Salt-template assisted preparation and electrochemical performance of MnO/C nanosheet composite electrode for lithium-ion battery

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A B S T R A C T

MnO/C nanosheet composites have been prepared by heating NaCl@Mn(Oleate)$_2$ particles at 600 °C with a heating rate of 10 °C min^{-1} under Ar atmosphere for 3 h, and NaCl@Mn(Oleate)$_2$ particles are obtained by coating NaCl powder with the solution of Mn(Oleate)$_2$/n-hexane. The effects of NaCl amount, heating temperatures and heating rates on the grain size and dispersity of MnO crystals are systematically investigated, respectively. The results show that NaCl plays an important role in providing the surface to fabricate the MnO/C nanosheet composites. The thickness of MnO/C nanosheet is influenced by the amount of NaCl, and its optimal amount is 7.5 g as the weight ratio of 12.146 to Mn(Oleate)$_2$. The dimension and morphology of the MnO nanocrystals embedded on the carbon nanosheets are affected by the heating rates and heating temperatures of NaCl@Mn(Oleate)$_2$ particles as well. On the other hand, the conductivity of the obtained composites is well improved during the lithiation/delithiation processes. Meanwhile, the aggregation of MnO nanoparticles is effectively mitigated by the construction of carbon network structure. MnO/C nanosheet composite electrodes exhibit a high reversible capacity of 783 mAh g^{-1} in the second cycle at a current density of 0.1 A g^{-1}, excellent cycling stability with a capacity retention of 71.7% and good rate performance as the anode in lithium ion battery. The synthetic procedure in the present study could be extended to prepare other metal oxide/carbon nanosheet composites for energy storage materials.

1. Introduction

The energy source is becoming more deficient with the rapid development of social economy. Extensive research works have been carried out to develop a new energy storage device, such as rechargeable lithium-ion batteries (LIBs), sodium-ion batteries, and supercapacitor, etc. [1,2]. Regarding the enlarged capacity of next-generation LIBs, great efforts have been made to prepare anode materials with novel structure to replace commercial graphite, such as transition metal oxides (Fe$_2$O$_3$, Fe$_3$O$_4$, Co$_3$O$_4$, NiO, SnO$_2$) [3–7]. Among the potential anode materials, MnO recently has recently attracted much attention owing to its high theoretical capacity (755 mAh g^{-1}), a low operation potential (1.032 V vs Li/Li$^+$), high abundance and low contamination to environment compared to other transition metal oxides [8,9]. However, the intrinsic conductivity of MnO is expected to be improved due to its poor rate capability and inferior cycling stability. It may be a good choice to coat or hybridize advanced carbon

nanomaterials on MnO particles to overcome the above disadvantages. The co-existed carbon ingredient could not only mitigate the stress in the formation and decomposition of Li$_2$O during cycling but also effectively inhibit the aggregation of MnO nanoparticles [10,11], as well as improve the electronic conductivity by using the carbon coating layer.

MnO-carbon based hybrid material electrodes with different morphologies and structures have been experimentally studied by using various carbon coating techniques recently. For example, various MnO/C materials have been prepared by adopting the biotemplating technology [8], a simple double-template strategy [12], free template method assisted with freeze drying [13], reduction reaction of MnO$_2$ or Mn$_3$O$_4$ [14,15], the pyrolysis of Mn-based compound and carbon materials (MnC$_2$O$_4$, manganese oleate, etc.) [16,17]. The experimental results indicate that the Li-ion storage properties of the obtained electrodes can be obviously improved by the coating technique. Monodisperse MnO/C microsphere electrodes have been fabricated

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by applying a green and facile biotemplating method. Large reversible specific capacity, outstanding cycling stability and good rate performance of 230 mAh g^{-1} at 3 A g^{-1} can be appreciated [8]. The carbon-coated MnO porous microsphere electrodes (MnO@C) are obtained by carbonization of the pyrrole coated porous Mn$_2$O$_3$, and they possess a specific capacity of 525.4 mAh g^{-1} at 0.1 A g^{-1} after achieving 100 cycles [18]. Jiang et al. annealed the MnO precursor/polydopamine core/shell nanostructure in an inert gas to get a peapod-like MnO/C heterostructure electrode, and it has a high reversible capacity of 1119 mAh g^{-1} at 0.5 A g^{-1} as anode material for LIBs [9].

The aforementioned experimental results also indicate that the nanocrystallization and self-assembly of the advanced materials can effectively improve the electrochemical performances, conductivity and charge/discharge rates of the obtained electrodes, on basis of the shorter transport path for electrons and ions than the bulk materials [19–22]. MnO nanoparticles with various morphologies and sizes loaded into carbon materials have been prepared by different methods. However, it is still a challenging work to prepare MnO nanocrystals with uniform cubic morphology and good dispersion embedded uniformly on the surface of carbon nanosheets.

Salt-template technology has been found to be favorable to prepare metal oxide nanocrystals with novel morphologies and good dispersion, since the salt crystals are both easily soluble and provide several wide crystal surfaces. AgCl hollow cube is prepared by using NaCl templates at ambient temperature [23]. By using sodium sulfate particles as a sacrificial template, uniform-sized ferrite nanocrystals and carbon materials with 2-D nanostructures are synthesized by heating metal-oleate complex [24]. With the surface assistance of NaCl crystals, Fe@C@PGC 2-D nanosheets have been synthesized by selecting Fe(NO$_3$)$_3$·9H$_2$O and C$_6$H$_{12}$O$_6$ as the metal and carbon precursor [25]. In this study, MnO/C nanosheet composites with regular hollow microcube morphology can be prepared by heating NaCl@Mn(Oleate)$_2$ particles at 600 °C for 3 h with a heating rate of 10 °C min^{-1} under Ar atmosphere, in which NaCl@Mn(Oleate)$_2$ particles are obtained by coating NaCl powder with the solution of Mn(Oleate)$_2$/n-hexane. The effects of the amount of NaCl, heating temperatures and heating rates on the grain size and dispersity of MnO crystals are experimentally investigated. The obtained MnO/C nanosheet composite electrodes exhibit a high reversible capacity, good cycling stability and excellent rate performance as lithium ion battery anodes. The synthetic procedure in the present study could be extended to prepare other metal oxide/carbon nanosheet composites for energy storage materials.

