The Effects Of Partially Substituting Manganese With Copper In LiMn$_2$O$_4$
Cathodic Material

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Abstract.

Although LiMn$_2$O$_4$ is a very promising material for use as cathodes in lithium ion batteries, it exhibits capacity fading on cycling. Substituting some of the Mn with a 3d metal may improve the stability of the material. In this research, LiMn$_{2-x}$Cu$_x$O$_4$ (where $x = 0.2$ and $0.4$) are synthesized and characterized by TGA, XRD and EDX. Cyclic voltammetry is also done to study their electrochemical characteristics. Results indicate improved thermal stability and some structural change in the material. Cyclic voltammetry results show the redox potentials have been shifted from those obtained from pure LiMn$_2$O$_4$ material.

Introduction

There are many advantages that can be obtained if LiMn$_2$O$_4$ is used in commercial lithium secondary batteries. Manganese is a very well known material in the battery industry [1, 2] and has been used as the main component in dry cells since 1860 [3]. It is less toxic than materials presently used in lithium secondary batteries such as nickel or cobalt. However, it suffers from capacity fading. Introducing copper into the crystal structure of the material may improve the stability of the material. The objective of this study is to see the changes in the characteristics of the material LiMn$_{2-x}$Cu$_x$O$_4$ (where $x = 0.2$ and $0.4$) synthesized by the soft chemistry route as compared to that of pure LiMn$_2$O$_4$ also synthesized by the same method.

Experimental

Stoichiometric amounts of lithium acetate, manganous acetate and copper oxide are used and stirred in ethanol for about half an hour. The materials are then mixed together and tartaric acid is slowly added to form a thick colloid. This is then slow heated until all the liquid has evaporated leaving a black precursor material. The material is grinded into fine powder. Thermogravimetric (TGA) analysis is done on the precursor. The material is then subjected to an annealing temperature of 600 °C for 24 hours. Characterization using XRD, FTIR and EDX are later done on the final products. Cyclic voltammetry is also done to look at the redox potentials of the new materials.

Results and Discussion

Fig 1, Fig 2 and Fig 3 shows the TGA traces of LiMn$_{1.4}$Cu$_{0.6}$O$_4$, LiMn$_{1.6}$Cu$_{0.4}$O$_4$ and LiMn$_2$O$_4$. 
respectively. The thermal profile of Figs 1 and 2 shows flatter traces in the temperature range of 380 °C to 780 °C as compared to the one in Fig 3. This is an indication that the materials with copper content seem to be more thermally stable compared to the pure LiMn$_2$O$_4$ material. The decrease in weight around the 800 °C region is also less for the material with more copper content, that is Fig 2. Generally, it can be said that the material substituted with copper has shown more thermal stability compared to the pure LiMn$_2$O$_4$ material.

XRD spectra of intensity against 2θ values for LiMn$_{1.8}$Cu$_{0.2}$O$_4$, LiMn$_{1.6}$Cu$_{0.4}$O$_4$ and LiMn$_2$O$_4$ is shown in Fig 4, Fig 5 and Fig 6 respectively. The spectra of the LiMn$_{1.8}$Cu$_{0.2}$O$_4$, LiMn$_{1.6}$Cu$_{0.4}$O$_4$ materials seem to have undergone some changes from the pure LiMn$_2$O$_4$ XRD spectra. The 34° peak seem to decrease in intensity as x increases. In fact the peak seem to have disappeared in Fig 5. The 56° peak also seem to have diminished in Fig 5 and disappeared in Fig 6. These are clear indications
that the materials have undergone some structural change. It is believed that the materials with copper content have undergone modifications of the cubic spinel structure.

Cyclic voltammograms of LiMn$_{1.8}$Cu$_{0.2}$O$_4$, LiMn$_{1.6}$Cu$_{0.4}$O$_4$ and LiMn$_2$O$_4$ are shown in Fig 7, Fig 8 and Fig 9 respectively. The CV traces were obtained at 25 mVs$^{-1}$ using LiMn$_{1.8}$Cu$_{0.2}$O$_4$, LiMn$_{1.6}$Cu$_{0.4}$O$_4$ and LiMn$_2$O$_4$ as the active material, carbon as the anode and Ag/AgCl as the reference electrode. The experiment was performed using Bio-Analytical Systems (BAS). Broad peaks are obtained and the redox potentials are as tabulated in Table 1. The redox peaks obtained for the pure LiMn$_2$O$_4$ agrees well with results from other researches [4-6]. It is observed that the redox peak of 3.62 V for the pure LiMn$_2$O$_4$ material has decreased to 3.02 V and 2.92 V for the LiMn$_{1.8}$Cu$_{0.2}$O$_4$ and LiMn$_{1.6}$Cu$_{0.4}$O$_4$ respectively. The 4.22 V peak for the pure LiMn$_2$O$_4$ material has also decrease to 4.12 V for both the LiMn$_{1.8}$Cu$_{0.2}$O$_4$ and LiMn$_{1.6}$Cu$_{0.4}$O$_4$ materials. However the decrease is only 0.1 V as compared to 0.5 and 0.6 V for the 3.62 V peak.
Table 1

<table>
<thead>
<tr>
<th>Material sample</th>
<th>ΔE (V) vs Ag/AgCl</th>
<th>ΔE (V) vs Li/Li⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMn₁.₈Cu₀.₂O₄</td>
<td>-0.3</td>
<td>3.02</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.12</td>
</tr>
<tr>
<td>LiMn₁.₆Cu₀.₄O₄</td>
<td>-0.4</td>
<td>2.92</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>4.12</td>
</tr>
<tr>
<td>LiMn₂O₄</td>
<td>0.3</td>
<td>3.62</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>4.22</td>
</tr>
</tbody>
</table>

Table 2 shows the EDX results for the LiMn₁.₈Cu₀.₂O₄ and LiMn₁.₆Cu₀.₄O₄ materials. The results show that the synthesis method is quite a viable way of obtaining the materials synthesized.

**Conclusion**

Partially substituting copper with manganese indicates that the new materials are more thermally stable than the pure LiMn₂O₄. The materials seem to have undergone some structural change as indicated by XRD results. The redox peaks of the new materials have decreased compared to those of the pure LiMn₂O₄. The synthesis route is also a viable way of obtaining stoichiometric samples of LiMn₁.₈Cu₀.₂O₄ and LiMn₁.₆Cu₀.₄O₄ materials.

**References**