Global Research and Development Inc.
Columbus, OH

Nano-Layered Oxygen Separation Membranes (SBIR Phase IIA)

Contract Number : DE-SC0013186

Global Research and Development Inc.

Project Period : August 25, 2018 to August 25, 2020

Principal Investigator- Don Karnes

U.S. DOE Advanced Manufacturing Office Program Review Meeting
Washington, D.C.
June 11-12, 2019

New technology being developed and demonstrated: nano-thickness membranes by scale-able manufacturing processes (for gas separation, SOFC, and water filtration)

Overview-SBIR Phase IIA

Project Title: Nano-Layered Oxygen Separation Membranes

Timeline:

Project Start Date: 08/25/2018

Budget Period End Date: 08/25/2019

Project End Date: 08/25/2020

Barriers and Challenges:

- Platform Technology for inorganic nano-thickness membranes.
- Converting from small flat supports to tubular supports
- Manufacture of tubular supports with nano surface roughness
- Deposition of 50-100 nm membrane layers
- Manufacturing and optimizing single tube cell during year 1
- Scaling up to multi-tube cells in year 2

Project Budget and Costs:

Budget	DOE Share	Cost Share	Total	Cost Share %
Overall Budget	$999,999	$0	$999,000	0%
Approved Budget (BP-1)	$500,000	$0	$500,000	0%
Costs as of 5/14/2019	$306,000	$0	$306,000	0%

Project Team and Roles:

- Don Karnes PI –Technical and Business Leadership
- Dr. Hendrik –Inorganic nano- thickness membrane expert
- Dr. Ralph Bauer –Inorganic nano-thickness membrane fabrication expert
- Mr. Yi Zhou- Inorganic nano-thickness membrane fabrication expert
- Mr. Dean Panik- membrane cell design and fabrication expert

AMO MYPP Connection:

- Improved energy efficiency for membrane separation technologies (much lower electricity cost)
- Lower operating temperature for inorganic membranes, resulting in lower life cycle costs for membranes
- Applies to applications that result in less electricity consumption and carbon foot print : O_2 production, SOFC, and water separation (purification).
- Creates new manufacturing capacity in the U.S. that can be automated to reduce manufacturing costs for membrane separation technologies

Project Objectives

1) Dramatically reduce the $/ton cost for oxygen so it can be used in coal powered plants to reduce CO_2 emissions. Presently cryogenic oxygen generation plant equipment is over 12% of the coal power plant construction costs, and the cost (primarily electricity) to produce the oxygen is over $24/ton (source DOE).

2) We have completed a SBIR Phase I and II and demonstrated the technology with high O_2 outputs in the 400-600°C. From material and manufacturing costs, we have projected that with our membrane technology scaled up, the capital equipment cost for generating oxygen would be less than 4% of the power plant construction costs. The cost to produce the O_2 would be less than $5/ton (again primarily electricity).

3) The objective of the Phase IIA is optimizing O_2 output from single tube cells, and demonstrating multi-tube modules. The multi-tube modules could then be stacked to produce various levels of total O_2 output, from 1-1000 tons/day as Phase III activities.

