Int. J. Electrochem. Sci., 8 **(2013)** 9764 - 9772

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Hydrogen Generation from the Reaction of Al-7.5 wt%Li-25 wt% Co/$NaBH_4$ Powder and Pure Water

Yu Wang, Ling Tong Zhou, Hui Yuan, Wei Hua Shen, Rui Tang, Mei Qiang Fan, Kang Ying Shu**

Department of Materials Science and Engineering, China Jiliang University, Hangzhou 310018, P R China
*E-mail: fanmeiqiang@126.com, shukangying@163.com

Received: 19 April 2013 / *Accepted:* 31 May 2013 / *Published:* 1 July 2013

Hydrogen generation from the hydrolysis of Al-7.5 wt% Li-25 wt% Co composite was evaluated in this paper. The composite had 100% hydrogen yield and good hydrogen generation performance at 323 K, including different Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ weight ratios and consecutive additions of $NaBH_4$. The combined effect of Li and Co on Al/$NaBH_4$ hydrolysis was attributed to the formation of alkaline solution and stable Co/$LiAl_2(OH)_7$ catalyst, which's catalytic activity was further increased by hydrolysis byproducts $Al(OH)_3$/$NaBO_2$. The optimized composite could be potentially applied as hydrogen sources for portable fuel cell.

Keywords: hydrogen generation; hydrolysis; Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite

1. INTRODUCTION

Sodium borohydride ($NaBH_4$) has been applied as hydrogen source for proton exchange membrane fuel due to its numerous advantages, such as high theoretic hydrogen density (10.8 wt%), good storability, and reaction controllability, etc [1,2]. $NaBH_4$ has bad hydrogen generation performance in alkaline solution, but it can be improved via adding some catalysts such as Pt-, Rh-, Co- and Ni-based catalysts [3].

However, there exists a problem between $NaBH_4$ concentration and catalyst stability in practical use because hydrolysis byproduct $NaBO_2$ has low solubility, deposits on catalyst surface and deteriorates catalyst activity when the concentration of $NaBH_4$ solution exceeds 20 wt% [4]. Recently, hydrolysis of solid-state $NaBH_4$/catalyst composites in limited water amount indicated high gravimetric hydrogen storage capacity. Ferreira [5] used Ni-Ru based catalyst/$NaBH_4$ powder (Ni-Ru:$NaBH_4$: 0.2 and 0.4 g/g) to obtain a viable gravimetric hydrogen generation of 6.3 wt% for portable application. However, the materials used for this method, including $NaBH_4$ and catalyst, are expensive.

Aluminum or aluminum alloy is another potential candidate for hydrogen generation as it has low cost, mild reaction conditions, et al [6, 7]. Combined hydrogen generation from Al/$NaBH_4$ composite might present higher hydrogen generation density and lower cost compared with hydrogen generation from Al hydrolysis and $NaBH_4$ hydrolysis separately. Dai [8] found that Al/$NaBH_4$/ NaOH/$CoCl_2$/H_2O composite could be readily controlled in hydrogen storage density, fuel conversion, and hydrogen generation rate. Soler [9] found that interaction from hydrolysis byproduct $Al(OH)_3$/$NaBO_2$ could be increased in hydrogen generation rates and yields by combining AlCo alloy with $NaBH_4$ in NaOH solution. However, strong alkaline must be used for sustainable hydrogen generation in the above method and strong alkaline solution is not easily handled.

In the present study, hydrogen generation from Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite in pure water is proposed for portable fuel cell. The Al/$NaBH_4$ weight ratios, microstructure and catalytic reactivity evolution of the hydrolysis byproduct were considered. This study aims to optimize Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite to obtain efficient hydrogen generation performance and fuel conversion.

