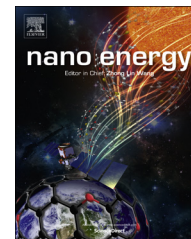




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RAPID COMMUNICATION

Soluble polysulphide sorption using carbon nanotube forest for enhancing cycle performance in a lithium-sulphur battery



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Cycle performance

Abstract

The rapid capacity decay of lithium-sulphur batteries has been a significant obstacle for practical application, which is generally considered to arise from dissolution of lithium polysulphide in the electrolyte and diffusion away from the cathode. As the lithium content in the polysulphide increases with further discharge, capacity decay occurs also from the passivating effects by the formation of insoluble sulphides, further amplified by volume increase. More recently, weakening of sulphur adhesion to carbon with progress in discharge is also an important factor in the sulphur cathode degradation. In order to overcome capacity decay caused by all the above mechanisms, we have prepared a composite cathode made of sulphur and high density carbon nanotube (HD-CNT) forest scaffold that is able to interfacially adsorb and volumetrically confine the polysulphide species and accommodate the expansion of sulphur discharge products effectively. This cathode demonstrates very high electrochemical stability and high discharge capacity up to 200 full discharge/charge cycles even with the use of the basic organic ether electrolyte where polysulphide shows high solubility, thus providing evidence for confinement and interfacial contact. Retention and surface adsorption favoured by minimizing the wall-to-wall distance between the aligned CNTs arise from a decrease in the

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reaction energy of the adsorption. Computational simulation of the interface between polysulphide species and carbon nanotube surface provides first-principle confirmation of improved binding between C and S in the polysulphides as wall-to-wall distance is decreased. The HD-CNT scaffold is self-binding and highly-conducting thus the conventional additives of binder and carbon black are also fully eliminated. A high discharge capacity of 812 mA h g^{-1} of sulphur (corresponding to 503 mA h g^{-1} of the whole cathode material mass) is stably retained after 200 cycles at 400 mA g^{-1} with a small average capacity decay of only 0.054% per cycle on average. These encouraging results provide novel approaches to designing and fabricating long cycle life cathode in a lithium-sulphur battery.

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Introduction

Lithium-sulphur batteries, which use sulphur (S) as cathode and lithium as anode, have attracted considerable attention because of their high theoretical capacity of 1675 mA h g^{-1} of elemental sulphur and high nominal theoretical energy density of 2500 W h kg^{-1} [1-5]. Sulphur is readily available particularly as a by-product of oil and natural gas desulphurization and poses less environmental risk than heavy metal based Co, Mn compounds or the phosphates that are presently used in Li-ion batteries. Therefore, sulphur is considered to be a very promising future cathode material for high energy-density rechargeable batteries. Despite its promising attributes, the Li-S battery is still plagued by various problems, and a rapid capacity fading with cycling is the key issue hindering its widespread practical utilization. Capacity degradation is ascribed to a combination of factors. The lithium polysulphides as they form during discharge can readily dissolve and diffuse in the electrolyte away from the cathode redox sites [6]. The lithium polysulphides are intermediate products of the electrochemical reduction of sulphur in the organic electrolyte. They can dissolve and diffuse from the cathode to the metallic lithium anode (and also in the reverse direction) causing parasitic reactions, which result in lithium anode corrosion, loss of active sulphur and low coulombic efficiency. As reduction progresses, the lithium polysulphides will finally result in the precipitation of insulating Li_2S and other insoluble compounds on the cathode surface, which inhibit transport of the lithium ions and reduce the battery capacity especially with cycling. The solid sulphides occupy 80% more volume than sulphur and thus enhance the passivating effect. Any unutilized sulphur can also have the passivating effect due to its insulating property.

To address these issues, some forms of carbon are usually added to the cathode due to their high conductivity, low weight and ready availability in porous structure [7-12]. But the capacity fading is still observed in the basic sulphur/carbon composite systems. Poor interfacial contact degradation due to the Li_xS detachment from the carbon surface during the discharge process has been shown recently to be an important issue [13]. Zheng et al. [13] recently proved that despite tendency towards volume expansion, weakening of C-S bonding with increasing lithium in the polysulphides can result in shrinking away of S from the C surface. Thus the interfacial contact between the lithium

polysulphides and carbon crucial for sustaining the redox reaction is degraded, inevitably leading to the formation of aggregated insoluble sulphides. Zheng et al. [13] added PVP to electrolyte and used ex-situ TEM to show evidence for improving the C-S bonding.

Most approaches reported in the literature have tended to consider additives that can further limit the solubility and diffusivity of polysulphides in the electrolyte. Just as the above-mentioned work by Zheng et al. [13], who have aimed to avoid loss of binding between C and the S products in the electrolyte by amphiphilic surface modification. Oxides sulphide captures, such as mesoporous silica [14], metal-organic framework (MOF) [10,15] and titania [16], have been introduced to improve the performance of the sulphur cathode. Several groups also demonstrate that the modification of sulphur electrode by polar polymer additives is consistently shown to improve the cycling performance [7,13,17]. In further improve the cycle stability, several precise structural innovations have been proposed, including the use of core-shell morphology [18,19], the graphite/lithium metal as a hybrid anode [20] and the introduction of an ion selective membrane [21]. Furthermore, the new electrolyte system based on an organic ether, such as dioxolane (DOL) and 1,2-dimethoxyethane (DME), as a solvent is developed because the carbonate solvents typically used in a lithium-ion battery are usually not suitable for Li-S batteries [22]. The rapid capacity fading arises from the dissolution of lithium polysulphides (Li_2S_n , $n=3-8$) into the organic ether electrolyte during the discharge-charge process. Finally, the large volume expansion due to the difference in density between sulphur and the solid lithium sulphide products coupled with the polysulphide dissolution will further accelerate the capacity fading during cycling.

Therefore, LiNO_3 additive has been introduced to stabilize the Li-metal surface. Meanwhile, the electrolyte with high Li salt concentrations has been used to reduce the dissolution of polysulphide by the common ion effect [23-25]. However, the additives will decrease the overall capacity of the battery and introduce additional costs. In this paper, we have focused on a solution that can improve the interfacial binding between C and the Li polysulphides through morphological control alone without any additives. In order to prove the concept we have intentionally used an electrolyte in which the polysulphides are very soluble.

Recently, carbon nanotube (CNT) has been combined with sulphur to form a cathode for lithium-sulphur battery, thus utilizing CNT's excellent electrical, thermal, and

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