Liquid Fuel Cells: A Promising Power for a Prosperous Future

By

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Outline

- **Sustainability**
- **Energy Services & Climate Change**
- **Fuel Cells**
  - Motivation, features and applications
  - HFCs (H_2/O_2 FCs) – challenges
- **DFAFCs & FAO**
  - Mechanism, Catalyst's poisoning & Kinetic enhancement outlook
  - FeOx/Au/Pt/GC nanoanode
  - Activity & Stability
  - Mechanism
- **Conclusion**

Sustainability

Sust. Society

is one that meets the needs of the **current generation** without sacrificing the ability to meet the needs of **future generations**.

Sust. Development

- is a strategic goal that can be reached using various approaches as "**Green chemistry**"

Green Chem. ***"Seek prevention, not cure"***

- designs chemicals and processes that generate and use fewer (or **preferably no**) **hazardous** substances.

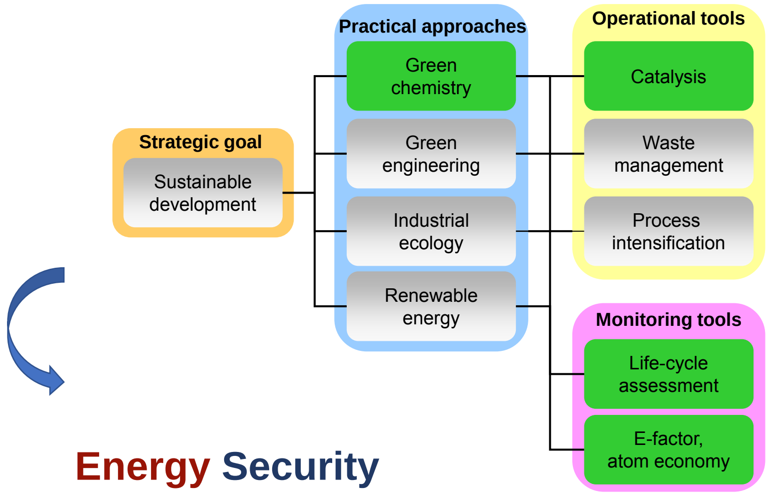
Transforming our world: the 2030 Agenda for Sustainable Development

September 2015 Plan of Action

17 Sust. Dev. GOALS

https://sdgs.un.org/2030agenda

Sustainability



Energy Security
Energy Equity
Environmental Protection

12 Principles of Green Chemistry

- Prevent **waste** instead of treating it.
- Design **atom-efficient** synthetic methods.
- Choose synthetic routes using **nontoxic** compounds where possible.
- Design new products preserving **functionality** while reducing toxicity.
- Minimize the use of **auxiliary** reagents and solvents.
- Design processes with **minimal energy** requirements.
- Preferably use **renewable** raw materials.
- Avoid unnecessary **derivatization**.
- Replace stoichiometric reagents with **catalytic cycles**.
- Design new products with **biodegradable** capabilities.
- Develop **real-time** & **on-line** process analysis & monitoring methods.
- Choose feedstocks and design processes that minimize the chance of **accidents**.

"Anastas, P.T. and Warner, J. (2000) Green Chemistry: Theory and Practice, Oxford University Press, ISBN 0-19-850698-8,

Quantifying Environmental Impact

- When are processes and products claimed to be "**efficient**", "**green**", "**environmentally friendly**", and "**Eco-friendliness**"?

Reactant conversion

- fraction of reactant molecules that have transformed to product molecules (regardless of which product it is).

Selectivity to a product P

- is the fraction (or percentage) of the converted reactant that has turned into this specific product P

$$\text{Yield of P} = \text{Conversion} \times \text{Selectivity of P}$$

- High conversions in short time ≡ smaller and safer reactors.
- High selectivity ≡ less waste, simpler & cheaper separation units.

E-factor

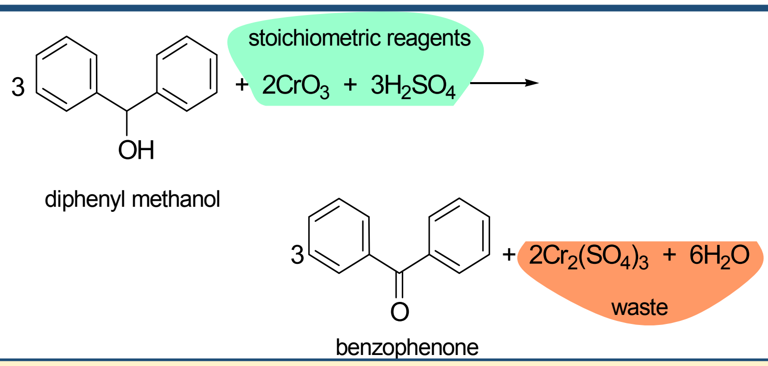
- is the quotient **$kg_{waste}/kg_{product}$**
- "**waste**" is everything (CO_2 or NO_x, water, common inorganic or heavy metal salts, and/or organic compounds) formed in the reaction except the desired product.

Atom Economy

- It refers to **how many** and **which** atoms of the reactants are incorporated into the products.

Gadi Rothenberg, Catalysis: Concepts and Green Applications 2008 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

Oxidation of diphenylmethanol to benzophenone



- Even for 100 % yield & selectivity, for every kilogram of benzophenone we generate 0.717 kg of chromium sulfate and 0.197 kg of water.

$$E - factor = (0.717 + 0.197)/1 = 0.914$$

Energy Services

- **Measure**
  - **A country's economic development.**
- **Essential for**
  - **clean water**
  - **Sanitation**
  - **Healthcare**
  - **Lighting**
  - **Heating**
  - **Cooking**
  - **Mechanical power**
  - **Transportation**
  - **Telecommunications**

In 2010

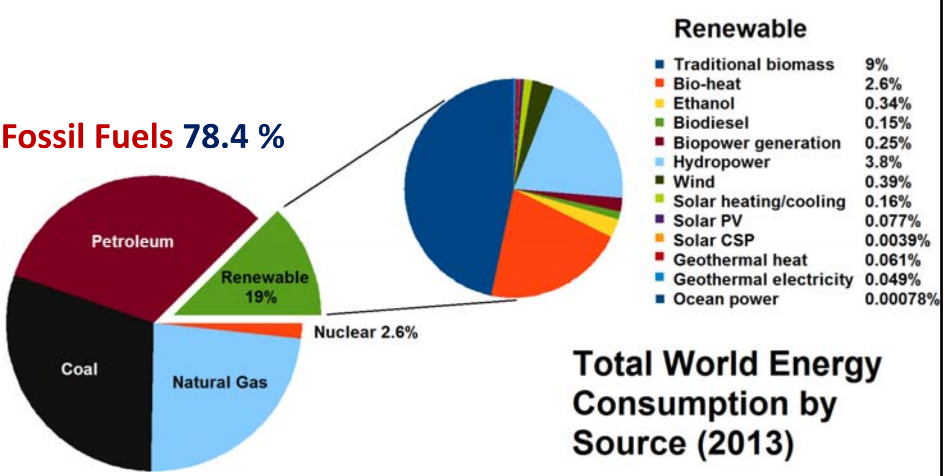
- **1.2 billion people are without access to electricity**
- **More than 2.7 billion people rely on the traditional use of biomass for cooking**

http://www.worldenergyoutlook.org/resources/energydevelopment/

Impact

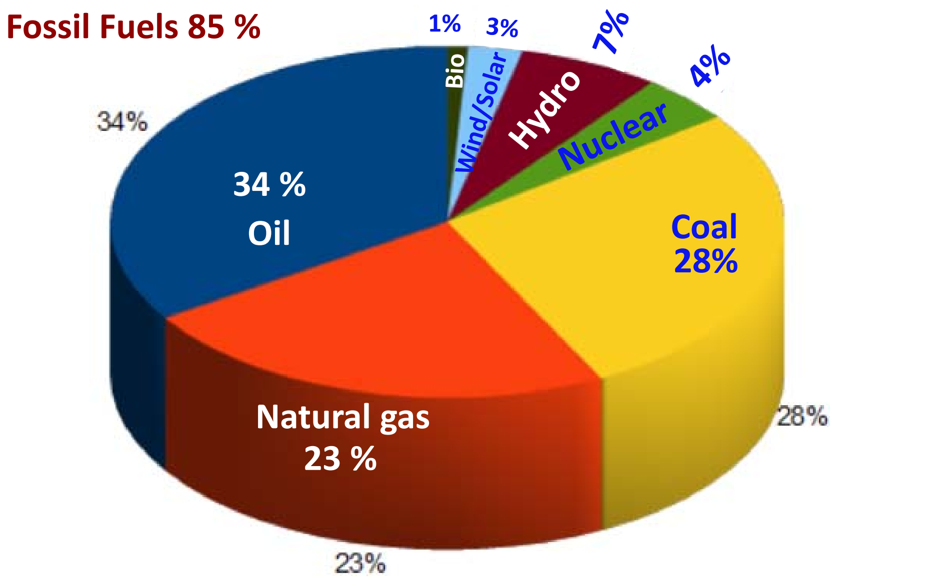
World Energy Consumption 2013

Fossil Fuels 78.4 %



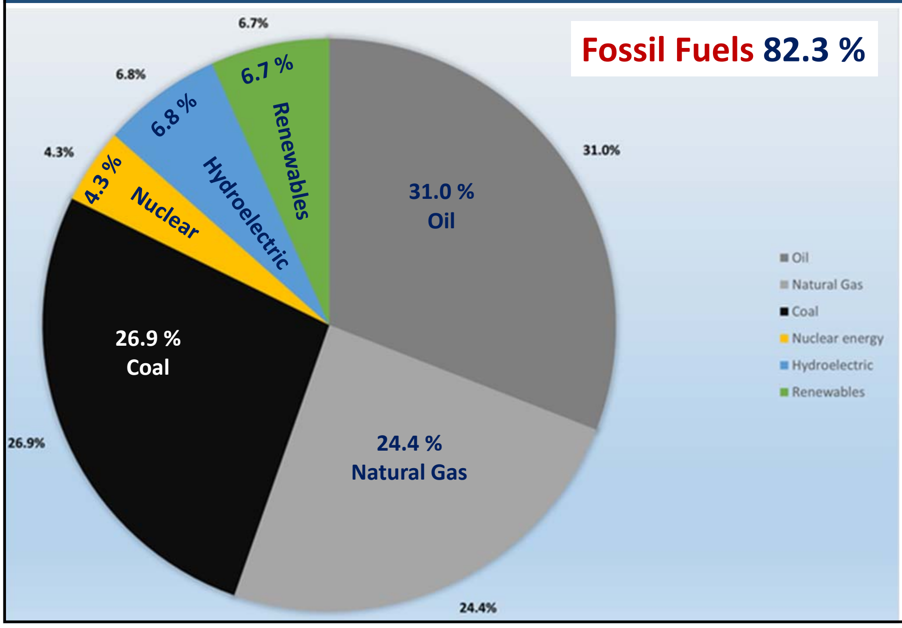
https://commons.wikimedia.org/wiki/File:Total_World_Energy_Consumption_by_Source_2013.png

