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Electrochemical Investigations of Cobalt-Doped LiMn$_2$O$_4$ as Cathode Material for Lithium-Ion Batteries

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ABSTRACT

A wide range ($y = 0.05$–$0.33$) of Co-doped LiCo$_y$Mn$_{2-y}$O$_4$ spinels were synthesized and electrochemically characterized. These Co-doped spinels showed improved specific capacity and capacity retention over pure spinels. Electrochemical impedance spectroscopy and the linear polarization resistance technique were used to determine the transport and electrochemical kinetic parameters of Co-doped spinels. The presence of Co in the spinel inhibits the passivation process occurring on the surface of the cathode. Also, Co increases the exchange current density and facilitates the charge-transfer reaction of the active material. The lower self-discharge observed for Co-doped spinels was attributed to their low surface areas. The cumulative capacity loss estimated for a pure spinel resulting from self-discharge in the first 30 h was 3 and 6 times larger than those estimated for Co-doped spinels with $y = 0.05$ and $y = 0.16$ in LiCo$_{y}$Mn$_{2-y}$O$_4$, respectively.

**Introduction**

Layered LiCoO$_2$ is currently used as a cathode material for production of commercial, high-energy-density lithium-ion batteries.1,2 Because of the high cost of Co and its toxicity, the three-dimensional LiMnO$_2$ spinel phase was studied extensively to substitute LiCoO$_2$ as the cathode material for Li-ion batteries.3-6 The Li insertion/deinsertion processes occur in the spinel phase in two composition ranges resulting in two voltage plateaus at 4 and 3 V vs Li/Li' for LiCo$_2$O$_4$.7,8 Attempts to substitute LiMnO$_2$ for LiCoO$_2$ in commercial Li-ion batteries have not been successful due to the lower specific capacity of the spinel and the fast capacity fade upon cycling.9-11

Efforts have been made to improve cycle life by controlling the capacity fading in LiMnO$_2$.12-16 The capacity fading has been attributed to spinel dissolution,12 the Jahn–Teller effect,12 and lattice instability13 at high oxidation levels. Baochen et al.14 found that cobalt-doped LiCo$_y$Mn$_{2-y}$O$_4$ improved cycling performance. According to Guohua et al.,15 LiCo$_{0.9}$Mn$_{1.1}$O$_4$ showed good cycle performance with an energy density of 370 Wh/kg at the 300th cycle. Recently, Sanchez and Tirado16 reported a new cobalt-substituted Li$_{1-y}$O$_{y}$Mn$_{2-y}$O$_4$ ($y = 4$) spinel phase reversible in a 3.3–2.3 V potential window. The capacity for the first cycle was 105 mAh/g. However, the initial capacity decreased sharply during the first five cycles, reaching values of about 110 and 85 mAh/g after 100 and 200 cycles, respectively.

In this study, a wide range ($y = 0.05$–$0.33$) of Co-doped LiCo$_y$Mn$_{2-y}$O$_4$ spinels were synthesized and electrochemically characterized. Electrochemical impedance spectroscopy (EIS) and the linear polarization resistance technique (LP) were used to determine the transport and electrochemical kinetic parameters of pure and Co-doped spinels.

The capacity fade rates of LiMnO$_2$ and LiCo$_{0.9}$Mn$_{1.1}$O$_4$ were studied and the active material loss during cycling was determined. Also, the effect of Co content on the self-discharge of pure and Co-doped LiMnO$_2$ was investigated.

**Experimental**

LiMnO$_2$ and Co-doped LiMnO$_2$ cathodes were prepared by a solid-state reaction between lithium carbonate (Aldrich, 99%), manganese carbonate (Aldrich, 99.5%), and cobalt oxalate hydrate (Aldrich, 99%). The mixture was preheated at 600 °C for 4 h and then heated at 750 °C for 3 days in air with intermittent grinding, followed by slow cooling (about 2 °C/min) to cool the sample to ambient temperature. LiCo$_{y}$Mn$_{2-y}$O$_4$ compounds with $y = 0$, 0.05, 0.06, 0.08, 0.16, and 0.33 were prepared.

The active material was mixed with carbon black and Teflon binder in a ratio of LiCo$_{y}$Mn$_{2-y}$O$_4$:carbon black:Teflon = 100:10:5 by weight and pressed into a thin film. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) studies were carried out to determine the particle size and the structure of the synthesized cathode materials. Electrochemical characterization of the cathode materials was carried out using Swagelok three-electrode cells presented in Fig. 1. The anode and reference electrodes were disks of lithium foil, and a sheet of glass fiber acted as the separator. The electrolyte contained 1 M LiPF$_6$ dissolved in a mixture of propylene carbonate (PC), ethylene carbonate (EC), and dimethyl carbonate (DMC) in a ratio 1:1:3.

