Available online at www.sciencedirect.com
ScienceDirect
Trans. Nonferrous Met. Soc. China 24(2014) 1425−1433

Transactions of Nonferrous Metals Society of China
www.tnmsc.cn

Flexible free-standing graphene-like film electrode for supercapacitors by electrophoretic deposition and electrochemical reduction

Yuan-yun DOU[1], Min LUO[1], Sen LIANG[2], Xue-ling ZHANG[1], Xiao-yi DING[1], Bin LIANG[1]

1. Key Laboratory of Energy Resources and Chemical Engineering, Department of Chemical Science and Engineering, Ningxia University, Yinchuan 750021, China;
2. Key Laboratory of Ningxia for Photovoltaic Materials, Ningxia University, Yinchuan 750021, China

Received 17 June 2013; accepted 5 March 2014

Abstract: Electrophoretic deposition in conjunction with electrochemical reduction was used to make flexible free-standing graphene-like films. Firstly, graphene oxide (GO) film was deposited on graphite substrate by electrophoretic deposition method, and then reduced by subsequent electrochemical reduction of GO to obtain reduced GO (ERGO) film with high electrochemical performance. The morphology, structure and electrochemical performance of the prepared graphene-like film were confirmed by SEM, XRD and FT-IR. These unique materials were found to provide high specific capacitance and good cycling stability. The high specific capacitance of 254 F/g was obtained from cyclic voltammetry measurement at a scan rate of 10 mV/s. When the current density increased to 83.3 A/g, the specific capacitance values still remained 132 F/g. Meanwhile, the high powder density of 39.1 kW/kg was measured at energy density of 11.8 W·h/kg in 1 mol/L H_2SO_4 solution. Furthermore, at a constant scan rate of 50 mV/s, 97.02% of its capacitance was retained for 1000 cycles. These promising results were attributed to the unique assembly structure of graphene film and low contact resistance, which indicated their potential application to electrochemical capacitors.

Key words: free-standing graphene-like film; supercapacitor; electrophoretic deposition; electrochemical reduction; flexibility

1 Introduction

Supercapacitor has attracted great attention for a wide and growing range of applications due to its high energy density, rapid charging and discharging rate, long cycling life and low cost compared to conventional dielectric capacitors [1,2]. So far, various materials, such as carbonaceous material [3,4], metal oxide [5], conducting polymers [6] and their composites [7,8], have been used as supercapacitor electrode materials. Among these materials, carbon is the widely used electrode materials for supercapacitor, including activated carbon (AC) [9,10], mesoporous carbon (MC) [11], carbide derived carbon [12], carbon xerogel [13] and carbon nanotube [14]. Although these porous carbon materials have high specific surface area, but the low conductivity and high contact resistance between electrode and current collector limit the application in high powder density supercapacitors [15].

Graphene, with a two-dimensional one-atom-thick planar sheet of sp^2 bonded carbon atoms, is the carbon material for potential application in electrochemical energy storage with various superior properties such as large specific surface area, high electrical conductivity and charge−carrier mobility, high mechanical strength and inherent flexibility [16−18].

Many methods, such as hydrothermal synthesis [19], vacuum filtration deposition [20], electrophoretic deposition [21], biotemplating method [22], have been carried out to prepare the grapheme-based carbon material with high effective surface areas, high electric conductivity and low contact resistance, which should be expected to exhibit better supercapacitor performance. ZHU et al [23] produced high surface areas carbon-based supercapacitors by activation of grapheme. MILLER et al [24] prepared vertically oriented graphene nanosheets directly on metal current collectors to minimize electronic and ionic resistances. YOO et al [25] fabricated the ultrathin supercapacitors by “in-plane”

Foundation item: Projects (21361020, 21061012) supported by the National Natural Science Foundation of China; Project (NZ12156) supported by the Natural Science Foundation of Ningxia, China Project (N-09-13) supported by Project of State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics of the Chinese Academy of Sciences

Corresponding author: Min LUO; Tel: +86-951-6892181; E-mail: luominjy@nxu.edu.cn

DOI: 10.1016/S1003-6326(14)63208-8

design to exploit the surface of each graphene layer for energy storage. However, synthesizing the graphene material with less agglomeration and manipulating the graphene nanosheets into controllable architectures film electrode were still challenges due to the hydrophobicity and staking interaction among graphene sheets.

