



## Original article

# Thermocells of carbon material electrodes and its performance characteristics

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## ABSTRACT

Thermocells in box and flat cell configurations were demonstrated via simplified design and cost effective materials like activated charcoal and potassium ferri/ferrocyanide solution and MWCNTs respectively. Employing saturated concentrations of potassium ferri/ferrocyanide in aqueous solution as electrolyte in combination with the electrodes resulted in a highly feasible redox-mediated electron transfer. Effects of concentration of potassium ferri/ferrocyanide (0.1 mM, 1 M and 4 M in aqueous medium) on the performance of the devices were analyzed. The electrolyte trapped in agar-agar gel functions as a solid like medium. In the case of box configuration the maximum power density attained being 22.463 W/m<sup>2</sup> yielding 20–30% of Carnot efficiency and 0.563 W/m<sup>2</sup> for MWCNT based flat cells reaching 0.5–18% higher than the Carnot efficiency. The efficiency of the thermocells at different  $\Delta T$  from 30 °C to 130 °C was reported. The power density increased by 14.92 times for activated charcoal thermocell operating in 1 M K<sub>3</sub>[Fe(CN)<sub>6</sub>]/K<sub>4</sub>[Fe(CN)<sub>6</sub>] at  $\Delta T = 60$  °C in comparison with MWCNT based thermocells at the same  $\Delta T$ . Other low cost electrode materials like activated charcoal, acetylene black were employed to study the performance of thermocells. Cells were connected in series and parallel to study the feasibility of performance improvement at different  $\Delta T$ .

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## 1. Introduction

Thermocells were the most attractive way for conversion of thermal energy to electrical energy and energy management. The vital merits of these systems were (i) absence of moving mechanical parts, (ii) complete and closed usage of electrolyte,

(iii) device lifetime and longevity, (iv) simplicity in fabrication, etc. The major sustainable energy source for thermocells being low grade sensible heat at  $\Delta T$  below 130 °C available from industrial waste effluent streams, geothermal activity, solar heating, solar thermal power plants, data storage systems, etc. Thermoelectric energy conversion was not feasible even though the solid-state thermoelectrics and Stirling engines

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### Nomenclature

#### Parameters symbols

$\eta$	efficiency of the thermocells
$r_{\text{ext}}$	external resistance
$I$	current
$I_{\text{sc}}, I_0$	short circuit current
$V$	electrode potential, voltage
$V_{\text{oc}}, V_0$	open circuit voltage
$T$	temperature
$C$	concentration of the electrolyte
$K$	thermal conductivity
$S$	Seebeck coefficient
$N$	number of electrons
$F$	Faraday's constant
$\Delta S_{\text{B,A}}$	reaction entropy for the redox couple
$\eta_r$	relative power conversion efficiency
$A$	cross-sectional area of the cell
$D$	the electrode separation distance
$\Delta T$	the temperature gradient between the two electrodes
$P_{\text{max}}$	maximum power output
$J_{\text{sc}}$	current density
$T_{\text{h}}$	temperature of hot electrode
$I_{\text{max}}$	maximum current
$P_{\text{max}}/\Delta T^2$	normalized area power density
$J_{\text{sc}}/\Delta T$	normalized area current density
MWCNTs	Multiwalled Carbon Nanotubes

were investigated in the literature, for efficient and effective harvest of low-grade heat to electrical energy [1], mainly due to the limitations on physical, material properties and high cost [2]. Furthermore, Stirling engine technology possesses demerits such as high initial cost and long-term reliability problems [3]. Thus thermocells utilizing the Seebeck effect of the electrolytes to produce electrical power becomes an attractive alternative for harnessing low-grade heat due to its simple design, direct thermal to electric energy conversion, continuous operation, low maintenance and zero carbon emission [4–6].

Investigation of thermocells to generate electricity through direct conversion of thermal energy was not an unheard phenomenon. Redox-type thermocells with aqueous potassium ferri/ferrocyanide solution had been studied in the literature for several decades [4–13]. The solution fills the space between two inert electrodes which were maintained at different  $\Delta T$  (Fig. 1). Thermocells are electrochemical cells where the voltage and current varies with the external resistance as  $r_{\text{ext}} \rightarrow 0$ ,  $I \rightarrow I_0$  (short circuit current) and as  $r_{\text{ext}} \rightarrow \infty$ ,  $V \rightarrow V_0$  (open circuit voltage). The efficiency of the thermocells,  $\eta$  based on Seebeck coefficient depends on temperature  $T$ , concentration of the electrolyte  $c$ , thermal conductivity  $k$ , as

$$\eta = \left( \frac{d\varphi^{(s)}}{dT} \right)^2 \left( \frac{Tc^0\lambda^0}{4} \right) \left( \frac{1}{kcp} \right)$$

The working principle of the thermocells has been depicted in Fig. 1. Under steady state conditions, Burrows [14] measured a power density ( $W$ ) of about  $0.9 \text{ W/m}^2$  at a  $\Delta T = 50 \text{ K}$ .

Quickenden and Vernon [15] measured  $w = 0.3 \text{ W/m}^2$  at  $\Delta T = 20 \text{ K}$  during the initial stage immediately after loading the cell. Thin layer redox-type cells [16,17] had been under research and development for several years. A value of  $w = 2.6 \text{ W/m}^2$  at  $\Delta T = 73 \text{ K}$  [16] and  $w = 3.2 \text{ W/m}^2$  at  $\Delta T = 50 \text{ K}$  [17] were reported as steady-state power densities. In all the previously reported literature the temperature gradients were less than  $100 \text{ K}$ . The reason could be usage of aqueous electrolyte solutions in atmospheric conditions or cells with no antipressure mechanism. The current work investigates the performance of the cells at temperatures above  $303\text{--}403 \text{ K}$ . The electrochemical Seebeck effect [18,19] for any redox reaction  $B \leftrightarrow ne^- + A$  and the Seebeck coefficient,  $S$ , in general was expressed as

$$S = \frac{\partial V}{\partial T} = \frac{\Delta S_{\text{B,A}}}{nF}$$

where  $V$  is the electrode potential,  $T$  is the temperature,  $n$  is the number of electrons involved in the reaction,  $F$  implies Faraday's constant, and  $\Delta S_{\text{B,A}}$  indicates the reaction entropy for the redox couple [20,15]. Aqueous potassium ferri/ferrocyanide solution had been used as the redox system due to its ability to reversibly exchange one electron per iron atom and produce a large reaction entropy, yielding Seebeck coefficient ( $>1 \text{ mV/K}$ ) and high exchange current [14,16,17,15,21,22]. Heat induced voltage generation in electrochemical cell containing ZnO nanoparticles possessing  $498 \text{ mV}$  with storage capacity of  $60 \text{ h}$  and exhibiting  $1.06\%$  efficiency of Carnot was already reported in literature [23] at an operating  $\Delta T = 30\text{--}50^\circ \text{C}$ . Apart from this thermodynamics aspects of thermal, chemical and electrochemical systems were extensively analyzed by several researchers in the literature [24].

The power conversion efficiency of a thermocell as modified by Hu et al. [25], expressed as

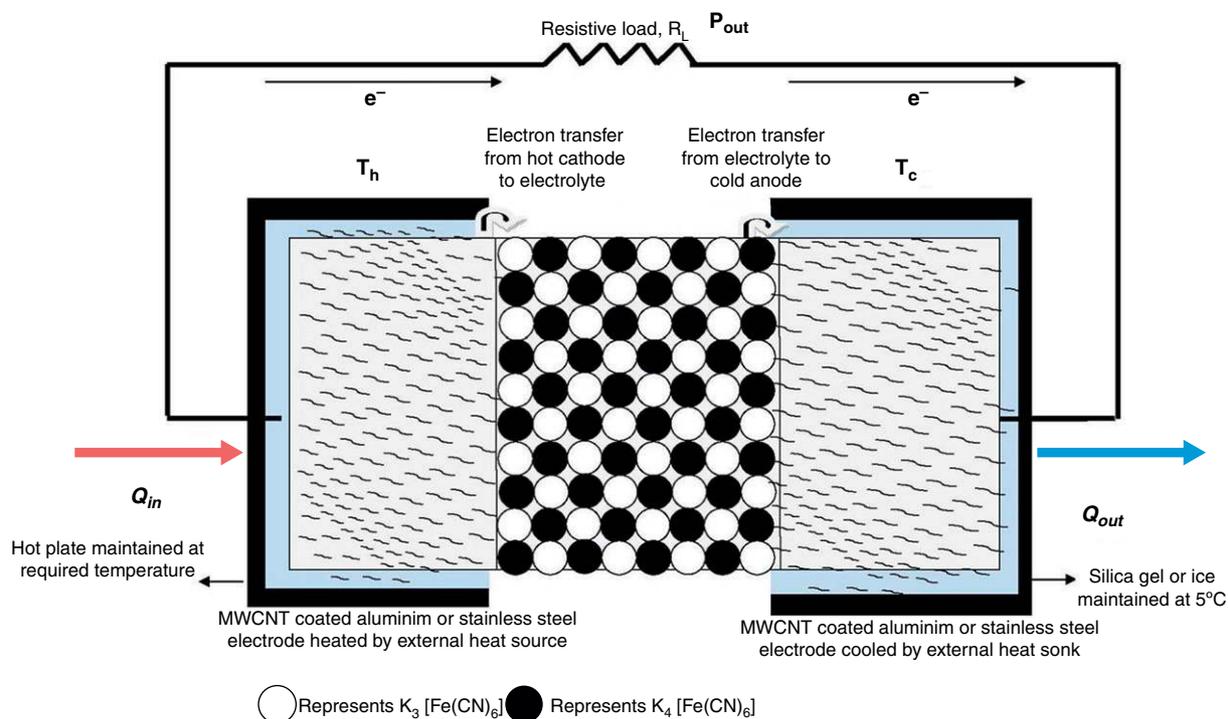
$$\eta = \frac{1/4 V_{\text{oc}} I_{\text{sc}}}{Ak(\Delta T/d)}$$

and the relative power conversion efficiency implied as  $\eta_r = \eta/(\Delta T/T_{\text{h}})$ , where  $V_{\text{oc}}$  is the open circuit voltage,  $I_{\text{sc}}$  represents the short circuit current,  $A$  indicates the cross-sectional area of the cell,  $d$  depicts the electrode separation distance,  $\Delta T$  is the temperature gradient between the two electrodes,  $k$  illustrates the thermal conductivity of the electrolyte (or the effective thermal conductivity of the electrolyte and separator), and  $T_{\text{h}}$  describes the temperature at the hot side.  $P_{\text{max}}$ , being  $1/4 V_{\text{oc}} I_{\text{sc}}$  and  $Ak(\Delta T/d)$  indicate the input thermal energy needed to maintain  $\Delta T$ .  $\Delta T/T_{\text{h}}$  corresponds to the Carnot efficiency.

In the present work we attempt to optimize the efficiency and the cost of construction of the thermocells employing simple design of the cell, electrodes, electrolyte and characterization techniques. This study aimed at fabricating a low cost device that can be practically integrated with industrial pipes, rooftops, solar power plants, etc. for extraction of power from sensible waste heat.

