High Performance Porous Anode Based on Template-Free Synthesis of Co$_3$O$_4$ Nanowires for Lithium-Ion Batteries

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A facile template-free synthesis is developed to directly grow cobalt oxide (Co$_3$O$_4$) nanowires (NWs) on stainless steel (SS) mesh substrate as anode for lithium ion batteries (LIBs). The directly grown Co$_3$O$_4$ NWs on SS mesh are prepared via an ammonia-evaporation-induced method followed by calcination at 300 °C in air. SEM images show a SS mesh-sketched structure with densely grown NWs and ordered meshes on it. Free from the tedious and economically unfavorable electrode fabrication, Co$_3$O$_4$ NWs on SS mesh electrode simplifies the process by a direct growing technique. Furthermore, it better addresses the cycling stability and rate performance issues of Co$_3$O$_4$ by improving both ion and electron transportation. The charge and discharge capacities are stabilized at around 850 mAh g$^{-1}$ after 30 cycles with various current densities. After 100 cycles charge and discharge, Co$_3$O$_4$ NWs on SS mesh electrode still remains a capacity of 766 mAh g$^{-1}$. Together with its outstanding mechanical strength and flexibility, this novel electrode may find many applications in different types of LIBs.

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1. Introduction

Lithium-ion batteries (LIBs) have been contributing tremendously to the evolution of modern electronic applications such as mobile phones, laptops, and other portable electronics, due to their high performance and reliability.[1] The broad implementation of LIBs in electrical transportation vehicles is still hindered by several constraints in terms of energy density, safety, and cost.[2] Currently, most of the commercialized LIBs utilize graphite as anode materials which possesses a theoretical specific capacity of 372 mAh g$^{-1}$, exhibits low cost, and a long cycle life.[3] However, the low packing density of carbon materials leads to a volumetric energy density, which is a critical parameter for a portable device.[4] Moreover, the dynamic solid-electrolyte interface (SEI) layer brings additional safety and cost concerns.[5] Silicon- and tin-based materials are also investigated because of their high specific capacities and abundance, yet their cycling performance is not satisfactory due to the intrinsic large volume change during cycling.[6–9] By comparison, transition metal oxides exhibit much higher capacity than carbon materials, but smaller volume change than Si materials, thus these materials play an important role in the development of high-performance LIBs anode.[10–12]

Among various transition metal oxides, cobalt oxide (Co$_3$O$_4$) has been extensively studied due to its high theoretical capacity (890 mAh g$^{-1}$), low cost, and facile synthesis.[13–15] Although many types of Co$_3$O$_4$-based materials have been reported as anode materials in LIBs, their practical application is still limited by the poor rate performance and cycling stability as a result of their intrinsic low conductivity, and low overall capacity caused by the usage of a large amount of binder and conductive agent during the electrode fabrication.[16,17] To address these issues, two main strategies have been applied. First, more efficient conductive components, such as carbon nanotubes and graphene, are mixed with Co$_3$O$_4$ with different methodologies to increase the conductivity.[18–20] For example, CNT/Co$_3$O$_4$ nanocomposites can deliver a capacity of 776 mAh g$^{-1}$ at a current density of 200 mA g$^{-1}$.[21] However, the overall capacity and the volumetric capacity are significantly sacrificed by the addition of CNT, binder and extra conductive materials like carbon black. Moreover, the weak bond between active materials and current collector may deteriorate during cycling, leading to a poor cycle life. Second, directly grown Co$_3$O$_4$ materials on binder-free and free-standing substrate are also applied to avoid the usage of inert components in the electrode. For example, mesoporous Co$_3$O$_4$ NW arrays were grown on titanium foil and a capacity of around 700 mAh g$^{-1}$ was retained at a cycling rate of 111 mA g$^{-1}$ after 20 cycles.[22] Co$_3$O$_4$ nanobelt arrays grown on titanium foil was reported[23] with an overall capacity of 770 mAh g$^{-1}$ at a current density of 177 mA g$^{-1}$ after 25 cycles, while traditional Co$_3$O$_4$
nanoparticle electrode faded rapidly to present a capacity of lower than 100 mAh g\(^{-1}\) after same cycle number. However, such strategies utilize titanium as the substrate, which suffers high cost and poor flexibility. Li et al.\(^{[24]}\) reported direct growth of \(\text{Co}_3\text{O}_4\) NW film on the surface of steel coin, and showed an initial capacity of around 700 mAh g\(^{-1}\). The cell was stable in first 50 cycles at a charge and discharge rate of 100 mAh\(^{-1}\), however, after 100 cycles, only around 300 mAh g\(^{-1}\) of the cell’s capacity was retained. Therefore, an efficient growth of \(\text{Co}_3\text{O}_4\) nanomaterials on a proper substrate with high specific capacity and good cycling stability is still highly desirable.

