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Combustion synthesis and characterization of substituted lithium cobalt oxides in lithium batteries

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Abstract

Substituted lithium cobaltates $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ (where M = Ni, Mg, Mn, Zn) have been synthesized by the combustion of mixtures obtained from aqueous solutions containing the respective metal nitrates, LiNO_3 , and urea in stoichiometric amounts. The mixtures, when dried and fired at 700°C, ignite and yield submicron-sized powders. Physical properties of the synthesized products are discussed in the light of structural (XRD, SEM) and spectroscopic (FTIR and Raman) measurements. XRD results show that most of the compounds have a structure similar to LiCoO_2 , while $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$ crystallises with the modified-spinel structure. FTIR and Raman measurements probed the cationic environment in $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ structures in order to investigate cation distribution and local distortion in the lithiated lattice. Performances of lithiated oxides as cathode materials in lithium batteries and substitutive effect on electrochemical properties have been investigated. Stable charge–discharge features have been observed for $\text{Li}/\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ cells cycled in the potential range from 3.0 to 4.2 volts when Ni and Zn dopants are used. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ solid solutions; Rechargeable lithium batteries; Raman; FTIR spectroscopy

Materials: $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ (M = Ni, Mg, Mn, Zn)

1. Introduction

Designing rechargeable lithium batteries with high specific energy and power, long cycle life, and rapid discharge rates is intimately linked to the availability of electrode materials. Among the cathode materials, lithiated transition-metal oxides (LTMOs) with either spinel (cubic) structure (LiMn_2O_4) or layered (rhombohedral) structure (LiCoO_2 and LiNiO_2) have been

proposed as advanced positive electrode materials for secondary lithium batteries [1–3]. The structure of LiCoO_2 belongs to the rhombohedral space group $R\bar{3}m$ (layered $\alpha\text{-NaFeO}_2$ -type structure) with lithium atoms in the 3a positions, transition-metal atoms in the 3b positions, and oxygen atoms in the 6c positions (with respect to hexagonal axes).

Recently, there has been intensive investigations on substituted LTMOs in which the effects of the substitution of the transition metal are interesting in terms of the structural and electrochemical properties. As LiCoO_2 and LiNiO_2 are isostructural, it is known that a solid solution $\text{LiCo}_{1-y}\text{Ni}_y\text{O}_2$ can be

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formed, showing advantages over the pure end members [4,5]. Various structural modifications of lithium cobaltate have been reported for doping or substitution in $\text{LiCo}_{1-y}\text{M}_y\text{O}_2$ with nickel [6], manganese [7], chromium [8], aluminum [9], titanium [10], and boron [9–11]. It is believed that doping with M-additives could stabilise the layered framework, which extends the cyclability and enhances the capacity of the electrochemical cell $\text{Li}/\text{LiCo}_{1-y}\text{M}_y\text{O}_2$ [5].

In the present paper, we report the synthesis of lithiated transition-metal oxides $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ doped with $\text{M} = \text{Ni}, \text{Mg}, \text{Mn}, \text{Zn}$. The products have been obtained by the combustion synthesis of aqueous solutions containing the respective metal nitrates, LiNO_3 , and urea in stoichiometric amounts. The structural modifications of LiCoO_2 induced by doping are investigated by X-ray diffraction, Raman scattering and FTIR spectroscopy. In addition, the electrochemical performance of $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ compounds in lithium cells is studied.

2. Experimental

2.1. Preparation of the Li–Co–M oxides

The doped $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ oxide samples were prepared by combustion synthesis of aqueous solutions. The salts of lithium, cobalt and doping substances were weighed as their nitrates in the required quantities. The contents were dissolved in distilled water (20 ml). The stoichiometric composition of the metal nitrates and urea mixtures was calculated on the total oxidizing and reducing valencies of the oxidizer and fuel which released the energy at a maximum [12,13]. The mixture of LiNO_3 with metal nitrates and urea, placed in a quartz crucible was rapidly calcined to 700°C for 3 h, ignited and yielded the product of the composition $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$. The resulting solid (black in color with lustre) was cooled to room temperature and pulverized for 3 h to a fine powder.

