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Carbon Coated MnO@Mn₃N₂ Core-Shell Composites for High Performance Lithium Ion Battery Anodes

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Carbon coated $MnO@Mn_3N_2$ core-shell composites $(MnO@Mn_3N_2/C)$ were synthesized at a simple approach by calcining MnO_2 nanowires with urea at 800 °C under ammonia atmosphere. Urea derived carbon nanosheets partially coated on pure phase $MnO @Mn_3N_2$ core-shell composites. Electrochemical measurements reveal that the $MnO@Mn_3N_2/C$ displayed high discharge capacities, excellent high-rate capability and enhanced cycling performance.

Rechargeable lithium-ion batteries (LIBs) have long been considered an attractive power source for future advanced transportation equipment and electric vehicles (EVs) over traditional rechargeable battery systems.¹ Carbon materials are most commonly used as anode materials in today's LIBs.² With the growing demand for high energy density secondary batteries, the low capacity of graphite (theoretical capacity: 372 mAh g⁻¹) has become limited for a wider applications.³ At present, novel anode materials and the related mechanism are extensively explored to improve capacity performance and rate capability. These include alloying or conversion reaction with silicon, tin-based alloy, metal oxides, metal hydrides, metal sulfides, metal fluorides and metal phosphides.^{1, 2, 4-7}

Recently, MnO with the theoretical capacity of 756 m Ah g^{-1} , was found reversibly formed and decomposed in subsequent cycles.⁸⁻¹³ Because of its low cost, environmental benignity, the high abundance of Mn and relatively lower thermodynamic equilibrium voltage (1.032 V vs. Li⁺/Li), MnO is considered as an attractive anode material for LIBs.¹² However, there still remain at least two issues greatly constraining the cycle and rate performance of MnO electrode: one is huge volume changes caused by the Mn in the oxide alloyed with lithium which normally results in the crushing and powdering of electrodes and continuous formation of the solid electrolyte interphase (SEI) in freshly exposed areas that appear in each cycle.^{2, 5, 11} The other is side reactions due to un-protected surface of single-phased materials, leading to continuous capacity loss.⁵ Up to now, a variety of methods have been devoted to

optimize MnO.^{8, 10-12, 14-21} It is well established that core-shell hybrid structures are currently recognized as the potential candidates to solve the above issues, which could improve the chemical and structure stability, prevent particles from aggregation, and lessen the compounded internal stresses.^{12, 21, 23}

Metal nitrides are also considered as a promising group of anode material for LIBs.^{1,9} They have superior chemical resistance properties, low and flat potentials close to that of lithium metal along with high molar density. Moreover, Li₃N, formed by the irreversible conversion reaction of metal hydrides and lithium, has an exceptionally high Li-ion conductivity (approximately 10^{-3} S cm⁻¹) which leads to more stable and complete SEI film, lower electrode/electrolyte interface resistance and facile distance for Li ion diffusion.^{24, 25} Recently, the electrochemical behavior of Sb₃N, Ni₃N, Co₃N, Fe₃N, VN as anode materials for LIBs have been investigated, and found that they can be indexed to conversion reaction mechanism.²⁶⁻²⁹ Generally, The MnO, Mn_3N_2 and carbon derived by organics formed in reducing atmosphere, so we can enhance both the Li⁺ transmittability and electronic conductivity of the MnO by coating both Mn₃N₂ and carbon in same synthesis condition with controlled ratio, it can be expected that the cycling and rate performance of MnO can dramatically improve with a slightly decreased capacity. ^{11, 25, 27} Unfortunately, considering the essentially high melting point and chemically inert behavior of metal nitrides, it still remains a challenge to synthesize core-shell structured MnO@Mn₃N₂ with high crystalline. Herein, we reported a simple approach to synthesize carbon coated MnO@Mn₃N₂ coreshell composites (MnO@Mn₃N₂/C) by calcining MnO₂ nanowires with urea at 800 °C under ammonia atmosphere. Such MnO@ Mn₃N₂ core-shell composites with partial carbon coating, produced by one-step synthesis approach, present a much better electrochemical performance than pure phase MnO, carbon coated Mn_3N_2 (Mn_3N_2/C) and carbon coated MnO (MnO/C), including higher capacity and excellent rate capability.

