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Electrochemical performance of Co–Al layered double hydroxide nanosheets mixed with multiwall carbon nanotubes

Ling-Hao Su · Xiao-Gang Zhang · Yang Liu

Abstract Regular hexagonal Co–Al layered double hydroxides (Co–Al LDH) were synthesized by urea-induced homogeneous precipitation. This material proved to be nanosheets by scanning electron microscopy and X-ray diffraction measurements. The electrochemical capacitive behavior of the nanosheets in 1 M KOH solution were evaluated by constant current charge/discharge and cyclic voltammetric measurements, showing a large specific capacitance of $192 \ F \cdot g^{-1}$ even at the high current density of $2 \ A \cdot g^{-1}$. When multiwall carbon nanotubes (MWNTs) were mixed with the Co–Al LDH, it was found that the specific capacitance and long-life performance of all composite electrodes at high current density are superior to pure LDH electrode. When the added MWNTs content is 10 wt%, the specific capacitance increases to $342.4 \ F \cdot g^{-1}$ and remains at a value of $304 \ F \cdot g^{-1}$ until the 400th cycle at $2 \ A \cdot g^{-1}$, showing that this is a promising electrode material for supercapacitors working at heavy load. According to the electrochemical impedance spectra, MWNTs greatly increase the electronic conductivity between MWNTs and the surface of Co–Al LDH, which consequently facilitates the access of ions in the electrolyte and electrons to the electrode/electrolyte interface.

Keywords Co–Al layered double hydroxides ·
Multiwall carbon nanotubes · Supercapacitor ·
Large current density

L.-H. Su · X.-G. Zhang (✉) · Y. Liu
College of Material Science and Engineering,
Nanjing University of Aeronautics and Astronautics,
Nanjing, Jiangsu 210016, People's Republic of China
e-mail: azhangxg@163.com

Introduction

Supercapacitors, also called electrochemical capacitors, have attracted great attentions [1–7] due to their high power density and good long-life behavior. They can be classified into two types according to their energy-storage mechanism: *electrical double layer* capacitors (EDLC) where the double-layer is charged and *faradaic* pseudo capacitors where reversible redox reactions proceed. Carbon materials are typical electrode materials for EDLC, while ruthenium oxide (RuO_2) is the best material for a *faradaic* pseudo capacitor whose specific capacitance is up to $760 \ F \cdot g^{-1}$ [8]. However, RuO_2 is expensive, and the capacitance of carbon is low. Therefore, it is very necessary to find new electrode materials. Layered double hydroxides (LDH) are of hydrotalcite-like structure, and they are used extensively in catalysis [9], adsorption [10], ion exchange [11], and even as templates [12, 13] for the preparation of nanomaterials. Recently, they are explored as electrode materials [14–16] for supercapacitors.

One possible application of supercapacitors is in electrical vehicles which need large current when it starting. Obviously, studies and improvements of the capacitive behavior of supercapacitors working at heavy load are very important for their practical applications. However, a large number of studies of supercapacitors are confined to low current conditions, and only a few papers [17] deal with capacitive performance at high current densities, like $2 \ A \cdot g^{-1}$. As far as Co–Al LDH is concerned, to our best knowledge, the highest current density for which the behavior has been reported is $1.2 \ A \cdot g^{-1}$. In our earlier works, we have synthesized Me double hydroxides (Me = Co and Ni)/TiO_2 nanotube composite electrodes [15] whose specific capacitance is up to $1,053 \ F \cdot g^{-1}$, indicating nanotubes are effectively improving the properties of LDHs.

