2013 DOE Bioenergy Technologies Office (BETO) Project Peer Review

Development of Biofuels Using Ionic Transfer Membranes

Phase III

May 20-23, 2013
Technology Area Review: Biofuels

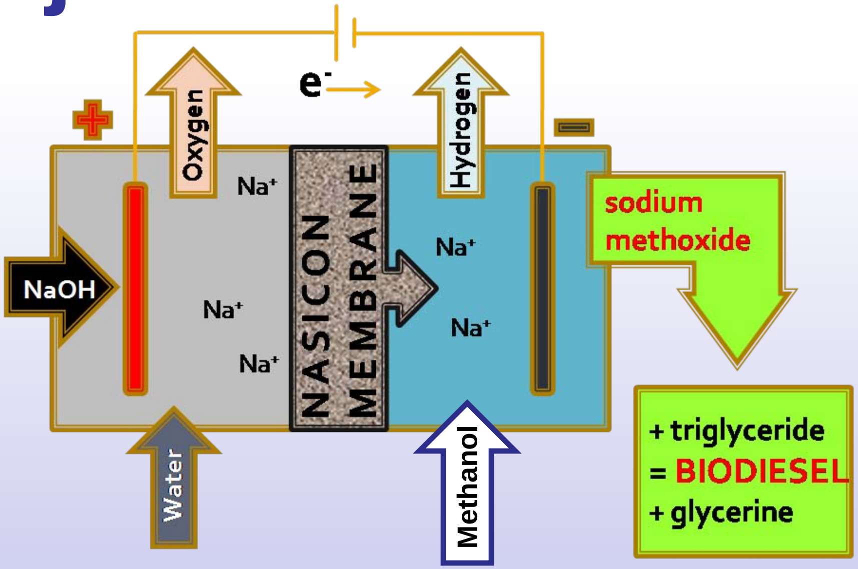
Principal Investigator: **Dr. Kris Lipinska**, University of Nevada Las Vegas

Investigators: **S. Balagopal**, Ceramatec Inc.
Dr. O. Hemmers, UNLV
Dr. C. Bae, Rensselaer Polytechnic Institute

Goal Statement & Project Overview - 1

What?

- **Sodium methoxide (SMO)** is an effective **catalyst for the trans-esterification** of vegetable **oils**, animal **fats** and recycled **greases**. An important **application** for these materials is **production of biodiesel**



Problem

- **Current production** of **SMO** uses high-purity **Na metal**, an **expensive raw material** that requires a **complex infrastructure** for safe handling. Other methods: make **SMO** from **Na/Hg amalgam**, but final product contains **toxic mercury**; other produces chlorine and has higher carbon footprint.

Solution!

- **This project** investigates an **Electrochemical Membrane Process (EMP)** to yield **high-purity SMO** from **low-cost** aqueous sodium hydroxide, using a *Sodium Super Ionic Conductor* **membrane: NaSICON.**

- The result is a **lower-cost, high-purity SMO** with **no contaminants** and **no waste stream**.

Goal Statement & Project Overview - 2

- Goal is to demonstrate an **energy-efficient**, **low cost Electrochemical Membrane System** (**EMS**) to produce Sodium Methoxide (**SMO**), on site and as needed, at a Biofuels Production Facility
- Demonstration of an integrated **SMO** unit with the Biofuel process will allow manufacturers the flexibility to evaluate other biomass feedstock's such as algal oil, and oils derived from other types of feedstocks
- **HIGH LEVEL objectives of the project**
  - Demonstrate the concept of selective transport Na^+ across the NaSICON Membrane for reaction with methanol to form a final product: **SMO**
  - Obtain highest concentration of **SMO** produced versus energy consumed
  - Demonstrate long-term performance of a membrane cell to produce **SMO**
  - Ability to scale up size of ceramic membrane and build & operate a robust & reliable modular and **scalable Multi-Tubular Unit**

Quad Chart Overview - 1

Timeline

- PHASE-III Start date: 10/1/2011
- PHASE-III End date: 12/31/2013
- Percent complete: 60%

Barriers

Barriers addressed

- Biggest engineering problem to be overcome: **scalability of membrane size and modularization of system footprint** to meet the production demand. System operation reliability and safety (ex. handling of gases).
- **Reduce commercial cost of production**: the cost to produce Sodium Methoxide (SMO) by the electrochemical process is anticipated to be in the $0.30 to $0.35/lbs of 28 wt% SMO solution in methanol.

Budget (DOE/Cost Share)

- Funding for FY11: $824K/$339K
- Funding for FY12: $726K/$186K
- Funding for FY13: $490k/$0K
- Years the project has been funded: 7 years with $697K average annual funding.

Partners

- Key Interactions: K. Lipinska, UNLV; S. Balagopal, Ceramatec Inc.; O. Hemmers, UNLV; C. Bae, RPI
- Project Management: Kris Lipinska, U. of Nevada Las Vegas

Overall Approach

THE PROJECT : Development of an electrochemical process producing high-purity **Sodium Methoxide - SMO** from low-cost aqueous sodium hydroxide, with the use of **NaSICON** membranes (Sodium SuperIonic Conductors).

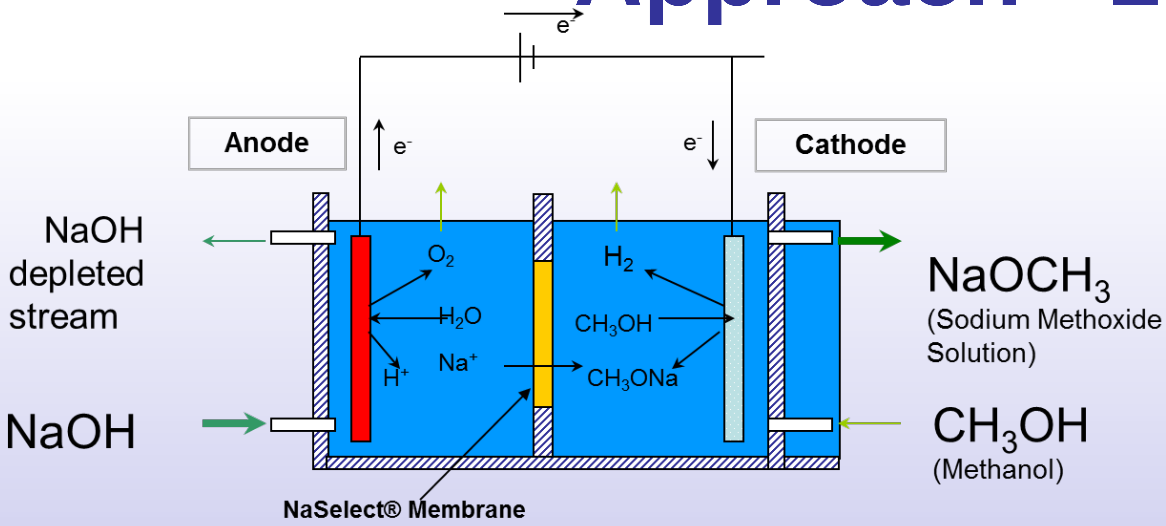
THE PROBLEM

- Our **SMO production** process is low-cost, but **highly caustic solution reduces** the stability of the **NaSICON** membrane and **decreases its lifetime and performance**.

3 BRANCHED APPROACH

- **Approach #1:** develop **tubular membranes** with higher burst pressure reliability (*as opposed to planar*) with better performance and **reduced energy consumption.**
- **Approach #2**: **coating materials** that conducts sodium ions and **that** extend membrane lifetime.
- **Approach #3**: **composition-structure-property-synthesis route relationship studies** to develop **membrane** materials that better withstand harsh operating conditions.

