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Letter

Sodium borohydride formation when Mg reacts with hydrous sodium borates under hydrogen

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ABSTRACT

In this work, we explored the possibility of $NaBH_4$ synthesis when Mg reacted with hydrous sodium borates under hydrogen. It was found that Mg could react with the water in molten hydrous borates to form MgO and release hydrogen, which can be used for $NaBH_4$ synthesis. Then remained Mg would react with formed anhydrous borate to form $NaBH_4$. $NaBO_2$ conversion rate was decreased with increase of the crystalline water content in the hydrous sodium borates. Based on experimental results, a mechanism of $NaBH_4$ formation when Mg reacted with hydrous sodium borates was suggested.

1. Introduction

Recently, sodium borohydride ($NaBH_4$) has been attracted more attentions as a hydrogen storage material for hydrogen generation [1–8] or as a fuel for the Direct Borohydride Fuel Cell (DBFC) due to its high hydrogen storage capacity [9–18]. It is considered that $NaBH_4$ recovery technology is an important issue when $NaBH_4$ is used as a hydrogen storage material because the $NaBH_4$ production cost is too high to be a hydrogen source right now [15,19,20]. Recently, several $NaBH_4$ synthesis methods have been developed such as ball-milling synthesis [21–23] and thermal synthesis [24–29]. Ball-milling synthesis is a convenient method by which borohydrides are formed through mechano-chemical reactions of borates with metal hydrides at room temperature. Thermal synthesis is a mass production method by which borohydrides are formed through chemical reactions of borates with metals and hydrogen by heating up to around 600 °C. For example, Mg reacts with $NaBO_2$ to form $NaBH_4$ and MgO under hydrogen atmosphere through following reaction:

$$2Mg + NaBO_2 + 2H_2 = NaBH_4 + 2MgO, \quad \Delta G = -342\ \mathrm{kJ/mol\ NaBH_4} \qquad (1)$$

It is considered that spent solutions after $NaBH_4$ hydrolysis can be used as the raw material for $NaBH_4$ recovery. Anhydrous $NaBO_2$ can be prepared by evaporation to remove water in the spent solution. However, it is considered that some hydrous $NaBO_2$ would remain when preparing anhydrous $NaBO_2$ in large scale. The anhydrous $NaBO_2$ is deliquescent and easy to form hydrous $NaBO_2$ when exposing to air. It is considered that the crystalline water in the borates would influence the $NaBH_4$ synthesis. However, it is not clear that the effect of crystalline water in hydrous borates on $NaBH_4$ synthesis.

In this work, we explored the possibility of $NaBH_4$ synthesis when Mg reacted with hydrous sodium borates under hydrogen atmosphere. Based on experimental results, a mechanism of $NaBH_4$ formation was suggested and discussed.

2. Experimental details

Mg powder (purity: 99.9%, <200 mesh), hydrous sodium borate $NaBO_2{\cdot}4H_2O$ (purity: 98%) and hydrogen (purity: 99.99%) were used as raw materials. The diagram of test apparatus for borohydride synthesis is as described in Ref. [26]. The confirmation of sodium borohydride formation was conducted by XRD analysis (RINT 1000, Cu K_α). Sample morphology observation and element distribution mapping were conducted by scanning electron microscopy and electron probe microanalysis (EPMA) analyses (EPMA-8705). $NaBO_2$ conversion rates were both determined by Sievert method through calculation of hydrogen consumption amount and by iodimetric analysis.

Hydrous borates with different contents of crystalline water were prepared by heating $NaBO_2{\cdot}4H_2O$ at different temperatures according to the result of differential scanning calorimetry (DSC) analysis (Simadzu DSC-60) as shown in Fig. 1. $NaBO_2{\cdot}2H_2O$ was obtained by heating $NaBO_2{\cdot}4H_2O$ at 90 °C for 12 h and

