Flower-like $K_{0.27}MnO_2$ as Cathode Materials for High-Performance Aqueous Sodium-ion Batteries

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Introduction

The emerging concerns over global energy supply have stimulated intensive investigation on new and clean energy technologies, such as electric vehicles (EVs) and electrical smart grid from wind and solar power.[1] Therefore, developing new battery technologies with comprehensive consideration of energy density, cost, safety and resource is desirable and necessary.[2] Aqueous sodium-ion battery (NIB) is a promising candidate among several aqueous energy storage technologies, which has recently attracted extensive interest due to its environmental benign and potential economic cost deriving from the natural abundance of Na resource. Furthermore, the electrochemical mechanism of NIB is similar to that of lithium-ion batteries (LIB) since Na and Li are based on the same periodic alkalis. Binessite-type A_xMnO_2 ($A = H^+$, Li^+, Na^+, K^+) are interesing compounds. They have a layered structure consisting of edge-sharing MnO_6 octahedra with a basal spacing of ~7 Å, which allow high mobility of the interlayer cations with fast kinetics and easy access of ions to the electrode/electrolyte interface. K_xMnO_2 with a typical layer structure can serve as an attractive cathode material for NIB. For K_xMnO_2, the synthesis method and microstructure are important to achieve high electrochemical performance.

Experimental

A facile topochemical method based on microwave assistance and heat treatment was employed to synthesize $K_{0.27}MnO_2$ microflowers. δ-MnO_2 microflowers were firstly synthesized via microwave-assisted route.[3] The obtained δ-MnO_2 microflowers were mixed with K_2CO_3 using ethanol as dispersant, and the ethanol was evaporated at 80 °C under stirring. The composite was collected and calcined in air at 500 °C for 2 h. Full cell was assembled by using PP (polypropene) as separator, commercial activated carbon (AC) as the counter electrode, and 1 mol L^{-1} Na_2SO_4 as electrolyte. The mass ratio of $K_{0.27}MnO_2$ to AC in the full cell is about 1:1 (weight ratio). Electrochemical measurements were carried out in full-cell configuration in coin cells (CR2032), which were investigated within the cut-off voltage window of 0–1.8 V.

Results and Discussion

The morphology of the sample was investigated by SEM (Figure 1). The SEM shows that the resulting sample of $K_{0.27}MnO_2$ maintained the flower-like morphology with a diameter of 1-1.5 μm (Figure 1a). From the high-resolution SEM image in Figure 1b, it can be seen that hierarchical structure of the microflowers is assembled with sheet-like crystals, and the typical thickness of the nanosheets is about 50 nm. This result demonstrate that stable microflower $K_{0.27}MnO_2$ can be successfully obtained via this facile topochemical method.

To estimate the potential application of the $K_{0.27}MnO_2$ microflowers as cathode in sodium-ion energy

storage device, full cell performance was investigated within the cut-off voltage window of 0.0–1.8 V. Figure 2a presents the discharge capacity and the corresponding Coulombic efficiency at 0.2 A g^{-1}. The initial charge and discharge capacities are 81.1 and 59.4 mA h g^{-1}, respectively; the corresponding Coulombic efficiency is 73.3%. In the third cycle, the Coulombic efficiency increases rapidly to 81.5%. After 100 cycles, the reversible capacity becomes 52.1 mA h g^{-1}, and the Coulombic efficiency increases to 94.2%. Furthermore, It can be clearly seen that the electrode shows an excellent cyclability with reversible capacity of 46.9 mA h g^{-1} after 200 cycles. Figure 5b shows the rate capability of KMO-500. At a current density of 0.1 A g^{-1}, the reversible capacity gradually decreases to 75.4 mA h g^{-1} after 10 cycles. The specific discharge capacities are 60.6, 54.8, 45.5, 42.2 and 34.0 mA h g^{-1} at current densities of 0.15, 0.2, 0.4, 0.5 and 0.8 A g^{-1}, respectively. When the current density is turned back from 0.8 to 0.15 A g^{-1}, the capacity can be well recovered to almost the original value. These results demonstrate that $K_{0.27}MnO_2$ exhibits excellent rate performance.

The flower-like structure offers a large surface area for surface reactions and enables fast insertion/extraction of Na^+ ions. Good crystallinity of the product provides stable structure and high electrical conductivity, which is favorable for the charge transport. Therefore, when evaluated as cathode materials for aqueous sodium-ion batteries, they exhibit high reversible capacity, excellent cyclability and remarkable rate capability. We believe our research will have profound meanings for renewable energy and large-scale electric energy storage devices.
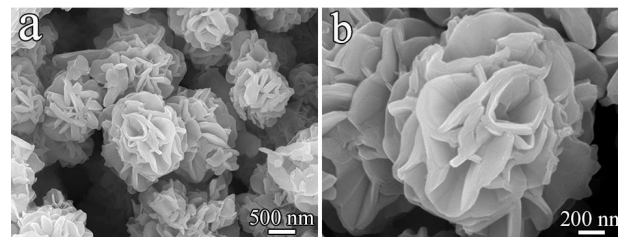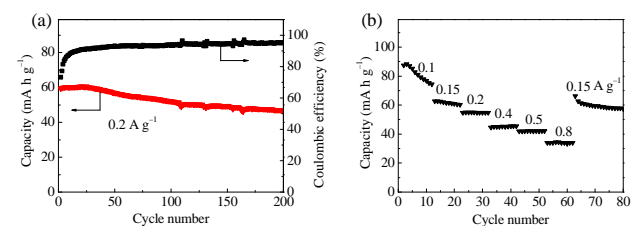

Figure 1. SEM images of $K_{0.27}MnO_2$.

Figure 2. (a) Cycling performances and the corresponding Coulombic efficiencies at a current density of 0.2 A g^{-1} in activated carbon/ $K_{0.27}MnO_2$ full cell. (b) Specific capacity at various current densities of $K_{0.27}MnO_2$.

References

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