

NONARRENIUS BEHAVIOR OF CERTAIN SOLID PROTONIC CONDUCTORS AT 200–420 K: COMPOUNDS OF ACIDIC SALT, HYDRATES OF POTASSIUM HYDROXIDE, INDIVIDUAL ALKALI

H. Takahashi^{1*}, Yu.M. Baikov², E.I. Nikulin²

¹Institute of Quantum Beam Science, Grad.School, Ibaraki University, Japan

²Ioffe Institute, Sankt-Petersburg, Russian Federation

*e-mail: haruyuki.takahashi.ssilab@vc.ibaraki.ac.jp

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 activity 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 certain representatives of three families of solid inorganic protonic conductors. Contrary to high temperature perovskites ceramic, in which hydrogen is “guest”, our attention is concentrated on inorganic materials, in which hydrogen is the part of “host”, first of all anions. But there is subtle difference between hydrogen containing anions, depended on “small” numbers circumstances: hydroxide ion is sooner keeper of basicity contrary to acidic ion. Besides of these fundamental aspects there is the special aspect due to the role of water molecules, which are not only in surrounding atmosphere, but also as the structural component of hydrates of both acidic salts and hydroxides. It is very interesting from both applied and basic point of view. The matter is that the amphoteric properties of water molecules sufficiently change the level of acidic-basic properties, which, according to widely spread idea, responsible namely for proton migration randomly as well as under the electric and/or chemical potential gradient. Therefore, for further discussion it is useful to consider separately the individual compounds, even like solid compound $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ or solid eutectic $\text{KOH}+\text{KOH}\cdot\text{H}_2\text{O}$, and hydrates of individual hydroxides. Of course, here authors do not claim to discuss various sides of such distinguished event as proton transport. We are simply trying to attract the attention of “protonic community” to seeming enough not important the deviation from Arrhenius –type dependence “ physico-chemical properties – temperature”. The matter is that the high-temperature phase of protonic conductors is characterized, as a rules, enough small E_{act} from linear curve $\ln(\sigma T)$ vs T^{-1} . Such simple curve is sufficient from applied (technological) point of view. However, it is not enough for intellectual treatment of available experimental data at the search of advanced materials.

To illustrate one's point of view by examples let us consider some our data relating to three different families of inorganic proton conductors studied in Ibaraki University (Japan) and Ioffe Institute (Russian Federation).

Hereafter the superprotonic phase of $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ is abbreviated to HT phase. The characteristic feature of $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ is that the HT phase is readily supercooled as a metastable state at room temperature [1]. Takeya et al. have investigated the stability of the supercooled state of HT phase [2]. They have proved that the phase is stable at room temperature for a few days under a dry atmosphere. The $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ enables us to examine the structural and the dynamical properties of the HT phase in wide temperature range. So it is considered to be a model material for investigating the superprotonic conduction mechanism in the solid acids. Takahashi et al [3] (Figure1) investigated the temperature change of the structure and the proton conduction for the HT phase of $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ in order to elucidate the nature of the superprotonic conduction in inorganic solid acids.

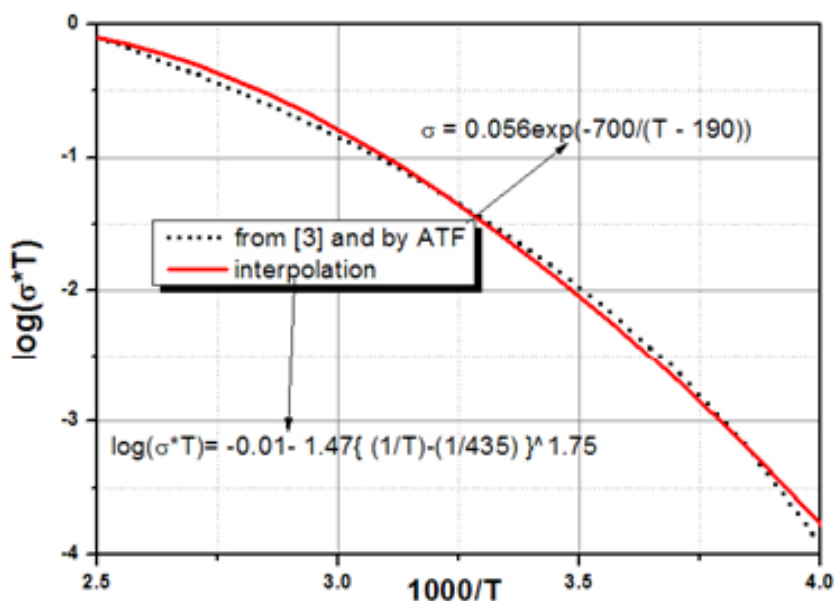


Figure 1. Different types of the presentation the same data from [3] on the conductivity of $\text{Cs}_2(\text{HSO}_4)(\text{H}_2\text{PO}_4)$ vs temperature: Vogel-Tamman- Fulcher (black dot curve) and traditional approach for physics of unordered system (red line).

Inorganic solid bases were discovered as protonic conductors historically simultaneously (1981-1982 years) with acidic salts. But because of any applied requirements solid alkali metal hydroxides (Li, Na, K, Cs, Rb) have not retained in concurrent run. Although they 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[4]. In the ensuing ~20 years (1980–2000), the number of publications dealing with the conductivity of alkali metal hydroxides has hardly risen over two dozens [5,6] . This should be attributed primarily to the pessimistic conclusions inferred from assessment of the potential application of these compounds , which were based on the 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 this presentation. The special team from Ioffe Institute has started also from molten eutectic NaOH-KOH as liquid phase of countercurrent technological columns.

