



Contents lists available at ScienceDirect

Journal of the Taiwan Institute of Chemical Engineers

journal homepage: www.elsevier.com/locate/jtice

Honeycomb polyaniline-dodecyl benzene sulfonic acid (hPANI-DBSA)/sulfur as a new cathode for high performance Li–S batteries

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ARTICLE INFO

Article history:

Received 27 December 2017

Revised 28 February 2018

Accepted 1 March 2018

Available online xxx

Keywords:

Lithium–sulfur battery

Honeycomb

Breath figure

Electrodeposition of sulfur

ABSTRACT

In the last few years, there has been a growing interest in lithium–sulfur (Li–S) batteries due to their high theoretical capacity of 1672 mAh/g, long life cycle, and low cost. However, Li–S batteries have been plagued with fast capacity loss and dissolution and diffusion of the polysulfides. In this study, honeycomb polyaniline-dodecyl benzene sulfonic acid (hPANI-DBSA) was prepared through the breath figure (BF) method, then, sulfur was electrodeposited on hPANI-DBSA and used to investigate the electrochemical properties of the Li–S cells. The hPANI-DBSA/S exhibit a higher capacity and excellent reversible capacity of 873.5 mAh/g after 100 cycles at 0.1 C. An initial specific capacity of 848 mAh/g at 0.2 C and coulombic efficiency of 99.3% over 100 cycles was achieved. The results suggest that this approach can also be useful for applying the Li–S cathodes for use in high capacity lithium–sulfur batteries.

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1. Introduction

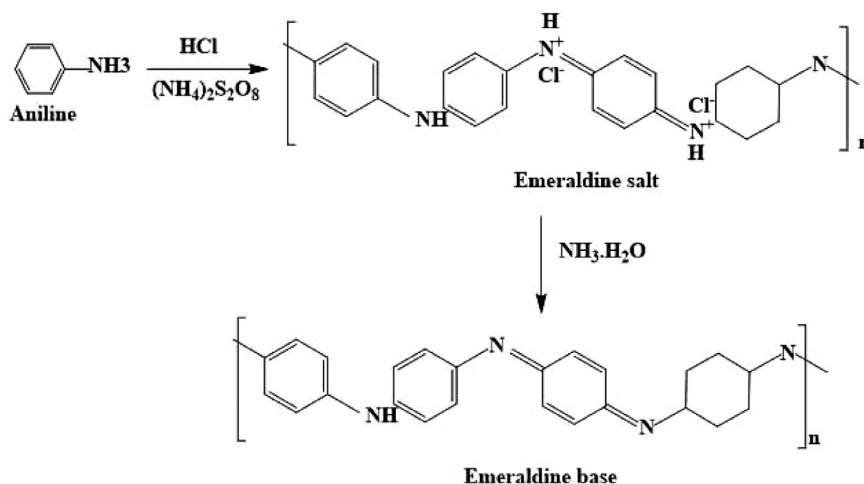
Higher energy density sources play a vital role in industrial development [1]. Recently, lithium–ion batteries have seen extensive applications, such as in portable electronic devices and in hybrid electric vehicles, owing to their long life cycle, low self-discharge rates, and high operating voltages [2–4]. Although these batteries have been gaining importance in recent years, previous research has demonstrated that they have a limited theoretical energy density and the high cost and that these issues limit their applications [5]. To overcome these disadvantages, the Li–S batteries are one of the most promising candidates on account of their high theoretical capacity of 1672 mAh/g, which is over five times more than that of Li–ion batteries. Also, the Li–S batteries are low-cost, sulfur is a highly abundant resource, non-poisonous and environmentally friendly [6,7]. However, there are numerous challenges in Li–S batteries, including the low conductivity of sulphur, the dissolution of polysulfides, the diffusion shuttling effect in the charge–discharge process, and the volumetric expansion of the cathodes [8–11]. To solve these problems, many researchers have proposed various methods [12,13]. They have been working to find an ideal matrix for sulfur-containing composites by including some properties such as a high electrical conductivity, an appropriate

structure for loading higher sulfur contents, a stable framework to sustain the strain generated by the volume changes of the active material during cycling, and the high electrochemical affinity for sulfur [14–18]. In recent years, the Li–S cathode composites have attracted much attention from researchers [19]. These composites can be divided into three categories: carbon/sulfur [20–22], polymer/sulfur [23–28], and metal oxide/sulfur [29–32] composites. In comparison, the soft polymers in the polymer/sulfur composites are more flexible. Polyaniline (PANI) has been widely used in the lithium secondary batteries owing to the chemical stability in the organic electrolyte and its adequate electrochemical conductivity. The porous structure can improve the electrochemical properties of the lithium–sulfur battery by increasing the contact surface area [33–35]. Nonetheless, further improvements are possible by making porous structure cathodes. This structure has the capability to adsorb the soluble lithium polysulfides formed during discharge [8,11,36], to increase the contact surface area, to reduce the dissolution of the active materials into the electrolyte, and has a faster charge transfer process. Therefore, we tried to fabricate a porous polymer structure cathode for Li–S batteries. For this reason, the conductive polyaniline was synthesized with high conductivity by means of doping agents like dodecyl benzene sulfonic acid (DBSA). Afterward, the honeycomb polyaniline-dodecyl benzene sulfonic acid (hPANI-DBSA) was prepared and sulfur was electrodeposited on the porous surfaces and applied as a new cathode and the electrochemical behavior of this cathode was investigated.

