# AOI 2: Modularization of Ceramic Hollow Fiber Membrane Technology for Air Separation

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# Project Description and Objectives

## Objective of project

- *Develop membrane stack and module for air separation and oxygen production using ceramic hollow fiber membrane technology*

## Strategic alignment of project to Fossil Energy objectives

- **Cost of Energy and Carbon Dioxide (CO2) Capture**
  - Pure oxygen instead of air for combustion of power plant produces CO2, no need to separate nitrogen from down stream;
  - Reduce the cost and simplify the system for CO2 capture.
- **Power Plant Efficiency Improvements**
  - Pure oxygen instead of air increases efficiency of power plant;
  - Cost-effective, reliable technologies to improve the efficiency of coal-fired power plants.

# Project Description

## Status at beginning of project

- Single membrane fabrication and performance testing;
- Single membrane design with traditional architecture, material system, and microstructure;
- No stack/module designs with traditional single membrane cells.

**Technology benchmarking (for air separation and oxygen production)**

- Cryogenic distillation;
- Pressure swing adsorption;
- Ceramic permeation membrane;
  - Simple system: dense mixed conducting membranes;
  - Producing high purity oxygen from air;
  - Economically competitive technology.

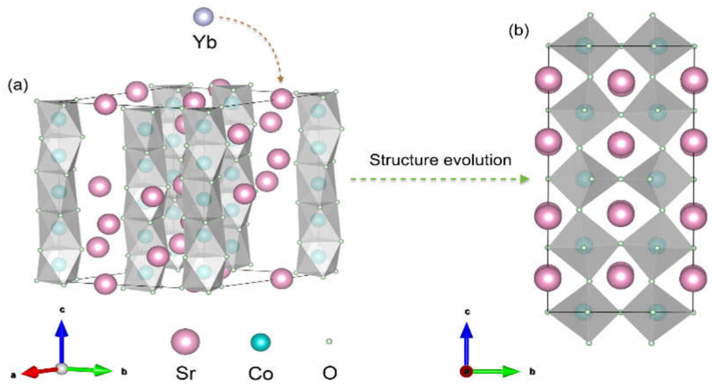
# Current Status of project

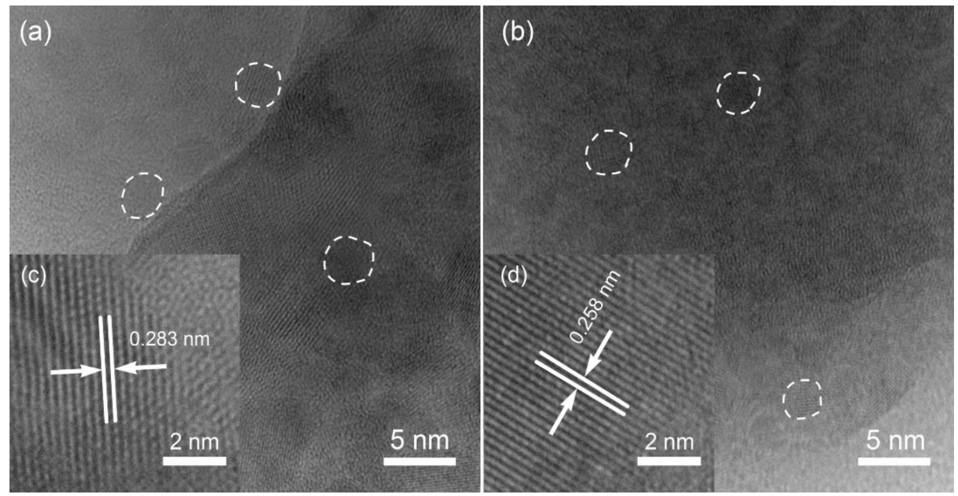
- New membrane design with novel architecture, material system, and microstructure:
  - ✓ Developed new membrane functional materials;
  - ✓ Determined material for device substrate;
  - ✓ Developed and optimized process for membrane device fabrication;
  - ✓ Performed preliminary oxygen permeate test.
- Finished tasks 2.1, 2.2, and 3.1
- No change of project goal/objectives;
- Market need: in addition to coal-fired power plants, oxygen has wide applications in industries

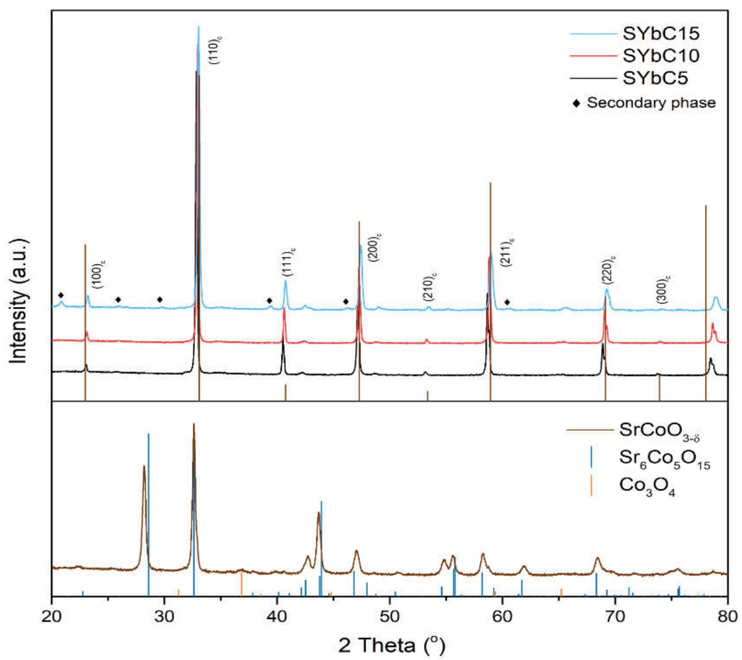
# Conferences attended and publications

- "Fabrication and characterization of an asymmetrical hollow fiber membrane for air separation and oxygen production", 4$^{th}$ Global Congress & Expo on Materials Science and Nanoscience, Amsterdam, Netherlands, Oct. 2018. (invited talk)
- "An asymmetrical hollow fiber membrane for oxygen permeation", Collaborative Conference on Materials Science and Technology, Beijing, China, Sept. 2018. (invited talk)
- *Journal of The Electrochemical Society*, 165 (13) F1032-F1042 (2018).
- *Journal of Solid State Electrochemistry*, 2018, 22:2929-2943.
- *Journal of Materials Chemistry A*, 2020 8 (20), 10450-10461.
- *ACS Applied Energy Materials*, 2020, 3, 2, 1831-1841.

