High Field MAS NMR and Conductivity Study of the Superionic Conductor LiH$_2$PO$_4$: Critical Role of Physisorbed Water in Its Protonic Conductivity

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ABSTRACT: LiH$_2$PO$_4$ (LDP) is a favored candidate for hydrogen fuel cells, but the mechanism of its high protonic conductivity remains unclear. A complicating factor has been the lack of resolution in the reported proton NMR spectra. We now report multinuclear magic angle spinning NMR in LDP at magnetic fields up to 21.2 T. 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$_2$O. The position and intensity for the H$_2$O peak depend on the H$_2$O content, implying fast exchange between the adsorbed H$_2$O and the O···H···O protons. $^{31}$P and $^7$Li NMR spectra and spin–lattice relaxation measurements showed that the proton hopping/exchange processes involve concerted hindered rotational fluctuations of the phosphate groups. Conductivity data from adsorbed H$_2$O-controlled samples clearly suggest that the mechanism of LDP’s protonic conductivity is dominantly the exchange (and hopping) of the adsorbed H$_2$O protons with the short O···H···O hydrogen bonds, in contrast to an earlier model that ascribed it to intermolecular hopping of O···H···O protons. The new findings enable us to modulate LDP’s protonic conductivity by several orders of magnitude via controlling physisorbed water.

1. INTRODUCTION

Understanding the mechanism of proton conduction in hydrogen-bonded solids is of considerable interest owing to their potential application as proton conduction electrolytes in fuel cells. Despite focused effort the basic mechanism remains unclear.1−3 The AH$_2$PO$_4$-type (A = Li$^+$, NH$_4$$^+$, K$^+$, Rb$^+$, Cs$^+$, TI$^+$) hydrogen-bonded lattices show various physical properties depending on the ionic radius of the cation A and the hydrogen bond lengths. For instance, at room temperature (RT) the protonic conductivity was measured to be 10$^{-10}$−10$^{-11}$ Ω$^{-1}$ cm$^{-1}$ for KH$_2$PO$_4$ (KDP) and 10$^{-9}$−10$^{-10}$ Ω$^{-1}$ cm$^{-1}$ for CsH$_2$PO$_4$ (CDP).6 In the so-called superprotonic phase transition at 230 °C, an increase of protonic conductivity by up to 4 orders of magnitude has been observed for CDP, resulting from rapid dynamic motion between different H-bonding environments and fast rotation of the phosphate ions.2 On the other hand, LiH$_2$PO$_4$ (LDP) exhibits an exceptionally high protonic conductivity (i.e., 10$^{-3}$−10$^{-5}$ Ω$^{-1}$ cm$^{-1}$) even at RT,7,9 but the underlying conduction mechanism has not been fully understood, thus suggesting an attractive research area.

A good protonic conductor generally involves O···H···O hydrogen bonds longer than 2.60 Å. The crystal structure of LDP determined by X-ray and neutron diffraction shows two types of O···H···O hydrogen bonds with different bond lengths of 2.677 and 2.561 Å connecting the tetrahedral PO$_4$ groups.4,10 In several earlier studies of LDP, fast interbond proton hopping was suggested to be responsible for the exceptionally high protonic conductivity—this conclusion being based on the correlation between temperature-dependent $^1$H spin–lattice relaxation and conductivity measurements.8,11,12 However, in the similar compound CDP, which also contains two different H-bonding environments, the interbond proton hopping was found to be very slow, together with low protonic conductivity (10$^{-9}$−10$^{-10}$ Ω$^{-1}$ cm$^{-1}$).8,13 More importantly, LDP is known to be hygroscopic, but whether or not the adsorbed H$_2$O plays any role in LDP’s protonic conductivity mechanism was not considered. This is important because earlier studies of several AH$_2$PO$_4$ compounds (A = Li, K, and Cs) had indicated the role of lattice dehydration or humidity in the conductivity mechanism. For example, the ionic conductivity of CDP and its composite with silica was found to increase, reversibly, above 230 °C in humid conditions, the conductivity being influenced by silica’s hydrophilicity.14 The acceleration of the conductivity could be induced by point defects generated in the ionic salt.
(CDP) near the surface between the ionic salt and silica.\textsuperscript{14} Similarly, a positive effect of high temperature steam on protonic conductivity of CDP/SiP\textsubscript{2}O\textsubscript{7}-based composite electrolytes has been reported.\textsuperscript{15} Observation of increase in ionic conductivity in Rh\textsubscript{3}H\textsubscript{4}P\textsubscript{2}O\textsubscript{7} under high humidity to suppress its lattice dehydration (i.e., loss of hydrogens and conversion to Rh\textsubscript{2}H\textsubscript{2}P\textsubscript{2}O\textsubscript{5}) has also been studied.\textsuperscript{16} The mechanism of protonic conductivity in KDP has been studied in detail.\textsuperscript{17} The mobile species were thought to result from a 3-fold rotation of H\textsubscript{2}PO\textsubscript{4}···O units about any axis leading to H···O···H···O units. The H···O···H bridge is dissociated under applied voltage to lead to H\textsuperscript{+} and OH\textsuperscript{-} moieties. But the role of surface adsorbed water was not mentioned. We note, in addition, that the role of physisorbed H\textsubscript{2}O in conductivity of conducting polymers such as polyaniline and silica glasses has been mentioned.\textsuperscript{18–21} High-performance CDP-based fuel cells have been reported and humidity was found to be helpful for their stable performance.\textsuperscript{22} Finally, in LDP itself, the role of humidity has been noted,\textsuperscript{9} but surprisingly, the conductivity was reported to decrease with increase in dampness, in contrast to CDP. In addition, the earlier NMR studies on LDP were carried out at the low frequency of 200 MHz for \textsuperscript{1}H, where spectral resolution was insufficient for assignment of peaks to specific O···H···O protons,\textsuperscript{11,12} adding to the impetus for the present undertaking.

