

# Materijali za konverziju energije

## Pt/C

‘I believe that water will one day be used as a fuel because the hydrogen and oxygen which constitute it, used separately or together, will furnish an inexhaustible source of heat and light. I therefore believe that, when coal deposits are oxidised, we will heat ourselves by means of water. Water is the coal of the future’

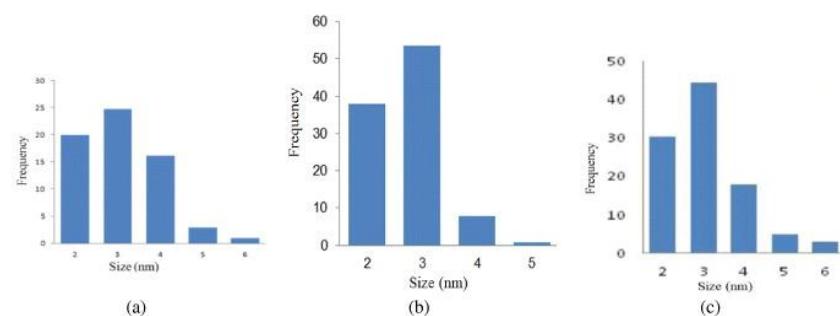
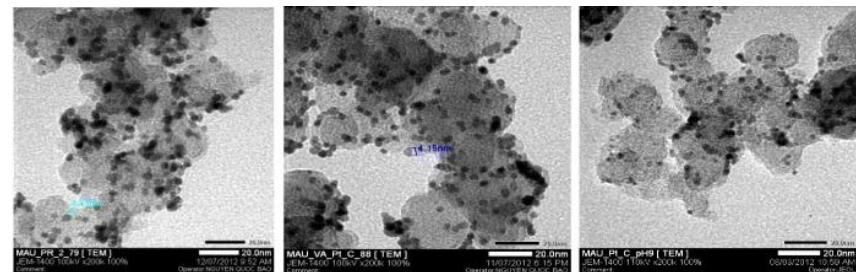
‘L’Île Mysterieuse’, Jules Verne, circa 1875.

# Pregled

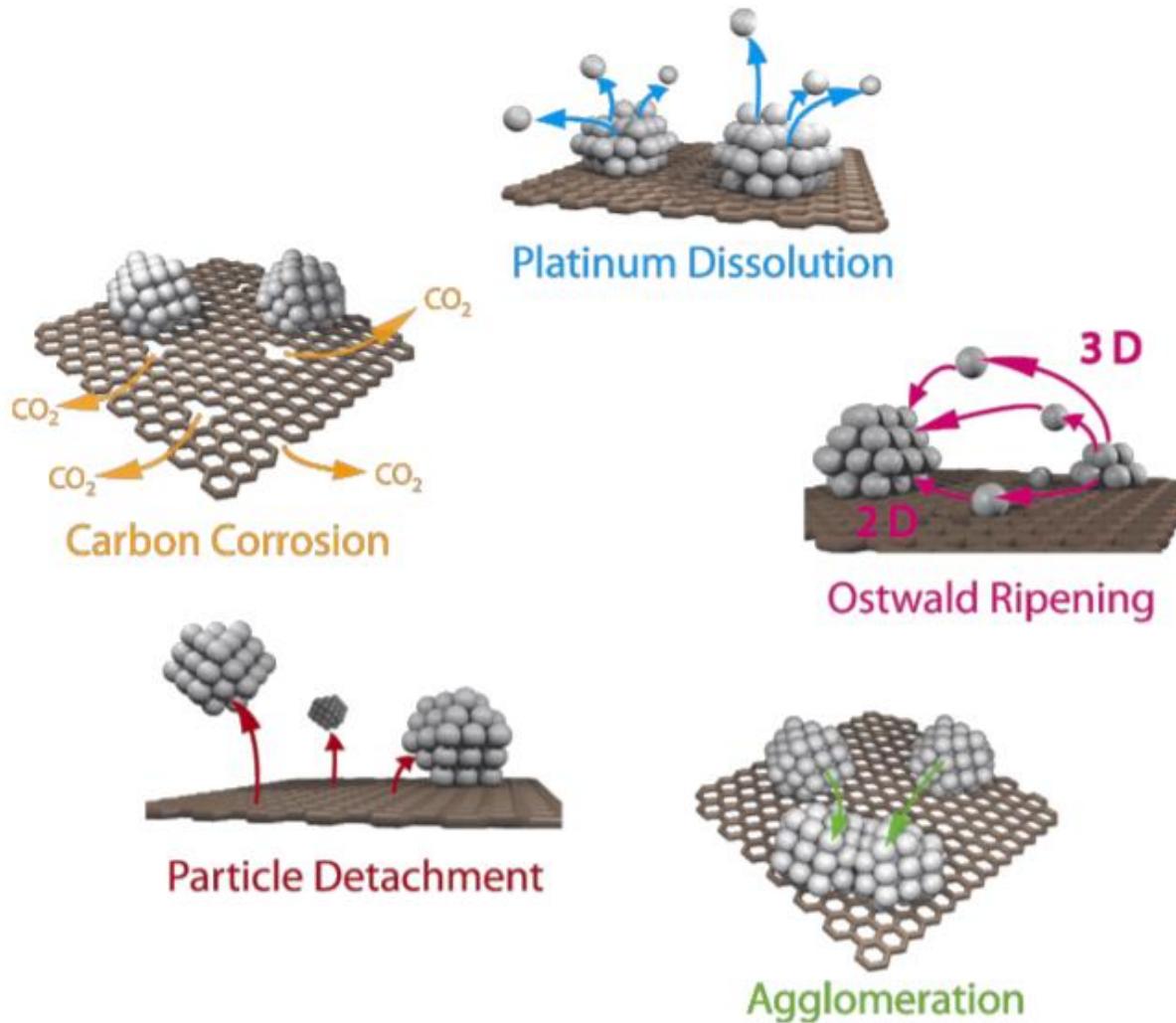
- Konverzija energije i trendovi
- Princip rada niskotemperaturske gorivne ćelije (PEMFC)
- Osnovne komponente
- Efikasnost rada FC
- Pt/C
- Degradacioni procesi Pt/C i metode njihovog ispitivanja
  - CO striping
  - IL-TEM
  - flow-cell-ICP-MS/OES
  - EIS
  - CI

# Pt/C

- Visoka aktivnost po jedinici mase
- Visoka aktivnost po jedinici površine
- **Stabilnost pri uslovima koji vladaju u realnoj gorivnoj čeliji**
  - Electrohemski aktivna površina ECSA
  - pH
  - Temperatura
  - Primjenjeni potencijal (start/stop operacije)
  - Čistoća goriva i oksidanta
- Razvoj novih ugljeničnih podloga



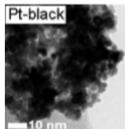
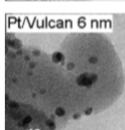
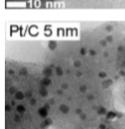
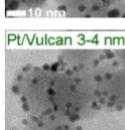
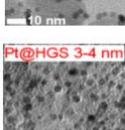
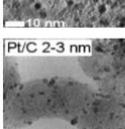
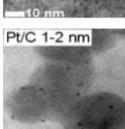
## Mehanizmi degradacije Pt/C katalizatora



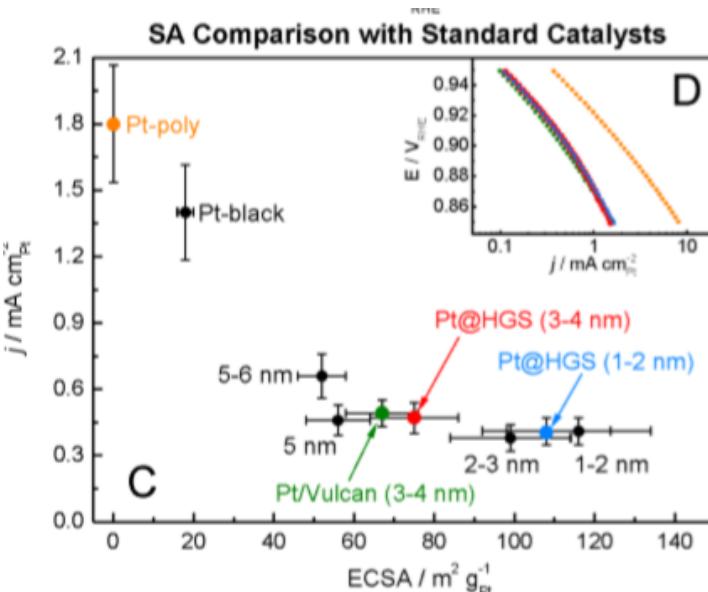
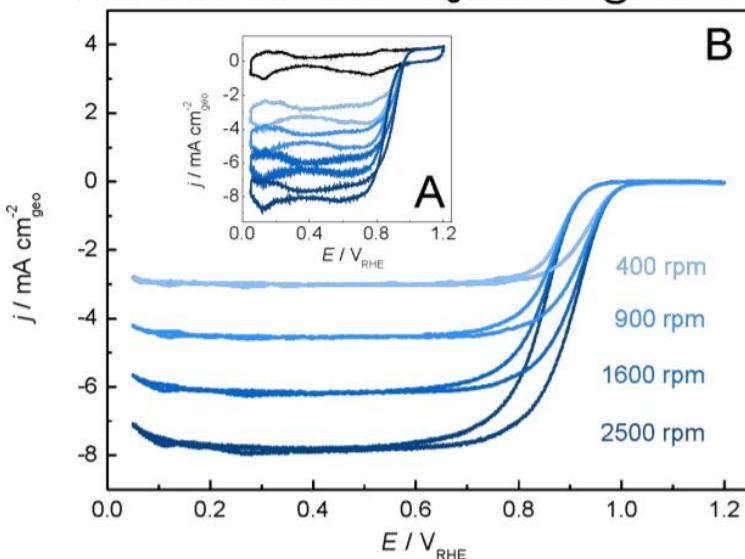
## Mehanizmi degradacije Pt/C katalizatora

- Ex-situ ispitivanje MEA
- Elektronska mikroskopija (SEM, TEM)
- Statistička obrada kako bi se dobili pouzdani rezultati
- Skup postupak
- Rešenje: ispitivanje mikrostrukture jednostavnijih sistema i posmatranje evolucije sistema pri uslovima koji vladaju u FC

