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A study on the Active Material FeS_2 in Battery Fabricated by Mechanical Alloying

Woo-Hyun Jung, In-Shup Ahn*, Hyo-Jun Ahn, Sung-Yeal Bae, Tek-Kyoung Sung, Tae-Bum Kim and You-Young Kim[a]
Division of Advanced Materials Science and Engineering & ITRC, Gyeongsang National University, Jinju, Gyeongnam-do, 660-701, Korea
[a]Jinju National University, Chiram-dong, Jinju-si, Gyeongsangnam-do, 660-758, Korea
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Abstract As the electrodes of secondary battery are made with sulfur compounds, excellent electrode system of environmental non-toxicity, high specific energy density and low material cost can be obtained. In this study, the FeS_2 fine compound powders for active material in the battery were synthesized by mechanical alloying. Fine Fe-53.5 wt.%S powders of 450 nm of mean size were fabricated by mechanical alloying for 60 hours at the horizontal attritor. As the mechanical alloying time increases, particle size of Fe-53.5 wt.%S was decreased and steady state of Fe-53.5 wt.%S compound powders was obtained at 30 hours. Fe-53.5 wt.%S cathode shows the excellent discharge capacity (1011 mAh/g).

Keywords : Mechanical alloying, Battery, Active materials, Metal sulfide

1. Introduction

In order to replace the Ni-Cd battery, which has the environmental problem, Li electrode battery has been developed since 1960. Because the Li metals is stable in the $LiClO_4$, liquid SO_2 nonaqueous electrolyte, active materials for cathode are used as the form of the $LiMn_2O_4$, and $LiCoO_2$ and $LiNiO_2$. However, these materials are very expensive and have low discharge capacity under 200 mAh/g-active materials.

Many transition metal sulfides have more than one reaction potential plateaus in Li-ion conducting electrolytes. The equivalent potential of one of the plateaus for each sulfide is around 1.5V vs Li+/Li. Among the various attractive cathode materials, metals sulfides are promising materials because of their high theoretical capacity[1-12]. As NiS synthesized by ball milling was reported[13,14] previously, the homogeneous NiS phase readily forms after ball milling for 12 hours under Ar atmosphere. The ball milled NiS particles are smaller than those of the starting materials and have a nanocrystalline structure. The NiS powders synthesized by mechanical alloying show good cycling properties, even after 100 cycles at 30°C. Li/FeS_2 battery has many attractive properties such as a high theoretical energy density and cheap and nontoxic materials. Primary cell, containing lithium salt dissolved in organic electrolytes, has been commercialized and is used in cameras, computer, camcorders and cellular phones. The discharging capacity of FeS_2 cathode increased as the powder size decreased according to the previous paper[15].

Mechanical alloying (MA) method is powerful processing to fabricate fine powder particles. However, the study of the iron sulfide system by mechanical alloying methode has not been com-

*Corresponding Author : [Tel : +82-55-751-5304; E-mail : ais@gsnu.ac.kr]

pleted.

The purpose of this research was to make fine compound powders for active materials of Li battery by MA methods and to characterized the properties of discharge capacity as a function of MA time.

2. Experimental Procedure

Iron (99.9%, -325 mesh) and sulfur (-100 mesh) powders were weighed in a 1:2(mol/mol) atomic ratio and sealed in a hardened stainless steel vial in a glove box with an Ar atmosphere. Milling was conducted using horizontal Zoz simoloyer and the grinding media was a 1/4" high Cr stainless steel ball (SUS 304). The charge ratio (mass of grinding balls/mass of powder charge) was kept constant at 40:1. To avoid cold welding, stearic acid ($CH_3(OH_2)_{16}CO_2H$) of 0.64 g was added. The rotating speed of the impeller was 1000 rpm for 4 min and 300 rpm for 1min alternatively. The maximum MA time was 60 hours. The structure of the ball-milled powder was characterized using by X-ray diffraction (XRD, Rigaku). The morphology of the iron sulfide powder prepared by mechanical alloying was characterized by scanning electron microscopy (SEM, JEOL). Mean particle size was analyzed by the laser diffraction method.

