

Ordered $\text{LaCO}_3(\text{OH})\text{-Co}_3\text{O}_4/\text{CMK-3}$ Nanocomposite as the Electrode Material for Electrochemical Capacitor

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Abstract: A novel ordered mesoporous carbon (CMK-3) hybrid composite for electrochemical capacitor, $\text{La-CoO}_x/\text{CMK-3}$, is prepared via an infusing method combined with solvothermal method. The composite is characterized by X ray diffraction and N_2 adsorption-desorption analysis techniques. It is observed that the La-CoO_x nanoparticles are loaded in the channels of mesoporous carbon. The electrochemical properties of composite are studied by cyclic voltammetry method. The results show that the $\text{La-CoO}_x/\text{CMK-3}$ composite has higher specific capacitance (443.7 F/g) in comparison with the pure CMK-3 (242.9 F/g). The $\text{La-CoO}_x/\text{CMK-3}$ composite electrode also shows excellent cyclic stability, suggesting its potential applications as the electrode materials for electrochemical capacitor.

Key words: electrochemical capacitor; composite; Co_3O_4 ; $\text{LaCO}_3(\text{OH})$; supercapacitor

1 Introduction

Undoubtedly, one of the great challenges in this century is energy storage. In order to satisfy the dramatic demanding for energy conversion and storage, it is vital to search for new energy materials [1]. Recently, supercapacitor or electrochemical capacitor has generated comprehensively studied as a particular device for energy storage and delivery.

Recently, porous inorganic material has attracted great interest in various fields [2-5], owing to the ability to interact with ions, atoms, and molecules. Among various porous materials, ordered mesoporous carbon (CMK-3) has been considered as possible nanomaterial with high energy storage capacity. The ordered mesochannel and large surface area of CMK-3 shorten the distance of ion diffusing and its high conductivity is in favor of transmitting the electron [6]. CMK-3 material was also used to functionalize other material, improving the electrical conductivity, mechanical and thermal properties [7-9].

Co_3O_4 is a new type electrode material for electrochemical capacitor with high reversible specific capacity.

However, only a few cover the $\text{Co}_3\text{O}_4/\text{carbon}$ composites [11, 12]. Shan et al. [11] prepared MWNTs/ Co_3O_4 composite electrode for supercapacitor and its specific capacitance is 200.98 F g^{-1} , which is greater than that of pure MWNTs. It is shown by studies that the electrochemical performances of $\text{Co}_3\text{O}_4/\text{carbon}$ electrode can be greatly improved by doping other elements into the composite [12]. Lanthanum with a special electron shell structure has obvious influence on the capabilities of many materials [13].

In this paper, $\text{La-CoO}_x/\text{CMK-3}$ composite for electrochemical capacitor was prepared by infusing method combined with solvothermal method. The microstructure and the electrochemical performances of the composite were also investigated. On the basis of the experiment results, a possible mechanism for improved electrochemical properties of $\text{La-CoO}_x/\text{CMK-3}$ composite was discussed in detail.

2 Experimental

2.1 Synthesis of CMK-3 and $\text{La-CoO}_x/\text{CMK-3}$

According to the method reported by Zhao et al. [14], SBA-15 mesoporous silica materials were synthesized using the triblock copolymer ($\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$) as the surfactant and tetraethylorthosilicate as the silica source.

CMK-3 was similar to the synthesis method described by Lee et al. [15].

The La-CoO_x/CMK-3 composites were synthesized by infusing method combined with solvothermal method. Typically, 0.38 g Co(NO₃)₂ · 6H₂O and 0.43 g La(NO₃)₂ · 6H₂O were dissolved in 8 ml ethanol solution in a Teflon vessel, 1 g CMK-3 was added to the Teflon vessel. The above mixture was stirred for 1 h at room temperature to make the CMK-3 dispersed completely in the solution. Then the precursor was reacted at 200°C for 4h using a low temperature solvothermal method. It can be found that the resulting substance still keep the wetness state. Then, the composite was dried under vacuum at 80°C and the obtained black powder was designated as La-CoO_x/CMK-3

2.2 Characterization

The prepared materials were characterized by transmission electron microscope (TEM, JEM-2010), X-ray diffraction (XRD) measurements (Bruker, D/Max-rB II), and N₂ adsorption and desorption experiments (Micromeritics, ASAP 2020). The surface area was calculated using the Brunauer Emmett Teller (BET) equation. Pore size distributions were calculated by Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherm.

