Constructing hierarchically porous MnO/C composite to induce diffusion kinetics for high-performance lithium-ion batteries

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Abstract: Hybridization with transition metal oxide is broadly realized as an attractive way to smash the capacity limitation of carbon-base materials upon lithium storage. However, the influence of metal ions on the fast reaction kinetics of the electrode is still a confusing topic. Herein, a common molten salt method is displayed to fabricate hierarchically porous MnO/carbon composites. The addition of LiCl and KCl induces the fluid reaction substance by forming molten salt at a high-temperatures to beneficially achieve the activation and breaking of the carbon particles. The abundant porous and homogeneou carbon skeletons validly raise the ion/electron diffusion and transferability to prevent MnO particles from agglomerating, thereby inducing the diffusion kinetic. Moreover, the hierarchical porous MnO/carbon composite offers a highly invertible capacity of 851 mAh g⁻¹ at 0.1 A g⁻¹ and outstanding cyclic performance. This work has opened up a path for metal oxidation/carbon composite materials in electrochemical energy storage.

1. Introduction
Carbon-base materials are considered to be the main focus for lithium storage owing to their benefits of high conductivity and porous structure[1-2]. The carbon-based lithium-ion batteries (LIBs) achieve lithium storage through the Li⁺ diffusion or the reversible redox potential in anode materials[3]. However, carbon-based LIBs have limited further applications because of their low capacity and slow diffusion reaction kinetics. As a result, developing high-capacity electrode materials with fast reaction kinetics is a currently hot topic.

Manganese oxides (MnOx) have a variety of oxidation states, high theoretical capacity, and low voltage (Li/Li⁺), demonstrating enormous potential in LIBs application[4]. However, the poor conductivity, severe volume expansion, and easy agglomeration still hinder the actual application of MnO-based materials. Hybridization with biomass carbon is a common and valid way to ameliorate these shortcomings of MnO-based materials in LIBs[5]. Luan et al[6] reported a simple strategy of hydrothermal reaction and calcination to construct N-doped carbon-coated MnO porous spheres. Zhang
et al\cite{7} confirmed MnO quantum dots@carbon nanotubes composite via a scalable electrospinning technique for high-performance LICs anode. So far, many metal oxide/carbon composites have been developed as electrode material, showing excellent electrochemical performances for LIBs\cite{8-9}. However, the influence of metal ions on the fast reaction kinetics of the electrode is still a confusing challenge.

In this paper, a common molten salt method is displayed to fabr icate hierarchically porous MnO/carbon composites, whose smaller size and better dispersion endue the electrode with high surface areas to cushion the volume expansion of the electrode, facilitating the transmission kinetics. In addition, the porous carbon could load with a large of active MnO, which increases the active sites of the composite. LiCl and KCl could form molten salt at high-temperat ures to beneficially achieve the activation and breaking of the carbon particles. Manganese acetate is used as a manganese source and activator to make the surface of the composite forming an abundant pore structure. The hierarchically porous MnO/carbon composites offer a highly invertible capacity of 851 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) and outstanding cyclic performance.

2. Materials and Methods

2.1. Synthesis of MnO/C composite

A certain amount of sucrose is dehydrated by concentrated sulfuric acid, then washed and dried. In a typical procedure, dehydrated sucrose (3.0 g, Shanghai Macleans Biochemical Technology Co., Ltd.), lithium chloride and potassium chloride(13.6 g and 16.4 g, 99.5\%, Aladdin Corp, AR), Mn(CH\(_3\)COO)\(_2\)·4H\(_2\)O (36.8 g, 99.5\%, Sinopharm Chemical Reagent Co., AR), and deionized water (200 mL) were mixed evenly, then churned at 80 °C for 0.5 h, drying in oven at 110 °C for 8 h. The mixtures were transferred into a inert reactor and kept at 800 °C for 2 h in Ar atmosphere. After allowing to stand at room temperature, the as-obtained products were washed in 1. 0 M HCl. As a comparison, the carbonized products of dehydrated sucrose without Mn(CH\(_3\)COO)\(_2\)·4H\(_2\)O activation in molten salt medium were named as BC.

