



High performance asymmetric supercapacitors using electrospun copper oxide nanowires anode



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ABSTRACT

We have fabricated, for the first time, an asymmetric supercapacitor (ASC) employing pseudocapacitive copper oxide (CuO) as anode and electrochemical double layer capacitive commercial activated carbon (AC) as cathode. The CuO is in the form of nanowires of diameter $\sim 30\text{--}50$ nm developed using an aqueous polymeric solution based electrospinning process. The ASC showed larger voltage window ($V \sim 1.6$ V) and specific capacitance ($C_S \sim 83$ Fg $^{-1}$) than a control symmetric electrochemical double layer capacitor (EDLC) ($V \sim 1.4$ V; $C_S \sim 33$ Fg $^{-1}$) fabricated using the AC. The ASC delivered specific energy densities (E_S) of 29.5, 23.5, 19.2 and 16.4 W h kg $^{-1}$ at specific power densities (P_S) 800, 1500, 4000 and 8400 W kg $^{-1}$, respectively. The performance of ASC is much superior to the control EDLC, which delivered E_S of 11, 10 and 8.8 W h kg $^{-1}$ at P_S 800, 1600 and 3900 W kg $^{-1}$, respectively. Owing to the larger abundance of copper in the earth's crust and promising charge storage properties achieved herewith, the present ASC could be developed as a commercial electrical energy storage device.

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1. Introduction

Deployment of electrical energy derived from renewable sources such as solar, water and wind demands efficient storage system such as batteries and supercapacitors [1,2]. Supercapacitors have gained considerable attention in recent years as an energy storage device due to their high power densities, fast recharge capability and long cycle life. Supercapacitors are classified into electric double layer capacitors (EDLCs) and pseudocapacitors according to charge storage mechanisms [3–6]. The EDLCs store electrical energy via accumulation of electric charges at an electrical double layer formed at an electrode–electrolyte interface. Carbons such as activated carbon, carbon nanotubes, and graphene are choices to build EDLCs; however, lower specific capacitance (C_S) and specific energy density (E_S) limit its application areas [7–9]. The pseudocapacitors provide several times larger C_S and E_S than EDLC through a faradic reaction at the electrode–electrolyte interface [10–12]. Transition metal oxides (TMO), layered materials, metal hydroxides, and conducting polymers show pseudocapacitance [9,13–18]. However, they suffer from a lower operating potential (V) window and E_S , which restricts their applications. Therefore, improvement of the E_S of the pseudocapacitors is crucial to meet the energy storage demands [19–21]. The E_S could be

increased by increasing the C_S and the V of the device as they are related by [9,22,23]

$$E_S = 1/2C_S V^2 \quad (1)$$

A large number of TMOs are reported with large theoretical C_S ~ 3500 Fg $^{-1}$, a brief review of which is available in recent articles [24–26]. One of the main issues in the electrode selection for pseudocapacitors is to unite high C_S , specific power density (P_S), and abundance for large scale production. Although materials such as Co $_3$ O $_4$ show large practical C_S (~ 3560 Fg $^{-1}$) [27] they are relatively lower abundant (<20 ppm) in the earth crust. On the other hand, materials such as MnO $_2$ with theoretical C_S (~ 1370 Fg $^{-1}$) are largely abundant (>2000 ppm) but their practical C_S are relatively lower (<400 Fg $^{-1}$) [24,26,28,29]. Therefore, materials of high abundance and large practical C_S are inevitable for fabrication of high performance commercial devices.

The other parameter for achieving higher E_S is V (Eq. (1)). The V depends on the difference in electrochemical potentials of the electrode material and the electrolyte. Therefore, for a given pseudocapacitive electrode, the V could be widened by choosing an electrolyte with much different electrochemical potential than the electrode material [19,30,31]. Towards this end, high operating voltage is reported using organic electrolytes (2.7 V) and ionic liquids (3.5 V) using this approach [32]. However, high cost, toxicity, low conductivity, flammability, and stringent device fabrication requirements restrict their use in large scales. Otherwise, aqueous

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electrolytes are environmentally benign and easy to handle but suffers from narrow operation voltage window (<1 V; theoretical stability window 1.23 V). This drawback is surpassed in asymmetric supercapacitors (ASCs) by combining a pseudocapacitor anode and an EDLC cathode.

