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Brain-like manganese monoxide microspheres as anode materials for lithium ion battery

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Abstract: Brain-like manganese monoxide (MnO) microspheres were synthesized by simple precipitation method with subsequent heat treatment. MnO with polyacrylonitrile (PAN) as a binder delivers an initial reversible specific capacity of 976.1 mAh g^{-1} and it remains at 912.3 mAh g^{-1} after 30 cycles. The excellent cyclic performance is attributed to the effective conductive network of cross-linked PAN that formed during the thermal treatment. FTIR, ex situ XRD and XAS were performed to investigate the excess reversible capacity of MnO. The results show that the excess capacity is partially ascribed to the interfacial lithium storage between nanosized Li_2O and Mn which is formed during the conversion reaction. The porous microspheres with large surface area also provide some active sites for lithium storage.

Keywords: brain-like; MnO; PAN; lithium ion battery

1. Introduction

The common battery system can hardly meet the increasing market demand of lithium ion battery in power batteries and large-scale energy storage. It is urgent to develop new electrode materials and critical technology for lithium ion battery.[1-5] As one of the most potential anode materials, transition metal oxides have widely been paid attention since the pioneering investigation by Poizot et al. on M_aO_b (M=Fe, Mn, Co, Ni, Ti, Cu, etc.) and M_aX_b(X=O, N, S, etc.) as anode materials for lithium storage.[6] Among these, manganese oxides have advantages of high theoretical capacity, low cost and environmental friendliness. In addition, MnO is the only end product of manganese oxides (including MnO, Mn_2O_3, Mn_3O_4 and MnO_2) when the electrode is recharged to 3.0 V (vs. Li/Li^+)[7]. MnO stands out consequently for its higher specific capacity and initial coulombic efficiency and better electrochemical performance. However, MnO still suffers from large volume expansion because of the conversion reaction during lithium intercalation and extraction. Inferior electrical conductivity, low efficiency and poor cycling performance of MnO always restrict its commercialization in the lithium ion battery industry.

Coating and structural specialization can somehow improve the electrochemical performance of MnO. Zhong et.al.[8, 9] investigated the electrochemical performance of both MnO nanoparticles and microspheres for lithium storage. Liu et.al.[10] reported on MnO/C nanocomposites with a reversible capacity greater than 680 mAh g^{-1} through a simple thermal decomposition of manganese benzoate. Zhang et.al. [11]loaded MnO nanoparticles inside of the nanotubes that synthesized by the pyrolysis of conjugated microporous polymer nanotubes and MnO–PCNTs deliver superior electrochemical performance. A 3D carbon framework has been introduced into a MnO yolk–shell structure by wang et.el. and it can prevent MnO from fracturing and agglomerating.[12] Though many efforts have been undertaken in the past decades to improve the electrochemical properties of MnO, it is still a long way for the application of MnO as anode