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Communications

Synthesis of High-Voltage (4.5 V) Cycling Doped LiCoO₂ for Use in Lithium Rechargeable Cells

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Introduction. Designing of high-performance cathode materials for lithium ion batteries is emerging as a major task in view of the wide range of applications ranging from cell phones to electric vehicles and also in medical equipment. Usually, lithiated transition metal oxides, namely, LiCoO₂, LiNiO₂, and LiMn₂O₄, are employed as cathode materials. However, among these mentioned materials, lithium cobalt oxide (LiCoO₂) is the most widely used in the majority of commercially available lithium ion batteries owing to its ease of synthesis and high reversibility.¹ In view of the advantages associated with LiCoO₂, the maximum attainable practical capacity is only around 137 mA·h/g when cycled in the voltage range 3–4.25 V, although the theoretical capacity is as high as 273.8 mA·h/g. Therefore, to obtain higher capacities, one has to charge the cells to high voltages (4.5 V).² However, such attempts failed to produce stable LiCoO₂ due to structural

changes taking place³ during cycling. Attempts to improve the cycleability beyond 4.25 V have been reported by some authors^{4,5} by doping with either Mg or Al. However, such results only report inferior capacities. Theoretical studies^{6,7} suggest that doping of LiCoO₂ with a transition metal ion leads to an increase in capacity whereas on the other hand non-transition-metal ion doping leads to an increase in voltage at the expense of capacity. To overcome the cycling problems at high voltages, very recently, Cho et al.^{8–10} demonstrated that coating of LiCoO₂ with ceramic materials such as Al₂O₃ and ZrO₂ is the only available option for obtaining stable capacities when cycled up to 4.5 V and this was confirmed by Dahn et al.² However, apart from these studies to the best of our knowledge there is no report on the stable cycling of doped LiCoO₂ at high voltages (4.5 V). Hence, we thought it timely to synthesize carefully doped LiCoO₂ involving dopant ions such as Mn, Cu, Fe, and Zn and present in this communication the physical and electrochemical characterization of the synthesized materials for use in lithium rechargeable cells. Moreover, the present method of synthesis is advantageous from a commercial and economic point of view.

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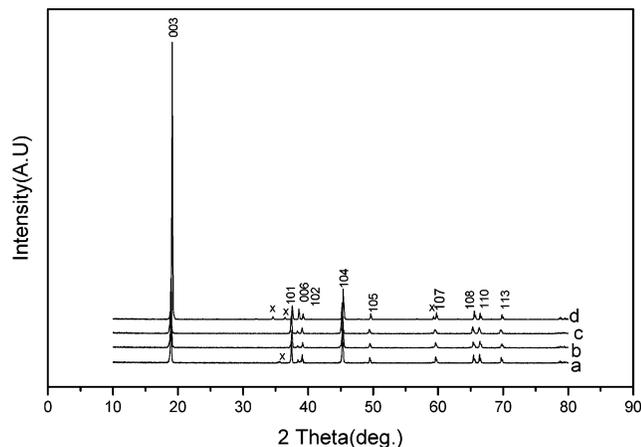


Figure 1. XRD patterns of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$, M = (a) Cu, (b) Mn, (c) Fe, and (d) Zn.

Experimental Section. $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ (M = Mn, Cu, Fe, and Zn) has been prepared by thoroughly mixing stoichiometric amounts of Co_3O_4 (>99.9% pure), Li_2CO_3 , and either $\text{Mn}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_3$, $\text{FeO}(\text{OH})$, or $\text{Zn}(\text{CH}_3\text{-COO})_2$, melted in an argon atmosphere at 550°C for 6 h, and then cooled. The synthesized powders were ground and mixed well before finally annealing at 850°C for 10 h and then cooled, mixed, and annealed further for 10 h. The mixture was cooled, mixed thoroughly, and subjected to physical and electrochemical characterization.

The prepared powders were characterized for their phase purity and structural features using powder X-ray diffraction (XRD, Rint 1000, Rigaku) using Cu $K\alpha$ radiation. The particle morphologies of the powders were recorded using a scanning electron microscope (JSM-5300E, Japan Electron Ltd., Japan).

