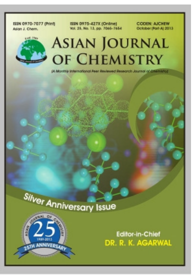
Asian Journal of Chemistry; Vol. 25, No. 14 (2013), 7749-7752

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14593



Preparation of Sodium Borohydride by Copper Electrolysis

QI-YONG ZHU*, CHUAN-GAO ZHU, FENG-WU WANG and YI-JUN WEI

Department of Chemistry & Chemical engineering, Huainan Normal University, Huainan 232001, P.R. China

*Corresponding author: Tel: +86 554 6863572; E-mail: zhuqiyong2651@163.com

(*Received*: 17 September 2012; *Accepted*: 13 July 2013) AJC-13800

The feasibility of preparing sodium borohydride by electrolyzing sodium metaborate has been demonstrated from the thermodynamic perspective and the cyclic voltammetry curves of different electrode materials were investigated. Furthermore, under the condition of copper as a working electrode, the changing relations between the cell current and working electrode potential were compared with different conditions, such as membrane, the concentrations of alkali and sodium metaborate. The copper electrode whose electrode potential is 1.17 V was chosen as a working electrode. In a home-made electrolytic cell which contains of cation-exchange membrane, sodium borohydride was prepared by electrolyzing sodium metaborate and the product was titrated using national standard method.

Key Words: Sodium borohydride, Electrode material, Cyclic voltammetry, Electrolysis, Current efficiency.

INTRODUCTION

The rapid development of fuel cells has drawn people's great interest in the field of energy and chemistry[1-5]. Among these researches, using hydrogen as raw material expedites the process of hydrogen energy economics in recent years. Researches focused on the preparation, storage and application of hydrogen have attracted worldwide attention[6-9]. As a kind of hydrogen storage material, sodium borohydride is used primarily by directly supplying hydrogen to the fuel cells[10-15]. However, with both the increasingly mature and the extensive application of fuel cell technique based on sodium borohydride, the expensive price for sodium borohydride is becoming the bottle-neck which limits the actual application of sodium borohydride in fuel cell production. Additionally, it is of significant importance to exploit a low-cost method to prepare sodium borohydride. There are several usual preparation methods, such as the Schlesinger and Brown[16], the Bayer[17], direct reduction[18], mechano-chemical reduction[19], microwave[20] and radiation[21]. However, all of these methods do not directly using sodium metaborate as raw material and consume a lot of metallic sodium (in theory, to prepare 1 mol sodium metaborate needs at least 4 mol metallic sodium produced by high temperature electrolysis). This leads to high production cost and heavy environmental pollution. Boron element is a scarce resource and the recovery utilization of sodium metaborate has attracted a wide attention of both governments and enterprises.

This article is focused on the research of multiaperture metal-electrocatalysis electrode which has a high efficiency in reducing BO_2^- to BH_4^-. According to the reported literature[22], the thermodynamic perspective was used to test the feasibility of preparing sodium borohydride by electrolyzing sodium metaborate. Then, using "electron" as reagents, which leads to a new hydrogen atom forming in cathode reducing $NaBO_2$ to $NaBH_4$, a new low-cost "green-chemical" method is exploited to prepare sodium borohydride.

EXPERIMENTAL

All regents used for this study were of analytical grade with no further purification. H_2SO_4, NaOH and sodium metaborate were purchased from Shanghai Chemical Reagent Co. Ltd.

Method: 100 mL, 1 mol/L H_2SO_4 is added into anode electric cell. In the meantime, 100 mL, 1 mol/L NaOH and 0.2 mol/L sodium metaborate are added into cathode electric cell. With copper electrode working as the cathode, lead electrode as the anode, electrolysis is conducted at atmospheric pressure and room temperature.

The products were characterized by XD-3 type polycrystalline X-ray powder diffraction (XRD). The diffraction conditions: Cu target, tube voltage 36 kV, tube current 40 mA. Quantitative analysis was conducted by the use of National Standard Method.

