

On the use of the reverse micelles synthesis of nanomaterials for lithium-ion batteries

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Abstract The reverse micelles procedure is a convenient route for the preparation of nanomaterials. Chemical reactions in aqueous media are carried out within a restricted volume, limited by the array of surfactant molecules. The versatility of this technique allows its use in the preparation of different electrode materials for lithium-ion batteries. The thermolysis of the reagents in aqueous solution in the micellar volume by contact with hot kerosene allows the preparation of LiCoO_2 , LiMn_2O_4 , and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ fine powders with good electrochemical behavior. The conversion electrode material Co_3O_4 was prepared with controlled particle size and microstructure by a precipitation reaction in the micellar volume. The electrochemical response found in lithium cells was excellent after optimizing the annealing procedure. Cobalt and iron oxalate nanoribbons and submicrometric rhombic particles of manganese carbonate have been prepared by the reverse micelles procedure and partially behave as conversion oxide electrodes. The electrochemical reaction with lithium of these new oxysalt materials takes place by a different conversion reaction than the corresponding oxide, and a surface capacitive contribution has also been detected.

Keywords Lithium batteries · Reverse micelles · Synthesis of nanoparticles · Transition metal oxides · Transition metal oxysalts

Introduction

In recent years, nanoscience has irrupted strongly in the battery materials field. Not only the performance of previously known materials was improved significantly by nanodisperison and nanostructuring, but also new materials and electrochemical reactions have emerged. A typical example is the reversible conversion reactions in which oxides can participate with the use of more than one electron per formula [1].

Among the numerous physical and chemical synthetic routes for nanomaterials, the use of swollen micelles is a straightforward method based on the restriction of the reaction volume to small solvent droplets stabilized by different arrays of surfactant and co-surfactant molecules [2]. When using the reagents in aqueous solutions, reverse micelles should be used in which water is constricted within the micellar volume surrounded by an oil medium. The solid products have controlled size and shape and remain well dispersed due to their separation from other particles during the synthesis by the surfactant molecules. Three different processes can be used to obtain nanoparticles by the reverse micelles methods: (1) mixing of different emulsions containing the necessary reagents in aqueous solution, which results in the coalescence of pairs of droplets and the formation of the solids in the resulting volume, (2) diffusion of one of the reagents through the oil phase and the surfactant molecular layer, and (3) activation of the reaction (e.g., thermolysis) within individual droplets [2].

In this work, different examples of application of the reverse micelles method to obtain cathode—layered LiCoO_2 and spinel LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ —as well as previously reported anodes—conversion Co_3O_4 [3] and transition metal oxysalts such as MnCO_3 [4], FeC_2O_4 [5], and CoC_2O_4 [6]—electroactive materials are compared.

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Cathode materials

The preparation of LiCoO_2 started with the formation of water-in-oil emulsions using 1 M aqueous LiNO_3 and $\text{Co}(\text{NO}_3)_2$ solutions in cyclohexane oil. The water/oil volumetric ratio was 1:10. The reverse microemulsion was stabilized using TRITON X-100 surfactant and 1-hexanol co-surfactant in volumetric oil/surfactant/co-surfactant ratio was 67:20:13. Attempts to prepare LiCoO_2 without the use of a co-surfactant were unsuccessful. Then, the reverse micelles were added to hot kerosene (180°C). The resulting poorly crystallized solid product was then separated from the solvents and annealed in air at different temperatures from 480 to 800°C . The product annealed at 800°C consisted of submicrometric particles with the $\text{O}_3\text{-LiCoO}_2$ structure and negligible amounts of impurities (Fig. 1). Moreover, ^7Li MAS NMR revealed mostly a single signal around 0 ppm resulting from ionic lithium in the interlayer space (Fig. 2). The micellar sample shows traces of 4-, 6-, and -6-ppm signals, commonly ascribed to overstoichiometry [7]. In contrast, these signals were significantly more intense for commercial LiCoO_2 .

The solid was cycled vs. lithium in two voltage windows, 3.0–4.2 and 3.0–4.5 V, providing 145 and 195 mAh/g in the first cycle and 135 and 140 mA/g in the 50th cycle, respectively (Fig. 3). These results show how the capacity values can reach values closer to the theoretical capacity of this solid when prepared by the reverse micelles method.