2.3 Electrochemical measurement

A working electrode was fabricated as follows: the electrode covered the mixture of the composite, carbon black and PTFE (75:20:5 wt %) was pressed on nickel foam and used as a working electrode. All electrochemical measurements were performed on a CHI 660C electrochemical workstation. The experiments were carried out in a standard three electrodes cell containing a platinum electrode as a counter and a saturated calomel electrode as a reference electrode. Cyclic voltammetry (CV) was measured in 6 M KOH aqueous solution within the potential range of -0.2-0.7 V. The specific capacitance (C) was calculated by the following equation:

$$C = \frac{Q}{m\Delta V} \quad (1)$$

where Q is the charge obtained from CV tests, m is

the mass of electrode and ΔV is the potential window.

3 Results and discussion

3.1 Structure and morphology characterization

The TEM image shown in Fig. 1(a) confirms that CMK-3 with high degree of ordered porous texture delivering arranged P6mm hexagonal structure. It can be clearly observed that the lineament of CMK-3 become somewhat unclear after the infusion and the thermal decomposition of metal nitrate, which demonstrating the nanoparticles uniformly dispersed inside the CMK-3 framework. The ordering of La-CoO_x/CMK-3 composites decrease compared with CMK-3 whereas no spots of metal oxides were detectable onto the surface, which is a further hint of the formation of the metal oxides inside the pore system.

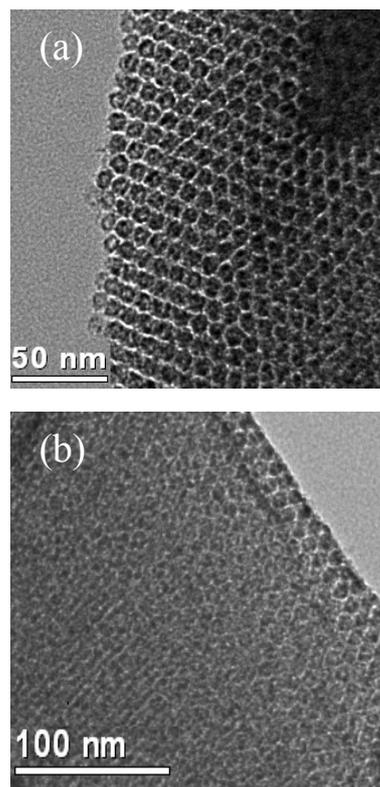


Fig. 1. TEM images of CMK-3 and La-CoO_x/CMK-3 electrodes

Small angle XRD patterns of CMK-3 are showed in Fig. 2. The obtained diffraction pattern presents certain degree of periodic order with a strong intensity from (100), (110) and (200) planes. The visible high index peak (200) indicates a highly periodic order in the ar-

