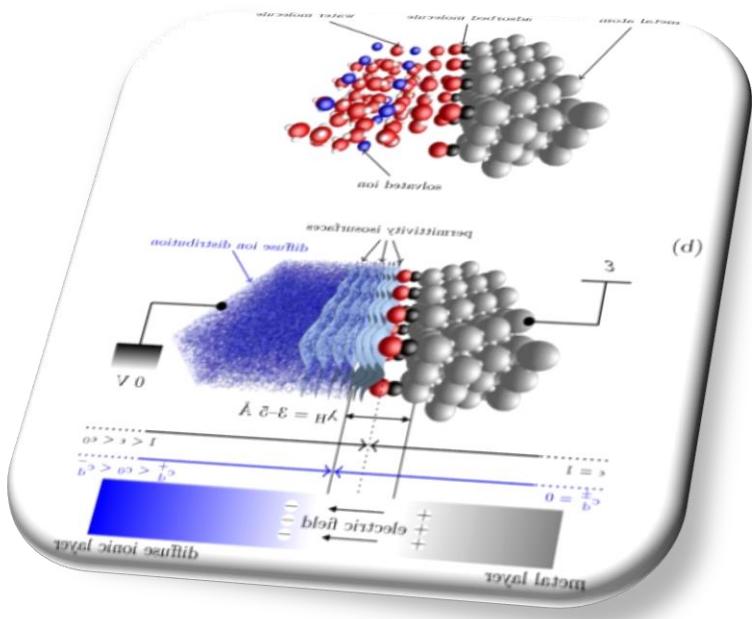


Savremeni pravci u razvoju ugljeničnih materijala za elektrohemijske kondenzatore

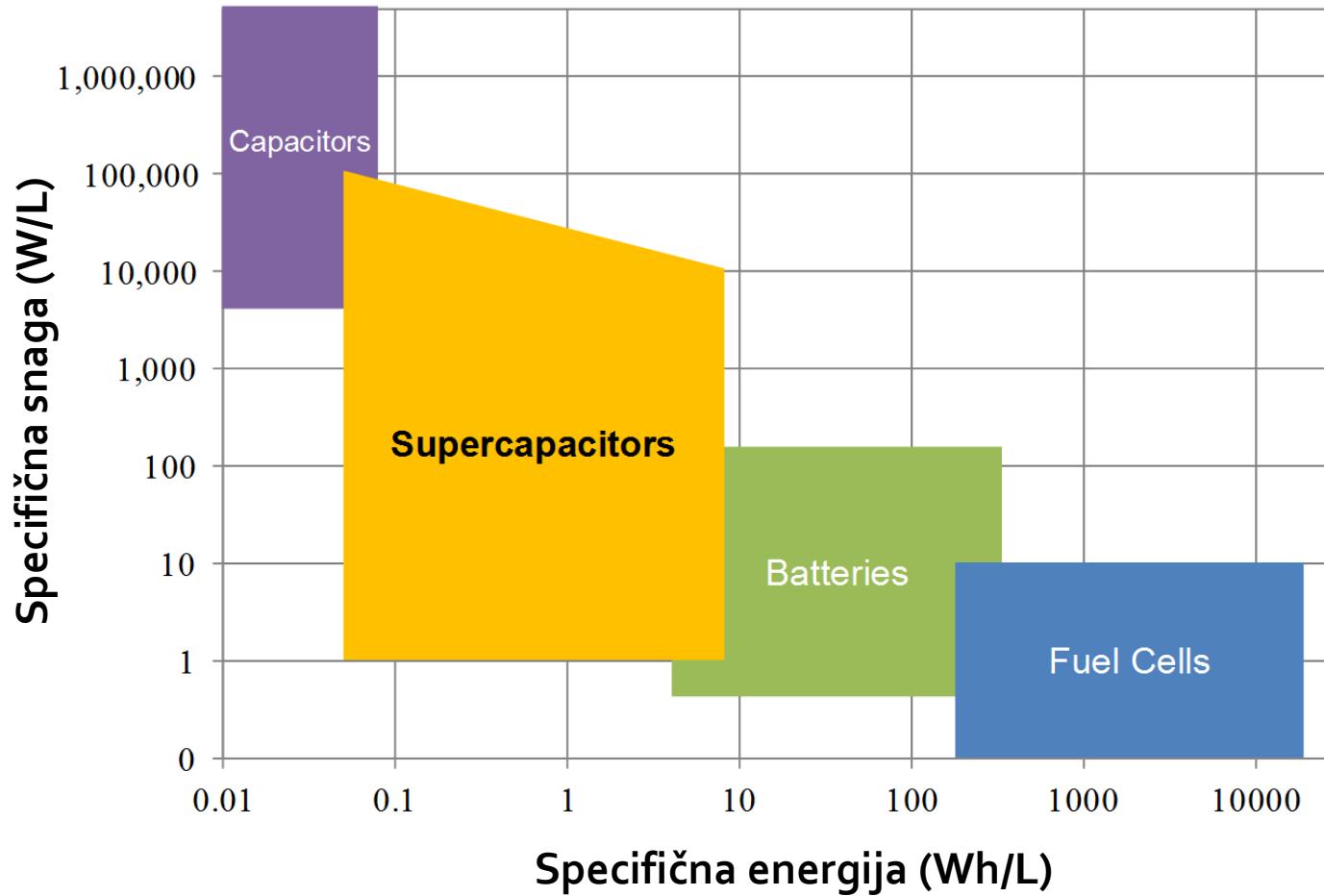


Igor Pašti

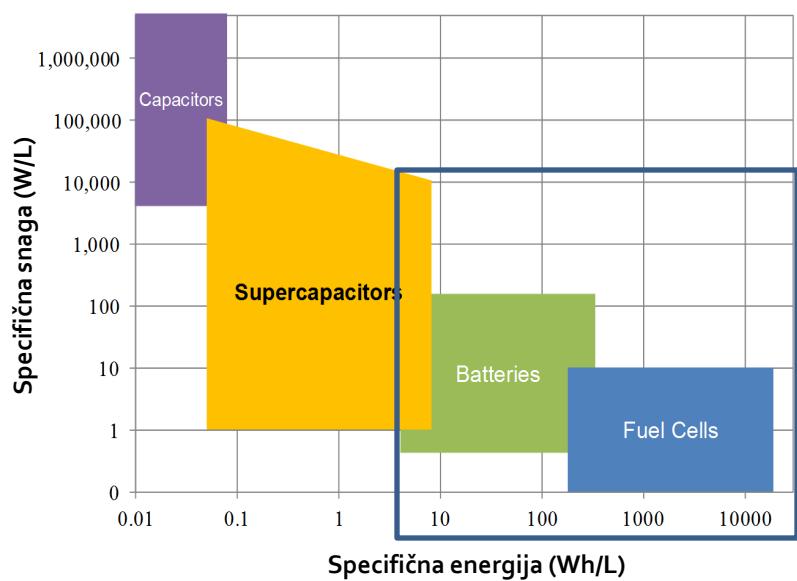
Univerzitet u Beogradu – Fakultet za fizičku hemiju

- Elektrohemskijsko skladištenje energije
- Elektrohemskijski kondenzator
- Materijali za elektrohemskijske kondenzatore
- Odabrani primeri
- Od laboratorije do police

Elektrohemjsko skladištenje energije

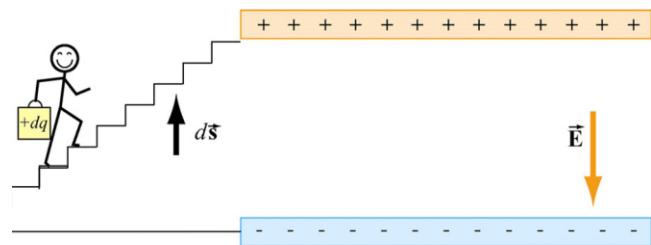


Elektrohemjsko skladištenje energije



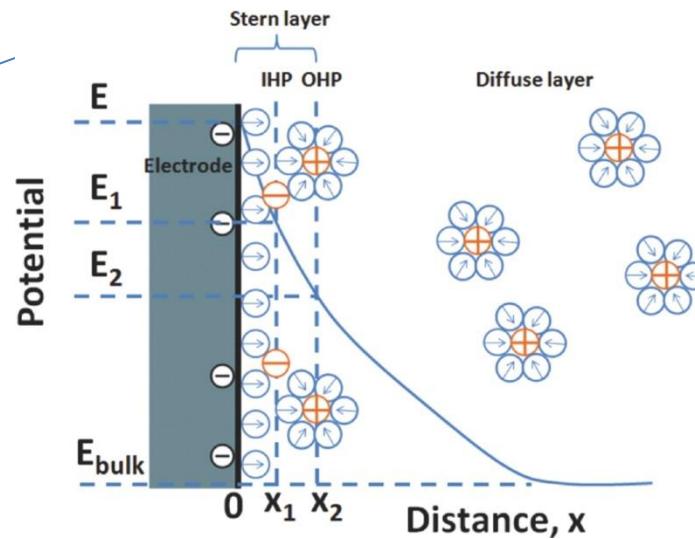
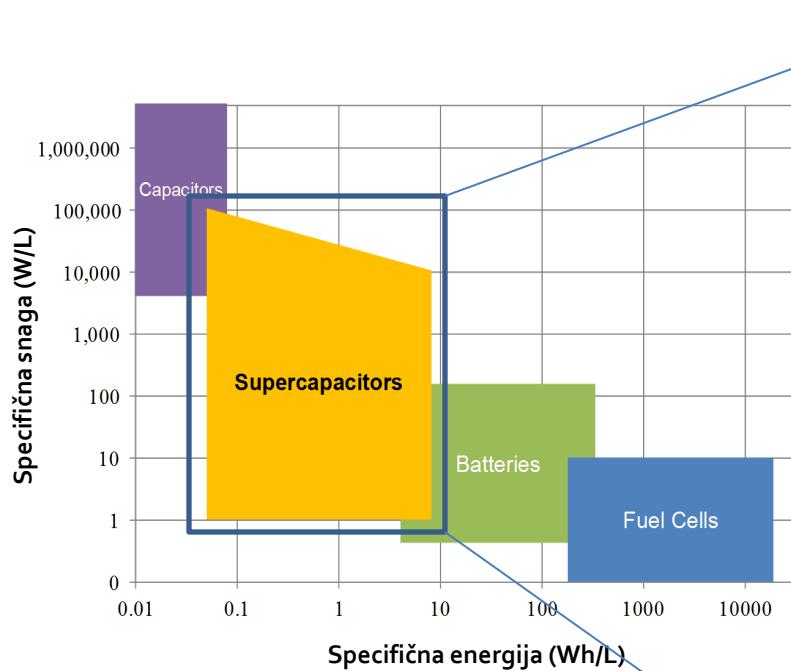
$$A + B = C + D$$

ΔG



Rad po mogu reaktanta
 $n \times F \times \varepsilon = -\Delta G$

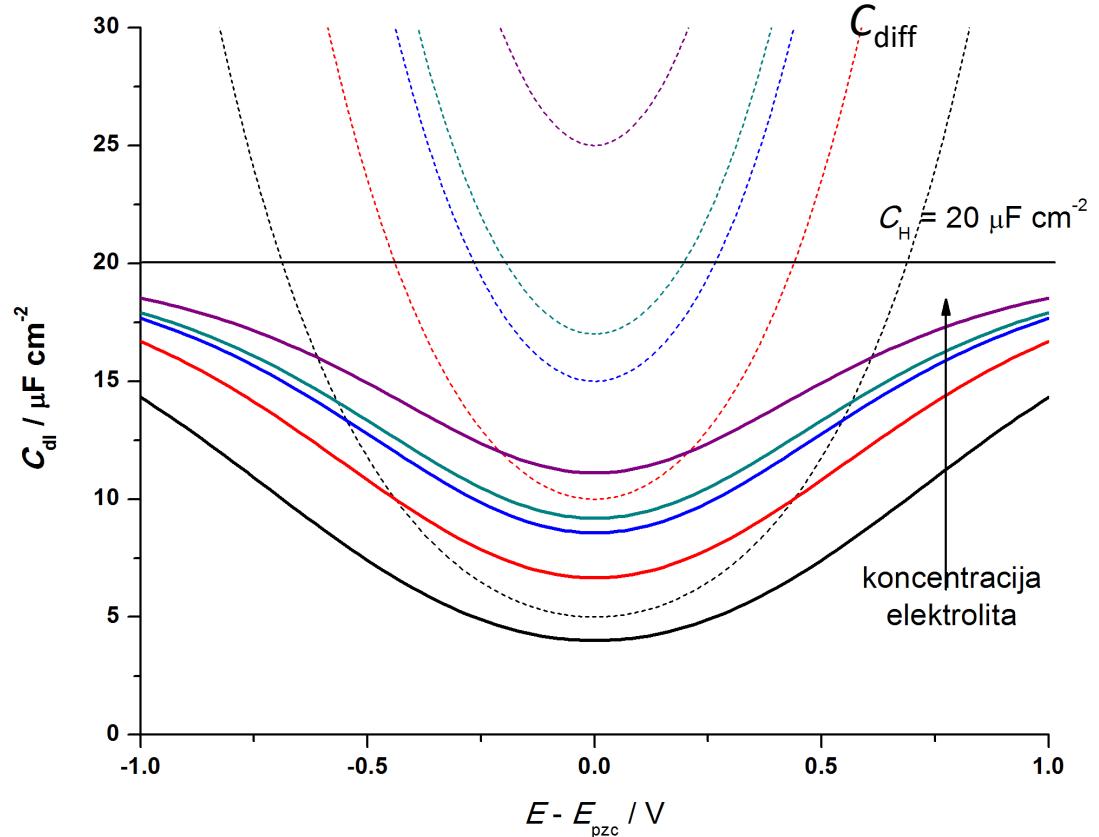
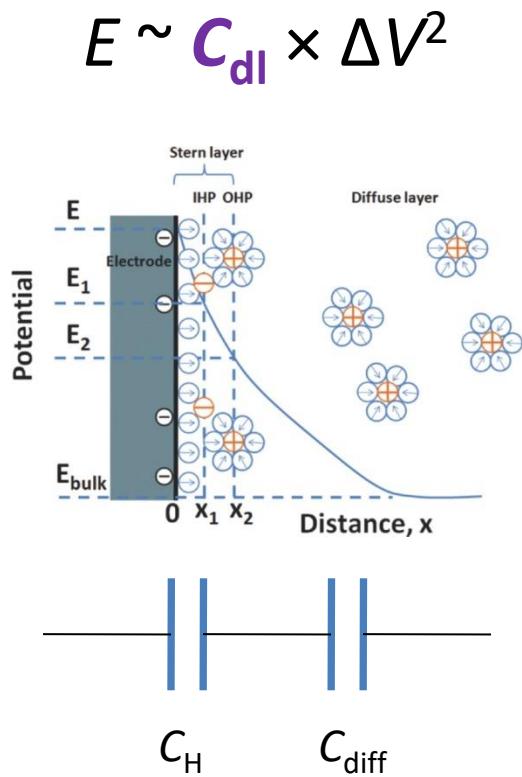
Elektrohemijsko skladištenje energije



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

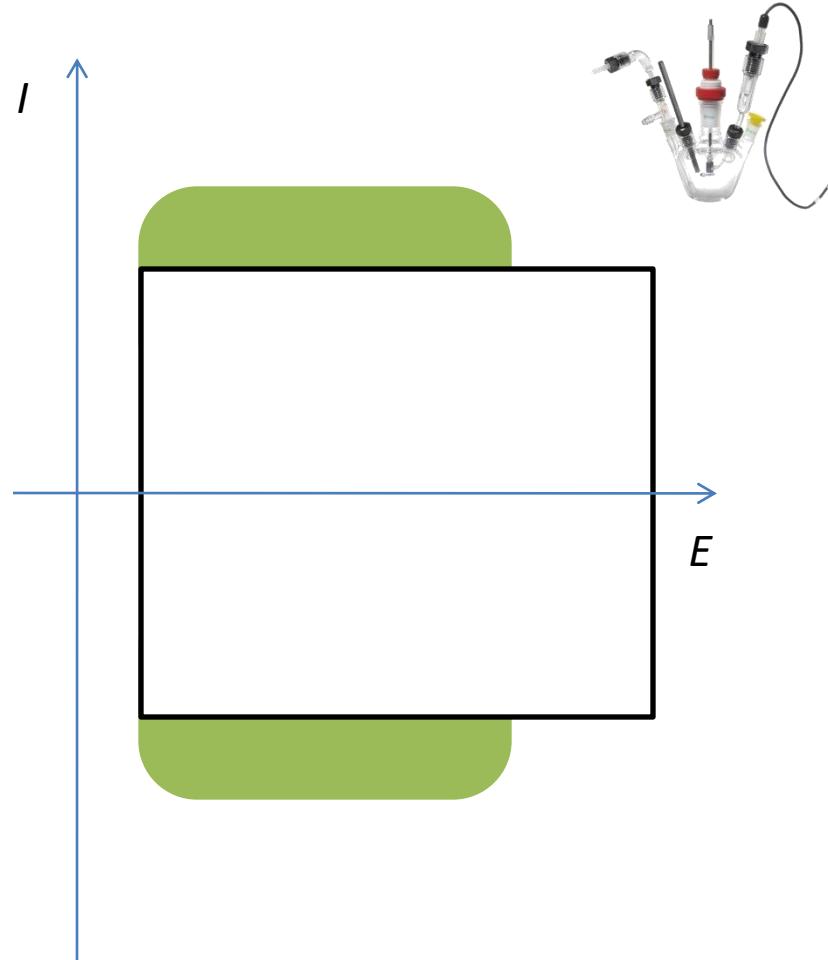
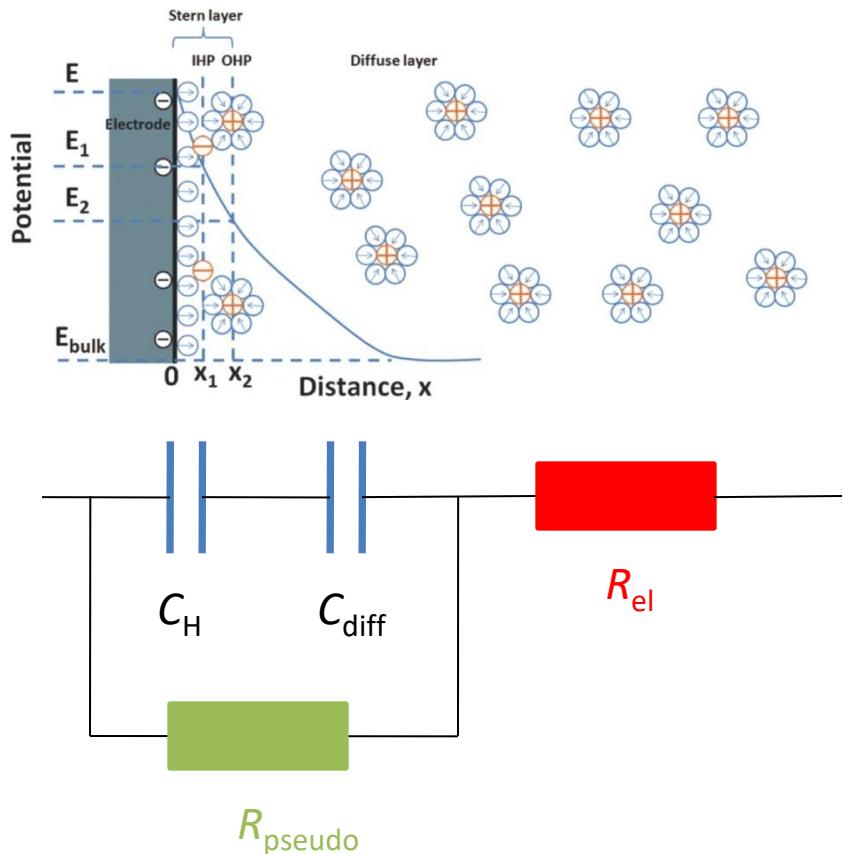
$$E \sim C_{dl} \times \Delta V^2$$

Elektrohemski kondenzator



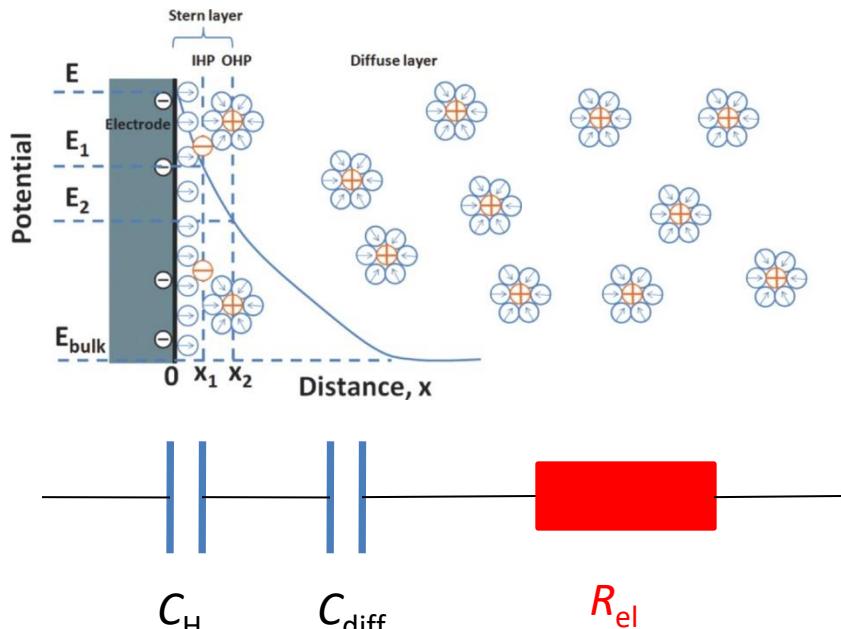
U odsustvu procesa razmene elektrona u koncentrovanim elektroličkim rastvorima, kapacitet EDS je oko $20 \mu\text{F cm}^{-2}$ za sve materijale. Cilj povećati površinu po jedinici mase.

