Potential and Challenges of Thermogalvanic Cells for Low-Grade Heat Harvesting

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INTRODUCTION

Flexible electronics may lead to a novel technological revolution with the upcoming 5G information era (Wang et al., 2019; Zhang et al., 2021). However, the traditional power supply with batteries cannot match the needs of flexible electronics. Hence, an advanced power source with flexibility, non-environmental dependency, and user-friendliness is urgently needed (Suarez et al., 2017; Fan et al., 2021). Immense but largely untapped low-grade heat from the human body, industry (e.g., data centers), and the environment (e.g., solar energy) is emerging into the research spotlight (Duan et al., 2021). Thermoelectric energy conversion technology is an approach for reusing the widely available low-grade heat, which has the potential to optimize energy efficiency and reduce energy consumption (Fan et al., 2021). Among the state-of-art options, thermogalvanic cells can generate electricity by the gain and loss of electrons at the two same electrodes under the action of a temperature-dependent redox ionic reaction (Lei et al., 2021; Li et al., 2021). In comparison with the conventional electronic thermoelectrics (Taroni et al., 2018; Chae et al., 2020) and ionic thermos capacitors (Al-zubaidi et al., 2017; Wu et al., 2021), thermogalvanic cells based on redox reactions are not only noise-free and environmentally friendly, but also they enable continuous conversion of low-grade heat to electricity (Gao et al., 2022). Moreover, the thermogalvanic cells hold the potential to enable an efficient, lightweight, continuous flexible power supply for the burgeoning flexible electronics (e.g., flexible screens and wearable medical electronics) (Liu et al., 2022; Peng et al., 2022; Zhang et al., 2022). This imposes the challenge of durably optimizing the performance of thermogalvanic cells in terms of thermopower (Duan et al., 2018), mechanical properties (Lei et al., 2021; Gao et al., 2022; Lei et al., 2022), and anti-freezing (Gao et al., 2021), among others. Although the previous researchers presented significant advances, thermogalvanic cells still have challenges in the field of low-grade heat harvesting and flexible power sources.

This article intends to summarize the potentials of the thermogalvanic cells from the working mechanism, and strategies for performance enhancement. In the end, the challenges of thermogalvanic cells in further applications are also comprehensively presented.

THE WORKING MECHANISM OF THERMOGALVANIC CELLS

The thermogalvanic cell is assembled by two identical electrodes and an electrolyte with a redox couple. The liquid-state electrolyte mainly comprises an organic ionic liquid or salt solution containing redox couples, such as Fe^{2+}/Fe^{3+}, I^-/I_3\(^-\), and Fe(CN)\(_6\)^3- /Fe(CN)\(_6\)^4-. The quasi-solid electrolyte includes gel matrix (gelatin, PVA, PAAM, etc.) and the doped redox couples mentioned previously. There are two main approaches for obtaining the quasi-solid electrolyte: (1) first, doping the redox couple into precursor solution and then gelling the solution and (2) first, obtaining the gel...
matrix and then immersing the redox couple. Once the two electrodes are given a temperature gradient, thermopower can be generated by the temperature-dependent redox reaction, \( A_{Ox} + n e \Leftrightarrow B_{Red} \). Temperature gradients cause two main sources of thermally induced voltage: 1) the entropy change of the redox reaction and 2) the thermodiffusion of all ions. The thermopower is denoted according to the Nernst equation as:

\[
S_V = \frac{E^0(T_h) - E^0(T_c)}{T_h - T_c} = \frac{S_A - S_B}{nF} + \frac{1}{nF}(\hat{S}_B - \hat{S}_A - n\hat{S}_{\text{electron}}),
\]

where \( S \), \( \hat{S} \), and \( \tilde{S} \) represent the partial molar entropy, Eastman entropy, and transport entropy, respectively. The standard electrode potential at the hot side \( (T_h) \) is denoted by \( E^0(T_h) \) and \( E^0(T_c) \) for the cold side \( (T_c) \). \( F \) and \( n \) represent Faraday’s constant and the number of electrons, respectively. In the aforementioned equation, the first term is the contribution from the redox couple and the second corresponds to the thermodiffusion of all ions and electrons.