2.2. Instruments

The structure of the samples was characterized by X-ray diffraction (XRD) using a diffractometer

(Philips model PW1830) with nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The diffraction patterns were taken at room temperature in the range of $5^\circ < 2\theta < 80^\circ$ using step scans. The step size and the scan rate were set at 0.1 and 0.2 degree/min, respectively. The particle morphologies of the materials were examined by scanning electron microscopy (SEM, Cambridge Instruments, Stereoscan 120). The vibrational spectra were characterized at 25°C by Raman scattering (RS) and Fourier transform infrared (FTIR) spectroscopy. RS spectra were collected in a quasi-backscattering configuration on the powder sample annealed at 700°C . A double monochromator (Raman-laser spectrometer, Jobin-Yvon U1000) with holographic gratings and a computer-controlled photon-counting system was used. The laser light source was the 514.5 nm line radiation from a Spectra-Physics 2020 argon-ion laser. A RS spectrum is the average of 12 scans obtained with a spectral resolution of 2 cm^{-1} . A low power laser excitation of 15 mW was used to prevent any decomposition of the sample. FTIR absorption spectra were recorded using an interferometer (Brucker IFS113v) at a spectral resolution of 2 cm^{-1} . In the studied region ($100\text{--}700 \text{ cm}^{-1}$), the spectrometer was equipped with a $3.5 \text{ }\mu\text{m}$ -thick beam splitter, a globar source, and a DTGS/PE far-infrared detector. Samples were ground to fine powders painted onto polyethylene slabs.

2.3. Electrochemical studies

Electrochemical measurements were carried out at room temperature (22°C) with cells which include a lithium metal foil as the counter-electrode, a positive electrode mixture composed of 90 weight percent (w/o) of active material, 5 (w/o) carbon black as a conductive agent, and 5 (w/o) polytetrafluoroethylene as a binder. The laboratory-scale $\text{Li}||\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ cells were housed in a Teflon laboratory-cell hardware employing a non-aqueous Li^+ ion conducting organic electrolyte. The electrolyte was a 1 M LiPF_6 in EC-DMC in 1:1 volumetric ratio. A microporous polypropylene film (Celgard 2500) was used as a separator. Quasi open-circuit voltage profiles were measured using intermittent charging as follows. A current density of 0.1 mA/cm^2 was supplied for 1 h, corresponding to a

lithium extraction of about 0.01 mol from 1 mol of the electrode material. This was followed by a relaxation time of 0.5 h before the next charging started. The charging was stopped when the closed-circuit voltage reached 4.2 V. The apparent lithium content of the charge–discharge compounds was estimated using the current passed and the mass of the electrode material.

3. Results and discussion

3.1. Structural studies

Fig. 1 shows the powder X-ray diffraction diagrams of doped lithium cobaltates calcined at 700°C. The XRD patterns of $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ samples are dominated by a strong Bragg peak located at ca. $2\theta = 19^\circ$ and Bragg peaks with medium intensity at 36 and 44° . Considering the intensity and position of the Bragg peaks, it is well known that patterns can

be indexed either to a rhombohedral unit cell ($\text{R}\bar{3}\text{m}$) of a layered structure or, because the c/a ratio equals 4.90, to a face-centered cubic unit cell ($\text{Fd}\bar{3}\text{m}$) of a spinel structure [14,15]. For some samples, we decided to index the XRD diagram assuming a modified spinel-like structure with $\text{Fd}\bar{3}\text{m}$ space group because this assignment is in good accordance with our spectroscopic data, as shown herewith. Thus the stoichiometric formula of the final product should be $\text{Li}_2[\text{Co}_{0.5}\text{M}_{0.5}]_2\text{O}_4$, which is the fully lithiated phase of spinel.

$\text{LiCo}_{0.5}\text{Mg}_{0.5}\text{O}_2$, $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ and $\text{LiCo}_{0.5}\text{Zn}_{0.5}\text{O}_2$ grow with the tendency of a layered $\alpha\text{-NaFeO}_2$ -type structure; their XRD patterns appear to be similar to those reported for LiCoO_2 [16]. In the diagrams of $\text{LiCo}_{0.5}\text{Mg}_{0.5}\text{O}_2$ and $\text{LiCo}_{0.5}\text{Zn}_{0.5}\text{O}_2$ powders, we detect the presence of a small amount of a second phase, while $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ powders appear to be a single phase. The rhombohedral $\text{R}\bar{3}\text{m}$ structure is based on alternative ordering of Li in the octahedral sites between $(\text{Co}_{0.5}\text{M}_{0.5}\text{O}_2)_n$ infinite