Electrochemical characterizations were performed in a 2032 coin cell type two-electrode assembly. A cathode mix was prepared by using 85% of the active material mixed with 15% Teflonized carbon. The prepared mix was coated onto aluminum foil using doctor blade technique and dried in an oven for 6–12 h at 120°C . The dried sheet of the cathode material was then roll-pressed for increased adherence of the cathode mixture onto the aluminum foil current collector. Circular disks of the cathodes were then punched and were used for fabricating the coin cell. The coin type cells were assembled in an argon-filled glovebox with the prepared circular disks of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ as the cathode and lithium (Cyprus Foote Mineral Co.) metal anode and with Celgard 3401 as the separator using 1 M LiPF_6 in 1:2 by volume ethylene carbonate (EC)/dimethyl carbonate (DMC) [Ube Chemical, Japan] as electrolyte solution. The galvanostatic cycling studies of the fabricated cells were performed at a C/5 rate in the voltage range 3.5–4.5 V using an automatic battery tester at room temperature.

Results and Discussion. Figure 1 presents the XRD patterns of the synthesized $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ [M = Mn, Fe, Cu, and Zn]. It can be observed from Figure 1 that all the patterns can be indexed to the $\alpha\text{-NaFeO}_2$ structure as all the fingerprint peaks, viz., 003, 101, 006, 102, 104, 108, and 110, are clearly assignable. The hexagonal lattice parameters of the synthesized powders were evaluated by using a least-squares fit and the

Table 1. XRD Lattice Constants a and c and c/a Ratio for Differently Synthesized Doped LiCoO_2

material	a	c	c/a
$\text{LiCu}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.817	14.059	4.991
$\text{LiMn}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.814	14.065	4.997
$\text{LiFe}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.817	14.088	5.001
$\text{LiZn}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.816	14.165	5.030

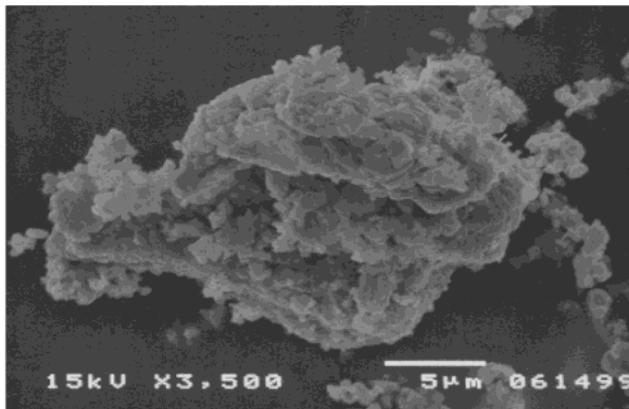


Figure 2. Typical SEM photograph of $\text{LiMn}_{0.05}\text{Co}_{0.95}\text{O}_2$.

values of a and c are presented in Table 1 along with the c/a ratio, an indicator of metal–metal layering distance. It is interesting to observe that the XRD patterns of Zn-doped LiCoO_2 shows the formations of some secondary phases and the intensity of 006 is higher than that of the 102 peak. This suggests the R -factor, i.e., the ratio of $[006/102]/101$ as suggested by Reimers et al.,¹¹ is higher and so results in the distortion of the hexagonal setting. Moreover, the abnormal intensity of the 003 peak may be ascribed to the inhomogeneous distribution of Zn and Co ions. However, in all other cases no such abnormality is observed, which can be confirmed by the perfect hexagonal setting. As can be seen, all other XRD patterns have a perfect 006/102 and 108/110 doublet splitting as seen in pristine LiCoO_2 ¹² and therefore could be inferred to have perfect layering involving the metal ions and oxygen atoms. As can be observed from Table 1, the values of a are similar while those of c are higher than the pristine LiCoO_2 with the c/a ratio of above 4.991, thereby suggesting improved layering characteristics and therefore the ions should exhibit excellent electrochemical behavior. Such an increase in lattice parameters is understandable in view of the higher ionic radii of the present dopant ions as compared to high spin cobalt (0.565 \AA). Our results confirm the reports available in the literature.¹³