2. EXPERIMENT SECTION

2.1. Preparation of Al-7.5 wt%Li-25 wt%Co alloy

Aluminum powder (99.9% purity and particle size of approximately 10 μm; Angang Group Aluminum Powder Co., Ltd., China), lithium sheet (99.9% purity; China Energy Lithium Co., Ltd.), micro Co powder (99.0% purity and particle size of approximately 70 μm; China Chemical Company, Ltd.) and $NaBH_4$ (98% purity; China Chemical Company, Ltd.) were used as starting materials. The designed Al-7.5 wt% Li-25 wt% micro Co were weighed and mixed in an argon-filled glove box. The total weight of the mixture was 3 g, and the ball milling was conducted using a QM−ISP3 planetary ball miller under 0.2 MPa to 0.3 MPa argon atmosphere. Ball-to-powder weight ratio corresponded to 20:1 at a milling time of 15 h and a rotation speed of 450 r/min.

2.2. Hydrogen generation

Hydrogen generation measurements were performed in a sealed 200 mL hydrogen reactor placed in a thermostatic bath at 323 K and attached to a condenser and a hydrogen generation collector. Generated hydrogen was collected in the cylinder at 298 K and 1 atm and measured from water level change. Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite including 0.3 g Al-7.5 wt%Li-25 wt%Co and 0.3 g $NaBH_4$, were pressed into a tablet before hydrolysis. The Al/$NaBH_4$ weight ratios were set as 1:1, 1:3 and 1:5. Pure water volume was 4 mL. In the consecutive experiments, successive addition of 0.4 g $NaBH_4$ and 2 ml H_2O $NaBH_4$ was added in the hydrolysis byproduct. Hydrogen generation yield was defined as the ratio of experimental hydrogen generation volume to the theoretical one. Hydrogen generation rate was calculated from the first bubble that evolved from the start of the test.

2.3 Microstructure analysis

Powder X-ray diffraction (XRD) patterns of the as-prepared samples were characterized using an X-ray diffractometer (Thermo ARL, Switzerland, model ARL X'TRA) over a range of diffraction angles (θ) from 2θ = 10° to 2θ = 80°, with Cu Kα radiation filtered by a monochromator. Scanning electron microscopy (SEM) observations were conducted using JSM-5610LV model (JEOL Company) equipped with INCA energy dispersive X-ray spectroscopy (EDS) measurements. The solid hydrolysis byproduct in the reactor was filtered using a vacuum pump, and then dried in an oven at 313 K.

3. RESULTS AND DISCUSSION

3.1 Hydrogen generation performance

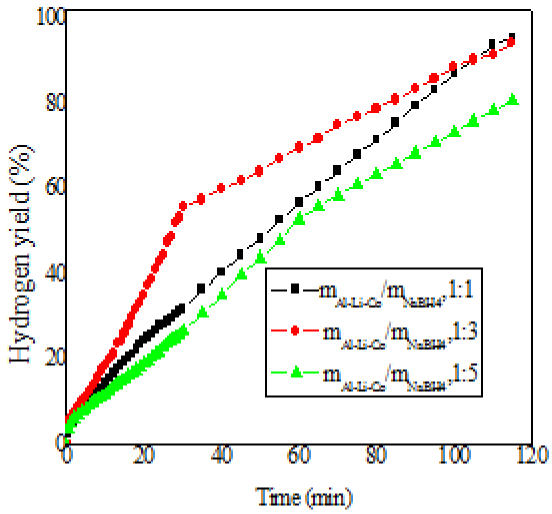


Figure 1. Effect of Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ weight ratios on hydrogen generation curves of Al-7.5 wt% Li-25 wt% Co/$NaBH_4$ composite.