One of the routes for improving the capacitance is to synthesize new materials with special structure, like mesoporous materials [18–20] and nanorods or nanowires [4, 21, 22] which provide large surface areas. However, there are only a few reports [23] about nanosheets acting as electrode material for supercapacitor. Nanosheets can, in fact, not only increase the specific area of materials but also decrease remarkably the diffusion distance for ions from the bulk electrolyte to the surface of active material when used as electrode material owing to their very thin thickness in the scale of nanometer. Therfore, in this article, we present a detailed examination of the high-current capacitive behavior of Co–Al LDH nanosheets synthesized by homogenous precipitation and compare it with the composite mixed with multiwall carbon nanotubes (MWNTs) by constant current charge/discharge, electrochemical impedance spectra, and cyclic voltammetry experiments assisted with scanning electron microscopy (SEM) images. Our intent is to illustrate the function of MWNTs in composite electrodes for improving the electrode stability and enhancing ion/charge transport properties at the electrode/electrolyte interface. SEM images and electrochemical measurements reveal that MWNTs adhere to the surface of Co–Al LDH particles, increase the electronic conductivity of composite electrode, and elevate specific capacitance and capacitance retention.

Experimentals

All chemicals used here were of analytic grade and, except the MWNTs, were used as received without any further treatment. MWNTs were purchased from Shenzhen Nano Port Co. Ltd (China). The tube length is given to be from 20 to 40 nm. After refluxing with dilute nitric acid for 6 h and rinsing with ultrapure water (18.32 MΩ cm), the MWNTs were filtered and dried under vacuum.

Co–Al LDH nanosheets were prepared via a method of homogeneous precipitation according to the literature [11], except replacing chlorides with nitrates as starting materials. Chiefly, a solution having concentrations of 10, 5, and 35 mM of $Co(NO_3)_2$, $Al(NO_3)_3$, and urea, respectively, was heated and refluxed at 95 °C under continuous magnetic stirring for 48 h. After filtering and washing with ultrapure water and anhydrous ethanol for several times, the resulting precipitant was dried at room temperature under ambient atmosphere.

An appropriate amount of treated MWNTs and/or LDH, 15 wt% acetylene black, and binder (PTFE) with 5 wt% of the total electrode mass were ultrasonically mixed with a little water to make a uniform paste then coated onto a piece of foamed Ni grid. After drying at 80 °C, it was pressed under a pressure of 20 MPa as a slice with a

thickness of about 0.2 mm. The total weight of the electrode was about 10 mg after subtracting the weight of Ni grid, which is used for calculating specific gravimetric capacitance of whole electrode. In composite electrodes, the content of MWNTs means its percentage of total electrode weight.

All the electrochemical measurements were performed in a conventional three-electrode system. A Pt foil (1 cm^2) and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The electrolyte used was 1 M KOH aqueous solution. A CHI-660B style electrochemical working station instrument was employed for CV, electrochemical impedance spectra (EIS) and constant current charge/discharge measurements. Electrochemical impedance spectra were measured at the open-circuit potentials of the electrodes, with frequencies varying from 0.01 to 100, 000 Hz with amplitudes of 0.005 V.

Results and discussion

The SEM images of the as-prepared Co–Al LDH are shown in Fig. 1. As can be seen, the Co–Al LDH has a lamellar morphology, and the sheets are almost regular hexagons with a mean lateral size of about 6 μm and a thickness of scores of nanometers. The sheets are so thin that another
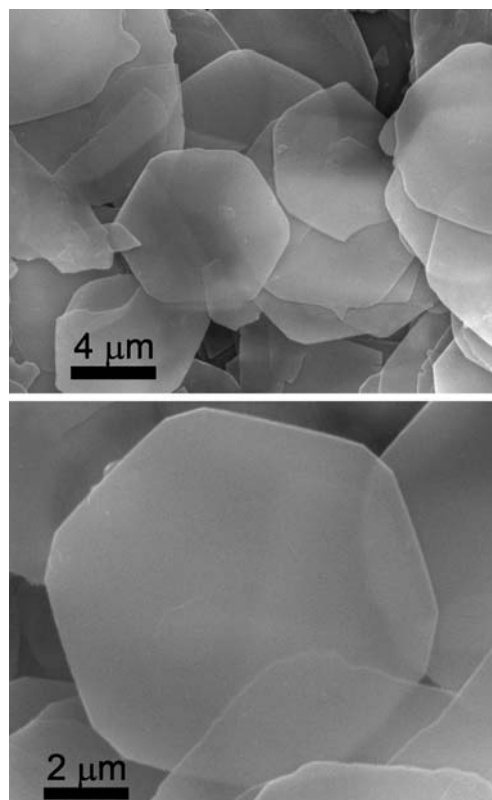
Fig. 1 The SEM images of the Co–Al LDH nanosheets prepared by homogeneous precipitation

sheet can even be clearly seen through one. The observation is in good accordance with the literature [11].

