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Effect of carbon on galvanically deposited cuprous oxide as flexible charge storage electrode

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ABSTRACT

Electroless deposition of cuprous oxide was carried out on Al foil and heat treated at 370 °C. Different combination of Carbon/Cuprous oxide composites were prepared and labelled as Al-2, Al-3 & Al-4. Scanning Electron microscopy (SEM) and energy dispersive X-ray (EDX) study revealed the formation of Cu_2O for Al-2. FTIR studies revealed presence of Cu_2O for non-heat treated Al-2 and CuO for heat treated Al-2. SEM micrograph showed the porous nature of Al-2, whereas, the least porosity was shown by Al-3. The resultant foils were electrochemically characterized using Cyclic Voltammetry, Electrochemical impedance spectroscopy and Galvanostatic Charge Discharge techniques. On deposition of carbon on cuprous oxide surface, capacitance value of the composite decreased. Among them capacitance of Al-2 was found to be 475 mF g^{-1} from the galvanostatic charge discharge studies. The capacitance was found to be 419.12 mF g^{-1} and 296.87 mF g^{-1} for Al-3 and Al-4 respectively.

1. Introduction

Due to continuous depletion of fossil fuel and increasing energy demand there is a need to develop a clean and sustainable source of energy [1]. The recent technological advancements have shown that there is an increasing need of micropower systems [2]. Charge storage electrodes, which are employed to be used as a new, sustainable and clean source of energy are now also being used as the small scale devices which can be used as a replacement of batteries in the microelectronics [2]. Electrochemical micro-capacitors with high power density can be coupled with energy harvesting devices to store the generated energy [3]. They find application in microelectronics, medical sensors etc. devices [2]. For devices such as microcapacitor it is observed that weight of the electrode materials, high power and energy density do not seem to change with the thickness of the electrode material [2]. In such charge storage electrodes use of aqueous electrolytes gives low internal resistance and high specific capacitance than organic electrolytes [4]. Carbonaceous materials usually exhibit low resistance and high stability and the usage of metal oxides exhibits high pseudocapacitance [4]. The active materials of charge storage electrodes include transition metal oxides, conductive polymers, graphene, carbon nanotube etc. and also their hybrids [3,5]. Cuprous and cupric oxide of varying morphologies, synthesized by different chemical routes has been widely explored for application as capacitors and batteries [6–11]. Contemporary research is focused on development of flexible charge storage electrodes [5,12,13]. Jiang et al. fabricated microcapacitor with VA-CNT electrodes which showed a specific capacitance of 428 μF cm^{-2} [5]. Copper oxide based and its composite charge storage electrodes have been reported in literature [14–16]. Cathodic electrodeposition method was employed to deposit copper oxide film at room temperature on stainless steel substrate by Patake et al. [16]. They reported capacitance of around 36 F g^{-1} for the film thickness of 0.6959 mg cm^{-2} [16]. Yu et al. showed the formation of 3D porous gear like copper oxide formed by annealing $Cu(OH)_2$ at 200 °C in air. These demonstrated an excellent supercapacitance of 348 F g^{-1} at a discharge current density of 1 A g^{-1} with an energy density of 43.5 Wh kg^{-1} with excellent cycle stability [17]. It has been demonstrated in the literature that an amorphous material exhibits superior performance compared to its highly crystalline form [1]. A crystalline structure owing to its difficulty in contraction and expansion; hinders ions from easy and fast diffusion within its lattice and compromising Faradaic reactions to be limited to the material surface [18]. In case of an amorphous material, the Faradaic reaction occurs not only on the surface but also throughout the bulk [19]. Superiority of amorphous material for charge storage applications has been well investigated.

The present work focuses on the synthesis and characterization of galvanically deposited cuprous oxide based flexible charge storage electrode and effect of carbon on its charge storage behaviour.

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2. Experimental

2.1. Materials

Copper sulphate (99.5%), Lactic acid (88–92 wt.%), Sodium hydroxide and Acetone were procured from Rankem, Merck Specialities, Fischer Scientific India Pvt. Ltd. and CDH, India respectively. All the chemical reagents were used as received without any further purification. Aluminium foil was procured from Alfa Aesar.

2.2. Synthesis of cuprous oxide, carbon coated aluminium foil by electroless deposition

2.2.1. Preparation of copper sulphate bath.

0.4 M copper sulphate was prepared in 3 M Lactic acid and 4 M sodium hydroxide solution. The bath was prepared according to the protocol reported in the literature by Wang et al. [20]. Initially 0.4 M copper sulphate was added to 3 M lactic acid with the addition of distilled water to make up the volume up to 50 ml. Then to this 4 M NaOH was added till the colour changed to dark blue and pH of the solution was approximately 9.0.

