IEEE SusTech2024
TECHNOLOGIES THAT IMPROVE AIR, WATER, ENERGY, FOOD AND HUMAN LIFE

Efficient, Cost-Effective Polymeric Materials Design for Clean Energy and Biomedical Technologies *via* Biomass Valorization

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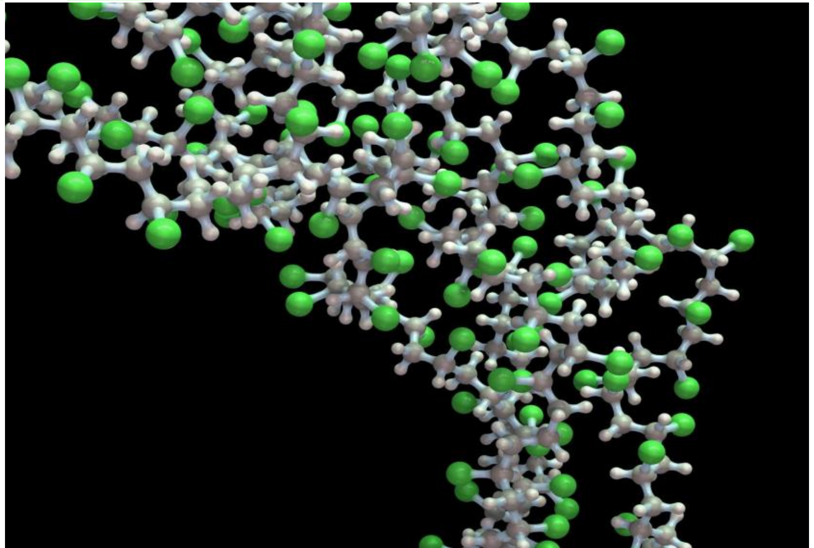
My Journey

B.S.	Chemical Engineering (2005) Bangladesh University of Engineering and Technology (BUET)
Ph. D.	Chemical and Biomolecular Engineering (2010) National University of Singapore
Post-doc	Materials Science and Engineering (2010-2013) (PI: Michael Hickner) Chemical Engineering (2013-2015) (PI: Andrew Zydney) Pennsylvania State University
Assistant Professor	Chemical and Biomolecular Engineering (2016-) University of Nebraska-Lincoln
Associate Professor	Chemical and Biomolecular Engineering (2022-) University of Nebraska-Lincoln
Vice-Chair	8A (Polymers)-MESD, AIChE (2022-2023)
Chair	8A (Polymers)-MESD, AIChE (2023-)
Associate Editor	Journal of Electrochemical Energy Conversion and Storage, an ASME journal (2023-)

Nanomaterials Lab

Polymers

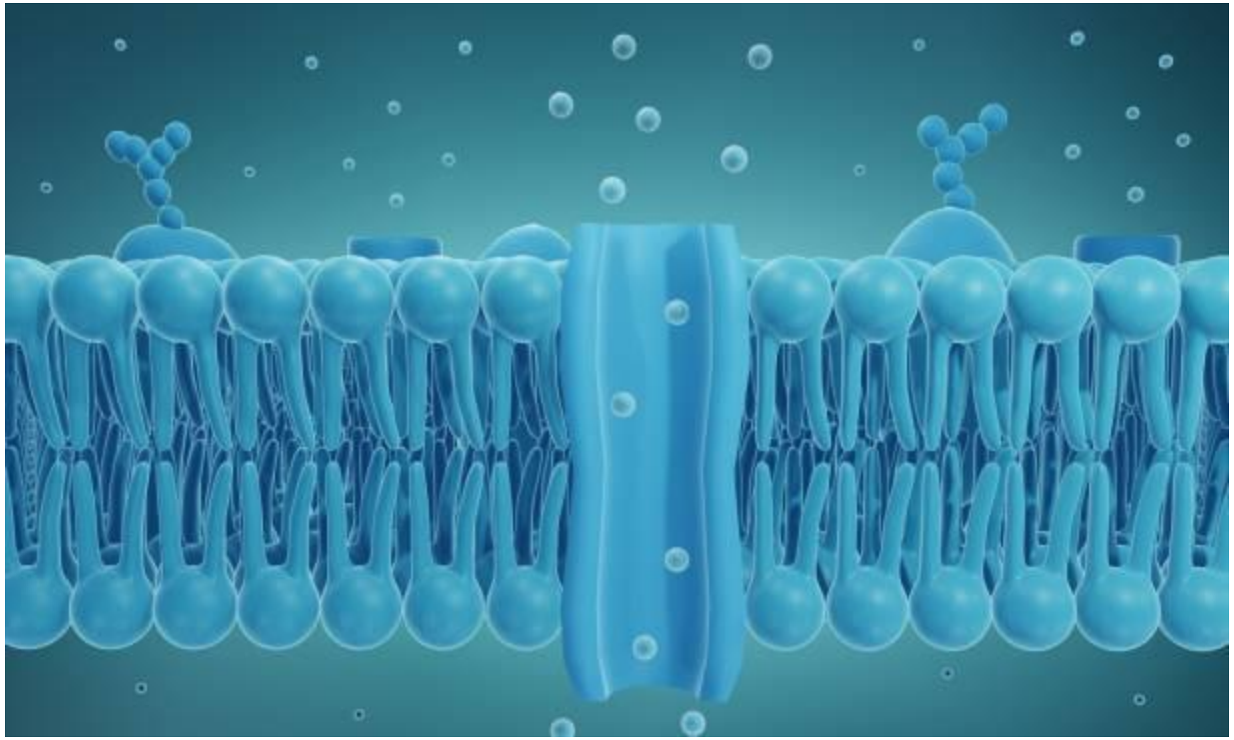


Honors/Awards

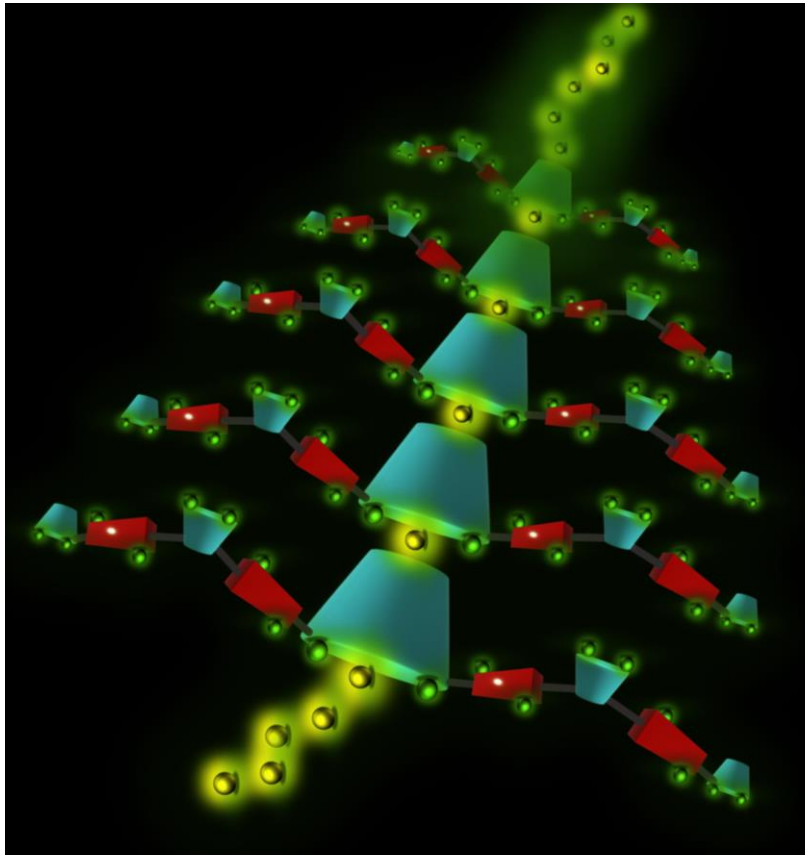
DOE Early CAREER Award (2019)
NSF CAREER Award (2018)
ACS PMSE Young Investigator Award (2023)
3M Non-Tenured Faculty Award (2021)
WEPAN Accelerator Core Concept Award (2022)
ASEE Midwest Conference Best Paper Award (2023)
EPSCoR First Award (2017)
Emerging Innovator of the Year Award (2020)
Edgerton Innovation Award (2021)
Harold and Esther Edgerton Junior Faculty Award (2019)

Nature-Inspired Polymers

Bringing the capabilities of ion channels, transporting nutrient ions in living systems, to the design of synthetic polymers to transport ions faster



Biological ion channels



Biological ion channel-inspired ionomers

Funded by:
DOE Office of Energy Early Career Award
3M Non-Tenured Faculty Award
Edgerton Innovation Award

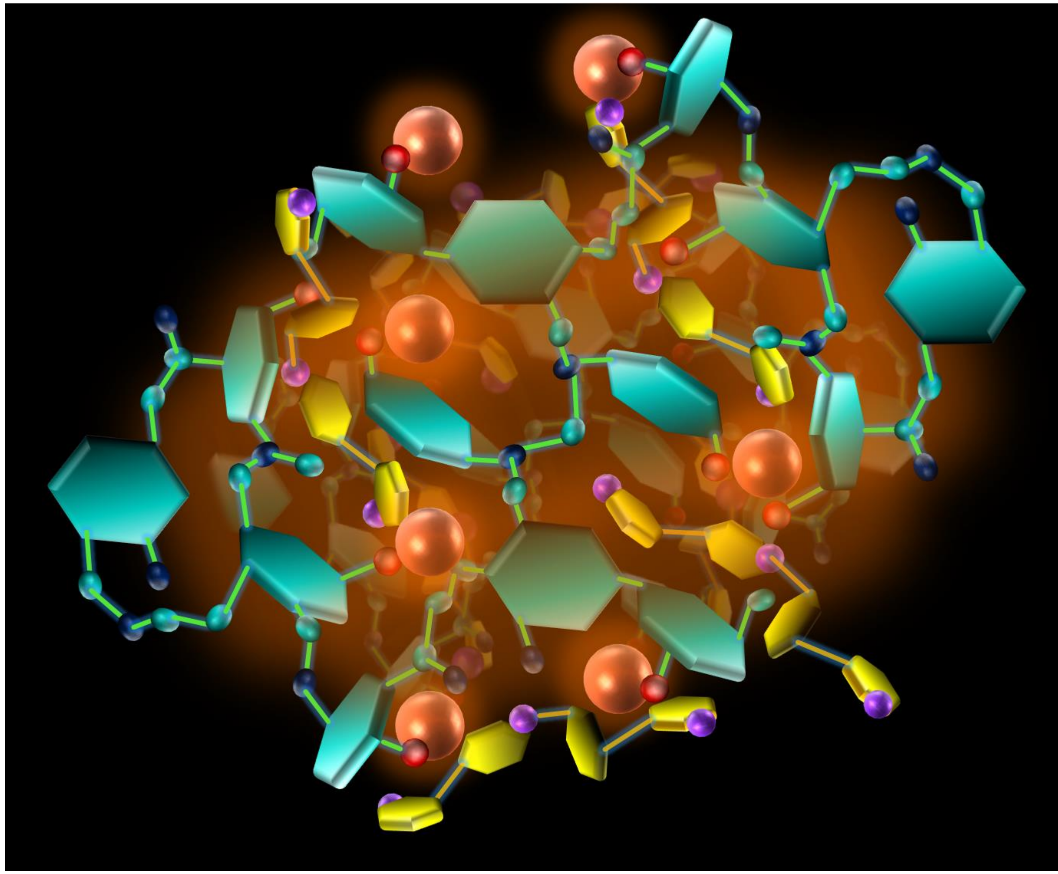
Plant-based Polymers

Bringing the capabilities of plant cell wall components to the design of green, low-cost, but efficient polymers

Funded by:
NSF-CBET (Electrochemical Systems)
NCESR (NPPD)

Forest/Ag residue

Plant-based wastes



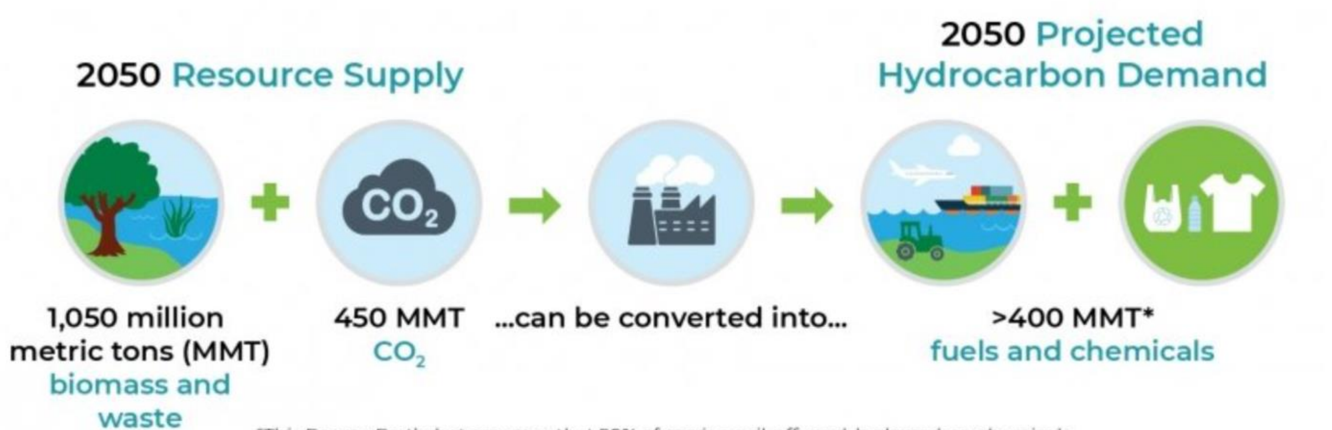
Plant-based polymers

Biomass Valorization to Support Bioeconomy

SEPTEMBER 12, 2022

Executive Order on Advancing Biotechnology and Biomanufacturing Innovation for a Sustainable, Safe, and Secure American Bioeconomy

Biomass sources	Possible Biomass production (tons)
Agricultural resources	150-800 million+
Timberland	32-63 million
Waste and By-product	180-220 million



*This Energy Earthshot assumes that 50% of marine, rail, off-road, hydrocarbon chemicals and 100% of aviation demand will be met by hydrocarbon fuels in 2050.

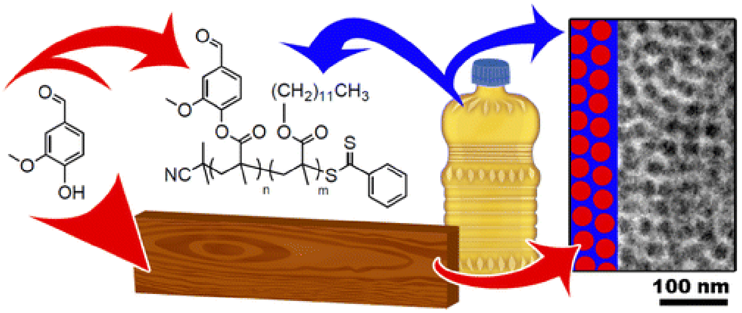
Lignin-based Value-Added Products

Valorizing untapped, conversion process waste streams (like, **lignin**) and producing novel bioproducts that capitalize on the biomass

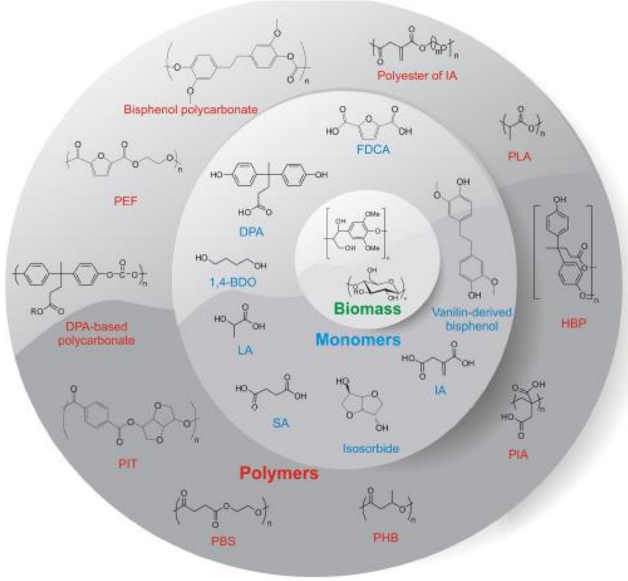
Amount of lignin produced worldwide:
- 50-70 million tons/yr by pulp and paper industries
- 100,000-200,000 tons/yr by cellulosic ethanol plants

Only a small percentage (1-2%) of this lignin is used to make value-added products:
- concrete additives
- carbonaceous materials
- stabilizing agents
- Chemicals (e.g., phenols from depolymerized lignin)
- Chemical building blocks for plastics
- functional copolymers (from monolignols)

Our goal:
- Lignin valorization-aid in **bioeconomy**
- Design low-cost, efficient energy materials-aid in **energy economy**



Epps et al, ACS Sus.Chem. Eng. **2014**

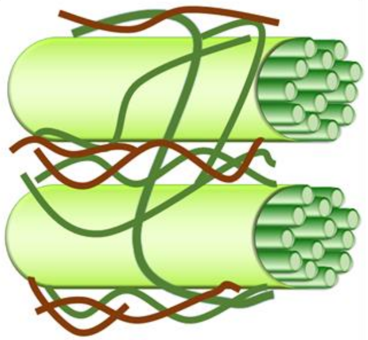


Delidovich et al, Chem. Rev. **2016**

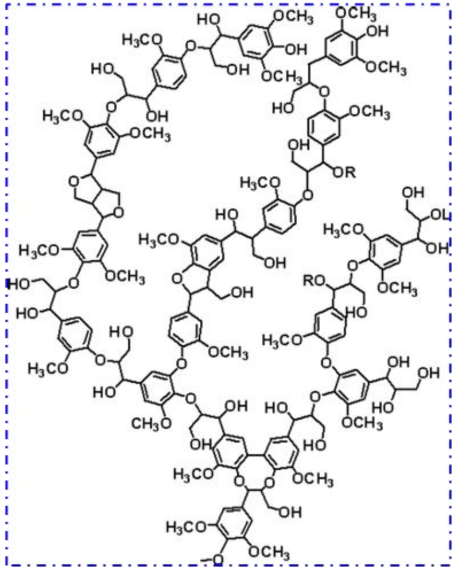
New Pathways towards Biomass Valorization and Sustainable Technologies

Tree/Plant

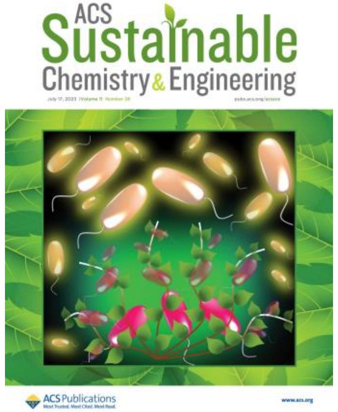
Wood



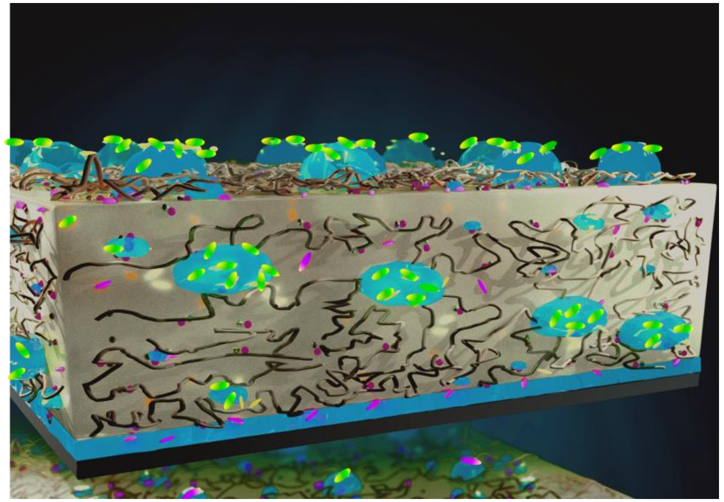
Plant cell wall



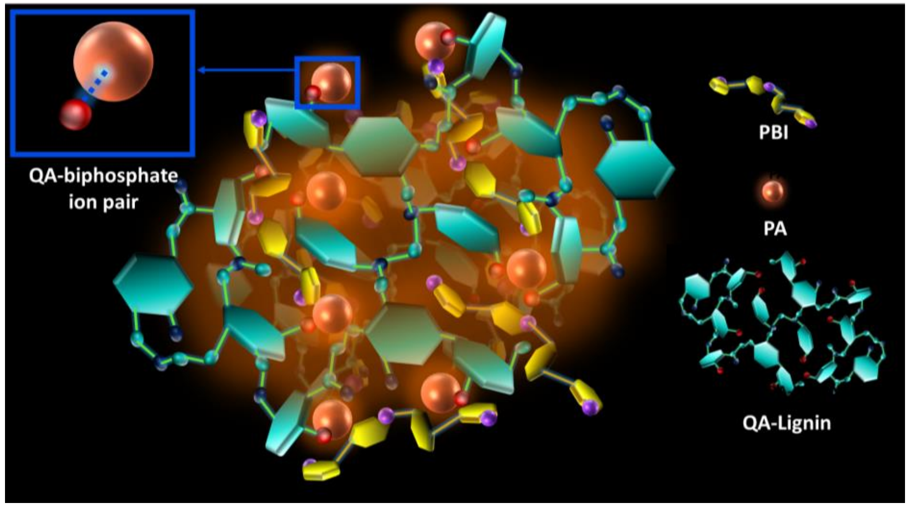
Lignin



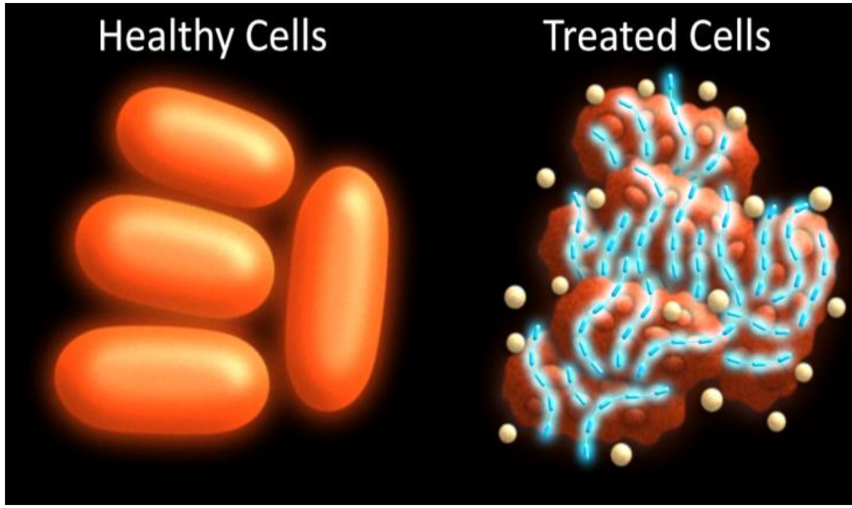
Dishari et al. ACS Sustainable Chem. Eng.(2023)



Improve conductivity at electrode-catalyst interfaces



Durable Materials for electrochemical systems

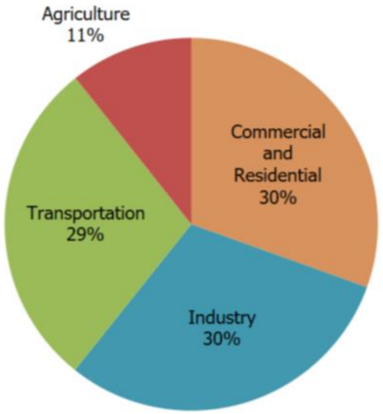


Fight against antibiotic resistance

Lignin-based Ionomer Binders for H-Fuel Cells

Clean Energy Technologies are key to Decarbonization Efforts

U.S. Greenhouse Gas Emissions by Economic Sector



Total U.S. CO_2 emission (2021): 6,340 Million Metric Tons

https://www.epa.gov/ghgemissions/sources-greenhouse-gas-emissions

Fuel Cells: produce electricity

Batteries: produce electricity

Electrolyzers: produce green hydrogen converts CO_2 to valuable products

Cost-Performance-Durability

Capture the CO_2 emission

Transition to technologies causing <u>no</u> CO_2 emission

Tesla

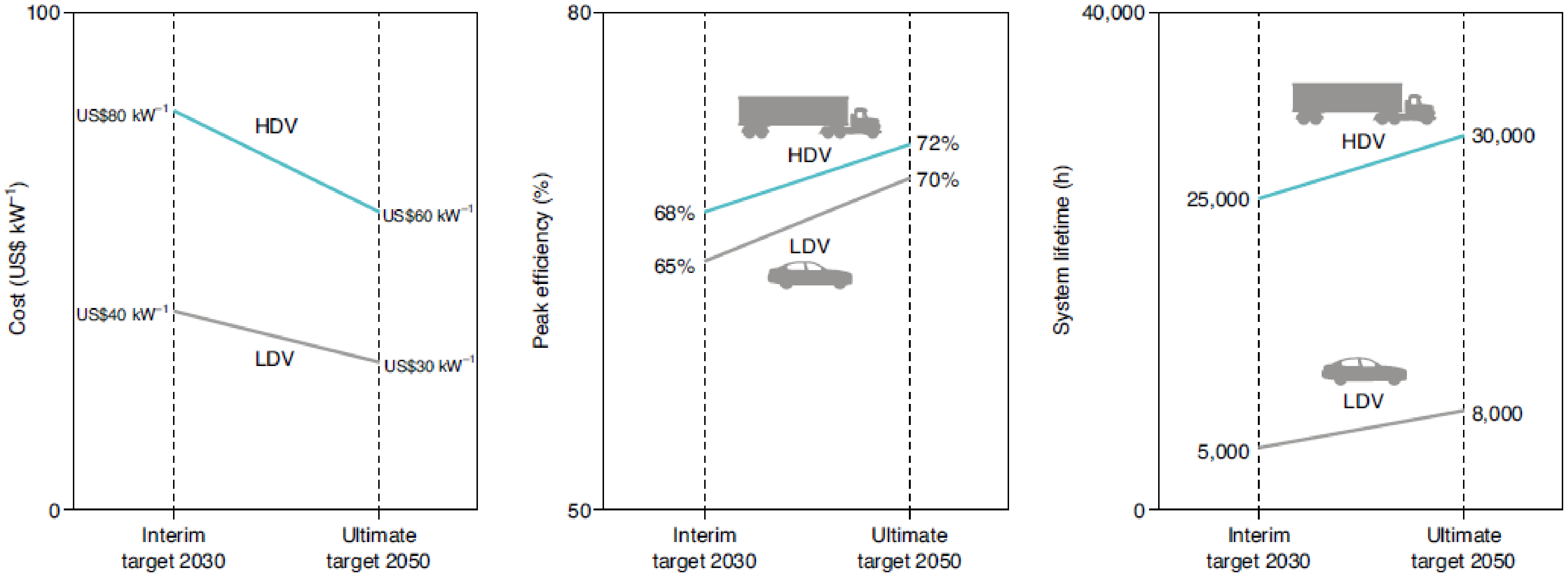
Daimler Truck

Clean Energy Devices: Cost-Performance-Durability

- A gasoline driven car emits 5 metric tons of CO_2/yr
- By 2050, hydrogen could meet 14% of the energy demand in the United states and 24% of world's energy needs.
- The recent roadmap of hydrogen economy emphasizes the need for accelerated investment in R&D for *hydrogen production*, *storage*, *energy conversion and storage devices*.