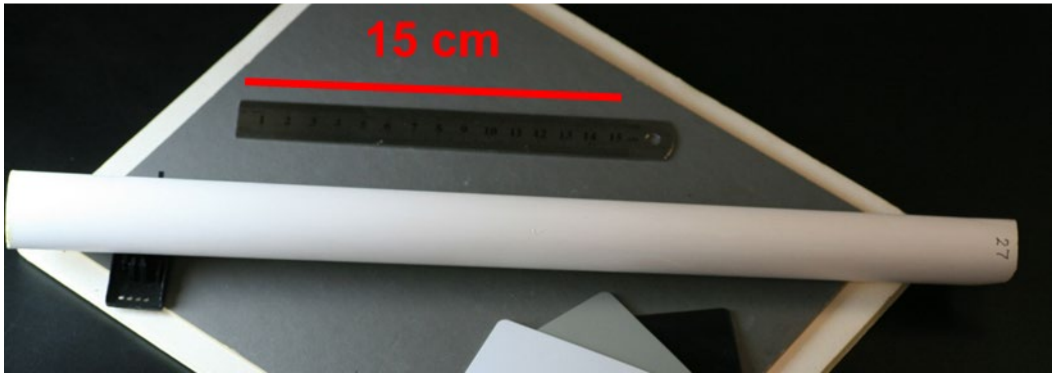
Technical Innovation

1) Present inorganic membranes for oxygen use extruded tubes that are 5-10% porous, with micro-scale surface roughness, thus requiring 10-300μm thick layers to coat the support. Thick layers must be heated to 700-900°C to achieve measurable O_2 permeance (output).
2) Our innovation is that we have developed a highly porous (38 vol%) ceramic support tube using a high-rate production process to fabricate the tube, which inherently creates a 25nm surface roughness for immediate nano-thick membrane deposition.
3) We deposit 50-150nm membrane on this surface to separate O_2 from air, while achieving more output with less pressure (electricity cost) at much lower temperatures (200-600°C).
4) Oxygen output per square meter of membrane surface is several times higher than micron thick membranes even at lower temperatures.
5) Impact: Capital equipment cost (1/3 of cryogenic oxygen) and operating costs (1/5 of cryogenic oxygen). The technology will significantly impact the current $26 billion/year cryogenic oxygen market. Oxygen will not have to be shipped. It can be made on site. This technology is scale-able down to personal oxygen units for individuals at 5-10 liters/min, to 1-5 ton/day units for hospitals, and 1000-3000 tons/day for steel mills and coal plants.

Technical Approach

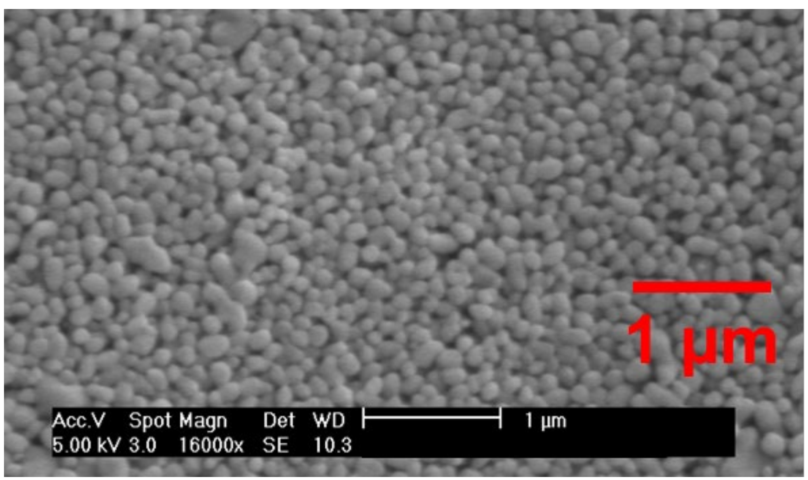
We have demonstrated both flat and tubular inorganic supports

The Support
Macro-scale:



Tubular Support Properties	Measured Value
Thickness	2 mm
Porosity	≤38%
Pore Size (surface)	~40 nm
Pore Size (bulk)	~80 nm
Surface Roughness	25 nm

Nano-scale:

