Journal of Materials Chemistry A



PAPER



Cite this: J. Mater. Chem. A, 2016, 4, 8421

Ultrahigh-rate-capability of a layered double hydroxide supercapacitor based on a selfgenerated electrolyte reservoir[†]

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A hierarchical CoAl–OH layered double hydroxide (H-OH-LDH) electrode was prepared *via* a continuous calcination–rehydration treatment of a plate-like CoAl–CO₃ layered double hydroxide (P-CO₃-LDH) array on a nickel foil substrate. The H-OH-LDH electrode shows a well-defined hierarchical structure with a greatly increased accessible interlaminar surface area, leading to improved electrochemical energy storage ability. Most significantly, the interlayer space of H-OH-LDH acts as an electrolyte micro-reservoir to store OH⁻ ions, which dramatically decreases the diffusion resistance of OH⁻ to the inner surface of LDH lamella, and consequently results in an ultrahigh-rate-capability (capacitance reservation of 66% when the current density increases from 1 to 100 A g⁻¹). The remarkable rate capability is superior to that of ever-reported transition metal oxide/hydroxide-based electrodes. In addition, an all-solid-state hybrid capacitor device was fabricated based on this H-OH-LDH electrode, exhibiting outstanding energy and power output (35.5 W h kg⁻¹ at 27.3 kW kg⁻¹) as well as excellent cycling stability. Therefore, this work demonstrates a new approach for the design and fabrication of LDH-based materials with self-generated electrolyte reservoirs, which have promising potential application in energy storage/conversion systems.

Received 14th March 2016 Accepted 2nd May 2016 DOI: 10.1039/c6ta02164f www.rsc.org/MaterialsA

1. Introduction

With the rapid depletion of global fossil fuels and environmental deterioration, the development of high-efficient energy storage/conversion devices arouses worldwide concern in both scientific and technological fields.¹⁻⁴ Supercapacitors (SCs) are a kind of important energy storage device due to their large capacitance, high power density and long cycling life.5-7 Among the several evaluation parameters of SCs, the rate capability is of vital importance,^{8,9} which ensures a fast charging-discharging rate and instantaneous high-power output, especially for applications in electric vehicles, aeronautics/astronautics and backup energy systems. Generally, SCs with carbon-based materials possess high rate capability and long cycling lifetime, but mediocre specific capacitance and energy density.¹⁰⁻¹² In contrast, SC materials based on a faradaic mechanism have satisfactory specific capacitance and energy density, but suffer from poor rate capability, as a result of the depressed ion

diffusion kinetics and large resistance.^{13–16} Recent advances in the improvement of rate properties of SC materials have been achieved by the incorporation of highly conductive species (*e.g.*, carbon nanotubes, carbon cloth, graphene and conductive polymers)^{6,17–19} or fabrication of nanostructured electrodes (*e.g.*, nanotubes, nanowires, and nanosheets).^{8,20,21} Although these materials have shown interesting performance, the construction of novel materials with large ion-accessible surface areas, facile ion-diffusion dynamics and consequent high rate capability still remains a challenging goal.

Transition metal layered double hydroxides (*e.g.*, Co, Ni, Fe or Mn-containing LDHs), whose structures are based on positively charged brucite-like layers and interlayer charge compensating anions,^{22–25} have shown outstanding performance in SCs, oxygen evolution reactions and electrocatalysis.^{26–30} During the redox reaction of LDHs, OH⁻ ions in the electrolyte are involved to induce a valence change of the transition metal for charge storage as SC materials.^{31,32} However, the transportation rate of OH⁻ is normally slow owing to the large diffusion resistance in the LDH gallery, resulting in poor unitization of the inner active surface and inferior rate capability. If OH⁻ ions can be stored in the interlayer space of LDHs, the ion diffusion distance would be shortened dramatically and the available active surface would be significantly increased.

