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Study of nanocellulose crosslinking with organic acids for improved proton conductivity in bio-based proton exchange membranes

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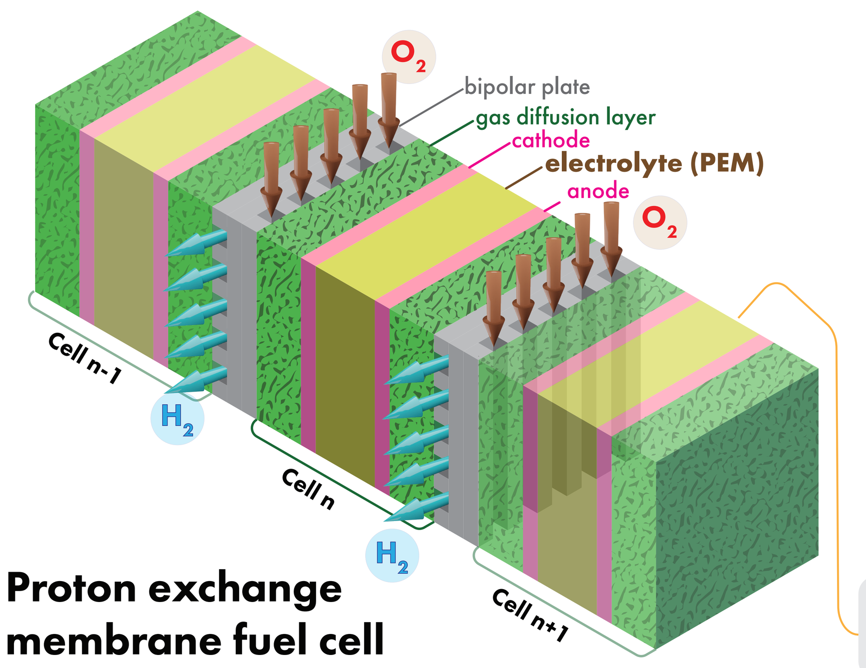
HYDROGEN FUEL CELL

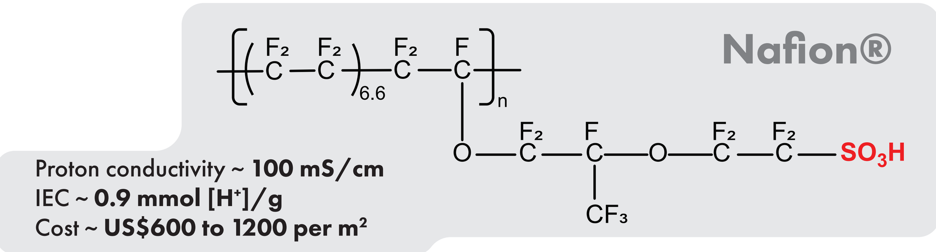
Fuel cell – core technological element of the sustainable **"Hydrogen society"**



Proton exchange membrane fuel cell (PEMFC)

Barriers for wide deployment of fuel cells:
> Cost of hydrogen
> Lack of infrastructure (e.g. fuelling stations)
> Cost of fuel cells (Pt in electrocatalyst, bipolar plates and proton exchange membrane)

Benchmark materials for PEM – perfluorinated sulfonic acid ionomers: Nafion®, Aquivion®, 3M®



Disadvantages: high-cost, non-recyclable

Purpose of this work:
Development of low-cost and efficient PEM based on nanocellulose