Copper oxide (CuO) nanostructures gained considerable attention recently owing to its lower toxicity, relatively larger abundance (~70 ppm), environmental stability, and desirable electrochemical properties [33,34]. We reported the highest C_S (~620 Fg^{-1}) ever achieved using CuO nanostructures recently in aqueous electrolytes in thin (<50 nm) and dense nanowires developed by electrospinning process [31]. A survey of literature shows that no ASC is reported using CuO as an electrode so far most likely due to the inferior C_S achieved before. Therefore, the high C_S achieved in CuO nanowires provide a possibility to fabricate high performance ASCs and study its characteristics. We used commercial activated carbon (AC) as cathode of the ASCs for commercial viability. The ASC delivered E_S of 29.5, 23.5, 19.2 and 16.4 W h kg^{-1} at P_S of 800, 1500, 4000 and 8400 W kg^{-1} , respectively, which is much superior to a control symmetric EDLC device fabricated using the AC. The devices could be cycled over 2000 times in the voltage range 0–1.6 V with 98% capacity retention.

2. Experimental details

The CuO nanowires were produced as reported before [35,36] using copper acetate monohydrate [$\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$; CuAc; 99%; R&M Chemicals] and polyvinyl alcohol (PVA; Mw-145000, Merck) as starting materials. In a typical synthesis, CuAc (1 g) was dissolved in 20 ml aqueous PVA solution (7 wt.% PVA in water) thereby forming a 0.63 M stock solution, which was stirred for 20 h at room temperature. The as-prepared solution was electrospun using a commercial electrospinning unit (Electroris, nanoLab, Malaysia) at 0.5 ml h^{-1} and at ~24 kV. The solid fibers were collected at a distance ~17 cm away from the spinneret. The relative humidity of the electrospinning chamber was maintained at ~30%. The as-spun fibers were calcined at 500 °C for 1 h in air to remove polymeric template and allow nucleation and growth of CuO nanowires.

Crystal structure of the material was studied by X-ray diffraction (XRD) technique using Rigaku Miniflex II X-ray diffractometer employing $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Morphology and microstructure of the materials were studied by scanning electron microscopic technique (7800F, FESEM, JEOL, USA). High resolution lattice images and selected area diffraction patterns were obtained using transmission electron microscope (TEM) operating at 300 kV (FEI, Titan 80–300 kV).

Supercapacitor electrodes were fabricated on pre-cleaned nickel foam substrates. The nickel foam was cleaned by degreasing in acetone, etching in 1 M HCl for 15 min, and subsequently washing in water and ethanol for 5 min each. The working electrode was prepared by mixing the CuO nanowires with polyvinylidene fluoride (PVDF) (Sigma Aldrich) and carbon black (Super P conductive, Alfa Aesar) in the ratio 75:15:10. The above mixture was stirred in N-methyl-2-pyrrolidinone for better homogeneity. The as-prepared slurry was then pasted on a nickel foam substrate (area ~1 cm^2) and dried in an oven at 60 °C for 24 h. The commercial AC electrode was also developed similarly. The dried electrodes were then pressed using a hydraulic press at a pressure of 5 ton. Electrochemical properties of the electrodes were studied by cyclic voltammetry (CV), galvanostatic charge–discharge cycling (CDC), and electrochemical impedance spectroscopy (EIS) in 6 M KOH electrolyte. The electrochemical characteristics of the CuO (mass loading ~2.5 mg) and AC (mass loading ~3.8 mg) electrodes were separately studied in the three-electrode configuration. A platinum rod and a saturated Ag/AgCl were used as the counter and the reference electrodes, respectively. A potentiostat–galvanostat (PGSTAT M101, Metrohm Autolab B.V., The Netherlands) employing NOVA 1.9 software was used for electrochemical measurements.

The ASCs were fabricated by assembling the CuO nanowire (anode) and the AC (cathode) electrodes separated by a glass microfiber filter (fioroni) in 6 M KOH. The amount of active materials for fabrication of ACS was calculated based on the charge balance between the electrodes such that the effective capacitance at each electrode is same (see Section 3 for details). A symmetric EDLC comprising of AC as both electrodes was used a control device. The capacitive properties of the ASC were obtained in two-electrode configuration at room temperature using the PGSTAT M101 potentiostat–galvanostat.

