The Properties of Layered Cathode Material LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 with Fe-doping

Li Mingli^{1,2,*}, Yu Qiong^{1,2}, Zhao Jie^{1,2}, Ma Lan^{1,2}, Xu Wei^{1,2}, Qin Guanghe^{1,2}

^{1}Ningbo Branch of China Academy of Ordnance Science, Ningbo 315103, China;
^{2}Ningbo United New Material Research Institute, Ningbo 315040, China)

Abstract. A layered cathode-active material LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 was synthesized by sintering the admixture of oxalate co-precipitation powder of Cobalt, Nickel, and Manganese and Li_2CO_3. The influence of Fe-doped on the structural and electrochemical properties of LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 was characterized by XRD, SEM, BET and electrochemical experiments. The results reveal that LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 with small amounts (≤6%) of Fe-doping keeps the α-NaFeO_2 layered structure. As the doping content increases, the lattice parameters increase and the random stacking happens. The average particle size is about 0.3-0.4 μm and the specific surface area decreases. The Fe-doping improved charge and discharge capacity. The 2% Fe-doped materials deliver an initial charge and discharge capacity of 243.2 and 167.4mAh∙g^{-1}.

1. Introduction

Lithium ion battery has been used widely as an energy source in a portable electronic device since it has been commercialized in Japan in the early of 1990’s. The cathode material is LiCoO_2 and many recent reports address the problem in synthesizing a cheaper, high-capacity, and safer layered cathode material then this. One of the promising candidates, LiNiO_2, has large capacity and good rate capabilities but shows a high instability in its layered structure at a high voltage above 4.5V which may result in a battery hazard on overcharge or under unexpected abuse conditions that it has failed to replace LiCoO_2. On the other hand, LiMn_2O_4, another candidate to replace LiCoO_2, shows good structural stability on overcharge but has low capacity and high reactivity with electrolyte at elevated temperature above 55℃.

A layered compound, LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2, which was first proposed by Ohzuku and Shaju K M, has been extensively studied as a promising cathode material for lithium ion batteries. It has many advantages over other candidates, such as a high discharge capacity, high rate capacity and good structural stability. It has the same crystalline structure as LiCoO_2 does, the R-3m, and is not simple solid solution of LiCoO_2, LiNiO_2 and LiMnO_2 due to the fact that formal charges on Co, Ni and Mn were estimated theoretically and confirmed experimentally to be +3, +2 and +4, respectively, instead of +3 for all 3d-metals as in the case of solid solution. This material shows the rechargeable capacity of about 200mAh∙g^{-1} in the voltage range from 2.5 to 4.6V. The thermal behavior of the fully charged state for LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 with electrolyte is much better than that of LiCoO_2 or LiNiO_2. Above all, LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2 is one of the most possible candidates with good electrochemical performances, safety, low toxicity and low cost.

However, there are a few drawbacks with LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2. The structure of LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2 (space group R3m) has a Li ion at the site of 3a, the transition metal ions at the 3b and the O ions at the 6c sites, respectively. With similar radius of the occupancy Li^+ ions and Ni^{2+} ions interchange
partially resulting disorder in the structure, which deteriorates the structural stability and the electrochemical performance. Partial substitution has been proved an effective method in modifying the electronic structure and improving the electrochemical performances of the cathode materials. Doping small amounts of additional ions such as Mg\(^4\), F\(^5\), Mo\(^6\) into the Li(Ni\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\))O\(_2\) lattice have been reported to improve structural stability and enhance the cycling performance. Si-F co-doping into Li(Ni\(_{1/3}\)Co\(_{1/3}\)Mn\(_{1/3}\))O\(_2\) have been reported by Kim. Composite doping was effective for the improvement of physical properties, which enhanced the capacity and thermal stability, even though the cells were cycled between 2.8V and 4.6V.

Lithium transition metal oxides LiMO\(_2\) (where M is a 3d transition metal) are amongst the most studied materials for high capacity cathodes in secondary lithium batteries. Generally, the structures of these materials are based on the sodium chloride lattice with the oxygen atoms in the close packed fcc sites and the cations filling all the octahedral interstices. In this paper, the role of 3d transition metal Fe on Fe-doping LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\) materials was analyzed. We synthesized different contents of Fe-doping LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\). The effects of Fe-doping on the structural properties, morphology and electrochemical performance were studied. The results were also compared with that of LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\).

