Studies on Bare and Mg-doped LiCoO₂ as a cathode material for Lithium ion Batteries

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Abstract

In this paper, we report on the preparation of bare and Mg-doped Li(MgₓCo₁₋ₓ)O₂ (x = 0, 0.03, 0.05) phases by a molten salt method and their electrochemical properties. They were prepared at 800 °C for 6 h in air. Rietveld refined X-Ray Diffraction data of bare (x = 0) and Mg-doped (x = 0.03, 0.05) compounds show a well-ordered hexagonal layer-type structure (a ~ 2.81 Å, c ~ 14.05 Å). Scanning Electron Microscopy (SEM) show hexagonal type
morphology at 800 °C. Powder density was close to 5.02 g cm$^{-3}$, which compares well with the theoretical value. Electrochemical properties were studied in the voltage range of 2.5-4.3 V vs. Li using Cyclic Voltammetry (CV) and galvanostatic cycling. CV studies on bare and Mg-doped LiCoO$_2$ show main cathodic and anodic redox peaks at ~ 3.9 V and ~ 4.0 V, respectively. Galvanostatic cycling of Li(Mg$_x$Co$_{1-x}$)O$_2$ (x = 0, 0.03, 0.05) showed reversible charge capacity values at the 60$^{th}$ cycle to be: 147 (±3) mAh g$^{-1}$ (x = 0), 127 (±3) mAh g$^{-1}$ (x = 0.03), and 131 (±3) mAh g$^{-1}$ (x=0.05) cycled at a current density of 30 mA g$^{-1}$. Capacity retention is also favourable at 98.5%.

**Keywords:** Molten salt method ; Mg-doped LiCoO$_2$ ; Cathode ; Electrochemical properties

### 1. Introduction

Commercial Lithium ion batteries (LIBs) consist of a LiCoO$_2$[1] or LiMn$_2$O$_4$[2, 3] LiNi$_{0.5}$Mn$_{1.5}$O$_4$[4, 5] or LiFePO$_4$[6] and other cathode as cathodes[7] and Graphite as anode[8, 9]. During the charging process, Li-ions are removed from the cathode and inserted in the anode and vice-versa during the discharging process. The commercial cathode is usually lithium cobalt oxide (LiCoO$_2$) due to its nice 4V redox potential and its well-ordered layered structure while the anode is usually graphite due its flat discharge-charge potentials at 0.2-0.3 V[10]. LIBs are very successful due to their high energy density, low self-discharge and low maintenance, making them suitable for portable equipment from wireless communications to mobile computing.

Studies have shown that commercial batteries made of LiCoO$_2$ can deliver a reversible capacity of 120-140 m Ah$^{-1}$. However, the capacities of the batteries fade when cycled at more than 4.2 V as it undergoes structural transformations due to various factors such as the preparation method, operating voltages and hexagonal structural transformations during cycling. The capacity fading can be reduced by suitable doping to the Co-sites,
nanophase coating or novel preparation methods[11]. It was shown theoretically from first principles and determined experimentally that the substitution of Al increases the performance of the LiCoO$_2$ cathode[12]. However, it has been reported that Al doping causes capacity fading upon cycling[13]. Since Mg is a light element, cheap and abundant it is considered as a substituent (dopant) for Co, Mg is shown to stabilize the layered structure and therefore increase the cycle ability of the cathode material [14, 15]. Previous studies also showed that the electronic conductivity of LiCoO$_2$ can be improved by Mg-doping[14, 16-22]. In this project, Li(Mg$_x$Co$_{1-x}$)O$_2$ (x = 0, x = 0.03 , x = 0.05) compounds were prepared by the molten salt method (LiNO$_3$:LiCl eutectic as the molten salt) at 800 °C, and their cathodic performance was studied in a voltage range of 2.5-4.3V at current rate of 30 mAg$^{-1}$ for up to 60 charge-discharge cycles.

