BS-ERA.NET

Networking on Science and Technology in the Black Sea Region

SEVENTH FRAMEWORK PROGRAMME

Universitatea Politehnica Timişoara

P-ţa Victoriei nr. 2
RO 300006 - Timişoara
Tel: +4 0256 403000
Fax: +4 0256 403021
rector@rectorat.upt.ro
www.upt.ro

Task II.1. Analysis of available data on the composition of the Black Sea waters

Meeting name: 3rd Regular meeting of the international team of HYSUFCEL

Name, role in the project: Assoc. Prof. Andrea Kellenberger, team member

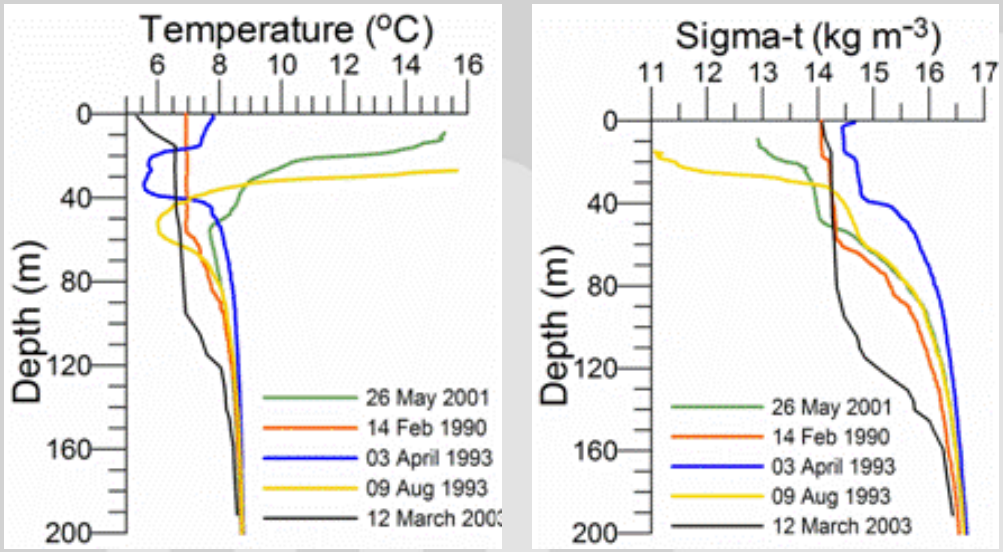
Institution: University Politehnica Timisoara

Timisoara, 05.11.2013

II.1.1. Characteristics of the Black Sea waters

Vertical stratification of the Black Sea waters into two zones:

- ***oxic layer:*** an upper layer between 0 - 100 m depth with low density and low salinity
- ***anoxic layer:*** a bottom layer below 150 m depth with high density and high salinity
- ***suboxic layer:*** an intermediate zone, with minimal concentrations of O_2 and H_2S



The physical and chemical properties of the Black Sea waters show extreme vertical variations depending on stratification.

Fig. 2. Vertical variation of temperature and conventional density depending on the season [3].

T. Oguz (Ed.), *State of the Environment of the Black Sea (2001 - 2006/7)*, Publications of the Commission on the Protection of the Black Sea against Pollution (BSC) 2008-3, Istanbul, Turkey.

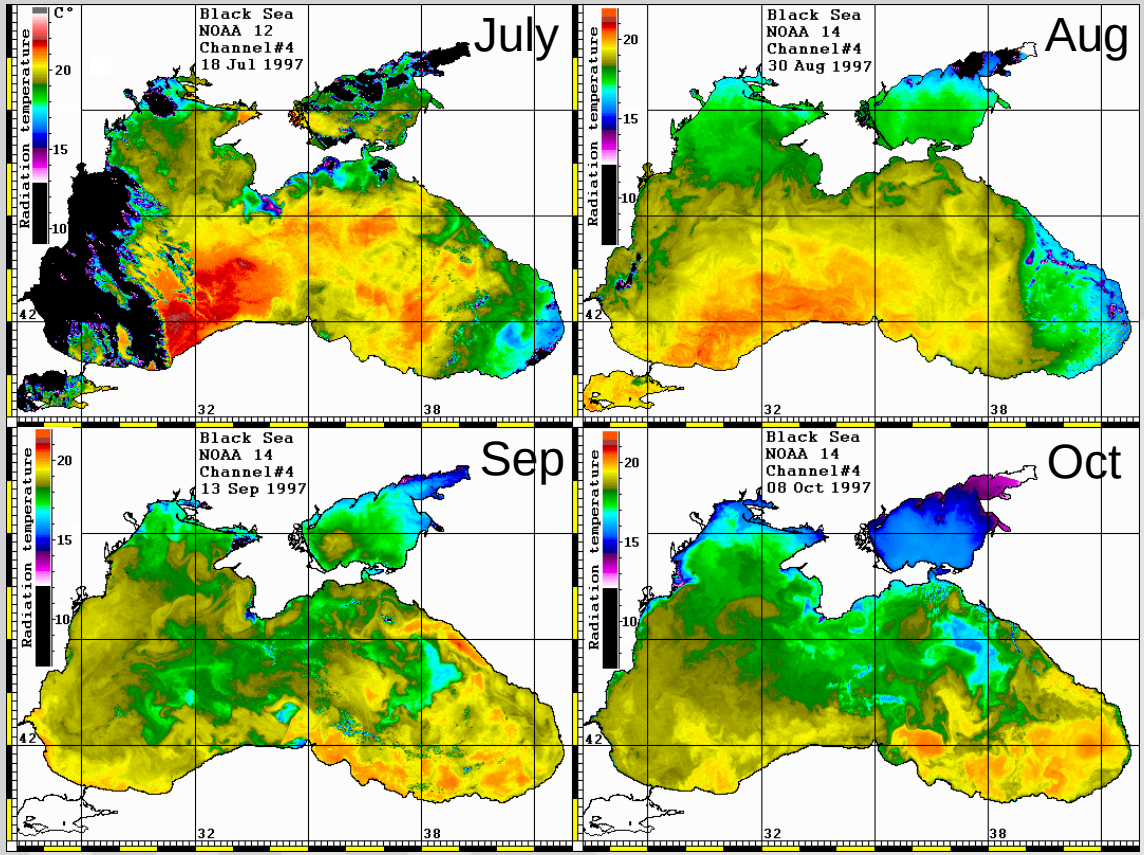
Oxic layer - salinity

Fig. 3. Variation profile of surface salinity in July [5].

Salinity from 17.1 to 18 ‰, except areas near the mouths of major tributaries, (Danube, Dniester and Dnieper) where salinity values are lower due to important contribution of freshwaters.

http://www.blackseaweb.net/maps/welcome.html - accessed 19.11.2012.

Oxic layer – surface water temperature



Winter:
-0.5°C in the north-west
9-10°C in the south-east

Summer:
surface water: 23-26°C
50 and 75 m depth: 7°C

The minimum temperature is not at the basin bottom, but in the layer located between 50-60 m and 80-90 m depth.

Fig. 4. Distribution map of surface temperature of the Black Sea depending on the season [7,8].

http://web.deu.edu.tr/atiksu/ana09/ana09.html - accessed 15.11.2012.
http://www.blackseaweb.net/satellite/welcome.html - accessed 15.11.2012.

Oxic layer – oxygen concentration

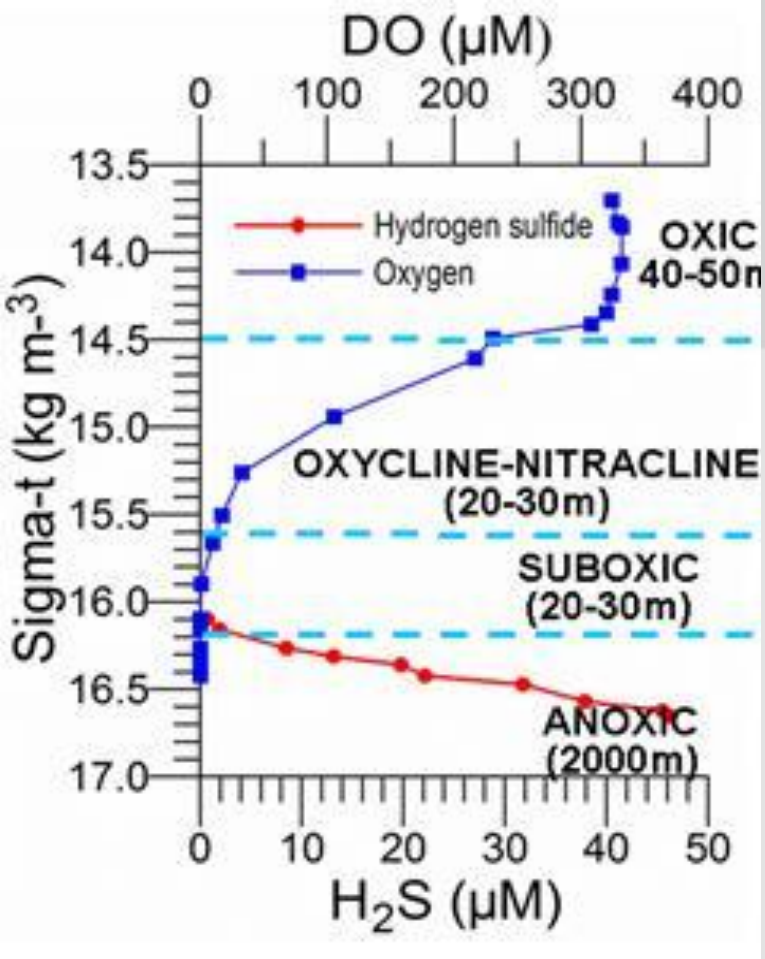
• Seasonal variations in oxygen concentration are within very large limits between 250-450 μM.

• The highest values of dissolved oxygen concentration are recorded at the end of February, corresponding to the lowest values of surface water temperatures.

• The temperature increase of the surface waters which begins in March, leads to a decrease of the oxygen concentration in the sub-surface layer down to 250 μM.

• Then, depending on the activity of phytoplankton in the summer months, oxygen concentration increases again above 350 μM.

Suboxic layer



The existence of suboxic layer can not be predicted theoretically, given the inverse relationship between oxygen and hydrogen sulfide concentrations. However the suboxic layer exists, with thickness ranging from 20 to 50 m. In the suboxic layer oxygen and hydrogen sulfide concentrations are extremely low, i.e. $O_2 < 10$ μM and $H_2S < 1$ μM.

