Electronic Supplementary Information

Affinity-Engineered Carbon Nanofibers as a Scaffold for Na Metal Anodes

Alessandro Susca,^a Jiapeng Liu,^a Jiang Cui,^a Nauman Mubarak,^a Junxiong Wu,^a Muhammad Ihsan-Ul-Haq,^a Francesco Ciucci^a and Jang-Kyo Kim^{a*}

^{a.} Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clearwater Bay, Kowloon, Hong Kong. * Corresponding author email: mejkkim@ust.hk



Figure S1. Different cell setups.



Figure S2. Coulombic efficiencies of half cells with pCNF as an anode scaffold, tested with repeated cycles at 3 mA/cm² with a loading of 3 mAh/cm². The data is presented for two identical cells for each carbonization temperature (650° C, 725° C, and 800° C).



Figure S3. TEM image (left) and XRD pattern (right) of pCNFs.



Figure S4. Plating and stripping voltage profiles of flat Cu half-cell for the first 10 cycles at a current density of 1 mA/cm².



Figure S5. Chronopotentiometric discharge/charge curve on a Cu foil at 30 μ A, in a half cell configuration versus Na⁺/Na. One charging cycle (partial stripping) was blocked at a potential of 10 mV. Overpotentials are highlighted with red circles.



Figure S6. Potential values of different substrates measured during Na deposition at a constant current of 30 μ A. Graphs are stacked in the X-direction and adjusted in the Y-direction to highlight the difference in overpotential and plateau between different substrates.



Figure S7. Ex-situ SEM image of Na deposited on a Zn plate at 1 mA/cm².

Note S1: DFT calculations

We performed the spin-polarized first-principle calculations using Vienna ab *initio* simulation package (VASP) [S1,S2] with plane wave basis set and a projector-augmented wave (PAW) approach [S3]. We set the kinetic energy cutoff at 520 eV and described the exchange-correlation using the Perdew-Burk-Ernzerhof (PBE) functional [S4] under the generalized gradient approximation (GGA) scheme. Graphene was modeled with a 4×4 supercell. As the bonding of Na metal with graphene is mainly ionic [S5,S6], the van der Waals correction was not considered due to its minor effect. To model the adsorption of Na atoms on the surface of Zn, ZnO, and Sn, we constructed the surface for both Zn and ZnO in 0001 index with 4 layers in 3×3 unit cell, for Sn in 001 index with 4 layers in 2×2 unit cell, respectively. At least 13 Å vacuum space was placed along the *c*-direction to cancel the interactions between different slabs. To model the bulk property in the bottom of slab model, the bottom two layers were fixed with the bulk lattice parameter. Considering that the lattice parameters along the *ab* plane in practical experiments would not deviate far from the bulk, we fixed them while relaxing all

other atoms using the conjugated gradient method until the energy reached a convergence criterion of 10^{-5} eV and the force became 0.02 eV/Å. The Brillouin-zone was sampled by Gamma centered k-meshes of $4 \times 4 \times 1$, $3 \times 3 \times 1$, $4 \times 4 \times 1$, and $4 \times 4 \times 1$ for graphene, ZnO (0001) surface, Zn (0001) surface, and Sn (001), respectively.

To study the Na adsorption on each substrate, we considered several different possible sites and finally selected only the sites with low energies, as shown in Figure S8. The adsorption reaction energy of Na, E_{ads} , was calculated as:

$$E_{ads} = E_{sys} - E_{substrate} - nE_{Na} \tag{S1}$$

where E_{sys} is the total energy of the substrate with one Na atom adsorbed on the surface after relaxation, $E_{substrate}$ is the energy of pure substrate, and E_{Na} corresponds to the energy of Na in gas phase. Charge difference plots are shown in Figure S9.



Figure S8. Top views of the relaxed structures of one Na atom adsorbed on different substrates: (a) graphene, (b) Zn (0001) surface, (c) ZnO (0001) surface, and (d) Sn (001) surface.



