Research Article

Synthesis and Characterization of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ as Cathode Materials for Lithium Ion Batteries at 55°C

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A series of materials based on the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ system were prepared by a sol-gel method, and their phase formation processes, crystal structures, and electrochemical performances were studied by thermogravimetric analyses (TG/DTG), X-ray diffraction (XRD), charge-discharge tests, and cyclic voltammetry (CV). The XRD patterns indicate that the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ powders with better crystalline structure could be obtained at calcining temperature 850°C for 20 h under air atmosphere and show that the chlorine addition may induce the change of lattice parameters. The charge-discharge tests show that both the specific capacities and capacity retentions of Cl-doped materials increase compared to the undoped material, especially for the capacity retention at the high-voltage region. At 55°C, the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-0.10}\text{Cl}_{0.10}$ cathode material shows the highest initial discharge capacity of 180.1 mAh·g⁻¹ and the best capacity retention with the value of 91.9% after 100 cycles in the region of 2.0–4.4 V at 0.1 C, while the initial discharge capacity is 208.2 mAh·g⁻¹ when the charge cutoff voltage is up to 4.6 V.

1. Introduction

Lithiumion batteries have been investigated extensively by people for their high working voltage, high energy density, and long cyclic life to be used in electronic devices and power tools. A significant challenge of lithiumion battery improvement is to find a proper cathode material as an attractive candidate of next-generation cathode materials to replace LiCoO_2 . Although LiCoO_2 is the predominant cathode material, its high cost and toxicity limit its further development. Recently, several other positive electrode materials, such as LiNiO_2 , LiMn_2O_4 , $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, and LiFePO_4 , have been researched [1–4]. However, LiNiO_2 suffers from safety and stability problems; LiMn_2O_4 has serious capacity fading problem during cycling, especially at higher temperatures, and LiFePO_4 suffers from lower conductivity [1–3]. Layer-structured $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode material has attracted much attention for it integrates the features of LiCoO_2 , LiNiO_2 , and LiMn_2O_4 with higher structural stability, higher capacity, lower cost, higher safety, and so on. It has been found that the predominant oxidation states of Ni, Co, and Mn are +2, +3, and +4,

respectively. Ni^{2+} and Co^{3+} are electrochemically active for redox reaction; however, Mn^{4+} is electrochemically inactive to stabilize the crystal structure [4, 5]. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ has been studied extensively because it has fast capacity fading due to the electrolyte decomposition and the structural decay of the electrode itself [6–8]. Moreover, the degree of capacity fading increases with the increase of charge cutoff voltage, in which is mainly due to gradual decaying of electroactive Co [4]. In general, it is believed that the valence of transition-metal ions changes during Li^+ intercalation and deintercalation. Tsai et al. [9] reported that the whole Ni^{2+} ions are oxidized to Jahn-Teller active Ni^{3+} ions, which two-step redox reactions of $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ occur during cycling, and the initial irreversible capacity is mainly due to that a part of Ni^{3+} and Ni^{4+} cannot be reduced to Ni^{2+} and also proved that the function of oxygen is to be the electron donor at the end of charge. It may be an effective way that partial O^{2-} substitution by F^- would enhance the electrochemical performance [10–12]. However, the fluorine addition could lower the conductivity as F^- is harder to lose electrons than O^{2-} . Li et al. [13] reported that chlorine

TABLE 1: Lattice parameters of the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ cathode material.

x	a (Å)	c (Å)	c/a	V (Å ³)	I_{003}/I_{104}
0.00	2.858	14.228	4.978	100.61	1.32
0.05	2.861	14.231	4.974	100.89	1.38
0.10	2.861	14.249	4.980	101.01	1.37
0.15	2.862	14.254	4.980	101.11	1.37

addition may increase the specific capacity and enhance the cyclic stability of $\text{LiNi}_{0.7}\text{Co}_{0.3}\text{O}_2$, which is conducive for their electrochemical performance due to that Cl^- is easier to lose electrons than O^{2-} . Sun et al. [14] also reported that Cl-doping has improved the high-rate capability of LiFePO_4 owing to the improvement of the Li^+ ion diffusion.