2. Experimental

Li(Mg$_x$Co$_{1-x}$)O$_2$ (x = 0, 0.03, 0.05) samples were prepared at 800 °C by the molten salt method. The molten salt method is one of the simpler one-pot methods and usually its reactivity will be faster when compared to solid state reaction methods and this method offers defect free highly crystalline layered structure materials and no mixing and/or repeated reheating of the compounds are needed[23-27]. The initial reactants, 0.88 moles of LiNO$_3$, 0.12 moles of LiCl, 1-x moles of (CH$_3$COO)$_2$Co and x moles of Mg(NO$_3$)$_2$ 4H$_2$O were weighed and heated in an alumina crucible at 800 °C in air for 6 h in a box furnace. After heating, the samples were cooled to room temperature before they were thoroughly washed with distilled water and filtered to remove the excess salts. They were then dried in an air oven at 70 °C for 12 h. The black crystalline powder obtained was used for further studies. The material was characterized by X-Ray Diffraction (XRD) using the (Empyrean, Panalytical) to determine the structure of Li(Mg$_x$Co$_{1-x}$)O$_2$ (x = 0, 0.03, 0.05). After XRD was
performed, Rietveld Refinement was carried out using TOPAS-R software to compare the data obtained with literature. Scanning Electron Microscope (SEM) (model JEOL JSM-6700F) was also used to examine the morphology of Li(MgₓCo₁₋ₓ)O₂ (x = 0, 0.03, 0.05). The density and BET surface area of the powders were evaluated by Gas pycnometer and tristar (Micromeritics, USA). To fabricate the coin cells, a slurry had to be made. The slurry was made by mixing Li(MgₓCo₁₋ₓ)O₂ (x = 0, 0.03, 0.05), super P carbon black and Polyvinylidene Fluoride (PVDF) in the weight ratio of 70:15:15, using N-Methyl-2-pyrrolidone (NMP) as a solvent, and it was stirred overnight before being spread on aluminum foil, which was the current collector. This was then dried at 70 °C before it was cut into electrodes. The coin cells were then fabricated inside a glove box filled with argon gas, and each coin cell consisted of a bottom cap, the composite cathode on aluminum foil, an 1M LiPF₆(EC;DEC) (Merck) as a electrolyte, a separator (Polypropylene-Cellguard), another few drops of electrolyte, Lithium foil and a top cap with O-ring and spring. It was then sealed with a press to form a coin cell of size 2016. After the coin cells were made in a glove box, electrochemical studies were performed using cyclic voltammetry (using Biologic, France) to determine the redox couple of the compounds. Galvanostatic cycling using Bitrode battery tester (USA) was done to evaluate the performance of the battery via charge-discharge cycling at ambient temperature, with further details given in [28-30].

3. Results and discussion

3.1. Structure and morphology

The XRD patterns of Li(MgₓCo₁₋ₓ)O₂ (x = 0, 0.03, 0.05) samples prepared at 800 °C are shown in Figure 1a. The lattice parameters were refined using known space group (Fd-3m) and positional parameters[19]. For clarity, the refined XRD patterns of LiCoO₂ are shown in Figure 1b. The obtained lattice parameters, Brunauer Emmett and Teller (BET)
surface area values, as well as experimental and theoretical densities of all compounds are given in Table 1. The XRD patterns of Li(Co_{1-x}Mg_x)O_2 (x = 0, 0.03, 0.05) samples are similar to NaFeO_2 and no impurity lines of Co_2O_4 or MgO lines were observed. The obtained lattice parameter values are similar to reported literature on bare and doped LiCoO_2 by solid state method and other methods[14, 18]. In brief LiCoO_2 showed a lattice parameter values \(a=2.819\text{ (5) Å, } c=14.052\text{ (8) Å}\) [1, 31], Levasseur et al. reported a lattice parameter values of \(a=2.8212\text{ (1) Å, } c=14.082\text{ (1) Å}\) for LiCo_{0.94}Mg_{0.06}O_2[20]. When doping with Mg^{2+} the Co^{3+} ions are substituted and therefore there will be a charge compensation mechanism (Co^{3+} to Co^{4+}) taking place or oxygen vacancies will be created which leads to structural defect stabilizing Co^{3+\text{\(\text{IS}\)}}} ions. With the increase in Co^{4+} ions and intermediated spin Co^{3+\text{\(\text{IS}\)}}} ions, there will be an enhancement in the conductivity compared to the un-doped LiCoO_2 [20].