Approach - 1



NaSelect™ Ceramic membrane

- Use **Na$^+$** transporting **NaSICON Membrane** in an electro-chem. cell to make **99.99% pure SMO**.
- Design **Prototype Cell** to transition from **Planar** to **Tubular** membrane.
- Develop a high-yield process to make large area **NaSelect™ Membrane**.
- Conceptualize design to configure **multiple Tubular Membranes** to increase production.
- Demonstrate modular unit making up to **50 lbs/day of SMO** at highest concentration.
- Complete a techno-feasibility process analysis for integration into Biofuels production.
- Development of **blocky ionic polymers** with nano-structured ionic channels **to coat** and to protect **NaSICON Membrane** surface.
- Development of **new NaSICON compositions** with lower fabrication temperature, lower energy consumption and improved mechanical properties.
- Attempt an alternative **glass-ceramic route** for **NaSICON synthesis** by controlled crystallization of a precursor **NaSICON glass** in order to fabricate dense, small grain size, mostly single-phase **NaSICON** with good electrical conductivity.

Approach – 2
Management Approach

- The **Project Management Plan (PMP)** is the primary **formal “guiding document”** for the project and is updated as necessary and transmitted to all participants.
- **Formal Reports**: quarterly **technical** and **financial** status **reports**; (planned vs. actual expenditures for the quarter); exception reporting (explaining a major deviation from the established schedule); and **semi-annual** update of the **PMP**.
- **Project Meetings**: include bi-annual technical project accomplishment meetings, which include all project participants; and informal meetings among PIs to resolve issues and exchange information.
- **UNLV lead PI**, as the overall project manager, communicates with all project participants by technical accomplishment reports; by periodic project updates and by informal meetings with co-PIs and representatives of the industrial participant.

Approach – 3
Milestones for Monitoring Progress

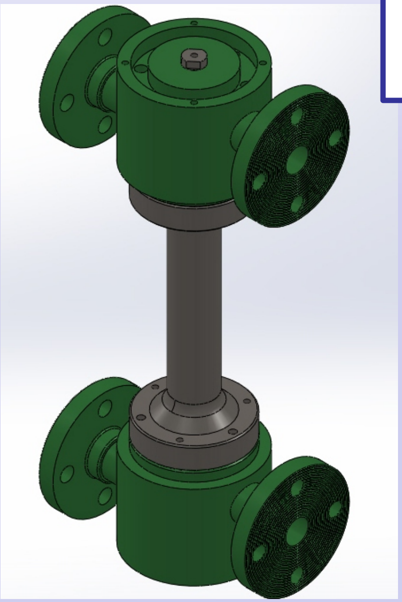
- **Key Milestones Summary**
  - Complete flow sheet and system design
  - Processing yield of NaSICON membranes: 70% of ceramic tubular membrane manufacturing yield
  - Process design maturity: 1000h of cell performance in NaOH to produce sodium methoxide, cell operation at 100 mA/cm^2 at 50C.
  - Demonstrate polymer coated NaSICON with stability over 1 week
- **Go/No-Go Decisions** are based on chemical & economic feasibility and operating parameters:
  - Design single membrane cell: 500h of cell operation to establish seal reliability
  - Assembly of skid: 100% dimension target to manufacture and assembly components.
  - Operation single membrane cells: 1000h of cell operation at 100 mA/cm2 within 1 volts of steady performance.
  - Cost target for Sodium methoxide: 100% payback and cost target to produce sodium methoxide
  - Demonstrate NaSICON ceramics produced by glass technology with sub-micron grain size and high-crystallinity

Approach – 4
Outline of Roles & Responsibilities

- **UNLV's Harry Reid Center for Environmental Studies (UNLV- HRC) manages** and **administers** the project according to the Statement of Project Objectives.
- **Ceramatec *Inc* is the industrial partner** in the project.
- **UNLV Office of Sponsored Programs** (OSP) assures that all **financial assistance agreements** are accomplished, and is the primary POC with DOE and with the industrial partner regarding contractual and financial matters.
- **Lead PI** plans, **directs** and **evaluates** the research assigned to UNLV as well as oversees and evaluates the work assigned to the industrial partner. The PI reports directly to the DOE.
- **Co-PI's** are responsible for individual **Tasks**.
- **Ceramatec's PI**: (1) leads the development and technology maturity activities, (2) is responsible for planning, directing and evaluating the work of the sub-contract including the schedule of milestones and deliverables; (3) reports directly to the **UNLV lead PI** on accomplishment of the work, (4) contractual and financial aspects are the responsibility of Ceramatec's business manager whose POC is UNLV's lead PI and OSP.

Technical Accomplishments - 1

Two prototype design concepts developed with Tubular NaSelect™ membrane with electrode configuration for design qualification.



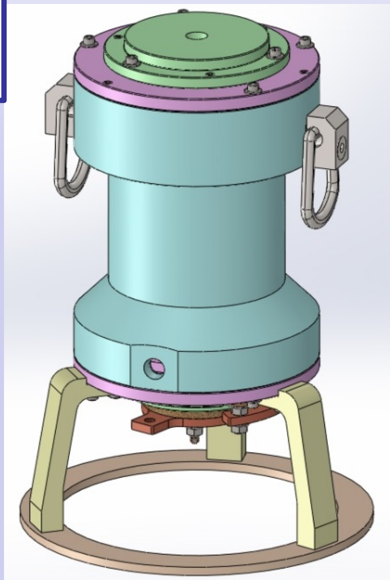
I. Canister design

- Modular concept
- Compact
- **Design and validation completed**

Single membrane cell

II. Rod & Mesh

- Non-Modular concept
- Compact when scaled
- **Single membrane cell tested**

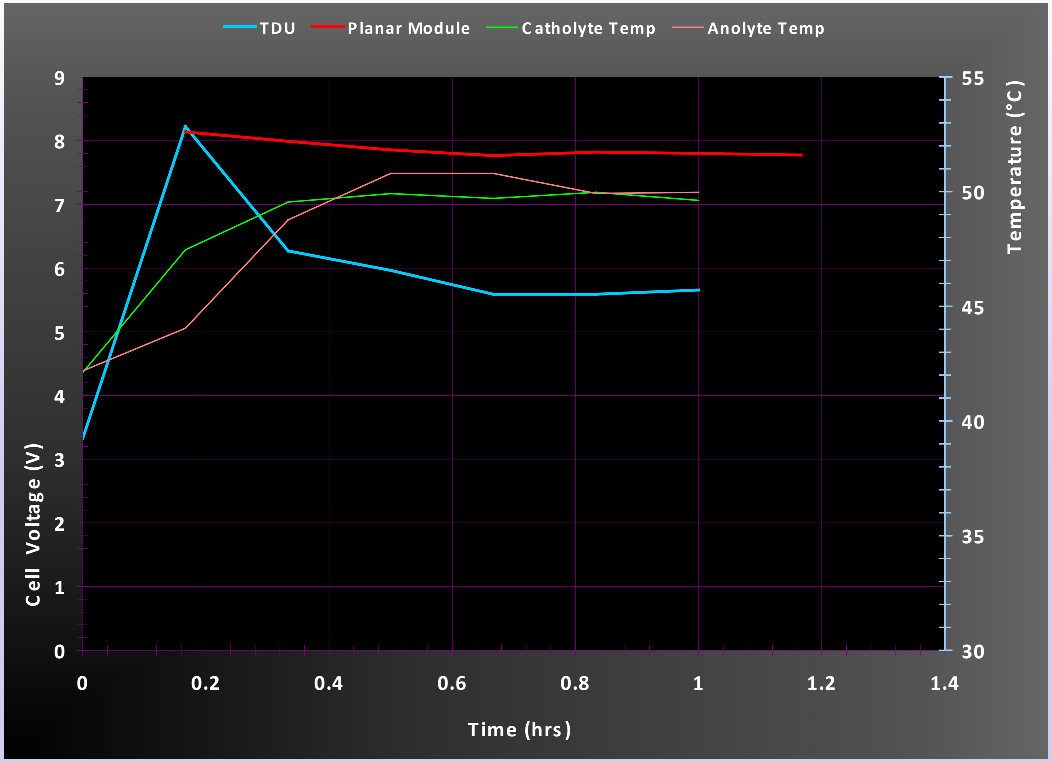


5 membrane cell

Technical Accomplishments - 2

Operating conditions:

