Abstract

LiMn$_2$O$_4$, LiCo$_{0.2}$Mn$_{1.8}$O$_4$, LiMn$_{1.9}$Ni$_{0.1}$O$_4$ gels were produced via Sol-Gel method. 100 ml sol-gel solutions were prepared and gel structure obtained after 4 hours with 250 rpm stirring speed, pH value of 7, 80 °C solution temperature. Gel structures were dried at 100 °C for 24 hours. Dried gel structures were calcined and crystallized at 800-850°C with 1 °C/min heating rate. Obtained powders were mixed with carbon black and PVDF binder with 80/10/10 ratio. Powder mixtures were laminated on 19 μm aluminum foil via Doctor Blade method. 2032 half cells were prepared for Galvanostatic test. Charge/Discharge performances of cathode materials were studied with 25, 50, 100 mA/g current density respectively for 50 cycles. Cyclic voltammetry (CV) technique was used to understand charge/discharge behavior in detail. X-ray diffraction (XRD) characterization method was used to observe crystallization level of the powders. Dopant elements do not form different compounds instead they decrease lattice parameter. Scanning electron microscopy (SEM) was used to identify powder morphology and size. Powder particles are not spherical or sharp edged instead have soft edges with facet structure and powder size varies between 250-1000 nm. Energy dispersive spectrometer (EDS) method was used to get compositional information. Powders exhibit desired composition with small deviations. X-ray diffraction (XRD) characterization method was used to observe crystallization level of the powders. Dopant elements do not form different compounds instead they decrease lattice parameter. Scanning electron microscopy (SEM) was used to identify powder morphology and size. Powder particles are not spherical or sharp edged instead have soft edges with facet structure and powder size varies between 250-1000 nm. Energy dispersive spectrometer (EDS) method was used to get compositional information. Powders exhibit desired composition with small deviations. SEM technique was also used to characterize electrochemically cycled cathodes. Cracks formation with Jahn-Teller distortion mechanism diminish with doping.

1. Introduction

Mainly cathode materials consist of spinel and layered structure materials. Commercially, LiCoO$_2$, LiMn$_2$O$_4$ and LiFePO$_4$ cathodes are used in lithium ion batteries. LiMn$_2$O$_4$ cubic spinel cathode material has been studied due to its low cost, environmental friendliness and easy preparation route [1]. Main disadvantage of this material is known as Jahn-Teller effect. During lithiation/delithiation process of Li ions cathode structures expand. As a result, cracks occur on cathodes and active material loses electrical contact which ends up with capacity loss. Mn$^{3+}$ ions are main reason of Jahn-Teller transformation. Mn$^{3+}$ disproportion into Mn$^{4+}$ and Mn$^{2+}$ ions and Mn$^{2+}$ dissolves in electrolyte which causes permanent Mn ion loss. That ion loss also leads to cubic-tetragonal transformation (5.6 %volume change) indirectly [2, 3]. The most common to overcome this negative effect is to dope cathode structure with another elements like Ni, Co, Al, Fe. Doped elements reduces amount of Mn$^{3+}$ ions and Jahn-Teller effect directly [4]. In doped systems, accurate stoichiometry is desired to control Mn valance state. Sol-gel method is the most relevant route to obtain that requirement. This method has some important advantages such as good stoichiometric control, production of sub-micron particle size, narrow particle size distribution and short process time [5]. Especially stoichiometry and particle size properties are very critical to obtain high specific capacity values. In this study, LiMn$_2$O$_4$, LiCo$_{0.2}$Mn$_{1.8}$O$_4$, LiMn$_{1.9}$Ni$_{0.1}$O$_4$ powders were synthesized by sol-gel method using citric acid as chelating agent. The main focus of this study to investigate doping effect of Ni and Co elements inside the LiMn$_2$O$_4$ structure.