Toyota Mirai

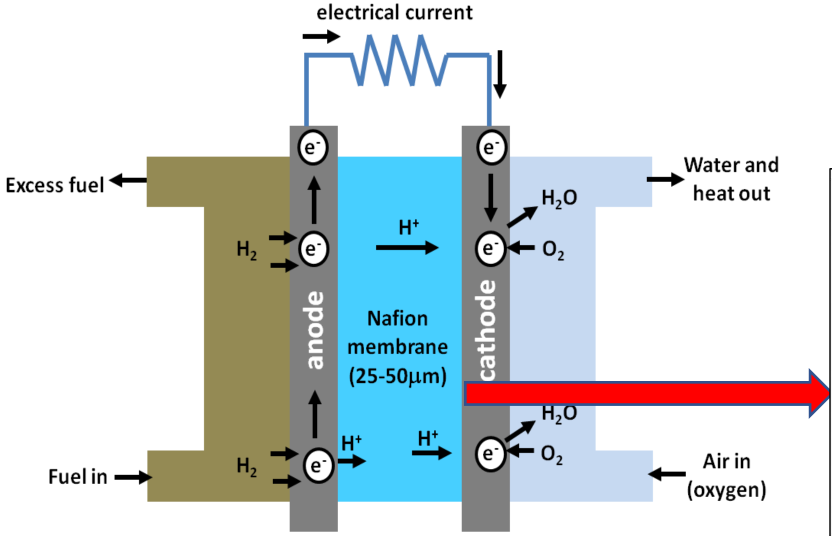
Million-Mile Fuel Cell Truck Consortium Target (2030): 25,000 h or *1-million-mile lifetime for long-haul trucks*.



- Fuel cell-based cars are eco-friendly.
- Fuel cell cars are 3 times more expensive than gasoline-driven cars
- **Cost-Performance-Durability**

Kusoglu, A. et al. Nature Energy 2021

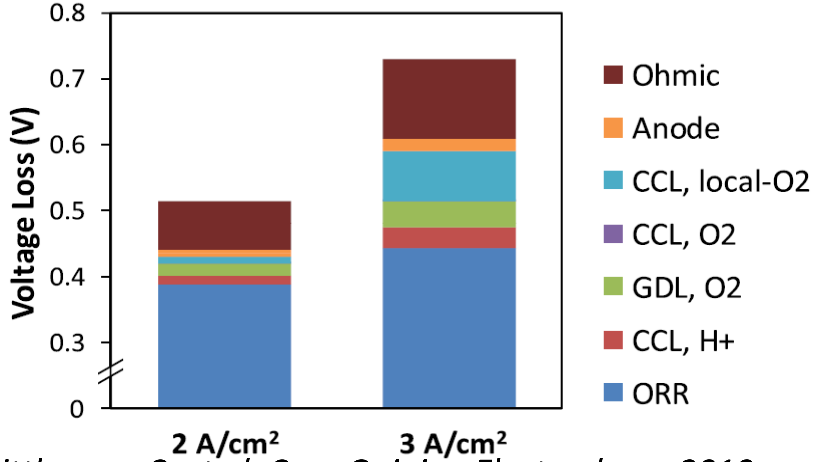
Technical Challenges of H-Fuel Cells



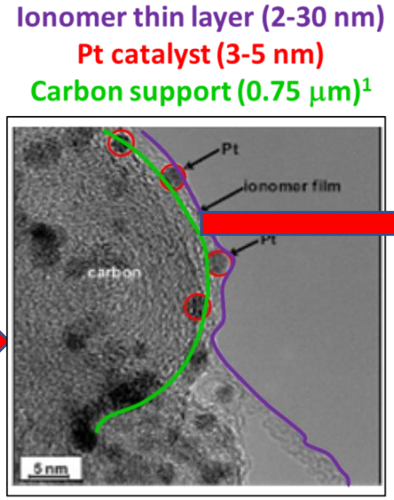
Proton exchange membrane fuel cell (PEMFC)

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

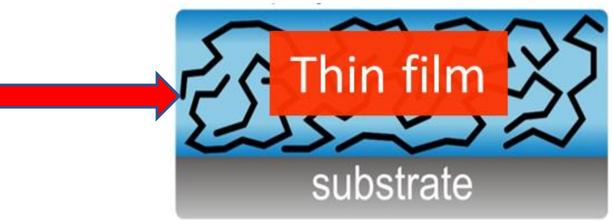
Cathode: $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$ **(ORR)**



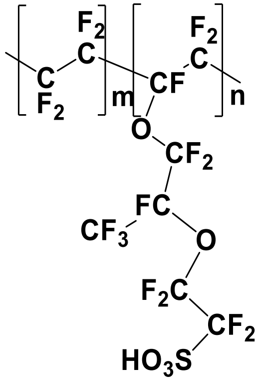
Gittleman, C. et al. Curr. Opinion Electrochem. 2019



Ionomer-catalyst interface



Dishari , S. K. et al. J .Phys. Chem. C 2019
Dishari , S. K. et al. J .Phys. Chem. C 2018
Dishari , S. K. et al. Macromolecules 2013



Nafion

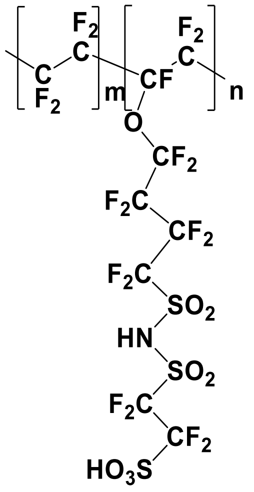
Issues with current state-of-the-art ionomer Nafion:

- **High ion transport resistance** at nanothin polymer-catalyst interface
  - makes ORR sluggish
  - negatively impacts power performance of fuel cells
- **Nafion is very expensive ($500/kg,** 2018 cost projection report, DOE-FCTO)
- **Nafion is fluorocarbon-based - not environment friendly.**

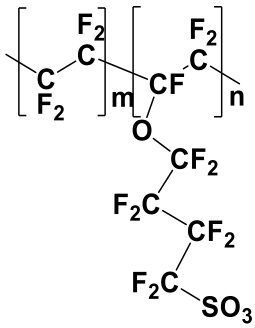
Ionomer thin film & interfacial behavior are neither well-understood nor attempted to improve significantly

We need **low-cost, efficient**, and **environment friendly ionomers**.

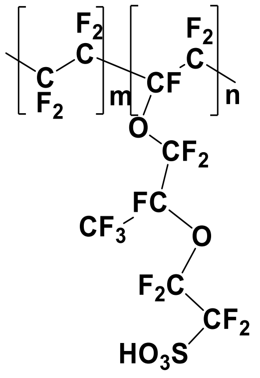
Ionomers exhibit poor conductivity in thin films



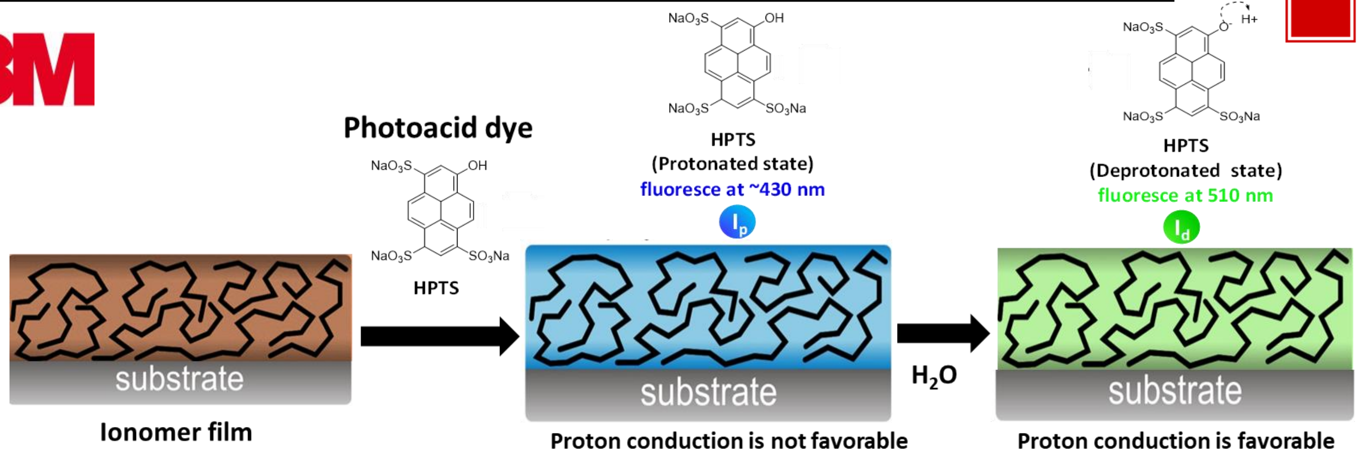
3M PFIA
IEC ~ 1.61 meq/g



3M PFSA
IEC ~ 1.21 meq/g



Nafion
IEC ~ 0.91 meq/g



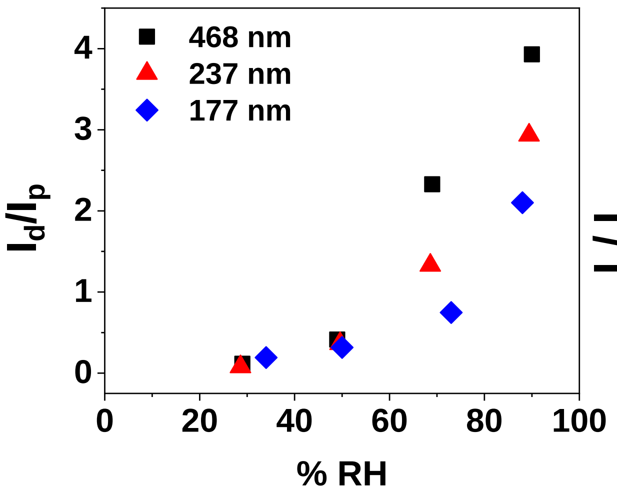
Ionomer film
(unstained)

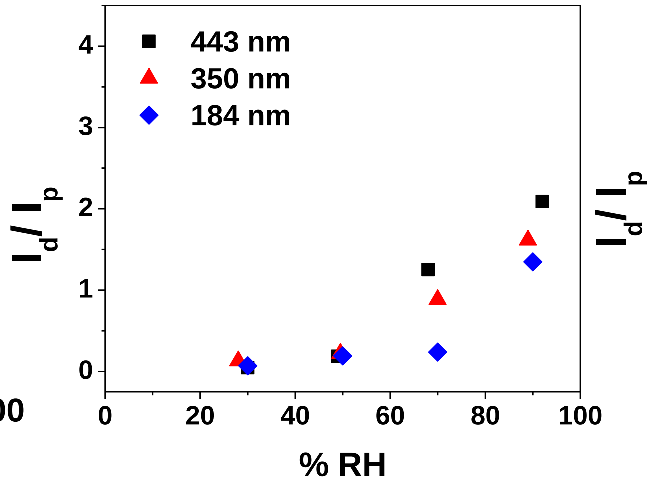
Proton conduction is not favorable
proton is not dissociated/not carried away
Blue fluorescence

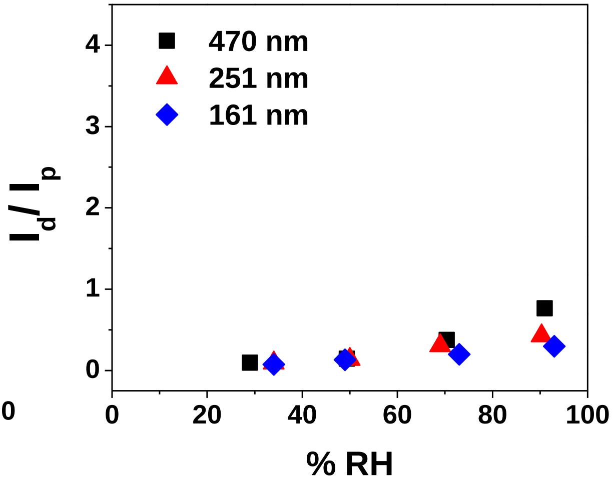
Proton conduction is favorable
Dissociated proton is carried away
Green fluorescence

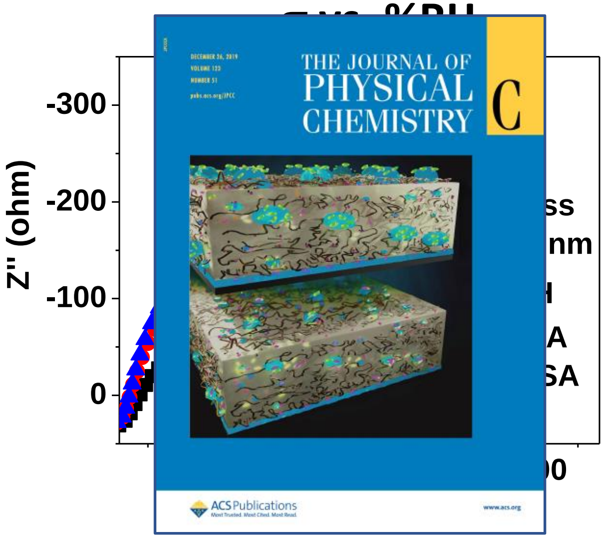
Incorporated HPTS within ionomer films

Higher I_d/I_p → Higher extent of proton conduction







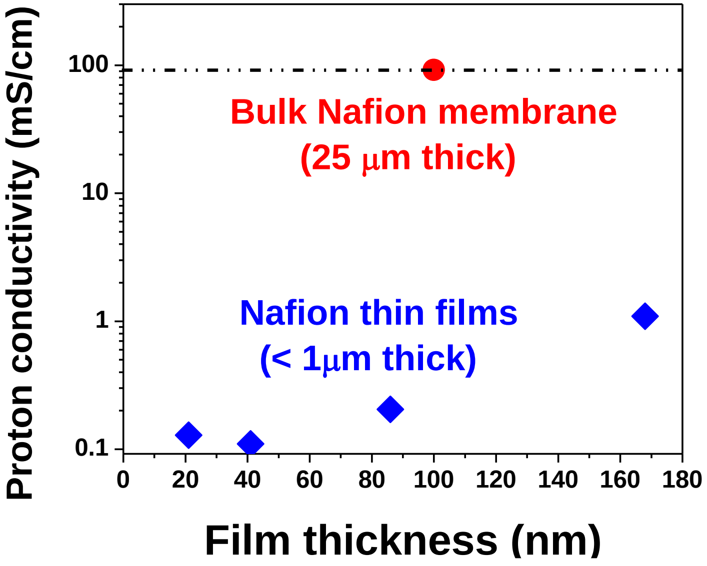


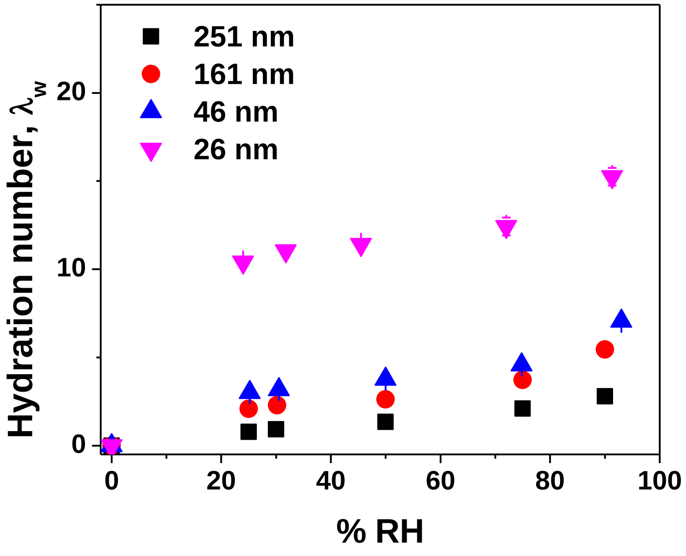
Dishari et al. J .Phys. Chem. C (2019)

Proton transport becomes weaker as the ionomer films become thinner.

Why is ion conductivity weak in thinner films?

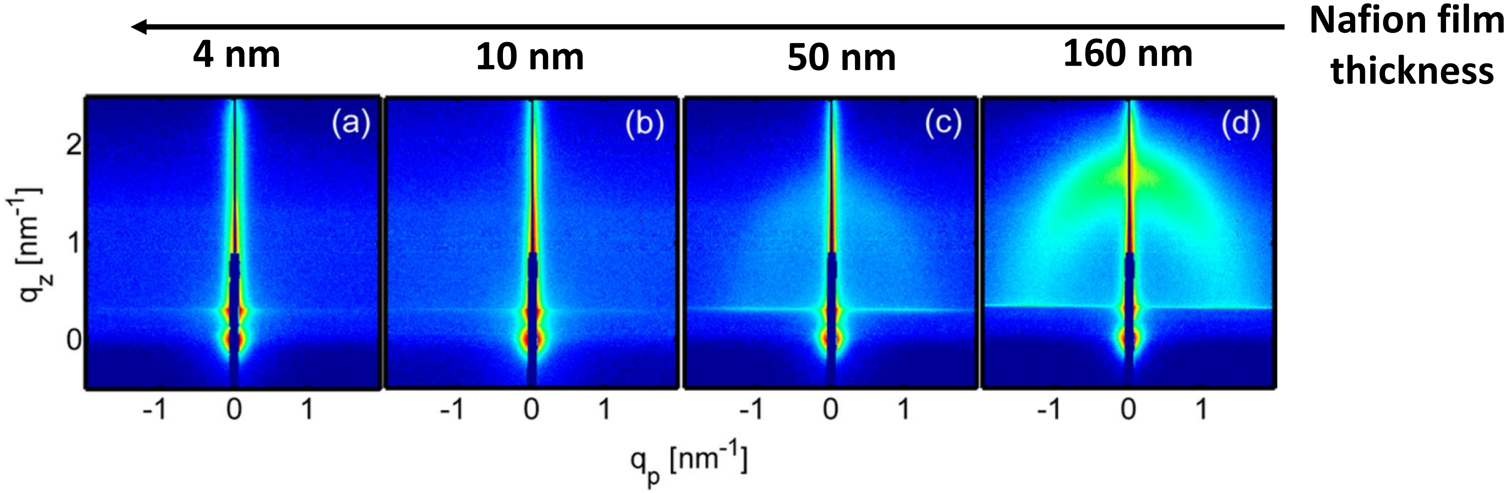
Thinner films: sorb water, but conduct protons poorly





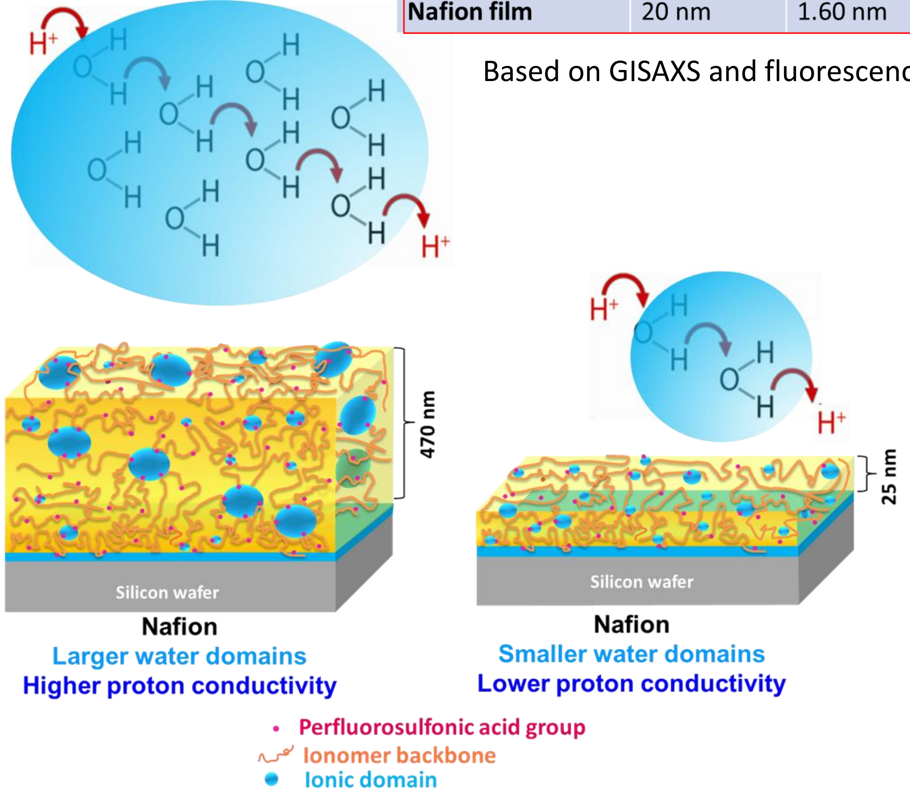
	Film thickness	Ionic domain size
Nafion membrane	25 μm	4 nm
Nafion film	470 nm	2.10 nm
Nafion film	20 nm	1.60 nm

Based on GISAXS and fluorescence



Poor phase separation in thinner films

Modestino et al. Macromolecules (2013)

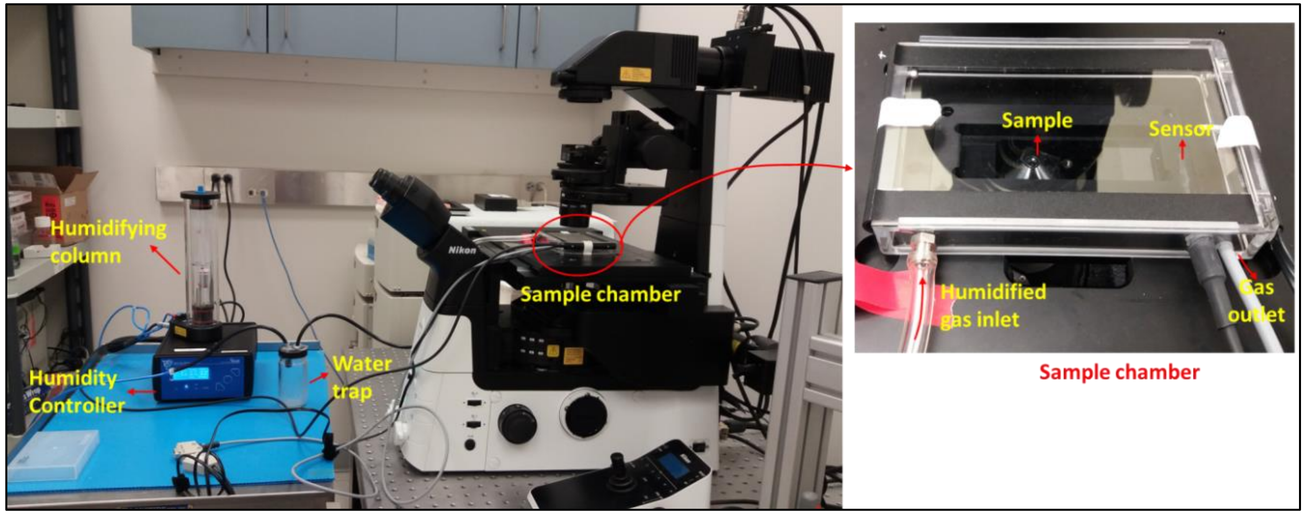


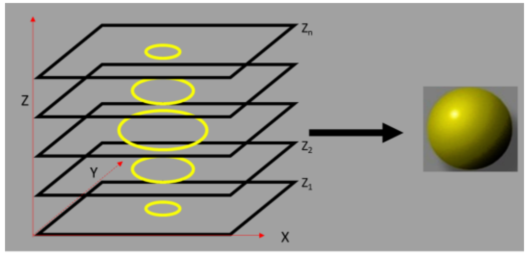
Not the water uptake, but the size of the water domains matters!

