Three-Dimensionally “Curved” NiO Nanomembranes as Ultrahigh Rate Capability Anodes for Li-Ion Batteries with Long Cycle Lifetimes

Xiaolei Sun, Chenglin Yan,* Yao Chen, Wenping Si, Junwen Deng, Steffen Oswald, Lifeng Liu, and Oliver G. Schmidt

The depletion of traditional energy resources has stimulated significant research interest in developing renewable energy sources, including solar radiation, wind, and waves. Because of the intermittent availability of these resources, the exploitation of their full potential requires the development of energy storage systems. Lithium-ion batteries (LIBs), as a class of energy storage devices, are now attracting great attention for applications in portable electronic devices and electrical vehicles. To meet the ever-increasing demand for efficient energy storage systems in hybrid electric vehicles and plug-in hybrid electric vehicles, LIBs must be developed further to improve their ability to deliver high power and their energy density with ensured safety in operation and reduced cost.

As a transition metal oxide, nickel oxide (NiO) is low cost, environmentally friendly, and abundant in nature. It is considered as one of the most appealing anode materials due to its high lithium storage capacity. However, the performance of the NiO anode has been limited by its poor electrochemical reactivity and large volume variation during the lithium uptake/release process. To address these issues, various nanostructured NiO anode materials have been fabricated to achieve improved electrochemical performance. Despite significant progress, the NiO electrodes are still far from commercialization. Therefore, new strategies for building advanced NiO electrodes with ultrafast power rates and long lifespans are urgently needed.

Recently, curved nanomembranes, an important family of functional materials, have attracted considerable interest because of their properties and potential applications in energy storage, fluidic sensor, bioanalysis, etc. In terms of LIBs, the large interstitial space in the curved nanostructure can efficiently increase the surface area accessible to the electrolyte, which allows lithium ions to intercalate at the interior and exterior of the curved nanomembranes and to accommodate large and frequent mechanical strain from the electrochemical reactions of the active materials with lithium ions.

Here, we report three-dimensionally “curved” NiO nanomembranes made using a simple fabrication technique followed by a thermal oxidation process, based on above considerations. The curved NiO nanomembranes exhibit both superior power rate and ultralong cycle life when utilized as the anode material for LIBs. The electrodes deliver a high capacity of 721 mAh g⁻¹ at 1.5 C (1 C = 718 mA g⁻¹) after 1400 cycles. Notably, even after cycling at an extremely high C-rate of 50 C (i.e., current density of 35 400 mA g⁻¹), the capacity is able to recover to the initial value when the current rate is set back to 0.2 C after 110 cycles. To the best of our knowledge, such impressive superior power rate and ultralong lifespan for nickel-oxide-based electrodes have not been reported previously.

The chemical composition of the product was determined by X-ray powder diffraction (XRD), as shown in Figure 1a. All three characteristic diffraction peaks can be assigned to NiO in the face-centered cubic phase (JCPDS card No. 47–1049). The corresponding Raman spectrum (see Supporting Information, Figure S1) reveals five broad peaks centered at 402, 520, 695, 879, and 1069 cm⁻¹, which are of vibrational origin and correspond to the one-phonon first-order transverse optical mode (TO, at 402 cm⁻¹), one-phonon longitudinal optical mode (LO, at 520 cm⁻¹), two-phonon modes (2TO, at 695 cm⁻¹), TO + LO (at 879 cm⁻¹), and 2LO (at 1069 cm⁻¹) modes, respectively.

Further, the composition and valence states of the material were investigated by X-ray photoelectron spectroscopy (XPS; Supporting Information, Figure S2), where the O 1s and Ni 2p core levels were examined. The O 1s spectrum consists of a main peak at 530.7 eV with a shoulder at 532.4 eV. The two regions in the Ni 2p spectrum could be assigned to the Ni 2p₁/₂ (870–885 eV) and Ni 2p₃/₂ (850–865 eV) spin-orbit levels, respectively. From these spectra it follows that Ni is at the surface, mainly in the Ni²⁺ state with some Ni³⁺ contribution, and no metallic Ni is observed.

