

Short communication

## Electrochemical properties of sodium/pyrite battery at room temperature

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### Abstract

We investigated sodium/pyrite battery because sodium and pyrite (natural FeS<sub>2</sub> ore) were very cheap materials. The sodium/pyrite battery showed high discharge capacity of 630 mAh g<sup>-1</sup>-FeS<sub>2</sub> with 50 mA g<sup>-1</sup>-FeS<sub>2</sub> at room temperature, which was higher than that of Li ion battery and Na/synthetic FeS<sub>2</sub> battery. First discharge curve had one plateau-shaped voltage region of 1.3 V, which disappeared and changed to sloping shape after second cycle. The discharge capacity decreased continuously by repeated charge–discharge cycling, and remained 85 mAh g<sup>-1</sup>-FeS<sub>2</sub> after 50th cycles.

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### 1. Introduction

Because of environmental issues and high oil price, many countries are extensively developing practical hybrid electric vehicles (HEVs) and electric vehicles (EVs). The success of these EVs depends primarily on the performances of the battery that is adopted for the vehicles and it is important to develop new types of batteries with high energy density and high specific power as well as to improve conventional batteries [1].

Ni/MH and Li battery have been good candidates because of high specific power and high energy density. However, raw materials of these batteries were more expensive than lead acid battery which has low energy density and environmental problem by Pb [2–4]. It is necessary to develop battery which has high specific energy density and is economical and environment-friendly.

Because of low material cost, many researches have been performed on electrochemical properties of various metal sulfides such as FeS<sub>2</sub> [5–9], CuS<sub>2</sub> [10,11], NiS<sub>2</sub> [10,12] and CoS<sub>2</sub> [10], etc. Metal sulfides could be used as cathode or anode material for lithium battery.

Especially, natural FeS<sub>2</sub> ore (pyrite) has been demonstrated to be potential electrode materials among of metal sulfides, because pyrite was a non-toxic material, high theoretical specific capacity of 894 mAh g<sup>-1</sup>-FeS<sub>2</sub> (4e<sup>-</sup>/FeS<sub>2</sub>) and cheap price (US\$ ~0.5 kg<sup>-1</sup>, compared to US\$ 30–80 kg<sup>-1</sup> for lithiated metal oxides) [13]. Li/FeS<sub>2</sub> battery was known as a primary battery, which has already been commercialized. Although Li/FeS<sub>2</sub> battery showed high theoretical capacity of 893 mAh g<sup>-1</sup>-FeS<sub>2</sub>, lithium is very expensive material. Sodium is an attractive anode material because of low material cost, high theoretical specific capacity of 1160 mAh g<sup>-1</sup>-sodium, and a high potential of -2.71 V compared to SHE [14]. Na/FeS<sub>2</sub> redox couple could be potential battery for electric vehicle because each electrode materials have many advantages.

However, there were only a few studies on the sodium battery using pyrite cathode at room temperature. Ahn and co-workers [15] reported that Na/synthetic FeS<sub>2</sub> battery showed the first discharge capacity of 447 mAh g<sup>-1</sup>-FeS<sub>2</sub>, and 70 mAh g<sup>-1</sup>-FeS<sub>2</sub> after 50th cycles at room temperature. Although the raw material cost of natural FeS<sub>2</sub> ore (pyrite) is cheaper than synthetic FeS<sub>2</sub>, there was no study about sodium battery using pyrite cathode.

In this study, we prepared sodium/pyrite battery and investigated the electrochemical property at room temperature. Also, we investigated the discharge process of sodium/pyrite using

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scanning electron microscopy (SEM), and energy dispersive X-ray spectrometer (EDS).