As shown in the mechanism diagram of Figure 1A, for the thermogalvanic cell with the redox couple, ferric/ferrous \( (Fe^{3+}/Fe^{2+}) \), the thermopower is zero without a temperature gradient. The redox couple \( (Fe^{2+}/Fe^{3+}) \) doped in the electrolyte of quasi-solid thermocell based on the thermogalvanic effect undergoes spontaneous redox reactions when heat flows across the cell. At the hot electrode, \( Fe^{3+} \) gains electrons from the electrode and is reduced to \( Fe^{2+} \), which leads to an increase in the standard potential \( E^0(T_h) \). In contrast, the reverse oxidation reaction occurs at the cold electrode, where \( Fe^{2+} \) is oxidized to \( Fe^{3+} \), accompanying the release of electrons to the electrode, lowering the standard potential \( E^0(T_c) \) at the cold electrode. The redox reactions at two terminals of the cell form a potential difference between the electrodes. Moreover, the redox reactions generate an ion concentration gradient inside the cell, which promotes the migration of ions and thus achieves continuous working.

**PERFORMANCE ENHANCEMENT OF THERMOGALVANIC CELLS**

For thermogalvanic cells, redox couples with different entropy differences can output a certain thermopower under a temperature gradient. Therefore, liquid thermogalvanic cells with different thermoelectric performances can be fabricated with electrolytes of organic solvents or aqueous solutions \( (Fe(CN)_6^{4-/3-}, Fe^{2+/3+}, \text{and } I^{-/3-}) \). For example, the thermopower of thermogalvanic cells using ferricyanide/ferrocyanide \( (Fe(CN)_6^{4-/3-}) \) and ferric/ferrous \( (Fe^{3+)/2+}) \) electrolyte solution as electrolytes is \( \sim 1.4 \text{ mV/K} \) and \( \sim 1.0 \text{ mV/K} \). In order to enhance thermoelectric performance, two strategies have been reported in thermogalvanic cell systems through two distinct mechanisms \( (Duan et al., 2021) \). One strategy is to increase the solvation structure entropy difference. Jiao et al. \( (2014) \) reported thermopower up to \( \sim 2.65 \text{ mV/K} \) using pure ionic liquids or ionic liquid mixture electrolytes, which is mainly attributed to the different solution environments between ionic liquids and aqueous systems. Moreover, the introduction of ionic...
liquids and the addition of organic solvents with appropriate solubility can also contribute to thermoelectric performances. The combination of 15 wt% methanol and Fe(CN)$_6^{4/-3}$- exhibits a thermopower of ~2.9 mV/K (Kim et al., 2017). Duan et al. (2018) tripled the thermopower to 4.2 mV/K by adding Gdm$^+$ and urea, reorganizing the solvated shell of Fe(CN)$_6^{4/-3}$- based on the chaotrope–chaotrope ionic bond interaction (Figure 1B). In addition to the approach of increasing the redox entropy difference, enhancing concentration ratio differences between redox species is another strategy. It has been reported that the introduction of thermosensitive nanogel (poly(N-isopropylacrylamide), PNIPAM) (Duan et al., 2019) (Figure 1C) and supramolecular (α-cyclodextrin) (Zhou et al., 2016) can boost the thermopower by establishing a larger redox species concentration difference across the cell.

