High Resolution Solid-State NMR Suggests a New Model of Protonic Conductivity in the Superionic Conductor LiH_2PO_4 : Critical Role of Physisorbed Water

J.J. Kweon, R. Fu, W.W. Brey (NHMFL); C.E. Lee (Korea U.); N.S. Dalal (FSU, Chemistry)

Introduction

Understanding the mechanism of proton conduction in solids and biophysical processes is of considerable interest, but despite focused effort the basic mechanism remains unclear. In particular, since proton NMR is the most direct technique for probing the structural and dynamic aspects of protons, NMR has been utilized to follow the mechanism of proton conduction in the most promising superionic material such as LiH_2PO_4 (LDP), however the measurements were made only at the low frequency of 200 MHz, where the spectral resolution was insufficient to lead to any definitive conclusions[1,2]. In this project, as part of the development of the VT facility on the 21.2 T (900 MHz) spectrometer, we have reinvestigated proton NMR on LDP at 300, 600 and (currently) 900 MHz on specifically prepared LDP samples. The results lead to a much enhanced understanding of the conduction mechanism: a critical role of physisorbed water, in contrast to that derived from the earlier low-resolution NMR studies.

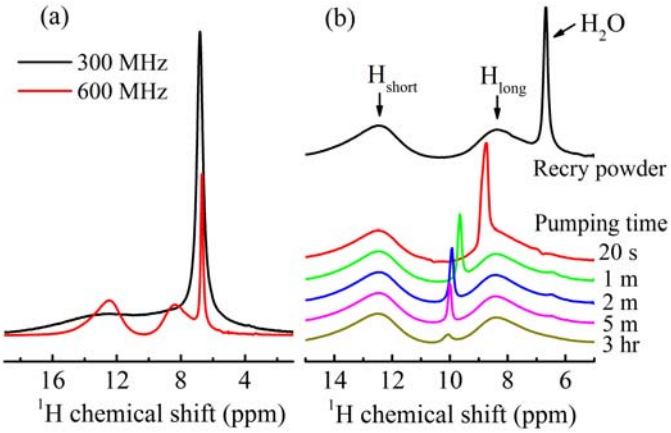

Fig. 1 (a) ^{1}H spectra at 300 and 600 MHz of recrystallized powder. (b) ^{1}H spectra at 600 MHz with systematic control of water by vacuum pumping.

Experimental

High-resolution NMR (MAS) measurements were made using LDP polycrystalline powder (99.99%), purchased from Aldrich, purified by recrystallization in double processed purified water at 30 ^oC. ^{1}H magic-angle spinning (MAS) NMR lineshape measurements on the LDP powder were performed with 300, 600 and 900 MHz spectrometers at NHMFL. Electrical conductivity was measured on pellet samples in an Ar filled glove box by using a conventional two-probe technique.

Results and Discussion

Fig. 1 (a) shows a comparison of the low-field, low-resolution and high-field, high resolution spectra (obtained using 13.5 kHz spinning speed). Clearly the high field spectra of Fig. 1 (b) provide much more detailed view. Two broad peaks can be assigned to the protons in two different hydrogen bonds, which do not show excessive dynamics, while the narrow peak corresponds to highly dynamic protons whose chemical shift depends on the sample drying condition. This resonance associated with the fast-water exchange arises from weak interaction between protons with short hydrogen bonds and adsorbed water molecules. Plots of amount of water in the sample (as measured by NMR) vs protonic conductivity showed clear proportionality, showing that the sample conductivity is controlled by the water content, in contrast to the earlier proposed model [1,2] based on just the hydrogen bonds. Detailed VT studies using the 900 MHz spectrometer are in progress.

Conclusions

Correlated high-field, high-resolution solid-state NMR and electrical conductivity measurements on the superionic conductor LiH_2PO_4 show that the mechanism of its protonic conductivity is the exchange of H_2O protons with its short hydrogen bonds. The protonic conductivity can be enhanced by several orders of magnitude by controlled exposure to water.

Acknowledgements

This work is supported by the NHMFL User Collaboration Grants Program. We gratefully acknowledge Peter L. Gor'kov and Jason Kitchen for developing a VT MAS probe for 900 MHz spectrometer.

References

[1] Kweon, J. J., *et al*., Applied Physics Letters, **98**, 262903 (2011).
[2] Kweon, J. J., *et al*., Applied Physics Letters, **101**, 012905 (2012).