Synthesis and Electrochemical Properties of LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} cathode materials by electrospun process

Chung-Soo Kang\textsuperscript{1}, Jong-Tae Son\textsuperscript{1,*}, Jung-Bin Im\textsuperscript{1}, Syed Abdul Monim\textsuperscript{1}, Hyo-Jin Jeon\textsuperscript{1}, Jong-pil park\textsuperscript{1}
\textsuperscript{1}Department of Nano-Polymer Science & Engineering, Chungju National University
Chungju, Chungbuk 380 - 702, Korea
* Jong-Tae Son (jit1234@cjnu.ac.kr)

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Introduction
The high energy density of LIBs has influenced their current commercial success, but the low rate capability of LIBs has limited their use in important applications such as hybrid electric vehicles (HEVs) and portable power tools that require fast charging and discharging at high power rates. To improve the rate performance and reduce the cost of the electrochemically active electrode, nanostructures materials are usually adopted to solve the kinetic problems associated with the solid-state diffusion of Li\textsuperscript{+} intercalation and electronic conductivity\textsuperscript{[1 ~ 3]}.

Electrospinning of a polymer solution is a novel and efficient fabrication method for preparation of fibrous membrane composed of ultrafine fibers with diameter of several micrometers to tens of nanometers\textsuperscript{[4]}. Electrospinning has the unique ability to produce nano-fibers of different materials with high specific surface area\textsuperscript{[5 ~ 7]}. Also, there have been very few reports on the synthesis of inorganic nano-fibers by electrospinning.

It was reported that nano-structured cathode materials always exhibited better electrochemical performance comparing with ordinary cathode materials, which could be partially ascribed to the decrease of diffused distance for Li\textsuperscript{+} in cathode materials\textsuperscript{[8 ~ 9]}. LiNi\textsubscript{1/3}Co\textsubscript{1/3}Mn\textsubscript{1/3}O\textsubscript{2} nanofibers as cathode materials for lithium ion batteries have been prepared successfully from sol-gel precursors using electrospinning method.

Experiment

2.1. synthesis

The solution for electrospinning was prepared from Polyvinylpyrrolidone[PVP], Deionized Water, Lithium nitrate[LiNO\textsubscript{3}], Nickel nitrate hexahydrate[Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O], Cobalt nitrate hexahydrate [Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O], Manganese nitrate tetrahydrate[Mn(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O], Lithium nitrate[LiNO\textsubscript{3}], Nickel nitrate hexahydrate [Ni(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O], Cobalt nitrate hexahydrate [Co(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O], Manganese nitrate tetrahydrate[Mn(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O] and Polyvinylpyrrolidone[PVP] were added to a solution of water. The mixture was vigorously stirred at room temperature for 24h.

2.2. Electrospinning

The prepared solution was placed in a plastic capillary. The distance between the capillary and the collector was 10cm and the applied voltage was 17kV. The nano-fibers were deposited on the collector, which was dried at 100°C in vacuum for 12h. The dried fibers were calcined at 500°C for 5h in air in order to eliminate the organic residues. The product was calcined at 800°C in atmosphere of Air And Oxygen.

2.3. Characterization

The morphology of the electrospinning fibers was observed with Scanning Electron Microscope. The crystal structure of the nanofibers was characterized by X-ray diffraction instrument.

For electrochemical testing, the cathode was prepared by mixing the nanofibers with Super P and PVdf(10wt%) in a weight ratio of 80 : 10 : 10. The mixture was dried for 24h at 120°C. The test cell was assembled with the cathode as prepared, lithium metal as anode and polypropylene film as separators. The assembling wa performed in an argon-filed glove box. Charge-discharge and Cyclic voltammogram experiments were performed in the voltage range of 3.0 - 4.5V. Impedance spectroscopy were carried out at room temperature. The frequency was varied from 0.2MHz to 3mHz with an alternating-current signal amplitude of 10mV. Nyquist plots(Z’ vs –Z”) were collected and analyzed using Zplot and Zview software.
Result and Discussion

The XRD pattern of the fibers at different heating atmospheres were applied. Figure 1 show the XRD patterns of (a) the calcined nanowire in atmosphere of Oxygen and (b) the calcined nanowire in atmosphere of Air. Both the XRD patterns of (a) and (b) correspond to the patterns of the LiNi⅓Co⅓Mn⅓O₂ without any impurity phase. The calculation from the calcined nanowire in Oxygen atmosphere of XRD pattern gave the unit cell parameters of a = 2.8567 Å, c = 14.2246 Å, cell volume = 100.5426 Å³ and the lattice parameter of the calcined nanowire in Air atmosphere calculated a = 2.8611 Å, c = 14.1964 Å, cell volume = 100.6431 Å³. When analyzing the above results, These results are assumed that the manganese to increase the structural stability by having a low balance.

