

Improved electrode characteristics of olivine–LiCoPO₄ processed by high energy milling

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Abstract

Olivine–LiCoPO₄ powders have been processed by mechanical grinding for time periods ranging from 0.5 to 10 h with conductive carbon contents of 0, 8 and 20% (w/w). In all cases the grinding process produces an amorphization of the crystalline materials and decreases both the crystallite and particle sizes. Secondary phases are detected by scanning electron microscopy and X-ray diffraction in the materials milled for times greater than 2 h without carbon. The addition of conductive carbon during the milling process decelerates the degradation of the material and secondary phases are not detected even after 10 h of grinding. The electrochemical performance of olivine–LiCoPO₄ is improved in all the materials milled for 0.5 h; a lower cell polarization and a larger reversible specific capacity are observed. These characteristics are enhanced in the materials grinded with conductive carbon, which also display a capacity retention with cycling clearly superior to that of the fresh LiCoPO₄. Ball milling LiCoPO₄ for times greater than 1 h is detrimental for the response of the electrode, independently on the amount of conductive carbon in the grinding media.

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1. Introduction

Since the demonstration of reversible electrochemical lithium insertion–extraction in LiFePO₄ in 1997 [1], olivine–transition metal phosphates have attracted much attention as an alternative to LiMO₂ (M=transition metal) layered materials as positive electrode for rechargeable lithium batteries. It is well documented that LiCoPO₄ crystallizes in the olivine structure, usually described in terms of a hexagonal close-packing of oxygen with Li and Co ions located in half of the octahedral sites and P in one eighth of the tetrahedral positions. The [Co–O₆] octahedra share four corners in the *cb*-plane being cross-linked along the *a*-axis by the PO₄ groups, whereas Li ions are located in rows, running along *a*, of edge-shared LiO₆ octahedra which

appear in between two consecutive [CoO₆]_∞ layers lying on the *cb*-plane.

Amine et al. demonstrated that lithium can be reversible removed from LiCoPO₄ at an average voltage of 4.8 V, with only a small contraction in volume of the olivine-framework [2]. The theoretical specific capacity of this material is of 167 Ah kg^{−1}. However, the practical use of LiCoPO₄ is precluded by its poor rate cyclability related to a electronic conductivity, which is the common limitation for olivine LiMPO₄ compounds. The use of olivine–LiCoPO₄ brings an additional problem; the oxidation of Co²⁺ to Co³⁺ (4.8–5.1 V) overlaps with the stability limit of the most used and stable liquid electrolytes for lithium batteries (LiPF₆ based) [3]. Hence the couple Co³⁺/Co²⁺ may be useful for the development of more reliable commercial lithium cells if the oxidation voltage was slightly decreased. This can be achieved improving the conductivity of the positive electrode, i.e. decreasing the polarization of the cell. Previous works on LiFePO₄ proved that the poor electrode conductivity, and hence

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the electrode polarization, may be alleviated by means of carbon coating [4]. Reducing the particle size of the active material also had a beneficial impact over the electrode conductivity. Indeed the particle size is a key factor in the lithium insertion process in many phosphates [5–7] and it is well documented that the electrochemical performance is improved when the particle size decreases and the material is amorphized [7–9].

We postulate that the electrochemical characteristics of LiCoPO_4 could be greatly improved (i) using a material of small particle size and (ii) producing a carbon/ LiCoPO_4 composite prior to the conformation of the electrode. For most type of materials mechanical grinding (MG) leads to materials in fine particle form, resulting in the modification of the electrochemical performance of electrode material for lithium batteries [9–11]. In the present work, a conductive carbon additive has been grinded together with the active material (LiCoPO_4) in order to form a highly conductive C/ LiCoPO_4 composite. We discuss the electrochemical behavior of olivine- LiCoPO_4 processed by mechanical grinding, focusing in two variables: the milling time and the amount of carbon added to the LiCoPO_4 powder for the milling process.