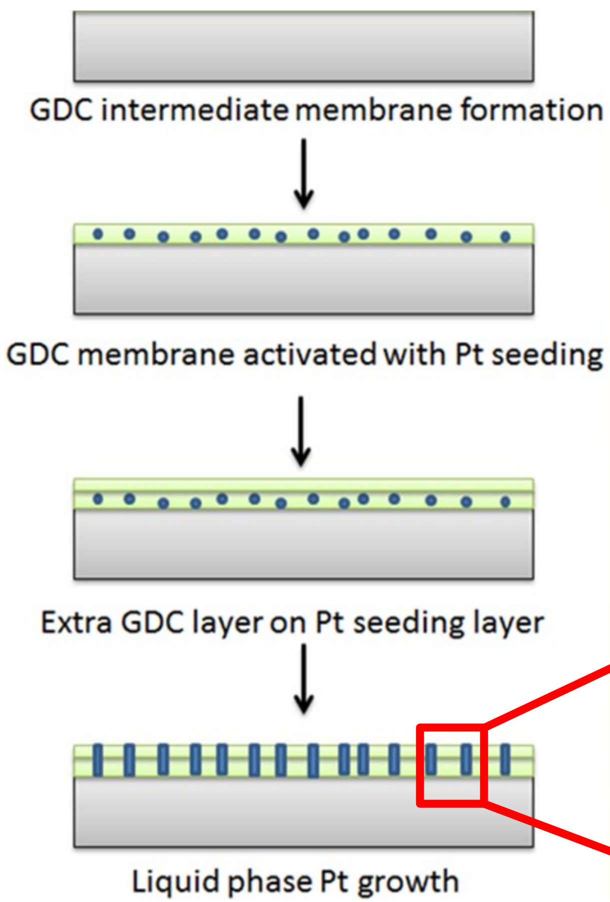


- Tubes withstand pressurization over 250 psi
- Tubes withstand rapid thermal cycling of >10°C/s to temperatures of 950°C

Technical Approach

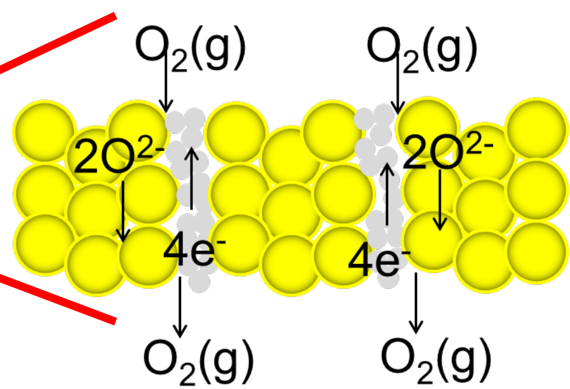
We have demonstrated nano-thickness membranes on the inorganic supports

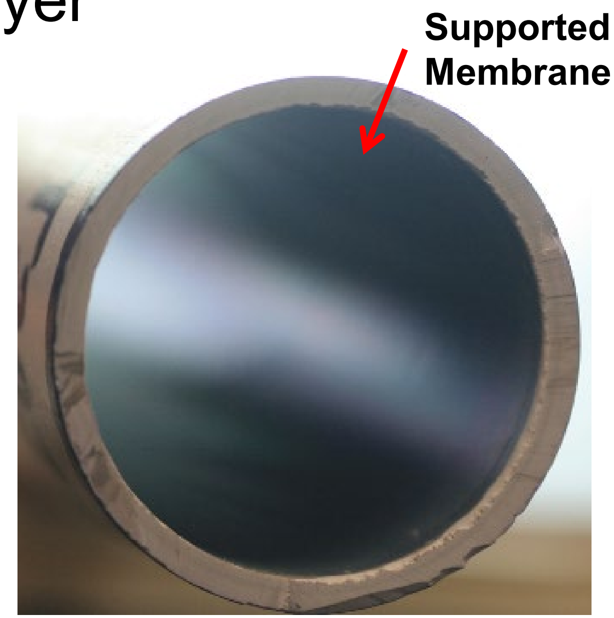
The Membrane



- Pt phase fills pores of GDC layer for a thickness of ~20nm, making a thin, dense dual phase layer
- O^{2-} anions transport through GDC, e- are conducted through Pt phase
- Highly selective and permeable due to thin, dense active layer