2. Experimental Procedure

LiMn$_2$O$_4$, LiCo$_{0.2}$Mn$_{1.8}$O$_4$, LiMn$_{1.9}$Ni$_{0.1}$O$_4$ gels were synthesized separately by using lithium acetate (LiOOCCH$_3$.2H$_2$O, Alfa Aesar), manganese acetate (Mn(OOCCH$_3$)$_2$, Alfa Aesar), nickel nitrate (N$_2$NiO$_6$.6H$_2$O, Alfa Aesar), cobalt nitrate (Co(NO$_3$)$_2$.6H$_2$O, Alfa Aesar) precursors. Citric acid (C$_6$H$_8$O$_7$, Alfa Aesar) was used as chelating agent with the mol ratio of 1/3 (Li/Acid). 32% ammonium solution (WMR) was used to adjust sol-gel solution pH to 7. 100 ml volume was used during gelation process. 250 rpm stirring speed and 80 °C solution temperature were kept constant during the synthesis. Complete gel structures were obtained after 4 hours of process. Obtained gels were dried at 120 °C for 12 hours. Dried materials were calcined at 300 °C for 6 hours. 800, 850, 800 °C temperature and 6, 8, 12 hours of duration were used as crystallization parameter for three different compositions. In every heat treatment process, 1 °C/min heating rate was used. Obtained powders were mixed with carbon black (Alfa Aesar) and PVDF binder -CH$_2$CF$_2$, Alfa Aesar) with 80/10/10 ratio respectively. NMP (Alfa Aesar) was added into the powder mixture to form a slurry before lamination process. The powder mixtures were laminated on a 19 μm aluminum foil substrate via Doctor Blade. Each
coating thickness was adjusted as 500 μm. Laminating speed was set to 20 mm/s. The laminates were dried at 100 °C for 1 hour before rolling operation. Double rolling process was applied on the coatings to get smooth and flat surface. CR2032 lithium ion cells were assembled. 1 M LiPF₆ in EC-DMC (Alfa Aesar) was used as electrolyte. Charge/Discharge tests (MTI BST8-WA) were made using 25, 50, 100 mA/g current densities for 50 cycles between 3-4.3 V. Cyclic voltammetry (Gamry Insturements Interface 1000) tests were carried out with 25 °C temperature, 0.02 mV/s scanning rate between 3-4.3 V operating voltage for first 3 cycles. The crystallinity of the powders were examined by X-ray diffraction method (Rigaku Miniflex, Cu Kα radiation) with 2°/min scanning rate, between 20 = 15°-70° diffraction angle. Scanning electron microscopy (JEOL-JSM-5410LV, 15 kV ) was used before and after charge/discharge test to identify powder morphology and size. Energy dispersive spectrometer (JEOL-JSM-5410LV, 15 kV) method was used before charge/discharge test to get compositional information.

3. Results and Discussion

Fig. 1. shows XRD graphs of LiMn₂O₄, LiCo₀.₂Mn₁.₈O₄, LiMn₁.₉Ni₀.₁O₄ powders.

XRD graphs show that cubic spinel structure was obtained successfully for all three powders. The impurities such as Li₂CO₃ and Mn₂O₃ that affect charge/discharge performance were not observed [6]. XRD graphs of doped powders are identical with un-doped material. Dopant element (Co, Ni) does not form different compounds instead they decrease the lattice parameters. Inducing another element into the structure increases Mn valence from 3⁺ to 4⁺. Decrease in ionic radius favors the formation of a structure having smaller lattice parameters (Mn³⁺ = 0.645 Å, Mn⁴⁺ = 0.530 Å). The transformation of Mn³⁺ to Mn⁴⁺ diminishes Jahn-Teller effect and improves charge/discharge performance of cathode material [7]. Fig. 2. shows the SEM images of LiMn₂O₄, LiCo₀.₂Mn₁.₈O₄, and LiMn₁.₉Ni₀.₁O₄ powders.

SEM images show that all powder particles are not spherical or sharp edged instead they have soft edges with facet structure. The size of the powders varies between 250-1000 nm. Charge/discharge performance highly depends on the powder size and morphology. Spherical shape and smaller size favors electrochemical reactions on the cathode surface thus improves cycling performance. The doped powders keep similar powder size and morphology compared to the un-doped powders. In that point of view, it is likely to mentioned that all three powder will exhibit the same level of reaction on the surface. Table 1. shows the EDS results of LiMn₂O₄, LiCo₀.₂Mn₁.₈O₄, LiMn₁.₉Ni₀.₁O₄ powders.

Table 1. The EDS results of powders

<table>
<thead>
<tr>
<th>Composition</th>
<th>MnO</th>
<th>CoO</th>
<th>NiO</th>
<th>Total</th>
</tr>
</thead>
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<tr>
<td>LiMn₂O₄</td>
<td>100.00</td>
<td></td>
<td></td>
<td>100.00</td>
</tr>
<tr>
<td>LiCo₀.₂Mn₁.₈O₄</td>
<td>91.10</td>
<td>8.90</td>
<td></td>
<td>100.00</td>
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<tr>
<td>LiMn₁.₉Ni₀.₁O₄</td>
<td>95.53</td>
<td></td>
<td>4.47</td>
<td>100.00</td>
</tr>
</tbody>
</table>
The EDS results show that theoretically calculated stoichiometric values were obtained after sol-gel process. Mn, Co and Ni elements tend to make bonds with oxygen atoms in the structure. In this consideration, the percentage of possible oxides were calculated in Table 1. This result proves that sol-gel is fast and precise method to obtain specific composition in short durations. Fig. 3. shows specific capacity-cycle graphs of LiMn$_2$O$_4$, LiCo$_{0.2}$Mn$_{1.8}$O$_4$, LiMn$_{1.9}$Ni$_{0.1}$O$_4$ cathodes at 25 mA/g current density.

