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**General synthesis of $x\text{Li}_2\text{MnO}_3 \cdot (1 - X)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/4, 1/3,$
and $1/2$) hollow microspheres towards enhancing the performance of
rechargeable lithium ion batteries**

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General synthesis of $x\text{Li}_2\text{MnO}_3 \cdot (1 - x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/4, 1/3, \text{ and } 1/2$) hollow microspheres towards enhancing the performance of rechargeable lithium ion batteries

Abstract

Well-crystallized and high-performance $x\text{Li}_2\text{MnO}_3 \cdot (1 - x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/2, 1/3, 1/4$) hollow microspheres are prepared through an in situ self-sacrificial template route. By precisely adjusting y values in the starting precursor, $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ porous microspheres, uniform $x\text{Li}_2\text{MnO}_3 \cdot (1 - x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ hollow microspheres are formed. Property testing of lithium ion batteries shows that an appropriate x value plays an important role in their electrochemical behavior: a higher x value leads to a higher specific capacity, but a worse cycling capability, and vice versa; when $x = 1/3$, the $x\text{Li}_2\text{MnO}_3 \cdot (1 - x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode shows a high specific capacity and a high capacity retention rate. In particular, the hollow microspheres with $x = 1/3$ achieved a reversible capacity as high as 203 mA h g^{-1} at 0.25C and 181 mA h g^{-1} at 1.0C over 200 cycles. A rate capacity as high as 191 mA h g^{-1} at 5.0C is obtained after 5 cycles stepwise from 0.25C to 5.0C . This work provides a general approach based on the use of an in situ self-sacrificial template to synthesize $x\text{Li}_2\text{MnO}_3 \cdot (1 - x)\text{LiMO}_2$ ($0 < x < 1$, $\text{M} = \text{Ni, Co, Mn}$, etc.) at various x values and other targeted materials in a morphology with hollow interiors, which is inaccessible through a wet chemistry route.

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General Synthesis of $x\text{Li}_2\text{MnO}_3 \cdot (1-x) \text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/4, 1/3$, and $1/2$) Hollow Microspheres towards Enhancing Performance in Rechargeable Lithium Ion Batteries

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Abstract.

Well-crystallized and high-performance $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/2, 1/3, 1/4$) hollow microspheres are prepared through a *in-situ* self-sacrificial template route. By precisely adjusting y values in the starting precursor, $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ porous microspheres, uniform $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ hollow microspheres are formed. Property testing in lithium ion batteries shows that an appropriate x value plays an important role in the electrochemical behavior: a higher x value leads to a higher specific capacity, but a worse cycling capability, and vice versa; when $x = 1/3$, does the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ electrode show a high specific capacity and a high capacity retention rate. Specially, the hollow microspheres with $x = 1/3$ achieved a reversible capacity as high as 203 mAh g^{-1} at 0.25 C and 181 mAh g^{-1} at 1.0 C over 200 cycles. A rate capacity as high as 191 mAh g^{-1} at 5.0 C is obtained after 5 cycles stepwise from 0.25 C to 5.0 C . This work provides a general approach based on the use of an *in-situ* self-sacrificial template to synthesize $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 < x < 1$, $\text{M} = \text{Ni, Co, Mn, etc.}$) at various x values and other targeted materials in a morphology with hollow interiors, which is inaccessible through a wet chemistry route.

Keywords: self-sacrificial template, lithium-excess, layered oxides, cathodes

1. Introduction.

With the growing pressure on resources and the growing environmental crisis, developing renewable energy to replace conventional fuel energy is now considered to be an essential technical issue.^{1,2} Rechargeable lithium-ion batteries (LIBs), due to their low cost, long cycle life, and lack of any memory effect, are expected to be widely used in new diverse applications, such as smart grids, electric or hybrid electric vehicles, and stationary energy storage.^{3,4} Their further development has been limited, however, by their low energy density and their high cost of cathode material. Lithium-excess manganese oxide layered structures, represented by the chemical formula $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 < x < 1$, $\text{M} = \text{Ni}, \text{Co}, \text{Mn}$), have undergone a flurry of research as cathode candidates owing to their high specific capacity ($> 200 \text{ mAh g}^{-1}$) and high operation potential ($> 3.5 \text{ V vs. Li/Li}^+$), as well as their low cost and high energy density ($> 900 \text{ Wh/kg}$).^{5,6} Electrodes comprising hierarchical architectures with hollow interiors exhibit outstanding electrochemical performances owing to the shorter paths for electron transport and Li^+ diffusion, the larger electrode-electrolyte contact area for Li^+ flux across the interfaces, and the more stable structural integrity due to their ability to alleviate the mechanical strain induced by volume changes during the repeated Li^+ insertion/extraction processes.⁶⁻¹² As expected, it has been demonstrated that the anode materials with hollow or core-shell microspheres such as CoMn_2O_4 ,⁶ MnCo_2O_4 ,⁷ ZnMn_2O_4 ,⁸ and $\text{Mn}_{1.5}\text{Co}_{1.5}\text{O}_4$,⁹ which are facilely-prepared, displayed high lithium-storage performance.