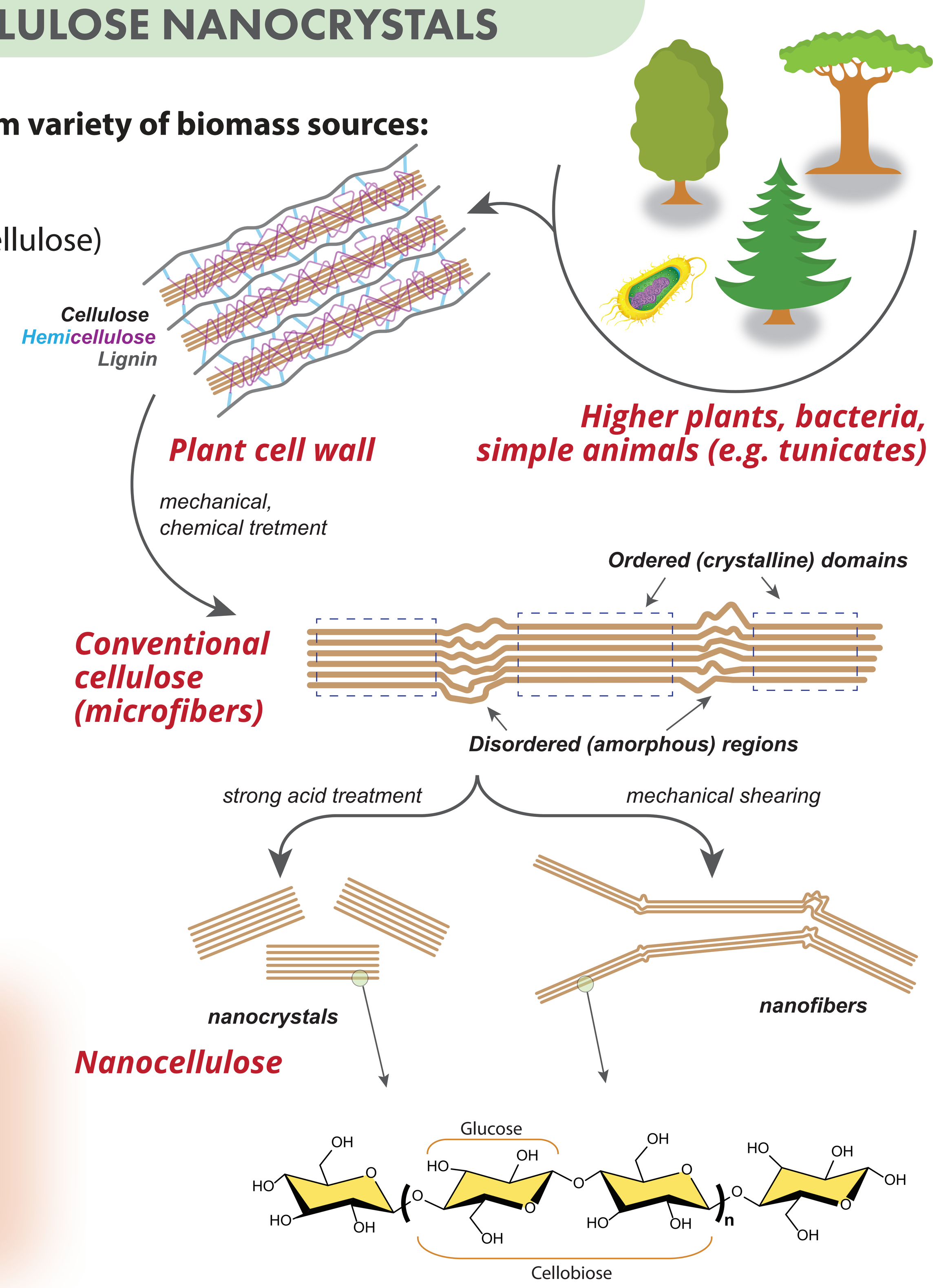
RESEARCH MATERIAL: CELLULOSE NANOCRYSTALS

Nanocellulose can be obtained from variety of biomass sources:
– acid hydrolysis (nanocrystals)
– mechanical shearing (nanofibers)
– microorganisms (bacterial nanocellulose)

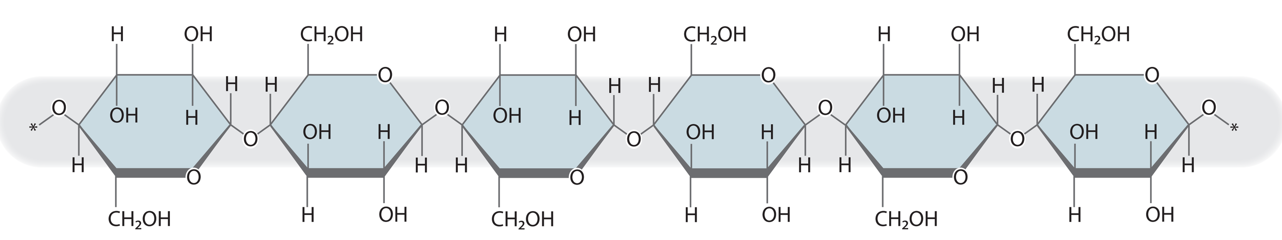
Characteristic properties:
– high mechanical strength
– low density and high surface area
– non toxicity and biodegradability
– flexibility

