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

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Substituted cobalt oxides, $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ ($M = \text{Mg}^{2+}$, Al^{3+} , and Ti^{4+}), have been synthesized using solid-state technique and their performance in a 2032-type lithium rechargeable coin cell is reported. The synthesized powders were structurally analyzed using X-ray diffraction (XRD) and the surface morphology evaluated with scanning electron microscopy. XRD patterns indicate that single-phase materials were formed involving Al-doped LiCoO_2 . 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. The doping involving 5% Mg resulted in a charge/discharge capacity of ~ 160 mAh/g at C/5 rate and remained stable even after 50 cycles. To the best of our knowledge, this is the first time that such high stable capacities have been obtained involving doped LiCoO_2 when cycled up to 4.5 V.

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Lithium-ion batteries are emerging as a major source of power in view of their varied 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 137 mAh/g in the voltage range 3–4.25 V even though the theoretical capacity is around 273.8 mAh/g. Therefore, to obtain higher capacities one must charge the cells to high voltages (4.5 V).² However, such attempts have failed to produce stable cycling LiCoO_2 due to structural changes taking place.³ Attempts to improve the cyclability beyond 4.25 V by doping have been reported by some authors.^{4,5} However, such doping resulted in only inferior capacities. Theoretical studies^{6,7} suggest that doping of LiCoO_2 with a transition metal ion leads to an increase in capacity whereas nontransitional metal ion doping leads to an increase in voltage at the expense of capacity. To overcome the cycling problems at high voltages, recently, Cho *et al.*^{8–10} demonstrated that the coating of LiCoO_2 with ceramic materials like Al_2O_3 , ZrO_2 , etc., delivers stable capacities even when cycled up to 4.5 V and was also confirmed by Chen and Dahn.² However, apart from these studies to the best of our knowledge there is no report on the stable cycling of doped LiCoO_2 at high voltages (4.5 V). Hence, we thought it timely to synthesize carefully doped LiCoO_2 and present in this communication the electrochemical performance of the synthesized materials in a lithium rechargeable cell. Moreover, the present method of synthesis is more commercially acceptable considering the economy and ease of the bulk production process involved.

Experimental

$\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ ($M = \text{Mg}, \text{Al}, \text{Ti}$) has been prepared using Co_3O_4 (>99.9% pure), Li_2CO_3 and either $\text{Mg}(\text{NO}_3)_2$, $\text{Al}(\text{NO}_3)_3$, or TiO_2 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 mixture was cooled, mixed thoroughly, and was 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 $\text{Cu K}\alpha$ 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. Cathode mix was prepared using 85% of the active material mixed with 15% Teflonized carbon. The prepared mix was coated onto an 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 on 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 glove box with the prepared circular disks of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ as cathode, lithium (Cyprus Foote Mineral Co.) metal anode, and with Celgard 3401 as separator in a nonaqueous electrolyte consisting of 1 M LiPF_6 in 1:2 by volume ethylene carbonate (EC)/dimethyl carbonate (DMC) (Ube Chemical, Japan). The charge/discharge galvanostatic cycling of the fabricated cells were performed at C/5 rate in the voltage range 3.5–4.5 V using an automatic battery tester at room temperature.

Results and Discussion

The XRD patterns of the synthesized metal-doped LiCoO_2 are presented in Fig. 1. It is clearly observed that all the finger print peaks, viz., 003, 101, 006, 102, 104, 108, and 110 are identifiable thereby suggesting the existence of *a*- NaFeO_2 structure. The hexagonal lattice parameters of the synthesized powders were evaluated using a least square fit and the values of *a* and *c* (± 0.002) are summarized in Table I along with the *c/a* ratio, an indicator of metal-metal layering distance. As can be observed from Table I the values of *a* and *c* are highest in Mg doping as compared to pristine LiCoO_2 or with Al or Ti doping with a *c/a* ratio of 4.995 thereby suggesting that all the investigated doped LiCoO_2 materials are lamellar, but the magnitude of *a* and *c* depends on the cations present in the slab (to compensate for the charge of the substituent) and therefore should exhibit excellent electrochemical behavior. Further, it can be seen from Fig. 1 the evolution of secondary phases marked “X” in the Ti-doped sample and may be assigned to the