Fig. 6. Concentration profiles of O_2 and H_2S versus conventional density in the center of the eastern gyre of the Black Sea during May 2003 [12].

http://www.ocean.washington.edu/cruises/Knorr2003/index.html- accessed 20.11.2012.

Anoxic layer

- low O_2 concentrations and high conc. of H_2S and sulfides.

- H_2S first occurs at depths of 100 m and its concentration increases sharply in the water column up to 500 m depth. Below this depth its concentration increases much slower, reaching a value of 400 μM at a depth of 2200 m.

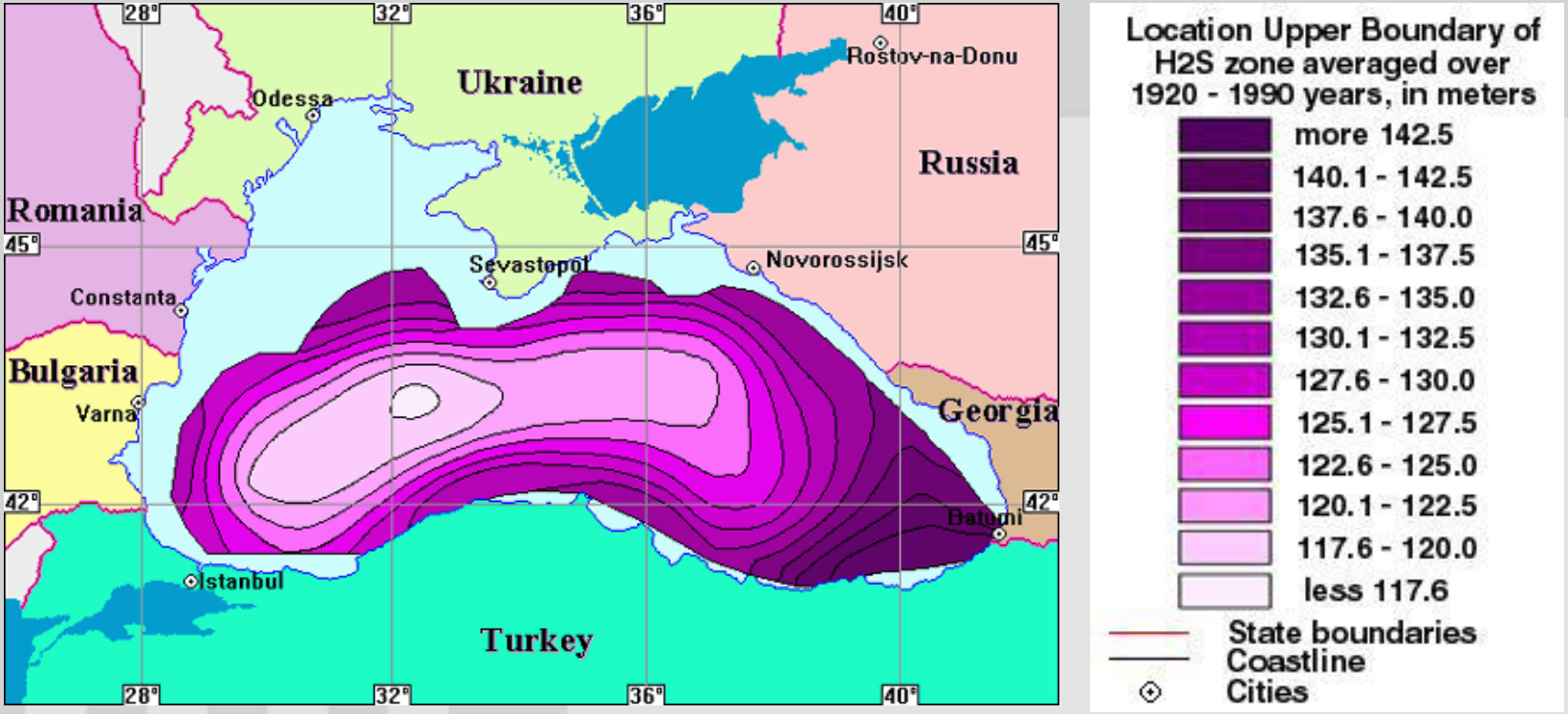


Fig. 10. Location of the upper boundary of H_2S zone averaged over 1920's-1980's [5].

http://www.blackseaweb.net/maps/welcome.html - accessed 19.11.2012.

II.1.2. Composition, chemical and physical properties of seawater

Seawater salinity (S) = the total amount of salt in grams dissolved in one kilogram of sea water, considering that bromide and iodide are expressed as chloride, carbonates are converted into oxides and organic substances are fully oxidized.

Chlorinity = the total amount of chlorides, bromides and iodides, expressed in grams contained in one kilogram of sea water, considering that bromide and iodide are expressed as chloride. Chlorinity can be easily determined by titration with silver nitrate.

Seawater density ρ is generally expressed as relative density, relative to the density of distilled water at 4°C, which is equal to unity.

Conventional density σ often used in practice, represents the difference between the density of sea water and fresh water.

$$\sigma = (\rho - 1) \times 1000$$

Table 2. Concentrations of major ions in seawater [26]

Major ion	Salinity S = 35.000‰			
	mg kg S^{-1}	g kg^{-1}	mmol kg^{-1}	mM*
Na^+	308.0	10.781	468.96	480.57
K^+	11.40	0.399	10.21	10.46
Mg^{2+}	36.69	1.284	52.83	54.14
Ca^{2+}	11.77	0.4119	10.28	10.53
Sr^{2+}	0.227	0.00794	0.0906	0.0928
Cl^-	552.94	19.353	545.88	559.40
SO_4^{2-}	77.49	2.712	28.23	28.93
HCO_3^-	3.60	0.126	2.06	2.11
Br^-	1.923	0.0673	0.844	0.865
$B(OH)_3$	0.735	0.0257	0.416	0.426
F^-	0.037	0.00130	0.068	0.070
Total		35.169		

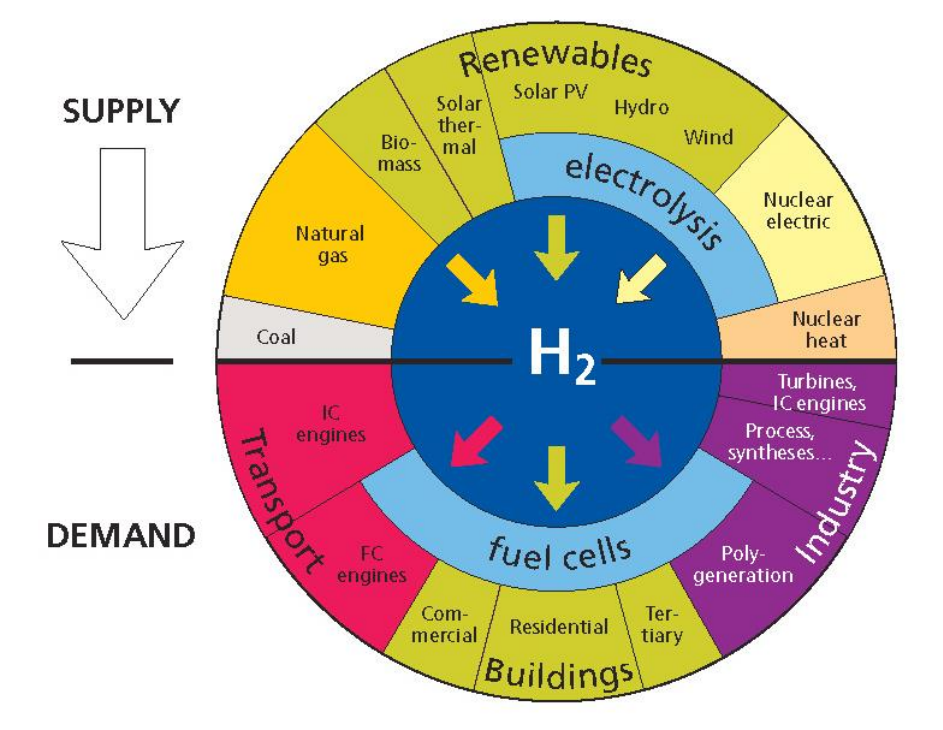
M.E.Q. Pilson, *An introduction to the chemistry of the sea*, Prentice-Hall, New York, 1998.

II.1.3. Composition of artificial seawater

A. Gravimetric salts					
Compound	Molar mass (g mol^{-1})	quantity (g kg^{-1} solution)		ion	conc. g kg^{-1}
				Cl^-	19.353
NaCl	58.44	23.926		Na^+	10.765
Na_2SO_4	142.04	4.008		SO_4^{2-}	2.711
KCl	74.56	0.677		K^+	0.387
$NaHCO_3$	84.00	0.196		HCO_3^-	0.142
KBr	119.01	0.098		Br^-	0.066
H_3BO_3	61.83	0.026		$B(OH)_3$	0.026
NaF	41.99	0.003		F^-	0.001
B. Volumetric salts					
Compound	Molar mass (g mol^{-1})	nr. of moles	Stock solution	ρ ($g\ mL^{-1}$)	ion	conc. g kg^{-1}
$MgCl_2 \cdot 6H_2O$	203.33	0.05327	1.0 M	1.071	Mg^{2+}	1.295
$CaCl_2 \cdot 2H_2O$	147.03	0.01033	1.0 M	1.085	Ca^{2+}	0.414
$SrCl_2 \cdot 6H_2O$	266.64	0.00009	0.1 M	1.013	Sr^{2+}	0.008
C. Distilled water up to 1000.00 g						

Task II.3. Enhancement of hydrogen evolution reaction on platinum cathode by proton carriers

Hydrogen economy



http://hho-hydrogen-energy.com/html/abouthydrogen.html

(1) **hydrogen production** from water using non-renewable energy sources (coal, atomic energy, thermonuclear energy) and renewable energy sources (sun, hydro, wind, currents, tides, biomass).

