

Short communication

Nanostructured manganese oxides as lithium battery cathode materials

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Abstract

We have designed and synthesized a novel nanocrystalline manganese oxide with a nanofibrous morphology by employing an electrodeposition process in the presence of a non-ionic surfactant. This unique nanoporous/nanocrystalline material effectively accommodates the structural transformation during lithium insertion and avoids deleterious morphological changes as observed in battery materials composed of large particles. Consequently, the material exhibits outstanding cycling stability in addition to its high discharge capacity.

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1. Introduction

Lithium-ion batteries are the current power sources of choice for portable electronics and promising candidates for use in electric vehicle applications. Further improvement of performance and simultaneous reduction in cost as well as material toxicity remain the subject of intensive research [1]. For example, novel cathode materials such as iron phosphates [2] and manganese oxides [3–5] are being developed to replace LiCoO₂ which dominates the current technology. Despite the great potential of manganese oxide-based cathodes, their utilization in batteries has been plagued by problems of moderate capacity and poor stability. There are many manganese oxide materials under study such as spinel LiMn₂O₄ [6], layered LiMnO₂ [7] and Na_{0.44}MnO₂ [8]. These materials, however, suffer from either low capacities or poor cycling stability which is believed to be a result of a co-operative Jahn-Teller effect associated with the presence of Mn³⁺ ions in an MnO₆ octahedron. Amorphous manganese oxides have shown some promise in addressing these issues by alleviating this co-operative effect. A Li_{1.5}Na_{0.5}MnO_{2.85}I_{0.12} [9] material has exhibited enhanced cycling stability, but its capacity needs to be delivered in a very wide voltage range (4.3–1.5 V) and its rate capability is far from satisfactory. In this report, we address the cycling stability and rate capability issues of a high-capacity manganese dioxide material by intro-

ducing a novel structural composition primarily consisting of two complementary aspects: nanoporosity and nanocrystallinity. A nanocrystalline material, unlike an amorphous one, will most likely exhibit a more levelled discharge profile and may alleviate problems associated with the co-operative Jahn-Teller effect. Both amorphous and nanocrystalline materials, however, often suffer from poor rate capability. This electrochemical deficiency can be mitigated by the creation of nanopores between the nanocrystals to generate a unique nanofibrous material.

2. Experimental

Synthesis of this nanostructured manganese oxide is accomplished via electrodeposition of manganese oxide in the presence of a surfactant, BrijTM 56 (C₁₆H₃₃(OCH₂CH₂)₈H). In a typical electrodeposition reaction sequence, 2.55 g of MnSO₄ is dissolved in 5 g of H₂SO₄ and 50 g of H₂O. Subsequently, 0.82 g of Brij 56 is added to the solution with vigorous stirring and a uniform milky solution is obtained which serves as the electrolyte for electrodeposition. F-doped SnO₂ glass, Pt mesh and Ag/AgCl are used as the working, the counter and the reference electrodes, respectively. A current density of 1 mA cm⁻² is employed and a 10-min deposition at 25 °C yields a dark brown film with a thickness of ~1 μm. Before being tested in a lithium battery cell, the electrodes are air dried at 100 °C for 4 h. For evaluation of the electrode in a lithium battery, a three-electrode cell was used (with lithium metal as both the counter and reference electrodes), while a solution of 1 M LiClO₄ in

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propylene carbonate was used as the electrolyte. Charge and discharge experiments were performed utilizing an Arbin battery testing system (Arbin Instruments, TX, USA). Transmission electron micrographs (TEM) were obtained on a Phillips CM 30 transmission electron microscope and scanning electron micrographs were recorded on a JSM scanning electron microscope. The Raman spectra were taken in the quasi-backscattering geometry using 100 mW of the 514.5 nm line of an Ar ion laser, focused to a line of $5 \text{ mm} \times 100 \text{ }\mu\text{m}$, as the excitation source. The signal was dispersed by a Spex 0.6 m triple spectrometer and detected with a liquid-nitrogen-cooled high-resolution charge-coupled-device detector array. Both the spectral resolution and the accuracy in the Raman shift are estimated to be $\sim 2 \text{ cm}^{-1}$.

