UNIVERSITY OF SOUTH CAROLINA

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NETL

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Intermediate Temperature Nano-Structured Ceramic Hollow Fiber Membranes for Oxygen Separation

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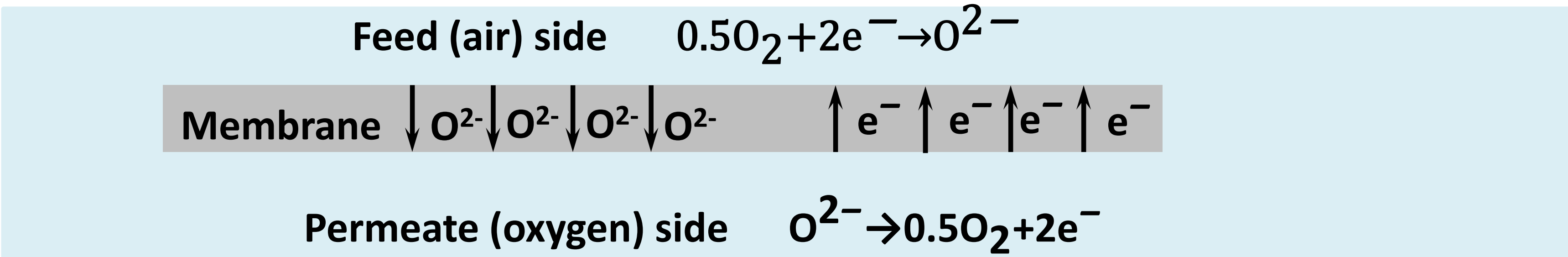
Technology and Aims

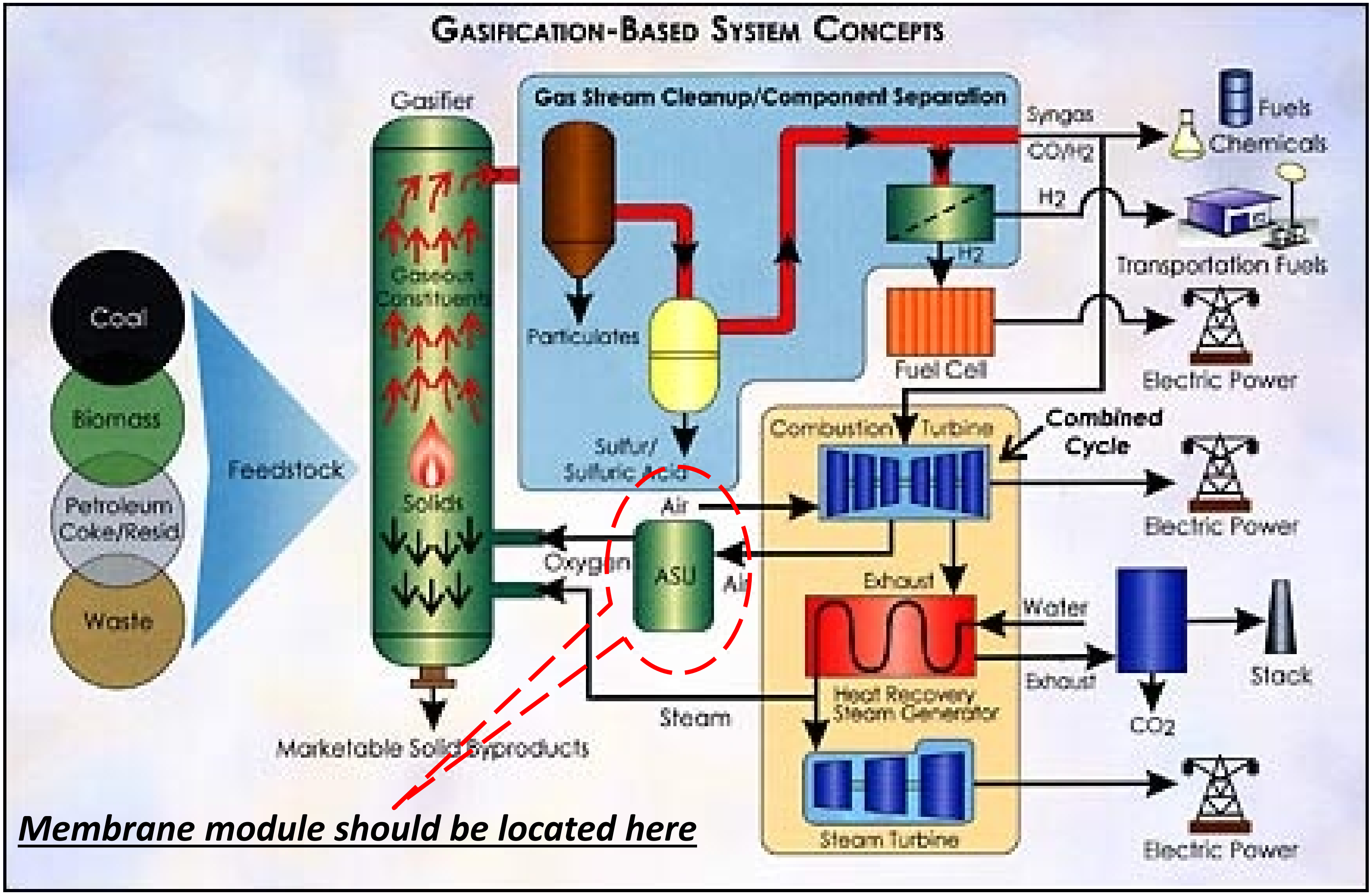
- Technology aims :
  - Improve production rate of high-purity oxygen from air;
  - Improve stability and reliability;
  - Reduce cost.

