Reversible SOFCs operating on CO$_2$ and CO$_2$/H$_2$O Performance, Stability & Reversibility aspects

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Reversible SOFCs operating on $\text{CO}_2$ and $\text{CO}_2/\text{H}_2\text{O}$
Performance, Stability & Reversibility aspects

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Reversible or Regenerative Fuel Cells

the concept

A closed-loop system for energy storage and on-demand power generation

- In a PEM or SOFC system $\text{H}_2\text{O}$ is separated into $\text{H}_2$ and $\text{O}_2$ by a solar (or other RES) powered electrolyzer
- In a SOFC system $\text{CO}_2$ is separated into $\text{CO}$ and $\text{O}_2$ by a solar (or other RES) powered electrolyzer \textbf{SOEC}
- The produced gases are stored in order to be supplied to the fuel cell (PEMFC or SOFC) when electricity is needed
Reversible Solid Oxide Cells (SOFC/SOEC)

An integrated solution: a unitized reversible system that can use \( \text{H}_2\text{O} \) and/or \( \text{CO}_2 \) as media.

**Convert Power to Fuel**
Using off-peak excess generating capacity, electricity generated by intermittent sources
- Excess or **Renewable Power** and **Steam** to **Fuel (H\(_2\))**
- Excess or **Renewable Power** and **CO\(_2\)** to **Fuel (CO)**
- Excess or **Renewable Power** and **CO\(_2\)** and **Steam** to **Syngas (\(\rightarrow\) Synfuels or valuable chemicals)** (e.g. via Fischer-Tropsch)

**Convert Fuel to Power**
Stored fuel (H\(_2\), CO) can be used to produce power on site and on demand.
Reversible Solid Oxide Cells (SOFC/SOEC)

An integrated solution: a unitized reversible system that can use H₂O and/or CO₂ as media.

Convert Power to Fuel
Using off-peak excess generating capacity, electricity generated by intermittent sources
Excess or Renewable Power and CO₂ and Steam to Syngas (Synfuels or valuable chemicals) (e.g via Fischer-Tropsch)

Example: SELySOS Project (FCH JU)

“Development of new electrode materials and understanding of degradation mechanisms on Solid Oxide High Temperature Electrolysis Cells”

http://selysos.iceht.forth.gr

WORKSHOP "Degradation Mechanisms in Solid Oxide Cells and Systems"
Reversible Solid Oxide Cells (SOFC/SOEC)

The RSOFC concept in Space Exploration: Many studies have showed the advantages of fuel cells for power production in space planetary missions. If the reactants for the power production can be taken directly from the planetary atmosphere the mass saving potential is huge.

A suitable example: Energy on Mars

The Martian atmosphere consists of 95.7% CO₂

- Electricity from solar power
- Storage of energy by electrolysis of CO₂ to CO
- Converting CO back to electricity in the same unit
- Production of liquid fuel from CO and hydrogen
- No transport of carbon, limited transport of hydrogen
- High operation temperature makes it easy to get rid of excess heat

“The energy supplied by these fuel cells is intended to be used as periodic supplement to the batteries which are the main power source during low or no solar power. Especially in the Martian winters this energy is needed to avoid serious oversizing of batteries or the necessity for radioactive devices. The overall target is to develop an energy storage system for Mars missions with significant mass saving by the use of reversible fuel cells and on-site reactants.”
Reversible SOFC/SOEC operating on CO\textsubscript{2}
Reversible SOFC/SOEC operating on CO₂

Challenges

SOFC on CO

Usually SOFC fuel contains H₂, H₂O, CO and CO₂ (CH₄) ▶ Dry CO/CO₂ mixture as fuel

- Risk of soot formation when
  - Intermediate temperatures (< 850°C – 900°C)
  - High CO concentrations (Boudouard: 2 CO → C₇gr + CO₂)
  - Presence of metals (anode and interconnects)

- Reduced reaction kinetics
  - Lower reaction kinetics with CO than with H₂
  - Redox instability (volume change, coarsening of the Ni-phase)
  - Thermal or overpotential sintering (Ni agglomeration)

- New chemistry when hydrogen is not present
  - H₂S impurities, other??
Reversible SOFC/SOEC operating on CO$_2$