3. Result and discussion

The CuO nanowires obtained by annealing the polymeric fiber had a diameter of ~30–50 nm with a dense packing of particles

of size ~10–20 nm (Fig. 1). The CuO nanowires had a monoclinic structure (Space group C12/c_1 , #15) with lattice parameters $a = 4.598 \text{ \AA}$, $b = 3.46 \text{ \AA}$, $c = 5.135 \text{ \AA}$ and $\beta = 99.30^\circ$, which correspond to reported values (PDF Card No.: 45-0937). Detailed analysis of material characterization is reported elsewhere [35].

It is imperative to understand the properties of the pseudocapacitive and carbon electrodes separately for fabrication ASCs for optimum performance. This is because an ASC is equivalent to two capacitors in series whose reciprocal of the effective capacitance is equal to the sum of the reciprocals of the individual capacitances ($1/C_{\text{eff}} = 1/C_{\text{anode}} + 1/C_{\text{cathode}}$). This relation follows that the effective capacitance will be lower than the lowest individual capacitance. Therefore, both electrodes of ASCs should have similar capacitance for maximum effective capacitance [37]. The similarity in capacitance follows a charge balance (as charge $q = CV$) $q_+ = q_-$, where q_+ is the charge stored at the anode and q_- is that at the cathode. The charge on each electrode is given by $q = C_S \times \Delta V \times m$ [38], where ΔV is the potential window, from which the mass on the respective electrode for optimum performance follows [22,37]

$$\frac{m_-}{m_+} = \frac{C_{S+}(\text{PC}) \times \Delta V_+}{C_{S-}(\text{EDLC}) \times \Delta V_-} \quad (2)$$

Although electrochemical properties of electrospun CuO nanowires are reported in our recent publication [35] a comparison with commercial AC was not accomplished for fabrication of ASCs. Fig. 2 compares the electrochemical properties of the CuO nanowires and AC electrodes. Fig. 2a shows the CV curves of CuO nanowire on Ni foam in 6 M KOH electrolyte at scan rates from 2 to 70 mV s^{-1} . It is seen from the CV graph that CuO electrode showed a pair of redox peaks at all scan rates originate from the faradic reaction of the active material indicative of pseudocapacitance. The CVs are almost symmetric, showing good reversibility of the oxidation and reduction process. The shapes of CV do not change as the scan rate increases from 2 to 70 mV s^{-1} , showing the good mass transport and electron conduction within the nanowire and small equivalent series resistance (ESR). The scan rate (v) dependence of voltammetric current (I) is analyzed to determine whether capacitance originates from surface redox or semi-infinite bulk diffusion. The anodic peak current (I_p) linearly varies with square root of scan rate (\sqrt{v}) which indicate that majority of capacitance originate from the semi-infinite bulk diffusion (supplementary information S1). In case of semi-infinite diffusion, I_p can be expressed by the Randle's–Sevcik equation at 25 °C [39,40],

$$I_p = 2.69 \times 10^5 \times n^{3/2} \times D^{1/2} \times A \times C_0 \times \sqrt{v} \quad (3)$$

where n is the number of electron transferred, A is the surface area of the electrode, D is the diffusion coefficient, v is the scan rate, and C_0 is the initial ion concentration. Based on slope of I_p vs v graph and Eq. (3), diffusion coefficients of the electrode material is found to be $1.3 \times 10^{-13} \text{ cm}^2 \text{ s}^{-1}$ which is higher than many such materials [40,41]. The anodic peak in the CV profile shifted towards positive potentials with increase in the scan rate and the cathodic peak to the negative potential on account of the internal resistance of the electrode material. The difference in anodic peak potential (E_A) and cathodic peak potential (E_C) is a measure of reversibility and internal resistance of the material [42]. The difference in potential ($E_C - E_A$) is found to be ~59 mV at a lower scan rate 2 mV s^{-1} . This smaller value indicates that the electrode material is highly reversible and has low internal resistance [43]. This could be attributed to the high diffusion coefficient and excellent electrical conductivity of CuO. The presence of the redox peaks resulted from oxidation and reduction between Cu_2O and CuO, which form the basis of the charge storage, is given by [44–46]

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