1. Introduction

Lithium-ion batteries (LIBs) with long cycle life, high energy density, high power density, and decent environmental friendliness have great potential to be widely employed as large-scale power sources for electric vehicles (EVs) and hybrid electric vehicles (HEVs).\(^1\)–\(^3\) The cathode materials have been extensively investigated because they play an important role in LIBs. Commercial LiCoO\(_2\), as a typical example, has been initially used as a cathode material since Sony Corporation introduced it into LIBs.\(^4\) However, the disadvantages of commercial LiCoO\(_2\) such as relatively high cost, low energy density, and toxicity have impeded its widespread application in the field of EVs and HEVs. Thus, the development of cathode materials with high energy/power density, low cost, and environmental friendliness is of great importance.\(^5\)

In recent years, the high-voltage Li-rich and Mn-based layered oxide cathode materials with the chemical composition of \(x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2\) (\(M = \text{Ni}, \text{Co}, \text{Mn}\)) have attracted an increasing attention owing to the high capacity (>250 mA h g\(^{-1}\)) when charged above 4.5 V, and high average operating potential.\(^6\)–\(^10\) Nevertheless, the Li-rich cathode materials suffer from a few of serious problems, which hindered them in the commercial application, such as the high irreversible capacity due to the oxidation of \(O^2-\) accompanying the extraction of Li\(^+\) at high working voltage (>4.5 V) during first cycle, the rapid voltage fading during subsequent cycles, and the inferior rate capability.\(^11\)–\(^15\) These obstacles have been overcome to some extent through some effective methods in the reported results. Reducing particle sizes to the nanoscale level has been considered as one of the most effective ways to improve the rate capability of Li-rich cathode materials due to the shortening of the lithium-ion diffusion length.\(^16\)–\(^18\) Moreover, the electrochemical performance of active material in LIB cathode is closely related to the morphology and particle size.\(^19\) Controlling of the morphology via the synthesizing strategies has made great progress, such as solid-state reactions,\(^20\)–\(^23\) co-precipitation,\(^22\)–\(^24\) microwave heating,\(^24\) hydrothermal process,\(^25\)–\(^27\) molten salt process,\(^28\)–\(^29\) sol–gel preparation,\(^30\)–\(^31\) and so on. Among them, the sol–gel method has been applied widely in the fabrication process of Li-rich materials with higher purity and smaller particle size. The process is based on the reaction between inorganic reagents (generally acetates) and fuels (e.g., urea, resorcinol–formaldehyde (RF), citric acid), which is an effective technique to synthesize electrode materials with nanoscale particle size.\(^31\)–\(^33\) The formation of organic carbon-gel are used to aid for metallic ions to achieve the homogeneous state during chemical reaction of RF. Gao and coworkers have successfully synthesized LiCoO\(_2\) cathode material via a facile RF sol–gel method to improve the rate performance, which exhibited a discharge capacity of 97.4 mA h g\(^{-1}\) at 2C.\(^32\) Chen
et al. prepared LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 by a carbon gel–combustion process using RF gel. As cathode material, it showed excellent rate capability and cycling performance, i.e., the average discharge capacity of 169.1 and 90.5 mA h g^{-1} at 0.5 and 50C, respectively.\(^3\)

In the study, the Li_{1-x}Ni_{x}Mn_{y}O_2 material was synthesized via a facile RF organic carbon gel approach, which is an effective technique to prepare electrode materials with the molecular-level. The initial in situ polymerization of resorcinol, formaldehyde, and metal acetate solution helps to achieve the uniformly mixing of raw materials. After calcination, the Li-rich oxide with well-formed layered structure was obtained, which exhibits much better electrochemical properties.

2. Experimental

2.1 Materials preparation

All the raw materials used were analytical purity grade and used as received without any further treatment. The synthesis process of Li_{1-x}Ni_{x}Mn_{y}O_2 samples through a facile solvothermal method is illustrated in Fig. 1. To start with, the starting materials of resorcinol (3.75 mL), formaldehyde (2.7778 g), lithium acetate (2.5968 g), manganese(II) acetate (2.9707 g), and nickel(II) acetate (1.0157 g) with a stoichiometric amount were dissolved in 40 mL absolute ethanol under magnetic stirring for 1 h at room temperature. Then the solution was transferred and sealed in a 100 mL Teflon-lined stainless steel autoclave with a volume filling ratio of 80%, which was kept at 85 °C for 72 h. After that, the solution was naturally cooled down to room temperature and then RF organic carbon-gel was obtained. Subsequently, RF organic carbon-gel was dried completely at 80 °C for 24 h and ground to be powder by using an agate mortar and pestle. Finally, the dried-gels was first calcined at 500 °C for 5 h and then at 850 °C for another 12 h (ref. 30) in alumina crucibles in air atmosphere before it is naturally cooled down to room temperature in the furnace.

