CARBON 86 (2015) 118–123

Available at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/carbon

A tubing shaped, flexible thermal energy harvester based on a carbon nanotube sheet electrode

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ARTICLE INFO

Article history:
Received 17 October 2014
Accepted 16 January 2015
Available online 22 January 2015

ABSTRACT

A tubing-shaped, flexible electrochemical thermal energy harvester (thermocell), which can be wound around various types of waste heat sources, was fabricated. The thermocell utilizes the temperature dependence of the ferri/ferrocyanide ($Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$) redox potential, providing a thermoelectric coefficient of ~1.4 mV/K. A highly porous carbon nanotube (CNT) sheet, which is wrapped onto a thin platinum (Pt) wire, was used as an electrode for the redox reaction. The electrode performance was examined by comparing the output powers from the thermocells using a bare Pt wire and CNT sheet wound electrodes. The CNT sheet electrode showed a higher output power from 8.5 to 15.6 μW, and the short-circuit current density (j_{sc}) was increased ~1.8 times compared to that of the Pt wire electrode. The performance of the CNT sheet based thermocell was examined according to the winding number of the CNT sheet, the temperature difference between the two electrodes and the operating temperature. The series connection of the thermocells, to demonstrate the voltage and power scaling, was also examined with an understanding of the primary internal resistance that limits the output electrical power.

1. Introduction

A tremendous amount of waste heat is released from everyday life, such as air-conditioning, vehicles, lighting, and home appliances. This waste heat is typical available at temperatures below 100 °C and released to surrounding environment. The use of a thermoelectric device is one of the possible ways of scavenging waste heat. Based on the Seebeck effect, a thermoelectric generator is capable of the direct conversion of temperature differences to an electrical voltage. In the past few decades, considerable efforts have been made to improve the conversion efficiency of thermoelectric generators [1–8]. However, the small thermoelectric coefficient (typically several tens to hundreds of microvolts per Kelvin) [9–12] remains an obstacle to the delivery a sufficient voltage and electric power, particularly when utilizing the temperature difference between the waste heat source and ambient environment. Inflexible and expensive thermoelectric materials have limited applicability to certain shapes of the heat source and large-area installations. Accordingly, researchers have focused on not only enhancing the thermoelectric performance, but also

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http://dx.doi.org/10.1016/j.carbon.2015.01.037
0008-6223/

on finding an alternative way to effectively harvest waste heat energy [13,14].

Liquid thermoelectric generators (*i.e.*, thermal electrochemical cells or thermocells) have recently attracted considerable attention in the thermal energy conversion [13,15–22]. A thermocell utilizes the temperature dependence of the redox potential of an electrolyte, which can provide a 10–100-fold higher thermoelectric coefficient (several millivolts per Kelvin) than those of conventional thermoelectric materials [13,23]. With the steady efforts in finding high-performance thermoelectric electrolyte and electrode materials, a low cost per watt of power conversion is envisioned as one of the major advantages of thermocell utilization. Using a flexible electrode and package materials to complete thermocell fabrication, the thermocell can be wrapped around the rounded heat sources without any degradation of performance.

In this study, a tubing-shaped, flexible electrochemical thermal energy harvester (thermocell), which can be wound around various types of waste heat sources, was fabricated. The thermocell utilizes temperature dependence of the ferri/ferrocyanide ($Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$) redox potential, providing a thermoelectric coefficient of 1.4 mV/K. A highly porous carbon nanotube (CNT) sheet that is wrapped around a thin platinum (Pt) wire was used as an electrode for the redox reaction. The performance of the thermocell was investigated quantitatively according to the winding numbers of the CNT sheet, temperature difference between the two electrodes and operating temperature of the thermocell. To demonstrate the voltage and power scaling, the series connection was also examined with an understanding of the internal resistance that limits the output electrical power.

2. Experimental section

2.1. Operation principle of a thermocell

The thermoelectric potential in a thermocell is generated by the temperature dependence of the free energy difference between reactant and product of a reaction taking place at the electrolyte–electrode interface [13,20,23]. The operation of a thermocell is described schematically in Fig. 1(a). The CNT sheet electrodes are placed at different temperature zones. The inter-electrode temperature difference generates an electrical potential difference because of the temperature dependence of the $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox potential.

When the cell is connected to an external electrical load, the thermally generated potential drives electrons in the external circuit so that an electrical current and power can be delivered. The continuous operation of a thermocell is achieved by the transport of the reaction product formed at one electrode to the other electrode, where it can then become a reactant. Natural convection based on the density gradient of the electrolyte can be a significant mode of transport in thermocells [20].

2.2. Fabrication of tubing-shaped, flexible thermocell

Aligned CNT sheets that are wrapped on a thin Pt wire were used as an electrode for improving thermocell performance. The most important advantage of nanocarbon electrodes is the characteristic high internal surface area, which can increase the number of available reaction sites per unit external area, resulting in increased power density [20]. The CNT sheets offer remarkable properties including high flexibility, thermal stability, high surface area (which can exceed 300 m^2/g) and ultra-low areal density (that can be below 3 μg/cm^2) [24,25]. To prepare the electrode, 1.0 cm width CNT sheet was continuously drawn from a sidewall of multi-walled CNT (MWCNT) forest using a dry-state spinning process (see Fig. 1(b)) and wrapped around a 200 μm diameter Pt wire using a connected rotating motor at 10 rpm. A percentile weight of CNT loading on the Pt wire can be easily controlled by the number of motor rotations. In order to find the optimal winding number of CNT sheets on a Pt wire, the winding number per unit Pt wire length was varied in the range 27–108 turns/cm with an interval of 27 turns/cm.

Fig. 1(c) presents the fabrication process of the thermocell used in this study. A highly flexible silicone tubing (Korea Ace Scientific) was used as a cell package with an inner and outer diameter of 3.0 and 4.5 mm, respectively. A 0.4 M potassium ferri/ferrocyanide (Sigma Aldrich) aqueous solution with a concentration close to saturation was used as the thermoelectric electrolyte. The electrolyte was prepared using deionized (DI) water and degassed prior to use by bath sonication. The freshly prepared electrolytes were incorporated immediately into the thermocell before commencing a series of measurements to avoid the effects of electrolyte degradation. The thermocell was assembled by inserting the CNT sheet electrodes in silicone tubing, followed by hot pressing both ends of the tubing at ~300 °C for 10 s. The electrolyte was injected into the cell through a syringe and the injection hole was sealed completely with epoxy.

2.3. Instruments and methods

Hot and cold temperatures were controlled by circulating water from a thermostatic bath (A&D Korea) with an accuracy of ±0.1 °C. The potential and current output from the cell was measured using a voltage–current meter (Keithley 2000 multimeter) to characterize the power output with respect to the external resistive loads. Scanning electron microscopy (SEM, Hitachi S-4700) was performed at an acceleration voltage of 10–15 keV.

3. Results and discussion

A tubing-shaped thermocell consisting of all flexible components, such as silicone tubing for packaging, CNT sheet electrodes and thermoelectric electrolytes, was fabricated to demonstrate the thermocell that is flexible enough to wrap onto the heat source of various shapes. The capability of power generation in the thermocell depends not only on the voltage, which is linearly proportional to the applied temperature difference, but also on the discharging currents. A large number of available reaction sites in the thermocell reaction result in increased power density. To prepare a thermocell electrode, two most important factors were considered in this study, which mainly determine the electrode performance: (1) the number of available reaction sites per unit external area, which is directly proportional to the reaction rate (*i.e.*, electric