研 究 終 了 報 告 書

「伝導性ポリマーによる熱充電可能な電気化学セルの創成」

研究期間： 2017年10月～2021年03月
研 究 者： 衛 慶碩

1． 研究のねらい

Energy recycling and reuse are among the most important global-scale priorities. One solution is the harvesting of energy from external environmental sources such as light, heat, vibration, motion, and electromagnetic radiation. Among these energy sources, thermal energy is ubiquitously distributed and can be converted to electrical energy by various approaches exploiting the Seebeck effect. Solid-state thermoelectric devices using inorganic semiconductors such as Bi_2Ti_3 are the most common strategy, and can potentially power Internet-of-things sensors without cables or batteries. However, Te is an expensive rare metal and environmentally damaging, so is unsuitable for large-area applications. Solid-state thermoelectric devices based on abundant and eco-friendly materials have been studied for many years.

Thermo-electrochemical cells, which rely on the potential difference generated by a redox couple at a different temperature, also convert thermal energy to electrical energy. In redox couple-based thermo-electrochemical cells, the thermopower (S_e) can be boosted to millivolts per Kelvin because the reaction entropy of the ions is extremely large. This advantage is important for practical applications because the efficiency of DC-to-DC converters improves at larger input voltages. Especially at low temperatures, such as human body temperature, the achievable temperature difference is considerably small. Thus far, research has focused mainly on redox-based thermoelectrical cells with aqueous media, for example, the ferrocyanide/ferricyanide redox couple with an S_e exceeding 1 mV K^{-1}.

The target of this study is to develop novel polymer-based thermally chargeable electrochemical cells aiming for a power density higher than 1 mW/cm^2 and an energy density higher than 1 Wh/kg (double-layer capacitor). The size of the cell is expected to be 1 cc (1 cm×1 cm×1 cm). Since we are using a water-based electrolyte, the target temperature range is from 5 degrees to 95 degrees.

The proposed project is divided into three steps. The first one is understanding and developing conducting polymer electrodes and screening the redox reaction to achieve high thermopower using half-reaction. The second one is employing two different redox couples with positive and negative reaction entropy using separation members. Finally, we are going to demonstrate the device using body heat for wireless communications.

2． 研究成果

（1）概要

There are four major achievements in 3 years.

1. The conducting polymer PEDOT/PSS film was reported to be an attractive electrode in thermoelectrochemical cells, as it shows an even lower charge transfer resistance than Pt.
2. Additives with a strong hydrogen bond will significantly increase the thermopower of $K_3Fe(CN)_6/K_4Fe(CN)_6$ up to 4 mV/K. Using a 6 cm^2 device, a power output of 1.6 mW was achieved. A 1 mW/cm^2 power density could be expected when the temperature difference is 73K.
3. Conducting polymer films shows the advantage of compatibility with insoluble redox couples such as Prussian blue analog materials, which facilitates determining the temperature-dependent redox potential of different materials. By appropriately combining redox couples, thermally regenerative electrochemical cells were realized, which could generate power during an environmental temperature change. The calculated energy density is around 0.1 Wh/kg.
4. We have demonstrated that polymer-based thermoelectrochemical cells could power Beacons and LEDs using body heat.

(2)詳細

研究テーマ A「Developing polymer electrode with low charge transfer resistance」

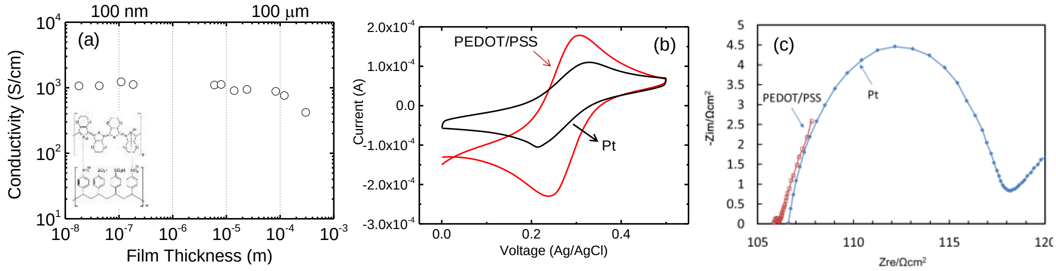

Figure 1. (a) Conductivity of the PEDOT/PSS films at different film thickness; (b) CVs of PEDOT/PSS and Pt electrodes at a scan rate of 10 mV/s in 1 M KCl; (c)Nyquist plots for various electrodes in a ca. 0.1 M $K_3Fe(CN)_6/K_4Fe(CN)_6$ solution.

