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Short communication

Alkaline sodium borohydride gel as a hydrogen source for PEMFC or an energy carrier for $NaBH_4$-air battery

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ABSTRACT

In this preliminary study, we tried to use sodium polyacrylate as the super absorbent polymer to form alkaline $NaBH_4$ gel and explored its possibilities for borohydride hydrolysis and borohydride electro-oxidation. It was found that the absorption capacity of sodium polyacrylate decreased with increasing $NaBH_4$ concentration. The formed gel was rather stable in the sealed vessel but tended to slowly decompose in open air. Hydrogen generation from the gel was carried out using $CoCl_2$ catalyst precursor solutions. Hydrogen generation rate from the alkaline $NaBH_4$ gel was found to be higher and impurities in hydrogen were less than that from the alkaline $NaBH_4$ solution. The $NaBH_4$ gel also successfully powered a $NaBH_4$-air battery.

1. Introduction

Sodium borohydride $NaBH_4$, a compound containing 10.6 wt% hydrogen, is now attracting considerable attentions as a hydrogen source for proton-exchange membrane fuel cells (PEMFCs) [1–15] and also an anodic fuel for the direct borohydride fuel cell (DBFC) [16–29]. In these applications, $NaBH_4$ is usually dissolved in alkaline solutions. However, when borohydride solutions were used for portable applications, some engineering problems were encountered. Among them, system orientation problem and hydrogen purity were two major concerns:

(1) System orientation problem in portable applications: In portable applications, it is hoped that power generation devices can be placed in all directions without orientation preference. However, when using a liquid fuel to power a fuel cell, a system orientation problem usually occurs as the fuel supply system has to be placed in some special directions, which would cause inconvenience in use.

(2) Impurities in generated hydrogen from borohydride hydrolysis: In principle, hydrogen generated from borohydride hydrolysis should be pure as hydrogen is the only gas product. However, when hydrogen was generated from a borohydride solution, some solution mist was brought out with the generated hydrogen. It was found that the mist could not be removed completely through a simple gas–liquid separation. As the mist contains solution components such as $NaBO_2$, $NaBH_4$, NaOH and H_2O, it is afraid that these alkaline impurities in hydrogen would accumulate in the anode side of the PEMFC and induce property deterioration.

In order to overcome these shortcomings, here we suggest a new storage form of sodium borohydride as the energy carrier. A super absorbent polymer (SAP) was applied to absorb sodium borohydride solution to form alkaline $NaBH_4$ gel. SAP is a commercialized product that is used in disposable diapers. It can absorb and hold on a large amount of water, as much as 200–800 times its weight in water.

In this preliminary study, we tried to use sodium polyacrylate as the SAP for formation of the alkaline $NaBH_4$ gel and explored its possibilities for borohydride hydrolysis and borohydride electro-oxidation. Before the application tests, the absorption behavior of sodium polyacrylate for alkaline $NaBH_4$

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solution and the storage property of the formed gel were investigated.

2. Experimental details

Alkaline $NaBH_4$ solution was first prepared by dissolving sodium borohydride (purity: 99%) in aqueous NaOH solution. Commercial sodium polyacrylate (30 mesh) was then added into the alkaline $NaBH_4$ solution to form the alkaline $NaBH_4$ gel. The obtained gel was filtrated to remove free solution. All these were done at room temperature around 20 °C. The absorption capacity is defined as the weight ratio of the absorbed alkaline $NaBH_4$ solution to the absorbent (SAP). The $NaBH_4$ amount in the gel was determined by hydrogen generation through $NaBH_4$ hydrolysis reaction catalyzed by Ni powder (Inco 255).

X-ray diffraction (XRD) analyses of the gel were carried out on a Rigaku-D/MAX-2550PC diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å).

