

Electrochemical Hydrogenations in a Solid Polymer Electrolyte Fuel Cell Reactor

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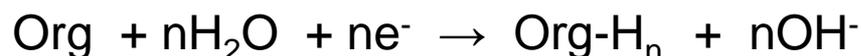
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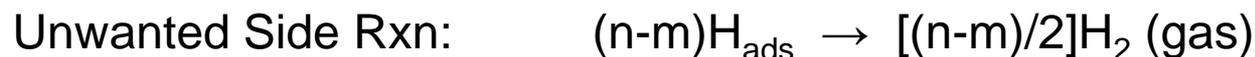
Traditional Electrochemical Reductions vs. Electrocatalytic Hydrogenations

Traditional Electrochemical Reductions Reactions at a high hydrogen overpotential cathode (e.g., Hg, Zn, Pb, or Cd) to suppress unwanted hydrogen gas evolution. Product selectivity is controlled by the electrode potential

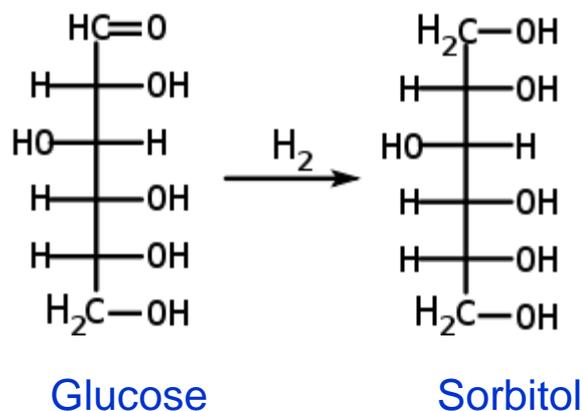


here the cathode potential is high and we minimize hydrogen evolution ($n\text{H}_2\text{O} + ne^- \rightarrow n\text{H}_{\text{ads}} + n\text{OH}^-$) by the choice of cathode material and by operating at near neutral pH.

Electrocatalytic Hydrogenation Reactions at a low hydrogen overpotential catalytic cathode (e.g., Raney nickel, Pt-black, Pd-black). Here we seek to electrochemically generate H species which chemically react with the organic reactant. Selectivity controlled by the chemical catalyst.



Electrochemical Reduction vs. Electrocatalytic Hydrogenation



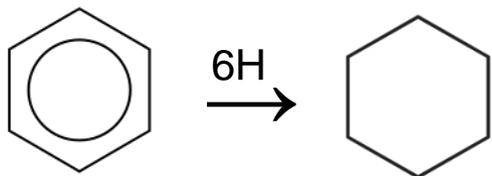
At a Zn(Hg) cathode, potential = -1.7 to -2.2 V vs SCE, Current Efficiency ~30%

At Ra-Ni, potential = -1.1 V vs SCE, Current Efficiency = 60-70%

Current Efficiency = (product formed)/(product that should have been made based on the current passed)

$$\text{Current Efficiency (\%)} \equiv \left[\frac{m F \cdot (\text{moles of Org} - H_m)}{\text{curren} \cdot \text{time}} \right] \cdot 100$$

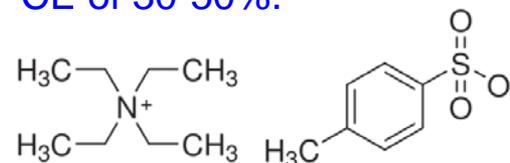
Examples of Electrocatalytic Hydrogenation of Aromatic Compounds - using H_2O as the Source of H



benzene

cyclohexane

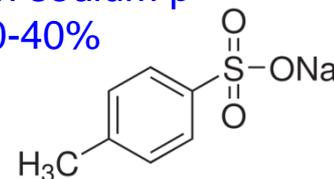
Raney nickel cathode and water/t-butanol solvent; a 1.0 M solution of benzene in 2.0 M tetramethylammonium p-toluenesulfonate was used (a hydrotropic salt which allows benzene to dissolve in water). CE of 30-50%.



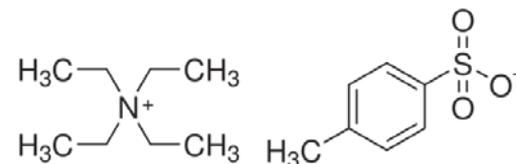
aniline

cyclohexylamine

Raney nickel cathode, water/butanol solvent with sodium p-toluenesulfonate supporting electrolyte). CE=20-40%

