A Versatile Variable Temperature Probe for the Ultra Wide Bore 21.2 T (900 MHz UWB) Spectrometer for High Resolution NMR of Solids

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Introduction

High resolution NMR employing cross-polarization and magic angle spinning (CPMAS) techniques has become a highly valuable method for elucidating the chemical structure and bonding of solids. High resolution NMR with variable temperature (VT) measurements enables the elucidation of the mechanism of the high proton conductivity in superprotonic conductor and the various types of phase transitions at the atomistic (microscopic) scale. We designed and fabricated a 3.2 mm double resonance MAS probe for VT experiments on the 900 UWB magnet, with added features to allow for low temperature experiments to 130 K.

Experimental

VT and bearing gas are both delivered to the stator through vacuum insulated glass dewars (Fig 1). Cooling the bearing gas not only lowers the sample temperature, but also allows for further sample thermal gradient reduction by matching the VT and bearing gas temperatures. The magic angle adjustor is located directly behind the stator housing, the short length of the contact between the screw mechanism and stator body serves to minimize thermal contraction and expansion effects that might lead to angle instability during wide VT experiments. High-resolution MAS NMR measurements were made using polycrystalline LiH_2PO_4 (LDP) powder, a superprotonic conductor, for elucidating the mechanism of its high protonic conductivity.

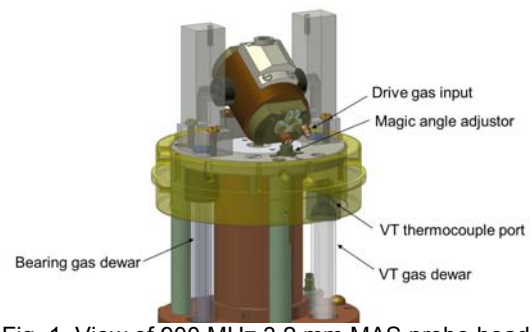

Fig. 1. View of 900 MHz 3.2 mm MAS probe head, showing VT, bearing, and magic angle adjustment components.

Results and Discussion

At 900 MHz, well-resolved ^{1}H NMR spectra are observed that are assignable to protons in the short and long O-H…O hydrogen bonds and a peak to physisorbed H_2O (Fig 2). The spectral characteristics of the adsorbed H_2O peak depend on the H_2O content, implying fast exchange between the adsorbed H_2O and the O-H…O protons. Parallel ^{1}H, ^{31}P and ^{7}Li NMR and protonic conductivity studies on samples containing (relatively) known amounts of adsorbed H_2O clearly suggest that the exchange between the adsorbed H_2O and O−H···O protons and interbond hopping of protons, in concert with the rotational fluctuation of the phosphate moieties is the dominant mechanism of LDP's protonic conductivity.[1]

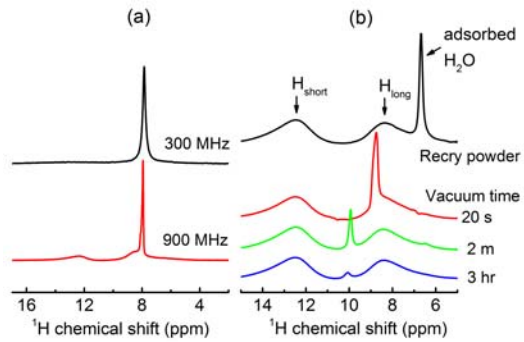

Fig. 2. (a) ^{1}H spectra at 300 and 900 MHz of recrystallized powder. (b) ^{1}H spectra at 600 MHz with a systematic control of adsorbed water by vacuum-pumping time.

Conclusions

Correlated high-field, high-resolution solid-state NMR and electrical conductivity measurements on the superionic conductor LDP show that the mechanism of its protonic conductivity is the exchange of H_2O protons mainly with its short hydrogen bonds and not the interbond hopping of protons between the O−H···O bonds.

Acknowledgement

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References

[1] Kweon, J.J., *et al*., J. Phys. Chem. C, **118**, 13387-13393 (2014).