Journal of Visualized Experiments

Asymmetric Thermoelectrochemical Cell for Harvesting Low-grade Heat under Isothermal Operation

--Manuscript Draft--

Article Type:	Invited Methods Article - JoVE Produced Video
Manuscript Number:	JoVE60768R1
Full Title:	Asymmetric Thermoelectrochemical Cell for Harvesting Low-grade Heat under Isothermal Operation
Section/Category:	JoVE Engineering
Keywords:	Thermoelectrochemical cell, low grade heat, efficiency, graphene oxide, Thermo-pseudocapacitive effect, polyaniline
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Additional Information:	
Question	**Response**
Please indicate whether this article will be Standard Access or Open Access.	Standard Access (US$2,400)
Please indicate the **city, state/province, and country** where this article will be **filmed**. Please do not use abbreviations.	Hong Kong

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June 9th, 2019

Dr. Benjamin Werth
Science Editor at *JoVE*

Dear Dr. Werth,

Please find enclosed a manuscript entitled "Asymmetric Thermoelectrochemical Cell for Harvesting Low-grade Heat under Isothermal Operation," by Kaiyu Mu, Xun Wang, Ka Ho Li, Shien-Ping Feng, submitted for consideration in Journal of Visualized Experiments.

Low-grade heat is abundant but its efficient recovery is still a great challenge. We invent an asymmetric thermoelectrochemical cell (aTEC) to efficiently convert low-grade heat into electricity. The aTEC is composed with graphene oxide (GO) cathode, polyaniline (PANI) anode and 1M KCl electrolyte. The cell generates a voltage due to the pseudocapacitive reaction of GO when heating from room temperature to a high temperature (40~90 ^{o}C), and then current is successively produced by oxidizing PANI when an external electrical load is connected. The aTEC demonstrates a remarkable temperature coefficient of 4.1 mV/K and a high heat-to-electricity conversion efficiency of 3.32% working at a high temperature of 70^{o}C as equivalent to 25.3% of Carnot efficiency, unveiling a new promising thermoelectrochemical technology for low-grade heat recovery. This is the first demonstration of heat-to-electricity conversion via isothermal heating; it is fundamentally different from the state-of-the-art systems with power generation coupled to temperature differential.

We believe this manuscript is well suit for *JoVE*. Our work opens a new game-changing technology for harvesting low grade heat. With further research and development, aTEC may find many applications, such as low power sensing and communication for smart cities and body heat-powered technologies.

We confirm that none of the material has been published or is under consideration for publication elsewhere. All authors have approved the manuscript and agree with its submission. We would be grateful if the manuscript could be reviewed and considered for publication in the journal. If you have any queries or questions, please do not hesitate to contact me. Thank you for your attention.

Sincerely,

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TITLE:

Asymmetric Thermoelectrochemical Cell for Harvesting Low-grade Heat under Isothermal Operation

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KEYWORDS:

thermoelectrochemical cell, low-grade heat, efficiency, graphene oxide, thermo-pseudocapacitive effect, polyaniline

SUMMARY:

Low-grade heat is abundant, but its efficient recovery is still a great challenge. We report an asymmetric thermoelectrochemical cell using graphene oxide as a cathode and polyaniline as an anode with KCl as the electrolyte. This cell works under isothermal heating, exhibiting a high heat-to-electricity conversion efficiency in low-temperature regions.

ABSTRACT:

Low-grade heat is abundantly available in the environment as waste heat. The efficient conversion of low-grade heat into electricity is very difficult. We developed an asymmetric thermoelectrochemical cell (aTEC) for heat-to-electricity conversion under isothermal operation in the charging and discharging processes without exploiting the thermal gradient or the thermal cycle. The aTEC is composed of a graphene oxide (GO) cathode, a polyaniline (PANI) anode, and 1M KCl as the electrolyte. The cell generates a voltage due to the pseudocapacitive reaction of GO when heating from room temperature (RT) to a high temperature (T_H, ~40–90 °C), and then current is successively produced by oxidizing PANI when an external electrical load is connected. The aTEC demonstrates a remarkable temperature coefficient of 4.1 mV/K and a high heat-to-electricity conversion efficiency of 3.32%, working at a T_H = 70 °C with a Carnot efficiency of 25.3%, unveiling a new promising thermoelectrochemical technology for low-grade heat recovery.

INTRODUCTION:

Ubiquitous low-grade heat energy (<100 °C) could be recycled and converted into electricity[1,2] but is instead wasted. Unfortunately, heat recovery is still a great challenge, because converting low-grade heat to electricity is usually inefficient due to the low temperature differential and the distributed nature of the heat sources[3]. Intensive research has been conducted in solid-state thermoelectric (TE) materials and devices for the past decades, but the scalable application of TE devices in a low-grade heat regime is limited by the low energy conversion efficiency (η_E) of <2%[4].

Alternative approaches based on the effect of temperature on electrochemical cells have been suggested as a solution to this problem, because the ionic Seebeck coefficient (α) of thermoelectrochemical cells (TECs) is much higher than that of TE semiconductors[5,6]. Thermogalvanic cells (TGC) utilize redox active electrolytes sandwiched between two identical electrodes to generate a voltage across the cell when a thermal gradient is applied. The commonly used aqueous $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ electrolyte in TGCs was reported to have an α of -1.4 mV/K and yield an η_E of <1%[7-11]. However, TGCs suffer the drawback of the poor ionic conductivity of the liquid electrolyte, which is around three orders of magnitude smaller than the electronic conductivity in TE materials. The electric conductivity could be improved, but this improvement is always accompanied by a higher thermal conductivity, which leads to a lower temperature gradient. Therefore, the η_E of TGCs is inherently limited due to the trade-off between the liquid electrolyte conductance and the temperature requirement for the desired redox reactions in each side of the electrode.