Dishari, S. K. et al. Cell Rep. Phys. Sci. 2023
Dishari, S. K. et al. JACS Au 2022
Dishari, S. K. et al. J .Phys. Chem. C 2019
Dishari, S. K. et al. J .Phys. Chem. C 2018
Dishari, S. K. et al. Macromolecules 2013

Ion transport is weak immediate next to substrate interface

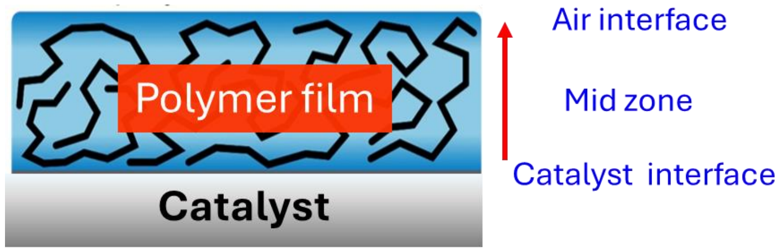
Set-up for performing humidity based confocal microscopy measurements of ionomer films and membranes.





Development of Z-stack image

Funded by:
NSF CAREER Award
NSF-CBET-Electrochemical Systems
3M Non-Tenured Faculty Award

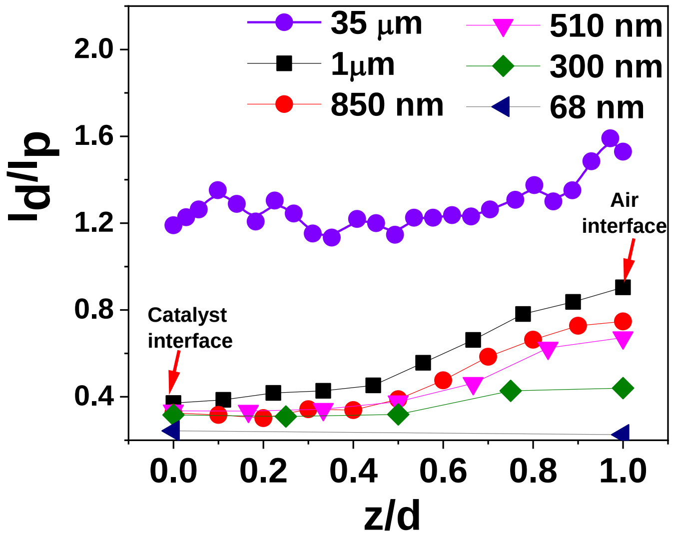


In thin film, proton conduction:

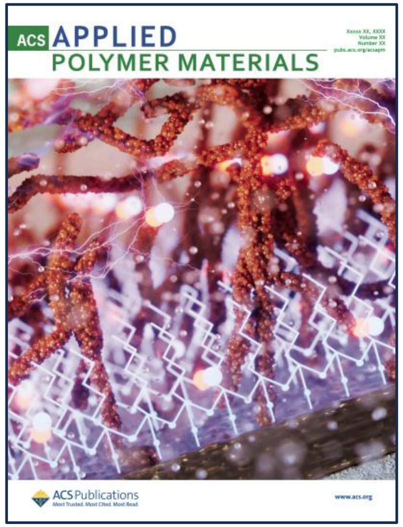
weak near substrate interface

relatively stronger near air interface

Proton conduction profile

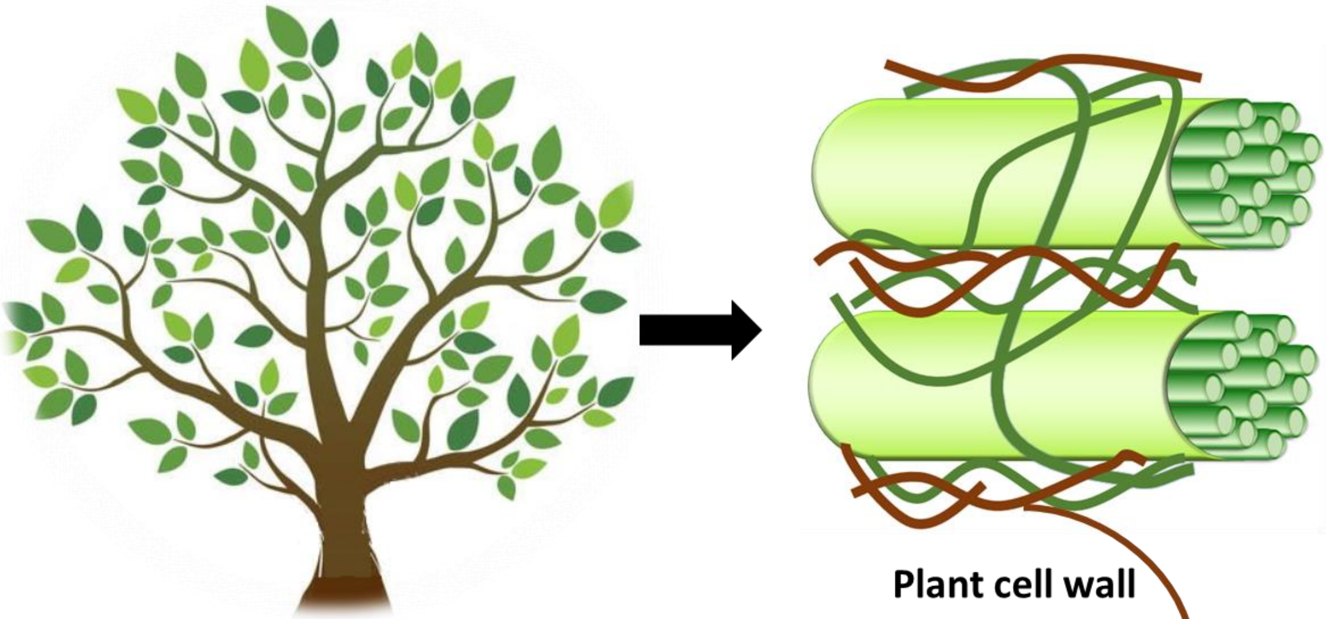


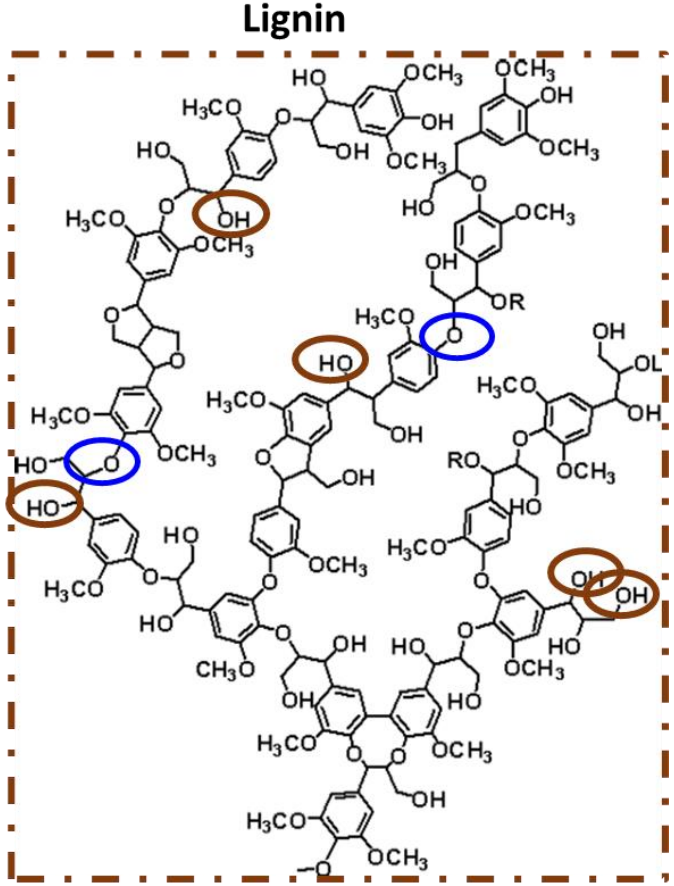
Nafion films and membranes are
exposed to humid air



Dishari, S. K. et al. ACS Appl. Polym. Mater. 2024
Dishari, S. K. et al. ACS Macro Lett. 2021

Why lignin-based ionomers?





Plant cell wall polymer Lignin

Offer unique molecular sorption sites/ transport pathways

- 3-dimensional, hyperbranched architecture
- Polar/hydrophilic groups (-OH, ether linkages)
- Facile functionalization/crosslinking site

Green, low-cost, naturally abundant material

Inexpensive ionomer → cost-competitive fuel cell

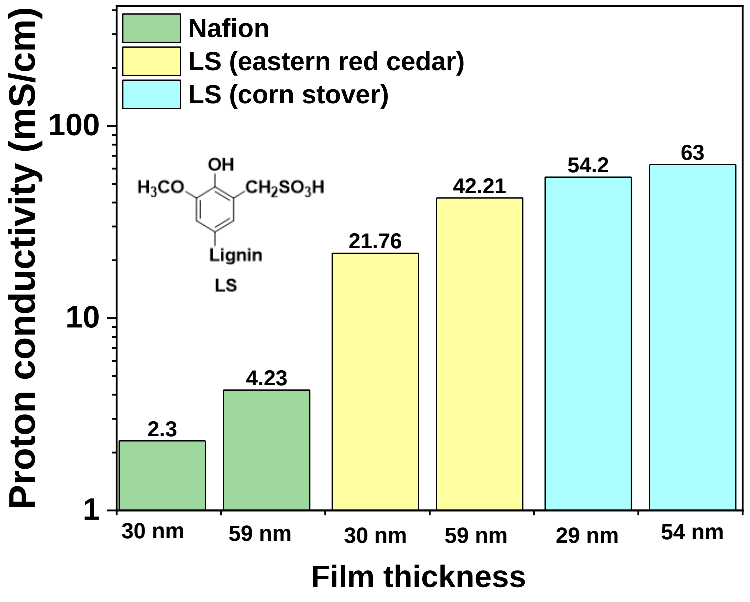
Dishari, S.K. et al, Frontiers in Chemistry ***2020***

Funded by:
NSF-CBET (Electrochemical Systems)
Nebraska Center for Energy Science Research Grant

Lignin-based ionomers offer ionic conductivity higher than Nafion in thin films

Lignin sulfonic acid ionomer (LS) synthesis

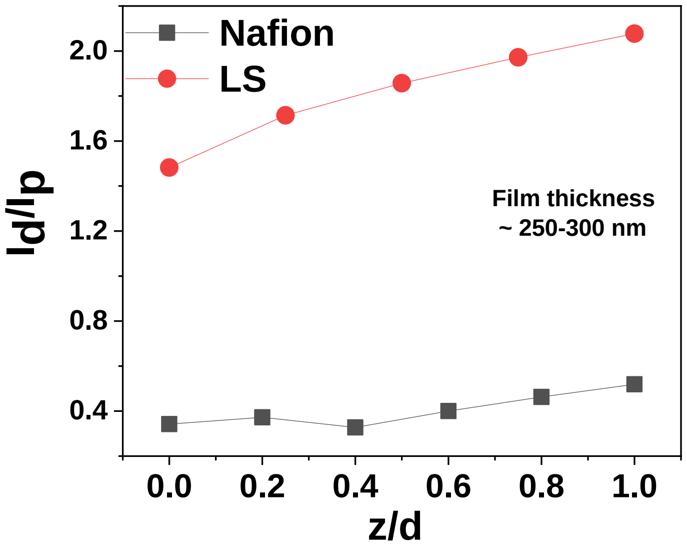
Average Conductivity



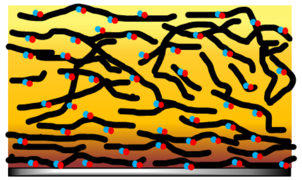
*Dishari, S.K. et al, Frontiers in Chemistry **2020***

Photographic image of Nafion-LS composite membrane

Proton conduction profile



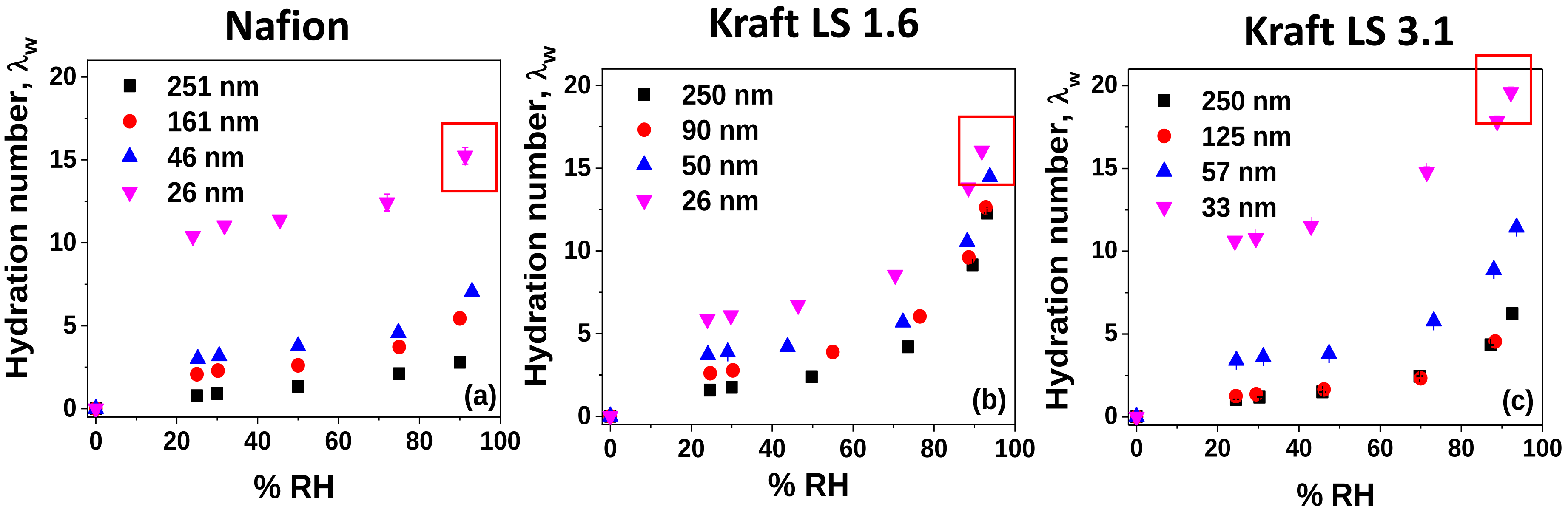
LS: non-linear

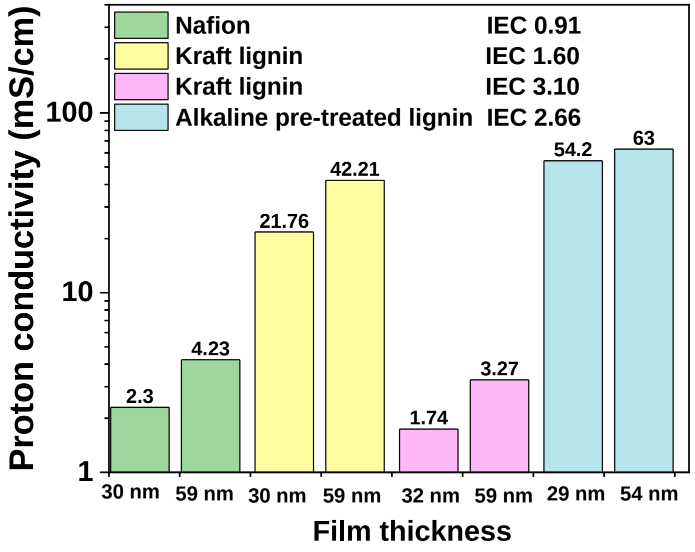


Nafion: linear

Non-linear LS: *likely leads to* *lesser number of point of contact with interfaces*

Water uptake is not directly correlated to proton conductivity of ionomer thin films





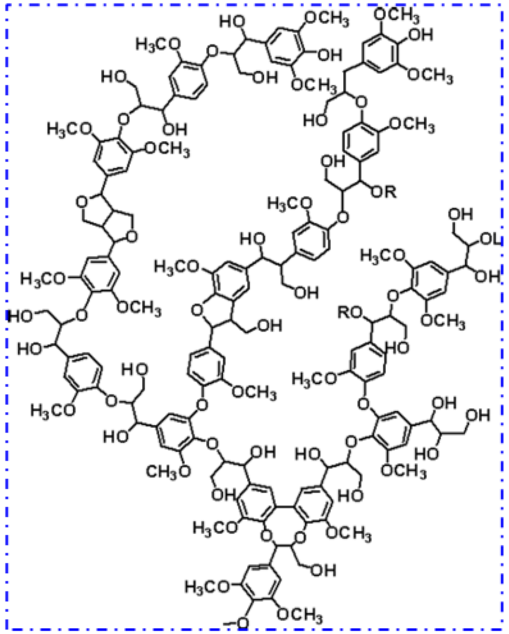
High water uptake does not necessarily lead to high proton conductivity

*Dishari, S.K. et al, Frontiers in Chemistry **2020***

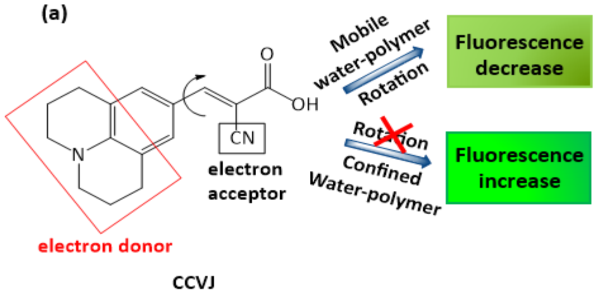
LS films are less dense, less stiff

Polymer	**IEC**	**Density (g/cc)**	
		Film thickness (~250 nm)	Film thickness (~25 nm)
Nafion	0.91	1.89	1.71
S-Radel	2.5	1.45	
Kraft lignin (LS)	1.6	**1.29**	**1.07**
Kraft lignin (LS)	3.1	**1.06**	**0.92**

Lignin-based ionomer films are less dense
in agreement with
3D hyperbranched architecture of lignin
which leaves free spaces
within macromolecular ionomer structure.

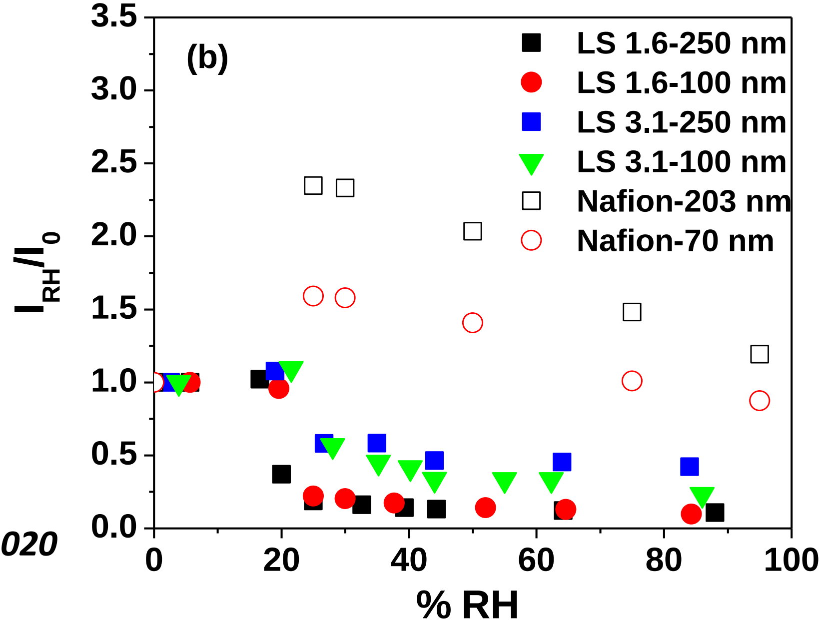


Films were stained with rotor probe CCVJ



*Dishari , S. K. et al. J .Phys. Chem. C **2018***
*Dishari, S.K. et al, Frontiers in Chemistry **2020***

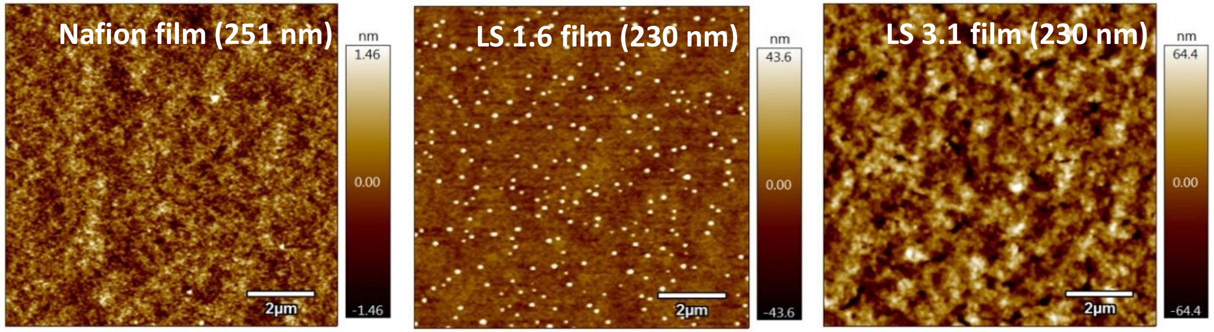
As the film stiffens at hydrated state, I_{RH}/I_0 increases

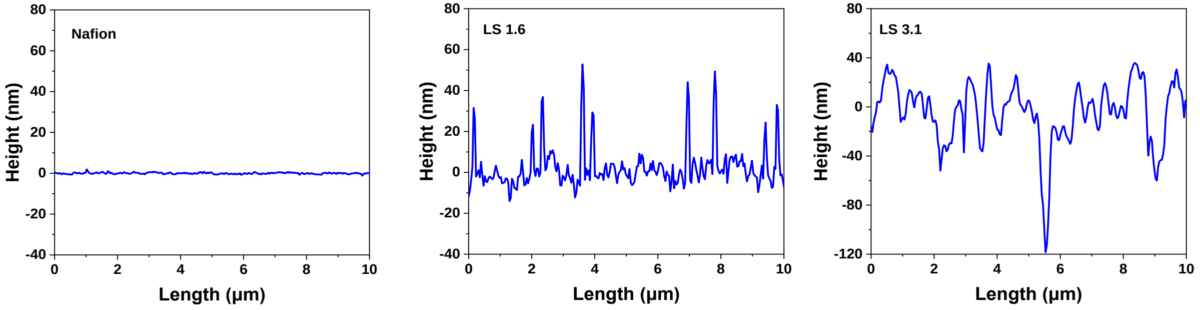


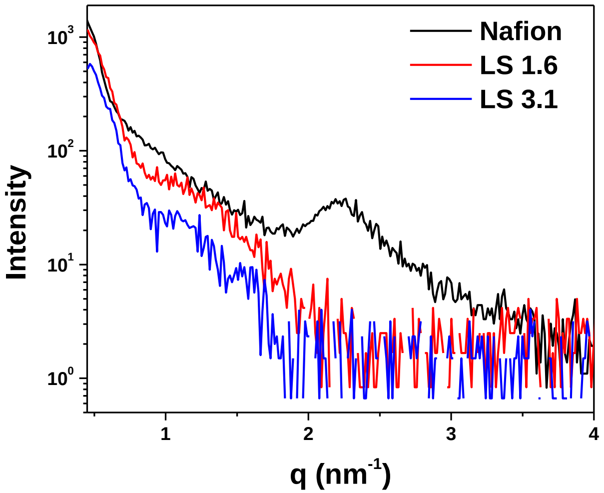
LS films did not stiffen upon hydration

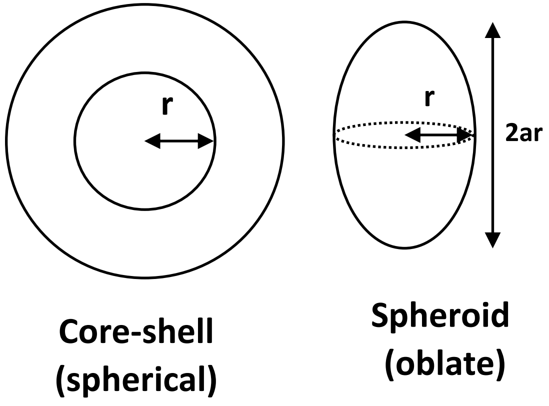
Water molecules have higher mobility in LS films

Morphological Features of LS vs Nafion films



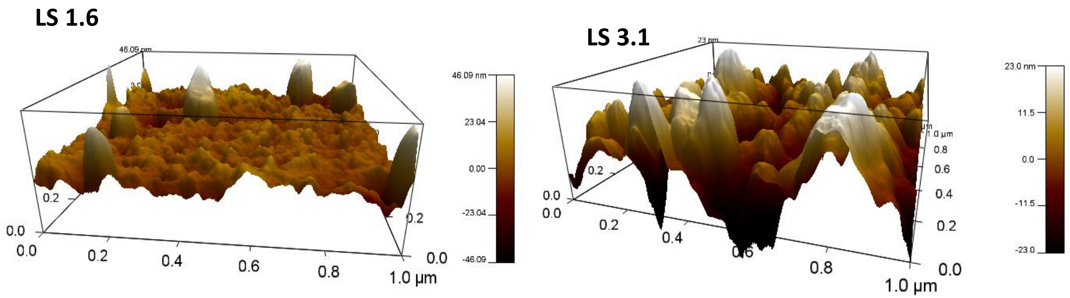






Ionic domain size: LS 1.6 > LS 3.1> Nafion

Model	Parameters	Nafion	LS 1.6	LS 3.1
Core-shell (spherical)	Average diameter (2r) (nm)	**1.85**	**10.50**	**8.95**
Oblate spheroid (ellipsoid)	Average diameter (2r) (nm)	**1.55**	**7.50**	**6.00**
	Aspect ratio (a)	1.00	5.50	4.50
	Length of long axis (2ar) (nm)	1.55	41.25	27.00



LS films had ellipsoidal features
Nafion films were featureless

Ionic domains are larger in LS films
as compared to Nafion films

Dishari, S.K. et al, Frontiers in Chemistry. **2020**

Conclusion: Lignin-based Ionomeric binders

- We innovated a novel range of ionomer using lignin to address and overcome the ion transport limitations in sub-micron thick films.

