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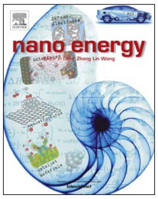

High thermopower of ferri/ferrocyanide redox couple in organic-water solutions

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ABSTRACT

Thermogalvanic cell (thermocell) represents a promising technology for converting low grade waste heat to electricity. For the cell to be attractive, however, the voltage generated for a given temperature difference has to be high. We report that the electrochemical thermopower can be more than doubled to 2.9 mV K^{-1} when an organic solvent with an appropriate solubility parameter is added to the aqueous electrolyte of ferri/ferrocyanide. This value is better than any reported for the redox couples in aqueous electrolyte as well as in organic solvents. The addition causes a significant rearrangement of the solvation shell, which leads to an increase in the entropy change of the overall redox system and thus an increase in the electrochemical thermopower. For an evaluation of thermoelectric conversion performance, a thermocell with a circulating electrolyte is fabricated as a candidate technology for harvesting thermal energy from liquid cooling systems. The maximum power density obtained, normalized to the square of the inter-electrode temperature difference (~4.1 °C), is 0.64 mW $m^{-2}K^{-2}$, which is approximately 1.8 times higher compared with the thermocell based on pure aqueous electrolyte.

1. Introduction

Low-grade thermal energy wasted from everyday life, such as heats released from body, car dashboard, solar panel, and external walls of building, is an attractive energy source when considering its abundance and low usability [1]. Thermoelectric generators based on semiconducting materials have been extensively studied to convert this waste heat into an electrical energy, based on the Seebeck effect [2–7]. However, the material issues of high cost and rarity have restricted their practical deployments.

A promising alternative to the conventional thermoelectric generator is thermogalvanic cell (thermocell), which has recently attracted considerable attention mainly due to the cost-effectiveness [8–12]. Extensive studies of advanced electrodes that utilize nanocarbon materials have led to outstanding electrode performance, including high surface area, ability to carry large current densities, and fast electron transfer kinetics [13–15]. Various redox couples in aqueous and non-aqueous electrolytes have also shown to offer the possibility of cheap and flexible device design suitable for harvesting waste heat [13,16–18]. For all these efforts, remarkable advances have been made to improve the conversion efficiency of the thermocell to 3.95%, relative to Carnot cycle efficiency, which makes the thermocell commercially viable [13,15,19]. Recently, thermally regenerative electrochemical systems have reported outstanding performance with an absolute efficiency of 5.7% assuming a heat recuperation efficiency of 50% [20–26].

The nature of the waste heat is such that the temperature difference between the heat source and the surrounding ambient is small. Therefore, development of a thermocell that can provide a high electric voltage in spite of the small temperature difference is of great importance. The proportionality constant (i.e., electrochemical thermopower, S_e) relating the temperature difference to the voltage is directly linked to the entropy change accompanying the redox reaction in the thermocell. In this work, we show that the electrochemical thermopower of aqueous $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ electrolyte, which has typically been used in the thermocell research, is improved by more than a factor of 2 (from 1.43 to 2.9 mV K^{-1}) by simply mixing an organic solvent with the aqueous electrolyte. The experiments using various organic

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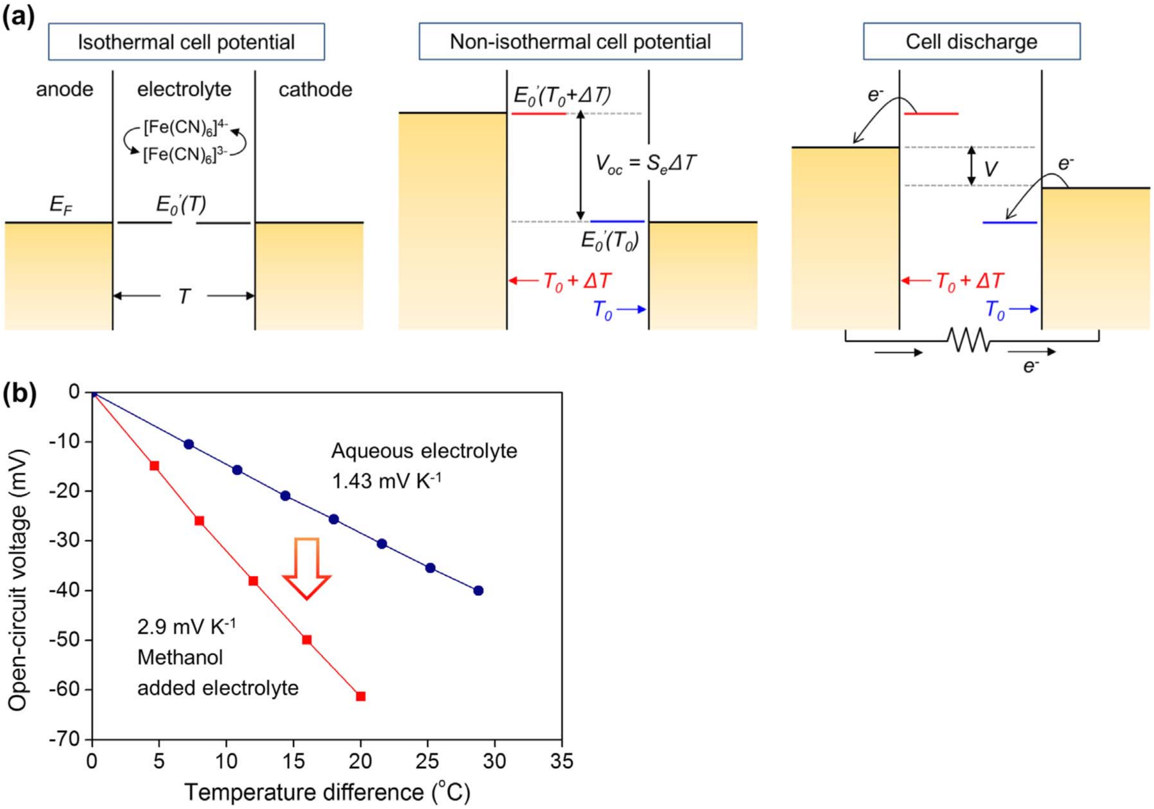

