

Hydrogen Adsorption MOF Design and Adsorption Characteristics

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ABSTRACT

The project discussed in this paper attempted to design and synthesize a hydrogen-adsorbing material suitable for fuel cell electric vehicles. The newly designed and synthesized $\text{Cu}_2(3,5\text{-pyridinedicarboxylate})_2$ metal complex displayed an extremely high volumetric uptake density for a physisorption material, despite the fact that its specific surface area was only about $1,000 \text{ m}^2 \text{ g}^{-1}$. It is believed that the realization of an increased number of adsorption sites per unit area and increased adsorption energy, in addition to the optimized design of pore shapes, were major factors in the achieved uptake performance.

1. Introduction

Climate change is a major issue facing humanity today, and one which should be urgently addressed. The enormous volumes of CO_2 released as a result of the evolution of human activities is believed to be one of the main causes of climate change, strongly necessitating the reduction of CO_2 emissions. Given this, research is pushing ahead on the fuel cell electric vehicle as an advanced mode of transport able to help curb CO_2 emissions. In fuel cell electric vehicles, the motor is driven by electricity generated in a chemical reaction between hydrogen stored in a high-pressure gas tank and oxygen in the air, and the only emission is water. However, the high-pressure hydrogen storage gas tanks occupy a large amount of space, and are also heavy. The use of materials for hydrogen storage that would help to enable the vehicle bodies to be reduced in size and fuel efficiency to be increased is therefore being studied.

Hydrogen storage materials can be broadly divided into two types, and both metal hydrides, which function by chemisorption, and hydrogen-adsorbing materials (with carbon materials and zeolite as representative examples), which function by physisorption, have been the subject of study. Hydrogen-adsorbing materials offer the advantage of producing less heat than metal hydrides when adsorbing and releasing hydrogen. This does away with the need for heat management systems, which can be expected to contribute to the reduction of vehicle size and weight. The issue, however, is overcoming the low adsorption volume of these materials.

Metal-organic frameworks (MOF) have recently become the focus of attention as adsorbent materials, and

numerous gas adsorption characteristics of these materials have been reported on^{(1), (2)}. Metal-organic frameworks are macromolecular crystals formed from a combination of metallic cores and organic ligands known as linkers. The appropriate selection of these elements makes it possible to adjust parameters including pore size and crystal system. This high degree of freedom of design is one of the appealing points of MOF.

The research discussed in this paper attempted to design and synthesize an original MOF optimized for application in hydrogen storage for fuel cell electric vehicles. The developed MOF realizes a higher level of hydrogen adsorption performance than an existing MOF (IRMOF-1⁽³⁾).

2. Design of Material

From considerations of driving distance, fitting space, speed of hydrogen filling and speed of hydrogen release, hydrogen-adsorbing materials employed in fuel cell electric vehicles should reconcile high mass storage density (wt%) and volumetric storage density (vol%) with low adsorption heat (ΔH). In order to increase the volume adsorbed, it is generally necessary to increase the number of adsorption sites and attempt to ensure an appropriate level of adsorption energy. In an MOF, the number of adsorption sites can be increased by lengthening the linkers to increase the material's specific surface area. However, when long linkers are employed, an excessive number of pores are created at the same time that the specific surface area increases, and this can reduce volumetric density and increase the space necessary for fitting the hydrogen storage tank. It is, therefore, important to appropriately

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control pore volume in order to help ensure that volumetric density does not decline. Analyses of the adsorption sites in IRMOF-1 conducted by the authors using neutron diffraction measurements and first-principle molecular dynamics calculations showed that the main adsorption sites surrounded the metallic cores⁽⁴⁾, indicating that it would also be important to realize a high-density configuration of metallic cores.

When utilizing physisorption materials, large amounts of hydrogen can be stored by increasing adsorption energy (adsorption heat), but this results in the production of high levels of heat when the hydrogen is stored, and filling speed declines. In order to realize filling times equivalent to those for gasoline engines, hydrogen adsorption heat should be controlled to 10 kJ mol⁻¹ or below. The hydrogen adsorption heat (ΔH) of IRMOF-1 is 4.8 kJ mol⁻¹⁽¹³⁾. Designing an MOF with a higher adsorption energy could be expected to increase adsorption volume, and methods of increasing adsorption energy were therefore investigated. The use of heterocycle linkers, in which atoms with a high electronegativity such as N, F or Cl have been partially substituted, is known to increase adsorptivity. This is supported by the analysis results shown in Fig. 1, calculated using first-principle calculations^{(6), (18), (19)} based on density functional theory (DFT)⁽⁵⁾, for the adsorption energy of hydrogen molecules and electron density (electrostatic potential) around adsorption sites in a benzene dicarboxylate (BDC) linker and metallic core model. It is predicted that hydrogen adsorption energy will tend to increase in areas in which electrons are localized, and the use of atoms displaying high electronegativity is therefore an effective method of increasing adsorption energy. In the metallic core, it is necessary to reduce the actual volume occupied by the atoms and to increase adsorption energy. A double-core structure known as a paddle wheel⁽¹⁵⁾ represented an effective candidate given

the fact that it has a comparatively low coordination number, can further reduce the actual volume occupied by the atoms in the metal cores, and is able to form high adsorption energy sites when the surface of the metal is exposed. Results for the hydrogen adsorption energy of double-core structures obtained using first-principle calculations^{(6), (18), (19)} based on DFT indicated that hydrogen adsorption energy would be 10-12 kJ mol⁻¹ in almost all cases if second-, third-, or fourth-row transition metal elements were used, and that there was no significant difference in adsorption energy between elemental species (Table 1). Cu, which is known to frequently synthesize metallic complexes with double-core structures⁽¹⁷⁾, was, therefore, selected as the metallic element.