The conventional methods such as hard templating, soft templating, and template-free synthesis have been proven to be effective approaches to hollow structures in solution chemistry.¹³ They were not applicable to the layered oxide cathode, however, since it required a high-temperature treatment to obtain the layered phase. Thus, it remains a challenge to develop a general strategy that allows morphology-controlled preparation of uniform hollow lithium-excess manganese-based electrode materials for LIBs with high performance. *In-situ*

self-sacrificial templating method, in which the precursor plays the roles of both the template and the reactant, is considered as a solution strategy and has been demonstrated for the preparation of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ hollow microspheres,¹⁰ $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ hollow microcubes,¹¹ and one-dimensional (1D) $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ microbars.¹⁴ There is, however, a lack of research into hollow layered $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($0 < x < 1$, $\text{M} = \text{Ni, Co, and Mn}$) oxides and the effect of the x value in the electrochemical performance in LIBs.

Herein, we report a general *in-situ* self-sacrificial template strategy to fabricate $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/4, 1/3$, and $1/2$) hollow microspheres. The whole strategy mainly consists of three steps, as illustrated schematically in **Figure 1**. Briefly, in step I, monodisperse $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ microspheres, which are fabricated by a solvothermal method, are transformed into spinel porous $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ microspheres, accompanied by the release of CO_2 gas and the migration of atoms. Importantly, the x value in the final product can be tuned by the ratio of Co to Mn atoms in the starting materials. In step II, $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ together with a certain amount of $\text{LiOH} \cdot \text{H}_2\text{O}$ is introduced into the holes and pores of the $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ microspheres through a simple impregnation method. Step III involves the introduction of nickel and lithiation, as well as the fusion of the mesopores, accompanied by the shrink of the walls, a phenomenon arising from the modified Kirkendall effect, which is attributed to the fast outward diffusion of Ni, Co, and Mn atoms and the slow inward diffusion of O atoms, leading to the final formation of the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/4, 1/3$, and $1/2$) hollow microspheres. When incorporating these hollow microspheres as cathode material in LIBs, the Li^+ ions could diffuse into the hollow microspheres through these pores by pathways with short distances and little resistance, favorably enhancing the electrochemical behavior. Battery testing results show that $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with $x = 1/3$ exhibits the best performance, indicating the high level of homogeneity between its Li_2MnO_3 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ components. The

present work offers a new strategy for the design of hollow interiors and composites with morphology-controlled lithium-excess manganese-based layered oxides for LIB applications.

2. Experimental Section

Material preparations for $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ and $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ hollow microspheres: The $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ microsphere precursors with different y values ($y = 1, 6/7, 3/5$ corresponds to different ratios of Co:Mn, 1:2, 1:2.5, and 1:4, and different x values of 1/4, 1/3, and 1/2 in the final product, respectively) were synthesized using a facile solvothermal method. Typically, 6 mmol $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ in the designated ratios (1:2, 1:2.5, and 1:4) were dissolved in 40 mL ethylene glycol (EG) in a Teflon-lined stainless steel autoclave with a volume of 50 mL to form a homogeneous solution, and then 30 mmol NH_4HCO_3 was added into the mixture under continuously stirring for 0.5 h. Finally, the autoclave was sealed in an electric oven at 200 °C for 20 h and naturally cooled to room temperature. The light purple precipitate was collected by centrifuge, washed with deionized water and absolute ethanol several times, and dried in a vacuum oven at 60 °C over-night for subsequent steps. To obtain $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ porous microspheres, the $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ precursors were further calcined at 600 °C for 5 h with a ramp rate of 4.0 °C min⁻¹ under atmospheric conditions.