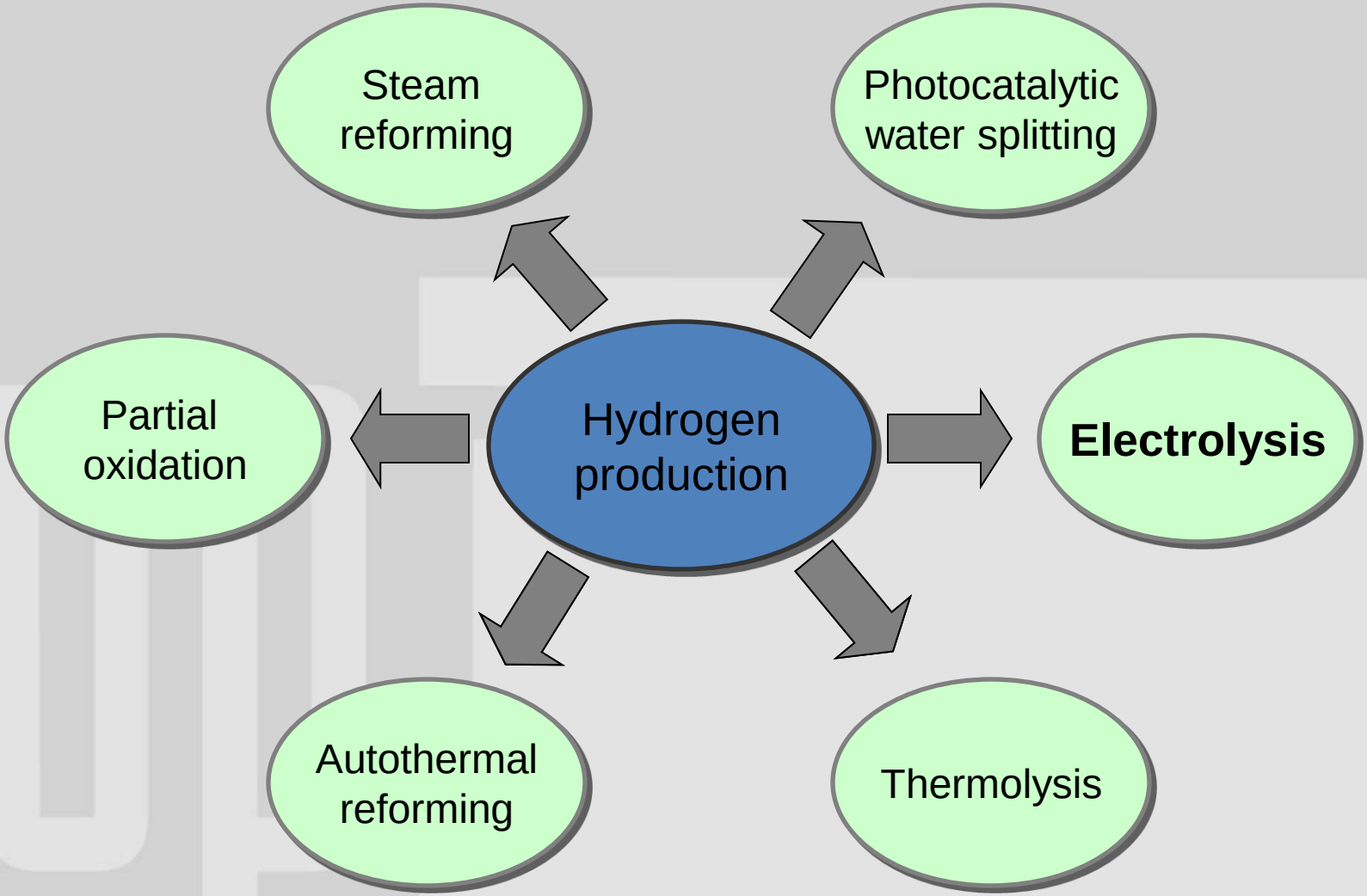
(2) **hydrogen delivery**, transportation and storage.

(3) **hydrogen utilization** in industry, transport (land, water and air) and home.

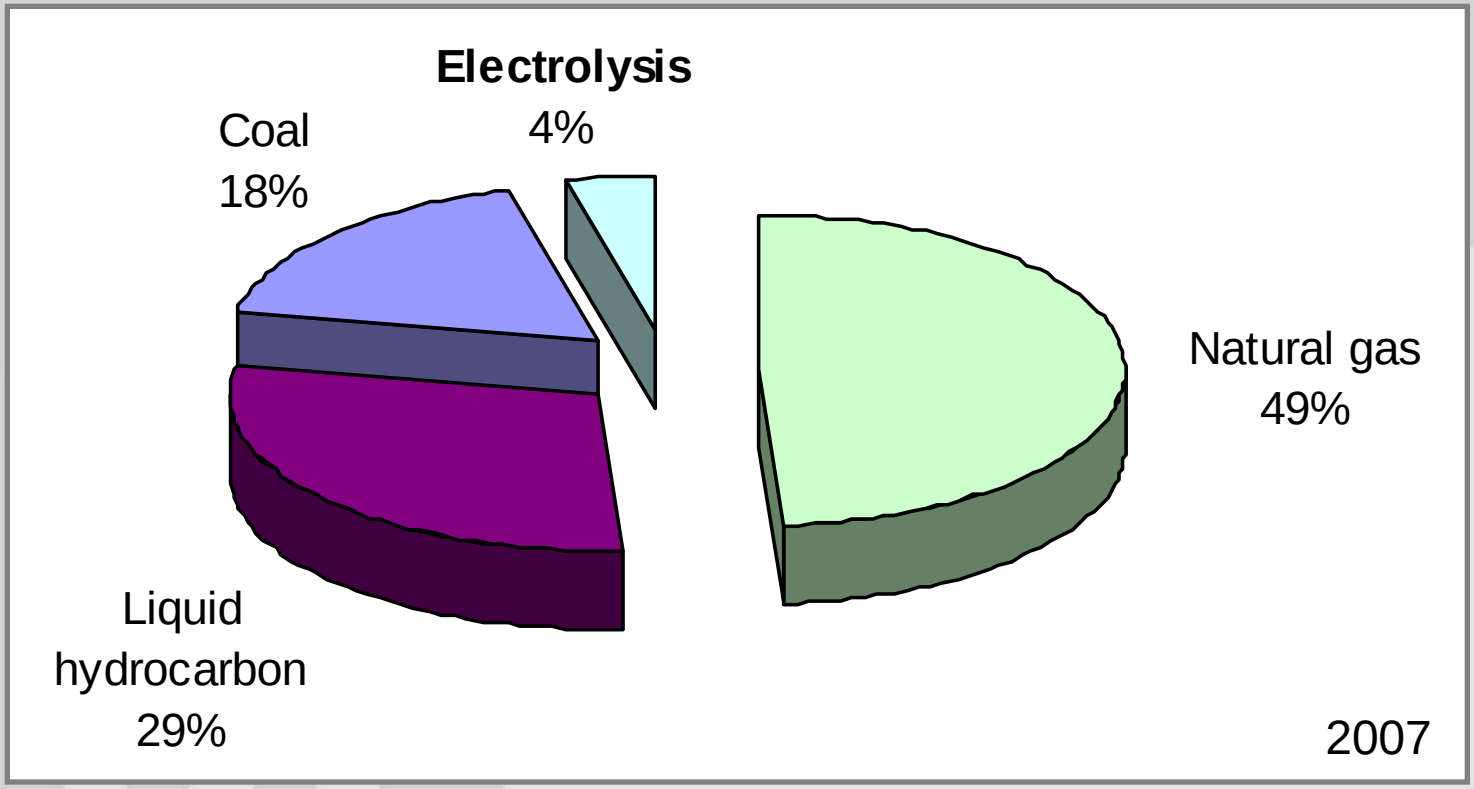
(4) problems of **material reliability** and system safety.

V.A.Goltsov, T.N. Veziroglu, L.F. Goltsova, Hydrogen civilization of the future – A new conception of the IAHE, *Int. J. Hydrogen Energy* 31 (2006) 153-159.

Hydrogen production

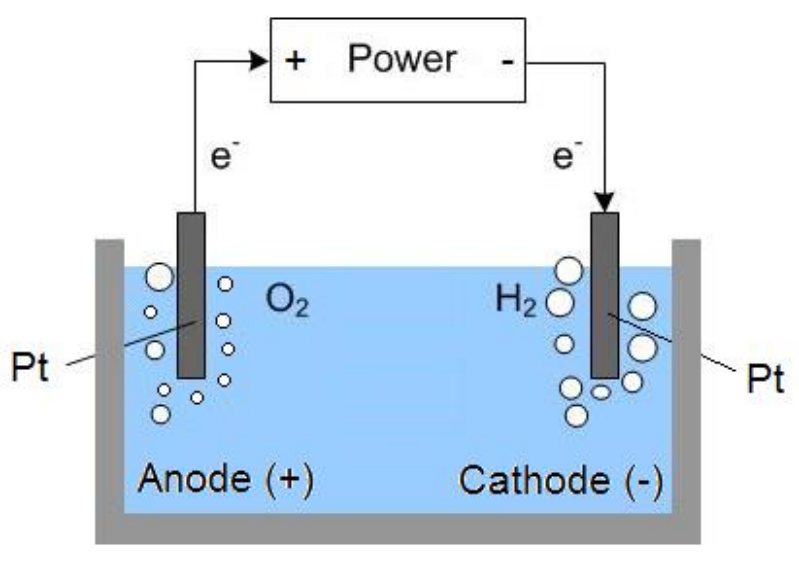


Hydrogen production sources



Water electrolysis

1800: William Nicholson and Anthony Carlisle used the battery invented by Alessandro Volta for the electrolysis of water.



A(+): $2\ H_2O \rightarrow O_2 + 4\ H^+ + 4e^-$ $\quad E^o = 1.23$ V

C(-): $2\ H^+ + 2e^- \rightarrow H_2$ $\quad E^o = 0$ V

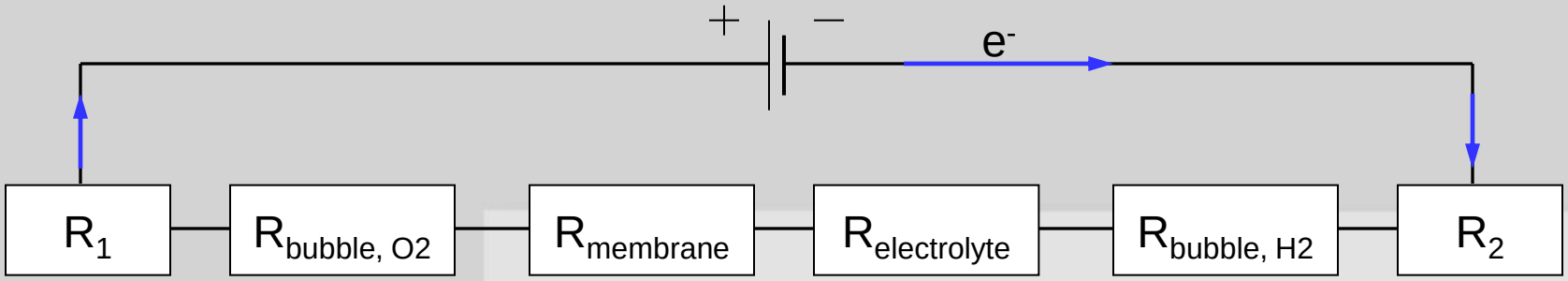
Overall reaction

$2\ H_2O \rightarrow 2\ H_2 + O_2$ $\quad \Delta E^o = 1.23$ V

$$\Delta E_{cell} = \Delta E^o + IR_{cell} + \Sigma\eta$$

Ways to reduce the cell voltage

R_{cell} = Σ of external circuit resistance, electrolyte, membrane, bubbles



Minimize R

High conductivity electrolytes

(acid or alkaline solutions)

