Computationally Guided Design of MULTIPLE Impurities Tolerant Electrode

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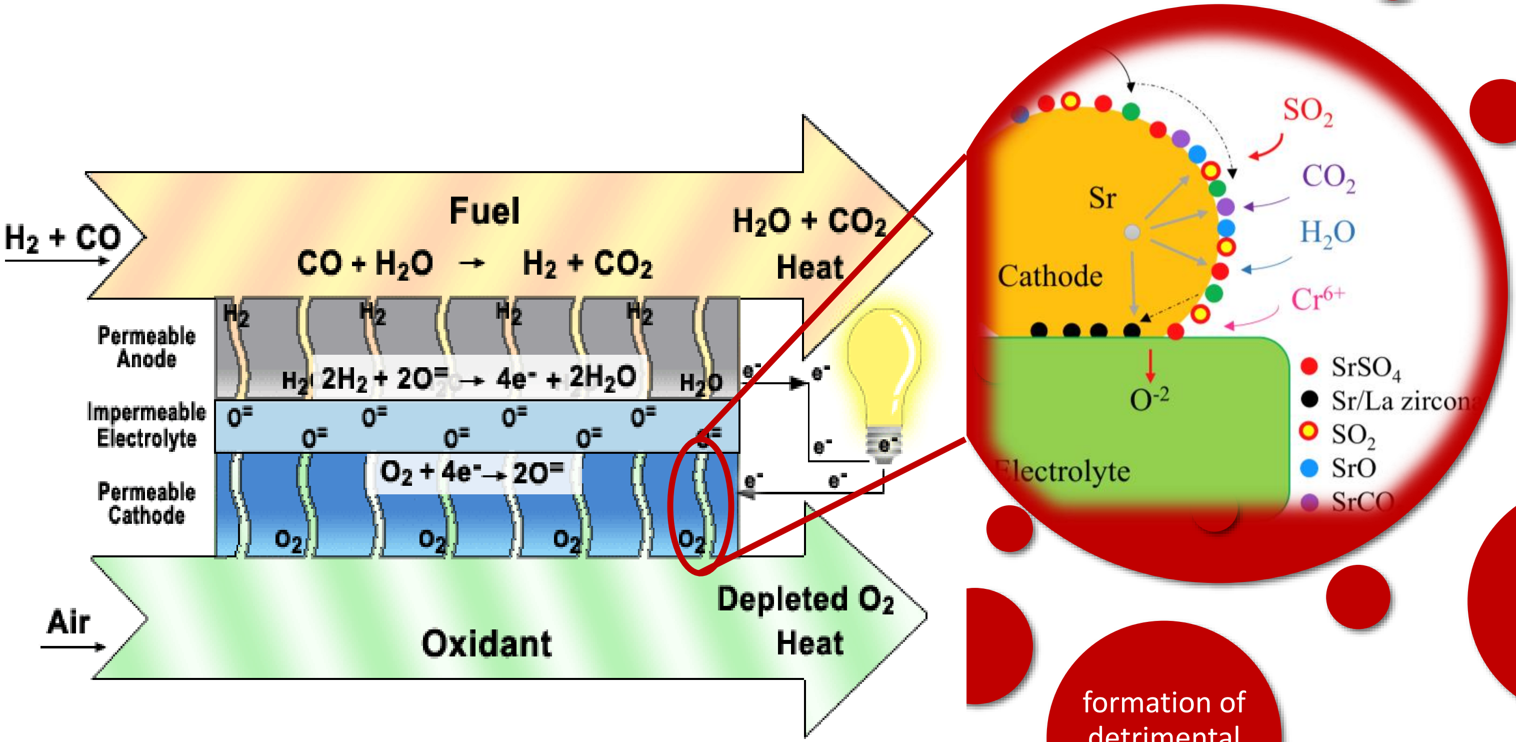
Introduction



compositional, morphological, and crystal structure changes

Activation, ohmic polarization changes

formation of detrimental phases

SOFC Development

Decreasing Activation Polarization by Maximizing the Rates of the ORR Reaction

Materials Compositional Design

Reducing Long-term Degradation due to the Effect of Single Air-contained Impurity

External Impurity Getter

GOAL:
Develop The Cathode Material with

1. **High Initial Power Density**
2. **Low Long-term Degradation Rate**

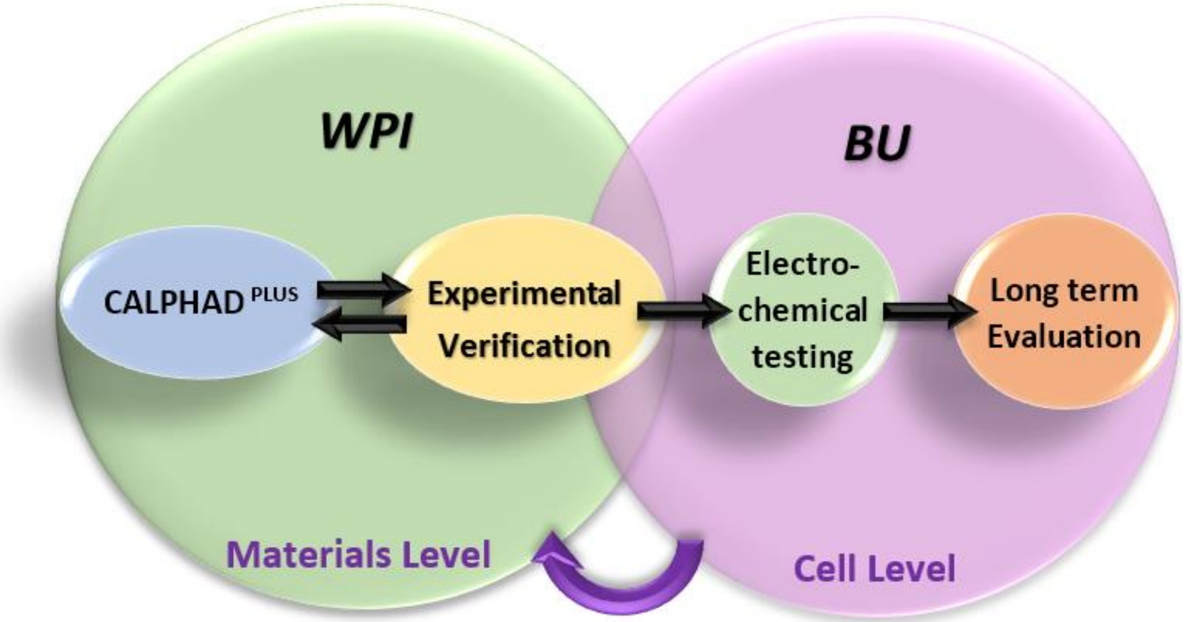
CURRENT LIMITATIONS with Trial-and-Error Approach:

