Flexible thermoelectric films from electrodeposited Bi$_2$Te$_3$ on recycled carbon fibre- Modulation of Seebeck coefficient by electrode pre-treatment

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Abstract. Recycled carbon fibre (RCF) sheets were electrodeposited with bismuth telluride (Bi$_2$Te$_3$), a state-of-art thermoelectric compound, to produce an n-type thermoelectric module which serves as a precursor to the development of a flexible thermoelectric module. The primary objective of this study is to determine the effects of electrode pre-treatment on the Seebeck coefficient and surface morphology of the RCF electrode. The RCF electrode pre-treatment methods include solvent cleaning via isopropanol, electrochemical polarization using phosphate buffer solution (PBS), and thermal annealing at 350°C with 5% hydrogen in argon gas. The main thermoelectric property, the Seebeck coefficient, which is a measure of the magnitude of an induced thermoelectric voltage due to the thermal gradient across the material, is reported. The surface morphologies and elemental composition of the post-electrodeposited carbon fibres were also studied and reported by Scanning Electron Microscopy (FESEM) and Energy Dispersive X-ray Spectroscopy (EDX). Electrochemical polarization method yielded -13.38 μV/K in Seebeck coefficient compared to -12.23 μV/K of control sample. Solvent cleaned and heat treated samples have lower Seebeck coefficient values of -10.70 μV/K and -10.71 μV/K respectively compared to control sample. SEM images show promising surface properties improvement of the electrodeposited RCF which have been subjected to pre-treatment.

1. Introduction

The use of carbon fibre in many industries, such as the aerospace and automotive industries, has risen lately due to its high specific strength and stiffness. However, carbon fibre is non-biodegradable and non-photodegradable, which makes it difficult to be disposed of. The introduction of the Landfill Directive (1999/31/EC) which bans carbon fibre from landfill disposal, hence leading to increased disposal costs of carbon fibre, has added to the need to recycle carbon fibres$^{[1]}$. As the strength of...
carbon fibre will be reduced due to the degradation of the fibre as a downside of recycling, hence, making its reuse to be very limited in critical load bearing applications\[^{[3]}\].

One such promising applications for re-using recycled carbon fibre (RCF) is the use of it as thermoelectric module as RCF is flexible, mechanically robust while exhibiting low electrical resistivity. Nevertheless, RCF alone possesses substantially low Seebeck coefficient, which could be easily tampered by depositing thin films of bismuth telluride (Bi\(_2\)Te\(_3\)) on its surface. Bi\(_2\)Te\(_3\) is a widely studied thermoelectric material owing to its high room temperature thermoelectric properties, electrodeposited Bi\(_2\)Te\(_3\) achieved a power factor of 1.97 mW/K\(^2\)m with a Seebeck coefficient of -188.5 \(\mu\)V/K\[^{[3]}\]. Electrodeposition is chosen as the best technique due to its many advantages such as low operating cost, large-area coverage, ambient temperature process, and relative ease of controlling film composition and thickness \[^{[4]}\]. In the past a few research works have successfully electrodeposited Bi\(_2\)Te\(_3\) films on RCF \[^{[1][5][6]}\], all of these research works have emphasised on the optimisation of the electrodeposition and post deposition process parameters to improve the Seebeck coefficient of RCF. However, no prior work has reported the effect of RCF electrode pre-treatment on the Seebeck coefficient. The recycling process may result in carbon fibre having decreased activity in active sites, decreased sensitivity to electrolytes or contain contaminants which could be removed via electrode pre-treatment. The reaction kinetics of an electrodeposition mechanism is governed by the interaction between electrode surface and electrolyte, therefore the removal of these contaminants could enhance electrochemical reactions. Pre-treatment methods performed in this study include solvent cleaning, heat treatment, and electrochemical polarization. This research work aims to study the modulation of Seebeck coefficient via pre-treatment techniques and also report the subsequent effect of pre-treatment techniques on the surface morphology and elemental composition of Bi\(_2\)Te\(_3\) electrodeposited RCF electrodes.

