Structural Transitions in Positive Electrodes for Li-Ion Batteries
the Vibronic Approach

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Abstract. We present the vibrational properties of manganese dioxides and lithiated oxides with either spinel-type and layered-type structure used as positive electrodes in Li-ion batteries. The local structure in $\gamma$-MnO$_2$ is investigated as a function of the intergrowth rate, $P_r$, of pyrolusite in the ramsdellite matrix and the phase evolution as a function of the degree of intercalation or deintercalation in 4-volt electrode materials Li$_{1-x}$CoO$_2$ and Li$_{1-x}$Mn$_2$O$_4$. Lattice dynamics are studied using either a classical group theoretical analysis or a local environment model. Raman and FTIR bands are identified on the basis of vibrational modes of polyhedral units which are building the structure. Structural modifications induced by intercalation-deintercalation process are examined.

1. Introduction

The recent interest in developing advanced rechargeable lithium batteries, such as lithium-ion type cells, has stimulated investigation on high-performance positive electrodes, the so-called 4-volt cathode materials [1-4]. Three lithiated systems with high operating voltage are presently known: LiCoO$_2$ and LiNiO$_2$, with the pseudo-layered $\alpha$-NaFeO$_2$ structure, and the 3-D spinel LiMn$_2$O$_4$. These structures are grown by numerous synthesis methods with substitution on the transition-metal site. To improve the electrochemical properties of the parent compounds, various materials have been tested forming the solid solutions LiCo$_{1-x}$M$_x$O$_2$ and LiMn$_{2-y}$M$_y$O$_4$ (M = monovalent or multivalent cation) which lead to successful results.

Since the electrochemical characteristics of the 4-volt materials depend on their crystal nature, size and shape, various kinds of preparation methods have been developed to improve the characteristics of these cathodes. Also, it has been pointed out that the rechargeability can be markedly improved and the fading loss upon cycling can be minimized for mixed or for substituted transition metal oxides. The current debate consists in the investigation of the local structure of these compounds because of the difficulty encountered in using powder x-ray and neutron diffraction for an unambiguous structural determination.

Among the local probes, vibrational spectroscopies, i.e. Raman scattering (RS) and Fourier transform infrared (FTIR), are techniques sensitive to the short-range environment of oxygen coordination around the cations in oxide lattices [5]. Since RS and FTIR techniques can solve the problem of phase determination when various environments are present. As a first approximation, spectra consist of a superposition of the components of all local entities present in the same material in contrast to diffraction data which gives a weighted average of similar interplanar spacings. The frequencies and relative intensities of the bands are sensitive to coordination geometry and oxidation states. Thus, spectra are less affected by the grain size or the degree of long-range order of the lattice.

In this contribution, we present the vibrational properties of manganese dioxides and materials with either spinel-type and layered-type structure used as positive electrodes in Li-ion batteries. We investigate the local structure in $\gamma$-MnO$_2$ as a function of the intergrowth rate, $P_r$, of pyrolusite in the ramsdellite matrix and the phase evolution as a function of the degree of intercalation or
deintercalation in Li_{1.4}CoO_2 and Li_{1.4}Mn_2O_4 4-volt electrode materials. Lattice dynamics are studied using either a classical group theoretical analysis or a local environment model. Raman and FTIR bands are identified on the basis of vibrational modes of polyhedral units which are building the structure. Structural modifications induced by intercalation-deintercalation process are examined.

2. Lattice dynamics of γ-MnO_2

Manganese oxides have long been known as materials of technological importance for catalytic and battery applications [6,7]. A major step was realized with the use of natural (NMD), electrochemically (EMD), chemically (CMD) and heat-treated (HTMD) prepared MnO_2 [8-9]. Polymorphism is common for MnO_2 which exhibits the largest structural complexity among the binary metal oxides. Manganese dioxides include α-MnO_2 (hollandite-type structure), γ-MnO_2 (nsutite structure), δ-MnO_2 (layered structure), λ-MnO_2 (spinel structure). The nsutite family is classified either as γ- or ε-MnO_2 depending on the quality of their X-ray diffraction patterns. Manganese dioxides, which were originally developed as positive electrode materials for commercial primary cells, are recently considered as promising cathodic materials for rechargeable lithium batteries [10].

