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.

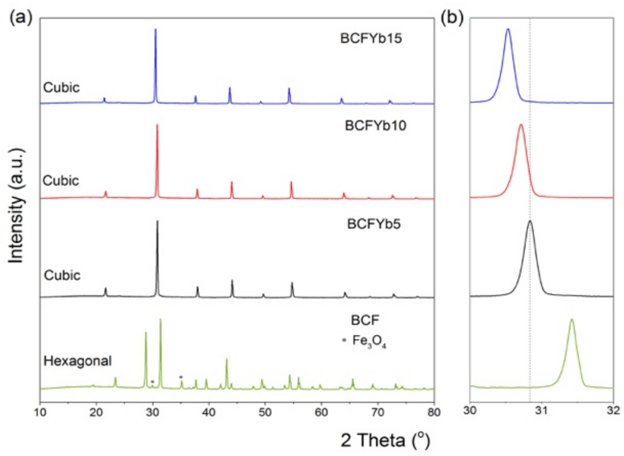
Current Status of project

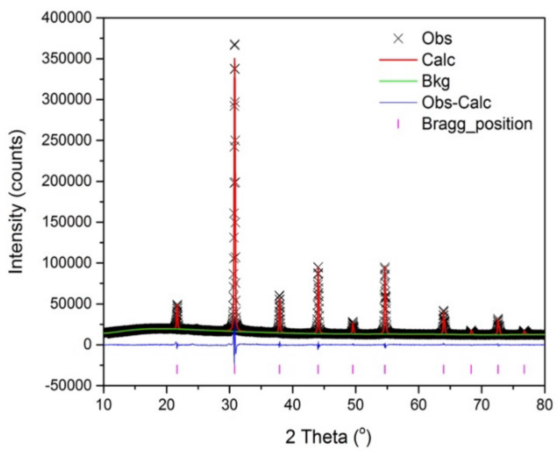
- New membrane design with novel architecture, material system, and microstructure;
- Significantly reduce capital cost of membrane cell and operating cost;
- Potentially improve reliability, durability, and endurance;
- Potentially enhance performance;
- Enabling flexible up-scaling for stack/module.
- 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", 4th 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.

Mixed conducting membrane materials



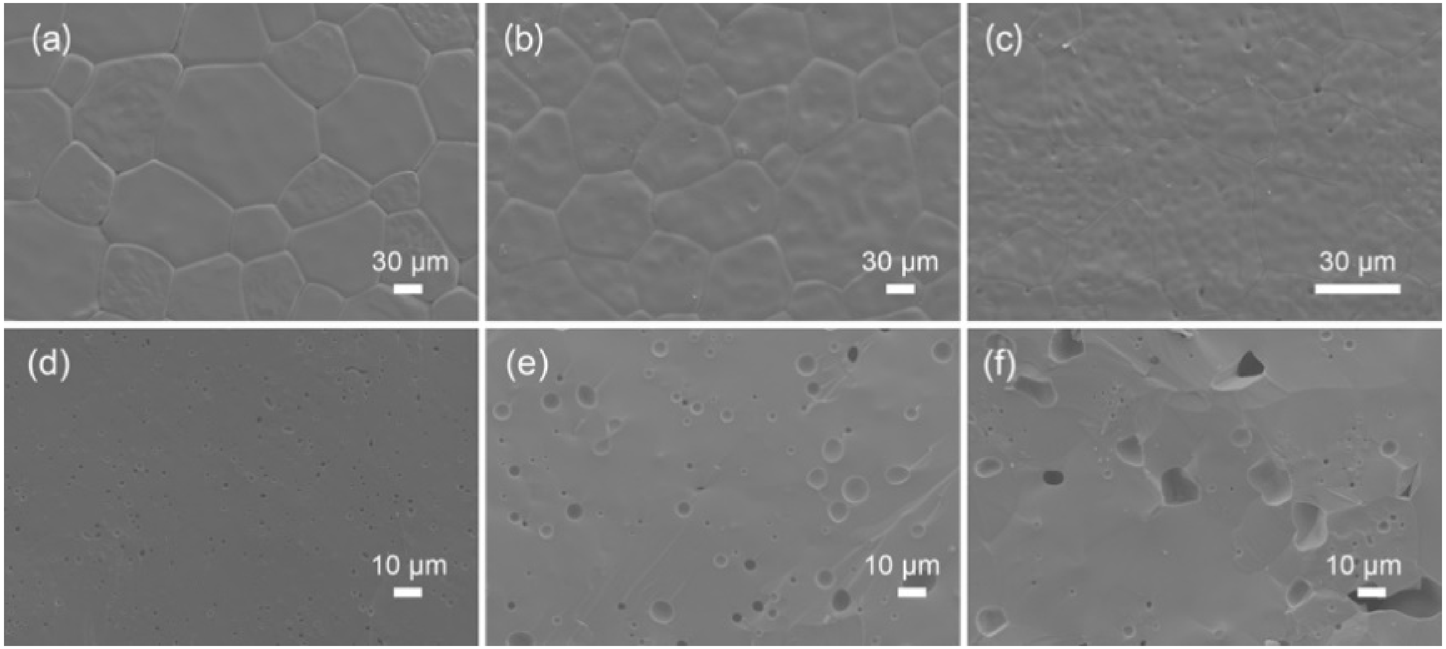


- Perovskite $BaCo_{0.7}Fe_{0.3-x}Yb_xO_{3-\delta}$ (x =0, 0.05, 0.10 and 0.15) BCF, BCFYb5, BCFYb10 and BCFYb15 (a); details of the selected 2θ range of 30-32° (b).
- XRD pattern and Rietveld refinement of BCFYb10

	x=0.05	x=0.10	x=0.15
a (Å)	4.1042(7)	4.1153(5)	4.1367(7)
V(Å^3)	69.136(56)	69.698(00)	70.791(99)
GOF (χ^2)	4.59	4.93	4.92
R_F (%)	3.15	2.57	2.56
R_{wp} (%)	3.59	3.77	3.82