Herein, we demonstrate a facile \textit{in-situ} growth of \(\text{Co}_3\text{O}_4\) NWs on the SS mesh current collector as a high-performance, template-free, binder-free, and flexible anode. Such a material possesses several features: (1) The avoidance of using binder and conductive agent, and the low density of stainless steel mesh as well effectively increase the total capacity; (2) The \textit{in-situ} growth ensures an intimate contact between the active material and the highly conductive current collector, leading to a superior rate-performance of the electrode; (3) The excellent mechanical property of SS mesh as well as the unique 2-D NW structure enables the electrode a long cycling stability; (4) The flexibility of the SS mesh provides more functionalities for broader applications. The demonstrated electrode here can deliver a high overall capacity of 855 mAh g\(^{-1}\) at a current density of 100 mA g\(^{-1}\), and the capacity retention is superior that 90% of its initial capacity (766 mAh g\(^{-1}\)) can still be retained after 100 cycles at a current density of 200 mA g\(^{-1}\).

2. Experimental

2.1. Materials Synthesis

SS mesh supported \(\text{Co}_3\text{O}_4\) NW electrodes were synthesized via a facile template-free growing method. As described in Scheme 1, cobalt nitrate hexahydrate (10 mmol, \(\text{Co(NO}_3)_2\cdot 6\text{H}_2\text{O}, \) Sigma-Aldrich, USA) and ammonia nitrate (5 mmol, \(\text{NH}_4\text{NO}_3, \) Sigma-Aldrich, USA) were dissolved in an aqueous solution of 50 ml containing 15 ml of 30 wt% ammonia. Then, it was slowly mixed under magnetic stirring for 10 min in air at room temperature. After that, the solution was transferred to a Petri dish and the preheating step was conducted by placing the covered Petri dish in the 90 °C oven for 2 h. Meanwhile, 500-SS (3 cm \(\times\) 3 cm) mesh was sonicated in DDI water and acetone for 15 min to remove both inorganic and organic impurities. Then it was soaked in 6.0 mol L\(^{-1}\) HCl for 15 min and rinsed with water thoroughly. Next, the pre-treated SS mesh was immersed in the precursor solution and kept at rest for 12 h at 90 °C. Finally, the SS mesh grown with \(\text{Co(OH)}_2\) NWs was rinsed with DDI water and dried in an oven at 60 °C, followed by calcination at 300 °C for 2 h in air with a ramping rate of 2 °C per minute to obtain \(\text{Co}_3\text{O}_4\) NWs.

2.2. Materials Characterizations

The crystal structure and phase composition of the samples obtained were examined by X-ray diffraction (XRD). Scanning electron microscopy (SEM) (Zeiss Ultra Plus, UK) and transmission electron microscopy (TEM) (FEI Philips CM300, USA) were utilized to investigate the morphology of the samples.