The MnO_2 nanowires (Fig. S1) were mixed with urea by manual agitation in mass ratio of 0, 200, 1000 wt % to prepare MnO, $MnO@Mn_3N_2/C$ and Mn_3N_2/C respectively. The mixtures were

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calcined in a tubular furnace at 800 °C under ammonia for 3 h with a careful controlled heating ramp (See Supporting Information). It is believed that the urea can continuously release ammonia to provide a reduced ambient and nitrogen-rich condition, which faciles the nitridation process. The urea derived carbon can improve the conductivity of the composites and as a functional dispersing agent to decrease the particle size of composites. For studying the effects of carbon, we have also calcined MnO₂ nanowires with 20 wt % sucrose at 800 °C under NH₃, in which the yielded sample denoted as MnO/C.



Fig. 1. XRD patterns of MnO (a), MnO@Mn_3N_2/C (b), Mn_3N_2/C (c) and MnO/C (d) with standard data.

XRD patterns of the MnO, $MnO@Mn_3N_2/C$, Mn_3N_2/C and MnO/C are shown in Fig. 1. The positions of diffraction peaks in the pattern of MnO and Mn_3N_2/C are well ascribed to the standard data respectively. It is indicated that without urea, the MnO_2 nanowires were hard nitride into metal nitrides. It can be observed that the $MnO@Mn_3N_2$ composites have both cubic phase of MnO and tetragonal phase of Mn_3N_2 . The sucrose derived carbon shows a weak diffraction peak at 25.8 (20) in the XRD pattern of MnO/C.



Fig. 2. HRTEM images of $MnO@Mn_3N_2/C$ (a), an expanded HRTEM images (b and c) for the marks (1) and (2) in (a), HRTEM images of MnO (d), Mn_3N_2/C (e) and MnO/C (f), respectively. EDX spectra (inset in c and d) showing the presence of Mn, C, N, O.

Fig. 2 shows the high-resolution transmission electron microscopy (HRTEM) images of the MnO@Mn₃N₂/C. It is revealed that clear lattice fringes had a space of around 2.11 Å corresponding to the (110) plane of tetragonal phase of Mn₃N₂ (Fig. 2c). The energy dispersive X-ray (EDX) spectrum confirms the chemical composition of Mn₃N₂, suggesting the Mn₃N₂ with high crystalline was coated on the surface of MnO. The HRTEM image of MnO (Fig. 2d) shows that the lattice fringes had a space of around 2.56 Å corresponding to the (111) plane of cubic phase of MnO. The EDX spectrum of MnO (Fig. 2d, inset) has indicated undetectable metal nitrides in MnO, being consistence with the XRD results. Fig. 2f shows the HRTEM images of MnO/C. It is clear that the MnO was uniformly modified with a film. The lattice fringes of the nanosheets on the surface of $MnO@Mn_3N_2/C$ (Fig. 2b) and Mn_3N_2/C (Fig. 2e, inset) had a space of around 3.45 Å corresponding to the (002) plane of carbon, and CHN analysis data show that the average carbon content in MnO@Mn₃N₂/C and Mn₃N₂/C were 3.04 and 4.31 %. It is indicated that urea derived carbon nanosheets were coated on the surface of compositess.



Fig. 3. Electrochemical impedance spectroscopic (A) at open circuit potential with an AC voltage of 5 mV amplitude in the 100 mHz to 100 kHz frequency range, The insets is the magnified curves. Cyclic voltammograms (B) of MnO/C (1), MnO@Mn₃N₂/C (2), Mn₃N₂/C (3) and MnO (4) electrodes with the first three cycles between 3.0 to 0.0 V (vs. Li⁺/Li) at a scan rate of 0.1 mV s⁻¹; Charge-discharge galvanostatic curves of MnO/C (5), MnO@Mn₃N₂/C (6), and Mn₃N₂/C (7) electrodes at rates of 100, 200, 500, 1000 and 2000 mA g⁻¹ between 3.00 and 0.05 V, and MnO (8) electrode with the first five cycles at rates of 100 mA g⁻¹ between 3.00 and 0.05 V.

