ACHIEVEMENTS AND PLANS

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GOALS

- To concentrate the sulfide ions for the needs of the fuel cell;
- To develop appropriate aeration system; mathematical modeling;
- To test different electrodes and techniques for high efficiency sulfide-driven fuel cell;
- To decide whether it is suitable to extract rare metals from the sea water.

Sulfide concentration

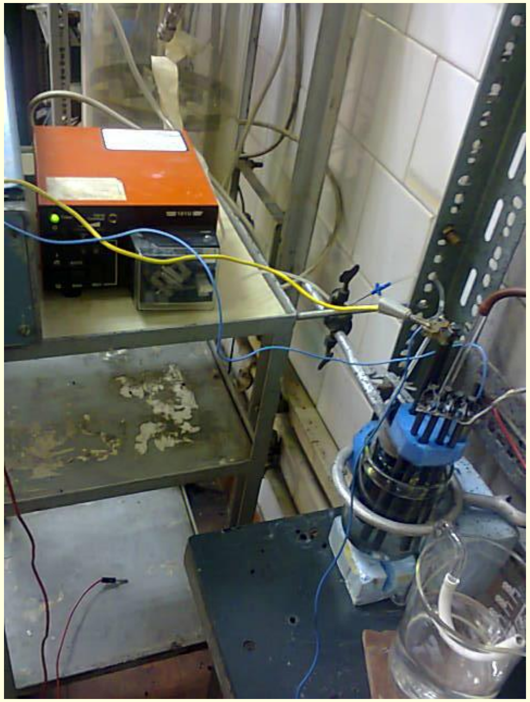
- By ion-exchange resin; eluation by NaOH or NaCl; or the resin was put into the anodic compartment of the fuel cell.
- By activated carbon.

- In both cases sulfides have been oxidized on the support to sulfite and sulfate.
- We hope, the sea water do not contain oxygen at large depths.

Fuel cell experiments

- Different electrodes for sulfide compartments – graphite, cobalt ions, embedded into GAC; zirconia; La-Ni-alloys;
- Different construction of the cell; electrode area in the oxygen compartment (GAC particles)
- Different membranes (OH^-, H^+) –depending on the electrode processes.

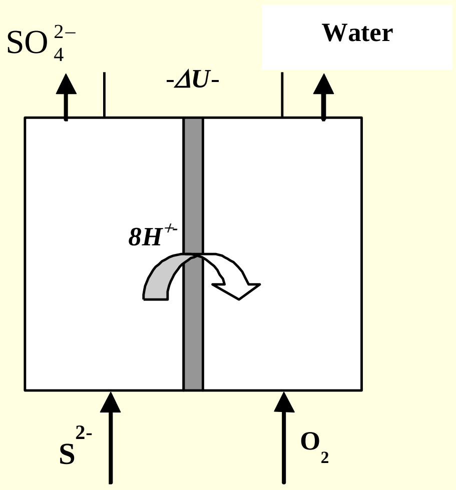
Aeration system; fuel cell



Electrode processes

- Anode: $S_2^- + 4H_2O - 8e- = SO_4^{2-} + 8H^+$, E_o= 0.149 V
- Cathode:$2O_2 + 8H^+ + 8e- = 4H_2O$, E_o=1.229 V

The net reaction: $S_2^- + 2O_2 = SO_4^{2-}$

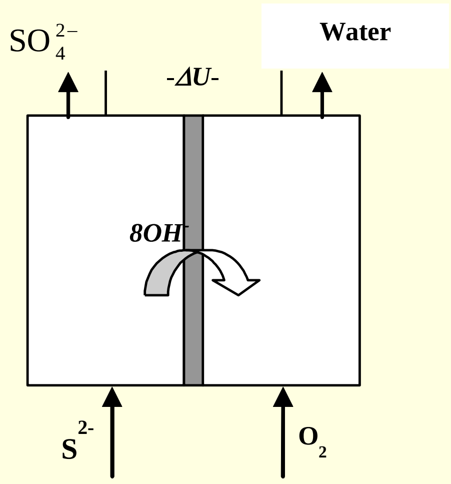


- Anode: $S_2^- + 6OH^- - 6e- = SO_3^{2-} + 3H_2O$, E_o= - 0.61 V

$SO_3^{2-} + 2OH^- - 2e^- = SO_4^{2-} + H_2O$

E_o= - 0.90 V; Total: -0.706 V.

- Cathode: $2O_2 + 4H_2O + 8e^- = 8OH^-$, E_o= 0.401 V



Spontaneous electrode reactions do not fit the required ones!