Fig. 1 shows hydrogen generation performance of Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite improves with weight ratios increasing from 1:1 to 1:3, and decreases from 1:3 to 1:5. Results show that interaction of Al/$NaBH_4$.hydrolysis was determined.. $Al(OH)_3$ or hydrated lithium aluminum hydroxide ($LiAl_2(OH)_7.2H_2O$) is a promoter for $NaBH_4$ hydrolysis; Demirci[10] confirmed that $Al(OH)_3$ powder could improve the hydrolysis kinetic of $NaBH_4$. On the contrary, $NaBO_2$ presents alkaline which was a good catalyst for Al hydrolysis. An electrochemical corrosion of Al was found in the hydrolysis process as Al alloys had high negative potential and micro galvanic cell might be formed [11]. Thus, the increased ion amount from $NaBH_4$ hydrolysis may stimulate the efficiency of micro galvanic cell of Al (or Li) and Co. The composites with weight ratios of 1:1 and 1:3 had approximate 95% efficiency. Their hydrogen generation value was up to 6.5wt% and 8.4 wt% if residual water was not considered. Compared to traditional hydrogen generation from Al hydrolysis and $NaBH_4$ alkaline solution with below 4 wt% hydrogen generation value [12-14], the Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite had better hydrogen generation performance, which can be further improved when the optimized Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite weight ratios was pursued.

Fig. 2 shows hydrogen generation curves of Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite ($m_{Al\text{-}7.5\ wt\%Li\text{-}25\ wt\%Co}/m_{NaBH4}$, 1:1) at different temperatures. Hydrogen generation performance of the composite improves as temperature increases. As illustrated in our previous work [15], several processes were found in hydrolysis. Hydrogen yield reaches 100% at temperature higher than 323 K and hydrogen generation rate soars quickly with temperature increasing Hydrolysis of AlLi including chemical reaction as well as electrochemical corrosion and self-hydrolysis of $NaBH_4$, occurs when Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite contacts with water, accompanied with $NaBH_4$ dissolution into water.. Then, Al hydrolysis was sustainably conducted and Co-based catalyst begins to stimulate $NaBH_4$ hydrolysis. Mass transfer, including the transfer of OH^-, H^+, BH_4^-, and BO_2^-, exists. The hydrolysis kinetic of Al, Li, and $NaBH_4$ as well as the transfer rate of OH^-, H^+, BH_4^-, and BO_2^- are proportional to temperature. Therefore, the hydrogen generation rate can be significantly accelerated with increased hydrolysis temperature in Fig. 2, and the hydrolysis reaction of the composite can be ended within 15 min at 343 K. Using the maximum hydrogen generation rate at different hydrolysis temperature, the activation energy of Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite ($m_{Al\text{-}7.5\ wt\%Li\text{-}25\ wt\%Co}/m_{NaBH4}$, 1:1) can be calculated (Fig. 3) 68.4 kJ/mol. Results show that the total hydrolysis process was controlled by chemical reaction and not by mass transfer.

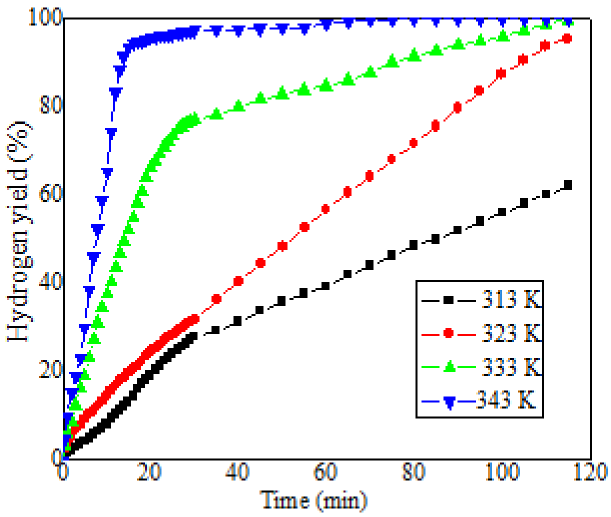


Figure 2. Effect of hydrolysis temperature on hydrogen generation curves of Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite at different temperature.