Membranes features:
– uniform thickness in casted membranes (aqueous solution)
– natural drying (no extra energy)
– suitable for mass production
– flat and stable after hot-pressing

"Eco-friendly, low-cost material platform for advanced materials development"

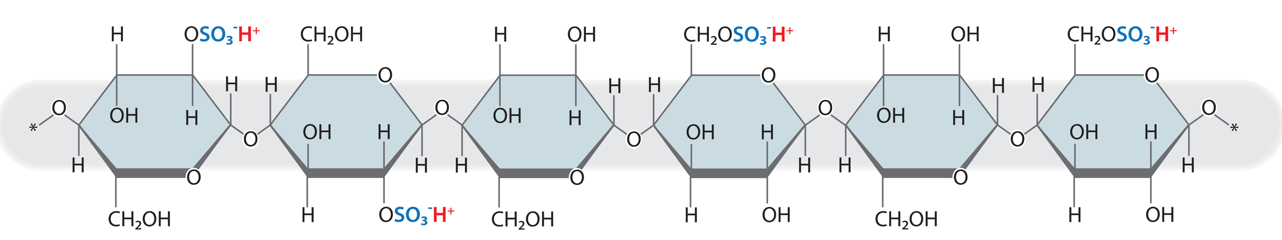


HYPOTHESIS OF THE STUDY



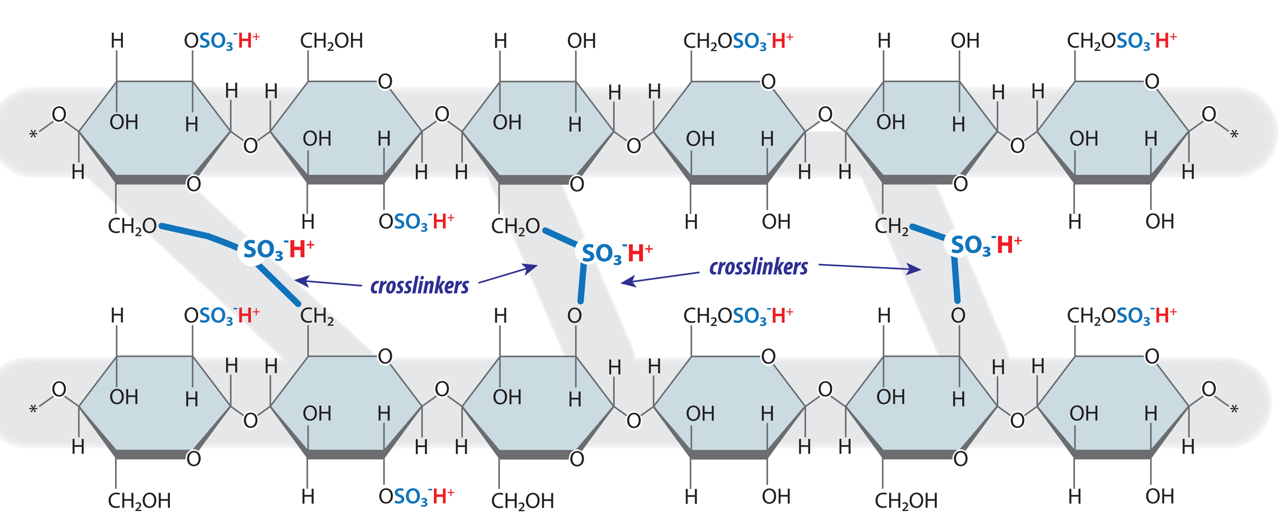
(a) Pristine cellulose without modification

Superior mechanical stability
Ultra-low proton conductivity
Deteoriation in humid environment