In the synthesis of LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, Mn (II), Ni(II), and Li(I) acetates were used in the starting aqueous solutions, giving 1 M solutions. The oil phase was kerosene and the surfactant SPAN 80 (sorbitan monooleate). The volumetric water/oil ratio was 1:5, and the surfactant was added in a 5% volume concentration. In contrast with the LiCoO_2 synthesis, no co-surfactant was needed in this case to obtain the desired mixed oxide. The

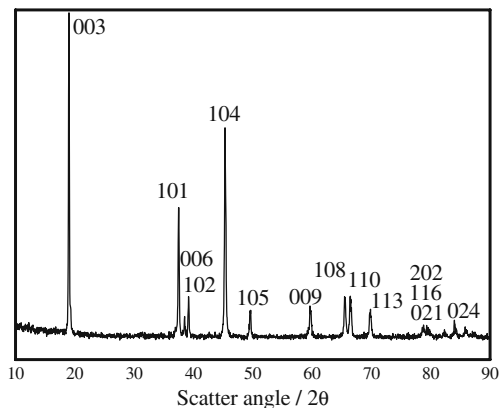


Fig. 1 XRD pattern of LiCoO_2 prepared at 800°C

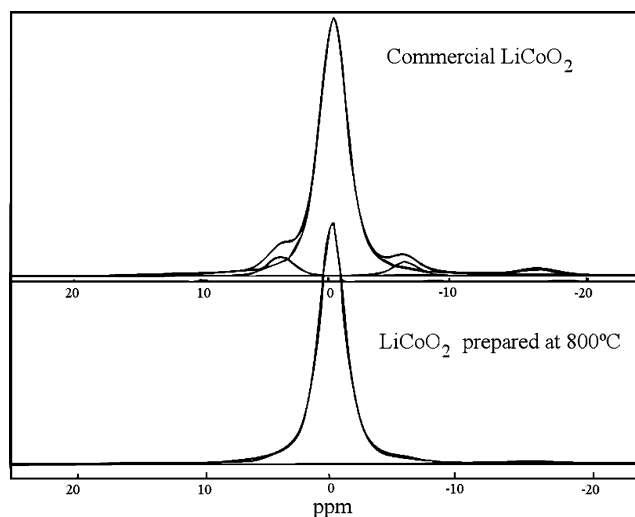


Fig. 2 ^7Li MAS NMR spectra of LiCoO_2 prepared from micellar precursors and commercial product

thermolysis of the micellar solutions was induced by addition to hot kerosene. The solids annealed between 600 and 800°C . Well-crystallized nanoparticles (approx. 200-nm diameter) of high-purity spinel structure solids were obtained at 800°C by this simple procedure (Figs. 4 and 5). For LiMn_2O_4 , traces of impurity are detectable.

The electrochemical results differ from LiMn_2O_4 to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The 4-V material could cycle with higher initial capacity on increasing preparation temperature, but with similar capacity retention irrespective of the annealing temperature. On the contrary, the high-voltage spinel showed similar initial capacity, but a sharp decrease on cycling for temperatures below 800°C (Fig. 6).

