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Application of Carbon Nanotubes, Cobalt and Molybdenum in a Dye-Sensitized Solar Cell

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Abstract: Continuous improvements to the performance of dye-sensitized solar cells (DSSCs) are sought after and alternative to the expensive platinum in the counter electrode is a major component to be considered. This study investigated the effect of applying molybdenum, cobalt and multi-walled carbon nanotubes (MWCNT) nano-powders to the counter electrode and MWCNT onto the photo anode at 1:1 wt.% with TiO2 and as a CNT stand-alone catalyst in the anode. Prepared catalytic pastes were directly applied onto the glass substrate by rolling a glass rod until evenly distributed within the active area of 1.4 cm^2. Dried impregnated TiO2 and CNT (photo anode) pastes and catalysts platinum, cobalt, molybdenum, CNT and various combinations in the counter electrode, the DSSCs were assembled and tested for respective performance. To calculate maximum power output, corresponding measured voltage and current for each DSC were recorded. Current-voltage and voltage-power graph were plotted and performance in terms of efficiency was calculated. It was found, based on the comparison of efficiencies that CNT saturating the catalyst films in photo anode was found to not produce power. It is still best to use TiO_2 as the conduction base in the photo anode; CNT can only be used as a dopant. With pureTiO2 in the anode, DSSCs with electrodes having tandems of Molybdenum-CNT and Cobalt-CNT at 1:1 wt.% were found to give highest efficiency, about 10 times than that of the platinum-based counter electrodes. These two DSC type also outperformed the other DSCs in terms of the cost to performance ratio on a laboratory setting.

Key Words: Dye-sensitized solar cell; carbon nanotube, molybdenum, cobalt, titanium oxide

1. INTRODUCTION

Alternative renewable and sustainable resources such as solar energy are gaining attention due to tremendous promise to trim down fossil fuel usage and carbon dioxide emission. Silicon-based is the leading solar cell type, however, its being expensive and Silicon's low-abundance, results to researching for possible competitor. One of the

promising and relatively inexpensive considerations is the dye-sensitized solar cells (DSSC) due to its cheap and eases of fabrication, being light, portable and flexible. DSSC is based on the concept of charge separation at an interface of two materials of different conduction mechanism (Graetzel, 2003).

The current structures for DSSCs are composed greatly of titanium oxide (TiO2) in the photo anode and platinum in the counter electrodes. These materials are prevalently used due to the efficiency and suitability as catalysts. Breakthrough on nano-technologies advances the production of more nano-materials that when applied to the existing DSSC components, yield better and higher efficiency. One interesting material to be added to DSSC is the carbon nanotubes (CNT), both in the photo anode and counter electrode. Molybdenum and cobalt having close similarity on electrical conductivity with Platinum are also considered to be possible replacements for platinum, a rare and expensive metal, in the counter electrode.

The objectives of this study include determination if cobalt and molybdenum and its respective tandems with CNT are competent with the platinum based counter electrode; identification which DSC combination, after replacing a component in the electrodes, will result to highest voltage and power output, and; test the performance of each fabricated DSC.

2. METHODOLOGY

2.1 Materials

Titanium dioxide (TiO2), used as catalyst in the photo anode, is naturally photo-electrochemical in nature. Its nanocrystalline structure serves as a matrix for sensitizing dyes. The high surface area of the semiconductor TiO2 layer allows adsorption of large number of dye molecules sufficient for effective light harvesting. The substrate used to support both the photo-anode and the counter-electrodes is indium tin oxide (ITO) doped glass. This is a transparent, electrically conducting glass. The ability of TiO2 to to attach well to the ITO layer improves electron dispersion to the ITO layer and diminishes recombination of photogenerated electrons with the triiodide species (Krasovec et al. 2009).

For the counter electrodes, platinum, cobalt, molybdenum and CNT nanopowders were considered. Generally, these materials used as catalyst in the counter electrode, have excellent electrical properties and have great electrocatalytic activities.

The ITO-doped glass substrate allows approximately 90% of incident light to percolate through the substrate and at the same time, gathering the diffused electrons from the TiO2 film and conducting it outward to an external load.

Halogen lamp, having a continuous spectrum near ultraviolet to infrared, similar to that of the sun (black body radiation) was used as the light source during the testing of the DSCs.