Hydrogen generation tests of the alkaline $NaBH_4$ gel were carried out in a three-neck flask (200 ml) as shown in Fig. 1. The alkaline $NaBH_4$ gel (30 g) was initially put at the bottom of the flask. The hydrolysis reaction was initiated by injecting the catalyst precursor solution with varied concentrations of $CoCl_2$ into the flask. The generated hydrogen was introduced into a mist catcher in which 75 ml of de-ionized water was added. The volume of generated hydrogen gas was measured by a wet gas flow meter and was transformed to the value in standard temperature and pressure (STP). The flask was immersed in a water bath to stabilize the temperature. No stirring was employed in the flask. The amount of mist in generated hydrogen was checked by measuring the pH change of water in the mist catcher using a pH meter after the hydrolysis test.

The $NaBH_4$-air battery was assembled by using a mixture of surface treated Zr-Ni Laves phase alloy AB_2 ($Zr_{0.9}Ti_{0.1}Mn_{0.6}V_{0.2}Co_{0.1}Ni_{1.1}$), Ni powder and Pd-C as the anode catalyst, carbon supported Pt as the cathode catalyst and the Na^+ form Nafion membrane (112) as the electrolyte. The preparation of the catalyst, anode and the battery figuration were described in our previous work [22,27,30].

3. Results and discussion

3.1. Formation of the alkaline $NaBH_4$ gel

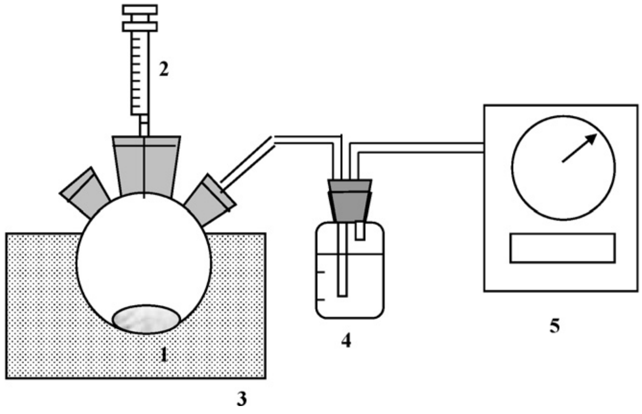


Fig. 1. Experimental setup for the hydrolysis reaction: 1: three-neck flask, 2: syringe, 3: water bath, 4: mist catcher, 5: gas meter.

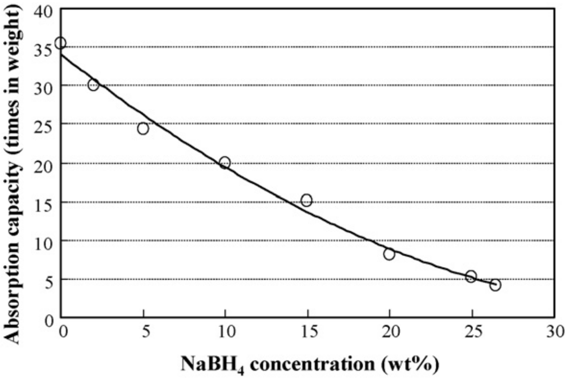
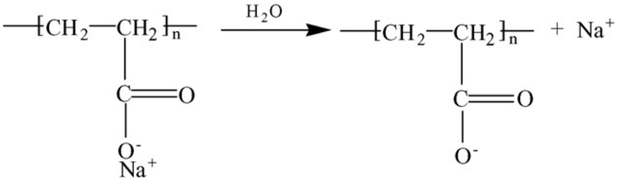


Fig. 2. Alkaline $NaBH_4$ solution absoption behavior of SAP. Alkaline $NaBH_4$ solutions contained 5 wt% NaOH.