The T-cell was assembled in a glove box filled with argon. The cathode had a diameter of 1.25 cm (an area of 1.23 cm$^2$) and a thickness of 70 μm with a total mass of 20 mg. It was heated in a minifurnace at 300 °C for 2 h in the glove box before assembling. The cathode and anode separation was approximately 3 mm. After the cell was assembled, it was left in the dry box for half an hour, enabling the electrolyte to disperse into the porous structure of the cathode. The cells were tested with a Bitrode (Bitrode Co., MI, USA) cycler with cutoff potentials of 3 and 4.3 V. Charge/discharge curves were obtained galvanostatically using a current density of 0.1 mA/cm$^2$.

Cyclic voltagammograms were obtained using a scan rate of 0.06 mV/s over a potential range of 3.0 to 4.3 V vs Li/Li'. EIS experiments were carried out at different states of charge on both pure spinel and Co-doped spinel electrodes with $y = 0.160$ in LiCo$_{y}$Mn$_{2-y}$O$_4$. The impedance data generally covered the frequency range from 0.002 Hz to 100 kHz with an ac voltage signal of ±5 mV, which ensured the electrode system to be under minimum perturbation. The Co-doped spinels were characterized by XRD using a Rigaku 405S5 diffractometer with...
Cu Kα radiation. The specific surface area was measured using a Micrometrics Pulse Chemisorb 2700 according to the Brunauer-Emmett-Teller (BET) single-point method with nitrogen physisorption. All samples were previously dried for half an hour under argon flow at 150 °C.

### Results and Discussion

The powder XRD patterns of the LiCo9Mn3-O4, for y = 0, 0.08, 0.16, and 0.330 are shown in Fig. 2. All samples were identified as a single-phase spinel with a space group Fd3m (oh7) where lithium ions occupy the tetrahedral (8a) sites; Mn2+, Mn3+, and Co3+ ions reside at the octahedral (16d) sites; and O2− ions are located at 32(e) sites. The estimated structure agreed with previous results obtained for pure spinel.15

The lattice constants of LiCo9Mn3-O4 (0 < y < 1) samples are presented in Fig. 3 as a function of the Co content in the oxide. The cubic lattice parameter “a” was estimated for the fully discharged electrode. Fully discharged spinel (x = 1 and y = 0) has a lattice constant value of 8.24 Å. Guohua et al.12 studied the cubic lattice constant “a” variation as a function of x for LiMn2+yMn3-yO4 (M = Cr, Ni, or Co). They found that a-values decreased with the deintercalation of lithium in the positive electrode. The variation of the lattice parameter was almost linear with an a-value of 8.042 Å for a charged electrode (Li0.9Mn3O4). As shown in Table I, in the Co-substituted spinel phases, the Mn–Mn and Mn–O interatomic distances decreased with increasing Co content thereby contributing to the spinel lattice contraction and to the decrease of the initial specific capacity of the doped spinel. The average Mn–Mn and Mn–O interatomic distances were calculated using the equation $R_{\text{Mn-Mn}} = a^2/24$ and $R_{\text{Mn-O}} = a(3u^2 - 2u + 0.375)$, respectively. The constant u = 0.265 is the oxygen positional parameter,6 considered constant for all samples. As shown in Fig. 3, the lattice constant decreased linearly with increasing Co content. For example when y = 1 in LiCo9Mn3-O4, the spinel lattice constant decreased to 8.09 Å.

The Li/LiCo9Mn3-O4 volume change during the cycling for y = 0 (V = 559.68 Å3 for a fully intercalated spinel and $V = 530.69$ Å3 for fully deintercalated), y = 0.16 (V = 551.37 Å3 for a fully intercalated and $V = 521.66$ Å3 for fully deintercalated) and y = 0.33 (V = 545.34 Å3 for fully intercalated and $V = 521.66$ Å3 a fully deintercalated spinel) was 6.9, 5.3, and 4.22%, respectively, which agreed with results reported in the literature.13 All Co-substituted phases were more reversible than repeated lithium insertion–deinsertion processes than the pure spinel. The stability of the structure increases with a decrease of the volume shrinkage. However, increasing the cobalt content in the spinel higher than y = 0.16 resulted in a very sharp decrease of capacity. Thus, the optimized Co content in the spinel should not exceed y = 0.16. The improvement of cycle performance was attributed to the stabilization of the octahedral sites in the spinel structure. The binding energies of MnO2 and CoO, are 946 and 1067 kJ/mol, respectively.13 The stronger CoO bond contributed to the overall stabilization of the spinel octahedral sites.

Figure 4 shows the BET surface area of pure and Co-doped spinels as a function of cobalt content in the oxide. As shown in this figure, substitution of cobalt increases the particle size and decreases the total surface area of the spinel up to 50%, which is beneficial for good capacity retention properties of the cathode both at room and at high temperatures.5 After the initial reduction, the spinel surface area remained independent of the Co content in the oxide. Similar results were obtained using SEM. As shown in Fig. 5, a small addition of Co (y = 0.05) resulted in a significant decrease in the surface area and differences in sample morphology between the pure and Co-doped spinel. The Co-doped samples consisted of aggregates of well-developed crystals.