- 100 mA/cm^2
- 20% NaOH
- 20% $NaOCH_3$



GOAL: to reduce energy consumption:

- Tubular membrane cell operates **~2.2V lower** than planar membrane cell
- **0.83 kWh/lb**. of SMO on **100%** basis

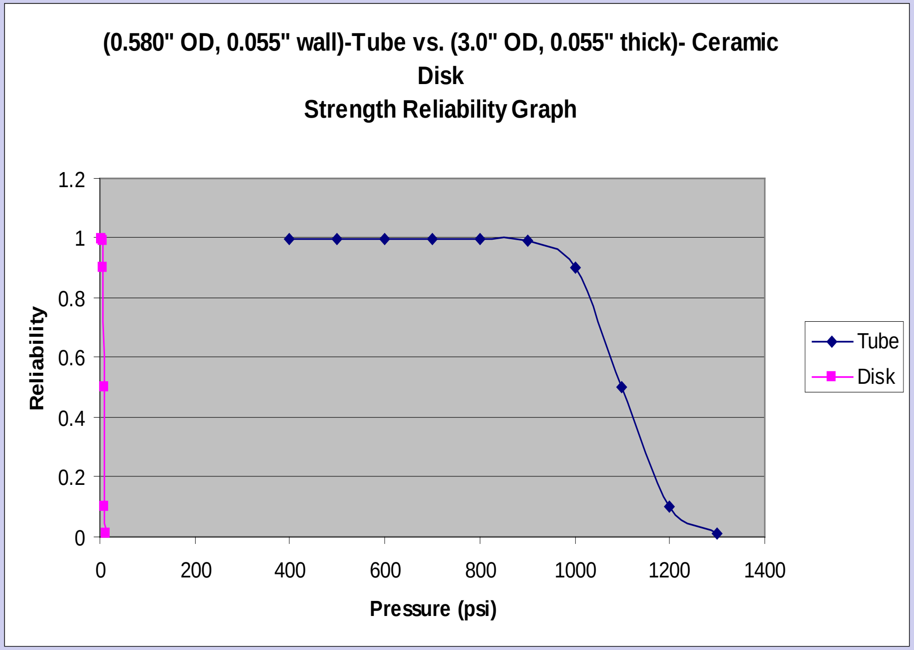
Technical Accomplishments - 3

Tubular NaSICON Membrane-based Cell Units allow operation:

- under higher flow and pressure drop conditions
- with lower number of cell seals
- with smaller footprint of device

ACHIEVEMENTS in manufacture of large area ceramics:

- Developed process to make **tubular NaSelect™ membrane**
- Transition from 0.8 inch diameter to 1.5 inch diameter membrane
- Increased ceramic production yield from 60% to 80%
- Implemented quality control measures to make robust membranes



→ Weibull reliability: NaSelect™ tubular membrane withstands > 400 psi pressure differential

Technical Accomplishments - 4

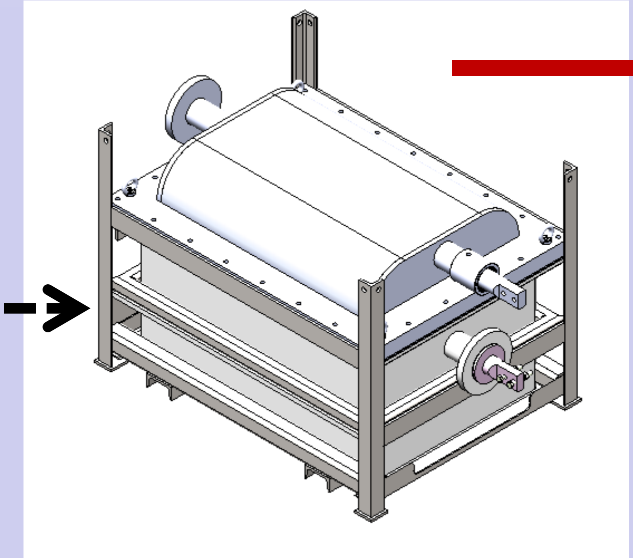
Design and manufacture **multi-Tubular Membrane-based Cell Unit** to increase processing through put.

