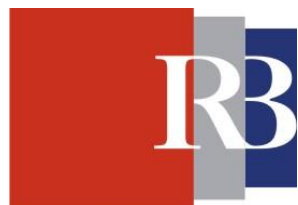


Impedance approach to hydrogen evolution at GC/Ru electrodes: influence of differently modified GC electrode supports



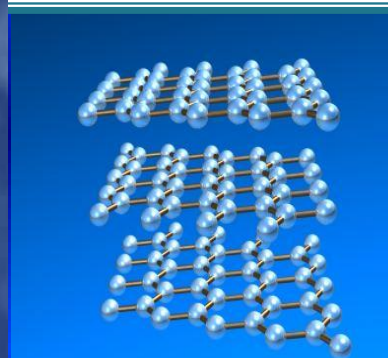
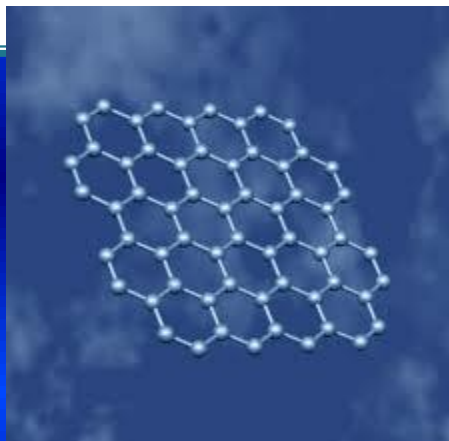
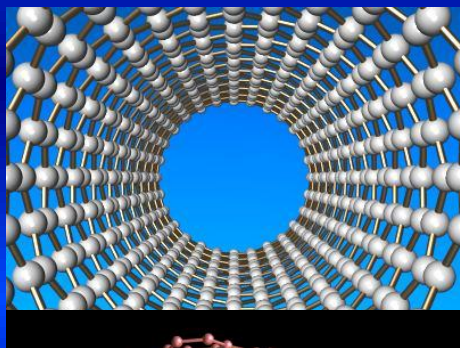
Višnja Horvat-Radošević
Katja Magdić
Krešimir Kvastek

Ruđer Bošković Institute, Zagreb, Croatia

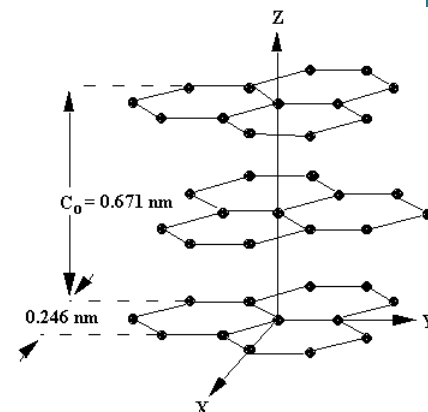
10th International Symposium on Electrochemical Impedance
Analysis, EIA 2014

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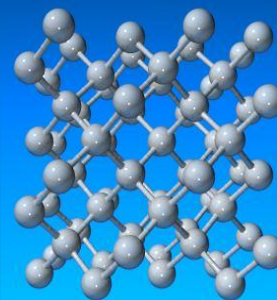
Carbon: allotropes & spin off products



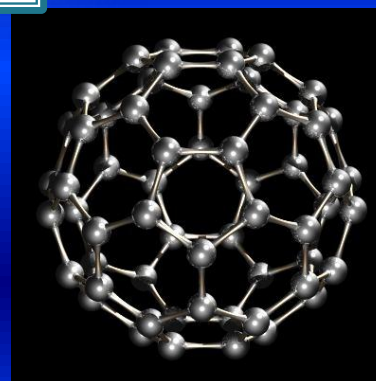
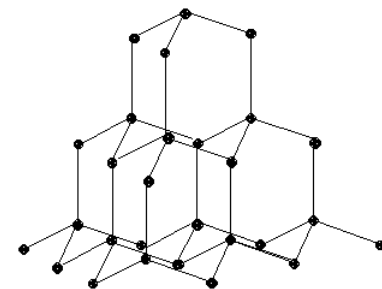
Graphite



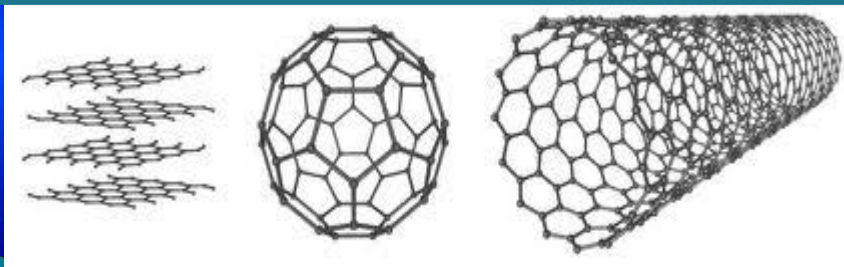
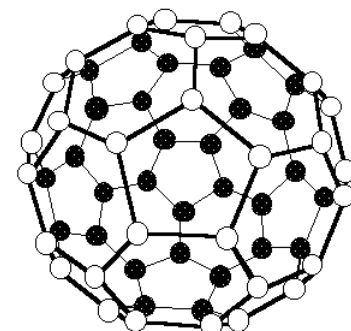
Optics, Nanoelectronics, (Bio)sensors,
Nanotechnology, Nanoscience,
Energy Conversion and Storage...



Diamond



Fullerene





EIS for carbon electrodes:

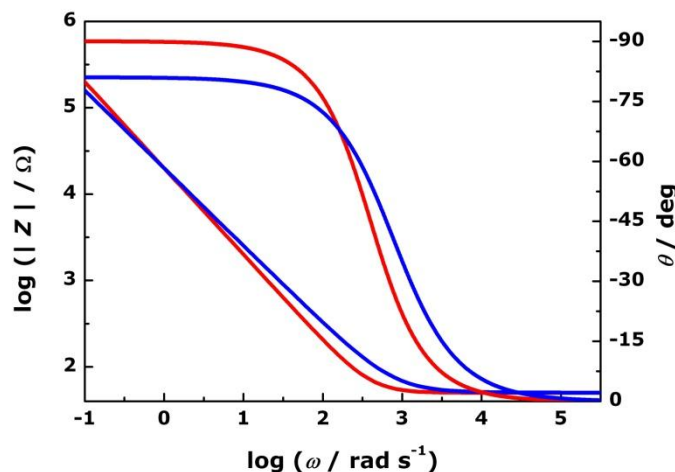
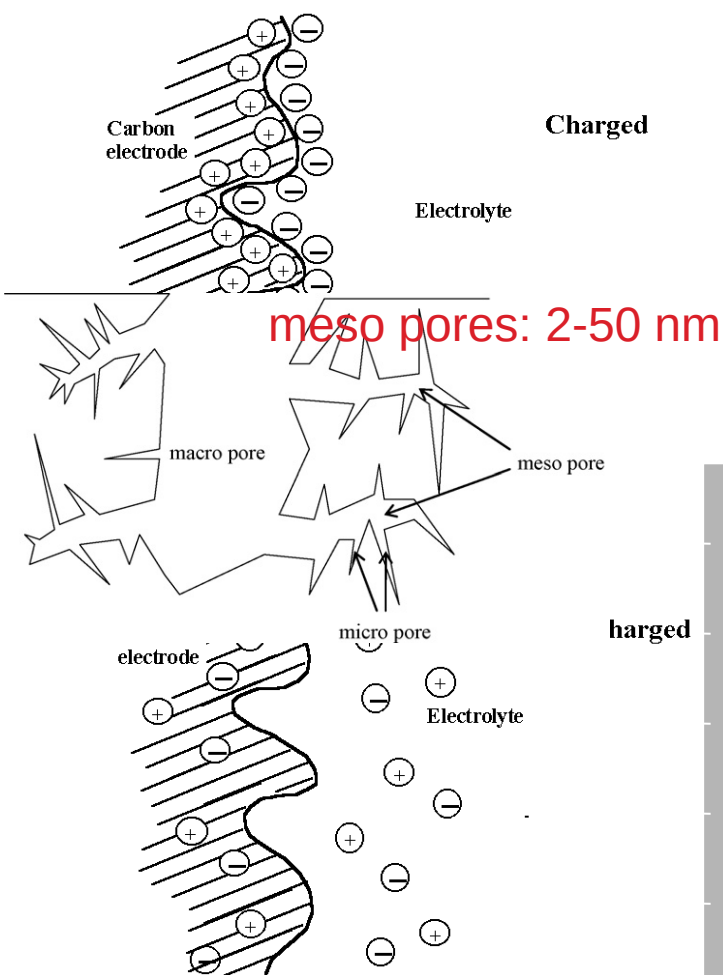
➤ **characterization and diagnostic tool of electrochemical devices**

ultracapacitors
supercapacitors
fuel cells
batteries

➤ **characterization of individual
electrodes**
electroanalysis
sensor properties
EDL and supercapacitors
electrocatalysis (batteries, fuel cells)

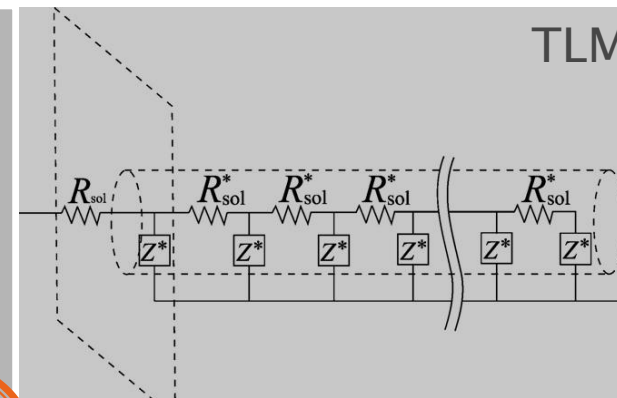
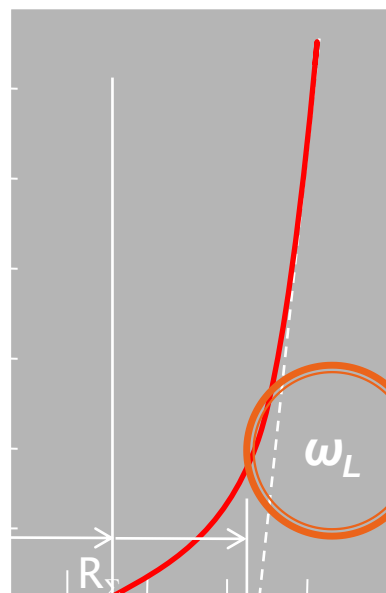
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$$Z_{pe}(i\omega) = \frac{1}{i\omega C}$$

$$Z_{CPE}(i\omega) = \frac{1}{Q(i\omega)^\alpha}$$



$$Z_{pf}(i\omega) = \sqrt{\frac{R_w}{i\omega C_{LF}}} \coth \sqrt{\frac{i\omega}{\omega_L}}$$

$$Z(i\omega) = \left(\left(Z(i\omega)_{\Sigma TL} \right)^{-1} \right)^{-1}$$



➤ Glassy carbon – general properties

- Good electronic conductor
- Resistive to chemical and thermal attack
- Impermeable to gas and solutions
- Low reactivity
- Low density and high proportion of closed porosity

Activation

- Thermal treatment
- Chemical oxidation
- Electrochemical oxidation

➤ as electrode material

- High potential window
- High chemical and physical stability

OSG's :

carbonyl
carboxyl
ketone
quinone
hydroxyl...

➤ as electrodes for energy storage devices

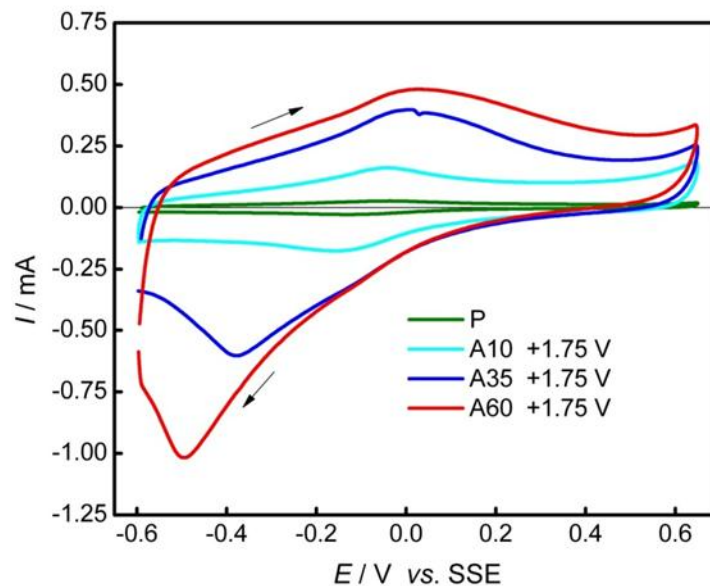
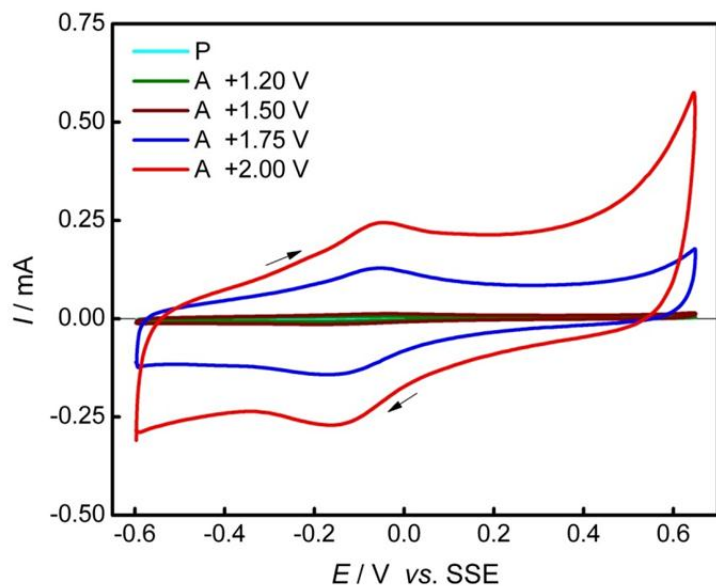
- High specific capacitance
- Low contact, active-layer and ionic resistances



GC-P: polished

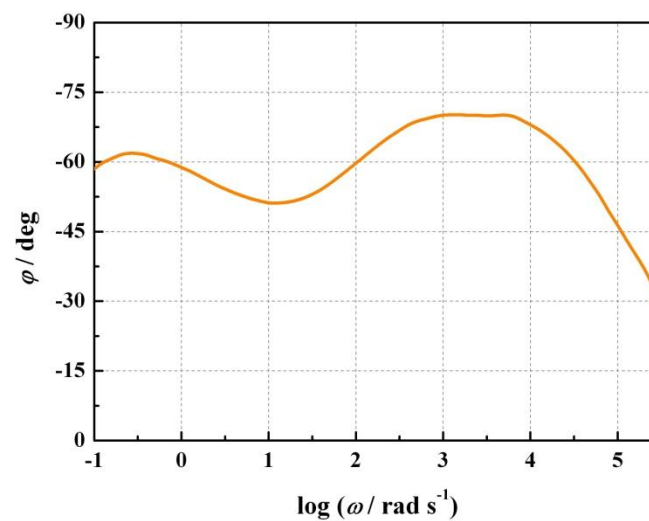
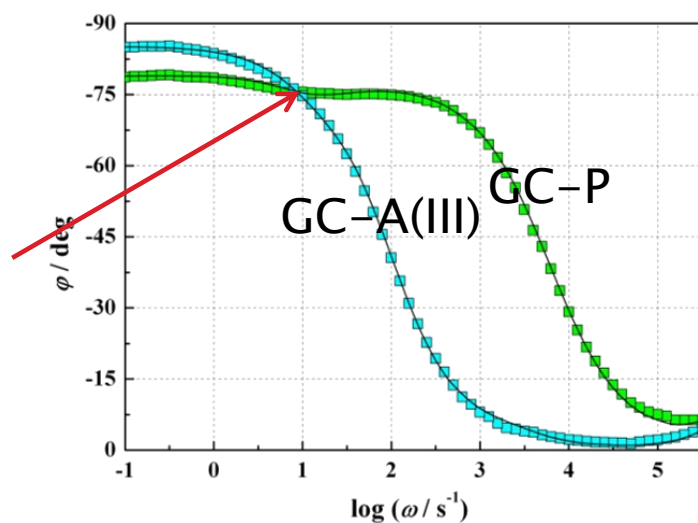
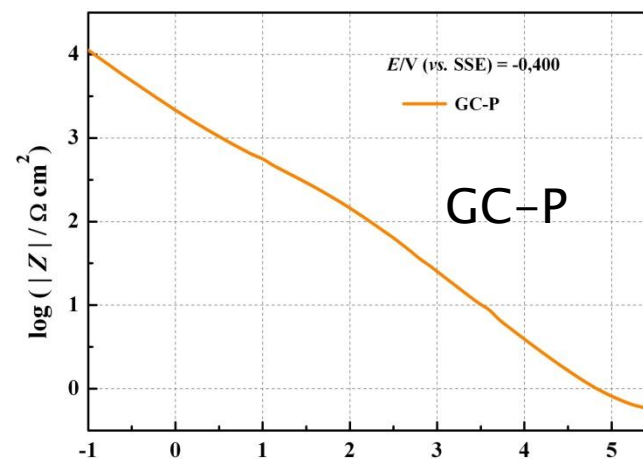
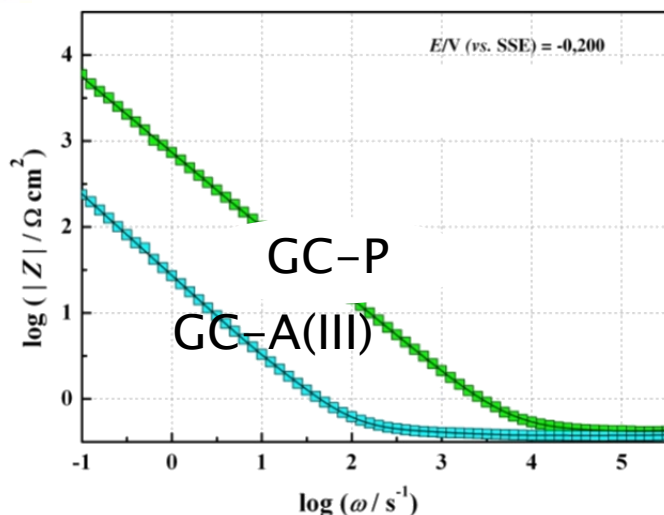
GC-A(III): mildly oxidized