To evaluate the electrochemical performance of the synthesized electrodes, CR-2032 coin cells were fabricated in an argon-filled glove box (MBRAUN 10, USA). Lithium metal foil was used as both the reference and counter electrode. A polypropylene membrane (high porosity, 20 μm micro porous, Celgard PP2075, USA) was used as a separator. 1 M LiPF\(_6\) dissolved in a mixed solution of ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 volume ratio, Novolyte, USA) was used as the electrolyte. The SS mesh with \(\text{Co}_3\text{O}_4\) NWs was punched into an appropriate size and directly made into batteries. As a comparison, the conventional electrode fabrication was done by scraping of the same \(\text{Co}_3\text{O}_4\) NWs from the SS mesh mixed with super-P (conductive carbon black) as a conductive material, polyvinylidene fluoride (PVDF) as a binder, forming a slurry in N-methyl pyrrolidone (NMP). Subsequently, it was casted onto a Cu foil current collector. The conventional \(\text{Co}_3\text{O}_4\) NW electrode consisted of 60% active material, 20% binder and 20% conductive material.

The cells were charged and discharged in a potential range of 0.01-3 V (versus Li/Li\(^+\)), same elsewhere in this paper unless specified, electrode potential of Li+/Li is -3.041 V versus Standard Hydrogen Electrode) on a battery testing station (Neware BTS-5 V 10 mA, China) to obtain charge and discharge profiles, cycling and rate capability data. Cyclic voltammetry (CV) between 0.01 V and 3 V and electrochemical impedance spectroscopy (EIS) were conducted on an electrochemical workstation (Versa Stat, Princeton Applied Research, USA). A scan rate of 1 mV s\(^{-1}\) was used in CV tests. All tests above were performed at room temperature.

3. Results and discussion

Fig. 1A and 1B show optical photographs of SS mesh before and after \(\text{Co}_3\text{O}_4\) NWs growth. The color change from grey to black
observed clearly indicates the successful growth of Co$_3$O$_4$ NWs. SS mesh has a great flexibility: Co$_3$O$_4$ NWs on SS mesh were not peeled off by considerable curling, which makes it promising for applications in flexible batteries.[25,26] Fig. 1C shows the XRD pattern of the SS mesh electrode with the diffraction peaks observed at 18.95°, 31.29°, 36.8°, 38.54°, 44.9°, 59.39° and 65.25°, which are indexed to (111), (220), (311), (222), (440), (511) and (440) planes of crystalline Co$_3$O$_4$, in accordance with the standard JCPDS Card NO. 42-1467.[15] No other obvious peaks can be observed, indicating the absence of any impurities.

The morphology of the Co$_3$O$_4$ NW mesh electrode is revealed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), which show that Co$_3$O$_4$ NW arrays directly and vertically grow without the use of any binder or carbon black. Co$_3$O$_4$ NW arrays are densely grown on SS mesh with a highly porous structure which facilitates the electrolyte diffusion and accommodates volume expansion upon Li insertion. In addition, the porous electrode structure and nanostructured active material are believed to provide huge surface area, large free volume, along with increased lithium-ion diffusion rate,[13,22,27–29] endowing the LIBs made from it with superior performance during charge and discharge process. The low magnification SEM image in Fig. 2A shows that electrode is highly porous and the meshes are not blocked by the growth of NWs. Fig. 2B shows the average diameter of NWs of 300 nm with some NWs interconnected with each other during the synthesis. Fig. 2C shows a typical TEM image of several Co$_3$O$_4$ NWs peeled off from the SS mesh with dimensions consistent with SEM results. In addition, surface roughness can be clearly observed, resulting in increased surface area between the electrode and electrolyte. The high crystallinity of Co$_3$O$_4$ NWs is revealed by the SAED pattern inset in Fig. 2C. The fringes observed in high-resolution TEM image in Fig. 2D also confirm crystalline Co$_3$O$_4$ NWs with the lattice distance of 0.233 nm measured corresponding to (222) plane.

