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Efficient construction of a $CoCO_3$/graphene composite anode material for lithium-ion batteries by stirring solvothermal reaction

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ABSTRACT

Transition-metal carbonates have recently been investigated as anode materials for lithium-ion batteries because of their relatively high capacity compared with that of the corresponding transition-metal oxides. In this work, a facile stirring solvothermal reaction is used to prepare a $CoCO_3$/graphene composite without the use of an additional organic chelating agent. The as-prepared $CoCO_3$/graphene composite exhibits a smaller cubic particle size of 1–2 μm and a larger specific surface area than the composite obtained by a traditional solvothermal reaction. The composite prepared with stirring delivers a highly reversible capacity of 602 mAh g^{-1} after 100 cycles. Even at a high current density of 2.0 A g^{-1}, the composite maintains charge–discharge capacities of 605/598 mAh g^{-1}. The composites contained the same amount of graphene, indicating that the improved electrochemical properties are attained independently of the amount of the graphene. In addition, the results of cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS)experiments also reveal that the $CoCO_3$/graphene composite electrode materials synthesised via a stirring solvothermal reaction exhibit substantially enhanced kinetics. The stirring solvo/hydrothermal reaction develops in this work is considered a promising candidate for efficiently preparing carbonate/graphene composites with better electrochemical properties for practical applications, without the use of an extra chelating agent.

1. Introduction

Lithium-ion batteries are considered one of the most efficient solutions to the energy and environmental crises. Various anode materials with high energy density and high cycling stability have been developed as potential substitutes for commercial graphite [1–4]. Among these materials, anodes based on transition-metal oxides [5–9] exhibit much higher capacities than graphite anodes, and almost all of the candidate transition-metal oxides have been studied in depth in works involving special morphological and composite modifications. According to the conversion mechanism, when used as anode materials for lithium-ion batteries, transition-metal carbonates should exhibit approximately the same or slightly lower lithium storage capacity than the related oxides. However, recent works have found that transition-metal carbonates deliver much higher capacity than the corresponding oxides [10–13]. In addition, metal carbonates can be facilely prepared at low temperatures without a high-temperature heat treatment. Metal carbonates are promising candidates for anode materials for lithium-ion batteries. Thus, works related to the performance of metal carbonates as anode materials have become common [14–18].

Because the electrochemical lithiation/delithiation mechanism of transition-metal carbonates is similar to that of transition-metal oxides, poor cycling stability resulting from their serious volumetric effect is also a bottleneck confronting the practical application of transition-metal carbonates as anode materials. One efficient approach to enhancing the stability of transition-metal carbonate electrodes relies on nanotechnology [19–22]. Zhao et al. prepared $CoCO_3$ nanoscale dumbbells through a hydrothermal synthesis route; as an anode material, the $CoCO_3$ dumbbells exhibited enhanced electrochemical performance compared with spherical $CoCO_3$ nanoparticles [23]. The $CoCO_3$ dumbbells delivered a capacity of 1042 mAh g^{-1} after 100 cycles at 200 mA g^{-1}. Another efficient approach is to form composites between transition-metal carbonates and other materials to restrict the defects induced by the volumetric effect [22,24]. Among the materials used in composites, graphene is considered one of the most efficient because of its ability to both serve as a buffer and offer a fast electron transport network [14,15]. Su et al. synthesised $CoCO_3$/graphene composites with improved cycling stability through a solvothermal route [10]. Their $CoCO_3$/GNS composites delivered capacities greater than 1000 mAh g^{-1}, which is much higher than theoretical values based on known lithium storage mechanisms.

Solvo/hydrothermal synthesis methods are popular for preparing

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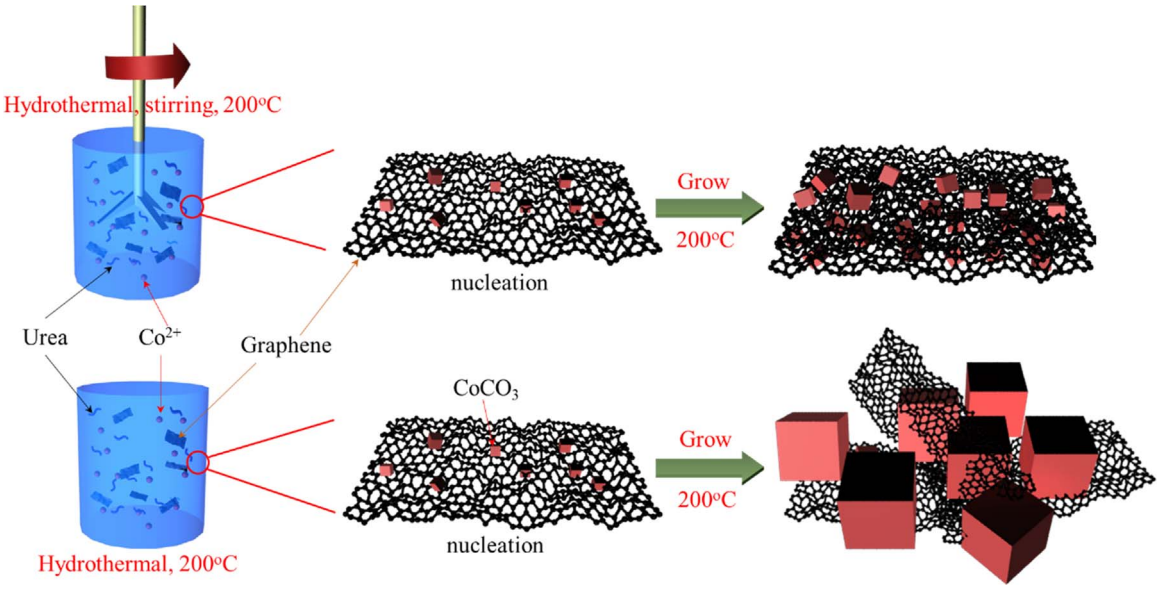

