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Facile Electrodeposition of Molybdenum sulfide on Nickel Foam surface as a highly efficient supercapacitor

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Abstract: Supercapacitor devices have significant attention owing to their rapid charge/discharge and high power density. Herein, Molybdenum sulfide is advantageous material for super-capacitors due to good conductivity and excellent electrochemical performance and it was synthesized by facile and effective electro-deposition technique. The fabricated electrode has been studied by SEM to construe the material morphology and the electrochemical experiments were performed to investigate the supercapacitive activity which indicate the good substitution of metal sulfide on Ni foam. The system exhibited an excellent capacitance with high energy and power densities of 1068.6 F/g with 133.57 Wh/kg and 870 W/kg, respectively, at 1 A/g and the capacitance was calculated from CV (1143.9 F/g at 5 mv/s). These results indicate that metal sulfides are promising materials for energy storage devices.

keywords: super-capacitor; electrodeposition; binder free electrode; Molybdenum sulfide.

1.Introduction

With the growth demand for energy, scientist's interest in creating a unique asymmetric energy storage technology with energy and power density concurrently has been encouraged [1, 2]. Super-capacitor's, also referred to as electrochemical capacitors, are gaining popularity in the energy storage field owing to high power density, good cyclic stability, rapid charge discharge and high safety compared to batteries [2, 3]. These capacitors are classified into three types, pseudo-capacitors that store charge by quick reversible oxidation-reduction reaction on the surface of material, electrical-double-layer super-capacitor which store charge through ions adsorption desorption at the electrolyte/electrode interface, and hybrid super-capacitors which combine both of these mechanisms to storage charges [4, 5]. According to their redox mechanism, pseudo-capacitors have more specific capacitance than EDLCs. The development of the structure's materials including the design of active electrode materials and current collectors, is the primary goal to enhance the SCs electrochemical performance. Various materials such as metal oxides, sulfides, phosphides, and polymers were evaluated for their high electrochemical performance as electrode materials [6, 7].

Transition metal sulphides are among the many reported electrode materials for hybrid super-capacitors that have significant advantages in a number of energy devices [8]. Due to their abundance of active sites, which award more faradic reaction, greater cyclic stability, cost-effective, non-toxicity, and improved electric conductivity [7, 9]

Molybdenum sulfide is a promising electrode with high capacitance due to the multiple oxidation state of Mo ion and the low electro negativity, large polarizability of sulfur ions sustains flexible structure morphology [4, 10]. The synthetic method should be controlled to produce materials with excellent cyclic stability and high rate capability. The MoS electrode was prepared by simple, versatile, and rapid technique. In electro-deposition process, the electro-active material is directly growth on the Ni foam surface as a template with a large surface area, high conductivity and porosity[11]. Moreover, this technique not only guarantees good contact with Ni foam substrate but also reduce the electrode internal resistance[12].

In this work, we report the molybdenum sulfide prepared via inexpensive, simple, green, and one-step electro-deposition technique for

capacitor applications. The work's main innovation is improved the electrochemical characteristics by the growth of material on the current collector and the absence of binders which reduce the resistive electrode material. At a current density of 1 A/g, the MoS/NF electrode showed a 1068.6 F/g specific capacitance.

2. Experimental Section

2.1 Reagents

Ni foam and all reagents were used in synthesis of electrode materials without further purification. Thiourea ($CS(NH_2)_2$), ethanol (C_2H_5OH), and ammonium hepta-molybdate tetrahydrate $(NH_4)_6Mo_7O_{24}.4H_2O$, were purchased from Alfa. Potassium hydroxide (KOH), hydrochloride acid (HCl), acetone, ethanol.

2.2. Preparation of MoS/Ni foam electrode

Prior to the electrodeposition, the Ni foam was cut into pieces (1 x 4 cm^2) and sonicated in HCl solution (3 M), water, and ethanol for 10 min for each solvent to remove surface contaminants. Finally, the sheets were dried in an oven for 10 h at 70 ℃ for 10 h under vacuum. The electrodeposition solution was prepared by a mixture of 5 mmol ($(NH_4)_6Mo_7O_{24}.4H_2O$) with 0.22 g of thiourea (CH_4N_2S). Using a three-electrode configuration with Ni Foam, Ag/AgCl electrode, and platinum plate as a working electrode, reference electrode, and counter electrode, respectively, the electrodeposition process was carried out using the cyclic voltammetry (CV) for 5 cycles with a voltage range of (-1.2 to 0.2 V) at a scan rate of 5 mv/s. The final sample was cleaned by thoroughly rinsing with water and ethanol, followed by a 10-hour drying period at 70 ℃. The weight of Ni foam before and after MoS deposition was calculated to estimate the loaded weight of MoS.

Material Characterization

The morphology of the prepared materials was estimated by the scanning electron microscopy (SEM, Hitachi s- 4800) to confirm the successful preparation.