Fig. 3A shows the first three CV curves of the electrode fabricated into a coin-type half-cell between 0.01 V and 3 V at a scan rate of...
respectively, the electrochemical Li⁺ insertion/extraction process occurring at spinel Co₃O₄ can be expressed as

\[ \text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- \rightarrow 4\text{Li}_2\text{O} + 3\text{Co} \]  

(2)

Two well-defined current peaks are observed from the initial cycle at 0.52 V (cathodic sweep) and 2.11 V (anodic sweep), respectively, corresponding to the first electrochemical reduction reaction of Co₃O₄ and the formation of solid electrolyte interface (SEI), and the oxidation of Co.[20,30] This observation is consistent with typical insertion/extraction behavior of Li⁺ in Co₃O₄. It is also found that the following CV curves are almost constant, indicating that SEI layer formed during the first cycle is highly stable.

The cycle stability and rate capability of SS mesh supported Co₃O₄ NW electrode and conventional Co₃O₄ NW electrode were investigated by galvanostatic discharge and charge measurements with various applied currents. As shown in Fig. 3B, the initial specific discharge and charge capacities of SS mesh supported Co₃O₄ NW electrode are 1106.9 mAh g⁻¹ and 855.1 mAh g⁻¹ at a current density of 100 mA g⁻¹, with a coulometric efficiency of 77.3%. The specific discharge capacity in the second cycle was 883.4 mAh g⁻¹ with capacity retention of 79.8% with respect to the first two cycles. In comparison, the specific capacities of the conventional Co₃O₄ electrode in first discharge and charge are 1129 mAh g⁻¹ and 782 mAh g⁻¹, respectively, and the coulometric efficiency is 69.3% as shown in Fig. 3C, significantly underperforming compared to Co₃O₄ NW mesh electrode. The specific discharge capacity in the second cycle is 801 mAh g⁻¹ and the capacity retention is 70.9%, which again are much lower than that of Co₃O₄ NWs on SS mesh. The large irreversible capacity during the first cycle is attributed to the irreversible conversion reaction of Co₃O₄ NWs with Li ions and the formation of an SEI layer by electrolyte decomposition and surface reaction on the active material. During the second cycle, the discrepancy in discharge and charge capacity is reduced, suggesting that most of the irreversible reactions including the formation of an SEI layer occur during the first cycle. Fig. 3D demonstrates the rate capabilities of SS mesh supported and conventional Co₃O₄ NW electrodes. The charge capacity of 625 mAh g⁻¹ is achieved at a current rate of 800 mA g⁻¹ for the mesh electrode, which is significantly higher than that of the conventional Co₃O₄ NW electrode (366 mAh g⁻¹). The superior rate capability of the Co₃O₄ NW SS mesh electrode is mainly attributed to the direct coupling of the active material onto the current collector thereby greatly enhancing the charge transfer properties. Furthermore, after 30 cycles conducted at varying current densities, the mesh-supported Co₃O₄ NW electrode is stabilized at around 850 mAh g⁻¹, with a flat plateau on the cycling curve, introducing the superior cycle stability of the electrode. The recoverable capacity in subsequent cycles also well implies the structural integrity of Co₃O₄ NWs on the SS mesh electrode. However, for the conventional Co₃O₄ NW electrode, an obvious drop in capacity is observed from the rate capability curve. This finding also corroborates the enhanced charge transfer obtained by direct coupling of Co₃O₄ NWs to the SS mesh current collector.