Sodium polyacrylate is known as a super absorbent polymer because it can absorb a large amount of water, as much as 200–800 times its own mass. In the dry powder state, the polymer chains are coiled and cross-linked. But when it is hydrated with water, the carboxyl groups dissociate into carboxylate ions as shown below:



$$-\!\left[CH_2-\underset{\substack{|\\ C=O\\ |\\ O^-\\ Na^+}}{CH_2}\right]_n- \xrightarrow{H_2O} -\!\left[CH_2-\underset{\substack{|\\ C=O\\ |\\ O^-}}{CH_2}\right]_n- + Na^+ \qquad (1)$$

The ions repel each other along the polymer chain, making chains uncoil and stretch out and then allowing more water to move into. The polymer then swells and forms a gel with high viscosity. The polymer gel exhibits both solid and liquid properties. Some salts like sodium chloride are found to greatly decrease the ability of polyacrylate to absorb water because water is drawn from the polymer to Na^+ and Cl^- ions.

When dry sodium polyacrylate powder was added into the alkaline $NaBH_4$ solution, a transparent gel was found to be formed. It suggests that the alkaline $NaBH_4$ solution was absorbed into the polymer like water. The absorption capacity is denoted as the weight ratio of the saturated gel to the dry powder. Fig. 2 shows the relation of absorption capacity with $NaBH_4$ concentration in the solution. The absorption capacity was found to be several ten times of the polymer mass and tended to decrease with increasing the $NaBH_4$ concentration in the solution. It is considered that $NaBH_4$ has similar effect as NaCl in decreasing water absorption ability of the polymer.

When the alkaline $NaBH_4$ gel was placed in different environments, the gel demonstrated some interesting behaviors as shown in Fig. 3. When the sodium borohydride gel was sealed in a bottle

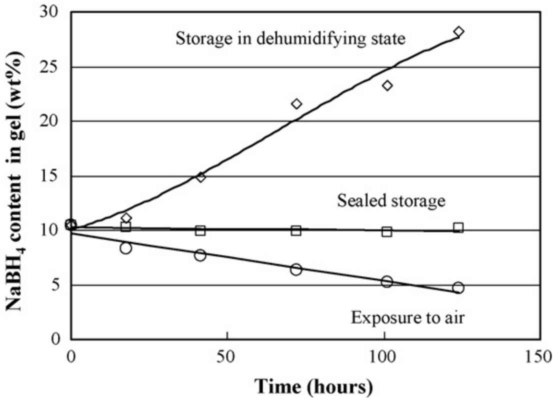


Fig. 3. Storage behaviors of the alkaline $NaBH_4$ gel under different atmospheres.

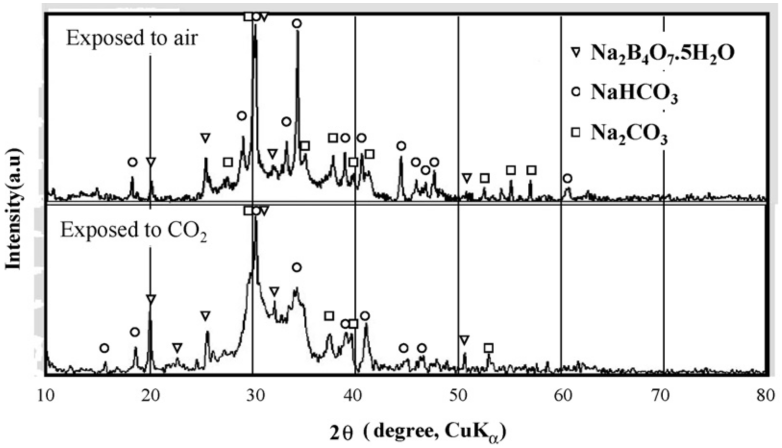


Fig. 4. XRD analysis of dried samples after alkaline $NaBH_4$ gel was exposed to air or CO_2.

without air, $NaBH_4$ concentration in the gel kept in constant. When the sodium borohydride gel was put together with some dehumidifying agent like CaO in a vessel, $NaBH_4$ concentration in the gel increased. It is suggested that water in the gel was evaporated and was absorbed by the dehumidifying agent so that $NaBH_4$ in the gel was condensed. When the sodium borohydride gel was exposed to air, it was found that $NaBH_4$ concentration in the gel decreased. In order to find the reason for that, the sample exposed to air for 2 months was subject to XRD analysis. It was found that $NaBH_4$ in the gel was decomposed to form $Na_2B_4O_7{\cdot}5H_2O$, $NaHCO_3$ and Na_2CO_3 as shown in Fig. 4. There was no $NaBH_4$ detected.