Taking into account the ionic radii [32] of the Mg^{2+} (0.72 Å), Co^{3+} (0.545 Å) and Co^{4+} (0.53 Å) it is expected that there will be an increase in the lattice parameters with doping as seen in Table 1. Also when examining the \(c/a\) ratios it is worth noting that all samples have values greater than 4.90. This indicates a low degree of hexagonal phase distortion and a lack of cation disorder. The Li(Mg_{0.05}Co_{0.95})O_2 shows the highest ratio of 5.00 making it structurally superior compared to the Li(Mg_{0.03}Co_{0.97})O_2 and the LiCoO_2 cathode materials and thus a better cyclability is expected.

SEM images of Li(Co_{1-x}Mg_x)O_2 (x = 0, x = 0.03 , x = 0.05) with different magnifications are shown in Figure 2(a-f), those of Li(Mg_{0.03}Co_{0.97})O_2 at different magnifications are shown in Figure 2c,d, while the results for Li(Mg_{0.05}Co_{0.95})O_2 prepared at different magnifications are shown in Figure 2e,f. The SEM images showed that the particles have a hexagonal shape, are of sub-micron size and that there are not many differences in the
Figure 1: (a) XRD patterns of Li(Mg$_{x}$Co$_{1-x}$)O$_2$ ($x = 0, 0.03, 0.05$) of all samples, (b) Rietveld refined X-ray diffraction pattern of LiCoO$_2$ synthesized using the molten salt method at 800°C. Vertical bars are Miller indices ($h k l$) as shown and indexed.
<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Parameter (Å) and cell volume (V)= (Å³)</th>
<th>Theoretical Density (g/cm³)</th>
<th>Experimental Density (g/cm³)</th>
<th>BET Surface Area (m²/g)</th>
<th>Reversible capacity at 5th and 60th cycle (mAh/g), Capacity fading (5-60 cyc.) %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li(Mg₀.₀₂Co₀.₉₈)O₂</td>
<td></td>
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<td></td>
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<tr>
<td>LiCoO₂</td>
<td>$a = 2.8153(4)$</td>
<td>5.053</td>
<td>5.01</td>
<td>2.40</td>
<td>156 ; 147</td>
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<td></td>
<td>$c = 14.0568(2)$</td>
<td></td>
<td></td>
<td></td>
<td>(5.7)</td>
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<tr>
<td></td>
<td>$c/a = 4.993$</td>
<td></td>
<td></td>
<td></td>
<td></td>
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<td></td>
<td>$V = 96.489$</td>
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<tr>
<td>Li(Mg₀.₀₅Co₀.₹₅)O₂</td>
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<tr>
<td>Li(Mg₀.₀₅Co₀.₹₅)O₂</td>
<td>$a = 2.8162(2)$</td>
<td>4.994</td>
<td>5.30</td>
<td>3.30</td>
<td>135; 127</td>
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<td></td>
<td>$c = 14.0627(2)$</td>
<td></td>
<td></td>
<td></td>
<td>(5.9)</td>
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<tr>
<td></td>
<td>$c/a = 4.993$</td>
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<td></td>
<td>$V = 96.589$</td>
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<tr>
<td>Li(Mg₀.₀₇Co₀.₹₃)O₂</td>
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<tr>
<td>Li(Mg₀.₀₇Co₀.₹₃)O₂</td>
<td>$a = 2.820(2)$</td>
<td>4.931</td>
<td>4.94</td>
<td>3.43</td>
<td>136;132</td>
</tr>
<tr>
<td></td>
<td>$c = 14.0936(7)$</td>
<td></td>
<td></td>
<td></td>
<td>(2.9)</td>
</tr>
<tr>
<td></td>
<td>$c/a = 4.997$</td>
<td></td>
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<td></td>
<td>$V = 97.133$</td>
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Figure 2: Scanning Electron micrographs of (a,b) LiCoO$_2$, (c,d) Li(Mg$_{0.03}$Co$_{0.97}$)O$_2$, (e,f) Li(Mg$_{0.05}$Co$_{0.95}$)O$_2$ with two different magnifications bar scale, 1µm.

