Georgia Tech Institute of Paper Science and Technology

Low temperature and high efficiency biomass fuel cell and bio-hydrogen production

Dr. Yulin Deng

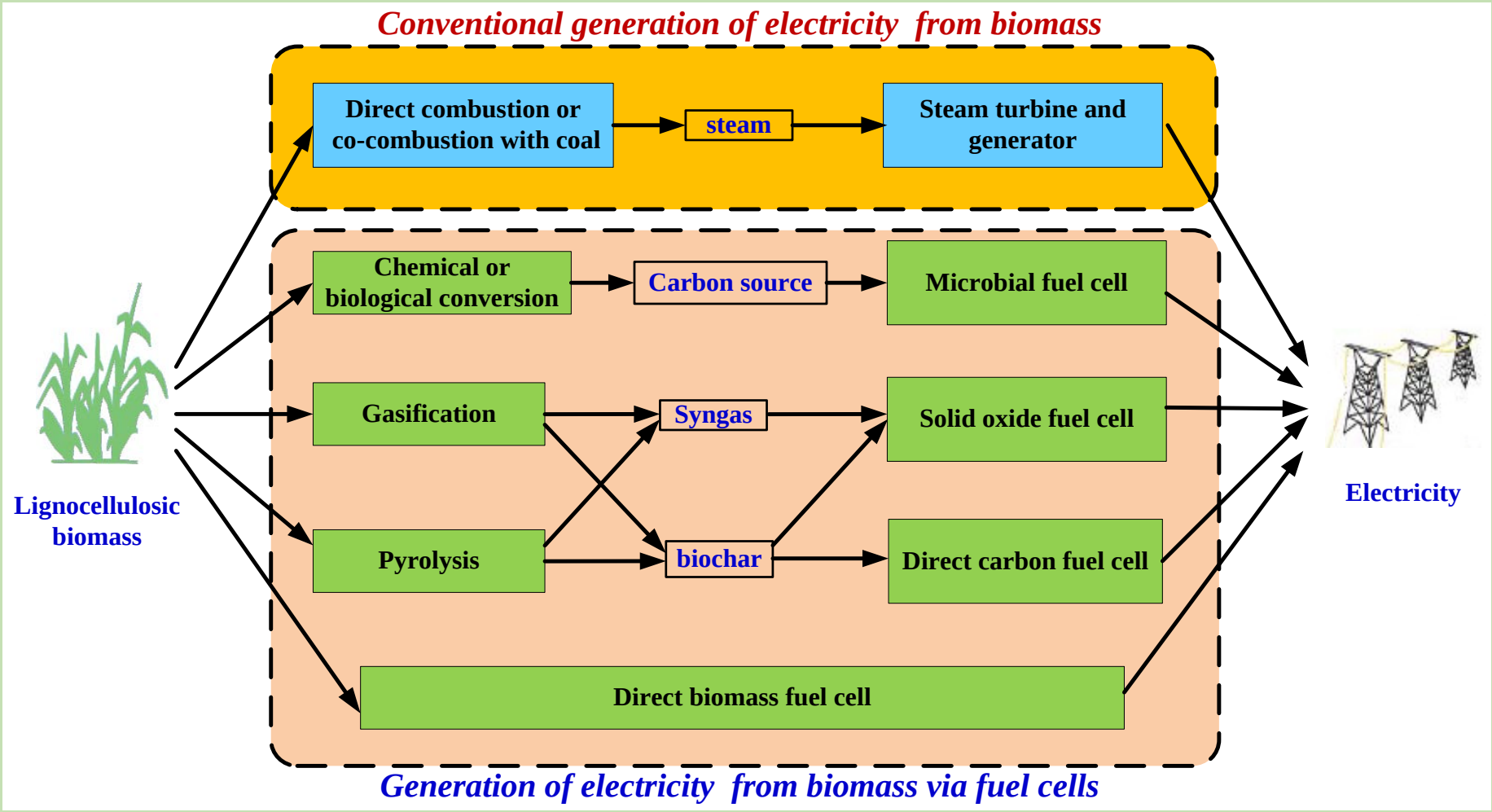
Professor

School of Chemical and Biomolecular Engineering

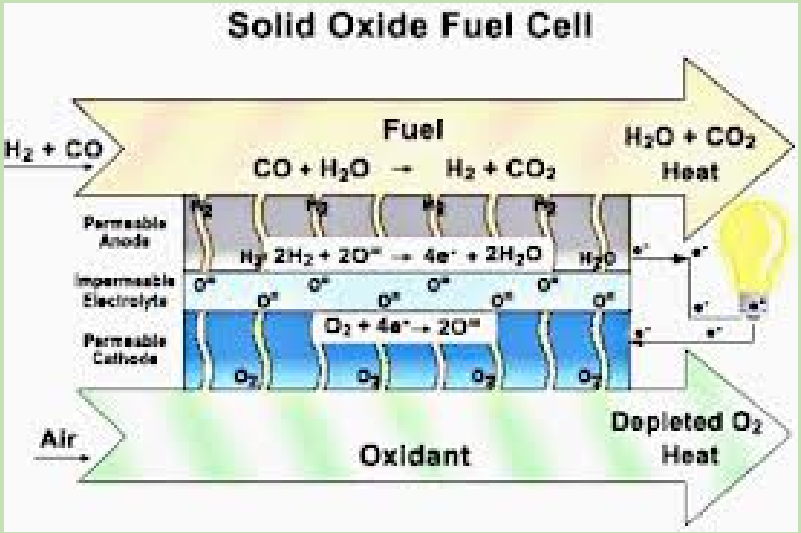
Renewable Bioproducts Institute

Georgia Institute of Technology

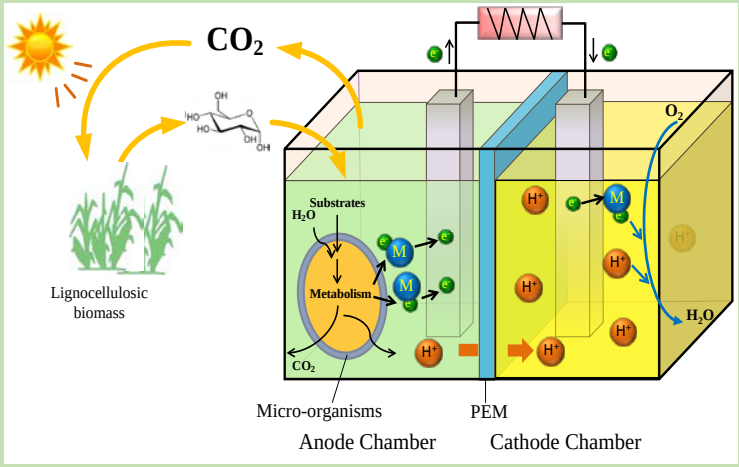
Methods to convert biomass to electricity



Current biomass fuel cells



Microbial fuel cell:



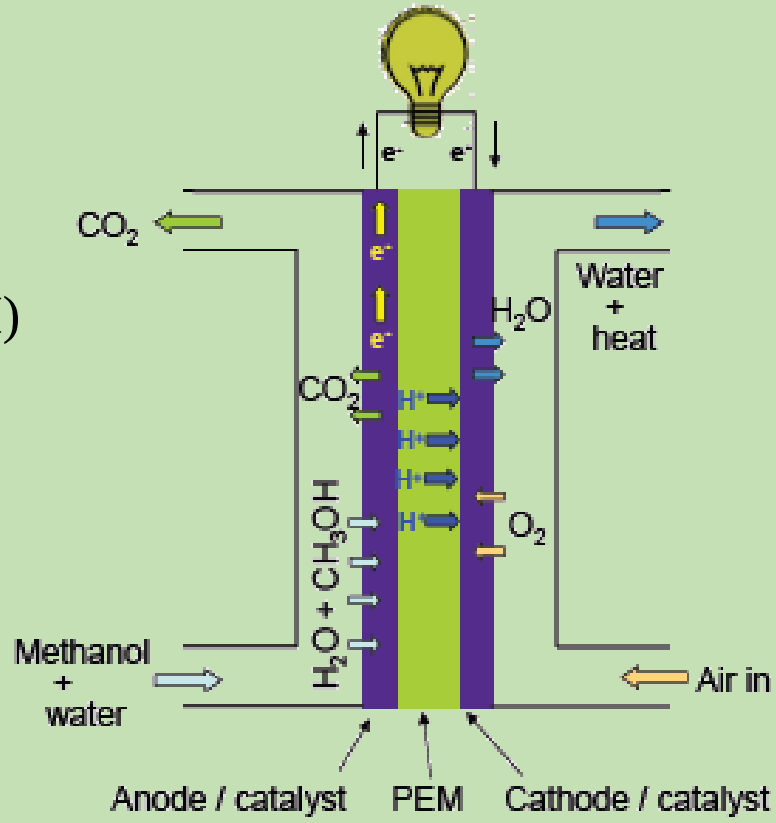
High temperature (>500 ^oC);
burn biomass to syngas

Restrict reaction conditions:
Easy to be contaminated;
Enzyme or fungus activity is very selective
Very low power output,