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[†] Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ta02164f

Herein, we report the design and construction of a hierarchical CoAl-OH LDH (defined as H-OH-LDH) array on a nickel foil substrate, by storing OH⁻ ions in the LDH gallery as a selfgenerated electrolyte reservoir. This is achieved based on the "memory effect" of LDH materials: calcination of carbonatecontaining CoAl-LDH (P-CO₃-LDH) at a moderate temperature induces the formation of layered double oxides (LDOs), and rehydration of LDOs in hydroxide aqueous solution leads to the recovery of the LDH structure with OH⁻ as the interlayer anion. The resulting H-OH-LDH electrode yields largely improved capacitance (1031 F g^{-1} at 1 A g^{-1}) compared with the P-CO₃-LDH electrode (588 F g^{-1} at 1 A g^{-1}). Most significantly, it exhibits a remarkable charge-discharge rate capability, retaining 66% of capacitance as the current density increases from 1 to 100 A g^{-1} , which originates from its electrolyte storage capability. In addition, an all-solid-state hybrid capacitor device was fabricated based on the H-OH-LDH electrode, which shows prominently enhanced energy and power output (35.5 W h kg⁻¹ at 27.3 kW kg⁻¹) as well as long-term stability.

2. Experimental

2.1. Preparation of the CoAl-LDH nanoplate array

The plate-like CoAl–CO₃ LDH (P-CO₃-LDH) array on a Ni foil substrate was prepared using a facile *in situ* growth approach similar to our previous work.²⁶ Typically, 15 mmol Co(NO₃)₂··6H₂O, 5 mmol Al(NO₃)₃··9H₂O, 2 mmol NH₄F and 50 mmol Co(NH₂)₂ were dissolved in 100 mL water, and then transferred into a Teflon lined stainless steel autoclave. A piece of precleaned Ni foil (size: 3 cm × 6 cm; thickness: ~100 µm) was immersed into the solution. Subsequently, the autoclave was sealed and maintained at 110 °C for 8 h. Finally, the substrate was rinsed thoroughly and a P-CO₃-LDH array was obtained on the surface of the Ni foil substrate. The mass loading of the active material is about 0.5 mg cm⁻².

2.2. Calcination of the P-CO₃-LDH array

One piece of the substrate-supported P-CO₃-LDH array was calcined in a H₂ stream at 500 °C for 240 min, with a heating rate of 2 °C min⁻¹. After calcination, the resulting product was slowly cooled to room temperature in a N₂ stream. The calcination process results in the phase transformation from CoAl-LDH to a Co–Al₂O₃–CoO hybrid structure.

2.3. Rehydration of the calcined product

The H-OH-LDH electrodes were prepared based on the "memory effect" of the LDH materials. Five pieces of the calcined product (Co–Al₂O₃–CoO) on the Ni substrate were rehydrated in a 0.5 M KOH solution at 60 °C in a N₂ atmosphere for 15, 30, 60, 90 and 120 min, respectively, to prepare the hierarchical H-OH-LDH electrode. For a comparison study, a piece of calcined product was rehydrated in a 0.5 M Na₂CO₃ solution at 60 °C for the construction of the hierarchical CoAl–CO₃ LDH (H-CO₃-LDH) electrode. After washing with distilled water and drying in a vacuum, H-OH-LDH and H-CO₃-LDH array electrodes were obtained.

2.4. Fabrication of the H-OH-LDH//AC SC device

The as-prepared H-OH-LDH array on the Ni foil substrate and activated carbon (AC) serve as the positive and negative electrode, respectively, for the fabrication of an asymmetric hybrid SC device. The negative electrode was prepared by mixing 80 wt% AC, 10 wt% acetylene black and 10 wt% polytetrafluoroethylene (PTFE) and coating the mixture on a nickel foam substrate. The PVA/KOH gel electrolyte was prepared as follows: KOH (3.36 g) and powdered PVA (6 g) were added into deionized water (60 mL); and then the whole mixture was heated to 85 °C under stirring until the solution became clear. Two strips of the positive and negative electrodes were dipped into the PVA/KCl solution for 10 min. Subsequently, the electrodes with a thin electrolyte coating were air-dried at room temperature for 4 h to vaporize excess water. The two electrodes were pressed together under a pressure of \sim 5 MPa for 10 min to obtain the final H-OH-LDH//AC asymmetric all-solid-state hybrid capacitor device.