Having confirmed the formation of metal ion doped materials, we examined the surface morphology of the synthesized materials using SEM. Figure 2 depicts a typical SEM photograph of the synthesized manganese doped LiCoO_2 powders. It is interesting to see that a different type of morphology is adopted by doping with metal ions. The SEM photographs reveal that the particle size is more than $3\text{ }\mu\text{m}$ in the case of Cu and Zn ion doping while on the other hand a slight reduction

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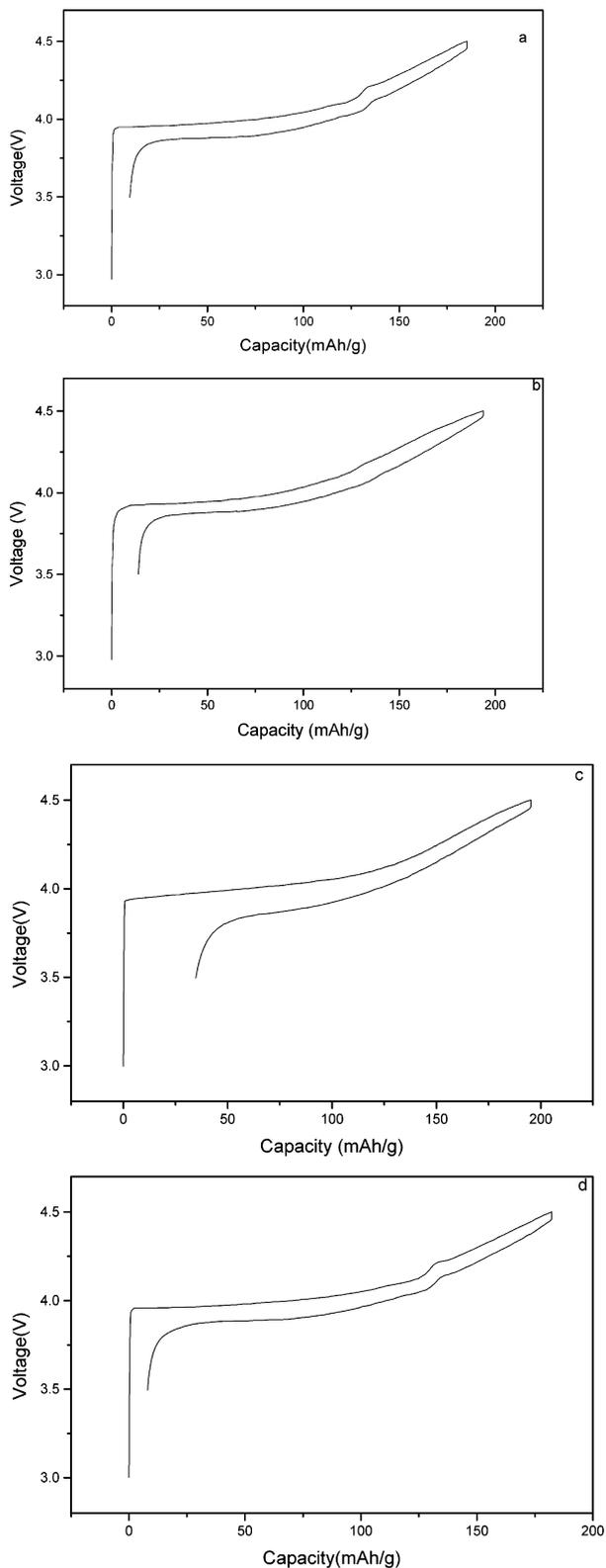


Figure 3. First charge/discharge patterns of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$, $M =$ (a) Cu, (b) Mn, (c) Fe, and (d) Zn.

in particle size is observed in the case of Fe dopant. Indeed, the SEM photograph of Mn doping is still exciting as each particle is made up of aggregates of smaller particles and forms a cluster. Such kind of reduction in particle size indicates that the lithium ions could easily insert and deintercalate due to reduction in path lengths.