N3 dye was applied as the sensitizer while iodide/triiodide is the redox couple in the electrolyte. Both are reportedly the best among the dye and redox couple selections for DSC researches.

2.2 DSSC Fabrication and Testing

This study has five stages: 1) preparation of dye solution and the electrolyte; 2) preparation of the TiO2 with or without CNT paste and impregnation to photo anode; 3) preparation of the metal catalysts paste and application to the counter electrode substrate; 4) DSC assembly, and; 5) testing and performance calculation.

10, 20 and 30 mg of N3 dye was dissolved each in 50 mL ethanol and then kept separately in bottles. Electrolyte was prepared by mixing 0.5M lithium iodide and 0.05M iodine in acetonitrile and then stored in a dark bottle.

A 5% acetic acid was gradually added into a pre-weighed 6 grams of Titanium (IV) oxide (TiO2) powder. Addition of 0.5 grams of polyethylene glycol (PEG) and a drop of Triton X-100 was added and mixing was continued using magnetic stirrer until consistency of the slurry became thick. For the CNT-TiO2 and pure CNT slurry preparation, similar process was employed, except 50% of TiO2 weight was replaced with 50% wt. for MWCNT and on the other, TiO2 was completely removed for the pure CNT photo anode DSC. The paste was impregnated onto the conductive side of the ITO glass, limited to

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the 1.4 cm² active area bounded and guided by scotch tapes on the four sides, heated for 30 minutes on 450 °C hot plate, then air-cooled, and submerged into dye solution for 30 hours.

As was done by Chen et al. (2010), CNT, molybdenum, cobalt and platinum nanopowders were dissolved in deionized water and ethanol and applied with Triton-X 100 for dispersion. 250 mg each of CNT, cobalt and molybdenum and platinum nanopowder was mixed with 5mL deionized water and 5 mL ethanol. For the CNT-metal combinations, 125 mg of CNT and 125 mg combination metal was applied. All these were then ultrasonically dispersed for an hour using a sonicator based on the CNT electrode preparation of Ramasamy et al (2008).
Another method employed platinum-based electrode where 10 mM PtCl4 and 0.05 M of HCl was prepared following the method used by (Chen et al, 2010). To check if there is difference in using PtCl4 and platinum nanopowder, another counter electrode catalyst was prepared following Chen's procedure but used platinum nanopowder instead of PtCl4. Each prepared pastes were then deposited to an active area of an ITO glass via. The steps undertaken for the deposition was the same as in the photo anode colloids deposition process. Each counter electrode was also heated for 30 minutes under 450 °C hot plate temperature.

Assembly of the DSC was done by putting active areas of the photo anode and counter electrodes in contact with each other. Parafilm spacer surrounded the active area to avoid short circuiting of the system. Binder clips held together the glass substrate while alligator clips were clamped at each edges of the anode and electrode. The prepared electrolyte was applied onto the assembled DSC prior to testing and evaluation.

Each fabricated cell was evaluated immediately after its assembly to maximize electrolyte before it dries up. Solarimeter, used to measure light irradiance, was positioned beside the tested cell, both equidistant to the light source and was positioned and tilted facing the halogen lamp where irradiance is at its maximum. Alligator clips were attached to the electrodes, negative part is at the counter electrode, and the electrical set-up in Figure 1.1 was configured. To get the current and voltage readings, millivolt meter and micro ammeter were used. The variable resistors were first set to get a reading of zero ohms. The corresponding current at zero voltage and resistance was recorded as Isc. Finding the value of Voc was done by disconnecting the resistors from the system. Resistors were re-attached and varied and corresponding current and voltage were recorded until maximum resistance or zero current was reached. I-V and P-V curves were graphed for each tested cell and fill factor and efficiencies were also calculated. Comparison of the cell performance was conducted and was variations were statistically supported by one-way analysis of variance (ANOVA).

The performance of the DSSC was determined. The most important performance descriptor for a photovoltaic cell is the current-voltage (I-V) plot. To measure current and voltage, electrical set-up as in Figure 1.1 is to be established.