Li-excess manganese-based layered oxide hollow microspheres were obtained through the introduction of nickel and the lithiation into porous $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ microspheres. In a typical procedure, 10 y mmol $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 10.8(6- y) mmol $\text{LiOH} \cdot \text{H}_2\text{O}$ (Li excess of 8%) were dispersed into 50 mL absolute ethanol, and then 10 mmol $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ hollow microsphere powders were added into the mixture. The ethanol was evaporated slowly under stirring in the fume hood at room temperature. The precipitate was ground manually for 5 min and then heated at 900 °C for 10 h in a pipe furnace with a ramping rate of 1.0 °C /min, followed by a

natural cooling to room temperature. Finally, the $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ ($x = 1/4, 1/3$, and $1/2$) hollow microspheres were formed.

Microstructural Characterization: The morphology and microstructure of the as-prepared samples were characterized by X-ray diffraction (XRD; Bruker D8 Advance diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$)), scanning electron microscopy (SEM; JEOL JSM 7500F, 5 kV) with JEOL energy-dispersive X-ray (EDX) spectroscopy and an EDX mapping system (30 kV), and transmission electron microscopy (TEM; JEM 2100F, 200 kV) with an EM-24015 scanning image observation device. The thermal performance of the as-prepared carbonates was characterized by thermogravimetric analysis (TGA; Shimadzu DTG-60H spectrometer from room temperature to 800 °C under air at a flow rate of 30 mL min⁻¹ with a ramp rate of 10°C /min; surface analysis by X-ray photoelectron spectroscopy (XPS; Kratos Axis Ultra DLD spectrometer)), with binding energy correction by referencing the C1s peak of adventitious carbon to 284.5 eV; and the element content by an inductively coupled plasma mass spectroscopy (ICP-MS, Perkin-Elmer Optima 2100DV).

Electrochemical Measurements: Electrochemical measurements were performed using coin cells (CR2025) assembled in a glove box filled with argon. During the electrode-prepared process, a mixture of as-prepared $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, Super-P (SP) carbon black, and poly(vinylidene fluoride) (PVDF, Mw: 534, 000, Sigma-Aldrich) in a weight ratio of 70 : 15 : 15 in N-methyl-2-pyrrolidone (99.5%, Sigma-Aldrich), was mixed into slurry. An aluminium foil with the size of 12 mm was used as the current collector, on which the active materials with the thickness of ~200 μm and the mass of ~2 mg were coated. The electrodes were dried for 10 h at 120 °C in a vacuum oven before use. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate (EC)–diethyl carbonate (DEC) (1:1 by volume). Galvanostatic tests of the assembled cells were carried out using a LAND CT 2001A system in the voltage range of 2.0–4.8 V (vs. Li⁺/Li) (we defined 1 C as 200 mAh g⁻¹).

3. Results and discussions.

Figure 2 presents SEM images of the $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ precursors at different y values (1, 6/7, and 3/5). We can observe the typical spherical morphology for the sample with $y = 1$ in **Figure 2a**. Close observation of **Figure 2b** reveals the monodisperse and uniform nature of the microspheres, which were $\sim 1.0 \mu\text{m}$ in diameter. According to the statistical data from one hundred particles (inset in **Figure 2a**), the average diameter of $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ microspheres with $y = 1$ was $\sim 1.0 \mu\text{m}$, smaller than those of the other two samples, which were $1.4 \mu\text{m}$ for $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ with $y = 6/7$, and $1.6 \mu\text{m}$ for $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ with $y=3/5$, respectively, as shown in **Figure 2c** and **Figure 2d**. The small size (low than $1.8 \mu\text{m}$ for all) and the narrow distribution ($0.5 \mu\text{m}$ for each) by the solvothermal method surpass the common co-precipitation method,^{15,16} which generally possesses the large size of more than $5 \mu\text{m}$ and the wide distribution of $3.0 \mu\text{m}$.