A thermally regenerative electrochemical cycle (TREC)[12-14] based on a battery system using a solid copper hexacyanoferrate (CuHCF) cathode and a Cu/Cu^+ anode was recently reported. TREC is configured as a pouch cell to improve the electrolyte conductance, showing an α of −1.2 mV/K and reaching a high η_E of 3.7% (21% of η_{carnot}) when operated at 60 °C and 10 °C. Nevertheless, one limit of TREC is that external electricity is required at the start of the process to charge the electrodes in each thermal cycle, leading to complicated system designs[14]. A TREC without this limitation can be achieved, but it suffers from a poor conversion efficiency of <1%[13]. The TREC system demonstrates that a sodium-ion secondary battery (SIB)-type thermocell consisting of two types of Prussian blue analogues (PBA) with different α values can harvest waste heat. The thermal efficiency (η) increases proportionally with ΔT. Moreover, η reaches 1.08%, 3.19% at ΔT = 30 K, 56 K separately. The thermal cyclability is improved using Ni-substituted PBA[15-18].

Alternatively, a thermally regenerative ammonia battery (TRAB) employs copper-based redox couples [$Cu(NH3)_4^{2+}$/Cu and Cu(II)/Cu] that operate with the reverse temperature gradient by switching the temperature of electrolyte co-operated with positive and negative electrodes, which produces a η_E of 0.53% (13% of η_{carnot}). However, this system is configured with two tanks full of liquid electrolyte, causing sluggish heating and cooling. Also, the ammonia stream in the system creates concerns regarding safety, leakage, and stability[19-21].

Here we present an asymmetric thermoelectrochemical cell (aTEC) for heat-to-electricity conversion that can be thermally charged and electrically discharged by continuous isothermal heating without maintaining a temperature gradient in a geometric configuration or switching temperatures in a thermal cycle. The aTEC uses asymmetric electrodes, including a graphene oxide (GO) cathode and a polyaniline (PANI) anode, and KCl as the electrolyte. It is thermally charged via the thermo-pseudocapacitive effect of GO and then discharged with the oxidation reaction of PANI. Notably, the aTEC exhibits a high α of 4.1 mV/K and attains a η_E of 3.32%, the highest ever achieved at 70 °C (25.3% of η_{Carnot}).

PROTOCOL:

1. Preparation of the graphene oxide electrode

1.1. Synthesis of graphene oxide via the modified Hummer's method

1.1.1. Steps 1.1.2 and 1.1.3 occur at a low temperature (<0 °C). Circulate ice water flowing through the external layer of a double wall glass beaker placed on a magnetic stirrer to create low temperature conditions for the reactants inside.

1.1.2. Mix 1 g of sodium nitrate ($NaNO_3$) with 100 mL of sulfuric acid (H_2SO_4, reagent grade, 95–98%) using slow stirring in the beaker.

1.1.3. Add 1 g of flake graphite into the sulfuric acid and stir for 1 h in the cold bath. Add 6 g of potassium permanganate ($KMnO_4$) gradually to the solution and stir the mixture for another 2 h.

1.1.4. The next step of the reaction takes place at a middle temperature (~35 °C). Change the ice water to 35 °C water and continue the oxidation of the graphite by stirring for ½ h.

1.1.5. The last step of the reaction takes place at a T_H (80–90 °C). Add 46 mL of deionized (DI) water (70 °C) into the reaction tank drop by drop. Note that that the reaction is strong. Add 140 mL of DI water and 20 mL of hydrogen peroxide (30% H_2O_2) in the reaction tank as the last step of the reaction. Make sure that golden particles of GO appear as a result.

1.1.6. Wash the product thoroughly with dilute hydrochloric acid (HCl) and DI water several times until the GO suspension reaches pH = 7.

1.1.7. Freeze the washed GO suspension overnight and dry it in a freeze dryer until water evaporates completely.

1.2. Preparation of the graphene oxide electrode

1.2.1. Mix the graphene oxide, carbon black, and PVDF in a mass ratio of 75:15:10 and put them in a glass bottle. Drip the solvent N-methyl-2-pyrrolidone (NMP) into the solid mixture and ensure the weight ratio of solvent and solid mixture is 4:1.

1.2.2. Prepare the paste by mixing at 2,000 rpm for 13 min and defoaming in 1,200 rpm for 2 min with a mixer.

1.2.3. Brush coat the paste on carbon paper until the coat is ~8–15 mg/cm^2 and dry it for 4 h at 40 °C.

2. Preparation of the polyaniline (PANI) electrode

2.1. Prepare 1 wt% carboxymethyl cellulose (CMC) aqueous solution by dissolving CMC powder in DI water by stirring for 10 h.

2.2. Mix 50 mg of leucoemeraldine-base PANI and 10 mg of carbon black in a beaker. Add 150 μL of 1 wt% CMC solution into the beaker and mix with a magnetic stirrer for 12 h.

2.3. Add 6 μL of 40% styrene-butadiene (SBR) solution into the mixture and stir for another 15 min.

2.4. Place a piece of carbon paper on the doctor blade coater and drop the mixed PANI slurry at the leading edge of the carbon paper.

2.5. Blade coat the slurry to produce a film 400 μm thick on the carbon paper. Dry the coating for 4 h at 50 °C.

3. Assembling the pouch cell

3.1. Cut titanium foil into small pieces 3.5 cm long and 2.5 cm wide to make current collectors and then connect each piece to a nickel tab with a 20 kHz ultrasonic spot welding machine.

3.2. Place the porous hydrophilic polypropylene-based separator between the GO electrode and the PANI electrode to avoid short circuits. Each electrode is paired with one current collector.

