



Transition metal oxides for sodium-ion batteries



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ABSTRACT

Rechargeable batteries have attracted significant attention in recent years because of aggravate environment problems. Lithium-ion batteries play an important role in our daily life and extensively used in portable electronic devices as well as hybrid electric vehicles. However, the uneven distribution and limitation of lithium resources have gradually aroused people's anxiety on lithium-ion battery sustainability. Sodium-ion batteries have been studied by many groups recently and potentially used as one of the next-generation rechargeable batteries due to the earth abundance and cost-effectiveness of sodium resources. The key to commercialize the promising sodium-ion rechargeable batteries mainly lies on the development of advanced electrode materials. Transition metal oxides are one of the oldest and most important electrode materials for sodium-ion batteries, and have been studied by many researchers for about 30 years, especially in recent five years. Here, with a main line of crystalline structure design for transition metal oxides, the whole research progress on transition metal oxides used for sodium-ion batteries has been reviewed, some important research results in recent five years are emphatically introduced, and the perspective on novel electrode materials development is also discussed.

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1. Introduction

Energy storage and energy conversion has become the basic need as well as the key issue concerning with our daily life [1–4]. With the increment concern about fossil fuel depletion, the renewable and cleaner power sources and energy storage devices such as solar radiation, wind and waves have been developed for the modern grid. To smooth out its variations, stability, reliability and efficiency, cost effective electrical energy storage devices are the main objective at all the time throughout the world [1,3]. Rechargeable Lithium batteries which are so called Li-ion batteries (LIBs) named by Sony Corp., commercialized for the first time in 1991 which get great interest and delivered high impact on the economy with beating into new market as well as installed in the power system of hybrid electric vehicles (HEV) and pure electric vehicles (EV) with a relatively affordable price. During the last two decades, a lot of research works have been focused on the development of LIBs towards high-energy/high-power performance, now LIBs become the prime candidate and as well as the essential part of grid energy storage. However, the large scale demand of Li forced the researcher to reconsider the feasibility of Li, which is not regarded as an abundant element in the Earth's crust. The resources of Li are most situated in South America area and huge investment is required to involve in mining [2,3]. So high-cost is a critical problem to use Li in batteries in future. Na is considered as a suitable candidate near to Li in alkali metal and also a low-cost material due to its abundance in the Earth's crust in different forms (e.g., sea salt, rock salt). Furthermore, Na has a similar reaction mechanism like Li. Thus, sodium-ion batteries (NIBs) have been considered as another promising energy storage device since from 2000s as well as in future that can fulfill the demand of the energy-storage market. Besides these advantages, there are some problems come to facing to use Na as an alternative of Li due to the fundamental differences between these two ions such as ionic radii, difference in electrochemical standard potential of Na/Na⁺ and Li/Li⁺ etc [2–4]. The size of Na⁺ (1.02 Å) is larger than Li⁺ (0.76 Å) and large interstitial space should be required in the host electrode materials which can accommodate Na⁺ and allow reversible rapid ions insertion and extraction. Unfortunately, graphite cannot develop hosted insertion material for Na⁺ ions while it is extensively used in LIBs [5]. Similarly, sodium cobalt oxide (Na_xCoO₂) with layered structure is reported with complex electrochemical curves while Li counterpart (LiCoO₂) is extensively used as positive electrode materials in LIBs [6].

In the past two decades, tremendous research efforts have been focused on Li⁺ insertion materials to enhance the storage efficiency of LIBs compared to Na⁺ insertion materials for energy storage. Research interests in Na⁺ insertion materials have been completely renewed with the increasing demand of global energy issue in 2010, and the ratio of publications on NIBs is drastically increasing. A lot of materials have been proposed for positive and negative electrodes of NIBs especially in the past 5 years, including transition metal oxides, polynomic compounds, carbon based materials, and so on [1,3,4].

Transition metal oxides are one of the promising electrode materials for its' high theoretical capacity, and have been developed and researched by many groups in the world. Delmas et al. [7] reviewed the early research progress on NIBs and in the past two years, some review articles on NIBs have also been published. Yabuuchi et al. [8] summarized the whole electrode materials development as well as iron and manganese based oxides [9] in 2014. Sawicki et al. [10–12] reviewed the positive and negative electrodes as well as electrolytes used in NIBs while Balogun et al. mainly introduced the carbon materials utilization in NIBs [13,14]. However, the detailed review on transition metal oxides used for NIBs is absented. In this paper, the transition metal oxides development for NIBs is focused, a main line of crystalline structure design for these materials runs through all the paper. Research progress and perspective on transition metal oxides for NIBs are also discussed in detail.

2. Structure classification of transition metal oxides

Layered transition metal oxides were proposed for NIBs in the early 1980s [15], and there are mainly two different kinds of structures, namely, O3-type and P2-type structure. O3-type structure is classified cation-ordered rock salt superstructure oxides [16] and the schematic illustration of this type material is shown in Fig. 1b. Oxygen usually form a cubic close-packed sublattice in these materials as a basic matrix and the transition metal (TM, TM=Ti, V, Cr, Mn, Fe, Co, Ni, Cu) can form octahedron when coordinate with six oxygen atoms along the c-axis direction. These TMO₆ octahedrons connect to each other by edge sharing, forming the TMO₂ layers. Between the TMO₂ layers, there can be two different Na⁺ occupancy sites (octahedral sites and prismatic sites) to accommodate Na⁺. These cations ordered alternate layers can be noted as NaO₂ and TMO₂ layers when observed perpendicular to 111 directions. O-type NaTMO₂ is named after the octahedral sites between the TMO₂ layers, and these sites can be easily formed by gliding of TMO₂ layers [17]. Oxygen packings can be notably distinguished, denoted as "A, B and C", respectively. In O3-type structure, oxygen packings are stacked alone in the sequence of AB-CA-BC (isostructural with CdCl₂), while the Na⁺ are accommodated in the octahedral sites with three different layers as shown in Fig. 1b. The same situation can take place when prismatic sites are formed with TMO₂ layers gliding, and P2-type structure (Fig. 1a) is named after the oxygen packing' stacking sequence following "AB-BA". What's more, the apostrophe (') on the right-top of O or P stands for their structure distortion.

P2 and O3-type layered materials were extensively studied for the rechargeable batteries with different electrochemical performances due to different Na⁺ distribution in interslab space. Only one Na⁺ occupancy sites are observed in O3-type structure which sharing six edges with TMO₆ octahedrons [8,18,19] while two different Na⁺ occupancy sites are found in P2-type structure. One of them shares faces with the upper and lower TMO₆ octahedrons

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