2. Experimental

Conventional solid-state reaction was employed to synthesize LiCoPO_4 from a stoichiometric mixture of Li_2CO_3 , Co_3O_4 and $(\text{NH}_4)_2\text{HPO}_4$. The mixture was first ground in an agate mortar, and then calcined in air at 350°C for 12 h to give a mixture of reactive oxides. After cooling, the powders were pressed into a pellet and annealed at higher temperatures (750°C) for 24 h in air. The samples were reground and reheated at 350°C for 9 h to ensure the homogeneity and purity of the final compound [2].

The LiCoPO_4 powder was produced by high-energy milling LiCoPO_4 coarse powders in a vibratory ball mill Spex CertiPrep (Model 8000), at room temperature. The grinding chamber and balls ($\varnothing = 10$ mm) were of stainless steel. The volume of the grinding chamber was about 150 cm^3 . The ball-to-powder weight was 22:1. Grinding experiments were performed in air at 1425 rpm. In order to evaluate the effect of the milling time and carbon additive over the electrochemical properties, different milling conditions have been used. In a first set of materials (sample A) the LiCoPO_4 powders were ball-milled for 0.5, 1, 2, 3 and 10 h. In a second set of experiments (sample B) LiCoPO_4 powders were milled for the same times, but in this case together with black carbon (super-S, MMM carbon, Belgium) in a 8 wt.%. In a last experiment, a 20% (w/w) of conductive carbon was added to LiCoPO_4 and ball-milled for 0.5 h (sample C).

X-ray diffraction (XRD) data were collected using a X Philips X'Pert automatic diffractometer with $\text{Cu K}\alpha$ radiation (1.5418 \AA) operating at 40 kV and 40 mV. Conditions of the scans were a measurement range of $10\text{--}80^\circ$, step size of 0.02° and counting time of 1.5 s. The average crystallite size for the five most intense diffraction peaks of LiCoPO_4 was evaluated by means of Scherrer formula [12]. For every peak, defined by its Bragg angle, the sample width (β_{sample}) was calculated by means to the experimental width (β_{exp}), measured as the full width

at half maximum (FWHM) and the instrumental broadening (β_{int}), determined from a polycrystalline NIST silicon standard [13,14]. The morphology of materials was studied by scanning electron microscopy (SEM) (Model Philips XL 30 equipped with an EDAX analyzer) and the compositional homogeneity was evaluated by energy X-ray dispersive spectroscopy (EDS).

Olivine- LiCoPO_4 electrodes were fabricated by mixing the corresponding active material (fresh LiCoPO_4 , sample A, sample B or sample C) with carbon black (Super S, MMM Carbon, Belgium) and Kynarfex 2801[®] (Elf-Atochem) used as binder. The ratio of LiCoPO_4 , C and binder was 75:20:5 (w/w/w). This means that the total carbon content of the electrode is the same in all cases, though for sample A all the carbon is added after the grinding process, for sample C before grinding, and for sample B in two steps (8% before and 12% after grinding). The positive electrode blend was conformed in 8 mm pellets of 30 mg in weight. Electrochemical measurements were performed using Swagelok cells comprising Li metal counter electrode with a 1 M solution of LiPF_6 in EC/DMC (1:1, v/v, Merck LP30) as the electrolyte. After assembling the cells in an argon filled glove box, they were connected to a MacPile battery tester for either potentiostatic or galvanostatic charge/discharge.

3. Results and discussion

3.1. Characterization of mechanically grinded (MG) LiCoPO_4

Fig. 1 shows the result of fitting the experimental XRD pattern for initial LiCoPO_4 to the olivine structure. All diffraction peaks are indexed according to JCPDS file no. 32-0552. The refined unit cell parameter calculated from XRD patterns are $a = 5.926(8)\text{ \AA}$, $b = 10.206(1)\text{ \AA}$, and $c = 4.706(8)\text{ \AA}$ corresponding to an orthorhombic cell, similar to those previously reported by other authors [2,15,16].

