

SOLID-STATE SCIENCE AND TECHNOLOGY

Electronic Conductivity of LiCoO_2 and Its Enhancement by Magnesium DopingH. Tukamoto^a and A. R. West

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ABSTRACT

LiCoO_2 , the active cathode material in commercial rechargeable lithium batteries, is shown to be a p-type semiconductor, associated with the presence of a small concentration of Co^{4+} ions. Its conductivity at room temperature can be increased by over two orders of magnitude, to $\sim 0.5 \text{ S cm}^{-1}$, by partial substitution of Co^{3+} by Mg^{2+} and compensating hole creation. The electrochemical performance of $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$ is comparable to that of LiCoO_2 ; a small reduction in capacity, associated with a reduction in Co^{3+} content, occurs but good reversibility is retained and, in contrast to LiCoO_2 , the Mg-doped material is single phase throughout the charge/discharge cycle.

Introduction

LiCoO_2 was found by Mizushima *et al.*¹ to have excellent reversibility for Li deintercalation/intercalation and, in its deintercalated form, to have a high potential of 4 V *vs.* Li/Li^+ in an organic electrolyte. After Plichta *et al.*^{2,3} reported the possibility of a practical 4 V Li battery using this material, it has been extensively investigated in both scientific and industrial communities. Now, it is the standard positive active material for the expanding Li-ion battery market.

Various reports of the solid-state chemistry of LiCoO_2 have been published. Ohzuku⁴ reported the phase behavior of $\text{Li}_{1-y}\text{CoO}_2$ at various levels of charge and discharge. The ionic conductivity was studied by Kikkawa⁵ and Morenda.⁶ The thermal stability of $\text{Li}_{1-y}\text{CoO}_2$ was investigated by Honders.^{7,8}

Here we report the results of an investigation into the conduction mechanism of LiCoO_2 and the influence of dopants on its conductivity and electrochemical performance.

Experimental

Reagents used for most of the work were Li_2CO_3 , $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and MgCO_3 ; these were found to be moisture-insensitive and were used undried. Samples were weighed in 5 to 10 g amounts, mixed in an agate mortar using acetone to form a paste, dried, and fired in Au foil boats, initially at 200°C for 2 h to expel NO_2 , CO_2 , and H_2O . After recrushing, samples were fired at 900°C for 20 h to complete reaction. Phase analysis was carried out by x-ray powder diffraction using Philips or Rigaku diffractometers, Cu K_α radiation.

For conductivity measurements, reacted powders were pressed into pellets, 10 mm diam and 1 mm thick and sintered at 800°C. Both ac and dc measurements were made. For ac impedance measurements, gold strip electrodes were attached to opposite pellet faces using liquid gold paste, which was dried and hardened by gradually heating to 600°C. The pellets were placed on a controlled-atmosphere

conductivity rig, inside a tube furnace whose temperature was controlled and measured to within 3°C. Impedance measurements were carried out using a combination of Hewlett-Packard 4192 and Solartron 1250/1286 instrumentation to cover the frequency range 100 mHz to 1 MHz. For dc measurements, a four-probe arrangement was used with metal electrodes on opposite pellet faces and point contact electrodes along the length of the pellets.

Electrodes for electrochemical measurements were fabricated from reacted powder (87 mass %) acetylene black (5 mass %), and polyvinylidene fluoride (PVDF) powder [8 weight percent (w/o)] which was mixed with *n*-methyl-2-pyrrolidone in a mortar. The mixture was pasted onto a $15 \times 15 \text{ mm}$, 120 mesh Al gauze to give a coverage of about 0.07 g cm^{-2} , which was then dried at 120°C. The electrodes were charged and discharged in a sealed glass cell with Li metal as reference and counterelectrodes and 1 M LiClO_4 dissolved in a 1:1 mixture of ethylene carbonate and diethylene carbonate as electrolyte. The electrochemical measurements were carried out in an Ar dry box.

