Effects of the particle properties on electrochemical performance of nanocrystalline $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode materials prepared by ultrasonic spray pyrolysis

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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 have 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 μm to 770 nm. Both samples have porous and partly hollow structure. 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 $\text{mAh} \cdot \text{g}^{-1}$, respectively, between 3.0 and 4.8 V at 0.1C rate. Discharge capacities at the 4 V potential region drop 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 0.1C than the finer particles, the cathode prepared from the submicron particles has a better rate capability with a retention of the discharge capacity that is 3 times higher at 4C rate.

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1. Introduction

Li-ion batteries (LIBs) are the most attractive energy storage devices for electronic 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 cyclability 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 have been studied widely to enhance the structural stability of LiMn_2O_4 cathodes during the charge/discharge process.

These are partial substitution of Mn in the spinel structure and 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 with Mn into LiMn_2O_4 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

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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 clearly present that both Al and Cu mono-substitutions have a positive effects on the working potential, and also the cycling performance of LiMn_2O_4 cathodes. However, the studies on Al and Cu bi-substitution with Mn in LiMn_2O_4 structure are limited. The literature shows that their amounts 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. Al and Cu bi-substitution joint effects on the electrochemical properties of LiMn_2O_4 were investigated and the results were compared with spinel LiMn_2O_4 in the literature. In addition to that, the effects of the particle properties on electrochemical performance were also studied 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 were 0.5 M Li^+ , 0.05 M Al^{3+} , 0.05 M Cu^{2+} , and 0.9 M Mn^{2+} . Enough 0.025 M 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 ± 1 °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. The residence time of the droplets was calculated as 65 s by assuming that the rate of droplets and the carried gas are equal. However, the real residence time can be obtained when the correction for gas flow rate due to temperature causes gas expansion. The real residence times, taking into account the gas expansion at 800 °C, was approximately 18 s.

X-ray powder diffraction patterns were obtained on the samples with a Phillips X'Pert diffractometer equipped with an X'Celerator detector, using $\text{CuK}\alpha$ 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 $0.2 \text{ mV} \cdot \text{s}^{-1}$ 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. The current density was around $0.38 \text{ mA} \cdot \text{cm}^{-2}$ for 1C.

3. Results and discussion

The XRD patterns of the prepared particles are shown in Fig. 1. All of the diffraction peaks for both samples could be indexed to a cubic spinel structure of LiMn_2O_4 (Fd-3 m 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. The lattice parameters for both $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ samples were 8.23 Å for both, a number close to that is correlated having relatively good cycle life for spinel LiMn_2O_4 materials [32]. Although Mn cations ($\text{Mn}^{3+} = 72 \text{ pm}$, $\text{Mn}^{4+} = 67 \text{ pm}$, 6-coordinate, octahedral) were substituted with cations of different sizes, ($\text{Cu}^{2+} = 87 \text{ pm}$ $\text{Al}^{3+} = 67.5 \text{ pm}$), the lattice parameter was not significantly affected by the cationic substitution.

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 1 for both $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles. The appearance of the (220) peak and the corresponding increment at the (220)/(311) intensity ratio indicates 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-dimensional CuO_4 chains, where copper is in the center of oxygen rectangle [33]. It is more likely that some Cu^{2+} cations occupy 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 compared to Cu^{2+} cation.

The stoichiometry of the synthesized cathode materials were investigated using EDS analysis (Fig. 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 while the atomic ratio of Al:Cu is around 1.3:1 for both samples. The amount of Mn is

Fig. 1. XRD patterns of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode materials.

slightly less than the targeted value for both samples, with an atomic ratio of Mn:Al and Mn:Cu 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. Fig. 3a, b, and c is of increasing magnification of particles from the 120 kHz USP method, and Fig. 3d, e, and f is 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 Eq. 1.

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

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 produce 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 to 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). Although the majority of the samples have smooth surface, some bigger particles exhibit rough surface. Magnified SEM images indicate that the particles are the aggregates of nanosized primary particles, consistent with our previous studies [18,22]. The general steps of the

particle formation mechanism for USP process are (i) evaporation of the solvent and precipitation when the droplets introduce the hot-zone, (ii) nucleation and formation of primary particles, and (iii) sintering to secondary particles with increased density and smooth surface. The effective sintering of the primary particles is a necessity to form secondary particles with a smooth surface. Sintering in USP method is an interactive step that is directly related with complex relation between gas flow rate, residence time, reaction temperature and precipitation.