Reversible reaction	Electrode potential [V]
$2SO_3^{2-} + 2H_2O + 2e = S_2O_4^{2-} + 4OH^-$	-1.12
$SO_4^{2-} + H_2O + 2e = SO_3^{2-} + 2OH^-$	**-0.93**
$SO_3^{2-} + 3H_2O + 4e = S + 6OH^-$	**-0.66**
$S_2^{2-} + 2e = 2S^{2-}$	-0.524
$S_4^{2-} + 2e = S^{2-} + S_3^{2-}$	-0.52
$2S_3^{2-} + 2e = 3S_2^{2-}$	-0.506
$S_3^{2-} + 2e = S^{2-} + S_2^{2-}$	-0.49
$S + 2e = S^{2-}$	-0.48
$3S_4^{2-} + 2e = 4S_3^{2-}$	-0.478
$4S_5^{2-} + 2e = 5S_4^{2-}$	-0.441
$5S + 2e = S_5^{2-}$	-0.34
$4S + 2e = S_4^{2-}$	-0.33
$2SO_4^{2-} + 4H^+ + 2e = S_2O_6^{2-} + 2H_2O$	-0.22
$2H_2SO_3(aq) + H^+ \; 2e = HS_2O^{4-} + 2H_2O$	-0.082
$S + H^+ + 2e = HS^-$	-0.065
$2HSO_3^- + 2H^+ + 2e = S_2O_4^{2-} + 2H_2O$	-0.013
$S_2O_3^{2-} + 6H^+ + 8e = 2S^{2-} + 3H_2O$	-0.006
$HSO_3^- + 5H^+ + 4e = S + 3H_2O$	0

Continued

19	$S_5^{2-} + 5H^+ + 8e = 5HS^-$	0.003
20	$S_2O_6^{2-} + 2e = 2SO_3^{2-}$	0.026
21	$S_4^{2-} + 4H^+ + 6e = 4HS^-$	0.033
22	$2HSO_3^- + 3H^+ + 2e = HS_2O_4^- + 2H_2O$	0.06
23	$S_4O_6^{2-} + 2e = 2S_2O_3^{2-}$	0.08
24	$S_3^{2-} + 3H^+ + 4e = 3HS^-$	0.097
25	$SO_4^{2-} + 4H^+ + 2e = SO_2(g) + 2H_2O$	0.138
26	$S(romb) + 2H^+ + 2e = H_2S\ (aq)$	0.142
27	**$SO_4^{2-} + 8H^+ + 8e = S^{2-} + 4H_2O$**	**0.149**
28	$SO_4^{2-} + 4H^+ + 2e = H_2SO_3\ (aq) + H_2O$	0.172
29	$S_2O_3^{2-} + 8H^+ + 8e = 2HS^- + 3H_2O$	0.2