# Poređenje aktivnosti različitih Pt/C katalizatora

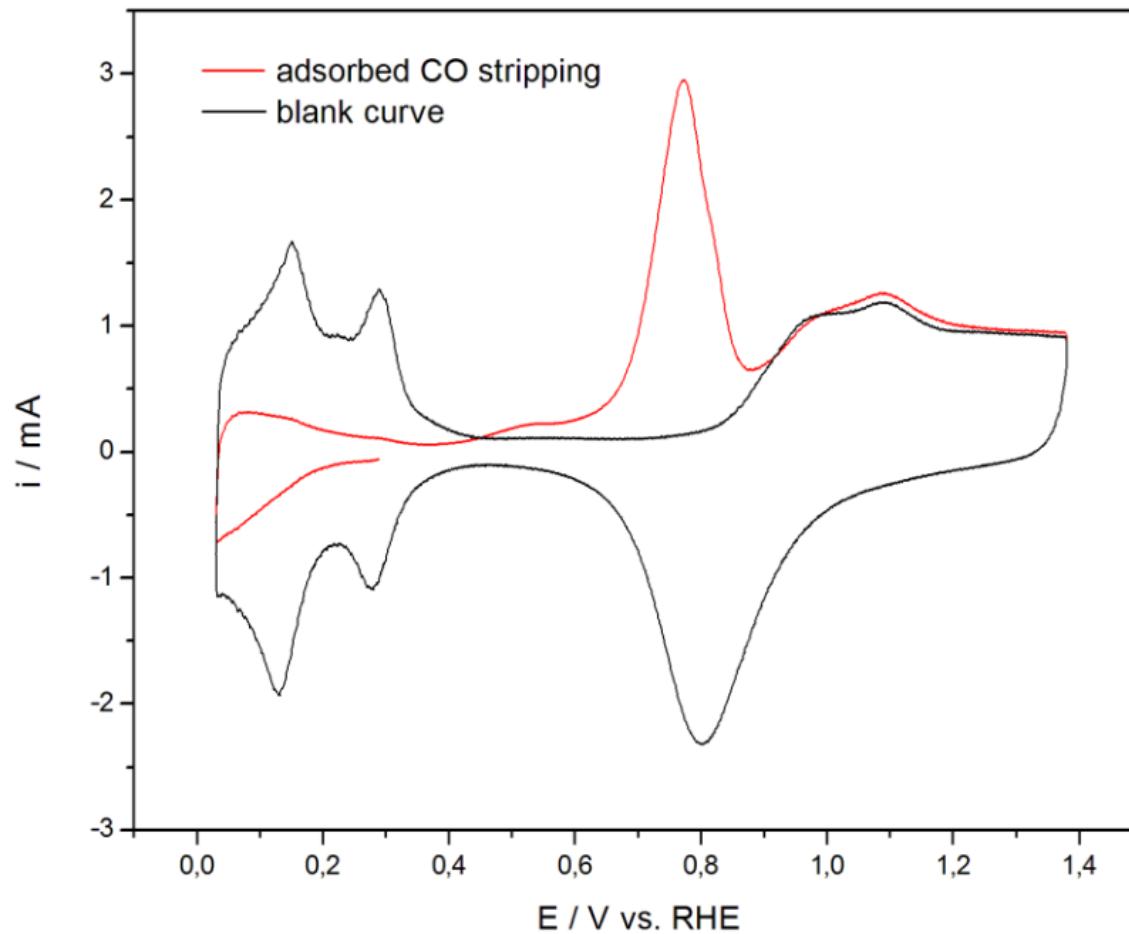
material	manufacturer	particle size [nm]	Pt content [wt %]	electrochemical active surface area [ $\text{m}^2 \cdot \text{g}^{-1}$ ]	specific activity in $\text{HClO}_4/\text{H}_2\text{SO}_4$ [ $\text{mA} \cdot \text{cm}^{-2} \cdot \text{Pt}$ ]	mass activity in $\text{HClO}_4/\text{H}_2\text{SO}_4$ [ $\text{A} \cdot \text{mg}^{-1} \cdot \text{Pt}$ ]
<b>Poly-Pt</b>	MaTeck	—	100	—	$1.8 \pm 0.27$ ( $0.43 \pm 0.039$ )	—
 <b>Pt-black</b>	Umicore	10–15	98	$18 \pm 2$	$1.4 \pm 0.22$ ( $0.27 \pm 0.024$ )	$0.26 \pm 0.07$ ( $0.049 \pm 0.010$ )
 <b>Pt/Vulcan 6 nm</b>	authors' lab	5–6	21	$52 \pm 6$	$0.66 \pm 0.10$ ( $0.14 \pm 0.013$ )	$0.34 \pm 0.09$ ( $0.073 \pm 0.015$ )
 <b>Pt/C 5 nm</b>	TKK	4.8	51	$56 \pm 8$	$0.46 \pm 0.07$ ( $0.11 \pm 0.012$ )	$0.26 \pm 0.08$ ( $0.062 \pm 0.014$ )
 <b>Pt/Vulcan 3-4 nm</b>	authors' lab	3–4	20	$67 \pm 6$	$0.49 \pm 0.06$ (—)	$0.32 \pm 0.07$ (—)
 <b>Pt@HGS 3-4 nm</b>	authors' lab	3–4	20	$75 \pm 11$	$0.47 \pm 0.07$ ( $0.095 \pm 0.009$ )	$0.35 \pm 0.09$ ( $0.071 \pm 0.017$ )
 <b>Pt/C 2-3 nm</b>	TKK	2.6	46	$99 \pm 15$	$0.38 \pm 0.06$ ( $0.093 \pm 0.008$ )	$0.37 \pm 0.11$ ( $0.092 \pm 0.022$ )
 <b>Pt@HGS 1-2 nm</b>	authors' lab	1–2	20	$108 \pm 16$	$0.41 \pm 0.06$ ( $0.10 \pm 0.009$ )	$0.44 \pm 0.13$ ( $0.11 \pm 0.026$ )
 <b>Pt/C 1-2 nm</b>	TKK	1–2	10	$116 \pm 18$	$0.41 \pm 0.06$ ( $0.084 \pm 0.008$ )	$0.47 \pm 0.14$ ( $0.097 \pm 0.024$ )