The low-magnification scanning electron microscopy (SEM) image in Figure 1b provides an overview of the morphology...
of the as-prepared product. Clearly, the product is composed of large quantities of curved nanomembranes with an average diameter around 10 μm and wall thickness of 25 nm. The representative high-magnification SEM and transmission electron microscopy (TEM) images (Figure 1c,d) reveal that the nanomembrane is rolled up around itself, resembling a scroll of parchment with open ends and smooth surface. The corresponding selected area electron diffraction (SAED, Figure 1e) pattern displays diffraction rings assigned to the (111), (200), (220), (311), and (222) planes, respectively. The result indicates the polycrystalline nature of face-centered cubic NiO, which is consistent with the XRD results. In the high-resolution TEM (HR-TEM) image (Figure 1f), it is observed that the ultrathin nanomembranes are built from numerous NiO nanocrystals around 8 nm in size that are randomly distributed without specific orientations, which is also in good agreement with the XRD and SAED results. This unique structure should result in excellent lithium storage as it combines efficient 3D electron transport, excellent connectivity with electronic and ionic sources, and short diffusion distance, which will be confirmed in the following by the electrochemical analysis.

To verify the excellent electrochemical performance of the curved NiO nanomembranes, Swagelok-type cells using the nickel oxide nanomembranes as the anode and lithium metal
as the counter electrode were assembled. The cyclic voltammetry (CV) profiles of the initial five cycles were recorded at a scan rate of 0.1 mV s\(^{-1}\) within the potential window of 0.02–3.0 V versus Li/Li\(^+\). As shown in Figure 2a, the profiles of the CV curves of the second and fifth cycles are similar, which is indicative of good cycling performance. However, there are significant differences between the first and the subsequent scans. In the first cycle, an intense peak located at around 0.5 V is observed in the cathodic scan, corresponding to the initial reduction of NiO to Ni, the formation of amorphous Li\(_2\)O (NiO + 2Li\(^+\) + 2e\(^-\) → Ni + Li\(_2\)O), and the formation of the solid electrolyte interphase (SEI) layer.\[^{14,25}\] This peak becomes weaker and shifts to about 1.07 V during the subsequent scans. The two broad peaks located at about 1.4 and 2.2 V in the anodic scan curves can be attributed to the decomposition of the SEI layer and the Li\(_2\)O decomposition (Ni + Li\(_2\)O → NiO + 2Li\(^+\) + 2e\(^-\)), respectively.\[^{15,26}\] The small shift of the peaks during the subsequent cycles may be due to the drastic lithium driven, structural, or textural modifications.\[^{11,25}\] However, a more surprising and interesting phenomenon found here is that the oxidation peak area increases progressively during the following cycles, which can also be detected at high scan rates (see Supporting Information, Figure S3), indicating that there might be an activating process or the partial decomposition of SEI on the surface of the electrode materials.\[^{17,21}\] In addition to the above-mentioned faradaic processes, the capacitive effects were also investigated using previously reported methodology to some extent.\[^{27,28}\] The capacitive contributions of electrochemical energy storage at different scan rates are illustrated in Figure S3 (Supporting Information). We analyzed the CV data and found that the percentage contribution of the faradaic part and the non-faradaic part to the overall charge storage depends on the sweep rate and the shifting of the main redox peaks. Capacitive processes become more obvious at higher sweep rates due to the rapid discharge/charge characteristics, and the diffusion of lithium ions into the inner surface of the curved NiO becomes more difficult.

Figure 2b shows representative discharge–charge voltage profiles of the NiO electrodes for the first five cycles at a current rate of 0.2 C within a cutoff voltage window of 0.02–3.0 V. The electrodes exhibit a potential plateau at ≈0.7 V during the first discharge. After the first cycle, this long potential plateau is replaced by a long sloped curve from 1.7 to 0.9 V, which is in agreement with the CV results. In addition, the first discharge and charge profiles deliver capacities of 1073 and 732 mAh g\(^{-1}\), respectively. The capacity loss of 31.8% is mainly attributed to the interfacial reaction between NiO and the electrolyte, which is commonly observed for most anode materials.\[^{29–31}\] Remarkably, the capacity of the electrodes continuously increases after the second cycle. The discharge capacity gradually increases to 742 mAh g\(^{-1}\) after 5 cycles, and the Coulombic efficiency steadily reaches a value higher than 99.0%. The increased capacity characteristic after the initial cycle is consistent with the observation that the oxidation peak current increases gradually in subsequent CV cycles, which can be ascribed to gradual electrochemical activation of the electrode material.
In order to gain a better understanding of the enhanced electrochemical performance of the curved NiO electrodes, impedance measurements were performed on NiO electrodes before cycling, and after the 1st, 3rd, and 5th cycles, as shown in Figure 2c. The measured impedance data were analyzed by fitting to an equivalent circuit (inset of Figure 2c), and a detailed illustration can be found in Supporting Information (Table S1). It consists of the electrolyte and cell components (R_e), surface film (R_{sf}), and charge transfer (R_{ct}) resistances, a constant phase element instead of pure capacitance (CPE_i) (due to the observation of a depressed semicircle), as well as Warburg diffusion impedance (W_s).

