Cyclic Olefin Copolymer based Alkaline Exchange Polymers and Reinforced Membranes

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Project ID #
FC307

Overview

Timeline

- **Project Start Date: Jan 1, 2019**
- **Project End Date : Dec 31, 2020**

Barriers

- **Performance**
- **Cost**
- **Durability**

Budget

- **Total Project Budget: $ 1,275,000**
  - Total Cost Share: $ 275,000
  - Total Federal Share: $ 1,000,000
  - Total DOE Funds Spent*: $ 0

* As of 3/01/19

Partners

- **Xergy Inc.**

  Bamdad Bahar

- **Los Alamos National Laboratory**

  Yu Seung Kim

Relevance

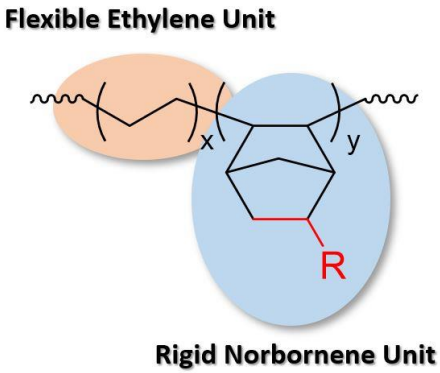
Objective

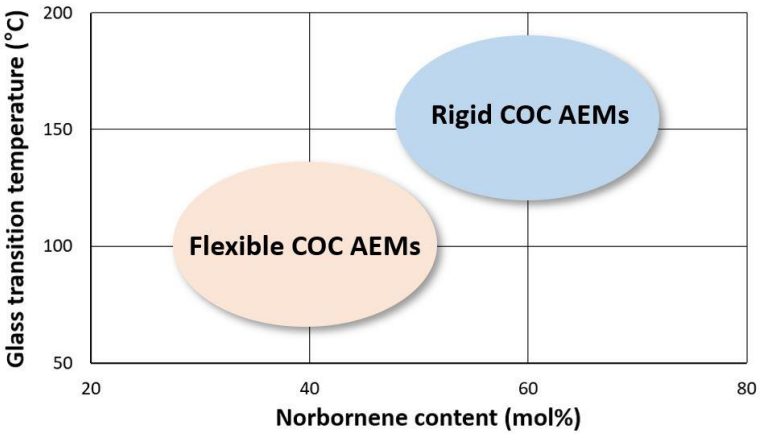
- Development of high-performance, low-cost AEMs by synthesis of a series of QA-functionalized cyclic olefin copolymers (COCs) and impregnation using reinforcement technology.

Technical Targets

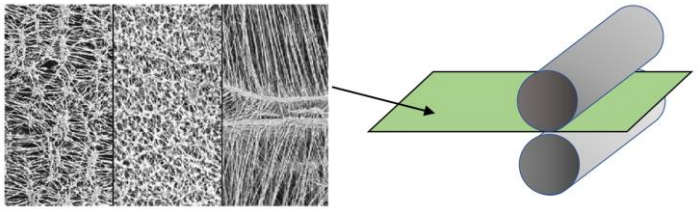
Technical Metrics	the-state-of-the-art AEM (m-TPN1)	2019 Target (Q4)	Ultimate Target (Q8)
Hydroxide conductivity (in-plane, 80 ºC)	112 mS/cm	60 mS/cm	120 mS/cm
Alkaline stability (1M NaOH, 95 ºC)	720 h, IEC drop <2%	500 h, <3%	1000 h, <3%
Tensile strength at break (50 ºC, 50% RH)	29 MPa	25 MPa	50 MPa
Elongation at break (50 ºC, 50% RH)	36%	35%	70%
Swelling ratio (OH^- form, 25 ºC)	16%	20%	10%
Area specific resistance (80 ºC; in fuel cell)	0.18 Ω cm^2	0.10 Ω cm^2	0.05 Ω cm^2