Fig. 1. Schematic of the differences between stirring solvothermal and traditional solvothermal reactions to prepare $CoCO_3$/graphene composites.

composites between metal oxides/carbonates and graphene [2,10,14,25]. Because of the functional groups of oxidative graphene, oxides/carbonates can be facilely grown on the surface of graphene. Usually, the addition of one or two complexing agents, such as polyvinylpyrrolidone (PVP) [10] or sodium dodecylbenzenesulfonate (SDBS) [11], is necessary to enable the construction of composites or to control the growth of $CoCO_3$ particles. In addition, most of the solvo/hydrothermal reaction mixtures remain still during the reaction, which may result in hysteresis of material diffusion and affect the growth of products.

In the present work, stirring is carried out during the solvo/hydrothermal process to obtain $CoCO_3$/graphene without the use of an additional complexing agent. The stirring minimises the hysteresis of the concentration deviation and changes the growth environment of the materials. Thus, compared with a $CoCO_3$/graphene composite prepared without stirring, a $CoCO_3$/graphene composite with a much more efficient structure and improved electrochemical properties was obtained under stirring conditions. The structure and performance of the $CoCO_3$/graphene synthesised with and without stirring are compared in depth. Such a strategy is promising for obtaining various composites (here, $CoCO_3$/graphene) with enhanced properties through solvo/hydrothermal reactions.

2. Experimental

Firstly, a 50 mL solution of deionised water and ethanol with a ratio of 2:1 (deionised water:ethanol) was prepared as the solvent. Then, 50 mg of oxidative graphene was added to the aforementioned solution, resulting in a graphene concentration of 1 mg mL^{-1} after ultrasonic dispersion for 30 min. Afterwards, 1.125 g of $Co(CH_3COO)_2{\cdot}4H_2O$ and 1.5 g of urea were added to the aforementioned solution and the resultant solution was stirred for 12 h. Finally, the solution was pulled into a 100-mL Teflon-lined autoclave, which was subsequently sealed. The reaction conditions were set as 200 °C for 6 h with stirring at various speeds during the whole reaction process. After the reaction, the precipitate was collected by centrifugation. The final $CoCO_3$/graphene, which was labelled as S-$CoCO_3$, was obtained after the precipitate was dried at 60 °C in a vacuum oven. Another sample of $CoCO_3$/graphene was synthesised using the same processes as those used to prepare S-$CoCO_3$ but without stirring during the solvothermal reaction. The final product was labelled as T-$CoCO_3$.

The phase of the $CoCO_3$/graphene was determined by X-ray diffraction (XRD); the samples were scanned at a rate of 4° min^{-1} from 10° to 80° on an X-ray diffractometer (Rigaku D/max-2200-PC) equipped with a Cu K_α radiation source. Thermogravimetry/differential scanning calorimetry (TG/DSC) of the reactions was performed on a thermogravimetric analyser (TGA/SDTA851) and a thermal analyser (STA 449 F3). Field-emission scanning electron microscopy (SEM, ZEISS SIGMA microscope) was used to characterise the morphologies of the ternary layered oxides. The surface area, including the pore distribution, was determined using a Brunauer–Emmett–Teller (BET) surface-area analyser (Micromeritics ASAP 2020). The structure of the $CoCO_3$/graphene composites was further characterised by high-resolution transmission electron microscopy (TEM, TECNAI G20). Furthermore, the surface environments of the $CoCO_3$/graphene were characterised by X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab 250Xi) using Al-Kα radiation.

The working electrodes were prepared as described in our previous work [26]. The galvanostatic discharge/charge tests were performed on a LAND battery test system (Wuhan, China) at room temperature within the electrochemical window from 0.001 to 3.0 V. The test current densities were varied from 100 to 2000 mA g^{-1}. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (CH Instruments CHI660E). The CV experiments were carried out within a potential window from 0 to 3.0 V (vs. Li/Li^+) and at a scan rate of 0.1 mV s^{-1}. EIS was carried out using a three-electrode cell with metallic Li foil as both the counter and reference electrodes and the $CoCO_3$/graphene as the working electrode.

3. Results and discussion

3.1. Materials characterisation

A schematic of the solvothermal reactions with and without stirring is shown in Fig. 1. During the long stirring period before the reaction, the Co^{2+} is attracted to the surface of the graphene via electrostatic interaction between the functional groups of the graphene and Co^{2+}. Upon decomposition of the urea, carbonate begins to appear on the surface of the graphene. Differences appear between the stirred and unstirred samples as the reaction proceeds. Because of the stirring, more efficient contact is achieved between the ions and graphene, which leads to the formation of more small $CoCO_3$ cubic particles rather than to the growth of $CoCO_3$ particles. However, in the absence of