GC-A(IV): strongly oxidized



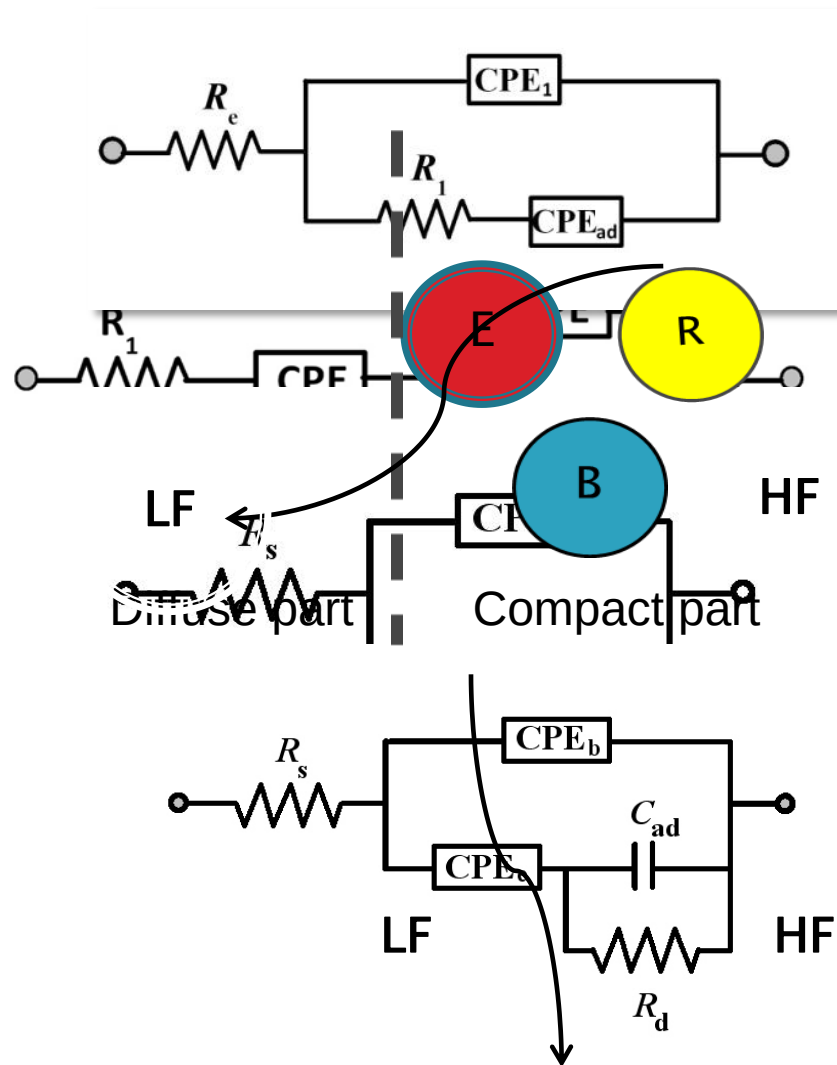
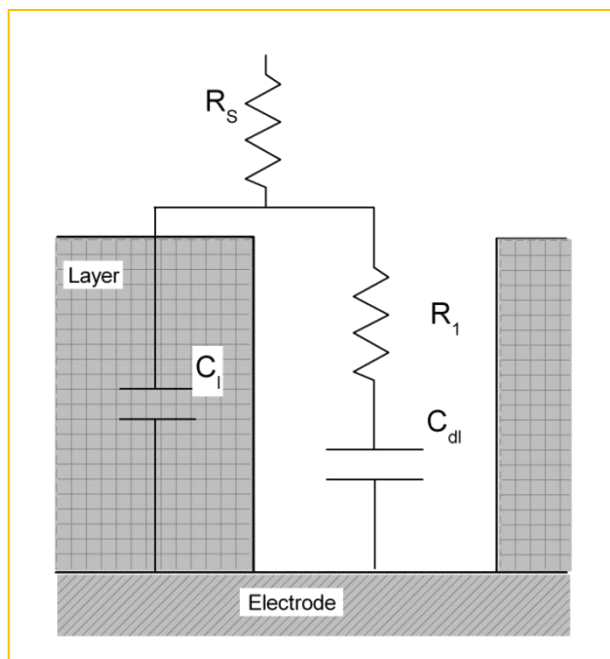
10th International Symposium on Electrochemical Impedance Analysis

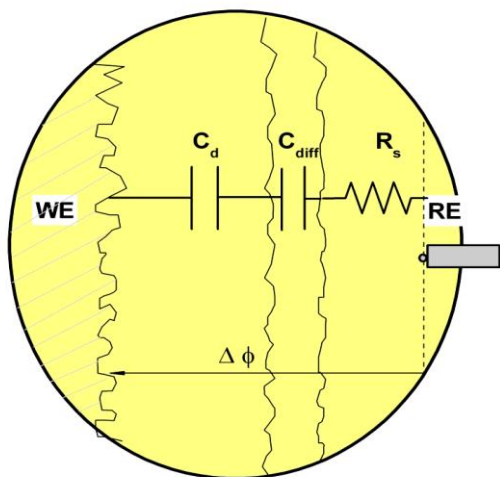
June, 1-5. 2014, Borovets-Rila Mountains, Bulgaria



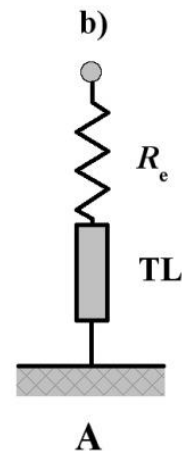
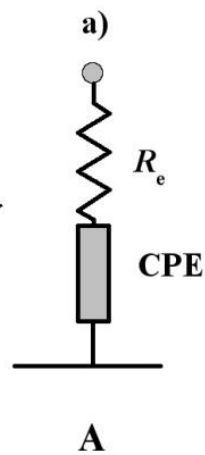
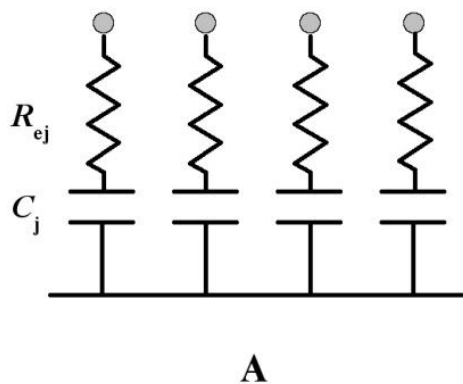
10th International Symposium on Electrochemical Impedance Analysis

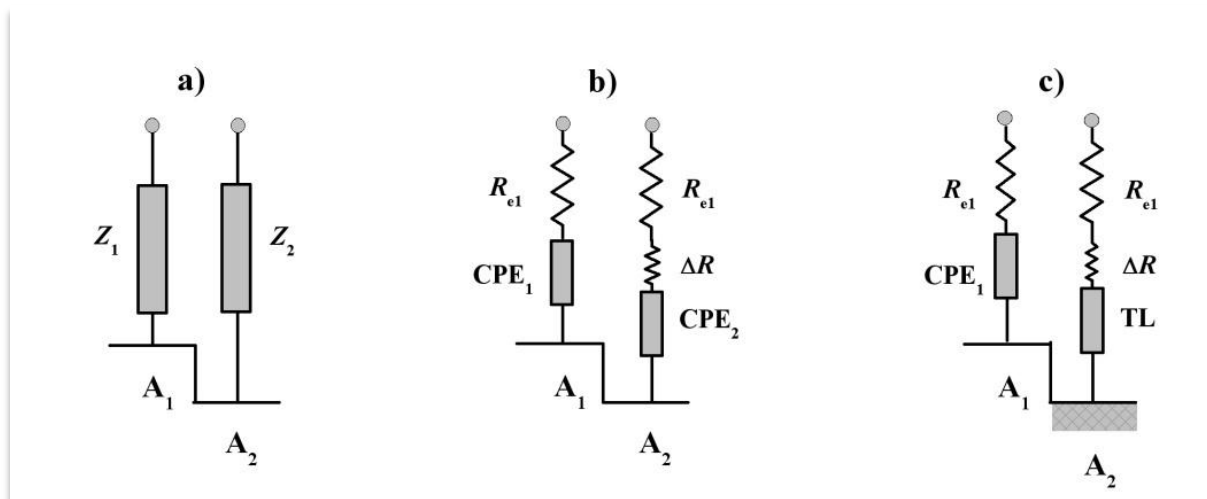
June, 1-5. 2014, Borovets-Rila Mountains, Bulgaria



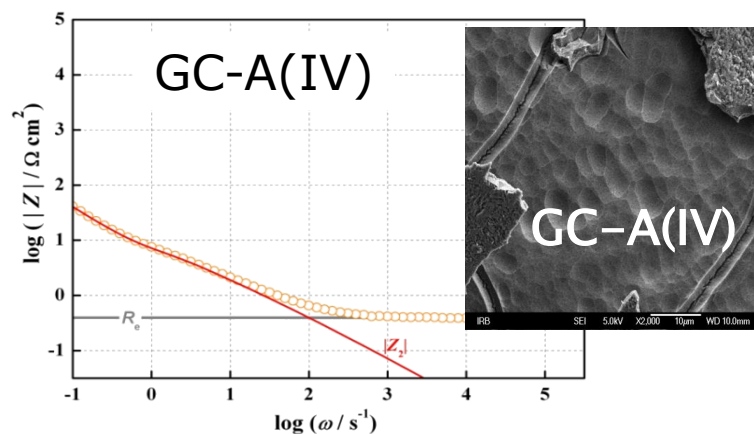
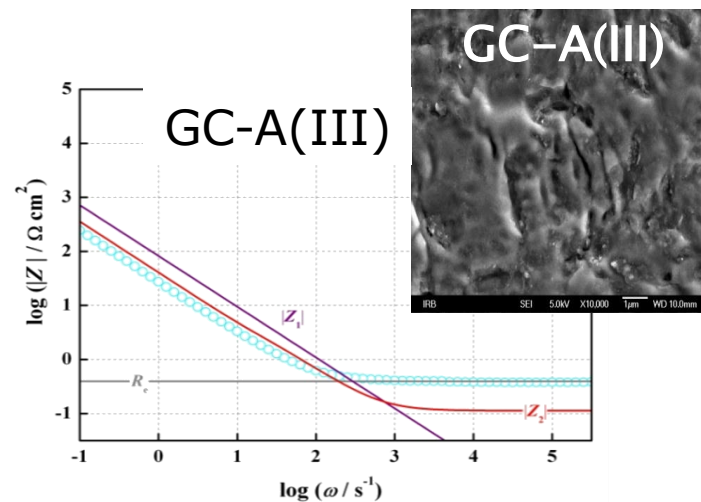
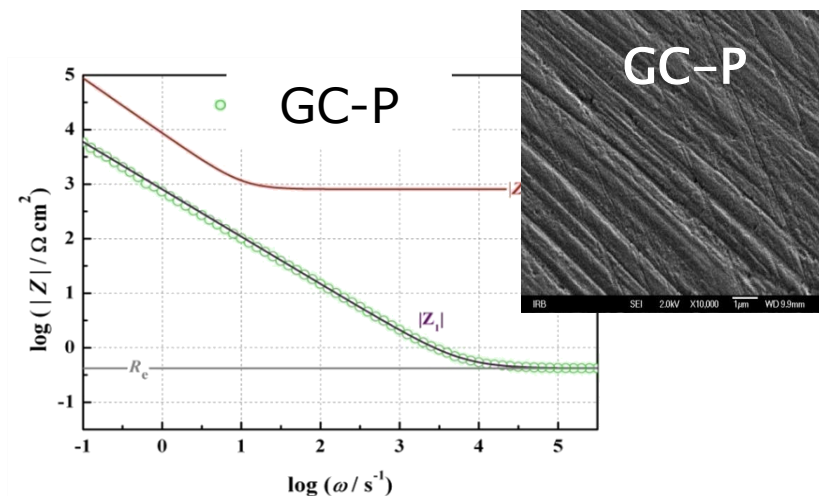


$$Z = \frac{\Delta\phi}{\sum_j I_j}$$





K. Magdić, K. Kvastek, V. Horvat-Radošević, *Electrochim. Acta*, 117 (2014) 310-321.



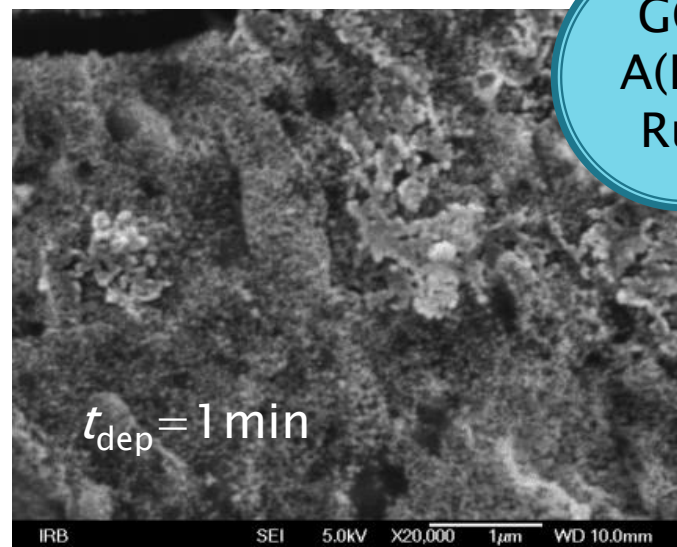
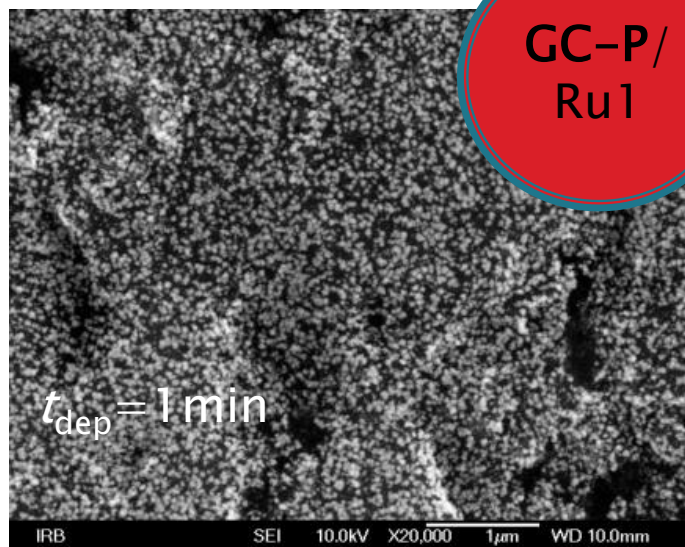


Formation of GC/Ru electrodes

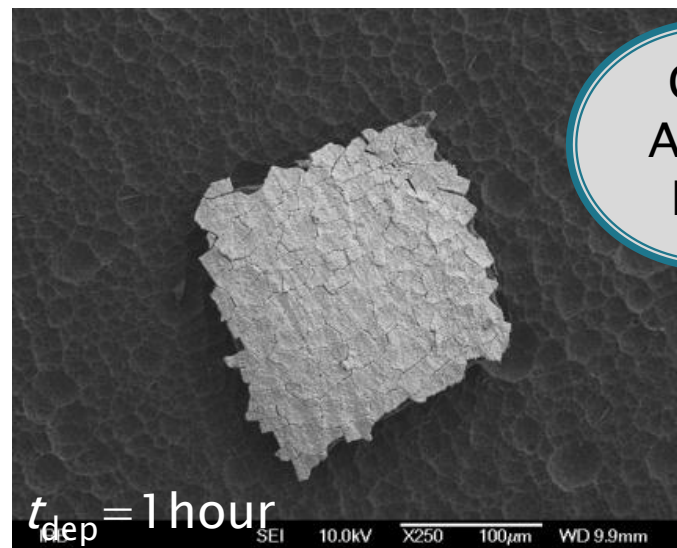
- Polished GC: **GC-P/Ru**
- Electrochemically activated GC: **GC-A(III-IV)/Ru**

Ru added to **GC-P** and **GC-A(I-IV)** by cathodic potentiostatic deposition from $(\text{NH}_4)_2\text{RuCl}_6/\text{H}_2\text{SO}_4$ at $E = -0.85 \text{ V}$ vs. SSE and various t_{dep} .