2.2. Structural characterizations and electrochemical measurements

Scanning electron microscopy (SEM, SU8010) test the shape and conformation of the MnO/C. The BET datas were tested by Micrometritics ASAP-2020 and the specific surface area and pore structure were quantified by nonlocal density functional theory (DFT). The XPS datas were evaluated on a SPECS spectrometer equipped (Thermo Scientific).

The electrode sheets used MnO/C, conductive agent and Binder (poly(vinylidene fluoride), PVDF) with a weight ratio of 8:1:1 in organic solvents (N-methyl-2-pyrrolidinone, NMP) to form an average slurry, then overlaid on Cu foil. The mass of active materials in the working electrode is 1.68 mg. The coin cells were assembled in an Ar-filled glovebox with lithium sheet as the counter electrode, Celgard 2400 as the separator and 1 M LiPF6 in ethylene carbonate (EC), dimethyl carbonate (DEC) and ethyl methyl carbonate (EMC) (1:1:1 Vol\%) is used as electrolyte. The cyclic voltammetry curve (CV) were tested on CHI 760D (Chenhua, Shanghai) workstation.
3. Results & Discussion

The shape and conformation of the MnO/C composite was probed by SEM. The MnO/C composite is constituted by the agglomeration of nanoparticles with relatively uniform size, which can be seen from the high magnification in Figure 1a. Figure 1b illustrates that the MnO/C composite is constituted by the cumulation of homogeneous particles, owing to the remarkable breaking action in the flowing liquid substance at a high-temperature. The C, O and Mn elemental mappings of the MnO/C in Figure 1c show that all elements are distributed uniformly. Moreover, the composition ingredients of the MnO/C composite were defined by XPS. As shown in Figure 1d, the obvious C, O and Mn peaks appeared in the survey spectrum. Mn 2p kernel layer (Figure 1e) displays two peaks at 641.7 eV (Mn 2p3/2) and 653.7 eV (Mn 2p1/2) with apart 12 eV, belonging to the feature of MnO[10]. The N2 adsorption-desorption isotherms of the MnO/C composite are shown in Figure 1f, which display the features of type-IV isotherms. The corresponding pore size is mainly distributed in the scope of 0.5-2 nm, computed by density function theory (DFT). The favorable specific surface area is 235.2 m² g⁻¹. In addition, the larger specific surface area of MnO/C helps to offer more storage void for Li⁺ and speed up the diffusion of ions/electrons, to promote the overall transmission kinetics in LIBs.

The electrochemical test of MnO/C electrode is demonstrated in Figure 2 (the loading mass of HNBC was set at 1.68 mg). The CV curve of the coin cell is displayed in Figure 2a. The peak at around 0.5 V in the first discharging cycle results from a layer of solid-electrolyte interphase (SEI) membranes formed on the surface of the electrode, which is associated with the conversion of MnO to metallic Mn. A peak at around 1.2 V in the first charging cycle is due to the reversible oxidization of Mn to MnO[11]. The specific reaction formula is as follows: Mn + Li₂O → MnO + 2Li⁺ + 2e⁻. Galvanostatic charging/discharging curves are displayed in Figure 2b, in which the selected cycles of MnO/C anode for LIBs were registered at 0.1 A g⁻¹ over a voltage scope of 0.01-3 V. The MnO/C electrode offers high capacity of 959 and 2250 mAh g⁻¹ at first cycle of charge and discharge, achieving an initial coulombic efficiency of 42.6%. The invertible capacity loss in the first cycle is resulted by the formation of the SEI membrane and the side reaction of the electrolyte. The cycling performance of the MnO/C, and BC electrodes at 0.1 A g⁻¹ is displayed in Figure 2c. After 3 cycles, the MnO/C, and BC electrodes exhibited high discharging capacity of 851 and 236 mAh g⁻¹. After 200 continuous cycles, they still delivered 801, and 212 mAh g⁻¹ with 94.1%, and 89.8% capacity retention, respectively. As displayed in Figure 2d, the specific capacities are 851, 498, 404, 271, 216, and 131 mAh g⁻¹ at 0.1, 0.2, 0.5, 1, 5, and 10 A g⁻¹,
demonstrating the MnO/C electrode has much better rate of performance than BC electrode owing to the different architectures. The abundant porous gap could avoid an accumulation of the MnO/C particles, accordingly, supplying more active sites and Li+ storage pathways.

