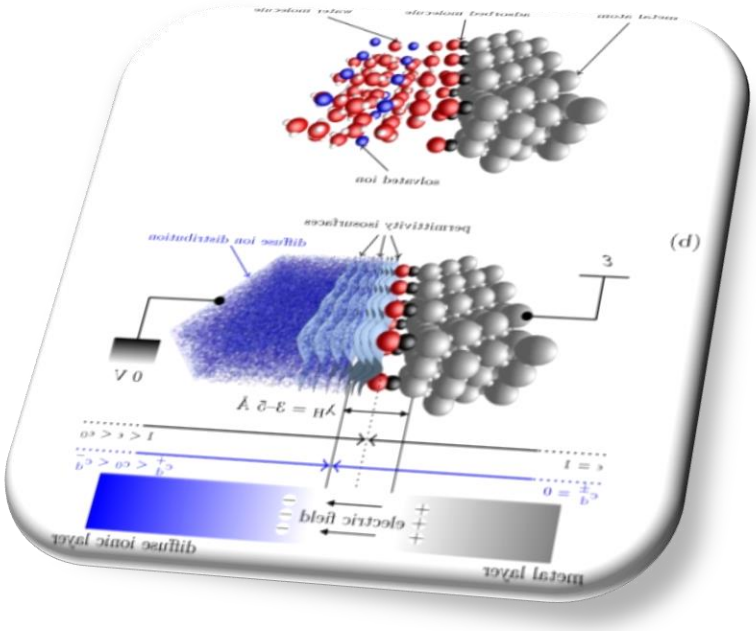
Savremeni pravci u razvoju ugljeničnih materijala za elektrohemijske kondenzatore

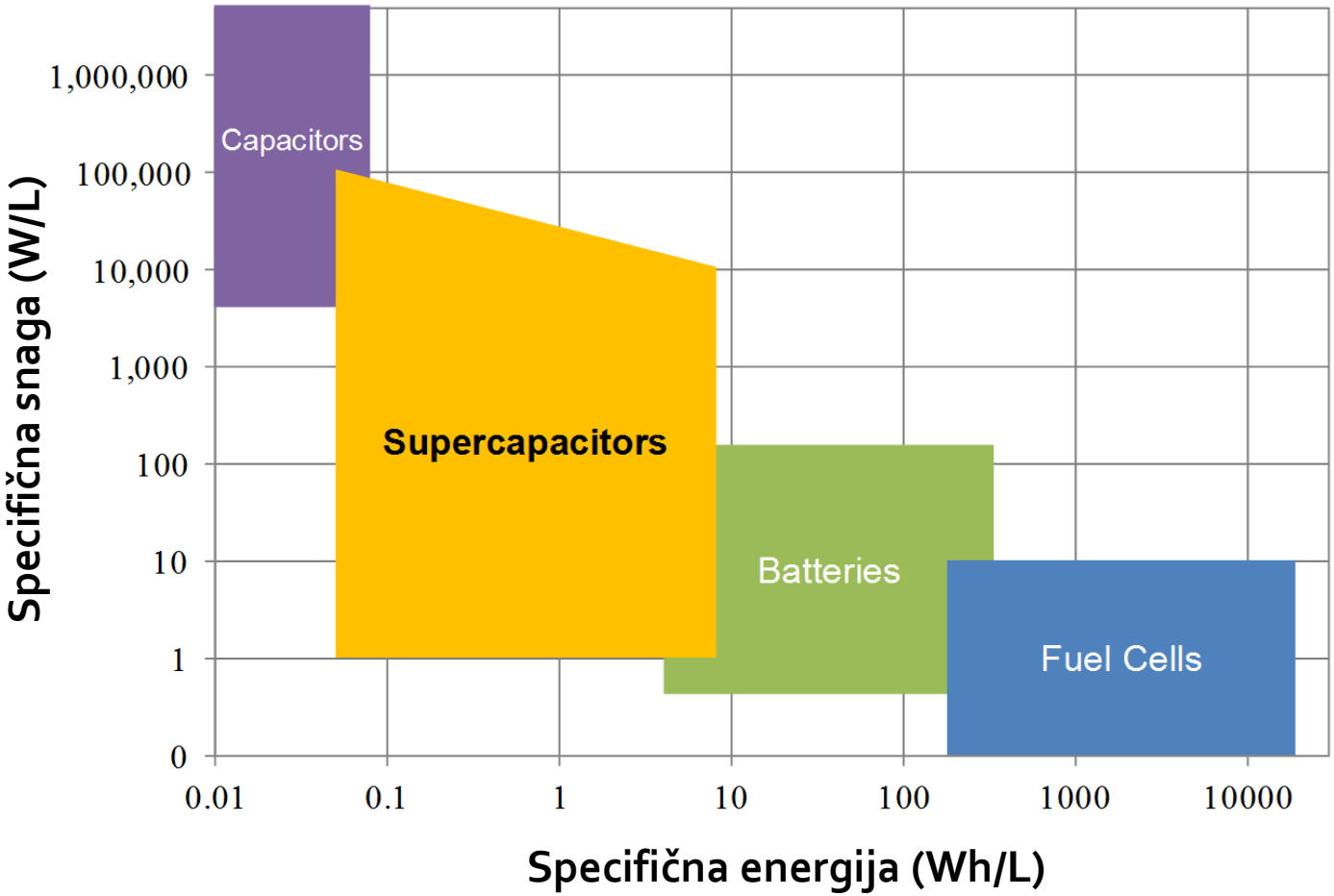


Igor Pašti

Univerzitet u Beogradu – Fakultet za fizičku hemiju

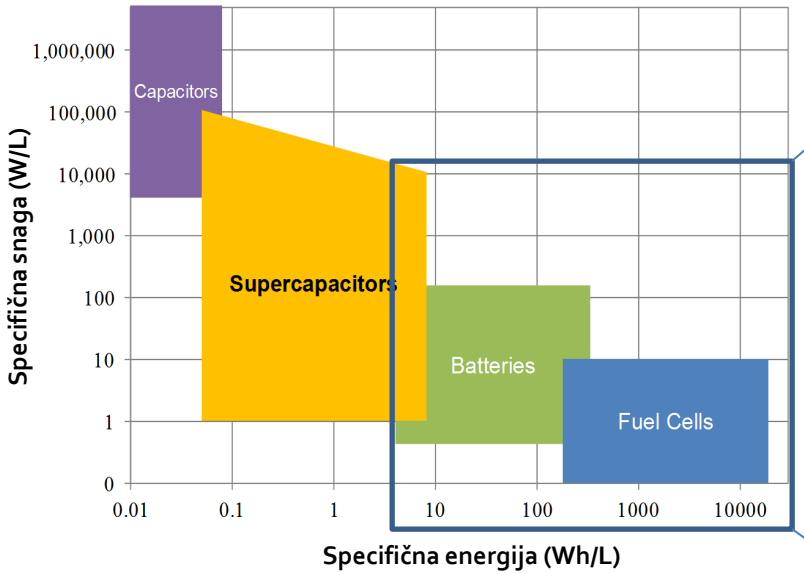
- Elektrohemijsko skladištenje energije
- Elektrohemijski kondenzator
- Materijali za elektrohemijske kondenzatore
- Odabrani primeri
- Od laboratorije do police

Elektrohemijsko skladištenje energije

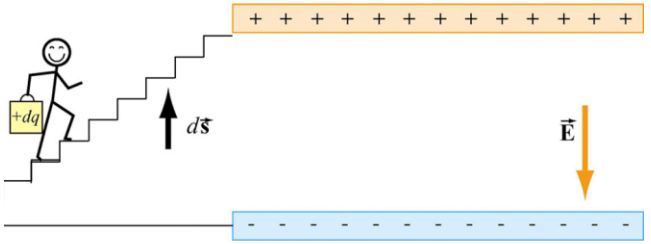


https://www.exponent.com/knowledge/alerts/2018/02/supercapacitors

Elektrohemijsko skladištenje energije



A + B = C + D ΔG

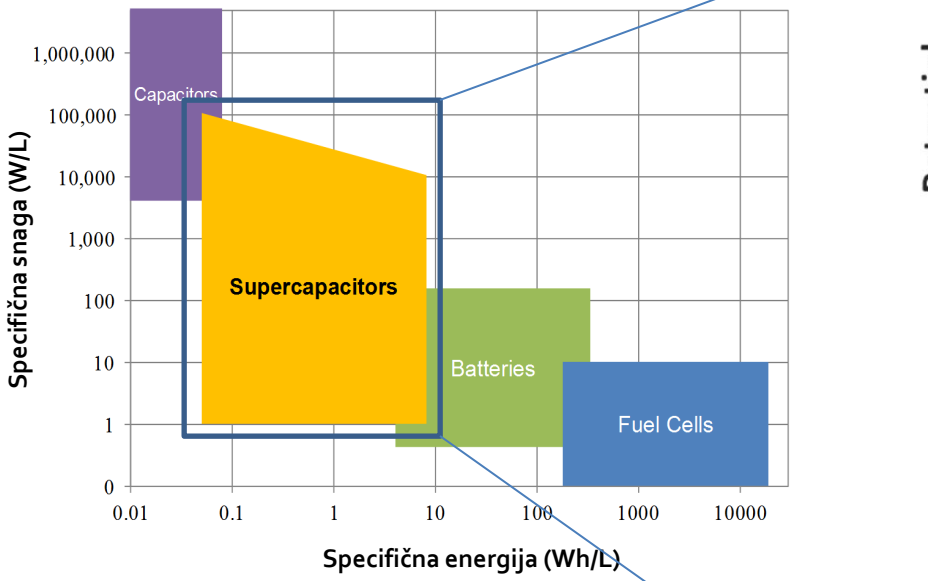


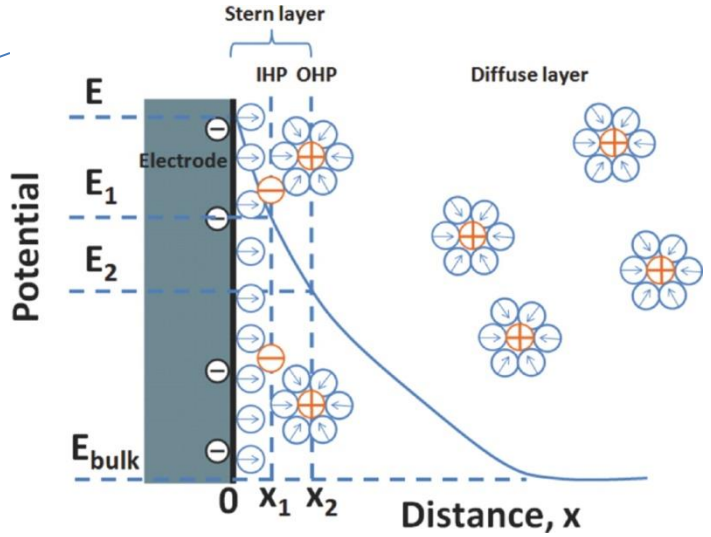
Rad po mogu reaktanta

$n \times F \times \varepsilon = -\Delta G$

https://www.exponent.com/knowledge/alerts/2018/02/supercapacitors

Elektrohemijsko skladištenje energije



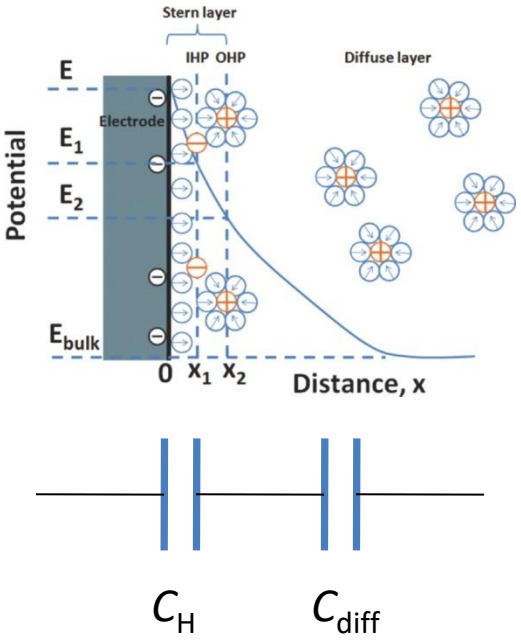


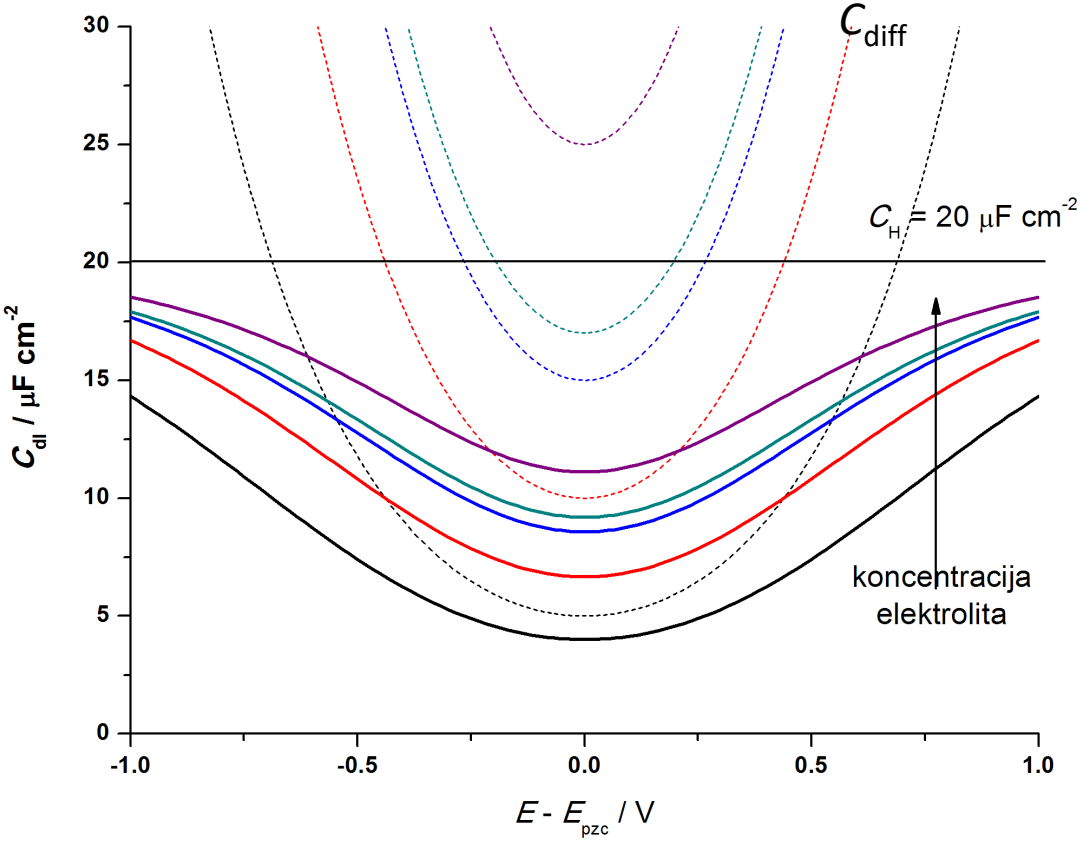
Energija skladištena u električnom polju koje se formira na faznoj granici elektronski/jonski provodnik

$$E \sim C_{dl} \times \Delta V^2$$

Elektrohemijski kondenzator

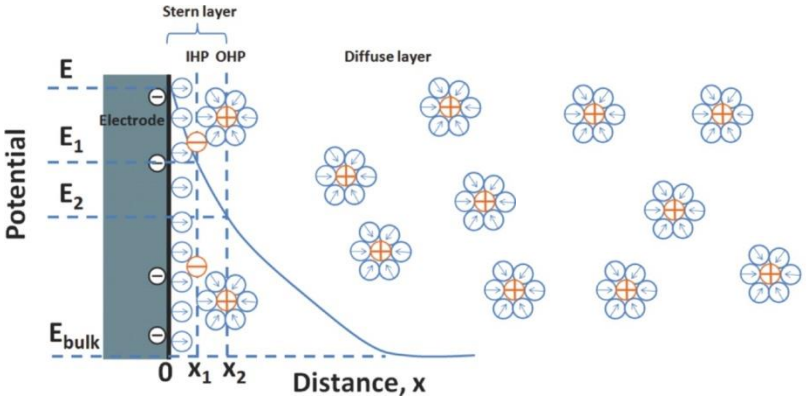
$$E \sim C_{dl} \times \Delta V^2$$

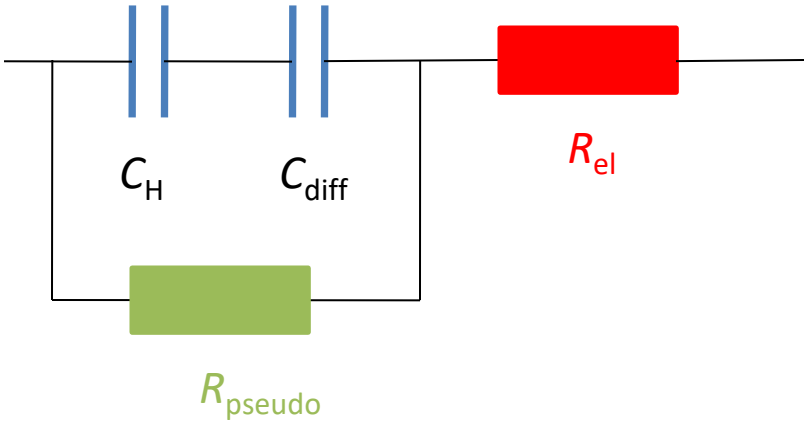


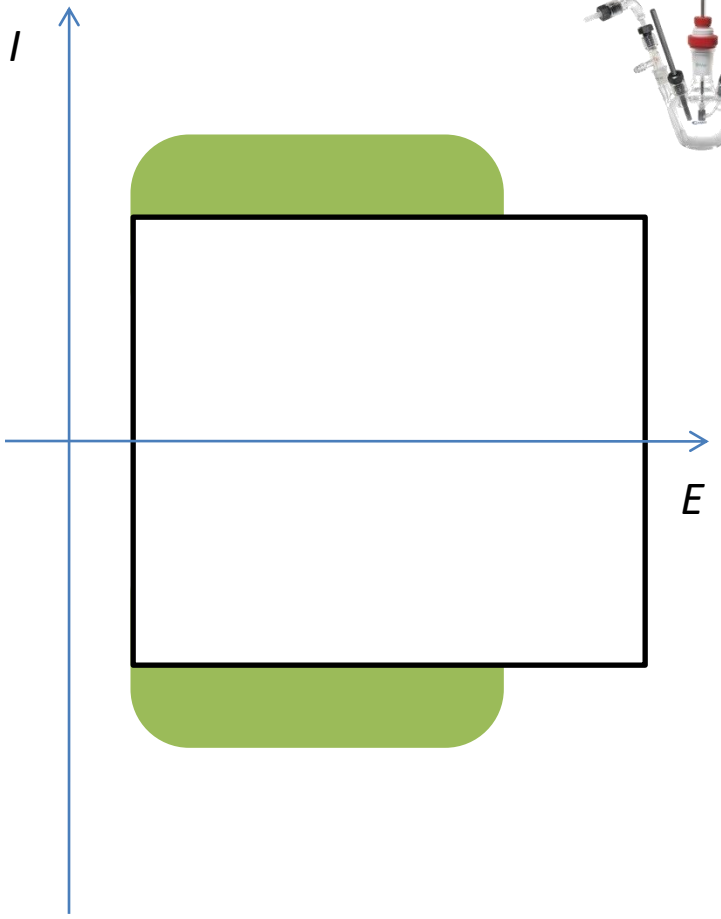


U odsustvu procesa razmene elektrona u **koncentrovanim** elektroličkim rastvorima, kapacitet EDS je oko 20 μF cm^{-2} za sve materijale. **Cilj povećati površinu po jedinici mase.**

Elektrohemijski kondenzator

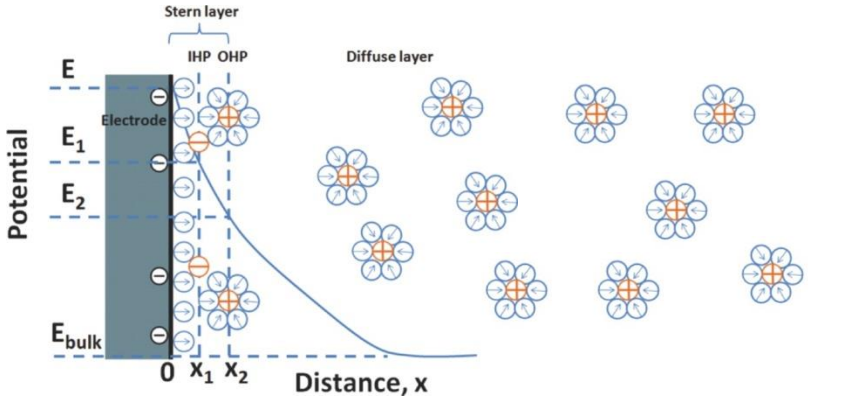


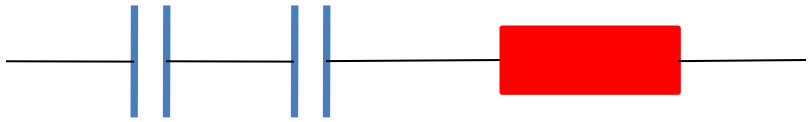




Kapacitivni odgovor može biti uvećan usled pseudocapacitivnih procesa na površini materijala (brza izmena elektrona).