2. Experimental methodology

2.1. Materials

Recycled carbon fibre sheets was made from poly-acrylonitrile (PAN) and obtained from Recycled Carbon Fibre Limited. The following materials were used for electrodeposition of Bi\(_2\)Te\(_3\) films: (a) bismuth nitrate pentahydrate (Bi(NO\(_3\))\(_3\)-5H\(_2\)O) from Sigma Aldrich Sdn. Bhd, (b) tellurium dioxide (TeO\(_2\)) from Sigma Aldrich Sdn. Bhd (c) 65% nitric acid (HNO\(_3\)) from R&M Chemicals. Materials used for RCF electrode pre-treatment are sodium chloride (NaCl), potassium chloride (KCl), sodium phosphate (Na\(_2\)HPO\(_4\)) potassium phosphate (KH\(_2\)HPO\(_4\)), magnesium chloride (MgCl\(_2\)), hydrochloric acid (HCl), and isopropanol (C\(_3\)H\(_6\)O). Gas involved for heat-treatment is forming gas (5% hydrogen in 95% argon supplied by Linde Malaysia.

2.2. Pre-treatment of RCF electrode

There are 3 methods of pre-treatment carried out for the RCF electrode prior to electrodeposition. The three pre-treatment methods that were investigated are solvent cleaning, electrochemical polarization, and heat treatment.

2.2.1. Solvent cleaning

The RCF working electrode was immersed and soaked in a 25 ml test tube filled with analytical grade isopropanol for 30 minutes. The carbon fibre was then dried in the 100°C pre-heated oven for 15 minutes.

2.2.2. Electrochemical polarization

The buffer solution for the electrochemical polarization was made with 8 g of NaCl, 0.2 g of KCl, 1.15 g of Na\(_3\)HPO\(_4\), 0.2 g of KH\(_2\)PO\(_4\), and 0.047 g of MgCl\(_2\) into a 800 mL of distilled water (. HCl was then added drop by drop to adjust the solution until it was slightly alkaline, whereby the pH of solution must be 7.4. Electrochemical polarization was carried out using a potentiostat with the cyclic voltammetry mode. The cyclic voltammetry was programmed to have a scan rate of 0.01 V/s. An
alternate potential was applied between 0 and 2 V vs Ag/AgCl using a potentiostat. The carbon fibre was then dried in the 100°C pre-heated oven for 15 minutes.

2.2.3. Heat treatment
The RCF electrode was annealed in a tubular furnace in a 5% hydrogen in 95% argon gas environment with a ramping of 10 °C/min, gas flow rate of 0.1 litres/min, annealing temperature of 350 °C, annealing duration of 2 hours. The samples were cooled down to room temperature before removing it from the furnace.

2.3. Electrodeposition of Bi$_2$Te$_3$ on RCF electrode
Bi$_2$Te$_3$ films were electrodeposited on RCF from an electrolyte solution consisting of 8 mM of Bi(NO$_3$)$_3$.5H$_2$O and 10 mM of TeO$_2$ in 1.3 M of 65% purity HNO$_3$. Bi$_2$Te$_3$ film was electrodeposited on RCF with a potentiostat (VersaStat-3, Princeton Applied Research). The electrodeposition process utilized a standard 3 cell electrodes configuration whereby a silver/silver chloride (Ag/AgCl) filled with 1 M of KCl was used as the reference electrode, the counter electrode was a platinum rod, and the working electrode was RCF and it was carried out for 1 hour. The electrodeposited RCF was dried at a temperature of 100 °C for a duration of 15 minutes in a gravity convection oven.

