SOFC Cathodes, Supports and Contact Layers

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Contents for cathodes

- Requirements for application in SOFCs
- LSM based cathodes
  - defects in TM perovskites
  - temperature limitations
- Mixed conducting cathodes
- Oxygen diffusion and exchange
- Drive for lower operating temperatures
- Contamination and durability issues
  - Cr poisoning
  - water vapour sensitivity
  - surface segregation

Oxygen reduction reaction

Oxygen vacancies are required for surface reaction as well as for bulk diffusion. Electrons are required for ionisation.
Triple phase boundary electrodes

- Electrocatalyst has high electronic conductivity, but low ionic conductivity
- Reaction site is “at” triple phase boundary
- LSM cathodes typical example
- Composites with good ionic conductor used to improve performance (e.g. LSM/YSZ cathodes)
- Capacitance is low (e.g. $10^{-5}$ F cm$^{-2}$)

Cathode reaction requires both electronic and (oxygen) ionic defects

In oxides this means transition metal constituents and oxygen non-stoichiometry (vacancies or interstitials)

Working overpotentials can change oxide stability or properties
Theory for porous single phase cathode


- Microstructure is very important ($a$, $\varepsilon$, $\tau$)

\[
R_{chem} = \left( \frac{RT}{2F^2} \right) \sqrt{\frac{(1-\varepsilon)c_0^2aD^*k^*}{\tau}}
\]

- Oxygen tracer diffusion coefficient
- Oxygen surface exchange rate constant
- Oxygen ion concentration in solid
- Volume specific surface area
- Porosity
- Tortuosity

Only gives ASR close to open circuit conditions (when gas and solid are close to being in equilibrium).
Targets

Cathode

\[ R_{\text{Chem}} = \left( \frac{RT}{4F^2} \right) \sqrt{\frac{\tau}{(1 - \varepsilon)ac_0^2D^*k^*}} \]

ASR = 0.15 ohm cm\(^2\)
For \( \tau = 2, \varepsilon = 0.3, a = 10^7 \text{ m}^{-1}, T = 1000\text{K} \)
Then \( D^*k^* > 10^{-14} \text{ cm}^3 \text{s}^{-1} \)
(Note: an ionic conductivity of 0.01 S/cm corresponds to \( D^* = 2 \times 10^{-8} \text{ cm}^2 \text{s}^{-1} \))
e.g. \( D^* > 10^{-8} \text{ cm}^2 \text{s}^{-1} \) and \( k^* > 10^{-6} \text{ cm s}^{-1} \)

For current collection need high electronic conductivity (e.g. 100s S/cm)

5 mm channels \( \sigma > 1,000 \text{ S cm}^{-1} \)

All require chemical and thermo-mechanical stability (CTE match)
Defects in TM perovskites e.g. La$_{1-x}$Sr$_x$MnO$_3$ (LSM)

- **Acceptor doping**
  
  \[
  2\text{SrO} \rightarrow 2\text{Sr}_{\text{La}} + 2\text{O}^\times_{\text{O}} + \text{V}^{\ddagger\ddagger}_{\text{O}}
  \]

- **Reduction**
  
  \[
  \text{O}^\times_{\text{O}} \rightarrow \text{V}^{\ddagger\ddagger}_{\text{O}} + 2e^- + \frac{1}{2}\text{O}_2(\text{g})
  \]

- **Electronic**
  
  \[\text{null} \rightarrow \text{e}' + \text{h}^\cdot \quad \text{Mn valency change}\]

- **Schottky**
  
  \[\text{null} \rightarrow \text{V}^{\prime\prime\prime}_{\text{La}} + \text{V}^{\prime\prime\prime}_{\text{Mn}} + 3\text{V}^{\ddagger\ddagger}_{\text{O}}\]

LSM in this range
Properties of LSM

D too low for single phase cathode
Need electrolyte (YSZ) to provide ionic conductivity and vacancies for oxygen reaction

\[ \Delta H_{k_s}^* = 128 \pm 21 \text{ kJ mol}^{-1} \]

