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# Fabrication of $Bi_2O_3$||AC asymmetric supercapacitor with redox additive aqueous electrolyte and its improved electrochemical performances

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ABSTRACT

A new asymmetric supercapacitor (ASC) was fabricated using flower like α-Bi2O3as negative and bio-waste derived activated carbon (AC) as positive electrodes with Li2SO4as electrolyte. Here, the fabricated ASC was operated over the potential range of 0-1.6 V and evaluated by cyclic voltammetry (CV), galvano static charge-discharge (GCD), electrochemical impedance spectroscopy (EIS) and cycle life. Further to improve the performance of ASC, KI was used as electrolyte redox additive with pristine (Li2SO4) electrolyte due to their possible redox reactions of iodine ions. Remarkably, a nearly threefold improved specific capacitance and energy density of 99.5 F $g^{-1}$and 35.4 Wh $kg^{-1}$respectively was achieved by adding of KI into $Li_2SO_4$ electrolyte, while it was only 29 F $g^{-1}$and 10.2 Wh $kg^{-1}$for pristine (Li2SO4) electrolyte used ASC at 1.5 mA $cm^{-2}$.

## 1. Introduction

It is well known that Li ion batteries and supercapacitors are the prominent energy storage gadgets in recent years. However, both devices have its own drawbacks like Li-ion batteries having the lower power density (~200 W $Kg^{-1}$) and less cycle life (< 1000 cycles) than supercapacitors (5 kW $kg^{-1}$ and ~10000 cycles). Similarly, supercapacitors (SCs) possess a lower energy density (3 to 7 Wh $kg^{-1}$) compared to batteries (25 to 150 Wh $kg^{-1}$) [1–3]. In order to enhance the energy density in supercapacitors, the asymmetric supercapacitors (ASCs) or hybrid capacitors were established without losing its power performance, since this asymmetric system is fabricated using both pseudocapacitive metal oxide (battery) type electrode (which is able to boost the energy density) for faradaic process and a capacitive carbon type electrode (which is able to boost the power density) for non-faradaic or capacitive process. However the performances of the ASCs in aqueous electrolytes need to be improved because the energy performance is low when compared with non-aqueous electrolytes. Thus recently motivated the researcher to find the innovative approach to improve their supercapacitors performance.

Mostly, the capacitance performances of supercapacitors are improved by varying or using different kind of electrode active materials and the ionic mediums are used as the electrolytes for charge storage in supercapacitors. Recently, an alternative approach is explored that modifying/adding redox active species in to the electrolytes in order to enhance the electrochemical performances [4] and achieved superior capacitance as well as energy density values. Especially, Su et al. [5] has proposed $K_3Fe(CN)_6$ or $K_4Fe(CN)_6$ as the redox additive in KOH electrolyte to increase the capacitance of Co-Al LDH (layered double hydroxide) electrode and achieved the improved capacitance of 712 F $g^{-1}$ and 317 F $g^{-1}$ for KOH + 0.1 M $K_3Fe(CN)_6$ and 1 M KOH + 0.1 M $K_4Fe(CN)_6$ but it is only 226 F $g^{-1}$ for KOH. Later, Roldan et al. [6,7] has improved the performance of the carbon based supercapacitor by using of hydroquinone in 1 M $H_2SO_4$ electrolyte and achieved the three fold of improved capacitance from 320 F $g^{-1}$ to 901 F $g^{-1}$. Then, followed by the above approaches many works are have been reported like indigo carmine [8], sodium lignosulfonate [9], p-phenylenediamine [10], m-phenylenediamine [11], KI [12], $Na_2S$/S [13] and $VOSO_4$ [14] as redox mediators or additives with electrolytes thus interestingly enhanced their capacitance/energy performance of the supercapaciors through redox reaction at electrode/electrolyte interfaces. However, this approach has not been applied so far in ASC, to further improve their capacitance/energy storage performance.

Besides, most of the ASCs are developed using carbon based materials as negative electrode and metal oxide/hydroxides as

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positive electrodes [15] since most of the metal oxides/hydroxide work or show their original behaviour in positive potential window. In contrast, in this work the metal oxide, $Bi_2O_3$ is used as a negative electrode since it involves in the redox reaction within the potential range of 0 to -0.8 V/-0.2 to -1 V as reported elsewhere [16,17] and activated carbon as a positive electrode for ASC because it is well known that carbon based materials can works at either positive and negative potential and there is no chemical reaction occurred in between the electrolyte and electrode. As well as, to the best of our knowledge $Bi_2O_3$ and *Eichhornia Crassipes* derived AC has not been studied in ASC so far. Further, the performance of ASC ($Bi_2O_3/Li_2SO_4$/AC) was improved using KI as redox additive in electrolyte ($Li_2SO_4$).

## 2. Experimental Methods and materials

### 2.1. Materials synthesis

For the preparation of flower like $\alpha$-$Bi_2O_3$, 3.12 g (6.43 mmol) of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 20 mL of nitric acid (4 M). Then, the desired amount of distilled water, isopropyl alcohol and N-methyl-2-pyrrolide were added consecutively into the above solution with continuous stirring. Further, 1 g (5.2 mmol) of citric acid was added. After stirring, 20 ml of NaOH (9 M) was added drop wise till the yellow color precipitate was observed and then the precipitate was kept at 80 °C for 4 h. The resulting yellow precipitate was collected by centrifugation, washed several times with deionized water as well as ethanol and dried at 70 °C for 4 h. Finally, the flower like $\alpha$-$Bi_2O_3$ sample was obtained by low temperature calcination at 400 °C for 2 h.

