

LiNi_{0.5}Mn_{1.5}O₄ Hollow Structures as High-Performance Cathodes for Lithium-Ion Batteries

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Lithium-ion batteries (LIBs), which are the dominant power source for portable electronics, have also gained enormous interest recently for large-scale applications, such as electric vehicles (EV), hybrid electric vehicles (HEV), and stationary energy storage.^[1] To meet the requirements of these applications, further improvements in terms of energy and power densities, safety, and lifetime are required. However, conventional micrometer-sized bulk electrode materials are reaching their inherent limits in performance and unable to fully satisfy the increasing demands. Nanostructured electrode materials hold the key to overcome the limits, especially the power density.^[1c,2] Taking the well-known cathode material LiMn₂O₄ as an example, various nanostructures, such as nanoparticles,^[3] nanowires,^[4] nanotubes,^[5] hollow spheres,^[6] and ordered mesoporous/macroporous materials,^[7] have been fabricated to improve the rate capability. When compared to pristine LiMn₂O₄, Ni-doped LiNi_{0.5}Mn_{1.5}O₄ shows significantly improved cycling performance and increased energy density.^[8] However, types of LiNi_{0.5}Mn_{1.5}O₄ nanostructures reported are rather limited, which is mainly due to undesirable particle growth during the essential high-temperature sintering process. During conventional synthesis of LiNi_{0.5}Mn_{1.5}O₄, the raw materials used are usually in micrometer scale and mixed by grinding or ball-milling methods. Atomic migration over micrometer scale during the subsequent high-temperature sintering process will likely lead to undesirable particle growth. Although the undesirable particle growth can be partly prevented by adding growth inhibitors, the resultant products are usually composed of irregular nano- or microparticles.^[8c,d] Thus, morphologically controlled synthesis of LiNi_{0.5}Mn_{1.5}O₄ nanostructures remains a great challenge.

Herein, we present a morphology-controlled synthesis of LiNi_{0.5}Mn_{1.5}O₄ hollow microspheres and microcubes with nanosized subunits by an impregnation method followed by a

simple solid-state reaction. The impregnation method provides homogeneous distribution of the reagents at nanoscale. As the distance for atomic migration is shortened significantly to several nanometers, the undesired particle growth during the annealing is effectively suppressed in the present synthesis. The resultant LiNi_{0.5}Mn_{1.5}O₄ hollow structures exhibit a discharge capacity of about 120 mA h g⁻¹, with excellent cycling stability and superior rate capability.

Figure 1 illustrates the procedure for the fabrication of LiNi_{0.5}Mn_{1.5}O₄ hollow structures. Uniform MnCO₃ microspheres and microcubes (Supporting Information, Figure S1

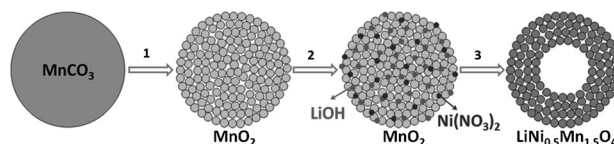


Figure 1. Illustration of the fabrication of LiNi_{0.5}Mn_{1.5}O₄ hollow microstructures (see text for details).

and S2) prepared by the precipitation method are employed as the precursors in the synthesis. In step 1, the MnCO₃ microspheres and microcubes are converted into MnO₂ by thermal decomposition at 400 °C according to 2MnCO₃ + O₂ → 2MnO₂ + 2CO₂. The microsphere/microcube morphology is retained after the annealing process (Supporting Information, Figure S3 and S4). Owing to the release of CO₂ in the thermal decomposition, the obtained MnO₂ microspheres/microcubes are highly porous. In step 2, LiOH·H₂O and Ni(NO₃)₂·6H₂O are introduced into the mesopores of the MnO₂ microspheres/microcubes by a simple impregnation method. The reactions involved in step 3 are multi-step and rather complicated. Briefly, it could involve the following processes: the dehydration of LiOH·H₂O (LiOH·H₂O → LiOH + H₂O); the decomposition of MnO₂ (4MnO₂ → 2Mn₂O₃ + O₂); the decomposition of Ni(NO₃)₂·6H₂O (2Ni(NO₃)₂·6H₂O → 2NiO + 4NO₂ + 12H₂O + O₂); and finally lithiation (8LiOH + 6Mn₂O₃ + 4NiO + 3O₂ → 8LiNi_{0.5}Mn_{1.5}O₄ + 4H₂O). The fusion of the mesopores and a mechanism analogous to the Kirkendall effect, that is, the fast outward diffusion of Mn and Ni atoms and the slow inward diffusion of O atoms, are proposed to be responsible for the formation of the hollow cavity in the LiNi_{0.5}Mn_{1.5}O₄ microspheres/microcubes.^[9]

