



Application of dye sensitized solar cell (DSSC) from dammar carbon - Fe₂O₃ (Iron (III) Oxide) composite counter electrode

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ABSTRACT

Huge interests in usage of organic carbon in preparing counter electrode for DSSC have increased extensively among the researchers. Composite-electrode using hydrocarbon of Dammar (*Canarium strictum*) (D) and Iron (III) Oxide Carbon nanoparticles (Fe₂O₃) were prepared as counter electrode (CE) for DSSC evaluation. Dammar rosin was chosen because of high carbon content and when combined with Fe₂O₃ under oxidation synthesis, the composite was found suitable to become as catalyst in DSSC counter electrode. Therefore, the use of composite electrode in exchange of Platinum (Pt) as a counter electrode is greener approach for DSSC advancement. The low cost organic CE composite was applied on flexible substrate using Blade technique to form thin films on conductor. The DSSC cells were fabricated using CE produced and referred as Pt and D-carbon-Fe₂O₃ for characterization. Thin films embedded in thick film substrate were cured at room temperature (25°C) with eased method approach. The conversion efficiency of the incident-photon-electrical-conversion efficiency (IPCE) was obtained as high as 6.7% for composite D-carbon Fe₂O₃ with fill factor (FF) of 0.64 while Pt system was obtained an efficiency of 6.5% with 0.66 FF. XRD test has revealed that the composite has been broaden from crystalline in structure to semi-crystalline with organic compounds shown in the spectra. The Electrical Impedance (EIS) test was carried out and the electrode performance has shown suitable for conductive catalyst in DSSC counter electrode with conductivity range of 10⁻⁴ S.cm⁻¹.

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1. Introduction

DSSC has becoming a new trail of photovoltaic applications where the technology is now focusing on a low cost energy generation. The adaptation of organic component of counter electrode was applied where D hydrocarbon was used. The low cost electrode as an alternative material of DSSC electrode from scarce material (Pt) was going to be replaced. D hydrocarbon was used in preparation of counter electrode from similar research in Alpine rosin carbon for mole-enhanced oxidation-composite. D carbon/ Fe₂O₃ were synthesized into an electrode to become a conductive catalysts and mediator electron mobility system. DSSC using hydrothermal process added with pyrolysis post-processes to form D carbon/Fe₂O₃ (CE1) composite

was obtained for photovoltaic performance of counter electrode. The composite of CE1 electrode was synthesized and further pyrolyzed for obtaining higher activated surface area of carbon-conducting material. The electrode to replace Platinum as catalysts is now as proposed (Abdin et al., 2013; Chandrasekaran et al., 2011; Chen et al., 2009).

The efficiency or IPCE for D carbon-composite (CE1) was evaluated. DSSC performances as properties of counter electrode were improved using CE1 with lower resistance of redox electrolyte and more stable system of catalytic material. In comparison, conventional counter electrode using Pt has degrading terminal contacts due to corrosive nature of metal-electrolyte corroded contacts (Ren et al., 2013; Xia et al., 2011). The electro-chemicals of DSSC were characterized for conductivity study using electrical impedance analysis (Chou et al., 2009; Huang et al., 2007; Grangvist et al., 2007). CE1 composite has given stabled heterojunction properties of photo electrochemical device and the electrode properties were further improved by sub-composite of transparent conducting polymer

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substrate for mobilizing electron more effectively. The efficient electron mobility enhances the regeneration of the electrochemical redox as well as reduces recombination properties (Lee et al., 2011; Li et al., 2014; Maçaira et al., 2013; Mekprasart et al., 2010)

2. Methodology

2.1. Preparation of organic carbon composite, CE1

CE1 composite was synthesized by using chemical reaction of hydrothermal process using solvent (Acetonitrile) with concentration of 0.3M and carbon composite with overnight stirring. The contained-weight compositions with ratio of 5:1 (Carbon: D) was further ball milled at 1200 rpm for 1 hr using the 1mm beads by planetary ball mill (Fritsch). The samples prepared were further sintered at 120 °C to eliminate solvent. The precipitated material obtained was further pyrolyzed under Nitrogen inert chamber at 500 °C and obtained carbon composite of CE1. The carbon sources (CE1 and Fe₂O₃) were made into ink-paste and applied onto a peel able polyurethane substrate to obtained a uniform thin film on transparent conductive component and left to dry for 8 hours. The samples were further heated at vacuum oven at 120 °C until dry thin film (50µm) of each samples were obtained.