GC	$t_{\text{dep}} = 1 \text{ min}$	5 min	30 min	50 min
GC-P/Ru	GC-P/Ru1	GC-P/Ru2	GC-P/Ru3	–
GC-A(III)/Ru	GC-A(III)/Ru1	GC-A(III)/Ru2	GC-A(III)/ Ru3	GC-A(III)/Ru4
GC-A(IV)/Ru	GC-A(IV)/Ru1	GC-A(IV)/Ru2	–	GC-A(IV)/Ru4

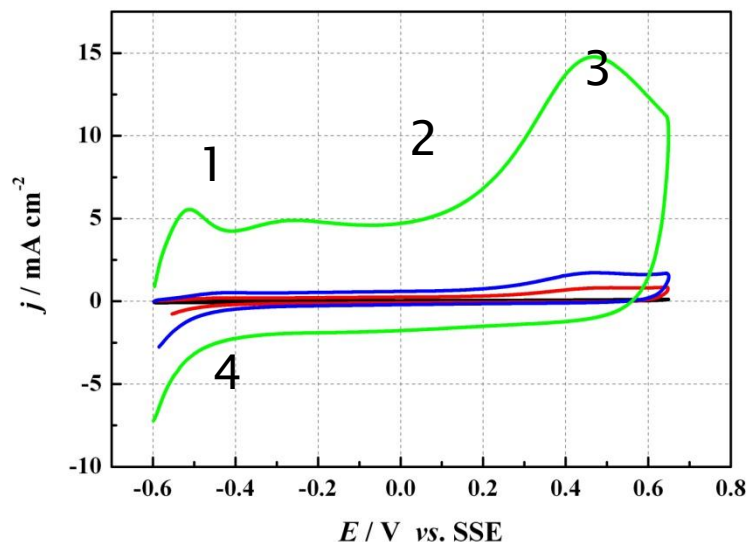


SEM images

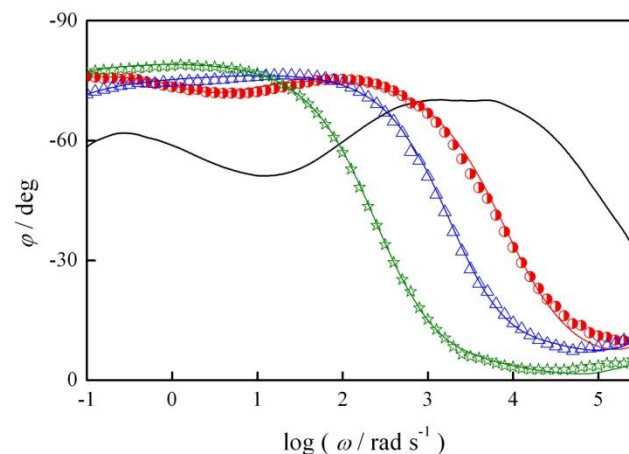
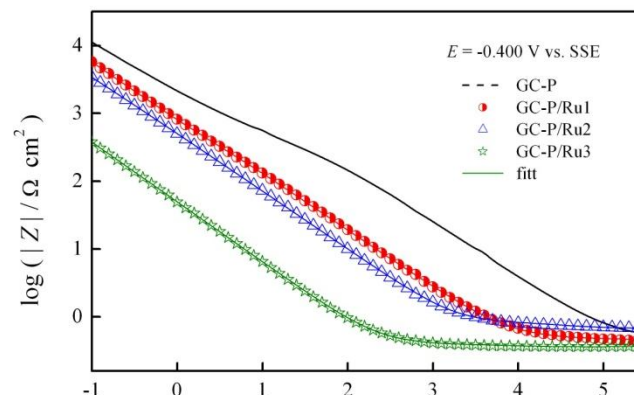




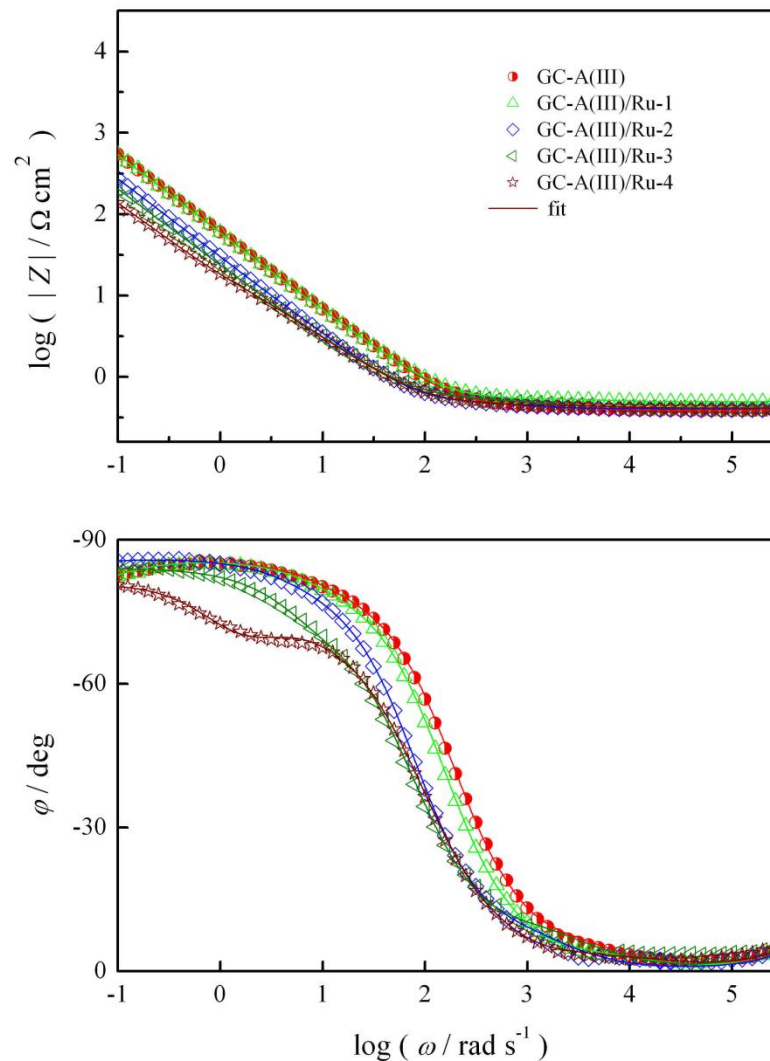
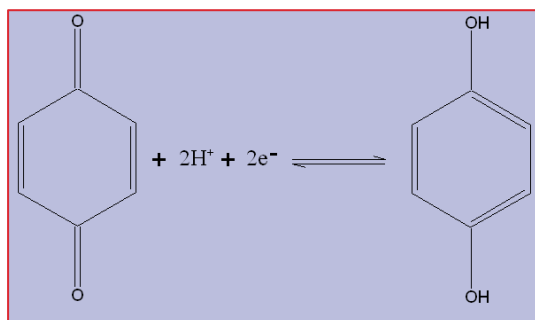
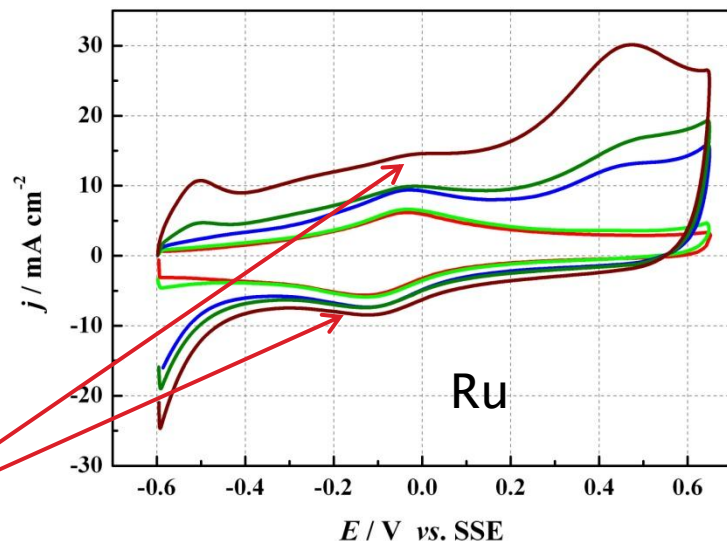
GC-P/Ru



- 1 – Hydrogen desorption, H UPD
- 2 – Ru oxidation to hydrated ox-hydroxide, $H_xRu_yO_z$
- 3 – Formation of hydrated RuO_2 at 0.45 V vs. SSE
- 4 – Hydrogen adsorption + reduction of Ru-oxides formed at 2 and 3

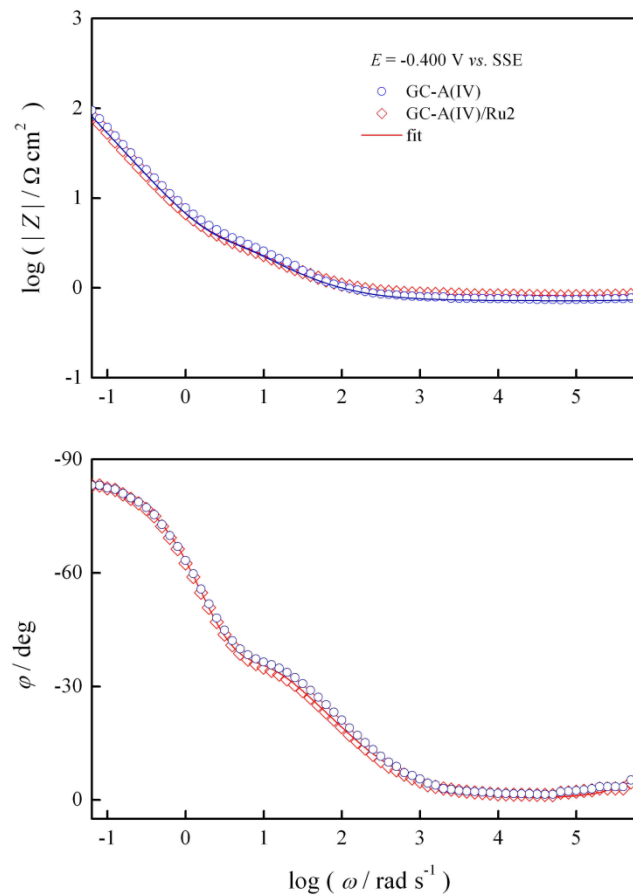
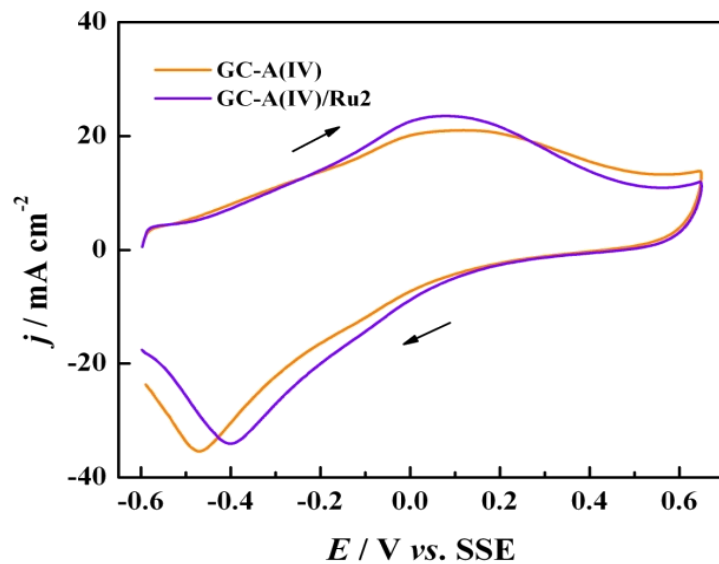


GC-A(III)/Ru



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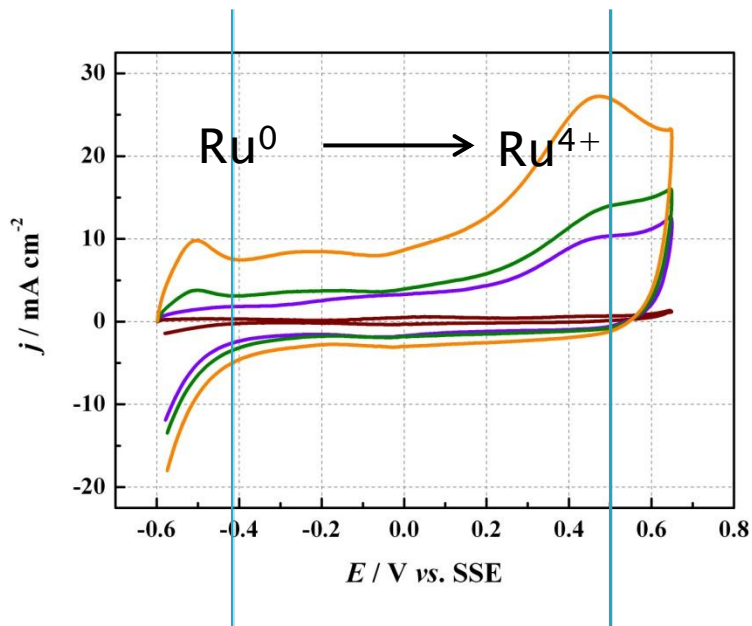
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Subtracted CVs

GC-P/Ru - GC-P

GC-A(III)/Ru - GC-A(III)

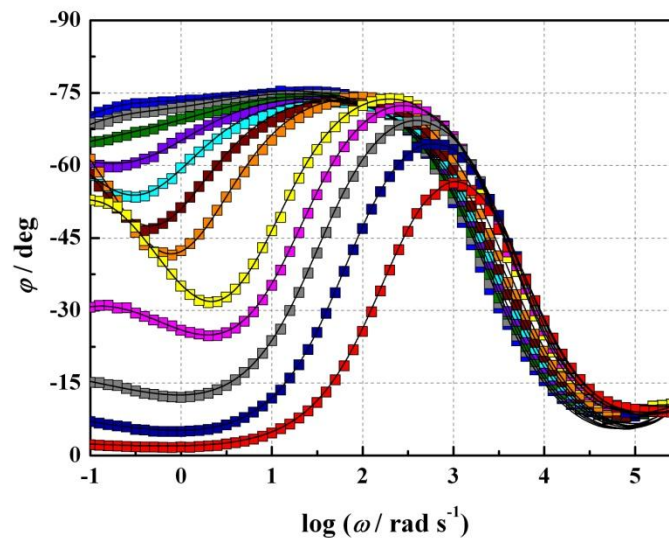
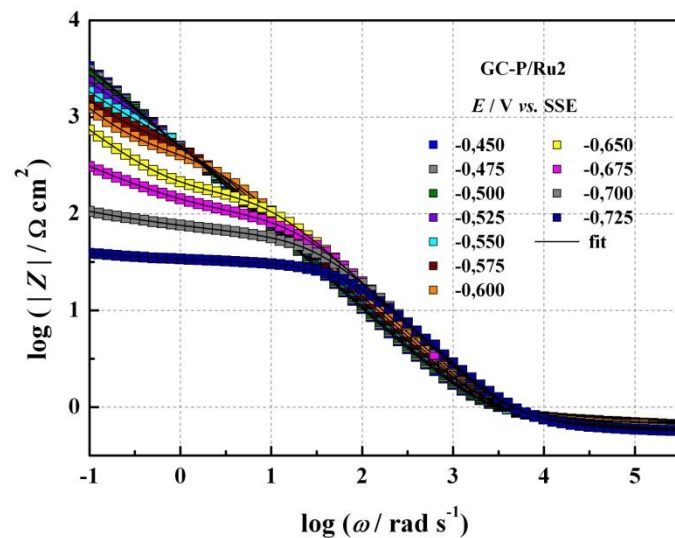


$$m_{\text{Ru}^*} = \frac{qM}{4F}$$

$t_{\text{dep}} / \text{min}$	$10^3 q / \text{C cm}^{-2}$	$10^5 (m)_{\text{Ru}^*} / \text{g cm}^{-2}$
GC-P/Ru		
1	6.32	0.16
5	11.93	0.31
30	93.55	2.43
GC-A(III)/Ru		
1	10.71	0.28
5	78.57	2.04
30	114,29	2.98
50	228,57	5.97

