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Short Communication

Synthesis and Electrochemical Study of Spinel $LiCu_{0.05}Mn_{1.95}O_4$ via a Solution Combustion Method as a Cathode Material for Lithium Ion Batteries

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Single-phase $LiCu_xMn_{2-x}O_4$ (x = 0 and 0.05) particles were synthesized by a solution combustion method at 600 °C for 3 h. Scanning electron microscopy revealed that the agglomeration of the sample decreased with Cu doped. The electrochemical properties of $LiCu_xMn_{2-x}O_4$ (x = 0 and 0.05) as a cathode material for rechargeable lithium-ion batteries was characterized by galvanostatic charge-discharge experiments, cyclic voltammetry and electrochemical impedance spectroscopy. Cu-substituted $LiCu_{0.05}Mn_{1.95}O_4$ exhibited excellent cycling stability with a capacity retention of 77.1% at a discharge rate of 1 C (1 C =148 mAh g^{-1}) after 500 cycles. $LiCu_{0.05}Mn_{1.95}O_4$ spinel had a high rate capability and reversible cycling performance, revealing that doping $LiMn_2O_4$ with Cu improves its electrochemical performance for use as a cathode in lithium-ion batteries.

Keywords: solution combustion method; Cu-doping; $LiMn_2O_4$; cathode materials; Lithium-ion batteries

1. INTRODUCTION

Lithium-ion batteries (LIBs) that provide high energy density at fast charge-discharge rates are needed because of the high power requirements of electric vehicles (EVs) and hybrid electric vehicle (HEVs) [1]. Therefore, extensive research has been carried out to improve the rate capability of cathode materials such as layered $LiNi_{0.5}Mn_{0.5}O_2$ [2], olivine $LiFePO_4$ [3], and spinel $LiNi_{0.5}Mn_{1.5}O_4$

[4], improved electrochemical performance was achieved. Spinel $LiMn_2O_4$ has been widely investigated as a promising cathode material for use in LIBs for EVs and HEVs because of its low cost, non-toxicity, and high safety and power density. However, an important issue restricting practical application of $LiMn_2O_4$ is rapid capacity fading, which is mainly caused by structural distortion *via* the Jahn-Teller effect. To suppress capacity fading in $LiMn_2O_4$, substitution of the Mn^{3+} ions with other ions such as Mg^{2+} [5], Ni^{2+} [6], Sn^{4+} [7], Al^{3+} [8], Fe^{2+} [9], Cu^{2+} [10] and F^- [11] has been studied. The results showed that ion doping is an effective way to improve the structural stability and electrochemical performance of $LiMn_2O_4$ as a cathode material. Among these materials, the Cu substitution spinel $LiMn_2O_4$ were studied only by a few researchers [12-19]. It was found that the structural stability and cycling performance of spinel $LiMn_2O_4$ can be enhanced by using of lesser Cu substitution, which can be ascribed to the stronger bond of Cu-O than that of Mn-O [14, 18]. Murali et al. [17] reported that $LiCu_xMn_{2-x}O_4$ ($0<x<0.5$) samples were synthesized by a sol-gel process. "Li/$LiMnCu_{0.1}Mn_{1.9}O_4$" cells show an initial discharge capacity of 105 mAh g^{-1} with 90.48% capacity retention after 60 cycles. Ebin et al synthesized nanocrystalline $LiCu_xMn_{2-x}O_4$ (x=0.2-0.6) particles by ultrasonic spray pyrolysis method and showed that the initial discharge capacities of $LiCu_{0.2}Mn_{1.8}O_4$ was 122 mAh g^{-1}, and the capacity retention was 55.74% after 50 cycles at 0.5 C [13]. Huang et al prepared Single-phase $LiCu_xMn_{2-x}O_4$ ($x\leq 0.10$) cathode materials by a molten-salt combustion method and $LiCu_{0.05}Mn_{1.95}O_4$ demonstrated that initial discharge specific capacity of 119.0 mAh g^{-1} with 95.0% capacity retention after 100 cycles at 0.5 C [19]. These results demonstrate that the Cu-doping can effectively improve the electrochemical performance of the $LiMn_2O_4$ material. However, the desired capacity retention and rate performance did not achieve.

In this paper, spinel $LiCu_xMn_{2-x}O_4$ (x = 0 and 0.05) particles were synthesized by a solution combustion method. Crystal structure, morphology, electrochemical properties and rate performance of the $LiCu_xMn_{2-x}O_4$ cathode materials for LIBs were investigated in detail.

