Cyclic Olefin Copolymer based Alkaline Exchange Polymers and Reinforced Membranes

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Rensselaer Polytechnic Institute

May 19, 2020

Project ID: FC307

Overview

Timeline

- **Project Start Date: Jan 1, 2019**
- **Project End Date : Jun 30, 2021**
- **Percent complete: 35%**

Barriers

- **C. Performance**
- **B. Cost**
- **A. Durability**

Budget

- **Total Project Budget: $ 1,275,000**
  - Total Federal Share: $ 700,000 (+ $300k for LANL)
  - Total Cost Share: $ 250,000
  - Total DOE Funds Spent*: $172,495
  - Total Cost Share Spent*: $35,971

* As of 03/30/2020

Partners

Co-PI, Yu Seung Kim

Los Alamos National Laboratory

- Ionomer-catalyst interface study
- MEA fabrication and fuel cell performance test

Xergy Inc. (RPI took over tasks since 01/2020)

- Reinforced composite membrane fabrication and characterization

Relevance

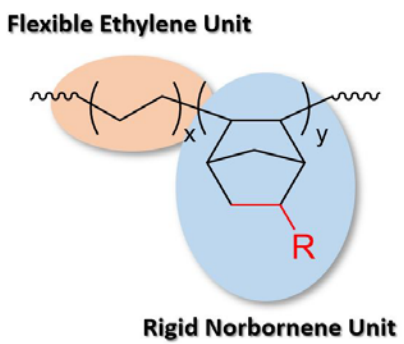
Objective

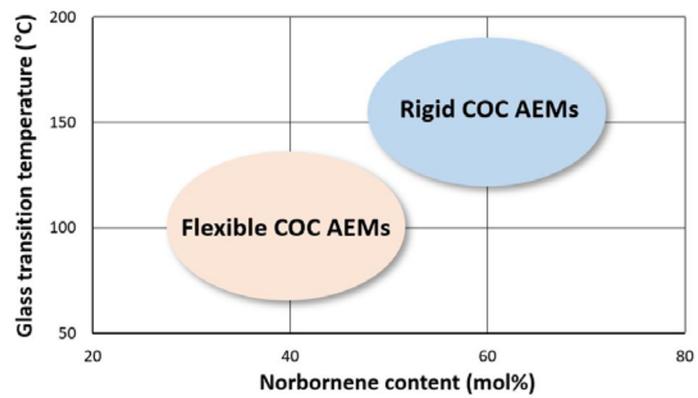
- Development of high-performance, low-cost AEMs by synthesis of a series of QA-functionalized cyclic olefin copolymers and impregnation using reinforcement technology.

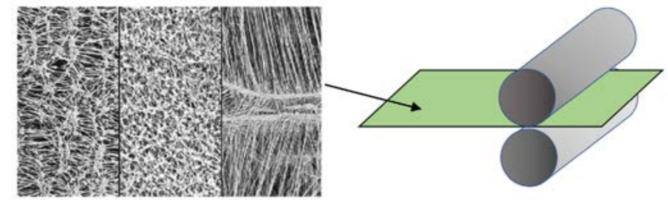
Technical Targets

Technical Metrics	the-state-of-the-art AEM (m-TPN1)	BP1 Target	Ultimate Target
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





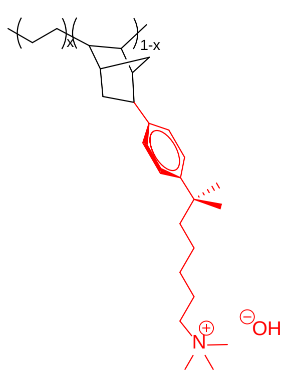


SEM image of porous substrates for reinforcement

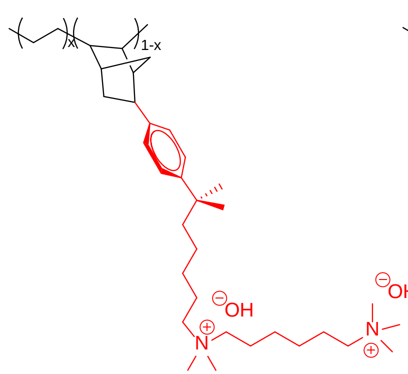
- ***Low cost*** **monomers and polymers**
- **No heteroatom (O or N) in the backbone → *High alkaline stability***
- **Excellent mechanical properties and dimensional stability due to high molecular weight**
- ***Tunable Rigidity*** **by varying the ratio of ethylene and norbornene/cyclic olefins in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

COC AEMs in the proposal

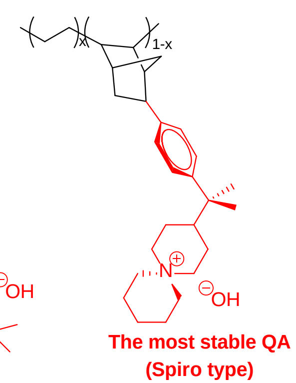
Additional COC AEMs



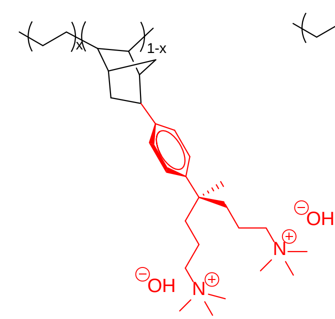
COC-TMA (1st gen.)



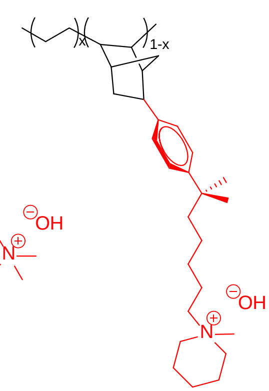
COC-N2 (2nd gen.)



COC-ASU (3rd gen.)