- **Characterization Detection of Nano-sized Secondary Phases**
- **Difficulty of Doing In-situ or In-operando Observation**
- **Detailed Reaction Mechanism Verification (Is it valid to do Accelerated Test?)**
- **Real Impacts of Multiple Gas Species on Cell/Stack Performance**

Novel Integrated Approach and Objectives

Phase I:

- Achieve the highest power densities of 1.5W/cm^2 at 800ºC
- Achieve a degradation rate of 0.4%/1000hrs under realistic operating conditions with simultaneously present, MULTIPLE impurities at the cell level.



Phase II:

- Achieve a degradation rate of 0.1%/1000hrs at the stack level

Tasks and Deliverables

Task 1. Project Management and Planning (Zhong)

Task 2. Literature Review of Existing Experimental Data (Zhong)

Task 3. CALPHAD^{PLUS} simulations (Zhong)

- Subtask 3.1 Simulations of cathode stability under various gas impurities
- Subtask 3.2 Simulations of cathode/electrolyte chemical compatibilities
- Subtask 3.3 Simulation of cathode point defect chemistry and electrical transport properties (ionic and electronic conductivities)

Task 4. Materials synthesis and electrical properties (Zhong & Gopalan)

- Subtask 4.1. Materials synthesis
- Subtask 4.2. Chemical stabilities under various gas impurity conditions
- Subtask 4.3. Electrical Conductivity and Conductivity Relaxation Experiments

Materials Level

Task 5. Fabrication of Single Cells Using the proposed cathode (Gopalan)

Task 6. Electrochemical Testing and Polarization Modeling (Gopalan)

- Subtask 6.1 Electrochemical testing
- Subtask 6.2 Polarization Modeling PLANNED

Task 7. Long-term degradation test (Gopalan) PLANNED

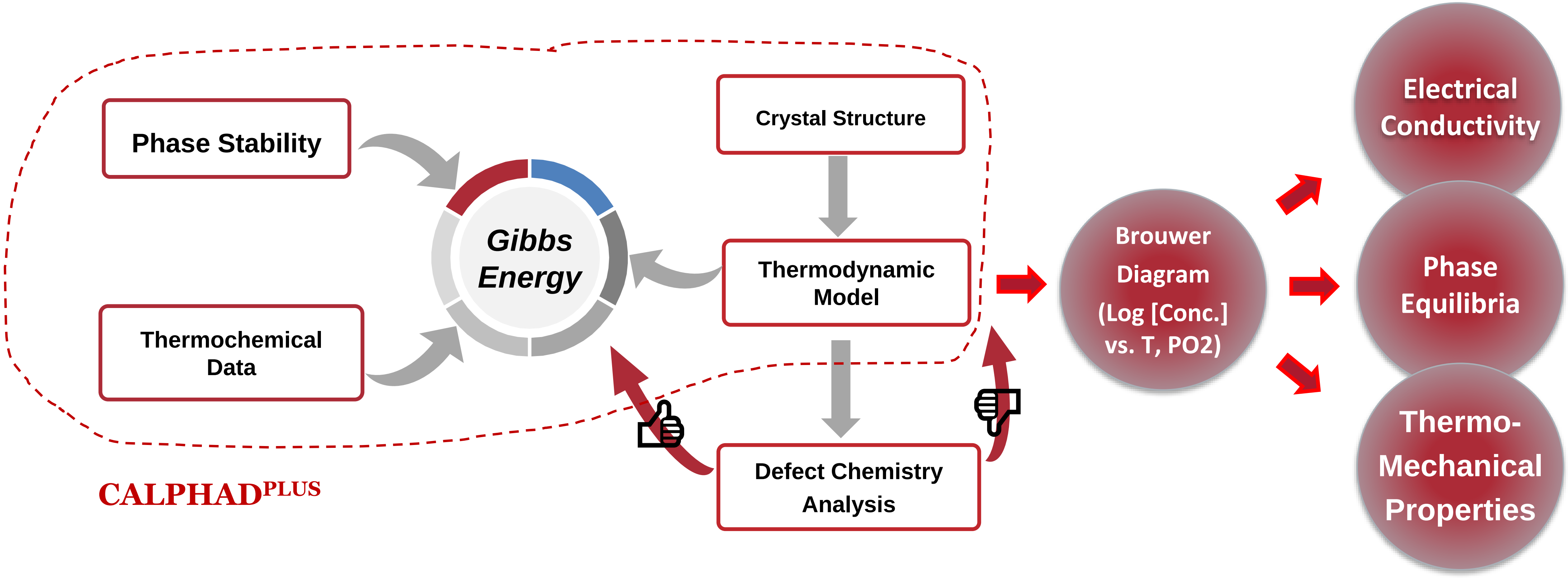
Cell Level

Materials Level Research

- Phase Stability (Thermodynamic Investigation)