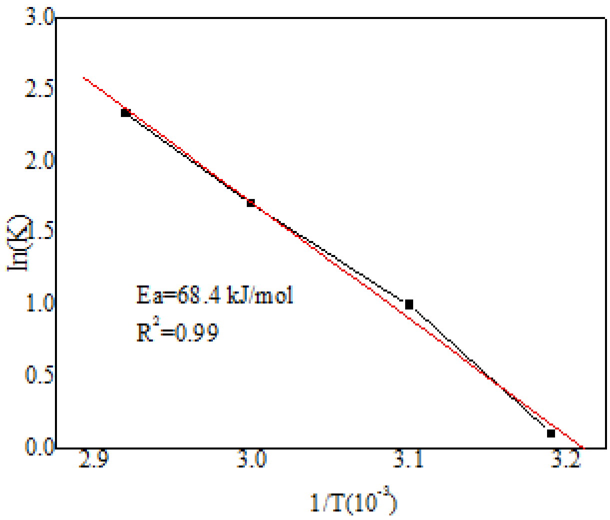


Figure 3. Arrhenius plots of the rate constants using the results in Figure 2.

Fig. 4 shows the hydrogen generation performance of the Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite with successive addition of 0.4 g $NaBH_4$ and 2 ml H_2O within 1h. Results indicate that hydrolysis byproducts of the Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite have high efficient catalytic reactivity on $NaBH_4$ hydrolysis. The hydrogen yield increases from 57% to 100 within 1 h and preserve 100% in the followed eight consecutive runs. The maximum hydrogen generation rate of the $NaBH_4$ hydrolysis increases with successive addition of $NaBH_4$. Its largest value arrived at fifth times and then its value decreased slowly. The results show that hydrolysis byproducts from Al-7.5 wt% Li-25 wt% micro Co have stable and high catalytic reactivity. The microstructure of hydrolysis byproducts will be elaborated in the followed section.

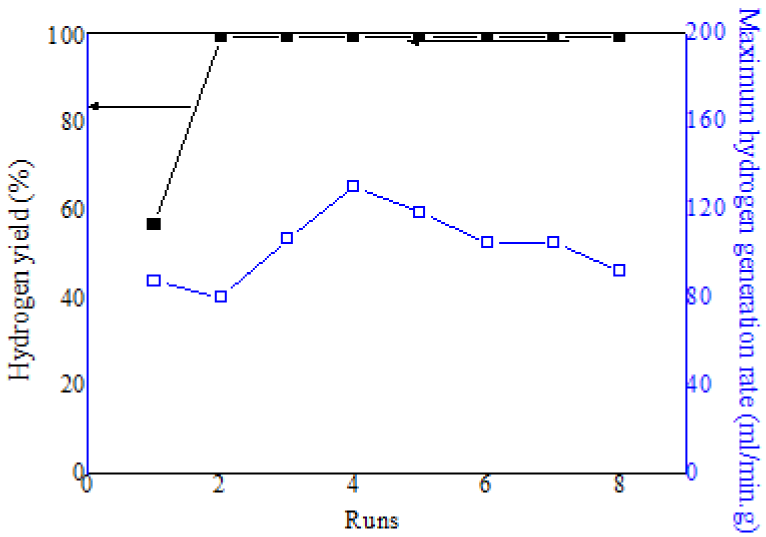


Figure 4. Hydrogen generation curves of Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ composite with successive addition of 0.4 g $NaBH_4$ and 2 ml H_2O.

3.2 Microstructure evolution before and after hydrolysis

Fig. 5 shows X-ray patterns of Al-7.5 wt%Li-25 wt%Co before and after hydrolysis. Peaks of AlLi and $Al_{0.94}Co_{1.06}$ phase were identified except Al and Co phase. After hydrolysis, peaks of $LiAl_2(OH)_7.2H_2O$, $Al(OH)_3$ (bayerite), and Co (Cubic phase (FCC)) were found. After eight consecutive runs of $NaBH_4$ hydrolysis, strong peaks of $NaBO_2$ were found except $LiAl_2(OH)_7.2H_2O$ and Co. But peaks of $Al(OH)_3$ had obviously weakened because of the hydrolysis byproduct of $NaBO_2$, which presents alkaline and dissolute $Al(OH)_3$. Combined with SEM results, the particle size of Al-7.5 wt%Li-25 wt%Co before hydrolysis ranged in several micrometers to tens of micrometers and numerous defects and small particles were accumulated together. It can be imaged that alloying leads to low particle size.

