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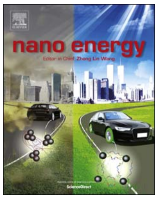

Enhanced performances of Li/polysulfide batteries with 3D reduced graphene oxide/carbon nanotube hybrid aerogel as the polysulfide host

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ABSTRACT

Li-S batteries, though promising for long-distance electrical vehicles, are still not practically viable mainly due to the short cycling life arising from the polysulfide shuttle. Herein, we demonstrate a Li/polysulfide battery with 3D nitrogen-doped reduced graphene oxide (rGO)/carbon nanotube (CNT) hybrid aerogel as the binder-free and self-standing host for liquid polysulfide-containing catholyte. Hetero-dopants of nitrogen and CNT additives are found to significantly improve the electrochemical performances due to the abundant active catholyte/electrolyte interfaces, high rate charge-transfer paths, and spatially uniform depositing/stripping of reactants. The final hybrid aerogel achieves long cycling stability (0.11% capacity fading rate for 400 cycles) and high rate capability (767 mAh/g_{sulfur} at 2 C rate) at a high areal sulfur loading weight of ~6 mg/cm^2.

1. Introduction

The lithium–sulfur (Li-S) battery holds great promise for powering next-generation long-distance (> 300 miles per charge) electric vehicles due to its much higher energy density and lower price comparing with that of commercial lithium intercalation-based Li-ion batteries. A Li-S cell undergoes a two-electron reaction ($S+2Li^{+}+2e^{-}\leftrightarrow Li_2S$), yielding a theoretical capacity of 1672 mAh/g and a theoretical energy density of 2567 Wh/kg, more than 6-fold higher than that of commercial Li-ion batteries (e.g. 387 Wh/kg of $LiCoO_2$/graphite battery) [1–5]. Nevertheless, the commercialization of Li-S batteries is still not viable due to their low rate-capability and short cycling life, arising from the insulating nature of reactants (both elemental sulfur and reduced Li_2S/Li_2S_2) and the known effect of polysulfide shuttle, respectively. The intermediates, i.e. high-order lithium polysulfides (Li_2S_x, $3\leq x\leq 8$), generated during discharge/charge cycles are highly soluble in the organic electrolyte, resulting in the repeated stripping/depositing of sulfur or Li_2S/Li_2S_2 from/onto the conductive frameworks of the cathode. The aggregation of these insulating products could seriously deteriorate the kinetics of the cell and make the active materials inaccessible. Meanwhile, the dissolved lithium polysulfides diffuse from cathode to Li anode, and are reduced to insoluble low-order lithium polysulfides. Active electrode materials are continuously consumed during the shuttle, leading to the low columbic efficiency and poor cycling life [6–8].

Intensive efforts have been dedicated to solving these challenges. The mostly adopted approach is to trap solid sulfur in porous carbonaceous nanostructures by a melting and infusing fabrication route. A variety of porous carbon structures were adopted, including the graphene [9], carbon nanotubes (CNT) [10], mesoporous carbon [11,12], microporous carbon [13], etc. Porous carbon interlayers between the cathode and separator were developed to suppress the polysulfide shuttle [12,14]. Also, different shuttle mediators (oxides [15–17], hetero-atom dopants [18–20], etc.) were found to be able to immobilize the polysulfides. Through these approaches, the cycling performances were improved, but the use of large amount of inactive materials (carbonaceous materials, polymer binders, metal current collectors, etc.) significantly decrease the energy density based on the total weight of the cathode. Binder-free, current collector-free, and self-standing conductive frameworks of carbonaceous electrode have been demonstrated to be promising to solve this issue, since the weight of metal current collector and polymer binder is reduced [21]. Meanwhile, three dimensional (3D) connected porous structures could promote the intimate electrolyte/electrode contact and the high-rate charge transfer, allowing the potential high areal loading of sulfur and thus high areal capacity.