2.2. Preparation of the photoanode (TNP-N719)

The photo anode of the TNP-N719 was prepared on the conductive glass of Flourine-doped tin-oxide (FTO) from Solaronix SA with conductivity of 7 Ohm.cm⁻² with care of pre-treatment. The cleaning with sonification in distilled water and alcohol mix was to clean the conductive surface on FTO without damaging the conductive coating. The FTO glass was dried in dry-chamber overnight to ensure cleaner substrate before further preparation. The Dye-incorporated Titanium dioxide (TNP) (Sigma Aldrich - 99%) paste ink was prepared. Ink composition of TNP-N719 (Di-tetrabutylammonium cis-bis (isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) Ruthernizer (Solaronix SA)) was applied to combine photo catalyzer and sensitizer dye into a single step process. The simpler process preparation for the active layer films of DSSC system was prepared on the pre-treat FTO glass previously prepared. The ink paste was applied onto prepared FTO glass using Blade technique and left to dry in vacuum oven with 120 °C for 2 hours. The preparation of TNP-719 of the photo-active layer film was prepared with molarity of TNP: N719 ratio of (1:0.0001) M.

2.3. Preparation of the counter electrode

Dammar resin was obtained from local supplier and placed in a vacuum oven to dry the sample at 60 °C. The synthesized D carbon- Fe₂O₃ composite was pyrolyzed at fix-bed reactor with Nitrogen inlet for 1 hr at 500 °C and quenched at room temperature to obtain an activated carbon of CE1. The black reddish residue was made into an ink paste and was applied onto Polyurethane flexible substrate with conductor embedded (metal-Poly Ethylene Oxide-PEO) and left to become thin film of CE1. The electrode was then further sintered in vacuum oven at 120 °C. The counter electrode was now ready for DSSC fabrication as a composite counter electrode. Another electrode thin film was also applied on the substrate from activated carbon Fe₂O₃ (FEO) film for comparative study. The conducting PEO used was hybridized with Copper (Solaronix SA) mix incorporating conducting polymer and metal as conductors. All samples were left to dry in vacuum oven and prepared using solution casting method at room temperature of 25 °C.

2.4. Preparation of electrolyte (Redox system)

The Acetonitrile (0.3M) was used as base solution from previous work as reviewed (Chou et.al, 2009) and the electrolyte was then mixed in the ratio of 1:1 of KI or NaI respectively and stired overnight. Additionally, Iodide (I₂) of molarity of 0.01M was mixed with the resulted electrolyte to obtain the Redox system which consists of I₃⁻/I⁻ for the oxidation-reduction mechanism of electron (e) permeability. The hoping placement of e in band gap energy system was made for the gap energy properties which operate within the redox system as flow of potential design. Acetonitrile with added functional salts as cations provided medium of electron movement and exchanges iodide ion provide the more complete redox oxidation-reduction process. The gapping engineering of electron available made flow of e to outer circuit of the device via the electrolyte/electrode system prepared for more electron density from resulted e-permeability.

2.5. Fabrication of DSSC cell - Hybrid DSSC FTO/Cu-PE

The photo anode TNP-N719 component prepared and CE1 counter electrode were ready as sample of electrodes for producing a complete DSSC cell. TNP-N719 where incorporated with FTO glass that was lay flat on surface. A few drops of electrolyte were placed onto the coated area and the ready adhesive CE was prepared. The incorporation of FTO/TNP-N719/Electrolyte/CE1/PU into a sandwiched type cell was made. DSSC Polyurethane cells were ready as a device of conductor FTO/metal/polymer substrates system. The FEO and CE1 device of thin films incorporated were fabricated. The formed sandwiched electrode/electrolyte/electrode system as DSSC system was ready for electrical study. The systems were aluminium-wrapped and stored in a

dark room and the structure of cells was as figured in Architecture A as a complete cell operation (Fig. 1).

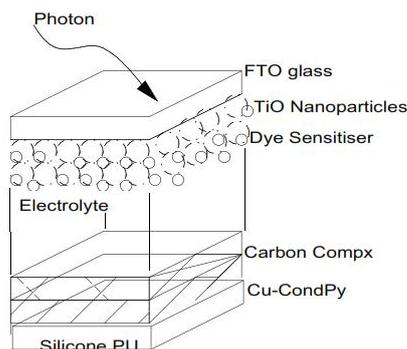


Fig. 1: DSSC Architecture A: A complete cell for DSSC operation

2.6. X-Ray diffraction spectroscopy of FEO-carbon film

XRD characterization was employed to investigate the crystalline structure and other chemical changes in the electrodes. The diffract gram of samples were used to study the crystalline nature of electro catalytic and permeability module of electron. The conductivity of the electrode composites CE1 was specified by the chemical structures and semi crystalline organic structure of the derived composites.

