SPECIAL ISSUE: Innovative Electrode Materials for Supercapacitors

Layered double hydroxides with larger interlayer distance for enhanced pseudocapacitance

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ABSTRACT The interlayer space of the layered materials is not always the electrochemical active area for contributing to the pseudocapacitive process. To our knowledge, few efforts have been devoted to investigating the effect of interlayer distance of layered double hydroxides (LDHs) on pseudocapacitors. Here, we obtained the CoAl-LDH with different interlayer distance *via* the reaction in aqueous media hydrothermally. Electrochemical characterization reveals that the CoAl(DS⁻ (dodecyl sulfate))-LDHs with an interlayer distance of 2.58 nm can deliver higher specific capacitance of 1481.7 F g⁻¹ than CoAl(SO₄²⁻)-LDH (0.87 nm, 1252.7 F g⁻¹) and CoAl(CO₃²⁻)-LDH (0.76 nm, 1149.2 F g⁻¹) at a discharge current density of 1 A g⁻¹. An asymmetric supercapacitor with the CoAl(DS⁻)-LDHs||activated carbon also shows a better electrochemical performance, including a high energy density of 54.2 W h kg⁻¹ at a power density of 0.9 kW kg⁻¹ and a long-term stability, in comparison with CoAl(SO₄²⁻)-LDH and CoAl(CO₃²⁻)-LDH||activated carbon.

Keywords: layered double hydroxides, interlayer distance, hydrothermal, asymmetric supercapacitors

INTRODUCTION

To meet ever-growing demand for electrochemical energy storage, there is an urgent need in finding out a new electrochemical energy storage device as the secondary battery often suffers from low power density and poor cycle life [1,2]. Electrochemical capacitors (ECs), as a new storage device can provide fast charge/discharge rate, high stability and high power density, which are widely considered as a potential substitute for secondary battery in some areas and have been attracting increasing attention in recent years [3–5]. Among different types of ECs,

pseudocapacitive transition metal-based oxides or hydroxides own a higher specific capacitance than carbon-based electric double-layer capacitors and a better stability than organic conducting polymer-based capacitors [6]. From a fundamental point of view, electrochemical energy storage of pseudocapacitive transition metal-based oxides or hydroxides is based mainly on the fast reversible multi-electron redox Faradaic reactions taking place on the surface of materials [1]. Thus, increasing the surface area of materials is essential for further improving their electrochemical performance. The ordered mesoporous structures with an ultrahigh surface area and the layered crystalline structures with an interlayer gap intercalated by ions can significantly enhance the accessible specific surface area [7,8]. However, ordered mesoporous structures have been considerably difficult to realize due to the using of hard or soft templates. And the layered crystalline structures with intercalation of ions only often occur in Li⁺ and a high-voltage nonaqueous electrolyte system [7]. In the alkaline and acid aqueous electrolyte system, the electrolyte ion is difficult to insert into an interlayer gap of layered materials because its space is usually less than one nanometer [9]. Much effort has been devoted to stripping the layered structured materials for improving pseudocapacitive performance [10].

Apart from the hard stripping work of layered structured materials, one effective approach has recently been reported to enhance the alkali metal ion batteries capacity and to enlarge the interlayer distance, which can relax the strain and lower the barrier for metal ion intercalation and diffusion [11]. Table S1 summarizes some of the results of the layered materials with tunable interlayer distance as an electrochemical energy storage materials.

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Therefore, the interlayer expansion is also a useful strategy to enhance the specific capacitance and rate performance of the layered materials.

Metallic layered double hydroxides (LDHs) as a typical layered material in the class of 2D hydrotalcite-like structure anionic clays, including CoAl-LDH [12], NiAl-LDH [13] NiMn-LDH [14] and CoNi-LDH [15,16] and so on, which interlayer space can be easily adjusted by intercalation of other molecules.

In this work, we use the CoAl-LDH as the model material to investigate the effect of CoAl-LDH with different interlayer distance on electrochemical performance. The typical SO_4^{2-} and sodium dodecyl sulfate (SDS) molecules can be intercalated into the interlayer of CoAl-LDH for increasing the interlayer distance from 0.76, 0.87 to 2.58 nm. The results of electrochemical measurements show that CoAl(DS^-)-LDHs with 2.58 nm interlayer spacing can deliver a higher specific capacitance of 1481.7 F g^{-1} than CoAl(SO_4^{2-})-LDHs (0.87 nm, 1252.7 F g^{-1}) and CoAl(CO_3^{2-})-LDHs (0.76 nm, 1149.2 F g^{-1}) at 1 A g^{-1} . Furthermore, an asymmetric supercapacitor (ASC) with CoAl-LDHs as positive electrode and activated carbon (AC) as negative electrode in 2 mol L^{-1} KOH electrolyte demonstrated the CoAl(DS^-)-LDHs||AC possessed an ultrahigh energy density of 54.2 W h kg^{-1} at a power density of 0.9 kW kg^{-1} and a high power density of 26.8 kW kg^{-1} at 29.8 W h kg^{-1} , as well as long-term stability, outperforming CoAl(SO_4^{2-})-LDHs||AC and CoAl(CO_3^{2-})-LDHs||AC ASCs. Our results suggest increasing the interlayer distance of LDHs material is an effective route for achieving high-performance supercapacitor electrode materials.