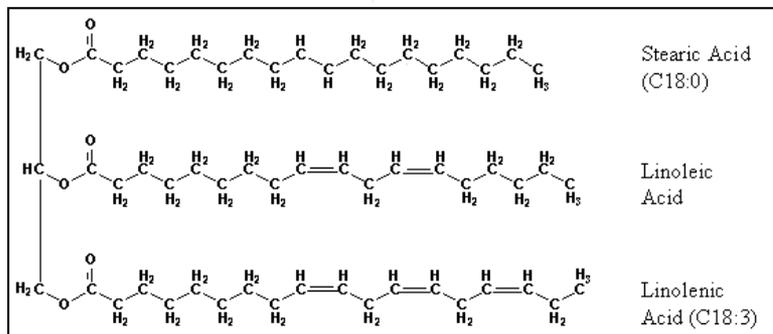
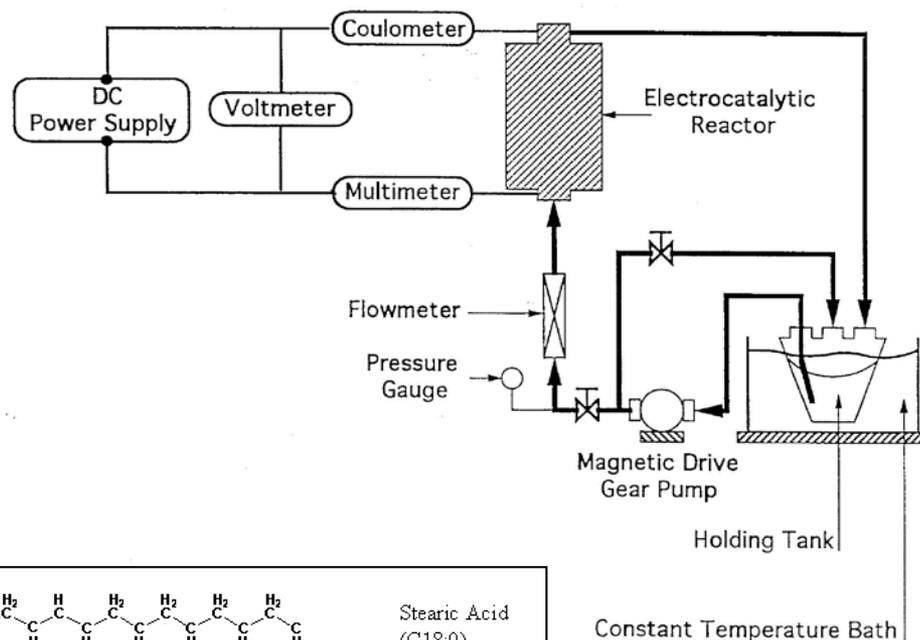
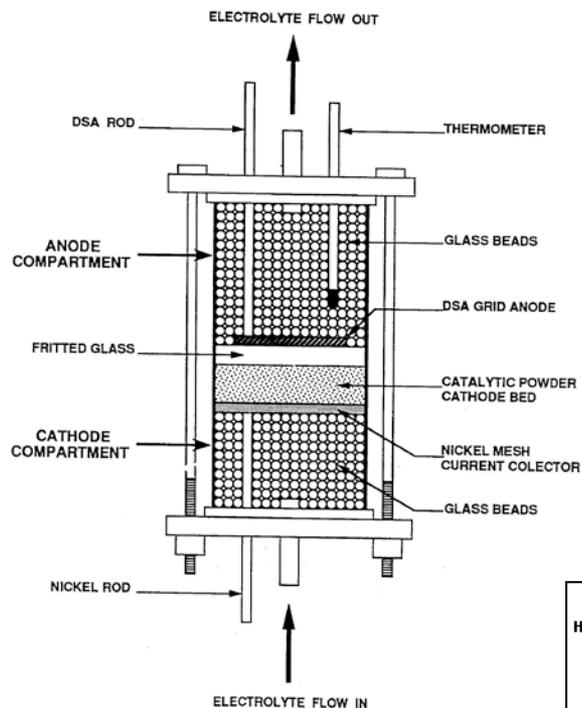


Ra-Ni cathode and water/butanol solvent. ; Quaternary ammonium cations form a hydrophobic layer on the cathode which promote organic substrate adsorption and reduction, with complete hydrogenation of the aromatic ring and nitro group. CE=40-70%.



Electrocatalytic Hydrogenation of Soybean Oil in a Flow-Through Reactor

Raney nickel powder cathode; Dimensionally stable anode (DSA) - titanium grid coated with IrO_2
 70°C; 1 atm.; solvent composition: 50/50 vol% t-butanol/water containing 1.0 M tetraethyl ammonium p-toluenesulfonate; current densities of 10-40 mA/cm²