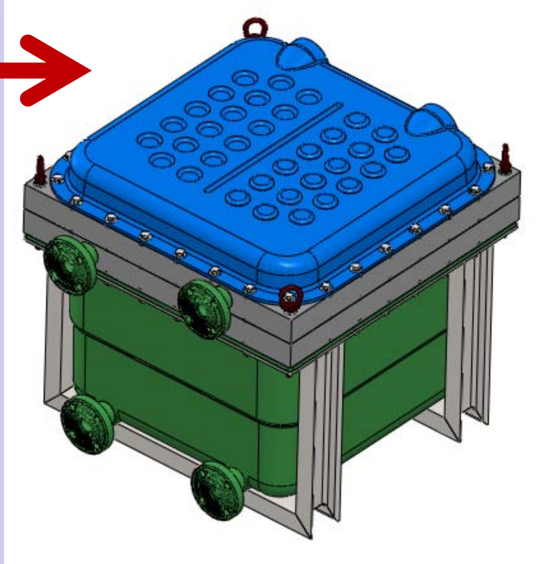
MODULAR DESIGN: 50 LBS/DAY SMO UNIT

Membrane canister in unit

Generation-1 UNIT: LARGE footprint

Generation-2 UNIT: SMALL footprint

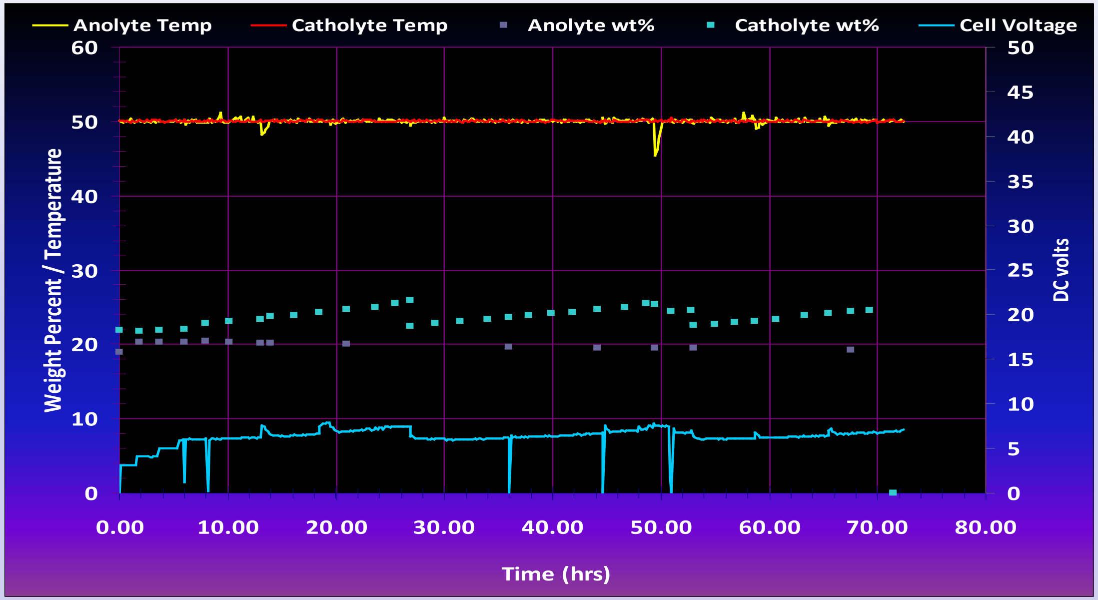


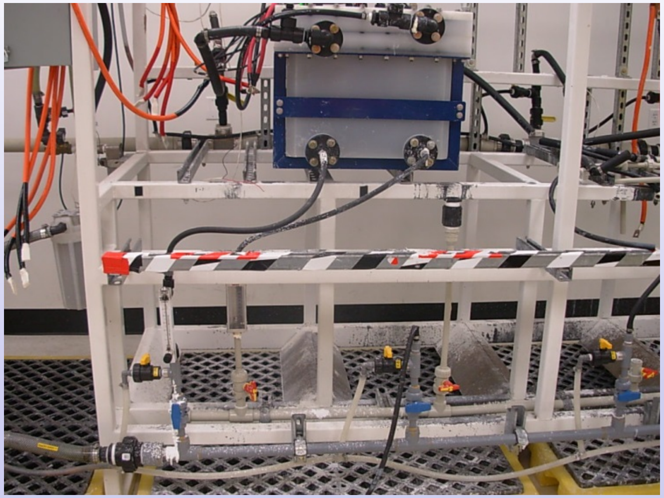


24x24x24 inches

Technical Accomplishments - 5

Generation 2 UNIT:
Module Operational Results





Operational Milestone:

- **Demonstrated batch unit operation at 100 mA/cm^2 to produce SMO**
- **Cell voltage increase from allowing concentration of SMO to increase from 18 to 25 wt%.**

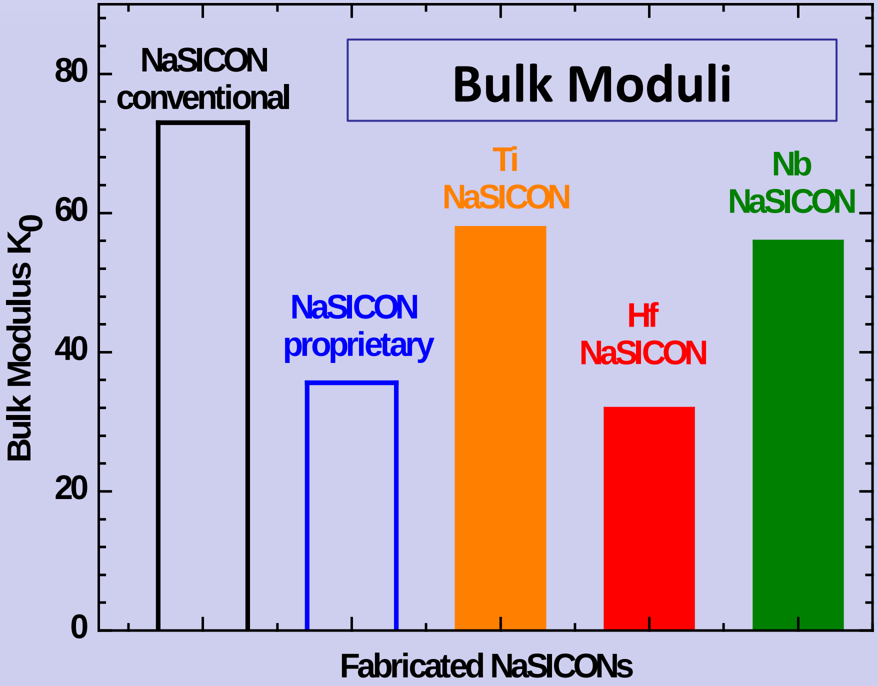
Technical Accomplishments - 6

Fabricated New NaSICON compositions: single-doping in the Zr-site

$Na_{1+x}\,Zr_2\,Si_x\,P_{3-x}\,O_{12}$

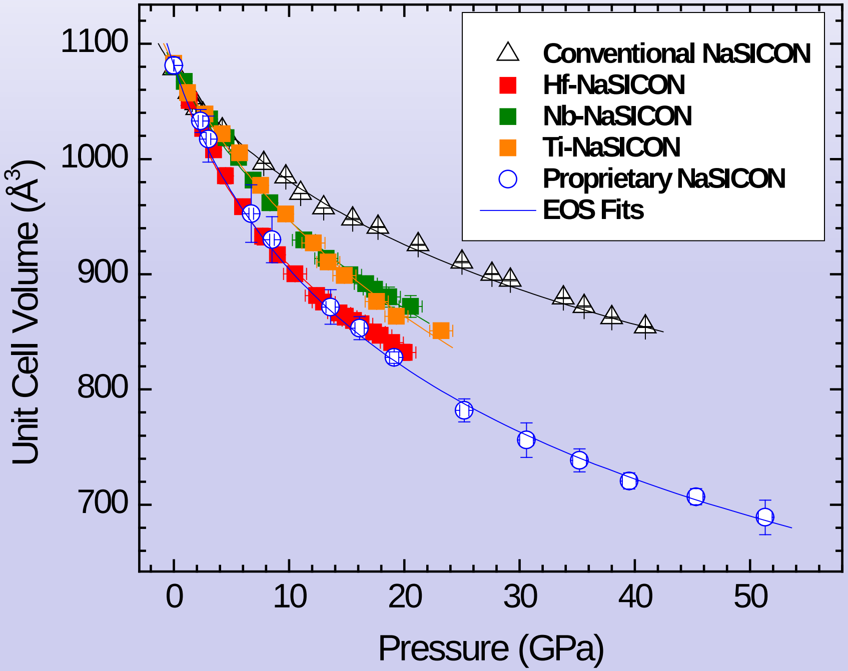
when x=2

$Na_3\,\{Zr_{2-x}\,A_x\}\,Si_2\,PO_{12}$



High-Pressure X-Ray Diff. in Diamond Anvil Cell:

Studied Compressibility and Bulk Modulus



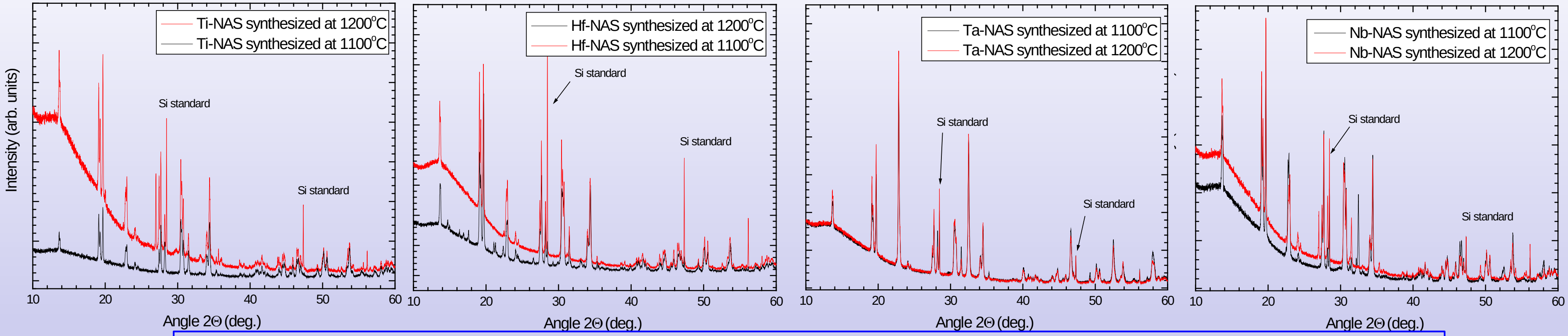
All New NaSICONs have:

- smaller **Bulk Moduli**, **more compressible** than the **conventional NaSICON**.
- have better ability to accommodate stress.