Cyclic voltammetry tests: It is a three-electrode system, comprising working electrode (Cu electrode), auxiliary electrode (Ni electrode) and reference electrode (saturated calomel electrode, SCE). HYL-A type DC power was adopted as electrolysis power. A self-designed two-electrode undivided electric glass cell was adopted as electric cell. The electrochemical measurement was performed in the LK98B II Microcomputer Electrochemical Analysis System (Tianjin Lanlike Chemical Electronics High-tech Corporation).

RESULTS AND DISCUSSION

Cyclic voltammetry tests on copper electrode: The cyclic voltammetry (CV) tests was conducted under the condition of working electrode (Cu electrode), auxiliary electrode (Ni electrode) and reference electrode (saturated calomel electrode, SCE), electrolytic solution (1 mol/L NaOH), scanning voltage (0.2-0.8 V), scanning speed (50 mV/s). The cathode and the anode were separated by cation exchange membrane. CV curves were obtained in Fig. 1. When scanning forward, first comes to the absorption of OH^-, then the absorption of oxygen atom producing from hydroxyl. Peak 1 and peak 2 is OH^- and oxygen atom adsorption peak, respectively. When scanning reverse, the successive formation of O_2^- $(HO_2)$and $OH(H_2O_2)$ due to desorption of the adsorbed containing-oxide anions. Peak 3 and peak 4 are OH^- and oxygen atom desorption peak, respectively[17]. There existed a turning point in the curve when the electric potential reaching -1.60 V, the moment when $NaBH_4$ was formed. The peak 5 occurs when the electric potential reaching 1.17 V, the moment highest production rate appeared. Formation of hydrogen began when another turning point existed with an electric potential of 1.23 V.

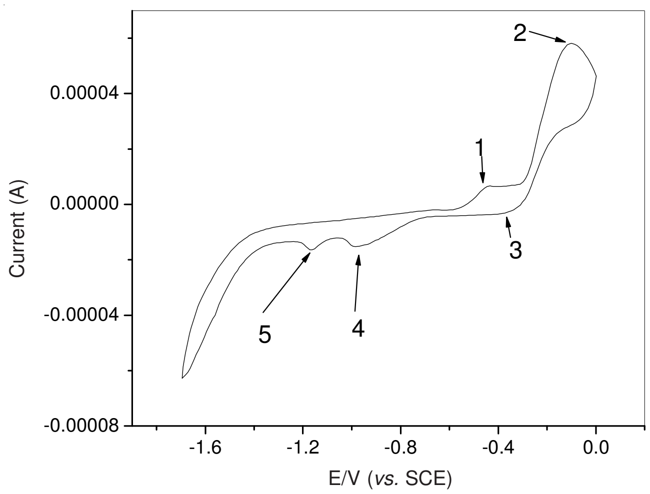


Fig. 1. Cyclic voltammetry curve of the $NaOH/NaBO_2$ system on working electrode (Cu electrode)

A blank experiment was in progress simultaneously under the same experimental condition, working electrode (Cu electrode), auxiliary electrode (Ni electrode) and reference electrode (saturated calomel electrode, SCE), electrolytic solution (1 mol/L NaOH), scanning voltage (0.2-0.8 V), scanning speed (50 mV/s). The cathode and the anode were separated by cation exchange membrane. Cyclic voltammetry curves were obtained in Fig. 2. According to the figure, peak 1 and peak 2 is OH^- and oxygen atom adsorption peak, respectively. Peak 3 and peak 4 are OH^- and oxygen atom desorption peak, respectively. However, reduction peak (peak 5) does not occur. It can be seen that peak 5 in Fig. 1 shows the formation reaction of $NaBH_4$. The actual reduction potential shifted due to the influence of oxide anion's adsorption and desorption.

