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Performance characteristics of Li//$Li_{1\pm X}CoO_2$ cells

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Abstract

Lithium cobalt oxides ($LiCoO_2$) with varying lithium stoichiometries viz., 0.97, 1, 1.03, 1.06 and 1.1 have been prepared by a solid-state high temperature technique. Structural determination of the synthesized powders with X-ray diffraction (XRD) reveals single-phase materials while the surface morphologies investigated with scanning electron microscopy (SEM) indicate different particle orientation with increase in lithium content. Electrochemical galvanostatic cycling studies of the synthesized powders in lithium 2032 coin type cells in the voltage range 3.5–4.5 V suggest that initial capacity fading is minimum in samples with lithium stoichiochiometries of either 0.97 or 1.03 and stable capacities are attained after the initial 10 cycles. The effect of lithium stoichiometry on the performance of $LiCoO_2$ in a lithium rechargeable cell is presented.

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1. Introduction

Lithium ion batteries are attractive due to their high voltage, high energy densities and wide range of applications [1]. The system involves the use of lithiated transition metal oxides as cathodes usually $LiCoO_2$, $LiNiO_2$ or $LiMn_2O_4$. Considering the ease of synthesis and reversibility [2], $LiCoO_2$ is the most preferred cathode material in the majority of commercial cells. The use of $LiCoO_2$ is expected to deliver a theoretical capacity of 273.8 mAh/g however in practice only 50% of this capacity is realized, i.e., only 0.5 mol of lithium can be extracted. Hence, in order to achieve higher capacities one has to cycle the cells

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to higher voltages viz., 4.5 V or employ either doping or coating the materials [3–5]. Marginal success has been reported by doping with tetravalent ions [6] but coating techniques has proven to be the only option. Normally, cycling beyond 4.25 V results in structural degradation thereby rendering inferior capacities [7] and hence other techniques have to be adopted. A thorough literature survey suggests that not much efforts have been attempted to investigate the role of lithium stoichiometry in $LiCoO_2$. In a recent study, Imanishi et al., [8] reported the electrochemical behavior of Li_XCoO_2 ($X > 1$) after oxygen treatment based on the XPS studies of Levasseur et al., [9]. However, the studies of Imanishi et al. were limited to first few cycles and were subjected to oxygen treatment but we believe that extended cycleability could often result in fading. Hence, based on this assumption, we found that it is noteworthy to carry out investigations for ascertaining the effect of lithium stiochiometry on the cycleability of $LiCoO_2$. Therefore, in this communication we present the synthesis and electrochemical behavior of Li_XCoO_2 in air using solid state technique in a lithium rechargeable cell when cycled up to 30 cycles in the voltage range 3.5–4.5 V.

2. Experimental

Li_XCoO_2 incorporating different amounts of lithium ($X = 0.97$, 1.03, 1.06 and 1.1) have been prepared by mixing stoichiometric amounts of Co_3O_4 (>99.9% pure), Li_2CO_3 melted in an argon atmosphere at 550 °C for 6 h and then cooled. The synthesized powders are ground and mixed well before first annealing at 800 °C for 10 h and then cooled, mixed and finally annealed for further 10 h. The synthesized materials were cooled, mixed and characterized both physically and electrochemically using different techniques.

X-ray diffraction (XRD, Rint 1000, Rigaku) using Cu Kα radiation were performed on the synthesized powders for analyzing the phase purity. Surface morphologies of the synthesized powders were investigated using a scanning electron microscope (JSM-5300E, Japan Electron Ltd., Japan).

ICP analysis were carried out for determining the composition of the synthesized materials.

Electrochemical behavior was carried out using a two-electrode 2032 coin cell assembly. The aluminum cathode disc was coated with a mixture containing 85% of the active material mixed with 15% teflonized carbon. The coating on aluminum foil has been done by using doctor blade technique and dried in an oven for 6–12 h at 120 °C. The dried sheet of the cathode material is then roll pressed for increased adherence of the cathode mixture onto the aluminum foil current collector. Circular discs 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 discs of Li_XCoO_2 as cathode, lithium (Cyprus Foote Mineral Co.) metal anode and with Celgard 3401 as separator using 1M $LiPF_6$ 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.