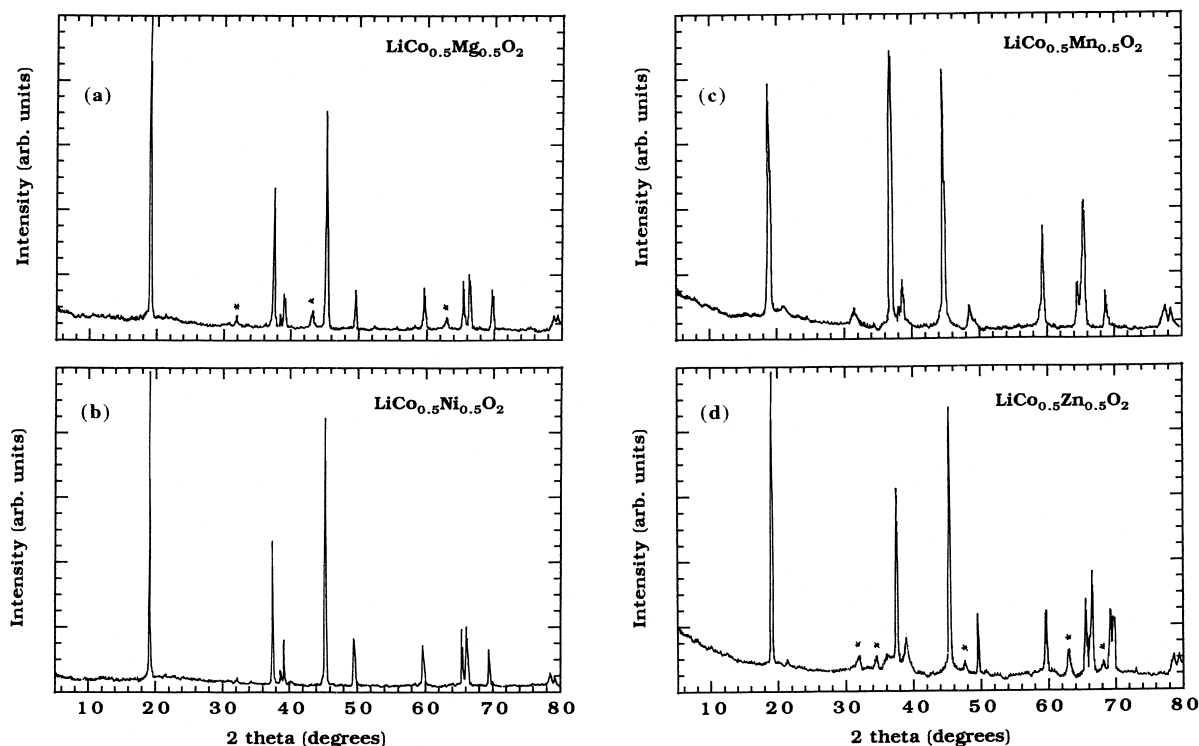


Fig. 1. X-Ray diffraction patterns of doped $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ with $\text{M} = \text{Ni}, \text{Zn}, \text{Mg},$ and Mn .

slabs formed by edge-sharing octahedra. Hexagonal cell parameters of the oxides prepared by different doping elements, which were calculated by least-squares refinement, are given in Table 1. These results reveal that the hexagonal-close-packed lattice is still maintained and both the metal–metal intrasheet distance (a_{hex}) and the metal–metal interlayer distance ($c_{\text{hex}}/3$) increase with doping. The $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ compound grown by combustion method exhibits XRD patterns with well-defined (006,102) and (108,110) doublets. The c/a ratio higher than the critical value 4.90 and the clear splitting of the (006) and (102) as well as (108) and (110) diffraction lines indicate that, as far as XRD patterns are concerned, an ordered distribution of lithium and transition-metal ions exists in the structure. On the other hand, the XRD diagram of $\text{LiCo}_{0.5}\text{Zn}_{0.5}\text{O}_2$ material (Fig. 1d) exhibits peaks due to impurities.

The substitution of Mn for Co expands the unit cell, which matches with the ionic radii of Co^{3+} and Mn^{3+} : 0.56 and 0.63 Å, respectively. In addition, the XRD patterns of $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$ display a drastic decrease of the (003)/(104) diffraction line intensity ratio caused by the Mn-additives. These results suggest that $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$ sample prepared by the combustion method at 700°C adopts a structural modification; thus we observe the formation of the modified-spinel structure for which the XRD patterns match based on Fd3m space group analogous to $\text{Li}_2\text{Ti}_2\text{O}_4$ (i.e. $\text{Li}_2\text{CoMnO}_4$), in which all cations occupy octahedral sites. In this modified-spinel structure, the oxygen atoms occupy fully the 32e sites and Li and Co fully occupy the 16c and 16d octahedral interstices, respectively, with very little cation mixing. This is slightly different than the normal spinel structure of LiMn_2O_4 , in which Li fully occupies

tetrahedral sites (Wyckoff position 8a in Fd3m). The XRD peaks of $\text{Li}_2[\text{Co}_{0.5}\text{Mn}_{0.5}]_2\text{O}_4$ prepared at 700°C were indexed assuming the cubic lattice parameter with $a = 8.331$ Å (Table 1). The degree of crystallinity, i.e. domain size, was examined by measuring the full width at half maximum (FWHM) for (004) peak at ca. $2\theta = 44^\circ$, which is found to be very sensitive to the synthesis temperature. The question of the local cationic order in $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ materials will be re-examined below by spectroscopic measurements.