Fuel cell

- Pt catalysts on anode and cathode
- Polymer ion-exchange membrane (PEM)
- Run at 60–100 °C

	Equation
Anode	$CH_3OH + H_2O \rightarrow 6\ H^+ + 6\ e^- + CO_2$ oxidation
Cathode	$\frac{3}{2}O_2 + 6\ H^+ + 6\ e^- \rightarrow 3\ H_2O$ reduction
Overall reaction	$CH_3OH + \frac{3}{2}O_2 \rightarrow 2\ H_2O + CO_2$ redox reaction



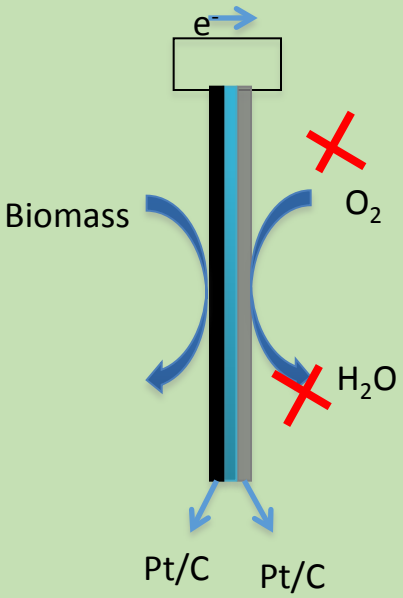
https://en.wikipedia.org/wiki/Fuel_cell

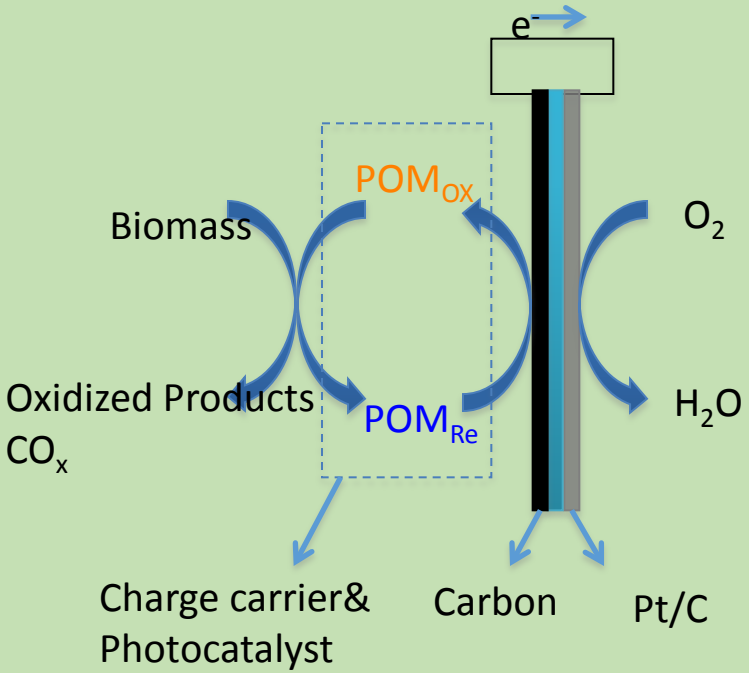
H_2 or CH_3OH are most common fuels. Low molecular alcohols such as ethanol, are ok, but conversion efficiency is low;

