HYDROGEN UPTAKE OF MECHANICALLY MILLED $LANI_5$-MWCNTS NANOCOMPOSITE

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Abstract - $LaNi_5$-MWCNTs nanocomposite was prepared by high-energy ball milling and their hydrogen storage capacity properties were studied by employing Sievert's volumetric instrument. Crystal structure, thermal stability, quantity, and nanostructured characterization of pristine and composite samples were performed by X-ray diffraction pattern, thermogravimetric and differential thermal analysis, field emission scanning and transmission electron microscopy methods. Channel and pore blocking of MWCNTs by $LaNi_5$ during synthesis method explains reduction of surface area of composite. Hydrogen uptake of commercial $LaNi_5$, pristine MWCNTs, and $LaNi_5$-MWCNTs nanocomposite was found to be 1.49, 0.07, and 1.53 wt.% measured at RT and hydrogen pressure of 4.0 MPa. Ball milling process and addition of MWCNTs to $LaNi_5$ alloy proved to be very critical to improve kinetics.

Keywords - Ball milling, Hydrogen storage; Nanocomposite; Crystal structure; Kinetics

I. INTRODUCTION

Pollution emerging from random use of various kinds of fossil fuels currently introduces an intimidating risk to a sustainable global growth and development. Depletion of fossil fuels is imminent in near future due to aggressive use by developing nations across the world. Only alternative to this growing and intimidating pollution problem is introduction of hydrogen based fuel cell economy. Currently hydrogen provides a sustainable solution for future energy crises and at the same time mitigates hostile environmental effects produced by combustion of fossil fuels. Thehydrogen based economy besides diminishing harmful effects can also significantly resolve present energy crisis related with increasing energydemands. Facile production, tremendous energy density, excessive presence, and nil pollution moulds hydrogen desirable and affordable fuel for on-board applications [1-4]. However, absence ofefficient, dependable, and inexpensive method that can reversiblystore hydrogen presently poses a significant challenge to general communities' approval and broader effective use of hydrogen as a fuel. Hydrogen storage capacity in variety of porous or non-porous mediums required to fulfill targets set by the US Department of Energy (DOE) for transport applications. DOE specific targets lay down for onboard hydrogen storage systems are 1.5 kWh/kg (4.5 wt.% of H_2) and 1.0 kWh/L (30 g H_2/L) for 2020; 1.8 kWh/kg (5.5 wt.% of H_2) and 1.3 kWh/L (40 g H_2/L) for 2025; and 2.2 kWh/kg (6.5 wt.% of H_2) and 1.7 kWh/L (50 g H_2/L) for latest [5, 6].

Currently chemisorption and physisorption type hydrogen uptake structures are considered as best solution to achieve longstanding storage targets. [7-9]. Physisorption in carbon nanotubes (SWCNTs & MWCNTs), fullerenes, clathrate hydrates, zeolites, and highly porous materials (MOFs and COFs) are treated as an accepted and easiest route of storing hydrogen conveniently [10-14]. Post activation of MWCNTs at elevated temperature, hysteresis are formed upon exposure to hydrogen. Moreover, weak physorption and chemisorption association is the reason for the formation of hysteresis in MWCNTs [15]. To approach DOE goals for conclusive hydrogen uptake, little dissociation temperature, medium pressure, fast kinetics, charging infrastructure, and safety are main criteria. Economical and productive hydrogen storage in MWCNTs build on characteristics such as morphology, irregularity, purification, pretreatment, high surface area, high pore volume, tunable structure etc. [16,17]. Various types of characteristics including tremendous surface area, vast pore volume, high stability, tunable geometry, porous and channel like structure etc. associated with MWCNTs qualifies it as a favorable candidate to store high hydrogen at moderate temperature and pressure [18-20]. Various productive and efficient measures including acid based treatment, annealing at elevated temperature, bromination, different types of etching, hydroxide activations etc. are implemented to improve overall hydrogen uptake in MWCNTs. [21-23]. Modifications in terms of forming metal or metal oxide or metal halide/MWCNTs composite is another important and efficient step to improve hydrogen storage capacity. Different types of MWCNTs composites are synthesized by various types of methods including in-situ reduction, ball milling, incipient wetness impregnation, sputtering etc.[24, 25]. Mg-MWCNTs composites prepared by ball milling shows a drastic enhancement in hydrogen uptake and kinetics. Addition of 5 wt.% single walled carbon nanotubes (SWCNTs) to Mg and ball milling for 10 h enhances hydrogen capacity up to 6.7 wt.% within 2 min [26]. Composites prepared from MWCNTs and magnesium nickel alloys by ball milling enhances specific surface area and blocks reconstruction of oxide layers on surface of composite samples [27].