Approach

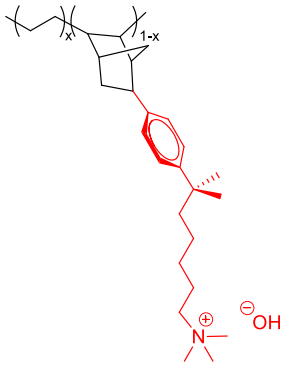




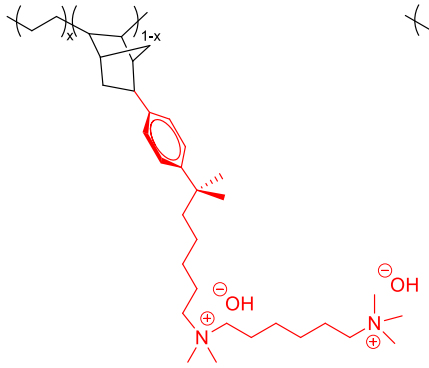
- ***Low cost*** **monomers and polymers**
- **No heteroatom (O or N) in the backbone → *High alkaline stability***
- **Excellent mechanical properties and dimensional stability due to high molecular weight**
- ***Tunable Rigidity*** **by varying the ratio of ethylene and norbornene/cyclic olefins in the backbone**
- ***Pore-filling reinforcement*** **for enhancing durability and extending lifetime of MEAs**



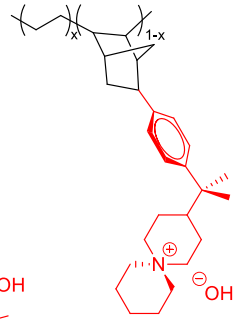
SEM image of porous substrates for reinforcement



COC-TMA (1st gen.)



COC-N2 (2nd gen.)



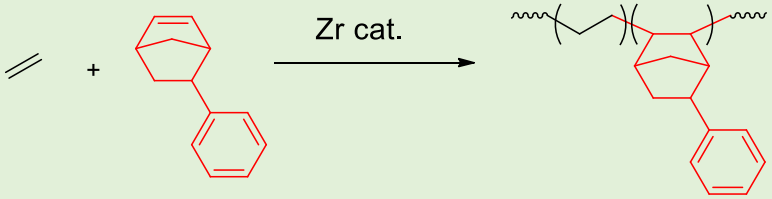
The most stable QA (Spiro type)

COC-ASU (3rd gen.)