Figure S9. Side views of charge density difference plots of one Na atom adsorbed on different substrates: (a) graphene, (b) Zn (0001) surface, (c) ZnO (0001) surface, and (d) Sn (001) surface. Light blue color indicates the charge loss, while yellow refers to charge accumulation.



Figure S10. (a) Discharge curve of a ZnO plate down to 5mV in a half-cell vs. Na⁺/Na, at a current of 30 μ A. (b) *Ex-situ* XRD patterns of the same ZnO plate before (light green) and after discharge (dark green). The magnified plot of the double peak at 54-55° is shown in inset.



Figure S11. (a) XRD patterns of ZnO@CNFs film containing 7.5% ZnAc₂ at the precursor level, obtained at different carbonization temperatures. (b) XRD pattern of ZnO@CNFs film containing 7.5% of ZnAc₂ precursor carbonized at 725 °C and discharged to 5mV in a half-cell vs. Na⁺/Na at a current of 30 μ A.

Note S2: Optimization of ZnO@CNF processing parameters

To optimize the ZnAc₂ content and the carbonization temperature for the best possible electrochemical performance of the electrodes, several processing parameters had to be taken into consideration. First, the ZnO content in the final product should be sufficient to serve as nucleation sites, but the solubility of ZnAc₂ in DMF was an issue. While stirring overnight was enough to fully dissolve up to 7.5 wt% of ZnAc₂, equivalent to a 3:2 ratio to PAN, a higher ZnAc₂ content was found to be excessive as some undissolved particles were partially suspended in the solution. When the mixture was electrospun, the resulting fibers presented severe agglomerates of ZnO. No ZnAc₂ content higher than 7.5% was considered in the following steps. Second, the electronic conductivity of the CNF network is highly dependent on carbonization temperature [S7]. A higher conductivity obtained at a higher carbonization.

The TGA was performed on the stabilized nanofibers with different amounts of ZnAc₂, 0, 5 and 7.5 wt%, as shown in Figure S12. There was a rapid mass loss between 600 and 800°C for all

materials studied. The mass retention was higher for the samples containing Zn: the high decomposition temperature of ZnO (1974 °C) allowed it to remain in the solid state in the studied temperature range. However, the loss derivatives varied depending on the amount of ZnAc₂: the derivative peak shifted from 730°C to 785°C for the fibers containing 5 and 7.5 wt%, respectively. No prominent derivative peak was found for the pCNFs without ZnAc₂, suggesting the loss was associated to the zinc additive. The XRD pattern (Figure S11) for the sample containing 7.5% of ZnAc₂ showed characteristic peaks of ZnO (in the form of hexagonal wurtzite) in the nanofibers uncarbonized or carbonized at 650 and 725 °C. However, these peaks were absent in the CNFs carbonized at 800 °C, suggesting a complete loss of ZnO. These CNFs carbonized at 800 °C burst open along the fiber, as shown in SEM and TEM images (Figure S13). Moreover, the average discharge capacities in the voltage range between 1 and 0 V were 270, 300 and 93 µAh cm⁻² respectively for the samples carbonized at 650, 725 and 800 °C. As a comparison, pCNF showed a discharge capacity of 190 µAh cm⁻². The increase in capacity is due to the contribution of ZnO nanoparticles whose intrinsic capacity is much higher than the carbon backbone. In view of the fact that ZnO is highly resistant to thermal treatment with a decomposition temperature of 1974 °C, the mass loss might arose from ZnO being chemically reduced by the surrounding carbon. The newly-formed metallic zinc was then close to its boiling point of 907 °C [S8], resulting in evaporation and bursting open from the fiber inside to escape. For instance, the CNFs containing 5 wt% ZnAc₂ lost most of ZnO after carbonization at just 725 °C, as expected from the TGA data. To maximize the electrical conductivity while maintaining sufficient ZnO particles in the fibers, the amount of ZnAc₂ in the precursor solution was set at 7.5 wt% and the carbonization temperature was kept at 725°C. These considerations were confirmed with overpotential and cyclic CE measurements, as reported in Figure S14: both the overpotential and cycle life presented the best performance for a carbonization temperature of 725°C, and the trend was inverted for a higher temperature of 800°C.



