

THE ELECTROCHEMICAL PROPERTIES OF SODIUM/IRON SULFIDE BATTERY USING IRON SULFIDE POWDER COATED WITH NICKEL

J. S. Kim¹, J. H. Yu¹, H. S. Ryu¹, K. W. Kim¹, T. H. Nam¹, J. H. Ahn², G. Wang^{1,3}
and H. J. Ahn¹

¹School of Materials Science and Engineering, *i*-Cube Center, WCUNGB, ReCAPT,
Gyeongsang National University, Jinju, 660-701, Korea

²Department of Chemical & Biological Engineering, Gyeongsang National University, Korea

³Department of Chemistry and Forensic Science, University of Technology Sydney, Australia

Received: February 17, 2011

Abstract. To develop the battery with low cost and high energy density, Na/TEGDME/FeS cell was prepared using Ni-plated FeS powder. Electrochemical properties of Na/FeS cells were investigated by cyclic voltammogram measurement and charge-discharge tests. The Na/FeS cell showed a high initial discharge capacity of 525 mAh/g-FeS in the current density of 0.1C-rate. The FeS electrode showed two reduction peak potentials at 0.87 and 1.39 V and broad one oxidation peak between 1.23 V and 2.3 V. The discharge products might be sodium sulfide of Na₂S_x (x = 1 to 5). The discharge capacity of 195 mAh/g-FeS was maintained after 150th cycle.

1. INTRODUCTION

Because of environmental issues and high oil price, many countries are extensively developing practical hybrid electric vehicles (HEVs), electric vehicles (EVs) and electricity storage system. The success of these applications depends primarily on the performances of the battery. Therefore, it is necessary to develop the electrode materials which have high specific energy density and low cost [1,2]. Especially, material cost is important for a large scale battery for HEVs, EVs, and electricity storage system. From this point of view, sodium is very promising anode material because of abundance. Thus, the sodium cost is lower than lithium [3].

Metal sulfides such as FeS, FeS₂, CuS, Cu₂S, NiS, Ni₃S₂, and NiS₂ are good candidates for cathode materials [4-13]. Especially, iron sulfides have been demonstrated to be potential electrode materials among metal sulfides due to nontoxicity and

high theoretical specific capacities. Na/FeS₂ cell showed high discharge capacity at the first cycle, but bad cycle performances with the rapid discharge capacity degradation [14,15]. However, the Li/FeS cell showed good cycle property when FeS electrode coated with metallic nickel [16,17]. Although FeS coated with nickel was a good cathode material, there was no report about the electrochemical property of Na/FeS battery.

In this work, we prepared FeS electrode coated with nickel. The electrochemical properties of Na/FeS cells were investigated from charge-discharge curves, CV, SEM, DSC data.

2. EXPERIMENTAL

We prepared iron sulfide (FeS) powder by mechanical alloying method. Pure iron and sulfur powders were weighed in an atomic ratio of 1:1. The grinding media were a set of six hardened-steel balls of 12.5

Corresponding author: H.J. Ahn, e-mail: ahj@gnu.ac.kr

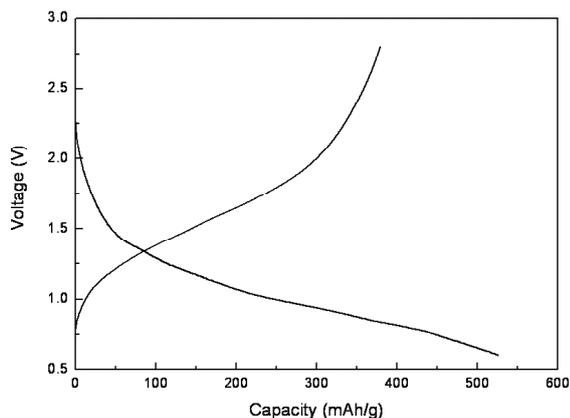


Fig. 1. The first charge and discharge curves of Na/FeS cell.

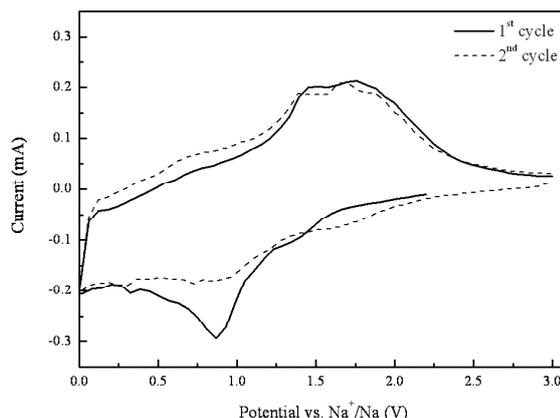


Fig. 2. Cyclic voltammogram of Na/FeS cell with scan rate of 0.1 mV/s.