World Primary Energy Consumption 2017



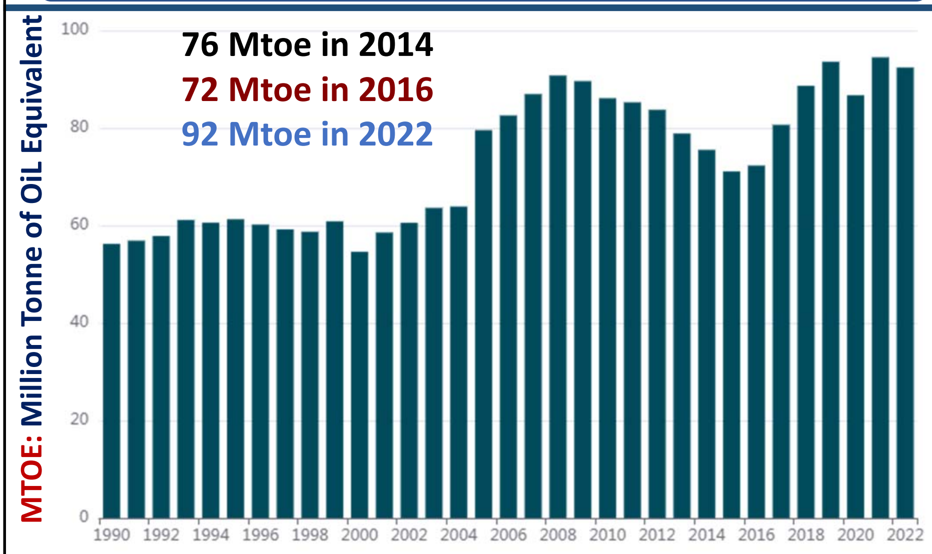
https://notalotofpeopleknowthat.wordpress.com/2018/06/15/bp-energy-review/

World Energy Consumption 2021



BP Statistical Review 2022

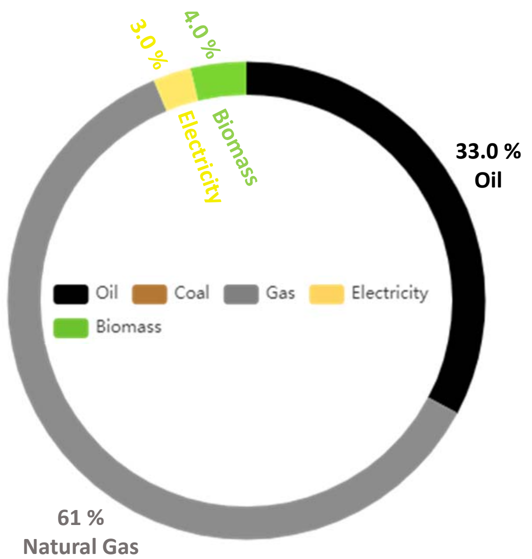
Total Energy Production in Egypt



1 toe = 11.63 megawatt-hours (MWh)
= 41.868 gigajoules (GJ)