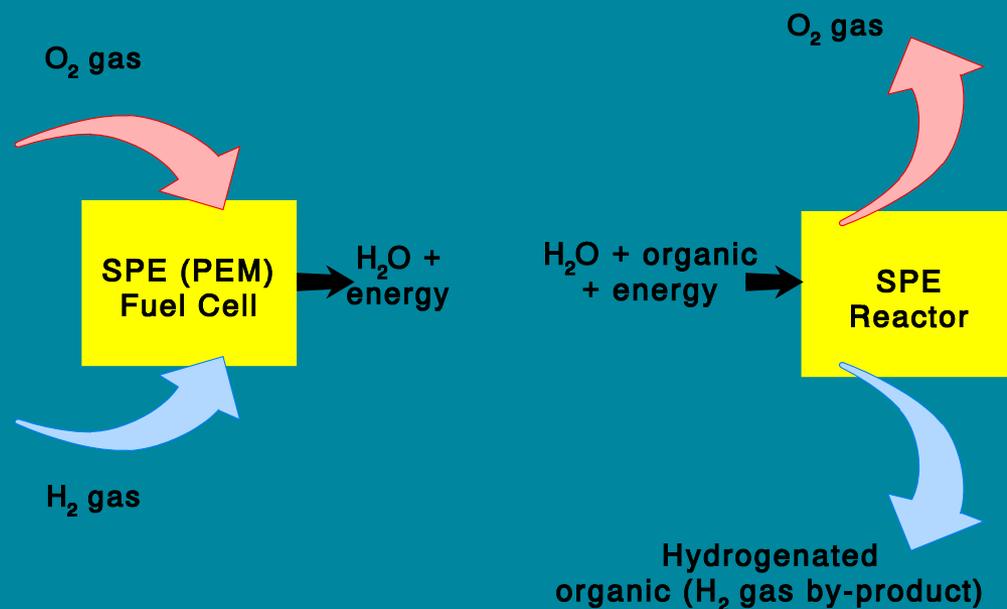


Complicating Factors of Electrochemical Routes to Hydrocarbon Syntheses

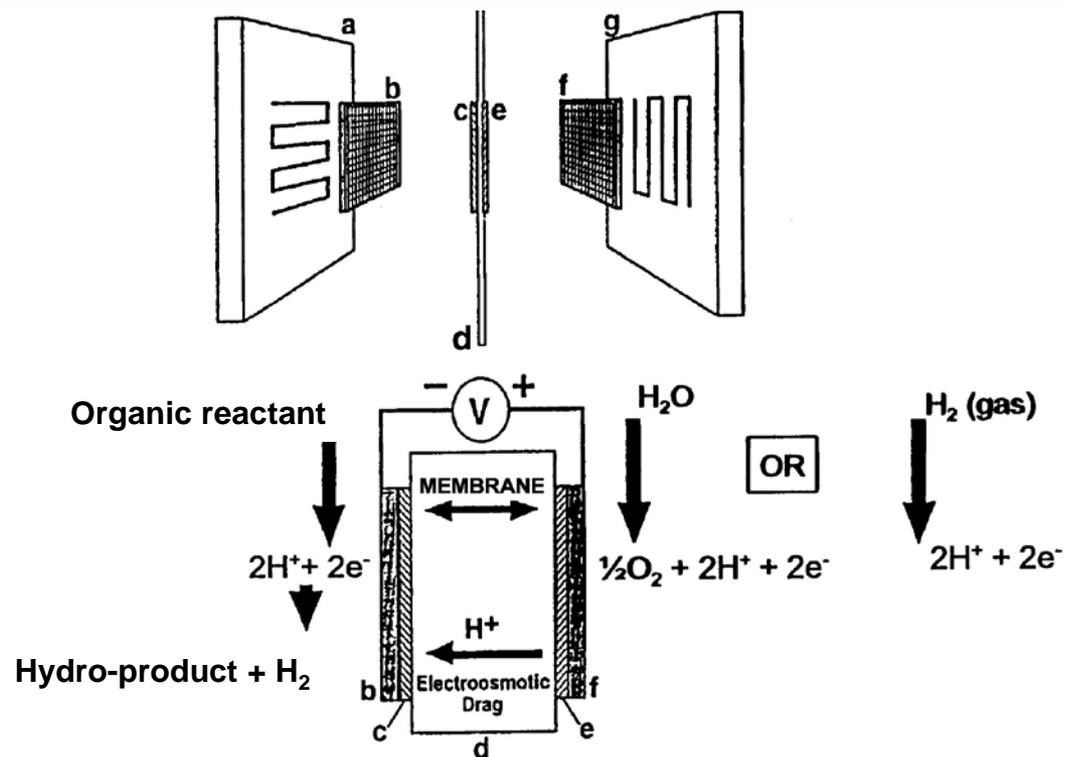
1. The rate of the electron transfer step at the anode or cathode during an electro-organic synthesis may be slow. To insure high current efficiencies, low current densities are used. This necessitates the use of high surface area electrodes (to get high conversion in a reactor of moderate size).
2. The high charge requirement of 96,487 coulombs (one Faraday) per mole of electrons is a detriment for electro-organic reactions, especially those that involve multiple electron transfer steps (this can be offset by using high MW starting materials).
3. It is difficult of carrying out organic electrochemical reactions in a liquid electrolyte
 - The organic substrate and/or product is not soluble in an aqueous electrolyte.
 - The ionically conducting supporting electrolyte salt is not soluble in the organic reactant or in solvents that solubilize the reactants/products).
 - It is difficult to use a vapor-phase organic reactant when the electrodes are immersed in liquid electrolyte
4. The requirement of having two reactions in an organic electrochemical reactor (an oxidation reaction at the anode and a reduction reaction at the cathode), where one reaction is often unwanted and where the product(s) of this unwanted reaction may interfere with the primary organic electrode reaction. To avoid problems, use a divided cell reactor (anode and cathode chambers are separated by a semi-permeable membrane).

For Organic Hydrogenation (reduction) Reactions: Carry Out an Indirect Electrocatalytic Hydrogenation Reaction in a Solid Polymer Electrolyte (Fuel Cell) Reactor

Run a Hydrogen/Oxygen Fuel Cell in Reverse



Principles of Operation of a Solid Polymer Electrolyte Reactor for Hydrogenation Reactions



- (a and g) Graphite (stainless steel) blocks with cross-patterned flow field.
- (b) Gas /oil permeable backing, cathode side.
- (c) Cathode thin film catalyst layer.
- (d) Nafion cation-exchange membrane.
- (e) Anode thin film catalyst layer.
- (f) Gas /water permeable backing, anode side.

Water vs. H₂ Gas as the Source of Hydrogen

Water as the Anode Feed:

Advantage – Hydrogen plant is not needed.

Disadvantage – Higher cell voltage (higher power requirements).
Reaction temperature at atmospheric pressure limited to $T < 100^{\circ}\text{C}$.
A robust and more costly ion-exchange membrane may be needed.