Elektrohemski kondenzator

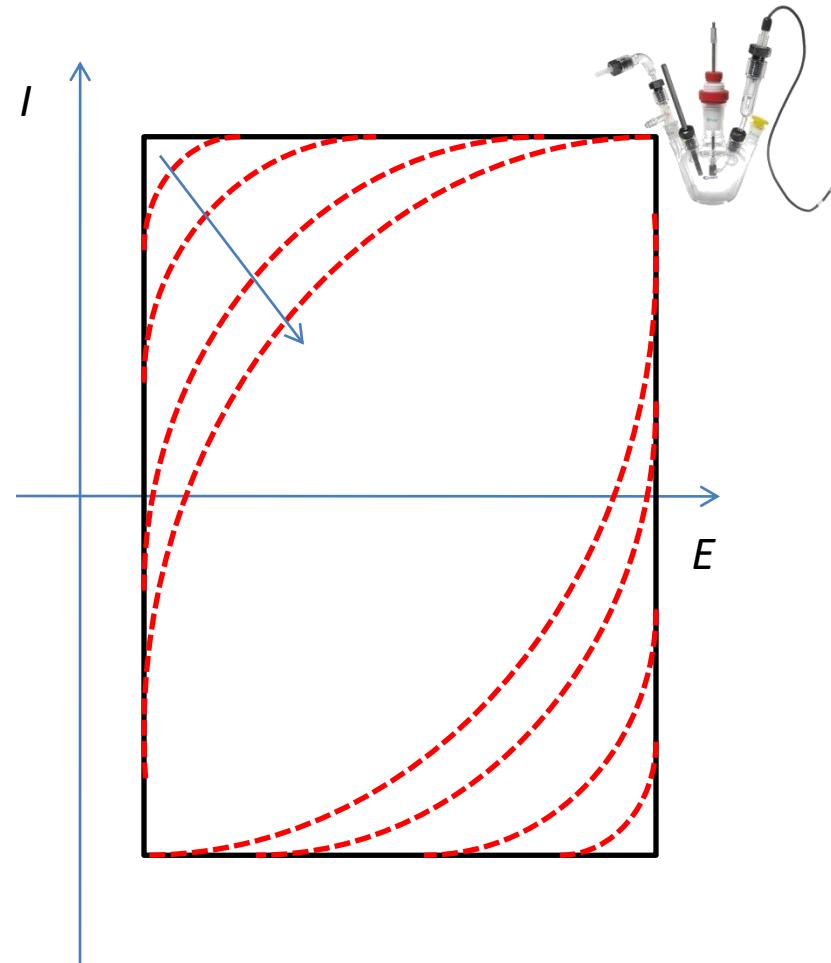


Kapacitivni odgovor može biti uvećan usled pseudocapacitivnih procesa na površini materijala (brza izmena elektrona).

Elektrohemski kondenzator

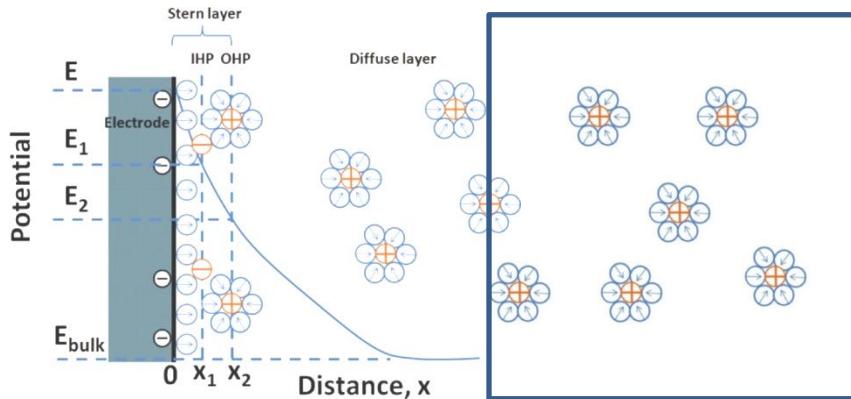


$$j_C = \frac{E}{R_e} e^{\frac{-t}{R_e C_{dl}}}$$

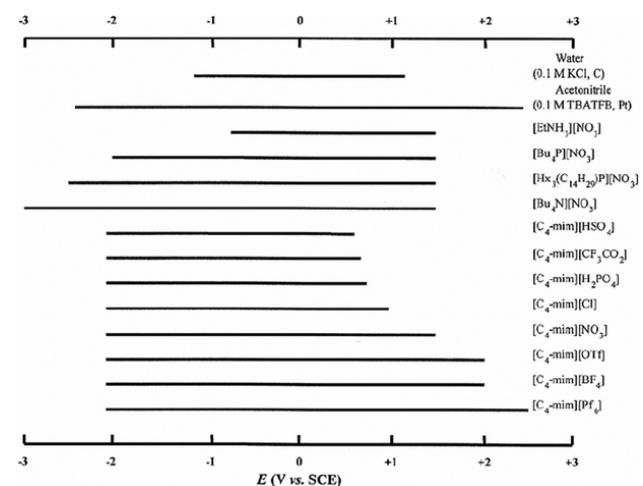
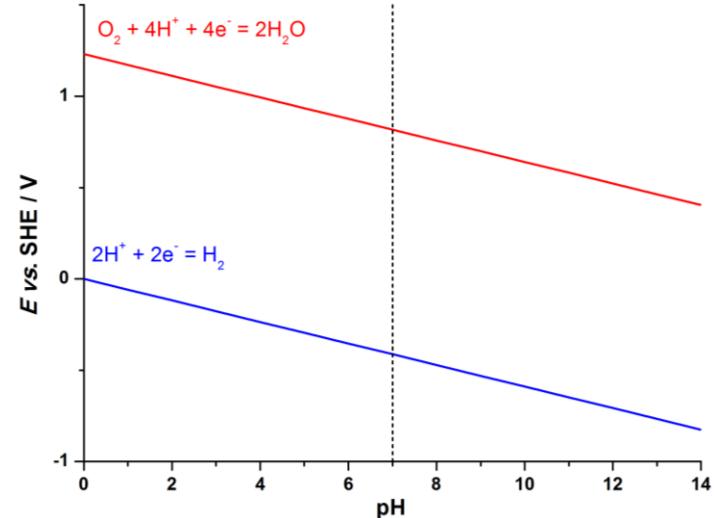
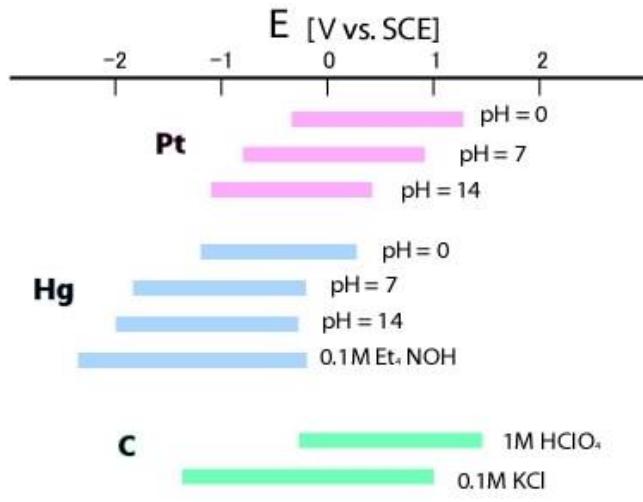


Otpor elektrolita takođe utiče na kapacitivni odgovor, neophodno je koristiti **koncentrovane elektrolite**.

Elektrohemijijski kondenzator



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



Elektrohemski kondenzator

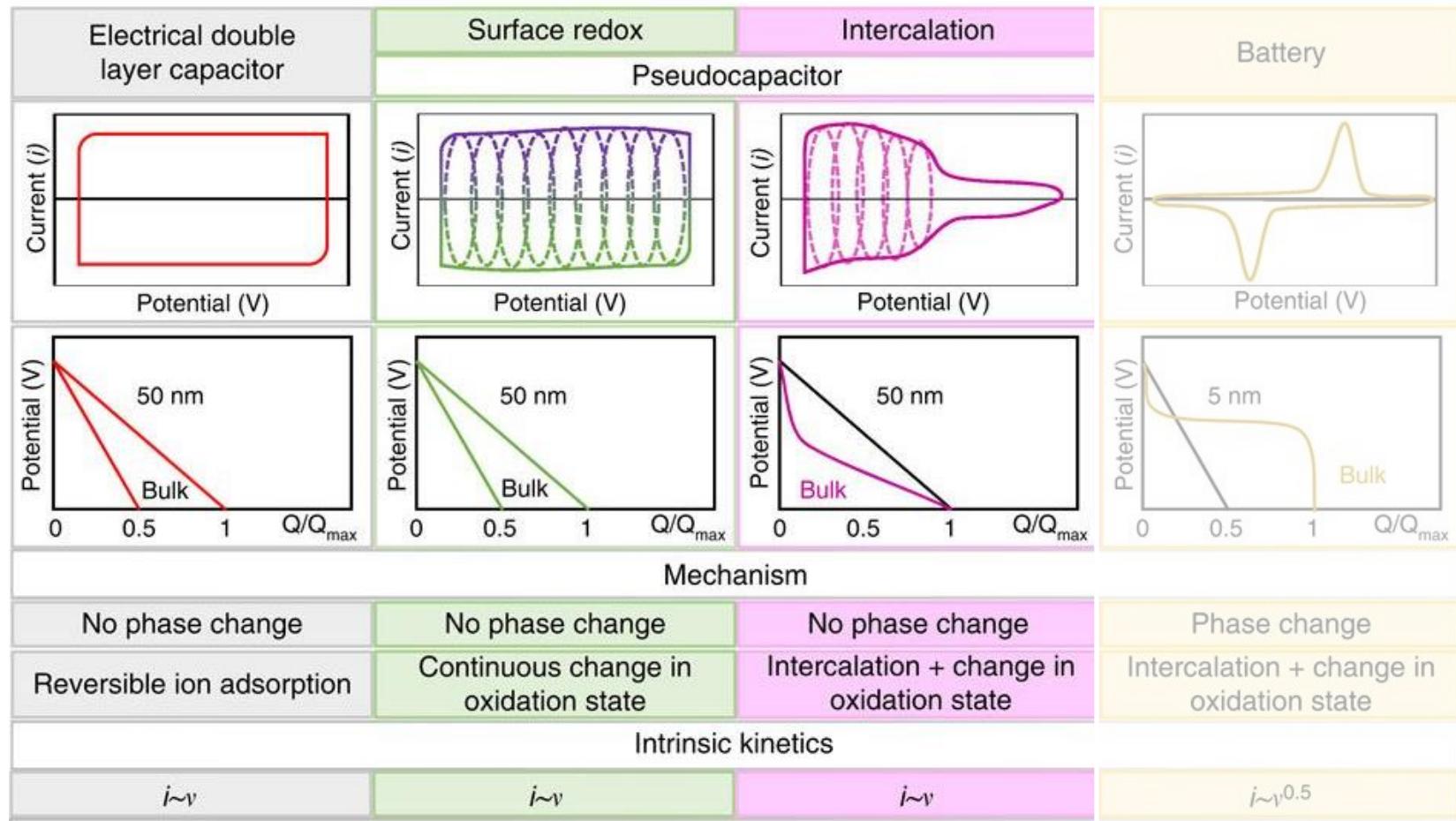
Elektrohemski dostupna površina u koncentrovanom elektrolitu

Pseudocapacitivni procesi

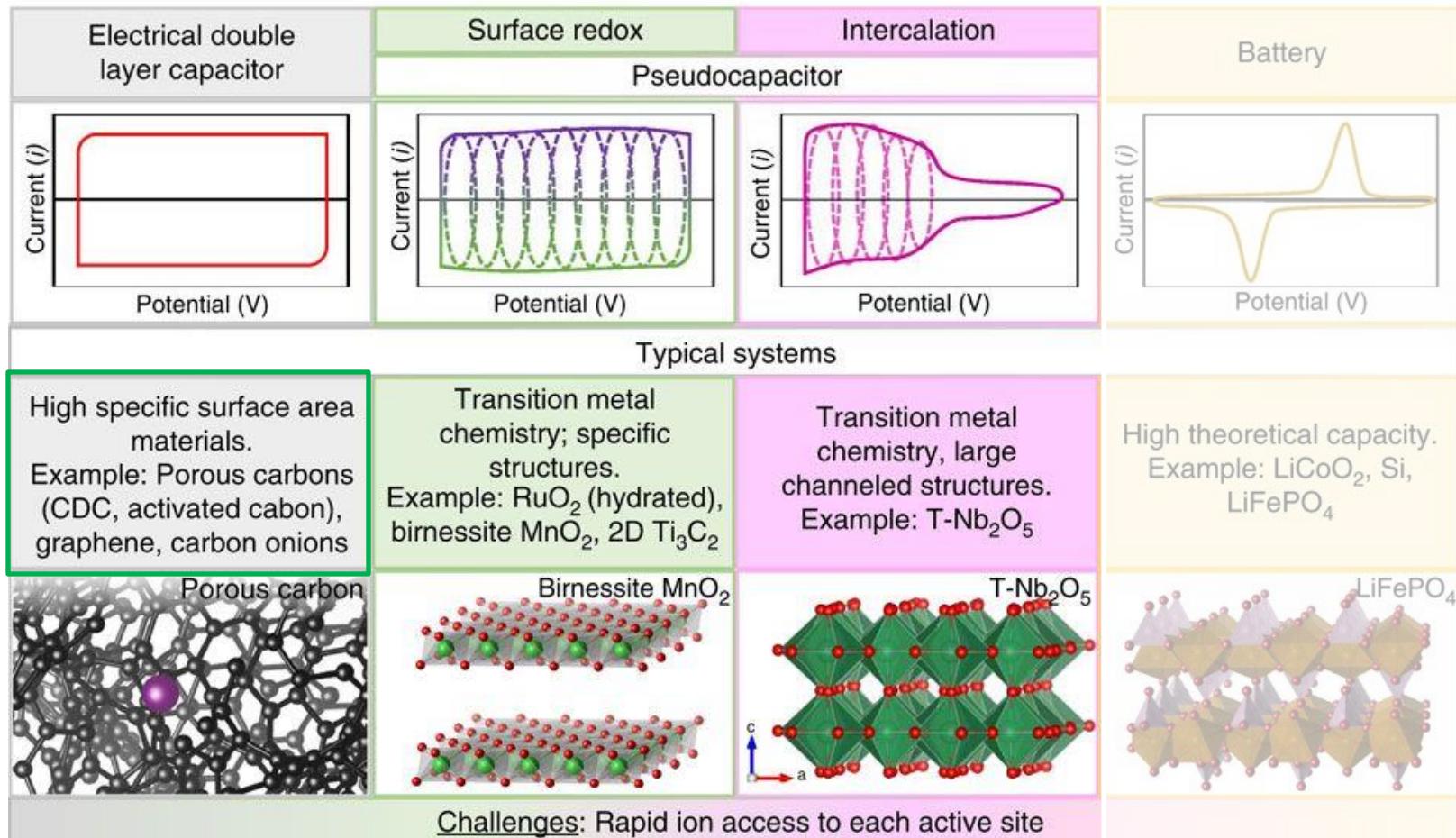
$$E \sim C_{dl} \times \Delta V^2$$

Elektrohemski prozor elektrolita.
Ireverzibilne elektrohemiske promene
elektrodnog materijala.

Materijali za elektrohemiske kondenzatore



Materijali za elektrohemiske kondenzatore

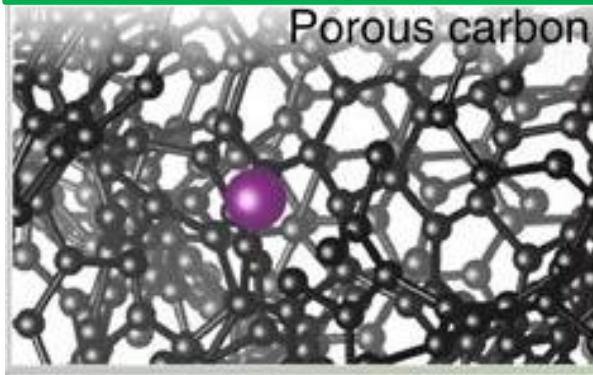


Materijali za elektrohemiske kondenzatore

$$20 \mu\text{F cm}^{-2} \times 1000 \text{ m}^2 \text{ g}^{-1} = 200 \text{ F g}^{-1}$$

High specific surface area materials.