3. Results and discussion

The ICP values determined based on relative molar ratios and also fixing the mol number of Li + Co as 2 for different lithium stoichiometries are presented in Table 1. We observe no oxygen defects for

Table 1
Composition analysis of Li_XCoO_2 by ICP

Target	Composition
Li = 0.97	$Li_{0.94}Co_{1.06}O_{1.95}$
Li = 1	$Li_{0.96}Co_{1.04}O_{1.97}$
Li = 1.03	$Li_{1.00}Co_{1.00}O_{2.00}$
Li = 1.06	$Li_{1.01}Co_{0.99}O_{2.0}$
Li = 1.1	$Li_{1.07}Co_{0.93}O_{2.01}$

samples with Li stoichiometries of 1.03, 1.06 and 1.1 but defects are observed for samples with lithium content of 0.97 and 1. Such defects have also been noted by Imanishi et al., [8]. Therefore, no oxygen treatment is necessary. Fig. 1(a–d) presents the XRD patterns of the synthesized materials with different lithium stoichiometries. It is observed that all the patterns exhibit clear finger print peaks viz., 003, 101, 006, 102, 104, 108 and 110 as well as the clear splitting of the doublets at 006/102 and 108/110 suggest the formation of α-$NaFeO_2$ structure therefore could be assigned to the space groug R-3m. One interesting point to note from the XRD patterns is that the intensity of 003 peak increases up to the lithium

