

CHAPTER III

EXPERIMENTS

3.1 Sample Preparations

The LiBH_4 ($\geq 90\%$ hydrogen-storage grade, Sigma-Aldrich) and LiAlH_4 ($>99.95\%$ hydrogen-storage grade, Sigma-Aldrich) were milled with a molar ratio of 1:1 in a stainless-steel vial (Evico Magnetic, Germany) using a SPEX SamplePrep 8000D DUAL Mixer/Mill (Figure 3.1B) to obtain $\text{LiBH}_4\text{-LiAlH}_4$ composite, denoted as LB-LA. Milling time and ball-to-powder weight ratio (BPR) were 5 h and 10:1, respectively. The LB-LA was dehydrogenated at $220\text{ }^\circ\text{C}$ for 15 min and milled for 5 h with BPR of 10:1, and denoted as LB-LA (220). The MWCNTs (Nano Generation Co. Ltd., Thailand) were treated at $100\text{ }^\circ\text{C}$ under vacuum for 1 h to remove oxygen and moisture. Treated MWCNTs (5 wt %) were milled with LB-LA (220) for 30 min with BPR of 10:1 to obtain LB-LA (220) doped with 5 wt % MWCNTs, denoted as LB-LA (220)-CNT. All samples were handled under a nitrogen atmosphere in a glove box (99.9% N_2) (Omni-Lab System, VAC) (Figure 3.1A).

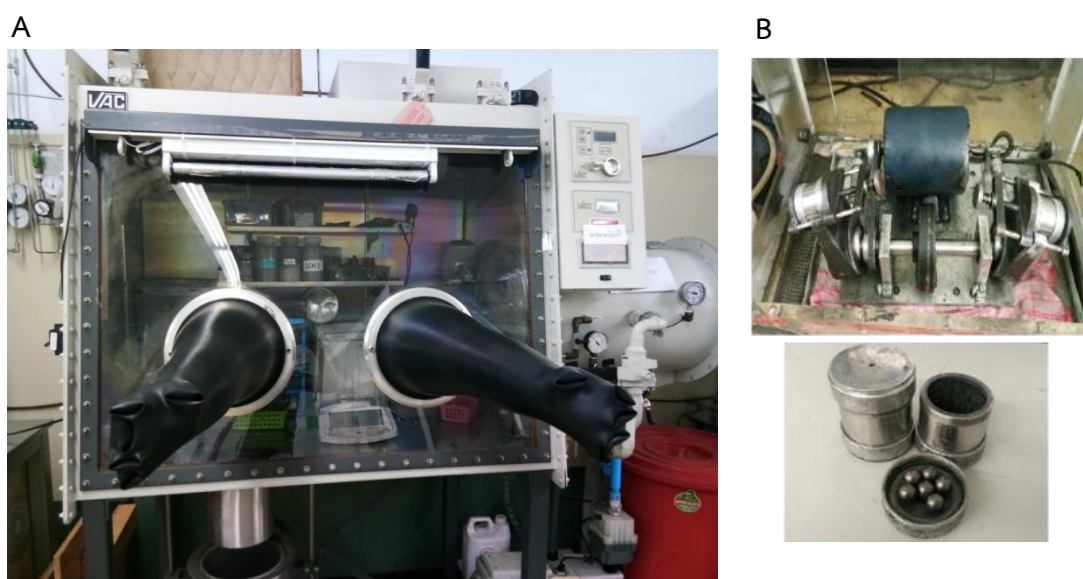


Figure 3.1 Glove box (Omni-Lab System, VAC) (A) and SPEX SamplePrep 8000D DUAL Mixer/Mill and stainless-steel vial (B).

3.2 Characterizations

3.2.1 Powder X-ray diffraction (XRD)

Powder X-ray diffraction (XRD) of as-prepared and de/rehydrogenated powder samples were carried out by using a Bruker D2 PHASER with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) (Figure 3.2A). The sample of approximately 7-10 g was packed in an airtight sample holder, covered by a poly (methyl methacrylate) dome (Figure 3.2B). All XRD experiments were conducted at room temperature. The scanning step was 0.02 $^\circ$ /s. The scanning 2θ was in the range of 10-80 $^\circ$.