morphology of the doped samples. The formation mechanisms are very complex as they depend on temperature and nature of the molten salt and metal ions. Further careful studies on the effect of different Co-salts, preparation temperature are in progress. The BET surface area are in the range, 2-4 m$^2$ g$^{-1}$ (Table1). The experimental density values are similar to the theoretical density values calculated from the XRD data.
Figure 3: Cyclic voltammograms of Li(Mg\textsubscript{x}Co\textsubscript{1-x})O\textsubscript{2} (x = 0, 0.03, 0.05): (a) LiCoO\textsubscript{2}, (b) Li(Mg\textsubscript{0.03}Co\textsubscript{0.97})O\textsubscript{2} and (c) Li(Mg\textsubscript{0.05}Co\textsubscript{0.95})O\textsubscript{2}. Scan rate: 0.058 mVs\textsuperscript{-1}. Voltage range: 2.5-4.3 V vs. (Li/Li\textsuperscript{+}). Only the 2\textsuperscript{nd} cycle is shown for clarity.

3.2. Electrochemical studies

Cyclic voltammograms of the cells, in the range of 2.5-4.3 V at ambient temperature at a scan rate of 0.058 mVs\textsuperscript{-1} are shown in Figure 3. For clarity cyclic voltammograms of the second cycles of Li(Mg\textsubscript{x}Co\textsubscript{1-x})O\textsubscript{2} (x = 0, 0.03, 0.05) are also shown in Figure 3. All
Figure 4: Graph of Voltage (V vs. (Li/Li⁺)) against Capacity (mAh/g): (a) LiCoO₂, (b) Li(Mg₀.₀₃Co₀.₉₇)O₂ and (c) Li(Mg₀.₀₃Co₀.₉₇)O₂. Voltage range, 2.5-4.3 V vs. Li; current rate: 30 mA g⁻¹. For clarity 2, 20 and 60 cycles are shown.
compounds showed a main anodic peak at ~4.0 V and the cathodic peak at ~3.8 V correspond to Co$^{3+/4+}$ redox couple[1, 31]. The origin of a minor peak (anodic peak) at 3.5 V is not clear at present.