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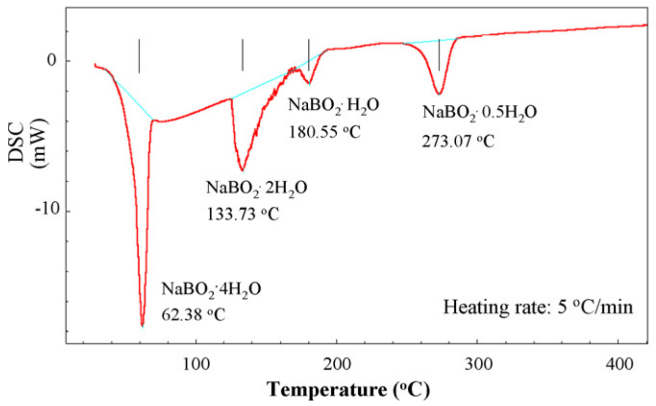


Fig. 1. DSC analysis of $NaBO_2{\cdot}4H_2O$ during heating.

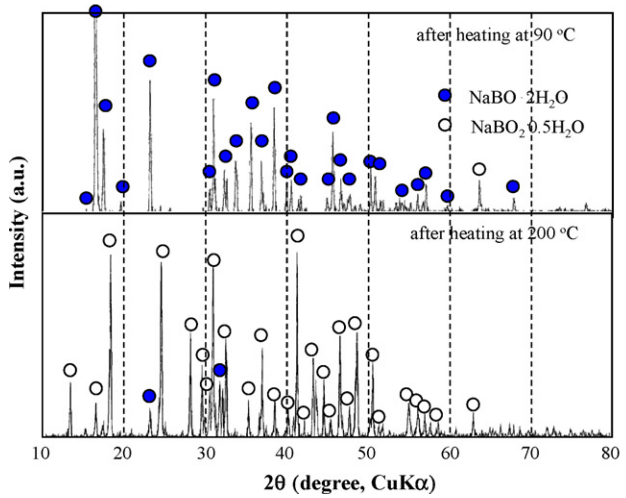


Fig. 2. XRD confirmation of $NaBO_2{\cdot}2H_2O$ and $NaBO_2{\cdot}0.5H_2O$ after heating $NaBO_2{\cdot}4H_2O$ at 90 °C and 200 °C respectively.

$NaBO_2{\cdot}0.5H_2O$ was obtained by heating $NaBO_2{\cdot}4H_2O$ at 200 °C for 12 h. Due to that dehydration peak of $NaBO_2{\cdot}2H_2O$ was close to that of $NaBO_2{\cdot}H_2O$, it was difficult to obtain pure $NaBO_2{\cdot}H_2O$ by dehydrating $NaBO_2{\cdot}2H_2O$. Therefore, we investigated the $NaBH_4$ formation behavior when Mg reacted with $NaBO_2{\cdot}2H_2O$ and $NaBO_2{\cdot}0.5H_2O$ respectively. The sample confirmations were done by XRD analysis as shown in Fig. 2.

Raw materials for sodium borohydride synthesis were well mixed in a glove box, and then put the mixture into a stainless steel reactor in which a thermocouple was placed in the reaction bed. The mole ratio of Mg to $NaBO_2$ in hydrous or anhydrous sodium borates was fixed to 2:1 or 4:1. The reactor was degassed during heating to 510 °C at a heating rate of 40 °C/min before introducing hydrogen (initial pressure: 3.0 MPa). After that, the reactor was heated to 600 °C at a heating rate of 5 °C/min and held at 600 °C under hydrogen atmosphere.

3. Results and discussion

3.1. *$NaBH_4$ formation*

Theoretically speaking, hydrogen in crystalline water of hydrous sodium borates can be directly used as a hydrogen source for $NaBH_4$ synthesis in thermodynamics. It was thought that Mg would react with $NaBO_2{\cdot}2H_2O$ through following supposed reaction:

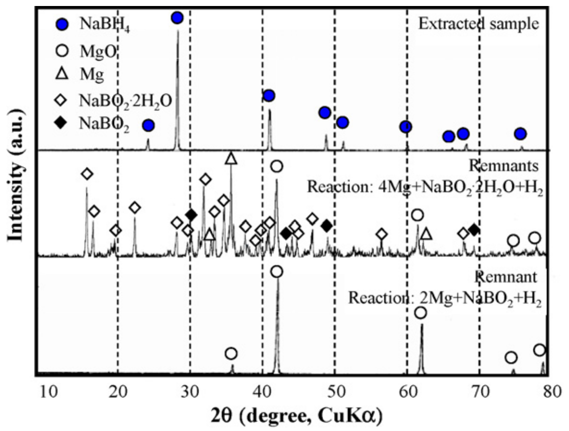


Fig. 3. XRD analyses of extracted samples and their remnants after Mg reacted with anhydrous borate or hydrous borates under hydrogen.

