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Unlocking the electrochemistry abilities of nanoscaled $Na_{2/3}Ni_{1/4}Mn_{3/4}O_2$ thin films

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ABSTRACT

Different thickness of $Na_{2/3}Ni_{1/4}Mn_{3/4}O_2$ thin films were deposited on stainless steel substrates by pulsed laser deposition technique. X-ray diffraction and field-emission scanning electron microscope results reveal that the thin film with highly preferred c-axis orientation is composed of homogeneous nano-sized grains. The charge/discharge tests indicate that the 0.55 μm thick film demonstrates a high initial discharge capacity of 175.3 $mAhg^{-1}$ and a retention of 91% after 30 cycles at a current density of 13 mAg^{-1}. Furthermore, as the current density increases from 13 to 130 mAg^{-1}, about 89% of its initial discharge capacity can be maintained, exhibiting excellent rate capability. These superior electrochemical properties would promote $Na_{2/3}Ni_{1/4}Mn_{3/4}O_2$ thin film to be a promising cathode material for sodium-ion micro-batteries.

1. Introduction

Thin film-based micro-batteries have been preferred as smaller electronic power sources due to their potential applications for complementary metal oxide semiconductor (CMOS) memory chips, smart cards, remote sensors, microelectromechanical systems (MEMS), implantable medical devices [1–4]. Numerous types of thin film electrodes with high energy density and electrochemical stability have been investigated for lithium-ion batteries (LIBs) [5–8]. However, the scarcity and uneven distribution of lithium result in the pursuit of alternative energy-storage materials [9,10]. Sodium-ion batteries (SIBs) hold much promise, owing to many advantages of sodium such as high abundance, wide distribution and suitable redox potential (only about 0.3 V above that of lithium) [11–15]. As a consequence, it is necessary and desirable to produce suitable thin film electrodes for sodium-ion micro-batteries.

Nowadays, a great variety of electrode materials have been researched for rechargeable SIBs. Among them, layered sodium transition metal oxides (Na_xMO_2, $0 \le x \le 1$, M = Mn [16], Ni [17], Fe [18], Co [19], V [20], etc. or their combinations [21–23]) are intensely studied as potential cathode materials. In particular, the Mn-based materials $Na_xM_yMn_{1-y}O_2$, which can provide large-sized tunnels for sodium ions (de-)intercalation, have shown outstanding properties. Bruce's group synthesized P2-$Na_{0.67}MnO_2$ by slow-cooled rout, which exhibited a capacity of 175 $mAhg^{-1}$ with good capacity retention. Then they also reduced the phase transitions by substituting Mn^{3+} ions with Mg^{2+} ions, and a content of 5% was sufficient to improve the cycling stability without affecting the capacity [24]. Lee et al. found that the diffusivity of Na-ions in the P2 structure was higher than that in the corresponding O3 structured Li compounds, which confirmed the superiority of P2-$Na_{2/3}Ni_{1/3}Mn_{2/3}O_2$ [25]. Recently, Zhao et al. showed that Ti substituted P2-$Na_{2/3}Ni_{1/4}Mn_{3/4}O_2$ (Ti = 0.20) could deliver a reversible capacity of 140 $mAhg^{-1}$ with the capacity retention over 92% after 25 cycles, even cycled at high upper cut-off voltage of 4.5 V [26].

Nevertheless, to date, very little work has been reported on the electrochemical behavior of Na_xMO_2 thin film despite some interesting results on powder. Compared to conventional compacted powder electrode, the thin film has close adhesion to the substrate, which could improve the electrical conductivity of active materials and drastically reduce charge transfer barrier. Besides, the thin film electrode is more appropriate for insight into the intrinsic properties of materials since it is free of additives and binders, which is an ideal system to measure the chemical diffusion coefficient for the fundamental studies [29].

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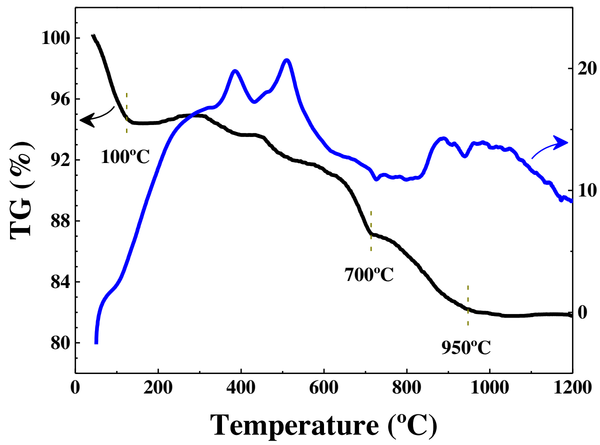

Fig. 1. TG/DTA curves of the as-prepared mixtures.