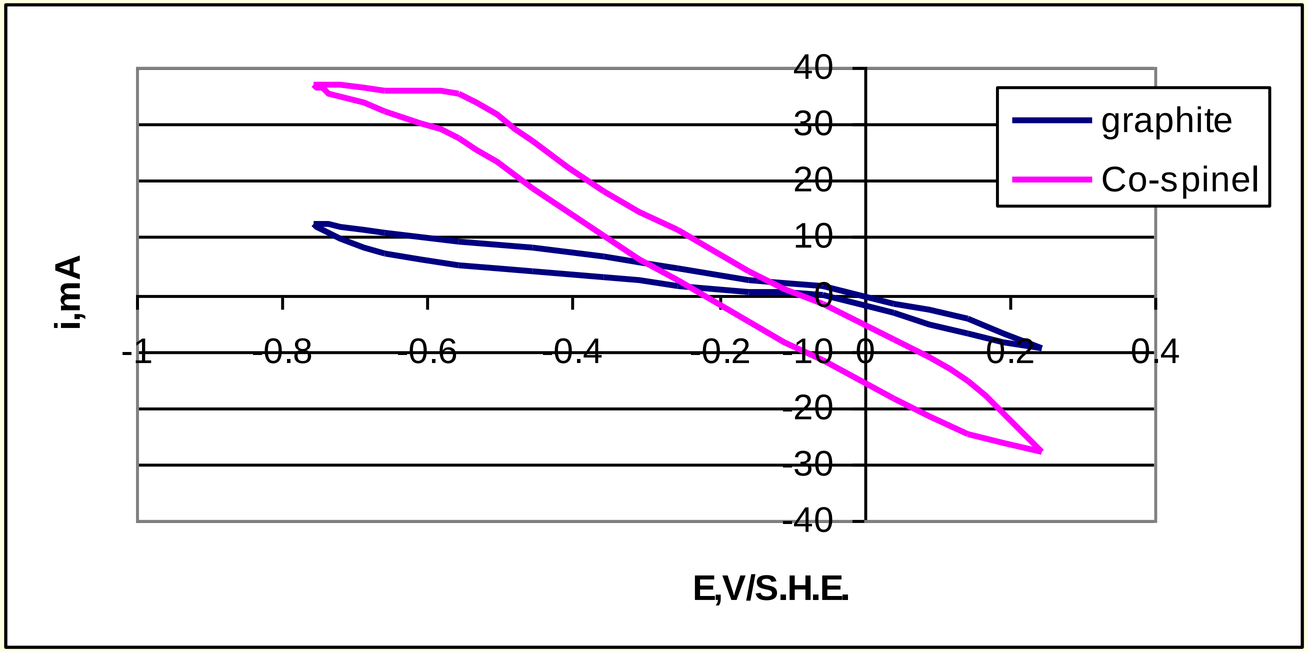
Maintenance of the required potential

- Suitable catalyst or
- Potentiostatic maintenance;
- Combination of both.

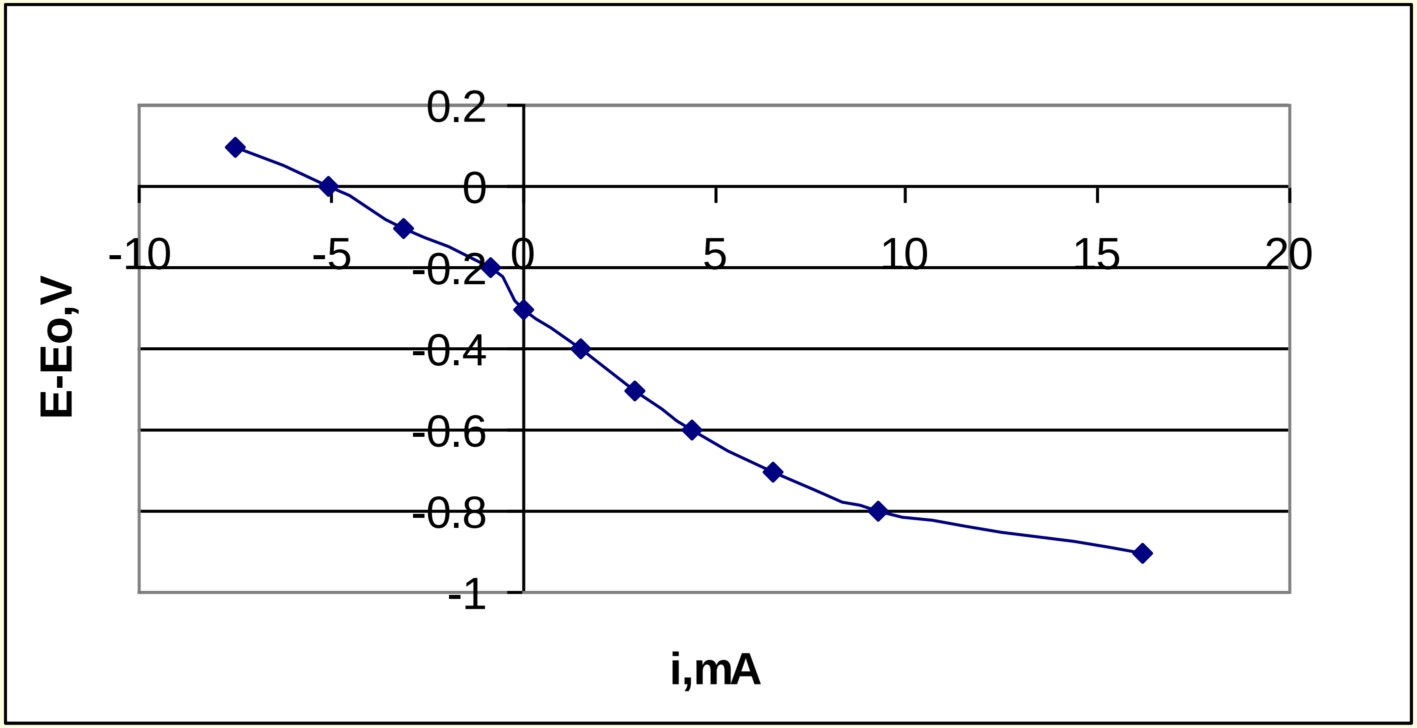
- Catalysts: Co-doped GAC;   GAC

Perovskite($La_{1.3}Sr_{0.7}NiO_4$); La-Ni-alloys; zirconia

VOLT-AMPERIC CHARACTERISTICS – COMPARISON (65 mg/l SULFIDE; 20^{O}C)



Polarization curve (Co-spinel)

