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Research Article

SiO_2 coated carbon interlayer for Li-S batteries

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Abstract

Lithium-sulfur batteries have received great attention because of the high theoretical specific capacity, natural abundance, low cost, and environmental friendliness of sulfur. However, poor cycling and C-rate performance limit the application of Li-sulfur batteries. Placing porous and highly conductive interlayer between separators and sulfur cathodes is an efficient approach to improve active materials' utilization and limit the polysulfide shuttle effect and thus enhance the electrochemical properties of Li-sulfur cells. Moreover, SiO_2 could further improve electrochemical performance via capturing large amount of polysulfides owing to the polar structure and strong chemical interactions. SiO_2 coated highly conductive carbon nanofibers were prepared and used as an interlayer in Li-sulfur batteries. The uniform coating of SiO_2 nanoparticles on carbon nanofibers were observed from SEM and TEM images. The cells with SiO_2 nanoparticles coated highly conductive carbon nanofiber (SiO_2@CNF) interlayers delivered high first discharge capacity of 1547 mAh/g and retained the specific capacity of around 916 mAh/g in 200 cycles at 0.2C. The cells with SiO_2@CNF interlayers also showed improved C-rate performance compared the cells without SiO_2@CNF interlayers. The enhanced electrochemical performance resulted not only from high polysulfides capturing ability of SiO_2 nanoparticles with high specific surface area but also highly conductive interconnected structure of carbon nanofibers. Highly porous structure of SiO_2@CNF led to large amount of polysulfide adsorption and highly conductive structure resulted in reutilization of adsorbed polysulfides and thereby improved reversible specific capacities.

Keywords: SiO_2, nanoparticles, nanofibers, coating, electrospinning

1. Introduction

Considering climate change and other environmental issues, developing energy storage and conversion systems is vital. Rechargeable batteries are also important for large-scale applications of electronics, electric vehicles and smart utility grids. Among rechargeable batteries, Li-sulfur batteries are gaining tremendous interest due to high theoretical capacity (1675 mAh/g), energy density (2567 Wh/kg, which is based on the redox reaction of 16 Li + S_8 = 8 Li_2S), low cost and environmentally friendliness of sulfur. However, the issues on large volume change of around 80% from S to Li_2S during cycling, poor electronic conductivity of sulfur and lithium sulfide and shuttle effect caused by the dissolution of polysulfides (Li_2S_x, $4 < x \leq 8$) have to be addressed to commercialize Li-sulfur batteries [1-4].

Many polysulfides dissolve in an electrolyte solution during cycling of the Li-sulfur cells. The capturing of polysulfides can suppress shuttling into the anode side and the cycling performance of the cell directly related to capturing polysulfides and reutilization of these trapped polysulfides. Placing conductive carbon layer between separator and cathode is an effective approach to limit the shuttle effect. However, carbon structures have poor interaction with polysulfides due to nonpolar structure of carbon materials. Metal oxides could improve chemical adsorption of polysulfides [2, 5, 6]. There are few numbers of research on utilization of SiO_2 as interlayer in Li-sulfur batteries. Belgibayeva et al [5] fabricated SiO_2/C nanofibers by using PVP and TEOS precursor solution. The initial discharge capacity was 1304 mAh/g and capacity was 934 mAh/g in 50 cycles at 0.1 C.

Electrospinning is a common method to prepare free standing highly porous CNFs. Highly porous structures provide large number of sites for polysulfide adsorption and high conductivity improves kinetics of the cells and thereby electrochemical performance. In this study, a facile approach was presented to fabricate high performance nanostructured interlayers that combine high polysulfide adsorption of SiO_2 nanoparticles and high conductive of CNFs for Li-sulfur batteries. Highly porous carbon nanofibers were prepared by using electrospinning and coating of SiO_2 nanoparticles were utilized to further improve the polysulfide adsorption. SiO_2 coating on CNFs were seen from

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SEM and TEM images. High reversible capacities were observed from the cells containing SiO_2@CNF interlayers.

2. Materials and Method

Polyacrylonitrile (PAN, 150000)/polystyrene (PS, 192000) were dissolved in dimethylformamide (DMF) and 10 wt.% polymer solution was used for electrospinning. The feeding rate was 1 ml/h, the tip to collector distance was 15 cm and applied voltage was 15 kV during electrospinning. After stabilization at 280 °C for 5h and carbonization at 800 °C for 2h, porous carbon nanofibers were obtained and SiO_2 nanoparticles were coated on CNFs via electrospraying. Scanning electron microscope (SEM) and tunneling electron microscope (TEM) were used for morphology study. EDX and X-ray diffraction (XRD) were used for structural characterization. Cycling tests were conducted at room temperatures using CR2032 coin cells.