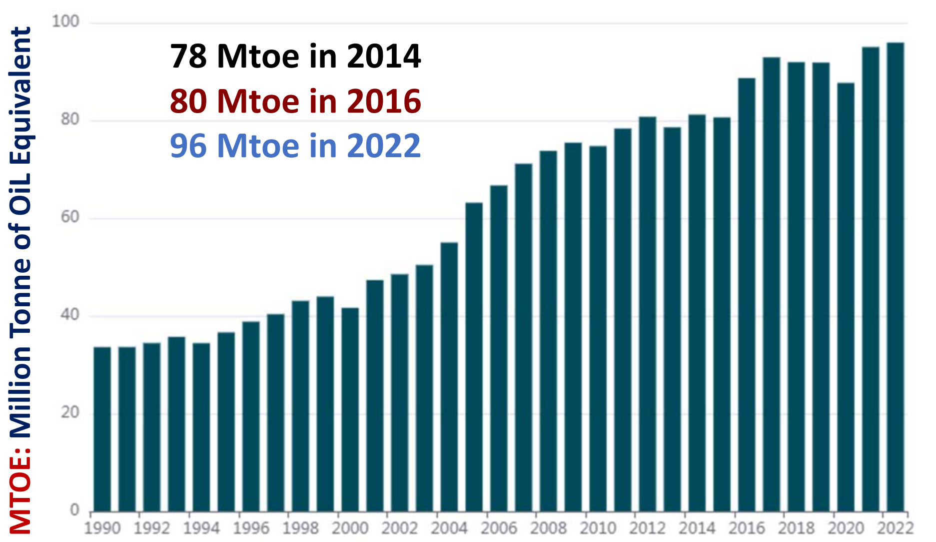
https://yearbook.enerdata.net/

Total Energy Production in Egypt



https://yearbook.enerdata.net/

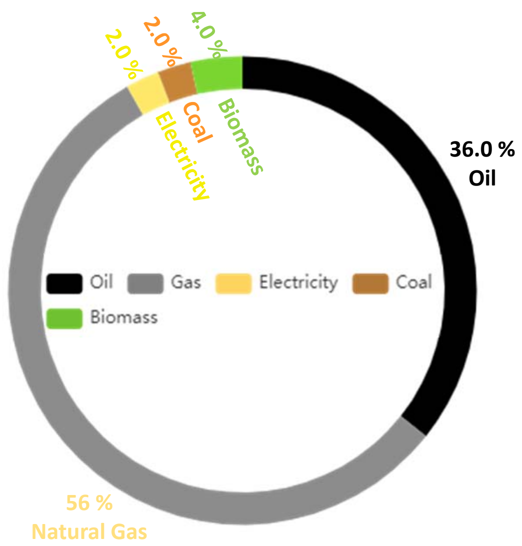
Total Energy Consumption in Egypt



4 Mtoe in 2022 Shortage

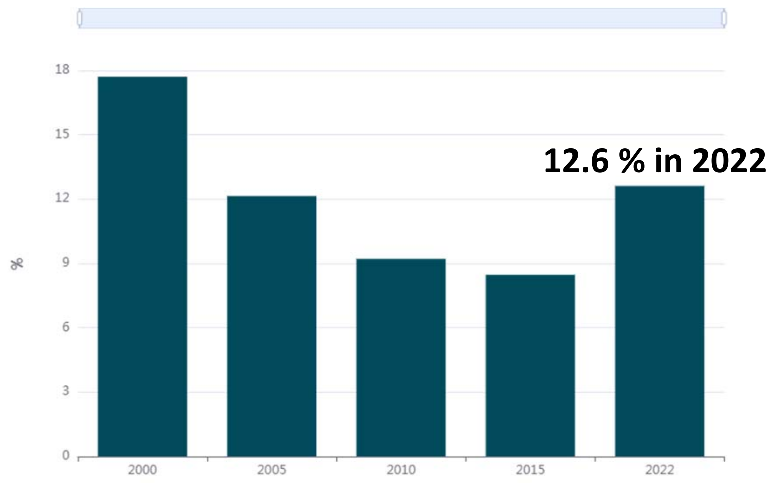
https://yearbook.enerdata.net/

Total Energy Consumption in Egypt



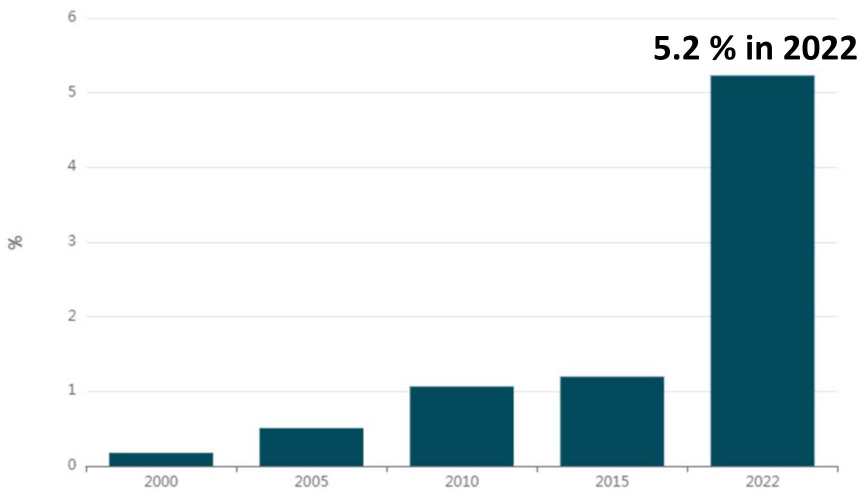
https://yearbook.enerdata.net/

Share of renewables in electricity production (incl. hydro)/Egypt



https://yearbook.enerdata.net/

Share of wind and solar in electricity production/Egypt



https://yearbook.enerdata.net/

Fossil fuels & Carbon emission

Non-renewable

Rapidly Depleted

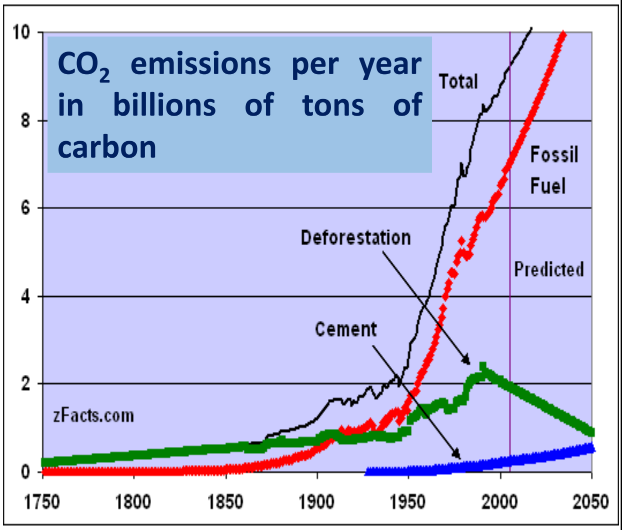
Little efficiency

Risky polluting

Noisy operation

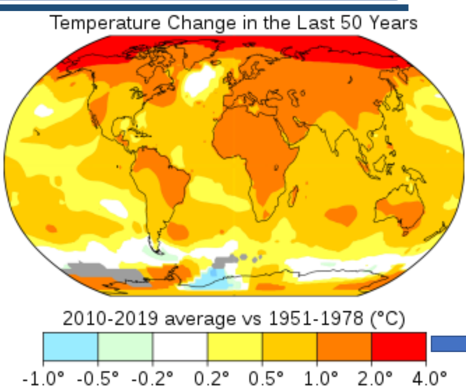
Huge Infra structure

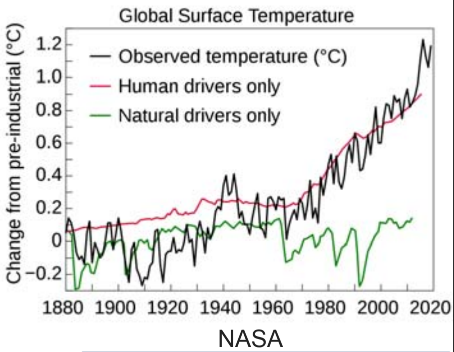
Climate Change



CO_2 emissions in 2014 ca. 7×10^{12} kg carbon/year

Climate change

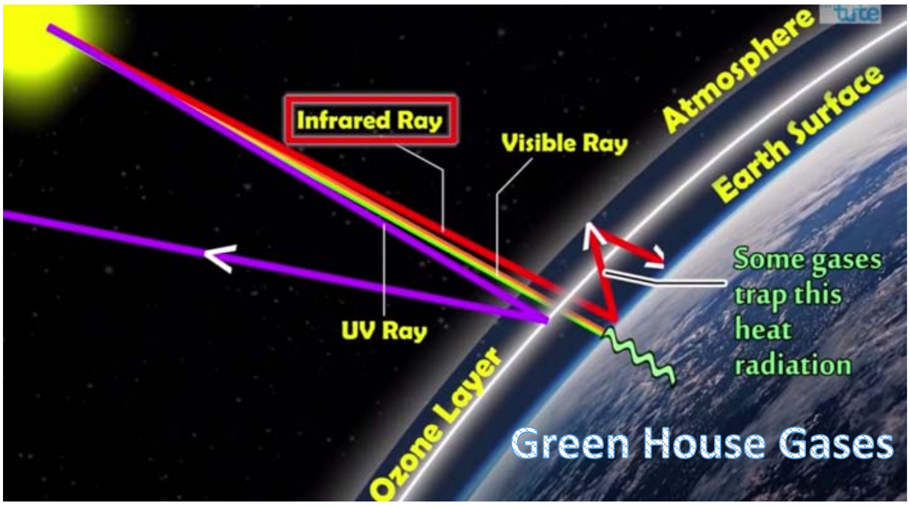




2016 UN conference in Marrakech

"The unprecedented momentum to combat **climate change** has to be irreversible and should be dealt as a matter of urgent priority"

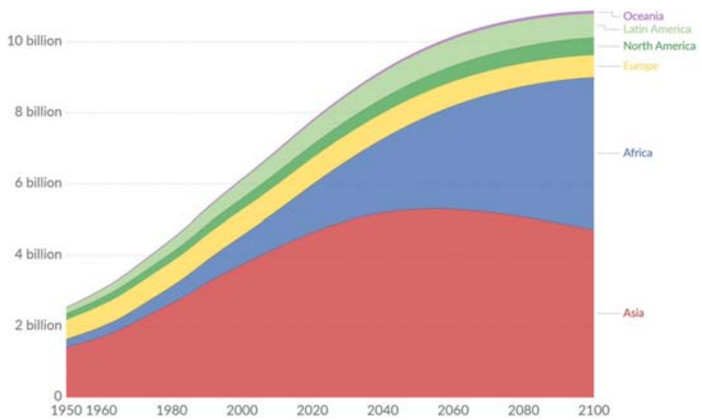
Green house effect



- CO_2
- H_2O vapor
- CH_4
- Chloroflouro Carbons

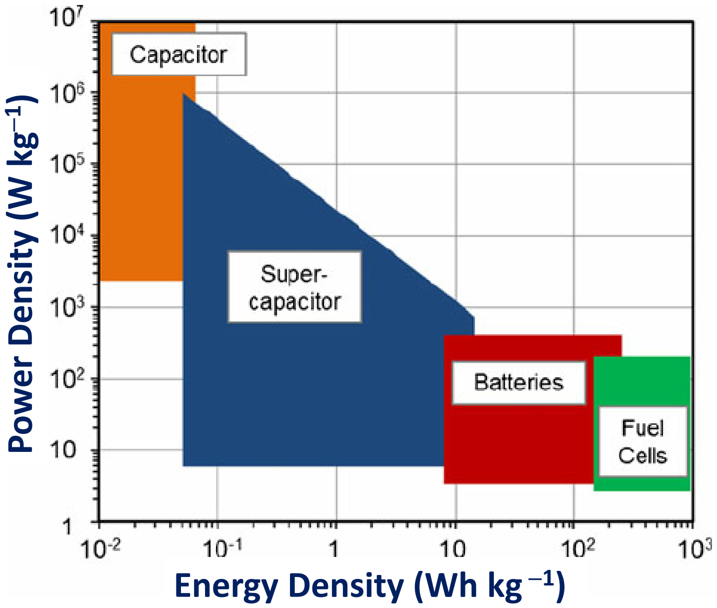
World population by region projected to 2100

World Energy Crisis



Ragone plot

Performance comparison of various energy-storing devices



Fuel Cells

- Enhanced Efficiency
- Reliability
- Robustness
- Safety
- Moving flexibility
- Low emissions (Clean Energy)
- Less Noisy
- Long-lasted
- Easily installed
- Economic

Efficiency

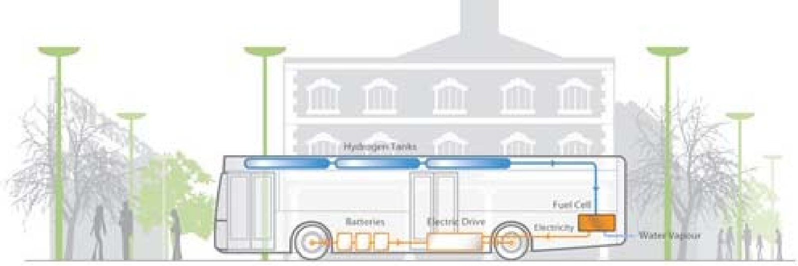
- Up to 60% in electrical energy conversion
- Up to 80% of electricity and heat

Emissions

- Up to 90% reduction in major pollutants

FCs are recommended for several stationary, portable and emergency backup power applications

Applications/ transportation



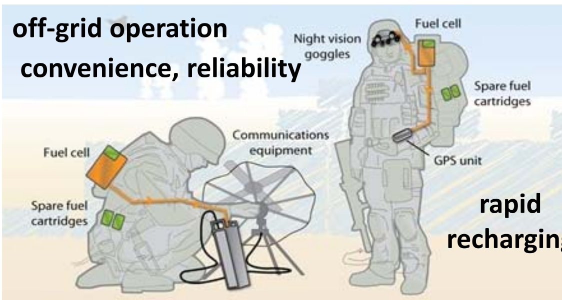
- Forklift trucks: airport baggage trucks etc
- Two- and three-wheeler vehicles such as scooters
- Light duty vehicles (LDVs), such as cars and vans
- Buses and trucks
- Trains and trams
- Ferries العبارات and smaller boats, Manned light aircraft
- Unmanned aerial vehicles (UAVs) طائرات بدون طيار and unmanned undersea vehicles (UUVs), for example, for reconnaissance استطلاع

Applications/ Portable (>5 W up to 500 kW)

- Military applications (portable soldier power, skid mounted fuel cell generators etc)

off-grid operation

convenience, reliability



rapid recharging

lower operating costs

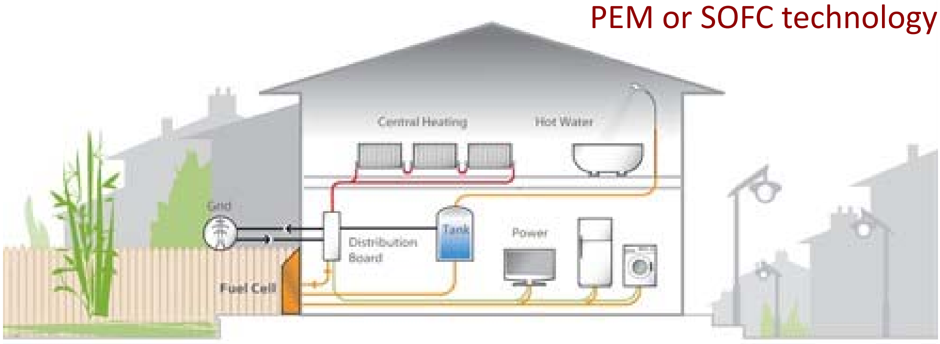
longer run-times compared with batteries

significant weight reduction

- Auxiliary Power Units (APU) (e.g. for the leisure راحة and trucking industries),
- Portable products (torches, vine trimmers المحراث etc)
- Small personal electronics (mp3 players, cameras etc)
- Large personal electronics (laptops, printers, radios etc),
- Education kits and toys.

Applications/ Stationary (0.5 – 10 kW)

PEM or SOFC technology



- Combined heat and power (CHP): overall efficiencies of 80-95%
- Uninterruptible power systems (UPS) : e.g., residential use.
- Primary power units

http://www.fuelcelltoday.com/applications/

Distributed Generation Systems, DGS

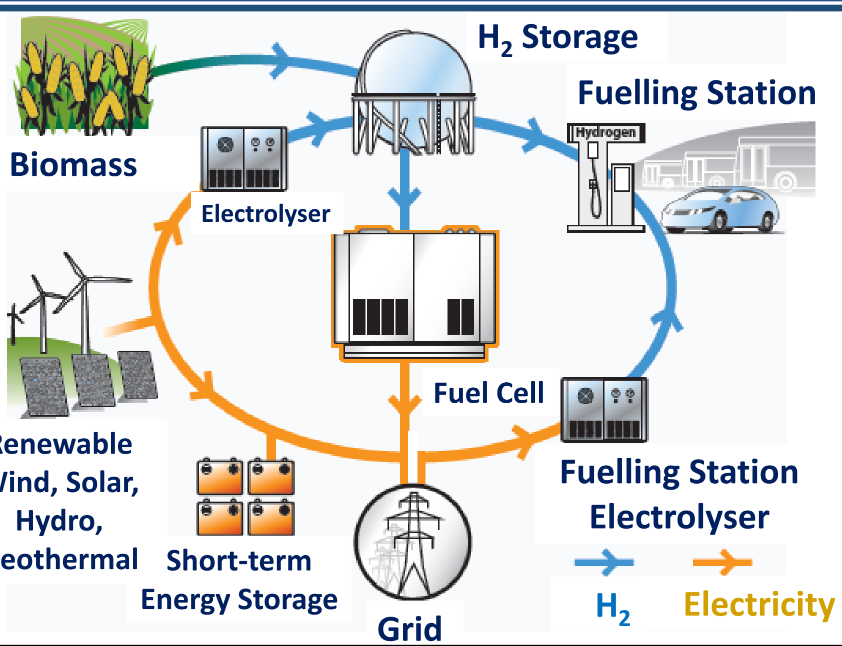
Generation systems located near the consumer not far away or central

- During transmission, distribution, and transformation, energy losses may exceed 32 %.

DGS saves

- Energy losses over long transmission and distribution lines
- Installation costs
- local voltage regulation
- Ability to add a small unit instead of a larger one during peak load conditions.