Challenges

SOEC on CO$_2$

Dry, pure CO$_2$ feed ▶ Ni–YSZ composites can be severely damaged by re-oxidation in pure CO$_2$ atmosphere & high temperatures

- Risk of soot formation when
  - Intermediate temperatures (< 850°C – 900°C)
  - High CO concentrations (Boudouard: 2 CO → C$_{gr}$ + CO$_2$
  - Presence of metals (anode and interconnects)

- Reduced reaction kinetics
  - Large resistance for CO$_2$ electrolysis related to the cathode (fuel) electrode kinetics
  - Redox instability
  - Thermal or overpotential sintering
  - Impurities
Reversible SOFC/SOEC operating on CO$_2$

Reversible electrodes’ requirements

✓ High electrocatalytic activity (CO oxidation, CO$_2$ reduction, ...)
✓ Redox stability
✓ Mixed ionic-electronic conductivity (MIEC)
✓ Tolerance to C-formation
Reversible SOFC/SOEC operating on CO$_2$

Fuel electrode materials

Perovskite structures $\text{ABO}_3$
- $\text{LaCrO}_3$

- Catalytically active
- Offer high ionic & electronic conductivity in reducing atmospheres
- Tolerant to carbon formation
- Thermally stable
- Chemically compatible with the electrolytes
- Dimensional stability upon redox cycling
- Mixed conducting materials
  - allow the geometric extension of the electrochemical reaction zone, TPB in the entire volume of the electrode
  - promote the electrochemical reaction in the SOEC fuel electrode

\[
\text{CO}_2 + \Box + 2\text{e}^- \rightarrow \text{CO} \rightarrow \text{V}_0^x
\]

$\text{V}_0^x$: oxygen vacancy in the lattice
$\text{V}_0^x$: oxygen ion
Reversible SOFC/SOEC operating on CO$_2$

A class of Substituted Lanthanum Chromites (LSC-M)

$$\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_x\text{M}_{1-x}\text{O}_3 \ [x=0.1, 0.5 \ & \ M= \text{Mn, Fe, Co, Ni}]$$

have been studied in CO fueled SOFCs and in SOEC/SOFC reversible operation on the CO$_2$ cycle

- Characterization ➔ understanding
- Performance evaluation & Testing under relevant conditions (SOFC/SOEC cycling)
Reversible SOFC/SOEC operating on CO₂

- **Starting point**: the entire class of materials prepared by a modified citrate/sol-gel route to be tested as CO/CO₂ fueled SOFC anodes:
  \[ \text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_x\text{M}_{1-x}\text{O}_3 \quad [x=0.1, 0.5 \quad \text{M= Mn, Fe, Co, Ni }] \]

- Evaluation of model button cells based on 1-2 mm thick YSZ electrolyte (900-1000 °C)

- Most active anode for a CO/CO₂ (9/1) fueled SOFC: \( \text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.9}\text{Fe}_{0.1}\text{O}_3 \) (LSCFe)

**Fuel cell performance**: current density at nominal potential \( V_{\text{nom}} = 0.65 \text{ V} \)

Compositions: \( \text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.9}\text{M}_{0.1}\text{O}_3 \)
La$_{0.75}$Sr$_{0.25}$Cr$_{0.9}$Fe$_{0.1}$O$_3$ (LSCFe)

Performance comparison test in a 4-cell short stack

<table>
<thead>
<tr>
<th></th>
<th>anode</th>
<th>anode current collector</th>
<th>electrolyte</th>
<th>cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 LSCFe cells</td>
<td>LSCFe/CGO sintered</td>
<td>NiO-unsintered</td>
<td>3YSZ (Kerafol)</td>
<td>LSM/YSZ + LSM as current collector</td>
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</tbody>
</table>

Operating conditions
90% CO - 10% CO$_2$ vs O$_2$, $T_{cell}$=950°C
Reversible SOFC/SOEC operating on $\text{CO}_2$

**Anode:** Ni-YSZ (as reference material)  
\[ \text{LSCFe: } \text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.9}\text{Fe}_{0.1}\text{O}_3 \]

