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Phase-tuned nanoporous vanadium pentoxide as binder-free cathode for lithium ion battery

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A B S T R A C T

Phase-controlled nanoporous vanadium pentoxide (V_2O_5) was prepared by electrochemical oxidation of vanadium foil as a binder-free cathode with high capacity and good cycling stability for lithium ion batteries. Increasing the annealing temperature led to the formation of a V_2O_5 film with preferential growth along the (001) plane on the as-prepared anodic film, resulting in enhanced Li ion diffusion and electronic conductivity. Thermal reduction of V_2O_5, depending on the annealing temperature, generated V_3O_7 and VO_2 (R), which affect both the cell capacity and stability. Appropriate development of the (001) plane and intermediate phases (such as V_3O_7 and VO_2) by thermal decomposition of the V_2O_5 lattice, determined by the annealing temperature, are key parameters for achieving high performance of the vanadium oxide cathode for Li ion batteries. The anodic V_2O_5 film annealed at 400 °C shows the highest discharge capacity of 170.1 mAh g^{-1} at fast charge/discharge rate (1.5 C) and good cycling stability for 100 cycles with a capacity retention of 91.4 %.

1. Introduction

Lithium ion batteries (LIBs) are superior power sources for energy storage systems and are widely used for electronic vehicles and portable electronics [1–3]. To meet the growing demands of advanced technologies, the development of electrode materials with high capacity, energy density, cycle stability, and safety is essential for next-generation LIB technology [4–6]. Graphite is the most widely used anode material [7,8], though alternatives including transition metals (Si, Sn, etc.) and metal oxides (SnO_2, TiO_2, etc.) with high specific capacities have been extensively investigated [9,10]. $LiCoO_2$ with a relatively high theoretical capacity (274 mAh g^{-1}) and good cyclability was first utilized as a cathode material by Goodenough and coworkers [11]. However, $LiCoO_2$ has become expensive due to the price surge of the Co component. In addition, the actual specific capacity is limited to 148 mAh g^{-1} because full-stoichiometric Li ions cannot be extracted due to irreversible transition of Li_xCoO_2 when 'x' is lower than 0.5 [12]. Similarly, other cost-effective cathode materials such as $LiMnO_2$ and $LiNiO_2$ have a relatively low actual specific capacity (140–150 mAh g^{-1}), even though the theoretical full-stoichiometric capacity is 285 and 275 mAh g^{-1}, respectively [13,14]. Thus, developing new cathode materials with high actual capacity, safety, and low cost is an important undertaking for LIBs.

Vanadium pentoxide (V_2O_5), which has the most stable state of vanadium (V^{5+}) of the multiple valence states (V^{2+}, V^{3+}, V^{4+}, and V^{5+}), is widely studied as a cathode material because of its low cost, simple synthesis, layered crystal structure for inter/deintercalation of Li ions, and high output voltage, all of which lead to high specific capacity [15]. In addition, V_2O_5 can react with up to 3 mol of Li ions, yielding respective specific capacities of 147, 294, and 441 mAh g^{-1} for the reactions with 1, 2, and 3 mol Li through the following phase transitions: (1) α-phase ($V_2O_5 - Li_{0.1}V_2O_5$ at 3.4 V); (2) ε-phase ($Li_{0.35}V_2O_5 - Li_{0.7}V_2O_5$ at 3.2 V); (3) δ-phase ($Li_{0.7}V_2O_5 - LiV_2O_5$ at 2.3 V); (4) γ-phase (Li $V_2O_5 - Li_2V_2O_5$ at 1.7–1.9 V); (5) ω-phase ($Li_2V_2O_5 - Li_3V_2O_5$) [16].

For practical use as a cathode material in LIBs, certain challenges must be overcome to improve the performance of V_2O_5; these include the relatively low diffusion coefficient of Li ions (10^{-12} to 10^{-14} cm^2 s^{-1}) in V_2O_5 [17,18], intermediate electrical conductivity (10^{-2} to 10^{-3} S cm^{-1}) [19,20], and irreversible phase transitions. Nanostructured V_2O_5 species, such as nanoparticles [21], nanowires

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