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Excellent cycle stability at elevated temperature (55 ºC) and high rate for spinel LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$ cathode material
Research highlights

- A series of LiNi_{0.5-x}Cu_xMn_{1.5}O_4 cathode materials were synthesized via a sol-gel method;

- The improvement of cycle stability at 55 % by Cu substitution is firstly reported;

- The LiNi_{0.45}Cu_{0.05}Mn_{1.5}O_4 material could achieve 115 mAh g^{-1} at 20 C discharge rate;

- The capacity retention at 55 % is 98 % after 100 cycles at 5 C discharge rate.
Improvement of cycle stability at elevated temperature and high rate for LiNi$_{0.5-x}$Cu$_x$Mn$_1.5$O$_4$ cathode material after Cu substitution

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Abstract: A series of Cu-substituted LiNi$_{0.5-x}$Cu$_x$Mn$_1.5$O$_4$ (x = 0, 0.03, 0.05 and 0.08) spinels have been synthesized using a sol-gel method. The results demonstrate that when x = 0.05, the sample (LiNi$_{0.45}$Cu$_{0.05}$Mn$_1.5$O$_4$) exhibits the best electrochemical performance, achieving 124.5 mAh g$^{-1}$ and 115.0 mAh g$^{-1}$ at the discharge rates of 5 C and 20 C with the capacity retention of 97.7 % and 95.7 % after 150 cycles, respectively. Besides, the excellent cycle stability at 55$^\circ$C has been demonstrated to retain 96.8 % of the maximum attainable discharge capacity (127.3 mAh g$^{-1}$) at the discharge rate of 5 C after 100 cycles. These data indicate that the LiNi$_{0.45}$Cu$_{0.05}$Mn$_1.5$O$_4$ cathode material has the real potential to be used for high power and high energy lithium ion battery in electric vehicle applications.

Keywords: A. Inorganic compounds; B. Sol-gel chemistry; C. X-ray diffraction; D. Electrochemical properties

1. Introduction

As a preferred secondary battery for portable electronic devices, the lithium-ion battery (LIB) is still at the forefront of the next-generation energy storage research. The growing demands to employ LIB
for high energy and high power density applications, such as electric vehicle (EV) and hybrid electric vehicle (HEV) have induced extensive research efforts worldwide [1]. The key factor for these applications lies in the research of new-type electrode materials that can improve the energy and power density of the LIB. Spinel LiMn$_2$O$_4$ cathode material has motivated researchers [2-6] to partially substitute manganese site by other transition metals to ameliorate the capacity fading. The resulting manganese oxides have exhibited desired charge-discharge behavior in the high 5 V region prompting these materials to be referred to as 5 V cathode materials.

Among the 5 V system spinels, LiNi$_{0.5}$Mn$_{1.5}$O$_4$ has been considered to be a particularly promising one due to its unique potential plateau at 4.7 V and its high theoretical discharge capacity of 147 mAh g$^{-1}$ [7, 8]. In addition, the spinel structure can provide a three-dimensional pathway for lithium-ion diffusion, which appears to provide about 20 ~ 30 % higher energy density than other cathode materials [9]. However, the possible electrolyte decomposition at high potential (~5 V) and negative reaction at high temperature (50 ~ 60 °C) may deteriorate the material’s capacity retention. To date, many attempts have been adopted to solve these problems, for example, coating the material with carbon [10], ZnO [11], AlPO$_4$ [12] or ZrO$_2$ [13] to prevent the active material from dissolving into the electrolyte at high potential and high temperature. Additionally, apart from the surface modification of LiNi$_{0.5}$Mn$_{1.5}$O$_4$, ion substitution in the material using Al [9], Cr [14], Co [15], Ti [16] and F [17] can result in an intrinsic improvement to the material’s electrochemical performance; in particular the rate performance. Wang et al [18] have synthesized Ru-doped LiNi$_{0.5}$Mn$_{1.5}$O$_4$ spinels with excellent rate performance at 10 C, but these ruthenium compounds are not realistic choices for cathode materials because of the high cost of ruthenium. As a 3d transition metal, Cu is an optional substitution element for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ because of its low cost and less toxicity than that of other transition metal elements.
such as Co and Cr. Yang et al [19] have carried out first principles computations to investigate the electronic, structural, and electrochemical properties of LiM₀.₅Mn₁.₅O₄ (M = Ti, V, Cr, Fe, Co, Ni, and Cu) and have found that Cu can potentially lower Li⁺ diffusion barrier which should make it a favorable substitution element in the LiNi₀.₅Mn₁.₅O₄ spinel. However, these authors failed to provide any research to define the high-rate capability and cycle performance of Cu-substituted LiNi₀.₅₋ₓCuₓMn₁.₅O₄ materials, especially the cycle stability at high rate and high temperature.