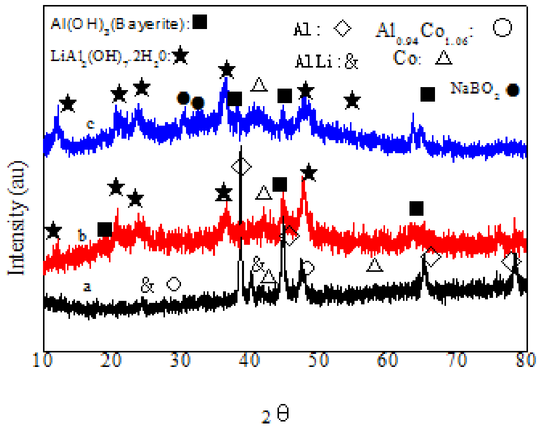


Figure 5. X-ray patterns of Al-7.5 wt% Li-25 wt% Co before (a) and after first (b) and eighth(c) runs.

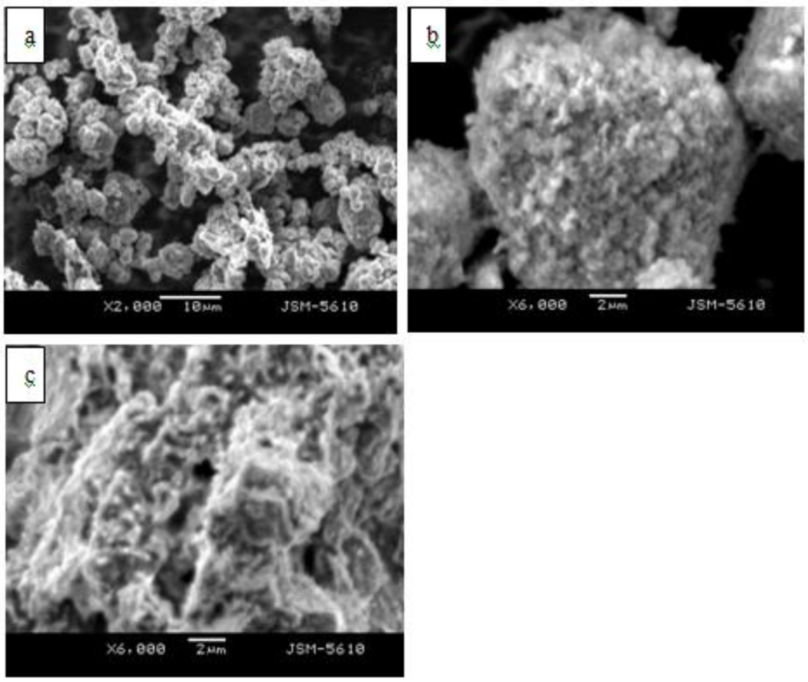
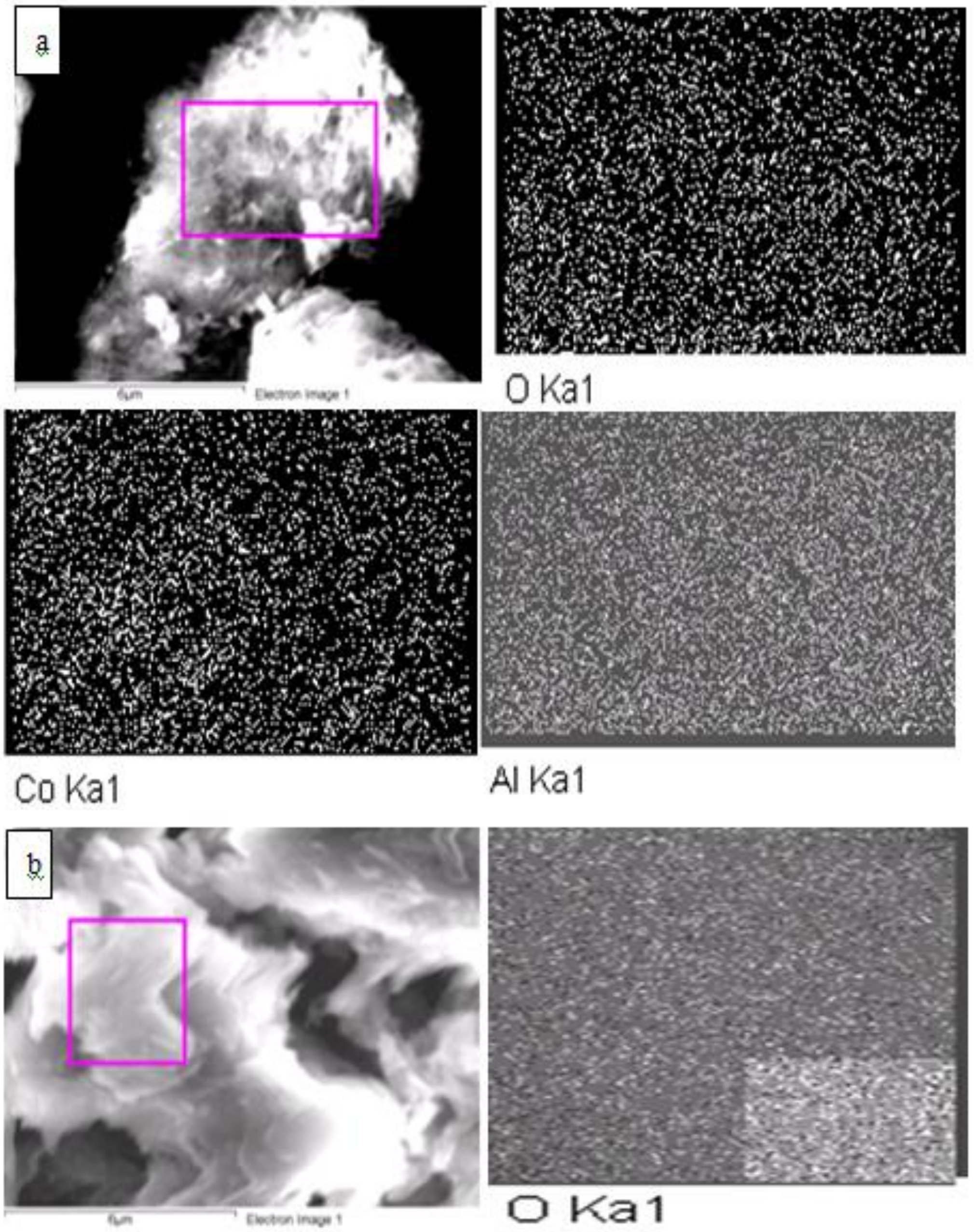


Figure 6. SEM of Al-7.5 wt% Li-25 wt% Co before (a) and after first (b) and eighth(c) runs.

After hydrolysis, several small flats and loose solids irregularly accumulated together and formed rough particles. Combined with XRD results, the flat was identified as $LiAl_2(OH)_7.2H_2O$; loose solids were identified as $Al(OH)_3$. After eight consecutive runs of $NaBH_4$ hydrolysis, the particle size became larger and flats became clear. Hollows in the particle also became large due to the dissolution of $Al(OH)_3$. It can be imaged that hydrolysis byproducts $Al(OH)_3$ or hydrated lithium aluminum hydroxide ($LiAl_2(OH)_7.2H_2O$) covers on Co surface and form Co/$Al(OH)_3$ catalyst, which improved the hydrolysis of $NaBH_4$ and resulted in more $NaBO_2$ generated. $NaBO_2$ reacted with $Al(OH)_3$ correspondingly. However, $LiAl_2(OH)_7.2H_2O$ has efficient stability in alkaline solution. The existence of $LiAl_2(OH)_7.2H_2O$ carriers guarantees high and stable catalytic reactivity of hydrolysis byproducts from Al-7.5wt%Li- 25 wt% Co in the solution.