3.3. Package the electrodes using aluminum laminated film. Seal the sides of the aluminum laminated film with a compact vacuum sealer for 4 s. Set the temperature of the top and bottom sealing parts as 180 °C and 160 °C separately.

3.4. Inject 500 μL of the 1 M KCl electrolyte into the pouch cell and allow to equilibrate for 10 min.

3.5. Extrude the excess electrolyte and seal the last side of the pouch cell in a -80 kPa vacuum chamber.

4. Setting up the temperature controlling system

4.1. Stack the pouch cell between two thermoelectric modules. Place thermocouples on the top and bottom sides of the cell. Apply thermal paste to all the interfaces to ensure good thermal contact.

NOTE: The temperature is controlled with LabVIEW code. Temperatures measured from the thermocouples are compared with the setting temperatures and the output voltage is determined by the difference between the real time temperature and setting temperature via a PID control. The voltage signals are transmitted to the power supply and are connected to the thermoelectric module. The closed-loop control guarantees a temperature measurement accuracy within ± 0.5 °C.

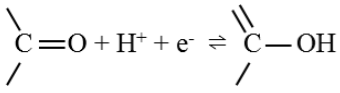
5. Electrochemical characterization

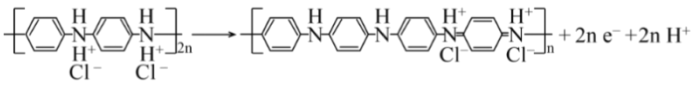
5.1. Perform the electrochemical tests of the cell using a potentiostat. Conduct the thermal charging in open circuit mode while carrying out the electrical discharging process at a constant current.

REPRESENTATIVE RESULTS:

The aTEC pouch cell was configured with asymmetric electrodes consisting of a GO cathode, a PANI anode, and filled with the KCl electrolyte. The thickness of the pouch cell shown in **Figure 1A** is 1 mm, which facilitates isothermal conditions between the two electrodes as well as efficient heat conduction. The scanning electron microscopy (SEM) images of the GO cathode and the PANI anode coated on carbon paper are shown in **Figure 1B** and **Figure 1C**. The porous structure increases the contact area between the active electrode materials and the electrolyte, thus optimizing the discharging current and the output power.

With the different work functions of the asymmetric electrodes, a built-in voltage (ΔV_0) was observed on the cell in open circuit conditions at RT (**Figure 2A**$_1$). When aTEC was heated from RT to T_H, heat triggered the pseudocapacitive reactions between functional groups containing oxygen (e.g., C=O bonds) and protons in the electrolyte at the GO-aqueous interface, thus the cell voltage (V_{oc}) increased as electrons moved to the surface of the GO (**Figure 2A**$_2$). When an external load was connected, the aTEC was discharged under the potential differential between electrodes at T_H, where the discharge capacity was mainly due to the oxidation of the PANI anode and the reduction of functional groups (**Figure 2A**$_3$), which can be presented as

Reduction: 

Oxidation: 

The voltages of aTEC during thermal charging and electrical discharging at T_H = 70 °C are shown in **Figure 2B**. The open circuit potential reached 0.185 V when the cell was heated from RT to T_H = 70 °C, where aTEC exhibited a high temperature coefficient ($\alpha = \partial V/\partial T$, where V is the electrode voltage and T is the temperature) of 4.1 mV/K. The discharging of aTEC was conducted under a constant current of 0.1 mA. The specific gravimetric capacity of the GO was 10.43 mAh/g while that of the PANI was 103.4 mAh/g. The heat-to-electricity conversion efficiency of aTEC can be calculated as the output electrical work (W) divided by input thermal energy, which can be expressed as

$$\eta_E = \frac{W}{Q_H + Q_{iso}} = \frac{\int V dq}{(1-\eta_{HX})\sum mC_p\Delta T + T_H\Delta S}$$

The output electrical work was calculated from the integration of discharging voltage over charge capacity while the input thermal energy consisted of the Q_H for heating the cell up from RT to T_H and Q_{iso} for heat absorbed during discharging at T_H. In the equation, q is the discharge capacity, η_{HX} is the efficiency of heat recovery, m is the mass of the active materials of electrodes and electrolyte, C_p is the specific heat, ΔT is the temperature difference between the operating temperature and RT, and ΔS is the reaction entropy change. Based on the discharging shown in **Figure 2B**, our aTEC attained a η_E of 3.32% at 70 °C, which is equivalent to 25.3% of η_{Carnot} (13.1%).

The isothermal operating of aTEC allows its use in many various scenarios. The aTEC can be charged by a hot pot with boiling water (**Figure 3**). The voltage of six aTECs connected in a series can reach >1 V. Our aTEC illustrated an excellent heat-to-electricity performance with a high temperature coefficient and energy conversion efficiency. The cell device performance and operating temperature window could be further improved by changing the composition of the electrolyte and using electrode materials with high α, low heat capacity, and robust functionalities. Our work sheds light on the design of thermoelectrochemical systems. With further research and development, aTEC has the potential to become a key technology for low-grade heat recovery.

FIGURE AND TABLE LEGENDS:

Figure 1: aTEC pouch cell. (A) Pouch cell configuration. The GO cathode and the PANI anode are assembled with the titanium (Ti) foil current collector and separated by the hydrophilic polypropylene separator. SEM images of **(B)** the GO cathode and **(C)** the PANI anode both coated on carbon paper.

Figure 2: aTEC charging and discharging. (A) Working principle of aTEC. **(B)** Open circuit voltage of the thermal charging process (red line) and electrical discharging curve (blue line) of the aTEC.

Figure 3: Demonstration of aTEC charged by a hot pot.

Table 1: Comparison of different TEC technologies for low-grade heat-to-electricity conversion.