Therefore, in order to improve the electrochemical performance of LiNi₀.₅Mn₁.₅O₄ by Cu substitution, we synthesized a series of Cu-substituted LiNi₀.₅₋ₓCuₓMn₁.₅O₄ cathode materials via a sol-gel method. The physical structure and electrochemical properties of all the synthesized samples were investigated systematically, particularly the optimal material’s cycle stability at elevated temperature (55 °C) and high rate.

2. Experimental

The LiNi₀.₅₋ₓCuₓMn₁.₅O₄ (x = 0, 0.03, 0.05, 0.08) powders were synthesized using a sol-gel method employing Li(CH₃COO)·2H₂O (99 %, AR), Mn(CH₃COO)₂·4H₂O (99 %, AR), Ni(CH₃COO)₂·4H₂O (98 %, AR), Cu(CH₃COO)₂·4H₂O (99 %, AR) and citric acid (99.5 %, AR) as raw materials. Stoichiometric amounts of all these acetates were dissolved in deionized water and stirred at 50 °C. An extra 5 mol % amount of lithium salt was added to compensate for lithium loss during calcinations. The citric acid solution acted as chelating agent for the polymeric matrix as it was added to the solution with continuous stirring. Next the pH value of the solution was adjusted to 7.0 by slow addition of ammonium hydroxide (25 ~ 28 %). After stirring for 5 h, the temperature was raised to 80 °C to promote the evaporation of water. This caused the solution to turn into a green viscous gel, which was dried at 120 °C in a vacuum oven for 12 h and then finely ground to yield a powder for subsequent
calcinations. To decompose the organic constituents, the powder was pre-sintered at 450 \degree C in air, and after grinding again, it was sintered at 800 \degree C for 12 h followed by an annealing treatment at 650 \degree C for 10 h in air. The resultant was a fine black powder which was subjected to physical characterizations and electrochemical performance tests.

The structural and crystalline phase analyses of the powders were conducted using powder X-ray diffraction (XRD, PTR-III, Japan) employing Cu K\alpha radiation with the scanning speed of 8 \degree min\(^{-1}\) between 10 \degree and 80 \degree. A Thermo electron corporation Fourier transform infrared (FTIR) spectrometer (Nicoletis10, China) was used for FTIR characterization. Each sample was subjected to an average of 100 scans taken between 700 and 400 cm\(^{-1}\). The morphology of the samples was observed by scanning electron microscopy (SEM, Hitachi S4800, Japan), 5 kV.

Electrochemical tests were carried out on CR2032 coin-type cells. The cathodes were prepared by mixing 80 wt.% of the experimental cathode material with 10 wt.% acetylene black and 10 wt.% polyvinylidene difluoride (PVDF) in N-methyl-2-pyrrolidone (NMP). The mixture was mixed by sonic oscillator for 30 min to get uniform slurry, which was coated on an aluminum foil and then dried completely under vacuum at 120 \degree C overnight. The cathode electrode films were punched into discs and then pressed under the pressure of 10 MPa. The resulting cathodes had an active material loading of about 2.8 (± 0.2) mg cm\(^{-2}\). Using lithium metal as anode, 1M LiPF\(_6\) in a 2:3 (by volume) mixture of ethylene carbonate (EC)/diethyl carbonate (DEC) as electrolyte and Celgard 2300 membrane as separator, the CR2032 coin-type cells were assembled in an argon-filled glove box (MIKROUNA Super (1220/750), China). The galvanostatic charged/discharged tests were performed at ambient temperature or elevated temperature (55 \degree C) using a standard battery cycle test system (LX-PCBT-138-32D, China) at different C-rates (1 C = 147 mA g\(^{-1}\)) between 3.5 V and 5 V. The cyclic
voltammetry (CV) tests were carried out on the electrochemical workstation (Gamry PCI4-750, America) at the test rate of 0.1 mV s\(^{-1}\) from 3.5 V to 5 V, and the electrochemical impedance spectroscopy (EIS) analysis was also carried out in the frequency range of 100 kHz to 0.01 Hz.