H₂ Gas as the Anode Feed:

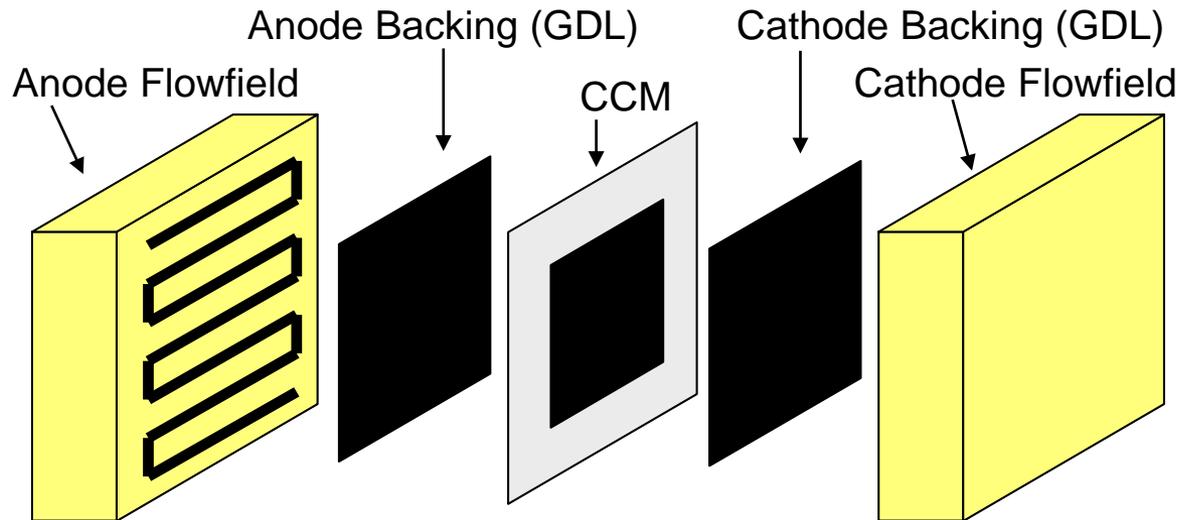
Advantage – Lower operating voltage (lower power requirements).
Unreacted H₂ gas can be recycled to the anode.
Wide range for reactor operating temperature ($T > 100^{\circ}\text{C}$ is possible).
Inexpensive (hydrocarbon) ion-exchange membrane can be used.

Disadvantage – How will H₂ gas be made?

The Heart of the Oil Hydrogenation Reactor – The Membrane-Electrode-Assembly (MEA)

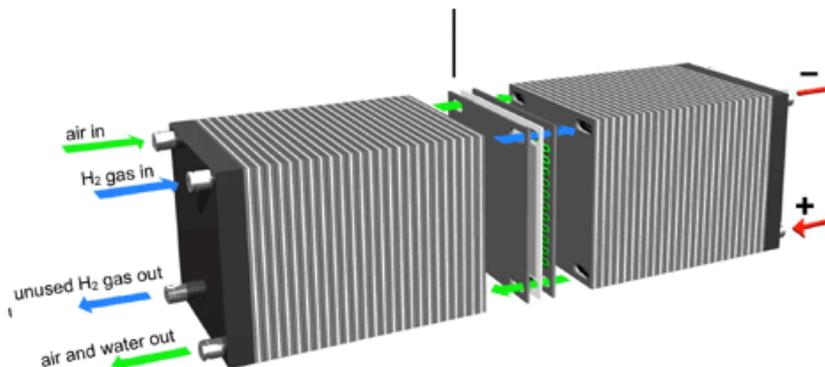
CCM=Catalyst Coated Membrane

GDL=Gas Diffusion Layer



Membrane-Electrode-Assembly (MEA) is composed of CCM and two GDLs.

MEA is inserted between the anode and cathode flowfield plates.



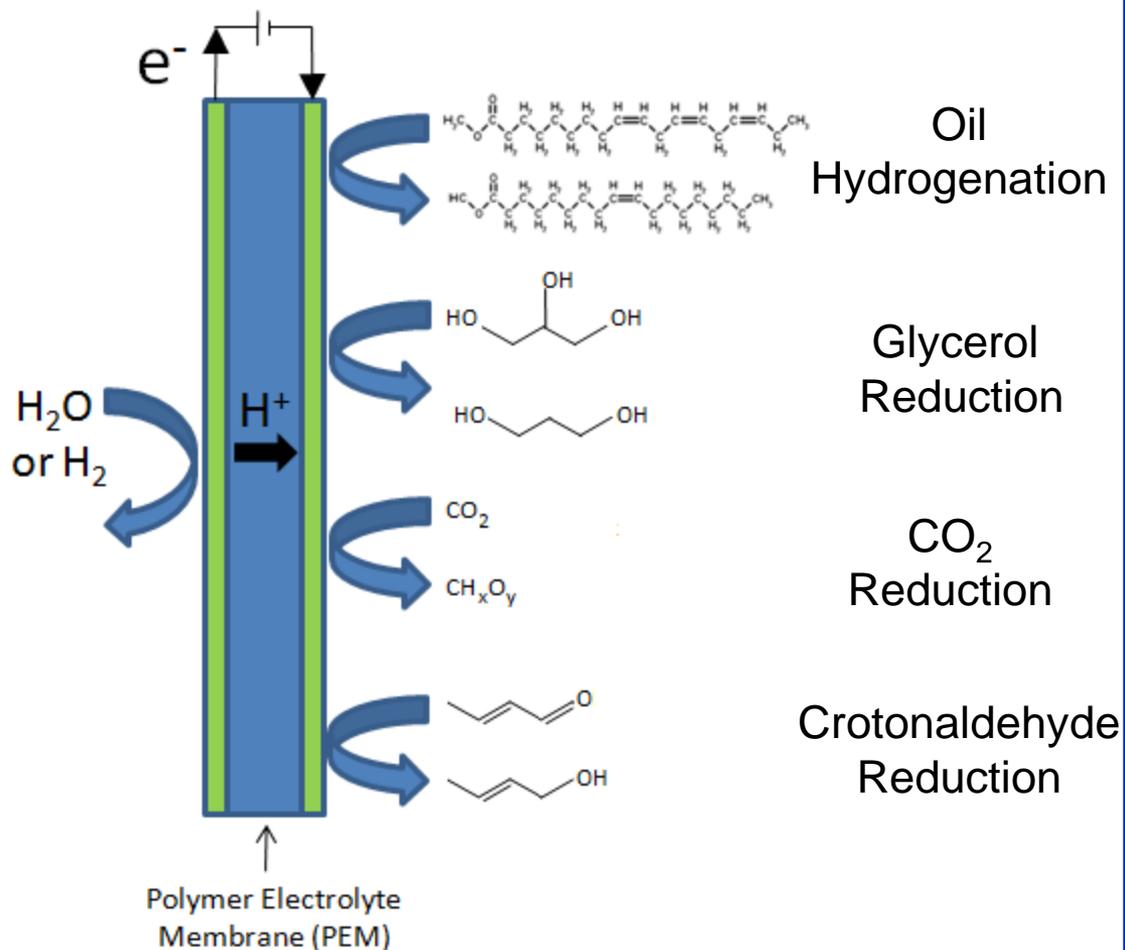
Multiple MEAs and flow distributors are arranged in series for a high electrode surface area “bipolar stack” design.