During the precipitation step, volume precipitation occurs, if the solute concentration at the center of the droplet is higher than or equal to the equilibrium saturation of the solute at the droplet temperature. On the other hand, if the concentration of the solute at the center is lower than the equilibrium saturation of the solute, the surface precipitation is active mechanism at the droplet. When the surface precipitation occurs, particles have thinner walls and open cavities in their centers [34,35]. The thinner surface parts can fall into the center. The cracked and rough surfaces were formed due to this phenomenon.

Fig. 2. EDS analysis of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode particles produced using (a) 120 kHz and (b) 2.4 MHz ultrasonic atomizers.

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

Fig. 3. SEM images of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode particles produced using a 120 kHz ultrasonic atomizer (a) $\times 1\text{K}$, (b) $\times 5\text{K}$ and (c) $\times 15\text{K}$ and using a 2.4 MHz ultrasonic atomizer (d) $\times 5\text{K}$, (e) $\times 10\text{K}$ and (f) $\times 50\text{K}$.

Fig. 4. Dark field STEM images of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode particles produced using a 120 kHz ultrasonic atomizer (a) $\times 5\text{K}$ and (b) $\times 10\text{K}$, and using a 2.4 MHz ultrasonic atomizer (c) $\times 20\text{K}$, (d) $\times 30\text{K}$.

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. Also removing of gas products originated from the decomposition of the citric acid can be a minor reason for the formation of porous and hollow structure.

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 cathode samples at the potential range between 3.0 and 4.8 V at 0.1 and 0.5C rates are shown in Fig. 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 0.1C rate, and 74 and $72 \text{ mAh} \cdot \text{g}^{-1}$, respectively, at 0.5C rate. Cathode particles produced by the 2.4 MHz atomizer exhibit 84 and $75 \text{ mAh} \cdot \text{g}^{-1}$ initial charge and discharge capacities, respectively, at 0.1C rate, and 69 and $65 \text{ mAh} \cdot \text{g}^{-1}$ initial charge and discharge capacities, respectively, at 0.5C rate. The initial capacity of $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ based cathodes slightly decreased for the smaller particles. The theoretical capacity of the spinel $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ is nearly $105 \text{ mAh} \cdot \text{g}^{-1}$ which is much lower than that of the pure spinel LiMn_2O_4 , which is $148 \text{ mAh} \cdot \text{g}^{-1}$. This is due to the substitution of active Mn with Al^{3+} and Cu^{2+} , which are electrochemically inactive in the 3.0–4.8 V potential region. The average oxidation state of the manganese in pristine spinel LiMn_2O_4 is +3.5. When electrode is charged, the oxidation state becomes +4. During the discharge, it is expected that manganese returns initial oxidation state. The oxidation state of manganese in $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ particles was

calculated as +3.61. The increasing average oxidation state of manganese leads to reduce in the capacity compared to pristine spinel LiMn_2O_4 . Moreover, the samples contain relatively lower Mn depending on Al and Cu amounts, which can also cause lower capacity. The crystallinity is another crucial factor effecting the capacity of the spinel particles [36,37]. The low crystallinity and structural defects such as occupation of metal ions on 8a tetrahedral sites and possibly 16c octahedral positions, which can block lithium diffusion, can result in the difference between the practical and theoretical capacities of the substituted sample.

Fig. 6 shows the cycle performance of cells containing the $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ based cathodes. The first 5 cycles were performed at 0.1C rate between 3.0 and 4.8 V, followed by 100 cycles at 0.5C rate, and finalized with 5 more cycles at 0.1C rate in order to compare the final capacity with the initial capacity. After the cycle performance test, discharge capacities measured at 0.1C rate decreased to 70 and $64 \text{ mAh} \cdot \text{g}^{-1}$ for particles produced using 120 kHz and 2.4 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 LiMn_2O_4 (with 720 nm particle and 30 nm crystallite size), also produced by the USP method as presented in a previous study [38]. In a similar study [39], Li and Cu co-doped spinel particles ($\text{Li}(\text{Li}_{0.05}\text{Cu}_{0.05}\text{Mn}_{1.90})\text{O}_4$) presents more stable structure than LiMn_2O_4 during charge-discharge process, as we observed for Al and Cu bi-substitution. The results indicate that substitution of Cu and Al in proper amounts can improve the cycle performance of pristine spinel LiMn_2O_4 cathodes.

Cyclic voltammetry (CV) results on cells with $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ electrodes before and after the cycle performance test, carried out in the potential range between 3.0 and 4.8 V at a sweep rate of $0.2 \text{ mV} \cdot \text{s}^{-1}$ are given in Fig. 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

Fig. 5. First charge-discharge capacities of cells containing $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode materials produced using (a) 120 kHz and (b) 2.4 MHz ultrasonic atomizers. Cells were cycled between 3.0 and 4.8 V, @0.1C and 0.5C.

