

Little-known catalytic and electrochemical activity of solid alkaline hydroxides for energy conversion and storage

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1 Introduction (Why alkaline hydroxides)

The effectiveness of chemical reactions used for energy conversion and storage is due to opportunity of ‘participants’ to activate mutually or one by one, e.g. the activation of dihydrogen as fuel by metallic electrodes. However, the crucial role, as a rules, play catalytic agents or electric field, particularly to finding new arrangements of processes and devices for energy conversion and storage. Recently new (or little known) combinations of electrolytes and electrodes were found and presented in our papers [1-3]. The main part of them are different forms of solid ALKALINE [4] hydroxides. There is some differences between hydroxide of alkaline and transition metals similar to nickel hydroxides: multi-valence state of cations, e.g Ni contrary K, and thermo-stability anions (OH⁻), e.g. KOH stable up to 800 K contrary Ni(OH)₂. (The latter relates also to alkaline and the alkali-earthy hydroxides.) These our hydroxide electrolytes have high protonic conductance as well as the ability to activate molecules of dihydrogen without any catalytic agents. Moreover, these hydroxides in solid state could work with cheap electrodes: intermetallic TiFe, metallic Sn, semiconducting Si and Ge.

2 Experimental part was described in detail in [1-4].

The main aspects of experiments were:

- i) all of solid samples were prepared from preliminary molten one;
- 2) electrodes were introduced into the melt under special atmosphere;
- 3) no experiment in air!

3 Methodology of isotopic exchange by Boreskov-Muzykantov

was modified for thermodynamic inequality of hydrogen isotopes. It was necessary because even at highest temperatures (400 K) H/D separation coefficient was 1.6.

4 Results and discussion

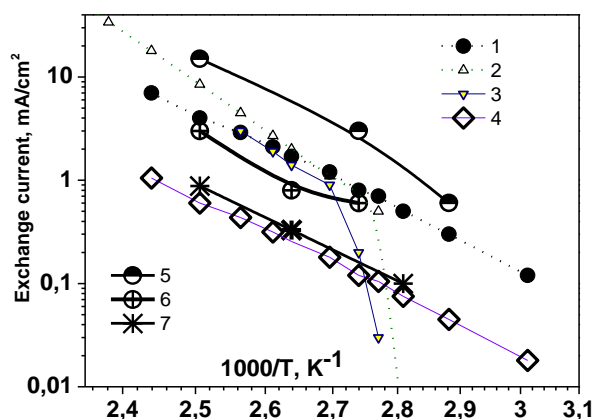


Fig. 1. To demonstrate the catalytic activity of hydroxide compounds under study the electrochemical exchange current on electrode/electrolyte interfaces - (1)- Pd-KOH.H₂O; (2)- Pd-KOH.H₂O ; (3)- Pd-KOH.H₂O; (4)- Pd-KOH.H₂O - compared with isotopic exchange between free hydroxides and dihydrogen: - (5) KOH.H₂O and 70 mmHg D₂; (6) KOH. NaOH and 70 mmHg ; (7) KOH.H₂O and Ti

Table 1. To demonstrate electrochemical activity of hydroxide compounds under study the electromotive forces of different electrochemical cells are presented.
The general formula of these cells is “C(graphite) – KOH·2H₂O (solid!!!) – “Second Electrode”

Second Electrode	OCP (E.M.F), mV		Remark
	H(protium)	D(80 at%)	
C	0	0	graphite
Ni	-130	-280	as reference
TiFe	-400	-450	before activation
p-Si	-400		20 Ohm.cm
n-Si	-440		0,3 Ohm.cm
Sn	-500		Electrolyte CsHSO ₄ , 425 K
Pt	-600		
Pb	-710		
n-Si	-850		20 Ohm.cm
Ti	-400	-500(?)	no activation
p-Si	-1200		0,05 Ohm.cm, dark
Sn	-1130	-1210	
TiFeHx	-1300	-1400	x<0,05

5 Conclusions

In spite of generalized point of view on the catalytic action our study is showing that solid hydroxides, at least alkaline ones in compound forms similar solid eutectics and crystalline hydrates [3], can activate dihydrogen (e.g. for H<>D isotopic exchange), have high protonic conductivity even at 250 K and can create of electrochemical cells working without any catalytic agents at room temperatures.

References

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