In the present study we utilized the much higher resolution afforded by the 300, 600, and 900 MHz solid-state NMR instrumentation, available at the National High Magnetic Field Laboratory (NHMFL). Indeed, using magic angle spinning (MAS) at these high frequencies (high fields), peaks from the different O···H···O protons were well resolved and easily assignable to the “long” and “short” hydrogen-bonded protons. An additional narrow peak was observed from adsorbed H\textsubscript{2}O that actually dominated the spectra. Parallel \textsuperscript{1}H and \textsuperscript{31}P NMR and protonic conductivity studies on samples containing (relatively) known amounts of adsorbed H\textsubscript{2}O clearly suggest that the exchange between the adsorbed H\textsubscript{2}O 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. This finding enabled us to control the protonic conductivity of LDP for the first time, by a careful control of physisorbed H\textsubscript{2}O, suggesting an additional important factor in the utility of LDP as a superionic material.

2. EXPERIMENTS

High-resolution MAS NMR measurements were made using polycrystalline LDP powder (99.99%), purchased from Aldrich, and purified by recrystallization in double processed purified water at 30 °C, following earlier reports.\textsuperscript{23–25} \textsuperscript{1}H MAS NMR line shape and spin–lattice relaxation time ($T_1$) measurements were made using 300, 600, and 900 NMR spectrometers on samples with a systematic control of physisorbed water by pumping. On the 300 and 600 MHz NMR spectrometers, 4 mm Bruker CPMAS double-resonance NMR probes and a 3.2 mm homemade Low-E MAS NMR probe were used with a spinning rate of 13.5 kHz. A locally designed and fabricated 3.2 mm CP/MAS double-resonance NMR probe was used on the 900 MHz spectrometer. In order to quantify relative signal intensity between the short and very long $T_1$ components, single-scan \textsuperscript{1}H NMR spectra were acquired right after the sample was first inserted into the magnet using the spin–echo pulse sequence to remove background \textsuperscript{1}H signal from the probe. Multiscan spectra with short relaxation delay did not show strong enough resonances from the long $T_1$ components. Adamantane (1.63 ppm, relative to TMS) was used as the chemical shift reference. A cross-polarization (CP) based heteronuclear $^{31}$P–$^1$H correlation spectrum with a spinning speed of 12.5 kHz was recorded at 600 MHz using a CP contact time of 50 μs and a recycle delay of 5 s with a spin-lock field of 35 kHz. Similarly, direct polarization (DP) was used to record single-scan $^{31}$P and $^1$Li spectra at 900 MHz using 13.5 kHz spinning speed, again acquired right after the sample was first inserted into the magnet. The chemical shifts for $^{31}$P and $^1$Li spectra were calculated from the $^1$H chemical shift based on their relative gyromagnetic ratios. A short recycle delay of 0.01 s was used in the saturation-recovery method for $T_1$ measurements of $^{31}$P and $^1$Li.

