Supporting Information

CoMn-layered double hydroxide nanowalls supported on carbon fibers for high-performance flexible energy storage devices

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Computational details

All calculations were performed with the periodic density functional theory (DFT) method using Dmol3 module in Materials Studio version 5.5 software package (Accelrys Software Inc.: San Diego, CA).¹ Cobalt-Manganese layered double hydroxide (CoMn-LDH), cobalt-aluminum layered double hydroxide (CoAl-LDH) and Co(OH)₂ were constructed with symmetry $P3_m^-1$. The CoMn-LDH was built based on the following lattice parameters: a=b=9.36 Å, c=7.61 Å (equivalent to $3 \times 3 \times 1$ in the a, b, c direction). The molar ratio of Co to Mn was set to be 2 : 1, *i.e.*, 6 Co atoms and 3 Mn atoms in the supercell. Each Mn(OH)₆ octahedron was surrounded by six Co(OH)₆ octahedra which ensures that Mn atoms will not occupy adjacent octahedra. Three carbonate anions were introduced into the interlayer space to keep the system neutral. CoAl-LDH was constructed with a=18.72 Å, b=9.36 Å, c=7.61 Å ($6 \times 3 \times 1$ in the a, b, cdirection). Three carbonate anions were also added to keep the model neutral. Co(OH)₂ was established with a=b=9.441 Å, c=4.768 Å (3 × 3 × 1 in the *a*, *b*, *c* direction). The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)² functional, together with effective core potentials with double numerical plus polarization quality basis, was utilized for the geometric optimization. During the calculations, the convergence tolerance was set as follows: energy = 1.0×10^{-6} Ha, force = 1.0×10^{-3} Ha/Å, displacement = 1.0×10^{-3} Å. The density of states and electron density of optimized structure were analyzed.



Scheme S1. Side view of the optimized CoMn-LDH supercell model (Blue: Co; Purple: Mn; Red: O; White: H; Grey: C).

Calculations

For the three-electrode configuration, the CoMn-LDH/CFs acts directly as the working electrode with a saturated Hg/HgO electrode as the reference electrode, a platinum plate as the counter electrode in 1.0 M LiOH. Specific capacitance from the charge/discharge curves was calculated according to:

$$C_s = \frac{I \times \Delta t}{m \times \Delta V} \tag{1}$$

where C_s (F/g) is the specific capacitance, I (A) refers to the discharge current, ΔV (V) represents the potential change within the discharge time Δt (s), and m (g) corresponds to the amount of active LDH material on the electrode.

Energy density and power density of the symmetric supercapacitor were estimated using the following equations:³

$$C = \frac{2 \cdot I \cdot \Delta t}{m \cdot \Delta V}$$
(2)

$$E = \frac{1}{2} \cdot C \cdot (\Delta V)^{2}$$
(3)7

$$P = \frac{E}{\Delta t}$$
(4)

$$P_{\text{max}} = \frac{\Delta V}{4 \cdot M \cdot R_{ESR}}$$
(5)

(5)

where C (F/g) is the measured specific capacitance; I (A) represents the discharge current; ΔV (V) refers to the potential change within the discharge time Δt (s); m (g) is the total mass of the active material from the electrodes; E (Wh/kg) refers to the energy density; P (kW/kg) corresponds to the average power density; P_{max} (kW/kg) is the maximum power density; M is the total mass of the two electrodes, and $R_{\text{ESR}}(\Omega)$ is the equivalent series resistance (ESR) of the supercapacitor.

Supplementary Figures



Fig. S1 EDS spectrum of the CoMn-LDH/CFs.



Fig. S2 XRD pattern and SEM image (inset) of the CoMn-LDH powdered sample.

The reflections of CoMn-LDH powdered sample can be indexed to a hexagonal lattice with *R3m* rhombohedral symmetry, commonly used for the description of LDH structures. No other crystalline phase was detected, indicating the high purity of the CoMn-LDH. A serious aggregation was observed from the SEM image. Therefore, the direct growth of CoMn-LDH on the surface of CFs presented in this work can effectively suppress the aggregation and increase the utilization of active species.



Fig. S3 The FTIR spectrum of the CoMn-LDH.



Fig. S4 CVs of the CoMn-LDH/CFs samples with different Co/Mn molar ratios at the same scan rate (normalized to the weight of active material).



Fig. S5 Specific capacitances of CoMn-LDH/CFs (mass loading of 0.5, 0.9, and 1.6 mg/cm²) at different current densities.



Fig. S6 (a) CVs of the CoMn-LDH/CFs and bare CFs at a scan rate of 20 mV/s; (b) galvanostatic charge-discharge curves for the CoMn-LDH/CFs and bare CFs at a current density of 2.1 A/g, respectively. The capacitance of CoMn-LDH/CFs is ~35 times higher than that of bare CFs, indicating the CFs substrate in this study delivers negligible capacitance.



Fig. S7 Typical SEM images for the CoMn-LDH/CFs before (a) and after 6000 cycles (b).



Fig. S8 Comparison of CVs for the CoMn-LDH/CFs and CoMn-LDH powered samples at the same scan rate (normalized to the weight of the active material).



Fig. S9 (a-c) SEM images and (d) EDS result of NiMn-LDH/CFs.



Fig. S10 The partial (a, b) and total (c) density of states for CoMn-LDH, CoAl-LDH and Co(OH)₂.



Fig. S11 The photograph of the flexible supercapacitor device (inset: cross-section image).



Fig. S12 Cycling performance of the flexible device at a current density of 6 A/g before and after bending to 120° for 100 times. The inset shows cycling performance of the device with a bending angle of 120° .



Fig. S13 Ragone plots of the flexible supercapacitor, in comparison with references.



Fig. S14 (a) Cycling performance for the supercapacitor device by using PVA/LiOH polymer electrolyte and 1 M LiOH aqueous electrolyte, respectively. (b) Specific capacitances of the supercapacitor device collected at different charge/discharge current densities.

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