



Short communication

A new form of manganese carbonate for the negative electrode of lithium-ion batteries

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ABSTRACT

A reverse micelles method is used in the synthesis of manganese carbonate. The use of cetyltrimethylammonium bromide surfactant and hexanol cosurfactant allows the preparation of a new monodispersed form of MnCO_3 . Particles with a regular shape and ca. 200 nm edges are observed by electron microscopy. The electrochemical reaction with lithium of the manganese carbonate leads to the formation of the manganese metal and lithium carbonate as the main side product, which yields higher capacity than graphite and good capacity retention. Submicron MnCO_3 could replace other more toxic and expensive anodes used in recent commercial Li-ion products.

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1. Introduction

Recently, a great variety of new compounds never imagined to be active electrode materials in lithium batteries have been proven to display interesting reversible reactions with lithium. Particularly, conversion electrodes involving transition metal oxides [1,2], and more recently transition metal fluorides [3,4], show a reduction of the metal ions to the metallic state together with the formation of lithium oxide or lithium fluoride, respectively. Recently, we were able to extend this process to submicrometric particles of manganese carbonate [5], iron and cobalt oxalate [6,7]. This study revealed that these compounds can be used directly as a conversion electrode vs. lithium. The discharge of lithium test cells takes place by a different conversion reaction that observed for the oxide produced during the thermal decomposition of the carbonate (MnO) or oxalate (FeO , CoO).

The use of highly dispersed materials has also emerged in the field of energy storage, particularly in advanced lithium-ion batteries, by improving their capacity, density of energy, power density and cycle life, simultaneously to a diminution of the production costs. In this work, we have introduced changes in the reverse micelles route to obtain finely divided MnCO_3 . The structural and electrochemical characteristics of the resulting product as active electrode material in lithium test cells are discussed with a view of its possible application in the anode of future Li-ion batteries.

2. Experimental

The synthesis of MnCO_3 was carried out by a reverse micelles procedure from water-in-oil microemulsions. First, two microemulsions (I and II) were obtained as follows. Microemulsion I contained cetyltrimethylammonium bromide (CTAB) as the surfactant, hexanol as the cosurfactant, isooctane as the hydrocarbon phase and 0.3 M manganese(II) nitrate solution as the aqueous phase. Microemulsion II has the same constituents as above except for having 0.3 M sodium hydrogen carbonate instead of iron sulfate as the aqueous phase. The weight fractions of the various constituents in these microemulsions are as follows: 16.76% of CTAB, 13.9% of hexanol, 59.29% of isooctane, and 10.05% of the aqueous phase. In a second step, both microemulsions were slowly mixed and stirred overnight on a magnetic stirrer. The resulting precipitate was separated from the apolar solvent and surfactant by centrifugation followed by rinsing with a 1:1 mixture of methanol and chloroform. Manganese carbonate obtained was subjected to a careful heating at 250 °C under vacuum.

X-ray diffraction (XRD) patterns were recorded on a Siemens D5000, using $\text{CuK}\alpha$ radiation and a graphite monochromator. The TEM images were obtained with a JEOL 2000 instrument working at 200 kV.

The cathode pellets were prepared as follows: a few milliliters of N-methyl-pyrrolidone were added to a mixture of the active material (60% in weight proportion), polyvinylidene fluoride (PVDF 10%) and carbon black (CB 30%) and then stirred until an homogeneous slurry was obtained. The slurry was then cast onto copper foil and heated to dryness at 120 °C. The Swagelok cells were assembled in an Ar-filled glove box (H_2O , $\text{O}_2 < 1$ ppm), using Li metal foil as the anode and a 1 M solution of LiPF_6 in diethyl

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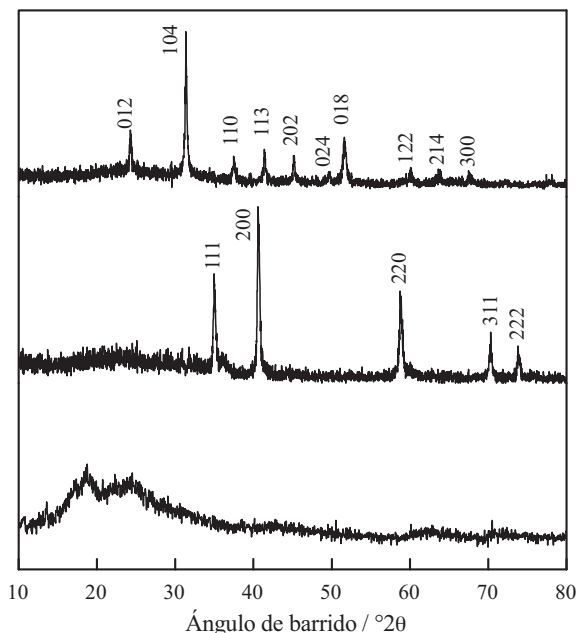