In this report, high-energy ball milling route is employed to synthesize MWCNTs-$LaNi_5$ composite. Sievert's volumetric instrument utilized to measure hydrogen storage capacity and kinetic characteristics of composite sample at RT and hydrogen pressure of 4.0 MPa and are compared with commercial $LaNi_5$ sample. Hydrogen uptake of composite are measured from storage capacity contributions of commercial $LaNi_5$ and purified MWCNTs performed at identical experimental surroundings. Improved kinetics in composite material is due to nanostructured character facilitated by ball milling and MWCNTs catalyst effects.

II. EXPERIMENTAL

High-energy ball milling used to synthesize MWCNTs-$LaNi_5$ composite adopting pristine MWCNTs and commercial $LaNi_5$ alloy as a starting material. Ceramic vial with different sizes of zirconia balls and sample inside are fitted in high-energy ball mill (Spex 8000). The ball milling duration to prepare composite sample was 4 h. Furthermore, Zirconia balls to sample powder ratio was fixed at 14:1. MWCNTs (98%), a reinforcing phase component of composite purchased from CNT Inc., Korea was purified by vigorous acid operation succeeded by bromination.

Crystal structure measurement of composite sample was performed by Rigaku D/MAX 2500 X-ray diffractometer (XRD) assembled with Cu-Ka radiation source (λ = 0.15418 nm). Morphological character study of pristine and composite samples were achieved by scanning electron microscopy and transmission electron microscopy methods. Thermogravimetric analysis and differential thermal analysis were used to determine thermal stability and residual amount of $LaNi_5$ in the composite. Surface area of purified and composite sample are measured by Brunauer-Emmett-Teller N_2 adsorption isotherm technique (BET, ASAP 2000). Sievert's volumetric instrument was used to measure hydrogen uptake study of $LaNi_5$-MWCNTs nanocomposite. Prior to each hydrogen uptake measurement, calculation of dead-volume of equipment was performed using a non-reactive helium gas.

Hydrogen storage data of $LaNi_5$ was utilized to cross-check calculated volume. In each hydrogen uptake measurement, 1 g of composite sample was used. Each composite sample was out-gassed for 3 h at 573 K under repeated evacuation up to 10^{-6}Torr before initiating hydrogen uptake measurement. Ideal gas equation calculation from pressure drop of hydrogen during experiment was utilized to measure hydrogen uptake. Data procurement for hydrogen uptake measurements was programmed by incorporating pressure transducer output to a PC via RS-232 apparatus. More information related to our hydrogen uptake measurements are reported in literature elsewhere [28].

III. RESULTS AND DISCUSSION

XRD pattern of $LaNi_5$-MWCNTs composite presented in Fig. 1 were analyzed to study crystalline structure. For XRD analysis, different types of peaks between 20 and 80^{o} are considered. The peaks at 20.3, 22.05, 30.2, 35.35, 41.35, 42.35, 43.95, 45.45, 59.45, 60.8, 63.1, 68.95, and 75.65^{o} correspond to $LaNi_5$ phase and peak at 25.45^{o} corresponds to MWCNTs phase. Peaks of $LaNi_5$ phase in composite sample are related to cubic P6/mmm (JCPDS File No. 65-3472). MWCNTs phase in composite sample at 25.45^{o} (002) belongs to hexagonal phase (JCPDS File No. 75-1621). All the peaks of composite sample are broader and less intense indicating nanostructured character.

