

Short communication

Synthesis and characterization of LiFeO_2 and $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ as cathode materials for Li-ion cells

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Abstract

The solution-combustion route is beneficial for fast and easy synthesis of cathode materials for Li-ion cells. LiFeO_2 synthesized by this method results in an amorphous phase that exhibits poor electrochemical activity with an initial specific capacity of only about 80 mAh g^{-1} and on annealing it transforms into an electrochemically inactive phase. On the other hand, $\alpha\text{-NaFeO}_2$ synthesized by a solution-combustion method and subjected to Na^+/Li^+ exchange by refluxing with LiBr solution in *n*-hexanol to obtain layered LiFeO_2 , exhibits an initial specific capacity of about 205 mAh g^{-1} with capacity fading after prolonged charge–discharge cycling. $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$, synthesized by the same route, shows a stable specific capacity of about 190 mAh g^{-1} .

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1. Introduction

Subsequent to the discovery of LiCoO_2 by the Goodenough group [1] in 1980, LiMO_2 ($M = \text{Co}, \text{Ni}$) compounds with layered $\alpha\text{-NaFeO}_2$ structures have been studied extensively [2] as cathode materials for Li-ion cells. However, both Co and Ni are expensive and toxic. Accordingly, Mn- and Fe-based compounds, such as LiMnO_2 [3], $\text{LiMn}_{1-y}\text{M}_y\text{O}_2$ [4] ($M = \text{Co}, \text{Ni}$ and Al), LiMn_2O_4 [5], LiFePO_4 [6] and LiFeO_2 [7–16], have been synthesized and investigated as cathode materials for Li-ion cells. It is noteworthy that, in the literature, the studies reported on layered LiFeO_2 [7–16] are scanty in relation to LiCoO_2 .

Layered LiFeO_2 cannot be synthesized by conventional high-temperature solid-state routes as it leads to different crystallographic forms of LiFeO_2 , namely α , β , and γ , depending on the synthesis conditions [12]. Furthermore, reversible intercalation and deintercalation of Li has not been possible in these phases owing to unfavorable crystallographic structures. Accordingly, various low-temperature methods have been adopted for the syn-

thesis of electrochemically active LiFeO_2 . For example, layered LiFeO_2 with the $\alpha\text{-NaFeO}_2$ structure was obtained by: (a) ion exchanging layered NaFeO_2 in $\text{LiOH}\cdot 2\text{H}_2\text{O}$ under hydrothermal conditions [13] and (b) hydrothermal reaction between FeOOH (or $\text{FeCl}_3\cdot\text{H}_2\text{O}$) and mixed-alkali flux comprising of $\text{LiOH}\text{--}\text{NaOH}$ (or $\text{LiOH}\text{--}\text{KOH}$) [14]. But LiFeO_2 obtained by these methods is not suitable as a cathode material in lithium-ion cells due to the migration of Fe to Li positions in the crystal lattice.

Kanno et al. [15] found corrugated-layer-structured LiFeO_2 to be electrochemically active. They synthesized LiFeO_2 from FeOOH using H^+/Li^+ ion-exchange reaction in the temperature range $100\text{--}500^\circ\text{C}$. But, this compound exhibited a fast capacity fade on cycling. Kim and Manthiram [16] reported synthesis of a nano-crystalline LiFeO_2 by oxidizing Fe^{2+} -species with lithium peroxide in aqueous lithium hydroxide followed by firing the precursors at varying temperatures between 200 and 800°C . The samples fired at low temperatures gave a discharge capacity of 140 mAh g^{-1} with good cyclability. On the other hand, samples heated at high temperatures exhibited a discharge capacity of only about 50 mAh g^{-1} .

A rapid, low-temperature solution-combustion method has been used to synthesize LiCoO_2 and also Mn- and Ni-substituted LiCoO_2 , by our group [17–19]. This route provides sub-micron

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size particles of the compounds in a short duration at temperatures as low as 350 °C. In the present study, we have synthesized LiFeO_2 at 350 °C by the rapid-combustion route using diformyl hydrazine as the fuel. This resulted in the formation of amorphous LiFeO_2 with poor electrochemical activity and annealing the sample resulted in an electrochemically inactive $\alpha\text{-LiFeO}_2$. As an alternative, $\alpha\text{-NaFeO}_2$ was synthesized from the solution-combustion method and then subjected to Na^+/Li^+ ion-exchange in *n*-hexanol. This procedure resulted in LiFeO_2 with a layered structure, which provided an initial specific capacity of 205 mAh g^{-1} as a cathode material for Li-ion cells. But the capacity faded rapidly on repeated charge–discharge cycling. Nevertheless, $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ synthesized by the similar route provided a stable specific capacity of 190 mAh g^{-1} as cathode material for Li-ion cells.