Thermogravimetric analysis (TGA) was used to optimize the sintering temperature to obtain the $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$ intermediate precursors. The results in **Figures 3a** show the weight losses of $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ with $y = 1$ *versus* the temperature as it increased from 25°C to 800°C . The weight loss might be categorized by two major factors: the first major weight loss (2.6%) resulted from the evaporation of absorbed water at relatively low temperature (such as 200°C), while the second prominent weight loss (34.32%) is the very significant decrease due to decomposition of $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ precursors into $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$, accompanied by release of CO_2 gas and migration of atoms. The TGA results for the other two samples, $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ with $y = 6/7$ and $y = 3/5$, show a similar decomposition trend after calcination, as indicated in **Figure S1a** and **Figure S1b** (*†Electronic SupplementaryInformation (ESI)*). Based on the TGA results, we chose 600°C as the calcination temperature for the synthesis of $\text{Co}_y\text{Mn}_{3-y}\text{O}_4$. **Figure 3b** shows the phase change from carbonate precursor to binary metal oxide after calcination. All diffraction peaks of $\text{CoMn}_2(\text{CO}_3)_3$ (top) could be indexed on the basis of the

hexagonal phase with space group $R\bar{3}c$ (no. 167). The XRD patterns of the as-calcined products (bottom) could be indexed as body-centered tetragonal (bct) phase ($a = 8.09 \text{ \AA}$, $c = 9.27 \text{ \AA}$, JCPDS no. 18-0408) with a distorted spinel structure owing to the well-known Jahn–Teller effect of manganese atom.¹⁷

The morphologies of the Mn-based binary metal oxides were characterized using SEM and TEM (**Figure 4**). It can be observed that the as-obtained samples from calcining $\text{CoMn}_2(\text{CO}_3)_3$ microspheres conserved the spherical morphologies in **Figure 4a** and **Figure 4b** while pores and void spaces also appear due to the CO_2 release in the TEM observations in **Figure 4c** and **4d**. We consider the formation of pores and void spaces in the metal oxides paves the way to the latter introduction of nickel and the lithiation in the next step to synthesize the hollow structure of the final products. The same transformation is also observed for the other two samples, $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ with $y = 6/7$ and $y = 3/5$, as shown in **Figure 4e** and **Figure 4f**.

To obtain the lithium-excess Mn-based oxides with hollow structures, the introduction of stoichiometric nickel and lithium into the aforementioned metal oxides take places through a simple impregnation process followed by post heat-treatment. Accordingly, the final products of the $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ microspheres with $y = 1$, $6/7$, and $3/5$ correspond to $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with $x = 1/4$, $1/3$, and $1/2$, respectively. For easy identification, we denoted $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ with $x = 1/4$, $1/3$, and $1/2$ as LNCM–1, LNCM–2, and LNCM–3, respectively. The FESEM image in **Figure 5a** shows that the as-calcined LNCM–1 sample is composed of uniform microspheres with diameter of $1.0 \text{ }\mu\text{m}$. The detailed observations in **Figure 5b** and **Figure 5c** reveal the hollow interiors from the broken parts in the FESEM image and the contrast between the center and the edge in the TEM image. The high resolution TEM (HRTEM) image in **Figure 5d** from the edge of the hollow microsphere displays an interplanar distance of $0.46 \text{ \AA}$, which should correspond to the (003) plane

spacing of the layered metal oxides in LNCM-1.^{18,19} Moreover, element mapping (**Figure 5e**) displays that the Mn, Co, Ni, and O elements (with Li inherently undetectable) are distributed uniformly across the hollow microspheres. The atomic ratio of Mn to Co, to Ni detected from the EDX spectrum are close to 2:1:1 (**Figure 5f**, with the Al signal from the aluminum substrate), in agreement with the theoretical ratio of elements in LNCM-1. The morphologies of the other two products LNCM-2 and LNCM-3 were also investigated by FESEM, and the results in **Figure 5g** and **Figure 5h** confirm a similar transition in the morphology. The atomic ratios could likewise be calculated from the EDX spectra in **Figure S2a** and **Figure S2b** (†ESI); for instance, 2.5:1:1 for LNCM-2 and 4:1:1 for LNCM-3, respectively. The precise chemical composition for LNCM-1 can also be determined as $\text{Li}_{1.36}\text{Ni}_{0.27}\text{Co}_{0.24}\text{Mn}_{0.56}\text{O}_{2.4}$ by the ICP-MS measurement, highly in agreement with the chemical formula $\text{Li}_{1.25}\text{Ni}_{0.25}\text{Co}_{0.25}\text{Mn}_{0.50}\text{O}_{2.25}$ within error limits.