Figure S12. TGA curves of pCNFs and ZnO@CNFs containing 5% and 7.5% ZnAc₂. The left graph represents the mass evolution, and the right one represents its derivative.



Figure S13. SEM (a) and TEM (b) images of ZnO@CNFs carbonized at 800°C.



Figure S14. Overpotential (left) and cyclic CE (right) of the ZnO@CNF electrodes containing 7.5wt ZnAc₂ carbonized at different temperatures.



Figure S15. TEM images of ZnO@CNFs with 7.5% ZnAc₂ carbonized at 725°C.



Figure S16. XPS spectra of (a) pCNFs and (b) ZnO@CNFs. High resolution scans of C 1s peaks of (c) pCNFs and (d) ZnO@CNFs, along with their deconvolution into different carbon functional groups.



Figure S17. TEM image of ZnO@CNFs after decomposition in air at 700°C.



Figure S18. SEM image of ZnO@CNF after enduring 200 plating/stripping cycles at 1 mA/cm². The sample was washed with hydrogen peroxide to remove the SEI layer after extraction from the cell and drying in vacuum overnight.



Figure S19. SEM image of pCNF network after discharging to 0 V in a half cell versus Na⁺/Na.

 Table S1. Comparison of electrochemical performance between the current work and other

 state-of-the-art recent scaffold materials for glyme-electrolyte Na metal batteries.

					Cycle	
		Half /	Current	Aerial	number /	
Material	Electrolyte	symmetric	Density	Capacity	Hr	REF.
Electrospun pCNF	NaCF3SO3	half	1	1	1500 cycles	Current work
Electrospun ZnO@CNE	NaCF3SO3	half	3	3	700 cycles	Current
		symmetric	1	1	1300 hr	WOIK
		symmetric	3	1	700 hours	
Pillared Mxene	NaPF6	half	4	4	500 cycles	[\$9]
		half	5	5	200 cycles	
		symmetric	3	3	300 hr	
		symmetric	5	3	200 hr	
Porous Al	NaPF6	half	1	0.5	1000 cycles	[S10]
		symmetric	0.5	0.5	1000 hr	
Carbon fibre paper	NaCF3SO3	symmetric	1	1	500 hr	[S11]
Reduced GO	NaCF3SO3	symmetric	1	1	600 hr	[S12]
			5	5	300 hr	
CNTs with O-groups	NaCF3SO3	half	1	1	1600 cycles	[S13]
5		half	3	1	1000 cycles	£}
		symmetric	3	1	1100 hr	
		symmetric	3	3	300 hr	
		symmetric	5	8	300 hr	
Carbon Microspheres	NaPF6	symmetric	0.5	1	3600 hr	[S14]
Carbon paper	NaCF3SO3	symmetric	5	1	1200 hr	[\$15]
CNFs with N- and O-	NaPF6	symmetric	1	1	1200 hr	[<u>S16]</u>
groups			2	1	1200 hr	
CNTs with N- and S-					1200 m	
groups	NaCF3SO3	symmetric	1	1	500 hr	[<u>S17]</u>
		symmetric	3	1	150 hr	
Sb2MoO6 microspheres	NaPF6	half	5	4	500 cycles	[S18]
-		symmetric	4	2	500 hr	
		symmetric	5	4	800 hr	
		symmetric	6	6	600 hr	
Sn nanoparticles in carbon buffer	NaPF6	half	2	1	500 cycles	[S19]
			2	5	250 cycles	
Hollow carbon fibers with N- and S-groups	NaCF3SO3	half	1	1	600 cycles	[S20]
		half	3	1.5	250 cycles	
		symmetric	1	1	1000 hr	



Figure S20. EIS spectra of symmetric cells made of ZnO@CNF electrodes after plating/stripping cycles at a high current of 3 mA/cm². The impedance parameters determined by fitting the EIS spectra with the equivalent circuit (in inset) are given in Table S2.

