Nickel foam supported mesoporous MnO$_2$ nanosheet arrays with superior lithium storage performance†

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Mesoporous MnO$_2$ nanosheet arrays have been directly grown on nickel foam current collectors and exhibited a reversible capacity as high as 1690 mA h g$^{-1}$ even after one hundred cycles at 100 mA g$^{-1}$. They also reveal good rate capability and excellent cycling stability.

Lithium-ion batteries (LIBs) are nowadays being broadly utilized in consumer electronics such as laptop computers, smart phones and digital cameras, and have recently emerged as a promising alternative to replace lead-acid batteries for energy storage in solar panels, electrical grids as well as hybrid electric vehicles. In order to fulfill the ever-growing demand for high energy and high power applications, developing LIB electrode materials having high-capacity, good rate capability and excellent cycling performance becomes greatly desired. In view of their large theoretical capacity, transition metal oxides (TMO) have been intensively investigated in the past decade for use as anode materials in LIBs. Manganese dioxide (MnO$_2$), among various TMOs, is particularly attractive in that it has higher theoretical capacity (1233 mA h g$^{-1}$) than many others, and is abundant in nature, low-cost as well as environmentally benign. Although different MnO$_2$ nanostructures have long been studied as electrode materials for supercapacitors, little attention was paid to their use as anode materials in LIBs.

Similar to other TMOs, MnO$_2$ based electrodes generally suffer from limited reversible capacity and fast capacity decay upon cycling because of the poor electrical conductivity (10$^{-8}$–10$^{-7}$ S cm$^{-1}$) of MnO$_2$ and the large volume change upon lithiation and de-lithiation. Attempts at fabricating nanocomposites consisting of MnO$_2$ nanostructures and electrically conductive carbon such as carbon nanotubes, amorphous carbon or graphenes have been made very recently, but only limited success was achieved. The specific capacity of these composites is still far below the theoretical prediction and the capacity value cannot be satisfactorily retained after extended cycling.

In this communication, we report direct growth of mesoporous MnO$_2$ nanosheet (NS) arrays on a nickel (Ni) foam current collector by simple and low-cost electrodeposition followed by a low temperature thermal annealing process (170 °C, 5 h, ESI†) in a nitrogen atmosphere. When using the Ni foam supported mesoporous MnO$_2$ NS arrays as anodes in LIBs, we find that the electrode can deliver a reversible capacity as high as 1690 mA h g$^{-1}$ even after one hundred cycles at a charge–discharge current density of 100 mA g$^{-1}$. 4.5 times higher than the theoretical capacity of graphite – the anode material currently being widely used in commercially available LIBs. More remarkably, the Ni foam supported mesoporous MnO$_2$ NS electrodes also exhibit very good rate capability and excellent cycling stability.

Fig. 1a shows a top view scanning electron microscopy (SEM) image of the electrodeposited MnO$_2$ NS arrays supported on the Ni foam current collector. MnO$_2$ was found to deposit uniformly and conformally over the entire skeleton of the Ni foam which consists...
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of an interconnected network of ribbon-like ligaments with the microscopic pores (Fig. S1, ESI†). A close inspection of the Ni foam surface reveals that the deposited MnO₂ can be characterized by a high density array of vertically aligned NSs having a thickness of 20–30 nm, as shown in Fig. 1b. These NSs are interconnected laterally, forming a highly open and porous structure, and firmly adhere to the underlying Ni foam. Extensive TEM investigation has been carried out in order to study the microstructural feature of the electrodeposited MnO₂ NSs. As shown in Fig. 1c, the NSs exhibit flexible silk-like morphology with a high degree of transparency, indicating that they are very thin. Upon closer examination, it is observed that the sheets are actually mesoporous with an average pore size of 8 nm, as revealed in Fig. 1d. These mesoscopic pores could result from the thermal decomposition of the electrodeposited hydroxides upon annealing, as reported for other nanostructures prepared in a similar way.15 Selected area electron diffraction (SAED) was performed to identify the crystal structure of the as-fabricated NSs (inset, Fig. 1d). A careful analysis confirms that these sheets consist of orthorhombic MnO₂ (COD database code: 900-3476). High resolution TEM (HRTEM) investigation reveals that these NSs are highly crystalline, and the measured interplanar spacings match those of orthorhombic MnO₂ very well, as shown in Fig. 1e. Besides, energy dispersive X-ray spectroscopy (EDX) was conducted to determine the composition of the NSs (Fig. 1f), which corroborates that the sheets are composed of manganese and oxygen. The carbon and copper peaks come from the carbon-coated copper grid.