Example: Porous carbons (CDC, activated carbon), graphene, carbon onions



Ugljenični materijali:

- Širok elektrohemiski prozor
- Hemijski inertni (relativno)
- Jeftini (relativno)

Obabrani primeri:

- Materijali izvedeni iz biomase
- Materijali izvedeni iz polimera
- Materijali na bazi grafena

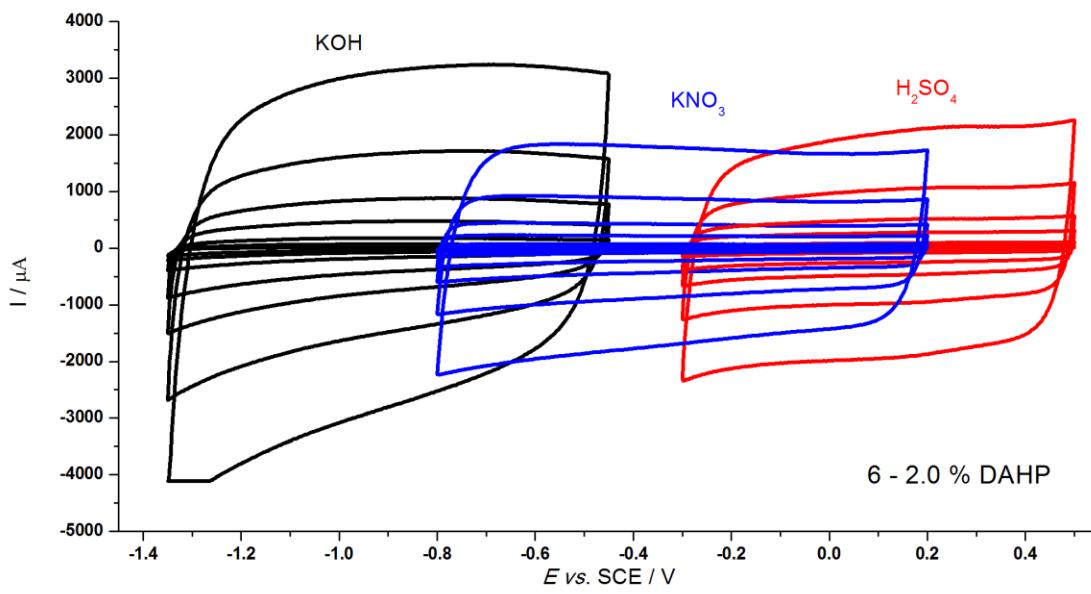
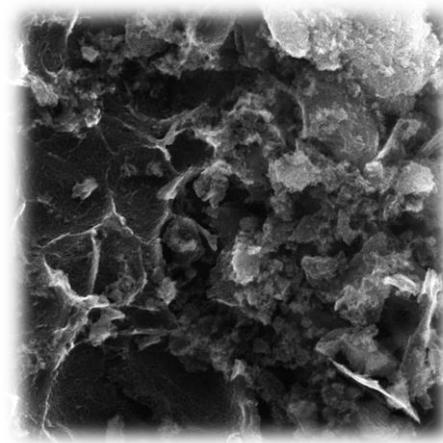
Materijali izvedeni iz biomase



Temperaturski tretman
Hemijska impregnacija



Aktivacija



Biomasa jer:

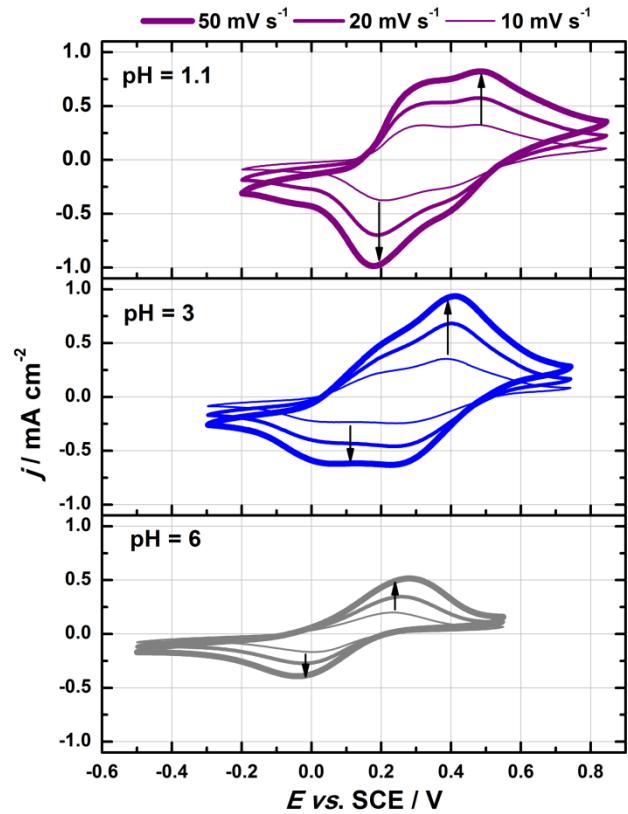
- Prirodno sadrži heteroatome
- Jeftina je lako dostupna
- Značajan ekološki aspekt
- Trenutno se najviše ispituje

kraft lignin

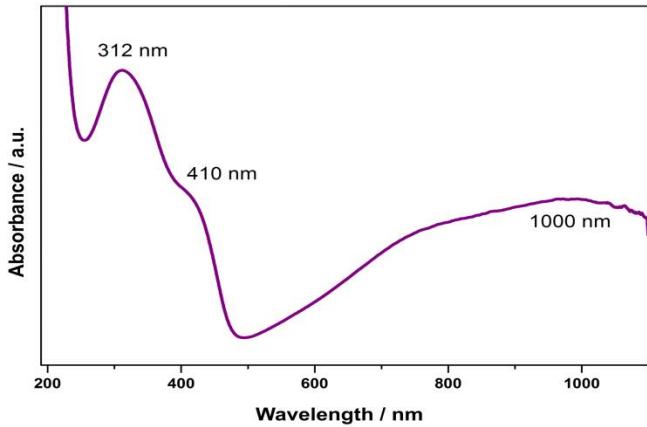
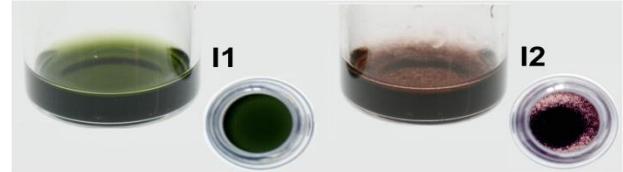
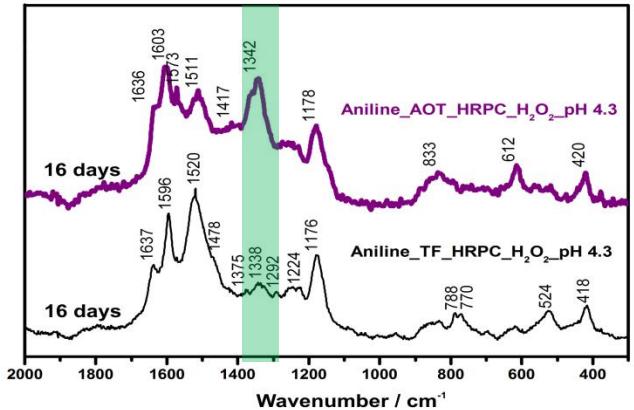
$-C_{\text{spec}}$ 100 – 200 F g⁻¹

Materijali izvedeni iz polimera

Provodni polimeri su interesantni materijali za elektrohemijske kondenzatore

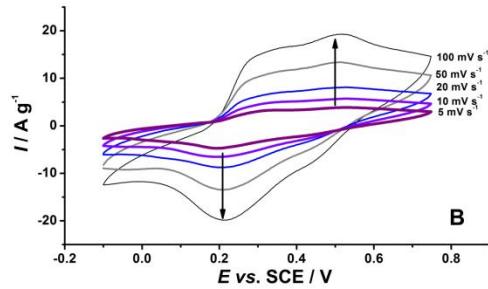
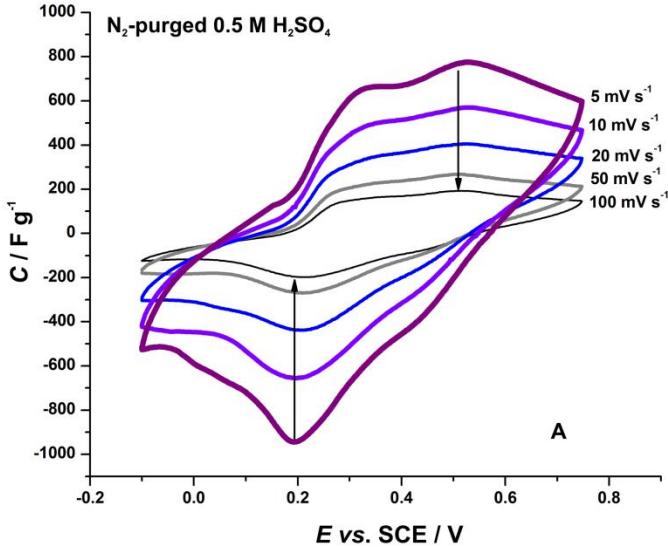


Gubitak redoks aktivnosti

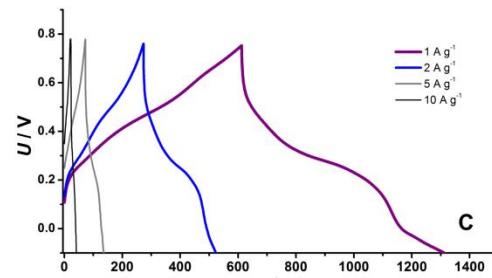


Capacitet potiče od redoks aktivnih grupa

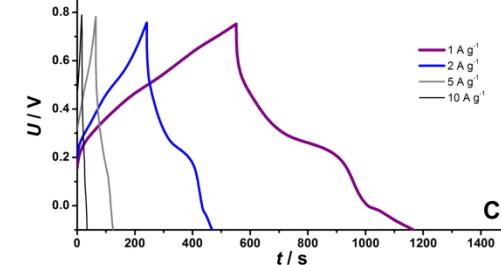
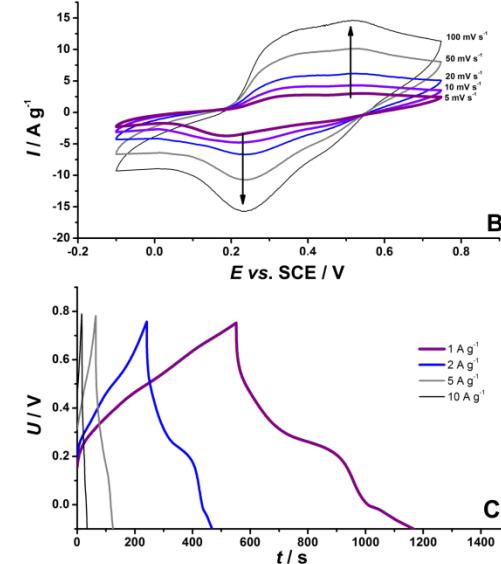
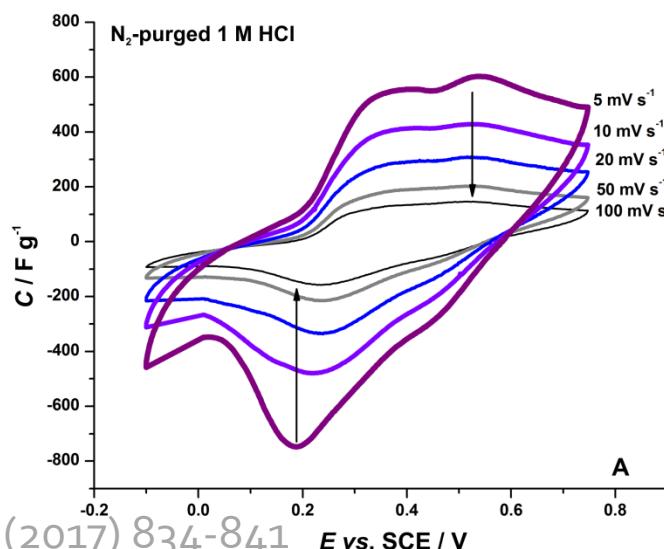
Materijali izvedeni iz polimera



Osetljivi na pH



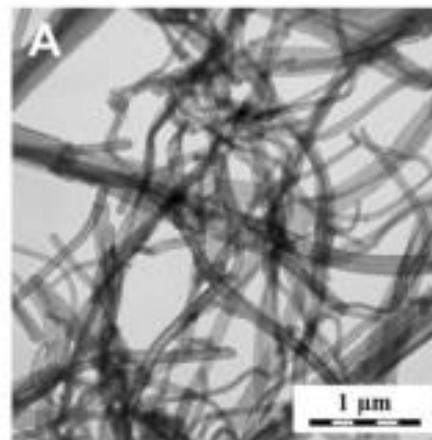
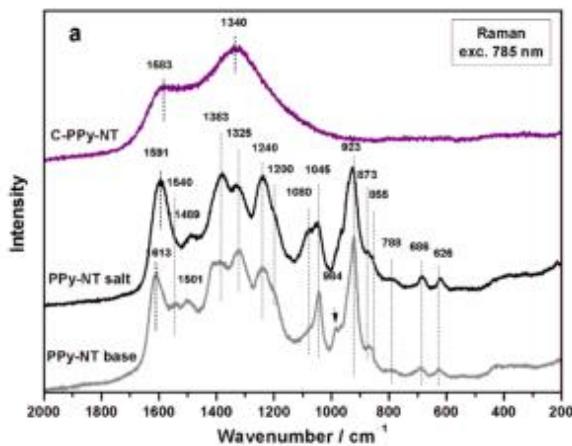
Osetljivi na ireverzibilne
promene



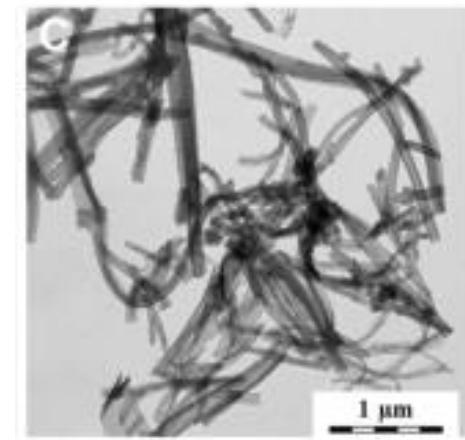
Materijali izvedeni iz polimera

Zadržava se polazna morfologija

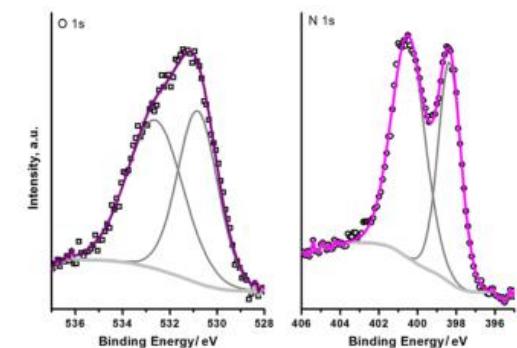
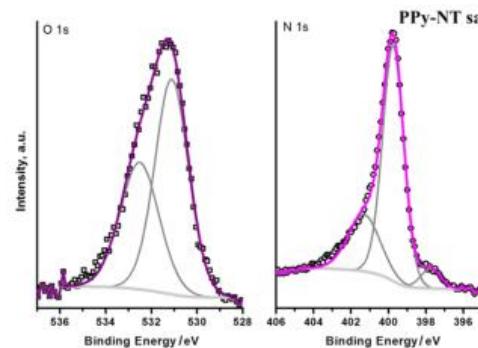
Karbonizacija polimernih nanostruktura



PPy NT

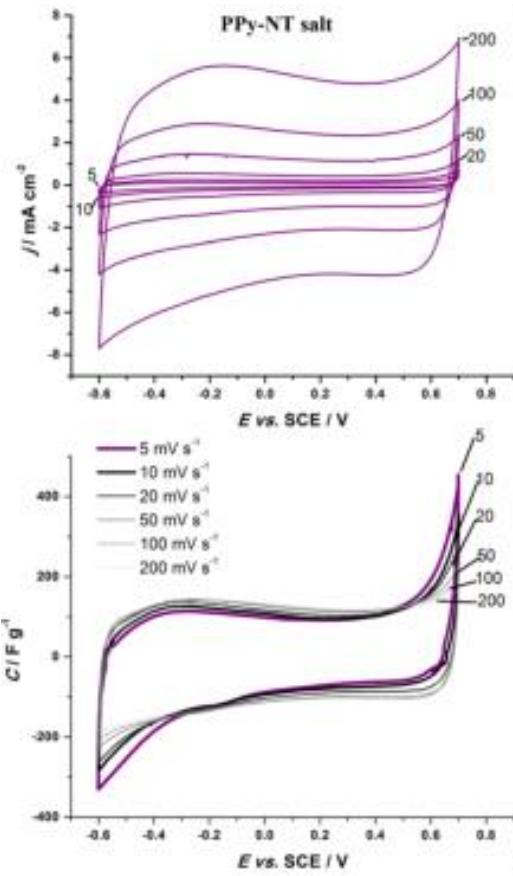


Carb-PPy NT

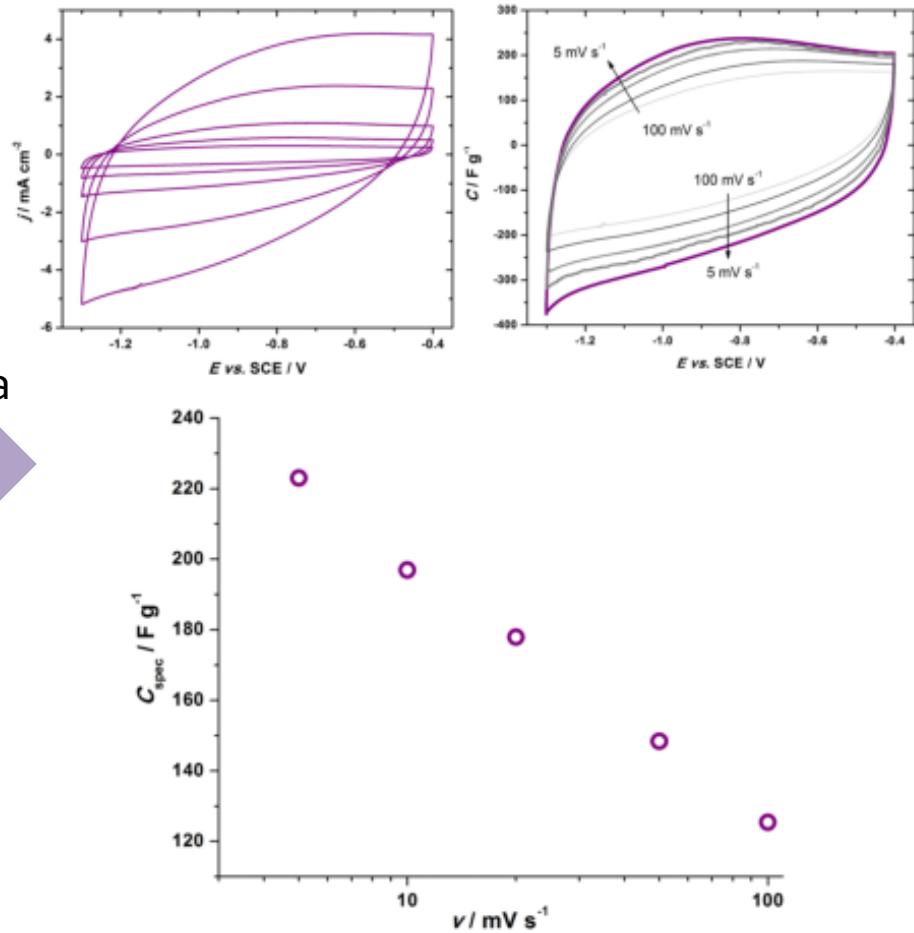


Ugradnja heteroatoma (pseudocapacitet)

Materijali izvedeni iz polimera



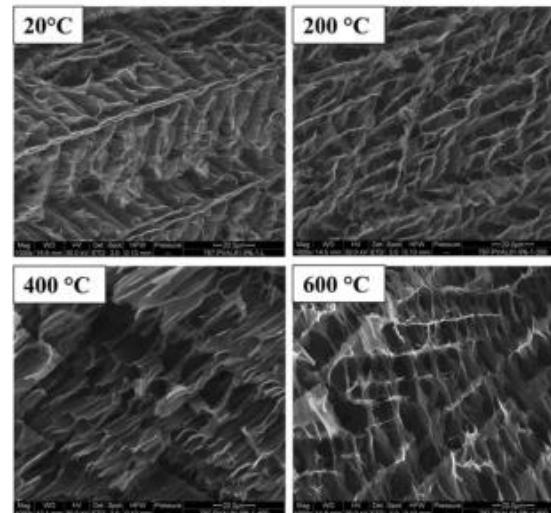
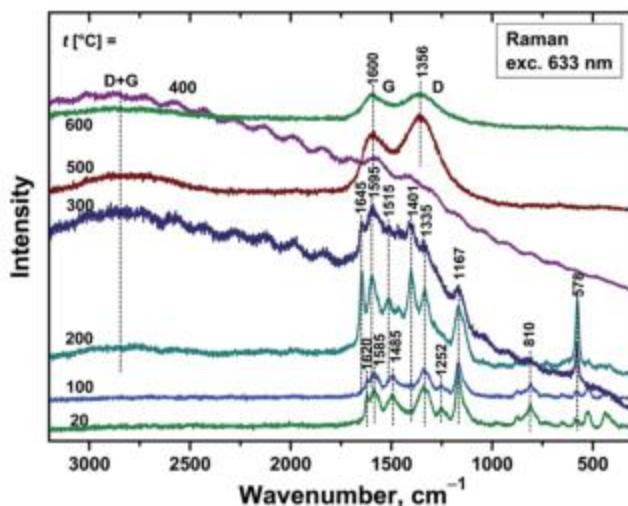
karbonizacija



Materijali izvedeni iz polimera



PANI aerogel to Carbogel



Temperature, °C	Specific surface area, m² 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

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.