- With ***3-dimensional , branched architecture***, lignin-based ionomers conduct ion efficiently due to larger ionic domains with high water mobility.

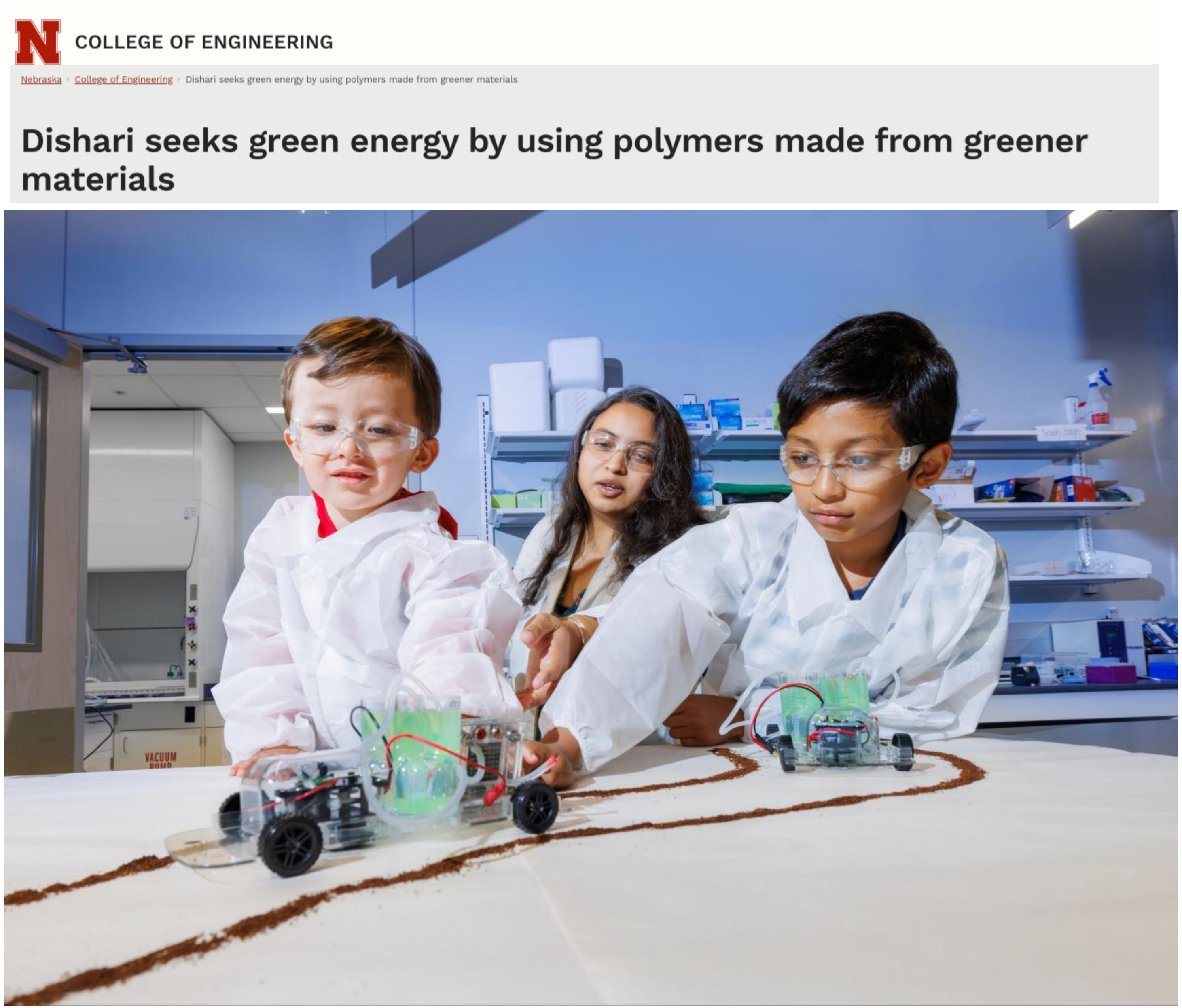
- The work demonstrates the potential of lignin-based ionomers and may lead to new ways of lignin valorization which can potentially aid in bio- and energy economy simultaneously.

- Lignin-based ionomers are **PFAS-free**.

- These ionomers can inform and guide the future design of ionomer-catalyst interfaces, highly proton-conductive catalyst binders and permselective bulk membranes as potential substitute of Nafion for fuel cells, electrolyzers, batteries, and more.

Dishari, S.K. et al, Frontiers in Chemistry. **2020**

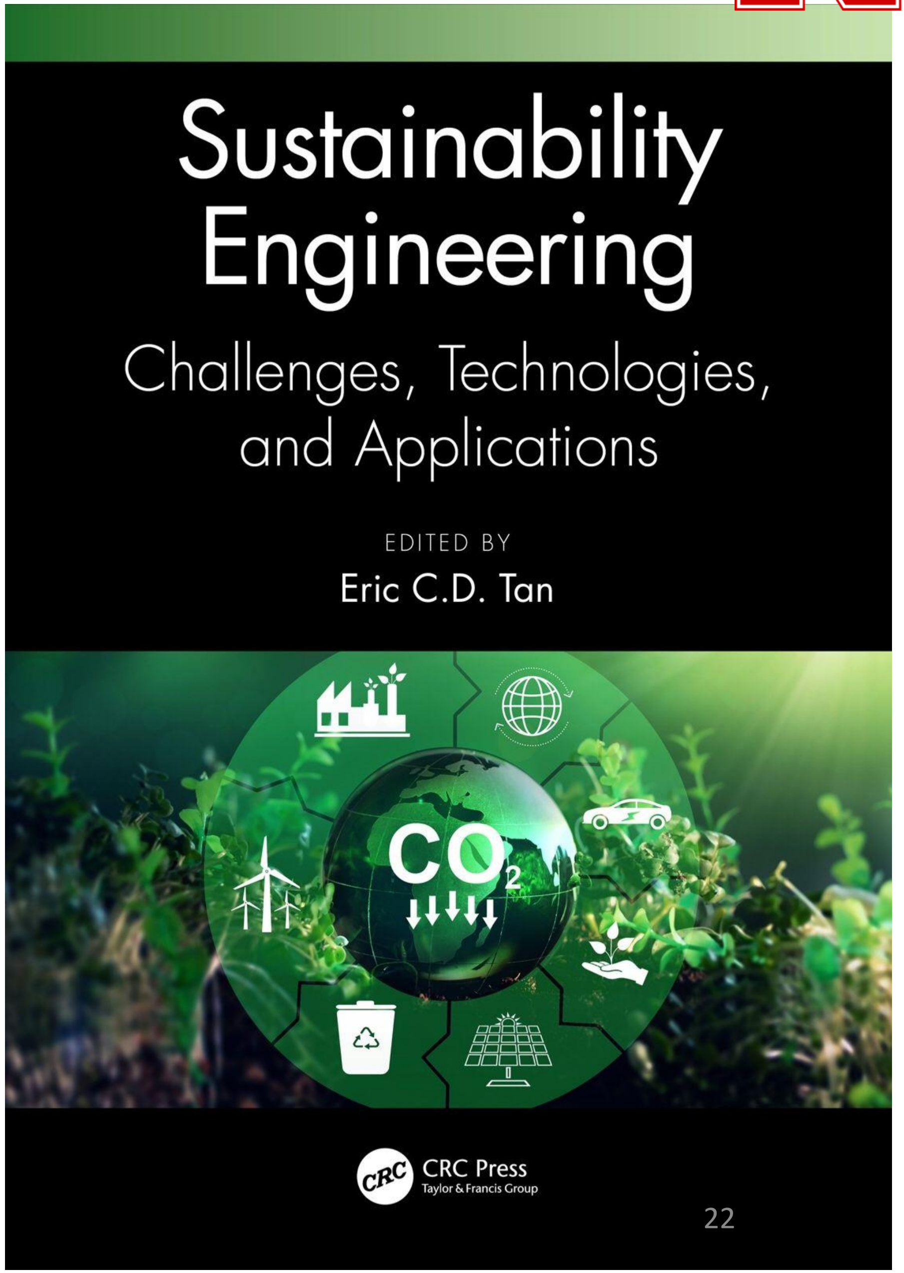
Green Energy using Green Materials



COLLEGE OF ENGINEERING

Nebraska › College of Engineering › Dishari seeks green energy by using polymers made from greener materials

Dishari seeks green energy by using polymers made from greener materials



Sustainability Engineering

Challenges, Technologies, and Applications

EDITED BY

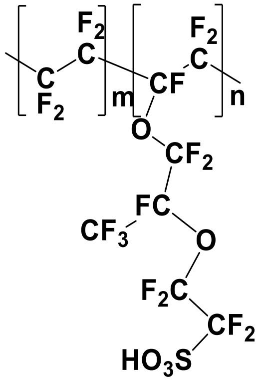
Eric C.D. Tan

CRC Press
Taylor & Francis Group

Designing Low-Cost, Green Polymer Electrolytes for High-Temperature Electrochemical Applications using Biorenewable Lignin

Funded by:
Edgerton Innovation Award

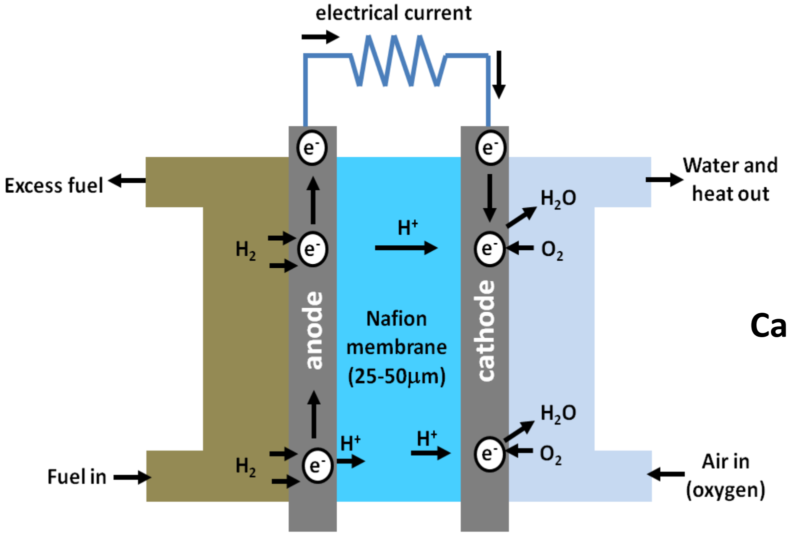
High Temperature H-Fuel Cells (PEMFCs): Challenges



Nafion

LT-PEMFCs: < 80 °C

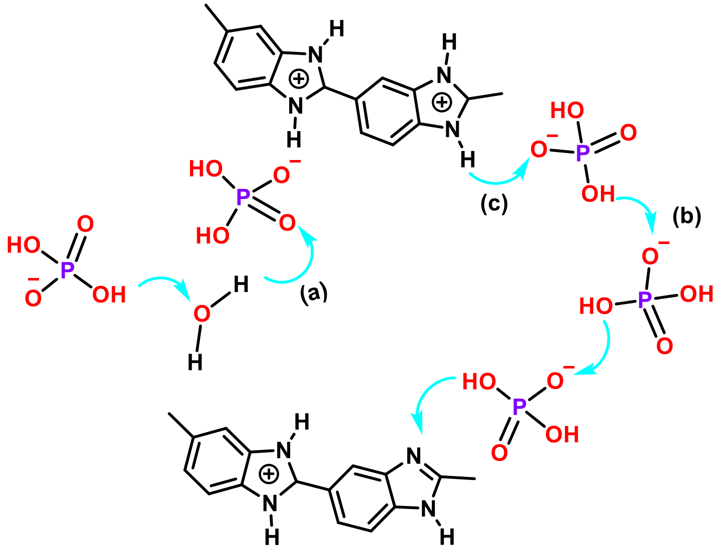
σ ~ 100 mS/cm at 80 °C



Proton exchange membrane fuel cell (PEMFC)

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $4H^+ + 4e^- + O_2 \rightarrow 2H_2O$ **(ORR)**



HT-PEMFCs: 80-200 °C

Phosphoric acid-doped PBI (PA-PBI)
(acid-base interaction)

σ ~ 120 mS/cm (80 °C)

σ ~ 157 mS/cm (140 °C)

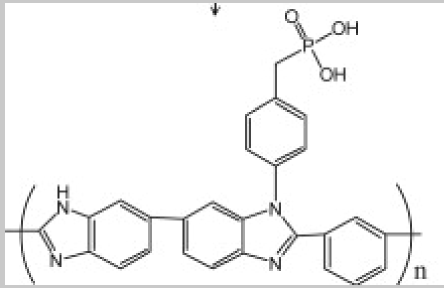
Attractive features of HT-PEMFCs

- Faster reaction kinetics (high energy efficiency)
- High tolerance to fuel/impurities
- Better heat and water management

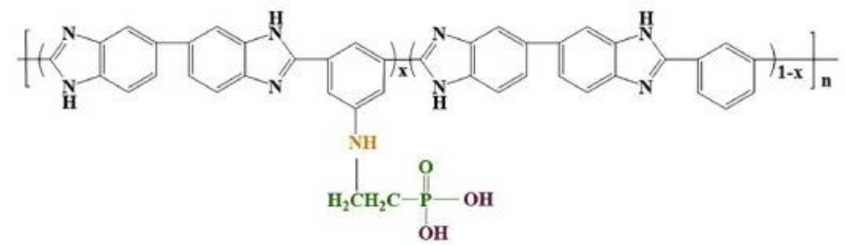
Drawbacks:

- PA leaching
- Reduced proton conductivity
- Catalyst poisoning

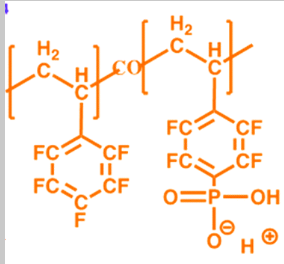
Approaches adopted to prevent PA leaching



Yu, L T et al. Int. J. Hydrog. Energy, 2020

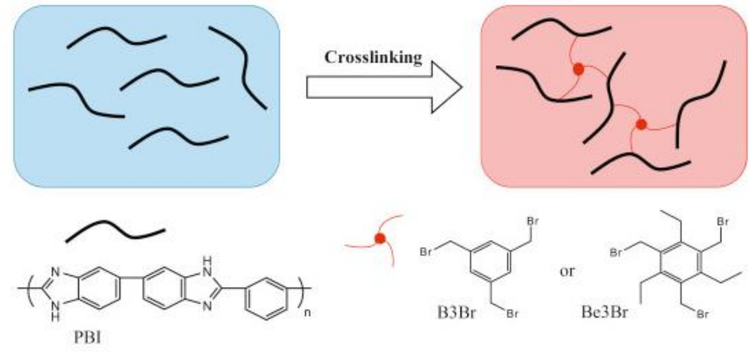


Liu G et al. Int. J. Hydrog. Energy, 2020



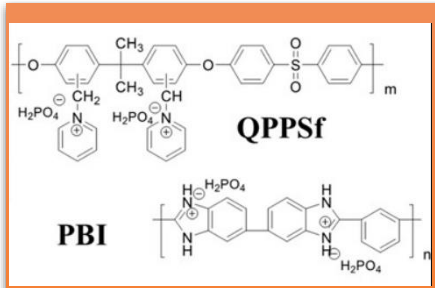
Arges, C G. et al. Mater. Adv., 2021

covalent functionalization of biphosphate groups to polymer backbone

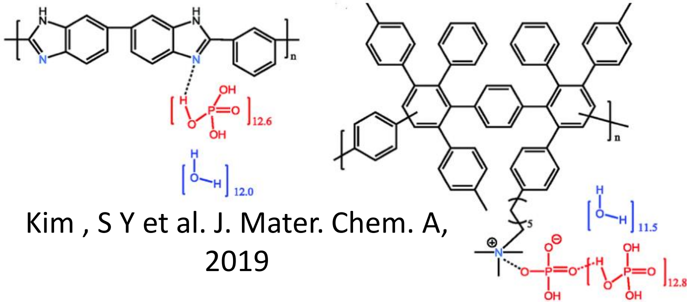


He, R et al. Int. J. Hydrog. Energy, 2018

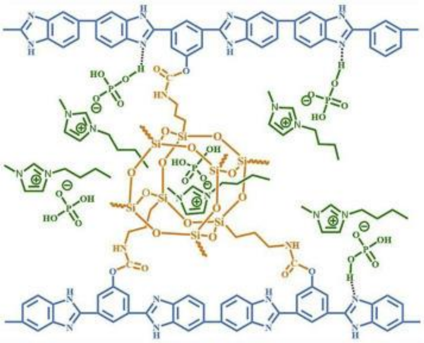
PBI crosslinking



Arges, C G. et al. ACS Appl. Energy Mater., 2020

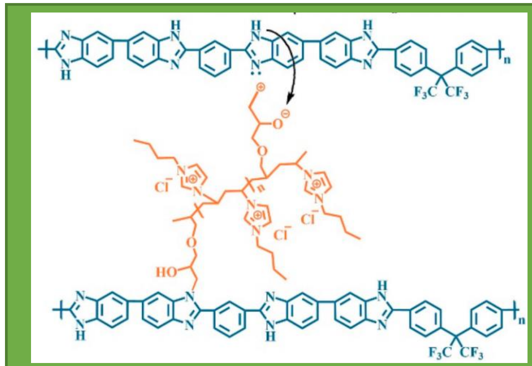


Kim , S Y et al. J. Mater. Chem. A, 2019

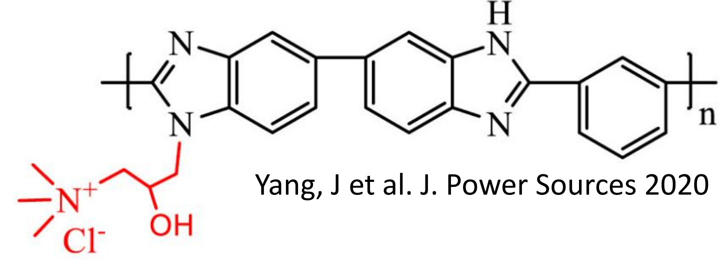


Wang, Z et al. Electrochimica Acta, 2018

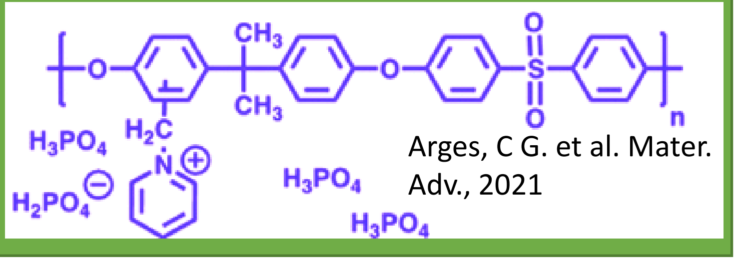
Incorporation of cationic groups in matrix



Wang, Z et al. Renewable Energy, 2021



Yang, J et al. J. Power Sources 2020



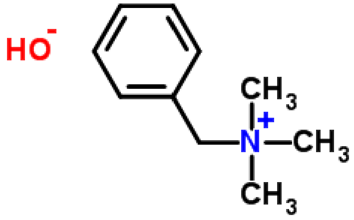
Arges, C G. et al. Mater. Adv., 2021

Grafting polymer backbone with cationic groups

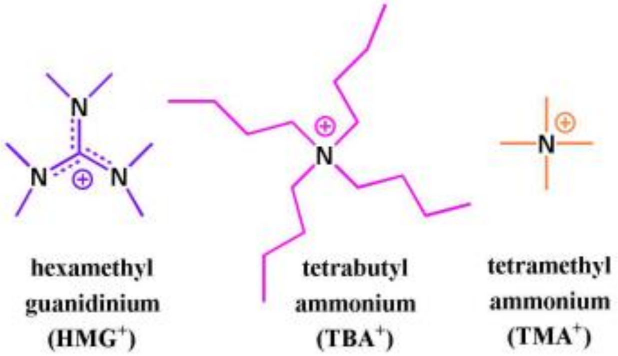
Quaternary ammonium groups used now to prevent PA leaching

Yang, J et al. J. Power Sources 2020

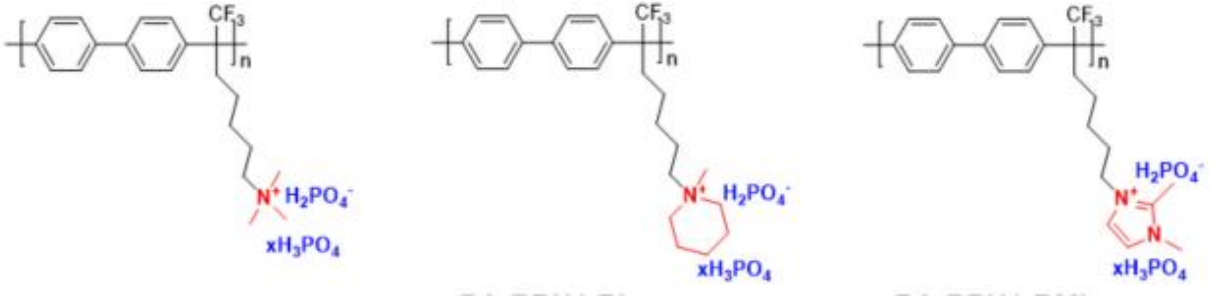
Wang, Z et al. Renewable Energy 2021



Kim S Y, et al. Joule 2021



Kim S Y, et al. J. Mater. Chem. A 2019



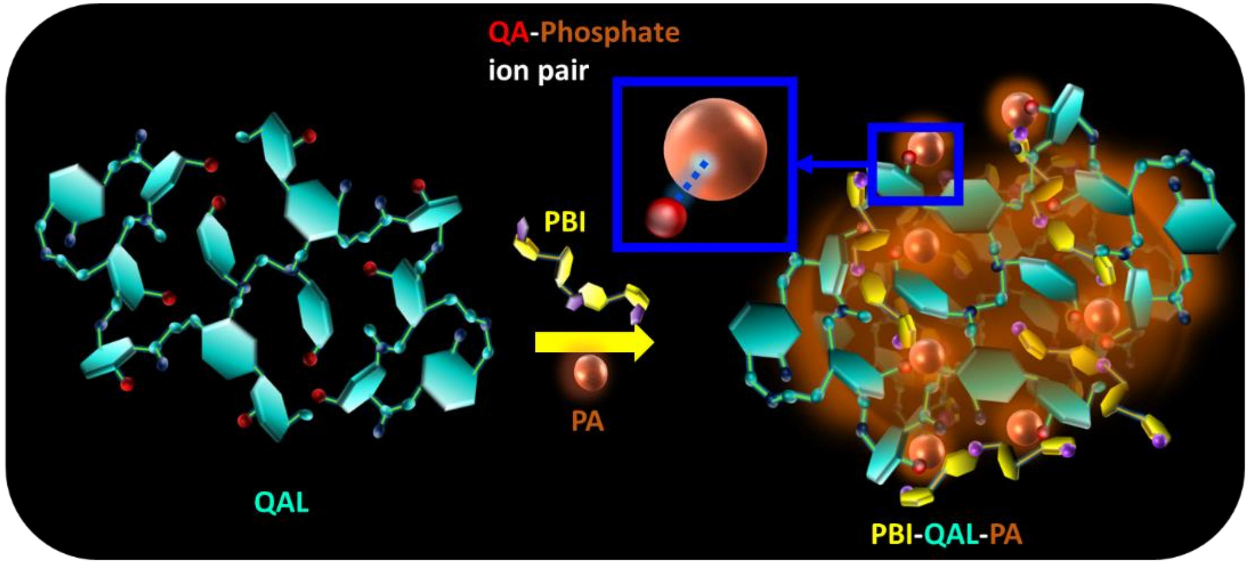
Bae, C et al. Energies 2020

Binding energy between:
PA and **PBI**: **17 kcal/mol**
PA and **quaternary ammonium groups**: **151 kcal/mol**

Many of these compounds are **synthetic/petroleum-derived**.
Sustainability, **Scalability** and **Disposability**??

