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Short communication

Thermal properties of alkaline sodium borohydride solutions

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ABSTRACT

Alkaline sodium borohydride solutions are potential hydrogen sources for fuel cells. Thermal properties of the $NaBH_4$–NaOH–H_2O ternary system were measured by DSC and temperature-rise calorimetry. Liquidus temperatures showed that it is possible to store and use the solutions well below 0 °C if NaOH concentration is less than 20 wt%. The solubility of sodium borohydride was found to be large in these solutions, but decreased with increasing NaOH concentration. The optimum composition for alkaline borohydride solutions seems to be 15 wt% $NaBH_4$ in 10 wt% NaOH considering both the liquidus temperature and hydrogen storage density.

1. Introduction

Sodium borohydride $NaBH_4$ is well known as a good reducing agent, and is attracting considerable attention as a potential hydrogen source for fuel cells due to the 10.6 wt% content of hydrogen [1–6]. $NaBH_4$ generates hydrogen by catalyzed hydrolysis:

$$NaBH_4 + 2H_2O = NaBO_2 + 4H_2, \quad (1)$$

and can be electrochemically oxidized in the direct borohydride fuel cell (DBFC):

$$BH_4^- + 8OH^- = BO_2^- + 6H_2O + 8e \quad (2)$$

In both cases, aqueous sodium borohydride solutions are stabilized to avoid slow hydrolysis by added hydroxides, usually sodium hydroxide. Concentrations of sodium hydroxide in borohydride solutions for hydrogen generation are usually 1–10 wt%. Concentrations of sodium hydroxide in DBFC applications are usually much higher due to 8:1 OH^- to BH_4^- in reaction (2). Liquidus temperatures and heat capacities of solutions are important in determining their storage and working temperatures. The solubility of $NaBH_4$ in alkaline solutions, which can be deduced from the liquidus line, determines the maximum hydrogen densities in these solutions. The hydrolysis reaction is an exothermic reaction with a large heat effect, so heat capacities of borohydride solutions are also important information for applications. However, there is little information available on these properties of borohydride solutions [10], especially for the $NaBH_4$–NaOH–H_2O ternary system. Therefore, we investigated liquidus temperatures of the $NaBH_4$–NaOH–H_2O system and measured heat capacity of solid $NaBH_4$ by DSC. Heat capacities of the solutions were obtained by temperature-rise calorimetry.

2. Experimental

Sodium borohydride was product of Rome and Haas Company, U.S.A. with a purity of 97%. Sodium hydroxide was commercially available A.R. grade. Borohydride solutions were prepared by dissolving $NaBH_4$ in previously prepared NaOH solutions.

DSC was done on Shimadzu DSC60. Alumina crucibles were used both for samples and references. α-Alumina powder with a purity of more than 99.5% was used as the reference material. During DSC measurements, the alumina crucibles were covered with small nickel plates to avoid vaporization of the solutions. Nitrogen gas flowed at a rate of 50 ml min^{-1} in the chamber. Liquid nitrogen was used as the cooling medium for low temperature measurements. At each measurement, the sample was first cooled to −100 °C at 5 K min^{-1} and then heated at 5 K min^{-1}. DSC samples were 10–20 mg.

The DSC baseline usually started to deviate when the temperature went above room temperature due to increased vaporization of solution samples. Using sealed sample cells did not fully solve the problem. To compensate, visual observations of solid disappearance during sample heating were used to correct the DSC results above room temperature.

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The heat capacity of solid $NaBH_4$ was measured by DSC through the three-step method: the temperature was first held at 30 °C for 5 min and then heated at a rate of 5 K min^{-1} to 80 °C and then held at 80 °C for another 5 min. This heating program was repeated for three times when the sample and reference crucible were in three different combinations: first both the sample and the reference crucibles were in empty, then α-alumina as the standard material with known heat capacity was put in the reference crucible while the sample crucible was kept in empty, and finally the sample to be tested was put in the reference crucible while the sample crucible was still in empty. Before the measurement, the $NaBH_4$ sample was preheated to remove possible humidity that will influence the result.

The heat capacities of NaOH–H_2O solutions and $NaBH_4$–NaOH–H_2O solutions were measured with a calorimeter from Shimadzu, Japan. A copper block (99.7%) was first heated in water to 80 ± 1 °C, and then put in solution samples at room temperature. The ΔT after equilibration was recorded and heat capacities of solutions were then calculated. Heat capacities of NaOH solutions obtained in this work were 3.88, 3.71, 3.62 J g^{-1} K^{-1} for 10, 20 and 30 wt% NaOH, respectively, which agree with the published results of 3.86, 3.71, 3.64 J g^{-1} K^{-1} correspondingly [9].