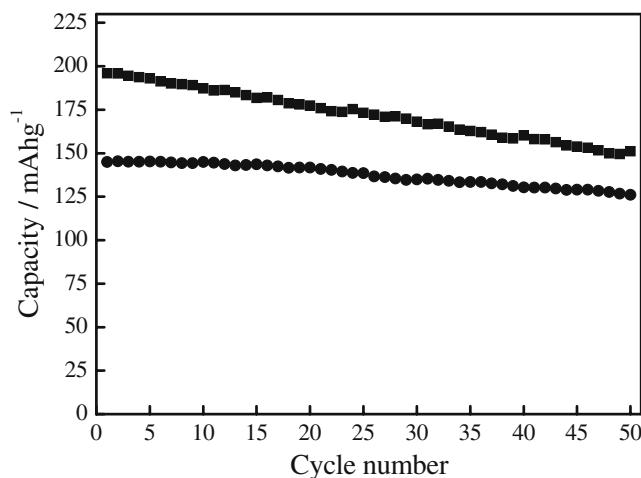
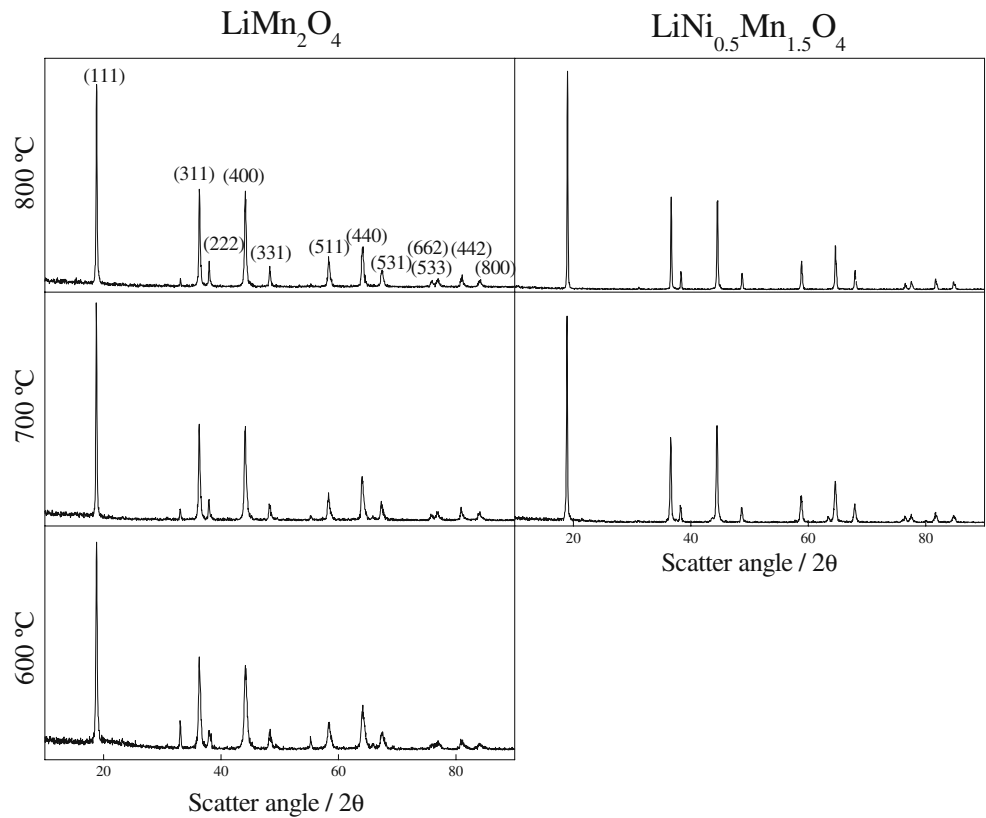


Fig. 3 Discharge capacities of Li/LiCoO_2 test cells galvanostatically cycled at $C/5$ in two voltage windows. Squares 3.0–4.5 V, circles 3.0–4.2 V

Fig. 4 XRD patterns of LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared at different temperatures



Anode materials

Concerning anode materials, the most successful method was the mixing of emulsions containing different reagents in separate aqueous solutions. In order to obtain Co_3O_4 , cobalt chloride and sodium hydroxide solutions provided two different aqueous phases within the reverse micelles. The oil phase was alternatively hexane or octadecene, and SPAN 80 was used as the surfactant [3]. By mixing both microemulsions, the precipitation of cobalt hydroxide

nanoparticles took place. After annealing, the resulting solid occurs as round aggregates of submicrometric particles with increasing size on increasing annealing temperatures from 600 to 800 °C. The particles form complex aggregates that were found particularly useful to achieve a good contact of the complete mass of the

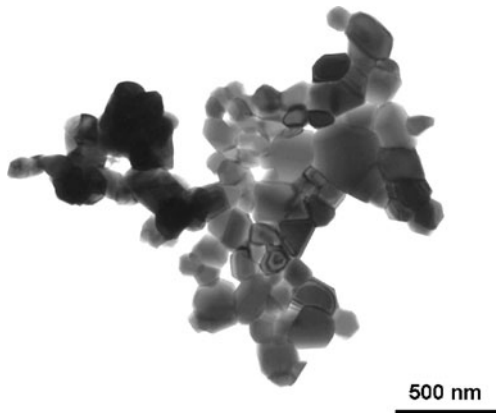


Fig. 5 Transmission electron micrograph of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared from reverse micelles and annealed at 800 °C