[\text{Sr}] = 0.2

\[ \Delta H_{D_b}^* = 270 \pm 13 \text{ kJ mol}^{-1} \]
Microstructure is very important (particle size, mixing, sintering temperature)
Compatible with YSZ (if A-site deficient)
Good CTE match to YSZ
Lowest operating T about 800°C
“Conditioning” on initial polarization (initial improvement in performance) probably due to changes in surface composition
Oxygen diffusion in TM perovskites

Temperature (°C)

1000          800     700       600           500                400

$D_T$ (cm$^2$/s)

$10^{-16}$  $10^{-15}$  $10^{-14}$  $10^{-13}$  $10^{-12}$  $10^{-11}$  $10^{-10}$  $10^{-9}$  $10^{-8}$  $10^{-7}$  $10^{-6}$  $10^{-5}$

$10^4/T$ (K$^{-1}$)

$La_{0.9}Sr_{0.1}CoO_3$

$La_{0.9}Sr_{0.1}FeO_3$

$La_{0.5}Sr_{0.5}(Mn_{0.8}Co_{0.2})_{0.6}Ni_{0.4}O_3$

$La_{0.6}Ca_{0.4}Co_{0.8}Fe_{0.2}O_3$

$Sm_{0.6}Sr_{0.4}CoO_3$

$Sm_{0.5}Sr_{0.5}CoO_3$

$Sm_{0.5}Sr_{0.5}CdO_3$

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

$La_{0.8}Sr_{0.2}Mn_{0.5}Co_{0.5}O_3$

$La_{0.8}Sr_{0.2}Mn_{0.8}Co_{0.2}O_3$

$La_{0.8}Sr_{0.2}MnO_3$
Co-containing cathodes

O vacancies that give high diffusivity also give high CTE

\[ \text{React with zirconia electrolytes} \]
\[ \text{Need an intermediate barrier layer (e.g. CGO)} \]

\[ \text{Tu et al., Solid State Ionics 117 (1999) 277–281} \]

\[ \text{Ln}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta} \]
Defects in La$_{1-x}$Sr$_x$CoO$_{3-\delta}$

Sr increases conductivity and induces metallic behaviour

Oxygen diffusion in $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_3$ at $p_{O_2}=0.21$ atm

$E_{\text{act}} = 1.84 \pm 0.02$ eV

ALS model for MIEC porous electrode

Effective cathode thickness increases with D and decreases with k and is usually $< 10 \mu m$

\[ l_\delta = \sqrt{\frac{D^*}{k^*}} \frac{(1 - \varepsilon)}{a\tau} \]

"Gerischer impedance"

\[ Z_{chem} = R_{chem} \frac{1}{1 + j\omega R_{chem} C_{chem}} \]

Large chemical capacitance controlled by deviation from stoichiometry, \( c_V \)
(e.g. 1F/cm\(^2\))

\[ t_{chem} = \frac{c_V}{c_O A} \frac{(1 - \varepsilon)}{a} \frac{1}{k^*} \]

\[ C_{chem} = \frac{2F^2(1 - \varepsilon)}{ART} c_V l_\delta \]

\( A \) is a thermodynamic factor for defects and is close to unity

Data for \( \text{La}_{0.6}\text{Ca}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 \) on SDC at 700°C (Adler et al. J. Electrochem Soc., 1996)
Surface exchange in La$_{0.6}$Sr$_{0.4}$CoO$_3$ and Sm$_{0.6}$Sr$_{0.4}$CoO$_3$ at p$_{O_2} = 0.21$ atm

Sensitive to rare-earth cation

Predicted $E_a$ for $R_p = 1.4$eV

Measured is 1.1eV
D* in LSC at 600°C

* Extrapolated from higher T
$k^*$ at 600°C

The graph shows the relationship between $K$ (in cm s$^{-1}$) and Sr doping ($x$) for different materials:

