Solar-induced direct biomass-to-electricity hybrid fuel cell using polyoxometalates as photocatalyst and charge carrier

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Solar Cell

Semiconductor solar cell

Dye sensitized solar cell
Fuel cell

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

H₂ or CH₃OH 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
Bottleneck of low temperature biomass direct fuel cell

- Pt cannot cleavage C-C bonds
  e.g. $\text{CH}_3\text{CH}_2\text{OH} + 3\text{H}_2\text{O} \rightarrow 2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^-$
  Pt: the final product can only be acetaldehyde (-2e\text{-}, 16.7%) or acetic acid (-4e\text{-}, 33.3%)
- easily being poisoned by impurities in fuels

Polymeric biomasses such as starch, lignin, and cellulose have not been directly used in alcohol fuel cell
Current biomass fuel cells

**Solid Oxide Fuel Cell**

- High temperature (>500 °C);
- Burn biomass to syngas

**Microbial fuel cell:**

- Restrict reaction conditions:
- Easy to be contaminated;
- Enzyme or fungus activity is very selective
- Very low power output,
The direct biomass fuel cell

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

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.
PS: what’s the POMs

- Keggin structure
- A central tetrahedral [PO₄] surrounded by 12 [MoO₆] octahedrons
- photo-sensitive: O→Mo ligand-to-metal charge transfer (O→M LMCT)

12-molybdophosphate, also as well known molybdenum blue
POMs in our life

POMs are not new chemicals ([PMo$_{12}$O$_{40}$]$^{3-}$ anion discovered in 1826): they have been widely used as Brønsted acid;

- Comparing with H$_2$SO$_4$ and other inorganic acids, POM is less corrosive.
- The Keggin ions are well-known to be thermally stable and reversibly reduced by accepting electrons. This makes them useful as catalysts for a range of organic reactions.
- Some POM's exhibit luminescence.
- POMs have unusual magnetic properties and have been used as storage devices
- Many potential medicinal applications have been reported, such as anti-tumoral and anti-viral applications.
- method of decontaminating water.
POM for pulp and paper industry

• It is not new for paper industry!
• Some potential "green" applications have been reported, such as a non-chlorine based wood pulp bleaching process
• However, it is used as oxidation agent rather than catalyst in pulping and bleaching (POM is consumed during the bleaching process)
Direct biomass fuel working mechanism

Excited to conduction band

Biomass oligomer, CO₂, etc.
Fabrication of the direct biomass fuel cell

(a) membrane electrode assembly (Nafion® 117 PEM, anode made of carbon cloth and cathode loaded with Pt/C catalyst) (b) graphite bipolar plate, (c) acrylic plastic end plate, (d) transparent glass vessel with PMo$_{12}$-starch solution, (e) pump, (f) oxygen inlet, (g) water and oxygen outlet.
Results

Voltage-current density and power-current density plots of different biomasses used in the PMo$_{12}$ reaction system in photo-thermal experiments;

Voltage-current density and power-current density plots of three repeated photo irradiation-discharge cycles with starch and PMo$_{12}$ reaction system (discharged at room temperature);
Summary for direct biomass fuel cell

- The power density is 0.72 mW/cm², 100 times higher than cellulose based microbial fuel cells;
- Close to the best microbial fuels;
- Still be 10 times lower than H₂ and CH₃OH fuel cells;
- The cell continuously run 24 hrs without reducing the efficiency
Possible reactions of lignin with POM

It is possible to output electrical power and produce high value chemicals using lignin-based fuel cell
Differences from traditional cells

- **Solar cell**: directly convert light to electricity
  - Biomass fuel cell: storage solar energy

- **Redox flow batteries**: charge and discharge
  - Biomass fuel cell: powered by biomass and sunlight

- **Alcohol fuel cell**: reactions occur on the Pt loaded anode
  - Biomass fuel cell: POM takes electrons from biomass while reducing its own valence state to Mo$^{5+}$ under light irradiation

- This novel solar-induced hybrid fuel cell offers a new design for converting biomass to electricity.
Advantages

- Combines photochemical and solar-thermal biomass degradation in a single chemical process.
- Does not use expensive noble metals as anode catalysts
- Directly powered by unpurified polymeric biomasses which could significantly reduce the fuel cell cost.
- Can use almost any biomass or their mixture: biomasses, such as starch, cellulose, lignin, and even switchgrass, wood powders, algae, poultry manufacture wastes and animal excrements
- Catalyst is chemical very stable, regenerable which can be used in Varity conditions
- POM is low cost: ~$30-50/lb
- Operation process is very simple: middle school students can made small cells in their home
- It can be used for large power plants and also small power output units
The work has brought broad attentions

- Featured by more than 50 internet websites, newspapers, radios, and sustainable organizations
- Some top scientists believe this is real groundbreaking discovery which opens a new way to use sustainable energies
Georgia Tech working on biomass-powered electricity

Georgia Tech researchers have developed a fuel cell that converts biomass directly to electricity with the help of a catalyst activated by solar or thermal energy.

The hybrid fuel cell can use a variety of biomass sources, including starch, cellulose, switchgrass, powdered wood, algae and waste from poultry processing.

Thank you!
Any Questions?