Table 1. The lattice parameter, average size of crystallites calculated from XRD results.

<table>
<thead>
<tr>
<th>Atmosphere</th>
<th>Parameter</th>
<th>Value (Å)</th>
<th>Sigma</th>
</tr>
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<tbody>
<tr>
<td>Oxygen</td>
<td>a</td>
<td>2.8567</td>
<td>0.0001</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>14.2246</td>
<td>0.0006</td>
</tr>
<tr>
<td></td>
<td>cell volume</td>
<td>100.5426</td>
<td>0.0066</td>
</tr>
<tr>
<td>Air</td>
<td>a</td>
<td>2.8611</td>
<td>0.0002</td>
</tr>
<tr>
<td></td>
<td>c</td>
<td>14.1964</td>
<td>0.0007</td>
</tr>
<tr>
<td></td>
<td>cell volume</td>
<td>100.6431</td>
<td>0.0113</td>
</tr>
</tbody>
</table>

The SEM morphology of LiNi½Co½Mn½O₂ fibers calcined in atmosphere of Oxygen shows that the diameter of the fibers are mainly around 100nm – 800nm, with minor less than 100nm, we could clearly investigate the agglomeration of calcined nano-powders in Air atmosphere. The fibers diameter could be controlled by adjusting the heating atmosphere and applied voltage. In samples calcined oxygen atmosphere, the reduction of agglomeration is considered by flowing gas. But that does not know the specific reasons.

The initial charge-discharge curves LiNi½Co½Mn½O₂ nanowires in the range of 3.0 – 4.5V at 0.5C are shown in Fig 3. All the charge-discharge profiles have a potential plateau around 3.6 – 3.8V, which matches well to the typical layer structured LiNi½Co½Mn½O₂. In the first cycle, the cathode materials show discharge capacity of 172.81 and 139.42mAh/g-1. The difficult solid state diffusion of Li⁺ was considered as a vital factor for the limitation in rate capability. The nanofibers might be used to reduce the diffusion distance of Li⁺ in the solid state.

As shown in the impedance results(Fig. 5), We speculated that the enhanced electrochemical properties resulted from the reduced interfacial resistance between cathode and electrolyte due to the heating atmosphere. These results matches with the XRD and SEM analysis. Transition metal layer and the surface shows the characteristics by the atmosphere during heat treatment. Thus, electrochemical impedance spectroscopy(EIS) suggest to be due to the above results.

Conclusions

The morphology of nanofibers was investigated by scanning electron microscope(SEM). The result show that the diameter of LiNi½Co½Mn½O₂ fibers was in the range of 100 - 300nm. X-ray diffraction(XRD) and electrochemical experiment were used to characterize its structure and electrochemical properties.
Figure 2. SEM and FE-SEM images of the LiNi\textsuperscript{1/3}Co\textsuperscript{1/3}Mn\textsuperscript{1/3}O\textsubscript{2} nanowire (a, b) SEM images of the calcined nanowire in Air atmosphere, (c, d) SEM images of the calcined nanowire in Oxygen atmosphere, (e, f) FE-SEM images of the calcined nanowire in Oxygen atmosphere

Figure 3. Initial Charge - discharge curves of (a) the calcined nanowire in Oxygen atmosphere, (b) the calcined nanowire of LiNi\textsuperscript{1/3}Co\textsuperscript{1/3}Mn\textsuperscript{1/3}O\textsubscript{2} in Air atmosphere

Figure 4. Performance cycles of (a) calcined nanowire in Oxygen atmosphere of LiNi\textsuperscript{1/3}Co\textsuperscript{1/3}Mn\textsuperscript{1/3}O\textsubscript{2}, (b) calcined nanowire in Air atmosphere of LiNi\textsuperscript{1/3}Co\textsuperscript{1/3}Mn\textsuperscript{1/3}O\textsubscript{2}
Nano-cathode materials using electrospinning are expected to have improving electrode properties due to the short diffusion distance of Li$^+$ cations and its high surface areas for enhancing kinetic process. This work has made an attractive nano-cathode materials for application in electric vehicles.

References