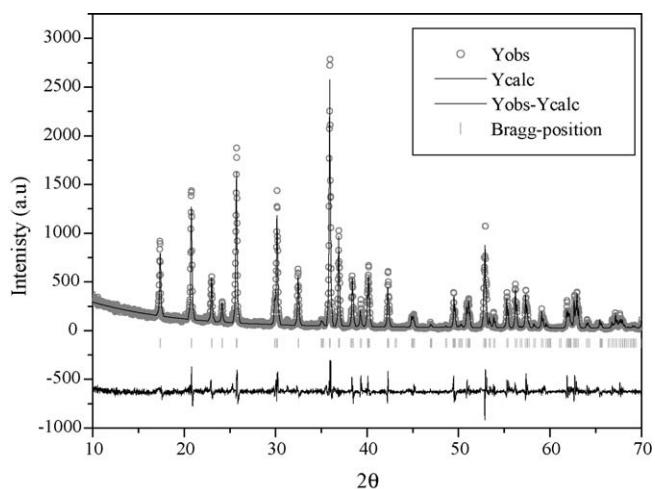


Fig. 1. Results of fitting the X-ray powder diffraction data corresponding to fresh olivine- LiCoPO_4 : experimental (points), calculated (solid line), assuming the $Pnmb$ space group, and the difference (bottom). Vertical bars represent the calculated Bragg position.

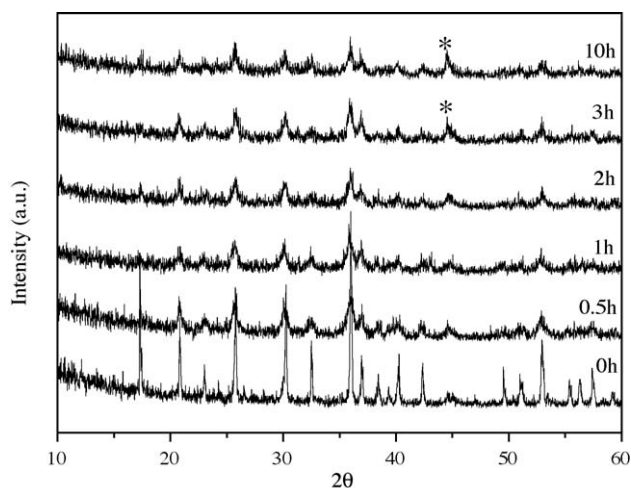


Fig. 2. Evolution of the XRD pattern of the ball milled LiCoPO_4 for different times in a Spex vibratory mill. After 3 h, a new diffraction peak appears due to a decomposition of olivine phase during the milling process (denoted by *).

Fig. 2 shows the evolution of XRD of the LiCoPO_4 initial olivine phase at different milling times. As consequence of milling process, there is a progressive broadening, and a decreasing of intensity in all diffraction peaks of the initial LiCoPO_4 , indicative of an amorphization process and a reduction in the crystallite size. This effect is more relevant at high diffraction angles. After 3 h of milling, a new diffraction peak appears at $2\theta = 44^\circ$. The intensity of this Bragg maximum increases with the milling time, suggesting the crystallization of a decomposition product of LiCoPO_4 as occurs in other systems [17,18]. The new crystalline phase could be identified as $\text{Co}_2\text{P}_2\text{O}_7$ (JCPDS card 40-0014), though it is not possible to observe other peaks from this crystalline phase, due to the overlapping of $\text{Co}_2\text{P}_2\text{O}_7$ diffraction peaks with those of LiCoPO_4 . The decomposition of LiCoPO_4 clearly results in the presence of crystalline $\text{Co}_2\text{P}_2\text{O}_7$, but it cannot be ruled out that other amorphous decomposition-products could be formed as well.