Technical Accomplishments - 7

Successfully Fabricated New NaSICON compositions

single-doping in the **Zr-site:** $Na_3\{Zr_{2-x}A_x\}Si_2PO_{12}$



Ti, **Nb**, **Ta**, and **Hf**- substituted **NaSICON** ceramics synthesized at **1100°C** and **1200°C**:
XRD patterns show progress of NaSICON crystallization as a function of synthesis T.

Partial Substitution of Zr-sites	Ionic Radius (Å)	Unit Cell Volume ($Å^3$)	Cell Param. *a* (Å)	Cell Param. *b* (Å)	Cell Param. *c* (Å)	Angle (deg.)
$Na_3Zr_2Si_2PO_{12}$	0.72	1084.72	15.64	9.04	9.22	123.74
Ti^{4+}	0.61	1082.79	15.62	9.04	9.21	123.65
Hf^{4+}	0.71	1081.56	15.62	9.03	9.22	123.75
Nb^{5+}	0.64	1080.33	15.61	9.02	9.22	123.63
Ta^{5+}	0.64	1076.24	15.60	9.01	9.22	123.73

NaSICON ceramics synthesized by solid state reaction at **1100°C**:
unit cell volume- V and cell parameters- a, b, c in function of **Zr** substitution by **Ti**, **Nb**,**Ta, Hf**
based on Rietveld structural refinements of XRD patterns.

Technical Accomplishments - 7

Successfully Fabricated New NaSICON compositions by single-doping in the Zr-site: $Na_3\{Zr_{2-x}A_x\}Si_2PO_{12}$

Partial Substitution of Zr-sites	Synthesis Temperature: 1100°C			Synthesis Temperature: 1200°C		
	% NaSICON Phase	% Zirconia Secondary Phase	% Other	% NaSICON Phase	% Zirconia Secondary Phase	% Other
$Na_3Zr_2Si_2PO_{12}$ (baseline comp.)	89.3	10.7	---	90.7	9.3	---
Ti^{4+}	**91.8**	**4.9**	3.3	73.7	6.8	19.5
Hf^{4+}	87.5	12.5	---	**92.0**	**8.0**	---
Nb^{5+}	86.0	3.8	10.2	**84.1**	**14.4**	1.5
Ta^{5+}	59.1	14.1	26.8	69.5	9.5	21

Hf-doped NaSICON is the **best** for further development:

- ✓ **lowest bulk modulus**
- ✓ **largest % of NaSICON phase**

Comparison of NaSICON ceramics synthesized at **1100°C** and **1200°C**:

- quantity of **NaSICON - primary crystalline phase** and
- quantity of **Zirconia - secondary crystalline phase** as a function of **Zr** substitution by **Ti**, **Nb**,**Ta, and Hf.**

(*All data based on Rietveld structural refinements of XRD patterns*).

Technical Accomplishments - 8

New Glass-Ceramic route for NaSICON synthesis

ROUTE

- First step: fabrication of **NaSICON glass.**
- Second step: controlled crystallization of NaSICON glass.
- Route alternative to solid state synthesis (=sintering of polycrystalline powders).

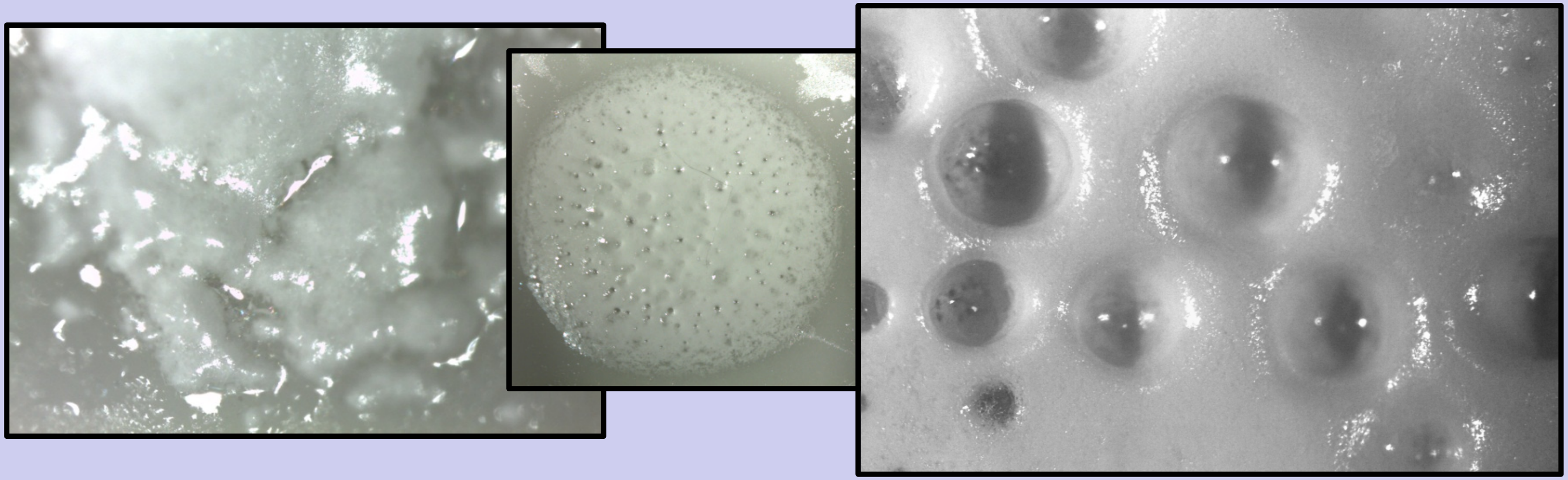
EXPECTED BENEFITS

- High-density NaSICON ceramics.
- Smaller NaSICON ceramics grain size.
- Single-phase NaSICON ceramics.
- Lower synthesis temperature.
- Better electrical conductivity.

Developed New NaSICON compositions with

double-atom doping in the **Zr-site:** $Na_3\{Zr_{2-(x+y)}(A_x B_y\} Si_2 PO_{12}$

First Fabricated NaSICON melts – glasses

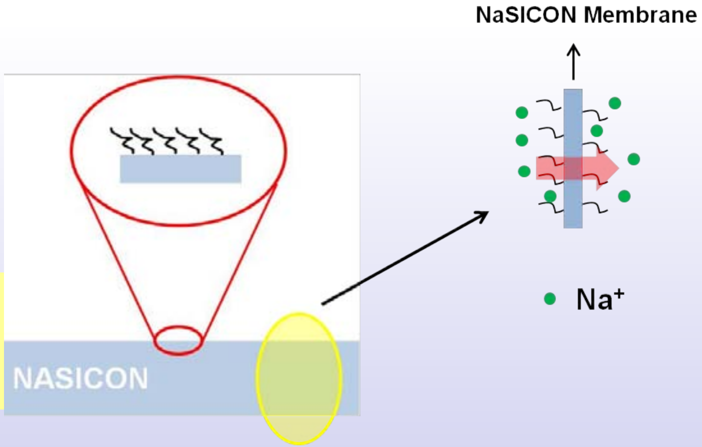


Technical Accomplishments - 9

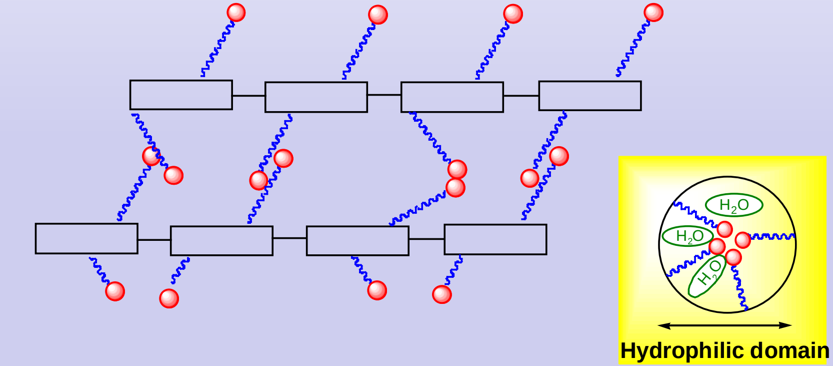
Goal: to **protect the surface** of NaSICON membrane.