Electricity Storage in Renewable Plants



Generation Systems: Comparison

	Reciprocating Engine	Diesel Turbine	Photo Voltaics	Wind Turbine	FCs
Capacity range	500 kW – 5 MW	500 kW – 25 MW	1 kW – 1 MW	10 kW – 1 MW	200 kW – 2 MW
Efficiency %	35	29 – 42	6 – 19	25	40 – 60
Capital cost ($/kW)	200 – 350	450 – 870	6600	1000	1500 – 3000
O&M cost ($/kW)	0.005 – 0.015	0.005 – 0.0065	0.001 – 0.004	0.01	0.0019 – 0.0153

FCs' Types

Based on the operating T

- **Low-temperature FCs: < 130°C**
  Alkali AFCs, proton exchange membranes PEMFCs, and phosphoric acid PAFCs FCs.
- **High-temperature FCs: (500–1000°C),**
  Molten carbonate (MCFCs) and Solid oxide (SOFCs) FCs

Based on the electrolyte nature

- **Solid** (polymer or ceramic) **electrolyte** (PEMFCs, SOFCs)
- **Liquid (aqueous or molten) electrolyte** (PAFCs, AFCs, MCFCs)

PEMFCs

- High power density,
- Fast start-up system,
- Low operation temperature,
- Low emissions,
- System robustness (the ability to withstand or overcome adverse conditions or rigorous testing)
- Ease transportation and storage
- High scalability

→ Electric vehicles & portable applications

Electric Vehicles

Toyota FCEV

- In Japan on December 15, 2014
- Travel up to 300 miles on a single tank of hydrogen

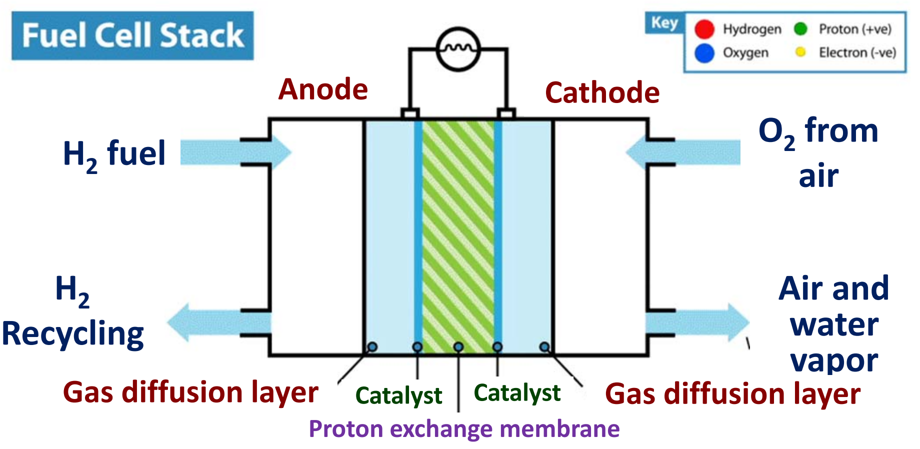
Honda FCV

- March 2016
- 70 MPa high-pressure hydrogen storage tank
- Travel up to 430 miles on a single tank of hydrogen

H_2 Fuel Cell Buses

Mercedes-Benz Fuel Cell Bus (O530) 2007–11

PEMFCs Components– H_2/O_2 FCs



Membrane electrode assembly (MEA):

- **Membrane**
- **Catalyst layers**
- **Gas diffusion layers (GDLs)**

Anode	$H_2 \rightarrow 2H^+ + 2e^-$	$E^o = 0$ V
Cathode	$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	$E^o = 1.229$ V
Overall	$2H_2(g) + O_2(g) \rightarrow 2H_2O\ (l)$	$E^o = 1.229$ V

Challenges H_2/O_2 FCs

- High cost of miniaturized hydrogen containers
- Potential risk in hydrogen
  - Using (H_2/air explosion)
  - Storing
  - Transporting
- Low gas-phase energy density

Energy Density = 0.017 MJ/m³

Liquid Fuels

Fuels?

Anything that can be oxidized at an electrode

e.g., gasoline; diesel and biodiesel; jet propellant (JP-8, JP-5); methane (natural gas); propane; biogas; ammonia; methanol ; ethanol ; butanol, etc.

Selection Criteria

- availability
- cost
- toxicity
- calorific value
- storage (gravimetric and volumetric density)
- fuel cell performance
- effect on performance degradation
- phase (solid, liquid, gas)
- water content (or other non reacting species such as CO_2)
- purity
- security of supply, carbon content, etc.

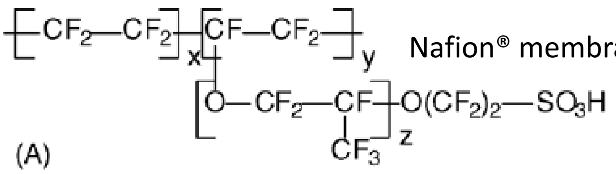
membranes?

Selection Criteria

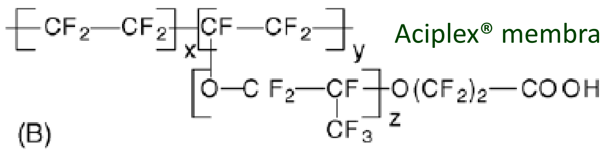
- Chemical and Electrochemical Stability
- Mechanical Strength and Stability
- Compatibility (good adhesion) to FCs components
- Extremely **low permeability** to reactants (H_2 , methanol, O_2) to maximize Coulombic efficiency
- High electrolyte transport to maintain uniform electrolyte content and to prevent local **drying**.
- High **proton conductivity** to support high currents with minimal resistive losses and **zero electronic conductivity**;
- Production **costs** compatible with the intended application.

Perfluorosulfonic acid polymer membranes

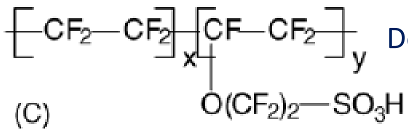
Derivatives of polytetrafluoroethylene (PTFE) possessing perfluoroether side chains with sulfonic acid end groups



Nafion® membrane (x = 6–10, y = z = 1)



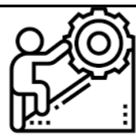
Aciplex® membrane (x = 6–8, y = 0–1, z = 1)



Dow® membrane (x = 3–10, y = 1)

Jochen Meier-Haack et al., Separation and Purification Technology 41 (2005) 207–220

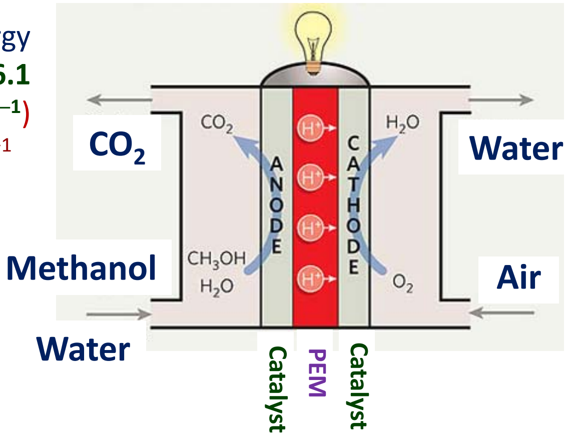
Challenge of Nafion



- High methanol **crossover**: even at low methanol concentrations, leading to a loss of coulombic efficiency and depolarization of the oxygen electrode reaction at the cathode.
- High **costs**: US \$ 600–700/m^2. Costs may be lowered if much thinner membranes are developed
- Operate only at **Low T** < 100°C.
  At higher T they dry out partially and lose their high proton conductivity.

Methanol/O_2 FCs

- High energy density (**6.1 kWh kg^{-1}**) 4.9 kWh L^{-1}

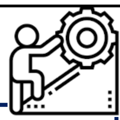


- Impressive hydrogen content
- Easy handling

Anode	$CH_3OH(aq) + H_2O(aq) \rightarrow CO_2(g) + 6H^+(aq) + 6e^-$	$E^o = 0.032$ V
Cathode	$3/2\,O_2(g) + 6H^+(aq) + 6e^- \rightarrow 3H_2O(l)$	$E^o = 1.229$ V
Overall	$CH_3OH(aq) + 3/2\,O_2(g) \rightarrow CO_2(g) + 2H_2O\ (l)$	$E^o = 1.197$ V

http://www.machine-history.com/Direct%20Methanol%20Fuel%20Cell

Challenge of DMFCs



- **Inherent toxicity**
- **Water Management**
  - dilution of the fuel ≡ lowering in Energy density
  - Water loss via **crossover** under electro-osmotic drag and molecular diffusion through the membrane
- **High fuel crossover through Nafion-based membranes**
  - necessitates lower fuel concentration < 2M. Higher than this reduces fuel utilization and decreases cell performance
- **Slow oxidation kinetics which necessitates a T> 100◦C for**
  - Fast oxidation kinetics
  - Better CO tolerance (Fast desorption of poisoning CO)
- **Damage of Nafion® membranes:** They operate at **< 100ºC**. To avoid drying out and losing the high proton conductivity.

Formic Acid

promising for **low-T** PEMFCs

- Small organic molecule, highly available, easily ionizable
- Pungent odor (early warning signs of exposure)
- Low carbon content but high hydrogen capacity (ca. 4.4 % by mass)
- high volumetric hydrogen content (53 g L^{-1} under standard temperature and pressure)
- high specific energy (5.3 MJ kg^{-1})
- high volumetric energy density (6.4 MJ L^{-1} at ambient conditions)
- Low toxicity & low odor threshold (attention to leaks)
- Easy and safe storage
- Non-flammable at moderate concentrations
- Involves **2 e^-** in oxidation with cleavage of two bonds.

FA is a renewable chemical for H_2 storage

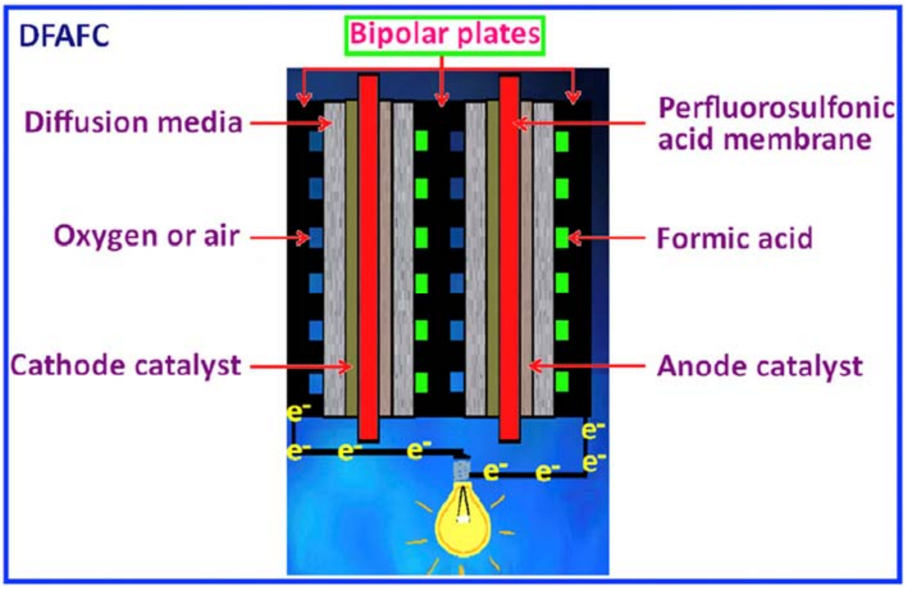
- **Dehydrogenation** of FA has a low ΔH_r; thus, H_2 can be produced from FA at moderate Ts **(< 100°C)**.
- less energy is required for H_2 production from FA
- **CO_2** (coproduct of FA dehydrogenation) can hydrogenate back to FA in water or organic solvents.
- FA can be a **renewable chemical** for H_2 storage

