Na$_2$S as a Potential Cathode Candidate for Room-Temperature Sodium-Sulfur Batteries

Elif Ceylan Cengiz$^{1,2}$, Sümeyye Yılmaz Uslukaya$^{3,4}$, Rezan Demir Çakan$^{2,3}$

$^1$Gebze Technical University, Material Science and Engineering Department, 41400, Gebze, Kocaeli
$^2$Gebze Technical University, Institute of Nanotechnology, 41400, Gebze, Kocaeli
$^3$Gebze Technical University, Chemical Engineering Department, 41400, Gebze, Kocaeli
$^4$Deva Holding, 41135, Kartepe, Kocaeli

Abstract

High temperature Sodium-Sulfur (Na-S) batteries are commercially available and widely used for stationary applications. However, operation at room temperatures is much more important due to the safety issues. Room-temperature Na-S batteries are safer and have higher capacity than that of high temperature Na-S batteries counterparts. In this work, sodium sulfide was synthesized under laboratory conditions and investigated as a potential cathode material.

1. Introduction

Lithium-Sulfur (Li-S) batteries have drawn attention by the battery society especially since 2009 with the properties of cheapness, abundancy and high theoretical energy density (2600 Wh/kg) of sulfur cathode. However, when taking into account cost issues, much cheaper and natural abundant sodium instead of lithium become a viable option. High temperature Sodium-Sulfur (Na-S) batteries have commercially been used in lots of industrial applications since 1960’s. However, they have safety problems due to their operation above 300 °C. Starting from 2006, Na-S batteries that can operate at room temperatures have been studied by the scientists [1-4].

Room-temperature Na-S batteries suffer from the same problems with its ancestor Li-S batteries; (i) high insulating nature of sulfur and the final discharge product Na$_2$S, (ii) polysulfide formation during cycling, (iii) huge volume expansion at the end of discharge, (iv) safety issues linked with metallic sodium anode.

In this work, we use Na$_2$S as cathode material instead of starting from sulfur. Since Na$_2$S is already in sodiated state, it can be coupled with non-sodium anodes (such as Sn, etc.) preventing the safety issues. At the same time, Na$_2$S has high theoretical capacity which is 666 mAh/g. By taking advantages of these, Na$_2$S was synthesized chemically and compared the electrochemical performances with commercial counterparts. Different ball milling times were tested to see its effect on electrochemical performance.

2. Experimental Procedure

2.1. Materials

Sulfur, toluene, 1.0 M lithium triethylborohydride in tetrahydrofuran (1M LiEt$_3$BH in THF), hexane, salts and solvents were purchased from Sigma-Aldrich.

2.2. Na$_2$S Synthesis

Since Na$_2$S is a highly hygroscopic material, all the procedure was done in a high purity argon filled glove box with oxygen and moisture content under 0.5 ppm. Na$_2$S synthesis was adapted from Cairns’ method [5]. According to this method, 128 mg sulfur was firstly dissolved in toluene for 2 minutes. After that, the solution was heated to 90 °C and stirred for 7 min to obtain nanometer sized particles. Then, the as-obtained Na$_2$S
2.3. Electrochemical Measurements

Carbon Ketjen Black-Na$_2$S was used as cathode. The aim of using Carbon Ketjen Black is to enhance the conductivity of cathode material which is because Na$_2$S is highly insulating material. To do so, Carbon Ketjen Black-Na$_2$S was ball milled with a ratio of 1:1.5 hours and 1 hour ball milling were tested. Hand milling in mortar for 15 minutes was also tested to see the effect. Besides that, to see the advantage of using synthesized Na$_2$S, commercial Na$_2$S was also tested galvanostatically with the same condition. In this comparison, both materials were hand milled with Carbon Ketjen Black in mortar for 15 minutes. The ratio of Na$_2$S and carbon was 1:1. Na$_2$S loading was ~4 mg/cm$^2$ for all the cells.