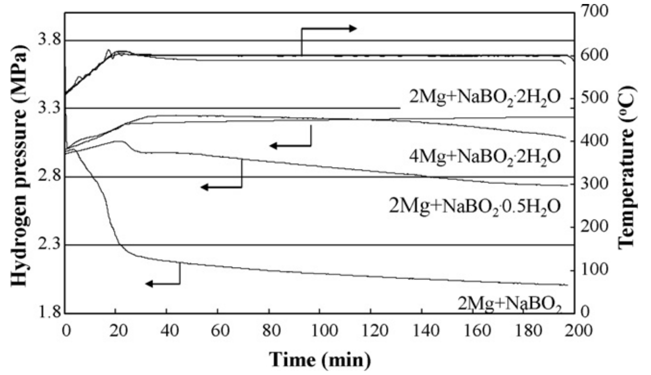


Fig. 4. Influence of crystalline water content in hydrous borates on hydrogen consumption behavior when Mg reacted with $NaBO_2{\cdot}xH_2O$ ($x = 0, 0.5, 2$) under hydrogen atmosphere.

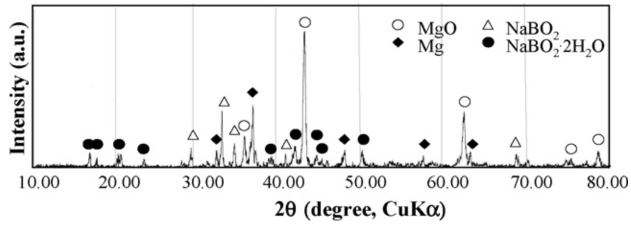


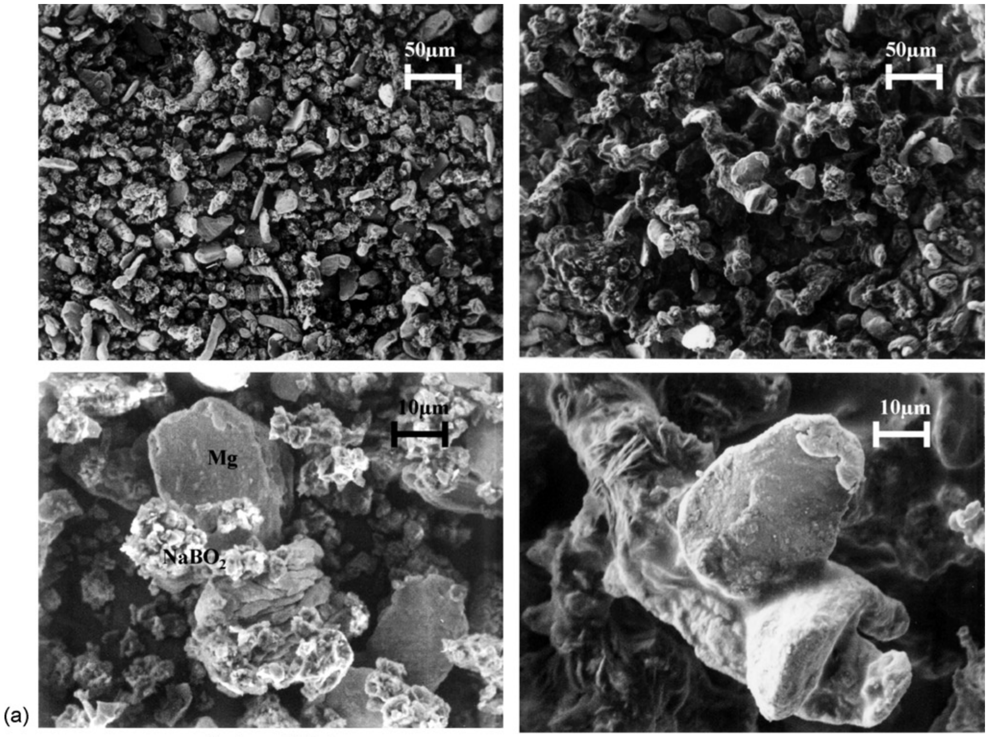
Fig. 5. XRD analysis of the sample after 2 mole of Mg reacted with 1 mole of $NaBO_2{\cdot}2H_2O$.