Results and Discussion

Initially, impedance measurements were carried out on pellets of LiCoO_2 in order to determine its conductivity as a function of temperature and investigate the nature of the conducting species. Impedance complex-plane plots of the data obtained indicated a very simple response; they showed a frequency-independent impedance with a large number of data points superimposed at a single point on the Z' axis. This gave the total resistance of the pellets directly. Since there was no indication of any low-frequency dispersion attributable to charge blocking at the sample electrode interface, it is concluded that the conduction mechanism is electronic and that any ionic conductivity is several orders of magnitude lower than that of the electronic conductivity.

The conductivity of LiCoO_2 was measured over the temperature range 25 to 700°C in three different atmospheres, Fig. 1. The Arrhenius plots are nonlinear, with increased slope and activation energy at lower temperature. They are also very atmosphere dependent, showing a lower conductivity at lower oxygen partial pressures. It is likely that oxygen is removed from the sample surface at lower oxy-

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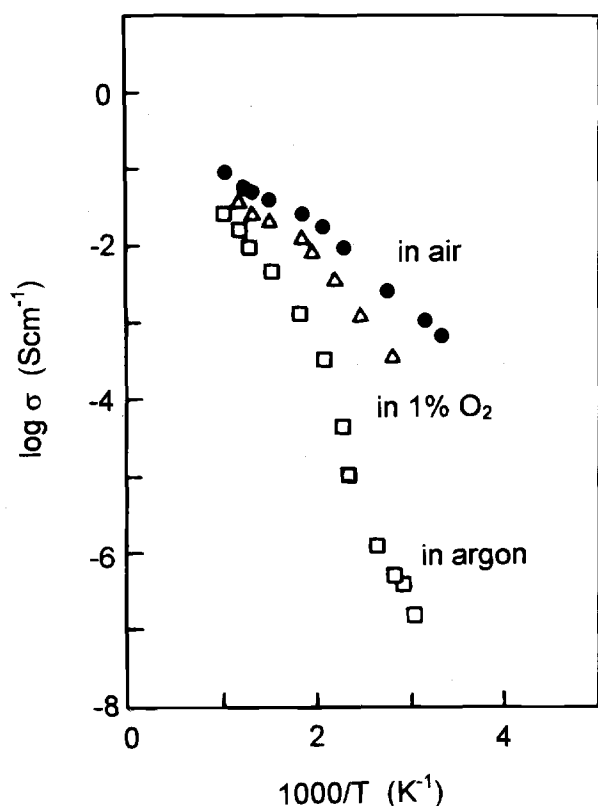


Fig. 1. Electronic conductivity of LiCoO_2 at various oxygen partial pressures.

gen partial pressures which leads to the generation of n-type carriers according to



Since the conductivity decreases at the same time as electrons are created by this process, the principal current carriers would appear to be holes which are cancelled by introduction of the n-type carriers. In addition, as the conductivity is atmosphere sensitive, the carrier concentration appears also to be atmosphere sensitive and, therefore, the conductivity is extrinsic rather than intrinsic.

The activation energies are higher at lower oxygen partial pressures, Fig. 1. This behavior is attributable to the existence of a distribution of energy levels for the acceptor states; these states are gradually filled by the electrons that are released as oxygen is desorbed. Consequently, the activation energy required to promote electrons into the available acceptor states, and thereby generate mobile holes in the valence band (assuming a band model for conduction), increases.

Having established that LiCoO_2 appears to be a p-type semiconductor, we attempted to increase the level of conductivity by deliberately doping with acceptors. A wide range of materials with nominal general formula $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$ were synthesized by solid-state reaction at 800°C , using the same conditions as outlined above but with appropriate partial substitution of an M oxide or oxysalt for Co. Products were characterized by powder x-ray diffraction and electrical conductivities at room temperature were determined by four-terminal measurements on pressed, sintered pellets.