- Microstructure (Core-shell structure)

CALPHAD^{PLUS} Approach



Experimental procedures

Pre-sinter

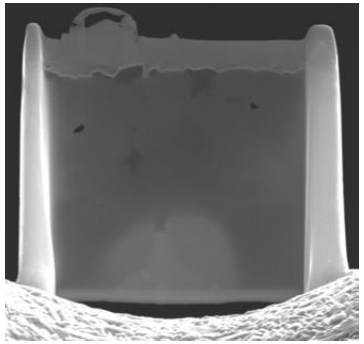
Press

Soaking under different impurities

XRD

SEM

FIB

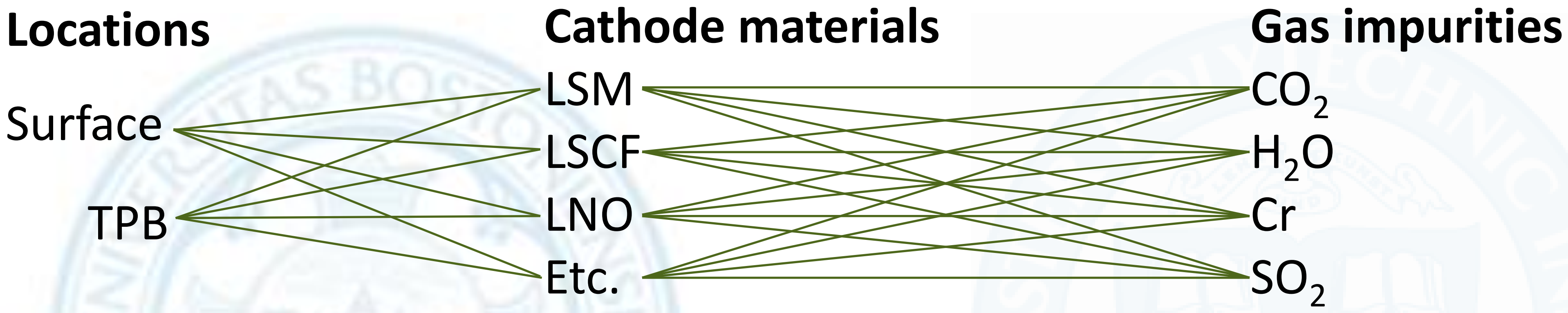


TEM

CALPHAD[*PLUS*]+experimental Investigation

Thermodynamic Databases

- Database Focusing on Perovskite/R-P phases
- Database Expanded to Consider Gas Impurities



