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

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ABSTRACT

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 0.5 $\times$ 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 $D_m$ values for the apparent chemical diffusion coefficient of lithium much higher by one order of magnitude than in microsized 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$_6$ octahedra, 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 pyrolysite 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 K$_2$MnO$_4$ and Mn$_2$O$_3$ [12] or by hydrothermal persulfate treatments of solid precursors like MnO$_2$ 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