

**SEPIOLITE AS AN ADDITIVE MATERIAL-CATHODE PREPARATION FOR LITHIUM SULFUR BATTERY**

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**Abstract:** Lithium-sulfur batteries have been considered as a promising next generation rechargeable energy storage system, owing to its high theoretical capacity and specific energy density. However, several critical problems arise the wide-scale commercial implementation of Li-S battery, namely low electrical conductivity of sulfur, dissolution of polysulfides in electrolyte, volume expansion of sulfur during discharge [1]. To overcome these difficulties, a variety of additives were added in to the positive electrode material. In this work, sieved Sepiolite has been chosen as an additive material to encounter the above challenges in lithium sulfur battery. Sepiolite powders were sieved through a 200 mesh sieve (particle size 74 microns) [2] and subjected to acid and thermal treatment prior to use. Sepiolite is a fibrous hydrated magnesium silicate which contains extended silicon-oxygen sheets, but the tetrahedral  $\text{SiO}_4$  groups forming these sheets are oriented to give fibrous character of the mineral. The acid pre-activation caused restrictions in possible crystal deformation during thermal treatment. The XRD patterns and FTIR spectra of the pure Sepiolite, sieved, acid treated and thermally treated samples were investigated and reported. From the XRD analyses, it is concluded that the Sepiolite structure has been collapsed and amorphous silica was formed. The stretching of Si-O in the Si-O-Si groups of tetrahedral sheet is observed in FT-IR spectra. From the SEM analysis, micro fibrous bundles morphology has been observed.

**Keyword:** lithium sulfur battery, electrode, Sepiolite, pre-treatment.

**1. Introduction**

Lithium-sulfur battery is one of the most promising electrochemical systems based on redox reaction. Rechargeable Li-S battery shows a high theoretical capacity of  $1675 \text{ mAhg}^{-1}$  and power density of  $2500 \text{ Wh kg}^{-1}$  which are 3-4 times greater than that of Li-ion batteries. In addition, sulfur is non-toxic, low cost, naturally abundant and eco-friendly [3]. The wide scale commercial implementation of Li-S batteries leads to loss of active material, capacity fading and self-discharge. The major problems arise in these batteries are insulating nature of sulfur, the dissolution of polysulfides and volume expansion of sulfur [4]. To overcome these remedies, a variety of nanostructure metal oxide additives were added into the positive electrode materials including lanthanum oxide, aluminum oxide, silicon oxide and titanium dioxide, with an expectation to utilize their high specific surface area and surface groups to adsorb lithium polysulfide dissolution [5]. In principle, Sepiolite-sulfur composite could lead to improved sulfur cathode materials for Li-S batteries.

Sepiolite is a porous and fibrous hydrated magnesium silicate with a large specific surface area (more than  $200 \text{ m}^2/\text{g}$ ) with high density of silanol group ( $-\text{SiOH}$ ) which explains the marked hydrophilicity of this clay with molecular formula of  $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$  [6]. Sepiolite structure is composed of blocks of two tetrahedral silica sheets sandwiching an octahedral sheet of magnesium oxide hydroxide. Therefore, Sepiolite has nano-sized channels containing water, which are approximately  $0.37 \text{ nm} \times 0.60 \text{ nm}$  [7]. The water is partly arranged (ordered) in these channels and water molecules are also bound to the magnesium cations of the Mg brucite-like ribbon edges that border the channels running along the length of the crystals. The blocks are not sheets but ribbons which are linked forming an open cavity (i.e., tunnel) similar to that of zeolites, in which water (zeolitic water) and exchange ions can be accommodated [8]. Each one of the  $\text{Mg}^{2+}$  cations located at the edges of the octahedral sheets (i.e., those with access to the tunnels) complete their octahedral coordination, for they are bound to two molecules of water (coordinated water). Sepiolite is also a good adsorbent for organic species because it exhibits a variety of attractive properties [9] and therefore used in a large spectrum of areas where its sorptive, catalytic, and rheological properties are exploited [10]. Different acid and thermal treatments modifying the structure and porosity of the silicate, change its surface and activity. The development of the porosity and of the number of acid centres and the size of the silica fibres in the solids are characterized as a function of the acid activation.