The advantage of SS mesh supported Co₃O₄ NWs which exhibit reduced internal resistance in batteries is confirmed by EIS conducted at fully discharged states of 0.01 V versus Li/Li⁺ (Fig. 4, the equivalent circuit is integrated in the figure). The electrolyte solution resistances (Rₛ) which can be obtained from the intercepts of Nyquist plots at high frequencies are very close since same electrolyte was used for these two electrodes. The diameter of the semi-cycle in the Nyquist plot represents the charge transfer resistance (Rct) of an electrode and W is the Warburg impedance.[31] The figure reveals that Rₛ of mesh supported Co₃O₄ NW electrode is 40 ohm lower than that of the conventional Co₃O₄ NW electrode. This is an indication that the electrochemical reactions in the directly grown Co₃O₄ NWs on SS mesh are faster, suggesting

![Fig. 3. CV curves of Co₃O₄ NWs on SS mesh. (Scan rate 1.0 mV s⁻¹, potential range 0.01-3.0 V) (A) Galvanostatic charge and discharge curves of the Co₃O₄ NWs on SS mesh (B) and the conventional Co₃O₄ NWs on copper foil (C). Co₃O₄ NWs on SS mesh and the conventional Co₃O₄ NW electrode at various current rates from 100 to 800 mA g⁻¹ with respect to the cycle number (D).](image-url)
that the faster electron conduction between the current collector and the active materials plays a critical role in the overall battery performance. In addition, the inclined lines in the low frequency region represent the mass-transfer controlled regions (so called the Warburg diffusion) and it can be interpreted that the lower slope of the line indicates swifter mass transport.[32] In comparison with the slopes in the Warburg diffusion region from the two different electrodes in Fig. 4, it confirms that the mass-transfer in the Co3O4 NW on SS mesh is enhanced, corresponding to the half-cell testing.

Also the diffusion coefficient (D) and the double layer capacitance (Cdl) for each electrode were calculated based on the Nyquist plot using equation as below.[33,34]

\[ Z'' = R_S + R_{ct} + \sigma_w \times \omega^{-0.5} \]  
\[ D = 0.5 \times \left( \frac{RT}{AF^2 \sigma_w C} \right)^2 \]  
\[ C_{dl} = \frac{1}{(\omega R_{ct})} \]  

Where \( \sigma_w \) is the Warburg impedance coefficient, \( \omega \) is the angular frequency \( = 2\pi f \), \( R \) is the gas constant, \( T \) is the absolute temperature, \( A \) is the area of the electrode surface, \( F \) is Faraday’s constant, \( C \) is the molar concentration of Li+ ions and \( n \) is the number of electrons involved in the electrochemical reaction. First of all, the relation of \( Z'' \) and \( \omega^{-0.5} \) was plotted to obtain the Warburg impedance coefficient, as presented in Fig. 5 since the slope represents \( \sigma_w \). The obtained values are 65.75 ohm s^{-0.5} and 16.65 ohm s^{-0.5} for the conventional Co3O4 NW electrode and the mesh supported Co3O4 NW electrode, respectively. Using the obtained Warburg impedance coefficient and the Equation (2), the diffusion coefficient of each electrode was calculated to be \( 3.31 \times 10^{-9} \text{cm}^2 \text{s}^{-1} \) and \( 5.16 \times 10^{-8} \text{cm}^2 \text{s}^{-1} \) for the conventional Co3O4 NW electrode and the mesh supported Co3O4 NW electrode, respectively, and the values are reasonable comparing with a previous report.[35] It clearly confirms that the mesh supported Co3O4 NW electrode has higher Li+ ion diffusivity to be able to enhance battery performance than the conventional Co3O4 NW electrode.
Table 1
Electrochemical impedance parameters.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$R_s$ (ohm)</th>
<th>$R_{ct}$ (ohm)</th>
<th>$\sigma_w$ (ohm s^{-0.5})</th>
<th>$D$ (cm² s^{-1})</th>
<th>$C_d$ (F)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co3O4 on SS mesh</td>
<td>4.63</td>
<td>81.74</td>
<td>16.65</td>
<td>5.16 x 10^{-4}</td>
<td>1.05 x 10^{-5}</td>
</tr>
<tr>
<td>Co3O4 on Cu foil</td>
<td>4.45</td>
<td>121.55</td>
<td>65.75</td>
<td>3.31 x 10^{-4}</td>
<td>1.31 x 10^{-5}</td>
</tr>
</tbody>
</table>

All electrochemical parameters from the EIS analysis are summarized in Table 1.