2. Experimental

Diformyl hydrazine (DFH) was prepared by drop-wise addition of formaldehyde (BDH) to a stoichiometric quantity of hydrazine hydrochloride (BDH) at 0 °C following the procedure reported by Ainsworth and Jones [20]. LiAsF_6 , ethylene carbonate (EC), dimethyl carbonate (DMC) and lithium ribbon (0.7 mm thick) were purchased from Aldrich. LiNO_3 and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was obtained from S.D. Fine Chemicals. $\text{Fe}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was prepared from a 1 M solution of oxalic acid and a 1 M solution of FeSO_4 in doubly distilled water as follows. Ferrous sulfate solution (100 ml) was taken in a beaker and heated to 80 °C. Oxalic acid solution (100 ml) was added drop-wise and the mixture was stirred at 80 °C for 12 h for completion of the reaction. The precipitate was filtered, washed repeatedly with double-distilled water and dried at 110 °C for 12 h under vacuum.

For the synthesis of LiFeO_2 , a mixture of LiNO_3 and $\text{Fe}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ was prepared in a minimum amount of water to get about 2 g of the product. LiNO_3 was taken 10% in excess of the stoichiometric requirement so as to compensate for any evaporation losses of Li as Li_2O . DFH (20 wt.% of the salts) was added to the mixture, stirred thoroughly and preheated at 80 °C for a few minutes to ensure homogeneity. The solution mixture was transferred to a wide mouthed petri-dish and introduced into a furnace, which was preheated to 350 °C. This resulted in fuel ignition with evolution of dense fumes and a solid residue was formed within a few minutes. The product was cooled to room temperature, dried in air and annealed at varying temperatures for 6 h. $\alpha\text{-NaFeO}_2$ was also synthesized similarly but by using NaNO_3 in place of LiNO_3 . $\alpha\text{-NaFeO}_2$ thus obtained was then subjected to ion-exchange by refluxing at 140–160 °C for 8 h in *n*-hexanol with eight-fold excess of LiBr to obtain layered LiFeO_2 . The product was then filtered, washed copiously with methanol and ethanol mixture and finally dried at 80 °C under vacuum for 12 h. $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ was obtained by Na^+/Li^+ ion-exchange of the corresponding sodium precursor, which was prepared by taking stoichiometric quantities of its constituent metal salts, namely NaNO_3 , $\text{Fe}(\text{COO})_2 \cdot 2\text{H}_2\text{O}$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

For electrochemical characterization, electrodes were prepared on an Al foil (0.2 mm thick) and cells were assembled in 1 M LiBF_4 dissolved in EC and DMC mixture of equal volumes as reported previously [17–19]. Lithium ribbon was used both for the counter and reference electrodes. The potential values reported are against a Li/Li^+ reference electrode.

The concentrations of sodium and lithium were estimated by flame photometry. Powder XRD patterns of the samples were recorded on a Siemens Diffractometer (Model D5005) using $\text{Cu K}\alpha$ radiation and the microscopic studies were made using Jeol Scanning Electron Microscope (Model JSM 5600LV). Cyclic voltammograms of the electrodes were recorded using an EG&G PARC Potentiostat/Galvanostat Model Versastat. Electrochemical impedance spectra were measured in the frequency range between 100 kHz and 10 mHz with an excitation signal of 5 mV by means of an EG&G PARC Electrochemical Impedance Analyzer (Model 6310). Galvanostatic charge–discharge cycling of the electrodes was carried out using a galvanostatic circuit that comprised a regulated dc power source, a high resistance and an ammeter in series with the cell. A digital multimeter with high input-impedance was used to measure the electrode potentials.