Formic Acid as a Hydrogen Carrier for Fuel Cells Toward a Sustainable Energy System, Advances in Inorganic Chemistry, Volume 70, 2017, Pages 395-427
https://doi.org/10.1016/bs.adioch.2017.04.002

FA is a renewable chemical for H_2 storage

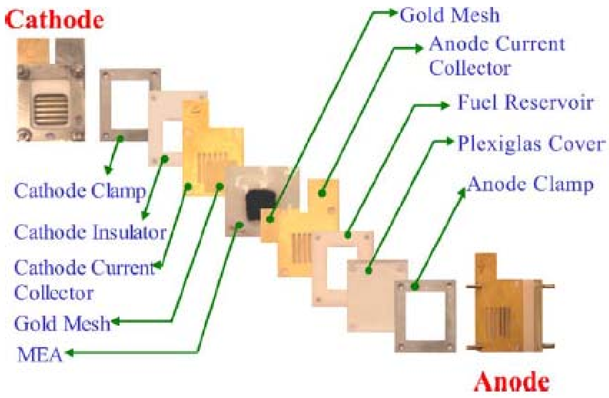
https://doi.org/10.1016/bs.adioch.2017.04.002	$\Delta_r H^0$ / $kJ\ mol^{-1}$	$\Delta_r G^0$ / $kJ\ mol^{-1}$
$HCOOH(l) \rightarrow H_2(g) + CO_2(g)$	+31.2	−33.0
$HCOOH(l) \rightarrow H_2O(l) + CO(g)$	+28.4	−13.0
$HCOOH(aq) \rightarrow H_2(g) + CO_2(g)$	+32.0	−43.2
$HCO_2NH_4(aq) \rightarrow H_2(g) + CO_2(g) + NH_3(g)$	+84.3	+9.5
$CH_4(g) + H_2O(g) \rightarrow 3H_2(g) + CO(g)$	+206.1	+140.9
$CO(g) + H_2O(g) \rightarrow H_2(g) + CO_2(g)$	−41.2	−28.6
$H_2O(l) \rightarrow H_2(g) + 1/2O_2(g)$	+285.8	+238.2
$NH_3(g) \rightarrow 3/2H_2(g) + 1/2N_2(g)$	+46.1	+16.5
$C_6H_{11}CH_3(l) \rightarrow 3H_2(g) + C_6H_5CH_3(l)$	+202.2	+93.3
$CH_3OH(l) + H_2O(l) \rightarrow 3H_2(g) + CO_2(g)$	+131.0	+9.0

DFAFCs



Miniature air breathing DFAFCs

2 cm × 2.4 cm × 1.4 cm DFAFCs at room temperature produced current density up to 250 mA/cm^2 and power density up to 33 mW/cm^2 at ambient conditions



- It runs successfully with formic acid concentration ranging from **1.8 and 10** M with little degradation in performance.

S. Ha et al. / Journal of Power Sources 128 (2004) 119–124

DFAFCs

- Easy handling
- Small crossover
  - Repulsion between $HCOO^-$/sulfuric gr. of Nafion
  - Allow high concentrated fuel and thinner membranes
- FA has a less poisoning impact to Pt-based electrocatalysts.
- DFAFCs have a higher theoretical open-circuit potential (1.48 V) than that of hydrogen fuel cells (1.23 V) and DMFCs (1.21 V).

DFAFCs

Anode

$$HCOOH(aq) \rightarrow CO_2(g) + 2H^+(aq) + 2e^- \qquad E^o = -0.25\ V$$

Cathode

$$1/2\ O_2(g) + 2H^+(aq) + 2e^- \rightarrow H_2O(l) \qquad E^o = 1.229\ V$$

Overall

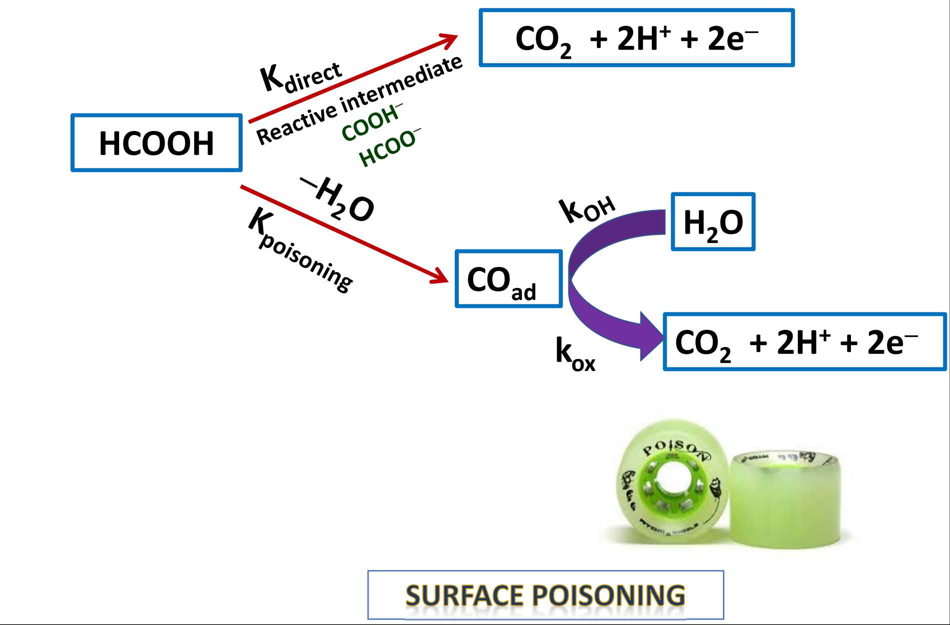
$$HCOOH(aq) + 1/2\ O_2(g) \rightarrow CO_2(g) + H_2O\ (l) \quad E^o = 1.48\ V$$

Challenge in DFAFCs

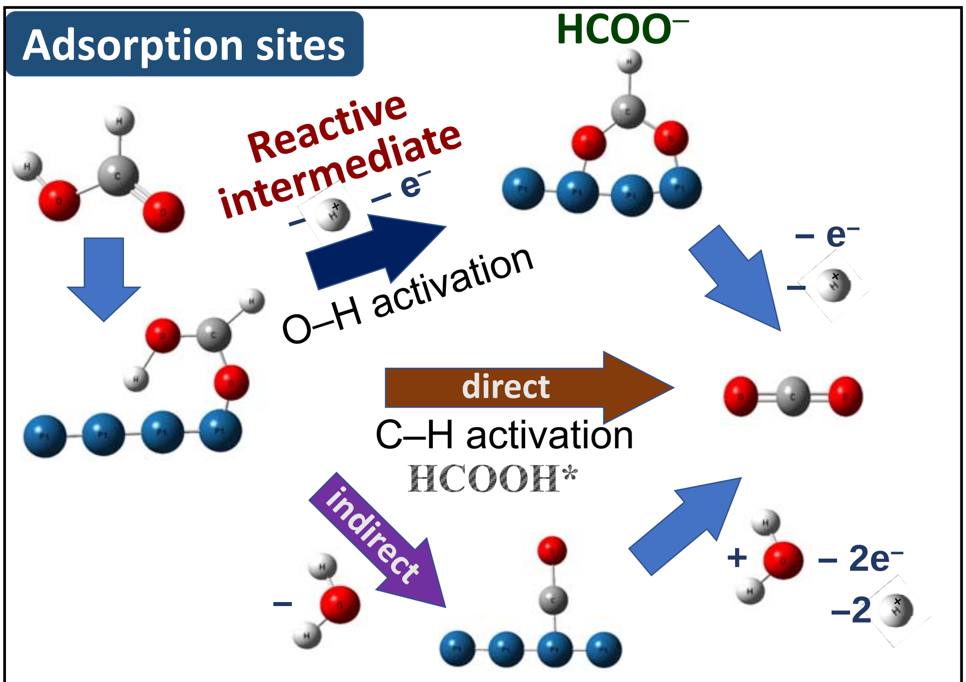
- Low (2,104 Wh L^{-1}) volumetric energy density of formic acid if compared to methanol (4,900 Wh L^{-1}).
  - This deficiency in DFAFCs is compensated by the 6X reduction in crossover through the Nafion™ membrane, allowing substantially higher fuel concentrations. (5– 12 M FA) Vs. (1–2 M Methanol)
- Poisoning with the CO intermediate
  - resulting from the "non-faradaic" dissociation of FA at Pt surface

Development of Efficient and Stable Electrocatalysts is required

Formic Acid Oxidation on Pt surface

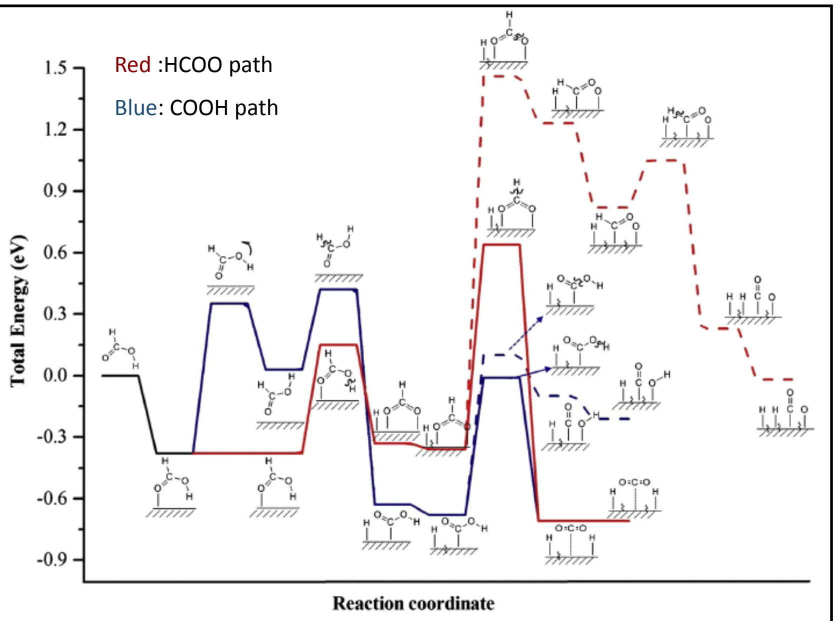


Adsorption sites



Gao et al. (2010), JACS doi:10.1021/ja1083317

Steps in FAO on Pt (1 1 1)



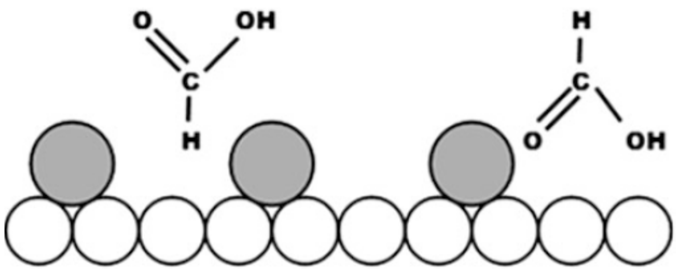
Solid red line: HCOOH*→HCOO*→CO_2*
solid blue line HCOOH*→COOH*→CO_2*
dashed red line: HCOOH*→HCOO*→HCO*→CO*
dashed blue line: HCOOH*→COOH*→CO*