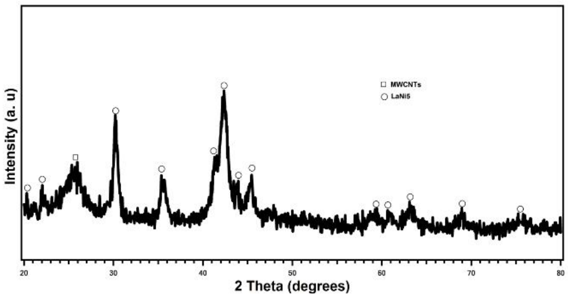

Figure 1. XRD pattern of $LaNi_5$-MWCNTs composite prepared by high-energy ball milling method.

TGA and DTA plot of composite material are presented in Fig. 2. In $LaNi_5$-MWCNTs composite, monotonous weight loss fall in the range 400–540°C is related to MWCNTsgasification. Paramount weight loss of composite interrelated to gasificationof MWCNTs at ~570°C is ~48%, demonstrates ~52% $LaNi_5$in composite. The initial amount of MWCNTs and $LaNi_5$ for the preparation of composite by ball milling was 1:1 ratio. The 2% higher amount of $LaNi_5$ indicated by TGA profile may be due to impurity. Furthermore, commercial $LaNi_5$ was used without purification for composite formation. Maximum rate of gasification of MWCNTs determined from DTA profile is 456°C.

A small peak at ~488^{o}C is related to oxidation of amorphous carbon. Both SEM and TEM profiles presented in Fig.3 indicates nanostructure morphology of composite sample. SEM image (a) and (b) belongs to pristine MWCNTs and $LaNi_5$/MWCNTs composite sample. TEM profile (a) and (b) corresponds to purified MWCNTs and $LaNi_5$-MWCNTs composite sample. Both SEM and TEM pattern of (b) and (d) profile indicates attachment of $LaNi_5$ with pristine MWCNTs.

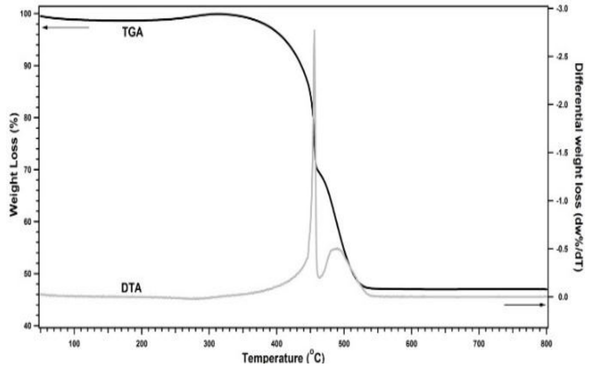

Figure 2. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) profiles of composite sample. Heating ramp used was 10°C/min.

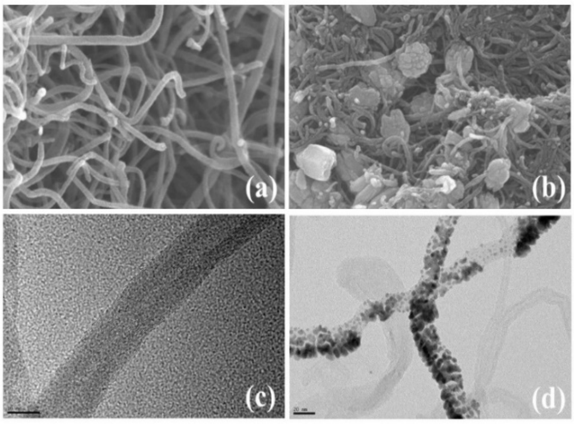

Figure 3. Scanning electron microscope (SEM) and transmission electron microscope (TEM) images of purified MWCNTs (a and c) and $LaNi_5$-MWCNTs composite sample (b and d). The scale bar for Fig. (a), (b), (c), and (d) is 500, 500, 10 and 20 nm respectively.

Fig. 4 (a) pattern shows nitrogen adsorption isotherm of purified and composite samples. According to IUPAC classification, pristine (■) and composite sample isotherm (●) belongs to closed type II isotherm [29]. The rise in adsorption isotherm of pristine and composite sample is assigned to filling of micropores [30]. Plot of $1/[V_A(P_O/P-1)]$ vs P/P_o of pristine MWCNTs (■) and composite (●) samples are presented in Fig. 4 (b). Legality of BET imitation in adjusting the experimental details, exclusively at high pressure is noticeable in Fig. 4 (b). Linear aggression equation presented below are used to measure slope and intercepts plots and also utilized to measure BET SSA.

$$\frac{1}{n[(P_O/P)-1]} = \frac{i}{cn_m} + \frac{c-1}{cn_m}\frac{P}{P_O}$$

BET adsorption isotherm model used for measurement of specific surface area of composite sample was 239 m^2/g. Composite shows less surface area as compared to purified MWCNTs sample (310 m^2/g). The reduction in surface area of composite sample is related to blocking of pores and channels of former during synthesis method [31, 32].

