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Microstructure and electrochemical properties of iron oxide film fabricated by aerosol deposition method for lithium ion battery

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HIGHLIGHTS

- Fe_2O_3 aerosol deposition film shows the high deposition speed.
- The electrochemical property of Fe_2O_3 aerosol deposition film is studied.
- The Fe_2O_3 aerosol deposition film shows the self-fitted microstructure.
- The Fe_2O_3 aerosol deposition film shows the high rate capability.

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ABSTRACT

The microstructure and electrochemical properties of Fe_2O_3 films, which are fabricated by an aerosol deposition (AD) method, are investigated in this study. For the high rate capability in Li ion battery, not only the nano-size grain but also the path for electrolyte is required in thin/thick electrode films. The microstructure is formed in Fe_2O_3 AD films. The Fe_2O_3 AD film shows the dense microstructure and the small grain size of a few nanometers. In particular, the space for electrolyte is also observed in the Fe_2O_3 AD film which has the dense microstructure. In addition, the AD method has the excellent deposition speed (1–10 min for 1 μm, 10 × 10 cm^2). In this manuscript, it is indicated that an Fe_2O_3 AD film has the excellent rate capability because of the self-fitted microstructure, which shows the path for electrolyte as well as the nano-size grains. In addition, the high capacity of 150 μAh cm^{-2} is also observed at the Fe_2O_3 AD film (the current density of 50 μA cm^{-2}, the film thickness: 300 nm).

1. Introduction

The nanomaterial is required for the high rate capability in Li ion battery. It is because the high surface area and the short length of Li-ion diffusion, due to the small grain size, can contribute to the high rate capability as well as the high capacity. In addition, the path for electrolyte is also necessary in a thin film which has the dense microstructure. However, in the dense film, it is difficult to obtain the appropriate microstructure which simultaneously shows the required conditions (such as the nano-size grain, the dense microstructure, the space for electrolyte etc.) without additives and an annealing process. Nevertheless, the aerosol deposition (AD) film has not only the nano-size grain and dense microstructure but also the space for electrolyte as shown in Fig. 1.

Recently, an AD method has gained considerable attention as a new promising film deposition process [1–5]. AD is the deposition method of a thin/thick film using fine particles as shown in Fig. 1. The fine particles, which are accelerated by an air compressor, are ejected through the nozzle and collide onto the substrate with high speed. Because of the fracture and plastic deformation of the primary particles, the dense ceramic film is formed at room temperature and the grain size of an AD film is very small approximately a few nanometers as seen in Fig. 1. Moreover, the pores are also formed among the agglomerated nano-grains during the AD process. The AD technology exhibits the following characteristics: i) the high deposition speed approximately 1–10 min for the thickness of 1 μm and the area of 10 × 10 cm^2, ii) the dense microstructure which consists of nano-size grains and pores among the agglomerated nano-grains, iii) the wide thickness range from submicron to hundreds micrometers, iv) the easy manufacture of a composite film and multi-layer, v) the easy manufacture of a flexible film through the use of a flexible substrate, vi) no use of heat

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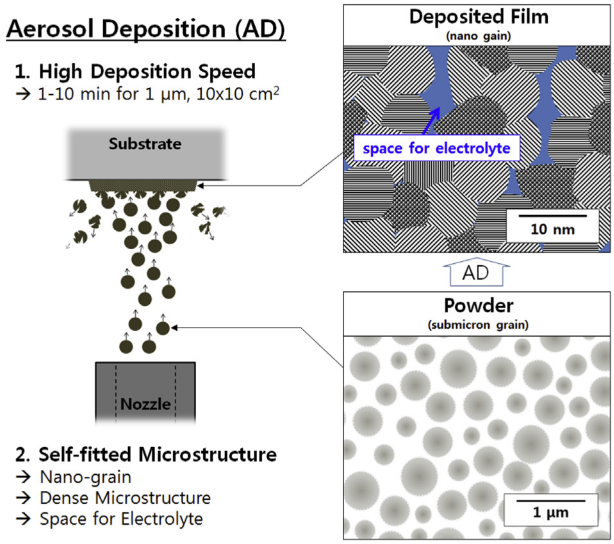

Fig. 1. Schematic diagram of aerosol deposition (AD) method: Not only the nano-size grain but also the path for electrolyte is formed an aerosol deposition (AD) film. The microstructure is formed because of the fracture and plastic deformation of the primary particles during the AD process. AD method shows the high deposition speed approximately 1–10 min for the thickness of 1 μm and the area of 10 × 10 cm^2.

treatment for densification etc. [1–5]. Until now, the various base technologies have been achieved (such as the optimization of AD equipment and the manufacturing technology of thick film and large size etc) and then, finally, the application of this technology is expanding [1–4].