range of symmetry cells, in agreement with the TEM observations

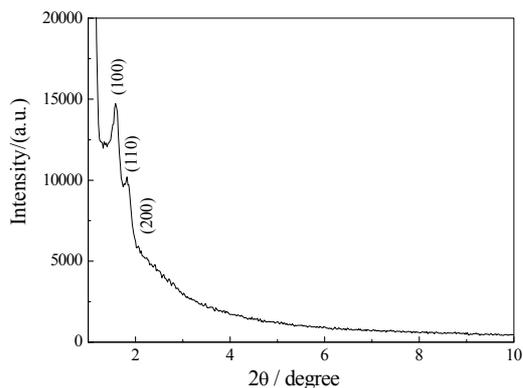


Fig. 2. Small angle XRD patterns of CMK-3

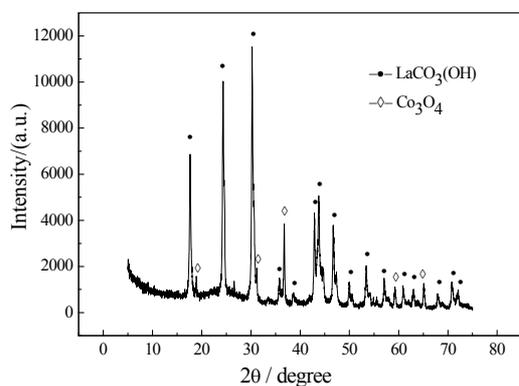


Fig. 3. XRD patterns of La-CoO_x/CMK-3 electrode

As it is seen from XRD pattern of La-CoO_x/CMK-3 electrode in Fig. 3, the characteristic peaks exhibit characteristic diffraction peaks of both LaCO₃(OH) and Co₃O₄. The characteristic peaks indexed to LaCO₃(OH) for the planes of (002), (110) and (103) which are consistent with data provided by PDF 24-0548. Characteristic diffraction peaks of Co₃O₄ (atlas 09-0418) are assigned to (111), (220) and (311) peaks.

N₂ adsorption/desorption isotherms and Barrett-Johnner-Halendar (BJH) mesopore size distributions of CMK-3 and La-CoO_x/CMK-3 electrode materials are presented in Fig. 4. It is obviously from Fig. 4a that the CMK-3 exhibits type IV isotherms with a distinct hysteresis loop, indicative of typical mesopore structure characteristic according to the IUPAC classification. An abrupt increase in adsorption volume of adsorbed N₂ is

observed which is generally associated with capillary condensation, suggesting the good homogeneity and small pore size of the samples^[16]. The pore size distribution curves (Fig. 4 b) of CMK-3 and La-CoO_x/CMK-3 electrode materials both possess a narrow distribution, which mainly originated from the existence of mesopores in CMK-3. The pore size of CMK-3 is centered at 3.78 nm while that of the La-CoO_x/CMK-3 is approximately 4.17 nm.

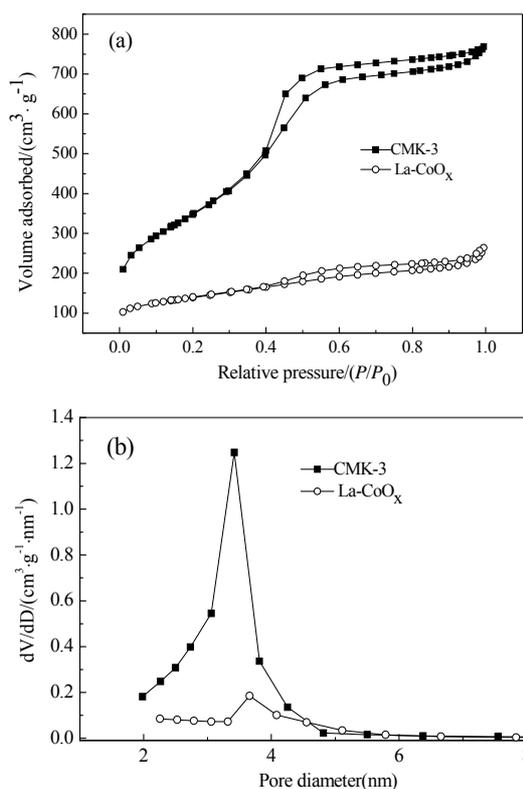


Fig. 4. N₂ adsorption-desorption isotherms (a) and pore size distribution (b) of CMK-3 and La-CoO_x/CMK-3 electrodes

