Development of thermo-electrochemical cells based on flexible nanocomposite electrodes with oxidized multi-walled carbon nanotubes coating

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Abstract. While conversion of low-grade waste heat into electricity is an important energy harvesting strategy, the thermo-electrochemical cells are one of the most promising devices for this application. This paper shows the study on thermo-electrochemical cell with polymer electrodes coated by oxidized multi-walled carbon nanotubes and the Fe(CN)63-/Fe(CN)64- based electrolyte. The developed cell demonstrates the current density values of more than 13 A/m2 and a specific power of 140 mW/m2. Hypothetical Seebeck coefficient was found equal to 0.7 mV/K by the calculation based on the temperature dependencies of the open circuit voltage.

1. Introduction
Conversion of low-grade waste heat (i.e. at temperatures < 150 °C) into electricity is a promising energy harvesting strategy. Low-grade waste heat gained from industrial or geothermal processes, solar heaters or collectors, biomass fermentation, human body, etc. by being a significant source of energy can be effectively harvested for electricity production. One of the key challenges regarding low-grade waste heat harvesting is an improvement of the devices efficiency while decreasing their cost [1-3]. Majority of studies shows the application of solid-state thermoelectric and Stirling engines for low-grade heat harvesting [2]. However semiconductors based thermoelectric have the insufficient efficiency at low temperatures due to low voltage range (μV/K). Meantime, Stirling engine technology demonstrates problems with long-term reliability while having high initial cost [1-3].

When comparing the devices’ efficiency in Wh/dollars, thermo-electrochemical cells shows advantages over Stirling engines or solid-state thermoelectric devices [1,2] due to their low cost. However, their low energy conversion efficiency and low real output power limit their commercial applications [3-6].

A typical thermo-electrochemical cell consists of two identical electrodes working at different temperatures in contact with an electrolyte containing a redox pair [7,8]. Temperature gradient
between electrodes causes oxidation of the redox pair on the anode (hot electrode) and reduction on the cathode (cold electrode) [6-8].

Aqueous ferri/ferrocyanide solution is an archetypical electrolyte system due to its large reaction entropy, high Seebeck coefficient (theoretical limit for aqueous solution is 1.4 mV/K) and high exchange current density [3].

Temperature difference between electrodes causes the oxidation of \([\text{Fe(CN)}_6]^{4-}\) ions on the hot electrode:

\[
[\text{Fe(CN)}_6]^{4-} \rightarrow [\text{Fe(CN)}_6]^{3-} \quad (1)
\]

and the reduction of \([\text{Fe(CN)}_6]^{3-}\) ions on cold electrode

\[
[\text{Fe(CN)}_6]^{3-} \rightarrow [\text{Fe(CN)}_6]^{4-} \quad (2)
\]

The potential difference is an important factor determining the device’s power output and characterized by the Seebeck coefficient:

\[
\mathcal{S} = \frac{\Delta S_{B,A}}{nF} = \frac{\partial \mathcal{V}}{\partial \mathcal{T}}
\]

The production of flexible devices is one of the promising trends in modern electronics. The thermocells flexibility can allow them to be used for heat harvesting from various non-planar heat sources such as heated pipeline, reactor or vessel, human body heat, etc. Flexible thermocells can be made of flexible body materials such as polyethylene terephthalate [9] and silicone [10] and flexible electrodes, typically based on carbon nanotubes. However, the device’s performance indicators (open-circuit voltage, short-circuit current and power output) is significantly limited by the low thermal conductivity of the body materials and low wettability of native multi-walled carbon nanotubes (MWCNTs) with aqueous ferri/ferrocyanide based electrolyte. This study shows the use of MWCNTs-based polymer composite with improved thermal [11,12] and electrical [13-15] conductivity allowing to increase the real temperature difference between internal electrodes surface (in the MWCNTs cover) in the cell and thus to improve the output open circuit voltage.

The MWCNTs show significant advantages including high electrical conductivity, flexibility, thermal stability, high surface area (i.e. 300-350 m\(^2\)/g for “Taunit-M” MWCNTs, used in current study) and ultra-low areal density [16-18]. Thus, MWCNTs become the most common electrode for modern thermal cells [1-3]. However, native CNTs have low wettability while interaction with aqueous electrolytes. Meantime, high wettability of oxidized MWCNTs allows increasing the charge transfer between electrolyte and MWCNTs electrode.

This study aims at performance indicators (open-circuit voltage, short-circuit current and power output) of thermo-electrochemical cell based on a flexible and heat conducting polymer electrodes coated by oxidized MWCNTs. Flexible cell body with well performance indicators provide have a potential applications as commercial battery based on thermo-electrochemical cells for waste heat gained from various sources such as industrial or geothermal processes, solar heaters or collectors, biomass fermention, human body heat, heated reactor, pipeline or vessel.