No one has reported to use polymer as direct fuel

The direct biomass fuel cell

- Polyoxometalates (POMs) used as photocatalysts
- POMs used as charge carrier



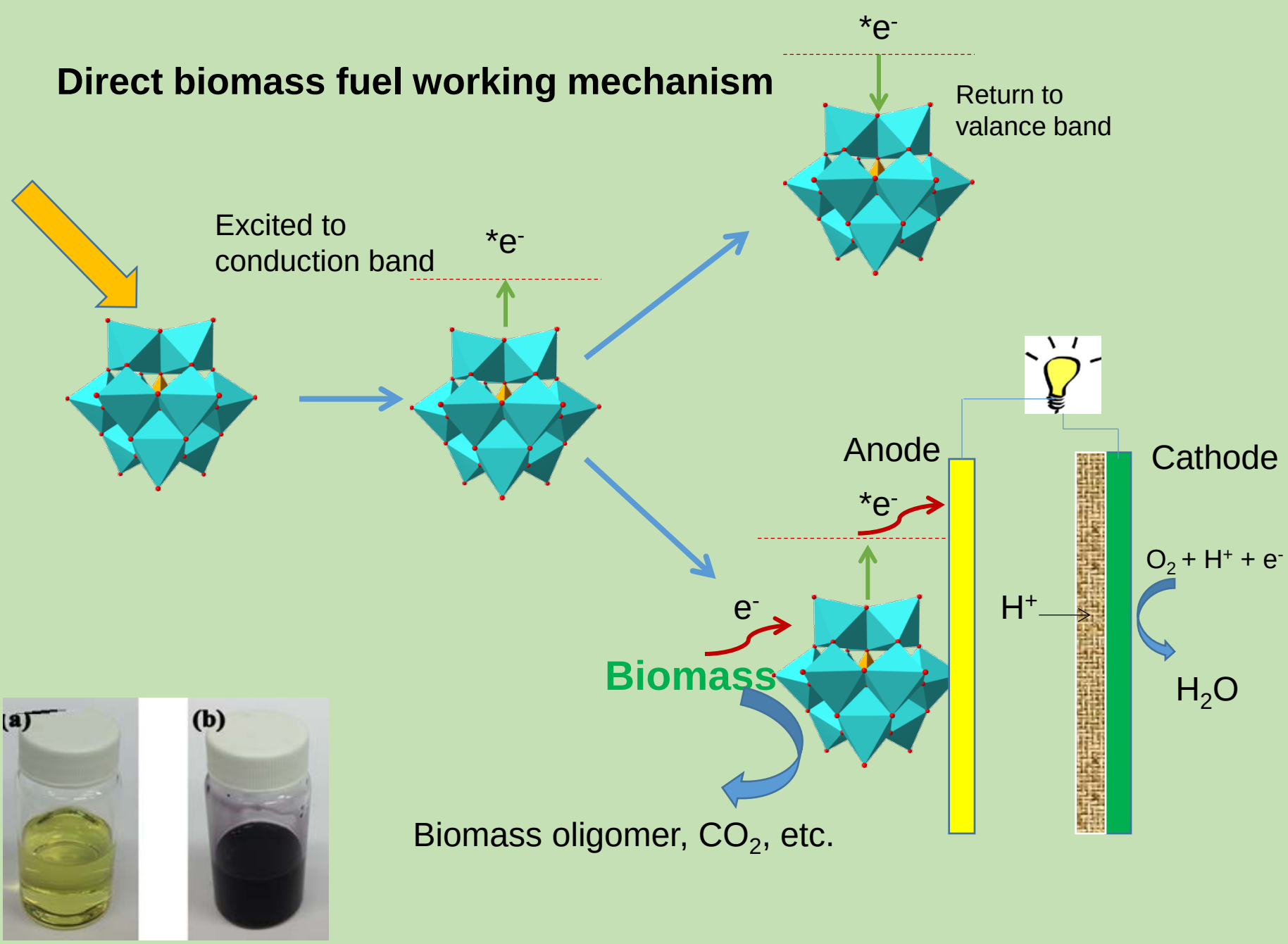


$$E(\text{biomass}) < E(\text{POM}) < E(\text{O}_2)$$

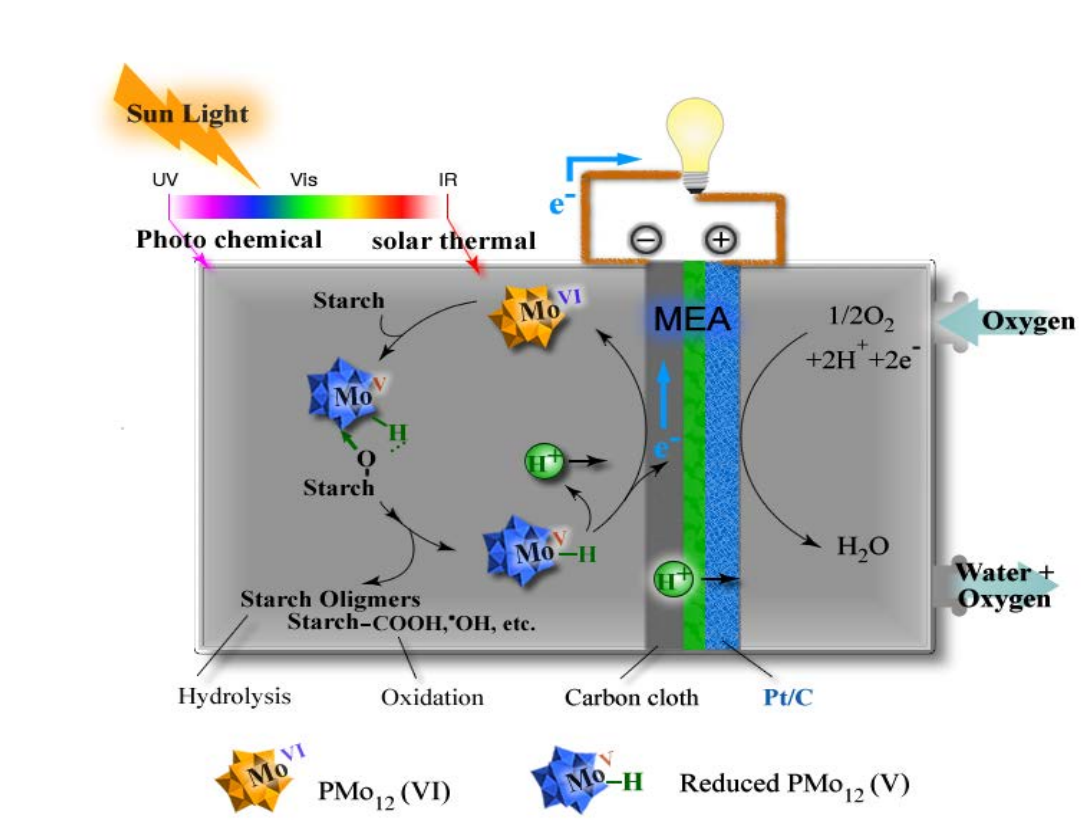
0.3-0.6V 0.6-0.9V 1.2V

Our key finding: We found a intermediate catalyst that can oxidize biomass under solar light irradiation or thermal treatment, but it can also transport the biomass charge to oxygen through an electric circle

Direct biomass fuel working mechanism



Mechanism of solar-induced biomass fuel cell



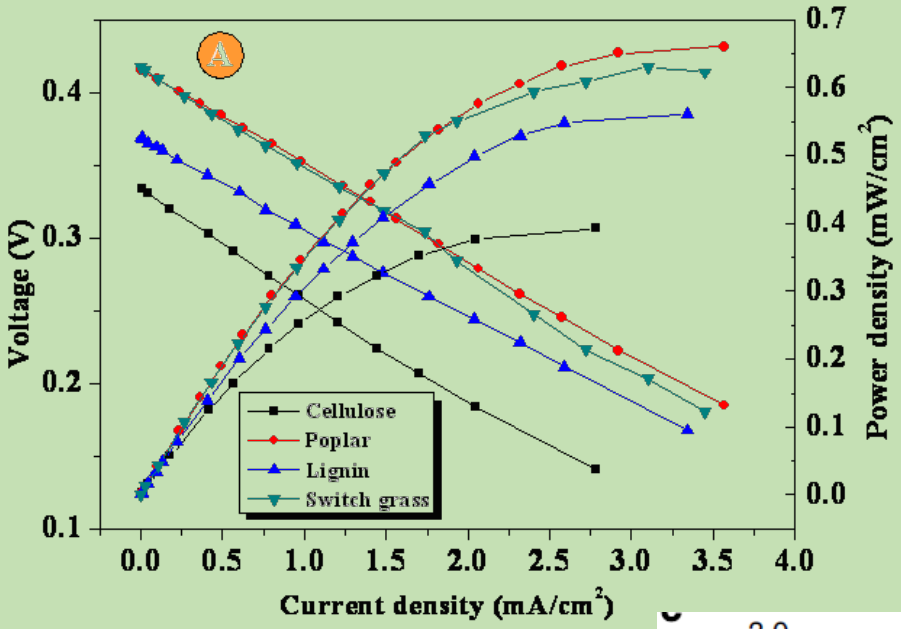
$$\text{Starch-O-}[HPMo^{VI}_{11}Mo^{V}O_{40}]^{3-} + [HPMo^{VI}_{11}Mo^{V}O_{40}]^{3-} \xrightarrow{anode} 2[PMo^{VI}_{12}O_{40}]^{3-} + \text{Oxidized starch oligmers} + 2e^- + 2H^+$$

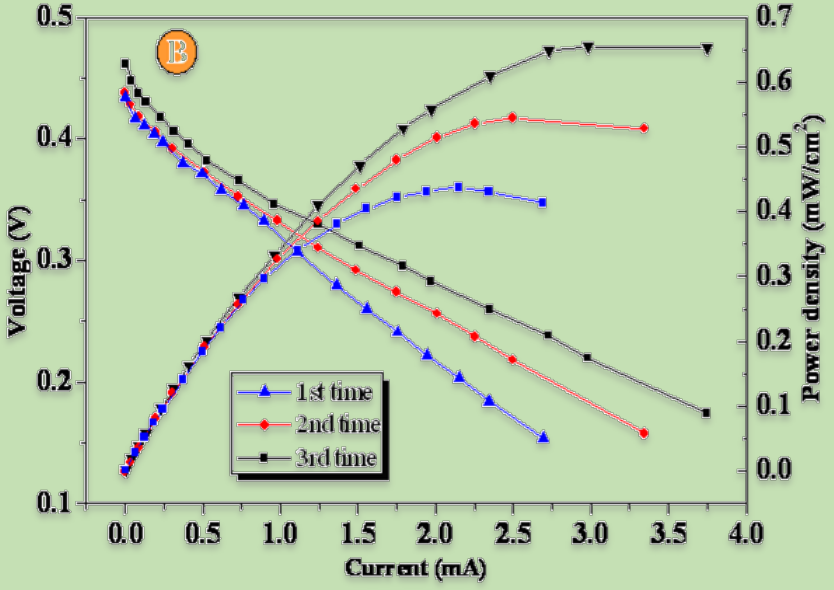
$$1/2\ O_2 + 2e^- + 2H^+ \xrightarrow{\text{cathode}} H_2O$$

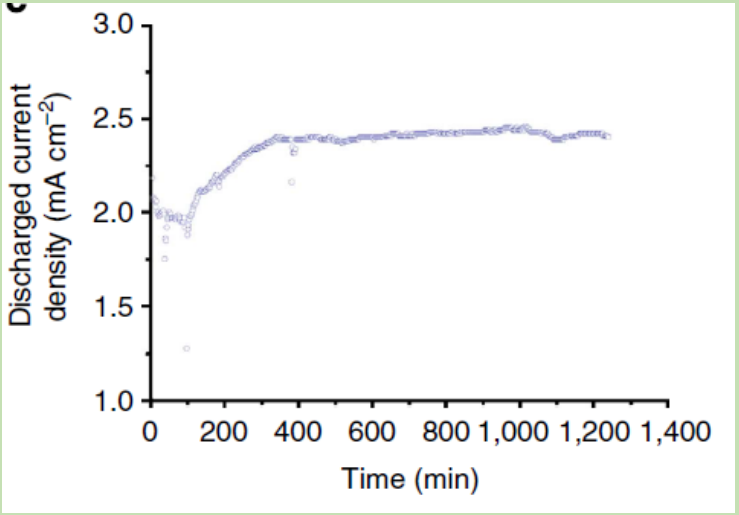
W. Liu, W. Mu, M. Liu, X. Zhang, H. Cai, Y. Deng, Solar-induced direct biomass-to-electricity hybrid cell using polyoxometalate as photo-catalyst and charge carrier, Nature Communications 5, (2014) 3208


Fisher Scientific
Fisher Scientific

Results







W. Liu, W. Mu, M. Liu, X. Zhang, H. Cai, Y. Deng, Solar-induced direct biomass-to-electricity hybrid cell using polyoxometalate as photo-catalyst and charge carrier, Nature Communications 5, (2014) 3208

Angewandte Chemie

VIP Biomass Conversion Very Important Paper

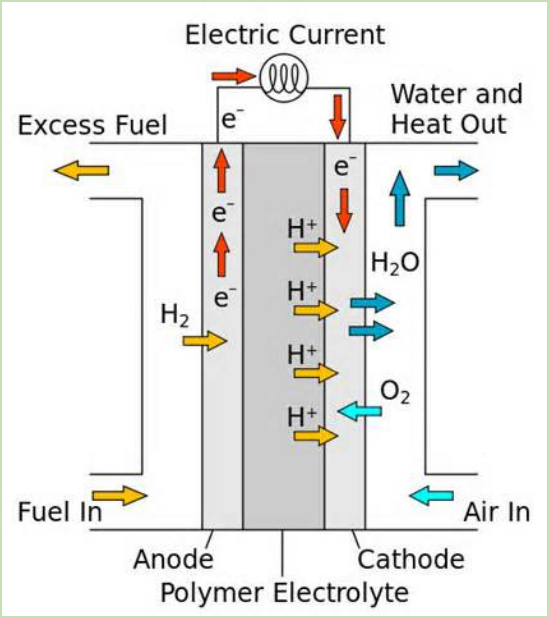
DOI: 10.1002/ange.201408226

High-Performance Liquid-Catalyst Fuel Cell for Direct Biomass-into-Electricity Conversion**