# Mixed conducting membrane materials

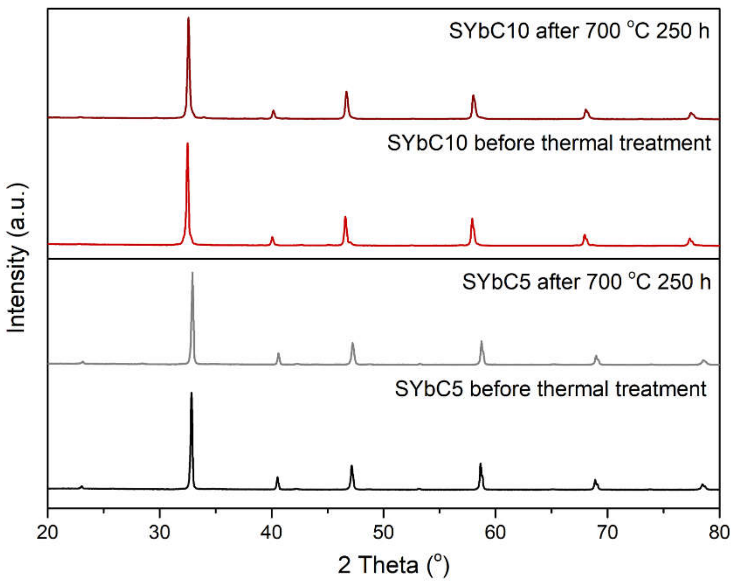


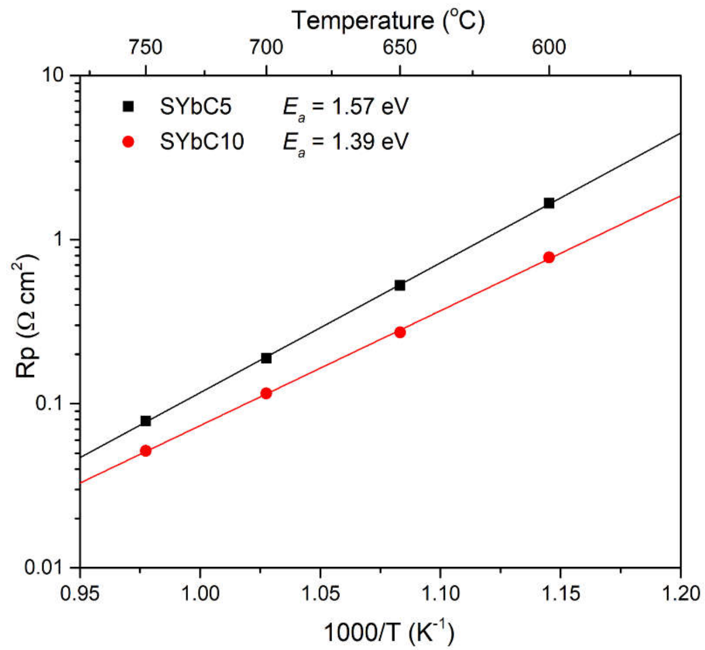




- $SrCoO_{3-\delta}$ is a good mixed conductor;
- Very complicated secondary phases are formed during synthesis process; difficult to obtain pure phase;
- Partial substitution of Sr by Yb may effectively stabilize the material phase, exhibiting a higher symmetrical perovskite phase.

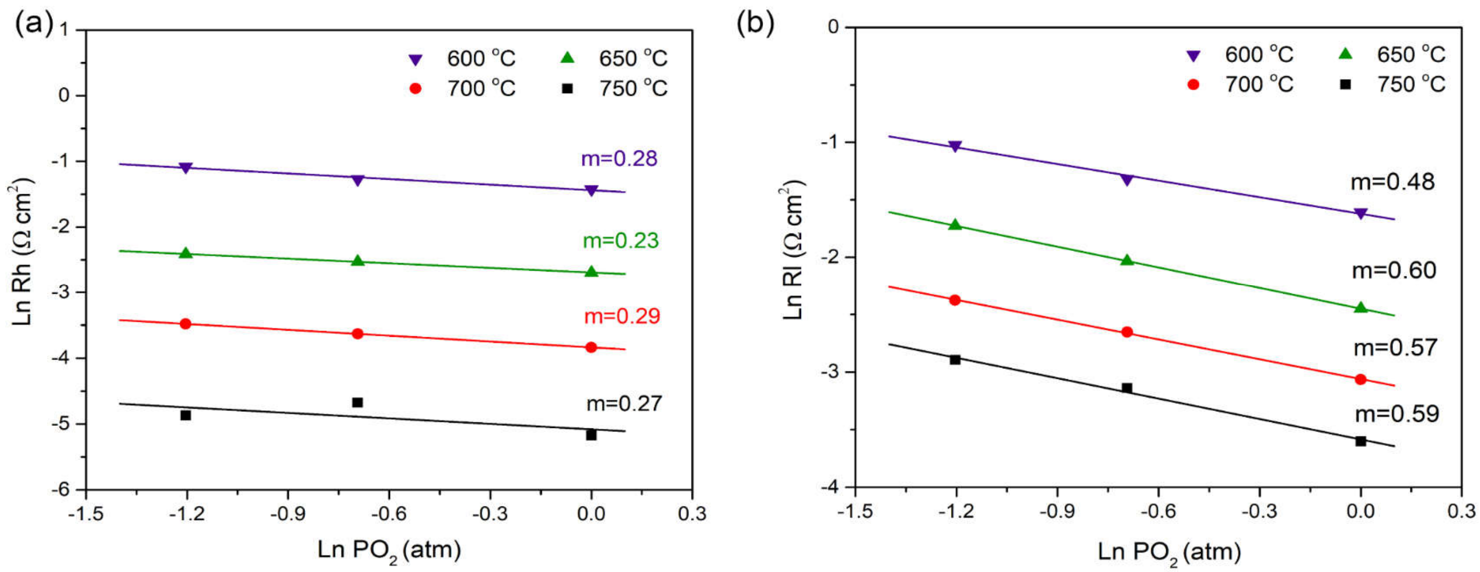
# Mixed conducting membrane materials




- Thermal stability of the materials
  - Both SYbC5 and SYbC10 demonstrated excellent thermal stability.
  - Polarization resistance for surface oxygen exchange decreases with increasing temperatures (thermal activation process).
  - Increasing Yb dopant from 5 mol% to 10 mol% resulted in a decrease in activation energy of the process;