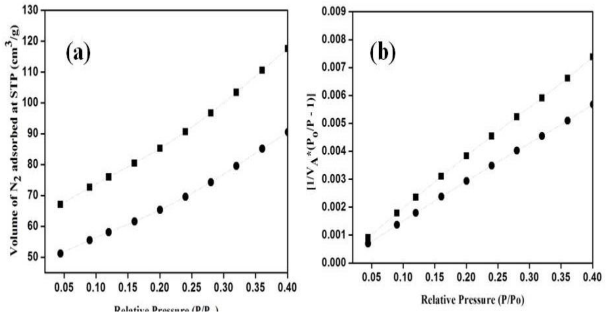

Figure 4. (a)N_2 adsorption isotherm profile of pristine MWCNTs and $LaNi_5$-MWCNTs composite (■and ●). (b) Plot of $1/V_a[(P_o/P-1)]$ vs P/P_o of purified MWCNTs and $LaNi_5$-MWCNTs composite (■ and●) shows linear fit in the relative pressure range of 0-0.4.

Hydrogen uptake of $LaNi_5$, pristine MWCNTs (inset), and $LaNi_5$-MWCNTs composite performed at similar experimental conditions are presented in Fig. 5. Hydrogen uptake of $LaNi_5$, purified MWCNTs, and $LaNi_5$-MWCNTs composite sample was found to be 1.49, 0.07, and 1.53 wt.% performed at room temperature and hydrogen pressure of 4.0 MPa. Hydrogen uptake of all the three materials reached equilibrium within one minute. However, adsorption kinetics is very low for $LaNi_5$ as compared to pristine and composite sample. More than 91% of hydrogen was adsorbed within 20 s of composite sample and less than 10% hydrogen was adsorbed within the same time for $LaNi_5$ performed at similar experimental conditions. Much improved kinetics of composite sample as compared to $LANi_5$ may be due to nanostructured morphology and surface activity imported by high-energy ball milling. Furthermore, enhanced kinetics in composite sample may be due to catalyst effect of MWCNTs also.

High hydrogen uptake and improved kinetics of composite materials as compared to $LaNi_5$ is due to addition of hydrogen uptakes of pristine MWCNTs and $LaNi_5$. Hydrogen adsorption capacity of composite sample is similar to the combination uptake of pristine MWCNTs and $LaNi_5$ sample and no hydrogen spillover effect was observed in our case as reported in literature.

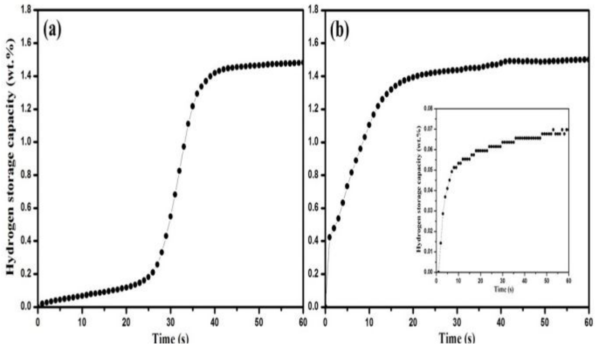

Figure 5. Hydrogen uptake profiles of $LaNi_5$ (a) and $LaNi_5$-MWCNTs composite (b) performed at RT and hydrogen pressure of 4.0 MPa. Inset (b) hydrogen storage capacity of pristine MWCNTs performed under similar experimental conditions.

CONCLUSION

Hydrogen uptake of $LaNi_5$, pristine MWCNTs, and composite samples performed at RT and hydrogen pressure of 4.0 MPa was found to be 1.49, 0.07, and 1.53 wt.%. Furthermore, hydrogen storage capacity was measured using Sievert's volumetric instrument. Spillover effect contribution in total hydrogen uptake of composite sample was found to be negligible. Surface area of purified and composite sample was found to be 310 m^2/g and 239 m^2/g. Enhancement of kinetic effects of nanocomposite sample as compared to pure sample is due to catalytic contribution of MWCNTs.