## 2. Experimental

Aqueous solution of  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  trapped in agar-agar gel was employed as electrolyte in the thermocells. The



**Fig. 1 – Schematic representation of the cross section and working principle of a thermocell.**

electrolyte had been studied at different concentrations such as 0.1 mM, 1 M and 4 M. The performance of activated charcoal, acetylene black, acetylene black + copper composite, activated charcoal copper composite (Sigma-Aldrich Co., USA), electrodes were directly compared using a box configuration whereas MWCNTs were used to fabricate flat electrochemical cell. The hot side electrode temperature was maintained at 35–135 °C while the cold side electrode temperature at ~5 °C, the two electrodes were 0.5 cm apart and the electrode dimension being 1.5 cm × 1.5 cm for box configuration and 22 cm × 24 cm for flat cell. The contacts were then covered by insulating M-seal (a chemical mixture of polyurethane resin base, diisodecyl phthalate, xylene, calcium oxide, ethylbenzene and diphenyl methane 4,4' diisocyanate which acts as a sealant) in order to prevent possible artifacts due to interaction between the copper wire and the electrolyte.

### 3. Construction of thermocell

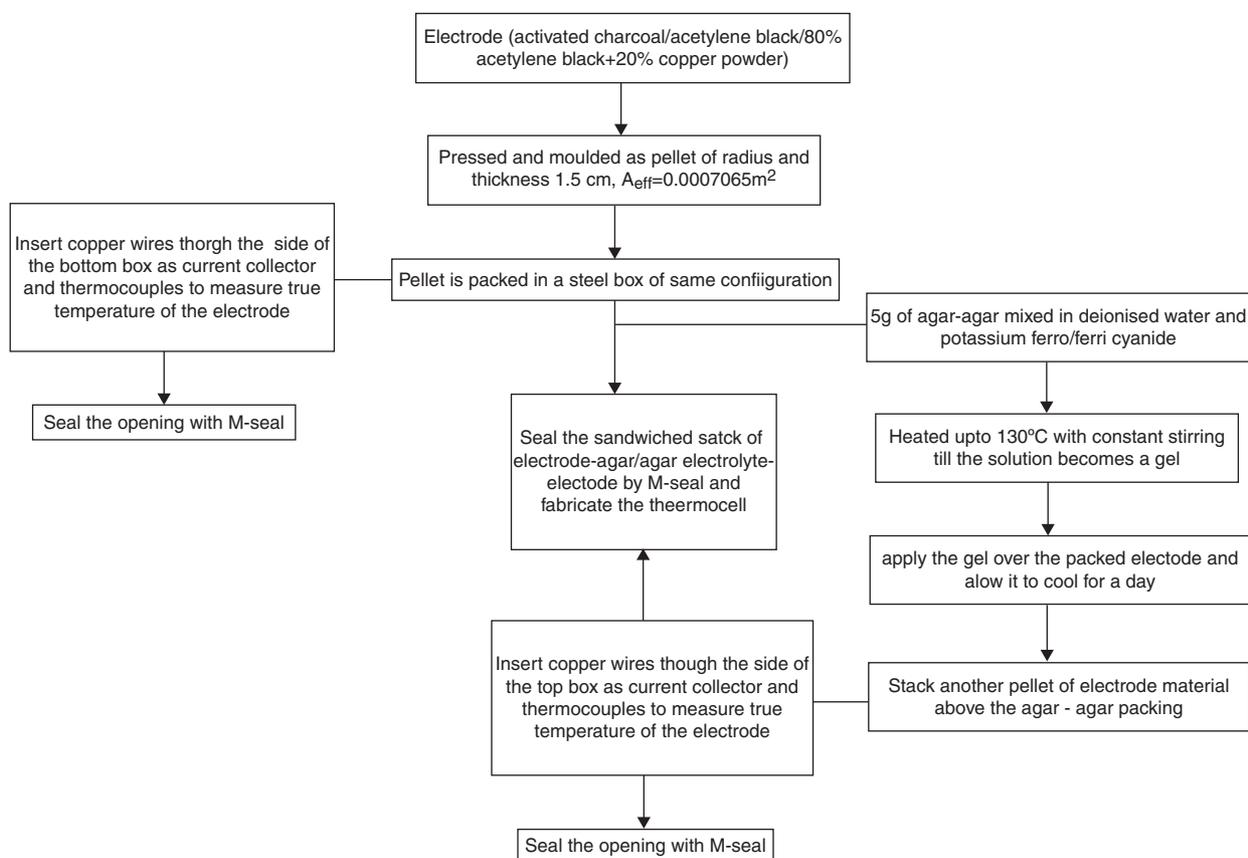
#### 3.1. Box configuration

Electrode materials (activated charcoal/acetylene black/80% acetylene black + 20% copper powder composite) were pressed and molded as a pellet of radius 1.5 cm and thickness 1.5 cm and effective area of the electrode being 0.007065 m<sup>2</sup>. The pellet was packed in a steel box of similar radius and height. Agar-agar powder (5 g) and appropriate weight of potassium ferri/ferrocyanide were mixed in 50 mL deionized water (Branstead Millipore, USA) depending upon the concentration under consideration (0.1 mM, 1 M and 4 M). The mixed solution was heated at 130 °C on a hot plate with constant stirring till the solution become a gel. The gel was applied

over the activated charcoal electrode and allowed to cool for a day. This packing was then covered by appropriate electrode material pellet and covered by the lid of the box. The copper wires were inserted through the side of the boxes (one at top and other at bottom) and the opening was sealed further by M-seal. K-type thermocouple wires were inserted inside the upper and lower electrode and sealed by M-seal. Thermocouple wires were connected to digital data acquisition system to measure the temperature of hot cathode and cold anode continuously during the experiments. By this setup direct measurement of the temperature of the electrodes was obtained instead of measuring the temperature of heat source and sink. The anode side was sealed with another steel cup to store ice and act as a heat sink. The heat sink was maintained at a temperature of 0–5 °C consistently. Thermocells were heated on the cathodic side using a digital hot plate. I–V discharge characterizations of the prepared thermocells were performed employing iviumstat spectroelectrochemical workstation employing galvanostatic linear sweep voltammetry technique (Fig. 2). The image of typical set up of thermocell has been depicted in Fig. 3.

#### 3.1.1. Flat cell configuration

Slurry of MWCNT in isoamyl acetate was prepared and spread to a thickness of 0.5 cm on an aluminum sheet of 22 cm × 24 cm area and the effective area of the electrode being 0.0528 m<sup>2</sup>. Isoamyl acetate was evaporated from the slurry by allowing the electrode to dry at room temperature. Agar-agar powder (5 g) and appropriate weight of potassium ferricyanide depending upon the concentration under consideration (1 M) were mixed in 50 mL deionized water (Branstead Millipore, USA). The mixed solution was heated at 130 °C on a hot plate

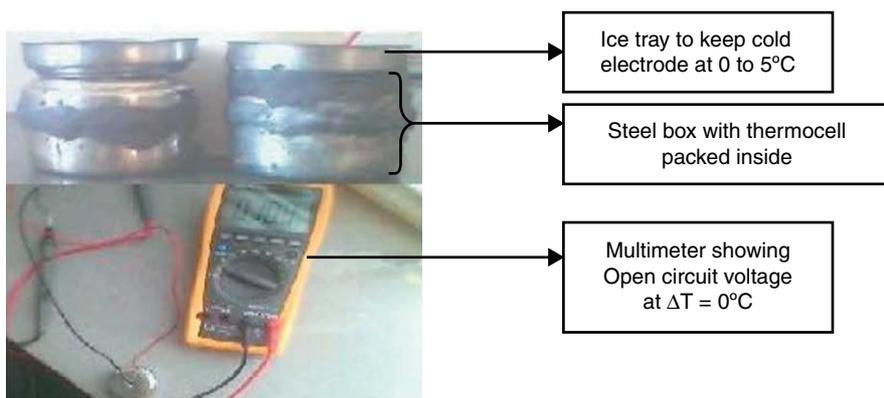


**Fig. 2 – Process sheet for construction of thermocell in box configuration.**

with constant stirring to form a gel. The gel was applied over the MWCNT electrode and allowed to cool for a day. This packing was then covered by identical MWCNT slurry coated polyethylene sheet on the top. The copper wires were inserted through the side of the cell and sealed by M-seal. K-type thermocouple wires were inserted inside the upper and lower electrode and sealed (Fig. 4). Temperature of the cold side (polyethylene side) always maintained at 5 °C by placing frozen silica gel packs (at 0 °C) over the cell. Image of the flat cell being as depicted below (Fig. 5).

### 3.1.2. *I-V discharge characterization of thermocells*

The thermocells were heated up to desired temperature and the  $\Delta T$  maintained till the experiments were completed. At the scan rate of 10 mA/s for box configuration and 20 mA/S for flat cells, the open circuit potential, short circuit current and *I-V* curves were measured employing Galvanostatic Linear sweep voltammetry. The current was kept constant at 10 mA or 20 mA as the case may be and the equilibration time being 30 s to measure the open circuit potential. The cell was discharged before proceeding to another temperature gradient.



**Fig. 3 – The image of typical set up of thermocell.**

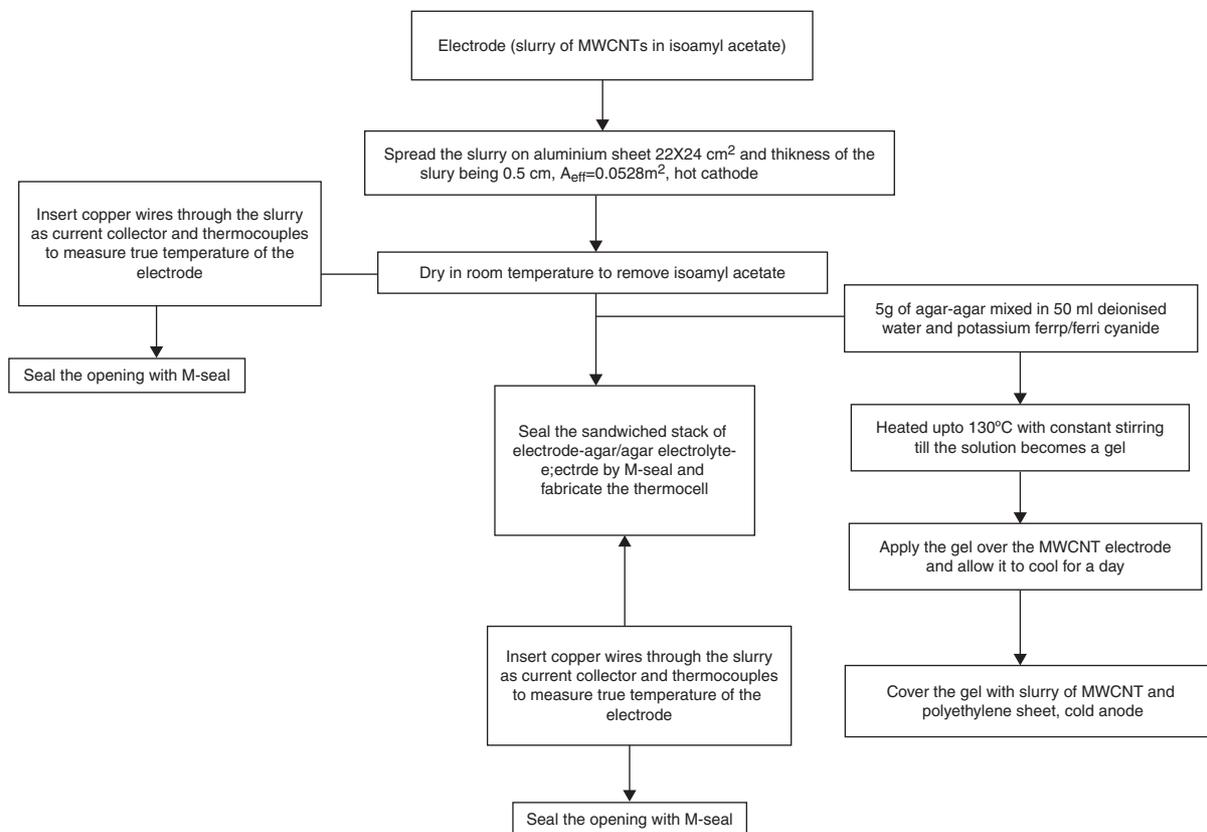


Fig. 4 – Image of the flat cell.