Contrary to the use of infused solid sulfur, liquid-type polysulfide-containing catholyte has been recently reported to be able to promote the homogeneous deposition of S or Li_2S/Li_2S_2, and improve the cell kinetics [21–26]. We have previously demonstrated the high performances of a Li/polysulfide cell with CNT sponge synthesized from chemical vapor deposition as the polysulfide host [21]. The key for Li/

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polysulfide battery is to achieve 3D highly porous conductive frameworks, and optimize the catholyte concentration and catholyte-to-carbon ratio [21]. Herein, we report a Li/polysulfide battery with 3D rGO/CNT hybrid aerogel as the conductive frameworks in cathode, which, compared to CNT sponge, can accommodate larger amount of liquid catholyte and therefore achieve a higher polysulfide loading volume and equivalent sulfur-to-carbon weight ratio. The aerogels were derived by a hydrothermal reaction and a following freeze-drying process. Nitrogen dopants were further introduced into the 3D electrode for adsorption of the dissolved polysulfides by a thermal annealing under the atmosphere of Ar/NH_3. The final nitrogen-doped rGO/CNT (NrGO/CNT) aerogel achieved high specific capacity (1150 mAh/g_{sulfur} for initial cycle), long cycling life (55.5% capacity retention after 400 cylces), high rate capability (767 mAh/ g_{sulfur} at 2 C rate) with a catholyte loading volume of 25 µL per miligram of rGO/CNT (equivalent to a S-to-C weight ratio of 1.6).

2. Methods

2.1. Preparation of aerogels

0.176 g of ascorbic acid was added to 20 ml of 2 mg/ml GO suspension (Nanjing XFNANO Materials Tech Co., Ltd), and the solution was then transferred into a 30 ml Teflon-lined stainless steel autoclave for hydrothermal treatment at 180 °C for 12 h. Then, the autoclave was naturally cooled to room temperature, and the black rGO hydrogel was washed with distilled water and freeze-dried to obtain the rGO aerogel. For the rGO/CNT hybrid aerogel, the same route was followed but the initial suspension contained 2 mg/ml of a mixture of acid-treated multi-walled CNT and GO (weight ratio is 1:4). To prepare nitrogen-doped rGO (NrGO) aerogel and nitrogen-doped rGO/CNT (NrGO/CNT) aerogel, the above two aerogels were thermally treated at 800 °C for 3 h under a mixture gas flow of Ar (40 sccm) and NH_3 (60 sccm). For the nitrogen-doped graphene (NG) aerogel, 5 mg/ml GO suspension was freeze-dried and then directly heat-treated at 800 °C for 3 h under Ar/NH_3 atmosphere without the hydrothermal reduction.

For the acid treatment of multi-walled CNT, 200 mg of multi-walled CNT (Diameter: 10–20 nm, length: 30–100 µm) was added into 80 ml of a mixture of 95% HNO_3 and 97% H_2SO_4 (1:3 by Vol.). The mixture was stirred and refluxed at 100 °C for 1 h to get a uniform black solution. The acid-treated CNT was collected by vacuum filtration and washed with abundant distilled water.

2.2. Preparation of polysulfide catholyte

The blank electrolyte was prepared by dissolving 1 M lithium bis(trifluoromethane)sulfonimide (LiTFSI) (Sigma Aldrich, 99.995%,) and 0.5 M $LiNO_3$ (Alfa Aesar, 99.999%,) in 1,3-dioxolane (DOL): dimethoxyethane (DME) (1:1 by volume). The polysulphide catholyte was synthesized by directly reacting elemental sulfur with stoichiometric Li_2S (molar ratio of S:Li_2S is 5:1) in blank electrolyte at 60 °C for 24 h to form 2 M Li_2S_6 (molar concentration calculated based on S atom).