Working principle of ceramic membrane for oxygen permeation



- At the feed (oxygen rich) side :
  - oxygen molecule combines with electrons from the permeate (oxygen lean) side, thereby being reduced to oxygen ion;
  - generated oxygen ion jumps into oxygen vacancy in dense membrane and migrates to the permeate side;
- At the permeate side (oxygen lean):
  - oxygen ion is oxidized to form O_2 and release electrons;
  - released electrons at the permeate side then transport back to the feed side, forming a closed-circuit loop within the membrane.

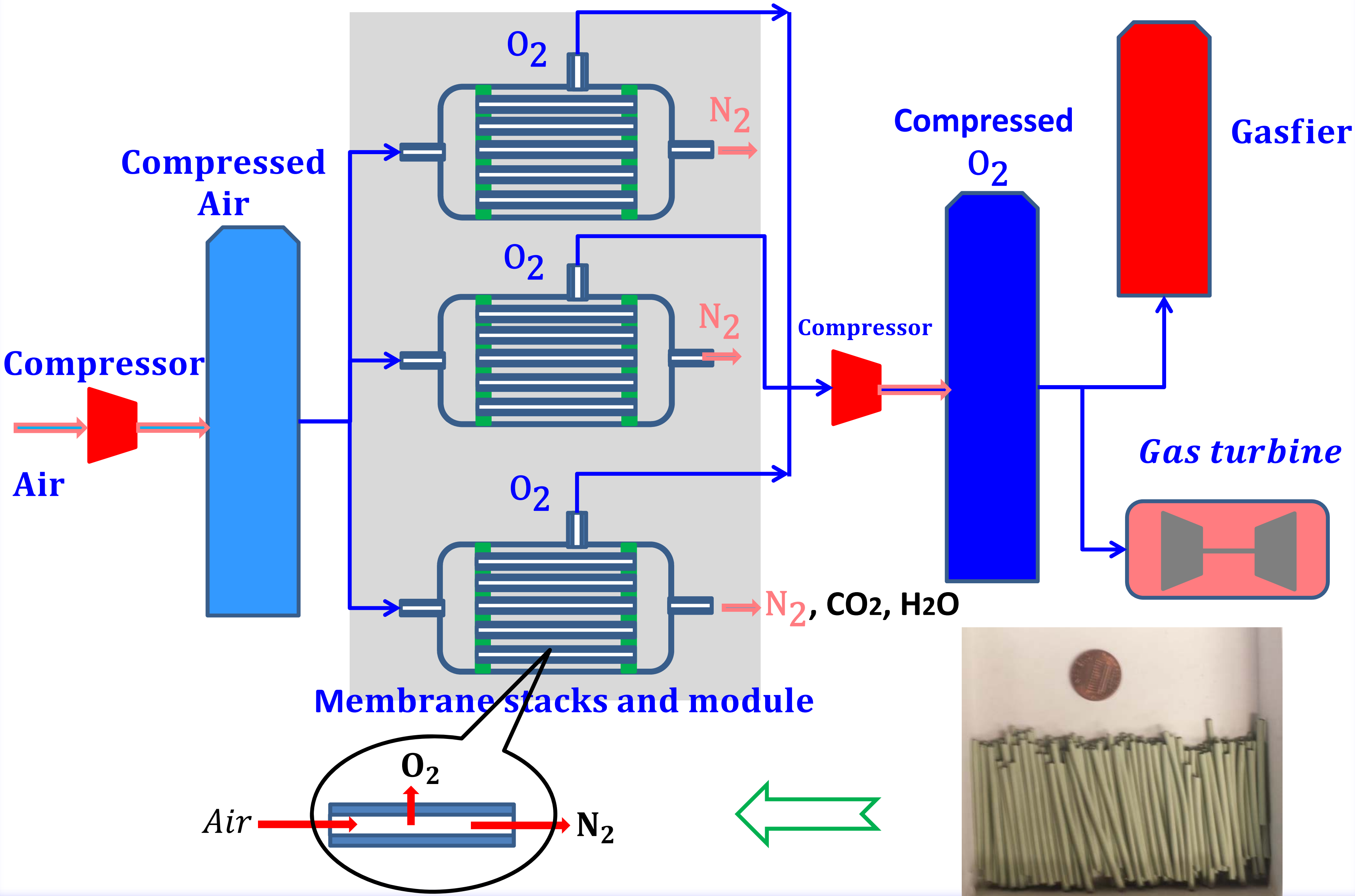
Technology in a gasification/CTL plant



<u>Membrane module should be located here</u>

This figure is adopted from the Office of Fossil Energy, Energy.gov

Integration of technology with plant



Project Goals and Commercial Viability

<u>Project goals:</u>