Fig. 1. XRD patterns of MnCO_3 sample. Top, at 250°C (Miller indices for the $R\bar{3}c$ calcite-type structure); medium, at 400°C (Miller indices for the $Fm\bar{3}m$ NaCl-type structure of MnO); and bottom, at 250°C totally discharged in lithium cell.

carbonate–ethylene carbonate (DEC:EC 1:1) as the electrolyte, supported by porous glass–paper Whatman disks. Galvanostatic and potentiostatic charge–discharge cycles were obtained by using a multichannel MacPile and Arbin systems at different rates.

3. Results and discussion

XRD patterns of manganese carbonate prepared by the reverse micelles method described in this work are shown in Fig. 1. Manganese carbonate shows a calcite-type rhombohedral structure. It is well known that the thermal decomposition of first row transition metal carbonates with a calcite structure yield oxide products in which the oxidation state of the transition metal depends markedly on the atmosphere [8].

The thermal behaviour in air of the manganese carbonate mineral form rhodochrosite is characterized by a double endothermic peak at about $560\text{--}660^\circ\text{C}$ followed by an exotherm at 670°C . The endothermic effect is attributed to the decomposition of the car-

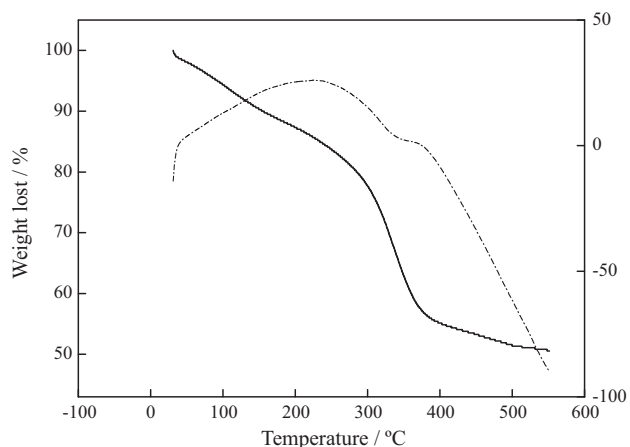


Fig. 2. TG–DTA curves in argon of MnCO_3 .

bonate and the exotherm to the oxidation of MnO to Mn_3O_4 [9]:



However, the mechanism of decomposition is rather complex in synthetic manganese carbonate. Pure carbonate starts to decompose at about 375°C [10].

To minimize the oxidation state of manganese, the carbonate product obtained from the micellar synthesis was studied by TGA–DTA under an argon atmosphere (Fig. 2). The traces show that the thermal decomposition was not completed until ca. 400°C . The calcite structure of manganese carbonate was retained up to 300°C .

The micrographs (Fig. 3) show well-crystallized particles with uniform size and pseudo-square shape habit. Electron diffraction and HREM images confirmed the calcite structure of the manganese submicron particles. Particles were defined by smooth edges on ca. 200 nm average size.

Fig. 4 shows electrochemical results from cells containing MnCO_3 submicron particles as active electrode material. The voltage profile reveals a sharp voltage drop and an extended plateau at 0.5 V. The plateau of the first discharge recorded at different discharge rates always extends to more than 1600 mAh g^{-1} . As expected for conversion electrodes the initial irreversible capacity is larger than in further cycles. In transition metal oxides, the redox processes for the first discharge are different as they involve an in situ nanodispersion together with the metal reduction process [1,2,11,12]. After this huge irreversible capacity, manganese

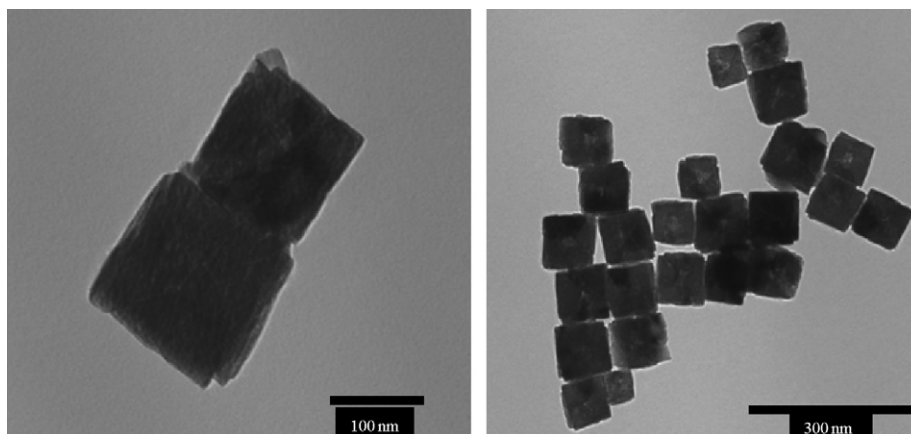


Fig. 3. TEM images for the MnCO_3 submicrometric particles.

