Ex-situ Li$^+$ doped into HKUST-1 and their application in hydrogen storage

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Abstract. The aim of this research is to know the influence of Li$^+$ doping into [Cu$_3$(BTC)$_2$] (BTC: benzene 1,3,5-tricarboxylate) or called as Hongkong University of Technology-1 (HKUST-1) structure through ex-situ modification under the solvothermal condition and testing for hydrogen storage. The HKUST-1 structure remains stable after Li$^+$ doping with variation 3, 5, and 10 wt.%, according to XRD analysis, however surface area of HKUST-1 changes significantly up to 1040.96 m$^2$/g after doped with 5 wt.% of Li$^+$ and gave impact to the hydrogen uptake. At temperature 30°C (1.4 bar), hydrogen uptake of Li$^+$ @HKUST-1 reached up to more twice than HKUST-1 without Li$^+$. In addition, the presence of Li$^+$ also increases hydrogen uptake at high temperature (80°C, 1.4 bar). Hydrogen uptake enhancement after doping with Li$^+$ could be due to Li$^+$ supplies additional active site to bind hydrogen molecules.

1. Introduction

Energy is urgently needed for modern society development. One of the promising alternative energies is hydrogen. Hydrogen combustion does not lead to the pollution and results in high energy density, which is almost three times than a petroleum [1]. The barrier in the utilization of hydrogen as an energy carrier is the storage system. Conventionally hydrogen storage used cryogenic tanks, which is neither efficient nor effective if be applied for the vehicle. In 2015, a target set by Department of Energy (DOE) of United State for hydrogen storage system is 5.5 wt.% on gravimetric capacity and 40 g L$^{-1}$ on volumetric capacity [2] under operational temperature (-40)-60 °C with pressure below 100 bar [1, 3].

Recently, several porous materials have been intensively explored, including Metal-Organic Framework (MOFs) as hydrogen storage materials. MOFs are hybrid materials of organic-inorganic, constructed from metal ions or metal-oxide clusters combined with organic ligands form crystalline porous coordination network [4]. MOFs can be used for hydrogen storage due to their porosity and active sites on both of ligand and metal [5]. MOFs store hydrogen effectively within reduced volume resulting in a high density [6].

HKUST-1 [Cu$_3$(BTC)$_2$] is a well-known type of MOFs frequently investigated materials in hydrogen storage [4, 7, 8]. In order to enhance the hydrogen uptake, HKUST-1 could be doped with
an electropositive metal. Based on the previous report [6], in-situ lithium and sodium ions doping into HKUST-1 can increase surface area and hydrogen uptake. Lithium ions act as additional binding sites to interact with hydrogen molecules [6]. In this present study, we investigate the influence of Li+ doping into HKUST-1 toward its structural changes and the hydrogen sorption properties. HKUST-1 was synthesized under the solvothermal condition and doped with a various amount of lithium ions (3, 5, 10 wt.%) through ex-situ modification in order to improve the hydrogen adsorption capacity of HKUST-1.

2. Materials and methods

2.1 Materials

H₂BTC (95%) and LiCl (8M) were purchased from Sigma Aldrich Germany, Cu(NO₃)·3H₂O (98%) and ethanol (96%) were commercially provided by Merck Germany. Deionized water was obtained from Bratapchem-Indonesia. All reagents were used as purchased without any further purification.

2.2 Synthesis of Li⁺ @ HKUST-1

HKUST-1 was prepared via the solvothermal method based on the previous literature procedures [4]. HKUST-1 was doped with Li⁺ through ex-situ modification from LiCl solution (8M) with a variation of 3, 5 and 10 wt.% Li⁺ in 1 g of HKUST-1. The solution of LiCl (1.027; 1.71; 3.42 mL) was added with HKUST-1 (0.97; 0.95; 0.90 g) in 24 mL ethanol: deionized water (1:1). The mixture was placed into Teflon vessels covered with stainless-steel autoclaves and heated in an oven MEMPRT (type 67 UN30) at 393 K for 12 h. After cooled, the obtained blue precipitate was filtered, washed with ethanol (96%) two times and dried at ambient temperature for 16 hours.

2.3 Hydrogen storage measurement

General procedures: the material (0.5 g) was activated under vacuum condition at 473 K for 1 h. Hydrogen storage measurement was tested using Sievert system as published by Suwarno et al. [9] at 30 and 80 °C with pressure from 0.2 to 1.5 bar. At each pressure, the measurement was conducted for 15 minutes.

2.4 Material characterization

The X-ray powder diffraction (PXRD) data as quantitative analysis were obtained on Rigaku Miniflex 600 Benchtop, using Cu as anode tube, Kα radiation (λ = 1.5406 Å), with the current and voltage under 30 mA and 40 kV (2θ = 5-50°) at a scan rate of 1°/min. The nitrogen sorption isotherms at 77 K were obtained from a Quadrasorp Evo (Quantachrome instruments). The samples were activated at 120 °C for 24 h prior measurement. The morphology and elemental compositions were observed using SEM-EDX FEI Inspect S50.