Recrystallized LDP powder was fabricated into a disk sample (12 mm diameter, 1 mm thickness) by uniaxially pressing in a cylindrical die at 4000 kg/cm\textsuperscript{2} in ambient atmosphere. DC and AC electrical conductivity measurements as a function of vacuum pumping time were made on the pellet samples in an Ar-filled glovebox by a simple two-probe technique using an Exttech MN15A Digital Mini multimeter for DC measurement and a Gamry Reference 600 potentiostat/galvanostat for AC measurement. Along with AC electrical conductivity measurement at 10 Hz, the change in the amount of adsorbed H\textsubscript{2}O was determined from the mass change of LDP the pellet as a function of pumping time. To measure humidity-dependent conductivity, three pellet samples were made using different pressures of 2000, 4000, and 6000 kg/cm\textsuperscript{2}. Simultaneous AC conductivity measurements were made on the three pellet samples at 20 Hz as a function of relative humidity at 40 °C inside a humidity-controlled chamber using three different lock-in amplifiers (Stanford Research Systems, Model SR830 DSP).\textsuperscript{26}

3. RESULTS AND DISCUSSION

3.1. Peak Assignment. Figure 1a shows a comparison of the low-field, low-resolution and high-field, high-resolution spectra obtained at RT using a recrystallized powder sample under the same humidity. A narrow peak at ~8 ppm was observed at 300 MHz, while three resonances were observed at

![Figure 1](https://example.com/image1.png)

**Figure 1.** (a) $^1$H spectra at 300 MHz using 7 kHz spinning speed (top), 600 MHz using 13.5 kHz (middle), and 900 MHz using 13.5 kHz (bottom) of the recrystallized LDP powder without vacuum pumping, showing resolution enhancement at high fields. The small peak with smaller chemical shift than the water exchange peak acquired at 600 MHz is background proton signal from a 3.2 mm homemade Low-E MAS NMR probe. (b) $^1$H spectra at 600 MHz with a systematic control of adsorbed water by vacuum-pumping time.
600 and 900 MHz: one at ~8 ppm and two broad peaks at 12.4 and 8.4 ppm. Figure 1b shows the $^1$H spectra with carefully H$_2$O-controlled samples, clearly indicating three well-resolved resonances. It is known that there is a direct correlation between the interoxygen (O−H···O) distance and the $^1$H NMR chemical shift. The resonance at a smaller chemical shift is attributed to the protons in the long hydrogen bonds, while the peak at a larger chemical shift to protons in short hydrogen bonds. Therefore, the two broad peaks at 12.4 and 8.4 ppm can be assigned to the two protons in two different hydrogen bonds: H1 with the longer O−H···O length of 2.677 Å and H2 of the shorter length of 2.561 Å. Their large line widths imply that the motion involving these protons is rather slow. The third, narrow peak, on the other hand, corresponds to highly dynamic protons. As shown in Figure 2, both broad peaks are directly coupled with phosphorus, as seen in the CP-based heteronuclear $^{31}$P−$^1$H correlation spectrum while this narrow peak is not, indicating the phosphorus in the tetrahedral PO$_4$ groups strongly couples with the protons in the two different H-bonding environments but does not have effective coupling with the highly dynamic water protons.

Interestingly, the position and intensity of the sharp peak vary in proportion to the sample’s H$_2$O content (controlled by the vacuum pumping time), showing that the H$_2$O protons experience a fast exchange with the short O−H···O protons. Since the H2 of the short hydrogen bond appears at 12.4 ppm and the water peak normally at 4.7 ppm, the exchange rate has to be much larger than their chemical shift difference of 7.7 ppm, i.e., $\gg$4620 Hz at 600 MHz. In the fast exchange limit, the observed chemical shift $\delta_{\text{obs}}$ appears in the position given by the mean of the chemical shifts $\delta_A$ and $\delta_B$ from the two species participating in the fast exchange process, weighted by their equilibrium concentrations $p_A$ and $p_B$ ($p_A + p_B = 1$): $\delta_{\text{obs}} = p_A \delta_A + p_B \delta_B$ (1)

It is quite possible that the water protons exchange with both the long and the short hydrogen bonds, but the NMR spectra under high water content shift the water peak toward that from the short ones, well past that from the longer ones. Clearly the exchange is dominated by the protons with the short bond lengths; otherwise the water peak could never go past that from the ones with the long bond lengths. Unfortunately, the peak from the long bond length H’s is covered by the strong water peak, and thus it is hard to follow its exchange under our conditions at any NMR frequency used. Nevertheless, it is clear that under higher water content the proton exchange is dominantly with protons from the short hydrogen bond lengths.