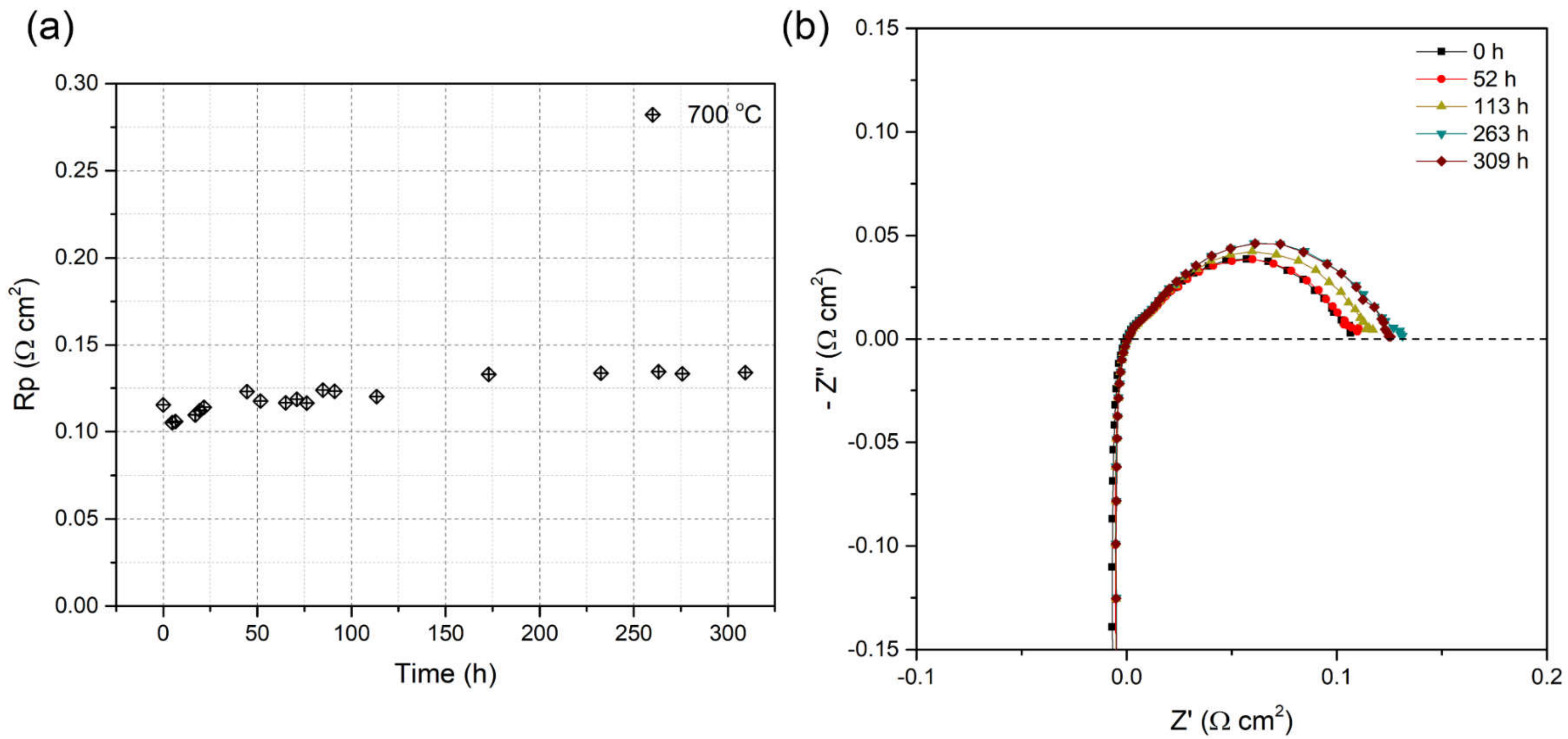
# Mixed conducting membrane materials




- Surface adsorption: $O_{2,g} \leftrightarrow O_{2,ad}$;
- Dissociation: $O_{2,ad} \leftrightarrow 2O_{ad}$;
- Charge transfer: $O_{ad} + 2e^{-} + V_{O}^{\cdot\cdot} \leftrightarrow O_{O}^{\times}$;
- Reaction order: (a) close to 0.25, charge transfer process (high frequency process);
- Reaction order: (b) close to 0.5, primarily contributed by dissociation (low frequency process)

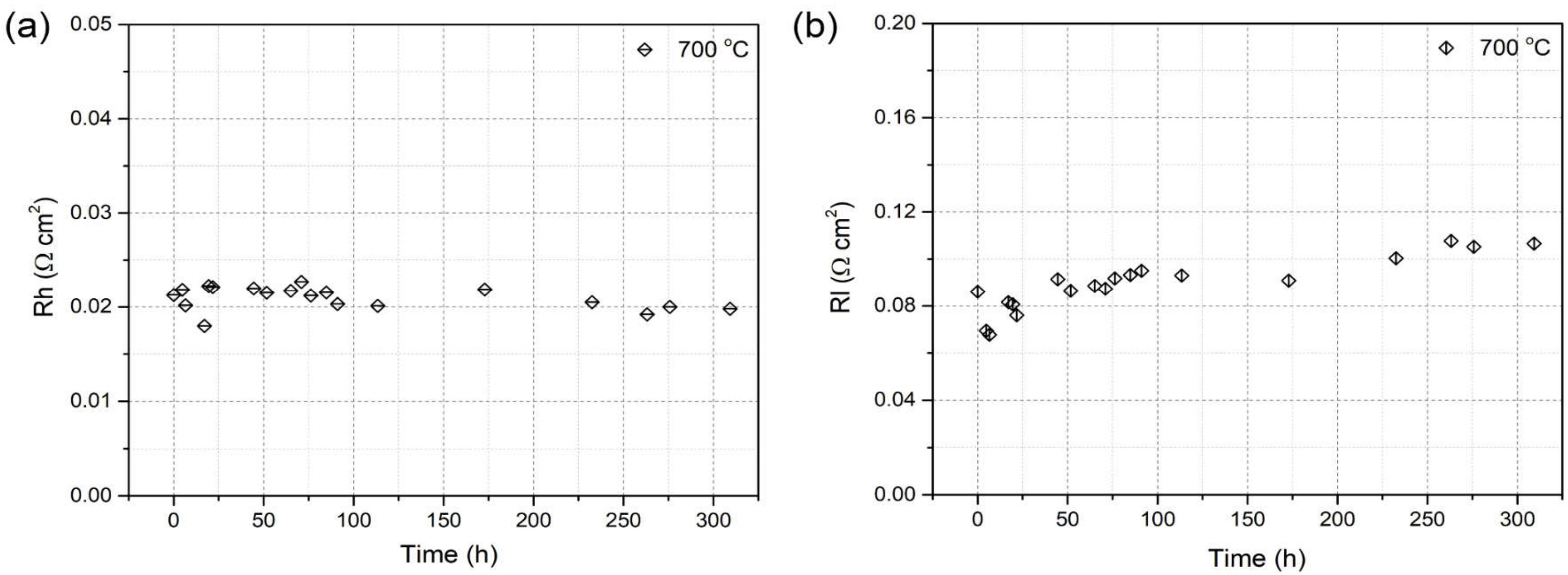
- Limiting steps of surface exchange processes
  - (a) high frequency charge transfer process;
  - (b) low frequency molecular dissociation process;

