HYDROGEN PRODUCTION FROM BLACK SEA WATER BY SULFIDE-DRIVEN FUEL CELL
HYSULFCEL

In present quarter the aim of the work was:

1. fabrication of the aggregate, working on hydrogen sulfide,
2. selection and preparation of membranes,

selection and preparation electrodes,

3. selection and preparation catalysts for experiment,
4. selection of technological regimes.

Aggregate

The aggregate, which consists of five assembled cells, has been fabricated from plexiglass. Nipples and electron conductors are embed in each of the cells.

The cells are separated from each other by corresponding membranes (cationic and anionic).

Electrode-catalysts (anode and cathode) are placed on the both sides of the membrane

Aggregate

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Electrodes

- In our researches we used metal gauze, content of which was determined by roentgen fluorescent analyzer in percent: Fe - 70, Cr - 17.55, Ni – 9.5, Mn - 1.61, Ti - 0.43 (contains also small quantity of V, Nb, Mo and Cu).
- Sulfidizing of 1M of the mentioned gauze in solution of Na_2S during 20 hours was carried out. After sulfidizing this metal gauze was used in the experiment as electrode-catalyst for working both in cathode and anode regimes.

Electrodes

- Complex sulfides (several sulfides together) are more active catalysts than each of them. PtS or PtS deposited by TiO_2, sometimes deposited by NiS, FeS, CoS, MoS are used substantially.
- Sulfidizing of the electrodes was made by their delay in Na_2S solution.

Membranes

- Ralex AM-PAD 08-17 was used as anion membrane and Nafion NN-115 – as cation membrane after corresponding treatment.
- Anion membrane was placed in water during 24 hours.
- Cation membrane was treated in the following way: the upper layer of the membrane was removed, and kept in 3% H_2O_2 on 80^0C temperature during 1hour. Then it was washed in distillate, kept for two hours in the warm distillate, then it was placed in 0.5M H_2SO_4 during one hour, then it was rinsed for 2-3 times in distilled water of temperature $80\text{-}90^0C$ and was kept in distillate.

Working

First, the second cell (containing H_2S) was filled by model solution and remained without current for 19 hours. In 1-st and 3-rd cells (containing correspondingly H^+ and S^{-2}) pH was changed, particularly, in 1-st cell (H^+) pH increased from 7.35 up to 9.2 and in 3-rd cell (S^{-2}) pH increased insignificantly: from 7.35 up to 7.45, pH was increased insignificantly also in 2-nd cell (H_2S) from 8.6 up to 8.9. Throughout this time 0.4mg/l S^{-2} ions passed to 3-rd cell (S^{-2}) through anionic membrane. So, we concluded, that in this system and in these solutions the anionic membrane transmit sulfur ion (small quantities) without current, and cationic membrane transmits sodium ions besides hydrogen, which may be the reason of pH increase.

Working

In the following series of the experiment we included only 2-nd cell (H_2S), which was filled by sulfide solution and 1-st and 3-rd cells were filled with water of the same pH. The conditions of the experiments were: i=0.1 mA/sm^2, V=10V, I=5 mA. Spheres filled with hydrogen appeared on the surface of the cathode after working 0.5 hours, therefore we decreased current (I=2.0 mA, V=4.0V). After 1 hour, concentration of sulfur ions in third cell (S^{-2}) was zero. During the work in this regime throughout one hour pH was not change in any of the cells. So, we assumed that exchange of H^+ and S^{-2} ions in the membranes didn't take place, because the circuit switched only in 2-nd cell didn't allowed ions to pass.

Working

The following experiments were continued by switching of internal and external circuits (Fig.1). At first, trial experiments were carried out in model electrolyte of sulfide water. The experiment continued for 3.5 hours. In order to supply electroconductivity 2 g/l Na_2SO_4 was added to all cells. The current of the internal circuit was the same as in the last case (I=2,0 mA, V=4,0 V). We changed the current of the external circuit from 2.5 mA up to 8.0 mA. and correspondingly the voltage changed from 3.5 V up to 5.0 V (Table 1). As it is obvious from the results of the experiment, pH increased in the first cell from 8.5 up to 9.6, it indicates, that Na^+ ions passed together with H^+ ions. As of 3-rd cell, pH there decreased from 7.35 to 2.6 (forming of sulfuric acid).

Working

Because of volatility of H_2S the concentration of the solution changed very rapidly, so the subsequent experiments were conducted in the electrolytes made from Na_2S instead of H_2S (2gr/l Na_2So_4 was added in all cells as background). The consequential series of the experiments were carried out. By the results (Table 1) of these experiments we determined correlation between the value of the voltage (correspondingly current) in external circuit and concentrations of S^{-2} ions, which transferred in the 3-rd cell (Fig.2). pH in the 3-rd cell abruptly decreased from 6.2÷7.3 to 2.95÷3.1 after increase of the current in external circuit, this implyies that transferred sulfide ions generated SO_4^{-2} ions.

Working

- . Thus, we consider that the best regime for the transfer of sulfur ions is: I_{int}=2.0 mA, V_{int}=1.4-2.3 V; $I_{ext.}$=1.7 mA, $V_{ext.}$=1.7-2.4 V. We studied the kinetic of the transfer of hydrogen sulfur from H_2S cell into S^{-2} cell (Table 2., Fig.2) in these selected conditions. As it is shown from the results, the maximal quantity of sulfur ions passes to anionic membrane during the first 15 minutes. During subsequent 0.5, 1.0, 2.0, 3.0 hours the concentration of sulfur ions doesn't change, and the change of pH is insignificant.

Conclusion

- Agregate working on hydrogen sulfide has been made;
- metal gauze of complex content has been selected and tested as electrode and catalyst;
- content of metal gauze is determined by X-ray fluorescence analyzer and sulfidizing of it is carried out;
- the membranes of anionic (RALEX AM-PAD) and cationic types (Nafion n-115) are selected and tested;

Conclusion

- the optimal conditions for transfer of the sulfur ion in anionic membrane are established;
- it is determined, that the maximal quantity of sulfur ions passes to anionic membrane during the first 15 minutes in selected regime. The increase of duration of the electrolysis doesn’t change the quantity of sulfur ions, which transferred into the cell.