3. Results and discussion

The morphologies of manganese oxides have been examined by scanning electron microscopy (SEM). Fig. 1 compares the results for two samples prepared with (Fig. 1b) or without (Fig. 1a) the Brij 56 surfactant. The addition of Brij 56 leads to the formation of hollow spherical shells of perforated manganese oxide. The shells bear superficial resemblance to

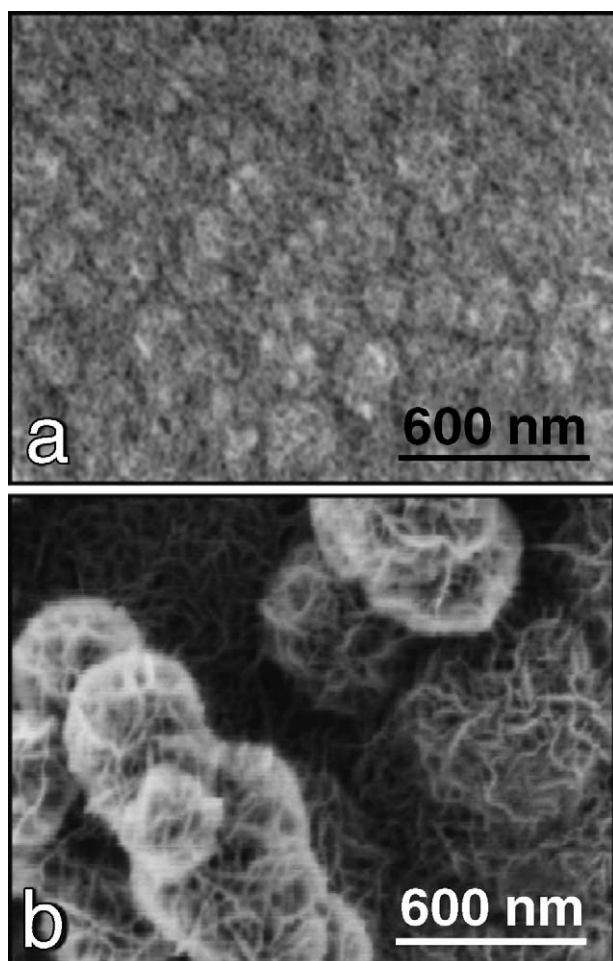


Fig. 1. SEM pictures of electrodeposited manganese oxides: (a) prepared in the absence of Brij 56; (b) in the presence of Brij 56.

synthetic porous aragonite, which is formed by the templating effect of bicontinuous microemulsion [10,11]. On the contrary, the control sample exhibits a relatively smooth surface. The structural difference of these two samples is also evident at the nanometer scale. Fig. 2a–e displays transmission electron micrographs of the two materials. While the control sample possesses a featureless morphology (Fig. 2a), the material prepared in the presence of the Brij 56 surfactant has an interesting flower-like structure which is nanofibrous in nature (Fig. 2b). Such a structural feature is distinctly unique with respect to nanometer-sized pores in mesoporous materials which can also be prepared using non-ionic surfactants as the templates [12]. While there have been discussions in the literature with regard to nanofibers of manganese oxide [13], our synthesis process produces a fiber width of $\sim 5 \text{ nm}$ in contrast to 60 nm for sodium manganese oxide fibers prepared by hydrothermal synthesis. Within the fibers, the manganese oxide is actually nanocrystalline, as evidenced by high-resolution TEM shown in Fig. 2c. The size of the nanocrystallites ranges from approximately $3\text{--}5 \text{ nm}$. Meanwhile, the electron diffraction pattern (shown in the inset of Fig. 2b) consists of a series of diffusive rings, indicative of short range ordering. The material does not exhibit any diffraction peaks using X-ray diffraction spectroscopy.

In perspective of the SEM and TEM observations, our manganese oxide material is composed of nanocrystallites which organize into nanofibers. Further arrangement of the nanofibers results in porous spheres. The phase of the crystallites can be identified by Raman spectroscopy, which effectively probes localized ordering. In Fig. 3, three main Raman peaks at 649 , 570 and 509 cm^{-1} are observed for the nanostructured manganese oxide (Fig. 3a). A comparison of these data with literature indicates that the material appears to be $\gamma\text{-MnO}_2$ with a very low concentration of pyrolusite $\beta\text{-MnO}_2$. In this structure, 1×2 tunnels (ramsdellite) dominate while 1×1 tunnels (pyrolusite) are also present [14]. The chemical compositions of the materials have been determined to be $(\text{Brij } 56)_{0.07}\text{MnO}_{1.96}$ by using a combination of thermogravimetric analysis (TGA) and a chemical titration process to determine the oxidation state of manganese [9].

