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Facile fabrication of cobalt oxalate nanostructures with superior specific capacitance and super-long cycling stability

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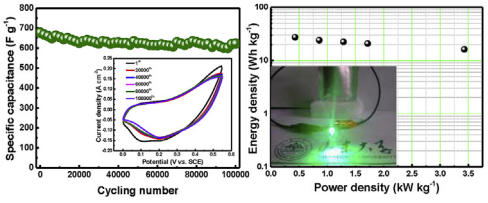
HIGHLIGHTS

- We fabricate cobalt oxalate-anchored cobalt foil electrode through anodization.
- The hybrid electrode presents superior specific capacitance of 1269 F g^{-1}.
- The hybrid electrode retains 91.9% after super-long cycling of 100,000 cycles.
- The present electrode has excellent flexibility and good mechanical properties.
- The asymmetric CoC_2O_4//AC supercapacitor shows high energy and power density.

GRAPHICAL ABSTRACT



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ABSTRACT

Transition metal oxalate materials have shown huge competitive advantages for applications in supercapacitors. Herein, nanostructured cobalt oxalate supported on cobalt foils has been facilely fabricated by anodization, and could directly serve as additive/binder-free electrodes for supercapacitors. The as-prepared cobalt oxalate electrodes present superior specific capacitance of 1269 F g^{-1} at the current density of 6 A g^{-1} in the galvanostatic charge/discharge test. Moreover, the retained capacitance is as high as 87.2% as the current density increases from 6 A g^{-1} to 30 A g^{-1}. More importantly, the specific capacitance of cobalt oxalate retains 91.9% even after super-long cycling of 100,000 cycles. In addition, an asymmetric supercapacitor assembled with cobalt oxalate (positive electrode) and activated carbon (negative electrode) demonstrates excellent capacitive performance with high energy density and power density.

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1. Introduction

In recent years, tremendous efforts have been made to develop energy storage devices such as supercapacitors and lithium batteries due to their wide applications in portable electronics, hybrid electric vehicles and smart electricity grids [1–3]. Supercapacitors have stimulated considerable interests for their functional ability to bridge the performance gap between traditional capacitors (high power output) and batteries/fuels cells (high energy-storage) with better power and energy densities, good rate capability as well as excellent cycling stability [4–8]. Based on the charge storage mechanism, supercapacitors can be divided into two

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kinds, electrical double-layer capacitors (EDLCs) and pseudocapacitors [9,10]. Although EDLCs have long lifespan, the low capacitance values (lower than 300 F g^{-1}) dramatically limit their wide utilization [11,12]. In contrast, pseudocapacitors exhibit higher capacitance (10–100 times) because the faradic redox reaction not only occurs on the surface but also near surface. Since the performance of electrodes is critical to practical applications of supercapacitors, how to design and construct high-capacity, low-cost and safe electrode materials turns to be a great challenge. Among numerous electrode materials for supercapacitor applications, transition metal oxides are widely studied due to multiple oxidation states of metal ions which facilitate redox reactions and higher charge storage within the potential range of water decomposition [13,14]. Cobalt-based pseudocapacitive electrode materials such as Co_3O_4 and $Co(OH)_2$ have attracted extensive attention due to high energy storage capacity, earth-abundant quantity and environmental benign nature. Unfortunately, large intrinsic electrical resistance, low rate capability and poor cycling stability impede their practical applications in supercapacitors [15]. Thus, great efforts are underway to look for efficient solutions to deal with these problems.

Nanostructuring has been proved to be an effective strategy that can dedicate a lot to the optimization of cobalt-based electrode properties owing to both the large surface area for increasing electrochemical active sites and short diffusion path for ions/electrons [16–19]. To further boost the charge transport and lower the electrical resistance, great progress has been witnessed in the design of additive/binder-free electrode architectures with nanostructured active materials grown directly on a current collector to avoid the “dead surface” in traditional slurry derived electrode. Anodization [20,21], hydrothermal [22], chemical vapor deposition [23], chemical reaction [24], electrodeposition [25,26] and electrospinning [27] are common fabrication methods. The cobalt-based electrodes synthesized by in-situ growth method indeed improve their electrochemical performances largely. Mesoporous cobalt oxide nanowires freely standing on nickel foam have been developed to show high specific capacitance of 1160 F g^{-1} and excellent cycling performance with 90.4% retention after 5000 cycles [18]. It is well known that transition metal oxalate materials are widely used as precursors to fabricate porous transition metal oxides (NiO [21,28], Mn_2O_3 [28], CeO_2 [29] and so forth) and porous mixed transition metal oxides [30–32]. As a matter of fact, the metal oxalate electrode materials can be fabricated by economic, scalable and environment-friendly synthesis methods, and show advanced electrochemical properties. However, related investigations about transition metal oxalates for energy storage are limited [33–37].

