Control of structure, strain and chemistry: a route to designer fuel cell interfaces
Control of structure, strain and chemistry: a route to designer fuel cell interfaces

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Main objectives of the project

1- Determine surface structure and chemistry of air electrode environment interfaces under operating conditions

2- Relate catalytic activity to surface structure and cation segregation effects

3- Probe strain and structure at *buried* interfaces (electrolyte/electrode)

4- Design and manufacture electrode structures with 2D and/or 3D engineered interfaces
Control of structure, strain and chemistry: a route to designer fuel cell interfaces

**Work Package 1 (WP1) – Cathode/Environment interfaces**

Analyse the factors governing the catalytic activity of both TPB and MEIC air electrodes as *bi-functional catalysts*

**Work Package 2 (WP2) – Electrode-Electrolyte: towards understanding buried interfaces in devices**

Explore the link between the transport processes detailed in WP1 and the assembly of tailored microstructures (WP3)

**Work Package 3 (WP3) – Engineered 2D and 3D Interfaces**

Offer new routes and alternate/improved cell morphologies
Control of structure, strain and chemistry: a route to designer fuel cell interfaces

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WP1: Cathode interfaces: \( \text{SrCoO}_{3-\delta} \) polymorphs

Synthesis via a citrate route. Highly reactive precursors calcined at 900 °C

*Slow cooling*  Hexagonal phase (H) \( \text{Sr}_6\text{Co}_5\text{O}_{15} \)

- Outstanding performance of the cubic phase
- Need to stabilise cubic phase at room temperature without detrimental of transport properties

De la Calle *et al.* Solid State Comm 2008 (10) 1924
Tailoring properties with subtle changes in the composition

Slight doping on the cobalt positions \( \text{SrCo}_{1-x}\text{B}_x\text{O}_{3-\delta} \) (\( B = \text{Sb, Mo} \) and \( x = 0.05, 0.1, 0.15 \) and 0.2) allow the stabilization of a perovskite 3C-arrangement.

Change of symmetry form tetragonal to cubic for \( x<0.2 \)
Tailoring properties with subtle changes in the composition: thermal expansion

Regular variation of the thermal expansion along the $\text{SrCo}_{1-x}\text{Sb}_x\text{O}_{3-\delta}$ ($0.05 \leq x \leq 0.2$) series without the presence of the abrupt changes observed in the undoped compound.
Tailoring properties with subtle changes in the composition: electrical conductivity

Increase of the electrical conductivity at intermediate temperatures ($T \leq 800 ^\circ C$) due to the stabilization of a 3D perovskite-like structure at RT

The highest conductivity value is presented by the $x = 0.05$ sample, reaching a maximum of 505 S·cm$^{-1}$ at 400 °C

J. Power Sources, 192, 132, 2009
Strained materials: Can we tune the surface defect structure of the catalysts?

In order evaluate the effect of the surface composition under operation condition thin films of these materials were grown under different strains.

**Tensile strain:**
substrate lattice parameter > thin film lattice parameter

**Compressive strain:**
substrate lattice parameter < thin film lattice parameter

SrCo$_{0.95}$Sb$_{0.05}$O$_{3-d}$ was chosen as optimum material from bulk studies.
SrCo$_{0.95}$Sb$_{0.05}$O$_{3-\delta}$ thin films: Strain tuning

**Graphical Representation:**

- **Compressive Strain:**
  - MgO
  - LSGM
  - STO
  - LSAT
  - NGO
  - LAO
  - GDC
  - YSZ

- **Tensile Strain:**
  - MgO
  - LSGM
  - STO

**Intensity (counts) vs. 2Theta (°):**

- Thickness = 30nm
SrCo$_{0.95}$Sb$_{0.05}$O$_{3-\delta}$ thin films: Strain tuning

- In-plane tensile
- In-plane compressive

STO (103)
LSAT (103)
NGO (103)
SrCo$_{0.95}$Sb$_{0.05}$O$_{3-\delta}$ thin films: AFM
SrCo$_{0.95}$Sb$_{0.05}$O$_{3-\delta}$ thin films: Anisotropic strain
SrCo$_{0.95}$Sb$_{0.05}$O$_{3-\delta}$ thin films: Electrical conductivity

- SCSO/STO in-plane tensile
- SCSO/NGO in-plane compressive
- Strain effect on the electronic conductivity
- SCSO/LSAT different activation energy $E_a$ of the electrical conductivity - effect of tetragonality?
- Possible under-stoichiometry of Sb in the thin film
WP2-Buried interfaces: polar and non polar terminations

LaAlO$_3$

n-type; metallic

p-type; insulating
WP2-Buried interfaces: Low energy ion scattering

\[ E_f = f(M_0, M_1, \theta) \times E_i \]

(a) Ion yield (a.u.)

(b) Area \(\text{Area}_{\text{La}}/\text{Area}_{\text{Al}}\) vs. temperature (°C)

Energy (eV)
WP2-Buried interfaces: crystal truncation rods

\[
F_{\text{sum}} = F_{\text{bulk}} + F_{\text{surf}}
\]

\[
F_{\text{bulk}} = \sum_{j=-\infty}^{0} F_{u} e^{2\pi i j} e^{j\alpha} = F_{u} \frac{1}{1 - e^{-2\pi i} e^{-\alpha}}
\]

\[
F_{u} = \sum_{j} f_{j} e^{\frac{B_{j} Q^{2}}{16\pi^{2}}} e^{2\pi i (hx_{j} + ky_{j} + lz_{j})}
\]

\[
F_{\text{surf}} = \sum_{j} f_{j} \theta_{j} e^{\frac{-B_{j} Q^{2}}{16\pi^{2}}} e^{2\pi i (hx_{j} + ky_{j} + lz_{j})}
\]
WP2-Buried interfaces-CTR different reciprocal lattice indices
WP2-Buried interfaces

- Fraw
- Bulk-Al terminated
- Bulk-La terminated
- Refined surface occupancy
- Optimised fit - relaxation and occupancy
WP2-Buried interfaces

![Diagram showing molecular structures and plots for RT, 10^{-10} Torr and 600°C, 10^{-10} Torr conditions. The plots display Δz values against nominal z-position (unit cell) for different temperatures and pressures, with La, Al, and O elements indicated.]