The nanostructured manganese oxide was deployed and tested as a thick film cathode without any binders in a lithium battery cell and the results are presented in Fig. 4. Fig. 4a shows the charge–discharge curves when the electrode is cycled between 2 and 4 V at a $C/6$ rate. The nanostructured manganese oxide exhibits a reversible capacity of 218 mAh g^{-1} at a discharge rate of $C/6$. Since the material contains $32 \text{ wt}\%$ of Brij 56 which is not electrochemically active, a capacity of 320 mAh g^{-1} would be obtained based only on manganese oxide and corresponds to a final composition of $(\text{Brij } 56)_{0.07}\text{Li}_{1.04}\text{MnO}_{1.96}$. With an average discharge potential of 2.9 V , this material delivers comparable energy density to manganese oxyiodide over a much narrower voltage window ($4\text{--}2 \text{ V}$ versus $4.3\text{--}1.5 \text{ V}$) [9]. Fig. 4b displays the cycling stability of the electrode at different discharging rates. The initial capacity increase during cycling is related to a structural transformation induced by lithium insertion rather than a release of the surfactant into the electrolyte. It is evident that the material displays a very stable cycling behavior with

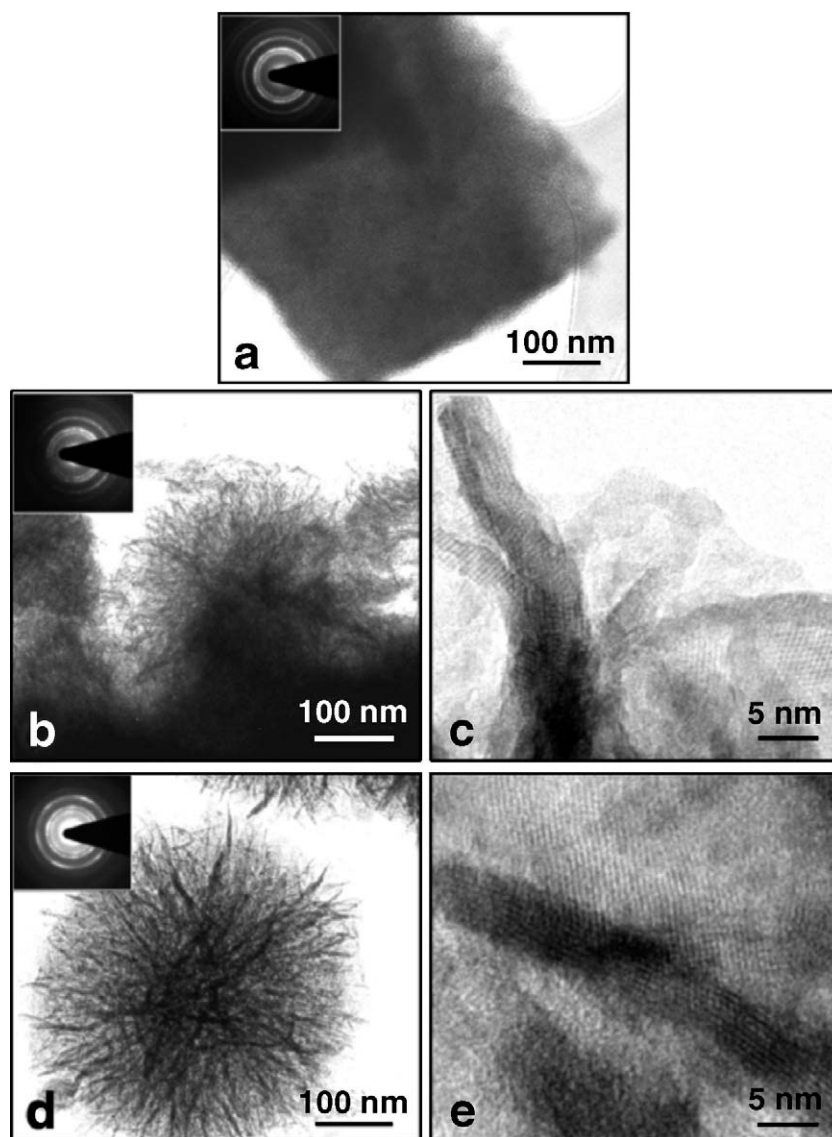


Fig. 2. TEM pictures of control and nanostructured manganese oxide samples: (a) control sample prepared in the absence of Brij 56; (b) sample prepared in the presence of Brij 56; (c) high resolution picture of sample in b showing the nanocrystalline structure; (d) sample in b cycled for 150 cycles; (e) high resolution picture of sample in d. Shown in the insets in a, b and d are the electron diffraction patterns.

minimal capacity degradation for 150 cycles. Possible structural transformation during cycling has been confirmed by a comparison of Raman spectra of fresh versus cycled samples as shown in Fig. 3. The vibrational modes attributed to the pyrolusite component (the peak at 570 cm^{-1} in curve a) disappear after cycling while those of ramsdellite remain [14]. This observation indicates that the 1×1 tunnel is less stable after lithium insertion.