3.2. Vibrational studies

The purpose of these studies is to investigate the local environment of cations in a cubic close-packed oxygen array of the $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ lattice using Raman scattering and FTIR spectroscopy. Vibrational modes, which correspond to vibrations involving primarily atomic motion of cations against their oxygen neighbors, are sensitive to the space group and consequently, these modes are very sensitive to the cationic local environment in the host matrix [17]. Fig. 2 shows the RS spectra of the doped lithium–cobalt oxides recorded at room temperature. According to a factor group analysis, the layered phase (R3m space group) exhibits only two Raman-active modes, i.e. the A_{1g} and the E_g species. The RS spectra (Fig. 2) of $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ ($M = \text{Ni}, \text{Zn}, \text{Mg}$) are dominated by two band at ca. 595 cm^{-1} (A_{1g} mode) and at ca. 485 cm^{-1} (E_g mode). For $\text{LiCo}_{0.5}\text{Zn}_{0.5}\text{O}_2$ a band with a weak intensity appears at ca. 550 cm^{-1} , which is attributed to the Zn–O bond. The RS results demonstrate clearly that the number of active modes is higher for the modified-spinel $\text{Li}_2[\text{Co}_{0.5}\text{Mn}_{0.5}]_2\text{O}_4$ structure than for the layered rhombohedral-like $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$ phase. The Raman band located at ca. 615 cm^{-1} can be viewed as the symmetric M–O stretching vibration of MO_6 groups with the A_{1g} symmetry in the O_h^7 spectroscopic space group. Its broadening may be related with the cation–anion bond lengths and polyhedral distortion occurring in $\text{Li}_2[\text{Co}_{0.5}\text{Mn}_{0.5}]_2\text{O}_4$. The RS peak at 495 cm^{-1} has the E_g symmetry, whereas the peaks located at lower frequency have the F_{2g} symmetry. Because the crystallographic anomaly strongly affects the Raman spectrum, we can definitely assume that the symme-

Table 1
XRD results obtained on doped $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ powders calcined at 700°C

Dopant	Space group	a (Å)	c (Å)	$I_{(003)}/I_{(104)}$
Mg	R $\bar{3}m$	2.858	14.138	1.28
Ni	R $\bar{3}m$	2.841	14.113	1.23
Mn	Fd3m	8.331	–	0.85
Zn	R3m	2.853	14.152	1.47