At a potential of 0.01-3 V, the CV curves of MnO/C anode at different scanning rates are demonstrated in Figure 3a. The capacitive and diffusion effect could be calculated by equations (1) and (2): [3, 12].

\[ i = k \nu^b \]  
\[ \log(i) = b \log(\nu) + \log(k) \]

where \( i \) demonstrates the peak current and \( \nu \) demonstrates scanning speed, the \( b \) value is generally considered to be the key point to evaluate the redox kinetics. Through previous research, the value of \( b \) near 0.5 shows a representative diffusion property, and the value of \( b \) near 1.0 displays a capacitive property dominated [48]. The logarithm of the anode current and the logarithm of the scanning rate fit almost a beeline at the potential of 2.99 V, indicating \( b \) values of 0.815 and 0.851 for the charge and discharge process at different scanning rates (Figure 3b). The calculation results of the \( b \) value display that the fast kinetics of the MnO/C anode is mainly owing to the capacitive behavior, and the redox reaction on the surface of the material helps to achieve the rapid insertion/deintercalation of Li⁺. Furthermore, the current response under stable voltage includes capacitive and diffusion. The quantitative comparison between capacitive and diffusion is mainly associated with the following equations: [3, 12].

\[ i = k_1 \nu + k_2 \nu^{1/2} \]  
\[ i/\nu^{1/2} = k_1 \nu^{1/2} + k_2 \]

where the \( k_1\nu \) displays capacitive current response and \( k_2\nu^{1/2} \) are connected with the current response provided by diffusion process. The main capacitance contribution of MnO/C electrode was calculated
as 62.1%, much higher than that of diffusion (Figure 3c). As illustrated in Figure 3d, the surface capacitance contribution of MnO/C electrode at 0.2, 0.4, 0.6, 0.8 and 1 mV s\(^{-1}\) is 48.1%, 55.0%, 62.1%, 68.9% and 75.1%. The proportion of capacitance contribution increases with the enhancement of sweeping speed. Typically, high capacitance contribution from MnO/C surface of the porous structure unique and rich MnO, facilitating rapid transfer of Li\(^+\) in the charging and discharging process.

Figure 3. a) CV curves of the MnO/C at different scanning rates. b) Relationship of peak currents and scanning rates in cyclic voltammetry process. c) Ratio of capacitive and diffusion currents at a scanning rate of 0.8 mV s\(^{-1}\). d) A ratio of the capacitive and diffusion at different scanning rates.

4. Conclusion
In summary, a common molten salt method is displayed to fabricate hierarchically porous MnO/carbon composites. The resultant MnO/C composite could resolve the influence of metal ions on the fast reaction kinetics of the electrode as follow: i) the porous carbon could load with a large of active MnO, which increases the active sites in the composite. ii) LiCl and KCl could form the liquid reaction medium at high temperatures to beneficially achieve the activation and breaking of the carbon particles. iii) Manganese acetate is used as a manganese source and activator to make the surface of the composite forming an abundant pore structure. As a consequence, the MnO/C composite-based electrode displays a high Li\(^+\) storage capacity of 851 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\), outstanding rate ability, and long-term cycle performance. The mechanism of metal ions on the rapid reaction kinetics of the electrode in this study could be widely applied for an energy storage system.

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