Solid Polymer Electrolyte Reactor

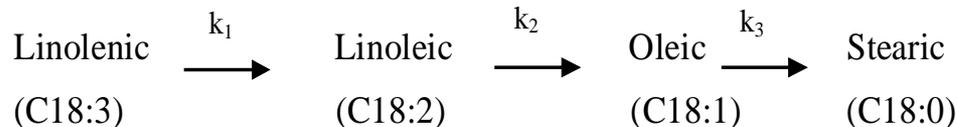
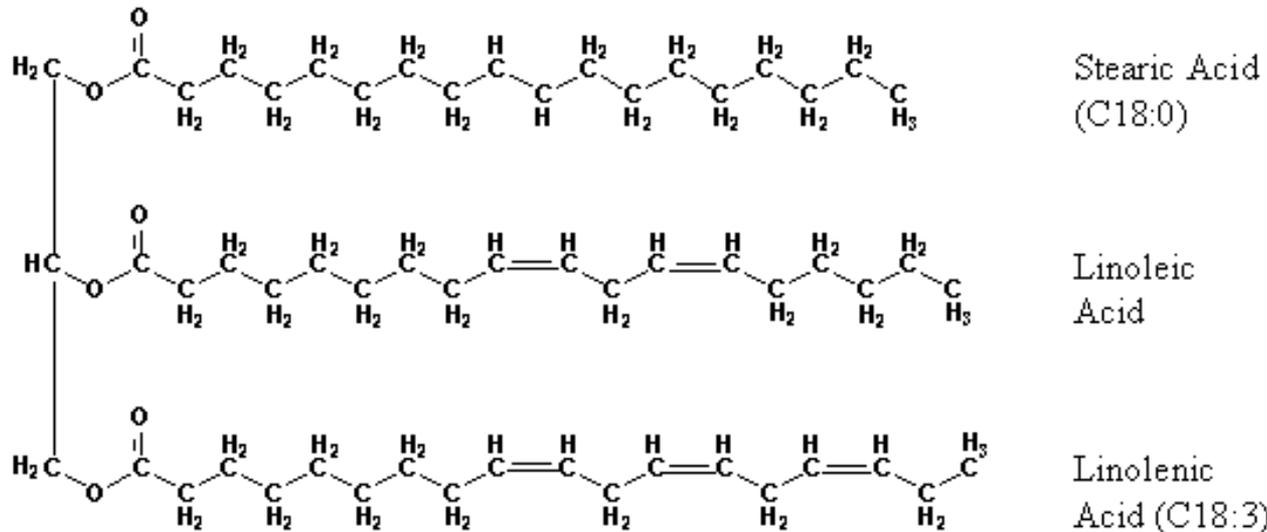
(slide from Prof. Levi Thompson)

- Mild temperatures and pressures
- Use electricity from renewable energy sources
- Reduced downstream separation and purification processes
- Can carry out thermodynamically unfavorable reactions by shifting the equilibrium
- Can use H_2O or H_2 as a hydrogen source



The Electrocatalytic Hydrogenation of Olefins – Unsaturated Fatty Acids in Soybean Oil

The goal of an oil hydrogenation reaction: Reduce the level of 18:3 fatty acids and increase the product melting point by decreasing the concentration of unsaturates (normally, an additional goal is to minimize the concentration of saturated stearic acid)



Reactor Operating Conditions

Electrodes: Pd-black or Pt-black cathode (for oil hydrogenation)
Pt-C (H₂ oxidation) or RuO₂ (water oxidation) anode

Cation-Exchange Membrane: DuPont's Nafion® 117

Electrode Area: single MEA (4 cm² or 25 cm²)

Gas Diffusion Layers: E-Tek, Inc. carbon cloth or Toray carbon paper

Applied Current Density: 0.10 - 0.20 A/cm²

Temperature: 50-120°C

Pressure: 1-4 atm.