ORR Polarization Voltammograms of Pt@HGS 1-2 nm

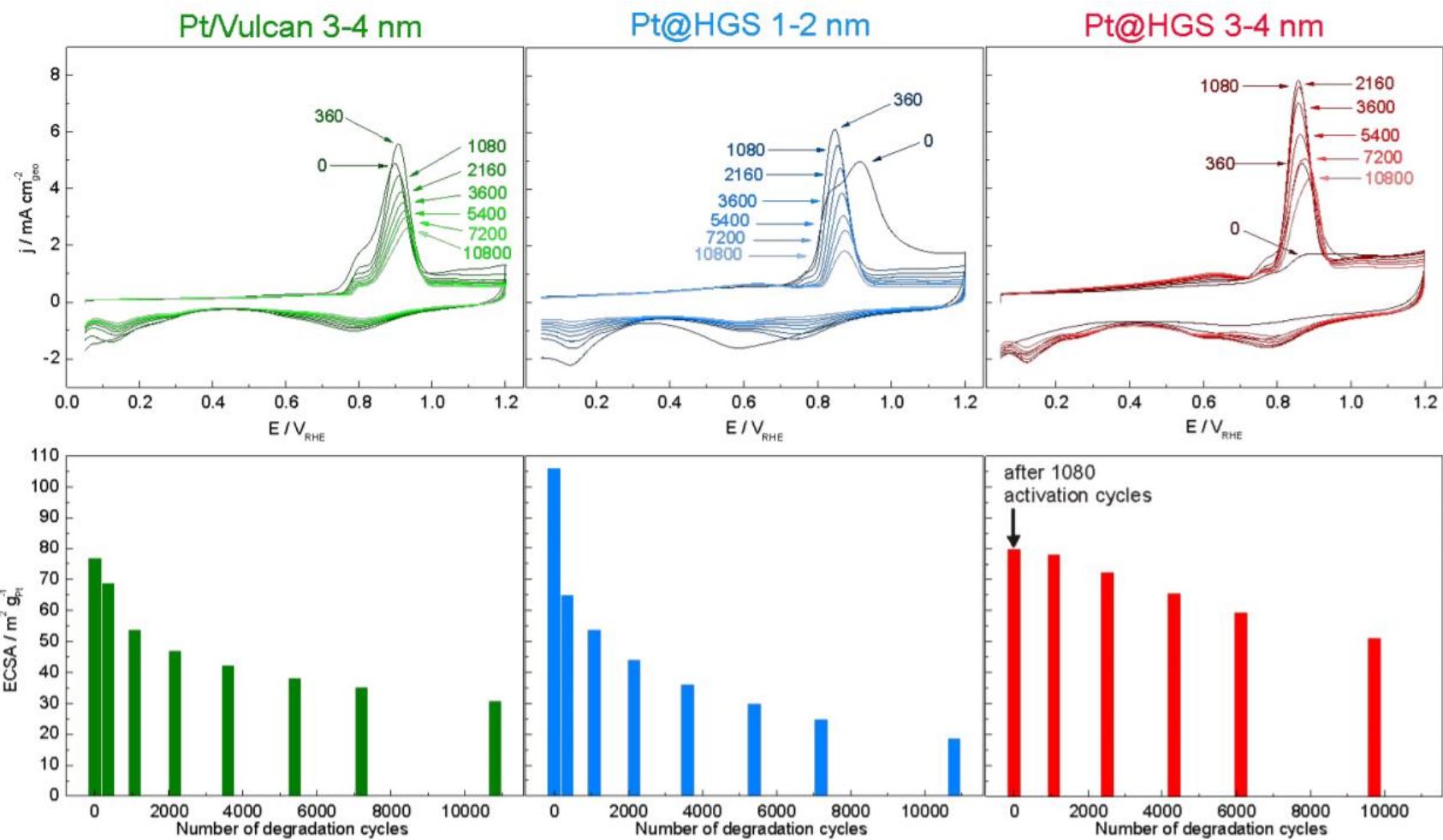


# Ispitivanje makroskopske stabilnosti

## CO-striping voltametrija

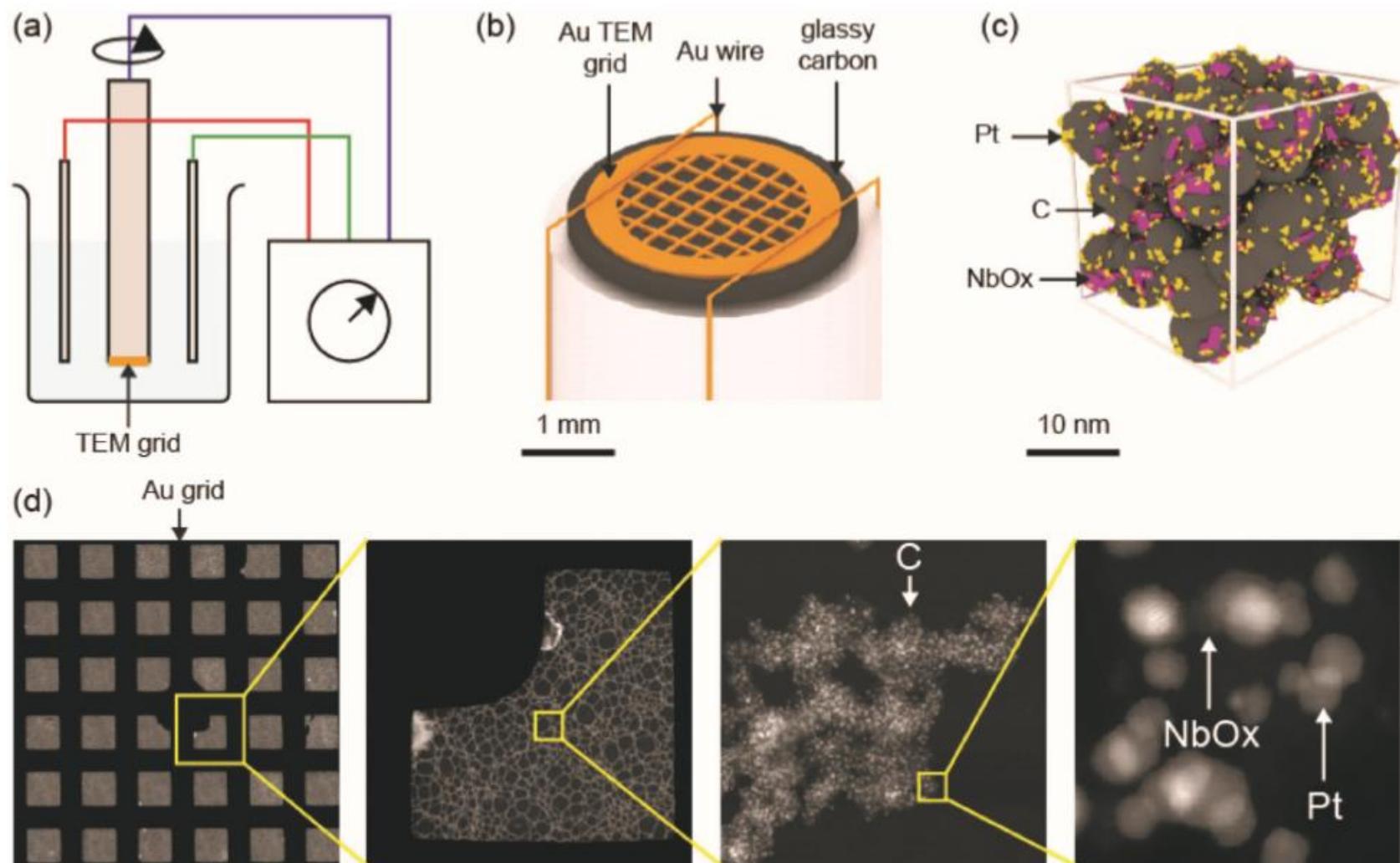


## CO-striping voltametrija

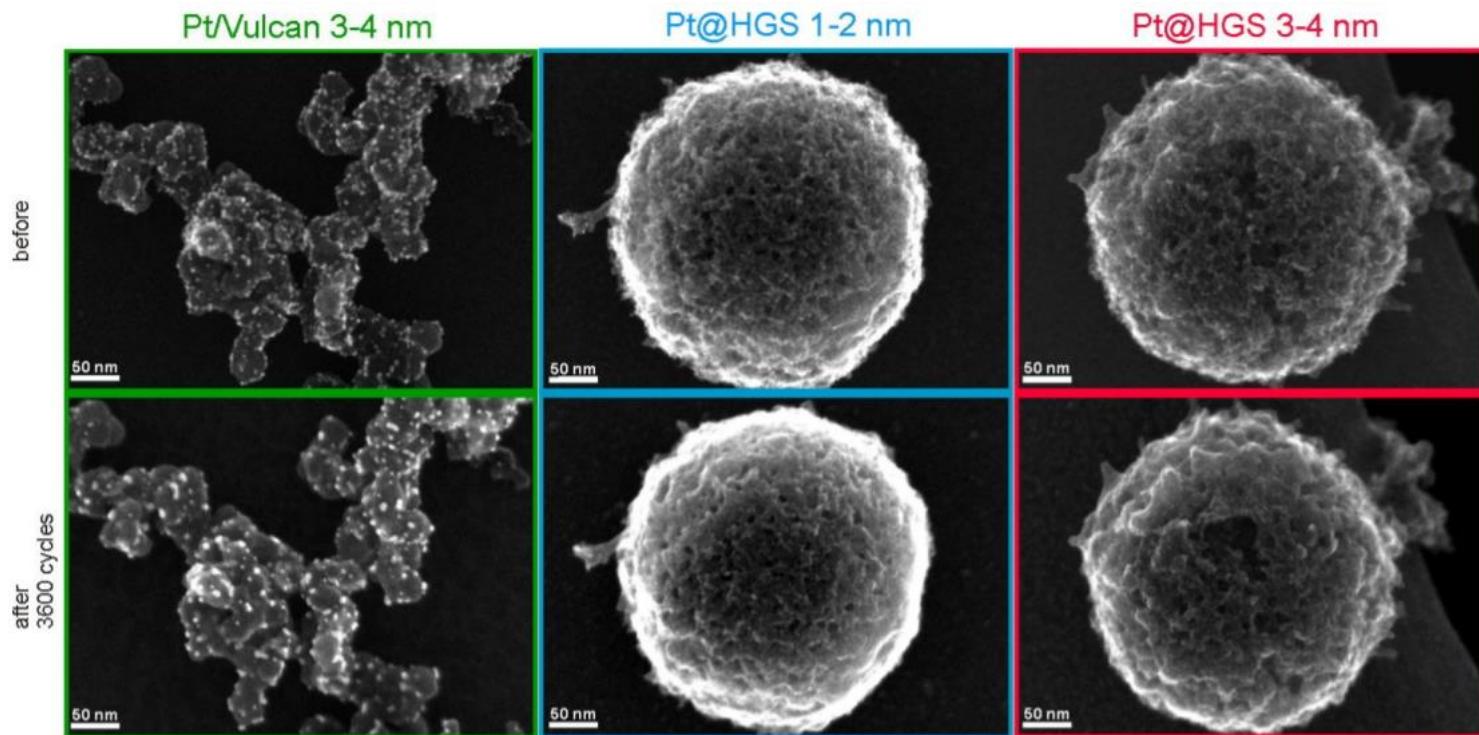


Razlozi za smanjenje ECSA: rastvaranje Pt, uticaj malih čestica 1-2 nm, kontakt izmešu čestica?