In Figure 2c the symbols represent the experimental data, whereas the continuous lines represent the fitted spectra. The as-prepared cell (=3.0 V) shows a single depressed semicircle in high frequency region, and the impedance of 14.77 Ω is mainly attributed to R_{sf}. The associated capacitance (CPE_{sf}) is 16.08 μF. It is noticed that the R_{sf}(ct) gradually decreased during cycling (from 26.66 to 11.45 Ω). Generally, the curved materials would loosen interior windings and expose the inner surfaces to the electrolyte during cycling. Thus, the activation of the internal wrapped active could contribute to the electrochemical reaction and the formation of a stable SEI layer, which would facilitate the lithium ion transfer at the interface between the electrolyte and the electrode. This natural phenomenon, in principle, should be reflected as the capacity increase after the first cycle, exhibiting excellent cyclic stability and rate capability.

Here, the representative discharge-charge voltage profiles of the NiO electrodes at various rates are shown in Figure 2d. As anticipated, the increase in current density gives rise to higher overpotential resulting from the kinetic effects of the electrode material, in terms of lower discharge plateau and higher charge potential. However, the discharge and charge curves under different rates still display a similar curve shape, demonstrating excellent rate performance.

The curved NiO nanomembrane electrodes also exhibit an impressive rate capability. Figure 3a shows the rate capability behavior over 110 cycles from 0.2 C to 50 C. The discharge capacities are 735, 699, 647, 582, 484, 374, and 240 mAh g⁻¹ at 0.2, 0.5, 1, 2, 5, 10, and 20 C, respectively. Notably, even after cycling at an extremely high C-rate of 50 C (i.e., current density of 35 400 mA g⁻¹), the capacity can recover to the initial value (about 710 mAh g⁻¹) when the current rate is set back to 0.2 C after 110 cycles. This remarkable rate capability can be repeated in another rate experiment cycling from 0.1 C to 50 C (see Supporting Information, Figure S4), which illustrates that the curved NiO anodes have very stable cycling performance.

The excellent rate capability is attributed to the short lithium diffusion distance in the curved NiO nanomembranes. We further evaluated the long life cycle performance of the NiO anodes. The data shown in Figure 3b has been recorded at 0.05 C for the initial four-cycles and then at 1.5 C current rate for the following cycles in the voltage range of 0.02–3.0 V. The NiO electrode shows excellent cycling stability with a capacity steadily increasing up to ≈1000 mAh g⁻¹ after 500 cycles. After that, the capacity gradually decreases to 721 mAh g⁻¹ after 1400 cycles, which is almost two times higher than that of the theoretical maximum capacity for graphite anodes (372 mAh g⁻¹).

As expected, these curved NiO nanomembrane anodes manifest ultrahigh rate capability and long term cycling stability compared to previously reported NiO-based anode materials (see Supporting Information, Table S2). The rise in
capacity is not surprising for the nanostructured NiO electrode, although it is rarely observed when an intercalation mechanism occurs. The plausible explanations are generally ascribed to the reversible growth of polymeric gel-like layers resulting from kinetically activated electrolyte degradation, a capacitive interface storage including electric double layer capacitance as well as an activating process in nanosheets, which can be confirmed from impedance spectra (Figure 2c). Recently, Zhou proposed an electrochemical catalytic conversion mechanism for lithium storage: during the charging process, the metal nanoparticles functioned as effective catalysts for the reversible formation/decomposition of some SEI components. To confirm this hypothesis, the discharge-charge profiles of NiO are also provided (see Supporting Information, Figure S5). The curves after the 100th cycle start losing their plateau-shape, indicative of the decomposition of SEI layers and polarization of electrodes upon cycling in the present of Ni as a catalyst. After 500 discharge-charge cycles, its original morphology is apparently retained with a remaining rough SEI layer (see Supporting Information, Figure S6). The structure expanded but did not break during cycling. These findings should be responsible for the enhanced reaction kinetics and improved performance. In other words, the excellent electrochemical properties are therefore related to the specific kinetic properties within the curved nanomembranes and the reversible formation/decomposition of some SEI components.