Active materials (Fe-53.5 wt.%S), poly vinylidene fluoride (PVDF, Aldrich Co., 20 wt.%) binder, acetylene black (AB, 30 wt.%) and 1-Methyl-2-pyrrolidinone (NMP, Aldrich Co.) solution were mixed for preparing FeS_2 composite electrodes. The obtained slurries were spread upon aluminum foil at room temperature in air using the Doctor-blade casting method. After evaporating solvent at 80°C in vacuum oven, the electrode foil was cut into disk shape electrodes (1.1 cm diameter). These electrode disk were dried in a vacuum at 80°C for 24h and then stored within the glove box. The thickness of the resulting composite cathode layer was ranged from 20 to 30 μm. Tetra Ethylene Glycol Dimethylether (10 ml)+$LiCF_3SO_3$ (1.56 g) was used as liquid electrolyte, and the Li/TG/FeS_2 cells were assembled in stainless steel cell holders made with a Swagelok-

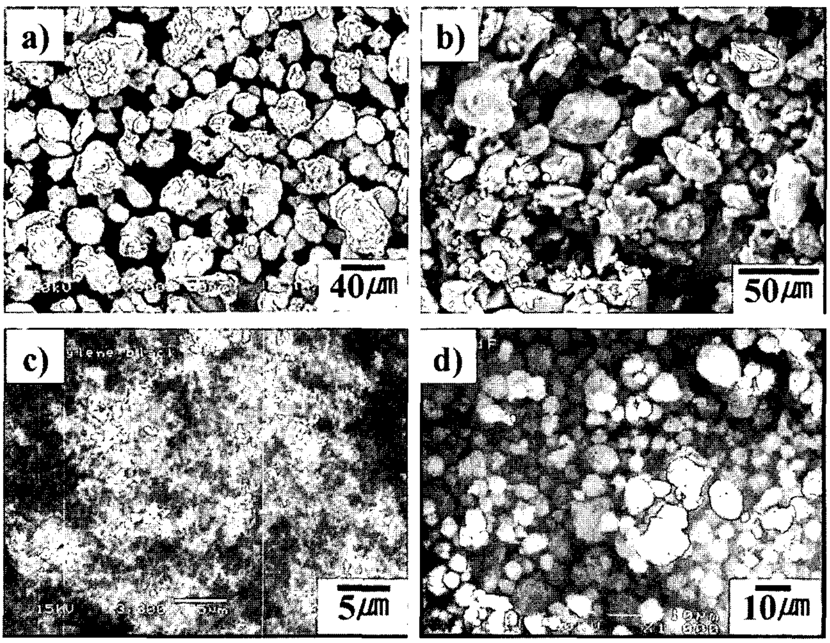

Fig. 1. SEM micrographs of raw powders for FeS_2 electrode; a) Fe, b) S, c) Acetylene Black, d) PVdF

type cell. The fabricated lithium sulfur cell was maintained for 1hr at 80°C, and then a discharge test was performed. The cells were discharged and charged galvanostatically. The potential sweep rate was 0.05 mV/s and the voltage ranged between 3.0 and 0.9V.

3. Result and Discussion

Fig. 1 shows the scanning electron microscopy (SEM) photos of Fe, S, carbon and PVdF powders used in this experiments. The mean particle size of irregular type iron was 24 μm(a), and sulfur powder (b) shows irregular shape with wide size distribution. Fig. 1(c) and (d) was SEM morphologies of carbon and PVdF powders, respectively. The powder size of carbon was submicron, and mean size of round shape PVdF powder was 5 μm.

Fig. 2 shows the SEM morphologies of the mechanically alloyed Fe-53.5 wt.%S for various times. The mechanically alloyed powders for 5 hours show finely fractured iron and sulfur powders, and partially agglomerated. The agglomerated Fe and S powder, and cold welded irregular shape powders can be observed in powder milled for 10 hours. After 20 hours milling, the mixed powders were fractured to fine compound particles, and particles were refined up to more at 20 hours milling.