#### 4. Results and discussion

The foregoing analysis indicated that sensible heat can be harnessed and converted to useful power via thermocells employing cost effective materials like activated charcoal, acetylene black copper composite, potassium ferri/ferrocyanide, steel boxes, M-seal and copper wires. Seebeck coefficient of 7.35 mV/K was measured for the activated charcoal electrode, 17.9 mV/K for 80% acetylene black + 20% Cu composite electrode and 20.9 mV/K for MWCNT electrode in 1 M potassium ferricyanide at temperature gradient of 60 °C proving the dependence of Seebeck coefficient on the thermodynamics of the redox couple as well as the thermal conductivity of the electrode material.

#### 4.1. Characterization of 0.1 mM potassium ferri/ferrocyanide and activated charcoal based thermocell

The I-V curve implied the current in mA and negative magnitude due to the discharging of the device. The maximum open circuit potential ( $V_{oc}$ ) achieved by the device functioning in 0.1 mM electrolyte being 0.6639 V and depending upon the operating  $\Delta T$  the value of  $V_{oc}$  varied from 0.0778 V to 0.6639 V. Fig. 6 depicts that as the  $\Delta T$  between hot and cold electrodes increases from 30 °C to 120 °C, the performance of the device fluctuated drastically.

Non-linear trend in the performance of the device with the  $\Delta T$  was observed. At  $\Delta T=30-70$  °C, the device showed good performance whereas the performance degradation started from 80 °C to 120 °C. The maximum current up to 10 mA at

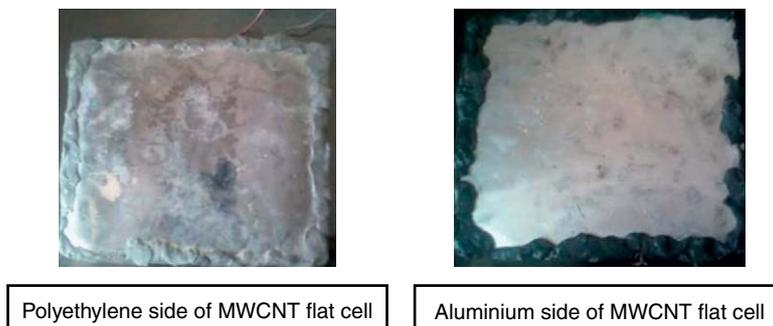
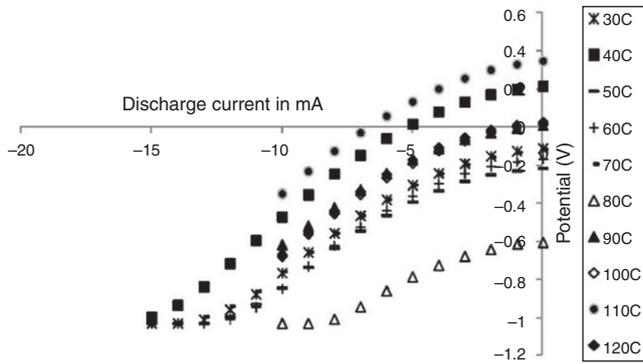


Fig. 5 – Process sheet for construction of thermocell in flat cell configuration.



**Fig. 6 – I-V discharge characteristics of 0.1 mM electrolyte filled activated charcoal based thermocells.**

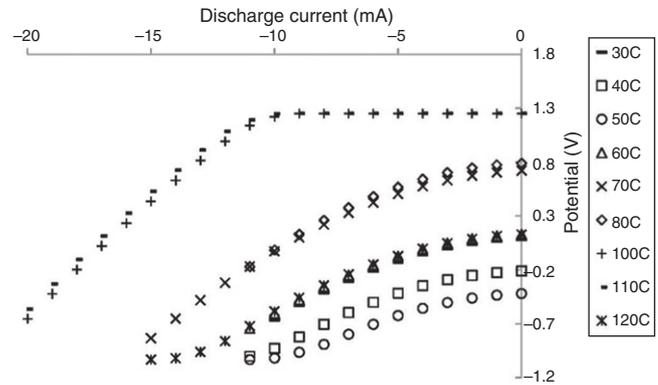
$\Delta T=80\text{--}120^\circ\text{C}$  and up to 15 mA at  $\Delta T=30\text{--}70^\circ\text{C}$  were noticed. The rationale behind this observation may be due to the vaporization of water from the gel at infinite dilution (0.1 mM) and plausible deterioration of the electrolyte beyond  $70^\circ\text{C}$ .

At  $\Delta T=40^\circ\text{C}$ ,  $P_{\max}=15.92\text{ mW}$  was observed, and the power density approximate to  $22.534\text{ W/m}^2$ . The power density observed being greater than that of ZnO, platinum and MWCNT electrode based thermocells reported in the literature [23,25]. The open circuit potential measured was 0.6639 V with higher  $I_{\text{sc}}$  and  $J_{\text{sc}}$  of 4.169 mA and  $5.9\text{ A/m}^2$ , respectively (Table 1). The power conversion efficiency of the device had been calculated employing the equation of Hu et al. [25], where  $A=0.0007065\text{ m}^2$ ,  $d=0.005\text{ m}$ ,  $k$  (thermal conductivity of activated charcoal) =  $0.51\text{ W/m/K}$ . The maximum power conversion efficiency was observed as 0.024. This value corresponds to ten times lower than the data reported for MWCNT and Pt thermocells [25].

#### 4.2. Characterization of 1 M potassium ferri/ferrocyanide and activated charcoal based thermocell

The effect of concentration of the electrolyte on the performance of the thermocell had been studied by increasing the electrolyte concentration to  $10^4$  times in the device. The open circuit potential of the device improved drastically with increase in the concentration of the electrolyte. The agar-agar gel was highly saturated with the electrolyte rather than water and resulted in a solid state device. The trend in the parameters such as open circuit potential, short circuit current, current and power density, efficiency and relative efficiency were low at lower temperature gradients from  $\Delta T=30\text{--}70^\circ\text{C}$  whereas high at  $\Delta T=80\text{--}110^\circ\text{C}$  and again at  $\Delta T=120^\circ\text{C}$  the trend falls. Fig. 2 depicts the I-V discharge characteristics of thermocells operating in 1 M electrolyte concentration at different  $\Delta T$  ranging from  $30^\circ\text{C}$  to  $120^\circ\text{C}$ . Fig. 7 infers that at higher concentration the trend in I-V characteristics appeared to be inverse to that of 0.1 mM operated thermocells. This could be attributed to the better heat conduction in solid phase device.

Thermocells show better performance at  $\Delta T=100^\circ\text{C}$  and  $110^\circ\text{C}$ , and beyond  $110^\circ\text{C}$  its performance degraded. The  $P_{\max}$  of the device was measured to be  $15.145\text{ mW}$  at  $\Delta T=110^\circ\text{C}$  and the power density being  $21.44\text{ W/m}^2$ . The open circuit

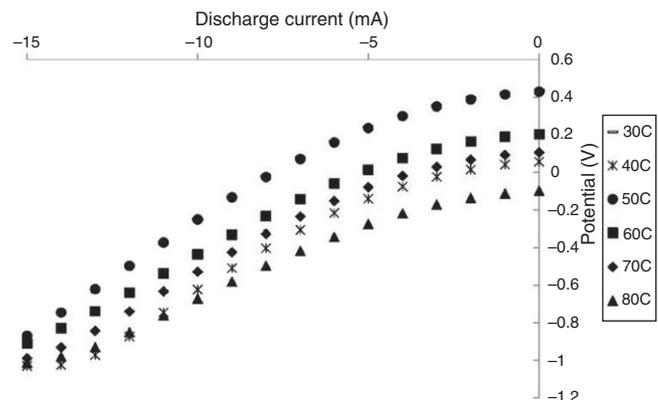


**Fig. 7 – I-V discharge characteristics of activated charcoal based thermocell operating in 1 M ferro/ferri electrolyte.**

potential measured to be 1.35 V with higher  $I_{\text{sc}}$  and  $J_{\text{sc}}$  values of 14.331 mA and  $20.2845\text{ A/m}^2$ , respectively in comparison to the 0.1 mM operated thermocells. The current density  $J_{\text{sc}}$  possessed the same order as reported but approximately three times lesser than the value obtained for MWCNT and two times lesser than that of Pt based thermocells. The maximum power conversion efficiency of 0.0671 observed at  $\Delta T=100^\circ\text{C}$ , being three times lower than the value reported for MWCNT and Pt thermocells whereas improved by three times in comparison with 0.1 mM operated device. Analogously, three times improvement in the power conversion efficiency, two times in open circuit potential were noticed with respect to the 0.1 mM operated devices (Table 2). It had been noticed  $10^3$  order of magnitude increment in the thermal stability of the device. Further improvement on the current density can be attained by changing the electrode material and by increasing the electrode area.

#### 4.3. Characterization of activated charcoal based thermocell in 4 M potassium ferri/ferrocyanide

Thermocells made of activated charcoal electrodes and 4 M ferri/ferro electrolyte had been investigated to understand the threshold limit of concentration of the electrolyte on the device performance. Fig. 8 depicts the performance



**Fig. 8 – I-V discharge characteristics of activated charcoal based thermocell operating in 4 M ferro/ferri electrolyte.**

**Table 1 – Characterization of 0.1 mM potassium ferri/ferrocyanide and activated charcoal based thermocell.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$I_{sc}$ (mA)	$E_{oc}$ (V)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	-1.031	-0.7288	0.0717	14.29	20.22646851	0.00239	0.017948734	0.983766234	1.82E-02
40	-5.9	-4.169	0.6639	15.92	22.53361642	0.016598	0.920320618	0.98427673	9.35E-01
50	0.1809	0.1278	-0.0139	13.95	19.74522293	-0.00028	0.00057239	0.984756098	5.81E-04
60	-0.4911	-0.3469	0.0388	13.78	19.50460014	0.000647	0.004206692	0.985207101	4.27E-03
70	-0.949	-0.6707	0.0653	14.48	20.49539986	0.000933	0.013289122	0.985632184	1.35E-02
80	3.976	2.809	-0.4644	9.611	13.60368011	-0.00581	0.384607873	0.98603352	3.90E-01
90	-2.369	-1.674	0.1208	6.608	9.353149328	0.001342	0.057978195	0.986413043	5.88E-02
100	-2.419	-1.709	0.1345	7.31	10.3467799	0.001345	0.06413638	0.986772487	6.50E-02
110	-2.419	-7.09	0.3345	3.51	4.968152866	0.003041	0.644454868	0.987113402	6.53E-01
120	-2.678	-1.892	0.1485	7.215	10.21231423	0.001238	0.074405315	0.987437186	7.54E-02