According to the XRD results and the different behaviors of the sodium borohydride gel in sealed state and by exposure to air, it is reasonable to suggest that CO_2 in air caused the $NaBH_4$ decomposition. In order to confirm this assumption, CO_2 was introduced into the sealed bottle in which alkaline $NaBH_4$ gel was placed. After 2 days, the sample was then dried in vacuum for XRD analysis. The XRD result as shown in Fig. 4 confirmed that the formation of $Na_2B_4O_7{\cdot}5H_2O$, $NaHCO_3$ and Na_2CO_3. Therefore, it can be concluded that $NaBH_4$ would be decomposed when the alkaline $NaBH_4$ gel is exposed to air or CO_2.

3.2. Hydrogen generation from sodium borohydride gel

3.2.1. $NaBH_4$ hydrolysis

In order to examine the hydrolysis properties of the alkaline $NaBH_4$ gel, we employed $CoCl_2$ solutions as the catalyst precursor and fixed amounts of $NaBH_4$ and $CoCl_2$ for hydrogen generation. Fig. 5 gives a comparison of hydrogen generation properties from the alkaline $NaBH_4$ gel and the alkaline $NaBH_4$ solution. When $CoCl_2$ solution was added into the alkaline $NaBH_4$ solution, $NaBH_4$ hydrolysis reaction took a longer incubation time and hydrogen generation was slow. The time for catalyst (Co-B alloy) formation from the catalyst precursor ($CoCl_2$) accounted for the delay of hydrogen generation. It was considered that $Co(OH)_2$ deposits were formed first when $CoCl_2$ solution was added into the alkaline $NaBH_4$ solution. After that, $Co(OH)_2$ was chemically reduced by $NaBH_4$ to form Co-B alloy. As a result, a long incubation time was needed to initiate the borohydride hydrolysis reaction. Furthermore, BH_4^- ions in the alkaline solution had to diffuse to Co-B alloy particles located at the bottom of the flask so that hydrogen generation rate was decreased.

When $CoCl_2$ solution was added into the alkaline $NaBH_4$ gel, $CoCl_2$ solution diffused along with gel particles. It was found that the alkaline $NaBH_4$ gel generated hydrogen faster after a shorter incubation time than the alkaline $NaBH_4$ solution. Because the size of the used sodium polyacrylate was around 30 mesh, it was considered that BH_4^- ions in alkaline gel particles could quickly diffuse to the surfaces of gel particles to form the Co-B catalyst.

As it was considered that $CoCl_2$ concentration in the catalyst precursor solution would influence the catalyst distribution on surfaces of the alkaline $NaBH_4$ gel particles, we investigated the effect of $CoCl_2$ concentration on the hydrolysis of the alkaline $NaBH_4$ gel as shown in Figs. 6 and 7. It was found that when $CoCl_2$ concentration was decreased, hydrogen generation needed longer incubation period. It suggests that when $CoCl_2$ solution was diluted, the chance for Co^{2+} ions to contact with BH_4^- was decreased so that it took longer time to form the Co-B catalyst on the surfaces of borohy-

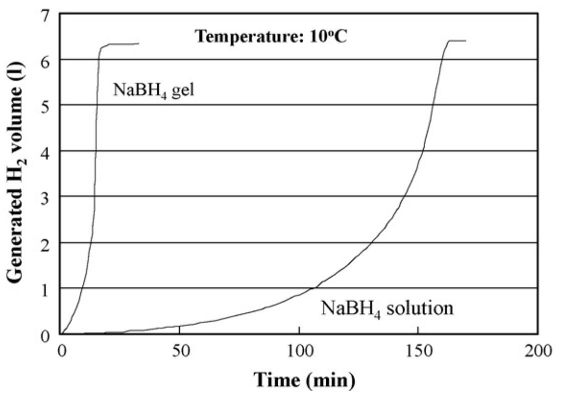


Fig. 5. Comparison of hydrogen generation from alkaline $NaBH_4$ gel and solution. (Weight of gel or solution: 30 g, catalyst precursor solution: 15.2 g of 0.067 M $CoCl_2$.)