The resultant products were initially characterized by X-ray diffraction (XRD) to identify the crystallographic structure and crystallinity, and the diffraction patterns are presented in Figure 2. Both patterns can be assigned to well-crystallized cubic spinel LiNi_{0.5}Mn_{1.5}O₄ (JCPDS Card No.: 80-2162, space group: *Fd* $\bar{3}m$, *a* = *b* = *c* = 8.170 Å), with

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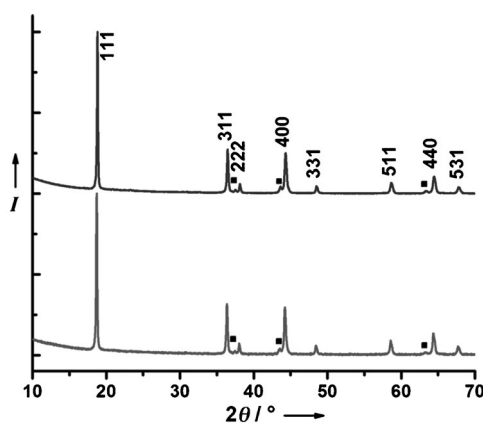


Figure 2. XRD patterns of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow microspheres (lower trace) and hollow microcubes (upper trace). ■ $\text{LiNi}_{1-x}\text{O}_2$.

minor residues peaks centered at $2\theta = 37.51, 43.62$, and 63.42° that can be attributed to $\text{Li}_x\text{Ni}_{1-x}\text{O}_2$.^[8a] This is a common impurity in the synthesis of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ when the Ni content x in the $\text{LiNi}_x\text{Mn}_{2-x}\text{O}_4$ spinel exceeds 0.2.

The morphology and microstructure of the products were examined by field-emission scanning electron microscope (FESEM). The low-magnification FESEM image (Figure 3a) reveals that the product is composed of uniform microspheres with diameters of $3.5\text{--}4.5\text{ }\mu\text{m}$. It is interesting to observe that a

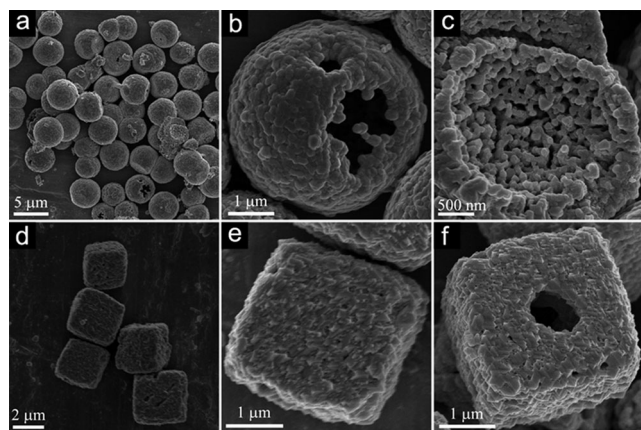


Figure 3. FESEM images of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ a)–c) hollow microspheres and d)–f) hollow microcubes.

significant fraction of the microspheres have cracks on their surface. A typical broken hollow microsphere is shown in Figure 3b; the hollow interior can be clearly observed from the broken part. From a broken hemisphere as shown in Figure 3c, it is revealed that the wall of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow microsphere is highly porous and composed of nano-sized/submicrometer-sized subunits. The wall thickness of the hollow microspheres is determined to be about 500 nm . The chemical composition of the products has been analyzed by energy-dispersive X-ray spectroscopy (EDX) (Supporting Information, Figure S5), which confirms an atomic Mn/Ni ratio of 3.0. The use of the pre-grown MnCO_3 as the precursor allows for the shape control of the resultant $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

hollow structures. For example, uniform and well-defined $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow microcubes with sizes of $3\text{--}3.5\text{ }\mu\text{m}$ (Figure 3d) can be obtained by replacing the MnCO_3 microspheres with microcubes. The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ microcubes have a rough surface (Figure 3e). From the broken part of a $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ microcube, the hollow interior can be identified unambiguously (Figure 3f).