2.5. Characterization

The X-ray diffraction (XRD) patterns were recorded on a Rigaku XRD-6000 diffractometer, using Cu-K α radiation ($\lambda = 0.1542$ nm) at 40 kV, 30 mA. The morphology was investigated using a scanning electron microscope (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV, combined with energy dispersive X-ray spectroscopy (EDX). Transmission electron microscopy (TEM) images were recorded with a Philips Tecnai 20 and JEOL JEM-2010 high-resolution TEM with an accelerating voltage of 200 kV in each case. X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCALAB 250 instrument (Thermo Electron) with Al Ka radiation. The XPS peaks were decomposed using mixed Gaussian-Lorentzian functions, nonlinear squares fitting algorithm, and Shirley-type background subtraction by using XPS peak fit software. Headspace gas chromatography (HS-GC) measurements were carried out using an HSS 80.65 Automatic Headspace Sampler (DANI, Italy) and a Model HP-7890 capillary GC equipped with a thermal conductivity detector (TCD) (Agilent Technologies, USA). The headspace sampler was operated at 60 °C with an equilibration time of 12 h. GC conditions were as follows: the capillary column at 40 °C; a carrier gas (high purity nitrogen) flow rate of 3.5 mL min⁻¹ 0.1 g of P-CO₃-LDH or H-OH-LDH sample was added into a H_2SO_4 solution (1.0 mol L⁻¹, 21.6 mL), sealed for a reaction of 4 h. The produced CO₂ gas from P-CO₃-LDH was injected immediately into the autosampler for HSGC measurements. The metal contents of samples were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Shimadzu ICPS-7500 instrument. The sample (0.02 g) was dissolved in 10 mL of HCl solution (1:1, v/v), followed by quantitative analysis of Co and Al. The analysis of C, H, and O elements was performed on a Perkin-Elmer Elementar vario elemental analysis instrument. The specific surface areas were calculated using the Brunauer-Emmett-Teller (BET) method with a degassing temperature of 100 °C. A CHI 660E electrochemical workstation (Shanghai Chenhua Instrument Co., China) was employed for all the electrochemical measurements. For the three-electrode configuration, a saturated Hg/HgCl₂

(SCE) electrode and a platinum plate serve as the reference and counter electrode, respectively. The EIS measurement was performed by applying an AC voltage of 5 mV amplitude in a frequency range 0.01–100 kHz at open circuit voltage in 1.0 M KOH solution.

3. Results and discussion

3.1. Characterization of P-CO₃-LDH and H-OH-LDH electrodes

The P-CO₃-LDH array on a Ni foil substrate was prepared via a hydrothermal method, which was further treated by a calcination-rehydration process to obtain the H-OH-LDH electrode (Scheme 1). The powder XRD pattern of the P-CO₃-LDH sample (Fig. 1, line a) displays a series of peaks at 2θ 11.58°, 23.43°, 34.86°, 59.74° and 60.85°, corresponding to the [003], [006], [012], [110] and [113] reflections of the LDH phase with CO_3^{2-} in its interlayer space. No other crystalline phase is detected, indicating a well-defined layered structure with high crystallinity. After calcination in a H₂ stream at 500 °C for 240 min, new diffraction reflections appear at 2θ 36.49°, 61.48° (ascribed to CoO phase) and 44.23° (assigned to the metal Co phase) (Fig. 1, line b), verifying the phase transformation from LDH to a metal/metal oxide hybrid. The spectrum of the rehydrated sample (Fig. 1, line c) shows [003], [006], [012] and [015] reflections of a typical LDH structure, indicating the recovery of the original layered structure. In comparison with the CO₃-LDH precursor, the [00*l*] diffractions of the recovered LDH shift to higher angles (for instance, [003] reflection moves to 11.80°, inset of Fig. 1) because of the anion substitution of CO_3^{2-} by OH⁻ anions in the interlayer gallery. The molecular formulae of P-CO₃-LDH and H-OH-LDH were determined to be [Co_{0.71}- $Al_{0.29}(OH)_2](CO_3^{2-})_{0.15} \cdot 0.51H_2O$ and $[Co_{0.71}Al_{0.29}(OH)_2]$ -(OH⁻)_{0.31}·0.45H₂O, based on ICP and C, H, and O elemental analysis. In addition, the anion exchange from CO_3^{2-} to $OH^$ after a calcination-rehydration process was further confirmed by the headspace gas chromatography (HSGC) analysis (ESI, Fig. S1[†]). The X-ray photoelectron spectroscopy (XPS) analysis (see details in the ESI, Fig. $S2^{\dagger}$) indicates that trace part of Co(II)