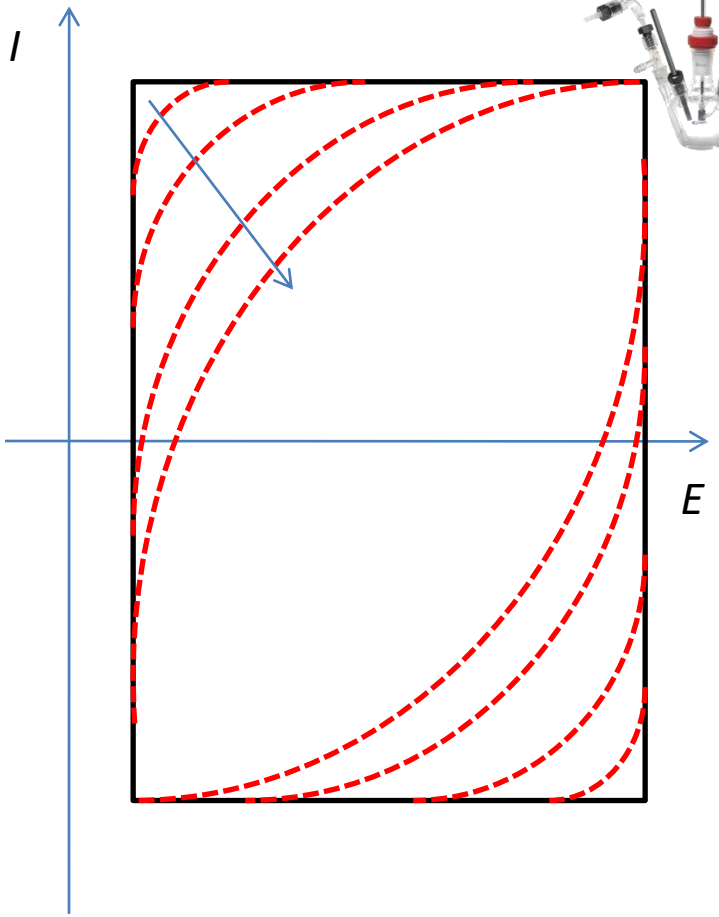
Elektrohemijski kondenzator

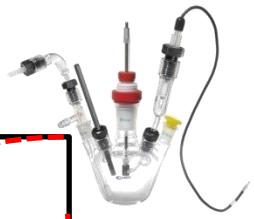




C_H C_{diff} R_{el}

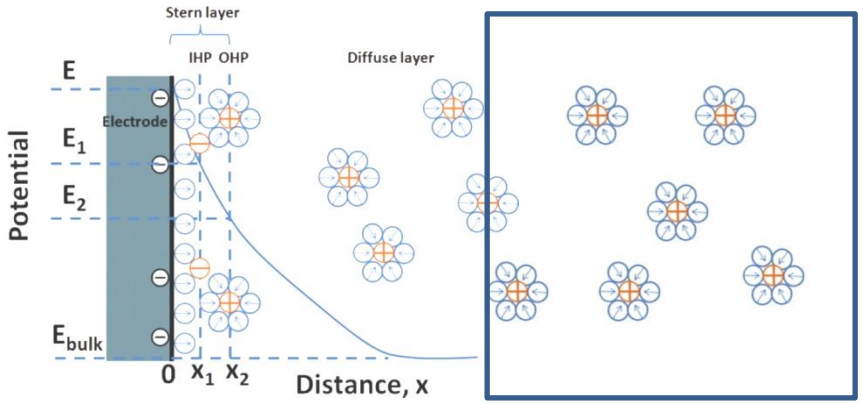
$$j_C = \frac{E}{R_e} e^{\frac{-t}{R_e C_{dl}}}$$



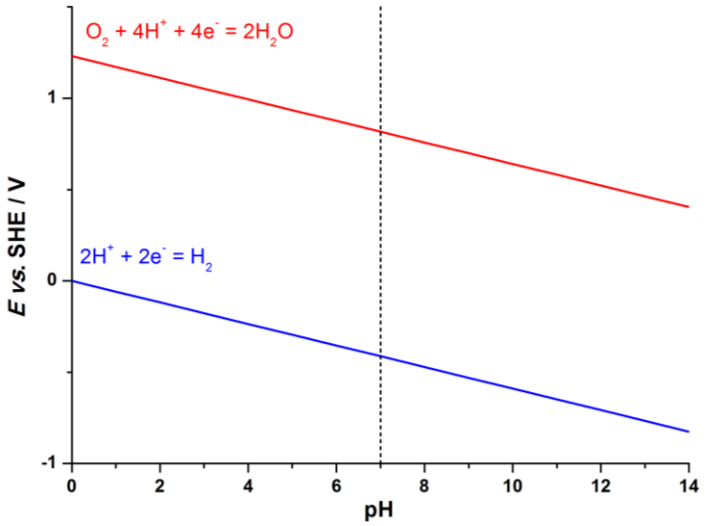


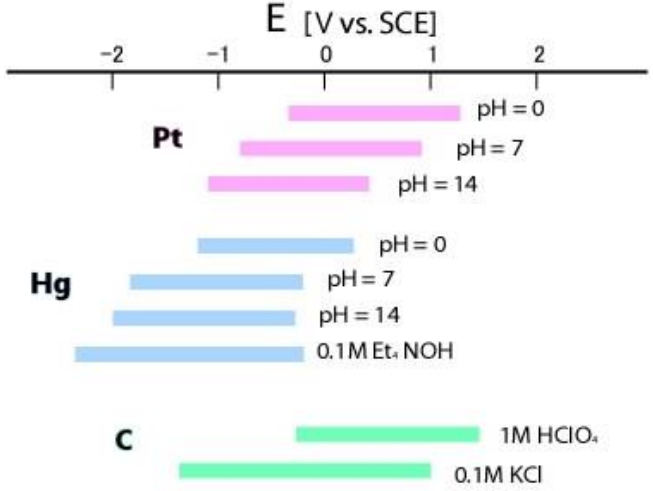
Otpor elektrolita takođe utiče na kapacitivni odgovor, neophodno je koristiti **koncentrovane elektrolite.**

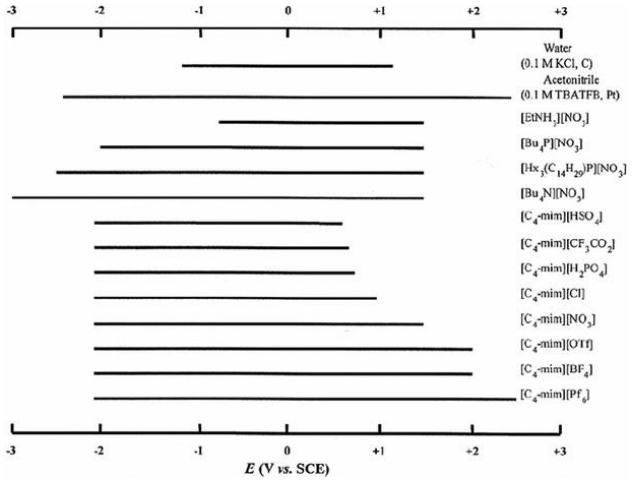
Elektrohemijski kondenzator



$E \sim C_{dl} \times \Delta V^2$







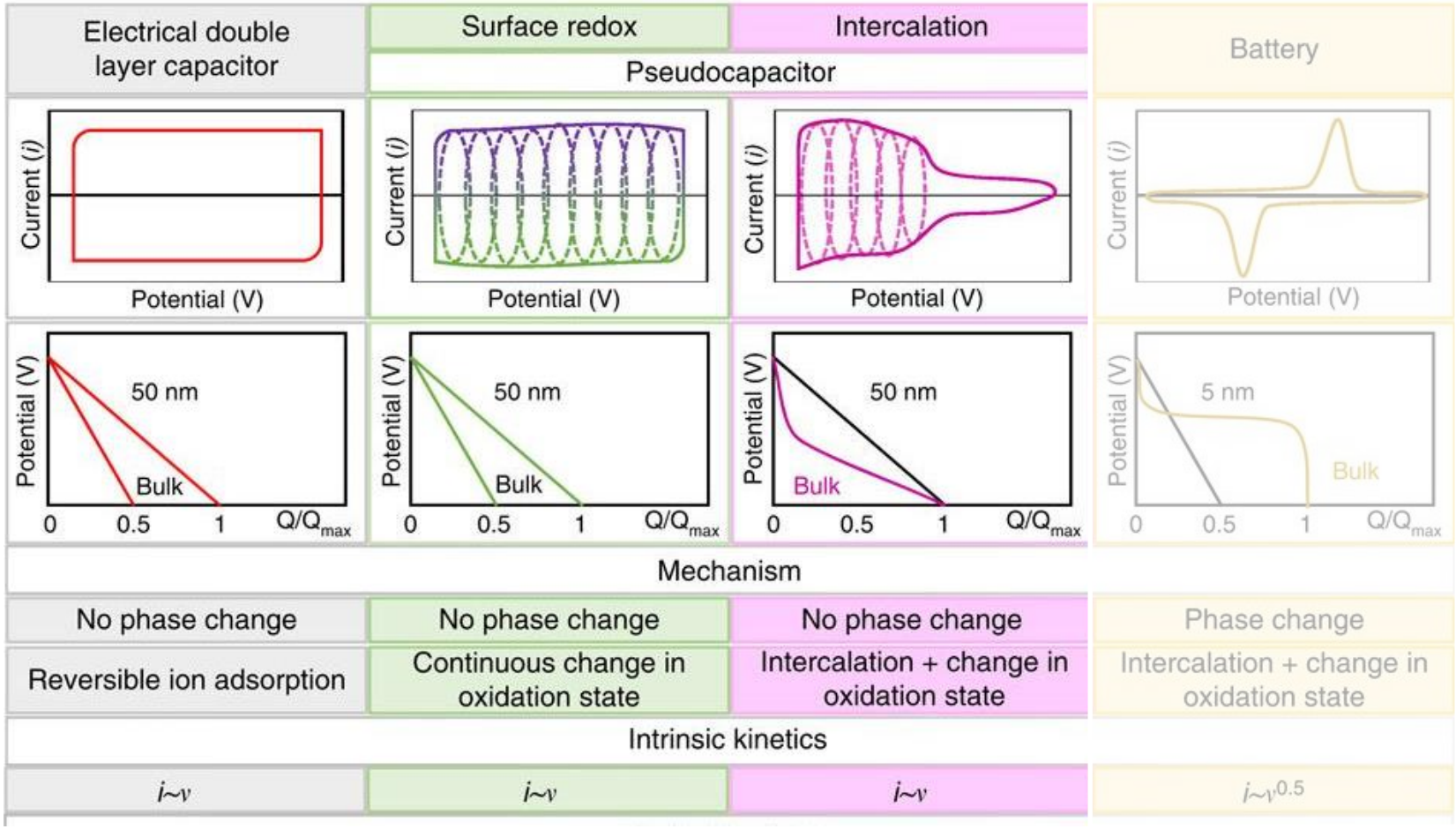
Elektrohemijski kondenzator

Elektrohemijski dostupna površina u koncentrovanom elektrolitu
Pseudocapacitivni procesi

$$E \sim C_{dl} \times \Delta V^2$$

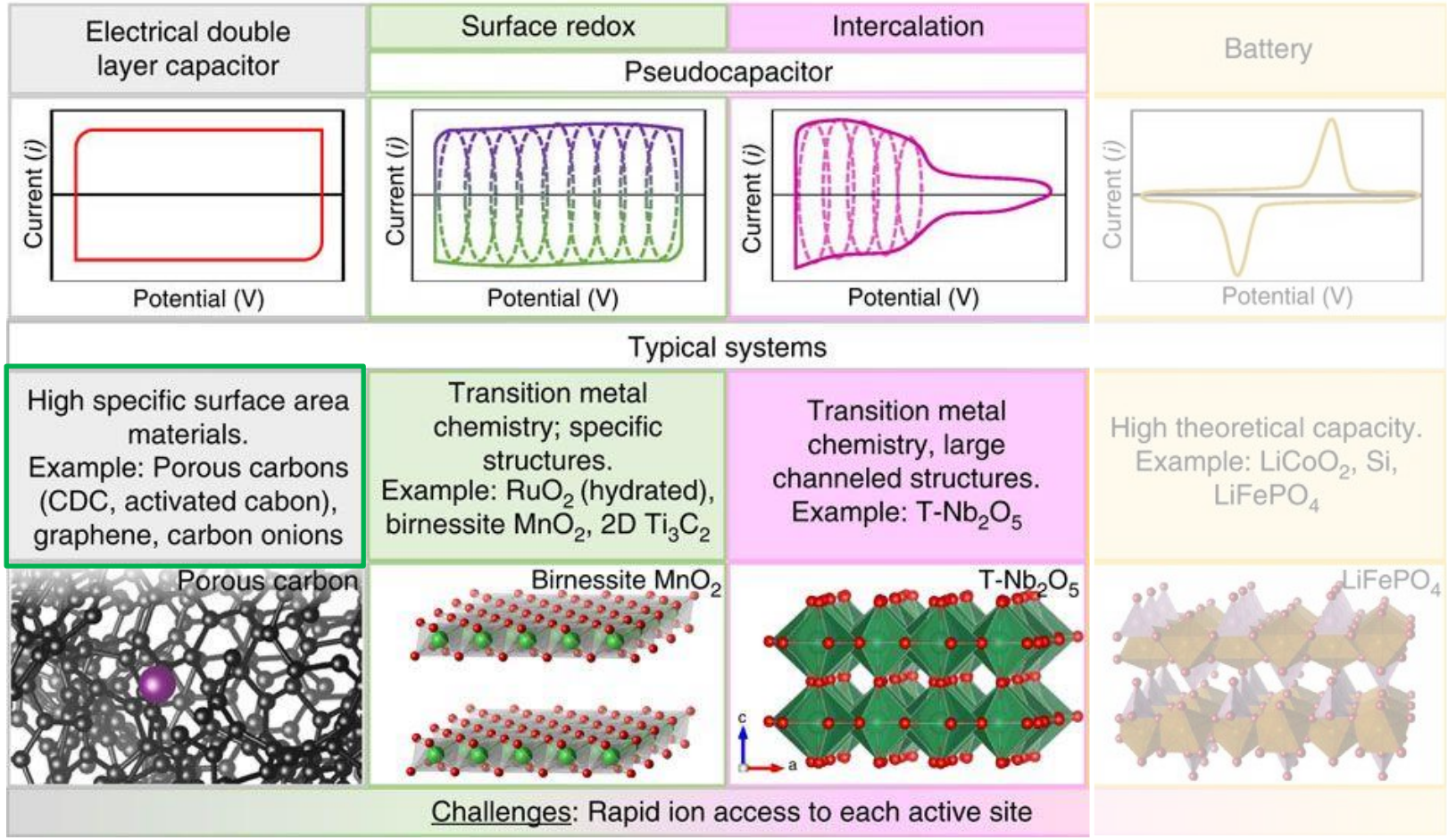
Elektrohemijski prozor elektrolita.
Ireverzibilne elektrohemijske promene elektrodnog materijala.