3. Results and discussion

The solution-combustion technique involves addition of a mild fuel to the metal nitrate solution and ignition of the fuel

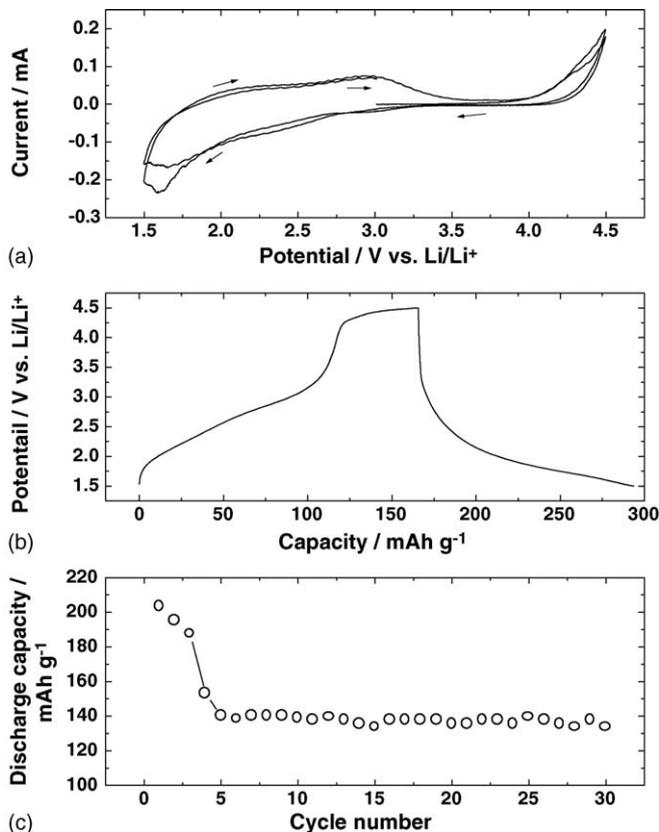


Fig. 1. (a) Cyclic voltammograms at a scan rate of 0.05 mV s^{-1} , (b) charge–discharge profiles at C/8 rate for second cycle, and (c) cycle-life data for the LiFeO_2 (ie) in 1 M LiBF_4 .

at a low temperature, usually around 350 °C [21]. During the ignition of the fuel, the temperature of the reactants rises rapidly decomposing the precursors, which results in the formation of the corresponding metal oxide. As this process is accompanied by emission of a large quantities of gases, viz. NO, NO₂, CO₂, H₂O, etc., the oxides are formed as fine particles with a sufficiently high surface-area. The time required to synthesize the oxide is only a few minutes. In the present study, this method is used to synthesize LiFeO₂, α-NaFeO₂ and α-NaFe_{0.9}Co_{0.1}O₂.

A structure field-map for LiMO₂ compounds is helpful in predicting their structures [22]. The structures of LiMO₂ are primarily dependent on the size of the M-cation. LiMO₂ compounds

with M = V, Cr, Co and Ni possess a layered rock-salt structure, while the compounds containing Fe and Ti adopt a disordered cubic rock-salt structure or a tetragonally ordered structure. The boundary of these two types of structures is located between V³⁺ and Fe³⁺. Depending on the synthetic procedure, it is possible to obtain layered LiFeO₂. Cubic α-LiFeO₂ was synthesized at temperatures >600 °C, monoclinic β-LiFeO₂ was obtained by annealing α-LiFeO₂ at <500 °C, tetragonal γ-LiFeO₂ was prepared at temperatures 500 °C, and rhombohedral layered-LiFeO₂ was obtained by ion-exchange of α-NaFeO₂ [12]. The XRD pattern of the LiFeO₂ synthesized by combustion method was found to correspond to essentially an amorphous phase.