3. Results and discussion

X-Ray diffractogram of HKUST-1 compared with Li⁺ @HKUST-1 are performed in Figure 1. Three basic peaks at 2θ: 6.73° (2 0 0); 9.47° (2 2 0) and 11.65° (2 2 2) are confirmed through similarities with the simulated pattern (CCDC: 112954). The diffraction patterns of HKUST-1 are remained unchanged after doped with Li⁺. It may be considered that the presence of Li⁺ does not chemically influence the HKUST-1 structure. Moreover, the absence of Li⁺ peaks in the diffractogram showed that HKUST-1 atoms are not chemically bonded with Li⁺ ions [6]. In addition, the presence of some impurities possibility such as Cu₂O (2θ: 36.43°) and CuO (2θ: 35.5° and 38.7°) are not observed in the obtained materials [10].

The determination of pore type, surface area, and pore volume distribution were performed using N₂ sorption isotherm measurement at 77 K. Figure 2 shows that before and after doping with Li⁺, the materials could be classified as microporous materials. Doped 5 wt.% of Li⁺ into HKUST-1 increases...
surface area from 713.28 up to 1040.96 m²/g with the smaller pore volume up to 0.048 cc/g which assumed that Li⁺ ions filled the HKUST-1 pores, as shown in Table 1.

![Diffractogram](image)

**Figure 1.** Diffractogram of doped HKUST-1 with Li⁺ and undoped HKUST-1 compared to simulated pattern #CCDC 112954.

![Nitrogen adsorption-desorption isotherm](image)

**Figure 2.** N₂ adsorption-desorption isotherm at 77 K of doped HKUST-1 with Li⁺ and undoped HKUST-1.

**Table 1.** Pore volume and surface area of doped HKUST-1 with Li⁺ and undoped HKUST-1.

| Sample           | Langmuir surface area (m²/g) | Pore volume (cc/g) |
|------------------|------------------------------|--------------------|
| HKUST-1          | 713.28                       | 0.068              |
| Li⁺ 3 wt.% @ HKUST-1 | 334.49                      | 0.108              |
| Li⁺ 5 wt.% @ HKUST-1 | 1040.96                     | 0.048              |
| Li⁺ 10 wt.% @ HKUST-1 | 314.84                      | 0.059              |
Figure 3. SEM-EDX Images of doped HKUST-1 with Li\(^+\) and undoped HKUST-1.

Table 2. Elements composition of doped HKUST-1 with Li\(^+\) and undoped HKUST-1.

| The material             | Element (wt%) |
|--------------------------|---------------|
|                          | C  | O  | Cu | Cl |
| HKUST-1                  | 33.68 | 19.40 | 46.92 | - |
| Li\(^+\) 5 wt.%@HKUST-1  | 30.13 | 21.19 | 47.69 | 0.99 |
| Li\(^+\) 10 wt.%@HKUST-1 | 25.79 | 19.04 | 49.25 | 5.91 |
EDX spectrum and HKUST-1 and Li⁺@HKUST-1 morphology were shown in Figure 3. The basic shape of HKUST-1 (in octahedral) remained similar after doped with Li⁺, however, the morphology is changed due to stirring process during the treatment which may break the HKUST-1 crystal. In addition, observed Cl elements in Table 2 is an indication that Li⁺ successfully doped into HKUST-1 since Li⁺ itself could not be observed by EDX analysis. Cl ions size are very small, 0.18 nm [11] which may diffuse to the HKUST-1 pores. The presence of Li⁺ and Cl in HKUST-1 also changed the element composition of HKUST-1 (C, O, and Cu) as listed in Table 2.

The hydrogen storage capacities at temperature 30 and 80 °C is shown in Figure 4. Hydrogen uptake enhancement of HKUST-1 could be due to Li⁺ ions supply additional active site to bind hydrogen molecules. At temperature 30 °C (1.4 bar), the maximum hydrogen uptake is 0.24 wt.%, obtained from Li⁺ 5 wt.%@HKUST-1. Additionally, the maximum adsorption capacity at 80°C (1.4 bar) is up to 0.18 wt.% obtained from Li⁺ 10 wt.%@HKUST-1. According to the previous study conducted by Anbia and Faryadas [6], in-situ doping about 16.9 wt% of Li⁺ gave hydrogen storage capacity at ambient temperature (14 bar) up to 8 mmol g⁻¹. The result indicates that electropositive metal ion embedding to HKUST-1 increases hydrogen uptake due to the increasing surface area and additional sites provided by the metal cations in the HKUST-1 environment. In overall, hydrogen storage capacity at temperature 80 °C is lower than temperature 30 °C. According to Lin et al. [4], interaction between hydrogen molecules and materials would be more effective at low temperature.

![Figure 4](image-url)

**Figure 4.** Hydrogen storage capacity of undoped HKUST-1 (A) and doped HKUST-1 with Li⁺ (B= 3 wt.%; C=5 wt.%; D=10 wt.%) at temperature (a) 30 °C (b) 80 °C.

4. Conclusion
Ex-situ doping of Li⁺ into HKUST-1 was successfully prepared and tested for hydrogen storage. The presence of Li⁺ does not chemically change the HKUST-1 structure but enhances hydrogen storage capacity up to 0.24 wt.% (for 5 wt.% of Li⁺) at 30 °C 1.4 bar. Due to its high surface area and porosity,
simple synthesis, and possible to store hydrogen. Li’@HKUST-1 can be a good candidate material for hydrogen storage. For the next study, the hydrogen uptake measurement should be conducted with longer time and optimized under higher pressure.

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