

CHAPTER III

EXPERIMENTAL SECTION

3.1 Chemicals

Table 3.1 Chemicals used in this work.

Chemicals	Formular	specification	Supplier
Lithium amide	LiNH_2	95 %	Aldrich
Lithium hydride	LiH	95 %	Aldrich
Titanium tetrafluoride	TiF_4	99 %	Acros Organics
Multiwall carbon nanotubes	MWCNTs	-	diameter of 20-50 nm, Nano Materials Research Unit

3.2 Apparatus

3.2.1 Glovebox and high-energy ball milling

Due to the sensitivity of hydride materials to air and moisture, all samples were handled under a nitrogen atmosphere in the glove box (Figure 3.1(A)). The ball milling was used for sample preparation (Figure 3.1(B)).

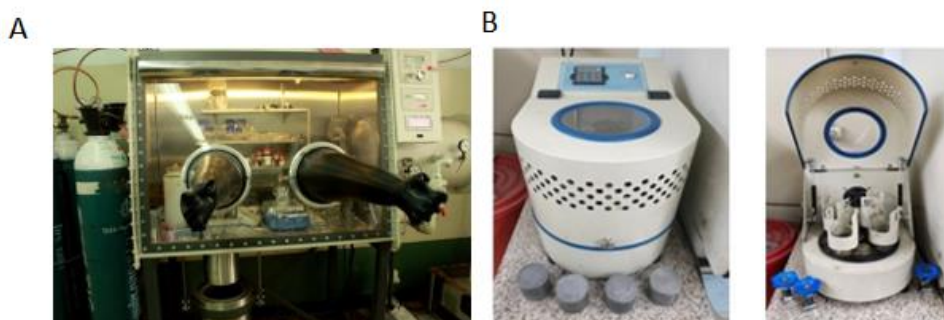


Figure 3.1 Glove box (Omni-Lab System, VAC) (A) and A QM0.4L Planetary Ball Mill, Nanjing Chishun Science & Technology (B).

3.3 Sample preparation

3.3.1 Compacted $\text{LiNH}_2\text{-LiH}$ doped with TiF_4 and MWCNTs

LiNH_2 was mixed with LiH by 1:1 molar ratio and milled for 5 h and 10 h with a ball-to-powder weight ratio of 20:1 and 580 rpm, respectively, to obtain $\text{LiNH}_2\text{-LiH}$ composites, denoted as LNL. LNL composite (5 h) was milled with 5.0 wt.% TiF_4 for 5 h and with MWCNTs for 10 min. The powder samples of LNL (10h) and LNL- TiF_4 -MWCNTs were compressed into the pellets under 200 Mpa using a pellet die set with 15 mm diameter to obtain the compacted samples of LNL and LNL- TiF_4 -MWCNTs, respectively. The densities of the LNL and LNL- TiF_4 -CNT pellets were ~ 0.7 and 1.00 g/cm^3 , respectively.

3.3.2 LiH-sandwiched $\text{LiNH}_2\text{-LiH-TiF}_4\text{-MWCNTs}$ pellets

LiH was pre-milled for 5 h and milled with 1 wt. % MWCNTs for 30 min. The powder sample of LNL (5h) obtained from 3.3.1 was sandwiched between MWCNTs-doped LiH by compressing under 200 MPa to obtain LiH-sandwiched LNL (Figure 3.2(A)). The amounts of MWCNTs-doped LiH layers were 10, 20, and 30 wt. % with respect to LNL content, and the obtained pellet samples were named LNL- 10% LiH, LNL- 20% LiH, and LNL-30% LiH, respectively.

3.4 Small hydrogen storage tanks containing compacted LNL, LNL- TiF_4 -MWCNTs and LiH-sandwiched LNL

All compacted samples ($\sim 2\text{-}3 \text{ g}$) were packed into separated cylindrical tanks with a packing volume of 21.7 mL (Figure 3.2(B-D)). Hydrogen diffusion inside the tank was improved by inserting the stainless-steel (SS) mesh sheets between the compacted pellets. Temperature profiles inside the tank were investigated using K-type thermocouples from SL heater (TC1, TC2, and TC3 inserted at the depths of 3, 2, and 1 cm, respectively) (Figure 3.2(C-D)).

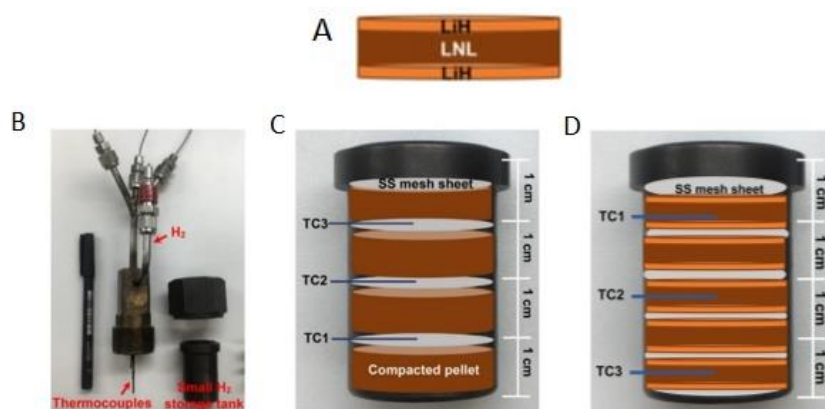


Figure 3.2 Schematic draw of LiH-sandwiched LNL pellet (A), the components of small hydrogen storage tank (B), and the positions of thermocouples along the tank length packed with compacted samples of LNL and LNL-TiF₄-MWCNTs (C) and LiH-sandwiched LNL (D).