Fig. 2a shows X-ray diffractions (XRD) patterns of the as-deposited NSs supported on Ni foam and a bare Ni foam for comparison. The peaks at 33.7°, 36.7°, 37.6°, 40.8° and 47.7° can be indexed to the diffractions from (301), (011), (400), (211) and (302) crystal planes of orthorhombic MnO₂, consistent with the above SAED results. Several features in the X-ray photoelectron spectroscopy (XPS) data also identify the dominant surface oxide as MnO₂. The position and line shape (sharp Mn 2p⁵/₂ peak at 641.6 eV, no satellites) of the Mn 2p doublet in Fig. 2b indicate majority Mn⁴⁺ chemistry with a minor Mn³⁺ component (small shoulder at ~640 eV).16 This assignment is supported by the O/Mn ratio determined from the metal oxide component of O 1s at 529.5 eV in Fig. 2d and Mn 2p peaks as ~1.9. Finally, the exchange splitting of ~5 eV for Mn 3s components shown in Fig. 2c corresponds to a valency of between 3 and 4 for Mn,17 while the symmetric shapes of Mn 3s peaks likely arise not from multiple chemical states but from one dominant state with a minor component, identified above as Mn⁴⁺ and Mn³⁺, respectively. The XPS data agree with the abovediscussed SAED and XRD results, further corroborating that the NSs are primarily composed of MnO₂ with little impurity of Mn³⁺ oxide.

The Ni foam supported mesoporous MnO₂ NSs were directly used as anodes in lithium-ion coin cells, and their electrochemical lithium storage performance was thoroughly evaluated in the potential range of 0.0–3.0 V vs. Li/Li⁺. Fig. 3a shows the cyclic voltammograms (CVs) of the first three cycles recorded at a scan rate of 0.05 mV s⁻¹. It is seen that upon the first scan, three cathodic peaks appear at 1.4, 0.8 and 0.1 V, respectively, corresponding to the reduction of manganese oxide to metallic manganese (Mn⁴⁺ to Mn⁰) as well as the formation of Li₂O and a solid electrolyte interphase (SEI) layer. Two anodic peaks located at 1.3 and 2.4 V are observed, which indicates that the re-oxidation of manganese may need two steps. During the second cycle, the cathodic peaks at 1.4 and 0.8 V disappear and the peak in the low potential region shifts from 0.1 to 0.3 V, suggesting an irreversible structural or textural change in the electrode materials due to the formation of Li₂O and metallic manganese.6 The CV curve of the third scan closely resembles that of the second scan, which manifests that the lithiation and de-lithiation processes are highly reversible from the second cycle onwards.

Fig. 3b depicts the charge–discharge potential profiles of the electrode tested at 100 mA g⁻¹ at different cycles. The well-defined potential plateau in the range of 0.35–0.75 V for lithiation and 1.0–2.0 V for de-lithiation is in good accordance with those of MnO₂ reported before.7 It is interesting to note that the capacity gradually increases with the increasing cycle numbers, as opposed to what people had observed in the same materials.6–14 It is assumed that the increase in capacity might originate from the increased number of vacancies and grain boundaries due to pulverization of the MnO₂ NSs upon cycling, where Li ions could be stored, as will be discussed below.18,19 Remarkably, after one hundred cycles, the capacity has been completely restored,
amounting to 1690 mA h g\(^{-1}\), even slightly higher than the initial capacity (i.e. 1643 mA h g\(^{-1}\)).

The cycling performance of the electrode was further evaluated at 100, 700 and 1000 mA h g\(^{-1}\), and the capacity as a function of cycle numbers was plotted in Fig. 3c. In all cases, the reversible capacity drops in the first few cycles, then increases over cycle numbers, and finally gets stabilized up to 100 cycles for the cell cycling at 100 mA g\(^{-1}\), 160 cycles for the cycling at 700 mA g\(^{-1}\) and 200 cycles for the cycling at 1000 mA g\(^{-1}\). No capacity fading was observed upon cycling for all the cells being tested. Actually, the increase in capacity over cycle numbers agrees well with the charge–discharge profiles shown in Fig. 3b and Fig. S2 (ESI†). Particularly, it is worth mentioning that for the cell cycling at 1000 mA g\(^{-1}\), the electrode can still maintain appreciable reversible capacity at about 900 mA h g\(^{-1}\) without any decay up to 200 cycles, indicating that the cell’s cycling performance is excellent even at high rates. More remarkably, the reversible capacity at 100 mA g\(^{-1}\) is far beyond the theoretical capacity of MnO\(_2\) (1233 mA h g\(^{-1}\)), which is, to the best of our knowledge, the highest reversible capacity for TMO. In fact, lithium storage capacity higher than theoretical prediction was also reported previously, both in anode and cathode materials \(^{20,22}\). In our case, we assume that the excess capacity can be attributed, on the one hand, to lithium storage in the formed gel-like polymeric SEI layer upon the first discharge (i.e. lithiation), as proposed by Tarascon et al. \(^{20,22}\) and well accepted for TMO; on the other hand, to lithium storage in the existing cavities and mesopores as well as the interface/surface of the crystallites in the NSs, \(^{18,19}\) given the fact that the NSs are mesoporous and contain a large number of grain boundaries and defects.