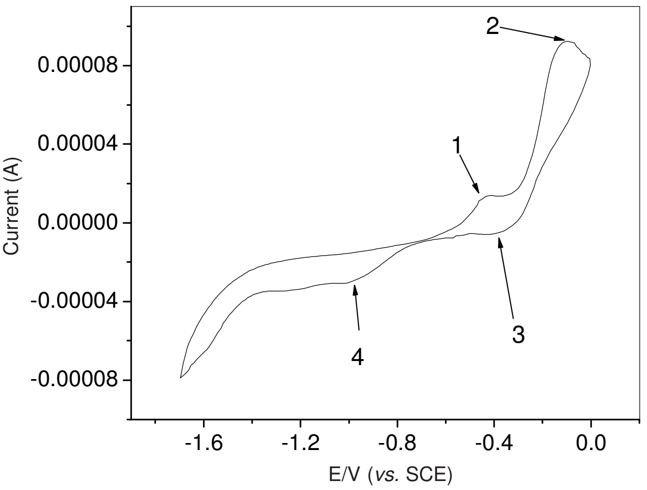


Fig. 2. Cyclic voltammetry curve of the NaOH system on working electrode (Cu electrode)

Influence of alkali concentration on the reaction: In the electrolysis process, main use of NaOH is conduction and inhibition hydrolysis of the product $NaBH_4$. Thus high concentration of NaOH will promote the reaction. However, over concentration increases the solution viscosity, which will inhibit bubbles detaching from the electrode. Large area of bubbles attached to the electrode surface is not only unfavorable for the products' adsorption but also for the conduction. Besides, over concentration will corrode cation exchange membrane and reduce its operating life. Consequently, the relationship between cell voltage and cell current under different alkali concentrations needed to be carefully compared to choose the most suitable concentration. Fig. 3 shows the relationship between cell voltage and current under different alkali concentrations when $NaBO_2$ concentration is 0.2 mol/L. According to Fig. 3, when the $NaBO_2$ concentration is 0.2 mol/L, cell current changes more quickly with the cell voltage in higher alkali concentration.

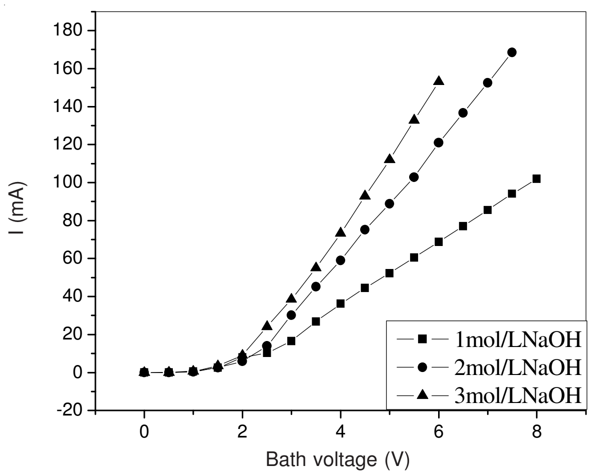


Fig. 3. Relationship between cell voltage and cell current under different alkali concentrations

Relationship between cell voltage and electrode potential under different alkali concentrations: Fig. 4 shows the

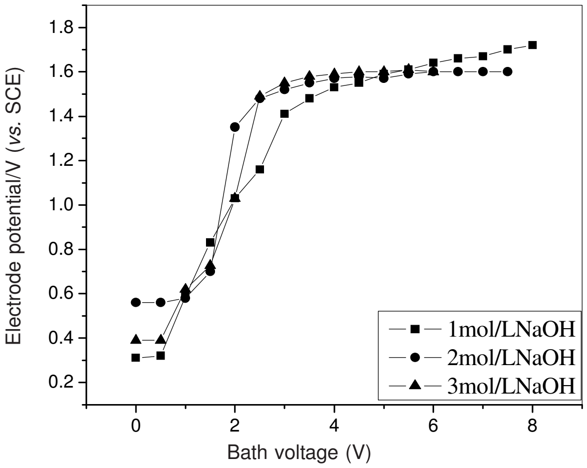


Fig. 4. Relationship between cell voltage and electrode potential under different alkali concentrations