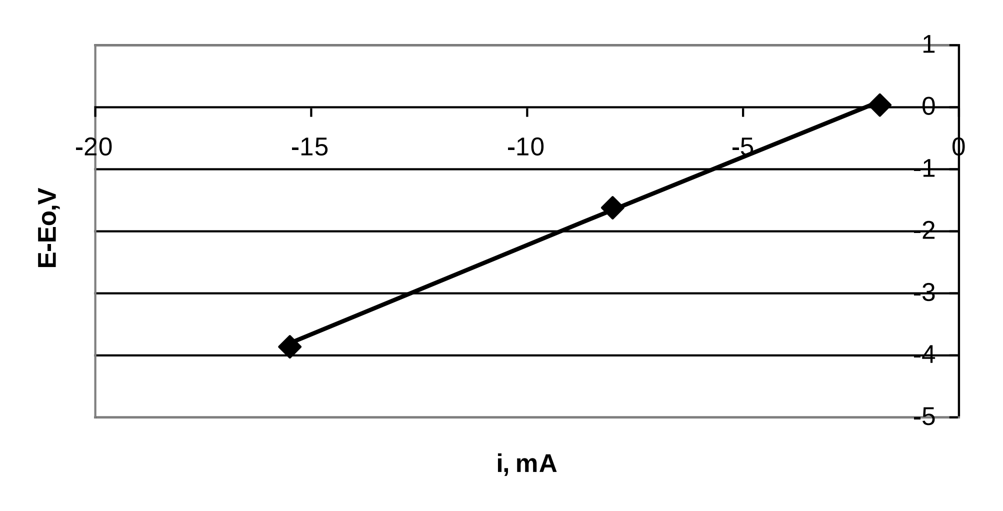


Tafel's plot-activation energy

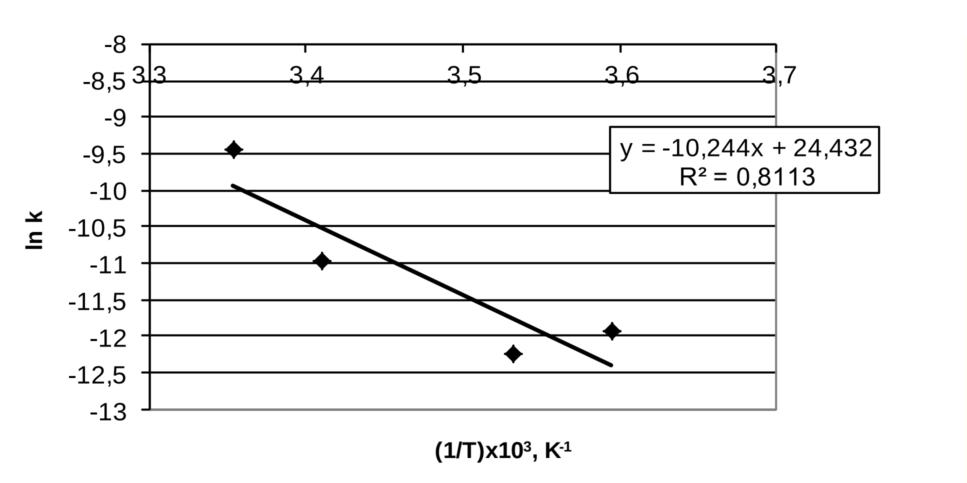
- $S_2^- + 4H_2O - 8e- = SO_4^{2-} + 8H^+$, E_o=0.149 V

R=0.29 Ω;