**Table 2 – Characterization of 1M potassium ferri/ferrocyanide activated charcoal based thermocell.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$I_{sc}$ (mA)	$E_{oc}$ (V)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	-0.9146	-0.6469	0.388	6.378	9.027600849	0.012933	0.00290252	0.983766234	0.00295
40	0.65	0.4592	-0.0448	11.45	16.20665251	-0.00112	0.000178422	0.98427673	0.000181
50	3.013	2.129	-0.2606	11	15.56970984	-0.00521	0.00384953	0.984756098	0.003909
60	-4.715	-3.331	0.4407	9.033	12.78556263	0.007345	0.00848778	0.985207101	0.008615
70	-14.15	-10.331	0.307	13.033	18.4472753	0.004386	0.015718474	0.985632184	0.015948
80	-14.15	-10.331	0.787	2	2.830856334	0.009838	0.035257765	0.98603352	0.035757
100	-20.2845	-14.331	1.35	13	18.40056617	0.0135	0.067117834	0.986772487	0.068018
110	-20	-14.13	1.35	15.145	21.43665959	0.012273	0.060160428	0.987113402	0.060946
120	-4.843	-3.421	0.3449	14.9	21.08987969	0.002874	0.003411086	0.987437186	0.003454

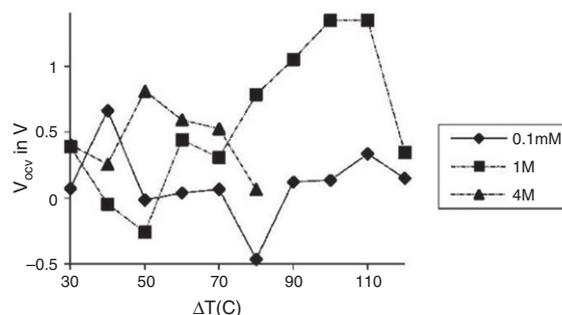
**Table 3 – Characterization of activated charcoal based thermocell in 4M potassium ferri/ferrocyanide.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$I_{sc}$ (mA)	$E_{oc}$ (V)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	-8.9469	-6.321	0.4049	15	21.23142251	0.013497	0.029596475	0.983766234	0.03008
40	-3.733	-2.637	0.2542	14.85	21.01910828	0.006355	0.00581371	0.98427673	0.00591
50	-9.03	-6.38	0.8118	14.06	19.90092003	0.016236	0.035935806	0.984756098	0.03649
60	-6.152	-4.346	0.593	14.5	20.52370842	0.009883	0.014901186	0.985207101	0.01512
70	-5.002	-3.534	0.5258	15.53	21.98159943	0.007511	0.009209091	0.985632184	0.00934
80	-10.64	-7.519	0.835	15.04	21.28803963	0.000798	0.002080264	0.98603352	0.00211

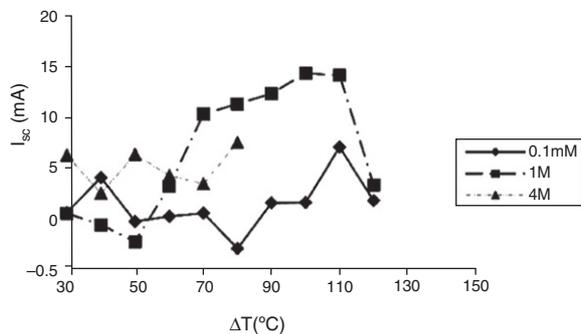
characterization of thermocells at 4M concentration of the electrolyte. From Table 3, the performance of the thermocell appeared uniform and identical for  $\Delta T=30-80^{\circ}\text{C}$  thereby demonstrating the thermal stability of the device up to  $80^{\circ}\text{C}$ .  $P_{max}=15.53\text{mW}$  was observed at  $\Delta T=70^{\circ}\text{C}$  and the power density measured to be  $21.98\text{W/m}^2$ . The open circuit potential of  $0.835\text{V}$  measured for the device, with  $I_{sc}$  and  $J_{sc}$  values as  $7.519\text{mA}$  and  $10.64\text{A/m}^2$ , respectively, in comparison with the  $0.1\text{mM}$  operated thermocells. In comparison to the current density  $J_{sc}$  measured for the MWCNT based device the present thermocell possessed  $J_{sc}$  approximately six times lesser value and four times lower value than that of Pt based thermocells [25]. The maximum power conversion efficiency was observed as  $0.0359$  (Table 3) and being eight times lower than the value reported for MWCNT and Pt thermocells whereas two times lower in comparison with  $0.1\text{mM}$  operated device. Although there was tremendous scope for utilizing the device at  $\Delta T<80^{\circ}\text{C}$  no improvement had been noticed in the power conversion efficiency, open circuit potential and the thermal stability of the device with increase in the electrolyte concentration to  $4\text{M}$ .

**4.4. Dependence of open circuit potential on  $\Delta T$  and concentration of the electrolyte**

Fig. 9 depicts the dependence of open circuit potential of the activated charcoal based thermocell on  $\Delta T$  and concentration of the electrolyte. The trend in the open circuit potential of thermocells operating at different concentrations of the electrolyte with  $\Delta T$  exhibit irregularity, even though a window of



**Fig. 9 –  $\Delta T$  and concentration of the electrolyte dependency of open circuit potential.**



**Fig. 10 –  $\Delta T$  and concentration of the electrolyte dependency of short circuit current.**

small  $\Delta T$  was maintained. For example, thermocell operating at 0.1 mM electrolyte concentration possessed the open circuit potential,  $V_{oc}$  of the order of 0.01 V at  $\Delta T$  30 °C, 50–100 °C and 120 °C, whereas at 40 °C and 110 °C an increase in  $V_{oc}$  being noticed (0.6639 V, 0.3345 V respectively). The rationale behind this anomalous behavior of the device, at  $\Delta T=110^\circ\text{C}$ , could be attributed to the fact that water in the electrolyte would have got vaporized and hence allowing solid phase electron transfer.

Analogously, in 1 M electrolyte concentration initial decrease in the value of  $V_{oc}$  with increase in  $\Delta T$  occurred from 30 °C to 50 °C. From  $\Delta T=60^\circ\text{C}$  to 110 °C  $V_{oc}$  increased linearly and decreased drastically at  $\Delta T=120^\circ\text{C}$ . This trend in  $V_{oc}$  with  $\Delta T$  could be attributed to the solid phase redox reaction at  $\Delta T$  ranging from 60 °C to 110 °C and degradation of the agar-agar gel and the electrolyte beyond 110 °C.

For thermocells operating at 4 M electrolyte concentration, as the cell opened up beyond 80 °C, a regular trend in  $V_{oc}$  was not observed. The data obtained at the rest of  $\Delta T$  ranging from 30 °C to 80 °C showed entirely reverse trend in comparison to those cells operating in lower concentration of the electrolyte. This may be due to the instability of the concentrated electrolyte toward thermal gradient imposed on the thermocells during their operation.

#### 4.5. Dependence of short circuit current on $\Delta T$ and concentration of the electrolyte

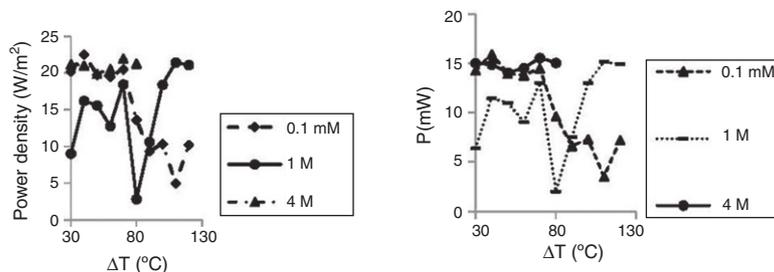
Fig. 10 represents the dependence of short circuit current,  $I_{sc}$  of the thermocells operating at all electrolyte concentrations and  $\Delta T$ . Identical trend between  $I_{sc}$  and  $V_{oc}$  at all

concentrations of the electrolyte as well as  $\Delta T$  had been observed. This clearly proved that the observed identical effect of the electrolyte concentration on  $V_{oc}$  and  $I_{sc}$  being analogous to  $I$  and  $V$  interrelated via Butler–Volmer kinetics for other electrochemical systems.

#### 4.6. Dependence of maximum power output and power density on $\Delta T$ and concentration of the electrolyte

The trend in  $P_{max}$  and the power density with electrolyte concentration and  $\Delta T$  are shown in Fig. 11. The maximum power output by thermocells operating at 0.1 mM electrolyte concentration remained constant from 30 °C to 70 °C and falls rapidly with increase in  $\Delta T$  from 80 °C to 120 °C. This could be attributed to the vaporization of water from the dilute electrolyte leading to performance degradation of the thermocell. Initial  $P_{max}$  value at  $\Delta T=30-70^\circ\text{C}$  being approximately 13.78–15.92 mW and falls suddenly to 5 mW at 80 °C and fluctuated between 9.611 and 3.51 mW throughout the experiment. Least value of 3.51 mW was noticed at  $\Delta T=110^\circ\text{C}$ . Analogous trend had been noticed for power density also. The power density remained constant from 30 °C to 70 °C and decrease rapidly with increase in  $\Delta T$  from 80 °C to 120 °C. Power density value showed less variation initially of around 20 W/m<sup>2</sup>, as the  $\Delta T$  increases, power density falls to 10 W/m<sup>2</sup> and then to 3 W/m<sup>2</sup> indicating the instability of the device at higher  $\Delta T$ . The reason behind this trend could be due to the change in thermionic processes beyond  $\Delta T=80^\circ\text{C}$ . In the case of thermocells operating in 1 M electrolyte concentration, although  $P_{max}$  and power density are higher than the cell operating at 0.1 mM electrolyte, the trend between  $P_{max}$  vs  $\Delta T$  and power density vs  $\Delta T$  remain unaltered. For thermocells operating in 4 M electrolyte, the  $P_{max}$  and power density measured being 14.06–15.53 mW at  $\Delta T=30-80^\circ\text{C}$  and 19.9–21.98 W/m<sup>2</sup>, respectively. This trend indicated that thermocells operating in this concentration range of the electrolyte were more efficient as it attains higher  $P_{max}$  and power density at lower temperature gradient. But the safety issues associated with the opening of the seals and the cell leading to cyanide evolution were hazardous and hence cannot be pursued further.

The characterization of activated charcoal electrode based thermocells with optimal electrolyte concentration as 1 M potassium ferricyanide solution trapped in agar-agar gel yielded a maximum power density of 21.437 W/m<sup>2</sup> at  $\Delta T=60^\circ\text{C}$ . The value being 14.92 times higher than that of MWCNT based thermocells at the same  $\Delta T$ . The power from a single thermocell of area 0.000765 m<sup>2</sup> proved to be insufficient



**Fig. 11 –  $\Delta T$  and concentration of the electrolyte dependency on (a)  $P_{max}$  (mW) and (b)  $P_{max}/A$  (W/m<sup>2</sup>).**

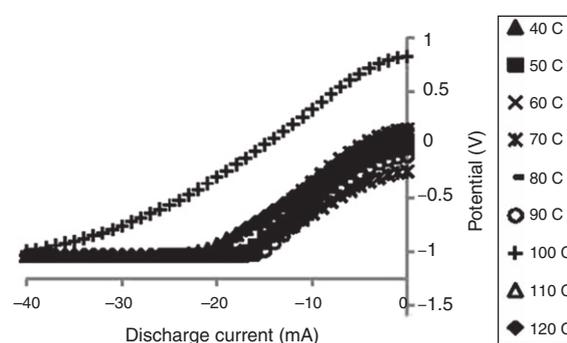
for practical application in small electronic devices like mobile batteries, health care devices, etc. Therefore, different cost effective electrode materials were experimented in a single box-type thermocell. In order to achieve higher power, box-type cells had been connected in series and parallel and characterized at  $\Delta T$  varying from 30 °C to 120 °C.