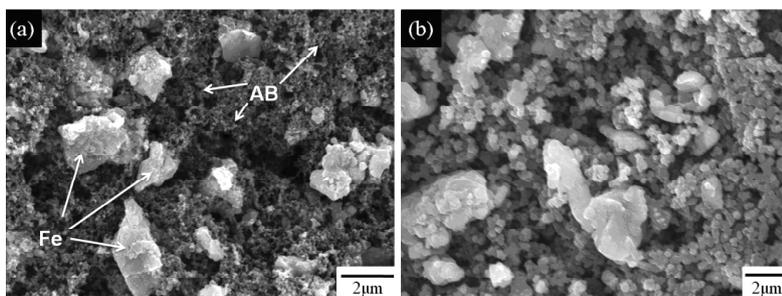


Fig. 3. Surface morphologies of (a) original FeS electrode and (b) electrode after the first discharge.

mm diameter. The charge ratio of ball to powder was kept constant at 20:1. Metallic nickel was coated on FeS powder by electroless plating method. Distilled water, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and FeS powder were mixed by vigorous stirring at 60 °C for 30 min and then dried in an oven at 60 °C for 3 h. The FeS electrode was prepared from nickel plated FeS powder of 60 wt.%, acetylene black (Alfa) of 20 wt.% and poly(vinylidene fluoride) (Aldrich) of 20 wt.% in acetone solvent. The prepared slurry was ultrasonicated for 20 min and then was mixed by attrition ball milling for 2 h. Finally, it was cast on a glass plate and then dried at room temperature until the solvent was evaporated completely. Electrolyte solution was prepared by dissolving 1M NaCF_3SO_3 (Aldrich) in TEGDME (Aldrich) electrolyte in an Ar glove box. The sodium electrode was prepared by cutting sodium ingot in an argon-filled glove box. The Na/FeS cell was assembled by stacking in turn the Ni-plated FeS cathode, porous polypropylene separator (Celgard® 2400) with 1M NaCF_3SO_3 in TEGDME electrolyte and sodium anode in a swagelock® type cell.

The cell was allowed to equilibrate open circuit voltage condition for 2 h before a discharge test. The cell was discharged to 0.6 V and charged to at

2.8 V with a constant current density of 61mA/g-FeS (0.1C-rate) by using a WBCS3000 (WonA Tech. Co.) at room temperature. Cyclic voltammograms (CV) were performed at the scan rate of 0.1 mV/s versus Na^+/Na at room temperature. The electrodes were analyzed by scanning electron microscopy (SEM, JSM 5600). The thermal properties of the discharge products were measured by differential scanning calorimetry (DSC, TA Instrument Inc.) with heating rate of 5 °C/min from 90 to 350 °C.

3. RESULTS AND DISCUSSION

Fig. 1 shows the first charge and discharge curves of the Na/FeS cell under a constant current density of 0.1 C at room temperature. The discharge curve has a slope-shape profile without a distinct plateau and a high specific discharge capacity of 525 mAh/g-FeS. The first charge curve has a specific capacity of 380 mAh/g-FeS and shows a slope-shape profile. The irreversible capacity is 145mAh/g-FeS that sodium atoms can not be transferred completely from the FeS electrode to the sodium anode and remains in the FeS electrode. From the phase diagram between sodium and sulfur, there are many kinds of sodium sulfides such as Na_2S , Na_2S_2 ,

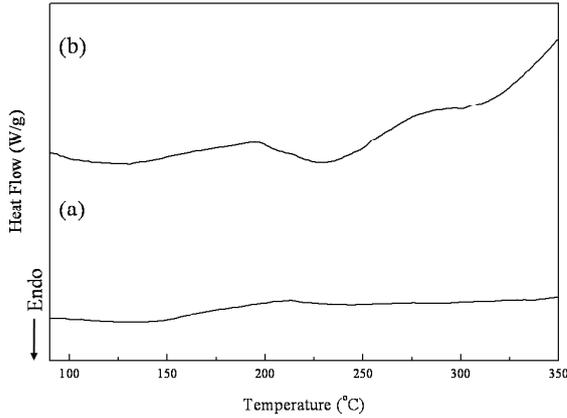


Fig. 4. DSC curves of (a) original FeS electrode and (b) electrode after the first discharge.