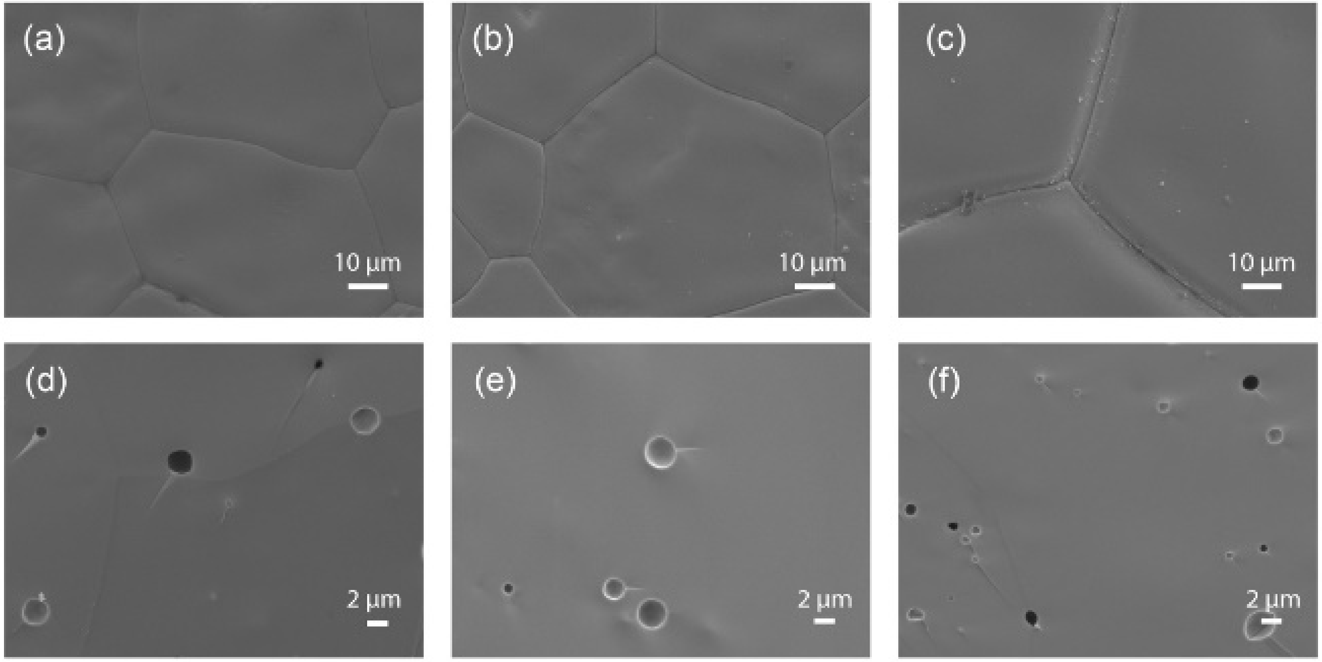
- impurity phase Fe_3O_4 generated in $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ sample due to large ionic size mismatch between Ba and Co/Fe;
- Very small amount of Yb-doping effectively stabilized the cubic structure of $BaCo_{0.7}Fe_{0.3}O_{3-\delta}$ to room temperature;
- Yb B-site doping shifted peak to lower angles, increased lattice parameter and cell volume.

Mixed conducting membrane materials



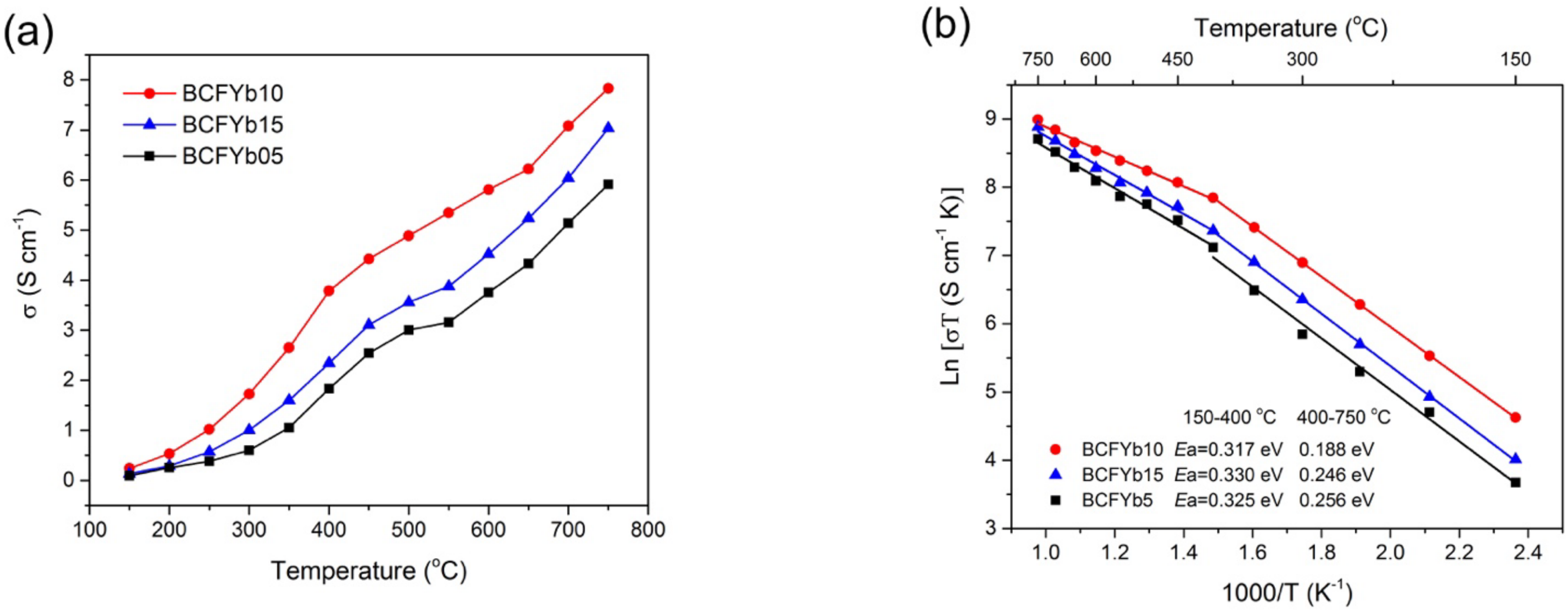
- Sintering ability of bulk materials
  - Surface (a, b and c) and cross-section (d, e and f) SEM images of bulk BCFYb5 (a, d), BCFYb10 (b, e) and BCFYb15 (c, f) sintered at 1190 ^{o}C in air for 6 h.
  - Measurement results: Relative densities of BCFYb5, BCFYb10 and BCFYb15 pellets reached 95.72%, 93.58% and 89.21% respectively;
  - Increasing Yb content, the pellets became harder to densify and average grain size decreased.