The goal of this work is to synthesize the Cl-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials and understand the effect of chlorine addition on the structure and electrochemical properties of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, especially at higher temperature. Because more and reliable results could be obtained by measuring the high temperature charge-discharge performance. To our knowledge, this is the first time to report Cl-doped $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials.

2. Experimental

2.1. The Preparation of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ Powders. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ ($x = 0.00, 0.05, 0.10, 0.15$) powders were prepared via a sol-gel route using citric acid as chelating agent. A stoichiometric amount of $\text{LiCH}_3\text{COO} \cdot 2\text{H}_2\text{O}$ (AR), $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR), $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR), $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (AR) and $\text{LiCl} \cdot \text{H}_2\text{O}$ (AR) was dissolved in deionized water, and then the aqueous solution of citric acid was added to the mixture of metal ion solution. The pH was adjusted to 7~8 by ammonium hydroxide. The reagent solution was stirred continuously at 80°C until homogeneous sol-gel formed. The resulting gel was dried at 120°C for 8 h and then heated at 500°C for 6 h to eliminate the organic residues. The powders were thoroughly ground and then calcinated at 850°C for 20 h in air and followed by quenching to room temperature.

2.2. The Characterization of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ Powders. TG/DTG was used to analyze the thermal process and phase formation process of the gel precursor from 50°C to 1000°C at a rate of 10°C/min under a nitrogen atmosphere.

The X-ray diffraction (XRD) with Cu K α radiation operated at 40 kV and 40 mA was used to analyze the crystalline structure of samples. The scan data were in the 2θ range from 10° to 90° in a step of 4°/min.

The electrochemical properties of samples were carried out using two-electrode coin cells (type CR2032) assembled in an argon filled glove box. The positive electrodes were prepared by blending 80% active material, 12% acetylene black, and 8% polyvinylidene fluoride in N-methyl-2-pyrrolidone (NMP). Then the slurry was spread on an aluminum foil as current collector using the Doctor-blade technique and

dried at 80°C for 10 h in a vacuum oven. Microporous polypropylene membrane (Celgard 2325) was used as the separator. The electrolyte is LB-315 which consists of a 1 M LiPF_6 solution in DMC : EMC : EC (1 : 1 : 1, v/v/v). The charge-discharge was tested in the potential range of 2.0~4.4 or 4.6 V at different rates at elevated temperature (55°C) by using the instrument Land2001T.

The cyclic voltammogram (CV) curves were obtained between the cutoff voltage ranges of 2.0~4.8 V on an IM6 electrochemical workstation at a scan rate of 0.1 mV/s.

3. Results and Discussion

3.1. TG-DTG Analysis. TG-DTG curves of the gel precursor of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-0.10}\text{Cl}_{0.10}$ are shown in Figure 1. There is little change in the two profiles. The first weight loss occurs at the range of 100~200°C, which corresponds to the removal of water molecules staying in the gel surface and the crystallization water of the acetates. The second weight loss is due to the decomposition of citric acid and the decomposition of anhydrous acetate to produce $\text{CH}_3\text{COCH}_3(\text{g})$ and metal carbonates in the temperature region of 200°C ~400°C [15]. A slow weight loss could be observed between 400~800°C in the curve, which is attributed to conversion of the metal carbonates into $\text{MO}(\text{s})$, $\text{CO}_2(\text{g})$, and $\text{CO}(\text{g})$. There is little weight loss to be observed over 800°C, which indicates that the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ phase has formed at around 800°C.