### 5. Construction of thermocell with different electrode materials

Electrolyte used in the current studies being 1M  $K_3Fe(CN)_6/K_4Fe(CN)_6$  aqueous solution trapped in agar-agar gel. The construction of box-type cell was done similar to previous study except for the electrodes. The electrode materials employed and their preparation were as follows:

1. Activated charcoal was mixed physically with copper powder in 80:20 wt.% ratio using mortar and pestle.
2. Five cells with activated charcoal as electrode material connected in series with copper wires.
3. A parallel connection of five cells (with activated charcoal and copper as electrode material) was connected with another set of five cells (with activated charcoal and copper as electrode material) in series.
4. Acetylene black was mixed with copper powder in 80:20 wt.% ratio using mortar and pestle.
5. Five cells with acetylene black copper powder composite as electrode material were connected in series.
6. A parallel connection of five cells (with acetylene black mixed with copper powder in 80:20 wt.% ratio as electrode material) in series connected with another set of five cells (with acetylene black mixed with copper powder in 80:20 wt.% ratio as electrode material).

When the mixture appeared fairly uniform, it was pressed and molded as a pellet of radius 1.5 cm and thickness 1.5 cm. The effective area of the electrode was 0.0007065 m<sup>2</sup> for a single cell and 0.003535 m<sup>2</sup> for five cells and 0.007065 m<sup>2</sup> for ten cells. The electrolyte gel was prepared as described in previous study. The hot side temperature was kept constant at 35–125 °C while the cold side temperature was ~5 °C and the two electrodes were 0.5 cm apart. The contacts were then covered by insulating M-seal to prevent possible artifacts due to interaction between the copper wire and the electrolyte.



**Fig. 12 – I–V discharge characteristics of 80% activated charcoal and 20% copper electrode filled thermocells.**

#### 5.1. I–V discharge characterization of thermocells with different electrode materials

The activated charcoal based thermocells were heated up to desired temperature and the  $\Delta T$  was maintained constant till the experiments were completed. At the scan rate of 10 mA/s,  $V_{oc}$  and I–V curves were measured employing Galvanostatic Linear sweep voltammetry. The current varied according to the discharge curve ranging from 15 to 25 mA and the equilibration time was set at 60 s or 90 s to measure the open circuit potential. The cell was then discharged before proceeding to next temperature gradient.

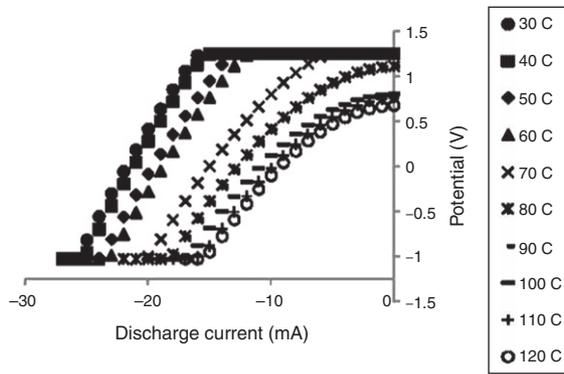
### 6. Results and discussion

#### 6.1. Characterization of a single 80% activated charcoal and 20% copper powder electrode based thermocell

From the non linear I–V characteristic curves (Fig. 12) and Table 4, it was observed that the maximum  $V_{oc}$  obtained being 0.827 V at  $\Delta T=100^\circ C$ . The trend in the performance observed to be unsteady with respect to the temperature variation and the potential of the device measured to be in the range of 0.01–0.2V at all  $\Delta T$ . Better results were noticed at  $\Delta T=100^\circ C$ , but still lower than pure activated charcoal electrode based thermocell which produced,  $V_{oc}=1.35 V$ . The maximum limiting current the device can withstand approximates to 15 mA at  $\Delta T=100^\circ C$ . At other temperature

**Table 4 – Characterization of a single 80% activated charcoal and 20% copper powder electrode based thermocell.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$I_{sc}$ (mA)	$E_{oc}$ (V)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	$S$ (mV/K)	Power conversion efficiency	Carnot efficiency	Relative efficiency
40	0	0	-0.027	0	0	-0.00068	0	0.983766234	0
50	-1.41443	-0.001	0.011	2.75E-03	0.00389	0.00022	7.62681E-05	0.98427673	0.000239
60	-6.36492	-0.0045	0.143	0.161	0.227546	0.002383	0.003718071	0.984756098	0.011638
70	0	0	-0.249	0	0	-0.00356	0	0.985207101	0
80	0	0	-0.072	0	0	-0.0009	0	0.985632184	0
90	0	0	-0.1	0	0	-0.00111	0	0.98603352	0
100	-21.2164	-0.015	0.827	3.101	4.386492	0.00827	0.043004826	0.986413043	0.134605
110	-2.82885	-0.002	0.046	0.023	0.032532	0.000418	0.000289945	0.986772487	0.000908

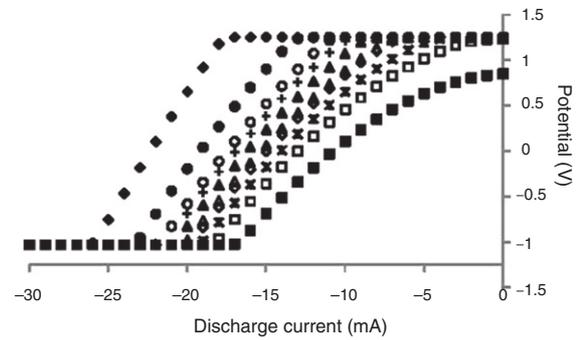


**Fig. 13 – I-V discharge characteristics of five activated charcoal electrode filled thermocells in series.**

gradients the current decayed to nearly 4 mA.  $P_{max}$  produced by the device being 3.101 mW and the maximum power density produced was 4.386 W/m<sup>2</sup> with a Seebeck coefficient of 0.00827 V/K. The values were nearly five times lower than pure activated charcoal electrode based thermocell which exhibited  $P_{max}$  as 15.145 mW and power density as 21.44 W/m<sup>2</sup>. The rationale behind the trend in the performance of the device would be attributed to the electrical and thermal conductivity mismatch of pure activated charcoal and copper coexisting in a non-homogeneous mixture. The difference in phononic vibration frequencies of both the materials may also attribute to the electron transport in the medium resulting in low power as compared to pure activated charcoal electrode based thermocell.

**6.2. Characterization of five cells with activated charcoal as electrode material connected in series tested immediately after fabrication**

The electrode area being five times that of a single cell i.e. 0.003535 m<sup>2</sup>. The experiment was conducted with an aim to improve the  $V_{oc}$  and the maximum power output of the device. From the I-V characteristics (Fig. 13) and Table 5, the maximum  $V_{oc}$  was obtained as 1.252 V and the maximum current the device can withstand as 26 mA. The trend showed good performance at  $\Delta T$  from 30 °C to 70 °C, with degradation after 70–120 °C. This could be attributed to the changes in



**Fig. 14 – I-V discharge characteristics of five activated charcoal electrode filled thermocells in series after 45 days.**

electrolyte at high temperatures. The  $V_{oc}$  obtained for single cell made of pure activated charcoal at  $\Delta T=100-110^{\circ}C$  were captured at  $\Delta T$  ranging from 30 °C to 70 °C for five cells in series.  $P_{max}$  obtained as 6.88 mW and power density of 1.992 W/m<sup>2</sup> at  $\Delta T=30^{\circ}C$  with a Seebeck coefficient of 0.04173 V/K had been measured. These values were three times lesser than the  $P_{max}$  of 15.145 mW and ten times less than power density of 21.44 W/m<sup>2</sup> for a single cell operating at  $\Delta T=110^{\circ}C$ . The decrement in the power obtained in series could be due to high internal resistance of the copper connecting wires which can be mitigated either by decreasing the length of the wires or by replacing with platinum wires. Feasible and low cost solution would be to increase the electrode area of a single cell instead of connecting many cells in series. Although five cells in series provided lesser power output than single cell, it would be favorable in a sense that if the electrode area had been increased, the device could harness sensible heat even at low  $\Delta T$  into useful power.

**6.3. Characterization of five cells with activated charcoal as electrode material connected in series tested after 45 days**

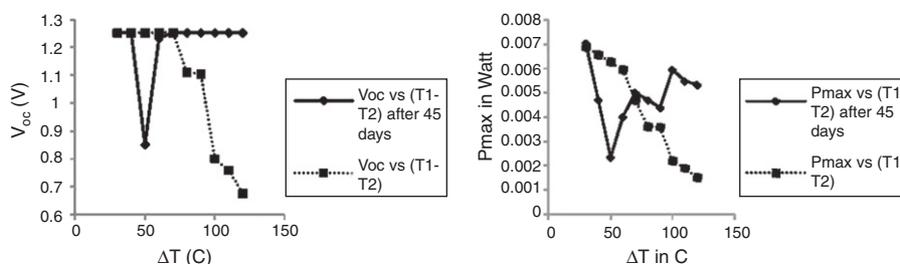
From the characteristic curves (Fig. 14), it was observed that  $V_{oc}$ ,  $I_{max}$ ,  $P_{max}$  and power density were identical in comparison with single cell tested immediately after fabrication. This uniformity of the values at all  $\Delta T$  without strong fluctuations implied that the device does not undergo self discharge or

**Table 5 – Characterization of 5 cells with activated charcoal as electrode material connected in series tested immediately after fabrication.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$E_{oc}$ (V)	$I_{sc}$ (mA)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	-6.22348	1.252	-0.022	0.006886	1.947949	0.041733	0.063658	0.98377	0.064709
40	-5.94059	1.252	-0.021	0.006573	1.859406	0.0313	0.045574	0.98428	0.046302
50	-5.65771	1.252	-0.02	0.00626	1.770863	0.02504	0.034723	0.98476	0.03526
60	-5.37482	1.252	-0.019	0.005947	1.68232	0.020867	0.027489	0.98521	0.027902
70	-4.24328	1.252	-0.015	0.004695	1.328147	0.017886	0.018602	0.98563	0.018873
80	-3.67751	1.11	-0.013	0.003608	1.020509	0.013875	0.012506	0.98603	0.012683
90	-3.67751	1.104	-0.013	0.003588	1.014993	0.012267	0.011057	0.98641	0.011209
100	-3.11174	0.8	-0.011	0.0022	0.622348	0.008	0.006101	0.98677	0.006183
110	-2.82885	0.759	-0.01	0.001898	0.536775	0.0069	0.004784	0.98711	0.004847
120	-2.54597	0.675	-0.009	0.001519	0.429632	0.005625	0.00351	0.98744	0.003555

