Phase transition and electrochemical capacitance of mechanically treated manganese oxides

Akira Taguchi, Sachio Inoue, Satoshi Akamaru, Masanori Hara,
Kuniaki Watanabe, Takayuki Abe *

Hydrogen Isotope Research Center, Toyama University, Gofuku 3190, Toyama 930-8555, Japan

Abstract

Mechanical grinding (MG) leads to a sequential phase transition of γ-MnO$_2$ to form the thermodynamically stable α-Mn$_2$O$_3$ and, subsequently, Mn$_3$O$_4$ depending on the duration of MG treatment. By MG treatment for 150 h, α-Mn$_2$O$_3$ became a predominant species. A subsequent transition to Mn$_3$O$_4$ was observed on further MG treatment for 200 h. The particle size of the resultant manganese oxides was reduced to as small as 20 nm after 300 h of MG treatment. The change in the specific capacitance of manganese oxides obtained was monitored by XRD and electrochemical experiments. It was observed that the specific capacitance of MG-treated manganese oxides depends on the amount of γ-MnO$_2$ left without phase transition.
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1. Introduction

Recently, the development of novel energy storage devices such as batteries and capacitors has been extensively studied in order to improve efficiency and reliability of electric utility systems such as solar-cell reservoirs or power quality regulators for computers, electric and hybrid vehicles, and fuel cell systems [1–4]. The oxide and hydroxide of ruthenium provide a good capacitance in aqueous and non-aqueous electrolyte systems [5,6]. However, the noble metal ruthenium, being expensive, has its own limitations. Hence, the fabrication of substitutional supercapacitive materials for ruthenium (hydro)oxides is gaining importance. Presently, several metal oxides and hydroxides, for example, those of Ni, Co, V, and Mn, are being studied extensively [8–10]. Among these, manganese oxide (MnO$_2$) is one of the promising materials for this purpose due to its availability, cost-effectiveness and non-toxicity.

The design and synthesis of manganese oxide electrodes is a key field for improving upon its electrochemical properties. In the case of super capacitor electrodes which comprise manganese oxide, it has been widely observed that MnO$_2$ exhibits a rather high performance in comparison to its other oxides such as Mn(OH)$_2$, Mn$_2$O$_3$, and Mn$_3$O$_4$ [11–13]. For example, amorphous hydrous manganese oxide (a-MnO$_2$·nH$_2$O) fabricated from MnSO$_4$·5H$_2$O solution via an anodic deposition yielded a specific capacitance in the range of 265–320 F/g between 0 to 1.0 V in 0.1 M Na$_2$SO$_4$ solution [12]. A thin film of MnO$_2$ electrode prepared by the dip-coating of colloidal MnO$_2$ exhibits an excellent specific capacitance value of unto 698 F/g that is comparable to the ruthenium (hydro)oxides [5,7,13].

However, a structural change in the active component of MnO$_2$ causes a loss of the electrochemical activity. This is due to of the significant change in the conductivity of manganese oxides—the conductivity of manganese oxides involving trivalent Mn(III) is rather low as compared to that of MnO$_2$ or amorphous manganese (oxyhydro)oxides involving Mn(IV); this is attributed to the Jahn–Teller distortion of the Mn^{III}O$_6$ octahedral [8,14]. A few reports pertaining to

* Corresponding author. Tel.: +81 76 445 6933; fax: +81 76 445 6931.
  E-mail address: abe@hrc.toyama-u.ac.jp (T. Abe).

the quantitative investigations of the content and capacitance of a mixture of MnO_2 and Mn_2O_3 have been published.

Much attention has been paid to a mechanical grinding (MG) technique by means of ball milling, which is a powerful tool to reduce the particle size or mix several components to homogeneous dispersion [15–17]. Besides these fine mixing, a phase transition by MG treatment has been reported by Wakamatsu et al. [18] and Kuznetsov et al. [19]. Wakamatsu et al. have shown that rutil and/or brookite were obtained by MG treatment of anatase [18]. The mechanical treatment of β-FeOOH caused the phase transition to FeO, via α-Fe_2O_3 and Fe_3O_4 as intermediate phases [19]. Depending on the duration of MG treatment, we observed a sequential phase transition of manganese oxides of γ-MnO_2 to α-Mn_2O_3 and then subsequently to Mn_3O_4. The resultant manganese oxides are suitable examples to investigate the relationship between the composition of manganese oxides and their capacitances. In this paper, we report a sequential phase transition of manganese oxides by MG treatment, and the change in the specific capacitances of the resultant manganese oxides.

2. Experimental

Commercially available MnO_2 (Kanto Chemical Co.) was mechanically ground using a planet type ball mill (Fritsch, pulverized 5). In a container (26 mm in diameter and 27 mm in height) with 30 balls (each 4 mm in diameter), 4 g of MnO_2 was placed and ground at 800 rpm for sufficient periods of time. Hereafter, these MG-treated samples are denoted as MG-*n*; where *n* is the period (in h). The structure and crystalline of the obtained samples were investigated by a powder X-ray diffraction (XRD, Philips, PW1825/00) and transmission electron microscopy (TEM, TOPCON, EM-002B).

