

Short communication

# Hydrogen generation from lithium borohydride solution over nano-sized platinum dispersed on LiCoO<sub>2</sub>

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## Abstract

A stoichiometric amount of hydrogen was generated by catalytic hydrolysis reaction of lithium borohydride solution over nano-sized platinum dispersed on LiCoO<sub>2</sub> (Pt-LiCoO<sub>2</sub>). The catalyst was characterized by X-ray diffraction (XRD), high-resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS). Analysis showed that the particles size of platinum was about 2 nm and they are dispersed on LiCoO<sub>2</sub>. The H<sub>2</sub> generation rate was expressed by the zero order rate equation and increased with an increase of the catalyst content. Compared with a mixture of Pt and LiCoO<sub>2</sub>, catalytic properties of Pt-LiCoO<sub>2</sub> was superior. The reason proposed for the higher catalytic activity of Pt-LiCoO<sub>2</sub> was the small platinum particle size.

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## 1. Introduction

A polymer electrolyte fuel cell (PEFC, PEM fuel cell) is the prime power source for FCV. One of the most widely envisioned sources of fuel for FCV is H<sub>2</sub>. Therefore, it is necessary to have a storage tank of H<sub>2</sub> to start the system on demand.

Hydrogen (H<sub>2</sub>) can be stored in tanks as compressed or liquefied H<sub>2</sub> or by adsorption on carbon materials [1–6]. It can also be stored in hydrogen storage alloys (hydrogen absorbing alloys) or as a chemical hydride, such as NaBH<sub>4</sub> [7–9], LiBH<sub>4</sub> [10–14] or NaAlH<sub>4</sub> [15], as well as in an organic hydride, such as methylcyclohexane or decalin [16]. Among these methods, attention has recently been given to the hydrolysis of chemical hydrides consisting of protide H<sup>-</sup> because of the large gravimetric and volumetric H<sub>2</sub> densities [7–12,14]. Chemical hydrides yield H<sub>2</sub> by the reaction with water at room temperature [7–12,14]. LiBH<sub>4</sub> has the highest gravimetric H<sub>2</sub> density of 37 wt.%, and therefore the lowest

weight requirement for the target duty [10–14]. However, the hydrolysis reaction of LiBH<sub>4</sub> is slow at ambient temperature [11–14]. In a previous paper, high H<sub>2</sub> pressure accelerated the hydrolysis reaction of LiBH<sub>4</sub>. The H<sub>2</sub> yield was only 50%, but still not sufficient [14]. In this paper, 100% of the stoichiometric amount of H<sub>2</sub> was generated when LiBH<sub>4</sub> solutions are hydrolyzed over catalytic nano-sized platinum dispersed on LiCoO<sub>2</sub>.

## 2. Experimental

### 2.1. Materials

Lithium borohydride (LiBH<sub>4</sub>, Wako Pure Chemical Industries, Ltd., Molecular weight: 21.78, density: 0.666 g cm<sup>-3</sup>) was used for the reaction with water. LiBH<sub>4</sub> is a white crystalline powder. The melting point is 541 K [17] and the rapid evolution of H<sub>2</sub> occurs at 653 K [17]. In a previous paper, we found that the H<sub>2</sub> generation by hydrolysis reaction of NaBH<sub>4</sub> was accelerated by applying metal-metal oxide catalysts such as Pt-TiO<sub>2</sub> and Pt-LiCoO<sub>2</sub> [8]. In this experiment, Pt-LiCoO<sub>2</sub>