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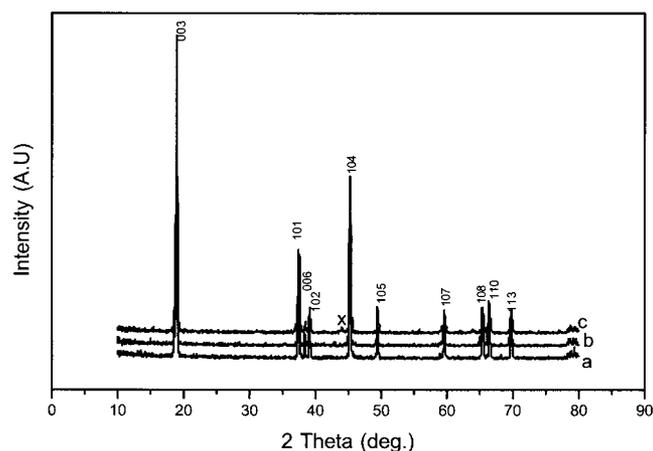


Figure 1. XRD patterns of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ M = (a) Al, (b) Mg, or (c) Ti.

emergence of spinel phases.¹¹ Our XRD results are in confirmation to earlier reports available for the synthesis of metal ion (Mg, Al, Ti) doped LiCoO_2 .¹¹⁻¹⁴

Having confirmed the formation of single-phase metal ion-doped materials, we examined the surface morphology of the synthesized materials using scanning electron microscopy (SEM). Figure 2 depicts the SEM photographs of the synthesized metal-doped powders. All the synthesized powders show particles of submicrometer size and therefore should aid the diffusion of lithium ions. Further, the particles exhibit a uniform distribution and are smaller than the parent LiCoO_2 .¹⁵

To confirm the electrochemical performance, we cycled the fabricated 2032 lithium coin cell galvanostatically from 3.5 to 4.5 V. The cells exhibited an open-circuit voltage of around 2.9 V (vs. Li metal). The first charge and discharge pattern for the cells incorporating the synthesized materials are shown in Fig. 3. It is observed in the Al doping (Fig. 3a) that the first charge is as high as 190 mAh/g, but the irreversible capacity is around 40 mAh/g in the first cycle. Moreover, phase change around 120-125 mAh/g is absent. However, interesting results are observed looking at the first cycle of the Mg doping (Fig. 3b). The first charge capacity is around 185 mAh/g but more than 90% of the capacity is retained in the first discharge or the irreversible capacity is only about 15-17 mAh/g. Moreover, Mg-doping also does not exhibit any phase transition such as in Al-doping at around 0.5 lithium extraction. Further, a different picture is seen for the first charge/discharge cycling of Ti-doped LiCoO_2 (Fig. 3c). First, the hump near the capacity of 120 mAh/g is observed even though the first charge and discharge capacities are 182 and 162 mAh/g, respectively. Having been encouraged by the preliminary performance of the synthesized powders, we were interested in carrying out the galvanostatic cycling studies up to 50 cycles so as to ascertain the stability of the initially observed high capacities.

Figure 4a-c presents the cycling behavior of the synthesized doped cathode materials in a lithium rechargeable 2032-type coin cell in the voltage range 3.5-4.5 V at the C/5 rate. It is seen from the figures that the cells employing Al doping (Fig. 4a) shows an initial capacity of around 160 mAh/g but fades slowly on cycling and

