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Improvement of the cycle life of $LiCoO_2$ powder by Sr doping

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ABSTRACT

Strontium doped $LiCoO_2$ cathode material for rechargeable lithium ion batteries were synthesized by starch assisted combustion route method. The structural characterization was carried out by X-ray powder diffraction and laser Raman spectroscopy. The sample exhibited a well-defined rhombohedral structure and the lattice parameters varied with the increasing strontium (Sr) content. Surface morphology of the synthesized materials was determined by Scanning electron microscope. The cathode materials consisted of highly ordered single crystalline particles with spherical shape. An increase of about two orders of magnitude in the electrical conductivity (5.9×10^{-3} S cm^{-1}) was observed for 10 mol%. Decrease of the electrode impedance was observed with increase in Sr content in system. Electrochemical properties were characterized by the assembled test cells using galvanostatic discharge studies that were carried out at a current rate of 0.1 C. Galvanostatic discharge profiles of coin cells fabricated with the synthesized powders show a significant enhancement in the discharge capacity during 5 mol% Sr doping $LiCoO_2$.

1. Introduction

$LiCoO_2$ is the most widely used cathode material for lithium ion batteries. Though it has a theoretical capacity of ~270 mAh g^{-1} practically only 120–160 mAh g^{-1} could be realized because of the fact that only 0.5 mole of lithium is extractable from one mole of $LiCoO_2$ in the voltage range 2.8–4.2 V [1–6]. In an attempt to extract more lithium per mole of $LiCoO_2$ considerable efforts were reported by applying higher voltages (~4.8 V), to the layered rhombohedral structure with Li–Co–O stacking in the order AB CA BC that has given way to the monoclinic form with the stacking pattern AA BB CC with little or no electrochemical performance as a cathode [7–10]. Thus, the stability of structure of $LiCoO_2$ is the most important parameter for obtaining good electrochemical performance and by stabilizing the structure it might be possible to extract lithium beyond the value realized. Accordingly, several efforts have been directed towards substituting cobalt by different transition elements such as Ni, Mn, Cr, and Fe [11–18]. In addition, extensive studies have also been carried out to substitute Co^{3+} in $LiCoO_2$ with non-transition elements like Mg^{2+} [8,9,19], B^{3+} [20,21], Al^{3+} [22,23], but only a marginal increase in cell potential from 4.2 to 4.3 V has been reported with associated capacity fading. While this capacity fading (>50% after 10 charge–discharge cycles) is large for Al^{3+} [22], a somewhat better capacity retention (~90% after 100 cycles) has been observed for Mg^{2+} and B^{3+} as dopants [19–21]. Having a much larger ionic radius of Sr^{2+} (~0.127 nm) than Co^{3+} (~0.063 nm), it is unlikely that Sr^{2+} would enter the $LiCoO_2$ lattice and substitute Co^{3+}. Instead, being a highly mobile ion, Sr^{2+} may migrate to the interlayer space stabilizing the layered framework of the $LiCoO_2$ structure. Fey et al. [22] have reported an improvement in capacity retention of $LiNi_{0.8}Co_{0.2}O_2$ powder doping with Sr. Recently, Subramania et al. [23] have observed an improved cyclability in $LiMn_2O_4$ compound doped with Sr. To the best of our knowledge, no study has been made on the Sr-doped $LiCoO_2$ composite cathode material. Here, we report the synthesis of Sr-doped $LiCoO_2$ composite powder by combustion technique for the first time. The influence of Sr on the phase transformation and electrical conductivity are discussed and correlated to the electrochemical properties of these composite cathode materials.

2. Experimental details

Sr-doped $LiCoO_2$ powders were synthesized using starch assisted combustion process by the following procedure. Stoichiometric amount of lithium hydroxide monohydrate ($LiOH.H_2O$) cobaltus (III) nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$) and strontium acetate $Sr(CH_3COO)_2{\cdot}1/2\,H_2O$ solutions were (metal ions ratio Li:Sr:Co: is $1{:}x{:}1-x$) mixed with starch solution. The obtained pink solutions were evaporated at 80 °C for 6 h with constant stirring. Continuous evaporation leads to the formation of dark pink coloured polymeric resin, which was further dried at 120 °C for 12 h to remove excess water, which lead to the formation of solid mass. Further, these intermediates were grounded and heat treated at 800 °C for 12 h.

