



Short Communication

Application of stabilized lithium metal powder and hard carbon in anode of lithium–sulfur battery



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ABSTRACT

Stabilized lithium metal powder (SLMP) can effectively compensate the irreversible capacity, increase energy density in the continuous charge–discharge process of lithium–sulfur battery, and provide more anode materials to match the need of the energy market in the future. A novel SLMP anode in which hard carbon (HC) was used as the additive and poly-vinylidene fluoride (PVDF) as binder was prepared in an argon-filled vacuum glove box. The new negative sheet provides greater surface for electrolyte infiltration, facilitates ion diffusion and improves the utilization of sulfur element. This new type of Li–S battery has a higher initial capacity of 1300.9 mAh/g and a better cyclic stability than cell using conventional lithium foil as anode.

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1. Introduction

Lithium–sulfur (Li–S) batteries, which have numerous appealing advantages, such as high gravimetric and volumetric energy densities of 2500 Wh kg⁻¹ and 2800 Wh L⁻¹ (assuming the complete reaction of sulfur with lithium to form Li₂S, respectively), environmental friendly and abundant sulfur storage, have attracted tremendous attention and are believed to be promising candidates for electric and hybrid electric vehicles [1,2]. However, commercialization of Li–S battery has been gravely hindered by several issues, such as the insulating of sulfur element, polysulfide dissolution, and large volume expansion of sulfur during cycling. In order to solve the above problems, enormous efforts have been demonstrated to overcome the insulating property of sulfur, to modify the properties of the SEI layer and prevent the dissolution of polysulfide by developing novel electrolyte [1,3–10]. However, few people pay attention to the anode problem of lithium–sulfur batteries, such as Li dendrite growth [11].

So far, stabilized lithium metal powder (SLMP) has been applied to anode to improve the performance of lithium-ion battery, especially for the first capacity and coulombic efficiency [12–16]. As a kind of innovative materials, SLMP can be safely operated in dry argon, can effectively compensate the irreversible capacity, increase energy density, and provide more anode materials to match the market demand in the future [13]. However, the effect of SLMP and hard carbon (HC) on Li–S cell performance has not been discussed in the present literature. In this work, a facile route to fabricate a new type of Li–S battery anode

using HC and SLMP is first introduced, and the corresponding performance is characterized and discussed.

2. Experimental

2.1. Materials and electrode fabrication

70 wt.% of sulfur (99.95%, analytically grade), 20 wt.% of Super p li (Super li Conductive Carbon Black) and 10 wt.% of PVDF (polyvinylidene fluoride) binder have been taken to prepare sulfur cathode in NMP (N-methyl-2-pyrrolidone). After that, the slurry was uniformly mixed and coated on nickel foam. After drying for 16 h at 60 °C under vacuum, the cathode was transferred into the glove box. The lithium anode was prepared by thoroughly mixing SLMP with 10–40 wt.% HC and 10 wt.% PVDF binder in NMP. Then the slurry was applied on nickel foam to make 0.3 mm thickness flattened film (compared to 0.2 mm thickness of ordinary lithium foil) using a doctor blade, and the negative film was placed on the heating plate for 10 h. The quality of both this new SLMP film and ordinary lithium foil is about 20–30 mg, and sulfur is about 6–8 mg in each cells. All the operation of lithium anode was carried out in the argon-filled vacuum glove box.

2.2. Coin-cell assembling and electrochemical measurements

2025 type coin-cell was assembled with the above positive and negative film using Celgard 2400 as separator, 1, 3-dioxolane (DOL) and Dimethyl Ether (DME) as the electrolyte solution (V_{DOL}:V_{DME} = 1:1), added with 1 M LiClO₄ and 1 M LiNO₃. The electrochemical properties test was carried on after cell placed for 24 h. The galvanostatic charge and discharge tests of Li–S cells were performed between 1.5 V

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and 3.0 V using a multi-channel battery test system (LAND CT2001A, China). The Cyclic Voltammetry (CV) of the Li-S cells was measured in electrochemistry working station (Potentiostat/Galvanostat Model 263A, sweep rate: 0.1 mV/s). Electrochemical impedance spectroscopy (EIS) was carried out on Signal Recovery Model 5210 over the certain test voltage (5 mV) and the frequency range from 10 MHz–100 KHz. All the above tests were carried out at room temperature.

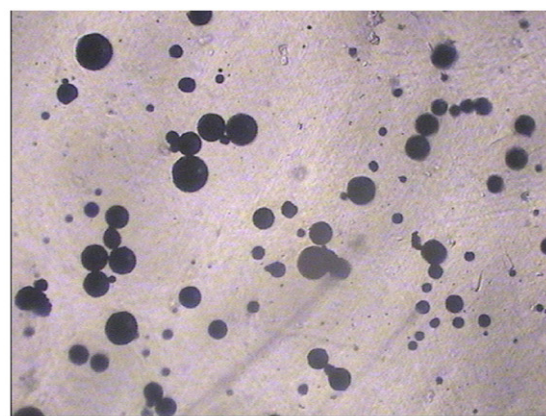
2.3. Morphology and structure characterizations

The surface morphology was observed through scanning electron microscopy (SEM, S4700, Hitachi). After charge–discharge cycles, the cathodes were soaked in the DME for 48 h before taking SEM and linear scans (Fig. 4). Morphology of SLMP was taken by microscope (SG fiber fineness meter, Shanghai), and the HC structure was measured via X-ray diffraction (XRD, Rigaku-3014).

