Electrochemical Fabrication of Monolithic Electrodes with Core/Shell Sandwiched Transition Metal Oxide/Oxyhydroxide for High-Performance Energy Storage

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Supporting Information

ABSTRACT: Transition metal oxides/oxyhydroxides (TMOs) are promising high-capacity materials for electrochemical energy storage. However, the low rate and poor cyclability hinder practical applications. In this work, we developed a general electrochemical route to fabricate monolithic core/shell sandwiched structures, which are able to significantly improve the electrochemical properties of TMO electrodes by electrically wiring the insulating active materials and alleviating the adverse effects caused by volume changes using engineered porous structures. As an example, a lithium ion battery anode of porous MnO sandwiched between CNT and carbon demonstrates a high capacity of 554 mAh g\(^{-1}\) even after 1000 cycles at 2 A g\(^{-1}\). An all-solid-state symmetric pseudocapacitor consisting of CNT@MnOOH@polypyrrole exhibits a high specific capacitance of 148 F g\(^{-1}\) and excellent capacitance retention (92% after 10000 cycles at 2 A g\(^{-1}\)). Several other examples and applications have further confirmed the effectiveness of improving the electrochemical properties by core/shell sandwiched structures.

KEYWORDS: lithium-ion batteries, electrodeposition, core/shell structure, transition metal oxide, flexible pseudocapacitors

1. INTRODUCTION

Transition metal oxides and oxyhydroxides (TMOs, TM = Mn, Co, Ni, etc.), as energy storage materials, have attracted increasing attention for lithium ion batteries (LIBs) and pseudocapacitors because of their high charge storage capability, relatively low cost, and environmental benignity. However, rapid capacity decay and poor rate performance hinder the applications of TMO electrodes for electrochemical energy storage. For example, when a MnO anode is charged to low potentials (<1 V vs Li/Li\(^+\)) in LIBs, the conversion reaction of MnO to nanosized Mn and Li\(_2\)O causes a significant volume change. Repeated cycling may break the electron pathway of MnO particles and solid electrolyte interphase (SEI). The fractured surface which is exposed to electrolyte consumes cyclable lithium ions and leads to capacity decay.

Porous TMO structures (such as porous nanospheres, porous nanoflakes, hollow oxide/C microspheres, etc.) have been reported to minimize the adverse effect of volume changes because engineered voids in the porous TMO anodes can accommodate volume changes during cycling. The poor rate capability of TMO electrodes mainly results from slow electron and ion transport. Carbon coating is widely used to enhance the electron conductivity of TMO electrodes. The coating also helps to stabilize the TMO/electrolyte interface, which is essential to high cycle life. Reducing the size of TMO particles decreases the diffusion length of lithium ions and enhances the rate capability of TMO electrodes. For example, nanocrystalline MnO thin film has been explored to shorten the transport length of electrons and lithium ions.

Although approaches such as pore engineering, size reduction, and carbon coating have been able to reduce adverse effects caused by volume changes, there still exist the strains induced by lithium insertion and extraction. A robust support or scaffold is able to adequately accept some of the strain during cycling and may improve the mechanical integrity of TMO electrodes. Conductive scaffolds are generally preferred because TMO is a poor electron conductor. Carbon nanotube (CNT) networks, foams, and carbon webs have been used to support TMO and conduct electrons. For example, Wei et al. presented a low-temperature synthetic route toward binder-free MnO\(_2\)/single-walled carbon nanotube (SWCNT) macrofilms which exhibit a high capacity of 1000 mAh g\(^{-1}\) and good capacity retention.
Generally, previous studies have shown that high-capacity TMO-based electrodes have been constructed with (1) porous structures to accommodate volume changes, (2) a robust scaffold to maintain the mechanical integrity, (3) a conductive network to decrease electric resistance, (4) short length to facilitate electron and ion transport, or (5) an appropriate SEI-stabilizing mechanism. Although modest strides have been achieved by some of these approaches, simultaneous realization of these five approaches is desired to significantly increase the electrochemical performance of TMO electrodes.