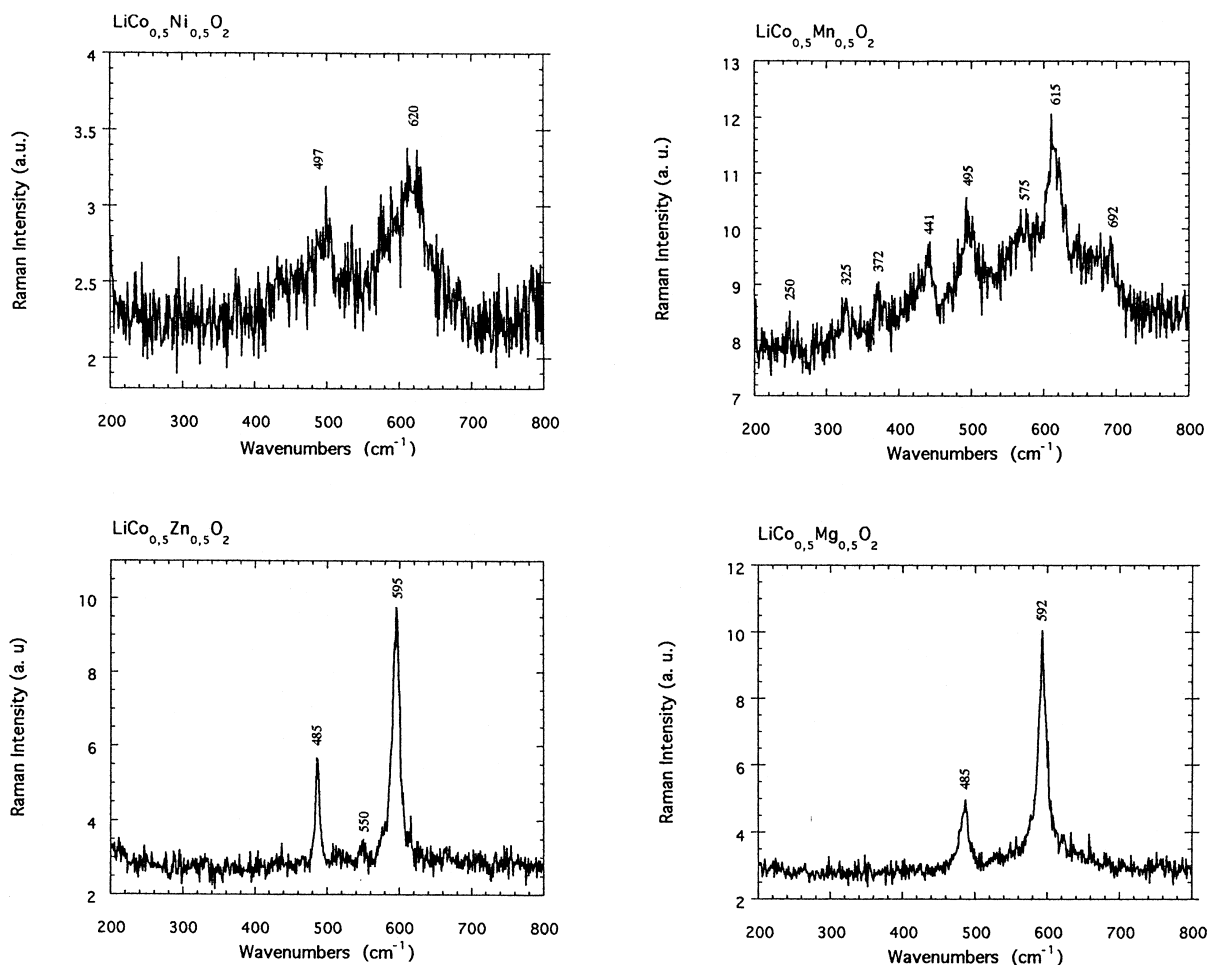


Fig. 2. Raman spectra of $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ compounds doped with $\text{M} = \text{Ni}, \text{Zn}, \text{Mg},$ and Mn .

try of the $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$ oxide synthesized at 700°C is of $\text{Fd}3\text{m}$.

Fig. 3 shows the FTIR spectra of doped $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ samples fired at 700°C for 5 h. The FTIR absorption spectra display features which can be divided into two parts: (i) The high-wavenumber region of strong absorption corresponds to the broad rock-salt band which has broken into several distinct components at ca. $400\text{--}600\text{ cm}^{-1}$, and (ii) the low-wavenumber region in which an isolated strong band is centered at ca. $240\text{--}260\text{ cm}^{-1}$.

The IR modes of crystalline LiCoO_2 can be predicted by factor group analysis with a Bravais cell which contains one molecule. The group factor

analysis of the D_{3d}^{55} spectroscopic symmetry yields four infrared-active modes [18]. Because FTIR spectroscopy is capable of probing directly the surrounding environment of the cation, we have studied the local environment of lithium ions in $\text{LiM}'\text{O}_2$ ($\text{M}' = \text{Co}, \text{Ni}, \text{Cr}$) materials [19]. It has been also demonstrated that the vibrational mode component of the LiO_6 octahedra appears invariably around 250 cm^{-1} [20]. Thus, the IR resonant frequency of LiO_6 groups appears at 269 cm^{-1} in LiCoO_2 (Fig. 3a). The IR absorption spectra of doped $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ microcrystalline powders (Fig. 3b, c and d) show that these compounds have the symmetry. The band situated at ca. 260 cm^{-1} is assigned with confidence

