A kinetic study of electrochemical lithium insertion in nanosized rutile $\beta$-MnO$_2$ by impedance spectroscopy

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The kinetics of the electrochemical lithium insertion reaction in nano-sized rutile $\beta$-MnO$_2$ has been investigated using ac impedance spectroscopy. The experimental kinetic data are obtained for a rutile compound synthesized by ball-milling the powder produced from the heat treatment of manganese nitrate salts. The results are discussed as a function of the Li content for $0 < x < 0.6$ and the number of cycles in the 4.1–2 V window. From a comparison with data obtained on the micro-sized oxide, an improved kinetics is found with $D_L$ values for the apparent chemical diffusion coefficient of lithium much higher by one order of magnitude than in micrösized oxide. Impedance behaviour of the ball-milled rutile $\beta$-MnO$_2$ vs cycles demonstrates a new system takes place from the second cycle, characterized by a significant improvement of Li diffusion by a factor 5 and a cathode impedance which decreases by a factor 2, remaining thereafter unchanged during cycling.

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1. Introduction

In the field of cathode materials for secondary lithium batteries, manganese oxides have unique and important advantages over other transition metal oxides due to their low toxicity, good capacity and inexpensive cost. Manganese oxides exist in various polymorphic forms and are made of MnO$_6$ octahedras, these basic units being linked by sharing edges and corners to give rise to different types such as $\alpha$, $\beta$, $\gamma$, and $\lambda$-types. For instance the hollandite form exhibits $(2 \times 2)$ while $\beta$-MnO$_2$ also called pyrolusite exhibits a rutile structure which contains the narrowest $(1 \times 1)$ channels. $\gamma$-MnO$_2$ contains domains of intergrown $\beta$-MnO$_2$ and ramsdellite MnO$_2$ with larger channels $(2 \times 1)$ and $\lambda$-MnO$_2$ is characterized by a three dimensional network of channels. The lowest size of the channels available for Li transport in the $\beta$-MnO$_2$ oxide framework makes this electrode material cannot provide much capacity. Indeed it has been found that the Li uptake inserted chemically or electrochemically into crystallized $\beta$-MnO$_2$ does not exceed 0.3 Li per mole of oxide at room temperature [1,2], and nearly 1 Li at temperatures around 100–C and 150–C [3,4].

Very recently, nanostructured materials have stimulated numerous works reporting the positive effect of the nanosized oxide particles mainly because of their substantial advantages in terms of mass transport [5–10]. Several groups have reported that at room temperature nanometer-sized [11–14] and mesoporous [15,16] $\beta$-MnO$_2$ show a higher electroactivity towards Li insertion than the conventional bulk oxide with a maximum Li uptake in the range 0.66–0.92 per MnO$_2$ unit in the first discharge. $\beta$-MnO$_2$ nanomaterials with different morphologies have been synthesized via a hydrothermal route using Mn(NO$_3$)$_2$ solutions [11], mixtures of KMnO$_4$ and MnCl$_2$ [12] or by hydrothermal persulfate treatments of solid precursors like MnO and Mn$_2$O$_3$ [13] or by simple heating a mixture of Mn(NO$_3$)$_2$ and acetylene black [14]. However, in spite of the afforded improvements, the electrochemical data available on nanosized and mesoporous $\beta$-MnO$_2$ only consist in the discharge–charge profile for one or several cycles and cycling data obtained in various voltage windows such as 4.5–1.5 V, 5–1 V, 4–1.5 V, 4.5–1 V. Even when the stark difference for the behaviour of bulk and nanosized $\beta$-MnO$_2$ is reported as being caused by kinetics, no work has focused on the kinetic of the electrochemical Li insertion reaction in nanosized $\beta$-MnO$_2$ [11–16]. Li diffusion process in the active material is essential for a good understanding of the cathode performance. This lack of kinetic data on nanosized rutile MnO$_2$ prompted us to investigate using ac impedance spectroscopy the kinetics of the Li insertion process into nanosized rutile MnO$_2$ prepared for the first time by ball-milling. The results reported here
2. Experimental

2.1. Powder preparation

The procedure used to obtain nanometric pyrolusite $\beta$-MnO$_2$ includes two steps. $\beta$-MnO$_2$ was first prepared by thermal decomposition of Mn(NO$_3$)$_2$ at 300 °C during 5 h. The latter is named microsized material in the text. During this decomposition, oxidation occurs leading to the formation of $\beta$-MnO$_2$ [11,14,17]. In a second step the latter was ground in a planetary ball mill at 500 rpm for 1 h, using tungsten balls and an agate jar.