$$4Mg + NaBO_2{\cdot}2H_2O = NaBH_4 + 4MgO, \quad \Delta G = -991\ \mathrm{kJ/mol\ NaBH_4} \tag{2}$$

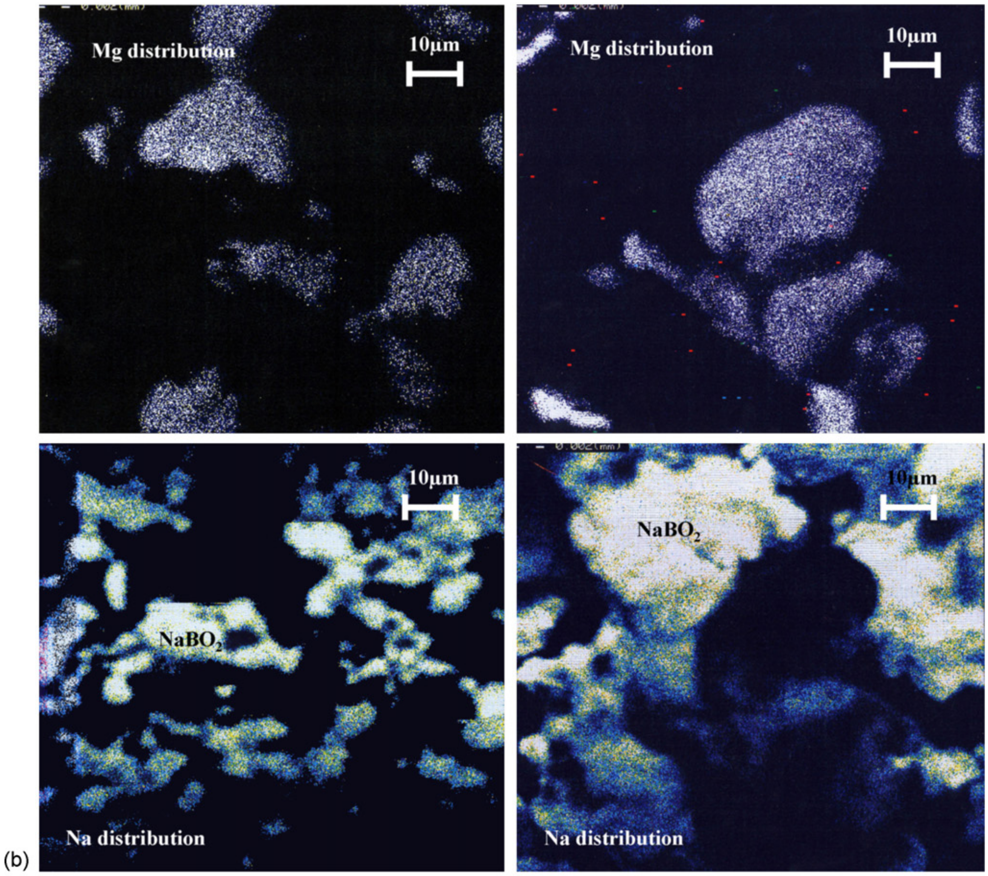
We calculated $NaBO_2$ conversion rates through Sievert method according to the gaseous hydrogen consumption of reaction (1) and measured by iodimetric measurement as shown in Table 1. It was found that there was some $NaBH_4$ formed when 4 mole of

Table 1
$NaBO_2$ conversion rates when Mg reacted with hydrous or anhydrous sodium borates.

