

Liquid Thermocells Enable Low-Grade Heat Harvesting

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Recently, two *Science* papers tackled the challenge of harvesting low-grade heat via liquid thermocells. One combines TGC and TDC to significantly enhance thermopower by an order of magnitude, and the other reveals the selectively thermosensitive crystallization/dissolution at two electrodes. These intriguing and inspiring advances in terms of materials, mechanisms, and performances are briefly introduced, and some remaining challenges and future directions are outlined for further thermopower improvement and practical implementation.

Low-grade heat (below 100°C) is distributed almost everywhere in our daily lives, such as body heat, solar heat, geothermal heat, vehicle exhaust, and especially the industrial waste heat.^{1–6} In the United States, >8,000 TWh per year is wasted as low-grade heat from the conventional power plants and the manufacturing industries.⁴ In China, about 15%–40% of the total fuel input turns to be the waste heat eventually.³ Despite the abundance, the low-grade heat is usually wasted without being efficiently harvested and utilized owing to the lack of viable, scalable, and cost-effective energy recovery technologies against the challenges like small temperature difference and the spatiotemporal variability in heat output.³ To date, there are only a few technologies available to harness the low-grade heat, such as thermoelectric (TE) energy conversion,^{2,6} thermomagnetic generator,³ thermo-osmotic energy conversion,³ thermally regenerative batteries,⁷ and so on. Among them, the all-solid electronic TE materials, which can directly convert the low-grade heat into electricity obeying the Seebeck effect, are mostly studied due to the advantages like no moving parts, noiselessness, small size, and easiness to integrate.² Traditional n-type or p-type electronic TE materials are usually focused on narrow-bandgap semiconductors like bismuth telluride alloys or

antimony telluride alloys that use electrons or holes as energy carriers, but they are suffering from low power output, low cost effectiveness, rigid structures, intrinsic parameter interdependence, etc.^{2,6,8}

Alternatively, the liquid thermocells, employing thermogalvanic or thermodiffusion mechanisms separately or synergistically, offer a more flexible way to achieve heat harvesting with additional merits like ambipolar, inexpensive, scalable, and flexible.^{1,9,10} As for thermogalvanic cell (TGC), the redox reaction happens at the two electrodes at different temperatures, generating electricity continuously for an external power load. As for thermodiffusion cell (TDC), cations and anions will be driven by the temperature difference without redox reaction to the two electrodes for charge accumulation and power supply when discharged externally.⁹ Currently, these two mechanisms have been separately investigated with different redox couples and liquid electrolytes, pursuing higher thermopower, cheaper price, higher robustness, simpler fabrication, and wider applications.¹ However, the liquid thermocells are still suffering from challenges like leakage problems in scalable encapsulation, still-limited thermopower, and low energy conver-

sion efficiency.^{1,9,10} The first challenge is partially relieved by resorting to the quasi-solid-state electrolytes, e.g., poly(sodium acrylate) and polyvinyl alcohol (PVA), poly(vinylidene fluoride-co-hexa-fluoro-propylene) (PVDF-HFP), and polyethylene glycol (PEG).⁹ But the other two challenges have remained unsolved.

Recently in *Science*, Han and colleagues from Southern University of Science and Technology and Massachusetts Institute of Technology innovatively integrated the gelatin $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ -based TGC and KCl-based TDC synergistically to achieve giant thermopower as high as 17.0 mV K^{-1} by subtly tailoring the types and molar concentrations of chemical species, water volume ratio in gelatin, pH value, and electrode materials, and the temperature gradient.⁹ For $\text{Fe}(\text{CN})_6^{4-}/\text{Fe}(\text{CN})_6^{3-}$ redox couples, the oxidation reaction happens at the hot electrode, releasing charges to the electrode; while the reduction reaction occurs at the cold electrode, attracting charges from the electrode. These redox reactions work together to generate a polarized built-in electric field pointing from the cold side to the hot side, which is consistent with the KCl-based TDC electric field, as shown in **Figures 1A–C**. From the Onsager transport theory, the total thermopower consists of the redox reaction contribution (17.9%), the thermodiffusion contribution of mobile ions (9.7% from $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$ and 62.2% from KCl), and the intrinsic thermopower of gelatin (10.2%). For practical long-term working, they further

