The research of hydrogen generation by sodium borohydride hydrolysis on nickel and cobalt catalysts for portable fuel cell

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At present, there is a trend to the increase of the energy demands of portable electronic devices of little and medium capacity, which are distributed more and more widely [1].

Existing batteries already can not assure their long-lasting continuous operation, and battery recharging requires connection to electrical network and takes much time [2]. These problems may be solved by using portable fuel cells (PFC) with replaceable cartridge for fuel storage since their specific parameters and continuous work time are higher than those of the batteries [1].

Hydrogen-air fuel cell with hydrogen generating cartridge is a promising portable power source. Hydrogen is produced in the reaction of hydrolysis of sodium borohydride $NaBH_4$ (SBH) which is stored in the cartridge [3,4]:

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2.$$

The application of SBH is determined by its high hydrogen capacity, the purity of hydrogen produced, and the easiness of SBH storage and transport.

In this work the process of SBH interaction with water with and without catalysts in model conditions is studied.

On fig. 1 are presented the dependence curves of hydrogen evolution efficiency and average hydrogen evolution rate on mole ratio SBH/water. Hydrogen evolution efficiency and its evolution rate related to SBH mass decreased with increasing the SBH/H_2O mole ratio.

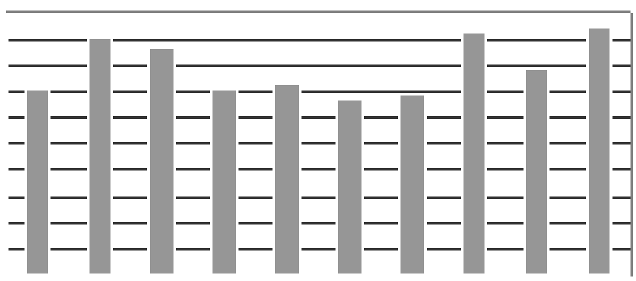
(a)

(b)
Fig. 1. Dependence curves of hydrogen evolution efficiency (a) and its average evolution rate related to SBH mass (b) on mole ratio SBH/water. 18 °C

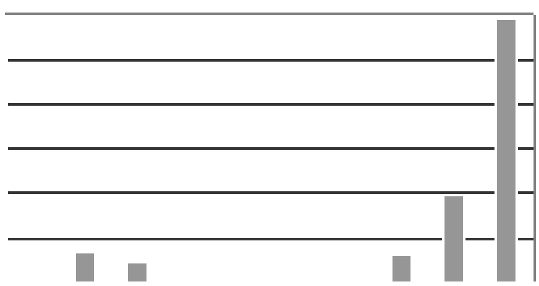
Having studied the dependence of SBH hydrolysis parameters on temperature, we determined that the process activation energy is 30 kJ mol^{-1}.

The purpose of further research was the selection of the catalysts for the SBH hydrolysis process.

On fig. 2 the comparative data of hydrogen evolution efficiency and its average evolution rate obtained on different catalysts are presented. It Electrolytical manganese dioxide (EMD), Mg and Ni/Mg do not catalyze SBH hydrolysis process, because hydrogen evolution efficiency and its average evolution rate on this substances is virtually the same as without them. The application of $LiCoO_2$, $NiCl_2$ and $CoCl_2$ essentially increases hydrogen evolution efficiency and its average evolution rate, the increase is most significant on two latter substances. This determined the interest to further studying of these catalysts.

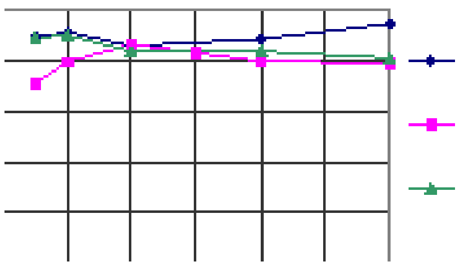


(a)