2. Experimental

2.1. Materials preparation
Ni(NO\(_3\))\(_2\)·6H\(_2\)O, Co(NO\(_3\))\(_2\)·6H\(_2\)O (all are 99.9% in purity) and Mn(NO\(_3\))\(_2\) (50% aqueous solution) with some 5wt.% PEG-1540 were dissolved in distilled water to obtain a starting solution. The aqueous solution of the metal nitrates and some 5wt.% PEG-1540 were dripped and mixed in a stirred reactor. The pH value of the mixture was regulated to 9 by changing the dripping rate of NH\(_3\)·H\(_2\)O. The temperature 60\(^\circ\)C, pH value 9 as well as the stirring speed of the mixture were controlled carefully. And the oxalic acid C\(_2\)H\(_2\)O\(_4\)·H\(_2\)O was added to get the oxalate co-precipitation. This led to the oxalate co-precipitation of Ni, Co and Mn with a homogeneous cation distribution. After rinsing filtering the precipitate was dried and the contents of Ni, Co and Mn were calculated by spectrophotometer. And then the co-precipitation was mixed with a stoichiometric amount of Li\(_2\)CO\(_3\) and Fe\(_2\)O\(_3\) at Fe molar content of 0%, 0.3%, 2%, 6% and ball-milled for 3h. 0.5% excess of lithium hydroxide was added to compensate for the Li loss by volatilization. The solid mixture was heated at 450\(^\circ\)C for 5h. By calcinating the powder at 900\(^\circ\)C for 15h was the final product obtained. All the above operations were carried out in air.

2.2. Materials characterization
The XRD measurement was carried out using a BDX-3300 diffractometer equipped with a monochromator and Cu target tube. The scan electron microscope (FESEM) study of the samples was performed by XL-30(PHILIPS) electron microscope. The specific surface area for each sample was analyzed by the Brunauer, Emmett, and Teller (BET) method using Quantachrome Instrument made in USA, in which a N\(_2\) gas adsorption was employed. Each sample was heated to 200\(^\circ\)C for 20 min to remove adsorbed water before measurement.

2.3. Preparation of lithium batteries
The cathode was prepared by mixing the active material with carbon black and polyvinylidene fluoride PVDF 7.5wt. % dissolved in n-methyl-2-pyrrolidinone (NMP) in a weight ratio of 80:10:10. The mixture was pressed onto a piece of Al foil used as the current collector and dried under vacuum at 120\(^\circ\)C for 12h. The laboratory pouch cells consisting of the cathode, the lithium foil as an anode, 1M LiPF\(_6\)-EC/DMC (1:1 in volume) as an electrolyte and Celgard 2400 as the separator were assembled into CR2430 type coin cells in an argon-filled glove box. Electrochemical properties were examined
were performed on the cells between 2.8 and 4.6 V versus Li/Li⁺ at 0.1 C of a constant current at 30°C with a Neware Battery Testing System.

3. Results and discussion

3.1 XRD analysis
XRD patterns of LiNi₁/₃Co₁/₃Mn₁/₃O₂ of Fe-doping for 0, 2%, 6% are shown in Fig. 1. and the peaks of (101), (006), (102), were magnified. The entire fingerprint peaks, i.e., (003), (101), (006), (102), (104), (105), (108), (110), and (113) are easily identifiable in the sample thereby suggesting the formation of the α-NaFeO₂ structure. The diffraction pattern shows a clear splitting of hexagonal characteristic doubles (006)/(012) and (018)/(110). These indicate that the samples possess typical layered characteristics and have R-3m layered structure without any impure phase. These two figures show that the oxalate co-precipitation powder of Cobalt, Nickel, and Manganese, Fe₂O₃, and Li₂CO₃ had solid-state reacted sufficiently and all the obtained materials are well crystallized and pure in phase.

Fig.1 Evolution of the XRD patterns of LiNi₁/₃Mn₁/₃Co₁/₃O₂, with different Fe contents, with an enlargement of a small region shown on the right.

3.2 Morphology and specific surface area analysis
The field-emission SEM (FESEM) images of LiNi₁/₃Co₁/₃Mn₁/₃O₂ materials of Fe-doping for 0, 0.3%, 2%, 6%, are shown in Fig. 2. The specific surface areas analyzed by BET method for each sample are showed in Table 1. The Fe-free LiNi₁/₃Co₁/₃Mn₁/₃O₂ has a relative uniform particle distribution ranging from 300 to 400 nm and has a well-shaped, smooth of crystals with sharp edges morphology. With increasing Fe content, the primary particle size and the shape of the primary particles do not obviously change, but the specific surface areas decreased according to Table 2. The morphology of D sample is particle-agglomerated, crumbling, and the specific surface area is nearly decreased by 50% than the sample of LiNi₁/₃Co₁/₃Mn₁/₃O₂. Therefore, the grains agglomerate much more closely as the Fe content increases, which is useful to the improvement of tap density.
Fig. 2 SEM images of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ for Fe-doping of (A)x=0, (B)x = 0.003, (C)x=0.02, (D)x=0.06.

Table 1 The specific surface areas analyzed by BET method for each sample

| Fe content | 0% | 2% | 6% |
|------------|----|----|----|
| specific surface area (m$^2$/g) | 5.355 | 4.043 | 2.869 |

3.3. Electrochemical properties

Fig. 3(A) shows the typical initial charge-discharge curves of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ materials with the content of Fe for 0, 0.003, 0.02 and 0.06. The cell was cycled between 2.8 and 4.6 V at a charge/discharge current density of 0.1C at room temperature. As shown in Fig. 3, all the cells display stable and smooth charge/discharge curves without any plateaus. This indicates that no spinel-related phases are formed during charging and discharging.