2.2 Materials characterization

The crystal structure of the as-prepared powder was characterized through powder X-ray diffraction (XRD, Bruker, D8 Advance, Germany) with Cu Kα radiation operated at 40 kV and 40 mA at a scanning rate of 1° min^{-1} within 2 theta range of 10–80°. The morphology of materials was observed by field-emission scanning electron microscopy (FESEM, Quanta 200, FEI, USA) and transmission electron microscopy (TEM, Tecnai G2 F20 S–TWIN, Japan). X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, USA) was performed to analyze the chemical valence states of Mn and Ni elements. The specific surface area of the samples was determined via Brunauer–Emmett–Teller (BET) procedure from nitrogen sorption isotherms at 77 K using a Quantachrome Autosorb-iQ2 gas sorptometer. The tap density was measured on a Quantachrome Autotap analyzer.

2.3 Electrochemical measurements

A two-electrode cell was used in the electrochemical characterization by galvanostatic charge/discharge cycling. The working electrode was fabricated by a slurry coating procedure. The slurry was prepared by mixing 80 wt% active materials, 10 wt% Super P conductive carbon black, 10 wt% polyvinylidene fluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The electrode slurry was uniformly dispersed and spread on treated aluminum foil as current collector. After drying at 120 °C for 12 h, the aluminum foil with the active materials was pressed under a pressure of 20 MPa. The single-sided cathode has a thickness of 0.033 mm with 3.8–4 mg active material loaded in each electrode. A metallic lithium foil served as the anode. 1 M LiPF_6 in a mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) with a volume ratio of 1 : 1 was used as the electrolyte and the Celgard 2400 was the separator. Finally, the cells with CR2025 coin-type half-cells were assembled in an argon-filled glove box with H_2O and O_2 concentrations below 1 ppm.

The charge–discharge performance of the cells was conducted using CT2001A battery testing system (LAND, Wuhan, China) between 2.0 and 4.8 V (vs. Li/Li+) at current densities of 20–400 mA g^{-1} (1C = 200 mA g^{-1}) at room temperature.

3. Results and discussion

The crystal phase structure of the Li_{1.2}Mn_{0.6}Ni_{0.2}O_2 sample was examined by XRD and shown in Fig. 2. The vast majority of the

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**Fig. 1** A schematic of RF organic carbon gel-assisted the formation process of Li_{1.2}Mn_{0.6}Ni_{0.2}O_2 sample.

**Fig. 2** XRD pattern of Li_{1.2}Mn_{0.6}Ni_{0.2}O_2 sample.
peaks can be well indexed to a hexagonal NaFeO₂ layered structure with space group R3m \((a = 2.86280(6) \text{ Å} \text{ and } c = 14.2608(8) \text{ Å})\) using the TOPAS software with \(R_{wp} = 7.242\%\), except the weak diffraction peaks between 20° and 25°. Two weak peaks at 20.9° and 21.7° can be indexed by (020) and (110) plane diffraction of the monoclinic \(\text{Li}_2\text{MnO}_3\) \((\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]_2\) \(\text{O}_3\)) structure corresponding to space group \(\text{C}2/m\). These two weak peaks are caused by the arrangement of \(\text{LiMn}_6\) cation, always occurring in the transition metal layers of \(\text{Li}_2\text{MnO}_3\) nano-domains, which is known to the characteristic peaks of Li-rich phase.\(^{34-37}\) No diffraction peaks of any other impurity phases are detectable in the whole XRD patterns, indicating a high purity of the as-prepared materials. In addition, the splitting of peaks corresponding to \(\text{(006)}/(012)\) and \(\text{(018)}/(110)\) planes are observed clearly, which are the signatures for the well layered hexagonal structure. The ratio of \(I(003)/I(104)\) was used to indicate the cation mixing of the layered structure.\(^{38,39}\) In this work, the ratio of \(I(003)/I(104)\) for the \(\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2\) sample is 1.44 and much more than 1.2, indicating a quite low level of \(\text{Li}^+/\text{Ni}^{2+}\) disorder. Similarly, a value of \(R\)-factor \((R = [I(012) + I(006)]/I(101))\) indicates the order degree of the hexagonal lattice.\(^{40,41}\) The \(R\) factor is 0.2997 in our case, suggesting better hexagonal ordering for the as-prepared material. This will then benefit the reversible insertion/extraction of lithium ion through the two-dimension channel built by \(\text{MO}_6\) and enhance the electrochemical performance.\(^{5,39}\)