Furthermore, the rate capability was examined by cycling the cell at various current densities in the same potential window. It is seen from Fig. 3d that the capacity can retain more than 50% when the current density changes from 100 to 1000 mA g\(^{-1}\). Actually, the major capacity drop occurs at the transition from 100 to 300 mA g\(^{-1}\). Afterwards, the capacity only reduces insignificantly with the increase in current density. It is also noted that the capacity values remain fairly stable over cycle numbers for a specific current density, demonstrating excellent rate capability of the electrode. In order to check the capacity restoration capability, the cell was further cycled at successively reduced current densities of 300 and 100 mA g\(^{-1}\). The restored capacity at 300 and 100 mA g\(^{-1}\) was found to be even higher than that measured previously and to increase over cycle numbers, consistent with the observation during the cycling test (Fig. 3c).

Besides, during the whole process, the Coulombic efficiency has been very high, close to 100% at all rates, indicating that the lithiation and de-lithiation processes are highly reversible.

The superior lithium storage performance of the Ni foam supported MnO\(_2\) NS electrode is believed to result from the unique structural feature of the NSs and their intimate contact with the underlying Ni foam. As shown in Fig. 1, the mesoporous MnO\(_2\) NSs are virtually grown vertically on the surface of the ligaments of Ni foam, forming open networks, which constitute, together with the micropores of the Ni foam, a hierarchical porous electrode offering a large electrolyte/electrode contact area. This can to the maximum extent facilitate the transport of electrolyte, ions and electrons, as evidenced by the sharp Warburg plot and relatively low charge transfer resistance of the electrode obtained by electrochemical impedance spectroscopy (Fig. S3, ESI†). Moreover, since the NSs are individually connected with the current collector, electron transfer can be accomplished very fast, which helps to improve the rate performance. Furthermore, the flexible ultrathin nature of the NSs and the wide inter-sheet space buffered by the electrolyte can better accommodate the volume change upon lithiation–de-lithiation, maintaining the intactness of the NSs and thereby the cycling stability. This is verified by the fact that the NSs still remain intact even after extended cycling tests at various current densities (Fig. S4, ESI†).

In summary, well-defined mesoporous MnO\(_2\) nanosheet arrays were directly grown on nickel foam current collectors, and exhibit extraordinarily high reversible capacity. Moreover, the MnO\(_2\) nanosheet electrodes also demonstrate very good rate capability and excellent cycling performance. It is assumed that the superior lithium storage performance results from the unique structural feature of the nanosheets and the intimate contact between the nanosheets and the current collector, which to the maximum extent facilitates the mass transport of lithium ions and the charge transfer processes. The nickel foam supported MnO\(_2\) nanosheet arrays hold great promise for use as high-performance anodes in lithium-ion batteries.

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Notes and references

Electronics Supplementary Information for

Nickel foam supported mesoporous MnO$_2$ nanosheet arrays

with superior lithium storage performance

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Experimental details

Sample preparation:

Before electrodeposition, the Ni foam (110 PPI, 480 g m$^{-2}$, 0.3 mm thick) was carefully cleaned with 6 M hydrochloric acid solution in an ultrasonic bath for 10 min, and then washed in sequence with copious de-ionized water ($\geq$ 18 MΩ·cm) and absolute ethanol. Afterwards, the Ni foam was dried at ambient temperature. The electrodeposition was performed in a two-electrode electrochemical cell using a piece of freshly cleaned Ni foam as working electrode and a platinum wire as counter electrode. The electrolyte was 0.02 M manganese acetate ($\geq$99%, Sigma-Aldrich) aqueous solution. A Keithley 2400 sourcemeter was used as a power supply. The deposition was conducted at room temperature at a current density of 10.5 mA cm$^{-2}$ for 3 min. After deposition, the Ni foam was thoroughly rinsed with de-ionized water and absolute ethanol for several times, and then dried in air. Subsequently, the sample was annealed in high-purity nitrogen (99.999%) at 170 °C for 5 h. The weight of the sample was measured before electrodeposition and after thermal annealing using a high precision electronic balance (Sartorius CPA225D) in order to calculate the mass of the deposited active materials.

