

Gorivne ćelije – fuel cells (FC)

Teme:

1. Niskotemperaturske gorivne ćelije – princip rada i osnovne karakteristike

Ili

2. Mehanizam reakcije redukcije kiseonika u kiseloj i/ili baznoj sredini

Zašto FC?

Elektromobilnost

DOE USA

Electromobility in Germany: Vision 2020 and Beyond

https://www.gtai.de/GTAI/Content/EN/Invest/_SharedDocs/Downloads/GTAI/Brochures/Industries/electromobility-in-germany.pdf?__blob=publicationFile

Tesla Gigafactory

<https://www.tesla.com/factory>

Daimler

<https://www.reuters.com/article/us-daimler-usa-diesel-idUSKBN13K1MG>

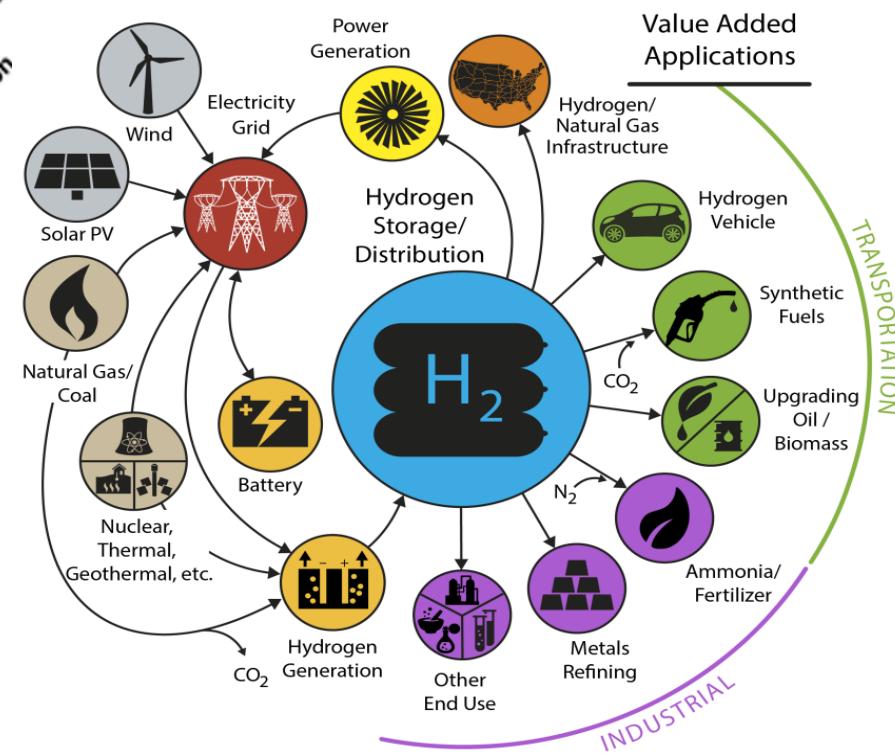
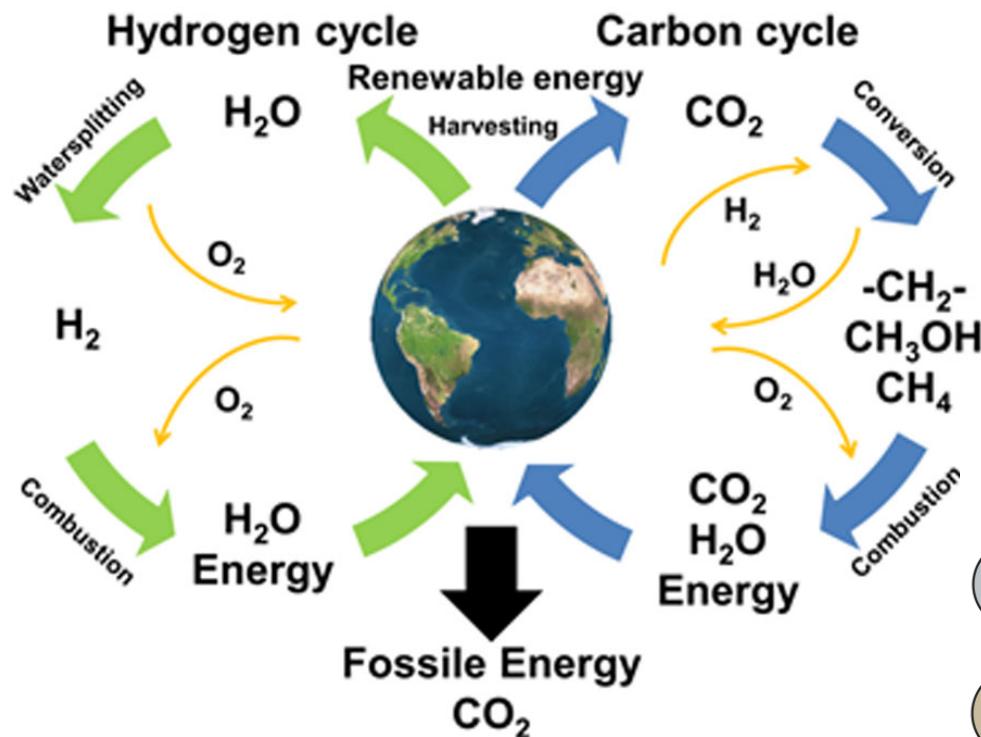
Modeli električnih vozila sa pogonom na gorivne čelije

<https://ssl.toyota.com/mirai/fcv.html>

<https://automobiles.honda.com/clarity-fuel-cell>

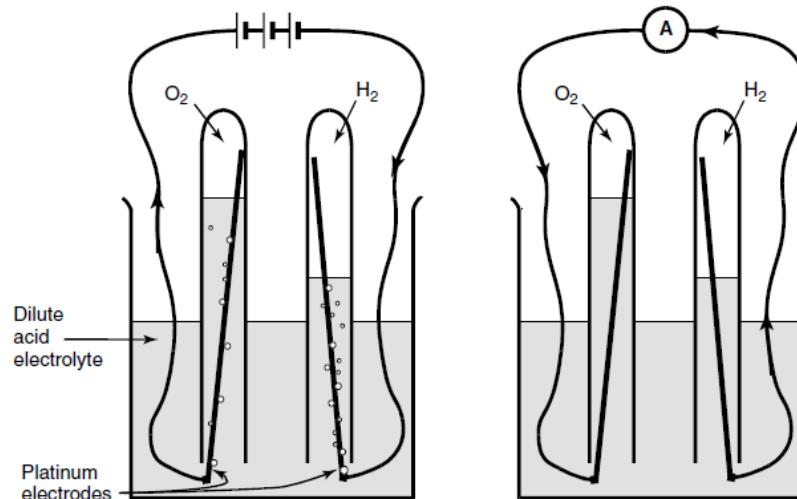
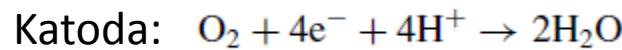
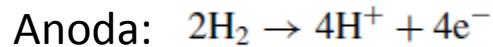
<https://www.hyundaiusa.com/tucsonfuelcell/index.aspx>

Ciklusi energije / ciklusi u prirodi

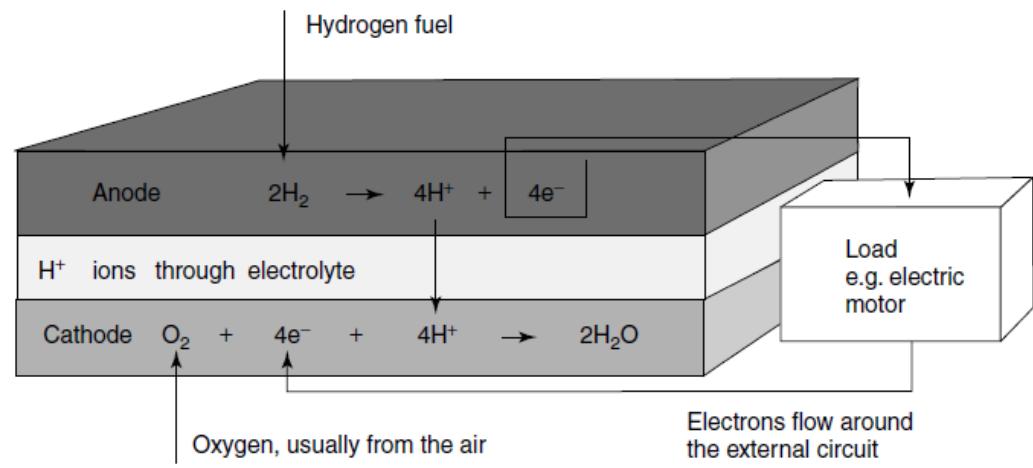
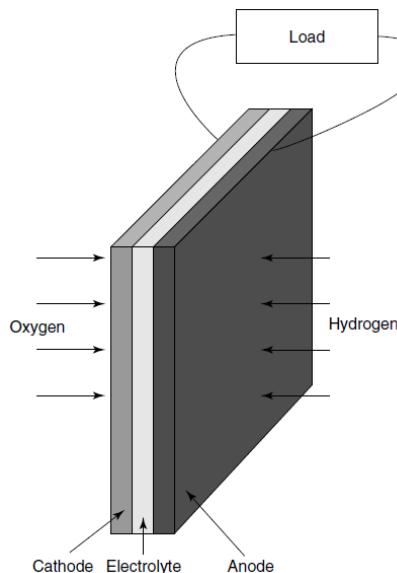


Vodonična gorivna čelija – Fuel Cell (FC)

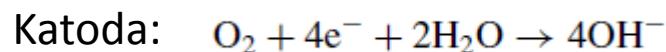
William Grove – 1839.