Galvanostatic cycling (charge and discharge) curves of bare and Mg-doped LiCoO$_2$ are shown in Figure 4. During charging, Li-ions are removed from Li(Mg$_x$Co$_{1-x}$)O$_2$ ($x = 0, 0.03, 0.05$), hence Co undergoes oxidation from Co$^{3+}$ to Co$^{4+}$. During discharging process, the reverse reaction occurs. We note Mg- ions are electrochemically inactive, are difficult to oxidize from Mg$^{2+}$ to Mg$^{3+}$ or Mg$^{4+}$ and it act as conducting matrix. All compounds showed a plateau at 3.9 V vs. Li, which is similar to the observed curves in the CV. We note that the hexagonal structural transformations (Monoclinic M $\rightarrow$ (Hexagonal) H$_2$, and H$_2$ $\rightarrow$H$_3$) [1, 33, 34] are completely suppressed in both bare and doped LiCoO$_2$, this may leads to improved capacity retention during. The capacity vs. cycle number plots are shown in Figure 5. Irreversible capacity loss during 1$^{st}$ cycle was observed in all cases and ICL values are in the range, 25-30 mAh g$^{-1}$. The cycling results clearly show that the LiCoO$_2$ ($x=0$) compound delivers a higher capacity compared to the other samples $x = 0.03$ and $x = 0.05$, which is expected due to the Mg that is electrochemical inactive. The reversible capacity at the end of 20$^{th}$ are 150 ($x=0$), 132 ($x=0.03$) and 135 ($x=0.05$) mAh g$^{-1}$ and corresponding capacity fading between 5 to 60 cycles are 3-6 % (Table1). The good cycling stability is due to a pure and well-ordered layered structure, with no cation mixing and uniform morphology as exampled by the XRD analyses and SEM images and other reasons like improved conductivity. Maldinov etal.[18] reported sol-gel derived Mg-doped LiCoO$_2$ showed a reversible capacity of 115 and 121 mAhg$^{-1}$ for bare and Mg-doped LiCoO$_2$, respectively and they showed 28 and 10 % capacity loss up to 40 cycles, cycled in the voltage range, 2.9-4.3V, at current rate of 30 mAg$^{-1}$. Levasseur etal.[19] reported a reversible capacities at 1$^{st}$ and 10$^{th}$ cycle, at current rate of C/20, the voltage range, 2.7-4.15V vs. Li are: 132 and 123 mAhg$^{-1}$ for
Figure 5: Graph of Capacity in (mAh\textsuperscript{−1}) against cycle number, (a) LiCoO\textsubscript{2}, (b) Li(Mg\textsubscript{0.03}Co\textsubscript{0.97})O\textsubscript{2}, and (c) Li(Mg\textsubscript{0.05}Co\textsubscript{0.95})O\textsubscript{2}. Voltage range, 2.5-4.3 V (Li/Li\textsuperscript{+}); current rate: 30 mA g\textsuperscript{−1}.

x=0, 134 and 122 mAh\textsuperscript{−1} for x=0.03 and 132 and 122 for x=0.05 mAh\textsuperscript{−1}. Kim et al. [35] reported x=0.03 sample deliver a reversible capacity of 130 mAh\textsuperscript{−1} at the end of 50\textsuperscript{th} cycle, where as x=0 sample deliver a reversible capacity of 80 mAh\textsuperscript{−1} at the end of 50\textsuperscript{th} cycle,
when cycled in the voltage range of 3.0-4.3V vs. Li and they prepared above mentioned samples using ball-milling followed by solid state reaction method. Sathiyamoorthi et al. [36] prepared using urea combustion/solid state method, they reported a reversible capacity of 96 and 86 mAhg$^{-1}$ for x=0 and x=0.2, cycled in the voltage range, 3.0-4.5V. Microwave assisted bare and x=0.1 doped LiCoO$_2$ by Zaheena et al. [37] showed a reversible capacity of 85 and 125 mAhg$^{-1}$ at the end of 20$^{th}$ cycle, cycle at C/10 rate and in the voltage range, 2.5-4.2V. Yin et al. [38] reported improved capacity retention with 1% Mg –doped LiCoO$_2$, they showed about 81 and 85 % capacity retention for bare and 1% Mg-doped LiCoO$_2$ after 50 cycles at current rate of 1C, in the voltage range, 3.0-4.5V. Very recently Nithya et al. [39] showed improved capacity with Cu, Mg co-doped LiCoO$_2$ and still capacity fading was not completely suppressed.

4. Conclusions

The compounds, LiCoO$_2$, Li(Mg$_{0.03}$Co$_{0.97}$)O$_2$ and Li(Mg$_{0.05}$Co$_{0.95}$)O$_2$ were prepared at 800 °C using the molten salt method. These samples were characterized using X-ray diffraction, scanning electron microscope and other electro-analytical techniques such as cyclic voltammetry and galvanostatic cycling. Galvanostatic cycling studies show LiCoO$_2$ delivering high and stable capacity of 147 mAhg$^{-1}$ at the end of the 60$^{th}$ cycle. Not much improvement were seen in the electrochemical performance of Mg-doped LiCoO$_2$ in comparison with the bare LiCoO$_2$ sample and further studies on the effect of the electrochemical performance of other Co/Mg-salts are in progress.
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