Low-grade waste heat can be harvested using electrochemical cells. However, the high cost of commonly used platinum electrodes limits their application. We developed poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) electrodes as an attractive alternative to platinum. a lower charge transfer resistance. The film shows high electrical conductivity (larger than 1000 S/cm, rapid electron transfer, and a lower charge transfer resistance (Figure 1). Two reasons can be proposed for the high rate of electron transfer and low contact resistance in devices using PEDOT/PSS. First, PEDOT/PSS is a mixed conductor, suggesting that both electrons and ions could be conducted inside the films. Compared with that of metal electrodes, the active area of PEDOT/PSS available for the redox reaction is larger because ions could migrate inside the films. Second, PEDOT/PSS films have a very high carrier density, which may be attributed to the proton doping of the polymers. After the redox reaction produces electrons, the films do not become insulating, which enables reactions to continue in the electrochemical cells.

研究テーマ B「Developing Novel approaches to increase the reaction entropy for thermo-electrochemical cells」

We have improved the thermopower of the redox by using additives and controlling the solvents. We found that using D_2O as the solvents showing a higher thermopower compare with H_2O. This may be related to solvent reorganization effects because D_2O has a larger dielectric constant than H_2O, and D_2O makes stronger H-bonds compared with H_2O. Based on this understanding, we have introduced an additive A for making a stronger hydrogen bonding with water. This significantly improved the thermopower from 1 mV/K to 4 mV/K (Figure 2a). With a temperature difference of 5K, the device shows more than 1 order magnetite higher power output. Using a 6 cm^2 device, we could achieve power as high as 1.6 mW. A 1 mW/cm^2 power density could be achieved when the temperature difference is 73K. (Figure 3 c and d). This device shows a very low internal resistance of 1.5 Ω due to the low charge transfer resistance using a polymer electrode. It could be easily used to boost commercial DC-to-DC converter LTC3108.

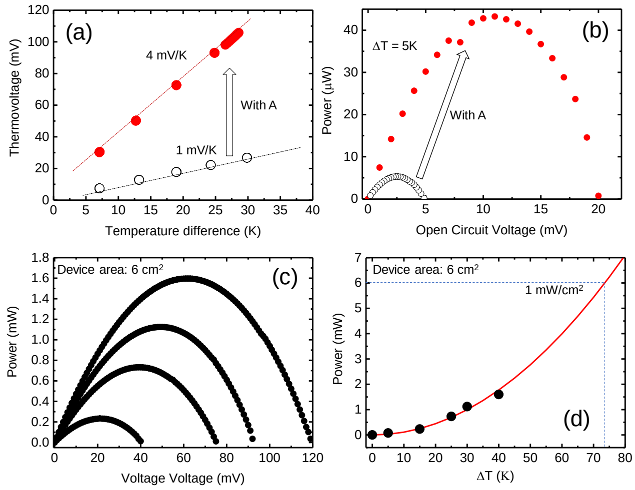

Figure 2. (a) Thermopower measurement (b) power output of $K_3Fe(CN)_6/K_4Fe(CN)_6$ with and without additive. (c) and (d) power output of a 6 cm^2 device with different ΔT.

研究テーマ C「Developing thermally chargeable cells by employing two redox couples」

One of the most significant advantages of PEDOT/PSS is its solution processability. In addition to soluble redox couples, we could study the electrochemical properties of insoluble redox couples such as Prussian blue (PB) analog compounds by hybridizing them with PEDOT/PSS via ball milling, which enables us to easily screen the redox potential of these compounds. If we can find and combine two redox couples with positive and negative reaction entropies using ion-selective members, we could realize a thermally regenerative electrochemical cycle. This cell will work in a range of temperatures above and below the crossover temperature, i.e., the temperature at which the potentials of two redox reactions are the same. We combined nickel ferrocyanide (NiHFC) with Fe^{2+}/Fe^{3+} using a cation separator, PB with $K_3Fe(CN)_6/K_4Fe(CN)_6$ using an anion Separator, and $K_xFe_y[Fe(CN)_6]$ with $K_xAg_y[Fe(CN)_6]$ (Figure 3). These cells were loaded with 100 Ω of resistance during measurements. When a temperature wave between 5 and 60 ° C was applied to the cells, they stably generated electricity, and peak power output was approximately 4 μW. The calculated energy density is around 0.1 Wh/kg. This value is lower than what we expect. We believed that is due to a relatively high resistance of separator and less efficient charge