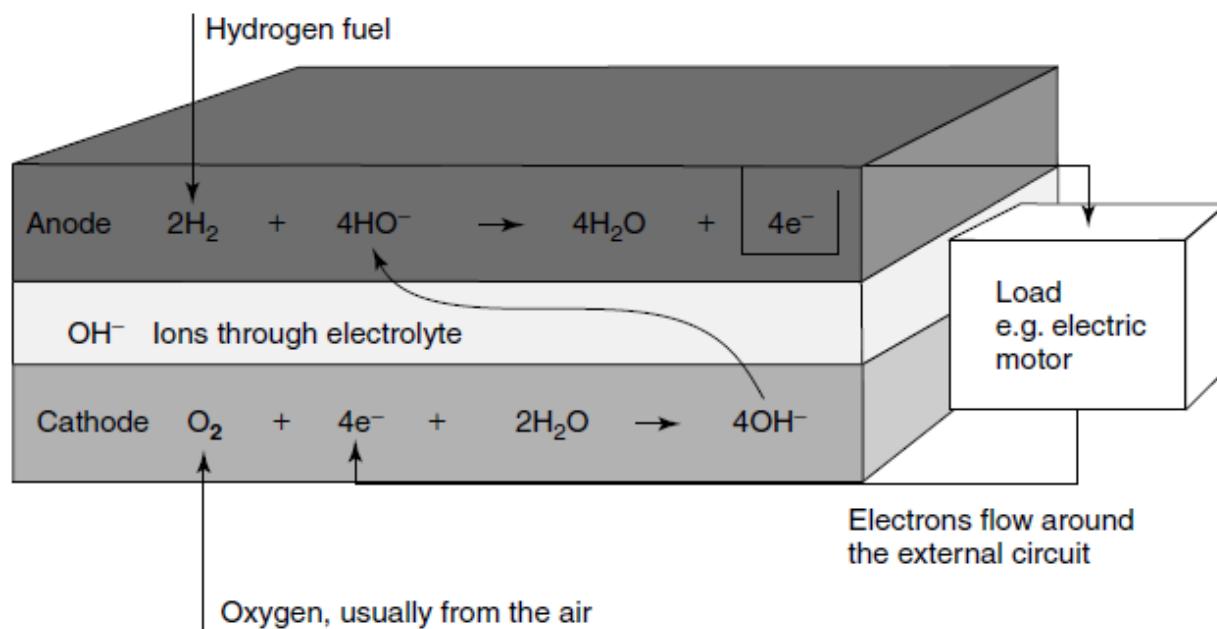
Membrana: provodnik H⁺ jona



Alkalna gorivna čelija – Alkaline Fuel Cell (AFC)

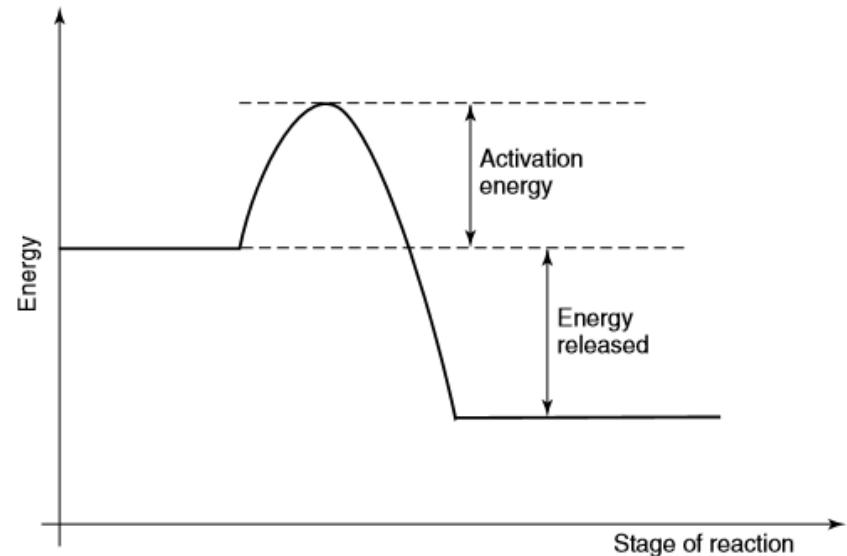


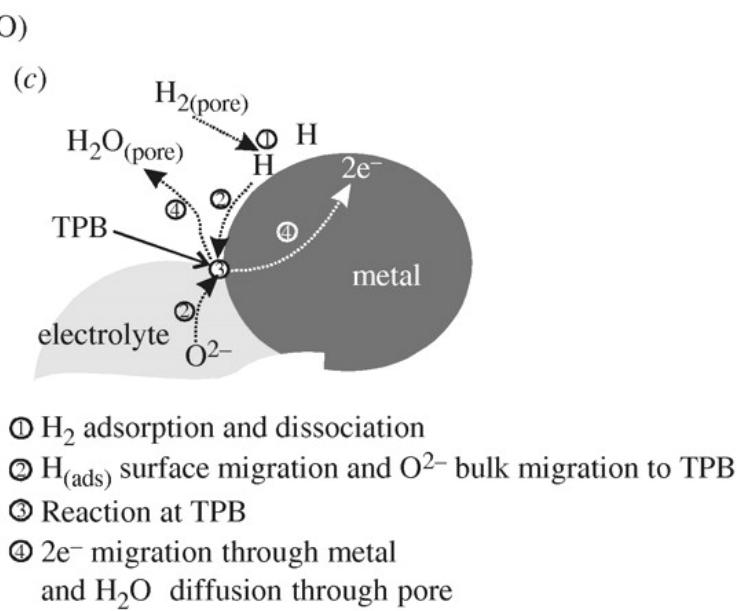
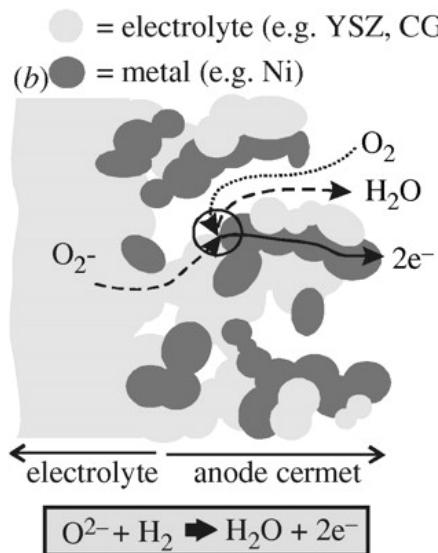
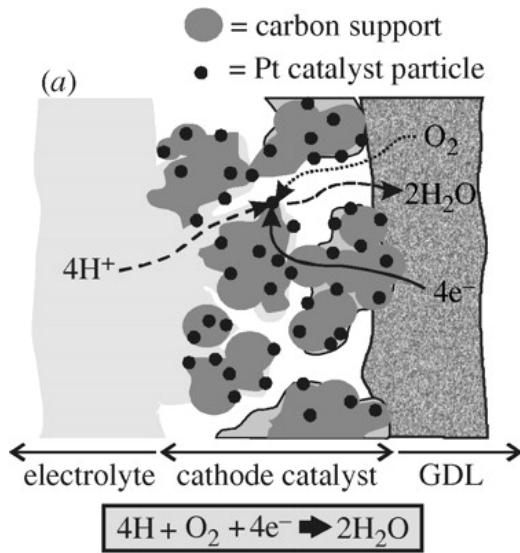
Membrana: provodnik OH^- jona



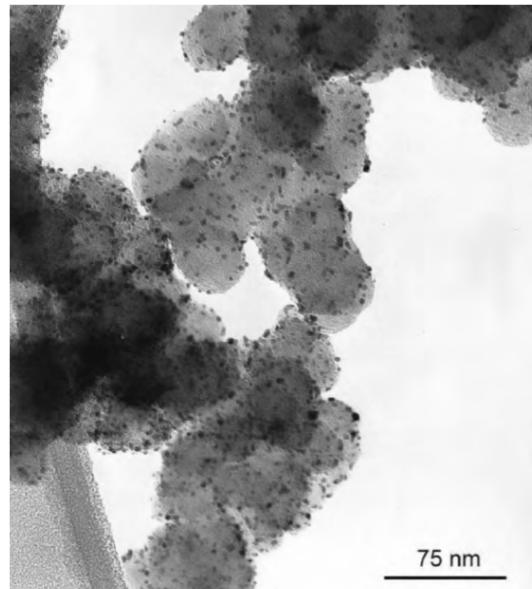
Kako ubrzati reakciju?

- katalizatori
 - povećanje temperature
 - povećanje specifične površine
 - gustina struje (cm^{-2})
 - dizajn struktura pora (mikrodizajn)
-
- Kontakt (granica) tri faze – $\text{H}_{2(g)}$, Elektrolit_(l), Elektroda_(s)



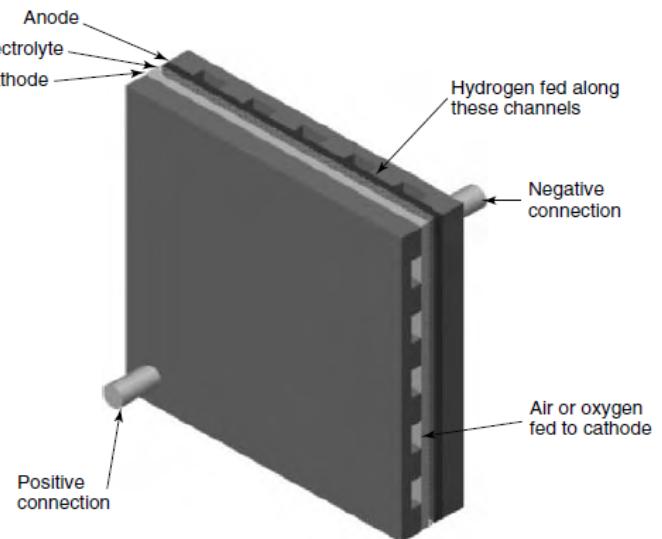
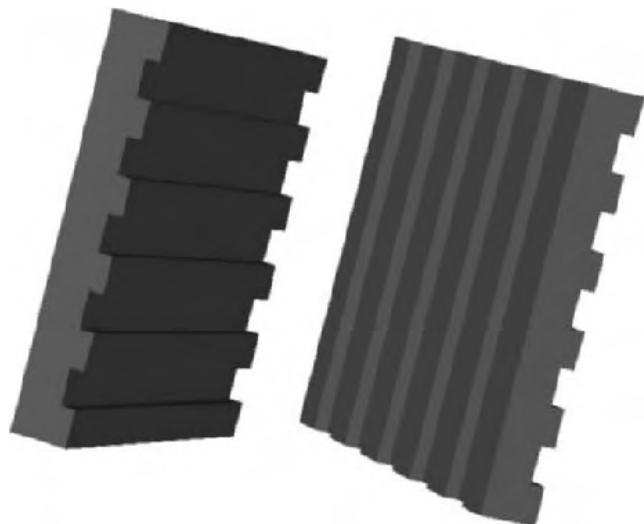
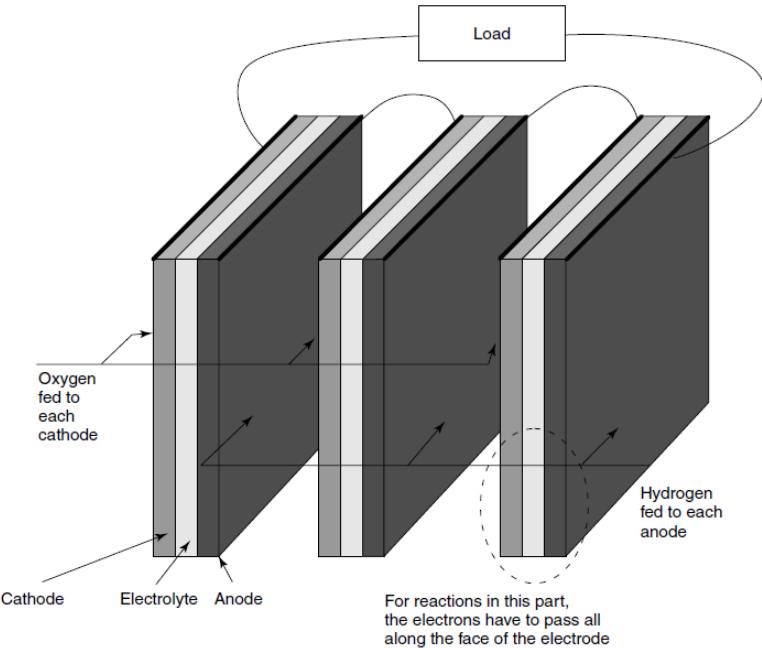