Tab. 1. Pore characteristics of CMK-3 and La-CoO_x/CMK-3 electrodes

Sample	$S_{BET}/(m^2 \cdot g^{-1})$	$V_t/(cm^3 \cdot g^{-1})$	Mean pore size/ nm
CMK-3	1258.0	1.19	3.78
La-CoO _x /CMK-3	364.9	0.35	4.17

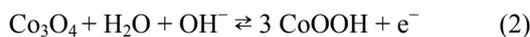
The pore characteristics, BET surface area, total pore volume (V_t) and mean pore diameter are shown in Tab. 1. The BET specific surface area is decreased from 1258.0

m^2/g for sample CMK-3 to $364.9 \text{ m}^2/\text{g}$ for sample La-CoO_x/CMK-3 composite. Similarly, the total pore volumes are found to decrease from 1.19 to $0.35 \text{ cm}^3/\text{g}$ after the La-CoO_x loading. This reduction in both surface area and pore volume after loading of La-CoO_x is mainly due to the increased density of the composite materials rather than the pore blocking by La-CoO_x.

3.2 Electrochemical characterization

Cyclic voltammetry is considered as an important method in supercapacitor has been developed to evaluate the potential possibility of materials used for capacitive deionization and meanwhile the electrochemical properties such as specific capacitance can be obtained. Fig. 5 shows the cyclic voltammograms of La-CoO_x/CMK-3 electrode recorded in 6.0 mol/L KOH solution at different scan rates between 5 and 100 mV/s . The curves show a rapid current response on voltage reversal at each end potential, indicating the high electrochemical reversibility of the sample.

A pair of redox peaks was observed at 5 mV/s scan rate, which correspond to the conversion between different cobalt oxidation states according to the following equation [17]:



The anodic peak exhibits at about 0.4 V , and a corresponding cathodic peak at about 0.18 V . The same inset has been found in the previous study [17] that identified it is derived from the pure Co_3O_4 , which proves that La didn't make a contribution to the redox reaction.

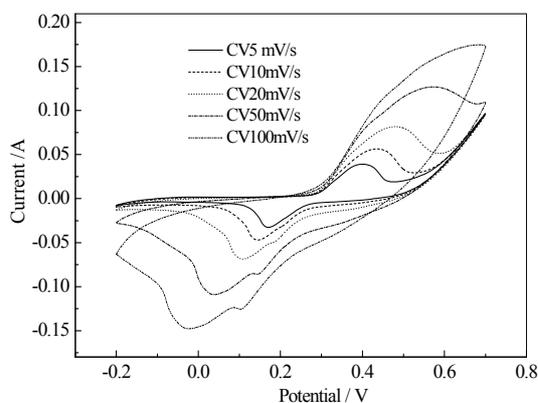


Fig. 5. Cyclic voltammograms of La-CoO_x/CMK-3 electrode at different scanning rate

The specific capacitances of CMK-3 and La-CoO_x/CMK-3 electrodes calculated from these CV curves are plotted in Fig. 6. The specific capacitance of La-CoO_x/CMK-3 was calculated to be 443.7 F/g at the scan rate of 5 mV/s , which reduces to 150.3 F/g at the scan rate of 100 mV/s , with specific capacitance retention of 33.8% . The specific capacitance of La-CoO_x/CMK-3 are higher than both that of CMK-3 (242.9 F/g for 5 mV/s) material at every given scan rate, showing good synergetic effect. La-CoO_x/CMK-3 also shows a much higher specific capacitance than that of $\text{Co}_3\text{O}_4/\text{carbon composite}$ [18] and pure Co_3O_4 [3]. It gives a clear proof that a synergic effect of La-CoO_x/CMK-3 composite electrode and CMK-3 makes an efficient energy extraction from either pure Co_3O_4 electrode or pure CMK-3 electrode. The result indicates that the crystal lattice of Co_3O_4 is distorted since La doping, which raises the diffusion rate of protons. The high specific capacitance is achieved ascribed to the unique nano-structure of the electrode.