The X-ray diffraction pattern of the Co–Al LDH prepared via the route of homogeneous precipitation is shown in Fig. 2, which is comparable to the compound $Co_6Al_2CO_3(OH)_{16}\cdot H_2O$ (JCPDS: 51-0045). The peaks of (003), (006), (012), and (018) planes with constant distance are typical for layered double hydroxides. No peaks for impurities are observed. The diffraction peaks of (003) and (006) are especially strong, while other peaks have relatively weak intensities, indicating that the crystal grew in definite direction. Calculated from the formula [24] $a=2d_{110}$ and $c=3/2(d_{003}+2d_{006}))$, respectively, the cell parameters a and c are 0.306 and 2.262 nm. The interlayer distance d_{003} is 0.756 nm, close to the value [25] reported, indicating the occupying of OH^- ions in the interlayer spaces.

Figure 3 provides the CV curves of the Co–Al LDH electrode at various rates and the relation of cathodic peak current ($I_{p,c}$) to scan rate (í). When the scan rate is 5 mV·s^{-1}, there are two well-defined waves at 409 and 219 mV (vs SCE), which belongs to the conversion of Co (II)/Co(III) [13]. When it increases, the anodic and cathodic peaks move toward positive and negative direction, respectively. Moreover, it can be observed that $I_{p,c}$ increases with scan rate and depends on í$^{1/2}$ linearly, confirming a diffusion-control of the electrode process.

To evaluate the electrochemical capacitive property of the Co–Al LDH nanosheets electrode, various constant current densities of 0.5, 1, and 2 A·g^{-1} were employed in chronopotentometric tests. The cutoff voltage varied between 0 and 0.5 V vs SCE. Typical charge/discharge curves are shown in Fig. 4. The specific capacitances (C_s) obtained from the Eq. 1 are listed in Table 1. It can be seen that the electrode made from the Co–Al LDH nanosheets has a good electrochemical reversibility (discharge/charge efficiency of
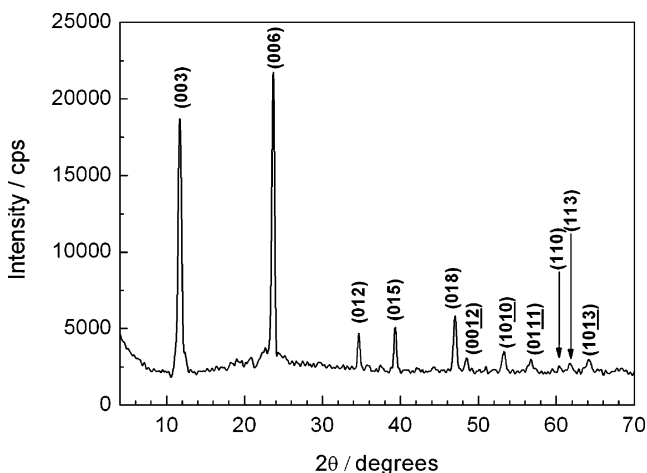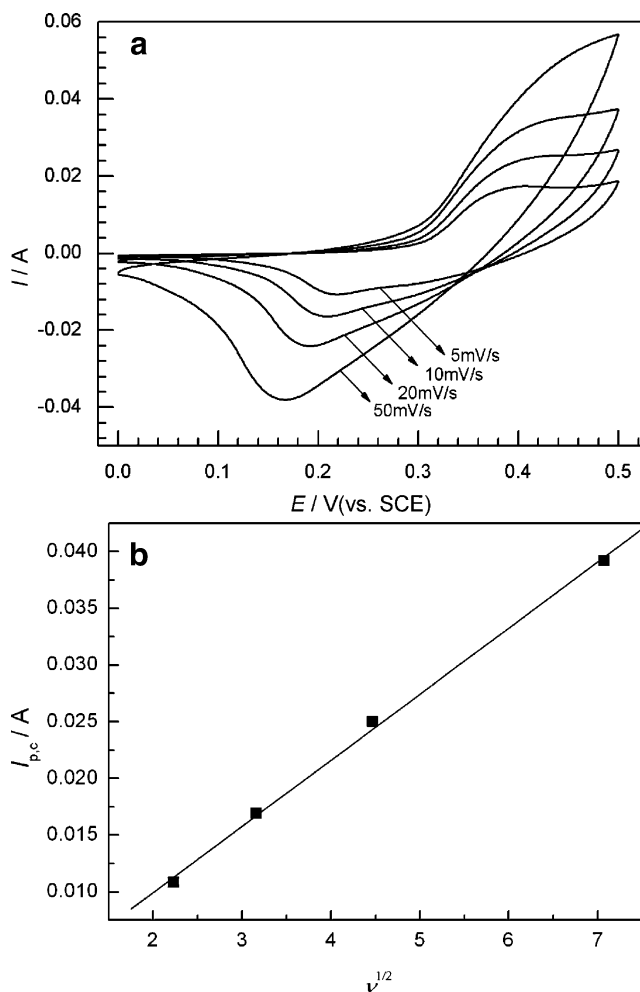
Fig. 3 a Cyclic voltammograms of Co–Al LDH electrode in 1 M KOH solution at various rates; b relationship of cathodic peak current of Co–Al LDH electrode with scan rate