i_o = 89 mA



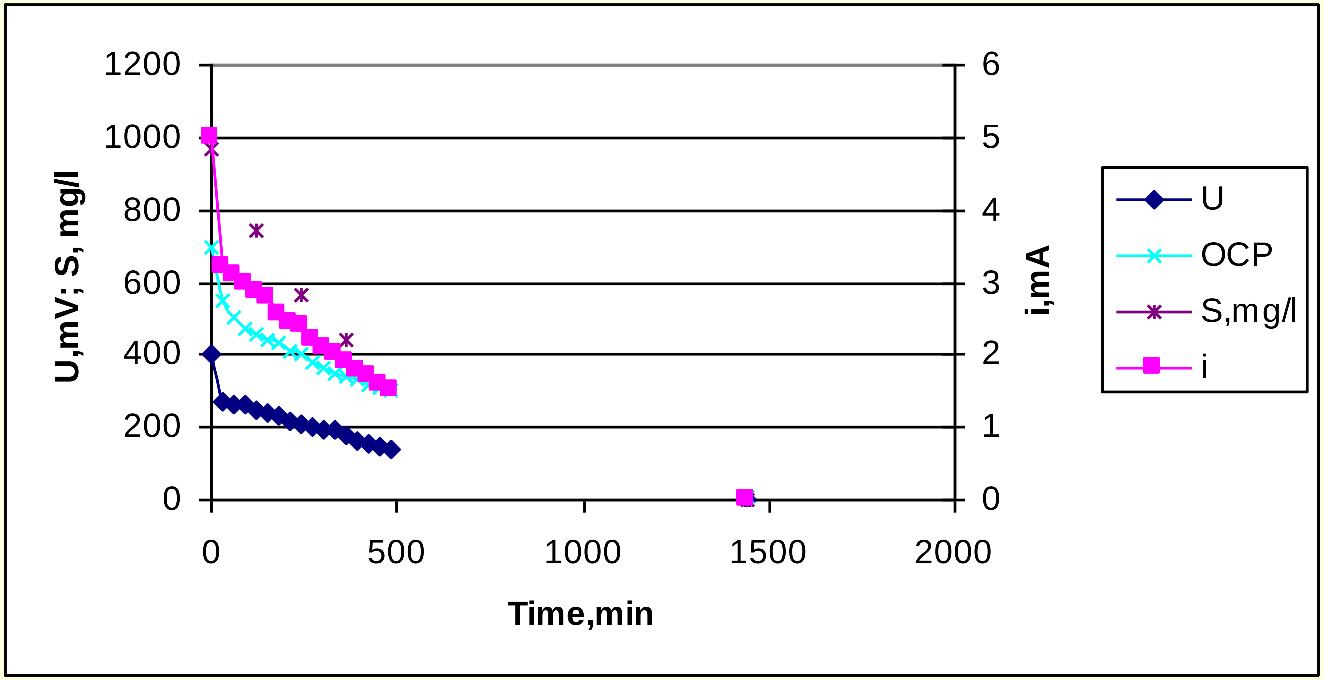
Arrhenius plot; 5 to 25ºC



Ea=20.4 kcal/mol or

85.18 kJ/mol

A SULFIDE-DRIVEN FUEL CELL-BATCH PROCESS;GRAPHITE ELECTRODES; NO CATALYST 970 mg/l sulfide



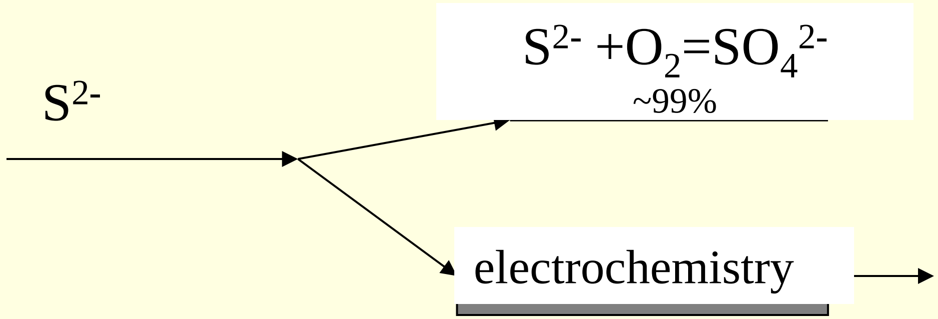
For 4 hours:

2.1 J

4.57 kJ stoichiometrically

Parallel competitive processes

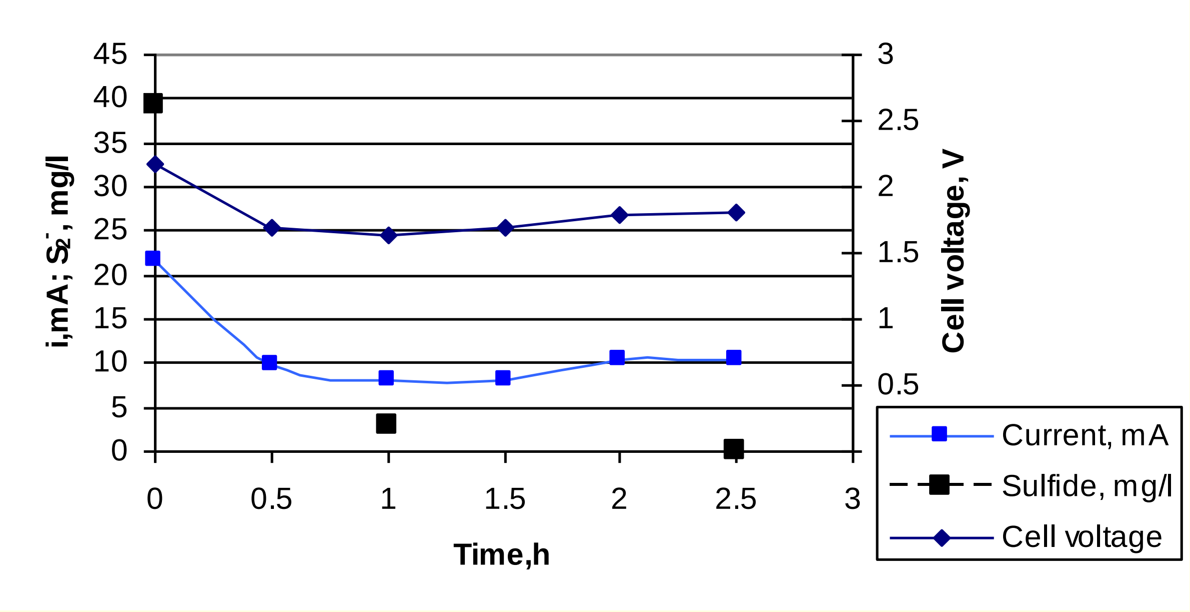
- How to overcome this?