Materijali izvedeni iz polimera

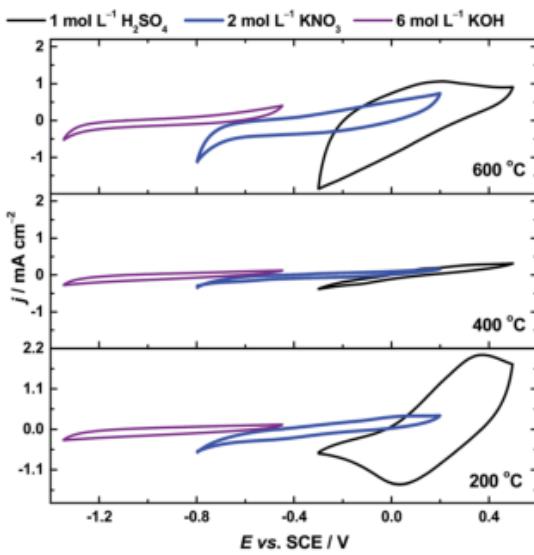
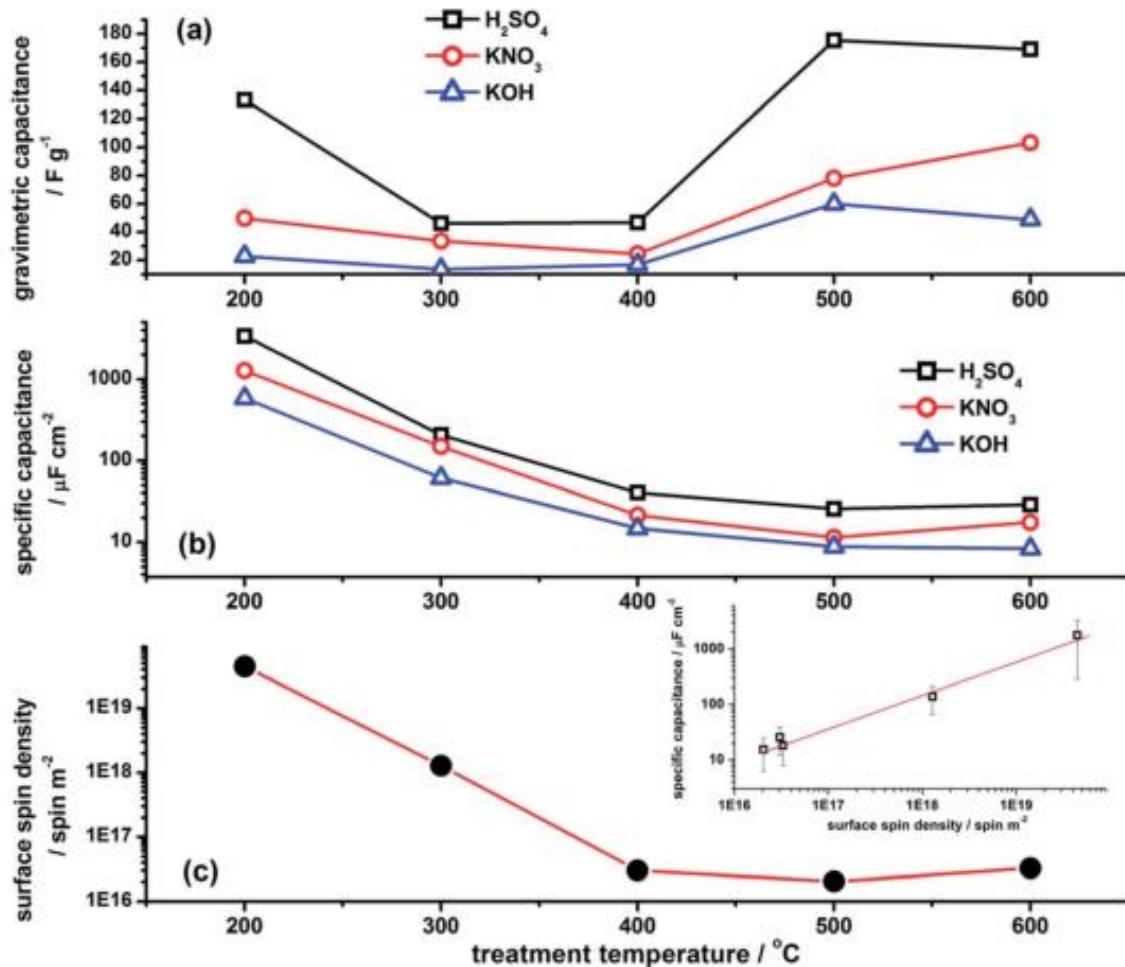
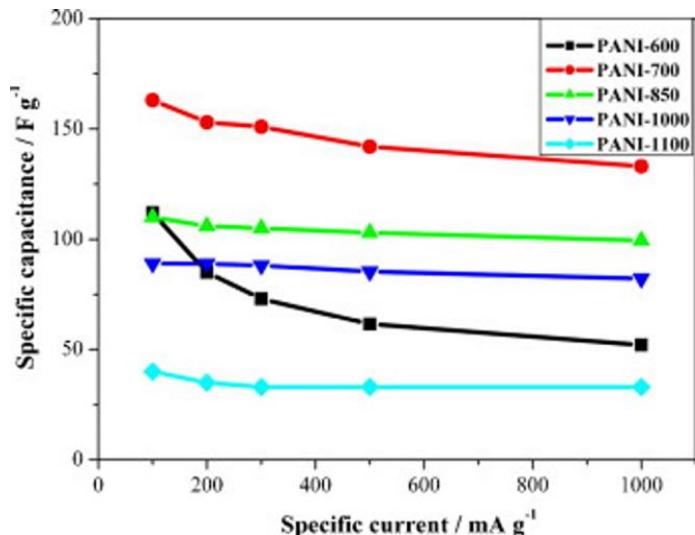


Fig. 10 Cyclic voltammograms of PANI aerogels heated to 200 °C (bottom), 400 °C (middle) and 600 °C (top) recorded in N₂-purged 1 M H₂SO₄, 2 M KNO₃ and 6 M KOH at the scan rate of 100 mV s⁻¹.



Materijali izvedeni iz polimera

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



Uticaj:

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

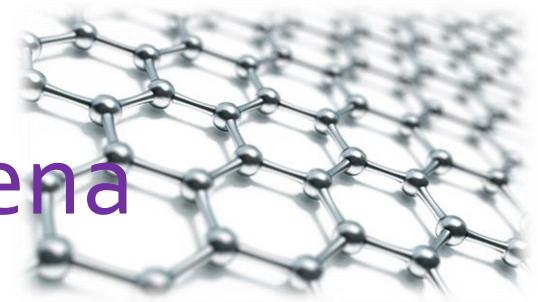
Najčešće korišćeni provodni polimeri:

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}

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"



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Videos

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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

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News

Maps

More

Settings

Tools

About 9,340 results (0.33 seconds)

Why Graphene is Amazing - Science in Society Archive

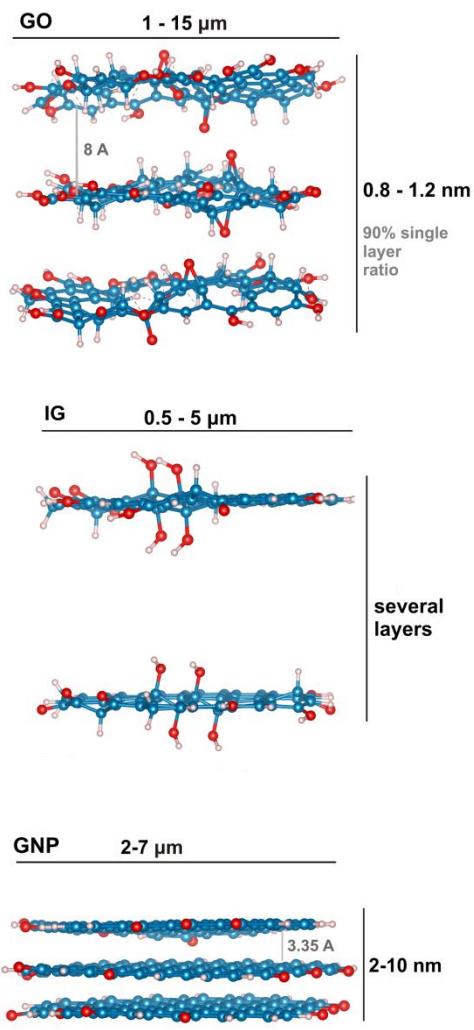
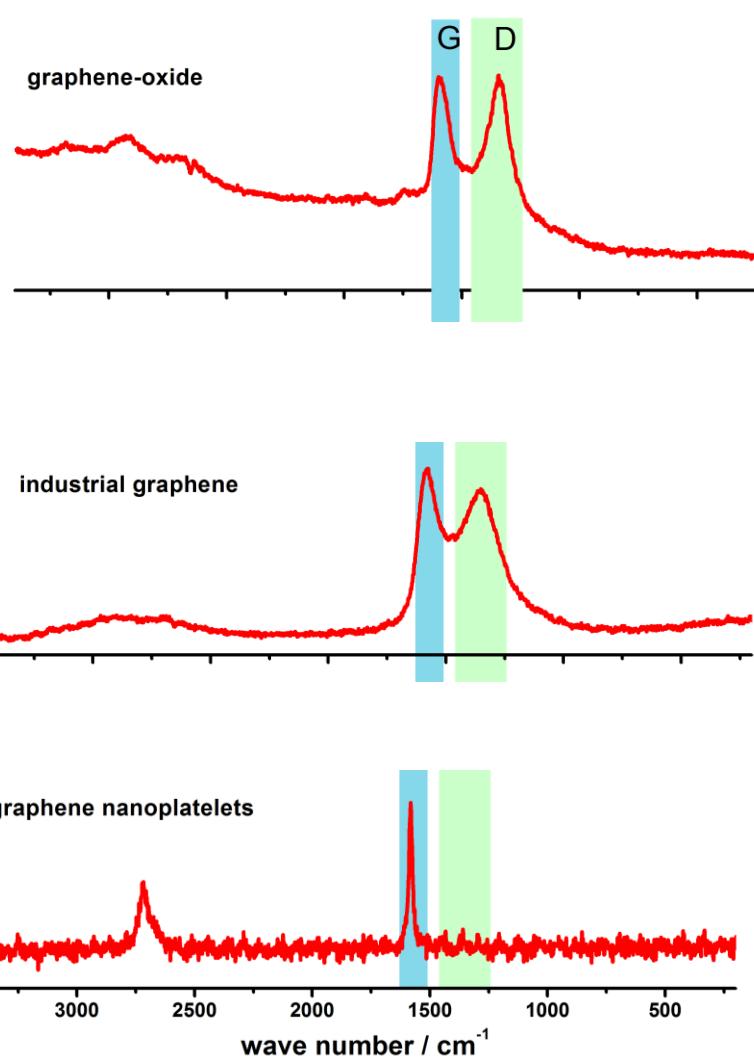
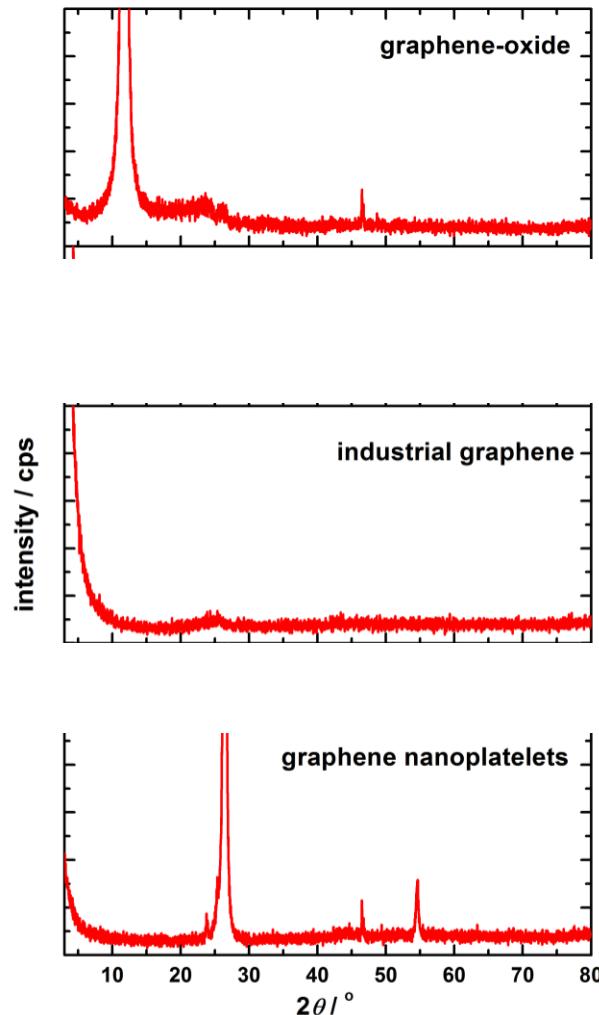
www.i-sis.org.uk/Why_Graphene_is_Amazing ▾

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

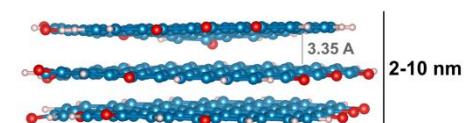
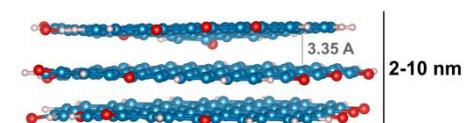
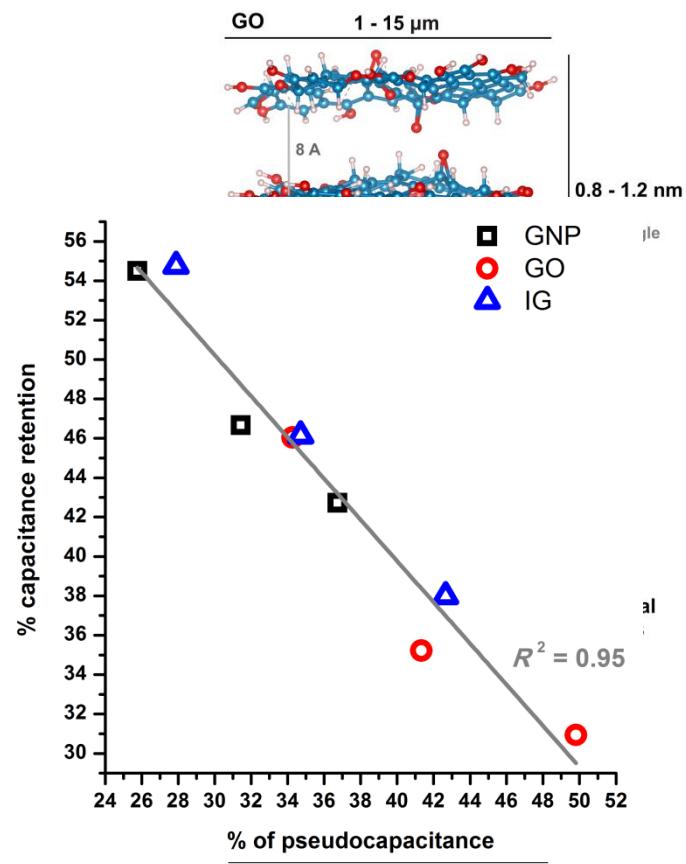
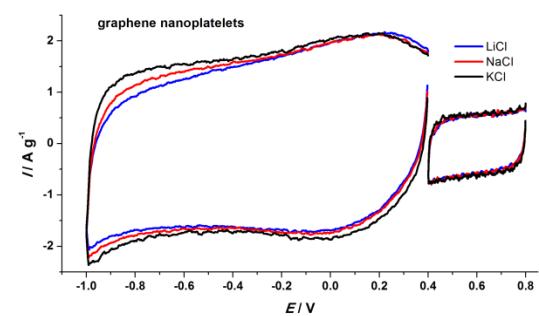
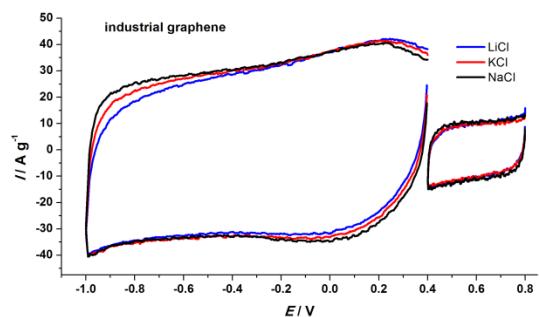
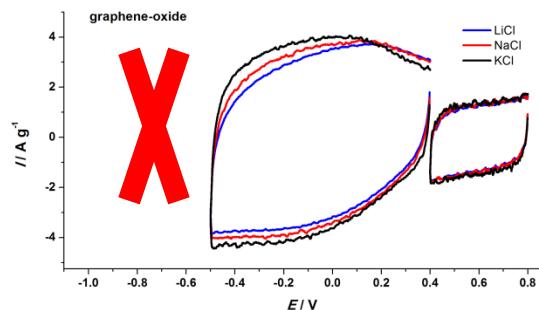
U realnosti, grafen