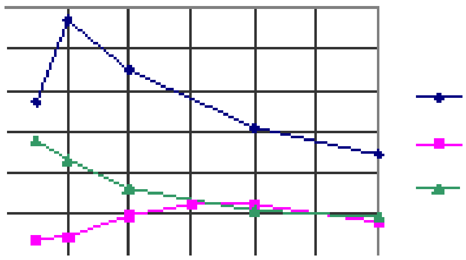


(b)
Fig. 2. Comparative data on hydrogen evolution efficiency (a) and hydrogen average evolution rate related to SBH mass (b) obtained without catalyst (1) and on different catalysts:
2 – $LiCoO_2$ (MERK); 3 – $LiCoO_2$ (FMC); 4 – EMD;
5 – Mg; 6 – Ni/Mg; 7 – Ni/Mg (heated);
8 – Ni/$LiCoO_2$; 9 – 6% $NiCl_2$; 10 – 6% $CoCl_2$.
Components ratio – 0.086 moles SBH/moles H_2O. 50 °C

On fig. 3 are shown the dependence curves of hydrogen evolution efficiency and its average evolution speed on $NiCl_2$ and $CoCl_2$ catalysts concentration in solution. As can be seen, hydrogen evolution efficiency depends slightly on concentration and is virtually the same for both catalysts. The analysis of the dependence of average evolution speed related to SBH and catalyst mass on concentration showed, that the optimal concentration of $NiCl_2$ solution is 4%, of $CoCl_2$ solution – 1%. The further studies of the catalysts were carried out using their optimal concentration.

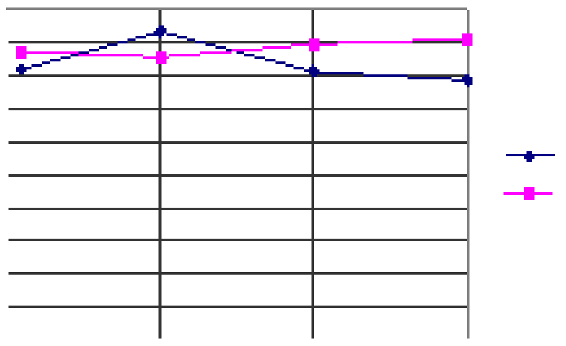


(a)



(b)
Fig. 3. Dependence curves of hydrogen evolution efficiency (a) and hydrogen average evolution speed related to SBH and catalyst mass (b) on $NiCl_2$, $CoCl_2$ and their mixture concentration.
50 °C. Components ratio – 0.086 moles $NaBH_4$/moles H_2O

The dependence of catalysts activity on temperature was studied. On fig. 4 the results of these experiments are shown. The data obtained were used for the calculation of activation energy, which constitutes 25 kJ/mol for $NiCl_2$ and 56.7 kJ/mol for $CoCl_2$.



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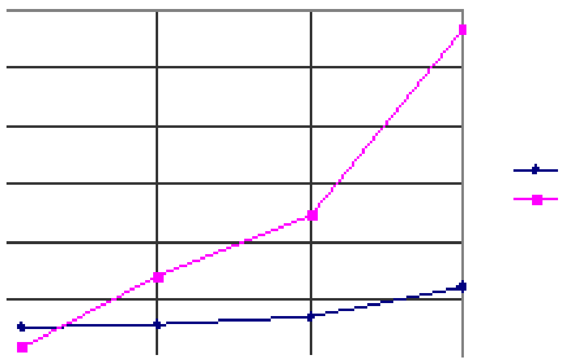
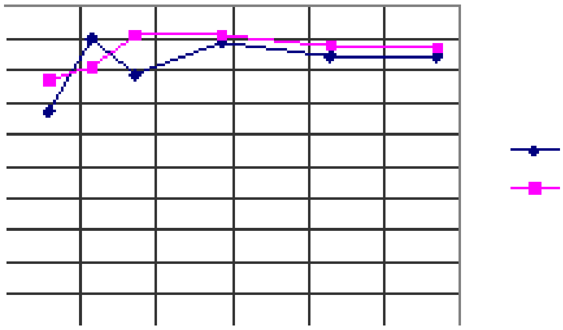


(b)

Fig. 4. Dependence curves of hydrogen evolution efficiency (a) and hydrogen average evolution rate related to SBH and catalyst mass (b) on temperature, obtained on 4% $NiCl_2$, 1% $CoCl_2$. 50 °C.

