Asian Journal of Chemistry; Vol. 25, No. 2 (2013), 1155-1156

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.12231

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# Study on the Anode Materials of Mn-$Co_3O_4$ for Lithium Ion Secondary Batteries

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(*Received*: 18 June 2011; *Accepted*: 31 August 2012) AJC-12064

The anode materials of $Co_3O_4$ for lithium-ion batteries are made by adding certain amount of manganese powder to $Co_3O_4$ and ball milling. Electrochemical properties of $Co_3O_4$ and Mn-$Co_3O_4$ powders are tested, respectively and the results are as follows: when the $Co_3O_4$ powder is independently used as the anode of lithium-ion batteries, the first charge and discharge efficiency is as low as 66 % with bad cycle performance; when Mn powder is added, the first charge and discharge efficiency is improved to 77 % with good cycle performance, the reversible capacity is still kept at 702 mAh $g^{-1}$ after 50 cycles and the coulomb efficiency is over 97 %.

**Key Words: Cobalt oxide, Mechanical ball milling, Manganese, Anode materials, Lithium ion battery.**

Lithium-ion secondary batteries are widely used as power sources for portable electronic products, such as mobile phones, laptops, camcorders and cameras. At present, carbon material is used for the anode of commercialized lithium-ion batteries and its theoretical capacity is 372 mAh $g^{-1}$. With the increase of demand for lithium-ion batteries with high capacity, people start to search for anode materials with high theoretical capacity. The anode materials of $Co_3O_4$ have higher reversible capacity than graphite, so they attract much attention as alternative materials for graphite[1-4]. This work reports the electrochemical properties of anode materials which are made by adding Mn powders to $Co_3O_4$ and ball milling.

**Preparation and surface characters of the electrode materials:** Precisely weigh out certain amount of $Co_3O_4$ powder, add 10 % analytically pure Mn powder, mix evenly and grind them with the rotating speed of 500 r/min in the QM-1SP04 planetary ball mill produced by Instrument Plant of Nanjing University for 0.5 h. Observe the surface appearance and the particle size of the samples with JSM-6360LV scanning electron microscope produced by Jeol.

**Test of electrochemical properties:** Mix the prepared powder samples with the binder, polyvinylidene fluoride and the conductive agent, acetylene black, with the proportion of 85:10:5, put a certain amount of N-methylpyrrolidone into it and mix well, then apply it to a 10 μm-thick copper foil and dry it. A CR2430 button cell is assembled with a 1.75 $cm^2$ disc as the work electrode, a metallic lithium disc as the auxiliary electrode, 1.0 mol $L^{-1}$ $LiPF_6$/[ethylene carbonate + dimethyl carbonate)] (with the volume ration of 1:1) as the electrolyte and a 20 μm-thick microporous polypropylene membrane as the separator. Carry out the constant current charge and discharge experiment in room temperature on the LAND CT2001A battery testing system produced by Wuhan Jinnuo Company.

**Scanning electron microscope analysis:** Fig. 1 shows the SEM image of Mn-$Co_3O_4$ powders. After ball milling, the diameter of particles is only several microns and evenly distributed.

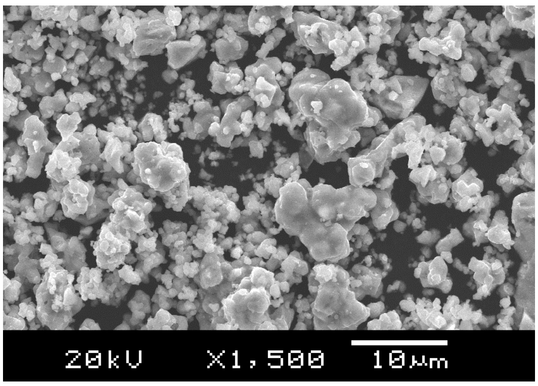


Fig. 1. SEM image of Mn-$Co_3O_4$ powders

**Electrochemical properties:** Fig. 2 shows the first three discharge and charge curves of the $Co_3O_4$ electrode. When the $Co_3O_4$ powder is independently used as the anode of lithium-ion batteries, the first discharge capacity is rather high, reaching 1200 mAh $g^{-1}$. Its first charge and discharge efficiency

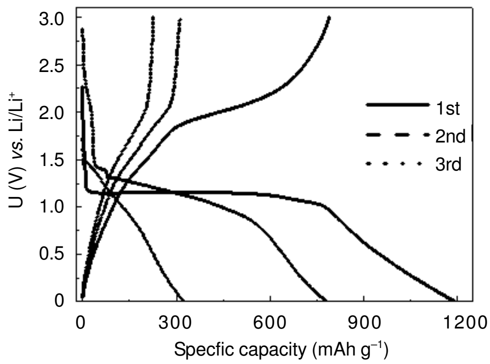


Fig. 2. First three discharge and charge curves of the $Co_3O_4$ electrode

is 66 %. Its first three charge capacities are 791, 312 and 226 mAh $g^{-1}$, respectively. Fig. 3 shows the first three discharge and charge curves of the Mn-$Co_3O_4$ electrode. When Mn is added, the first discharge capacity is 1049 mAh $g^{-1}$ while the first charge and discharge efficiency increases to 77 %. Its first three charge capacities are 814, 784 and 777 mAh $g^{-1}$. The attenuation speed slows down significantly.