**2. Experimental****2.1. Material preparation:**

A sepiolite powder was purchased from Sigma Aldrich (product in Spain), HCl in Nice Company and 200-Mesh sieve in Alfa Aesar. Acid treatment was carried out using 6 moles of HCl at ambient temperature for 24 h. The mineral particles were filtered and washed with deionised water several times, then dried at  $40^\circ\text{C}$  in an oven. The pre-treated sieved

sepiolite powder was obtained. In thermal treatment method, stoichiometric ratio of pre-treated sepiolite and sublimed sulfur were grinded together in a ceramic boat and then heated at 155°C for 12 h in a tubular furnace under Ar gas. Again, the sample is heated at 320°C for 6h and cooled down to room temperature. The sample was further milled and dried to obtain powder.

## 2.2 Characterization

The structure and composition of the sieved sepiolite/sulfur were examined by using X-ray Diffraction (PAN Analytical XPERT-PRO with Cu K $\alpha$  radiation) and the FTIR spectrometer recorded in the range of 4000-400 cm<sup>-1</sup> using (Thermo Nicolet 380 Instrument Cooperation and KBr pellets). The structural morphology was characterized by scanning electron microscope (SEM FEG Quanta 250).

## 3. Result and discussion

The XRD patterns of raw and thermally heated sepiolite are shown in Fig(2). The intensity of diffraction patterns of sepiolite is relatively weak, which shows that the used sepiolite powders have many impurities. The intensity of the diffraction peak at  $2\theta=7.45^\circ$  is disappeared in acid treated thermally activated samples [11]. Acid treatment increases the surface area because it virtually destroys the minerals and porous amorphous silica. The amorphous phase has been maintained even though the pretreatment has been followed.

Fig (3) shows the FT-IR spectra to optimize the functional groups and frequency range. In FT-IR analyses the OH band at 3567cm<sup>-1</sup> characterized by weak bending is ascribed to the presence of OH groups in the octahedral sheet. This is presenting the zeolitic water in the channels and bound water coordinated to magnesium in the octahedral sheet. The C-G stretching vibrating in the external surface of sepiolite has been appeared at 1660 cm<sup>-1</sup>. The vibrational peaks appearing at 1209 cm<sup>-1</sup> and 1026 cm<sup>-1</sup> represent the stretching of Si-O in the Si-O-Si groups of tetrahedral sheet. Besides, the appearance of absorbance bands at 799cm<sup>-1</sup> indicated the presence of quartz in raw sepiolite [11]. Thus the functional vibration groups have been studied in sepiolite samples.

The morphology of sepiolite was examined by SEM. It is evident that the sepiolite powders are composed of short micro fibrous bundles. Although, the fibrous morphology of the particle was exhibited, a more randomly oriented structure resulting from breaking of the bundles was also observed. A destructive breaking of the primary particles and forming aggregation result in thicker bundles. Therefore, the appropriate thermal treatment temperature is significant to improve the pore structure and surface properties of sepiolite.

## Conclusion

The acid treatment has been made for the sieved (200 mesh) Sepiolite using HCl for making a coating on sulfur electrode for Li-S batteries. Also the acid treated sepiolite materials were thermally treated for 600°C. The pure and acid thermally treated sepiolite samples were characterized using XRD, FT-IR and SEM analyses. In the XRD pattern it is observed that the sepiolite structure collapsed and amorphous silica was formed. The thermal activation of sepiolite removes the water molecules in the channels, which can release or create the active adsorption sites.