Materijali za elektrohemijske kondenzatore



Adaptirano iz Nature Communications volume 7, Article number: 12647 (2016)

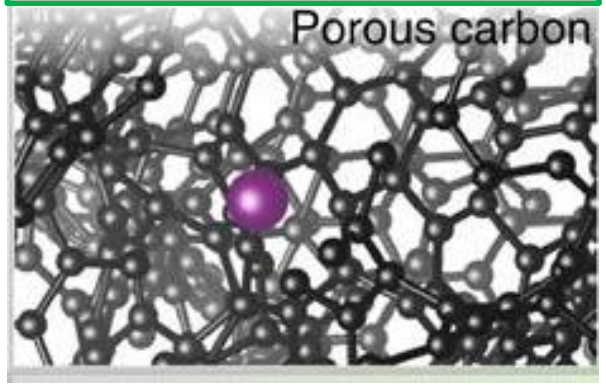
Materijali za elektrohemijske kondenzatore



Adaptirano iz Nature Communications volume 7, Article number: 12647 (2016)

Materijali za elektrohemijske kondenzatore

High specific surface area materials.
Example: Porous carbons (CDC, activated cabon), graphene, carbon onions



20 µF cm^{-2} × 1000 m^2 g^{-1} = 200 F g^{-1}

Ugljenični materijali:

-Širok elektrohemijski prozor

-Hemijski inertni (relativno)

-Jeftini (relativno)

Obabrani primeri:

-Materijali izvedeni iz biomase

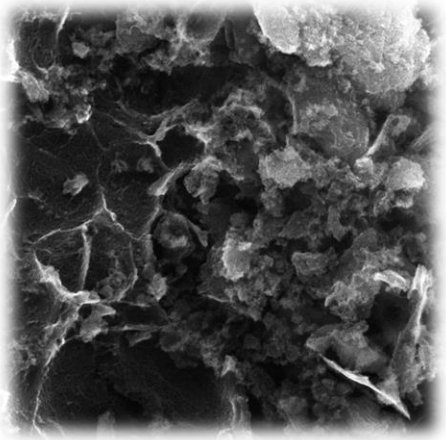
-Materijali izvedeni iz polimera

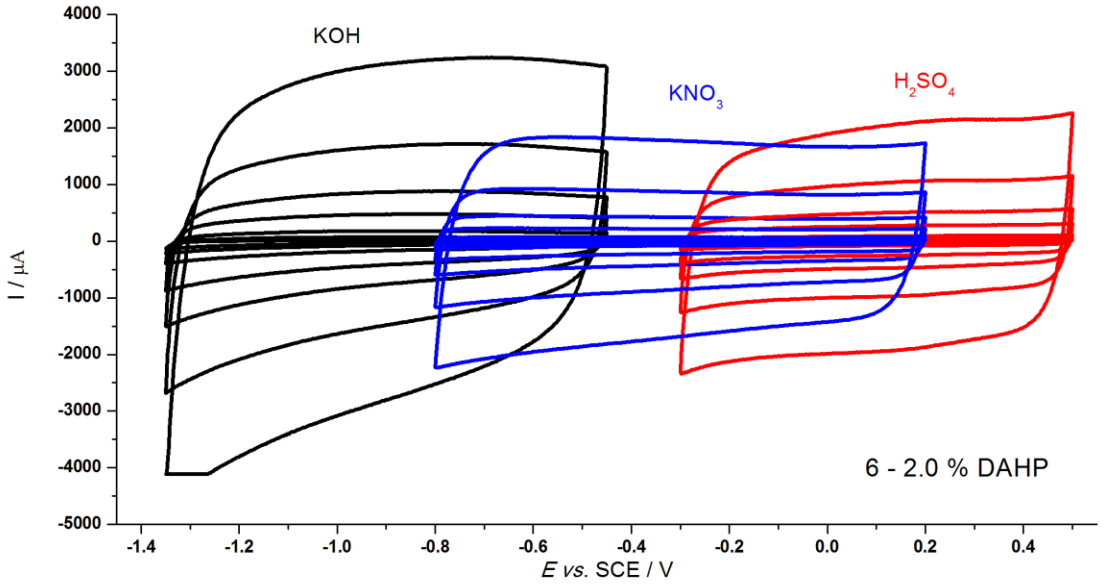
-Materijali na bazi grafena

Materijali izvedeni iz biomase

Temperaturski tretman
Hemijska impregnacija

Aktivacija





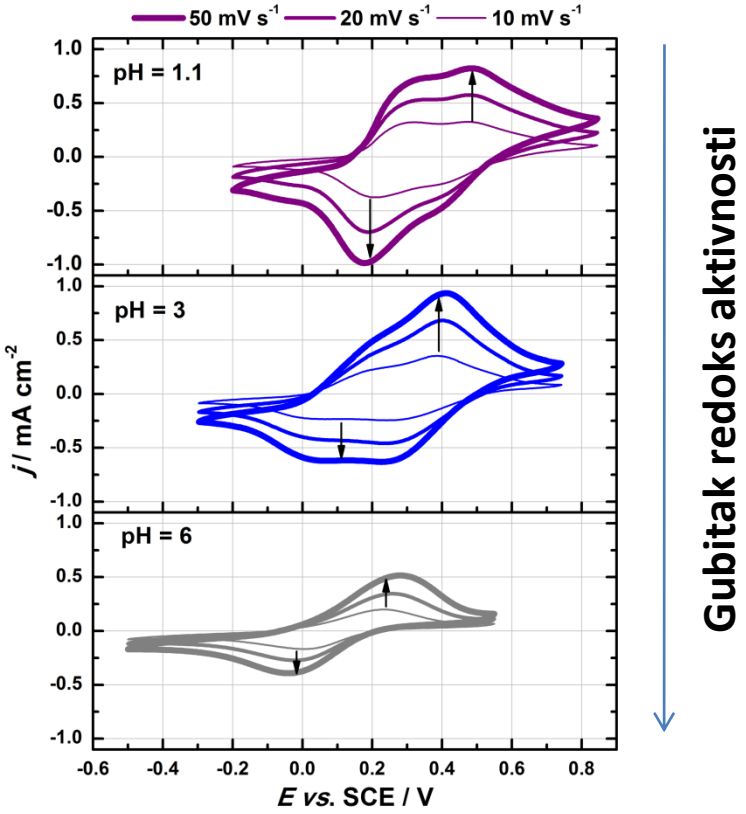
Biomasa jer:

- Prirodno sadrži heteroatome
- Jeftina je lako dostupna
- Značajan ekološki aspekt
- Trenutno se najviše ispituje kraft lignin

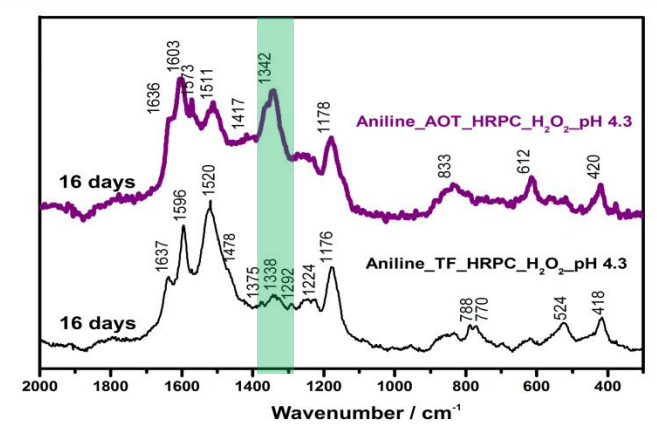
-C_{spec} 100 – 200 F g^{-1}

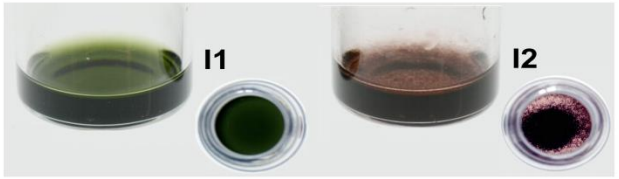
Materijali izvedeni iz polimera

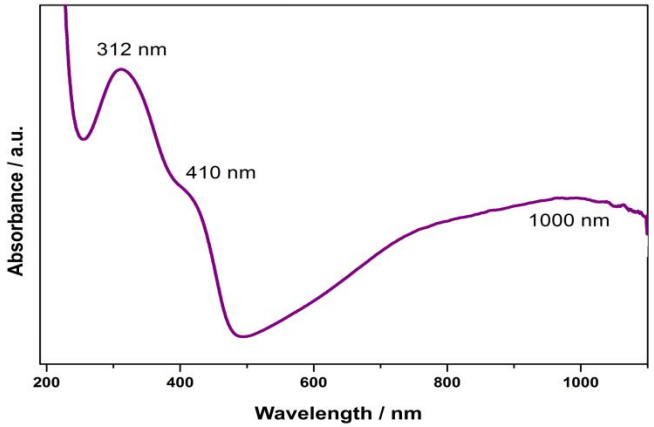
Provodni polimeri su interesantni materijali za elektrohemijske kondenzatore



Capacitet potiče od redoks aktivnih grupa

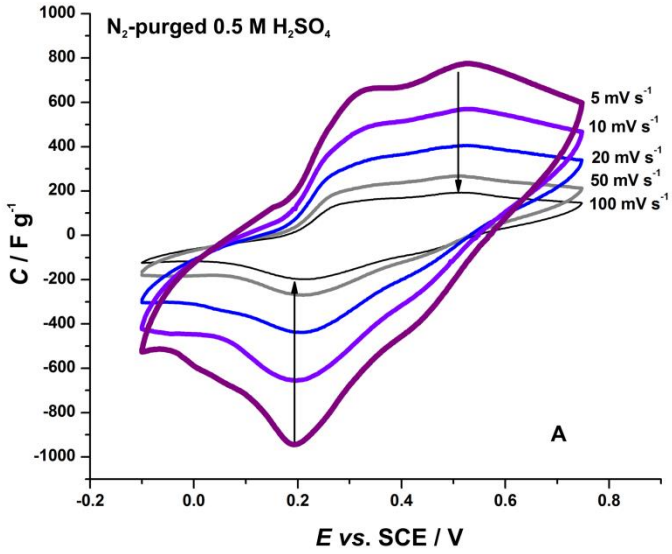


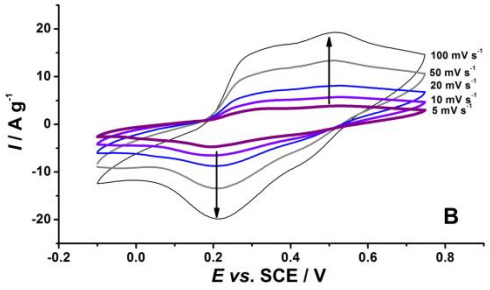


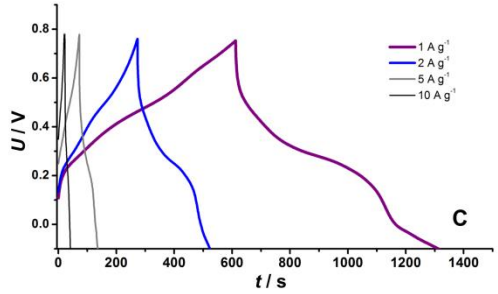


Pašti et al. Electrochimica Acta 258 (2017) 834-841

Materijali izvedeni iz polimera

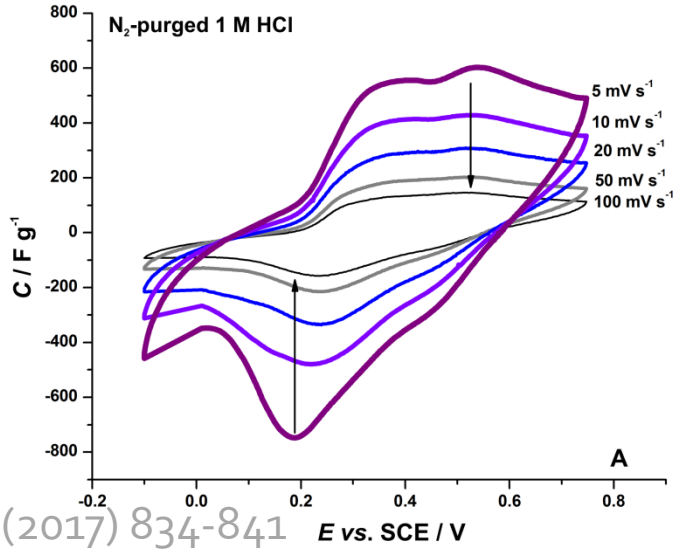


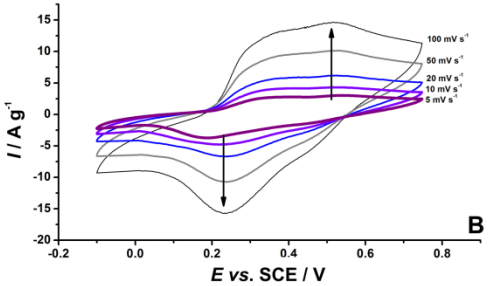


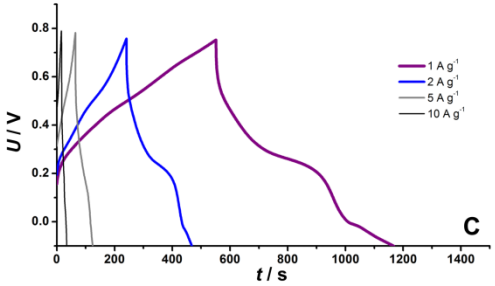


Osetljivi na pH

Osetljivi na ireverzibilne promene



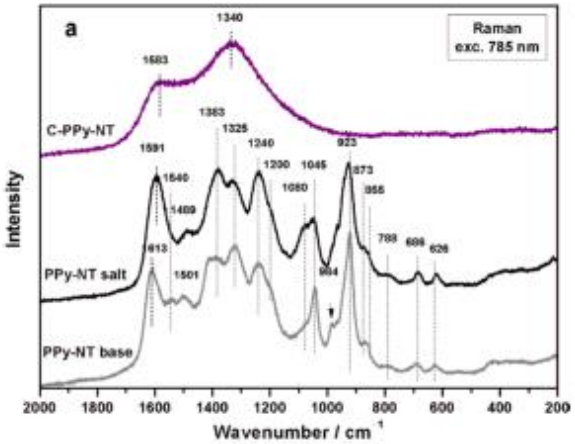




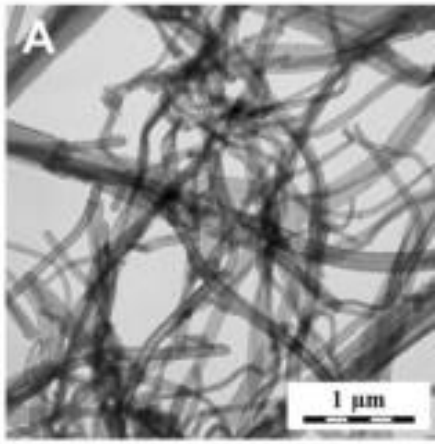
Pašti et al. Electrochimica Acta 258 (2017) 834-841

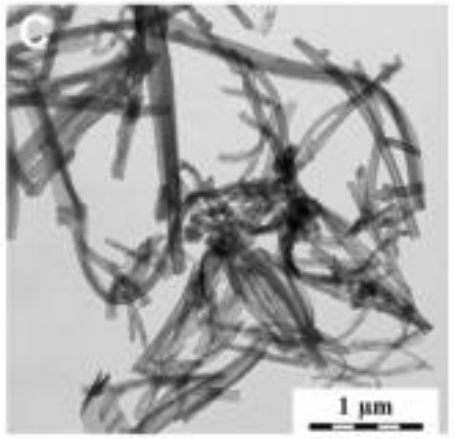
Materijali izvedeni iz polimera

Karbonizacija polimernih nanostruktura

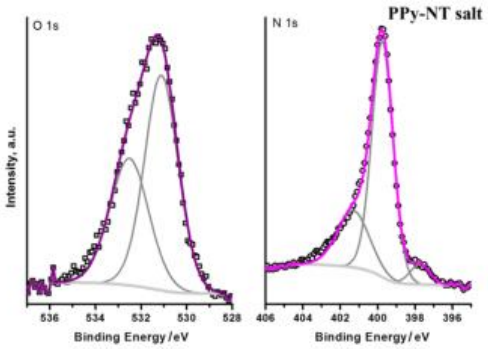


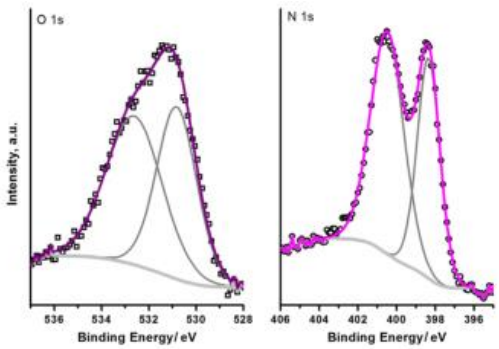
Zadržava se polazna morfologija





PPy NT **Carb-PPy NT**

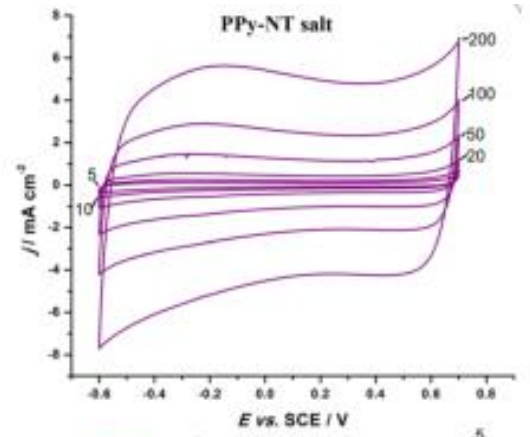


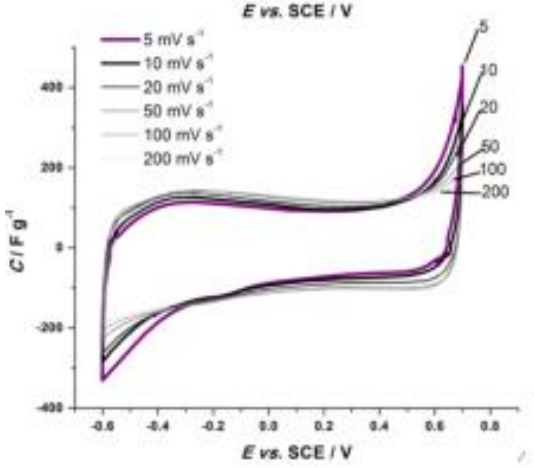


Ugradnja heteroatoma (pseudocapacitet)

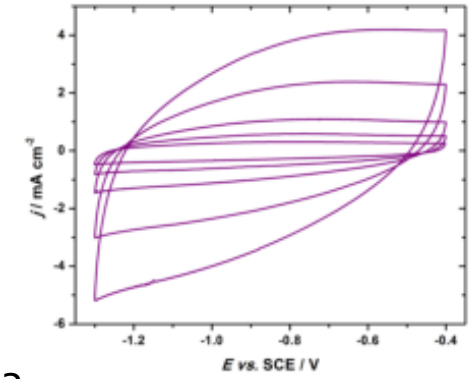
Ćirić-Marjanović et al. The Journal of Physical Chemistry C 118 (2015) 14770-14784

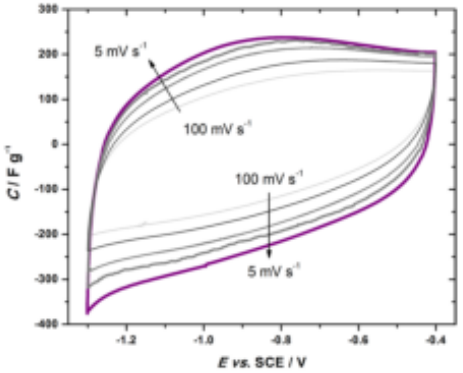
Materijali izvedeni iz polimera

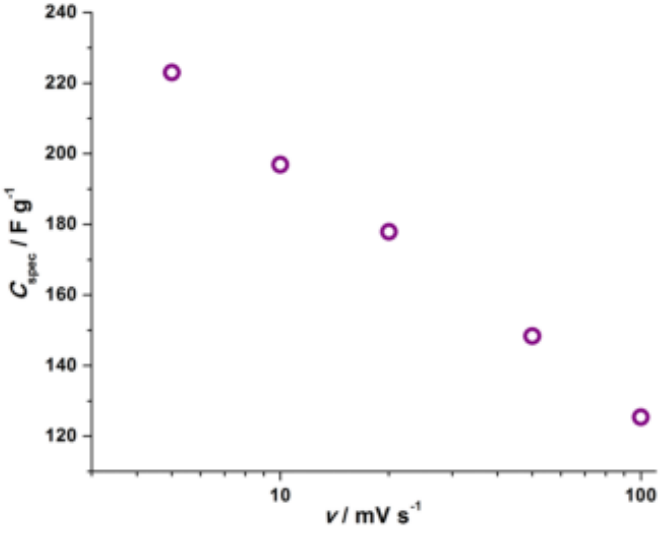




karbonizacija







Ćirić-Marjanović et al. The Journal of Physical Chemistry C 118 (2015) 14770-14784

Materijali izvedeni iz polimera

PANI aerogel to **Carbogel**

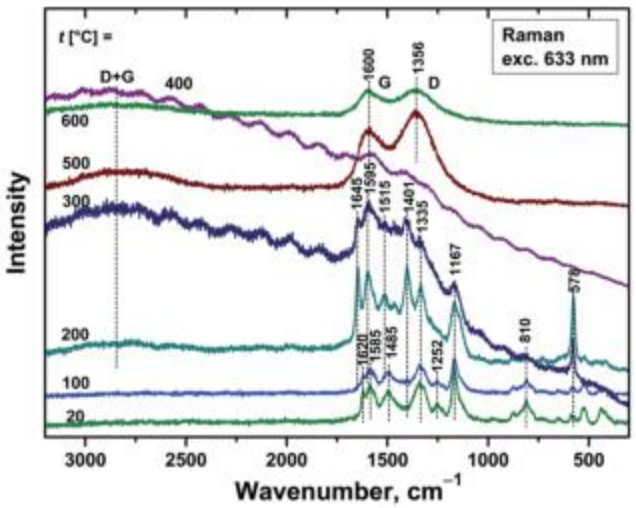


Fig. 4 Raman spectra of the PANI aerogel after exposure to various temperatures. Excitation wavelength: 633 nm.