Dual Phase Design

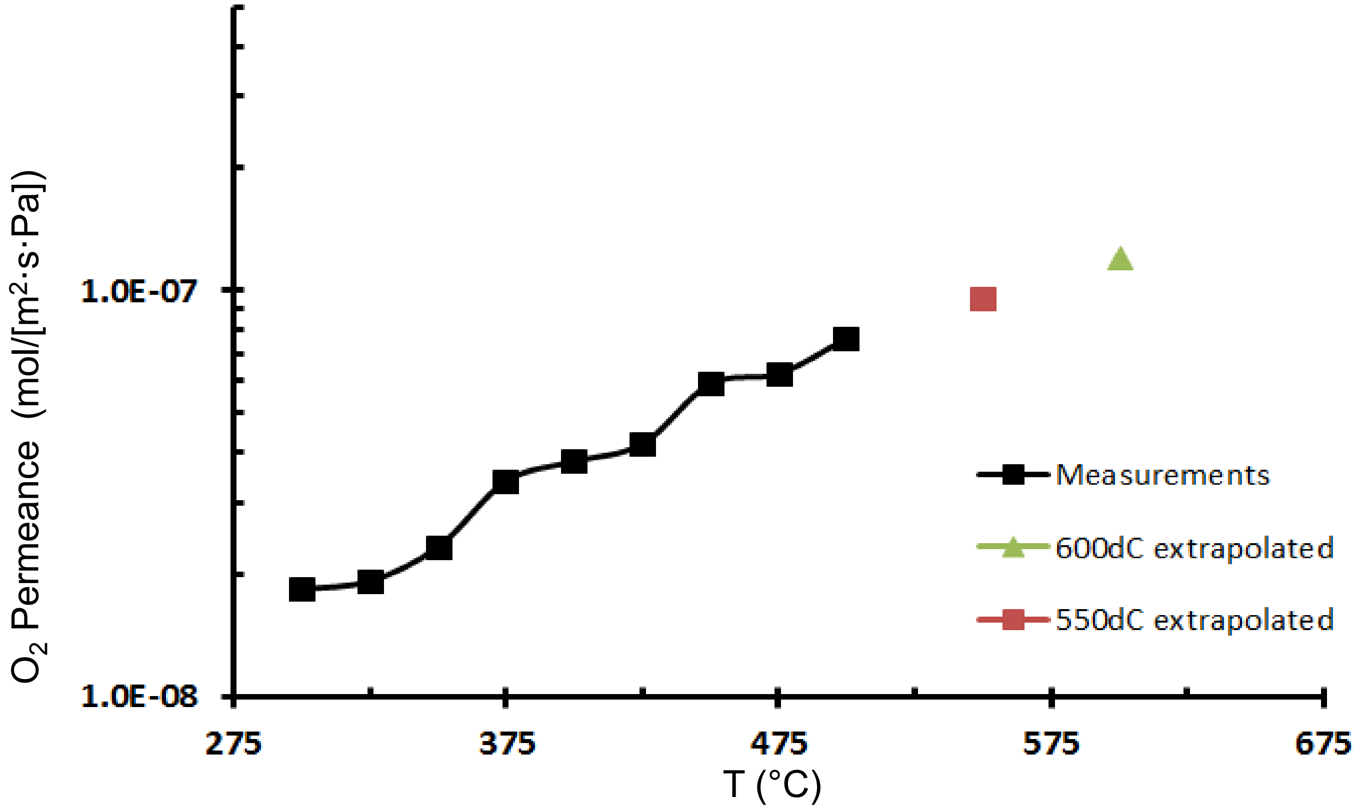




Nano-Layered Oxygen Separation Membranes

Results and Accomplishments

- Membrane demonstrates high selectivity and permeance between 200 to 600°C.
- Selectivities of >200 even at temperatures as low as 200°C



Measurements at 575°C, with a feed pressure of 250 psi yield an O_2 flow rate of 230 Lpm/m^2