3.5 Characterizations

3.5.1 Chemical compositions and structure

3.5.1.1 Powder x-ray diffraction (PXD)

Powder x-ray diffraction (PXD) experiments were done using a Bruker D8 ADVANCE with Cu K α source ($\lambda = 0.15406$ nm). The pellet sample was ground and packed in the sample holder covered with a poly (methylmethacrylate)(PMMA) dome (Figure 3.3) under a nitrogen-filled glove box. The experiments were investigated at the 2θ range and the scanning step of $10\text{--}80^\circ$ and $0.02^\circ/\text{s}$, respectively.



Figure 3.3 An airtight sample holder covered with a PMMA dome.

3.5.1.2 Fourier transform infrared spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) spectra were collected using an attenuated total reflection (ATR) mode (a Bruker T27/Hyp 2000) in 4000-400 cm^{-1} wavenumber range with 64 scans (Figure 3.4).



Figure 3.4 FTIR spectrometer of Tensor 27-Hyperion 2000 (Bruker).

3.5.1.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) experiments were carried out at the Suranaree University of Technology (SUT), National Nanotechnology Center (NANOTEC) and Synchrotron Light Research Institute (SLRI) joint research facility, Synchrotron Light Research Institute (Public organization), Thailand (Figure 3.5). A PHI5000 Versa Probe II (ULVAC-PHI Inc., Japan) with Al $K\alpha$ (1.486 keV) radiation as an excitation source was used. The powder samples were deposited on the sample holder using carbon glue tape in the glove box. Prior to the measurements, the samples were placed in the high vacuum chamber (1×10^{-8} mbar) for 2 h. The high-resolution scan of each element was collected using a pass energy of 46.95 eV and a step size of 0.05 eV. 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 was analyzed using MultiPak software version 9.6.0 (ULVAC-PHI, Japan). Peak fitting was performed after Shirley background subtraction. The symmetrical Gaussian-Lorentzian function was used to approximate the line shapes of the fitting components.

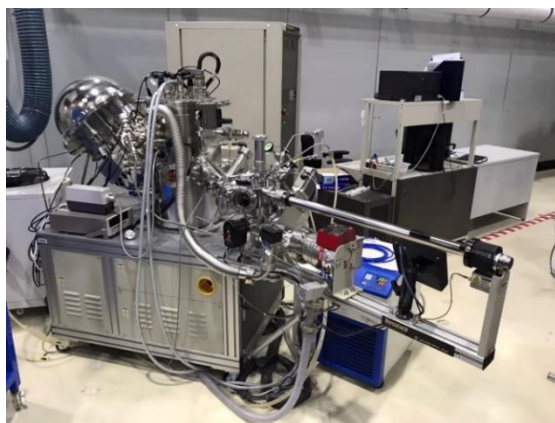


Figure 3.5 X-ray photoelectron spectroscopy at Suranaree University of Technology (SUT), National Nanotechnology Center (NANOTEC) and Synchrotron Light Research Institute (SLRI).

3.5.2 Hydrogen sorption properties

3.5.2.1 Simultaneous thermal analysis (STA) coupled with mass spectroscopy (MS)

Hydrogen desorption was characterized by differential scanning calorimetry (DSC) and thermogravimetry (TG) using a Netzsch (STA 449 F3 Jupiter) (Figure 3.8). The sample (~15 mg) was heated to 500 °C (5 °C/min) under 50 mL N₂/min. The relative signals of H₂ and NH₃ released from the sample were investigated by mass spectroscopy (MS) using a Netzsch QMS 403C (Figure 3.6).



Figure 3.6 STA 449 F3 Jupiter coupled with QMS 403C (Netzsch).