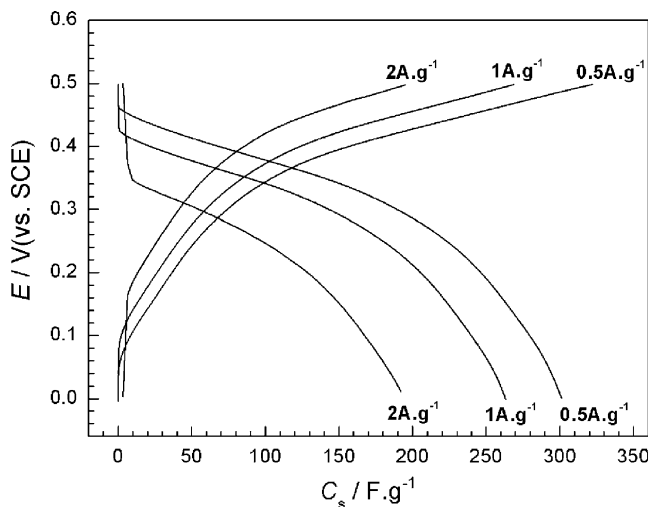Fig. 2 The XRD pattern of the Co–Al LDH prepared by homogeneous precipitation

Fig. 4 The charge/discharge curves of the Co–Al LDH electrode in 1 M KOH solution at various current densities

Table 1 Specific capacitances of the Co–Al LDH electrode at various current densities