2.7. Electrical Impedance Spectroscopy (EIS)

EIS was carried out to study the internal resistances and charge transfer properties of the electrodes. Electrode samples of cured film of Fe_2O_3 and CE1 composites were placed in a sample holder with conductors fitting (3-electrodes system) for undergoing the frequency response analysis. NaI was used as the base electrolyte or as Reference electrode. The EIS test revealed frequency response analysis for evaluating the bulk resistance and circuits system involved in the analysis. Bulk resistance, R_b is the overall conductivity behavior and the equivalent circuits involved were analyzed. The EIS was evaluated by using Nyquist plot where obtained frequency response trend was used for evaluating conductivity of the electrode system. The accelerated response of EIS measured conductivity of samples containing composite using Hioki Impedance Spectroscopy at 25°C .

2.8. Thin film characterization

The activated carbon of reddish organic composite material was evaluated using field emission scanning electron microscopy (FESEM) for structural and morphological study. For comparative electrode performance study, CE1 and Fe_2O_3 composites were evaluated as thin film counter electrode system. Film morphology was characterized to view structural characterization

property of Nano-morphological aspects. The Nano-structures enhanced CE composite in the electrodes material of which structure hopping of electron is being explained. The porous structure of composites analyzed explained electron hoping mechanism by electron tunneling in the porous molecular structure. The study of the relationship between Fe_2O_3 and CE1 interactions between molecular interfaces were analyzed

2.9. Incident photon-to-current conversion efficiency (IPCE) analysis

The current-to-voltage or J-V curve of the DSSCs with CE1 and Pt counter electrodes were measured under a light intensity of $100 \text{ mW}\cdot\text{cm}^{-2}$. The CE1 and Pt electrode performances were viewed with respected conductivity and evaluation of respected photovoltaic cell's performance. The IPCE was calculated using the following formula with a symbol η (IPCE) is defined as:

$$\eta = (J_{sc} \cdot V_{oc} \cdot FF) / I_0$$

where J_{sc} is the short circuit current, V_{oc} , the open circuit voltage, FF, fill factor and a solar photon flux spectrum (A.M 1.5) with value of $100 \text{ mW}\cdot\text{cm}^{-2}$ (Chou et al., 2009; Chen et al, 2009; Maçaira et al, 2013; Li et al, 2014).

3. Results

Effects on D carbon composite as DSSC system utilizing CE1 were indicated. The composite electrodes on electrical conductivity and its differentiated Pt/CE1 conversion efficiency characteristics were viewed. The properties of the conductivity evaluated by EIS has resulted R_b value evaluation for Fe_2O_3 and CE1 respectively. The efficiency of photovoltaic conversion (IPCE) application was determined for Pt and CE1 for photoelectron photo-electron performance for the carbon counter electrode produced. The investigated structures and corresponded electrical conductivity was also reviewed as additional relationships to performance.

Photocurrent performance or J-V curve of the DSSCs with CE1 and Pt composite were measured under a light intensity of $100 \text{ mW}\cdot\text{cm}^{-2}$. IPCE of Pt and CE1 electrodes performance were to view corresponded performance of photo-conversion efficiencies of both specified electrodes. The IPCE of this study indicated that the performance of CE1 was comparable to the Platinum as counter electrode performance. The CE1 carbon composite electrode functioned comparative performance with metal (Pt) catalytic material of the electrodes. The conductivity of composite of hydrocarbon CE1 showed conductivity with superior catalyst system was successfully applied as counter electrode. IPCE of both composite electrodes were achieved at 6.3 and 6.7% respectively and CE1 counter electrode produced for Pt replacement has now being proposed as successful.

3.1. XRD characterization

The broad spectral view of electrode material was shown in CE1 and formed a stable hybrid metal-organic-system composite film. The chemically synthesized hydrocarbon D is expected to improve the electrode catalyst system since higher carbon content of oxidation as provided in the semi crystalline structure. The study of interactions between molecular interfaces was analyzed where pattern of CE1 material prior of synthesis process showed highly crystalline catalytic material. On the other hand, high semi crystalline organic composite structure was obtained for the synthesis material of CE1. Conductivity of electrode materials were cross-referenced in XRD analysis and indicated that chemical structure has been broadened significantly through oxidized composite material (Fig. 2).