2. EXPERIMENTAL

$LiMn_2O_4$ and Cu-substituted $LiCu_{0.05}Mn_{1.95}O_4$ were prepared by a solution combustion method. $LiNO_3$ (AR, Aladdin) was used as lithium resource, $Mn(CH_3COO)_2{\cdot}4H_2O$ (AR, Aladdin) acted as manganese resource and $Cu(CH_3COO)_2{\cdot}H_2O$ (AR, Tianjin Kemiou) was dopant, which were weighted according to a stoichiometric ratio of 1:1.95:0.05 (Li:Mn:Cu) with a total mixture mass of 4 g and placed into a 300-mL crucible. Then, the 9 mol L^{-1} nitric acid were added to the mixture. Finally, the mixture was heated in a muffle furnace at 600 °C for 3 h. $LiCu_xMn_{2-x}O_4$ powders were obtained after cooling to room temperature. Cathodes for LIBs were prepared with a weight ratio of 80% active material, 10% acetylene black, and 10% polyvinylidene fluoride. The electrolyte was 1 M $LiPF_6$/ethylene carbonate + diethylene carbonate (1:1(v/v)), and the counter electrode was Li metal.

The structures of the materials were studied by powder X-ray diffraction (XRD, D/max-TTRIII, Rigaku, Japan) using Cu K_α radiation. Lattice parameters were obtained using Jade 5.0 software. The morphology of the samples were observed by scanning electron microscopy (SEM; Quanta-200, FEI, Hillsboro, OR, USA).Galvanostatic charge-discharge experiments were performed using a Land electric test system (CT2001A; Wuhan Jinnuo Electronics Co., Ltd., China) at a current density of 1 C between 3.0 and 4.5 V (*vs*. Li/Li^+). Cyclic voltammetry (CV) was carried out using an electrochemical workstation (IM6ex; Zahner Elektrik GmbH & Co. KG, Germany) from 3.60 to 4.50 V (*vs*. Li/Li^+). Electrochemical impedance spectroscopy (EIS) of cells was measured using the same electrochemical workstation by applying an AC voltage of 5 mV in the frequency range of 0.1 Hz to 100 KHz.

3. RESULTS AND DISCUSSION

3.1 X-ray diffraction analysis

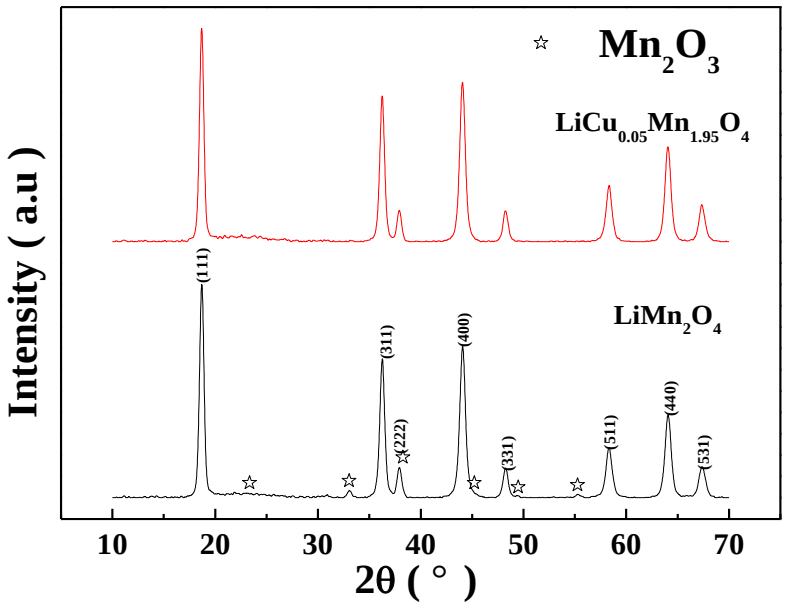

Figure 1. XRD patterns of $LiMn_2O_4$ and Cu-substituted $LiCu_{0.05}Mn_{1.95}O_4$.

The XRD patterns of $LiMn_2O_4$ and Cu-substituted $LiCu_{0.05}Mn_{1.95}O_4$ presented in Fig. 1 exhibit the characteristic diffraction peaks of cubic spinel $LiMn_2O_4$ with the Fd3m space group (JCPDS, PDF35-0782) corresponding to the eight crystal planes of (111), (311), (222), (400), (331), (511), (440), and (531). There is no marked difference in the crystal structure after Cu substitution. This indicates the addition of Cu does not change the spinel structure of $LiMn_2O_4$. The XRD pattern of $LiCu_{0.05}Mn_{1.95}O_4$ is consistent with a single phase, while a small amount of an impurity phase is

detected in the pattern of $LiMn_2O_4$, and can be identified as Mn_2O_3. The lattice parameters and unit cell volumes of the materials are summarized in Table 1.