	$NaBO_2$		$NaBO_2{\cdot}0.5H_2O$		$NaBO_2{\cdot}2H_2O$		$NaBO_2{\cdot}4H_2O$	
	Sievert method	Iodimetric analysis	Sievert method	Iodimetric analysis	Sievert method	Iodimetric analysis	Sievert method	Iodimetric analysis
2 Mg	61.0%	63.5%	26.1%	28.8%	0	0	–	–
4 Mg	–	–	–	–	9.2%	12.3%	0	0



anhydrous $NaBO_2$ hydrous sodium borate



anhydrous $NaBO_2$ hydrous sodium borate

Fig. 6. (a) SEM pictures of mixtures of Mg with anhydrous $NaBO_2$ or hydrous sodium borate after heating to 510 °C. (b) Mg and Na distribution in mixtures of Mg with anhydrous $NaBO_2$ or hydrous sodium borate after heating to 510 °C.

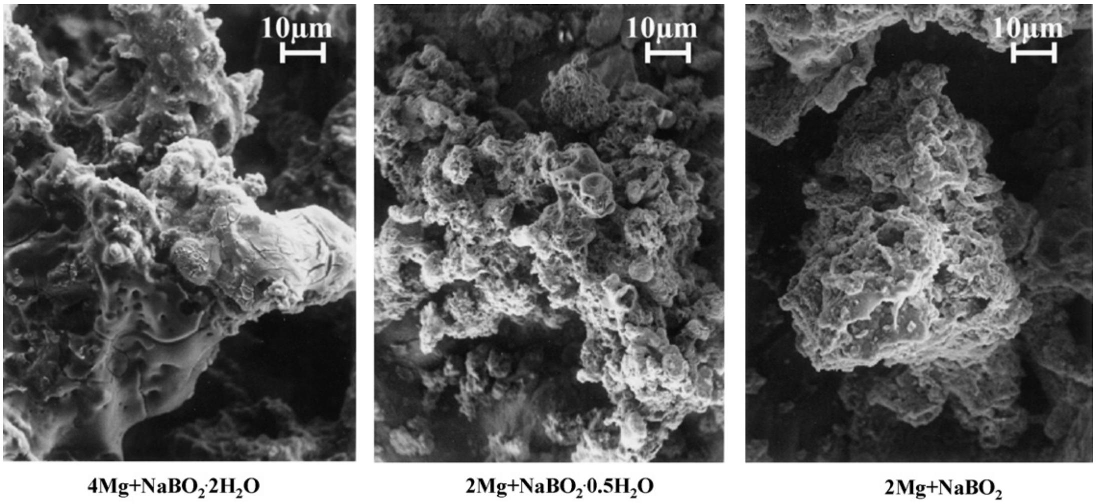


Fig. 7. SEM pictures of the mixtures after Mg reacted with anhydrous sodium borate or hydrous sodium borate under hydrogen.

Mg reacted with 1 mole of $NaBO_2{\cdot}2H_2O$ though the $NaBO_2$ conversion rate was lower than that of the reaction (1), but no $NaBH_4$ was formed when 4 mole of Mg reacted with 1 mole of $NaBO_2{\cdot}4H_2O$.

In order to confirm the $NaBH_4$ formation, we extracted the product by anhydrous ethylenediamine with a purity of 99%. Hardened filter paper was used to separate the extraction solution from remnants. White powders were obtained by evaporating the extraction solution under 0.01 MPa at room temperature. The obtained powders were subjected to XRD analysis for qualitative identification of the borohydride formation. The XRD peaks clearly demonstrate the existence of $NaBH_4$ when 4 mole of Mg reacted with 1 mole of $NaBO_2{\cdot}2H_2O$ as shown in Fig. 3. It can be seen that the remnants contained MgO, $NaBO_2$, some unreacted Mg and $NaBO_2{\cdot}2H_2O$.