Fig. 1 XRD patterns of (a) $P-CO_3-LDH$, (b) $Co-Al_2O_3-CoO$ and (c) H-OH-LDH samples scratched from the substrate. The inset shows the amplified [003] reflection of $P-CO_3-LDH$ and H-OH-LDH samples.

is oxidized to Co(m) after the calcination-rehydration treatment.

The SEM image of the precursor P-CO₃-LDH array (Fig. 2A) shows that platelet-like sheets (\sim 1 µm in lateral size) are oriented perpendicularly to the substrate, with plenty of interparticle macropores and an array thickness of \sim 3.6 µm. Energy dispersive X-ray (EDX) spectroscopy (ESI, Fig. S3†) displays a homogeneous distribution of cobalt, aluminum and oxygen elements throughout the whole nanoplate array. The corresponding TEM image (Fig. 2B) shows a smooth surface for a single nanoplatelet with a thickness of \sim 9 nm (ESI, Fig. S4A†). A series of lattice fringes with an interplanar distance of \sim 0.256 nm is observed in the HR-TEM image (Fig. 2C), corresponding to the [012] plane of the CoAl-LDH phase. The calcination product inherits the morphology feature of the P-CO₃-LDH array precursor, as shown in the SEM image (Fig. 2D). The HR-TEM image (Fig. 2E) of a single nanoplatelet reveals an uniform



Scheme 1 (A) The synthetic process of the H-OH-LDH array on a Ni foil substrate. (B) Schematic diagram of $P-CO_{x}$ -LDH and H-OH-LDH.



Fig. 2 SEM and TEM images of (A)–(C) P-CO_3-LDH, (D)–(F) Co– Al_2O_3-CoO and (G)–(I) H-OH-LDH arrays.

distribution of Co/CoO nanoparticles immobilized on the substrate, with two identified interplanar distances of \sim 0.208 and \sim 0.266 nm attributed to the [111] plane of the metal Co and CoO phase, respectively.

Interestingly, after the rehydration process, a large number of secondary tiny LDH nanoplates are grown on the surface of original LDH nanoplatelets (Fig. 2G), giving rise to a hierarchical architecture. The thickness of the H-OH-LDH film is ~3.6 μ m (inset of Fig. 2G), in accordance with that of the P-CO₃-LDH array. EDX mapping analysis (ESI, Fig. S5†) illustrates that cobalt, aluminum and oxygen elements are well-distributed in the H-OH-LDH array. TEM and SEM images reveal a plate size of ~50 nm (Fig. 2H) and thickness of ~8 nm (ESI, Fig. S4B†) for the secondary LDH nanoplates. A lattice fringe of ~0.256 nm is observed (Fig. 2I), corresponding to the [012] plane of the CoAl-LDH phase, in accordance with that of the precursor P-CO₃-LDH (Fig. 2C).

Time-dependent experiments were carried out to optimize the rehydration time of the H-OH-LDH array electrode, which was monitored by SEM images (Fig. 3). No apparent nanoplate subunit is observed on the surface of original nanoplatelets with a short rehydration time (15 min, Fig. 3A); a time of 30 min leads to the obvious growth of sub-nanoplates (Fig. 3B). As the reaction time is further prolonged, the LDH sub-nanoplates grow much bigger and more densely with a well-defined platelike morphology and decreased macropore size (Fig. 3C and D). After 120 min of the rehydration process, the whole surface of the electrode is completely covered by the secondary LDH nanoplates (Fig. 3E). The XRD patterns of these H-OH-LDH (Fig. 3F) samples display a gradually enhanced reflection intensity of [003], [006] and [012] with the increase of rehydration time, indicating the growth process of the H-OH-LDH phase.