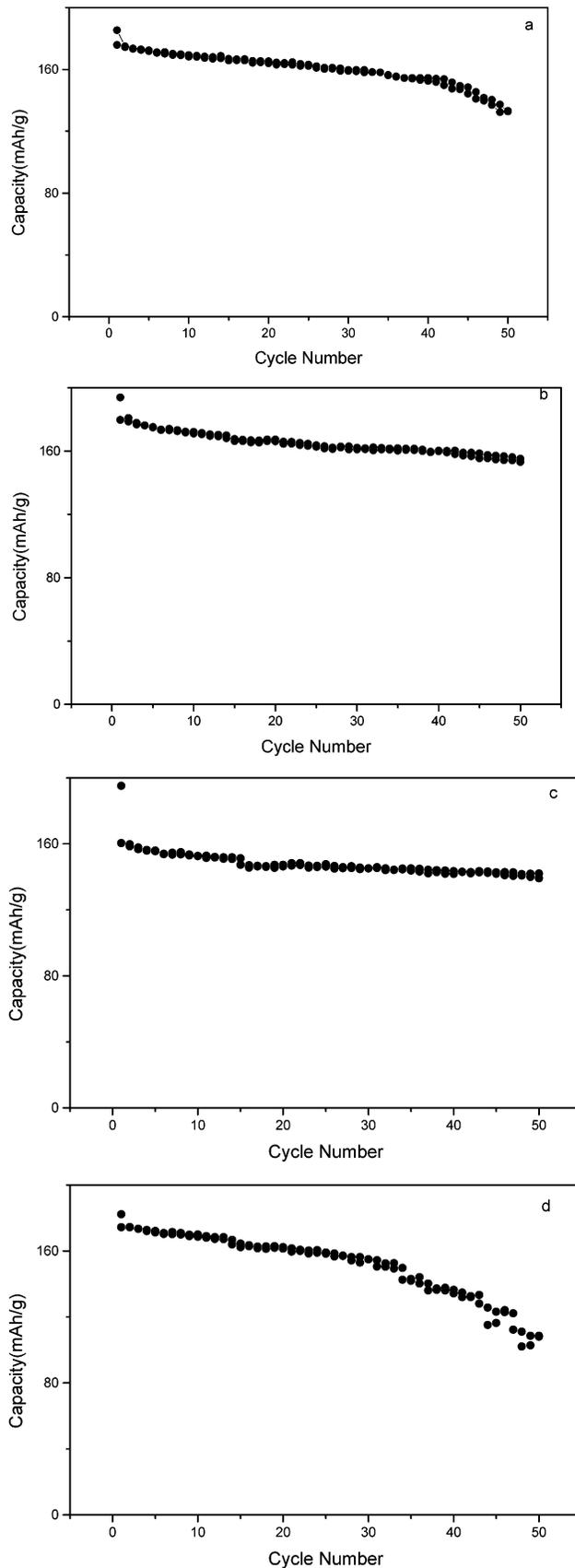


Figure 4. Galvanostatic cycling at a C/5 rate in the voltage range 3.5–4.5 V of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$, $M =$ (a) Cu, (b) Mn, (c) Fe, and (d) Zn.

Electrochemical performance of the fabricated 2032 lithium coin cell was evaluated galvanostatically by

cycling the cells from 3.5 to 4.5 V. The cells exhibited an open circuit voltage of around 3.0 V (vs Li metal). The first charge and discharge pattern for the cells incorporating the synthesized materials are presented in Figure 3. It is observed that all the cells employing the doping elements exhibit high first charge of around 190 mA·h/g but the irreversible capacity is different and depends on the dopant ions. The first cycle irreversible capacities in the case of Mn, Cu, and Zn are similar and is ~ 15 mA·h/g when cycled up to 4.5 V and hence could be potential materials for use in lithium ion batteries. Further, it is interesting to note that the irreversible first cycle capacity of $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{O}_2$ is very large (~ 40 mA·h/g), thereby suggesting poor cycleability at high voltages (4.5 V). A comparison of the first charge and discharge profile suggests the existence of two phase oxidation/reduction in the case of Cu and Zn doped LiCoO_2 (Figure 3a,d) and hence could lead to inferior capacities on extended cycling like in the case of pristine LiCoO_2 . Thus, we observe a phase change around 130–135 mA·h/g in these materials. It is worthwhile to recall here that the XRD patterns also confirm the existence of some secondary phases marked “x” in these materials. However, such phase changes are not noticeable in the case of $\text{LiFe}_{0.05}\text{Co}_{0.95}\text{O}_2$ and $\text{LiMn}_{0.05}\text{Co}_{0.95}\text{O}_2$ (Figure 3b,c) and hence is expected to deliver stable capacities on high-voltage cycling. Encouraged by the preliminary performance of the synthesized powders, we were interested in carrying out the extended galvanostatic cycling studies (50 cycles) so as to ascertain the stability of the initially observed high capacities.

