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Porous $LiNi_{0.5}Mn_{1.5}O_4$ microspheres with different pore conditions: Preparation and application as cathode materials for lithium-ion batteries

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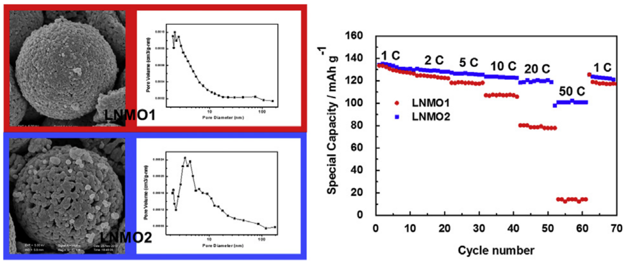
HIGHLIGHTS

- Porous $LiNi_{0.5}Mn_{1.5}O_4$ microspheres are produced through a simple two-step method.
- The pore condition is able to be altered by changing the lithium sources.
- Microspheres with larger pores exhibit excellent rate and cycle performance.
- Tinier pores coupled with larger surface area show distinct disadvantages.

GRAPHICAL ABSTRACT



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ABSTRACT

Here two types of $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO) microspheres with different pore conditions are prepared through a facile two-step method. Initially, nickel manganese carbonate microspheres are obtained through a solvothermal reaction, and then they are heated with different lithium sources to obtain the two products. Scanning electron microscopy images clearly disclose that the two types of microspheres are respectively covered with dense tinier pores and sparse larger pores while both of their interiors are constituted by nanoparticles in similar size. Nitrogen adsorption/desorption analyses indicate that their maximum pore diameters are 2.2 nm and 3.5 nm. As cathodes of lithium ion batteries, the LNMO microspheres equipped with larger pores exhibit much more excellent electrochemical performance especially in terms of rate performance, achieving a discharge capacity of 101.7 mAh g^{-1} even at 50C, while their counterparts only receive 14.3 mAh g^{-1} coupled with severe polarization. And the capacities of them respectively maintain at 102.9 and 67 mAh g^{-1} after 100 cycles at 20C. Their distinct performance is suggested due to both the pore parameter and its related surface area.

1. Introduction

During the last decades, a wide range of transition metal oxides have been investigated and developed into electrode materials of lithium-ion batteries (LIBs). Among them, high-voltage $LiNi_{0.5}Mn_{1.5}O_4$ (LNMO), [1] as a derivative of spinel $LiMn_2O_4$, has

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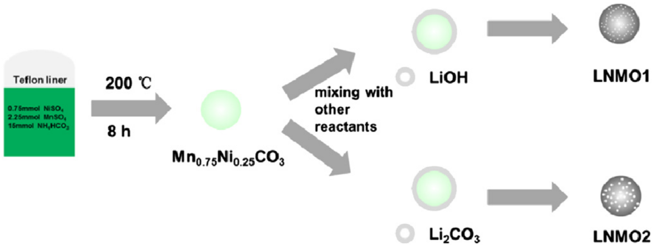

Scheme 1. Schematic illustration of the formation of two types of LNMO microspheres.

been considered as one of the hottest cathode candidates, which possess the advantages of considerably improved energy density, abundant raw materials and good stability. Generally, attributing to the theoretical capacity at 146.7 mAh g^{-1} and the high working voltage at 4.7 V, LNMO shows 20% and 30% higher energy density than conventional $LiCoO_2$ and $LiFePO_4$, respectively [2,3].

Apart from the inherent properties of the material, other attributes, including particle size, pore structure and morphology are also important and should be optimized [4]. Therefore, LNMO nanostructures with different morphologies, such as nanoparticle [5,6], nanorod [7], hierarchical micro-nano structure [8], porous nanorod [9], hollow microsphere or microcube [10], appear to be interesting, as they lead to improved kinetic performance by reducing the transport path lengths of lithium ions and electrons. However, some nanostructured materials with high surface area increase the incidence of undesirable electrode/electrolyte reactions [4]. Moreover, the situation may deteriorate in LNMO due to its high operation voltage, which nearly reaches the window of stability of the electrolyte solutions [11,12]. Porous micron materials, therefore, are reasonable to be designed in this case. Specifically, their relative high interfacial and continuous porous transport pores network, allowing for efficient ion transport thereby improving the rate capability of the LIBs [13]. Moreover, it has been established that microspheres, including $LiCoO_2$ [14],