COC-2TMA

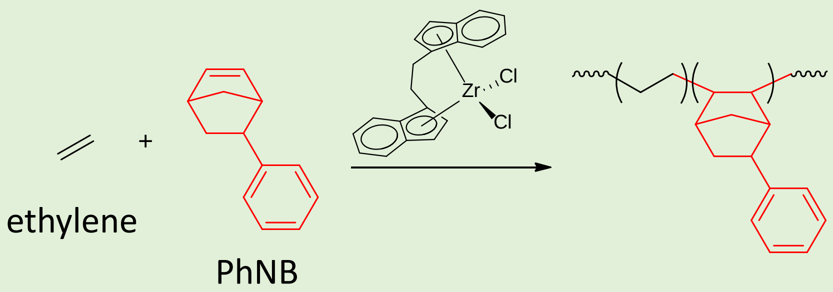


COC-PIP

Approach / Milestone

Milestone 1.1	**Synthesis of COCs (Q1–Q6)**	Polymer synthesis with high molecular weight (>100 kg/mol), ethylene composition (10–50 mol%)
Milestone 1.2	**Friedel-Crafts bromoalkylation of COCs (Q3–Q6)**	Optimization of synthetic process that gives degree of functionalization (30–90% of phenyl ring of COC)
Milestone 1.3	**Ionic functionalization of COCs (Q3–Q6)**	Optimization of polymer functionalization that affords COC AEMs with IEC = 1.5–2.5 mequiv./g
COC AEM Synthesis - *Go/No-Go decision* (Q6)		Demonstration of polymer AEMs that satisfy 50% of metric IDs 1 through 6
Milestone 2, 6	**Reinforced Composite Membrane (Q3–Q9)**	Fabrication of reinforced membranes with targeted thickness levels (25, 20, 15 mm)
Milestone 3, 7	**Ex-situ Membrane Characterization (Q3–Q9)**	Development of reinforced AEMs with IEC = 1.5–2.5 mequiv./g.
Milestone 4	**Ionomer-hydrogen oxidation catalyst interface (Q2–Q6)**	The RDE experiments will be performed using COC thin film coated HOR catalyst electrodes.
Milestone 8	**Ionomer-oxygen reduction catalyst interface (Q3–Q7)**	The RDE experiments will be performed using COC thin film coated ORR catalyst electrodes
Milestone 9.1	**MEA fabrication and fuel cell performance test (Q5–Q10)**	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 9.2	**AEM and AEM fuel cell durability (Q6–Q10)**	ASR after 1000 h AEMFC operation at ≥ 60°C and constant current condition (0.6 A/cm^2): ≤ 0.06 W cm^2.

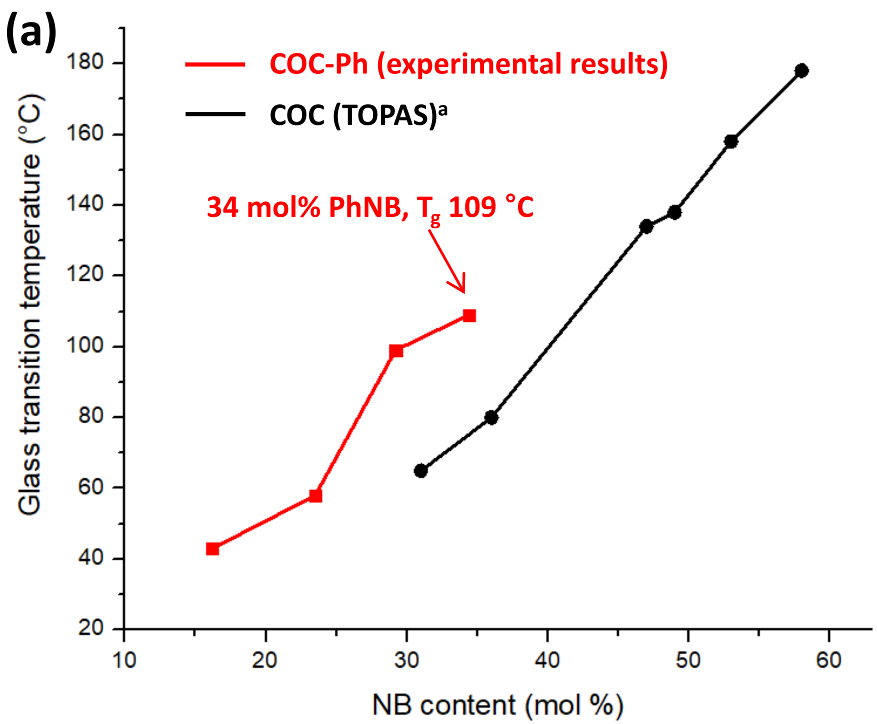
Accomplishments: Synthesis of COCs

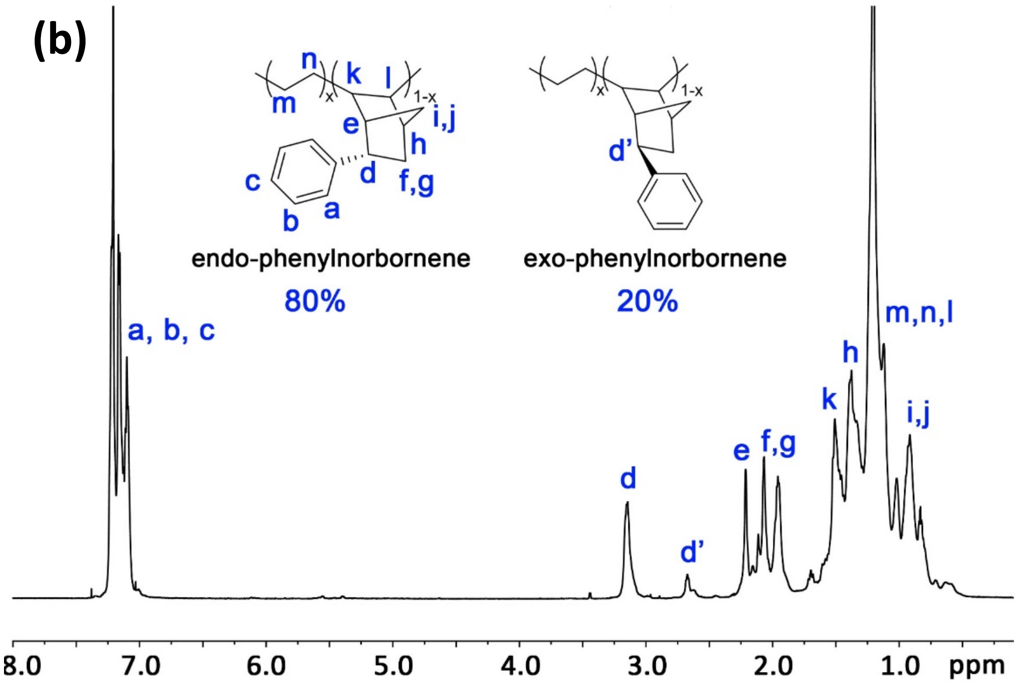


T_g tunable Ethylene-phenyl norbornene copolymer was successfully synthesized using Zr catalyst [(EBI)$ZrCl_2$].

