Highly Disperse Cathode Materials for Lithium Ion Batteries Prepared by Mechanical Activation

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Abstract

Synthesis of a series of cathode materials for lithium ion batteries by mechanical activation has been investigated. It is shown that the materials are characterized by submicron particle size and the presence of structural disordering. These characteristics positively influence the electrochemical properties of insertion cathodes (*e. g.*, $LiMn_2O_4$ − 3 V, LiV_3O_8 − 3 V, $Li_3Fe_2(PO_4)_3$ − 2.8 V) and cathodes with poor electronic conductivity (*e. g.*, $LiFePO_4$ − 3.4 V). Due to the highly disperse state of the materials, their practical capacity increases as a result of the enhanced utilized volume of particles and the occurrence of insertion/extraction processes of lithium ions in the kinetic regime, which is important for the design of high-speed batteries. The positive effect of structural disordering lies in the higher stability of defect structures to lithium ions insertion and, as a result, to better cyclability.

INTRODUCTION

Lithium and lithium-ion rechargeable batteries offer higher operative voltage and energy density than do other rechargeable battery systems and are successively applied in different portable electronic devices [1]. A wide variety of electrode materials capable of reversibly inserting/extracting lithium ions have been investigated (Fig. 1). $LiCoO_2$, $LiNiO_2$, $LiNi_{1-x}Co_xO_2$, and $LiMn_2O_4$ with working potential of about 4 V and practical capacity ~120 mA h/g are considered to be the most attractive cathode materials of the first generation. Lower potential cathode materials possessing higher specific capacity, such as LiV_3O_8 (>200 mA h/g), have become an area of active interest in view of recent achievements in electronics. Over the last few years, framework structured compounds containing polyanions, such as PO_4^{3-}, SO_4^{2-} and AsO_4^{3-} have been actively investigated.

Among them, $LiFePO_4$ is considered as a candidate for large-scale batteries for electric vehicles [2].

The capacity of lithium batteries is limited mostly by electrode materials. For a long time,
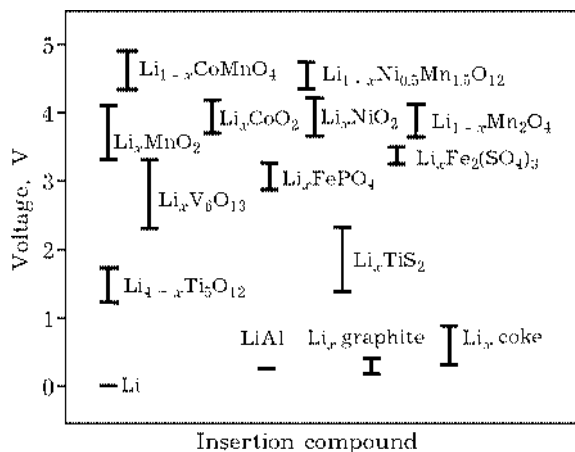

Fig. 1. Electrochemical potentials for some cathode and anode materials *vs.* metallic Li.

only perfect crystalline and micron-sized materials were considered to possess the best properties. However, recently, it has been established that higher dispersity when particles are submicron and even nanosized increases the practical capacity of cathode materials and promotes the occurrence of insertion/extraction process of lithium ions in kinetic regime, which is important for the design of high-speed batteries [3]. Moreover, positive influence of structural disordering of lithium and transition metal oxides on their electrochemical characteristics has been revealed which consists in higher stability of defect structure to insertion of additional lithium ions and, as result, in better cyclability. The presence of structural defects, especially surface defects, in the case of highly disperse electrode materials leads to the absence of sharp structural changes during insertion/extraction of lithium ions and, as a result, to smoother discharge curves.

To prepare highly disperse materials, sol-gel and other solution techniques carried out at moderate temperatures are generally used to prepare phase homogeneous compounds with reproducible composition and controllable morphology and microstructure. To obtain highly disperse cathode materials, the authors have developed a mechanochemical approach [4]. This study reports some results of studies on the properties of a series of cathode materials prepared by mechanical activation (MA) in comparison with similar materials synthesized by the ceramic method.