- Nije ravan
- Ima defekte
- Skup je

Materijali na bazi grafena

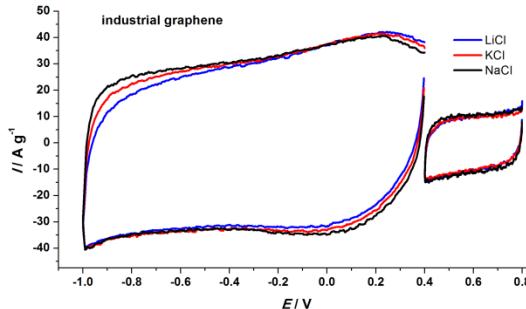
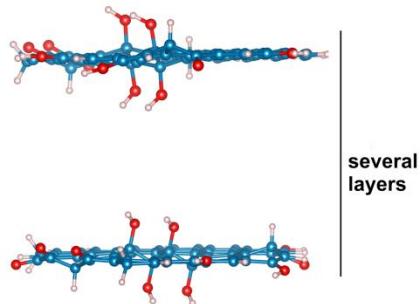


Materijali na bazi grafena

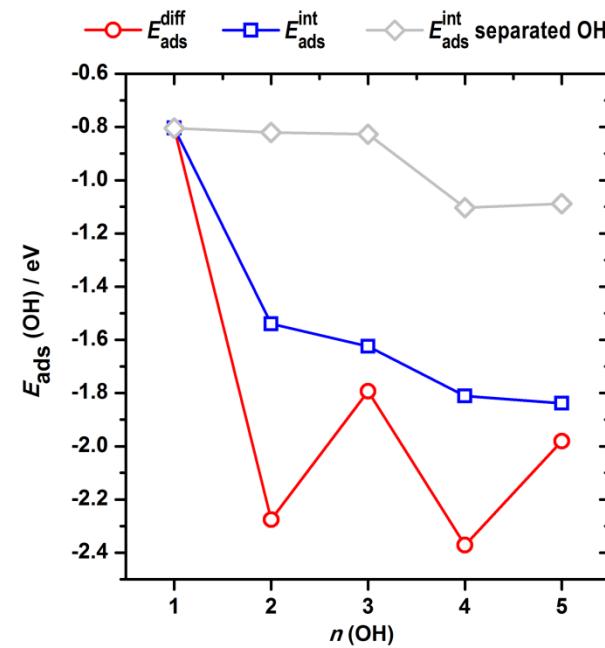
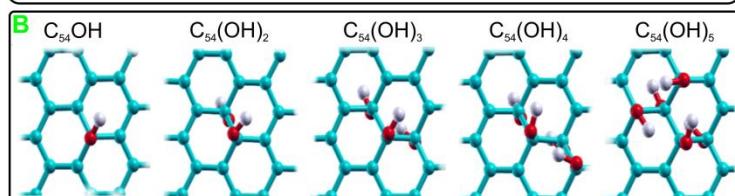
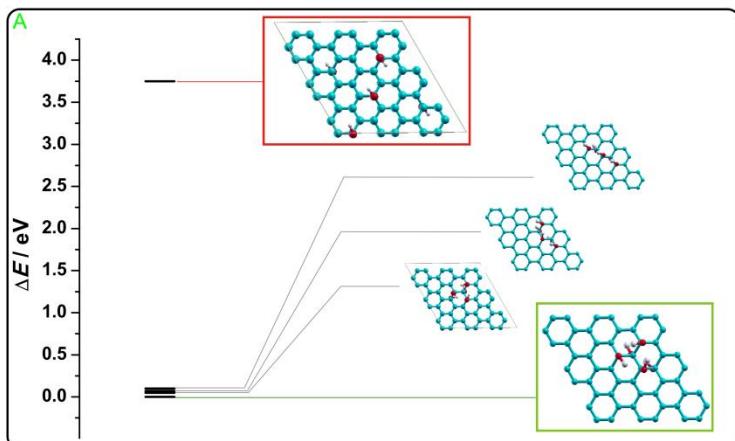


Materijali na bazi grafena

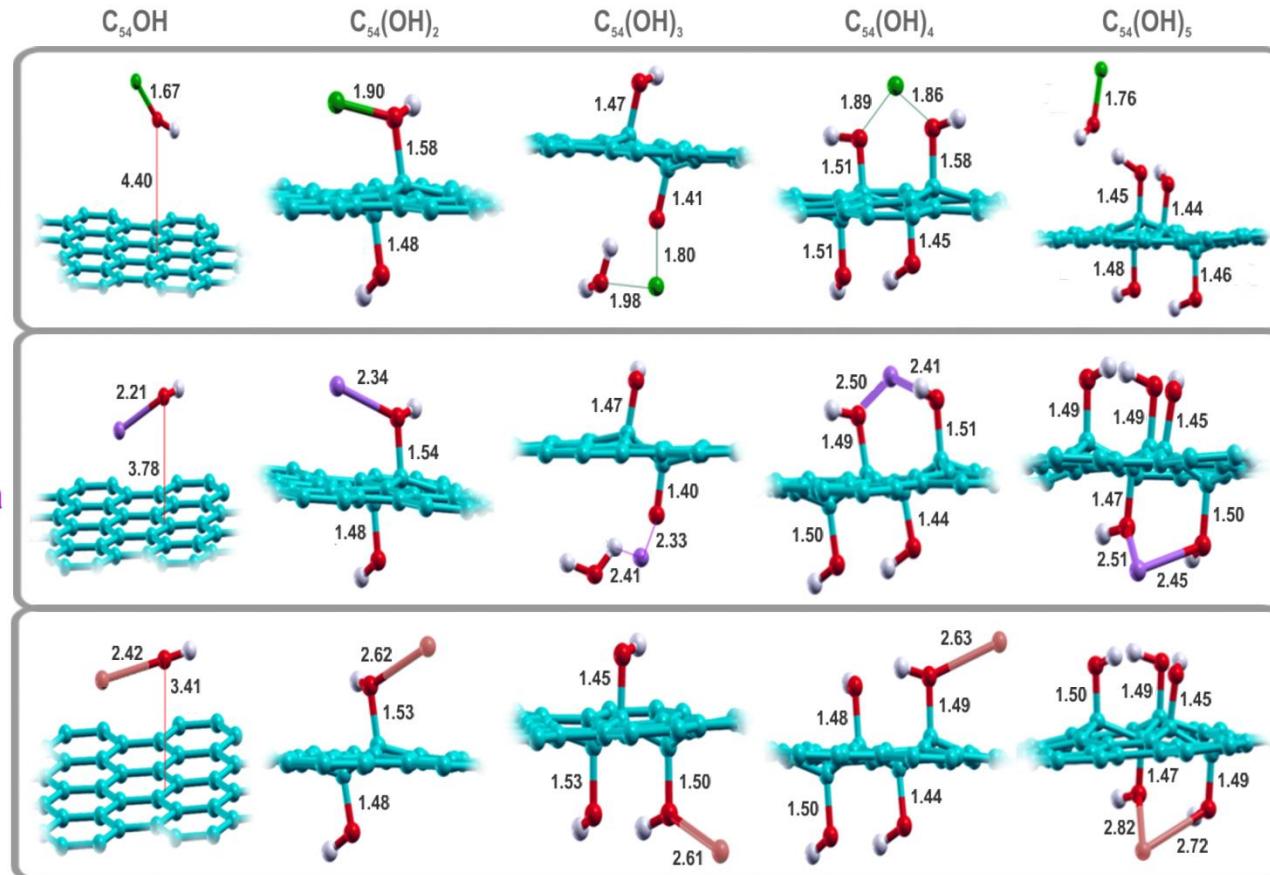
IG 0.5 - 5 μm



Odakle potiče kapacitet?

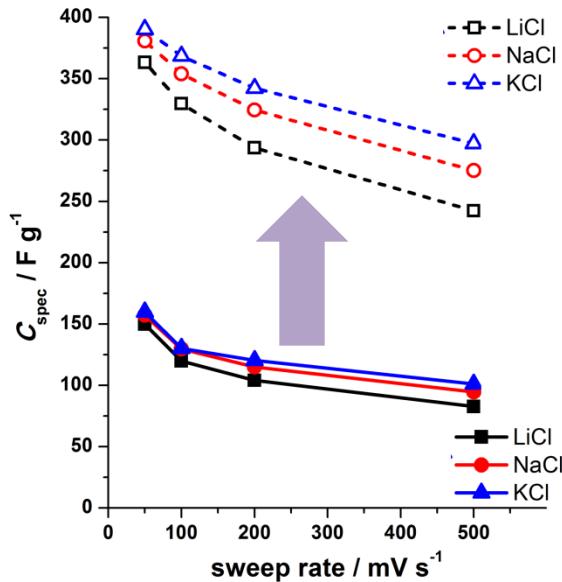
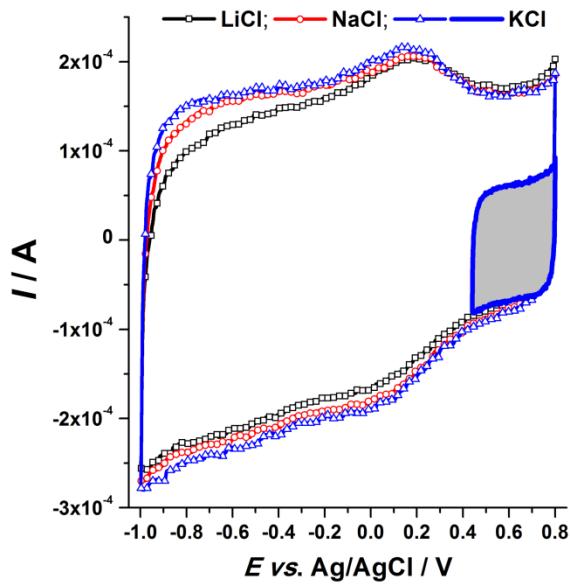


Materijali na bazi grafena

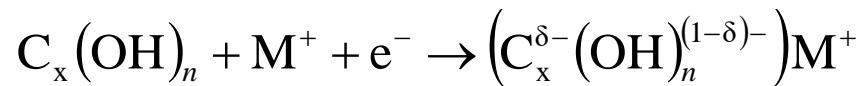
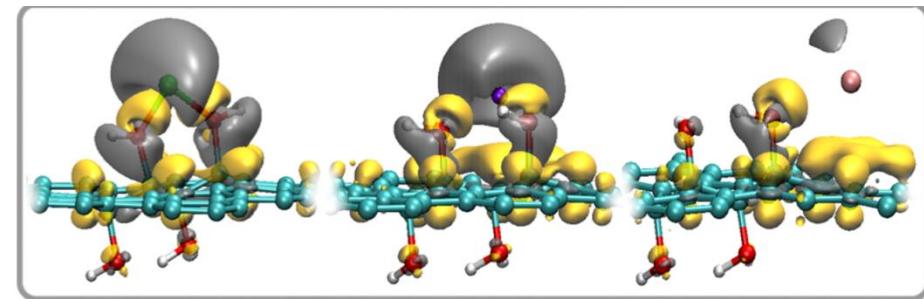


Aglomerisane
funkcionalne
grupe stabilizuju
interakciju sa M^+

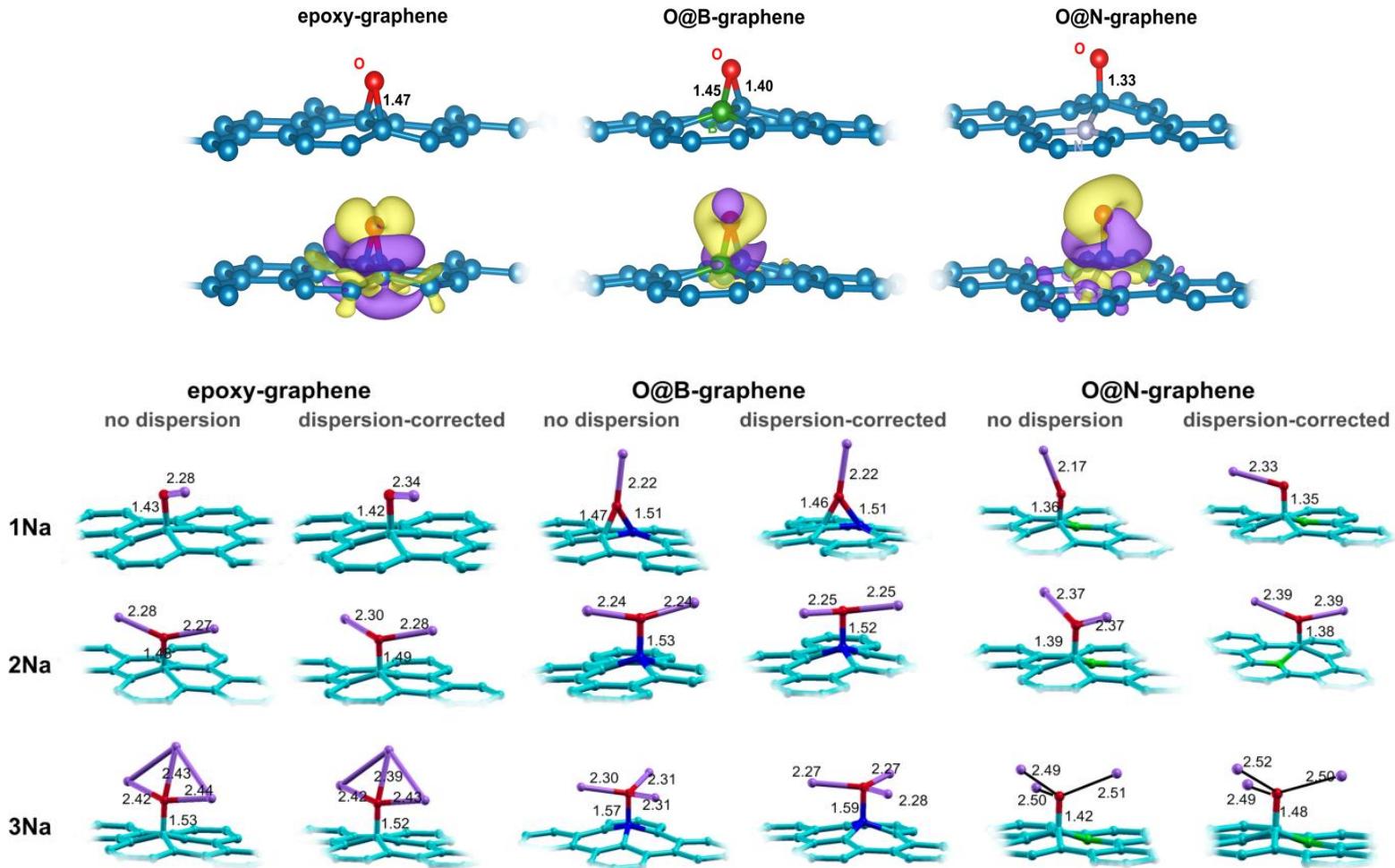
Materijali na bazi grafena



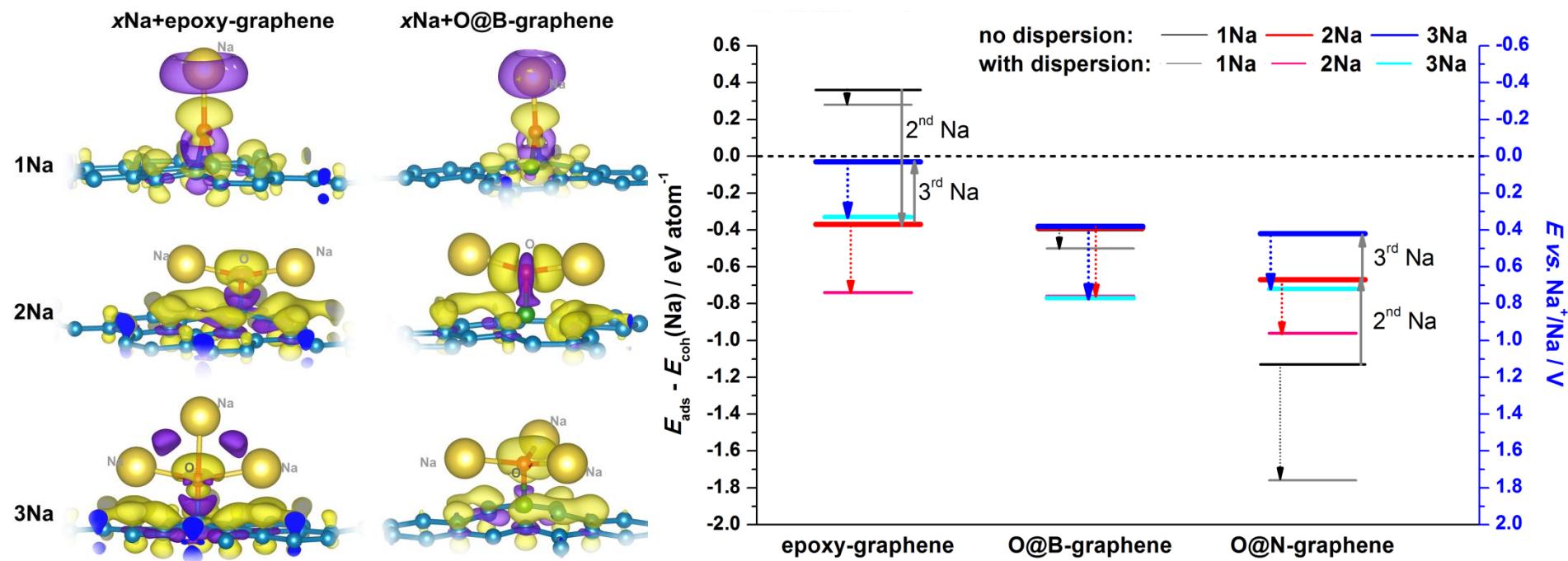
Pseudocapacitet
aktiviran na
negativnim
potencijalima



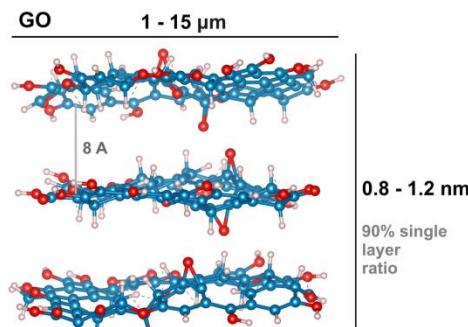
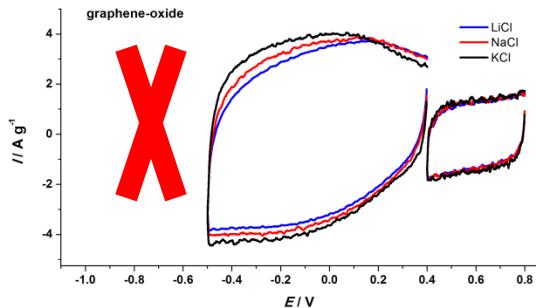
Materijali na bazi grafena