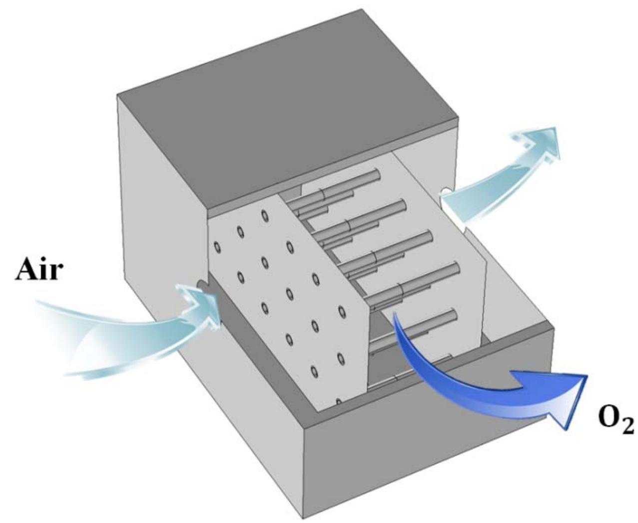
- *Intermediate temperature nanostructured ceramic hollow fiber membranes for oxygen separation*
  - *Obtain high performance and enhanced durability;*

<u>Vision for project goals for commercial viability:</u>

- *Reducing temperatures provides advantages:*
  - *Widen material selections for membrane stack and ancillary system;*
  - *Improve durability;*
  - *Reducing system and operating cost.*
- *Nanostructured ceramic hollow fiber designs:*
  - *Enhancing performance;*
  - *Improving specific oxygen flux.*

Maturity of Technology R&D

- State-of-the-art
  - High operating temperatures (>750 °C);
  - Material development and membrane cell fabrication;
  - Single cell testing and characterization;
  - Planar design;
  - Tubular design;
- Remaining work at the end of the ongoing project:
  - Stack development