The morphological structure of the as-prepared \(\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2\) sample is observed by SEM and TEM. From Fig. 3(a and b), the size of the primary particles is in the range of 50–200 nanometers, which aggregate with each other to form a porous network structure. Furthermore, Fig. 3(e) shows that these nanoparticles are in an irregular polyhedral shape with smooth surface and densely stacked in a plane to form a stable network flake structure. The tap density of this sample is determined to be 1.46 g cm\(^{-3}\), which is lower than spherical \(\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2\) material due to the existence of some tiny cavities between the nanoparticles.\(^42\) Such a structure could increase the specific surface area to be 6.9 m\(^2\) g\(^{-1}\) compared to the spherical counterpart,\(^43\) which contributes significantly to shortening the diffusion path of lithium ions and further raising the high rate capacity. Moreover, there are some tiny cavities observed between these nanoparticles in the densely stacked planes, resulting from the gas release during the decomposition of RF organic carbon-gel and ethanoates. These cavities could accelerate the electrolyte penetration, which is also contributed to the improvement of the cycling performance of the material.

To obtain more information about the chemical states of the as-prepared samples, X-ray photoelectron spectroscopy (XPS) measurement was employed. XPS spectra for Mn 2p and Ni 2p of samples are shown in Fig. 3(e and f). The Mn 2p spectra exhibits two major peaks at 642.68 and 654.08 eV, and the spin-energy separation is about 11.4 eV. Four signals are observed in the Ni 2p XPS spectra, in which two main sharp peaks of Ni 2p\(_{1/2}\) and Ni 2p\(_{3/2}\) are located at 854.93 and 872.47 eV with a spin-

![Fig. 3](a–c) SEM and (d) TEM images of \(\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2\) sample. The inset in (d) shows HRTEM image taken from the red circle. (e and f) XPS spectra of Mn 2p and Ni 2p of \(\text{Li}_{1.2}\text{Mn}_{0.6}\text{Ni}_{0.2}\text{O}_2\) sample.

![Fig. 4](a) Initial charge–discharge curves of the initial charge–discharge curves at different rates. (b) dQ/dV curves at the first three cycles at 0.1C. (c) Rate capability and (d) cycling performance at 2C of \(\text{Li}_{1.2}\text{Ni}_{0.2}\text{Mn}_{0.6}\text{O}_2\) sample. Mass of the active material loaded in one electrode: 3.8–4 mg.
Table 1

| Preparation method                              | Initial discharge capacity       | Capacity retention | Ref. |
|------------------------------------------------|---------------------------------|--------------------|------|
| Solution method using carbon felt as a carrier  | 288 mA h g\(^{-1}\) at 0.1C      | 96.4% (246.8 mA h g\(^{-1}\)) at 0.1C after 40 cycles | 39   |
| Hydrothermal reaction                           | 298.5 mA h g\(^{-1}\) at 0.1C    | 76.3% at 2C after 150 cycles | 42   |
| Solution combustion synthesis                   | 185.8 mA h g\(^{-1}\) at 2C     |                    |      |
| Sol–gel method                                  | 252.3 mA h g\(^{-1}\) at 0.1C    | 86.7% at 1C after 40 cycles | 48   |
| Ice templating combined coprecipitation strategy| 152.4 mA h g\(^{-1}\) at 2C      |                    |      |
| Amorphous complex method                        | 282.0 mA h g\(^{-1}\) at 0.125C  | 138 mA h g\(^{-1}\) at 2.5C after 100 cycles | 49   |
| Inverse microemulsion route                     | 280.1 mA h g\(^{-1}\) at 0.1C    | 91.1% (188.7 mA h g\(^{-1}\)) at 2C after 50 cycles | 50   |
| Organic carbon gel assisted-synthesis           | 207.1 mA h g\(^{-1}\) at 2C      |                    |      |
|                                                 | 221.0 mA h g\(^{-1}\) at 0.1C    | 81.0% (180.0 mA h g\(^{-1}\)) at 0.1C after 50 cycles | 51   |
|                                                 | 248.0 mA h g\(^{-1}\) at 0.125C  | 81.0% (210.0 mA h g\(^{-1}\)) at 0.125C after 30 cycles | 52   |
|                                                 | 273.3 mA h g\(^{-1}\) at 0.1C    | 93.4% (183.7 mA h g\(^{-1}\)) at 2C after 150 cycles | This work |