3. Results and discussion

3.1. Liquidus temperatures of the NaOH–H_2O binary system

Peak temperatures during the heating process are nearer to the equilibrium states and thus suitable for the determination of transformation temperatures. Fig. 1 shows more than one peak in the heating process for some NaOH solutions. The liquidus temperature was taken as the final peak temperature, e.g. −11.55 °C for 10 wt% NaOH. Liquidus line is shown in Fig. 2. There is a eutectic transition at −32.9 °C and 20 wt% NaOH. The results in Figs. 1 and 2 are consistent with the phase diagram published in ref. [7]. As there are different crystal forms of NaOH·xH_2O (x = 7, 5, 4, 3.5, 2, 1) reported in ref. [7], the DSC curves for some solutions showed several peaks during heating. A discussion for these phase transitions will not be elaborated here as liquidus temperatures of the solutions are our main interest in this work.

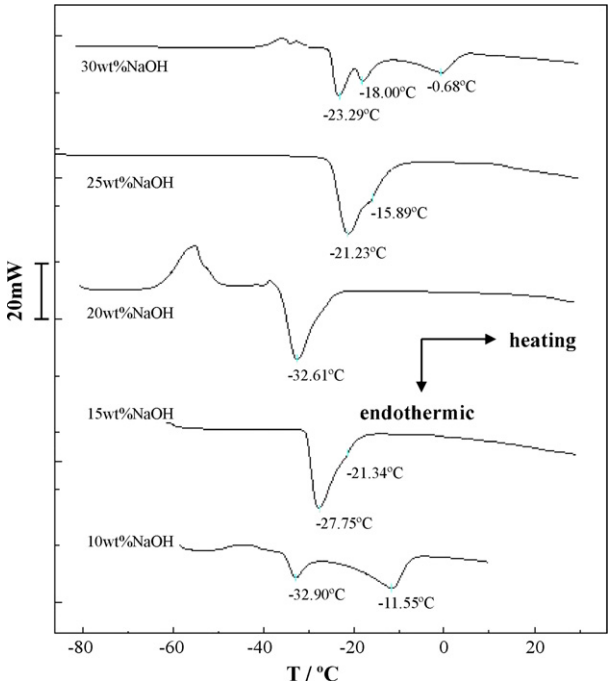

Fig. 1. DSC curves for NaOH solutions.

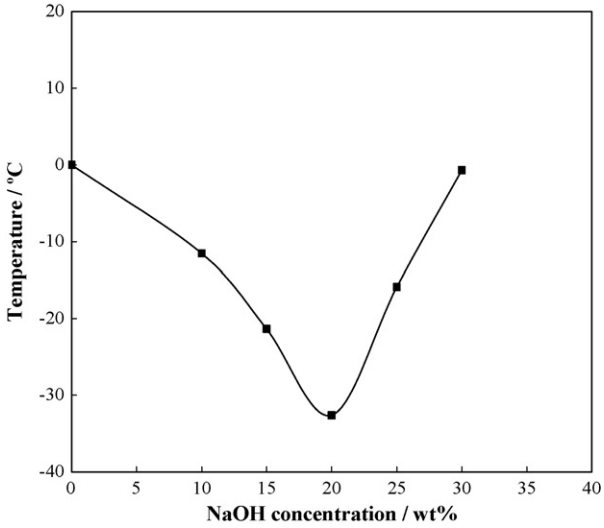

Fig. 2. Liquidus line for the NaOH–H_2O system determined by DSC.

3.2. Liquidus temperatures of the $NaBH_4$–NaOH–H_2O ternary system

Ternary compositions can be regarded as a $NaBH_4$–x wt% NaOH pseudo-binary system. Fig. 3 shows selected DSC curves for $NaBH_4$–10 wt% NaOH pseudo-binary compositions. The liquidus