Metallic lithium was used as anode and Whatman-type glass fiber material was used as separator. 1M NaClO$_4$ (Sodium perchlorate - from Sigma-Aldrich) salt containing Propylene Carbonate (PC – from Sigma Aldrich) was used as electrolyte. 0.1 ml electrolyte was used in the prepared cells.

Galvanostatic cycling measurements were performed with C/10 current density (1C corresponds to a current density to reach the theoretical cell capacity at 1 hour) using a galvanostat/potentiostat VMP3 at room temperature. The voltage range is between 1.2-2.8 V vs Na$^+$/Na.

2.4. Structural Characterization

The X-ray powder diffraction (XRD) patterns of Na$_2$S powders were recorded on a Bruker D8 Advance diffractometer (θ - 2θ mode, Co Kα radiation λ = 1.7903 Å, and a linear position-sensitive detector) with an air tighten beryllium (Be) window covered sample holder.

3. Results and Discussion

X-Ray Diffraction (XRD) was used to detect whether Na$_2$S particles was successfully synthesized or not. Since Na$_2$S is a highly hygroscopic material, sample holder which was covered by an air-tighten beryllium window was used for XRD process. **Fig. 1** shows the X-Ray Diffraction pattern of Na$_2$S particles which was synthesized under laboratory conditions. Sharp peaks which are located in the figure are corresponded to the Na$_2$S signals which present that crystalline sodium sulfide particles can be successfully synthesized by Cairns’ method.

**Fig. 1.** X-Ray Diffraction pattern of synthesized Na$_2$S particles.

**Fig. 2** shows the comparison of the synthesized Na$_2$S cells as a function of ball-milling time. **Fig. 2a** presents the charge-discharge profile of the cells. One discharge plateau behavior was observed for all the cells which is typical for carbonate-based electrolytes used in sulfur-based batteries. This is because quasi-solid state reactions occurs in carbonate based electrolytes, unlike ether-based electrolytes. **Fig. 2b** shows the discharge capacities as a function of cycle number. It can be seen from the figure that discharge capacity decreases with increasing ball-milling time. Moreover, hand-milled Na$_2$S-Carbon Ketjen Black composite gave the best result. In fact, it was expected that the discharge capacity increases with the increasing ball-milling time. However, increasing ball-milling time might cause decomposition of the structure. Additionally, agglomeration of nanometer sized Na$_2$S particles with increasing ball milling time might occur.
Fig. 2. Comparison of the cells with synthesized Na$_2$S as a function of ball-milling time. a) Galvanostatic charge-discharge profiles at C/10, b) discharge capacities as a function of cycle number.

To show the effectivity of using synthesized Na$_2$S particles, the cell with commercial Na$_2$S and Carbon Ketjen Black composite (1:1) cathode was also tested. In these cells, cathode composite was prepared with mortar. The comparison is shown in Fig. 3. Galvanostatic charge-discharge profiles are presented in Fig. 3a. Like seen in Fig. 2a, one plateau discharge profile behavior is observed for both of the cells. Discharge capacities as a function of cycle number is demonstrated in Fig. 3b. While 196 mAh/g discharge capacity is obtained for the cell with synthesized Na$_2$S during the first cycle, the cell with commercial Na$_2$S presents 102 mAh/g discharge capacity. After first cycle, both of the cells show fast capacity fading which is more severe in the cell with commercial Na$_2$S. After 20 cycles, the cell with synthesized Na$_2$S have more discharge capacity of 135 mAh/g than commercial one which has 18 mAh/g. This better capacity can be attributed to the nanometer particle size of synthesized Na$_2$S which enables more surface area.

4. Conclusions

In this work, Na$_2$S was synthesized under laboratory conditions and effect of the composite treatment was investigated. Different ball milling times were observed. With increasing ball milling time, discharge capacities decreased. Keeping that result in mind, the composite was prepared via mortar. The as-prepared composite gave better performance than the composites prepared with ball mill. This result is associated with agglomeration of particles and decomposition of particles with increasing ball-milling time. The effectivity of synthesized Na$_2$S was also tested by comparison with commercial one. Consequently, synthesized Na$_2$S resulted better discharge capacity because of the smaller particle size.
References