- To stop the parasite reaction (purging with nitrogen);
- Select suitable catalyst
- To enhance the anode process by suitable potential.

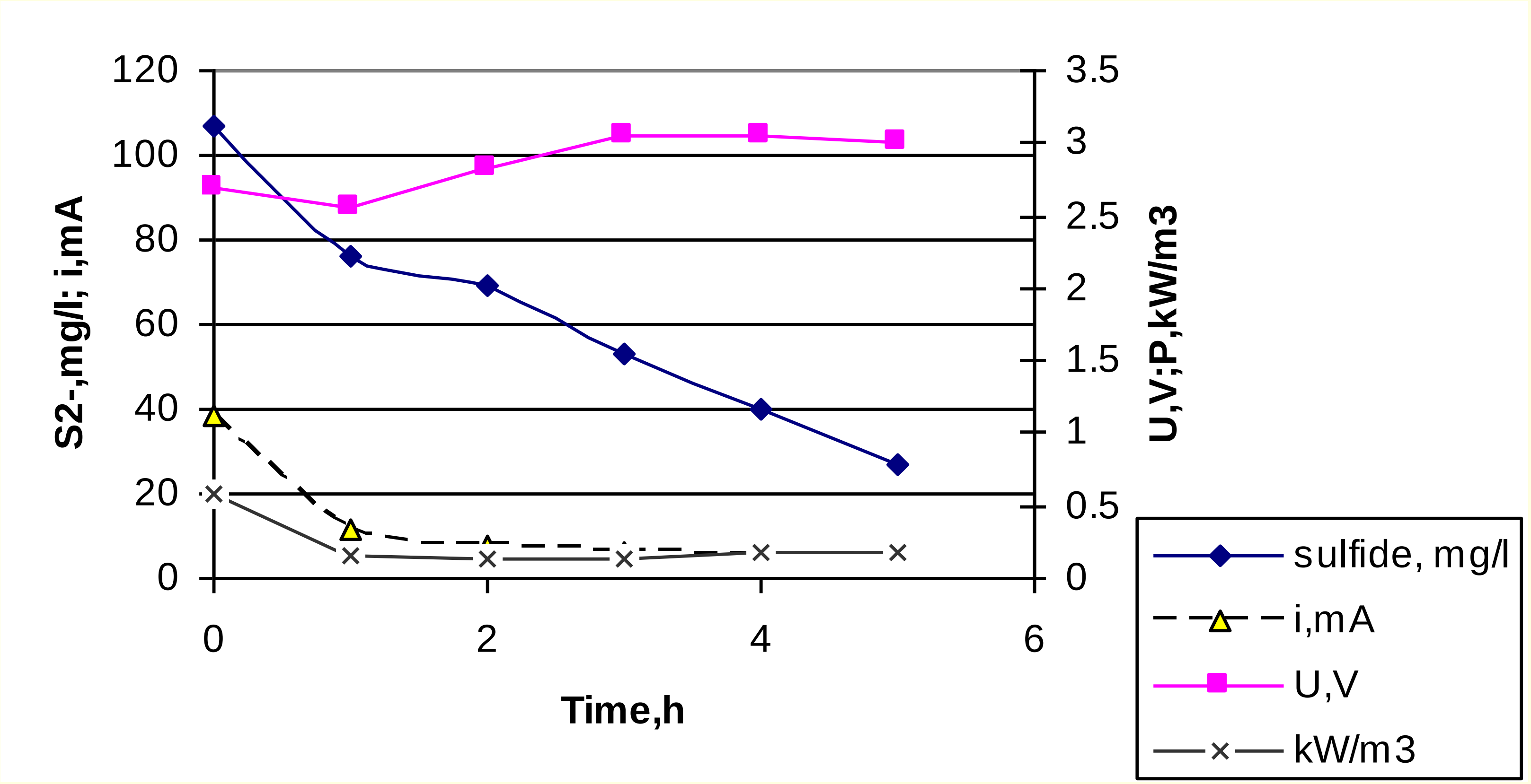
THE CATALYST IN A SULFIDE-DRIVEN FUEL CELL-BATCH PROCESS; anode potential: -1.0 V/SCE