EXPERIMENTAL SECTION

Synthesis of CoAl-LDHs

CoAl(DS^-)-LDHs: in a typical synthesis, 1 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.5 mmol $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$, 5 mmol hexamethylenetetramine (HMTA) and 4 mmol sodium dodecyl sulfate (SDS) were dissolved into 40 mL of deionized water in a three-neck flask of 1000 mL with a magnetic stirring under bubbling nitrogen to minimize dissolved carbonate. After 5h, the above solution was then transferred to a 50 mL Teflon-lined autoclave and heated for 10 h at 100°C . After the autoclave was cooled down to room temperature, the precipitates were collected by washed and dried at 60°C .

CoAl(SO_4^{2-})-LDHs were prepared by replacing the SDS with Na_2SO_4 while keeping an other reaction parameters unchanged.

CoAl(CO_3^{2-})-LDHs were prepared by a method similar to the above, but without adding SDS or Na_2SO_4 .

Characterizations

The products were characterized using X-ray diffraction (XRD, Bruker AXS D8 Advance), transmission electron microscopy (TEM, JEM-2100), Fourier transform infrared spectra (FT-IR, Nicolet 380) and X-ray photoelectron spectroscopy (XPS, ESCALAB 250 Xi). Thermogravimetry analysis (TGA) was performed on a thermal analyzer (SDTQ600) under nitrogen at a heating rate of 5°C min^{-1} . The BET surface was measured using an apparatus (Bel Japan Inc).

Electrochemical measurements

To fabricate electrode, a mixture consisting of active materials (80 wt.%), conductive materials (acetylene black, ATB, 10 wt.%) and binder (polytetrafluoroethylene, PTFE, 10 wt.%), which was coated onto a porous nickel foam sheet, and then dried at 80°C for 12 h. The electrochemical measurements of individual electrodes were carried out in 2 mol L^{-1} KOH in a three-electrode system, in which active materials, a platinum foil and an Ag/AgCl electrode were used as working, counter and reference electrodes, respectively. The ASCs have a two-electrode system which is composed of CoAl-LDHs as the positive electrode and AC as the negative electrode. In ASC system, the mass balanced electrodes are based on the principle of the charges stored at positive electrode and negative electrode is equivalent (see the Supplementary information for the detail method) [17,18]. Electrochemical measurements of cyclic voltammogram (CV) and electrochemical impedance spectroscopy (EIS) were conducted using a CHI 660E electrochemical workstation. Galvanostatic charge-discharge cycle tests were performed on a CT2001A LAND test system.

The specific capacitance, energy density, and power density of the supercapacitors can be investigated from the charge/discharge test as well as in the following equation [19]:

$$C_m = \frac{2 \times i_m \int U dt}{U^2 \Big|_{U_i}^{U_f}}, \quad (1)$$

$$E = \frac{i_m \int U dt}{3.6}, \quad (2)$$

$$P = \frac{3600 \times E}{t}, \quad (3)$$

where C_m is the specific capacitance of the supercapacitor

Figure 1 (a) XRD patterns and (b) FT-IR spectra of CoAl(DS[−])-LDH, CoAl(SO₄^{2−})-LDH and CoAl(CO₃^{2−})-LDH; XPS patterns of Al 2p (c) and Co 2p (d) for CoAl(DS[−])-LDH, and (e) S 2p spectra for CoAl(DS[−])-LDH and CoAl(SO₄^{2−})-LDH; (f) XPS patterns of C 1s for CoAl(DS[−])-LDH and CoAl(CO₃^{2−})-LDH. (g) Schematic illustration of the layered CoAl(CO₃^{2−})-LDH, CoAl(SO₄^{2−})-LDH and CoAl(DS[−])-LDH.

($F g^{-1}$), I_m is the specific current of the charge-discharge ($A g^{-1}$), $\int U dt$ is the integral current area; U is the potential (V) with initial and final values of U_i and U_p respectively; P is the power density ($W kg^{-1}$); E is the energy density ($W h kg^{-1}$); and t is the discharge time (s). In the ASC, m is the total mass of active materials.