2.2.2. Coating of aluminium foil

Aluminium foil was dipped in the copper sulphate bath for 45 min at a temperature of 65 °C. After 45 min strips were taken out and grey red colouration was observed on the surface of the aluminium foil. The coated foil was then washed with deionised water then acetone and air dried.

2.2.3. Heat treatment of cuprous oxide deposited aluminium foil

The prepared cuprous oxide coated Aluminium foil were heat treated for half an hour at 370 °C. Then the foils were washed with acetone and dried in air.

2.2.4. Deposition of carbon

Carbon in the form of carbon soot was deposited on bare Aluminium foil and cuprous oxide coated Aluminium foils by using wax candle. Strips were kept at a distance of 2 cm from the flame for deposition of Carbon soot.

2.2.5. Preparation methodology of each strip

2.2.5.1. Carbon deposited aluminium strip (C/Al). Carbon deposition was carried out with the help of candle on the Aluminium strips. The sample was labelled as Al-1.

2.2.5.2. Heat treated cuprous oxide modified aluminium strip (HT/Cu_2O/Al). After deposition of cuprous oxide on the Aluminium foil, the foil was kept for heating at 370 °C in furnace for 30 min. This sample was labelled as Al-2.

2.2.5.3. Carbon deposited cuprous oxide modified aluminium strips and then heat treatment at 370 °C (HT/C/Cu_2O/Al). Aluminium strips were modified by deposition of cuprous oxide as mentioned above. Then the strip was thoroughly washed with distilled water and acetone. Deposition of Carbon was carried out with Candle flame, the modified strip was kept at a distance of 2 cm from the flame. A black coating was observed on deposition of carbon and then these strips were kept for heat treatment at a temperature of 370 °C for 30 min. This sample was labelled as Al-3.

2.2.5.4. Carbon deposited aluminium strip modified by depositing cuprous oxide and heat treatment at 370 °C (HT/Cu_2O/C/Al). Aluminium foil was modified by the deposition of Carbon soot on the surface and then modifying it with the cuprous oxide deposition carried out at a temperature of 65 °C. Then the strips were again washed in distilled water and acetone and then kept in furnace for 30 min at 370 °C. This sample is labelled as Al-4.

3. Characterization

3.1. X-ray diffraction (XRD) measurement

Characterization of the carbon soot was carried out using XRD. The powder was analysed within 2θ range of 20° to 80°. X-ray diffraction was recorded on Rigaku Miniflex 600 diffractometer (Rigaku Corporation, Japan).

3.2. Scanning electron microscopy (SEM)

Surface morphology and elemental analysis was carried out by using Scanning electron microscope (SEM) JEOL 6010LA (Japan). The foils were characterized by cutting into small strip and adhered on Carbon tape for analysis.

3.3. FTIR analysis

FTIR spectra of the samples were carried out by scratching off the coating from the aluminium substrate into KBr powder followed by KBr pellet technique using Nicolet 5700 FTIR (USA).

3.4. Electrochemical measurements

Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS) and Galvanostatic Charge Discharge (CD) were carried out using AUTOLAB PGSTAT 302 N (Netherlands). Measurements were carried out using a three electrode assembly where sample, Pt wire, Ag/AgCl were used as working, counter and reference electrode respectively. The electrolytic medium was 0.1 M NaOH. CV and EIS data analyses were done using Nova 1.10.1.9 module provided with Autolab.

4. Results & discussion

For a metal oxide to be used as charge storage electrode, it should be electronically conducting, metal can exhibit two or more than two oxidation state, protons can freely intercalate into oxide lattice which on reduction allows easy conversion of O^{2-} to OH^-. The metal oxide based electrode which was synthesized was evaluated based on those criteria.

4.1. Electroless deposition of cuprous oxide

It is based on the principle of galvanic displacement [20]. Growth rate of formation of Cu_2O nanooctahedra is dependent on the reducibility of the metal substrate. If the reducibility of the metal substrate is fast

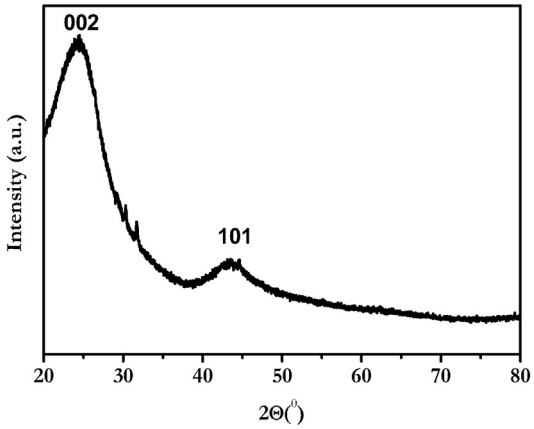

Fig. 1. X-ray diffraction pattern of the carbon soot.