RESULTS AND DISCUSSION

Lithium manganese spinel $Li_{1 \pm x}Mn_2O_4$

Lithium manganese spinel $LiMn_2O_4$ (space group $Fd\bar{3}m$) is one of the promising cathodes for rechargeable lithium batteries due to its lower cost and less toxicity compared with $LiCoO_2$. $LiMn_2O_4$ cycles in the range 4 and 3 V [5]. Cycling is accompanied by Li intercalation-deintercalation processes: $LiMn_2O_4 - Li^+ \leftrightarrow \lambda\text{-}MnO_2$ and $LiMn_2O_4 + Li^+ \leftrightarrow Li_2Mn_2O_4$, and oxidation-reduction of Mn ions, respectively. This compound is generally employed as a 4 V cathode material since the capacity fades severely around 3 V due to an irreversible structural rearrangement resulting from the Jahn − Teller distortion (when the concentration of Mn^{3+} becomes >50 %) and cathode destruction. It is well known that in the Li − Mn − O system, there is a number of stoichiometric and defect Li − Mn spinel phases (Fig. 2). The composition of the stoichiometric phases is described by the general formula $Li_xMn_{2-x}O_4$ ($0 \leq x \leq 1.33$). In Fig. 2, they are arranged on the line connecting Mn_3O_4 ($x = 0$) and $Li_4Mn_5O_{12}$ ($x = 1.33$). Defect spinels are described by the general formula $Li_2O \cdot yMnO_2$ ($y > 2.5$); they are arranged on the line between $Li_4Mn_5O_{12}$ and $\lambda\text{-}MnO_2$ in Fig. 2. Their structure is characterized by the presence of cation vacancies; all manganese ions are in the oxidation state 4+. It was shown that $Li_2Mn_4O_9$ and $Li_4Mn_5O_{12}$ are characterized by high capacity and cycling stability at 3 V [6]. These
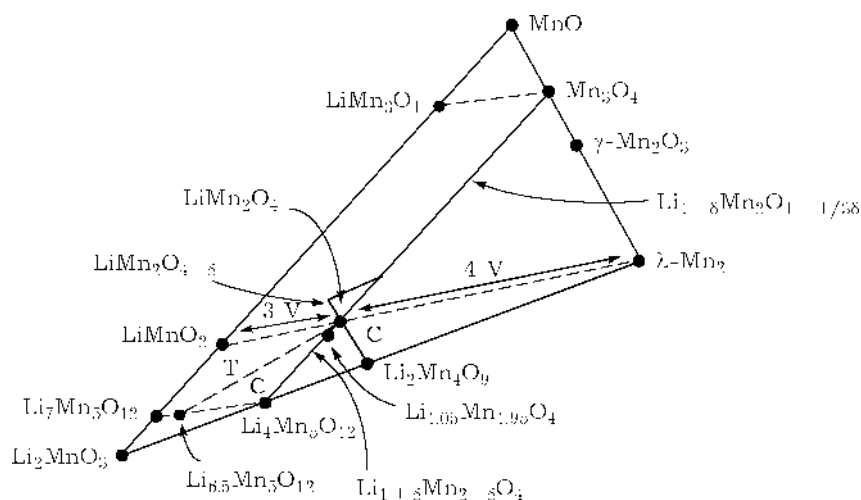