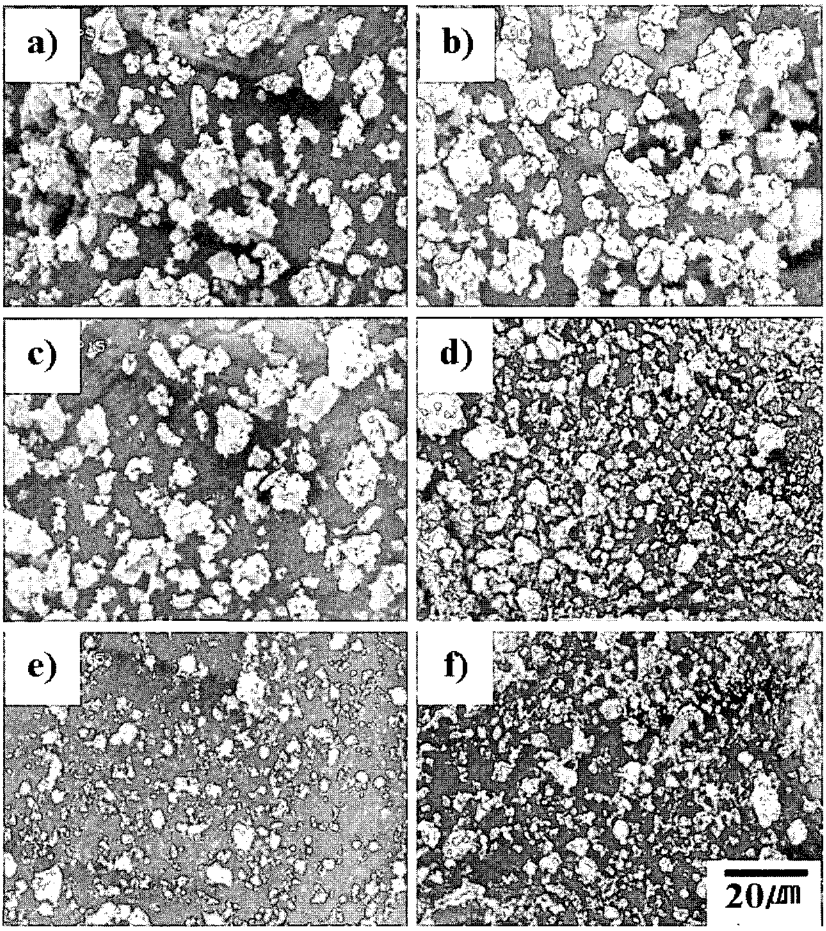

Fig. 2. SEM micrographs of mechanical alloyed Fe-53.5 wt.%S powders with milling time; a) 5h, b) 10h, c) 20h, d) 30h, e) 40h and f) 60h

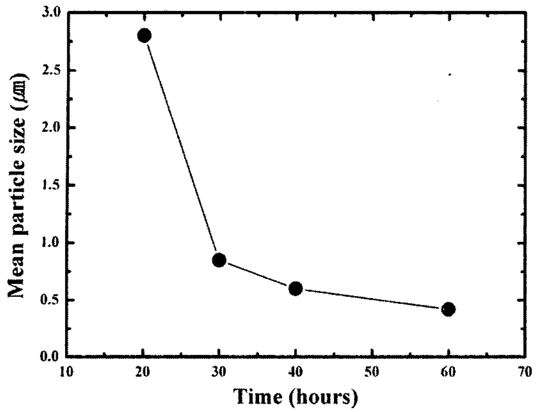

Fig. 3. Variation in mean particle size of mechanically alloyed Fe-53.5 wt.%S powders with milling time.

The particle size did not decrease considerably after 30 hours milling. As the MA times increases, particle shape was changed to round form. This phenomena depend on the steady state between the repeated cold welding and the fracture.

Fig. 3 shows the mean particle size of mechanically alloyed Fe-53.5 wt.%S measured by N4 PLUS particle size analyzer. The mean particle size of 20 hours mechanically alloyed powders was 2.8 μm, and decreased to 0.85 μm at 30 hours. The mean sizes of powders milled for 40 hours and 60 hours were 0.64 μm and 0.45 μm, respectively. From the 30 hours milling, it was considered that the steady state of alloying was obtained.

Fig. 4 shows the XRD pattern of mechanical alloyed Fe-53.5 wt.%S for various times. Alloy phase was not formed until 5 hours milling, however the FeS_2 peak was appeared at 20 hours milling, and FeS_2 (Pyrite) phase was formed at 30hours milling by consuming the iron element completely. FeS_2 phase has partially changed FeS phase after 40 hours milling, because FeS phase was stable at high temperature. It is considered due to the high mechanical energy accumulated in FeS2 powders by MA. As the milling time increases to 60 hours, the diffraction peak intensity was lowered because of particle size refining effect.

Fig. 5 shows the SEM images of FeS_2 cathode surface prepared by MA, before discharge test. As shown in the the image FeS_2 cathode is homogeneouly dispersed.

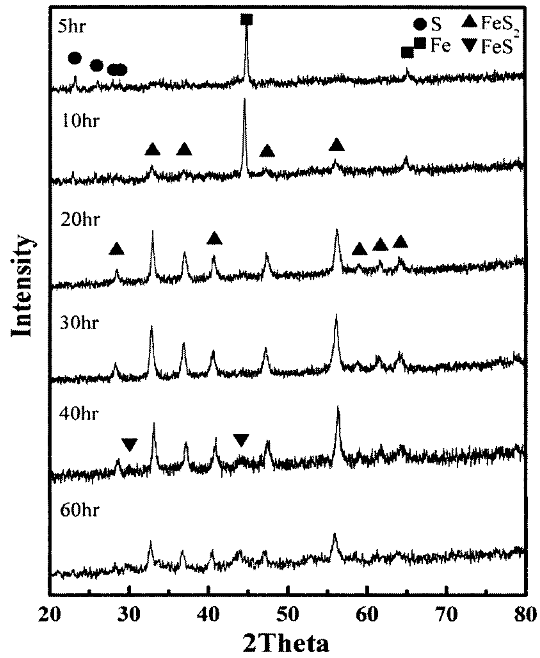

Fig. 4. XRD patterns of mechanically alloyed Fe-53.5 wt.%S powders with milling time.