Despite the extensive structural transformation during lithium insertion, which is often responsible for capacity degradation in many manganese oxide materials, the nanostructure of our manganese oxide remains intact (see Fig. 2d and e). While local ordering is different as evidenced by the presence of oriented lattice fringes along the direction of the nanofiber (Fig. 2e), Fig. 2d shows the basic shape of the nanofiber persists during this transformation process. It is well known that phase trans-

formation often leads to major morphological change which in turn may be responsible for poor long term stability. This situation, however, appears to be effectively addressed by using a nanocrystalline/nanofibrous structure.

In summary, we have designed and synthesized a novel manganese oxide material with nanofibrous morphology using an electrodeposition process employing a non-ionic surfactant. This unique nanoporous/nanocrystalline material effectively accommodates the structural transformation during lithium insertion and avoids deleterious morphological changes as observed in battery materials composed of large particles. Consequently, the material exhibits outstanding cycling stability in addition to its high discharge capacity. Further improvement in capacity may be achieved by extraction of the organic surfactant while preserving the nanostructure of manganese oxide. In addition, the rate capability of the material can be improved

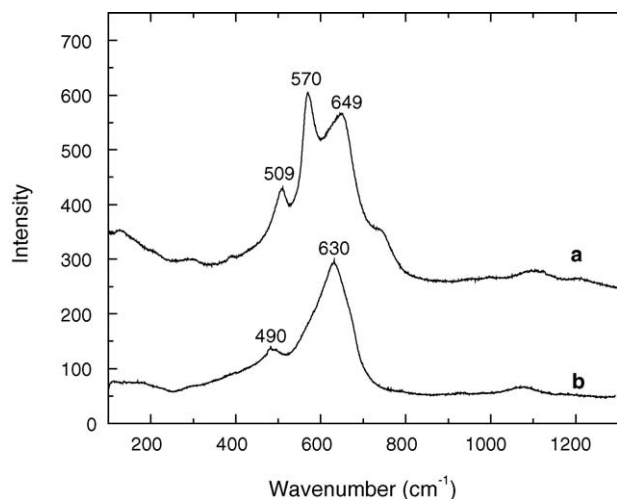


Fig. 3. Raman spectra of the nanostructured manganese oxide: (a) as-prepared; (b) after cycling for 150 cycles.

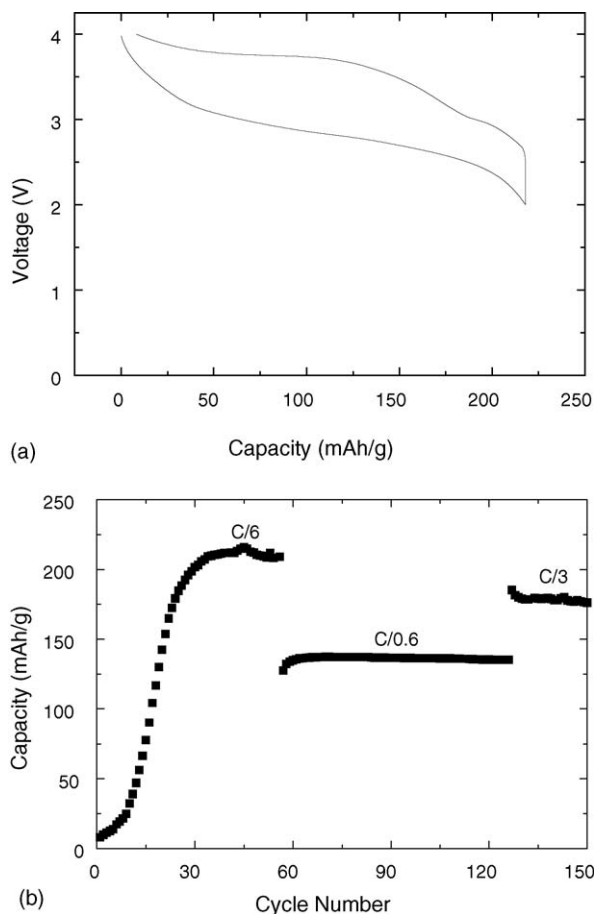


Fig. 4. (a) Charge–discharge curves of the nanostructured manganese oxide electrode after 150 cycling test shown in b. The electrode was discharged at a rate of C/6; (b) cycling stability of the nanostructured material.

with an enhancement in electronic conductivity via appropriate chemical additives.

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