The growth of secondary LDH nanoplates can be explained by the dissolution-recrystallization mechanism in an inorganic synthesis reported previously.³³⁻³⁷ In alkaline solution, hydrolysis of CoO and Al_2O_3 results in the formation of Co(OH)₂ and Al(OH)₄⁻, respectively. Al(OH)₄⁻ diffuses to the surface of Co(OH)₂ and enters into the Co(OH)₂ lattice to form CoAl-LDH seeds on the surface of original nanoplates



Fig. 3 SEM images of H-OH-LDH samples with different rehydration times: (A) 15 min, (B) 30 min, (C) 60 min, (D) 90 min and (E) 120 min. (F) XRD patterns of the H-OH-LDH samples synthesized with different rehydration times on the Ni foil substrate.

(eqn (1)-(4)). Then the seeds induce the gradual growth of secondary LDH nanoplates along the perpendicular direction to the Al_2O_3 substrate owing to the steric hindrance effect.

$$CoO + H_2O \leftrightarrow Co(OH)_2$$
 (1)

$$Al_2O_3 + 3H_2O \leftrightarrow 2Al(OH)_3$$
 (2)

$$Al(OH)_3 + OH^- \leftrightarrow Al(OH)_4^-$$
(3)

$$a\text{Co(OH)}_{2} + \text{Al(OH)}_{4}^{-} + x\text{H}_{2}\text{O} \leftrightarrow \\ [\text{Co}_{a}\text{Al(OH)}_{2a+2}](\text{OH}) \cdot x\text{H}_{2}\text{O}(s) + \text{OH}^{-}$$
(4)

N₂ adsorption-desorption measurements were performed on the bare Ni substrate, P-CO3-LDH and H-OH-LDH to study the surface area and porosity of these samples. As shown in Fig. S6 (ESI^{\dagger}), the Ni substrate does not show obvious N₂ adsorption-desorption behavior; while P-CO3-LDH and H-OH-LDH exhibit typical IV isotherm with a H3-type hysteresis loop $(P/P_0 > 0.4)$. No limiting adsorption in the high P/P_0 region is observed, indicating the presence of mesopores.³⁸ This is further confirmed by the pore size analysis based on the isotherms (inset of Fig. S6,† ESI), in which both the H-OH-LDH and P-CO₃-LDH consist of a mesopore distribution in the range of 2-6 nm. Significantly, the specific surface area of H-OH-LDH triples over that of P-CO₃-LDH (332 vs. 112 m² g⁻¹) due to its largely enhanced accessible surface arising from the hierarchical structure. By virtue of its increased surface area and the unique hierarchical porous structure, the H-OH-LDH electrode would afford more active sites at the electrode/electrolyte interface to efficiently facilitate the faradaic redox reactions.

Subsequently, cyclic voltammetry (CV) measurements were carried out to investigate the effect of hydration time (from 15 to 120 min) on the electrochemical properties of H-OH-LDH electrodes (Fig. S7,† ESI). All five samples demonstrate similar electrochemical behavior with a pair of anodic/ cathodic peaks in a potential range from -0.2 to 0.55 V, corresponding to the reversible redox reaction of Co(II), Co(III) and Co(IV) associated with OH⁻ according to the following chemical formula:

 $LDH-Co(OH)_2 + OH^- \leftrightarrow LDH-CoOOH + H_2O + e^-$ (5)

$$LDH-CoOOH + OH^- \leftrightarrow LDH-CoO_2 + H_2O + e^-$$
 (6)

However, the CV curves derived from the five samples show apparently different integrated areas at the same scan rate. The current of anodic/cathodic peaks enhances first upon increasing the hydration time and reaches the maximum with a hydration time of 90 min. A further increase of the hydration time leads to the decline of the anodic/ cathodic current, which is attributed to the depressed ion penetration into the inner H-OH-LDH electrode owing to the excess secondary LDH nanoplates. Therefore, the sample with a hydration time of 90 min was selected for the following electrochemical tests.