Figure 6a–e shows galvanostatic charge-discharge profiles obtained for LiCo9Mn3-O4 electrodes with y = 0, 0.050, 0.060, 0.160, and 0.330, respectively. For all samples, two distinct plateaus were observed during charging and discharging the electrode which are characteristic of the
spinel LiMn$_2$O$_4$ structure. These plateaus correspond to a reversible two-stage process which includes insertion and deinsertion of Li ions in Li$_{1-y}$Co$_y$Mn$_{2-y}$O$_4$. As shown in Fig. 6b and c, both plateaus are easily distinguished in the presence of small amounts of dopant (Co). They tend to merge into one plateau as the concentration of doped Co in LiMn$_2$O$_4$ increases from $y = 0.16-0.33$ (Fig. 6d and e). A large capacity loss was observed when cycling the undoped spinel (Fig. 6a) compared to the Co-doped spinel (Fig. 6b-e).

Figure 7 shows typical galvanostatic cycling curves for the pure and Co-doped spincels. For all Co-doped spincels, the capacity fades decreases substantially with cycle number. Increasing the Co content in the spinel from $y = 0$ to 0.05 and 0.06 resulted in an increase of the specific capacity and improvement in cycling performance of the cathode active material. With a Co content in the spinel of $y = 0.16$, a small reduction in the initial capacity was observed. However, as shown in Fig. 7, after the initial decrease in capacity, the $y = 0.160$ capacity line crosses the capacity decay lines of $y = 0.0, 0.050$, and 0.050 after 5, 12, and 30 cycles, respectively. Consequently, after 85 cycles, the specific capacity of Co-doped spinel with $y = 0.160$ is 100 mAh/g compared with specific capacities of 90, 82, and 65 mAh/g for $y = 0.050$, 0.060, and 0.0, respectively. Similar results were obtained for Co-doped spincels with $y = 0.120$ and 0.140. Co concentrations higher than $y = 0.160$ in LiCo$_{2}Mn_{2.8}O_{4}$ resulted in a reduced initial capacity of 70 to 80 mAh/g.

Figure 8 shows the capacities of Co-doped spincels at the 1st and 50th cycles and the capacity loss per cycle as a function of Co content in LiCo$_{2}Mn_{2.8}O_{4}$ cathode. The capacity loss per cycle was calculated by averaging the capacity loss over the first fifty cycles. The capacity loss
per cycle is largest for pure spinel. When increasing the cobalt content in the spinel, the capacity loss of the cathode per cycle reached a minimum when the Co content in the spinel was \( y = 0.160 \). With a further increase in Co content, the capacity loss per cycle showed a slight decrease. However, a cobalt content in the spinel higher than \( y = 0.16 \) in \( \text{LiCo}_5\text{Mn}_2\text{O}_4 \) resulted in a reduced initial capacity of 70–80 mAh/g. Thus, an optimized mixed cobalt content, the capacity loss per cycle showed a slight decrease. However, a cobalt content in the spinel higher than \( y = 0 \) in \( \text{LiCo}_5\text{Mn}_2\text{O}_4 \) resulted in a reduced initial capacity of 70–80 mAh/g. However, the capacity decreased to 81 mAh/g after 85 cycles. From the initial capacity of 109 mAh/g estimated after the 2nd cycle, the capacity decreased to 81 mAh/g after 85 cycles. The Co-doped spinel with \( y = 0.160 \) in \( \text{LiCo}_5\text{Mn}_2\text{O}_4 \) showed a low capacity fade of only 7 mAh/g in the first 85 cycles.

**Fig. 8.** Capacity and capacity loss per cycle as a function of Co content \((y)\) in \( \text{LiCo}_5\text{Mn}_2\text{O}_4 \) cells. The observed decrease in the peak height and estimated capacity as a function of cycling are in agreement with the observed capacity loss from the galvanostatic charge–discharge profiles presented in Fig. 7. The pure spinel showed a very large capacity fade. From the initial capacity of 107 mAh/g, the capacity decreased up to 65 mAh/g after 65 cycles. The Co-doped spinel with \( y = 0.06 \) shows a large capacity fade after 85 cycles. From the initial capacity of 109 mAh/g estimated after the 2nd cycle, the capacity decreased to 81 mAh/g after 85 cycles. The Co-doped spinel with \( y = 0.160 \) in \( \text{LiCo}_5\text{Mn}_2\text{O}_4 \) showed a low capacity fade of only 7 mAh/g in the first 85 cycles.