3.2. X-Ray Diffraction Analysis. Figure 2 shows the typical X-ray diffraction patterns of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ ($x = 0.00, 0.05, 0.10, 0.15$) cathode materials by calcining at 850°C for 20 h in air atmosphere. The XRD patterns of samples show that no impurity phase exists, which indicates that the samples have the hexagonal $\alpha\text{-NaFeO}_2$ structure (space group, $R\bar{3}m$). The clear peak splits of (006)/(102) and (108)/(110) doublets exhibit a high degree of ordered hexagonal layered structure. Table 1 presents the lattice parameters of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ ($x = 0.00, 0.05, 0.10, 0.15$) cathode materials. The integrated intensity ratio of (003)/(104) peak is more than 1.2 for all samples, and the biggest ratio 1.38 is obtained when the chlorine content is 0.10, suggesting that a small amount of Cl^- substitution for O^{2-} could suppress occupancy of Li^+ layers by Ni^{2+} and be conducive to the performance during electrochemical cycling [16]. The crystal structure has a little difference after chlorine doping, indicating the heteroelement has been incorporated into the $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ structure [17, 18]. The increase of lattice parameter a may be attributed to the valence balance by the chlorine doping leading to Mn^{4+} (0.53 Å) transform to Mn^{3+} (0.58 Å) or Co^{3+} (0.545 Å) transform to Co^{2+} (0.65 Å) in these compounds [19], while the increase of lattice parameter c may be due to the difference of radius between Cl^- (1.81 Å) and O^{2-} (1.40 Å). Furthermore, the c/a ratio is greater than 4.9, which reveals a high cation ordering of the synthesized compounds [20].

FIGURE 1: TG/DTG curves of the gel precursor of (a) $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and (b) $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-0.10}\text{Cl}_{0.10}$.

FIGURE 2: XRD patterns of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ cathode materials.

FIGURE 3: Initial charge-discharge curves of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ cathode materials.

3.3. Electrochemical Studies. The initial charge-discharge curves of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ ($x = 0.00, 0.05, 0.10, 0.15$) over a voltage range of 2.0–4.4 V at 55°C are shown in Figure 3. As for the initial discharge capacity, the materials exhibit 170.2, 178.9, 180.1, and 179.7 $\text{mAh}\cdot\text{g}^{-1}$, respectively, and the initial coulombic efficiencies are 90.4%, 93.3%, 93.0%, and 95.7%, respectively, for $x = 0.00$ to 0.15 at a current rate of 0.1 C. The 95.7% initial coulombic efficiency may be the highest value for $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in the world as we have known.

That the Cl-doped materials have higher discharge capacities than bare materials is attributed to the valence balance caused by chlorine addition, which may lead Ni^{3+} and Ni^{4+} to almost be completely reduced to Ni^{2+} , decreasing the initial irreversible capacity [9]. Another reason is due

to that Cl-doped materials have lower electrostatic repulsions between O–M–O interlayers in the process of Li^+ insertion/deinsertion for Cl^- has one valence electron less than O^{2-} , which is beneficial for the removal of Li^+ insertion/deinsertion [13]. Furthermore, the initial irreversible capacity loss of the materials also may be involved with the formation of surface electrolyte interphase (SEI) film [21].

The cyclic performance and rate capability of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ ($x = 0.00, 0.05, 0.10, 0.15$) cathode materials are illustrated in Figure 4. All cells were operated by the steps of 2 cycles at 0.1 C, 3 cycles at 0.15 C, 5 cycles at 0.25 C, 87 cycles at 0.5 C, and the final 3 cycles at 0.1 C between 2.0 V and 4.4 V. At the 97th cycle the discharge

FIGURE 4: Cyclic performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ cathode materials at different rates.

FIGURE 5: Initial charge-discharge curves of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ cathode materials.

capacities at 0.5 C are 101.2, 125.7, 139.1, and 129 $\text{mAh}\cdot\text{g}^{-1}$, which are 70.6%, 83.7%, 91.9%, and 85.5% of the 11th cycle at 0.5 C for $x = 0.00$ to 0.15, respectively. And after 100 cycles the capacities at 0.1 C are 82.4%, 89.9%, 91.8%, and 89.3% of the initial discharge capacity at 0.1 C, respectively.

It is worth noting that Cl-doped materials exhibit high discharge specific capacity, excellent cyclic stability, and good rate performance. The ion radius of Cl^- is larger than O^{2-} , expanding pathway for Li^+ to intercalate and deintercalate. Moreover, Li et al. [13] reported that Li^+ can be more freely deintercalated due to that Cl^- is easier to lose electron than O^{2-} . However, the structural stability slightly decreases with the increase of chlorine content; one reason may be for larger lattice parameters c and V and the other may be due to valence balance. So the capacity retention for $x = 0.15$ is lower than that with the chlorine content of 0.10.