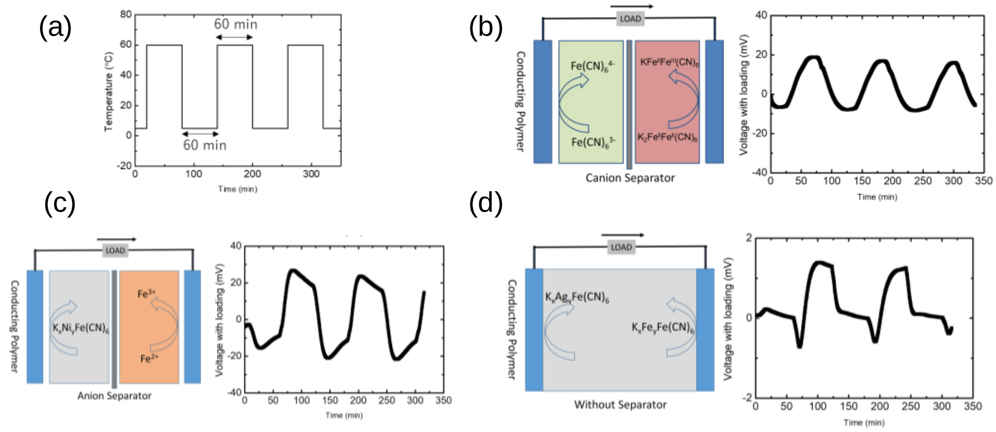

Figure 3. (a) Temperature changes applied to the cells (60 min cycles between 5 and 60 °C); voltage output of the devices combining (b) PB–PEDOT/PSS with $Fe(CN)_6^{3-/4-}$; (c) NiHCF–PEDOT/PSS with $Fe^{2+/3+}$; (d) $K_xAg_y[Fe(CN)_6]$ with $K_xAg_y[Fe(CN)_6]$

transfer of PB analog compounds on the conducting polymer surface. Nevertheless, the concept is proof in this project. The temperature change of the environment is important; however, a temperature difference between different electrodes does not need to be maintained.

研究テーマ D「Demonstration using body heat」

We have designed and fabricated the polymer-based thermoelectrochemical cells for demonstration. Four cells are connected in series to get a high voltage. As shown in Figure 4, the device with dimensions of 6 cm × 5 cm × 2 cm provided a maximum power output of 20 μW by putting it in hand. The achieved temperature difference is smaller than 3K, but it still drives the DC–DC converted. This device is sufficient to power an array of LEDs and Beacon sensors for wireless

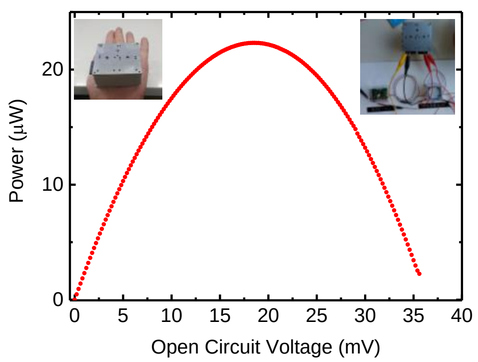

Figure 4. Power–output of thermoelectrochemical cells using body heat; inset: digital photograph of the devices

communication. This is the first example of polymer-based thermoelectrochemical cells that could be used to power sensors for wireless communication using body heat. Importantly, this device shows good stability for more than half a year. This demonstration is very encouraging for practical applications.

3．今後の展開

While the basic principle of the thermoelectrochemical cell itself has a long history, this is the first example of a polymer-based thermoelectrochemical cell to drive a practical device with a temperature difference of only a few degrees. The development of energy conversion devices using low-temperature heat sources that have not been used in the past will help to curb the growth of energy consumption and the development of self-powered sensors. This will contribute greatly to solving the problems of energy and environmental policies.