The corresponding X-ray powder diffraction (XRD) pattern provide the information on crystallinity and crystal phase of the LNCM-1 product, as indicated in **Figure 6a**. All the diffraction patterns can be readily indexed to the rhombohedral layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, together with characteristics typical of Li_2MnO_3 -based compounds at 20–25° (2 θ),²⁰ corresponding to the ordering of Li and Mn atoms in the transition metal layers of the Li_2MnO_3 component with space group *C2/m*. These characteristics are also present in the other two samples, LNCM-2 and LNCM-3, as indicated in **Figure S3** (†ESI). The oxidation states of transition metal ions in the LNCM-1 sample were analyzed by XPS. The binding energies were corrected by referencing the C 1s peak of adventitious carbon to 284.5 eV. The Co 2p spectrum (**Figure 6b**) shows two major peaks with binding energy values at 779.8 and 794.7 eV, assigned to the Co 2p_{3/2} and Co 2p_{1/2} peaks, respectively, with a spin-orbit splitting of ~14.9 eV.^{21,22} The presence of two weak shake-up satellite peaks at 789.4 and 804.2 eV is detected at about 9.8 eV above the Co main line, a fingerprint of Co(III) cations, which further

confirms the presence of the Co(III).²³ After a refined fitting, the appearance of two weak peaks at 780.7 and 796.0 eV demonstrated the coexistence of Co(II). The Mn 2p spectrum in **Figure 6c** features two main spin-orbit lines for 2p_{3/2} at ~641.9 eV and 2p_{1/2} at ~653.8 eV with separation of 11.9 eV, indicating the dominant Mn(IV) cation. A pair of less prominent peaks at 644.0 and 655.3 eV are characteristic of the Mn(III) cation.²⁴ The Ni 2p XPS spectrum in **Figure 6d** shows that the most intense Ni 2p_{3/2} peak is located at 854.3 eV, accompanied by a shake-up peak at about 860.6 eV, which is characteristic of the Ni(II) cation, in agreement with the peaks reported for Ni²⁺ in LiNi_{0.5}Mn_{1.5}O₄.²⁵ Additionally, two less prominent peaks at 855.8 eV and 873.0 eV (by using a Gaussian fitting method) are observed and indicate the presence of Ni³⁺.²⁶ Thus, the above results confirmed that the LNCM-1 with hollow interiors are produced from the *in-situ* self-sacrificial template.

To demonstrate the application value of the hollow micro-/nanostructured manganese-based materials, the three samples, LNCM-1, LNCM-2, and LNCM-3, were investigated as cathode materials for LIBs. As shown in **Figure 7a**, all the charge-discharge profiles show typical electrochemical behavior for the various LNCM-1, LNCM-2, and LNCM-3. During the charging at a potential below 4.4 V, the capacity can be ascribed to the deintercalation of Li⁺ ions accompanied by the concomitant oxidation of Ni²⁺ to Ni⁴⁺ and Co³⁺ to Co⁴⁺ within the active LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ component. The plateau near 4.4–4.6 V corresponds to the removal of lithium from the Li₂MnO₃ component accompanied by oxygen evolution.¹⁹ The charge capacity of LNCM-1, LNCM-2, and LNCM-3 are observed to be approximately 263, 299, and 276 mAh g⁻¹, respectively. These results should be attributed to the electrochemical activation of the corresponding Li₂MnO₃ component, which is consistent with the XRD results. The discharge capacities for the first cycle are 246 mAh g⁻¹ for LNCM-1, 259 mAh g⁻¹ for LNCM-2, and 284 mAh g⁻¹ for LNCM-3. It is evident that much higher discharge capacities can be delivered by these lithium-excess manganese-based oxide electrodes based

on an appropriate x value, which may possess a higher level of homogeneity between the Li_2MnO_3 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ components. The potential plateaus and reproducibility of the charge–discharge profiles of LNCM–1 are in good agreement with its differential capacity dQ/dV plots in **Figure 7b**. Two strong anodic peaks at 3.81 V and 4.49 V are derived from the oxidation of Ni^{2+} to Ni^{4+} and Co^{3+} to Co^{4+} as well as the loss of Li_2O from Li_2MnO_3 . The corresponding 4.5 V peak however cannot be found in the subsequent cycles. This indicates that Li_2MnO_3 will not be recovered, and the substitutional $\text{LiMnO}_2 \rightarrow \text{MnO}_2$ transformation accounts for the subsequent high reversible capacity, which is also reflected by the increased intensity of the following cycles at 3.81 V. During the discharge process, a strong peak at 3.75 V should be ascribed to the reduction of Ni^{4+} to Ni^{2+} and Co^{4+} to Co^{3+} . The $\text{MnO}_2 \rightarrow \text{LiMnO}_2$ transformation is responsible for the appearance of the peak at 3.28 V from the 2nd cycle.^{18,27-}