Kontakt (granica) tri faze



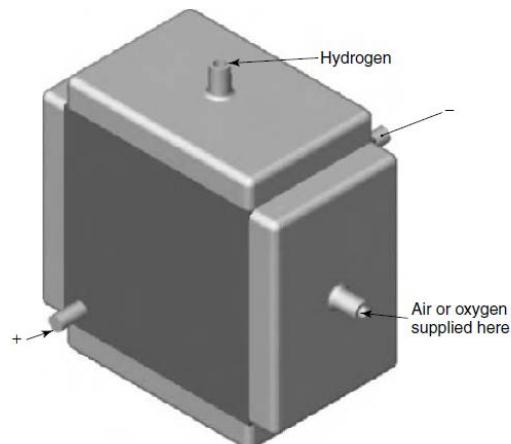
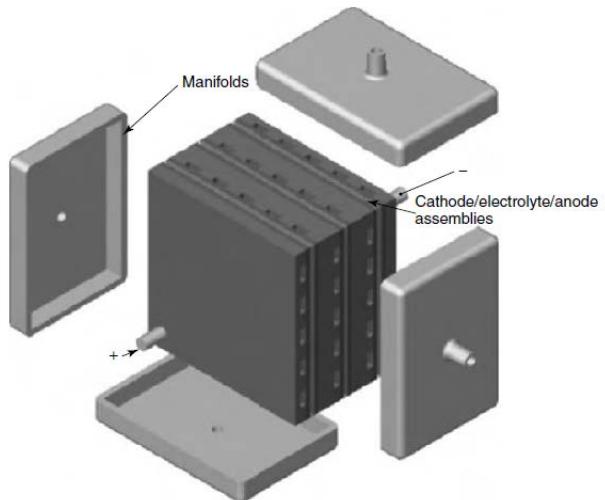
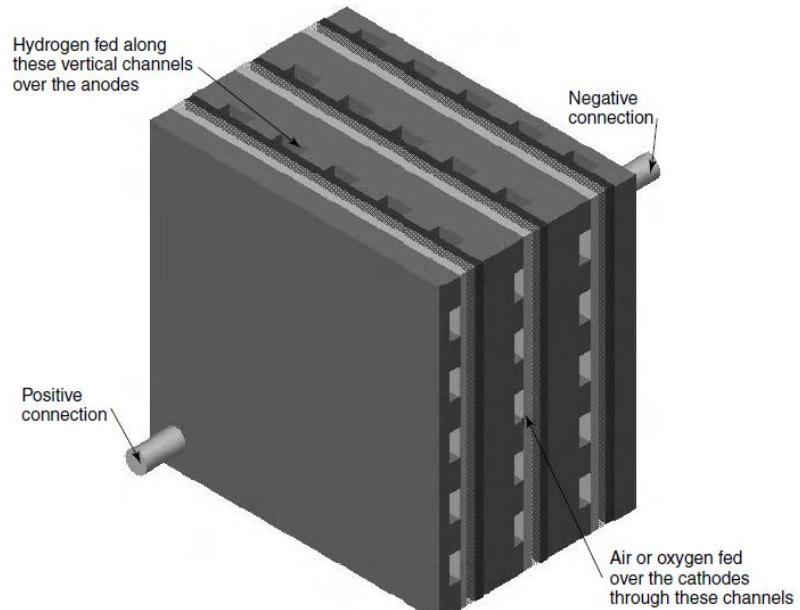
Povezivanje gorivnih čelija – fuel cell stack

- Prosto redno povezivanje – veliki padovi napona zbog dugog puta elektrona
- Rešenje: bipolarne ploče (prednosti/mane)



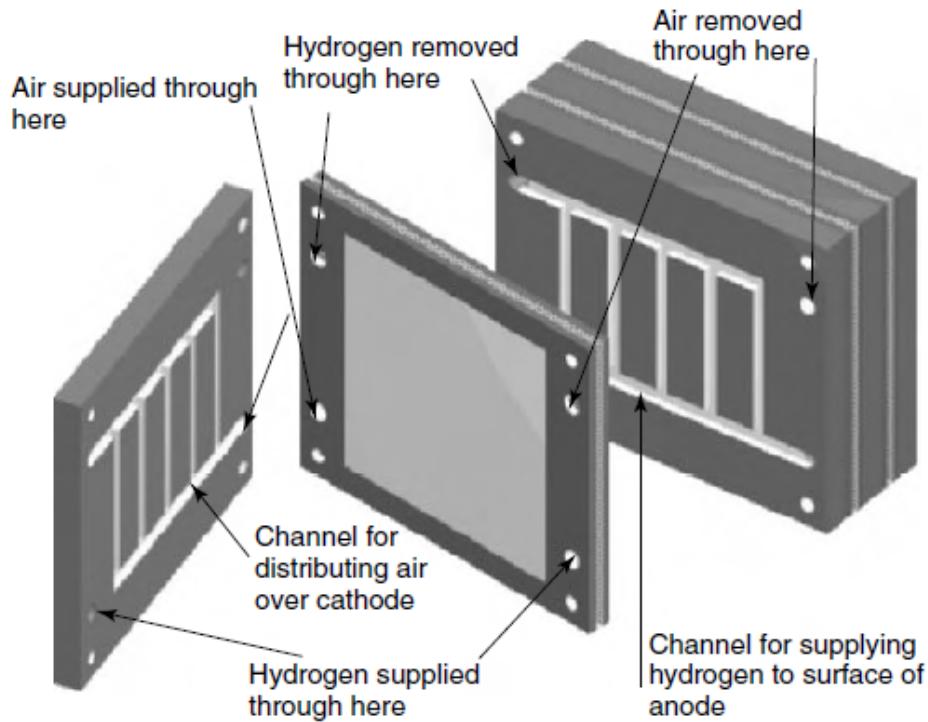
Povezivanje gorivnih čelija – fuel cell stack

- Dotok gasa, hlađenje, odvođenje nastale vode
- Veći pritisak i protok gasa zbog hlađenja
- Zbog različitih pritisaka unutar čelija podložna je curenju gasa (gas leakage)
- Eksterno povezivanje (external manifold)



Povezivanje gorivnih čelija – fuel cell stack

- Interno povezivanje (internal manifold)



- Često najskuplja komponenta koja se teško pravi
- Grafit ili nerđajući čelik

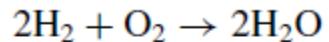
Veličine za poređenje gorivnih čelija

- gustina struje (mA cm^{-2}) na određenoj vrednosti napona, tipično 0,6 ili 0,7 V
 - gustina snage – snaga po jedinici zapremine (kW m^{-3} ili kW L^{-1})
 - Specifična snaga- snaga po jedinici mase (W kg^{-1})
 - Cena – ($\$ \text{ kW}^{-1}$)
 - Vek trajanja ili broj ciklusa
-
- Efikasnost i mogućnost povećanja snage (scalability)
 - Relativno jednostavan dizajn sa malo pokretnih delova
 - Niska emisija CO_2
 - Tih rad
 - Vodonik - prednost i mana
 - CHP (combined heat and power)

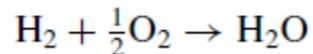
Efikasnost i napon otvorenog kola

$$P=V^*I$$

$$E=V^*I^*t$$



Gibsova slobodna energija



$$\text{Rad} = q * V = -2Ne^*V = -2F * E_{\text{ms}}$$

$$\Delta G_{\text{molar}} = -2F * E_{\text{ms}}$$

$$E_{\text{ms}} = -\Delta G_{\text{molar}}/2F$$

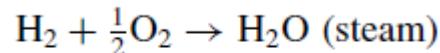
Form of water product	Temperature (°C)	$\Delta \bar{g}_f$ (kJ mol ⁻¹)
Liquid	25	-237.2
Liquid	80	-228.2
Gas	80	-226.1
Gas	100	-225.2
Gas	200	-220.4
Gas	400	-210.3
Gas	600	-199.6
Gas	800	-188.6
Gas	1000	-177.4

Efikasnost i limit efikasnosti

- vetroturbina $E_{\max} = 0.58 * E_{\text{kinetic}}$
- Carnoov ciklus $= \frac{T_1 - T_2}{T_1} = \frac{675 - 325}{675} = 0.52 = 52\%$

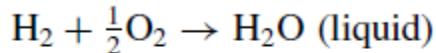
$$\text{Efikasnost FC} = \frac{\text{električna energija po molu goriva}}{\Delta H_f} = \frac{\Delta G_f}{\Delta H_f}$$

