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Tailoring the lattice structure of manganese oxides under electric field and improving the supercapacity of them

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ABSTRACT

Electrical field can tailor the lattice structure and morphology of manganese oxides during their synthesis and improve their supercapacities. Manganese oxides as Hausmannite Mn_3O_4 nanoparticles and/or Bernessite δ-MnO_2 nanolayers, were synthesized under electric field by titration of $MnSO_4{\cdot}H_2O$ and H_2O_2 solution into dilute NaOH solution at 90 °C. The sample without electric field has the main phase as Mn_3O_4 and some of δ-MnO_2. When a high electric field is applied, the percentage of δ-MnO_2 in the samples increases with the electric field rapidly. A pure δ-MnO_2 sample is obtained when an applied electric field above 0.6 kV·cm^{-1}. The supercapacity is improved in the samples synthesized with high electric field, in which the main phase is the δ-MnO_2. However, the deterioration of the properties is observed in the pure δ-MnO_2 sample. Therefore, synthesis under the electric field can tailor the crystalline structure of manganese oxides to improve the supercapacity respectively.

1. Introduction

MnO_2 received much attention as a candidate active material of supercapacitor with economy and its outstanding characteristics [1–9]. In fact, the different polymorphous with a composition near to MnO_2 are totally called as manganese dioxide. Several different crystalline structures of MnO_2 have been synthesized, such as, α, β, δ, γ, λ [10,11]. The polymorphous are constructed by interlinked MnO_6 octahedra with different pattern such as sharing corner, line, and face, and thus they possess tunnels or interlayers with gaps of different magnitudes, which cations or protons can be inserted/extracted into/from and thus involve electrons transfer as transition of Mn^{4+}/Mn^{3+} to be responsible for the pseudocapacitance behavior. There have been some approaches to the polymorphous of MnO_2. The nanoparticles of α-MnO_2 were synthesized by the redox reaction between stoichiometric quantities of $MnSO_4$ and $KMnO_4$ in the solutions [12–13]. Nanorods of *β*-MnO_2 were acquired by the hydrothermal treatment of aqueous solution of $Mn(NO_3)_2{\cdot}4H_2O$ [14]. Nanowires/nanorods of γ-MnO_2 were prepared from $MnSO_4$ using $(NH_4)_2S_2O_8$ as an oxidizing agent [15]. Nanoplatelets of δ-MnO_2 were prepared by following the same route of synthesis of α-MnO_2, but with double the stoichiometric amount of $KMnO_4$ [16]. λ-MnO_2 can be obtained by delithiation of $LiMn_2O_4$ [17]. Furthermore, some new technologies, such as preparation of nanorod array [18], using graphene to replace acetylene black [19] to improve the surpercapacity performance of MnO_2. The supercapacity performances of the different structured MnO_2 were comparing each other [10,11], and the charge storage ability of them is sorted as α-MnO_2 ≥ δ-MnO_2 > γ-MnO_2 > λ-MnO_2 > β-MnO_2 in series. Mn_3O_4 can be yield by heating MnO_2 at high temperature or other chemical method [20–22]. The spinel structured Mn_3O_4 is also reported as an active material of supercapacitors with good performance, although is studied less sufficiently than MnO_2.

In some cases, materials with a single phase cannot reach their best performance on a certain characteristics. Piezoelectrics have their best d33 (a kind of piezoelectric constant) in multiple phase boundaries typically as a physical effect [23], while TiO_2 has its best catalyst properties as hybrid phases of anatase and rutile as a chemical effect [24]. Therefore, as supercapacitor materials, manganese oxides with coexistence of multiple phases or valences also would've taken into account carefully in order to optimize their characteristics and get the outstanding performance. Electric field could control the morphology of ZnO during its synthesis as deposition of zinc salts solution into alkaline dilute solution. ZnO nanoparticles were obtained without electric field, but ZnO nanowires were prepared under the electric field over 0.4 kv·cm^{-1} using the same deposition [25]. Crystalline structure can be also tailored by electric field during synthesis of $CaCO_3$ nanostructures. The calcite structure with cubic-like morphology was obtained generally without electric field, the vaterite structure with the morphologies of nanorods and nanoflower was formed under the high electric field, and the mixture phases were obtained with mild electric

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field [26]. In this study, the electric field effects on the synthesis of manganese oxides were studied and their supercapacities were also checked.