# Mixed conducting membrane materials



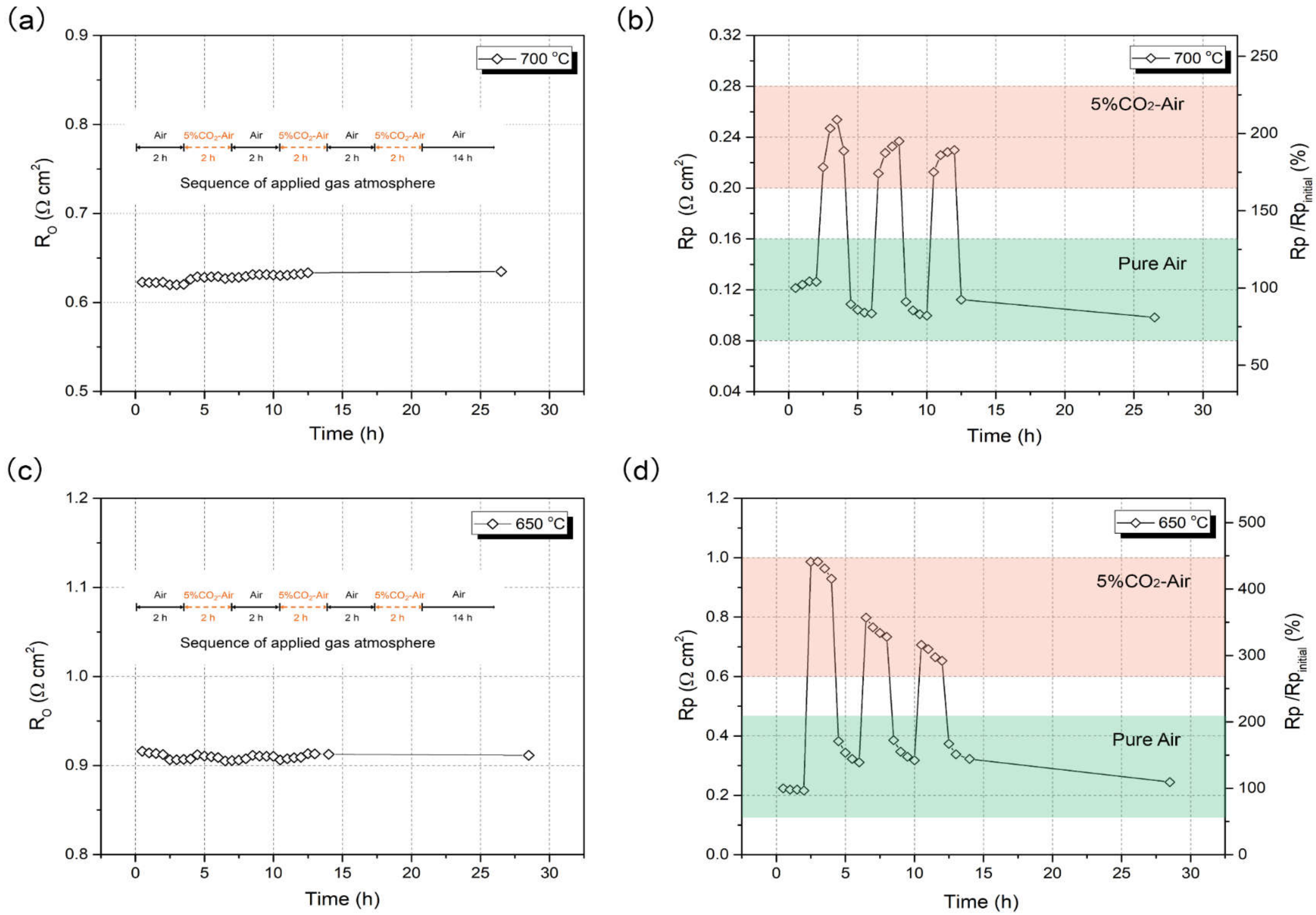

- Durability test was carried out using a symmetrical cell with SYbC10 electrode at 700 °C in air for ~ 300 h;
- Polarization resistance $R_p$ fluctuates in the first 50 hours, then increases a little bit between 50 and 175 h. Beyond 175 h, $R_p$ gradually approaches an equilibrium state.

# Mixed conducting membrane materials




- $R_h$: scatters in the 1st 100 hrs, but gradually stabilizes (to a value a little bit lower than those recorded at the start of the test).
- $R_l$: fluctuates in the 1st 25 hrs, and stabilizes around 300th h;
- $R_h$ : associated with charge transfer process (oxygen anion formation and incorporation into vacancy). In the 1st 100 hrs, reorganization and stabilization of surface vacancy distribution; beyond 100 hrs, surface vacancy and electronic structure stabilize.
- $R_l$ : related to dissociation process of adsorbed O2. Surface Sr segregation leads to certain change of surface catalytic property (1st 25 hrs, a small amount of surface Sr segregation; beyond 25 hrs, surface Sr segregation reaches an equilibrium state)

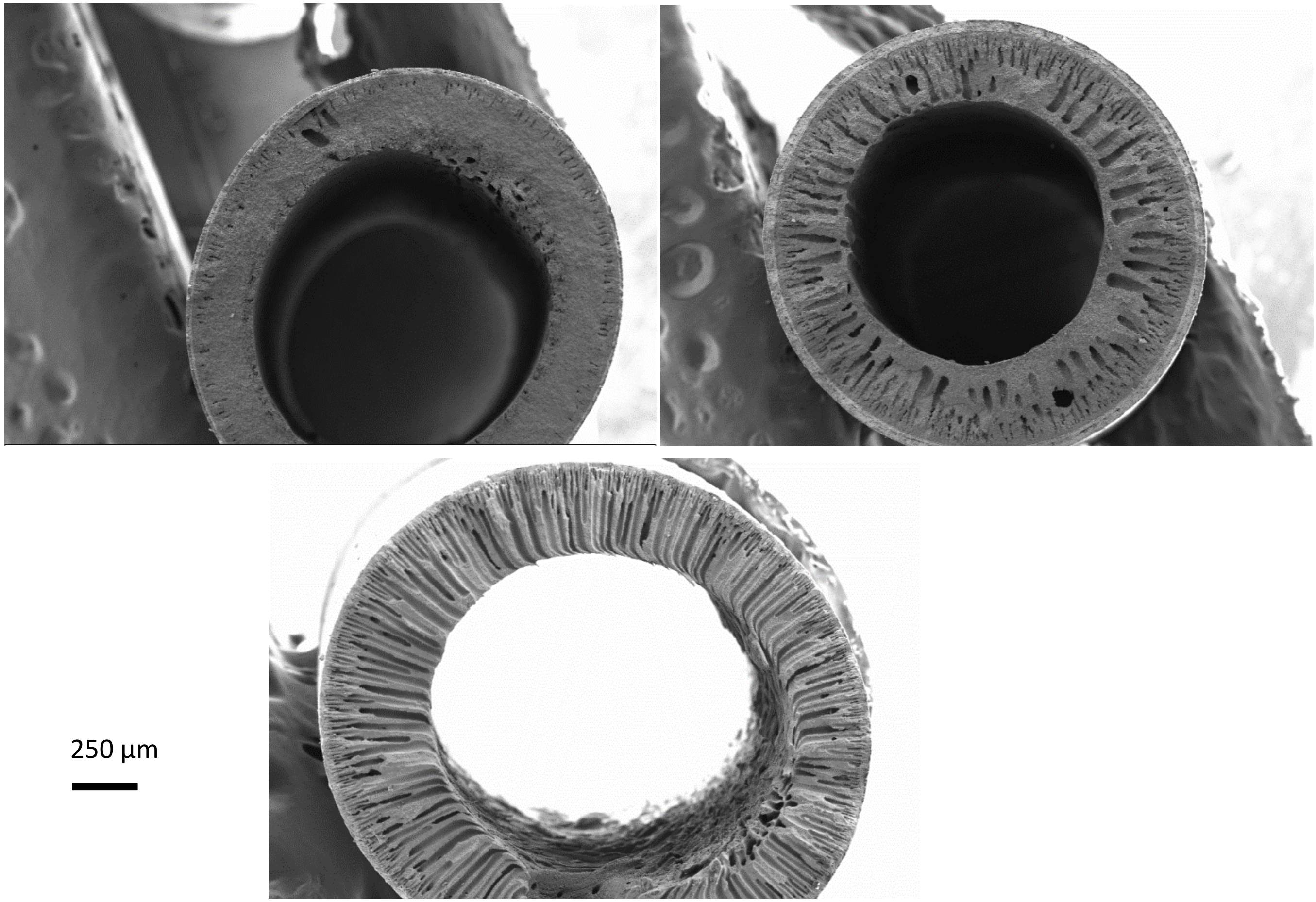
# Mixed conducting membrane materials




Stability in CO2 containing air: cycling between pure air and 5% $CO_2$-air

- Ro is stable, only shows a bit thermal aging process; Rp sensitive to CO2 but reversible;
- Due to adsorption/desorption of surface carbonaceous species and reversible reactions .