3. Results

Fig.1 shows the SEM image of SiO_2@CNF interlayer. Nanosized SiO_2 coated highly porous CNFs were observed. CNFs could employ as a buffer for volume change of active material. CNFs also capture polysulfides and improve active material utilization owing to highly porous and conductive structure. Moreover, uniformly distributed SiO_2 nanoparticles on CNFs further improve polysulfide migration because of strong chemical interaction between SiO_2 and polysulfides.

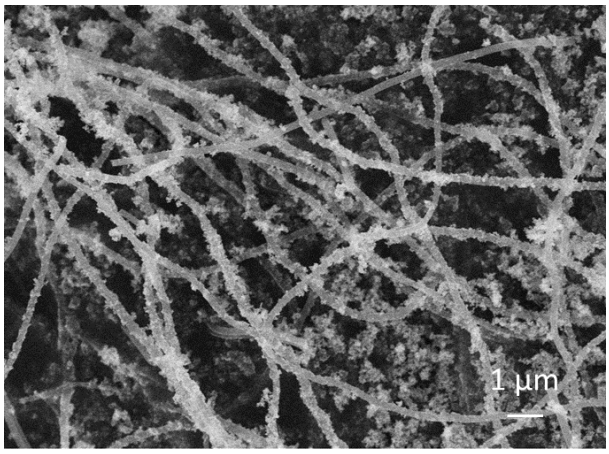

Fig. 1 SEM images of SiO_2@CNFs

TEM image of SiO_2@CNFs is also given in Fig.2 to prove uniform coating of SiO_2 on nanofibers. SiO_2 nanoparticles have amorphous structure with polar groups that is beneficial for chemical adsorption of polysulfides.

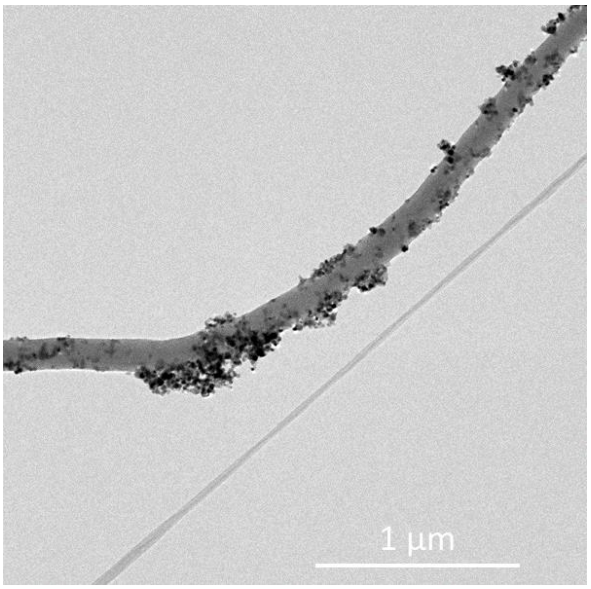

Fig. 2 TEM images of SiO_2@CNFs

Fig. 3 shows XRD spectra of SiO_2@CNFs. The large peak at around 23º is the characteristic of amorphous structure of carbon and SiO_2 which was also reported by Liu et al [7] for biomass derived SiO_2 containing carbons. SiO_2 coating was also proved by EDX spectra given in Fig.4.