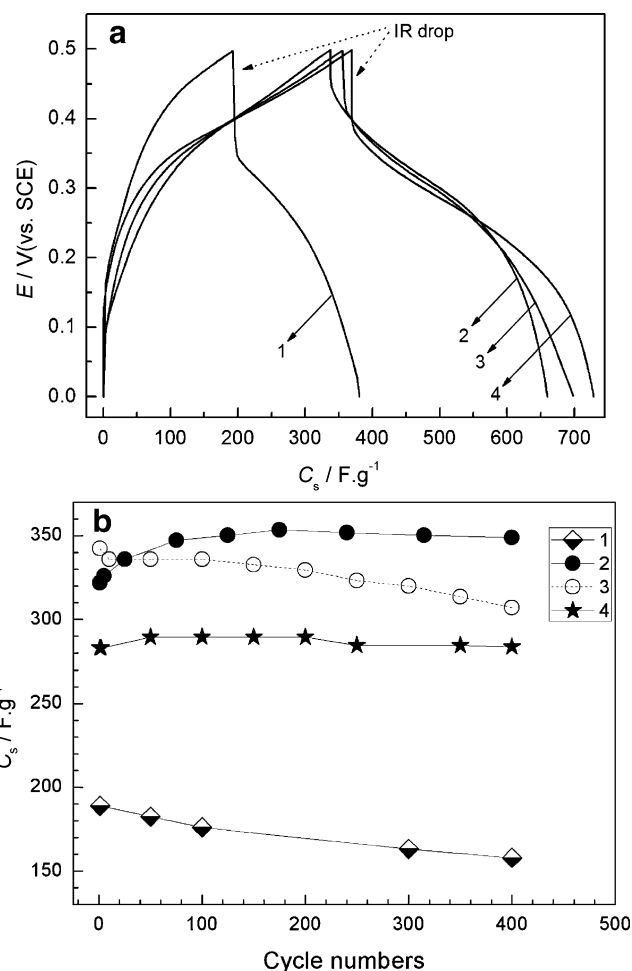| Current density $(A \cdot g^{-1})$	Specific capacitance (C_s) $(F \cdot g^{-1})$		Discharge/charge efficiency (%)
	Charge	Discharge	
0.5	322.3	301.3	93.5
1.0	269.0	263.2	97.8
2.0	195.2	192.0	98.4

more than 93%) and a large capacitance of 192 F·g^{-1} even at a current of 2 A·g^{-1}, indicating that the Co–Al LDH prepared by homogeneous precipitation is a promising material for supercapacitors.

$$C_s = \frac{I \Delta t}{m \Delta V} \quad (1)$$

To elevate the electrochemical capacitive properties at heavy load, MWNTs were mixed with the Co–Al LDH nanosheets to make composite electrodes. Typical charge/discharge curves are shown in Fig. 5a. As can be seen in Fig. 5a, the charge/discharge curve for pure LDH nanosheets electrode at 2 A·g^{-1} is not an ideal straight line but bends seriously, indicating that not a simple double-layer charging but a *faradaic* reaction is proceeding. In addition, there are clearly large *IR* drops at the starting stages of either charge and discharge curves. Probably, this has to be ascribed to high contact resistance among particles of Co–Al LDH.

Although *IR* drops are involved in MWNTs/LDH composite electrodes, their extents are smaller than for pure LDH electrodes, suggesting that the MWNTs increase the electronic conductivity. Moreover, the constant current charge/discharge curves of MWNTs/LDH composite electrodes are more linear than for pure LDH electrodes, indicating better electrochemical properties. Compared with Co–Al LDH's 192.0 F·g^{-1}, their capacitances are in the range of 283.3~342.4 F·g^{-1} when the content of MWNTs varies from 5 to 20 wt%. Although the amount of added MWNTs is small, the enhancement of C_s is surprisingly large.

Figure 5b provides the long-life performances of various electrodes at the current density of 2 A·g^{-1}. It is shown that both pure LDH and composite electrodes have good capacitance retention of no less than 85%, but composite electrodes have higher specific capacitance than pure LDH. It is well known that MWNTs have no electrochemical activity in KOH solution in the range of 0~0.5 V vs SCE. Hence, the most probable reason for the better performance of composite electrodes is the combination of the redox behavior of pure LDH with the good electronic conductivity of MWNTs. In other words, pure LDH provides *faradaic* basis of cyclic stability, while multiwall carbon nanotubes contribute to the electronic contact.

