Supporting Information

Artificial Electrode Interface Enables Stable Operation of Freestanding Anodes for High-Performance Flexible Lithium Ion Batteries

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Fig. S1 Digital images of the self-rolled-up process of NFO microtubes. (a) NFO nanomembranes deposited on the Al substrate with sacrificial layer. Inset is the optical image on NFO nanomembranes. (b) Etching of the sacrificial layer under the NFO nanomembranes. (c) Final products of self rolled-up the NFO microtubes. scale bar for the digital images: 1 cm.



Fig. S2 (a) Cycling stability and columbic efficiency of the NFO nanomembranes (inset scheme) at a current density of 10 mA cm⁻².

The cycling performance and coulombic efficiency of the NFO nanomembranes is presented in Fig. S2. The sample was cycled under the current density of 10 mA cm⁻² discharge/charge in the voltage range from 0.40 to 3.0 V. The capacity drastically decreases to 25% of the initial capacity at the 200th cycle, indicating the unstable nature of nanomembranes due to the intrinsic strain. In addition, upon electrochemical cycling, the rapid capacity fade and poor reversible capacity are observed in the NFO nanomembranes.



Fig. S3 (a) Raman spectrum of a single NiFe₂O₄ microtube materials. (b) X-ray diffraction (XRD) patterns of the NFO microtubes.

The corresponding Raman spectrum (Fig. S3a) reveals four broad peaks centered at 320, 484, 580, and 700 cm⁻¹. The peak at 320 cm⁻¹ represents the E_g vibrational modes, 484 cm⁻¹ peak represents the T_{2g} vibrational mode, the peaks at 580 and 700 cm⁻¹ represent the A_{1g} vibrational modes of the NFO.¹ In the XRD pattern (Fig. S3b), all the reflections of NFO microtubes are in good agreement with the standard pattern of the cubic phase NiFe₂O₄ (JCPDS No. 054-0964).



Fig. S4 TEM image of NFO tube.

The nanostructure of the NFO was further elucidated by transmission electron microscopy (TEM) (Fig. S4). Uniform contrast is observed in the image, which clearly reveals the smooth surface of the NFO tube.



Fig. S5 SEM image of the freestanding electrode made of NFO microtubes interwoven with CNTs.

The SEM image of the freestanding electrode is shown in Fig. S5, revealing that the excessive CNTs interweave with each other, serving as the conductive matrix for the freestanding electrode. Giant NFO microtubes are embedded in the conductive matrix.



Fig. S6 Raman spectrum of PAAm/gelatin gel.

The Raman spectrum from the PAAm/gelatin gel was also plotted (Fig. S6). Vibrational bands for the various molecular components of gelatin, acrylamide, and PAAm were assigned.² PAAm/gelatin (1450, 1648, 2875 and 2935 cm⁻¹).³



Fig. S7 CV curves of the second and third cycle of the (a) P-C-NFO, and (c) C-NFO electrode at a scan rate of 0.1 mV s⁻¹. Galvanostatic discharge/charge profiles in the second and third cycle of (b) P-C-NFO, and (d) C-NFO electrode at a current density of 200 mA g^{-1} .

Electrochemical behaviors at second and third cycles in CV curves are similar for both of the P-C-NFO and C-NFO electrode. A cathodic peak at around 0.82 V is attributed to the reduction of NFO into Fe and Ni. Two anodic peaks, identical to the those in the first cycle, still presents, which are ascribed to the oxidation of Fe and Ni. As shown in Fig. S7a, CV curves of the third cycle almost overlaps with the second cycle for the P-C-NFO electrode, indicating high reversibility of the capacity. The galvanostatic discharge/charge profile of the P-C-NFO electrode (Fig. S7b) confirms the high reversibility of the capacity as it immediately stabilizes at 910 mAh g⁻¹ and coulombic efficiency reaches 99.0%. On the

contrary, obvious differences in CV curves of the second and third cycles of the C-NFO electrode (Fig. S7c) are observed. Correspondingly, the capacity decays obviously as shown in galvanostatic charge/discharge profiles (Fig. S7d). In specific, the discharge capacity of C-NFO dramatically decreases to 648 mAh g⁻¹ after 3 cycles.



Fig. S8 (a) Cycling stability and (b) columbic efficiency of the P-C-NFO, C-NFO and NFO electrode at a current density of 200 mA g^{-1} .

The P-C-NFO electrode reaches the maximum capacity of 1100 mAh g⁻¹ and retains the capacity of 777 mAh g⁻¹ after 220 cycles (Fig. S8a). The coulombic efficiency is stabilized at 99.43 % at the end (Fig. S8b). By contrast, the capacity fades quickly for the C-NFO and NFO electrode. Only 30 % and 48 % of the initial capacity after 50 cycles is preserved for the C-NFO and NFO electrode, respectively. In addition, the NFO and C-NFO electrode can only deliver 390 and 337 mAh g⁻¹ (discharge capacity) after 50 cycles, respectively. Therefore, the PAAm/gelatin gel not only improves the cycling stability but also enhances the capacity of the NFO based freestanding electrode.



Fig. S9 Ex situ SEM images of the P-C-NFO electrode after 500 charge/discharge cycles. Fig. S9 displays the morphology of the P-C-NFO electrode after 500 charge/discharge cycles. Tubular shape of NFO tubes are still observed, indicating the excellent structural integrity of the P-C-NFO electrode enabled by the PAAm/gelatin gel.