The X-ray diffraction (XRD) patterns of γ-MnO_2 powders are always of rather poor quality and consist at best of a small number of sharp and broad lines on top of a diffuse background. This experimental fact led to De Wolff to propose a structural model of γ-MnO_2 based on the observation that rutile and ramsdellite structures have similar arrangements along their a and c axes and differ only by the width of the infinite strings of MnO_6 octahedra along the b axis [11]. This suggests that γ-MnO_2 could be described as an irregular intergrowth of elements of ramsdellite and pyrolusite. The structure of γ-MnO_2 can be seen as an intergrowth of pyrolusite blocks, called De Wolff defects [11], within a ramsdellite matrix. The chains of octahedra show changes in their growth direction, giving rise to zig-zag tunnels and resulting in crystallographic twinning. CMDs, EMDs and HTMDs do not exist without any defects. In the comprehensive description of the γ-MnO_2 structure proposed recently by Chabre and Pannetier [12], based on two kinds of defects, intergrowths and twinning, within the ramsdellite structure, the rate of pyrolusite intergrowth (structural parameter) is called Pr that is the fraction of single chain slabs in a given double chain (ramsdellite) framework. Simulations of X-ray diffraction patterns enabled to determine the amount of these defects [12]. Such results can be used to differentiate structurally the various γ-MnO_2 compounds that can be prepared for Li battery applications. The usual range of Pr for γ-MnO_2 compounds is as follows. CMDs are generally close to ramsdellite (Pr < 40 %), EMD are visualized with 40 < Pr < 60 %, and HTMD samples become close to pyrolusite.

Several manganese dioxide samples were studied among which two mineral specimens of MnO_2: the tetragonal rutile-type pyrolusite β-MnO_2 (from Thuringe, Germany) and the orthorhombic ramsdellite R-MnO_2 (from New Mexico). The manganese dioxide structure consists of edge- and corner-sharing MnO_6 octahedra that have tunnels of various sizes on the order of molecular dimensions. All MnO_2 structures can be described as a distribution of Mn^{4+} cations (having a small ionic radius of 0.53 Å) in the interstices of a more or less close-packed network of oxygen atoms. The manganese dioxide can be classified according the nature of the polymerization of MnO_6 units and the number of MnO_6 octahedral chains between two basal layers to form tunnel (T_{m,n}) openings [13]. The T_{1,1} group includes two chemically pure forms, the pyrolusite β-MnO_2 (T_{1,1}) and the ramsdellite R-MnO_2 (T_{12}).

As pointed out by many workers the total diffracted X-ray intensity is very small for any γ-MnO_2 except pure pyrolusite and ramsdellite. Synthetic nsutites exhibit a range of XRD patterns which are interpreted to be the result of variation in the concentration of pyrolusite microdomains. The changes in X-ray line sharpness, number, and position for the nsutite patterns are in agreement with that expected in going from a low (29%) to a high (75%) concentration of De Wolff defects. The structural parameter, Pr, has been determined using the procedure described by Chabre and Pannetier [12]. We observe that most of the studied γ-MnO_2 samples exhibit a structural parameter in the vicinity of Pr = 40 % that correspond to the EMD-type manganese oxides.

A careful examination of the results published earlier by different workers and of those that are more recently appeared shows discordance regarding the Raman spectra of manganese oxides due to the general peculiarity of low Raman activity of vibrational features in manganese dioxide. MnO_2 was not found to be Raman active by Strohmaier and Hercules [14] and Kapteijn et al. [15] whereas Gosztola and Weaver [16] and Bernard et al. [17] reported well-defined spectra of this oxide. The Raman