Fig. 5 The curves of constant current charge/discharge (**a**) and specific capacitances vs cyclic number (**b**) of various electrodes in 1 M KOH solution at a current density of 2 A·g^{-1}. *1* Pure LDH, *2* 5 wt%, *3* 10 wt%, and *4* 20 wt% MWNTs
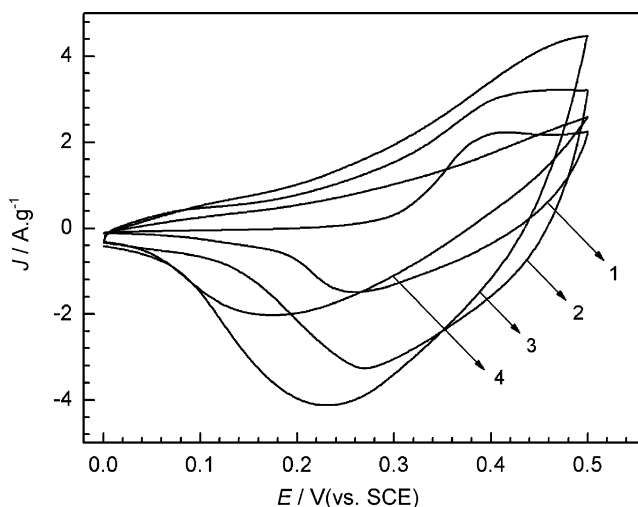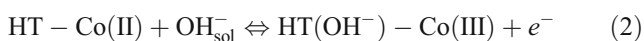

Fig. 6 Cyclic voltammograms of *1* pure LDH, *2* 5 wt%, *3* 10 