According to reaction (2), $NaBH_4$ formation would have nothing to do with the hydrogen pressure. However, from experimental results as shown in Fig. 4, it can be seen that hydrogen pressure increased first, and then decreased during reaction. It indicated that Mg would firstly react with $NaBO_2{\cdot}2H_2O$ to produce $NaBO_2$ and hydrogen by following reaction:

$$2Mg + NaBO_2{\cdot}2H_2O = 2MgO + NaBO_2 + 2H_2,\quad \Delta G = -324.4\,kJ/mol\,H_2 \tag{3}$$

Then remained Mg would react with $NaBO_2$ and hydrogen to form $NaBH_4$ by reaction (1). As a result, $NaBH_4$ was formed when 4 mole of Mg reacted with 1 mole of $NaBO_2{\cdot}2H_2O$.

In order to confirm the suggested $NaBH_4$ formation hypothesis when Mg reacted with hydrated sodium borate, we tried to use 2 mole of Mg to react with 1 mole of $NaBO_2{\cdot}2H_2O$ under hydrogen. It was found that hydrogen pressure increased but no hydrogen pressure drop occurred as shown in Fig. 4. The obtained sample was subjected to XRD analysis. It was found that no $NaBH_4$ was formed as shown in Fig. 5, but X-ray diffraction peaks clearly showed the existence of formed MgO. Through iodimetric measurement, no $NaBH_4$ formation was confirmed also.

The morphology and EPMA mapping after heating the mixture ($Mg + NaBO_2{\cdot}2H_2O$) to 510 °C is shown in Fig. 6(a) and (b) respectively. It can be seen that molten hydrous borates were generated. Fig. 7 shows the morphologic observation after Mg reacted with hydrous or anhydrous sodium borate under hydrogen. It was found many small pores remained in the molten substance, but no molten substance was formed when Mg reacted with anhydrous borate. It was considered that these pores were brought by hydrogen evolution when Mg reacted with H_2O in the molten $NaBO_2{\cdot}2H_2O$.

Fig. 4 shows the influence of crystalline water content in hydrous sodium borates on the hydrogen consumption behavior when Mg reacted $NaBO_2{\cdot}xH_2O$ ($x = 0, 0.5, 2$) under hydrogen. It was found that the more the crystalline water content in hydrous sodium borates, the higher the hydrogen pressure would go up. It reconfirmed that hydrogen was generated during heating the mixture of Mg and hydrous sodium borates.

From Fig. 4, it also can be seen that the hydrogen consumption rate (hydrogen pressure drop vs. time) was decreased with increasing the crystalline water content in the hydrous sodium borates. It is known that the more the crystalline water content in the hydrous sodium borates, the more MgO would be formed according to reaction (3). The thick layer of MgO on the Mg surfaces would significantly impede $NaBH_4$ formation from reaction (1). As a result, $NaBO_2$ conversion rate and kinetic properties of $NaBH_4$ formation were decreased.

3.2. *$NaBH_4$ formation mechanism*

From these experimental results and discussion above, it can be supposed that $NaBH_4$ would be formed by following steps when Mg reacted with hydrous borates:

(1) hydrous borates melted and coated on surfaces of Mg particles when heating to 510 °C;
(2) Mg reacted with H_2O in the molten borates to form anhydrous borates and release hydrogen;
(3) MgO was formed on surfaces of the Mg particles;
(4) after all H_2O in the molten borates was consumed, remained Mg reacted with anhydrous borate and hydrogen to form $NaBH_4$.

It is interesting to note that the crystalline water in hydrous sodium borates can be used as a hydrogen source for $NaBH_4$ synthesis. It is important for simplification of $NaBH_4$ recovery process and cost reduction of $NaBH_4$ production.

4. Conclusions

Mg can react with anhydrous borate to form $NaBH_4$. Mg would react with crystalline water in hydrous sodium borates to form anhydrous borate and release hydrogen, which can be used for $NaBH_4$ synthesis. Then remained Mg would react with formed anhydrous borate to form $NaBH_4$. $NaBO_2$ conversion rate was decreased with increase of the crystalline water content in the hydrous sodium borates.

