

CRYSTALLINE HYDRATES OF POTASSIUM HYDROXIDE AS NEW ADVANCED PROTONIC CONDUCTORS FOR 250 – 420 K

E.I. Nikulin*, Yu.M. Baikov

Ioffe Institute, Sankt-Peterburg, Russian Federation

*e-mail: e.nikulin@mail.ioffe.ru

Solid ionic conductors which are arousing presently an ever increasing interest in connection with progress in the development of both electrochemical methods of energy conversion and storage and other related electrochemical devices, have become a subject of active research for basic sciences and application area alike. Significantly, these materials should not only have a high ionicity, but be electrochemically active as well, i.e. be capable of supporting operation in heterogeneous systems of the type of electrode–electrolyte–electrode. Modifications of available materials by way of complicating their composition and structure is considered presently an efficient intellectual approach. Following them we are considering a family of solid inorganic protonic conductors based on alkali metal hydroxides (Li, Na, K) and water. Here attention is focused not on the individual KOH as solid hydroxide, but on their derivatives as well obtained by variation of the chemical composition, structure, and texture. Complication of the composition and texture is reached here through formation, accordingly, of the corresponding crystalline hydrates and eutectic mixtures. The impressive differences in the character and magnitude of the conductivity observed in the new products are both of pure basic and distinctly applied interest.

Solid hydroxides of alkali metals became a subject of interest in the field of ionic conductors of solids more than 40 years ago. As an impetus to this, served successful application of $\text{KOH}\cdot 0.5\text{H}_2\text{O}$ as a molten electrolyte for use in fuel cells in spacecraft [1]. Interestingly, in the ensuing ~20 years (1980–2000), the number of publications dealing with investigation of the ionic conductivity of alkali metal hydroxides has hardly risen over two dozens (see [2–6] and references therein). This should be attributed primarily to the pessimistic conclusions inferred from assessment of the potential application of these compounds, which were based on noticeable amounts of impurities in interaction with the ambient medium (*as a joke: It is impossible to keep KOH in hip pocket together with money*). However, these aspects are outside the scope of the present paper.

In the recent ten years it has turned out, however, that chemical and structural complication of hydroxides based on NaOH, KOH, and H_2O gives rise to development of materials which have a high protonic conductivity and retain electrochemical activity in the 400–250 K temperature region, a feature of considerable potential [7-10]. These results provided a driving force to a broad spectrum of basic studies. The attention is focused primarily on a comparative study of protonic conductivity and self-diffusion of hydrogen species in the crystalline hydrates and eutectics by isotopic method and aiming to possibly low temperature.

The physico-chemical properties of three types of compounds under study and/or discussion are well known and was described in considerable detail in literature only in protonated form. We have not enough much D₂O and have missed the phase diagram study in detail of deuterated forms. Nevertheless, data on figure 1 could be considered as the isotopic effect: monohydrate KOH·H₂O (T_{melt}=419 K, mhH or mhD), the dihydrate KOH·2H₂O (T_{melt} =315 K, dhH or dhD) and the eutectics KOH + KOH·H₂O (T_{melt}= 375 K, ewH or ewD). Here “mh”, “dh” and “ew” mean “monohydrate”, “dihydrate” and “eutectic” correspondingly. Capital letters “H” or “D” means isotopic form of proton Protium or Deuterium. New, unavailable data were obtained for conductivity at temperature up to 200 K. It has turn out that temperature behavior of the conductivity turned out below room temperatures far from classic Arrhenius-type (i.d linear ln(σ) or ln(σT) vs T⁻¹).

