

Hierarchically-structured nanocrystalline lithium rich layered composites with enhanced rate performances for lithium ion battery



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ABSTRACT

Li-rich layered composite cathode material: $1/2\text{Li}_2\text{MnO}_3 \cdot 1/2\text{LiMn}_{1/2}\text{Ni}_{1/2}\text{O}_2$ with a hierarchically-structured flake morphology is firstly synthesized with a solvent-controlled organic route. X-ray diffraction evidences a pure lithium-rich layered phase of as-fabricated materials. Transmission electron microscopy investigated that each single flake possesses a highly crystalline nature and it composed by numerous hierarchically-structured plates around 20 nm. Electrochemical performances demonstrates that flake cathode delivered a significantly enhanced rate capability as compared to conventional particles prepared by regular co-precipitation method. The specific capacity of flakes cycled at 0.1 and 1 C were 210 and 155 mAh/g, respectively. Cyclic voltammetry represents distinct intercalation mechanisms between two samples, in which a higher lithium diffusivity is derived by flakes with respect to particle ones. Electrochemical impedance profiles shows that the charge-transfer resistances of flake cathodes could be effectively suppressed with respect to particles after cycled at elevated discharge rates. This study provides an alternative approach for synthesizing morphologically-tailored Li-rich layered cathode and virtually proves the ability to tolerant high current input and can preserve a good cycling retention.

1. Introduction

Rechargeable Li-ion batteries (LIBs) that power most of today's portable electronics are presently under huge development for electric vehicles (EVs) [1]. A worldwide progress has been made in searching the preferable cathode materials for backup battery of EVs. In fact, both high energy densities and high output power are universally considered as key criterions for future significance [2]. United States Department of Energy (U.S. DOE) is currently supporting exploratory research on one of the advanced cathode materials: Li_2MnO_3 -stabilized $\text{LiMn}_{1-x}\text{Ni}_x\text{O}_2$ (LR-NMC) [3]. This composite material, so called as Li-rich layered oxides (LLOs), was first developed by Thackeray et al. at Argonne National Lab. in 2007 [4]. It usually delivers an ultimate high reversible capacities (> 250 mAh/g) at the sufficient operating voltage (> 4.4 V vs. Li/Li+) [5,6]. Concerning its dominated energy densities, LLOs is considered to be the most preferable cathode material for the future application of EVs [7].

The energy density of LIBs is not only determined by material's intrinsic chemistry, such as the theoretical capacity and operation voltage, it is also contributed by its extrinsic properties, for example, particle sizes, morphologies and dimensions [8]. In recent years, much attention has been paid on nanostructured materials for LIBs since its

shorter lithium ion diffusion distances and much more superficial active sites than bulk ones, and usually deliver high specific capacity and superior rate performances [9,10]. Needless to say, low-dimension electrodes with various morphologies, including nanorods [11], nanosheet [12], or nanotubes [13], offer tremendous opportunities for academic research owing to their unique physicochemical properties. These materials can either act as building blocks to form secondary hierarchical structures or share exclusive properties occurred between these primary nanostructures [14,15]. Because of their interesting features and electrochemical benefits, investigations on morphologically-tailored electrodes meets explosive growth [16–18].

Although nano-scale cathode/anodes could be obtained by various syntheses, including sol-gel [19], co-precipitation [20], hydrothermal [21], mechanochemical activation [22] and wet chemical process [23], the development of hierarchical structures with specific morphological designs needs further studies, especially for the electrode-electrolyte interactions. Empirically, large surface area frequently leads to easy reaction with the electrolyte, and then changes the surface composition during charge/discharge processes [24,25]. It permits a greater electrode-electrolyte reaction under elevated current densities. Nanostructures would not release the innerstress but induce rearrangement or collapse of the crystal structure, resulting in a rapid decay of

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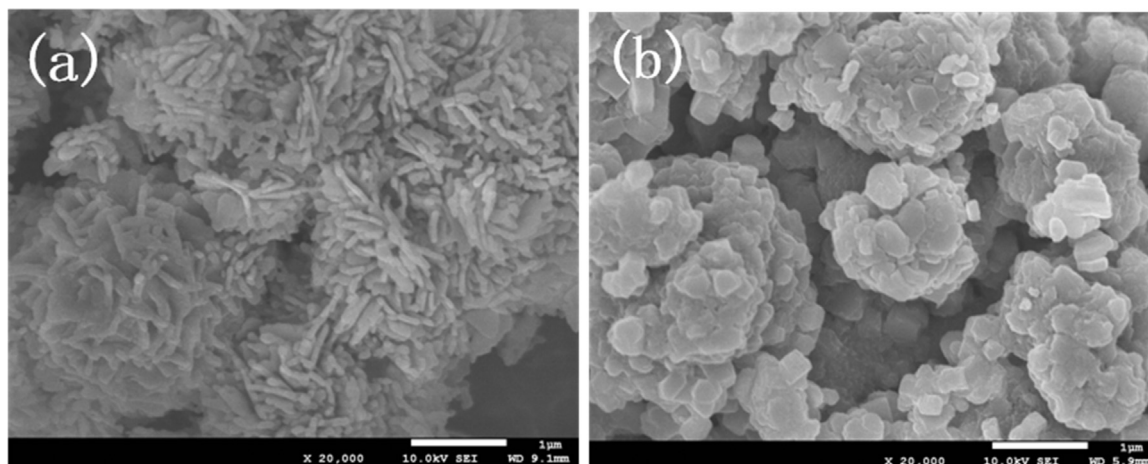


Fig. 1. SEM images of as-fabricated LLOs with different morphologies: (a) intercalated-flake (b) aggregated particle.

specific capacity once the surface changes are obvious [26,27]. Based on previous considerations, the obtained cathode material requires a suitable size/scale with preferable morphologies so as to achieve good electrochemical performances, yet to avoid undesired side reactions [28]. Moreover, other requirements should also be included, such as relatively low cost, less toxicity and good thermal stability related to better safety for realistic commercial application.