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was selected because it is on the excellent catalyst for releasing  $H_2$  from the  $NaBH_4$  solution. Pt-LiCoO<sub>2</sub> was synthesized using a conventional impregnation method as described in the previous paper [8]. Dinitrodiammine platinum (II) nitric acid solution [ $Pt(NO_2)_2(NH_3)_2$ , 33 ml, Pt content of  $50\text{ g l}^{-1}$ , Tanaka Kikinzoku Kogyo K.K., Japan] and lithium cobaltate powder (LiCoO<sub>2</sub>, Nippon Chemical Industrial, product name Cellseed 5, average particle size:  $5.9\ \mu\text{m}$ ) were mixed. The mixture was held at 523 K for 5 h. The dried powder was calcined for 2 h in air at 723 K, thereby coating Pt on the metal oxide. Thus, a catalyst, in which Pt was coated on LiCoO<sub>2</sub>, having Pt content of 1.5 wt.% (Pt-LiCoO<sub>2</sub>), was obtained. The mixture of Pt particles (Tanaka Kikinzoku Kogyo K.K. Japan, AY-1010, averaged diameter: 1–10  $\mu\text{m}$ ) and LiCoO<sub>2</sub> contained 1.5 wt.% of Pt was used as a reference specimen.

## 2.2. Characterization

The amount of  $H_2$  generated was determined as follows. Each amount of catalysts (3.8–76 mg) and 25 mg of  $LiBH_4$  were packed into an Erlenmeyer flask having a volume of 100 ml, and subsequently 5 g of water was added at room temperature (296 K) by use of a syringe. Then,  $H_2$  generation amounts were determined from the change in level of the volumetric burette in a gas analyzer made by Sibata Scientific Technology, Ltd., Japan. The gas generated was identified as  $H_2$  by a gas chromatograph. Crystalline structure of the catalyst was investigated by a wide angle X-ray diffraction (XRD). The X-ray diffraction pattern was recorded with  $Cu\ K\alpha$  radiation ( $\lambda = 0.154\text{ nm}$ ) at 50 kV and 300 mA filtered by a monochromator using a Rigaku Denki Rint-TTR over a range of diffraction angle ( $2\theta$ ) from  $30^\circ$  to  $55^\circ$ . The apertures of the first, second and third slits were 0.5, 0.5 and 0.15 mm, respectively. The morphology was observed by high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2010FEF) using an acceleration voltage of 200 kV. Specimens for HRTEM observed were sonicated in ethanol for 5 min then loaded onto 200 mesh copper grids. Energy dispersive X-ray spectroscopy (EDS) is a method used to determine the energy spectrum of X-ray radiation. The composition of Pt-LiCoO<sub>2</sub> was measured by EDS.

## 3. Results and discussion

An XRD pattern of Pt-LiCoO<sub>2</sub> is shown in Fig. 1. Five characteristic peaks of rhombohedral Pt ( $2\theta = 37.4^\circ$ ,  $38.4^\circ$ ,  $39.1^\circ$ ,  $45.3^\circ$  and  $49.5^\circ$ ) marked by Miller indices (1 0 1), (0 0 6), (0 1 2), (1 0 4) and (0 1 5) are observed in the  $2\theta$  range from  $30^\circ$  to  $55^\circ$  [18]. The diffraction peaks of Pt [18] are not detected. This suggests the presence of nano-Pt particles.

Fig. 2 shows a HRTEM image of Pt-LiCoO<sub>2</sub>. The Pt-LiCoO<sub>2</sub> particles that appear in the HRTEM image indicate the presence of many dark areas. Some of those are marked by arrows in the figure. The size of the dark areas is about 2 nm. EDS analysis is specific to the region marked by plus

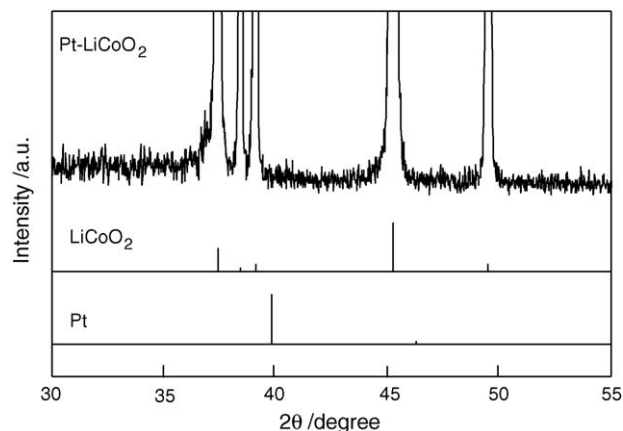


Fig. 1. XRD pattern of Pt-LiCoO<sub>2</sub>, together with the data of LiCoO<sub>2</sub> (JCPDS file No. 50-653) and Pt (JCPDS file No. 04-0802).

