



Full paper

Ultra-microporous carbons encapsulate small sulfur molecules for high performance lithium-sulfur battery

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ABSTRACT

Lithium-sulfur (Li-S) batteries are one of the most promising energy storage systems with high energy density. However, they suffer from fast capacity fading due to the shuttle of the dissolved polysulfides. Using small sulfur molecules (S_{2-4}) as cathodes can avoid the shuttle problem, but the preparation of ultra-microporous carbon to encapsulate S_{2-4} is challenging. Here, we report a Li-S battery with an excellent cycling performance by using a unique ultra-microporous carbon (UMC) with a uniform pore size of 0.55 nm. The UMC was synthesized from PVDF via a facile pyrolysis process to only accommodate small S_{2-4} molecules and eliminate large S_8 molecules. This S/UMC composite electrode is compatible with the carbonate-based electrolyte used in Li-S batteries. The resulting battery shows a typical discharging profile with only one long potential plateau because the reductions from cyclo- S_8 to dissolved polysulfides and consequence shuttle problem are avoided. The S/UMC composite retains a capacity of about 852 mAh g^{-1} and Coulombic efficiency approaching 100% after 150 cycles at 0.1 C and delivers a long-term cycling at 1 C for 1000 cycles with only around 0.03% capacity loss per cycle. We also tested this S/UMC composite electrode in Na-S systems and observed similar electrochemical behaviour. These results indicate that the S/UMC composite is a promising candidate as an electrode material in Li-S and Na-S batteries and related systems.

1. Introduction

As a typical representative of the most promising electrochemical energy storage systems, lithium-sulfur (Li-S) batteries have attracted numerous efforts due to its high theoretical specific capacity (1675 mAh g^{-1}) and energy density (2600 Wh kg^{-1}) as well as its low cost [1,2]. However, the Li-S batteries still face the challenges resulting from two intrinsic defects of cycloocta sulfur (cyclo- S_8) in the cathode. First, the intermediate products from cyclo- S_8 , dissolved polysulfides (Li_2S_m , $m \geq 4$), transport between the cathode and the anode with unfavorable reactions during charging-discharging process, leading to the “shuttle” problem [3,4]. Another essential problem is the typical insulation of the active materials (cyclo- S_8) and the final products (Li_2S) [5]. These two problems may cause loss of active sulfur, limited sulfur utilization and the consequent fast capacity fading of the Li-S batteries. These problems have attracted many researchers during the past decade, and various strategies have been attempted to improve the sulfur cathode performance [6–10].

The traditional strategies focused on design of the sulfur-based

composites with electronically conducting substrates, like carbon [11–14], conductive polymers [15], and metal oxides [16]. Although some of the dissolved Li_2S_m ($m \geq 4$) can be confined in the substrates with improved conductivity, the shuttle problem and the consequent loss of active sulfur still have not gotten basic settlement. In order to radically eliminate the problems originated from the intrinsic defects of cyclo- S_8 , a new strategy for sulfur-based composites with novel structure has been recently proposed. Instead of the aggregated cyclo- S_8 , the small sulfur allotropes (S_{2-4}) are used [17]. Different from the conventional cyclo- S_8 , the small S_{2-4} can directly transform into the insoluble Li_2S_2 and Li_2S which are the ultimate products in the Li-S battery discharging process. Since the unfavorable dissolved Li_2S_m , the intermediate products from cyclo- S_8 , are fundamentally avoided during discharging of the small S_{2-4} , the shuttle problem can be essentially solved and good cycling stability is expected to be obtained. Furthermore, as both the S_{2-4} and the products (Li_2S_2 and Li_2S) are insoluble in the electrolyte, the Li-S battery can operate well without loss of the active S_{2-4} species. In this method, the challenge is how to make the sulfur exist as the metastable small S_{2-4} molecules instead of the stable cyclo-

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S₈. To control the sulfur at molecular level, one feasible way is to facilitate the sieve effect of porous carbon with specific pore size, i.e. making the small sulfur molecules to be inserted and confined in the pores of the carbon substrates, while the sulfur molecules with bigger size would be excluded outside of the carbon substrates. Ultra-microporous carbon with pore size of about 0.55 nm is desired to prepare S_{2–4}/carbon composites, because 0.55 nm is an optimum size to separate S_{2–4} from the other sulfur molecules (Fig. S1). However, it is difficult to control the carbon pore size uniformly at so ultra-micro level, despite the importance of developing carbons with controlled porosity is well known [18]. As a result, although it is believed that the S_{2–4}/carbon composites promise Li-S battery with satisfactory electrochemical properties, the correlative studies are comparatively rare.

X. P. Gao et al [19] first proposed the small sulfur molecules for long stability of Li/S battery in 2010 and prepared porous carbon spheres with pore size of about 0.7 nm to accommodate the sulfur. Later, the follow-through work [20] explored the electrochemical behaviour further, but the larger sulfur molecules in the pores make the consequent irreversible capacity loss inevitable. Moreover, the microporous carbon derived from metal-organic frameworks (MOF) [21–23] or biomass [24] was proposed, but the carbon pores larger than 1 nm are still unavoidable. An organic-organic assembly method was used to prepare the microporous carbon with pores of 0.46 nm [25]. The S/C composite based on the carbon shows good cycling stability, but the rate performance (about 600 mAh g⁻¹ at 1 A g⁻¹) is limited due to the narrow pore size. In 2012, Y. G. Guo et al [26] reported small S_{2–4} confined in the microporous carbon with dominant pore size of about 0.5 nm, based on which, high performance S/C composite cathodes were achieved. However, the preparation and regulation of the porous carbon with uniform pores in ultra-microporous size are difficult either through hydrothermal reaction with surfactant [27] or by tunable KOH activation technique [28]. To summarize, although these complicated approaches are tried to prepare the microporous carbon, the precise regulation of carbon pores in size of 0.55 nm is still a challenge.