**Table 6 – Characterization of 5 cells with activated charcoal as electrode material connected in series tested after 45 days.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$E_{oc}$ (V)	$I_{sc}$ (mA)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	-6.36492	1.252	-22.5	7.043	1.992221	0.041733	0.064460644	0.983766	0.065524
40	-4.24328	1.252	-15	4.695	1.328147	0.0313	0.041600799	0.984277	0.042265
50	-3.11174	0.851	-11	2.34	0.662023	0.01702	0.020094173	0.984756	0.020405
60	-3.67751	1.233	-13	4.007	1.133593	0.02055	0.033374334	0.985207	0.033875
70	-4.52617	1.252	-16	5.008	1.41669	0.017886	0.040493061	0.985632	0.041083
80	-4.24328	1.252	-15	4.695	1.328147	0.01565	0.036886827	0.986034	0.037409
90	-3.9604	1.252	-14	4.382	1.239604	0.013911	0.033479284	0.986413	0.03394
100	-5.37482	1.252	-19	5.947	1.68232	0.01252	0.044218043	0.986772	0.044811
110	-4.9505	1.252	-17.5	0.005478	1.549505	0.011382	0.039663773	0.987113	0.040182
120	-4.80905	1.252	-17	0.005321	1.505233	0.010433	0.037550102	0.987437	0.038028

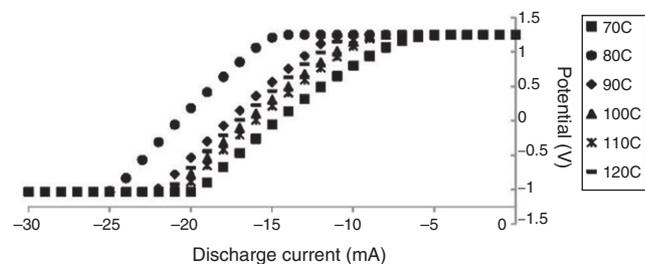


**Fig. 15 – (a)  $V_{oc}$  and (b)  $P_{max}$  vs  $\Delta T$  of five activated charcoal electrode filled thermocells in series with respect to time.**

degradation of chemicals employed over time. Thus thermocell can be a feasible technology for long term usage without performance degradation over time (Table 6).

**6.4. Characterization of parallel connection of five cells (with activated charcoal as electrode material) in series connected with another set of five cells (with activated charcoal as electrode material)**

The electrode area would be ten times that of a single cell i.e. 0.007065 m<sup>2</sup>. This experiment was carried out with an aim to improve the  $I_{sc}$  and  $P_{max}$  of the device. From the  $I-V$  characteristics (Fig. 15), open circuit potential and  $I_{max}$  were observed to be 1.252 V and 22 mA, respectively (Fig. 16). The trend showed steady performance at  $\Delta T=70-120^\circ C$ . The  $P_{max}$  and power density obtained being 6.57 mW and 0.932 W/m<sup>2</sup>, respectively, at  $\Delta T=80^\circ C$  with a Seebeck coefficient of 0.01565 V/K. The power obtained being identical to that of a single series of five cells with half the power density. The plausible reason for this behavior might be the internal resistance developed

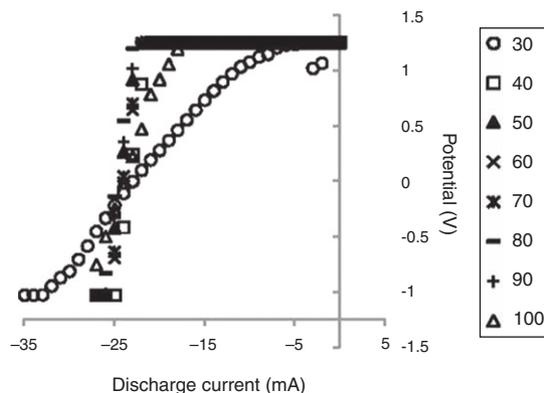


**Fig. 16 –  $I-V$  discharge characteristics of parallel combination of two series sets of five activated charcoal electrode filled thermocells.**

by the copper connecting wires. Hence feasible and low cost solution would be increasing the area of a single cell instead of connecting many cells in series/parallel (Table 7).

**6.5. Characterization of a single 80% acetylene black and 20% copper powder electrode based thermocell**

From the non linear  $I-V$  characteristic curves (Fig. 17), the maximum  $V_{oc}$  obtained was 1.252 V which remained constant for the whole range of  $\Delta T$  studied. The maximum limiting current the device can withstand being nearly constant around 33 mA. The trend of performance observed to be quite steady with the maximum power produced by this device being 7.83 mW and the maximum power density produced was 11.07 W/m<sup>2</sup> at  $\Delta T=80^\circ C$  with a Seebeck coefficient 0.04173 V/K. These values vary very slightly within the range of  $\Delta T$  employed. The power and power density were nearly



**Fig. 17 –  $I-V$  discharge characteristics of 80% acetylene black and 20% copper electrode filled thermocells.**

**Table 7 – Characterization of parallel connection of 5 cells (with activated charcoal as electrode material) in series connected with another set of 5 cells (with activated charcoal as electrode material).**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$E_{oc}$ (V)	$I_{sc}$ (mA)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
70	-2.12314	1.252	-15	4.695	0.664544	0.017886	0.01068444	0.98563	0.01084
80	-2.9724	1.252	-21	6.573	0.930361	0.01565	0.01453447	0.98603	0.01474
90	-2.54777	1.252	-18	5.634	0.797452	0.013911	0.01211492	0.98641	0.012282
100	-2.40623	1.252	-17	5.321	0.753149	0.01252	0.01113511	0.98677	0.011284
110	-2.26469	1.252	-16	5.008	0.708846	0.011382	0.01020647	0.98711	0.01034
120	-2.40623	1.252	-17	5.321	0.753149	0.010433	0.01056844	0.98744	0.010703

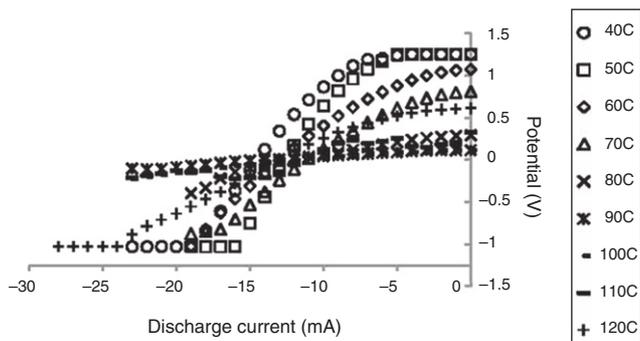
**Table 8 – Characterization of a single 80% acetylene black and 20% Copper powder electrode based thermocell.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$E_{oc}$ (V)	$I_{sc}$ (mA)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	-32.5548	1.252	-23	28.796	10.18967	0.041733	0.032947	0.98377	0.03349
40	-32.5548	1.252	-19	28.796	10.18967	0.0313	0.031894	0.98428	0.032403
50	-33.9703	1.252	-17	30.048	10.6327	0.02504	0.03225	0.98476	0.03275
60	-33.9703	1.252	-19	30.048	10.6327	0.020867	0.031282	0.98521	0.031752
70	-33.9703	1.252	-17	30.048	10.6327	0.017886	0.03037	0.98563	0.030813
80	-33.9703	1.252	-17	30.048	10.6327	0.01565	0.029509	0.98603	0.029927
90	-35.3857	1.252	-15	31.3	11.07573	0.013911	0.029892	0.98641	0.030304
100	-33.9703	1.252	-17	30.048	10.6327	0.01252	0.027927	0.98677	0.028302

twice that of activated charcoal copper composite electrode based thermocell (3.101 mW and 4.386 W/m<sup>2</sup>, Table 8). This might be accounted due to higher thermal conductivities of pure acetylene black as compared to pure activated charcoal. Thus acetylene black and copper composite might act as better electrode material than activated charcoal and copper mixture to extract power consistently at both higher and lower  $\Delta T$  ranges unlike single activated charcoal cell which can extract more power at high  $\Delta T$  only.

**6.6. Characterization of five cells with 80% acetylene black and 20% copper powder electrode based thermocells**

From the I-V characteristics (Fig. 18),  $I_{max}$  and the maximum  $V_{oc}$  were obtained as 23 mA and 1.252 V, respectively. The trend showed good performance at low  $\Delta T$  (30–40°C), but continuous degradation occurred after  $\Delta T=40^\circ\text{C}$  and up to  $\Delta T=120^\circ\text{C}$ .  $P_{max}$  value of 4.7 mW and power density being 0.6645 W/m<sup>2</sup> at  $\Delta T=40^\circ\text{C}$  with a Seebeck coefficient of 0.0313 V/K. The power obtained being lesser than that of

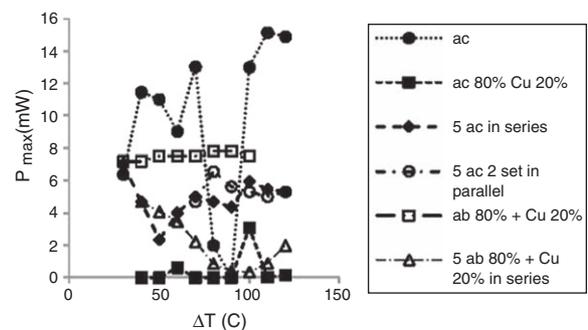


**Fig. 18 – I-V discharge characteristics of five 80% activated charcoal and 20% copper electrode thermocells in series.**

activated charcoal series and power density was three times less than 1.992 W/m<sup>2</sup> at  $\Delta T=30^\circ\text{C}$  (Table 9). This behavior of the device in series may be due to difference in thermal conductivities of pure acetylene black and copper which coexist in a non-homogeneous mixture. The difference in the phononic vibrations frequencies of the materials may lead to reduction in the rate of electron transfer resulting in lower power output compared to pure activated charcoal electrode based thermocell series.

**6.7. Dependence of  $P_{max}$  on  $\Delta T$  and electrode assemblies**

From Fig. 19, it can be inferred that  $P_{max}$  being obtained from a single thermocell of different electrode assembly combinations. The trend showed that there are fluctuations in  $P_{max}$  over all  $\Delta T$  range and higher the  $\Delta T$  (100°C or 110°C) higher would be the power output of a single cell. On the other hand, a drastic fall in  $P_{max}$  being observed in the case of activated charcoal and copper composite with practically negligible power at almost all  $\Delta T$  except at 100°C. The series and parallel combinations of five and ten activated charcoal



**Fig. 19 –  $P_{max}$  vs  $\Delta T$  characteristics of different electrode assemblies.**

**Table 9 – Characterization of 5 cells with 80% acetylene black and 20% Copper powder electrode based thermocells.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$E_{oc}$ (V)	$I_{sc}$ (mA)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	-2.12314	1.252	-0.015	4.7	0.66454	0.0313	0.00416	0.98428	0.004227
40	-1.84006	1.252	-0.013	4.07	0.57594	0.02504	0.003494	0.98476	0.003548
50	-1.84006	1.072	-0.013	3.48	0.49314	0.017867	0.002902	0.98521	0.002945
60	-1.55697	0.809	-0.011	2.22	0.3149	0.011557	0.001799	0.98563	0.001825
70	-1.69851	0.289	-0.012	0.87	0.12272	0.003613	0.000681	0.98603	0.000691
80	-1.9816	0.115	-0.014	0.4	0.05697	0.001278	0.000308	0.98641	0.000312
90	-1.69851	0.117	-0.012	0.35	0.04968	0.00117	0.000261	0.98677	0.000264
100	-1.55697	0.323	-0.011	0.89	0.12573	0.002936	0.000643	0.98711	0.000652

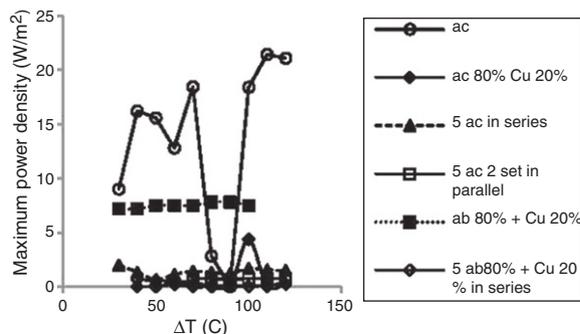
thermocells generated power approximately 33% of that produced from a single activated charcoal thermocell at higher  $\Delta T$ . The  $P_{max}$  from acetylene black and copper powder composite observed to be a constant value at different  $\Delta T$  ranges, but still lesser than  $P_{max}$  from pure activated charcoal cell. Alternatively, combination of acetylene black and copper cells five in series can capture very low  $\Delta T$  to produce substantial amount of power but the device do not perform well at higher  $\Delta T$ .