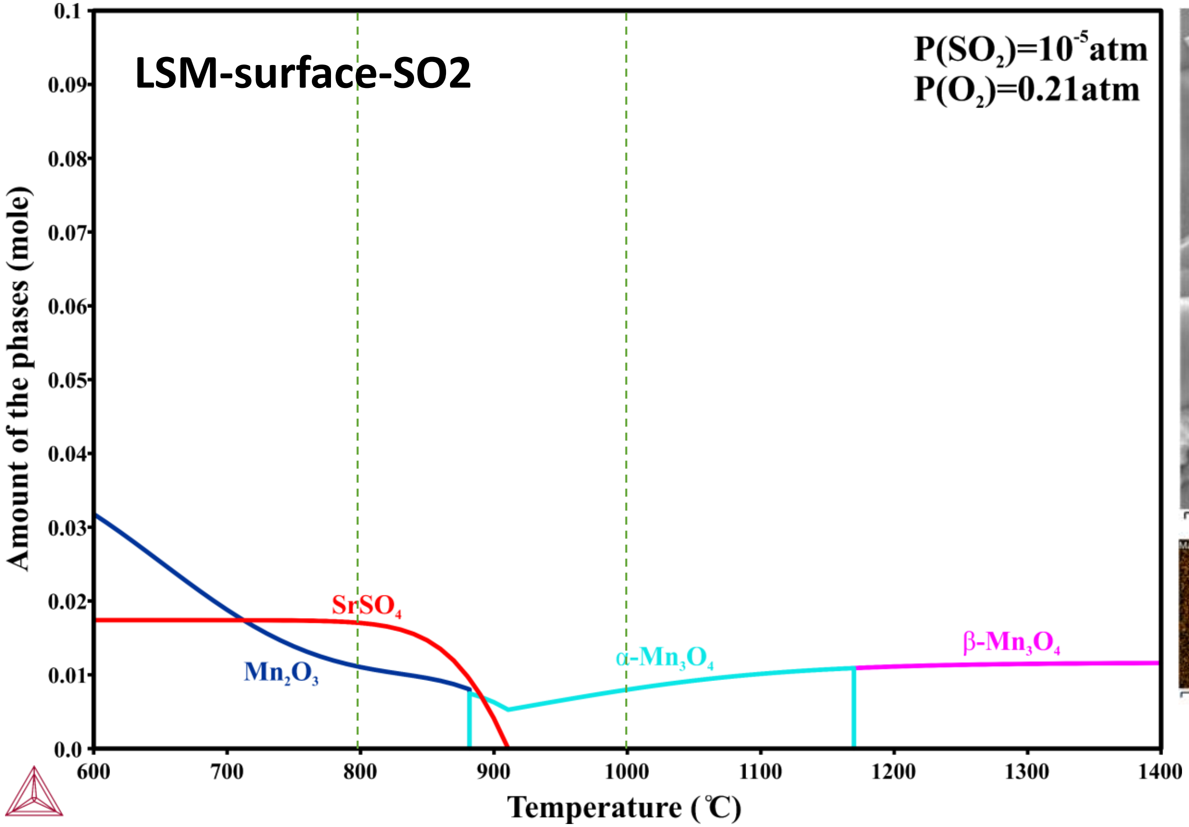
Multiple Impurities

Cr $+H_2O$

SO_2 $+Cr+H_2O$

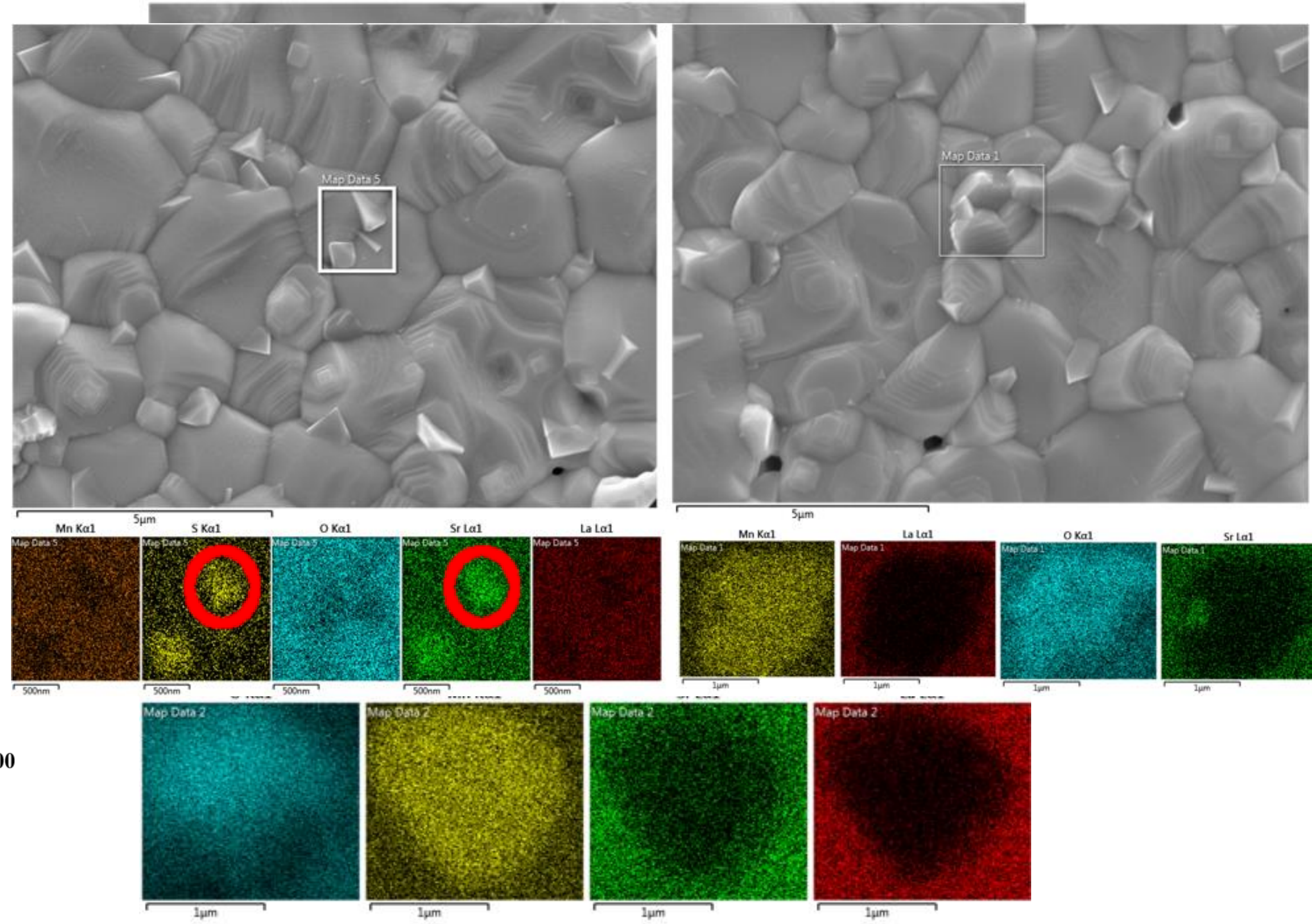
SO_2 $+Cr+H_2O+CO_2$

Example of Thermodynamic Investigation



LSM at 800℃ for 2 days with 10ppm SO_2+Dry air

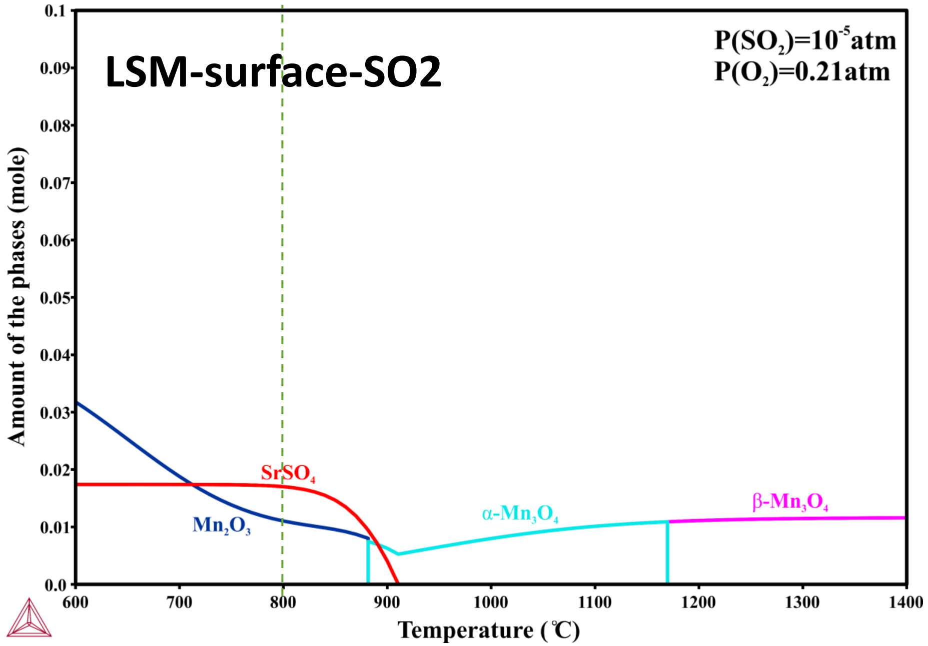
LSM at 1000℃ for 2 days with 10 ppm SO_2 + Dry air