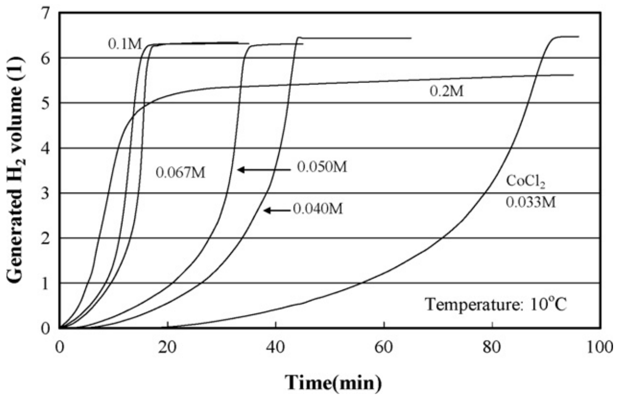


Fig. 6. Effect of $CoCl_2$ concentration on hydrogen generation behavior of the alkaline $NaBH_4$ gel. $CoCl_2$ amount was fixed at 0.13 g.

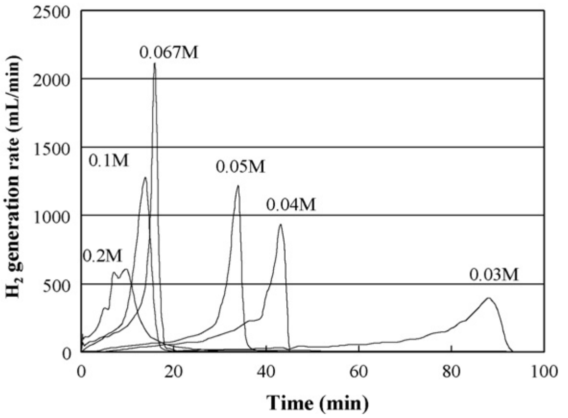


Fig. 7. Effect of $CoCl_2$ concentration on hydrogen generation rate of the alkaline $NaBH_4$ gel. $CoCl_2$ content: 0.13 g.

dride gel particles. As a result, hydrogen generation showed a longer incubation time as shown in Fig. 6.

With increasing $CoCl_2$ concentration, hydrogen generation rate from the $NaBH_4$ gel was first increased but then decreased as shown in Fig. 7. As the added $CoCl_2$ amount was kept the same, the volume of $CoCl_2$ solution decreased with increasing $CoCl_2$ concentration. As a result, the formed catalyst could not be homogeneously deposited on the surfaces of gel particles when the volume of $CoCl_2$ solution was too small. Therefore, for borohydride hydrolysis in alkaline $NaBH_4$ gels, there was optimum concentration for the catalyst precursor solution.

3.2.2. Impurity in the generated hydrogen

When hydrogen gas evolves from the alkaline solution containing NaOH, $NaBO_2$ and $NaBH_4$, it inevitably takes some mist out of the solution. The pH value of water in the mist catcher can qualitatively indicate the impurity content in the generated hydrogen. The final pH values after the hydrolysis tests are tabulated in Table 1. From Table 1, it can be seen that the pH value changed little when using the alkaline $NaBH_4$ gel, while the value apparently increased when using a solution. It indicates that less mist was produced by using the gel, mainly due to larger surface tension for bubbles.