relationship between cell voltage and electrode potential under different alkali concentrations when the $NaBO_2$ concentration is 0.2 mol/L. According to Fig. 4, changing relationships between cell voltage and electrode potential under different alkali concentrations reveal a similar rule: electrode potential changes more quickly with the cell voltage in higher alkali concentration although the margin was narrow. Since solution viscosity increases with the increase of alkali concentrations, bubbles attached to the electrode surface cannot quickly detach, which leads to the delay of voltage variation. Therefore, several sections of the curve exist some extant of crossing and overlapping.

According to Figs. 3 and 4, the relationship between cell voltage and electrode potential together with relationship between cell voltage and cell current share the same changing regularity: both of them change more quickly with increasing alkali concentration. There into, changing relationship between cell voltage and electrode potential displays tiny variation with different alkali concentration, some sections even indicate repetition phenomenon. Cell current changes more quickly with the cell voltage when the alkali concentration is increasing, whereas high alkali concentration will increase solution viscosity, which may cause many unfavorable factors. Through considering synthetically with Fig. 4, 1 mol/L is the most suitable NaOH concentration.

Influence of $NaBO_2$ concentration on the reaction: High concentration of $NaBO_2$ will promote the reaction equilibrium moving towards the $NaBH_4$-forming direction, however, over concentration increases the solution viscosity, which will inhibit bubbles separating from the electrode. Large area of bubbles attached to the electrode surface is not only unfavorable for the products' adsorption but also for the conduction. The effect of cell current and cell electrode potential under different $NaBO_2$ concentrations on the cell voltage were studied, respectively. As shown in Fig. 5, when NaOH concentration is 1 mol/L, cell current changes more slowly with the cell voltage in higher $NaBO_2$ concentration. This is because high solution viscosity inhibits bubbles detaching from the electrode surface. Besides, a large sum of bubbles distribute among the solution, which definitely reduces the conductivity of the solution.

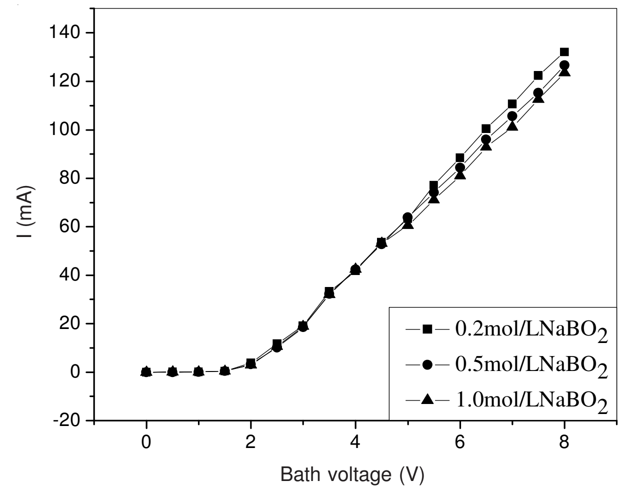


Fig. 5. Relationship between cell voltage and cell current under different $NaBO_2$ concentrations

According to Fig. 6, changing relationships between cell voltage and electrode potential under different $NaBO_2$ concentrations reveal a similar rule: electrode potential changes more quickly with the cell voltage in higher increasing $NaBO_2$ concentration although the margin was narrow. Since solution viscosity increases with the increase of alkali concentrations, bubbles attached to the electrode surface cannot quickly detach, which leads to the delay of voltage variation. Therefore, several sections of the curve exist some extant of crossing and overlapping.