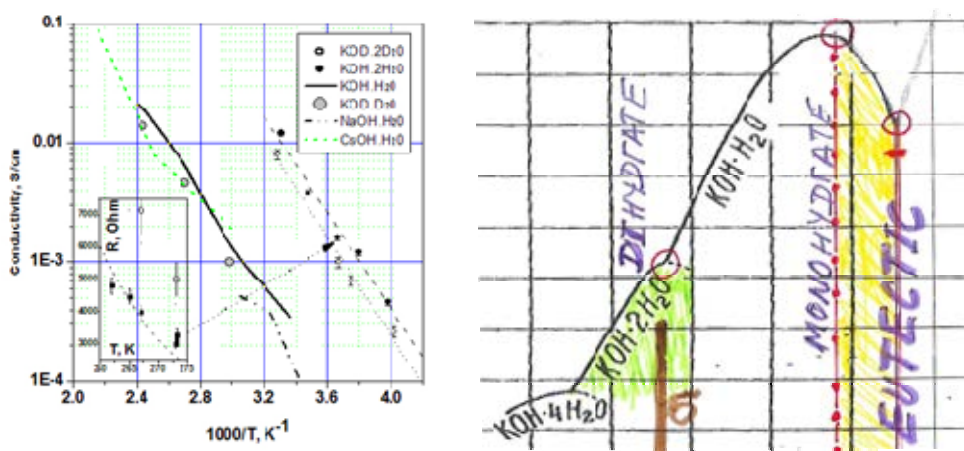


Figure 1. Conductivity of some hydrates of different alkaline metals. (Our collection)

Figure 2. Pa.r.t of phase diagram KOH–H₂O [11]. Three main points described in text.

Specific features of conductivity measurements. For determination of the electrical conductivity of crystalline hydrates, a version of dc measurements with an electrochemical cell of some types ‘(Ti, or Sn|) KOH·nH₂O|C’ (n = 0.5; 1; 2) was developed. The EMF of them is approximately 1.15 V. Four-electrodes arrangements were used. Such cells can operate into an external ohmic load as rechargeable batteries for over 100 h, with a current output of up to 200 μA at 320–410 K for n = 1, and at 260–320 K for n = 2. **More important:** in such cells the electrolyte is not in direct contact with the outer medium. Cell on figure 3 seems primitive, but effective.

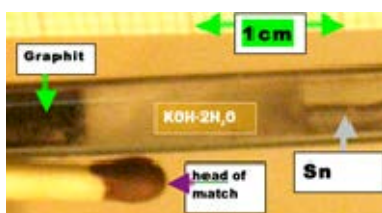


Figure 3. Glass tube at 300 K, left-graphite, middle-electrolyte, right Sn wire; 1.2 V.

The interest in complex hydroxide-based compounds stems from the possibility: 1) of these compounds to operate at close to room temperatures, 2) of their competitive protonic conductivity and 3) of electrochemical activity achievable *without the use of expensive catalysts*. 4) The low melting temperature of these compounds is suitable for the development of a variety of electrochemical devices, including modest-sized low-power supplies etc. [12-14]. 5) Physical and electrochemical properties of these materials are the object of the real intellect-intensive investigations to advance the electrochemistry of solid electrolytes not only in technologies, but also for basic researches.

Saying about proton conductivity of materials under our study and slightly advertising them we are omitting to prove the existence of namely charge and mass transfer at temperature under 250 K. The matter is that the experiment arrangement is not so simple to present it on half page of thesis. Moreover, more some of them must be discussed in wider circle. Therefore, we would like to present only two experimental facts concerning the mechanism of charge and mass transport below 220 K. On figure 4 one presented the temperature run of conductivity of mono- and dihydrate of KOH up to 200 K. Let us to highlight two features. First of all, there are no difference which could be related to isotopic effect ($H < > D$), contrary to results on figure 1 at temperature near 273 K ($1000/T > 3.7$). Secondly, there are the pictures characterized for the glass transitions at freezing the electrolyte. In spite of the similarity of electrochemical cells, like on figure 3, the similarity of curve's run could be related only for mono- and dihydrate KOH. It is may be explained by the leading role of phase transformations solid $KOH \cdot nH_2O$ according phase diagram on figure 2. In certain sense it would be considered as the role of hydrogen species in this electric properties.