In this work, we developed a binder-free monolithic electrode with core/shell sandwiched TMO fibers to realize these five strategies. Manganese is taken as an example here, and more TMOs are demonstrated in Supporting Information (SI). The fabrication procedure is illustrated in Figure 1. First, manganese oxyhydroxide is electrodeposited on a commercial CNT paper. Second, the obtained CNT@MnOOH fibers are coated with polymerized furfuryl alcohol (PFA). Third, heat treatment produces porous manganese oxide (pMnO) which is sandwiched between carbonized PFA and CNTs core to form a composite electrode. The carbon shell isolates MnO from electrolyte and may minimize the side reactions caused by the volume change of MnO materials. The composite electrode delivers a high capacity of 554 mAh g\(^{-1}\) even after 1000 cycles at 2 A g\(^{-1}\). The active material/electrolyte interface is also important to manganese oxide-based pseudocapacitors. We further apply the core/shell sandwiched structure to pseudocapacitor applications by coating CNT@MnOOH with polypyrrole (PPy) because PPy has a high electron conductivity (100–1000 S m\(^{-1}\)). The CNT@MnOOH@PPy electrode exhibits an outstanding electrochemical capacitance of 457.5 F g\(^{-1}\). A symmetric all-solid-state capacitor consisting of two CNT@MnOOH@PPy electrodes shows good capacitance retention of 92% after 10000 cycles at 2 A g\(^{-1}\). Both lithium ion and pseudocapacitor applications demonstrate that our core/shell sandwiched electrodes could significantly improve the electrochemical performance of TMO-based energy storage devices.

2. EXPERIMENTAL SECTION

2.1. Preparation of CNT@MnOOH. Carbon nanotube paper (Chengdu Organic Chemicals Co. Ltd.) was pretreated at 1000 °C for 2 h in forming gas (95% Ar and 5% H\(_2\)). Manganese oxyhydroxide was coated on CNT by a pulsed electrodeposition technique in an aqueous solution of 0.1 M MnSO\(_4\)·H\(_2\)O, 0.1 M Na\(_2\)SO\(_4\), and 0.1 M CH\(_3\)COONa. A platinum foil and Ag/AgCl electrode were used as the counter and reference electrodes, respectively. In a typical procedure, a series of 1.3–1.8 V pulses (1 s on and 15 s off) were applied between the CNT and reference electrodes at room temperature. The thickness of the MnOOH layer could be controlled by the pulse number. For experimental details and characterization of MnOOH, see the previous literature.

2.2. Synthesis of Core/Shell Sandwiched Structure. Typically, about 0.06 g of oxalic acid was added to 8 mL of furfuryl alcohol (PFA) and agitated until oxalic acid was fully dissolved. The CNT@MnOOH sample was dipped in the solution for 30 s and then removed. With heat treatment at 90 °C for 6 h, the FFA coating was solidified and partially polymerized. The dip-coating step was repeated multiple times to increase the polymer coating on the CNT@MnOOH fibers. The obtained sample was placed in a tube furnace and annealed at 250 °C for 60 min to polymerize the coating. A subsequent heat treatment at 600 °C for 2 h in forming gas carbonized the PFA coating and converted MnOOH to MnO. Due to the loss of water molecules, a porous MnO (pMnO) layer was sandwiched between the CNTs and carbonized PFA, which was denoted as CNT@pMnO@C. After the annealing treatment, MnO was dissolved in an ~6 M HCl solution. The weight loss was used to estimate the MnO load (1.4 mg cm\(^{-2}\), 70 wt %) in CNT@pMnO@C. PPy was electrodeposited by a series of anodic pulses (0.9 V vs Ag/AgCl, 1 s on and 10 s off for 30–60 cycles) in a solution of 1 M LiClO\(_4\) and 5 vol % pyrrole monomer. After washing with deionized water and drying in air at 50 °C for 2 h, a monolithic CNT@...
MnOOH@PPy electrode was obtained. The electrodeposited MnOOH was around 2.1 mg cm$^{-2}$.

2.3. Material Characterization. X-ray diffraction (XRD) patterns of all samples were collected on a Rigaku D/Max III X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). The sample morphologies were observed with a Zeiss Ultra 55 scanning electron microscope (SEM) and a high-resolution transmission electron microscope (HRTEM, FEI Technai F20S). X-ray photoelectron spectroscopy (XPS) was conducted with an ESCALab MKII spectrometer with Mg Kα X-ray as the excitation source.

2.4. Electrochemical Measurements. All samples for LIBs were assembled with lithium into coin cells (CR2032) in an argon-filled glovebox. Celgard 2320 and 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate/diethyl carbonate (1:1:1 by volume) were used as separator and electrolyte, respectively. Cyclic voltammograms (CV) were measured in the range of 0.01−2 V at a rate of 0.2 mV s$^{-1}$. Electrochemical impedance spectra (EIS) were obtained in the frequency range of 100 kHz to 10 mHz with a potentiostat (BioLogic VSP, France). The galvanostatic charge/discharge was carried out using a CT2001A test system (Land Electronic Co., China) between 0.01 and 2 V.