The crystalline structure was determined by X-ray diffraction using an X'pert PRO (PANalytical) diffractometer with Cu Kα radiation (λ = 0.15405 nm) and employing a scanning rate of 5° min^{-1}. The structure of the powders was characterized by Raman studies using NRS-3100 JASCO with 514 nm argon laser. The

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particle size and morphology was examined using scanning electron microscope (SEM) Hitachi S-3000H model. For SEM studies the samples are coated with Au sputtering using fine coat ion sputter JFC-1100 model instrument. The electrical conductivity was measured using two-probe conductivity system from room temperature to 150 °C on circular pellets of diameter of ∼10 mm and thickness of ∼2 mm. The impedance spectra were recorded using a schlumber 610 electrochemical interface and frequency response analyzer. The frequency range was 0.001 Hz to 100 kHz and the amplitude of the perturbation signal was 30 mV. The electrochemical performance was studied by assembling 2016 coin-type cells. Typical cathode was prepared from a slurry of the synthesized Sr-doped $LiCoO_2$ powder (80%), acetylene black (10%) and (polyvinylidene fluride) PVDF binder (10%) in n-methyl pyrrolidinone (NMP) solvent. The slurry was coated on an aluminium foil (current collector) and was dried at 110 °C in an oven for 12 h. It was then pressed under a pressure of 4 tonne in.$^{-2}$, for 1 min. Finally, circular discs of 18 mm in diameter were cut and used as cathode. The cells were assembled using Li metal as anode and $LiPF_6$ in EC: DMC (1:1, vol%) as electrolyte within an argon filled glove box. The cut-off voltages were 4.5 V for charging (deintercalation of Li-ions from $LiCoO_2$) and 3.0 V for discharging (intercalation of Li-ions into $Li_{0.5}CoO_2$), respectively, at a current rate of 0.1 C.

3. Results and discussions

3.1. XRD studies

X-ray diffraction patterns of Sr-doped $LiCoO_2$ compounds are presented in Fig. 1(a)–(e). The lattice parameters of the synthesized powders were calculated for (0 0 3) and (1 0 4) planes using the formula

$$\frac{1}{d^2} = \left(\frac{4}{3}\right)\left[\frac{h^2+hk+k^2}{a^2}\right] + \left(\frac{l^2}{c^2}\right) \qquad (1)$$

where ($h\,k\,l$) are Miller indices of the plane concerned and a and c are the lattice constants. The lattice parameter a indicates the metal–metal intralayer distance while c represents the interlayer spacing [24]. Lattice substitution by elements with larger ionic radii often leads to expansion of the unit cell parameters. Thus, considering the large difference in ionic radii of Sr^{2+} in (∼0.132 nm) compared to Co^{3+} (∼0.063 nm), the observed increase in the a and c values in Sr-doped $LiCoO_2$ composites can be explained. For a cation-disordered rocksalt structure, we know that the c/a should be 4.899($\sqrt{24}$) [25]. As seen from Table 1, the c/a value for 10 mol% Sr-doped $LiCoO_2$ is 4.875, indicating the existence of cation disorder in the lattice. Intensity ratio value $I_{(003)}/I_{(104)}$ increases with increasing molar concentration in Sr-doped $LiCoO_2$ composites and decreases to 0.98 for 10 mol% of Sr, less than the critical value of 1.2 [26], suggests that cation mixing happens at higher doping level. The 10 mol% Sr-doped sample has merged form of the (0 0 6) and (1 0 2) as well as (1 0 8) and (1 1 0) diffraction lines indicate that a disordered distribution of lithium and transition metal ions exist in the structure [27]. At the same time, when the doping amount is too high, the structure of the $LiCoO_2$ is found to be different, with the appearance of impurity phase. The crystallite size of the synthesized Sr-doped $LiCoO_2$ powders were calculated using FWHM data for the (0 0 3) and (1 0 4) planes by Scherrer [28] formula. The calculated crystallite size are found to be 89, 118, 196, 288 and 369 nm for strontium concentration 0, 1, 3, 5 and 10 mol%, respectively. This crystallite size variation has a direct impact on the electrical and electrochemical performances of the system.

Table 1
The lattice parameters of Sr-doped $LiCoO_2$ powders.