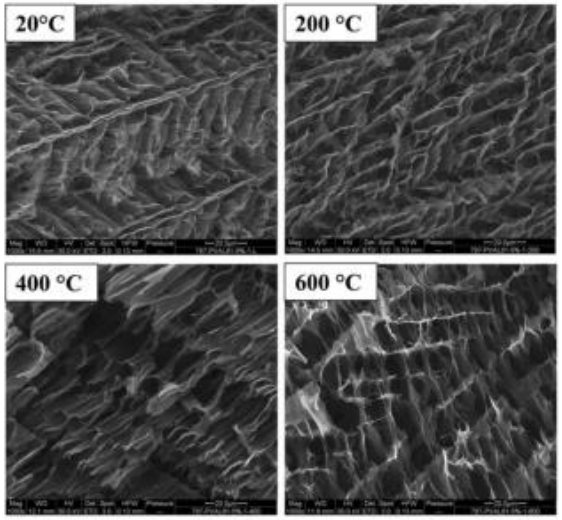


Fig. 5 Micrographs of aerogels exposed to various temperatures.

Temperature, °C	Specific surface area, $m^2 g^{-1}$	Pore diameter, μm
20	12	5.3
100	10.6	43.4
200	3.92	24.1
300	22.5	18.2
400	115	17.9
500	680	39.2
600	588	11.4

Bober et al. Journal of Materials Chemistry A 7 (2019) 1785-1796

Materijali izvedeni iz polimera

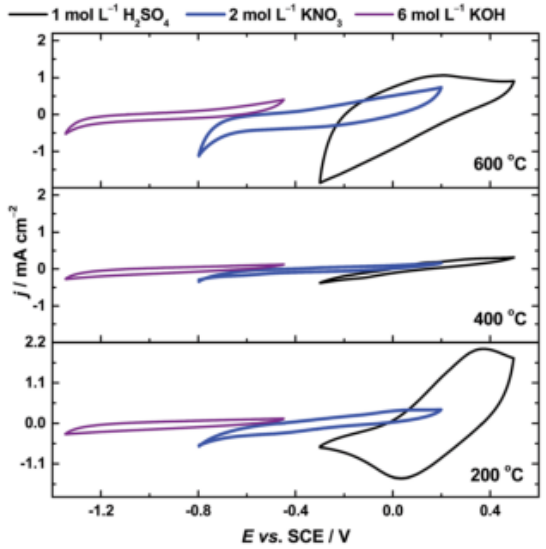
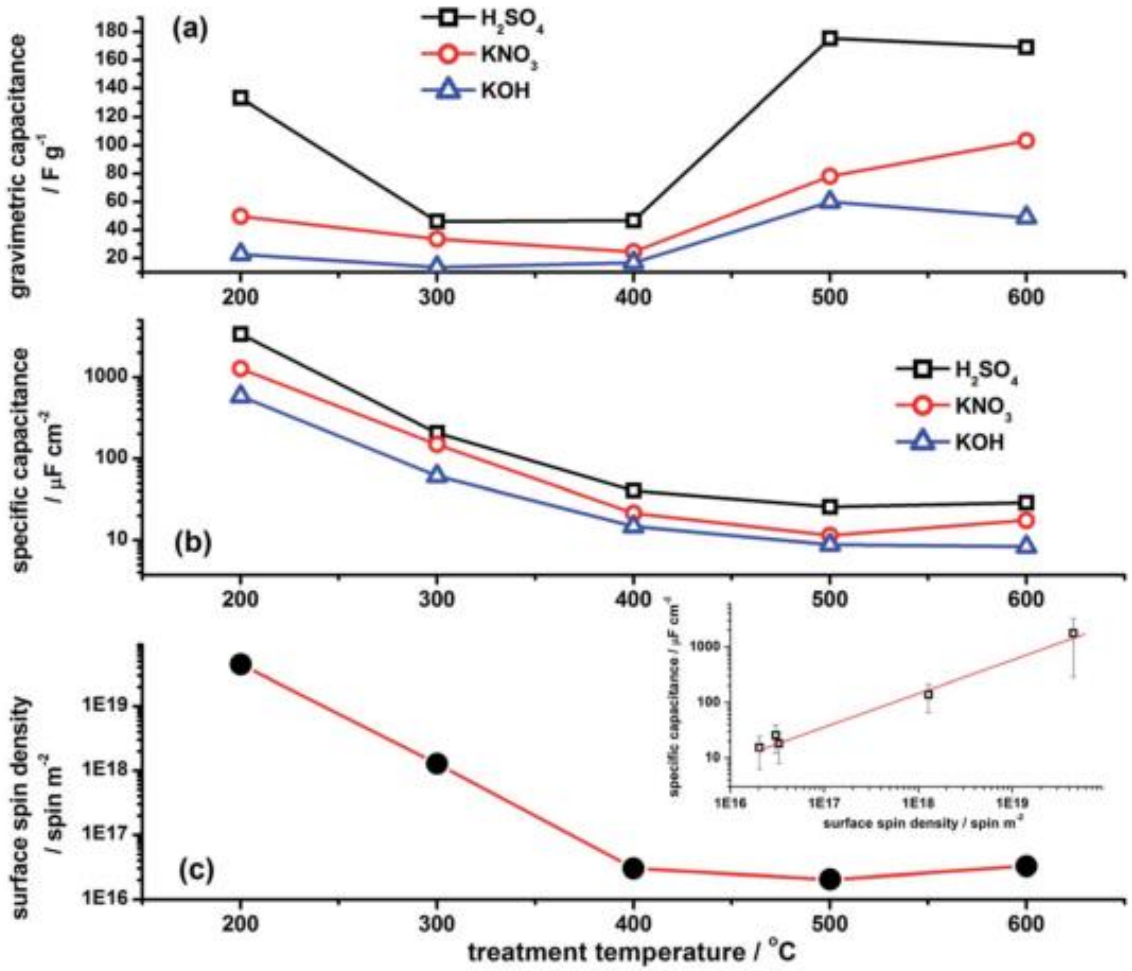


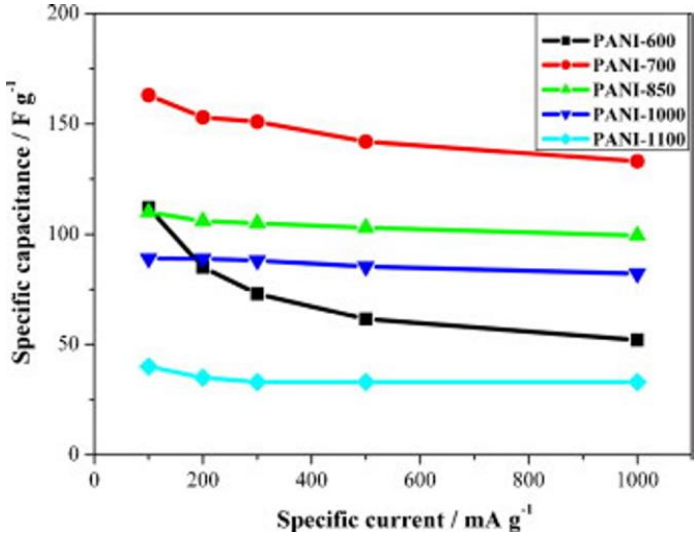
Fig. 10 Cyclic voltammograms of PANI aerogels heated to 200 °C (bottom), 400 °C (middle) and 600 °C (top) recorded in N_2-purged 1 M H_2SO_4, 2 M KNO_3 and 6 M KOH at the scan rate of 100 mV s^{-1}.



Bober et al. Journal of Materials Chemistry A 7 (2019) 1785-1796

Materijali izvedeni iz polimera

Electrochimica Acta, 55 (23), pp. 7021-7027



Uticaj:

1. Temperature karbonizacije
2. Morfologije prekursora
3. Dopanta
4. ...

Najčešće korišćeni provodni polimeri:

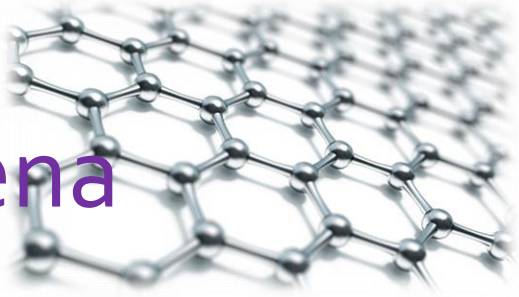
1. Polianilin (PANI)
2. Polipirol (PPy)

Kapaciteti:

1. "Čist" – do 400 F g^{-1} (i do 70% pseudocapaciteta)
2. Kompoziti do 1000 F g^{-1}

Pregled – Pašti et al. Synthetic Metals 246 (2018) 267-281

Materijali na bazi grafena



Google "graphene is unique"

All Images News Videos Maps More Settings Tools

About 29,200 results (0.37 seconds)

It is this unique structure that gives the material its incredible and extensive array of features, as well. One of its unique properties is that, in a single layer

Google "graphene is perfect"

All Images Videos News Maps More Settings Tools

About 11,300 results (0.39 seconds)

Will be graphene the material of the future? - ResearchGate

https://www.researchgate.net › post › Will_be_graphene_the_future_material

12 answers

Google "graphene is amazing"

All Images Videos News Maps More Settings Tools

About 9,340 results (0.33 seconds)

Why Graphene is Amazing - Science in Society Archive

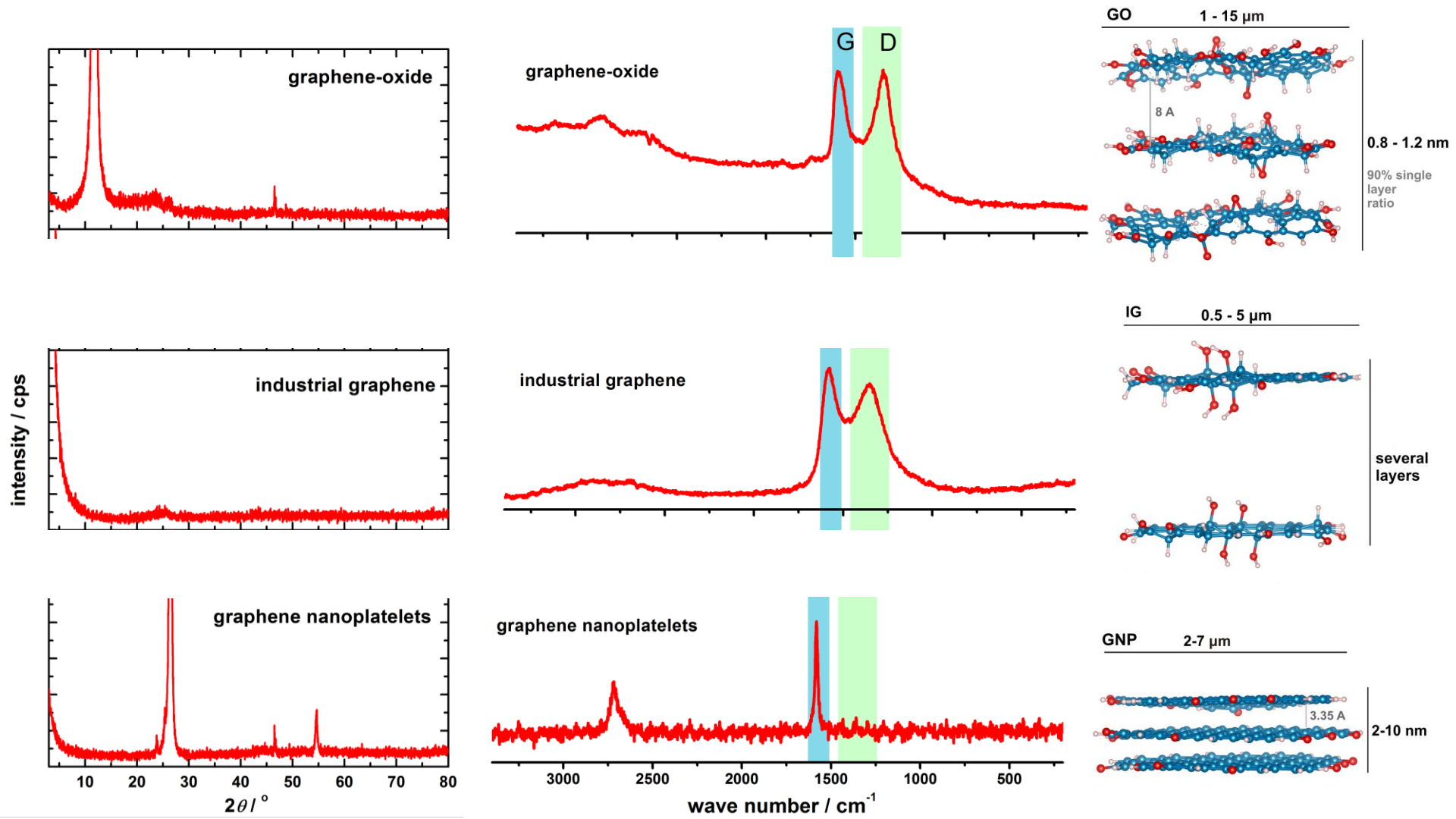
www.i-sis.org.uk › Why_Graphene_is_Amazing

Jul 15, 2013 - Why **Graphene is Amazing**. Graphene's unusual electronic structure enables it

U realnosti, grafen

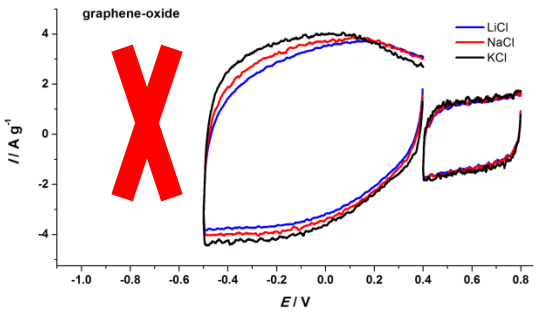
- Nije ravan
- Ima defekte
- Skup je

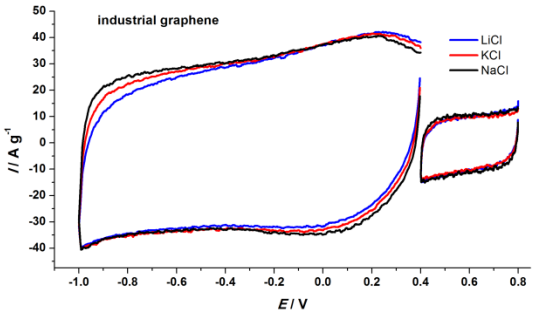
Materijali na bazi grafena

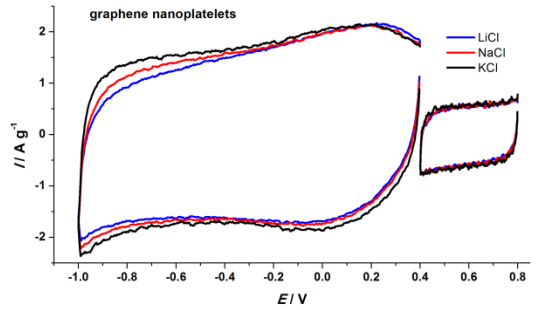


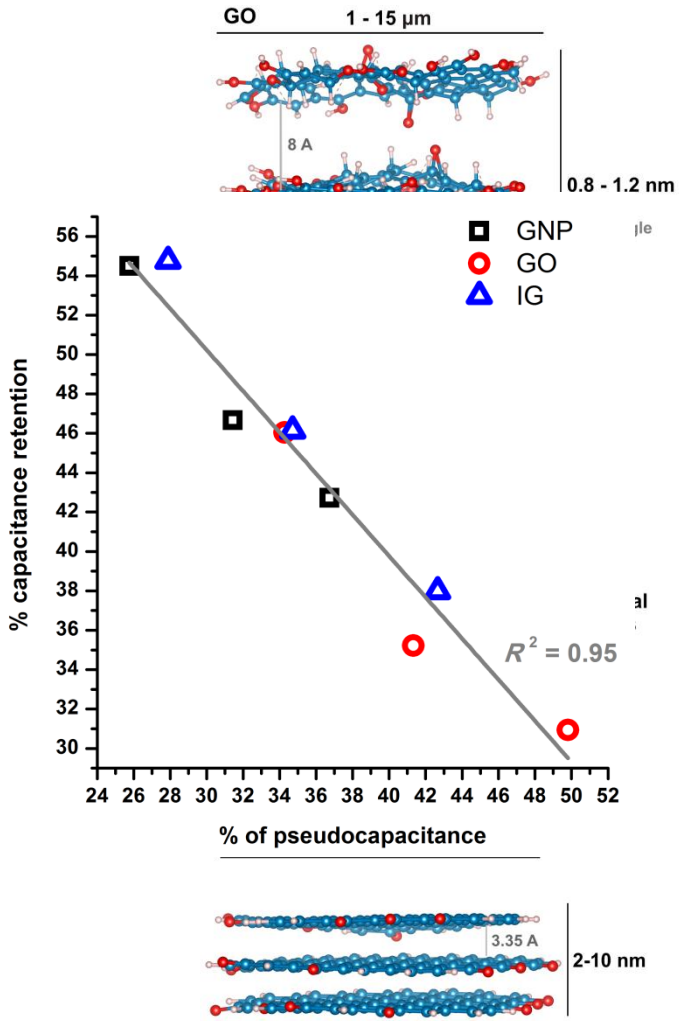
Gutić et al. Int. J. Electrochem. Sci 11 (2016) 8662-8682

Materijali na bazi grafena



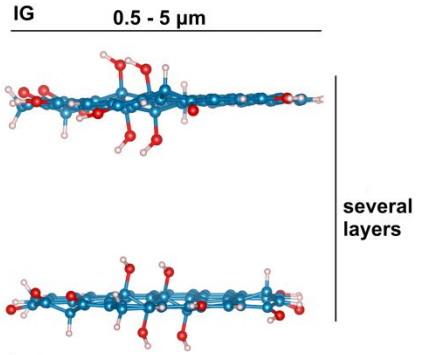


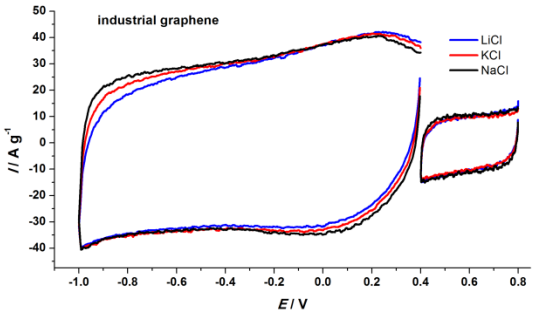




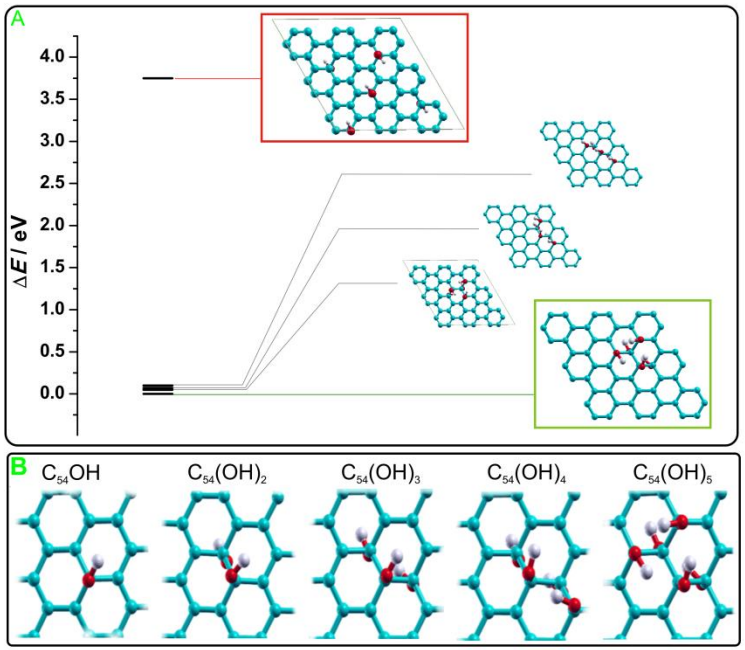
Gutić et al. Int. J. Electrochem. Sci 11 (2016) 8662-8682