Fig. 6 represents the initial discharge profiles of Li/FeS_2 cells with current density of 50 mA/g at room temperature for Fe-53.5S powders prepared by MA. The discharge capacity of FeS_2 cathode made by 20 hours and 30 hours milling shows 447 mAh/g and 1011 mAh/g, respectively. However, discharge capacity was decreased as the MA time increased, because of FeS phase functioned as impurity. The discharge curves of 30 hours alloying have only one plateau at about 1.5V. FeS_2 cell prepared by 30 hours milling have a good property for the application as primary Li/FeS_2 batteries. The discharge reaction at 1.5V was known to give a mixture of plate-shaped lithium sulfide and amorphous Fe as final product. The reduction of FeS_2 in the discharge occurs simultaneously in two steps (reaction 1 and 2) at room temperature[16].

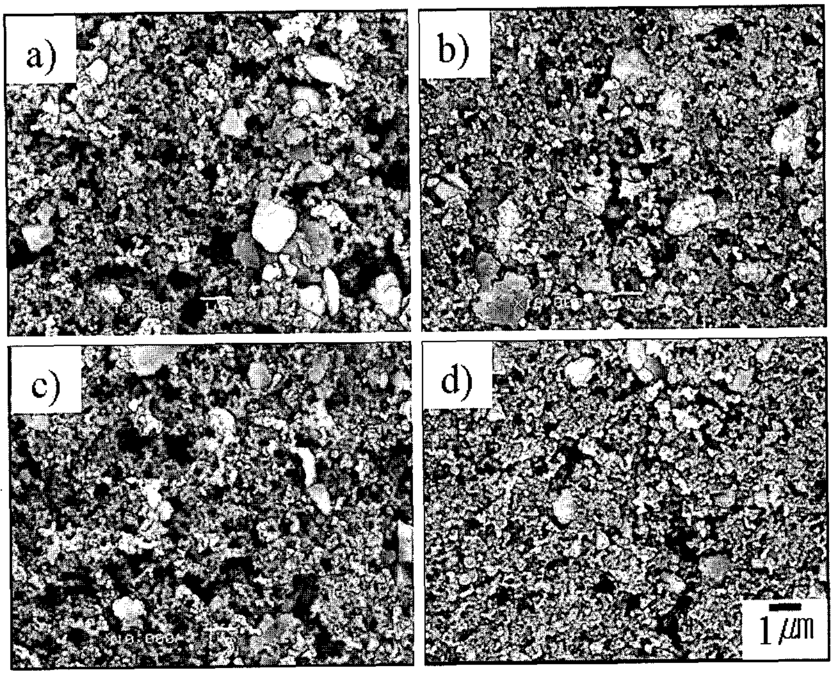

Fig. 5. SEM micrographs of FeS_2 cathode prepared by MA before discharge test; a) 20h, b) 30h, c) 40h and d) 60h

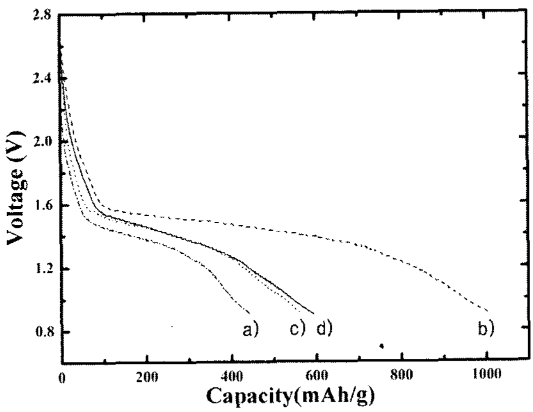

Fig. 6. Initial discharge profile of Li/FeS_2 cell with milling time at room temperature; a) 20h, b) 30h, c) 40h and d) 60h