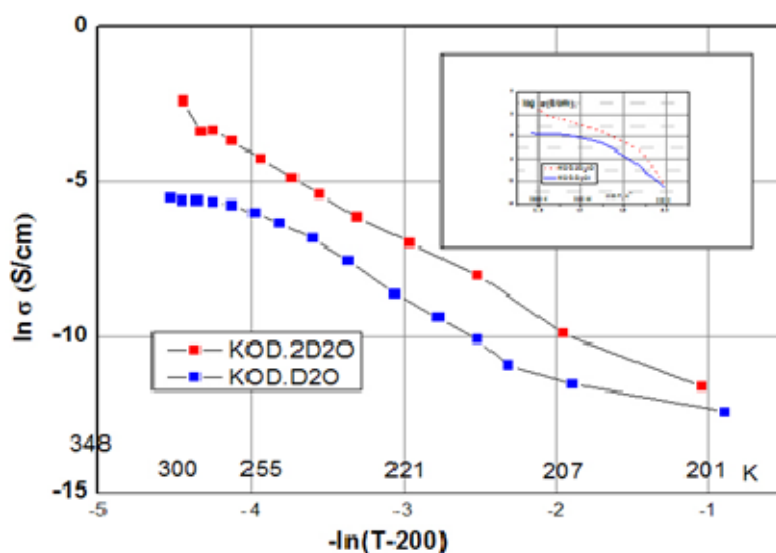


Figure 4. Special forms of 100%-Deuterated hydrates of KOH at different temperatures, to study the conductivity presented in ADF form with $\alpha \approx 0.33$.

In the course of these searches we have undertaken to search principal effect for mechanism of proton transfer in our materials, namely protonic Hall effect [13]. On

figure 5 it is presented experimental data which could be interpret as influence of switch on magnetic field perpendicular to total current.

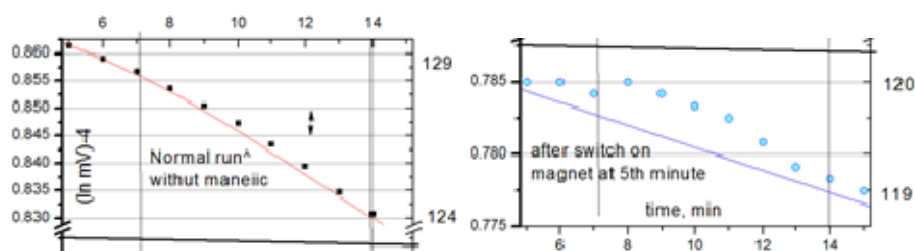


Figure 5. In special cells like on figure 3 was add two electrodes perpendicular current flow. The run of data shown on the left. After switching the magnetic field enough strong effect could be watch (blue points) on the right. Then after off at 8th minute could be watch the relax. Such effect repeated many times.

A totally different **conclusion** about the prospects in both basic and applied sciences evolves with respect to complex compounds based on alkali metal hydroxides. Two types of complication have been considered, namely, a purely chemical one, through formation of crystalline hydrates and a physico-chemical approach involving formation of eutectics. Materials of both types have been studied, and they demonstrated a high protonic conductivity ($>10^{-3}$ S/cm) at temperatures below 370 K, and the crystalline hydrates, down to room temperatures. This is essentially a new family of inorganic protonic conductors. Variation of their composition and texture appears to be a potentially promising approach for both basic science and as a contribution to new emerging technologies.

References

1. Stephen P.M.S, Howe A.T.// Solid State Ion. 1980. V.1. 5. P.461.
2. Baikov Yu.M.,// Sov. Electrochem.1982. V.18. 10. P.1256 (in English).
3. Haas K.H., Schindewolf U. // J. Solid State Chem. 1984. V.54. P. 342.
4. El'kin B.Sh.// Solid State Ion. 1990. V. 37. P. 139-145.
5. Spaeth M., Kreuer K.D. et al// Solid State Ion. 1997. V.97.P. 291.
6. Spaeth M., Kreuer K.D.,et al // J. Solid State Chem. 1999.V.148 .P. 169.
7. Baikov Yu.M.,// Solid State Ion. 2007. V.178. 10. P. 487.
8. Baikov Yu.M.// J. Power Sources 2009. V.183. 371.
9. V.M. Egorov et al// Phys. Solid St. 2009. V.51. P.33.
10. Baikov Yu.M.,// Solid State Ion. 2010. V.181. P. 545.
11. Gmelin// Handbook of Inorganic Chemistry 1963 . V.22. Kalium
12. Baikov Yu.M. Melekh B.T.et al. //Tech. Phys. Lett. 2010.V. 36. 5.P. 45
13. Nikulin E.I. et al// Phys. Solid State .2014. V. 56. 5. 1095
14. Baikov Yu.M. et al//Tech.Phys.Let// 2014 . V.40. 6 .P.557-560