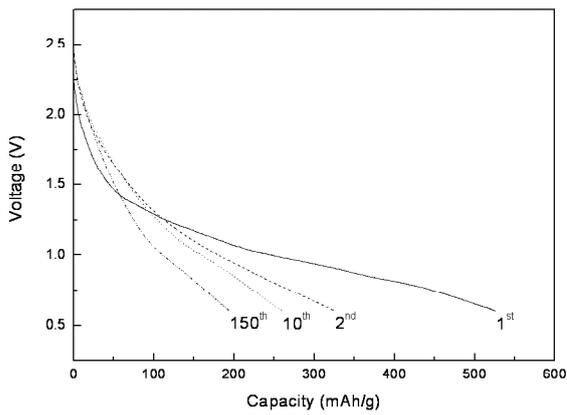
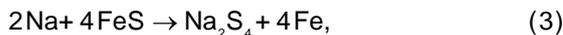
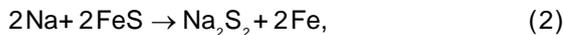
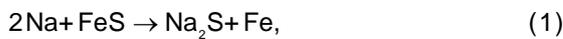


Fig. 5. Change of discharge curves of Na/FeS cell until the 150th cycle.

Na_2S_4 , and Na_2S_5 . A discharge process of the Na/FeS cell could be explained as follows.



The theoretical capacities of Na_2S , Na_2S_2 , Na_2S_4 and Na_2S_5 are 610, 305, 152, and 122 mAh/g-FeS, respectively. Theoretical capacity of Na_2S_2 , Na_2S_4 and Na_2S_5 is lower than the first discharge capacity of 525 mAh/g shown in Fig. 1. Therefore, the discharge process should include the formation of Na_2S phase.

Fig. 2 shows CV curves of the Na/FeS cell for the first and second cycles. The FeS electrode shows two reduction peak potentials at 0.87 and 1.39 V and broad one oxidation peak at the range

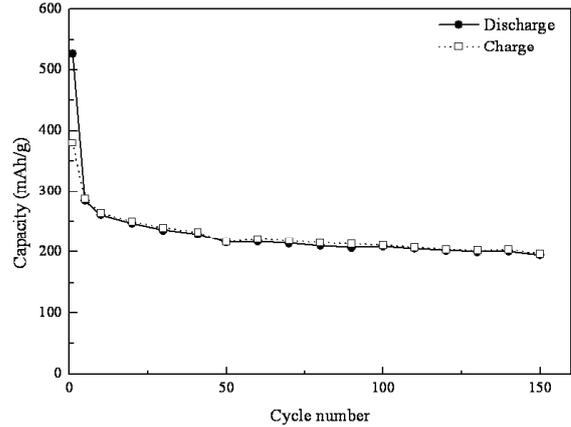


Fig. 6. Cyclic performance of Na/FeS cell until the 150th cycle.

between 1.23 V and 2.3 V. CV curve coincided with the first charge and discharge curves shown in Fig. 1. The peak intensity of reduction reaction decreased at the second cycling, which could be related to decrease of the second discharge capacity.

Fig. 3 shows the changes of SEM images in the FeS electrode after discharge reaction. The original FeS electrode represented a mixture of FeS powder and acetylene black. After the first discharge reaction, particles size of FeS electrode increased.

Fig. 4 shows the change of DSC curves after the first discharge reaction. The original FeS electrode had no endothermic peaks, but the broad endothermic peak was observed in the discharged electrode at the temperature range between 200 and 280 °C. Endothermic peak according to melting point of sodium (97 °C) was not observed after discharge reaction. Since the melting point of Na_2S and FeS are 974 °C and 1194 °C, respectively, the existence of these compounds could not be identified at this temperature range. From the sodium and sulfur phase diagram, the melting temperature of Na_2S_4 and Na_2S_5 is 235 °C and 237 °C, respectively. Therefore, endothermic peak from 200 to 280 °C could be related to melting of Na_2S_4 and Na_2S_5 . From the DSC and discharge curve, final products of the first discharge reaction were Na_2S_4 , Na_2S_5 and Na_2S phases. Therefore, a discharge process of Na/FeS cell could be explained from Eqs. (1), (3), and (4)

Fig. 5 shows the change of discharge curves of the Na/FeS cell during 150 cycles. The second discharge curve showed steeper slopes than the first discharge curve and had discharge capacity of 260 mAh/g.