Table S2. Solution resistance (R_sol), charge-transfer resistance (R_CT) and SEI resistance (R_SEI) parameters as modelled from the EIS data in Figure S20.

	R_sol	R_CT	R_SEI
Initial	6.2	10	9.0
10 cycles	6.3	5.2	4.4
50 cycles	6.2	5.7	4.8
100 cycles	6.9	6.3	4.6

Note S3: Cyclic stability of the ZnO@CNF electrode in commercial carbonate electrolytes

Carbonate-based electrolytes would be the optimal choice for Na batteries, due to their low cost and high oxidation potential for use with a wider range of cathode materials [S21,S22]. However, the high reactivity of Na to such electrolytes and the formation of unstable SEI layers make them unsuitable, and the development of stabilizing additives is still at an early stage. Here, we tested the electrochemical performance of the electrodes in 1M NaClO₄ in EC:PC. Our aim was to confirm that the increase in plating uniformity achieved by the ZnO@CNF electrodes played a significant stabilizing role even when the SEI stability was severely undermined. The test was run using a thick Whatman GF/D glass fiber separator to replace the thin polymeric Celgard 2400 used in other part of this work, see Figure S1, because the latter separator was prone to be damaged by dendrites in such a hostile environment. The half-cell tests were used to evaluate the Coulombic efficiencies when cycled against pure Na metal, as shown in Figure S20a. It should be noted that given the instability of the pure Na counter-electrode in this electrolyte, such tests can only give indicative information [S23]. Even so, the presence of a 3D conductive CNF network significantly increased the CE compared to a flat Cu current collector and the pCNFs. While still far from satisfying the requirements for practical application, the above result highlights the importance of a 3D current collector in reducing the local current density, controlling the growth of Na, and reducing the amount of material lost due to SEI instability. Moreover, the ZnO@CNF electrode gave rise to twice as many stable plating/stripping cycles than the pCNF counterpart before the irreversible capacity loss happened.

Cyclic tests were performed using the symmetric cells made from the neat Na and ZnO@CNF+Na electrodes, as shown in Figure S20b and c. The voltage profiles of the first 100 cycles for both electrodes are discussed as follows:

(1) For both electrodes, the first cycle (highlighted as Number 1) had a large overvoltage, attributed to stripping of Na from the bulk Na plate which was covered by a thick SEI layer formed during cell aging. All cells were aged for 12 hr prior to the cyclic tests.

(2) For both electrodes, the second cycle proceeded with a much lower overvoltage until 85-90% of the total loading (Number 2), where the freshly-deposited Na was fully stripped causing the overvoltage to revert to high values similar to the first cycle. This observation indicates that almost 10-15% of the freshly deposited Na was lost in each cycle due to parasitic reactions, so that new Na had to be supplied afresh from the bulk. A similar phenomenon was reported previously [S24, S25]. These values are compatible with the CEs found in the half-cell tests. (3) For the Na-Na cell, the voltage profile decreased with increasing cycle (Number 3), signifying gradual degradation of stripping and plating behavior. For the ZnO@CNF cell, in contrast, the voltage profile remained very stable for 100 cycles after the first.

(4) At the 19th cycle, the Na-Na cell experienced a short circuit (Number 4) because the overgrown dendrites likely perforated the glass fiber separator. After a short circuit, the cell continued to cycle with a minimum hysteresis (Number 5), as expected.



Figure S21. Electrochemical performance of cells coupled with EC:PC electrolyte containing 1M NaClO₄. (a) Coulombic efficiencies of a Cu current collector, pCNF and ZnO@CNF. Voltage profiles of (b) pure Na and (c) ZnO@CNF symmetric cells for the first 100 cycles.