Sr (mol%)	d (Å)	a (Å)	c (Å)	c/a	$I_{(003)}/I_{(104)}$
0	4.678	2.821	14.034	4.975	1.23
1	4.682	2.844	14.046	4.939	1.39
3	4.688	2.853	14.064	4.929	1.48
5	4.690	2.860	14.070	4.920	1.87
10	4.695	2.889	14.085	4.875	0.98

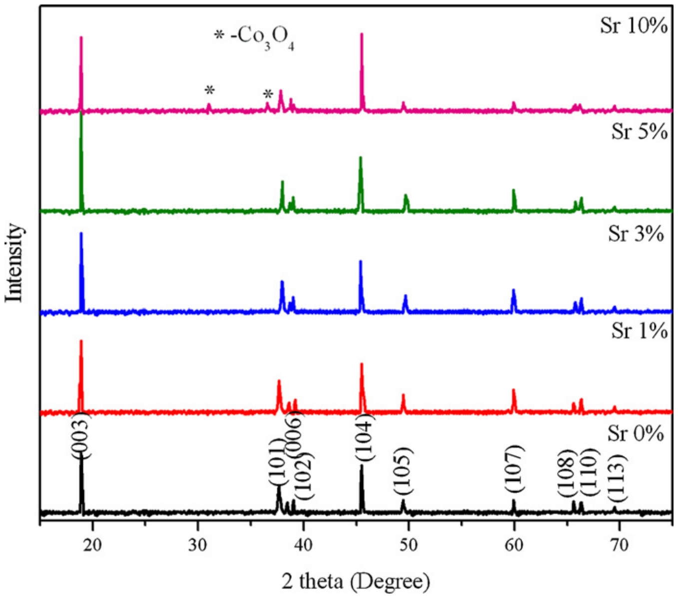

Fig. 1. X-ray diffraction patterns of the Sr-doped $LiCoO_2$ powders prepared by starch assisted combustion route method.

3.2. Raman studies

Fig. 2 shows Raman spectra of pristine and 10 mol% of Sr-doped $LiCoO_2$ compounds synthesized by combustion route method. It is observed that intensity of the Raman peaks increased and FWHM of the peak decreased with increase of Sr content. This may be due to an increase in grain size. The Raman spectrum of pristine $LiCoO_2$ was dominated by strong band around at 594 cm^{-1} accompanied by a still broader band at 484 cm^{-1} and these peaks are assigned as A_{1g} and E_g vibration modes in the hexagonal R-3m space group, which are in good agreement with those reported by Lee et al. [26]. The Raman studies reveal that the synthesized pristine $LiCoO_2$ is of high purity. However, at high doping level 10 mol% of Sr, an additional peak is observed at 686 cm^{-1} [26], which is ascribed to the formation of impurity Co_3O_4 phase. This reveals that single phase structure is observed only at lower strontium doping level, whereas the impurity phase co-exist at higher dopant level. No change in

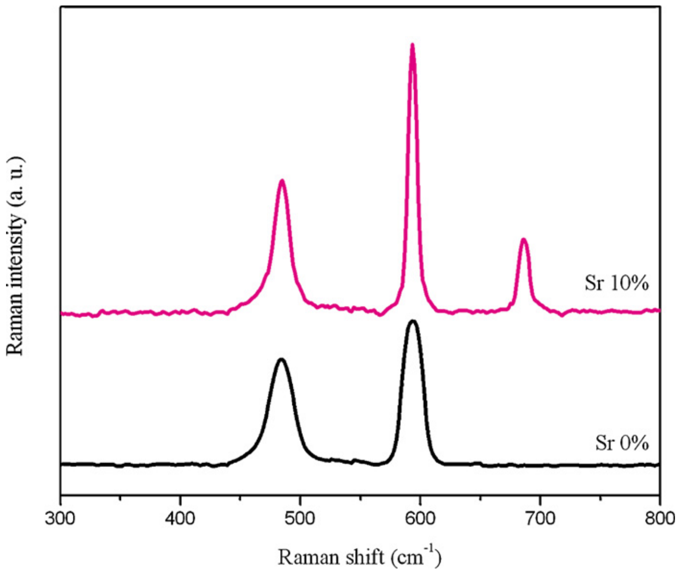

Fig. 2. Raman spectra of Sr-doped $LiCoO_2$ powders: 0 mol% Sr and 10 mol% Sr.