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**FIGURE CAPTIONS**

**Figure 1:** Images of (a) Sepiolite ore and (b) Sepiolite powders(c) Structure of Sepiolite

**Figure 2:** XRD patterns of pure, sieved, Acid treated sepiolite and thermally treated at 600 °C

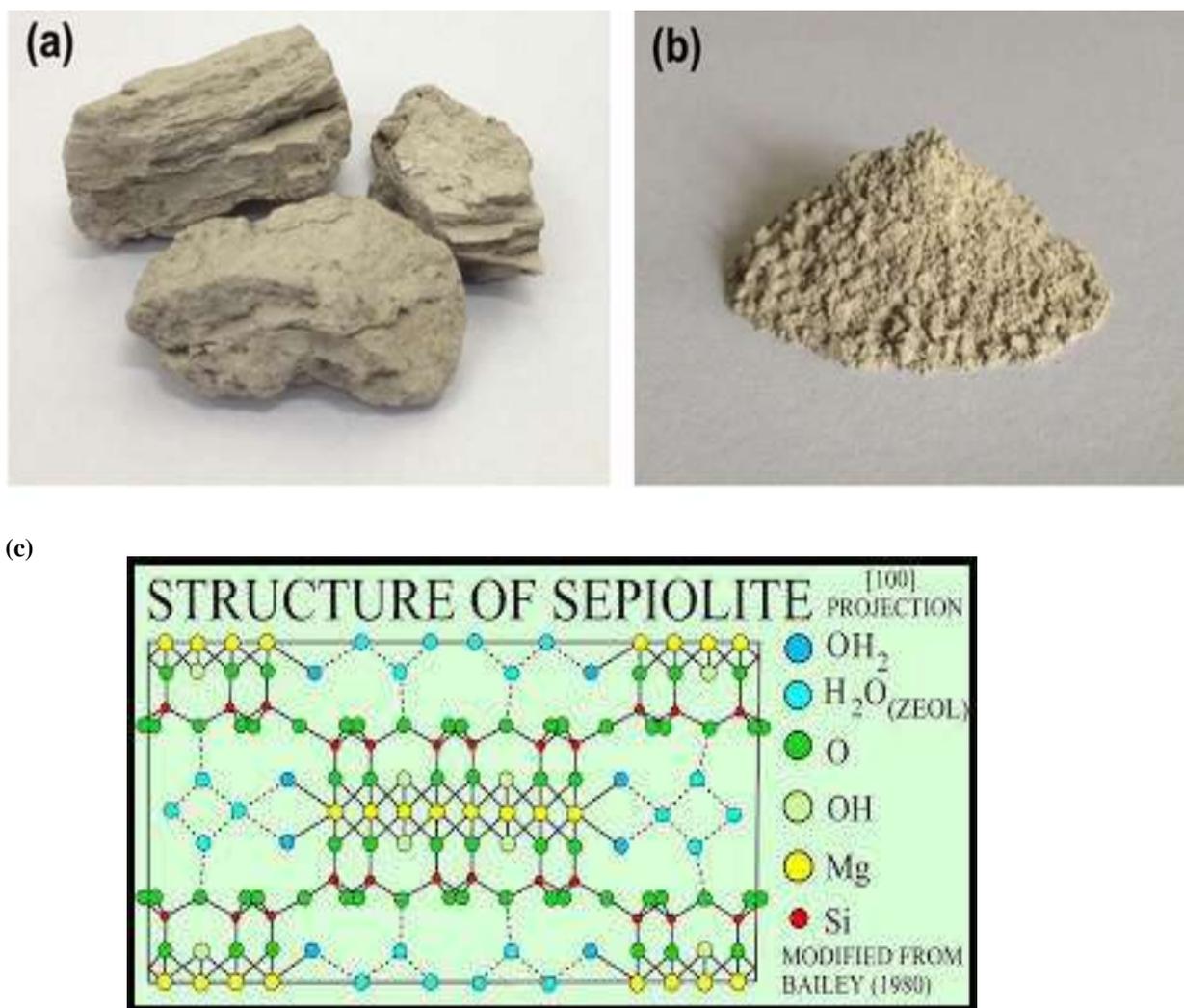
**Figure 3:** FT-IR spectra of pure, sieved, acid treated sepiolite and thermally treated at 600°C