In summary, we have demonstrated novel curved NiO nanomembranes fabricated by rolled-up nanotechnology followed by a thermal oxidation process. As anode materials for LIBs, these nanostructured materials exhibit impressive results, i.e., ultrafast power rate (50 C), a high capacity of 721 mAh g⁻¹ at 1.5 C, and long lifetime (1400 cycles). This work demonstrates the great potential of curved NiO nanomembranes for the design of high power LIBs. Furthermore, we believe that this method can be easily extended to fabricate other high-rate capability anodes and cathodes.

**Experimental Section**

**Materials Preparation:** Positive photoresist (AR P-3510, Allresist GmbH) as a sacrificial layer was spin-coated on a Si wafer at 3500 rpm for 35 s; this was followed by a hotplate baking step at 90 °C for 5 min. The non-stoichiometric nickel oxide nanomembranes were then deposited by electron beam evaporation. Oxygen flowed in the chamber at a pressure of about 8 × 10⁻⁵ mbar during the entire deposition process. The resulting non-stoichiometric nickel oxide nanomembranes were subsequently rolled-up into curved nanomembranes immediately after being immersed into acetone. Large quantities were collected after rinsing away the photoresist thoroughly and dried in a super critical point dryer (CPD). Then, the obtained materials were placed in an air-flowing tube furnace, which was then heated to a temperature of 400 °C for 1.5 h.

**Materials Characterization:** The samples were characterized by XRD using a Philips PW 1050 diffractometer (Co Kα radiation) and Raman spectroscopy using InVia Raman microscopes (Renishaw) with the excitation wavelength at 442 nm. The XPS measurements were further carried out using a PHI 5600 CI (Physical Electronics) spectrometer to check the chemical state of the elements constituting the samples. The morphologies of the samples were investigated by SEM (DSM982 Gemini, Germany) and TEM (FEI Titan ChemiSTEM 80–200).

**Electrochemical Characterization:** Electrochemical measurements were performed with Swagelok-type cells using Li foil as the counter electrode. The working electrode was prepared by mixing the active material, carbon black, and Na-alginate at a weight ratio of 80:10:10 in distilled water. The resultant slurry was then uniformly pasted onto a current collector (copper foil, Goodfellow) and dried in a vacuum oven at 80 °C for 12 h. These cells were assembled in an argon-filled glove box (H₂O < 0.1 ppm, O₂ < 0.1 ppm, MBraun, Germany). The electrolyte was 1 m LiPF₆ dissolved in a mixture of ethylene carbonate (EC), diethyl carbonate (DEC) and dimethyl carbonate (DMC) (1:1:1 by weight, Merck) containing 2.0 wt% vinylene carbonate (VC, Aldrich). Glass fibers (GF/D) from Whatman were used as separators. The two-electrode Swagelok type cells were galvanostatically discharged and charged in the voltage range of 0.02–3.0 V vs. Li/Li⁺ by an Arbin BT2000 system. CV tests were carried out between 0.02–3.0 V at various sweep rates ranging from 0.1 to 10 mV s⁻¹. In the case of electrodes prepared for EIS studies, a three-electrode Swagelok type cell was employed with the third electrode (also a lithium metal foil) used as the reference, and the evolution of the equivalent circuit parameters as a function of cycle number was investigated for a fixed voltage of 3.0 V. The frequency range was varied from 100 kHz to 10 mHz with an AC signal amplitude of 5 mV. Both the CV and EIS measurements were performed at room temperature using a Zahner-elektrik IM6 instrument (Germany).

**Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

**Acknowledgements**

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Supporting Information


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Figure S1. Raman spectrum of the as-prepared curved NiO nanomembranes.
Figure S2. XPS spectra of the as-prepared curved NiO nanomembranes.
Figure S3. CV profiles of the initial five-cycles in the potential window of 0.02-3.0 V at different scan rates.
Table S1. Impedance parameters derived using equivalent circuit model for the curved NiO electrode before cycling and after the 1st, 3rd, and 5th cycle.

<table>
<thead>
<tr>
<th>NiO electrodes</th>
<th>$R_s$ (Ω)</th>
<th>CPE$_{sf+ct}$ (µF)</th>
<th>$R_{sf+ct}$ (Ω)</th>
<th>$Z_w$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>before cycling</td>
<td>3.302</td>
<td>16.08</td>
<td>14.77</td>
<td>125.7</td>
</tr>
<tr>
<td>after 1st cycle</td>
<td>2.731</td>
<td>151.83</td>
<td>26.66</td>
<td>83.49</td>
</tr>
<tr>
<td>after 3rd cycle</td>
<td>3.184</td>
<td>215.45</td>
<td>17.67</td>
<td>107.6</td>
</tr>
<tr>
<td>after 5th cycle</td>
<td>4.858</td>
<td>138.08</td>
<td>11.45</td>
<td>78.33</td>
</tr>
</tbody>
</table>

Figure S4. Rate capability of the curved NiO nanomembrane electrodes.
Table S2. Summary of the electrochemical performance of various NiO anodes.

<table>
<thead>
<tr>
<th>NiO-based anodes</th>
<th>Maximum Rate Capability</th>
<th>Cycle Numbers/Capacity</th>
<th>Voltage Range</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Curved NiO nanomembranes</td>
<td>50 C</td>
<td>1400 cycles/~721 mAh g⁻¹</td>
<td>0.02-3.0 V</td>
<td>Our work</td>
</tr>
<tr>
<td>Mesoporous NiO crystals</td>
<td>40 C</td>
<td>1000 cycles/~468 mAh g⁻¹</td>
<td>0.01-3.0 V</td>
<td>[1]</td>
</tr>
<tr>
<td>NiO nanofibers</td>
<td>11.1 C</td>
<td>100 cycles/~583 mAh g⁻¹</td>
<td>0.005-3.0 V</td>
<td>[2]</td>
</tr>
<tr>
<td>NiO nanocone arrays</td>
<td>10 C</td>
<td>100 cycles/1058 mAh g⁻¹</td>
<td>0.02-3.0 V</td>
<td>[3]</td>
</tr>
<tr>
<td>Nanoporous NiO films</td>
<td>10 C</td>
<td>100 cycles/540 mAh g⁻¹</td>
<td>0.02-3.0 V</td>
<td>[4]</td>
</tr>
<tr>
<td>NiO nanowall</td>
<td>-</td>
<td>85 cycles/890 mAh g⁻¹</td>
<td>0.005-3.0 V</td>
<td>[5]</td>
</tr>
<tr>
<td>Mesoporous NiO nanosheets</td>
<td>10 C</td>
<td>80 cycles/1043 mAh g⁻¹</td>
<td>0.02-3.0 V</td>
<td>[6]</td>
</tr>
<tr>
<td>Hollow NiO microspheres</td>
<td>1.4 C</td>
<td>50 cycles/550 mAh g⁻¹</td>
<td>0.02-3.0 V</td>
<td>[7]</td>
</tr>
<tr>
<td>NiO nanoparticles</td>
<td>-</td>
<td>50 cycles/200 mAh g⁻¹</td>
<td>0.01-3.0 V</td>
<td>[8]</td>
</tr>
<tr>
<td>NiO nanofoams</td>
<td>5 C</td>
<td>40 cycles/670 mAh g⁻¹</td>
<td>0.01-3.0 V</td>
<td>[9]</td>
</tr>
<tr>
<td>NiO nanotubes</td>
<td>-</td>
<td>20 cycles/180 mAh g⁻¹</td>
<td>0.01-3.0 V</td>
<td>[10]</td>
</tr>
</tbody>
</table>
Figure S5. Representative discharge-charge voltage profiles for the 2nd, 10th, 100th, 1000th, and 1400th cycles at a rate of 1.5 C, with the 0.05 C for initial four cycles.

Figure S6. SEM image of a single curved NiO after 500 discharge-charge cycles. The scale bar is 20 µm.

Supplementary References


