Atomic Scale Analyses of Planar Defects in Cross-section Nanorods of K\(^+\) Stabilized α-MnO\(_2\)

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Manganese oxides with tunnel structures have attracted wide attentions because of their potential applications in rechargeable batteries, ionic exchange, molecular absorption and catalysis. For utilizations as electrode in batteries, knowledge on how the tunneled structures in one-dimensional (1D) nanorods facilitate ionic transport will lead to a better understanding of the structure-property relationship. Manganese oxides can form various kinds of tunnel structures [1]. Figs. 1a-d show four types of the tunnel structures in MnO\(_2\), namely 1×1, 2×2, 2×1 and 2×3 structures with various tunnel sizes. In most cases, these tunnels are partially occupied by different cations (e.g. K\(^+\), Ag\(^+\), Ba\(^{2+}\)) and water molecules. To simplify the analyses, here, the atomic occupations within tunnels are not included in these schematics. For 1×1 and 2×1 tunnel structures (Figs. 1a and 1c), it is found that the tunnels are pure 1×1 and 2×1 ones, while for 2×2 and 2×3 tunnel structures (Figs. 1b and 1d), besides 2×2 and 2×3 tunnels, the 1×1 tunnels are intercalated. The K\(^+\) stabilized α-MnO\(_2\) possess the 2×2 structure. Recently, it was found that many planar defects exist in K\(^+\) stabilized α-MnO\(_2\) [2]. However, the detailed atomic configurations associated with these planar defects are unknown. In this presentation, we report detailed characterizations on these planar defects.

The tunneled manganese oxide based materials tend to form 1D rod morphology spontaneously. Although the length of rods is about a micron, their diameter is about few to tens of nanometer. Thus, one of the most challenging issues in the study is to prepare cross-section samples of individual rods allowing direct probing the tunnel structure and defects at atomic scale. The results we report here are from the TEM samples prepared using the ultramicrotome method. The nanorod powders were first imbedded in epoxy resin. Then, solidified resins were mechanically cut into slices at the feeding step size of 500 nm using the Leica EM UC7 with a diamond knife.

Fig. 2a is a low magnification BF-STEM image clearly showing that there are many planar defects across the \{110\} planes in the K\(^+\) stabilized α-MnO\(_2\) with the 2×2 structure. One of the plan defects is shown in Fig. 2b. The planar defect is marked by arrows. It is found that the local defect regions correspond to a 2′×1′ tunnel structure with its structural schematic shown in Fig. 2c. This 2′×1′ structure has a perfect intergrowth with the up and bottom 2×2 structure. In addition, this newly identified 2′×1′ tunnel structure is different from the previous 2×1 tunnel structure although their largest tunnel sizes are the same. In the 2′×1′ tunnel structure, beside the 2×1 ones, many 1×1 tunnels are intercalated as shown in Fig. 2c. Besides, many other planar defects are also refined in this study [3].
References:

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Figure 1. Schematics of (a) 1×1, (b) 2×2, (c) 2×1 and (d) 2×3 tunneled structures viewing along [001] tunnel direction. The largest tunnel size in each structure is 2.3 Å×2.3 Å, 4.6 Å×4.6 Å, 4.6 Å×2.3 Å and 4.6 Å×6.9 Å, respectively. Lattice vectors of a and b are labeled. Two types of MnO₆ octahedra indicated by different colors have a relative lattice shift of c/2 along tunnel direction.

Figure 2. (a) Low magnification BF-STEM and (b) atomic resolution HAADF images viewing along the tunneled direction showing planar defects along {110} plane. Atomic resolution image in (b) was obtained from the defect marked by the arrow in (a). Two types of circles overlaid on Mn columns in (b) indicate the corresponding Mn atoms having a relative shift of c/2 along tunnel direction. The location of the planar defect is indicated by arrows in (b). (c) Schematic of the 2′×1′ tunnel structure. Lattice vector a and b are indicated.