Research on Modification of Ni-rich Lithium Ion Battery by MgO

Rui He1,2, Lihui Zhang1,2, Wen Li1,2, Aijia Wei1,2, Zhenfa Liu1,2*
1Institute of Energy Resources, Hebei Academy of Science, Shijiazhuang, Hebei Province, 050081, China
2Hebei Engineer Research Center for Water Saving in Industry, Shijiazhuang, Hebei Province, 050081, China
* Corresponding author’ email: kxyherui@163.com

Abstract: Rich Nickel transition metal oxides with layered structure are promising cathode materials for LIBs. However, their poor cycling performance limits the expansion of their applications. In my article MgO was used to modify the Ni-rich materials. The crystal structure of the Rich Nickel materials was studied by X-Ray Diffraction(XRD) and Scanning Electron Microscope(SEM). The electro-chemical performance was studied by charge-discharge test. Our results showed that, in the charge/discharge measurement, the electrochemical performance of MgO modified sample is better than unmodified sample. As well as when the MgO radio was 2%, the sample showed the optimum properties. The initial discharge capacity was 184 mAh/g and 155 mAh/g at 0.1C and at 1C, respectively. After 100cycles at 1C, the discharge capacity kept 90% at 1C.

1. Introduction
Compared with lead-acid batteries and nickel-chromium batteries, Lithium ion batteries have some competitive advantages, such as high energy density, less pollution and no memory effect. Therefore, it is widely used in electronic products, power tools and mobile phones[1,2]. With the increasing improvement of production, living standards and increasing concern for environmental issues, lithium ion-powered electric cars have been advocated and gradually entered people's life at present. Meanwhile, a large number of high-end electronic products powered by lithium ion batteries, such as handheld computers and smart phones, are also leading the fashion trend of an era[3,4]. All of these are put higher demand to lithium ion batteries. So the development of advanced anode materials is particularly increasingly urgent. Li[Ni1-x-yCoxMny]O2 materials have higher theoretical capacity of 200 mAhg−1 than that of traditional anode materials, such as LiCoO2, LiMn2O4 and LiFePO4. The layered ternary anode materials combine the advantages of the three materials through the synergistic effect of Ni-Co-Mn, and it has got a lot of attention in the battery industry.

In our study, MgO was used to modify the Ni riched lithium-ion battery anode material via solid-state method. The affect of MgO modification on the structure and electrochemical property was studied.

2. Experimental

2.1. Materials
Blank and MgO modified Ni-rich NCM materials were compound by solid state methods. A ratio of LiOH, precursor NCM811 and MgO was blended and muddlered for 8 h at 150 r/min by dry technique. The compound were sintered at 400°C for 4 h and 800°C for 10 h at 3°C/min.

2.2. characterization
The crystal texture of the blank and modified materials was recognized by powder XRD (ULTIMA IV, Rigaku) with Cu Kα radiation at a step of 0.02° in the range of 10-90°. The samples were tested at 25°C. The morphologies of the materials were researched by scanning electron microscopy (SEM, Quanta 450, FEI)

2.3. Electrolytes measurement
A working electrode was prepared as follows: A coating slurry was prepared by adding 80% LiNi0.8Co0.1Mn0.1O2 (NCM811), 10% poly-vinylidene fluoride, and 10% carbon conductor dispersed in N-methyl pyrrolidone (NMP, Aldrich). The mixture was spread onto an aluminum foil and dried at 80°C for 12H. The electrodes were cut into wafer and have a diameter of 12mm. The counter electrode was lithium foil. The electrolyte was 1 mol/L LiPF6. In an argon-filled glove box (Super (1220/750), Mikrouna, Germany), the Coin-type half cells (CR2032) were assembled. These cells test were carried out at an automatic galvanostatic unit between 2.8 and 4.3 V.

3. Results and Discussion
Blank and MgO-modified NCM811 samples’ X-ray diffraction patterns are manifested in Fig. 1. From Fig. 1 displays that, all of the samples exhibit a typical layered structure in accordance with LiCoO2. The XRD pattern displays that MgO does not change the crystal structure of NCM811. In the XRD patterns, the peak splits of (006)/(102) and (108)/(110) show that all samples have an ordered layered structure.

Fig. 2 shows the SEM images of blank and MgO-modified NCM811. Fig. 2(a) shows the pristine NCM811, and Fig. 2(b) (c) and (d) show the SEM of different concentration MgO modified samples. SEM images displays that all of the samples retained the spherical shape, and there is no obvious difference in morphology between the pristine and MgO-modified ncm811 samples.
Fig. 2 SEM of blank NCM811 and MgO-modified NCM811

Fig. 3 displays the first discharge capacity of blank NCM811 and MgO modified NCM811 from 2.8 to 4.3V at 0.1C at 25°C. The initial specific capacity of pristine NCM811 and MgO modified NCM811 (1wt%, 2wt%, 4wt%) is 170mAh/g, 177 mAh/g, 184 mAh/g and 180 mAh/g, respectively. There is a distinct plateau at about 3.7V on every discharge curve. From Fig. 3 it can be seen that the discharge capacity of MgO modified NCM811 sample is higher than the blank sample, and when the concentration of MgO is 2wt%, the discharge capacity reaches the optimal value.

Fig. 3 First discharge capacity of pristine NCM811 and MgO-modified NCM811
Fig. 4 Cycle performance of blank NCM811 and MgO-modified NCM811

Cycle performance of blank NCM811 and MgO-modified NCM811 patterns at 1C are show in Fig. 4. First discharge capacity of blank and MgO-modified NCM811 (1wt%, 2wt%, 4wt%) is 152 mAh/g, 154 mAh/g, 155 mAh/g and 155mAh/g at 1C at 25°C. After100 cycles the capacity is 82 mAh/g, 116 mAh/g, 123mAh/g and 140 mAh/g.

4. Conclusion
We modified MgO on the NCM811 material via solid state method. The MgO does not change the crystal structure of NCM811. The SEM expounded that all the samples have the irregularly shape and there is no obvious difference in morphology. The discharge capacities of pristine NCM811 and MgO-modified NCM811 remain at 54%, 75%, 90% and 79%, respectively.

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References
[1] Goodenough, J. B. and Park, K. S. (2013) The Li-ion rechargeable battery: a perspective. J. Am. Chem. Soc, 135, 1167.
[2] Tarascon, J. M. and Armand, M. (2001) Issues and challenges facing rechargeable lithium batteries. Nature, 414, 359.
[3] Andre, D., Kim, S. J., Lamp, P., Lux, S. F., Maglia, F., Paschos, O., and Stiaszny, B. (2015) Future generations of cathode materials: an automotive industry perspective. Journal of Materials Chemistry A, 3, 6709.
[4] Hy, S., Liu, H. D., Zhang, M. H., Qian, D. N., Hwang, B. J., and Meng, Y. S. (2016) Performance and design considerations for lithium excess layered oxide positive electrode materials for lithium ion batteries. Energy & Environmental Science, 9, 1931.