## Identical location – SEM/STEM

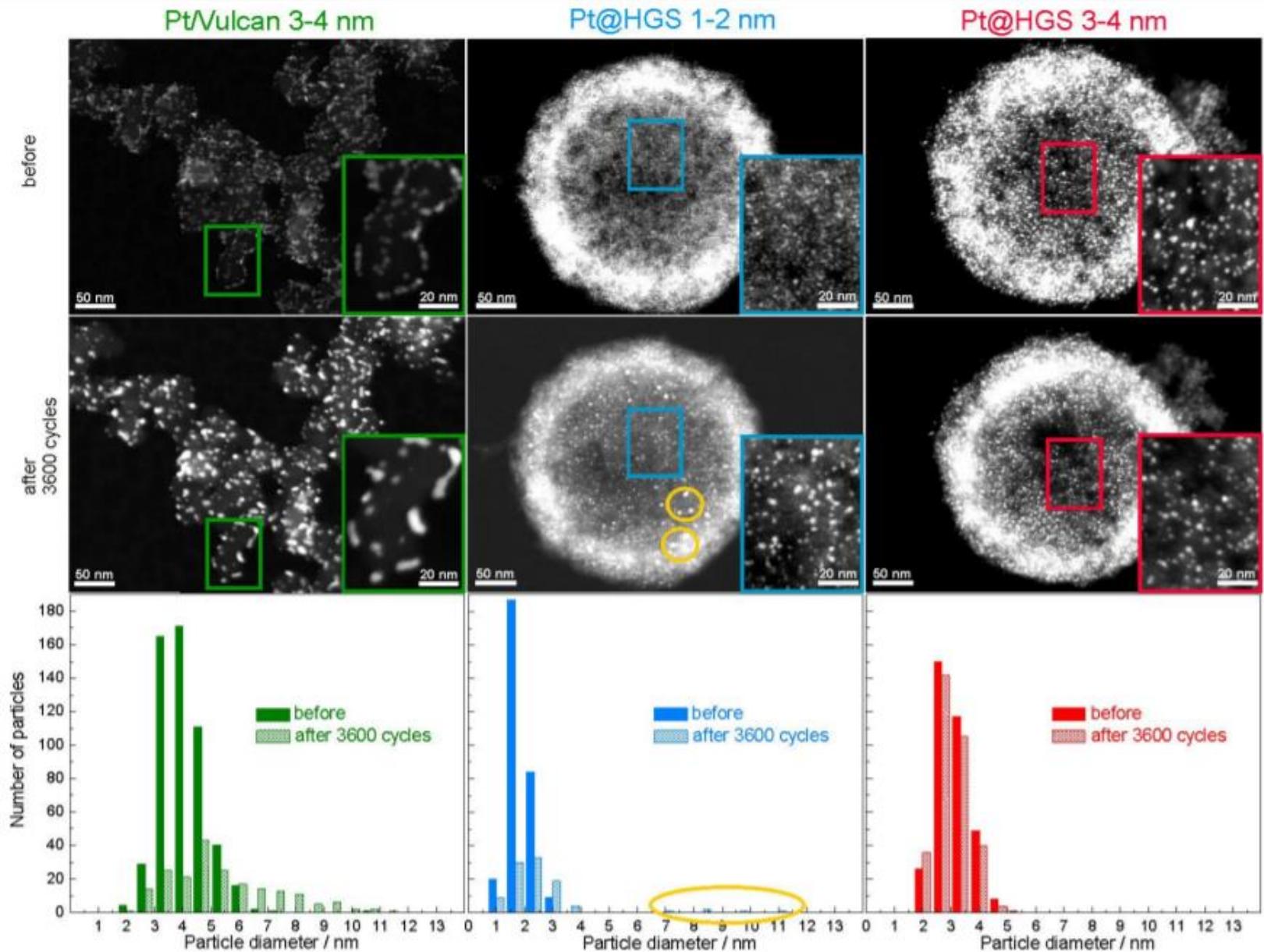


## IL-SEM



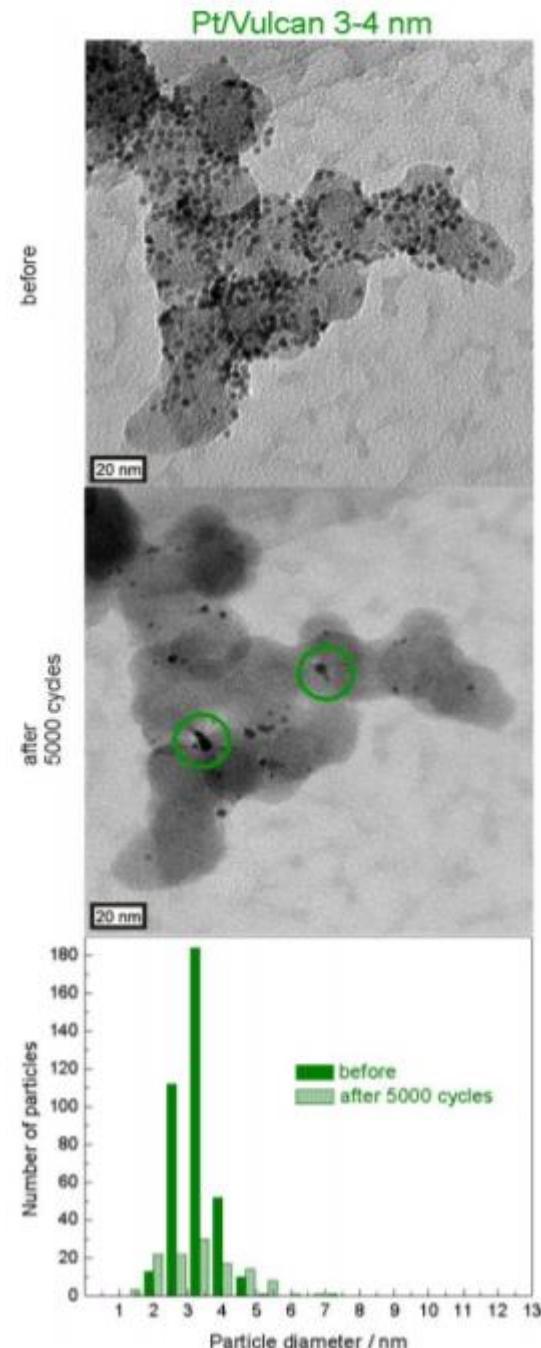
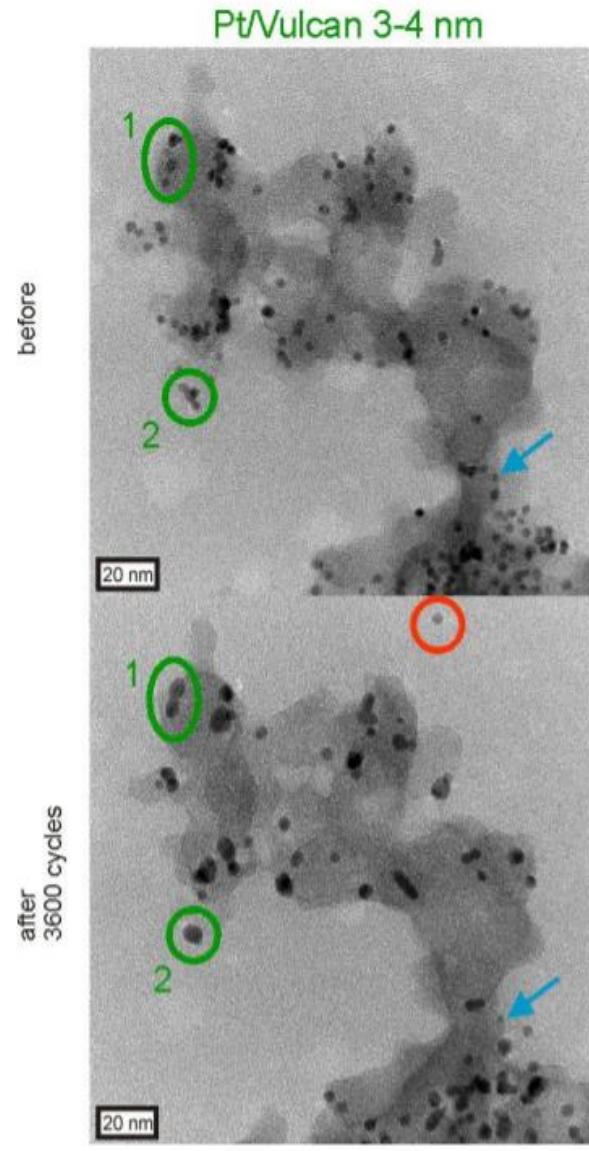
- Nema degradacije podloge od ugljenika
- Aglomeracija Pt čestica na Pt/Vulcan uzorku

# Dark field IL-STEM



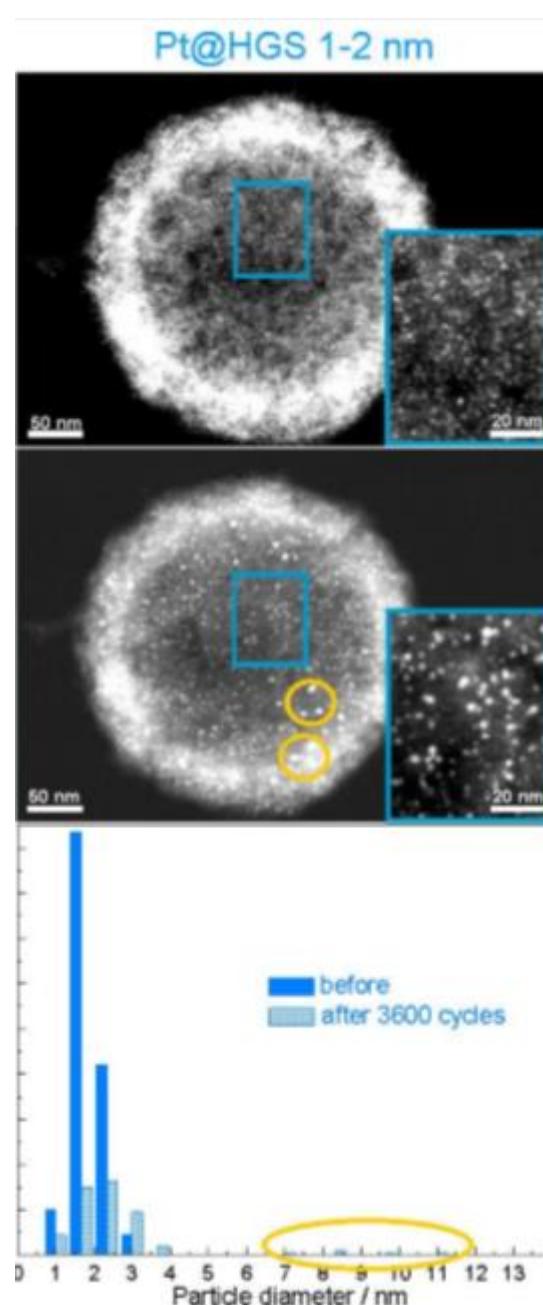
## Degradacija Pt/Vulcan 3-4 nm

- Smanjenje ukupne količine platine
- Povećanje veličine čestica
- Aglomeracija kao posledica blizine čestica
- Otkidanje čestica
- Inicijalno dolazi do povećanja veličine čestica dok nakon više hiljada ciklusa preovladava rastvaranje Pt



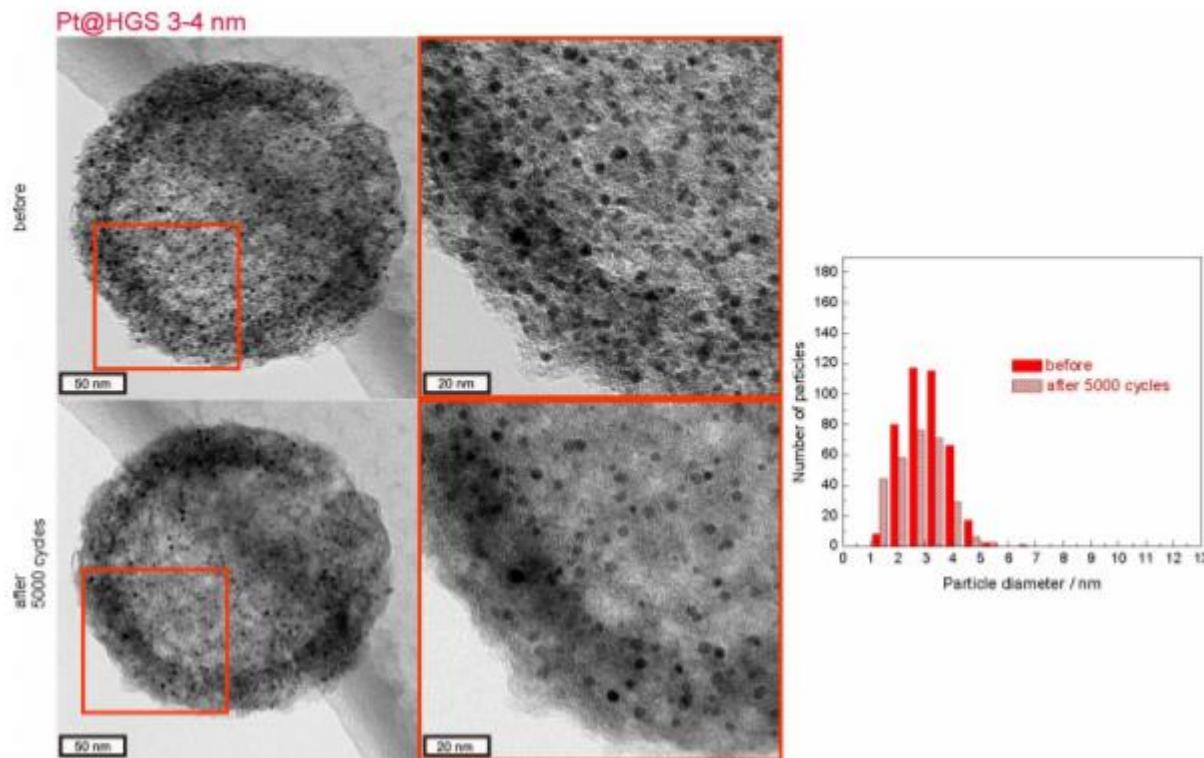
## Degradacija Pt/HGS 1-2 nm

- Drastično smanjenje ukupne količine platine
- Povećanje veličine čestica
- Rastvaranje kao poledica male veličine čestica
- Gubitak od 60% čestica izmešu 1-3 nm
- Delimična aglomeracija kroz rastvaranje i redepoziciju (Ostwald)