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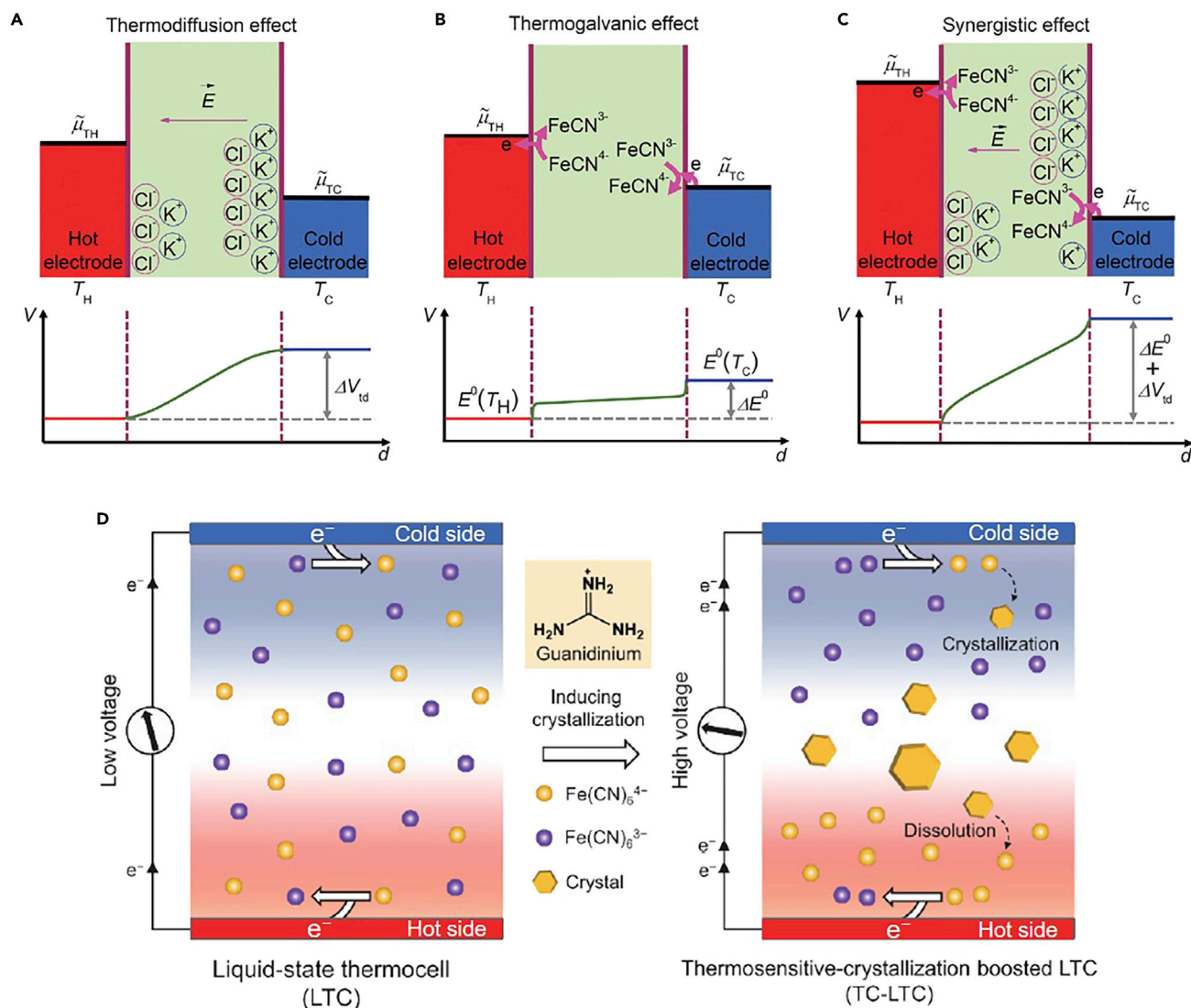