It was necessary to reconcile a high metallic core density with the formation of communicating pore spaces in creating the framework. It was also necessary to realize an arrangement of elements that would not destroy the metal exposure sites (cap sites) formed due to the paddle wheel structure⁽¹⁵⁾. The use of offset layering of monolayers formed from a combination of triangular and hexagonal pores maintained the cap sites while helping to enable the triangular sites to be maintained as communicating pores.

The bond angles between the paddle wheels⁽¹⁵⁾ and the linkers were 90°, and in order to realize a triangular framework with bond angles of 60°, it was necessary to maintain the paddle wheel structure in an unstable state. It was therefore proposed that the paddle wheels should be inclined from a perpendicular alignment in order to produce a structure with minimal distortion of the bond angles. Curved linkers were employed to realize this configuration.

The MOF pore size was optimized in order to balance adsorptivity with mobility of hydrogen atoms, and was made approximately twice the size of hydrogen molecules.

Based on the above, it is considered that there are specific guidelines that should be followed in the design of

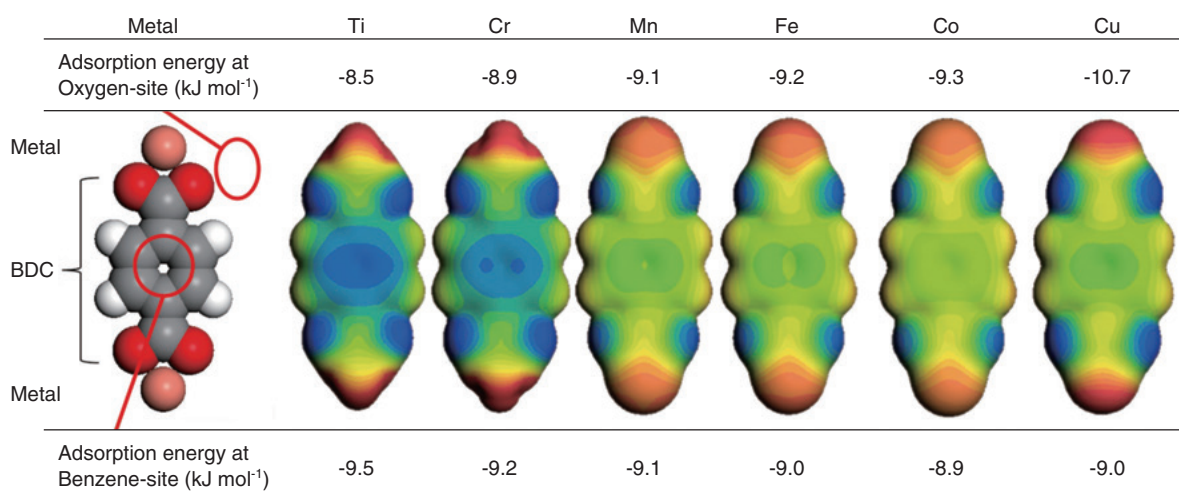


Fig. 1 Electrostatic potential and adsorption energy

* Calculated with VASP-LDA-PAW. ** The red areas correspond to positively charged areas and blue areas to negatively charged areas in the electrostatic potential map. The adsorption energy tends to be larger when there is greater negative charge, or where the electrons are localized.

Table 1 Adsorption energy of paddle wheel

Core atom	Adsorption energy (kJ mol ⁻¹)	Core atom	Adsorption energy (kJ mol ⁻¹)	Core atom	Adsorption energy (kJ mol ⁻¹)
Li	-11.3	V	-11.0	Zr	-11.7
Be	-10.2	Cr	-11.0	Nb	-11.7
B	–	Mn	-11.0	Mo	-10.9
Na	-11.3	Fe	-11.3	Rh	-11.4
Mg	-10.7	Co	-9.7	Pd	-11.3
Al	-12.2	Ni	-11.2	Cd	–
K	–	Cu	-11.3	La	–
Ca	-10.5	Zn	-10.9	Ce	–
Sc	-10.3	Ga	–	Pt	-12.0
Ti	-9.4	Y	-10.2		

*[-] Does not form paddle wheel structure.