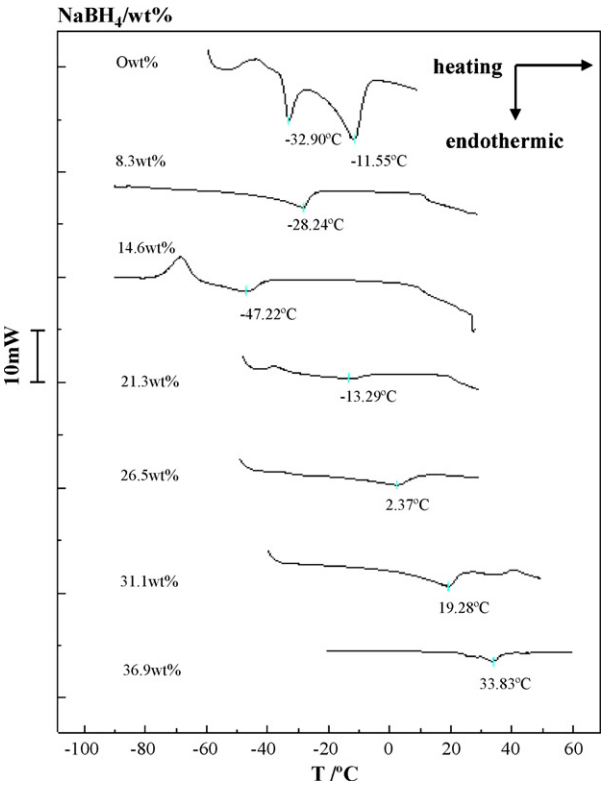

Fig. 3. DSC curves for the $NaBH_4$–10 wt% NaOH solutions.

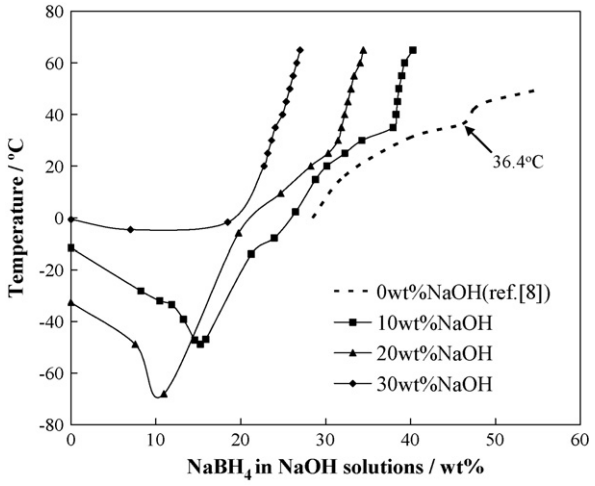

Fig. 4. Liquidus lines for $NaBH_4$–*x* wt% NaOH solutions.

Table 1
Heat capacities of $NaBH_4$–NaOH–H_2O solutions

Solutions	Heat capacity ($J\,g^{-1}\,K^{-1}$)
10 wt% NaOH + *x* wt% $NaBH_4$	
10 wt% NaOH + 0 wt% $NaBH_4$	3.88
10 wt% NaOH + 8.3 wt% $NaBH_4$	3.84
10 wt% NaOH + 15.3 wt% $NaBH_4$	3.78
10 wt% NaOH + 21.3 wt% $NaBH_4$	3.71
10 wt% NaOH + 26.5 wt% $NaBH_4$	3.67
20 wt% NaOH + *x* wt% $NaBH_4$	
20 wt% NaOH + 0 wt% $NaBH_4$	3.71
20 wt% NaOH + 7.6 wt% $NaBH_4$	3.70
20 wt% NaOH + 14.1 wt% $NaBH_4$	3.68
20 wt% NaOH + 19.7 wt% $NaBH_4$	3.61
20 wt% NaOH + 24.5 wt% $NaBH_4$	3.60
30 wt% NaOH + *x* wt% $NaBH_4$	
30 wt% NaOH + 0 wt% $NaBH_4$	3.62
30 wt% NaOH + 7.0 wt% $NaBH_4$	3.60
30 wt% NaOH + 13.1 wt% $NaBH_4$	3.54
30 wt% NaOH + 18.4 wt% $NaBH_4$	3.52

line is shown in Fig. 4. Liquidus temperatures are depressed by addition of $NaBH_4$ in the 10 wt% NaOH. The liquidus line beyond the eutectic point reflects the solubility of $NaBH_4$ in the solutions at different temperatures. The low liquidus temperatures of $NaBH_4$ solutions suggest they can be stored and used in cold environments without freezing. Solubilities of $NaBH_4$ are large and thus ensure high hydrogen storage densities. From Fig. 4, liquidus temperature is the lowest at 10 wt% $NaBH_4$ in 20 wt% NaOH. The solubility of $NaBH_4$ significantly decreased with increasing NaOH concentration.

In the $NaBH_4$–H_2O binary system, the transition at 36.4 °C in Fig. 4 corresponds to transition of the solid phase from $NaBH_4$ to $NaBH_4{\cdot}2H_2O$ at lower temperature in 0 wt% NaOH. [8]. Similar transitions in the liquidus lines in NaOH solutions are assumed to correspond to the transformation between $NaBH_4$ and $NaBH_4{\cdot}2H_2O$.

3.3. Heat capacities

According to the differences in the plateau heights, the average heat capacity between 30 and 80 °C for solid $NaBH_4$ was obtained as $2.95\,J\,g^{-1}\,K^{-1}$ or $111.7\,J\,mol^{-1}\,K^{-1}$.

The measured heat capacities of $NaBH_4$ in 10–30 wt% NaOH are given in Table 1.

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