HCOOH decomposition on Pt(111): A DFT study J. Scaranto, M. Mavrikakis / Surface Science (2015)

Mechanisms of Enhancement

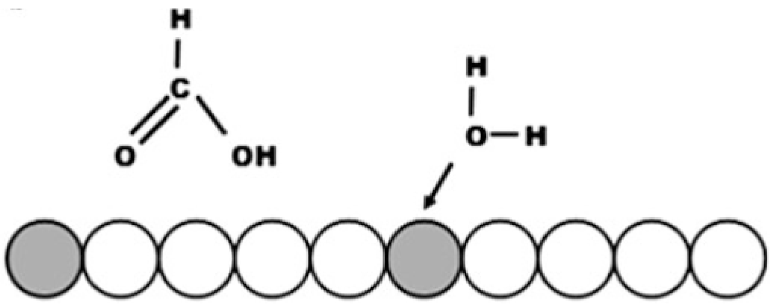
Ensemble or third-body effect

- adatoms or alloys to preferentially orient the adsorption mode (by steric hindrance) of FA in the CH-down direction (Dehydrogenataion Enhancement)



(Lecture Notes in Energy 9) Meng Li, Radoslav R. Adzic (auth.), Minhua Shao (eds.)-Electrocatalysis in Fuel Cells_ A Non- and Low- Platinum Approach-Springer-Verlag London (2013)

- **Bifunctional mechanism**
  - **increase availability of activated hydroxyl groups (Dehydration Enhancement)**

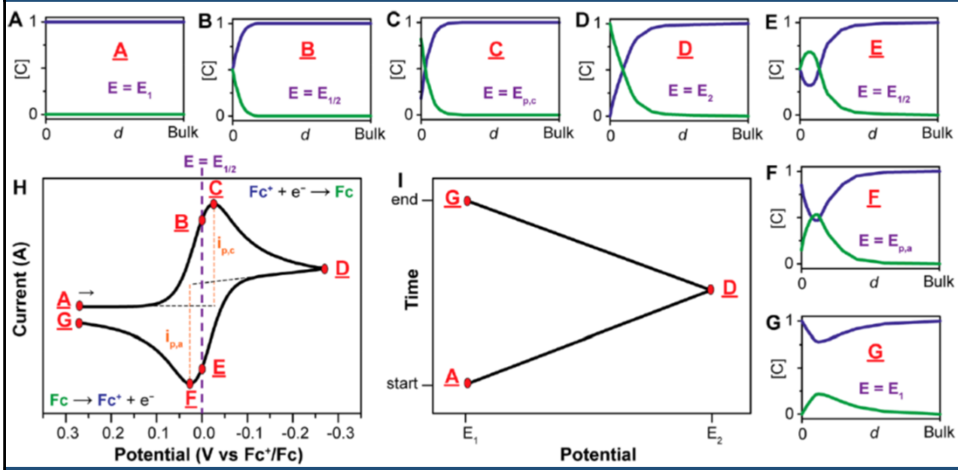


- **Electronic effect**
  - **Tuning the Pt/CO_{ads} bonding**

Cyclic voltammetry

- powerful in acquiring qualitative information about electrochemical reactions.
- rapidly provides considerable information on the **thermodynamics** of redox processes and the **kinetics** of heterogeneous electron transfer reactions and on coupled chemical reactions or adsorption processes.
- offers a rapid location of **redox** potentials of the electroactive species, and convenient evaluation of the effect of media on the redox process.
- consists of scanning linearly the potential of a stationary working electrode (in an unstirred solution), using a triangular potential waveform.
- The resulting current–potential plot is termed a **cyclic voltammogram.**

CV of reversible reduction of a 1 mM ferrocenium (Fc^+ : $[Fe(Cp)2]^+$ (Cp = cyclopentadienyl)) solution to ferrocene (Fc), at a scan rate of 100 mV s^{-1}.

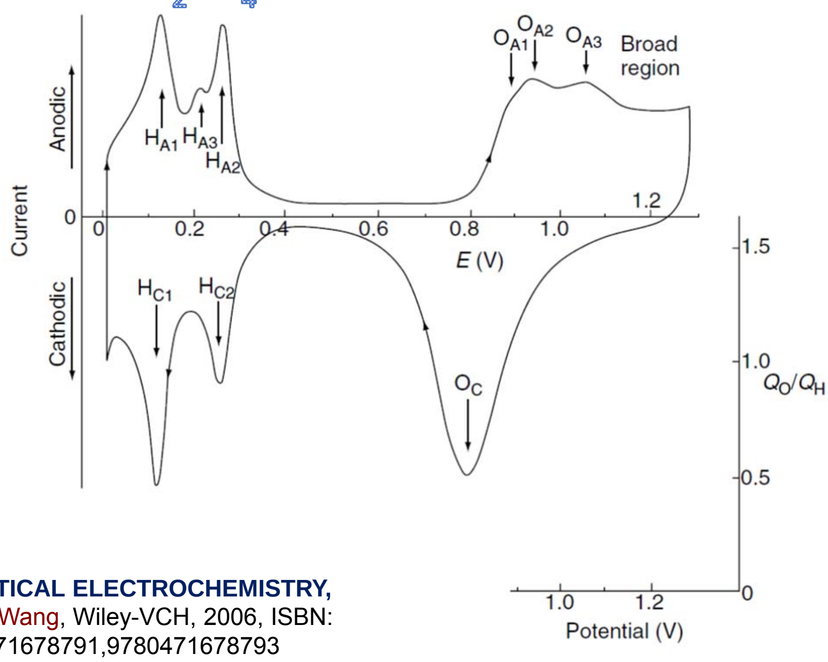


$$E = E^{0\prime} + 2.3026\frac{RT}{F}log\frac{[Fc^+]}{[Fc]}$$

$$Fc^+ \rightleftharpoons Fc$$

J. Chem. Educ. 2018, 95, 197–206

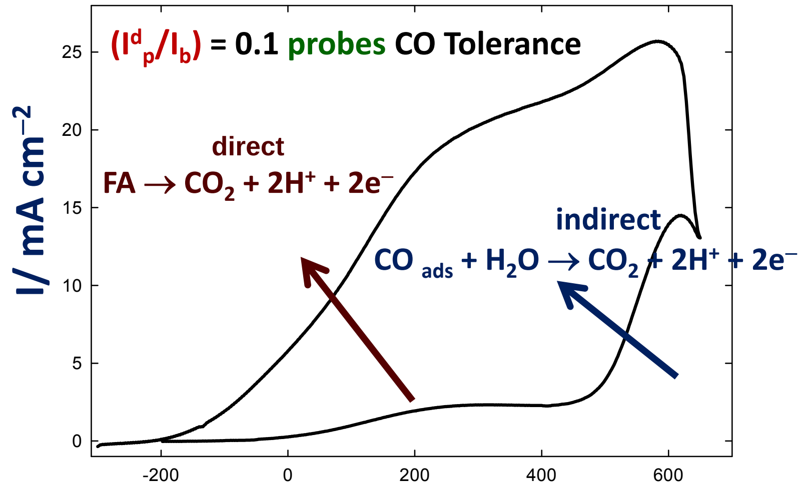
CV in 0.5 M H_2SO_4 at Pt electrode



ANALYTICAL ELECTROCHEMISTRY, Joseph Wang, Wiley-VCH, 2006, ISBN: 0471678791,9780471678793

FAO on Pt electrode

(I^{d}_{p}/I_{p}^{ind}) =0.2 Probes electrocatalytic activity



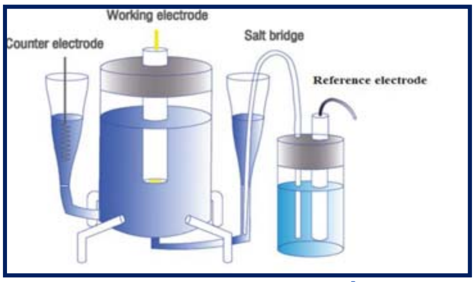
E/ mV vs. Ag/AgCl/KCl (sat.)

CV in 0.3M HCOOH (with pH 3.5) at Pt electrode. Potential scan rate:100 mV s^{-1}

Experimental Setup

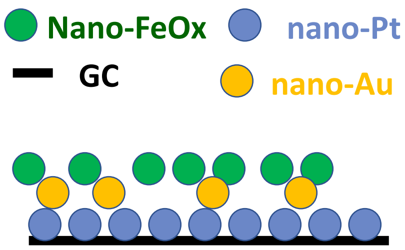
Biologic BP-300 Potentiostat
Dual channel electrochemical workstation. EIS capability.
Analog Ramp Generator.
EC-lab software

Working electrodes:
Glassy carbon (GC) rod (d = 3.0 mm)
Pt electrode (d = 1.6 mm)
Spiral Pt wire : Counter electrode
Ag/AgCl/KCl (sat.): Reference electrodes



Two-compartment three-electrode glass cell

FeOx/Au/Pt/GC



nano-Pt

potentiostatic at −0.2 V for 300 s

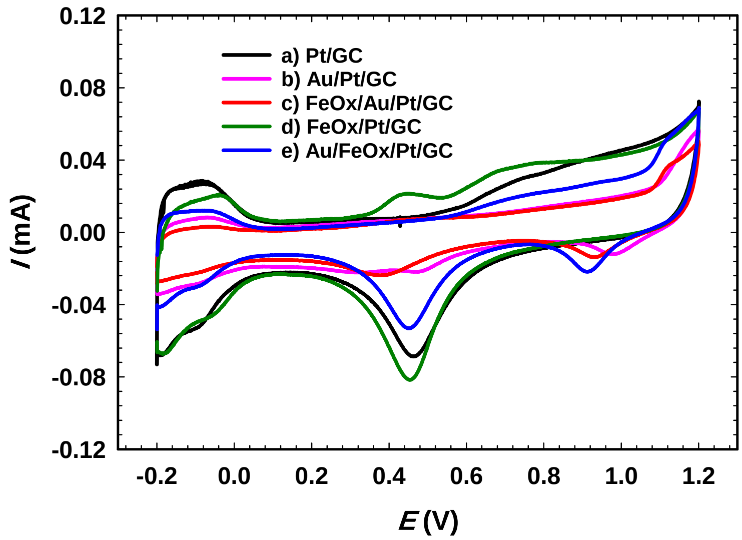
nano-Au

0.1 M H_2SO_4 containing 2.0 m mol L^{-1} $K[AuCl_4]$ at −0.2 V

nano-FeOx

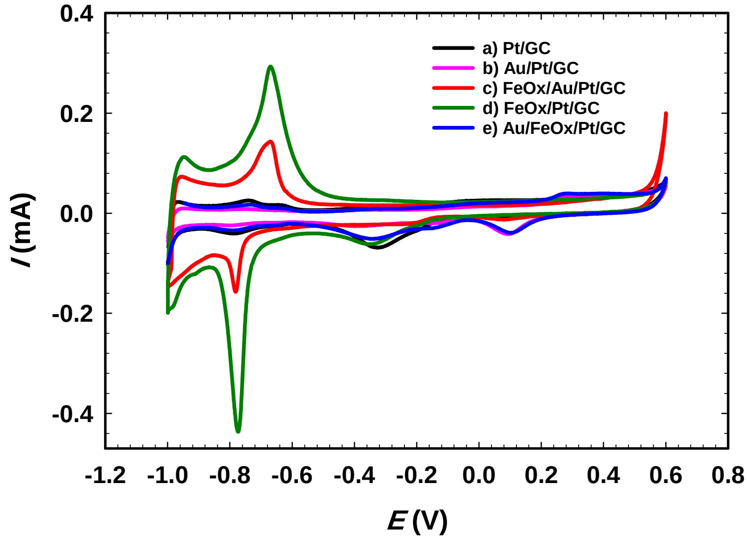
- 2 cycles between – 0.855 and – 1.205 V at 100 mV/s^{-1} in 0.02 mol L^{-1} $FeSO_4.7H_2O$