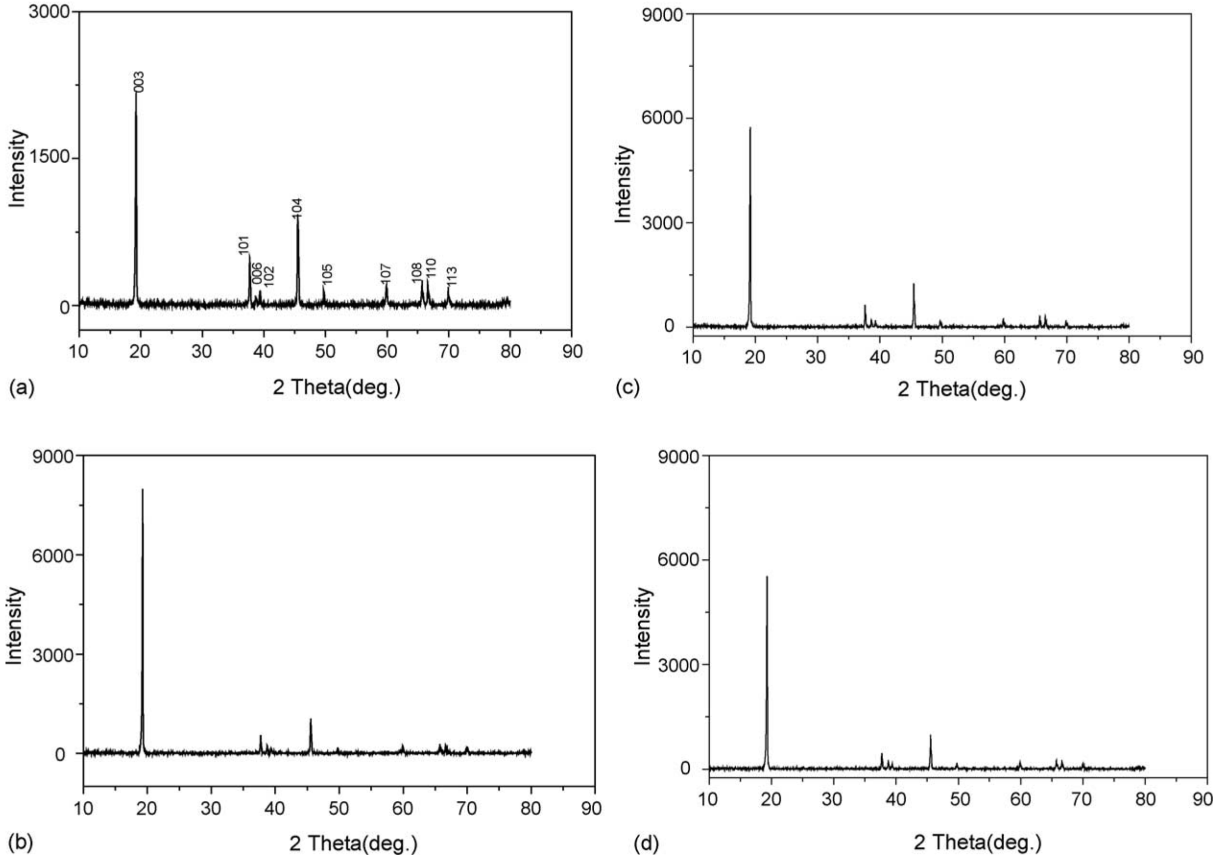

Fig. 1. XRD patterns of Li_XCoO_2 X = (a) 0.97, (b) 1.03, (c) 1.06 and (d) 1.1.

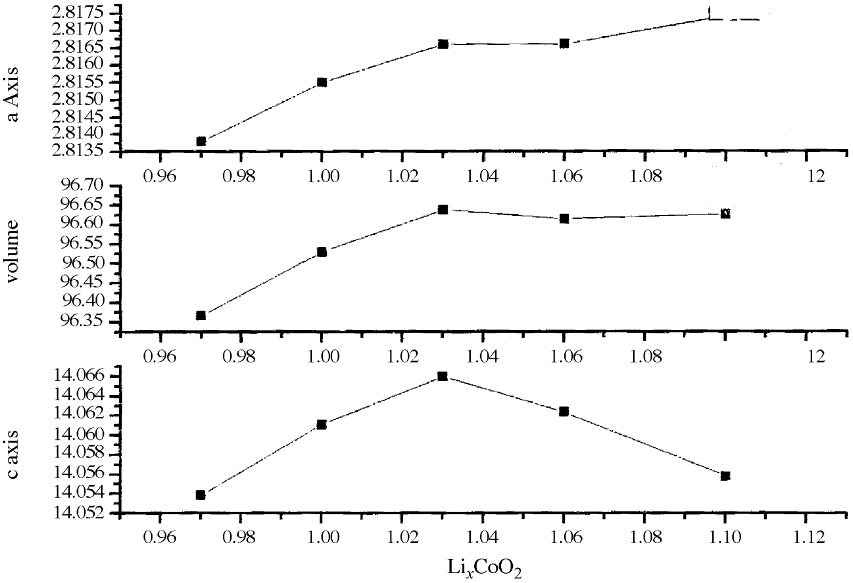

Fig. 2. Lattice constants “a” and “c” of Li_XCoO_2 $X = 0.97$, 1.00, 1.03, 1.06 and 1.1.