Materijali na bazi grafena

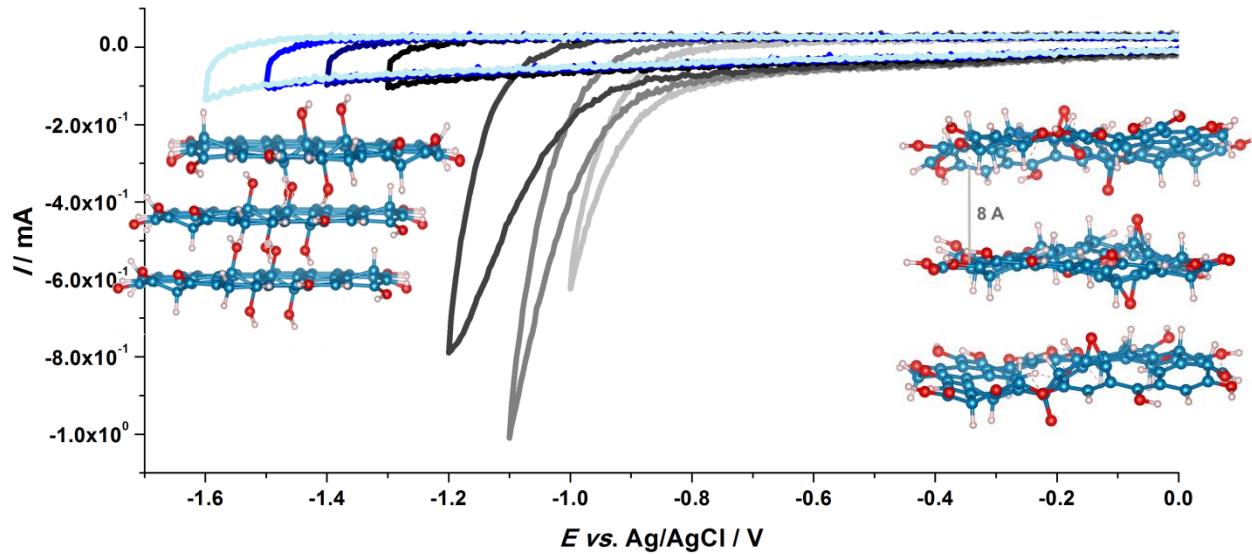


Materijali na bazi grafena

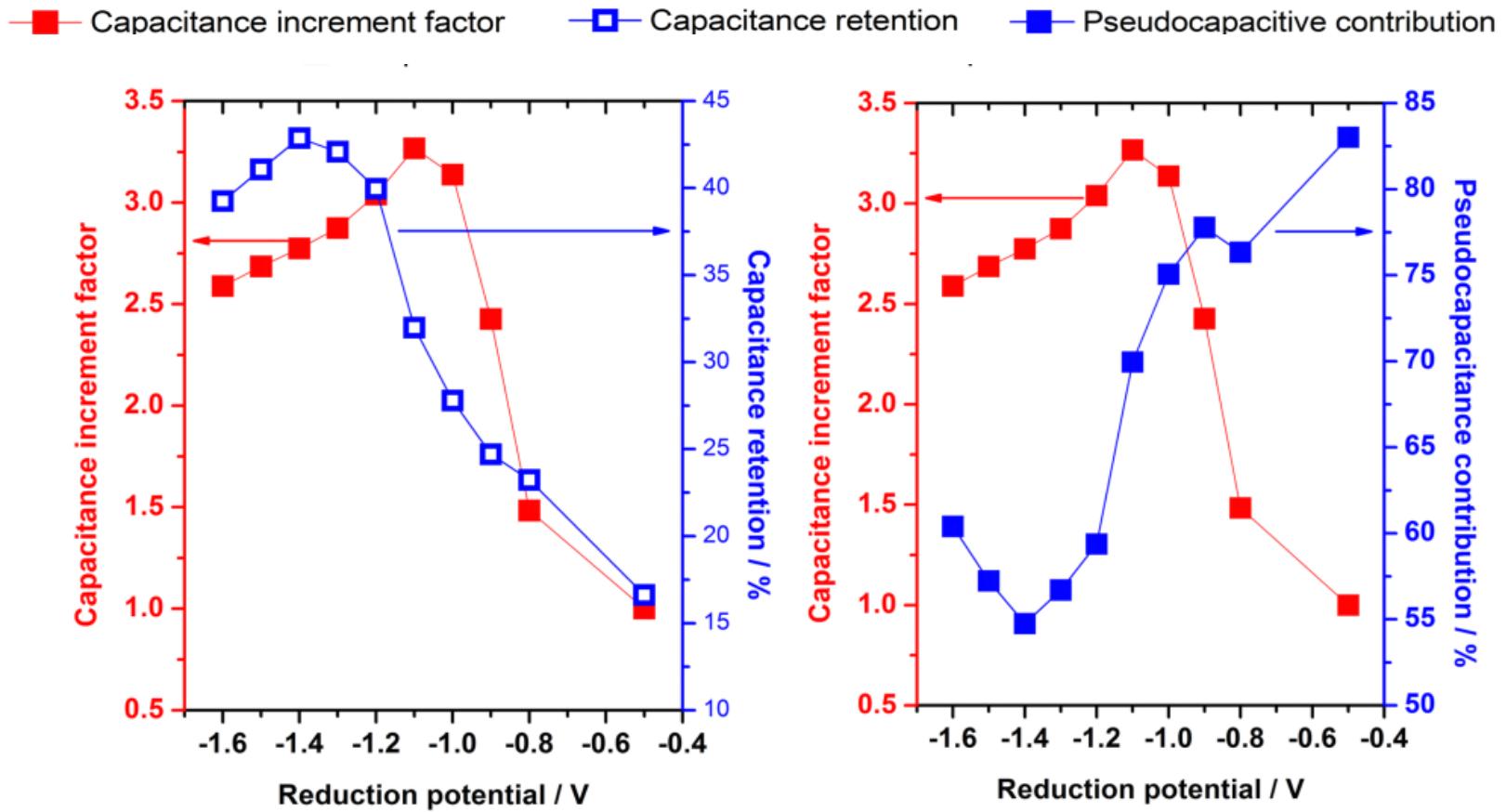


Grafen oksid je neprovodan

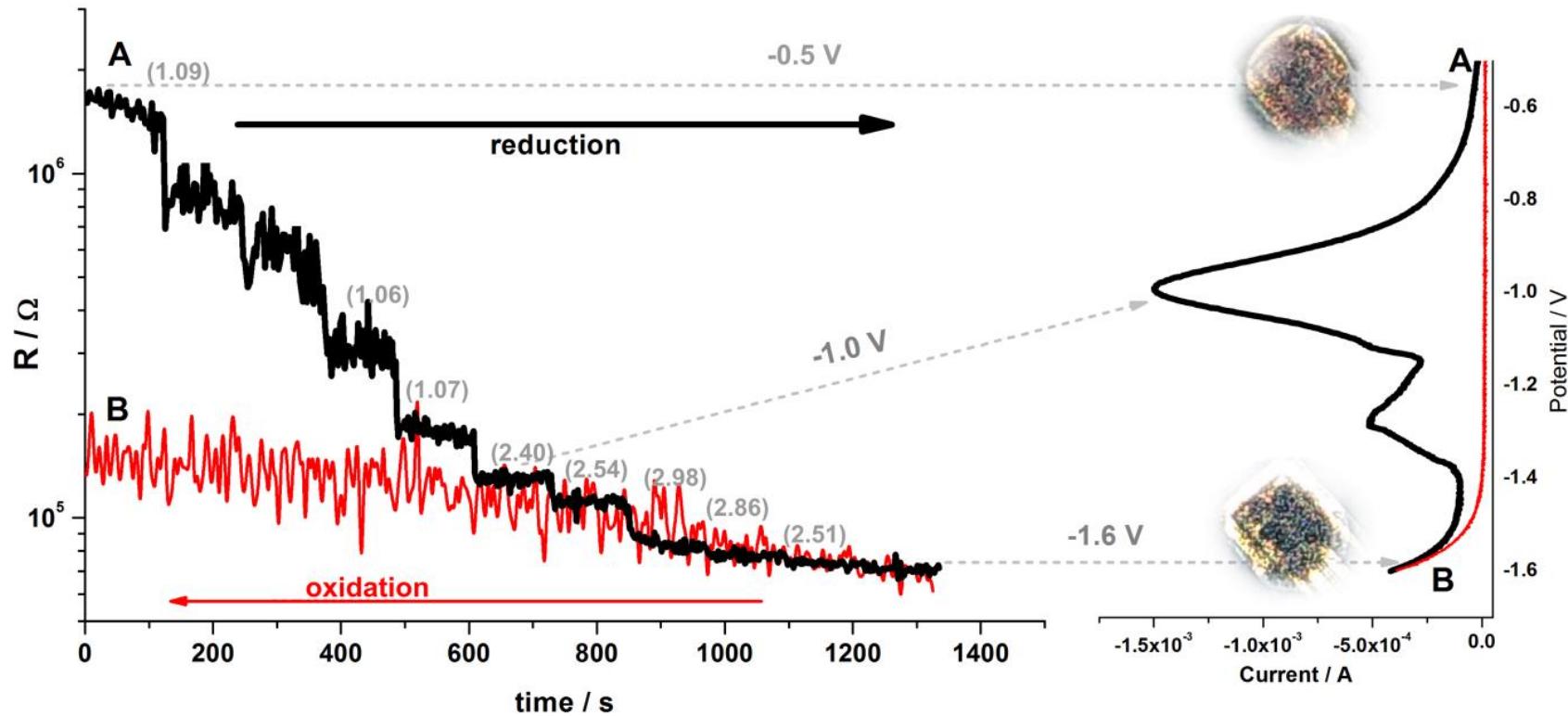
Ima mali kapacitet



Materijali na bazi grafena

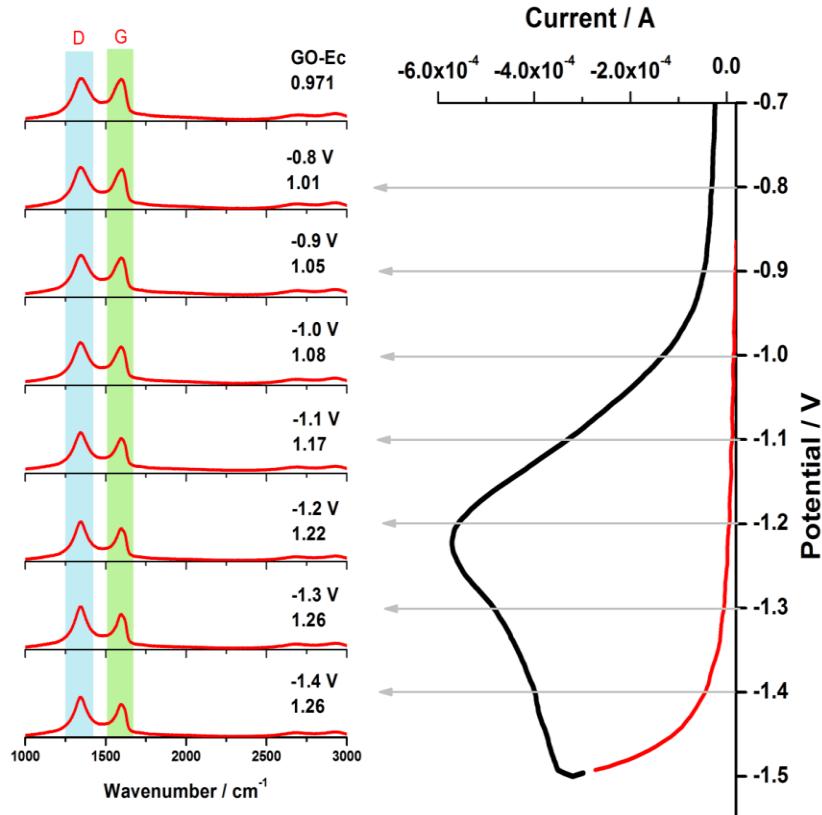
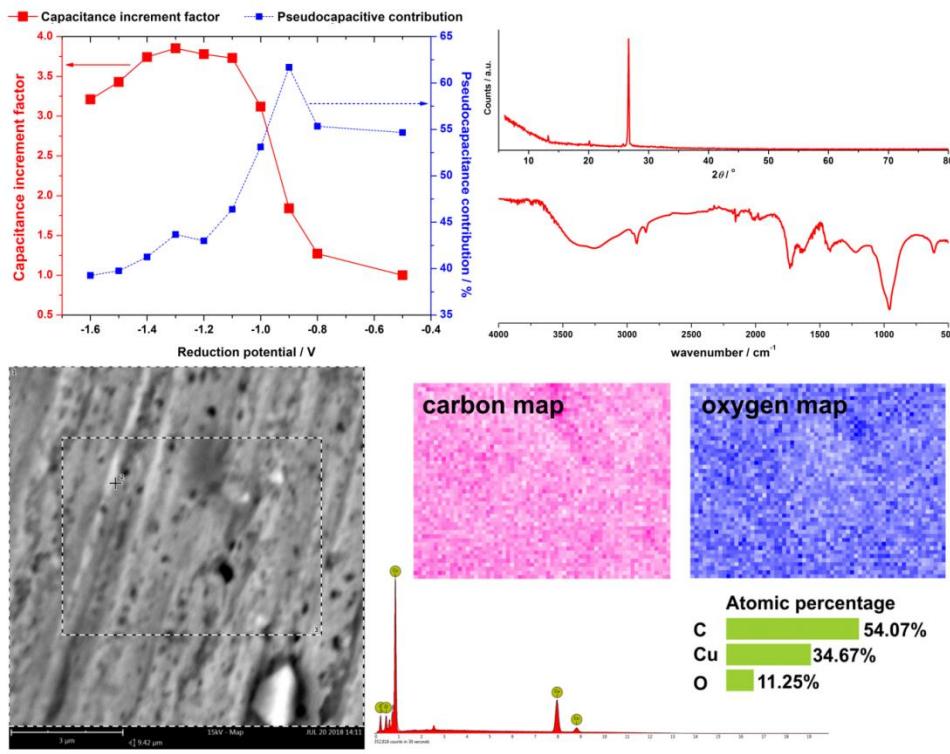


Materijali na bazi grafena



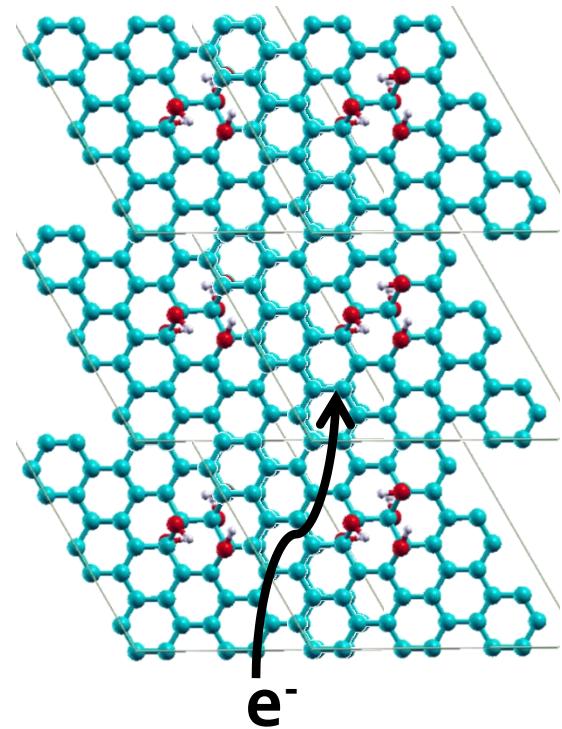
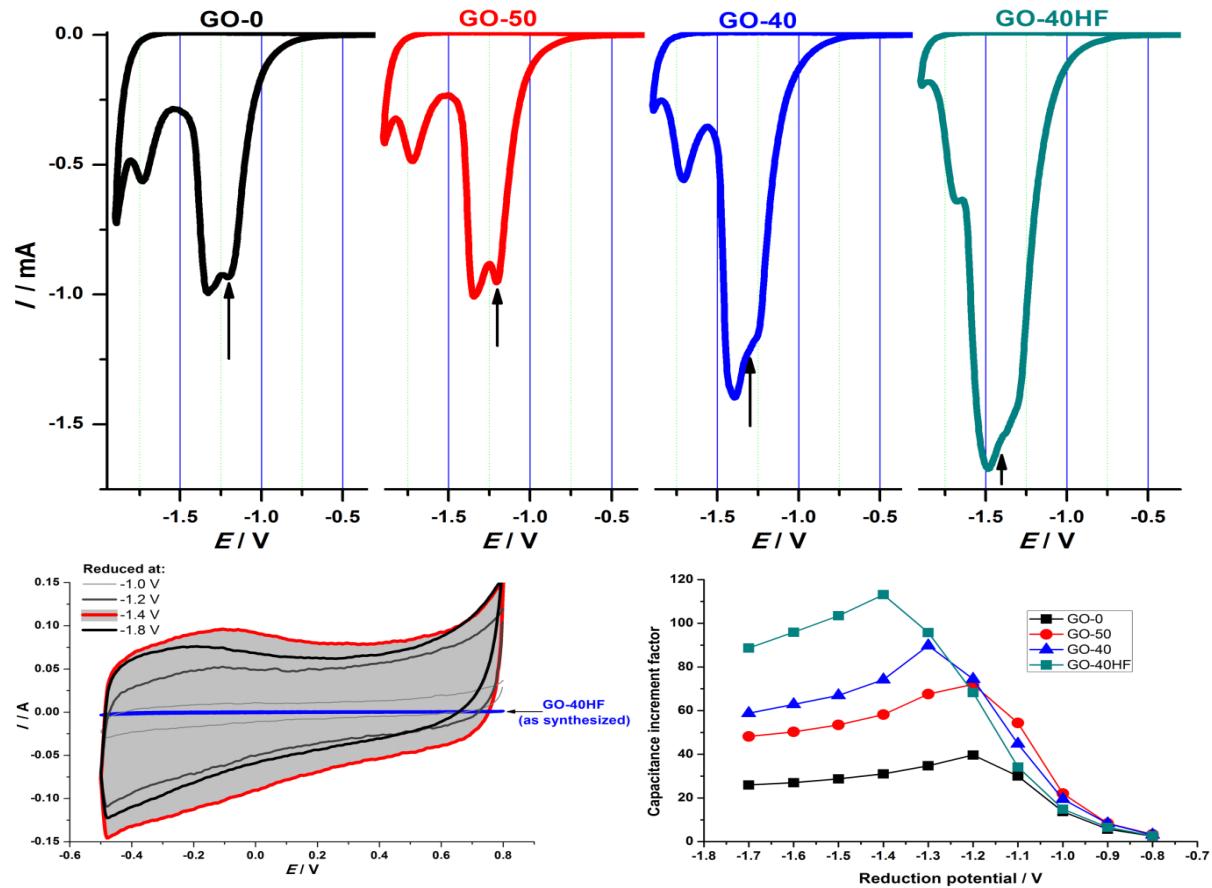
Maksimum kapaciteta =
balans između provodljivosti i koncentracije površinskih kiseoničnih funkcionalnih grupa