The manganese oxides prepared by the MG treatment were electrochemically investigated. Manganese oxide that had been treated for a specific time was mixed with a small amount of polytetrafluoroethylene (PTFE), which was used as a binder, and carbon powder (10 wt.%). A few drops of *n*-methylpyrrolidine were added to the mixture to prepare the sample paste. A Pt plate (10 mm × 10 mm), used as a current collector, was immersed in concentrated nitric acid for 2 h and dried in an oven at 80 °C; subsequently, it was washed with distilled water. The sample paste was spread on the Pt plate, and it was dried at 60 °C for 3 h. The amount of manganese oxides on the composite plate was measured by subtracting the weight of the Pt plate from that of the plate with the sample. In the case of the manganese oxides containing a mixture of γ-MnO_2, α-Mn_2O_3, and Mn_3O_4, the composition of each component was calculated from the relative peak intensity for the most intense peak of each. Cyclic voltammetry (CV) was carried out in 1 M KOH aqueous solution using a three-electrode system with a Pt counter electrode and a saturated calomel electrode (SCE) under potential control conditions (EG&G, potentiostat Model 263A).
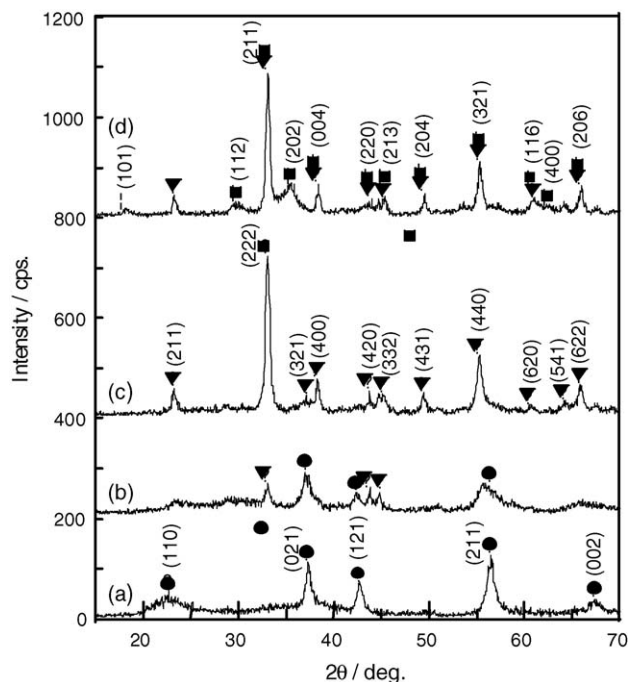

Fig. 1. X-ray diffraction patterns of manganese oxides of (a) untreated (MG-0), (b) MG-80 (an offset by 200 cps.), (c) MG-120 (an offset by 400 cps.) and (d) MG-300 (an offset by 800 cps.). Symbols (●), (▼) and (■) correspond to the peaks of γ-MnO_2, α-Mn_2O_3, and Mn_3O_4, respectively.

3. Results

The manganese oxide used in this study was γ-MnO_2 (nsutite, JCPDS 4-779 and 17-510), and its XRD pattern is shown in Fig. 1(a). Its particle size could not be estimated due to the very low diffraction intensity and the poor resolution of diffraction signals. The poor crystallinity is probably due to the presence of a small structural defect in γ-MnO_2 [8]. The phase composition and crystalline structure of γ-MnO_2 changed significantly after the MG treatment. As shown by the XRD pattern in Fig. 1(b), new diffraction signals assignable to α-Mn_2O_3 appeared at 2θ of 32.9°, 42.8° and 43.6° after the MG treatment for 80 h (MG-80). These peaks could be indexed to (2 2 2), (3 2 0) and (3 3 2), respectively; subsequent grinding for 120 h (MG-120) supported this observation. The diffraction signal of the α-Mn_2O_3 phase (bixbyite, JCPDS 31-825 and 41-1442) intensified and those of γ-MnO_2 almost completely disappeared during the duration of this MG treatment. The particle sizes of the obtained α-Mn_2O_3 were calculated with the diffraction signals of (2 2 2), (4 4 0), and (6 2 2), and were found to be 16.0, 13.4, and 15.6 nm, respectively, using the Scherrer's equation. Furthermore, on increasing the duration of MG treatment up to 300 h (MG-300), some diffraction signals corresponding to Mn_3O_4 (hausmannite, JCPDS 1-1127) appeared along with α-Mn_2O_3 signals.

Fig. 2 shows a change in the intensities of the diffraction signals of γ-MnO_2, α-Mn_2O_3, and Mn_3O_4, depending on