Mixed conducting membrane materials



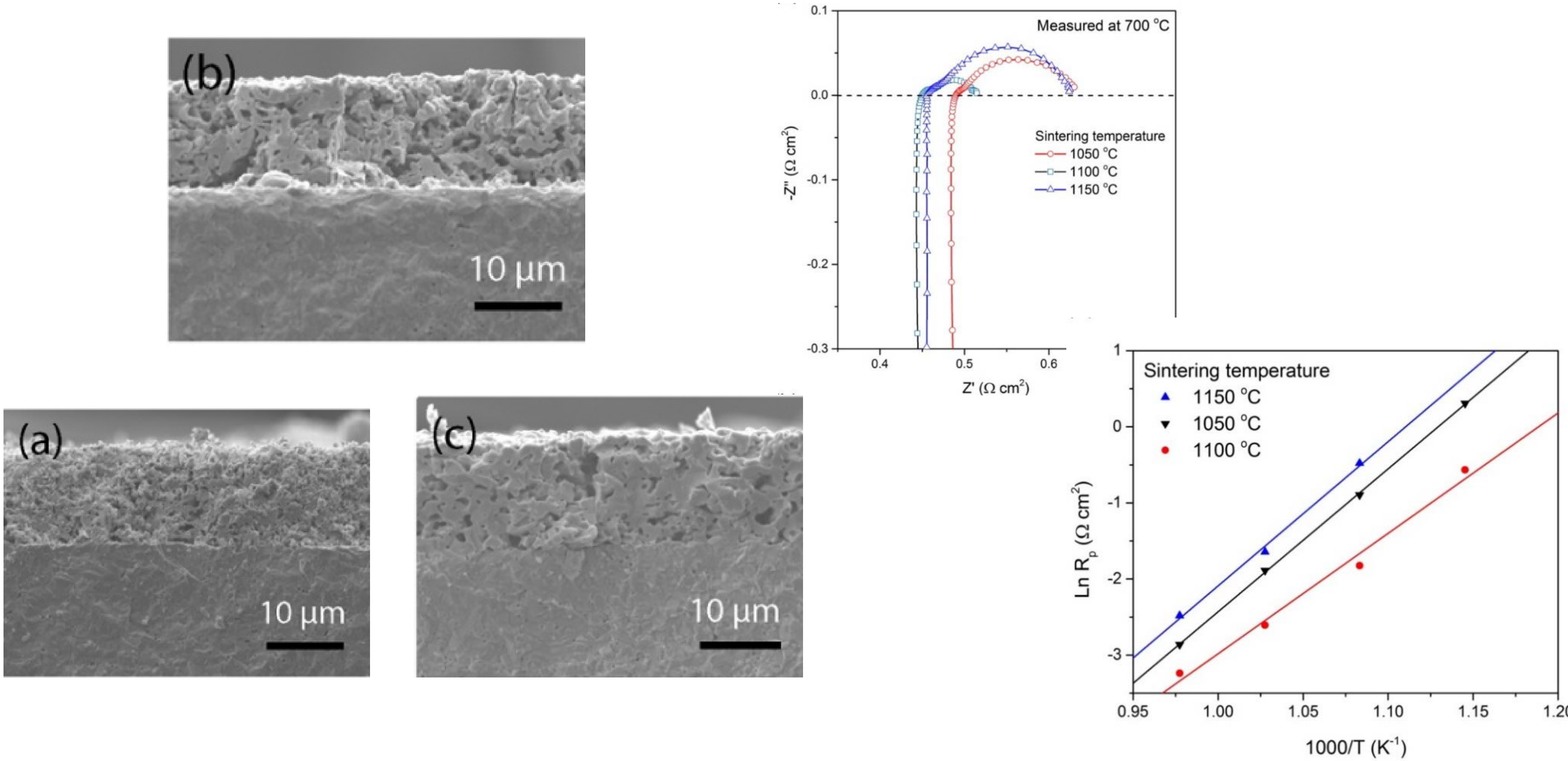
- Sintering ability of bulk materials
  - Surface (a, b and c) and cross-section (d, e and f) SEM images of bulk BCFYb5 (a, d) sintered at 1190 ^{o}C in air for 6 h, bulk BCFYb10 (b, e) sintered at 1220 ^{o}C in air for 6 h and bulk BCFYb15 (c, f) sintered at 1260 ^{o}C in air for 6 h;
  - Yb dopant is a sintering inhibitor;
  - The competing effect of Yb inhibiting and sintering temperature leads to increased average grain size.

Mixed conducting membrane materials



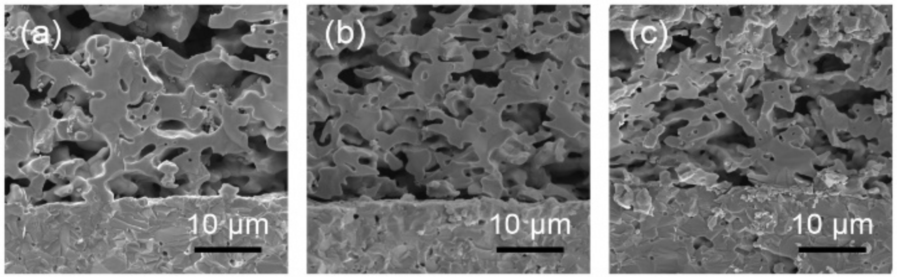
- Temperature dependent electrical conductivity of bulk in air
  - 150-450 °C, conductivity increased exponentially with temperatures; beyond 450 °C, increased in a little bit low rate. Arrhenius plot showed two regions with different Ea;
  - Mixed conductor: co-presence of electron holes and oxygen vacancies; high temp loss lattice oxygen and partial annihilation of electron holes; lead to observable conductivity change@450 °C;
  - Charge carriers conducted through route of strongly overlapped B-O-B bond, and Zerner double exchange process of B^{n+}-O^{2-}-$B^{(n+1)+} \rightarrow B^{(n+1)+}$-$O^{-}$-$B^{(n+1)+} \rightarrow B^{(n+1)+}$-$O^{2-}$-$B^{n+}$.