(b) Partially sulfonated cellulose

Low mechanical stability
Improved proton conductivity
Solubility in water

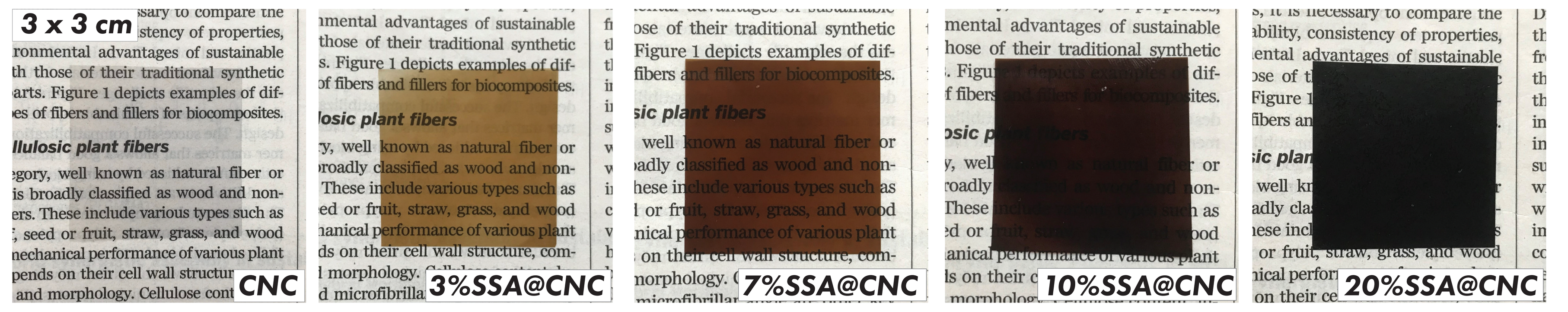


(c) Sulfonated cellulose crosslinked with organic sulfonic acid

Good mechanical stability
Stability in boiling water
Improved chemical stability
Controlled ion-exchange capacity
Appropriate proton conductivity

The study aims to clarify what is more important for the proton conduction: **"backbone sulfonation"** or **"sulfonation via added crosslinker"**. Therefore investagation of these factors on proton conductivity and mechanical properties is planned. Materials will be designed with a various content of two types of sulfonation.