The rate capabilities of the Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) sample are shown in Fig. 4(c). The charge–discharge rate is increased successively from 0.1 to 2C, and then decreased back to 0.1C. The discharge capacities of the Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) electrodes are 273.2, 263.0, 233.4, 215.0, and 190.9 mA h g\(^{-1}\) at 0.1, 0.2, 0.5, 1, and 2C discharge rates. Furthermore, the high specific capacity could be reversibly recovered 98.7% of the initial discharge capacity (269.6 mA h g\(^{-1}\)) after the rate is decreased back to 0.1C, indicating a superior rate performance for Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) cathode material. The excellent rate capability can be related to the densely stacked structure. The interior cavities not only accommodates volume change during cycles but also serves as a reservoir of electrolyte and provides more contact area between the electrode and electrolyte. The special structure of the samples comprised of nanoparticles significantly contributes to the remarkable enhancement of electrolyte penetration, charge transfer and ion diffusion, eventually giving rise to the fast lithiation/delithiation reaction kinetics.

In addition, to further evaluate the electrochemical performance of the as-prepared Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) sample, the cell is charged/discharged at 0.1C with a reduced polarization for cell activation in the first cycle and then charged/discharged at 2C in the following cycles. Fig. 4(d) exhibits a relatively high initial discharge capacity of 196.7 mA h g\(^{-1}\). The discharge capacity is slightly increased to be 204.9 mA h g\(^{-1}\) in the first three cycles due to the activation of Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) cathode material. Surprisingly, a much higher discharge capacity of 183.7 mA h g\(^{-1}\) can be achieved at the completion of 150 cycles with the capacity retention of 93.4%. Table 1 summarizes the electrochemical properties of Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) sample in comparison with previously reported results. The improved electrochemical properties in our case are superior to or on par with those of the reported Li\(_{1.2}\)Mn\(_{0.6}\)Ni\(_{0.2}\)O\(_2\) samples prepared through complex process such as solution combustion synthesis and an ice templating combined coprecipitation method. Again, such an excellent electrochemical performance is mainly due to the fact that the stable network flake structure with the nanosized and densely stacked structure can greatly facilitate the diffusion length for Li\(^+\) and electrolyte penetration.

4. Conclusions

In summary, the Li\(_{1.2}\)Ni\(_{0.2}\)Mn\(_{0.6}\)O\(_2\) sample with a high rate performance as cathode material of LIBs was successfully prepared through a facile RF carbon gel-assisted synthesis route in this work. The RF carbon gel is beneficial to the formation of molecular-level dispersion of metal ions, and then results in the well-crystallized Li\(_{1.2}\)Ni\(_{0.2}\)Mn\(_{0.6}\)O\(_2\) nanocrystals with high purity. An excellent electrochemical performance of Li\(_{1.2}\)Ni\(_{0.2}\)Mn\(_{0.6}\)O\(_2\) is achieved due to the stable network flake structure. The sample can deliver an initial discharge capacity of 273.2 mA h g\(^{-1}\) at a current density of 20 mA g\(^{-1}\) between 2.0 and 4.8 V. Moreover, a high discharge capacity of 196.7 mA h g\(^{-1}\) can be achieved at 2C with a capacity retention of 93.4% after 150 cycles. The Li\(_{1.2}\)Ni\(_{0.2}\)Mn\(_{0.6}\)O\(_2\) cathode material prepared by a facile RF organic carbon gel method shows a promising practical potential in high energy density and long cycle life lithium-ion batteries.
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