2. Experiments

2.1. Synthesis of manganese oxides

Manganese oxides (Mn_3O_4 or MnO_2) powders were synthesized according to the chemical reaction as

$$3MnSO_4 + H_2O_2 + 6NaOH = Mn_3O_4 + 3Na_2SO_4 + 4H2_O \quad (1)$$

$$\text{or } MnSO_4 + H_2O2 + 2NaOH = MnO_2 + 2H_2\ O + Na_2SO_4 \quad (2)$$

Here, there is no purposeless impurity introduced using H_2O_2 as oxidizer, and thus it is reasonable to adopt above reaction to synthesis Manganese oxides. An electric field is applied to tailor the ratio of the different polymorphous during synthesis. The synthesis system is as same as our synthesis of $CaCO_3$ nanoflowers and our patent described [25,26]. The injecta was prepared by dissolving 3.38 g $MnSO_4{\cdot}H_2O$ (0.02 mol) and 3 ml (2.27 g ~ 0.02 mol) 30% H_2O_2 in 10 ml deionized water and then transferred into a syringe. The base solution was prepared by dissolving 1.6 g NaOH into 200 ml deionized water in a stainless steel vessel. The vessel was linked to the ground of high voltage power served as counter electrode. The syringe was fixed on the ejector jet pump. The syringe nozzle was linked with a perfusion tube, which the other end was fixed on an entry needle. The entry needle simultaneously served as an electrode, to which a high electric field of 0–0.6 kV·cm^{-1} can be applied, and the distance to the counter electrode is 10–25 cm in our laboratory systems. After the base solution was heated to a target temperature (90 °C) which was stirred quickly by magnetic stirrer, the injecta solution was injected into it while a high electric field was applied on the synthesis system. In our experiments, 0 and 6 kV electric field was employed and 80 μl·min^{-1} perfusion flow was fixed. After the perfusion, obtained black slurry was filtered and washed several times by deionized water. Through the drying at 60 °C × 24 h, the black powders were prepared.

2.2. Characterization

All the powders samples were checked by the specific surface area (SSA, Bj builder specific surface area analyzer, SSA-3200), the X-ray diffraction (XRD, a Philips Diffractometer, X'Pert-Pro MPD), and Field emission scanning electron microscopy (FE-SEM, Zeiss supra55).

2.3. Preparation of working electrode

Total amount ~1 g of Manganese oxides, acetylene black, and 60% polytetrafluoethylene (PTFE) emulsion according to the ratio of 75:20:5 was weighted. PTEF emulsion was transferred in a small beaker and 5 ml ethanol alcohol was added into demulsify. MnO_2 and acetylene black were ground in a mortar sufficiently, and then put into the above-mentioned small beaker. After an ultrasonic dispersion for 1.5 h, syrup was formed. Electrodes were prepared on high-purity Ni foam as the current collector. The syrup was coated and dried several times on both side of Ni foam (1 cm × 1 cm with 1 mm thickness) homogenously. After that, the yielded Ni foam with the active materials was subjected with a slight pressure of 8 Mpa and then solidified at 200 °C × 2 h. The prepared electrode was dipped in the solution of 1 M Na_2SO_4 for 12 h.