3.2. Electrochemical energy storage properties of the H-OH-LDH electrode

To further illustrate the role of interlayer OH⁻ ions and the hierarchical structure in the enhancement of electrochemical performance, CV and galvanostatic charge-discharge (CD) measurements were carried out on P-CO₃-LDH, H-OH-LDH and H-CO₃-LDH (obtained by rehydration in Na₂CO₃ solution, Fig. S8,† ESI) electrodes. In comparison to the bare substrate, the three LDH electrodes show increased areas of CV curves by multiple orders of magnitude (Fig. 4A), indicating that their charge-storage capabilities are derived from the active materials. The H-OH-LDH array electrode shows a pair of anodic/ cathodic peaks at 0.30 V/0.21 V, leading to a potential separation ($\Delta E_{\rm p}$) of 0.09 V. This value is as expected much lower than that of the H-CO₃-LDH (0.13 V) and P-CO₃-LDH (0.15 V) electrodes, indicating a better reversibility of the H-OH-LDH electrode. CV curves (Fig. 4B) show that the peak current of H-OH-LDH increases with an insignificant change in the curve shape, and the peak potential shifts slightly as the scan rate increases, suggesting its good conductivity and facile ion transport kinetics.

The CD curves (Fig. 4C) exhibit a typical capacitive behavior for P-CO₃-LDH, H-CO₃-LDH and H-OH-LDH electrodes. On the basis of the discharge branch, the specific capacitance of the H-



Fig. 4 (A) CV curves of the P-CO₃-LDH, H-CO₃-LDH and H-OH-LDH electrodes (scan rate: 40 mV s⁻¹). (B) CV curves of the H-OH-LDH electrode collected at various scan rates. (C) Galvanostatic CD curves of P-CO₃-LDH, H-CO₃-LDH and H-OH-LDH at 1 A g⁻¹. (D) Galvanostatic CD curves of the H-OH-LDH electrode at various current densities. (E) Specific capacitance as a function of current density. (F) Electrochemical impedance spectra of the P-CO₃-LDH, H-CO₃-LDH and H-OH-LDH electrodes.

OH-LDH electrode is calculated to be 1031 F g^{-1} at a current density of 1 A g^{-1} , which is 1.8 and 1.2 times that of P-CO₃-LDH (588 F g^{-1}) and H-CO₃-LDH (883 F g^{-1}) electrode, respectively. In addition, the H-OH-LDH electrode shows the smallest IR drop at the same charging–discharging rate, demonstrating the lowest internal resistance of the electrode. For supercapacitor materials, a low internal resistance is crucial for improving the capacitance and reducing unwanted power consumption. Furthermore, the CD curves (Fig. 4D) of the H-OH-LDH electrode display little deviation with the increase of current density, even at a rather high discharging rate of 100 A g^{-1} , indicating a facilitated ion diffusion and excellent stability during the redox reaction.

Generally, the specific capacitance of a Faradaic capacitor would decline sharply with increasing current density, resulting in poor rate capability. The specific capacitances of the three samples derived from the CD curves at different chargedischarge current densities are shown in Fig. 4E. The P-CO₃-LDH and H-CO₃-LDH electrodes display a mediocre capacitance reservation of 32% and 53%, respectively, when the current density increases from 1 to 40 A g^{-1} . In the case of the H-OH-LDH electrode, its specific capacitance decreases slowly along with the increase of current density, with 74% retention (758 F g^{-1}) of its original capacitance (1031 F g^{-1}) when the current density reaches 40 A g^{-1} . It is worth noting that even if the current density increases to as high as 100 Ag^{-1} , the H-OH-LDH electrode achieves a remarkable capacitance retention rate of 66%, which is obviously higher than the reported rate capability of transition metal oxide/hydroxide electrodes (summarized in Table 1).