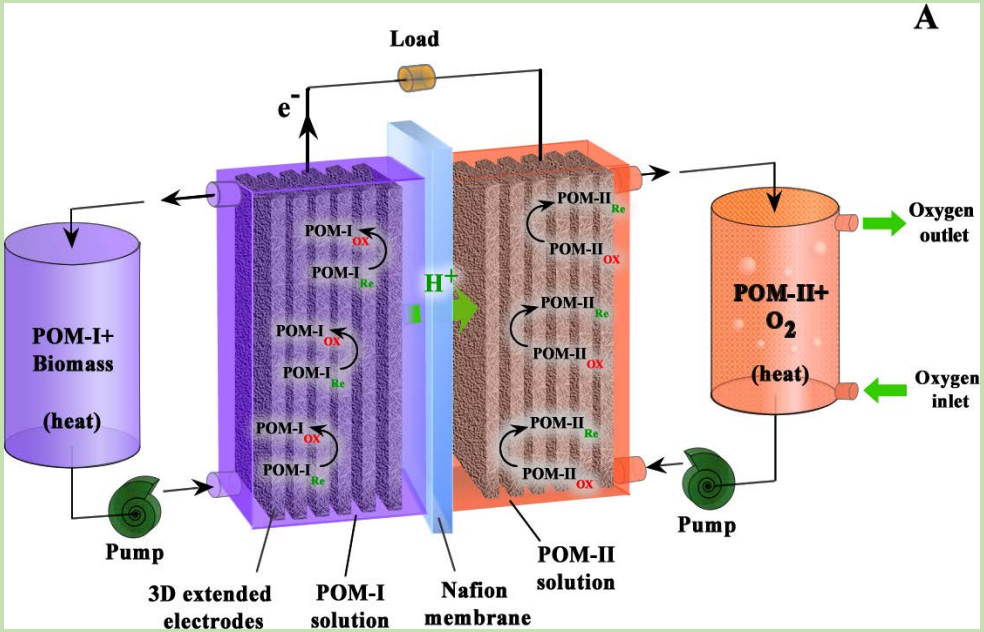
*Wei Liu, Wei Mu, and Yulin Deng**

- Completely remove noble metal
- Change gas-solid surface reaction to liquid-liquid or liquid-gas reactions
- Increase the total number (so the total surface area) of anode and cathode electrodes
- Improve the power density

Traditional fuel cell

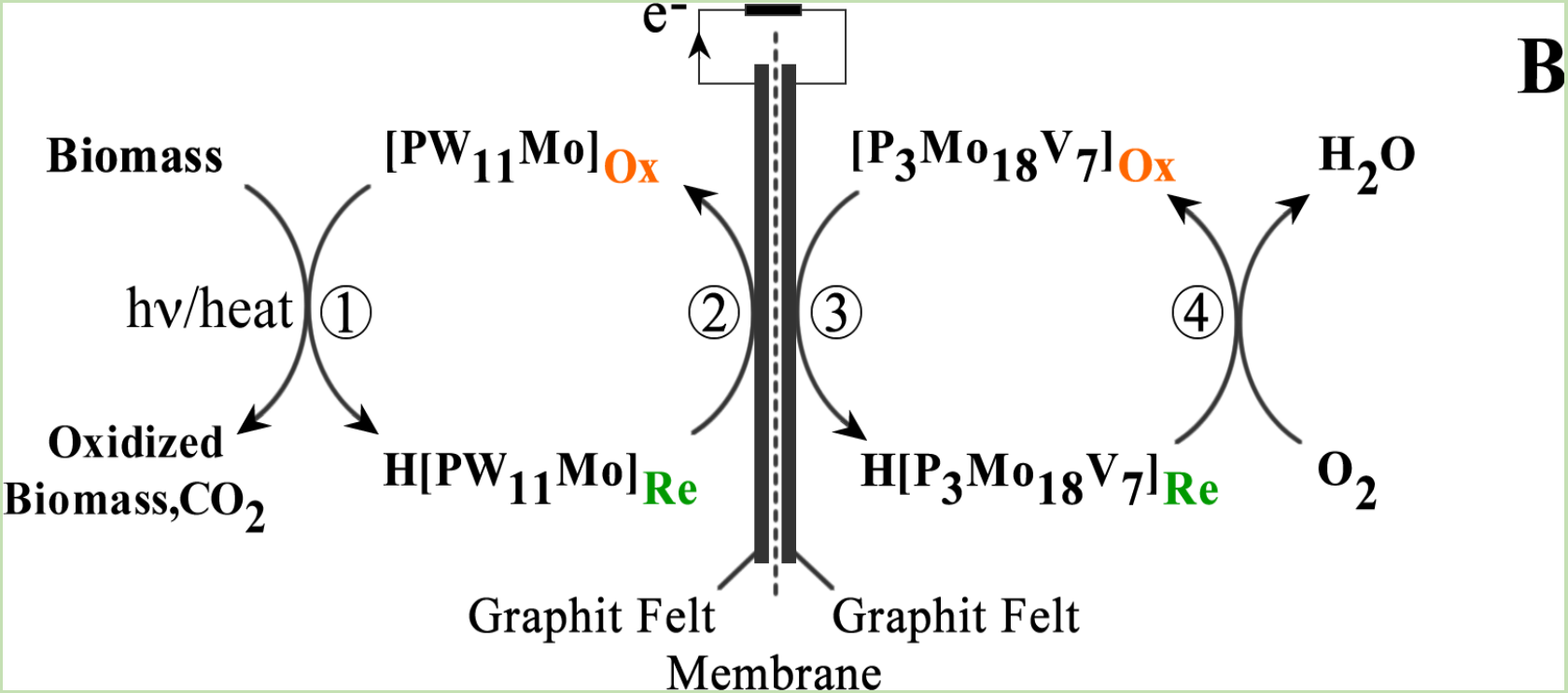


3-D liquid fuel cell



W. Liu, W. Mu, and Y. Deng, High-Performance Liquid-Catalyst Fuel Cell for Direct Biomass-into-Electricity Conversion, Angew. Chem., Int Ed, (2014), 53 (49), 13558

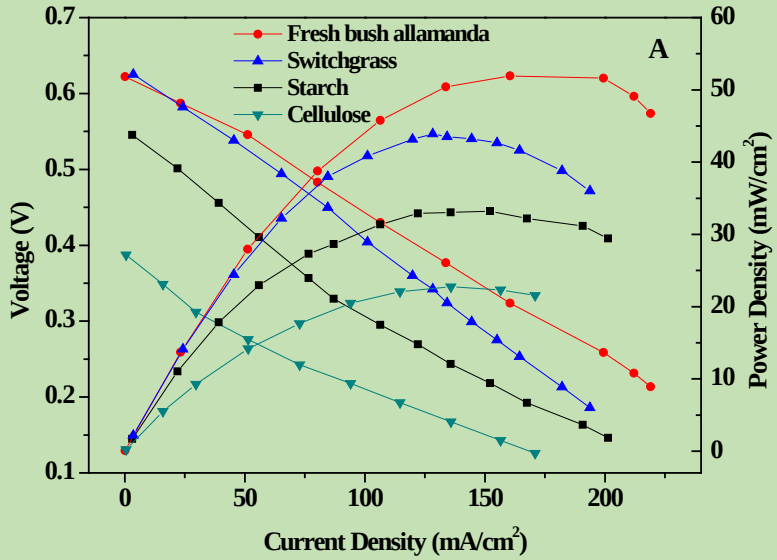
Liquid Catalyst Fuel Cell Mechanism

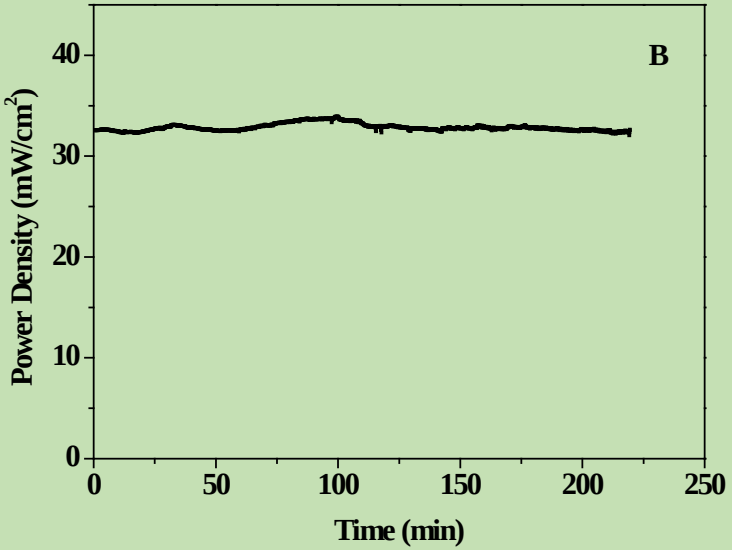


W. Liu, W. Mu, and Y. Deng, High-Performance Liquid-Catalyst Fuel Cell for Direct Biomass-into-Electricity Conversion, Angew. Chem., Int Ed, (2014), 53 (49), 13558