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REFERENCES

[1] Y. Jun, S. Andrea, W. Christopher, and J. S. Donald, "High capacity hydrogen storage materials: attributes for automotive applications and techniques for materials discovery," Chemical Society Reviews, vol. 39, pp. 656-675, Feb. 2010.

[2] C. Hui-Ming, Y. Quan-Hong, and L. Chang, "Hydrogen storage in carbon nanotubes," Carbon, vol. 39, pp. 1447-1454, Aug. 2001.

[3] Z. Li, "Progress and problems in hydrogen storage methods," Renew Sustainable Energy Review, vol. 9, pp. 395-408, August 2005.

[4] L. M. Reddy and S. Ramaprabhu, "Hydrogen adsorption properties of single-walled carbon nanotube—nanocrystalline platinum composites," International Journal of Hydrogen Energy, vol.33, pp. 1028-1034, Feb. 2008.

[5] S. U. Rather and K. S. Nahm, "Hydrogen uptake of high-energy ball milled nickel-multiwalled carbon nanotube composites," Materials Research Bulletin, vol.49, pp. 525-530, Jan. 2014.

[6] J. L. Mendoza-Cortes, W. A. Goddard, H. Furukawa, and O. M. Yaghi, "A covalent organic framework that exceeds the DOE 2015 volumetric target for H2 uptake at 298 K," Journal of Physical Chemical Letters, vol. 3, pp. 2671-2675, Aug. 2012.

[7] T. Heine, L. Zhechkov, and G. Seifert, "Hydrogen storage by physisorption on nanostructured graphite platelets," Physical Chemistsry Chemical Physics, vol. 6, pp. 980-984, Feb. 2004.

[8] S. Chaudhuri and J. T. Muckerman, "First-principles study of Ti catalyzed hydrogen chemisorption on an Al surface: a critical first step for reversible hydrogen storage in NaAlH4," Journal of Physical Chemistry B, vol.109, pp. 6952-6957, April 2005.

[9] Zuttel, "Materials for hydrogen storage," Materials Today, vol.6, pp. 24-33, Sept. 2003.

[10] M. Rzepka, P. Lamp, and M. A. De la Casa-Lillo, "Physisorption of hydrogen on microporous carbon and carbon nanotubes," Journal of Physical Chemistry B, vol. 102, pp. 10894-10898, Dec. 1998.

[11] O. V. Pupysheva, A. A. Farajian, and B. I. Yakobson, "Fullerene nanocage capacity for hydrogen storage," Nano Letters, vol. 8, pp. 767-774, Mar. 2008.

[12] H. P. Veluswamy, R. Kumar, and P. Linga, "Hydrogen storage in clathrate hydrates: Current state of the art and future directions," Applied Energy, vol. 122, pp. 112-132, June 2014.

[13] S. Bordiga, J. G. Vitillo, G. Ricchiardi, L. Regli, D. Cocina , A. Zecchina et al., "Interaction of hydrogen with MOF-5," Journal of Physical Chemistry B, vol. 109, pp. 18237-18242, Sept. 2005.

[14] L. A. N. Jianhui, C. Dapeng, and W. Wang, "Li-doped and nondoped covalent organic borosilicate framework for hydrogen storage," Journal of Physical Chemistry C, vol. 114, pp. 108-114, Jan. 2010.

[15] H. B. Seyed, T. T. Theodore, and S. Muhammad, "Chemisorption, physisorption and hysteresis during hydrogen storage in carbon nanotubes," International Journal of Hydrogen Energy, vol. 39, pp. 1390-1397, Jan. 2014.

[16] R. Strobel, J. Garche, P. T. Moseley, L. Jorissen, and G. Wolf, "Hydrogen storage by carbon materials," Journal of Power Sources, vol. 159, pp. 781-801, Sept. 2006.

[17] Kaylene, R. Siegmar, H. Michael, and G. Werner, "Carbon nanostructures: an efficient hydrogen storage medium for fuel cells," Fuel Cells Bulletin, vol. 4, pp. 9-12, Nov. 2001.