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For the evaluation of the long-term cycling stability of the LNCM electrodes, the electrodes were galvanostatically discharged and charged at 0.25 C for 200 cycles (**Figure 8a**). All three electrodes exhibit a noticeable slight capacity decline after 5 cycles. Among them, LNCM–2 shows the best cycling performance, and it can maintain a discharge capacity of 203 mAh g^{-1} for the 200th cycle, compared with the values of 175 mAh g^{-1} for LNCM–1 and 165 mAh g^{-1} for LNCM–3, respectively. The capacity retention curves (defined as: discharge capacity for certain cycle/1st cycle discharge capacity $\times 100\%$), which would reflect the overall application performance, give the clear order of $\text{LNCM-2} > \text{LNCM-1} > \text{LNCM-3}$. Obviously, the different x values in the layered oxides are most likely to be the reasons for the different electrochemical performances. It is well known that the level of homogeneity between the Li_2MnO_3 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ components and the degree of crystallinity in the structure of the lithium-excess manganese-based oxides will determine the electrochemical performance in LIBs.²⁹ A high or low dosage of the Li_2MnO_3 component

may introduce partial disorder in the layered oxides: the activity of Li_2MnO_3 at a low x value such as $1/4$ was inadequate; however, the irreversibility and sluggishness of Li_2MnO_3 at a high x value such as $1/2$ dominated the lithium insertion/extraction process. Considering that a high current density is significant for practical batteries when fast discharge/charge is required, we further evaluated the LNCM electrodes at the relatively high rate of 1 C (**Figure 8b**). The discharge/charge capacities of the 200th cycle were 155/156 mAh g^{-1} for LNCM-1, 181/183 mAh g^{-1} for LNCM-2, and 140/143 mAh g^{-1} for LNCM-3, respectively, showing a similar trend to those at the 0.25 C rate. It is worth pointing out that, even after 200 cycles at 1.0 C, LNCM-2 can also retain a discharge capacity of 181 mAh g^{-1} , be comparable to the existing state-of-the-art manganese-based micro- and nanostructured bars reported recently,¹⁴ higher than that in most other reports on Li-excess manganese oxides.^{18,19, 29-34} For example, $\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2$ microspheres delivered a capacity of 170 mAh g^{-1} at 1.0 C after 50 cycles,²⁹ and $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ nanomaterials obtained 160 mAh g^{-1} at a rate of 1.0 C over 100 cycles.³⁴ The high performance should be credited to the high level of homogeneity between the Li_2MnO_3 and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ components at an appropriate x values such as $1/3$, as well as the well-crystallized micro-/nanostructures with hollow interiors produced by the *in-situ* self-sacrificial template method. The structural integrity of the samples could be demonstrated by the preservation of the hollow spherical morphology after 200 charge/discharge cycles in **Figure S4a** and **Figure S4b** (†ESI).

The rate capability of the cathode material is an important performance indicator for grid-scale electricity storage and electric vehicle applications. **Figure 9** shows the rate capabilities of LNCM-1, LNCM-2, and LNCM-3 from the 0.25 C to the 5 C rate. The LNCM-2 electrode was clearly superior by comparison in both rate capability and specific capacity. The test began with the current density of 0.25 C, where the discharge capacity of the LNCM-2 electrode was consistently $\sim 255 \text{ mAh g}^{-1}$ for the first five cycles. When the current

density was increased in steps to 0.5, 0.75, 1.0, and 2.0 C, the capacity decrease was very small for a battery material. Even after a 20-fold increase in the discharge rate to 5 C, a discharge capacity of $\sim 191 \text{ mAh g}^{-1}$ or 75% of the capacity at 0.25 C (255 mAh g^{-1}), could still be retained. The discharge capacity when the current density was returned to 0.25 C was $\sim 253 \text{ mAh g}^{-1}$, which was only marginally lower than the value before the discharge rate increased. In contrast, the LNCM-1 and LNCM-3 electrodes with different x values exhibit lower capacities, which are 236 mAh g^{-1} at 0.25 C and 167 mAh g^{-1} at 5.0 C for LNCM-1, 247 mAh g^{-1} at 0.25C and 153 mAh g^{-1} at 5.0 C for LNCM-3, respectively.