Fig. 3 shows the XRD patterns of milled C (8 wt. %)/ LiCoPO_4 powders (sample B), after various milling times together with that of the initial material ($t = 0$). A progressive decrease in global intensity and broadening of diffraction peaks is observed, both features being less noticeable than in the milling of LiCoPO_4 (Fig. 2). The absence of extra peaks for long milling times indicates that LiCoPO_4 does not decompose into other crystalline oxides. These results suggest that the carbon coating prevents the decomposition of LiCoPO_4 and the crystallization of secondary phases during the high energy milling process.

The effect of the carbon addition in the milled blend is more clearly observed in Fig. 4, where the XRD patterns of the samples milled during 0.5 h but with different amounts of carbon, ranging from 0% (A), 8% (B) and 20% (C) are compared to the initial one. The evolution of the global intensity and broadening of peaks with the carbon content indicates that the amorphization of the fresh LiCoPO_4 is less severe with higher carbon amounts. The amorphization process due to milling decelerates as the carbon content increases. This is also evidenced from the particle

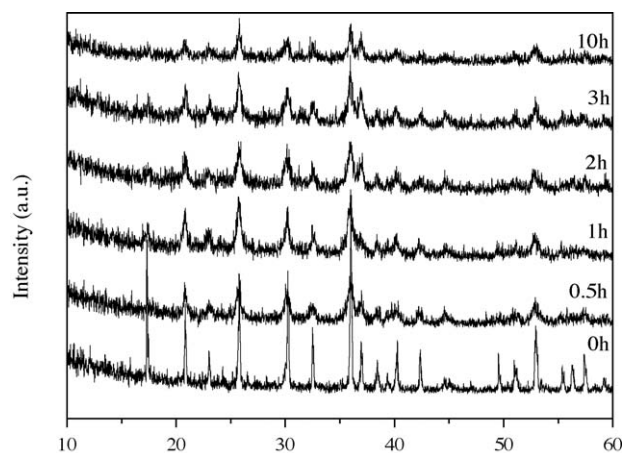


Fig. 3. X-ray diffraction patterns of LiCoPO_4 powders after mechanically grinding with 8% carbon for selected times. No extra peaks appear, indicating the absence of decomposition and recrystallization of the powders during the milling process.

size reduction, i.e. the size of the crystallites that can be estimated from the well known Scherrer formula [12]. The average crystallite size of the non-milled sample, 930 nm, dramatically decreases down to 200 nm for the samples milled during 0.5 h without carbon (A), and down to 220 nm (B) and 270 nm (C) when the carbon added is 8% and 20%, respectively.

Given the intimate physical contact of the LiCoPO_4/C powders with the impacting balls as well as with the vessel walls, some contamination from the milling tools is unavoidable. The chromium, iron and nickel contaminants have been determined by EDS analysis on the powders obtained after different milling times without carbon (sample A) and with carbon (sample B and sample C). All the samples milled for times inferior to 3 h (with either 0%, 8% or 20% of carbon) displayed similar results, being the total amount of polluting elements (Cr, Fe and Ni) around the 0.9% in all the cases. These contents are negligible, if we take into account the detection limit of this technique (1%). For superior milling times, only the samples milled with carbon present a greater percentage of the polluting iron (4%).

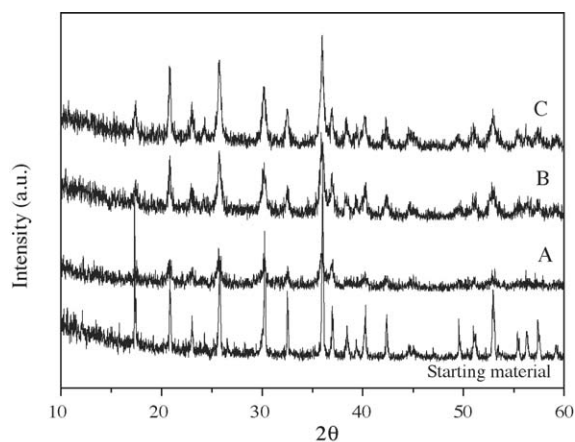


Fig. 4. Compared XRD from materials grinding for 0.5 h with different amounts of carbon added. A = 0% C, B = 8% C and C = 20% C.

