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Publication Date

2017-05-01

DOI

10.1016/j.jelechem.2017.03.031

Peer reviewed

**Effects of the particle properties on electrochemical performance of nanocrystalline
LiAl_{0.1}Cu_{0.1}Mn_{1.8}O₄ cathode materials prepared by ultrasonic spray pyrolysis method**

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Abstract

Nanocrystalline $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles were prepared by the ultrasonic spray pyrolysis using nitrate salts at 800°C in air atmosphere. The effects of ultrasonic frequency (120 kHz and 2.4 MHz) of the atomizer on the particle properties were investigated by X-ray diffraction, scanning and transmission electron microscopy, and energy dispersive spectroscopy. In addition, cyclic voltammetry and galvanostatic tests were performed to study the influence of the particle structure on the electrochemical behavior in Li-ion battery half-cell. Particle characterization studies reveal that the $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles had a nanocrystalline spinel structure. The secondary particles have a spherical morphology and the average particle size of the samples decreases with increase in frequency from $3.5\ \mu\text{m}$ to $770\ \text{nm}$ ($0.77\ \mu\text{m}$). Both samples had porous and partly hollow structures. The initial discharge capacities of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles produced using 120 kHz and 2.4 MHz atomizers are 82 and $75\ \text{mAhg}^{-1}$, respectively, between 3.0 and 4.8V at $0.1\ \text{C}$ rate. Discharge capacities at the 4V potential region dropped to 85% of the initial values for both samples after 110 cycles. Although the micron-sized $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles exhibit higher capacity at $0.1\ \text{C}$ than the finer particles, the cathode prepared from the submicron particles had a better rate capability with a retention of the discharge capacity that is 3 times higher at $4\ \text{C}$ rate.

Keywords: nanostructure, spinel, cathode materials, Li-ion batteries, ultrasonic spray pyrolysis

1. Introduction

Li-ion batteries (LIBs) are the devices of choice for applications that require high energy density, efficiency and environmental friendliness. For example, these batteries are widely used in daily life in electronic devices cell phones and laptop computers. Uncertainty in fossil fuel sources and environmental concerns has intensified interest in the application of LIBs in electrical vehicles (EV) [1-3]. Variants of the spinel LiMn_2O_4 are a promising candidates as cathode in LIBs due to their high safety and low toxicity, as well as the high abundance and low cost of manganese (Mn) compared to the cobalt (Co) in layered LiCoO_2 . However, spinel LiMn_2O_4 usually shows inferior cycleability due to manganese dissolution and changes in the crystal lattice and fracture of the structure due to a cooperative Jahn-Teller distortion [4-6].

Two approaches to enhance the structural stability of LiMn_2O_4 cathodes during the charge/discharge process are partial substitution of Mn in the spinel structure or coating of the cathode particle surfaces [7-10]. Several studies showed that partial aluminum (Al) substitution for Mn in the spinel LiMn_2O_4 structure improves the cycling performance, although there is a slight capacity reduction due to the decreased amount of electroactive Mn^{3+} [11-15]. In the case of copper (Cu) substitution for Mn, Murali et al. [16] reported an increase in the average discharge potential compared to unsubstituted LiMn_2O_4 spinels. Additionally, an appropriate amount of Cu substitution also improved the structural stability and reduced the capacity fading upon cycling [17,18]. Recently, bi-substitution of the spinel structure has been proposed to obtain better electrochemical properties by the combined influence of two metal cations. Prabu *et al.* [19] prepared Li and Al bi-substituted $\text{Li}(\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8})\text{O}_4$ cathodes and emphasized that the structural integrity of this sample was improved by the Al substitution on the 16d octahedral manganese sites. Fey et al. [20] investigated the effect of Al and chromium (Cr) bi- substitution on the electrochemical properties of LiMn_2O_4 spinel cathodes. According to their results, Al

enhanced the high voltage capability in $\text{LiAl}_y\text{Cr}_{0.5-y}\text{Mn}_{1.5}\text{O}_4$ cathodes. On the other hand, it reduced the capacity, and had negative effects on capacity retention. Cu substitution improves the rate capability in bi-substituted spinel structures due to its higher electronic conductivity [21]. On the other hand, Cu^{2+} ions have low stability in Cu and iron (Fe) bi-substituted spinel structure, and can occupy Li^+ positions (8a tetrahedral sites) and vacant 16c octahedral sites that limit the diffusion of Li^+ ions. Thus, Li^+ ions show quasi-reversible behavior in the spinel structure [22]. Previous studies show that Al and Cu substitution should be tuned carefully to improve the electrochemical performance of the spinel cathode and minimize the penalty in capacity.