Components ratio – 0.086 moles $NaBH_4$/moles H_2O

On fig. 5 the dependence curves of hydrogen evolution efficiency and its average evolution rate on mole ratio SBH/H_2O are presented. It can be seen from the figure that the volume of produced hydrogen related to SBH mass depends slightly on components ratio, and average hydrogen evolution rate decreases with increasing this ratio.



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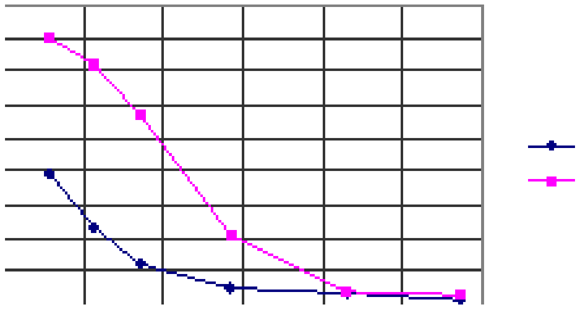
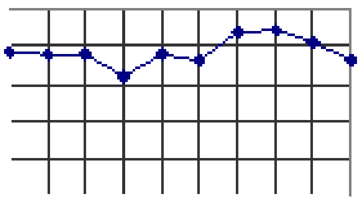


(b)
Fig. 5. Curves of dependence of hydrogen evolution efficiency (a) and its average evolution rate related to SBH and catalyst mass (b) on mole ratio SBH/H_2O, obtained on catalysts:
4% $NiCl_2$, 1% $CoCl_2$. 50 °C

The research of $CoCl_2$ catalyst stability was carried out, the results of which are shown on fig. 6 the curves of hydrogen evolution efficiency and its average evolution rate on multiple usage of $CoCl_2$ catalyst are shown. The hydrogen evolution efficiency slightly differed on repeated usage of catalyst, and the average hydrogen evolution rate decreased by 60% after tenfold usage. The research is carried out to increase the stability of this catalyst.



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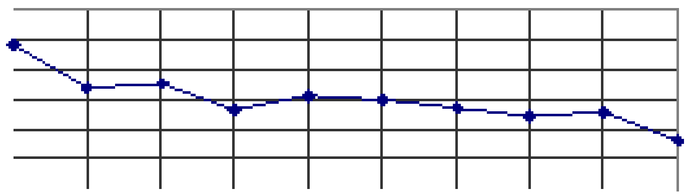

(b)
Fig. 6. Dependence curves of hydrogen evolution efficiency and its average evolution rate on the number of experiment, obtained on catalysts: 4% $NiCl_2$, 1% $CoCl_2$. 50 °C.
Components ratio – 0.086 moles $NaBH_4$/moles H_2O

Also the mixture $NiCl_2$ + $CoCl_2$ (1:1) was used as a catalyst of SBH hydrolysis process. On fig. 4 are presented the dependence curves of hydrogen evolution efficiency and its average evolution rate on this catalyst concentration. The average hydrogen evolution speed decreased with increasing the catalyst concentration. The catalytic activity of the mixture exceeded that of $NiCl_2$ only at concentrations lower than 3%. Further research of dependence of this catalyst activity on different factors is now carried out.

Basing on the results of the study carried out it can be concluded, that $NiCl_2$ or $CoCl_2$ are the active catalysts of SBH hydrolysis. The optimal concentration of $NiCl_2$ in the solution is 4%, of $CoCl_2$ – 1%. The stability of $CoCl_2$ decreases by 60% after tenfold usage. The research of these catalysts mixtures activity is carried out.

It is planned to carry out the research of activity of different catalysts in the electrooxidation reaction of hydrogen produced by SBH hydrolysis process.

References

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