## Degradacija Pt/HGS 3-4 nm

- Male promene u aktivnosti kao i mnogo manje smanjenje količine Pt
- Najverovatniji proces je rastvaranje Pt
- Povećanje broja čestica veličina oko 1-2 nm
- Uticaj podloge jer nema ukrupnjavanja čestica kao kod Pt/Vulcan 3-4 nm

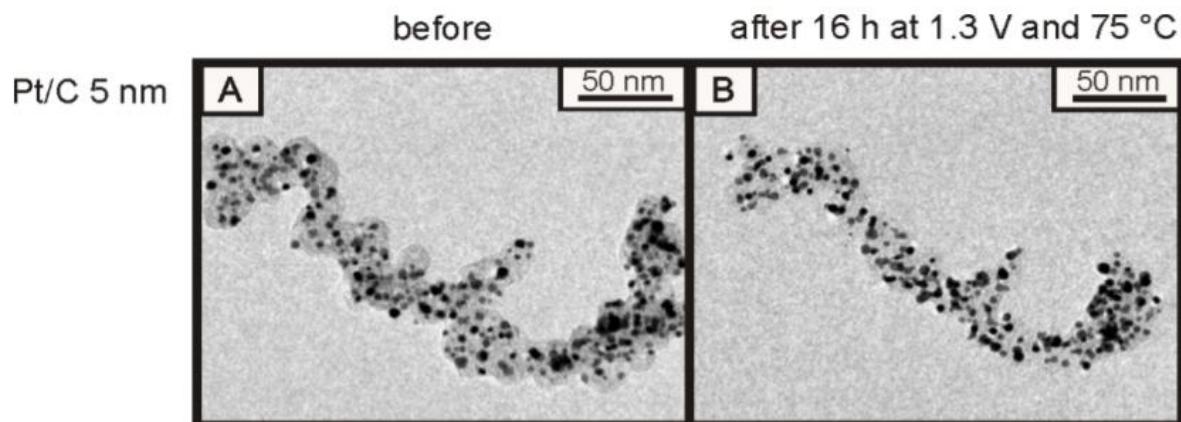
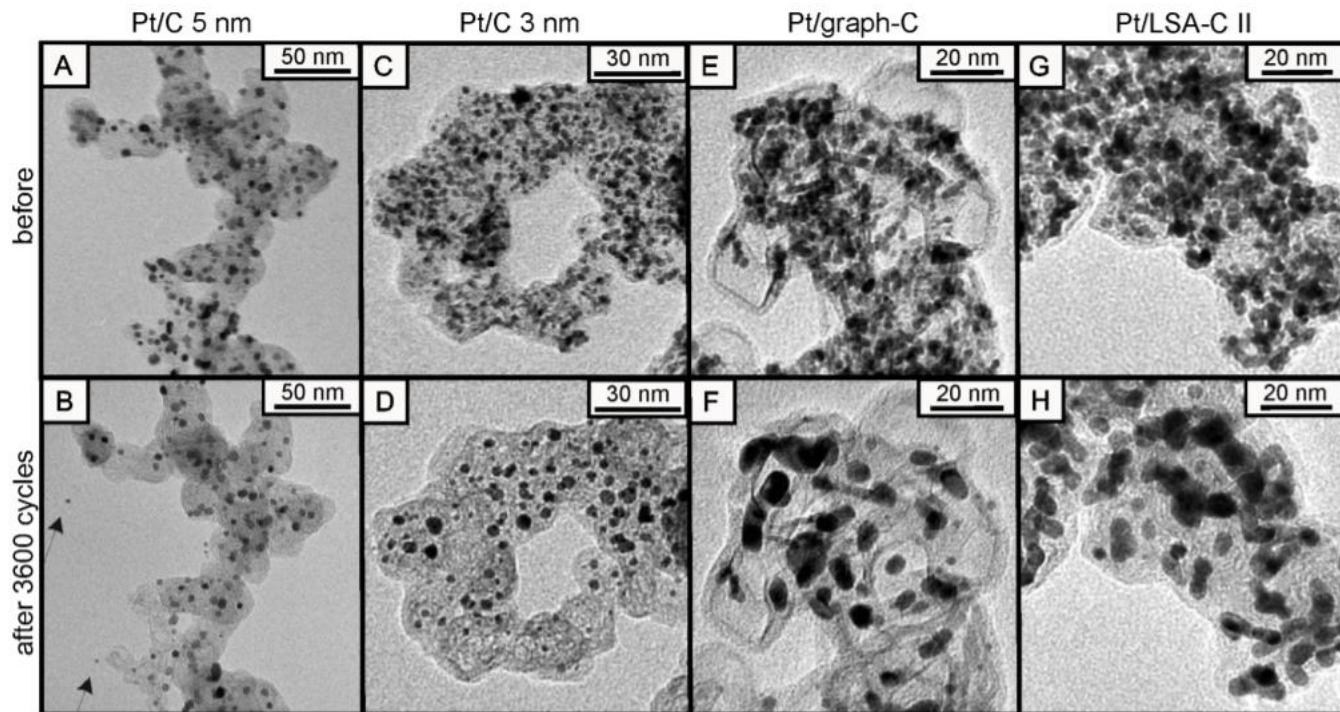


## Zaključak na osnovu IL-SEM/STEM

- Na sobnoj temperaturi i pri primenjenim uslovima ne dolazi do degradacije različitih ugljeničnih podloga
- rastvaranje Pt se javlja kod sva tri katalizatora
- rastvaranje Pt je najintenzivnije sa čestica veličina oko 1-2 nm
- Podloga ima uticaja na ukrupnjavanja čestica kod Pt/Vulcan 3-4 nm dok HGS smanjuje mogućnost ukrupnjavanja

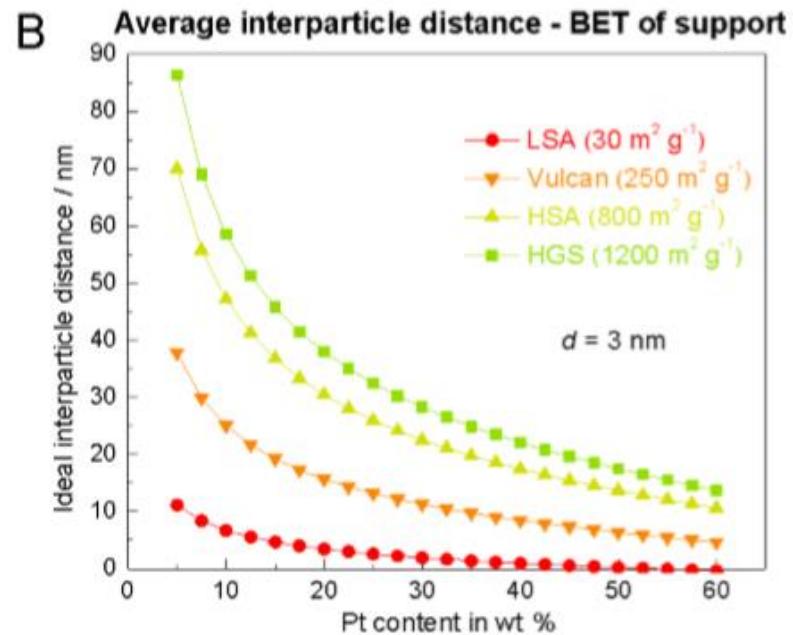
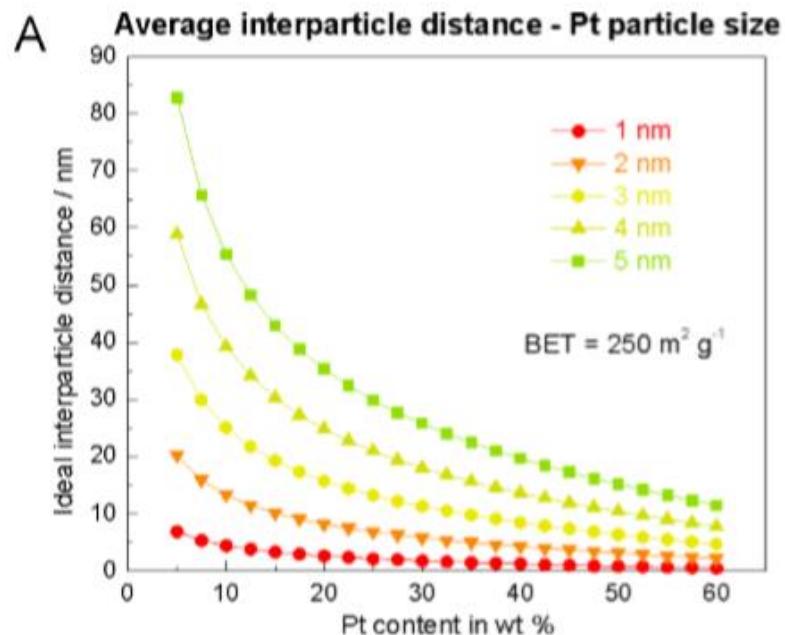
## Uticaj rastojanja mešu česticama na osnovu IL-SEM/STEM