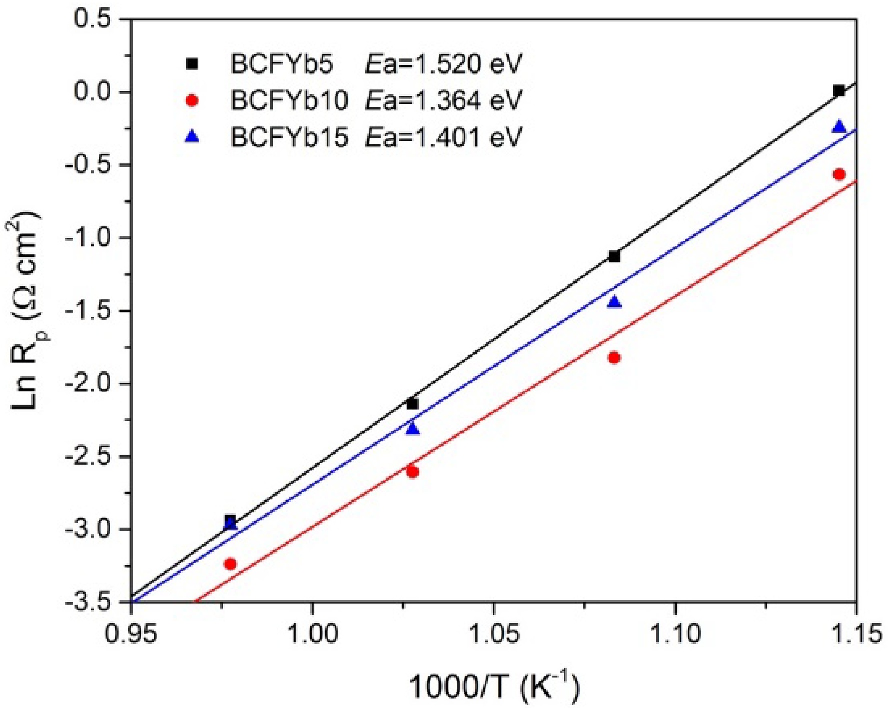
Mixed conducting membrane materials



- Sintering temperature effect on porous surface electro-catalytic property
  - Symmetrical cells BCFYb10|SDC|BCFYb10 sintered at 1050 °C (a), 1100 °C (b) and 1150 °C (c) in air for 2 h;
  - Electrochemical impedance spectra at different temperatures in air;
  - Arrhenius plots of polarization resistance measured at 600-750 °C.

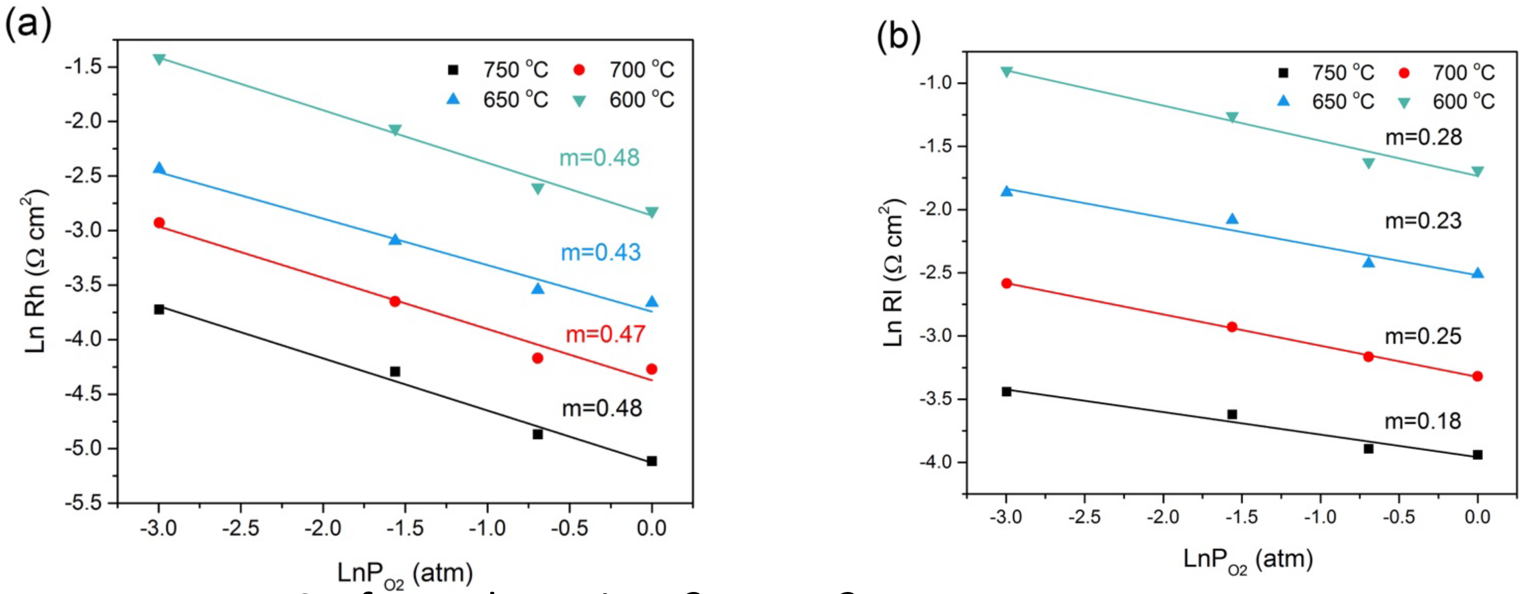
Mixed conducting membrane materials





- Sintering temperature effect on porous surface electro-catalytic property
  - Symmetrical cells sintered at 1100 ^oC in air for 2 h: BCFYb5 (a), BCFYb10 (b) and BCFYb15 (c) cathode on SDC electrolyte;
  - Arrhenius plots of polarization resistance measured at 600-750 ^oC.
  - BCFYb10 demonstrated better performance: lower Rp and Ea