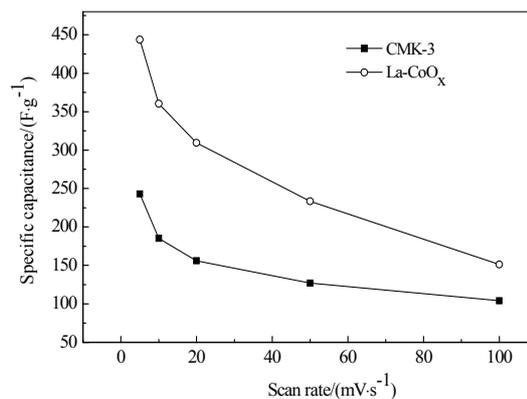


Fig. 6. Specific capacitance of CMK-3 and La-CoO_x/CMK-3 electrodes at different scanning rate

The specific capacitances decrease with respect to the increase of the scan rate, which can be attributed to the decrease of the electrolyte starvation near the La-CoO_x/CMK-3 electrode surface and the reduction of internal resistance effect at high concentration electrolyte [19]. Hence, the specific capacitance obtained at the lowest scan rate is believed to be close to that of full utilization of the electrode material.

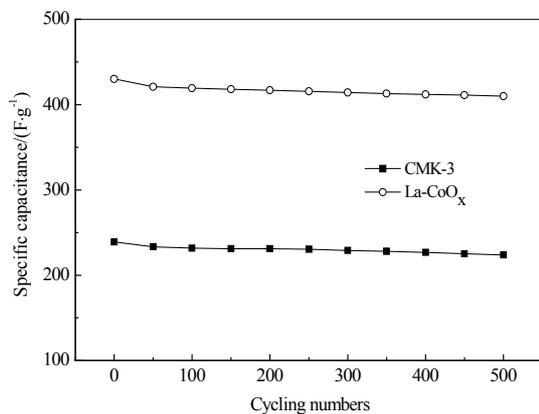


Fig. 7. Cycling performance of CMK-3 and La-CoO_x/CMK-3 electrodes within 500 cycles

Fig. 7 exhibits the cycling ability of CMK-3 and La-CoO_x/CMK-3 electrodes within 500 cycles at the scan rate of 5 mV/s. After 500 cycles, the specific capacitance retention for CMK-3 and La-CoO_x/CMK-3 electrodes is found to be 93.6% and 95.3%, respectively. The cycling ability of La-CoO_x/CMK-3 electrode reveals a stable specific capacitance during consecutive cycle test. The La-CoO_x/CMK-3 material may have great potential for electrochemical capacitor in energy storage.

4 Conclusions

In this paper, a CMK-3 hybrid composite, LaCO₃(OH)-Co₃O₄/CMK-3, is prepared via an infusing method combined with solvothermal method used for electrochemical capacitor. It is confirmed to be LaCO₃(OH)-Co₃O₄/CMK-3 from XRD analysis. The TEM image confirms that CMK-3 with high degree of ordered porous texture. The ordering of the LaCO₃(OH)-Co₃O₄/CMK-3 composite decrease compared to CMK-3. A reduction in both surface area and pore volume for CMK-3 after loading of LaCO₃(OH)-Co₃O₄ is mainly due to the increased density of the composite materials rather than the pore blocking by LaCO₃(OH)-Co₃O₄.

The curves show a reduction with a pair of current peaks. The inset derived from the pure Co₃O₄, which proves that La didn't make a contribution to the redox reaction. The LaCO₃(OH)-Co₃O₄/CMK-3 composite has

higher reversible capacities of 443.7 F/g, which is much higher than that of CMK-3, Co₃O₄/carbon composite and pure Co₃O₄. The high specific capacitance is achieved ascribed to the unique nano-structure of the electrode. The composite exhibits a stable cycle life after 500 cycles. This result persuades us to accept the LaCO₃(OH)-Co₃O₄/CMK-3 composites as a promising electrochemical capacitor material.

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