3. Results and discussion

The XRD patterns of LiNi\(_{0.5-x}\)Cu\(_x\)Mn\(_{1.5}\)O\(_4\) (x = 0, 0.03, 0.05, 0.08) materials are shown in Fig. 1. All the samples appear to be indexed in a well-defined cubic spinel phase with the very intense peaks at the (111), (311) and (400) planes [20]. Normally one obtains an XRD spectrum for LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) material that contains peaks at 37.5 °, 43.6 ° or 63.3 ° are indicative of the presence of NiO or Li\(_x\)Ni\(_y\)O [21] impurities. As shown in Fig. 1, these peaks are absent in the XRD spectra of our materials indicative of the highly pure products. In addition, the crystal lattice parameters, determined by refining the data with MDI Jade software, are 8.1536 Å for LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\), 8.1544 Å for LiNi\(_{0.47}\)Cu\(_{0.03}\)Mn\(_{1.5}\)O\(_4\), 8.1585 Å for LiNi\(_{0.45}\)Cu\(_{0.05}\)Mn\(_{1.5}\)O\(_4\) and 8.1571 Å for LiNi\(_{0.42}\)Cu\(_{0.08}\)Mn\(_{1.5}\)O\(_4\), respectively. A careful comparison on the location of (400) diffraction peak in the range of 43 ° ~ 46 ° (Fig. 1(b)) reveals that the peak position of the samples shifts to lower angles after Cu substitution, indicating that Cu substitution could cause the lattice expansion due to the slightly larger ionic radius of Cu\(^{2+}\) (0.73 Å) than that of Ni\(^{2+}\) (0.69 Å) [22]. Besides, as the amount of Cu increases in the spinel, we have observed no significant diffraction peaks for CuO: therefore, we conclude that Cu has been doped into the crystal structure of the spinels.

Except for the XRD analysis, the ordered P4\(_3\)32 phase is proved to appear three new peaks in the FTIR spectroscopy at about 646, 464 and 430 cm\(^{-1}\), which are normally absent in the other structure (disordered Fd3m phase) because of peak broadenings [23, 24]. As Fig. 2 shown, three IR absorption bands at 648, 468 and 429 cm\(^{-1}\), are observed from the FTIR spectra of all the samples between 700
and 400 cm\(^{-1}\), demonstrating that all the annealed samples have the P\(4_3\overline{3}2\) space group.

The scanning electron microscopy images under different magnifications of LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) and Cu-substituted samples are shown in Fig. 3. From the observation of (b) and (c), the morphology of the overall particles is more spherical with a slight second-level agglomeration, when the Cu content increases to 0.03 and 0.05. The special morphology would be beneficial to increase the contact area of active material with the electrolyte, resulting in fast electrochemical reaction and diffusion kinetics.

To examine the effectiveness of Cu substitution on improving the rate capability of LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\), the specific capacities of the bare and Cu-substituted samples at different charge-discharge rates are investigated and the results are exhibited in Fig. 4. As shown, due to the ohmic polarization and electrode polarization, the capacities of all the samples decrease with the charge-discharge rate increases. However, from the insert of Fig 4(a), we have found that this decreased trend has been reduced by Cu substitution. Thereinto, the sample LiNi\(_{0.45}\)Cu\(_{0.05}\)Mn\(_{1.5}\)O\(_4\) exhibits the highest discharge capacities, achieving 129.6, 129.2, 125.5, 122.2 and 114.8 mAh g\(^{-1}\) at rates of 0.5, 1, 2, 3 and 5 C, respectively. By contrast, 129.2, 127.8, 123.6, 116.0 and 97.2 mAh g\(^{-1}\) could be obtained from the pristine material at the same rates. It has been reported that a larger crystal lattice can be able to provide larger diffusion channels and hence lower activation energy to facilitate faster lithium ion transportation [18]. Therefore, the results together with those from the analysis of structure and morphology prompts one to assume that the rate capability of the Cu-substituted cathode materials is greatly improved due to the enhancement of lithium ion diffusion and electrochemical reaction kinetics afforded by the addition of Cu. In addition, it is clear to see that the discharge capacity at 0.5 C decreases slightly after doping with Cu. In the case of LiNi\(_{0.42}\)Cu\(_{0.08}\)Mn\(_{1.5}\)O\(_4\), we could achieve a discharge capacity that is only 94.1 % of the unmodified LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\) at the rate of 0.5 C. The lower
capacity may be due to the following reasons: First, as the Cu-content (x) in the spinel increases, there is a corresponding decrease in the Ni-content (0.5-x), which is the major contributor to the capacity at 5 V. Second, the 5 V capacity in LiNi_{0.5}Mn_{1.5}O_{4} is produced by Ni^{4+}/Ni^{2+} redox couple, which is a two-electron transfer reaction, by contrast, the Cu-substituted cathode materials produce their capacity through a one-electron transfer reaction [25], which compromises the material’s capacity vis-à-vis the LiNi_{0.5}Mn_{1.5}O_{4} material. Besides, as the content of Cu in the spinel increases, part of Cu^{2+} may be prone to occupy the tetrahedral sites [26], leading to a blockage of lithium ion transportation. Therefore, the suitable content of Cu substitution (x = 0.05 in this work) can improve the rate capability of LiNi_{0.5}Mn_{1.5}O_{4}, but excessive introduction of Cu in the spinel structure may reduce the capacity of the cells, playing a negative effect on the material’s electrochemical performance.