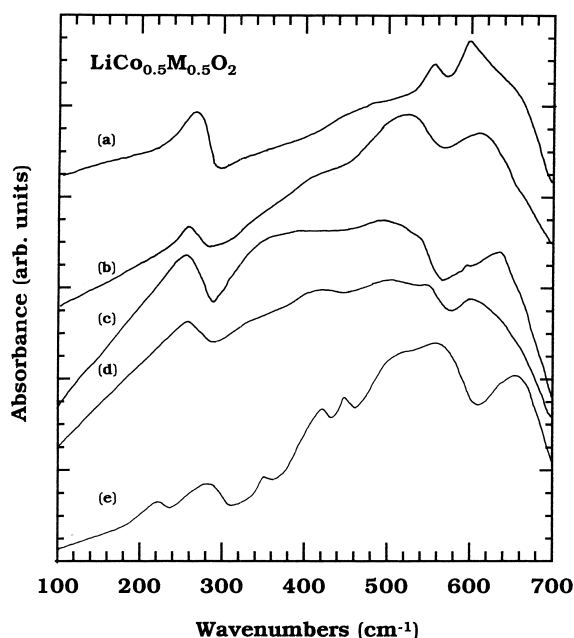


Fig. 3. FTIR spectra of (a) LiCoO_2 and $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ compounds doped with (b) Ni, (c) Zn, (d) Mg, and (e) Mn.

to an asymmetric stretching vibration of the Li^+ ion with O^{2-} nearest neighbors in $\text{LiCo}_{0.5}\text{Ni}_{0.5}\text{O}_2$, $\text{LiCo}_{0.5}\text{Zn}_{0.5}\text{O}_2$ and $\text{LiCo}_{0.5}\text{Mg}_{0.5}\text{O}_2$. The high-frequency band of the FTIR absorption spectra located at ca. 580 cm^{-1} is attributed to the asymmetric stretching mode of CoO_6 group, whereas the low-frequency bands at ca. 420 and 530 cm^{-1} are assigned to the bending modes of O–M–O chemical bonds. The shape of the FTIR spectrum of the $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$ product (Fig. 3e) shows the character of the modified-spinel $\text{Li}_2[\text{Co}_{0.5}\text{Mn}_{0.5}]_2\text{O}_4$ structure (Fd3m space group). The high-frequency bands of the FTIR absorption spectrum of $\text{Li}_2[\text{Co}_{0.5}\text{Mn}_{0.5}]_2\text{O}_4$ located at ca. 650 cm^{-1} are attributed to the asymmetric stretching modes of CoO_6 and MnO_6 groups. The IR resonant frequency of LiO_6 groups appears at 280 cm^{-1} . As a result, a breakdown in the Raman and IR selection rules is observed in the modified-spinel structure, which may explain the observation of broad bands (disorder) and the fact that the number of modes increased for $\text{Li}_2[\text{Co}_{0.5}\text{Mn}_{0.5}]_2\text{O}_4$. In conclusion, analysis of the Raman scattering and FTIR absorption spectra of doped lithium cobaltates has shown the modified-

spinel structure of $\text{Li}_2[\text{Co}_{0.5}\text{Mn}_{0.5}]_2\text{O}_4$ with Fd3m symmetry and the layered structure of $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ (M = Ni, Zn, Mg) with R3m symmetry. It has also demonstrated the local environment of cations against oxygen neighbors, i.e. lithium and transition-metal atoms reside in octahedral interstices of the modified-spinel matrix.

3.3. Electrochemical charge–discharge features

The electrochemical behavior of substituted $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ was examined in lithium-containing test cells employing a non-aqueous electrolyte. The Li metal acted as both counter and reference electrodes, while $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ was treated as the working electrode. The electrodes are separated by a porous membrane soaked in an electrolyte of 1 M LiPF_6 in 1:1 (v/v) mixture of EC-DMC. Fig. 4 shows the first charge–discharge curves at 22°C for the $\text{Li}||\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ non-aqueous cells operated under galvanostatic conditions. The initial open-circuit voltages of freshly prepared cells were around 2.9 V. The cells were charged and discharged at a current density of 0.1 mA/cm^2 , while the voltage is monitored between 3.0 and 4.2 V.

In the potential domain 3.0–4.2 V, the charge–discharge curves correspond to the voltage profiles characteristic of the lithiated transition-metal oxide cathode materials associated with lithium occupation of octahedral sites, in agreement with previous work [21–23]. The voltage profiles of the cells $\text{Li}||\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ exhibit a potential slightly lower than for the pure LiCoO_2 phase. This could be due to the different crystallographic texture and morphology of $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ cathodes. Since the electronic band structure of substituted $\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_2$ materials is affected by the presence of M atoms it should be remarked that the fully intercalated phase is not recovered after the first discharge. The capacities of the first charges are far larger than any subsequent discharges for the cells which contain doped cathode materials. This capacity decrease is more severe for the modified-spinel $\text{LiCo}_{0.5}\text{Mn}_{0.5}\text{O}_2$ compound. This behavior is attributed to the quasi-spinel phase in which the cations are located only in octahedral sites with the existence of cation mixing. These studies also demonstrate that the layered-type cathodes yield significantly inferior capacities of 140