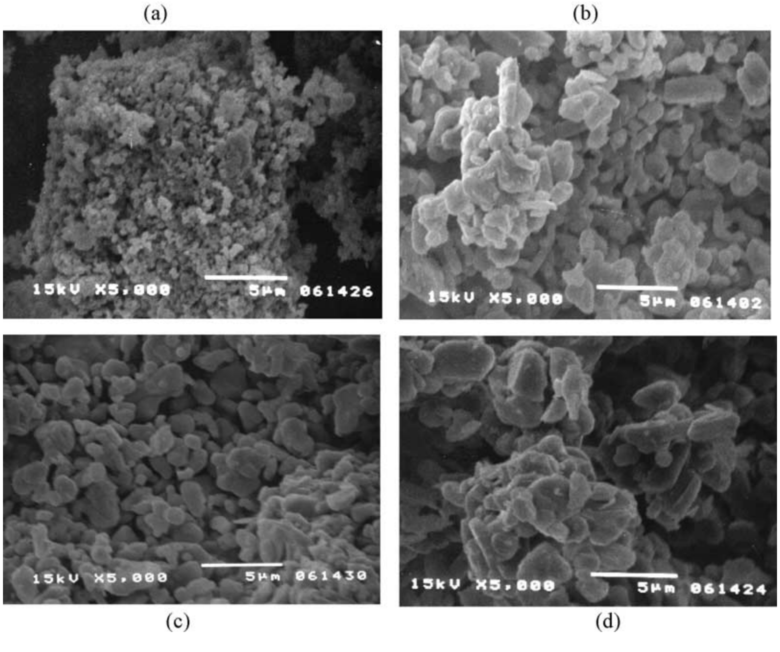

Fig. 3. SEM photograph of Li_XCoO_2 $X =$ (a) 0.97, (b) 1.03, (c) 1.06 and (d) 1.1.

stoichiometry of 1.03 and beyond this level the intensity reduces and becomes constant with further increase in Li-stoichiometry. Moreover, the 006 and 102 peaks are well developed in lithium deficient materials (Li = 0.97) but the 006 peak grows and almost matches the intensity of the 102 peak in lithium rich samples. These observations could be ascribed due to the inhomogeneous distribution of lithium in the 3a sites (lithium). Further, it is interesting to look at the trends of the lattice constants ‘‘a’’ and ‘‘c’’ (Fig. 2): with increasing contents of lithium both lattice constants increase up to a Li content of 1.03, but the values of ‘‘c’’ decrease at higher lithium contents (>1.03). This suggests that at higher lithium stoichiometries the intercalation/deintercalation of lithium ions is hindered resulting in poor cycleability of these lithium rich materials.

The SEM photographs depicted in Fig. 3(a–d) indicates plate type morphology. The particles in the lithium deficient materials are closely packed and exhibit agglomeration whereas the particle size grows with increase in lithium content. Thus, it can be said that lithium rich materials should have decreased electrochemical activity than lithium deficient materials due to an increase in lithium diffusion path lengths.

The first charge/discharge behavior of Li//$Li_XCoO_2$2032 type coin cells are presented in Fig. 4(a–d). All the fabricated cells using the synthesized materials exhibit an open circuit voltage (OCV) of 3 V