Decrease wire length
Increase cross-section area
Conductive wire material

Ways to reduce the cell voltage

Ση = activation overpotential + concentration overpotential

Electrode kinetics – Butler Volmer equation $$i = i_o\left(e^{\alpha f\eta} - e^{-(1-\alpha) f\eta}\right)$$

$$\eta = 2.303\frac{RT}{(1-\alpha)F}\log i_o - 2.303\frac{RT}{(1-\alpha)F}\log|i|$$

Tafel equation $$\eta = a + b\cdot\log|i|$$

Temperature increase

Minimize *η*

Catalysis in the solution

Catalytic materials (high i_o)

High surface area electrodes

Catalysis by proton carriers

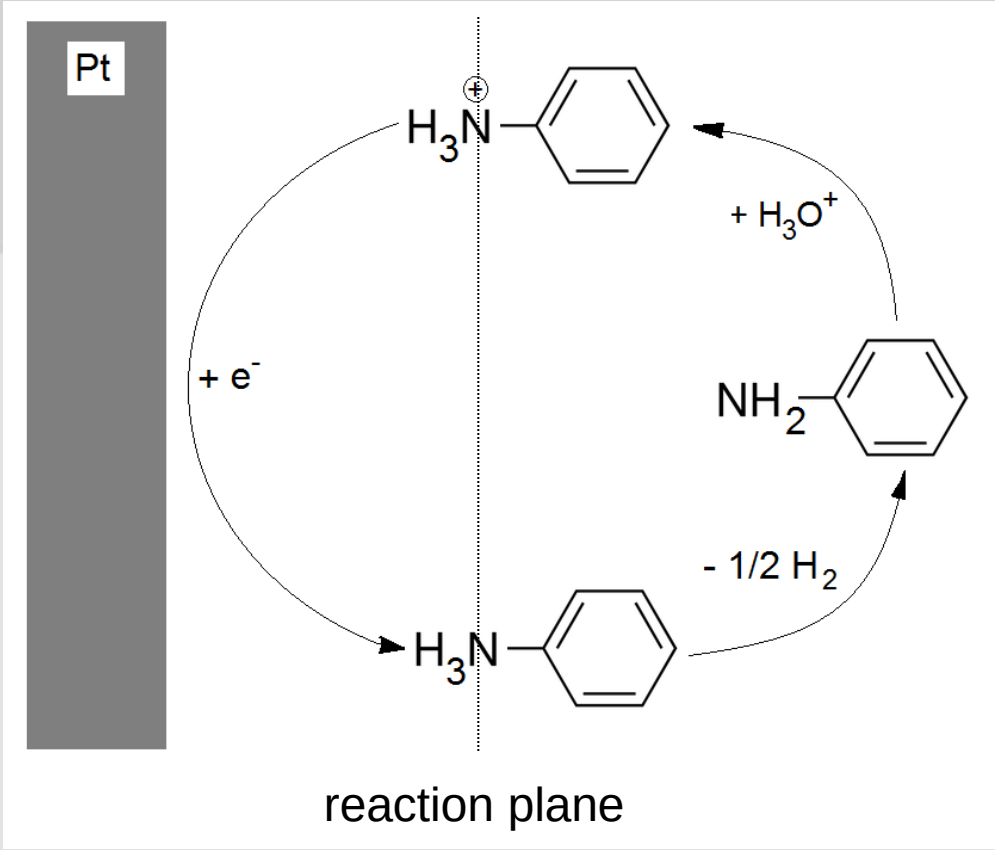
$R–NH_2 + H_3O^+ \leftrightarrow R–N^+H_3 + H_2O$

$R–N^+H_3 + e^- \rightarrow [R–NH_3]$

$2[R–NH_3] \rightarrow H_2 + R–NH_2$

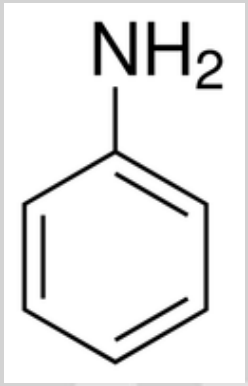
increase H^+ conc.

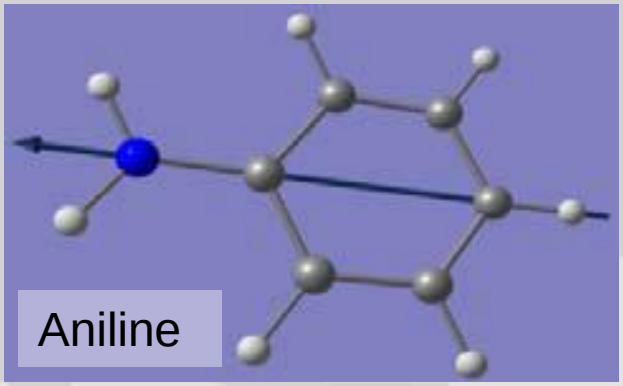
increased reaction rate



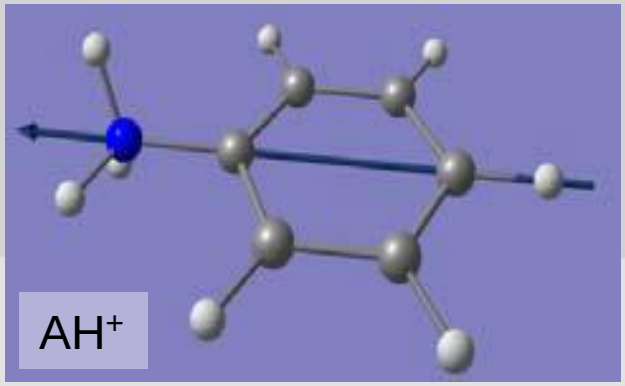
Proton carriers: aniline (A) & benzylamine (BA)