Electrochemical impedance spectroscopy (EIS) measurements were performed to examine the electron transfer and ion diffusion properties of the three electrodes (Fig. 4F), which represent a characteristic semicircle over the high frequency range and a linear part in the low frequency region. The chargetransfer resistance (related to the diameter of the semicircle) of H-OH-LDH is calculated to be 2.1 Ω , much smaller than that of P-CO₃-LDH (9.8 Ω) and H-CO₃-LDH (4.1 Ω), indicating a lower resistance of the H-OH-LDH electrode. The liner part of Nyquist plots of the H-OH-LDH electrode exhibits the largest slope among the three electrodes, indicating the lowest OH⁻ diffusion resistance of the H-OH-LDH electrode, which is responsible for its ultrahigh-rate-capability.

Table 1Comparison study of the rate capability between the H-OH-LDH electrode in this work and previously reported oxide/hydroxidematerials

Materials	Capacitance (F g ⁻¹)	Rate capability	Ref
NiCo-LDH	$2275 (1 \text{ A g}^{-1})$	$44\% (25 \text{ A g}^{-1})$	39
CoAl-LDH	$584 (1 \text{ A g}^{-1})$	$39\% (40 \text{ A g}^{-1})$	40
MoS ₂ @Ni(OH) ₂	516 (2 A g^{-1})	$48\% (10 \text{ A g}^{-1})$	15
Co(OH) ₂	$1116 (1 \text{ A g}^{-1})$	$38\% (10 \text{ A g}^{-1})$	41
MnOOH@NiO	$1890 (2 \text{ A g}^{-1})$	$64\% (20 \text{ A g}^{-1})$	42
NiCo ₂ O ₄	$1045 (5 \text{ A g}^{-1})$	$56\% (20 \text{ A g}^{-1})$	21
H-OH-LDH	$1031 (1 \text{ A g}^{-1})$	$74\% (40 \text{ A g}^{-1})$	This work
	,	$66\% (100 \text{ A g}^{-1})$	

In addition, the ion diffusion kinetics study based on CV curves (see details in the ESI, Fig. S9†) illustrates a low OH⁻ diffusion resistance of the H-OH-LDH electrode as well. The results indicate that the interlayer CO_3^{-2-} of P-CO₃-LDH and H-CO₃-LDH decreases the mass transport of OH⁻ ions through spatial hindrance (Fig. 5A). However, the H-OH-LDH electrode offers abundant OH⁻ ions from a self-generated electrolyte reservoir, which enhances the diffusion of OH⁻ to be involved in the faradaic redox reactions (Fig. 5B). Furthermore, the water contact angles of P-CO₃-LDH and H-OH-LDH films are 23° and 26°, respectively, indicating a negligible wettability change after the calcination–rehydration treatment (Fig. S10,† ESI). Therefore, the ultrahigh rate performance of the H-OH-LDH electrode is mainly attributed to its facile diffusion dynamics with the assistance of interlayer OH⁻.

To further evaluate the SC performance of the H-OH-LDH electrode, an asymmetric all-solid-state hybrid capacitor device was fabricated by using H-OH-LDH, activated carbon/Ni foam and a PVA/KOH film as the cathode, anode and electrolyte, respectively (defined as H-OH-LDH//AC, Fig. 6A). The total mass of the active materials on the positive and negative electrodes is 1.0 and 6.5 mg, respectively, according to the balance of the specific capacitance of the two electrodes (Fig. S11,† ESI). Fig. 6B shows the CV curves of the optimized supercapacitor device at various scan rates within a potential window of 0 to 1.5 V. Unlike the electrochemical feature of H-OH-LDH in a threeelectrode system, this all-solid-state device displays a quasirectangular CV geometry as an electric double layer capacitor. Galvanostatic CD curves (Fig. 6C) at various current densities show a high level of linear correlation and symmetrical shape with a quick response, indicating an ideal capacitive behavior.