Table 1. Lattice parameters of $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_4$ cathode materials

Cathode material	Lattice parameter (Å)	unit cell volume $(Å)^3$
$LiMn_2O_4$	8.2142	554.3
$LiCu_{0.05}Mn_{1.95}O_4$	8.2219	555.8

The lattice parameter increased from 8.2142 to 8.2219 Å after doping with Cu, which is because Mn^{3+} ions (0.0645 nm) are substituted by larger Cu^{2+} ions (0.087 nm) in $LiCu_{0.05}Mn_{1.95}O_4$. The expansion of the lattice crystal could provide more space for Li intercalation and deintercalation. The presence of Cu^{2+} could prevent the lattice from shrinking during the deintercalation process because of the large volume of the Cu-doped crystals [20, 21].

3.2 Surface morphology

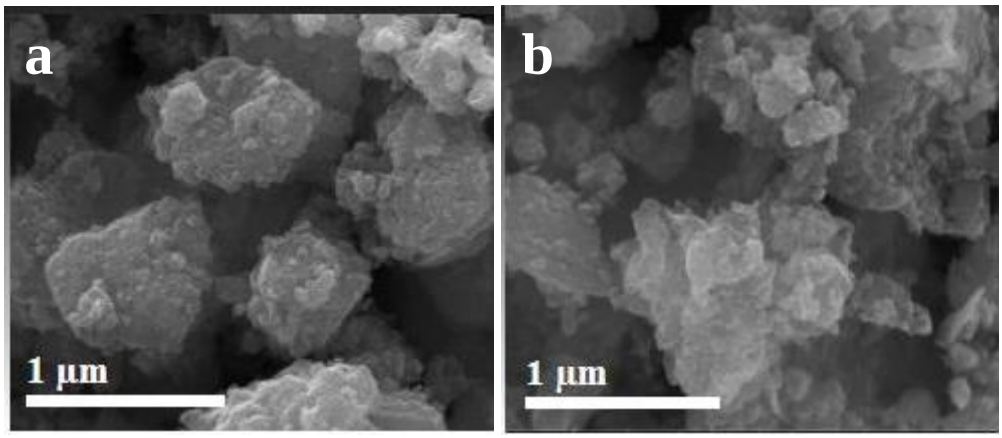

Figure 2. SEM images of $LiCu_xMn_{2-x}O_4$ (a: x = 0, b: x = 0.05).

Fig. 2(a and b) represents the typical SEM images of pristine $LiMn_2O_4$ and Cu substituted $LiCu_{0.05}Mn_{1.95}O_4$ and the size distribution ranges are from 40 to 400nm. Comparing these two micrographs of the samples, obvious difference of the particle morphology could be observed. As shown in Fig. 2, $LiMn_2O_4$ product agglomerated seriously while the agglomeration of the sample decreased and the particle sizes decreased with Cu doped. The results indicate that the Cu doping can restrain the agglomeration. On the other hand, the smaller particle sizes of materials may increase the

electrode-electrolyte contact area and reduce lithium-ion-diffusion distances, and then improve the electrochemical performance of cathode materials [1].

3.3 Galvanostatic charge-discharge studies

The discharge capacities and capacity retention of the $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_4$ cathode materials were measured; the results are shown in Fig. 3(a) and Table 2. $LiMn_2O_4$ exhibited an initial capacity of 115.1 mAh g^{-1} and capacity retention of 49.3% after 500 cycles. In contrast, $LiCu_{0.05}Mn_{1.95}O_4$ exhibited an initial capacity of 110.9 mAh g^{-1} and capacity retention after 500 cycles of 77.1%. Fig. 2(b) shows the C-rate capabilities of the $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_4$ cathode materials.

For both compounds, the discharge capacity decreased with increasing C-rate, which is caused by the low diffusion rate of the Li ions in the $LiMn_2O_4$ particles. At 5 C, $LiCu_{0.05}Mn_{1.95}O_4$ retained a discharge capacity of 80 mAh g^{-1}, while $LiMn_2O_4$ hardly discharges. These results indicate that doping $LiMn_2O_4$ with Cu has a remarkable effect on its cyclic behavior. This is because Cu doping can limit the Jahn-Teller effect as well as increasing structural stability as Cu-O bonds are stronger than Mn-O bonds [13].