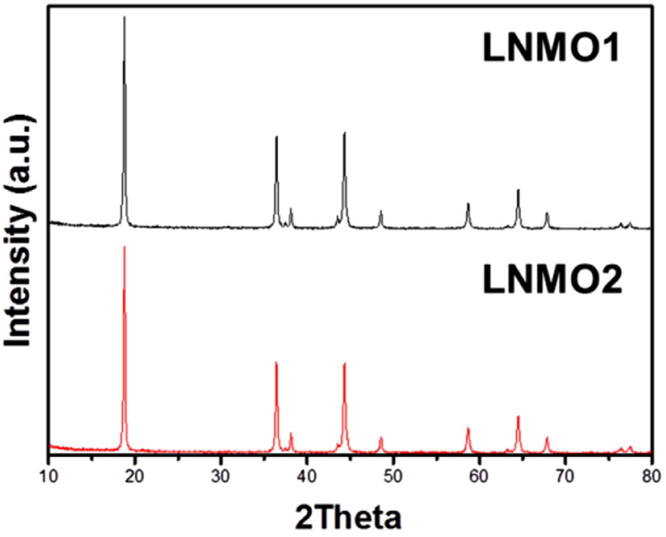

Fig. 2. XRD patterns of the two products.

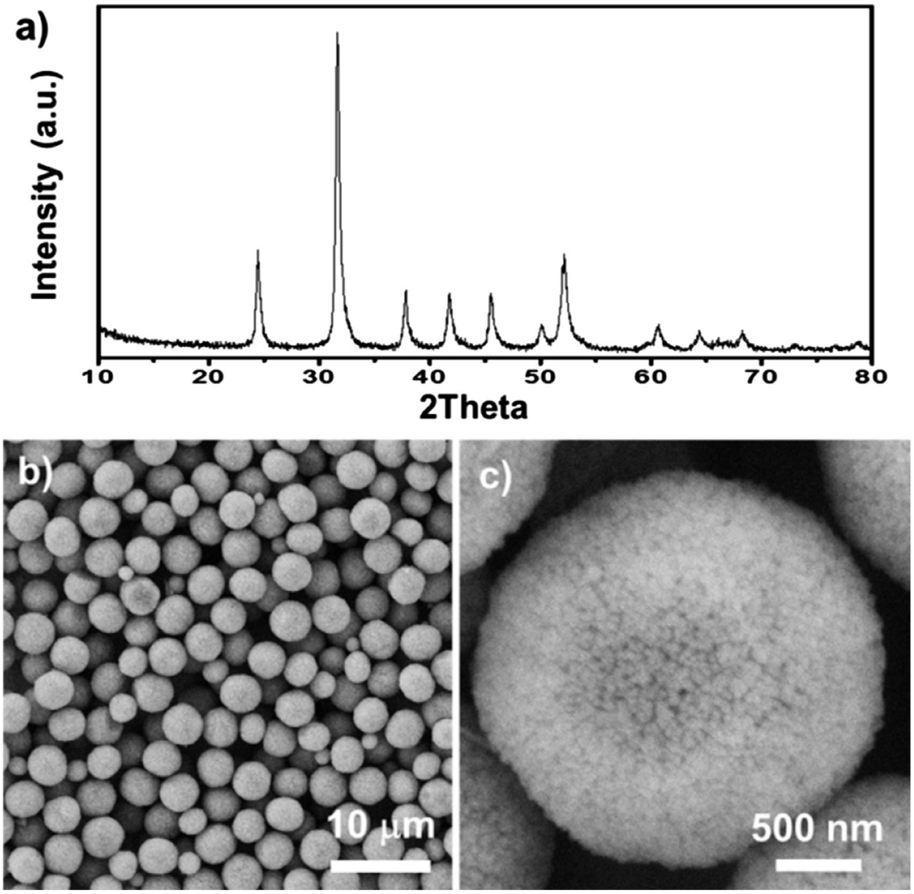

Fig. 1. XRD pattern (a) and SEM images under different magnifications (b, c) of $Mn_{0.75}Ni_{0.25}CO_3$.