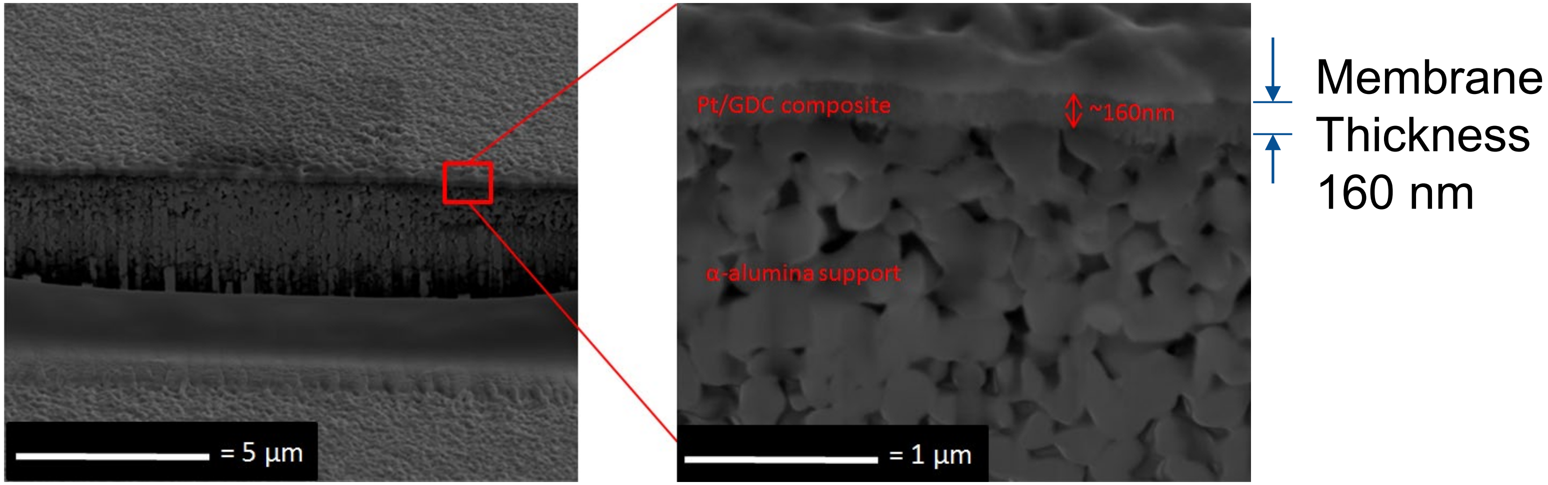
Results and Accomplishments

- Equipment for up scaling production of tubular supports has been purchased with designs started on commercial scale equipment.
- Nano-particle dispersions, layer deposition onto tubular support, and layer thermal processing for a complete membrane is accomplished within 24 hours. All processes are readily scaleable.

- 2nd generation single tube characterization cell testing is underway, improvements already demonstrated in cell manufacturing, assembly/disassembly are being implemented into the multi-tubular module design.

Results and Accomplishments

- SEM cross-section of membrane and support microstructure



- High angle images of deposited membrane layers

Tubular Nano-Layered Oxygen Separation Membranes

Remaining phase IIA tasks to be completed over the next 15 months

Task 3: Characterization of single tube modules
Subtask 3.1: Functional and lifetime characterization of O_2 membranes
Subtask 3.2: Structural Characterization
Subtask 3.3: Characterization of tubular membranes and cell stability
Subtask 3.4: Verification of tubular membrane performance by one of two large cryogenic oxygen manufacturers
Task 4: Assembly and characterization of a multi-tubular demonstration module
Task 5: Design concepts for 1…10 ton per day, 100…500 ton per day, and IGCC facilities

Dramatic Projected Cost Reductions for Oxygen Production compared to Cryogenic Oxygen Production (Currently a $26 billion/year market)

Material cost/m^2 comparison: Nano-thick membrane vs 300 micron membrane

Structure	200 nm	300 µm
Support	$36/m^2	$44/m^2 can vary depending on base material
Membrane		
GDC	$0.025/m^2	$38.90/m^2
Pt	$1.11/m^2	$1660/m^2
Total	$47.14/m^2	$1742.90/m^2

Note: Table made assuming Pt costs of $29,159/kg. Other prices quoted at industrial volumes.

We have laid out an automated factory to make tubes, coat tubes, and assembly multi-tube modules. The cost for the modules are $200/m2 of membrane surface area, so total cost per square meter of membrane is less than $250/m^2. This results in the oxygen plant being less than 4% of the coal fired power plant, and the ongoing cost to produce the O_2 (primarily electricity to run the compressor) is around $5 per ton, compared to over $24/ton for cryogenic oxygen.

Transition (beyond DOE assistance)

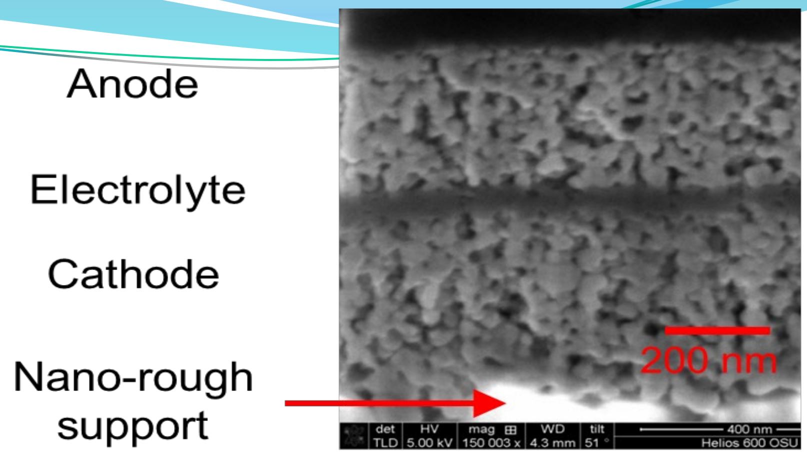
- We anticipate being at TRL-6 at end of Phase IIA
- We are in discussion with two large commercial cryogenic oxygen producers who are monitoring our progress and demonstration cells. We hope they will license the technology for scale up, 100 ton/day plus units.
- For after the Phase IIA, We are currently seeking funding for a larger demonstration unit, 1-5 ton/day pilot unit (hospital market, and small power plants). We are seeking cost share funds to propose a Phase IIC project.
- We are also seeking industrial partners and investors to pursue Solid Oxide Fuel Cells with this nano-thickness membrane technology. Technology also enables very high SOFC outputs at lower temperatures (400-600°C)

