Synthesis and Electrochemical Characterization of High Voltage Cycling LiMg0.05Co0.95O2 as Cathode Material for Lithium Rechargeable Batteries

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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, LiCoO2, LiNiO2, and LiMn2O4 as cathode material and also as lithium source. However, among these materials, lithium cobalt oxide (LiCoO2) 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 LiCoO2, the maximum attainable practical capacity is only around 140 mA/h/g in the voltage range of 3-4.2 V even though its theoretical capacity is around 273 mA/h/g. Therefore, to obtain larger capacities one must charge the cells to high voltages (4.5 V).2 Hence, we examined about synthesizing LiMg0.05Co0.95O2 samples and then those electrochemical characteristics to overcome a cycle problem due to the high upper cut-off voltage.

Experimental
LiMg0.05Co0.95O2 has been prepared using Co(NO3)2 (>99%), Li2CO3 and either Mg(NO3)2, Al(NO3)3, or TiO2 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 LiPF6 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) LiCoO2 observed that all peaks, viz., 003, 101, 006, 102, 104, 108, and 110 are identifiable thereby suggesting the existence of a-NaFeO2 structure. Moreover, single-phase structure is observed for the as-prepared LiCo0.95Mg0.05O2 material doped with Mg, Al, Mn, Fe and Cr. The synthesized LiCoO2 powers 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 LiCoO2 without doping.3 Figure 1 depicts the SEM photographs for LiMg0.05Co0.95O2.

Figure 1. The SEM photograph for LiMg0.05Co0.95O2.

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 LiMg0.05Co0.95O2 that the first charge is as high as 185 mA/h/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 mA/h/g after 50 cycles. The performance of LiCoO2 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 LiCo0.95Mg0.05O2 cathodes in the initial two cycles.

References