Electrochemical characterization



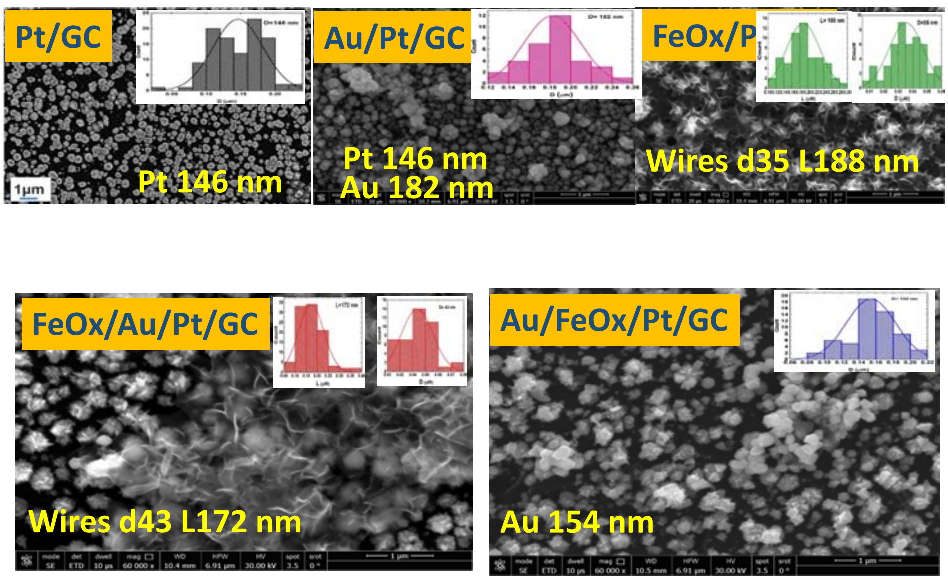
CVs in 0.5 mol L^{-1} H_2SO_4 at 50 mV/s.

Electrochemical characterization



CVs in 0.5 mol L^{-1} NaOH at 50 mV/s.

SEM



EDX

Au/Pt/GC

Element	Weight %	Atomic %	Error %
C K	28.34	85.14	9.16
O K	0.82	1.86	35.15
PtL	13.18	2.44	15.66
AuL	57.65	10.56	7.88

FeOx/Pt/GC

Element	Weight %	Atomic %	Error %
C K	68.72	87.77	6.18
O K	10.58	10.14	17.19
FeK	2.35	0.65	12.32
PtL	18.35	1.44	14.2

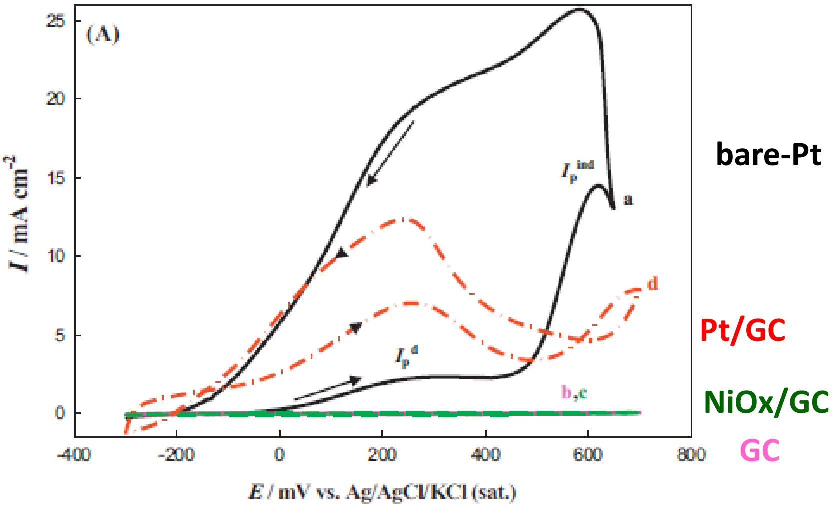
FeOx/Au/Pt/GC

Element	Weight %	Atomic %	Error %
C K	42.55	85.71	8.2
O K	4.71	7.12	16.76
FeK	2.2	0.95	11.09
PtL	8	0.99	24.74
AuL	42.54	5.22	11.06

Au/FeOx/Pt/GC

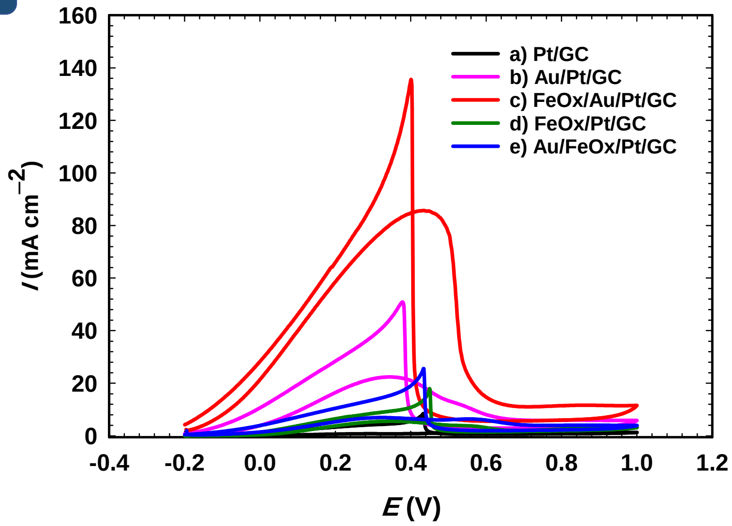
Element	Weight %	Atomic %	Error %
C K	44.79	90.47	8.22
O K	1.77	2.68	30.15
FeK	0.81	0.35	23.51
PtL	9.65	1.2	20.19
AuL	42.98	5.29	11.78

Activity



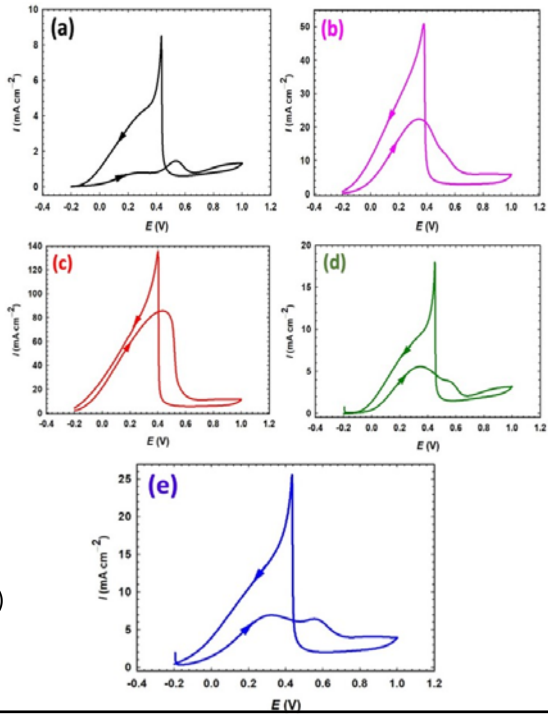
FAO at (a) Pt, (b) GC, (c) NiOx/GC and (d) Pt/GC catalysts in 0.3 mol L^{-1} FA (pH 3.5) at a scan rate of 100 mV/s.

Activity



FAO at (a) Pt/GC, (b) Au/Pt/GC, (c) FeOx/Au/Pt/GC, (d) FeOx/Pt/GC and (e) Au/FeOx/Pt/GC catalysts in 0.3 mol L^{-1} FA (pH 3.5) at a scan rate of 20 mV/s.

Activity



FAO at (a) Pt/GC, (b) Au/Pt/GC, (c) FeOx/Au/Pt/GC, (d) FeOx/Pt/GC and (e) Au/FeOx/Pt/GC catalysts in 0.3 mol L^{-1} FA (pH 3.5) at a scan rate of 20 mV/s.

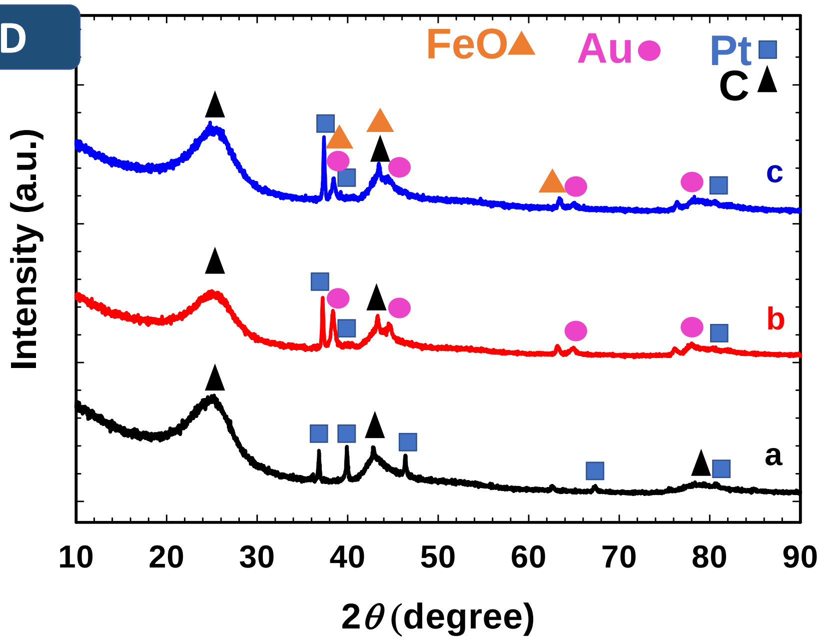
Activity

Electrode	ECSA (cm^2)	I_p^d (mA cm^{-2})	I_p^{ind} (mA cm^{-2})	I_b (mA cm^{-2})	I_p^d/I_p^{ind}	I_p^d/I_b	E_{onset} (mV)
Pt/GC	0.438	0.71	0.72	7.86	0.99	0.09	**126**
Au/Pt/GC	0.056	21.94	2.0	47.40	10.97	0.46	**10**
FeOx/Au/Pt/GC	0.028	83.71	0.00	129.28	∞	0.65	**−110**
FeOx/Pt/GC	0.249	5.44	0.80	16.50	6.80	0.33	**42**
Au/FeOx/Pt/GC	0.157	6.80	1.8	23.20	3.78	0.29	**−15**

