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Synthesis, structural, magnetic and electrochemical properties of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ prepared by a sol–gel method using table sugar as chelating agent

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ABSTRACT

Table sugar (sucrose) was used as a new and cheap chelating agent to prepare $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$. X-ray diffraction (XRD) shows that the powder adopts the α-$NaFeO_2$ layered structure with space group $R\bar{3}m$. The high value of c/a above 4.97 indicates a well-ordered rhombohedral lattice. The refined degree of cationic mixing of 2.4% remains fixed upon cycling. The fatigue of the material used as a positive electrode of a Li-cell has been investigated by scanning and transmission electron microscopy (SEM and TEM) as well as the magnetic measurements in the initial, charged and discharged state at low C/10 rate over the 10th first cycles. Small cracks are observed after cycling, despite the low C-rate and the voltage range limited to 3.0–4.2 V in which only the Ni is electrochemically active. This fatigue, however, has no sizeable impact on the capacity: the initial capacity ≈150 mAh g^{-1} was retained at the 10th cycle (*ca.* 97%).

1. Introduction

The desire to develop a sustainable transportation system, the necessity to lower our dependence on fossil fuel, and the demand for a clean and secure energy supply in the near future are pushing the development of low- or zero-emission electric and hybrid electric cars powered by a new generation of electric energy storage (*e.g.* batteries and supercapacitors) and conversion (*e.g.* fuel cells) systems. In the sector of portable electronics such as hand-held communication devices, computers, and cordless tools, batteries often function as the main power sources and thus greatly influence the performance and reliability of these devices [1,2]. Among all the types of batteries, lithium-ion batteries have attracted most attention, because the theoretical energy density (both gravimetric and volumetric) of established electrode materials is the highest among all the mobile energy storage systems, with very good cycling life and safe operation [3,4].

Lithium cobalt oxide ($LiCoO_2$), initially introduced in 1980 [5], has been one of the most widely used positive electrode material in commercial lithium-ion batteries due to its high reversible capacity (130–150 mAh g^{-1}), its high working voltage, reasonable cycle-life (300–500 cycles) and its easy preparation. However, its high cost, toxicity, and the thermal instability of Li_xCoO_2 phases limit its further use in newly developed multifunctional portable devices and electric vehicle systems. Thus, extensive research has been carried out to explore alternative positive electrode materials belonging to the same family of lamellar compounds [6,7].

Stoichiometric $LiNiO_2$ is difficult to synthesize. During cycling, lithium occupies nickel sites (antisite defect), which results in structural instability and capacity deterioration [8]. Partial substitution of Ni for Co reduces the concentration of antisite defects [9], while partial substitution of Ni by Mn stabilizes the lamellar structure [10]. $LiNi_{1-x-y}Co_xMn_yO_2$, used as positive electrodes in lithium-ion batteries can be synthesized by various methods. However, their structure, electrochemical performance and morphology depend on the synthesis route [11–15]. Also, the $LiNi_yMn_yCo_{1-2y}O_2$ $(0 \le y \le 0.5)$ compounds show better thermal stability in organic electrolytes [16]. That is why

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$LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, having improved cyclability and thermal stability, lower cost and less toxicity, has been extensively studied as an attractive candidate of next-generation positive electrode material in lithium-ion batteries to replace $LiCoO_2$. However, the severe capacity fading and relatively poor rate capability limit its use in lithium-ion batteries for electric vehicles and hybrid electric vehicles. In $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (NMC), Ni, Co and Mn are in 2+, 3+ and 4+ oxidation states, respectively. Ni is responsible for the cycling capacity in the operating voltage range 3.0–4.2 V as its valence changes from Ni^{2+} to Ni^{4+} [9], except the Ni^{2+} ions that are on the Li-sites, this antisite defect being detrimental to the electrochemical properties [17,18]. Above 4.2 V, the cobalt ions begin to switch to the Co^{4+} valence state [9], but this is detrimental to the thermal stability, since it increases the risk of oxygen release that can generate thermal runaway [19].

Many methods including the solid state synthesis [20], the sol–gel method [21,22], the combustion method [23], the co-precipitation method [24–29], the molten salt method [30], the hydrothermal synthesis [31], thermal polymerization [17], self combustion reaction [32,33] have been used to synthesize NMC. Among these methods, solid-state reaction easily leads to impure phases [15], and the sol–gel method with selected chelating agent has been widely adopted as the preferred technique to produce NMC with good cationic distribution. In addition, this technique makes possible the synthesis of nanosized particles, which has two advantages: it increases the effective surface area of the powder with the electrolyte and it increases the lithium intercalation efficiency by reducing the electron path inside the material that has a poor electronic conductivity [34]. Singh et al. [22] investigated the role of citric acid content on synthesis of NMC and its effect on electrochemical performance. Deng et al. [25] prepared NMC nano-structured powders by hydroxide co-precipitation using ammonia as chelating agent that plays an important role in preventing phase separation and in improving homogeneity of the products. Samarasingh et al. [35] have investigated the feasibility of the Pechini method for the preparation of NMC with characteristics appropriate for Li-ion battery positive electrodes. However, the preparation of the $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ solid solution with excellent electrochemical performance is still challenging [36].