2.4. Characterisation
2.4.1. Seebeck coefficient
The main thermoelectric property investigated and measured in this study is the Seebeck coefficient. The schematic for this measurement is as shown in figure 1. The formula for Seebeck coefficient is given by equation (1):

$$\alpha = \frac{\Delta V}{\Delta T} = \frac{V_H - V_C}{T_H - T_C} \quad (1)$$

The open circuit voltage ($V_{OC}$) obtained between the $V_H$, voltage on hot end and $V_C$, voltage on cold end is denoted as $\Delta V$ (in millivolts), temperature difference between $T_H$, temperature on hot end and $T_C$, temperature on cold end is denoted as $\Delta T$ (in Kelvin). The measurement was carried out with the hot end temperature at 40 °C and cold end at room temperature. Based on (2), $\alpha$ is Seebeck coefficient of both copper ($\alpha_{CU}$) and electrodeposited RCF ($\alpha_{CF}$), thus the Seebeck coefficient of electrodeposited RCF is calculated by equation (2) as shown below:

$$\alpha_{CF} = \alpha_{CU} - \alpha \quad (2)$$

Figure 1. Experimental setup for Seebeck coefficient measurement

2.4.2. Field emission scanning electron microscopy (FESEM) and energy dispersive x-ray (EDX)
The FESEM micrographs were obtained from the FEI Quanta 400 to observe the homogeneity of Bi$_2$Te$_3$ deposition on RCF strands. The elemental composition of bismuth and tellurium in the electrodeposited RCF was obtained using the EDX analysis.
3. Results and discussion

3.1. Effect of electrode pre-treatment on Seebeck coefficient

The RCF is pre-treated using 3 main methods namely the solvent cleaning with isopropanol, electrochemical polarization using phosphate buffer solution (PBS), and heat treatment. These methods were chosen based on the suitability on the carbon electrode and the availability of resources to perform said pre-treatment. Each method is used separately prior to electrodeposition of Bi$_2$Te$_3$ on RCF. The final Seebeck coefficient values are obtained averaged from several sets of experiment for each method and compared to a control sample which has not undergone any prior pre-treatment methods. The values are tabulated in table 1 below:

Table 1. Seebeck coefficient of Bi$_2$Te$_3$ electrodeposited RCF corresponding to different pre-treatment methods.

| Pre-treatment methods         | Seebeck coefficient (µV/K) |
|-------------------------------|----------------------------|
| Control                       | -12.23                     |
| Electrochemical polarization  | -13.38                     |
| Solvent cleaning              | -10.70                     |
| Heat treatment                | -10.71                     |

As shown in Table 1, among the three electrode pre-treatment, electrochemical polarization achieved the highest Seebeck coefficient of -13.38 µV/K while the other two pre-treatment (solvent cleaning and heat treatment) resulted in drop of Seebeck coefficient value compared to the control sample. The RCF electrode properties that can be altered using the electrochemical polarization technique are electronic structure, wettability and surface oxides. In addition to that, electrochemical polarization also induces microstructural changes on the RCF electrode with minimal oxidation whereas the other pre-treatment techniques leads to extensive probability of oxidation.

Solvent cleaning method works by the principle of dissolving the adsorbed contaminants from the surface. An electrode is said to be activated as cleaned active sites are made ready for electron transfer. Heat treatment/annealing can also be used to remove physically adsorbed surface contaminants by the modulation of temperature and environment of annealing. Both these methods prepared activated RCF electrode which are readily susceptible for electron transfer. In other words, more contaminants or oxides may have formed on the “activated” surface of the pre-treated RCF from solvent cleaning and heat treatment method. This hypothesis may be valid as seen in the low Seebeck coefficient values of these 2 pre-treatment methods compared to a control sample. The low values of Seebeck coefficient postulated limited electrodeposition of Bi$_2$Te$_3$ occurring on surface due to the newly adsorbed contaminants/oxides. This hypothesis is further strengthened by the presence of more elemental oxygen in solvent cleaned and heat treated samples as compared to control sample as obtained in EDX analysis tabulated in table 2.