To test the improvement of Li^+ transmittability and electronic conductivity of the MnO, the electrochemical impedance spectroscopy (EIS) was conducted to study the dynamics for lithium

insertion and extraction in samples (Figure 3A). According to the Nyquist plots, MnO, MnO/C, MnO@Mn₃N₂/C and Mn₃N₂/C electrode had R_{CT} value of 409, 126, 108, 91 Ω , respectively, revealing significantly lower charge-transfer resistance by coating with carbon and the nitride also have benefit to improve electronic conductivity. Generally, the diffusion coefficient of Li ions (D_{Li+}) can be calculated by the method described in the supporting information. D_{Li+} of MnO, MnO/C, MnO@Mn₃N₂/C and Mn₃N₂/C electrode were 1.16×10^{-10} cm² s⁻¹, 1.07×10^{-9} cm² s⁻¹, 2.68×10^{-9} cm² s⁻¹, and 3.84×10^{-9} cm² s⁻¹. It can be seen that after coat with carbon, the D_{Li+} of MnO/C was approximately larger ten times than MnO, while with the increase of Mn₃N₂ in the composite, the D_{Li+} increased signally, highlighting facile of Li+ ion diffusion in coating layer and the Li⁺ ion diffusion can be controlled by change the ratio of carbon and Mn₃N₂.

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The first three cyclic voltammogram (CV) curves of MnO/C, MnO@Mn₃N₂/C, Mn₃N₂/C and MnO are shown in Fig. 3B (1-4) respectively. It is observed that the MnO/C and MnO@Mn₃N₂/C electrodes have sharp peaks at around 0.40 V in the first two anodic scanning processes, the latter is broader due to its two phase crystals which result in complicated electrochemical reactions. These peaks were vanished in the third cycle and much broader peaks appeared at around 0.7 V for MnO/C and 0.6 V for MnO@Mn₃N₂/C. Single broad cathodic peak around 1.25-1.3 V was found in all three cycles. It is revealed that the cathodic peak shapes and current intensities of MnO@Mn₃N₂/C were maintained better than MnO/C, indicating higher reversible capacity of MnO@Mn₃N₂/C and better kinetics for lithium insertion and extraction.²¹ Mn₃N₂/C electrodes had broad anodic peaks at 0.4 V, 0.7 V and 0.8 V along with cathodic peaks at 1.4 V. The peak shapes maintained well but the peaks shape were broad and current intensities were low, suggesting the Mn₃N₂/C electrodes had stable structure but bad kinetics for lithium insertion and extraction. Because of low activity, the CV curves of MnO shows unapparent redox peak. Fig. 3B (5-8) show the chargedischarge curves of MnO/C, MnO@Mn₃N₂/C, Mn₃N₂/C and MnO at different specific rates respectively. The MnO@Mn₃N₂/C exhibited excellent rate capability with initial discharge capacities of 1193 (100 mA g^{-1}) , 545 (200 mA g^{-1}) , 436 (500 mA g^{-1}) , 342 (1 A g^{-1}) , and 264 mA h g^{-1} (2 A g^{-1}). It is worthwhile noted that the performance of MnO@Mn₃N₂/C was significantly improved in comparison with MnO/C and Mn₃N₂/C, which displayed the capacities of 1080 (100 mA g⁻¹), 298 (200 mA g⁻¹), 233 (500 mA g⁻¹), 183(1 A g⁻¹), and 155 mA h g $^{-1}$ (2 A g $^{-1}$) for MnO/C, and 697 (100 mA g $^{-1}$), 213 (200 mA g⁻¹), 166 (500 mA g⁻¹), 128 (1 A g⁻¹), and 105 mA h g⁻¹ (2 A g⁻¹) for Mn₃N₂/C respectively. The capacity of bare MnO was below 100 mA h g^{-1} after first cycle shows quit low activity. These results demonstrate that MnO@Mn₃N₂/C not only can enhance the capacity but also improve the rate capability. In addition, the discharge potential plateau of MnO@Mn₃N₂/C, as same as MnO, was higher than that of MnO, indicating higher capacity of MnO@Mn₃N₂/C than Mn_3N_2/C .