The aforementioned electrochemical testing results indicate that, among the three samples, LNCM-2 exhibit the highest reversible capacity and rate capability as well as the best cycling stability. The substitution of an appropriate amount of Li_2MnO_3 (x value) into the layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ oxide should account for this results: different x values result in different degrees of homogeneous structural integration of the layered character of $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. The higher the level of homogeneity between these two components and the higher the degree of crystallization are, the better the electrochemical performance. More importantly, the well-crystallized micro-/nanostructures with hollow interiors, produced by the *in-situ* self-sacrificial template method, are advantageous for shortening the electron and lithium diffusion lengths, providing an appropriate contact area between the active materials and the electrolyte, facilitating efficient diffusion of electrolyte into the inner regions of the electrode, and accommodating the volume changes associated with repeated Li^+ insertion and extraction.

4. Conclusion.

In summary, we have developed a general and facile approach involving *in-situ* self-sacrificial templates to synthesize an extensive series of lithium-excess manganese oxide micro-/nanostructures with hollow interiors. These cathode materials for LIBs exhibit high specific

capacity, long cycling life, and good rate capability, highlighting the advantages of hollow micro-/nanostructures for high performance. More importantly, it is anticipated that the present *in-situ* self-sacrificial template route will be extended to the design of other micro-/nanostructures with well-defined hollow interiors for broad applications in energy storage/conversion systems.

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Notes and references.

Electronic Supplementary Information (†ESI) is available: additional TGA result, EDX data, XRD patterns, and SEM images.

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Figures and captions:

Figure 1. Schematic illustration of the formation of hollow $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ microspheres by three steps; the x values are determined by the y values.

Figure 2. Field emission SEM (FESEM) images of $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ precursors with different y values: (a, b) $y = 1$; (c) $y = 6/7$; and (d) $y = 3/5$. The insets show the corresponding particle size distribution histograms gathered from one hundred particles.

Figure 3. (a) TGA curves for the carbonate precursor in flowing air. (b) XRD patterns of the $\text{CoMn}_2(\text{CO}_3)_3$ precursor (top) and the resulting porous CoMn_2O_4 sample (bottom) after calcining at 600 °C for 5 h.

Figure 4. Low and high magnification SEM (a, b) and TEM (c, d) images of CoMn_2O_4 microspheres; SEM images of the other two samples: $\text{Co}_y\text{Mn}_{3-y}(\text{CO}_3)_3$ microspheres with (e) $y=6/7$ and (f) $y = 3/5$.

Figure 5. Characterization of LNCM-1 sample: (a–b) low- and high-magnification FESEM images of the as-prepared product; (c) detailed view of the sample (TEM images) and (d) HRTEM image from the edge of the hollow microsphere; (e) elemental mapping of a hollow microsphere and (f) the corresponding EDX spectrum. FESEM images of the other two samples: (g) LNCM-2 and (h) LNCM-3 samples.

Figure 6. (a) Representative XRD pattern for the as-formed LNCM–1 hollow structures. XPS spectra of the LNCM–1 hollow microspheres: (b) Co 2p, (c) Mn 2p, and (d) Ni 2p.

Figure 7. (a) Initial charge–discharge voltage profiles for the electrodes containing LNCM–1, LNCM–2, and LNCM–3 in the voltage range of 2.0–4.8 V vs. Li at the 0.25 C rate. (b) Differential capacity dQ/dV (Q : capacity; V : voltage of the cells) plots for the first 3 cycles for LNCM-1 at the 0.25 C rate.

Figure 8. Cycling performances for the electrodes containing LNCM–1, LNCM–2, and LNCM–3 at the rates of (a) 0.25 C and (b) 1.0 C.

Figure 9. Rate performances for cycling between 2.0 and 4.8 V at different rates for the three samples: LNCM-1, LNCM-2, and LNCM-3.