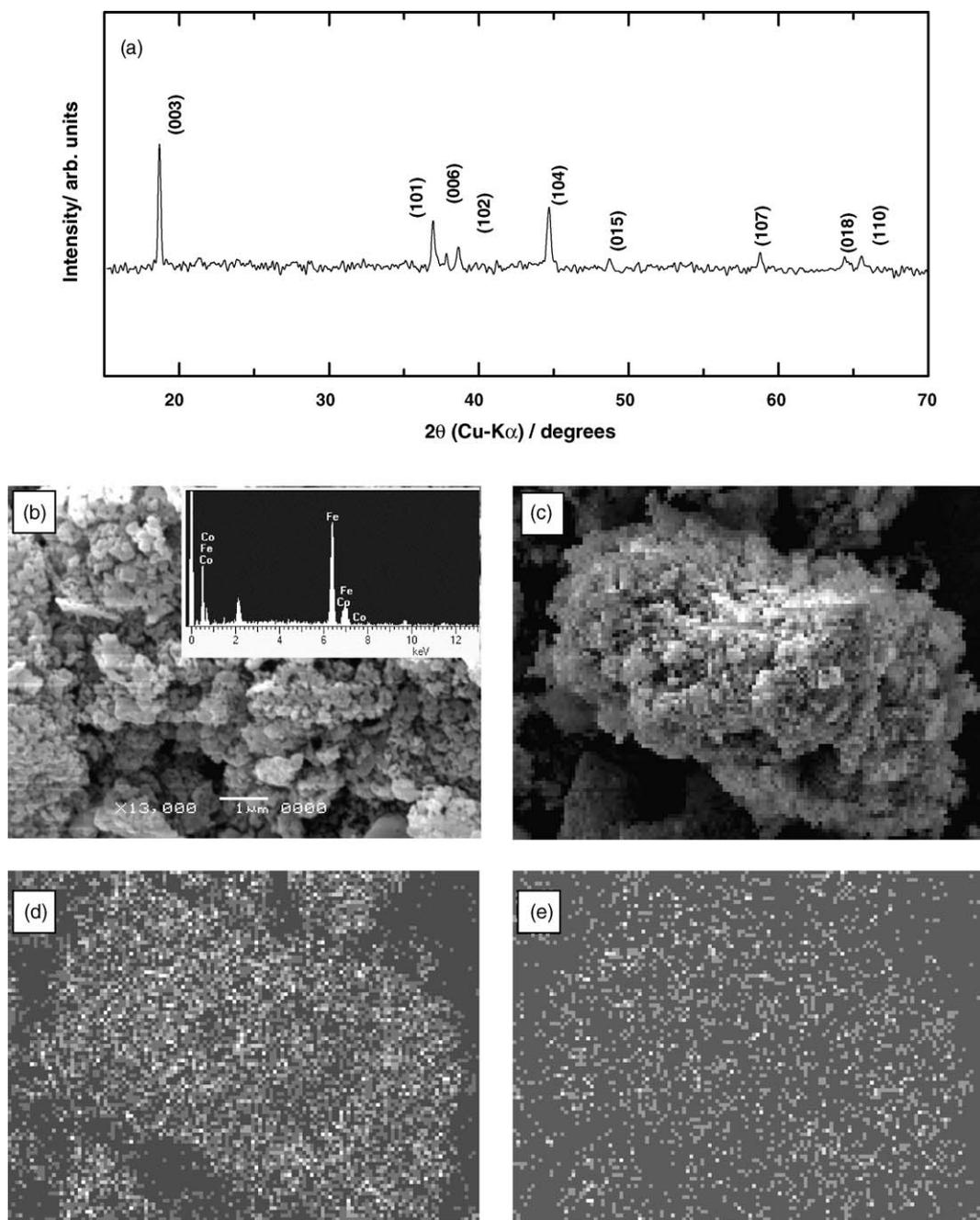


Fig. 2. (a) Powder XRD pattern of LiFe_{0.9}Co_{0.1}O₂, (b) SEM image with EDAX spectrum as inset, (c) selected area EDS dot mapping, (d) EDS dot mapping for Fe, and (e) EDS dot mapping for Co in LiFe_{0.9}Co_{0.1}O₂.

Charge–discharge cycling of this compound at the C/8 rate was performed in the voltage range between 1.5 and 4.5 V. Initially, a discharge capacity of 85 mAh g^{-1} was obtained that gradually faded and attained a steady value of about 50 mAh g^{-1} . This indicates that there was a structural rearrangement of the compound during charge–discharge cycling. On annealing the amorphous LiFeO_2 at 800°C for 6 h, a crystalline $\alpha\text{-LiFeO}_2$ was formed. Crystalline LiFeO_2 did not exhibit any electrochemical activity.