Method: **coating** of the membrane by polymer that allows for effective transport of Na+ ions.

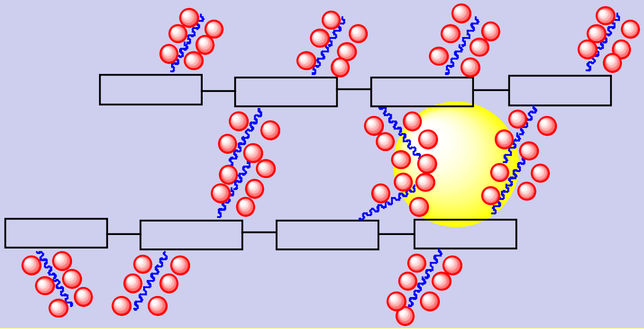
Material proposed: **blocky ionic polymers**, Na+ ion-conducting.



Developed: ***Random* sodium ion-functionalized polymer for NaSICON coating material,** in which sodium sulfonate groups are randomly located in polymer but the coating polymer caused resistance in transporting **Na+** ions.



- ▭ Rigid aromatic polymer
- 〰 Sulfonated side chain
- ● Sodium sulfonate groups



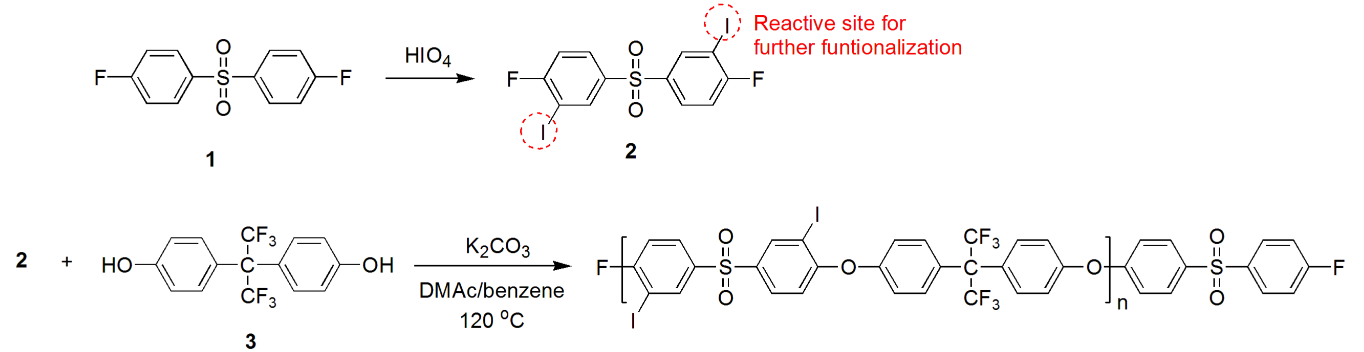
- ▭ Rigid aromatic polymer
- 〰 Sulfonated side chain
- ● Sodium sulfonate groups

Developed: ***Blocky* sodium ion-functionalized graft copolymer** for more efficient Na^+ transport.
Under Development: ***Blocky* copolymers** where sodium sulfonate groups are more localized in nano-scale domains, creating more favorable morphology for better transport of **Na+** ions in the coating material.

Technical Accomplishments - 10

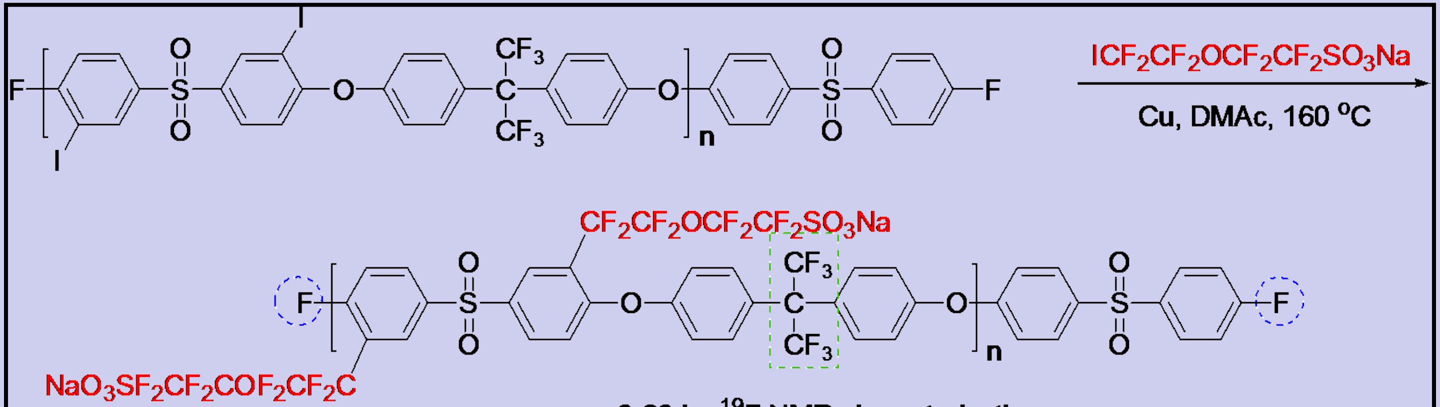
Graft Side Chain Precursors

- iodonated oligosulfones with different chain lengths in order to attach hydrophilic units to hydrophobic polysulfone chains.
- ooligosulfones with average molecular weight 6.1-17.3 kg/mol were prepared by adjusting the ratio of compounds 2 and 3 in polycondensation reaction.



Sodium Sulfonated Graft Side Chains

- The iodine group in the oligomer was converted to sodium sulfonate groups using copper-catalyzed coupling reaction



n = 8-20 by ^{19}F NMR characterization

Relevance to Advancement of Renewable Energy – 1

- **SMO** is an **effective catalyst to produce biofuels** by the transesterification of oils, animal fats, recycled greases, and oils from edible and non-edible feedstock.
- Commonly used methods to produce **SMO** are all **energy intensive** and **environmentally hazardous**.
- Onsite storage of **SMO** presents a safety hazard with stringent requirements for nitrogen blanketing for moisture control and basins for waste spill containment.
- This project **Develops, Demonstrates** and **Deploys** a **NEW**, inexpensive method to produce **SMO** at a desired concentration in methanol, on-site, and on-demand with very low concentration of impurities.
- Our process has a **21-26% lower carbon footprint** than other methods based on lifecycle analysis.
- **NaSICON fabrication route** based on **glass-ceramic technology** will produce glass-derived NaSICON with pore-free texture, very small grain size, and negligible grain boundary effects with **reduced energy barrier for Na^+ transport** and enhanced the material's ionic conductivity.
- Successful **polymer coating of NaSICON surface** will allow manufacturing of thinner membranes and thereby reduce power consumption of the electrochemical process, promoting more **energy-efficient and cost-effective** SMO catalyzed biodiesel production.
- This novel technology **benefits Biofuels'** and other industries that use **SMO.**
- Once the maturity of the **SMO technology** is demonstrated at **Biofuel facility**, the plants can then independently **integrate** the **SMO technology** for processing non-edible oils feeds derived from plants (*ex. jatropha, algae..*)

Relevance to Advancement of Renewable Energy – 2

- **NEW! Electrochemical Membrane Process (EMP) with NASICON membrane:** high-purity **SMO** output from low-purity low-cost NaOH input + no hazardous waste generation.
- Over 400,000 MT (Measurement Ton = 40 cubic feet) of **SMO** is **imported into the U.S**. Main supplier is China.
- **26% less energy**: when using the **EMP** to produce **SMO** compared to current fabrication methods.
- **40% less expensive,** based on a detailed cost analysis: to produce **SMO** at 500 kg/day compared to current SMO fabrication methods.
- **Extended lifetime,** 14 months demonstrated, 24 months projected: **EMP** cell lifetime is **surpassing expectations** in continuous cell operation.
- **On-site production of SMO** catalyst using **EMP** projected**:** scalable process, reduces transportation costs, avoids inventory and shelf-life costs, and reduces safety hazards.
- Ultimately a **“one-step process**” or **“zero inventory option”** is envisioned by **integrating** the on-site **SMO** generation with the downstream **Biodiesel process**.