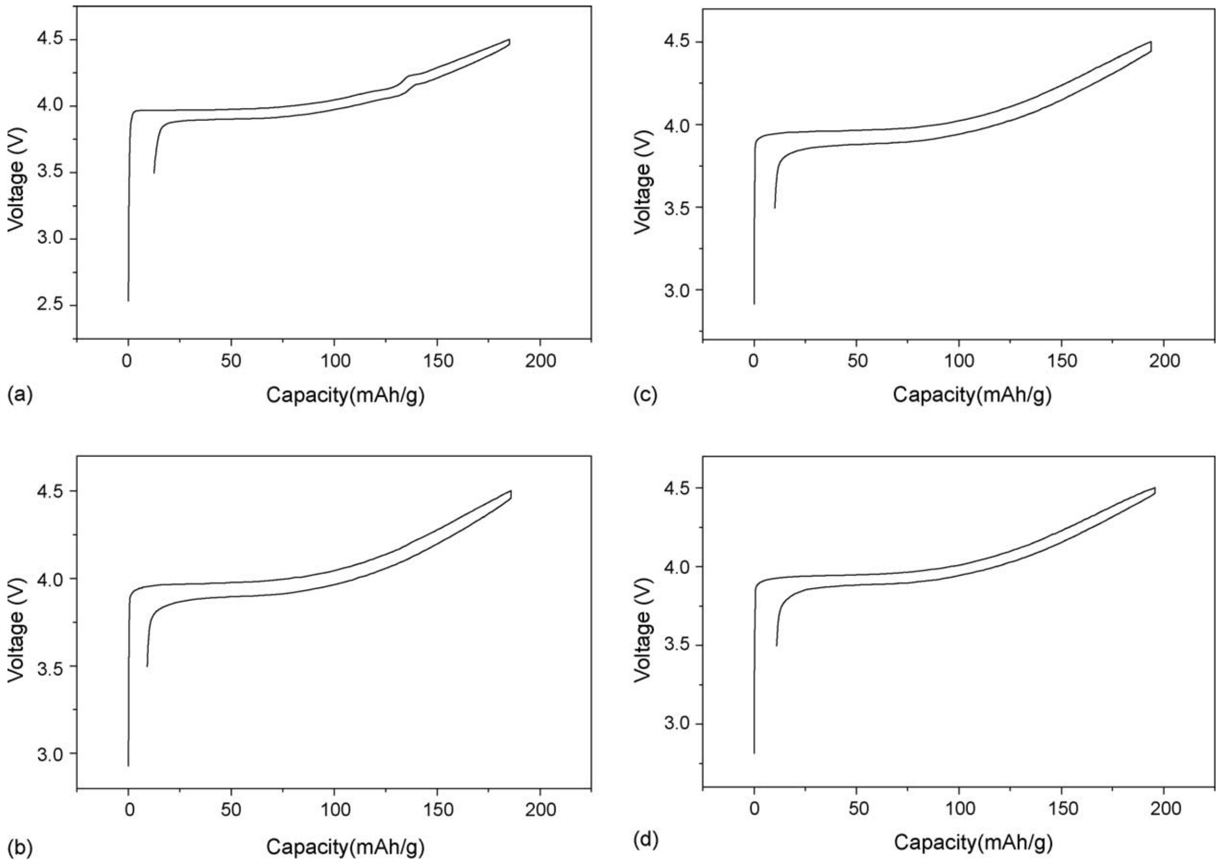

Fig. 4. First charge/discharge patterns of Li_XCoO_2 X = (a) 0.97, (b) 1.03, (c) 1.06 and (d) 1.1.

(versus lithium metal). The cells were cycled in the voltage range 3.5–4.5 V. It can be seen from Fig. 4a that a hump is observed around 4.2 V indicating a change from rhombohedral to monoclinic ($Li_{0.5}CoO_2$). However, it is interesting to note that such phase changes are not observed in lithium rich materials. Further, all the materials in the first charge show a flat plateau around 4 V but at very high lithium stoichiometry (Li = 1.1) there seems to be a lowering of the plateau to around 4.95 V and also higher charging capacity of around 195 mAh/g. However, the first irreversible capacities in all cases are similar, i.e., ~12 mAh/g. The lowering of the voltage plateau could be linked to the increased lithium concentration thus leading to inhomogeneous distribution. The phase change as observed in Fig. 4a is considered to hinder the long cycleability of the materials [7] and so we were interested to carryout the extended cycling (30 cycles) in the voltage range 3.5–4.5 V.

The cycling of the synthesized powders in a lithium rechargeable coin cell is presented in Fig. 5(a–d). It is interesting to note that all the materials show excellent cycleability in the investigated 30 cycles. The initial discharge capacity of around 175 mAh/g are exhibited in the case of lower lithium contents (0.97 and 1.03) whereas the patterns of higher lithium stoichiometry (1.06 and 1.1) are around 185 mAh/g. The cycling patterns remains the same up to 10 cycles beyond which higher lithium stiochiometric samples (Li = 1.1) fade to around 140 mAh/g. It is interesting to note that either of lithium stoichiometry viz., 0.97

