# Ion Conducting Polymers (Ionomers) from Waste Lignin for Electrochemical Devices

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### Background

- Maximize the use of renewable energy resources
- Minimize carbon footprint through reduction of green house gases •
- Increase energy productivity



#### **Reactions:**

Facts

- Anode:  $H_2(g) \rightarrow 2H^+ + 2e^-$ Cathode:  $\frac{1}{2}O_2(g) + 2H^+ + 2e^- \rightarrow H_2O(l)$ 1. High ion transport resistance at polymer/catalyst
- interface
- 2. Expensive
- 3. Not environment friendly

We need alternate ionomer formulations for energy conversion and storage devices which are cheap, efficient and environment-friendly.

### ~276.6 million automobiles are in the U.S. Emitting around >1273 Gt CO<sub>2</sub>/yr

### **Objectives**



- New ways to utilize locally abundant plant resources/ feedstock
- Innovative ranges of value-added materials from waste of • biorefineries
- Potential alternate, cheap, efficient, environment friendly ionomers for energy conversion and storage devices
- Aid in both **bioeconomy and energy economy**

### **Ionomers From Kraft Lignin for Renewable Energy Applications**

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Featured in a special collection "Women in Science: Chemistry" under "Green Chemistry" section

### Lignin sulfonate lonomer



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

1798

Am) score 7

TOTAL V

### Sulfonation of Kraft Lignin and its Properties in Thin Films

#### **Step-by-step procedure of sulfonation:**



#### Gives water insoluble ionomer (LS x) Important!



#### Conductivity vs. film thickness @ 90%RH

#### Hydration number of Nafion, LS 1.6, LS 3.1



#### High water uptake does not necessarily lead to high proton conductivity

#### **Proton conductivity trend:**

### LS 1.6 > LS 3.1 $\geq$ Nafion, even in ~20 nm thick films

## Lignin sulfonate films are less dense, do not stiffen and larger ionic domains -make proton conduction facile

#### **Film density**

		Film Density (g/cc)	
Polymer	IEC	~250 nm	~25 nm
Nafion	0.91	1.89	1.71
S-Radel	2.5	1.45	-
LS1.6	1.6	1.29	1.07
LS3.1	3.1	1.06	0.92

#### Water-polymer mobility



Low density of LS agrees with its **3-dimensional branched architecture** which leaves free volumes within macromolecular ionomer structure.

*Lignin sulfonate* films *do not* antiplasticize/stiffen upon hydration Water molecules have higher mobility

By fitting the RSAXS profiles in core-shell (spherical and oblate spheroid (ellipsoid) models in a software,

*Nafion films antiplasticize* significantly

Size of ionic domain: LS 1.6 > LS 3.1 > Nafion Ion conductivity: *LS* 1.6 > *LS* 3.1 > *Nafion* 



### Ion Conductivity of Lignin Sulfonate (LS) from Alkaline Pretreated Lignin (Corn Stover) and Organosolv Lignin (Eastern Red Cedar)







Lignin sulfonate (LS) from organosolv lignin (eastern red cedar) shows conductivity higher than Nafion at similar IEC (~0.91-0.98)

Eastern Red Cedar

#### Ion conductivity of lignin sulfonate (LS) from corn stover is higher than Nafion

## Conclusions

- We innovated a novel range of ionomer using Kraft lignin to address and overcome the ion transport limitations of sub-micron thick films.
- Unlike commercial lignosulfonate, our lignin-based ionomers are not water soluble which makes them suited for practical application where water-mediated ion conduction is needed.
- Ionomers from Kraft lignin provided about an order of magnitude higher ion conductivity over current stateof-the-art ionomer Nafion 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.
- Ionomers designed using lignin from corn stover and eastern red cedar also showed superior performance over Nafion.
- The work demonstrates the potential of lignin-based ionomers, especially as catalyst binder, and may lead to new ways of lignin valorization which can potentially aid in bio- and energy economy simultaneously.

## **Future Work Plan**

- Synthesize lignin sulfonate ionomer (LS) using extracted lignin from corn stover and eastern red cedar -alkaline pretreated, bionic liquid-extracted, organosolv –vary MW, PDI and IEC in each case systematically
- Explore –OH and –SO<sub>3</sub>H content (NMR), % of individual monolignols (MS), Degree of crystallinity • (GIWAXS)
- Explore how pretreatment process, MW, PDI, IEC of LS alter nanostructure of LS ionomer in thin films.  $\bullet$
- Maximize ion conductivity by controlling nanostructure, ionic domain characteristics, wetting behavior, ion ٠ mobility and film density.
- Explore *bulk membrane* ( $\leq$  50 µm thick) vs. thin film (< 1 µm thick) behavior- demonstrate the *potential of* LS as separator and catalyst binder.

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