In this work, an ultra-microporous carbon (UMC) with uniform 0.55 nm pores was designed and prepared by polyvinylidene fluoride (PVDF) pyrolysis according to our previous work [29,30] for accommodating small sulfur molecules (S_{2–4}) for Li-S battery. Compared to the previous studies, the method is very simple and economic, as only one-step pyrolysis process is needed for the UMC preparation. Both the characterization and the electrochemical performance promise that S/C composite based on the UMC is a potential cathode for high performance Li-S batteries and even for other related energy storage devices such as Na-S batteries.

2. Experimental

Preparation of the UMC and S/UMC composite: The UMC was prepared from PVDF via a facile pyrolysis process. The PVDF powder (Kynar 761, Arkema Co.) was directly carbonized at 800 °C for 2 h in tube furnace at flowing nitrogen (99.999%) atmosphere with a heating rate of 10 °C min⁻¹. Without any subsequent treatment, the UMC with abundant ultra-micropores was obtained. The prepared UMC was used to accommodate the small sulfur molecules. The mixture of the UMC

and sublimed sulfur (Aladdin, 99.5%) in various mass ratios (S:UMC=2:8, 4:6, 6:4) was sealed in vacuum glass vessels and heated at 155 °C for 20 h. The heating rate was 10 °C min⁻¹ from room temperature to 115 °C and slowed down to 0.5 °C min⁻¹ in the range of 115–155 °C. Then, the temperature was raised to 300 °C and kept for 2 h to remove the redundant sulfur outside the UMC. Consequently, the S/UMC composite was obtained, and the S/UMC composites prepared in sulfur/carbon mass ratio of 2:8, 4:6 and 6:4 were denoted as S/UMC-1, S/UMC-2 and S/UMC-3, respectively.

Material characterization: The porosity of the UMC before and after loading sulfur was characterized by nitrogen adsorption/desorption measurements with ASAP 2460 (Micromeritics, USA). The specific surface area (S_{BET}) and the pore size distribution were calculated with the conventional Brunauer-Emmett-Teller (BET) method and the density function theory (DFT) method, respectively. The total pore volume (V_t) was obtained based on the N₂ adsorption amount at a relative pressure of 0.99. The morphology with a mapping analysis of the elements was observed with scanning electron microscopy (SEM, Hitachi4800) and energy dispersive X-ray spectrometer (EDS). The actual sulfur content in the S/UMC composites was tested by thermal gravimetric analysis (TGA, DTG-60A) with a heating rate of 10 °C min⁻¹ under nitrogen atmosphere. The characterization of the UMC and S/UMC composites was studied with X-ray diffraction (XRD) using Cu Kα radiation and Raman spectra at 514 nm. The sulfur molecules with sizes were optimized and calculated with nonlocal DFT in the DMol3 module of the Materials Studio 7.0 program using the BLYP functional based on a DNP group.

Electrochemical measurements: The S/UMC composites were mixed with super-P acetylene black, and La132 binder in mass ratio of 8:1:1 in isopropyl alcohol and deionized water (1:3 in mass) as dispersing solvent to prepare cathode for Li-S batteries. After spread onto the current collector and dried at 70 °C under vacuum, the cathodes were punched into pellets with a diameter of 10 mm and a sulfur loading of about 1 mg cm⁻². CR2025-type coin cells were assembled using the prepared cathode with lithium as anode, Celgard®2300 separator and 30 μL electrolyte in the argon-filled glove box. For S/UMC-1 and S/UMC-2 cathodes, the used electrolyte was 1 mol L⁻¹ lithium hexafluorophosphate (LiPF₆) in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (v/v=1:1), while for S/UMC-3 cathode, the electrolyte was 1 mol L⁻¹ lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in the solution of 1,3-dioxolane (DOL) and dimethoxymethane (DME) (v/v=1:1) with 0.4 mol L⁻¹ LiNO₃ addition. Electrochemical behaviour of the coin cells was performed by the cyclic voltammetry (CV) in the scan rate of 0.1 mV s⁻¹ in the potential range of 1.0–3.0 V on a CHI600e electrochemical workstation. The constant current charge-discharge experiments with the coin cells were carried out between 1.0 V and 3.0 V on a LAND CT2001A battery test system. The cycling performance was evaluated at 0.1 C, and the rate performance was evaluated at 0.1, 0.2, 0.5, 1, 2 and 5 C.

3. Results and discussion

Schematic illustration showing the preparation process of S/UMC is presented in Fig. 1. The UMC with abundant ultra-micropores with the

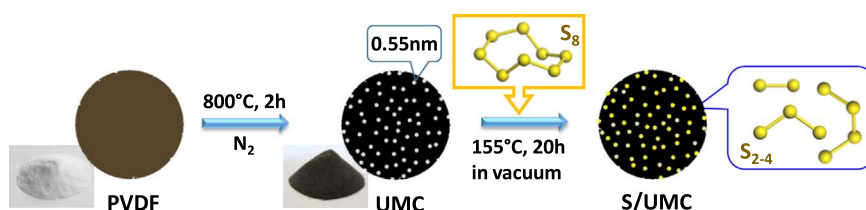


Fig. 1. Schematic illustration of the preparation of S/UMC by one-step pyrolysis treatment of PVDF powder at 800 °C for 2 h under N₂, followed by encapsulating small S_{2–4} molecules based on the pore size confinement through heating the mixture of UMC with melting sulfur.

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