Fig. 2. Section of the Li − Mn − O phase diagram. C − cubic structure, T − tetragonal structure.
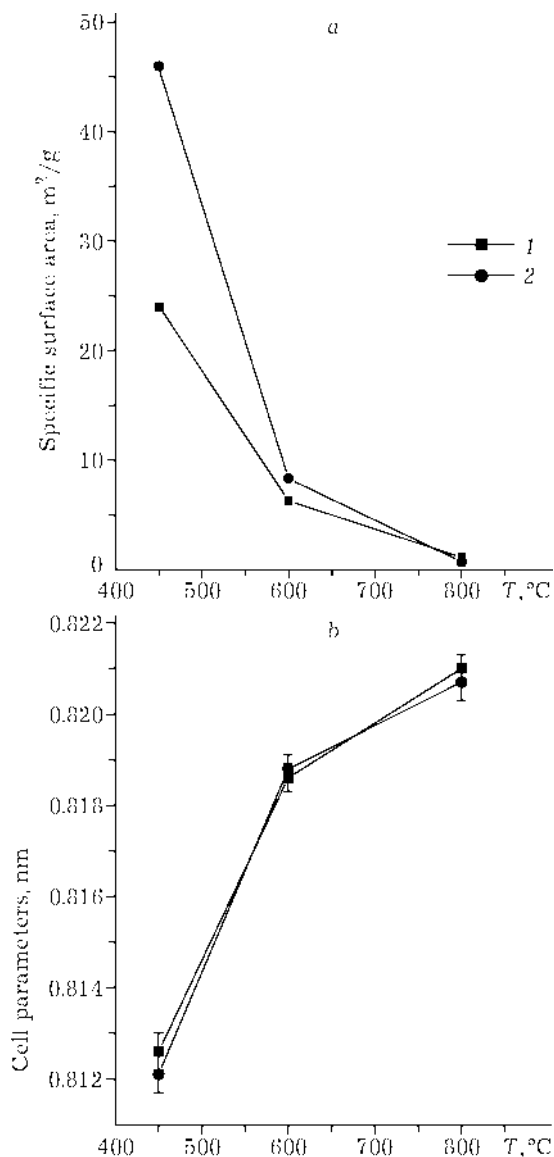
Fig. 3. Specific surface area (*a*) and lattice parameters (*b*) of $LiMn_2O_4$ prepared using MA *vs.* MA time and temperature of subsequent heat treatment. Time of MA, min: 1 (*1*), 10 (*2*).

spinels are prepared at temperatures below 400 °C because of the higher stability of Mn^{4+} ions at moderate temperatures.

In our studies, we investigated the possibility of synthesizing $LiMn_2O_4$ by MA of mixtures of different lithium (LiOH, Li_2CO_3) and manganese (MnO, Mn_2O_3, MnO_2) reagents in an AGO-2 planetary mill. The experimental conditions are described elsewhere [7]. In the case of MnO_2, we observed direct synthesis of low-crystalline lithium manganese oxide with a spinel structure (space group $Fd\bar{3}m$). To increase crystallinity (in mixtures with MnO_2)

and to complete synthesis (in the case of MnO and Mn_2O_3), the products were heated at 450–800 °C. The specific surface area of the samples reached 90 m^2/g and sharply decreased at elevated temperatures (Fig. 3, *a*). According to electron microscopy data, the heated samples were loose agglomerates with an average particle size of about 100–200 nm. The synthesized spinels were characterized by a decreased cell parameter as compared with ceramic samples (<0.824 nm) (see Fig. 3, *b*), evidencing an increased average degree of oxidation of manganese ions (>3.5+) because $R_{Mn^{4+}} < R_{Mn^{3+}}$. According to IR and ^7Li NMR spectroscopy, the samples are characterized by two kinds of disordering: cationic vacancies $(Li_{1-x}\square_x)[(Mn^{4+}Mn^{3+})_{2-y}\square_y]O_4$ (where $\square$ is a vacancy) and cationic mixing $Li_{Td} \leftrightarrow Mn_{Oh}$ [8].

The prepared samples were tested electrochemically in a galvanostatic cell Li/*EC*, DMC + $LiPF_6$/$LiMn_2O_4$, *C* over two ranges: 3.5–4.5 and 2.2–3.5 V at cycling rate *C*/10* (Fig. 4). It was found that the $LiMn_2O_4$ samples prepared by MA and subsequent heat treatment at 600 °C are characterized by higher capacity (~0.75–0.8 Li**) and better cyclability at 3 V compared with ceramic samples due to higher concentration of defects, facilitating adaptability of the material to volume changes induced by insertion of additional Li ions. However, these samples show worse characteristics when cycling at 4 V as a result of low concentration of Mn^{3+} ions.

Lithium vanadium oxide $Li_{1+x}V_3O_8$

Layered-structured $Li_{1+x}V_3O_8$ (space group $P2_1/m$) is attractive as a 3 V cathode material characterized by high capacity (~200 mA h/g), stability in air, and facile preparation. It can reversibly incorporate up to 3.8 Li (*x* = 0.2) due to reduction of V^{5+} to V^{4+} and V^{3+}. The synthetic conditions of $Li_{1+x}V_3O_8$ considerably influence the capacity and cyclability of

*Cycling rate is denoted as *C*/*n*, where *C* is the theoretical capacity, and *n* is charge/discharge time at a given current density.