[18] Liu, Y. Y. Fan, M. Liu, H. T. Cong, H. M. Cheng, and M. S. Dresselhaus, "Hydrogen storage in single-walled carbon nanotubes at room temperature," Science, vol. 286, pp. 1127-1129, Nov. 1999.

[19] F. L. Darkrim, P. Malbrunot, and G. P. Tartaglia, "Review of hydrogen storage by adsorption in carbon nanotubes," International Journal of Hydrogen Energy, vol. 27, pp. 193-202, Feb. 2002.

[20] X. Li, H. Zhu, L. Ci, C. Xu, Z. Mao, B. Wei et al., "Hydrogen uptake by graphitized multi-walled carbon nanotubes under moderate pressure and room temperature," Carbon, vol. 39, pp. 2077-2079, May 2001.

[21] C. Liji, Z. Hongwei, W. Bingqing, X. Cailu, and W. Dehai, "Annealing amorphous carbon nanotubes for their application in hydrogen storage," Applied Surface Science, vol. 205, pp. 39-43, Jan. 2003.

[22] S. Mirershadi, A. Reyhani, S. Z. Mortazavi, B. Safibonab, and M. K. Esfahani, "The effects of bromine treatment on the hydrogen storage properties of multi-walled carbon nanotubes," International Journal of Hydrogen Energy, vol. 36, pp. 15622-15631, Oct. 2011.

[23] M. Shi-chun, T. Hao-lin, Q. Sheng-hao, P. Mu, and Y. Run-zhang, "Hydrogen storage in carbon nanotubes modified by microwave plasma etching and Pd decoration," Carbon, vol. 44, pp. 762-767, April 2006.

[24] R. Zacharia, S. U. Rather, S. W. Hwang, and K. S. Nahm, "Spillover of physisorbed hydrogen from sputter-deposited arrays of platinum nanoparticles to multi-walled carbon nanotubes," Chemical Physics Letters, vol. 434, pp. 286-291, Feb. 2007.

[25] S. U. Rather, R. Zacharia, S. W. Hwang, M. Naik, and K. S. Nahm, "Hydrogen uptake of palladium-embedded MWCNTs produced by impregnation and condensed phase reduction method," Chemical Physics Letters, vol. 441, pp. 261-267, June 2007.

[26] C. Z. Wu, P. Wang, X. Yao, C. Liu, D. M. Chen, G. Q. Lu, H. M. Cheng, "Hydrogen storage properties of MgH2/SWNT composite prepared by ball milling," Journal of Alloys and Compound, vol. 420, pp. 278-282, Aug. 2006.

[27] J. L. Bobet, E. G. Grigorova, M. Khrussanova, M. Khristov, P. Stefanov, P. Peshev, and D. Radev, "Hydrogen sorption properties of graphite-modified magnesium nanocomposites prepared by ball-milling," Journal of Alloys Compounds, vol. 366, pp. 298-302, March 2004.

[28] R. Zacharia, K. Y. Kim, A. K. M F. Kibria, and K. S. Nahm, "Enhancement of hydrogen storage capacity of carbon nanotubes via spill-over from vanadium and palladium nanoparticles," Chemical Physics Letters, vol. 412, pp. 369-375, Sept. 2005.

[29] F. Li, Y. Wang, D. Wang, and F. Wei, "Characterization of single-wall carbon nanotubes by N2 adsorption," Carbon, vol. 42, pp. 2375-2383, July 2004.

[30] M. Eswaranoorthy, R. Sen, and C. N. R. Rao, "A study of micropores in single-walled carbon nanotubes by the adsorption of gases and vapors," Chemical Physics Letters, vol. 304, pp. 207-210, April 1999.

[31] F. Schuth, A. Wingen and J. Sauer, "Oxide loaded ordered mesoporous oxides for catalytic applications," Microporous Mesoporous Materials, vol. 44-45, pp. 465-476, April 2001.

[32] Q. Hu, J. Pang, N. Jiang, J. E. Hampsey, and Y. Lu, "Direct synthesis of palladium-containing mesoporous carbon," Microporous Mesoporous Materials, vol. 81, pp. 149-154, June 2005.

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