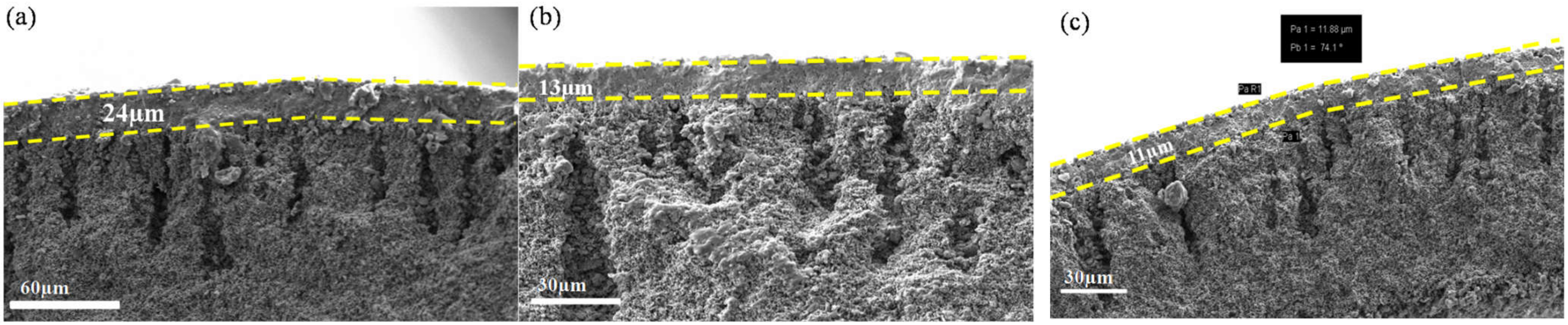
# Fabrication of hollow fiber membrane

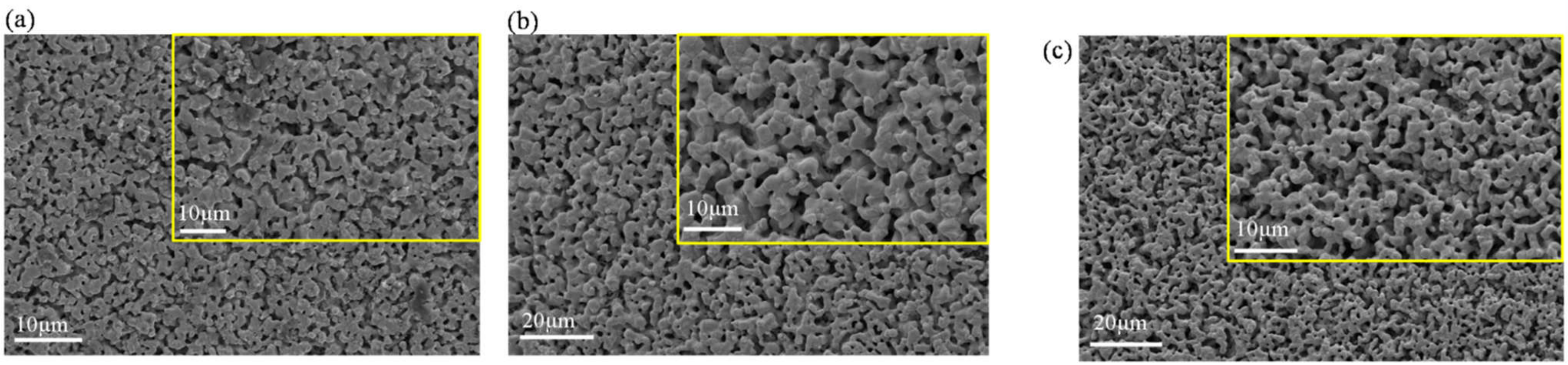



Fabrication of hollow fiber substrates :

- Process optimization
- Radially well-aligned micro-channels, open at the inner surface for facile gas diffusion