**Specific capacity is expressed either in mA h/g or in the number of Li ions per formula unit of the cycling compound.
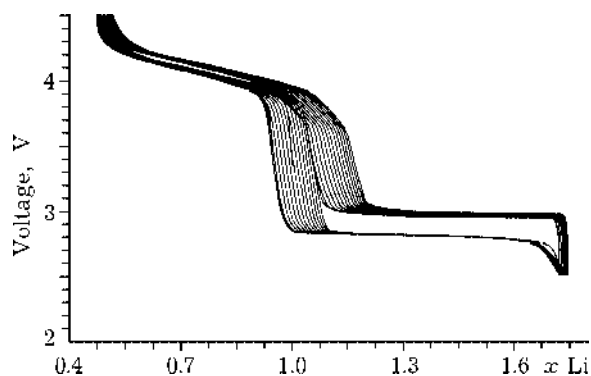
Fig. 4. Galvanostatic discharge curves of $LiMn_2O_4$ prepared using MA ($T = 600\,°C$).

$Li_{1+x}V_3O_8$. The decreased particle size, as well as crystallinity, enhances practical capacity at average and high discharge rates because of decreased diffusion path length [9−11].

We have shown that direct mechanochemical synthesis of $Li_{1+x}V_3O_8$ ($0.07 < x < 0.2$) can be realized in mixtures of LiOH (Li_2CO_3) and V_2O_5 [12]. Before electrochemical testing, the samples were heated at 200−400 °C. The products were characterized by low crystallinity as compared with the samples synthesized by the solid state method and via melting (Fig. 5). Specific surface area of the samples was about 2−4 m^2/g. The samples steadily cycled in the range 3.7−1.2 V; their specific capacity at different cycling rates exceeded the capacity of the samples prepared in the solid state and in melt and comprised
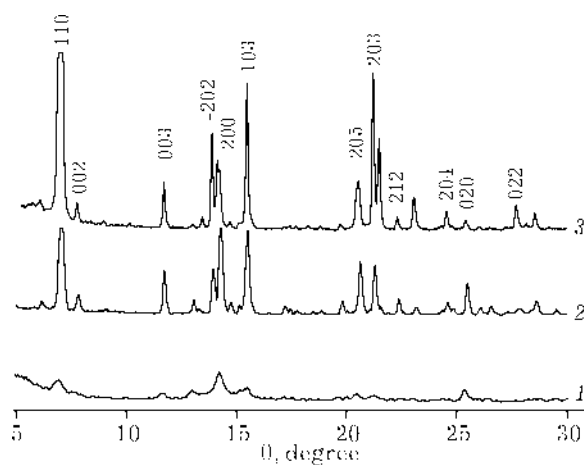
320 mA h/g at a rate of $C/10$ and 250 mA h/g at a rate of $C/5$ (Fig. 6). The discharge curve had smoother form without clear steps characteristic of the high-temperature samples.

Lithium 3d metal phosphates

Over the last few years, interest in framework structured compounds of lithium and transition metal ions with polyanions, such as PO_4^{3-}, SO_4^{2-} and AsO_4^{3-}, has developed enormously. Increased Li intercalation voltage for these compounds as compared with corresponding oxide systems is associated with the strong bond covalency in the X−O polyanion and decreases the potential of the Me^{n+1}/Me^n pair $vs.$ Li/Li^+ as a result of the Me−O−X inductive effect [2].

