Synthesis of Lithium Intercalation Oxides based on Manganese and Copper by the Sol-gel Method.

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Abstract

The current generation of lithium-ion batteries uses $LiCoO_2$ or $LiNiO_2$ as cathodes. In contrast to $LiCoO_2$ and $LiNiO_2$ systems, it is easy to synthesize a Mn-based cathode that contains more than one Li per formula unit. $LiCuO_2$ is also a promising electrode material for lithium batteries and it seems to be an attractive candidate as a new electrode material. $LiCoO_2$ and graphite have layered structures and $LiMn_2O_4$ has a tunnel-like framework and both structures are useful for the insertion and de-insertion of lithium guest ions into host materials with minimal physical alteration of the host structure.

Therefore, in this work attempts have been made to mix both transition metals of copper and manganese to form mixed Lithium manganese copper oxide as cathodic materials for lithium batteries, and the lithiated intercalation cathode materials (LiM_2O_4, M=Mn, Cu) were synthesized by the sol gel method. The elements, Mn and Cu were chosen because a Mn-based cathode can easily accommodate more than one lithium per formula unit while Cu has an advantage of lower cost and safety. Various ratios of Mn and Cu acetates, lithium hydroxides were used as starting materials with tartaric acid as the gelating agent. The dried samples were calcined at 800 °C. Structural changes were observed when Cu was introduced into $LiMn_2O_4$. Mixed oxides of $Li_2Mn_xCu_yO_z$ were formed.

The structure of the calcined materials was characterized by XRD, EDX and SEM. The XRD patterns for LiM_2O_4 (M=Mn, Cu) agree with the literature while those containing both Mn and Cu form mixed oxides with different stoichiometries (shown by the EDX results) depending on the starting mol ratios. SEM shows particle sizes of all these oxide materials is about the same, i.e. 6 micrometer.

Keywords: lithium intercalation compounds, sol-gel, XRD, TGA, FTIR and SEM).

1. Introduction

Lithium intercalation compounds have attracted much interest as cathode materials for lithium rechargeable batteries[1–3] due to their relatively high theoretical discharge capacity[4]. At present, $LiCoO_2$ is widely used commercially but 4V $LiMn_2O_4$ is an excellent alternative material in view of its low cost, environmental harmlessness and easy availabity of raw materials. The only drawback is when the cathode material is charged/discharged at 4 V, a progressive fade in capacity on cycling is observed[5-8] especially at elevated temperatures. The capacity fading comes primarily from the structure, i.e. the Jahn-Teller distortion and Mn dissolution at the end of the discharge, which will depend very much on the method of preparation of the materials.

Many methods for preparation of lithium intercalated materials have been carried out. The solid-state reaction between oxides[9,10] has been used extensively. This method requires heat treatment at relatively high temperatures and does not provide good control on the crystalline growth, compositional homogeneity, morphology and microstructure. As a consequence, final products consist in relatively large particles with broad particle size distribution. In addition, the spinel $LiMn_2O_4$ from solid-state reactions usually contains some phase impurities, which are detrimental to the electrochemical performance. In order to overcome or partly alleviate this serious problem, one effective solution is the use of sol-gel methods. This method has

many advantages over the solid-state reactions such as homogeneous mixing at the atomic or molecular level, good stoichiometric control, low synthesis temperature, short heating time, good crystallinity, uniform particle size and small diameter, even at the nanometer level[11,12]. To overcome the fading capacity problem in $LiMn_2O_4$, some transition metals such as Co, Ni, Cr, Fe, etc.[13,14] were introduced to partially substitute Mn in the lattice structure.

The micron sized cathode materials are known to exhibit improved electrochemical properties. Their behaviour is rather complicated and it is necessary to obtain more insight into the relationship between synthesis, microstructure and properties. In this work, lithiated intercalation materials, $LiMn_2O_4$, $LiCu_2O_2$ and $Li_2Mn_xCu_yO_z$ were synthesized and characterized. The sol gel method was used to obtain the micron sized powder materials. Cu was introduced in $LiMn_2O_4$ to partially substitute the Mn in the lattice structure so as to obtain a one-phase compound with good structural and thermal stability for the improved fading capacity. Characterization of the synthesized materials will be carried out.