It has been reported that an AD film could be used for the various applications such as piezoelectric devices, sensors, biodevices etc. [1–5]. In this study, another application was considered. That is the thin film Li ion battery which can be used for various devices such as medical devices, thinner portable electronics, defibrillators and neural stimulators, smart cards, wireless sensors, harvesting devices etc. [6,7]. In thin film battery, the Li-based alloys (such as Li, Li_2Sn_5, Li_2Si_5 etc.) have been employed for the anode [7]. Hence, in order to replace Li alloys with a cheap material, the microstructure and electrochemical properties of an Fe_2O_3 AD film were investigated in this study. Fe_2O_3 has been well-studied as a promising candidate for the anode in Li ion battery. It has the high theoretic capacity of 1007 mAh g^{-1} as well as the competitive price [8–25]. The Fe_2O_3 film has been fabricated by aerosol-based processes at which the film is not deposited at room temperature and the solution is used for the deposition source [23–25]. Therefore, they are different from this AD process at which the film is deposited at room temperature and the mixture of air and powder is used. Through the Fe_2O_3 AD films, we show that AD films can be used for the electrodes in thin film Li ion battery. In particular, an Fe_2O_3 AD film was expected to have the high rate capability due to the exceptional microstructure (nano-size grain & dense microstructure & the path for electrolyte). The dense microstructure means that an AD film is not separated from a substrate.

2. Experimental procedure

Fe_2O_3 films were fabricated on the stainless steel plate by an AD method, using the commercial powder (Fe_2O_3, >99%, Sigma Aldrich). The powder was mixed with the dried air to form an aerosol flow in the aerosol chamber. The aerosol flow, which was transported through a tube to a nozzle, was accelerated by an air compressor and ejected into the deposition vacuum chamber through a rectangular-shaped nozzle (25 × 0.8 mm^2). The vacuum chamber was evacuated using a rotary pump with a mechanical booster. The compressed air, which was dried through a dehumidifying filter, was used as the carrier gas at a flow rate of 20 l/min. The deposition equipment is described in detail elsewhere [1–4]. The crystal structure was examined by a Rigaku D/max-RC X-ray diffractometer. The microstructure was observed using a scanning electron microscope (SEM, JSM-5800; JEOL CO., Tokyo, Japan) and a transmission electron microscope (TEM, JEM 2100F; JEOL CO., Tokyo, Japan). In order to confirm the electrochemical properties of Fe_2O_3 AD films, the prepared Fe_2O_3 AD films (thickness: 0.3 μm and 1.7 μm) and a metallic lithium foil were used as the working electrode and the counter electrode. A 1 M $LiPF_6$ [the mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 v/v)] was used as the electrolyte and a polypropylene film (Celgard 2400) was chosen for the separator. The cell was assembled in an argon-filled glove box, using coin-type cells (CR 2016). It was cycled at the voltage range from 0.01 to 4.0 V using VMP3 (Bio Logic SAS, France) and the current density was 0.05–5 mA cm^{-2}.

3. Result and discussion

The crystal structure and microstructure of an Fe_2O_3 AD film were investigated as exhibited in Figs. 2–3. Fig. 2 shows the X-ray diffraction (XRD) patterns of Fe_2O_3 powder and an AD film. As seen in this figure, the peaks for any secondary phase were not detected. In addition, the peaks were broader in an Fe_2O_3 AD film than Fe_2O_3 powder and it might be due to the small grain size (a few nanometers) of the Fe_2O_3 AD film as seen in Figs. 2 and 3. Thus, it could be expected that an Fe_2O_3 AD film was well-deposited. The microstructures of Fe_2O_3 powder and an AD film were exhibited in Fig. 3. The particle size of Fe_2O_3 powder was observed to be submicron-scale and an Fe_2O_3 AD film showed the nano-size grains as shown in Fig. 3. During the AD process, the grain size was reduced from submicron-scale to nano-scale. The formation of nano-scale grain size is a normal phenomenon in AD film as indicated in Fig. 1. The nano-scale grain size might be also an important factor. It is because the high surface area and the short length of Li-ion diffusion can contribute to the high capacity and rate capability. However, the nano-scale grain size could be not good for the conductivity. In addition, the Fe_2O_3 AD film showed not only the nano-size grains but also the path for electrolyte as marked with yellow

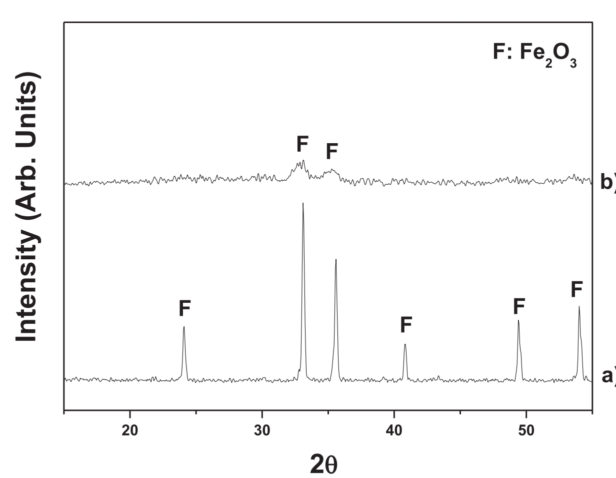

Fig. 2. X-ray diffraction (XRD) patterns of Fe_2O_3 (a) powder and (b) aerosol deposition (AD) film: No secondary phase is found. The peaks of Fe_2O_3 AD film are broader than them of Fe_2O_3 powder because of the nano-size grains of Fe_2O_3 AD film.