The CE1 has shown broad semi-crystalline structure as the catalyst electrode. The XRD spectra have showed distinctive materials of broad aspects of nature-derived composite as indicated. The figures in CE1 carbon showed semi crystal structures with peaks as illustrated in Fig. 2(a). Peaks of original Fe_2O_3 (a) is highly crystalline in nature and the chemically broaden peaks existed for functional composite as shown in Fig. 2(b). These showed complex organic structures of CE1 have significant differentiation with natural structure of Fe_2O_3 . The carbon chemical-oxidation showed conductive organic-carbon composite thin film of electrode produced. The highly conductive CE1 was essentially due to more conductive electron tunneling of complex organic material. The composite material was identified as indefinitely high carbon organic complex of composite material.

Morphological view was conducted using Field Emission Scanning Electron Microscopy (FESEM) and showed nanoparticles structure of metal-organic composite was suitable for elect catalyst. The porous

nature of electrode obtained supported more of electron-hop mechanism achieved by Nano technological development.

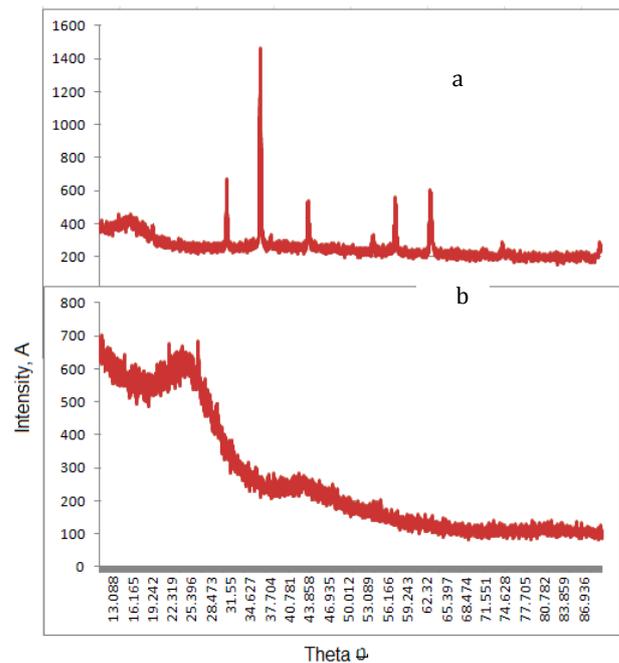


Fig. 2: XRD patterns of sample (a) Fe_2O_3 and (b) CE1

The Nano size of the molecules provided more Nano-porous structure indicating more electron interface for conductivity. The porous structure was needed as an efficient electron transfer tunnels provided by CE1 composite for DSSC application. The electrodes carbon labeled FEO was another composite reviewed and structure of Nano-particle material advances electron permeability in electrode material as viewed in Fig. 3. Sample of activated carbon of palm kernel cake (PKC-AC) was also viewed as comparative study.

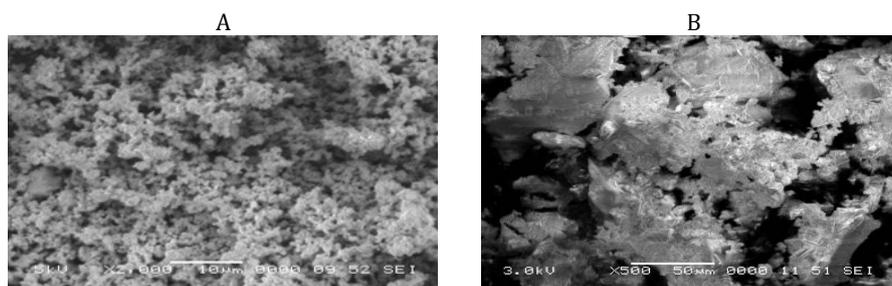


Fig. 3: Morphology images of Fe_2O_3 (A) and CE1 (B)