RESULTS AND DISCUSSION

Fig. 1 shows XRD pattern of as-prepared CoAl(CO₃^{2−})-LDH, CoAl(SO₄^{2−})-LDH and CoAl(DS[−])-LDH. There is an important difference between three LDHs shown in peak positions of XRD. The CoAl(CO₃^{2−})-LDH revealed a typical layered LDH structure and had a certain degree of similarities with those reported previously [20]. Since our synthetic LDH with a Co/Al = 2, all the main peaks of the CoAl(CO₃^{2−})-LDH sample are well corresponding to hexagonal phase Mg₄Al₂(OH)₁₂CO₃·3H₂O (JCPDS 51-1525, a typical layered structure of LDH with

hexagonal stacking) and the calculated (d_{003}) basal spacing of 0.76 nm demonstrate that the interlayer anions should be CO₃^{2−} and water molecules [21]. The XRD patterns of CoAl(DS[−])-LDH and CoAl(SO₄^{2−})-LDH show the main peak of (003) moving from 2θ of 11.2°, 10.1° to 2.1°, which is corresponding to the basal spacing increasing from 2θ of 0.76 nm, 0.87 nm to 2.58 nm, respectively. The significant increasing of LDH interlamellar distance was caused mainly by the intercalation of SO₄^{2−} and DS[−] molecule into the interlayer spaces. In addition, the long-chain DS[−] molecules likely form a perpendicular monolayer in the LDH interlamellar spaces [22,23]. The corresponding schematic diagrams of CoAl(CO₃^{2−})-LDH, CoAl(SO₄^{2−})-LDH and CoAl(DS[−])-LDH were presented in Fig. 1g.

FT-IR analysis was used to confirm the existence of different interlayer anions, as shown in Fig. 1b. The peaks centered at 1629 cm^{−1} correspond to the bending vibra-

Figure 2 TEM and HRTEM images of the as-obtained (a–b) $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, (c–d) $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and (e–f) $\text{CoAl}(\text{DS}^-)$ -LDH samples.

tions of water molecules in the interlayer or adsorbed on the surface. In the spectrum of $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, peaks at 1355 and 790 cm^{-1} are ascribed to the presence of intercalated CO_3^{2-} ion. The absorption peak of $\text{CoAl}(\text{SO}_4^{2-})$ -LDH in 1128 and 600 cm^{-1} is attributable to the asymmetric and symmetric stretching vibration of S=O and S–O bonds, respectively. As for the spectrum of $\text{CoAl}(\text{DS}^-)$ -LDH, the peak at 1469 cm^{-1} are related to the bending vibrations of $-\text{CH}_2-$ in alkyl chains of DS^- , while a series of relatively weak bands in the range 1200 to 1000 cm^{-1} are mainly ascribed to stretching mode of sulfate (OSO_3^-) [24].

To confirm the chemical compositions of the samples, we performed XPS analysis. Firstly, compositional elements of the $\text{CoAl}(\text{DS}^-)$ -LDH, $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and $\text{CoAl}(\text{CO}_3^{2-})$ -LDH can be identified by the full survey scanned XPS spectra, as shown in Fig. S1a–c. Fig. 1c reveals the Al 2p spectra of $\text{CoAl}(\text{DS}^-)$ -LDH with a peak at a binding energy of 74.9 eV, the result related to the Al^{3+} species in the form of Al–OH [25]. The Co 2p spectra (Fig. 1d, $\text{CoAl}(\text{DS}^-)$ -LDH) exhibited two main peaks at 781.7 eV and 797.7 eV with a spin-orbit splitting of 16 eV, corresponding to Co $2p_{2/3}$ and Co $2p_{1/2}$, respectively [26]. Depending on the full-spectra (Fig. S1a–c), the Al 2p and Co 2p spectra of $\text{CoAl}(\text{DS}^-)$ -LDH and $\text{CoAl}(\text{SO}_4^{2-})$ -LDH are similar to that of $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, further indicating the $\text{CoAl}(\text{DS}^-)$ -LDH and $\text{CoAl}(\text{SO}_4^{2-})$ -LDH possess the similar composition structure. From the S 2p spectra (Fig. 1e), the apparent peaks are observed at

around 168.9 eV, which can be assigned to $-\text{SO}_4^{2-}$, confirming the presence of DS^- and SO_4^{2-} in the $\text{CoAl}(\text{DS}^-)$ -LDH and $\text{CoAl}(\text{SO}_4^{2-})$ -LDH, respectively [27]. CO_3^{2-} ions usually have the stronger Coulombic attraction with the LDH layer than other ions [28]. For comparison, all the three C 1s spectra of the $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and $\text{CoAl}(\text{DS}^-)$ -LDH were shown in Fig. 1f. Except that the same main peak of 284.77 eV of the three materials is corresponding to adventitious carbon, the another main peak of $\text{CoAl}(\text{CO}_3^{2-})$ -LDH at 288.90 eV can be attributed to carbonate ions [29]. This result also demonstrated that there was no CO_3^{2-} in the $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and $\text{CoAl}(\text{DS}^-)$ -LDHs.

Fig. 2 displays the typical TEM images of the CoAl -LDHs from low to high magnifications. As it can be seen, the $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and $\text{CoAl}(\text{DS}^-)$ -LDH samples exhibit the irregular sheet-like shapes, as shown in Fig. 2a, c, e. From the edge folds of the sheets, HRTEM images of Fig. 2b, d, f demonstrated the lattice spacing of (003) of $\text{CoAl}(\text{CO}_3^{2-})$ -LDHs increasing from 0.76, 0.87 to 2.58 nm after intercalation of SO_4^{2-} and DS^- molecules into the interlayer spaces, which are in good agreement with the above XRD, FT-IR and XPS results.