The electrochemical properties of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow structures were initially investigated by cyclic voltammetry (CV). The first five consecutive CV curves are shown in the Supporting Information, Figure S6. The CV curves for the first two cycles differs significantly from those for the following cycles, and no significant alteration in the CV behavior is observed from the third cycle onwards. From these stabilized CV curves, two pairs of redox peaks associated with the $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ couples can be observed in the high-voltage region of $4.60\text{--}4.85\text{ V}$. A pair of minor peaks owing to the $\text{Mn}^{3+}/\text{Mn}^{4+}$ couple can also be observed at about 4 V . In stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, which has an ordered spinel structure, the oxidation state of Mn is $+4$. However, some oxygen deficiency appears during the high temperature calcination, and this reduces a small fraction of Mn^{4+} to Mn^{3+} .

To evaluate the rate capability, the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow microspheres were cycled at various charge/discharge rates ranging from 0.1 to 20 C over a potential window of $3.5\text{--}5.0\text{ V}$. A rate of $n\text{ C}$ corresponds to full charge/discharge of the theoretical capacity in $1/n$ hour, and 1 C is 147 mAh g^{-1} for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. For $n > 1$, the constant current charge step is followed by an additional constant voltage charge step till the current drops to $n/10\text{ C}$; that is, the cells are first charged at $n\text{ C}$ to 5.0 V , after 5.0 V is reached, the potential is kept at 5.0 V until the current decreases to one tenth of its initial value. Typical charge and discharge profiles are shown in Figure 4a. In good agreement with the CV results, the discharge curves have a dominant plateau at about 4.7 V and a minor plateau at about 4.0 V . With increasing current density, the discharge capacity only decreases slightly, indicating the excellent rate capability. For the charge curves, the voltage step only contributes a relatively small fraction (ca. 10%) to the total charge capacity. The cycling performance at various rates is shown in Figure 4b. Strikingly, the discharge capacity (118 mAh g^{-1}) at 1 C is even larger than that at lower current densities ($0.1, 0.2$, and 0.5 C). A similar phenomenon has been reported by Lazarraga et al.^[10] As the current density increases from 1 to $2, 5, 10$, and 20 C , the discharge capacity decreases slightly from 118 to $117, 115, 111.5$, and 104 mAh g^{-1} , respectively. After the high rate measurement, the current density is reduced back to 5 C , and a discharge capacity of about 116 mAh g^{-1} can be recovered. The cycling performance of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow microspheres at $1, 2$ and 5 C are shown in Figure 4c. Stable cycling performance was obtained for all three rates. For example, after 200 cycles at 2 C , 96.6% of the initial capacity can be retained. The cycling performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow microcubes was also investigated (Supporting Information, Figure S7). It delivers a discharge capacity of 124 mAh g^{-1} at 2 C , which only decreases slightly to 121 mAh g^{-1} after 200 charge/discharge cycles, corresponding to 97.6% of its initial capacity. When compared to state-of-art $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$