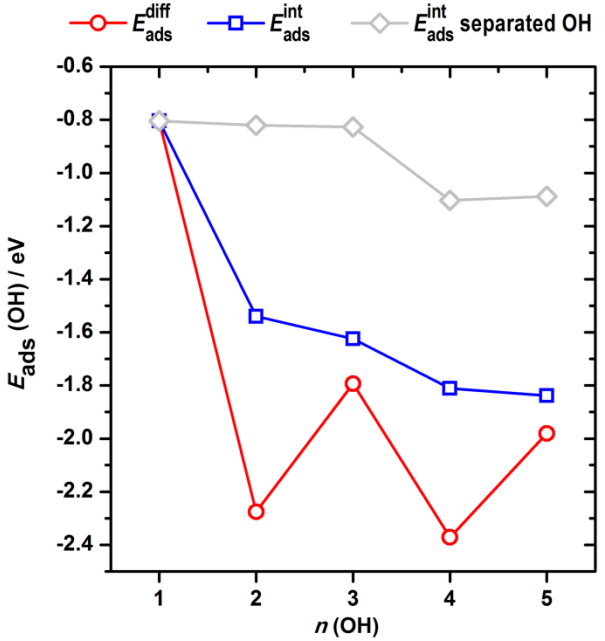
Materijali na bazi grafena





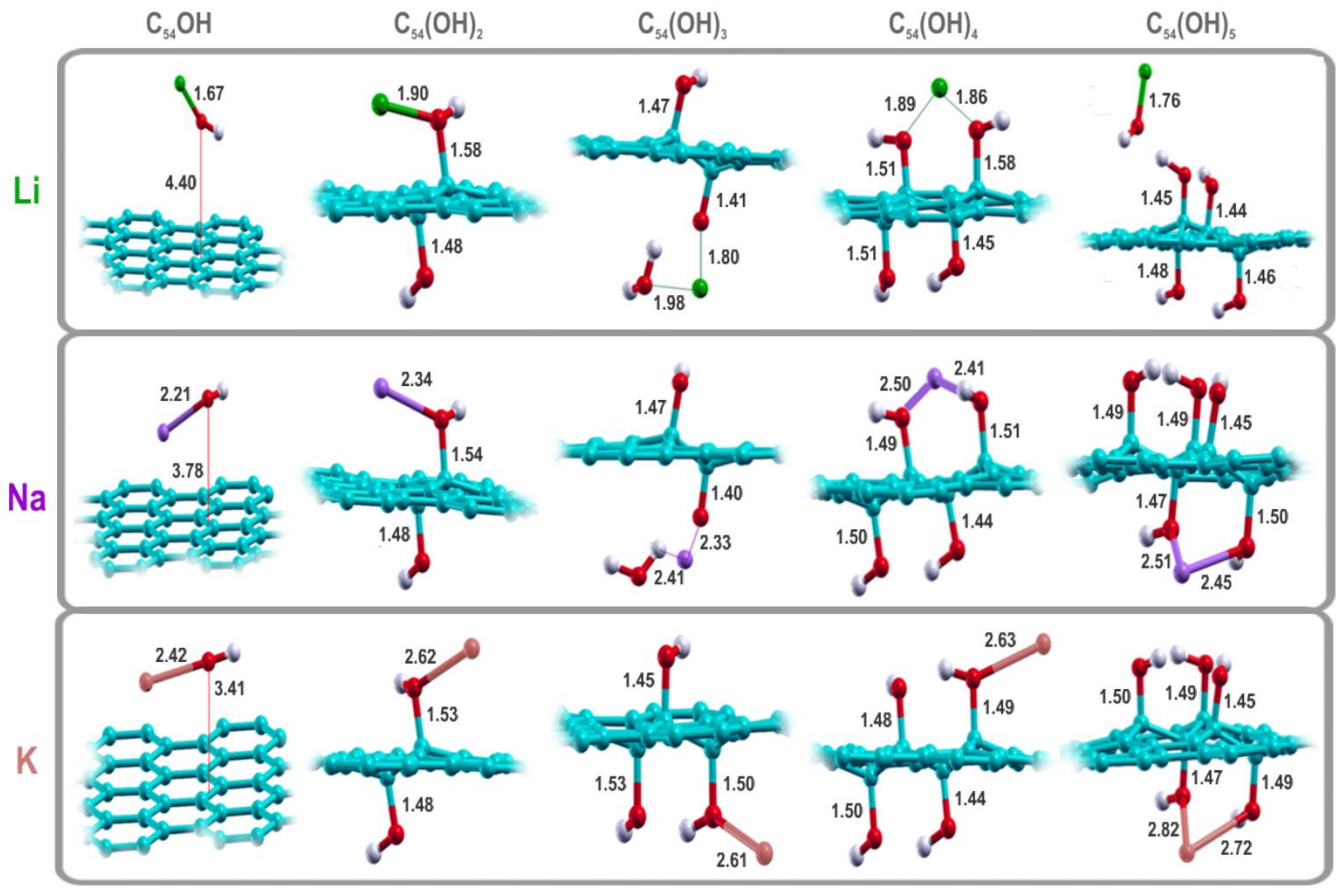
Odakle potiče kapacitet?





Dobrota et al. RSC Advances 6 (2016) 57910-57919

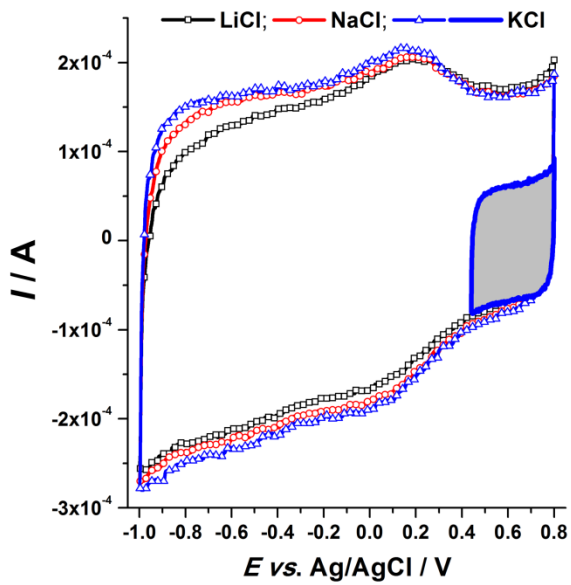
Materijali na bazi grafena

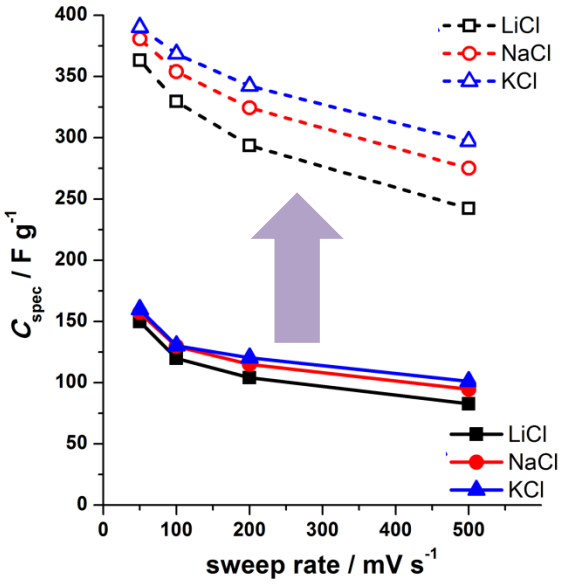


Aglomerisane funkcionalne grupe stabilizuju interakciju sa M^+

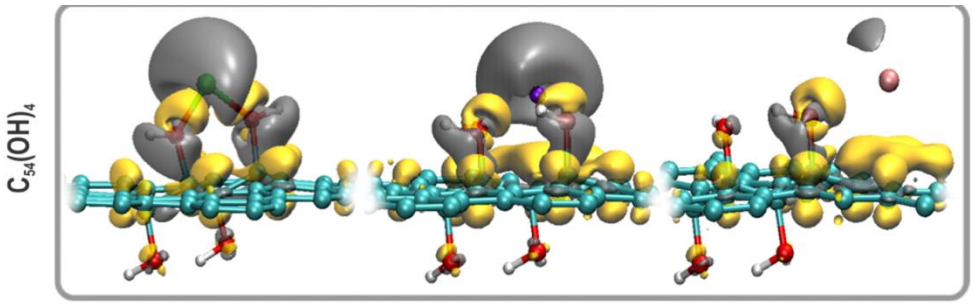
Dobrota et al. RSC Advances 6 (2016) 57910-57919

Materijali na bazi grafena





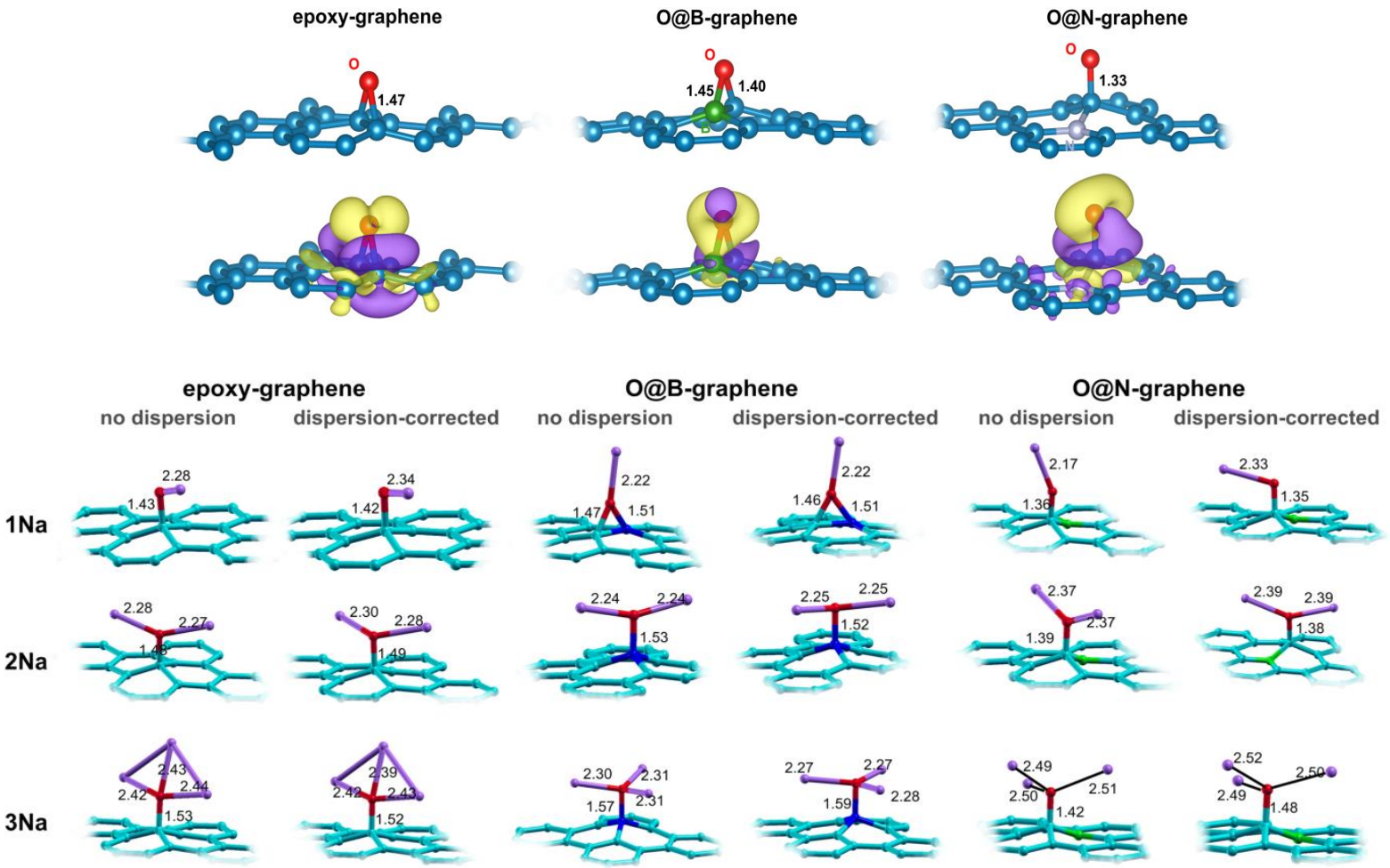
Pseudocapacitet aktiviran na negativnim potencijalima



$$C_x(OH)_n + M^+ + e^- \rightarrow \left(C_x^{\delta-}(OH)_n^{(1-\delta)-}\right)M^+$$

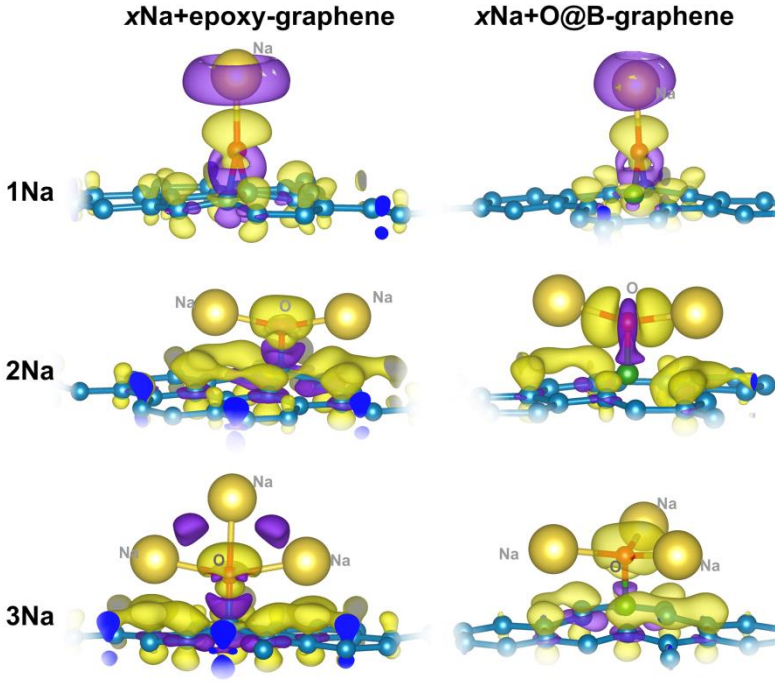
Dobrota et al. RSC Advances 6 (2016) 57910-57919