**Determination of electrochemical kinetic parameters for pure and Co-doped spindels using linear polarization and EIS techniques.** The reversible intercalation–deintercalation of Li\(^+\) ions has been studied extensively in layered structures. Since it has been assumed that the diffusion of Li\(^+\) ions within the insertion compound is rate-limiting, the fundamental electrochemical investigations have been limited to studies of Li\(^+\) ionic diffusion. However, the charge-transfer resistance is also an important kinetic parameter, especially in the case of high Li\(^+\) ion mobility within the host.

Linear polarization and EIS techniques were used to determine the total resistance, [charge-transfer resistance \((R_s)\), surface-layer resistance \((R_d)\), and ohmic resistance \((R_e)\)] and exchange current density \((i_0)\) of pure and Co-doped spindels. The experimental procedure was performed as follows: the electrode was charged under constant-current mode to a fully charged state (4.3 V vs Li/Li\(^+\)). After the open-circuit potential (OCP) stabilized, linear polarization and EIS experiments were carried out. Then the electrode was discharged for a certain period of time and the same measurements were conducted. The procedure was repeated until the electrode was discharged to the cutoff potential of 3.0 V vs Li/Li\(^+\).

**Fig. 9.** Cyclic voltammograms obtained for samples with \( y = (a, \text{top}) 0.06 \) and \( b, \text{bottom} \) in \( \text{LiLiCo}_5\text{Mn}_2\text{O}_4 \) after the 2nd and 85th cycles are shown in Fig. 10a and b. The observed decrease in the cell Voltage (V)

**Fig. 10.** Cyclic voltammograms obtained for samples with \( y = (a, \text{top}) 0.06 \) and \( b, \text{bottom} \) in \( \text{LiLiCo}_5\text{Mn}_2\text{O}_4 \) after the 2nd and 85th cycles.

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**Fig. 7.** Cyclic voltammograms of \( \text{LiLiCo}_5\text{Mn}_2\text{O}_4 \) cells at a 0.06 mV/s rate.
The total resistance determined by using the LP technique was equal to the charge-transfer resistance only when the electrode ohmic resistance was negligible. In such a case, the charge-transfer current across an interface of active surface area \( A \) is given by

\[
i = A n F k a_0 \exp(-\gamma - \beta n F v/RT) - a_0 \exp(\beta n F v/RT)
\]

where \( k \) is the charge-transfer rate constant, \( n = 1 \) for Li\(^+\) ion transfer, and \( \gamma \) is the overpotential. The insertion-ion activities in the electrolyte and electrode are represented by \( a_0 \) and \( a_\gamma \). At low overpotentials, linearization of the Butler–Volmer equation results in

\[
R_t = \frac{RT}{n F i_0} = \frac{\eta}{i} \quad \text{and} \quad i = A n F k a_0 \exp[(-\gamma - \beta n F v/RT)]
\]

where \( i_0 \) is the exchange current density. However, when the ohmic resistance is not negligible eq 2 estimates a sum of the ohmic resistance and the charge-transfer resistance. Thus, the exchange current density is underestimated. EIS enables a determination of the charge-transfer resistance and an evaluation of the exchange current density without interference of the ohmic resistance.

The Nyquist plots obtained at different states of charge for pure spinel and Co-doped spinels \( y = 0.160 \) are shown in Fig. 11a and b, respectively. For both the pure spinel and the Co-doped spinel two semicircles were observed. The semicircle at the low-frequency region represents the charge-transfer resistance and the nonfaradic processes occurring at the electrode–electrolyte interface. Thus, the faradic contribution may be presented as shown in Fig. 11a by a charge-transfer resistance \( R_t \) and by a Warburg impedance \( (Z_n) \) which includes diffusion-controlled processes in the solid. The model assumes that the spinel forms a rough but continuously interconnected, porous solid of low bulk resistance, \( R_b < R_e \), where \( R_b \) is the electrolyte resistance. At lower frequencies, uniform charging of the electrode surface results in formation of classical double-layer capacitance in the nonfaradic branch of the Nyquist plot. Thus, the nonfaradic contribution in the circuit can be represented by the electrolyte resistance \( R_e \) and by the double-layer capacitance \( C_{dl} \).

It is reasonable to assume that the second semicircle is due to the electrolyte decomposition product formed as a result of oxidation-reduction processes occurring on the surface of the electrode. A surface-layer model was used to fit the data. An equivalent circuit for this model is presented in Fig. 11a; \( R_s \) represents the insertion-ion resistance and \( C_{dl} \) is the capacitance of the surface layer. The data were fitted using Solartron impedance graphing and analysis software ZView (Scribner Associates, Inc.).