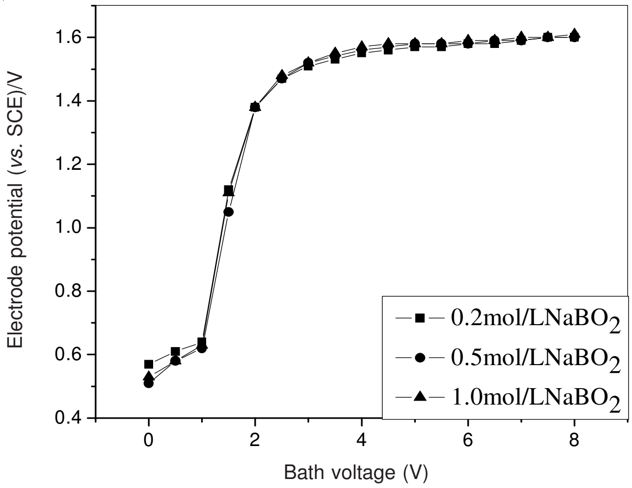


Fig. 6. Relationship between cell voltage and electrode potential under different $NaBO_2$ concentrations

Influence of membrane on cell voltage and cell current: Fig. 7 shows the relationship between cell voltage and cell current under the condition of cation membrane, ceramic membrane and no membrane, respectively. According to Fig. 7, changing rate of cell current with cell voltage in a descending order is: no membrane > cation membrane > ceramic membrane.

Characterization of product sodium borohydride: Fig. 8 shows the XRD pattern of the product sodium borohydride. When the 2θ values of the as-synthesized sample are locates at 25.14°, 28.88° and 41.20°, the diffraction peak occurs and

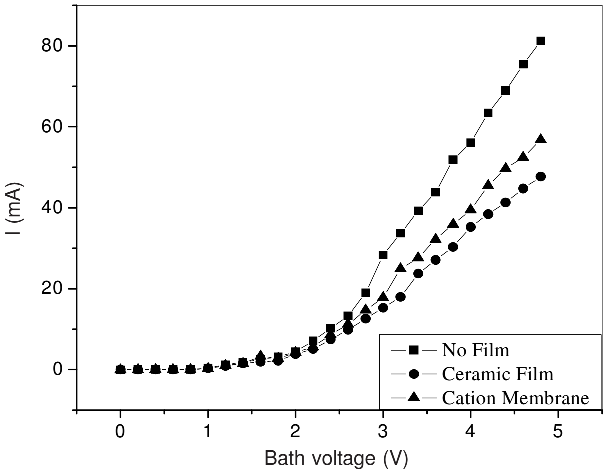


Fig. 7. Influence of membrane on cell voltage and cell current

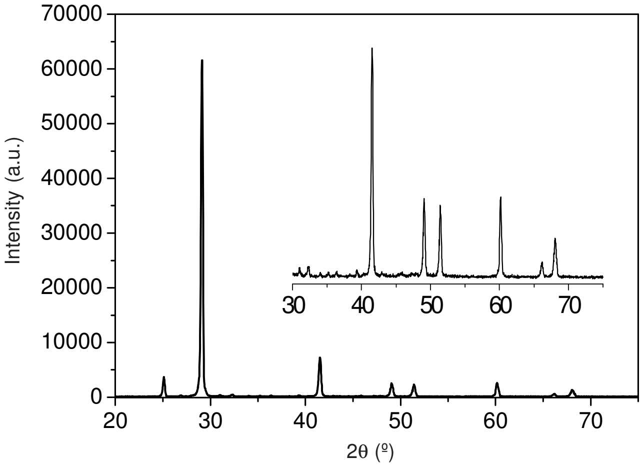


Fig. 8. XRD pattern of the as-synthesized sample

the d value is 2.176, 3.079 and 3.546, respectively. Compared with standard d value of sodium borohydride 2.18, 3.08 and 3.55, the formation of sodium borohydride can be proved. Theoretical yield is 0.106 g, actual yield is 0.016 g and current efficiency is 15.1 %.

