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Review

A review on integrating nano-carbons into polyanion phosphates and silicates for rechargeable lithium batteries

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ABSTRACT

Lithium metal phosphate (Li_2MPO_4) and silicates (Li_2MSiO_4) (where M = Fe, Mn, and Co) are promising polyanion cathodes for rechargeable lithium batteries, owing to the inherent merits such as low cost, decent electrochemical property, and high stability. However, these merits have often been undermined by insufficient energy and power delivery due to poor Li extraction/insertion kinetics. It is generally believed that the extremely low conductivity, i.e. $\sim 10^{-9}$ s cm^{-1} for phosphates and 10^{-12}–10^{-16} s cm^{-1} for silicates at room temperature, in combination with slow Li ion diffusion could account for such sluggish Li cycling kinetics. To address this critical issue, it is essential to integrate well-defined nano-carbons such as one-dimensional (1D) carbon nanotube (CNT), two-dimensional (2D) graphene, and their three-dimensional (3D) assembly into polyanion materials. By constructing hybrid architectures, integrated composites could afford much improved activity towards Li storage versus the bare ones. In this short review, we summarize recent advance in integrating CNT, graphene, and their 3D assemblies into $LiMPO_4$ and Li_2MSiO_4 cathodes, with particular emphasis on how the cathodes interact with carbon materials and their mechanism. We also conclude some general rules to engineer such integration structures to maximize their utilization towards Li storage.

Contents

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1. Introduction

Rechargeable lithium batteries (RLBs) have currently taken dominating position for energy supply in portable electronics. They have further found increasing application in automobile and renewable energy [1]. Clearly, further penetration of RLBs into these large scale systems needs to afford higher energy density and power capability than currently available. Thus, it is of necessity to search for better electrode materials which could fulfil harsh requirements to store high amounts of lithium in a reversible and rapid way. In addition, electrodes should meet other decisive criteria such as light weight, low cost, high safety, and environmental benignity [2].

While high-capacity anode materials have been widely developed, cathode materials have not yet witnessed such improvements. A balanced development of both electrodes is essential to achieve an increase in specific energy. As layered $LiCoO_2$ and spinel $LiMn_2O_4$ are instable under abused condition with the risk of oxygen release, intrinsically more stable polyanion materials of phosphate ($LiMPO_4$, where M = Fe, Mn, and Co) were introduced by Goodenough et al. in 1997 [3]. Replacement of O by PO_4 group has greatly raised the stability and potential of Fe^{2+}/Fe^{3+} up to 3.4 V (versus Li^+/Li, unless otherwise stated). However, it also added the formula weight, leading to a limited available capacity, around 170 mAh g^{-1} and energy density of 580 Wh kg^{-1} [4].

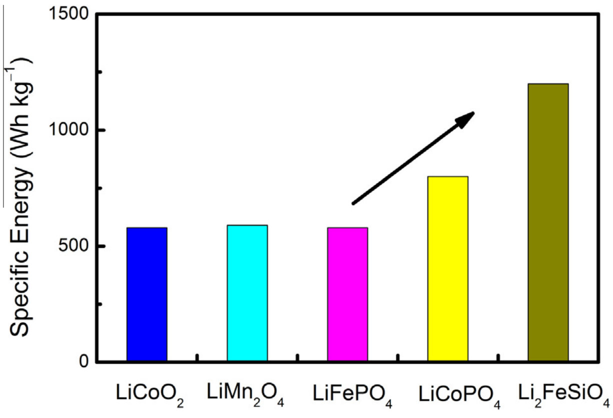

Fig. 1 – Diagram of energy density for conventional and new polyanion cathode materials. (A colour version of this figure can be viewed online.)

Although substitution of Fe by Mn [5,6] and Co [7,8] results in a higher potential and energy density (Fig. 1), such materials have their intrinsic disadvantages. More importantly, phosphate materials exhibit extremely low electronic conductivities ($\sim 10^{-9}$ s cm^{-1}), which make a sluggish Li extraction/insertion kinetics and poor lithium storage property.

Search for polyanion cathode also led to the discovery of orthosilicate Li_2MSiO_4 (where M = Fe, Mn, and Co) cathode, as proposed by Thomas in 2005 [9]. As a new class of cathodes, Li_2MSiO_4 has been attracting broad interest [10,11]. The massive abundance, low cost, environmentally benignity and promising electrochemical properties, offer the appealing prospect to fabricate reliable cathodes for next generation batteries. More importantly, Li_2MSiO_4 could realize two-electron transfer through M^{2+}/M^{4+} redox reaction, leading to a much higher capacity up to 330 mAh g^{-1}. This capacity is about twice that of conventional cathodes and thus could substantially boost the specific energy of RLBs. Similarly, the silicates have suffered from the inherently low electronic conductivity (10^{-12}–10^{-14} s cm^{-1}) and slow ion diffusivity (10^{-12}–10^{-16} cm^2 s^{-1}), which reduces the power capability of the cell.

To mitigate such a kinetics issue encountered in both types of polyanion cathodes, it is highly desirable to take advantage of sophistic material strategies. Several approaches such as nanoarchitecture design, surface engineering, and integrating conductive reagents have been adopted for this purpose and shown perspective [12]. Among them, integrating nano-carbons including carbon nanotube (CNT), graphene (including reduced graphene oxide (rGO)), and their assembly into polyanion materials seems to be an ideal strategy. Both CNT and graphene present unique conjugated π electron systems, which make them ideal additive for electrically wiring electrode materials. More importantly, functional nanocarbon possess a strong adhesive ability to bond material particles, through electrostatic interaction, π–π stacking, hydrophobic effect, etc. The integrating systems thus may generate some new properties caused by the cooperative effects between the two types of components. By taking advantage of the synergetic effect between the two components, these composites afford a superior capacity and fast charge transfer capability, opening up new possibilities for designing electrodes even adopting insulating materials. Furthermore, CNT, graphene, and their assembly as can be viewed, respectively, as one-, two-, and three-dimensional