Fig. 3 presents TGA curves of the $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and $\text{CoAl}(\text{DS}^-)$ -LDH. As it can be observed in Fig. 3, the first weight loss (16.4 wt.%) for the $\text{CoAl}(\text{CO}_3^{2-})$ -LDH and (16.5 wt.%) for $\text{CoAl}(\text{SO}_4^{2-})$ -LDH occurred at the low temperature (ca. 20–230°C) is at-

tributed to the release of surface water. The second weight loss (11.6 wt.%) for $\text{CoAl}(\text{CO}_3^{2-})$ -LDH and (11.9 wt.%) for $\text{CoAl}(\text{SO}_4^{2-})$ -LDH respectively occurred temperature range of 230–320°C and 230–420°C, which is corresponding to removal of water intercalated in the inter-layer galleries and the partial dehydroxylation of the LDH sheets. The third weight loss (8.7 wt.%) for $\text{CoAl}(\text{CO}_3^{2-})$ -LDH and (12.1 wt.%) for $\text{CoAl}(\text{SO}_4^{2-})$ -LDH occurred at the next high temperature range can be attributed to the dehydroxylation of the layers as well as removal of volatile species (CO_2) and SO_2 arising from the interlayer carbonate anions [30]. As for the $\text{CoAl}(\text{DS}^-)$ -LDH, the percentage of weight loss is different from the $\text{CoAl}(\text{CO}_3^{2-})$ -LDH and $\text{CoAl}(\text{SO}_4^{2-})$ -LDH. Undoubtedly, the first weight loss (9.5 wt.%) below 160°C originated from a removal of water physically adsorbed on the external surface. The second and the main degradation step, occurred at the temperature between 180 and 500°C, result from the removal of gallery water, dehydroxylation of the LDH sheets, as well as the partial decomposition of the intercalated DS^- organic long-chain molecules. The last weight loss (13.5 wt.%) above 500°C mainly corresponds to further decomposition of the intercalated DS^- long-chain molecules.

Electrochemical properties of synthetic LDH samples were first evaluated by CV, galvanostatic charge-dis-

Figure 3 A thermogravimetric curve for $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and $\text{CoAl}(\text{DS}^-)$ -LDH.

charge and EIS measurements using three-electrode system. Fig. 4a shows the typical CV curves of $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and $\text{CoAl}(\text{DS}^-)$ -LDH in the voltage range from 0 to 0.45V (vs. Ag/AgCl) at a scan rate of 10 mV s^{-1} . Two pairs of apparent redox peaks of each curve indicate that pseudocapacitive characteristics arose from Faradaic reactions, which are as follows:

It can also be clearly seen that the order of area sur-

Figure 4 (a) Cyclic voltammograms, (b) galvanostatic charge-discharge curves, (c) specific capacitances at different current densities and (d) Nyquist plots of $\text{CoAl}(\text{CO}_3^{2-})$ -LDH, $\text{CoAl}(\text{SO}_4^{2-})$ -LDH and $\text{CoAl}(\text{DS}^-)$ -LDH.

rounded by the CV curves is CoAl(DS⁻)-LDH, CoAl(SO₄²⁻)-LDH and CoAl(DS⁻)-LDH, implying that increasing of LDH interlamellar distance by the intercalation of long-chain DS⁻ or SO₄²⁻ molecule is related to enhancing the capacitive behavior of the LDH electrode. The corresponding galvanostatic charge-discharge profiles at 1 A g⁻¹ (Fig. 4b) reveal a voltage plateau in the charge-discharge process, which is in agreement with the CV curves and the previous reports in the literature [8,15]. Additionally, significantly extended charge-discharge time of CoAl(DS⁻)-LDH electrode indicated its improved charge storage capacity. Fig. 4c gives the plot of specific capacitance of CoAl(CO₃²⁻)-LDH, CoAl(SO₄²⁻)-LDH and CoAl(DS⁻)-LDH that are calculated by the Equation (1) based on the discharge curves at different current densities. The CoAl(DS⁻)-LDH shows the specific capacitance is as high as 1481.7, 1228.2, 1141.5, 1070.0, 1042.1, 962.5, 942.9 and 856.7 F g⁻¹ at discharge current densities of 1, 2, 4, 8, 10, 16, 20 and 32 A g⁻¹, respectively. This performance of CoAl(DS⁻)-LDH, at corresponding current densities, is much higher than CoAl(SO₄²⁻)-LDH, CoAl(CO₃²⁻)-LDH supercapacitors, and even higher than some carbon-based CoAl-LDH nanocomposites, such as fluorinated graphene/CoAl-LDH (1222 F g⁻¹, 1 A g⁻¹, 0.5 V) [31], and graphene foam/CoAl-LDH (775.6 F g⁻¹, 0.5 A g⁻¹, 0.4 V) [32].