Figure S22. SEM image of the side view of Na agglomerate ("island") grown on top of pCNFs. Na loading is 1 mAh/cm² and plating current is 3 mA/cm².



Figure S23. EDS elemental maps of Na plated on pCNFs at 3 mA/cm².



Figure S24. EDS maps of Na and carbon on a ZnO@CNF current collector after Na plating at 3 mA/cm².



Figure S25. *Ex-situ* SEM images of sodium-plated ZnO@CNFs at different capacities and different current densities. Average fiber diameters were taken from 20 independent measurements using each SEM image.

Note S4: Prediction of plated Na thickness

The volume of Na plated on the electrode surface can be predicted according to Equation S2 [S26]:

$$V = \frac{Q}{n_{Na} \cdot F} \cdot \frac{M_{Na}}{\rho_{Na}}$$
(S2)

where *F* is the Faraday constant (96458.3 $C mol^{-1}$); n_{Na} (= 1) is the number of transferred electrons per Na ion; and M_{Na} and ρ_{Na} are the molar mass (22.99 $g mol^{-1}$) and the density ($0.971 g cm^{-3}$) of metallic Na, respectively. *Q* is the charge of plated Na in Coulombs (1 mAh = 3.6 C). Assuming perfectly uniform Na plating over the whole ZnO@CNF surface whose diameter is also assumed uniform, the total volume of Na deposit, *V*, can be described by Equation (S3) by analogy with the volume of a hollow cylinder:

$$V = \frac{\pi L}{4} (D^2 - d_0^2)$$
(S3)

where d_0 is the diameter of bare fibers, D is the fiber diameter after Na plating, and *L* is the estimated length of whole fiber network. In this case, an average value $d_0 = 165 nm$ is measured from the SEM image (Figure S25-1). Using the estimated BET surface area ($= 7.1 m^2 g^{-1}$) and the typical loading (= 2.27 mg) per unit area of the ZnO@CNF electrode, the total surface area of fiber network, $A = 161.2 cm^2$, is obtained. Therefore, $L = 31.1 \cdot 10^3 m$ is derived from $A = \pi \cdot d_0 \cdot L$. Combining Equations (S2) and (S3) yields:

$$D = \sqrt{\frac{4Q}{\pi \cdot L \cdot n_{Na} \cdot F} \cdot \frac{M_{Na}}{\rho_{Na}}} + d_0^2$$
(S4)

The fiber diameters ($^{D_{measured}}$) were measured using the *ex-situ* SEM images of ZnO@CNFs taken after Na plating at different areal capacities, as shown in Figure S25. Each final diameter is the average of 20 independent random measures taken from the images. After complete re-

stripping of Na on the fiber, the fiber diameter was found ~41 nm larger than the bare fiber, see Figures S25-1 vs S25-8. The difference is attributed to the SEI layer which was formed on the surface of Na layer and remained even after stripping of Na layer. Thus, the thickness of the SEI layer, t_{SEI} , was taken into account in the final prediction.



Figure S26. SEM images of ZnO@CNF anode scaffold infused with 6 mAh/cm² of Na taken at different magnifications.



Figure S27. Cyclic performance of a symmetric cell having pure Na electrodes measured at a current density of 0.5 mA/cm².



Figure S28. Cross-section of ZnO@CNF electrode after 40 cycles in a symmetric setup at 1

mA cm⁻².

References

[S1] G. Kresse, J. Furthmüller, Phys. Rev. B 1996, 54, 11169.

- [S2] G. Kresse, J. Furthmüller, Computational Mater. Sci. 1996, 6, 15-50.
- [S3] P. E. Blöchl, Phys. Rev. B 1994, 50, 17953.
- [S4] J. P. Perdew, K. Burke, M. Ernzerhof, Phys. Rev. Lett. 1996, 77, 3865.
- [S5] M. Liu, A. Kutana, Y. Liu, B. I. Yakobson, J. Phys. Chem. Lett. 2014, 5, 1225-1229.