Fig. 1. (a) Energy diagrams depicting the operation of thermocell involving $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox ions. (b) Temperature dependence of the electrode potential difference over a range of temperature difference from 0 to 30 °C.

solvents revealed that a solvent with the Hildebrand solubility parameter in the range between 19.7 and 34.9 $MPa^{1/2}$, such as acetone, *N*-methyl-2-pyrrolidone (NMP), isopropyl alcohol (IPA), *N,N*-dimethylformamide (*N,N*-DMF), ethanol, dimethyl sulfoxide (DMSO), methanol, *N*-methylformamide (NMF), propylene glycol (PG), and ethylene glycol (EG) can produce a significant improvement in S_e in the solvent-water solution.

To maximize the power output delivered from the thermocell, the electrochemical thermopower (S_e) is optimized with respect to the ratio of organic solvent to water. With the optimized conditions, a practical thermocell is fabricated to demonstrate the utilization of a cooling stream for maximizing the power density.

2. Experimental section

2.1. Measurement of electrochemical thermopower of electrolytes

The electrochemical thermopower (S_e) of electrolyte was determined using a U-shaped cell shown in Fig. S1a. The U-shaped cell consists of two half cells surrounded by water pockets and the temperature of each compartment is controlled by the circulating cold (left) and hot (right) water stored in thermostatic baths (A & D, AD-RC08), providing a ± 0.1 °C control of the water temperatures. The distance between the two half-cells is 8.5 cm. Platinum disk electrodes (Digi-ivy, A102) were used to measure the potential difference generated by the temperature difference of the two half-cells. A thermocouple (K-type, TECPEL, DTM-318) was inserted in close proximity to the electrode for each half-cell. An output voltage from the cell was recorded using a multimeter (Keithley, 2000).

The temperature coefficient of electrode potential, which is relevant to S_e, was measured using electrochemical cells equipped with a three-electrode setup (Fig. S1b). Platinum working (Digi-ivy, A102) and auxiliary electrodes (Digi-ivy, A115), and Ag/AgCl reference electrode (Digi-ivy, A111) were used for cyclic voltammetry (Digi-ivy, DY2100) to measure the formal potential of redox ions. The working and auxiliary electrodes were fully immersed in the cell. The temperature was precisely controlled by circulating water through the bath, while the reference electrode was placed at an ambient temperature of 25 °C.

2.2. Fabrication of thermocell and the performance evaluation

Performance of thermocell was evaluated using an electrochemical flow cell system shown in Fig. S2 and S3. The outer case of the cell and the spacer are made of polyether ether ketone (PEEK). Stainless steel plates (SUS 304) at both sides are used as collecting electrodes. The collecting electrode has an array of 3 by 3 square holes, each of which is 3 mm in length with a pitch of 1 mm, and the spacer has a 1×1 cm^2 square hole for facilitating ion diffusion between the two half cells. Single wall carbon nanotube (SWNT) (Hanwha chemical, ASP-100F) sheets prepared by vacuum filtration were attached onto the collecting electrode using a carbon paste and were used as an electrode for thermocell reaction. The preparation of SWNT electrode is described in our previous work [27]. As shown in Fig. S2, the electrolyte stored in a temperature-controlled bath was circulated through the cell by a peristaltic pump (Longer Pump, BT100–2J). The flow rate of electrolytes was controlled in the range of 13–66 mL min^{-1} by adjusting the rotational speed of the peristaltic pump. The potential and current output from the cell was measured using a voltage–current meter (Keithley, 2000). A load resistor array was used for characterizing power output versus resistive load.

2.3. Instruments and methods

Ionic conductivity of electrolyte was measured using a conductivity meter (Metter Toledo, S-230). Fourier transform infrared spectroscopy (Thermo Scientific, Nicolet 6700) was used to analyze the characteristic