Nanoflake δ-MnO$_2$ deposited on carbon nanotubes-graphene-Ni foam scaffolds as self-standing three-dimensional porous anodes for high-rate-performance lithium-ion batteries

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HIGHLIGHTS

- δ-MnO$_2$ is in-situ grown on nanocarbon materials.
- δ-MnO$_2$-CNTs-G-NF can accommodate the volumetric change during cycling process.
- δ-MnO$_2$-CNTs-G-NF shows an excellent capacity of 1357 mAh g^{-1} at 0.4 A g^{-1}.
- A high rate capactiy of 490 mAh g^{-1} is attained at 4.0 A g^{-1} over 700 cycles.

ARTICLE INFO

ABSTRACT

The electrification of transportation necessitates the growth of high-power-density lithium ion batteries. However, traditional graphite anodes in lithium ion batteries perform poorly especially when charged or discharged under high current density. In this work, we deposit nanoflake δ-MnO$_2$ on the carbon nanotubes-Graphene-Nickel foam compound matrix and apply it as a self-standing anode without binder or conductive agent. This composite buffers volume change, enables more electrochemical active sites, boosts the conductivity of electrode materials and facilitates lithium-ion diffusion. The resulting lithium ion batteries with the composite anodes show improved cycle life and enhanced rate performance, yielding a high specific capacity of 1250 mAh g^{-1} for 350 cycles at 0.4 A g^{-1} and 490 mAh g^{-1} over 700 cycles at 4.0 A g^{-1}.

1. Introduction

Amongst all the various energy storage devices, lithium ion batteries (LIBs) have generally been regarded as one of the most widely used secondary energy sources for portable electronic equipment like smartphones, tablet computers and mobile power packs. However, large scale applications on the electrification of transportation and MW-class battery storage units are growing rapidly. To meet the requirement for electric vehicles (EVs), it is essential to explore novel anode materials with a high specific capacity as well as superior rate and cycling performance as alternatives to the current graphite anodes in LIBs [1–3]. Hence, in recent years, high-capacity anode materials such as transition-metal oxides [4–9], silicon [10–14] and metal Li [15,16]

have been widely investigated as alternatives for these traditional carbon-based anodes.

Manganese dioxide (MnO$_2$), as one of the most potential transition-metal oxides, has arisen increasing attention owing to its high theoretical capacity (∼1230 mAhg^{-1}), low equilibrium voltage vs. Li/Li$^+$ [17,18], low-cost and environmental benignity [19,20]. However, several acknowledged challenges still exist and block the application of MnO$_2$ anodes in LIBs. These include rapid capacity fading, poor rate performance and low columbic efficiency caused by large volume expansion during the cycling processes and low electrical conductivity which is intrinsic.

In-depth studies have been carried out to ameliorate the above-mentioned problems of MnO$_2$-based anode materials, such as different
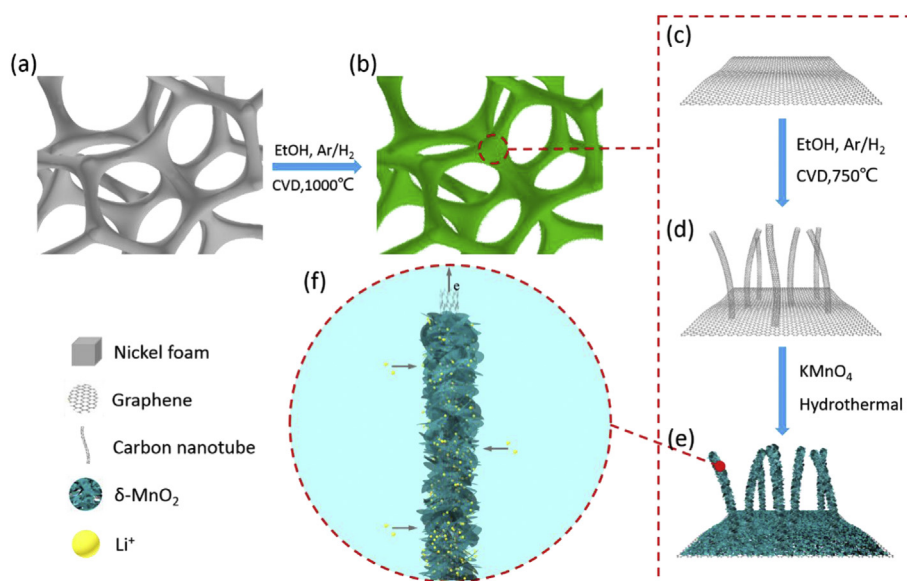