The first discharge capacities of the four samples with the content of Fe for 0, 0.3%, 2%, 6%, are 135.7, 148.6, 167.4 and 142.3 mAh·g$^{-1}$, respectively. Table 3 shows the initial charge and discharge capacities of Fe-doping materials increase compared to Fe-free LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$. Moreover, the Fe-substituted materials exhibit higher charge voltages according to Fig. 3A.

The cycling performance for the prepared Fe-doping materials is illustrated in Fig. 3(B). Both samples exhibited no better cycle abilities compared to Fe-free LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$. Nevertheless, the Fe-added material has the higher reversible capacity of 127.6mAh·g$^{-1}$ than that of LiNi$_{1/3}$Mn$_{1/3}$Co$_{1/3}$O$_2$ (119.8mAh·g$^{-1}$) after 10 cycles. The voltage plateau at 3.75V for LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (x = 0) is assigned to its Ni$^{2+}$/Ni$^{4+}$ reaction.

It is seen that the lithiation (discharge) plateau rises monotonously when the amount of Fe-doping increases from 0 to 0.02 for LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ (Fig. 3.A), but does not with the Fe content of 6%. This implies that the rise of discharge voltage plateau of Fe-doped LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ results from the polarization effect rather than from the drop of chemical potential of the material due to Fe doping. Actually Ceder and co-workers predicted that Fe doping lowers the operation voltage of LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$. The polarization effect becomes more severe with increasing Fe content. The reason for the decreased capacity of the Fe-doped LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$ is more complicated.

On one hand, the Fe$^{3+}$ ion is possibly electrochemically active for the cutoff charge/discharge voltages in this work (2.8-4.6V). Therefore, the active species increased with Fe$^{3+}$ content increasing in LiNi$_{1/3}$Co$_{1/3}$Mn$_{1/3}$O$_2$. Also, the expansions for lattice parameters of Fe-doping samples represent larger room for the moving of lithium, as the mobility of the Li$^+$ ions decreases more for the Fe-doped host than for the Fe-free one.

On the other hand, it is deduced that the doped Fe atoms tend to occupy the 3a sites as well as the 3b sites, especially after deep charge of the Fe-doping materials. The Fe atoms at the 3a sites hinder the diffusion of the Li ions also located at the 3a sites. This will lead to decrease of ionic conductivity and increase of polarization of the material. Because of this, a sudden decrease of Li ion mobility takes...
place. This will lead to “irreversible capacity” and descending capacity retention. This phenomenon can occur for almost all kinds of LiNi1/3Co1/3Mn1/3O2 doped, but the degree is different.

However, as the mobility of the Li+ ions increases more for the Fe-doped host than for the Fe-free one, the discharge capacity of Fe-doped LiNi1/3Co1/3Mn1/3O2 is more obvious. The lost capacity for this reason can be recovered by sufficiently decreasing the current density for discharge. As Fe3+ is introduced into LiNi1/3Co1/3Mn1/3O2 by mixing the co-precipitates of Ni2+, Co3+ and Mn4+ with fine Fe2O3 powder in this work, it becomes difficult for the Fe3+ ions to distribute homogeneously in the final product when the Fe content is high. This might be also an important reason for the poor cycling performance of high-content (≥6%). Above all of these critical points, the impacts of Fe doping show positive effects on the discharge capacity but does not improve the cycling performance of LiNi1/3Co1/3Mn1/3O2.

Fig.3 (A) Initial discharge curves          (B) Cyclic performances profiles
of samples with Fe-doping of 0, 0.3%, 2%, 6%, cycled at a current density of 0.1C in the voltage of 2.8-4.6V.

4. Conclusions
Fe-substituted LiNi1/3Co1/3Mn1/3O2 have been prepared by firing the co-precipitates of Ni, Co and Mn hydroxides. All the prepared materials have α-NaFeO2 layered structure without any impure phase as LiNi1/3Co1/3Mn1/3O2 does. All the materials have a relative uniform particle distribution ranging from 300 to 400 nm and have a well-shaped, smooth of crystals with sharp edges morphology. The morphology does not change much by adding Fe, but the specific surface areas were decreased.

Comparison of the electrochemical performances of Fe-free and Fe-doped LiNi1/3Co1/3Mn1/3O2 indicates that Fe-doping series of materials show better discharge capacities. This maybe related to the expansion of lattice parameter a and c for LiNi1/3Co1/3Mn1/3O2 materials with increasing Fe content, improves the diffusion of its Li+ ion. Also, Fe-doping makes the delithiation potential plateau of LiNi1/3Co1/3Mn1/3O2 higher indicating the electrochemical activity was improved.

However, it seems that Fe doping cannot improve the reversible cycling electrochemical performances of LiNi1/3Co1/3Mn1/3O2. The reversible discharge capacity of Fe-substituted LiNi1/3Co1/3Mn1/3O2 drops for different reasons. According to the analysis of XRD the integrity of layered structure declines by Fe-doping due to the disordered occupation of the doped Fe ions at the 3a sites. In contrast, low-content (2%) Fe doping improves the charge and discharge capacity of LiNi1/3Co1/3Mn1/3O2.

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