**Cathode:** LSM-YSZ (50:50) & LSM as current collector

**Electrolyte:** YSZ [d=20 mm, thickness: 1 mm, 300 $\mu$m, 150 $\mu$m]

- Ni-YSZ or Perovskite (LSCFe)
- YSZ
- LSM-YSZ
- LSM

Screen printed electrodes  
Sintering profiles: LSM-YSZ & LSM: 1150°C  
Ni-YSZ: 1350°C  
LSCFe: 1200°C

Fuel current collectors: Pt / oxidant current collectors: Au

**Operation @ 900-1000°C**
- Reference measurements: $\text{H}_2$ vs $\text{O}_2$ SOFC mode
- $\text{CO}_2$ electrolysis mode (pure $\text{CO}_2$ feed)
- $\text{CO}-\text{CO}_2(70:30 \%)$ vs $\text{O}_2$ SOFC mode

Equilibrium for soot formation in $\text{CO}/\text{CO}_2$ at different pressures

WORKSHOP "Degradation Mechanisms in Solid Oxide Cells and Systems"
Reversible SOFC/SOEC operating on CO₂

Testing facility

Lab test station equipped with
- button cell test fixture (Probostat NorECS)
- 5x5 cell fixture

Controlled by iFix industrial automation system

Button cell test fixture

- cathode current collector
  - Al₂O₃ tube: sample holder
  - Al₂O₃ tube: cathode gas supply
- thermocouple sealant: gold ring or ceramic
- anode current collector
  - Pt mesh
- silica tube: anode gas supply
- external current & signal (temperature) collectors
- Cathode gas inlet & outlet
- Anode gas inlet & outlet
Reversible SOFC/SOEC operating on CO$_2$

Reference conditions: H$_2$ vs O$_2$

Ni-YSZ/8YSZ (300μm)/LSM-YSZ/LSM vs LSCFe/CGO/8YSZ (300μm)/LSM-YSZ/LSM

![Graph showing potential vs current density for Ni-YSZ and LSCFe at T=1000°C.](image)
Reversible SOFC/SOEC operating on CO$_2$

Reference cell Ni-YSZ//8YSZ (300μm)//LSM-YSZ/LSM

**CO-CO$_2$ fuel cell**

- **Current density @ 0.7 V**
  - 900°C: 484 mA cm$^2$
  - 950°C: 558 mA cm$^2$
  - 1000°C: 568 mA cm$^2$

**CO$_2$ electrolysis**

- **Current density @ 1.1 V**
  - 900°C: 545 mA cm$^2$
  - 950°C: 861 mA cm$^2$
  - 1000°C: 1024 mA cm$^2$
Reversible SOFC/SOEC operating on CO₂

Reference cell Ni-YSZ//8YSZ (300μm)//LSM-YSZ/LSM

CO-CO₂ fuel cell

Constant FC operation
1000°C under V = 0.6 V
Degradation: 1.8 mA cm⁻²/min

Initial performance
Final performance

52% degradation after 160min of operation

Fast, severe degradation
Reversible SOFC/SOEC operating on CO₂

Reference cell **Ni-YSZ//8YSZ (300μm)//LSM-YSZ/LSM**

**CO₂ electrolysis**

Constant SOEC operation
1000°C under V = 1.1 V
Degradation: 4.8 mA cm⁻²/min

- Initial performance
- Final performance

64% degradation after 120min of operation

Fast, severe degradation
Reversible SOFC/SOEC operating on CO$_2$

LSCFe/CGO//8YSZ(300 μm)//LSM-YSZ/LSM

**CO$_2$ electrolysis**

**CO$_2$ fuel cell**

Current density / mA/cm$^2$

Potential / V

Potential / V

Current density / mA/cm$^2$

Potential / V

Potential / V

Potential / V

i / mA cm$^{-2}$

i / mA cm$^{-2}$

T$_{cell}$ = 1000°C

T$_{cell}$ = 1000°C

Ni-YSZ

LSCF
Reversible SOFC/SOEC operating on CO₂

LSCFe/CGO//8YSZ(300 μm)//LSM-YSZ/LSM

**CO₂ electrolysis**

Current density @ 1.1 V
- 900°C: 412 mA cm⁻²
- 950°C: 572 mA cm⁻²
- 1000°C: 762 mA cm⁻²