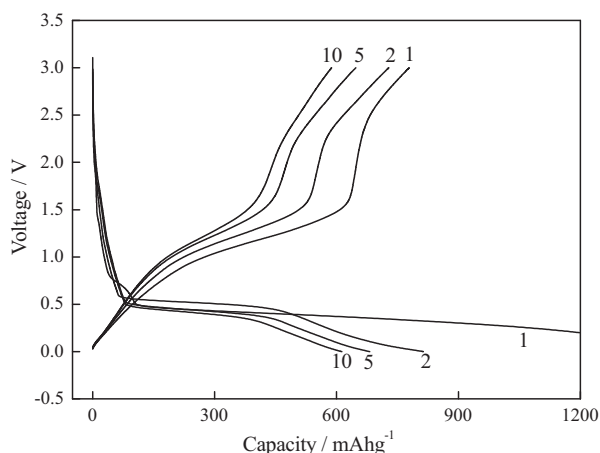


Fig. 4. Charge–discharge curves of electrochemical cells with lithium anode using MnCO_3 as active cathode material.

carbonate, presents reversible capacities the 2nd to 25th cycles between 750 and 450 mAh g^{-1} .

The initial irreversible capacity is large as commonly found in conversion electrodes, and the Faradaic nature of this process is discussed below. The discharge process leads to an X-ray amorphous product after the first discharge (see Fig. 1), the crystallinity was not recovered during additional charge–discharge cycles. Analogous to previous conversion electrode materials, the first step could be associated with the formation of manganese metal, according to



The reaction proposed in this study is based on previous experience in other oxysalt conversion electrodes such as iron [6] and cobalt [7] oxalate. In those systems ^{57}Fe and XAS spectroscopies unequivocally evidenced metal reduction at 0V and reoxidation upon charge.

Although the nanodispersed nature of the reaction products does not allow the identification of the crystalline phases of Mn metal or MnCO_3 , the electrode discharged to 0V was annealed at 300 °C under vacuum for 7 h. The resulting XRD pattern showed broadened lines ascribable to the cubic Mn phase. Particularly, the (222) peak which does not overlap with the support signals was clearly visible. Further studies of spectroscopic and magnetic properties are now in progress.

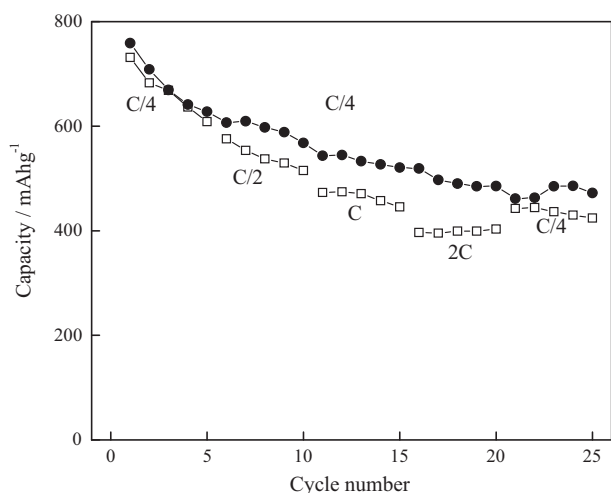


Fig. 5. Capacity vs. cycle number of MnCO_3 at same rate (C/4) and at different rates (C/4, C/2, C, 2C and C/4).

