



Binding mechanism of sulfur and dehydrogenated polyacrylonitrile in sulfur/polymer composite cathode

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H I G H L I G H T S

- Binding mechanism of sulfur and dehydrogenated polyacrylonitrile is proposed.
- C/H molar ratio is about 6 in the thermally stable structure.
- The upper limit for sulfur content in the composite is 56 wt%.
- Higher sulfur content will result in poor electrochemical performance.

A R T I C L E I N F O

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A composite consisting of sulfur/dehydrogenated polyacrylonitrile is one of the most promising cathode materials for use in rechargeable lithium–sulfur batteries. However, the reported sulfur contents have been low, less than 50 wt%, which compromise the intrinsic high specific capacity and energy of elemental sulfur and hence decrease significantly the specific energy of the composite. To identify the potential to further increase the sulfur content, we elucidate the binding mechanism of sulfur and polyacrylonitrile in their composite. The heat treatment experiments at varying timespans with excess sulfur showed a constancy of sulfur content after a critical length of timespan, indicating the saturation of sulfur in the structure of dehydrogenated polyacrylonitrile. Based on molecular structure and size consideration, it is proposed that the binding involves the formation of an 8 membered ring of sulfur embedded between 4 heterocyclic rings of dehydrogenated polyacrylonitrile. From this model and experimental results, we show that there exists an upper limit of sulfur content in the sulfur/dehydrogenated polyacrylonitrile composite at 56 wt%.

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1. Introduction

The lithium-ion battery first introduced by Sony in 1991 is considered the most successful and most widely applied portable energy storage system. While specific energy of the battery has improved over time using more innovative cell design, the specific energy limit appears to have been reached [1,2]. Because the specific capacities of commercial cathode materials such as LiCoO_2 , LiFePO_4 , LiMn_2O_4 [2–5] (all less than 170 mA h g^{-1}) are no match for the current anode materials such as lithium (3861 mA h g^{-1}), silicon (4200 mA h g^{-1}) and even lithium intercalated graphite (372 mA h g^{-1}), cathode material appears to be a limiting factor for enhancing the specific energy of a battery [2]. From this

consideration, it is obvious that cathode materials with higher specific capacities are required to improve the specific energy and enhance energy storage efficiency.

Of all known cathode materials, sulfur offers one of the highest theoretical specific capacities, 1672 mA h g^{-1} at a working voltage of 2.1 V vs. $\text{Li}^+/\text{Li}^\circ$, with a large specific energy of 2600 W h kg^{-1} , assuming a complete reaction to Li_2S [6]. This value is 6.5 times that of the existing $\text{LiCoO}_2/\text{graphite}$ system ($\sim 400 \text{ W h kg}^{-1}$) [7]. Sulfur, an abundant, cheap and less toxic material, is a promising choice as a high energy density cathode material for rechargeable lithium batteries. The use of sulfur as a cathode material does however pose problems, due to the high solubility of intermediate products (Li_2S_x , $4 \leq x \leq 8$) in commonly used liquid electrolytes [8], the large volume change between sulfur and Li_2S phases [7], and the insulating nature of sulfur, which leads to the use of low sulfur contents in cathode composites [9–12].

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To overcome these challenges, there have been several efforts focused on finding a host material, within which sulfur can be contained, to absorb polysulfides, provide conductive paths for electron transfer, and accommodate large volume change. There have been different approaches reported such as graphene-wrapping [13], hollow carbon nanofiber-encapsulation [7], multi-walled carbon nanotube addition [10,11,14], encapsulating sulfur into micropores or mesopores of carbon spheres [9,15], making composites with conductive polymers [14,16,17], mesoporous carbons [18,19], acetylene black [20], and graphene [21], using novel electrolytes [19,22,23], protection of lithium anode and cathode surfaces by coating conductive polymers [24,25]. Of all approaches, the sulfur/dehydrogenated polyacrylonitrile (S/DPAN) composites have shown the best results both in terms of specific capacity and cyclability [14,16,26]. However, the reported sulfur contents are within 36–53 wt% [14,16,26,27], which are low and significantly decreases the specific energy of the composite. Therefore, identifying the maximum sulfur content that can be achieved in this composite system is important for further research and development in this direction.

The sulfur/dehydrogenated polyacrylonitrile composite system was first introduced by Wang et al. [16]. From X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR) and Raman analysis, the authors concluded that sulfur is present in the elemental state (S_8) in the composite. Furthermore, they proposed a reaction scheme and suggested that the elemental sulfur is embedded in the heterocyclic ring of dehydrogenated PAN. However, Yu et al. [26] argued that elemental sulfur in the form of S_8 is too large to be embedded in the heterocyclic ring of DPAN. In view of these reports, we propose a more comprehensive binding scheme for the formation of S/DPAN composite, in which an 8 membered ring of sulfur embedded between 4 heterocyclic rings of dehydrogenated polyacrylonitrile. From the theoretical calculations and confirmed by experimental results, we show that the upper limit of sulfur content for the sulfur/dehydrogenated polyacrylonitrile composite, prepared from the mixture of polyacrylonitrile and excess sulfur, is 56 wt%. This indicates that whatever the effort to improve the electrochemical performance of this S/DPAN composite, the theoretical specific capacity of the composite is reduced to $\sim 936 \text{ mA h g}^{-1}$. As a consequence, the maximum specific energy of the composite is $\sim 1176 \text{ W h kg}^{-1}$, assuming a complete reaction to Li_2S at the average discharge potential of 1.8 V vs. Li^+/Li^0 . This specific energy is less than a half of the expected specific energy of a cathode consists of pure sulfur ($\sim 2600 \text{ W h kg}^{-1}$) [6]. This fact may serve as a criterion for the practical application of this composite as cathode material for lithium–sulfur batteries. Further increase of sulfur content will result in poor electrochemical performance, such as a reduced reversible capacity.