In the present work, we report for the first time an efficient in-situ anodization strategy to fabricate hybrid electrode materials with nanostructured cobalt oxalate-anchored cobalt foil. After the facile and easy scaled-up synthesis, the nanostructured cobalt oxalate successfully grows on the substrate with good adhesion as an additive/binder-free electrode for supercapacitors. The as-prepared materials demonstrate superior specific capacitance, excellent rate capability and super long lifespan. To the best of our knowledge, it is the first time to systematically investigate cobalt oxalate synthesized by anodization as electrode materials for supercapacitors. Particularly, it is worth mentioning that the cycling stability (91.9% of the initial specific capacitance is retained even after 100,000 cycles) is overwhelming to most transition metal oxides and comparable to carbonaceous electrode materials. This paves the way for the application of Co-based materials for supercapacitors. In addition, an asymmetric supercapacitor has been constructed based upon cobalt oxalate and activated carbon. The asymmetric supercapacitor shows excellent capacitive performance with high energy density and power density.

2. Experimental

2.1. Preparation of cobalt oxalate electrode materials

The nanostructured cobalt oxalate electrode was synthesized by means of a one-step in-situ electrochemical method (anodization). A two-electrode electrochemical cell with a DC stabilized power supply (Wenhua, China) was employed to prepare the electrode. Degreased and sealed commercial cobalt foil was used as the anode substrate for the growth of cobalt oxalate. A smaller cobalt foil acted as the cathode. Anodization was performed in a 0.5 M oxalic acid aqueous solution at a constant voltage of 40 V for 15 min at room temperature. After the reaction, the anodized samples were rinsed with deionized water for several times to remove the residual acid, followed by drying in air.

2.2. Characterization

The phase formation of the as-obtained samples was characterized by X-ray diffraction (XRD) using a XD-3 diffractometer (Beijing Purkinje General Instrument Co., Ltd, China) equipped with Cu Kα radiation. Scanning electron microscopy (SEM, LEO 1530 VP) was employed to observe the surface morphology and structure of the cobalt oxalate electrode before and after cycling stability measurement. In addition, thermogravimetric analysis (TGA, Mettler-Toledo) and differential scanning calorimetry (DSC) experiments of the cobalt oxalate dihydrate were carried out in air at a heating rate of 5 °C min^{-1}.

2.3. Electrochemical measurements

Pseudocapacitive properties of the nanostructured cobalt oxalate electrode were measured using a potentiostat (CHI660E, Shanghai, Chenhua) with a three electrode configuration. The prepared cobalt oxalate was used as the working electrode, the bright Pt foil as the counter electrode and an SCE electrode (in saturated KCl solution) as the reference electrode. The electrochemical tests were carried out in a 2 M KOH aqueous solution at room temperature. Cyclic voltammetry (CV), galvanostatic charge/discharge and electrochemical impedance spectroscopy (EIS) were conducted, and the stability of the electrode was evaluated through CV measurements at a scan rate of 100 mV s^{-1} in a potential window from 0 to 0.55 V (*vs.* SCE). Electrochemical impedance measurements were performed by means of an impedance spectrum analyzer (ZAHNER, Zennium) in a frequency range from 0.01 Hz to 100 kHz with a 5 mV amplitude at open circuit potential as well as at different biased potential during charging/discharging process.

An asymmetric supercapacitor was assembled using the cobalt oxalate as the positive electrode and an activated carbon (AC) electrode as the negative electrode. The preparation process of the AC electrode and the assembling method of the supercapacitor were described in our previous work [21]. Electrochemical measurements of the asymmetric supercapacitor were conducted using the CHI 660E potentiostat, including cyclic voltammetry and galvanostatic charge/discharge in the 2 M KOH aqueous solution.

3. Results and discussion

As illustrated in Fig. 1a, anodization was utilized to synthesize a hybrid electrode with cobalt oxalate in-situ growing on the surface of cobalt foil. The cobalt foil serves as the substrate and also the current collector, ensuring intimate contact between the cobalt oxalate nanostructures and the substrate which is beneficial for

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