FIGURE 6: Cyclic performance of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ cathode materials at different rates.

Figure 5 shows the initial charge-discharge curves when the charge cutoff potential is up to 4.6 V at 0.1 C. The initial discharge capacities are 202.1, 206.2, 208.2, and 207.7 $\text{mAh}\cdot\text{g}^{-1}$, respectively, and the initial coulombic efficiencies are 83.4%, 86.0%, 85.6% and 91.1% for $x = 0.00$ to 0.15, respectively. The initial coulombic efficiency decreases with the increase of charge cutoff potential. Figure 6 shows the cyclic performances and rate capabilities of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ ($x = 0.00, 0.05, 0.10, 0.15$) cathode materials between 2.0 V and 4.6 V. All cells were operated by the steps of 2 cycles at 0.1 C, 3 cycles at 0.15 C, 5 cycles at 0.25 C, and the final 50 cycles at 0.5 C. The discharge capacities of the 11th cycle at 0.5 C are 166.4, 170.9, 175.6, and 171.1 $\text{mAh}\cdot\text{g}^{-1}$, respectively; and at the 60th cycle the discharge capacities are 71.2%, 83.4%, 92.2% and 80.6% of the 11th cycle at 0.5 C for $x = 0.00$ to 0.15, respectively. It is worthy to note that the discharge capacity increases but leads to fast capacity fading with the increasing of cutoff voltage, especially for the bare material. Kim et al. [19] have reported that the capacity fading is mainly due to the Co dissolution during cycling in high voltage cutoff. However, the Cl^- doping leads to improvement in capacity retention at the high-voltage region, which indicates that chlorine addition has enhanced the electrochemical performance.

3.4. Cyclic Voltammetry (CV). Figure 7 presents the first cyclic voltammogram curves of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ cathode materials in the voltage range of 2.0–4.8 V at a scan rate of 0.1 mV/s. Evidently two redox peaks at 4.078/3.632 V and 4.608/4.497 V are found in the curve of bare sample, indicating that two phase transitions occurred in the charge-discharge process. Shaju et al. [4] have reported that the large redox peak and the small redox peak are corresponding to $\text{Ni}^{2+/4+}$ and $\text{Co}^{3+/4+}$, respectively. It is reported that the capacity fade of the layer-structured

FIGURE 7: Cyclic voltammograms for the first curves obtained from $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ for (a) $x = 0.00$; (b) $x = 0.05$; (c) $x = 0.10$; (d) $x = 0.15$.

cathode materials is associated with structural transitions from hexagonal to monoclinic to hexagonal modifications at potentials above 4.1 V [22, 23]. There is only one redox peak in the curves of Cl-doped materials, which means that Cl^- , as a doping material, suppresses the structure transitions from hexagonal to monoclinic structure.

4. Conclusions

The $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{2-x}\text{Cl}_x$ ($x = 0.00, 0.05, 0.10, 0.15$) cathode materials have been successfully synthesized by a sol-gel method. Partial O^{2-} substitution by Cl^- increases the lattice parameters c , and V . $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{1.90}\text{Cl}_{0.10}$ cathode material shows higher initial discharge capacity of $180.1 \text{ mAh}\cdot\text{g}^{-1}$ at 0.1 C in a voltage range of 2.0–4.4 V, and

the capacity retention was 91.9% after 100 cycles at 55°C , while for the undoped material they are $170.2 \text{ mAh}\cdot\text{g}^{-1}$ and 82.4%, respectively. It should be confirmed that a small amount of Cl doping could improve the cyclic property of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ a great deal and also increase the discharge capacity. Although the initial discharge capacity increases when the charge cutoff voltage is up to 4.6 V, the capacity retention and rate capability for the bare material decrease. Chlorine addition has improved the electrochemical performance in the higher charge cutoff voltage. CV shows that only one redox peak is observed for Cl-doped materials, which means that there is no structural transition from hexagonal to monoclinic in this area. Chlorine doping has been demonstrated to be a good way for improving the property of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_{1.90}\text{Cl}_{0.10}$

would be a promising candidate cathode material for next generation Li-ion battery.

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