Target Hydro-Oil Iodine Value (IV): 60-110 (17-55% reduction in the number of double bonds)

Reactor Operation: Batch recycle mode (small reactor, holding tank, and recirculation pump) with RBD soybean oil, IV 132 (from C&T Refinery, Charlotte, NC)

Analysis of Experimental Data

Reactor Operation:

Current Efficiency (CE)

$$\text{CE}(\%) = \frac{\text{moles of oil double bonds hydrogenated}}{\text{total moles of H generated at the cathode}} \times \frac{100}{2}$$

Production Rate (PR) and Power Consumption (PC) for fatty acid hydrogenation

$$\text{PR} = i \left(\frac{\text{CE}}{100} \right) \left(\frac{1}{\left[\frac{\Delta IV}{IV_{\text{init}}} \right] \times 1.054 \times 10^6} \text{ kg / C} \right) \times (1 \times 10^4 \text{ cm}^2 / \text{m}^2) (3600 \text{ s / h})$$

(1.054 x 10⁶C is the charge required to fully saturate one kilogram of soybean oil)

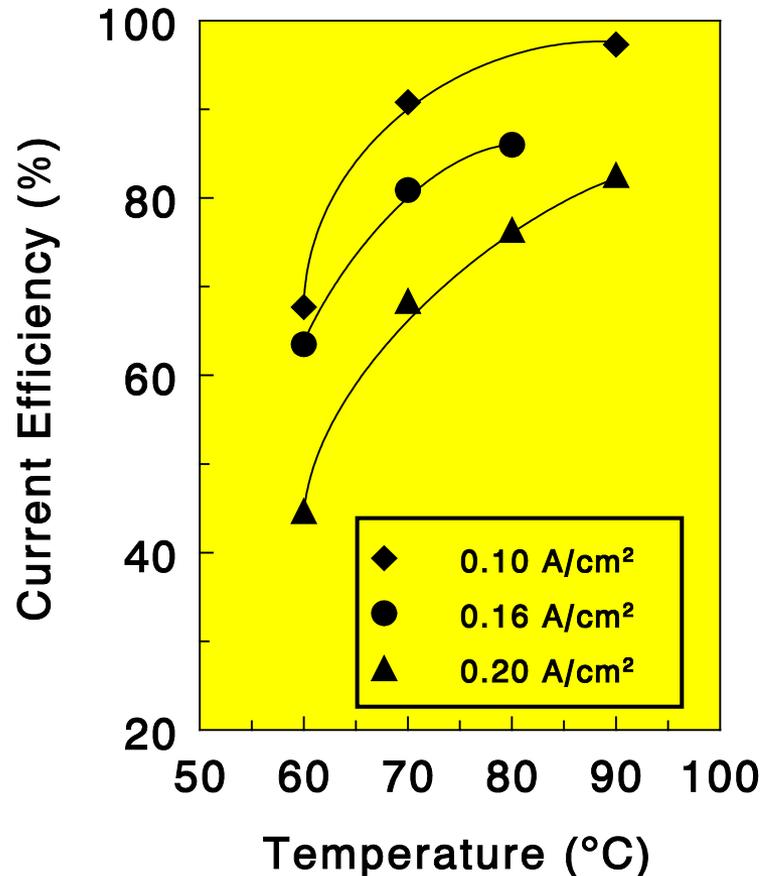
$$\text{PC} = \frac{i V (2.78 \times 10^{-7} \text{ kWh / J}) (1 \times 10^4 \text{ cm}^2 / \text{m}^2) (3600 \text{ s / h})}{\text{PR}}$$

Reactor Performance with H₂ Gas and Water Feeds

Cathode	T (°C)	Fatty Acid Profile				IV (132)	Cell V	CE(%)	% trans
		C18:0 (4%)	C18:1 (24%)	C18:2 (53%)	C18:3 (7.3%)				
Hydrogen Gas as the Anode Feed, $i=0.20$ A/cm²									
Pd	60	22	30	33	3.8	94		45	9.2
Pd	70	22	30	33	3.7	92	0.25	68	10.5
Pd	80	26	26	33	4.0	90		76	6.7
Pd	90	28	28	31	3.5	86		83	6.8
Water as the Anode Feed, $i=0.10$ A/cm²									
Pt	60	20	25	40	4.5	102	1.6	40	1.3
Pt	80	13	25	46	5.3	114	1.6	28	0.8
Pd	60	26	31	30	2.9	85	1.6	59	7.7
Pd	70	25	31	30	2.8	86	1.7	58	8.4
Pd	80	24	31	30	3	92	1.9	56	7.5
Chemical Catalytic Hydrogenation									
Ni	140	6	64	16	1.2	90			41

With water as the anode feed: (1) higher voltage drop and (2) lower hydrogenation current efficiency