Fig. 6A compares the cycling performance of the Co3O4 NWs—SS mesh electrode with conventionally prepared electrode from casting Co3O4 NWs based slurry on a copper current collector. The Co3O4 NWs mesh electrode is first cycled at a current density of 100 mA g$^{-1}$ followed by a current density of 200 mA g$^{-1}$. In the first 20 cycles at 100 mA g$^{-1}$, the capacity increases gradually from ~850 to ~880 mA g$^{-1}$. After 100 cycles at 200 mA g$^{-1}$, the electrode still possesses a capacity of 766 mA g$^{-1}$, maintaining 90% of the initial capacity. To the best of our knowledge, this is the best cycling performance among all the directly growing methods. By comparison, the battery with the conventional Co3O4 electrode is cycled at 100 mA g$^{-1}$, but the cyclic performance is far inferior to that of Co3O4 NWs on SS mesh, suggesting the enhanced durability due to direct growth of the active material onto the current collector.

As mentioned in the introduction, electrode materials being directly synthesized on current collector have been reported. To be convenient, a battery’s capacity is usually presented based on electrode’s area. The areal capacity of Co3O4 NWs on SS mesh after 100 cycles was calculated to be 0.675 mAh cm$^{-2}$ at a charge/discharge rate of 0.173 mA cm$^{-2}$. The above capacity is very competitive, namely, two to three times that of the reported values in the peer-reviewed articles published in recent years.\[36,37\]

Fig. 6B shows an optical photograph of Co3O4 NWs on SS mesh after 100 cycles. A coin cell was assembled at fully-charged state to obtain the cycled electrode, which was subsequently washed with dimethyl carbonate (DMC) and water to remove any residue electrolyte or by-product from electrode reactions. The electrode retained its black color which confirms that Co3O4 NWs are still firmly attached to SS mesh even after the electrochemical process. The SEM image in Fig. 6C further reveals the morphology of the cycled electrode, which shows virtually no de-attachment of Co3O4 NWs from the SS mesh. It is easy to see that the 3D array of the fresh electrode is well maintained even after repeated lithiation/delithiation processes. Compared to Fig. 2A, the pores on the mesh have not vanished although the size of these pores have diminished after cycling, thus still contributing efficient pathways for Li$^+$ diffusion in the electrolyte. An obvious increase in the average diameter of Co3O4 NWs can be observed from Fig. 6D with an average diameter of 400 nm, which is approximately 100 nm greater than its initial size. This volume expansion is ascribed to the lithiation during the discharge process.

4. Conclusions

The SS mesh–supported Co3O4 NW electrode was successfully synthesized via a binder- and template-free growth method for LIBs. It was formed on the SS mesh substrate with the original net structure of the mesh. We suggested that the unique morphology of the material and the structure of the electrode are responsible for the superior performance in LIBs, which were confirmed by various structural, morphological and electrochemical characterizations. Consequently, Co3O4 NWs on the SS mesh anode exhibited 855.1 mAh g$^{-1}$ of initial capacity at a current density of 100 mA g$^{-1}$, which corresponds to the theoretical capacity of Co3O4. After 100 cycles at 200 mA g$^{-1}$, 766 mAh g$^{-1}$ of battery’s capacity was obtained and the capacity retention was around 90%. Furthermore, it presents a capacity of 655 mAh g$^{-1}$ at 800 mA g$^{-1}$ of the current density which is 300 mA g$^{-1}$ higher than the capacity of conventionally prepared electrode of Co3O4 NWs. These results suggest that SS mesh-supported Co3O4 NW electrode is highly promising as an efficient anode for LIBs.

Author information

Notes
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References