Fig. 1. Schematic illustration of preparing self-standing δ-MnO₂-CNTs-G-NF hybrids. (a, b) The 3D framework of NF and graphene-nickel foam (G-NF). (c–e) Schematic surface morphology of synthesized G-NF, CNTs-G-NF and δ-MnO₂-CNTs-G-NF, respectively.
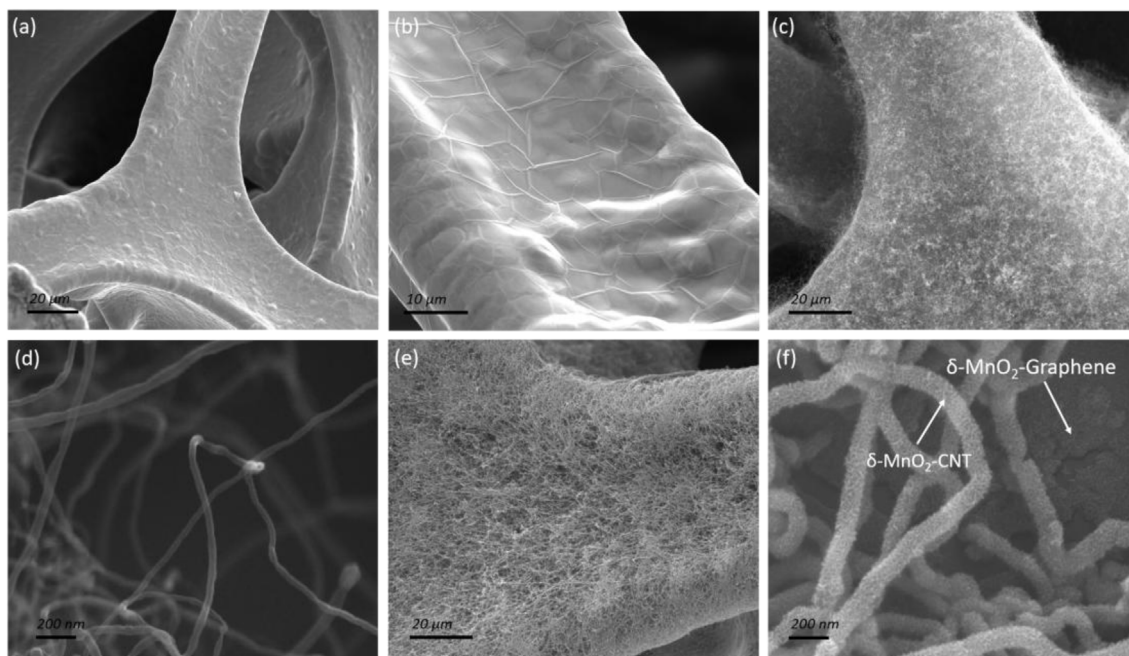

Fig. 2. SEM images of (a) surface of NF; (b) NF coated with graphene; (c, d) low and high magnification of CNTs grown G-NF substrate; and (e, f) low and high magnification of synthesized δ-MnO₂-CNTs-G-NF hybrid.

MnO_2 polymorphs (α-MnO_2 [21–24], β-MnO_2 [25,26], γ-MnO_2 [27–29], δ-MnO_2 [30,31]), morphology control to buffer volume change (nanocrystal [25], nanorods [21], nanoflakes [30]), composite design with carbon-based nanomaterials to enhance its conductivity [18,22,27,32], and combination with three-dimensional (3D) conductive matrixes to prepare self-standing electrode materials (steel plate [33], nickel foam [23,28,34], graphene [24,30,31]). Zhang et al. [32] reported an optimized microstructure δ-MnO_2/carbon nanotubes (CNTs) composite which delivered 903 mAh g^{-1} reversible capacity at 0.24 A g^{-1} and exhibited a good rate capacity of 540 mAh g^{-1} at a current density of 2.4 A g^{-1}. Yu et al. [24] prepared free-standing graphene/α-MnO_2 nanotube films as LIBs anodes, which delivered 686 mAh g^{-1} of reversible capacity at 0.1 A g^{-1} and 208 mAh g^{-1} at a higher current density of 1.6 A g^{-1}. However, considering the poor

conductivity and mediocre rate performance of MnO_2, the improvement on its ion diffusion, electrical conductivity is still worthy to be anticipated.

Herein, we construct a novel 3D self-standing composite and consider using δ-MnO_2 to grow on conductive nanocarbon materials and making the porous nickel foam as framework to achieve self-stand electrodes, which avoids the use of non-conducting binder. In the design, we use porous, conductive and robust NF to load nanocarbon and δ-MnO_2, fabricate *in-situ* grown δ-MnO_2 to enhance connection with carbon materials and increase composite conductivity, choose porous δ-MnO_2 nanosheets to enable more catalytic sites and shorter ion diffusion path. Besides, δ-MnO_2 nanoflakes and the overlapped δ-MnO_2-CNT clusters provide enough room for product accumulation and volume changing during the cycling process. Compared with previous works,