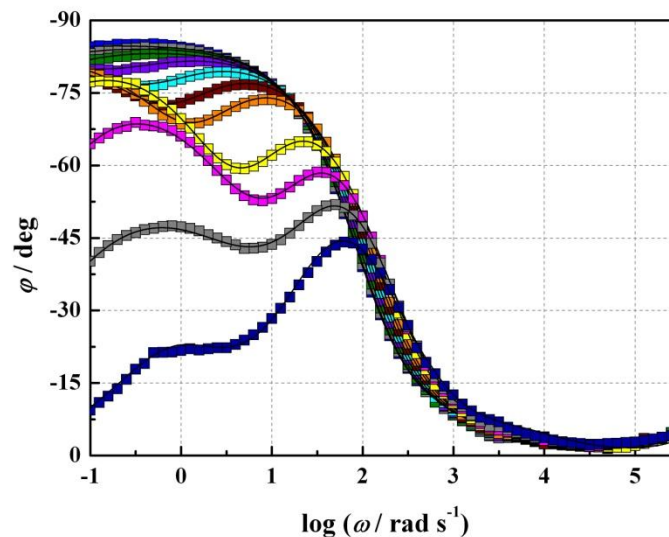
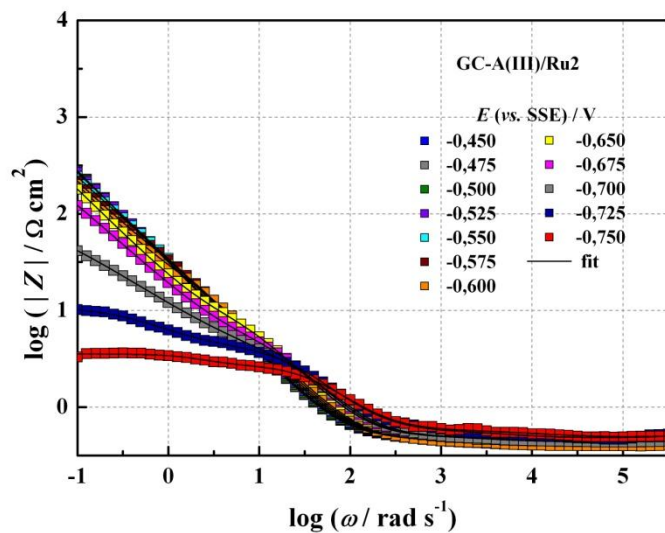


GC-P/Ru2



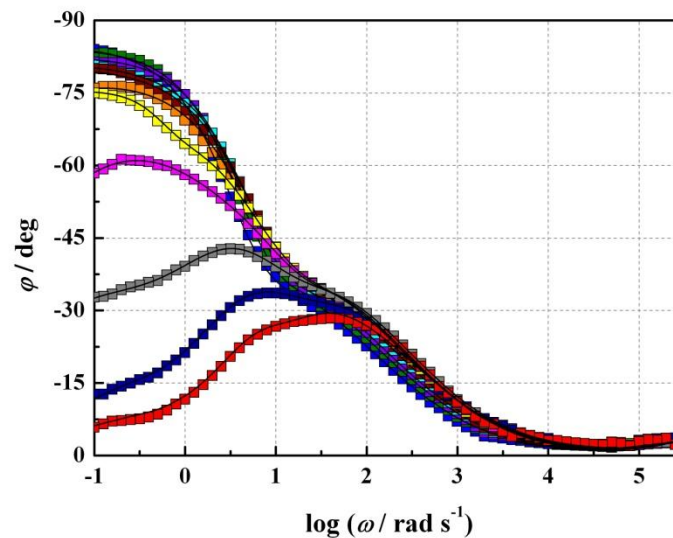
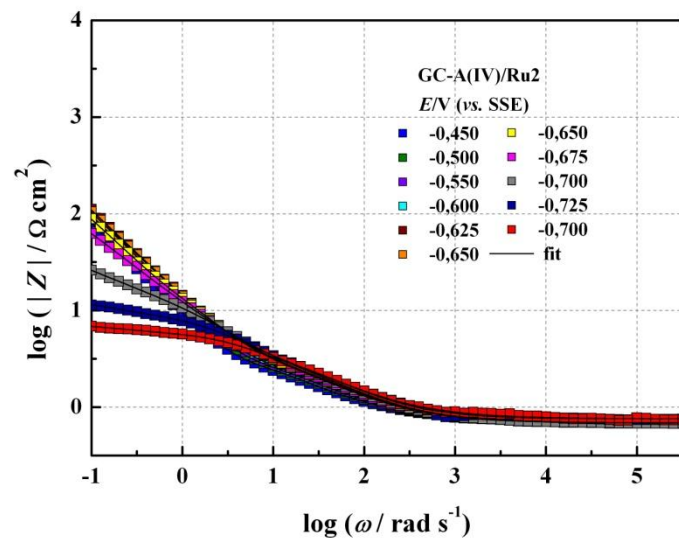


GC-A(III)/Ru2





GC-A(IV)/Ru2



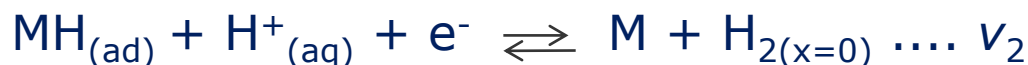


Hydrogen evolution reaction, HER

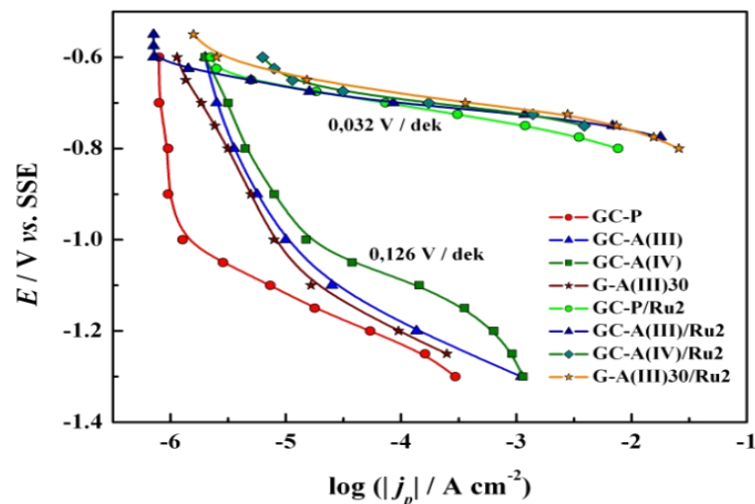
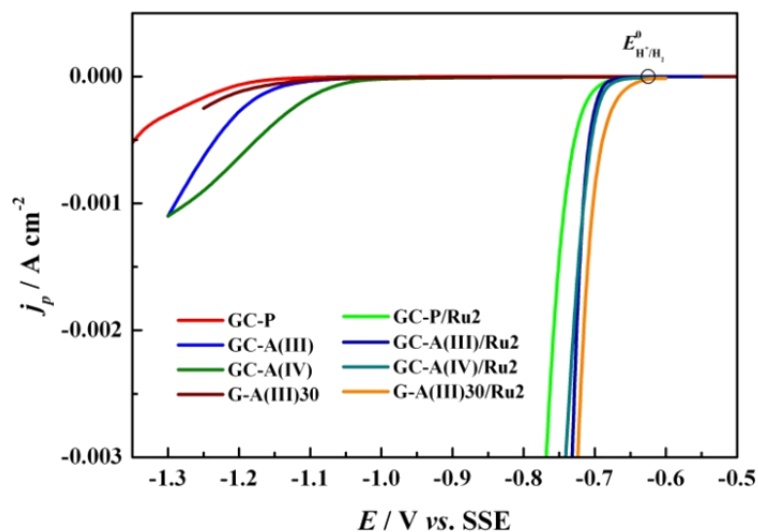
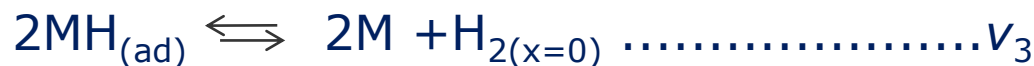
$$E^0(\text{H}^+/\text{H}_2) = 0.00 \text{ V vs. NHE}$$



$E > E^0$
H UPD

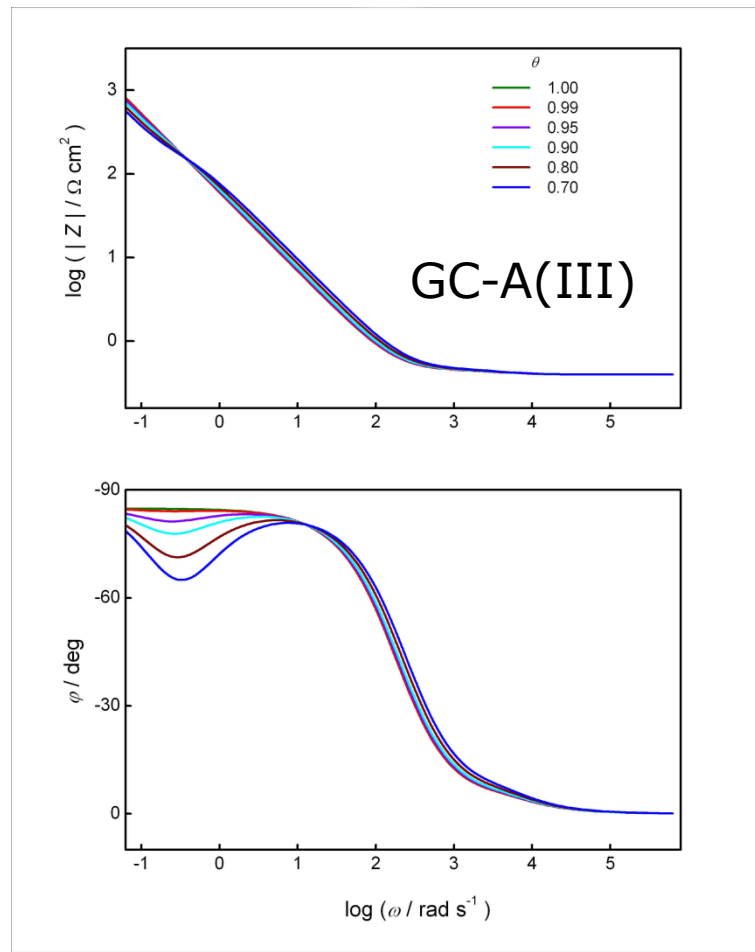
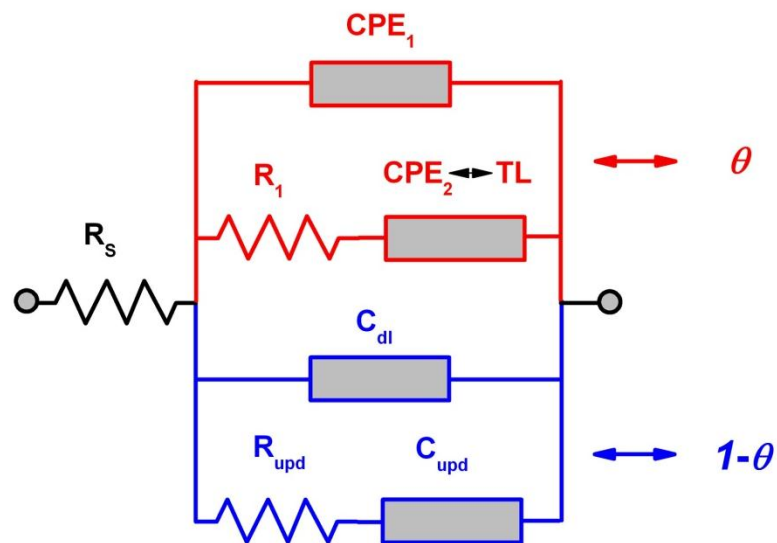


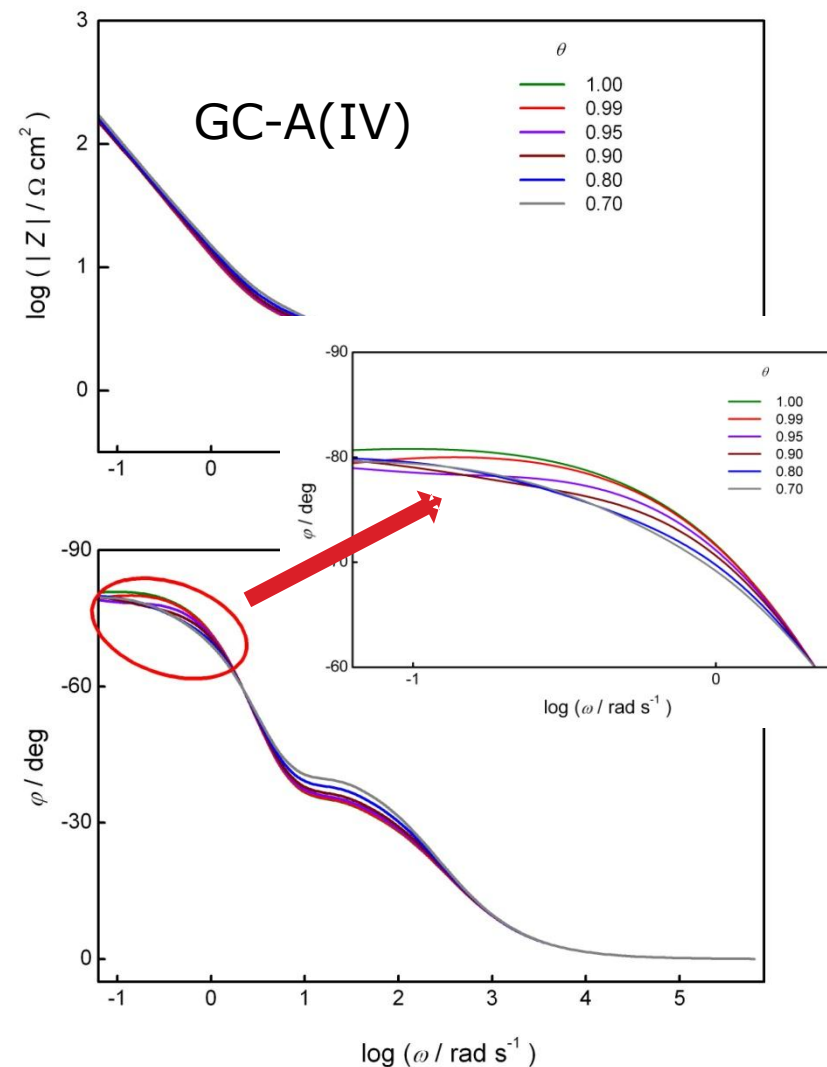
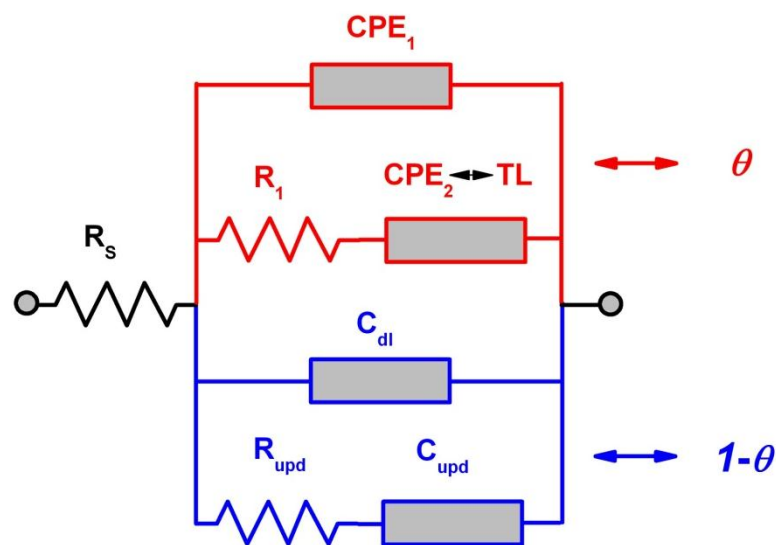
$E < E^0$
H OPD