The activated carbon (AC) was prepared from *Eichhornia crassipes* by $ZnCl_2$ activation as reported by us earlier [12]. Briefly, the dried small pieces of *Eichhornia crassipes* were pulverized and pre-heated at 200 °C for overnight. Then, 20 g of pre-heated sample was activated in 20% of $ZnCl_2$ for 24 h. It was then carbonized at 700 °C for 2 h under Ar atmosphere. The carbonized sample was washed several times using dis. $H_2O$ with desired amount of HCl until the pH reached neutral. The washed samples were dried at 100 °C for overnight.

### 2.2. Characterizations of $\alpha$-$Bi_2O_3$ and AC

The prepared electrode active materials are characterized by various techniques such as X-ray diffraction (XRD, X'Pert PRO PANalytical X-ray Diffractometer with $CuK_\alpha$ radiation), SEM (Quanta 200 ESEM). In addition, the Nitrogen adsorption–desorption measurements were also performed for activated carbon using Micromeritics ASAP 2010 surface area analyzer.

### 2.3. Fabrication of Electrodes/Asymmetric supercapacitors

The positive (AC electrode) and negative ($\alpha$-$Bi_2O_3$ electrode) electrodes for ASCs were prepared by drop-casting method [18]. First, the slurry was prepared by mixing of AC or $\alpha$-$Bi_2O_3$ (20 mg), carbon black (2 mg) and polyvinylidene fluoride (PVDF, 2 mg) in 0.4 ml of N-methyl-2-pyrrolidone (NMP). Then, 12 $\mu$L of slurry was spread onto the stainless steel with an area of 1 $cm^2$ and dried at 50 °C for overnight. The loaded active material on electrode (AC or $\alpha$-$Bi_2O_3$) was calculated to be 0.6 mg (excluding carbon black and PVDF mass). Finally, ASCs (1 M $Li_2SO_4$ or 0.06 M KI added 1 M $Li_2SO_4$) were fabricated as sandwich type electrode, where electrolyte (1 M $Li_2SO_4$ or KI added 1 M $Li_2SO_4$) immersed polypropylene sheet was used as separator.

### 2.4. Electrochemical characterizations of Electrode/Asymmetric supercapacitor

The electrochemical performance of the individual, AC and $\alpha$-$Bi_2O_3$ electrodes were tested by cyclic voltammetry (CV) in 1 M $Li_2SO_4$ using three electrode system (AC or $\alpha$-$Bi_2O_3$ as working electrode, Pt wire as counter electrode and Ag/AgCl as reference electrode). Also, the electrochemical properties of the ASCs were examined through cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance (EIS). Here, EIS measurements were accomplished by applying an AC voltage with 10 mV amplitude in the frequency range of 10 mHz to 1 MHz at open circuit voltage (OCV). However, all the electrochemical tests were carried out at room temperature using Bio-Logical SP150 electrochemical instrument.

The areal capacitance ($C_a$) from cyclic voltamogram was obtained using the follows relations [19],

$$C_a = \frac{\int Idv}{2\Delta VSA} \tag{1}$$

Where, $\int Idv$ is the integral area of CV curve, $\Delta$V is the potential difference, s is the scan rate and A is the area of active material in electrolyte

The cell capacitances ($C_{cell}$) of the ASCs were calculated using the following equation [12],

$$C_{Cell} = \frac{I}{M(dv/dt)} \tag{2}$$

where, I is the applied current density, dv/dt is average slope of the discharge curve and and M is the total mass of the active material in both electrodes.

The real ($C'$) and imaginary ($C''$) capacitance of the electrode is calculated using the following equation [20,21],

$$C' = \frac{Z''(\omega)}{\omega|Z(\omega)|^2} \tag{3}$$

$$C'' = \frac{Z'(\omega)}{\omega|Z(\omega)|^2} \tag{4}$$

Where, $Z'(\omega)$ and $Z''(\omega)$ are the respective real and imaginary parts of the complex impedance $Z(\omega)$, $\omega$ is the angular frequency and it is given by $\omega = 2\pi f$.

## 3. Results and Discussion

### 3.1. Characterization of $\alpha$-$Bi_2O_3$ and AC

The XRD pattern of $\alpha$-$Bi_2O_3$ and AC are given in Fig. 1 (a, b). The diffraction patterns of $Bi_2O_3$ inferred the formation of pure monoclinic crystalline $\alpha$-$Bi_2O_3$ (JCPDS No 041-1449). The prepared AC shows (Fig. 1b) a broad carbon peak between ~20° and ~30°, which indicates that the prepared AC is graphitic carbon with presence of amorphous carbon structure [22]. In addition a small broad peak is also noted about ~44° and is attributed to the presence of $sp^2$ hybridized carbon of aromatic structures in AC [23,24]. The observed two peaks in the Raman spectrum as shown in Fig. 1b (inset) elucidates the formation of graphitic carbon. The obtained band at 1349 $cm^{-1}$ relates to $sp^3$ configuration of D (disordered)-band which is due to the carbon-dangling bond vibration. Another band at about 1562 $cm^{-1}$ corresponds to $sp^2$ configuration of graphitic (G-band) nature of carbon which is due to C = C stretching vibration [12]. Moreover, the calculated intensity ratio ($I_D/I_G$) of D and G bands is 0.98 which is nearly equal to 1. It infers that the prepared AC is graphitic carbon (stacking of $sp^2$ hybridized carbon plane) with less content of amorphous carbon structure (plane defects). The morphology of the $\alpha$-$Bi_2O_3$