Additional Technology

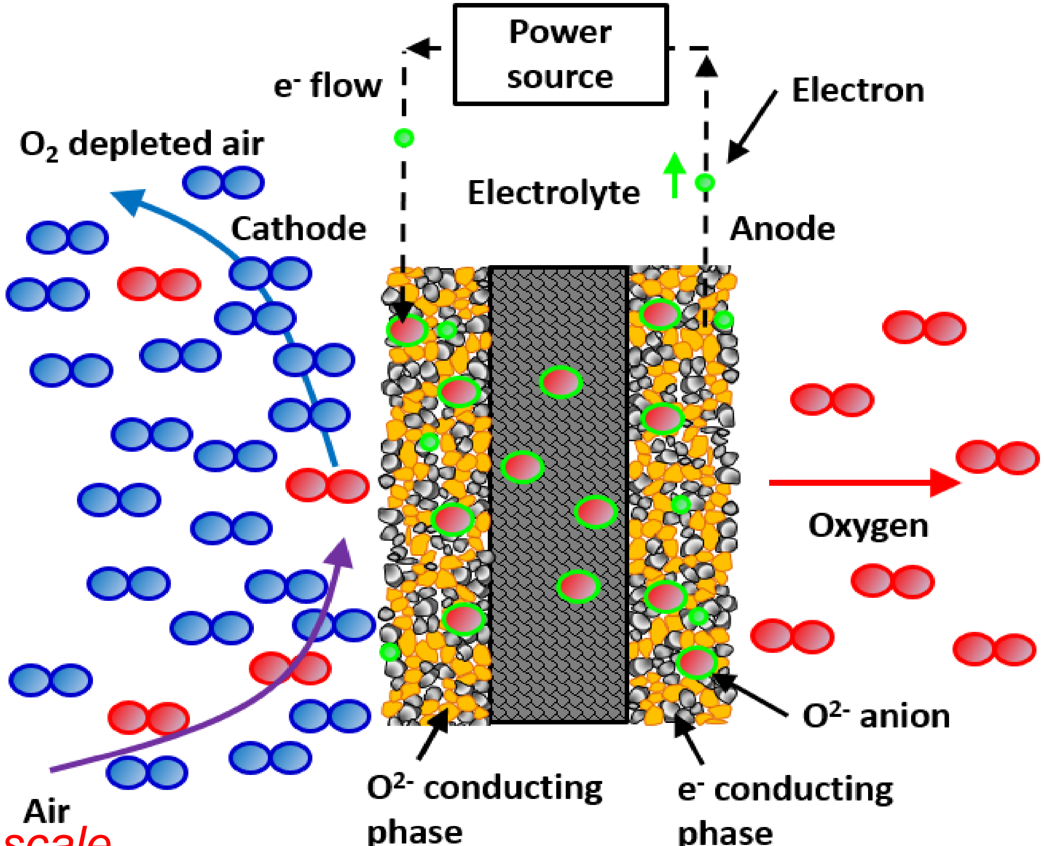
Nano-Thickness Membranes

Oxygen pump basics

All layers total 800 nm

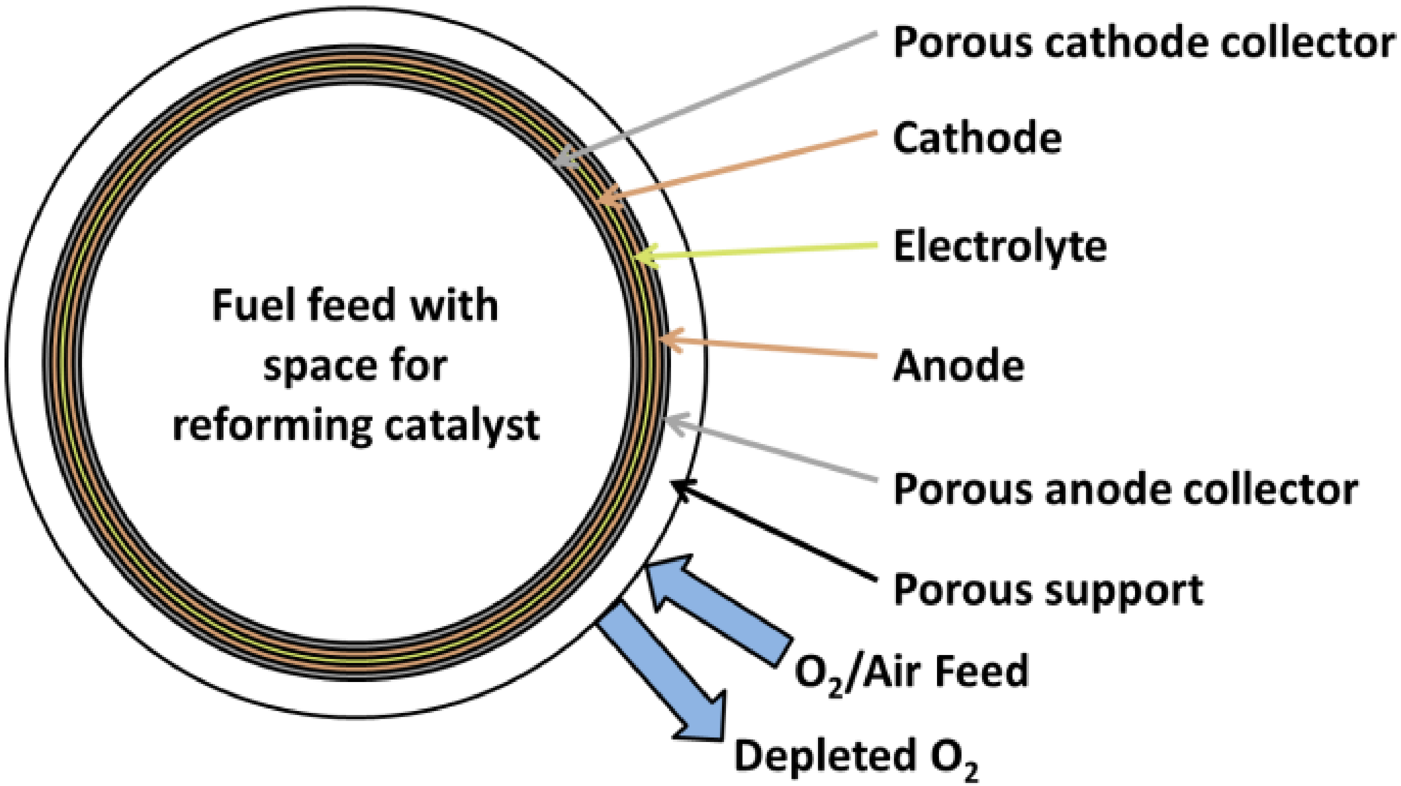


- Electrochemically driven transport device
- Voltage difference at electrodes drives oxygen anions through electrolyte
- Changing applied voltage changes O_2 permeate pressure