Another important issue is the impact of particle properties such as particle size, morphology and crystallinity, on the electrochemical performance. [23,24]. Matsuda and Taniguchi [25] demonstrated that the smaller specific areas and larger crystallite sizes lead to better cycle performance for sub-micron size LiMn_2O_4 cathodes. These properties strongly depend on the production process. Ultrasonic spray pyrolysis (USP) is a versatile, single-step particle preparation technique that allows good control of morphology, size, crystallinity and chemical composition. The particle properties can be adjusted by changing the frequency of atomizer, concentration of precursor, reaction temperature, gas flow rate, and residence time in the reaction zone [25-30].

In this study, bi-substituted spinel $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode particles were produced by a USP method using two different atomizer frequencies to obtain particles of different sizes. The effects of the particle properties on electrochemical performance were then investigated by voltammetric and galvanostatic electrochemical characterization methods.

2. Experimental

Nanocrystalline spinel $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles were produced by the ultrasonic spray pyrolysis method. The precursor solution was prepared by dissolving a stoichiometric amount of LiNO_3 , $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in distilled water. The ion concentrations of the precursor solution was 0.5M Li^+ , 0.05 M Al^{3+} , 0.05 M Cu^{2+} , and 0.9M Mn^{2+} . Enough 0.025M citric acid, used as a complexing agent, was added to adjust the pH of the precursor solution. Precursor solutions were atomized using either an ultrasonic nebulizers with a resonant frequency of 120 kHz (Sonaer) or 2.4 MHz (Sonaer-241PG). The aerosol stream was introduced into a horizontal quartz tube set inside a tube furnace at 800°C with a temperature control of $\pm 1^\circ\text{C}$ by air flow. The flow rate of the air used as a carrier gas was fixed at 2.5 l/min. The heated length and diameter of the quartz tube are 600 and 76 mm, respectively. The particles obtained by the decomposition of the metal nitrate aerosol droplets were collected in washing bottles connected to the outlet of the quartz reactor.

X-ray powder diffraction patterns were obtained on the samples with a Phillips X'Pert diffractometer equipped with an X'Celerator detector, using Cu $K\alpha$ radiation (1.541874 Å), covering an angular range from 10° to 90° with a step size of 0.0167. The morphologies and compositions of the spray-pyrolyzed materials were examined with a JEOL JSM 7500F field emission scanning electron microscope, equipped with an energy dispersive x-ray detector (EDS, Noran system S1X, Thermo Electron Corp., Model 6714A01SUS-SN).

Electrochemical analyses were performed using cyclic voltammetry and charge-discharge tests on 2032 type coin cells. The cells were composed of a lithium metal negative electrode isolated from the positive electrode by a polypropylene separator. 1 M LiPF_6 in ethylene carbonate:diethylene carbonate (EC:DEC, Novolyte) was used as the electrolyte. The positive electrodes contained 80% $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$, 10% acetylene black, and the rest polyvinylidene

difluoride (PVDF) binder. These materials which included 20 mg active cathode material, were dispersed in 1-methyl-2-pyrrolidione (NMP) and acetone, and the resultant slurry was spread onto aluminum foil using the doctor blade technique. The coated aluminum foil was dried in a vacuum dryer at 120°C for 12 h and then rolled to achieve good adherence between the coated material and the aluminum foil. The coin cells were assembled inside a glove box with a high-purity argon-gas atmosphere. A BioLogic MPG-2 battery test station was used in electrochemical characterization studies. Cyclic voltammetry (CV) was performed between 3.0 and 4.8 V potentials at a scanning rate of 0.2 mV.s⁻¹ at 30°C in an environmental test chamber. The cells were cycled galvanostatically between 3.0 and 4.8 V potentials at 0.1 to 4C charge-discharge rates.