Fig. S10 Rate capability of C-NFO electrode.

The capacity of C-NFO is also calculated based on the entire mass of the C-NFO electrode. The C-NFO electrode shows inferior capacity (267 mAh g-1) at low current density of 100 mA g-1, which is attributed to its poor initial coulombic efficiency (35%). Moreover, obvious performance degradation is observed as capacity continuously decreases along during the rate test.



Fig. S11 Digital photographs of the freestanding cathode (Left) and anode (Right). The scale bar is 2.5 cm.



Fig. S12 Galvanostatic discharge/charge profile of the P-C-NFOIP-C-LMO full battery (a) and P-C-LMO cathode (b) at the current density of 200 mA g^{-1} .

Fig. S12a displays charge/discharge profiles of the P-C-NFOIP-C-LMO battery at a current density of 200 mA g⁻¹ between 2.0 and 4.1 V. The full battery displays that the discharge voltage is larger than 2.7 V. Fig. S12b shows the discharge voltage of the cathode is 4.1 and 4.0 V. Based on these values and charge voltage of P-C-NFO of 1.5 V, theoretical discharge voltage of the full battery should be around 2.5 V. The deviation is attributed to the formation of Li_2O on the anode during the charging process, which makes the anode tend to behave like a lithium counter electrode.



Fig.S13. (a) The top view of the flexible P-C-NFO||C-LMO full battery. The aluminum foil (b) and copper foil (c) as contact pads for the cathode and anode in the flexible P-C-NFO||C-LMO full battery

The sheet resistance of the C-LMO and P-C-NFO electrode is 66.0 and 91.2 Ω /sq.



Fig. S14. Elastic force-separation curve and stress-separation curve performed by AFM force spectroscopy on P-C-NFO electrode (a, b) and C-LMO electrode (c, d).

The dynamic mechanical behavior is recorded for P-C-NFO and C-LMO electrode under deformation. The behavior obeys the Sneddon model. Accordingly, Young's modulus is determined as 102 MPa for the P-C-NFO electrode, and 80 MPa for the C-LMO electrode. This indicates the excellent mechanical performance of freestanding electrodes, which ensures their performance in real applications.



Fig. S15. Reversible capacity of the P-C-NFO (a), and C-LMO (b) at a current density of 200 mA g^{-1} .

$R_{s}\left(\Omega ight)$	$R_{\text{SEI}}(\Omega)$	$Q_{SEI}\left(S\ s^n\right)/n$	$Q_{ct}\left(S \ s^n\right) / \ n$	$Q_{ca}\left(S\ s^{n}\right)/n$
9	69	1.5×10 ⁻⁵ /0.84	1.7×10 ⁻² / 0.28	2.7×10 ⁻¹ / 1.0

Table S1. Parameters of elements in equivalent circuit of C-NFO electrode.

Table S2. Parameters of elements in equivalent circuit of P-C-NFO electrode.

$R_s(\Omega)$	$R_{SEI}(\Omega)$	$Q_{SEI}\left(S \; s^n\right) / \; n$	$R_{ct}(\Omega)$	$Q_{ct}\left(S\;s^n\right)/n$	W (S s ^{0.5})	$Q_{ca}\left(S\;s^{n}\right)/n$
9	168	2.6×10 ⁻³ / 0.66	162	2.1×10 ⁻⁵ / 0.77	2.7×10 ⁻²	1.3×10 ⁻¹ / 0.66

Table S3.	The comparison	of electrochemical	performances	of transition	metal oxide-
based ano	des in LIBs.				

Materials	aterials Rate Capability (mAh g ⁻¹)		Cycling Performance (mAh g ⁻¹)	Ref.
P-C-NFO	441 at 5000 mA g ⁻¹	0.4-3.0 V	777 after 220 cycles at 0.2 A g ⁻¹	This work
CoFe ₂ O ₄ /rGO nanoparticles	330 at 2000 mA g ⁻¹	0.01-3.0 V	700 after 200 cycles at 1 A g ⁻¹	[4]
Ni _x Fe _y O _z @rGO nanocomposite	388 at 5000 mA g ⁻¹	0.01-3.0 V	388 after 500 cycles at 5 A g ⁻¹	[5]
Core-Shell NiFe ₂ O ₄ @TiO ₂ Nanorods	202 at 5000 mA g ⁻¹	0.01-3.0 V	1034 after 100 cycles at 0.1 A g ⁻¹	[6]
NiFe ₂ O ₄ nanoplates	173 at 5000 mA g ⁻¹	0.01-3.0 V	880 after 100 cycles at 0.1 A g ⁻¹	[7]
Porous Fe ₂ O ₃ nanosheets	433 at 20000 mA g ⁻¹	0.01-3.0 V	877 after 1000 cycles at 2.01 A g ⁻¹	[8]
Graphene/Mn ₃ O ₄ nanocomposite	308 at 2000 mA g ⁻¹	0.005-3.0 V	802 after 100 cycles/0.1 mA g ⁻¹	[9]
MnCo ₂ O ₄ nanosheet array	215 at 7000 mA g ⁻¹	0.05-3.0 V	460 after 30 cycles at 800 mA g ⁻¹	[10]
MnO/C nanopeapods	463 at 5000 mA g ⁻¹	0.02-3.0 V	525 after 1,000 cycles at 2000 mA g ⁻¹	[11]

Note: rGO = Reduced Graphene Oxide

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