Conceptual design of stack with hollow fiber membranes

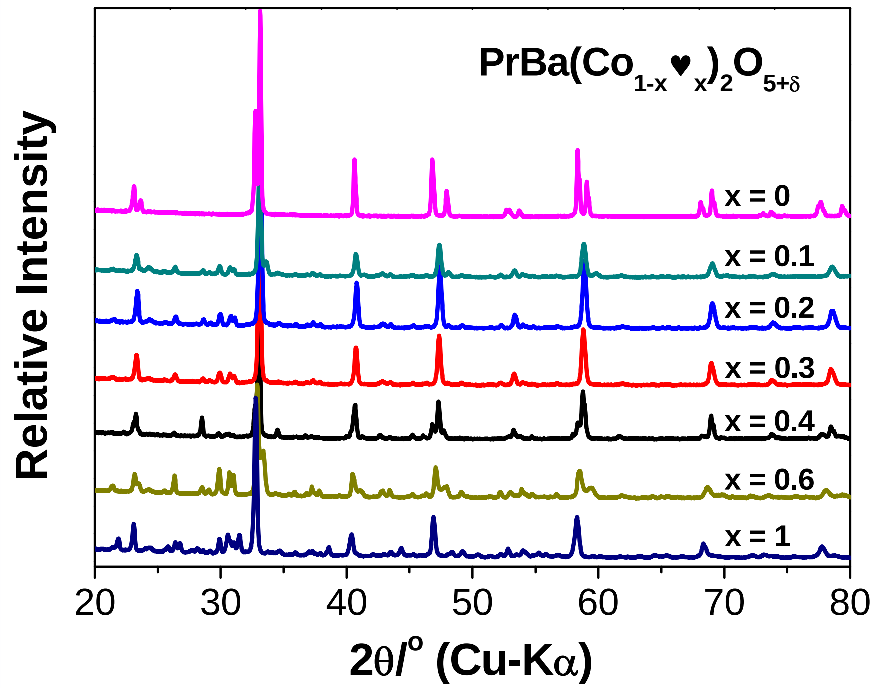
Commercial Benefits

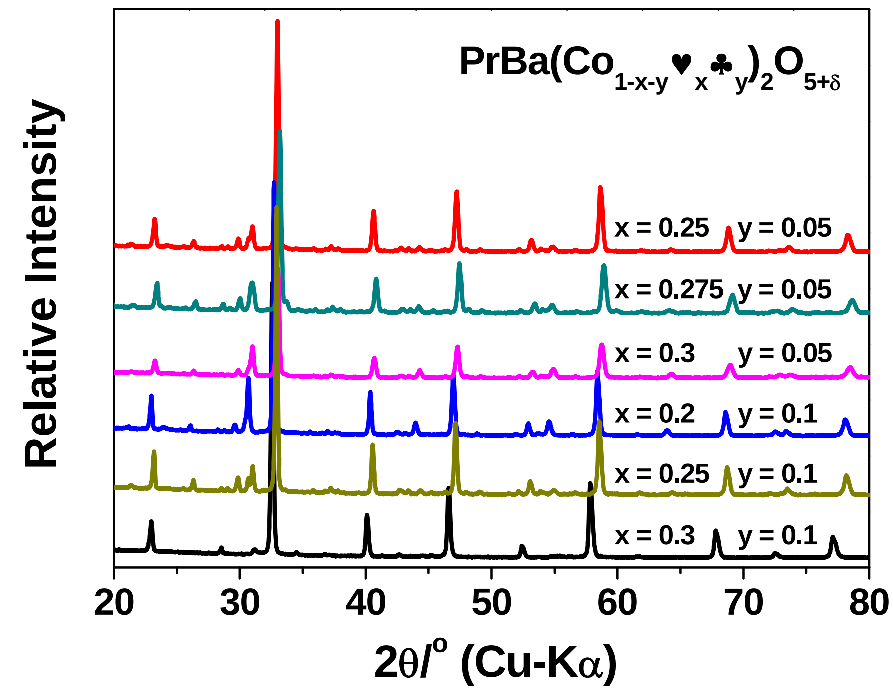
- Commercial Benefits
  - Cost-effective technology for pure oxygen generation from air with highly specific volumetric oxygen flux.
- Justification
  - Pretty simple system: dense mixed conducting membranes;
  - Generating pure oxygen from air;
  - Significantly reducing capital investments;
  - Reducing membrane dimensions (with diameters at millimeter or sub-millimeter scales) may significantly improve specific volumetric oxygen generation flux.
  - Lowering temperatures also reduces operating cost and ancillary components cost.