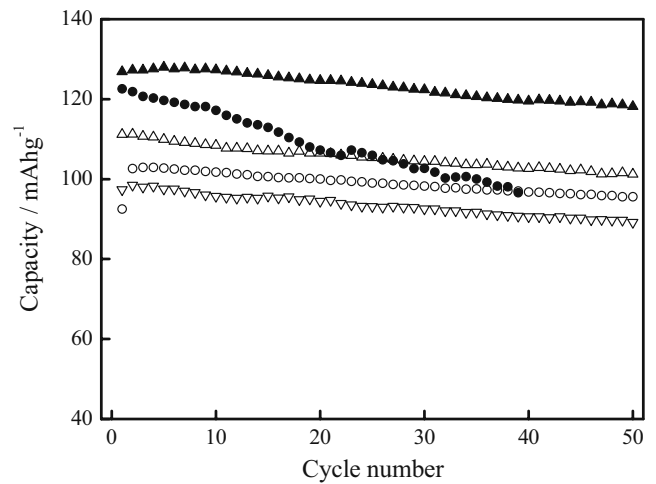
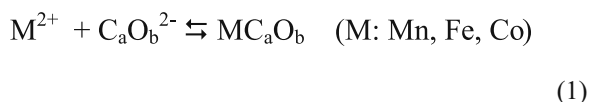


Fig. 6 Cycling behavior of LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ nanopowders prepared by the reverse micelles procedure and annealed at various temperatures. *Hollow symbols* LiMn_2O_4 , *full symbols* $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, *closed and open triangles* 800 °C, *open and closed circles* 700 °C, *inverted triangle* 600 °C

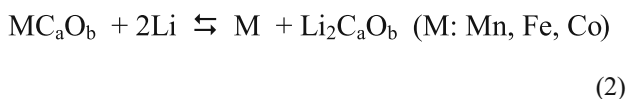
electrode material with the electrolyte solution in organic solvents used in the lithium test cells. Irrespective of the oil phase, reversible capacities higher than 800 mAh/g could be obtained during 20 cycles for the solid annealed at the higher temperature. Lower capacities (approx. 400 mAh/g) but better capacity retention were observed by annealing at 600 °C [3].

Finally, the use of the reverse micelles procedure has recently allowed the utilization for the first time of different first-row transition metal oxysalts as active electrode material in lithium test cells. MnCO_3 [4], FeC_2O_4 [5], and CoC_2O_4 [6] have already been reported. The three compounds can be prepared as nanoparticles by mixing reverse micelles that contain the divalent metal ions in solution and soluble salts of the anions. Special care was taken in the preparation of Fe(II) oxalate to avoid oxidation by using an Ar atmosphere. Thus, the following general precipitation reaction takes place:



The differences are: MnCO_3 is formed as prismatic submicrometric particles with a calcite structure, while the oxalates are obtained as di-hydrates $\text{MC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ in the form of nanoribbons and an orthorhombic structure that differs from the monoclinic phase. The precipitation reaction requires a careful control over the atmosphere to avoid Fe^{2+} oxidation.

The electrochemical behavior of the dehydrated solids is characterized by high values of both reversible and irreversible capacities (Table 1) and an improved behavior as compared with the oxides that can be produced by the thermal decomposition of the oxysalts. The observed capacities are particularly prominent for the oxalates in which the theoretical capacity for a pure conversion reaction should lead to values closer to that of graphite (372 mAh/g):



Moreover, ^{57}Fe Mössbauer spectroscopy revealed that Fe (II) is never recovered after the first discharge, while XAS

Table 1 Theoretical capacities and observed values (mAh/g)

Electrode material	Theoretical conversion capacity	Observed first discharge capacity	Observed reversible capacity
MnCO_3	466	1,500	600
FeC_2O_4	372	1,600	700
CoC_2O_4	365	1,600	900