Materijali na bazi grafena



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

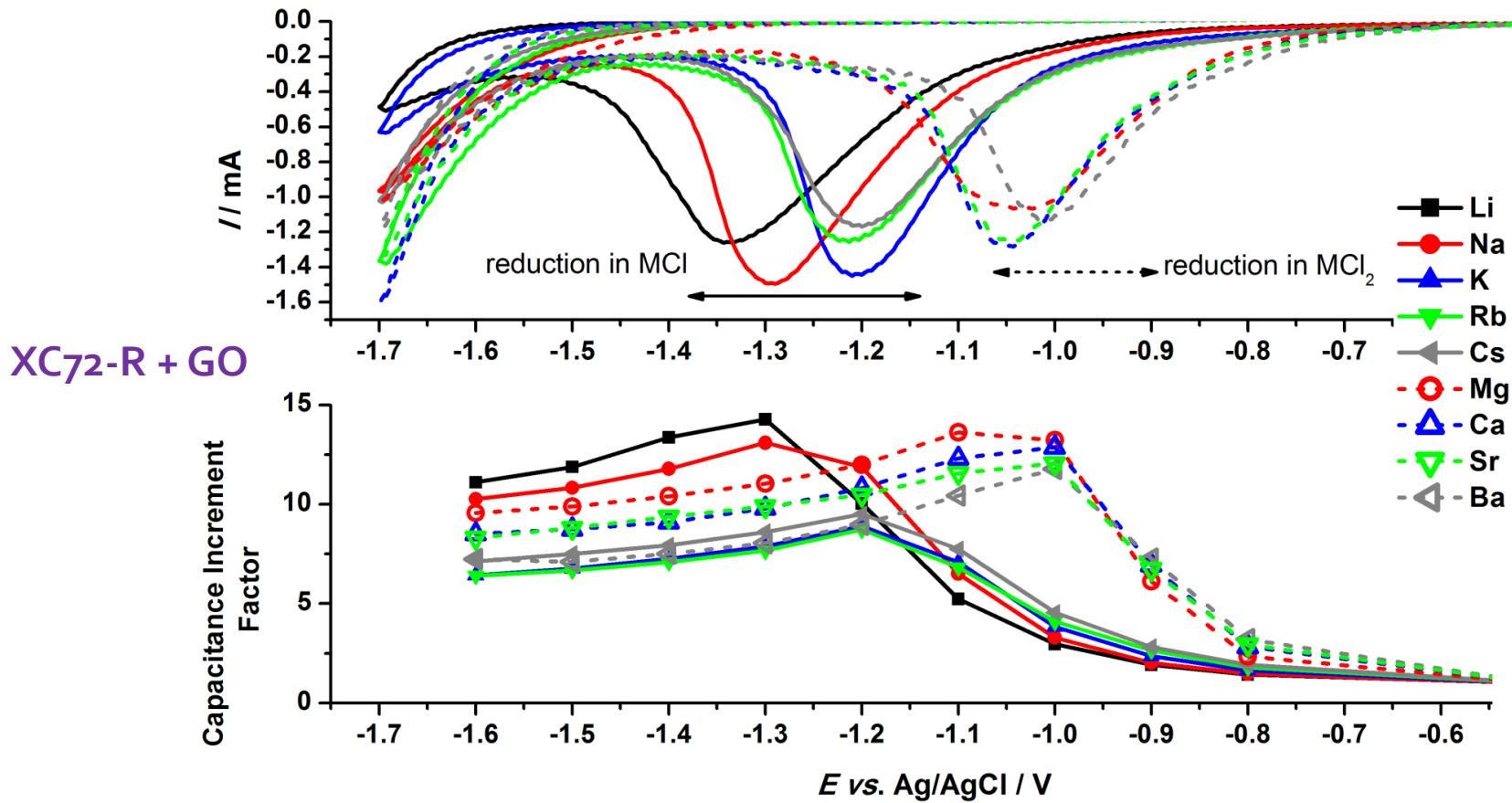
Materijali na bazi grafena



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

Materijali na bazi grafena

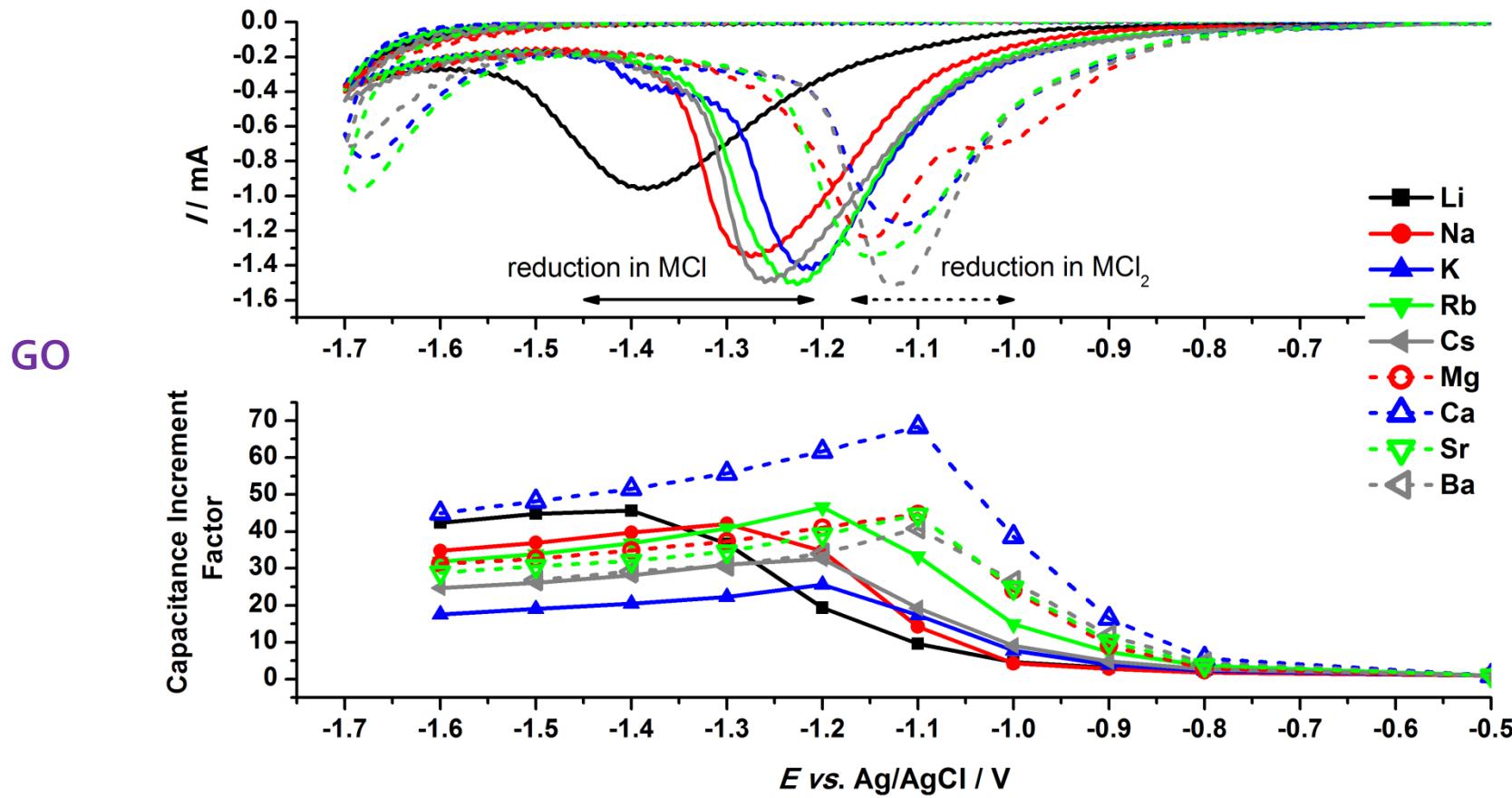
Redukcija na datom potencijalu, Merenje C



R_u oko 50 Ohm

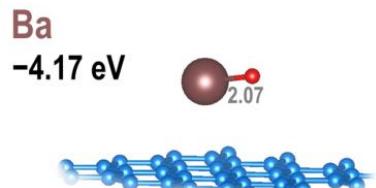
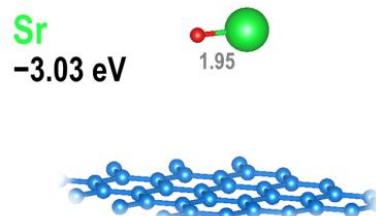
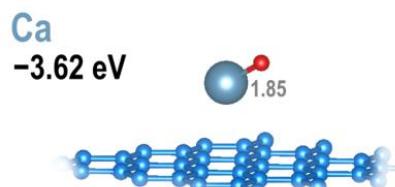
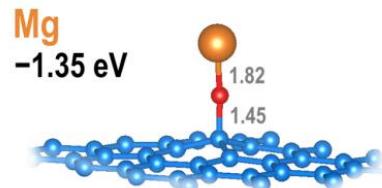
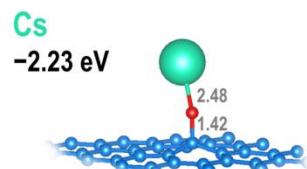
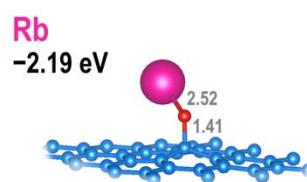
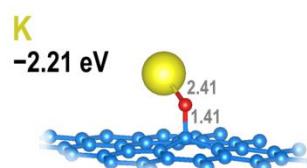
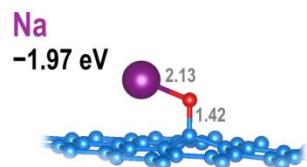
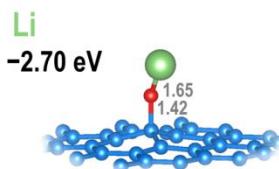
Materijali na bazi grafena

Redukcija na datom potencijalu, Merenje C



Materijali na bazi grafena

DFT

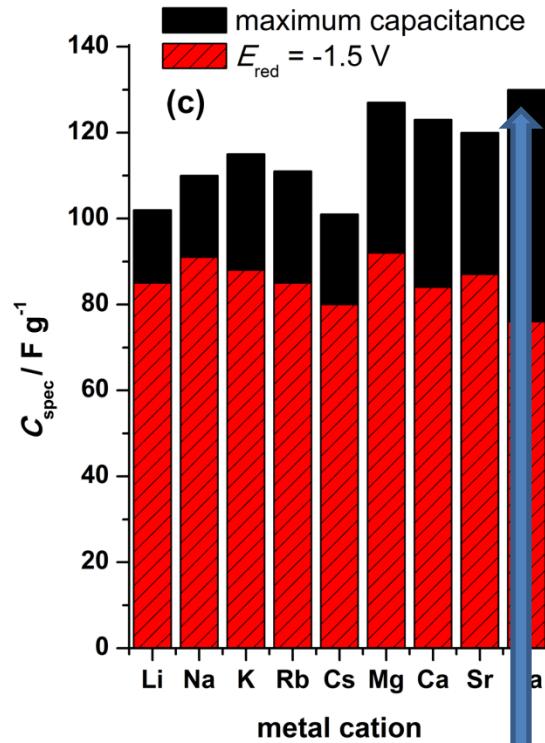
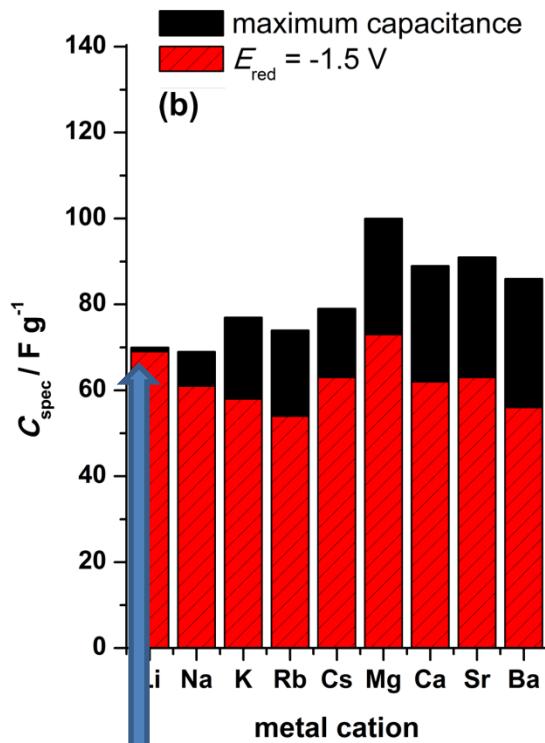
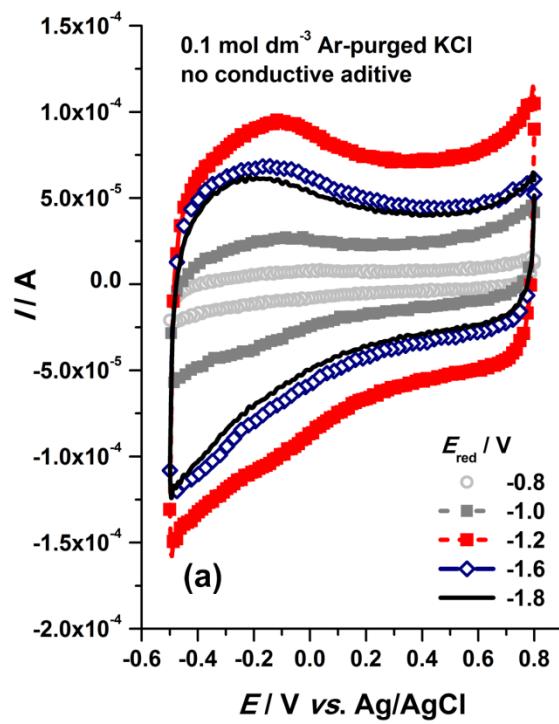


(i mnogi drugi primeri
uticaja inertnog
elektrolita koji nije samo
kroz R_e – elektrokataliza
HER i ORR na platinskim
metalima i ugljenicima)

Materijali na bazi grafena

Redukcija na datom potencijalu, Merenje C

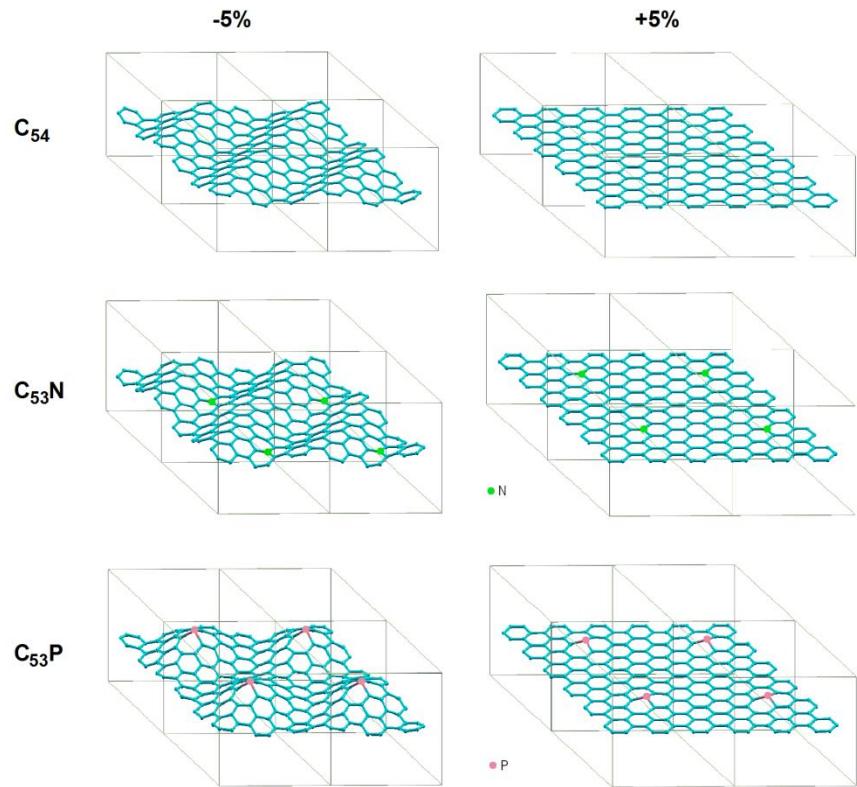
Praktična primena



Materijali na bazi grafena

Kapaciteti:

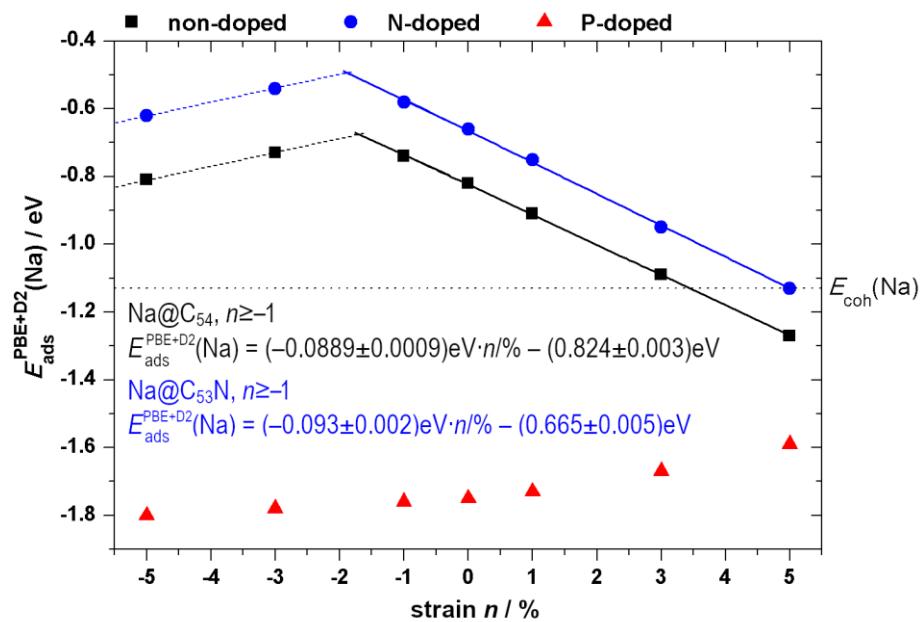
1. "Čist" – do 400 F g^{-1} (i do 70% pseudocapaciteta)
2. Kompoziti do 1000 F g^{-1} i više
3. Realno gledano, grafen je skuplji od platine
4. Navodno, postoji komercijalni kondenzatori na bazi grafena (curved graphene technology)