Membrane Materials

- *Surface exchange and bulk diffusion: two typical processes involved in gas separation ceramic membranes;*
- *Significance of obtaining surface exchange coefficient and bulk diffusivity;*
  - *Quantitative understanding surface exchange and transport mechanism in ceramic membranes;*
  - *Design membrane materials with better performance;*
- *Characterization*
  - *Electrical conductivity relaxation (ECR) measurement;*
  - *Inverse algorithm to extract electrochemical kinetic property.*

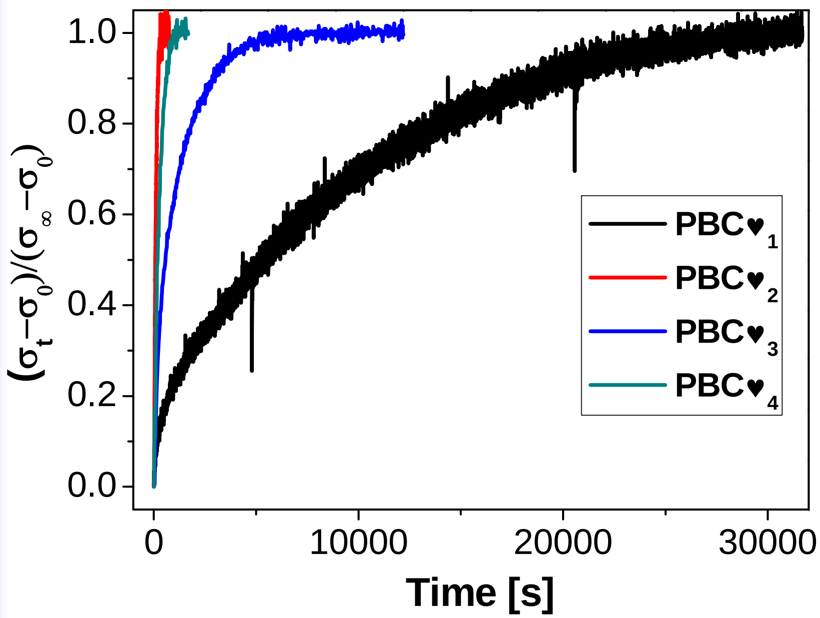
Material Synthesis





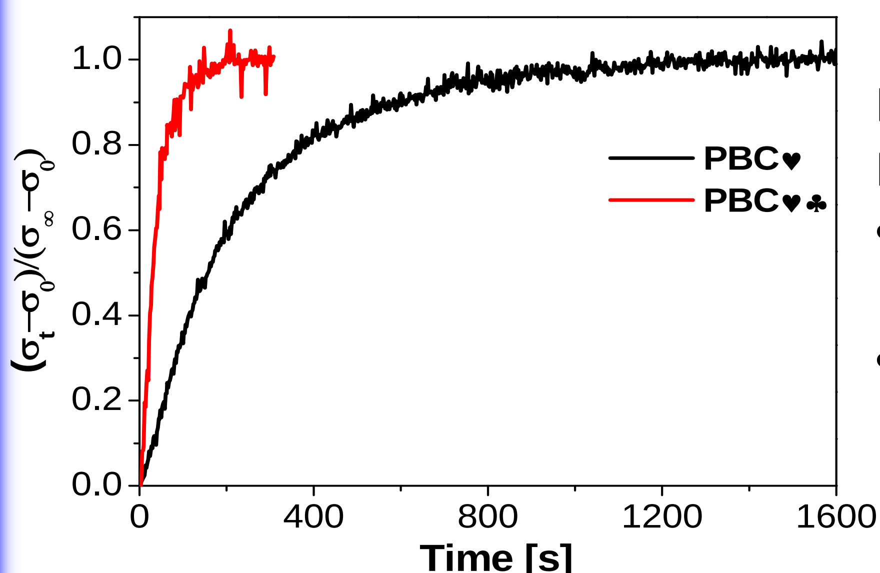
XRD patterns of $PrBa(Co_{1-x}♥_x)_2O_{5+\delta}$ and $PrBa(Co_{1-x-y}♥_x♣_y)_2O_{5+\delta}$ oxides at room temperature in air.