2.2. Structural characterization

XRD diffraction experiments were performed with a Inel Cps 300 diffractometer using the Cu Kα radiation ($\lambda = 1.54056$ Å). The morphology of the sample has been examined with a Philips XL 30 scanning electron microscope.

2.3. Electrochemical measurements

The electrolyte used was 1 mol L$^{-1}$ LiPF$_6$ in ethylene carbonate (EC) and DiEthyl carbonate (DEC) solution (1:2, v/v). The working electrode consisted of a stainless steel grid (12 mm diam., 0.2 mm thickness) with a geometric area of 1 cm$^2$ on which the cathode material was pressed (5 t/cm$^2$). The cathode was made of a mixture of active material (80 wt%), acetylene black (7.5 wt%), graphite (7.5 wt%) and teflon as binder agent (5%). The film is obtained by mixing the oxide powder, carbon and teflon. Electrochemical studies were carried out in two-electrode cells (Swagelok$^\text{TM}$ type) for the galvanostatic measurements and cycling tests. In that case a lithium foil was used both as reference and auxiliary electrode. Galvanostatic experiments were made with a MacPile apparatus. For GITT measurements, each electrode was discharged by the application of cathodic current (100 µA) for 1 h. After this interval, the discharge current was switched off and the potential of the electrode allowed to equilibrate up to voltage remained less than 0.2 mV for 1 h.

Impedance measurements were performed using a three-electrode cell in the frequency range $4 \times 10^{-5}$–$7 \times 10^{-3}$ Hz with an E.G.G. 273A apparatus connected with a Solartron SI 1255 frequency analyser driven by an IBM computer. The reference and counter electrodes consisted respectively of a lithium wire in a separated compartment and a high surface gold wire. The excitation signal was 10 mV peak to peak. The equilibrium potential was considered to be reached when the drift in open circuit voltage remained less than 0.2 mV for 1 h.

3. Results and discussion

Fig. 1 shows the XRD diffraction patterns of the prepared powder compared with that of the starting compound (Fig. 1). The whole pattern can be indexed on the basis of a $\beta$-MnO$_2$ rutile single phase (space group P4$_2$/mm). The lattice parameters calculated from XRD data are $a = 4.381$ Å and $c = 2.877$ Å in good agreement with those of the starting material ($a = 4.398$ Å and $c = 2.873$ Å, JCPDS 71-0071). In the $\beta$-MnO$_2$ rutile structure, each metal atom is surrounded by six oxygen atoms and octahedral share edges to form single chains of octahedral extending along the c axis, giving a (1 × 1)-tunnel structure (Fig. 2). The broader peaks found for all the diffraction lines of the nanosized powder prepared by ball-milling technique suggest a smaller grain size, corresponding to a nanosized material. The mean crystallite size calculated from the

![Fig. 1. Comparison of the X-ray diffraction patterns (Cu Kα) of (a) the microsized material and (b) the nano-sized $\beta$-MnO$_2$.](image1)

![Fig. 2. Crystal structure along the 001 direction of rutile $\beta$-MnO$_2$. Mn is located in octahedral sites.](image2)
behaviour between bulk and nanosized rutile clearly outlines the higher specific capacity exhibited by the nanosized compound, i.e. 190 mAh g⁻¹ corresponding to a Li uptake of 0.62Li/β-MnO₂ (Fig. 4b), about six fold greater than that found for the commercial β-MnO₂ with only 30 mAh g⁻¹ (Fig. 4a). This capacity value is in good accord with that found for β-MnO₂ nanorods obtained from the hydrothermal persulfate treatments of various manganese oxides [13] and nanotubes [12] or mesoporous β-MnO₂ [16]. Larger values near 1 Li per mole of oxide are reported in some cases for β-MnO₂ nanocrystals/acylene black composites [11] and mesoporous crystalline β-MnO₂ [15]. Even at C/10, the specific capacity obtained with the ball-milled compound is much higher with 120 mAh g⁻¹ (Fig. 4c). Such an increase of the electrochemical reactivity of β-MnO₂ as the size of the crystallite decreases is in agreement with other works [11–14] and has been also reported in the case of mesoporous β-MnO₂ [15,16].