From the Nyquist plots in Fig. 4d, CoAl(CO₃²⁻)-LDH, CoAl(SO₄²⁻)-LDH and CoAl(DS⁻)-LDH electrodes possess almost the same charge transfer resistance, which is represented by the diameter of the semicircle in the high-frequency region. The most noteworthy difference comes from the slope in the Warburg region (low frequency), which is related to solid-state ion diffusion in bulk material. It is very clearly seen that the CoAl(DS⁻)-LDH exhibited a steeper slope compared with CoAl(SO₄²⁻)-LDH and CoAl(CO₃²⁻)-LDH, suggesting the CoAl(DS⁻)-LDH electrode possessed a high ion mobility and diffusion. In addition, the higher Knee frequency (10.0 Hz) of CoAl(DS⁻)-LDH electrodes than CoAl(SO₄²⁻)-LDH (8.3 Hz) and CoAl(CO₃²⁻)-LDH (3.8 Hz), further demonstrates the more accessible interlayer space of CoAl(DS⁻)-LDH. Furthermore, Fig. S2 shows the frequency dependent specific capacitance values of LDHs, calculated from impedance measurements. The appreciably higher specific capacitance values of CoAl(DS⁻)-LDH electrodes in a wide range from low to high frequency demonstrate their high power performance and excellent rate response. The equivalent electrical circuit for the R(CR)(QW) model simulated by the ZSimpWin programme (inset in Fig. S2) and the fitted parameters (Table S2) are

in good agreement with the discussion above.

To evaluate the ASC performance of the CoAl(CO₃²⁻)-LDH, CoAl(SO₄²⁻)-LDH and CoAl(DS⁻)-LDH as the positive electrode material in real cell, we select the activated carbon with an excellent electric double-layer capacitance property at -1.0 to 0.0 V as the negative electrode material (see Fig. S3). Fig. 5a shows typical CV curves for the CoAl(DS⁻)-LDH||AC, CoAl(SO₄²⁻)-LDH||AC and CoAl(CO₃²⁻)-LDH||AC in 2 mol L⁻¹ KOH electrolyte with various scan rates at 0.0-1.7 V. It can be easily observed that the CV curves of CoAl(DS⁻)-LDH||AC display a larger integrated area than those of CoAl(SO₄²⁻)-LDH||AC and CoAl(CO₃²⁻)-LDH||AC, suggesting the better capacitive behavior of CoAl(DS⁻)-LDH||AC. Fig. 5b reveals the comparison of galvanostatic charge-discharge behavior for the CoAl(DS⁻)-LDH||AC, CoAl(SO₄²⁻)-LDH||AC and CoAl(CO₃²⁻)-LDH||AC at 1 A g⁻¹. As expected, because of the CoAl(DS⁻)-LDH with a better electrochemical performance, the CoAl(DS⁻)-LDH||AC possess the much longer charge-discharge time, which has a specific capacitance of 137.8 F g⁻¹ based on the total active materials superior to the CoAl(SO₄²⁻)-LDH||AC and CoAl(CO₃²⁻)-LDH||AC. Fig. 5c also shows the specific capacitances of an asymmetric cell calculated by the Equation (1) according to the discharge curves as the function of different discharging current densities. With increasing current density, the specific capacitances decrease gradually as the diffusion limits the movement of electrolyte ions at high current densities, because of time constraint and only the active outer surface and the bigger size of pore volume utilized for charge storage. Nevertheless, the CoAl(DS⁻)-LDH||AC still maintains a good rate in its performances, such as the CoAl(DS⁻)-LDH||AC with a 74.2 F g⁻¹ at a very high current density of 32 A g⁻¹, retained 53.8% of its initial capacitance obtained in 1 A g⁻¹, and the CoAl(SO₄²⁻)-LDH||AC and CoAl(CO₃²⁻)-LDH||AC respectively retained 32.0% and 28.0% of their capacitance when the charge-discharge rate increased from 1 to 32 A g⁻¹.

Cycling stability of ASC also is the critical issue for its practical application, and the cycle charge-discharge testing was employed to examine the cycle stability. Fig. 5d shows a long-term cycling performance of the CoAl(CO₃²⁻)-LDH||AC cell retaining more than 87% of initial capacitance after 5000 charge-discharge cycles at a current density of 20 A g⁻¹, which is significantly better than the retention of 49% for CoAl(SO₄²⁻)-LDH||AC and 61% for CoAl(CO₃²⁻)-LDH||AC cell.

The energy and power densities of ASCs devices have been further evaluated. As showed in Fig. 6, the Ragone

Figure 5 (a) Cyclic voltammograms at different scan rates and (b) charge-discharge curves at a current density of 1 A g^{-1} and corresponding specific capacitance in different cell voltages for CoAl-LDH||AC in 2 mol L^{-1} KOH solution. Specific capacitances (c) and cycle stability (d) of CoAl(CO_3^{2-})-LDH||AC, CoAl(SO_4^{2-})-LDH||AC and CoAl(DS^-)-LDH||AC.