Figure 1. Schematics for Liquid Thermocells Working with Various Mechanisms

(A) Thermodiffusion effect, (B) thermogalvanic effect, (C) synergistic effect, and (D) enhanced thermogalvanic effect through thermosensitive crystallization/dissolution. Reproduced from Han et al.⁹ and Yu et al.¹⁰

demonstrated a quasi-continuous working mode by assembling a symmetric Cu | Au | thermocell | Au | Cu laminar structure with a small temperature difference of 8.5 K near room temperature. The as-fabricated thermocell device could be charged in 55 min, and discharged in 10 s, and implemented for 100 cycles within 5 h. Thanks to its high flexibility, they applied the serially connected 25 thermocell elements to power wearable electronics in a near-room temperature environment by harvesting body heat with a voltage output of

2.2 V and an electrical energy of 3.5×10^{-5} J per single thermal charging process.

Writing in *Science* more recently, Yu and colleagues from Huazhong University of Science and Technology innovatively added guanidinium cations (Gdm^+) in the $\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$ aqueous electrolyte to selectively induce thermosensitive crystallization/dissolution at the cold/hot electrodes separately, as shown in Figure 1D, generating a persistent concentration

gradient of redox ions within the volumetric electrolyte.¹⁰ In TGC, the thermopower is dependent on the entropy difference (ΔS) between the redox ions and the concentration ratio difference (ΔC_r) between the hot and cold electrodes. In the pristine electrolyte, ΔC_r equals to zero at steady state, and thermopower is only determined by ΔS . After adding the Gdm^+ cations, a huge ΔC_r was built and, synergistically with ΔS , boosted the thermopower up to 3.73 mV K^{-1} , which is enhanced more than 2.5 times. Further investigations

revealed that the cation additives should have strong ability to induce crystallization of $\text{Fe}(\text{CN})_6^{4-}$ and high thermosensitive solubility of $\text{Fe}(\text{CN})_6^{4-}$ associated crystals. Moreover, the effective thermal conductivity was only $0.4 \text{ W m}^{-1} \text{ K}^{-1}$ because of the suppression of thermal convection in the liquid electrolyte by the crystallization. To evaluate the energy conversion efficiency, the authors adopted the Carnot-relative efficiency and coupled with the figure-of-merit of the traditional TE materials. The Carnot-relative efficiency was as high as 11%, far surpassing the conventional TGCs by 18.5 times and breaking the commercially viable limit of 5%. As a proof-of-concept application, they connected 20 units in series to generate an open-circuit voltage of 3.1 V, a short-circuit current of 120 mA, and a power output of 96 mW in maximum under a temperature difference of 50 K, enough to power an electric fan, a LED array, a thermohydrrometer, and a smart mobile phone.

These two recent important progresses on liquid thermocells in terms of materials, mechanisms, and performance to harvest low-grade heat are intriguing and inspiring. One combines TGC and TDC together for the first time to significantly enhance the thermopower by one order of magnitude, and the other reveals the selectively thermosensitive crystallization/dissolution at two electrodes to enhance the thermopower significantly. Despite recent breakthroughs, liquid thermocells still suffer

from low power output and large internal resistance, limiting their potential applications. More effort can be devoted to further exploring new mechanisms for boosting thermopower, revealing the coupling/decoupling of TGC and TDC mechanisms, thermodynamic analysis of the thermopower limit, manipulating the ion/mass transport selectively, improving the ionic conductivity, reducing the overpotential at the electrode-electrolyte interface, and so on. On the other hand, distinct from solid TE materials, liquid thermocells involve a complex system of electrodes, redox couples, chemical species, and hydrogel matrix (if any). More theoretical analysis should be conducted on the optimization of the cell performance and energy conversion efficiency. In addition, one advantage of liquid thermocells is their low cost,¹⁰ enabling new opportunities to explore innovative cell designs and mass production of large-scale, low-cost, versatile thermocells with the help of advanced manufacturing technologies. We hope these advances highlighted here can stimulate greater interests and attentions on further exploring ionic electrolyte materials and devices to enrich the understanding of the working mechanism and broaden the boundaries of low-grade heat harvesting.

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