DISCUSSION:

The aTEC converts thermal energy into electricity via a thermal charging process when heating from RT to T_H and a successive electrical discharging process at T_H. Getting rid of the dependence on a temperature gradient or a temperature cycle like the TGC and TREC, aTEC allows isothermal heating operation during the entire charging and discharging processes. Thermal induced voltage is based on the pseudocapacitive effect of GO because heating facilitates the chemisorption of protons on the oxygen functional groups of GO, causing the pseudocapacitive reaction at the GO-aqueous interface. PANI contributes little to the increased voltage but provides electrons in the discharging process. The utilization of the KCl electrolyte keeps the charge of the electrode-electrolyte interface balanced during the reaction and improves the conductivity of the whole cell. The system is nontoxic and environmentally friendly, which makes it ideal for commercial applications. Other alternatives for the electrolyte can be chloride salt, such as NaCl, because chloride ions play an essential role in the oxidation reaction of PANI in the discharging process.

Unlike technologies based on thermal gradients or thermal cycles, aTEC is unique and has potential for practical applications due to its low cost, flexibility, light weight, its isothermal and continuous thermal charge/electrical discharge process, and the ability to form stacks of cells. The aTEC achieves a high α of 4.1 mV/K and a high ηE of 3.32% (equivalent to 25.3% of η_{carnot}) at 70 °C, which is superior to existing techniques for low-grade heat harvesting. A comparison of aTEC and other TEC techniques is shown in **Table 1**.

The cyclability performance of aTEC is still unsatisfactory. This may be improved by adding a redox couple into the electrolyte or changing the electrode materials. Prussian blue analogs (PBA) are likely to make a better anode electrode for aTEC, because the negative temperature coefficient of some PBAs can help enhance the efficiency of aTEC. An aTEC with improved cyclability has great potential for commercial use, such as recovering waste heat from an air conditioner.

ACKNOWLEDGMENTS:

The authors acknowledge constructive discussion with Prof. D.Y.C. Leung and Dr. Y. Chen (The University of Hong Kong), Prof. M.H.K. Leung (City University of Hong Kong), Dr. W. S. Liu (Southern University of Science and Technology), and Mr. Frank H.T. Leung (Techskill [Asia] Limited). The authors acknowledge the financial support of General Research Fund of the Research Grants Council of Hong Kong Special Administrative Region, China, under Award Number 17204516 and 17206518, and Innovation and Technology Fund (Ref: ITS/171/16FX).

DISCLOSURE:

The authors declare no competing financial interests.

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Figure

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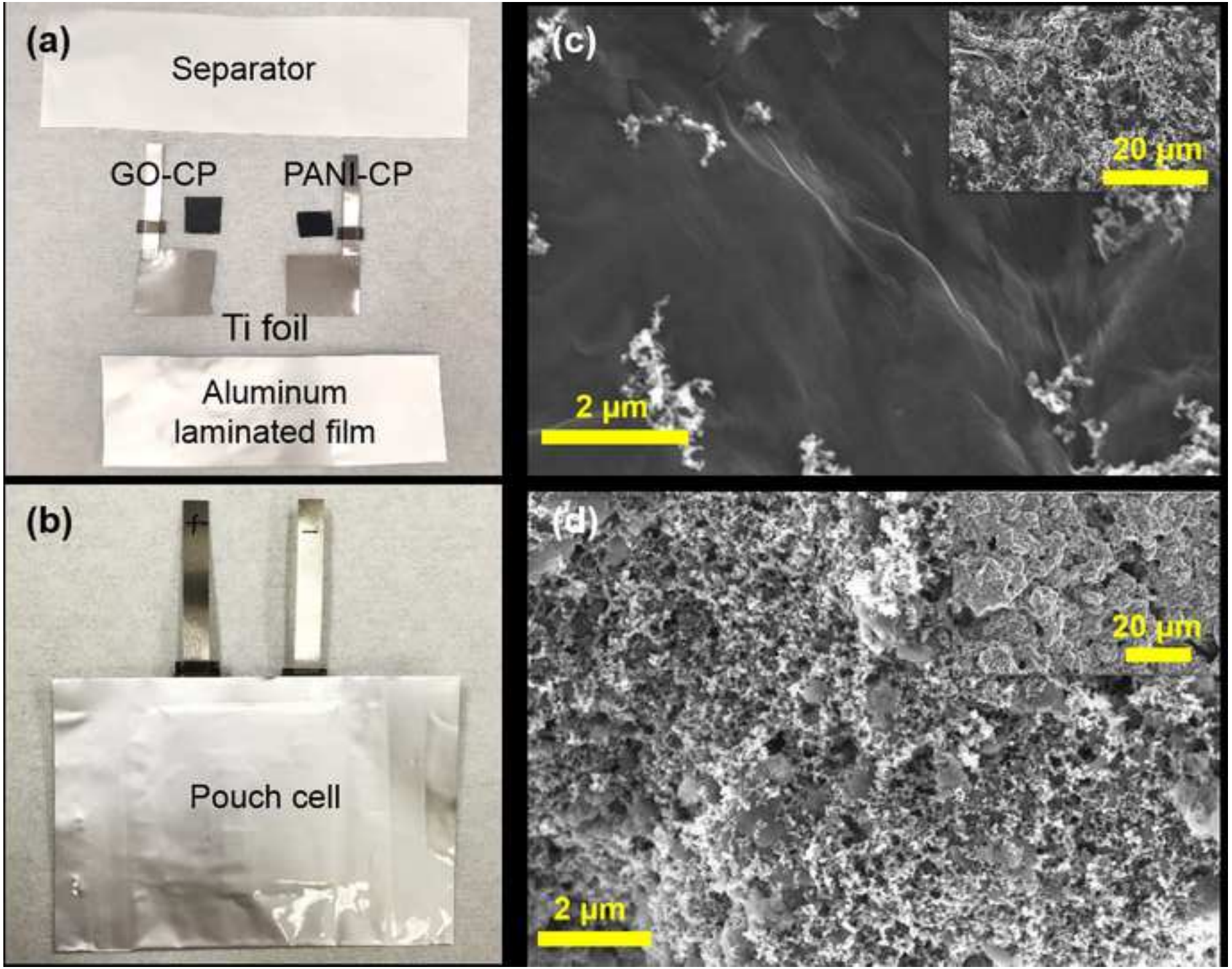