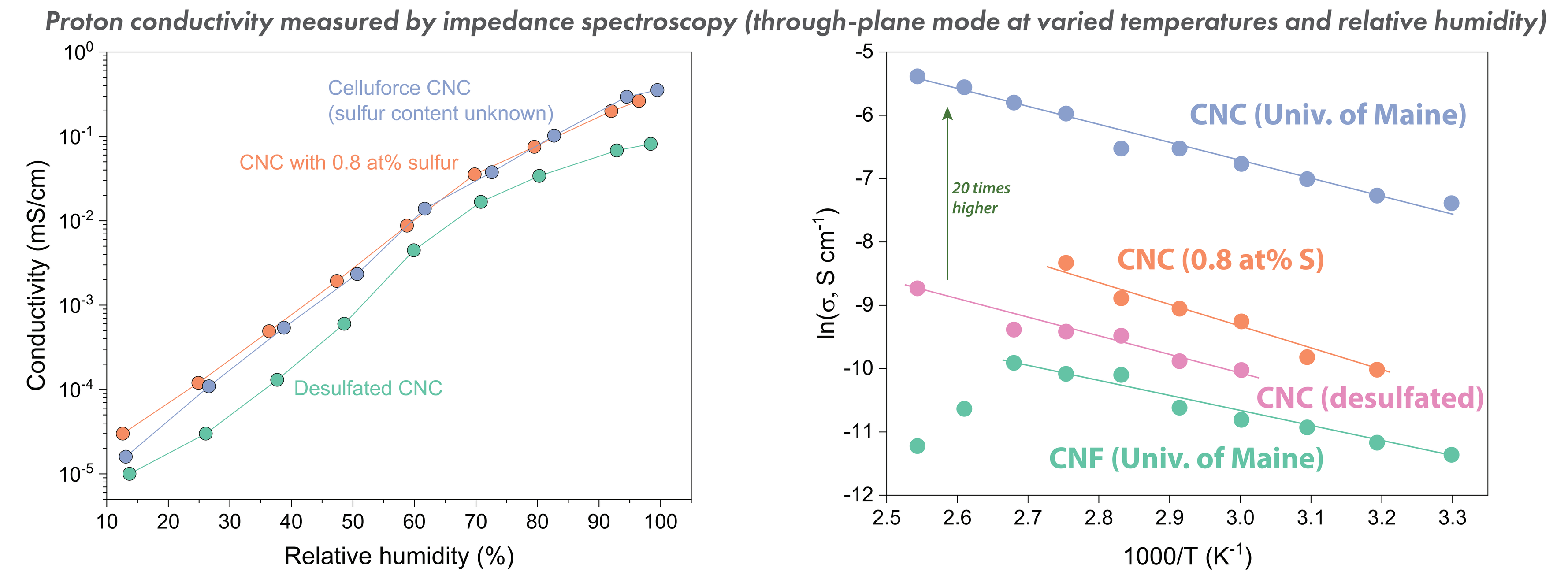
MACROSCOPIC MORPHOLOGY



Cellulose nanocrystal-based membranes: influence of crosslinking amount: the mebranes visually change but chemically similar to CNC (XPS, FTIR) and crosslinker can be chemicaly accomodated.

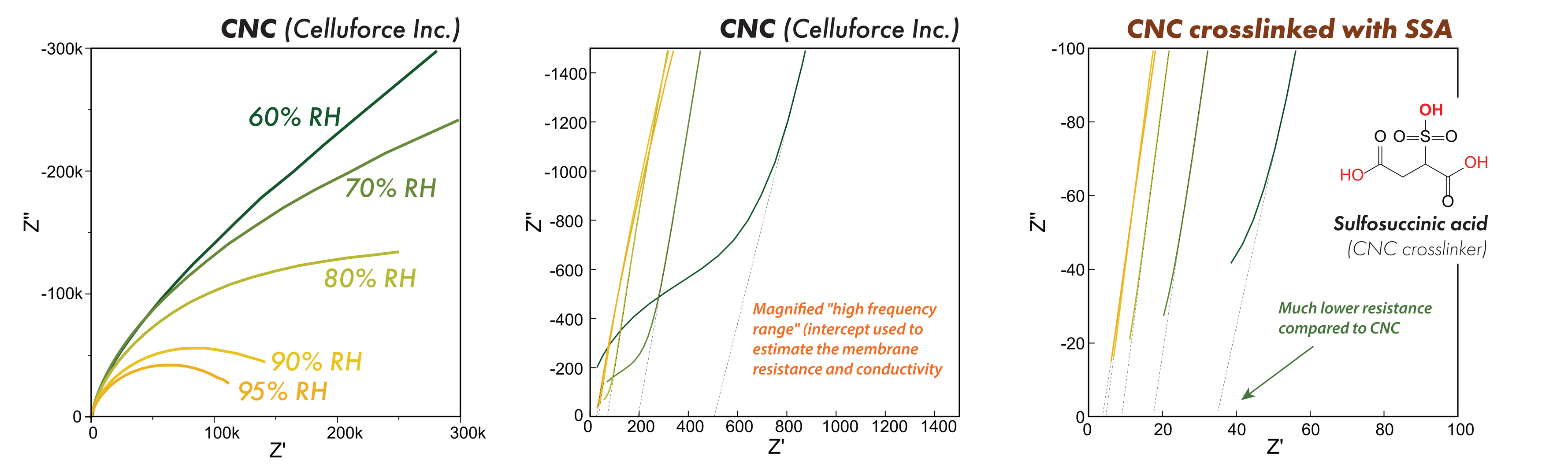
PROTON CONDUCTIVITY IN CNC WITH BACKBONE SULFONATION

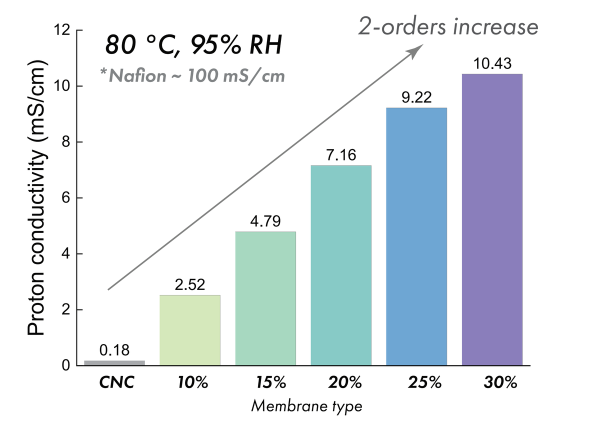
Proton conductivity measured by impedance spectroscopy (through-plane mode at varied temperatures and relative humidity)