Fig. 6. Cycling performance of cells containing $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode materials produced using (a) 120 kHz and (b) 2.4 MHz ultrasonic atomizers. Cells were cycled between 3.0 and 4.8 V, @0.1C and 0.5C.

Fig. 7. Cyclic voltammograms before and after cycling of cells containing $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode materials produced using (a) 120 kHz and (b) 2.4 MHz ultrasonic atomizers. Cells were cycled between 3.0 and 4.8 V, @ $0.2 \text{ mV} \cdot \text{s}^{-1}$.

originating from the $\text{Mn}^{3.5+}$ to $\text{Mn}^{3.75+}$ and $\text{Mn}^{3.75+}$ to Mn^{4+} reversible transitions. It is assumed that the 3.9 V peak is due to the intercalation and deintercalation of Li^+ into spinel $\text{Li}_x\text{Al}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ over a composition range of $0.5 < x < 1$. Similar to pristine spinel LiMn_2O_4 , two phases, cubic λ - 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 [31,38]. Yang et al. [21] reported that Cu^{2+} cations can be oxidized to Cu^{3+} in the spinel $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$, with a calculated voltage of the $\text{Cu}^{2+}/\text{Cu}^{3+}$ redox couple 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 appears in cells containing the highly substituted spinel, $\text{LiCu}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [16,21].

Fig. 8. Charge-discharge rate performance of cells containing $\text{LiAl}_{0.1}\text{Cu}_{0.1}\text{Mn}_{1.8}\text{O}_4$ cathode materials.

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 ($\text{mAh} \cdot \text{g}^{-1}$) at					
	0.1C	0.2C	0.5C	1C	2C	4C
120 kHz	80	72	64	55	42	16
2.4 MHz	75	70	64	60	52	42

Although there is no obvious high-voltage peak observed in the CV, cathodic and anodic peaks of the bi-substituted particle samples slightly shifted at the higher potentials (which can be also observed in the charge-discharge curves, Fig. 5) compared to galvanostatic discharges of cells containing the pristine LiMn_2O_4 cathode particles produced by USP method at 800°C [38].

Fig. 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 0.1C to 4C. 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 effect, which shortens the Li^+ diffusion pathway in the structure resulting in a better rate capability at high C-rates.

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 120 kHz and 2.4 MHz 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 (770 nm) particles had a lower discharge capacity at 0.1C rate in a half-cell configuration compared to the one with larger average particle size (3.5 μm) particles. However, the submicron particles exhibited better rate capability, and it was observed that smaller particles had higher capacity 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 4C rate, retaining over 50% of the capacity delivered at 0.1C. The capacity fade after >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 bi-substituted cathode materials.

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References

- [1] B. Scrosati, J. Garche, Lithium batteries: status, prospects and future, *J. Power Sources* 195 (2010) 2419–2430.
- [2] Y. Wang, G. Cao, Developments in nanostructured cathode materials for high-performance lithium-ion batteries, *Adv. Mater.* 20 (2008) 2251–2269.
- [3] L. Su, Y. Jing, Z. Zhou, Li ion battery materials with core-shell nanostructures, *Nano* 3 (2011) 3967–3983.
- [4] X. Li, Y. Xu, C. Wang, Suppression of Jahn-Teller distortion of spinel LiMn_2O_4 cathode, *J. Alloys Compd.* 479 (2009) 310–313.