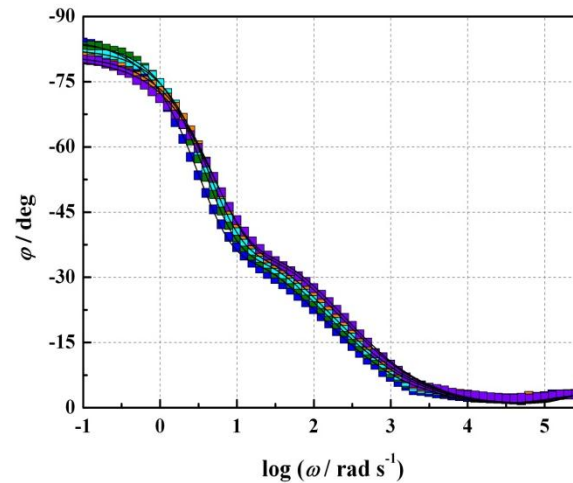
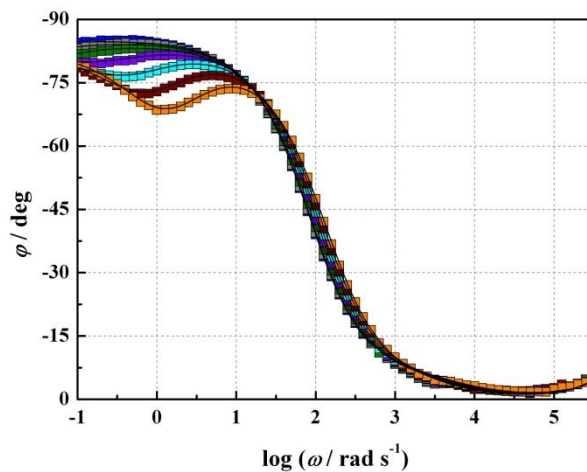
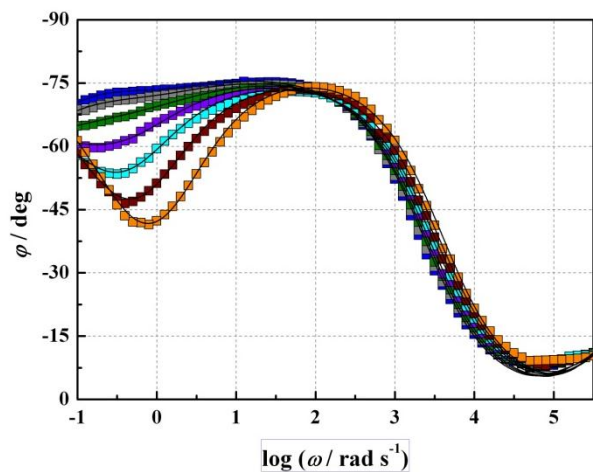
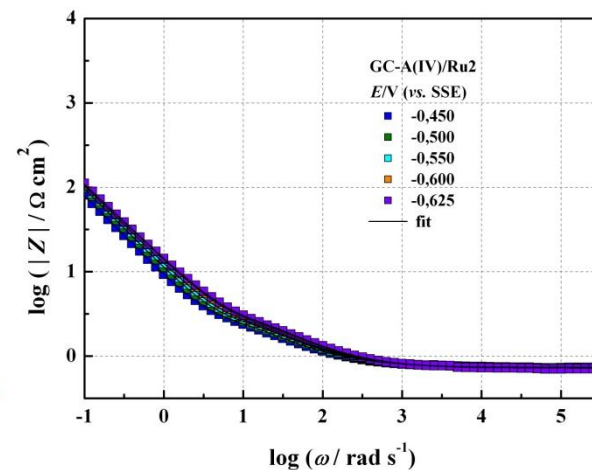
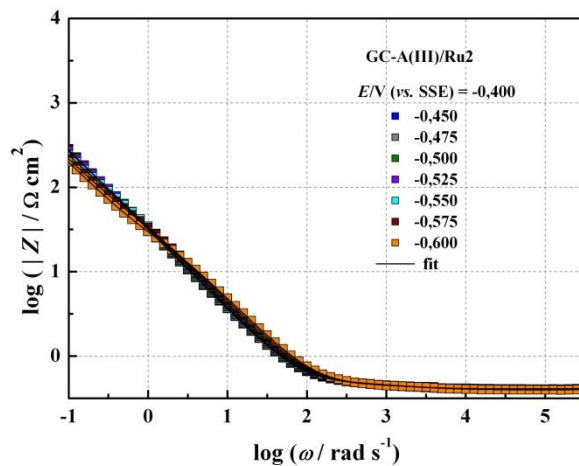
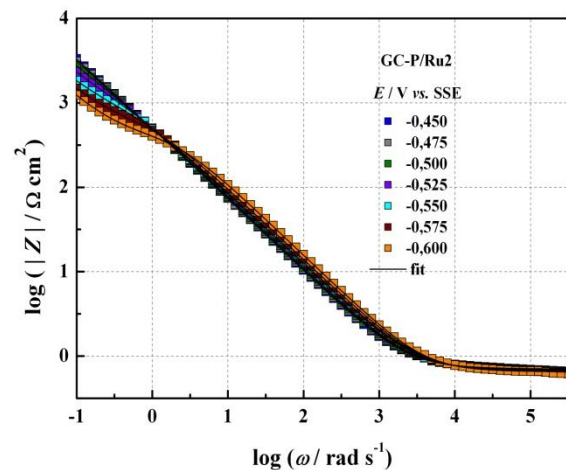
$$E = -0.60 \text{ V vs. SSE}$$





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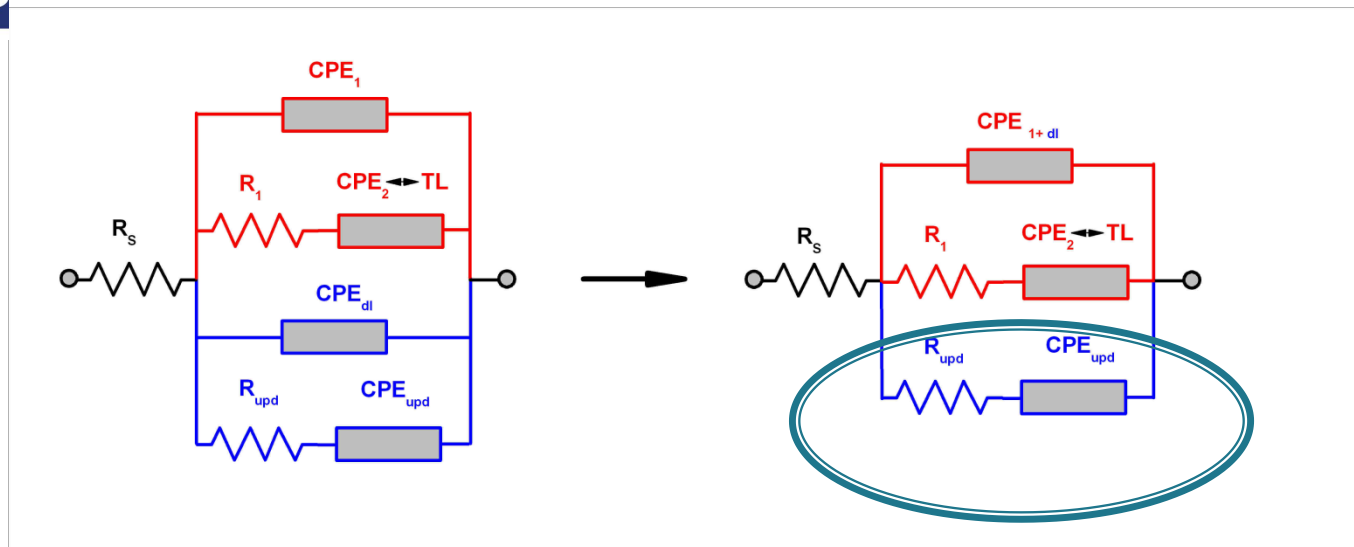
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GC-P

GC-A(III)

GC-A(IV)

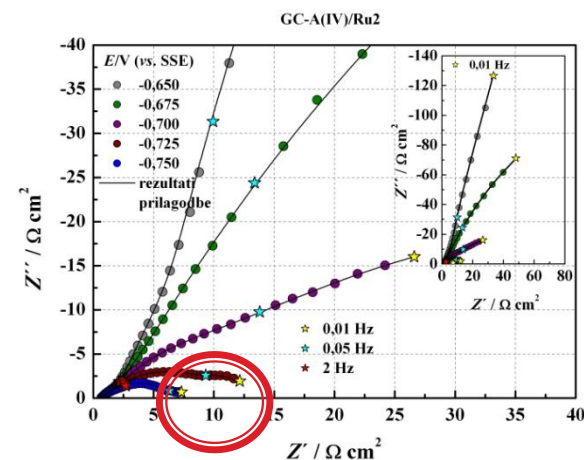
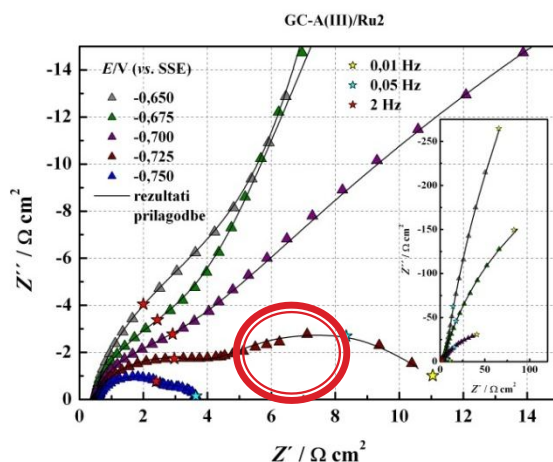
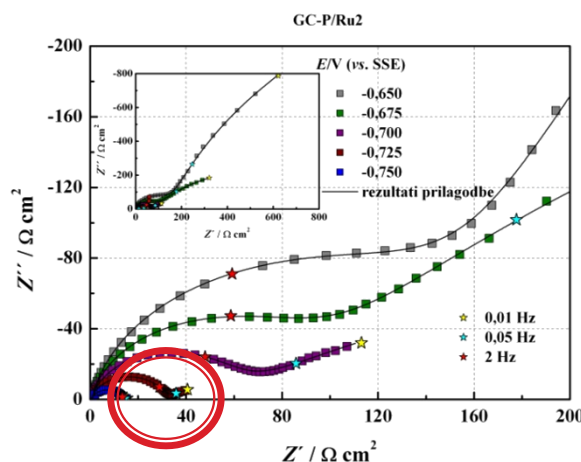


Electrode	E/ V vs.SSE	$R_{\text{upd}}/$ $\Omega \text{ cm}^2$	$Q_{\text{upd}}/$ $\Omega^{-1} \text{ s}^{\alpha} \text{ cm}^{-2}$	α
GC-P/Ru2	-0.55	1361	2.6×10^{-3}	0.78
	-0.60	528	5.4×10^{-3}	0.85
GC-A(III)/Ru2	-0.55	330	7.4×10^{-3}	0.86
	-0.60	61	17.8×10^{-3}	0.91

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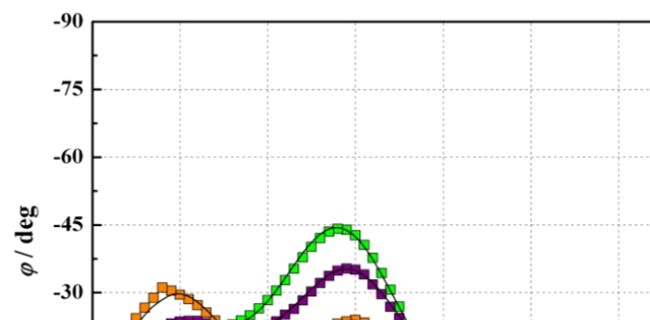
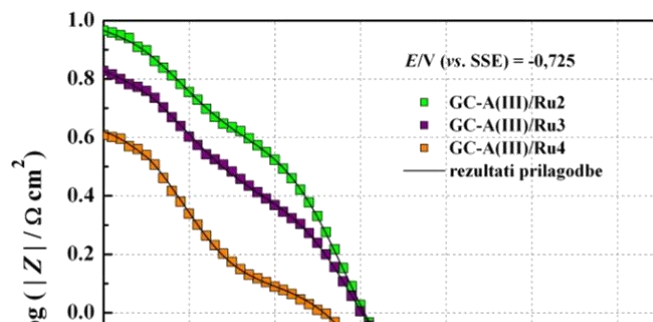
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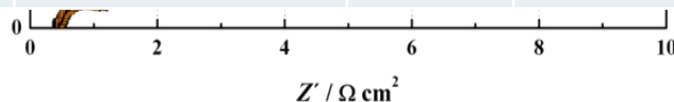
Electrode	$R_{ct}/\Omega \text{ cm}^2$	$Q_{ad}/\Omega^{-1} \text{ s}^{\alpha} \text{ cm}^{-2}$	α	$R_{ad}/\Omega \text{ cm}^2$	$R_{HER}/\Omega \text{ cm}^2$
GC-P/Ru2	31	251×10^{-3}	0.44	*38	69
GC-A(III)/Ru2	3.6	305×10^{-3}	0.76	6.4	10
GC-A(IV)/Ru2	*8	* 553×10^{-3}	0.76	*7	15
* $rsd < 15\%$					

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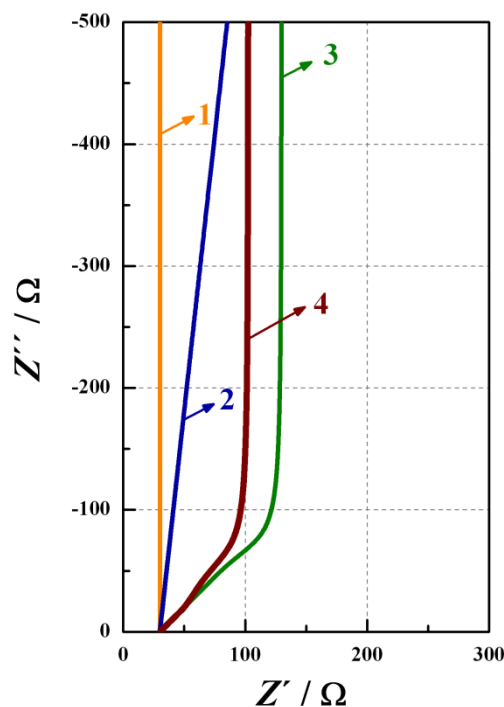
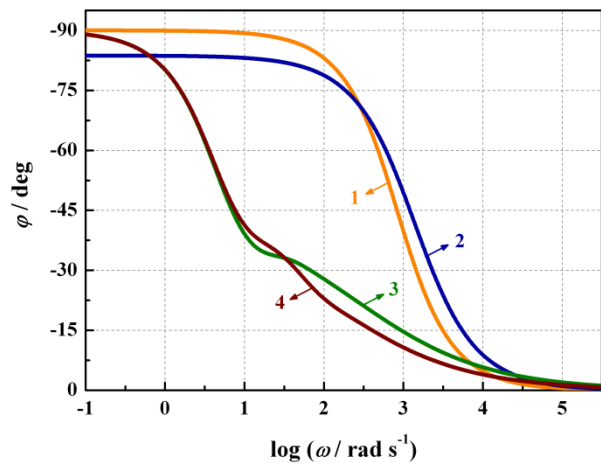
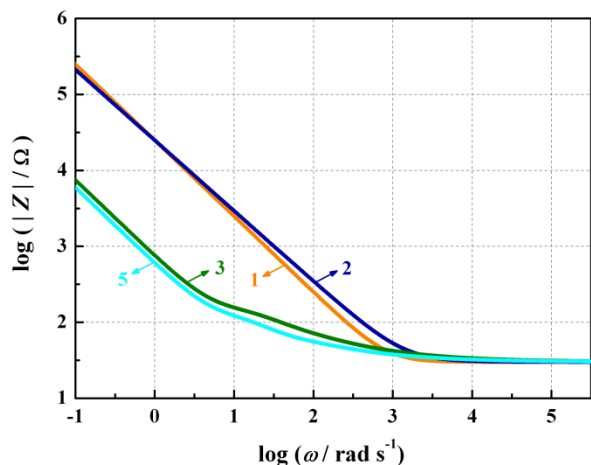
Electrode	$R_{ct}/\Omega \text{ cm}^2$	$Q_{ad}/\Omega^{-1} \text{ s}^\alpha \text{ cm}^{-2}$	α	$R_{ad}/\Omega \text{ cm}^2$	$R_{HER}/\Omega \text{ cm}^2$
GC-A(III)/Ru2	3.6	305×10^{-3}	0.76	6.4	10.0
GC-A(III)/Ru3	2.2	371×10^{-3}	0.77	4.8	7.0
GC-A(IV)/Ru4	0.82	651×10^{-3}	0.82	3.9	4.7
Pt/Ru	0.60	534×10^{-3}	0.78	2.1	2.7





THANK YOU FOR YOUR ATTENTION !