- Red squares: $La_{1-x}Sr_xCoO_{3-d}$
- Blue triangles: $Sm_{1-x}Sr_xCoO_{3-d}$

The data points indicate that high Sr content is needed to achieve certain $k^*$ values.
Low temperature composite cathodes

70% La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_3$
30% Ce$_{0.8}$Gd$_{0.2}$O$_2$
Composite

Esquirol, Kilner and Brandon, Solid State Ionics, 2004
Conductivity of LSC/CGO composites

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE ppm/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO</td>
<td>12.5</td>
</tr>
<tr>
<td>20%LSC/CGO</td>
<td>13.7</td>
</tr>
<tr>
<td>30%LSC/CGO</td>
<td>14.8</td>
</tr>
<tr>
<td>LSC</td>
<td>20.4</td>
</tr>
</tbody>
</table>
Low temperature composite cathodes

50% $\text{Gd}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$
50% $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_2$

Composite

Huang et al. J. Power Sources (2008)
Oxygen surface exchange on thin film cathode materials

Thickness is much less than $D^*/k^*$, so rate is controlled by surface exchange.

$$k = \frac{RT}{4F^2 R_s c_O}$$

- **BSCF** cathodes have excellent initial performance but degrade rapidly in air.
- Surface carbonation forming $\text{BaCO}_3$ is a major problem.

**Dense thin film electrodes**

Cr poisoning

Cr released from steel components as CrO(OH)$_2$ vapour
At cathode this is reduced to Cr$_2$O$_3$: $2\text{CrO(OH)}_2 + 2\text{e}^- \rightarrow \text{Cr}_2\text{O}_3 + 2\text{H}_2\text{O} + \text{O}_2^-$
Reacts with Sr in cathode to give SrCrO$_4$
Need coating on steel to prevent Cr evaporation

I. Vinke, SOFC IX, 2007
“K$_2$NiF$_4$”-structured oxides with oxygen excess


With no Sr or Ba hope to avoid some of the degradation issues
Because defects are oxygen interstitials performance under polarisation is not enhanced (as it is with oxygen deficient oxides)
“K₄NiF₄”-structured oxides with oxygen excess (2)

Performance of LNO cathodes

F. Chauveau et al, ECS Transactions, 25, 2557 (2009)
Final comments on cathodes

• LSM needs ionic conductor (YSZ) to give composite with TPBs and percolating ionic pathways.
  – LSM composites good for higher T (e.g. > 800 C)

• Transition metal perovskites good mixed conductors and some can be used as single phase cathodes
  – E.g. LSCF (with CGO barrier layer) at T > 700 C.
  – Below 700 C needs composite to boost ionic conductivity

• Composites also allow better CTE matching

• In general, the higher the intrinsic activity the lower the stability (chemical and mechanical)
  – High Ba, Sr and/or Co contents bring problems

• Would like better tolerance of Cr, H₂O and CO₂
Thank you for your attention!

Questions on cathodes?
Supports and contact/protective layers
Cell supports

• Requirements
  – Mechanical support for cell structure
  – Sufficient gas transport to electrode (conflicts with previous)
  – Sufficient electronic conductivity
  – CTE match to cell
  – Stable to chemical changes in environment
  – Easy and cheap to manufacture

• Options
  – Anode
  – Cathode
  – Electrolyte
  – Interconnect (metal)
  – Inert material
Anode support (Ni-based)

Advantages
- Popular (e.g. Juelich, Versa, Topsoe)
- Good performance
- Internal reforming

Disadvantages
- Expensive Ni content (but better than cathode support)
- Poor redox tolerance
- C-deposition problems
Anode support (ceramic)

- **Advantages**
  - No redox or C-deposition problems

- **Disadvantages**
  - Poor electronic conduction (difficult current collection)
  - Unreliable impregnation of catalyst
  - Still at research stage
Electrolyte support (e.g. Hexis)