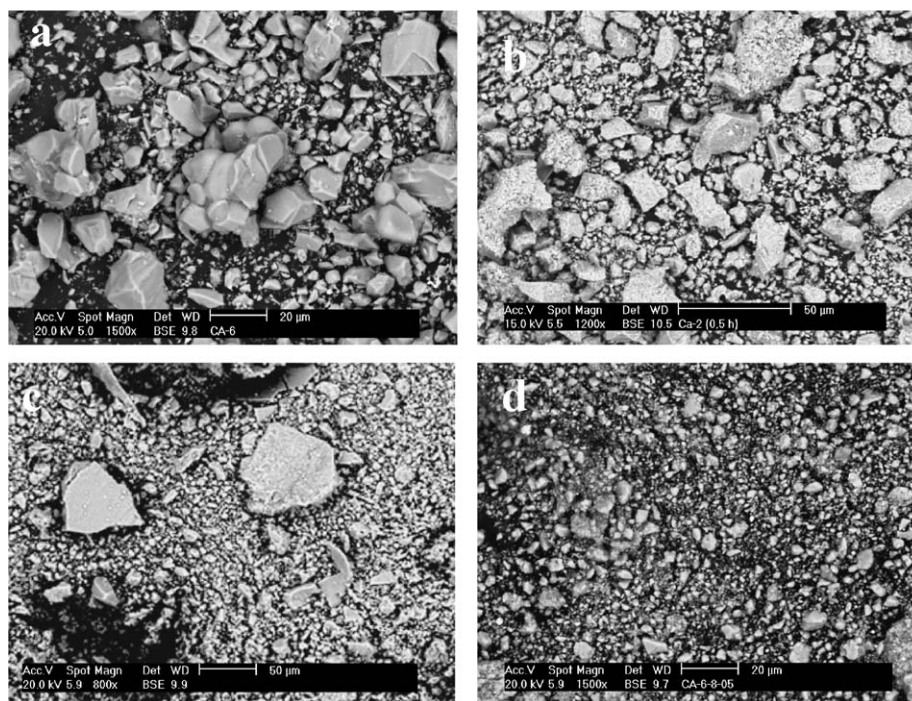


Fig. 5. SEM micrographs of (a) fresh LiCoPO_4 , (b) LiCoPO_4 milled for 0.5 h, (c) LiCoPO_4 milled for 10 h and (d) $\text{LiCoPO}_4 + 8\% \text{ C (w/w)}$ milled for 0.5 h.

The particle size is a key factor on the electrochemical reactivity of iron phosphates [5–7]. Electrochemical activity is favored for a given material when prepared as a highly disperse sample; i.e. for samples with high specific surface. The size and morphology of initial LiCoPO_4 and all the mechanically grinded samples were studied by SEM using a BES detector. Possible compositional changes were also followed by means of EDS analyses. Since this technique is semi-quantitative, and results for elements lighter than sodium are no trustworthy, only the atomic ratio P:Co of particles was analyzed. Fig. 5a shows the electronic micrography of the initial compound LiCoPO_4 . Polyhedral particles of irregular shape are distinguished in either dispersed forms or forming aggregates. The larger particles size does not exceed 100 nm. Only particles of LiCoPO_4 are detected by the semi-quantitative compositional analyses. In Fig. 5b and c the micrographs of the samples A for milling times of 0.5 and 10 h are compared. The milling process entails the appearance of morphologic changes: the particles of polyhedral form of the initial LiCoPO_4 are disaggregated until forming a combination of dispersed particles and greater particle aggregates. As inferred from XRD the mechanical process also produces the diminution of the crystallite size. However, in the samples grinded during 10 h the size of aggregates increased up to 50 nm in some cases (Fig. 5c). This effect can be ascribed to formation of secondary phases in the material, as the $\text{Co}_2\text{P}_2\text{O}_7$ phase identified by XRD (Fig. 2). Since the atomic ratio P:Co of $\text{Co}_2\text{P}_2\text{O}_7$ is identical to that of LiCoPO_4 it is not possible to distinguish the two materials by means of EDS. It should also be noticed that this technique does not provide information about a possible Li loss due to the local heating and long milling times. Such a lithium loss will also result in the oxidation of Co^{2+} to Co^{3+} that will be very