2. Materials and methods

2.1. Materials

A flexible polymer composite based on MWCNTs (“Taunit-M” [18] produced by NanoTechCenter LLC, Russia) and ethylene-1-octene copolymer (Lucene LC370 TM produced by LG Chem Ltd, South Korea) was used as an flexible electrode materials. A laboratory roller mixer UB-6175 (UGNLab, Russia) was used for sample processing. Processing took place at the temperature of 120±3°C and treatment time of 5-30 min. The details on polymer preparation methodology can be found in [14].

The electrode was covered with MWCNTs in order to get a greater specific surface area. The following oxidation of MWCNTs allowed increasing their wettability.
MWCNTs oxidation was carried out in two-necked flask with backflow condenser. The reaction temperature was maintained at 100-105°C and controlled with thermometer. Concentrated nitric acid (HNO₃) was used as an oxidizing agent in MWCNT/acid ratio equal to 1/20. Oxidation process continued for 2 h. After the oxidation completion, the products were rinsed with distilled water till the neutral pH. Separation of reaction products was performed by decantation with the following vacuum filtering and drying at 60 °C for 48 h. The details on oxidation technique can be found in [19].

Mixture of aqueous 0.3 M solution of the mixture of two components: potassium ferricyanide (III) K₃[Fe(CN)₆] and potassium ferrocyanide (II) K₄[Fe(CN)₆] with a molar ratio of 1/1 was used as an electrolyte.

2.2. Measurement and characterization technique

Figure 1 shows the schematic representation of the studied thermo-electrochemical cell with the electrodes made of composite sheets (1x1 mm size and 0.7-0.8 mm thickness). The composite sheets were coated with a MWCNTs by spreading their ethanol-based suspension (1 wt.%) and the following drying for 1 hour at 60 °C. Separator was placed between the electrode sheets. Electrolyte was introduced into the interelectrode space and sealed with a rubber gasket on perimeter.

3. Results and discussion

A SEM study of electrodes (figure 2a and 2b) proved the presence of 1 μm thick oxidized MWCNTs layer over polymer composite. The used separator (figure 2c) consisted of 10-20 μm thick polypropylene fibers. The MWCNTs distribution in the composite was shown as uniform (figure 2d).

Figure 3 shows the output power-voltage and current-voltage characteristics of the developed cell. The open-circuit voltage (U) and short-circuit current (j) increases with temperature difference increase, resulting in a parabolic power output (P) curves (figure 3a and 3b). The Seebeck coefficient is found to be ~ 0.7 mV/K (figure 3c). The output power of a thermo-cell also increases with an increase in the temperature gradient (figure 3d).
Figure 2: SEM image of components of the cell: (a) – electrode structure; (b) – cover oxidized MWCNTs layer; (c) – separator; (d) – fracture of polymer nanocomposite.

Figure 3. Electrophysical properties of thermocells: (a) – power output – open-circuit voltage and (b) – short-circuit current – open-circuit voltage dependences for different temperature; (c) and (d) – temperature dependences of open-circuit voltage and power output respectively.
Maximum output power increases from 26 mW/m² (ΔT = 20°C) to 140 mW/m² (ΔT = 50°C) (figure 3a). At the maximum temperature difference used in the experiment (hot electrode temperature T_hot = 75°C, ΔT = 50°C), the cell showed a current density of 13 A/m² and a voltage of 40 mV.

The obtained result (output power) is not as high as has been shown in literature for the best performers (i.e. non-flexible carbon nanotube aerogel sheet onto metal electrodes demonstrated the maximum power output of 6.6 W/m² [1]), however high enough for polymer flexible cells. The difference in results can be explained by the high resistance of the polymer electrode. The best values of output power for flexible thermo-electrochemical cell have been shown about 76 – 230 mW/m², as per [10] while current study shows the output power of 140 mW/m². However worth noting that in [10] these values have been obtained for tube-shaped flexible thermo-cell. The maximum output power for the flat thermo-electrochemical cells did not exceed 1 mW/m² as per [9].

Literature review shows the short-circuit current density of 0.39 A/m² and open-circuit voltage of 5 mV [10] for flexible thermo-cells compared to 13 A/m² and 40 mV, respectively, gained in current study. The different result can be explained by a higher real temperature gradient between the internal surfaces of the electrodes.

4. Conclusion
This paper shows the results of the study on the performance indicators (open-circuit voltage, short-circuit current and power output) of thermo-electrochemical cell with the flexible and heat- and electricity-conducting polymer electrodes coated with oxidized MWCNTs. The study showed that the polymer composite electrode with high thermal conductivity can improve thermo-electrochemical cell performance. Flat flexible thermo-electrochemical cell with polymer electrodes coated with oxidized MWCNTs showed the maximum output power of 140 mW/m², a current density of 13 A/m² and a voltage of 40 mV. Thus, the developed thermocells can be potentially applied for economically convenient harvesting untapped supplies of low-grade heat.