** Value calculated with VASP-LDA-PAW.

an MOF hydrogen-adsorbing material produced for use in a fuel cell electric vehicle. These are:

- (1) In order to increase the rate of hydrogen adsorption, it is necessary not to focus exclusively on increasing the specific surface area per unit weight, but also to increase the density of hydrogen adsorption sites as much as possible.
- (2) The space occupied by the atoms forming the framework themselves (dead space) should be reduced as much as possible.
- (3) In order to increase hydrogen adsorptivity, heterocycles

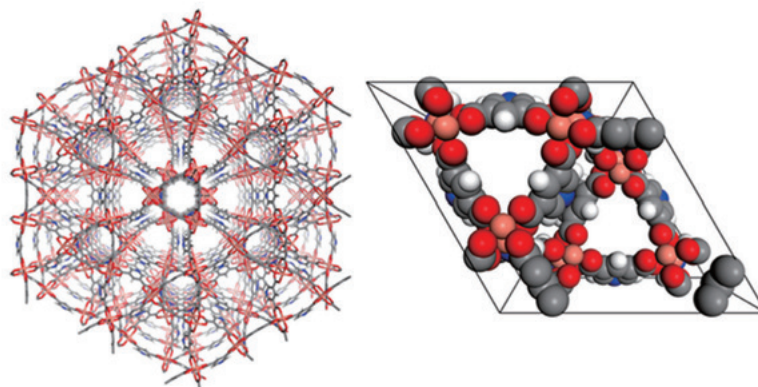
and high-electronegativity atoms that strengthen electron localization should be employed.

- (4) Space for sufficient hydrogen mobility should be created, pores that produce dead space should be reduced and the rate of diffusion should be increased.

Next, Cu₂(3,5-pyridinedicarboxylate)₂ (Cu₂PDC₂) was proposed and designed with comprehensive consideration of factors including the feasibility of experimental synthesis while making use of the freedom of design offered by MOF. The structure of the Cu₂PDC₂ is shown in Fig. 2(a).

This structure features a curved linker, and is formed

(a)



(b)

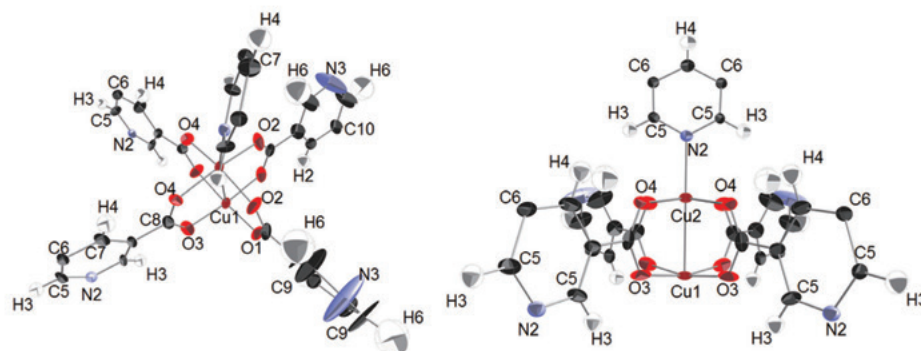


Fig. 2 (a) Overall view of Cu₂PDC₂ (left) and the unit cell (right). The space group is *P6₃mc* (blue: nitrogen; red: oxygen; gray: carbon; orange: copper); (b) The structure of Cu₂PDC₂. The two figures are the same structure from different angles.

Table 2 The calculated and experimentally measured density of adsorption sites, pore ratio, and adsorption energy in Cu_2PDC_2 and IRMOF-1

	Density of adsorption site (nm^{-3})	Pore ratio (cc cc^{-1})		Adsorption energy (kJ mol^{-1})	
		Calc.	Exp.	Calc.	Exp.
IRMOF-1	3.8	0.77	0.86	-9.4	-4.8
Cu_2PDC_2	8.9	0.50	0.46	-16.5	-6.0

from a basic framework [Fig. 2(b)] created by the bonding of 3,5-pyridinedicarboxylate (PDC), a linker containing N, which promotes electron localization, and Cu. This basic framework forms two-dimensional sheets with pores of approximately 6 Å and approximately 11 Å through planar bonding [Fig. 3(a)], and a three-dimensional structure of ABAB stacks is created by bonding between Cu and some of the N in the PDC [Fig. 3(b)]. The space groups are $P6_3mc$. These ABAB stacks overlap in 60° twists centering on the c-axes, and the respective layers are characterized by continuously changing pores of sizes between 6 Å and 11 Å, as shown by A in Fig. 3(a), and communicating pores of 6 Å, as shown by B [Fig. 3(a), right].

Table 2 shows the density of adsorption sites, pore ratio, and adsorption energy as predicted from the crystal

structure of Cu_2PDC_2 . The adsorption energy for typical adsorption sites was calculated using first principle calculations^{(6), (18), (19)} based on DFT (adsorption energy tends to be overestimated by DFT⁽⁴⁾). The density of adsorption sites was calculated from the number of typical adsorption sites displaying a high level of adsorption energy. Figures calculated from Connolly surfaces (using Materials Studio manufactured by Accelrys) are used for the pore ratio. For the sake of comparison, experimental values⁽¹³⁾ are also shown. The pore volume was estimated to be $0.5 \text{ cm}^3 \text{ g}^{-1}$ or less, and the number of adsorption sites per unit volume to be twice that of IRMOF-1. The crystals themselves were porous, with a dense atomic arrangement. The pore occupancy ratio per unit volume was approximately 1/2. In addition, hydrogen adsorption energy was high in comparison to IRMOF-1, and overall an increase in the rate of adsorption could, therefore, be expected.

3. Synthesis of Designed Material

3.1. Study of Synthesis Conditions

For the synthesis of the proposed Cu_2PDC_2 complex, (a) the state of coordination of the metallic cores and (b) the bonding energy of the metallic cores and the ligands were focused on.