wt%, and *4* 20 wt% MWNTs/LDH composite electrodes in 1 M KOH solution at a scan rate of 5 mV·s^{-1}
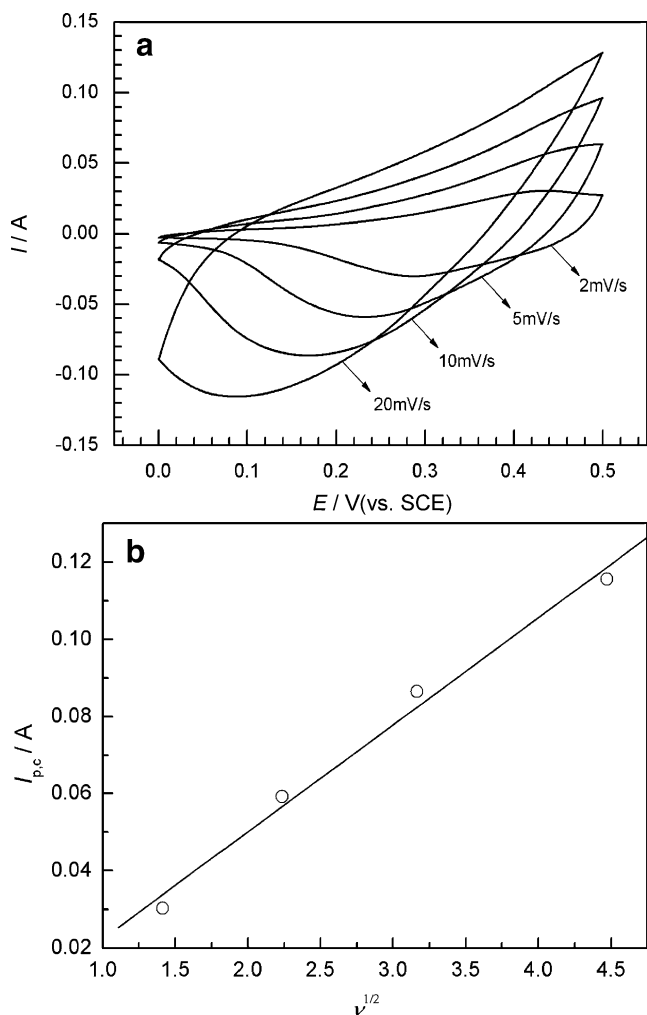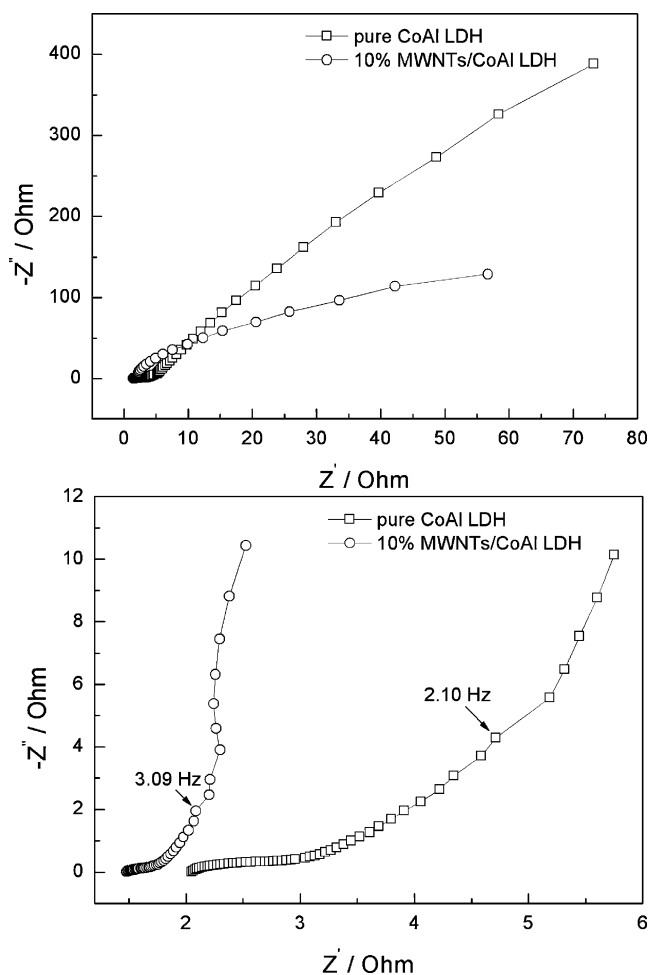
Fig. 7 **a** Cyclic voltammograms of 10 wt% MWNTs/LDH composite electrode in 1 M KOH solution at various scan rates; **b** relationship of cathodic peak current of 10 wt% MWNTs/LDH composite electrode with scan rate

