

Hydrogen adsorption/desorption on lithium alanat catalyzed by Ni/C for sustainable hydrogen storage

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Abstract

LiAlH₄ alloy has demonstrated the potentially to become one of the hydrogen storages with high storage capacity. In this research, the formation of LiAlH₄ alloys with dope and undope Ni/C catalysts and characterization and testing of hydrogen adsorption/desorption capacities using these alloys have been carried out. The alloy was made by the milling method and the resulting alloy was characterized using XRD analysis. The adsorption capacity test of the alloy was carried out by the gravimetric method at various pressures. The adsorption capacity of the LiAlH₄ alloy by adding additives in the form of Ni/C as much as 5% w/w. It was proven to increase the hydrogen adsorption capacity compared to undoped catalyst with the highest storage capacity at a pressure of 3 bar of 13.06% w/w compared to undoped a catalyst of 9.84% w/w at the same pressure. Meanwhile, the highest hydrogen desorption capacity was 53.56% w/w (dope catalyst) and 41.75% w/w (undope catalyst).

Keywords: Hydrogen Storage, LiAlH₄, Ni/C and Alanate

Article Info

Alloy LiAlH₄ menunjukkan berpotensi untuk menjadi salah satu hydrogen storage dengan kapasitas penyimpanan yang tinggi. Pada penelitian ini, pembentukan alloy LiAlH₄ dengan dan tanpa katalis Ni/C serta karakterisasi dan uji kapasitas adsorpsi/desorpsi hydrogen dengan menggunakan alloy tersebut telah dilakukan. Pembuatan alloy dilakukan dengan metode milling dan alloy yang dihasilkan dikarakterisasi menggunakan analisis XRD. Uji Kapasitas adsorpsi dari alloy dilakukan dengan metode gravimetri pada tekanan bervariasi. Kapasitas adsorpsi dari alloy LiAlH₄ dengan menambahkan zat aditif berupa Ni/C-sebanyak 5 % b/b terbukti meningkatkan kapasitas adsorpsi hydrogen dibandingkan tanpa katalis dengan kapasitas penyimpanan tertinggi pada tekanan 3 bar sebesar 13,06 % b/b dibanding tanpa katalis sebesar 9,84% b/b/ pada tekanan yang sama.. Sementara itu kapasitas desorpsi hydrogen tertinggi sebesar 53,56% b/b (dengan katalis) dan 41,75% b/b (tanpa katalis).

Keywords: Hydrogen Storage; LiAlH₄; Ni/C and Alanat

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INTRODUCTION

Renewable energy is becoming an attractive trend to replace fossil fuels, whose availability is decreasing over time. Fuel cells are classified as environmentally friendly energy-producing devices, which are predicted to become one of the future energy sources that have high efficiency with very low levels of

pollution. If the fuel used is hydrogen, the fuel cell is a device that produces energy without emissions [1]. As an energy source, hydrogen has several advantages, which make it an ideal candidate for meeting future energy needs. Hydrogen is the lightest element, the most abundant, does not pollute with the by-products of combustion of water, and can be produced from

various sources [2][3][4]. Besides, hydrogen has a very high heating value with LHV 120 MJ/kg. For comparison, gasoline has a heating value of 43 MJ/kg. Hydrogen is the lightest molecule of all molecules (molecular weight = 2.016), consequently, it has a density of 0.0899 kg/m³ which is 7% of the density of air [2].

Hydrogen storage has become an important issue and a major challenge in the use of hydrogen as a fuel [5]. Alanate is considered capable of meeting the targets set by the DOE (Department of Energy) of the United States as a hydrogen storage material due to its high gravimetric and volumetric storage capacity, and relatively safer operating conditions [6]. Alanate as a good hydrogen storage material for example is LiAlH₄ [7] [8]. LiAlH₄ (Lithium alanate) is seen as a potential hydrogen storage material because of the theoretically large storage capacity of hydrogen in the solid-state. To increase the adsorption capacity of the LiAl alloy, additives were added as reported by Sazelee and Ismail [9].

In this study, a hydrogen adsorption capacity test was carried out using a LiAl alloy with the addition of an additive, namely Ni/C catalyst in order to see its effect on the adsorption of hydrogen gas.