plot of CoAl(DS^-)-LDH||AC device displayed a high energy density of 54.2 W h kg^{-1} at a power density of 0.9 kW kg^{-1} and a high power density of 26.8 kW kg^{-1} at 29.8 W h kg^{-1} . The performance of this CoAl(DS^-)-LDH||AC is much higher than most of carbon based symmetrical supercapacitors (less than 10 W h kg^{-1}) [33] and many of pseudocapacitor electrode materials reported recently, including metal oxide, sulfide-based and hydroxide ASCs, such as NiO||GR (39.9 W h kg^{-1}) [34], $\text{Co}_3\text{O}_4\text{@MnO}_2$ ||GO (17.7 W h kg^{-1}) [35], CoS_x ||GR (14.7 W h kg^{-1}) [36], CNT/Ni(OH) $_2$ ||rGO (35 W h kg^{-1}) [37], Ni-Mn LDH/rGO||AC (33.8 W h kg^{-1}) [38], Co-Al LDHs-CNTs||AC (28 W h kg^{-1}) [39], GO/NiAl-LDHs||AC (21 W h kg^{-1}) [40], $\text{Ni}_x\text{Co}_{1-x}$ LDH-ZTO||AC (23.7 W h kg^{-1}) [41] and AC||Co(OH) $_2$ buds/Ni foam (20.3 W h kg^{-1}) [42].

In contrast, the CoAl(CO_3^{2-})-LDH||AC ASC only exhibited the highest energy density of 40.8 W h kg^{-1} at a power density of 0.8 kW kg^{-1} and the highest power density of 11.8 kW kg^{-1} at a energy density of 9.9 W h kg^{-1} . The improved electrochemical performance of the CoAl(DS^-)-LDH might be largely attributed to its structural features. Although, the CoAl(CO_3^{2-})-LDHs have a higher BET surface of $60.54 \text{ m}^2 \text{ g}^{-1}$ than the CoAl

Figure 6 Ragone plots of CoAl-LDH||AC. The values reported from other LDH and hydroxide based ASCs are inserted for comparison.

(DS^-)-LDH ($58.36 \text{ m}^2 \text{ g}^{-1}$) and CoAl(SO_4^{2-})-LDH ($41.50 \text{ m}^2 \text{ g}^{-1}$) (Fig. S4). The larger interlayer spacing of CoAl(DS^-)-LDH, with an interlayer distance of 2.58 nm , will facilitate more electrolyte ions into the inner space of LDH, which leads to a higher electrochemical activity because of the pseudocapacitance originating from a fast and reversible Faradaic reaction between electrolyte and active electrode material. Thus, it is believed that the

supercapacitor performance of LDH could be markedly enhanced by increasing its layer distance from the insertion of some long chain molecules.

CONCLUSIONS

In summary, we have synthesized CoAl-LDHs with different interlayer distances by intercalation of different anion ions under hydrothermal conditions. The CoAl(DS⁻)-LDHs with an interlayer distance of 2.58 nm exhibits a much higher specific capacitance of 1481.7 F g⁻¹ than the of CoAl(CO₃²⁻)-LDH (0.76 nm) and CoAl(SO₄²⁻)-LDH (0.87 nm) at a discharge current density of 1 A g⁻¹. An ASC based on this CoAl(DS⁻)-LDHs also shows a better electrochemical performance, including high energy density, power density, and cycling stability. This work shows that larger interlayer spacing, allowing more electrolyte ions to be stored, results in a higher electrochemical activity. These results indicate that our strategy could be expanded to further prepare the other LDHs with different interlayer distance for enhancing its pseudocapacitive performance.