- [5] B. Ebin, S. Gürmen, C. Arslan, G. Lindbergh, Electrochemical properties of nanocrystalline $\text{LiFe}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.2\text{--}1.0$) cathode particles prepared by ultrasonic spray pyrolysis, *Electrochim. Acta* 76 (2012) 368–374.
- [6] T.Y.S. Panca Putra, M. Yonemura, S. Torii, T. Ishigaki, T. Kamiyama, Structure and electrochemical performance of the spinel LiMn_2O_4 synthesized by mechanical alloying, *Solid State Ionics* 262 (2014) 83–87.
- [7] R. Thirunakaran, A. Sivashanmugam, S. Gopukumar, R. Rajakajshmi, Cerium and zinc: dual-doped LiMn_2O_4 spinels as cathode material for use in lithium rechargeable batteries, *J. Power Sources* 187 (2009) 565–574.
- [8] D. Arumugam, G. Paruthimal Kalaignan, Synthesis and electrochemical characterizations of nano- La_2O_3 -coated nanostructured LiMn_2O_4 cathode materials for rechargeable lithium batteries, *Mater. Res. Bull.* 45 (2010) 1825–1831.
- [9] W.-S. Yoon, K.Y. Chung, K.-W. Nam, K.-B. Kim, Characterization of LiMn_2O_4 -coated LiCoO_2 film electrode prepared by electrostatic spray deposition, *J. Power Sources* 163 (2006) 207–210.
- [10] D. Liu, Z. He, X. Liu, Increased cycling stability of AlPO_4 -coated LiMn_2O_4 for lithium ion batteries, *Mater. Lett.* 61 (2007) 4703–4706.
- [11] I. Taniguchi, D. Song, M. Wakihara, Electrochemical properties of $\text{LiM}_{1/6}\text{Mn}_{11/6}\text{O}_4$ ($M = \text{Mn, Co, Al and Ni}$) as cathode materials for Li-ion batteries prepared by ultrasonic spray pyrolysis method, *J. Power Sources* 109 (2002) 333–339.
- [12] B.J. Hwang, R. Santhanam, D.G. Liu, Y.V. Tsai, Effect of Al-substitution on the stability of LiMn_2O_4 spinel synthesized by citric acid sol-gel method, *J. Power Sources* 102 (2001) 326–331.
- [13] W. Cho, W. Ra, J. Shirakawa, M. Nakayama, M. Wakihara, Synthesis and electrochemical properties of nonstoichiometric $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_{4-6}$ as cathode materials for rechargeable lithium ion battery, *J. Solid State Chem.* 179 (2006) 3534–3540.
- [14] K.-S. Lee, H.J. Bang, S.-T. Myung, J. Prakash, K. Amine, Y.-K. Sun, Synthesis and electrochemical properties of spherical spinel $\text{Li}_{1.05}\text{M}_{0.05}\text{Mn}_{1.9}\text{O}_4$ ($M = \text{Mg and Al}$) as a cathode material for lithium-ion batteries by co-precipitation method, *J. Power Sources* 174 (2007) 726–729.
- [15] M.A. Kebede, M.J. Phasha, N. Kunjuzwa, L.J. le Roux, D. Mkhonto, K.I. Ozoemena, M.K. Mathe, Structural and electrochemical properties of aluminium doped LiMn_2O_4 cathode materials for Li battery: experimental and ab initio calculations, *Sustainable Energy Technologies and Assessments* 5 (2014) 44–49.
- [16] K.R. Murali, T. Saravaman, M. Jayachandran, Synthesis and characterization of copper substituted lithium manganate spinels, *J. Mater. Sci.:Mater. Electron.* 19 (2008) 533–537.
- [17] R. Thirunakaran, B.R. Babu, N. Kalaiselvi, P. Periasamy, T.P. Kumar, N.G. Renganathan, M. Raghavan, N. Muniyadi, Electrochemical behavior of $\text{LiM}_y\text{Mn}_{2-y}\text{O}_4$ ($M = \text{Cu, Cr; } 0 \leq y \leq 0.4$), *Bull. Mater. Sci.* 24 (2001) 51–55.
- [18] B. Ebin, S. Gürmen, G. Lindbergh, Electrochemical properties of nanocrystalline $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.2\text{--}0.6$) particles prepared by ultrasonic spray pyrolysis, *Mater. Chem. Phys.* 136 (2012) 424–430.
- [19] M. Prabu, M.V. Reddy, S. Selvasekarapandian, G.V. Subba Rao, B.V.R. Chowdari, (Li, Al)-co-doped spinel, $\text{Li}(\text{Li}_{0.1}\text{Al}_{0.1}\text{Mn}_{1.8})\text{O}_4$ as high performance cathode for lithium ion batteries, *Electrochim. Acta* 88 (2013) 745–755.
- [20] G.T.-K. Fey, C.-Z. Lu, T.P. Kumar, Solid state synthesis and electrochemical characterization of $\text{LiM}_y\text{Cr}_{0.5-y}\text{Mn}_{1.5}\text{O}_4$ ($M = \text{Fe or Al; } 0.0 < y < 0.4$) spinels, *Mater. Chem. Phys.* 80 (2003) 309–318.