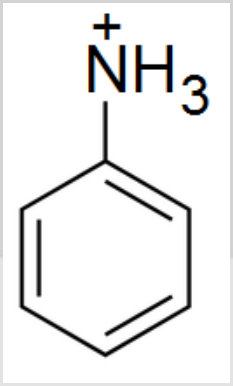
μ = 1.603 D

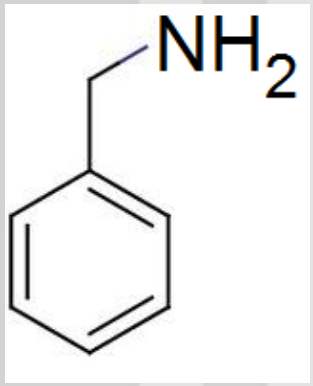


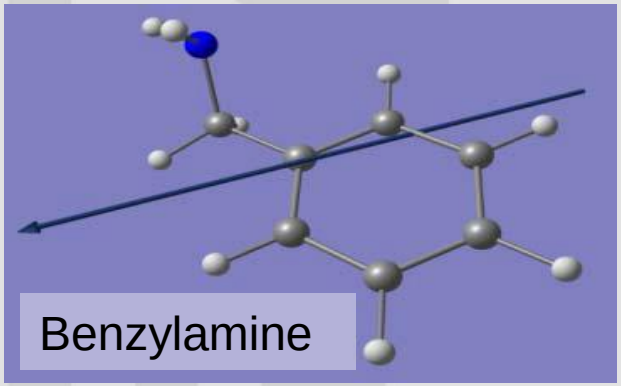


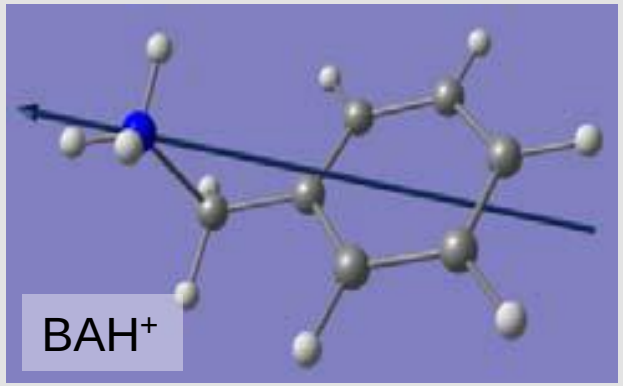
μ = 7.461 D

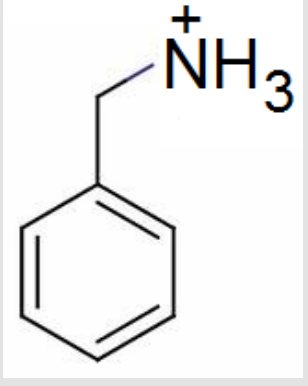








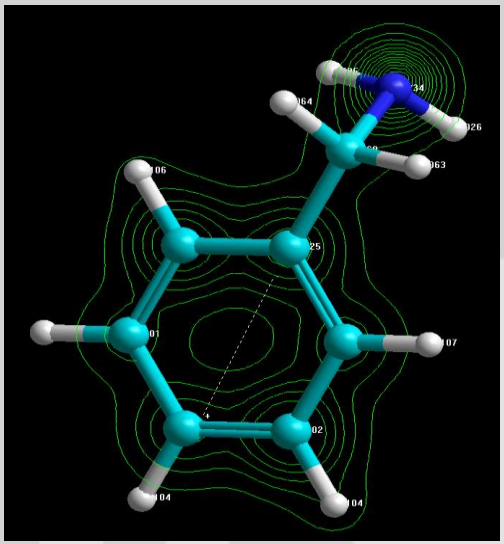




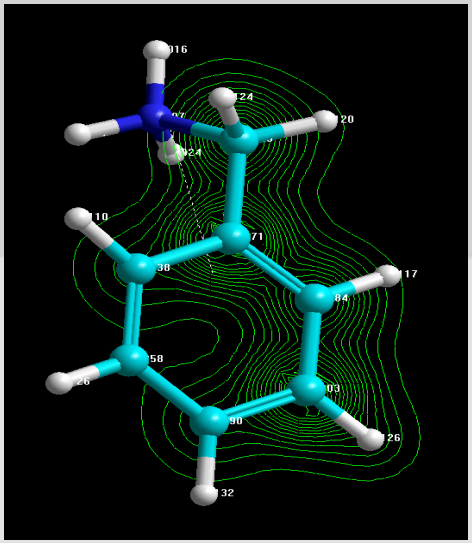
Dipole moment μ = 1.779 D μ = 9.441 D

AH^+ = anilinium cation BAH^+ = benzyl ammonium cation

Proton carriers: aniline & benzylamine



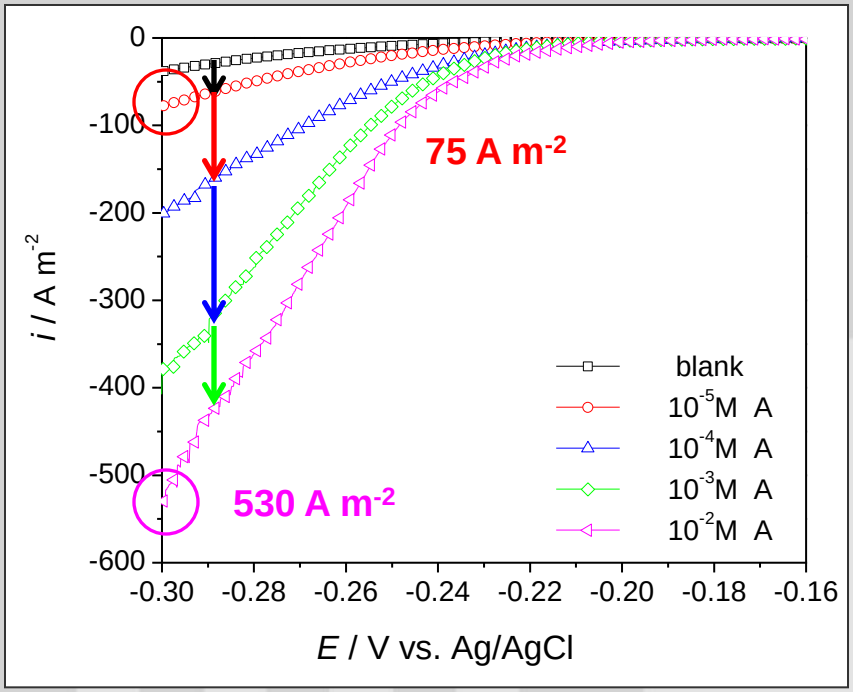
Benzylamine

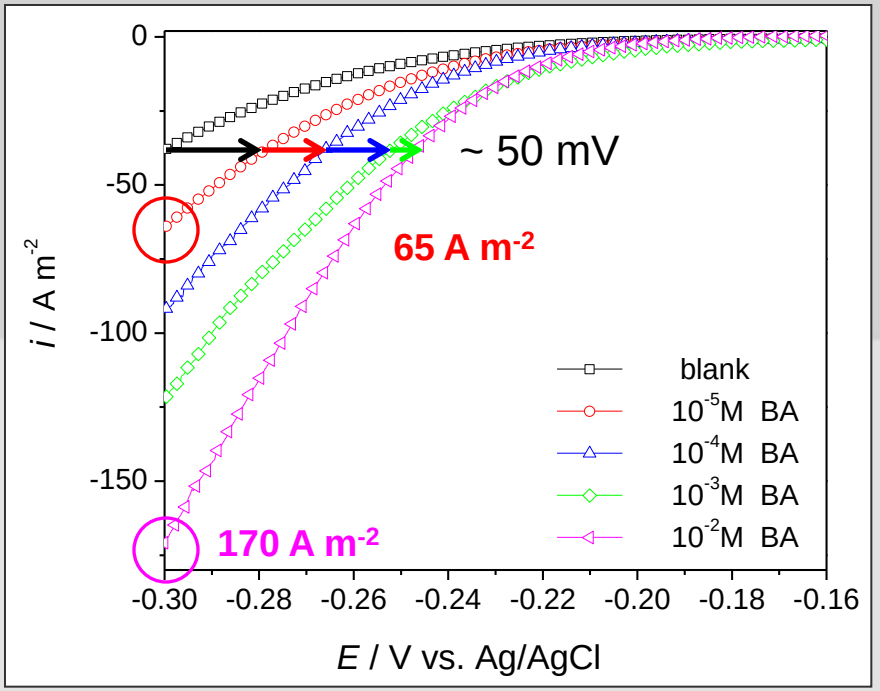


Benzyl-ammonium

Electron densities of benzylamine and benzyl-ammonium molecules

Linear polarization curves





Low concentrations: comparable catalytic effect

High concentration: catalytic effect aniline >> benzylamine

Tafel plots – kinetic parameters

$$\eta = 2.303\frac{RT}{(1-\alpha)F}\log i_o - 2.303\frac{RT}{(1-\alpha)F}\log|i|$$

transfer coefficient

exchange current density

Tafel slope

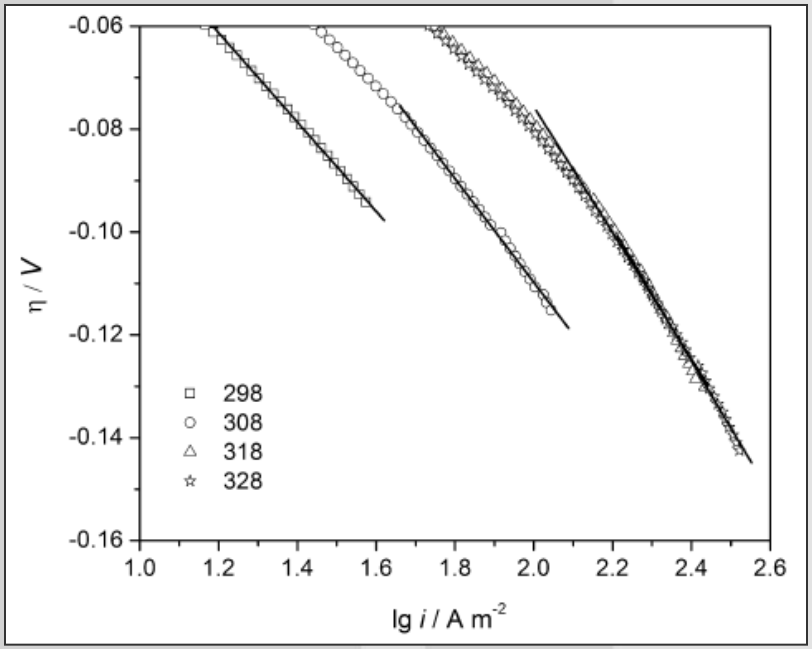


Table 1 – Kinetic parameters for HER in 0.5 mol L^{-1} H_2SO_4 at different temperatures.

T [K]	$-b$ [mV dec^{-1}]	$1-\alpha$	i_o [A m^{-2}]
298	87	0.68	2.9
308	101	0.58	7.6
318	122	0.48	25.1
328	130	0.45	28.8

Tafel plots – kinetic parameters

10^{-5} M benzylamine 10^{-2} M

Table 2 – Kinetic parameters for HER in 0.5 mol L^{-1} H_2SO_4 with 10^{-5} M BA at different temperatures.

T [K]	$-b$ [mV dec^{-1}]	$1-\alpha$	i_o [A m^{-2}]
298	88	0.68	5.8
308	109	0.54	21.9
318	129	0.46	32.5
328	141	0.45	34.7

Table 3 – Kinetic parameters for HER in 0.5 mol L^{-1} H_2SO_4 with 10^{-2} M BA at different temperatures.

T [K]	$-b$ [mV dec^{-1}]	$1-\alpha$	i_o [A m^{-2}]
298	103	0.57	22.9
308	119	0.49	41.7
318	129	0.45	51.3
328	140	0.42	66.1

Table 4 – Kinetic parameters for HER in 0.5 mol L^{-1} H_2SO_4 with 10^{-5} M A at different temperatures.

T [K]	$-b$ [mV dec^{-1}]	$1-\alpha$	i_o [A m^{-2}]
298	94	0.63	6.9
308	100	0.59	11.0
318	121	0.45	28.2
328	136	0.43	40.7

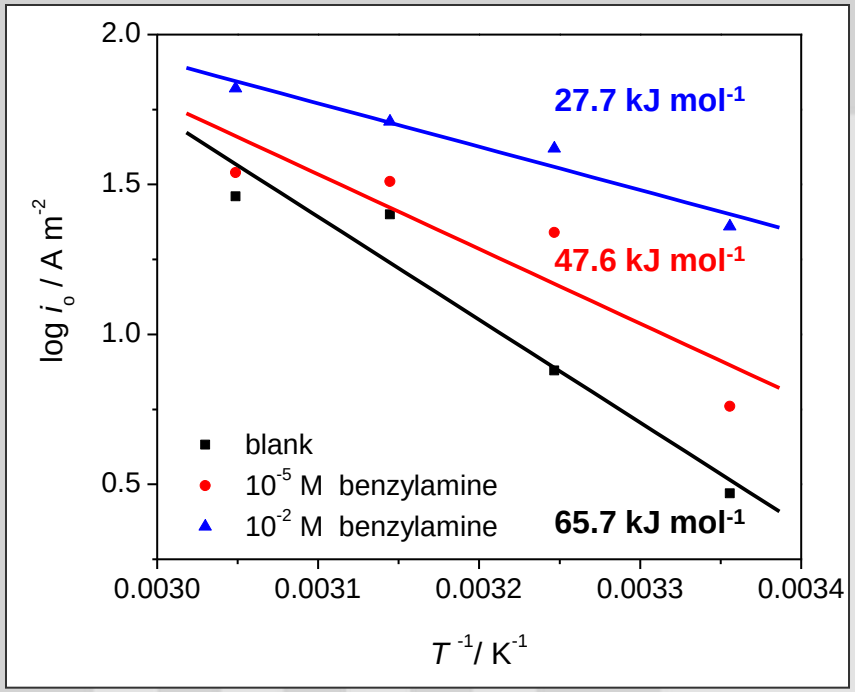
Table 5 – Kinetic parameters for HER in 0.5 mol L^{-1} H_2SO_4 with 10^{-2} M A at different temperatures.