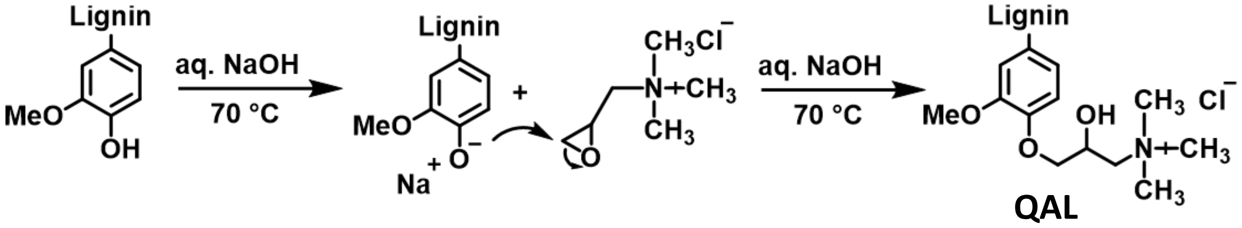
Why lignin-based cationic polymer electrolytes?

Cationic lignin (QAL) for HT-PEMFCs



Current challenges.
- PA loss from membrane
- Moderate conductivity
- Low stability of conductivity
- Low durability
- Cost

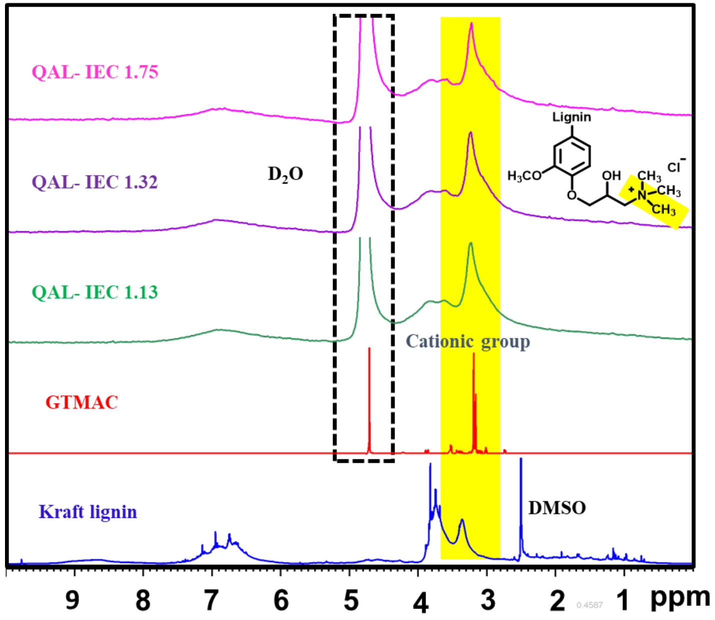
What lignin does to address these challenges.
- Elevates PA capture by ion-pair interaction
- Retains PA within the membrane
- Improves membrane proton conductivity at high T
- Maintains stable conductivity for extended hours
- Good thermal, chemical and mechanical stability

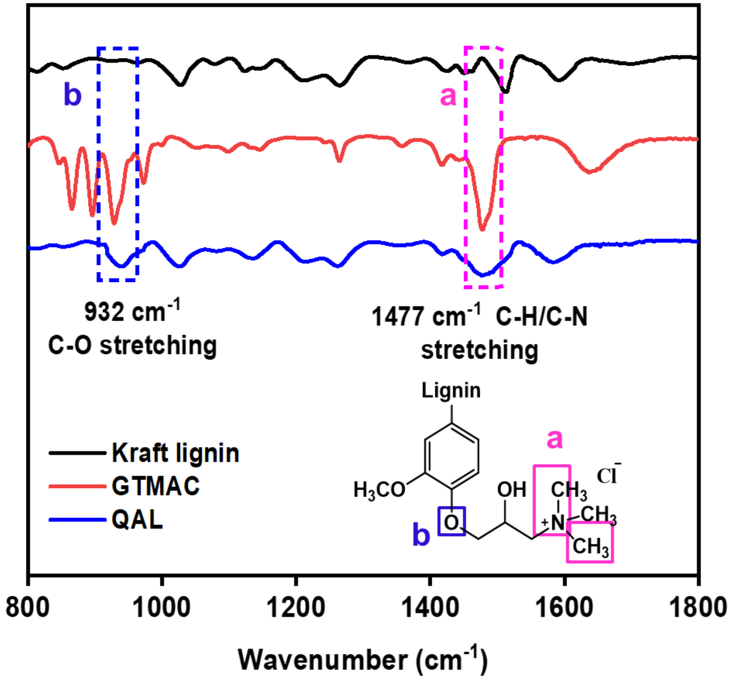


Polymer	IEC
Lignin: GTMAC (1:1.5)	1.13
Lignin: GTMAC (1:1.7)	1.32
Lignin: GTMAC (1:2.0)	1.75

Dishari, S.K. et al, manuscript under preparation, ***2024***

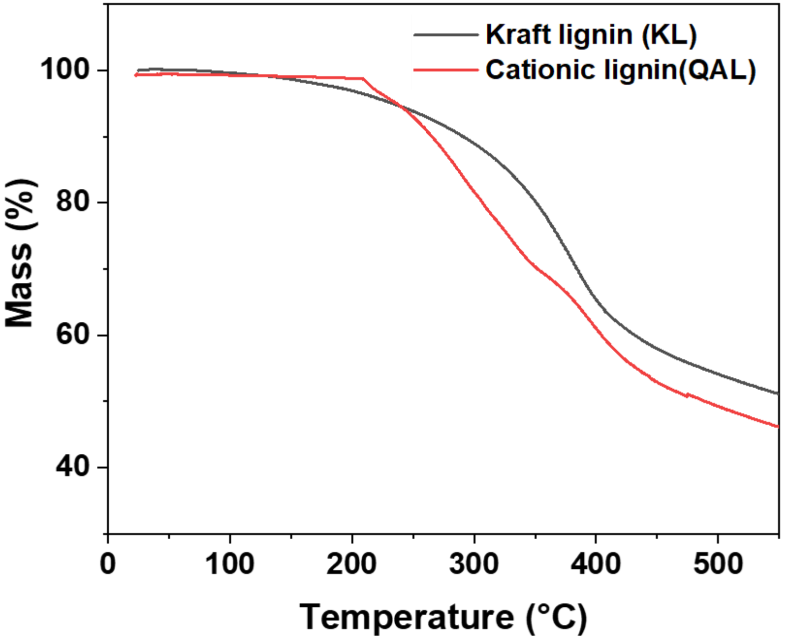
Cationic Lignin (QAL)





^{1}H NMR:
Quaternary amine protons (-N(CH$_3$)$_3^+$):
2.49-3.36 ppm in QAL

FT-IR:
1477 cm^{-1}: **C-H and C-N stretching** vibration of QA
932 cm^{-1}: **C-O stretching** vibration (ether) of QA

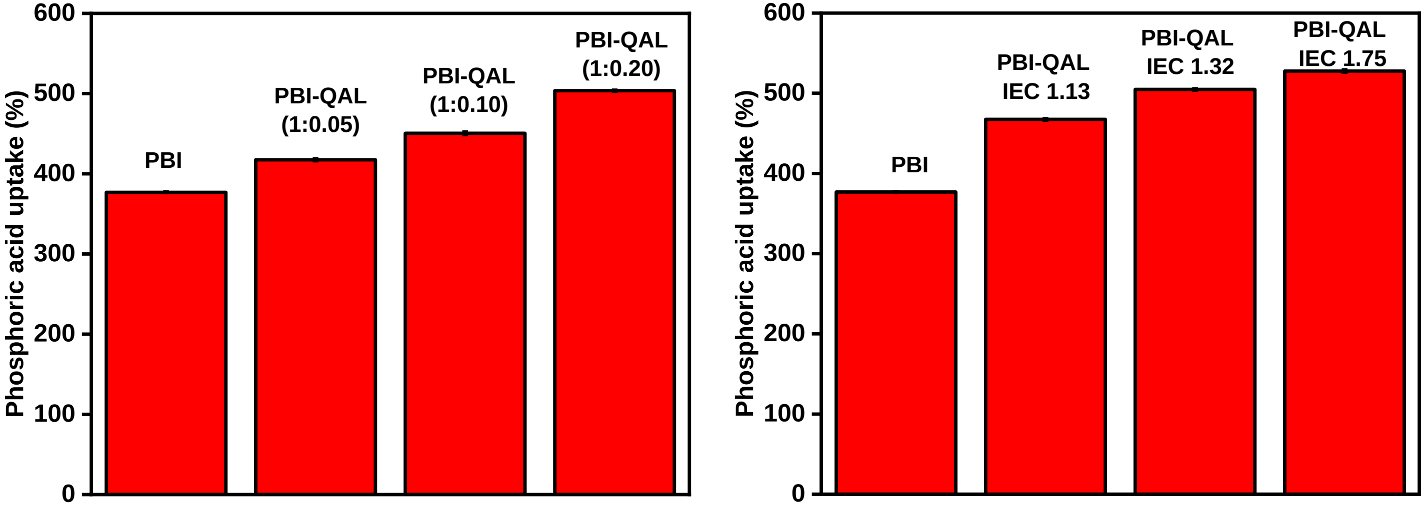


Within typical HT-PEMFC operation range (~100-200 °C), QAL did not show any sign of degradation

High Thermal Stability/Durability

*Dishari, S.K. et al, manuscript under preparation, **2024***

PA-doped PBI-QAL Membranes: PA uptake



- Incorporation of cationic QAL elevated the PA uptake by the PBI-QAL composite membranes.
- The higher the QAL content was, the higher the PA doping was experienced.

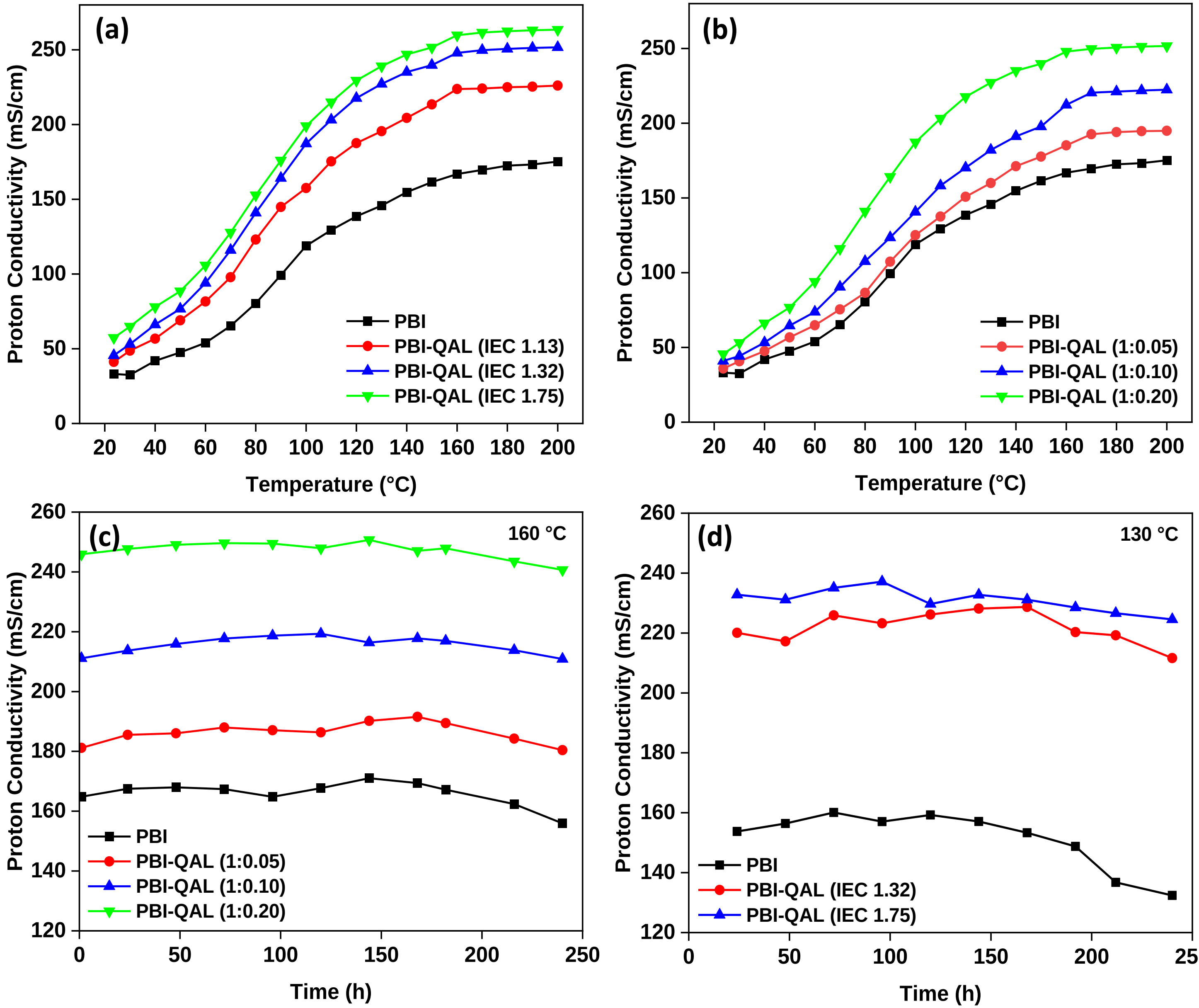
- Elevated PA uptake within PBI-QAL membrane could be attributed to:

- **Porous structure of lignin offering additional void volume to capture and store more PA** within membrane matrix than traditional PBI membranes

- **Strong ion-pair interaction between <u>cationic QAL</u> and <u>anionic phosphate of PA.</u>**

*Dishari, S.K. et al, manuscript under preparation, **2024***

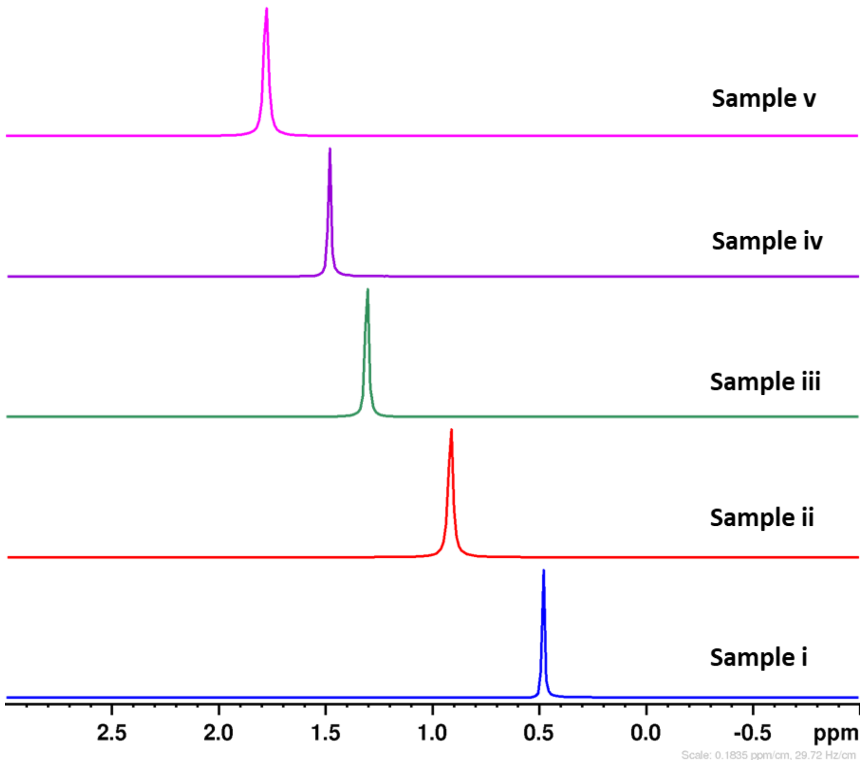
PA-doped PBI-QAL Membranes: Conductivity



*Dishari, S.K. et al, manuscript under preparation, **2024***

- **PBI-QAL membranes always showed proton conductivity higher than pure PBI membranes**.
- pure PBI membrane: 175 mS/cm
  PBI-QAL membrane: 225 mS/cm (IEC 1.13)
  251 mS/cm (IEC 1.32)
  264 mS/cm (IEC 1.75)
- When PBI-to-QAL ratio was varied from 1: 0.05 to 1: 0.2 while maintaining IEC of QAL constant, proton conductivity increased.
- In a 240-h long stability study at 160 °C, the conductivity of PBI-QAL membranes remained almost the same (only 2% drop over 240 h) while maintaining consistently higher proton conductivity over PBI membranes
- **At a relatively lower T** (130 °C) at which the stability has been identified as an issue for PBI, PBI-QAL membranes showed much more **stable conductivity over 240 h-operation**.
- **Cationic QAL** as a **low-cost**, **eco-friendly**, **stable,** and **durable alternate to synthetic cationic variants** to enable ion-pair interactions

Ion-pair interaction: ^{31}P NMR



PA: QAL: PBI mass ratio

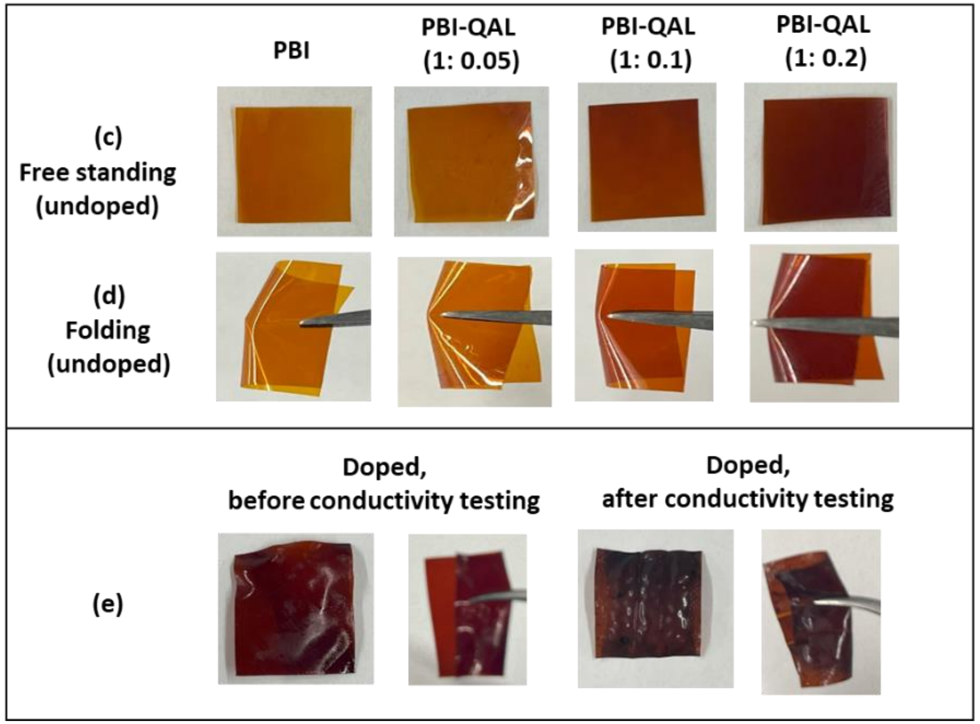
1: 0.4: 0.6

1: 0.3: 0.7

1: 0.2: 0.8

1: 0.1: 0.9

1: 0.0: 1.0

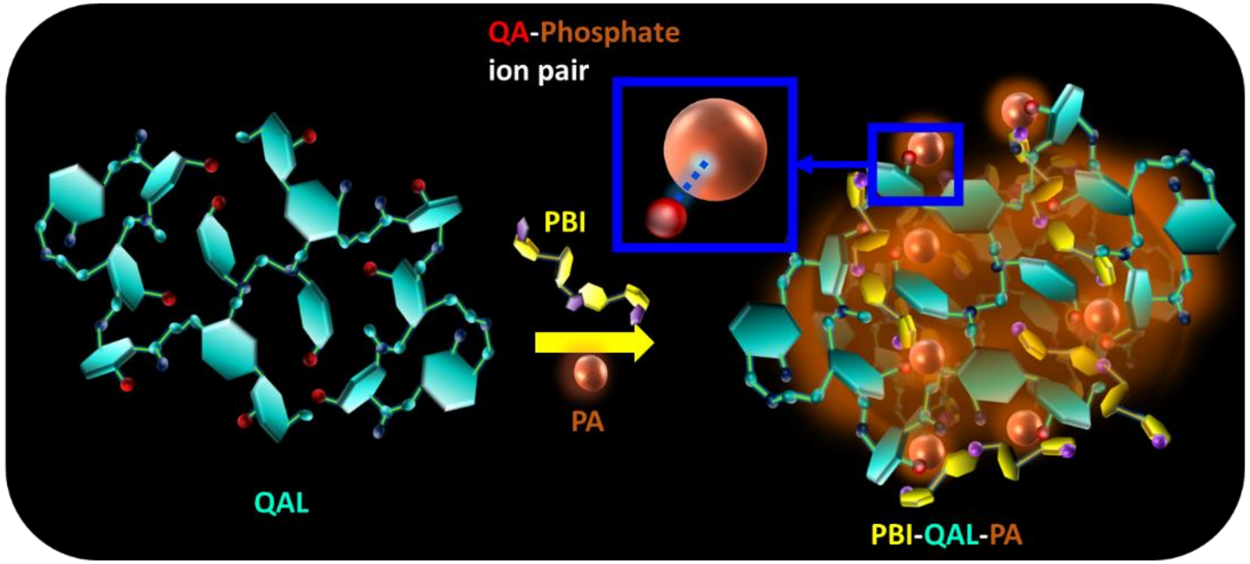


A **downfield shift of peaks with increasing QAL content** was an indicative of **increased ion-pair interactions** between phosphate anions of PA and quaternary ammonium cations of QAL.

Dishari, S.K. et al, manuscript under preparation, ***2024***

Conclusions: Lignin for HT-PEMFCs

Cationic lignin (QAL) for HT-PEMFCs



- We innovated a novel class of ***cationic polyelectrolyte using lignin*** to address and overcome PA leaching from PBI membranes in HT-PEMFCs.

- With ***3-dimensional , branched architecture of lignin*** and ***high ion-pair interaction energy,*** QAL elevates PA capture and retains PA within the membrane. This elevates the proton conductivity of membranes over extended hr of operation a high temperature.

- QAL is **PFAS-free**.

- These ionomers can inform and guide the future design of membranes for high-temperature electrochemical applications.

Fighting against Antibiotic Resistance: Designing antimicrobial materials

Funded by:
Nebraska Collaboration Initiative Grant
Voelte-Keegan Bioengineering Grant
3M Non-Tenured Faculty Award
Edgerton Innovation Award

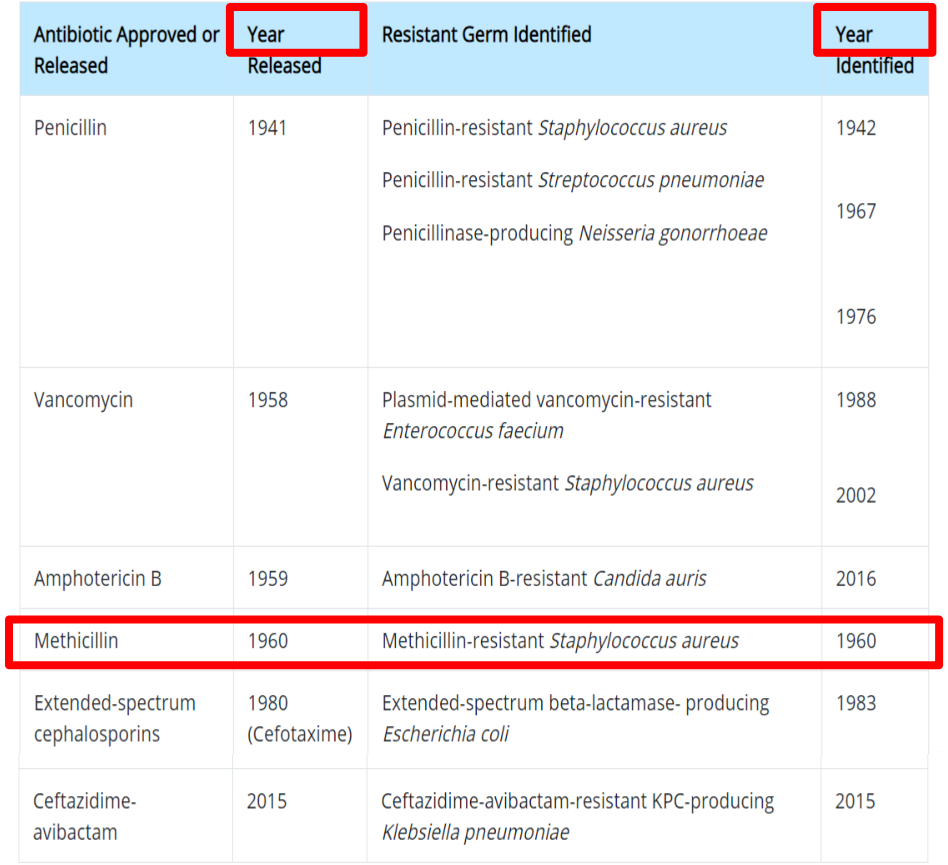
University of Nebraska Medical Center

DEPARTMENT OF PATHOLOGY AND MICROBIOLOGY
CENTER FOR STAPHYLOCOCCAL RESEARCH (CSR)

Kansas Lipidomics Research Center

Antibiotic-resistant bacteria

✓ Antibiotic resistant bacteria is one of the biggest health concerns.
✓ Overuse and misuse of the antibiotics has caused the emergence of antibiotic resistant bacteria.
✓ Each year (in U.S.) more than **2.8 million people are getting infected by antibiotic-resistant bacteria**
✓ and more than **35,000 people die**.
✓ If no action is taken, drug-resistant diseases could cause 10 million deaths each year by 2050.