# Fabrication of hollow fiber membrane

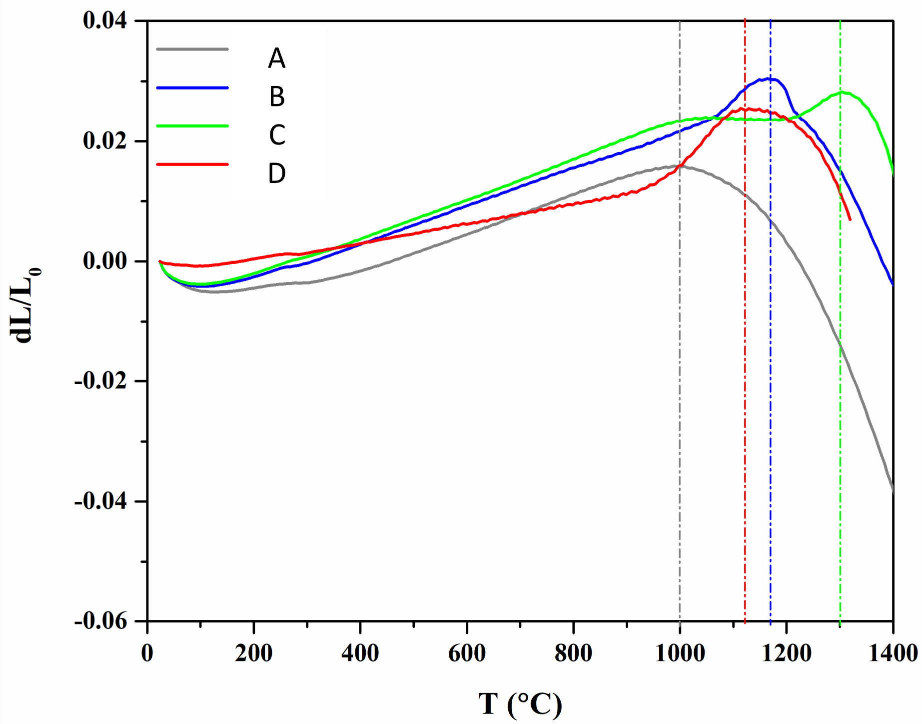


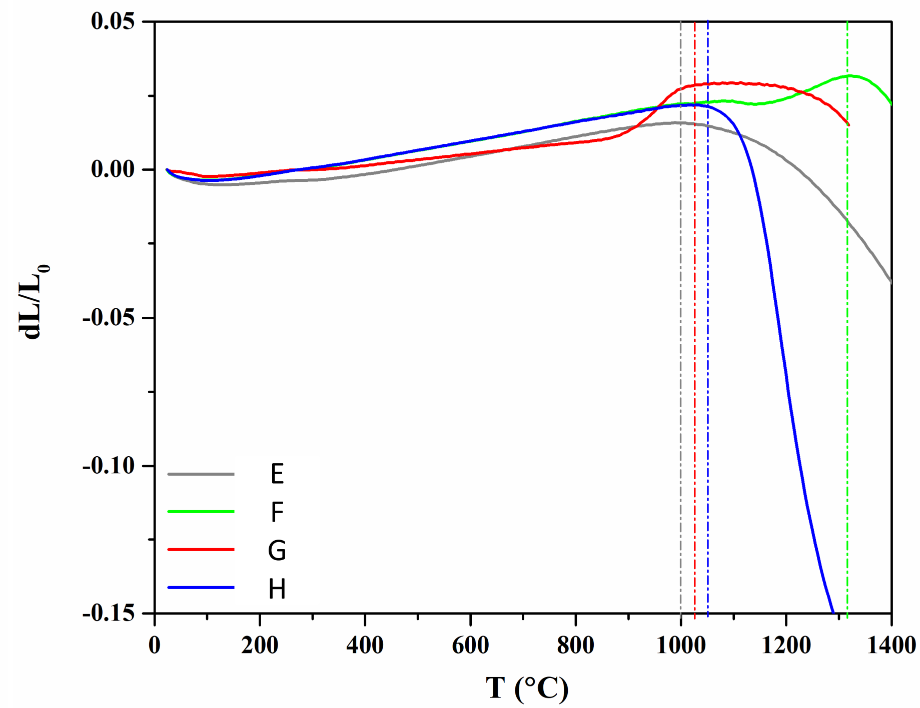




Process optimization of functional layer fabrication

- Solution/slurry compositions
- Coatings

# Fabrication of hollow fiber membrane

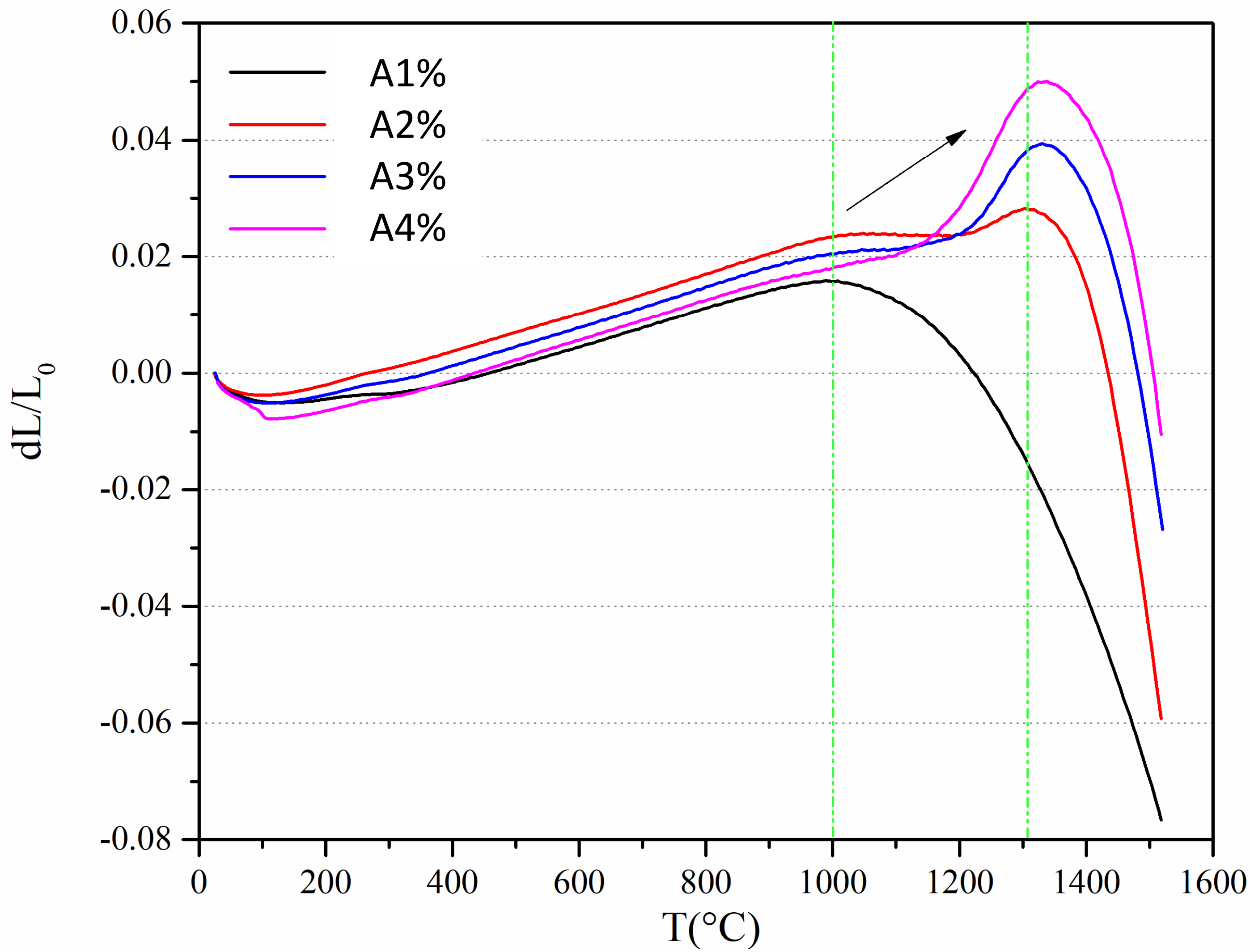



Sintering behavior and modifications:

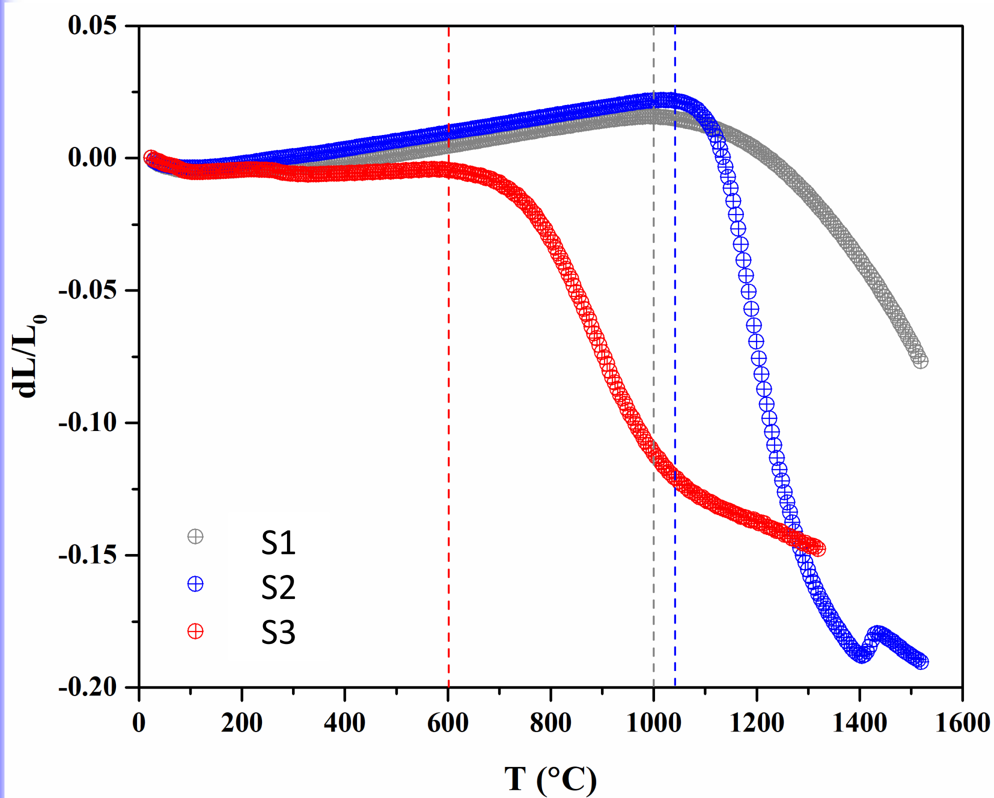
- Sintering behaviors of substrates are systematically measured;
- Sintering behaviors are modified with a set of sintering aids.

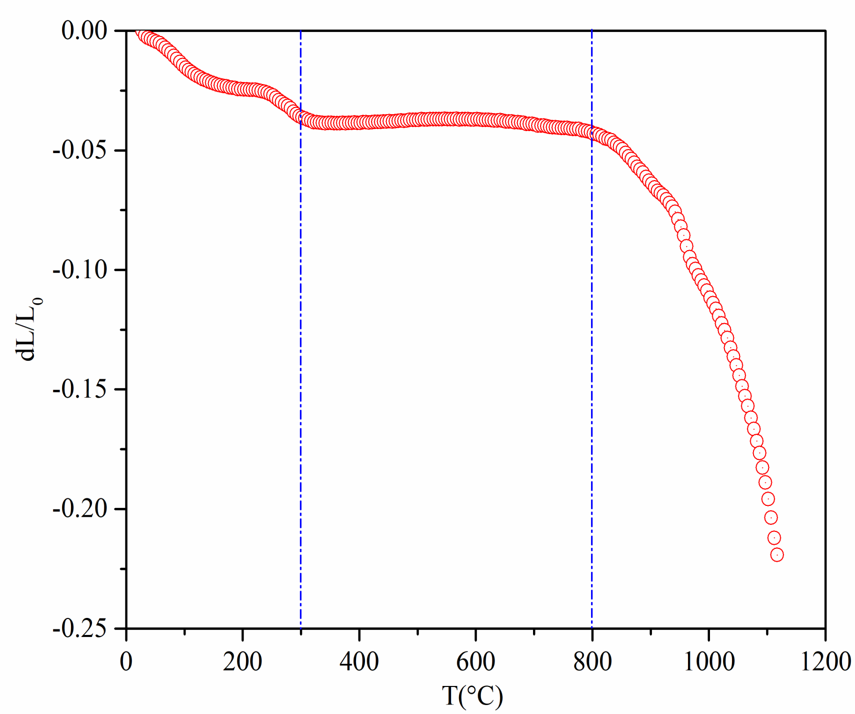
# Fabrication of hollow fiber membrane




Contents of sintering agent may significantly affect sintering behavior of substrates.