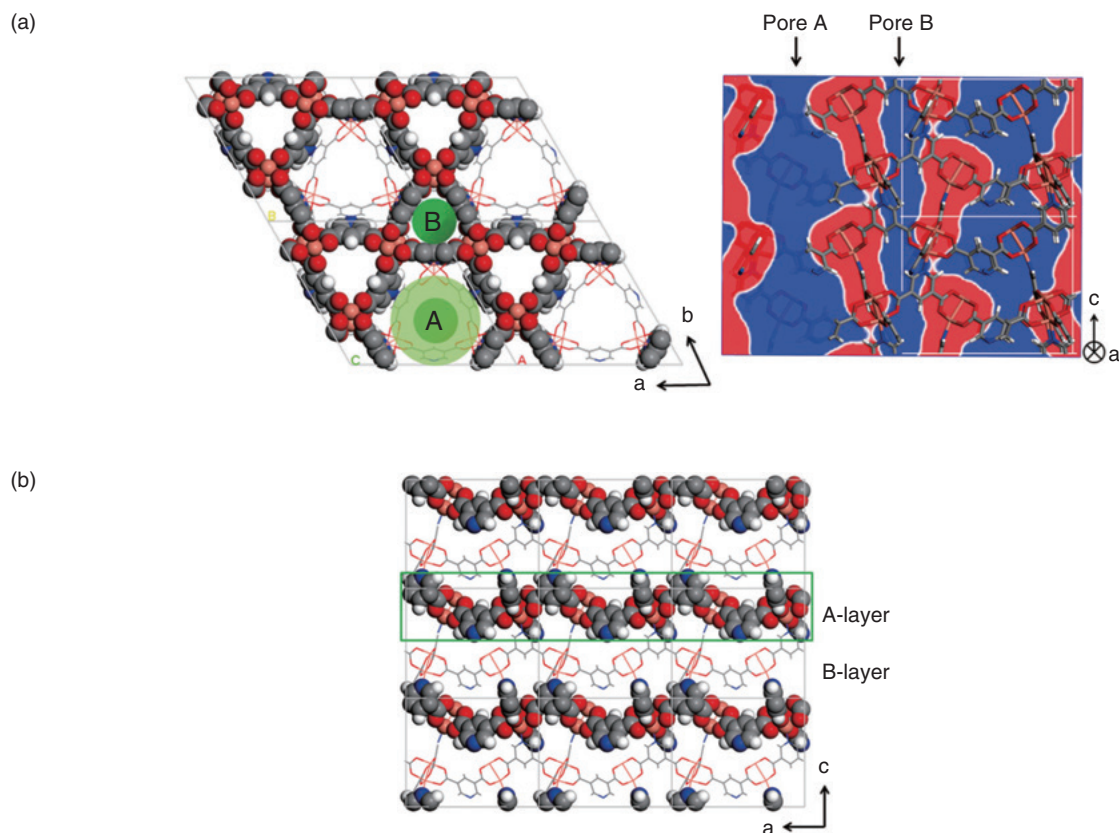


Fig. 3 (a) Pores observed from the c-axis (left) and the a-axis (right). The blue portions indicate pores in the figure to the right. Pore A consists of holes with $\phi = \sim 11$ Å and $\phi = \sim 6$ Å. Pore B is made up of holes with $\phi = \sim 6$ Å; (b) The A-B stacking sequence. The rectangle shows single layer.

(a) Coordination state of metallic cores and selection of starting materials

As Fig. 4 shows, the complex has a particular coordination state, forming structures termed paddle wheels, with Cu atoms as the metallic cores. Copper(II) acetate, which has the same structure, was, therefore, selected from among the copper salts for use in synthesis. 3,5-Pyridinedicarboxylic acid (PDC acid), a precursor of PDC, was used as the linker.

The solvent forming the reactive site for the synthesis of the complex should possess the property of maintaining the paddle wheel structure of the copper(II) acetate dissolved in it. To verify this condition, the coordination state of the metal ions in the solution was measured⁽¹⁶⁾ by means of Cu K-edge X-ray absorption fine structure (XAFS) measurements taken using SPring-8⁽¹⁴⁾ high-brilliance X-rays. Water (H₂O), ethanol (EtOH), dimethylformamide (DMF), and diethylformamide (DEF), which are standard solvents for the synthesis of complexes, were the substances under consideration for use as the solvent. Figure 5 shows XAFS spectra for copper(II) acetate dissolved in each of the solvents. A peak occurring around 8985 eV, shown as the red broken line in the figure, reflects the paddle wheel configuration. This peak is not present in water, indicating the collapse of the paddle wheel structure. It is believed that the coordination of the acetic acid ions could not be maintained in water, which has a high polarity (water's specific permittivity is 80, while figures for EtOH and DMF are around half this). Water was, therefore, removed from the list of potential solvents. The paddle wheel structure was maintained in the other solvents, and EtOH, DMF, and DEF were therefore selected as synthesis solvents.