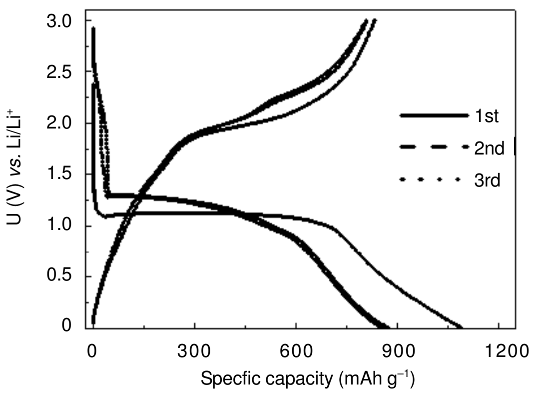


Fig. 3. First three discharge and charge curves of the Mn-$Co_3O_4$ electrode

Fig. 4 shows the cycle performance of the electrodes. Fig. 5 shows coulomb efficiency of the electrodes. According to the two figures, we can clearly see that the reversible capacities of the $Co_3O_4$ electrode attenuate to below 200 mAh $g^{-1}$ after 5 cycles and its coulomb efficiency is also low. After 50 cycles, the reversible capacities attenuate to 63 mAh $g^{-1}$. The Mn-$Co_3O_4$ electrode is better. After 50 cycles, the reversible capacity stays to 702 mAh $g^{-1}$, which is 86.2 % of the first capacity and its coulomb efficiency is above 97 %.

## Conclusion

When $Co_3O_4$ powder is used as anode in a lithium ion battery, the first charge and discharge efficiency is only 66 %

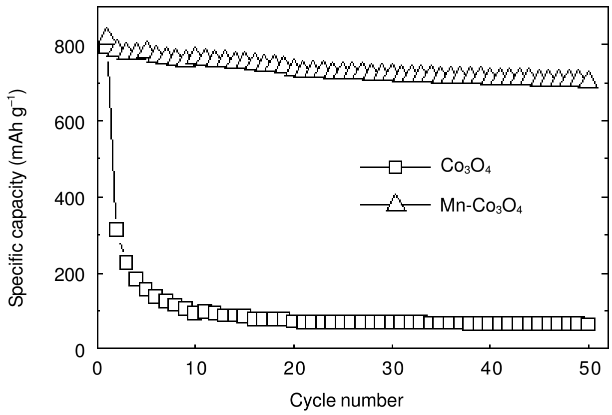


Fig. 4. Cycle performance of the electrodes

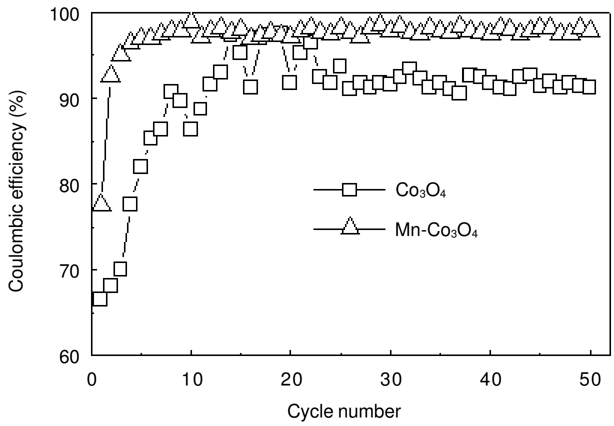


Fig. 5. Coulomb efficiency of the electrodes

and the cycle performance is bad. Adding manganese powder improves the first charge and discharge efficiency of the electrode to 77 %. The cycle performance is good. After 50 cycles, the reversible capacity stays to 702 mAh $g^{-1}$ and coulomb efficiency is above 97 %. So it is likely to become substitution material of the carbon anode in lithium ion battery.


## ACKNOWLEDGEMENTS

This work was supported by the Science Development Fund of Tianjin Agricultural University, P.R. China.


## REFERENCES


1. F. Huang, Z.Y. Yuan, H. Zhan, Y.H. Zhou and J.T. Sun, *Mater. Lett.*, **57**, 3341 (2003).
2. G.X. Wang, Y. Chen and K. Konstantinov, *J. Power Sour.*, **109**, 142 (2002).
3. P.A. Connor and J.T.S. Irvine, *Electrochim. Acta*, **47**, 2885 (2002).
4. Y.-M. Kang, K.-T. Kim and J.-H. Kim, *J. Power Sour.*, **133**, 252 (2004).