3.2. Role of Water in LDP System. A clue to the lack of role of interbond hopping was suggested by the widths of the proton peaks: the widths of the peaks from both sites of the O−H···O protons are broad and almost equal, as can be seen in Figure 1b, implicating that any underlying interbond proton hopping motion is slow on the millisecond time scale. This is also indicated by the fact that spin–lattice relaxation times of these two broad components were around 160 s for recrystallized powder without drying and around 230 s under vacuum pumping for 5 min and showed no temperature dependence within the experimental temperature range from 280 to 330 K. The derived inference is that the interbond proton hopping is very slow, in sharp contrast to an earlier proposed mechanism for LDP’s $^1$H superionic conductivity. Conductivity measurements were then undertaken to support the above conclusion from NMR that proton conductivity in LDP is strongly associated with the adsorbed H$_2$O. Figure 3 shows the plots of the relative intensity (solid squares, left axis) of the fast exchanged proton resonance of the recrystallized powder and the DC electrical conductivity (solid circles, right axis) of the recrystallized powder pellet as a function of vacuum-pumping time. The $^1$H signal intensities were normalized to that from the unpumped sample.
and the activation energies as a function of pumping time. and those in the short $O\cdot\cdot\cdot H$ bonds is the primary mechanism underlying the superprotonic conductivity in LDP. Thus, the mechanism of proton conductivity in LDP must involve hopping between water protons and $O\cdot\cdot\cdot H\cdot\cdot\cdot O$ bonds, with the water acting as a catalyst for the intermolecular H hopping and conduction under applied electric fields.

An important question is whether the observed protonic conductivity is due to just conduction via a surface layer of water or does the water act as a catalyst promoting the conductivity involving the hopping of the LDP hydrogens. To answer it, we note that LDP shows high conductivity of $10^{-4}$ $\Omega^{-1}$ cm$^{-1}$ at RT and relative humidity of 50%. At this ambient condition, the moisture adsorbed by the pellet was $\sim$1 wt % or in terms of volume percentage, $\sim$2.5 vol %. For a given LDP pellet (1 cm$^2$ area by 1 mm thickness), the resistance of the LDP pellet containing $\sim$1 wt % of moisture was measured to be $\sim$1 k$\Omega$. To distinguish the contributions to the proton conductivity due to the interconnected water, LDP, and the interactions between water and LDP, we have measured and estimated the resistance due to each of these factors. We confirm that the resistance of just the interconnected water and just the LDP are very high compared to that of the LDP containing $\sim$1 wt % moisture. First, the resistance $R_w$ due to the interconnected water in the pellet can be estimated by

$$R_w = \frac{l}{\sigma_w A(2.5\%)}$$  \hspace{1cm} (2)

where $\sigma_w$ is the conductivity of distilled water which we have measured to be $7 \times 10^{-6}$ $\Omega^{-1}$ cm$^{-1}$ at RT, $l$ is the thickness of the pellet, $A$ is the area of the pellet, and 2.5% is the filling factor of the adsorbed moisture. From this, we calculated the resistance due to the interconnected water to be $\sim$560 k$\Omega$. Second, we have measured the resistance of LDP at 0% relative humidity which is equal to the resistance of just the LDP crystals to be $\sim$1 $\times$ 10$^{12}$ $\Omega$ at RT. Both resistances are very high compared to that of the LDP containing a minor amount of moisture. Therefore, the high proton conductivity of LDP is due to adsorbed water interacting with protons in LDP rather than purely interconnected surface water.

3.3. $^{31}$P and $^7$Li Measurements Support the New Mechanism of Protonic Conductivity. In order to gain further understanding of the conduction mechanism, we measured $^{31}$P and $^7$Li spectra and relaxation times. Figures 6 and 7 respectively show single-scan $^{31}$P and $^7$Li DP-MAS spectra at 21.2 T at a spinning speed of 13.5 kHz. Two peaks are seen in the $^{31}$P spectra; their relative intensity changes as the water is depleted via pumping on the sample. The smaller peak can be assigned to the minority phosphate groups with the water is depleted via pumping on the sample. The smaller peak can be assigned to the minority phosphate groups with the water acting as a catalyst for the water protons and not just hydrogen-bonded to each other. The condition of high protonic conductivity is also that of strong exchange between the water protons and the LDP hydrogens. Conductivity measurement on highly dehydrated samples provides the background conduction due to just proton hopping within the LDP’s $O\cdot\cdot\cdot H\cdot\cdot\cdot O$ bonds, which is orders of magnitude too low compared to that shown by hydrated samples. Thus, the mechanism of proton conductivity in LDP must involve hopping between water protons and $O\cdot\cdot\cdot H\cdot\cdot\cdot O$ protons, with the water acting as a catalyst for the intermolecular H hopping and conduction under applied electric fields.