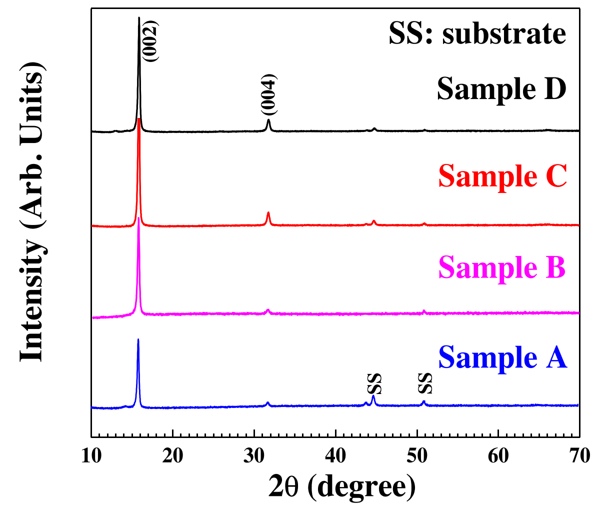

Fig. 2. XRD patterns of NNMO thin films.

In this work, in order to explore the electrochemical properties of $Na_{2/3}Ni_{1/4}Mn_{3/4}O_2$ thin films, we fabricated the samples on stainless steel substrates by pulsed laser deposition (PLD). In a variety of film-growth methods, PLD shows many advantages, for example, high texture, good crystallinity, easy to control thickness and uniformity, and direct stoichiometry transfer from the target to the film [30–32]. Electrochemical tests indicate that the 0.55 μm thick film behaves high capacity, excellent cycling performance and rate capability.

2. Experimental

The target for laser sputtering was prepared by the conventional solid state reaction method. NaOH (99.99%), MnO_2 (99.9%) and NiO (99.9%) were mixed using ball mill. These mixtures were calcined firstly at 750 °C for 24 h, then at 1000 °C for 12 h in air. A 248 nm laser beam, provided by the KrF excimer pulsed laser, was focused onto the surface of the target. The laser energy intensity and repetition frequency were 2 J/cm^2 and 10 Hz, respectively. Different thickness of $Na_{2/3}Ni_{1/4}Mn_{3/4}O_2$ (NNMO) thin films were deposited on stainless steel (SS) and SiO_2/Si (SOS) substrates at 750 °C in an oxygen partial pressure of 65 Pa for 30 min (Sample A), 60 min (Sample B), 120 min (Sample C) and 240 min (Sample D), respectively, followed by in-situ annealing for 60 min. Afterwards, all the samples were stored under an inert atmosphere.

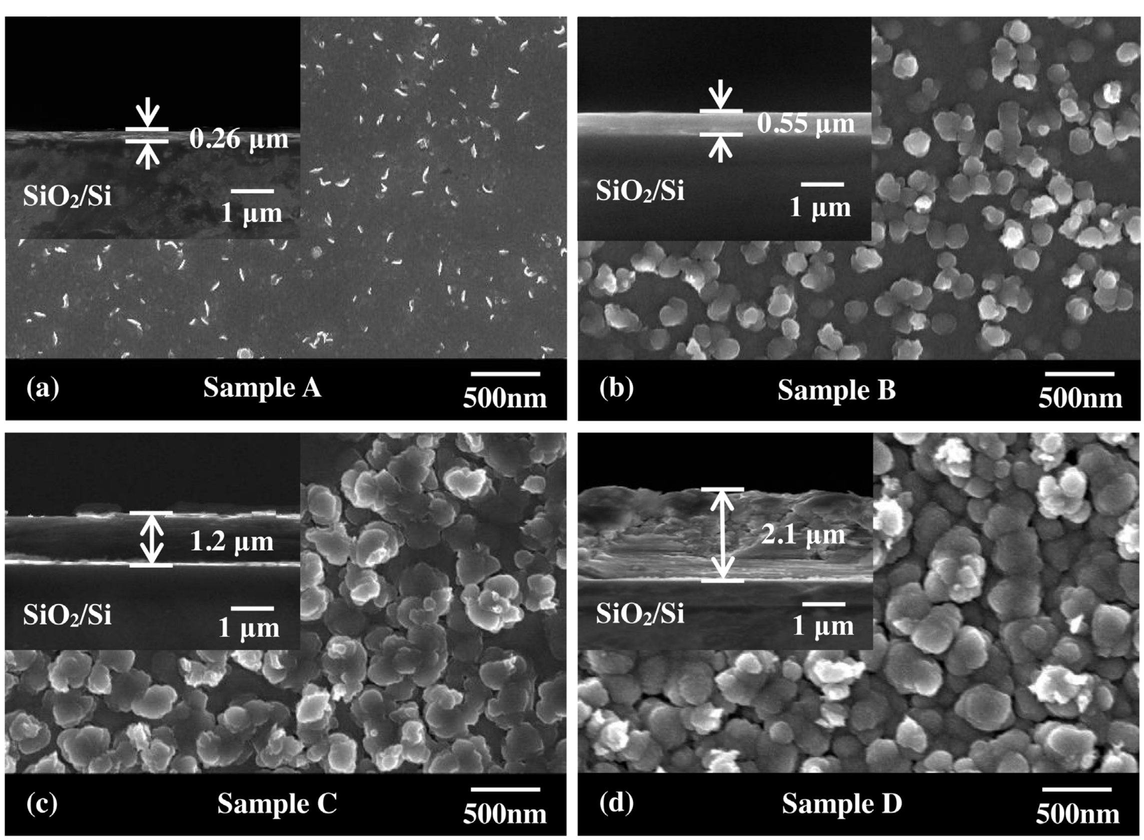

Fig. 3. FSEM images of the NNMO films on SS substrates, and (inset) cross-sectional views of the NNMO films on SiO_2/Si substrates.