In the present work, table sugar was used as chelating agent to prepare nano-sized $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ by a sol–gel route, providing us with a simple and cost effective synthesis process. Now, the NMC material is being adopted in commercial batteries we find the use of inexpensive table sugar is an important improvement to reduce the production cost. The effect of specific preparation conditions on the structure, morphology, magnetic and electrochemical properties of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ are also reported.

2. Experimental

$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ was synthesized by a wet-chemical method using table sugar as polymeric agent. The use of sucrose with CH_2OH groups has the advantage of lowering the polymerization temperature (<350 °C). Stoichiometric amounts of lithium acetate, nickel acetate, manganese acetate and cobalt acetate were dissolved in distilled water and mixed with an aqueous solution of 1.5 mol L^{-1} table sugar to give the ratio metal/sugar = 1.5. The pH-value was adjusted to 7–8 by addition of ammonia solution. The resulting solution was stirred at 80 °C for 6 h to obtain a clear viscous gel. The gel was dried in an oven at 120 °C for 12 h. The dried powder was ground and precalcined at 400 °C for 4 h in air to eliminate the organic substances and cooled to room temperature by turning off the furnace. A crystalline sample was formed by heating the precursor at 900 °C for 12 h in air.

Apparatus used for characterization of NMC samples have been described elsewhere [37]. Briefly, X-ray diffraction experiments were carried out with a STOE STADIP diffractometer (Mo-$K_{\alpha 1}$-radiation, $\lambda = 0.70926$ Å) in Debye–Scherrer mode. We used glass capillaries, which were filled in argon atmosphere. To investigate the powder after electrochemistry the said Swagelok cells were disassembled and the electrodes were washed in dimethylcarbonate (DMC) to remove electrolyte residues. After drying, the remaining powder was filled in glass capillaries in argon atmosphere.

To get information about the morphology and the particle size of the electrode composite electron microscopy investigations were performed. A Gemini 1530 (Zeiss) SEM (Scanning Electron Microscope) with primary energy of 10 keV, working distance of 5 mm and intense – SE – detector was used. For SEM the powder was placed on a carbon pad. Images with higher magnification were taken with a CM20 (FEI/Philips) TEM (Transmission Electron Microscope) in bright field at 200 kV acceleration voltage. For TEM the powder was dispersed in DMC and one drop of the dispersion was placed on a carbon coated copper grid.

To ensure a high electronic conductivity, 80:10:10 (wt.%) mixture of active material, polyvinylidene difluoride (PVdF) as a binder and super P carbon as a conduction material respectively was grinded in a mortar. About 15 mg of the mixture were pressed with 90 MPa (5 t at ⌀ 13 mm) on aluminum mesh and dried for 24 h in a vacuum oven at 100 °C. Swagelok®-based cells were assembled in an argon-filled glove box with lithium foil as anode, 1 mol L^{-1} $LiPF_6$ in an ethylenecarbonate (EC) and dimethylcarbonate (DMC) mixture in the ratio EC:DMC (1:1) as electrolyte (NOVOLYTE, USA) and a glassfiber sheets (Whatmann®-GF/D 2.7 μm) as separator. Electrochemical experiments were carried out with a multichannel potentiostat-galvanostat (VMP 3, Bio-Logic, France). The cells were galvanostatically charged and discharged at 25 °C in the voltage range 3–4.2 V, for reasons outlined in the introduction. The achievable capacity depends on the C-Rate. A nC rate is defined by the current, which is set to achieve a fully charge or discharge of the electrochemical cell in a C/n hour, assuming that one lithium per mol of $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ could be inserted or de-intercalated. Due to the first faraday law a specific current of 27.8 μA mg^{-1} could be calculated for C/10. This quite low C-rate was used to prevent kinetic limitations during electrochemical cycling.

Magnetic measurements were performed with a Magnetic Property Measurement System (Quantum Design) equipped with SQUID magnetometers. Magnetization *vs.* temperature was measured from 2 to 325 K in zero-field cooled (ZFC) and field cooled (FC) mode. For ZFC the sample was cooled down without applied field and the magnetization was measured during heating (2 K/min) at a field of 200 Oe. For FC the sample was cooled down with an applied field of 200 Oe and the magnetization was recorded during the cooling process. Magnetization *vs.* field at 5 and 50 K was measured by looping the magnetic field, starting from the maximum field of 10 kOe, under static field conditions.

3. Results and discussion

3.1. Structural and microstructural characterization

The XRD pattern of $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ is shown in Fig. 1. All reflections are indexed in agreement with the rhombohedral α-$NaFeO_2$ structure ($R\bar{3}m$ space group) without any impurity. The (0 0 6,1 0 2) and (1 0 8,1 1 0) reflections are clearly separated, which has been recognized as a criterion for the formation of a highly ordered layered structure [38]. The XRD pattern of the as-prepared sample is shown in Fig. 1a together with the calculated profile, based on the rhombohedral structure model derived from $LiCoO_2$ by a randomly mixed occupation of the 3d-transition