The selected starting materials (copper(II) acetate and

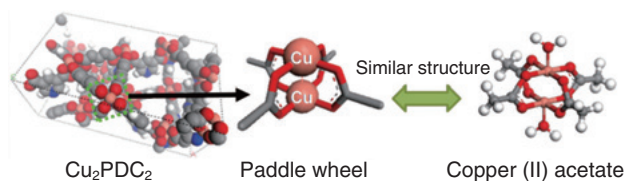


Fig. 4 Structure of Cu₂PDC₂ and coordination state of Cu

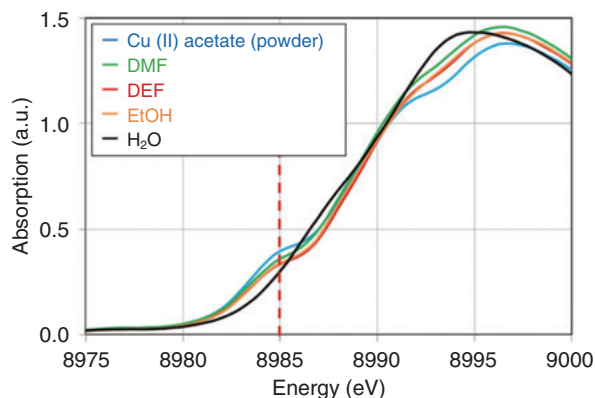


Fig. 5 XAFS spectra of Cu acetate with solvent

PDC acid) were dissolved in each of the candidate solvents, and the status of synthesis was studied. This produced blue solutions of the type shown in Fig. 6. Scanning electron microscopy (SEM) showed the sediment precipitated out of the solution to be spherical aggregates (Fig. 6, right). Analysis indicated that these aggregates were an amorphous-like substance with an identical composition to Cu₂PDC₂ complex (see Fig. 7). It had, therefore, not been possible to obtain a Cu₂PDC₂ complex.

(b) Reexamination of conditions with focus on bonding energy between metallic cores and ligands

The bonding energy between the metallic cores and the ligands was focused on to help enable modification of the synthesis reaction conditions, and the energy diagram shown in Fig. 8 was formulated.

The energy ΔH produced by the reaction $2\text{Cu} + 2\text{PDC} \rightarrow \text{Cu}_2\text{PDC}_2$ (MOF), as determined by first-principle calculations based on DFT^{(6), (18), (19)}, was a negative figure (-46 kJ mol^{-1}), and it was predicted that the target synthesis reaction (the reaction pathway to the right in Fig. 8) could occur. At the same time, the simple bonding energy of Cu and PDC (as the energy generated by the reaction, ΔH) is also a negative figure (-5.6 kJ mol^{-1}), and it was

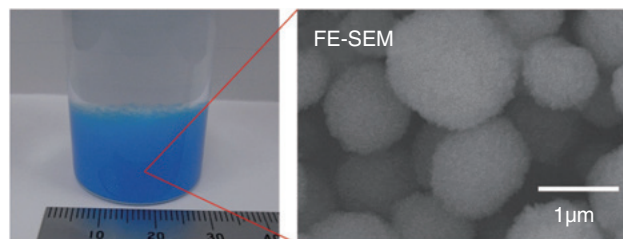


Fig. 6 SEM image of the precipitated aggregate

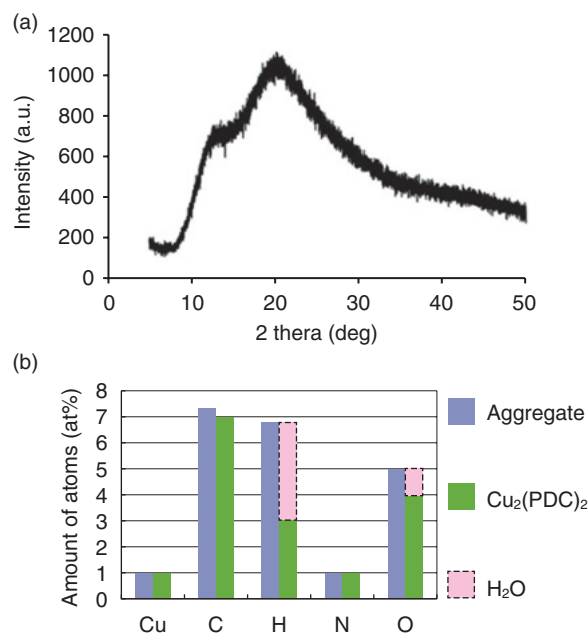
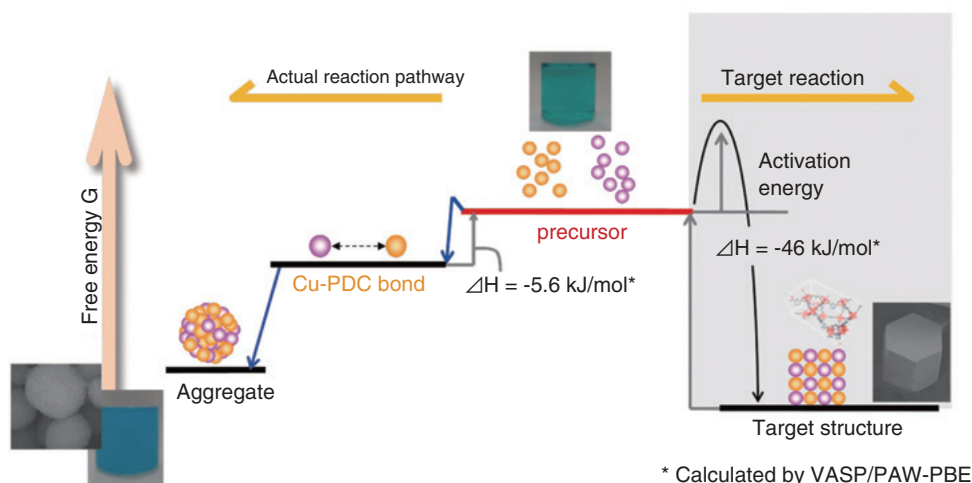


Fig. 7 Analysis results of the precipitated aggregate (a) XPRD spectrum; (b) The results of component analysis.