Due to complexity of co-existed phases and synthesizing difficulties, there are limited studies focus on the morphology controlling of lithium-rich layered composite. Recently, Luo et al. [29] and Fan et al. [30] reported the synthesis of Li-rich layered microspheres by solvothermal method and both showed enhanced rate capabilities. Other work was done by Yang et al. [31], whose described the synthesis of nanoplate-like $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMnO}_2$ by hydrothermal technique with pyrolysis reduction process. However, a rather poor rate capability was resulted in nanoplates as compared to nanoparticles. It was assumed that a longer in-plane diffusion pathway within the non-preferable intercalation plane is responsible for the performance failure. Except for the operating limitations, other issues concerning hydrothermal procedure, such as the low production-yield and high costs related to the expensive autoclave, are also raised [32].

In this study, a feasible process has successfully developed for preparing flake-like LR-NMC by using polar aprotic solvent with controlled solvation properties. There is no need to apply high pressure, such as hydrothermal conditions or any complicated flux instruments as previously mentioned. One of the critical approaches is to confine the primary particle size as well as its dimensions to ensure a facilitated Li-ion diffusion. The attempt to understand the typical morphological evolution has been undertaken. In aspect of battery performances, the correlated working principle and lithium intercalating mechanism are detailed discussed. As-fabricated flake cathodes with an opened facet along the preferable diffusion pathway would benefit its electrochemical properties, and ultimately deliver a superior rate capability as compared to the conventional LR-NMC.

2. Experimental section

LR-NMC powders were synthesized with the ratio of Li:Mn:Ni=6:3:1 in respect to $0.5\text{Li}_2\text{MnO}_3 \cdot 0.5\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$. In case of fabricating flake cathode, firstly, stoichiometric amounts of LiNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were dissolved in a DMAc (Dimethylacetamide) solvent with continuously stirring. Then, the anhydrous dicarboxylic acid with the identical molar weight of metal salts was added to the previous batch. Distinctively, the solution color immediately turned from pale green to dark black. The detail controlling steps and solvation procedures will be discussed later. After a prolonged drying process, the resulting product was calcined at 700°C

for 10 h in air atmosphere to obtain crystallized powders. The micro-meter particle was synthesized by the conventional carbonate coprecipitation process [33] using D.I. water as solvent.

X-ray diffraction (XRD, D2-Phaser, Bruker) was employed to identify the crystalline phase of the synthesized materials using Cu K α radiation. The powder morphology was observed by field emission scanning electron microscope (FESEM, JSM-7600, JOEL). The detailed atomic structure was investigated by high resolution transmission electron microscopy (HRTEM, JEM-ARM200FTH, JEOL), in which the sample was placed on the Lacey carbon film featured copper grid. The selected area electron diffraction (SAED) was achieved by applying 2D Fourier transform of high resolution atomic image in Gatan Digital Micrograph software. Fourier transform infrared spectroscopy (FTIR, Bruker, Vertex 80v and Tensor 27) was utilized by detecting reflection signal in a wavelength range from 2000 to 700 cm^{-1} with a spectral resolution of 2 cm^{-1} .

For electrochemical characterizations, the cathode electrode was fabricated with the ratio of active material: super P: binder (Commercialized CMC)=80:15:5. The electrolyte solution was 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) in a 1:2 volume ratio. The CR2032 type coin cell was assembled in the argon-purged glovebox using lithium foil as a counter electrode with a controlled environmental condition. The cyclic voltammetry was performed by varying the voltage sweep rate continuously from 1 to 5 mV s^{-1} in the potential range between 2 and 5 V. The electrochemical impedance spectroscopy was carried out in the frequency range from 100 MHz to 10 mHz at an open circuit state.

3. Results and discussion

SEM images of as-synthesized LR-NMC powders are shown in Fig. 1. The cathode material obtained by aprotic solvent system exhibits an intercalated flake morphology. The average size of each cluster is measured about $2\text{ }\mu\text{m}$ and the thickness of a single flake is around 50 nm. In contrast, the material fabricated by traditional method displays a nodular morphology with a severe powder aggregation. The size of secondary particle size is approximately $4\text{ }\mu\text{m}$. The influence of solvent system on the powder morphology was significantly emphasized.

In general, the crystal growth mechanism can be explained by the stages of precursor dissolution and nucleation, oriented crystal growth and alignment by self-assembly, aggregation and partial dissolution and complete re-crystallization [34]. It is suggested that the distinct solvation reaction is responsible for the particular morphology transformation. When metal nitrates are dissolved in the DMAc solvent, the hydroxyl protons of oxalic acid will form strong bonds with the NO_3^- , simultaneously splitting the $\text{M}^{\text{n}+}-(\text{NO}_3^-)_n$ ion pairs [35]. Afterwards,

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