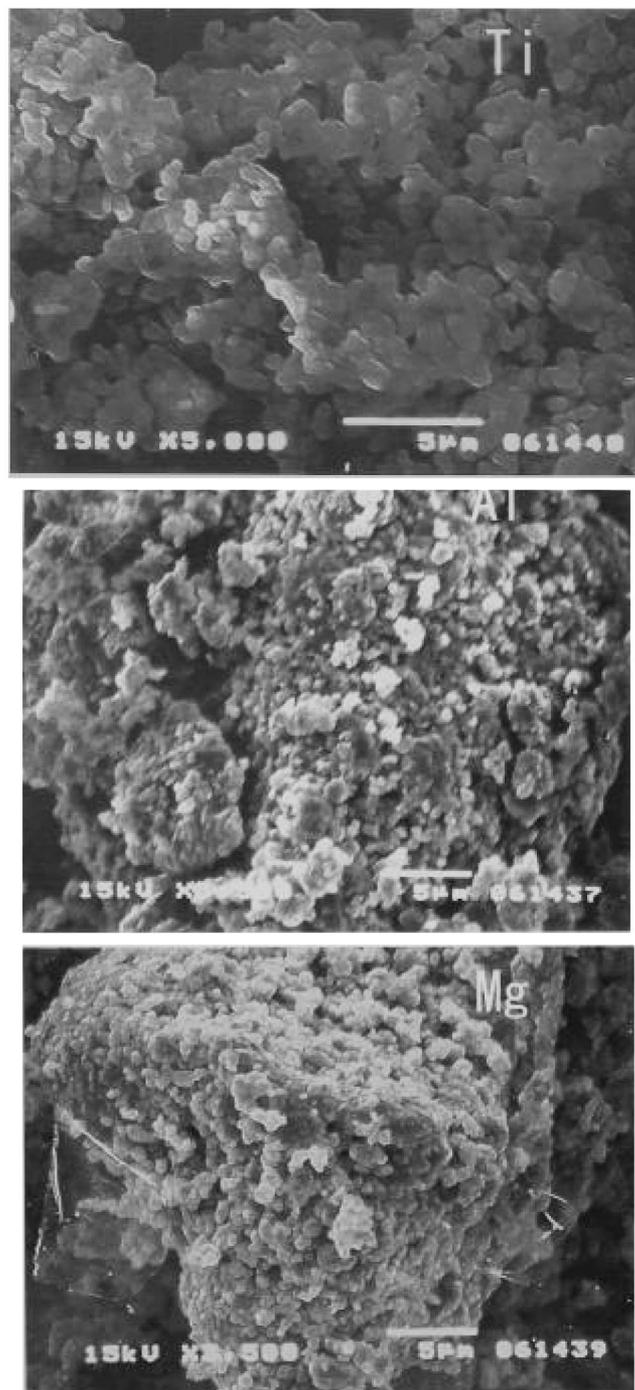


Figure 2. SEM photographs of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$.

retains a capacity of approximately 140 mAh/g. Such fading has also been observed by other authors^{4,12} and is as expected theoretically.⁷ Excellent cyclability of Mg-doped material (Fig. 4b) is exhibited over the investigated 50 cycles, *i.e.*, there only being a difference of ~ 8 mAh/g from the first to the 50th discharge capacities. This result looks interesting as to our knowledge this is the first time such stable high voltage capacities have been obtained even though some authors suggest improved performance up to 4.25 V range involving Mg-doped LiCoO_2 .¹¹ The enhanced performance of Mg doping cycling up to 4.25 V has been ascribed to enhanced electronic conductivity. Finally, the cyclability of Ti-doped LiCoO_2 (Fig. 4c) even though it looks attractive in the initial cycles, fades to

Table I. XRD lattice constants a , c and c/a ratio for different synthesized doped LiCoO_2 .

Material	a (Å)	c (Å)	c/a
$\text{LiAl}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.813	14.066	5.000
$\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.818	14.075	4.995
$\text{LiTi}_{0.05}\text{Co}_{0.95}\text{O}_2$	2.812	14.015	4.984