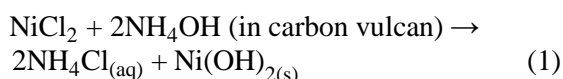
MATERIALS AND METHODS

Materials

The materials used include hydrogen and nitrogen gas 99.9% UHP from Samator, 99% granular Lithium powder trace metal basis from Aldrich, 99.99% aluminum powder with a size of 10-40 mesh, from Aldrich, Carbon Vulcan XC-72R (Fuel Cell Store), and Nickel from Aldrich.

Methods

The catalyst fabrication is carried out by reducing the NiCl₂·6H₂O compound which has been mixed with Carbon Vulcan. The first step is to mix and dissolve the NiCl₂·6H₂O and carbon Vulcan in the water and stirring for 24 hours while dropping NH₄OH for 4 hours to bind Cl to the solution, thus forming reaction 1.



The reaction product filtered and washed with distilled water to remove NH₄Cl then heated in the oven to evaporate the distilled water and the sintered for 4 hours at a temperature of 400°C to form a reaction 2. Ni(OH)₂/C → NiO/C + H₂O (2)

Finally, it was heated while flowing hydrogen gas for 2 hours at a temperature of 450°C using a horizontal

furnace OTF-1200X from MTI KJ group, to reduce the NiO show in reaction 3.



After obtaining the Ni/C catalyst, the LiAl alloy has formed by mixing Lithium granular powder and Aluminum powder with a size of 10-40 mesh using the ball milling method with the HEM-E3D tool for 3 hours. All operations on the sample were carried out under a dry nitrogen atmosphere in a glove box to prevent reaction with moisture and oxygen in the air. The alloy is inserted into the reactor then hydrogen gas is flown at pressure variations while measuring the reactor temperature using a temperature detector.

Data Analysis

The measurement results are carried out by calculating the capacity using equation 4:

$$\text{Adsorption capacity of H}_2 = \frac{w_3 - w_2}{w_2 - w_1} \times 100\% \quad (4)$$

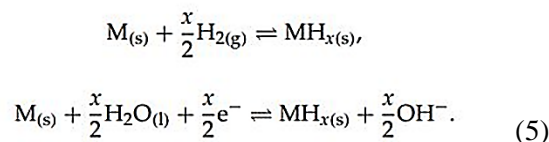
i.e :

W₁ = blank reactor weight

W₂ = the weight of reactor + alloy

W₃ = the weight of reactor + alloy + hydrogen gas

The reaction of metal hydrides formation can be seen in reaction 5.



RESULTS AND DISCUSSION

Characterization of Alloy LiAl-Ni/C

The experimental data was supported by XRD characterization of the fabricated alloy of LiAl-Ni/C to identification the diffraction peaks in the compound from X-Ray diffraction. Diffractogram of LiAl-Ni/C is presented in Figure 1.

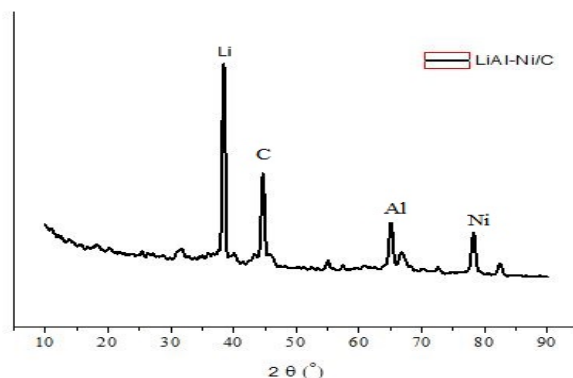


Figure 1. Diffractogram of LiAl-Ni/C alloy

Figure 1 indicated the diffractogram of LiAl alloy doped with Ni/C. The diffraction peaks at $2\theta = 44-45^\circ$ is determined as Carbon, as refers to JCPDS no. 74-2232 [15]. Furthermore, the solely metal was indicated at $2\theta = 35^\circ$ and 38° as lithium metal, $2\theta = 78^\circ$ regarded as Nickel-metal based on JCPDS number 03-065-2865 [16]. Those respected diffractogram peak showed that alloy with Ni/C catalyst has been successfully doped in to LiAl alloys.

Hydrogen Gas Adsorption-Desorption Capacity

The interaction of hydrogen molecules or their adsorption in materials can be categorized into three processes: a) physisorption, in which hydrogen does not dissociate, but there are van der Waals interactions to form weak bonds with the surface of the material. b) chemisorption, in which hydrogen molecules first dissociate into individual atoms which migrate to the material and then form chemical bonds with the material. The hydride bonds are quite strong with an enthalpy of formation (ΔH_f) of $100-200 \text{ kJmol}^{-1} \text{ H}_2$ and binding energies in the range 2-4 eV [10].