16 – 40 mol% of PhNB

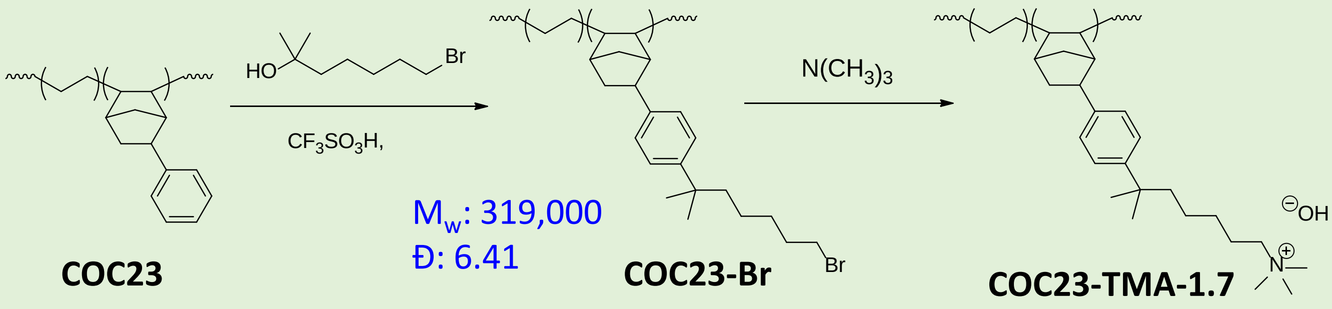
Catalyst activity : 2.87-5.42 x 10^6 g/mol·h





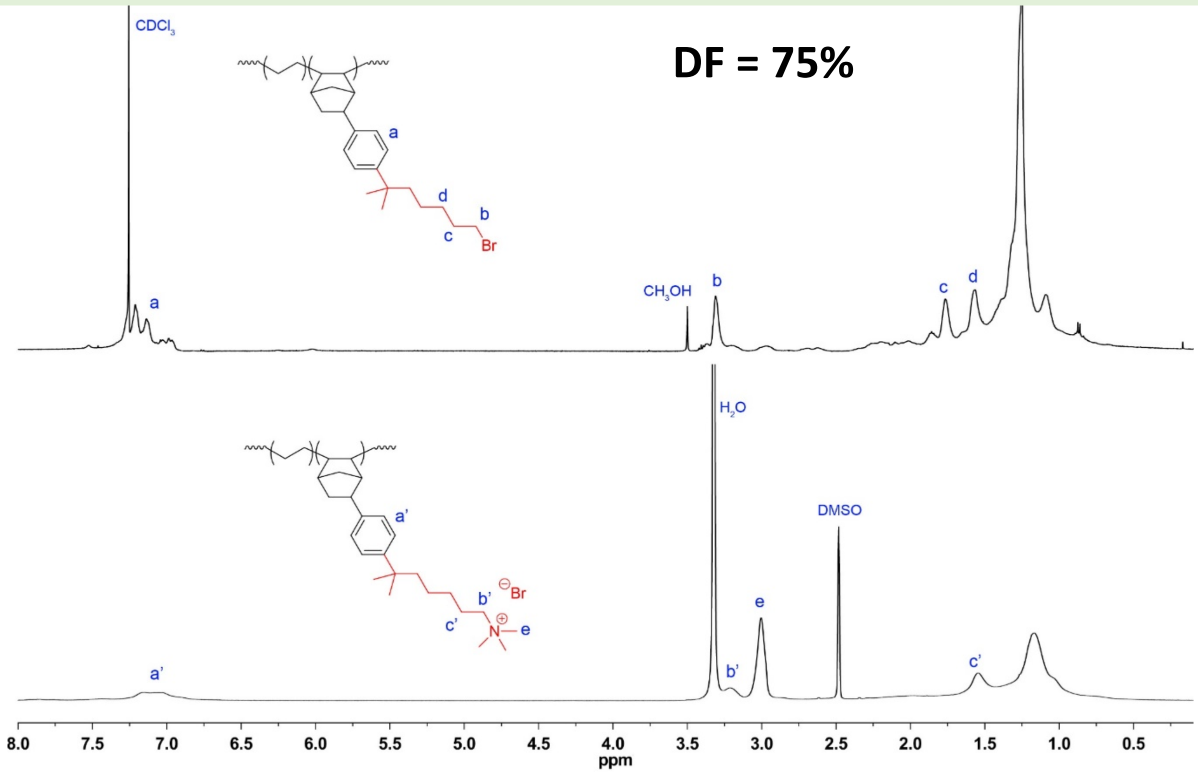
- As the PhNB content of COC-Phs increase, the T_g of the polymers increase from 43 °C to 109 °C