Milestone & go-no-go decision

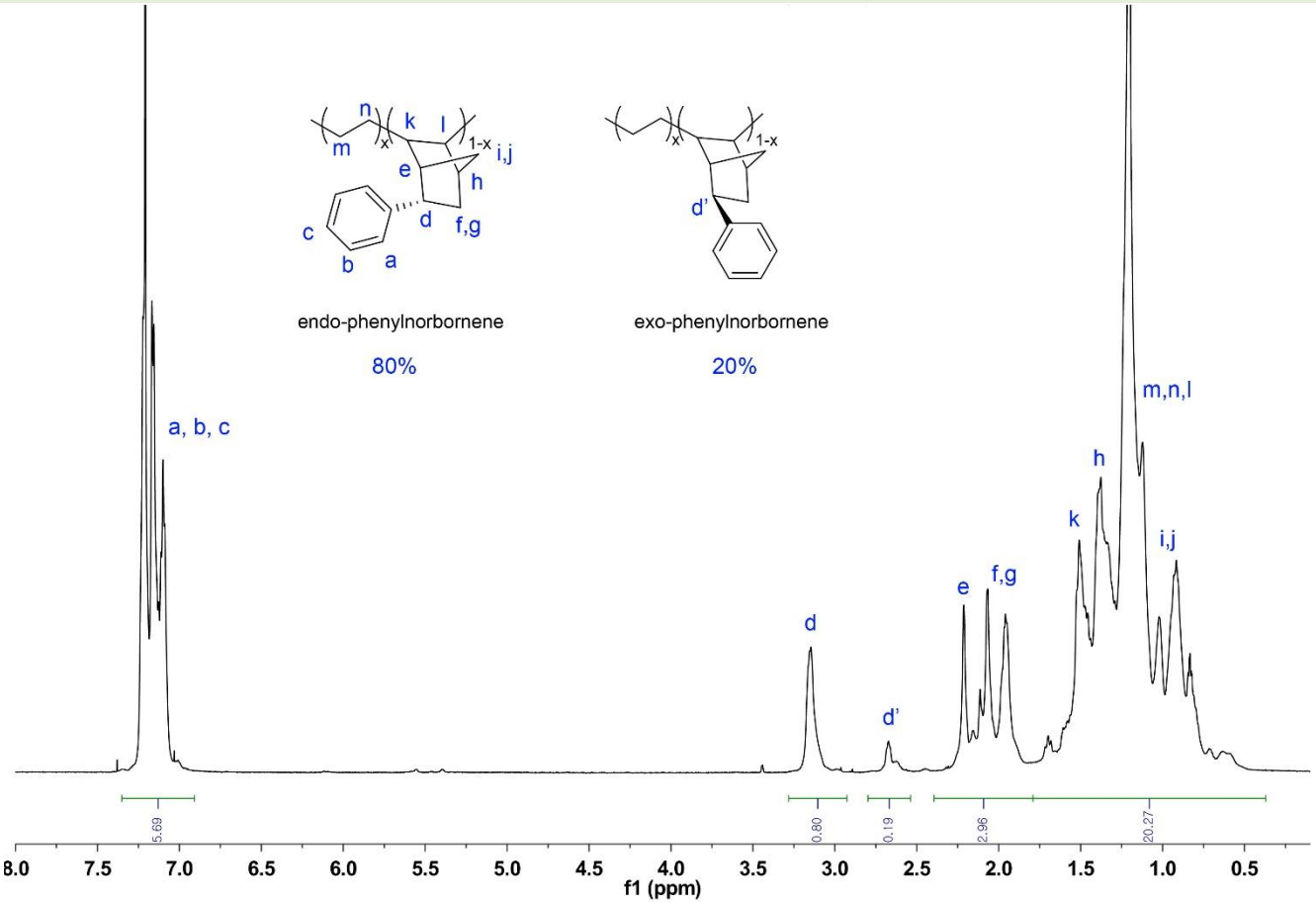
Milestone 1.1	**Synthesis of COCs (Q1–Q4) ← current status**	Polymer synthesis with high molecular weight (>100 kg/mol), ethylene composition (10–50 mol%)
Milestone 1.2	**Friedel-Crafts bromoalkylation of COCs (Q3–Q5)**	Optimization of synthetic process that gives degree of functionalization (30–90% of phenyl ring of COC)
Milestone 1.3	**Ionic functionalization of COCs (Q3–Q7)**	Optimization of polymer functionalization that affords COC AEMs with IEC = 1.5–2.5 mequiv./g
COC AEM Synthesis - *Go/No-Go decision* (Q4)		Demonstration of polymer AEMs that satisfy 50% of metric IDs 1 through 6
Milestone 2	**Reinforced Composite Membrane (Q3–Q7)**	Fabrication of reinforced membranes with targeted thickness levels (25, 20, 15 mm)
Milestone 3	**Ex-situ Membrane Characterization (Q3–Q7)**	Development of reinforced AEMs with IEC = 1.5–2.5 mequiv./g.
Milestone 4.1	**Ionomer-hydrogen oxidation catalyst interface (Q2–Q4)**	The RDE experiments will be performed using COC thin film coated HOR catalyst electrodes.
Milestone 4.2	**Ionomer-oxygen reduction catalyst interface (Q3–Q5)**	The RDE experiments will be performed using COC thin film coated ORR catalyst electrodes
Milestone 5.1	**MEA fabrication and fuel cell performance test (Q5–Q8)**	AEM fuel cell peak power density > 1 W/cm^2 for a MEA employing COC AEM and low PGM or non-PGM loading catalysts (< 0.1 mg_{Pt}/cm^2).
Milestone 5.2	**AEM and AEM fuel cell durability (Q6–Q8)**	ASR after 1000 h AEMFC operation at ≥ 60°C and constant current condition (0.6 A/cm^2): ≤ 0.06 W cm^2.