Fig. 6 shows cyclic performance of Na/FeS cell until the 150th cycle. The Na/FeS cell shows rela-

tively the good capacity retention until the 150th cycle. A large decline of the discharge capacity appeared until 10 cycles, and then fade rate of the capacity diminished substantially to 195 mAh/g-FeS. This cycle performance of the Na/FeS cell is better than Na/synthesized FeS₂ and Na/natural pyrite cells [14,15].

4. CONCLUSION

We investigated the electrochemical properties of Na/FeS cell using the Ni-plated FeS electrode fabricated by electroless plating method. From the result of CV measurements, the Na/FeS electrode shows two reduction peak potentials at 0.87 and 1.39 V and broad one oxidation peak at the range between 1.23 V and 2.3 V. The discharge curve of the Na/FeS cell has a slope-shape profile without a distinct plateau and a high specific discharge capacity of 525 mAh/g-FeS. The Na/FeS cell shows relatively the good capacity retention of 195 mAh/g-FeS until the 150th cycle.

ACKNOWLEDGEMENT

This research was supported by the Basic Science Research (2010-0015934) and PRC (2010-0002179) program through the National Research Foundation of Korea.

REFERENCES

- [1] N. Sato // *J. Power Sources* **70** (2001) 99.
- [2] M. Ikoma and N. Fujioka // *Kagaku Kogyo* **45** (1998) 49.
- [3] J.L. Sudworth and A.R. Tilley, *The Sodium Sulfur Battery* (Chapman & Hall, London, 1985).
- [4] E. Strauss, S. Calvin, H. Mehta, D. Golodnitsky, S.G. Greenbaum, M.L. den Boer, V. Dusheiko and E. Peled // *Solid State Ionics* **52** (2003) 164.
- [5] G. Ardel, D. Golodnitsky, K. Freedman, E. Pled, G.B. Appetecchi, P. Romagnoli and B. Scrosati // *J. Power Sources* **152** (2002) 110.
- [6] S.H. Yang and Q.C. Horn // *Electrochim. Acta* **2613** (2001) 46.
- [7] J.W. Choi, G. Cheruvally, H.J. Ahn, K.W. Kim and J.H. Ahn // *J. Power Sources* **158** (2006) 163.
- [8] B.C. Kim, K. Takada, N. Ohta, Y. Seino, L. Zhang, H. Wada and T. Sasaki // *Solid State Ionics* **2383** (2005) 176.
- [9] A. Debart, L. Dupont, R. Patrice and J.M. Tarascon // *Solid State Sci.* **640** (2006) 8.
- [10] A. Hayashi, T. Ohtomo, F. Mizuno, K. Tadanaga and M. Tatsumisago // *Electrochim. Acta* **893** (2004) 50.
- [11] J.S. Kim, D.Y. Kim, G.B. Cho, T.H. Nam, K.W. Kim, H.S. Ryu, J.H. Ahn and H.J. Ahn // *J. Power Sources* **864** (2009) 189.
- [12] S.C. Han, K.W. Kim, H.J. Ahn, J.H. Ahn and J.Y. Lee // *J. Alloys Compd.* **247** (2003) 361.
- [13] J.S. Kim, H.J. Ahn, H.S. Ryu, D.J. Kim, G.B. Cho, K.W. Kim, T.H. Nam and J.H. Ahn // *J. Power Sources* **852** (2008) 178.
- [14] T.B. Kim, J.W. Choi, H.S. Ryu, G.B. Cho, K.W. Kim, J.H. Ahn, K.K. Cho and H.J. Ahn // *J. Power Sources* **1275** (2007) 174.
- [15] T.B. Kim, W.H. Jung, H.S. Ryu, K.W. Kim, J.H. Ahn, K.K. Cho, G.B. Cho, T.H. Nam, I.S. Ahn and H.J. Ahn // *J. Alloys Compd.* **304** (2007) 449.
- [16] S.H. Kim, Y.J. Choi, D.H. Kim, J.H. Jung, K.W. Kim and H.J. Ahn // *Surface Review Lett.* **35** (2008) 15.
- [17] B.C. Kim, K. Takada, N. Ohta, Y. Seino, L. Zhang, H. Wada and T. Sasaki // *Solid State Ionics* **2383** (2005) 176.