For comparison, the Fig. 4 (b) represents the discharge curves of LiNi_{0.5}Mn_{1.5}O_{4} and LiNi_{0.45}Cu_{0.05}Mn_{1.5}O_{4} at different rates. In both cases, there is a voltage plateaus at 4.6 ~ 4.8 V reflecting the reduction of Ni^{4+}/Ni^{2+} redox couple. The weak plateau at 3.9 ~ 4.0 V, characteristic of the Mn^{4+}/Mn^{3+} redox couple is almost invisible, suggesting that annealing process reduces the formation of Mn^{3+}. Furthermore, at higher currents (increasing discharge rates), the Cu-free sample (LiNi_{0.5}Mn_{1.5}O_{4}) exhibits a gradual decrease in capacity with a lower voltage platform, due to the ohmic voltage drop and electrode polarization. The operating voltage of LiNi_{0.5}Mn_{1.5}O_{4} at 5 C is 4.55 V with a discharge capacity of 97.2 mAh g^{-1}. In contrast, the Cu-substituted sample (LiNi_{0.45}Cu_{0.05}Mn_{1.5}O_{4}) exhibits a stable operating voltage of 4.63 V, with a discharge capacity of 114.8 mAh g^{-1}. These results illustrate that the electrode polarization can be suppressed effectively and good rate capability can be obtained by Cu substitution.

The rate capability as the cathodes are cycled is an important parameter for practical applications.
For further research on this, we have charged the cells at 1 C and discharged at 20 C for 150 cycles. Fig. 5 details the results. It is notable that the Cu-substituted sample (LiNi_{0.45}Cu_{0.05}Mn_{1.5}O_{4}) delivers the discharge capacity of 115.0 mAh g\(^{-1}\), and after 150 cycles, it still can retain 95.7 % of the initial capacity (114.2 mAh g\(^{-1}\)), exhibiting excellent cycle stability at high rate. On the other hand, the Cu-free sample (LiNi_{0.5}Mn_{1.5}O_{4}) could reach only 82.8 % of the initial discharge capacity (94.5 mAh g\(^{-1}\)), revealing poor cycle stability at high rate.

The capacity fading at elevated temperature is another significant limiting factor for LiNi_{0.5}Mn_{1.5}O_{4} spinels in practical applications. Therefore, we have investigated the cycle stability at elevated temperature (55 °C) of the Cu-free and Cu-substituted samples by charging the cells at 1 C and discharging at 5 C for 100 cycles at 55 °C, accompanied by 150 cycles at room temperature (RT) for comparison. The results shown in Fig. 6(a) indicate that both samples exhibit satisfactory cycle stability at RT, and the Cu-substituted sample delivers higher discharge capacity (124.5 mAh g\(^{-1}\)) with a capacity retention of 97.7 % after 150 cycles, compared with the Cu-free one (116.0 mAh g\(^{-1}\), 97.5 %). Nevertheless, when cycled at 55 °C (Fig. 6 (b)), the discharge capacity of LiNi_{0.5}Mn_{1.5}O_{4} decays rapidly from 116.1 mAh g\(^{-1}\) at the first cycle to 100.0 mAh g\(^{-1}\) at the 100\(^{th}\) cycle which is only 86.2 % of the initial discharge capacity. By contrast, the capacity fading is reduced for the Cu-substituted sample LiNi_{0.45}Cu_{0.05}Mn_{1.5}O_{4}, which could achieve 127.3 mAh g\(^{-1}\) at maximum and 123.2 mAh g\(^{-1}\) at the 100\(^{th}\) cycle, with 98.0 % of the initial discharge capacity (125.7 mAh g\(^{-1}\)) retained. The capacity fading rate is only 0.02. It can be inferred that faster lithium ion mobility in the Cu-substituted sample may give rise to better high-rate performance including lower polarization and better structural stability by preventing the pile-up of lithium ions on the surfaces of the particles [18].

