

A novel composite anode based on lithium transition metal nitrides for lithium ion batteries

Y. Liu, K. Horikawa, K. Hanai, N. Imanishi, A. Hirano
and Y. Takeda

Department of Chemistry, Faculty of Engineering, Mie
University, Kamihama-cho, Tsu, Mie 514-8507, Japan

Research for new Li-storage materials with an improved capacity possesses a challenge for Li-ion batteries. Recently, we have developed a series of low cost lithium transition metal nitrides with the modified morphology characteristics^{1,2}. These compounds were found to show large capacities of 700-900 mAh g⁻¹ and excellent capacities retention. However, lithium must be extracted from the nitrides in an initial anodic oxidation; thereby these anodes cannot directly combine with the typical high potential cathodes such as LiCoO₂ and LiMn₂O₄ to constitute cells. This deterrent can be overcome by introducing a certain amount of cobalt oxides into the nitrides based electrodes. As found, cobalt oxides can thermodynamically extract lithium from the lithium transition metal nitrides that leads to a delithiated state of the nitrides and to form metallic Co and Li₂O. On the other hand, cobalt oxide within the electrodes shows inactive toward lithium in a limited potential range after the first cycle. Thus, lithium transition metal nitrides can be directly treated as being in a delithiated state and is mainly responsible for the continue Li-reaction. Fig.1 shows charge and discharge curves of the Co₃O₄-Li_{2.6}Co_{0.2}Cu_{0.2}N composite electrode. The voltage trends of the electrode showed high coincidence from cycle to cycle that indicates a single phase reaction and good charge reversibility.

The initial faradaic yield with the composite electrode was ca.100% and reversible capacity was ca.500 mAh g⁻¹ after tradeoff the weight ratio between Li_{2.6}Co_{0.2}Cu_{0.2}N and Co₃O₄. An increase in the Li-reactive potential compared with the commercial graphite is in favor for avoiding the Li-deposition. The composite anode systems were found to show good capacity retention with cycling, as shown in Fig.2. More important, we found that the composite anodes have a friend interfacial compatibility with the solid-state electrolytes, e.g., poly (ethylene oxide) (PEO)-Li-salt composite, which is believed to be superior to the liquid electrolytes and difficult to be operated with the commercial carbonaceous anodes. We are at present investigating the cells with the proposed novel anodes that might lead to high energy density of lithium-ion cell.

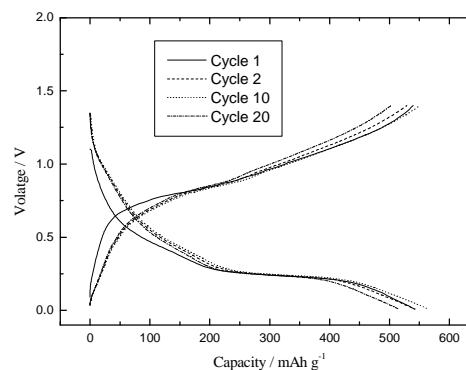


Fig.1. Charge/discharge curves of the Co₃O₄/Li_{2.6}Co_{0.2}Cu_{0.2}N electrode with the electrolytes of LiPF₆/EC+DMC in the potential range of 1.4~0.01 V, vs.Li/Li⁺, i_c=i_d=0.15 mA cm⁻²,

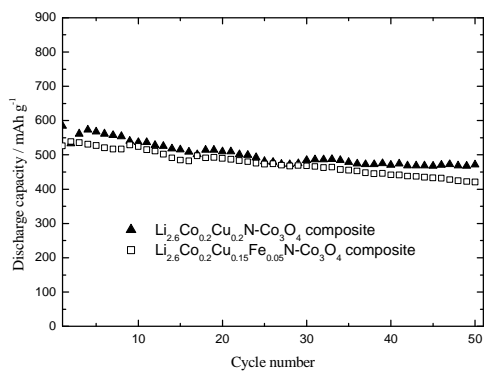


Fig.2. Cycling performance of the composite electrode.

References

- [1] Y. Liu, T. Matsumura, N. Imanishi, T. Ichikawa, A. Hirano and Y. Takeda, *Electrochemistry Communications*, 6(2004)632
- [2] Y. Liu, K. Horikawa, M. Fujiyosi, N. Imanishi, A. Hirano and Y. Takeda, *J. Electrochem. Soc.*, in press