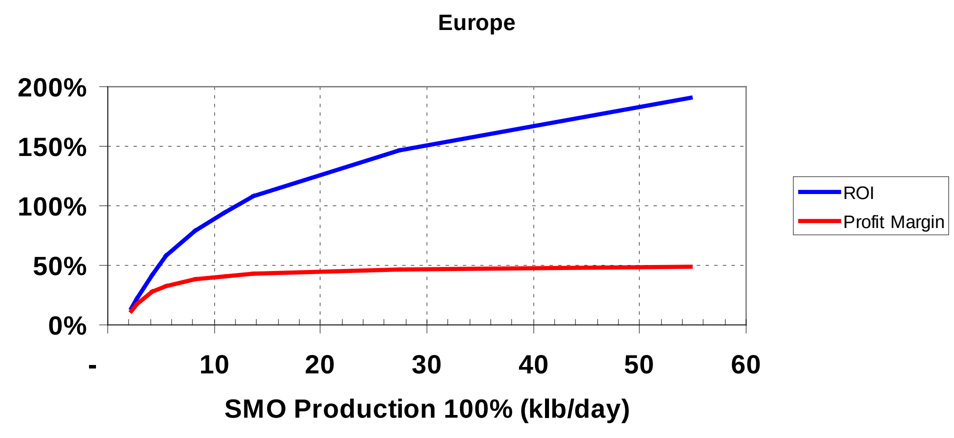
Critical Success Factors – 1

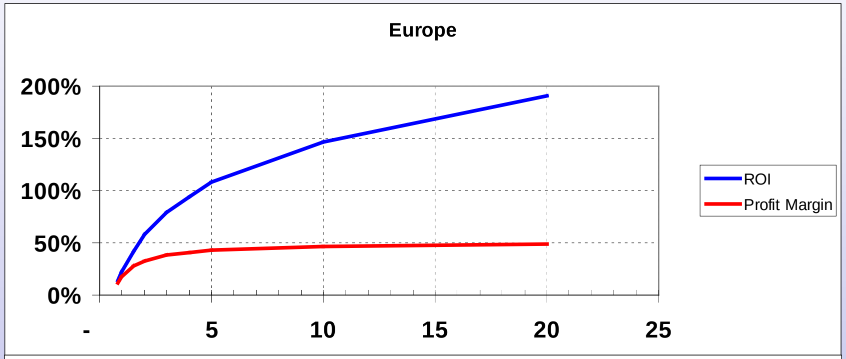
Techno-Economics: CAPEX and OPEC Costing for a 3300 lbs/day SMO of solids basis and higher system for payback target of < 2 years and return of investment of > 30%

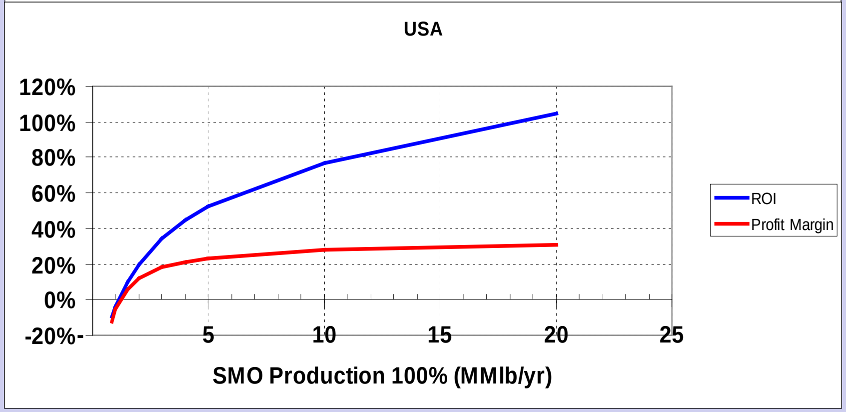
- Replacement items:
  - **NaSelect™ membranes replacement** : once in **24 months**
  - **Cell Components**: electrode and plastics – once in **5 yrs.**
- Device Operating Conditions:
  - Current density: 100 mA/cm^2, Cell Voltage: 3.38 volts at 50^oC
- Cost breakdown of equipment including cell lines (Tubular Membranes) and site services are lumped