2. Experimental
2.1. Synthesis

$LiMn_2O_4$, $LiCu_2O_2$ and $Li_2Mn_xCu_yO_z$ were synthesized by the sol–gel method using tartaric acid as a chelating agent. A stoichiometric amount of high purity

lithium hydroxide, manganese acetate and cupric acetate (Table 1) were dissolved in distilled water and mixed with an aqueous solution of 1.0 M tartaric acid. The solution was constantly maintained at pH between 4.5 to 5.5. The resulting solution was mixed with a magnetic stirrer to obtain a clear viscous gel and heated at ca. 90 ∘C for 5–6 h to form the powder. The powdered precursor was calcined at 800 ∘C.

Table 1 Type and mole of salts used to synthesize the oxide materials.

Sample	Salt	Moles used
A	$LiOH.H_2O$ $Mn(CH_3COO)_2.H_2O$	0.071 0.143
B	$LiOH.H_2O$ $Cu(CH_3COO)_2.H_2O$	0.071 0.141
C	$LiOH.H_2O$ $Mn(CH_3COO)_2.H_2O$ $Cu(CH_3COO)_2.H_2O$	0.071 0.036 0.107
D	$LiOH.H_2O$ $Mn(CH_3COO)_2.H_2O$ $Cu(CH_3COO)_2.H_2O$	0.071 0.071 0.071
E	$LiOH.H_2O$ $Mn(CH_3COO)_2.H_2O$ $Cu(CH_3COO)_2.H_2O$	0.071 0.107 0.036

2.2. Characterization

X-ray powder diffraction patterns were recorded at room temperature in PHILIPS PW 1840 diffractometer, with CuKα radiation. The patterns were taken at room temperature with 2θ ranging from 10° to 80°.

Energy dispersive analysis of X-ray (EDAX) was performed with a PHILIPS PV3800 to determine the composition of the materials. EDAX is attached to a scanning electron microscope. The particle morphology was examined by scanning electron microscopy (PHILIPS 515) operated at 15 kV.

The morphology and average particle size was studied using an SEM (PHILIPS Model 515). Thermogravimetric (TG) analysis were carried in the temperature range of 40 to 900 ^oC in flowing air. Infra red spectral studies in the range of 400 - 4000 cm^{-1} were done using a Perkin Elmer FTIR Spectrometer Spectrum 200 system with a spectral resolution of 4 cm^{-1}. Fine powders of the compounds were mixed with KBr and pressed to give translucent pellets.

3. Results and Discussion

The XRD pattern of sample A (LiM_2O_4) matched that of other researchers[15,16] with high intensity peaks at 36.5^o, 44° and 64° and minor peaks at 19°, 58° and 68° showing that after calcination in air at 900^oC, crystalline spinel structure of $LiMn_2O_4$ was formed. For sample B ($LiCu_2O_2$), the XRD pattern matched that of the JCPDS

pattern with a maximum peak at 39.0^o. Sample C has highest Cu:Mn ratio followed by samples D and E. The XRD patterns shows dominant peaks of $LiCu_2O_2$ and weaker peaks of $LiMn_2O_4$ for sample C and vice-versa for sample E. For sample D, the XRD pattern showed both $LiCu_2O_2$ and $LiMn_2O_4$ peaks evenly. As there are no references to compare the XRD patterns of these three materials, the metal ratio in these compounds was determined from the EDAX analysis.