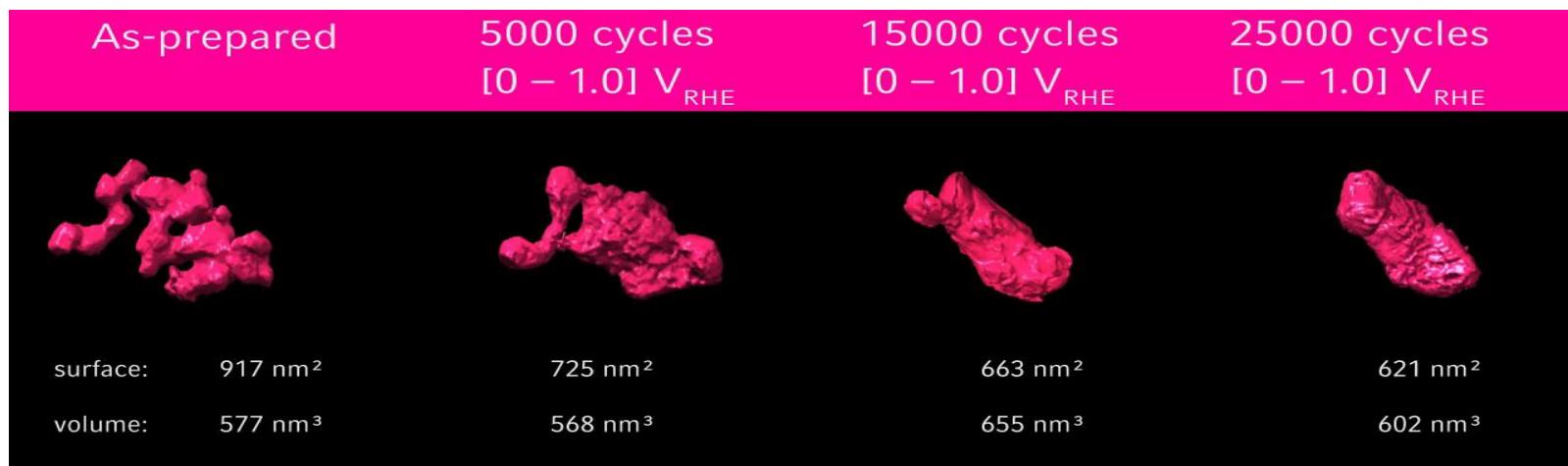
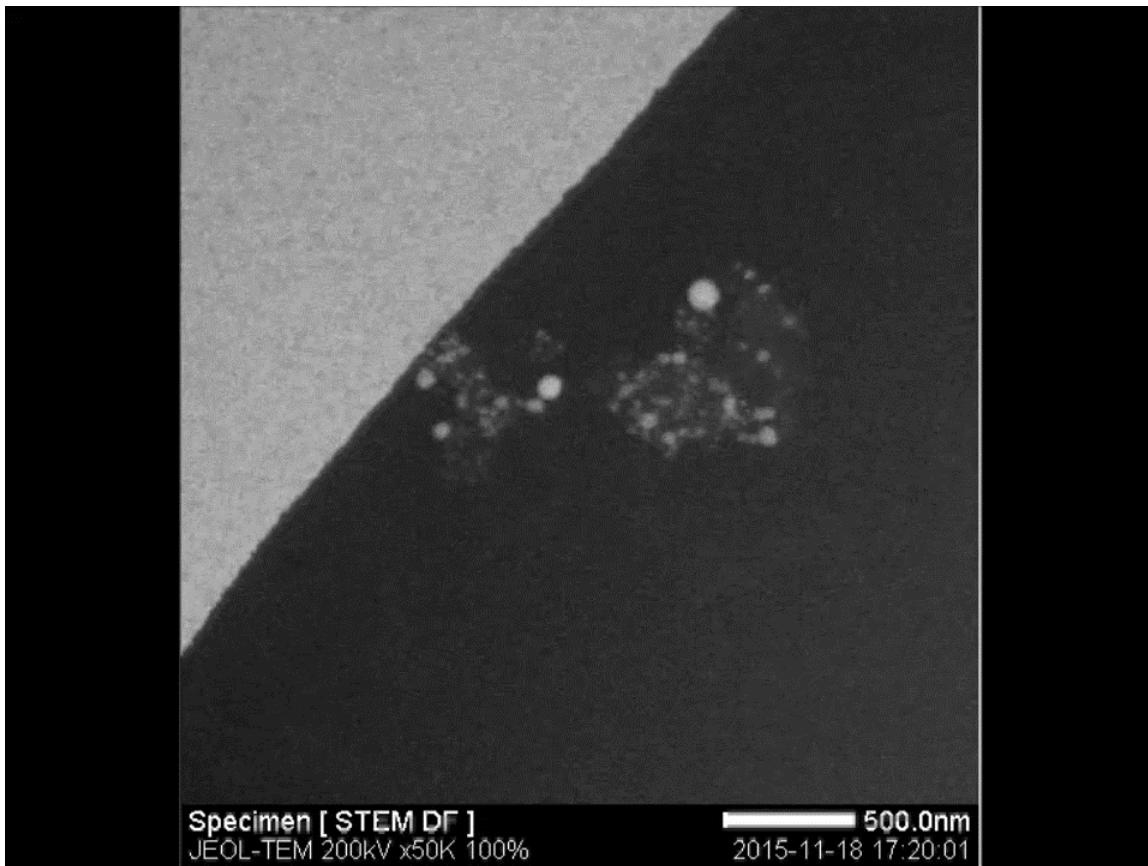
- Inicijalna količina platine
- Specifična površina podloge
- Veličina nanočestica
- Homogena distribucija čestican na nosaču
- Zagrevanje ugljenika kako bi se sprečila korozija (stabilnost vs. manja površina)



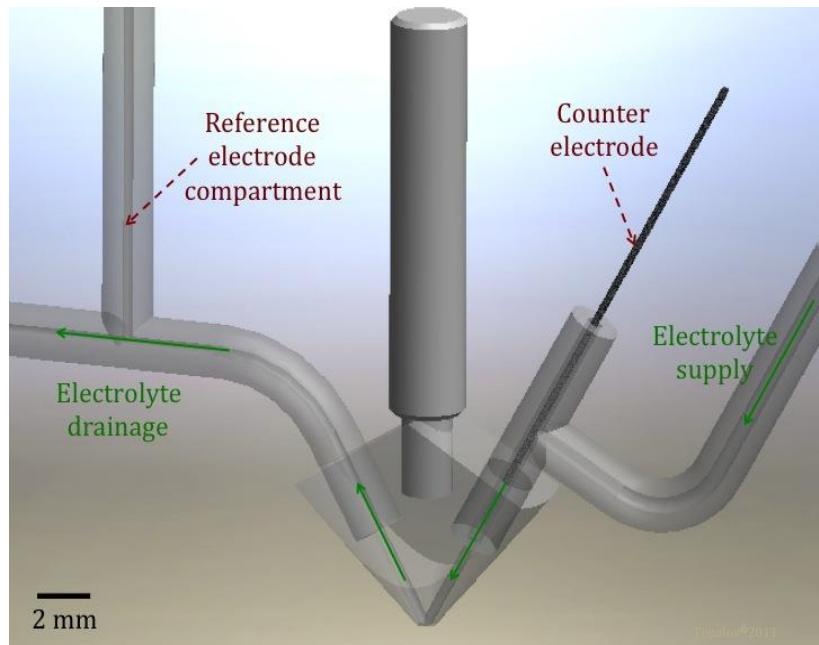
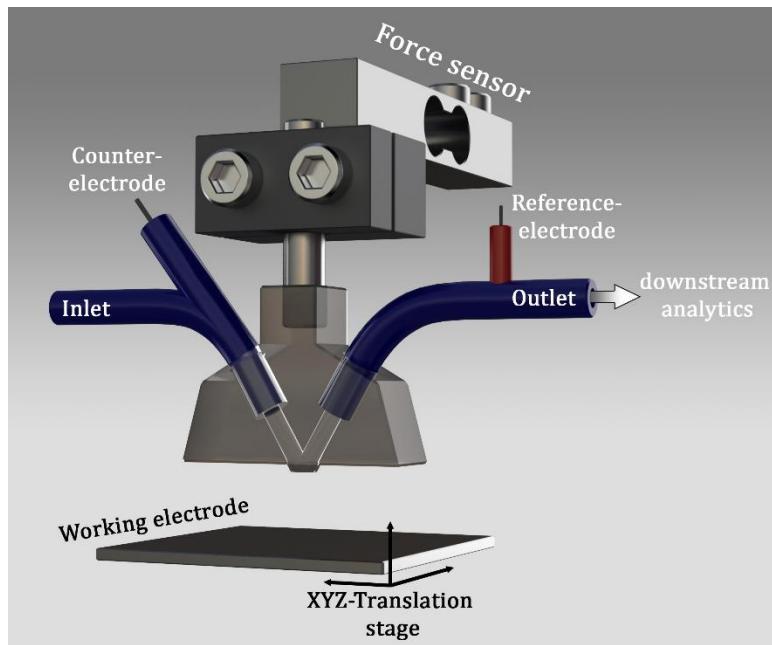
## Idealno rastojanje između nanočestica

$$l = \sqrt{\frac{\pi}{3\sqrt{3}} \cdot 10^{-3} \cdot \rho_{\text{Pt}} \cdot \left( \frac{100 - L_{\text{Pt}}}{L_{\text{Pt}}} \right) \cdot A_S \cdot d^3 - d}$$