LHV – lower heating value



$$\Delta \bar{h}_f = -241.83 \text{ kJ mol}^{-1}$$

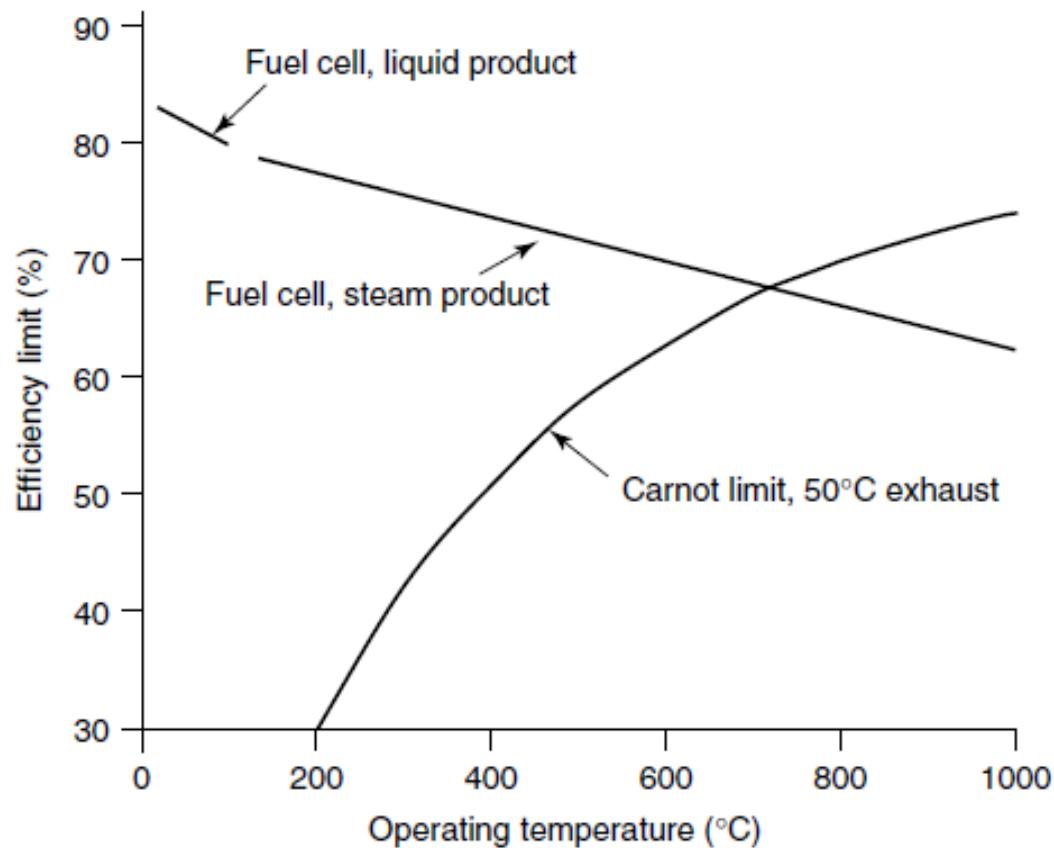
HHV – higher heating value

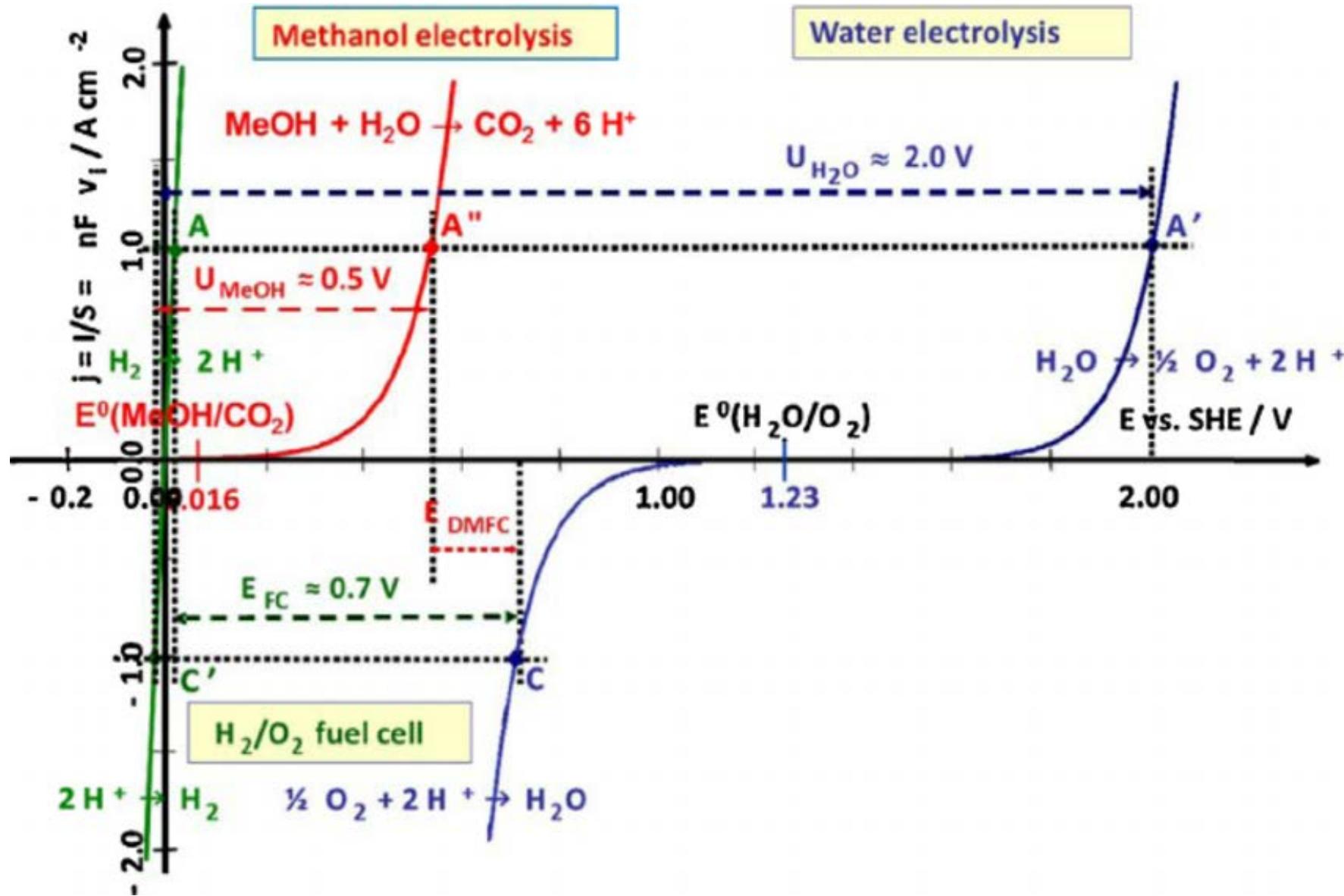


$$\Delta \bar{h}_f = -285.84 \text{ kJ mol}^{-1}$$

Form of water product	Temp °C	$\Delta \bar{g}_f, \text{ kJ mol}^{-1}$	Max EMF V	Efficiency limit %
Liquid	25	-237.2	1.23	83
Liquid	80	-228.2	1.18	80
Gas	100	-225.2	1.17	79
Gas	200	-220.4	1.14	77
Gas	400	-210.3	1.09	74
Gas	600	-199.6	1.04	70
Gas	800	-188.6	0.98	66
Gas	1000	-177.4	0.92	62

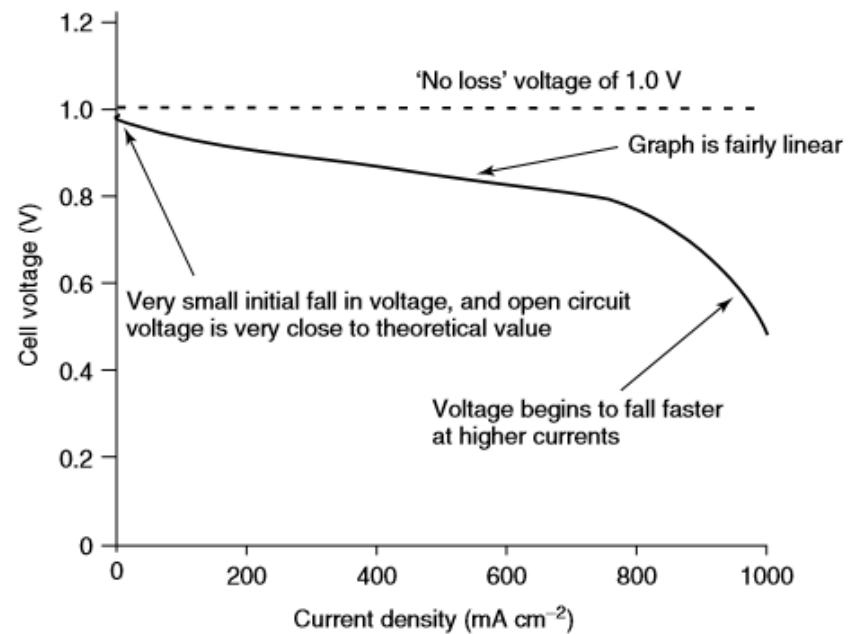
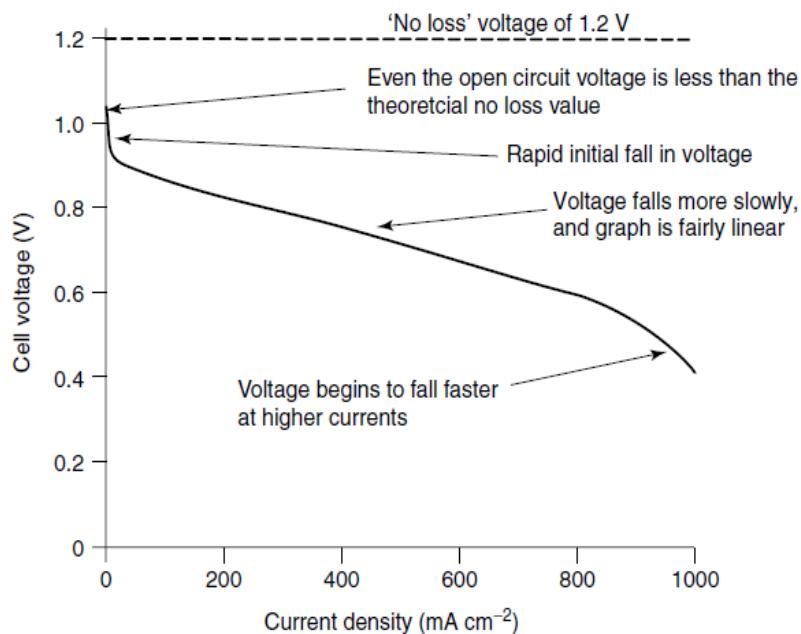
Efikasnost i limit efikasnosti





