

Characterization of Solid Acid Electrolyte $\text{CsH}_5(\text{PO}_4)_2$ by NMR SpectroscopySeen Ae Chae,[†] Young Eun Lee,[†] Oc Hee Han,^{†,‡,*} Dong Hoon Kim,[§] and Hong-In Lee[§][†]Daegu Center, Korea Basic Science Institute, Daegu 702-701, Korea. *E-mail: ohhan@kbsi.re.kr[‡]Graduate School of Analytical Science and Technology Chungnam National University, Daejeon 305-764, Korea[§]Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea

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The electrolyte is one of the most important constituents of fuel cells (FCs), and determines the application areas, the performance, and the operation temperature range. The high proton conductivities of solid acids in specific temperature ranges have made them as excellent candidates for FC electrolytes.¹ Solid acids are both an acid and salt in a solid state, and can generally be described as $\text{M}_a\text{H}_b(\text{XO}_4)_c$, where M is Cs, Rb, K, Na, or NH_4 and X is P, S, As, or Se. Ever since CsHSO_4 (CHS) electrolyte was demonstrated for FCs by Halie *et al.*¹ various solid acid electrolytes for FCs have been reported.^{2,3} Even better performance than that with CHS was reported with CsH_2PO_4 (CDP) only, or with CDP/Si-oxide composites in humidified conditions.^{2,3} All of the CDP in the CDP/ SiP_2O_7 composite electrolyte was observed by X-ray diffraction (XRD) to convert to $\text{CsH}_5(\text{PO}_4)_2$ (CPDP) at 220 °C and higher, indicating that the good conductivity of this composite electrolyte over 150-250 °C was mainly from CPDP, not CDP.³

Solid acid electrolytes have been characterized primarily by XRD. However, solid-state nuclear magnetic resonance spectroscopy (SS-NMR) can be more powerful. SS-NMR can be used to directly observe nuclei, detect light atoms and phases without a long-range order, and provide dynamics information such as ionic movement and molecular motion in more detail. Two hydrogens in CDP were identified by ^1H magic angle spinning (MAS) NMR spectroscopy.⁴ Static ^1H and ^{31}P NMR experiments on a single crystal of CDP at different temperatures indicated that the reorientation of H_2PO_4^- anions plays an important role in the proton conduction of CDP.⁵ The hydrogen dynamics of CPDP were studied at various temperatures by static ^1H NMR,⁶ and recently, the results were reported for ^{31}P and ^{133}Cs MAS NMR spectra of CDP and ^1H , ^{31}P , and ^{133}Cs MAS NMR spectra of the mixture of CDP and CPDP were reported.⁷ The peaks corresponding to each compound were assigned, but the ^1H peaks of the mixture of CDP and CPDP were not clearly assigned due to the possible overlapping of the signals for CPDP and CDP.⁷ In this work, the ^1H , ^{31}P , and ^{133}Cs MAS NMR spectra of pure CPDP with clear peak assignments are presented, and the confirmation of the purity of CPDP is demonstrated, which is not possible with XRD techniques.

Since the stoichiometric mole ratio of H_3PO_4 and Cs_2CO_3 for CPDP synthesis is 4:1, as described by $4\text{H}_3\text{PO}_4 + \text{Cs}_2\text{CO}_3$

$\rightarrow 2\text{CsH}_5(\text{PO}_4)_2 + \text{H}_2\text{O} + \text{CO}_2\uparrow$, CPDP was prepared as follows. First, 16 mmol H_3PO_4 (85 wt %, $d = 1.685 \text{ g/mL}$, Sigma Aldrich, USA) was placed into a 50-mL beaker, and 4 mmol Cs_2CO_3 (99.995%, Sigma Aldrich) was added. All of the reagents were weighed for accurate stoichiometric matching. The reagent mixture slurry was stirred well with a glass bar prior to carefully adding 1 mL of distilled water into the slurry to dissolve all the Cs_2CO_3 , and stirred more until the solution became transparent. The transparent solution was transferred to a clean beaker and kept at 100 °C for 24 h. The synthesized CPDP powder was identified with X'Pert PRO-MPD XRD (Philips, Netherland). All NMR spectra were obtained on a 14.1 T unity INOVA NMR spectrometer (Varian, USA) using a MAS probe for 2.5-mm zirconia rotors spun at 20 kHz for ^{31}P and ^{133}Cs experiments and at 22 kHz for ^1H spectroscopy. For ^{31}P and ^{133}Cs spectra, 2- μs pulse widths were used without ^1H decoupling. To acquire ^1H spectra, a depth pulse sequence with an excitation pulse width of 5 μs and a train of two 180° pulses of 10- μs were used to remove the background signal. The repetition times of 10, 12, and 30 s, and 16, 32, and 4 scans were used for ^1H , ^{31}P , and ^{133}Cs NMR acquisition, respectively. The chemical shifts for ^1H , ^{31}P , and ^{133}Cs NMR spectroscopy were referenced to an ex-

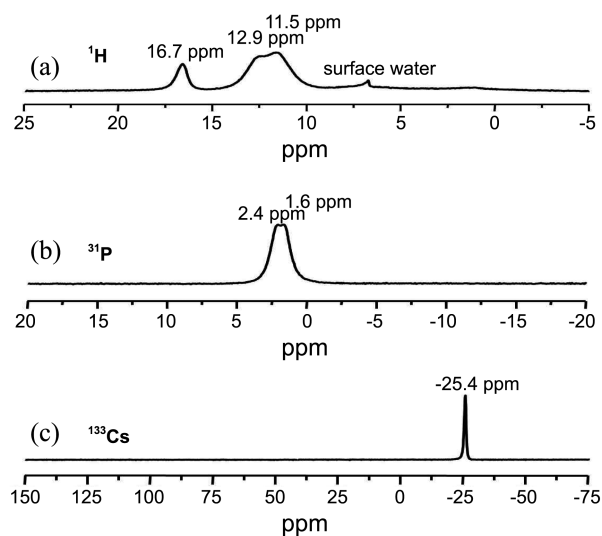


Figure 1. (a) ^1H , (b) ^{31}P , and (c) ^{133}Cs MAS NMR spectra of $\text{CsH}_5(\text{PO}_4)_2$.