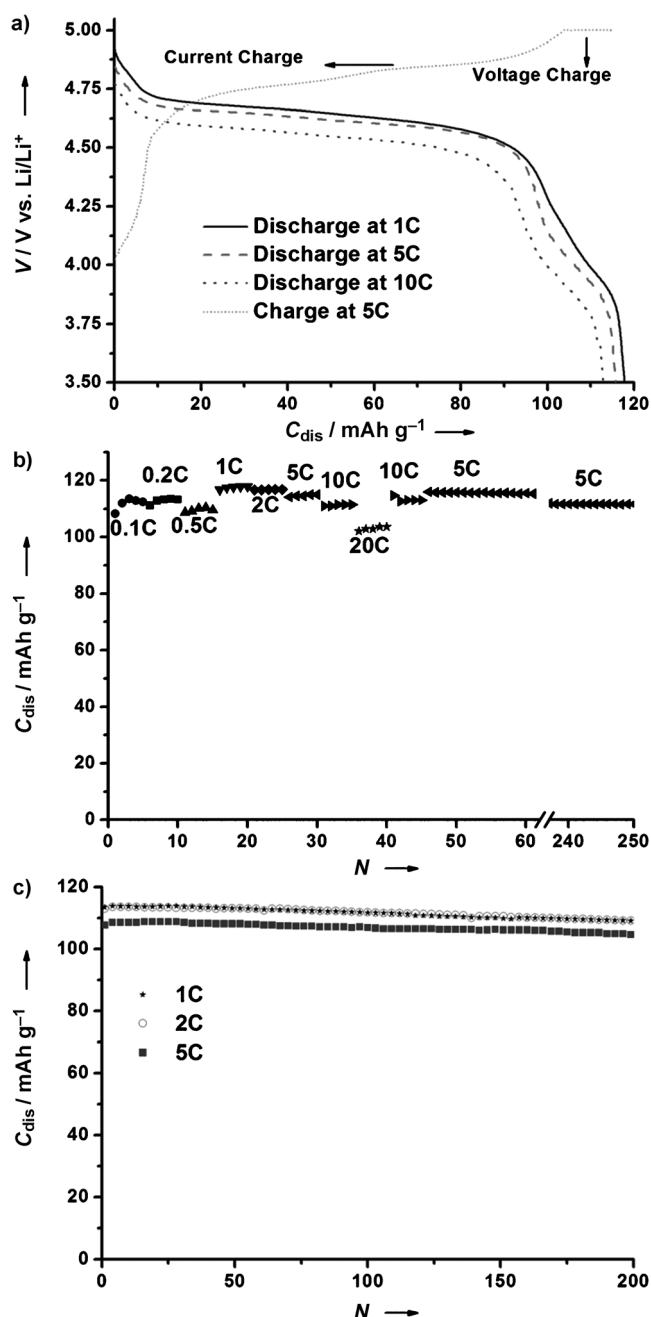


Figure 4. a) Charge/discharge profiles at 1C, 5C, and 10C between 3.5–5.0 V; b) cycling performance at various rates (0.1C–20C); c) cycling performance at 1C, 2C, and 5C for 200 cycles. C_{dis} = discharge capacity; N = cycle number.

materials in literature,^[8b] it was found that our material exhibits a slightly lower capacity, but better rate and cycling performances.

The excellent rate capability and cycling stability of these LiNi_{0.5}Mn_{1.5}O₄ materials might be attributed to the unique nano/micro hierarchical structure. Specifically, the nanosized/submicrometer-sized building blocks provide short distances for Li⁺ diffusion and large electrode–electrolyte contact area for high Li⁺ flux across the interface, leading to better rate capability. Second, the structural strain and volume change associated with the repeated Li⁺ insertion/extraction process-

es could be buffered effectively by the porosity in the wall and interior void space, thus improving the cycling stability. Finally, the Ni substitution increases the average oxidation state of Mn from 3.5 for LiMn₂O₄ to about 4 for LiNi_{0.5}Mn_{1.5}O₄, thus effectively suppress capacity fading caused by Mn dissolution and Jahn–Teller distortion.

In summary, uniform LiNi_{0.5}Mn_{1.5}O₄ hollow microspheres/microcubes with nanosized building blocks have been synthesized by a facile impregnation approach. The resultant LiNi_{0.5}Mn_{1.5}O₄ hollow structures deliver a discharge capacity of about 120 mAh g⁻¹ with excellent cycling stability. They also exhibit exceptional rate capability up to 20C. The superior electrochemical performance suggests the use of these LiNi_{0.5}Mn_{1.5}O₄ hollow structures as cathode materials for high-power lithium-ion batteries. The synthesis strategy demonstrated herein is simple and versatile for the fabrication of other metal-doped LiMn₂O₄ cathode materials.

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