- $S_2^- + 2O_2 - 8e^- = SO_4^{2-}$, $E_o = -0.705$ V

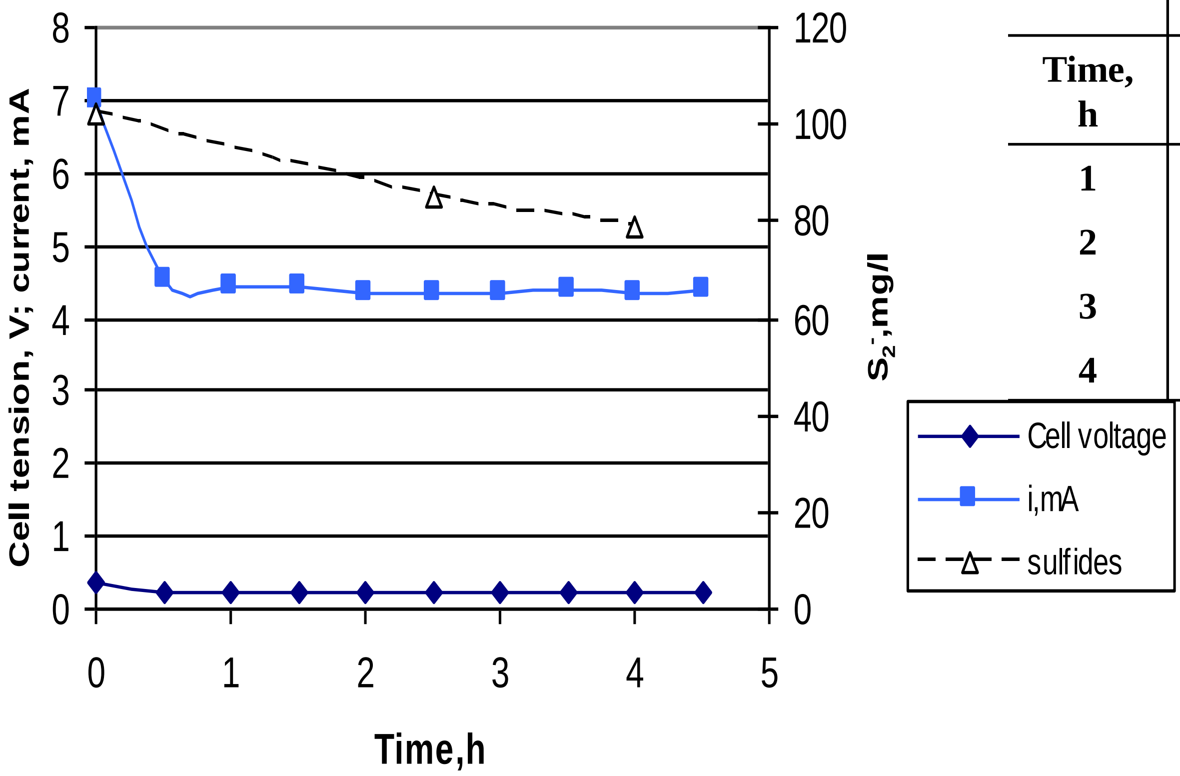


Time, h	Produced energy, J	Stoichiometric yield, J	Product
1	84.2	110.4	sulfites
2.5	171.5	172.4	sulfates

THE CATALYST IN A SULFIDE-DRIVEN FUEL CELL-BATCH PROCESS; anode potential: -1.0 V/SCE



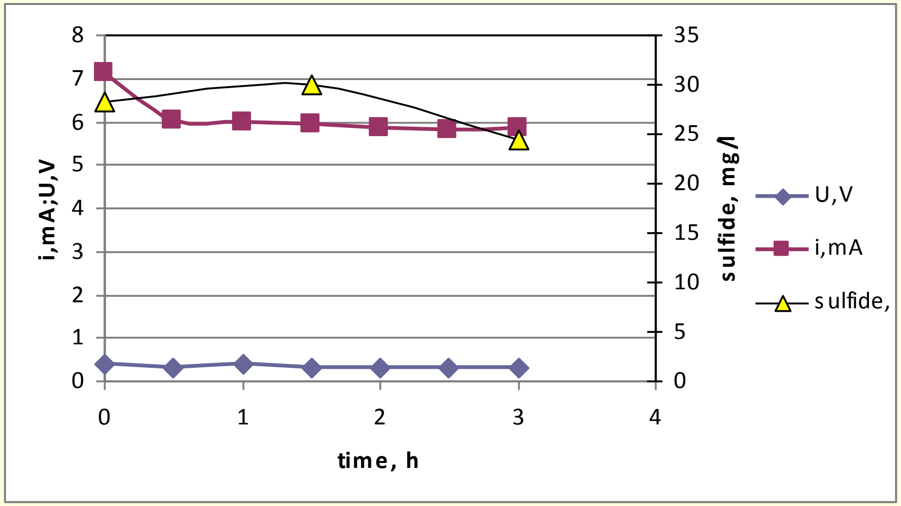
THE CATALYST IN A SULFIDE-DRIVEN FUEL CELL- CONTINUOUS PROCESS (0.035 l/);