detrimental for the electrochemical performance of the milled samples.

Fig. 5d shows the micrograph of a sample B with 8 wt.% in carbon milled for 0.5 h. An intimate mixture between the active material and carbon is obtained. The milling process entails an evolution of the morphology as that observed in the case of milling without carbon additives; the large aggregates of particles is disaggregated in smaller crystallites, but in this case the addition of conductive carbon produces a more homogenous distribution of the particle size. In none of the milled powders from sample B other particles than those of the pure olivine phase have been detected.

3.2. Electrochemical study of MG materials

Fig. 6 shows the first charge–discharge cycle of Li cells bearing the sample A (grinding without carbon) as the positive electrode. The electrochemical response of the initial LiCoPO_4 electrode is improved for low grinding times (0.5 h); larger amounts of lithium ions can be reversibly extracted from and inserted into LiCoPO_4 . Longer milling times are detrimental to the electrochemical performance of the electrode. As commented above, among other factors, it can not be discarded that Co^{2+} gets oxidized to Co^{3+} under the milling process. Fig. 6 also shows that during the charge of the cells using the samples milled for 2 and 3 h a new electrochemical process appears at 4 V. This process might be due to the irreversible oxidation of the decomposition products of LiCoPO_4 ; crystalline $\text{Co}_2\text{P}_2\text{O}_7$ detected by XRD and SEM or more likely an unidentified amorphous compound. The sample milled for 10 h is electrochemically inactive.

The electrochemical results of the materials from sample B (milling with 8 wt.% carbon) are shown in Fig. 7. All the

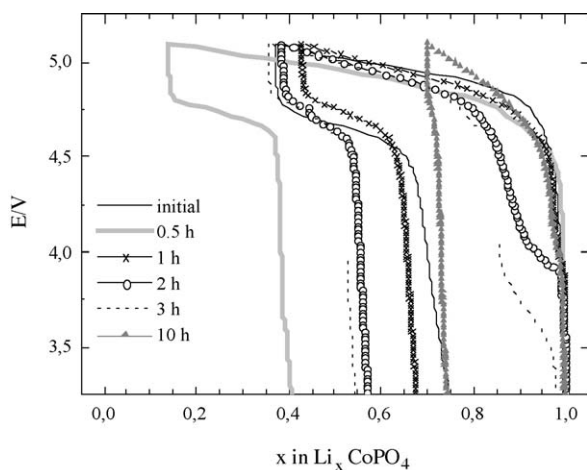


Fig. 6. Voltage–composition plot obtained during electrochemical lithium de-insertion/insertion in LiCoPO_4 samples processed through different milling times (0, 0.5, 1, 3 and 10 h). Voltage scan was 20 mV h^{-1} .

materials present similar electrochemical behavior when used as positive electrode in lithium cells. The voltage–composition curves are parallel suggesting a similar mechanism for the lithium de-insertion–insertion process. In all cases the shape of the voltage–composition curves also indicates that the lithium de-insertion–insertion is a reversible reaction, however a noticeable lost of capacity is observed. Hence, it cannot be ruled out that some side-reaction, such as the electrolyte decomposition, occur when Li cells are charged up to very high voltages. The milling process for short times has a positive effect on the electrode characteristics. It can be observed that the oxidation of cobalt, proceeding at 5.02 V in the initial LiCoPO_4 for $x=0.5$, occurs at a lower voltage in the samples milled for 0.5 and 1 h. As a result of the lower cell polarization, the electrodes comprising C/LiCoPO_4 composites deliver a higher specific capacity within the electrochemical stability window of the electrolyte. While milling LiCoPO_4 with a carbon additive for short times improves the performance of the electrode, the grinding process