Experimental results



Layered perovskite $PrBa(Co_{1-x}♥_x)_2O_{5+\delta}$

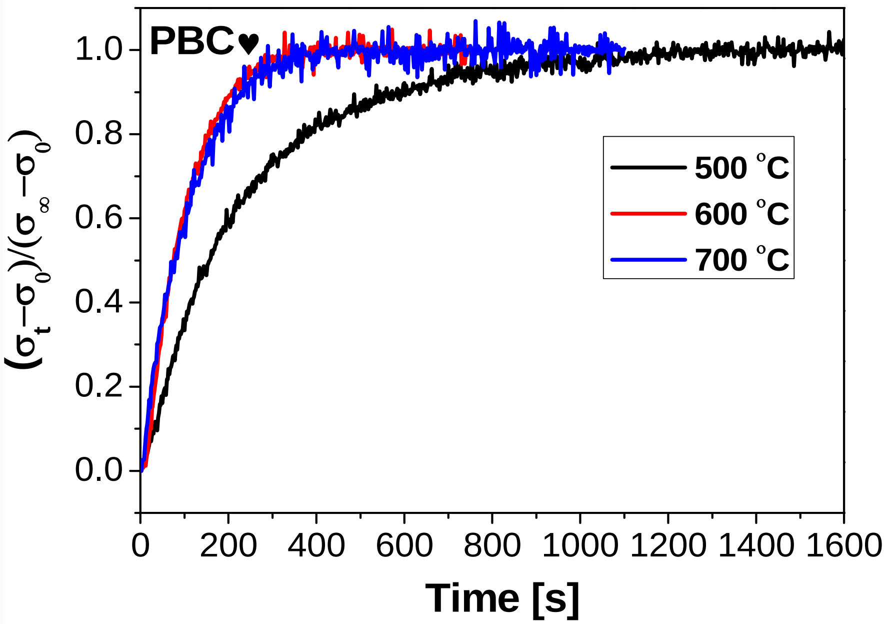
- oxygen partial pressure changes from 0.1 to 0.01 atm at 600 °C;
- dopant "♥" and doping level significantly affect relaxation behavior



Layered perovskite $PrBa(Co_{0.7}♥_x)_2O_{5+\delta}$ and $PrBa(Co_{0.7}♥_{x-y}♣_y)_2O_{5+\delta}$

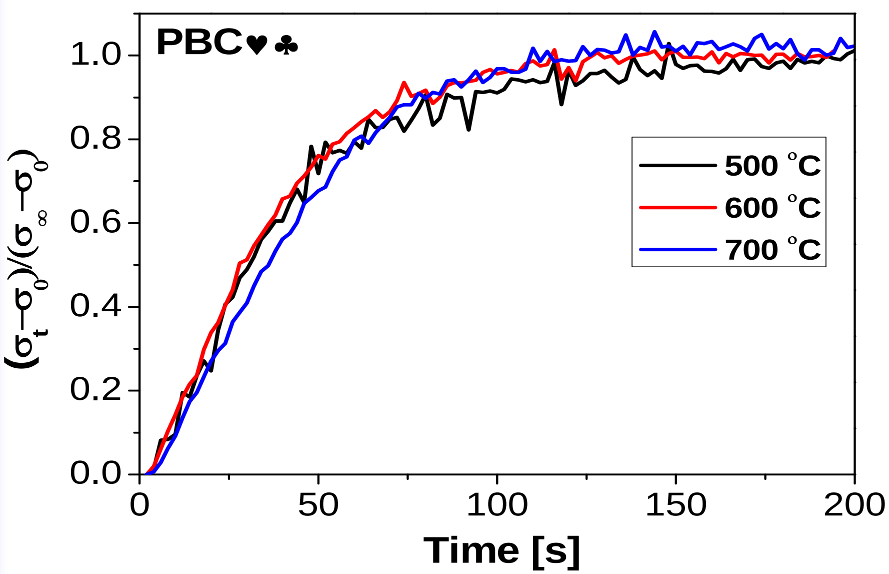
- oxygen partial pressure step change from 0.1 to 0.01 atm at 500 °C
- dopant "♣" and doping level significantly improve relaxation behavior