Fig. 8 Reaction pathway and energy diagram of Cu_2PDC_2

predicted that a reaction promoting simple bonds between Cu and PDC (the reaction pathway to the left in Fig. 8) might also occur. However, given the fact that aggregates were formed rather than the target structure, Cu_2PDC_2 (MOF), it was considered that the reaction activation barrier for the formation of Cu_2PDC_2 (MOF) (the reaction pathway to the right in Fig. 8) is higher than the reaction activation barrier for simple bonding between Cu and PDC (the reaction pathway to the left in Fig. 8). It is believed that as a result, the simple bonding reaction between Cu and PDC (the reaction pathway to the left in Fig. 8), for which the reaction activation barrier is lower, occurs preferentially and more rapidly, and aggregates are formed. It was, therefore, necessary to study conditions that would restrict and control the formation of aggregates by simple bonding between Cu and PDC, and promote the target Cu_2PDC_2 (MOF) synthesis reaction (the reaction pathway to the right in Fig. 8). The addition of acids and other auxiliary agents is available as a method of controlling reaction rate. The successful dissolution of aggregates and synthesis of crystalline MOF by competitively promoting a reaction between metal ions and organic ligands has been reported⁽¹⁷⁾. The acid to be used as an additive was therefore studied from the perspective of its potential for disassembling aggregates (detaching bonds between Cu and PDC) and maintaining the Cu paddle wheel structure.

Figure 9 shows the colors of the solutions produced by adding various acids to the aggregates and spectra for each solution obtained using ultraviolet absorption visible spectroscopy (UV-vis). Like XAFS results, UV-vis spectra reflect the coordination state of metal ions.

In each case, the addition of the acids resulted in the solution becoming clear, and dissolved the Cu-PDC aggregates. For the acetic acid, the fact that no changes could be observed in the UV-vis spectra indicated that the Cu paddle wheel structure was maintained. Given this, acetic acid could be considered an additive that was able to control the speed of bonding of Cu and PDC while

maintaining the Cu paddle wheel structure. Based on the results discussed above, copper(II) acetate, PDC acid and acetic acid were selected as starting materials and EtOH, DMF, and DEF were selected as reaction solvents satisfying the conditions indicated in the guidelines for the synthesis of a Cu_2PDC_2 complex. The complex was synthesized by optimal adjustment of proportion, time and temperature in relation to these substances.

3.2. Method of Synthesis

With regard to the solvents, no crystals were precipitated when the candidate EtOH was employed, and crystals of low purity were obtained when DEF was employed. It was, therefore, decided to use DMF as the synthesis solution. The proposed Cu_2PDC_2 complex crystals were obtained by placing DMF (N,N-

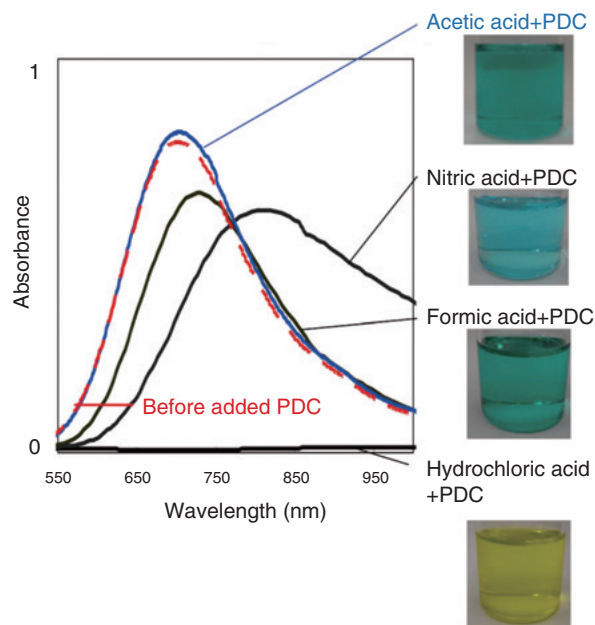


Fig. 9 Pictures and UV-vis spectra of solution when various acids are added

dimethylformamide; CAS No. 68-12-2) 9.89 ml, copper(II) acetate monohydrate (CAS No. 6046-93-1) 51.3 mg and PDC acid (3,5-pyridinedicarboxylic acid (CAS No. 499-81-0) 85.9 mg in a vial bottle and dissolving them by ultrasound, following which acetic acid (CAS No. 64-19-7) 0.11 ml was added and the substance was stored for a week at 70°C. Following this, the solvent was repeatedly replaced by CHCl_3 (trichloromethane; CAS No. 67-66-3) at room temperature in order to remove guest molecules. The crystals obtained were comparatively uniform, measuring slightly less than 100 μm in the longitudinal direction and around 50 μm in the lateral direction.