The composition of Li, Mn, Cu in $Li_2Mn_xCu_yO_z$ (structures C, D and E) determined by EDAX and that used during preparation is given in Table 2. Results show the values of the compositions of Li, Mn and Cu from EDAX and those used during preparation are very close. As Cu and Mn are respectively most stable in (II) and (IV) oxidation state, it is reasonable to assign the samples C, D and E as $LiMn_{0.5}Cu_{1.5}O_{2.5}$, $LiMnCuO_3$ and $LiMn_{1.5}Cu_{0.5}O_{3.5}$. The content of oxygen in these materials increases with the content of manganese(IV) because of the higher oxidation state of manganese(IV) compared to copper(II).

Table 2. Comparison between material used during synthesis and results from EDAX.

Sample	Atoms	Relative amount of atoms used during synthesis	% atoms shown in EDAX	Lithium intercalation materials
C	Li Mn Cu	1.0 0.5 1.5	- 25.09 74.91	$LiMn_{0.5}Cu_{1.5}O_{2.5}$
D	Li Mn Cu	1.0 1.0 1.0	- 51.49 48.51	$LiMn_{1.0}Cu_{1.0}O_3$
E	Li Mn Cu	1.0 1.5 0.5	- 75.36 24.64	$LiMn_{1.5}Cu_{0.5}O_{3.5}$

Since the particle size is also an important factor for cycling performance, particle morphology and particle size of the materials were examined by SEM. The variation in the shape, size and surface morphology of the grains in the materials C, D and E are shown in Figure 1. It is found that the grain size for these materials synthesized by the sol-gel method is small, about 6 μm. No significant change in size and shape was observed though the ratio C:Mn is different.
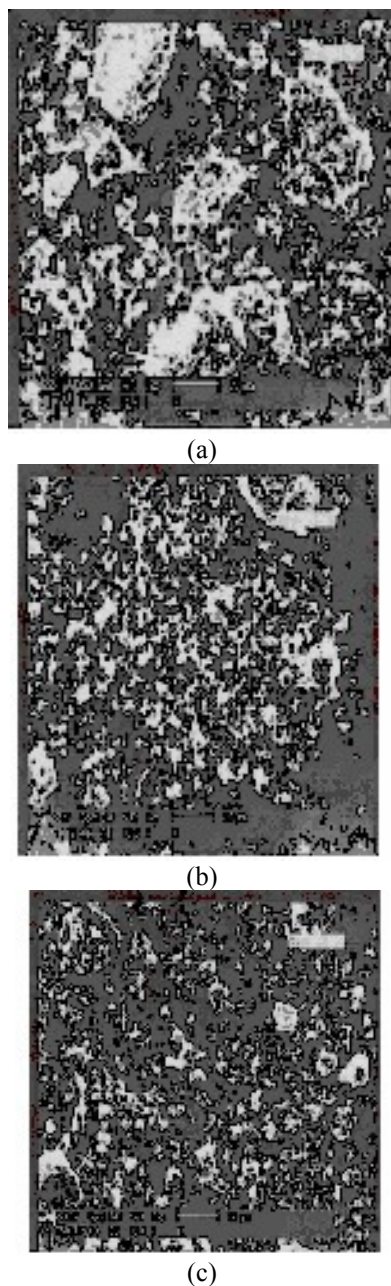
(a)

(b)

(c)

Figure 1. SEM micrographs at a magnification of 1500X of samples C, D and E ($Li_2Mn_xCu_yO_z$) synthesized by the sol-gel method. Sample C= (a), Sample D = (b) and Sample E = (c).

The formation temperature of an oxide sample from its precursor can be determined from the TG curve. For sample A, two distinctive weight losses at 103^oC and between 393 to 470^oC were observed. From the percentage weight loss, the former can be attributed to residual water removal and the latter due to combustion of the tartaric acid, acetate ions and other organic species and the solid state formation the oxide phase. Thus, the formation temperature of A begins at 393^oC and sample is thermally stable up to 900^oC. Similar TG curve was observed for sample B but the two weight losses occurred at lower temperatures (91^oC and $266-332^oC$). In both samples A and B, more than 50% of weight losses occur