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Scheme 1. Preparation of polyaniline.

2. Material and methods

2.1. Materials and chemicals

All the chemicals were of analytical grade. Aniline (99.5%), which needs to be distilled twice under reduced pressure and stored at a low temperature, dodecyl benzene sulfonic acid (DBSA), ammonium persulfate (APS), Lithium bis(trifluoromethanesulfonylimide ((LiTFSI), 1,3-dioxolane, and 1,2-dimethoxyethane were used without any purification.

2.2. Instruments

The infrared spectra of the PANI and PANI-DBSA were recorded on a Unicam Galaxy Series FT-IR 5000 spectrophotometer (using KBr pellets) in the region between 400 and 4000 cm^{-1} . For the conductivity, powder samples were pressed (11 tons of pressure) and placed between two metal plate arrangements and the conductivity was measured by using a potentiostat SP-150, Bio-Logic (frequency range 0.1 Hz to 10⁶ Hz). The surface morphology of the honeycomb PANI-DBSA and hPANI-DBSA/S were studied by using a scanning electron microscope (Jeol 5400). The statistical analysis was performed with the SPSS software. The electrochemical measurements were recorded on a potentiostat (Biologic VSP 300, France).

2.3. Synthesis of the polyaniline

The polyaniline was synthesized by chemical methods, as reported [37]. In a flat bottom flask, 5 mL of distilled aniline was dissolved in 100 mL of HCl (1 mol/L) and cooled to 0–4 °C using an ice bath. A total of (15.62 g) of APS was dissolved in (250 mL) of HCl (1 mol/L) and added slowly into the flask solution. As soon as it was added to the solution, pink color appeared, which then, turned into deep blue. After 5 min, the product, green colored polyaniline–HCl, precipitated out from the solution. The polymerization was completed by stirring at 30 °C for 24 h. The precipitate was filtered, washed with HCl (1 mol/L) for several times and stirred in a flask containing aqueous ammonia solution (1 mol/L). To ensure the completion of de-doping, the blue precipitate was stirred for 3 h at room temperature. The resultant black PANI was filtered and washed with water and acetone to remove the unreacted materials. Finally, the black PANI was collected and it was then kept overnight in an oven at 80 °C for drying. The synthesis steps are illustrated in Scheme 1.

2.4. Synthesis of the PANI doped with DBSA (PANI-DBSA)

PANI-DBSA was synthesized by chemical methods, as reported [37]. In a flat bottom flask, (2.8 g) of aniline was mixed with (7.3 g) of DBSA and (100 mL) of distilled water to form a homogeneous milky white dispersion of Anilinium-DBSA complex. The flask was placed into an ice bath containing salt (0–5 °C). Then, 5.2 g of APS was dissolved in 50 mL of distilled water and added slowly into the flask over 30 min at the mentioned temperature. After 24 h, the dark green suspension of the doped PANI powder was precipitated with 150 mL of acetone. The precipitant was filtered off and washed with deionized water for several times and its pH value was the same as that of the deionized water. Then, the product was filtered and dried at 60 °C for 48 h. The synthesis steps are illustrated in Scheme 2.

2.5. Preparation of the honeycomb film

The honeycomb PANI-DBSA film preparation procedure is performed in a box with a thermometer and a hydrometer. The thin honeycomb films were prepared by direct casting PANI-DBSA chloroform solution onto the copper substrate under a moist airflow (relative humidity *ca.* 80%). The dark green thin films covering an area of 1 cm^2 were left behind after the complete evaporation of the solvent and water within 20–30 s. The control experiments had airflows of different humidity and concentrations of the PANI-DBSA chloroform solution [38]. Scheme 3 shows a schematic representation of the design for the experimental setup.

2.6. Electrodeposition of sulfur on the honeycomb structure

Sulfur electrodeposition was performed in a two-electrode system in a different concentration of Na₂S aqueous solution at room temperature, the honeycomb PANI-DBSA structure was used as the substrate. Using gold foam as a working electrode, the counter electrode was of honeycomb polymer. For electrodeposition of sulfur on a honeycomb polymer substrate, a constant current (5 mA/cm²) was applied to the cell using a SP-150 Potentiostat–Bio-Logic. To investigate the effect of the time and concentration on the amount of homogeneous deposition of sulfur on the honeycomb surface, various times (10 min, 15 min, 20 min, 30 min) and various concentrations (0.18 mol/L, 0.1 mol/L, 0.04 mol/L, and 0.02 mol/L) were employed.

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