The electrochemical properties of CNT@MnOOH@PPy electrodes were characterized in a 0.1 M Na$_2$SO$_4$ solution with a Ag/AgCl reference electrode. A symmetric pseudocapacitor of two CNT@MnOOH@PPy electrodes was assembled with a gel electrolyte composed of 10:10:1 mass ratio of poly(vinyl alcohol) (PVA, MW = 145000), KOH, and KI in a pouch cell (Kapak SealPAK 400, Ampac Flexibles). Among all the electrochemical characterizations, the specific capacity/capacitance of samples is based on electrodes or full cells.

3. RESULTS AND DISCUSSION

Commercial CNT paper, as the scaffold, is used to load the active material because of its good electron conductivity and flexibility. Figure 2a shows that the average CNT diameter is around 45 nm. When positive voltage pulses are applied between CNTs and Pt counter electrodes in a Mn$^{2+}$-containing solution, flake-like manganese oxyhydroxide is coated on the CNT surface as shown in Figure 2b. The coating thickness could be controlled by the pulse number. Typically, about 60 nm thick MnOOH is produced by eight cycles of 1.3 V pulses. By dipping into a mixture of FFA and oxalic acid multiple times, the CNT@MnOOH sample is coated with PFA as shown in Figure 2c. A subsequent heat treatment in forming gas drives off water molecules and reduces MnOOH to MnO, which is confirmed by the XRD analysis in Figure 2g. Due to the loss of water, the volume of electrodeposited MnOOH on the CNT surface shrinks and generates porous structures. The PFA coating is carbonized to form a carbon shell which sandwiches MnO with the CNT core (Figure 2d). To observe the sandwich structure, the CNT core is pulled out of a CNT@MnO@C fiber. Figure 2e shows the transmission electron microscope (TEM) morphologies of the CNT core and MnO. It can be seen that the surface of MnO is coated by a thin layer of carbon, which is converted from PFA. The HRTEM image in Figure 2f clearly shows the interface between amorphous carbon and crystalline MnO. The lattice fringe in the crystalline region of Figure 2f corresponds to the (111) plane. The XRD patterns in Figure 2g confirm the appearance of MnO phase (JCPDS card no. 78-0424) after
annealing. The Mn 2p spectrum in Figure S1 shows two peaks at 653.0 and 641.0 eV, corresponding to the signals of Mn$^{2+}$ 2p$_{1/2}$ and 2p$_{3/2}$, respectively. The XPS analysis further confirms the valence of Mn is 2+ in conjunction with XRD and HRTEM results.

Figure 3a shows the CV curves of CNT@pMnO@C at a scan rate of 0.2 mV s$^{-1}$ between 0.01 and 2 V (vs Li/Li$^+$). A reduction peak between 0.75 and 0.5 V appears only in the first cycle. It is related to the SEI formation according to previous reports. The reduction peak at 0.5 V and oxidation peak at 1.3 V are attributed to the following conversion reaction: MnO + 2Li$^+$ + 2e$^-$ ↔ Mn + Li$_2$O. The voltage gap between the two redox peaks may be due to kinetic resistance and thermodynamic hysteresis. The peak at 0.2 V in the anodic scan results from both MnO and CNT. Figure 3b shows the charge/discharge curves of CNT@pMnO@C at 1 A g$^{-1}$. It delivers an initial capacity of 1290.3 mAh g$^{-1}$ (electrode basis) with a Coulombic efficiency of 63.1%, which is comparable to other transition metal oxide anodes. A capacity loss between the first two cycles is ascribed to the inevitable formation of SEI films on the surface of the anode. The plateau below 0.7 V corresponds to the lithiation of MnO and CNT, which is in agreement with the CV analysis.