Complete liquid based biomass fuel cells

Starch based fuel cell





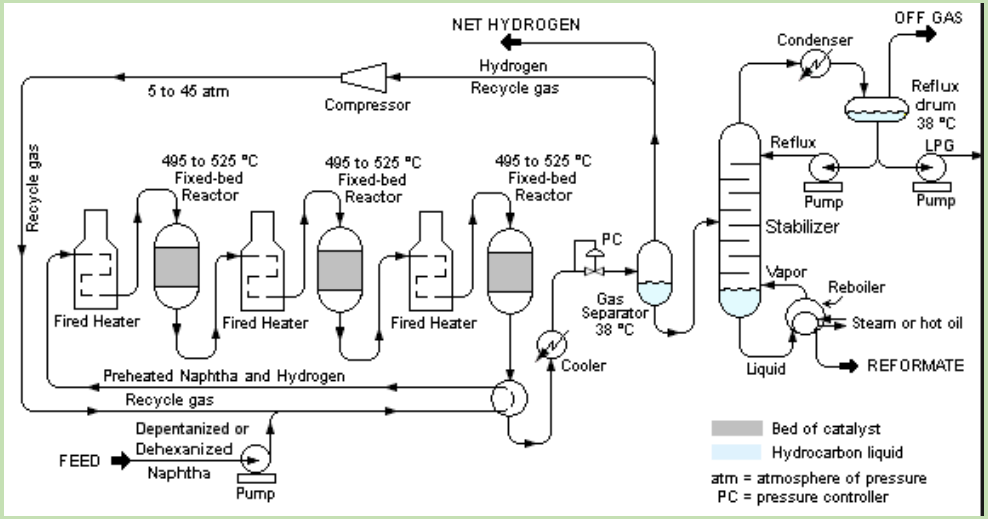
Fuel cell efficiency can be as high as 95%, but heat engine thermal conversion efficiency is usually 35-40%

W. Liu, W. Mu, and Y. Deng, High-Performance Liquid-Catalyst Fuel Cell for Direct Biomass-into-Electricity Conversion, Angew. Chem., Int Ed, (2014), 53 (49), 13558

A generic electrolysis approach for high efficiency conversion of native biomasses to hydrogen

Hydrogen production

Petroleum reforming and coal gasification: 96% of the global hydrogen



http://en.wikipedia.org/wiki/Catalytic_reforming

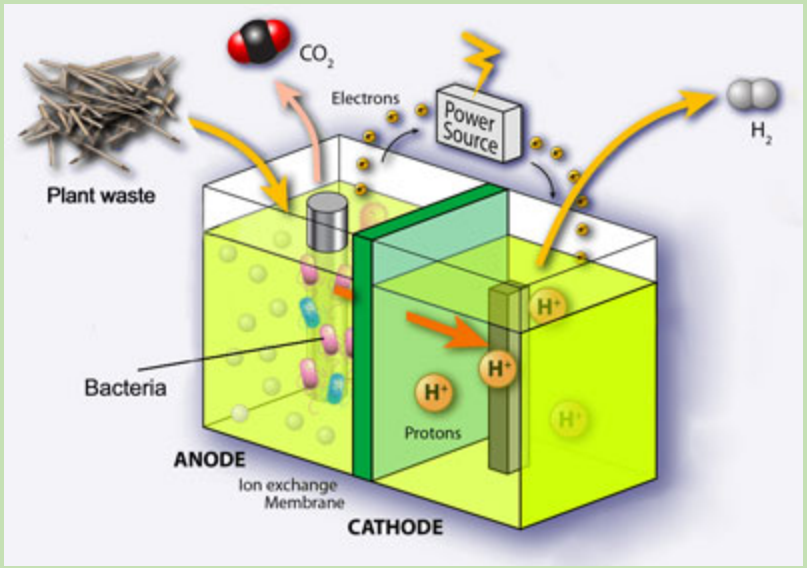
$$C_mH_n + mH_2O\,(g) \longrightarrow mCO + (m + 0.5\,n)\,H_2$$

$$C_mH_n + 2mH_2O\,(g) \longrightarrow mCO_2 + (2m + 0.5\,n)\,H_2$$

$$CO + H_2O\,(g) \longleftrightarrow CO_2 + H_2$$

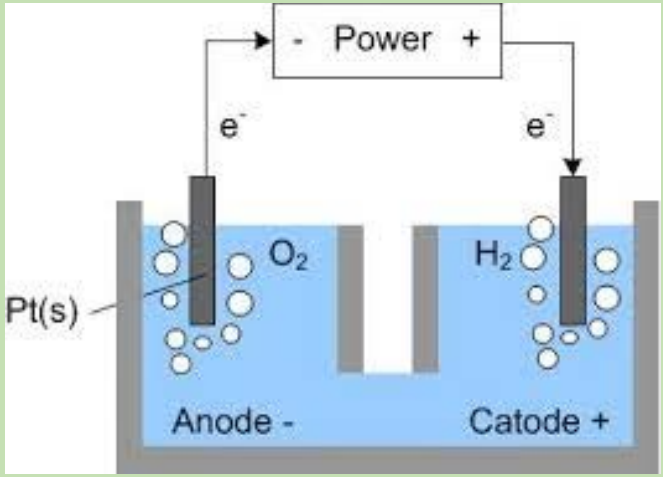
$$CH_3OH + H_2O\,(g) \longleftrightarrow CO_2 + 3H_2$$

Bio-hydrogen



http://www.rsc.org/chemistryworld/News/2011/February/11021103.asp

Water splitting for hydrogen



$2H_2O \Rightarrow O_2(g) + 4H^+ + 4e^-$

$4H_2O + 4e^- \Rightarrow 2H_2(g) + 4OH^-$

Over-potential: ca. 0.95 V for oxygen over graphite anode

Pt or noble metal catalyst must be used.

Even with Pt catalyst: 1.8 V total potential and the energy of 4.3 kWh $Nm^{-3}H_2$ was generally required

Water-alcohol electrolysis for hydrogen

$$Pt - CH_3OH \rightarrow Pt - CO + 4H^+ + 4e^-$$

$$Pt - CO + H_2O \rightarrow Pt(site) + CO_2 + 2H^+ + 2e^-$$

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

$$CH_3OH + H_2O \rightarrow HCOOH + 4H^+ + 4e^-$$

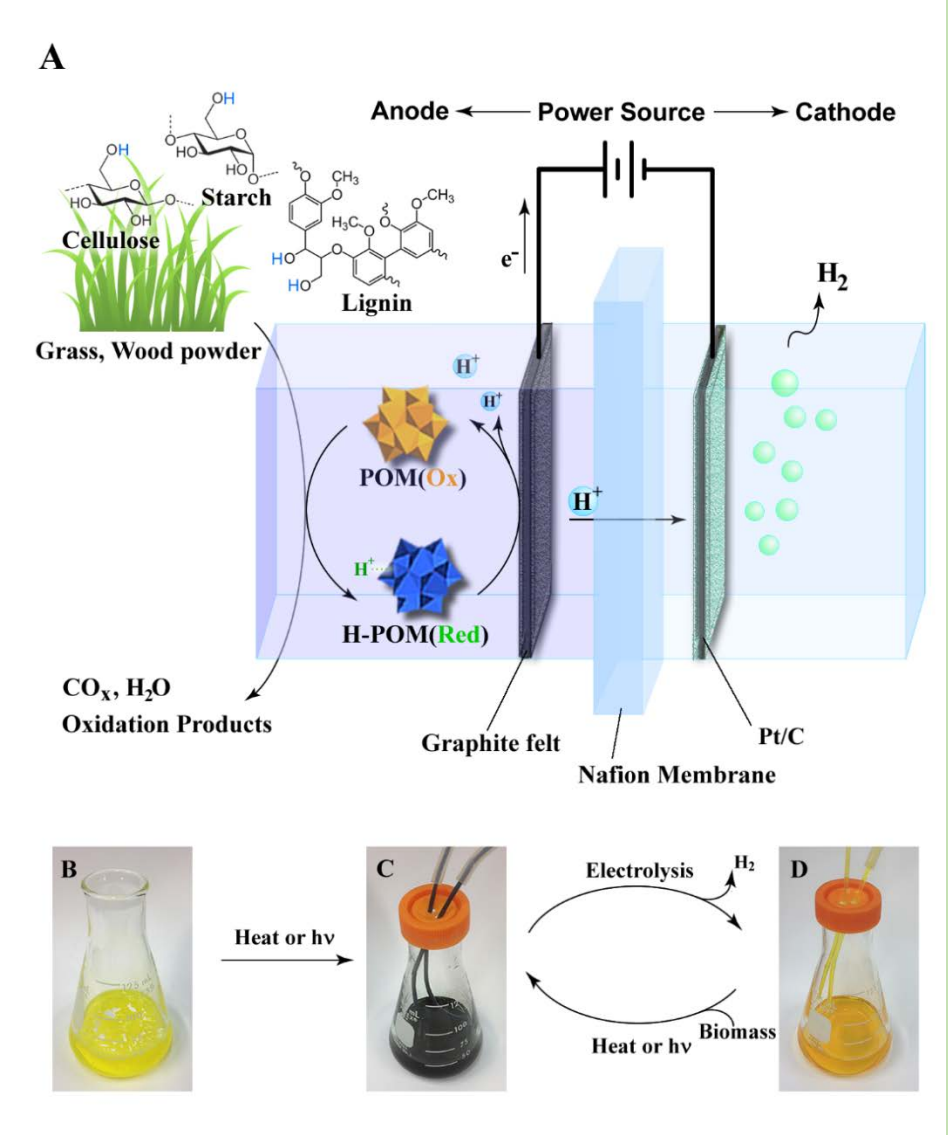
$$CH_3OH \rightarrow HCHO + 2H^+ + 2e^-$$

Reduce the electrolysis potential significantly.