Figure 2

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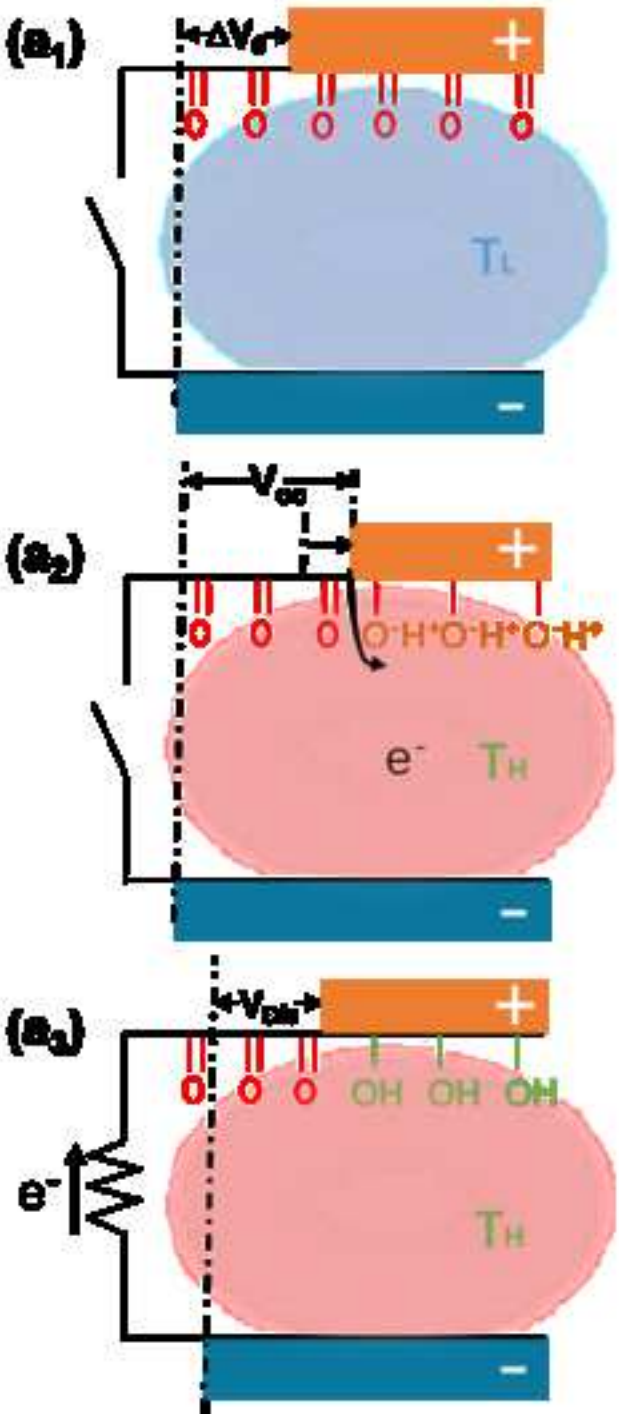