**LiMn$_2$O$_4$, LiCo$_{0.2}$Mn$_{1.8}$O$_4$, LiMn$_{1.9}$Ni$_{0.1}$O$_4$ cathode materials showed 108, 103, 126 mAh/g specific charge capacity and 76%, 80%, 85% capacity retention rate after 30 cycles respectively.** Doping LiMn$_2$O$_4$ powder dramatically increases capacity retention especially with Ni content. Decreasing Mn$^{3+}$ quantity eliminates volumetric expansion which called Jahn-Teller distortion. In addition to this, Mn$^{3+}$ disproportion reaction can not take place and Mn$^{2+}$ dissolution in electrolyte (permanent loss of Mn$^{3+}$ ion) is hindered [7, 8]. Ni doped powder also shows higher specific capacity values due to an increase in ionic conductivity. Increase in ionic conductivity decreases Li-Li repulsive forces thus Li ions delithiate faster in the same duration and exhibits higher specific capacity values [9]. Fig. 4. shows specific capacity-cycle of LiMn$_{1.9}$Ni$_{0.1}$O$_4$ cathodes at 25, 50, 100 mA/g current densities and Coulombic efficiency of all cathode materials. LiMn$_{1.9}$Ni$_{0.1}$O$_4$ cathode materials showed 128, 118, 68 mAh/g specific charge capacity and 85%, 89%, 99% capacity retention rate after 50 cycles at 25, 50, 100 mA/g current densities, respectively. High current density means Li ions have less time to travel between cathode and anode material. In lesser duration, some Li ions become unable to complete that travel so that the capacity value decreases [10]. Fortunately, that mechanism hinders Mn$^{3+}$ disproportion and Jahn-Teller formation thus capacity retention increases. Li ion diffusion rate is still sufficient enough at 2x current density and there is 10 mAh/g drop in charge capacity value. On the other hand, when system works with 4x current density Li ion diffusion becomes insufficient. Coulombic efficiency values increase with increase in cycle number for all cathode materials. This behavior is explained by stable SEI (Solid Electrolyte Interface) formation after the first few cycles [11]. Fig 5. shows SEM images of LiMn$_2$O$_4$, LiCo$_{0.2}$Mn$_{1.8}$O$_4$, LiMn$_{1.9}$Ni$_{0.1}$O$_4$ cathodes after the electrochemical tests.
The SEM images show that the coatings were able to stay attached on the aluminum substrate surface even at high current densities. However, LiMn\(_2\)O\(_4\) cathode exhibits several cracks on the surface. This result is well expected and points Jahn-Teller transformation. In the presence of Mn\(^{3+}\) ions Mn\(^{2+}\) dissolve in electrolyte after disproportion reaction. During discharge, Li ions are unable to find host material to lithiate due to permanent loss of Mn\(^{3+}\) ions. As a result, the same amount of Li ions generate structure with less Mn\(^{3+}\) ions and form Li\(_2\)Mn\(_2\)O\(_4\) which has tetragonal structure. This cubic-tetragonal transformation leads crack and affect charge/discharge performance negatively. Fig. 6. shows CV graphs of LiMn\(_2\)O\(_4\), LiCo\(_{0.2}\)Mn\(_{1.8}\)O\(_4\), LiMn\(_{1.9}\)Ni\(_{0.1}\)O\(_4\) cathodes.

CV graphs show that delithiation and lithiation processes are driven by two step reversible oxidation and reduction reactions. In first reaction half of the Li ions delithiate from the structure and in second reaction the rest of Li ions are extracted. Reaction voltages are ((4.09 V – 3.94 V);(4.20 V – 4.05 V)), ((4.03 V – 3.96 V);(4.16 V – 4.11 V)), ((4.09 V – 3.92 V);(4.21 V – 4.09 V)) respectively. Anodic and cathodic peak voltage difference decreases with the existence of doping elements. Less peak difference points that less volume expansion occurs inside the structure during cycling [12, 13]. In Fig. 6. a. electrical conductivity decreases with an increase in cycle number. This result is obtained due to the loss of contact (crack formation) between active material and aluminum substrate (Jahn-Teller mechanism) thus capacity value decreases with an increase in the cycle number. In Fig. 6. c. reactions peaks are softer than other CV graphs. Softer reaction peaks indicate high ionic conductivity in the system. As a proof, Ni doped cathode performed high capacity values at high current densities [14].

4. Conclusion

In this study, Co and Ni doped LiMn\(_2\)O\(_4\) cathodes are produced via sol-gel route. The specific capacity-cycle and CV results suggest that Ni doping is the best choice to increase both capacity value and capacity retention rate even at high current densities.

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References