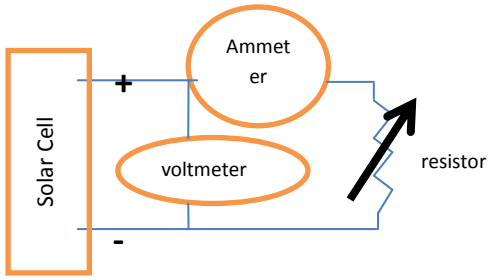

Figure 1.1 DSSC Testing Set-up.

Digital multi-meters, micro ammeter and millivolt meters, are used to accurately capture the minute readings during testing of DSSC. Applied onto the system are varying amounts of single-turn potentiometer where varying resistance of the system becomes possible to provide equivalent voltage and current measurements. Power is then calculated and is the product of voltage and its corresponding current. Highest power calculated was noted.

2.3 Design of experiment

Taguchi $L_9 3^4$ array orthogonal array was initially the proposed design of experiment meant to be used in this study to provide near optimal design parameters. However, given the results of the

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Taguchi analysis (first batch of fabricated DSC), it was deemed necessary to conduct second batch of fabricated DSC and analyse using One-way analysis of variance (ANOVA). The ANOVA applied was to determine whether there is significant difference among the eight assembled DSC.

3. RESULTS AND DISCUSSION

The actual experimentation involved two batches: Taguchi Array Experiment and verification experiment. The Taguchi Array Experiment (first batch) is composed of 9 fabricated DSC while the verification experiment (second batch) has eight different solar cells and was fabricated as a follow-on experiment to the Taguchi Array Experiment results.

The first batch of DSCs had the following compositions following the Taguchi design with the respective calculated efficiencies.

Table 1. Taguchi Array Experimental Results

DSSC Type	Photo Electrode	Counter Electrode	Dye Con'c Mg dye: 50mL EtOH	Cal'd Power, mW/cm^2
1	TiO_2	Pt	10	$4.04E10^{-3}$
2	TiO_2/CNT	Pt/CNT	30	n.d
3	CNT	CNT	20	n.d
4	TiO_2	Mo/CNT	20	$4.61E10^{-4}$
5	TiO_2/CNT	CNT	10	n.d
6	CNT	Mo	30	n.d
7	TiO_2	CNT	20	$1.70E10^{-5}$
8	TiO_2/CNT	Co	10	n.d
9	CNT	Co/CNT	30	n.d

Calculated efficiencies of DSC types 1, 4 and 7 are 0.011%, 0.00166% and 0.000046%, respectively. It is apparent that DSC types 2, 3, 5, 6, 8 and 9 had non detectible (n.d) power output and they commonly have 50% or 100% CNT in the photo anode. CNT is likely not sensitized by the dye molecule possible because the band gap of CNT is higher compared to the energy of the excitons, thus electrons in the highly concentrated CNT were not excited and released. In addition, it could be due to the low dye adsorption capacity of the CNT and that CNT's optical absorption property competes with dye's light harvesting capacity thereby reduced solar conversion efficiency of the dye. With these three successful results, mean effect for each of the four factors were calculated and showed that ideally, 100% TiO_2, 100% metal using platinum at 10 mg dye concentration is the optimum combination in a DSC system. However, since only three of nine DSCs provided power output, data cannot singly be a basis to draw a conclusion. Hence, another set of DSC were fabricated having eight varying counter electrode components but fixing 100% TiO_2 in the photo anode and using 20 mg dye concentration, results presented in Table 2.

Table 2. Verification Experimental Results

DSSC Type	Trial 1 Max Power, mW/cm^2	Trial 2 Max Power, mW/cm^2	Average Max Power, mW/cm^2	Efficiency, %
TiO_2 - CNT	0.033	0.026	0.029	0.0635
TiO_2 – Mo	0.007	0.005	0.006	0.0137
TiO_2 – Co	0.006	0.005	0.006	0.0133
TiO_2 – Co/CNT	0.049	0.045	0.047	0.0982
TiO_2 – Mo/CNT	0.052	0.044	0.0488	0.10025
TiO_2 – Pt	0.004	0.003	0.003	0.00745
TiO_2 – Pt/HCl	0.030	0.021	0.024	0.0489
TiO_2 – $PtCl_4$/HCl	0.007	0.008	0.008	0.0183

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From Table 2, calculated maximum power in trial 1 is generally higher than in trial 2. The reducing power over time is attributed to the drying up of electrolyte due to prolonged exposure to the light. It is likely that because of the 2 cm x 2 cm size of the test cell and no sealant were applied on all sides, electrolyte evaporates/escapes rapidly out of the system, weakening the electron recombination in the redox couple.