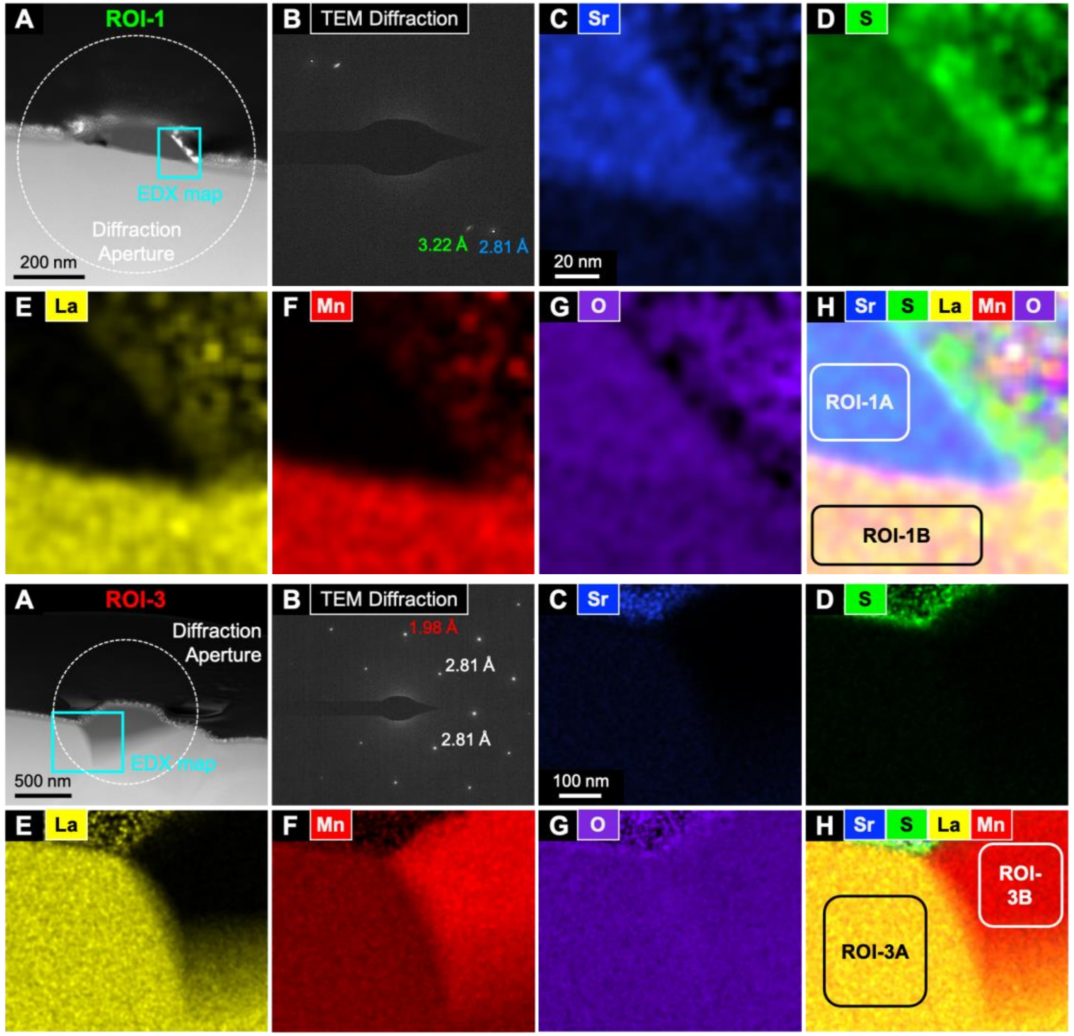


SrSO4 will form at lower temperature condition. And the threshold can be well predicted through CALPHAD.

There is no signal of sulfur element on the surface of the entire sample.