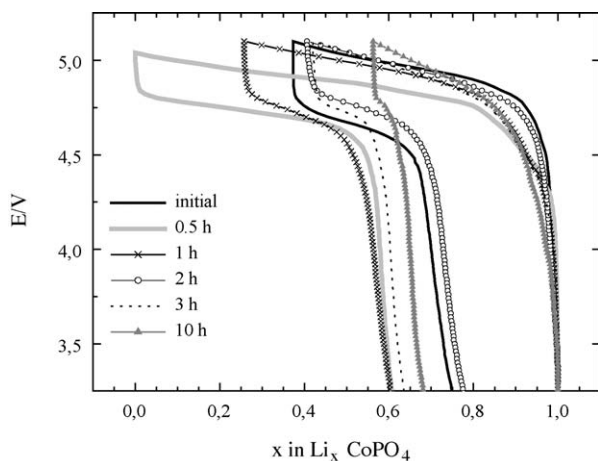


Fig. 7. Voltage–composition curve obtained from the charge–discharge of a $\text{Li/LiCoPO}_4 + \text{C}$ (8%, w/w) cells (scan 20 mV h^{-1}). The $\text{LiCoPO}_4 + \text{C}$ (8%, w/w) composite was obtained by ball-milling during different times.

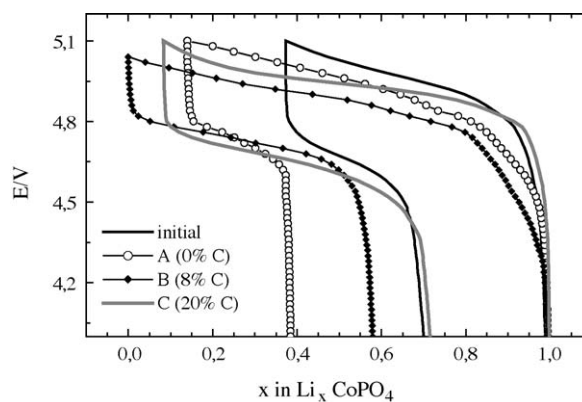


Fig. 8. Comparison of the first charge–discharge cycle of Li cells using composites $\text{LiCoPO}_4 + \text{C}$ as positive electrode (scan 20 mV h^{-1}). Composites were obtained by mechanical grinding LiCoPO_4 for 0.5 h with different amounts of carbon.

for times greater than 1 h reduces the specific capacity delivered by the electrode.

The electrochemical behavior of the different samples milled for 0.5 h are compared to the initial one in Fig. 8. In all cases milled materials display a higher capacity than the starting material. The highest specific capacity is obtained when LiCoPO_4 is milled with carbon owing to a better interface between carbon and LiCoPO_4 and to the reduction of the active material particle sizes. The effect of MG is also reflected in the cells polarization, i.e. voltage differences between discharge and charge curves. It can be seen in Fig. 8 that polarization of the cells decreases with milling, so that the grinding process seems to cause an increase in the electronic conductivity of the electrode that is more notorious in materials milled with carbon (samples B and C). Therefore, adding the conductive carbon during the grinding processing clearly favors the electronic conductivity of the electrode. This voltage shift of few millivolts is very beneficial for lithium batteries operating near the limit of the electrolyte decomposition. Interestingly, the sample milled with 8% carbon displays a lower polarization than that milled with 20% C, suggesting that there is no a linear correlation between the amount of carbon added in the grinding media and the electronic conductivity of the electrode.

