Electrochemical properties study on NCM622 by in suit modification of Mg and F

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Abstract: With the rapid development of portable electronic products and electric cars, higher requirements are put forward for the performance of high energy density lithium ion battery. Nickel-rich layered metal oxides with higher energy density and lower raw material cost are considered as ideal cathode materials for lithium ion batteries. However, the structural defects and unstable interfacial chemical properties make the electrochemical properties degrade and reduce the safety of the material. Based on the previous work, this project synthesized NCM622 materials by solid phase method, and studied the influence of F, Mg and MgF2 on the comprehensive electrochemical properties of NCM622 materials. The relationship between microstructure and electrochemical properties of the materials was studied.

1. Introduction

In recent years, with the popularity of electronic products, the demand for batteries, especially lithium ion batteries, is increasing [1,2]. As cars enter homes, air pollution in large and medium-sized cities in China is mainly caused by automobile exhaust emissions. One of the effective ways to deal with the fuel and pollution of automobiles is to develop electric vehicles. Lithium-ion batteries have attracted the attention of many scholars because of their advantages of low cost, environmental protection, low toxicity, no memory effect and high energy density [3]. However, as a power battery, lithium ion battery anode material must have a high specific capacity. At present, the cathode materials used in lithium ion batteries mainly include lithium iron phosphate, ternary materials (NCM) and lithium cobalt oxides [4,5,6]. Lithium iron phosphate has high safety and long cycle life, but it has poor conductivity. Lithium cobalt oxide is toxic and easy to pollute the environment. At present, most manufacturers mainly use 333,523 ternary materials, a few manufacturers use model 622. The main advantage of NCM622 materials over high nickel ternary materials is that they have good cyclic stability. In order to further improve its capacity and loop performance, we studied the modification of NCM622 by Mg and F.

2. Experimental

2.1 Materials synthesis

Pristine and in suit MgF2 modified NCM622 materials were prepared via solid-state methods. All chemicals were A.R. purity. A stoichiometric ratio of Li2CO3, precursor NCM622, NH4F or...
Mg(NO3)2 were mixed, and mix them well by stirring at 150 r/min. Then the slurry was dried by dry technique. The mixture was calcined at 500°C for 4h at 5°C/min and 750°C for 10h.

2.2 Materials characterization

The crystal structure and microstructure were identified by powder X-ray diffraction (XRD, ULTIMA IV, Rigaku) with Cu Kα radiation at a step of 0.02° in the range of 10-90°. The surface morphologies of the electrodes were researched by scanning electron microscopy (SEM, Quanta 450, FEI).

2.3 Electrochemical measurements

The working electrode was prepared as follows: A coating slurry was prepared containing 80% pristine and MgF2 modified NCM622, 10% poly-vinylidene fluoride (PVDF), and 10% carbon conductor (Super P) dispersed in N-methyl pyrrolidone (NMP, Aldrich). The mixture was stirred well and spread uniformly over an aluminum foil. The aluminum foils coated with cathode materials were cut into wafer with the diameter of 14mm. Then the wafer was dried at 105°C for 12 hour under vacuum. After the working electrode was prepared. The lithium foil was used as a counter electrode. The electrolyte was 1 mol/L LiPF6 in ethylene carbonate (EC)/diethyl carbonate (DEC)/ethyl methyl carbonate (EMC)(1:1:1 in volume ratio). Coin-type half cells (CR2032) were assembled in an argon-filled glove box (Super (1220/750), Mikrouna, Germany) with the water and oxygen content less than 0.1ppm. The Charge/discharge test was performed on an automatic galvanostatic unit between 2.8 and 4.3 V at different charge/discharge rates at room temperatures.

3. Results and Discussion

Fig.1 XRD patterns of F, Mg and MgF2 modified NCM622

Fig. 1 shows the XRD pattern of cathode electrode material NCM622 synthesized by doping F, Mg and MgF2. As can be seen from Fig. 1, the prepared material belongs to the hexagonal crystal system, and the space group is R-3m. And the structure is α-NaFeO2 type lamellar structure. The peak (111) of the hexagonal crystal system with the structure of α-NaFeO2-type layered structure will split into the peak (006) and (102). The peaks (220) of the hexagonal system split into peaks (108) and (102). Therefore, the degree of two-dimensional order of the layered structure can be measured by the degree of the diffraction peaks (006)/(102) and (108)/(110). And the clear split of (006)/(102) and (108)/(110) peaks indicate that the samples have an ordered layered structure.[7]
Fig. 2 SEM images of pristine (a) and modified samples (F(b), Mg(c) and MgF2(d))

Fig. 2 is the SEM image of the sample modified by F, Mg and MgF2. As can be seen from the Fig. 2, the particles of the sample modified by fluorine, magnesium and magnesium fluoride have smaller particle size and are more uniform than the pristine sample, especially the surface of the MgF2 modified sample become smooth.

Fig. 3 Discharge curve of different samples modified by F, Mg and MgF2

Fig. 3 illustrates the first discharge curve modified by F, Mg and MgF2. It can be seen that the first discharge specific capacity of different substances modified sample is greater than that of the pure sample. The first discharge capacity of Mg-modified NCM622 obtains the largest discharge capacity.

Fig. 4 shows the cycling performance of F and Mg modified NCM622 materials. Table1 shows the cycling performance data. From the Fig and Table, it can be seen that the material of Mg modified obtains the best cycling performance. And the electrochemical properties of modified samples are superior to the pristine sample. The first discharge capacity of Mg modified NCM622 reaches 157.7mAh/g, and after 100 cycles the capacity efficiency is 89.1%, which is 35.3% higher than pristine NCM622 sample.
Fig. 4 Cycling performance of different samples modified by F, Mg and MgF2

Table 1 Cycling data of pristine and MgF2 modified samples

| Sample            | Capacity (mAh/g) | Capacity efficiency (%) |
|-------------------|------------------|-------------------------|
|                   | First cycle      | 100th cycle             |
| NCM622            | 155.6            | 83.7                    | 53.8 |
| F-NCM622          | 156.8            | 113.8                   | 72.6 |
| Mg-NCM622         | 157.7            | 140.5                   | 89.1 |
| MgF2-NCM622       | 157.7            | 136.0                   | 86.2 |

4. Conclusion
The modification of by F and Mg on NCM622 has been studied in this paper. XRD pattern indicate that the samples have an ordered layered structure. And the Mg modified sample has showed the best electrochemical properties. The capacity efficiency of Mg modified sample is 35.3% higher than pristine NCM622 sample.

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