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The suppression of lithium dendrite growth in lithium sulfur batteries: A review

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ABSTRACT

Lithium sulfur batteries (LSBs) are attractive owing to the high theoretical capacities of sulfur cathode active material (1672 mAh g^{-1}) and lithium anode active material (3862 mAh g^{-1}), which leads to a specific energy of approximately 2600 Wh kg^{-1}. However, for any rechargeable batteries employing lithium metal as the anode, a major failure mechanism is uncontrolled dendrite formation, which presents serious safety issues, low Coulombic efficiency and poor cycle performance. Recently, researchers make great effort to overcome these problems. Here we summarize some methods for suppressing lithium dendrite growth based on the failure mechanism of LSBs, mainly including novel separator, anode modification and electrolyte modification. We also discuss the advantages and disadvantages of different methods and point out the challenges that still needed to be addressed for building better LSBs.

Contents

1. Introduction

In view of application in emerging markets, such as energy renewal and sustainable road transport, new and high performance storage systems urgently needed. Of the various rechargeable battery types, lithium ion batteries (LIBs) dominate the consumer electronics market over the past two decades and the

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electrical vehicle (EV) applications in recent years, mainly because of their high specific energy (typically around 120–240 Wh kg^{-1}) compared with lead acid batteries, Ni/MH batteries [1,2], high capacity and good cycle stability [3–5]. However, the limited theoretical specific energy, as well as higher cost of LIBs, make their very difficult to meet the higher demands [6,7]. Therefore, it is necessary to develop the new energy storage system with higher specific density.

Lithium sulfur battery (LSB) represents one of the most promising high energy candidate compared to LIB due to the high theoretical capacities of sulfur cathode active material (ca. 1672 mAh g^{-1}) and lithium anode active material (ca. 3862 mAh g^{-1}), which leads to a specific energy of approximately 2600 Wh kg^{-1} [8–10]. In general, the LSB consisted of a lithium metal anode, an organic electrolyte, and a sulfur composite cathode [11,12]. Because sulfur is in the charged state, the battery operation starts with discharge [13]. During the discharge reaction, lithium metal is oxidized at the anode to produce lithium ions and electrons. The lithium ions produced move to the cathode through the electrolyte internally while the electrons travel to the cathode through the external electrical circuit. Sulfur is reduced to produce lithium sulfide by accepting the lithium ions and electrons at the cathode [14].

Similar to LIBs, lithium dendrite growth is unavoidable when lithium metal used as the anode. Unlike LIBs, lithium polysulfides form in the cathode and dissolve in the electrolyte during charge and discharge cycle, which is in direct contact with the metallic anode and leads to a much more complicated system with the coexistence of lithium dendrites and lithium polysulfides [15,16]. Generally, dendrite formation mainly induced by inhomogeneous distribution of (1) the current density on the electrode surface, and (2) the concentration gradient of lithium ions at the electrolyte/electrode interface [17–20]. Lithium dendrites may pierce the polymer separator, resulting in short circuit and subsequent thermal runaway of the cell. Meanwhile, the bottom of the lithium dendrites prefers to lose lithium first because the dendrite lithium possesses higher reactivity than plate lithium [21,22]. It rapidly dissolves at the local region, and breaks away from the anode during the de-lithiation, leading to the formation of “dead Li” that is detached from the current collector and contributes no capacity. This also decreases the efficiency and stability of lithium anode in metallic lithium batteries [22]. Recently, the electrolyte additive [23], solid state electrolytes [24], carbon anode [25], hybrid anode structure, protected lithium anode [26], as well as novel separator, electrolyte and anode [27–29] were used to handle the dendrite problems. However, these strategies rarely involve the electrochemical behaviors (nucleation and growth of lithium dendrites) of the anode in LSBs. Moreover, the previous review papers mainly described the comprehensive, systematic work related to Li-sulfur battery systems [30], discussed LSB’s electrode and cell parameters [31], investigated the attainable gravimetric and volumetric energy density with single method for protecting lithium metal anodes [32], and gave guidance based on the real applications of LSBs [33]. However, these reviews mainly focus on obtaining superior battery performance. For practical application, the safety and stability of anode are particularly important. Therefore, it is necessary to summarize and compare the suppression methods of the lithium dendrite growth in the LSBs, searching effective strategies to improve the safety and practicality of LSBs.

In this review, focus gave the approaches to suppress the lithium dendrite growths from separator, anode and electrolyte based on the main failure mechanisms of LSBs. We also discuss the advantages and disadvantages of different methods and pointed out the challenges that still needed to address for building better LSBs.

2. Main failure mechanism

In order to search effective suppression methods for the lithium dendrite growth, it is necessary to investigate the main failure mechanisms of LSBs. When employing lithium metal as the anode, two major failure mechanisms are typically associated with the application of LSBs. On the one hand, the problem of continuous lithium erosion is compounded with the dissolved polysulphides that also get involved in the passivation film formation [34,35]. On the other hand, uncontrolled lithium dendrite formation is a main reason for the failure of LSBs [36,37]. Differently, the former causes serious attenuations of cycle performance and specific capacity [38], while the latter leads to lower Coulombic efficiency and serious safety problems caused by cell short circuit [39].

Qie et al. [40] investigated the failure mechanism of LSBs by using low-cost carbon nanofibers (CNFs) as carbon hosts and dissolved liquid lithium polysulfide (LPS) solution (1 M Li_2S_6 in blank electrolyte) as a starting active material. The result showed that the thickness of the residual lithium after cycling (120 μm) was less than half of that of the fresh lithium chip (250 μm), which suggested more than half of the lithium metal was “eaten” up by the migrated LPS during the cycles. Lu and his co-worker [41] demonstrated that the formation of porous interphase on the surface of residual lithium metal anode was able to increase the cell impedance and result in an early termination of the LSBs. Therefore, the serious lithium metal corrosion and electrolyte decomposition were one main reason for the failure of the LSBs.

To overcome the problems of lithium dendrite growth, Chang et al. [42] reported a fundamental understanding of the growth mechanism of dendrites under working conditions by the in situ ^{7}Li magnetic resonance (Fig. 1). The chemical shift imaging showed that mossy types of microstructure grow close to the surface of the anode from the beginning of charge, while dendritic growth was triggered much later. Compared a series of cells charged at different current densities, the results showed that at high charge rates, there was a strong correlation between the onset time of dendrite growth and the local depletion of the electrolyte at the surface of the electrode observed both experimentally and predicted theoretical. Therefore, high charge rates could cause the growth of lithium dendrites, which led to the lower Coulombic efficiency and safety issues.

Although there are two main failure mechanisms and they have different effects on performances of LSBs. The lithium dendrite growth on the surface of lithium metal anode is particularly important due to it related to the security issue. The above mechanism studies show that LSBs failure is mainly attributed to the side reactions between the electrode and the electrolyte. In the following, we summarize and compare the methods of suppressing the growth of lithium dendrites based on the failure mechanisms.

3. Suppression method

Recently, with the development of cathode materials and electrolytes in LSBs, the safety of the LSBs anode become one of the more urgent challenges in order to reach practicality of LSBs. Faced with these challenges, the researchers raised three routes for suppressing the growth of lithium dendrites (Table 1), which are separator [43–45], anode [46–51] and electrolyte [52–58]. All these methods are able to suppress the growth of lithium dendrites to a certain extent.