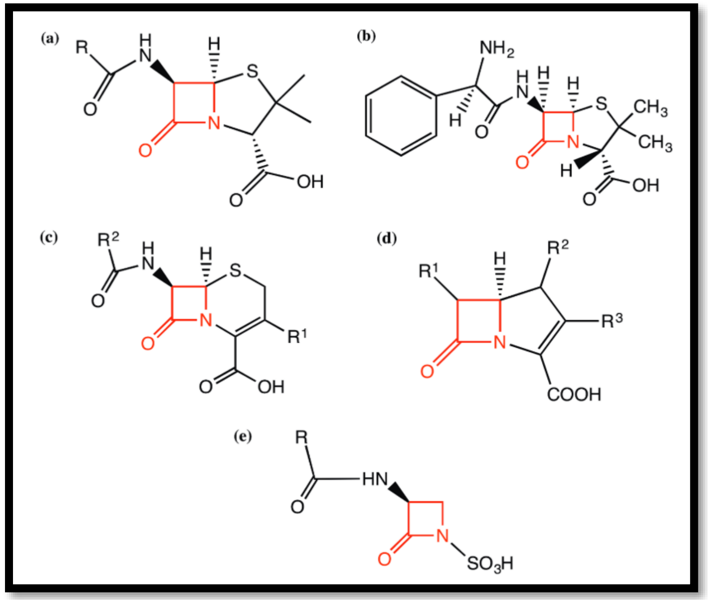
Antibiotic Approved or Released	Year Released	Resistant Germ Identified	Year Identified
Penicillin	1941	Penicillin-resistant *Staphylococcus aureus* Penicillin-resistant *Streptococcus pneumoniae* Penicillinase-producing *Neisseria gonorrhoeae*	1942 1967 1976
Vancomycin	1958	Plasmid-mediated vancomycin-resistant *Enterococcus faecium* Vancomycin-resistant *Staphylococcus aureus*	1988 2002
Amphotericin B	1959	Amphotericin B-resistant *Candida auris*	2016
Methicillin	1960	Methicillin-resistant *Staphylococcus aureus*	1960
Extended-spectrum cephalosporins	1980 (Cefotaxime)	Extended-spectrum beta-lactamase- producing *Escherichia coli*	1983
Ceftazidime-avibactam	2015	Ceftazidime-avibactam-resistant KPC-producing *Klebsiella pneumoniae*	2015

Center for Disease Control and Prevention
World Health Organization

Antibiotics to treat bacterial infections

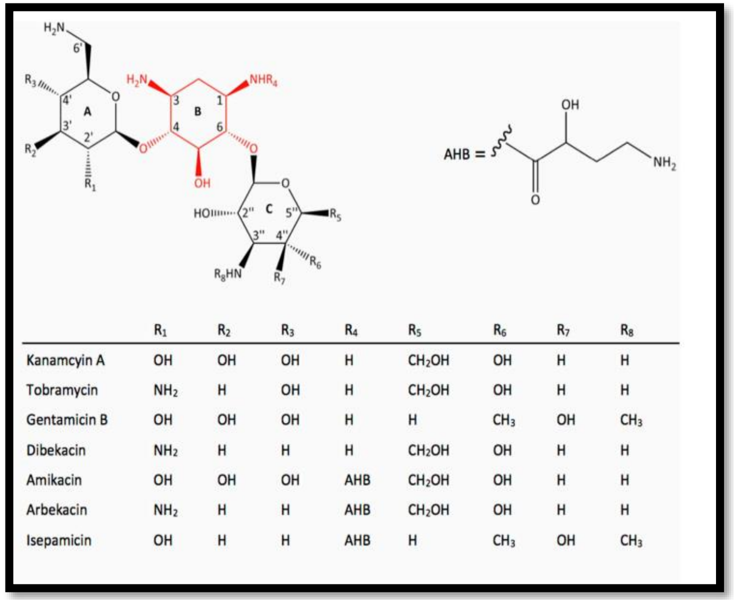
PLoS Comput. Biol. **2016**, *12* (6).
Front. Cell. Infect. Microbiol. 2013, *4*.

β-lactam antibiotics



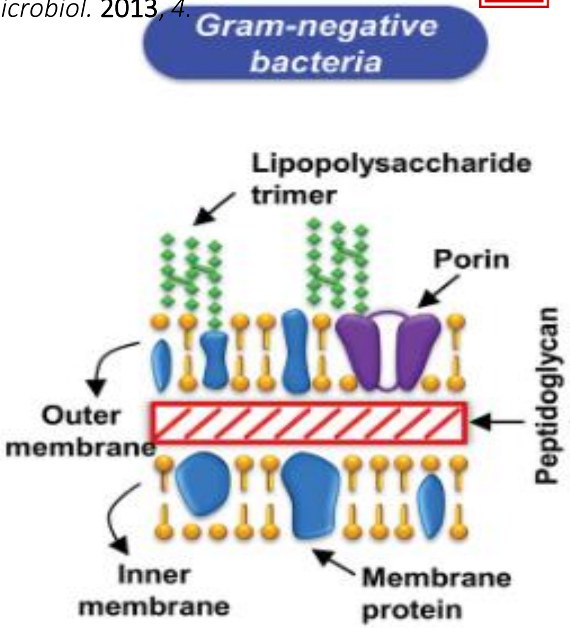
- Penetrate the bacteria cells through porins
- Bind to target proteins in cytoplasmic membrane
- Inhibit the cell wall biosynthesis
- Show bacteriolytic activity

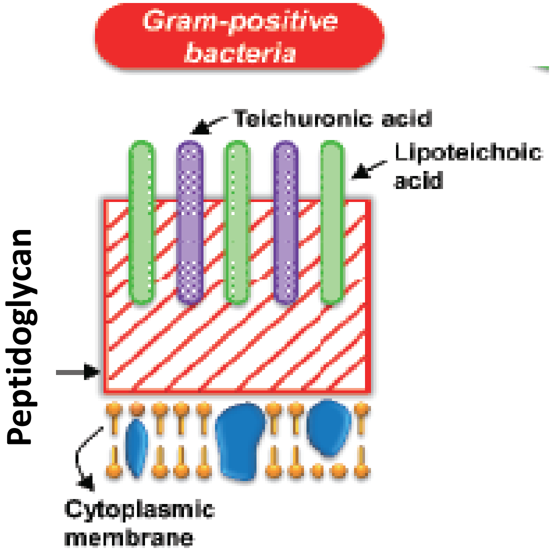
Aminoglycosides



	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
Kanamcyin A	OH	OH	OH	H	CH_2OH	OH	H	H
Tobramycin	NH_2	H	OH	H	CH_2OH	OH	H	H
Gentamicin B	OH	OH	OH	H	H	CH_3	OH	CH_3
Dibekacin	NH_2	H	H	H	CH_2OH	OH	H	H
Amikacin	OH	OH	OH	AHB	CH_2OH	OH	H	H
Arbekacin	NH_2	H	H	AHB	CH_2OH	OH	H	H
Isepamicin	OH	H	H	AHB	H	CH_3	OH	CH_3

- Drug permeate into the cell and bind to ribosome inside the cell
- Damage DNA bases of bacteria (*E. coli*)
- Inhibit protein synthesis
- Cause cell death

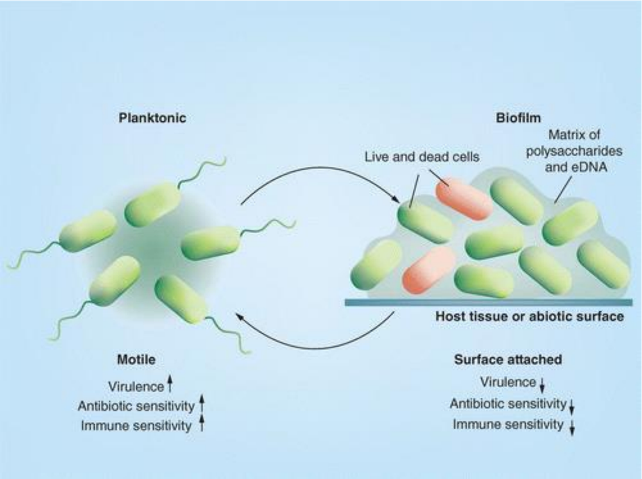


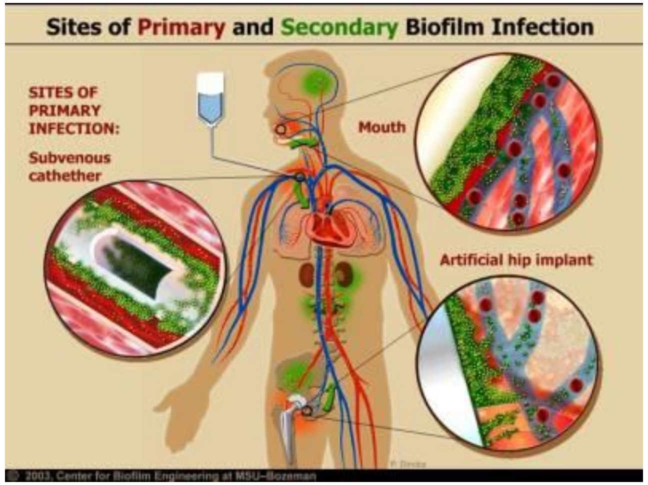


Many Gram-negative and Gram-positive bacterial strains, including the **ESKAPE pathogens** become resistant to drugs **by altering their outer cell envelope.**

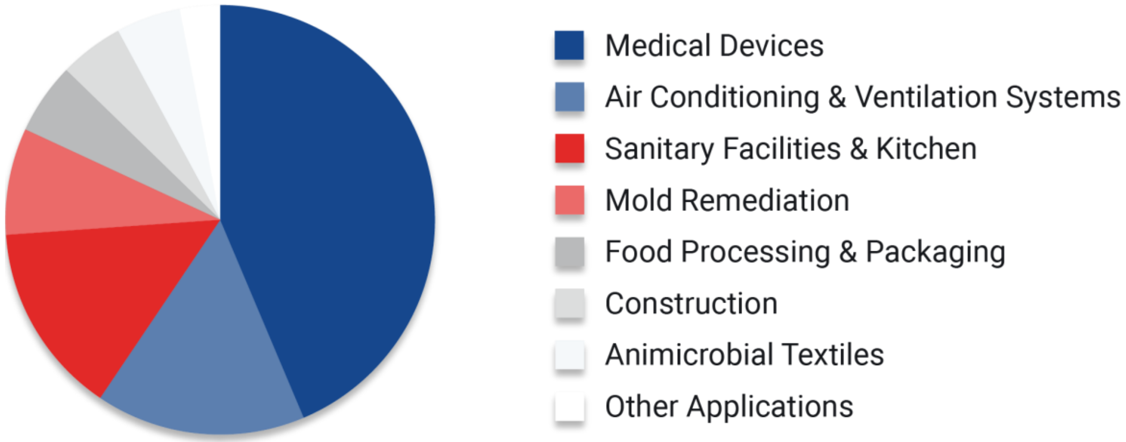
Antimicrobial coatings

Bacterial biofilms, forming over healthcare equipment, are one of the major causes of *hospital-acquired infections*.

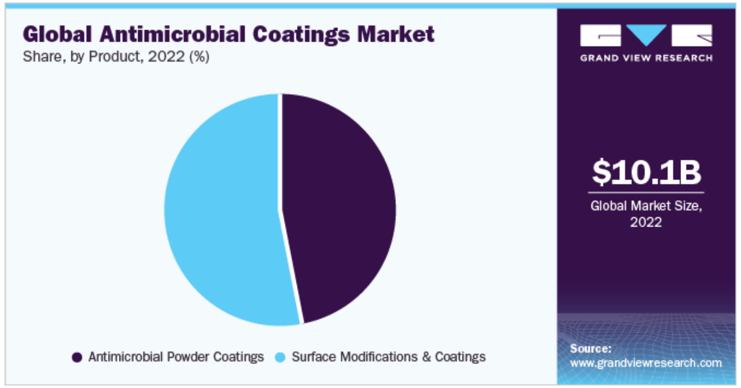




Global Antimicrobial Coatings Market Share, By Application, 2020 (%)



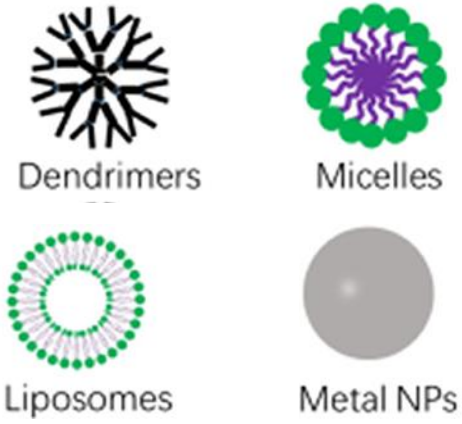
Source: www.grandviewresearch.com



There is a growing need to develop innovative and effective **antimicrobial coatings** for medical equipment, touch surfaces, wound healing materials, food packaging, water supply lines and many more.

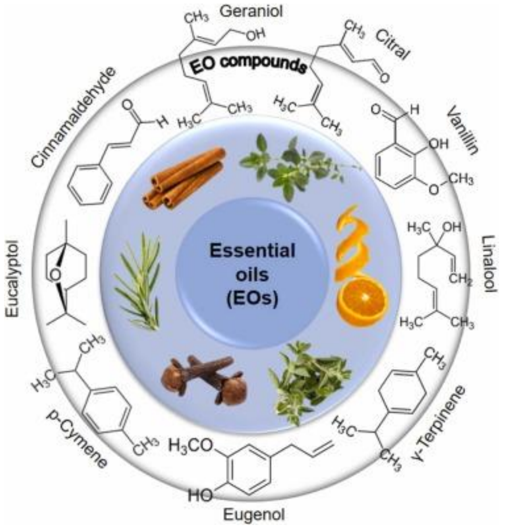
Different classes of antimicrobial materials

Nano-derived antimicrobials



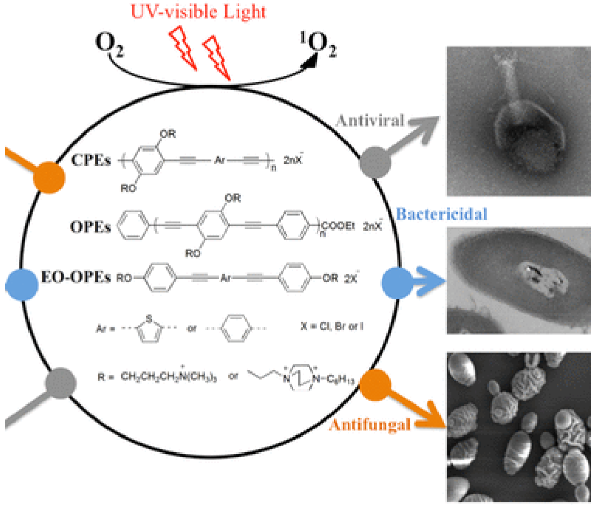
Wang D-Y, et al. Front. Chem. 2019, 7:872.

Natural-based antimicrobials



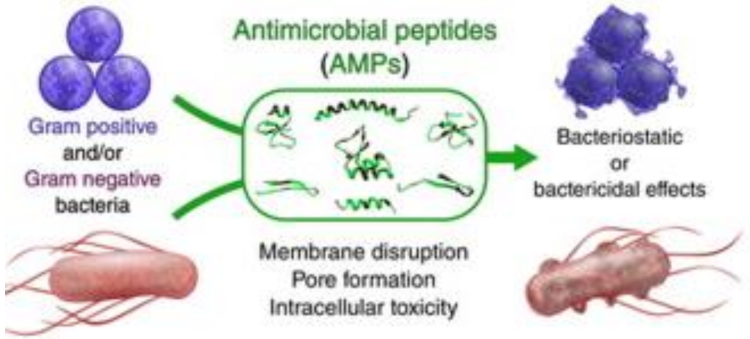
Renata Fialho, R., et al., Food Packag. Shelf Life, 2022 , 31

CPEs/OPEs



Whitten, D. et al. *ACS Appl. Bio Mater*., **2023**

Antimicrobial peptides (AMPs)



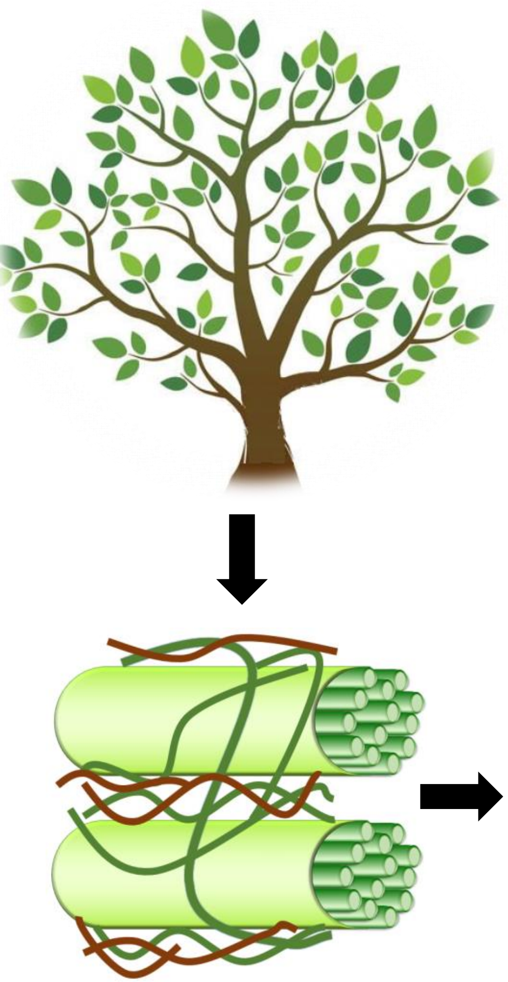
Ageitos J.M., et al. Biochem. Pharmacol., 2017 ,133, 117-138

Cationic functionalities for non-specific binding: bypass specific targeting modes

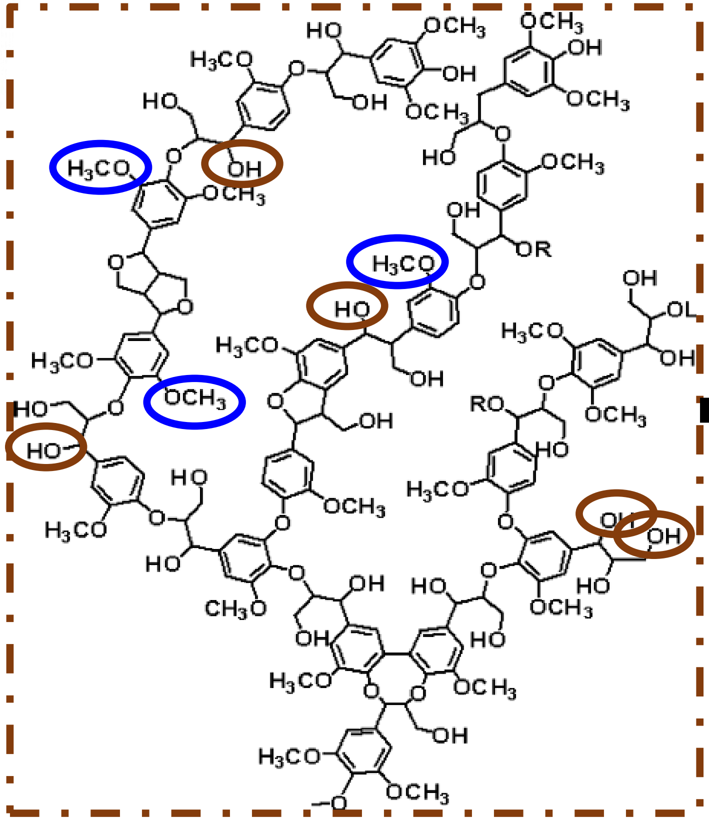
Critical barriers:
High costs, non-abundant sources, complex fabrication, disposability, environmental sustainability

Utilization of natural and renewable feedstocks for the fabrication of green and eco-friendly antimicrobial materials is needed

Lignin: Opportunities for antimicrobial applications



Plant cell wall



Lignin

Plant cell wall polymer Lignin

- 3-dimensional, hyperbranched architecture
- -OH and –OCH$_3$ groups render antimicrobial properties
- Facile functionalization (-OH)-ample scope of cationization **(Green synthesis)**
- Tune the side chain structure
  - **attain high antimicrobial properties**
  - **limit cytotoxicity to mammalian cells**

Green, low-cost, naturally abundant bio-renewable materials

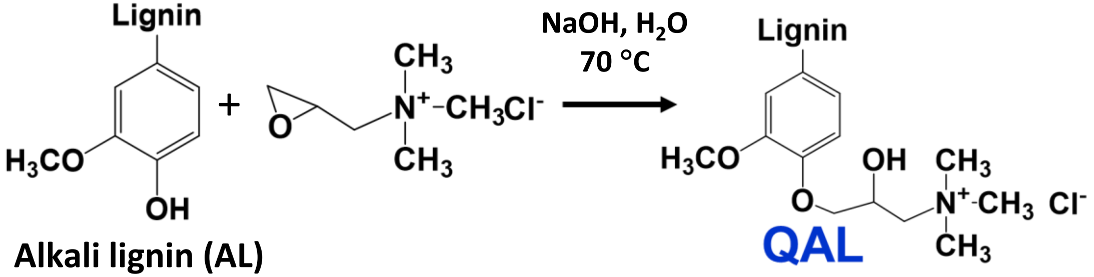
Every year, the U.S. spends ~$55 billion to handle hospital-acquired infections and antibiotic resistance

Lignin-based cheap, effective antimicrobials can be produced & made available in resource-limited, remote places

Significantly aid the remote/war-zone medical facilities and save lives

Cationic lignin as antimicrobial material

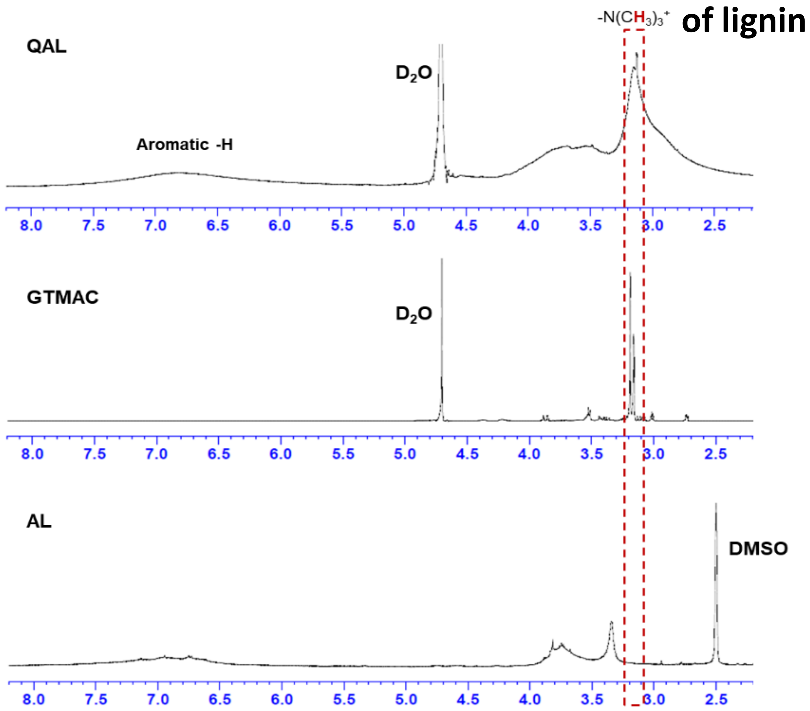
Lignin modification to impart cationic functionalities that can potentially kill antibiotic-resistant bacteria