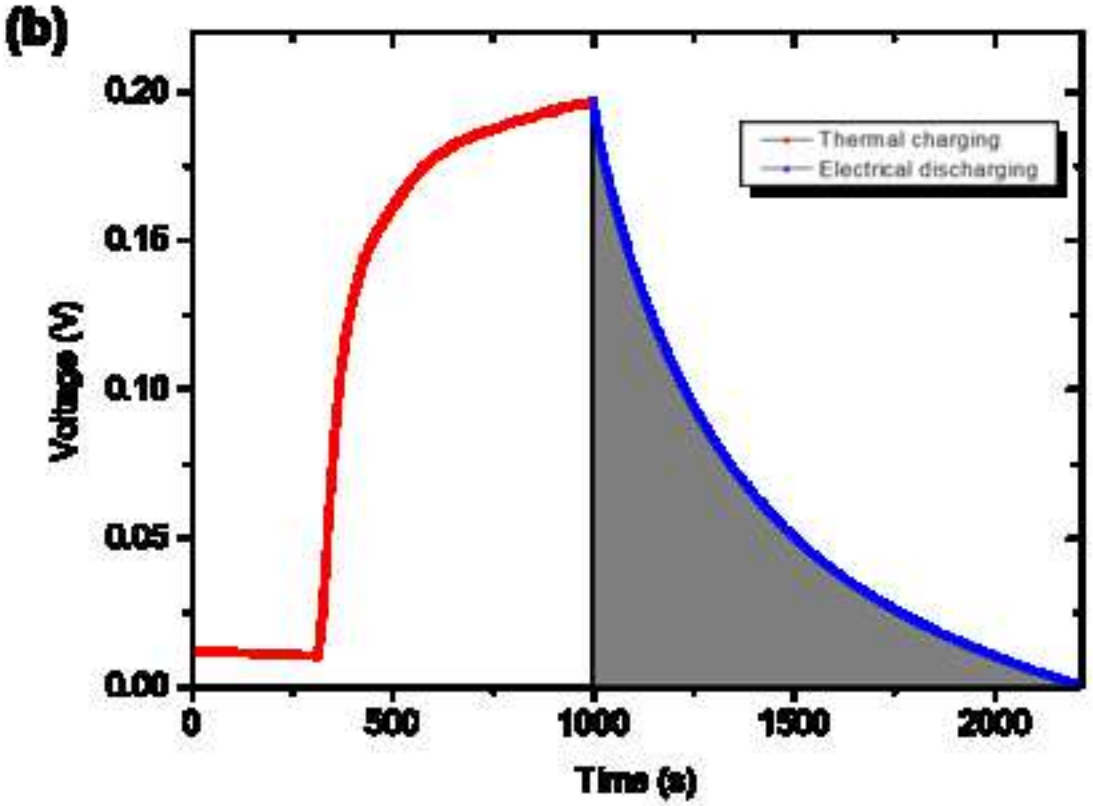

Figure 3

Table 1 Click here to access/download;Table;Table 1.xlsx

Operating mode	*TEC system*	*Structure and Materials*	*α (mV/K)*	*η_E (η_E/η_{Carnot})*
Temperature gradient (continuous operation based on the temperature-dependent redox potentials at the hot and cold sides)	TGC	Electrode: Multi-walled carbon nanotubes (MWCNT) based electrode Electrolyte: $K_3Fe(CN)_6/K_4Fe(CN)_6$	1.4	0.24% -1.40%
		Electrode: Carbon-based material Electrolyte: $K_3[Fe(CN)_6]/(NH_4)_4[Fe(CN)_6]$ or $Fe_2(SO_4)_3/FeSO_4$	1.85	0.11% -0.40%
		Electrode: CNT aerogel sheets Electrolyte: $K_3Fe(CN)_6/K_4Fe(CN)_6$	1.43	0.55% -3.95%
Temperature gradient	RFB	Electrode: carbon cloth Flow electrolyte: $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ and V^{3+}/V^{2+}	3	1.80% -15%
Temperature cycle	TREC	Electrode: CuHCF and Cu Electrolyte: $NaNO_3$ and $Cu(NO_3)_2$	1.2	3.70% -25%
		Electrode: NiHCF and Ag/AgCl Electrolyte: KCl	0.74	1.60% -13%
		Electrode: $KFe^{II}Fe^{III}(CN)_6$ and $K_3Fe(CN)_6/K_4Fe(CN)_6$ with carbon cloth Electrolyte: KNO_3	1.45	0.72% -6.00%
		Electrode: Cu		0.86%

	TRAB	Electrolyte: $Cu(NO_3)_2/NH_4NO_3$	–	-6.10%
		Electrode: Cu Flow electrolyte: $Cu(NO_3)_2/NH_4NO_3$	–	0.70% -5.00%
Temperature cycle	aTEC	Electrode: GO and PANI Electrolyte: KCl	4.1	3.32% (25.3%)

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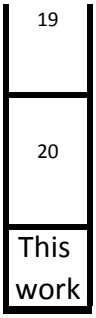
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Table of Materials

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Name	Company	Catalog Number	Comments
Alumina laminated film	Showa Denko	SPALF C4	
Carbon black	Alfa Aesar	H30253.22	
Carbon paper	CeTech Co. Ltd	W0S1009	
Carboxymethyl cellulose (CMC)	Guidechem company		
DC Power supply	B&K Precision	Model 913-B	
Doctor blade coater	Shining Energy Co. Ltd		
Gamry	Gamry Instruments	Reference 3000	
Graphite	Sigma-Aldrich	332461-2.5KG	
Mixer	Thinky	ARE-250	
Nickel tab	Tianjin Iversonchem company		4 mm width
N-Methyl-2-pyrrolidone (NMP)	Sigma-Aldrich	443778-1L	
Polyaniline (leucoemeraldine base)	Sigma-Aldrich	530670-5G	
potassium permanganate (KMnO4)	Sigma-Aldrich	223468-500G	
Separator	CLDP		25 um thickness
Sodium nitrate (NaNO3)	Sigma-Aldrich	S5506-250G	
Styrene butadiene	Tianjin Iversonchem company	BM400	
Sulfuric acid	Sigma-Aldrich	320501-2.5L	
Thermoelectric modules	CUI Inc.	CP455535H	
Titanum foil	Qingyuan metal		0.03 mm thickness

Revision Report for JoVE60768

Asymmetric Thermoelectrochemical Cell for Harvesting Low-grade Heat under Isothermal Operation

Kaiyu Mu, Xun Wang, Ka Ho Li, Shien-Ping Feng

We thank the editor for handling the manuscript review and the reviewers for their detailed and insightful comments. The manuscript has been revised to reflect the comments of editor and all reviewers. A detailed revision/rebuttal report is included below, and all revised text in the manuscript and supplementary material is marked in blue for convenience.

Editorial comments

General:

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues.

Response: We thank the editor for his/her comments. We have thoroughly proofread the manuscript.

2. Please ensure that the manuscript is formatted according to JoVE guidelines–letter (8.5" x 11") page size, 1-inch margins, 12 pt Calibri font throughout, all text aligned to the left margin, single spacing within paragraphs, and spaces between all paragraphs and protocol steps/substeps.

Response: We thank the editor for the suggestion on the format and we have updated the format according to the requirements.

3. If possible, please write equations using Word's equation editor.

Response: We thank the editor for his/her comments. All equations are correctly formatted.

4. Please include at least 6 key words or phrases.

Response: We thank the editor for his/her suggestion. The key word 'Thermo-pseudocapacitive effect' has been added as shown in line 41, page 1.

5. For in-text formatting, corresponding reference numbers should appear as numbered superscripts (without brackets) after the appropriate statements.

Response: We thank the editor for his/her comment. The reference format has been revised accordingly.