**Figure 4:** SEM images of pure, sieved, acid and thermally treated sepiolite

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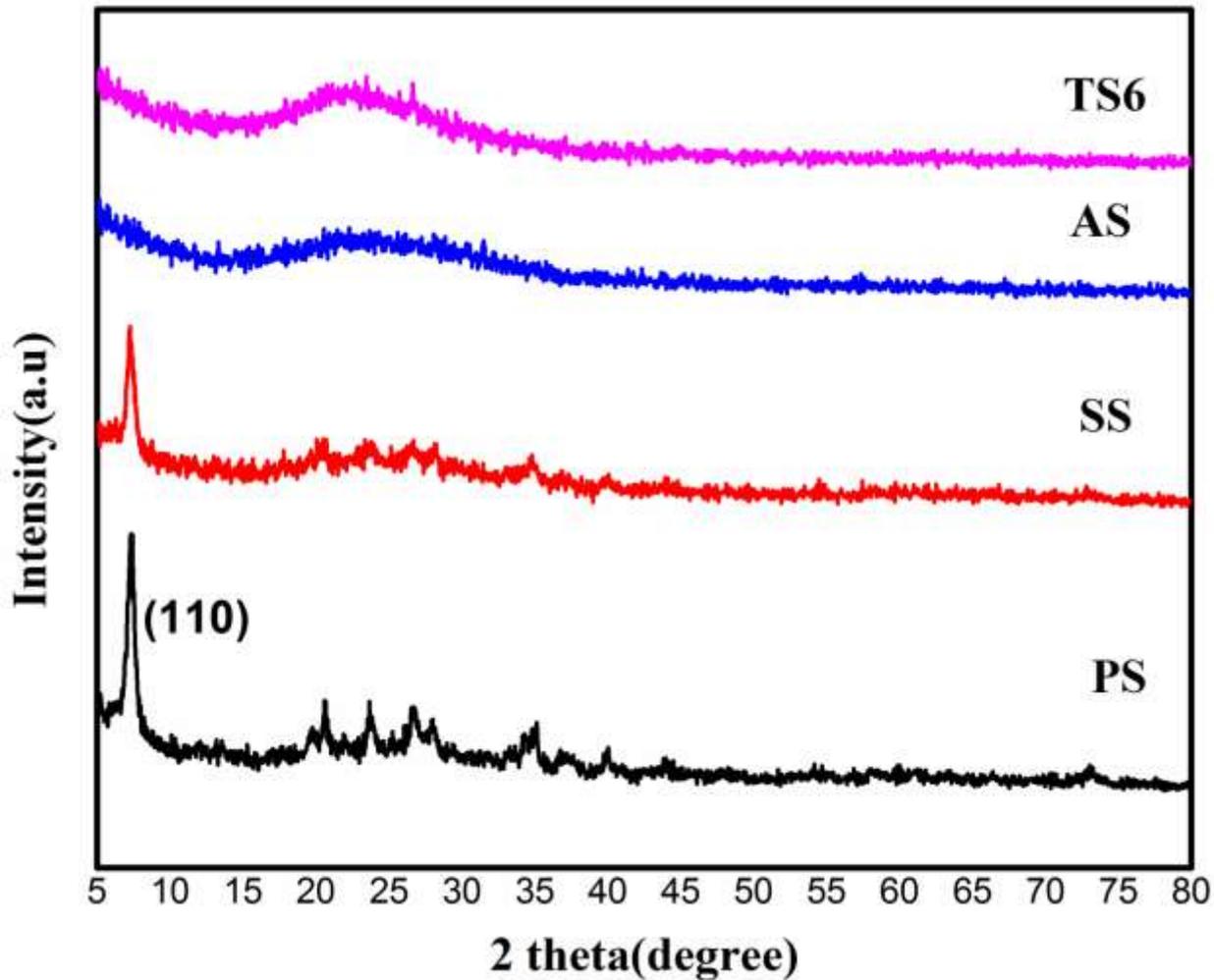
**Figure 1**