Padovi napona čelije – gubici

- potencijal otvorenog kola je niži od teorijske vrednosti
- nagli pad potencijala na početku pri malim gustinama struje
- linearan pad napona na srednjim gustinama struje
- nagli pad potencijala pri velikim gustinama struja



- Interdisciplinarnost i različiti pojmovi
 - overvoltage/overpotential, polarisation, irreversibility, losses, voltage drop
-
- aktivaciona polarizacija
 - unutrašnje struje, prolazak goriva kroz membranu (intenal currents, fuel cross-over)
 - pad napona na otporima (Ohmic losses)
 - transport mase (mass transport losses, concentration losses)

Aktivaciona polarizacija

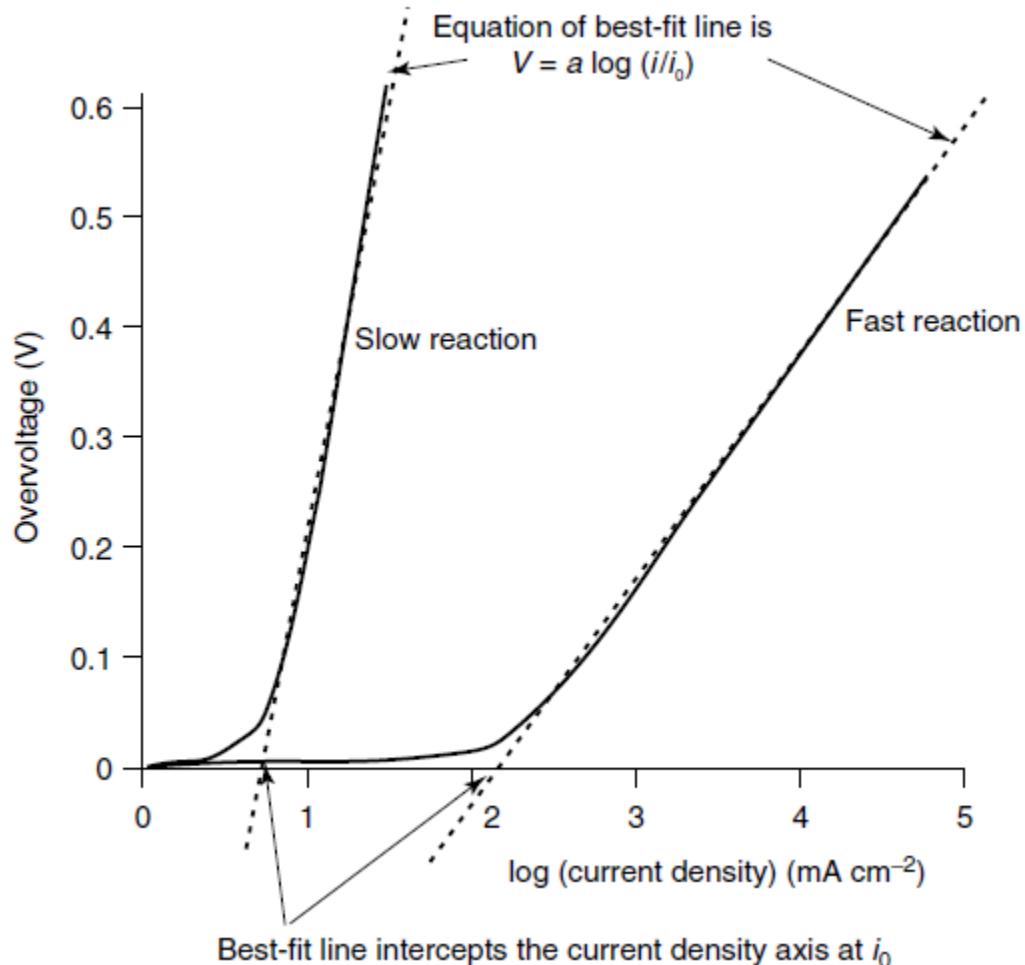
$$\eta = A \ln\left(\frac{i}{i_0}\right)$$

$$A = \frac{RT}{2\beta F}$$

- β je oko 0,5 za oksidaciju vodonik
- 0,1-0,5 za redukciju kiseonik

$$V = E - A \ln\left(\frac{i}{i_0}\right)$$

$$i = i_0 e^{\frac{2\beta F \eta}{RT}}$$

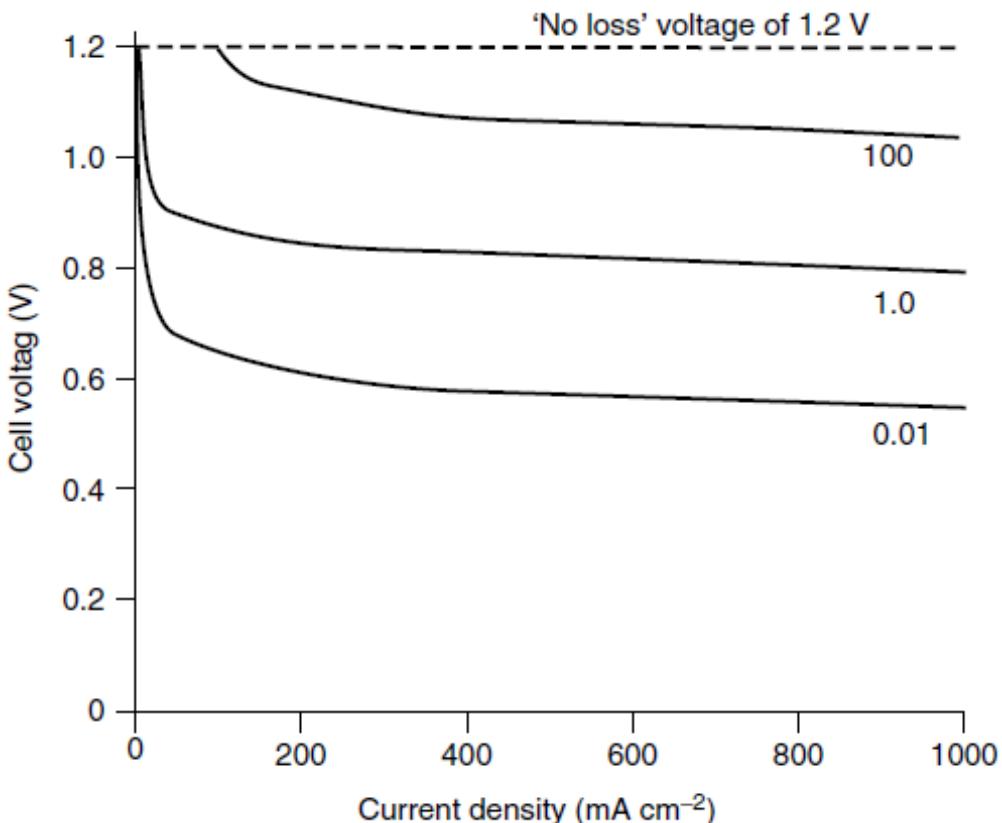


$$V = E - A \ln \left(\frac{i}{i_0} \right)$$

$i_0 = 0,01; 1,0; 100$

$A = 0,06 \text{ V}$

Metal	$i_0 (\text{A cm}^{-2})$
Pb	2.5×10^{-13}
Zn	3×10^{-11}
Ag	4×10^{-7}
Ni	6×10^{-6}
Pt	5×10^{-4}
Pd	4×10^{-3}



$I_{0\text{(anoda)}} = 200 \text{ mA cm}^{-2}$ za $I_{0\text{(katoda)}} = 0,1 \text{ mA cm}^{-2}$

Kako povećati i_0 ?

- povećanje temperature; pri promeni sa $70\text{ }^{\circ}\text{C}$ na $800\text{ }^{\circ}\text{C}$ i_0 se povećava 100 puta
 - upotrebom boljih katalizatora
 - povećanjem „hrapavosti“ elektrode (roughness factor)
 - povećanjem koncentracije reaktanata
 - povećanjem pritiska
-
- aktivaciona polarizacija je najvažnija kod nisko-temperaturnih gorivnih ćelija
 - najveća je na katodi kod vodonične gorivne ćelije
 - Aktivaciona polarizacija se može javiti kao problem na obe elektrode kod drugih tipova gorivnih ćelija

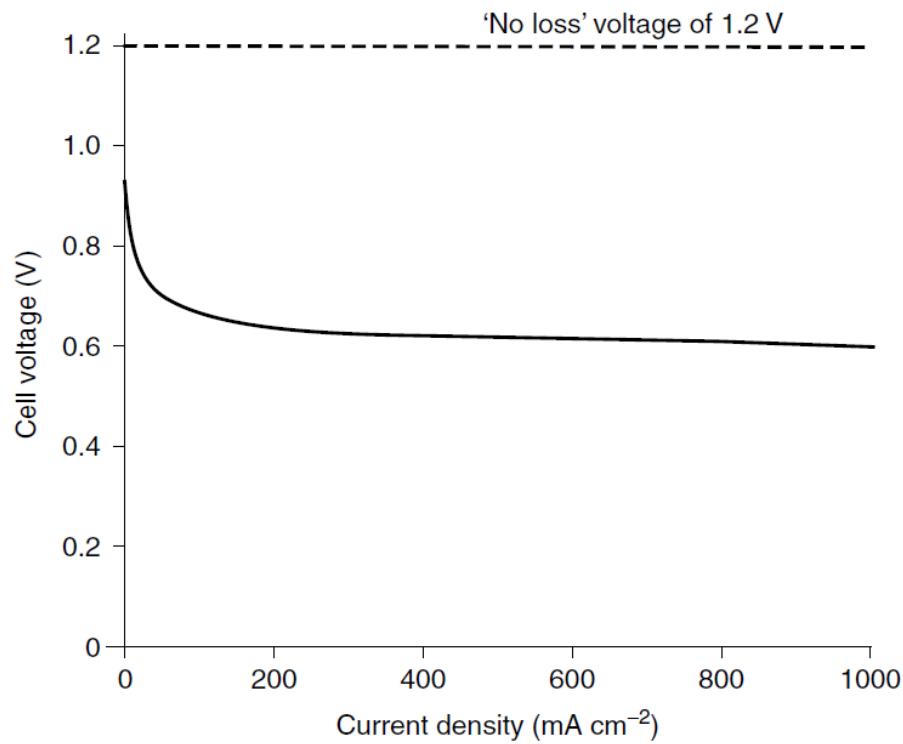
Unutrašnje struje i prolazak goriva kroz membranu