Similar to the properties of crystalline LiFeO_2 observed in the present study, electrochemical inactivity for LiFeO_2 synthesized at low temperatures has been reported by Sakurai et al. [23]. In order to study the effect of the annealing temperature on the electrochemical activity of LiFeO_2 synthesized by combustion route, samples were annealed at several temperatures between 500 and 800°C and subjected to charge–discharge cycling. There was a gradual decrease in discharge capacity with increase in annealing temperature. It is concluded that amorphous LiFeO_2 synthesized from the combustion route possesses a higher electrochemical activity than the annealed crystalline samples.

Layered $\alpha\text{-NaFeO}_2$ was synthesized from the combustion route and then subjected to Na^+/Li^+ exchange to obtain $\text{LiFeO}_2(\text{ie})$ [“ie” stands for ion-exchange]. The XRD pattern of $\text{LiFeO}_2(\text{ie})$ agreed well with the pattern reported for the layered LiFeO_2 . The pattern was indexed as a hexagonal unit cell with space group: $R\bar{3}m$. The unit cell parameters obtained using least-square-fitting procedure were: $a = 2.9446 \text{ \AA}$ and $c = 14.5851 \text{ \AA}$.

Cyclic voltammograms of layered $\text{LiFeO}_2(\text{ie})$ are shown in Fig. 1(a) in the voltage range between 1.5 and 4.5 V. There are broad peaks at 3 and 1.69 V, respectively, in the anodic and cathodic sweeps. Although sharp current peaks are not present in the cyclic voltammogram, $\text{LiFeO}_2(\text{ie})$ was found to provide attractive values of charge–discharge capacity as described below.

The charge–discharge profiles during cycling of $\text{LiFeO}_2(\text{ie})$ for the second cycle are shown in Fig. 1(b). It is seen that both during charging and discharging the effective capacity window lies below 3 V. This charge–discharge profile agrees well with the profile reported for the layered LiFeO_2 [24]. There is a large irreversible capacity loss during the initial charge–discharge cycles. The coulombic efficiency obtained for the first cycle is about 76%. However, there was a gradual increase in the efficiency with increase of cycle number and this attained 98–99% after about 15 cycles. Although the reasons for the behaviour are not understood, almost all studies reported on LiFeO_2 show similar behaviour [11,14,15]. The cycle-life data are shown in Fig. 1(c). The initial discharge capacity was about 205 mAh g^{-1} that faded to about 140 mAh g^{-1} after five cycles. Thereafter, the capacity remained stable over about 30 charge–discharge cycles conducted during the study.

Subsequent to the studies on $\text{LiFeO}_2(\text{ie})$, attempts were made to partially substitute Fe with Co. Accordingly, $\text{NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ was prepared by the solution-combustion method and subjected to Na^+/Li^+ ion-exchange to obtain $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$. The XRD pattern for $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ is shown in Fig. 2(a). The pattern obtained was indexed as hexagonal unit cell with $R\bar{3}m$ space

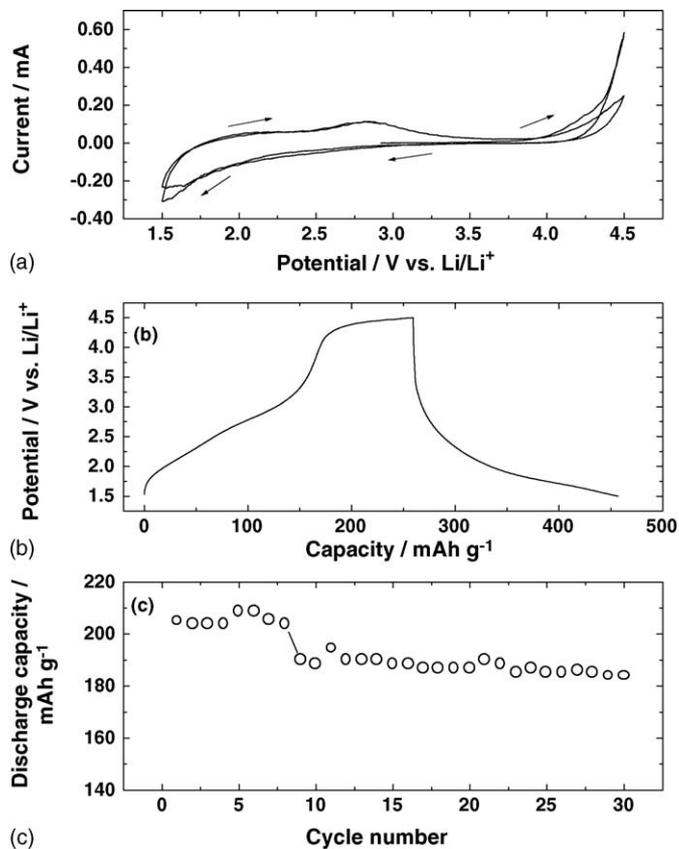


Fig. 3. (a) Cyclic voltammogram at a scan rate of 0.05 mV s^{-1} , (b) charge–discharge profile at C/8 rate for second cycle, and (c) cycle-life data of $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$.