Electrochemical measurements

.The electrochemical tests of electrodes

Through a potentiostat, the deposited electrodes were tested electrochemically utilizing cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) methods. With a platinum counter electrode, the electrochemical characteristics were tested versus Ag/AgCl in 1 M KOH. The fabricated electrodes were activated by 50 cycles of the CV technique from 0 to 0.5 V at a 50 mV/s scan rate before taking the data due to unstable capacitive performance. Afterward, the CV measurements were analyzed at different scan rates (5-50 mV/s) at 0 V to 0.5 V followed by the GCD measurements with the same voltage window for various current densities (1-20) A/g. Finally, the EIS measurements were carried out at frequencies ranging from 0.1 to 105 Hz using the open circuit potential (OCP) with an amplitude of 5 mV. To conduct the specific capacity (Cs, C/g) of different as-synthesized electrodes, the CV data at various scan rates were used as follows:

$$C = \frac{\int i\, dV}{m \times \nu \times \Delta V}$$

where, i (A), C (Fg^{-1}), ν (vs^{-1}), ΔV (V), and m (g) are the current, specific capacitance, scan rate, potential window, and mass of active material in working electrode in three electrode system.

Moreover, the specific capacity (Cs, C/g) and specific capacitance (C, F/g) depending on the GCD results can be conducted as follows;

$$C = \frac{i \times \Delta t}{m \times \Delta V}$$

where, Δt (s) and I (A) are discharge time and current.

The power and energy densities were calculated as follows.

$$E = \frac{1}{2} C V^2$$

$$P = \frac{E}{t}$$

3. Results and Discussion section

3.1. Characterization of materials

SEM image showed the rougher surface of Ni foam with cracks due to the deposition of MoS on Ni foam. Clearly, the porous nanostructure has a lot of free space, which is good for allowing electrolytes to get into the

material of electrode quickly for redox reaction and storage of charge.

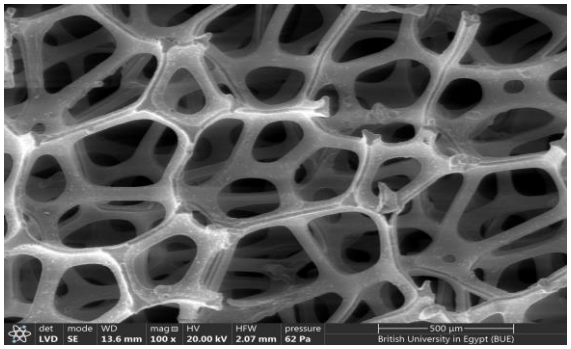

Fig.1 SEM image of MoS/Ni foam.

3.2. Electrochemical evaluation

The MoS that was deposited on the NF surface was electrochemically tested and compared to the pristine Ni Foam that had been produced in 1M KOH under the same conditions using a 3-electrode system, as seen in Fig. 2. Firstly, Fig. 2 compares the results of the cyclic voltammetry (CV) tests performed on the manufactured catalysts using an operating potential window of 0- 0.5 V with a scan rate of 5 mV/s. The figure shows one pair of redox peaks for MoS/NF curve, suggesting the involvement of battery-type components in the redox reaction. The MoS/NF electrode shows redox peaks at ~0.39 V (oxidation) and 0.26 V (reduction) indicating the redox process. The figure shows redox peaks due to the reaction of the alkaline electrolyte with the active materials of the electrode.

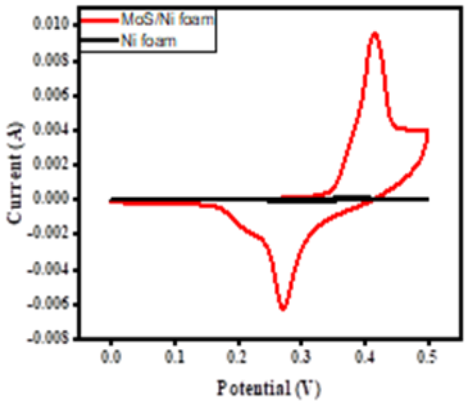

Fig.2 CV curves of Ni foam supported MoS and pure Ni foam at 5mv/s.

Moreover, the cyclic voltammetry studies of electrode were performed at different scan rates of 5-50 mV/s with an operating voltage window of (0-0.5V). Fig.3a shows that the reduction and oxidation peaks for all electrodes shifted to lower and higher potentials, respectively, with the increase of scan rate in regard to the internal