- uvek prisutna mala elektronska provodljivost membrane
- prolazak malih količina goriva kroz membranu i oksidacija koja ne daje elektrone
- nekoliko mA cm^{-2}
- procena vrednosti merenjem potrošnje gasova pri naponu otvorenog kola
- Modelovanje otpora članom i_n

$$V = E - A \ln \left(\frac{i + i_n}{i_0} \right)$$

Current density (mA cm^{-2})	Voltage (V)
0	1.2
0.25	1.05
0.5	1.01
1.0	0.97
2.0	0.92
3.0	0.90
4.0	0.88
5.0	0.87
6.0	0.86
7.0	0.85
8.0	0.84
9.0	0.83

If the internal current density is 1.0 mA cm^{-2} , then the open circuit voltage will drop to 0.97 V



Pad napona na otporima (Ohmic losses)

- Pad napona na elektrodama i kretanje jona kroz elektrolit
- Iz Omovog zakona $U = I \cdot R$
- $\Delta V = i \cdot r$; i – gusitna struje; r – otpor jedinice površine
- otpor veza menju ćelijama u seriji kao i otpor bipolarnih ploča

$$\Delta V_{\text{ohm}} = ir$$

- Upotreba elektroda što veće provodljivosti
- Dobar dizajn ćelije smanjuje otpor veza u seriji kao i otpor bipolarnih ploča
- Upotreba što tanjeg elektrolita (diskutabilno)

Transport mase (mass transport losses, concentration losses)

- smanjenje koncentracije gasova uz elektrodu u zavisnosti od struje koja protiče kroz ćeliju
- zavisi od načina cirkulacije gasova unutar same ćelije i koliko brzo se potrošeni gas može nadoknaditi
- Teško je analitički modelovati usled uticaja mnogo faktora (fluktuacije parcijalnih pritisaka, uticaj azota, isparavanje nastale vode)
- Koristi se empirijska formula oblika

$$\Delta V_{\text{trans}} = m \exp(ni)$$

Kombinovanje različitih tipova otpora

$$V = E - \Delta V_{\text{ohm}} - \Delta V_{\text{act}} - \Delta V_{\text{trans}}$$

$$V = E - ir - A \ln \left(\frac{i + i_n}{i_0} \right) + m \exp(ni)$$

$$\Delta V_{\text{act}} = A \ln \left(\frac{i}{i_0} \right) = A \ln(i) - A \ln(i_0)$$

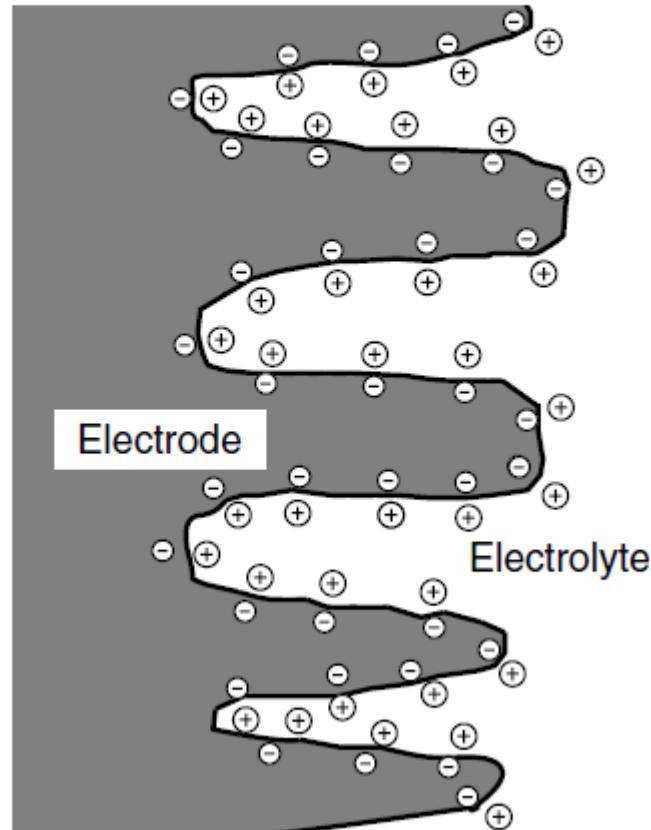
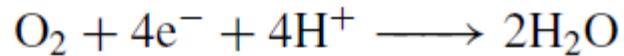
$$E_{\text{oc}} = E + A \ln(i_0)$$

$$V = E_{\text{oc}} - ir - A \ln(i) + m \exp(ni)$$

Dvojni električni sloj

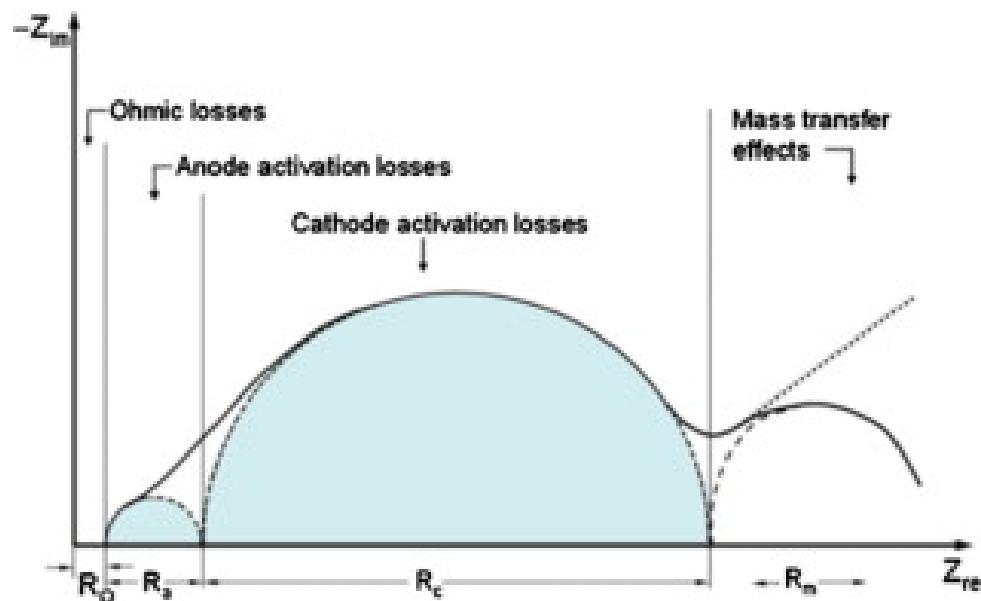
Formiranje usled:

- difuzionih efekata
 - reakcije između elektrona i jonskih vrsta
 - nametnutog nadnapona
-
- Verovatnoća reakcije zavisi od gustine elektrona na elektrodi i H^+ jona unutar elektrolita. Veća gustina nanelektrisanje odgovara većoj struci
 - Stvaranje kondenzatora odgovorno za aktivacionu polarizaciju
 - Veći napon na DL veća brzina procesa ali i veća polarizacija
 - Efekat katalizatora – veća struja uz što manje nagomilavanje nanelektrisanja unutar DL
 - Dobre dinamičke karakteristike zbog prisustva DL



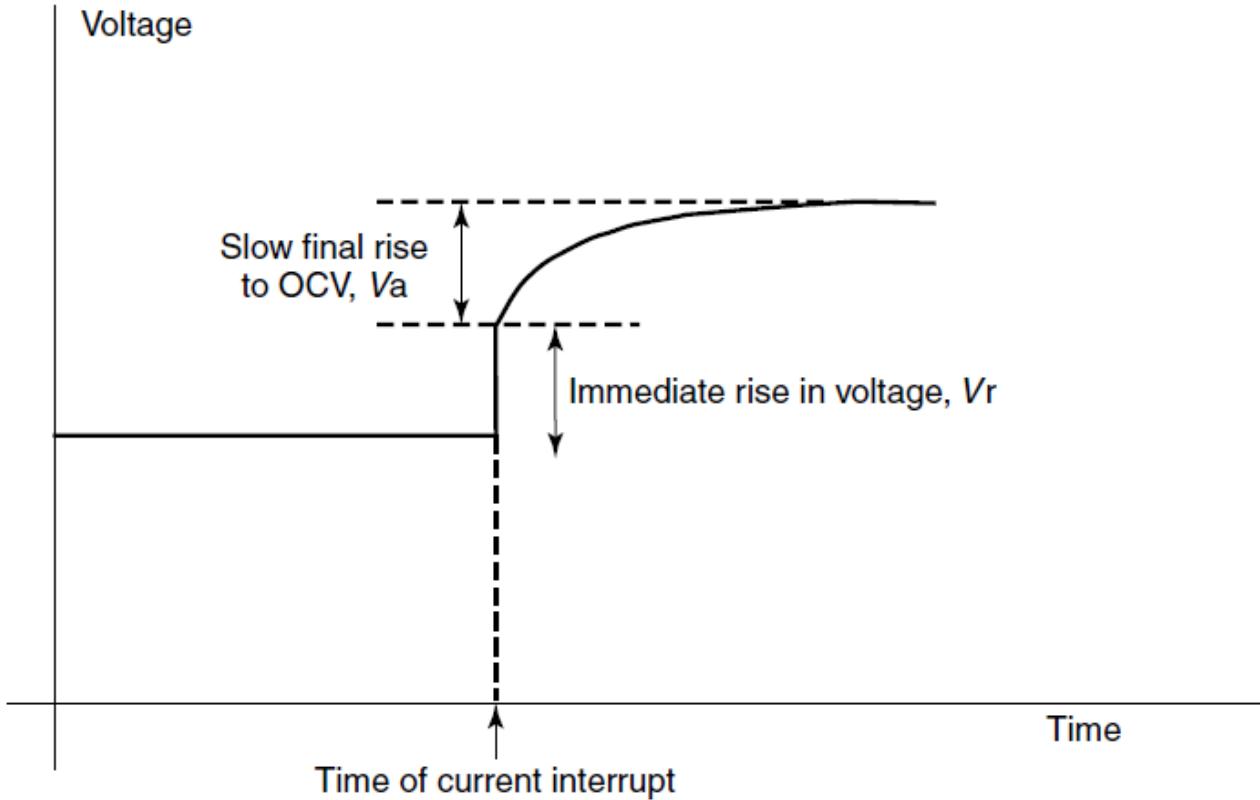
Metode za određivanje tipa dominantnog otpora