Fig. 4. Variation in specific capacities versus cycle numbers of

MnO@Mn₃N₂/C (\blacksquare), Mn₃N₂/C (\blacktriangle), MnO/C (\square) and MnO (\triangle),

under different rates of 100 mA g-1, 200 mA g-1, 500 mA g-1, 1 A g-1 and 2 A g-1 between voltage limits of 3.00 and 0.05 V.

Fig. 4 shows the rate and cycle performances of MnO@Mn₃N₂/C, Mn₃N₂/C, MnO/C and MnO. After 60 cycles with current density constantly changing, the reversible capacity of MnO@Mn₃N₂/C can still maintain above 626 mA h g 1 with current density of 100 mA g⁻¹, while the MnO/C retained a capacity of 261 mA h g^{-1} , that of the Mn₃N₂/C was 329 mA h g^{-1} and that of MnO faded to less than 25 mA h g⁻¹ after 30 cycles with current density changing to 500 mA g⁻¹. Fig. S2 shows that the coulombic efficiency of as-prepared batteries use MnO@Mn₃N₂/C, Mn₃N₂/C, MnO/C and MnO as anode, during 60 cycles, the coulombic efficiency of MnO@Mn₃N₂/C changes little, from 61% to 59%, while Mn₃N₂/C and MnO/C changes from 61% to 17% and 12%, respectively. The coulombic efficiency of MnO was lower than 9% after 25 cycles. Fig. S3 shows that the high ionic conductivity of Li₃N can be clearly seen on the surface of electrode, which was generated by decomposing of Mn₃N₂. It is believed that the excellent capacity retention for MnO@Mn₃N₂/C after cycling is attributed to the core-shell structure of Mn₃N₂ and MnO, partial carbon coating and high crystalline with pure phase which greatly facilitates the kinetics of Li⁺ insertion and extraction

The above results clearly reveal that MnO@Mn₃N₂/C exhibits significantly improved performance in comparison with the MnO/C and Mn₃N₂/C samples. Actually, the as-developed MnO@Mn₃N₂/C also outperforms Mn₃N₂ reported by Fu, who fabricated Mn₃N₂ thin films by magnetron sputtering, and the reversible capacity of Mn_3N_2 thin films was 579 mA h g⁻¹ at 80 mA g⁻¹.²⁷ Notably, this work provides at least three significant observations for the distinct improvement of electrochemical performances in the samples of MnO@Mn₃N₂/C: 1) Mn₃N₂, as shell coated on the surface of MnO, with higher discharge potential plateau than MnO, would firstly react with lithium conversed to Mn and Li₃N, while the Li₃N could demonstrate a complete SEI film on electrode, which may greatly improve the stability of the electrode and facilitate kinetics of lithium insertion and extraction;¹³⁻¹⁵ 2) This ammonia nitridation approach assisted by urea, produces highly crystalline pure phase Mn₃N₂/C and MnO without introducing reducing agent including other elements. In that case, the composites have robust

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homogeneous structures, which may greatly decrease the possibility of the reunion and collapse of nanostructures; 3) Urea derived carbon nanosheets coated on the surface of crystalline $MnO@Mn_3N_2/C$, which produced an efficient electronic and ionic conducting network, could obviously enhance electronic conductivity, facilitate the electron transport and greatly decrease the Ohmic energy loss.^{12, 23, 24}

Conclusions

In summary, we have successfully developed a reliable strategy to synthesize high crystalline MnO@Mn₃N₂/C with the assistance of sucrose. The MnO@Mn₃N₂/C delivered superior lithium-storage capability during 60 cycles with current density changes randomly form 100 to 2000 mA g⁻¹. The conspicuous improvement for rate and cycle performance could be attributed to core-shell structure of Mn₃N₂ and MnO, partial carbon coating and high crystalline with pure phase. Taking the excellent electrochemical performance and facile fabrication into consideration, the presented MnO@Mn₃N₂/C is envisaged to be a competitive candidate anode material of high-performance LIBs. Furthermore, this approach can be easily extended to fabricate various carbon coated core-shell structure metal nitrides/metal oxides composites.

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Notes and references

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