The H-OH-LDH//AC device exhibits a high specific capacitance of 125 F g⁻¹ at 1 A g⁻¹ and maintains 98 F g⁻¹ at 32 A g⁻¹ (Fig. 6D), indicating an outstanding rate performance. As a comparison study, the P-CO₃-LDH//AC device shows a lower capacitance (96 F g⁻¹) at 1 A g⁻¹ and inferior capacitance retention (34.3% from 1 A g⁻¹ to 16 A g⁻¹). The Ragone plot of the H-OH-LDH//AC device (Fig. 6E) illustrates a maximum energy density of 44.8 W h kg⁻¹ (at a power density of 0.85 kW kg⁻¹) and power density of 27.3 kW kg⁻¹ (at an energy density of 35.5 W h kg⁻¹) at an operating voltage of 1.5 V. The energy density and rate capability of the H-OH-LDH//AC device in this



Fig. 5 Schematic illustration of the redox process in (A) P-CO₃-LDH and H-CO₃-LDH, and (B) H-OH-LDH electrodes. The interlayer pink area in (B) represents the self-generated electrolyte reservoir of H-OH-LDH.



Fig. 6 (A) A schematic diagram illustrating the architecture of an asymmetrical SC device fabricated with the H-OH-LDH and activated carbon electrode. (B) CV curves collected at scan rates between 20 and 200 mV s⁻¹. (C) Galvanostatic CD curves of the device at various current densities. (D) Specific capacitances of H-OH-LDH//AC, H-CO₃-LDH//AC and P-CO₃-LDH//AC capacitors as a function of current density. (E) Ragone plots of the H-OH-LDH//AC device in this work, in comparison with the reported supercapacitors.^{21,43–47} (F) Cycling performance of the H-OH-LDH//AC device at a current density of 4 A g⁻¹.

work are comparable with or superior to those of previously reported supercapacitors (*e.g.*, $Co_3O_4//carbon$, $Co(OH)_2@VN//carbon$, $V_2O_5//carbon$, $NiCo_2O_4@Au//carbon$ and CoO@NiO//rGO supercapacitors,^{21,43-46}), but slightly lower than the $NiCo_2O_4/carbon$ cloth (CC)//rGO device.⁴⁷

Cycling life test on the device was carried out at a current density of 4 A g^{-1} by a galvanostatic charge-discharge technique, which shows a capacitance retention of 92% over 2000 cycles (Fig. 6F). The charge-discharge curves for the last 20 cycles (inset of Fig. 6F) still exhibit isosceles triangle characteristics with good coulombic efficiency. Furthermore, the structure and morphology of the H-OH-LDH electrode (Fig. S12,† ESI) did not undergo obvious change after 2000 charge-discharge cycles, indicative of its excellent cycling stability. Moreover, the self-discharge curve (Fig. S13,† ESI) undergoes a rapid decrease within the first several hours, but shows a stable output voltage of \sim 0.8 V after 4.5 h and an almost 50% retention of the initial charge potential after 24 h. In addition, the H-OH-LDH//AC SCD with an area of \sim 5 cm² can continuously drive a mini-fan after charging to 1.5 V (Movie S1,† ESI), further demonstrating its prospective application as an energy storage device.

4. Conclusions

In summary, a hierarchical CoAl–OH-LDH array was successfully fabricated *via* a facile and effective approach based on the "memory effect" of LDH materials. The H-OH-LDH exhibits a well-aligned hierarchical structure with an enhanced specific surface area and suitable mesopore distribution, which significantly improves the energy storage capacity of the electrode. It is noteworthy that the H-OH-LDH electrode presents an ultrahigh rate performance, arising from the facilitated electrolytediffusion dynamics induced by an ion micro-reservoir in the LDH interlayer space. Furthermore, the hierarchical H-OH-LDH electrode is assembled into an all-solid-state supercapacitor, which exhibits superior energy and power output. Therefore, this facile and cost-effective strategy to achieve a hierarchical electrode with a self-generated electrolyte reservoir offers new opportunities for the design and fabrication of high-performance solid-state devices.

Acknowledgements

This work was supported by the 973 Program (Grant No. 2014CB932102) and the National Natural Science Foundation of China (NSFC). M. Wei particularly appreciates the financial aid from the China National Funds for Distinguished Young Scientists of the NSFC. The authors thank Dr Hailong Li (South China University of Technology) for his help in HSGC measurements.

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