Results are summarized in Table I. Single-phase products were obtained with $\text{M} = \text{Mg}, \text{Cr}, \text{Ni}, \text{B}, \text{Al}$, and Ga . Most of these, apart from Mg and possibly Ni , are trivalent and could substitute directly for Co^{3+} without affecting the electronic structure and conductivity. Consistent with this observation, of these various dopants only Mg led to a significant increase in conductivity, Table I. The temperature dependence of the conductivity of undoped and Mg -doped LiCoO_2 is compared in Fig. 2. The conductivity of the doped material shows very little temperature dependence, and at room temperature is two orders of magnitude higher than that of undoped LiCoO_2 .

The next step was to investigate the effect of varying the Mg dopant concentration; results are shown in Fig. 3 for measurements in air at room temperature; the conductivity decreased initially and then increased rapidly to achieve a constant value for $x \geq 0.04$. Not all samples of LiCoO_2 showed this minimum at intermediate dopant contents, although all showed an overall increase in conductivity, reaching an approximately constant value at higher dopant levels.

In order to investigate further the stoichiometry of Mg -doped LiCoO_2 and elucidate the possible mechanism of Mg doping, a preliminary phase diagram study of the system $\text{Li}_2\text{O}-\text{Co}_2\text{O}_3-\text{MgO}$ was carried out, with the results shown in Fig. 4. Data correspond to the reaction of samples in air at 900°C . Under these conditions, Co is expected to be present predominantly as Co^{3+} , but as discussed later, some

Table I. Results of doping experiments on conductivity and phase purity of LiCoO_2 .

M^a	Impurity phase(s)	Conductivity ^b	M^a	Impurity phase(s)	Conductivity ^b
Mg	None	9.9×10^{-1}	Mn	$\text{Li}_2\text{MnO}_3, \text{Co}_3\text{O}_4$	1×10^{-6}
Ca	CaO	5.6×10^{-3}	Fe	Unknown	1.4×10^{-3}
Sr	SrCO_3	1.2×10^{-3}	Rh	LiRhO_2	1.2×10^{-3}
Ba	BaCO_3	4.3×10^{-6}	Ni	None	7.6×10^{-4}
Sc	LiScO_2	2.0×10^{-3}	Cu	CuO	5.0×10^{-3}
Y	$\text{LiYO}_2, \text{Y}_2\text{O}_3$	6.7×10^{-4}	Zn	ZnO	1.8×10^{-2}
La	Unknown	1.8×10^{-3}	Cd	CdO	1.5×10^{-3}
Ce	CeO_2	3.9×10^{-3}	B	Single phase	3.4×10^{-6}
Pr	Pr_6O_{11}	3.7×10^{-3}	Al	Single phase	1.6×10^{-3}
Nd	Unknown	4.7×10^{-3}	Ga	Single phase	1.3×10^{-3}
Ti	Co_2O_3	1×10^{-6}	In	LiInO_2	1.6×10^{-3}
Zr	$\text{Li}_2\text{ZrO}_3, \text{ZrO}_2$	4.2×10^{-4}	Si	SiO_2	1.5×10^{-3}
Hf	$\text{Li}_2\text{HfO}_3, \text{HfO}_2$	4.2×10^{-4}	Ge	$\text{Li}_2\text{CoGeO}_4$	1×10^{-6}
V	Li_3VO_4	5.8×10^{-4}	Sn	$\text{Li}_2\text{SnO}_3, \text{SnO}_2$	1×10^{-3}
Nb	Li_3NbO_4	2.3×10^{-5}	Pb	$\text{Li}_2\text{PbO}_3, \text{PbO}$	3.1×10^{-3}
Ta	Co_3O_4	1.7×10^{-6}	Sb	Unknown	2.7×10^{-6}
Cr	None	2.0×10^{-4}	Bi	LiBiO_2	2.7×10^{-4}
Mo	Unknown	1.3×10^{-4}	Te	$\text{Co}_6\text{TeO}_{16}$	9.3×10^{-6}
W	$\text{Li}_2\text{WO}_4, \text{Li}_4\text{WO}_5$	3.4×10^{-5}			

^a All doped materials have nominal composition $\text{LiM}_{0.05}\text{Co}_{0.95}\text{O}_2$.