3.3. Analysis of Synthesized Material

Figure 10 shows an SEM image of the synthesized Cu_2PDC_2 crystals. These were hexagonal columnar crystals that reflected the $P6_3mc$ symmetry of the basic framework. The results of X-ray powder diffraction (XRPD) using SPring-8 high-brilliance X-rays (Fig. 11) and single crystal analysis⁽¹³⁾ verified that the structure of the crystals was identical to that proposed in Fig. 2. In addition, there was an almost complete one-to-one correspondence between the diffraction peaks obtained using XRPD and diffraction peaks that had been optimized by calculations [Fig. 11(b)]. The synthesized Cu_2PDC_2 was, therefore, judged to be of high purity.

The results of a structural defect analysis by means of Rietveld refinement also corresponded well with a projected complete structure with no defects, suggesting that the crystals displayed an extremely low rate of defects⁽¹³⁾. In addition, the same analysis indicated that the difference in intensity between the values measured using XRPD and the calculated diffraction peaks was an effect of residual solvents such as DMF remaining in the pores⁽¹³⁾.

The specific surface area of the crystals was measured at 1003 m^2g^{-1} and 1033 m^2g^{-1} by the Brunauer Emmett Teller (BET) method and the Langmuir method, respectively. The median pore size was measured at 8.9 Å by means of the

Horvath-Kawazoe method^{(11), (12)} (using a cylinder model). Because the crystal structure is porous, the value for specific surface area is comparatively high, but the figure is low in comparison to already known high specific surface area MOF⁽⁷⁾⁻⁽¹⁰⁾. Pore sizes of 6 Å and 11 Å have been calculated, and the synthesized crystals are considered to display a value intermediate between these. (An application was made to The Cambridge Crystallographic Data Centre for registration of this Cu_2PDC_2 crystal structure, and it has been registered as CCDC 791274.)

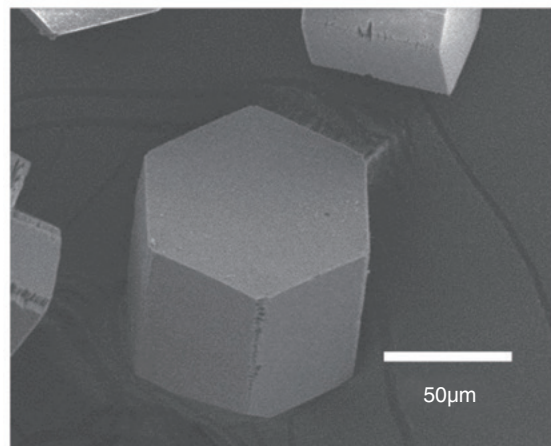


Fig. 10 SEM image of the synthesized Cu_2PDC_2 crystals

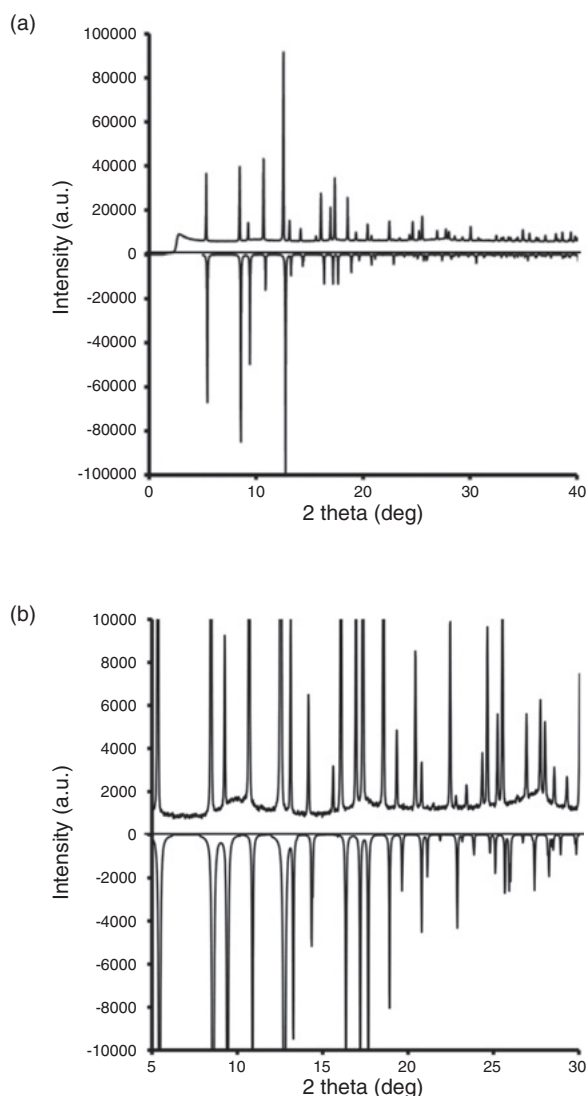


Fig. 11 XRPD spectrum of synthesized Cu_2PDC_2 crystals. (a) (Top) Diffraction pattern measured by SPring-8. (Bottom) Simulated pattern. FWHM = 0.05. $\lambda = 1.54056$ Å; (b) Highly magnified image of the low-intensity area of (a). Slight differences in peak positions are caused by differences in the lattice parameters between the actual crystal and a model crystal optimized by an LDA calculation. Measured peaks show a nearly one-to-one correspondence with the simulated peaks.