1

$$Z(i\omega) = \frac{1}{i\omega C}$$

2

$$Z_{CPE}(i\omega) = \frac{1}{Q(i\omega)^\alpha}$$

3

$$Z_{TL}(i\omega) = \sqrt{\frac{R_W}{i\omega C_{LF}}} \coth \sqrt{\frac{i\omega}{\omega_L}}$$

4

$$Z(i\omega) = \left((Z(i\omega)_{\Sigma_{TL}})^{-1} \right)^{-1}$$



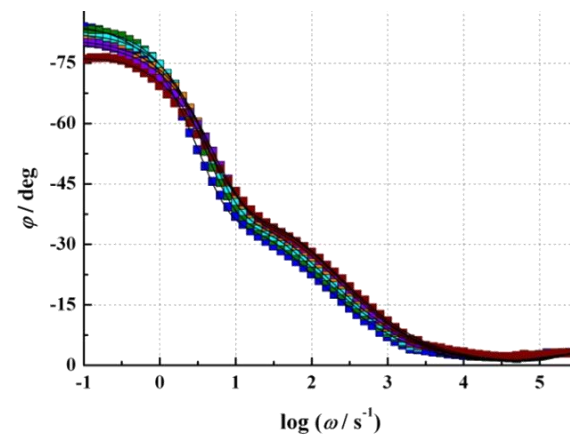
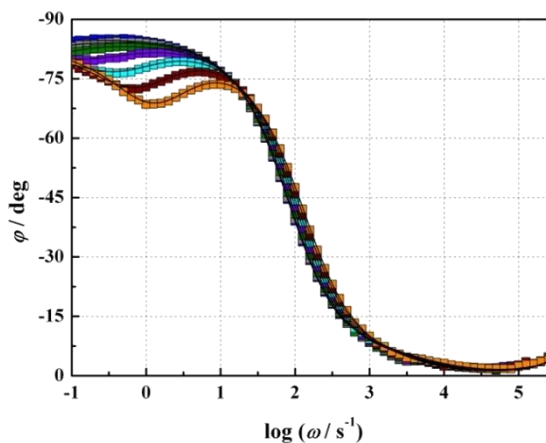
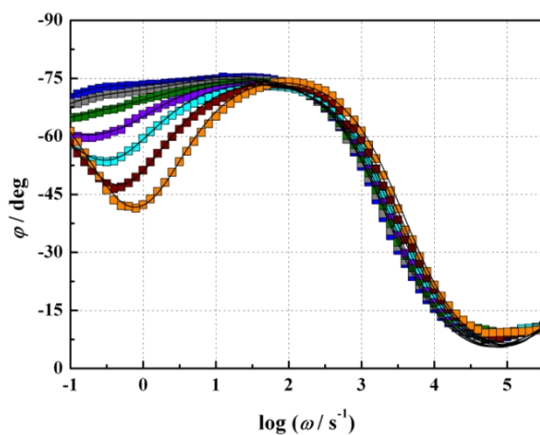
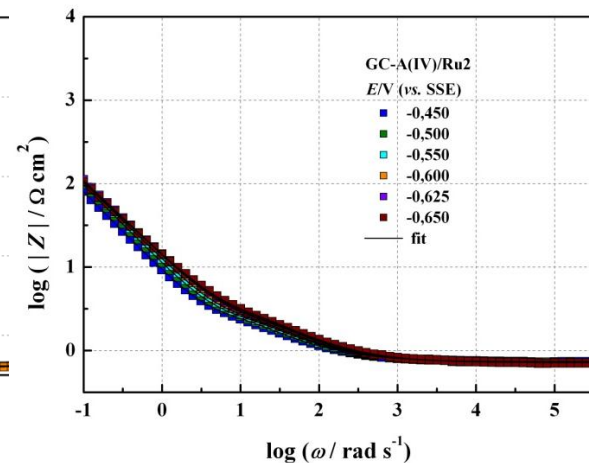
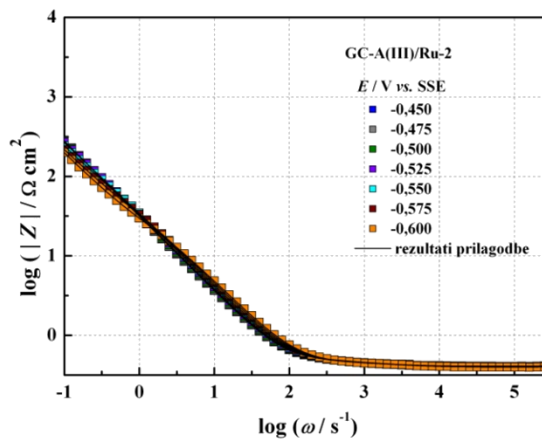
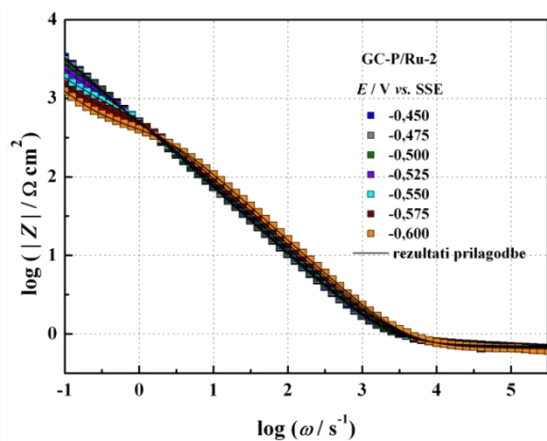
$E = -0.725 \text{ V vs. SSE}$

Electrode	$R_{ct}/\Omega \text{ cm}^2$	$Q_{ad}/\Omega^{-1} \text{ s}^\alpha \text{ cm}^{-2}$	α	$R_{ad}/\Omega \text{ cm}^2$	$R_{HER}/\Omega \text{ cm}^2$
GC-A(III)/Ru2	3.6	305×10^{-3}	0.76	6.4	10.0
GC-A(III)/Ru3	2.2	371×10^{-3}	0.77	4.8	7.0
GC-A(IV)/Ru4	0.82	651×10^{-3}	0.82	3.9	4.7
Pt/Ru	0.60	534×10^{-3}	0.78	2.1	2.7

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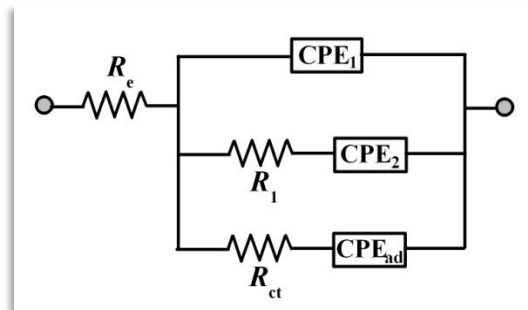
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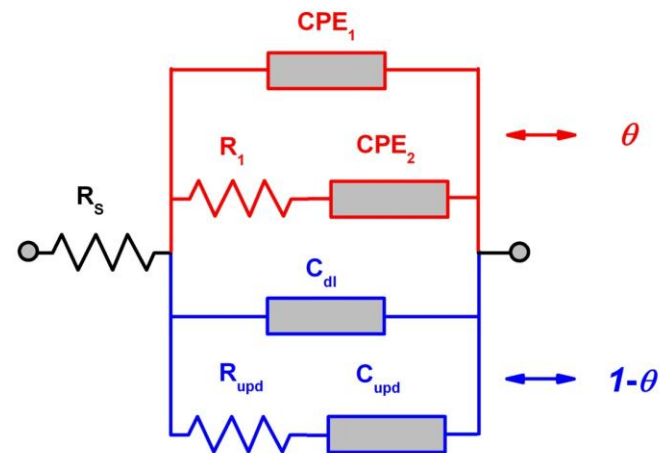
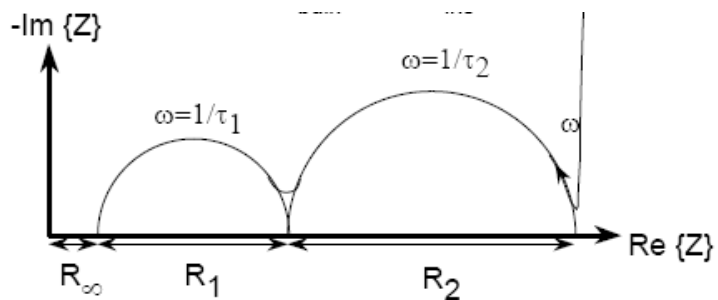
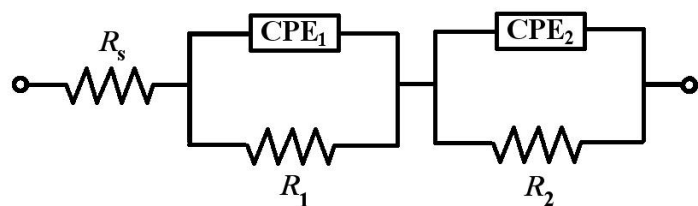


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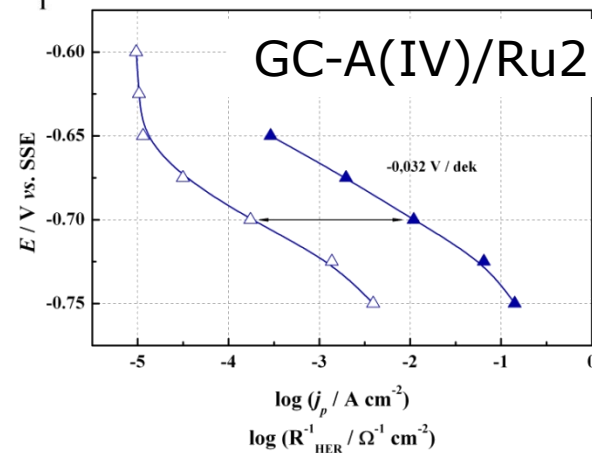
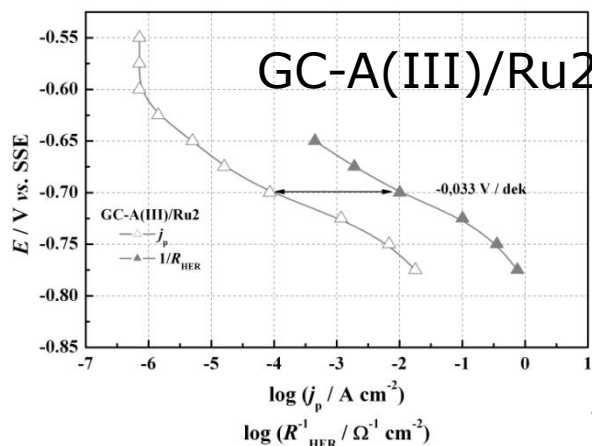
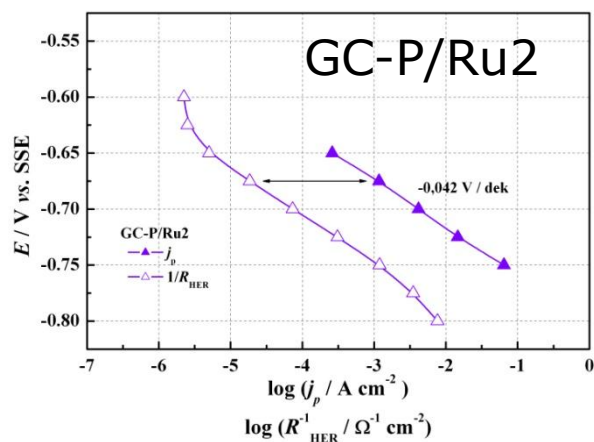




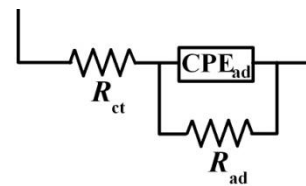
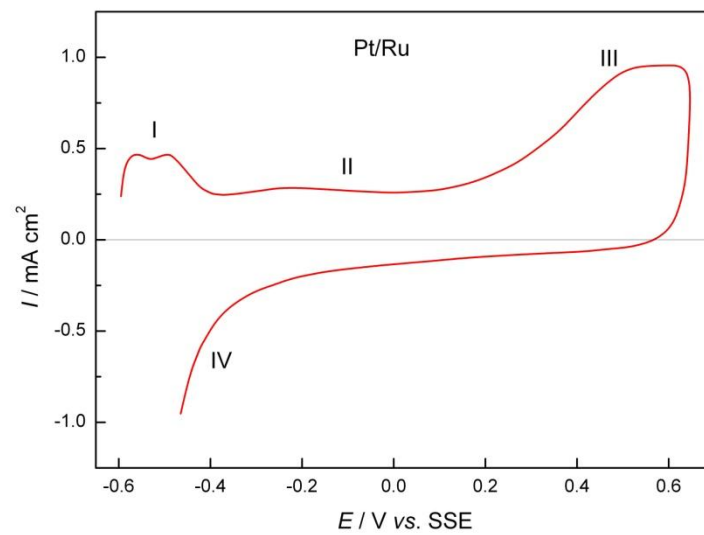
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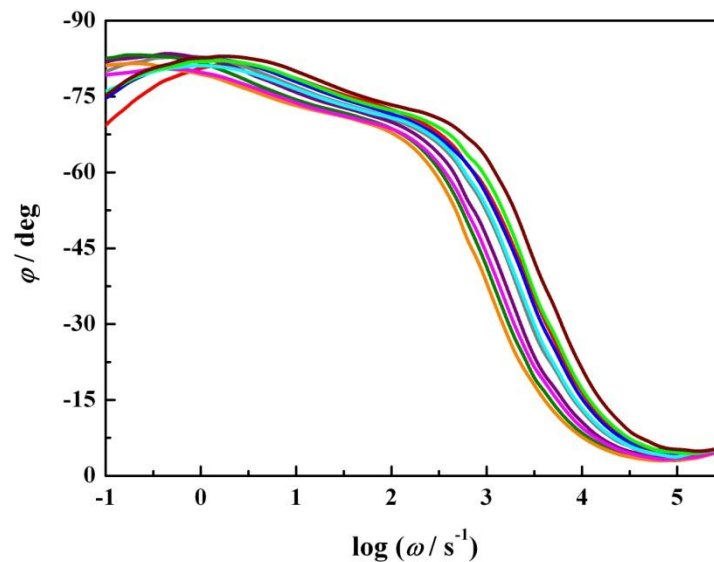
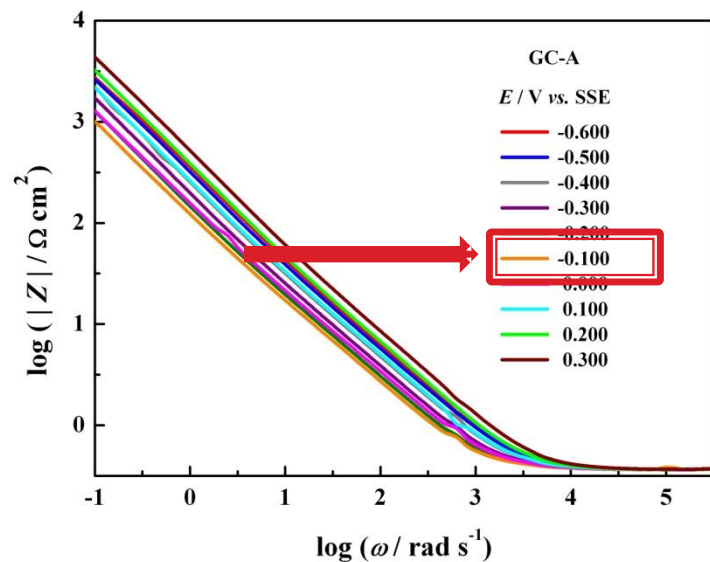