3. Results and Discussion

The XRD patterns of the prepared particles are shown in Figure 1. All of the diffraction peaks of for both samples could be indexed to a cubic spinel structure of LiMn₂O₄ (Fd-3m space group), consistent with JCPDS Card No: 01-088-1026. In this spinel structure, 32 oxide ions form a face centered cubic lattice, where lithium and manganese ions occupy 8a tetrahedral sites and 16d octahedral sites, respectively [31]. Crystallite sizes of the particles were determined by the Scherrer equation using the (111), (311) and (400) peaks in the XRD patterns. Instrumental broadening was taken into account to obtain accurate crystallite size in the calculation.

Furthermore, lattice parameters of the samples were obtained by the least squares method. The crystallite sizes of the cathode particles were determined to be around 40 and 55 nm for the samples produced using the 120 kHz and 2.4 MHz atomizers, respectively. Besides, †The lattice parameters for both LiAl_{0.1}Cu_{0.1}Mn_{1.8}O₄ samples were 8.23 Å for both, which is preferred a number close to that which is correlated to for spinel LiMn₂O₄ materials having relatively good

cycle life [32] [for spinel \$\text{LiMn}_2\text{O}_4\$ materials](#). Although Mn cations ($\text{Mn}^{3+} = 72$ pm, $\text{Mn}^{4+} = 67$ pm, 6-coordinate, octahedral) were substituted with cations of different sizes, ($\text{Cu}^{2+} = 87$ pm $\text{Al}^{3+} = 67.5$ pm), the lattice parameter was not affected by the substitution of Cu and Al with Mn. The XRD patterns were also used to estimate the occupancies of ions on the lattice sites. The (220) peaks are observed for both samples, (although they are weak) suggesting that there are some transition metals ions such as Cu^{2+} in the tetrahedral 8a lithium lattice sites. The integrated intensity ratios of the (400)/(311) and (220)/(311) peaks are indices of the extent of occupancy of the substituent ions in the tetrahedral 8a lithium sites [20] and are given in Table for both $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles. [A rise](#)The appearance of the (220) peak and the corresponding increase in the (220)/(311) intensity ratio indicates [increasing-increased](#) occupancy of the substituent cations in the tetrahedral 8a lithium lattice sites. In this case, the particles produced using 2.4 MHz atomizer had [a](#) slight cationic disorder. Lithium copper oxide structures (Li_2CuO_2 , $\text{Li}_3\text{Cu}_2\text{O}_4$, LiCuO_2) have [one-one](#)-dimensional CuO_4 chains, where copper is in the center of oxygen rectangle [33]. It is more likely that some Cu^{2+} occupies the tetrahedral 8a lithium lattice sites rather than the Al^{3+} cation which is more similar in [size](#) to Mn^{3+} and Mn^{4+} than Cu^{2+} . Thus, Al can occupy the octahedral sites easier than Cu which can lead to a more effective substitution with Mn cations when compared to Cu.

Table 1. Integrated peak intensity ratios of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles produced using 120 kHz and 2.4 MHz atomizers.

Atomizer	I(400)/I(311)	I(220)/I(311)
120 kHz	0.68	0.06
2.4 MHz	0.84	0.14

The stoichiometries of the synthesized cathode materials were investigated using EDS analysis (Figure 2), wherein the percentages of the individual elements has been confirmed with an exception of Li. It is not possible to detect lithium by EDS because of its low atomic number. The nominal atomic ratios of Al:Cu, Mn:Al and Mn:Cu used in the precursor solutions are 1:1, 18:1 and 18:1. However, in the EDS data, the amount of Al is slightly higher than Cu in the samples ~~with while the an~~ atomic ratio of Al:Cu is around 1.3:1 for both samples. ~~The amount of Mn is slightly less than the desired-targetted value for both samples, with an atomic ratio of Mn:Al and Mn:Cu are of~~ around 13:1 and 17:1 respectively.