^b Conductivities at room temperature. By comparison, undoped LiCoO_2 had a conductivity $1 \times 10^{-3} \text{ S cm}^{-1}$.

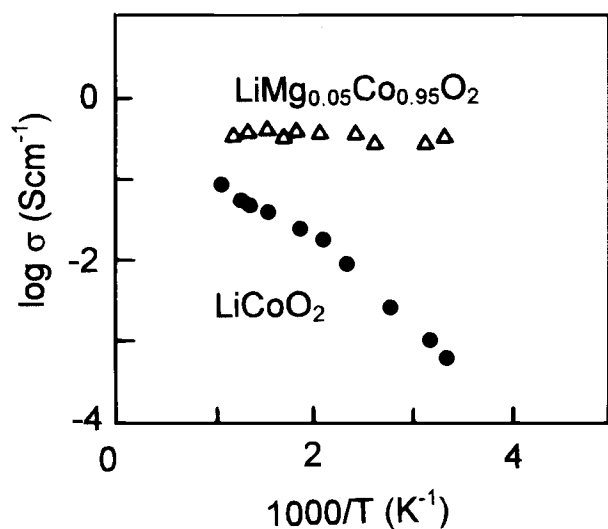


Fig. 2. Comparison of electronic conductivity of LiCoO_2 and $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$. Measurements made in air.

oxidation to Co^{4+} has probably occurred. The phase-diagram is therefore a pseudoternary diagram since, although it represents correctly the cation contents, the oxygen contents may vary.

The main result of the phase-diagram study is that a range of LiCoO_2 solid solutions forms in the direction of the hypothetical composition " $\text{LiMgO}_{1.5}$ " or " $\text{Li}_{1.33}\text{Mg}_{1.33}\text{O}_2$." This means that Mg substitutes for Co in a 1:1 ratio in the general formula, but that an additional mechanism of charge compensation, discussed later, is required to take account of the different charge states of Mg and Co. A practical problem in accurately determining the phase-diagram concerns the possibility of compositional change associated with lithia loss by volatilization during firing.

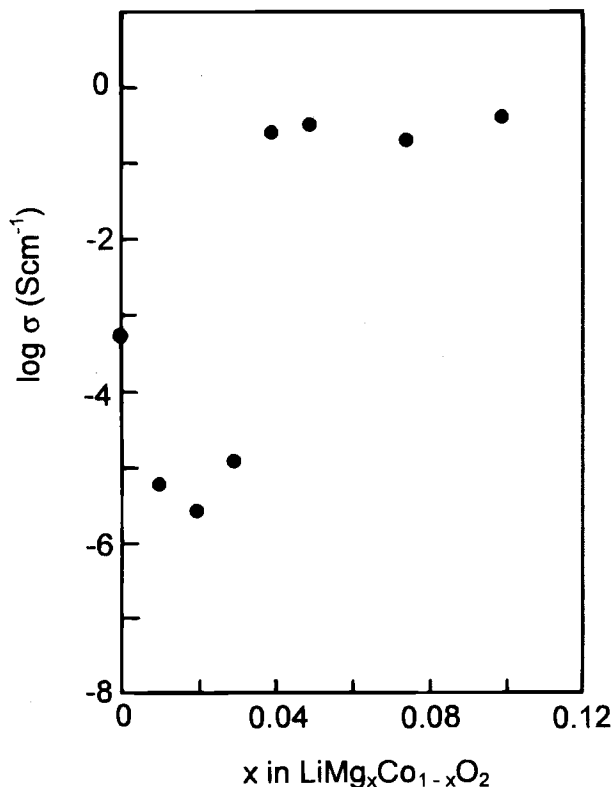


Fig. 3. Dependence of electronic conductivity of $\text{LiMg}_x\text{Co}_{1-x}\text{O}_2$ on Mg content, data measured in air at room temperature.