Table 2. Discharge capacities and capacity retention of $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_4$ cathode materials

Cathode material	Initial discharge capacity (mAh g^{-1})	Discharge capacity after 500 cycles (mAh g^{-1})	Capacity retention (%)
$LiMn_2O_4$	115.1	56.7	49.3
$LiCu_{0.05}Mn_{1.95}O_4$	110.9	85.5	77.1

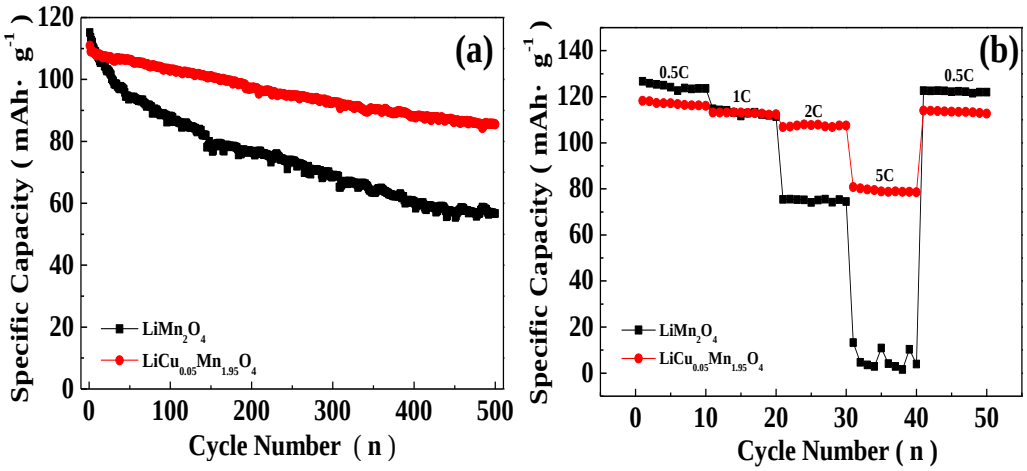

Figure 3. (a) Cycle performance at a current of 1 C and (b) discharge capacity *vs.* cycle number at various current rates from 0.5 C to 5 C (1 C = 148 mA g^{-1}) for $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_4$.

3.4 Cyclic voltammetric studies and Electrochemical impedance spectroscopy (EIS)

Typical CVs of $LiMn_2O_4$ and Cu-substituted $LiCu_{0.05}Mn_{1.95}O_4$ electrodes in the potential range of 3.6-4.5 V at a scan rate of 0.05 mV s^{-1} are depicted in Fig. 4(a) and (b), respectively. The electrochemical behavior of Li/$LiMn_2O_4$ and Li/$LiCu_{0.05}Mn_{1.95}O_4$ cells was tested before the cells were used for galvanostatic charge-discharge studies at various current rates in the range of 0.5-5 C. CVs of both cells were also measured after the completion of 50 cycles at various current rates in the range of 0.5-5 C. For $LiMn_2O_4$, in the first cycle, the two redox peaks are well separated and narrow. However, after 50 cycles, both anodic and cathodic peaks are broader and closer to each other with weaker peak intensity compared with in the first cycle, which is ascribed to possible Jahn-Teller distortion. In contrast, $LiCu_{0.05}Mn_{1.95}O_4$ after 50 charge-discharge cycles at different rates showed peaks similar to the initial ones, indicating less polarization and better reversibility. Based on these results, doping $LiMn_2O_4$ with Cu could markedly improve its reversibility and electrochemical performance [20].