To determine what role the surface coating plays in the electrochemical properties of manganese oxide and CNT composite electrodes, a CNT@MnOOH sample is cut into two identical electrodes. One of the two electrodes is coated with PFA and the other is not. Both of them are then treated according to the same procedures. Figure 2g shows similar XRD patterns for the two composite samples (with and without carbon coating). A sample of CNT/MnO/C with the same ratio as that of CNT@pMnO@C was fabricated by directly mixing CNT, MnO, and carbon black. Their EIS spectra (Figure 3c) show the similar characteristics of a semicircle and linear tail. Generally, the short high-frequency intercepts and semicircle diameter show that the CNT@pMnO@C has a resistance slightly lower than that of CNT@MnO and CNT/MnO/C. The galvanostatic cycling properties of the composite samples and a CNT electrode are measured at 2 A g$^{-1}$. As shown in Figure 3d, an initial capacity of about 221.2 mAh g$^{-1}$ is observed for the CNT electrode. After a decrease of 46.2% in the first few cycles, the specific capacity of CNT approaches a stable value of 119 mAh g$^{-1}$. The CNT@pMnO@C electrode delivers an initial capacity of 1196.8 mAh g$^{-1}$ and decreases to 678 mAh g$^{-1}$ in the 10th cycle. Meanwhile, its Coulombic efficiency increases from 63.1% to almost 100%. After 1000 cycles, the CNT@pMnO@C sample even retains a capacity of 554 mA h g$^{-1}$. The CNT@MnO sample without carbon coating shows an initial capacity (1344 mAh g$^{-1}$) higher than that of CNT@pMnO@C. However, it decreases rapidly to 330 mAh g$^{-1}$ after 100 cycles. The CNT/MnO@C has a relatively low initial capacity of 727.2 mAh g$^{-1}$ and decreases to 184.6 mAh g$^{-1}$ in 100 cycles. These results indicate that the cycling properties are improved for the sample with carbon coating. Since the dehydration and reduction of electrodeposited MnOOH generate porous structures during heat treatment in forming gas, it is conceivable that the extra empty space sandwiched between the CNT core and carbon shell could accommodate the volume change of MnO during lithiation. The surface carbon could also isolate MnO from electrolyte. Conversely, MnO in the sample without carbon coating is exposed to liquid electrolyte during cycling. The adverse effect caused by volume changes could not be effectively managed.

Figure S2 shows the postmortem SEM images of CNT@pMnO@C. Basically, the fibrous morphology of the CNT@pMnO@C composite was retained, indicating that the core/shell sandwiched structures were robust upon electrochemical cycling. Therefore, our core/shell sandwiched structure is able to significantly improve the cyclability of high capacity MnO anodes in lithium ion batteries.
The good electrochemical properties of the sandwiched Li-ion anodes prompted us to consider whether the sandwich structure could be applied to other electrochemical energy storage systems. Py is electrodeposited on the CNT@MnOOH (Figure 4a) to form a core/shell sandwiched MnOOH electrode (Figure 4b). By comparing the SEM images of CNT and CNT@MnOOH samples, the thickness of the MnOOH layer is estimated to be around 65 nm. The pseudocapacitor properties of CNT@MnOOH with and without PPY coating are compared in a 0.1 M Na2SO4 solution at scan rates of 2–100 mV s−1. The rectangular shapes in Figure 4c, d indicate that the CNT@MnOOH samples with and without PPY coating both exhibit typical pseudocapacitive properties.32,43−51 Their specific capacitances are calculated by integrating the CV curves and are shown in Figure 4e. The CNT electrode provides a capacitance of 27.4 F g−1 (at 2 mV s−1). It only decreases 20% when the scan rate increases 50 times. The good capacitance retention is due to the electrical double layer mechanism.32,49,52 As compared to the CNT electrode, the CNT@MnOOH electrode demonstrates a significantly increased capacitance because of the pseudocapacitive contribution of MnOOH. However, the capacitance decreases 41.5% when the scan rate increases from 2 to 100 mV s−1. The relatively rapid capacitance decrease at high rates typically results from kinetic resistances because of the thick MnOOH.32,40,53 Figure 4e shows that PPY coating significantly increases the specific capacitance of CNT@MnOOH by 157.5 F g−1. This implies that the CNT core is not sufficient to effectively conduct electrons for such a thick MnOOH layer despite its good electron conductivity.34,39,54,55 For the CNT@MnOOH@PPY sample, the PPY coating improves the utilization of MnOOH and results in a high capacitance of 457.5 F g−1. To confirm the role of PPY, the electrochemical impedances of the two electrodes are compared in Figure 4f, which shows that the kinetic process is enhanced by PPY coating on CNT@MnOOH due to its relatively low impedance.32,50

A symmetric all-solid-state capacitor of CNT@MnOOH@PPY is assembled with a gel electrolyte, which consists of PVA and KOH. As shown in Figure 5a, the capacitor demonstrates a well-defined rectangular shape, indicating the pseudocapacitive behavior. The CNT@MnOOH@PPY capacitor is galvanostatically charged and discharged at varied current densities. Figure 5b shows that all of the charge curves are symmetrical with their corresponding discharge branches, as well as their good linear voltage−time profiles, indicating good capacitive behavior of the composite structure. The CNT@MnOOH@PPY capacitor delivers 148 F g−1 (full cell basis) at 1 A g−1.