The galvanostatic cycling behavior of the synthesized doped cathode materials were evaluated in a lithium rechargeable 2032 type coin cell in the voltage range 3.5–4.5 V at a C/5 rate and are presented in Figure 4a–d. It is observed from the figures that the cells employing Cu and Zn doping (Figure 4a,d) show initial discharge capacities of around 165–170 mA·h/g but fade slowly on cycling and retain a capacity of approximately 130 and 110 mA·h/g, respectively. Such kind of fading has also been observed by other authors in the case of LiCoO_2 ³ and has been ascribed due to the different phase changes taking place on cycling. It is interesting to observe the excellent cycleability exhibited by either Fe or Mg doped material (Figure 4b,c) over the investigated 50 cycles. However, as indicated elsewhere, Fe doped LiCoO_2 has the highest irreversible capacity and hence delivers a stable capacity of around 145 mA·h/g after 50 cycles. Further, looking at the cycleability of $\text{LiMn}_{0.05}\text{Co}_{0.95}\text{O}_2$, we observe not only good stable capacities delivered at high-voltage cycling (4.5 V) but also

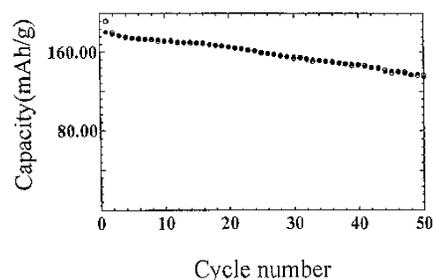


Figure 5. Galvanostatic cycling at a C/5 rate in the voltage range 3.5–4.5 V of LiCoO_2 .

at the same time delivery of the highest capacities of ~ 158 mA·h/g. This result looks very interesting as to our knowledge this is the first time such stable high-voltage capacities are obtained, even though some authors suggest improved performance up to 4.5 V involving only coating of LiCoO_2 .⁸ The enhanced performance of Mn doping cycling up to 4.5 V can be ascribed to the absence of phase changes. Last, the cycleability of Mn doped LiCoO_2 [Figure 4b] delivers initial discharge capacities of around 180 mA·h/g and becomes stabilized from the 15th cycle and delivers a capacity of ~ 158 mA·h/g at the 50th cycle. Thus, we can say that doping with manganese could deliver high capacities and also produce good high-voltage cycling cathode materials. Moreover, LiCoO_2 synthesized under identical conditions delivers only a discharge capacity of around 138 mA·h/g after 50 cycles (Figure 5). Further, a comparison of our capacities with that obtained by coating^{8–10} of LiCoO_2 indicates that our results are superior in view of the high capacities obtained in a narrow voltage range of 3.5–4.5 V in contrast to values of ~ 165 mA·h/g reported by Cho et al.,⁸ in the voltage range 2.75–4.4 V.

Conclusion. We may therefore conclude that doped LiCoO_2 materials synthesized by the present technique result in enhanced stable capacities at high voltages (4.5 V). Thus, we demonstrate for the first time that the material, $\text{LiMn}_{0.05}\text{Co}_{0.95}\text{O}_2$, is a promising cathode material for use in lithium rechargeable cells delivering capacities of 158 mA·h/g at a C/5 rate when cycled between 3.5 and 4.5 V.

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