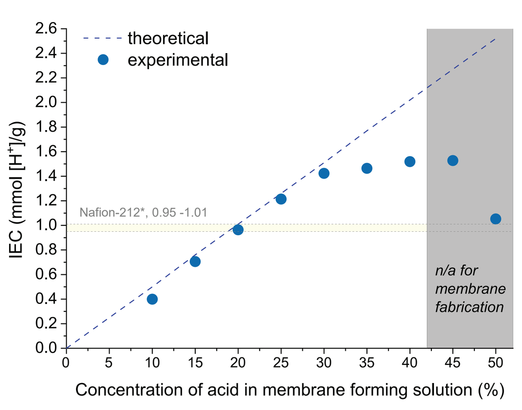


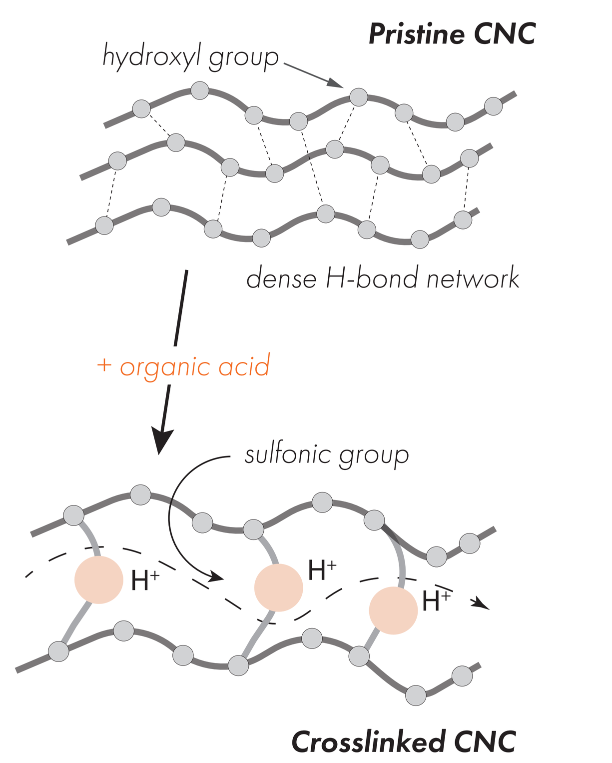
– The technological process for CNC fabrication (acid hydrolysis) results in a different values of sulfonation
– Understanding/utilization of backbone sulfonation can have significant impact on final conductivity
– ***The differences of the proton conductivity can be higher than 20 times (desulfated vs. CNC Univ. of Maine)***

PROTON CONDUCTIVITY IN CROSSLINKED CNC









– CNC is a promising biopolymer platform for developing novel PEM via the sulfonic acid crosslinking pathway
– The structural integrity of the sulfosuccininc acid crosslinked CNC membranes with up to 35% of the acid in membrane forming mixture
– Chemical structure confirmed via XPS and FTIR, IEC measurements shows that acid is bound via esterification route, stable even at higher temperatures (>100 C)
– ***More than 100 times increase in conductivity of crosslinked membranes compared to source CNC (Celluforce, Inc. Canada)***

CONCLUSIONS

Results of this work compared to literature shows that utilization of acid crosslinking of crystalline nanocellulose allows substantial increase in the proton conductivity (2 orders of magnitude) while backbone sulfonation has a smaller impact.

– Considering high gas barrier of nanocellulose membranes PEMs with competitive properies (specific resistance and mechanical stability) can be fabricated

– CNC membranes present an environmentally friendly and substantially lower cost option compared to industrial benchmarks (e.g. Nafion).

– Essentially , these "paper" based PEMs can find their niche application in portable low cost applications (e.g. unmanned aerial or underwater vehicles)

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THE LYTH LAB

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