The electrochemical impedance spectroscopy is measured to determine the kinetic parameters of the
electrode process. Before the EIS measurements, all the samples were cycled for 3 cycles at 0.2 C to obtain relatively stable and identical status. The Nyquist plots for Cu-free sample and Cu-substituted sample are shown in Fig. 7. The spectra is typically consist of a semi-circle in the high to medium frequency region resulted from the charge-transfer process and the inclined line at low frequency is attributed to lithium ion diffusion in the spinel. The EIS is fitted by the equivalent circuit inserted in Fig. 7, where $R_e$ is the ohmic resistance, $R_{ct}$ and CPE are the charge transfer resistance and the constant phase element of the double-layer, respectively, $Z_w$ is Warburg impedance. The fitting results show that the charge transfer resistance ($R_{ct}$) decreases from 297 ohm (LiNi$_{0.5}$Mn$_{1.5}$O$_4$) to 149 ohm (LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$) after Cu substitution, indicating a significant improvement of the electrochemical reaction kinetic.

The cyclic voltammograms of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$ are represented in Fig. 8. The anodic sweeps of both samples have two main distinguished peaks at 4.78 V and 4.81 V corresponding to the Ni$^{2+}$/Ni$^{3+}$ and Ni$^{3+}$/Ni$^{4+}$ redox couples, but there is only one cathodic peak presents above 4.62 V suggesting an indistinguishable difference of the phase transition steps between [Ni$_{0.5}$Mn$_{1.5}$]O$_4$/Li$_{0.5}$[Ni$_{0.5}$Mn$_{1.5}$]O$_4$ and Li$_{0.5}$[Ni$_{0.5}$Mn$_{1.5}$]O$_4$/Li[Ni$_{0.5}$Mn$_{1.5}$]O$_4$ upon the insertion of Li$^+$ into the spinel. Besides, the weak peaks at about 4.0 V and 4.4 V are corresponding to the Mn$^{3+}$/Mn$^{4+}$ and Cu$^{2+}$/Cu$^{3+}$ redox couples [19], respectively. It is notable that the potential difference between the anodic and cathodic peaks of Ni$^{2+}$/Ni$^{4+}$ redox couples decreases from 0.19 V and 0.16 V to 0.17 V and 0.13 V after Cu substitution, indicating the enhancement of the reversibility in the electrode reaction by reducing the electrochemical polarization and accelerating lithium ion intercalation/de-intercalation.

On the other hand, for the coin-type cell systems, the electrode can approximately be regarded as a flat one and the peak current density can be represented as follows: $i_p = 2.69 \times 10^5 n^{3/2} A D_{Li}^{1/2} v^{1/2} C_0$, where n
is the number of electrons involved in the electrochemical reaction, \( A \) is the surface area of the electrode, \( C_0 \) is the concentration of \( \text{Li}^+ \), \( D \) is the diffusion coefficient of \( \text{Li}^+ \), and \( \nu \) is the scan rate.

Since \( i_p \propto D^{1/2} \) [27], the diffusion coefficient of \( \text{Li}^+ \) is higher in the Cu-substituted electrode than that of the Cu-free electrode. In summary, the improvement of electrochemical reversibility, lithium ion diffusion and ionic conductivity by Cu substitution can produce better cycle stability than unmodified \( \text{LiNi}_{0.45}\text{Mn}_{1.5}\text{O}_4 \), especially at high rate and high temperature.