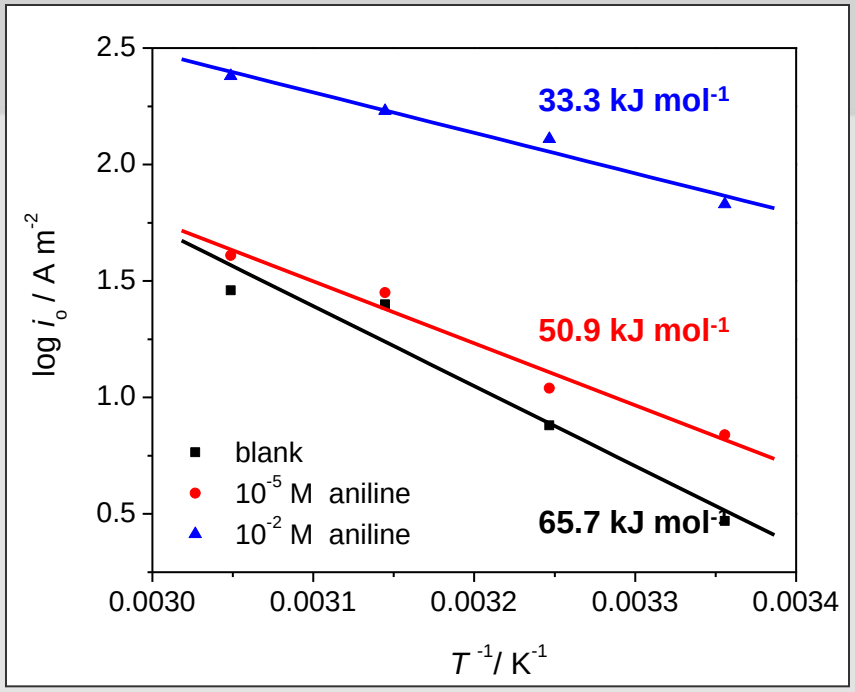
T [K]	$-b$ [mV dec^{-1}]	$1-\alpha$	i_o [A m^{-2}]
298	110	0.54	67.6
308	126	0.47	128.8
318	147	0.40	169.8
328	168	0.35	239.9

10^{-5} M aniline 10^{-2} M

Apparent activation energy

$$E_a = -2.303 \frac{\partial(\log i_o)}{\partial(T^{-1})}$$





HER - mechanism

1. Volmer reaction - hydrogen adsorption

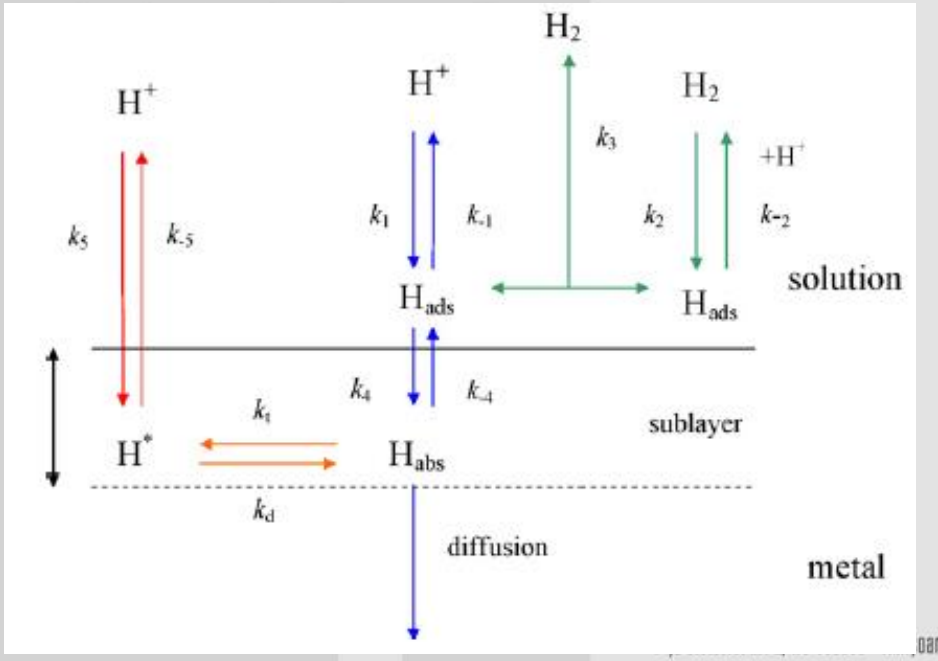
$$H^+ + M + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} MH_{ads} + H_2O$$

2. Heyrovsky reaction – electrochemical desorption

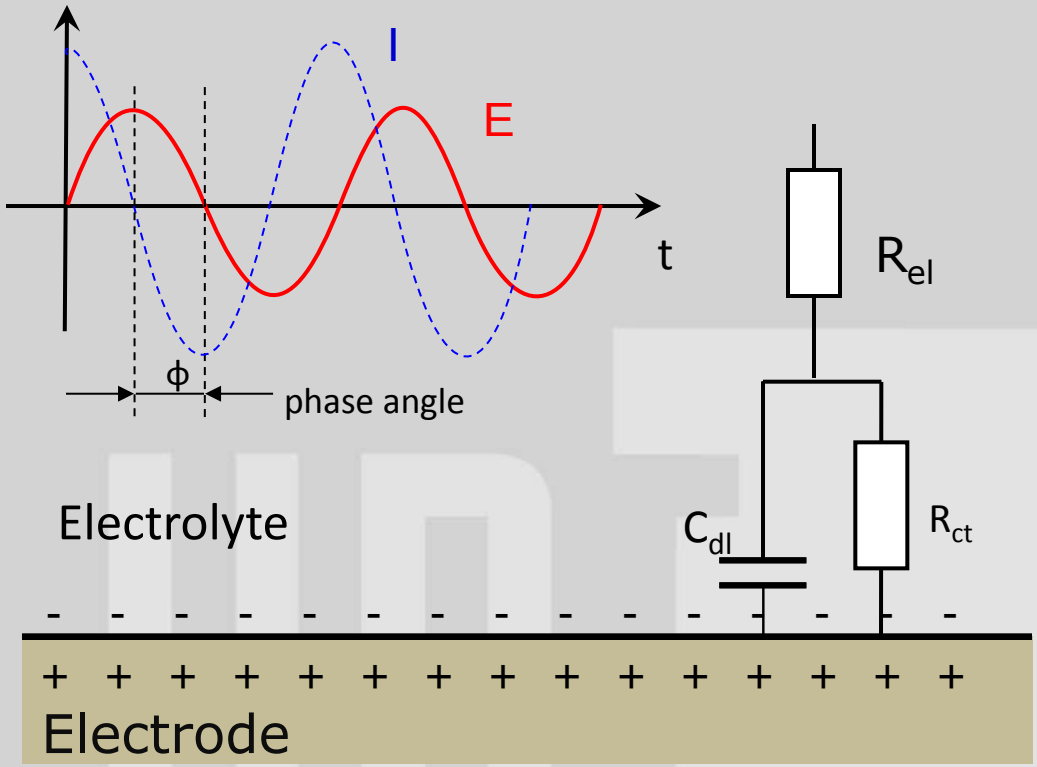
$$MH_{ads} + H^+ + e^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} M + H_2$$