The charge process occurs in one step with a quasi-voltage plateau located around 3.2 V and then a continuous voltage increase for Li extraction up to 4 V. As expected from previous works, an irreversible capacity of 0.15 F/mol of oxide is observed corresponding to the trapping of 0.15 Li ions in the structure (Fig. 4b).

Cycling experiments for the nanosized β-MnO₂ have been performed as a function of the C rate with the cycling limits 4.1–2 V (Fig. 5). After the irreversible capacity loss observed for the first

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**Fig. 3.** SEM micrographs of the nano-sized β-MnO₂ (a and b) and the microsized material (c and d).

**Fig. 4.** Comparison of the first discharge–charge profiles of microsized (a: C/20) and nano-sized rutile β-MnO₂ (b: C/20; c: C/10) at room temperature. Inset: OCV discharge curve obtained from GITT measurements.

**Fig. 5.** Evolution of the Faradaic yield and the specific capacity for micro and nano-sized β-MnO₂ as a function of the number of cycles and C rate performed in the 4.1–2 V potential range.
cycle, whatever the discharge–charge rate applied, an excellent capacity retention is observed at least for 35 cycles. Indeed, at the lowest rate (C/20), the capacity first declines from its initial value of \(\approx 185 \text{ mAh g}^{-1}\) to remain stable from the second cycle at 150 mAh g\(^{-1}\). A similar attractive stability of the capacity is obtained even at a higher discharge rate (C/10) with a capacity value of 90 mAh g\(^{-1}\) over at least 40 cycles. The excellent reversible behaviour for the Li insertion reaction into nanosized \(\beta\)-MnO\(_2\) can be directly seen in Fig. 6 where all the discharge–charge profiles vs cycles 2–35 recorded at C/20 rate superimpose to deliver 150 mAh g\(^{-1}\) without any capacity variation and any polarization. It is noteworthy to observe that there is a significant change in the discharge–charge profile vs cycles (shape, working voltage). Indeed, from the second cycle, the discharge–charge curves clearly show the same S-shape with a higher discharge potential (3.10 V instead of 2.8 V in the first discharge) and the disappearance of the large hysteresis phenomenon seen in the first cycle. These new characteristics seem to indicate that after the first cycle, further Li intercalation takes place in a “new” host lattice corresponding to Li\(_{0.15}\)MnO\(_2\) without any further phase transformation. Stable capacity values in the range 150–200 mAh g\(^{-1}\) can be found in literature for cycling experiments performed in different voltage windows in the case of nanosized and mesoporous compounds [11–16].

In order to get more information about the stability of the host lattice, we have compared XRD experiments for an electrode of nanosized \(\beta\)-MnO\(_2\) before cycling, after first discharge and after 35 cycles at C/20 (Fig. 7). For the discharged sample \(\beta\)-Li\(_{0.15}\)MnO\(_2\) the XRD pattern is not modified except a small shift of some peaks showing a very low expansion of the a parameter of 4.424 \(\AA\) against 4.389 \(\AA\) for the pristine material, i.e. less than 1\%, while the c parameter of 2.866 \(\AA\) is unchanged. After cycling (Fig. 7c) all the typical diffraction peaks of the rutile structure still appear with a slight intensity decrease and with no evidence of a structural transformation to spinel LiMn\(_2\)O\(_4\) or other phases, the a and c lattice parameters of the cycled material being close to that of the starting one with values of 4.426 \(\AA\) and 2.876 \(\AA\), respectively. The present finding shows that lithium insertion progresses topotactically retaining the initial structure framework of \(\beta\)-MnO\(_2\) in the potential window 4.1–2 V. Insertion of lithium ions provokes a weak expansion of the lattice parameter along these tunnels leading to a stress in the particle which is more easily released in a nanosized particle than in a large particle. Larger capacities obtained in the enlarged cycling limits like 5–1 V as in [14] are possible to be reached at the expense of a capacity decrease due to the emergence of the LiMn\(_2\)O\(_4\) spinel phase.