Example of Thermodynamic Investigation



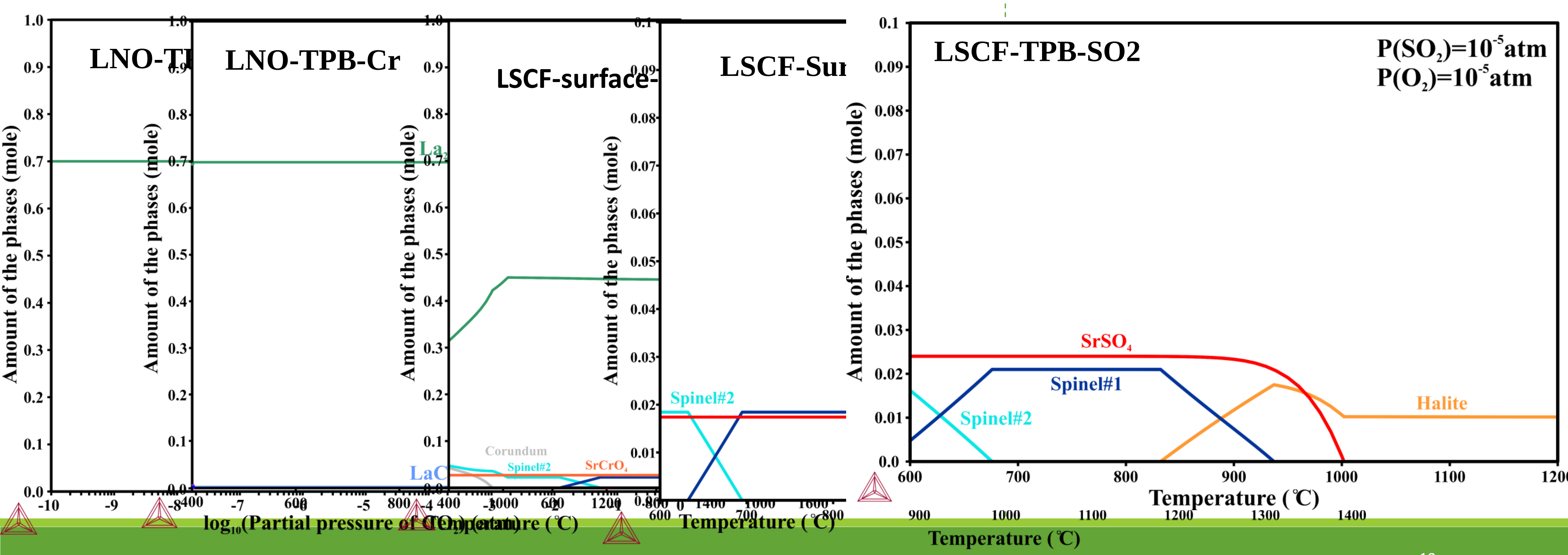


SrSO4

Mn2O3

Additional Examples

Both surface and TPB were considered



Conclusions from Thermodynamic Investigations

The impact from single impurity:

Impurity	impact
CO_2	No impact to LNO No reaction with LSM at operation temperature, but $SrCO_3$ may form during thermal cycles LSCF has worst CO_2 resistance
Cr	LSCF: $SrCrO_4$ prefers to form on the surface LSM: Cr preferred to react with Mn LNO: no impact on TPB, but will decompose on the surface
H_2O	It is mainly helping increasing the Cr gas species concentration
SO_2	LSCF: LSCF has bad S tolerance LSM: S prefer to react with Mn on the surface LNO: very sensitive to S

The impact from multiple impurities

The reaction under SO_2+Cr can be different from which under single impurities

Accelerated stress tests (AST)

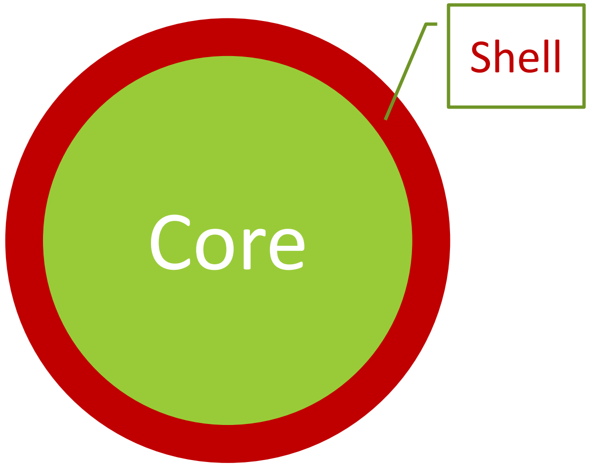
The reaction mechanism under AST and real operation condition may be different

Core-Shell Microstructure

Molten salt synthesis (MSS) is being pursued to synthesize core-shell structures of cathode materials; the goals are two-fold

- High performance
- High tolerance to attack by Cr-impurity from ferritic stainless steel interconnect

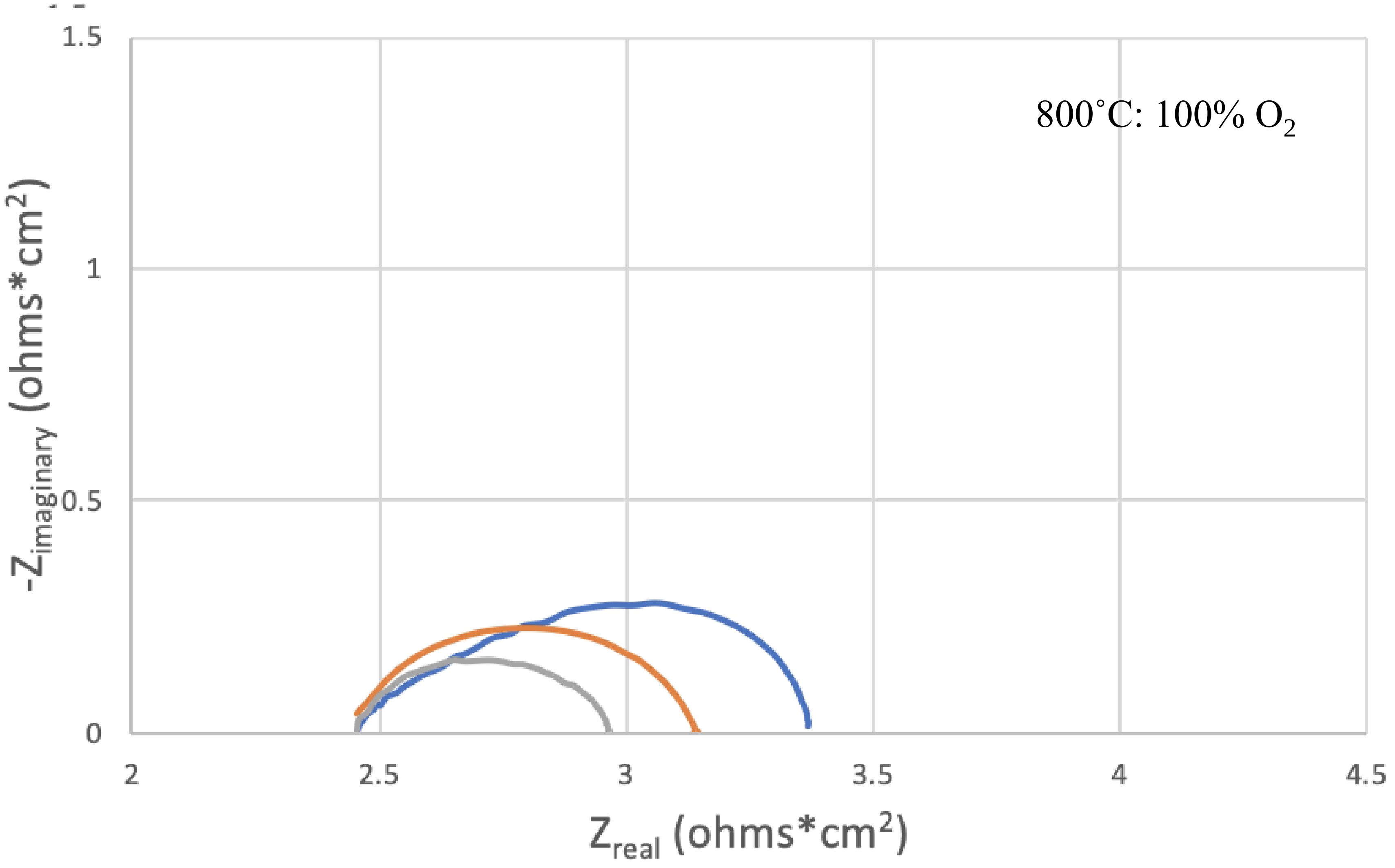
The core materials are excellent MIECs such as LSCF and LNO; and the shell materials we want to explore are LSM (for high performance) and LSCr (for high Cr-impurity tolerance)



