Abstract—Pyrite (FeS₂) is a promising candidate for cathode materials in batteries because of its high theoretical capacity, low cost and non-toxicity. In this study, nano size iron disulfide thin film was prepared on graphite substrate through a new method as battery cathode. In this way, acetylene black and poly vinylidene fluoride were used as electron conductor and binder, respectively. Fabricated thin films were analyzed by XRD and SEM. These results and electrochemical data confirm improvement of battery discharge capacity in comparison with commercial type of pyrite.

Keywords—Nano pyrite, Thin film, Battery cathode, capacity.

I. INTRODUCTION

FeS₂ is a non-toxic, “green” material, available in abundance at low cost with high electrochemical capacity. The development of compact, light-weight batteries offering high-energy densities are of enormous interest in industry as well as research for applications in miniaturized electronic devices as well as in electric vehicles (EV) and hybrid electric vehicle (HEV). Substantial amount is being invested by advanced nations for the research and development of new battery materials and technology that potentially could increase energy storage and reduce cost. Lithium batteries offer higher energy density compared to other rechargeable systems but they also contain mercury, various types of lead-acid batteries involve water, and nickel-based batteries involve cobalt oxides. For these reasons, many researchers are working on alternative battery technologies.

Pyrite has for a long time been synthesized chemically for studies in solar cells [1], [2], but its efficiency is very low (1%) [3]. It has been used in commercial lithium primary cells [4], [5] and high-temperature thermal batteries [6], [7]. Li/FeS₂ battery was known as a primary battery, which has already been commercialized. Although Li/FeS₂ battery showed high theoretical capacity of 893mAh g⁻¹, lithium is a very expensive material. Zinc is an attractive anode material because of low material cost, high theoretical specific capacity Zn/FeS₂ redox couple could be potential battery for electric vehicle because each electrode materials have many advantages.

Thin film batteries have attracted notable attention in recent years along with developments in microelectronic devices. In order to develop long-lasting and high-energy efficient micro-batteries to meet the requirement of microelectronic systems, much effort has been spent devising new cathode materials or improving the electrochemical properties of traditional materials. The pyrite films have been prepared by chemical vapor transport[8], MOCVD [9], sulfuration of iron films, spray pyrolysis [10], sulfuration of sprayed iron oxide films, magnetron sputtering [11] and molecular beam deposition, solgel, chemical bath deposition, vacuum deposition, chemical vapor deposition and Chemical Spray pyrolysis. In these all methods pyrite synthesis and thin film preparation (deposition) was done simultaneously.

In this study, we prepared sodium/pyrite electrochemical battery with zinc as a anode and thin film pyrite as a cathode and was investigated the electrochemical property at room temperature. Also, we investigated the discharge process of zinc/pyrite using XRD, ICP, SEM, Voltametric measurement.

II. EXPERIMENTAL DETAILS

A. Materials

To prepare FeS₂ cathode the active material was synthesized nano sized pyrite by hydro thermal method and poly vinylidene fluoride [PVdF, Aldrich Chem. Co., 5wt.%] is used as binder, acetylene black (Alfa Aesar, 4wt.%) as conducting agent, and N methyl-pyrrolidone (NMP, Aldrich) as a solvent for used binder.

B. Experimental Method

The first step of FeS₂ cathode preparation was making homogeneous slurry by mixing synthesized nano sized pyrite with binder and conducting agent by using solvent. Pyrite film was prepared by homogeneous spray method on graphite with 14cm² area substrate in 90°C. Electrochemical cell contains the Zn plate as anode electrode by equal size of graphite (substrate of pyrite cathode), by 7mm distance as an optimum distance in the 0.5 molar sulfuric acid as electrolyte and thin film pyrite as cathode electrode. To investigate of the effect of nano size active material two cathode electrode by micro and nano pyrite was prepared according to identical procedure.

The uniformity structure and morphology of prepared thin film by spray method were investigated by field emission scanning electron microscope (FESEM, Hitachi s-4160).

C. Electrochemical Investigation

Prior to the electrochemical study there is a circuit contain 100Ω resistance, prepared electrochemical cell as energy source and two multi meter. One of multi meters is to measure the current and is at series condition by resistance and another one is a potential meter that is parallel with circuit. Both multi
meters are connected to data logger software (DMM 2.02) to record the open circuit potential and dead voltage of battery.

In order to evaluate the performance of synthesized nano sized pyrite based cathode for the electrolyte system generally used in commercial lithium batteries and optimize pyrite acetylene black ratio we have studied the discharge profile of Zn/FeS2 cells with 0.5 molar acid sulfuric solutions at room temperature also capacity of this cell has been calculated.

Fig. 4 shows the discharge curves for Zn/FeS2 cell with this electrolyte. A plateau is observed at 1V in the red curve as the optimum ratio of pyrite to acetylene black 10 and specific capacity is 24mAh/g.

III. RESULTS AND DISCUSSION

Fig. 1 shows FESEM images of the thin film preparation surface at 90°C.

Uniform distribution of binder, conductor and active material is observed. In our previous studies the 10–15 mm-thick cathode foil was prepared by dispersing fine pyrite powder D.B casting method, on casting of the composite cathode, FeS2 tends to settle to the bottom, as its density is twice as other composition so The distribution of pyrite over the thickness of the cast cathode is, therefore, non homogeneous. In this spray method because of simultaneity of mixing and distribution this settling does not happen.

Fig. 2 shows open circuit potential curve of pyrite-graphite electrodes in different active material size of nano and micro in comparison with the graphite electrode in the absence of pyrite was prepared according to an identical procedure without the addition of pyrite. The value of the OCP is 787-mv in 0.5 mol L-1 H2SO4 without pyrite and that in the presence of 230nm and 390 nm pyrite is 1313 and 1497 mV, respectively. It is clear that the OCPs are greatly influenced by the active material size.

Fig. 3 Current increasing caused by pyrite layer on graphite and increase due to decrease in pyrite size from 200µm to 333nm
Fig. 4 Maximum specific capacity in FeS$_2$/AB 10 and its potential plateau (red curve)

Fig. 3 shows the effect of the size of pyrite powder on the current of the electrochemical cell. The capacity of the cell can be calculated from area under current curve, in this way it is observed decrease size of pyrite powder from 200µm to 333nm improve capacity of cell from 2.7mAhg$^{-1}$ to 5.05mAhg$^{-1}$.

The current curve of the graphite electrode without pyrite was also recorded for comparison. No reduction reaction peaks are observed in the control experiment. No electrochemical reactions occur on the graphite-alone electrode and all of the electrochemical signals observed in the pyrite–graphite electrode are ascribed to the redox reactions of pyrite. This reaction can be represented by:

$$\text{FeS}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{FeS} + \text{H}_2\text{S}$$

The second one is the reduction of S$^0$ possibly formed during the handling and preparation of samples. The proposed reaction is:

$$\text{S} + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{S}$$

IV. CONCLUSION

Prepared slurry from FeS$_2$ and binder were successfully deposited on graphite substrates at 90°C using a new spray method, without the use of other expensive method such as chemical vapor deposition. Particle size effect on performance of this cell was investigated and nano sized active material make higher open circuit potential and current .Prepared cathode with this method was optimized by comparison between different FeS$_2$ acetylene black ratios.

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REFERENCES