3.2. The effect of hydrocarbon-FEO/CE1 composite's conductivity

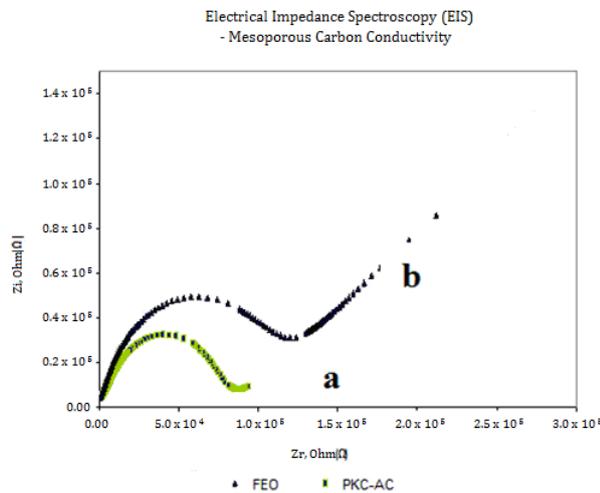
Electrode conductivity of organic composite material was observed by using EIS and from the frequency response analysis, the mechanisms of electron transport system of the composite was analyzed. The different addition of carbon composite in CE has determined unique conductivity of the electrode. The impedance plot characteristics presented in Fig. 4 showed a frequency response of

Fe_2O_3 and activated carbon from PKC-AC. The result showed that the quality of the conductivity from the value of Rb was varied with different type of composite used. The conductivity shown in figure of carbon composite was viewed in Fig. 4(a). The respected Rb of the analysis was obtained from the admittance value of conductivity (σ) and was calculated according to equation:

$$\sigma = t/(A.R_b)$$

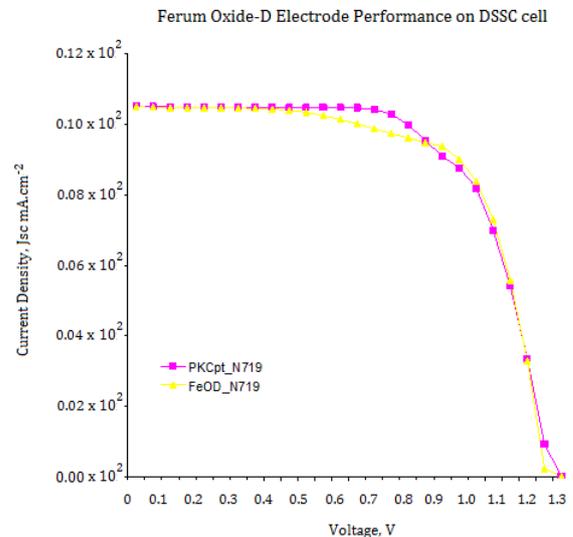
Where t and A is thickness and area respectively while R_b is the bulk resistance of the admittance value of impedance plot analysis.

From the Fig. 4(a), the value of conductivity was higher for PKC-AC composite compared to FEO composite. It was proven that organic composite



(a)

when prepared with synthesis activation of energy may performed as catalyst for electrode system as shown and the value of the conductive composite was conducted from the admittance plot for each composited materials.



(b)

Fig. 4: Impedance Plot of (a) Fe_2O_3 and (b) CE1 counter electrode efficiency performance

The IPCE of electrode material plot was viewed as in Fig. 4(b) and found respected conversion efficiency values. The conductivity value obtained for CE1 as electrode was a better performance of IPCE with a conversion of 6.7%. The compared composite studied (Pt) electrode has shown a comparable performance as shown in Fig. 3(b). The trends of IPCE plot determined proven the performance and also as indicated in EIS. The performed material is increasing in conductivity of CE composite system determined with respected organic electrode composite used. CE1 carbon has been identified as good electro-chemical composite which post good catalytic in electron transport system for DSSCs.

4. Conclusion

The results indicated that Dammar when combined with metal oxide of Fe_2O_3 composite electrode has produced good photovoltaic cell performance of counter electrode in DSSCs. The IPCE for counter electrode depends on the type of carbon/metal oxide used and also the organic composite material used in the electrode. Activated carbon was also found suitable for counter electrode which obtained from pyrolysis of Palm Kernel compound (PKC AC) and was used as source of carbon compositions. Photovoltaic performance (IPCE) is depended on electrode's conductivity in which the composite properties have played a significant role as counter electrode. CE1 composite was able to performed functional material as electro-catalysis composite comparable to Pt as electrode for

solar cell. The conductivity of catalytic behaviour in composite material of the Fe_2O_3 and CE1 composite electrodes was found in the range of good conductivity of $(1.2 \times 10^{-5}) \text{ S.cm}^{-2}$. IPCE of CE1 has resulted good catalytic electrode with the conversion efficiency of 6.7% with fill factor (FF) of 0.64 while Pt system efficiency of 6.5% with 0.66 FF were obtained. XRD revealed that the composite has broad shown spectra of chemical structure as the semi-crystalline (organic). The performance of organic hydrocarbon composite modification has obtained good CE carbon composite with best conductivity performance suitable for new DSSC counter electrode system.

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