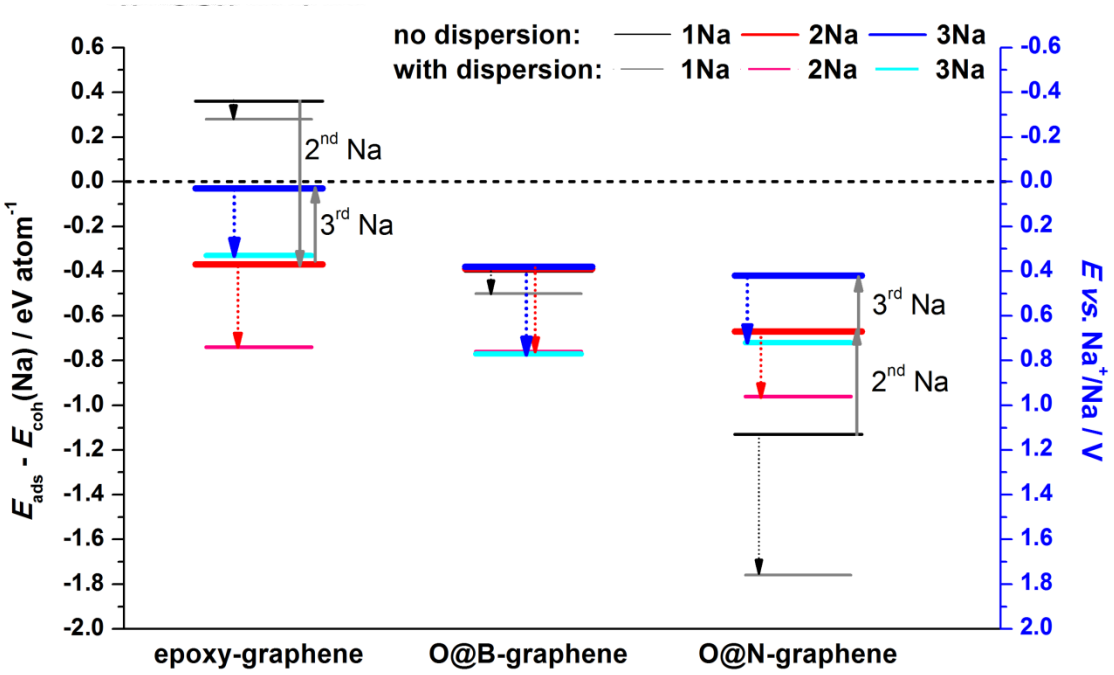
Materijali na bazi grafena



Diklić et al. Electrochimica Acta 297 (2019) 523-528

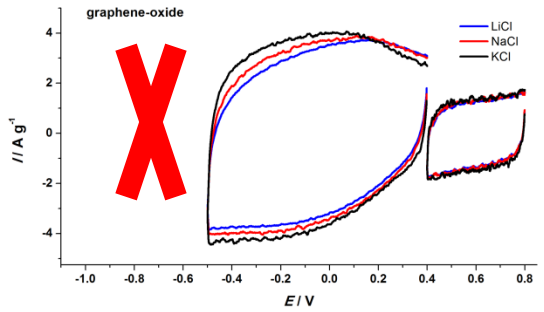
Materijali na bazi grafena

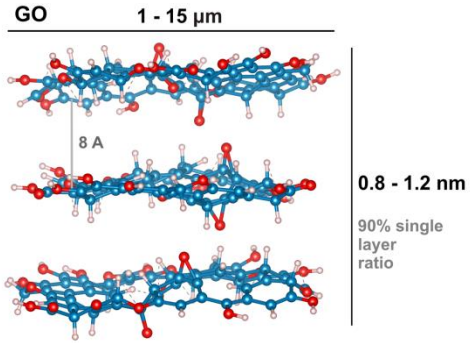




Diklić et al. Electrochimica Acta 297 (2019) 523-528

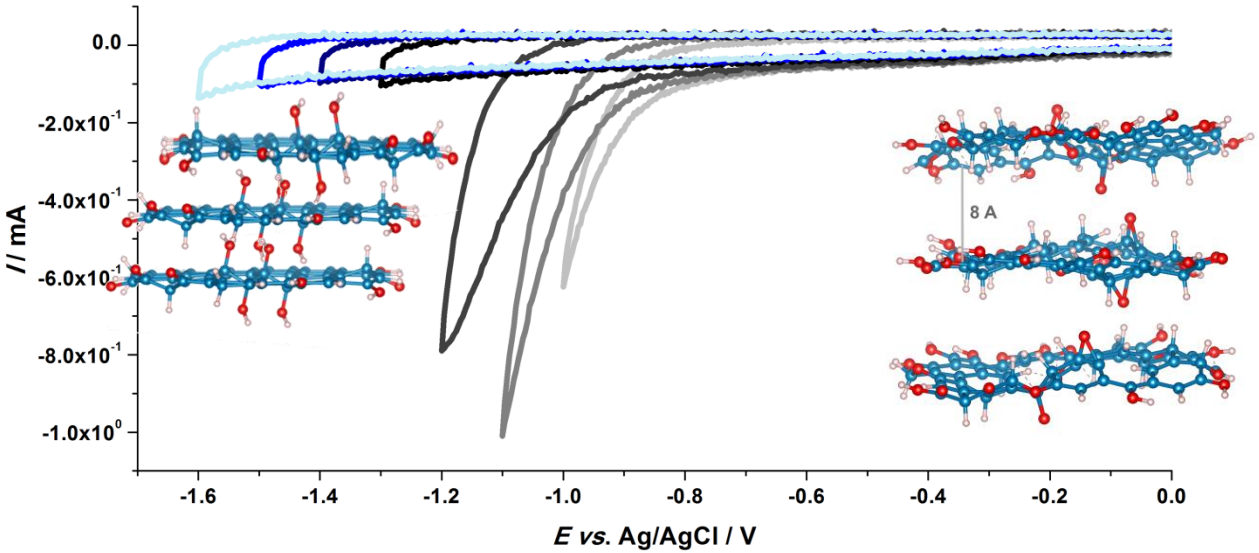
Materijali na bazi grafena





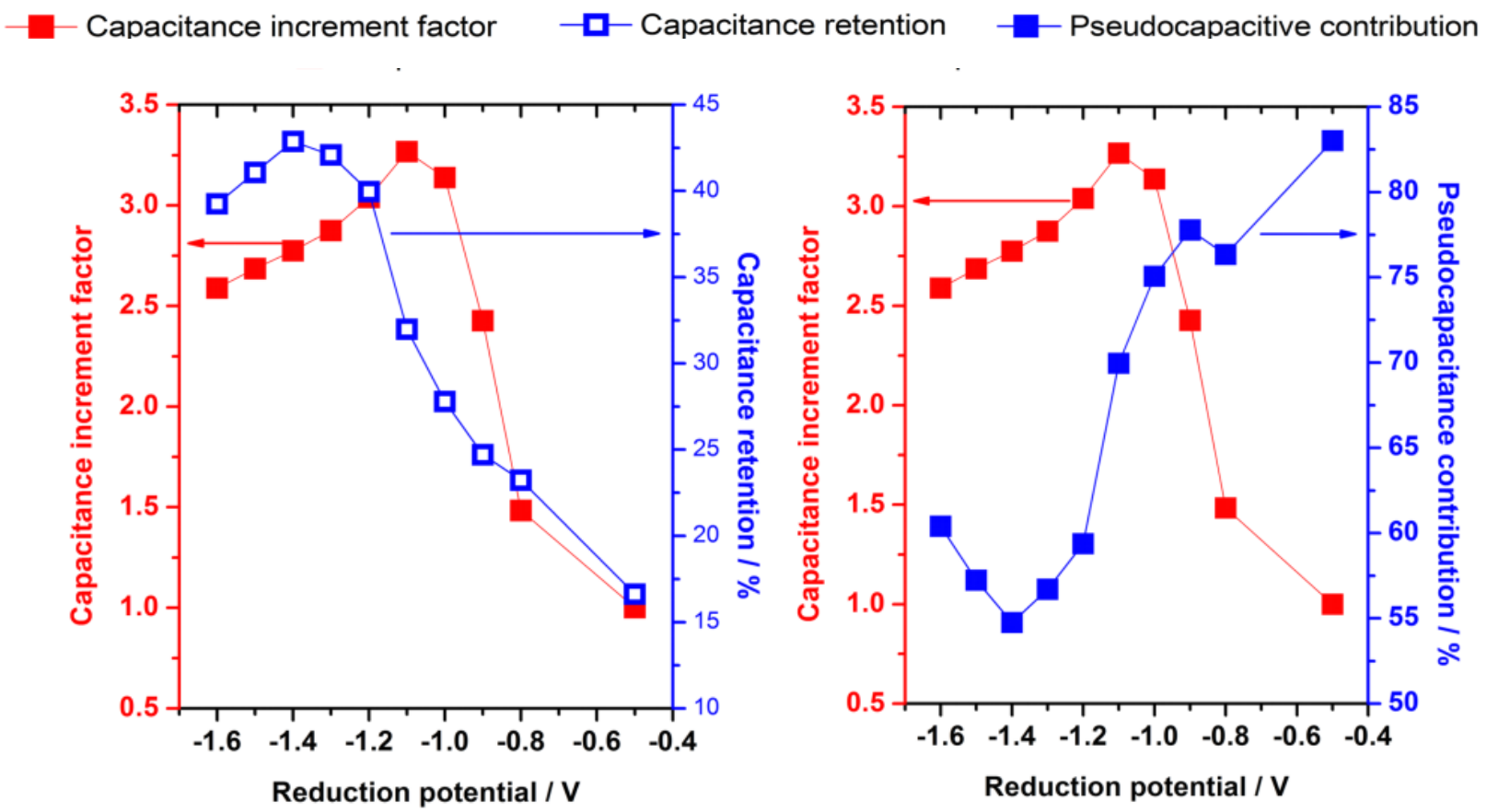
Grafen oksid je neprovodan

Ima mali kapacitet



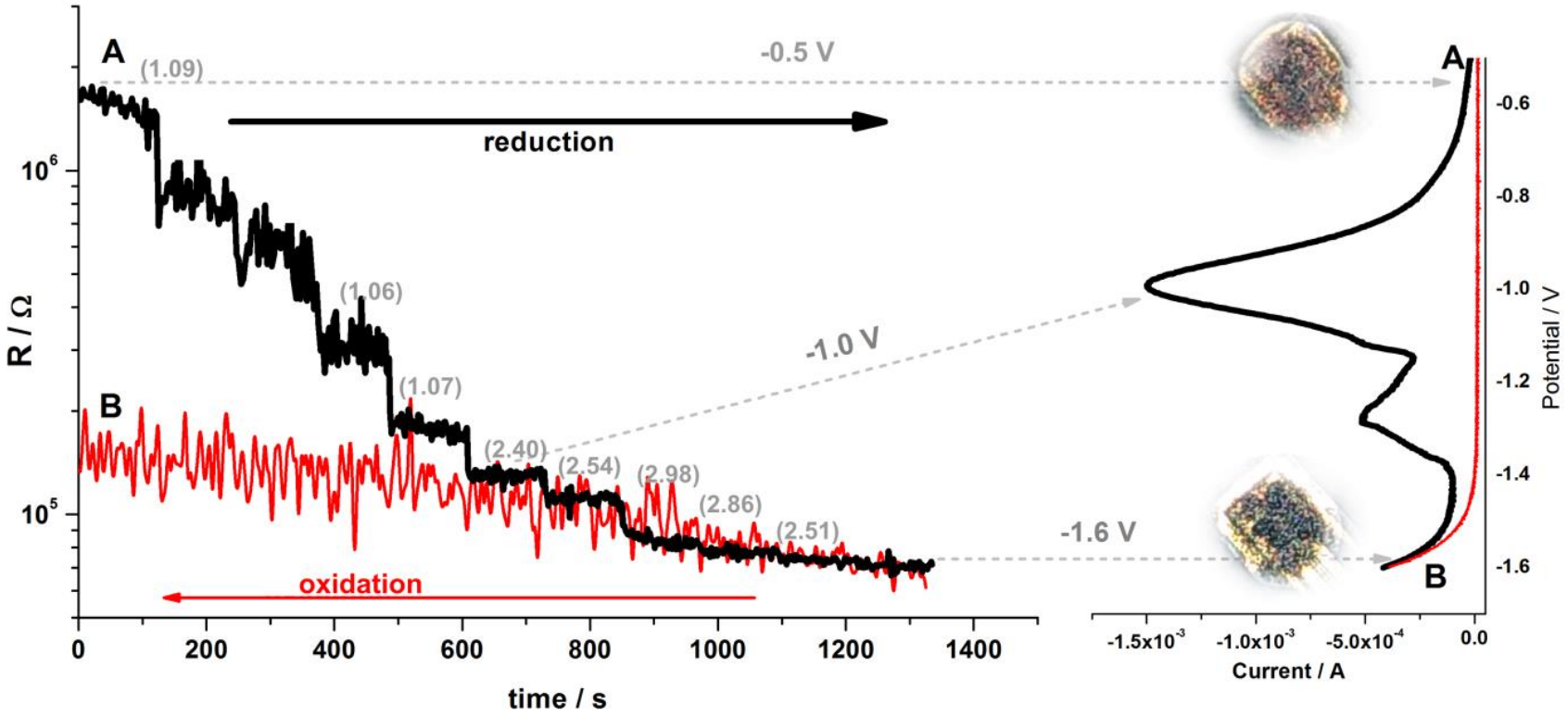
Gutić et al. Physical Chemistry Chemical Physics 20 (2018) 22698-22709

Materijali na bazi grafena



Gutić et al. Physical Chemistry Chemical Physics 20 (2018) 22698-22709

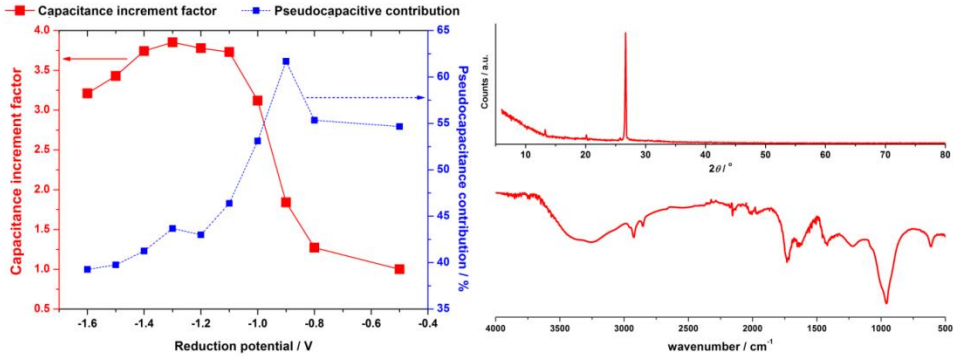
Materijali na bazi grafena

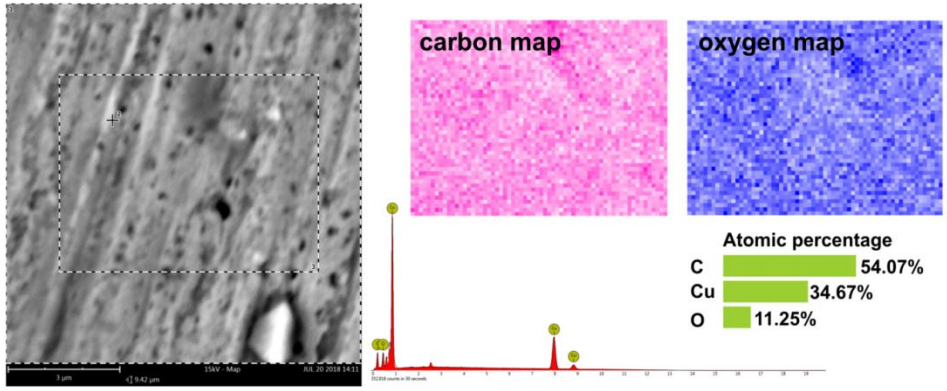


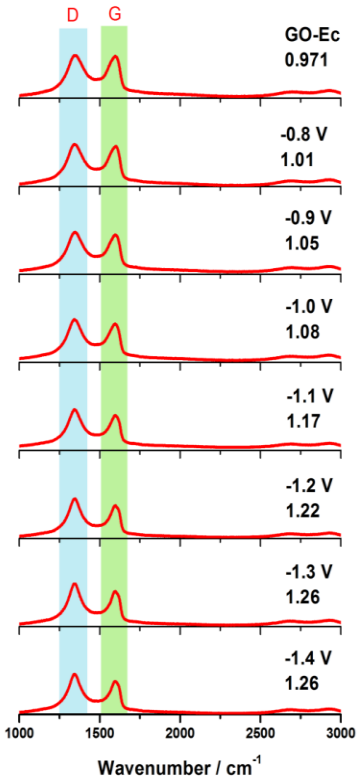
Maksimum kapaciteta =
balans između provodljivosti i koncentracije površinskih kiseoničnih funkcionalnih grupa

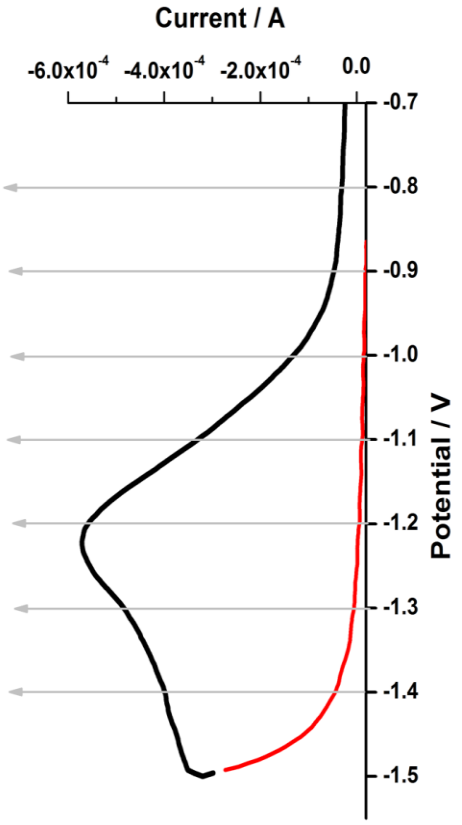
Gutić et al. Physical Chemistry Chemical Physics 20 (2018) 22698-22709

Materijali na bazi grafena





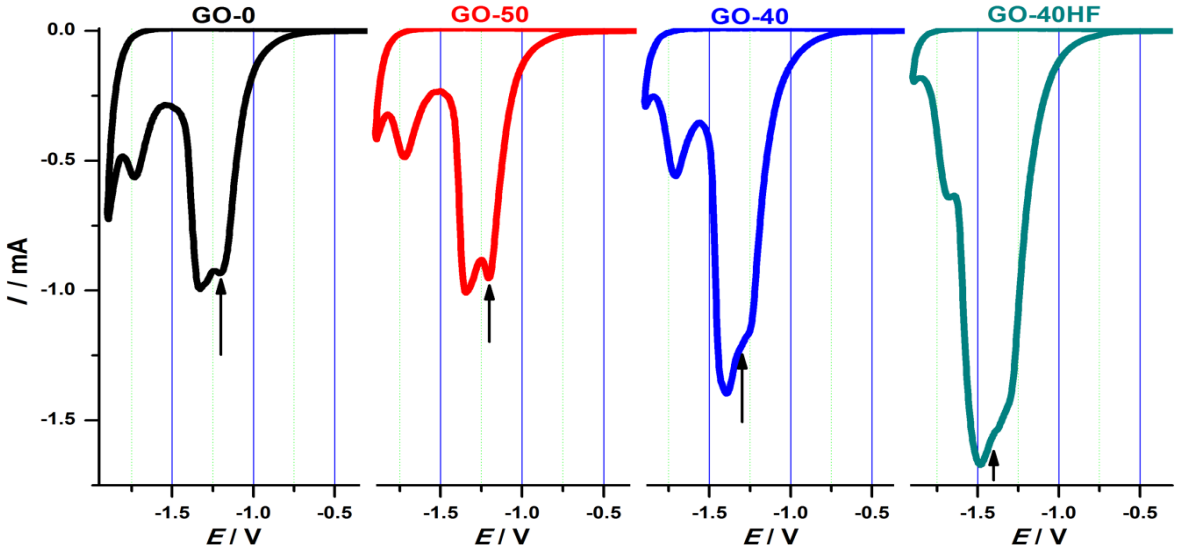


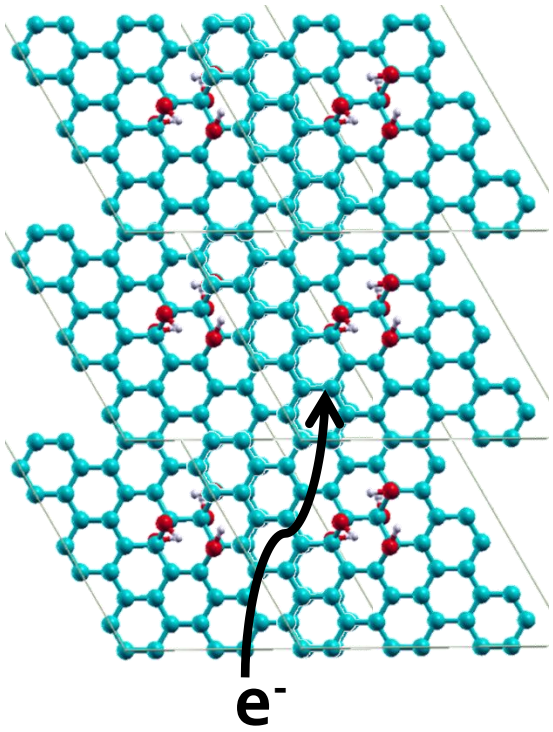


Generalno ponašanje za svaki GO (koji smo do sada testirali)

Gutić et al. Physical Chemistry Chemical Physics 20 (2018) 22698-22709

Materijali na bazi grafena





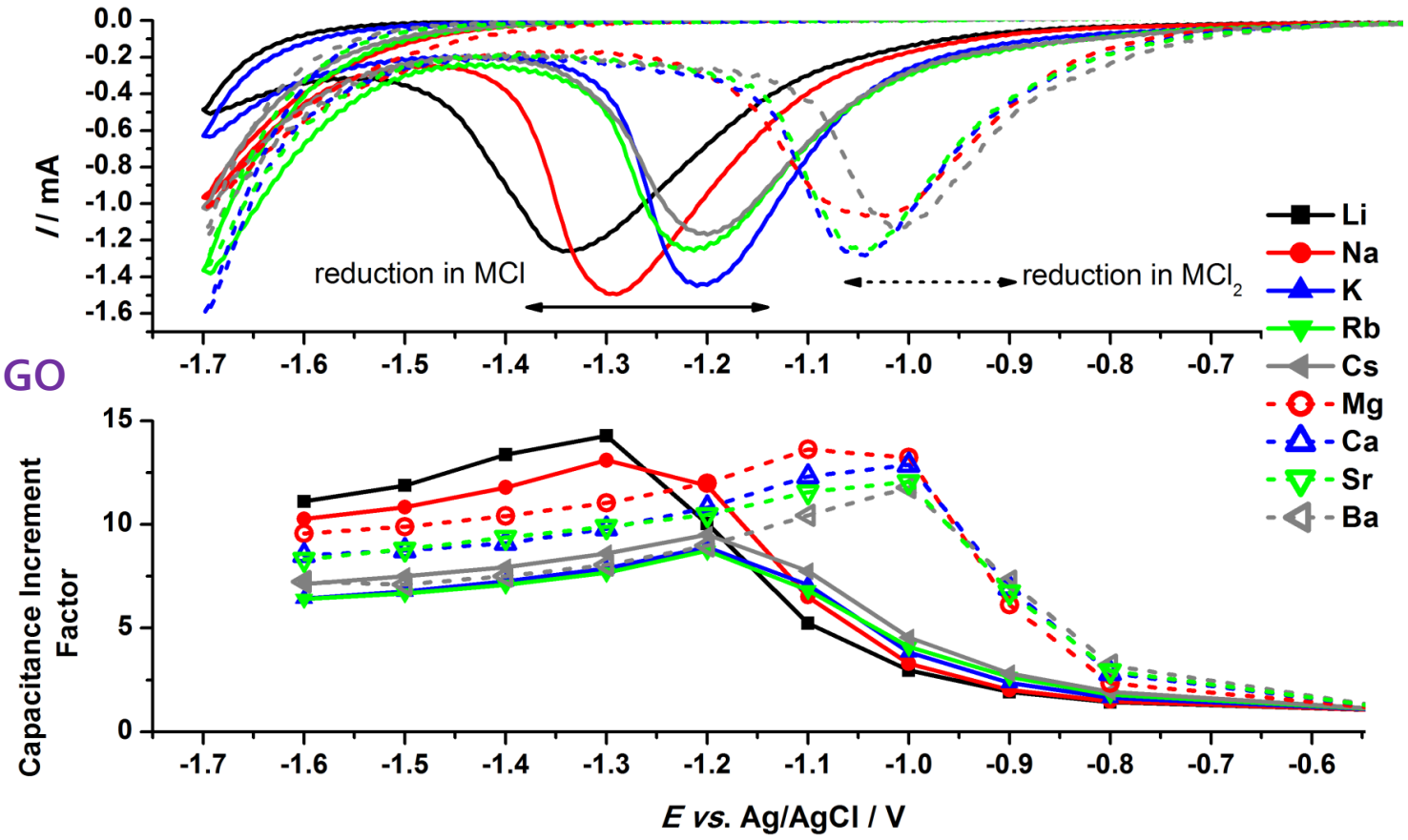
Generalno ponašanje za svaki GO (koji smo do sada testirali)