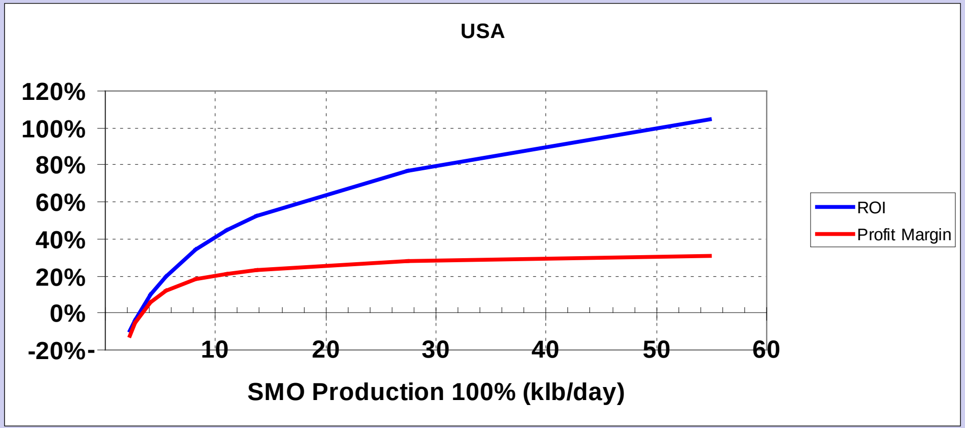
Critical Success Factors– 2

Analysis ROI & Profit Margin





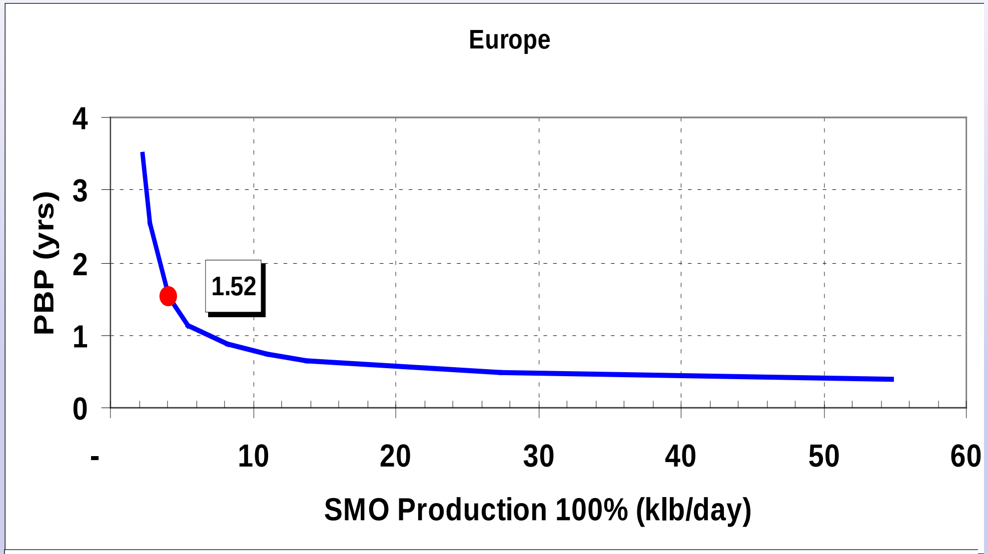


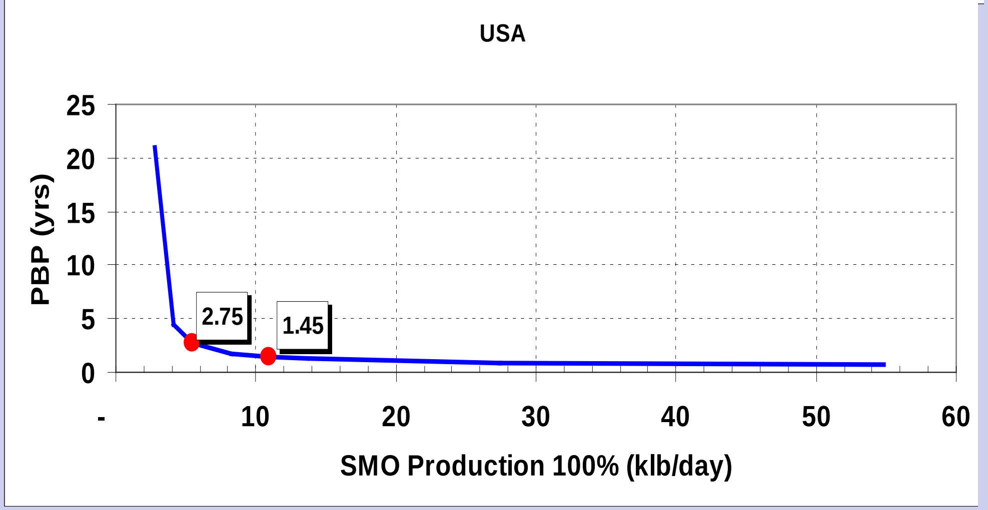


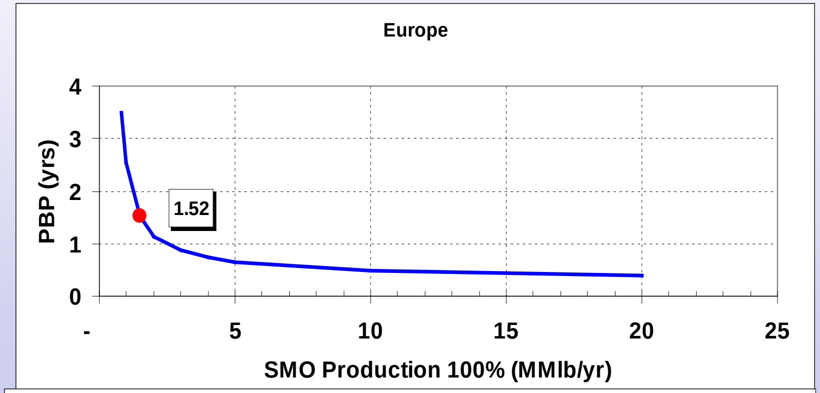
ROI is attractive past 2000 lbs./day

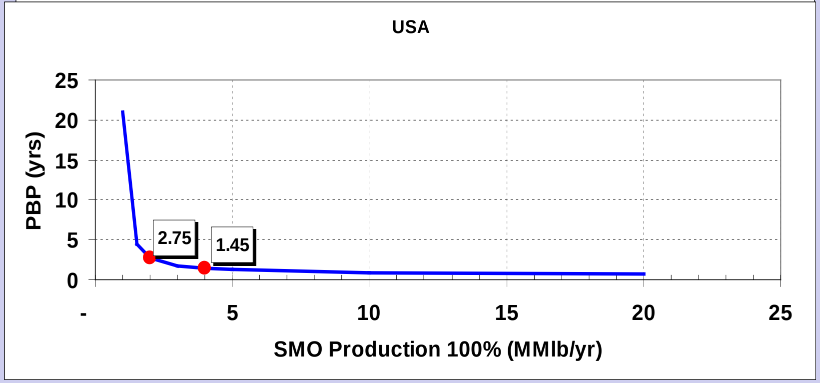
Critical Success Factors– 3

Cost Analysis Pay Back Period (PBP)









PBP looks good at production rates **> 4,000 lb./day** in Europe and **5,000 lb./day** in USA

Future Work

- Demonstrate up to **1000 hours of operation** of **Generation-2 Unit** after design qualification to make sodium methoxide.
- Modify design according to lessons learned from the demonstration to maximize **reliability** and **low-cost** operation of **Unit.**
- Synthesize a final blocky ionic **polymer**, by connecting Na-sulfonated oligomer and non-sulfonated high-molecular polymer and use it for coating the surface of **NaSICON ceramics**.
- Evaluate the **NaSICON** fabrication route based on glass-ceramic technology to produce **glass-derived NaSICON** from selected **new compositions** in light of Na-conductivity and working lifetime in the **Unit**.
- Develop reliable and robust **Unit** to produce a maximum concentration of **Sodium Methoxide-SMO** with near zero leak in **Unit** system and meet product (SMO) requirements and moisture specification for product.
- Carry out Field Analysis of Technology at a **Biodiesel Facility** and complete a feasibility analysis for installation

SUMMARY

Approach:

- Developed and attained target specifications in an unique concept that uses an Electrochemical Process with a selective Sodium Transport **NaSICON Membrane** to produce **SMO** as well as other Alkali Alcoholates.

Technical accomplishments:

- Developed a low-cost process to synthetize **NaSelect™** ceramic material and produce large-sized Membranes that allow the scale up of devices.

Relevance:

- Successfully designed **Prototype Cell** to increase active working surface area of the **Unit** and developed multiple **NaSelect™ Membrane-based Unit** configurations.

Critical Success factors and challenges:

- In the process of demonstrating Modular **Cell-Unit** capable to produce up to **50 lbs./day of SMO** which is scalable to large production size.

Future Work:

- Long term operation of **Cell-Unit** planned in facility.

Technology Transfer:

- In discussion with **Industrial customers** to evaluate this technology in the field.

ABREVIATIONS USED

- **NaSICON**: ceramic membrane, sodium (**Na**) **S**uper**I**onic **CON**ductor
- **NaSelect™**: proprietary composition of NaSICOn ceramic
- **SMO**: **S**odium **M**et**O**xide
- **EMP**: **E**lectrochemical **M**embrane **P**rocess
- **DCP**: **D**own **C**ell **P**rocess
- **TDU**: **T**echnological **D**emonstration **U**nit

Publications, Presentations, and Commercialization

- **PATENTS**: Two **U.S. Patents** have been received for this technology
- **PRESENTATIONS**:
  - First Annual STEM Summit: Science, Technology, Engineering and Mathematics, Las Vegas, NV, Jan 14-15, 2013 Development of Biofuels Using Ionic Transfer Membranes; K. Lipinska *et al*.
  - 2011 DOE Biomass Program Review Integrated Biorefineries Platform IBR & Infrastructure, Washington D.C. Feb. 1-3, 2011: Development of Biofuels Using Ionic Transfer Membranes, Phase II; K. Lipinska, O. Hemmers, C. Bae and S. Balagopal
  - American Physical Society - APS March Meeting, Dallas, TX, March 21-25, 2012: Synthesis, Microstructure and Properties of Complex Nasicon-Type Ceramics; K. Lipinska, O. Hemmers, J. Romin, P. Kalita, S. Sinogeikin, S. Balagopal, A. Nickens
- **COMMERCIALIZATION**: Currently in communication with three major industrial users in the field of Chemicals, Biodiesel and Pharmaceutical for evaluation of this technology.

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- Thank you!