Still too expensive: Pt catalyst, high materials cost, electric energy is still too high

$$\text{Biomass} + x\text{H}_2\text{O} + y\text{POM}_{(\text{oxdized})} \xrightarrow{\Delta \text{ or } h\nu} \text{Oxidized products} + n\text{CO}_2 + y\text{H-POM}_{(\text{reduced})} \quad (1)$$

$$\text{H-POM}_{(\text{Red})} \xrightarrow{\text{Anode}} \text{POM}_{(\text{Ox})} + \text{H}^+ + \text{e}^-$$

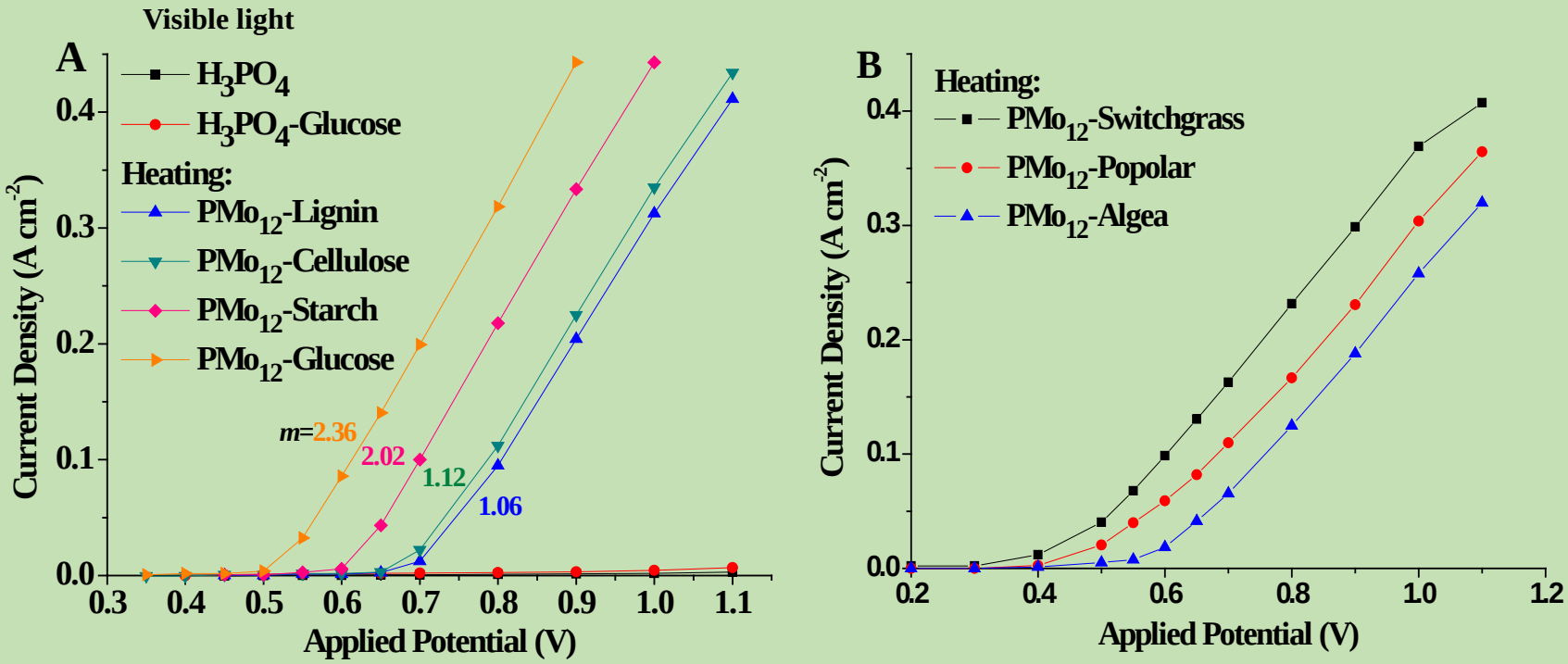


$$\text{H}^+ + \text{e}^- \xrightarrow{\text{Cathode}} \tfrac{1}{2}\,\text{H}_2$$

Catalytic reaction is in the solution but not on the electrode surface: no noble metal is needed

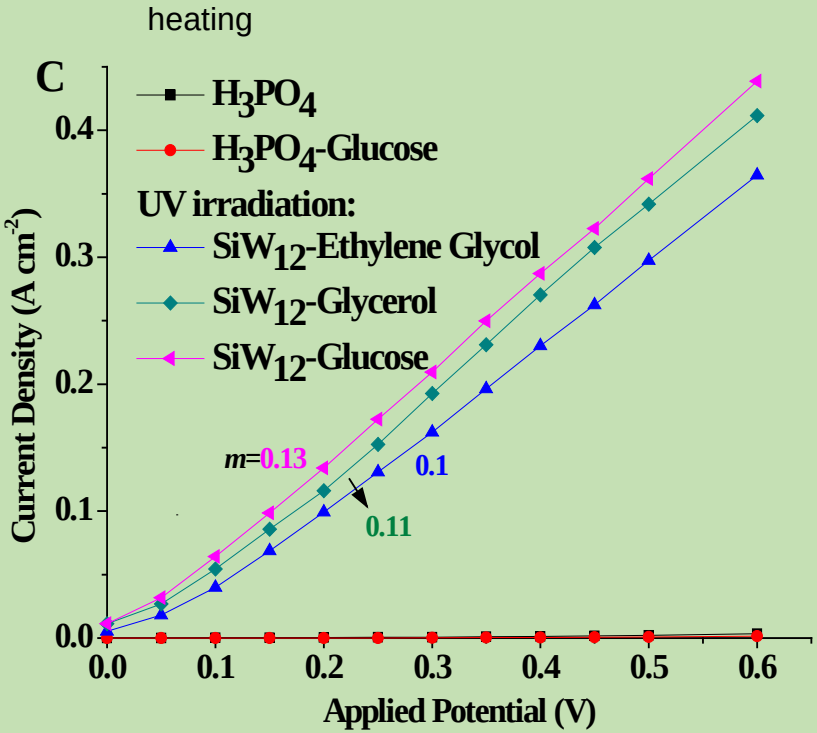
$$2\text{Starch-OH} + 2[\text{PMo}^{\text{VI}}{}_{12}\text{O}_{40}]^{3-} \xrightarrow{\text{light or heat}} \text{Starch-O-}[\text{HPMo}^{\text{VI}}{}_{11}\text{Mo}^{\text{V}}\text{O}_{40}]^{3-} + [\text{HPMo}^{\text{VI}}{}_{11}\text{Mo}^{\text{V}}\text{O}_{40}]^{3-} + \text{Oxidized starch oligomrs}$$

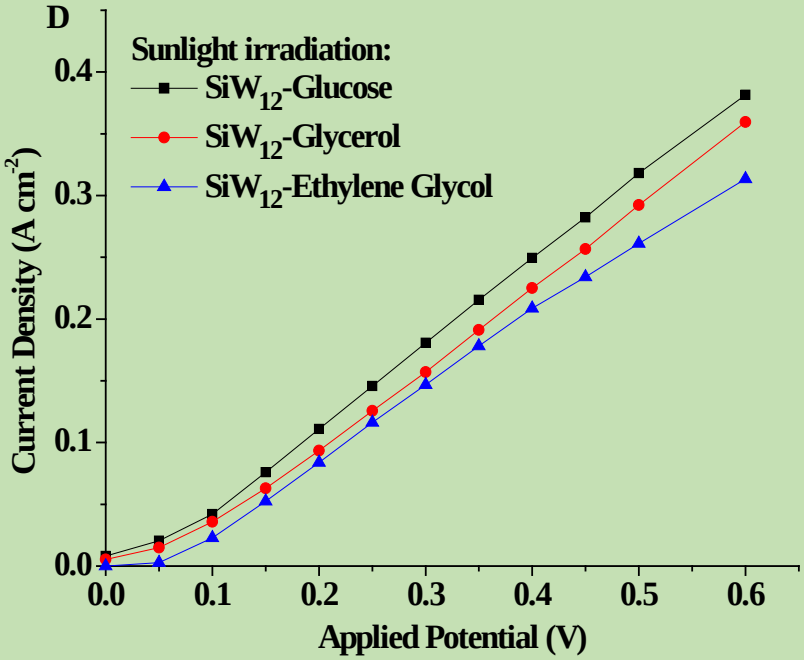
Using phosphomolybdic acid ($H_3PMo_{12}O_{40}$, noted as PMo_{12})



