Development of Thermocells Driven by Volume Phase Transition of Hydrogel Nanoparticles

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論 文 名　：Development of Thermocells Driven by Volume Phase Transition of Hydrogel Nanoparticles
（ハイドロゲルナノ粒子の体積相転移によって駆動される熱化学電池の開発）

区　　分　：甲

論　文　内　容　の　要　旨
Thesis Summary

The Sustainable Development Goals (SDGs), which advocate an integrated approach to solve development problems in the three dimensions of society, economy, and environment, are the major subject of concern in the next decade. However, the energy crisis and environmental problems caused by the massive use of non-renewable energy have become the biggest challenge to sustainable development. Waste heat, as an exhaust from the process of primary energy consumption, and as a low-grade energy widely distributed in the environment, is a renewable resource with high reuse value. In particular, the ultra-low-quality waste heat, which accounts for the highest proportion, lacks low-cost and efficient harvesting methods. The development of highly efficient thermoelectric conversion devices that is simple and mass-producible is key for the use of thermal energy. Although among many thermoelectric conversion technologies, there have been some commercial examples of using thermoelectric generator to harvest high-quality waste heat. Improvement of output power density and conversion efficiency in a temperature range of ultra-low-quality waste heat without using toxic and/or minor metals is required for the practical use of these technologies.

Thermocells, or thermo-electrochemical cells, provide an option for the harvesting low-temperature heat owing to their advantages of low-cost and flexibility of components. Thermocells consist of an aqueous solution of redox-active electrolyte pair and electrodes. The gap of the equilibrium potential of the redox species provided between electrodes in response to temperature difference induces a redox reaction on each electrode resulting in a thermoelectrical conversion. A continuous thermo-voltage generated by thermocell is based on the temperature change. The capacity can be defined as Seebeck coefficient that is used to describe the voltage produced by per unit temperature difference.

In this thesis, the author describes a novel liquid-state thermocell based on the aqueous electrolyte with thermal responsive hydrogel nanoparticles. This thermocell utilizes the volume phase transfer process of the nanoparticles near the ambient temperature, which can generate very high voltage and output power under a condition of low temperature and sm1all temperature range, thereby achieving efficient harvesting of ultra-low-quality waste heat. Compared with the research in other thermocell fields, this thesis uses simple and safe aqueous electrolyte to achieve thermoelectric conversion efficiency and record-breaking output power beyond other more complex and expensive thermocells by introducing stimuli-responsive polymer materials. This thesis also proposes the design rationale for this novel thermoelectric conversion system by screening and optimizing the components of the thermocell. Moreover, the improvement of the practical

design of the cell device in this thesis shows that this thermocell has the possibility of commercialization and practicality. The author believes that the simple, inexpensive, and non-toxic thermoelectric conversion technology in this thesis for ultra-low quality waste heat harvesting will give a fundamental insight into design of energy conversional devices using stimuli-responsive smart materials and provide a direction for the development of flexible energy chargers for wireless devices including portable smart devices and sensors.

In chapter 2, a new thermoelectric conversion mechanism based on the proton-responsive redox reaction and the pH response of hydrogel nanoparticles was proposed. Quinhydrone and acrylic acid-containing thermal responsive hydrogel nanoparticles were used to illustrate this mechanism. This thermocell showed a high Seebeck coefficient of -6.7 mV K^{-1} and $+6.1$ mV K^{-1}, which is beyond the maximum value ever reported for liquid-state thermocells. The success of this concept involving entropy-driven phase transition opened a new arena for investigating high performance thermocells and became the cornerstone of follow-up research.

In chapter 3, the design rationale of thermocell using thermal sensitive hydrogel nanoparticles were discussed. Through the screening of redox species, electrolyte salts, and nanogel particles, the conditions necessary to achieve optimal thermocell performance were determined. The combination of 2,7-AQDS and acid-containing thermal responsive hydrogel nanoparticles achieved the highly efficient conversion of temperature differences to electrical energy at physiological temperature. The thermocell showed a high Seebeck coefficient of -9.5 mV K^{-1}, which exceeds those of reported liquid-phase thermocells. The screening process presented in this study provides a guide for the rational design of high-performance thermocell systems based on hydrogel nanoparticles. The optimal electrolyte composition shown by the experimental results was also used in subsequent studies.

In chapter 4, by assembling a planar liquid-state thermocell device with low inter-electrode spacing, engineering strategies for optimizing cell performance were discussed. The author used flexible carbon nanotube buckypaper as an electrode with a larger effective surface area to increase the number of redox reaction sites, and therefore, can effectively increase the current and power per unit electrode area. In addition, a laser-processed porous polytetrafluoroethylene film was employed as a separator to maintain a stable temperature gradient at an electrode spacing of 50 μm. By optimizing the impact of natural convection, mass transfer, and heat transfer, the use of separators in the individual cells increased the overall power density. Through the improving of LTC device design, a high output power of 0.82 mW m^{-2} K^{-2} can be achieved at temperature between 33 and 37 °C. The use of flexible and low-cost carbon electrode materials and the design of the ultra-thin cell size meet a variety of ultra-low-quality waste heat harvesting applications. Moreover, the high output power density that can be generated by a small temperature difference within the body temperature range is very attractive result.

Thermocells using temperature-sensitive polymer electrolytes are a new field of research. This pioneering study has given a new direction to research related to thermoelectric conversion and provided a promising solution for future energy problems in a sustainable society. Crucially, this thermocell uses simple, inexpensive, and non-toxic materials to achieve a high Seebeck coefficient and output power density. We believe that our findings will spur the development of ultra-low-quality waste heat harvesting devices such as wearable devices to harvest human body heat.