Characterization:

The morphology of the as-prepared MnO$_2$ nanosheets was examined by scanning electron microscopy (FEI Quanta FEG650), and their crystal phase and microstructure were investigated by X-ray diffractometry (PanAnalytical X’pert Pro) and transmission electron microscopy (FEI TITAN ChemSTEM 80-200 kV, probe corrected), respectively.

The surface chemistry of manganese oxide nanosheets was probed by X-ray photoelectron spectroscopy (XPS) using an ESCALAB 250 Xi system (Thermo Scientific) equipped with a monochromated Al Kα X-ray source, a hemispherical electron energy analyzer, a magnetic lens, and a video camera for viewing the analysis position. Uniform charge neutralization was provided by beams of low-energy ($\leq$10 eV) Ar$^+$ ions and low-energy electrons guided by the
magnetic lens. The standard analysis spot of ca. 900×600 μm² was defined by the microfocused X-ray source. The measurements were performed at room temperature in an ultra-high vacuum chamber with the base pressure <5×10⁻¹⁰ mbar; the charge neutralization device produced ca. 2×10⁻⁷ mbar partial pressure of Ar during measurements. The energy of the monochromated Al Kα X-ray source was measured to be within <0.2 eV from 1486.6 eV. The binding energy (BE) scale of the analyzer was calibrated to produce <50 meV deviations of the three standard peaks from their standard values: 83.98 eV for Au 4f⁷/₂, 368.26 eV for Ag 3d⁵/₂, and 932.67 eV for Cu 2p₃/₂. The aliphatic C 1s peak was observed at 284.6 eV. High-resolution elemental XPS data in C 1s, O 1s, Mn 2p, and Mn 3s regions were acquired with the analyzer pass energy set to 20 eV (corresponding to energy resolution of ca. 0.36 eV) and the step size set to 0.1 eV. All the spectra were acquired in normal emission with an effective analyzer collection angle of ca. 30°. Advantage software package (Thermo Fisher Scientific) was used to fit the elemental spectra and to quantify the standard “atomic ‰” elemental compositions based on calibrated analyzer transmission functions, Scofield sensitivity factors, and effective attenuation lengths for photoelectrons from the standard TPP-2M formalism.

**Electrochemical measurements:**

The electrochemical performance was evaluated by cyclic voltammetry (CV), galvonastatic charge/discharge technique and electrochemical impedance spectroscopy (EIS) using a Biologic VMP3 battery tester. The tests were made using 2032 type coin cells with the Ni foam supported MnO₂ nanosheet arrays as working electrode and Li metal as counter as well as reference electrodes. The electrolyte consists of LiPF₆ dissolved in EC: DMC (1:2 vol%). Celgard 2300 membranes were used as separator. The cells were assembled in an argon filled glove box (JACOMEX, Germany) where the moisture and oxygen levels were kept below 0.5 ppm.
Supplementary Figures

Figure S1. (a) Overview and (b) Zoomed view SEM micrographs of the nickel foam (110 PPI, 480 g m\(^{-2}\), 0.3 mm thick) used in the experiments.
Figure S2. Charge/discharge profiles of the cells measured at current densities of (a) 700 mA g\(^{-1}\) and (b) 1000 mA g\(^{-1}\).
Figure S3. (a) The electrochemical impedance spectra (EIS) of the MnO₂ NS electrode measured at different cycling intervals. Insets: zoomed view (upper right) and the fitted impedance values (lower right). Equivalent circuit models of (b) the as-assembled fresh cells and (c) the cycled cells, where \( R_{el} \) refers to the electrolyte resistance, \( Q_{sei} \) the constant phase element of the SEI layer, \( R_{sei} \) the resistance of the SEI layer, \( Q_{dl} \) the constant phase element of the double layer, \( R_{ct} \) the charge-transfer resistance, and \( W_{o} \) the Warburg impedance. Frequency range: 1 mHz – 1 MHz.

It is seen that all the Nyquist plots consist of a large depressed semicircle followed by a straight slope. The depressive nature originates from the existence of a Li⁺ ion migration process through the surface film of the electrode (e.g. SEI layer) in the high frequency region and a charge transfer process between the electrode and electrolyte in the medium frequency region. A sharp Warburg in the low frequency region indicates fast diffusion of Li⁺ ions to the electrode.
**Figure S4.** SEM micrographs showing the morphology of the Ni foam supported MnO$_2$ NSs subjected to charge/discharge for 70 cycles at various current densities. After disassembling, the electrode was ultrasonicated in isopropanol for 10 min in order to remove the remaining electrolyte. (a) Overview and (b) Zoomed view.