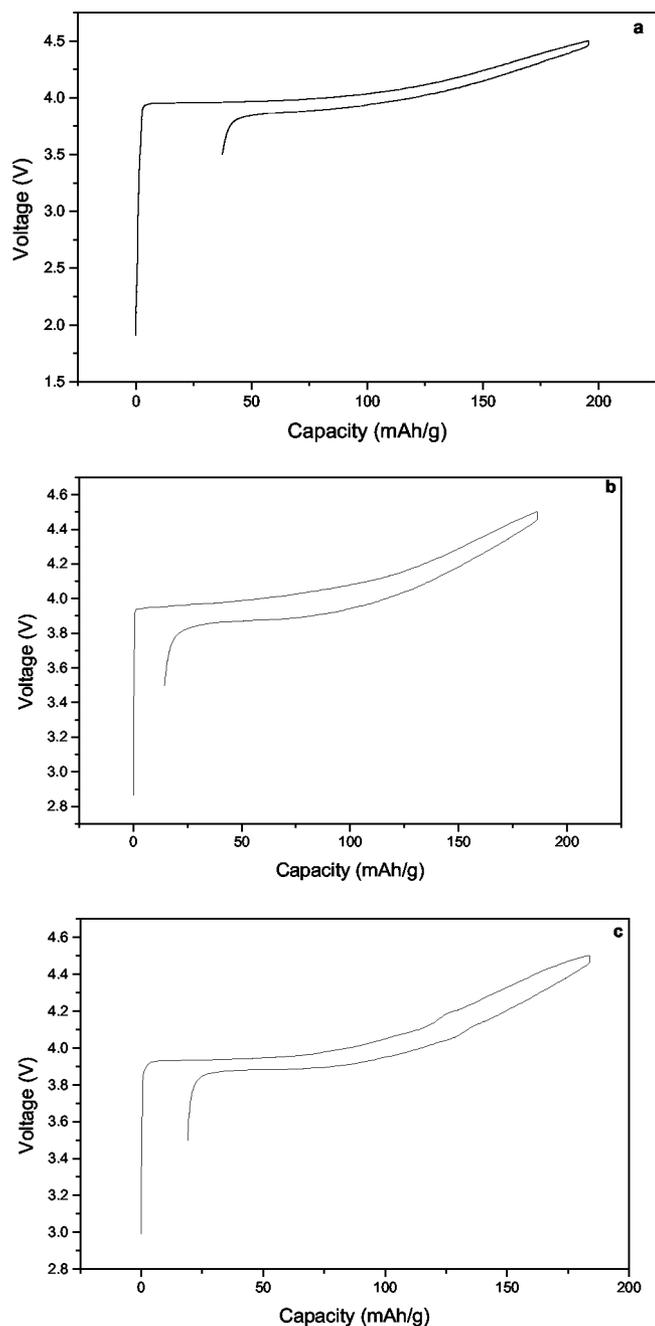


Figure 3. First charge/discharge patterns of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ M = (a) Al, (b) Mg, or (c) Ti.

a stable value of around 143 mAh/g. The drop in capacity can be ascribed due to the phase changes encountered around a capacity of 125 mAh/g and also due to inactive Ti present. Thus, we can say that doping with divalent magnesium may deliver high capacities and also produce good high voltage cycling cathode materials. A comparison of our capacities with that obtained by coating⁸⁻¹⁰ 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 mAh/g reported by Cho *et al.*,⁸ in the voltage range 2.75-4.4 V.

Conclusion

We may therefore conclude that metal-doped LiCoO_2 materials synthesized by the present procedure results in enhanced electrochemical activity. It has been demonstrated for the first time that the

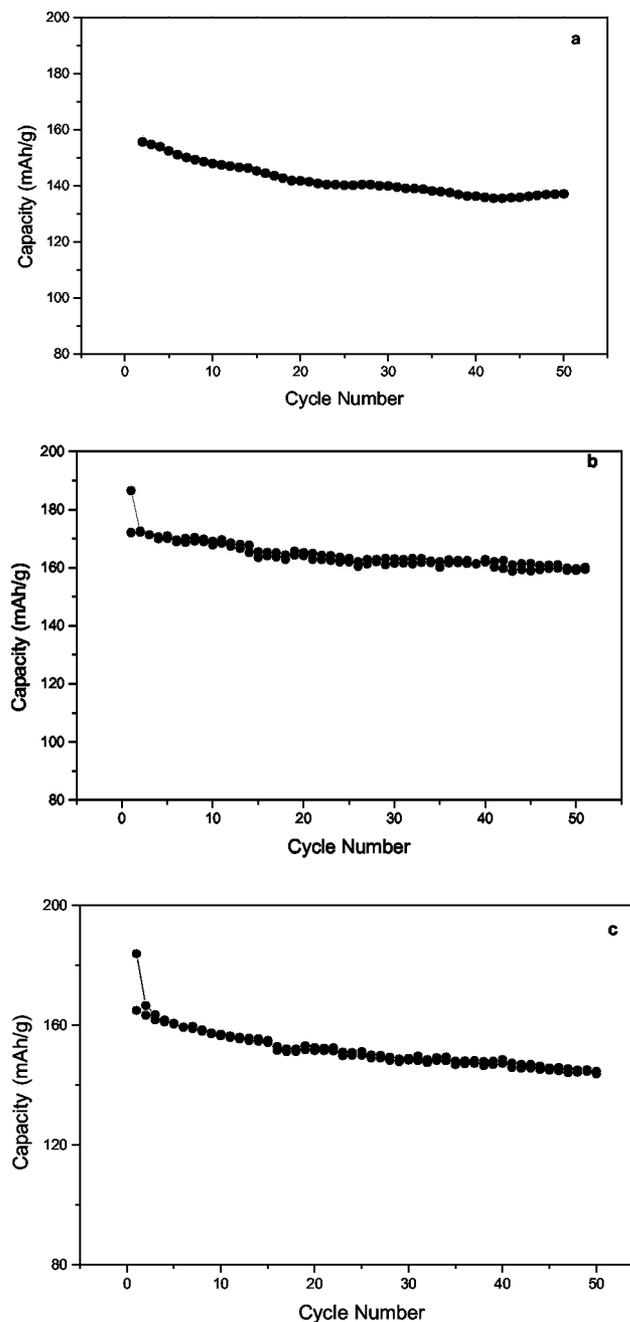


Figure 4. Galvanostatic cycling at C/5 rate in the voltage range 3.5 to 4.5 V of $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ M = (a) Al, (b) Mg, or (c) Ti.

material, $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$, is a promising high voltage cycling (4.5 V) cathode material delivering capacities of 160 mAh/g at C/5 rate for use in lithium rechargeable cells.

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