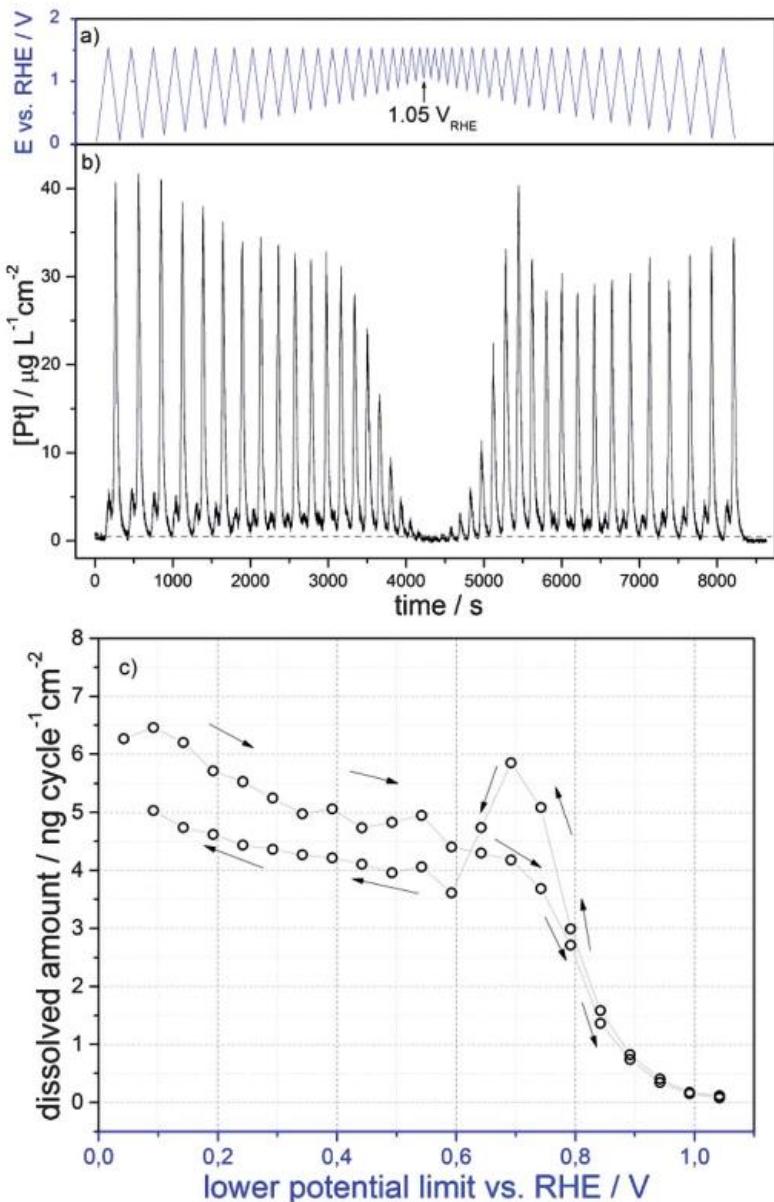




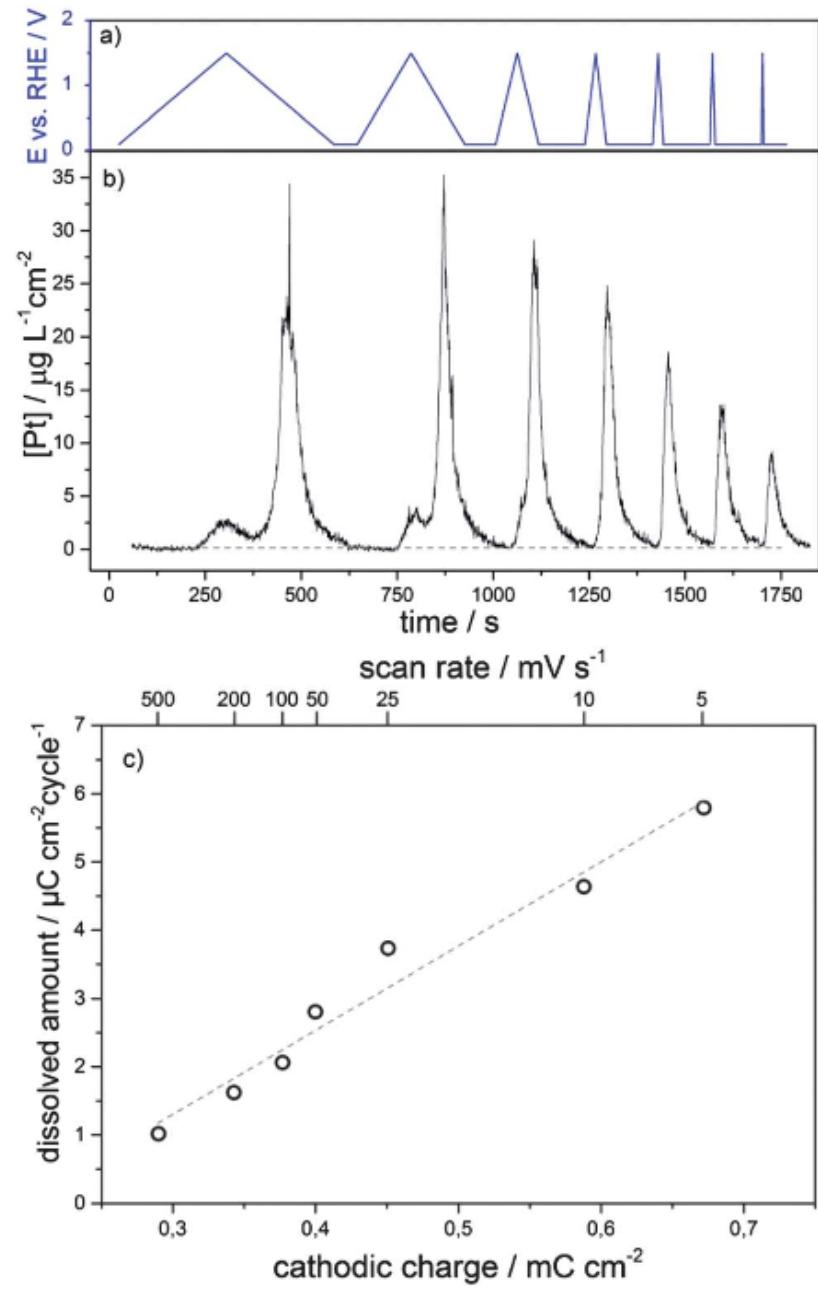
## Flow cell – ICP-MS/OES



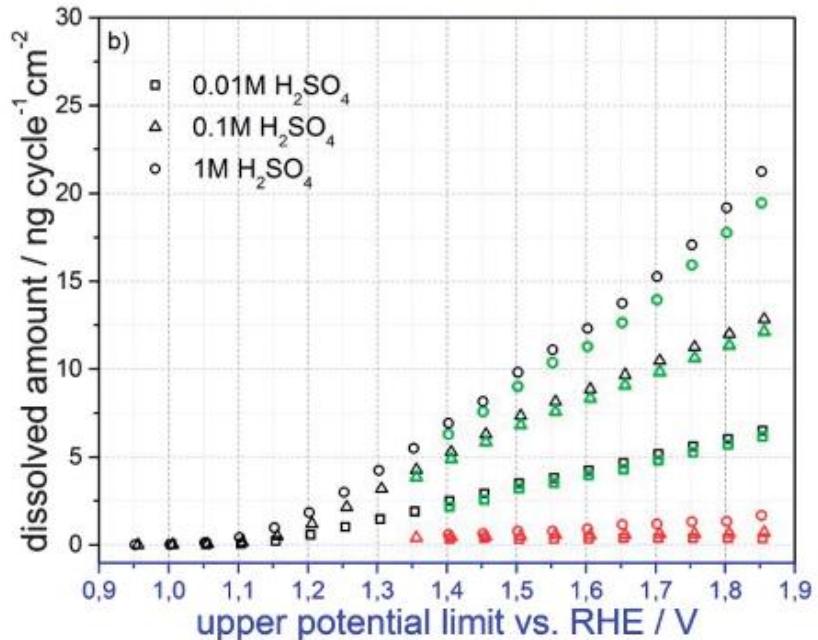
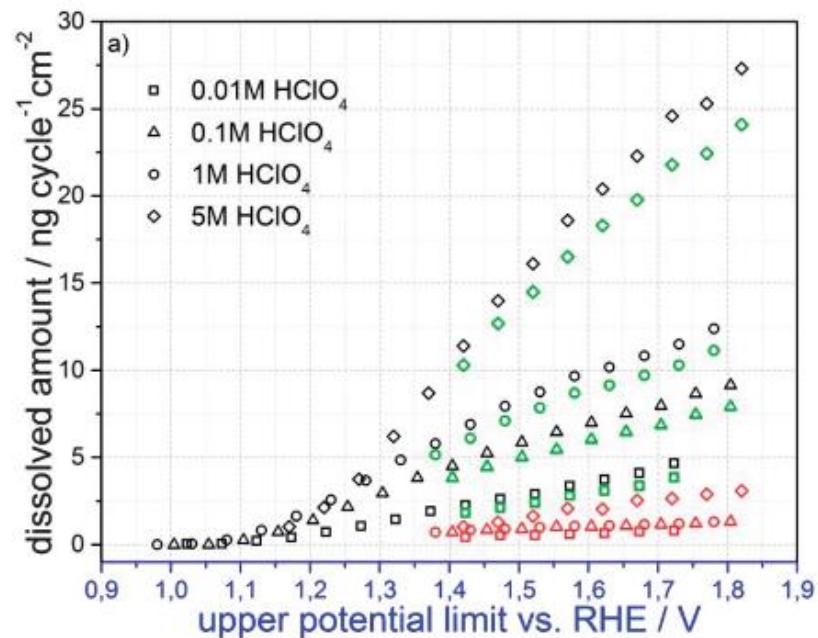
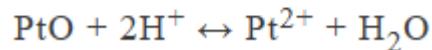
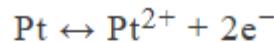
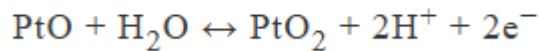
## Uticaj krajnjih potencijala na rastvaranje Pt