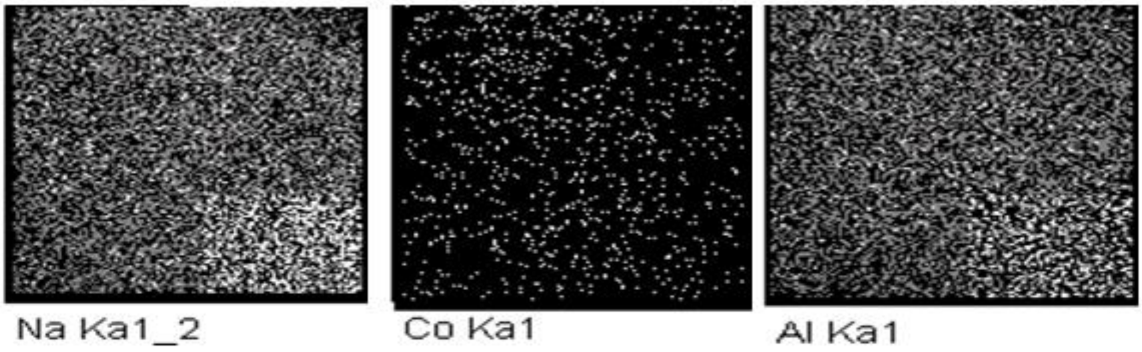


Figure 7. EDS of Al-7.5 wt% Li-25 wt% Co after first (a) and eighth (b) runs.

In addition, $NaBO_2$ deposition on catalyst surface affects the catalytic reactivity of the hydrolysis byproducts. Fig. 7 shows the EDS mapping of Al-7.5wt%Li- 25 wt% Co/$NaBH_4$ composite after hydrolysis. Intensive distribution of Co into EDS mapping of Al, O, and Co was obtained in the hydrolysis byproduct of Al-7.5wt%Li- 25 wt% Co /$NaBH_4$ composite, which indicates the catalyst Co distributed into carriers $LiAl_2(OH)_7.2H_2O$ and $Al(OH)_3$. Co powder was distributed in $LiAl_2(OH)_7.2H_2O$ or $Al(OH)_3$ and formed highly active catalyst. But EDS mapping of Co became sparse and Na occurs in the hydrolysis byproducts of Al-7.5wt%Li- 25 wt% Co/$NaBH_4$ composite in eight consecutive runs of $NaBH_4$ hydrolysis. This condition indicates that some insoluble $NaBO_2$ covers and accumulates on the surface of catalyst. Further compared with element percentages in Tables 1 and 2, the concentration of Al and Co decreased; concentration of O and Na increased. Results show that the presence of $NaBO_2$ is critical in decreasing catalytic reactivity of the catalyst.

Table 1. Element percentages of the hydrolysis byproducts of Al-7.5 wt% Li-25 wt% Co/$NaBH_4$ mixture ($m_{Al\text{-}7.5\ wt\%Li\text{-}25\ wt\%\ Co}$ /m_{NaBH4} 1:1).

Element	Weight (%)	Atomic (%)
O K	37.75	58.36
Al K	31.19	28.60
Co K	31.06	13.04
Total	100.00	

Table 2. Element percentages of the hydrolysis byproducts of Al-7.5 wt% Li-25 wt% Co /$NaBH_4$ mixture ($m_{Al\text{-}7.5\ wt\%Li\text{-}25\ wt\%\ Co}$ /m_{NaBH4} 1:1) after eighth addition of 0.4 g $NaBH_4$ and 2 ml H_2O.