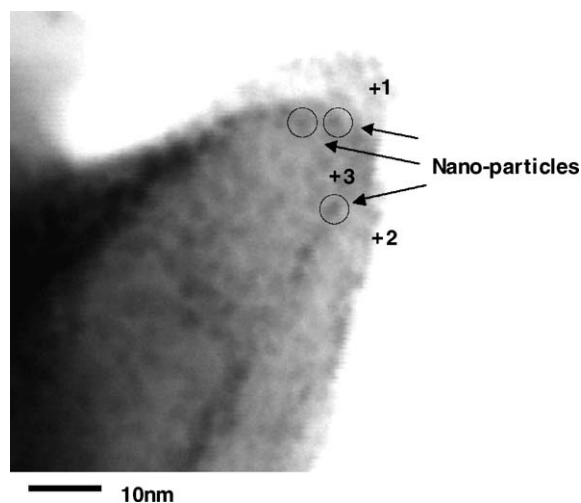


Fig. 2. HRTEM image of Pt-LiCoO<sub>2</sub>.

signs. The electron beam could be focused on about 5 nm and the EDS analysis cover the area of the support. The EDS results show that the catalyst consists of Co, Cu, Pt and O, as shown in Fig. 3. No other elements are measured by EDS. The copper detected by EDS is caused by the grids. Because of the lightweight, Li is not observed in EDS. The peak intensity of O increases with increasing of that of Co. This

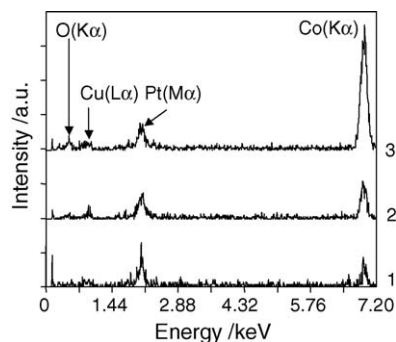
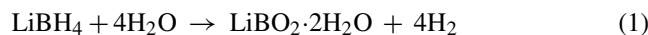


Fig. 3. EDS spectra of Pt-LiCoO<sub>2</sub>.

indicates that O detected by EDS comes from LiCoO<sub>2</sub>. Thus, we found that the dark areas in Fig. 2 are nano-Pt particles. The relative intensity of Pt (Intensity of Pt/intensity of Co) decreases from the surface to the inside. Thus, analysis results show that Pt-LiCoO<sub>2</sub> is a nano-composite material in which nano-Pt particles are dispersed on the surface of the LiCoO<sub>2</sub> particles.

The hydrolysis reaction of LiBH<sub>4</sub> is shown as follows [14]



The H<sub>2</sub> generation capacity of this reaction is 8.6 wt.% when the weight of water is taken into account. In a fuel cell application, if the water produced by the fuel cell is redirected to LiBH<sub>4</sub>, then the H<sub>2</sub> generation capacity is 37.0 wt.%. The reaction profiles of LiBH<sub>4</sub> for the reaction with water carried out at 296 K are shown in Fig. 4. Without using catalysts, the H<sub>2</sub> yield slowly increases with time and approaches only 10% at 1800 s. The catalytic activity comparison is also shown in Fig. 4. Pt-LiCoO<sub>2</sub> (Pt-LiCoO<sub>2</sub>/LiBH<sub>4</sub>:15%) gives constant hydrolysis rate up to 87% conversion. We found that 100% of the stoichiometric amount of H<sub>2</sub> was generated in 1200 s as little as 15% of the catalyst. The 15% refer the weight ratio of Pt-LiCoO<sub>2</sub> and LiBH<sub>4</sub>. The hydrogen generation rate of Pt-LiCoO<sub>2</sub> is 2.4 times higher than that of the mixture of the Pt particles and LiCoO<sub>2</sub>. The H<sub>2</sub> generated by Pt-LiCoO<sub>2</sub> catalyzed LiBH<sub>4</sub> hydrolysis increases linearly with time. Thus, the H<sub>2</sub> generation rate is expressed by the following zero order rate equation.

