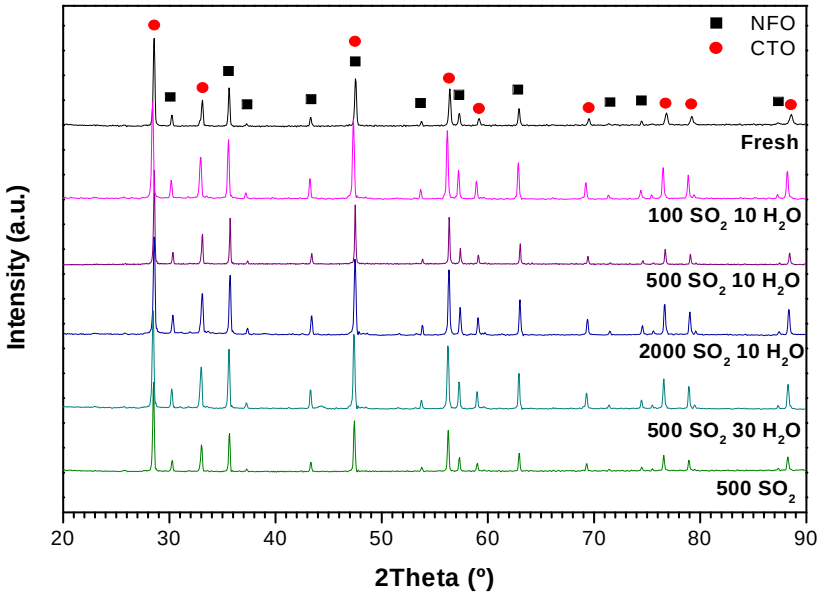
- Electronic conductor (doped ZnO) and ionic conductor (Y-Sc stabilized ZrO_2) are stable against CO_2 and SO_2
- Raman, XRF, Elemental Analysis and SEM (coupled with EDS and WDS) confirmed the stability



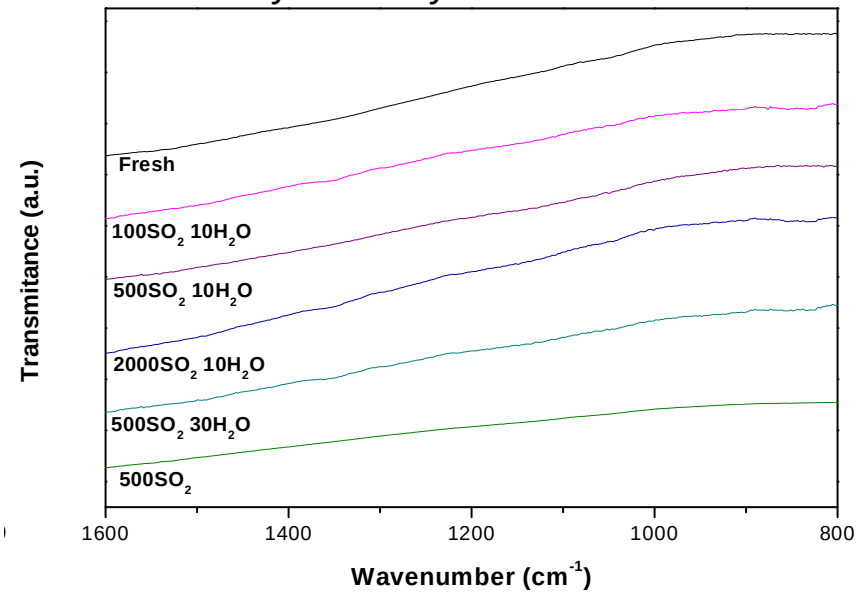
Imperial College London

Results

CTO-NFO
$Ce_{0.8}Tb_{0.2}O_2$–Ni_2FeO_4



- Electronic conductor (spinel) and ionic conductor (doped CeO_2) are stable against CO_2 and SO_2
- Raman, XRF, Elemental Analysis and SEM (coupled with EDS and WDS) confirmed the stability
- Tested as catalyst in asymmetric membranes



Imperial College London

Conclusions

- Single phase MIECs are not stable under CO_2/SO_2 atmospheres
- Certain materials show a competitive interaction with CO_2 and SO_2
- Electronic conductors are less stable, but in certain cases this has low impact on the oxygen transport
- Certain materials have shown high stability under all the conditions studied and present the potential of being used in OTM for oxyfuel combustion processes

Imperial College London

Thank you for your attention

Dr. Jose M. Bermudez
Dr. Marcos Millan