Effect of Temperature and Current Density on Reactor Performance



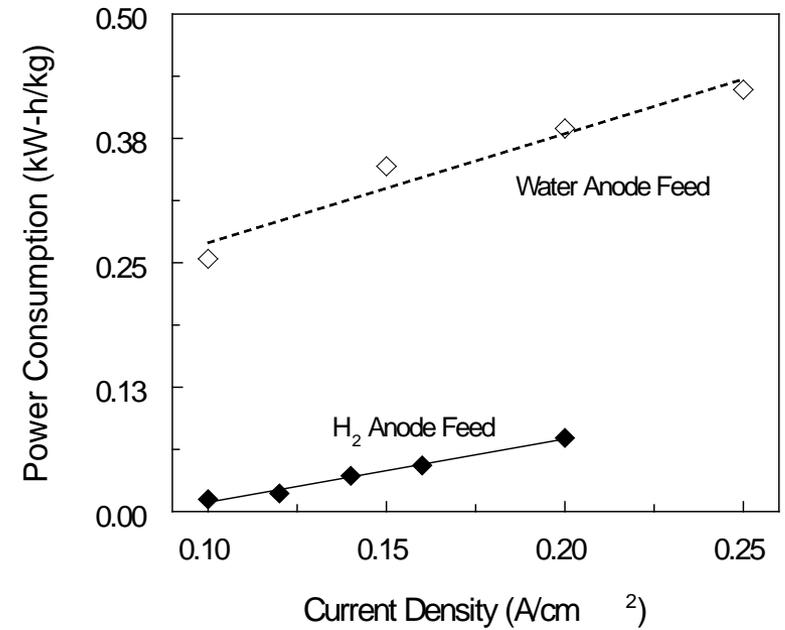
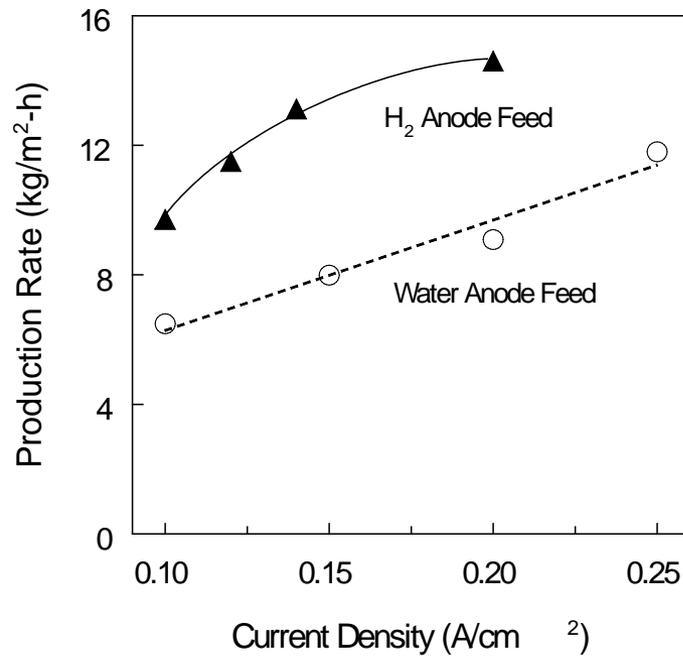
Pd-black cathode, 1 atm H₂ gas, 30 ml/min oil feed flow rate.

Oil product: a 32% reduction in double bonds

Current efficiencies with H₂ gas were always higher than those with water as the anode feed and source of H

Production Rate and Power Consumption

IV 90 soybean oil product



Hydrogenation Selectivity Studies – $i=0.10$ A/cm², 60°C, and water as the anode feed

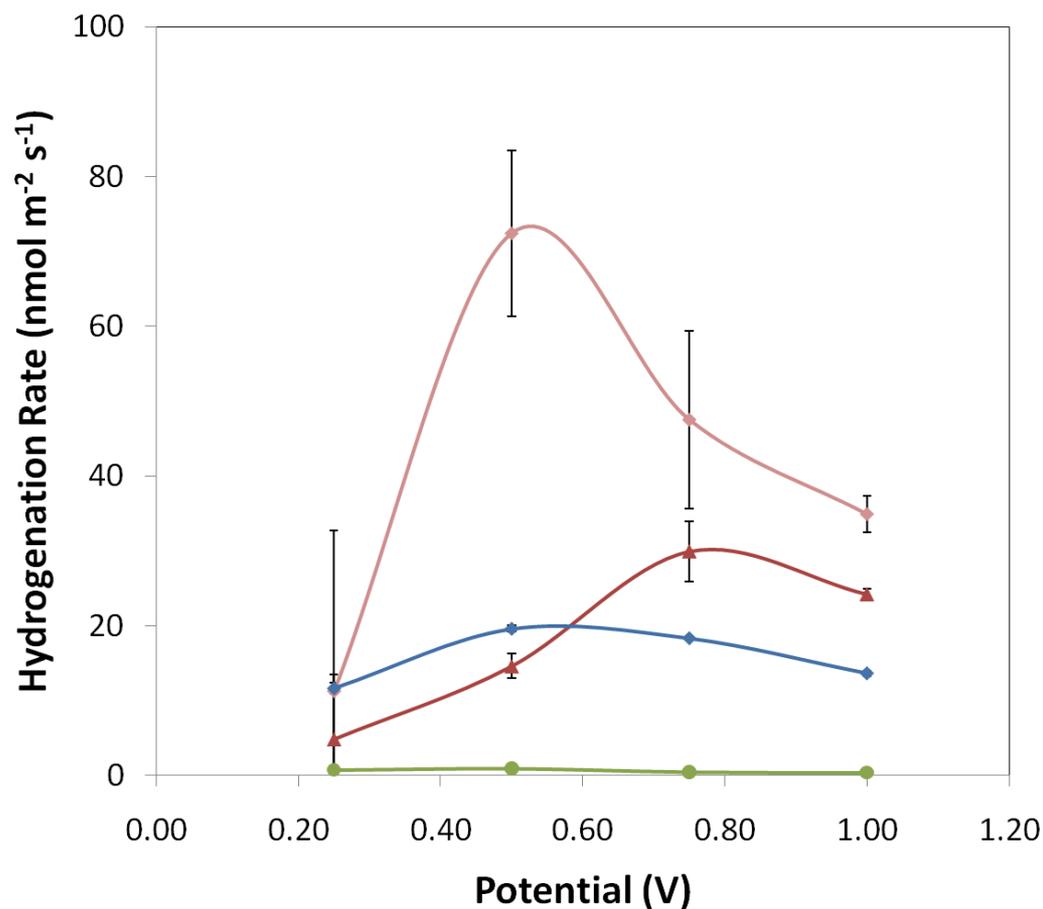
Cathode conditions	Fatty acid profile (%)				IV	% Trans isomers
	C18:0	C18:1	C18:2	C18:3		
Base case (2 mg/cm ² Pd-black cathode)	23.8	28.9	32.5	3.6	91	6.5
High oil flow rate with turbulence promoter	12.2	41.8	32.6	2.3	98	9.1
High oil flow rate, turbulence promoter and Pd-Co Cathode*	5.3	38.5	42.5	2.3	113	9.5

* Pd-Co cathode (1 mg/cm² each) was prepared by making a MEA with the Nafion membrane in the Co²⁺ counterion form. Before adding oil to the reactor, water was added to the anode and cathode and current was passed. H⁺ displaced Co²⁺ in the membrane and ferrous ions were deposited on the Pd.