Gutić et al. Physical Chemistry Chemical Physics 20 (2018) 22698-22709

Materijali na bazi grafena

Redukcija na datom potencijalu, Merenje C

XC72-R + GO



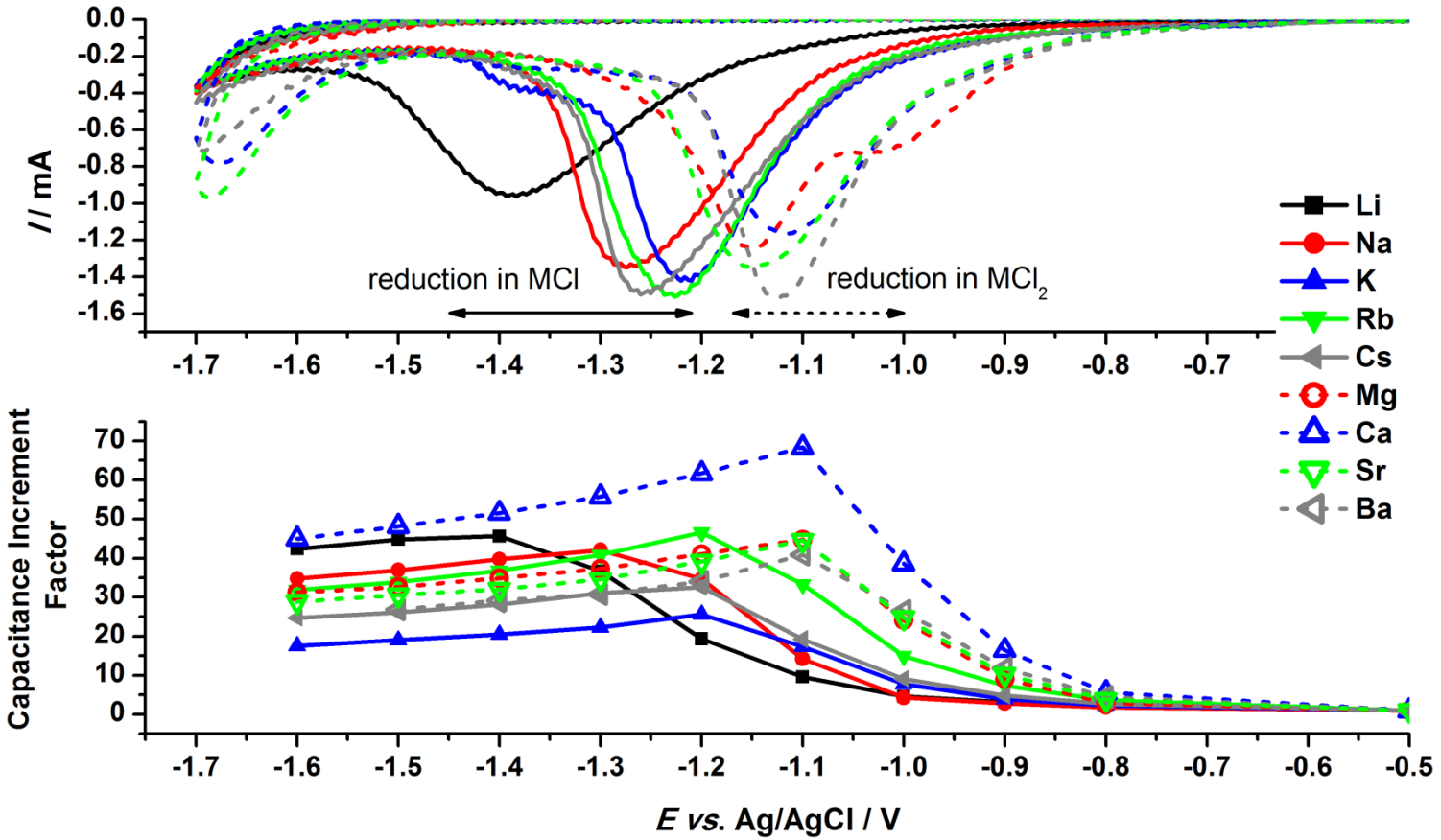
R_u oko 50 Ohm

Karačić et al. Electrochimica Acta 297, 112-117

Materijali na bazi grafena

Redukcija na datom potencijalu, Merenje C

GO

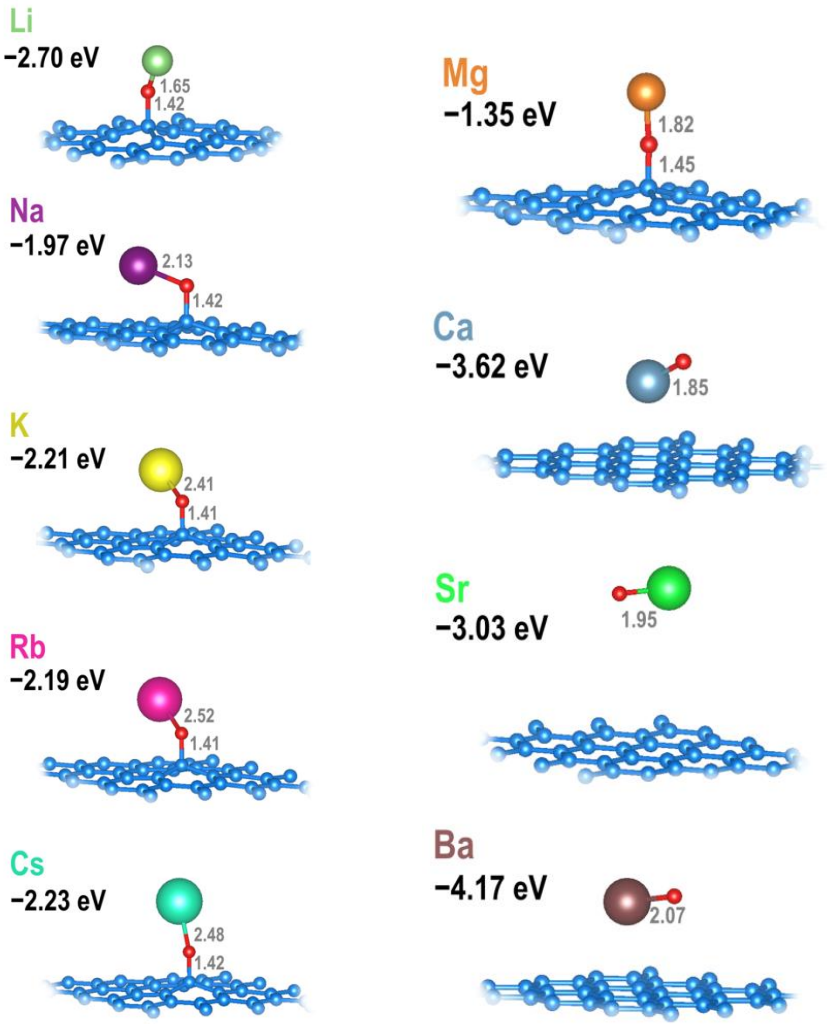


R_u oko 50 Ohm

Karačić et al. Electrochimica Acta 297, 112-117

Materijali na bazi grafena

DFT



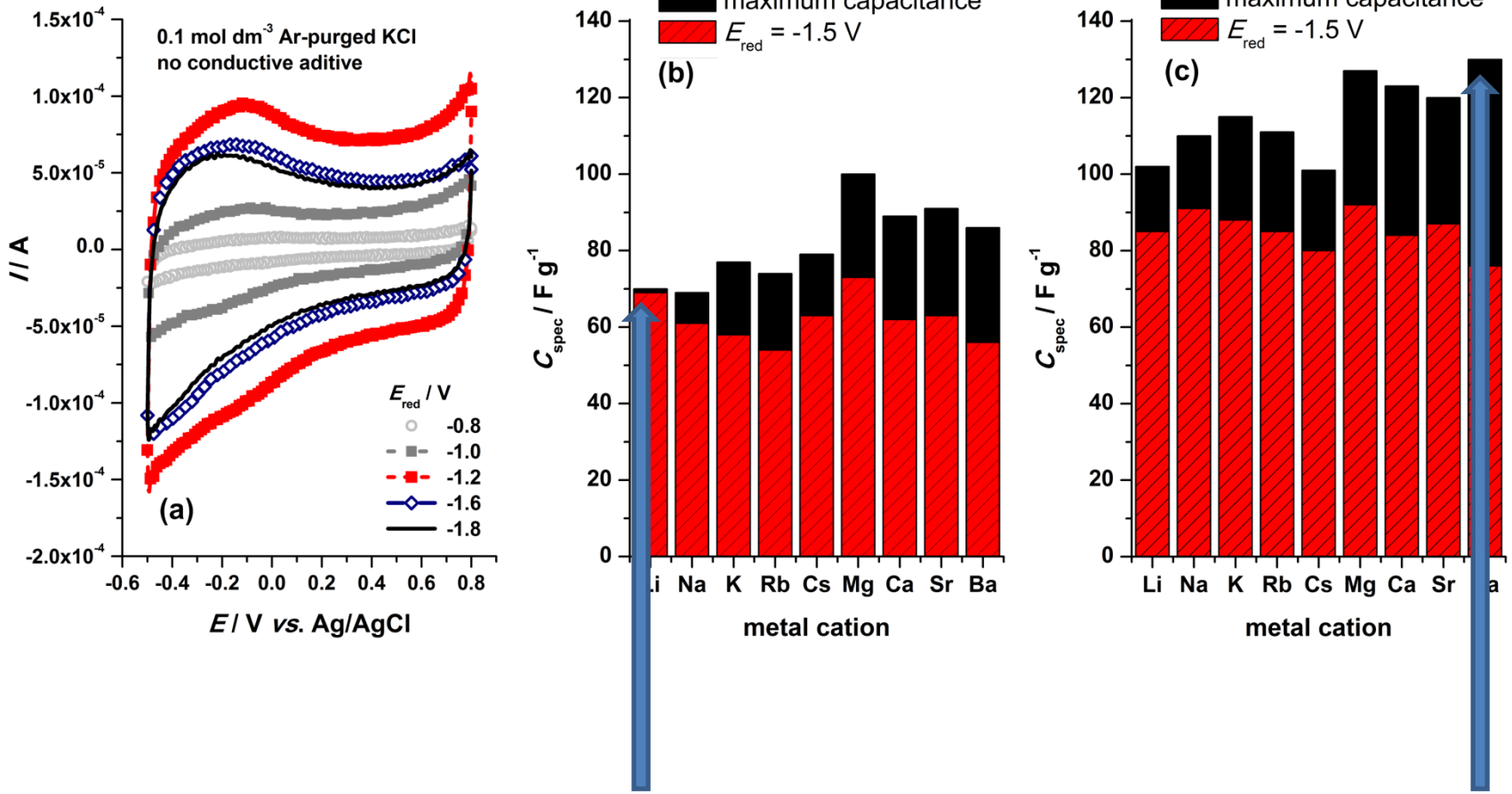
(i mnogi drugi primeri uticaja inertnog elektrolita koji nije samo kroz R_e – elektrokataliza HER i ORR na platinskim metalima i ugljenicima)

Karačić et al. Electrochimica Acta 297, 112-117

Materijali na bazi grafena

Redukcija na datom potencijalu, Merenje C

Praktična primena

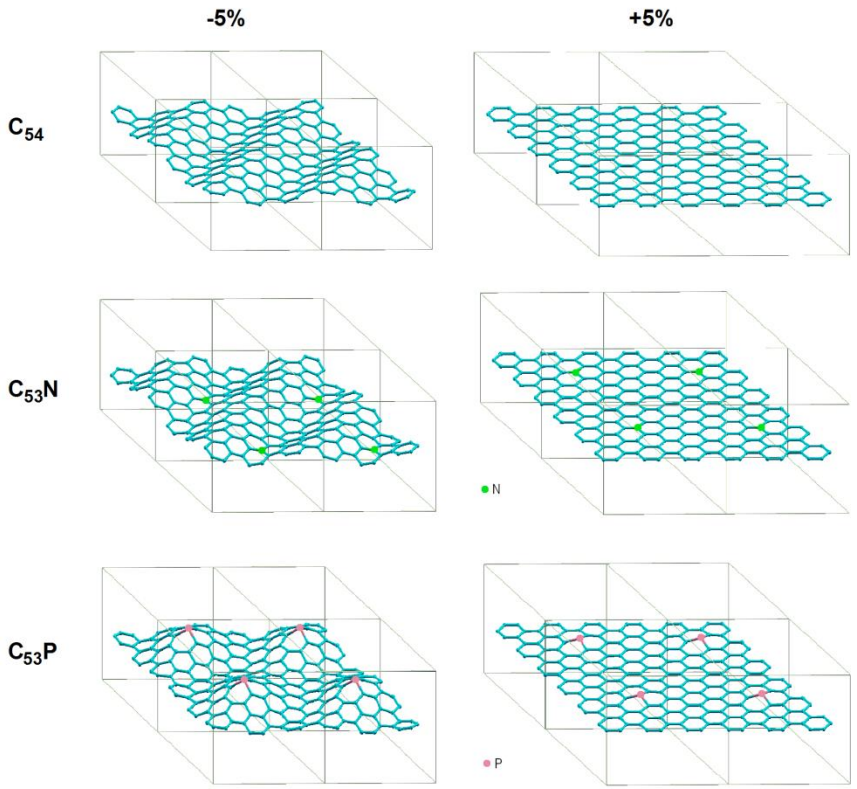


Karačić et al. Electrochimica Acta 297, 112-117

Materijali na bazi grafena

Kapaciteti:

1. "Čist" – do 400 F g^{-1} (i do 70% pseudocapaciteta)
2. Kompoziti do 1000 F g^{-1} i više
3. Realno gledano, grafen je skuplji od platine
4. Navodno, postoje komercijalni kondenzatori na bazi grafena (curved graphene technology)



Dobrota et al. Appl. Surf. Sci, submitted, available @ arXiv

Materijali na bazi grafena

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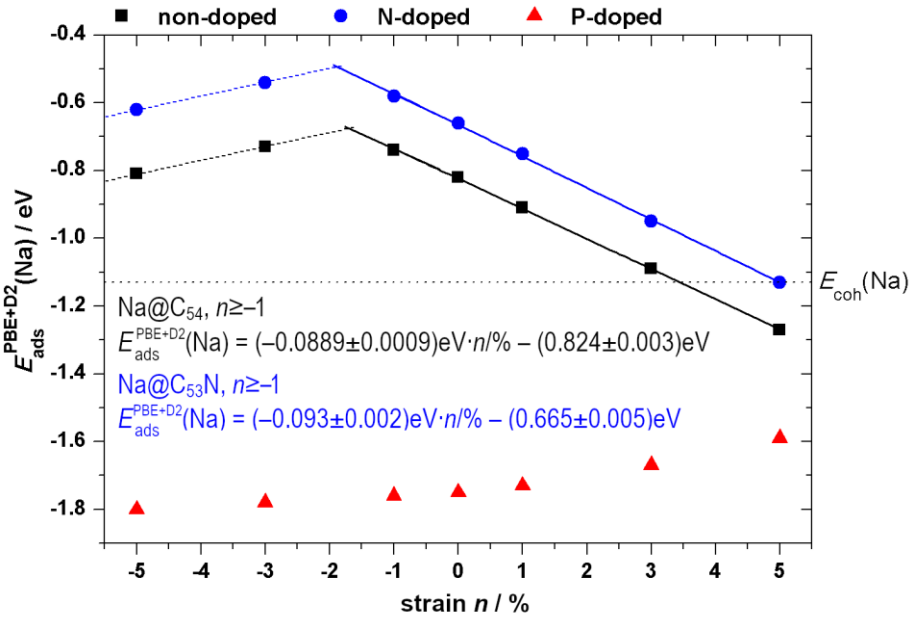
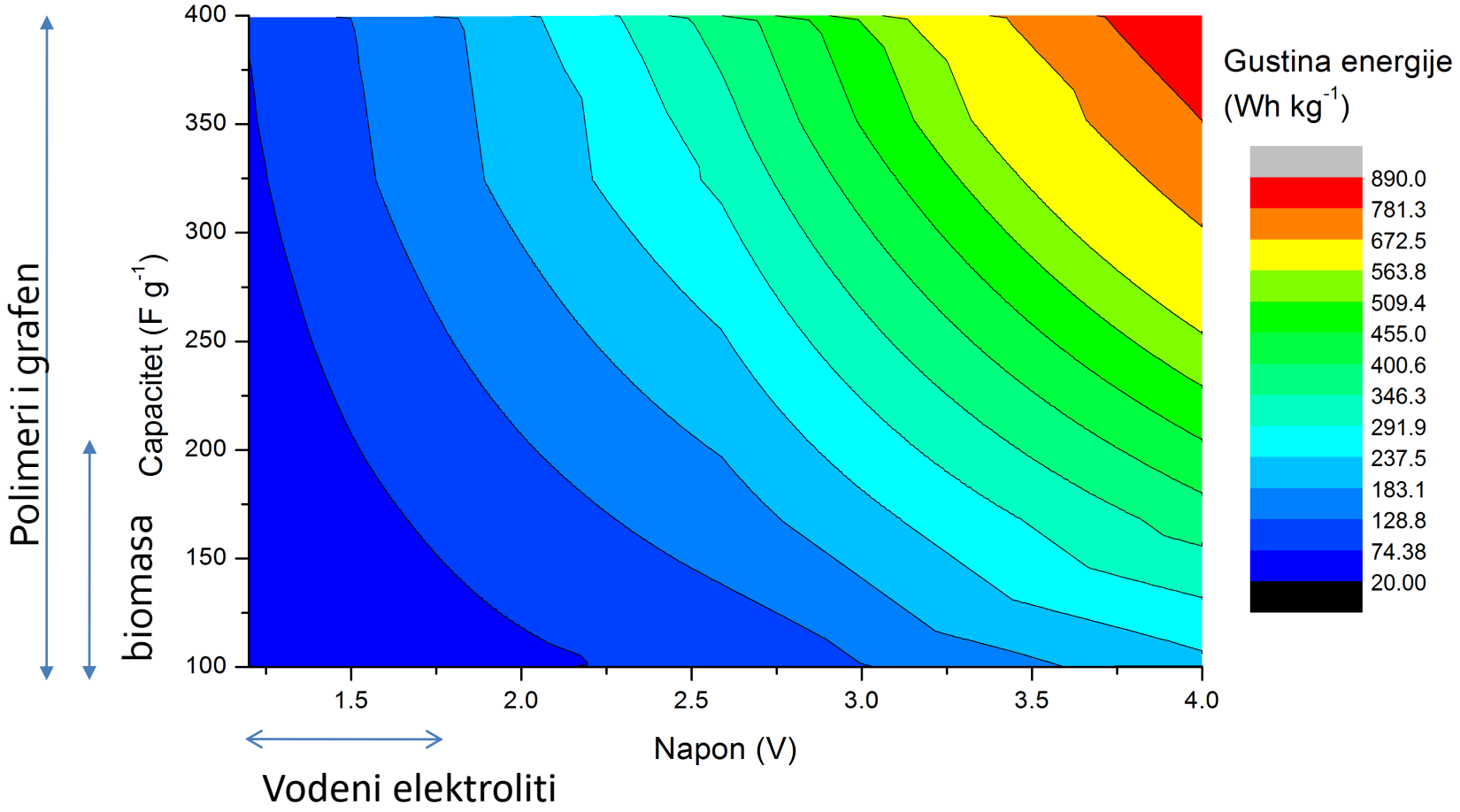