Experimental results



Layered perovskite $PrBa(Co_{0.7}♥_x)_2O_{5+\delta}$

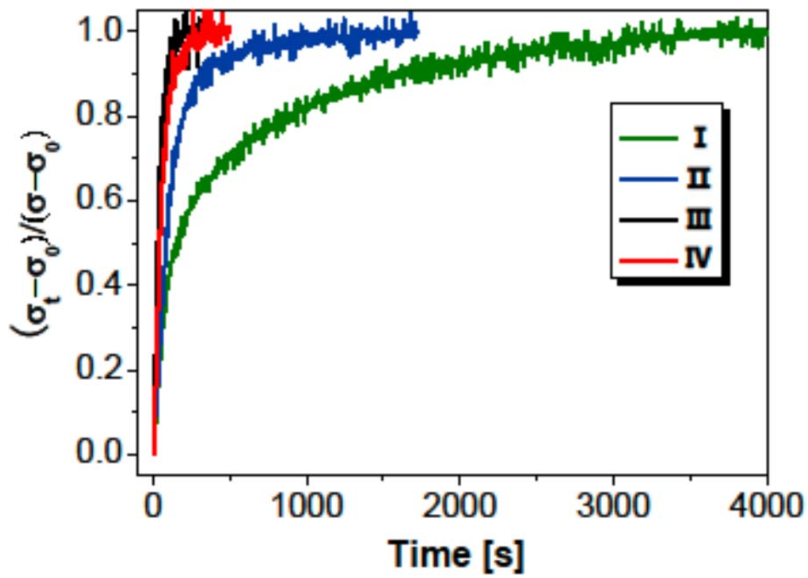
- oxygen partial pressure step change from 0.01 to 0.1 atm at different temperatures;
- Reduce temperature (to 500 °C), ECR property deteriorates

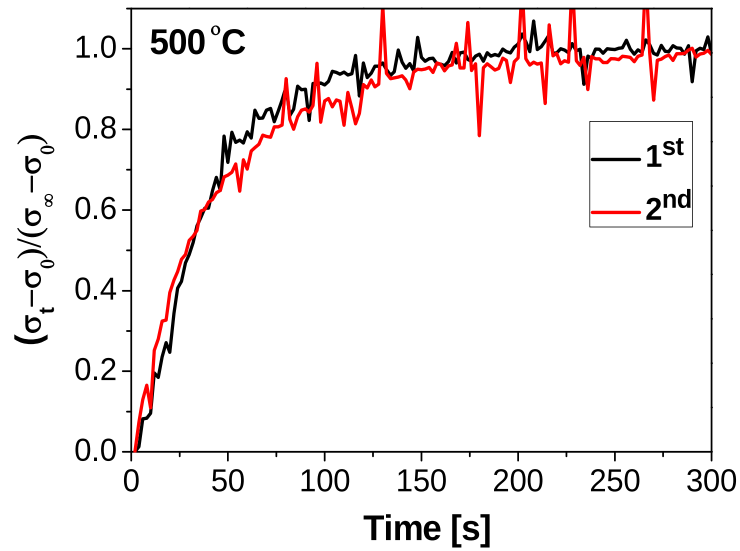


Layered $PrBa(Co_{0.7}♥_{x-y}♣_y)_2O_{5+\delta}$

- oxygen partial pressure step change from 0.1 to 0.01 atm at different temperatures;
- Reducing temperature has little effect on ECR property, suitable for low temperature membranes;
- **Lower temperature ECR measurement will be performed**.