For practical applications, we think four issues need to be considered:

(1) Higher power and enhanced thermal charging capabilities;

(2) Durability and the cost of materials;

(3) Actually environment for application development;

(4) Collaboration with material and device manufacturers

For the next step, we are getting support from NEDO 先導研究プログラム from the middle of this year (体温で IoT デバイスを駆動する熱化学電池の開発). This project is leading by AIST and supported by Toyo Ink SCHD and Nippon Shokubai. Toyo Ink SCHD is a leading company for printing electronics and flexible devices, and Nippon Shokubai holds a large market share of superabsorbent polymers for gelation. We are aiming at the devices with higher power density and flexibility than the current one, and by overwhelmingly increasing the number of applicable low-temperature heat sources through research and development. The success of starting a new project for practical application has to thank the support of JST PRESTO. Scifos activities are also very helpful to find the collaborators for the NEDO project.

4．自己評価

The development of polymer-based thermoelectrochemical cells with a high power density was highly appreciated. Especially the demonstration for powering BLE sensors using body heat. The successful proof-of-concept of thermally chargeable cells is also evaluated. On the other hand, the initial numerical target for the high energy density of thermally chargeable cells remains challenging. In the next step, our industry colleagues are going to push forward with us to realize flexible organic thermoelectrochemical cells using body heat for energy harvesting and health monitoring.

The scope of my research has been greatly expanded in the three years by the active discussion with researchers in this Energy Harvesting field. I strongly feel that this is a very important asset for me to survive in my long research career in the future.

５． 主な研究成果リスト

（１）代表的な論文（原著論文）発表

研究期間累積件数：10件

1. "Poly(3,4-Ethylene Dioxythiophene)/Poly(Styrene Sulfonate) Electrodes in Electrochemical Cells for Harvesting Waste Heat", Y. Wang, M. Mukaida, K. Kirihara, L. Lyu and Q.S. Wei, *Energy Technol.*, **2020**, 8, 1900998. (Journal Cover)

This paper report that poly(3,4-ethylene dioxythiophene)/poly(styrene sulfonate) (PEDOT/PSS) films as an attractive alternative to platinum electrodes, as they show a lower charge transfer resistance. PEDOT/PSS also offers the advantage of compatibility with insoluble redox couples such as Prussian blue analog materials, which facilitates determining the temperature-dependent redox potential of different materials.

2. "Enhanced Power Output in Polymer Thermoelectric Devices through Thermal and Electrical Impedance Matching", M. Mukaida, K. Kirihara, and Q.S. Wei, *ACS Appl. Energy Mater.*, **2019**, 2, 6973. (Journal Cover)

This paper reported the simulation for maximizing the power outputs using benchmark materials. We have used organic thermoelectric materials for demonstration. Conceptually, this approach applies to thermoelectrochemical cells. It suggested a very low interfacial resistivity is needed if we are trying to make flexible thermoelectric or thermoelectrochemical cells.

3. "Extracting Carrier Mobility in Conducting Polymers From Photoinduced Charge Transfer Reaction", Q.S. Wei, M. Mukaida, and T. Ishida, *J. Phys. Chem. C*, **2018**, 28, 15922.

This paper suggested PEDOT/PSS have a high carrier density because of the proton doping. In the thermoelectrochemical cells, after the redox reaction produces electrons, the films do not become insulating, which enables reactions to continue in the electrochemical cells.

（２）特許出願

（３）その他の成果（主要な学会発表、受賞、著作物、プレスリリース等）

主要な学会発表

1. Qingshuo Wei, Heat-to-electricity Conversion utilizing Conducting Polymers, *MRS Fall Meeting* 2018, Boston, 2018/11/30 (Invited)
2. Qingshuo Wei, Gel electrolytes for thermoelectrochemical cells, *The 9th NANOTEC-NMRI joint research meeting,* Thailand, 2019/8/29 (Invited)
3. 衛 慶碩, PEDOT/PSS electrodes in electrochemical cells for waste heat harvesting, *電気化学秋季大会*, 山梨, 2019/9/6
4. Qingshuo Wei, Masakazu Mukaida, Kazuhiro Kirihara, and Shohei Horike, Conducting polymer electrodes in electrochemical cells for waste heat harvesting, *PowerMEMS2019*, Poland 2019/12/5.

5. Masakazu Mukaida, Kazuhiro Kirihara, and Qingshuo Wei, Enhanced Power Output in Polymer Thermoelectric Devices through Thermal and Electrical Impedance Matching, *ICACC 2020*, Florida, 2020/1/28 (Invited)