Fig. 8 EIS spectra of pure LDH and 10 wt% MWNTs/LDH electrodes in 1 M KOH solution

For further understanding of the capacitive characteristics of MWNTs/LDH composite electrodes, cyclic voltammograms at various rates were recorded. The CV curves of pure LDH and MWNTs/LDH composite electrodes at scan rate of 5 mV·s^{-1} are plotted in Fig. 6. For pure LDH, the CV curve is not an ideal rectangle shape. And there are a couple of redox peaks at about 0.27 and 0.38 V (vs SCE) which correspond to the transformation of Co(II)/Co(III). According to the viewpoint of Scavetta et al. [26], OH$^-$ ions replace interlayer anions rapidly as soon as the electrode is dipped into KOH solution so that the redox reaction can be written as:

$$HT - Co(II) + OH_{sol}^- \Leftrightarrow HT(OH^-) - Co(III) + e^- \qquad (2)$$

where HT stands for hydrotalcite-like compound.

For composite electrodes, their CV shapes are not of rectangle shapes either, but they are approaching it. Peak potentials are basically the same as for pure LDH except some

slight shift. The anodic and cathodic peak areas are greater than for pure LDH, anticipating higher electrochemical capacitance. For example, Fig. 7 shows the CV curves at various rates and the relation of cathodic peak current ($I_{p,c}$) to scan rate for 10 wt% MWNTs/LDH composite electrodes as a comparison with pure Co–Al LDH (see Fig. 3). It can be seen that $I_{p,c}$ increases with scan rate for both electrodes and that $I_{p,c}$ both depends on i$^{1/2}$ linearly, confirming that a
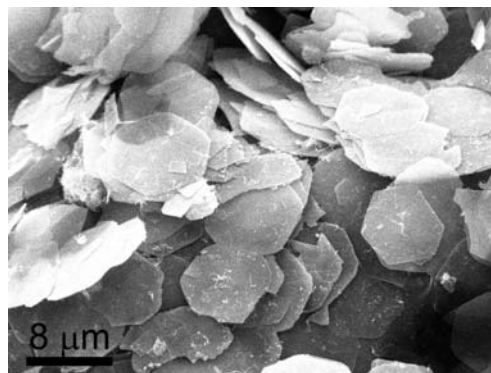
Fig. 9 The SEM image of 10 wt% MWNTs/LDH electrode

diffusion-controlled process taking place. According to the Eq. 3, provided that both electrodes have same number of n, A, and $C_O{}^*$, which is almost the case, diffusion coefficients (D_{LDH} and D_{com}) for pure LDH and 10 wt% MWNTs/LDH composite electrodes are compared. From Eq. 4, it is evident that MWNTs improve the diffusion coefficient of the electrode enormously.

$$i_p = (2.69 \times 10^5) n^{3/2} A D_O^{1/2} C_O^* v^{1/2} \qquad (3)$$

$$\frac{D_{com}}{D_{LDH}} = \left(\frac{(i_{p,c}/v^{1/2})_{com}}{(i_{p,c}/v^{1/2})_{LDH}} \right)^2 = \left(\frac{0.02774}{0.00583} \right)^2 = 22.6 \qquad (4)$$

The fact that MWNTs increase the conductivity of the electrode can also be derived from the EIS. The EIS spectra of both electrodes exhibit a semicircle at higher frequency region and a straight line at lower frequency region (cf. Fig. 8). For pure Co–Al LDH electrode, the impedance spectrum shows a straight line of almost 45° from 1.74 to 0.01 Hz, corresponding to the diffusion control process in CV curves. As for 10% MWNTs/LDH composite electrode, there appears a straight line from 0.26 to 0.02 Hz with some deviation. However, the knee frequency for 10% MWNTs/ LDH composite electrode is 3.09 Hz, higher than pure Co–Al LDH electrode (2.10 Hz), which means that the former is a more rapidly charged and discharged electrode than the latter. Moreover, it can be clearly seen from Fig. 8b that inner resistance and contact resistance between particles in the composite electrode are smaller than pure Co–Al LDH. The results confirm the suggestion that MWNTs play a key role in increasing the conductivity of the composite electrode.

Figure 9 gives a straightforward SEM observation for 10% MWNTs/LDH composite electrode. It can be explicitly seen that MWNTs are uniformly attached to the surface of LDH nanosheets. As well known, MWNTs have good electronic conductivity and large surface areas which can improve the contact of LDH with the electrode. Based on these facts, we speculate that MWNTs, when mixed with LDH, set up a fairly conductive network owing to their huge surface area and entangled structure, which ensures facile charge-transfer and mass-transfer processes.

Conclusion

A composite material of hexagonal multiwall carbon nanotubes and, for the first time, Co–Al layered double hydroxide nanosheets obtained from homogeneous precipitation, was studied as electrode material for supercapacitors at high currents. Constant current charge/discharge and cyclic voltammetry measurements show that LDH/MWNTs composite electrodes have better electrochemical performance and long-life cyclic stability at high current density than pure LDH. When the content of MWNTs added is 10 wt% in the composite, the specific capacitance increases from 192.0 F·g^{-1} of pure Co–Al LDH to 342.4 F·g^{-1} and keeps still 304 F·g^{-1} up to the 400th cycle at a constant current of 2 A·g^{-1}. The reason for the better behavior of the composite is the good electronic conductivity of MWNTs and their large surface area. SEM image show that MWNTs are attached to the surface of the LDH, which provides better interconnections of the Co–Al LDH particles and decreases contact resistance.

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