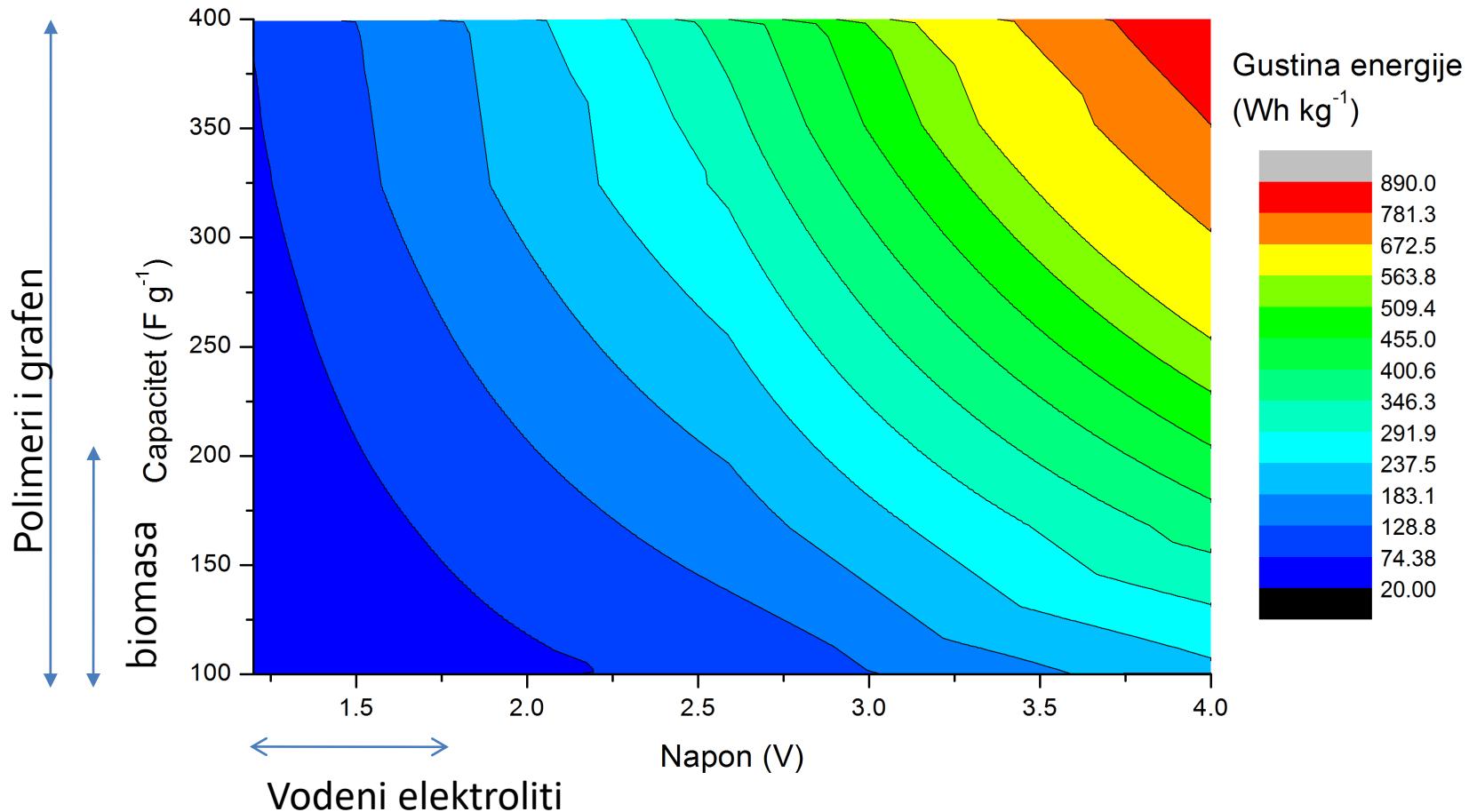
Materijali na bazi grafena

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
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(curved graphene technology)

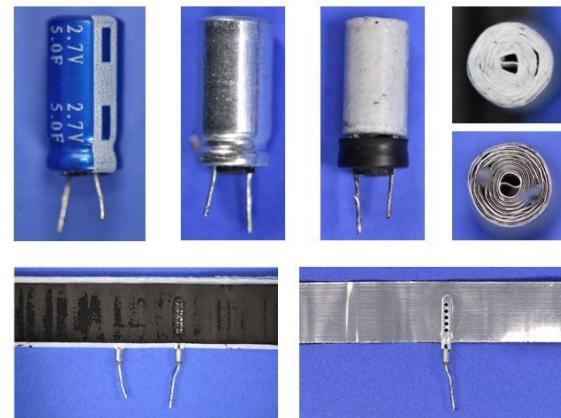
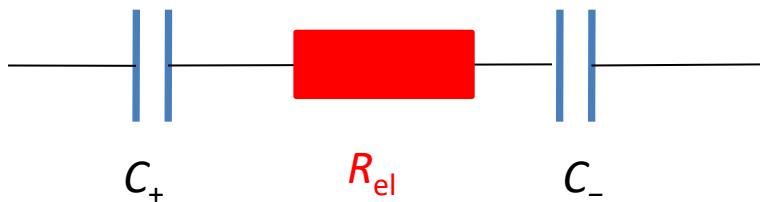


Od laboratorije do police



Od laboratorije do police

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



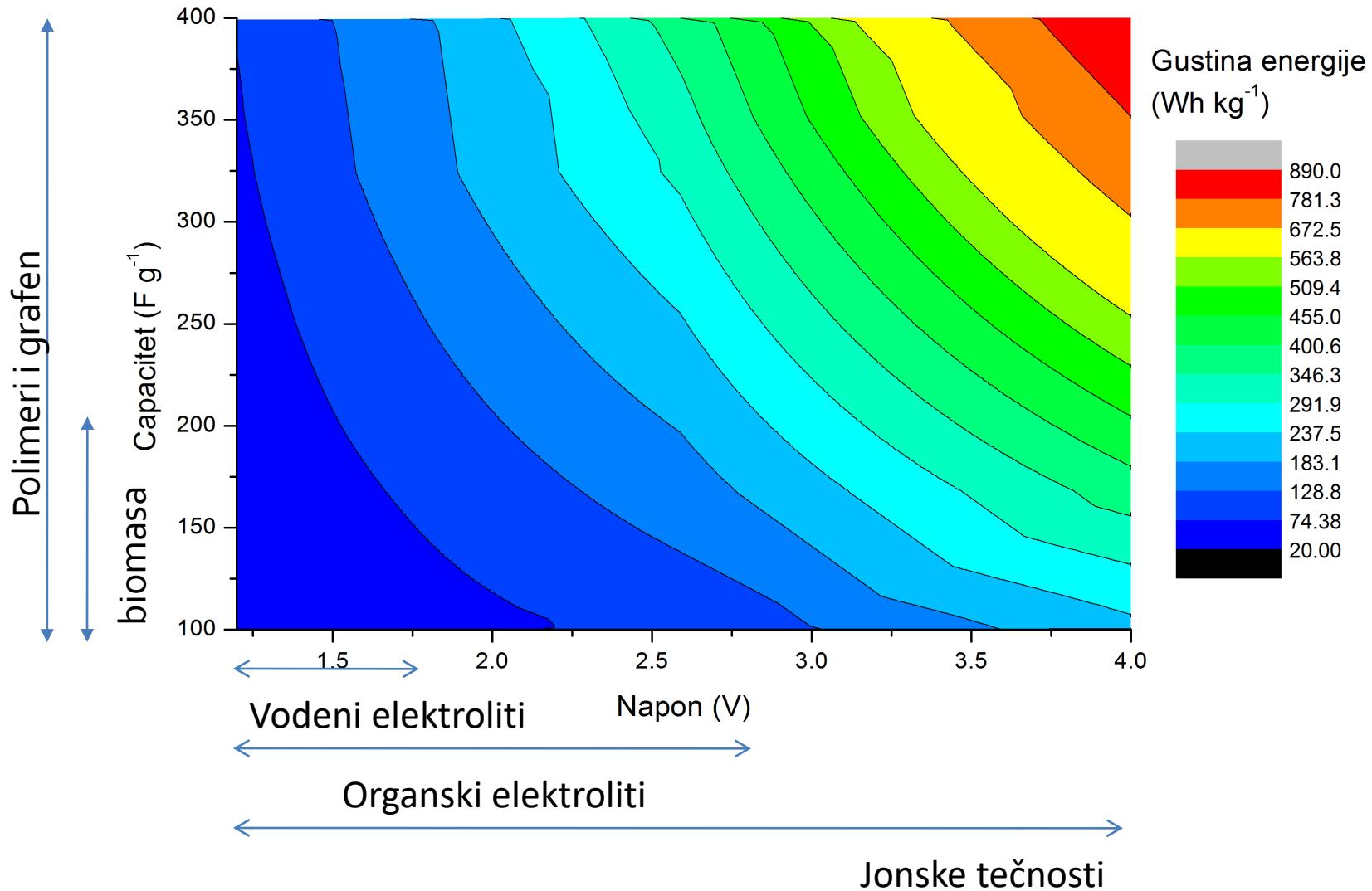
U naučnoj literaturi kapaciteti su računati u odnosu na **masu aktivnog materijala**

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

Od laboratorije do police

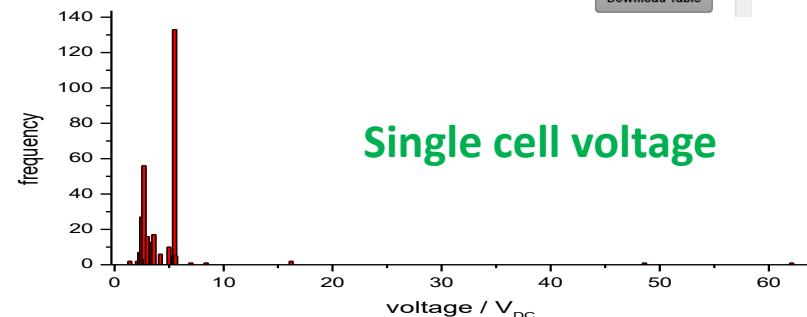
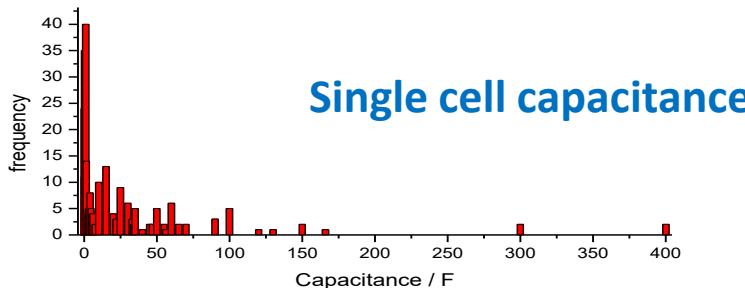


Od laboratorije do police

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

Applied Filters: Capacitance <input type="button" value="X"/>																	
Results per Page 25 <input type="button" value="▼"/> Page 1/1																	
Compare Parts	<input type="checkbox"/>  <input type="checkbox"/>  Image	Digi-Key Part Number	Manufacturer Part Number	Manufacturer	Description	Enter Quantity		Minimum Quantity <input type="button" value="?"/>	Packaging	Series	Part Status	Capacitance	Tolerance	Voltage - Rated	ESR (Equivalent Series Resistance)	Lifetime @ Temp.	
						<input type="button" value="▼"/>	<input type="button" value="▲"/>										
	<input type="checkbox"/>  <input type="checkbox"/>  Image	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 <input type="button" value="?"/>	PowerStor XV	Active	300F	-5%, +10%	2,7V	4.5 mOhm	1500 Hrs @ 65°C	
	<input type="checkbox"/>  <input type="checkbox"/>  Image	604-1091-ND	DZH-2R5D307S57T	Eina America	CAP 300F -20% +80% 2.5V T/H	34 - Immediate	484,13000 kr	1 Non-Stock <input type="button" value="?"/>	Bulk <input type="button" value="?"/>	DZH	Active	300F	-20%, +80%	2,5V	30 mOhm	2000 Hrs @ 60°C	
	<input type="checkbox"/>  <input type="checkbox"/>  Image	283-4175-ND	XB3550-2R5307-R	Eaton	CAP 300F 10% 2.5V THROUGH HOLE	10 - Immediate	89,76000 kr	1	Bulk <input type="button" value="?"/>	PowerStor XB	Active	300F	±10%	2,5V	7 mOhm	1500 Hrs @ 70°C	
	<input type="checkbox"/>  <input type="checkbox"/>  Image	SCCY62V307VSB-ND	SCCY62V307VSB	AVX Corporation	CAPACITOR 300F 2.7V SOLDER LUG	0	79,90275 kr	40 Non-Stock <input type="button" value="?"/>	Bulk <input type="button" value="?"/>	SCC	Active	300F	-5%, +25%	2,7V	-	1000 Hrs @ 60°C	
	<input type="checkbox"/>  <input type="checkbox"/>  Image	CDHC301K2R3SR-ND	CDHC301K2R3SR	Cornell Dubilier Electronics (CDE)	CAP 300F -5% +10% 2.3V T/H	0	Obsolete	-	Bulk <input type="button" value="?"/>	CDHC	Obsolete	300F	-5%, +10%	2,3V	25 mOhm	1000 Hrs @ 50°C	

Results per Page 25 Page 1/1



Od laboratorije do police

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

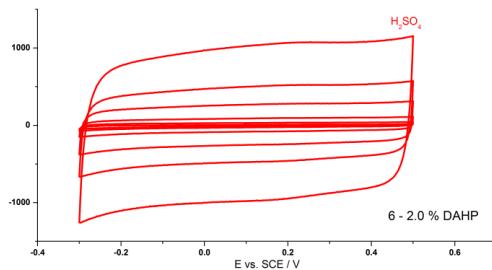
Device	Supercapattery								Battery	
	Supercapacitor				Hybrid					
	EDLC	Pseudocapacitor			Capacitive Hybrid		Others (Supercabattery)			
Electrode Material	NFCS	NFCS	CFS	NFCS	CFS	NFCS	CFS	NCFS		
	+	+	+	+	+	+	+	+		
	NFCS	CFS	CFS	NCFS	NCFS	NCFS	NCFS	NCFS		
Specific energy (Wh kg ⁻¹)	102 (IL), 6.7 (aq.)	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.

Od laboratorije do police

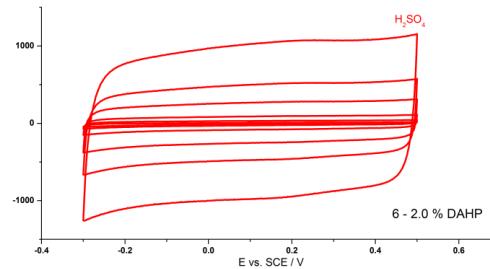
Simetrični EDL superkondenzator

Negativna elektroda AC



$$C_{\text{spec}} = 150 \text{ F g}^{-1}$$

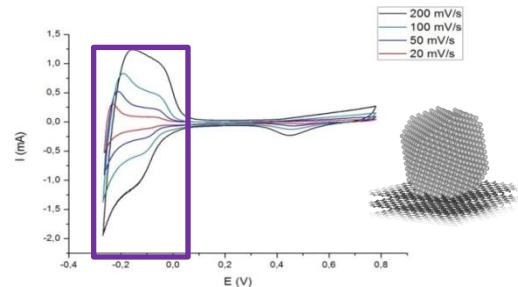
Pozitivna elektroda AC



$$C_{\text{spec}} = 150 \text{ F g}^{-1}$$

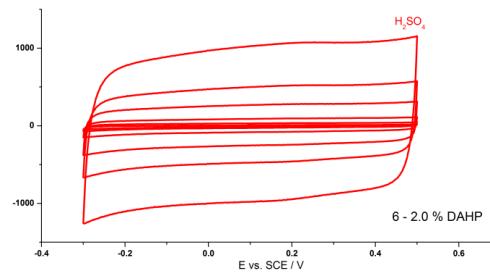
Hipotetički hibridni Pd-Carbon sistem

Negativna elektroda nano Pd



$$C_{\text{spec}} = 3000 \text{ F g}^{-1}$$

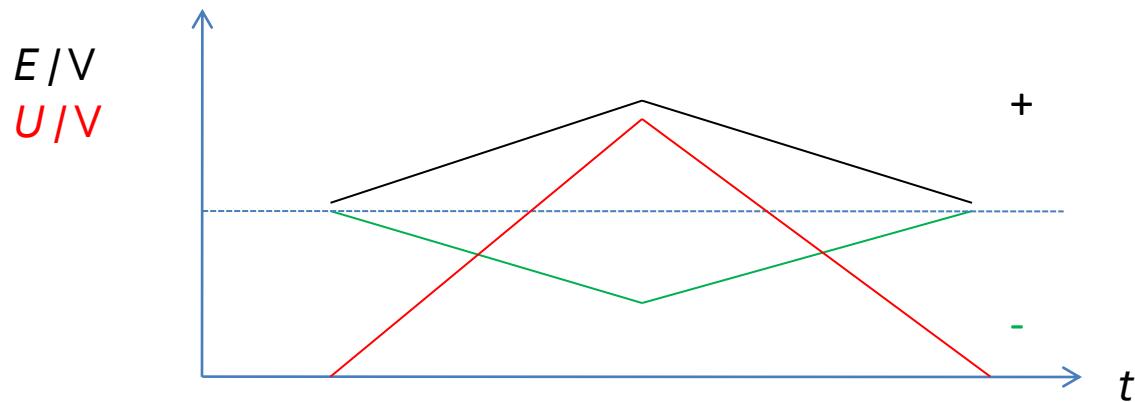
Pozitivna elektroda AC



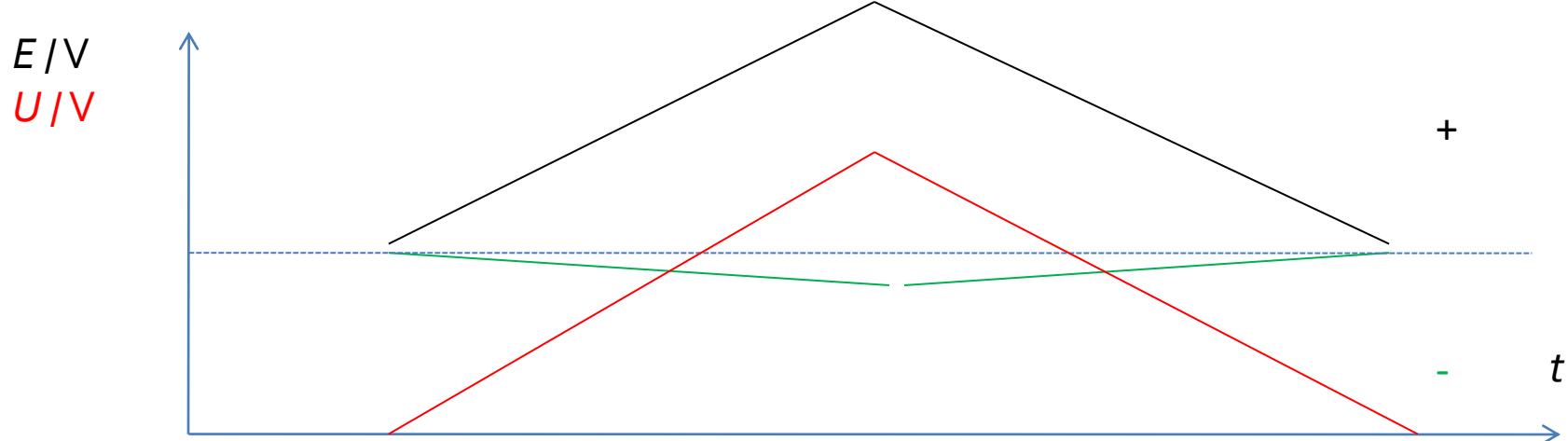
$$C_{\text{spec}} = 150 \text{ F g}^{-1}$$

Od laboratorije do police

Simetrični EDL superkondenzator



Hipotetički hibridni Pd-Carbon sistem



Umesto zaključka

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