# Fabrication of hollow fiber membrane

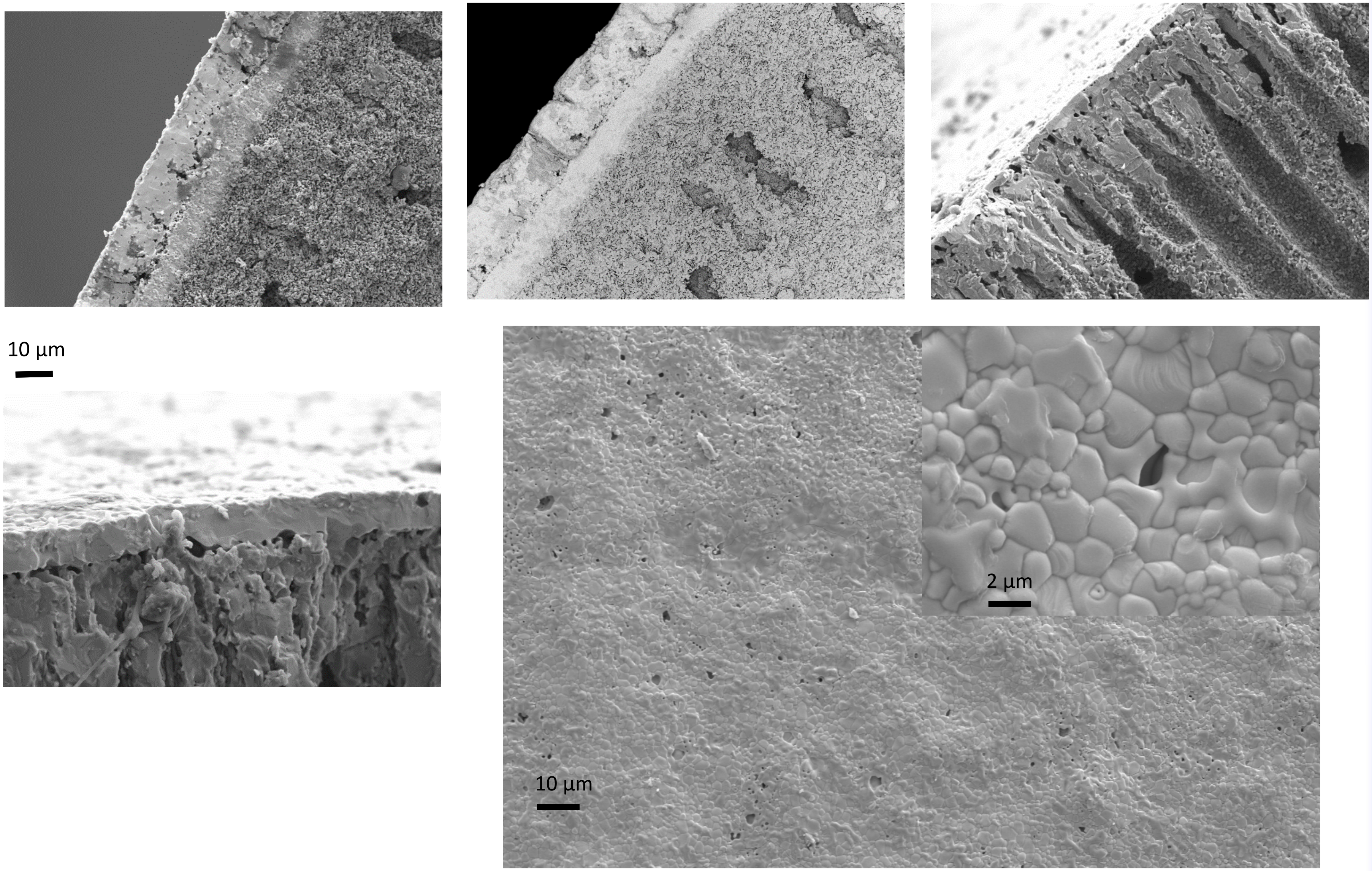


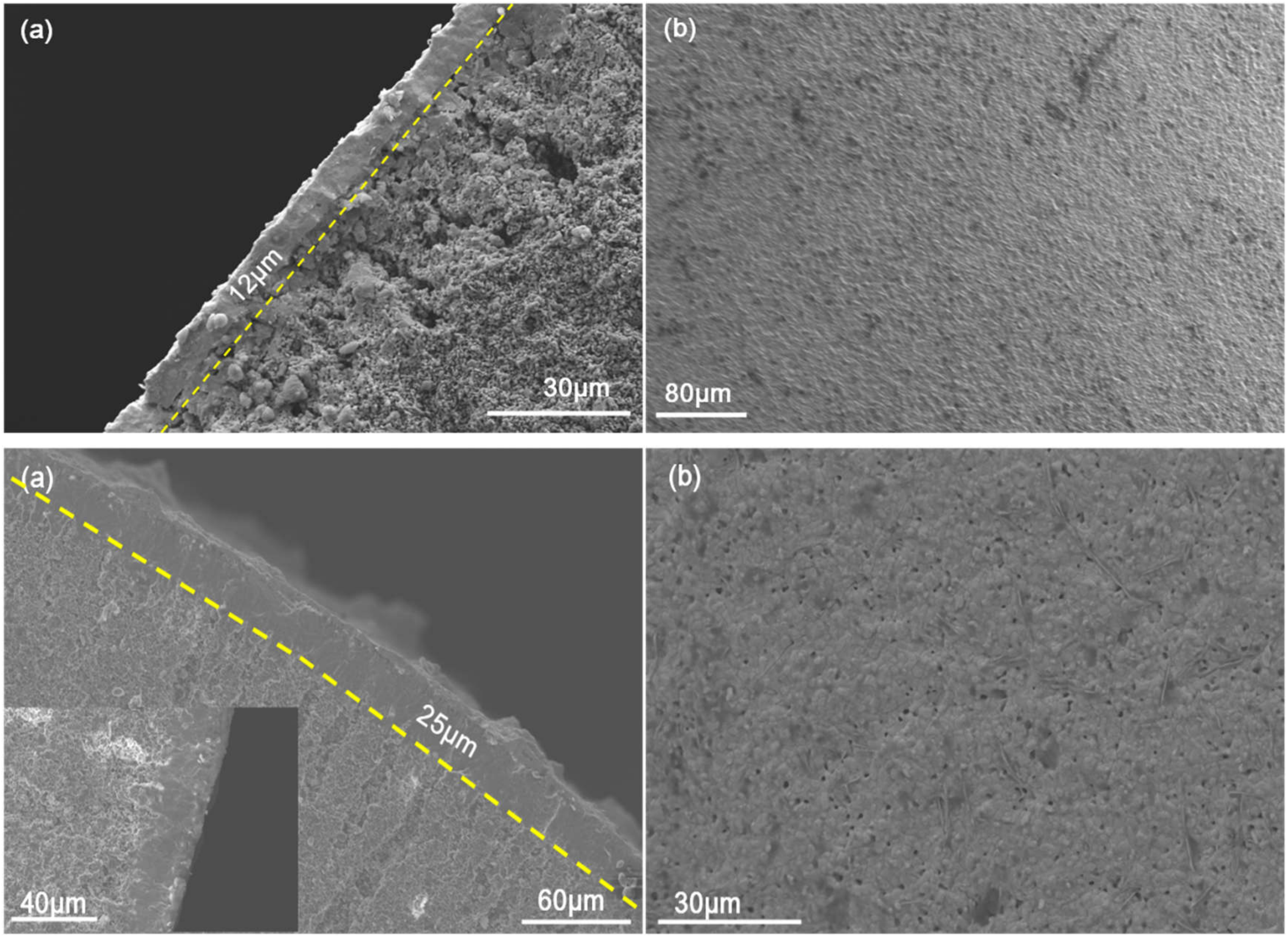

Sintering curves allow us to

- Match sintering behavior of substrate with functional layers;
- Critical step to densify functional layer while remaining microstructure of substrate.