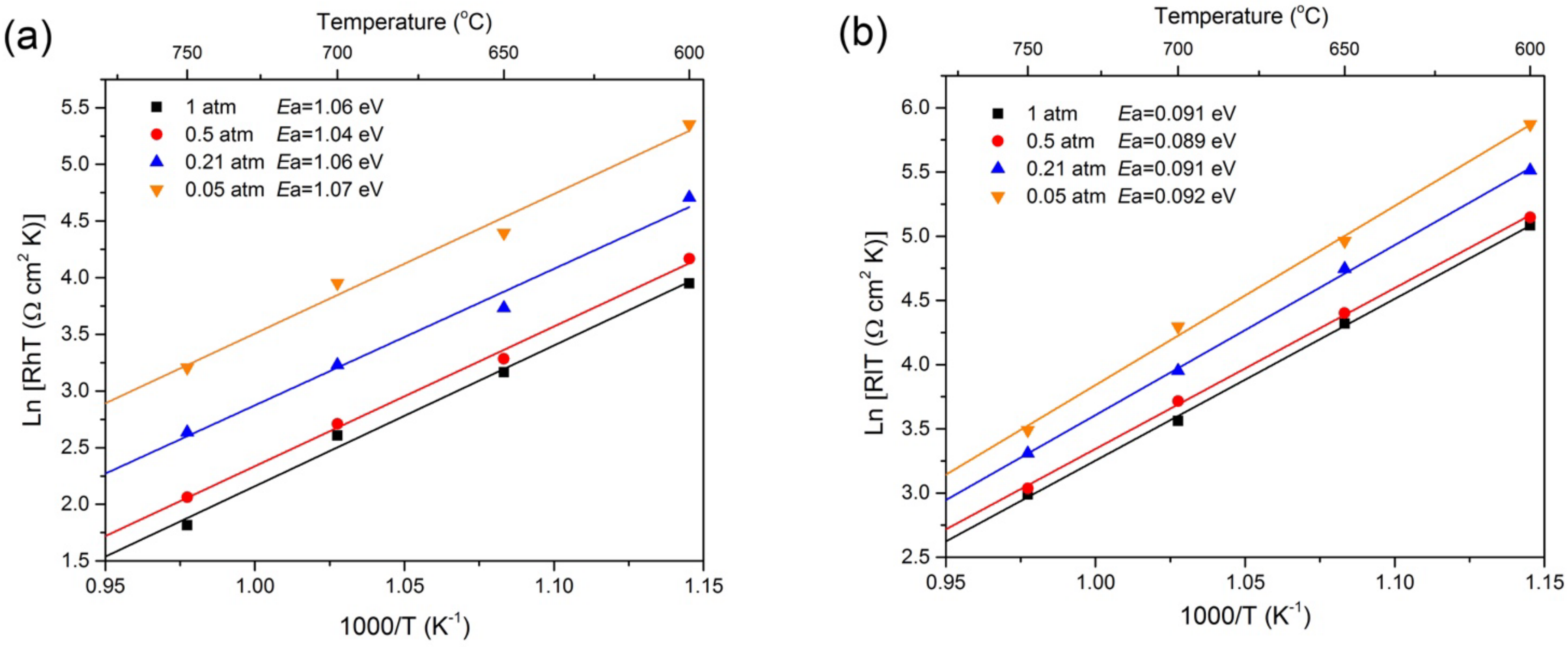
Mixed conducting membrane materials



- 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 0.5, primarily contributed by dissociation;
- Reaction order: (b) close to 0.25, charge transfer process;

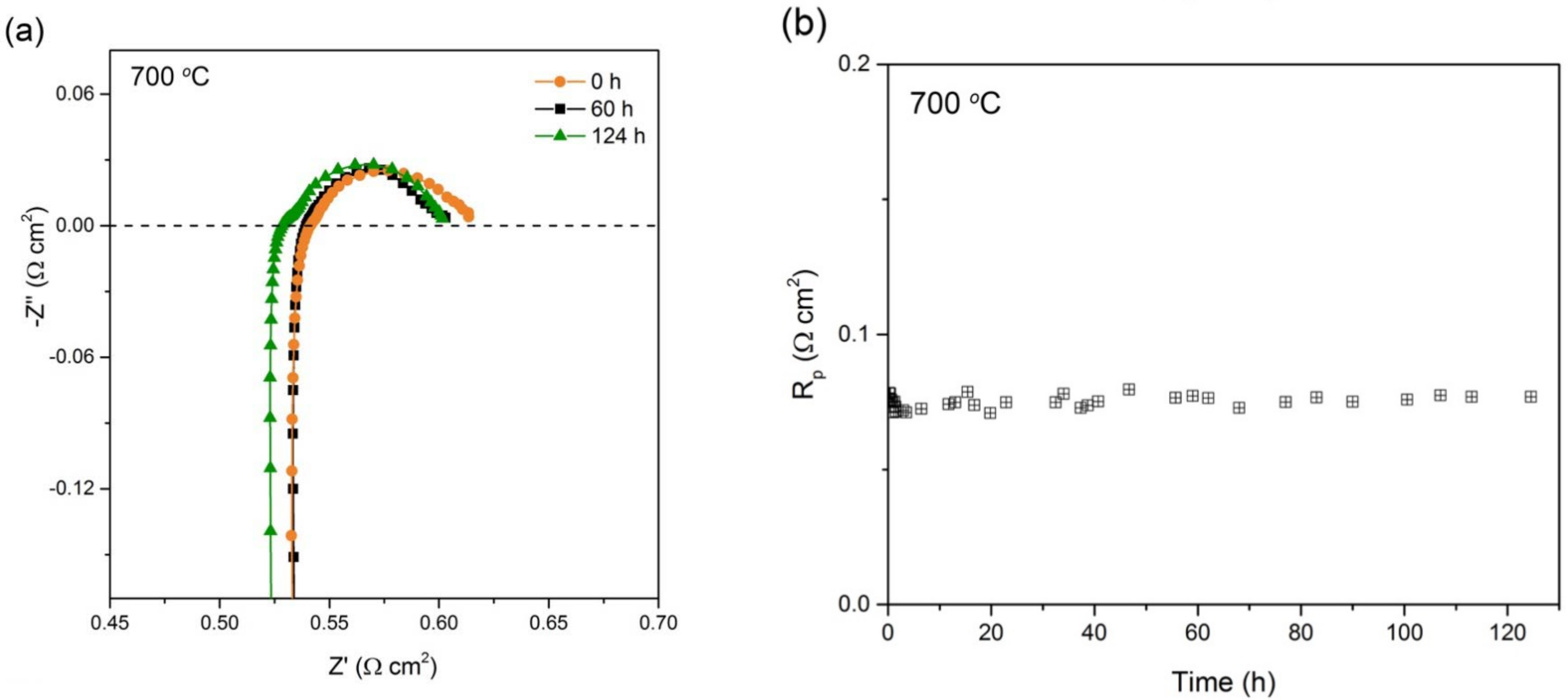
- Surface exchange processes
  - polarization resistance vs. applied oxygen partial pressure at different temperatures, and corresponding reaction orders;
  - (a) polarization resistance associated with high frequency arc;
  - (b) polarization associated with low frequency arc;

Mixed conducting membrane materials



- Surface exchange processes: dominant process for BCFYb10
  - Arrhenius plot of polarization resistance under different oxygen partial pressures;
  - (a) Ea in range of 1.04~1.07 eV for surface oxygen dissociation process;
  - (b) Ea in range of 0.089~0.092 eV for charge transfer process;
  - Oxygen dissociation is a dominant process;

Mixed conducting membrane materials



- Durability test for BCFYb10 in air at 700 °C for over 120 h
  - EIS was measured intermittently during the test;
  - Ohmic resistance slightly decreased probably due to thermal aging of various bonding;
  - Polarization resistance remained relatively constant, indicating good stability of BCFYb10.