## 2. Experimental

### 2.1. Preparation of the pyrite cathode and the electrolyte

Natural pyrite ( $\text{FeS}_2$ , Chile) was ball-milled for 6 h and the powder was sieved (400 mesh). A pyrite electrode was prepared from a suspension of 50 wt% elemental pyrite powder, 25 wt% acetylene black (Alfa Aesar) and 25 wt% poly(vinylidene fluoride) (PVdF, Aldrich Chem. Co.) in *N*-methyl-pyrrolidone (NMP, Aldrich). The suspension was mixed to make homogeneous slurry for 1 h by high energy ball-milling. The slurry was spread upon aluminum foil as current collector using doctor-blade method at room temperature. The composite film was dried at  $80^\circ\text{C}$  for 12 h in an air oven and was cut into disk electrodes. The pyrite electrode film had about  $30\ \mu\text{m}$  thickness and  $1.54\ \text{cm}^2$  area.  $\text{NaCF}_3\text{SO}_3$  (99.9%) and tetraethylene glycol dimethylether (TEGDME) were used after purification by molecular sieve and vacuum heat treatment. Electrolyte solution was prepared by dissolving 1 M  $\text{NaCF}_3\text{SO}_3$  in TEGDME electrolyte in a dry glove box. Sodium electrode was prepared by cutting from sodium ingot in argon gas atmosphere.

### 2.2. Preparation and electrochemical measurements

The sodium/pyrite battery was assembled by stacking celgard which hold the 1 M  $\text{NaCF}_3\text{SO}_3$  in TEGDME electrolyte between the pyrite cathode and the sodium anode in a swagelock<sup>®</sup> type cell. The battery was discharged to 0.8 V and charged to at 2.8 V and a constant specific current of  $50\ \text{mA g}^{-1}\text{-FeS}_2$  by using a WBCS3000 (WonA Tech. Co.) at room temperature. The battery was allowed to equilibrate OCV condition for 1 h before a discharge test. The electrode was analyzed by scanning electron microscopy (SEM, JEOL JSM 5600) and energy dispersive X-ray spectrometer (EDS, Oxford).

## 3. Results and discussion

Fig. 1 shows the first discharge–charge profile of sodium/pyrite battery at room temperature. The sodium/pyrite battery has the first discharge capacity of  $630\ \text{mAh g}^{-1}\text{-pyrite}$ , which is higher than one of Na/synthetic  $\text{FeS}_2$  battery [15], and lower than one of the Li/pyrite batteries of  $772\ \text{mAh g}^{-1}\text{-pyrite}$  [8]. The sodium/pyrite battery has plateau-shaped voltage region of 1.3 V. The first charge capacity is  $450\ \text{mAh g}^{-1}\text{-FeS}_2$  and charge curve is slope-shaped.

From the phase diagram between sodium and sulfur, there are many kinds of sodium sulfides, such as  $\text{NaS}_2$ ,  $\text{Na}_2\text{S}_3$ ,  $\text{Na}_2\text{S}_2$ ,  $\text{Na}_3\text{S}_2$  and  $\text{Na}_2\text{S}$  [16]. During discharge reaction, iron sulfide can be reduced by following reactions:

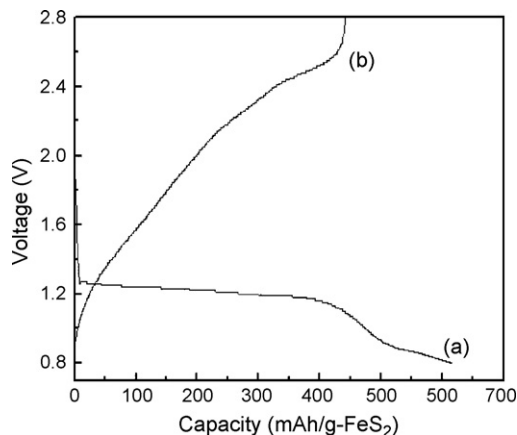


Fig. 1. The first discharge–charge profiles of sodium/pyrite battery. (a) First discharge and (b) first charge.