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References

[1] V.C.Y. Kong, F.R. Foulkes, D.W. Kirk, J.T. Hinatsu, Int. J. Hydrogen Energy 24 (1999) 665.
[2] R. Aiello, J.H. Sharp, M.A. Matthew, Int. J. Hydrogen Energy 24 (1999) 1123.
[3] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, N.C. Spencer, M.T. Kelly, P.J. Petillo, M. Binder, Int. J. Hydrogen Energy 25 (2000) 969.
[4] S. Suda, Y.M. Sun, B.H. Liu, Y. Zhou, S. Morimitsu, K. Arai, Y. Zhou, N. Tsukamaoto, Y. Candra, Z.P. Li, Met. Mater. Korea 7 (2001) 73.
[5] D. Hua, Y. Hanxi, A. Xinping, C. Chuansin, Int. J. Hydrogen Energy 28 (10) (2003) 1095.
[6] J.-H Kim, H. Lee, S.-C. Han, H.-S. Kim, M.-S. Song, J.-Y. Lee, Int. J. Hydrogen Energy 29 (3) (2004) 263.
[7] B.H. Liu, Z.P. Li, S. Suda, J. Alloys Compd. 415 (1–2) (2006) 288.
[8] M. Aya, A. Midillib, I. Dincerc, J. Power Sources 157 (1) (2006) 104.
[9] S. Amendola, P. Onnerud, M. Kelly, P. Petillo, S. Sharp-Goldman, M. Binder, J. Power Sources 84 (1) (1999) 130.
[10] Z.P. Li, B.H. Liu, K. Arai, S. Suda, J. Electrochem. Soc. 150 (7) (2003) A868.
[11] B.H. Liu, Z.P. Li, S. Suda, J. Electrochem. Soc. 150 (3) (2003) A398.
[12] M.V. Mirkin, H. Yang, A.J. Bard, J. Electrochem. Soc. 139 (8) (1992) 2212.
[13] E. Gyenge, Electrochim. Acta 49 (6) (2004) 965.
[14] H. Dong, R. Feng, X. Ai, Y. Cao, H. Yang, C. Cha, J. Phys. Chem. B 109 (21) (2005) 10896.
[15] Z.P. Li, B.H. Liu, K. Arai, S. Suda, J. Alloys Compd. 404–406 (2005) 648.
[16] Z.P. Li, B.H. Liu, J.K. Zhu, S. Suda, J. Power Sources 163 (1) (2006) 555.
[17] B.H. Liu, S. Suda, J. Power Sources 164 (1) (2007) 100.
[18] B.H. Liu, Z.P. Li, S. Suda, J. Power Sources 175 (1) (2008) 226.
[19] C. Ponce de Leon, F.C. Walsh, D. Pletcher, D.J. Browning, J.B. Lakeman, J. Power Sources 155 (2) (2006) 172.
[20] J.-H. Wee, J. Power Sources 155 (2) (2006) 329.
[21] Z.P. Li, B.H. Liu, N. Morigasaki, S. Suda, J. Alloys Compd. 354 (1/2) (2003) 243.
[22] Z.P. Li, B.H. Liu, K. Arai, N. Morigasaki, S. Suda, J. Alloys Compd. 356–357 (2003) 469.
[23] E. Jeon, Y. Cho, J. Alloys Compd. 422 (2006) 273.
[24] Y. Kojima, T. Haga, Int. J. Hydrogen Energy 28 (2003) 989.
[25] S. Suda, N. Morigasaki, Y. Iwase, Z.P. Li, J. Alloys Compd. 404–406 (2005) 643.
[26] Z.P. Li, B.H. Liu, J.K. Zhu, N. Morigasaki, S. Suda, J. Alloys Compd. 437 (2007) 311.
[27] B.H. Liu, Z.P. Li, J.K. Zhu, N. Morigasaki, S. Suda, Energy Fuels 21 (3) (2007) 1707.
[28] B.H. Liu, Z.P. Li, N. Morigasaki, S. Suda, Int. J. Hydrogen Energy 33 (2008) 1323.
[29] B.H. Liu, Z.P. Li, N. Morigasaki, S. Suda, Energy Fuels 22 (2008) 1894.