6. JoVE cannot publish manuscripts containing commercial language. This includes trademark symbols (™), registered symbols (®), and company names before an instrument or reagent. Please limit the use of commercial language from your manuscript and use generic terms instead. All commercial products should be sufficiently referenced in the Table of Materials and Reagents.

For example: Thinky Mixer ARE-250, Guidechem, Sigma-Aldrich, Omega, Gamry, etc.

Response: We thank the editor for his/her comment. The manuscript has been checked thoroughly. The detailed information on the materials has been added in the Table of Materials.

Protocol:

1. Please ensure the protocol is written in the imperative, except for separate 'NOTE's.

Response: We thank the editor for his/her comment. Grammar of the protocol is revised in imperative tense.

.

2. Please split up longer Protocol steps so that individual steps contain only 2–3 actions and a maximum of 4 sentences.

Response: We thank the editor for the suggestion. The protocol steps have been correctly rearranged.

3. There is a 10 page limit for the Protocol, but there is a 2.75 page limit for filmable content. If revisions cause the highlighted portion to be more than 2.75 pages, please highlight 2.75 pages or less of the Protocol (including headers and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol.

Response: We thank the editor for the information. The protocol contents for filming have been highlighted in blue from page 3 to page 5.

4. For each protocol step, please ensure you answer the "how" question, i.e., how is the step performed? Alternatively, add references to published material specifying how to perform the protocol action. If revisions cause a step to have more than 2-3 actions and 4 sentences per step, please split into separate steps or substeps.

Response: We thank the editor for pointing this out. The protocol has been checked thoroghtly.

Figures:

1. Please remove the embedded figures from the manuscript.

2. Please combine all panels of each figure into single image files (i.e., 3 in total).

3. Figure 1b: Please explain which SEM image is which. Also, the scale bar labels are hard to read.

Response: We thank the editor for his/her comment. All figures have been rearranged and replaced with higher resolution.

Discussion:

1. Please include a Discussion section that explicitly covers the following in detail in 3–6 paragraphs with citations:

a) Critical steps within the protocol

b) Any modifications and troubleshooting of the technique

c) Any limitations of the technique

d) The significance with respect to existing methods

e) Any future applications of the technique

Response: We thank the editor for his/her comment. The discussion section has been revised.

Acknowledgment and Disclosures:

1. Please include an Acknowledgements section, containing any acknowledgments and all funding sources for this work.

2. Please include a Disclosures section, providing information regarding the authors' competing financial interests or other conflicts of interest. If authors have no competing financial interests, then a statement indicating no competing financial interests must be included.

Response: We thank the editor for his/her comment. Acknowledgements and Disclosures section has been added in line 349 and line 352, page 11 respectively.

References:

1. Please ensure that the references appear as the following: [Lastname, F.I., LastName, F.I., LastName, F.I. Article Title. Source. ***Volume*** *(Issue), FirstPage – LastPage (YEAR).] For more than 6 authors, list only the first author then et al.*

2. Please do not abbreviate journal titles.

Response: We thank the editor for his/her comment. The reference section has been revised in the right format.

Table of Materials:

1. Please ensure the Table of Materials has information on all materials and equipment used, especially those mentioned in the Protocol.

Response: We thank the editor for his/her information. The table of Materials has been revised.

Reviewer #1:

Accept

Response: We appreciate the reviewer's acceptance on the publication of this work.

Reviewer #2:

Manuscript Summary:

This paper reports the asymmetric thermoelectrochemical cell for heat-to-electricity conversion under isothermal operation without exploiting thermal gradient or thermal cycle. It is an interesting work.

Response: We thank the reviewer for his/her comment and the interest on this work.

Major Concerns:

This paper can be considered for publication in "Journal of Visualized Experiments" after addressing the following issues:

(1) In the part of introduction, the author should divide this part into two or three paragraphs. Line 76, the ηE can reach more than 0.5% using aqueous Fe(CN)63-/Fe(CN)64- electrolyte in thermogalvanic cell, as reported by many literatures. Therefore, some important references should be cited, including Nano-Micro Lett. (2016) 8: 240.; RSC Adv., 2015, 5, 97982.

In addition, the author should explain clearly the motivations of choosing the graphene oxide (GO) as cathode, choosing a polyaniline (PANI) as anode, and KCl as electrolyte?

Response: We thank the reviewer's for providing more information on efficient TGC systems. TGC based on $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ electrolyte could yield energy conversion from 0.1% to 1% as shown in the reference cited.

Thermal- induced voltage is based on the pseudocapacitive effect of GO since heating facilitates the chemisorption of protons on the oxygen functional groups of GO, causing the occurring of pseudocapacitive reaction at the GO-aqueous interface. PANI contributes little to the increased voltage but provides electrons in the discharging process. The utilization of KCl electrolyte keeps the charge of electrode-electrolyte interface balanced during reactions and improves the conductivity of the whole cell, which is also nontoxic and environmentally friendly for the broader application. The alternatives for the electrolyte can be Cl^- based salt like NaCl, as Cl^- plays an essential role in the oxidation reaction of PANI in discharging process. The related sentences have been revised correspondingly in the revised manuscript (highlighted in blue in line 271 on page 7).

(2) In the part of experimental section, this part is very long and the author should simplify and combine some sections. Actually, an illustration may well express the production process.

Response: We thank the reviewer for this comment. The key steps have been extracted in the experimental section. We are trying our best to provide all the useful and important experimental details to the readers. The illustration of the production process will be present in the JoVE video protocol.

(3) In the Representative results section, it is very simple and very little discussion can be observed in this part. Therefore, more discussion should be added it in this part.

Response: We thank the reviewer for his/her comment. The discussion part has been extended in line 263 page 7.

(4) Line 195, it would be helpful to list the equation for calculating the temperature coefficient.

Response: We thank the reviewer for his/her comment. The calculation equation has been added in line 235, page 6.

