

Synthesis and Electrochemical Characterization of High Voltage Cycling $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$ as Cathode Material for Lithium Rechargeable Batteries

Meijing Zou, Bohua Deng, Masaki Yoshio
Department of Applied Chemistry, Saga University,
Honjyo 1, Saga 840-8502, Japan

Introduction

Lithium-ion batteries are emerging as a major power source for their wide applications ranging from cell phones to electric vehicles as also in the medical field. The system usually involves the use of lithiated transition metal oxides, namely, LiCoO_2 , LiNiO_2 , and LiMn_2O_4 as cathode material and also as lithium source. However, among these materials, lithium cobalt oxide (LiCoO_2) is the most widely used cathode material in the majority of commercially available lithium-ion batteries owing to its ease of synthesis and high reversibility.¹ Despite the advantages of LiCoO_2 , the maximum attainable practical capacity is only around 140 mAh/g in the voltage range of 3-4.2 V even though its theoretical capacity is around 273 mAh/g. Therefore, to obtain larger capacities one must charge the cells to high voltages (4.5 V).² Hence, we examined about synthesizing $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$ samples and then those electrochemical characteristics to overcome a cycle problem due to the high upper cut-off voltage.

Experimental

$\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$ has been prepared using Co_3O_4 (>99.9%), Li_2CO_3 and either $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, or TiO_2 and etc. as precursor materials. Stoichiometric amounts of the mentioned materials were thoroughly mixed and melted in an argon atmosphere at 550°C for 6 h and then cooled. The synthesized powder is ground and mixed well before finally subjecting to further annealing at high temperature of 850°C for 10 h and then cooled, mixed, and repeated annealing for a further 10 h. The synthesized powders were structurally analyzed using X-ray diffraction and the surface morphology evaluated with scanning electron microscopy (SEM).

Electrochemical studies were carried out in the voltage range 3.5-4.5 V vs. Li metal using 1 M LiPF_6 in ethylene carbonate/dimethyl carbonate as electrolyte.

Results and discussions

The XRD patterns of the synthesized metal-doped (Mn, Mg, Cr, Fe, Zn, Zr, Al, Cu, Sn, Ti, and Bi) LiCoO_2 observed that all peaks, viz., 003, 101, 006, 102, 104, 108, and 110 are identifiable thereby suggesting the existence of $\alpha\text{-NaFeO}_2$ structure. Moreover, single-phase structure is observed for the as-prepared $\text{LiCo}_{0.95}\text{Mg}_{0.05}\text{O}_2$ material doped with Mg, Al, Mn, Fe and Cr. The synthesized LiCoO_2 powders with metal-doping of Mn, Mg, Mn, Fe, Al, Zr, Cu, Sn and Ti show particles exhibiting a uniform submicrometer size and the particles are smaller than that of parent LiCoO_2 without doping.³ Figure 1 depicts the SEM photographs for $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$.

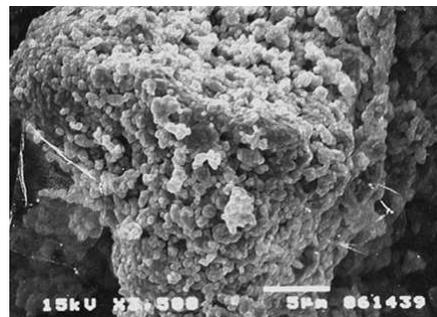


Figure 1. The SEM photograph for $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$.

To evaluate the electrochemical performance, we cycled the fabricated 2032 coin cells galvanostatically from 3.5 to 4.5 V. The first charge and discharge pattern for the cells incorporating the synthesized materials are shown in Figure 2. It is observed for $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$ that the first charge is as high as 185 mAh/g, and more than 90% of the capacity is retained in the first discharge. Excellent cycleability of Mg-doped material is exhibited over the investigated long time cycling with only capacity loss of about 8 mAh/g after 50 cycles. The performance of LiCoO_2 doped with other cations was also investigated. It was found that the improved performance when cycled up to 4.5 V does not depend on the suppressed phase transition around 4.2V. Other factors will be proposed based on the investigation of doping with a great variety of metal cations.

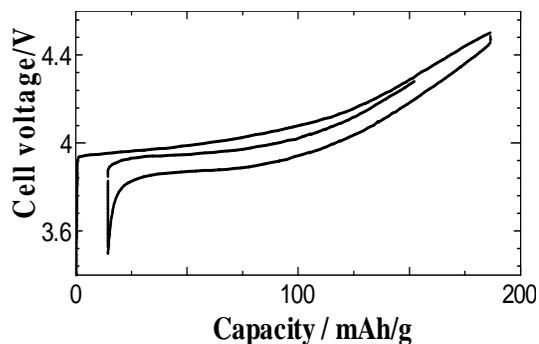


Figure 2. The charge/discharge curves for $\text{LiCo}_{0.95}\text{Mg}_{0.05}\text{O}_2$ cathodes in the initial two cycles.

References

1. C. Julien and S. Gastro-Garcia, *J. Power Sources*, **97/98**, 290 (2001).
2. Z. Chen and J. R. Dahn, *Electrochem. Solid-State Lett.*, **5**, A213 (2002).
3. M. Zou, M. Yoshio, S. Gopukumar, and J. Yamaki, *Chem. Mater.*, **15**, 4699 (2003).