It has been reported that assembly of GO sheets on a solid substrate was a good way to prevent the aggregation of GO after reduction [26]. Given that the difficulty of directly assembling the graphene electrode materials, an alternative strategy was proposed to firstly prepare the graphene oxide film electrode materials by electrophoretic deposition (EPD), and then electrochemically reduce the GO films to graphene-like films by removing the oxygen-contained groups (OCGs) with the recovery of conjugated structure. In the process of fabricating the electrode materials, EPD was seen as one of the economical and versatile processing techniques for depositing various types of functional films due to unique microstructures, complex shape and rapid production times [27], while electrochemical reduction has been developed to achieve the reduction of GO to graphene due to its fast and green nature [28]. Herein, a flexible self-standing graphene-like membrane electrode material with large capacitance, low contact resistance and good cycling stability was developed. The graphene-like materials were obtained by a two-step process. In the first step, negative charged GO nanosheets suspended in an organic liquid migrated toward a positive electrode to form a homogeneous film with unique microstructure and complex shape by electrophoretic deposition. In the second step, the GO films were reduced by electrochemical reduction method, after the removal of OCGs of GO by electrochemical reduction, some micro-channels in the graphene-like film were left, which can significantly permeate electrolyte to facilitate ion transport. The influences of electrophoretic deposition voltage and time on the electrochemical properties were investigated.

2 Experimental

2.1 Preparation of ERGO film electrode

2.1.1 Synthesis of GO

Graphene oxide was synthesized from graphite flakes (Sinopharm Chemical Reagent Co. Ltd., China) by a modified hummer’s method. Briefly, graphite (2 g) and $NaNO_3$ (1 g) were mixed with H_2SO_4 (50 mL, 98%) in a 500 mL beaker. The mixture was stirred for 30 min within an ice bath. While maintaining stirring, $KMnO_4$ (5 g) was dissolved to the suspension and the mixture was continuous stirred for 30 min. The ice bath was then removed, and the mixture was stirred at 35 °C for 2 h. As the reaction progressed, the mixture gradually became pasty, and the color turned into brownish. Then 50 mL H_2O was slowly added to the pasty. The reaction temperature was rapidly increased by adding the boiling water (100 mL), and the color of solution changed to yellow. At the end, 15 mL of 30% H_2O_2 was added to the mixture. The precipitate was washed with excess water for several times. Further purified solution could be achieved by repeating centrifugation for several times until neutral pH, the graphene oxide (GO) powder was collected after freeze drying for 2 d.

2.1.2 Electrophoretic deposition of graphene oxide film

The as-obtained graphene oxide powers were transferred into alcohol and acetone mixed liquor to form stable graphene oxide colloids after ultrasonication with a concentration of 0.5 mg/mL. Electrophoretic deposition of graphene oxide was performed using a cell consisting of nickel plate as cathode and a graphite plate as anode. The two electrodes were placed parallel to each other and separated by 10 mm. The area of contact of each electrode with the GO slurry was 2 cm^2. The samples used were listed in Table 1 together with electrophoretic deposition parameters (deposition voltage and deposition time), in which GO-30-5 signified that the deposition voltage was 30 V and the deposition time was 5 min, and the corresponding electrochemically reduced sample was designed as ERGO-30-5.

Table 1 Electrophoretic deposition parameters of electrode films

Electrode film	Deposition voltage/V	Deposition time/min
GO-20-10	20	10
GO-30-2	30	2
GO-30-5	30	5
GO-30-8	30	8
GO-30-10	30	10
GO-30-15	30	15
GO-30-20	30	20
GO-40-10	40	10
GO-50-10	50	10

2.1.3 Electrochemical reduction of graphene-like film electrode

After deposition, the GO film on the graphite substrate was electrochemically reduced by cyclic voltammetry method from −1.2 to 0 V in 0.1 mol/L phosphate buffer solution (PBS, pH=6) at a scan rate of 10 mV/s. As-prepared ERGO film electrode was then rinsed with water and dried at room temperature for electrochemical characterization.

2.2 Characterization of materials

X-ray diffraction (XRD, D/MAX 2200P, Rigaku,