(5) It would be valuable to compare the ηE with other types of thermo cells.

Response: We thank the reviewer for this suggestion. We added table 1 for the detailed comparison (include η_E) between our aTEC and current thermoelectrochemical systems.

Minor Concerns:

(6) Some typos, in line 196, "efficiency o aTEC", should be "efficiency of aTEC"?

(7) Several letters in equation after line 197 are not in the right form.

Response: We thank the reviewer for his/her comment. We have thoroughly checked the spelling and the formatting of this manuscript.

Reviewer #3:

This paper report on the protocol of aTEC, GO cathode, polyaniline anode, and 1M KCl electrolyte. I think the description on the experiment is OK. However, authors should consider the following

1. The aTEC is charged by heating (and negatively charged by cooling). At high temperature, the charged (and limited) charge was be extracted by discharging process. In the actually use, the capacity is a significant parameter. So, authors clearly state the capacity per cathode/anode weight.

Response: We thank the reviewer for the positive comment on experiment description and the suggestion. The The specific gravimetric capacity of GO is 10.43 mAh/g while that of PANI is 103.4 mAh/g. The related sentences have been revised correspondingly in the revised manuscript (highlighted in blue in line 237 on page 6).

2. In the actual operation, the aTEC need thermal cycle. OR the aTEC no longer convert thermal energy to electronic energy. The description "isothermal operation without exploiting thermal gradient or thermal cycle" is misleading. Should be change to "isothermal operation without exploiting thermal gradient" .

Response: We thank the reviewer for pointing out the misleading expression on the system. The isothermal operation without thermal cycle is actually referred that the aTEC is charged by heating the cell to a high temperature and the discharging process is conducted on the same high temperature. We have revised the statement (highlighted in blue in line 53 on page 2).

3. The ideal of the aTEC was reported with use of secondary battery materials. For example, T. Shibata, at al. Appl. Phys. Express, 11(2018)017101, T. Shibata, et al. Sci. Reps.. 8(2018)14784, Y. Fukuzumi, et al. Energy Technol, 6(2018)1865, T. Shibata, ChemSelect, 4(2019)8558. These papers should be appropriately cited.

Response: We thank the reviewer for the suggestion. The secondary battery materials mentioned in these paper have great potential to be used on the thermoelectrochemical system. These paper have been cited as reference 17-20.

Reviewer #4:

Authors report the electrolyte thermoelectric energy harvester using Graphene oxide and PANI as electrode material. The content of paper seem to be good but several issues should be addressed as following:

- The device concept seems not clear. This device concept is same as thermal charging of supercapacitor?

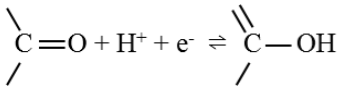
Response: We thank the reviewer's for his/her comment. The concept of our aTEC is to generate a voltage between two different electrodes isothermally at a high temperature. Due to the thermopseudocapacitive effect of oxygen functional groups, graphene oxide (GO) obtains a high positive temperature coefficient over 4 mV/K. Meanwhile, polyaniline(PANI) shows an negligible voltage response to temperature, thus building a voltage difference between GO cathode and PANI anode by heating the two electrode simultaneously. The voltage generated at high temperature enables the cell to be discharged or power electric devices under the reduction of GO and oxidation of PANI successively. The concept is totally different from the thermal charging of supercapacitor which is generally composed by two identical carbon-based materials and operated independently from redox reaction.

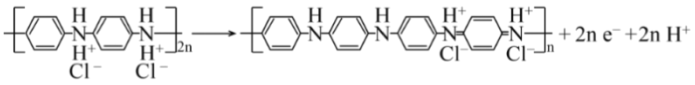
- What is the role of KCl? What will be different for other electrolytes?

Response: We thank the reviewer's for his/her comment. The utilization of KCl electrolyte keeps the charge of electrode-electrolyte interface balanced during reactions and improves the conductivity of the whole cell, which is also nontoxic and environmentally friendly for the broader application. The alternatives for the electrolyte can be Cl- based salt like NaCl, as Cl- plays an essential role in the oxidation reaction of PANI in discharging process. The related sentences have been revised correspondingly in the revised manuscript (highlighted in blue in line 270 on page 7).

- *What is the reaction at GO cathode side, PANi anode side? Reaction equations should be written.*

Response: We thank the reviewer's for his/her comment. The reactions of GO and PANI can be presented respectively as:

Reduction: 

Oxidation: 

The reactions has been added and highlighted in blue in line 232 on page 6.

- *What is contribution of K+ and Cl- into the redox reaction?*

Response: We thank the reviewer's for his/her comment. The utilization of KCl electrolyte keeps the charge of electrode-electrolyte interface balanced during reactions and improves the conductivity of the whole cell, which is also nontoxic and environmentally friendly for the broader application . The alternatives for the electrolyte can be Cl- based salt like NaCl, as Cl- plays an essential role in the oxidation reaction of PANI in discharging process. The related sentences have been revised correspondingly in the revised manuscript (highlighted in blue in line 270 on page 7).

- *If the KCL concentration is different, how is effect*

Response: We thank the reviewer's for pointing this out. As the main function of KCl is to improve the conductivity of the cell and participate in the reaction of PANI, the concentration of KCl has little effect on the operation of the device and limited influence on the discharging current.

- *What is the pore diameter of separator?*

Response: We thank the reviewer's for his/her comment. We choose the commercial separator of lithium battery and the porosity is 50%.

- *How much is internal resistance?*

Response: We thank the reviewer's for his/her comment. The internal resistance of a cell is less than 10 Ω.

- *Also, paper organization should be revised.*

Response: We thank the reviewer's for his/her suggestion. The manuscript has been reorganized and revised.