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References
[1] Im H and Kim T 2016 High-efficiency electrochemical thermal energy harvester using carbon nanotube aerogel sheet electrodes. Nat. Commun. 7 10600 doi.org/10.1038/ncomms10600
[2] Hu R, et al. 2010 Harvesting waste thermal energy using a carbon-nanotube-based thermo-electrochemical cell. Nano Lett. 10 838 doi.org/10.1021/nl903267n
[3] Dupont M F, MacFarlane D R and Pringle J M 2017 Thermo-electrochemical cells for waste heat harvesting – progress and perspectives. Chem. Commun. 53 6288 doi.org/10.1039/C7CC02160G
[4] Quickenden T I and Mua Y 1995 A review of power generation in aqueous thermogalvanic cells. J. Electrochem. Soc. 142 3985 doi.org/10.1149/1.2048446
[5] Gunawan A, Lin C H and Buttry D A 2013 Liquid thermoelectrics: review of recent and limited new data of thermogalvanic cell experiments. Nanosc. Microsc. Therm. 17 304 doi.org/10.1080/15567265.2013.776149
[6] Burmistrov I, Kovyneva N, Gorshkov N, Gorokhovsky A, Durakov A, Artyukhov D and Kiselev N 2019 Development of new electrode materials for thermo-electrochemical cells for waste heat harvesting. Renew. Energy Focus 29 42 doi.org/10.1016/j.ente.2019.02.003
[7] Kim K and Lee H 2019 Diglyme-based thermoelectrochemical cells operable at both subzero and elevated temperatures. Energy Technol. Online doi.org/10.1002/ente.201900857
[8] Alzahrani H A H, Buckingham M A, Marken F and Aldous L 2019 Success and failure in the incorporation of gold nanoparticles inside ferri/ferrocyanide thermogalvanic cells. *Electrochem. commun.* **102** 41 doi.org/10.1016/j.elecom.2019.03.007

[9] Im H, Moon H G, Lee J S, Chung I Y, Kang T J and Kim Y H 2014 Flexible thermocells for utilization of body heat. *Nano Res.* **7** 443 doi.org/10.1007/s12274-014-0410-6

[10] Yang H D, Tufa L T, Bae R M and Kang T J 2015 A tubing shaped, flexible thermal energy harvester based on a carbon nanotube sheet electrode. *Carbon* **86** 118 doi.org/10.1016/j.carbon.2015.01.037

[11] Muratov D, Kuznetsov D, Ilinykh I, Burmistrov I and Mazov I 2015 Thermal conductivity of polypropylene composites filled with silane-modified hexagonal BN. *Composites Science and Technology* **111** 40 doi.org/10.1016/j.compsecitech.2015.03.003

[12] Mazov I, Burmistrov I, Ilinykh I, Stepashkin A, Kuznetsov D and Issi J-P 2014 Anisotropic thermal conductivity of polypropylene composites filled with carbon fibers and multiwall carbon nanotubes. *Polym. Compos.* **36** 1951 doi/abs/10.1002/pc.23104

[13] Burmistrov I, Gorshkov N, Ilinykh I, Muratov D, Kolesnikov E, Anshin S and Mazov I 2016 Improvement of carbon black based polymer composite electrical conductivity with additions of MWCNT. *Compos. Sci. Technol.* **129** 79 doi.org/10.1016/j.compsecitech.2016.03.032

[14] Burmistrov I, Gorshkov N, Ilinykh I, Muratov D, Kolesnikov E, Yakovlev E and Mazov I 2017 Mechanical and electrical properties of ethylene-l-octene and polypropylene composites filled with carbon nanotubes. *Compos. Sci. Technol.* **147** 71 doi.org/10.1016/j.compsecitech.2017.05.005

[15] Burmistrov I, Gorshkov N, Anshin S, Kolesnikov E, Kuskov K, Ilinykh I, Issi J-P, Vikulova M and Kuznetsov D 2019 Enhancement of percolation threshold by controlling the structure of composites based on nanostructured carbon filler. *J. Electron. Mater.* **48** 5111 doi.org/10.1007/s11664-019-07287-3

[16] Gong K, Yan Y, Zhang M, Su L, Xiong S and Mao L 2005 Electrochemistry and electroanalytical applications of carbon nanotubes: a review. *Anal. Sci.* **21** 1383 doi.org/10.2116/analsci.21.1383

[17] Zhang M, Fang S, Zakhidov A, Lee S B, Aliev A and Williams C 2005 Strong, transparent, multifunctional, carbon nanotube sheets. *Science* **309** 1215 doi.org/10.1126/science.1115311

[18] Tkachev A, Mikhailo Z and Burakova E 2009 Investigation of methods for improving the activity of catalysts for producing carbon nanostructural materials. *Theor. Found. Chem. Eng.* **43** 739 doi.org/10.1134/S0040579509050212

[19] Burmistrov I, Muratov D, Ilinykh I, Kolesnikov E, Godymchuk A and Kuznetsov D 2016 The effects of liquid-phase oxidation of multiwall carbon nanotubes on their surface characteristics *IOP Conference Series: Materials and Engineering.* **112** 012004 doi.org/10.1088/1757-899X/112/1/012004