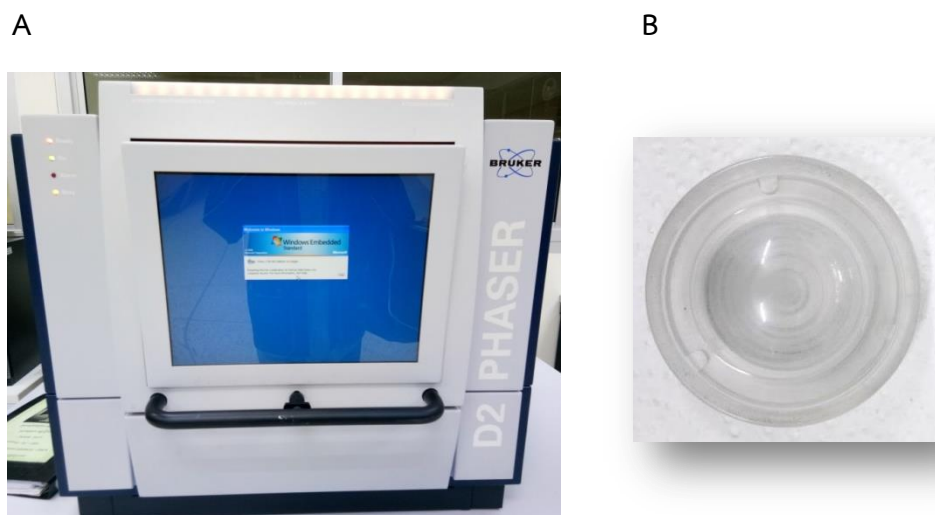


Figure 3.2 A Bruker D2 Phaser Powder X-ray diffractometer (A) and sample holder, covered by a poly (methyl methacrylate) dome (B).

3.2.2 Fourier transform infrared spectroscopy (FTIR)

The powder samples of milled LB-LA, LB-LA (220), and LB-LA (220)-CNT were investigated by Fourier Transform Infrared Spectrophotometer (FTIR) using a Bruker Tensor 27-Hyperion 2000 (Figure 3.3). The mixture of sample powder and anhydrous KBr was ground in the mortar with the weight ratio of \sim 1:10 (sample powder: KBr), and pressed under a specific pressure into a pellet of 1 cm diameter. The KBr pellet containing the sample was assembled in the instrument, where it was on the infrared direction. The spectra were collected in the wavenumber range of 4000-400 cm^{-1} with 64 scans for both sample and background. To accomplish the final spectrum, subtraction of the sample spectrum with that of the background was done.



Figure 3.3 A Bruker Tensor 27 Fourier transform infrared spectrophotometer.

3.2.3 X-ray photoelectron spectroscopy (XPS)

The X-ray photoelectron spectroscopy (XPS) was carried out at the SUT-NANOTEC-SLRI joint research facility, Synchrotron Light Research Institute (Public Organization), Thailand (Figure 3.4), using a PHI5000 Versa Probe II (ULVAC-PHI Inc., Japan) with Al K_{α} (1.486 keV) radiation as an excitation source. The powder samples were deposited on the sample holders by using carbon glue tape in the glove box under N_2 atmosphere. Prior to the measurements, all prepared samples were placed in a high vacuum chamber (1×10^{-8} mbar) for 2 h. The high-resolution scan of each element was collected using pass energy and a step size of 46.95 and 0.05 eV, respectively. Dual-beam charge neutralization (low energy electron and ion beam) method was used to minimize sample charging. The binding energy was calibrated with respect to the C 1s peak (284.8 eV). The data were processed and analyzed using MultiPak software version 9.6.0 (ULVAC-PHI, Japan). Peak fitting was performed after Shirley background subtraction and a symmetrical Gaussian-Lorentzian function was used to approximate the line shapes of the fitting components.



Figure 3.4 X-ray photoelectron spectroscopy at Synchrotron Light Research Institute (SLRI).

3.2.4 Solid-state nuclear magnetic resonance spectroscopy (NMR)

Solid-State ^{27}Al , magic-angle spinning nuclear magnetic resonance (MAS NMR) spectra were recorded by a Bruker ASCENDTM 500 spectrometer (Figure 3.5A). The samples were tightly packed in a zirconia end-capped tube (Figure 3.5B). All experiments were performed at 302 K using a BL4 VTN probe for 4 mm outer diameter rotors. The ^{27}Al chemical shifts were detected in parts per million (ppm) relative to neat aluminum oxide (Al_2O_3). Spinning speed (ν_r), excitation pulse length, and the number of scans were 8 kHz, 9.8 μs , and 1000, respectively.

A



B



Figure 3.5 A Bruker AscendTM 500 Solid-State magic-angle spinning nuclear magnetic resonance (MAS NMR) spectrometer (A) and zirconia end-capped tube (B).

3.2.5 Optical microscopy

Morphology of samples was characterized using an optical microscope (BX51, Olympus America Inc., USA) (Figure 3.6A). As-prepared LB-LA, LB-LA (220), and LB-LA (220)-CNT were sandwiched between microscope glass slides wrapped with Kapton tape to prevent oxidation from air and moisture (Figure 3.6B). The experiments were carried out under LBD, ND25, and ND6 transmitted light and all micrographs were collected using an Olympus XC50 camera with a color charge-coupled device.