Namely then the high proton mobility was observed not only in molten, but also in high-temperature solid phase [7].

In the recent ten years it has turned out, however, that chemical and structural complication of hydroxides based on NaOH, KOH, and H₂O gives rise to development of materials which have a high protonic conductivity and retain electrochemical activity in the 400–250 K temperature region. This is the feature of considerable potential [9, 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.

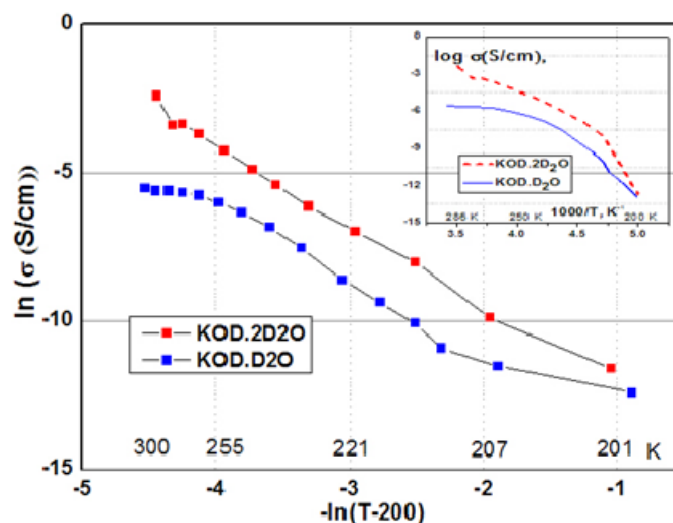


Figure 2. Special presentation the data on the conductivity of crystalline hydrates of potassium hydroxide in the form as well monohydrate as dihydrate of deuterated compounds. Isotopic effect is not discussed here. In insert: the more frequently used presentation are shown in the framework of this theses. Ln-ln mastab allows to indicate the power law parameter.

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. These two families on which our attention is focused above are not individual NaOH and 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 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.

In the framework of announced topic in the title the next two pictures relates to sooner fundamental problem of protonic transport in solids. Nevertheless, these data

allows to do some general conclusion that PROTON TRANSPORT is now not understand fully. The necessary explanation is in figure captions.

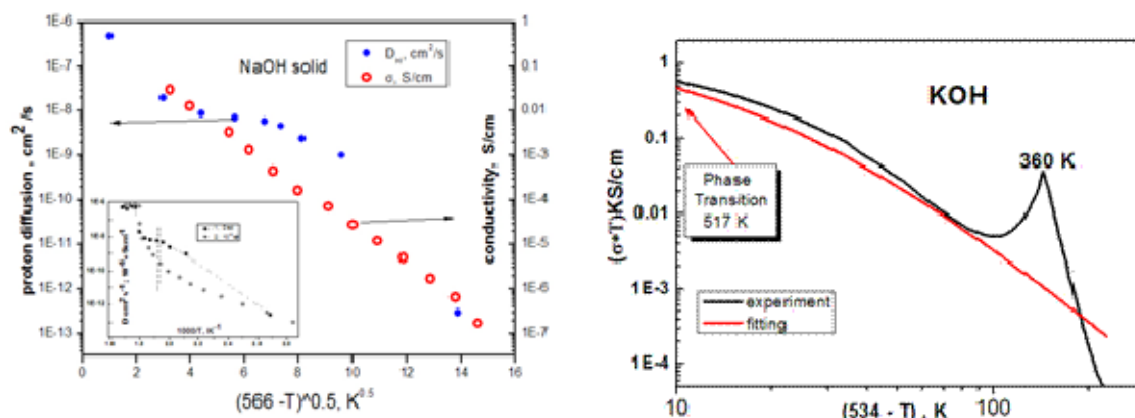


Figure 3 (left) and **Figure 4** (right) show different forms of the presentation of the conductivity in solid individual hydroxides (NaOH left, KOH right) at temperature below approximately 500 K, i.d. phase transformations into superionic states [8,11].

For both materials there are remarkable deviation from simple Arrenius's form and possible using presentation based on physical theories on disordered materials. For NaOH there is couple of interesting phenomena:

- 1) evident difference Arrenius's law (insert) and power law and
- 2) different temperature run of conductivity (red circles) and self - diffusion of proton measured by isotopic method (blue points).

The same difference take place for KOH, (but not shown here). For KOH is most interesting the strong peaks at 360 K [11] accompanied by slow relaxation of another physico-chemical properties.

References

1. Cyisholm C.R.I., Haile, S.M. //Solid State Ionics. 2000. V.136-137. P. 229.
2. Takeys S., Hayashi S.V., Fujihisa H., Honda K. // Solid State Ionics. 2006. V.177. P. 483.
3. Takahashi H., Suzzuki Y., Sakuma T. // Solid State Ionics. 2016. V. 285. P. 155.
4. Stephen P.M.S., Howe A.T. // Solid State Ion. 1. (5). 1980. 461.
- 5 El'kin B. Sh. // Solid State Ion. 1990. V. 37. P. 139-145.
6. Spaeth M., Kreuer K.D., Maier J. // J. Solid State Chem. 1999.V.148 .P. 169.
7. Baikov Yu.M. // J. Power Sources. 2009. V.183. P. 371.
8. Baikov Yu.M. // Solid State Ion. 2012. V.208. P. 17-24.
9. Baikov Yu.M., Melekh B.T., Korkin I.V. // Tech. Phys. Lett. 2010. V. 36. (5). P. 45.
10. Nikulin E.I., Baikov Yu.M. // Phys. Solid State. 2014. V. 56. 5. 1095.
11. <http://www.solidionic.com>.