The charge-transfer resistance values obtained from EIS are compared in Fig. 12 with those estimated using an IP technique. The LP measurements were performed on both pure and Co-doped spinels at different states of charge using a potentiodynamic method at a scan rate of 1 mV/s. As shown in Fig. 12, the charge-transfer resistance values for pure spinel \( y = 0 \) were higher than those estimated for Co-doped spinels with an optimized cobalt content of \( y = 0.160 \). The charge-transfer resistances for both the pure spinel and Co-doped spinel were independent of state of charge (SOC). The average charge-transfer resistance values estimated for pure and Co-doped spinels at different states of charge are 0.27 Ω g (19.9 Ω) and 0.171 Ω g (11.6 Ω), respectively. The presence of Co decreases the charge-transfer resistance and facilitates the charge-transfer reaction in the active material, which is favorable for battery operation.

The exchange current density values were estimated using eq 2 at different states of charge for pure and Co-doped spinel. The charge-transfer resistances used to calculate the exchange current density were estimated by fitting the ac-impedance data and are presented in Fig. 12. The calculated exchange current densities are plotted as a function of the SOC in Fig. 13. The average exchange current densities of the Co-doped spinel \( y = 0.160 \) and the pure spinel are 150.63 and 95 mA/g, respectively. The surface area of the pure spinel determined by BET was approximately 5.5 m\(^2\)/g, which converts the exchange current density into 1.729 × 10\(^{-8}\) A/cm\(^2\). This value agrees with the exchange current density value of 1.3 × 10\(^{-8}\) A/cm\(^2\) reported in the literature by Kanoh et al.\(^{11}\) for LiMn\(_2\)O\(_4\). The surface area of the Co-doped spinel determined by BET was 2.32 m\(^2\)/g, which converts the exchange current density into 6.49 × 10\(^{-8}\) A/cm\(^2\).

Figure 14 shows the dependence of \( C_{dl} \) values of pure spinel and Co-doped spinel as a function of SOC. The values of \( C_{dl} \) estimated for both the pure spinel (average value of 22.5 μF) and Co-doped spinel (average value of 25.32 μF) were independent of the SOC. The results indicated that the effective surface area of the electrode does...
not increase significantly with time due to the complete flooding of the electrode with the electrolyte.

Since \( R_s = \rho(l/A) \) and \( C_{sl} = \epsilon(\A/l) \), the surface-layer resistance should increase, while the surface capacitance should decrease with the increase of the surface-layer thickness, \( l \). As shown in Fig. 14, the capacitance of the surface layer is almost independent of the SOC for both the pure and Co-doped spinels, indicating that the thickness of the surface layer formed initially on the surface of the electrode remains constant. Note that the EIS experiments were performed initially on a fully charged electrode. The values of the surface-layer capacitance estimated for the pure spinel at different SOCs were in the range of 3.26—1.9 \( \mu \)F. These values were smaller compared with surface-layer capacitance values estimated for Co-doped spinel (8.16—6.4 \( \mu \)F), indicating that a thicker surface layer formed on the pure spinel. The presence of Co in the spinel inhibits the passivation processes occurring on the surface of the cathode.

According to Fig. 15, the \( R_s \) values are independent of SOC for both the pure and Co-doped spinel. The \( R_s \) value estimated for the pure spinel increases from 0.11 \( \Omega \)g (8.7 \( \Omega \)) for a fully charged electrode to 0.18 \( \Omega \)g (13.7 \( \Omega \)) for a fully discharged electrode. The observed increase of resistance is due to slow growth of the film as a function of time. Also, \( R_s \) for the Co-doped spinel increased from 0.04 \( \Omega \)g (2.9 \( \Omega \)) to 0.07 \( \Omega \)g (4.7 \( \Omega \)), in agreement with the estimated decrease of \( C_{sl} \) from 3.26 to 1.9 \( \mu \)F and 8.16 to 6.4 \( \mu \)F for pure and Co-doped spinel, respectively. Thomas et al.\(^{20}\) reported from their impedance analysis of polycrystalline \( \text{Li}_1\text{CoO}_2 \) that the rate of growth of the surface layer was rapid over the first 6 h after the construction of the cell and thereafter the films grow slowly.

\[ D_{Li^+} = \frac{1}{2FSB} \left[ \frac{V_m \, dE}{dx} \right]^2 \]  