$$\frac{-1}{4} \frac{d[\text{LiBH}_4]}{dt} = \frac{d[\text{H}_2]}{dt} = k \quad (2)$$

where  $k$  is the rate constant. This indicates that H<sub>2</sub> generation rate is controlled by the catalyst. It is revealed that the H<sub>2</sub> generation rate  $k$  using Pt-LiCoO<sub>2</sub> is remarkably improved compared to the mixture of Pt particles and LiCoO<sub>2</sub>, as shown in Fig. 4. We suggest that the high surface area of the nano-Pt particles in Pt-LiCoO<sub>2</sub> results in the high H<sub>2</sub> generation rate. The H<sub>2</sub> generation rate using Pt-LiCoO<sub>2</sub> is 0.1% conversion s<sup>-1</sup> and similar to the rate of NaBH<sub>4</sub> using the same catalyst [8].

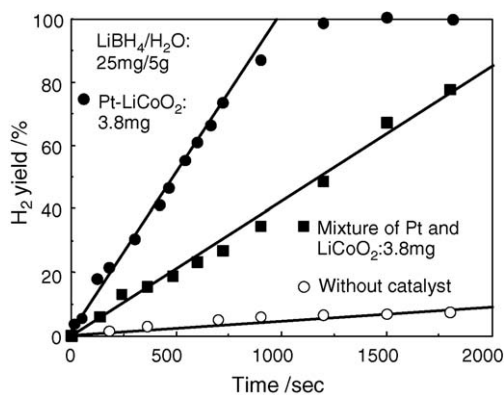


Fig. 4. Hydrogen production profiles for the reaction of LiBH<sub>4</sub> with water using different catalysts at 296 K.

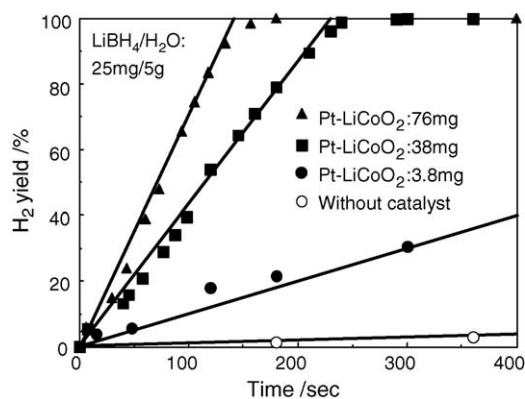


Fig. 5. Hydrogen production profiles for reaction of LiBH<sub>4</sub> with water using different amount of Pt-LiCoO<sub>2</sub> catalyst at 296 K.

The H<sub>2</sub> production profiles as a function of time by the different amounts of Pt-LiCoO<sub>2</sub> are plotted in Fig. 5. Pt-LiCoO<sub>2</sub> amount accelerates the H<sub>2</sub> generation rate (Pt-LiCoO<sub>2</sub>: 3.8–76 mg, H<sub>2</sub> generation rate: 0.1–0.7% conversion s<sup>-1</sup>). The relation between  $k$  and the catalysts content  $C$  (mg) is linear as shown in

$$k = 0.0436 + 0.00917C \quad (3)$$

This also indicates that the hydrolysis reaction involves the surface reaction of LiBH<sub>4</sub> adsorbed on the catalyst. Above H<sub>2</sub> yield of 90%, diffusion controlled first order kinetics may dominate the reaction at the very low LiBH<sub>4</sub> concentration. The catalysts were not consumed during the hydrolysis and are reusable.