SEM images of nanocrystalline spinel $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles prepared by the USP method are shown in Fig. 3. Figures 3.a,b, and c are of increasing magnification of particles from the 120 kHz USP method, and figures 3.d, e, and f are of increasing magnification of particles from 2.4 MHz. Both samples possess nearly spherical morphologies although the ones prepared at the lower ultrasonic are less perfect ~~in~~ shape and more appeared to have burst apart. Particles from both types of samples display some cracks and pores on their surfaces, and broken parts can be clearly observed. Fig. 3 clearly shows the effect of nozzle frequency on the obtained particle sizes, which decreased by increasing ultrasonic frequency as expected considering the aerosol droplet and particle formation mechanisms. Aerosol droplet size is directly related to frequency of the atomizer (f), density of the solution (ρ), and surface tension of the solution (γ) [27]. The mean diameter of the aerosol droplets can be estimated by equation 1.

$$D = 0.34 (8 \cdot \pi \cdot \gamma / \rho \cdot f^2)^{1/3} \quad (\text{Eq. 1})$$

The calculated droplet sizes for distilled water are 17.1 and 2.3 μm for frequencies of 120 kHz and 2.4 MHz, respectively. The average particles size can be estimated using the aerosol droplet

size and assuming full densification of the reacted material. Higher atomizer frequencies produces finer particles due to the decreasing aerosol droplet size assuming all other conditions are equal. The particle sizes for sample produced using the 120 kHz atomizer range from 10 and 0.7 μm , with an average particle size of around 3.5 μm . The particle sizes for sample produced using the 2.4 MHz atomizer vary between 2500 nm (2.5 μm) and 140 nm (0.14 μm), and the average particle size is around 770 nm (0.77 μm). Magnified SEM images indicate that the particles are aggregates of nanosized primary particles, consistent with our previous studies [18,22].

According to STEM images (Fig. 4), the particles have interior pores and partially hollow structures. This indicates that the decomposition and nucleation on the aerosol surface is the active mechanism for the particle formation. When the aerosol droplet was introduced into the hot zone, the metal nitrates decomposed to form oxides and simultaneously nucleated on the surface. Rapid oxide formation on the surface partly insulates the interior of aerosol droplet resulting in pores and partly hollow structure under these experimental conditions.

The initial charge and discharge curves of Li half-cells containing the $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ based cathodes of the two materials between 3.0 and 4.8 V at 0.1 and 0.5 C rates are shown in Figure 5. The first charge and discharge capacities of the sample prepared using the 120 kHz atomizer are 93 and 82 $\text{mAh}\cdot\text{g}^{-1}$, respectively, at 0.1 C rate, and 74 and 72 $\text{mAh}\cdot\text{g}^{-1}$, respectively, at 0.5 C rate. Particles produced by the 2.4 MHz atomizer exhibits 84 and 75 $\text{mAh}\cdot\text{g}^{-1}$ initial charge and discharge capacities, respectively, at 0.1 C rate, and 69 and 65 initial charge and discharge capacities, respectively, at 0.5 C rate. The initial capacity of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ based cathodes slightly decreased ~~when the particle size was decreased to submicron range for the smaller particles, and as slight cationic disorder caused by occupation of the substitution ions on the 8a tetrahedral sites.~~ The theoretical capacity of the spinel $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ is nearly 105

mAhg⁻¹ which is much lower than that of the pure spinel LiMn₂O₄ ~~of, which is~~ 148 mAh.g⁻¹. This is ~~because due to the~~ substitution of active Mn with -Al³⁺ and Cu²⁺ cations, which are electrochemically inactive ~~Al³⁺ and Cu²⁺ cations atin the~~ 3.0 - 4.8 V potential region ~~reduces the amount of electrochemically active Mn³⁺ cations~~. The difference between the practical and theoretical capacities may be due to the low crystallinity and structural defects such as occupation of metal ions on 8a tetrahedral sites and ~~maybe on possibly -Li⁺ diffusion pathway~~ (16c octahedral positions), which can block lithium diffusion.

Figure 6 shows the cycle performance of cells containing the LiAl_{0.1}Cu_{0.1}Mn_{1.8}O₄ based cathodes. The first 5 cycles were performed at 0.1C rate between 3.0 and 4.8 V, followed by 100 cycles at 0.5 C rate, and finalized with 5 more cycles at 0.1 C rate in order to compare the final capacity with the initial capacity. After the cycle performance test, discharge capacities measured at 0.1 C rate became decreased to 70 and 64 mAhg⁻¹ for particles produced using 120 kHz and 2.3 MHz atomizers, respectively, which correspond to a 15% capacity fade for both samples. The cycle performance of Cu and Al substituted spinel structure is better than that of pristine LiMn₂O₄ (with 720 nm particle and 30 nm crystallite size), also produced by the USP method ~~in as~~ presented in a previous study, however [34]. ~~Substitution~~ This indicates that substitution of Cu and Al in proper amounts can improve the cycle performance of pristine spinel LiMn₂O₄ cathodes.