group. The lattice parameters obtained were: $a = 2.9316 \text{ \AA}$ and $c = 14.5364 \text{ \AA}$.

An SEM image of $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ is shown in Fig. 2(b) with the EDAX pattern inset. To check the homogeneity of the $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$, Energy Dispersive Spectra (EDS) dot mappings were recorded for Fe and Co in the sample. Fig. 2(c) shows the selected area for the dot mapping, and Fig. 2(d) and (e) shows EDS dot mappings for Fe and Co, respectively. EDAX pattern (inset to Fig. 2(b)) indicates the Fe and Co ratio to be about 9:1, thus confirming the composition. The dot mappings (Fig. 2(d) and (e)) suggest that the sample is homogeneous with a uniform distribution of Fe and Co.

A cyclic voltammogram of the $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ recorded in the voltage range between 1.5 and 4.5 V is shown in Fig. 3(a). The voltammogram shows broad cathodic and anodic peaks at 1.6 and 3 V, respectively, similar to the voltammetric behaviour of $\text{LiFeO}_2(\text{ie})$. Charge–discharge cycling of the $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ was performed in the voltage range between 1.5 and 4.5 V. The voltage profiles of the sample (Fig. 3(b)) with the initial specific capacity value of about 205 mAh g^{-1} are similar to $\text{LiFeO}_2(\text{ie})$. The Coulombic efficiency is low during initial cycling and it increased on repeated cycling as in the case of $\text{LiFeO}_2(\text{ie})$. On cycling, a stable capacity of about 190 mAh g^{-1} is obtained after 30 charge–discharge cycles conducted during the study (Fig. 3(c)). The stable value of the reversible capacity obtained