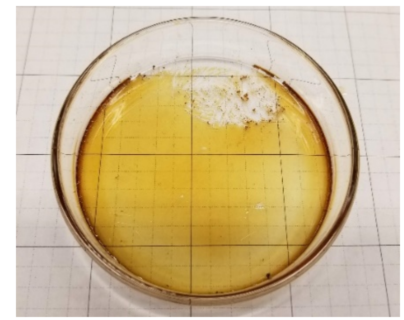
Accomplishments: Synthesis of COC-TMA

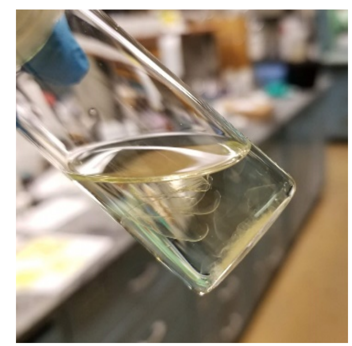


Soluble in MeOH, EtOH, and 65% IPA in H2O

IEC = 1.70 meqiv./g



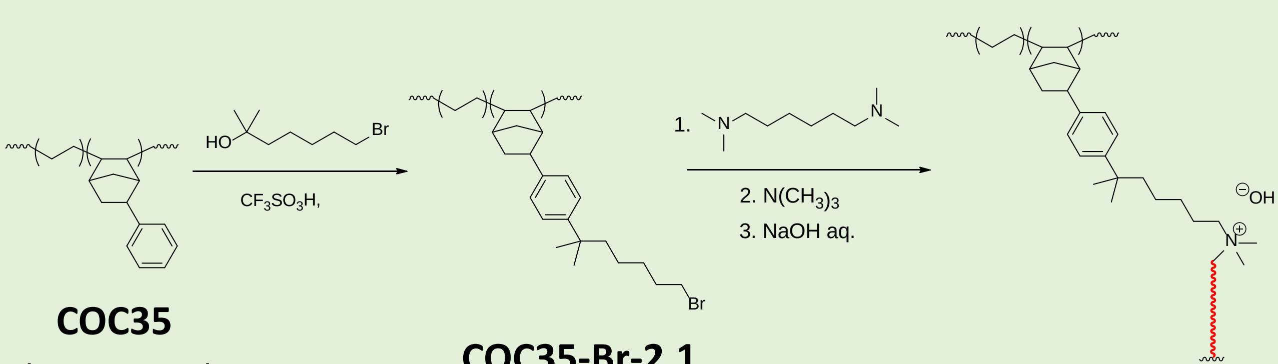




The synthesis of COC23-TMA-1.7 was successful, but dimensional stabilities and mechanical properties of the membranes were insufficient. The membranes broke into pieces during amination.

Accomplishments: Crosslinked COC-TMA

Simultaneous amination and crosslinking strategy



COC35

PhNB: 35 mol%

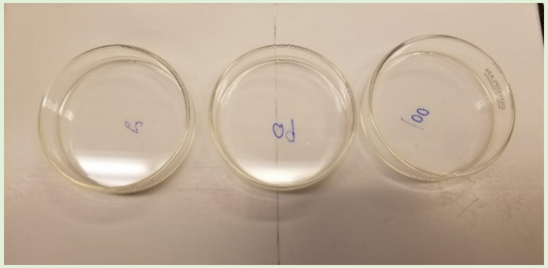
M_w: 97,000

Đ: 1.96

COC35-Br-2.1

Degree of functionalization: 75%

XL-COC35-TMA-2.1



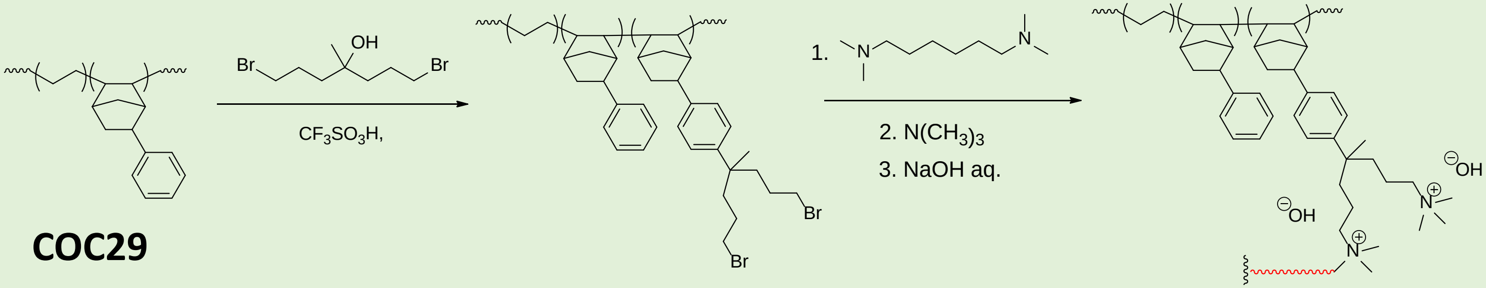
AEM	Diamine crosslinker	Degree of crosslinking[a]	Titration IEC before TMA reaction	IEC(mequiv./g)		In-plane swelling (%, OH^-)	OH^- σ (mS/cm)		
				^{1}H NMR	Titration		30 °C	60 °C	80 °C
XL60-COC35-TMA-2.1	0.3 eq.	55%	1.14	2.07	1.98	27%	49	69	**102**
XL100-COC35-TMA-2.1	0.5 eq.	80%	1.65	2.07	1.96	**20%**	39	57	**78**

[a]Calculated by titration IEC before the reaction with $N(CH_3)_3$, [b]measurement conditions: 50 °C, 50% RH

- Crosslinked COC-TMAs showed better mechanical properties than non-crosslinked COC-TMA, but it is still insufficient for fuel cell applications. The membranes were easily torn during handling (*no mechanical property measured*).
- Pore-filling reinforcement is required for better mechanical properties.
- Go/No-Go decision point target: **OH^- conductivity 60 mS/cm** at 80 °C, **20% swelling ratio** (OH- form)