Accomplishments: Synthesis of COCs (M1.1)



- Ethylene-phenylnorbornene copolymer (62 wt% PhNB) was successfully synthesized using Zr catalyst.

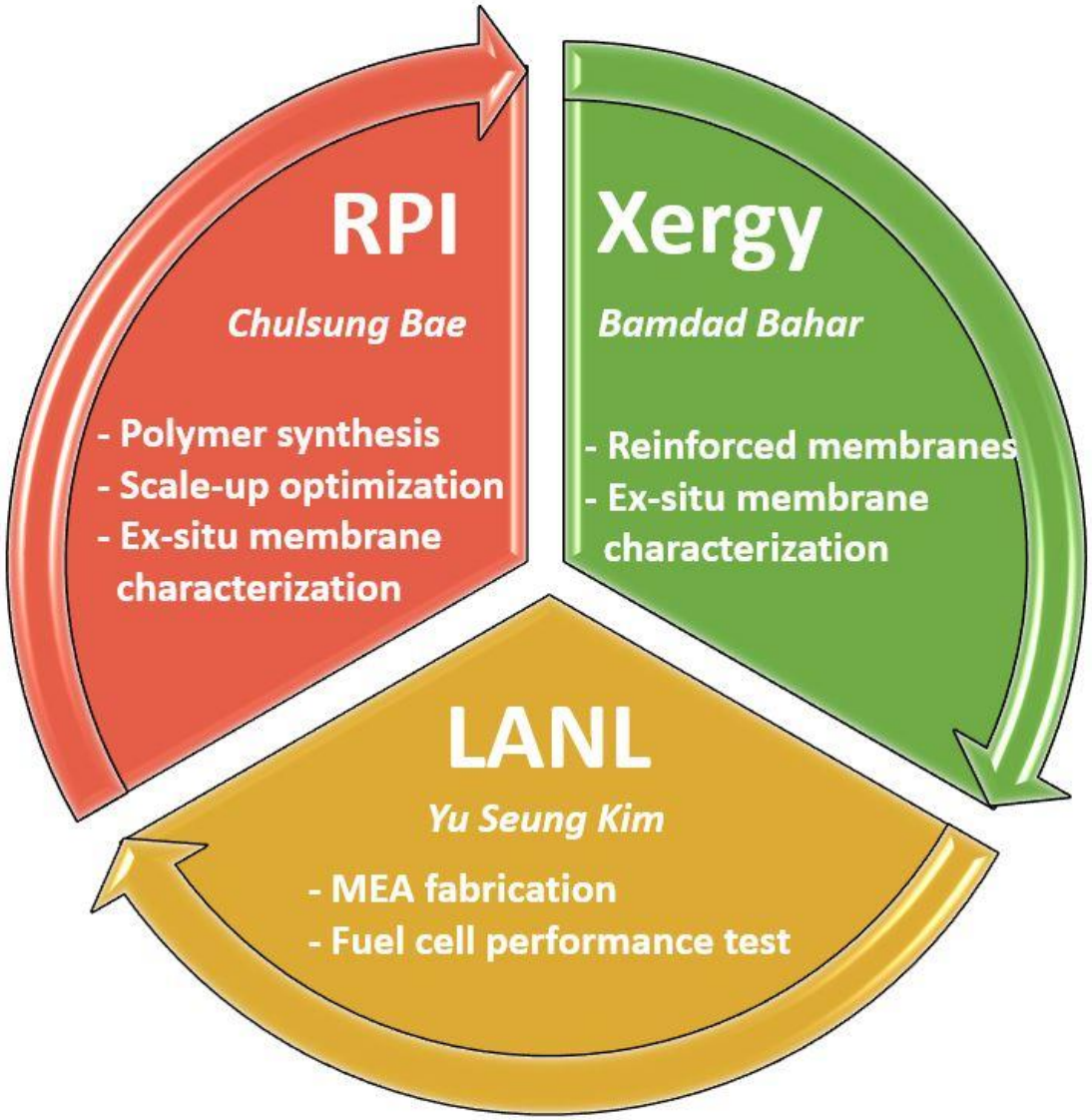
Activity : 3.12 x 10^6 g/mol·h



Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

This project started on January 2019, and it was not reviewed last year.