Regarding the long term cycling behavior of Li/LiCoPO_4 previous authors reported only the 2 [2], 3 [16] and up to 10 first cycles [19] of a Li/LiCoPO_4 cell. In the later study a low-temperature synthesis route produced an improved LiCoPO_4 material with an initial charge capacity of 140 Ah kg^{-1} that fell down to 60 Ah kg^{-1} in the 10th cycle (current density 0.5 mA cm^{-2}). Fig. 9 shows our results obtained from cycling Li cells (C/5 and C/10) using the initial LiCoPO_4 and the $\text{LiCoPO}_4/8\% \text{ C}$ composite ball milled for 0.5 h. At a C/5 rate the capacity fading with cycling in the initial LiCoPO_4 is very pronounced, with a progressive decrease from 80 Ah kg^{-1} in the first cycle down to 10 Ah kg^{-1} in cycle 40th. A better performance is achieved at the slower scan rate of C/10 for the first 20 cycles, followed by an abrupt drop of capacity down to 10 Ah kg^{-1} in a longer term cycling. Independently on the cycling rate both the specific capacity and capacity retention

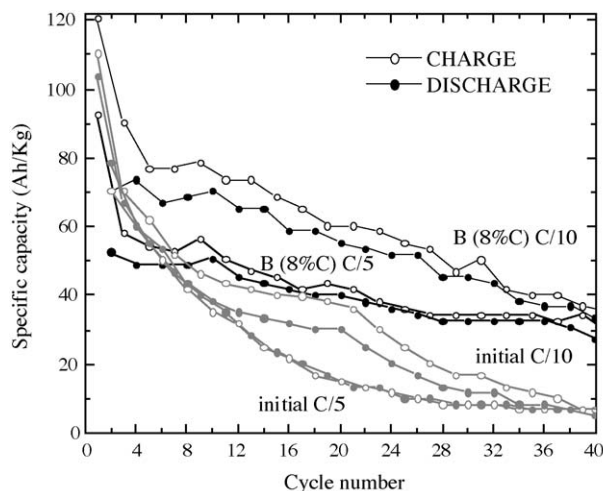


Fig. 9. Capacity of Li/LiCoPO₄ Li cells vs. cycle number for the initial LiCoPO₄ compound, and electrodes of LiCoPO₄/8% C at cycling rates of C/5 and C/10. Cut-off voltages were 5.1 and 3.5 V.

with cycling of the MG material is clearly superior to that of the fresh LiCoPO₄. At a C/5 in the cycle 20 the specific capacity of the milled material (40 Ah kg⁻¹) doubles that of the fresh material (20 Ah kg⁻¹), being this improvement more critical in cycle 40 with specific capacities of 10 Ah kg⁻¹ and 30 Ah kg⁻¹ for the fresh and milled materials, respectively. At C/10 the milled material displays also a higher specific capacity and a better retention with cycling than the fresh LiCoPO₄. It is worth mentioning that in all cases a higher irreversible capacity lost is observed between the charge and discharge of the cell at a given cycle for the slower cycling rate (C/10), in spite of the generally improved electrochemical behavior with respect to the slower rate C/5. This indicates that the electrolyte decomposition is certainly more effective at low than at high rates.

4. Conclusions

The electrode characteristics of olivine–LiCoPO₄ are improved by high energy ball milling for 0.5 h; the smaller particle size leads to a better electrode conductivity, which results in a lower cell polarization, an increasing of the reversible specific capacity and a better capacity retention with cycling. All these features are more pronounced when LiCoPO₄ is mechanically grinded with conductive carbon. The presence of carbon additives in the grinding media enables a good carbon coating that enhances the electrical conductivity of the electrode. The ball milling process for times greater than 1 h deteriorates the response of the electrode, regardless the presence of conductive

carbon in the grinding media. These results demonstrate that ball milling of LiCoPO₄ powders for very short times with conductive carbon is an adequate and convenient route to enhance its application as electrode material.

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