Table 2. Effects of pre-treatment on the elemental composition.

| Pre-treatment methods | C  | O  | Te | Bi |
|-----------------------|----|----|----|----|
| Control               | 65.81 | 14.15 | 11.37 | 8.67 |
| Solvent cleaning      | 53.00 | 18.77 | 19.88 | 8.35 |
| Heat treatment        | 51.15 | 17.69 | 12.07 | 19.09 |
3.2. Effect of electrode pre-treatment on surface morphology

FESEM images as shown in figure 2 reveal possible improvements in surface morphologies and topographies of RCF substrate subjected to prior pre-treatment. FESEM images revealed more uniform coatings of Bi$_2$Te$_3$ on the RCF substrate subjected to pre-treatment in comparison to the non-pre-treated ones as shown in figure 2. Pre-treatment of electrodes are widely performed to condition the surface morphologies and topographies of the electrode prior to electrodeposition. Since reaction kinetics of electrodeposition is controlled by electrode-electrolyte interface, an improved surface condition should influence the uniformity of electrodeposition as better electron-transfer kinetics for a redox system is achieved. The increased Seebeck coefficient of electrodeposited RCF after electrochemical polarization is owing to the improved uniformity of Bi$_2$Te$_3$ deposition on RCF strands. These findings indicate the plausibility of developing a flexible thermoelectric module from recycled carbon fibre which could potentially be used as a flexible energy harvester with possible applications in wearable devices, medical and sensors.

![Figure 2. FESEM image of RCF (a) uncoated (b) electrodeposited RCF (control) (c) electrodeposited RCF after electrochemical polarization (d) electrodeposited RCF after solvent cleaning (e) electrodeposited RCF after heat treatment](image-url)

4. Conclusion

Electrodeposition technique was employed in this study to deposit thin films of Bi$_2$Te$_3$ on the surface of RCF electrode. The choice of RCF electrode pre-treatment technique has an impact on the Seebeck coefficient as well as the surface morphology of electrodeposited Bi$_2$Te$_3$ on RCF. Amongst all pre-treatment techniques, only electrochemical polarization enhanced the Seebeck coefficient from -12.23
µV/K (control) to -13.38 µV/K with a 9.4% increment in its Seebeck coefficient value. Whereas solvent cleaned and heat treated samples exhibited decrement in Seebeck coefficient values compared to that of control sample owing to oxidation of Bi$_2$Te$_3$ films.

References
[1] Pang E J X, Pickering S J, Chan a., Wong K H and Lau P L 2012 N-type thermoelectric recycled carbon fibre sheet with electrochemically deposited Bi$_2$Te$_3$ J. Solid State Chem. 193 147–53
[2] Pimenta S and Pinho S T 2011 Recycling carbon fibre reinforced polymers for structural applications: Technology review and market outlook Waste Manag. 31 378–92
[3] Yoo B Y, Huang C-K, Lim J R, Herman J, Ryan M a., Fleurial J-P and Myung N V 2005 Electrochemically deposited thermoelectric n-type Bi$_2$Te$_3$ thin films Electrochim. Acta 50 4371–7
[4] Ma Y, Johansson A, Ahlberg E and Palmqvist A E C 2010 A mechanistic study of electrodeposition of bismuth telluride on stainless steel substrates Electrochim. Acta 55 4610–7
[5] Jagadish P R, Li L P, Chan A and Khalid M 2016 Effect of Annealing on Virgin and Recycled Carbon Fiber Electrochemically Deposited with N-type Bismuth Telluride and Bismuth Sulfide Mater. Manuf. Process. 31 1223–31
[6] Jagadish P R, Khalid M, Amin N, Li L P and Chan A 2017 Process optimisation for n-type Bi$_2$Te$_3$ films electrodeposited on flexible recycled carbon fibre using response surface methodology J. Mater. Sci. 52 11467–81
[7] Swain G M 2007 Handbook of Electrochemistry ed C Zoski (Amsterdam: Elsevier) chapter 5 pp 111–153