The XRD data available on lithiated \(\beta\)-MnO\(_2\) are not detailed and are rather contradictory. XRD experiments performed on nanosized \(\beta\)-MnO\(_2\) [14] indicate that Li insertion results in the emergence of a new tetragonal phase from x = 0.25 with the same symmetry and a structure very close to that of the pristine material. A limited expansion of the lattice perpendicular to the \(1 \times 1\) tunnel is found with the a parameter increasing by 3\% while the c parameter remains constant. However the new peaks of this tetragonal phase would be located with 2 theta shifts of a few degrees which cannot account for an expanded phase with the same symmetry.

Fig. 7. (a) X-ray diffraction patterns for the nanosized rutile \(\beta\)-MnO\(_2\) (a), after first discharge (b) and after 35 cycles at C/20 rate (c) (+: graphite and stainless steel grid).

The numerical values of the apparent chemical diffusion \(D_i\) are calculated [23] using Eq. (1), when the angular frequency of the ac perturbation \(\omega \approx 2D_i/\ell^2\):

\[
D_i = \left[ \frac{V_m (dE/dx)_x}{F \sqrt{S}} \right]^2
\]

where \(V_m\) is the molar volume of the compound \((=33.20 \text{ cm}^3 \text{ mol}^{-1})\), \(S\) is the apparent geometric surface area of the electrode \((2 \text{ cm}^2)\) and \((dE/dx)_x\) is the slope, at fixed \(x\), of the equilibrium potential composition curve (inset Fig. 4); \(L\) is the
maximum length of the diffusion pathway (cm). In the present 
case, determining  in unambiguously is rather difficult. The 45° 
straight line is therefore considered as a criterion for semi infinite 
diffusion behaviour, although this cannot be proven further based 
on the frequency values. The analysis of the Warburg impedance 
of the system plotted in the complex plane  or  allows to get the Warburg prefactor  and then to 
calculate  for different  values. Fig. 9 illustrates the continuous 
increase of  vs  in Li$_x$β-MnO$_2$. According to Eq. (1), this trend 
indicates a decrease in the apparent chemical diffusion  when  increases. More precisely, the evolution of the values for  vs  in 
Li$_x$β-MnO$_2$ is reported in Table 1. Two sets of data are evidenced 
with high  values for low lithium contents ( 0.2), between 
2 × 10$^{-10}$–5 × 10$^{-10}$ cm$^2$ s$^{-1}$. Then  slightly decreases to reach 
lower values around 1.2 × 10$^{-10}$ cm$^2$ s$^{-1}$ before being stabilized 
in the Li composition range 0.2 ≤  ≤ 0.5. The slower kinetics of Li 
transport evidenced for  x 0.4 make the electrochemical performances 
of the material is affected when the C rate increases as it 
can be observed on the discharge curves (Fig. 5). The Li transport 
is highly anisotropic since it occurs along the c direction in the 
small (1 × 1) tunnels where repulsive Li–Li interactions increase. 
This can explain the decrease of  with  x insofar the rigid three-
dimensional tunnel structure of the compound remains practically 
unchanged during Li accommodation (Fig. 7). Li transport is found to 
be slower than in nanosized rutile TiO$_2$ [22] by one order of 
magnitude for  y 0.2 and by half a decade for  x 0.5. The values 
reported in the present work are the first one for a nanosized 
rutile MnO$_2$. Using the Basu and Worrell’s potentiometric method 
and the surface value as the apparent geometric surface area of 
similar composite electrodes, lower values have been found for  (≈6 × 10$^{-11}$ cm$^2$ s$^{-1}$ for 0.02 ≤  ≤ 0.08) in the microsized β-MnO$_2$ 
phase derived from Mn(NO$_3$)$_2$ precursor [2].