- [21] M.-C. Yang, B. Xu, J.-H. Cheng, C.-J. Pan, B.-J. Hwang, Y.S. Meng, et al., *Chem. Mater.* 23 (2011) 2832–2841.
- [22] B. Ebin, S. Gürmen, G. Lindbergh, Preparation and electrochemical properties of spinel $\text{LiFe}_x\text{Cu}_y\text{Mn}_{1-z}\text{O}_4$ by ultrasonic spray pyrolysis method, *Ceram. Int.* 40 (2014) 1019–1027.
- [23] Y. Cai, Y. Huang, X. Wang, D. Jia, X. Tang, Long cycle life, high rate capability of truncated octahedral LiMn_2O_4 cathode materials synthesized by a solid-state combustion reaction for lithium ion batteries, *Ceram. Int.* 40 (2014) 14039–14043.
- [24] X. Lv, S. Chen, C. Chen, L. Liu, F. Liu, G. Qiu, One-step hydrothermal synthesis of LiMn_2O_4 cathode for rechargeable lithium batteries, *Solid State Sci.* 31 (2014) 16–23.
- [25] K. Matsuda, I. Taniguchi, Relationship between the electrochemical and particle properties of LiMn_2O_4 prepared by ultrasonic spray pyrolysis, *J. Power Sources* 132 (2004) 156–160.
- [26] B. Ebin, E. Yazici, S. Gürmen, Production of nanocrystalline silver particles by hydrogen reduction of silver nitrate aerosol droplets, *Trans. Nonferrous Metals Soc. China* 23 (2013) 841–848.
- [27] B. Ebin, O. Gencer, S. Gurmen, Simple preparation of CuO nanoparticles and submicron spheres via ultrasonic spray pyrolysis (USP), *Int. J. Mater. Res.* 104 (2) (2013) 199–206.
- [28] W.-N. Wang, A. Purwanto, I.W. Lengggoro, K. Okuyama, H. Chang, H.D. Jang, Investigation on the correlations between droplet and particle size distribution in ultrasonic spray pyrolysis, *Ind. Eng. Chem. Res.* 47 (2008) 1650–1659.
- [29] B. Ebin, E. Arig, B. Ozkal, S. Gurmen, Production and characterization of ZnO nanoparticles and porous particles by ultrasonic spray pyrolysis using a zinc nitrate precursor, *Int. J. Miner. Metall. Mater.* 19 (7) (2012) 651–656.
- [30] B. Ebin, C. Toparli, S. Gurmen, Preparation and magnetic characterization of Fe/metal oxide nanocomposite particles by means of hydrogen reduction assisted ultrasonic spray pyrolysis (USP-HR), *Int. J. Mater. Res.* 104 (5) (2013) 483–488.
- [31] M. Wakihara, H. Ikuta, Y. Uchimoto, Structural stability in partially substituted lithium manganese spinel oxide cathode, *Ionics* 8 (2002) 329.
- [32] M.S. Whittingham, Lithium batteries and cathode materials, *Chem. Rev.* 104 (2004) 4271–4301.
- [33] H. Arai, S. Okada, Y. Sakurai, J.-I. Yamaki, Electrochemical and structural study of Li_2CuO_2 , LiCuO_2 and NaCuO_2 , *Solid State Ionics* 106 (1998) 45–53.
- [34] V. Jokanović, A.M. Spasić, D. Uskoković, Designing of nanostructured hollow TiO_2 spheres obtained by ultrasonic spray pyrolysis, *J. Colloid Interface Sci.* 278 (2004) 342–352.
- [35] V. Jokanović, M.D. Dramićanin, Ž. Andrić, T. Dramićanin, M. Plavšić, S. Pašalić, M. Miljković, Nanostructure designed powders of optical active materials Me_xSiO_y obtained by ultrasonic spray pyrolysis, *Opt. Mater.* 30 (2008) 1168–1172.
- [36] X. Zhang, H. Zheng, V. Battaglia, R.L. Axelbaum, Electrochemical performance of spinel LiMn_2O_4 cathode materials made by flame-assisted spray technology, *J. Power Sources* 196 (2011) 3640–3645.
- [37] F.P. Nkosi, C.J. Jafta, M. Kebede, L. le Roux, M.K. Mathe, K.I. Ozoemena, Microwave-assisted optimization of the manganese redox states for enhanced capacity and capacity retention of $\text{LiAl}_x\text{Mn}_{2-x}\text{O}_4$ ($x = 0.0$ and 0.3) spinel materials, *RSC Adv.* 5 (2015) 32256–32262.
- [38] B. Ebin, V. Battaglia, S. Gürmen, Comparison of 4 V and 3 V electrochemical properties of nanocrystalline LiMn_2O_4 cathode particles in lithium ion batteries prepared by ultrasonic spray pyrolysis, *Ceram. Int.* 40 (5) (2014) 7029–7035.
- [39] J. Hao, H. Bai, J. Liu, F. Yang, Q. Li, C. Su, J. Guo, Synthesis and electrochemical properties of spinel $\text{Li}(\text{Li}_{0.05}\text{Cu}_{0.05}\text{Mn}_{1.90})\text{O}_4$ by a flameless combustion method, *J. Alloys Compd.* 668 (2016) 200–205.