\[ \text{where } F \text{ is the Faraday constant, } S \text{ the apparent geometrical area of the positive electrode, } V_m \text{ the molar volume of Li}_{1-y} \text{Co}_y \text{Mn}_{2+y} \text{O}_4, dE/dx \text{ the slope of the OCP vs mobile ion concentration } x \text{ at each } x \text{ value, and } L \text{ is the maximum length of the diffusion pathway. The OCP curves showed a similar loss of resolution of the two plateaus for Co-doped LiMn}_2\text{O}_4 \text{ as observed during galvanostatic cycling of these materials (Fig. 6b-e). The Warburg coefficient was obtained from the slope of Re } Z \text{ vs } \omega^{1/2} \text{ or } -\text{Im } Z \text{ vs } \omega^{1/2}. \text{ The } D_{Li^+} \text{ values as a function of } x \text{ for both } y = 0 \text{ and } y = 0.16 \text{ in Li}_{1-y} \text{Co}_y \text{Mn}_{2+y} \text{O}_4 \text{ are presented in Fig. 16. As shown in Fig. 16 for } y = 0 \text{, the } D_{Li^+} \text{ is in the range } 9.20 \times 10^{-12} \text{ to } 2.6 \times 10^{-10} \text{ m}^2/\text{s}, \text{ in agreement with the diffusion coe}fi-
cient reported in the literature.\textsuperscript{11} For Co-doped spinel, the diffusion coefficient \( D(x) \) was estimated to be in the range \( 2.4 \times 10^{-12} \) to \( 1.4 \times 10^{-11} \) m\(^2\)/s, which is higher than the value estimated for the pure spinel. Guyomard and Tarascon\textsuperscript{6} reported a value of \( 10^{-8} \) cm\(^2\)/s independent of SOC. Recently, Barker et al.\textsuperscript{26} reported a range of \( (0.2-2.2) \times 10^{-8} \) cm\(^2\)/s, with fairly complex dependence on SOC, and Striebel et al.\textsuperscript{28} reported a value of \( 2.5 \times 10^{-11} \) for LiMn\(_2\)O\(_4\), thin films measured using the galvanostatic intermittent technique (GITT). The values quoted for the diffusion coefficient are accurate to within an order of magnitude because of the difficulties involved in estimating the true electrochemical area of the cathode material.

The partial conductivity of lithium ion \( \sigma_{Li^+} \) was calculated using the equation

\[
\sigma_{Li^+} = \frac{FD}{V_{nuc}} \left( \frac{dE}{dx} \right)^{-1}
\]

In Fig. 17, the partial conductivity, \( \sigma_{Li^+} \), is presented for \( y = 0 \) and 0.16 as a function of \( x \) in Li\(_{1-y}\)Co\(_y\)Mn\(_2\)O\(_4\). As shown in this figure, for \( y = 0 \), the Li\(^+\) partial conductivity varies from (1.2 to 7.2) \( \times 10^{-5} \) S/cm. Higher values were estimated for Co-doped spinel (\( y = 0.16 \)) which were in the range between 8 \( \times 10^{-5} \) and 1.85 \( \times 10^{-4} \) S/cm. The observed low \( \sigma_{Li^+} \) value indicates a predominant contribution of electronic conductivity to the total conductivity in the spinel.

Self-discharge studies.—Self-discharge up to 6-12\% in the first month occurs in oxidized LiMn\(_2\)O\(_4\), LiCoO\(_2\), and LiNiO\(_2\) electrodes.\textsuperscript{8,10} The capacity loss depends upon factors such as the cathode and cell preparation, the nature and purity of the electrolyte, temperature, and the storage time. Self-discharge losses can be both reversible and irreversible. The reversible capacity loss is recovered by charging the cell while the irreversible capacity loss is not recoverable and contributes to the overall capacity fade of the cell. The self-discharge processes are caused in the charged state of the electrode by the highly oxidizing and reducing character of the electrode materials and the electrolyte, respectively.\textsuperscript{9}

Figure 18 shows the initial voltage decay for pure and Co-doped fully charged spinels upon storage in 1 M LiPF\(_6\)-PC:EC:DMC (1:1:3) electrolyte. The self-discharge rate in the case of the pure spinel is 41.5 mV/day compared with 31.2 mV/day for Co-doped (\( y = 0.160 \)) spinels. Thus, Co stabilizes the spinel structure while reducing the self-discharge rate. The lower self-discharge rate of Co-doped spinels can be also attributed to their low surface areas (Fig. 4 and 5) compared with the high surface area of pure spinels. The larger particle size of Co-doped spinels results in lesser contact between the active material and the electrolyte, thus decreasing the rate of both the electrode and the electrolyte decomposition.

Potentiostatic experiments were also carried out to determine the nature of the discharge process occurring at the cathode. The cathode was oxidized up to 4.3 V and the potential was kept constant during the experiment. Under these conditions, one measures the floating current, that is, the current required to counterbalance the self-discharge. The floating current and the capacity loss for a pure spinel are shown in Fig. 19a, and in Fig. 19b-d for Co-doped spinels. The cumulative capacity losses for pure and Co-doped spinels are compared in Fig. 20. The capacity loss estimated for pure spinel resulting from self-discharge in the first 30 h is 3 and 6 times larger than those for Co-doped spinel with \( y = 0.06 \) and 0.160, respectively. These results are in agreement with the voltage decay curves presented in Fig. 18.

The effect of storage on the cycling ability of Co-doped spinels was also investigated. Figure 21 shows the results obtained for an oxidized Co-doped spinel (\( y = 0.16 \)) before and after storage for 150 h. The cell cycled after 150 h of storage showed a larger capacity fade with increasing number of cycles, compared to a cell which was cycled fresh. This capacity loss can be attributed to passive-film formation resulting from the electrolyte-decomposition products.