2. Experimental

2.1. Material preparation procedure

A sulfur (Sigma–Aldrich[®], 100-mesh particle size) and PAN (Sigma–Aldrich[®], average $M_w = 150,000$) mixture was ball milled (Fritsch, pulverisette 7) at a weight ratio of 4:1 for 5 h with ethanol as the dispersant. The resulting mixture was dried at 50 °C for 3 h in a vacuum oven and then annealed at 300 °C in argon. The heat treatment time was varied from 0.5 h to 4 h. Fig. S1 in Supplementary data shows the flow chart of preparation of the S/DPAN composites.

2.2. Material characterization

The crystalline phases of the samples were studied by X-ray diffraction analysis (XRD, D8 Discover, Bruker) equipped with Cu-

$K\alpha$ radiation, with a scan speed of 4° per minute ranging from 10° to 90° . The chemical transformation of the composites during the heat treatment process was investigated by Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27). The composite surface morphology was examined by field emission scanning electron microscopy (FE-SEM, Leo-1550, Zeiss) equipped with energy-dispersive X-ray spectroscopy (EDX, EDAX, Ametek Genesis V5.2). The particle size distribution, the calculation of geometric mean diameter $d_{g,p}$ and geometric standard deviation σ_g were done via a random sampling of particles from the FE-SEM images [28]. The interior structures of the samples were observed using transmission electron microscopy (TEM, CM10, Philips). The sulfur, carbon, hydrogen and nitrogen contents of the samples were analyzed using the elemental analyzer (CHNS, Vario Micro Cube, Elementar). The thermal decomposition behavior of the samples was determined by a thermogravimetry (TG)–differential thermal analysis (DTA) apparatus (TA instruments, Q-600). A temperature ramp mode at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ was applied in a N_2 atmosphere.

2.3. Electrochemical measurements

The composite cathode comprised 80 wt% S/DPAN (or S/PAN) with 10 wt% ketjenblack (EC600JD, Akzo Nobel) and the rest was polyvinylidene fluoride (PVdF) (Kynar, HSV900) as the binder. These materials were dispersed in 1-methyl-2-pyrrolidinone (NMP, Sigma–Aldrich, $\geq 99.5\%$ purity). The resultant slurry was spread uniformly onto a nickel foam disc (MTI, $\geq 99\%$ purity) of 1 cm in diameter and $\sim 800 \mu\text{m}$ in thickness. After drying in a vacuum oven at 50 °C for 12 h, the electrode was pressed at 8 MPa by a hydraulic presser in order to achieve a good contact between active material and nickel foam. The average weight of S/DPAN composite was $\sim 10\text{--}12 \text{ mg}$ per electrode ($\sim 12.7\text{--}15.3 \text{ mg cm}^{-2}$). The electrochemical performances of the S/DPAN composite samples were investigated using coin-type cells (CR2025). Each cell is composed of a lithium metal negative electrode and the S/DPAN composite positive electrode, separated by a microporous polypropylene film. 1 M LiPF_6 in a mixed solvent of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethylene carbonate (DEC) with 1:1:1 weight ratio (LP71, Merck Chemicals) was used as the liquid electrolyte. The coin cells were assembled in a Braun glove box filled with high purity argon gas (99.9995% purity). The cells were tested galvanostatically on a multi-channel battery tester (BT-2000, Arbin) between 1 and 3 V at 0.2 C charge/discharge rate (current density = 334.4 mA g^{-1}). Applied currents and specific capacities were calculated on the basis of the weight of sulfur in the cathode. The cyclic voltammetry (CV) measurements were carried out using a multi-channel potentiostat (VMP3, Biologic). CV was performed between 1 and 3 V vs. Li^+/Li^0 at a scan rate of 0.1 mV s^{-1} . All electrochemical measurements were conducted at $\sim 25 \text{ }^\circ\text{C}$.

3. Results and discussion

In order to monitor the structural change during heat treatment, the variation of carbon/hydrogen (C/H) weight ratio and sulfur content was studied while varying heat treatment time from 0.5 to 4 h. S/DPAN-X ($X = 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4$ h of heat treatment time) were used to indicate the S/DPAN composites after different heat treatment times, and S/PAN was used to indicate the sample without heat treatment. The carbon, sulfur, nitrogen and hydrogen contents were identified by the elemental analysis. Fig. 1a represents the effect of the heat treatment time on carbon/nitrogen (C/N) and carbon/hydrogen (C/H) weight ratios in the composite. The C/N ratio remains constant, which was found to be about 2.57, corresponding to that of the PAN formula; thus PAN and its

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