## Uticaj brzine polarizacije na rastvaranje Pt

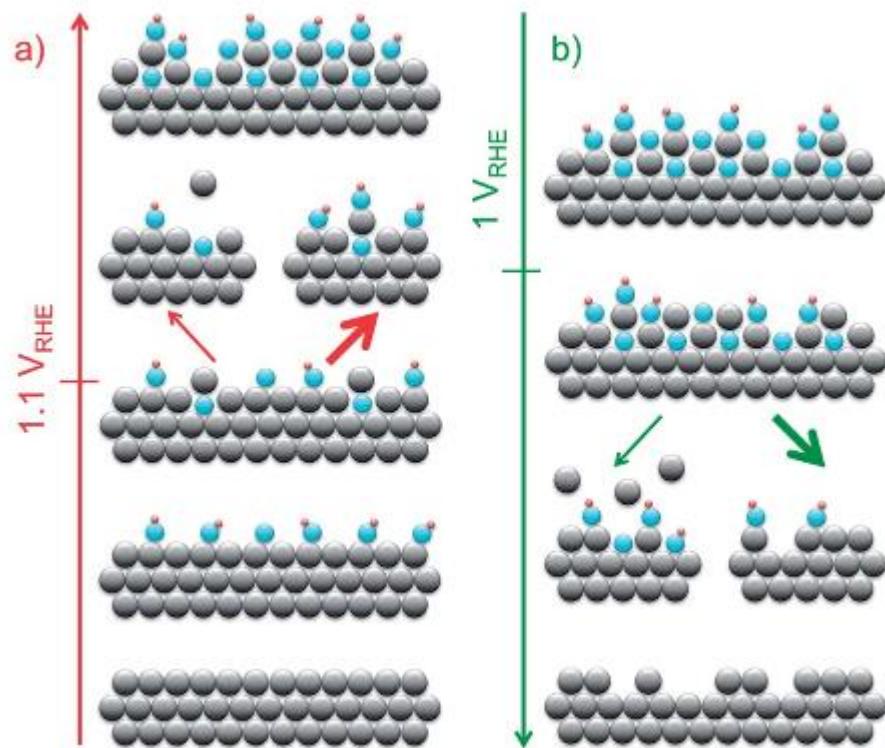


## Uticaj koncentracije $\text{H}^+$ jona u elektrolitu na rastvaranje Pt

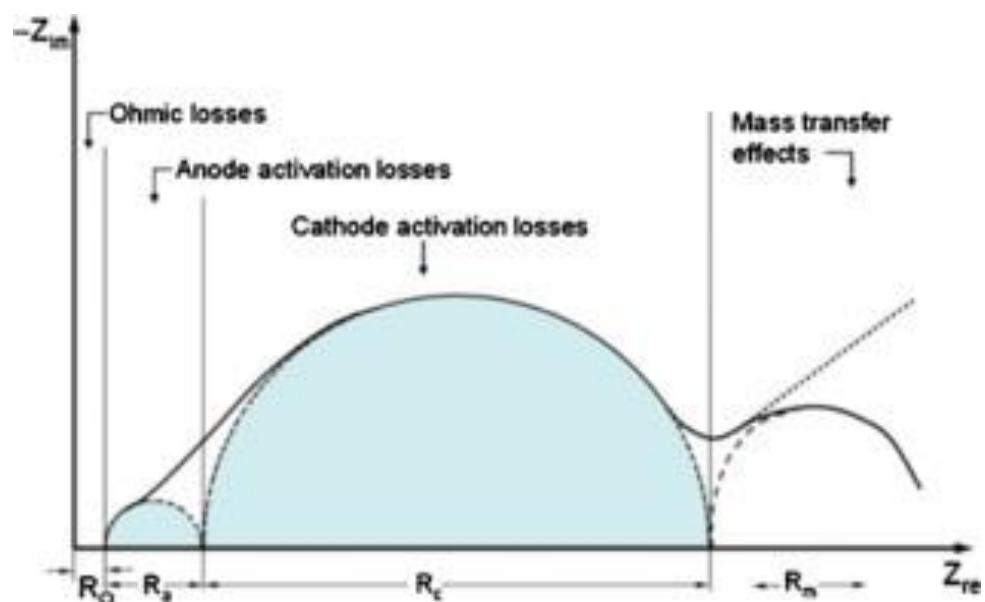


## Shema rastvaranja Pt na potencijalu oko 1,1 V vs. RHE

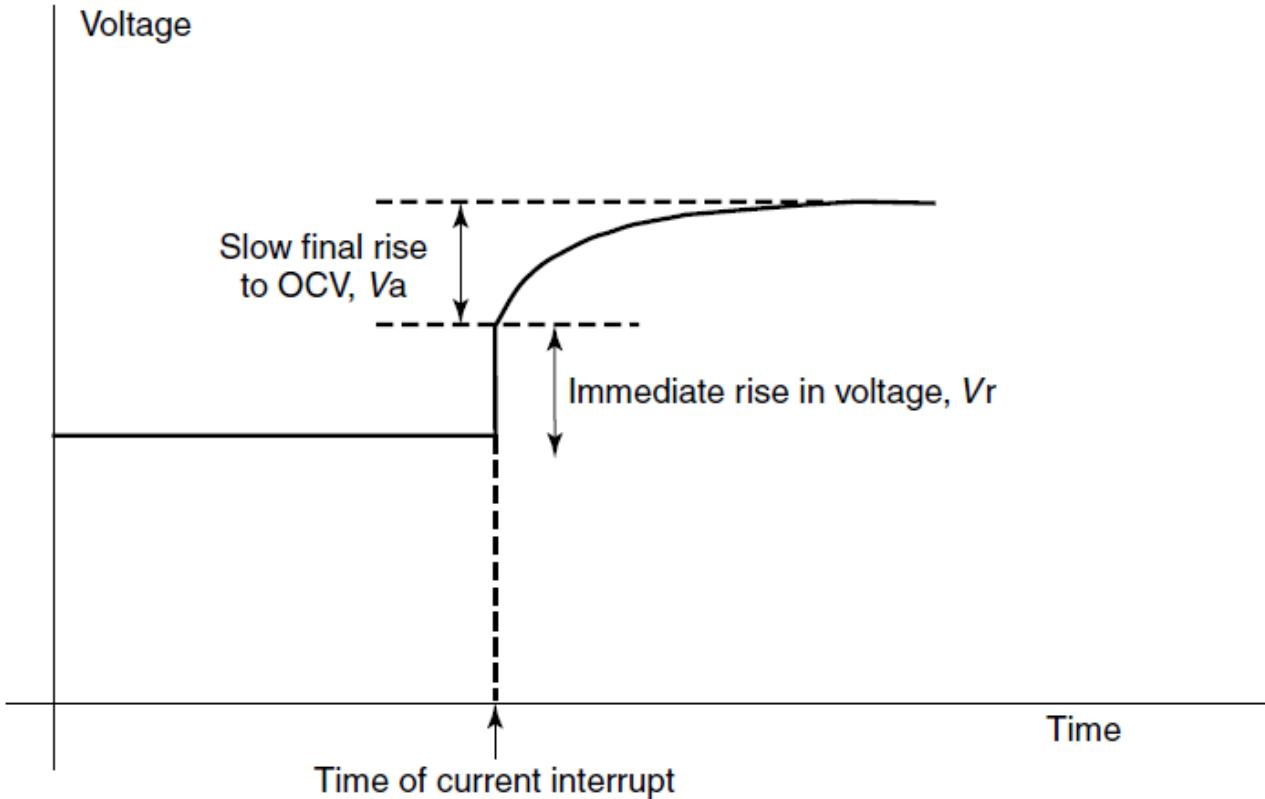
- Povećanje brzine polarizacije smanjuje brzinu rastvaranja
- Povećanje koncentracije H<sup>+</sup> jona povećava brzinu rastvaranja



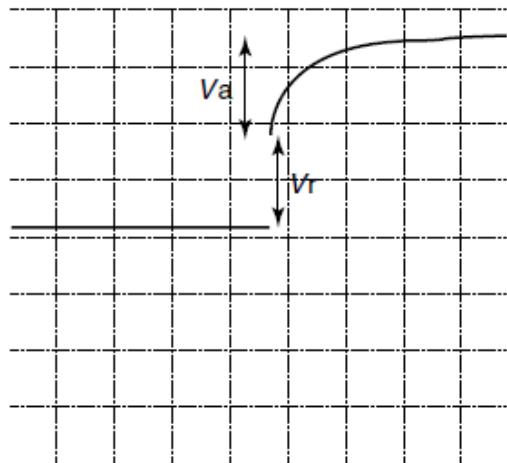
## Elektrohemija impedansna spektroskopija (EIS)



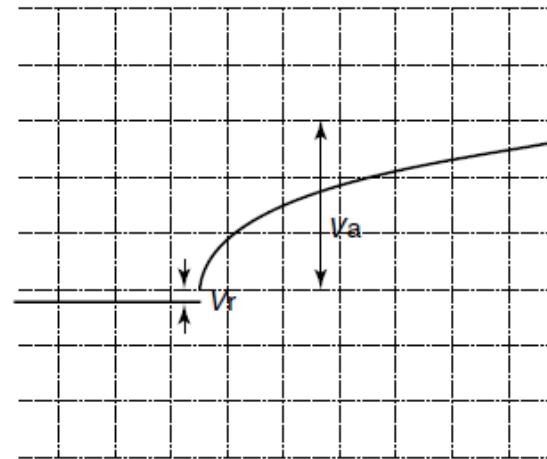
## Current interrupt technique (CI)



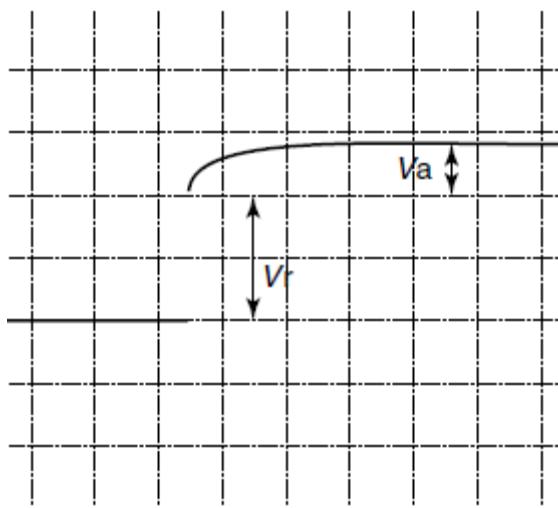
PEMFC



DMFC



SOFC



Reference:

1. J. Larminie and A. Dicks, Fuel Cell Systems Explained, 2<sup>nd</sup> edition, John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England ISBN 0-470-84857-X
2. Angel A. Topalov,Serhiy Cherevko, Aleksandar R. Zeradjanin, Josef C. Meier,Ioannis Katsounaros and Karl J. J. Mayrhofer, Towards a comprehensive understanding of platinum dissolution in acidic media, Chem. Sci.,2014,5,631-638
3. Josef C. Meier, Carolina Galeano, Ioannis Katsounaros, Jonathon Witte, Hans J. Bongard, Angel A. Topalov, Claudio Baldizzone, Stefano Mezzavilla, Ferdi Schüth and Karl J. J. Mayrhofer, Design criteria for stable Pt/C fuel cell catalysts, Beilstein J. Nanotechnol. 2014, 5, 44–67