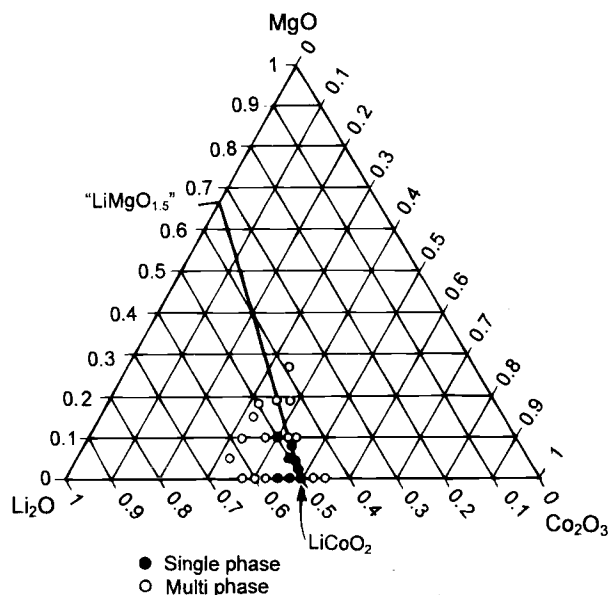
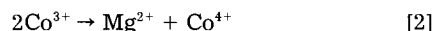


Fig. 4. Phase diagram of the Li_2O - MgO - Co_2O_3 system.

In addition, for lithia-rich compositions, it is very difficult to eliminate CO_2 , so Li_2CO_3 appears as an impurity phase instead of Li_2O . At this stage, we are unable to confirm whether or not LiCoO_2 also forms a limited solid solution by means of variation in the Li:Co ratio. A limited region of lithia-rich solid solution formation is indicated in Fig. 4, but this may instead be associated with partial lithia loss during heating.

There appear to be three possible simple charge balance mechanisms to compensate for the 1:1 substitution of Co by Mg. These involve creation of: oxygen vacancies, interstitial cations (both Li and Mg), and holes. We discount the first two since these would involve major disruption of the crystal structure of LiCoO_2 which is an ordered, layered, rock salt superstructure. In addition, these are ionic compensation mechanisms which should not influence the level of electronic conductivity whereas, in fact, large changes in conductivity occur.

The third mechanism can be written as



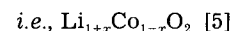
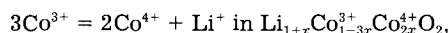
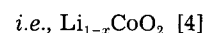
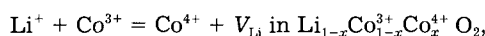
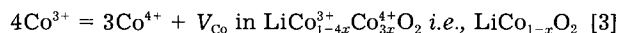
Note that this way of writing solid-solution mechanisms implies compositional change and the partial replacement, in the crystal structure, of species on the left side of the equation by those on the right. It is not a chemical equation and while charge balance must be preserved, mass balance clearly can not. This particular mechanism involves the generation of holes, i.e., Co^{4+} ions and thereby, a mixed 3+, 4+ valence state of Co. It is consistent with the increased conductivity observed on Mg doping (but not with the decrease seen at low Mg contents, see later).

The general formula of the solid solutions may be written as $\text{LiMg}_x\text{Co}_{1-x}\text{O}_2$; $0 < x < 0.10$. Variations of the lattice parameters a and c of the hexagonal unit cell as a function of composition x are shown in Fig. 5; a projection of the crystal structure of LiCoO_2 is also shown in Fig. 5. Both parameters, but especially c , show a linear increase with x . This increase is attributed to the introduction of Mg, which is significantly larger than Co, into the crystal structure and more than offsets the tendency of Co-O bonds to shorten and for the unit cell parameter to contract on oxidation of Co from 3+ to 4+.