Accomplishments: Crosslinked COC-2TMA

Simultaneous amination and crosslinking strategy



COC29

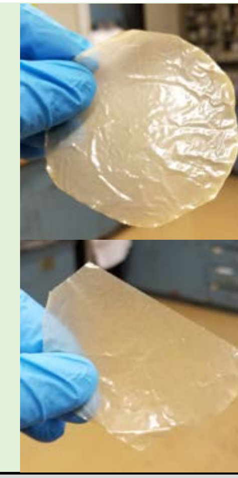
PhNB: 29 mol%

M_w: 111,000
Đ: 2.06

COC29-2Br-1.9

XL-COC29-2TMA-1.9

Degree of functionalization: 30%



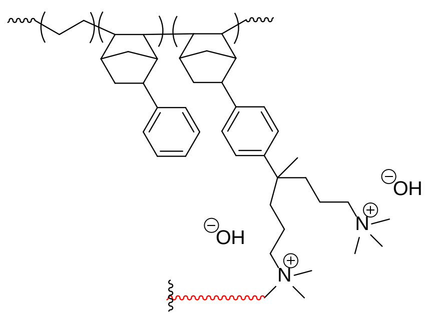
AEM	Diamine crosslinker	Degree of crosslinking[a]	Titration IEC before TMA reaction	IEC(mequiv./g)		In-plane swelling (%, OH^-)	Tensile stress[b]	Elongation at break[b]	OH^- σ (mS/cm)		
				^{1}H NMR	Titration				30 °C	60 °C	80 °C
XL40-COC29-2TMA-1.9	0.2 eq.	38%	0.72	1.91	1.83	18%	17	17	N/A	N/A	N/A
XL60-COC29-2TMA-1.9	0.3 eq.	57%	1.08	1.90	1.89	18%	19	42	N/A	N/A	N/A
XL100-COC29-2TMA-1.9	0.5 eq.	85%	1.60	1.89	1.87	**20%**	**21**	**94**	53	85	**105**

[a]Calculated by titration IEC before the reaction with $N(CH_3)_3$, [b]measurement conditions: 50 °C, 50% RH

- Crosslinked COC-2TMAs showed better mechanical properties than crosslinked COC-TMAs. They are strong enough for handling, and most of properties are meeting with Go/No-Go decision point target
- Interestingly, tensile stress and elongation at break increased with increasing of the degree of crosslinking.
- Go/No-Go decision point target: **OH^- conductivity 60 mS/cm** at 80 °C, **20% swelling ratio, 25MPa tensile tress, and 35% elongation at break**

Accomplishments: Alkaline Stability

1M NaOH Solution at 95 °C for 250 h (as of early March 2020)



XL-COC29-2TMA-1.9

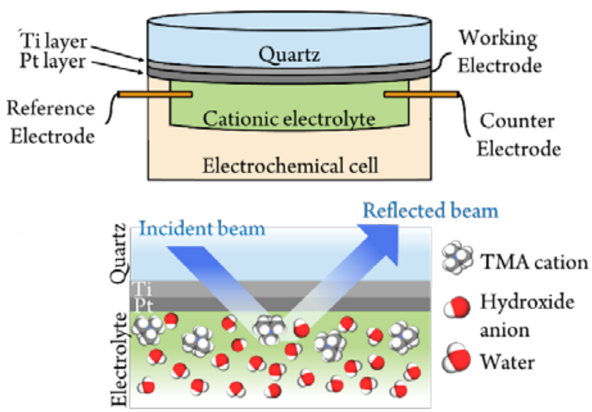
Samples	IEC(mequiv./g)		**IEC(mequiv./g) after 250 h**
	^{1}H NMR	Titration	
XL60-COC29-2TMA-1.9	1.90	1.89	**1.92**
XL100-COC29-2TMA-1.9	1.89	1.87	**1.91**

- No sign of chemical degradation after 250h test in 1M NaOH Solution at 95 °C
- Go/No-Go decision point target: **Alkaline stability, less than 3% degradation (IEC) in 1M NaOH aq. at 95°C for 500 h**

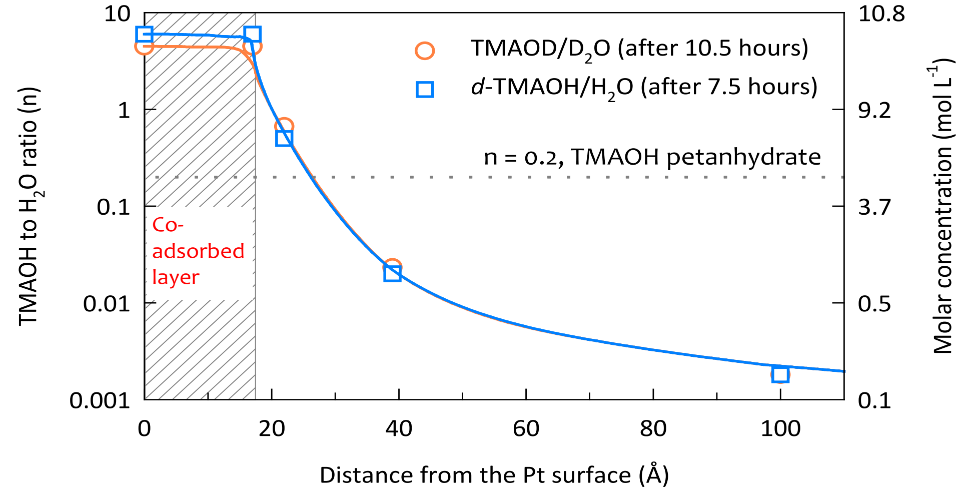
Accomplishments: catalyst interaction

Cation adsorption on alkaline HOR catalysts

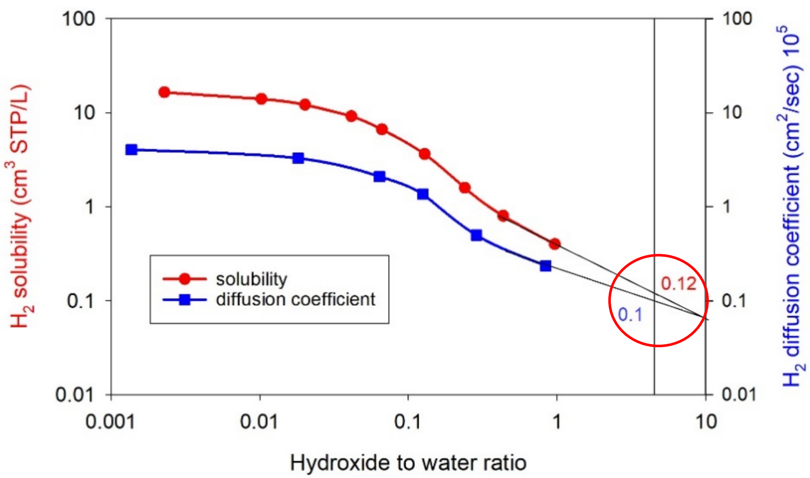
Schematics of electrochemical cell
for neutron reflectometry (NR) experiment