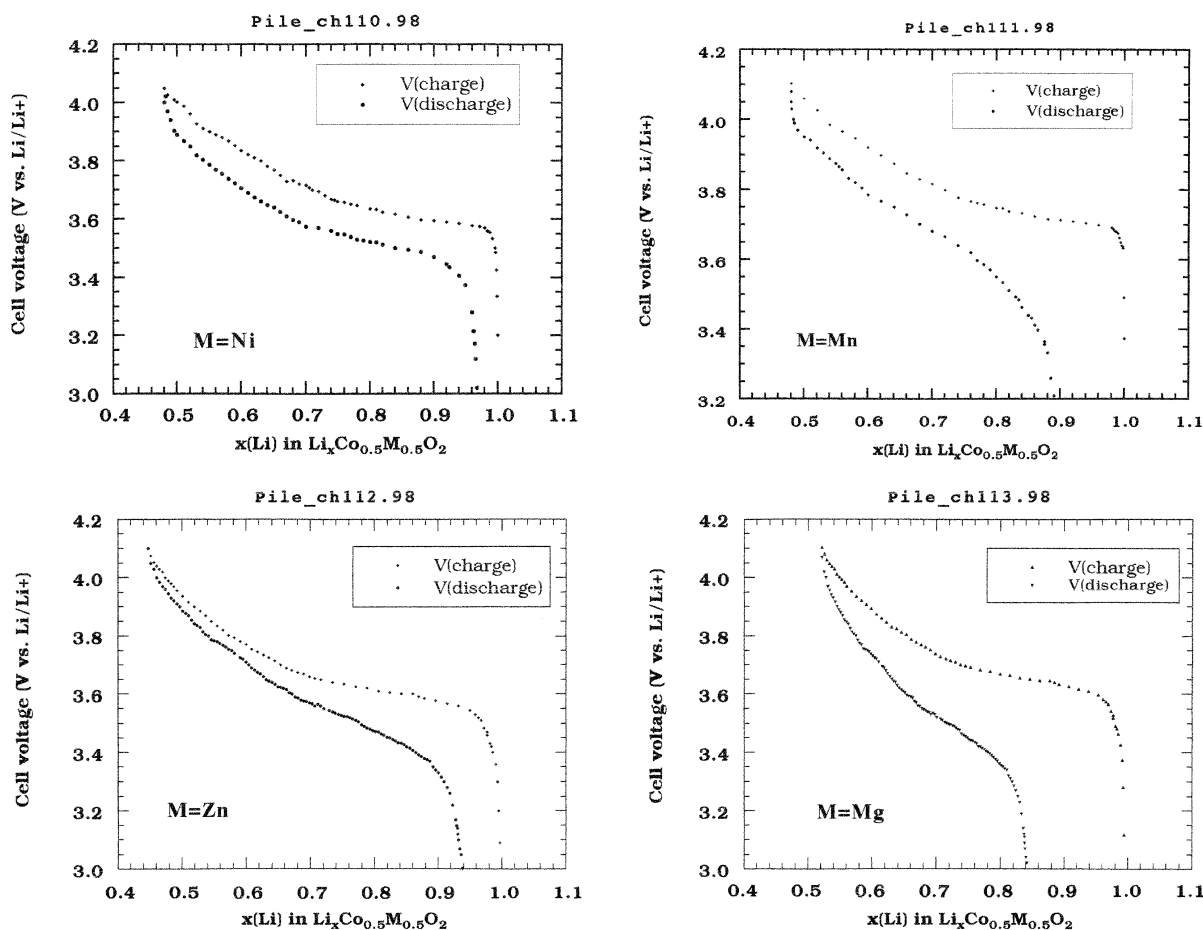


Fig. 4. Charge–discharge profiles of Li//LiCo_{0.5}M_{0.5}O₂ cells with M = Ni, Zn, Mg, and Mn. Electrochemical measurements were carried out at current density 0.1 mA/cm² in the voltage range 3.0–4.2 V.

mAh/g compared to the theoretical value of 164 mAh/g when discharged to a cut-off voltage of 2.8 V. The improved performance of the Li||LiCo_{0.5}Zn_{0.5}O₂ cell is evident (Fig. 4) from the following factors: (i) the rate at which the capacity is lost on cycling is reduced, (ii) the capacity retention is comparable to the Ni-substituted compounds, but the cell potential is inferior in the entire length of charge–discharge. However, the low capacities of the samples are also indicative of heavy migration of doping metal within the oxide slab (into the lithium sites), which gives a more three dimensional character to the product, consistent with vibrational spectra. As a concluding remark, it can be pointed out that for doped cathode materials prepared by the combus-

tion method electrochemical features are less, i.e. specific capacity after the first discharge, than their parent compounds LiNi_{1-y}Co_yO₂ synthesized by wet chemistry.