Reaction Rates Depend on the Applied Current (Potential) and the Chemical Catalyst

Results from the lab of Prof. Levi Thompson



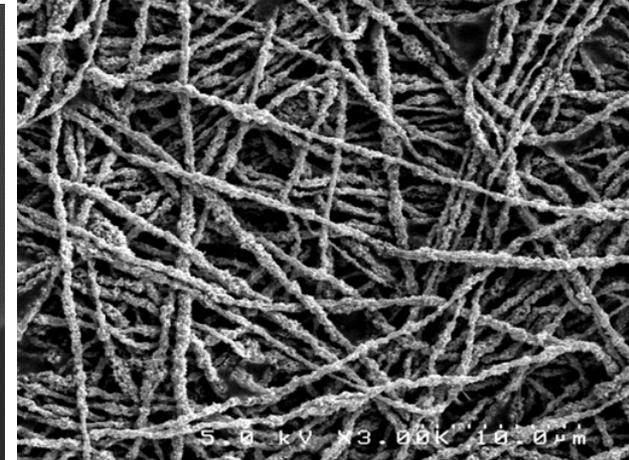
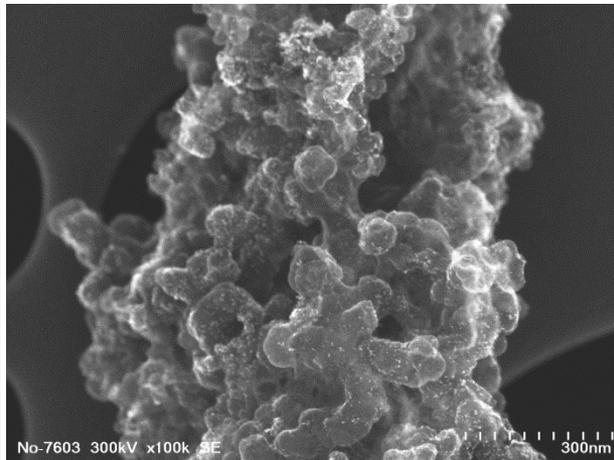
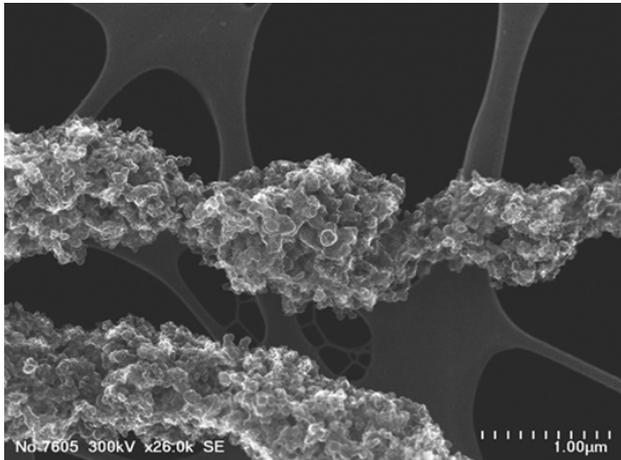
- **Pd/W₂C catalysts have high rates**
Hydrogenation rate is a strong function of potential

T = 70 ° C, P = 1 atm H₂, Flow rates = 100 mL min⁻¹ H₂ and oil
Anode: 1 mg/cm² 20% Pt/C Cathode: 1 mg/cm² various catalysts

Background – Nanofiber Electrodes

A particle/polymer nanofiber mat performs exceptionally well as a cathode in a H₂/air fuel cell. Such electrode designs can also be exploited for electrosynthesis in a SPE reactor

- Low Pt loading (0.05-0.10 mg/cm²)
- Excellent long-term durability (after accelerated carbon corrosion tests)
- Commercial Pt/C catalyst (Johnson-Matthey and TKK) with a Nafion + poly(acrylic acid) binder



From Karren More, ORNL

Nanofiber Composition

65-72 wt.% Pt/C

13-23 wt.% Nafion

12-15 wt.% PAA

W. Zhang and P. N. Pintauro, “High Performance Nanofiber Fuel Cell Electrodes”, *ChemSusChem*, **4**, 1753-1757 (2011).

M. Brodt, R. Wycisk, and P. N. Pintauro, “Nanofiber Electrodes with Low Platinum Loading for High Power Hydrogen/Air PEM Fuel Cells”, *Journal of the Electrochemical Society*, **160**, F744-F749 (2013). 21



Conclusions

Electrochemistry can be used indirectly to hydrogenate organic substrates at moderate temperatures, at high current densities, and with high current efficiencies (minimal current lost due to H₂ generation).

Use chemical catalysts to perform the hydrogenation

Use electrochemistry to generate H on the chemical catalyst surface

Carry out the reaction in a solid polymer electrolyte reactor (a fuel cell run in reverse)

No need for a supporting electrolyte

No need for a solvent, for liquid organic reactant/product

High electrode contact area for vapor phase organic reactants

This technology seeks to exploit the intersection of electrochemistry and chemical catalysis.

SPE reactors and electrocatalytic reactions can/should be utilized for a reversible hydrogen carrier organic liquid fuel systems, to achieve high current density operation for high yield and reversible reactions.

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