Orthorhombic $LiFePO_4$ with an ordered olivine structure is the most attractive compound in this class of materials. It is characterized by high discharge voltage (3.4 V) and relatively high theoretical capacity − of about 170 mA h/g. Its electrochemical performance is enhanced at moderately elevated temperatures, and no evidence of troublesome reactions is observed. The main drawback is poor electronic conductivity and, as a consequence, poor rate performance. However, it was shown that disperse materials prepared at relatively low temperatures are characterized by enhanced electro-
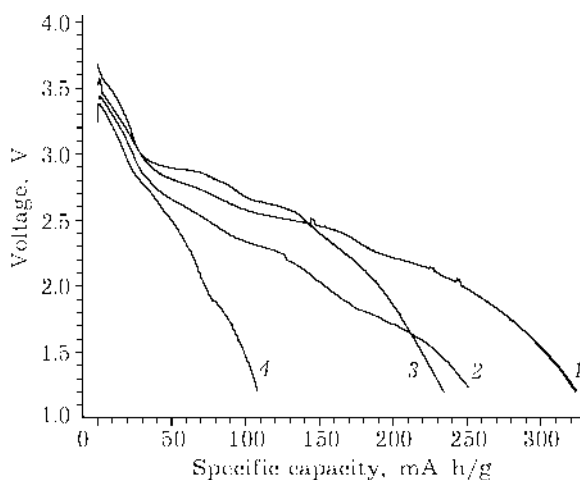

Fig. 5. X-ray patterns for $Li_{1.07}V_3O_8$ prepared using MA (1) and after subsequent heat treatment at 400 °C (2) in comparison with $Li_{1.07}V_3O_8$ prepared by melting at 680 °C (3).

Fig. 6. First discharge curves of $Li_{1.07}V_3O_8$ prepared using MA (1, 3) and by melting (2, 4) at rates of $C/10$ (1, 2) and $C/5$ (3, 4).
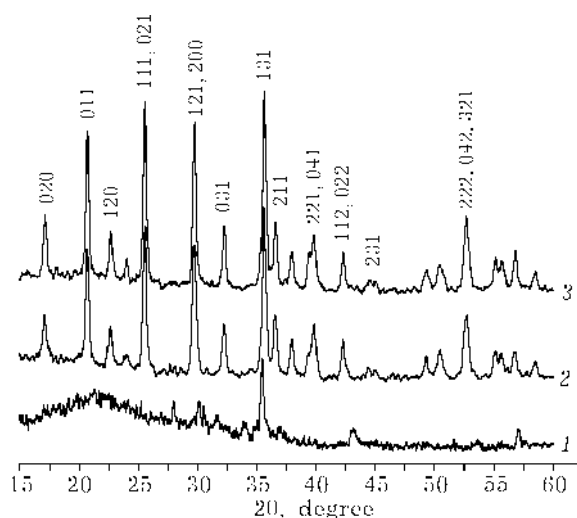
Fig. 7. X-ray patterns of LiFePO$_4$ prepared from nonactivated (1) and activated (2, 3) mixtures and by heat treatment at 400 (1, 2) and 600 °C (3).

Fig. 8. Discharge curves for LiFePO$_4$ prepared using MA: 1, 2 — the first and second discharge curves.

chemical characteristics as compared with high-temperature samples due to the increased volume of LiFePO$_4$ particles utilized [13–15].

We prepared LiFePO$_4$ by preliminary MA of the mixture of FeC$_2$O$_4 \cdot$ H$_2$O, NH$_4$H$_2$PO$_4$, and LiOH or Li$_2$CO$_3$ followed by heat treatment at 400–600 °C in an Ar atmosphere [16]. All the samples were single phase LiFePO$_4$ with an ordered olivine structure (space group Pnmb) and with a specific surface area of 3–6 m^2/g. Note that no noticeable interaction was observed in nonactivated mixtures heated at 400 °C, whereas the samples heated at 600 °C were characterized by phase inhomogeneity (Fig. 7). The capacity of the sample prepared using MA and heat treated at 600 C was about 120 mA h/g in the range 2.6–4.2 V with a very small capacity loss after the first cycle (2–3 %) (Fig. 8).

Two extra Li ions can be theoretically inserted into rhombohedral R–Li$_3$Fe$_2$(PO$_4$)$_3$ to form Li$_5$Fe$_2$(PO$_4$)$_3$ at 2.8 V. Practical capacity and cyclability are determined by the synthesis conditions. It was shown [17] that after grinding in a ball mill, the capacity of Li$_3$Fe$_2$(PO$_4$)$_3$ increased to 1.5–1.6 Li instead of 1.1 Li ions for non-milled sample. Moreover, two plateaus (at 2.8 V and 2.65 V) were observed instead of only one plateau at 2.8 V for untreated sample.