At present, we do not fully understand the conductivity decrease observed at low Mg contents in some samples of LiCoO_2 but offer the following possibility.

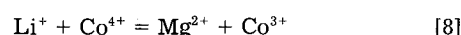
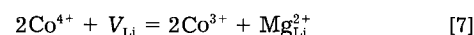
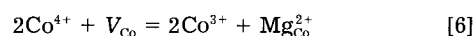
We speculate that the nominally pure LiCoO_2 is defective and contains a small amount of Co^{4+} with at least three plausible mechanisms of charge compensation; it

could be compensated by vacancies on either the Co or Li sublattices, or by incorporation of extra Li, as follows



Compared to stoichiometric LiCoO_2 , formulas 3 and 5 lead to Li-rich materials whereas Eq. 4 leads to Li deficiency. Given the possibility of a small amount of lithia loss by volatilization during synthesis mechanism 4 seems the most likely.

Upon addition of Mg^{2+} to defective LiCoO_2 , the concentration of Co^{4+} decreases initially, as indicated by the decrease in conductivity. There are three simple mechanisms by which this can occur; Mg^{2+} substitutes either onto the Co vacancies, the Li vacancies or directly substitutes for Li, as follows



Since mechanism 4 is regarded as the most probable mechanism for formation of defective LiCoO_2 then mechanism 7 is the most likely one for incorporating small amounts of Mg^{2+} to explain the observed electrical properties.

The discharge characteristics of various Mg-doped compositions are shown in Fig. 6. With increasing x , two effects are seen, a decrease in discharge capacity and a change in discharge profile. The reduction in capacity is attributed to a reduction of Co^{3+} content: only Co^{3+} and not Co^{4+} may be oxidized upon removal of Li during charging. In the subsequent discharge profile of Li_xCoO_2 (not shown) and in compositions with low Mg content, e.g., $x = 0.01$, Fig. 6, there is a flat potential range toward the end of the discharge cycle. This plateau is attributed to the

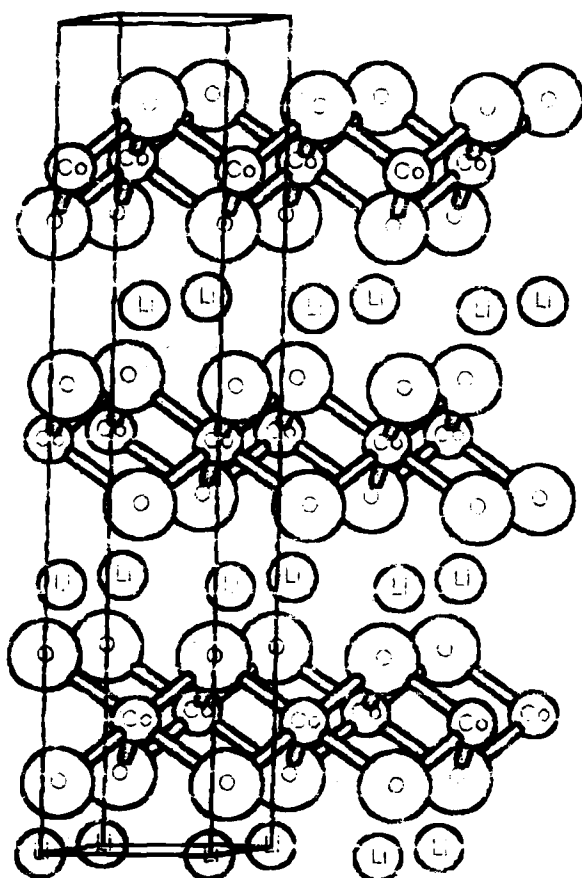
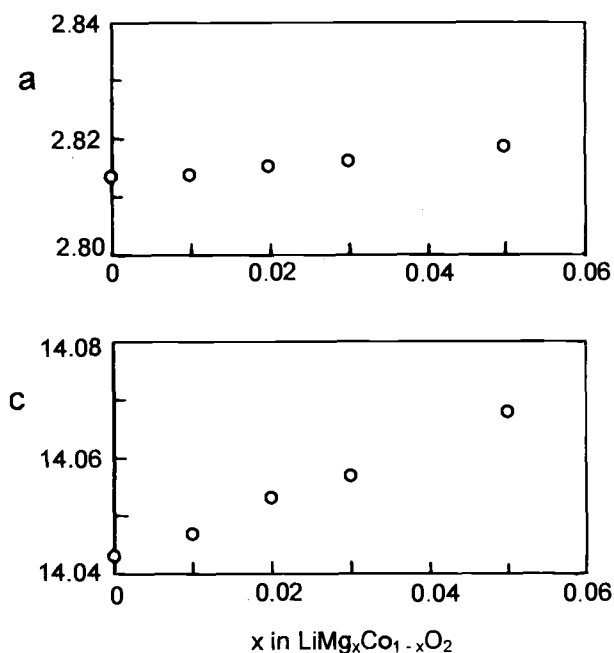