**CO₂ fuel cell**

Current density @ 0.7 V
- 900°C: 285 mA cm⁻²
- 950°C: 327 mA cm⁻²
- 1000°C: 378 mA cm⁻²

Stability & adequate performance in reversible operation
Reversible SOFC/SOEC operating on CO$_2$

LSCFe/CGO//8YSZ(300 μm)//LSM-YSZ/LSM

CO$_2$ electrolysis

24h SOEC operation @ 1000°C under V = 1.1 V
Degradation: 2.3 μA cm$^{-2}$/min

Stability & adequate performance in reversible operation
Reversible SOFC/SOEC operating on CO₂

CO₂ electrolysis ($I_{cell}=0.9$ A)

Accelerated test on ELE – FC cycling

20 min ELE / 30 min FC

ESC cell
LSCFe AFL
CGO interlayer
8YSZ, 150 μm electrolyte
YSZ/LSM cathode
LSM cathode CC

degradation rate 0.25 mV min⁻¹
Summary & key findings

- A class of substituted Lanthanum Chromite (LSC-M) perovskite materials has been developed and evaluated for their performance in reversible SOEC/SOFC operating on CO$_2$/CO

- The material found to have the highest intrinsic activity for the reversible operation was $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.9}\text{Fe}_{0.1}\text{O}_3$ (LSCFe)

- LSCFe employed as fuel electrode of an RSOFC operating on CO$_2$ exhibited adequate performance, tolerance to carbon formation, redox stability and sufficient round trip efficiency under SOFC-SOEC cycling
Further steps

Realizing a complete reversible pressurized SOC system operating on CO₂
Further steps

Exploiting SOCs’ operational flexibility

Ni-YSZ//8YSZ//LSM-YSZ/LSM vs LSC-Fe/CGO//8YSZ//LSM-YSZ/LSM

The same unit tested for different processes

Water electrolysis

Water & CO₂ co-electrolysis

Electrolyte thickness: 1.5 mm, T=1000°C
Further steps

Exploiting SOCs’ operational flexibility

LSC-Fe/CGO//8YSZ//LSM-YSZ/LSM

Stability in water electrolysis

- electrolyte thickness: 1.5 mm
- Loadings
  - LSC-Fe: 19.93 mg cm\(^{-2}\)
  - CGO: 13.81 mg cm\(^{-2}\)
  - LSM-YSZ/LSM: 13.70 mg cm\(^{-2}\)
Further steps

Exploiting SOCs’ operational flexibility

**LSC-Fe/CGO//8YSZ//LSM-YSZ/LSM**

- Stability in water & CO$_2$ co-electrolysis

- Electrolyte thickness: 1.5 mm

**Loadings**
- LSC-Fe: 19.93 mg cm$^{-2}$
- CGO: 13.81 mg cm$^{-2}$
- LSM-YSZ/LSM: 13.70 mg cm$^{-2}$

**Graphs**

- 23.5% H$_2$O - 23.5% CO$_2$ / H$_2$
  - $V = 1.3$ V
  - $T_{cell} = 900^\circ$C

- Plot showing $i / mA cm^2$ vs. Time / h

- Plot showing $Z_{Re} / \Omega cm^2$ vs. $Z_{im} / \Omega cm^2$
Summary & perspectives

Benefits of R-SOFC
- Vastly expands applications
- Environmental benefits
- Potential to reduce manufacturing cost by using a common device for power generation, electrolysis, and reversible modes
- In SOFC mode (low emission) and in utilizing renewable energy in electrolysis mode

Open issues
- Degradation/Lifetime
  - Oxygen electrode delamination
  - Electrolyte stability
  - Seals
  - Chromium migration
  - Interconnect scale growth & resistance
  - Electrode microstructure (Electrode coarsening)

Manufacturing aspects
thank you

thanks to:

**esa**

**FCH**

**SELySOs** Project (671481)

**RSOFC for Mars exploration**

ESA Contracts: 21767/08/NL/LvH and 4000108849/13/NL/EK