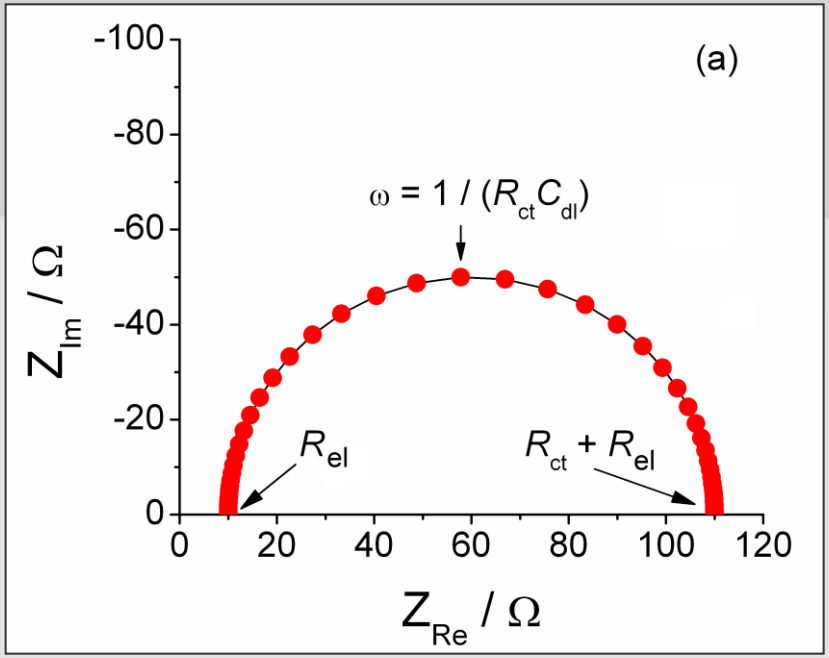
3. Tafel reaction – chemical desorption

$$2MH_{ads} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} 2M + H_2$$



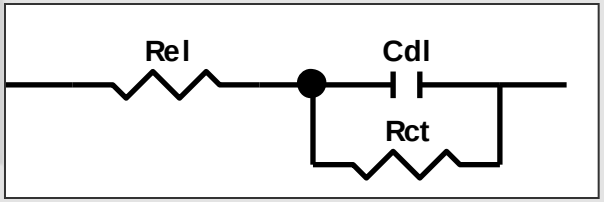
Electrochemical impedance spectroscopy





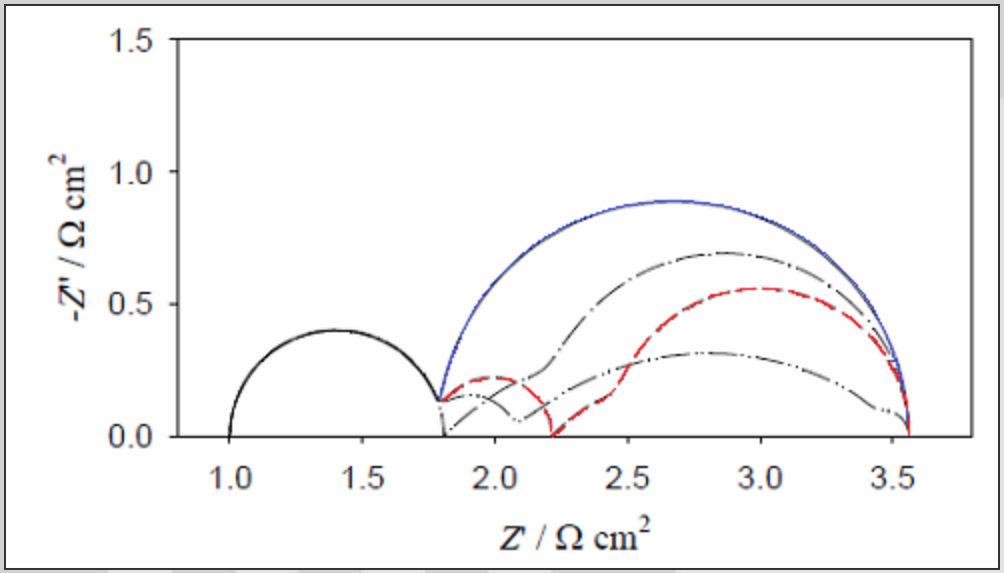
Nyquist plot

$$Z(j\omega) = R_{el} + \frac{R_{ct}}{1 + j\omega R_{ct} C_{dl}}$$



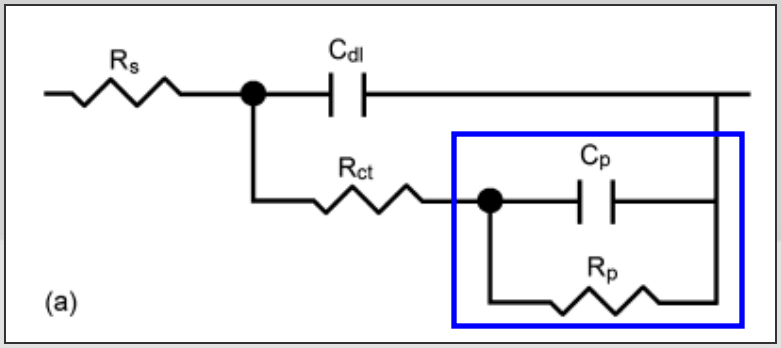
equivalent electrical circuit

Electrochemical impedance spectroscopy

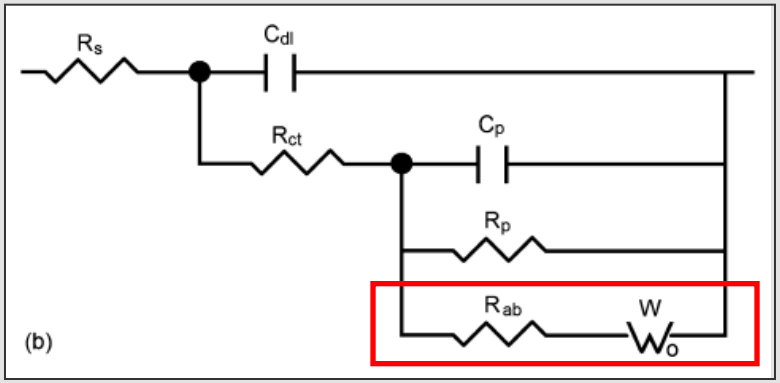


Simulated complex plane plots for HER

equivalent electrical circuit

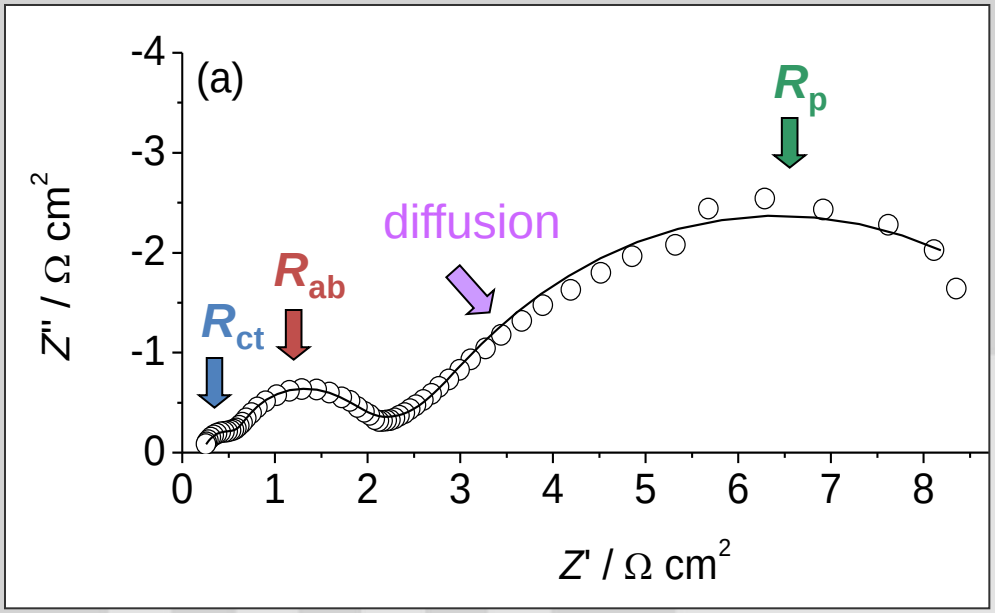


no hydrogen absorption



hydrogen absorption

Electrochemical impedance spectroscopy

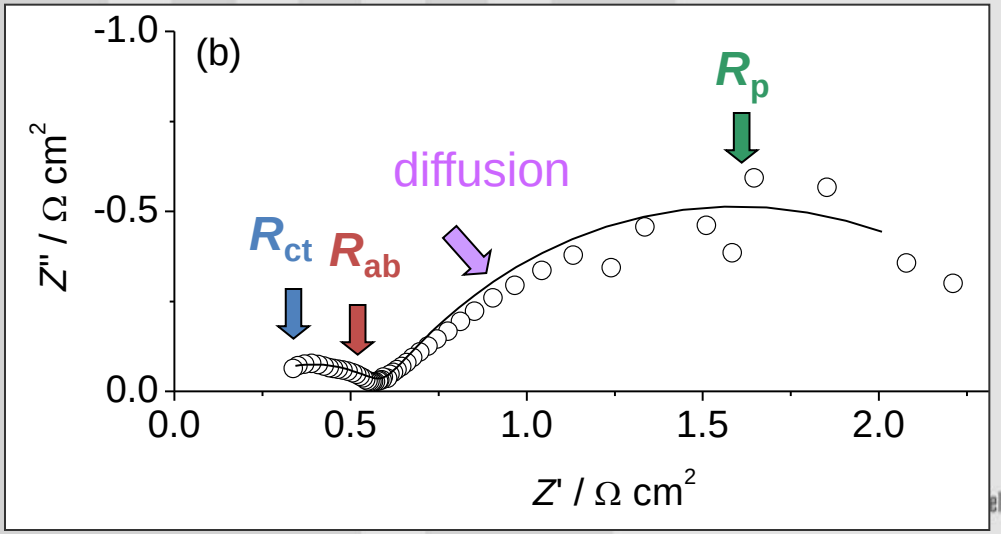


low η (η = -0.25 V)

R_{ct} = 0.43 Ω cm²

R_{ab} = 1.15 Ω cm²

R_p = 9.76 Ω cm²



high η (η = -0.45 V)