Conclusion

The feasibility of preparing sodium borohydride by electrolyzing sodium metaborate has been verified by the obtained product. Also, some exploration has been made to improve experimental conditions. Combined with the result of upper experiment, this system still needs to be improved and optimized. Further working emphases will be focused on improving current efficiency and ameliorating electrode materials. New electrode materials such as alloy and metal materials with oxygenated film will be tried. The final purpose is to integrate the whole reaction in a hydrogen supply system to realize the boron-circulating based hydrogen energy utilization.

ACKNOWLEDGEMENTS

This work is supported by the fund of Department of Education of Anhui Province (KJ2009A135, KJ2010A309).

REFERENCES

1. L. Guetaz, S. Escribano and O. Sicardy, *J. Power Sources*, **212**, 169 (2012).
2. Y. Huang, H. Huang, Y. Liu, Y. Xie, Z. Liang and C. Liu, *J. Power Sources*, **201**, 81 (2012).
3. T.S. Hwang, M.J. Tarca and S.Y. Park, *IEEE T. Power Electr.*, **27**, 3605 (2012).
4. F. Ishak, I. Dincer and C. Zamfirescu, *J. Power Sources*, **212**, 73 (2012).
5. T. Kitahara, H. Nakajima and M. Morishita, *J. Power Sources*, **214**, 100 (2012).
6. S.Y. Chae, J.B. Yadav and O.S. Joo, *Int. J. Energy Res.*, **36**, 1044 (2012).
7. M.Q. Fan, S. Liu, W. Q. Sun, Y. Fei, H. Pan and K.Y. Shu, *Renew. Energy*, **46**, 203 (2012).
8. A. Molino, G. Braccio, G. Fiorenza, F.A. Marraffa, S. Lamonaca, G. Giordano, G. Rotondo, U. Stecchi and M. La Scala, *Fuel*, **99**, 245 (2012).
9. X.G. Yang, Q. Ye and P. Cheng, *Int. J. Heat Mass Transfer*, **55**, 4754 (2012).
10. N.A. Choudhury, J. Ma and Y. Sahai, *J. Power Sources*, **210**, 358 (2012).
11. D.H. Duan, S.B. Liu and Y.P. Sun, *J. Power Sources*, **210**, 198 (2012).
12. V.G. Minkina, S.I. Shabunya, V.I. Kalinin, V.V. Martynenko and A.L. Smirnova, *Int. J. Hydrogen Energy*, **37**, 3313 (2012).
13. P.L. Ng, A. Jamaludin, Y. Alias, W.J. Basirun, Z.A. Ahmad and A.A. Mohamad, *J. Appl. Polym. Sci.*, **123**, 2662 (2012).
14. S. Tominaka, *Chem. Commun.*, **48**, 7949 (2012).
15. C.W. Tsai, H.M. Chen, R.S. Liu, J.F. Lee, S.M. Chang and B.J. Weng, *Int. J. Hydrogen Energy*, **37**, 3338 (2012).
16. H.I. Schlesinger and H.C. Brown, Method of Preparing Alkali Metal Borohydrides, US Patent 2534533 (1950).
17. K. Yoshitsugu and H. Tetsuya, *Int. J. Hydrogen Energy*, **28**, 989 (2003).
18. Z.P. Li and B.H. Liu, *J. Alloy Compd.*, **354**, 243 (2003).
19. P.M. Jeffers and S.H. Bauer, *Inorg. Chem.*, **20**, 1698 (1981).
20. D.N. Bingham, B.M. Wilding, K.M. Klingler, W.T. Zollinger and K.M. Wendt, Method of Forming a Chemical Composition, US Patent 20050077170 A1 (2005)
21. V.C.Y. Kong, F.R. Foulkes and D.W. Kirk, *Int. J. Hydrogen Energy*, **24**, 665 (1999).
22. J.Q. Wang, Y.P. Sun and Z.H. liang, *J. Taiyuan Univ. Technol.*, **37**, 539 (2006).