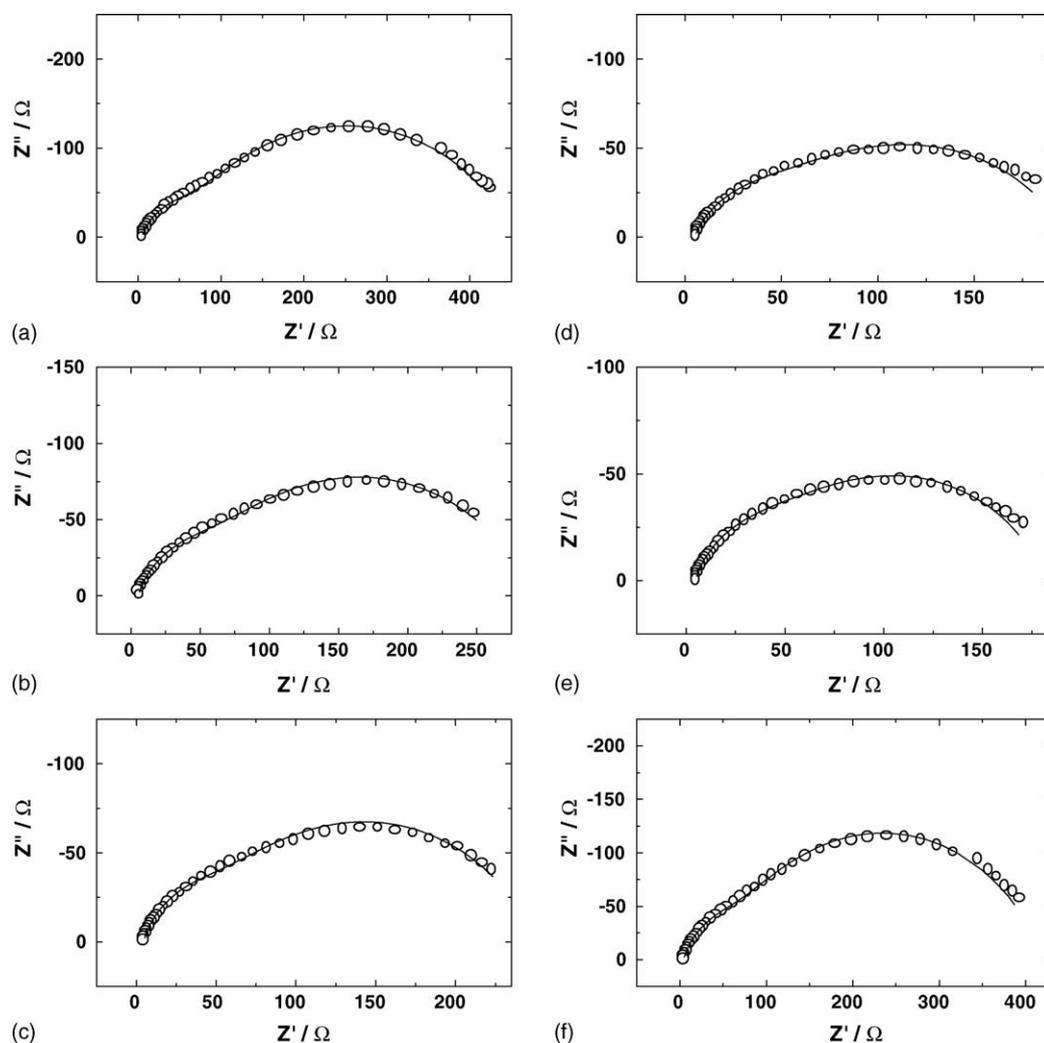


Fig. 4. Nyquist plots of $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ at SOC (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8, and (f) 1. Symbols represent the experimental data and lines the fit results.

for the $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ is possibly due to the stabilization of the layered structure by Co.

Impedance spectra for the $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ at several state-of-charge (SOC) values are shown in Fig. 4. The impedance plot

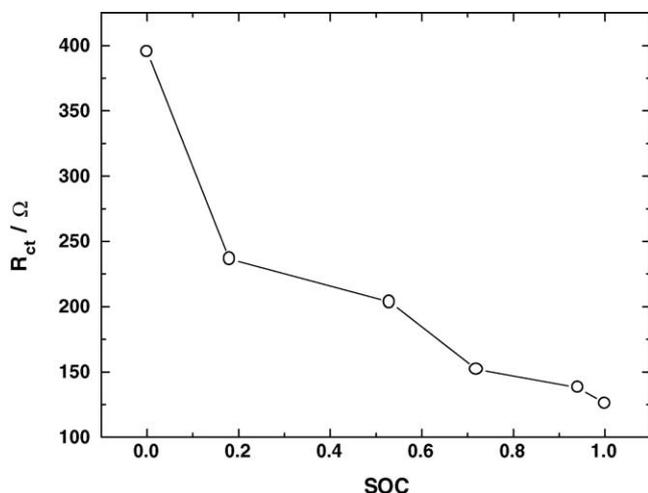


Fig. 5. Variation in R_{ct} with SOC for $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$.

shows two overlapping semicircles, which are assigned to the surface-layer resistance (R_f) and charge-transfer resistance (R_{ct}), respectively. The circuit code $R(RQ)(RQ)$ and the equivalent circuit program by Boukamp [25] were used for fitting. The variation in charge-transfer resistance (R_{ct}) for $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ with the state-of-charge (SOC) is shown in Fig. 5. There is a decrease in R_{ct} with an increase of SOC of the electrode in accordance with other cathode materials reported in the literature [26,27].

4. Conclusions

A solution-combustion technique has been successfully employed in the synthesis of electrochemically active LiFeO_2 and $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$. Synthesis of NaFeO_2 and $\text{NaFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ by the combustion method and Na^+/Li^+ exchange provided respective lithiated oxides. On the other hand, LiFeO_2 synthesized directly from solution-combustion exhibited poor electrochemical activity. Although the capacity value of 190 mAh g^{-1} obtained for $\text{LiFe}_{0.9}\text{Co}_{0.1}\text{O}_2$ is lower than 240 mAh g^{-1} obtained for layered LiMnO_2 , it is higher than 130 mAh g^{-1} generally reported for LiCoO_2 .

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