Experiments to date

- LSCF (core) – LSM (shell) [Core-Shell nanoparticles or CSNP]
  - Symmetrical cells of the configuration LSCF (core) – LSM (shell)/GDC/ LSCF (core) – LSM (shell) and LSCF/GDC/LSCF have been fabricated
  - Impedance spectra of these cells have been obtained as a function of temperature and oxygen partial pressure
  - Significant reductions in electrode polarization were observed in electrodes featuring the core-shell electrodes compared to standard LSCF electrodes
- A new method using the molten salt method has also been developed which coats the LSCF surface continuously (invention disclosure filed)
  - Symmetrical cells of the configuration LSCF – LSM [new method]/GDC/ LSCF – LSM [new method]
  - The new coating method results in even more significant polarization reductions

Impedance Tests



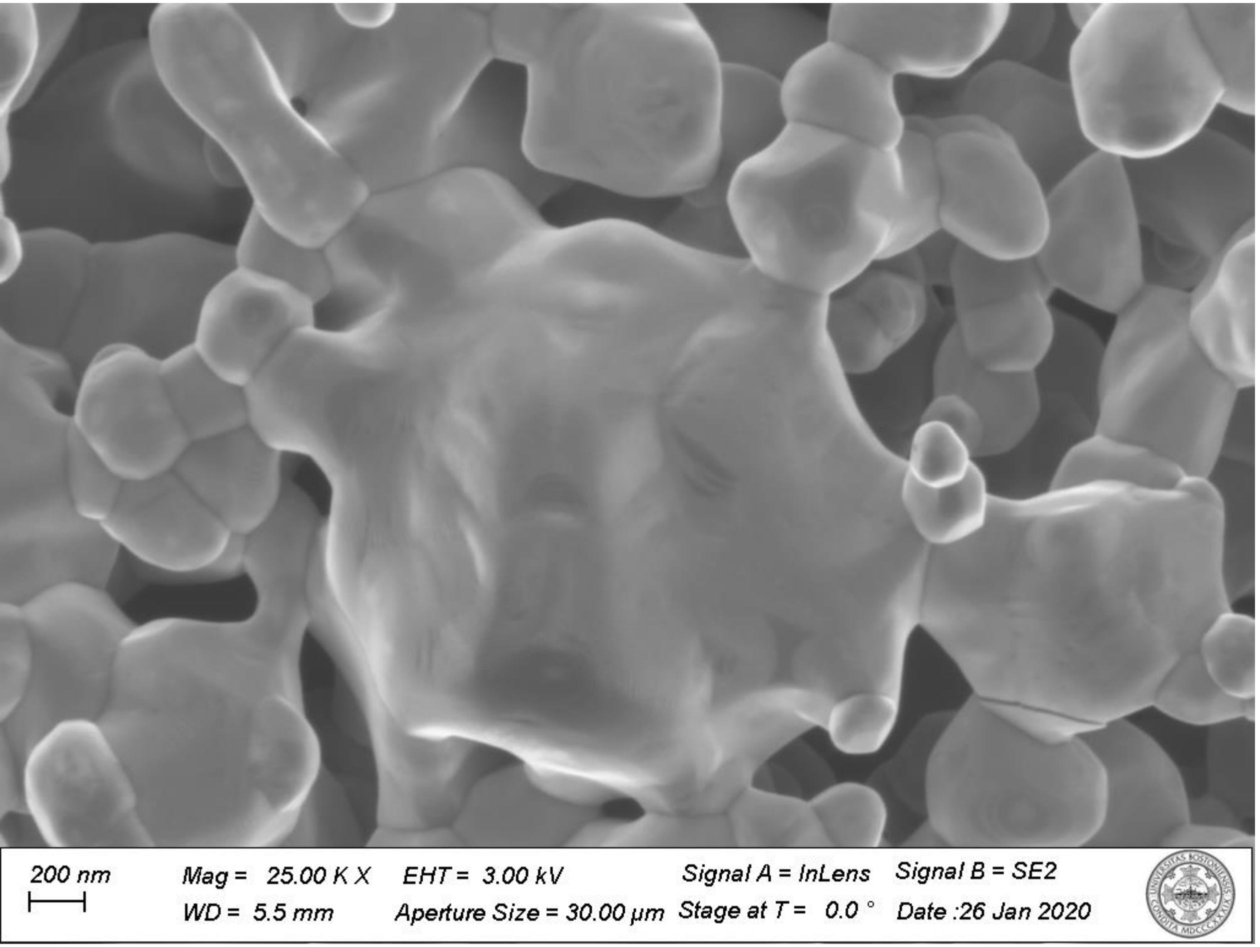
Blue: LSCF-baseline

Orange: 3:1 mass ratio LSCF-LSM CSNP

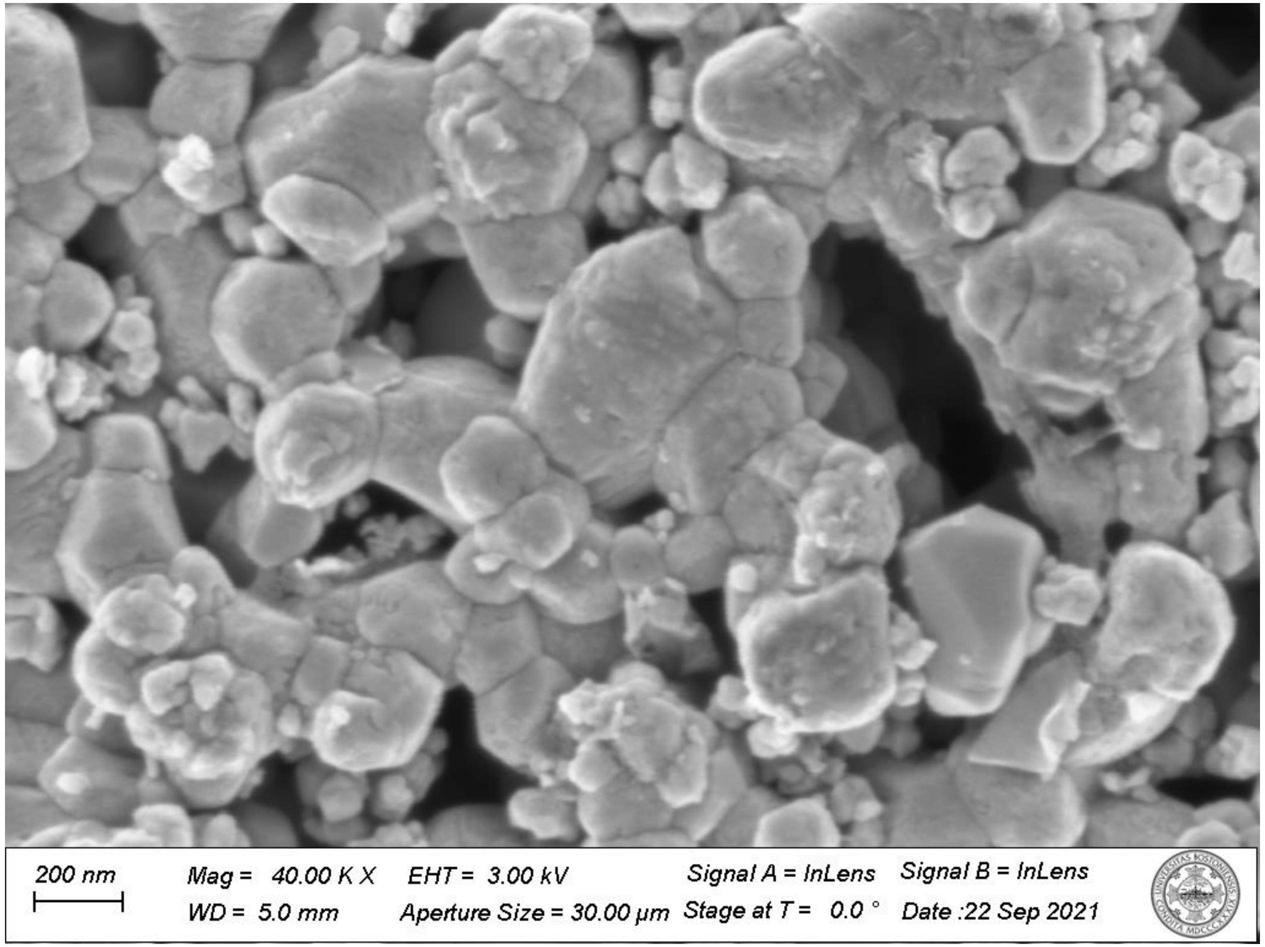
Gray: New Method

Sintered Substrate compared to New MS Method

Substrate (LSCF)



New Method (LSCF coated with LSM)



Summary and Future Work

1. The impact of single impurity and multiple impurities to the cathode surface and TPB was systematically investigated with *CALPHAD*^{PLUS} and thermodynamic experiments
2. The accelerated stress tests may have different mechanism than the real operation.
3. Core-shell nanoparticle electrodes prepared with two different molten salt synthesis result in significantly reduced polarization resistances.
4. Cells of the type Stainless steel current collector/LSCF (Core)-LSCr (Shell) /GDC/ LSCF (Core)-LSCr (Shell)/Stainless steel current collector will be fabricated
5. The impedance spectra of such cells will be obtained as a function of temperature and oxygen partial pressure
6. We also plan to apply a constant DC current to these cells and investigate the polarization of the cells over 500 h

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Thank you !