3.3. $NaBH_4$-air battery using sodium borohydride gel

Fig. 8 shows a performance comparison of the test cell when using alkaline $NaBH_4$ solution and alkaline $NaBH_4$ gel. The alkaline $NaBH_4$ solution and gel contained 5 wt% of $NaBH_4$ and 7.5 wt% of NaOH. It was found that whether using the alkaline $NaBH_4$ solution or gel, the test cell demonstrated the same performance when the current density was lower than 80 mA cm^{-2}. However, when the operation current density was over 80 mA cm^{-2}, the cell performance was decreased if using the alkaline $NaBH_4$ gel to power the cell. It is considered that the diffusion of BH_4^- ion in the gel was slower than that in the solution. The alkaline $NaBH_4$ gel behaved like a sustained release capsule that is widely used in medicine. When the cell was operated at large currents, BH_4^- ion diffusion rate in the gel could not catch up with the electro-oxidation rate of BH_4^- at the anode so that the limiting current was reached. It seems that mass transport property in the gel is not as good as that in liquid due to large viscosity. Increasing working temperature may somewhat enhance mass transport property in gel, but it may still be inferior to that in a solution. In our future research scope, how to improve BH_4^- ion diffusion rate in the gel and shorten diffusion distance of BH_4^- ions to anode would be key points to improve the cell performance.

Table 1
The pH value of water in the mist catcher when using $CoCl_2$ solution as the hydrolysis catalyst precursor

	De-ionized water	Using $NaBH_4$ solution[a,c]	Using $NaBH_4$ gel[b,c]
pH value	6.90	8.27	7.16

[a] Alkaline $NaBH_4$ solution: 10 wt% of $NaBH_4$ and 5 wt% of NaOH, 30 g.

[b] Alkaline $NaBH_4$ gel: 30 g.

[c] Using a solution containing 0.13 g of $CoCl_2$ and 15.07 g of water as the catalyst precursor.

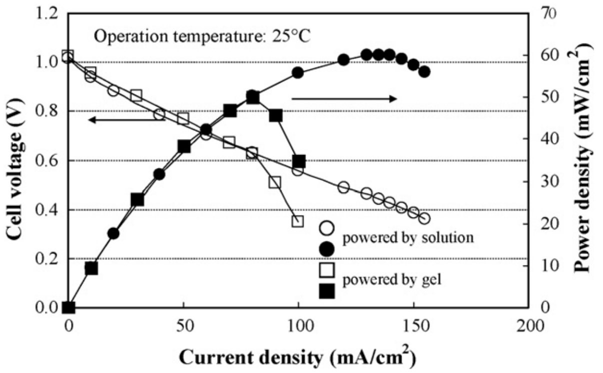


Fig. 8. Performances of the test cell powered by alkaline $NaBH_4$ solution or gel.

4. Conclusions

Sodium polyacrylate can be used as a super absorbent for absorption of alkaline $NaBH_4$ solution to form an alkaline $NaBH_4$ gel. The alkaline $NaBH_4$ gel should be stored in sealed container without CO_2. If the gel is exposed to air for a long time, $NaBH_4$ in the gel would absorb CO_2 to form $NaHCO_3$ or Na_2CO_3 and lose the function as a hydrogen or energy carrier.

Alkaline $NaBH_4$ gel can be used for generation of clean hydrogen to supply PEMFCs. For hydrolysis of borohydride in alkaline $NaBH_4$ gels, there was optimum concentration for the catalyst precursor solution.

Alkaline $NaBH_4$ gel can also power a $NaBH_4$-air battery but was found to give a smaller limiting current than a $NaBH_4$ solution.