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molecules. In the CP-based two-dimensional heteronuclear 1H−31P correlation spectrum of Figure 2, two broad 1H resonances from the long and short hydrogen bonding in the LDP lattice are shown to be directly coupled with phosphorus, while a small 31P peak (∼0 ppm) associated with adsorbed water is not shown because it does not have effective coupling with the two protons in the two different hydrogen bonds.

Figure 7 shows single-scan 7Li spectra of recrystallized LDP powder under different conditions. Together with the main peak, we see a narrow component whose intensity decreases with increasing of vacuum-pumping time. This small and narrow component has a very short T1 (∼0.1 s), as compared to the main peak (∼1200 s). Again, it appears to arise from interaction between LiO4 and surrounding water molecules. The narrow and the broad peaks could be easily separated via deconvolution. It should be noted that the intensities of both the 31P and the 7Li peaks related to the adsorbed water are rather small as compared to the signals from the rest of the LDP lattice, indicating that only the tetrahedral PO4 groups and Li moieties in the surface area are interacting with the adsorbed water molecules. LiO4 tetrahedra are linked by their vertices forming [100] isolated chains and have weak interaction with surrounding water molecules. Therefore, LiO4 moieties are likely to have no direct contribution to LDP’s high protonic conductivity.

Figure 8 shows the schematic of the proton exchange model of LDP with adsorbed H2O molecules. Since the inter-oxygen bond in the short hydrogen bonds (H2) is 2.561 Å, the hydrogen bond between H2 and its oxygen is relatively weak, so that the H2 proton can be easily attracted by the nearby water molecules adsorbed by the H3PO4− anions and LiO4 tetrahedra. With the addition of the proton, the water molecule becomes H2O2−, an ion contradicting the standard two-proton ice rule, thus resulting in pushing a proton away to the neighboring H2O molecule. As the H2 proton is attracted away by the water molecule, its place can be easily replaced by a proton from other water molecules, thus resulting in a fast exchange between the H-bonding proton H2 and the adsorbed water molecules. We conclude that this H2O proton exchange in concert with the rotational fluctuations of the PO4 moieties is the dominant mechanism of LDP’s exceptionally high protonic conductivity.

The above results suggested that LDP’s conductivity could be modulated by controlling the amount of surface adsorbed water. This was indeed found to be the case. Figure 9 shows the conductivity of three different pressed LDP pellets (red: 2000 kg/cm²; green: 4000 kg/cm²; blue: 6000 kg/cm²) under cyclic humidity conditions at ambient pressures. For all samples, as the humidity is increased from 10% to 50%, the resulting conductivity increases by an order of magnitude. More importantly, when the humidity is cycled, the conductivity oscillates accordingly, implying that the physically adsorbed water is the driving force for the conductivity. The slow humidity response is consistent with the hydrogen bonding-driven water adsorption/desorption process. The conductivity...
can also be controlled by squeezing the water out of the powder during the pellet fabrication. For samples made under 2000, 4000, and 6000 kg/cm² pressures, the water content was driven away by 7.8%, 10.9%, and 12.0%, respectively. As a consequence, the conductivity is lower for samples prepared under more strongly squeezed (more strongly pressed) samples, and vice versa. The proton conductivity of LDP can be well controlled by the adsorbed water content through humidity and pressure. We stress that the present work is distinctly different from the earlier studies on CDP\textsuperscript{13,14,22} and RDP,\textsuperscript{16} where humidity was used to control the sample dehydration at high temperatures close to 250 °C. The current study shows that LDP's conductivity can be modulated reversibly which should add a new dimension to its potential applications in the fields of fuel cells and humidity sensors based on hydrogen-bonded proton conductors.

4. 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\textsubscript{2}O protons mainly with its short hydrogen bonds and not the interbond hopping of protons between the O−H−O bonds. While water is known to play a role in other hygroscopic conducting systems, such as some polymers like polyanilines,\textsuperscript{18} the current work is the first report on the role of water in proton conduction in the LDP type hydrogen-bonded solids, in both single crystal and powder form. In fact, the presently proposed mechanism is a significant improvement over an earlier proposed model\textsuperscript{11,12} wherein the role of water was not recognized.

Finally, we have shown that LDP’s protonic conductivity can be modulated reversibly by factors of several orders of magnitude via controlled exposure to water, a result of high relevance in the utility of LDP in hydrogen fuel cells and related applications, and possibly for proton conduction in other classes of hydrogen-bonded solids.

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Notes
The authors declare no competing financial interest.

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