4. Hydrogen Storage Performance

The material's rate of hydrogen adsorption was measured using a pressure composition temperature (PCT) measurement apparatus. Figures 12(a) and (b) respectively show the amount of adsorbed hydrogen (wt%) at 293 K and the mass of adsorbed hydrogen (g L^{-1}) per crystal unit volume at 293 K. The amount of hydrogen adsorbed increased with increase in the pressure of the hydrogen, and was 0.77 wt% at 8.92 MPa [Fig. 12(a)]. This is a higher rate of hydrogen adsorption than IRMOF-1 (the broken line in Fig. 12), and is believed to demonstrate the validity of the design guidelines proposed by the authors. In addition, the figure of 8.66 g L^{-1} for the mass of adsorbed hydrogen per crystal unit volume at 8.92 MPa is approximately twice the figure for IRMOF-1 [Fig. 12(b)]. This is an extremely high figure for a physisorption material. In particular in the case of application in a vehicle, a high hydrogen volumetric adsorption density is able to contribute significantly to the reduction of tank volume.

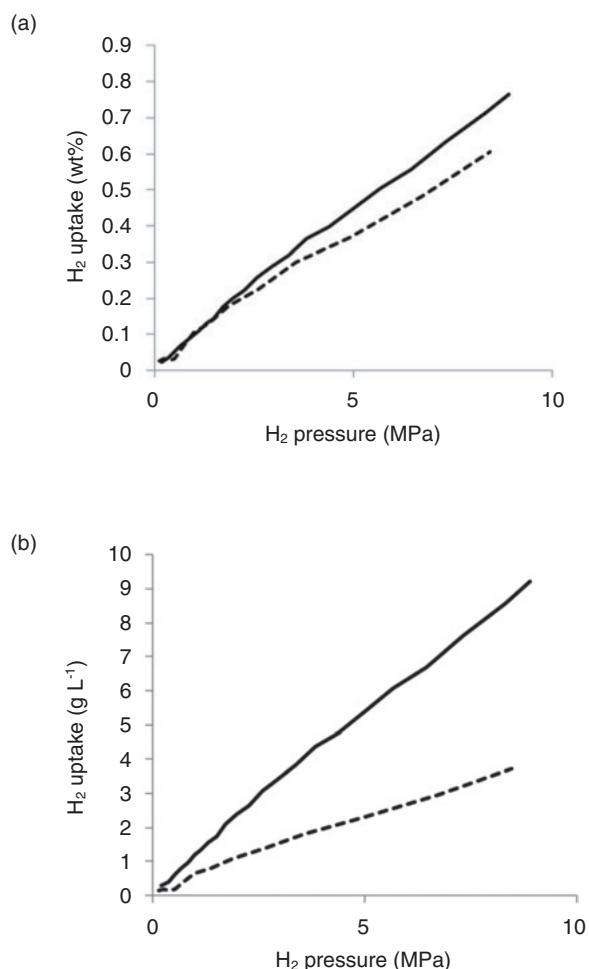


Fig. 12 Hydrogen uptake properties of synthesized Cu_2PDC_2 . (a) Gravimetric uptake at 293 K, 10 MPa; (b) Volumetric uptake at 293 K, 10 MPa. Values for IRMOF-1 are shown for comparison (dashed line).

The Cu_2PDC_2 adsorption energy, calculated using a van't Hoff plot of adsorption isothermal curves at various temperatures, was 6.0 kJ mol^{-1} . This figure is approximately 1 kJ mol^{-1} higher than IRMOF-1 (Table 2). This adsorption energy figure is lower than the figure projected at the initial stage of design, but the qualitative tendency for an increase over the figure for IRMOF-1 accords with the aims established for the project.

It is believed that the factors which helped to enable the material to achieve a figure approximately twice that of IRMOF-1 for amount of adsorbed hydrogen [Fig. 12(b)] despite its specific surface area of around $1000 \text{ m}^2 \text{ g}^{-1}$ were the fact that it possesses twice the adsorption sites per unit volume, its high adsorption energy, and its effective combination of small and large pores.

5. Conclusion

The research discussed in this paper attempted to design and synthesize a hydrogen-adsorbing material optimized for use in a fuel cell electric vehicle. Despite having a specific surface area of around $1000 \text{ m}^2 \text{ g}^{-1}$, the synthesized Cu_2PDC_2 complex achieved a figure of 8.66 g L^{-1} for maximum mass of adsorbed hydrogen, approximately twice the figure for IRMOF-1. The realization of an increased number of adsorption sites per unit volume and increased adsorption energy, in addition to a design focus on the shape of the pores, are considered to be the factors that contributed to this result. The authors believe that a focus on the micro- and nano-levels using sophisticated analytic techniques and the prediction of properties by means of computational science represent useful tools in the study of the structure of hydrogen storage materials and their design.

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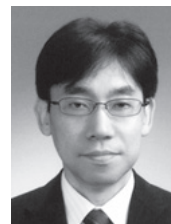
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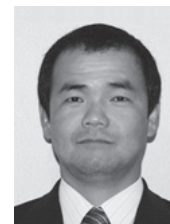
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