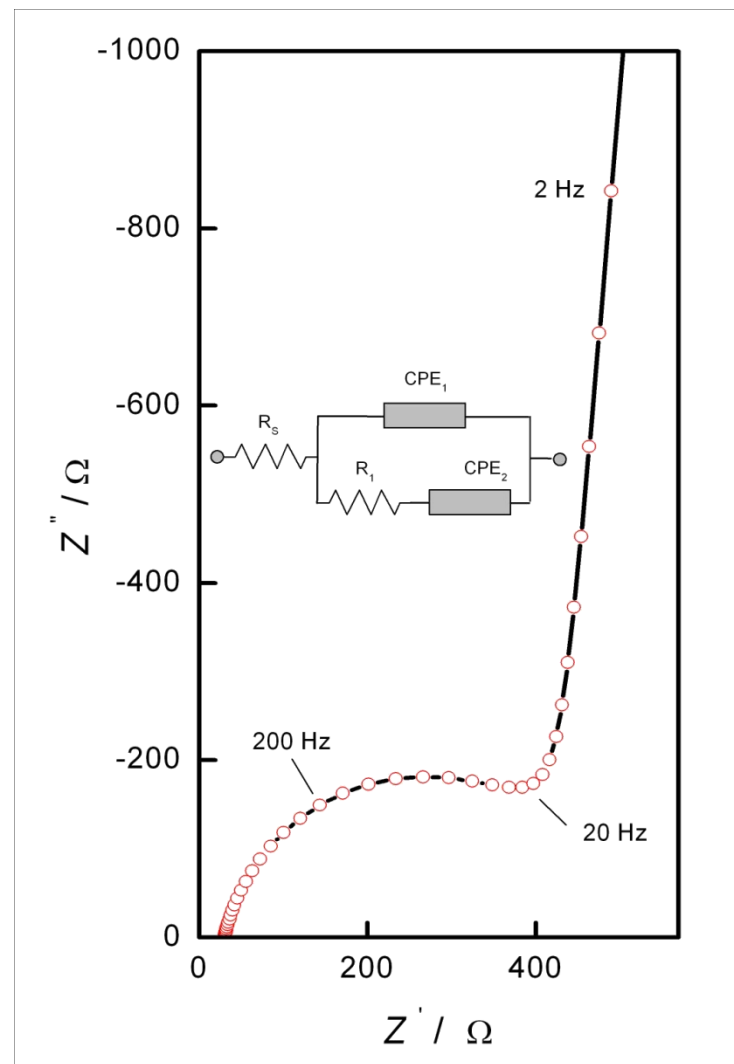
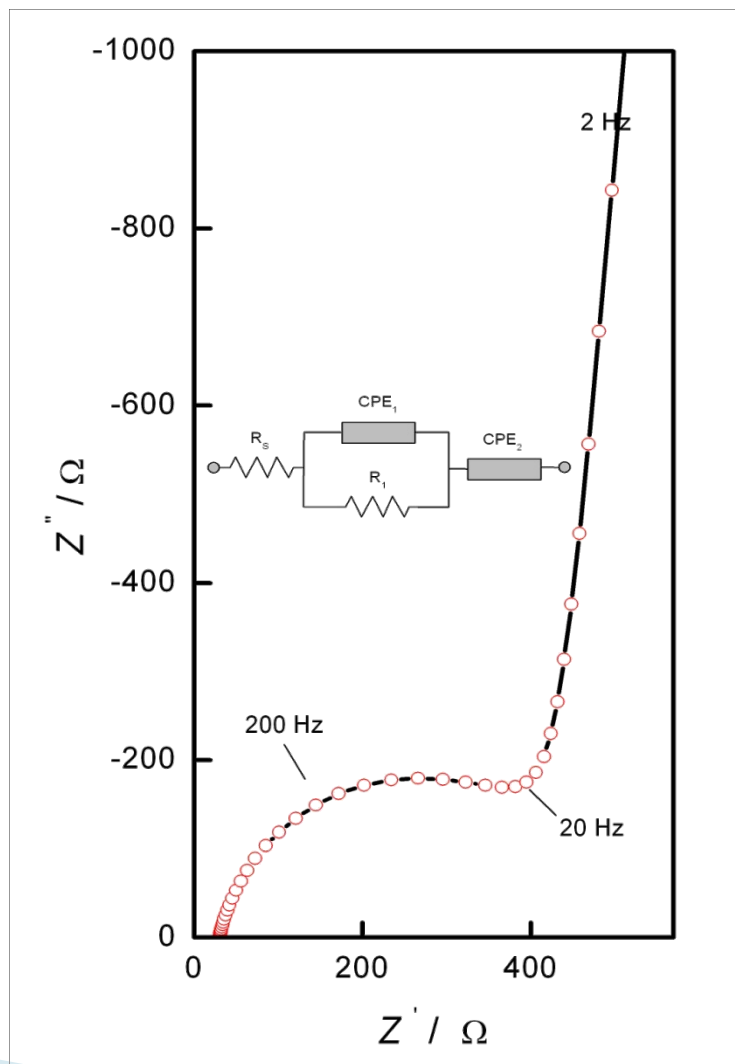


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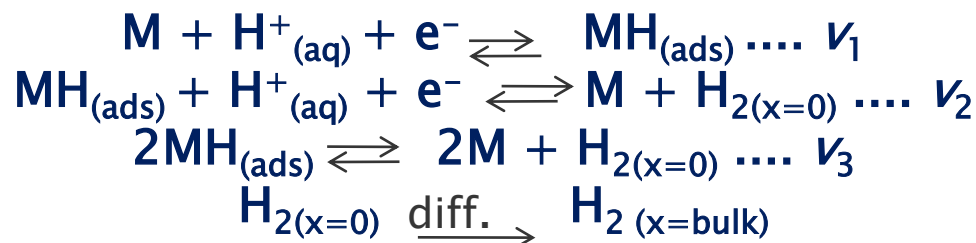


Fourth Regional Symposium on Electrochemistry
South-East Europe, RSE-SEE 4
Ljubljana, Slovenia, May 26-30, 2013



REACTION OF HER

Kinetics and impedance equation at metal surfaces:



$$\begin{aligned}
 r_e &= -I_f/F = -(\nu_1 + \nu_2) \\
 r_\theta &= (q/F) d\theta/dt = \nu_1 - \nu_2 - 2\nu_3 \\
 r_c &= J_{\text{diff}(\text{x}=0)} = -D(dc/dx)_{\text{x}=0} = \\
 &\quad \nu_2 + \nu_3
 \end{aligned}$$

$$\begin{aligned}
 \Delta I_f &= a_1 \Delta E + a_2 \Delta \theta + a_3 \Delta c_0 \\
 qi\omega \Delta \theta &= b_1 \Delta E + b_2 \Delta \theta + \\
 b_3 \Delta c_0 \quad FM(\omega) \Delta c_0 &= d_1 \Delta E + \\
 &\quad d_2 \Delta \theta + d_3 \Delta c_0
 \end{aligned}$$

$$a_1 = -F(\partial r_e / \partial E)_{\theta, c}$$

$$a_2 = -F(\partial r_e / \partial \theta)_{E, c}$$

$$a_3 = -F(\partial r_e / \partial c_0)_{E, \theta}$$

$$Y_f(i\omega) = Z_f^{-1}(i\omega) = \Delta I_f(i\omega) / \Delta E(i\omega) = a_1 + a_2 \Delta \theta / \Delta E + a_3 \Delta c_0 / \Delta E$$

$$Y_f(i\omega) = a_1 + (a_2 b_1 Q + a_2 b_3 d_1 + a_3 d_1 P + a_3 b_1 d_2) / (PQ - b_3 d_2)$$

$$b_1 = F(\partial r_\theta / \partial E)_{\theta, c}$$

$$b_2 = F(\partial r_\theta / \partial \theta)_{E, c}$$

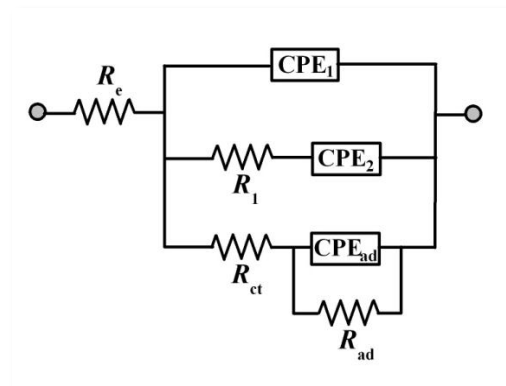
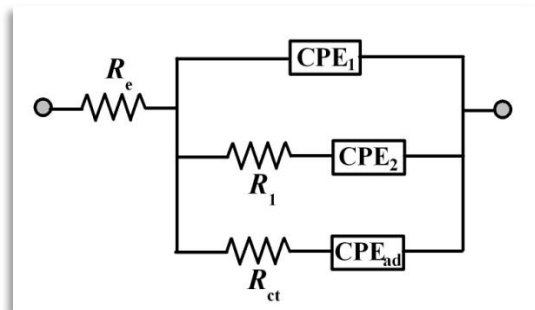
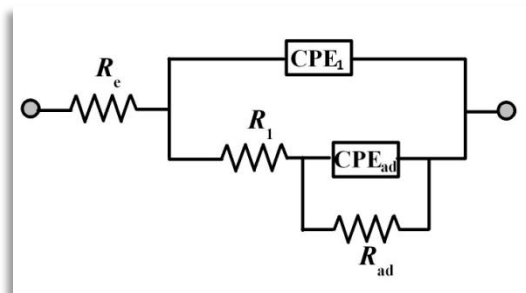
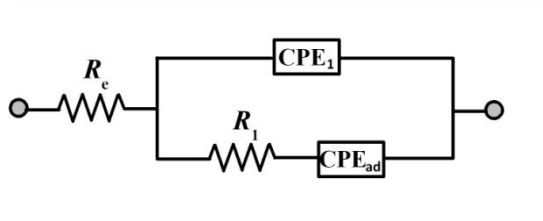
$$b_3 = F(\partial r_\theta / \partial c_0)_{E, \theta}$$

$$\begin{aligned}
 P &= qi\omega - b_2 \\
 Q &= FM(i\omega) - d_3
 \end{aligned}$$

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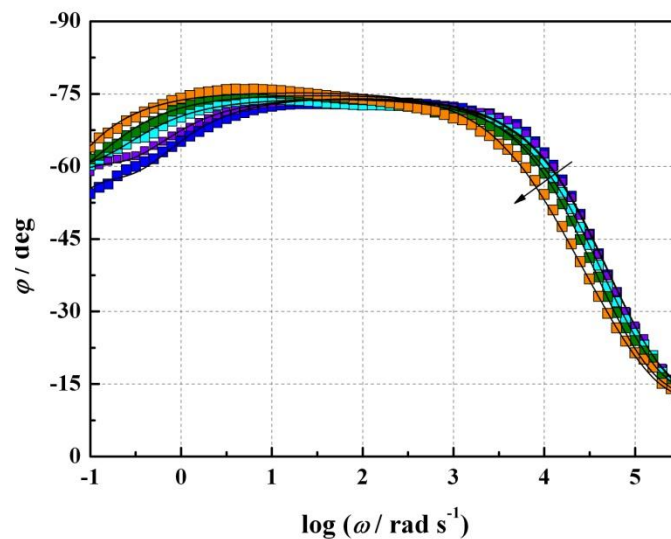
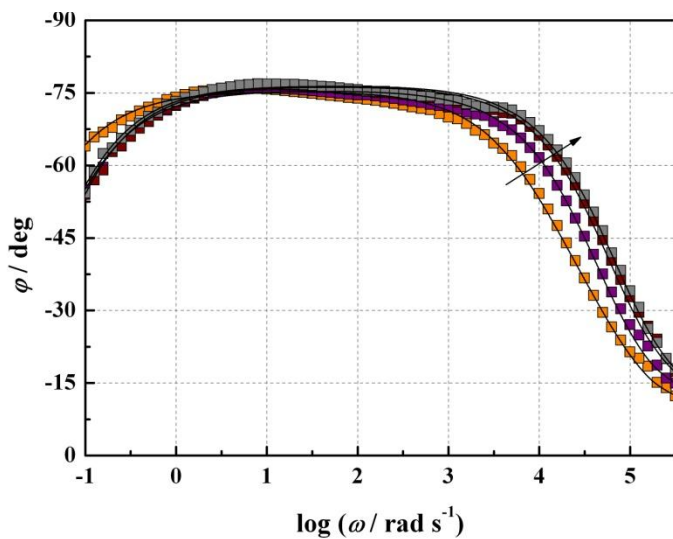
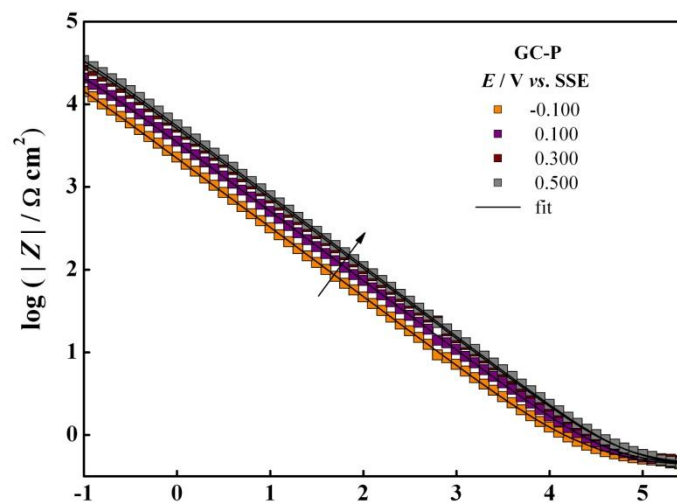
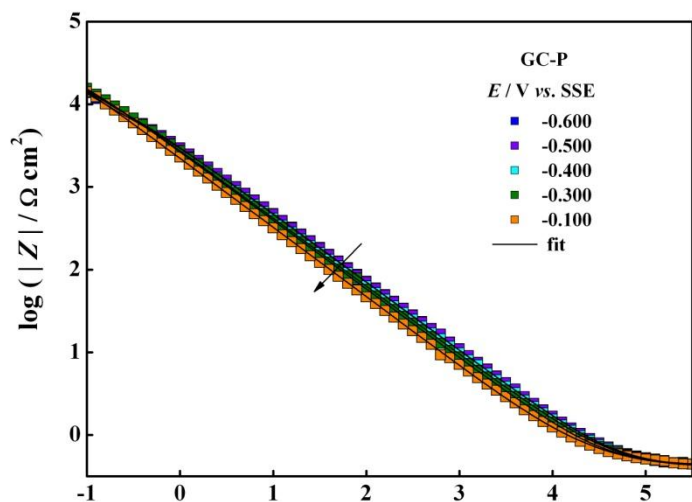


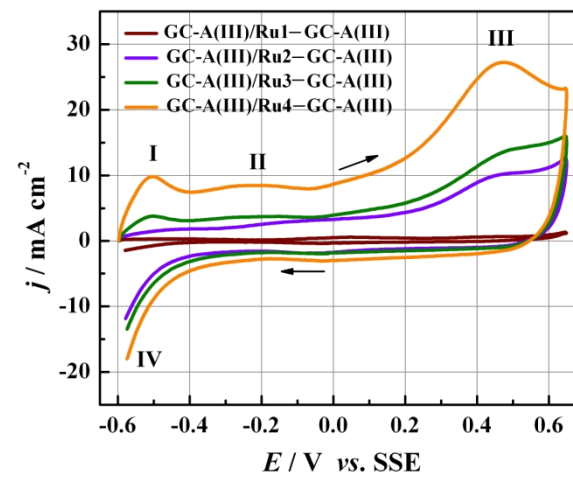
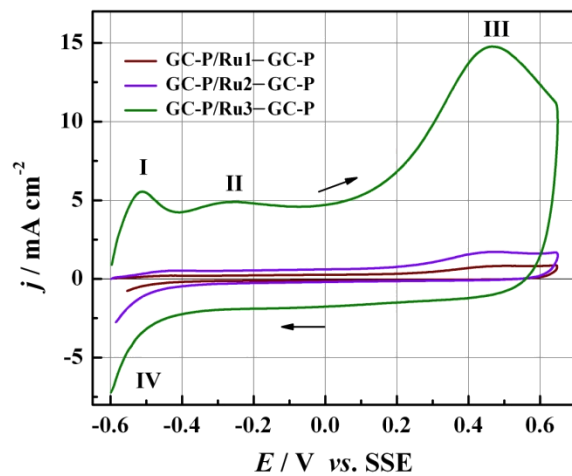