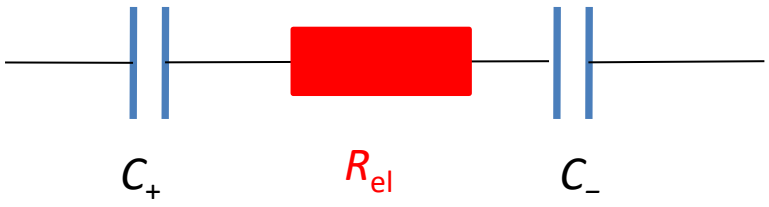
Dobrota et al. Appl. Surf. Sci, submitted, available @ arXiv

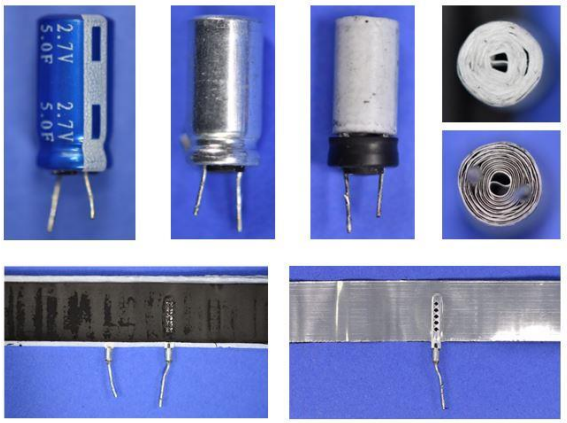
Od laboratorije do police



Od laboratorije do police

U realnoj ćeliji (kondenzatoru) postoje dve kapacitivne elektrode, pa je rezultujući kapacitet (kod simetričnog kondenzatora) 1/2 capaciteta jedne elektrode





U naučnoj literaturi kapaciteti su računati u odnosu na **masu aktivnog materijala**

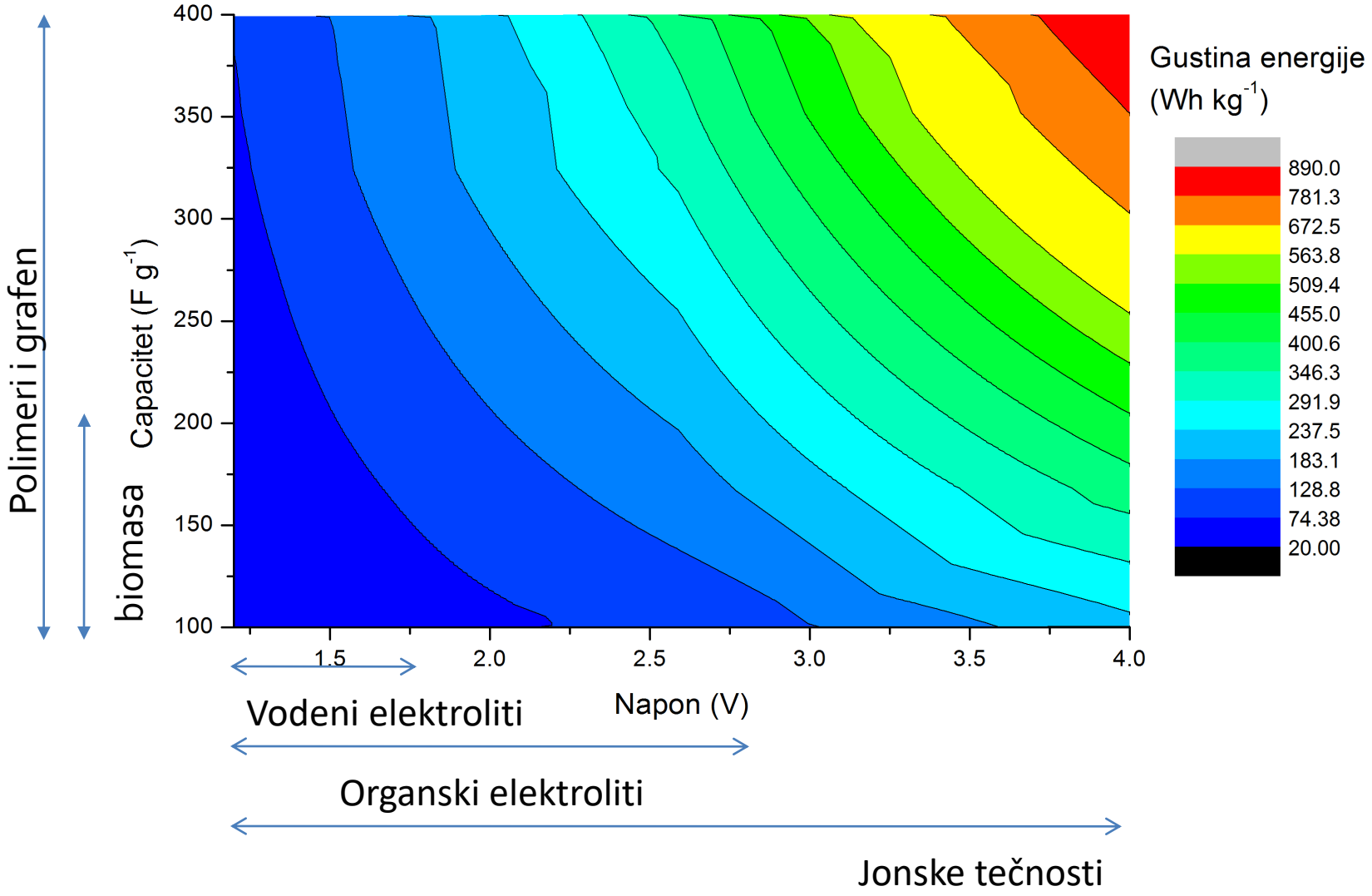
Od laboratorije do police

U naučnoj literaturi kapaciteti su računati u odnosu na **masu aktivnog materijala**

Product Type	Capacitance	Voltage	ESR (DC)	Specific Power	Specific Energy	Weight	Volume
SCA0500	500 F	2.85 V	0.7 mOhm	80 kW/kg	5.1 Wh/kg	0.111 kg	0.079 L
SCA0750	750 F	2.85 V	0.6 mOhm	66 kW/kg	5.8 Wh/kg	0.147 kg	0.107 L
SCA1200	1200 F	2.85 V	0.29 mOhm	73 kW/kg	5.4 Wh/kg	0.253 kg	0.178 L
SCA1800	1800 F	2.85 V	0.27 mOhm	46.4 kW/kg	6.0 Wh/kg	0.337 kg	0.240 L
SCA3200	3200 F	2.85 V	0.18 mOhm	34.6 kW/kg	6.8 Wh/kg	0.533 kg	0.390 L

https://www.skeletontech.com/

Od laboratorije do police



Od laboratorije do police

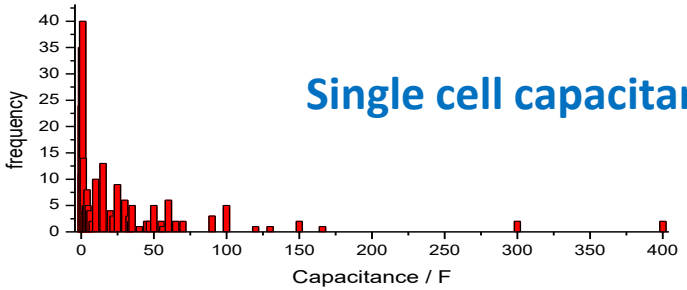
Skoro sva istraživanja koriste vodene elektrolite, ali praktično nijedan komercijalni sistem

Applied Filters: Capacitance

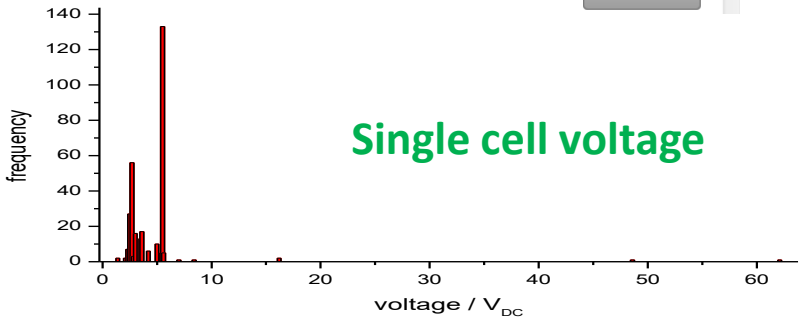
Results per Page 25 Page 1/1 Enter Quantity Download Table

Compare Parts	Image	Digi-Key Part Number	Manufacturer Part Number	Manufacturer	Description	Quantity Available	Unit Price SEK	Minimum Quantity	Packaging	Series	Part Status	Capacitance	Tolerance	Voltage - Rated	ESR (Equivalent Series Resistance)	Lifetime @ Temp.
		283-4210-ND	XV3550-2R7307-R	Eaton	CAP 300F -5% +10% 2.7V T/H	0 Standard Lead Time 24 Weeks	86,50000 kr	1	Bulk	PowerStor XV	Active	300F	-5%, +10	2,7V	4.5 mOhm	1500 Hrs @ 65°C
		604-1091-ND	DZH-2R5D307S57T	Elna America	CAP 300F -20% +80% 2.5V T/H	34 - Immediate	484,13000 kr	1 Non-Stock	Bulk	DZH	Active	300F	-20%, +80%	2,5V	30 mOhm	2000 Hrs @ 60°C
		283-4175-ND	XB3550-2R5307-R	Eaton	CAP 300F 10% 2.5V THROUGH HOLE	10 - Immediate	89,76000 kr	1	Bulk	PowerStor XB	Active	300F	±10%	2,5V	7 mOhm	1500 Hrs @ 70°C
		SCCY62V307VSB-ND	SCCY62V307VSB	AVX Corporation	CAPACITOR 300F 2.7V SOLDER LUG	0	79,90275 kr	40 Non-Stock	Bulk	SCC	Active	300F	-5%, +25	2,7V	-	1000 Hrs @ 60°C
		CDHC301K2R3SR-ND	CDHC301K2R3SR	Cornell Dubilier Electronics (CDE)	CAP 300F -5% +10% 2.3V T/H	0	Obsolete	-	Bulk	CDHC	Obsolete	300F	-5%, +10	2,3V	25 mOhm	1000 Hrs @ 50°C

Results per Page 25 Page 1/1 Download Table



Single cell capacitance



Single cell voltage

Od laboratorije do police

Potencijalna rešenja – **novi elektroliti** i **novi sistemi** (pseudokondenzatori, hibridi)

Device	Supercapattery							
	Supercapacitor			Hybrid				Battery
	EDLC	Pseudocapacitor		Capacitive Hybrid		Others (Supercabattery)		
Electrode Material	NFCS	NFCS	CFS	NFCS	CFS	NFCS	CFS	NCFS
	+	+	+	+	+	+	+	+
	NFCS	CFS	CFS	NCFS	NCFS	NCFS	NCFS	NCFS
Specific energy (Wh kg^{-1})	102 (IL), 6.7 (aq.)	3.6	26.6	230	261	–	208.6	250
Max specific power (kW kg^{-1})	111.6	24.7	13	59	25	–	3	1.5
Cycling life (cycles)	>10,000	>5,000	>5,000	>1,000	>10,000	–	>1,000	<1,200
Electrolyte type	IL, aq.	aq.	aq.	IL	IL	–	organic	organic
References	Lewandowski et al., 2010; Hou et al., 2015	Zhou et al., 2012	Huang et al., 2015	Zhang F. et al., 2013; Zhang L. et al., 2013; Yu and Chen, 2016a	Ortaboy et al., 2017	–	Zhou et al., 2016	**

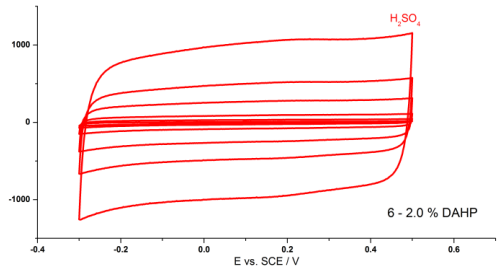
**NFCS, Non-Faradaic Capacitive Storage = Electrical Double Layer Capacitance) Storage; CFS, Capacitive Faradaic Storage = Pseudocapacitive Storage; NCFS, Non-Capacitive Faradaic Storage = Battery-Type Storage; ** data from web: https://en.wikipedia.org/wiki/Lithium-ion_battery#cite_note-7. The colors represent different charge storage mechanisms and relevant devices.*

Yu & Chen, Front. Chem., 18 April 2019 | https://doi.org/10.3389/fchem.2019.00272

Od laboratorije do police

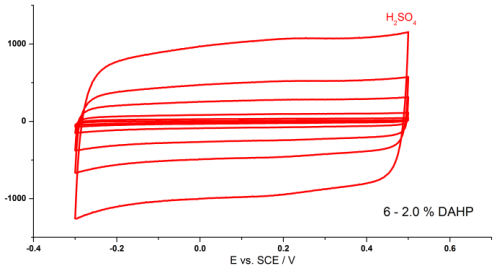
Simetrični EDL superkondenzator

Negativna elektroda AC



C_{spec} = 150 F g^{-1}

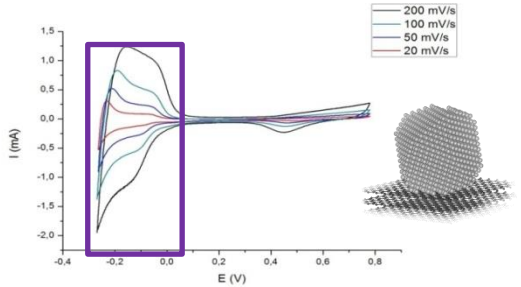
Pozitivna elektroda AC



C_{spec} = 150 F g^{-1}

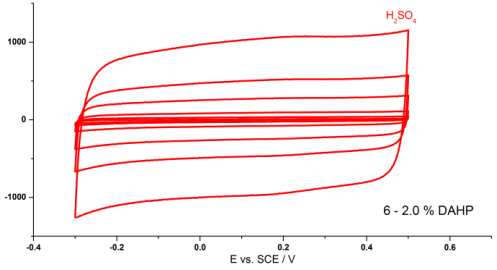
Hipotetički hibridni Pd-Carbon sistem

Negativna elektroda nano Pd



Pd + H^{+} + e^{-} = Pd-H C_{spec} = 3000 F g^{-1}

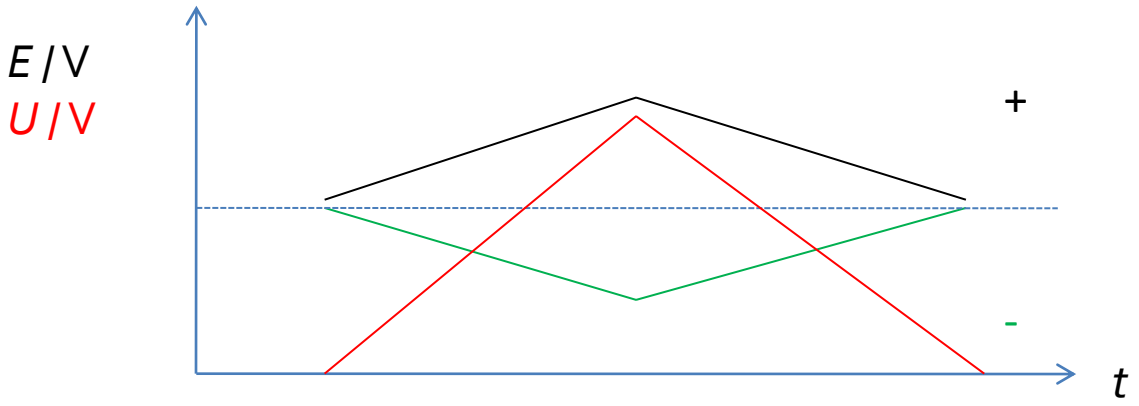
Pozitivna elektroda AC



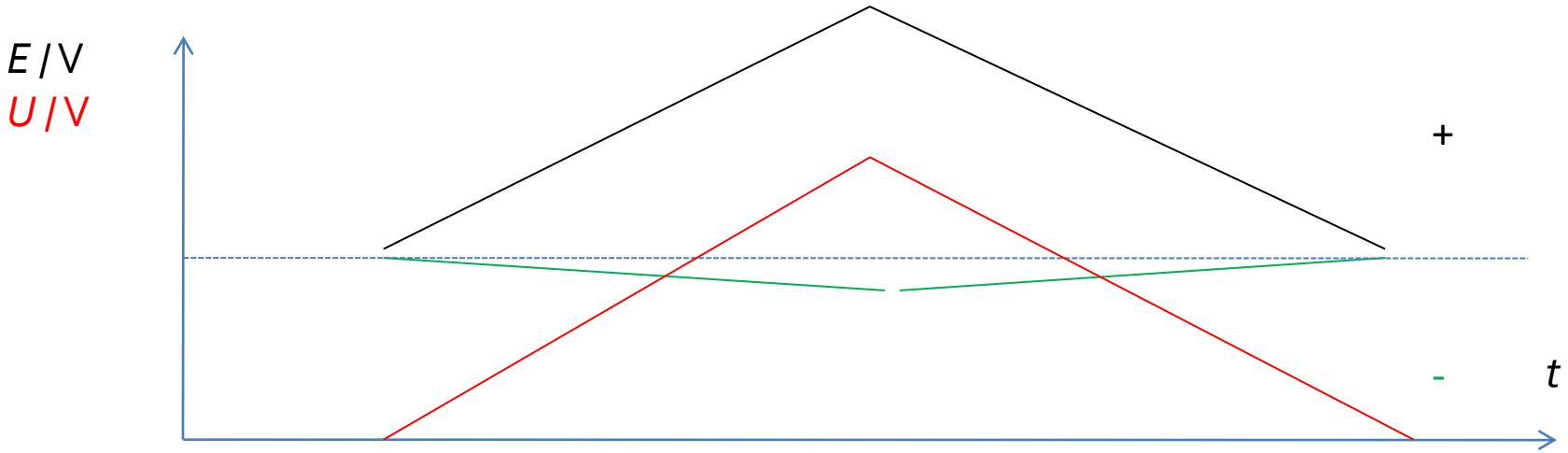
C_{spec} = 150 F g^{-1}

Od laboratorije do police

Simetrični EDL superkondenzator



Hipotetički hibridni Pd-Carbon sistem



Umesto zaključka

- Ugljenični materijali za elektrohemijske kondenzatore: širok elektrohemijski prozor
- Velika površina, hemijska inertnost
- Fokus na pseudokapacitet
- Grafen je skuplji od platine
- AC: 900 $/ton