![Fig. 9. Evolution of the imaginary part of the Warburg impedance—Z$_{im}$ vs $\omega^{-1/2}$](image)

**Table 1**

<table>
<thead>
<tr>
<th>x in Li$_x$β-MnO$_2$</th>
<th>$D_{Li}$ (cm$^2$ s$^{-1}$ × 10$^{-10}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>1.8</td>
</tr>
<tr>
<td>0.1</td>
<td>5.4</td>
</tr>
<tr>
<td>0.2</td>
<td>3.0</td>
</tr>
<tr>
<td>0.4</td>
<td>1.2</td>
</tr>
<tr>
<td>0.5</td>
<td>1.2</td>
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Fig. 10 shows the comparison of ac impedance diagrams recorded for the starting microsized Li$_{0.08}$β-MnO$_2$ and the nanosized Li$_{0.1}$β-MnO$_2$. A decrease for the charge transfer resistance ($R_{ct}$) from 80 to 60 (for the microsized compound and nanosized material, respectively. This indicates an improve of electron transfer kinetics for nanosized compound. The micro-sized rutile sample exhibits a much larger cathode impedance at $7 \times 10^{-3}$ Hz by a factor 10, $|Z| = 3020 \Omega$ against only $340 \Omega$ for the nanosized oxide. This huge discrepancy reflects the more attractive electrochemical characteristics allowed by the nanosize effect in terms of effective electrochemical surface area, kinetics of charge transfer and Li diffusion. A promoting effect for Li insertion is induced by the nanocrystalline structure of this compound which facilitates the Li insertion with a better kinetics than in bulk material.

The kinetic behaviour of the nanosized rutile has been also examined as cycling proceeds at C/20 rate between 4.1 V and 2 V. The evolution of Nyquist diagrams vs cycles for the composition Li$_{0.4}$β-MnO$_2$ is shown in Fig. 11. An interesting point is that cathode impedance decreases by a factor two after the initial cycle showing further Li insertion–extraction proceeds in a new material as suggested by the higher working voltage of 3 V achieved against 2.8 V for discharge one (Fig. 3). From cycle 2 to cycle 20 all the impedance diagrams superimpose. As seen from Fig. 12, the Warburg’s pre-factor during cycling is about half that found for the first discharge which indicates a significantly faster Li transport by a factor 5: $D_{||} \approx 6 \times 10^{-10}$ cm$^2$ s$^{-1}$ for cycles 2 and 20 against $1.2 \times 10^{-10}$ cm$^2$ s$^{-1}$ in cycle 1. The present finding confirms that after initial cycle, further lithiation proceeds in a quite different material working at higher potential (3 V) and characterized by a faster Li diffusion. These characteristics are well consistent with the stable cycling data reported in Figs. 5 and 6.

4. Conclusions

AC impedance spectroscopy has been applied to the study of Li transport in nanosized rutile MnO$_2$ synthesized by ball milling the powder resulting from the heat-treatment of Mn(NO$_3$)$_2$ at 300°C. In comparison with the micro-sized material, the ball-milled rutile exhibits a lower cathode impedance and a better charge transfer kinetics. For the first time $D_{||}$ values ($\approx$ a few $10^{-10}$ cm$^2$ s$^{-1}$) are achieved for this rutile-type oxide in a wide composition range $0 < x < 0.5$. The values of the apparent chemical diffusion coefficient $D_{||}$ are much higher, i.e. by one order of magnitude than in microsized oxide. We show that from the second cycle, Li transport is faster than during the initial discharge–charge process by half an order of magnitude. This is consistent with the new discharge–charge fingerprint observed from cycle 2 with S-shape curves at a higher working voltage ($\approx$3 V instead of 2.75 V) combined with a high efficiency of the redox process in lithiated rutile Li$_{0.15}$MnO$_2$. Good cycling properties are achieved in the 4.1–2 V potential range with stable specific capacities of 150 mAh/g and 90 mAh/g at C/10 and C/5, respectively. This can be explained by a negligible structural change during lithium accommodation. The present finding has allowed to illustrate the strong nanosize effect on the electrochemical properties of a Li host lattice.
References