**6.8. Dependence of maximum power density on  $\Delta T$  and electrode assemblies**

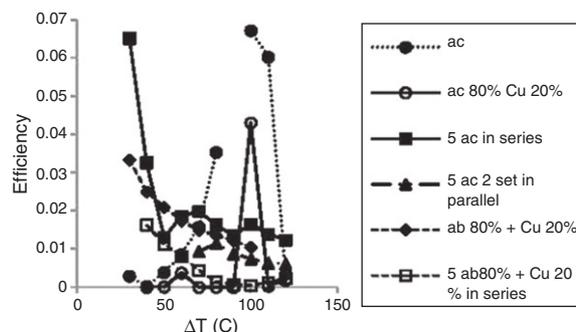
The trend in Fig. 20 being similar to  $P_{max}$  in Fig. 19 except for the difference in scale of the parameters plotted.

**6.9. Dependence of efficiency on  $\Delta T$  and electrode assemblies**

According to Fig. 21, at low  $\Delta T$ , efficiency of activated charcoal cells in series observed to be high and drastically falls with increment in  $\Delta T$ . On the other hand, activated charcoal electrode based thermocell had higher efficiencies at higher  $\Delta T$ . The trend in acetylene black thermocells showed that higher efficiencies were obtained at lower  $\Delta T$  and slowly reduced as  $\Delta T$  increased. All other assemblies showed identical trend as a single activated charcoal thermocell. It must be noted that though actual efficiencies were lesser than 1%, the efficiency accounts for approximately 20–30% of Carnot efficiency.



**Fig. 20 – Maximum power density vs  $\Delta T$  characteristics of different electrode assemblies.**

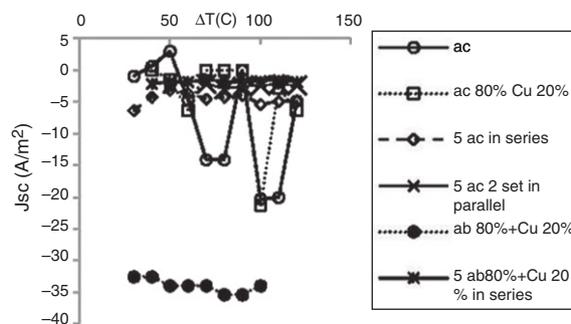


**Fig. 21 – Efficiency vs  $\Delta T$  characteristics of different electrode assemblies.**

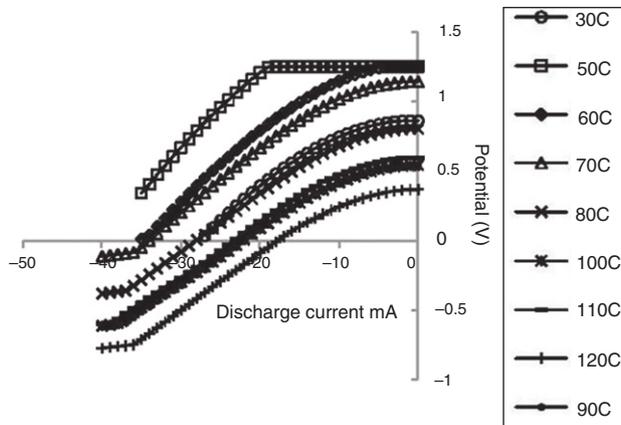
**6.10. Dependence of  $J_{sc}$  on  $\Delta T$  and electrode assemblies**

From Fig. 22, it could be seen that high and uniform power density were observed in case of single acetylene black-copper composite electrode based thermocell. The trend can be reasoned by the availability of free electrons in  $sp^2$  hybridized orbitals of acetylene black and d electrons in copper. These electrons contribute to high electron transfer rate and current density. Conversely, combination of such cells in series had very low current density. Activated charcoal single cells showed sudden increase in  $J_{sc}$  at  $\Delta T$  ranging from 100 °C to 110 °C.

From all the above described studies, it could be concluded that the best performance characteristic at high  $\Delta T$  had been shown by acetylene black single cell while acetylene black and copper composite electrode based single cell generated better and uniform performance characteristic at lower  $\Delta T$ . The series and parallel connected cells although showed



**Fig. 22 –  $J_{sc}$  vs  $\Delta T$  characteristics of different electrode assemblies.**



**Fig. 23 – V vs I characteristics of flat cell using CNT as electrode material.**

consistent results, it was not significant due to high internal resistance developed in the device.

Thus from the experimental results it can be inferred that activated charcoal generated higher power output at high  $\Delta T_s$  and acetylene black produced high power output at low  $\Delta T_s$ . When the cells were connected in series and parallel, huge power dissipation happened due to the copper connecting wires. Consequently, it was concluded that instead of connecting cells in parallel or series, utilizing highly conducting materials like multi wall carbon nanotube coatings on a flat flexible plate with large surface area would mitigate both low power output and high internal resistance effects.

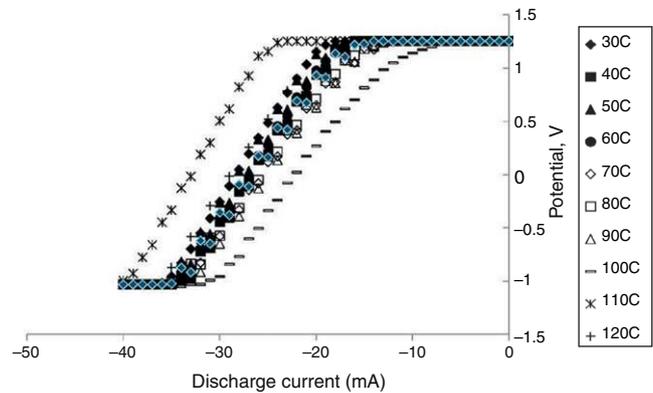
## 7. Characterization of flat cell with CNT as electrode material

A flat and flexible cell was prepared using Aluminum sheet of 0.3 mm thickness, 4 cm  $\times$  4 cm area as hot anode side, plastic transparency sheet of 0.3 mm thickness and 4 cm  $\times$  4 cm area as cold cathode side. A paste made of CNT and acetone was spread evenly using a spatula on each of these sheets up to a thickness of 0.5 cm.  $K_3Fe(CN)_6/K_4Fe(CN)_6$  aqueous solution trapped in agar-agar gel was then applied over the dried surface of one of the electrodes and this whole assembly was sealed using M-seal on all four sides.

From Fig. 23 it can be inferred that the  $I$ - $V$  characteristics showed a very uniform and well defined trend.  $V_{oc}$  was maximum at  $\Delta T=40^\circ C$  and  $\Delta T=50^\circ C$  with a value of 1.252 V while maximum  $I_{sc}$  was at 0.04 A,  $P_{max}=0.0109$  W, while maximum power density equals to  $6.84$  W/m<sup>2</sup>, maximum  $J_{sc}$  as  $21.875$  A/m<sup>2</sup> and the Seebeck coefficient of  $0.02504$  V/K at  $\Delta T=40$ - $50^\circ C$  (Table 10).

### 7.1. Characterization of MWCNT based flat cell (1 M potassium ferri/ferrocyanide)

The current dimension investigated being 22 cm  $\times$  24 cm. Fig. 24, implied that the  $V_{oc}$  of MWCNT based flat cell being consistently at 1.252 V on all  $\Delta T$ . The trend in  $I$ - $V$  characteristics was uniform without any fluctuation.  $I_{sc}$  varies from 20 to 40 mA within the range of  $\Delta T$  considered.



**Fig. 24 – I-V characteristics of 22 cm  $\times$  24 cm MWCNT based flat thermocell.**

From Fig. 25, irrespective of  $\Delta T$ ,  $V_{oc}$  appeared to be a straight line (constant). The maximum voltage fluctuated between 1.252 V and 1 V for  $\Delta T$  from  $30^\circ C$  to  $130^\circ C$ . The fall of maximum voltage decreased to 1 V at  $\Delta T=100^\circ C$  and increased again to 1.252 V at  $\Delta T=110$ - $130^\circ C$ . The trend in power density and current density is identical with respect to  $\Delta T$ . Both  $J_{sc}$  and power density were in the range of  $0.4$  A/m<sup>2</sup> (W/m<sup>2</sup>) to  $0.2$  A/m<sup>2</sup> (W/m<sup>2</sup>) with a drop noticed at  $\Delta T=100^\circ C$  and subsequent increase to initial value. The values  $I_{sc}$  and  $I_{max}$  overlapped and lie between 20 mA and 40 mA at all  $\Delta T$ . From Fig. 26a and Table 11, it can be inferred that 20-65% Carnot efficiency being achieved by the device at  $\Delta T$  ranging from  $30^\circ C$  to  $100^\circ C$ . At  $\Delta T=120^\circ C$  and  $130^\circ C$ , the device power conversion and relative efficiency became equal to that of Carnot efficiency. The device power conversion and relative efficiencies were 2% higher than Carnot efficiency at  $\Delta T=120^\circ C$  and 2% lower than Carnot efficiency at  $\Delta T=130^\circ C$ . At  $\Delta T=110^\circ C$ , the power conversion efficiency and relative efficiencies of the thermocell were approximately 18% higher than the Carnot efficiency. This high efficiency could be attributed to the plausible change in the thermionic processes at higher temperatures and high thermal conductivity of MWCNTs. The error analysis on power conversion efficiency of MWCNT based flat thermocell by conducting the characterization studies after 120 and 180 days of the fabrication from Fig. 26b. It was seen that the reproducibility of the data lies well within the experimental error limit and the performance of the device remained unaffected after 180 days from the day of its fabrication.