Spektroskija elektrohemijeske impedanse (EIS)

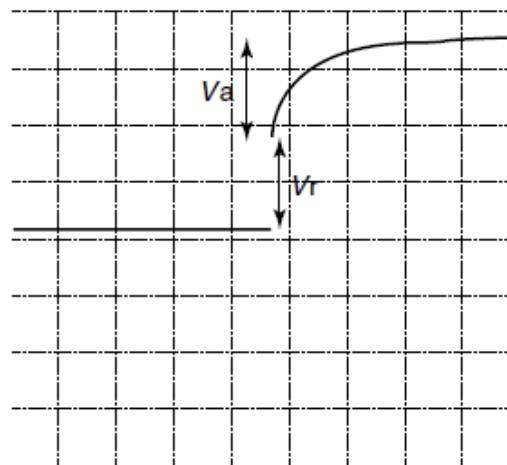


Metode za određivanje tipa dominantnog otpora

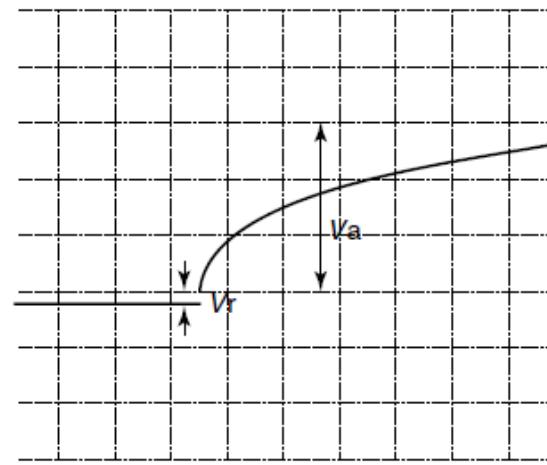
Current interrupt technique



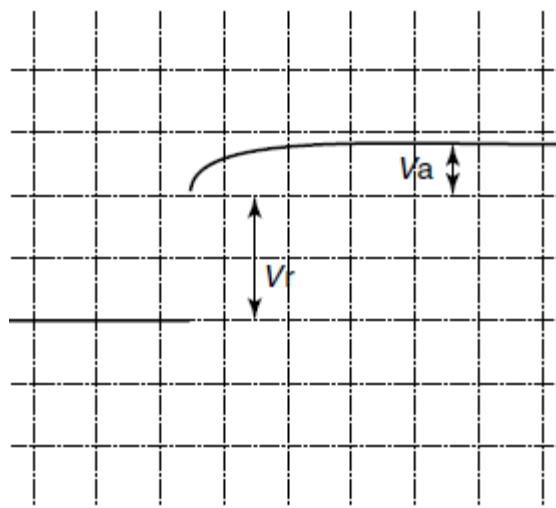
PEMFC



DMFC



SOFC

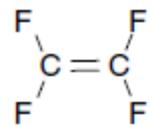
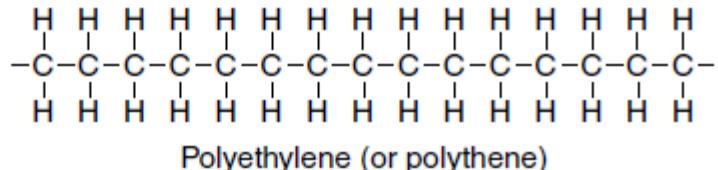
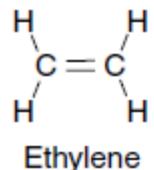


PEMFC – Proton Exchange Membrane Fuel Cell

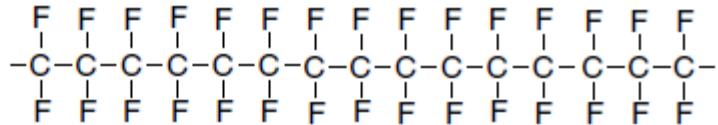
- elektrolit je membrana provodna za vodonične jone
 - sa obe strane je porozna elektroda sa katalitičkim materijalom
 - MEA – membrane electrode assembly
 - serijsko povezivanje pomoću bipolarnih ploča
 - radi na niskim temperaturama, nema korozivnih/štetnih tečnih rastvarača, lako i brzo se pokreće što je pogodno za primenu u prenosivim uređajima i transportu
 - $28 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$ na početku, sad $< 0,2 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$
 - mogućnost proširenja (scalable)- od nekoliko W, preko nekoliko kW do MW
-
- Sličnosti svih tipova PEMFC:
 - elektrolit
 - struktura elektrode i tip katalizatora
-
- Razlike:
 - Raspodela vode
 - Hlađenje
 - Struktura bipolarnih ploča
 - Tip goriva. Čist H_2 , čist O_2 , vazduh

Polimerni elektrolit

- često je tajna i pod patentnom zaštitom
- Sulfonatna grupa na fluoro polimerima

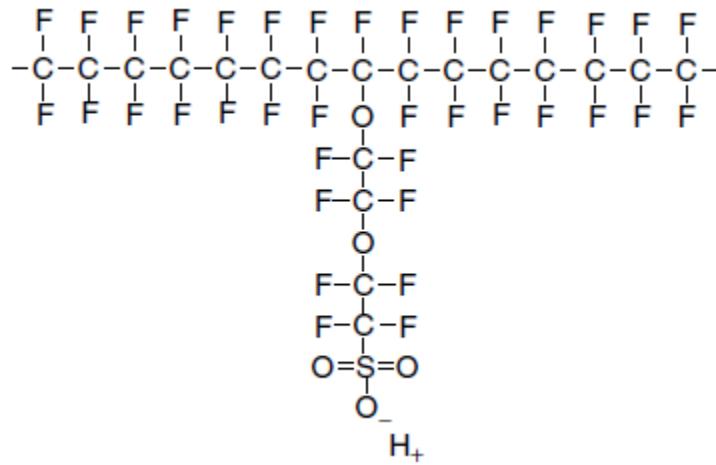


Tetrafluoroethylene



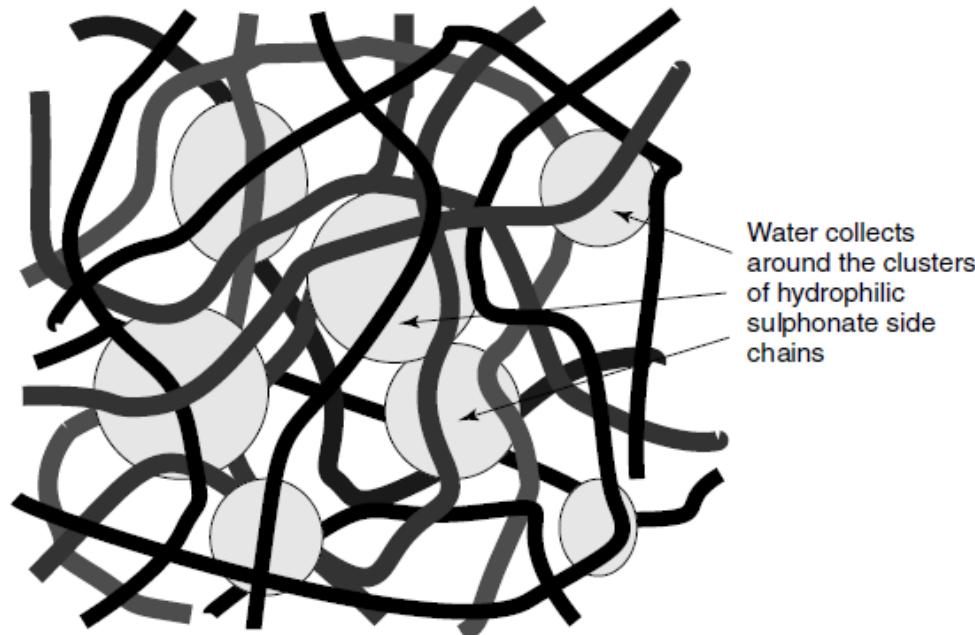
Polytetrafluoroethylene (PTFE)

- Dugotrane i otporne na različite hemijske agense
- Hidrofobne (sprečavaju začepljenja membrane vodom)
- Jonomer (ionomer)



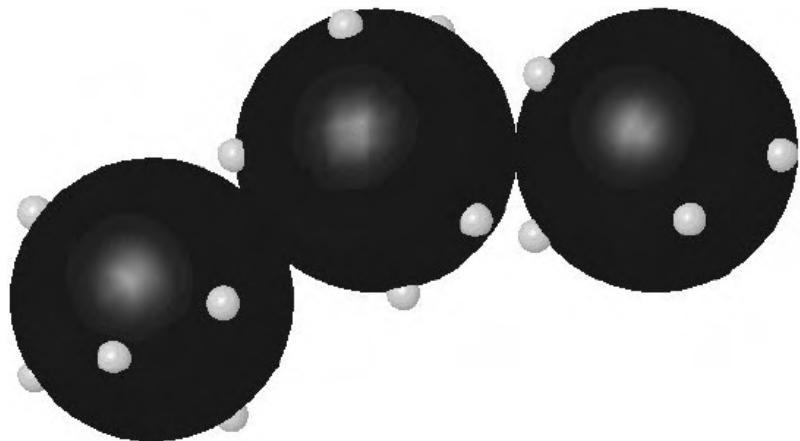
Polimerni elektrolit

- grupisanje bočnih lanca koji su hidrofilni
- povećanje mase od 50% usled apsorpcije vode
- specifična provodljivost $0,1 \text{ S cm}^{-1}$
- hemijska inertnost i stabilnost
- mehanička postojanost i mogućnost pravljenja tankih filmova
- kiselost
- apsorbuju dosta vode
- dobri protonski provodnici uz dobru hidriranost materijala