A 10 kW-scale H<sub>2</sub> generator using a NaBH<sub>4</sub> solution and Pt-LiCoO<sub>2</sub> showed during 30,000 s no decrease of the H<sub>2</sub> generation rate [19]. It is suggested that Pt-LiCoO<sub>2</sub> has the long-term stability of the nano-disperse catalyst particles. As the generation of H<sub>2</sub> is irreversible on board, our chemical hydride system may be effective as a hydrogen storage system for fuel cell uninterrupted power supply (FCUPS) or for any emergency power source. As stated above, the catalytic properties of nano-sized Pt dispersed on LiCoO<sub>2</sub> (Pt-LiCoO<sub>2</sub>) are superior to that of the mixture of Pt and LiCoO<sub>2</sub>.

## 4. Conclusions

Hydrogen generation using lithium borohydride solution was accelerated some factor by applying Pt-LiCoO<sub>2</sub> catalyst. HRTEM, EDS and XRD measurements revealed that Pt-LiCoO<sub>2</sub> was a nano-composite material where nano-Pt particles of about 2 nm were dispersed on LiCoO<sub>2</sub>. It was found that 100% of the stoichiometric amount of H<sub>2</sub> was generated by the Pt-LiCoO<sub>2</sub> catalyst.

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## References

- [1] L. Schlapbach, A. Züttel, *Nature* 414 (2001) 353.
- [2] A.C. Dillon, K.M. Jones, T.A. Bekkedahl, C.H. Kiang, D.S. Bethune, M.J. Heben, *Nature* 386 (1997) 377.
- [3] R. Chahine, T.K. Bose, *Int. J. Hydrogen Energy* 19 (1994) 161.
- [4] Y. Kojima, N. Suzuki, *Appl. Phys. Lett.* 84 (2004) 4113.
- [5] Y. Ye, C.C. Ahn, C. Witham, B. Fultz, J. Liu, A.G. Rinzler, D. Colbert, K.A. Smith, R.E. Smalley, *Appl. Phys. Lett.* 74 (1999) 2307.
- [6] C.C. Ahn, Y. Ye, B.V. Ratnakumar, C. Witham, R.C. Bowman Jr., B. Fultz, *Appl. Phys. Lett.* 73 (1998) 3378.
- [7] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, *J. Power Sources* 85 (2000) 186.
- [8] Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, *Int. J. Hydrogen Energy* 27 (2002) 1029.
- [9] Z.P. Li, B.H. Liu, K. Arai, N. Morigazaki, S. Suda, *Int. J. Hydrogen energy* 356–357 (2003) 469.
- [10] P.M. Dunn, C.J. Egan, W.L. Harbison, G.K. Pitcher, *Proceedings of the 26th Interso. Energy Conversion Eng. Conf.* (3), 1991, p. 527.
- [11] V.C.Y. Kong, F.R. Foulkes, D.W. Kirk, J.T. Hinatsu, *Int. J. Hydrogen Energy* 24 (1999) 665.
- [12] R. Aiello, J.H. Sharp, M.A. Matthews, *Int. J. Hydrogen Energy* 24 (1999) 1123.
- [13] A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron, Ch. Emmenegger, *J. Power Sources* 118 (2003) 1.
- [14] Y. Kojima, Y. Kawai, M. Kimbara, H. Nakanishi, S. Matsumoto, *Int. J. Hydrogen Energy* 29 (2004) 1213.
- [15] B. Bogdanović, M. Schwickardi, *J. Alloys Compd.* 253–254 (1997) 1.
- [16] E. Newson, T. Haueter, P. Hottinger, F. Von Roth, G.W.H. Scherer, Th.H. Schucan, *Int. J. Hydrogen Energy* 23 (1998) 905.
- [17] B.D. James, M.G.H. Wallbridge, *Metal tetrahydroborates*, *Progr. Inorg. Chem.* 11 (1970) 99.
- [18] “Powder Diffraction File, ” Database Manager T.M. Kahmer, Editor-in-Chief W.F. McClune, Editor of Calculated Patterns S. N. Kabekkodu, Staff Scientist H. E. Clark, International Center for Diffraction Data (JCPDS), Pennsylvania USA, 2001.
- [19] Y. Kojima, K. Suzuki, K. Fukumoto, Y. Kawai, M. Kimbra, H. Nakanishi, S. Matsumoto, *J. Power Sources* 125 (2004) 22.