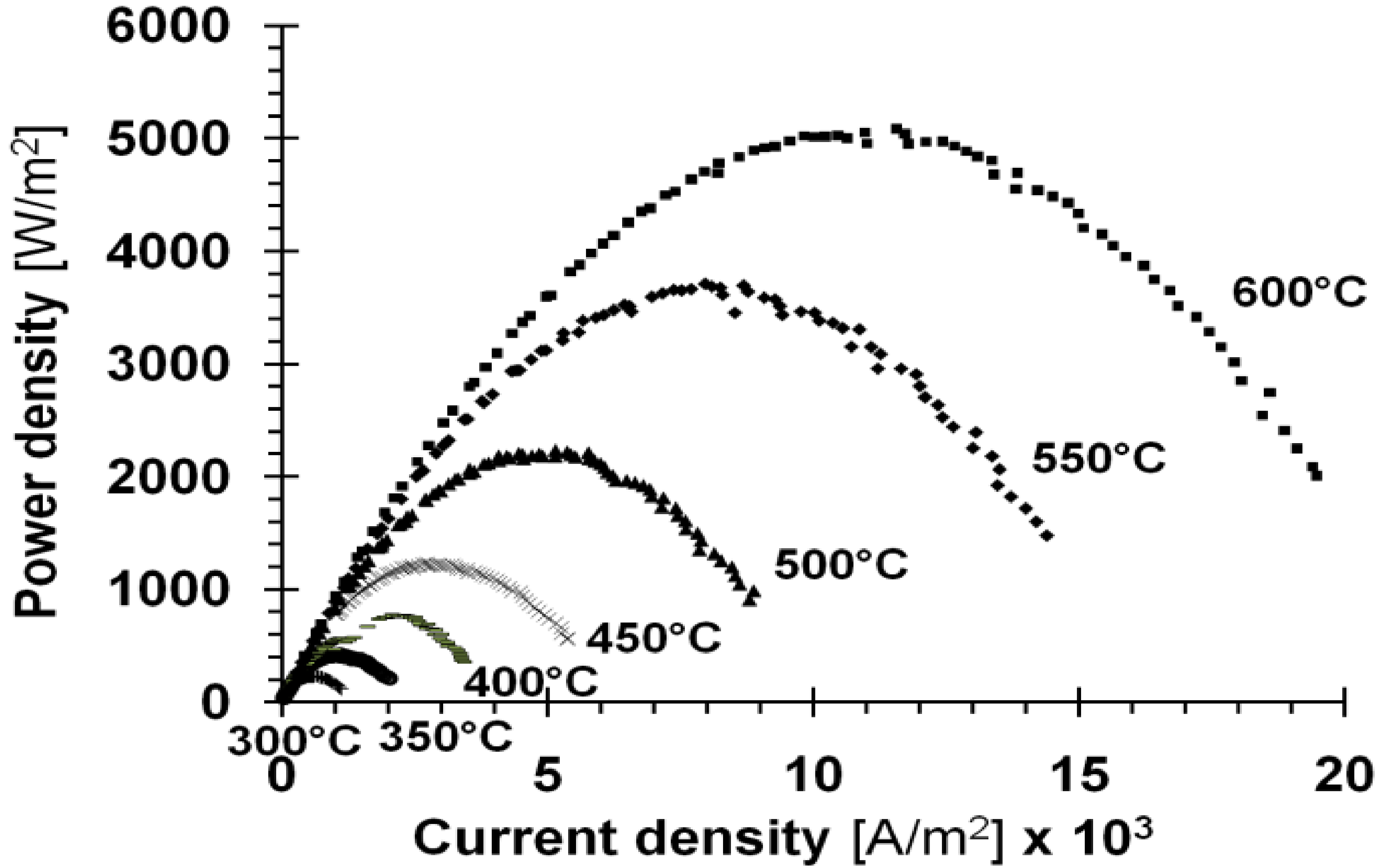
*not to scale

Additional Technology for Nano-Thickness Membranes



Tubular Support SOFC

SOFC - Significant power in 400-600°C range



5kW SOFC Projected Stack cost $/kw

* Platinum wire $175 (5 kw) based on current wire size. Wire size could be much less to to carry current level $75-$175 (5kw).

5kW stack cost (20 -22mm ID X 558 mm long tubes)
≤600°C temperature

Cell power density (W/m^2)	**5,000 (W/m^2)**
Material 5kW SOFC stack (today in low volume)	
Anode material	**$36.74**
Electrolyte material	**$0.01**
Cathode material	**$36.73**
Seals	**$15.88**
Support Material	**$39.11**
Platinum wire *	**$175.00**
Tube end plates	**$36.96**
Total material stack cost	**$340.43**
Stack direct labor @ $35.00/ hr.	
Support tubes, coating, containment	**$51.24**
Assembly & test	**$43.75**
Factory burden @ 4 X direct labor	**$204.96**
Total stack cost	**$640.38**
Stack cost per kW **	**$128.00**

****Potential to be under $100/kW**