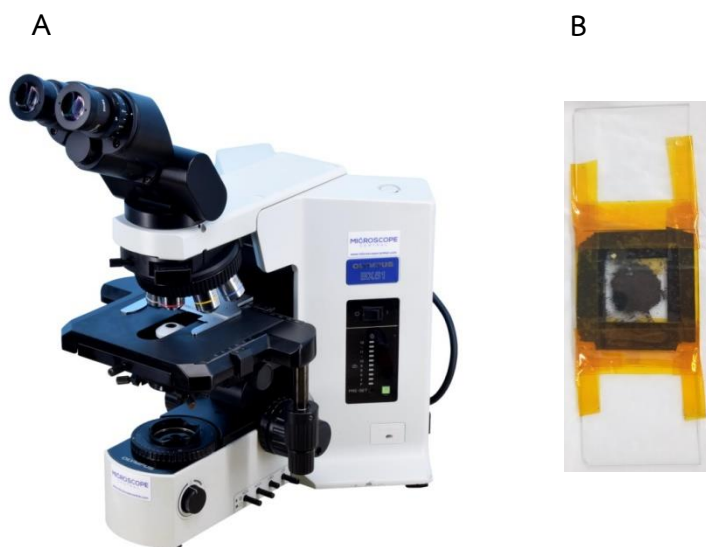


Figure 3.6 An Olympus optical microscopes (A) and sandwiched glass slides of sample. (B) (<https://microscopecentral.com/products/olympus-bx51-microscope>).

3.2.6 Kinetic measurements

Dehydrogenation kinetics and reversibility were investigated using a laboratory-scale setup of a Sievert-type apparatus (Figure 3.7 and 3.8) (Rapee Gosalawit-Utke et al., 2014). The powder samples (100-200 mg) was packed in a high pressure stainless steel sample holder (316SS, Swagelok) under argon atmosphere of the glove box and transferred to the Sievert-type apparatus. Two K-type thermocouples (-250–1,300 °C, SL heater) were attached to the sample holder and the furnace to measure the temperature of the system. Pressure transducers (C206, Cole Parmer) in the pressure range of 0-500 psig and 0-3000 psig were used to measure the pressure change due to hydrogen desorption and absorption, respectively. Thermocouples and pressure transducers were connected to an AI 210I module convertor data logger (Wisco), measuring and transferring (every 1 s) the pressure and temperature changes of the sample to the computer for further evaluation. Dehydrogenation was carried out at 400 °C under 7 mbar H₂ and rehydrogenation was at 400 °C under 80 bar H₂ for 16 h. Once the pressure of the system was constant, the amount of hydrogen released was calculated by the pressure change (Δp) and the following equations: Once the pressure reading was constant over a period of time, the amount of hydrogen release and uptake was calculated by the pressure change (ΔP) using the following equations:

$$(\Delta P)V = nRT \quad (3.1)$$

$$H_2 \text{ desorbed (wt. \%)} = [(n \times 2.0158)/\text{sample weight}] \times 100 \quad (3.2)$$

where P, V, and T are hydrogen pressure (atm), volume of the system (L), and temperature (K), respectively, n is the number of hydrogen moles (mol), and R is gas constant (0.0821 L atm K⁻¹ mol⁻¹).

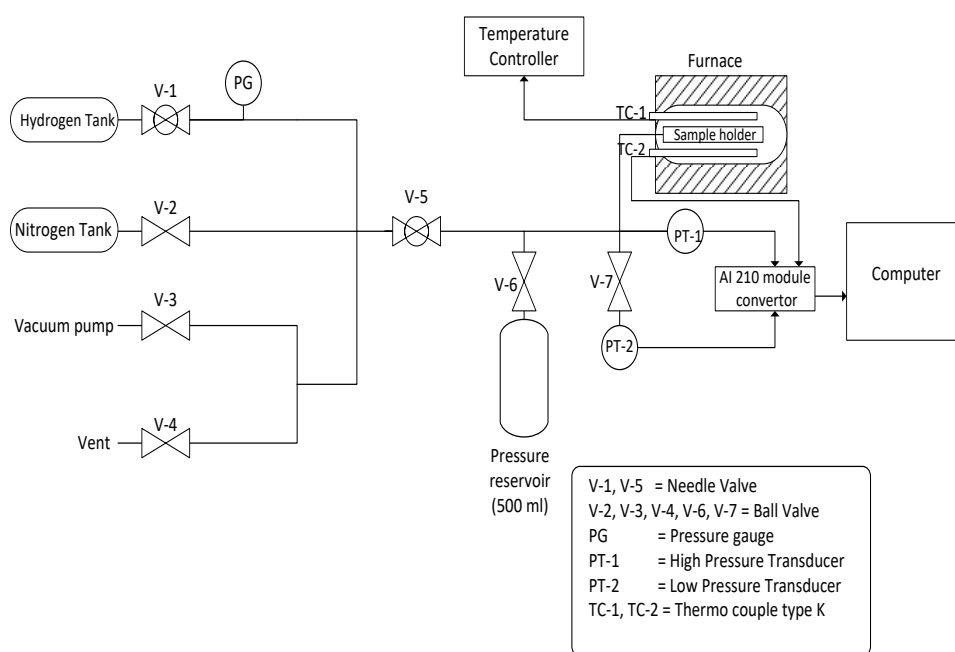


Figure 3.7 Schematic diagram of Sievert-type apparatus.



Figure 3.8 Laboratory-scale setup of Sievert-type apparatus.

3.3 References

Gosalawit-Utke, R. Meethom, S. Pistidda, C., Milanese, C., Laipple, D., Saisopa, T., and Dornheim, M. (2014). Destabilization of LiBH_4 by nanoconfinement in PMMA-co-BM polymer matrix for reversible hydrogen storage. *Int. J. Hydrogen Energy*, 39, 5019–5029.