Tetramethyl ammonium hydroxide (TMAOH) concentration profile
on Pt after chronoamperometry at 0.1 V vs. RHE



Hydrogen solubility & diffusion coefficient as a
function of TMAOH to water ratio



- NR experiments showed that cation hydroxide concentration in the adsorbed layer on Pt HOR catalyst is extremely high which may significantly reduce hydrogen permeability.
- NR study further showed that the thickness of the co-adsorbed layer of tetraethyl ammonium hydroxide is ~2 times thinner (Technical backup slide 2)

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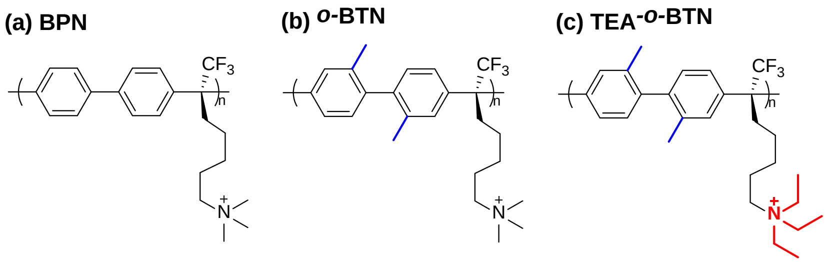
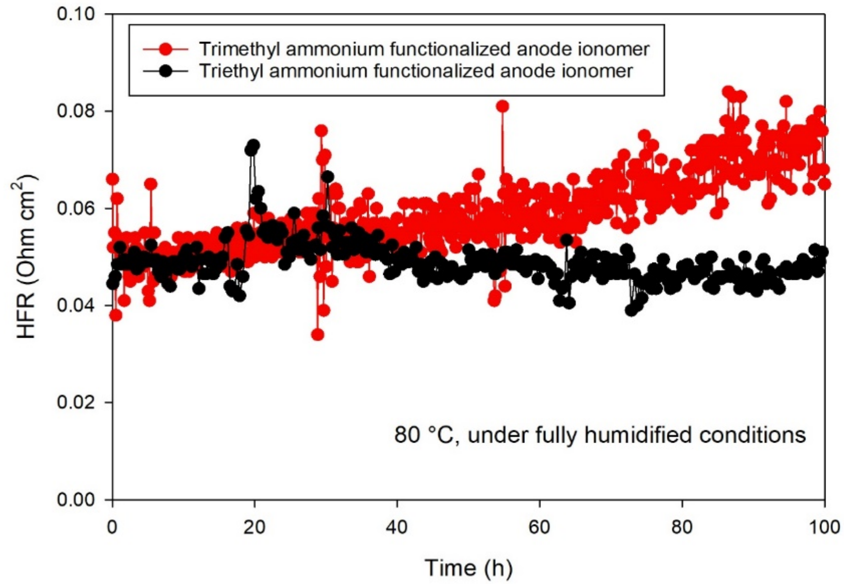
Accomplishments: Model ionomer study

Model ionomers

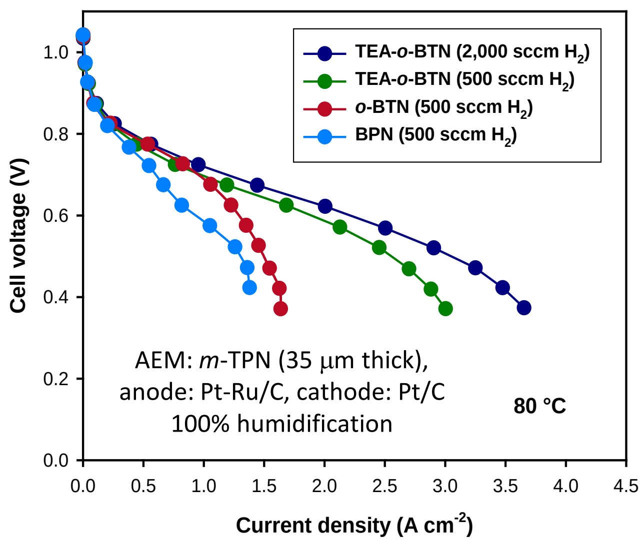


(a) poly(biphenyl alkylene); (b) poly(o,o'-bitolyl alkylene); (c) tetraethyl ammonium hydroxide (TEAOH) functionalized o-BTN

High frequency resistance change of two MEAs over time



Impact of anode ionomer on H_2/O_2 AMFC performance



- TEAOH functionalized ionomer (TEA-*o*-BTN) shows much higher performance and stability due to less adsorbing characteristics.
- TEA-*o*-BTN ionomer will be used for project performance evaluation.

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Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

2019 AMR Reviewers' Comments and responses

• The project's tasks are all relevant, but moving chemical durability up earlier is suggested.

- Chemical durability test was performed in 1M NaOH aq. at 95°C for 250 hours, and LX60-COC29-2TMA-1.9 and LX100-COC29-2TMA-1.9 didn't show any degradations. IECs of the AEMs were preserved after the test. The results of 500 h test will be reported in following year.

• The project team could perhaps provide a better breakdown of synthesis risks and mitigations.

- The detail synthetic scheme was provided in accomplishments section.

Collaborations – Project team

Rensselaer Polytechnic Institute

- Project lead
- COC based AEMs synthesis
- Fabrication of pore-filled reinforced membranes (with Xergy)

Los Alamos National Laboratory

- Ionomer-catalyst interface study
- MEA fabrication and fuel cell performance test

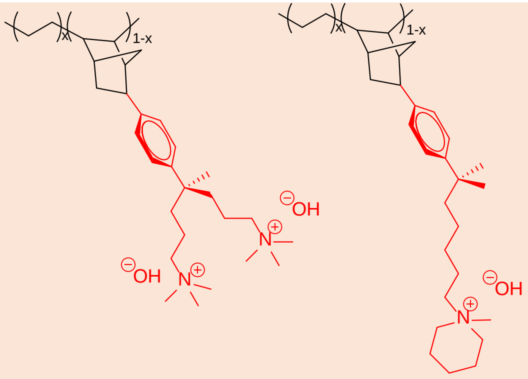
Remaining Challenges and Barriers

- **Scale up synthesis and cost reduction**
- **Mechanical properties improvement and membrane casting optimization of pore-filled reinforced membranes**
- **Compatibility study of COC AEMs with support materials for pore-filled reinforced membranes**