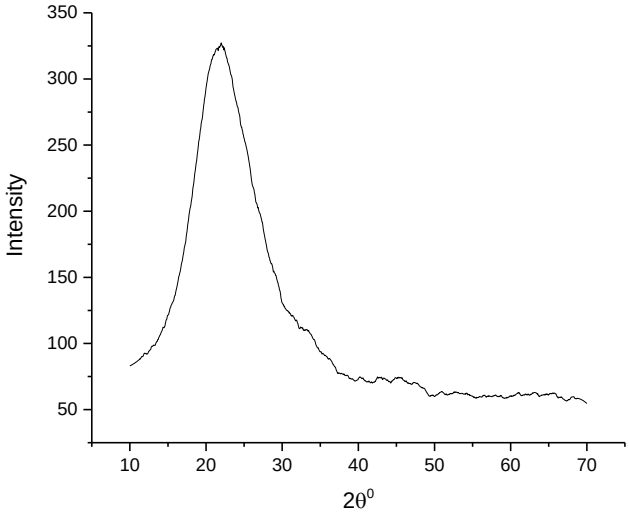

Fig. 3 XRD spectra of SiO_2@CNFs

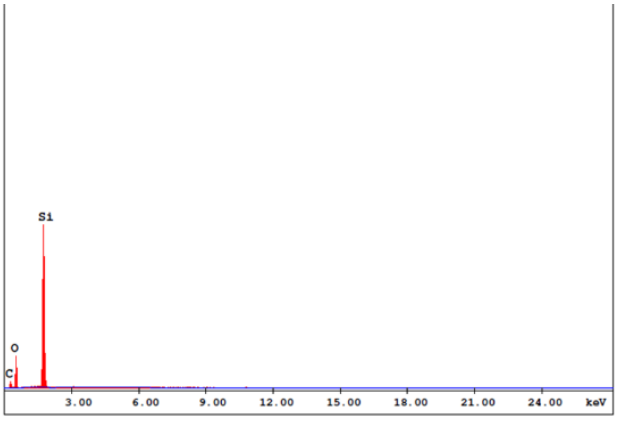

Fig. 4 EDX spectra of SiO_2@CNFs

Cycling performance of the cells with SiO_2@CNF interlayer is seen in Fig. 5. Initial discharge capacity of the cells with SiO_2@CNF interlayer was 1547 mAh/g whereas that of the cell without interlayer was 884 mAh/g. The corresponding sulfur utilization were 92% and 53%, respectively, for the cells with and without SiO_2@CNFs. Better sulfur utilization could be attributed to polar structure of SiO_2 nanoparticles and highly conductive CNFs. Liu et al [7] also reported better cycling performance for the cells with SiO_2 containing hard carbons and the results were attributed to keeping polysulfides on the cathode side owing to polar structure of SiO_2 and highly conductive structure of carbons.

Reversible capacity for the cell with SiO_2@CNF interlayer in 200 cycles was around 950 mAh/g while the cell without interlayer delivered specific capacity of around 223 mAh/g. The capacity decay was 0.2% per cycle for the cells with SiO_2@CNF interlayer. However, the capacity decay was 0.38% per cycle for the cells without interlayer. The result could be explained limited polysulfide shuttling resulted via strong chemical interaction between SiO_2 nanoparticles and polysulfides. Zhang et al [8] prepared SiO_2 coated separators for Li-sulfur batteries and improved cycling performance was attributed to efficient suppression of polysulfide shuttling.

C rate performance is also given in Fig.6. C-rate was changed from 0.2 C to 2 C and then back to 0.2 C. The cells with SiO_2@CNF interlayer delivered higher specific capacities at all C rates. The specific capacities were around 1180 mAh/g, 1030 mAh/g, 820 mAh/g, 710 mAh/g at 0.2, 0.5, 1 and 2C, respectively. However, the cells without interlayer showed poor C rate performance with low specific capacities because of severe shuttling of polysulfides. The capacities were 515 mAh/g, 385 mAh/g, 260 mAh/g, 100 mAh/g at 0.2, 0.5, 1 and 2C, respectively. Moreover, as the C rate was back to 0.2 C, the cells with SiO_2@CNF interlayer delivered high capacity of around 1160 mAh/g. Strong interaction between Si-O bond and polysulfides led to better sulfur utilization while CNFs acted as a second current collector and improve reutilization of active material and thus led to better C rate performance.

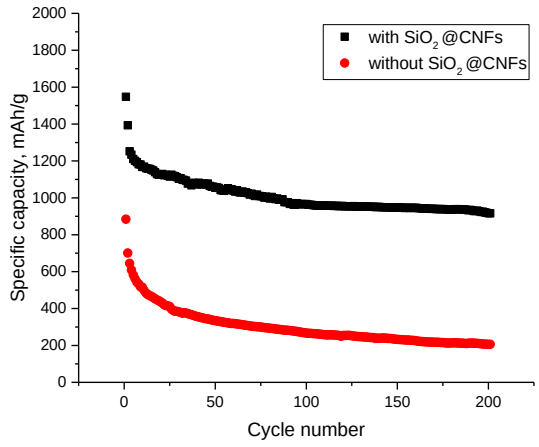

Fig. 5 Cycling performance of SiO_2@CNFs

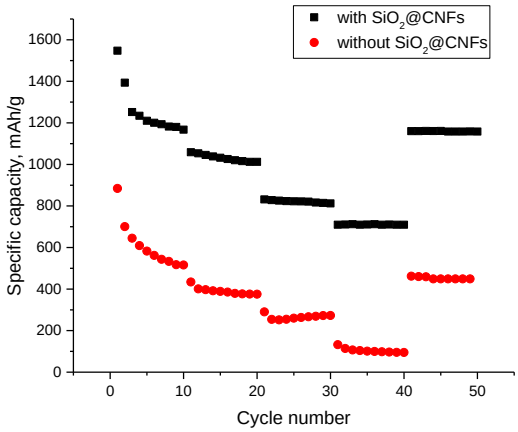

Fig. 6 C-rate performance of SiO_2@CNFs

4. Conclusion

High performance SiO_2@CNF interlayers were fabricated via electrospinning and uniform nanolayer of SiO_2 nanoparticles were coated on CNFs to combine large polysulfide adsorption ability of SiO_2 nanoparticles and high conductivity of CNFs. Due to the facile and effective approach that combines high polysulfide chemisorption of SiO_2 nanoparticles and highly conductive porous interconnected nanostructured carbon nanofibers, high reversible capacities and improved C rate performance was observed.

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