![Fig. 18. The cathode voltage decay as a function of storage time in 1 M LiPF\(_6\)-PC:EC:DMC (1:1:3).](image)

![Fig. 19. Cumulative capacity (left ordinate) and floating current (right ordinate) for Li/LiCo\(_y\)Mn\(_{1-y}\)O\(_4\) cells with \( y = (a) 0, (b) 0.160, (c) 0.06, \) and (d) 0.050.](image)
Substitution of Co in Li,Mn,O₄ increases the particle size and decreases the total surface area of the spinel by up to 50%, which is beneficial for good capacity retention properties of the cathode. After the initial reduction of the surface area observed for $y = 0.05$ in LiCo,Mn₂O₄, the spinel surface area remained independent of the Co content in the oxide. Increasing the Co content in the spinel from $y = 0$ to $y = 0.05$ and 0.06 resulted in an increase in initial capacity and a decrease in capacity fade during cycling. With a Co content in the spinel of $y = 0.160$, a small reduction in the initial capacity was observed. However, after the initial decrease in capacity, the $y = 0.160$ sample capacity curve crossed the capacity decay curves of $y = 0$, 0.060, and 0.050 after 5, 12, and 30 cycles, respectively. The specific capacity of a Co-doped spinel with $y = 0.160$ is 100 mAh/g compared with specific capacities of 90, 82, and 65 mAh/g estimated for $y = 0.050$, 0.060, and 0, respectively. Similar results were obtained for Co-doped spinels with $y = 0.120$ and 0.140.

The charge-transfer resistance for the pure and Co-doped spinels were 4.27 Ohm g (19.9 Ω) and 0.171 Ω g (11.62 Ω), respectively. The charge-transfer resistance values for both the pure and Co-doped spinels were independent of SOC. The average exchange current density estimated for Co-doped spinel ($y = 0.160$) and pure spinel are 6.59 x 10⁻⁴ and 1.73 x 10⁻⁴ A/cm². The presence of Co increases the charge-transfer resistance and facilitates the charge-transfer reaction in the active material, which is favorable for battery operation.

The surface resistance values, ($R_s$) were independent of SOC and varied from 0.11 Ω g (8.7 Ω) for a fully charged electrode to 0.18 Ω g (13.7 Ω) for a fully discharged electrode. The observed increase of the resistance was due to the slow growth of a passive film on the surface of the cathode as a function of time. The observed increase of $R_s$ values is in agreement with the estimated decreases of $C_{dl}$ from 3.26 to 1.9 μF and 8.16 to 6.4 μF for pure and Co-doped spinels, respectively. The lithium-ion diffusion coefficient ($D_L$) for Co-doped spinel was estimated to be in the range 2.4 x 10⁻¹¹ to 1.4 x 10⁻¹¹ m²/s as a function of SOC and was found to be higher than the value estimated for the pure spinel (9.2 x 10⁻¹² to 2.6 x 10⁻¹² m²/s). The Li⁺ partial conductivities estimated in Co-doped spinel (in the range between 8 x 10⁻⁶ and 1.85 x 10⁻⁴ S/cm) were higher than those estimated for pure spinels (1.2-7.2 x 10⁻⁶ S/cm).

The larger particle size of Co-doped spinel resulted in less contact between the active material and the electrolyte, contributing to decrease of the rate of electrolyte and electrode decomposition, and consequently, to a smaller self-discharge rate.

**Conclusions**

Substitution of Co in Li,Mn,O₄ increases the particle size and decreases the total surface area of the spinel by up to 50%, which is beneficial for good capacity retention properties of the cathode. After the initial reduction of the surface area observed for $y = 0.05$ in LiCo,Mn₂O₄, the spinel surface area remained independent of the Co content in the oxide. Increasing the Co content in the spinel from $y = 0$ to $y = 0.05$ and 0.06 resulted in an increase in initial capacity and a decrease in capacity fade during cycling. With a Co content in the spinel of $y = 0.160$, a small reduction in the initial capacity was observed. However, after the initial decrease in capacity, the $y = 0.160$ sample capacity curve crossed the capacity decay curves of $y = 0$, 0.060, and 0.050 after 5, 12, and 30 cycles, respectively. The specific capacity of a Co-doped spinel with $y = 0.160$ is 100 mAh/g compared with specific capacities of 90, 82, and 65 mAh/g estimated for $y = 0.050$, 0.060, and 0, respectively. Similar results were obtained for Co-doped spinels with $y = 0.120$ and 0.140.