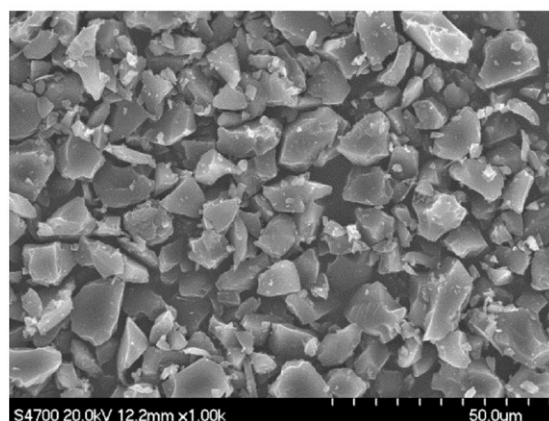
3. Results and discussion

From the image of SLMP showing in Fig. 1a, the particles have different size and the range of them is 20–50 μm . The composite anode of SLMP and HC can effectively improve the safety and cycling performance of the Li-S battery. The electrode surface area using SLMP as anode is larger than that of the ordinary lithium foil, which allows more complete contact with the electrolyte and greater effective current density. From the SEM image of HC in Fig. 1b, HC has different size and shape, no reunion, irregular grain orientation. HC can be obtained from the cross-linked resin thermal decomposition around 1000 $^{\circ}\text{C}$, such carbon at a high temperature above 2500 $^{\circ}\text{C}$ is difficult to be graphitized [17,18]. As has random sorting, uneven size, structural stability and high reversible specific capacity (usually 500–700 mA/g), thereby Li-S battery with adding HC has a longer cycle life, higher specific capacity and better safety performance. The XRD diffractogram (Fig. 1c) contains apparent peaks at 23.9, 43.7 and 79 $^{\circ}$ which correlated to the (002), (100) and (110). In order to easily estimate the number of carbon sheets arranged as single layers, Liu et al. [19] defined an empirical parameter R that involves the ratio of the (002) peak height against the 2-theta axis. In our work, the R of 2.5 suggests the less fraction of single layers.

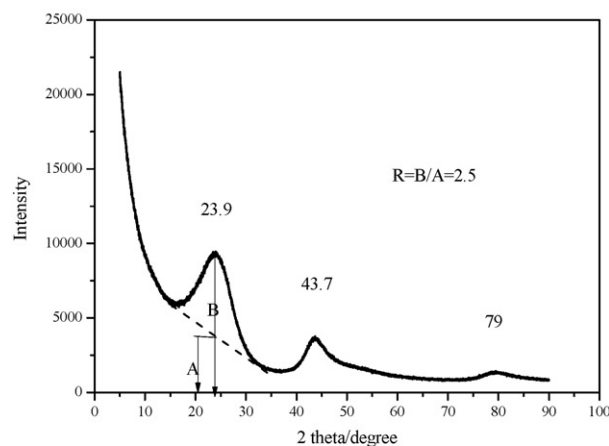
The initial charge/discharge curves at 50 mA/g current density of the Li-S batteries are shown in Fig. 2a. Both six discharge profiles have two-voltage plateaus: a higher one at 2.3 V~ and a lower one at 2.0 V~. When adding 10–30% HC to SLMP anode, the charge and discharge capacity for the first time of Li-S battery is higher than ordinary electrode, especially after adding 20% HC, the initial discharge capacity reaches 1300.9 mAh/g. It is noteworthy that battery overcharge phenomenon occurred when using traditional lithium foil as anode. Overcharge capacity of 80 mAh/g indicates serious shuttle effect appeared during charging and discharging. As for the use of HC, this first overcharge phenomenon has weakened. The rate performances of the different content of HC are presented in Fig. 2b. From the figure, battery with 20% HC has a relatively high specific capacity and best rate capability in all the samples. In contrast, anode having 40% HC shows lower capacity and electrode using ordinary lithium foil performs lowest capacity at the rate of 1000 mA/g, indicating that battery rate performance with the addition of about 20% HC can be obviously improved. Cycling performances at different current density of cells are shown in Fig. 2c, d and e. From the picture Fig. 2c and d, the discharge specific capacity of the battery using ordinary lithium foil suddenly dropped and the battery in 50–60 cycles prone serious overcharge phenomenon leading to the termination of life, which may be closely related to the accumulation of polysulfide and lithium dendrite. Charging and discharging of Li-S battery using lithium foil at high current density, such as 1000 mA/g (Fig. 2e) shows the lowest specific capacity. The specific capacity and cycle stability was significantly improved with 10% or 20% HC used. This is probably because HC has played a huge role in the continuous cycle, can inhibit



(a)



(b)



(c)

Fig. 1. (a) Microscope image of SLMP, (b) SEM image of hard carbon(HC), (c) XRD pattern of the HC material.

the ongoing shuttle effect and the constant growth of the lithium dendrites on negative electrode surface in a certain degree.

The cyclic voltammetry curves of Li-S cells are shown in Fig. 3a. The curve exhibits an oxidation peak at 2.50 V and two reduction peaks at 1.9–2.0 V and 2.3 V. The two reduction peaks were possibly attributed to the reactions of sulfur to low state polysulfide ions (Li_2S_n , $n \geq 4$) and further to solid state $\text{Li}_2\text{S}/\text{Li}_2\text{S}_2$. The voltage of the two reduction peaks is basically consistent with the voltage plateau of the first charge and discharge curve as shown in Fig. 2a. The second reduction peak of the Li-S battery using common lithium foil corresponding to the low voltage, indicating that this battery has poor reversibility. When 20%

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