[S6] K. T. Chan, J. B. Neaton, M. L. Cohen, Phys. Rev. B 2008, 77, 235430.

[S7] B. Zhang, F. Kang, J. M. Tarascon, J. K. Kim, Prog. Mater. Sci. 2016, 76, 316-380.

[S8] W. M. Haynes, CRC Handbook of Chemistry and Physics, CRC Press 2011

[S9] J. Luo, C. Wang, H. Wang, X. Hu, E. Matios, X. Lu, W. Zhang, X. Tao, W. Li, *Adv. Funct. Mater.* 2019, *29*, 1805946.

[S10] S. Liu, S. Tang, X. Zhang, A. Wang, Q. H. Yang, J. Luo, *Nano Letters* 2017 17, 5862-5868.

[S11] Q. Zhang, Y. Lu, M. Zhou, J. Liang, Z. Tao, J. Chen, *Inorganic Chem. Frontiers* 2018, 5, 864-869.

[S12] A. Wang, X. Hu, H. Tang, C. Zhang, S. Liu, Y.-W. Yang, Q.-H. Yang, J. Luo, *Angew. Chem. Int. Ed.* 2017, *56*, 11921-11926.

[S13] C. Chu, N. Wang, L. Li, L. Lin, F. Tian, Y. Li, J. Yang, S. Dou, Y. Qian, *Energy Storage Mater*. 2019, *23*, 137-143.

[S14] H. Ye, C. Y. Wang, P. F. Wang, P. Wang, T. T. Zuo, Y. X. Yin, Z. J. Zheng, J. Cheng, F. F. Cao, Y. G. Guo, *Nano Energy* 2018, *48*, 369-376.

[S15] P. Li, T. Xu, P. Ding, J. Deng, C. Zha, Y. Wu, Y. Wang, Y. Li, *Energy Storage Mater*. 2018, *15*, 8-13.

[S16] Z. Zheng, X. Zeng, H. Ye, F. Cao, Z. Wang, ACS Appl. Mater. Interfaces 2018, 10, 30417-30425.

[S17] B. Sun, P. Li, J. Zhang, D. Wang, P. Munroe, C. Wang, P. H. L. Notten, G. Wang, *Adv. Mater.* 2018, *30*, 1801334.

[S18] X. Lu, J. Luo, E. Matios, Y. Zhang, H. Wang, X. Hu, C. Wang, H. Wang, J. Wang, W. Li, *Nano Energy* 2020, *69*, 104446.

[S19] H. Wang, E. Matios, C. Wang, J. Luo, X. Lu, X. Hu, Y. Zhang, W. Li, *J. Mater. Chem.* A 2019, 7, 23747-23755.

[S20] X. Zheng, P. Li, Z. Cao, W. Luo, F. Sun, Z. Wang, B. Ding, G. Wang, Y. Huang, *Small* 2019, *15*, 1902688.

[S21] X. Zheng, H. Fu, C. Hu, H, Xu, Y. Huang, J. Wen, H. Sun, W. Luo, Y. Huang, J. Phys. Chem. Lett. 2019, 10, 707-714.

[S22] A. Ponrouch, D. Monti, A. Boschin, B. Steen, P. Johansson, M. R. Palacín, J. Mater. Chem. A 2015, 3, 22-42.

[S23] D. I. Iermakova, R, Dugas, M. R. Palacín, A. Ponrouch, J. Electrochem. Soc. 2015, 162, A7060.

[S24] A. Rudola, D. Aurbach, P. Balaya, Electrochem. Commun. 2014, 46, 56-59.

[S25] R. Dugas, A. Ponrouch, G. Gachot, R. David, M. R. Palacin, J. M. Tarascon, J. Electrochem. Soc. 2016, 163, A2333.

[S26] A. Mahapatro, S. K. Suggu, Adv. Mater. Sci. 2018, 3, 1-9.