Collaborations – Project team



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Remaining Challenges and Barriers

- **Synthesis of COC AEMs**
  - **Optimization of copolymerization and Scale up synthesis**
  - **Synthesis of COC AEMs with high anion conductivity and high durability**

- **Fabrication of reinforced composite membranes**
  - **Compatibility of COC AEMs with porous support materials**
  - **Production of robust ultra-thin composite membrane**

Proposed Future Work

Remainder of FY 2019

- **Synthesis of COC AEMs (RPI)**
  - **Ethylene phenylnorbornene copolymerization with various composition (10-40 mol% PhNB)**
  - **Friedel-Crafts bromoalkylation of COCs (30–90% DF of phenyl ring of COC)**
  - **Synthesis of COC AEMs with IEC = 1.5–2.7 mequig./g**

- **Fabrication of reinforced composite membranes (Xergy)**
  - **Demonstration of COC AEMs composite membranes that satisfy Q4 Metrics**

- **MEA fabrication and fuel cell performance test (LANL)**
  - **Preparation of soluble ionomer dispersions and catalyst ink**
  - **Investigation of catalyst layer and AEM compatibility**
  - **Measurement of alkaline membrane fuel cell performance using 1st year COC AEMs**

Any proposed future work is subject to change based on funding levels.

Proposed Future Work

FY 2020

- **Synthesis of COC AEMs (RPI)**
  - **Synthesis of COC AEMs with IEC = 1.5–2.7 mequig./g**
  - **Ex-situ membrane characterization.**

- **Fabrication of reinforced composite membranes (Xergy)**
  - **Demonstration of COC AEMs composite membranes that satisfy Q8 Metrics**
  - **Scale-up r2r fabrication process for ultra-thin, ultra-strong and ultra high-performance COC AEMs composite membranes**

- **MEA fabrication and fuel cell performance test (LANL)**
  - **Electrode optimization of alkaline membrane fuel cell performance using 2nd year COC AEMs**
  - **Measurement of alkaline membrane fuel cell stability using COC AEMs**

Any proposed future work is subject to change based on funding levels.

Technology Transfer Activities

- Team has Initiated a joint venture between RPI (Chulsung Bae) and Xergy Inc., and established Orion Polymer Corp. to supply research grade ionic polymers and membranes samples (both free-standing and reinforced) to clients. Orion will seek license agreement from RPI for the scale-up synthesis of COC ionic polymers.

- Xergy Inc. will initiate discussions with 3rd party companies regarding commercial product sales.

- RPI and Xergy have joint IPs on composite membranes

- Manufacturing scale-up
  - RPI and Xergy have had membrane scale-up activities supported by DOE ARPA-E, STTR, EERE programs
  - Xergy has two roll-to-roll composite membrane production lines

Summary

Objective: Development of high-performance, low-cost AEMs by synthesis of a series of quaternary ammonium-functionalized cyclic olefin copolymers (COCs) and impregnation using reinforcement technology.

Approach: Development of COCs with tunable backbone rigidity. Incorporating alkyl chain-tethered cations of different structures to the polymer by simple post-functionalization method. Impregnating ionic polymers into a mechanically stable matrix (reinforced AEM). Demonstrating the membranes' performance and durability in fuel cells using Pt-base and precious group metal-free (PGM-free) catalysts

Accomplishments:

Ethylene-phenylnorbornene copolymer (62 wt% PhNB) was successfully synthesized using Zr catalyst (*Activity : 3.12 x 10^6 g/mol·h*)

Collaborations:

We have a diverse team of researchers including national lab, university, and industry.
Rensselaer Polytechnic Institute: Synthesis and characterization of ionic polymers

Xergy Inc.: Reinforced composite membrane fabrication and characterization.

Los Alamos National Laboratory: MEA fabrication and fuel cell performance test.