Time, h	Rate of sulfide/sulfate conversion, mg/h		
	Faraday's law	Stoichiometric	Ratio
1	0.73	0.606	1.2
2	0.73	0.812	0.9
3	0.69	1.124	0.61
4	0.63	1.424	0.44

THE CATALYST IN A SULFIDE-DRIVEN FUEL CELL- CONTINUOUS PROCESS (0.12 l/h); anode potential: -0.1 V/SCE

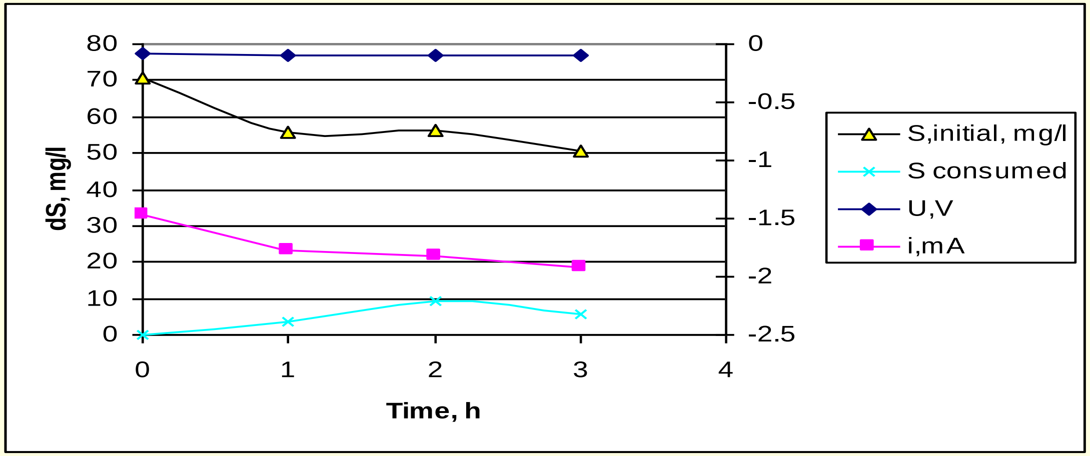
- **$S2- + 4H2O - 8e- = SO_4^{2-}$ + 8H+, Eo=0.149 V**



	Rate of sulfide/sulfate conversion, mg/h		
Time, h	Faraday's law	Stoichiometric	Ratio
0	1.06	2.29	0.46
1.5	0.883	0.647	1.365
3	0.872	0.976	0.893
Average	0.938	1.304	0.72

THE CATALYST IN A SULFIDE-DRIVEN FUEL CELL-CONTINUOUS PROCESS (0.12 l/h); anode potential: -0.1 V/SCE

- S2- + 4H2O - 8e- = SO_4^{2-} + 8H+, Eo=0.149 V



	Rate of sulfide/sulfite conversion, mg/h		
Time, h	Faraday's law	Stoichiometric	Ratio
1	0.354	0.4212	0.84
2	0.3625	1.093	0.332
3	0.394	0.6588	0.60
Average	0.37	0.7243	0.59

	Rate of sulfide/sulfate conversion, mg/h		
Time, h	Faraday's law	Stoichiometric	Ratio
1	0.2656	0.4212	0.63
2	0.2719	1.093	0.25
3	0.2955	0.6588	0.4485
Average	0.2776	0.7243	0.443

How to continue?

- To improve the catalyst;
- To avoid oxygen in the sulfide compartment;
- To reduce the cell ohmic resistance drastically (high salinity, better ion exchange membrane); reduction of the ohmic resistance of the electrodes;
- To increase the surface/volume ratio.

General issues for discussion

- To select the best catalyst (if any)
- To select ion-exchange resin or else for sulfide concentration;
- To check the feasibility for rare earths extraction;
- To compose the pilot-plant equipment (including hydrogen production);
- To outline the terms and dead lines for these activities. To plan them.

THANK YOU FOR THE ATTENTION!