Proposed Future Work

FY 2021

- **Synthesis and analysis of COC AEMs (RPI)**
  - **Crosslinked COC-2TMA and COC-PIP**
  - **Fabrication of pore-filled reinforced membranes**
  - **Ex-situ membrane characterization**



COC-2TMA **COC-PIP**

- **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 employing COC AEMs**

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

Summary

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

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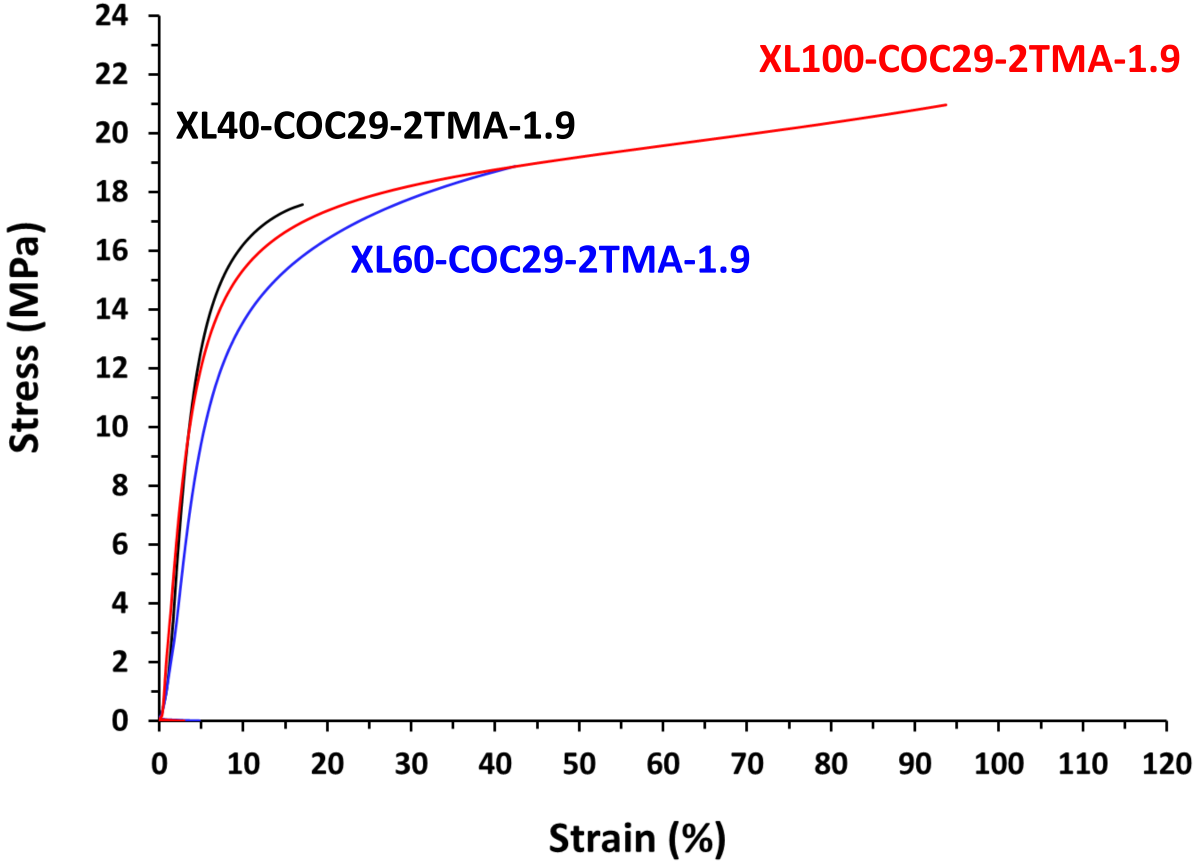
Alkaline stability (1M NaOH, 95 ºC)	720 h, IEC drop <2 %	500 h, <3%	1000 h, <3%	**250 h, No degradation**
Tensile strength at break (50 ºC, 50% RH)	29 MPa	25 MPa	50 MPa	**21 MPa**
Elongation at break (50 ºC, 50% RH)	36%	35%	70%	**94%**
Swelling ratio (OH^- form, 25 ºC)	16%	20%	10%	**20%**
Area specific resistance (80 ºC; in fuel cell)	0.18 Ω cm^2	0.10 Ω cm^2	0.05 Ω cm^2	**(0.048 Ω cm^2)** [a]

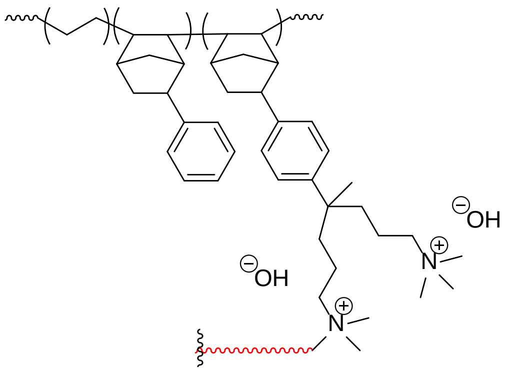
[a]Calculated from hydroxide in-plane conductivity, ASR = L/σ

Technical Backup Slides

Mechanical Properties of XL-COC29-2TMA-1.9

Stress-strain curve (measured at 50 °C and 50% RH)