$$FeS_2+2Li^{+}+2e^{-} \rightarrow Li_2FeS_2(FeS+Li_2S) \quad (1)$$

$$Li_2FeS_2(FeS+Li_2S)+xLi+xe^{-} \rightarrow Li_2+xFeS_2 \quad (2)$$

Fig. 7 (a) and (b) are the XRD patterns of FeS_2 cathodes prepared by mechanically alloyed for 20 hours and 30 hours, respectively. The pattern of FeS_2 cathodes before discharge is the same with the pattern after discharge in Fig. 7 (a), in which the residual amount of FeS_2 was shown after discharge test. This means that the first discharge did not occur enough with 435 mAh/g as shown in Fig. 6 in spite of FeS_2 compound with mono phase. The new phase of Li_2FeS_2 was appeared after discharge test, which was formed at the result of $2Li+FeS_2$ reaction as shown in Fig. 7 (b). It could be considered that the FeS_2 compound fabricated by 20 hours milling may be different composition or incomplete alloying compound, which should be analyzed in more detail.

Fig. 8 shows the variation of discharge capacity of Li/FeS_2 cell prepared by MA for 30 hours with the cycle number. During cycling, cell shows a rapid capacity fade. After the 10 th cycle, the capacity remains only 291 mAh/g. It is well known that the main factors affecting cycle life of lithium/sulfur batteries are formation of lithium polysulfides (Li_2Sn) soluble in electrolyte and insoluble lithium sulfide (Li_2S) in the cathode film on discharging. Soluble lithium polysulfides can give rise to a shut-

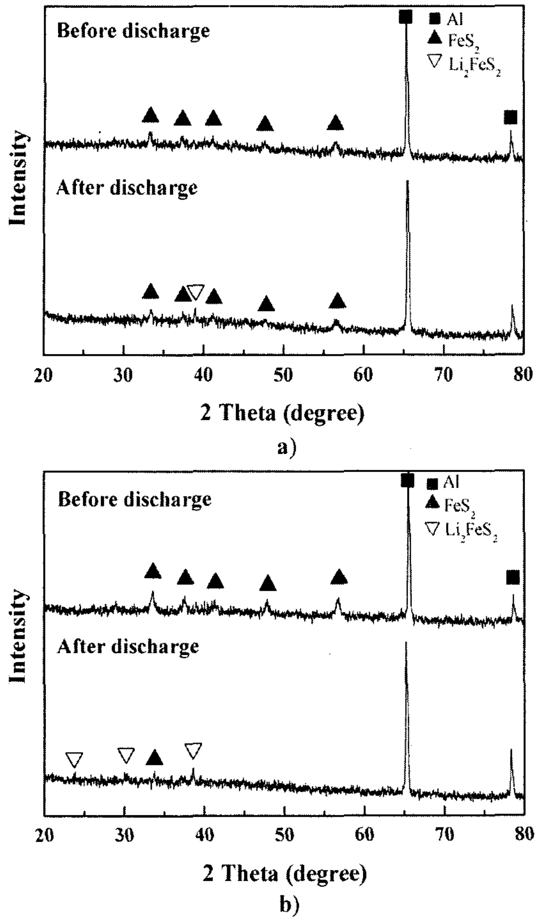

Fig. 7. XRD patterns of FeS_2 cathode prepared by MA for a) 20h and b) 30h.

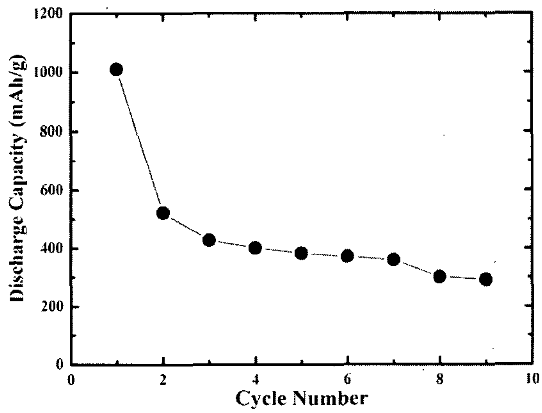

Fig. 8. Cyclic performance of Li/FeS_2 cell of 30 hours mechanical alloying.

tle mechanism, which in turn results in the decrease of the discharging capacity during repeated cycling. The insoluble lithium sulfide cannot be fully reduced to the long chain sulfur during charging, and the active sulfur available was therefore decreased during repeated cycling[17].

4. Conclusion

1. The FeS_2 compound powders fabricated by MA after 20hours have crystal structure of pyrite.
2. As the mechanical alloying time increases, particle size of Fe-53.5S decreased, and steady state of FeS_2 compound alloy powders was obtained 30 hours mechanical alloying.
3. The cell of FeS_2 cathode made by MA for 30 hours has the excellent discharge capacity (1011 mAh/g).
4. Cycle life of Li/FeS_2 cell prepared by MA for 30 hours shows a rapid capacity fade.

Acknowledgements

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