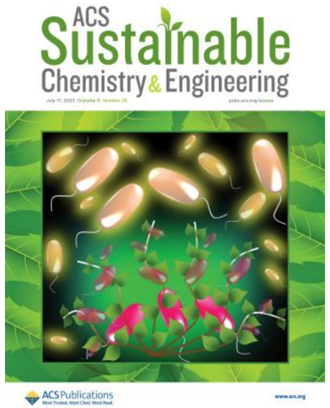
Alkali lignin (AL)
Norway Spruce

QAL

^{1}H NMR

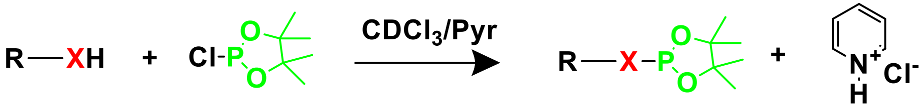


Successful modification of lignin

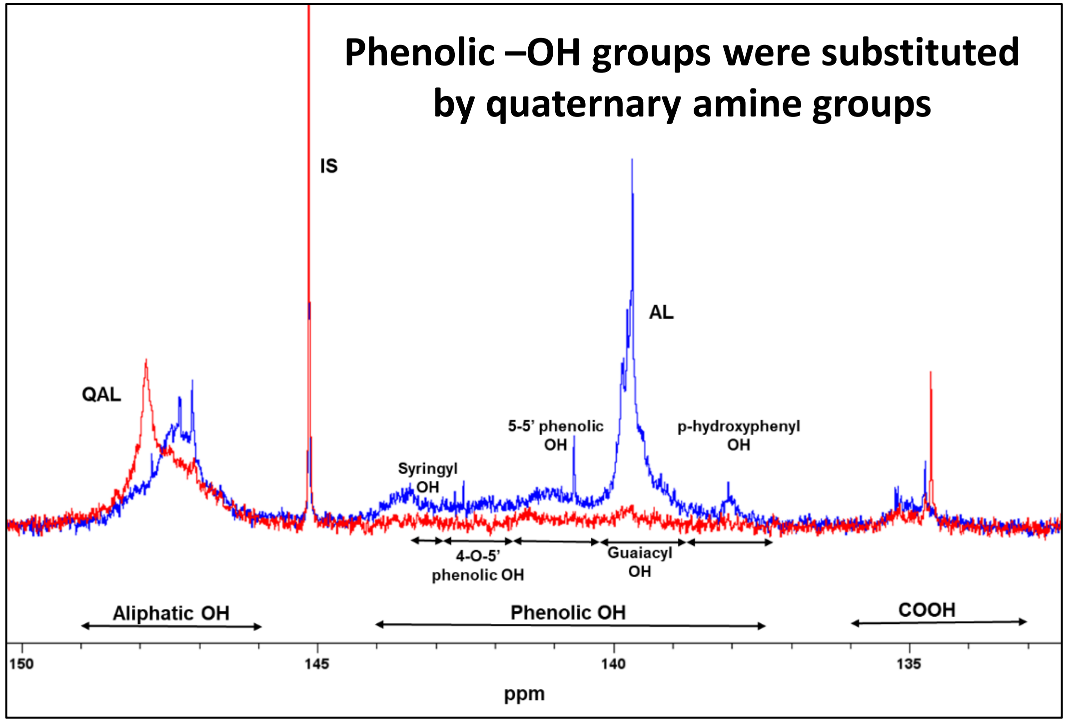


Dishari et al,
ACS Sustainable.Chem. Eng.
2023

^{31}P NMR



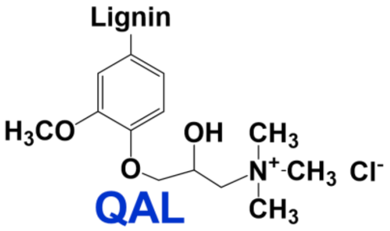
-XH= -OH (aromatic/aliphatic), -COOH

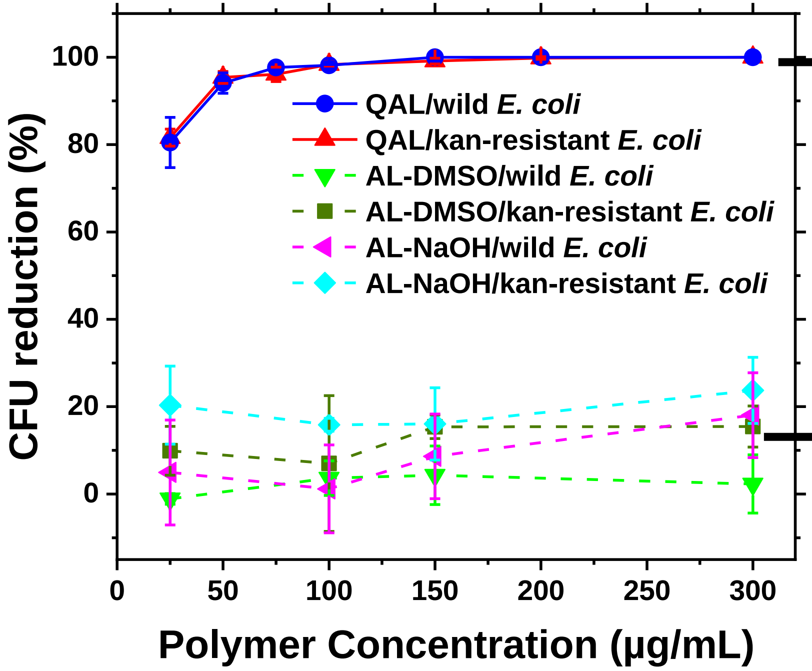


Phenolic –OH groups were substituted by quaternary amine groups

Components	AL mmol/g	QAL mmol/g
Total phenolic -OH	**4.24**	**0.57**
Aliphatic -OH	2.33	2.35
-COOH	0.41	0.26

Lignin cationization improves antimicrobial efficacy





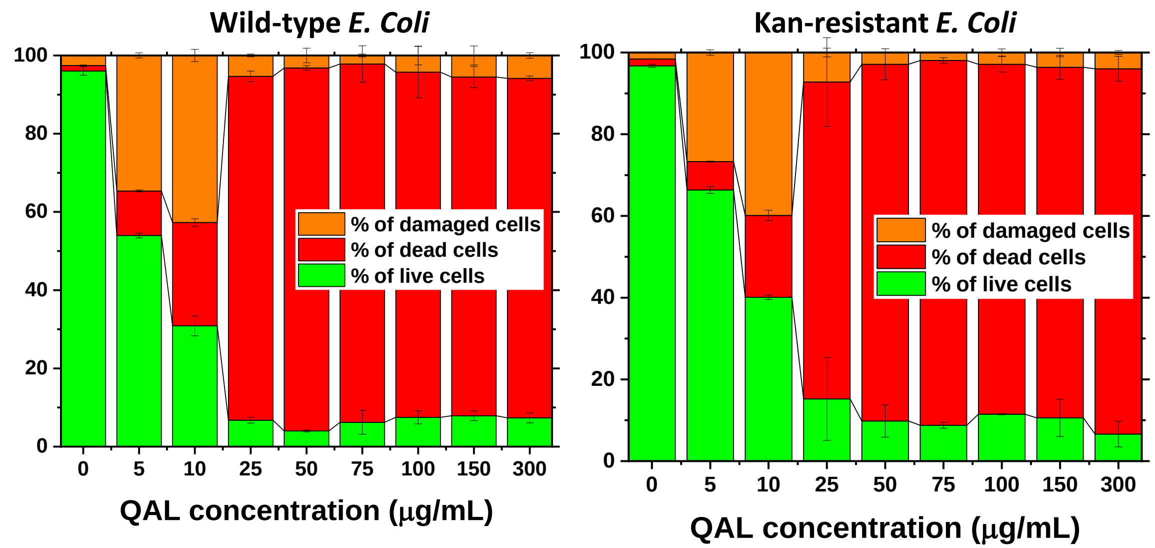
Cationic Lignin (QAL)

Unmodified Lignin

Antimicrobial activity was substantially enhanced by cationization of lignin

Dishari et al, ACS Sus.Chem. Eng. **2023**

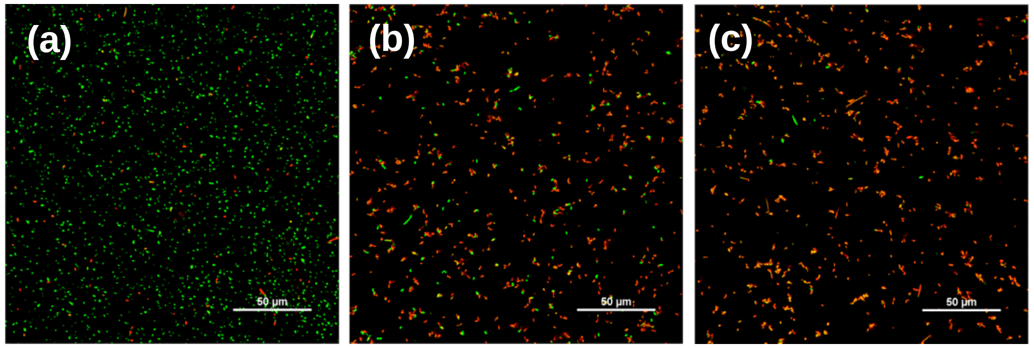
Live/dead assay



1-h treatment with 50 µg/mL of QAL

can kill ~ 90% of wild type and resistant bacteria (damage 4% more cells)

Green: alive
Red: dead

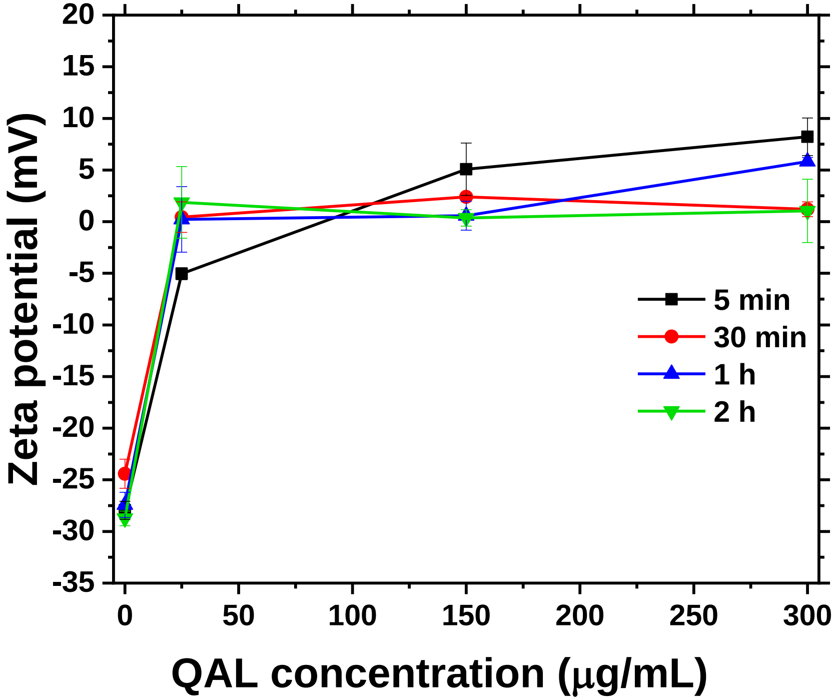


0 µg/mL QAL **25 µg/mL QAL** **150 µg/mL QAL**

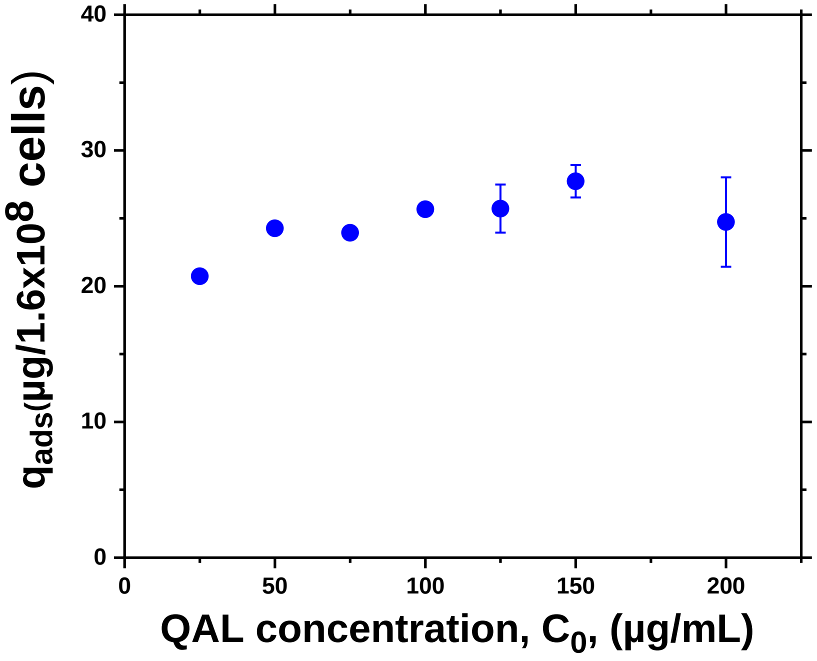
Cell membranes were compromised to different extent upon treatment with QAL

Antimicrobial action mechanism of cationic lignin

Antimicrobial process was majorly driven by
electrostatic adsorption of the incoming QAL onto the surface of bacteria



Bacterial lost its negative charges when treated with QAL



Langmuir monolayer adsorption of QAL onto the surface of bacteria

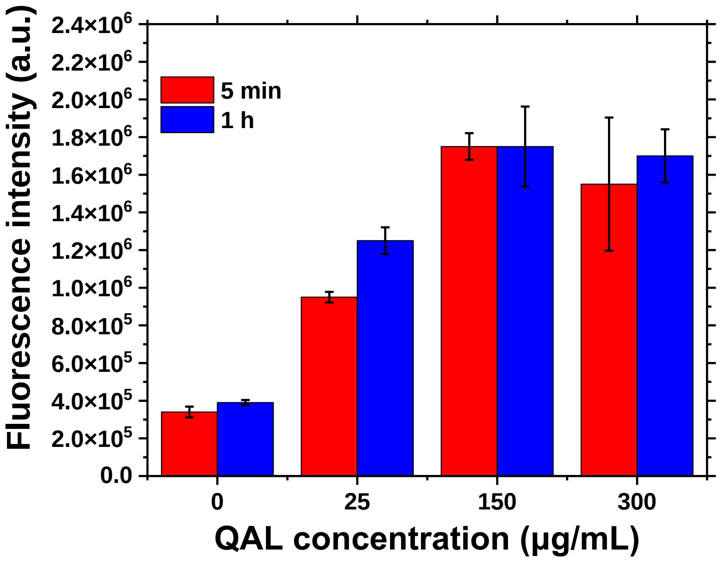
Untreated *E. coli*

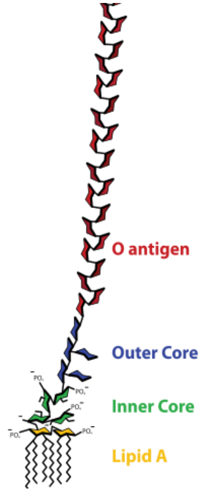
Treated *E. coli*

Neutralization destabilizes bacterial membrane

Dishari et al, ACS Sus.Chem. Eng. **2023**

QAL causes membrane permeabilization

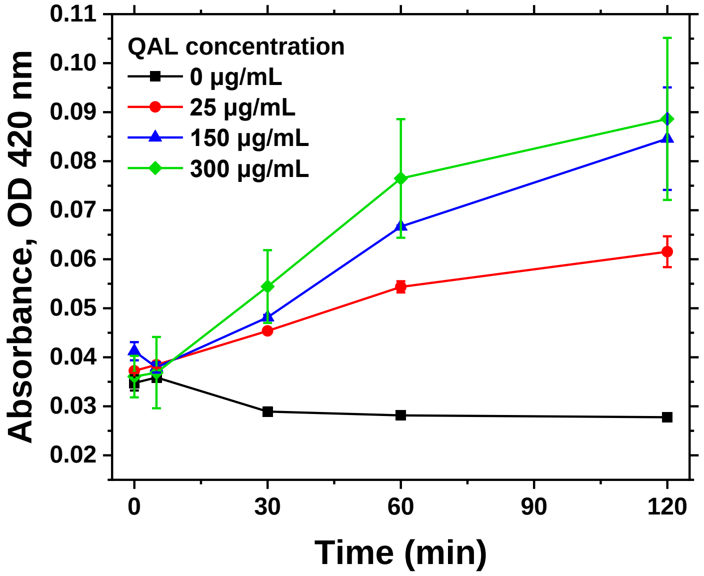




Structure of outer membrane

Nile red staining

- Nile red dye fluoresces in lipid-rich environments
- Fluorescence intensity increases with increasing QAL indicating lipid exposure
- Lipid exposure corresponds to disruption of the outer bacterial membrane



ONPG (ortho-nitrophenyl-β-galactoside) test

- Inner membrane permeability of *E. coli* increased with QAL concentration nd treatment time
- Absorbance corresponds to leakage from cytoplasm

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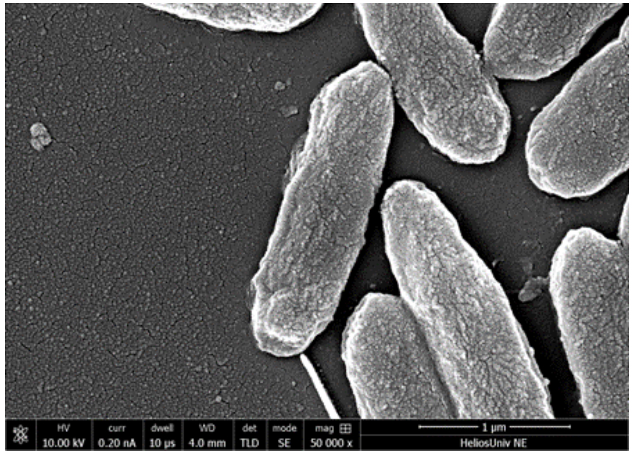
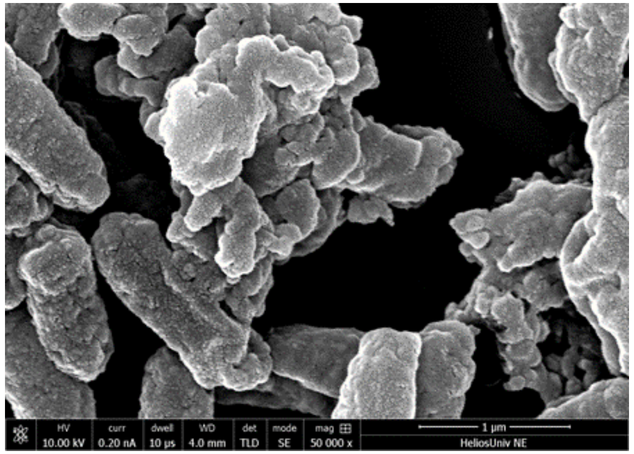
Alterations of bacteria cell-envelope after QAL treatment

Untreated *E. coli*

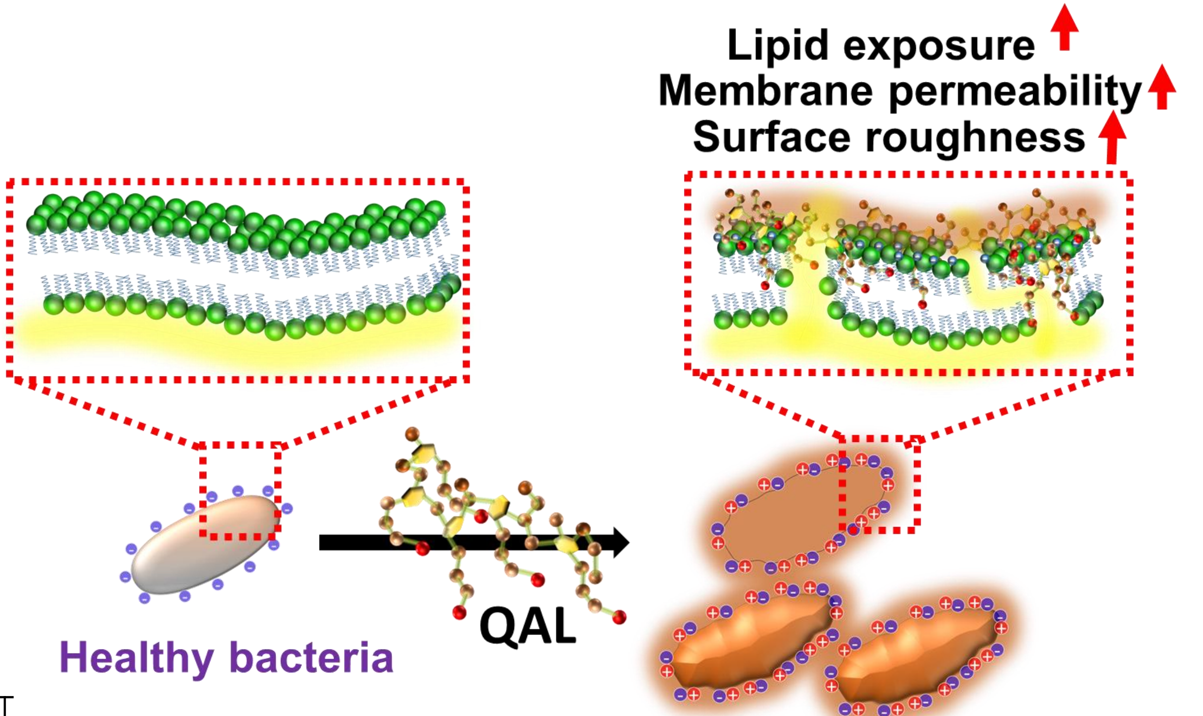


QAL: 0 μg/ml

Treated *E. coli*



QAL: 150 μg/ml



Lipid exposure ↑
Membrane permeability ↑
Surface roughness ↑

Healthy bacteria

Electrostatic adsorption-driven bactericidal effect

Morphological changes (SEM)

Cell wall roughens (AFM)

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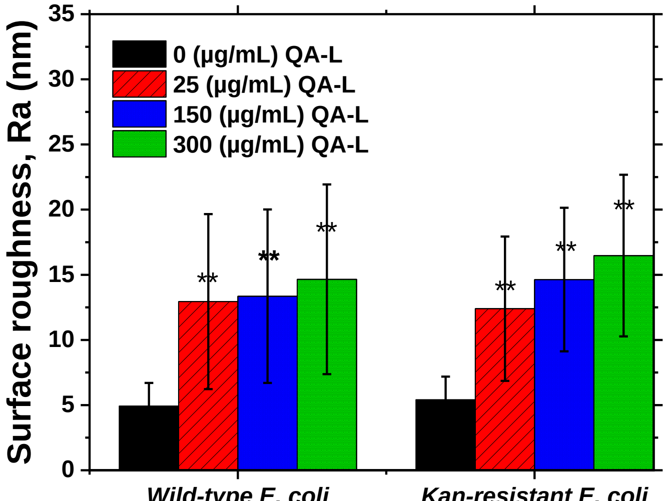
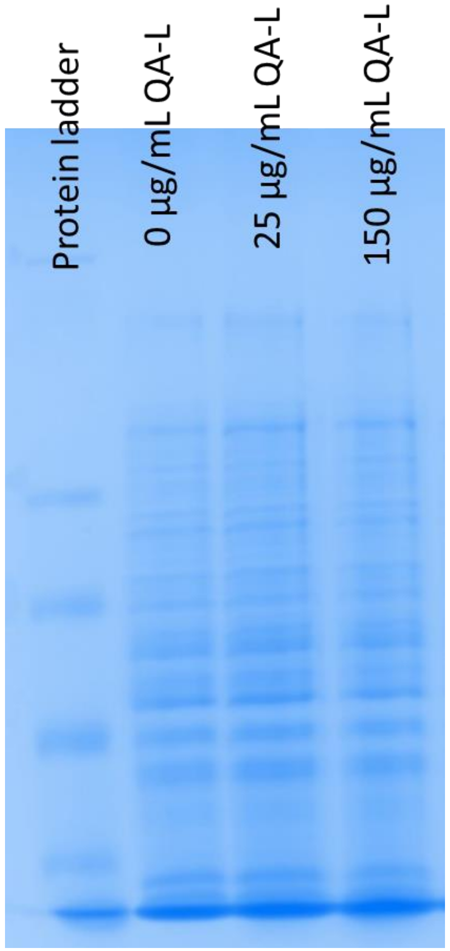


QAL likely destabilizes
the outer and inner membrane of bacteria
due to
electrostatic adsorption-driven bactericidal effect

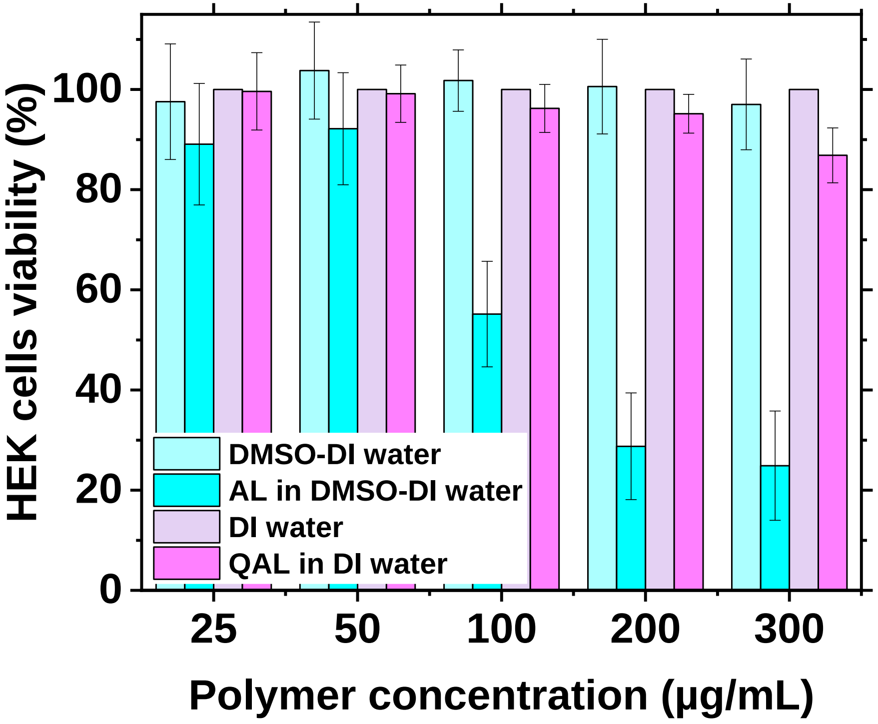
QAL is not cytotoxic to human cells!