2.4. Electrochemical measurements

An electrochemical study was carried out at 20 ± 2 °C in a glass cell of capacity 70 ml to load a manganese-oxides-working-electrode, Pt auxiliary electrodes, a reference electrode, and an aqueous solution of 0.1 M Na_2SO_4 as the electrolyte. A saturated calomel electrode was used as the reference electrode, and potential values are reported against the reference electrode. Electrochemical studies were carried out using a potentiostat-galvanostat Princeton Applied Research model Parstat-2273.

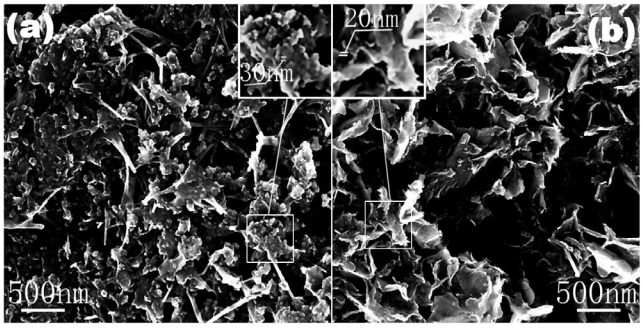

Fig. 1. SEM of the samples, (a) without electric field (b) with electric field 0.4 kV·cm^{-1}.

3. Results and discussion

The morphologies of the crystalline powders synthesized from solution method are often related to the lattice cell structures due to their crystallization characteristics. Near round particles often are obtained for the cubic cells, and plate-like morphology powders can be acquired for layer structured cells easily. Fig. 1 showed the SEM graphs of the Manganese oxides samples without electric field as Fig. 1(a) and with an electric field of 0.4 kV·cm^{-1} during their synthesis as Fig. 1(b). There are two kinds of morphologies in the graphs, particles and platelets. Small platelets are imbedded in large amount of nanoparticles in Fig. 1(a), but only a slight numbers of nanoparticles dispersed on the large amount of nanosheets in Fig. 1(b) contrarily. More details can be observed in the insets of Fig. 1. The nanoparticles can have a grain size of ~30 nm and the nanosheets have the thickness of ~20 nm. Combining crystalline characteristics with the profiles of XRD of the samples as shown in Fig. 2, the nanoparticles were indexed as tetragonal hausmanite Mn_3O_4 and the nanosheets or nanoplatelets as layer structured birnessite δ-MnO_2. The ratio of Mn_3O_4:δ-MnO_2 as 6:4 can roughly be estimated statistically in the sample without electric field from Fig. 1(a), while Mn_3O_4 only take a proportion less than 10% in the sample with electric field as shown in Fig. 1(b).

The percentages of each phase take a direct proportion to their intensities of XRD peaks approximately, and can be estimated out as

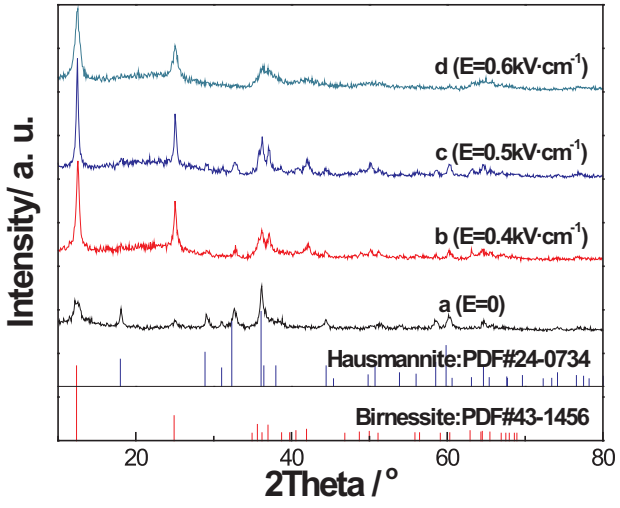

Fig. 2. XRD profiles of the samples synthesized under the different electric field, a:0 kV·cm^{-1}, b:0.4 kV·cm^{-1}, c:0.5 kV·cm^{-1}, d:0.6 kV·cm^{-1}.