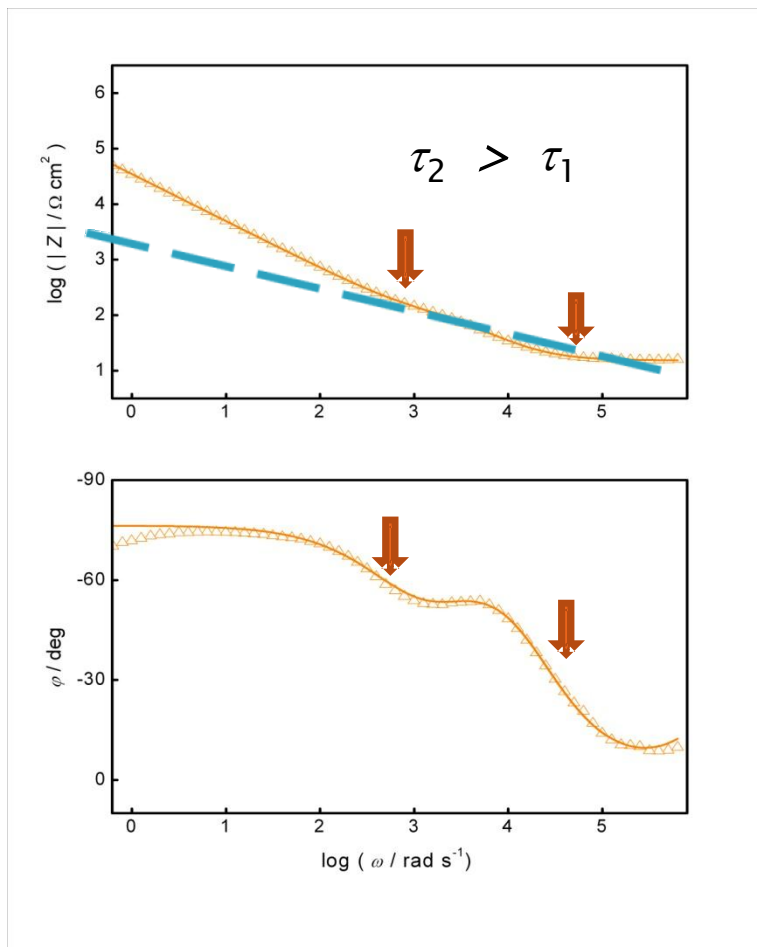
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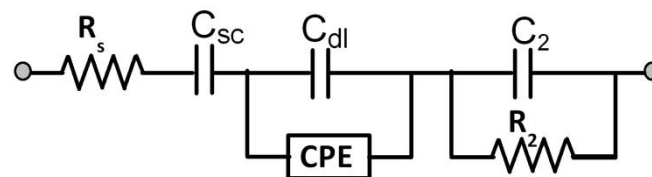
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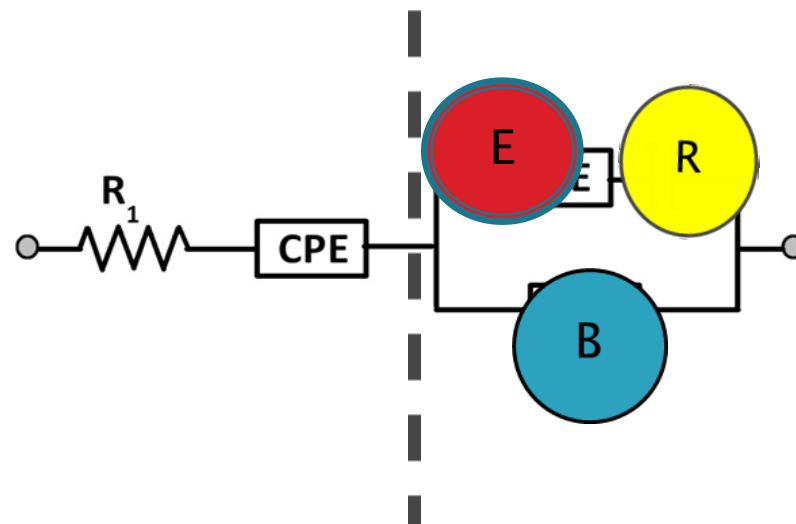




Anodically treated boron-doped diamond/ H_2SO_4



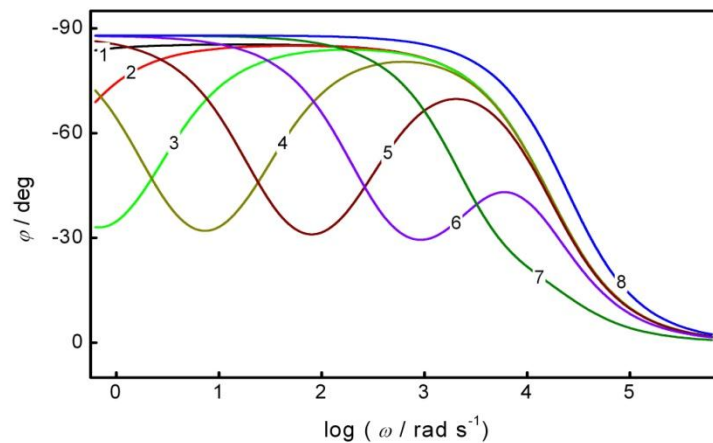
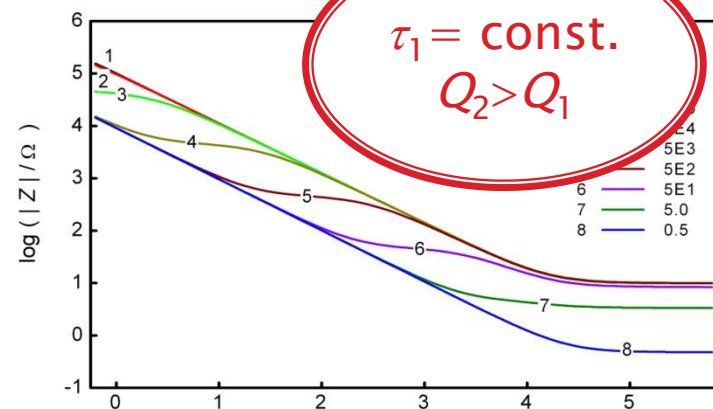
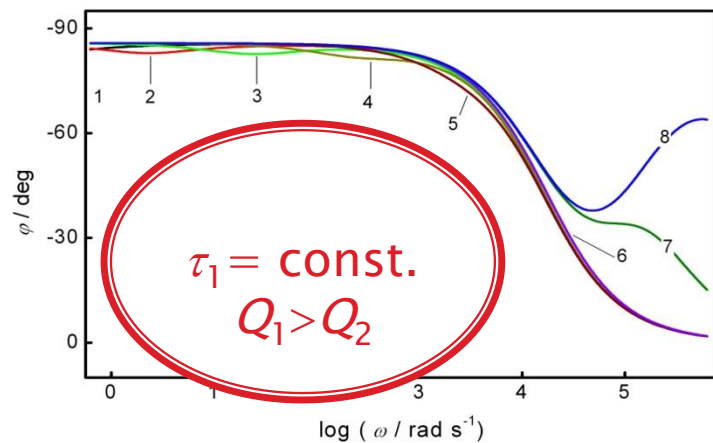
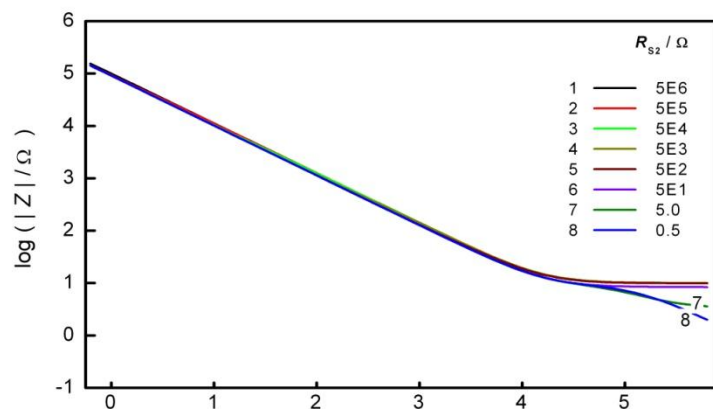
Polished and oxidized GC/ KCl



Diffuse part

Compact part

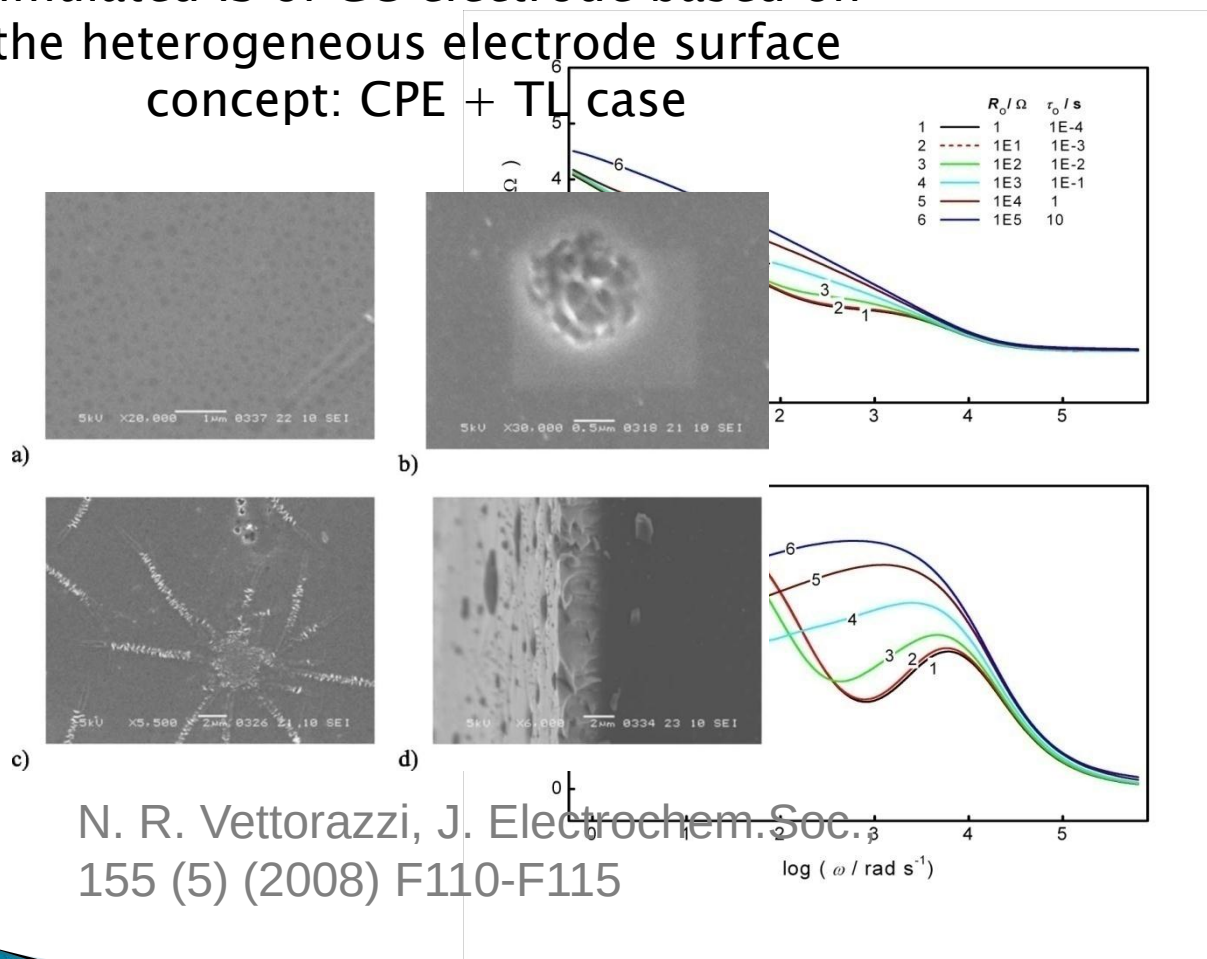
Simulated IS of GC electrode based on the heterogeneous electrode surface concept: Two different CPEs case



$$Z(i\omega) = \left\{ \left[R_{s1} + \frac{1}{Q_1(i\omega)^{\alpha_1}} \right]^{-1} + [R_{s2} + R_0(i\omega\tau_0)^{-p} \coth(i\omega\tau_0)^p]^{-1} \right\}^{-1}$$

Simulated IS of GC electrode based on
the heterogeneous electrode surface

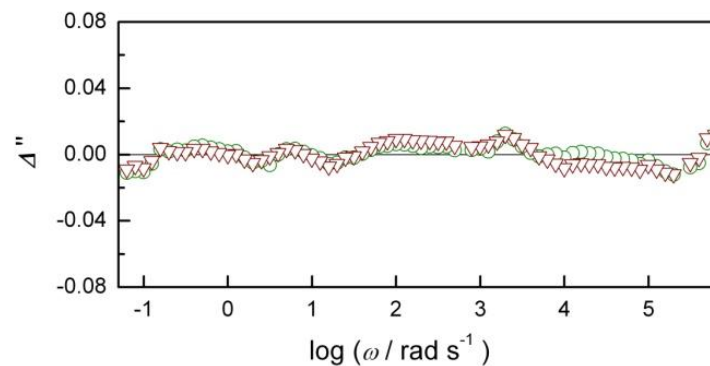
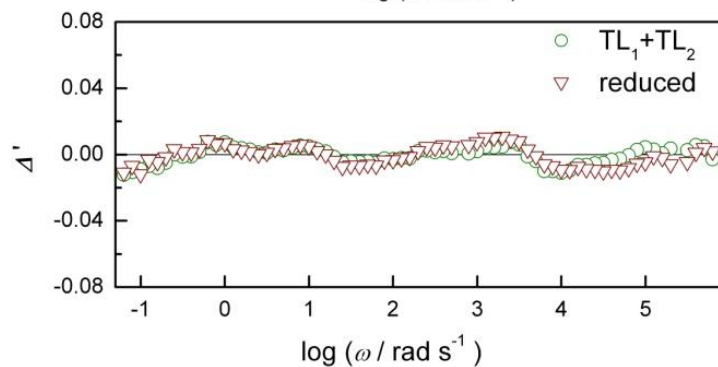
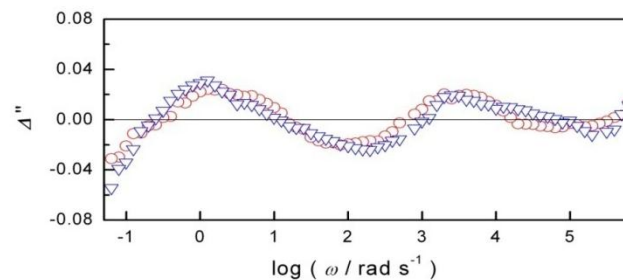
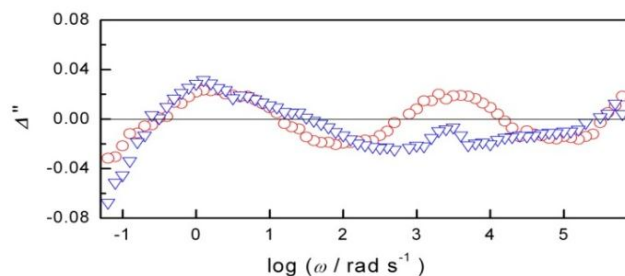
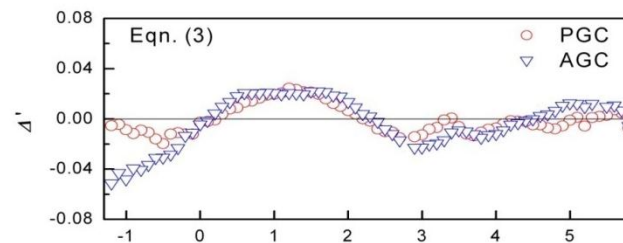
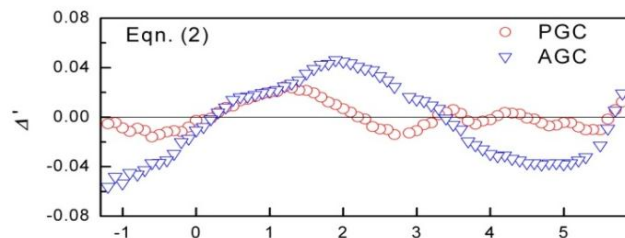
concept: CPE + TL case



N. R. Vettorazzi, J. Electrochem. Soc.
155 (5) (2008) F110-F115

$$\Delta'_k = \frac{Z'_k(\text{exp}) - Z'_k(\text{cal})}{|Z_k(\text{exp})|}$$

$$\Delta''_k = \frac{Z''_k(\text{exp}) - Z''_k(\text{cal})}{|Z_k(\text{exp})|}$$

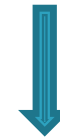


General Procedure for Analysis of Impedance Spectra

- **Experiment**
- **Regulation**
- **Small signal**
- **Measurements**



Theory
Matem. eqns.
Linearization
Calculations



➤ **Electrical Equivalent Circuits**

Comparison ➔ Choice ➔ Interpretation