4. Conclusion

The positive electrode materials LiCo_{0.5}M_{0.5}O₂ (M = Ni, Mg, Zn, and Mn) have been synthesized using a combustion procedure at 700°C. Structural features suggested by X-ray diffraction show that doped lithium cobaltates have an essentially ordered rock-salt structure, while Mn-doped LiCoO₂ exhibits a modified-spinel structure (Li₂CoMnO₄). These

results are well-confirmed by vibrational spectroscopy, i.e. Raman scattering and FTIR absorption. The analysis of the Raman and FTIR absorption spectra shows that the local environment of the doped lithium–cobalt oxides is in good agreement with structural models including R3m and Fd3m space groups. The charge–discharge profiles of $\text{Li}||\text{LiCo}_{0.5}\text{M}_{0.5}\text{O}_4$ cells using positive electrodes prepared by combustion method temperatures were recorded at lower voltages than for high-temperature materials. The capacities of the first charges are far larger than any subsequent discharges for the cells which contain doping species.

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References

- [1] T. Ohzuku, in: *Lithium Batteries, New Materials, Developments and Perspectives*, Elsevier, Amsterdam, 1993, p. 239.
- [2] R.J. Gummow, M.M. Thackeray, *Solid State Ionics* 53–56 (1992) 681.
- [3] D. Guyomard, J.M. Tarascon, *Solid State Ionics* 69 (1994) 222.
- [4] C. Delmas, I. Saadoune, *Solid State Ionics* 53–56 (1992) 370.
- [5] T. Ohzuku, A. Ueda, M. Nagayama, Y. Iwakoshi, H. Komori, *Electrochim. Acta* 38 (1993) 1159.
- [6] I. Saadoune, C. Delmas, *J. Solid State Chem.* 136 (1998) 8.
- [7] R. Stoyanova, E. Zhecheva, L. Zarkova, *Solid State Ionics* 73 (1994) 233.
- [8] C.D.W. Jones, E. Rossen, J.R. Dahn, *Solid State Ionics* 68 (1994) 65.
- [9] G.A. Nazri, A. Rougier, K.F. Kia, *Mater. Res. Soc. Symp. Proc.* 453 (1997) 635.
- [10] W. Huang, R. Frech, *Solid State Ionics* 86–88 (1996) 395.
- [11] R. Alcantara, P. Lavela, J.L. Tirado, R. Stoyanova, E. Zhecheva, *J. Solid State Chem.* 134 (1997) 265.
- [12] S.S. Manoharan, K.C. Patil, *J. Am. Ceram. Soc.* 75 (1992) 1012.
- [13] S. Chitra, P. Kalyani, T. Mohan, R. Gangadharan, C. Julien, *Indian Patent* (1999) under process.
- [14] E. Rossen, J.N. Reimers, J.R. Dahn, *Solid State Ionics* 62 (1993) 53.
- [15] B. Garcia, P. Barboux, F. Ribot, A. Kahn-Harari, L. Mazerolles, N. Baffier, *Solid State Ionics* 80 (1995) 111.
- [16] A. Ueda, T. Ohzuku, *J. Electrochem. Soc.* 141 (1994) 2013.
- [17] C. Julien, A. Rougier, G.A. Nazri, *Mater. Res. Soc. Symp. Proc.* 453 (1997) 647.
- [18] R.K. Moore, W.B. White, *J. Am. Ceram. Soc.* 53 (1970) 679.
- [19] A. Rougier, G.A. Nazri, C. Julien, *Ionics* 3 (1997) 170.
- [20] M. Nazri, D. Curtis, B. Yebka, G.A. Nazri, C. Julien, in: *Paper presented at the 193th Meeting of The Electrochem. Soc., San Diego, CA, 3–8 May, 1998.*
- [21] A. Rougier, I. Saadoune, P. Gravereau, P. Willman, C. Delmas, *Solid State Ionics* 90 (1996) 83.
- [22] W. Huang, R. Frech, *Solid State Ionics* 86–88 (1996) 395.
- [23] C.D.W. Jones, E. Rossen, J.R. Dahn, *Solid State Ionics* 68 (1994) 65.