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- Simon P, Gogotsi Y. Materials for electrochemical capacitors. *Nat Mater*, 2008, 7: 845–854
- Lv W, Li Z, Deng Y, *et al.* Graphene-based materials for electrochemical energy storage devices: opportunities and challenges. *Energy Storage Mater*, 2016, 2: 107–138
- Zhou C, Zhang Y, Li Y, *et al.* Construction of high-capacitance 3D CoO@polypyrrole nanowire array electrode for aqueous asymmetric supercapacitor. *Nano Lett*, 2013, 13: 2078–2085
- Li X, Chen Y, Huang H, *et al.* Electrospun carbon-based nanostructured electrodes for advanced energy storage—a review. *Energy Storage Mater*, 2016, 5: 58–92
- Liang J, Li F, Cheng HM. Carbons: multi-functional energy storage materials. *Energy Storage Mater*, 2016, 2: A1–A2
- Xiao Y, Liu S, Li F, *et al.* 3D hierarchical Co₃O₄ twin-spheres with an urchin-like structure: large-scale synthesis, multistep-splitting growth, and electrochemical pseudocapacitors. *Adv Funct Mater*, 2012, 22: 4052–4059
- Brezesinski T, Wang J, Tolbert SH, *et al.* Ordered mesoporous α-MoO₃ with iso-oriented nanocrystalline walls for thin-film pseudocapacitors. *Nat Mater*, 2010, 9: 146–151
- Shi Y, Guo B, Corr SA, *et al.* Ordered mesoporous metallic MoO₂ materials with highly reversible lithium storage capacity. *Nano Lett*, 2009, 9: 4215–4220
- Xie L, Hu Z, Lv C, *et al.* Co₂Ni_{1-x} double hydroxide nanoparticles with ultrahigh specific capacitances as supercapacitor electrode materials. *Electrochim Acta*, 2012, 78: 205–211
- Liu XM, Zhang YH, Zhang XG, *et al.* Studies on Me/Al-layered double hydroxides (Me = Ni and Co) as electrode materials for electrochemical capacitors. *Electrochim Acta*, 2004, 49: 3137–3141
- Liang Y, Yoo HD, Li Y, *et al.* Interlayer-expanded molybdenum disulfide nanocomposites for electrochemical magnesium storage. *Nano Lett*, 2015, 15: 2194–2202
- Lu Z, Zhu W, Lei X, *et al.* High pseudocapacitive cobalt carbonate hydroxide films derived from CoAl layered double hydroxides. *Nanoscale*, 2012, 4: 3640–3643
- Wang B, Williams GR, Chang Z, *et al.* Hierarchical NiAl layered double hydroxide/multiwalled carbon nanotube/nickel foam electrodes with excellent pseudocapacitive properties. *ACS Appl Mater Interfaces*, 2014, 6: 16304–16311
- Zhao J, Chen J, Xu S, *et al.* Hierarchical NiMn layered double hydroxide/carbon nanotubes architecture with superb energy density for flexible supercapacitors. *Adv Funct Mater*, 2014, 24: 2938–2946
- Chen H, Hu L, Chen M, *et al.* Nickel–cobalt layered double hydroxide nanosheets for high-performance supercapacitor electrode materials. *Adv Funct Mater*, 2014, 24: 934–942
- Cheng Y, Zhang H, Varanasi CV, *et al.* Improving the performance of cobalt–nickel hydroxide-based self-supporting electrodes for supercapacitors using accumulative approaches. *Energy Environ Sci*, 2013, 6: 3314–3321
- Cao Y, Xiao Y, Gong Y, *et al.* One-pot synthesis of MnOOH nanorods on graphene for asymmetric supercapacitors. *Electrochim Acta*, 2014, 127: 200–207
- Xiao Y, Cao Y, Gong Y, *et al.* Electrolyte and composition effects on the performances of asymmetric supercapacitors constructed with Mn₃O₄ nanoparticles–graphene nanocomposites. *J Power Sources*, 2014, 246: 926–933
- Chen Y, Pang WK, Bai H, *et al.* Enhanced structural stability of nickel–cobalt hydroxide via intrinsic pillar effect of metaborate for high-power and long-life supercapacitor electrodes. *Nano Lett*, 2017, 17: 429–436
- Tang Z, Tang C, Gong H. A high energy density asymmetric supercapacitor from nano-architected Ni(OH)₂/carbon nanotube electrodes. *Adv Funct Mater*, 2012, 22: 1272–1278
- Ogawa M, Hiramane M. Direct correlation between nanostructure and particle morphology during intercalation. *Cryst Growth Des*, 2014, 14: 1516–1519
- Zhao H, Nagy KL. Dodecyl sulfate–hydrotalcite nanocomposites for trapping chlorinated organic pollutants in water. *J Colloid Interface Sci*, 2004, 274: 613–624
- Klopprogge JT, Wharton D, Hickey L, *et al.* Infrared and Raman study of interlayer anions CO₃²⁻, NO₃⁻, SO₄²⁻ and ClO₄⁻ in Mg/Al-hydrotalcite. *Am Miner*, 2002, 87: 623–629
- Jiang Y, Chen D, Song J, *et al.* A facile hydrothermal synthesis of graphene porous NiO nanocomposite and its application in electrochemical capacitors. *Electrochim Acta*, 2013, 91: 173–178
- Liu X, Wang C, Dou Y, *et al.* A NiAl layered double hydroxide@carbon nanoparticles hybrid electrode for high-performance asymmetric supercapacitors. *J Mater Chem A*, 2014, 2: 1682–1685
- Xiao Y, Su D, Wang X, *et al.* Ultrahigh energy density and stable supercapacitor with 2D NiCoAl Layered double hydroxide. *Electrochim Acta*, 2017, 253: 324–332
- Wang G, Zhang L, Zhang J. A review of electrode materials for electrochemical supercapacitors. *Chem Soc Rev*, 2012, 41: 797–828
- Prasanna SV, Kamath PV. Anion-exchange reactions of layered double hydroxides: interplay between Coulombic and H-bonding interactions. *Ind Eng Chem Res*, 2009, 48: 6315–6320
- Yu G, Hu L, Liu N, *et al.* Enhancing the supercapacitor performance of graphene/MnO₂ nanostructured electrodes by conductive wrapping. *Nano Lett*, 2011, 11: 4438–4442
- Abellán G, Coronado E, Martí-Gastaldo C, *et al.* Hexagonal na-