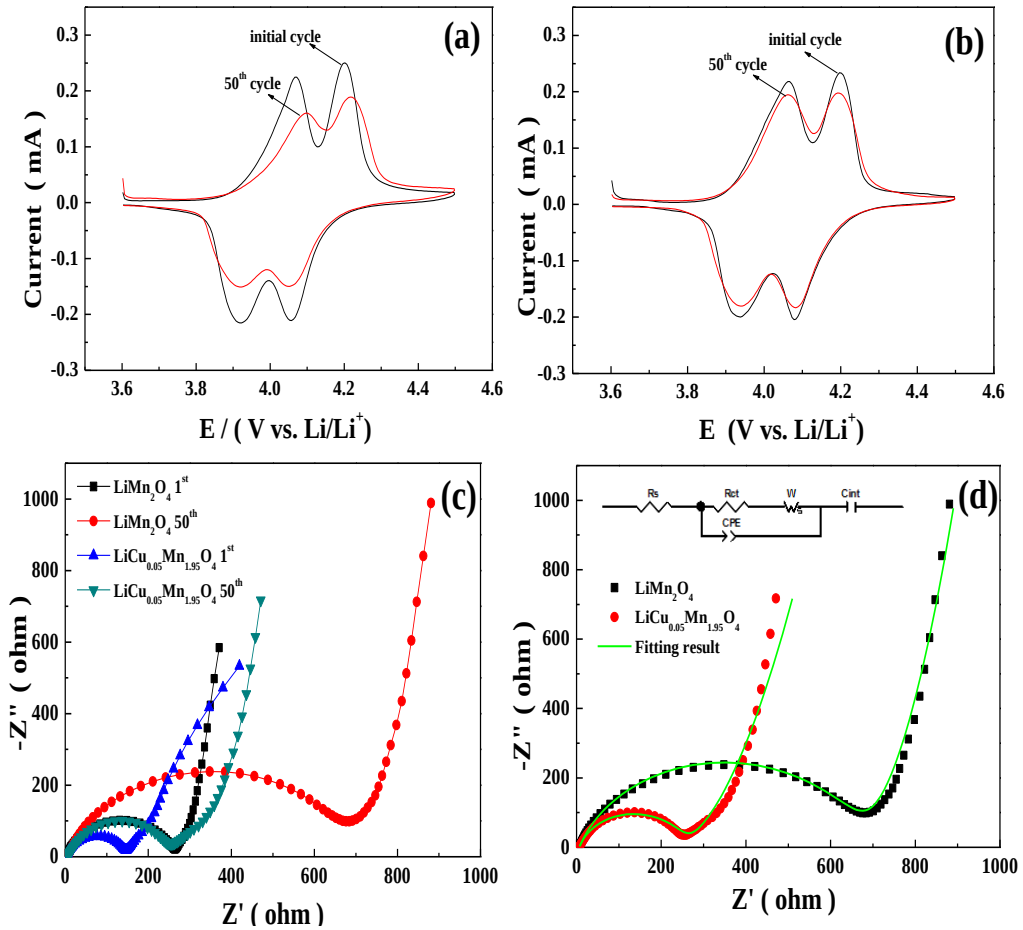

Figure 4. Typical CV curves of initial and 50th cycles for (a) $LiMn_2O_4$ and (b) $LiCu_{0.05}Mn_{1.95}O_4$. (c) Nyquist plots of initial and 50th cycles for $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_4$. (d) Nyquist plots of 50th cycles for $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_4$. Inset is the equivalent circuit used to fit the EIS data.

EIS of the $LiMn_2O_4$ and Cu-doped $LiCu_{0.05}Mn_{1.95}O_4$ cathode materials was performed to help rationalize their cycle life and rate capability characteristics. Nyquist plots of $LiMn_2O_4$ and $LiCu_{0.05}Mn_{1.95}O_4$ after 50 charge-discharge cycles at different rates are shown in Fig. 4(c). The charge transfer resistance (R_{ct}) of $LiMn_2O_4$ increased considerably after 50 charge-discharge cycles at different rates, whereas that of $LiCu_{0.05}Mn_{1.95}O_4$ increased only slightly. This means charge transfer occurs more easily in $LiCu_{0.05}Mn_{1.95}O_4$ than in $LiMn_2O_4$, which is consistent with the high rate capability and good cyclability of $LiCu_{0.05}Mn_{1.95}O_4$ illustrated above.

Table 3. Fitting values of electrochemical parameters obtained from EIS data

	Cathode material	
Parameter	$LiMn_2O_4$	$LiCu_{0.05}Mn_{1.95}O_4$
R_s (Ω)	6.073	7.156
R_{ct} (Ω)	653.2	247

The EIS data were analyzed using the equivalent circuit given in the inset of Fig. 4(d) and the respective parameters are shown in Table 3. $LiCu_{0.05}Mn_{1.95}O_4$ exhibited an R_{ct} of 247 Ω, which is lower than that of $LiMn_2O_4$ (653.2 Ω). This indicates that Cu doping could effectively enhance the ability of Li ions to diffuse in the spinel during the charge-discharge process.

This result suggests that Cu-doped $LiCu_{0.05}Mn_{1.95}O_4$ should show high rate capability, as observed in Fig. 3.

4. CONCLUSIONS

Single-phase $LiCu_{0.05}Mn_{1.95}O_4$ spinel was synthesized using a solution combustion method. $LiCu_{0.05}Mn_{1.95}O_4$ produced by this method exhibited a capacity retention of 77.1% at a discharge rate of 1 C (1C=148 mA g^{-1}) after 500 cycles, showing excellent cycling stability. $LiCu_{0.05}Mn_{1.95}O_4$ showed good reversibility and a high peak current in electrochemical studies, which are favorable for electrodes in LIBs. EIS analysis suggested $LiCu_{0.05}Mn_{1.95}O_4$ had improved cycling performance with smaller charge transfer resistance compared with those of $LiMn_2O_4$, resulting in high rate capability.

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