SDS-PAGE



E. coli proteins did not degrade upon treatment

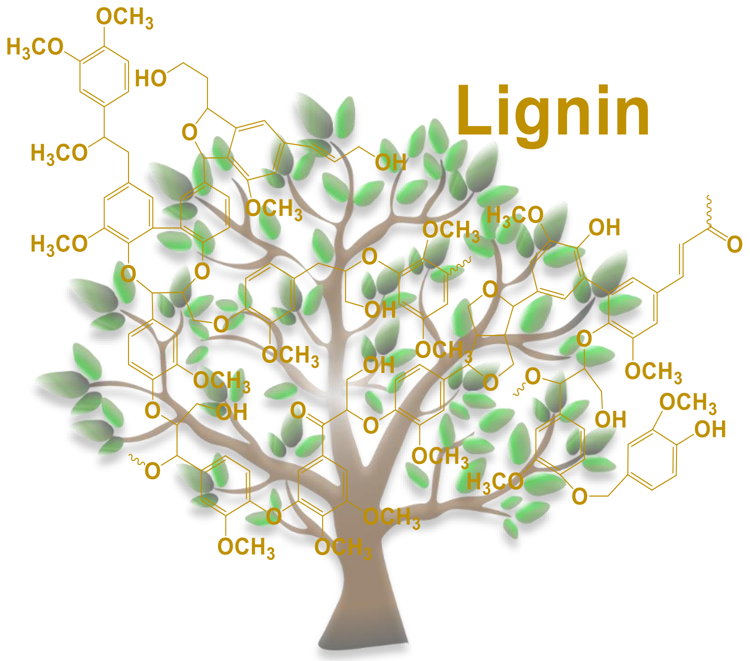
Bacteria did not produce any protein with different MW



Cationic QAL **was not/minimally cytotoxic against HEK293 cells: 90–100% cell viability** up to a concentration range (0–300 µg/mL) in which QAL achieved 100% CFU reduction

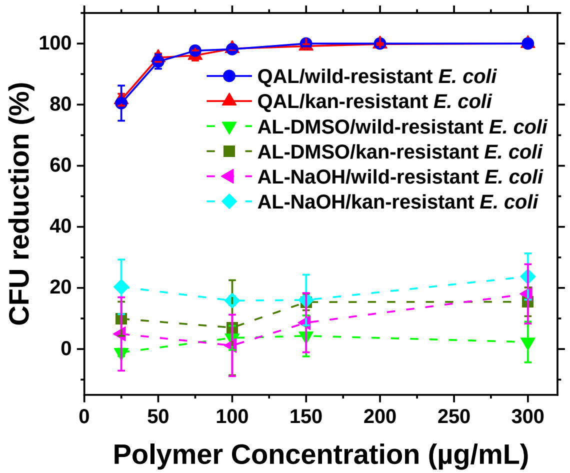
Dishari et al, ACS Sus.Chem. Eng. **2023**

Conclusions: Lignin-based antimicrobials

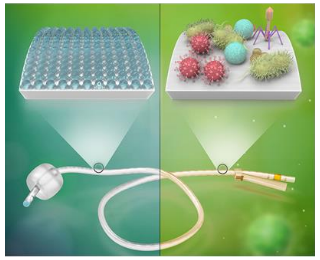


Lignin: Great potential as antimicrobial

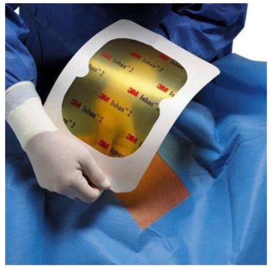
- Low cost
- Abundant raw material that allows scalability of the processes
- Biocompatible: not harmful against human cells
- Modifiable functional groups
- Second most abundant natural material on earth
- Residues easy to dispose of



Applications that our science and materials can impact



Implantable device

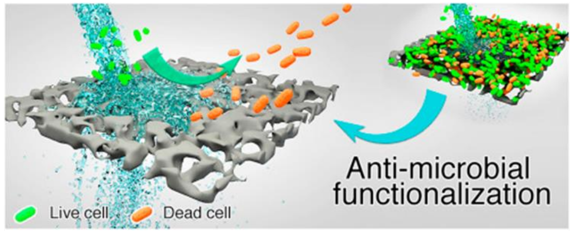


Wound-healing materials
Antimicrobial incise drape

Coating for
food processing equipment

Packaging materials for food safety

Touch surfaces



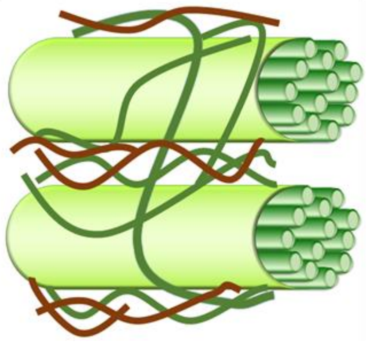
Water treatment

Energy technologies requiring understanding of material-microbe interactions

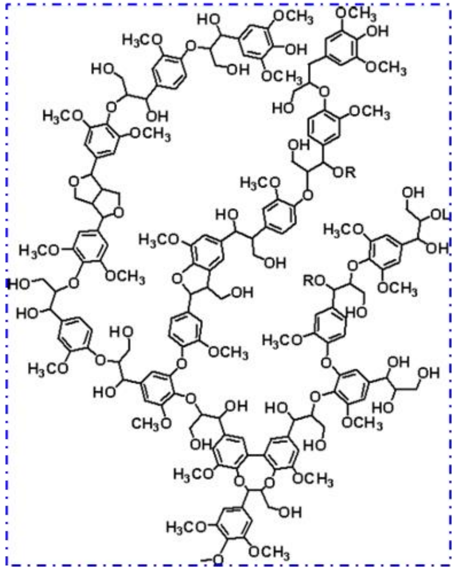
Conclusions

Tree/Plant

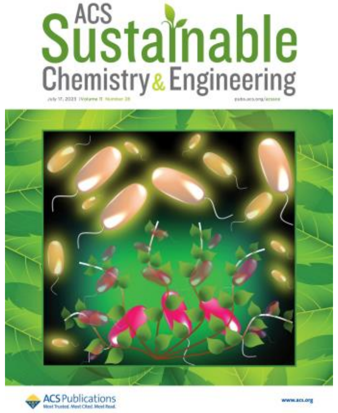
Wood



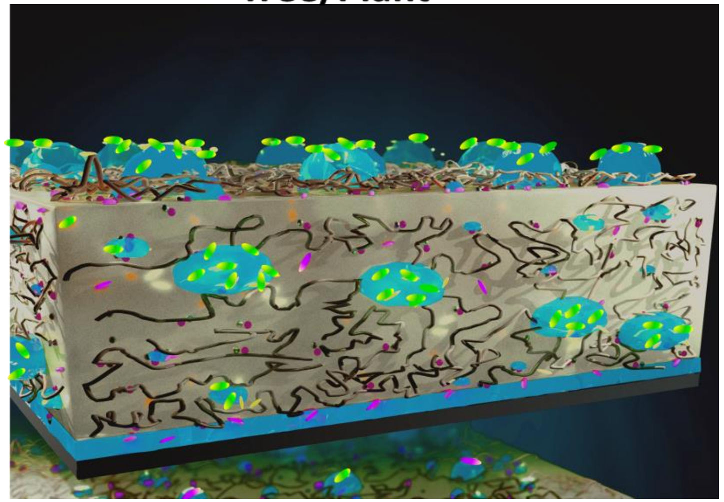
Plant cell wall



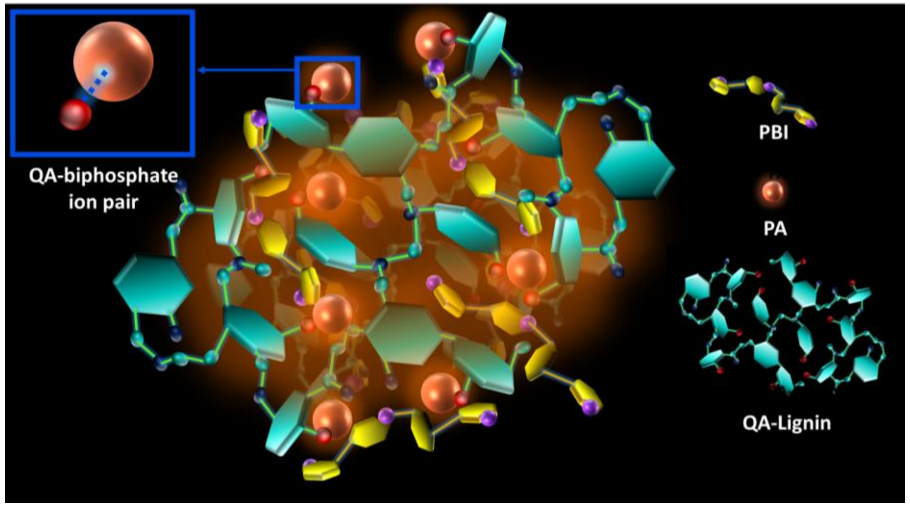
Lignin



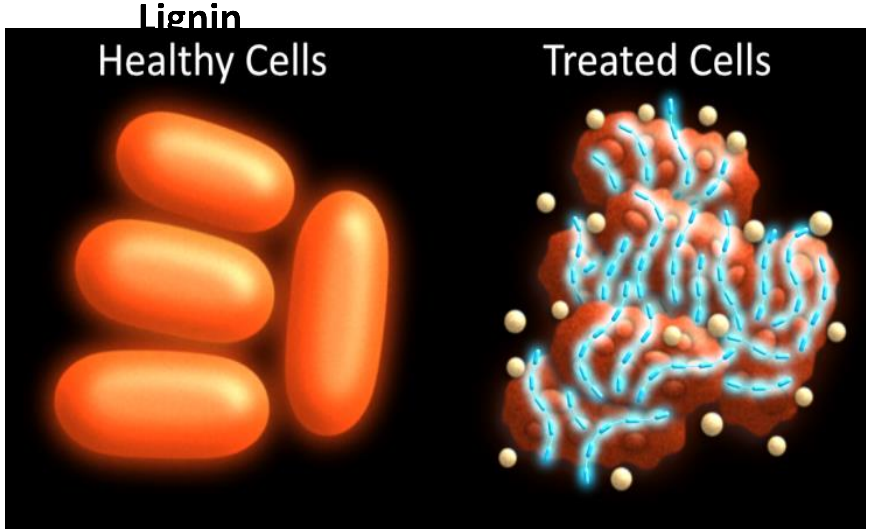
Dishari et al. ACS Sustainable Chem. Eng.(2023)



Improve conductivity at electrode-catalyst interfaces



Durable Materials for electrochemical systems



Fight against antibiotic resistance

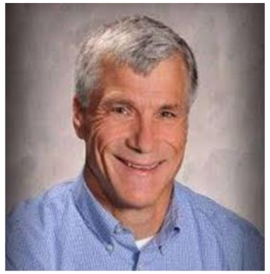
New Pathways towards Biomass Valorization and Sustainable Technologies

Collaborators and Funding Sources

Collaborators


Kevin Yager
Brookhaven
National Lab


Gregory Su
Adv. Light Source
Berkeley Lab


Mike Yandrasits
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Ratul Chowdhury
Iowa State Uni.


Vitaly Alexandrov
UNL


Oleh Khalimonchuk
UNL


Rassel Raihan
UT Arlington


Martha Morton
UNL


Rajib Saha
UNL


Vinai Thomas
UNMC

Funding Sources

NSF CAREER Award: DMR (Polymer)
NSF-CBET (Electrochemical Systems)

DOE Office of Science
Early CAREER Award

3M Non-Tenured Faculty
Award

NASA Nebraska
Space Grant

Nebraska Public Power District
Always there when you need us

Nebraska Center for
Energy Science Research
Grant (NPPD)

IDeA EPSCoR NEBRASKA

Nebraska EPSCoR
First Award

Research Council Faculty Seed Grant
Nebraska Collaboration Initiative Grant
Edgerton Innovation Award
Layman Award
NCMN Core Facility Grant

Graduate Students and Post-doc


Ehsan Zamani (PhD)
R&D Engineer
Intel


Seefat Farzin (PhD)
Formulation Chemist
Syngenta


Tyler Johnson (BS, MS)
Materials Engineer
Medtronic


Oghenetega Obewhere
(PhD, current)
NSBE Award


Rajesh Keloth
(PhD, current)
National Overseas Award


Karen Acurio Cerda
(PhD, current)
Fulbright Scholar


Sourav Sutradhar
(PhD, current)


Moses Dike
(PhD, current)


Shyambo Chatterjee
Post-doc

Female: 14
Underrepresented: 16
First-generation college students: 6

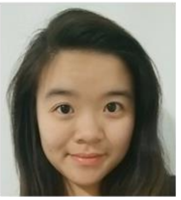
Undergraduate Students

Industries/Govt. Agencies


Serena Tenhumberg
Production Process Engineer
Syngenta


Catherine Nouva
Engineer I
Cargill


Jackson Goddard
Formulation Engineer
Syngenta


Nina Zeng (NNCI-REU)
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Reckitt


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Neb. Dept of Env. & Energy


Ashley Miller
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Isabelle Koehler
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Monolith


Giovanni Cruz-Mojica
Process Engineer
Prairie Catalytic

Grad School


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3D Systems Corp.


Tyler Johnson
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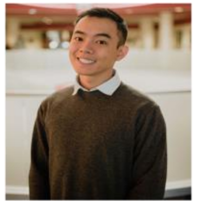
Medtronic


Kai Shen Choong
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PhD (current)
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Alyssa Grube
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PhD (current)
UNL-CHME


Fernando Pesantez
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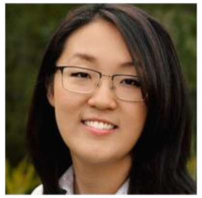
PhD (current)
U. Albany (SUNY)


Maria Carter
UNL-BSE
PhD (current)
U. Colorado Boulder

On progress


Juliana Rodriguez
McNair Grad
UNL-BSE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Mathew Koenig
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UNL-CHME

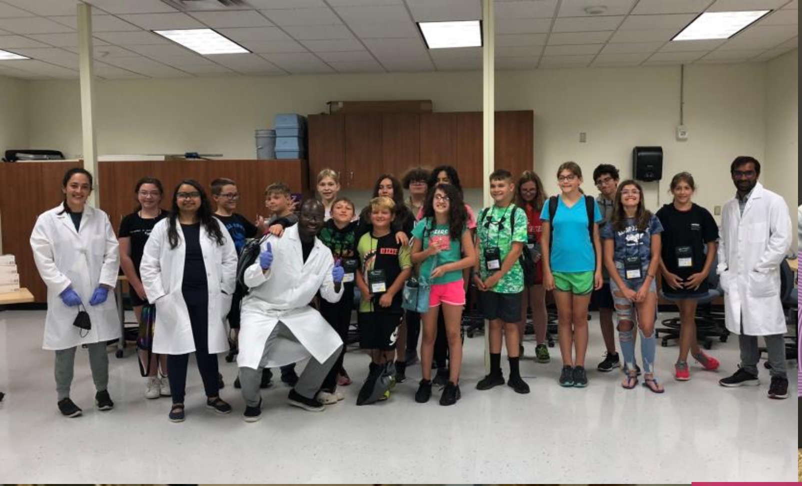

Will Johnson
BS
UNL-CHME


Nate Wagner
BS
UNL-CHME


Tyler Ishman
(NNCI-REU)
Lockhaven Uni.

Diversity Matters!

Student Impact Matters!

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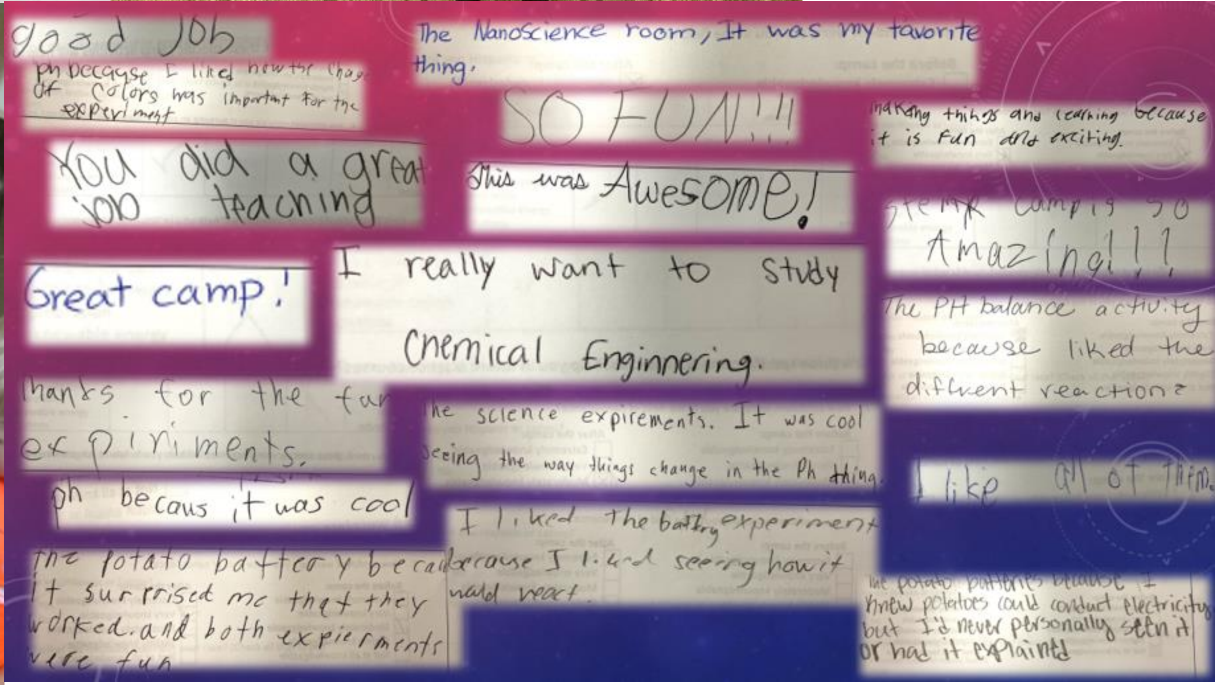


good Job

ph because I liked how the chag of colors was important for the experiment

The Nanoscience room, It was my favorite thing.

SO FUN!!!

making things and learning because it is Fun and exciting.

You did a great job teaching

This was Awesome!

stem camp is so Amazing!!!

Great camp!

I really want to study Chemical Enginnering.

The PH balance activity because liked the diffrent reactions

thanks for the fun expiriments.

The science expirements. It was cool seeing the way things change in the Ph thing.

I like all of them.

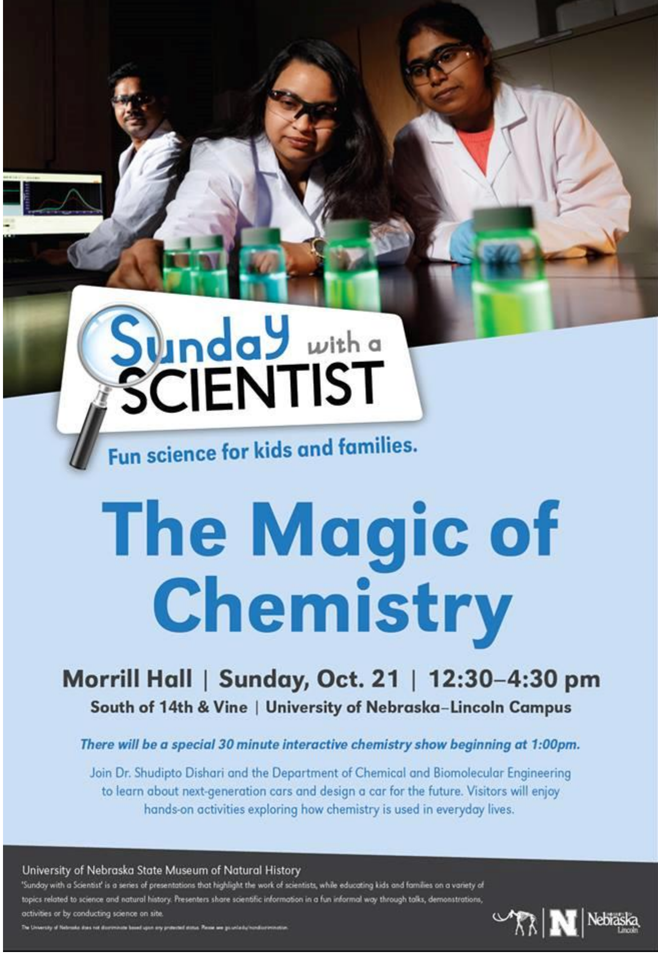
ph becaus it was cool

I liked the battry experiment because I liked seeing how it would react.

the potato battery because it surprised me that they worked. and both expierments were fun

the potato batteries because I knew potatoes could conduct electricity but I'd never personally seen it or had it explaind

Thank you!



Sunday with a SCIENTIST

Fun science for kids and families.

The Magic of Chemistry

Morrill Hall | Sunday, Oct. 21 | 12:30–4:30 pm

South of 14th & Vine | University of Nebraska–Lincoln Campus

There will be a special 30 minute interactive chemistry show beginning at 1:00pm.

Join Dr. Shudipto Dishari and the Department of Chemical and Biomolecular Engineering to learn about next-generation cars and design a car for the future. Visitors will enjoy hands-on activities exploring how chemistry is used in everyday lives.

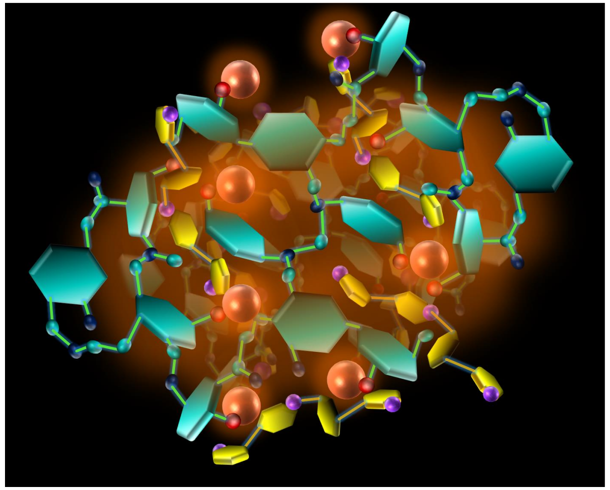
University of Nebraska State Museum of Natural History

'Sunday with a Scientist' is a series of presentations that highlight the work of scientists, while educating kids and families on a variety of topics related to science and natural history. Presenters share scientific information in a fun informal way through talks, demonstrations, activities or by conducting science on site.

The University of Nebraska does not discriminate based upon any protected status. Please see go.unl.edu/nondiscrimination.

Conclusions

- We innovated a novel range of ***ionomer using lignin*** to address and overcome the ion transport limitations of sub-micron thick films.
- With ***3-dimensional , branched architecture***, lignin-based ionomers conduct ion efficiently due to larger ionic domains with high water mobility.
- The work demonstrates the potential of lignin-based ionomers and may lead to new ways of lignin valorization which can potentially aid in bio- and energy economy simultaneously.
- Both classes of ionomers are **PFAS-free**.
- These ionomers can inform and guide the future design of ionomer-catalyst interfaces, highly proton-conductive catalyst binders and permselective bulk membranes as potential substitute of Nafion for fuel cells, electrolyzers, batteries, and more.



Lignin-derived ionomers