- nosheets from the exfoliation of Ni^{2+} - Fe^{3+} LDHs: a route towards layered multifunctional materials. *J Mater Chem*, 2010, 20: 7451–7455
- 31 Peng W, Li H, Song S. Synthesis of fluorinated graphene/CoAl-layered double hydroxide composites as electrode materials for supercapacitors. *ACS Appl Mater Interfaces*, 2017, 9: 5204–5212
- 32 Masikhwa TM, Madito MJ, Momodu DY, *et al.* High performance asymmetric supercapacitor based on CoAl-LDH/GF and activated carbon from expanded graphite. *RSC Adv*, 2016, 6: 46723–46732
- 33 Hall PJ, Mirzaeian M, Fletcher SI, *et al.* Energy storage in electrochemical capacitors: designing functional materials to improve performance. *Energ Environ Sci*, 2010, 3: 1238–1251
- 34 Luan F, Wang G, Ling Y, *et al.* High energy density asymmetric supercapacitors with a nickel oxide nanoflake cathode and a 3D reduced graphene oxide anode. *Nanoscale*, 2013, 5: 7984–7990
- 35 Huang M, Zhang Y, Li F, *et al.* Facile synthesis of hierarchical Co_3O_4 @ MnO_2 core-shell arrays on Ni foam for asymmetric supercapacitors. *J Power Sources*, 2014, 252: 98–106
- 36 Dubal DP, Gund GS, Lokhande CD, *et al.* Controlled growth of CoS_x nanostrip arrays (CoS_x -NSA) on nickel foam for asymmetric supercapacitors. *Energ Tech*, 2014, 2: 401–408
- 37 Salunkhe RR, Lin J, Malgras V, *et al.* Large-scale synthesis of coaxial carbon nanotube/ $\text{Ni}(\text{OH})_2$ composites for asymmetric supercapacitor application. *Nano Energy*, 2015, 11: 211–218
- 38 Li M, Cheng JP, Wang J, *et al.* The growth of nickel-manganese and cobalt-manganese layered double hydroxides on reduced graphene oxide for supercapacitor. *Electrochim Acta*, 2016, 206: 108–115
- 39 Yu L, Shi N, Liu Q, *et al.* Facile synthesis of exfoliated Co-Al LDH-carbon nanotube composites with high performance as supercapacitor electrodes. *Phys Chem Chem Phys*, 2014, 16: 17936–17942
- 40 Zhang L, Yao H, Li Z, *et al.* Synthesis of delaminated layered double hydroxides and their assembly with graphene oxide for supercapacitor application. *J Alloys Compd*, 2017, 711: 31–41
- 41 Wang X, Sumboja A, Lin M, *et al.* Enhancing electrochemical reaction sites in nickel-cobalt layered double hydroxides on zinc tin oxide nanowires: a hybrid material for an asymmetric supercapacitor device. *Nanoscale*, 2012, 4: 7266–7272
- 42 Yang S, Cheng K, Ye K, *et al.* A novel asymmetric supercapacitor with buds-like $\text{Co}(\text{OH})_2$ used as cathode materials and activated carbon as anode materials. *J Electroanal Chem*, 2015, 741: 93–99

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Supplementary information Supplementary information is available in the online version of the paper, including part of XPS and BET curve of synthetic materials.

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层状双羟基复合金属氧化物层间距调控及其电容器性能研究

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摘要 在电化学储能过程中, 层状结构材料中较窄的层间距一般会抑制电解液离子的嵌入, 进而限制其层间内部结构在电化学储能过程中的充分利用. 本文分别选用3种不同尺寸的阴离子 (CO_3^{2-} , SO_4^{2-} , DS^- (十二烷基硫酸根)), 通过简单的一步水热过程, 成功对 CoAl-LDH (层状双羟基复合金属氧化物)进行插层, 获得了3种具有不同层间距的复合材料: $\text{CoAl}(\text{CO}_3^{2-})\text{-LDH}$ (0.76 nm), $\text{CoAl}(\text{SO}_4^{2-})\text{-LDH}$ (0.87 nm), $\text{CoAl}(\text{DS}^-)\text{-LDHs}$ (2.58 nm). 超级电容器性能研究表明, 在 1 A g^{-1} 充放电电流密度下, 3种材料单电极比电容表现出与其层间距大小的一致性, 即 $\text{CoAl}(\text{DS}^-)\text{-LDHs}$ (1481.7 F g^{-1}) > $\text{CoAl}(\text{SO}_4^{2-})\text{-LDH}$ (1252.7 F g^{-1}) > $\text{CoAl}(\text{CO}_3^{2-})\text{-LDH}$ (1149.2 F g^{-1}). 此外, 将3种材料与活性炭 (AC) 组建非对称超级电容器, 结果表明: 基于电极材料总质量, $\text{CoAl}(\text{DS}^-)\text{-LDHs}||\text{AC}$ 展现了 54.2 W h kg^{-1} 的高能量密度和长循环寿命, 且显著高于 $\text{CoAl}(\text{SO}_4^{2-})\text{-LDH}||\text{AC}$ 和 $\text{CoAl}(\text{CO}_3^{2-})\text{-LDH}||\text{AC}$ 非对称电容器. 该方法为寻找新型高性能超级电容器用层状结构材料提供了新的途径.