Fig. 5. Lattice parameters (in Å) of $\text{LiMg}_x\text{Co}_{1-x}\text{O}_2$ with increasing magnesium content; crystal structure projection of LiCoO_2 : the hexagonal unit cell is outlined. In the vertical, c , direction the oxide ions form a cubic close-packed array and the layers of octahedral sites between adjacent pairs of oxide layers are fully occupied by Li and Co, alternately.

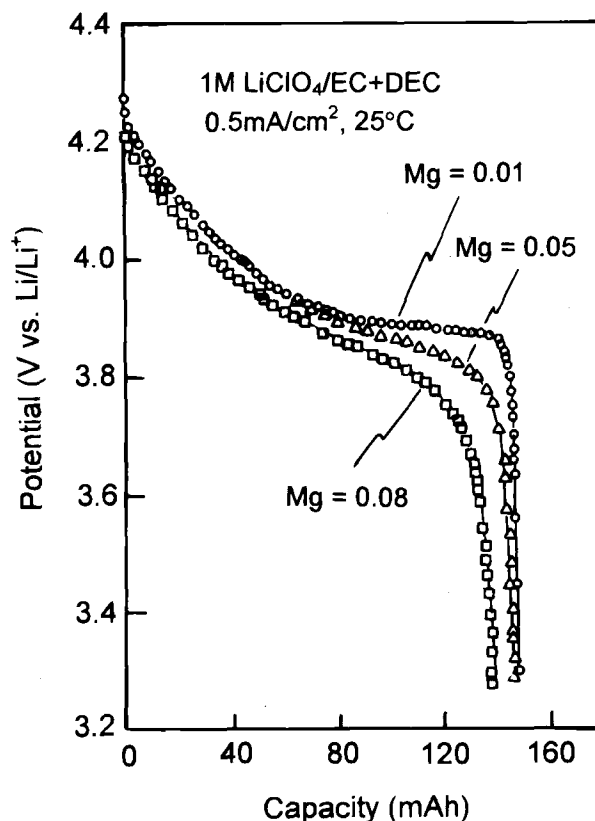


Fig. 6. Comparison of discharge curves of $\text{LiMg}_x\text{Co}_{1-x}\text{O}_2$ with various magnesium contents.