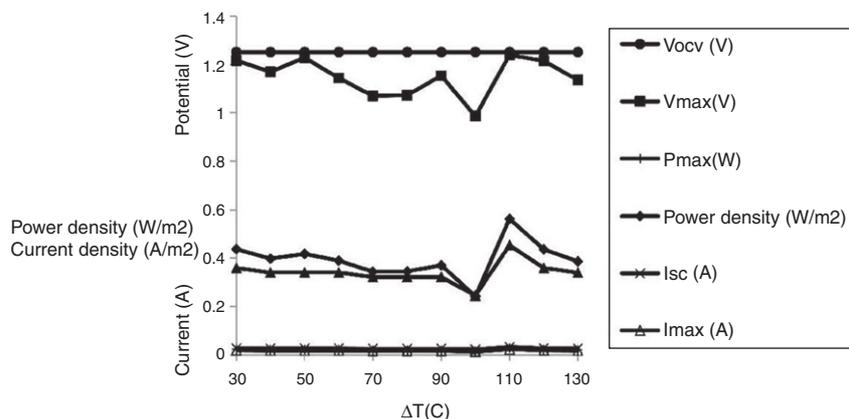
Thus from the above results, it can be concluded that MWCNT based flat cells performs efficiently than any other devices investigated in the current work. Although the maximum power density achieved by the device being  $\sim 0.6$  W/m<sup>2</sup>, the consistent performance of the device at all temperature gradient need to be highlighted.

## 8. Cost analysis of the device

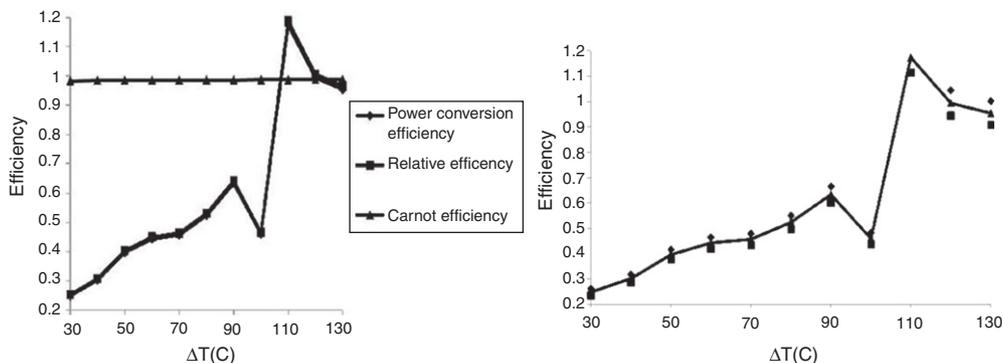
As the cost of MWCNTs have gone down a lot, in the current market MWCNTs of 10-20 nm size and >95% purity obtained from Chinese academy of Sciences was sufficient to produce

**Table 10 – Characterization of flat cell with CNT as electrode material.**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$E_{oc}$ (V)	$I_{sc}$ (mA)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	-16.875	0.862	-0.027	5.819	3.636563	0.028733	0.118842	0.98428	0.12074
40	-21.875	1.252	-0.035	10.955	6.846875	0.02504	0.134252	0.98476	0.13633
50	-21.875	1.252	-0.035	10.955	6.846875	0.020867	0.111877	0.98521	0.113557
60	-21.25	1.143	-0.034	9.716	6.072188	0.016329	0.085045	0.98563	0.086285
70	-17.5	0.804	-0.028	5.628	3.5175	0.01005	0.043107	0.98603	0.043717
80	-13.75	0.534	-0.022	2.937	1.835625	0.005933	0.019996	0.98641	0.020271
90	-13.75	0.543	-0.022	2.987	1.866563	0.00543	0.0183	0.98677	0.018545
100	-14.375	0.596	-0.023	3.427	2.141875	0.005418	0.01909	0.98711	0.019339



**Fig. 25 – Variation of  $V_{oc}$ ,  $V_{max}$ ,  $P_{max}$ ,  $J_{sc}$ , power density,  $I_{sc}$  and  $I_{max}$  of the 22 cm x 24 cm flat thermocell with  $\Delta T$ .**



**Fig. 26 – Variation of power conversion efficiency and relative efficiency of the device, with Carnot efficiency and  $\Delta T$ .**

**Table 11 – Characterization of MWCNT based flat cell (1M potassium ferri/ferrocyanide).**

$\Delta T$ (C)	$J_{sc}$ (A/m <sup>2</sup> )	$E_{oc}$ (V)	$I_{sc}$ (mA)	$P_{max}$ (mW)	$P_{max}/A$ (W/m <sup>2</sup> )	S	Power conversion efficiency	Carnot efficiency	Relative efficiency
30	0.3598485	1.252	0.019	0.023123	0.4379356	0.041733	0.248827045	0.983766234	0.252933102
40	0.340909091	1.252	0.018	0.02106	0.398863636	0.0313	0.302169422	0.98427673	0.306996409
50	0.340909091	1.252	0.018	0.022104	0.418636364	0.02504	0.39643595	0.984756098	0.40257273
60	0.340909091	1.252	0.018	0.020592	0.39	0.020867	0.443181818	0.985207101	0.4498362
70	0.321969697	1.252	0.017	0.01819	0.344507576	0.017886	0.456733529	0.985632184	0.463391452
80	0.321969697	1.252	0.017	0.018241	0.345473485	0.01565	0.523444674	0.98603352	0.530858904
90	0.321969697	1.252	0.017	0.019618	0.371553	0.013911	0.633328977	0.986413043	0.642052517
100	0.2462121	1.252	0.013	0.012818	0.2427652	0.01252	0.459782576	0.986772487	0.465945881
110	0.4545455	1.252	0.024	0.029736	0.5631818	0.011382	1.173295417	0.987113402	1.188612589
120	0.3598485	1.252	0.019	0.023085	0.4372159	0.010433	0.9936725	0.987437186	1.006314644
130	0.3409091	1.252	0.018	0.020448	0.3872727	0.009631	0.95351233	0.987745098	0.965342507

0.4 W/m<sup>2</sup> of power density in a flat cell. Moreover, the other materials employed in the fabrication of the thermocell constituted (i) potassium ferrocyanide and ferricyanide, (ii) agar-agar gel, which cost around Rs. 500/kg. Hence the fabrication cost of a single flat cell of MWCNT electrodes being Rs.10 and the power gained by this expenditure is around 0.4 W/m<sup>2</sup> approximately 0.22\$ per 0.4 W/m<sup>2</sup>. The cost further came down upon usage of electrode materials like activated charcoal, acetylene black and copper powder. Thus for thermocells made of activated charcoal, acetylene black and copper powder Rs.10 was the expense for a gain of 22 W/m<sup>2</sup>, approximately 0.22\$ per 22 W/m<sup>2</sup> which in turn being much more cost effective than any other thermocells demonstrated in the literature [25].

## 9. Perspectives and summary

The performance and efficiency of box configuration thermocells operating in activated charcoal, acetylene black and copper composite electrodes, agar-agar gel trapped potassium ferri/ferricyanide electrolyte had been studied. The Seebeck coefficient of 7.35 mV/K was measured for the activated charcoal electrode at 1M potassium ferricyanide at  $\Delta T = 6^\circ\text{C}$  and seven times higher than the value of 1.4 mV/K reported by Hu et al. [25] employing MWCNTs and 0.4M potassium ferricyanide at  $\Delta T = 60^\circ\text{C}$ , proving the fact that the thermodynamics of the redox couple and electrode material governs the Seebeck coefficient. The  $J_{sc}$  and power density ( $P_{max}$ ) generated by the activated charcoal electrodes in 0.1 mM, 1M and 4M potassium ferricyanide were 3.976 A/m<sup>2</sup>, 20.495 W/m<sup>2</sup> and 20.2845 A/m<sup>2</sup>, 21.437 W/m<sup>2</sup> and 9.03 A/m<sup>2</sup>, 21.98 W/m<sup>2</sup>, respectively, whereas that of the other electrode materials were discussed in other sections. The normalized current density at  $\Delta T = 60^\circ\text{C}$  for all the three concentrations of electrolyte mentioned above were  $J_{sc}/\Delta T$ , 0.066 A/m<sup>2</sup> K, 0.338 A/m<sup>2</sup> K and 0.151 A/m<sup>2</sup> K, respectively. The rationale behind this lower value of normalized current density might be due to the lower thermal conductivity of the activated charcoal electrodes. The normalized area power density,  $P_{max}/\Delta T^2$  of  $5.7 \times 10^{-3}$  W/m<sup>2</sup> K<sup>2</sup>,  $5.96 \times 10^{-3}$  W/m<sup>2</sup> K<sup>2</sup> and  $6.11 \times 10^{-3}$  W/m<sup>2</sup> K<sup>2</sup> for 0.1 mM, 1M and 4M electrolyte respectively were measured. It was reported in the literature that the Pt electrodes generated a  $J_{sc}$  of 48.4 A/m<sup>2</sup> and a  $P_{max}$  of 1.02 W/m<sup>2</sup>, corresponding to a  $J_{sc}/\Delta T$  of 0.81 A/(m<sup>2</sup> K) and a  $P_{max}/\Delta T^2$  of  $2.8 \times 10^{-4}$  W/(m<sup>2</sup> K<sup>2</sup>). The graphite sheet electrodes generated a  $J_{sc}$  of 36.6 A/m<sup>2</sup> and a  $P_{max}$  of 0.76 W/m<sup>2</sup>, corresponding to a  $J_{sc}/\Delta T$  of 0.61 A/(m<sup>2</sup> K) and a  $P_{max}/\Delta T^2$  of  $2.1 \times 10^{-4}$  W/(m<sup>2</sup> K<sup>2</sup>). Hence the current methodology would positively pave way for cost effective tapping of sensible heat and converting it in to useful power.

With different electrode materials, it was concluded that activated charcoal electrode thermocell had produced the highest maximum power of 15.145 mW and power density of 21.44 mW/m<sup>2</sup> at  $\Delta T = 100^\circ\text{C}$ . Thus making material best suited for use in industrial applications where waste heat in the range of  $\Delta T = 100^\circ\text{C}$  being available. Acetylene black had produced a maximum power of 4.7 mW with maximum power density of 0.6645 mW/m<sup>2</sup> and current density as 35.38 A/m<sup>2</sup>. By achievement of 18% higher efficiency than Carnot efficiency

at  $\Delta T = 110^\circ\text{C}$  for MWCNT based thermocells, real time applications of waste heat harnessing from thermal power plants, solar power plants, processing industries, etc. becomes plausible and best suited to extract the power from low temperature gradients across roofs, panels, bioreactors, etc.

The foregoing analysis aimed at development of thermocells which can harvest the waste heat or low grade sensible heat into useful power. In the current investigation cost of the thermocells had been tremendously brought down by cost effective materials like activated charcoal, boxes made of low quality steel and electrolyte trapped in agar-agar gel. By using optimal concentration of electrolyte as 1M and using appropriate electrode material, the power obtained had been improved by 14.92 times as seen in recent literature. To demonstrate thermocells in harnessing solar heat as well as low grade heat dissipated by storage devices and super computers and converted into power, experiments were performed employing flat cells. The future work in this regard aims at (i) demonstrating the device on flexible substrates in a real time data monitoring environment like exhaust pipes, chimneys, hot water pipes, etc. (ii) Studying the effects of vibrations of the heat transfer pipe on the phononic vibrations in the thermocells, (iii) designing a complete product from scratch, (iv) Integrating power storage devices and charge regulators into thermocells to harness waste thermal energy from solar panels, waste heat from Concentrated solar power plants, thermal heat generated in electronic devices like mobiles, tablets, laptops, etc. Although the current flat and box configuration thermocells produced consistent and constant power output for the maximum of 45 days, operational lifetimes of years to decades would be more desirable. Since the available waste energy being free and unlimited from several sources, relatively high conversion efficiencies of the presently improved thermocells and its cost effectiveness becomes a preferred task in the future.

## Conflicts of interest

The authors declare no conflicts of interest.

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