Available online at www.sciencedirect.com
ScienceDirect
Materials Letters 61 (2007) 3189–3192
materials letters
www.elsevier.com/locate/matlet

In-situ fabrication and characterisation of nanostructured Mn_3O_4 powders for electronic and electrochemical applications

K. Konstantinov *, Y. Tournayre, H.K. Liu

University of Wollongong, Institute for Superconducting and Electronic Materials, 2522 Wollongong, NSW, Australia

Received 19 January 2006; accepted 5 November 2006
Available online 21 November 2006

Abstract

A spray pyrolysis approach has been used to obtain in-situ single-phase nanocrystalline Mn_3O_4 powders with spherically shaped particles. Ethanol or water-based solutions were sprayed at temperatures in the range of 450–750 °C. Ethanol-based solutions led to carbon-contaminated powders at low temperatures and to particles with low porosity. Water-based solutions, however, are suitable for obtaining single-phase nanomaterials with a high specific surface area, up to 45 m^2/g. The crystal size is less than 10 nm for spraying temperatures below 550 °C.

Keywords: Mn_3O_4; Spray pyrolysis; In-situ process; Nanomaterials; Porosity

1. Introduction

Trimanganese tetroxide (Mn_3O_4) is one of the most stable oxides of manganese, and it has a variety of important applications. In a pure form it is used to manufacture ferrites for electronic applications [1]. It is also used as a starting material for fabrication of Li–Mn–O rechargeable batteries [2]. This material is an active catalyst for oxidation of methane and CO [3] and promotes the selective reduction of nitrobenzene [4] and the combustion of organic compounds between 373 and 773 K, which is of interest for solving air-pollution problems [5]. For all these applications it is desirable to use nanostructured Mn_3O_4 powders with enhanced surface area. So far, a limited number of papers regarding the synthesis of such materials have been published [6–11]. Different methods such as sol–gel, co-precipitation, and solvothermal and hydrothermal methods have been applied. Although these can allow the composition and morphology of Mn_3O_4 powders to be controlled, they either use elevated temperatures, which increases the crystal size and reduces the surface area, or they are not cost-effective and easily applicable for industrial use.

The present paper reports the in-situ synthesis of nanostructured Mn_3O_4 powders with enhanced surface area by using a spray-solution approach, which has been proven to be a productive and easily scalable method for industrial applications.

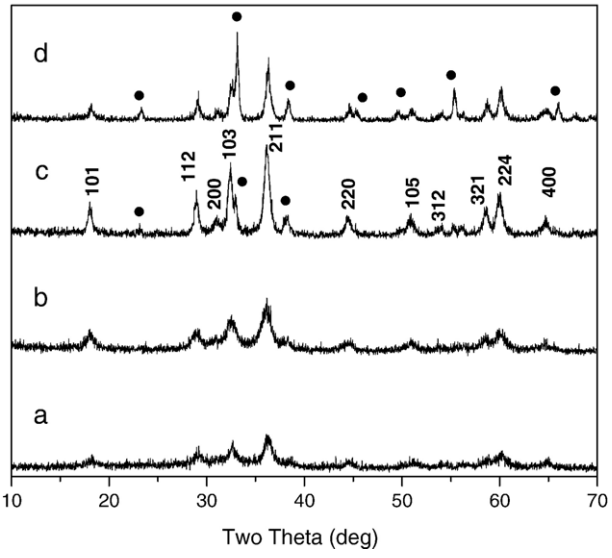

Fig. 1. XRD patterns of powders obtained from ethanol-based solutions and sprayed at 450 °C (a), 550 °C (b), 650 °C (c) and 750 °C (d), respectively. The Miller indexes of the Mn_3O_4 phase are shown for material sprayed at 650 °C and the peaks of the Mn_2O_3 phase are marked by (●).

* Corresponding author. Tel.: +61 2 42215765; fax: +61 2 42215731.
E-mail address: konstan@uow.edu.au (K. Konstantinov).

0167-577X/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2006.11.020

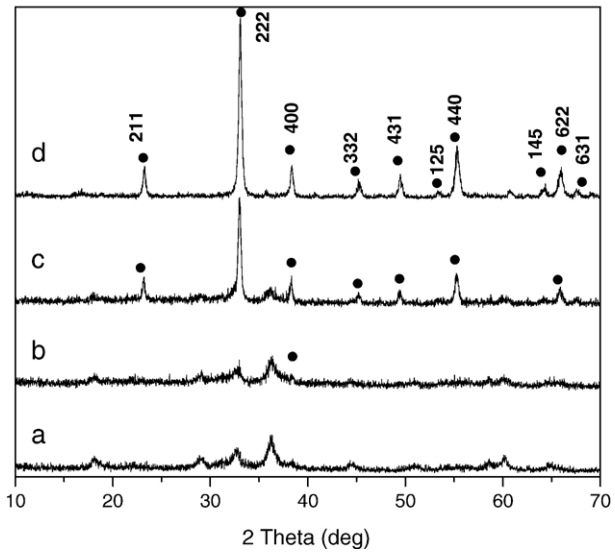

Fig. 2. XRD patterns of powders obtained from water-based solutions and sprayed at 450 °C (a), 550 °C (b), 650 °C (c) and 750 °C (d), respectively. The Miller indexes of the Mn_2O_3 phase are shown for material sprayed at 750 °C, and the peaks of this phase are marked by (●).