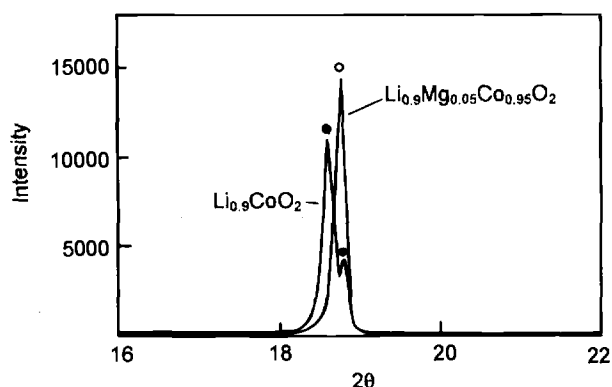


Fig. 7. Comparison of XRD patterns of $\text{Li}_{0.9}\text{CoO}_2$ and $\text{Li}_{0.9}\text{Mg}_{0.05}\text{Co}_{0.95}\text{O}_2$.

existence of two discrete crystalline phases of different Li contents, as reported by Okzuku.⁴ At higher Mg contents, this flat region is lost, and instead a gradual decay in potential occurs, indicative of a single, homogeneous solid solution range over the entire range of lithium contents studied.

Additional evidence for the existence of a two-phase region in samples of low Mg content is shown in x-ray powder diffraction patterns of two deintercalated samples, parts of which are shown in Fig. 7. Deintercalated LiCoO_2 shows clearly the presence of two peaks whereas the corresponding Mg-doped sample with $x = 0.05$ at the same level of deintercalation shows only a single peak.

The reversibility of LiCoO_2 and Mg-doped LiCoO_2 ($x = 0.05$) to charge and discharge is compared in Fig. 8. Both show good reversibility up to 30 cycles. Thus, the Mg substitution has not caused any decrease in electrochemical reversibility but has given a large increase in the electronic conductivity. The capacity of the Mg-doped sample is slightly less than that of LiCoO_2 , which may be attributed to a decrease in concentration of the active Co^{3+} ions.

Conclusions

LiCoO_2 exhibits p-type semiconductivity as shown by the atmosphere sensitivity of the conductivity of undoped LiCoO_2 and the enhanced conductivity on acceptor doping with Mg. The p-type semiconductor appears to be associated with the presence of a small concentration of Co^{4+} ions. The detailed defect structure of LiCoO_2 is, however, not well understood at present. Two mechanisms for incorporation of Mg^{2+} are postulated. Undoped LiCoO_2 may be Li-deficient with small concentrations of equal numbers

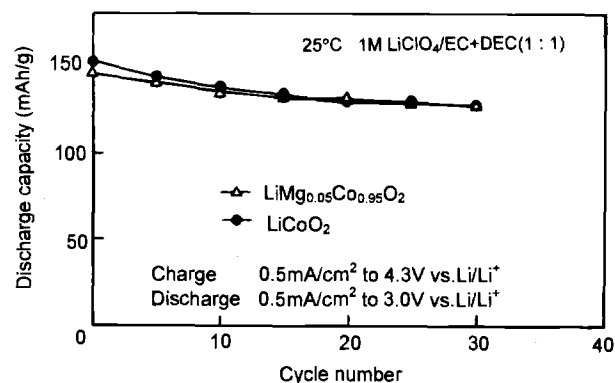


Fig. 8. Charge retention characteristics of $\text{LiMg}_{0.05}\text{Co}_{0.95}\text{O}_2$ and LiCoO_2 .

of Li vacancies and Co^{4+} ions. At low Mg contents, the Li vacancies are occupied by Mg and the Co^{4+} concentration is reduced, leading to a decrease in conductivity. At higher Mg contents, Mg^{2+} substitutes onto Co sites, leading to the creation of an equal number of Co^{4+} ions for charge balance and the conductivity increases.

The electrochemical performance of Mg-doped LiCoO_2 is comparable to that of undoped LiCoO_2 in terms of reversibility but shows a reduction in capacity associated with the reduction in Co^{3+} content. However, Mg-doped LiCoO_2 remains as a single-phase material throughout the charge/discharge cycle, in contrast to LiCoO_2 , and this may lead to improved long-term stability on cycling.

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