Experimental results





Layered $PrBa(Co_{0.7}\heartsuit_{x-y}\clubsuit_{y})_2O_{5+\delta}$ – **synthesis conditions** (temperatures)

- Synthesis powder materials are calcinated at different temperatures;
- oxygen partial pressure step change from 0.1 to 0.01 atm at different temperatures;

Performance repeatability of $PrBa(Co_{0.7}\heartsuit_{x-y}\clubsuit_{y})_2O_{5+\delta}$ material:

- measured with oxidation step from oxygen partial pressures of 0.1 to 0.01 atm;
- Pretty good.

Electrochemical Kinetic Property Extraction

Given: $\bar{\sigma}(t)_{meas}$ $\quad$ $Find\text{: } D \text{ and } k$

$$Minimize\text{: } S(D,k) = \int_0^t [\bar{\sigma}(D,k,t)_{simu} - \bar{\sigma}(t)_{meas}]^2 \, dt$$

Subject to: $\frac{\partial C_v}{\partial t} = \nabla \cdot (D \nabla C_v)$ $\quad$ $C_v(x,y,z,0) = C_0$ $\quad$ $-D\frac{\partial C_v}{\partial n}|_{surface} = k(C_v - C_\infty)$

[*Journal of The Electrochemical Society*, **162** (9) F951-F958 (2015)]

Dopants/levels			k_{chem} [cm s^{-1}]			D_{chem} [cm^2 s^{-1}]		
♣	♥	Co	500 °C	600 °C	700 °C	500 °C	600 °C	700 °C
0.05	0.25	0.70	2.55×10^{-2}	1.17×10^{-2}	9.64×10^{-3}	1.92×10^{-3}	2.16×10^{-3}	1.92×10^{-3}
	0.275	0.675	1.27×10^{-2}	3.13×10^{-3}	4.77×10^{-4}	1.55×10^{-3}	3.13×10^{-3}	3.08×10^{-3}
	0.30	0.65	1.52×10^{-4}	2.81×10^{-4}	9.16×10^{-5}	6.20×10^{-3}	6.04×10^{-3}	2.88×10^{-3}
0.10	0.20	0.70	1.20×10^{-4}	1.72×10^{-3}	1.96×10^{-4}	1.56×10^{-3}	3.65×10^{-3}	4.54×10^{-3}
	0.25	0.65	3.20×10^{-7}	2.26×10^{-4}	6.30×10^{-4}	2.48×10^{-5}	7.77×10^{-4}	1.93×10^{-3}
	0.30	0.60	4.42×10^{-4}	1.31×10^{-3}	3.13×10^{-4}	6.60×10^{-4}	1.74×10^{-3}	2.29×10^{-3}

Electrochemical Kinetic Property Extraction

Dopants/levels			Extracted parameters @700 °C and property analysis					
♣	♥	Co	k [cm/s]	D [cm^2/s]	t_{relax}/τ_k	t_{relax}/τ_D	log(Bi)	Property limited by
0.05	0.25	0.70	9.64×10^{-3}	1.92×10^{-3}	7.92×10^{1}	3.04×10^{2}	0.584	both
	0.275	0.675	4.77×10^{-4}	3.08×10^{-3}	1.41×10^{3}	1.47×10^{2}	-0.982	both
	0.30	0.65	9.16×10^{-5}	2.88×10^{-3}	7.50×10^{3}	1.64×10^{2}	-1.66	Surface exchange
0.10	0.20	0.70	1.96×10^{-4}	4.54×10^{-3}	3.67×10^{3}	1.14×10^{2}	-1.51	Surface exchange
	0.25	0.65	6.30×10^{-4}	1.93×10^{-3}	1.07×10^{3}	2.35×10^{2}	-0.658	both
	0.30	0.60	3.13×10^{-4}	2.29×10^{-3}	2.41×10^{3}	2.48×10^{2}	-0.988	both

Fabrication of Hollow Fiber Membranes