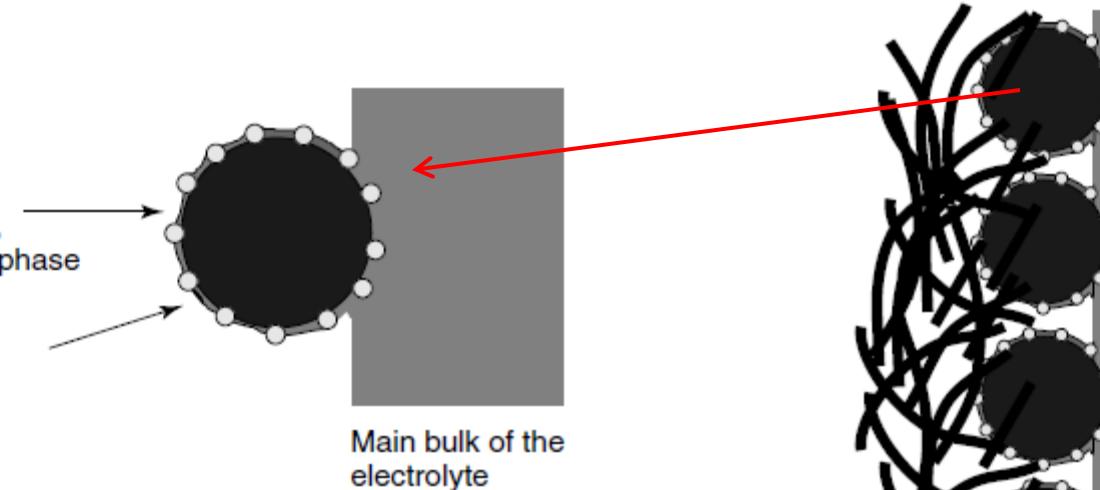
Elektrode i njihova struktura

- Nanočestice platine na nosaču od ugljnika (Carbon Black, Vulkan XC72, KetjenBlack,...)
- Što sitnije čestice kako bi se dobila što veća aktivna površina

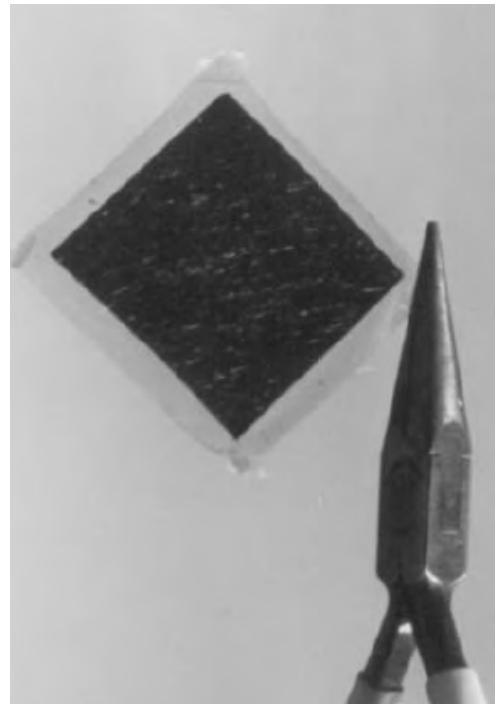


- Fiksiranje Pt/C na ugljnični papir – gas diffusion layer/current collector uz dodatka PTFE
- Toplo presovanje na 140 °C

A thin layer of electrolyte also reaches the catalyst, promoting the three-phase contact between electrolyte, reactant gas, and electrode catalyst.



MEA - Bez obzira gde je pravljena, kojom metodom, koja kompanije, izgledaće slično, radiće na sličan način i zahtevaće isti tretman tokom rada.



Comparison of Fuel Cell Technologies

Fuel Cell Type	Common Electrolyte	Operating Temperature	System Output	Electrical Efficiency	Combined Heat and Power (CHP) Efficiency	Applications	Advantages
Polymer Electrolyte Membrane (PEM)*	Solid organic polymer poly-perfluorosulfonic acid	50 - 100°C 122 - 212°F	<1kW – 250kW	53-58% (transportation) 25-35% (stationary)	70-90% (low-grade waste heat)	▪ Backup power ▪ Portable power ▪ Small distributed generation ▪ Transportation ▪ Specialty vehicles	▪ Solid electrolyte reduces corrosion & electrolyte management problems ▪ Low temperature ▪ Quick start-up
Alkaline (AFC)	Aqueous solution of potassium hydroxide soaked in a matrix	90 - 100°C 194 - 212°F	10kW – 100kW	60%	>80% (low-grade waste heat)	▪ Military ▪ Space	▪ Cathode reaction faster in alkaline electrolyte, leads to higher performance ▪ Can use a variety of catalysts
Phosphoric Acid (PAFC)	Liquid phosphoric acid soaked in a matrix	150 - 200°C 302 - 392°F	50kW – 1MW (250kW module typical)	>40%	>85%	▪ Distributed generation	▪ Higher overall efficiency with CHP ▪ Increased tolerance to impurities in hydrogen
Molten Carbonate (MCFC)	Liquid solution of lithium, sodium, and/or potassium carbonates, soaked in a matrix	600 - 700°C 1112 - 1292°F	<1kW – 1MW (250kW module typical)	45-47%	>80%	▪ Electric utility ▪ Large distributed generation	▪ High efficiency ▪ Fuel flexibility ▪ Can use a variety of catalysts ▪ Suitable for CHP
Solid Oxide (SOFC)	Yttria stabilized zirconia	600 - 1000°C 1202 - 1832°F	<1kW – 3MW	35-43%	<90%	▪ Auxiliary power ▪ Electric utility ▪ Large distributed generation	▪ High efficiency ▪ Fuel flexibility ▪ Can use a variety of catalysts ▪ Solid electrolyte reduces electrolyte management problems ▪ Suitable for CHP ▪ Hybrid/GT cycle

*Direct Methanol Fuel Cells (DMFC) are a subset of PEM typically used for small portable power applications with a size range of about a subwatt to 100W and operating at 60 - 90°C.

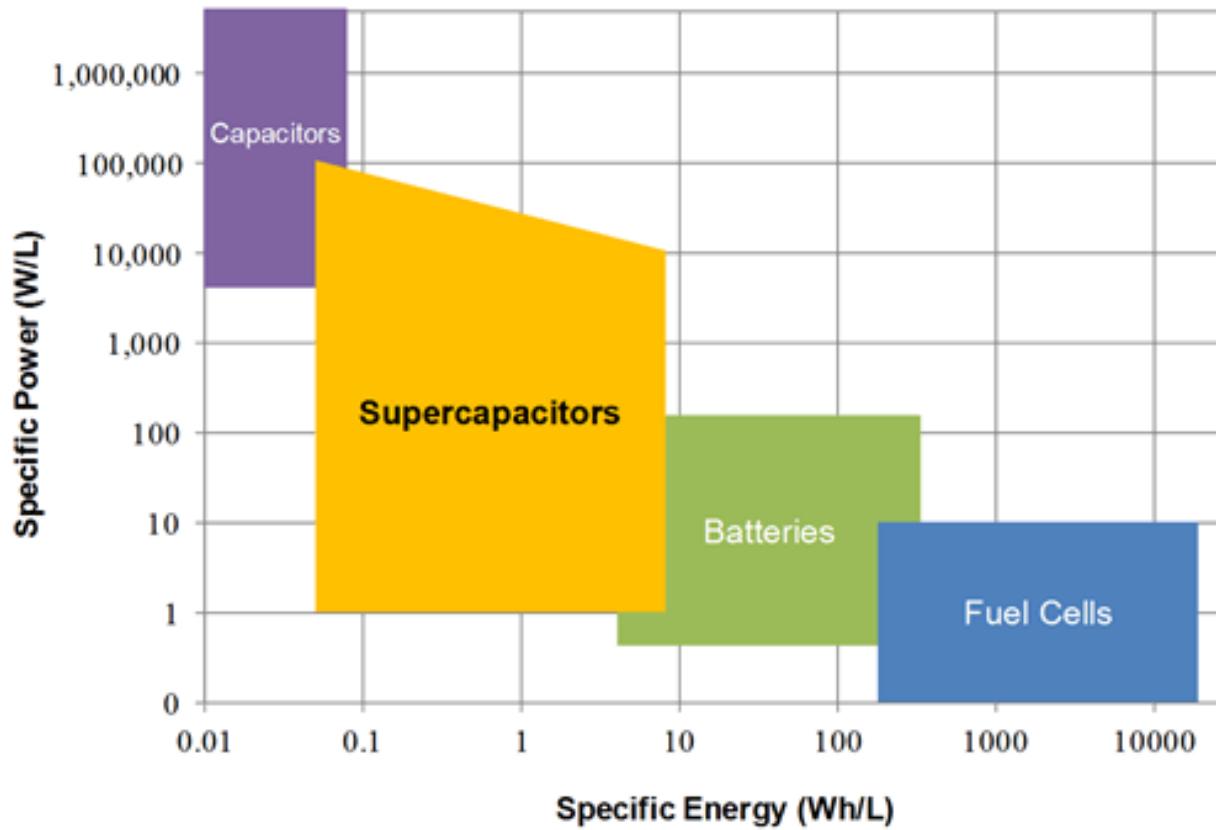
For print copies of this fact sheet, please call the DOE Energy Efficiency and Renewable Energy Information Center at 877-EERE-INF(0)/877-337-3463.

December 2008



U.S. Department of Energy Hydrogen Program
www.hydrogen.energy.gov

Poređenje superkondenzatori vs. baterije vs. gorivne ćelije



What Are Batteries, Fuel Cells, and Supercapacitors?

Martin Winter and Ralph J. Brodd, *Chem. Rev.* 2004, 104, 10, 4245–4270

superkondenzatori vs. baterije vs. gorivne ćelije

Property	CAP-XX Supercapacitors	Capacitors	Fuel Cells	Batteries
Charge/Discharge Time	Milliseconds to Seconds	Picoseconds to Milliseconds	10 to 300 hrs. Instant charge (refuel).	1 to 10 hrs
Operating Temperature	-40 to +85°C	-20 to +100°C	+25 to +90°C	-20 to +65°C
Operating Voltage	2.3 to 2.75V	6 to 800V	0.6V	1.25 to 4.2V
Capacitance	100mF to 1500F	10pF to 2.2mF	N/A	N/A
Life	50,000+ hrs Unlimited cycles	>100,000 cycles	1,500 to 10,000 hrs	150 to 1,500 cycles
Weight	1 g to 230g	1g to 10kg	20g to >5kg	1g to >10kg
Power Density	10 to 120 kW/kg	0.25 to 10,000 kW/kg	0.001 to 0.1 kW/kg	0.005 to 0.4 kW/kg
Energy Density	1 to 10 Wh/kg	0.01 to 0.05 Wh/kg	300 to 3,000 Wh/kg	8 to 600 Wh/kg
Pulse Load	Up to 100A	Up to 1000A	Up to 150mA/cm ²	Up to 5A