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**LIST OF SYMBOLS**

- $a_1$: insertion ion activity of oxidized species
- $a_2$: insertion ion activity of reduced species
- $A$: effective surface area, m²/g
- $B$: Warburg coefficient, Ω s¹/²
- $C_{dl}$: double-layer capacitance, μF
- $C_a$: surface-layer capacitance, μF
- $D_L$: diffusion coefficient of Li ion in positive electrode, m²/s
- $E$: open-circuit potential, V
- $F$: Faraday's constant, 9.6487 C/equiv
- $i$: current per unit of mass, A/g
- $i_0$: exchange current per unit of mass, A/g
- $Im$: imaginary
- $k$: rate constant
- $l$: surface-layer thickness, m
- $n$: number of electrons
- $R$: gas constant, 8.314 J/(mol K)
- $Re$: real
- $R_b$: bulk resistance, Ω
- $R_e$: electrolyte resistance, Ω
- $R_r$: charge-transfer resistance, Ω
- $R_s$: surface-layer resistance, Ω
- $S$: apparent geometric area, m²
- $t$: time, s
- $T$: temperature, K
- $U$: oxygen positional parameter
- $V$: unit cell volume, cm³
- $X$: molar volume, cm³/mol
- $X_{Li}$: stoichiometric coefficient for positive electrode, Li₉Co₅Mn₇O₄
- $y$: dopant (Co) concentration
- $Z$: impedance, Ω
- $Z_{W}^{0}$: Warburg Impedance, Ω
- $\beta$: symmetry factor, dimensionless
- $\epsilon$: permittivity
- $\sigma$: conductivity, S/cm
- $\omega$: angular frequency, Hz
- $\eta$: overpotential, V
- $\rho$: resistivity

**REFERENCES**

Oxygen Reduction Characteristics of Heat-Treated Catalysts Based on Cobalt-Porphyrin Ion Complexes

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ABSTRACT

Oxygen reduction characteristics of graphite electrodes modified with aggregated cobalt-porphyrins heat-treated at various temperatures and then impregnated in Nafion polymer were investigated systematically. The aggregated cobalt-porphyrin compound was adsorbed on graphite powder and then heat-treated at various temperatures ranging from 200 to 1200 °C. The catalysts were evaluated for electroreduction performances of oxygen on modified electrodes in sulfuric acid solutions. The electrocatalytic performances of catalysts as measured in rotating ring-disk electrodes showed that the most effective catalytic activity for oxygen reduction was attained for the aggregated cobalt-porphyrin compounds on graphite powder heat-treated at temperatures between 600 and 800 °C. The electrocatalytic performances of catalysts as measured in rotating ring-disk electrodes showed that the most effective catalytic activity for oxygen reduction was attained for the aggregated cobalt-porphyrin compounds on graphite powder heat-treated at temperatures between 600 and 800 °C. The surface concentration of Co and N in the temperature range 600-800 °C, it appeared that the increased catalytic activity originated from the well-dispersed Co-N bonds and from fragments of the original molecules still retaining the cobalt bound to nitrogen atoms. In the higher temperature region, Co-N bonds were no longer detected, and the presence of cobalt in the metallic states (13-Co) in the catalysts was confirmed by X-ray diffraction analysis. From the results of the stability tests, the pyrolyzed cobalt porphyrin electrode systems were found to be more stable than the nonheat-treated catalysts.

Introduction

Polymer electrolyte fuel cells (PEFCs) are particularly attractive for transportation and other small-scale on-site power source applications because of their high power density at low temperature operations. In the cathodes of PEFCs, platinum supported on carbon is usually used as the catalyst for electroreduction of oxygen. Since Pt is an expensive metal with a relatively limited abundance, various kinds of non-Pt catalysts have been explored.

The metalloporphyrins, phthalocyanines, and related compounds have been extensively investigated in detail as possible catalysts for oxygen reduction. Although metalloporphyrin compounds show some catalytic ability, heat-treated porphyrin compounds adsorbed on carbon have been revealed to exhibit higher activity and stability as compared with nonheat-treated ones.

Yeager et al. reported that during the heat-treatment of carbon supported metalloporphyrins at temperatures above 700 °C, macrocycles are pyrolyzed to yield a carbonaceous layer with substantial surface nitrogen as the adsorption sites. The metal may also be present on the surface in the form of small oxide particles, which are to some extent stabilized on this type of surfaces in acid electrolytes. On the other hand, van Veet et al. have explained that metal-Nx moiety of the chelate is the structural feature associated with the high activity of the heat-treated macrocycles on the surface of carbon materials. However, different views about this activity and stability have been reported by other workers and this point is still not resolved.

In the previous work, it has been shown that the cobalt-porphyrin ion complexes, which are electrostatic agglomerates of cobalt tetraakis(4-carboxyphenyl) porphyrin (CoTCPP, anionic) and cobalt tetraakis[1-methyl-4-pyridyl] porphyrin (CoTMPyP, cationic) have a catalytic activity for the reduction of molecular oxygen in acidic solutions.