Compare

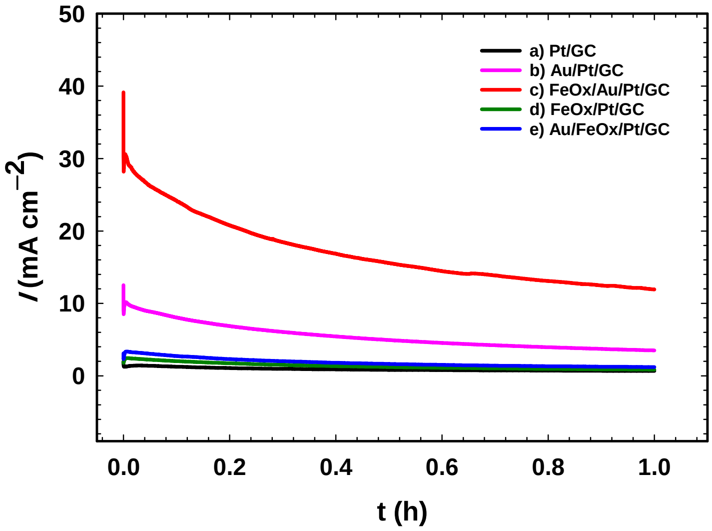
Electrode	I_p^d/I_p^{ind}	I_p^d/I_b	Ref.
6Pt/PVA	0.18	0.13	[42]
Pt black	0.24	0.11	[21]
6Pt/GO	0.26	0.15	[42]
Pt/C	0.29	0.20	[21]
3Pt3Pd/PVA	0.49	0.26	[42]
Mn/Pt/GC	3.13	0.50	[43]
NiOx/Pt/GC	3.33	0.40	[44]
PtPd/GC	7.33	0.32	[30]
Pt/MWCNTs-GC	7.5	0.45	[45]
Au/Pt/GC	10.97	0.46	This work
FeOx/Au/Pt/GC	∞	0.65	This work

XRD



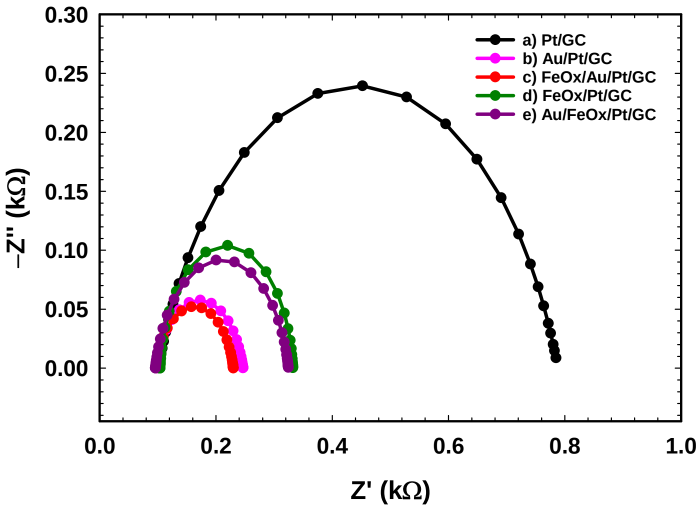
XRD patterns of (a) Pt/GC, (b) Au/Pt/GC and (c) FeOx/Au/Pt/GC

Stability



The *i-t* relations obtained during FAO for the (a) Pt/GC, (b) Au/Pt/GC, (c) FeOx/Au/Pt/GC, (d) FeOx/Pt/GC and (e) Au/FeOx/Pt/GC catalysts in 0.3 mol L^{-1} FA (pH 3.5) at 0.15 V.

EIS

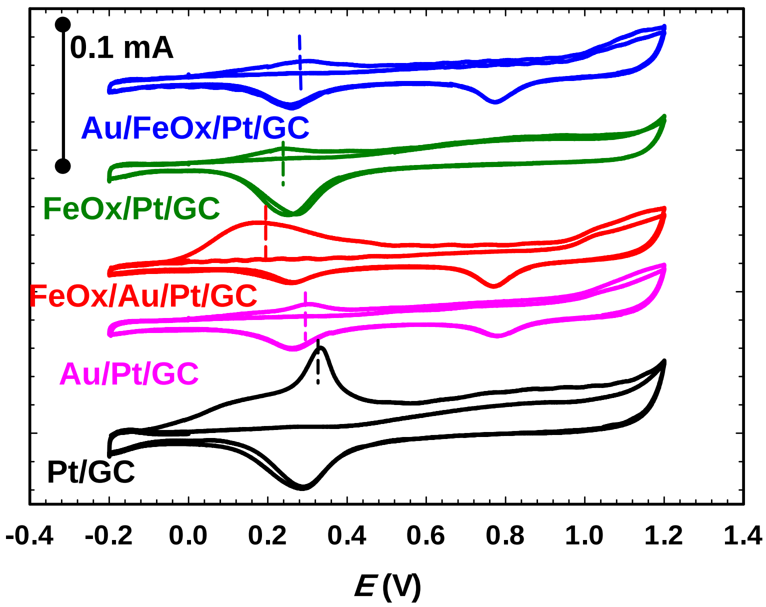


Nyquist plot at 0.15 V for (a) Pt/GC, (b) Au/Pt/GC, (c) FeOx/Au/Pt/GC, (d) FeOx/Pt/GC and (e) Au/FeOx/Pt/GC catalysts in 0.3 mol L^{-1} FA (pH 3.5).

EIS

Electrode	R_s [kΩ]	R_{ct} [kΩ]
Pt/GC	0.100	0.687
Au/Pt/GC	0.097	0.149
FeOx/Au/Pt/GC	0.096	0.133
FeOx/Pt/GC	0.103	0.2284
Au/FeOx/Pt/GC	0.095	0.2288

CO Stripping



Oxidative stripping of CO from the (a) Pt/GC, (b) Au/Pt/GC, (c) FeOx/Au/Pt/GC, (d) FeOx/Pt/GC and (e) Au/FeOx/Pt/GC catalysts in 0.5 mol L^{-1} Na_2SO_4 (pH 3.5) at a scan rate of 20 mV/s.

Tafel

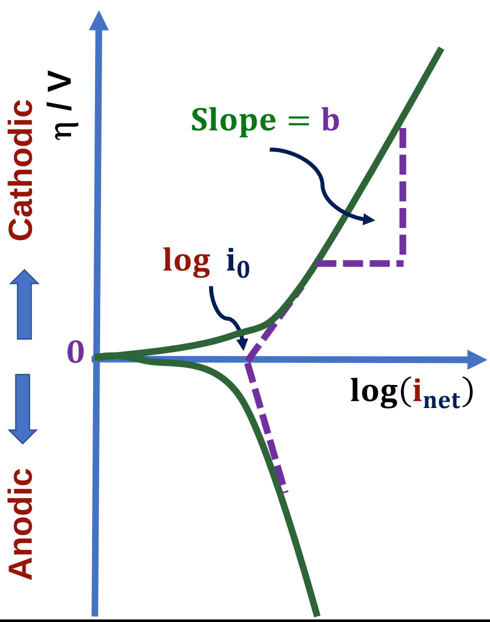
$$\eta = \frac{2.303\ RT\log\ i_0}{\alpha nF} - \frac{2.303\ RT}{\alpha nF}\log(i_{net})$$

$$\eta = a - b\log(i_{net})$$

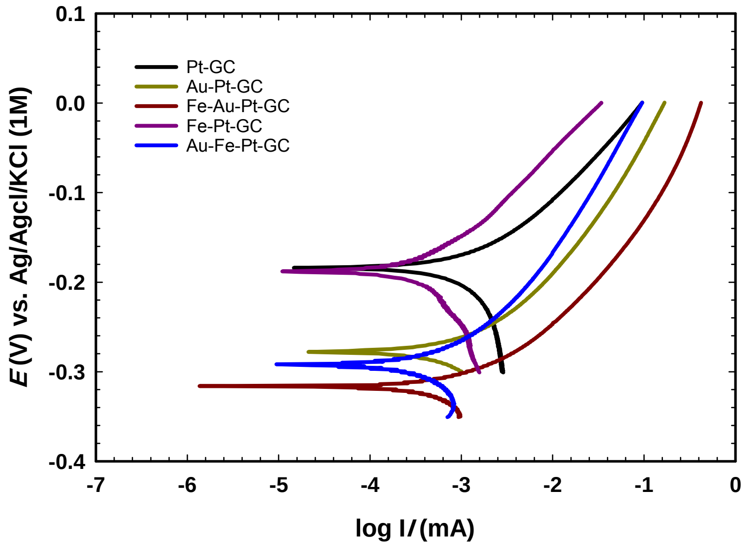
$$a = \text{intercept} = \frac{2.303\ RT\log\ i_0}{\alpha nF}$$

$$b = \text{slope} = \frac{2.303\ RT}{\alpha nF}$$

$$\log\ i_0 = \frac{-a}{b}$$



Tafel



Tafel plots of (a) Pt/GC, (b) Au/Pt/GC, (c) FeOx/Au/Pt/GC, (d) FeOx/Pt/GC and (e) Au/FeOx/Pt/GC catalysts in 0.5 mol L^{-1} Na_2SO_4 (pH 3.5).

Tafel

Electrode	Anodic Tafel slope (mV/decade)	I_0 (mA)
Pt/GC	105.4	
Au/Pt/GC	99.2	
FeOx/Au/Pt/GC	73.7	highest
FeOx/Pt/GC	100.9	
Au/FeOx/Pt/GC	83.2	

Mechanism

$Fe(OH)_2 \leftrightarrow FeOOH + H^+ + e^-$ (1)

$HCOOH_{ads} + FeOOH \rightarrow CO_2 + Fe(OH)_2 + H^+ + e^-$ (2)

$COads + FeOOH + H_2O \rightarrow Fe(OH)_2 + CO_2 + H^+ + e^-$ (3)

Addition of Eqs. 1 and 2 gives:

$HCOOH_{ads} \rightarrow CO_2 + 2H^+ + 2e^-$ (4)

Addition of Eqs. 1 and 3 gives:

$CO_{ads} + H_2O \rightarrow CO_2 + 2H^+ + 2e^-$ (6)

Conclusion

- nano-FeOx improved FAO **bifunctionally** via
  - providing the hydroxyl group moiety required to catalyze the CO oxidation of the indirect route of FAO
  - modifying the **electronic** structure of Pt surface.
  - facilitating the **charge transfer** during the CO oxidation via a catalytic mediation with the **$FeOOH/Fe(OH)_2$** reversible transformation.
- nano-FeOx geometrically **favored** the CO adsorption
- Nano-Au played the **third-body** role mitigating the CO adsorption and improving the electronic properties of Pt.


Thank You