Calculated average power and efficiency were consistently highest at DSC with counter electrode tandem Co/CNT and Mo/CNT. Cobalt, classified as a ferromagnetic material, is characterized to have an unbalanced electron spins near the nucleus where the electron spins generate a charged field (http://www.thecdi.com/cdi/images/documents/facts/COBALT_FACTS-Magnetic_Alloys.pdf). This charged field accelerates electrons to move to the conduction band. Given that CNT is both a conductor and a semiconductor, the band gap is narrower, increasing the rate and density of electron flow. This, along with the strong attachment of Cobalt nanoparticles to the walls of CNT, likely influenced the electrical conductivity of the counter electrode catalyst. The more electrons are given off from the counter electrode, the more electrons become available to the electrolyte and regenerated back to the TiO2 photo anode, then higher voltage and amperage output.

Molybdenum atom bonds and interacts with CNT strongly and involves significant charge transfer because Carbon atoms tend to approach the Mo atoms, interaction energy of this was calculated to be at ~3.5 eV, carbon-molybdenum strong coupling or bond is identified as the metal-induced gap states (Dag., S, 2003). From the work of Garcia-Fuente et al. (2013), molybdenum monoatomic wires encapsulated in carbon nanotubes "showed that bonding between transversal orbitals of Mo and the p orbitals of the C atoms leads to electronic charge transfer towards the Mo orbitals", thus, molybdenum tends to lose charge when inside a carbon nanotube.

The improved electron densities in the counter electrode for Co/CNT and Mo/CNT could have influenced the electron regeneration of the electron-acceptor in the electrolyte which in turn, donates back to the photo anode.

Zhu et. All (2009) and Choi et al. (2010) both reported that CNT counter electrodes compete or had higher efficiency that platinum electrode. This supports the results why CNT performance was higher than the platinum-based electrodes. Its combination with either cobalt or molybdenum intensified the efficiency due to the respective characteristics of these two metals.

The over-all efficiencies for this study are relatively lower compared to the reported literature efficiency of between 3% and 11%. This may be attributed to the usage of the halogen lamp as the energy source. While the other studies with higher efficiencies used the standard testing condition for DSSC set at 1,000 W/m2 (1 sun),. temperature of 25 °C, air mass 1.5 (AM 1.5) spectrum, the halogen lamp used in this study is equivalent to the range of 400-513 W/m2, AM and temperature not considered. Another reason is the size of the test cell possibly affecting and limiting light collection.

Statistical analysis tool Minitab 15 used to do ANOVA at 95% confidence being the second batch of DSSC have one dependent (efficiency) and eight independent variables (varying eight DSC type). It suggests that the efficiency means of Trial 1 and Trial 2 are significantly the same, meaning the mean efficiency is statistically equal in both runs and possibly the replicates do not have significant interference during the testing conditions. Significant difference among the efficiency means of the eight DSC's suggests that the eight solar cells are statistically different from each other.

4. CONCLUSIONS

A major finding from this study is that DSSC's with large amount of CNTs onto the photo anode did not produce detectable power output. Although previous

related studies suggested possibility of CNT being added onto the electrode, doping or minute amount will make it work but not increasing it more than 0.3 wt. % or worse by fully replacing TiO2 with CNT. Application of CNT to the photo anode was found to hinder electron excitement and movement since this material is not highly sensitized by the N3 dye. Cobalt and molybdenum were found to be great alternatives to both platinum and CNT as catalyst in the counter electrode. Based on the results of the experiment, application of molybdenum and cobalt as an alternative to CNT and Platinum to DSSC counter electrode supports electron regeneration for the solar cell electrical system. The highest calculated power was recorded at the molybdenum/CNT and cobalt/CNT electrodes. These combinations outperformed as well the efficiency of the other fabricated solar cell. Maximum recorded efficiency was at 0.10025% followed by 0.0982% and 0.0635% for TiO2-Mo/CNT, TiO2-Co/CNT and TiO2-CNT, respectively. These two DSC consistently tops even considering the cost to performance ratio, on a laboratory scale level.

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