Pore-filled reinforced membranes

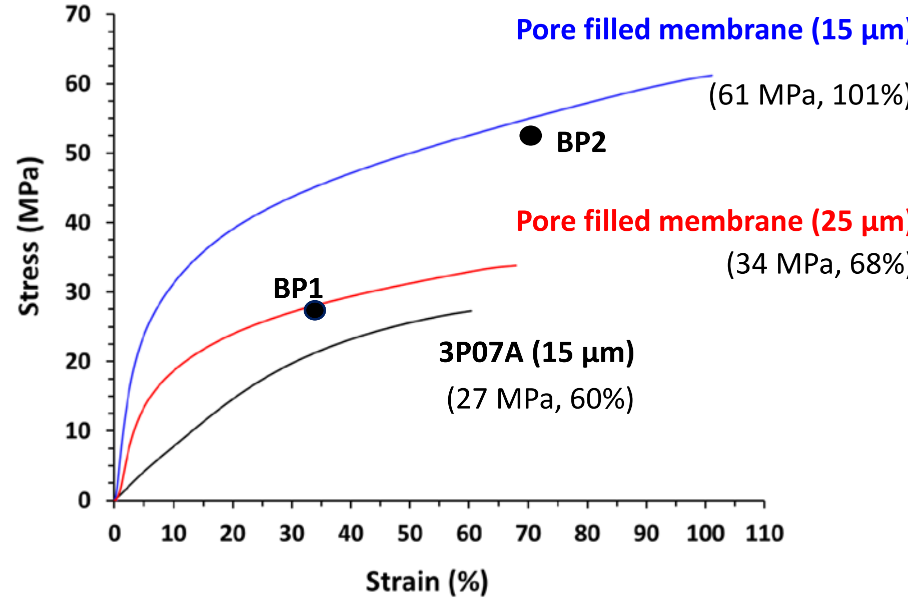
High Molecular Weight Polyethylene

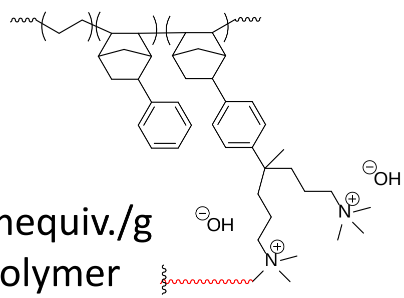
Porous substrate

Thickness: 15-20 µm

Porosity: 83%

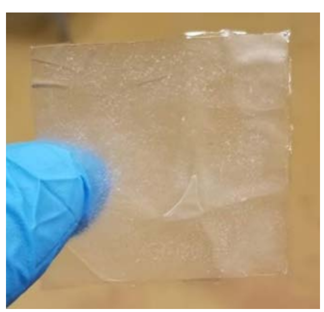
Stress-Strain curves at 50 % RH 50°C





2.4 mequiv./g for polymer

Pore-filling



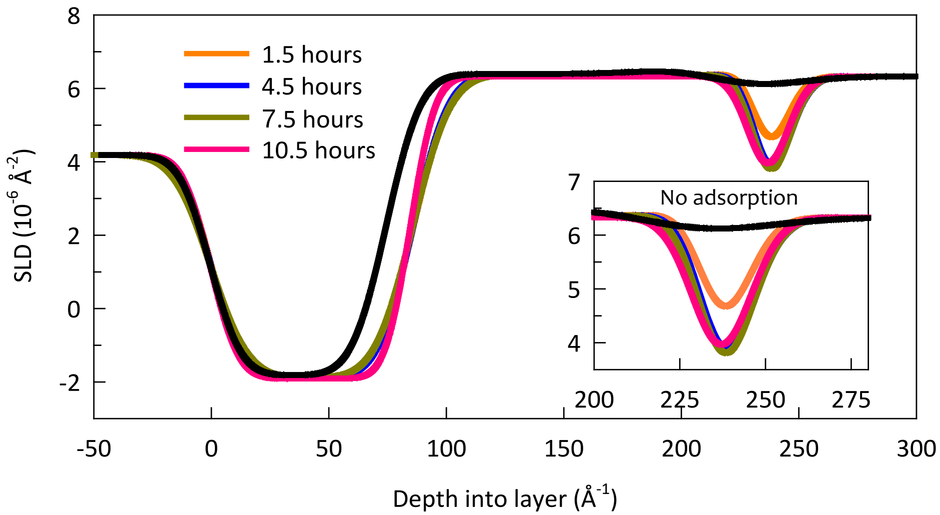
PE-XL100-COC29-2TMA-2.13

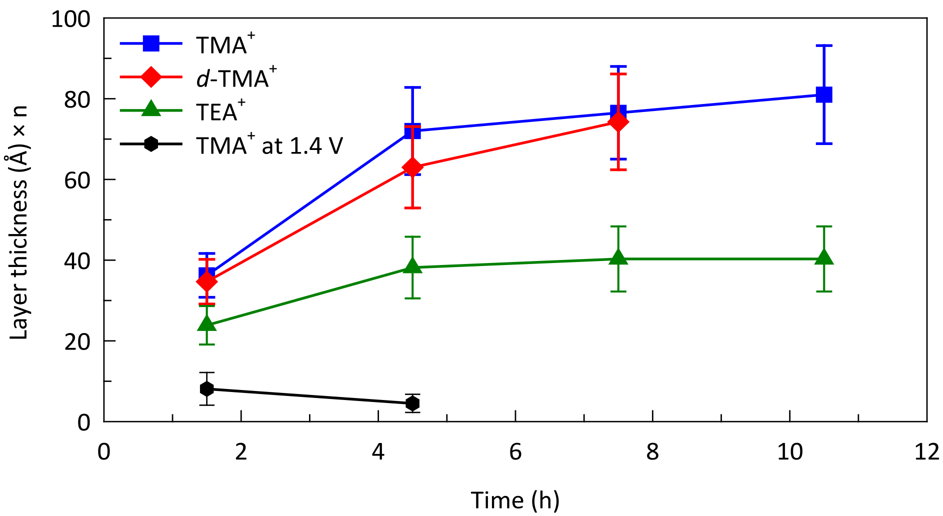
Titration IEC = 2.13 mequiv./g
(pore-filled Reinforced COC AEM)

Degree of crosslinking: 70%
(calculated by titration, 1.46 mequiv./g)

TEAOH adsorption on Pt electrode

SLD profiles of NR as a function of distance from the surface from fitting the experimental NR data





- NR SLD profile shows

1) TEAOH adsorption is cumulative.
2) The highest adsorption occurs at 0.1 V vs. RHE (HOR potential).
3) The concentration of TEAOH is high (TEAOH to water: ~ 5).
4) The thickness of adsorbed layer of TEAOH, however, ~2 times thinner than TMAOH.

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