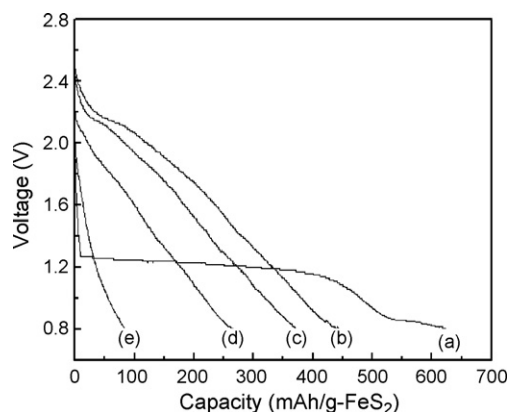


Fig. 2. The changes of discharge curve of sodium/pyrite battery with cycle. (a) First discharge, (b) second discharge, (c) third discharge, (d) fifth discharge, and (e) 50th discharge.



The theoretical capacities by Eqs. (1)–(5) are 149, 299, 447, 673 and  $897\ \text{mAh g}^{-1}\text{-FeS}_2$ , respectively. The first discharge capacity of  $630\ \text{mAh g}^{-1}\text{-pyrite}$  was similar to  $673\ \text{mAh g}^{-1}\text{-FeS}_2$  by formation of  $\text{Na}_3\text{S}_2$ .

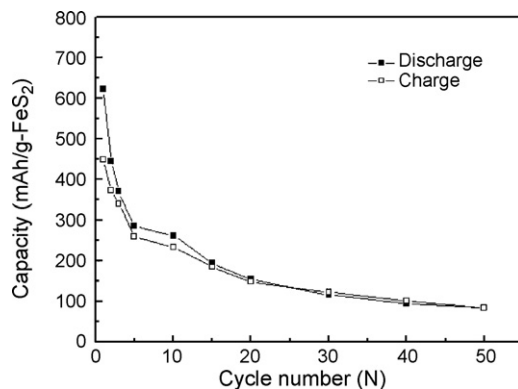


Fig. 3. Change of capacity as a function of cycle life of sodium/pyrite battery.

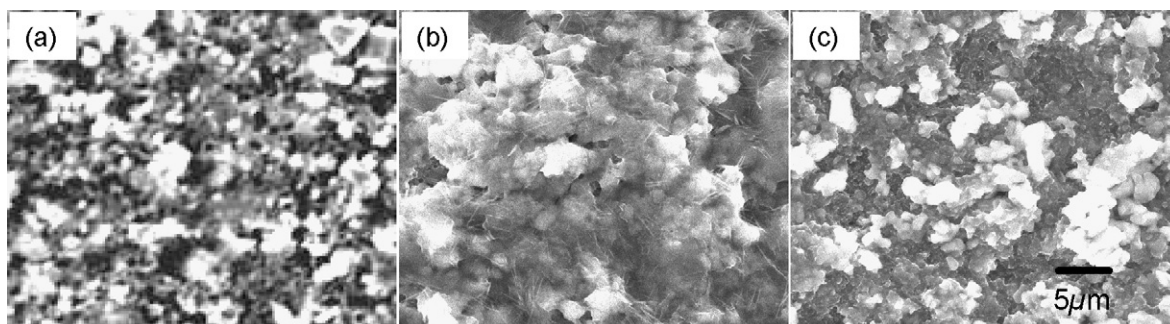


Fig. 4. SEM images of pyrite electrode. (a) Original pyrite electrode, (b) after the first discharge and (c) after the first charge.