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References

[1] H.I. Schlesinger, H.C. Brown, A.E. Finholt, J.R. Gilbreath, et al., J. Am. Chem. Soc. 75 (1953) 215.
[2] V.C.Y. Kong, F.R. Foulkes, D.W. Kirk, J.T. Hinatsu, Int. J. Hydrogen Energy 24 (1999) 665.
[3] R. Aiello, J.H. Sharp, M.A. Matthew, Int. J. Hydrogen Energy 24 (1999) 1123.
[4] S.C. Amendola, S.L. Sharp-Goldman, M.S. Janjua, M.T. Kelly, P.J. Petillo, M. Binder, J. Power Sources 85 (2000) 186.
[5] 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.
[6] 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.
[7] S. Suda, Y.M. Sun, B.H. Liu, Y. Zhou, S. Morimitsu, K. Arai, N. Tsukamoto, M. Uchida, Y. Candra, Z.P. Li, J. Appl. Phys. A72 (2001) 209.
[8] Y. Kojima, K. Suzuki, K. Fukumoto, M. Sasaki, T. Yamamoto, Y. Kawai, H. Hayashi, Int. J. Hydrogen Energy 27 (2002) 1029.
[9] Dong Hua, Yang Hanxi, Ai Xinping, Cha Chuansin, Int. J. Hydrogen Energy 28 (2003) 1095.
[10] C. Wu, H. Zhang, B. Yi, Catal. Today 93–95 (2004) 477.

[11] J.-H. Kim, K.-T. Kim, Y.-M. Kang, H.-S. Kim, M.-S. Song, Y.-J. Lee, P.S. Lee, J.-Y. Lee, J. Alloys Compd. 379 (2004) 222.
[12] A. Zaluska, L. Zaluski, J. Alloys Compd. 404–406 (2005) 706.
[13] Jin-Ho Kim, Ho Lee., Sang-Cheol Han, Hyun-Seok Kim, Min-Sang Song, Jai-Young Lee, Int. J. Hydrogen Energy 29 (2004) 263.
[14] B.H. Liu, Z.P. Li, S. Suda, J. Alloys Compd. 415 (2006) 288.
[15] Murat Ay, Adnan Midilli, Ibrahim Dincer, J. Power Sources 157 (2006) 104.
[16] S. Amendola, P. Onnerud, M. Kelly, P. Petillo, S. Sharp-Goldman, M. Binder, J. Power Sources 84 (1999) 130.
[17] Z.P. Li, B.H. Liu, K. Arai, S. Suda, J. Electrochem. Soc. 150 (2003) A868.
[18] B.H. Liu, Z.P. Li, S. Suda, J. Electrochem. Soc. 150 (2003) A398.
[19] Michael V. Mirkin, Hongqium Yang, Allen J. Bard, J. Electrochem. Soc. 139 (1992) 2212.
[20] E. Gyenge, Electrochim. Acta 49 (2004) 965.
[21] B.H. Liu, Z.P. Li, S. Suda, Electrochem. Acta 49 (2004) 3097.
[22] B.H. Liu, Z.P. Li, S. Suda, Electrochem. Acta 50 (2005) 3719.
[23] H. Dong, R. Feng, X. Ai, Y. Cao, H. Yang, C. Cha, J. Phys. Chem. B 109 (2005) 10896.
[24] J.-H. Kim, H.-S. Kim, Y.-M. Kang, M.-S. Song, S. Rajendran, S.-C. Han, D.-H. Jung, J.-Y. Lee, J. Electrochem. Soc. 151 (2004) A1039.
[25] Z.P. Li, B.H. Liu, K. Arai, K. Asaba, S. Suda, J. Power Sources 126 (2004) 28.
[26] Z.P. Li, B.H. Liu, K. Arai, S. Suda, J. Alloys Compd. 404–406 (2005) 648.
[27] Z.P. Li, B.H. Liu, J.K. Zhu, S. Suda, J. Power Sources 163 (2006) 555.
[28] B.H. Liu, S. Suda, J. Power Sources 164 (2007) 100.
[29] B.H. Liu, Z.P. Li, S. Suda, J. Power Sources 175 (2008) 226.
[30] Z.P. Li, E. Higuchi, B.H. Liu, S. Suda, J. Alloys Compd. 293–295 (1999) 593.