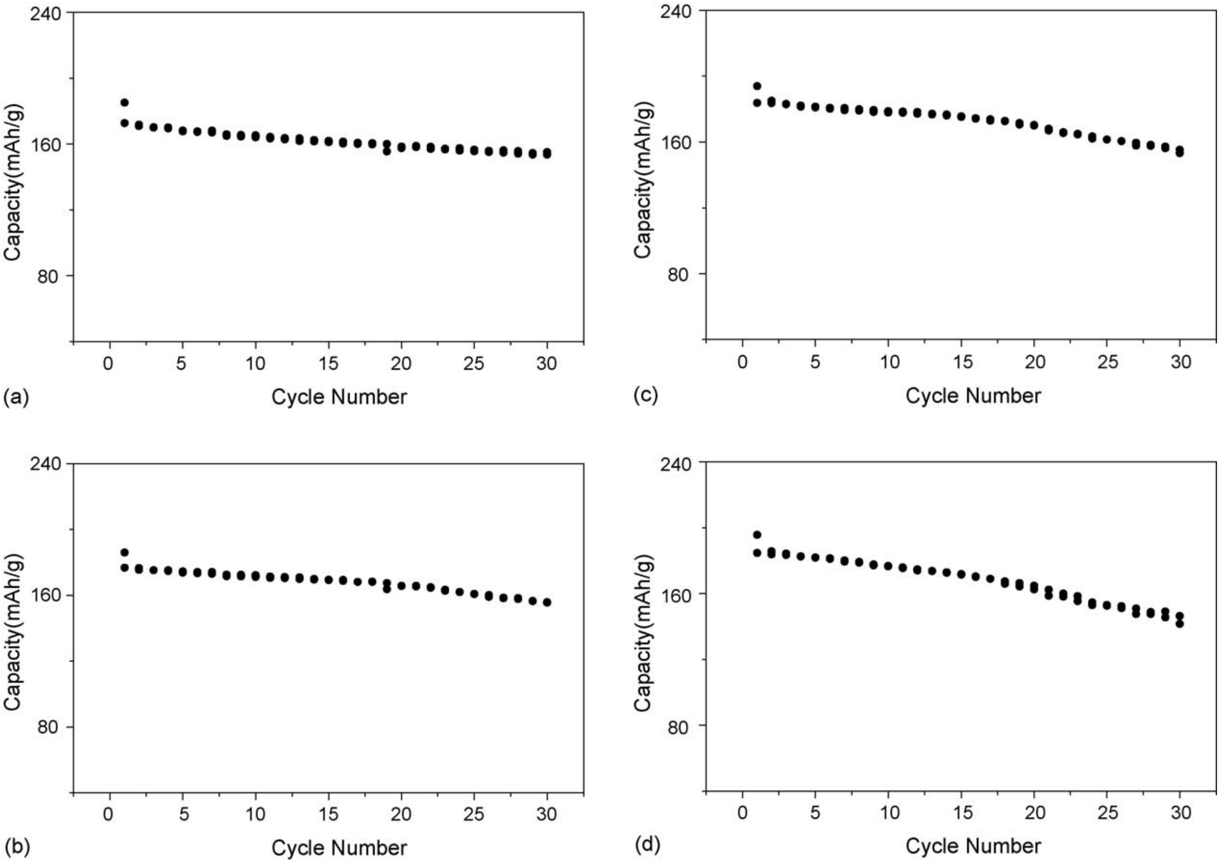

Fig. 5. Galvanostatic cycling at C/5 rate in the voltage range 3.5–4.5 V of Li_XCoO_2 X = (a) 0.97, (b) 1.03, (c) 1.06 and (d) 1.1.

or 1.03 show stable cycling thereby exhibiting a final discharge capacity of around 160 mAh/g at the end of 30 cycles. Therefore, we can say that in lithium compositions of either 0.97 or 1.03 the capacity retention of more than 90% is achieved. Our results reported herein are superior to those published by Imanishi et al. [8], as we have demonstrated that by annealing in air at 800 °C there is no oxygen defects in the investigated compositions ($X = 1.03$, 1.06 and 1.1). Further, high capacities of around 160 mAh/g either for lithium stoichiometry of 0.97 or 1.03 in a narrow cycling range of 3.5–4.5 V are obtained as against the reported value of 160 mAh/g in a much wider range of 2.5–4.52 V [8]. Results of high voltage cycling of stoichiometric $LiCoO_2$ has already been reported in our earlier communication [10].

4. Conclusion

We may therefore conclude that solid solutions have been prepared up to lithium stoichiometry of 1.1 and either slightly lithium deficient or rich materials ($Li_{0.97}CoO_2$ and $Li_{1.03}CoO_2$) delivers stable high capacities of ~160 mAh/g over the investigated 30 charge/discharge cycles in the voltage range 3.5–4.5 V.

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