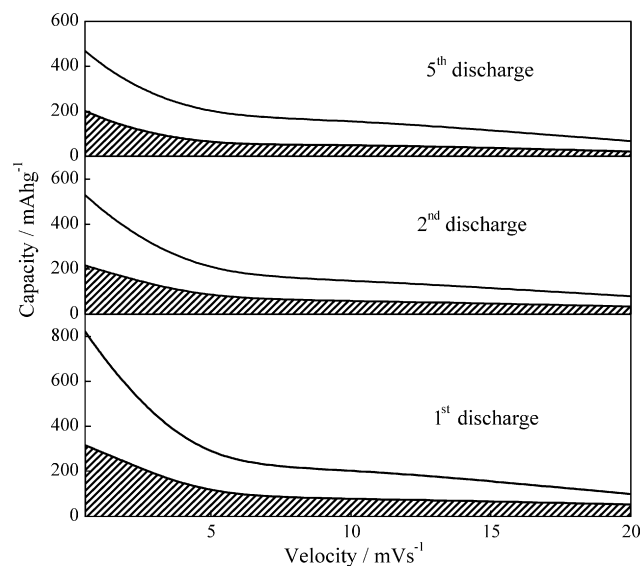


Fig. 6. Capacity vs. sweep rate in step-potential electrochemical spectra of manganese carbonate in the 0.01–3.0V potential window for discharges 1, 2, and 5. Filled region, Faradaic contribution in total capacity; non-filled region, capacitive contribution.

The reactions of the carbonate with the electrolyte are the principal reason of the large irreversible capacity during the first discharge until Mn nanoparticles are protected by a coating layer of lithium carbonate. It is normal that SEI layer of the negative electrodes of lithium-ion batteries contains lithium carbonate and alkyl carbonates, in which it is produced by the irreversible reactions with the electrolyte characteristic of the passivation phenomena [13]. However, the high reactivity of the Mn nanoparticles obtained by the reduction of manganese carbonate allows the recombination process during cell charge of successive cycles.

The cycling experiments in Fig. 5 show the reversible capacity of manganese carbonate for 25 cycles at constant C/4 rate, as compared with varying rates (C/4, C/2, C, 2C and C/4 again). Even cycling at the higher 2C rate, manganese carbonate maintains capacities of ca. 400 mAh g^{-1} . When the rate is decreased to C/4 from 2C, capacity is recovered, reaching similar values than in constant C/4 rate.

The theoretical capacity values calculated for reaction (2) is 466 mAh g^{-1} . In previous studies, conversion electrodes exhibit an extra irreversible capacity that could be ascribed to both the for-

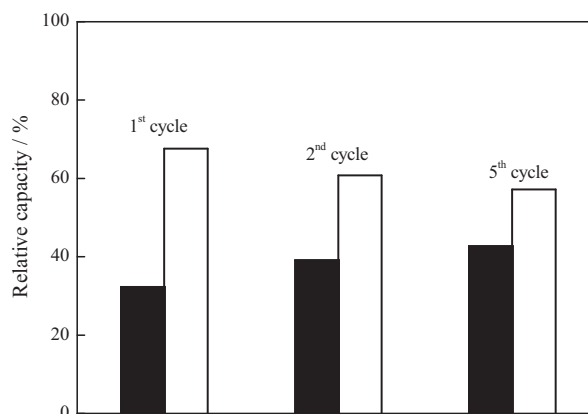


Fig. 7. Relative capacity in first, second and fifth cycles of manganese carbonate electrodes at 0.5 mVs^{-1} . Black bars (Faradaic capacity) and white bars (non-Faradaic capacity).

mation of a SEI and extended electrolyte degradation. For MnCO_3 , reversible capacity is also higher than theoretical capacity obtained in reaction (2). We have carried out a study of the possible contribution of Faradaic and non-Faradaic (capacitance) to the global observed values in order to understand the origin of the extra capacity [14].

The results are shown in Fig. 6. It is clear that the first discharge is mostly irreversible and overpasses the theoretical capacity. The contribution of irreversible reactions with the electrolyte is demonstrated. In the first discharge, the Faradaic capacity is close to the theoretical capacity of the proposed conversion reaction. On further cycles, the Faradaic capacity decreases slower than non-Faradaic capacity. This fact means that extra capacity mainly comes from non-Faradaic origin. In Fig. 7, it is shown the relative contribution of Faradaic and non-Faradaic capacity with increasing cycles at a defined rate (0.5 mV s^{-1}). Thus, it is easily observable how the Faradaic capacity increases its relative contribution as cycling progresses. Capacitive phenomena show smaller relative contribution on a larger number of cycles, being responsible for the decrease in total capacity in the first cycles.

4. Conclusions

The reverse micelles synthesis induces the formation of submicrometric particles of manganese carbonate with square-shaped habit. Electrochemical characterizations show good values of capacity even at high rates. Capacity is retained above 372 mAh g^{-1}

even at 2C. The new form of MnCO_3 is a promising material to be used as alternative anode in lithium-ion batteries.

Acknowledgments

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