Rhombohedral Li$_3$Fe$_2$(PO$_4$)$_3$ is usually prepared from monoclinic Na$_3$Fe$_2$(PO$_4$)$_3$ by ionic exchange in a melted or concentrated solution of LiNO$_3$. We studied the possibility of an

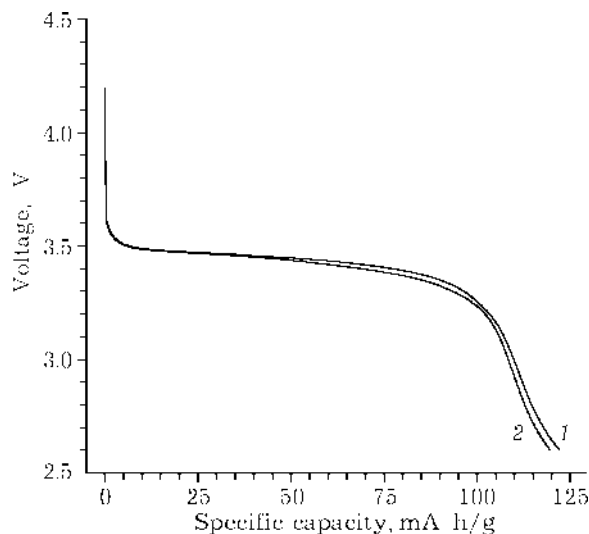exchange reaction in the solid state in the course of MA. It was found that ionic exchange is realized in mixtures of Na$_3$Fe$_2$(PO$_4$)$_3$ with solid LiNO$_3$ and Li$_2$SO$_4$ (Fig. 9), but does not occur in mixtures with LiOH. The products were washed with water to remove NaNO$_3$ or Na$_2$SO$_4$ and dried at 100 °C. Chemical analysis showed that the degree of ionic exchange reached 65 %. Interestingly, preliminary MA of Na$_3$Fe$_2$(PO$_4$)$_3$ hinders its ionic exchange with LiNO$_3$ solution, and no transformation of monoclinic Li$_3$Fe$_2$(PO$_4$)$_3$ into R–Li$_3$Fe$_2$(PO$_4$)$_3$ occurs during MA. Since the lithium salts were carefully dried
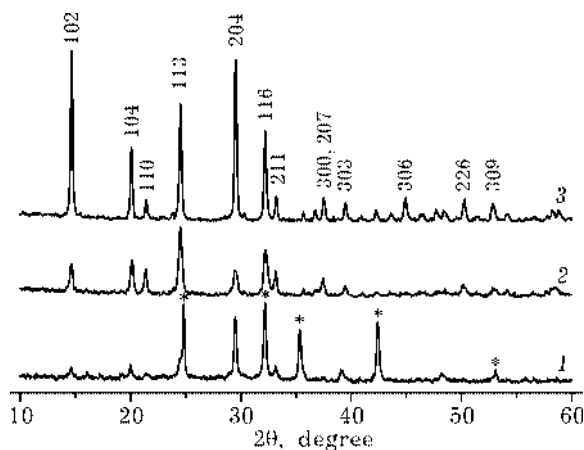

Fig. 9. X-ray patterns for R–Li$_3$Fe$_2$(PO$_4$)$_3$ prepared via solid state mechanochemical ion exchange with LiNO$_3$ (1, 2) and in solution (3): 1 – without washing from LiNO$_3$, 2 – after washing; * LiNO$_3$.

before MA and their melting points were drastically different, the solid state mechanism of exchange reaction is more likely than the mechanisms via solution or melt. Note that these exchange reactions are, as a rule, realized in highly energetic activators only.

CONCLUSION

Thus, based on some examples it has been demonstrated that MA can be successfully used for the synthesis of highly disperse and structurally disordered cathode materials for lithium ion batteries. These parameters positively influence the electrochemical behavior of insertion cathodes, leading to increased practical capacity and structural stability to insertion and extraction processes of Li ions.

Acknowledgement

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