during the second stage, i.e. oxidation-decomposition reaction. It appeared that the tartaric acid acted as a fuel in the pyrolysis of the molecular precursors (Cu and Mn acetates) and thus expedited the decomposition process. For samples D, three distinct weight losses were observed as shown in Fig 2. Similar curves were also obtained for samples C and E. The first is due to water removal ($88-100^oC$), the second ($250-296^oC$) and the third ($356-469^oC$) due to oxidation-decomposition reaction. In all cases, there was also a very small weight loss at $\sim800^oC$ which can be attributed loss in lithium due to its sublimation[17].
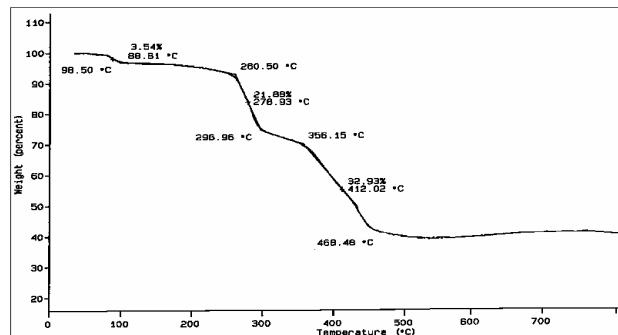

Figure 2. TGA curve for sample D, $LiMn_{1.0}Cu_{1.0}O_3$.

Table 3 Weight loss temperatures ranges from TGA experiments.

Samples	Weight loss temperatures	
A ($LiMn_2O_4$)	$103\ ^oC$	Water
	$393 - 470\ ^oC$	Tartaric acid, Acetates
B (LiCuO)	$91\ ^oC$	Water
	$266 - 332\ ^oC$	Tartaric acid, Acetates
C, D, E	$88 - 100\ ^oC$	Water
	$250 - 296\ ^oC$	Tartaric acid, Acetates
	$356 - 469\ ^oC$	Decomposition ad oxidaition

As for infrared spectroscopy, this study gives information on the local structure of the materials. It is sensitive to the short range environment of oxygen coordination around the cations in the metal oxide samples. The peaks are also sensitive to oxidation states, and remain relatively unaffected by the degree of long-range order. As our objective is to obtain pure oxide materials with small particle size, any residual organic compounds present from the synthesis process can easily be detected.

For samples A after calcinations at 800^oC, many peaks attributed to acetate ions, tartaric acid ($1600 – 1800$ cm^{-1}) and hydroxide ($3000-3800$ cm^{-1}) disappear indicating all organic molecules have been evaporated. This shows that the calcination temperature is sufficient for Li-Mn compounds, $LiMn_2O_4$, to form. For sample E, no peaks were observed after calcination at 800^oC.

This could possibly due the inclusion of Cu is sufficiently enough to give the correct ratio of Mn:Cu to

form the Li-Mn-Cu compounds with no impurities at a calcination temperature of 800°C. However, slight differences are seen in the other samples whereby apart from peaks due to LiCu$_2$O$_2$, peaks at 864, 1508, 1458 cm^{-1} due to hydroxyacetates, i.e. Li(OH)$_x$(CH$_3$COO)$_y$, are also present. This suggests that the amount of Cu used will affect the materials synthesized. And that a higher calcinations temperature and amount of Cu are needed to avoid these impurities.

4. Conclusion

The formation temperature of lithiated intercalation materials, LiMn$_2$O$_4$, LiCu$_2$O$_2$ and Li$_2$Mn$_x$Cu$_y$O$_z$ by the sol gel method was found to be between 300 – 500°C which is rather lower compared to other methods. Small grain size of 6.0 μm was formed. From the XRD, TGA and FTIR results, formation of one-phase compound of Li$_2$Mn$_x$Cu$_y$O$_z$ using a calcination temperature of 800°C can only be achieved when the ratio of Li:Mn:Cu is 1.0:1.5:0.5. Higher Cu content results in a mixture of the oxide phases.

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