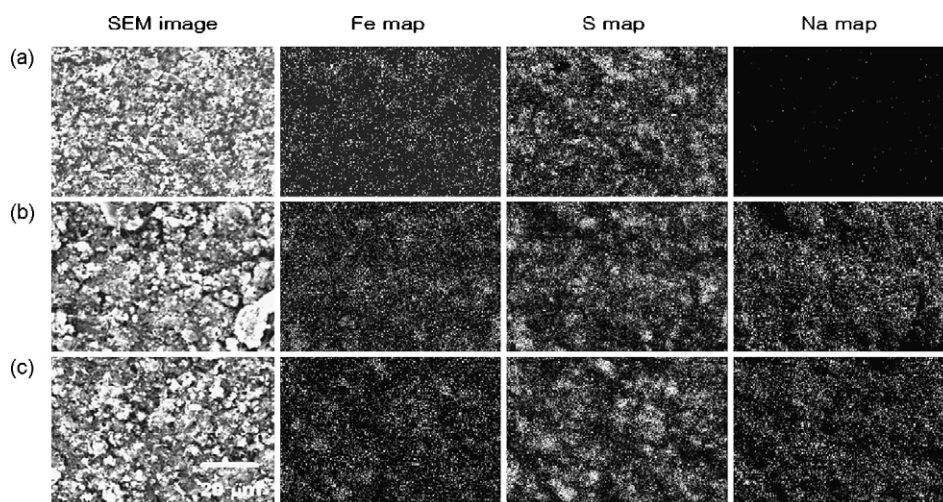


Fig. 5. SEM photographs and EDS mapping data of pyrite electrode. (a) Original pyrite electrode, (b) after the first discharge and (c) after the first charge.

Fig. 2 shows change of discharge curves with repeated charge–discharge cycles. After second cycle, the discharge curve showed slopping phenomena without any plateau-shaped region. This result is similar to one of Na/synthetic  $\text{FeS}_2$  battery [15]. However, Li/ $\text{FeS}_2$  battery [8] and Na/S battery [17] showed plateau-shaped region after repeated cycle.

Fig. 3 shows the change of discharge capacity and charge capacity as a function of cycling numbers. The sodium/pyrite battery shows sharp decline of discharge capacity over the next few cycles, and then fade rate of the capacity diminished substantially to  $85 \text{ mAh g}^{-1}\text{-FeS}_2$  after 50th cycles.

Fig. 4 shows the SEM photographs of pyrite electrode after charge and discharge. Original pyrite electrode represents a homogeneous mixture of each material. Surface morphology of pyrite electrode changes to an agglomerated shape during discharge reaction. Agglomerated shape of electrode after discharge in sodium/pyrite battery is similar to one of Li/S battery which was occurred by dissolution of lithium polysulfides in electrolyte [18]. During discharge process, it might be possible to dissolve the sodium polysulfides. However, the agglomerated shape did not recover to original one by charge process.

Fig. 5 shows SEM photographs and EDS mapping data of pyrite electrodes. Original electrode shows homogeneous mixing of iron and sulfur which caused by intermetallic compound of  $\text{FeS}_2$ . For discharged pyrite electrode, the sodium uniformly distributed on sulfur. After charge, sodium still exists

Table 1

EDS result of pyrite electrode after charge and discharge of sodium/pyrite battery

Electrodes	Major elements (at.%)		
	Sulfur	Iron	Sodium
(a) Original pyrite electrode	67	33	0
(b) Pyrite electrode after the first discharge	34	15	51
(c) Pyrite electrode after the first charge	45	21	34

in pyrite electrode, which means partially recovery to original cathode.

Table 1 represents composition of pyrite electrode after discharge and charge from EDS result. After discharge, the discharging product might be  $\text{Na}_3\text{S}_2$  because atomic ratio of Na to S is 3:2 by EDS result, which coincided with the first discharge capacity of reaction (3).

However, pyrite electrode contains sodium element after charge, which meant the irreversible process. The irreversible capacity should be related with decrease of discharge capacity with cycling shown in Fig. 3.

#### 4. Conclusion

The first discharge capacity of sodium/pyrite battery is  $630 \text{ mAh g}^{-1}\text{-FeS}_2$ . The discharge capacity continuously decreases with cycling, and remains  $85 \text{ mAh g}^{-1}\text{-FeS}_2$  after 50th

cycles, which should be related with irreversible reaction of sodium. First discharge curve has one plateau-shaped voltage region of 1.3 V, which disappears and changes to sloping shape after second cycle.

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