Testing the storage capacity of hydrogen gas to see the effect of adding a Ni/C catalyst on pressure variations obtained data as in Figure 2.

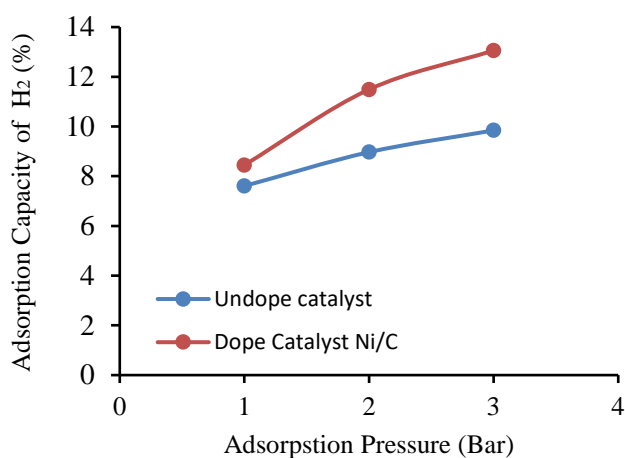


Figure 2. Hydrogen gas adsorption capacity curves on alloys with dope and undope catalyst and at variations in pressure

Figure 2 shows a difference in the adsorption capacity of LiAl alloys with dope and undoped catalysts and the effect of pressure. It appears that nickel with carbon matrix (Ni/C) has significantly increase hydrogen adsorption capacity until 13.057w/w% at 3 Bar. Meanwhile, the desorption capacity has also increased compared to alloys that are not doped with a catalyst, which is shown in Figure 3.

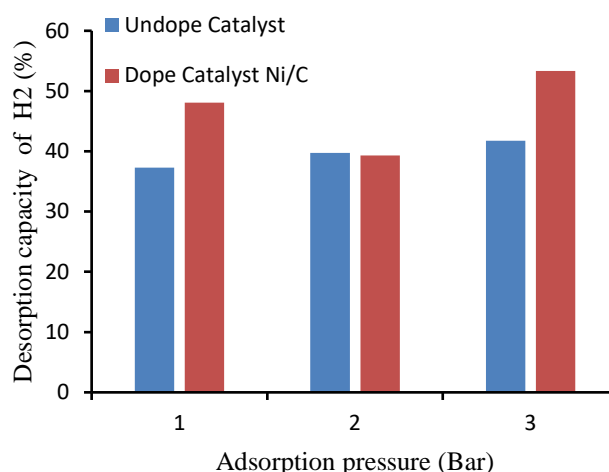


Figure 3. Curves of H_2 gas desorption capacity on alloys with dope and undope a catalyst at the various of adsorption pressure conditions.

The desorption capacity of the alloys doped with Ni catalysts has a higher capacity. This is because Ni/C catalysts have high stability in the adsorption/desorption of hydrogen [11] and able to achieves the equilibrium that might overcome the resistance of dissociation and diffusion of hydrogen molecules. This phenomenon would decrease the activation energy [12], [13]. The addition of a carbon matrix was also an advantage in inhibiting catalyst aggregation and thus improve the performance of the catalyst [14].

In addition to the adsorption doped and undoped catalyst, adsorption was also carried out at various pressures, namely 1, 2, and 3 Bar. The experimental results have shown the adsorption capacity increasing with increasing the pressure. This is in accordance with the ideal gas equation ($PV = nRT$) [9]. Experimental data of the adsorption capacity of hydrogen on pressure variations are attached in Table 1.

Table 1. The Adsorption Capacity of Hydrogen at the Various of Pressure

Pressure (bar)	Adsorption Capacity of Hydrogen (w/w%)	
	Undoped Catalyst	Doped Catalyst Ni/C
1	7.61	8.45
2	8.97	11.49
3	9.84	13.06

CONCLUSION

The doped Ni/C catalyst onto LiAl alloy has significantly increased the adsorption capacity of hydrogen gas. Furthermore, highest adsorption pressure exerted would also increase the hydrogen gas adsorbed. LiAl alloys doped with Ni/C alloy has supported by X-ray diffractogram characterization at respected peaks mentioned by JCPDS database.

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