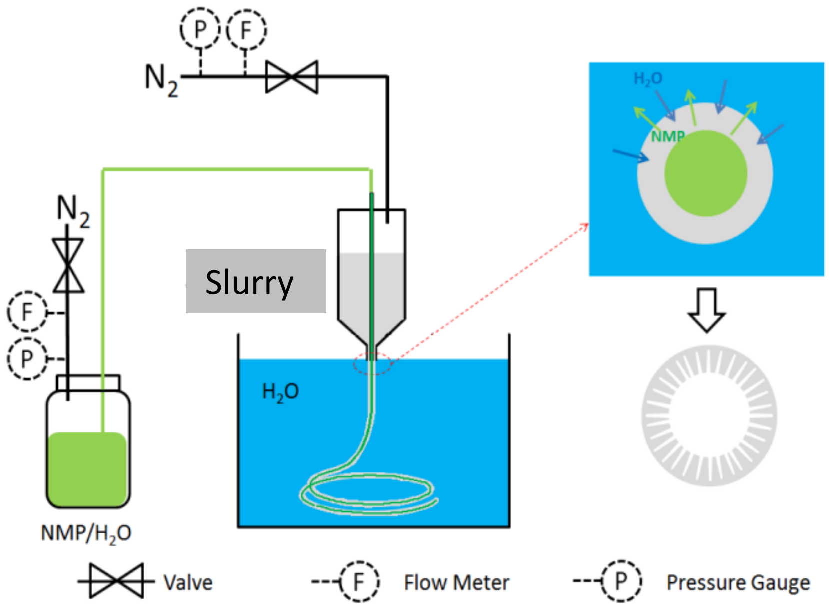
Fabrication of hollow fiber members

Slurry preparation for extrusion

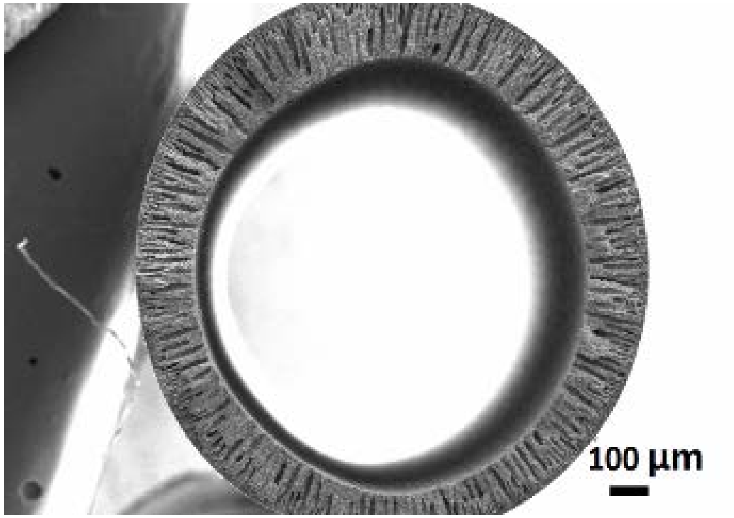
Powder materials *synthesis*

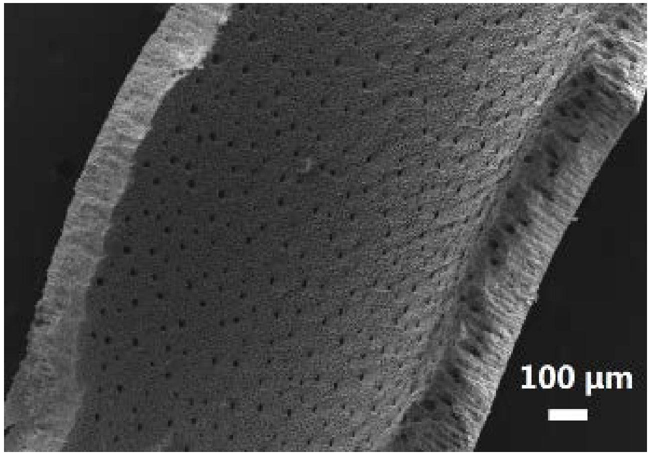
Raw *materials*

Fabrication of hollow fiber members



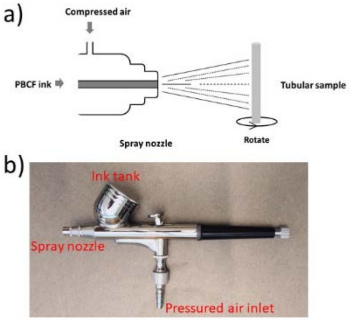
Fabrication of hollow fiber members

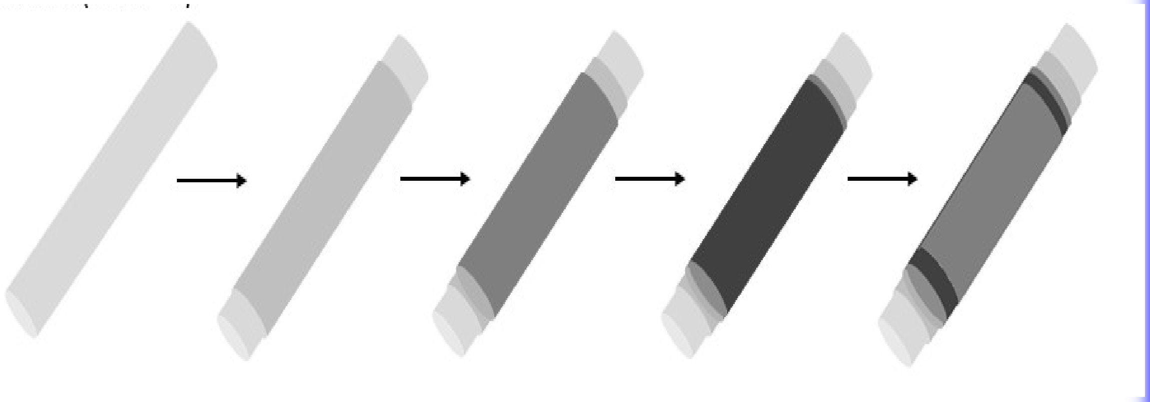


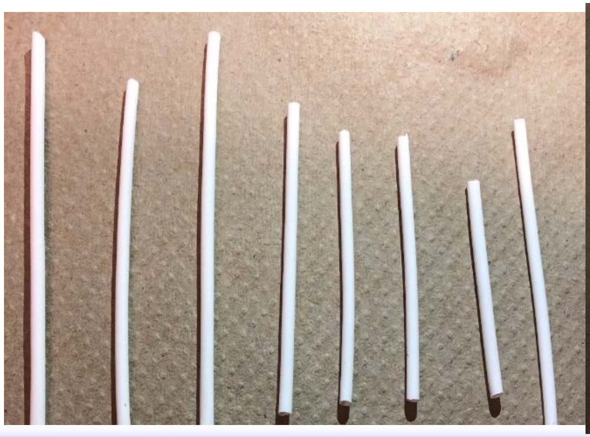


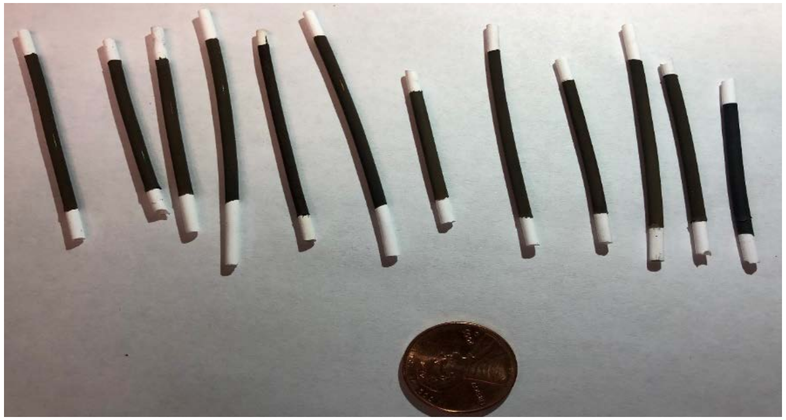
Fabrication of hollow fiber members

Solution preparation for functional layer coatings

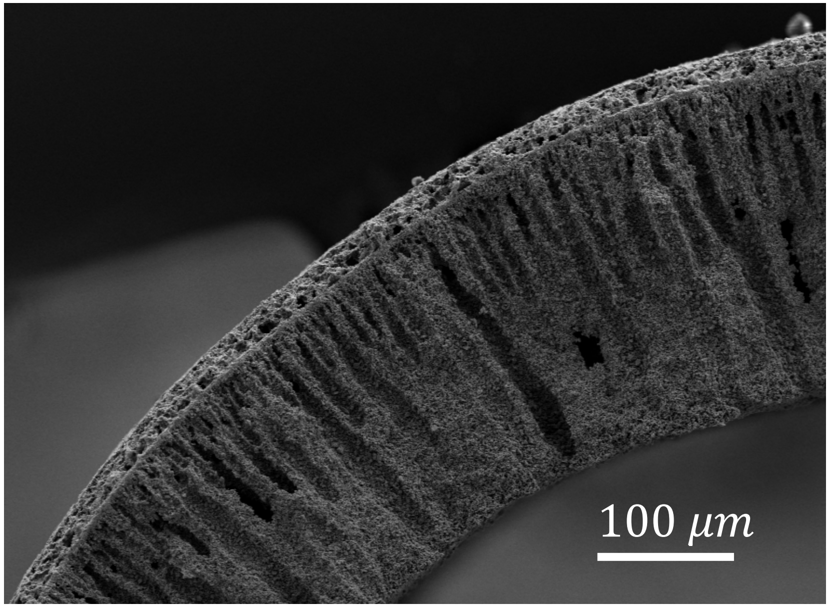


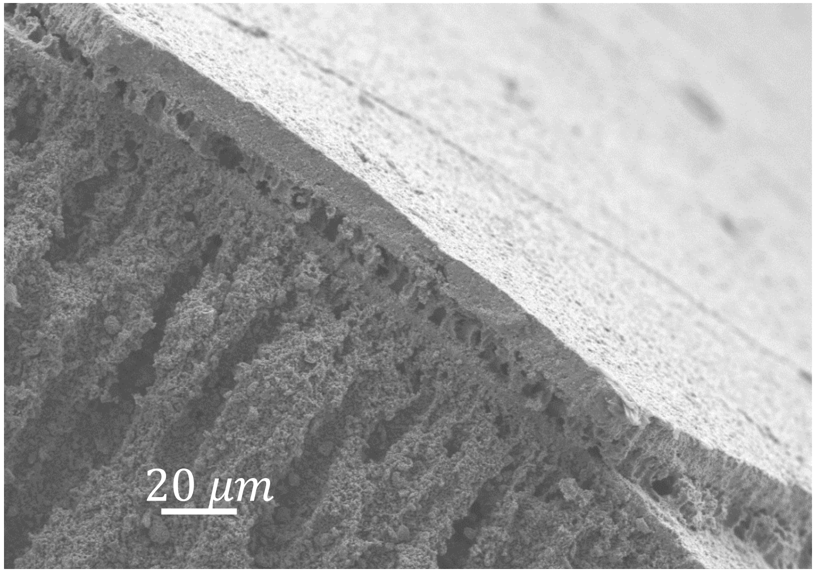