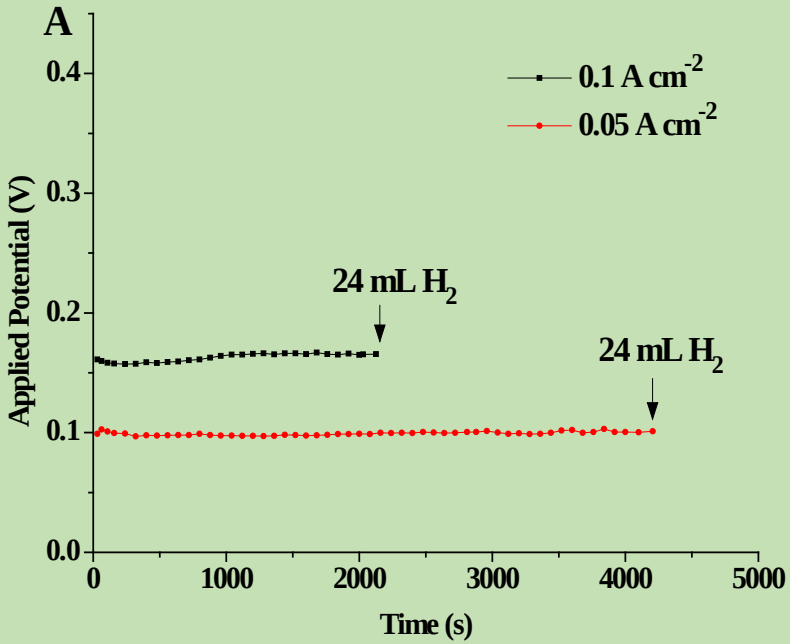
Starch-O-$[HPMo^{VI}_{11}Mo^{V}O_{40}]^{3-}$+$[HPMo^{VI}_{11}Mo^{V}O_{40}]^{3-}$ +Oxidized starch oligomers $\xrightarrow{light\ or\ heat}$ 2Starch-OH + 2$[PMo^{VI}_{12}O_{40}]^{3-}$

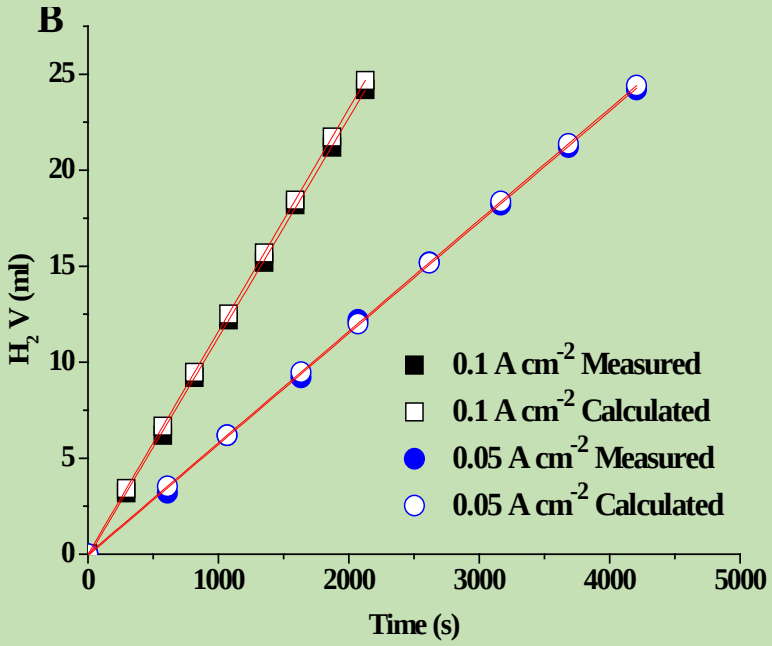
Using silicotungstic acid ($H_4SiW_{12}O_{40}$ noted as SiW_{12})





Using phosphomolybdic acid ($H_3PMo_{12}O_{40}$, noted as PMo_{12})



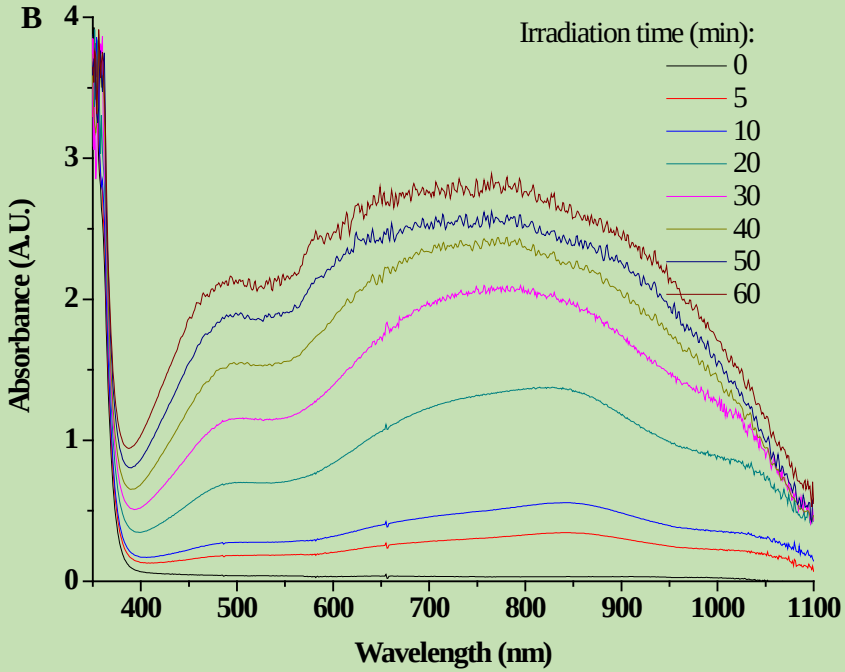


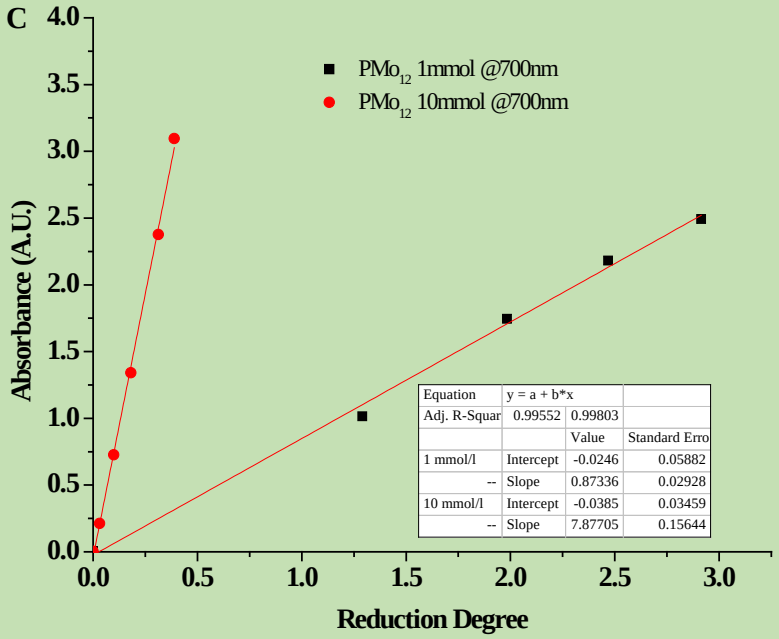
$H_4SiW_{12}O_{40}$ (SiW_{12})-glucose solution

Solid line: calculated value according to Faraday's law.

What is the POM reduce degree?

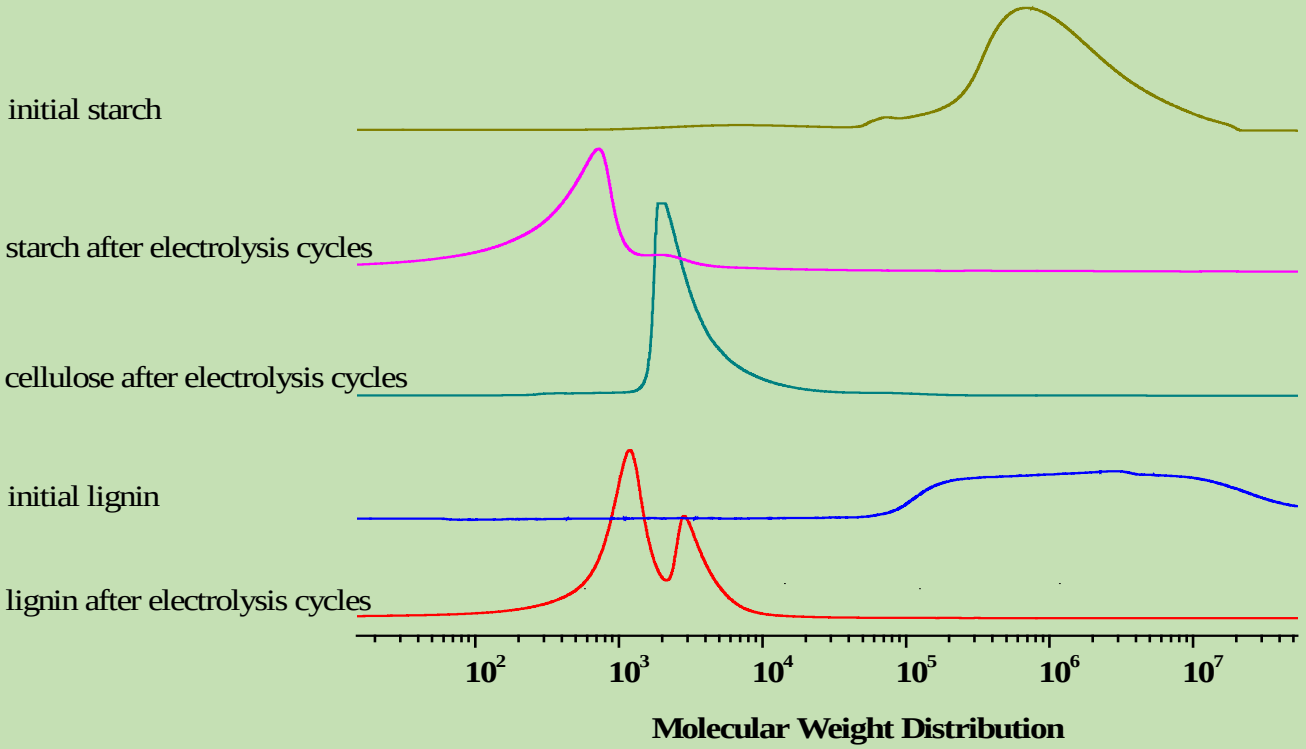
- Theoretically, $H_3[PMo_{12}O_{40}]$ has 12 *Molybdenum* elements, the maximum reduce degree is 12. However, practically, 3-4 reduce degree was obtained.
- Different POMs has different reduction degree.
- Reduction degree also depends on the chemistry of biomass, concentration, reaction time, and temperature of the reaction