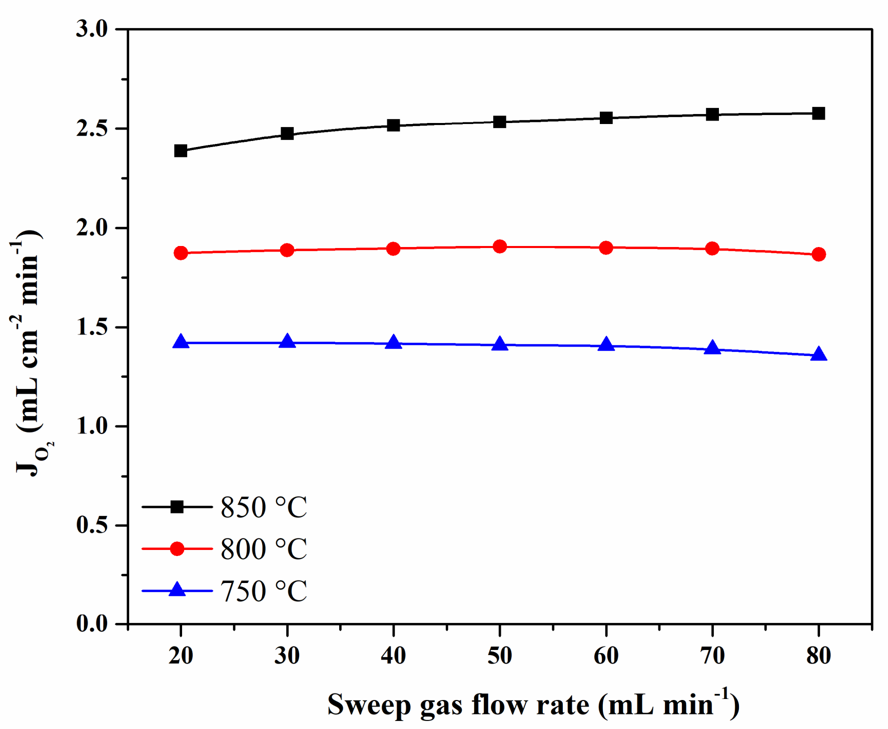
# Fabrication of hollow fiber membrane

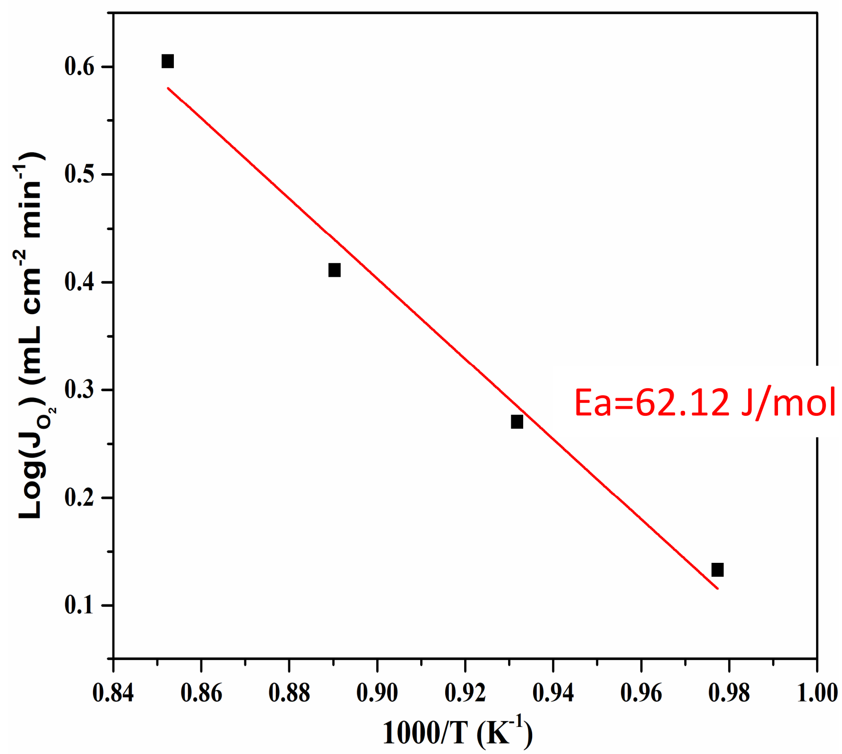


# Fabrication of hollow fiber membrane



# Oxygen Permeation Testing Results




- Feed side: ambient air;
- Permeate side: Argon sweep gas;
- Operation in intermediate temperature 750 – 850 oC;
- Permeation flux Increases with temperature, process is thermally activated;
- Not sensitive to flow rate of sweep gas, oxygen evolution is not a limiting step.

# Future work/next steps

- Refinement and finish up optimizations of single membrane cell fabrication and characterization;
- Systematic oxygen permeation testing and characterization of single membrane cells;
- Assembly of stacks with single membranes;
- Stack testing and characterizations;
- Modeling and analysis.

# Market Benefits/Assessment

– Oxygen has wide applications in industries:
  - Energy (oxygen combustion/gasification, improve efficiency, enable CO2 capture, etc.);
  - Manufacturing (metal production, glass production, welding, plasma cutting, pulp and paper production, refining)
  - Environmental (water and wastewater treatment);
  - Healthcare
  - Others (chemicals, pharmaceutical and biotechnology, etc.)

– Oxygen needs are/will be intensive in these industries.
  - Technology advancement and/or Innovations are needed to fulfill these needs.

– The technology studied in this project:
  - Low cost, reliable technology for high purity oxygen production from air;
  - Has up-scaling flexibility for oxygen production at different scales.

# Technology-to-Market Path

- The technology, if successful, can be directly integrated into gasification based power plant system to achieve FE goals/objectives:
  - As an oxygen supply module integrated into the system (replace air supply unit);
  - Improve efficiency of power plant system (no nitrogen involvement);
  - Enable cost-effective, efficient, and reliable CO2 separation and capture.
- The technology can also be a stand-alone oxygen production unit/system
  - Can be scaled for oxygen production at different scales (directly transferred to market);
  - Relevant companies (Praxair, Airgas) might be interested in this technology (integrated into their oxygen production systems);
- Remaining technology challenges:
  - Fabrication process optimization for single membranes;
  - Stack assembly, testing, and characterization;
  - Modeling and analysis.

# Concluding Remarks

- Applicability to Fossil Energy and alignment to strategic goals
  - Low cost technology for pure oxygen production from air;
  - Up-scaling flexibility (stack, module);
  - Can be used as oxygen supply unit, incorporated into gasification based power plant system; (replace air supply unit)
  - Improve efficiency of power plant system;
  - No nitrogen involved in the system, enable cost-effective, efficient, and reliable CO2 separation/capture.
- **Project's next steps and current technical challenges**
  - Keep doing what were planned in the project;
    - Single membranes: fabrication, testing, characterization;
    - Stack assembly, testing, and characterization;
    - Modeling and analysis
  - Current technical challenges;
    - Technical challenges could pop-up during the course;
    - E.g.: takes longer time than planned due to complexity of process and various uncertainties.

# Acknowledgments

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Post-docs and Graduates