HEMISTRY

ISSUES OF ANODE AND CATHODE MATERIALS FOR RECHARGEABLE LITHIUM -ION BATTERIES

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Abstract. *The development of novel battery systems, such as Si-lithium sulphide (Li_2S), will have a significant impact on applications that require high specific energy, such as batteries for electric vehicles and portable electronics. The problems of rechargeable lithium-ion batteries related to anode materials such as the huge volume change during cycling, pulverization, rapid degradation during the process of introduction and extraction of lithium may be solved with application of nanostructured silicon anodes. On the cathode side, it is important to encapsulate lithium sulfide in the best way possible with highly-conductive materials.*

Keywords: *lithium-ion batteries, nanostructured silicon anodes, conjugated polymers, sulfur based cathodes, energy capacity, Coulombic efficiency.*

Due to the unique characteristics, rechargeable lithium-ion batteries (LIB) are widely used in various industries: in power systems for smoothing peak loads, as traction batteries for electric transport, in energy storage systems produced by alternative sources, uninterruptible power supplies, etc [1-4].

In many LIB, brought to the stage of commercialization, the anode is made of graphite (primarily synthetic). At the same time, today's LIBs with a negative graphite-based electrode can not provide ever-increasing requirements, since its practical capacity has approached its theoretical limit.

It is known, that the energy capacity of any battery depends on the capacity of the active materials of the positive and negative electrodes. Thus, it is possible to increase the energy capacity of the battery by replacing existing active materials with more energy-intensive ones.

Since Li metal has the issue of dendrite formation and is not safe as anode, silicon can be considered as one of the promising materials for the negative electrode of the LIB. Moreover it has the highest theoretical capacity in comparison with other materials. The lithium-rich intermetallic compound has the following composition: Li4,4Si (Li22Si5), it corresponds to a specific capacity of 4200 mAh / g, which is in order of magnitude higher than the theoretical capacity of graphite [5]. However, an almost threefold increase of the specific volume and major structural changes, caused by alloying, result in destruction of the electrode. In addition, silicon has low electron conductivity and low diffusion coefficient of lithium ions. It is expected that a decrease of the size of the active silicon particles to the nanolevel will have a positive effect on the cyclic behavior of the electrodes due to a decrease of internal mechanical stresses.

Lately, the ways of synthesis of various nanostructured silicon materials are actively developed: silicon nanowires (NWs), silicon nanotubes (NTs), hollow silicon nanospheres, that can attract a larger volume of material during lithium penetration / extraction compared to micro- and nanoparticles [6-7].

Various Si nanostructures have been designed, which successfully overcome the materials and interface problems; and Si anode with stable cycling up to 6000 cycles has been reported [6–8].

Currently $LiCoO_2$ (LCO) and $LiFePO_4$ (LFP) cathodes are most widely used in commercial Li-ion batteries [1]. The layered oxide $LiCoO_2$ cathode can be easily manufactured in large scale and is stable in air. Its practical capacity is ~140 mAh/g and the theoretical capacity is 274 mAh/g upon full charge. Besides low practical capacity, $LiCoO_2$ has other noticeable disadvantages, namely, low thermal stability, high material cost and toxicity of cobalt [1].

$LiFePO_4$-based cathode materials (practical capacity ∼150 Ah/kg) are attracting much attention in the past decade due to their low cost and low environmental impact [1]. Compared to $LiCoO_2$, $LiFePO_4$ also offers a number of advantages, such as stability, cycle life, and temperature tolerance (−20 to 70°C). Nevertheless, the low electronic conductivity ($< 10^{-9}$ S cm^{-1}) and the low diffusion coefficient of Li+ ion ($\approx 10^{-14}$ cm^2 s^{-1}) of LFP may result in losses in capacity during high-rate discharge [9**]**.

Sulfur based cathodes are one of the most promising candidates to satisfy an emerging market demands. The beauty of S is attributed to its very low cost, low density, low toxicity, and, most of all, high theoretical specific capacity of 1672 mAh g^{-1}. [10, 11]

Combined with the Si or lithium metal anodes, the S-based full batteries can achieve four or five times of the theoretical specific energy of the existing C– $LiCoO_2$ system, with reduced cost. However, practical applications are currently hindered by several obstacles [10]. These predominantly relate to the insulating nature of sulfur and lithium sulfides, which require addition of conductive additives (hence lowering the active sulfur mass fraction), pronounced capacity fading on cycling and an internal redox shuttle that lowers Coulombic efficiency [11]. The cell capacity is reduced due to active material loss, dissolution of intermediate lithium polysulfides (Li_2S_x, $4 \leq x \leq 8$) in the electrolyte. To retain polysulfides within the cathode structure, one can use the approach of encapsulating sulfur in a conductive polymer matrix, Functional groups of which can bind lithium polysulphides.

In [11] the theoretical calculations were performed to elucidate the interaction between lithium polysulfides/sulfides and various conducting polymers, namely ,poly(3,4-ethylenedioxythiophene) (PEDOT), polyaniline (PANI) and polypyrrole (PPY). It was found that all three conducting polymers were capable of forming strong interactions with lithium polysulfides/sulfides. Overall, the binding energies were found to follow the order: PEDOT > PANI > PPY. This order is consistent with the electrochemical cycling results of conductive polymer-coated hollow sulfur nanospheres, which showed that coating with PEDOT led to the best cycling performance among the three polymers [11].

It is expected that, in the case of lithium sulphide, conductive polymers will exhibit excellent results as materials for encapsulation.

For an effective development of high energy density batteries, the development of high capacity electrode materials, for both positive and negative electrode, is an essential factor.

From this point of view, as the perspective direction one can consider the obtaining of hybrid cathode materials based on conjugated polymers. Conducting polymers represent a promising class for cathodes owing to: their inherently conducting nature which can facilitate electronic conduction, their elastic and flexible nature which can partially accommodate the volumetric change during cycling. On the anode side, nanostructuring is successful in extending the cycle life of silicon anode.

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