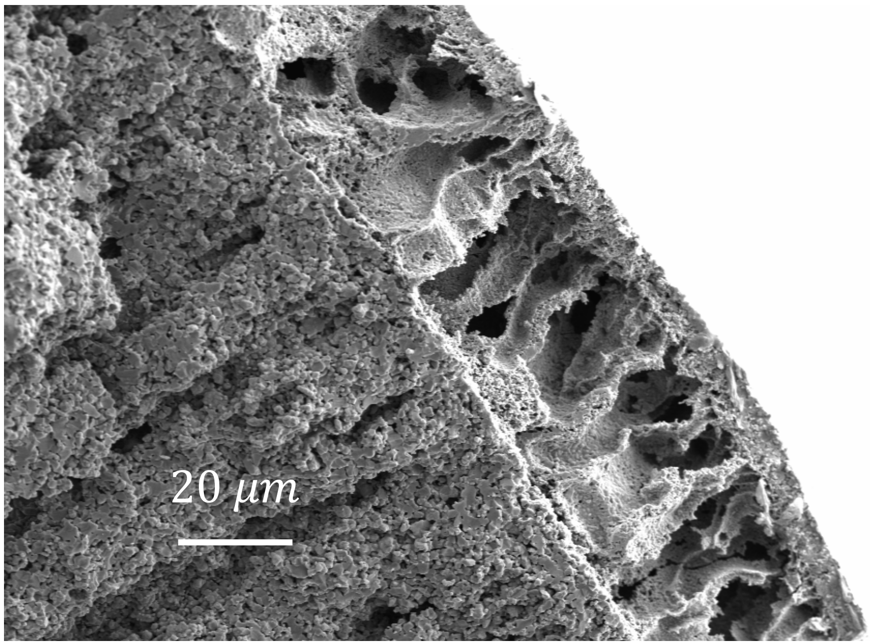
Fabrication of hollow fiber members

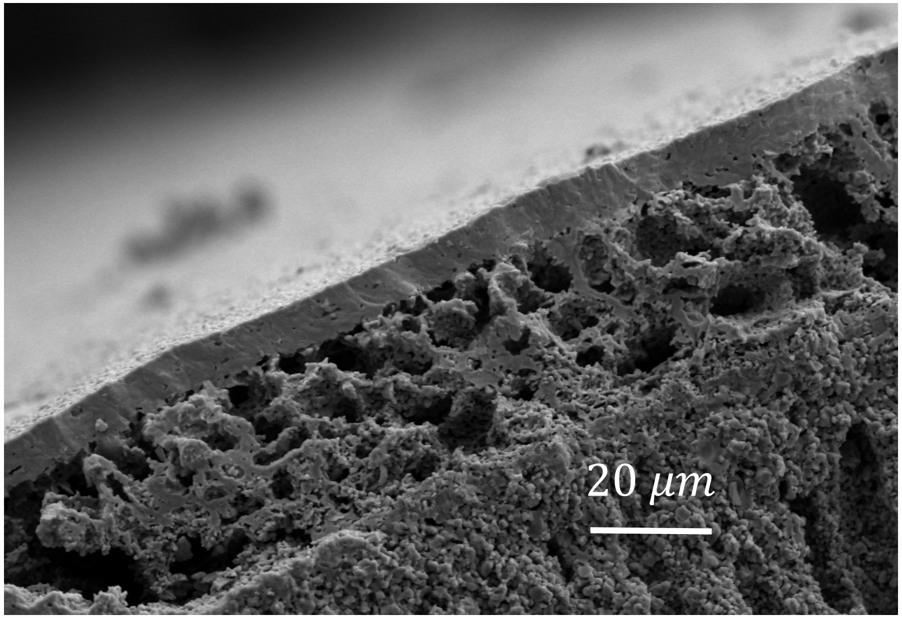




- Fabrications of multiple functional layers for single membranes
  - Thin functional layers;
  - Porous layer and dense layer exist alternatively.

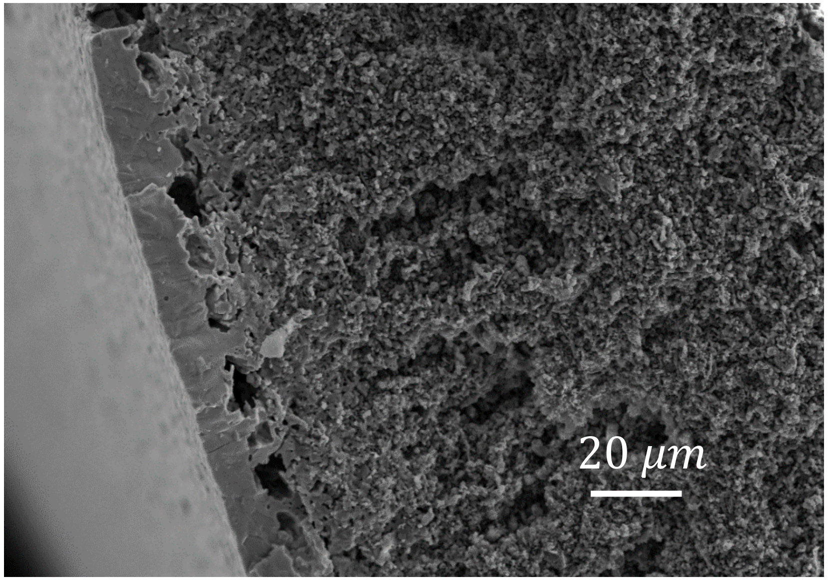
Fabrication of hollow fiber members

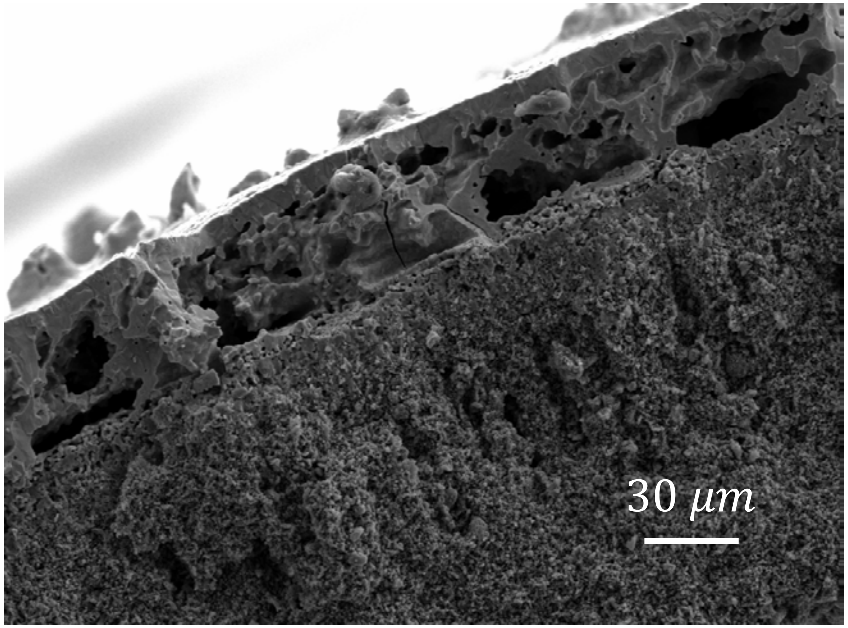




- Fabrications of multiple functional layers for single membranes
  - Optimizations for fabrication processes;
  - Challenge: fabrication of thin film dense layer on porous functional layer.

Fabrication of hollow fiber members





- Fabrications of multiple functional layers for single membranes
  - Optimizations for fabrication processes;
  - Challenge: fabrication of thin film dense layer on porous functional layer.

Future work/next steps

- Further screening materials for membrane applications;
- Finish up optimizations of fabrications for multiple functional layers and single membrane cells;
- Testing and characterization of single membranes;
- 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., fabrication process optimization: takes longer time than planned due to complexity of process

Acknowledgments

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Post-docs and Graduates