Element	Weight (%)	Atomic (%)
O K	68.44	77.20
Na K	20.04	15.74
Al K	9.76	6.53
Co K	1.76	0.54
Total	100.00	

Therefore, the improved hydrogen generation performance of Al-7.5wt%Li- 25 wt% Co/$NaBH_4$ composite can be elaborated in the following. The formation of AlLi and $Al_{0.94}Co_{1.06}$ alloy leads to uniform distribution of Co into Al matrix and produce Al-Li and Al-Co active center. When Al-7.5wt%Li- 25 wt% Co contacts with water, the active center reacted with water and generated Co/$LiAl_2(OH)_7.2H_2O$ or Co/ $Al(OH)_3$. $LiAl_2(OH)_7.2H_2O$ and $Al(OH)_3$ are good catalyst carriers and promoters for $NaBH_4$ hydrolysis. As $Al(OH)_3$ can dissolve in alkaline solution, the loss of catalyst carrier decreases catalyst activity in some degrees.

4. CONCLUSIONS

Hydrogen generation from the hydrolysis of Al-7.5 wt% Li-25 wt% Co/$NaBH_4$ composites in water was investigated. The composite had 100% hydrogen yield and good hydrogen generation performance at 323 K, including different Al-7.5 wt%Li-25 wt%Co/$NaBH_4$ weight ratios and consecutive additions of $NaBH_4$. The combined effect of Li and Co on Al/$NaBH_4$ hydrolysis was attributed to the formation of alkaline solution and stable Co/$LiAl_2(OH)_7$ catalyst, which's catalytic activity was further increased by hydrolysis byproducts $Al(OH)_3$/$NaBO_2$. Compared to traditional hydrogen generation from Al or $NaBH_4$ alkaline solution, Al-7.5 wt% Li-25 wt% Co/$NaBH_4$ composites have high hydrogen generation value and it can be potentially applied as hydrogen sources for portable fuel cell.

ACKNOWLEDGMENT
This work was financially supported by the National Science Foundation of China (Project Nos. 21003112, 11175169).

References

1. E.Y.Marrero-Alfonso, J.R.Gray, T.A. Davis, M.A. Matthews. , *Int. J. Hydrogen Energy*, 32(2007) 4723.
2. U.B. Demirci, O. Akdim, P. Miele. , *Int. J. Hydrogen Energy*, 34 (2009) 2638.
3. B. H. Liu, Z.P. Li. *J. Power sources*, 187(2009) 527.
4. J. H. Kim, K. T. Kim, Y. M. Kang, H.S. Kim, M. S. Song, Y. J. Lee. *Int J Hydrogen Energy*, 29(2004) 263.
5. M.J.F Ferreira, L. Gale, V.R. Fernandes. *Int J Hydrogen Energy*, 35(2010) 9869.
6. Y. D. Zhen, Y.F. Liu, T.Yoshihisa, K. Yutaka. *J. Am. Ceram. Soc.* , 88 (2005) 2975.
7. M.Q. Fan, L.X Sun, F. Xu. *Energy Fuel*, 23(2009) 4562.
8. H.B. Dai, G. L. Ma, X.D Kang., P. Wang. *Catalysis Today*, 170(2011) 50.
9. L. Soler, J. Macanas, M. Munoz. *Int. J. Hydrogen Energy*, 32(2009) 4702.
10. U.B. Demirci, A.P. Miele. *J Power Sources* 192 (2009) 310.
11. M.Q. Fan, S. Liu, W. Q. Sun. *J New Materials for Electrochemical System*, 14(2011) 259.
12. Z.Y. Deng, Y.B. Tang, L.L. Zhu. Int J Hydrogen Energy, 35(2010) 9561.
13. E.D.Wang, P.F Shi, C.Y Du. J Power Sources, 181(2008) 144.
14. K. Yoshisugu, S. Kenichirou, F. Kazuhiro. *J Power Sources*, 125(2004)22.
15. M.Q. Fan, L.X. Sun, F. Xu. *Int. J. Hydrogen energy*, 37(2012) 4571.