2. Experimental section

2.1. Materials

All reagents were of analytical grade without further purification. MnCl$_2$·4H$_2$O (99%) and NaCl (99%) were purchased from Sinopharm Group Co. Ltd. Sodium oleate was purchased from TCI Shanghai.

2.2. Sample preparation

Manganese oleate complex (Mn(Oleate)$_2$) was prepared according to a reported procedure [26]. In a typical synthesis, 3.9583 g MnCl$_2$·4H$_2$O and 12.1780 g of sodium oleate were dispersed in a mixture solvent, which was consisted by 80 mL distilled water, 40 mL ethanol and 70 mL hexane. The above mentioned solution was heated at 70 °C for 4 h. When the reaction was completed, the Mn(Oleate)$_2$ existing in the upper organic layer was washed with 30 mL distilled water for three times in a separatory funnel. The organic layer was dried to form Mn(Oleate)$_2$ in a waxy solid at 70 °C for 12 h in air.

The MnO/C nanosheet was prepared according to the following procedure: 5 mol L^{-1} NaCl solution was added into anhydrous ethanol with vigorous stirring, immediately forming a cloudy suspension mingled with NaCl crystals [23]. The NaCl crystals were obtained after

the separation of the NaCl cloudy suspension and dried at 50 °C for 12 h. 7.5 g of NaCl powder was dispersed in Mn(Oleate)$_2$/n-hexane solution, which was composed of 0.6175 g Mn(Oleate)$_2$ and 10 mL n-hexane. NaCl@Mn(Oleate)$_2$ fine powder was in-situ formed by grounding mechanically along with n-hexane volatilizing in this process. The NaCl@Mn(Oleate)$_2$ particles were then heated to 600 °C at a heating rate of 10 °C min^{-1} under Ar atmosphere for 3 h. After being cooled, the products were washed with distilled water and dried at 50 °C for 24 h. The influences on the grain size and dispersity of MnO crystals were systematically investigated by controlling the different influence factor. The detailed information is mentioned in Table S1. The amount of NaCl and Mn(Oleate)$_2$ is controlled to 1.5, 2.5, 3.5, 5, 7.5 and 10 g. The heating temperature is altered to 400, 600 and 750 °C. The heating rate is changed to 5, 10 and 15 °C min^{-1}, respectively.

2.3. Characterization

The X-ray diffraction (XRD) patterns were obtained on a Rigaku MiniFlex600 diffractometer with CuKα (λ = 1.5406 Å), controlling an operation voltage and current of 40 kV and 15 mA, respectively. The SEM and FESEM images were taken with Quanta 200 environmental scanning and Quanta 600 F field emission scanning electron microscopy, respectively. TEM images were recorded on a JEM-200c transmission electron microscope, by using an electron kinetic energy of 200 kV. The X-ray photoelectron spectra (XPS) were recorded with the Axis Ultra spectrometer from Kratos Analytical Ltd. The binding energy reference was taken at 284.6 eV for the C 1 s peak arising from surface hydrocarbons. The Raman spectra were measured by using an Invia Raman microscope (wavelength = 532 nm, light power = 20 mW) between 200 and 1200 cm^{-1} at room temperature. Thermal analysis was determined on TGA-DSC analysis (Q1000DSC + LNCS + FACS Q600SDT) at a heating rate of 10 °C min^{-1} from 25 to 800 °C under air atmosphere.

2.4. Electrochemical measurements

The CR2032 coin-type cells were assembled in an argon-filled glove box for evaluating the electrochemical performance of prepared materials. The working electrode was consisted of 80 wt% MnO/C nanosheet composites as active material, 15 wt% acetylene black, and 5 wt% polyvinylidene fluoride (PVDF) binder. The slurry was formed by milling the above mentioned three components with the assistance of anhydrous ethanol as a solvent. Then the mixture was coated on the Al foil disks with the diameter of about 12 mm. The loading mass of MnO/C composite on the electrode is about 3 mg cm^{-2}, and the actual capacities are calculated on basis of the mass of MnO/C composite. To assemble the working electrode, lithium metal disk was selected as counter electrode and Celgard 2400 microporous membrane was used as a separator. 1 M LiPF$_6$ was adopted as the electrolyte which was dissolved in dimethyl carbonate (DMC)/diethyl carbonate (DEC)/ethylene carbonate (EC) with 1:1:1 vol ratio. The galvanostatic charge/discharge tests were conducted over a voltage window of 0.05−3 V on LAND CT-2001A battery cyclers at 25 °C. The actual capacity was calculated based on the mass of MnO/C composites, and the detailed was shown in the following equation:

$$\text{Actual capacity} = I \cdot T / m_{\text{(MnO/C composites)}} \quad [I: \text{ current (mA)},$$

T: time (h), m: mass (g)].

3. Results and discussion

The morphology of the MnO/C nanosheet composites was investigated by SEM, FESEM and TEM images in Fig. 1. The MnO/C nanosheet composites are formed, and hollow cubic morphology are maintained after the NaCl cubic crystals removing as shown in Fig. 1a