2. Experimental procedures

Ethanol and water-based spraying solutions with a concentration of 1 M were prepared by using manganese (II) nitrate tetrahydrate. The solutions were sprayed in a vertical spray pyrolysis unit at various furnace temperatures in the range of 450 to 750 °C. The flow rate was 3 mL/min.

The phase composition, morphology, and chemical composition of materials were studied by X-ray diffraction (XRD) analysis (Philips PW1730 diffractometer with Cu Kα radiation), scanning electron microscopy (SEM), and energy dispersive X-ray analysis (EDX) using a JEOL JSM 6460A instrument. The particle size distribution and specific surface area were investigated by particle size analysis (Malvern Mastersizer) and a gas sorption technique (Nova 1000 instrument) using the BET method.

3. Results and discussion

Fig. 1 presents the XRD results for sprayed powders obtained with spray temperatures between 450 and 750 °C using ethanol solutions. The materials exhibit a nanostructured, tetragonal Mn_3O_4 Hausmannite single-phase (PDF file 08-0017) with lattice parameters

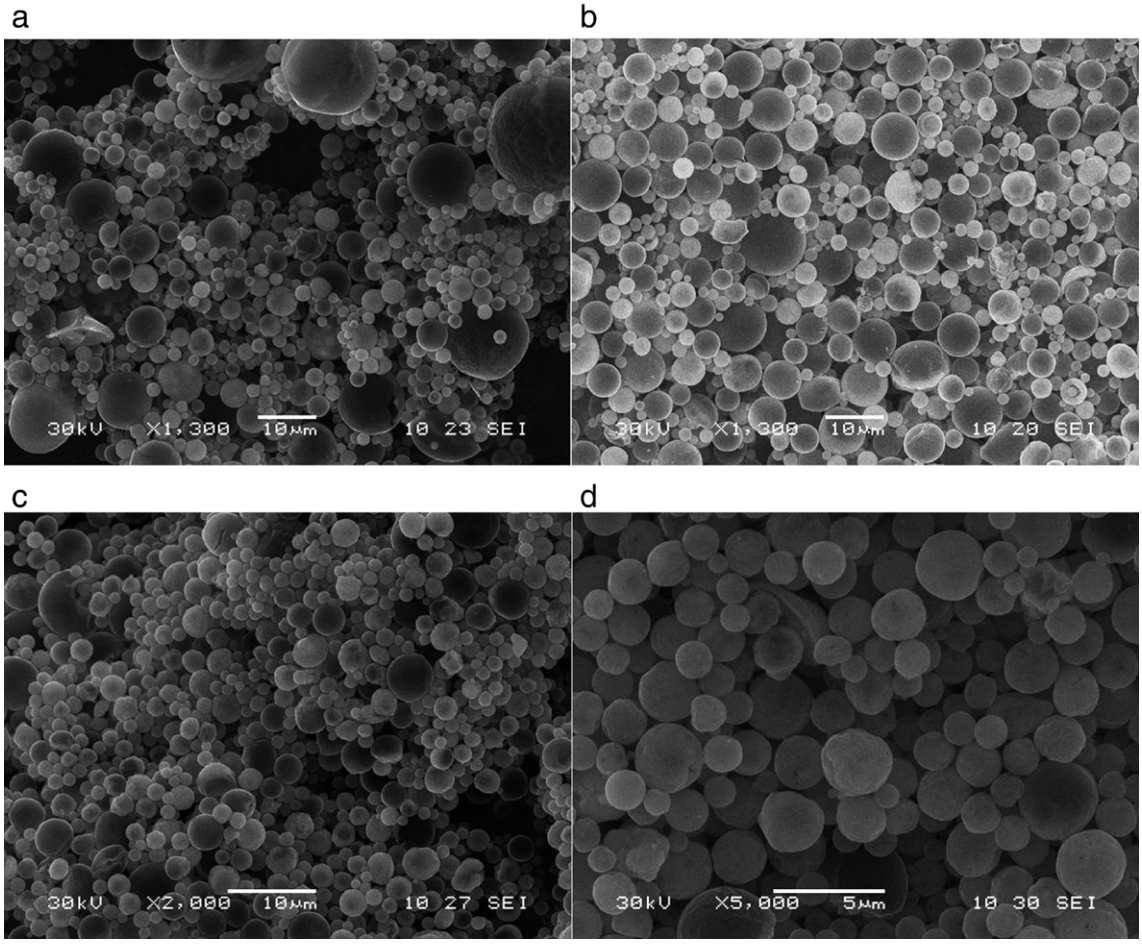

Fig. 3. SEM photographs of manganese oxide powders obtained from ethanol-based solutions and sprayed at 450 °C (a), 550 °C (b), 650 °C (c) and 750 °C (d), respectively.