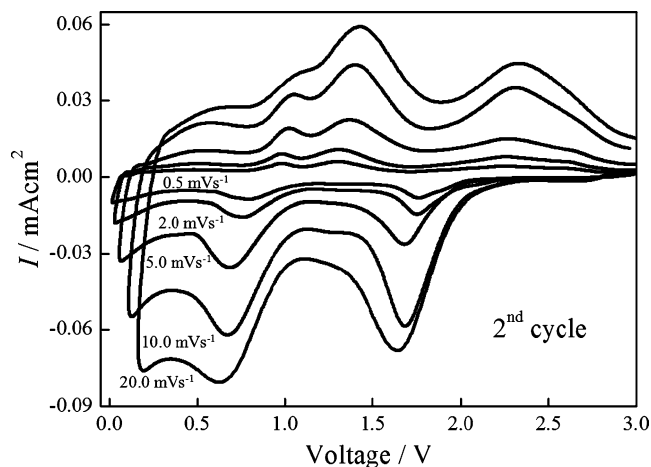


Fig. 7 Step potential electrochemical spectra obtained at different rates in Li/ CoC_2O_4 cells

showed that Co(II) is reduced during cell discharge and reoxidized during charge [6]. FTIR showed that the integrity of the oxalate ions is preserved on cycling [5, 6].

Further complexity in the electrochemical behavior results from a marked hysteresis. The polarization changes linearly with the logarithm of the rate, and this behavior can be ascribed to mass transfer controlled reactions [8, 9]. However, the origin of the extra capacity requires further analysis. By using the method developed by Dunn and co-workers [10], step-potential electrochemical spectra were obtained at different rates, ν (Fig. 7).

A linear relationship was found between the intensity measured at different voltages by using the following equation:

$$i(V)/\nu^{1/2} = k_1\nu^{1/2} + k_2 \quad (3)$$

where constants k_1 and k_2 are related to current contributions from surface capacitive and diffusion-controlled Faradaic effects, respectively (Fig. 8).

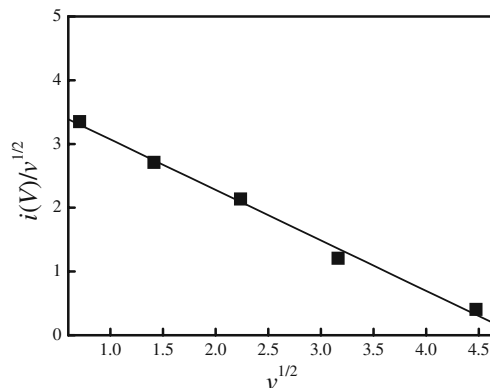


Fig. 8 Plot of $i(V)/\nu^{1/2}$ versus $\nu^{1/2}$ from SPES curves recorded at different rates

The results for the first discharge were indicative of the contribution of initial reactions with the electrolyte, being mostly irreversible and overpassing the theoretical capacity [6]. On successive cycles, the Faradaic capacity gets closer to the theoretical capacity of the proposed conversion reaction, while the extra capacity comes most probably from double-layer capacitive effects.

Conclusions

The versatility of the reverse micelles technique allows its use in the preparation of different electrode materials for lithium-ion batteries. Concerning cathode materials, a suitable technique is the thermal decomposition of the micelles which can be achieved by putting the emulsion in contact with a hot organic solvent such as kerosene. Thus, it was possible to obtain LiCoO_2 using TRITON X-100 surfactant, *n*-hexanol co-surfactants and cyclohexane as the oil phase, and LiMn_2O_4 and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ using SPAN80 surfactant and kerosene oil. On the other hand, for conversion of oxide electrodes, it was possible to prepare Co_3O_4 materials with controlled particle size and microstructure by mixing two emulsions that contained reverse micelles formed in hexane or octadecene oils. The precipitation reaction took place by the coalescence of two different reverse micelles containing aqueous solutions of NaOH and cobalt chloride, respectively. After sintering, single-phase submicrometric particles that interconnect into larger, spherical aggregates can be obtained with spherical shape. The electrochemical response found in lithium cells was excellent after annealing at 600°C , with capacities of up to approx. 800 mAh/g and good capacity retention. Recently, we have studied several examples of oxysalts which partially behave as conversion oxide electrodes.

Among them, iron and cobalt anhydrous oxalates in the form of nanoribbons and submicrometric rhombic particles of manganese carbonate can be prepared by the reverse micelles method by mixing separate emulsions containing the cation and the anion. The electrochemical reaction with lithium of these new oxysalt materials takes place by a different conversion reaction than the corresponding oxide. Thus, ^{57}Fe Mössbauer data unequivocally showed that iron is reduced to the metallic state during cell discharge, while it is partially reoxidized during charge to a +3 oxidation state.

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