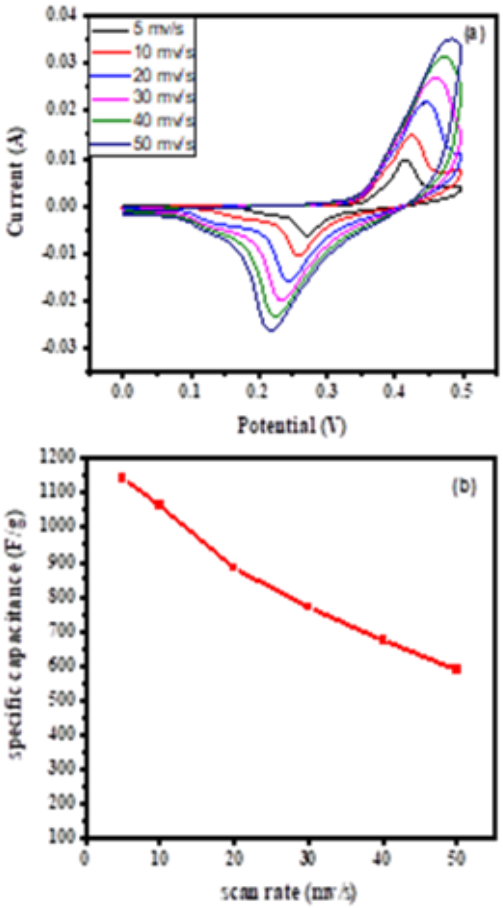

Fig.3 Cyclic voltammetry curves (a) and (b) specific capacitance as a factor of scan rate of MoS/Ni foam electrode at different scan rate.

resistance of the electrode and the quick interfacial rate kinetics demonstrating that the redox processes are diffusion-controlled negative potentials, respectively due to the fast transfer of electrons on the electrode surface at high scan rates. Moreover, the scanning rate and capacitance relationship was displayed in Fig.3b showing that at lower scan rate, the specific capacitance of fabricated electrode was enhanced to 1143.9 F/g due to the susceptibility of active site for the penetration of the electrolyte.

The GCD measurements of Mo sulfides electrode were examined at different current densities (1- 20 A/g) in 1 M KOH electrolyte at a potential of 0-0.5 V as shown in Fig. 4a. The specific capacitance was calculated from GCD curves, and their values were 1068.7 F/g, 848.46 F/g, 651.2 F/g, 338.4 F/g, and 230 F/g at 1-20, respectively, (Fig.4.b). generally, when

current density increases, the charge transfer process accelerates, and the transfer rate outpaces in the redox reaction. This resulted in a progressive drop in capacitance.

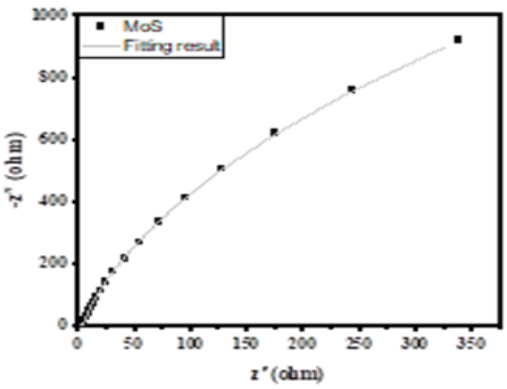

Fig.4 (a) GCD curves of MoS/Ni foam at current density (1, 3, 5, 10, and 20 A/g), (b) specific capacitance in relation to current density.

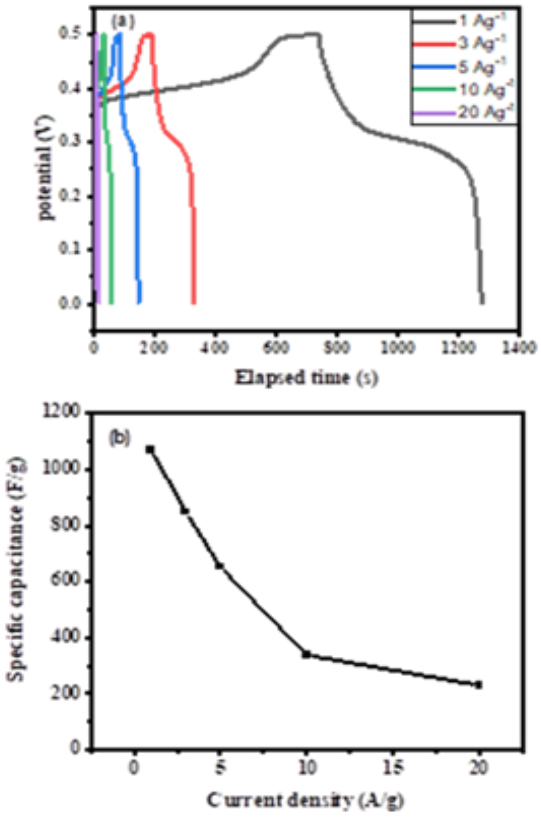

Fig.5 EIS spectrum of MoS/Ni foam electrode with frequency range (0.1-100 KHz).

EIS measurements were studied to examine the conductivity of fabricated electrode with frequency range (0.1-100 KHz). The Nyquist plot for MoS/Ni foam electrode was exhibited in Fig.5. In the region of low frequency, the straight line appears that pointing to the OH^- ions diffusion into the electrode.

Conclusion

In summary, Molybdenum sulphide was directly grown on the substrate surface (Ni foam) to produce MoS/NF. In the preparation process, the electrode is fabricated without binder or any additives that enhancing the electrode conductivity. The surface morphology of the electrode was construed using SEM and Three electrodes were subjected to electrochemical experiments using CV, GCD, and EIS to determine how well the electrode was constructed (1068.6 F/g specific capacitance at 1 A/g).

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