Figure 4. SEM images of (a) CNT@MnOOH and (b) CNT@MnOOH@PPy. CV curves of (c) CNT@MnOOH and (d) CNT@MnOOH@PPy at varied scan rates. (e) The relation of specific capacitance of CNT, CNT@MnOOH, and CNT@MnOOH@PPy with respect to scan rates. (f) Nyquist plots of CNT@MnOOH and CNT@MnOOH@PPy.
After being cycled for 10000 times at 2 A g\(^{-1}\), it still retains 92% of its initial capacitance as shown in Figure 5c. A capacitor similar to CNT/MnOOH/PPy fabricated by directly mixing (see SI) delivers 51 F g\(^{-1}\) at 1 A g\(^{-1}\) (Figure S3a) and only maintains 49% of its initial capacitance after 5000 cycles (Figure S3b). These analyses indicate that the all-solid-state capacitor of CNT@MnOOH@PPy has a superior cyclability due to the core/shell sandwiched structure.

The fabricated solid-state device is flexible and able to be bent. As shown in Figure 5d, the CV curves are measured when bent to 90° and 150°. Figure S4 indicates that the device is able to cycle at different bending states. The overlapping of CV curves and high capacitance retention at different bending angles demonstrate good flexibility. It is believed that the good cyclability and flexibility are related to our electrodeposition technologies. Because the electrodeposition produces the conformal coating on the conductive surface, all CNT surfaces are coated with MnOOH and PPy. The three components CNT, MnOOH, and PPy are continuously interlocked to form a monolithic structure. The internal CNT and external PPy provide rapid electron-conducting pathways and meanwhile act as mechanical supports to prevent MnOOH from detaching off the conducting network. Such a core/shell sandwiched structure improves the electrochemical and mechanical properties of energy storage devices. The core/shell sandwiched structures are further extended to other TMO systems (Figures S5–S7). We explored the sandwiched structure of nickel and cobalt oxyhydroxide with CNT cores and PPy shells (see details in SI). The monolithic structures demonstrated generally improved electrochemical properties due to the rapid electron pathway and protective carbon shell.

4. CONCLUSION

We demonstrated monolithic TMO-based electrodes with enhanced electrochemical properties by conformally electrodepositing core/shell sandwich structure. The composite structures are applied to LIBs and pseudocapacitors. Due to the rapid electron pathway provided by the internal CNT and external surface layer, the rate properties of TMO electrodes are significantly improved. For example, the engineered pores in CNT@pMnO@C electrodes accommodate the volume change of MnO during lithiation and delithiation and manage the capacity decay. A high capacity of 554 mAh g\(^{-1}\) is maintained after 1000 cycles at 2 A g\(^{-1}\). A symmetric all-solid-state pseudocapacitor consisting of CNT@MnOOH@PPy has been demonstrated with 92% capacitance retention after 10000 cycles. The monolithic core/shell sandwich structure could also provide electrodes with flexibility due to extrinsically interlock effects, which are enabled by the conformal electrodeposition. The good electrochemical properties of the composite structures make TMOs promising for high-performance electrochemical storage devices. More importantly, the method of fabricating core/shell sandwich structures is a general approach to address the issues which are related to electron/ion conduction and volume change in electrodes with high-capacity active materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b06073.

XPS and postmortem analyses. Electrochemical properties of CNT/MnOOH/PPy. Combined tests of electrochemical cycling and bending. SEM images, experimental details, and electrochemical properties of the CoOOH and NiOOH sandwiched by CNT and PPy (PDF)
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Notes
The authors declare no competing financial interest.

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REFERENCES
(17) Wang, S.; Ren, Y.; Liu, G.; Xing, Y.; Zhang, S. Peanut-like MnO@C Core–Shell Composites as Anode Electrodes for High-Performance Lithium Ion Batteries. Nano letters 2014, 6, 3508–3512.
(25) Zhang, J.; Wang, K.; Xu, Q.; Zhou, Y.; Cheng, F.; Guo, S. Beyond Yolk–Shell Nanoparticles: Fe3O4@Fe3C Core@Shell Nanoparticles as Yolks and Carbon Nanoparticles as Shells for Efficient Lithium Ion Storage. ACS Nano 2015, 9, 3369–3376.


(56) Shi, Y.; Pan, L.; Liu, B.; Wang, Y.; Cui, Y.; Bao, Z.; Yu, G. Nanostructured Conductive Polypyrrole Hydrogels as High-Perform-