Table 1. Chemical shifts of ^1H , ^{31}P , and ^{133}Cs NMR peaks of $\text{CsH}_5(\text{PO}_4)_2$ and CsH_2PO_4

Compound	^1H (ppm)	^{31}P (ppm)	^{133}Cs (ppm)
$\text{CsH}_5(\text{PO}_4)_2$	16.7, 12.9, 11.5	2.4, 1.6	-25.4 ^b
CsH_2PO_4 ^a	14.3, 10.9	-5.6	46.4 ^b

^afrom Reference 7. ^bChemical shift was corrected in this work.

ternal H_2O at 4.80 ppm, aqueous 85% H_3PO_4 at 0 ppm, and 1 M CsCl solution (Sigma Aldrich, USA) at 0 ppm, respectively.

Figure 1 shows the ^1H , ^{31}P , and ^{133}Cs MAS NMR spectra of CPDP, and the chemical shifts of peaks are summarized in Table 1. Crystallographically, five H sites, two P sites and one Cs site exist in CPDP structures⁸ and strong hydrogen bonds in CPDP were observed to consist of 4 OHs with similar OH bond lengths, with the other OH having a shorter bond length.⁹ Since stronger hydrogen bonding results in larger ^1H chemical shifts, the peak at 16.7 ppm in the ^1H MAS NMR spectrum is assigned to the H with the shortest OH bond length (the stronger hydrogen bonding), and the rest of the peaks at 12.9 and 11.5 ppm are assigned to the other 4 Hs. The ^1H spectrum in Figure 1(a) also confirms that the 10.9-ppm peak in the ^1H MAS spectrum of the mixture of CPDP and CDP in our previous report⁷ was not from the CPDP. The two peaks with 1:1 peak areas in the ^{31}P MAS NMR spectrum in Figure 1(b) and the single peak in the ^{133}Cs MAS NMR spectrum in Figure 1(c) correspond to the two P sites and the single Cs site in the CPDP, respectively. The comparison of the ^{31}P MAS NMR spectra of the mixture of CPDP and CDP in Figures 2(a) and 2(b) clearly indicates that continuous wave ^1H decoupling broadened the line widths of the signals of both compounds. This line broadening is due to the interference of ^1H decoupling and molecular motions/sample spinning at similar frequencies.¹⁰ These results suggest that ^{31}P MAS NMR experiments for solid acids are more advantageous without ^1H decoupling, especially at fast spinning rates over a few tens of kHz.

Even when the powder XRD patterns had CPDP signals only, the H_3PO_4 remaining in the CPDP was easily observed by ^{31}P MAS NMR spectroscopy as the signal near 0 ppm, as shown in Figure 2(c). This H_3PO_4 cannot be easily detected by XRD, but ^{31}P MAS NMR spectroscopy is useful to investigate the purity of the synthesized CPDP. In addition, much longer ^{31}P T_1 relaxation times of the solid acids than those of liquid H_3PO_4 allow for the detection of even small amounts of H_3PO_4 in CPDP with short pulse repetition delay times. When the amount of H_3PO_4 was less used than the stoichiometry for CPDP synthesis, a mixture of CDP and CPDP was produced. However, too much H_3PO_4 left excess H_3PO_4 in the CPDP product. Collecting pure CPDP from the mixtures is very difficult. Therefore, it is crucial to match the amounts of reagents precisely. The inaccurate ^{133}Cs chemical shifts previously reported due to the misread concentration

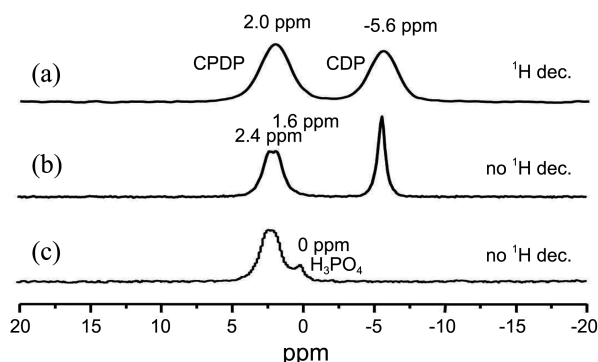


Figure 2. ^{31}P MAS NMR spectra of the mixture of $\text{CsH}_5(\text{PO}_4)_2$ and CsH_2PO_4 (a) under ^1H continuous wave decoupling condition, (b) without ^1H decoupling, and of (c) the mixture of $\text{CsH}_5(\text{PO}_4)_2$ and H_3PO_4 without ^1H decoupling.

of a reference CsCl solution⁷ are corrected by adding 25.3 ppm to the previous chemical shifts. The ^{133}Cs chemical shift is found to be extremely sensitive to the concentration of Cs^+ ions in the solution.

In summary, ^1H , ^{31}P , and ^{133}Cs MAS NMR spectra of pure CPDP have been presented and interpreted for the first time, and MAS MMR spectroscopy has been demonstrated to be more advantageous than XRD techniques to confirm the purity of CPDP, especially when liquid impurities such as H_3PO_4 are present. These NMR results will contribute to the better understanding of the behavior of protons in CPDP electrolytes.

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