4. Conclusions

The sol-gel method followed by an annealing treatment is used to synthesize Cu-substituted \( \text{LiNi}_{0.5-x}\text{Cu}_x\text{Mn}_{1.5}\text{O}_4 \) (\( x = 0, 0.03, 0.05, 0.08 \)) cathode materials. Physical properties analysis results demonstrate that all the samples have a well-defined cubic spinel structure containing \( \text{P4}_3\text{32} \) space groups. Discharge capacities of 129.6, 129.2 and 114.8 mAh g\(^{-1}\) at 0.5, 1 and 5 C, are achieved from the Cu-substituted sample (\( \text{LiNi}_{0.45}\text{Cu}_{0.05}\text{Mn}_{1.5}\text{O}_4 \)), which are far greater than the corresponding Cu-free sample (\( \text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \)). In particular, we have found that the Cu-substituted material delivers excellent rate cycle performance, retaining 95.7 % of the initial capacity (114.2 mAh g\(^{-1}\)) at the discharge rate of 20 C after 150 cycles. In addition, high cycle stability at elevated temperature (55 °C) has been demonstrated to reach 127.3 mAh g\(^{-1}\) at the discharge rate of 5 C, with 2.0 % capacity fading after 100 cycles. The considerable rate capability and cycle stability at high rate and elevated temperature of \( \text{LiNi}_{0.45}\text{Cu}_{0.05}\text{Mn}_{1.5}\text{O}_4 \) cathode material will provide new opportunities for high power, high energy density LIB in electric vehicle applications.

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References


Figure Captions

**Fig. 1.** (a) XRD patterns of LiNi$_{0.5-x}$Cu$_x$Mn$_{1.5}$O$_4$ (x=0, 0.03, 0.05, 0.08); (b) Detailed XRD patterns of LiNi$_{0.5-x}$Cu$_x$Mn$_1$O$_4$ (x=0, 0.03, 0.05, 0.08) between 43° and 46°.

**Fig. 2.** FTIR spectra of LiNi$_{0.5-x}$Cu$_x$Mn$_{1.5}$O$_4$ (x=0, 0.03, 0.05, 0.08).

**Fig. 3.** SEM images under different magnifications of LiNi$_{0.5-x}$Cu$_x$Mn$_{1.5}$O$_4$: (a) x=0; (b) x=0.03; (c) x=0.05; (d) x=0.08.

**Fig. 4.** (a) Discharge capacities of LiNi$_{0.5-x}$Cu$_x$Mn$_{1.5}$O$_4$ (x=0, 0.03, 0.05, 0.08) as a function of cycle number and charge-discharge rates; (b) The discharge curves of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$ at different rates.

**Fig. 5.** Rate cycle performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$ at 20 C (charge rate: 1 C).

**Fig. 6.** Cycle performance of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$ at (a) 5 C (RT, charge rate: 1 C); (b) 5 C (55 °C, charge rate: 1 C).

**Fig. 7.** EIS spectra of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$ electrodes.

**Fig. 8.** Cyclic voltammograms of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$ electrodes.
Figure 1.
Figure 2.
Figure 3.
Figure 4.

(a) Discharge capacity / mAh g$^{-1}$ vs. cycle number for different C-rates and compositions with varying x values.

(b) Potential vs. (Li/Li$^+$) / V for different compositions of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ and LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$ at different C-rates.
Figure 5.

Charge rate: 1 C
Discharge rate: 20 C
Figure 6.

(a) Discharge capacity / mAh g\(^{-1}\) vs. Cycle number

- LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\)
- LiNi\(_{0.45}\)Cu\(_{0.05}\)Mn\(_{1.5}\)O\(_4\)

Charge rate: 1 C
Discharge rate: 5 C

(b) Discharge capacity / mAh g\(^{-1}\) vs. Cycle number

- LiNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\)
- LiNi\(_{0.45}\)Cu\(_{0.05}\)Mn\(_{1.5}\)O\(_4\)

Charge rate: 1 C
Discharge rate: 5 C

RT vs. 55°C
Figure 7.
Figure 8.

(a) LiNi$_{0.5}$Mn$_{1.5}$O$_4$
(b) LiNi$_{0.45}$Cu$_{0.05}$Mn$_{1.5}$O$_4$

- Ni$^{2+}$/Ni$^{4+}$
  - 4.82 V
- Cu$^{2+}$/Cu$^{3+}$
  - 4.65 V
- Mn$^{3+}$/Mn$^{4+}$
  - 4.62 V