- Advantages
  - Flexible choice for anode
  - Some redox tolerance even with Ni-based anodes

- Disadvantages
  - Limited to high operating T (e.g. 900°C)
  - Fragile
  - Expensive interconnector (e.g. CrFeY)
Metallic support (e.g. Ceres Power, DLR)

- Advantages
  - Mechanically robust
  - Cheap material
  - Good for lower temperatures
  - Easy to seal

- Disadvantages
  - Tricky processing
Inert supported (e.g. LGFCS)

- **Advantages**
  - Cheap material
  - Some redox tolerance

- **Disadvantages**
  - In-plane design has difficult current collection
Need for contact and protective coatings

- Used with metallic interconnects/bipolar plates
- To improve (lower) contact resistance between metal and cathode
  - Target contribution to ASR < 20 mΩ cm²
  - Corresponds to approx. 1% reduction in power density
- To reduce contamination of cathode by Cr-containing vapour evaporating from metal
  - Target for cathode ASR to increase by < 1%/kh
- Applied as a coating(s) on the interconnect on cathode side
Corrosion scales on interconnect alloys

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Ti</th>
<th>Si</th>
<th>Al</th>
<th>Nb</th>
<th>Andere</th>
</tr>
</thead>
<tbody>
<tr>
<td>F18TNb</td>
<td>78</td>
<td>19.4</td>
<td>0.12-0.5</td>
<td>0.12</td>
<td>0.46</td>
<td>0.02</td>
<td>0.17</td>
<td>Mo 1.7</td>
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<tr>
<td>ITM</td>
<td>70</td>
<td>26</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Y 0.06</td>
</tr>
<tr>
<td>Crofer 22APU</td>
<td>Rest</td>
<td>20-24</td>
<td>0.3-0.8</td>
<td>0.2</td>
<td></td>
<td>0.5</td>
<td>0.5</td>
<td>Cu 0.5</td>
</tr>
<tr>
<td>Crofer 22 H</td>
<td>Rest</td>
<td>20-24</td>
<td>0.3-0.8</td>
<td>0.2</td>
<td>0.1-0.6</td>
<td>0.1</td>
<td>0.2-1.0</td>
<td>W 1.0-3; La 0.04-0.2; Cu 0.5; S 0.006</td>
</tr>
</tbody>
</table>

After 1000hrs exposure in air at 800°C all interconnects form a Cr and/or (Cr,Mn) oxide layer

Often there are 2 layers: inner Cr₂O₃ and outer (Mn,Cr)₃O₄ spinel

Evaporation of Cr species poisons cathode

M. Zahid
Protective coatings

Physical properties of spinels

Thermal expansion & conductivity

T. Kiefer, M. Zahid, F. Tietz, D. Stöver, H.-R. Zerfaß,
Electrochemistry, eds.: S. Linderoth et al.,
Roskilde, Denmark (2005), 261-266
Application of Mn-Co-O spinels as protective layer

Figure 2. Interfacial ASR between a LSF cathode and a coated Crofer22 APU interconnect as a function of time at 800°C in air, in comparison with that between a LSF cathode and a bare Crofer22 APU interconnect under the same test conditions.

Electroplated or PVD Co coating on interconnect

Available commercially as Sandvik Sanergy HT

Coatings improve performance

MnCo$_{1.9}$Fe$_{0.1}$O$_4$ protective coating on Crofer 22APU

10000 hrs with constant degradation rate achieved!
Final comments on coatings

• Protective and contact coatings need to be optimised for particular interconnect alloys and cathodes

• Protective coatings
  – Ideally should be dense
  – Should be able to absorb Cr in solid solution
  – Can reduce alloy corrosion rates
  – Should not react to produce insulating phases
  – Transition metal spinels currently favoured for stainless steel interconnects
  – If not used, then need Cr-tolerant cathodes

• Contact coatings
  – Ideally should be porous (compliant)
  – Transition metal perovskites currently favoured
Thank you for your attention!

Questions on supports and coatings?