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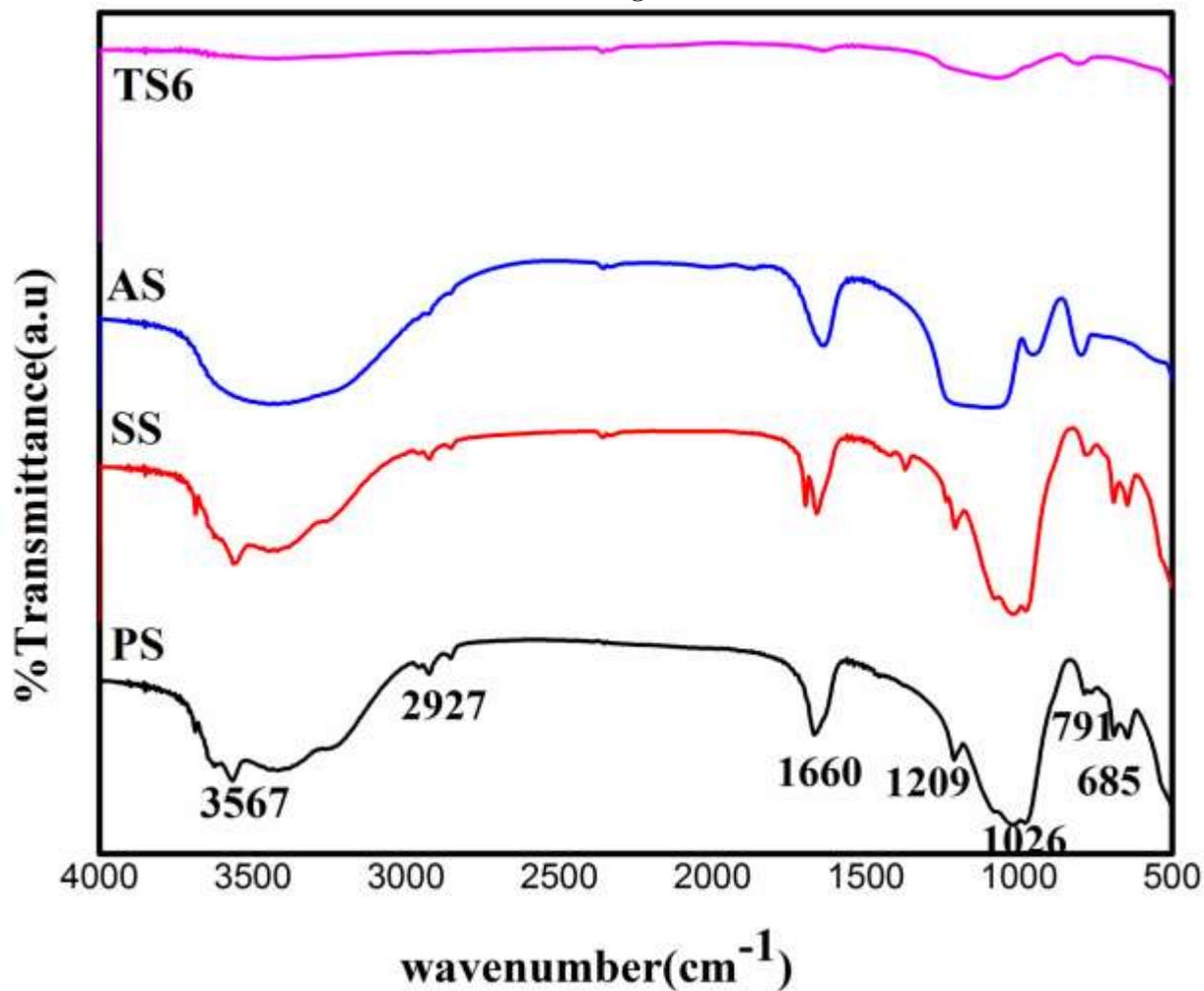
Figure 2



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Figure 3



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**Figure 4**