3.5.2.2 Sievert-type apparatus for tank scale

Titration measurements were carried out using a test station automatically controlled by a program created in the Labview® environment (Dansirima et al., 2019), (Thiangviriyaya et al., 2019), (Thongtan et al., 2018). The small hydrogen storage tanks packed with the compacted samples were assembled with other components of the sample holders for titration measurement (Figure 3.7). The direct-acting plunger solenoid valves (a Bürkert Type 0255) were used to control hydrogen consumption and liberation during de/rehydrogenation. The pressure change during the experiments was detected by a pressure transducer (0–3000 psig, an OMEGA Engineering PX309–3KGI). Temperature, pressure, and mass flow rate profiles were transferred to the computer using the module data loggers (a National Instruments NI USB-6009 and a Wisco AI210). Hydrogenation was carried out at isothermal conditions ($T_{\text{set}} = 330 \text{ }^{\circ}\text{C}$) under 10–15 bar H_2 . Dehydrogenation was at $T_{\text{set}} = 330 \text{ }^{\circ}\text{C}$ and began with the hydrogen pressure of 15 bar, remaining after hydrogenation. A mass flow controller (MFC, a Bronkhorst EL-FLOW selected F-201CV) with the operating range of 0–1.0 standard L/min (SLM) was used to measure the content of hydrogen desorbed.

The volume of hydrogen gas was achieved by integrating the peak area of hydrogen mass flow rate (SLM) versus time (min) plot. Total hydrogen storage capacity, defined as the combination of material hydrogen capacity and hydrogen content remaining after absorption was calculated as following equations.

$$V_{STP} = \frac{P_s V_s T_{STP}}{T_s P_{STP}} \quad (3.1)$$

$$n_{H_2} = \frac{V_{STP}}{22.4 \text{ L}\cdot\text{mol}^{-1}} \quad (3.2)$$

$$H_2 \text{ capacity (wt. \%)} = \frac{n_{H_2} \times 2.016 \text{ g/mol}}{\text{sample weight (g)}} \times 100 \quad (3.3)$$

where V_{STP} (L) and V_s (SL) are volumes of hydrogen gas at standard temperature and pressure condition (STP, $T_{STP} = 273.15 \text{ K}$ and $P_{STP} = 1.0133 \text{ bar}$) and at the standard condition of MFC ($T_s = 296.15 \text{ K}$ and $P_s = 1.0156 \text{ bar}$), respectively. n_{H_2} (mol) is hydrogen mole and standard molar volume is 22.4 L/mol .

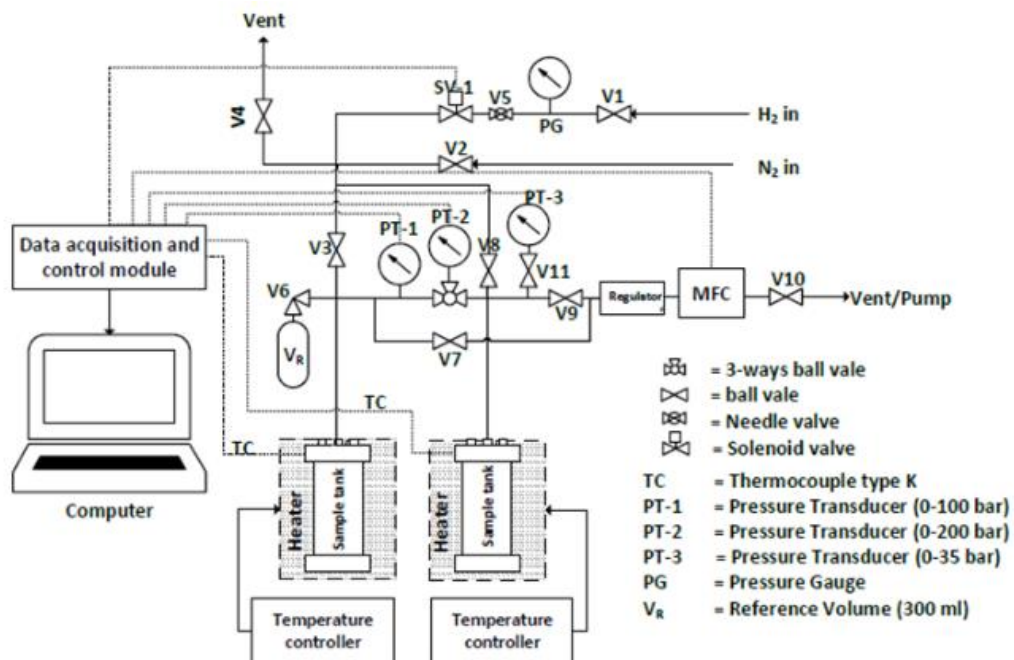


Figure 3.7 Schematic diagram of Sievert-type apparatus.

3.6 References

- Dansirima, P., Thiangviriyaya, S., Plerdsranoy, P., Utke, O., and Utke, R. (2019). Small hydrogen storage tank filled with $2\text{LiBH}_4\text{-MgH}_2$ nanoconfined in activated carbon: reaction mechanisms and performances. *Int. J. Hydrogen Energy*, *44*, 10752-10762.
- Thiangviriyaya, S., Plerdsranoy, P., Sitthiwet, C., Dansirima, P., Thongtan, P., Eiamlamai, P., Utke, O., and Utke, R. (2019). $\text{MgH}_2\text{-TiF}_4\text{-MWCNTs}$ based hydrogen storage tank with central heat exchanger. *Int. J. Hydrog. Energy* *44*, 20173–20182.
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