Cycling Cyclic voltammetry (CV) results on cells with LiAl_{0.1}Cu_{0.1}Mn_{1.8}O₄ electrodes before and after the cycle performance test, carried out in the potential range between 3.0 and 4.8V, at a sweep rate of 0.2mVs⁻¹ are given in Figure 7. The first CV curves depict two reversible charge peaks at 4.1 and 4.3 V, and discharge peaks at 4.1 and 3.9 V originating from the Mn^{3.5+} to Mn^{3.75+} and Mn^{3.75+} to Mn⁴⁺ reversible transitions. It is assumed that the 3.9 V peak is due to the intercalation and deintercalation of Li⁺ into spinel Li_xAl_{0.1}Cu_{0.1}Mn_{1.8}O₄ over a composition range

of $0.5 < x < 1$. Similar to pristine spinel LiMn_2O_4 , two phases, cubic $\lambda\text{-MnO}_2$ and cubic $\text{Li}_{0.5-x}\text{Al}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ ($0 < x < 0.5$) coexist in the 4.1 V region [31,34]. *Yang et al.* [35] reported that Cu^{2+} cations can be oxidized to Cu^{3+} in the spinel $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and the with a calculated voltage of the $\text{Cu}^{2+}/\text{Cu}^{3+}$ redox couple is of 4.44 V vs Li^+/Li . Cu substitution into the spinel shifts the voltage plateau to higher values and a new discharge voltage plateau around 4.9 V appeared appears at high level of Cu substituted in cells containing the highly substituted spinel, $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [16,35]. However, there is no obvious high-voltage plateau peak sign was not observed on in the CV results and low level of Cu and Al the bi-substituted spinel preserved the potential plateau seen in galvanostatic discharges of cells containing of the pristine LiMn_2O_4 spinel.

Figure 8 exhibits the discharge rate capability of cells containing $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathodes particles during cycling between 3.0 and 4.8 V at increasing C rates from 0.1 C to 4 C. The mean capacities of the cathodes at different C-rates are given in Table 2. The cell containing the cathode material made using the 2.4 MHz frequency nozzle showed somewhat lower discharge capacity at 0.1C rate compared to the one with the material made at 120 kHz, but outperformed it at higher rates. The performance was particularly impressive at the 4C rate, with nearly 56% of the low rate capacity retained. This is probably due to the finer particle size, which shortens the Li^+ diffusion pathway in the structure resulting in a better rate capability at high C-rates.

Table 2. Mean discharge capacities of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ electrodes at increasing C-rates.

$\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ Atomizer Type	Mean capacities (mAhg ⁻¹) at					
	0.1 C	0.2 C	0.5 C	1 C	2 C	4 C
120 kHz	80	72	64	55	42	16

2.4 MHz	75	70	64	60	52	42
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4. Conclusion

Nanocrystalline $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles were successfully produced in two different particle size range by ultrasonic spray pyrolysis using 120kHz and 2.4MHz frequency atomizers. Particle characterization studies showed that particle size directly depends on the atomizer frequency used during the synthesis by USP method. The crystallite size, composition of the particles and particle morphologies were largely unaffected by the change in atomizer frequency. The cathode material with submicron-sized (0.77 μm) particles had a lower discharge capacity at 0.1 C rate in a half-cell configuration comparing to the one with larger average particle size (3.5 μm) particles. However, the submicron particles exhibited better rate capability, as higher capacity retention was observed at increasing C-rates. The discharge capacity of the cell containing the submicron $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles was 3 times greater than that with the micron size particles at 4 C rate, retaining over 50% of the capacity delivered at 0.1C. The capacity fading exhibited after more than 100 cycles was equal to nearly 15% of initial capacity for both samples. The results indicate that judicious partial Al and Cu substitution for Mn can improve the cycle performance of the spinel LiMn_2O_4 and that changing the particle size affects the rate capability of the substituted cathode materials.

Acknowledgements

We would like to thank Istanbul Technical University Research Fund (ITU-BAP) for a fellowships for Burçak Ebin to perform his research at Lawrence Berkeley National Laboratory,

Berkeley, CA, USA. This work was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

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