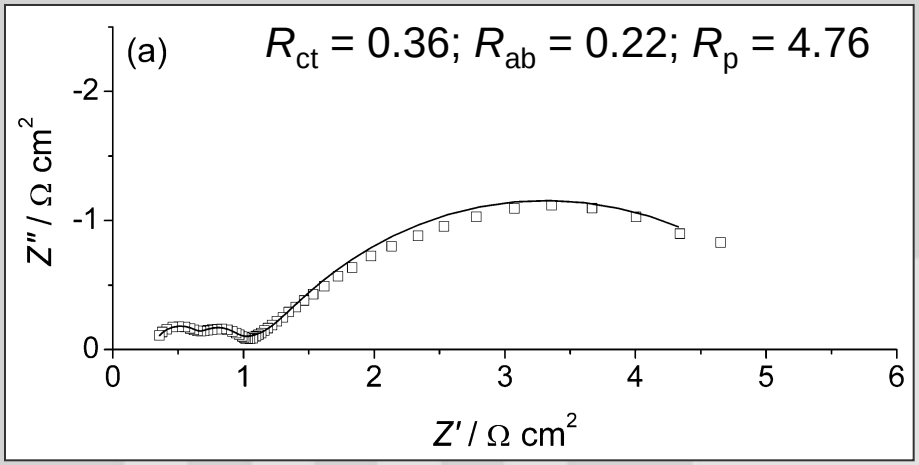
R_{ct} = 0.15 Ω cm²

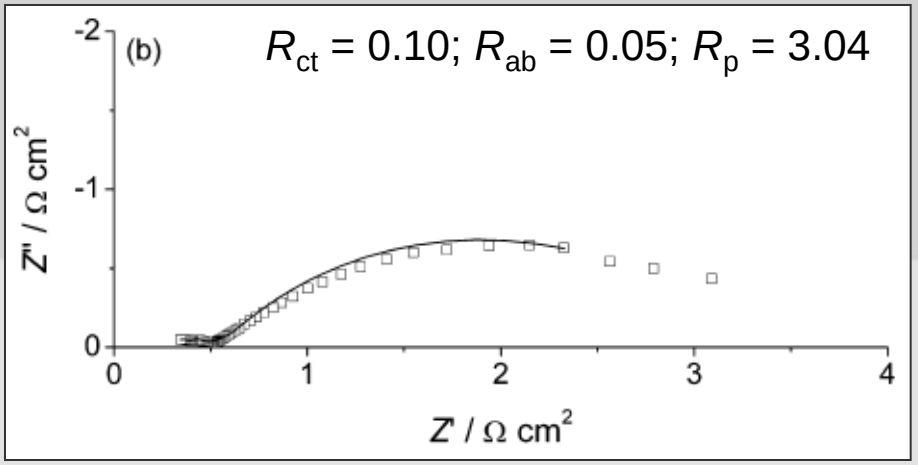
R_{ab} = 0.06 Ω cm²

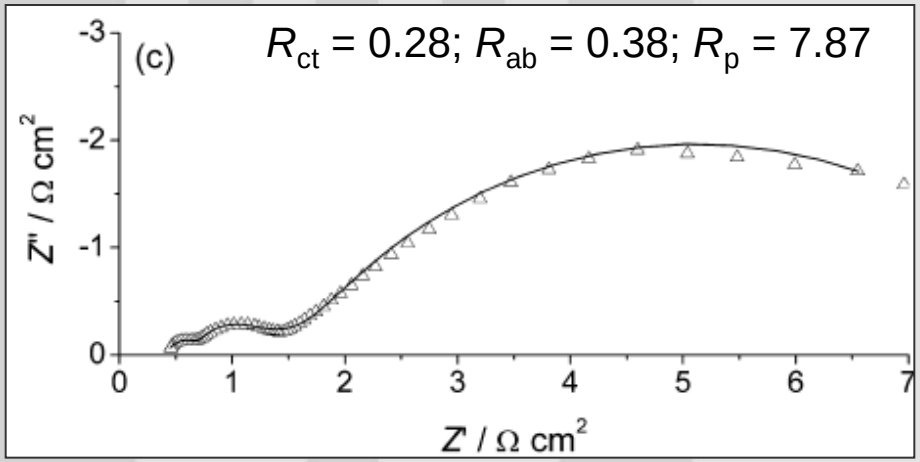
R_p = 2.06 Ω cm²

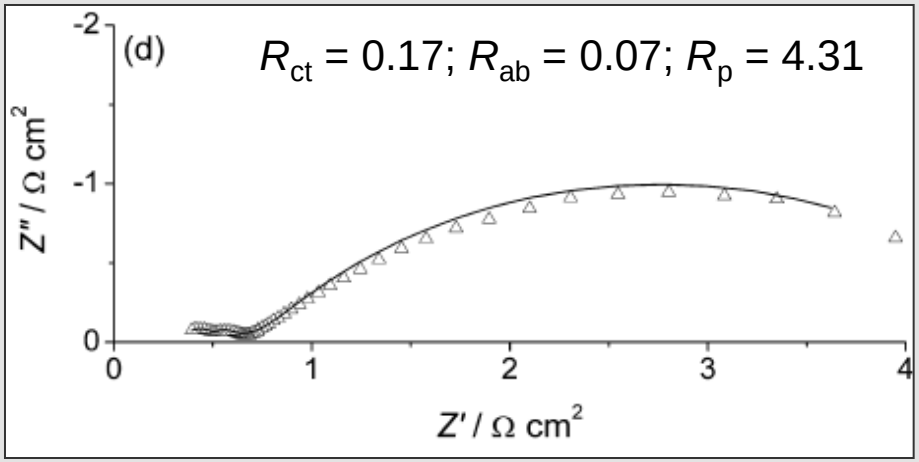
Electrochemical impedance spectroscopy

10^{-5} M benzylamine 10^{-2} M









10^{-5} M aniline 10^{-2} M

Electrochemical impedance spectroscopy

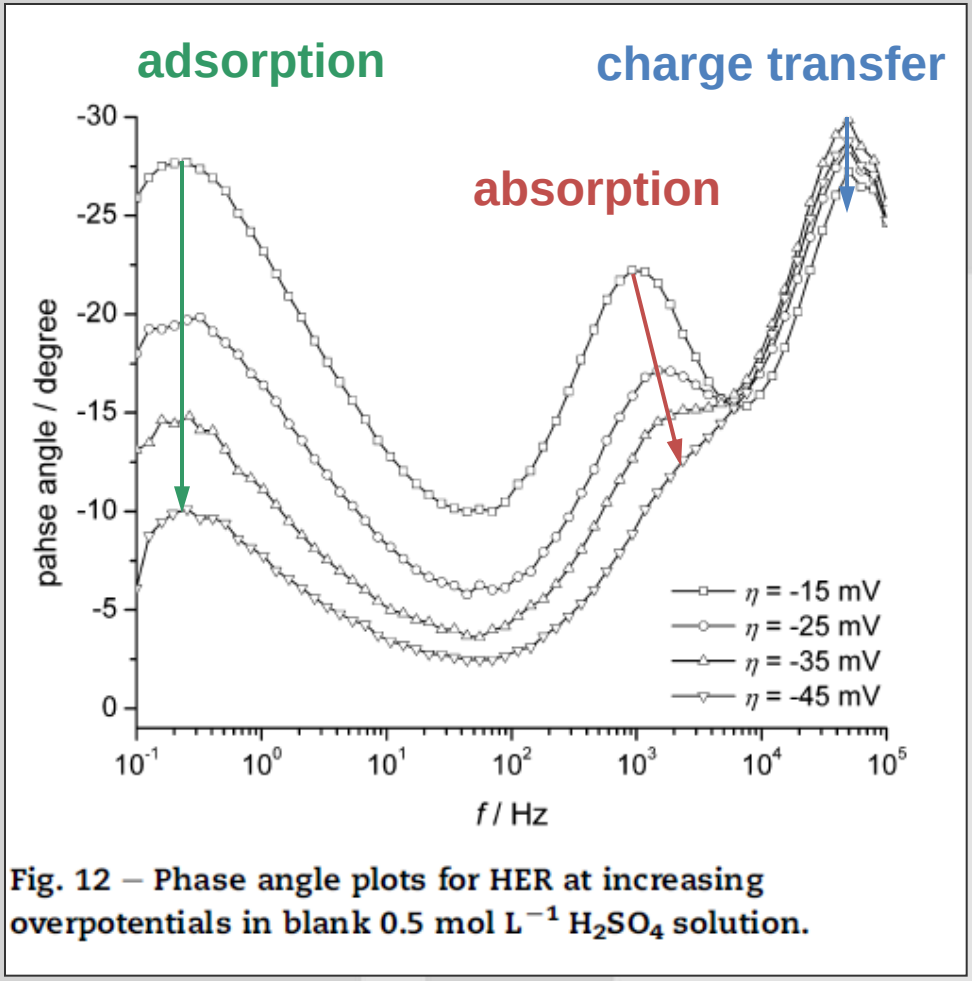


Fig. 12 – Phase angle plots for HER at increasing overpotentials in blank 0.5 mol L^{-1} H_2SO_4 solution.

Charge transfer
Adsorption
} potential independent

Absorption – potential dependent

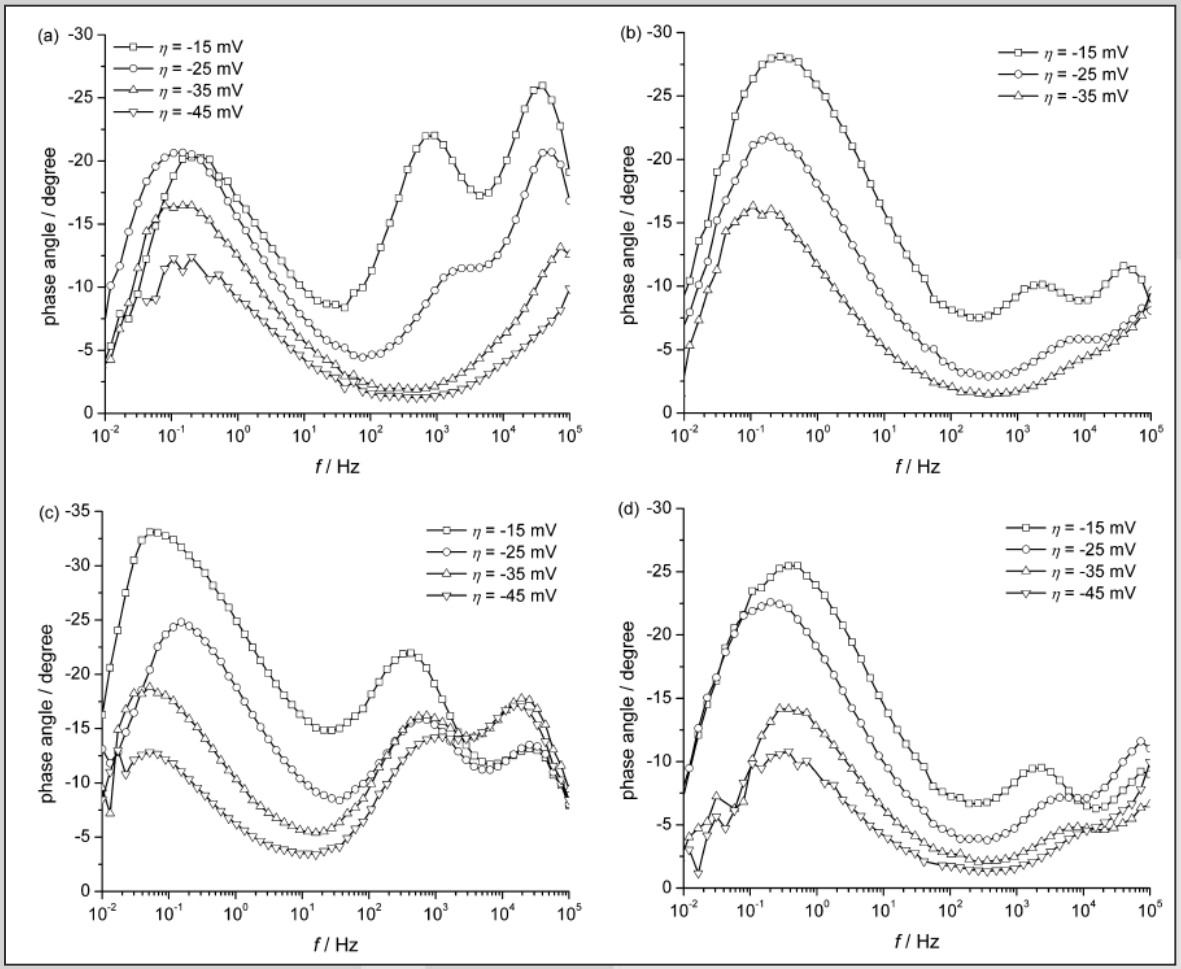
τ_{ct} = 9.2 μs ⇒ very fast

τ_{abs} = 0.255 ms ⇒ fast

τ_{ads} = 2.17 ms ⇒ slow

Electrochemical impedance spectroscopy

10^{-5} M benzylamine 10^{-2} M



τ_{ct} = 5.1 µs / 1.8 µs

τ_{abs} = 0.063 ms / 0.011 ms

τ_{ads} = 1.38 ms / 0.72 ms

τ_{ct} = 8.0 µs / 2.5 µs

τ_{abs} = 0.168 ms / 0.018 ms

τ_{ads} = 3.49 ms / 1.11 ms

10^{-5} M aniline 10^{-2} M

CONCLUSIONS

- HER is catalyzed by aromatic amines present in the solution;
- the amines increase the proton concentration at the metal-electrolyte solution interface due to the protonation of nitrogen atoms;
- the exchange current density values increase almost 10 times in the presence of benzylamine and more than 20 times in the presence of aniline;
- activation energy considerably drops in the presence of amines;
- kinetic parameters are strongly related to molecular parameters: dipole moment and molecular surface;
- impedance measurements showed that in the presence of amines HER is accelerated as a result of faster charge transfer resistance.

ACKNOWLEDGMENTS

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Phd. student Raluca Cretu

Prof. dr.eng. Nicolae Vaszilcsin

R. Cretu, A. Kellenberger, N. Vaszilcsin, Enhancement of hydrogen evolution reaction on platinum cathode by proton carriers, *International Journal of Hydrogen Energy,* 38 (2013) 11685-11694.

THANK YOU

FOR YOUR ATTENTION!

P-ța Victoriei nr. 2, RO 300006 - Timișoara, Tel: +4 0256 403000, Fax: +4 0256 403021, rector@rectorat.upt.ro, www.upt.ro