2.3. Measurements and characterizations

2032-type coin cells were assembled in an Ar-filled glove box (O_2 and H_2O less than 1 ppm) for testing the Li/polysulfide batteries. The aerogels were cut into thin rectangular plates of about 2 mg. The coin cell was assembled with the Li metal foil as the anode, Celgard 2400 membrane as the separator, and thin aerogel plate soaked with Li_2S_6 cathodlyte as the cathode. The soaked volume of Li_2S_6 catholyte is 25 µL per miligram of rGO/CNT, equivalent to a sulfur-to-carbon weight ratio of 1.6. The areal loading weight of sulfur is about 6 mg/cm^2. The Li/polysulfide cells were first discharged to 1.7 V, and then cycled between 1.7 and 2.8 V at different rates (1 C=1672 mA/g_{sulfur}) by a battery cycler (LAND CT2001A). The AC impedance measurement was conducted for the freshly assembled Li/polysulfide cells by a CHI electrochemical workstation (CHI660E) from 100 kHz to 0.1 Hz.

Scanning electron microscopy (SEM) was taken with a Hitachi SU8200. After the 100 cycles at 0.25 C rate and at charged state, the aerogels were detached from the cells and washed with DOL to remove the lithium salt (mainly LiTFSI and $LiNO_3$) and dried in the glove box for following SEM and EDS characterization. XRD measurements were performed with a Panalytical instrument (X′Pert 3 Powder). Raman spectra were measured by a confocal Raman spectrometer (HORIBA LabRAM HR Evolution).

3. Results and discussions

The 3D porous electrode is key for a Li/polysulfide battery, which is required to soak large amount of liquid catholyte and to provide abundant active electrode/catholyte interface for redox reactions of polysulfide species. Graphene sponges fabricated from different processes (template CVD, freeze-drying, etc.) have been recently studied for applications as sorbents of oil or organic solvents, due to its ultra-low density, large specific surface area, and high adsorption capacity

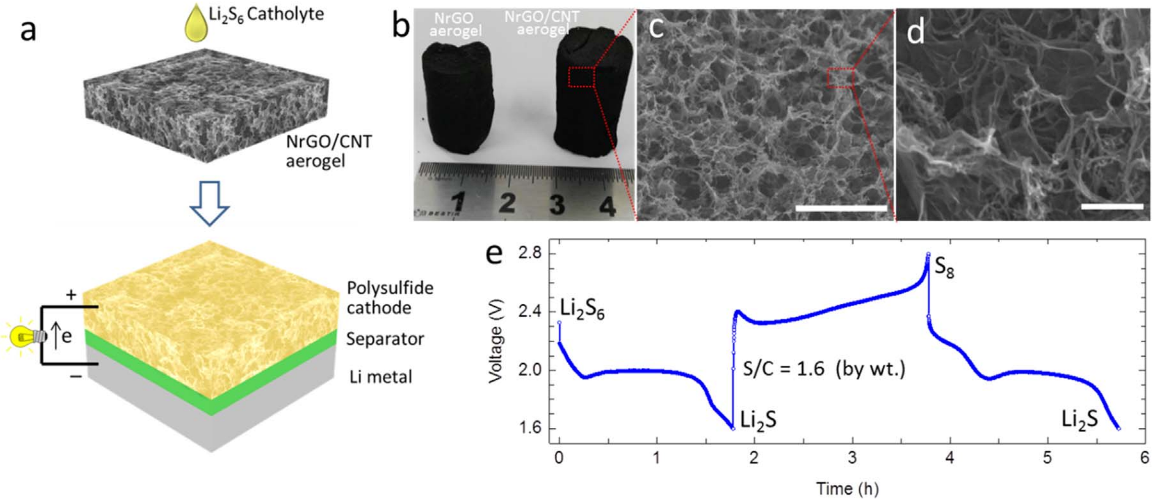

Fig. 1. Li/polysulfide batteries. (a) A scheme of the Li/polysulfide battery with 3D graphene aerogel as the host for Li_2S_6 catholyte in the cathode. (b) A photo of NrGO and NrGO/CNT aerogel. The SEM image of a NrGO/CNT aerogel at low (c) and high (d) magnification. (e) The typical voltage profile of a Li/polysulfide battery. The scale bar for (c) and (d) is 50 µm and 500 nm, respectively.