Rechargeable Lithium-Sulfur Batteries with Binder-Free Carbon Nanotube Electrodes

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Introduction

Electrical energy storage systems are becoming critical for a sustainable and green world.[1] High energy rechargeable batteries are one of the most promising options for electric vehicles and grid energy storage. Lithium–sulfur (Li-S) batteries, which utilize the high theoretical capacity of sulfur (*i.e.*, 1,672 mAh g^{-1}), can enable packaged cells with two to three times higher energy densities than current Li-ion batteries.[2] However, a lot of challenges associated with insulating sulfur, soluble intermediate polysulfides, and shuttling effect exist. Although significant improvements have been achieved in recent years, detailed understanding and further improvements are still needed.

Binder-free carbon nanotube electrodes, which have shown unique properties, have been developed for Li-S batteries in our group. We present here a highly reversible Li/dissolved polysulfide battery utilizing a binder-free, self-standing multiwalled carbon nanotube (MWCNT) electrode.[3]

Experimental

The binder-free, self-standing MWCNT electrode was prepared by a dispersion-filtration method. Polysulfide catholyte was prepared by mixing sulfur powder and lithium sulfide within an ether-based electrolyte (1 M $LiCF_3SO_3$ and 0.1 M $LiNO_3$ in dimethoxy ethane (DME)/1,3-dioxolane (DOL) (1:1 v/v)) at an elevated temperature. CR2032 coin cells were assembled with the MWCNT electrodes, polysulfide catholyte, polypropylene separator, and lithium foil.

Results and Discussion

The cell configuration of a Li/dissolved polysulfide cell with a MWCNT electrode is displayed in Figure 1. The cell with an open circuit voltage (OCV) of ~ 2.28 V was initially charged to 3.0 V followed by full discharge and charge in the voltage range of 3.0 – 1.8 V.

XPS was used to identify the composition of the charged and discharged MWCNT electrodes before and after washing with electrolyte solvent. There is no obvious binding energy shifts among these four samples for the elements F 1s and C 1s, excepting the reduction in peak intensity due to the removal of $LiCF_3SO_3$ and electrolyte by washing. Figure 2 presents the S $2p_{1/2}$ and S $2p_{3/2}$ dual peaks with an intensity ratio of ~ 1:2 arising from spin orbit coupling. The peaks at 171.1 and 169.8 eV are only present before washing, and are characteristic of the soluble $LiCF_3SO_3$. The two strong peaks at low binding energies (161.9 and 160.4 eV) are only observed in the discharged MWCNT electrodes, and are assigned to Li_2S. The peak intensities do not decrease after washing, indicating that the discharged product Li_2S is insoluble.

Figure 3 presents the extended cycling and Coulombic efficiency of the Li/dissolved polysulfide cells. Reversible capacities after 50 cycles remain high at 1,411 mAh g^{-1}, 1,317 mAh g^{-1}, and 1,179 mAh g^{-1} at, respectively, C/10, C/5, and C/2 rates. The capacities obtained are more than double those of the control Li/dissolved polysulfide cell with Teflon-bonded Super P electrode and conventional sulfur electrodes. The Coulombic efficiency is > 95% with a degradation trend similar to that observed for the capacity. The capacity retention and Coulombic efficiency are higher under high-rate conditions because higher rate leads to a lower retention time of the dissolved polysulfides within the electrolyte per cycle, resulting in a suppression of the migration of polysulfides to the lithium anode side and a decrease in the loss of active material.

In summary, we have demonstrated highly reversible Li/dissolved polysulfide cells, utilizing an intertwined, free-standing MWCNT paper as a host electrode. The high capacities obtained are attributed to the unique MWCNT electrode architecture, facilitating charge transport, formation of amorphous charge and discharge products, and trapping of polysulfides and cycled products within the MWCNT electrode. This system offers a new way to solve the long-term reversibility obstacle facing rechargeable Li-S batteries and provides guidelines for designing electrode architectures and cell configurations to achieve high energy density batteries. With the further developments of solid electrolytes that can eliminate the contamination of polysulfides on the lithium metal anode, Li/dissolved polysulfide batteries could become promising for practical applications.

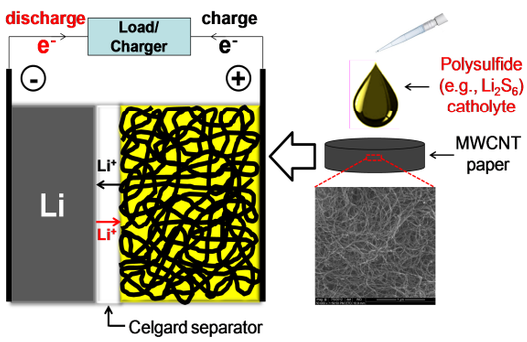

Fig. 1. Schematic configuration of a Li/dissolved polysulfide cell with a binder-free MWCNT electrode.

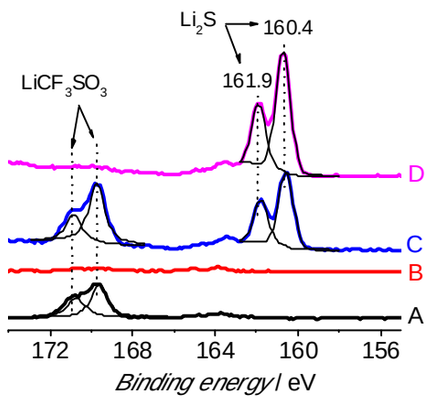

Fig. 2. S 2p XPS spectra of the MWCNT electrodes: (A) charged electrode without washing, (B) charged electrode washed with electrolyte solvent, (C) discharged electrode without washing, and (D) discharged electrode washed with electrolyte solvent.

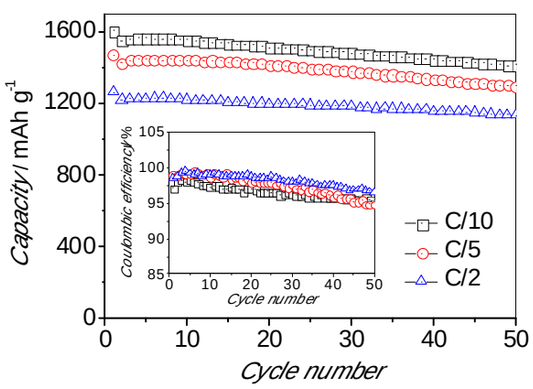

Fig. 3. Cycle life and Coulombic efficiency of the Li/dissolved polysulfide cells with MWCNT electrodes.

References

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