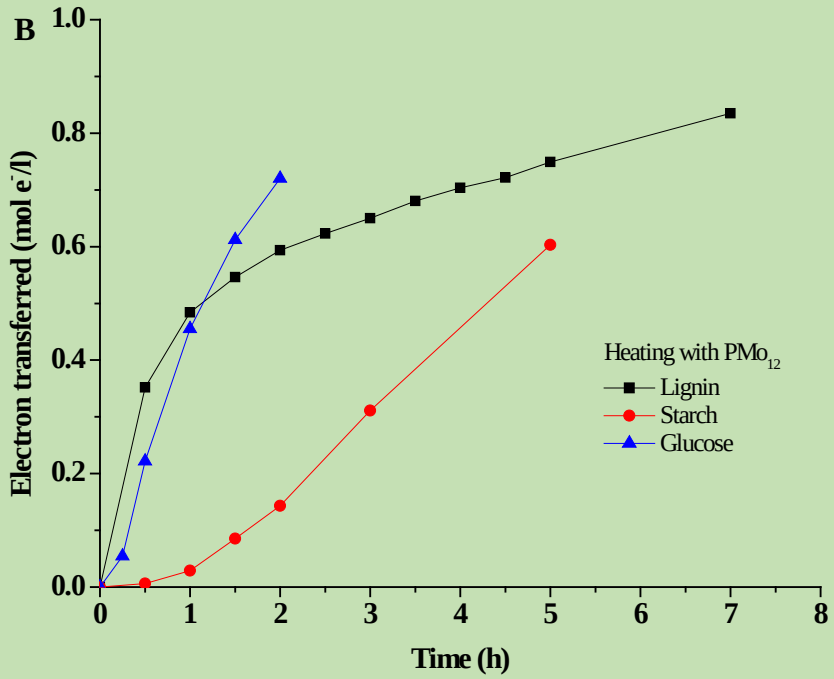
What are the residual products of the biomass

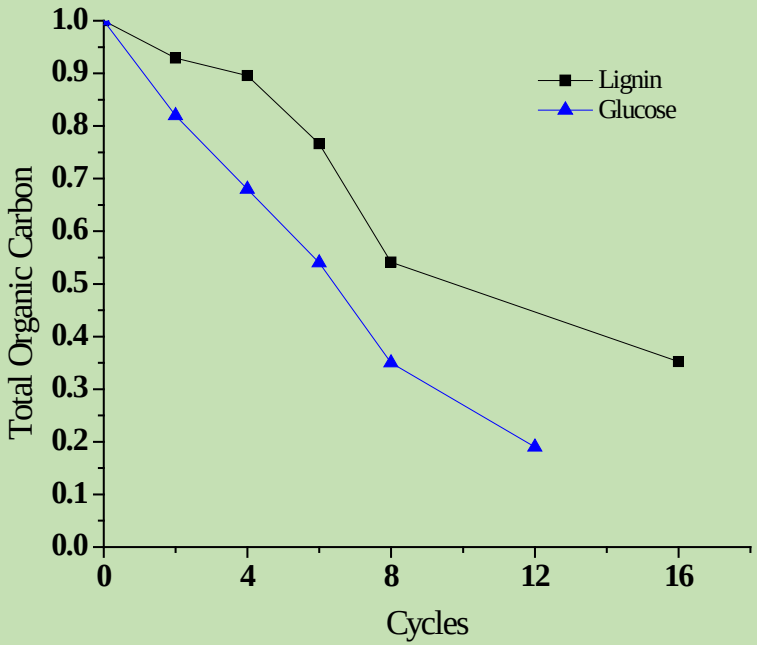
- Polysaccharides such as starch, glucose, cellulose, can completely converted to H_2 and CO_2
- Aromatic or aliphatic chemicals are difficult react with POM by heating, but can completely converted to CO_2 by light irradiation in the presence of POM
- The residual products also depends on the POM concentration, type of POM, reaction temperature and reaction time



Total organic residuals in the biomass solution

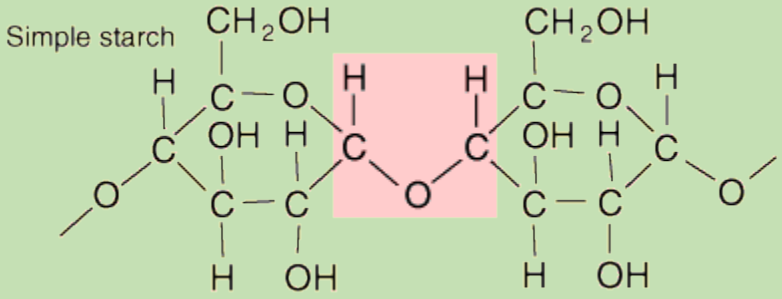
Originally, biomass is particle suspension. It turned to soluble liquid after reaction.

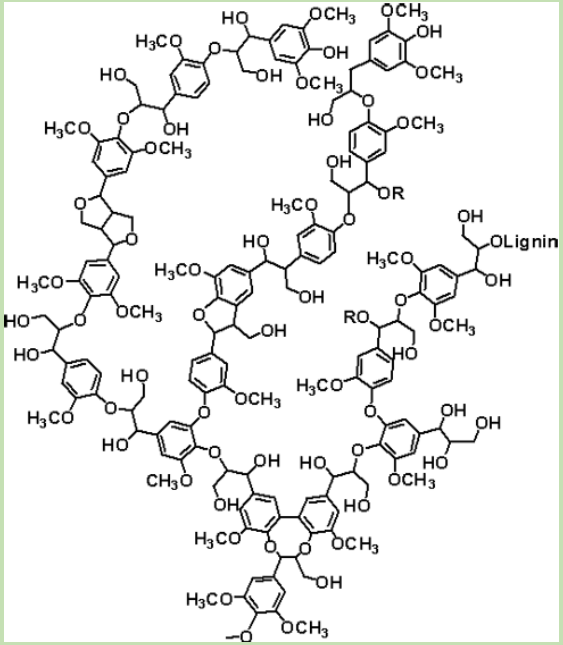




How many hydrogen atoms in the biomass can be converted to H_2 gas?

- Which depends on the chemistry of biomass, reaction conditions, POM chemistry, reaction time.
- For some polysaccharides such as starch, glucose, all H atoms can be completely converted to H2 gas. However, for the H atoms in aromatic or aliphatic molecules, high temperature reaction or photo radiation is needed





Conclusions

- Low temperature direct biomass fuel cell was developed. This fuel cell is different from traditional fuel cell, solar cell, and flow cell
- The fundamentals and mechanisms of the approach are completely different from traditional water splitting electrolysis.
- The approach is generic which can be used for almost all native biomasses, including solid powders of wood, grass, starch, cellulose, lignin etc.
- No complicated pretreatment or purification is needed
- Noble metal is no longer needed for anode. The catalytic redox reaction occurs in the solution but not on anode surface.
- The catalyst POM is very stable and low cost (about $100/kg), which will significantly reduce the cost of H_2 production.
- The electric energy consumption is extremely low, which is only about 16.7% of the energy consumption of electrolysis of water.

Acknowledgement

- Chinese Scholarship Council
- Renewable Bioproducts Institute at Georgia Tech
- Wei Liu, Sudhir Sharma, Arie Mulyadi, Wei Mu, Xu Du, Zhe Zhang, Professor Art Ragauskas

Tanks! Questions?