Although the ionic mobility of liquid-state thermocells is more prominent, the leakage risk of electrolyte solutions poses challenges for thermogalvanic cell packaging (Gao et al., 2021). To this end, quasi-solid-state thermogalvanic cells (e.g., hydrogel with redox couples) emerge due to the decoupling of mechanical and ionic properties of solid and liquid, respectively. Wu et al. (2017) and Yang et al. (2016) fabricated the quasi-solid thermocell based on Fe(CN)$_6^{4/-3}$- (p-type), using poly(sodium acrylate) and PVA, which obtained the different thermopower of −1.09 and −1.21 mV/K, respectively. These values exhibit a slight decrease compared to the equivalent condition in an aqueous solution, attributed to the poor ion transport in the gel matrix. On the contrary, Zhou et al. (2018) introduced the polymer–ion interaction between $I_3^-$ and the polymer containing starch and polyvinylpyrrolidone (PVP), achieving the enhancement of +0.86 mV/K in liquid $I^-_1/ I^-_3$ solution to +1.54 mV/K. In addition, Taheri et al. (2018) further studied the relationship between PVDF, PVD-HFP, and cobalt bipyridyl redox. Results show that only strongly interconnected polymer chains and redox reactants affect entropy changes of the redox reaction. Otherwise, the change of thermopower is negligible. However, the maximum power densities obtained with PVDF (6 mW/m$^2$) and PVDF-HFP (4.5 mW/m$^2$) are significantly reduced compared to liquid MPN-based electrolyte (48 mW/m$^2$), which is mainly due to the limited convection that impairs the mass transport. Zhou and Liu, (2018) achieved a high thermopower as high as −9.9 mV/K first through the combination of acetone and isopropanol. This report demonstrates the evaporation phase transition of acetone on the boost of entropy and the enhancement of the concentration gradient, which verifies the possibility of enhancing the thermoelectric performance through the vapor–liquid phase transition. Based on the gelatin containing KCl, NaCl, KNO$_3$, and Fe(CN)$_6^{4/-3}$-, Cheng-Gong et al. (2020) gained a prominent thermopower of +17 mV/K through the thermodiffusion of KCl, NaCl, and KNO$_3$, as well as the thermogalvanic effect of Fe(CN)$_6^{4/-3}$- (Figure 1D). In addition to the studies on the enhancement of thermoelectric performance, the anti-freeze performance (Gao et al., 2021), mechanical properties (Gao et al., 2022), and p-n-type conversion (Duan et al., 2019) are also the focus of research.

In addition, electrode materials are also critical to realizing the thermoelectric performance enhancement. Compared with the commonly used metal electrodes, carbon-based electrodes and conducting polymer electrodes have high-efficiency and flexibility advantages. The Carnot efficiency of the thermogalvanic cells with multi-walled CNTs is 200% superior to that of platinum (Hu et al., 2010). By adjusting the composition of the CNTs and GO composites, an output power of 460 mW/m$^2$ and a Carnot efficiency of 2.6% were obtained (Romano et al., 2013). Moreover, the PEDOT–Tos conductive polymer electrodes also demonstrated comparable electrical properties to platinum (Wijeratne et al., 2017). Benefiting from the intrinsic flexibility and stretchability, the non-metal electrode enlarges the potential of thermogalvanic cells in the field of flexible electronics benefiting from the intrinsic flexibility and stretchability.

**CONCLUSION**

This study briefly describes the mechanisms and the potential of thermogalvanic cells in low-grade heat harvesting. The trend from liquid-state cells to quasi-solid-state cells and two key factors affecting thermoelectric performance are summarized. Several strategies are introduced for improving thermoelectric performance in the liquid-state and quasi-solid-state thermogalvanic cells. Although current research has yielded advances such as excellent thermoelectric performance output and flexible mechanical properties, there are still some overlooked challenges to address:

1) Poor ionic conductivity: in comparison to conventional solid-state thermoelectric materials, the ionic thermoelectric electrolytes exhibit insufficient conductivity because the ionic mobility is lower than that of electrons. In particular, the weakening of convection in the quasi-solid-state matrix results in much lower ionic conductivity than that of liquid electrolytes.

2) Mismatched thermopower of n-type thermogalvanic cells: the series connection of p-type and n-type cells is a common assemble method, which can enlarge the capacity of the modules for practical applications. However, the current reports mainly focus on the performance enhancement of p-type thermocells. The scarcity of n-type thermocells sufficiently matching the thermopower of p-type thermocells remains to be further investigated.

**AUTHOR CONTRIBUTIONS**

WG contributed to the conception of the study. HM wrote the first draft of the manuscript. All authors contributed to manuscript revision and read and approved the submitted version.
