* research\_question

**How can the architecture of quasi-solid-state polymer electrolytes be engineered to enhance ionic conductivity, leading to improved thermoelectric and mechanical performance in high-performance thermal batteries?**

background\_survey

* The development of quasi-solid-state polymer thermoelectrics is driven by the immense potential of liquid-based thermogalvanic cells, which exhibit giant Seebeck coefficients. Among them, some of the most widely studied redox pairs include ferro/ferricyanide ([Fe(CN)₆]³⁻/⁴⁻), ferrous/ferric ions (Fe²⁺/Fe³⁺), iodide/triiodide (I⁻/I₃⁻), copper ions (Cu⁺/Cu²⁺), and various cobalt complexes,etc. For instance, liquid systems based on the [Fe(CN)6]⁴⁻/[Fe(CN)6]³⁻ redox pair have demonstrated an S value enhancement from a baseline of 1.4 mV/K to an astonishing 4.2 mV/K through solvation shell engineering.
* However, the practical application of these high-performance liquid systems is severely hampered by inherent issues of leakage and bulkiness. To address this, polymer matrices are utilized to create quasi-solid-state gels, which provide crucial mechanical support, prevent leakage, and suppress thermal convection. This transition, however, introduces a core conflict: the polymer network, while ensuring stability, inevitably increases internal resistance by hindering ion transport, resulting in low ionic conductivity and poor power densities, often below 0.20 mW m⁻² K⁻². Therefore, current research focuses on overcoming this challenge through multi-faceted design strategies, including optimizing the polymer network architecture for low tortuosity, incorporating S-enhancing additives like urea directly into the gel, and using conductive fillers such as CNTs to reduce interfacial resistance. The ultimate goal is to engineer advanced polymer systems that synergistically balance mechanical robustness with high electrochemical performance, paving the way for next-generation flexible and wearable thermoelectric devices.
* background\_survey

**1. The Inevitable Shift from Liquid to Quasi-Solid-State**

Thermogalvanic cells, based on redox pairs, have garnered significant attention due to their giant Seebeck coefficients on the order of mV/K, showing immense promise for low-grade heat harvesting. Among them, some of the most widely studied redox pairs include ferro/ferricyanide ([Fe(CN)₆]³⁻/⁴⁻), ferrous/ferric ions (Fe²⁺/Fe³⁺), iodide/triiodide (I⁻/I₃⁻), copper ions (Cu⁺/Cu²⁺), and various cobalt complexes, etc.Liquid-based systems, exemplified by [Fe(CN)6]⁴⁻/[Fe(CN)6]³⁻, have demonstrated Se values that can be boosted from a baseline of 1.4 mV/K to an astonishing 4.2 mV/K through solvation shell engineering., However, the inherent leakage risk and bulky design of liquid electrolytes severely hinder their practical application, especially in scenarios requiring flexibility, portability, and safety (e.g., wearable devices).

To overcome these obstacles, research has shifted towards quasi-solid-state thermoelectric materials. The core idea is to utilize a polymer matrix to solidify the liquid electrolyte into a gel form. This strategy aims to combine the high thermoelectric performance of liquids with the mechanical stability and safety of solids.

**2. The Core Role of Polymers: More Than Just a ‘Solidifier’**

In quasi-solid-state polymer systems, the polymer plays multiple critical roles:

**Mechanical Support & Leakage Prevention:** The polymer network confines the liquid electrolyte, fundamentally solving the leakage problem and endowing the device with excellent mechanical properties such as flexibility, stretchability, and even self-healing capabilities.

**Suppression of Thermal Convection:** This is crucial for maintaining a stable temperature difference (ΔT). The polymer network effectively prevents the macroscopic flow of liquid molecules, thereby significantly reducing heat transfer by convection and ensuring that thermal energy is efficiently used for power generation rather than being quickly dissipated.

**Ion Transport Pathway:** The microscopic porous structure within the polymer network constitutes the channels for redox ion migration between the two electrodes.

**3. Performance Issues of Quasi-Solidification**

Despite the clear advantages, the transition from liquid to quasi-solid-state is not without its costs. The literature and extensive research highlight a core conflict:gaining mechanical stability often comes at the expense of electrochemical performance.

**High Internal Resistance is the ‘Culprit’:** The polymer chains are inherently insulating. Their network structure inevitably increases the path length and tortuosity for ion migration, hindering their free movement. This leads to a higher internal resistance compared to the pure liquid counterpart.

**Manifestations of Performance Degradation:**

**Low Ionic Conductivity (σ\_ionic):** The ionic conductivity of quasi-solid-state systems is typically much lower than that of their corresponding liquid systems.

**Low Power Density (P\_max):** As high internal resistance limits the current output, the peak power density of the device decreases significantly.

**Quantification of Performance:** A commonly used normalized power density metric, P\_max / ΔT², vividly illustrates this issue. As noted in the literature, the value for most quasi-solid-state devices hovers at a low level of **< 0.20 mW m⁻² K⁻²**⁹, far from the threshold for practical applications.

**4. Key Material Systems and Design Strategies**

Current research focuses on resolving the aforementioned core conflict, primarily by targeting the polymer matrix and the electrolyte itself.

**A. Polymer Matrix Selection and Design:**

**Hydrogels:**Using water as the solvent, they are the mainstream choice. Common polymers include:

**Poly(vinyl alcohol) (PVA):** Forms a network through physical cross-linking (freeze-thaw cycles), simple and effective.

**Polyacrylamide (PAM):** Forms a stable network via chemical cross-linking, with good mechanical properties.

**Natural Polymers:** Such as gelatin, cellulose, and alginate, offering benefits of biocompatibility and low cost.

**B. Design Strategies for Performance Enhancement:**

**Optimizing Network Architecture:**

**Constructing Interconnected Channels:** Designing porous networks with low tortuosity and high connectivity is key to reducing internal resistance. This can be achieved by tuning cross-linking density or introducing porogens.

**Incorporating Hydrophilic/Ionic Groups:** Introducing groups like sulfonate or carboxylate onto the polymer chains can enhance affinity for water or ions, thereby promoting ion transport.

**Synergistic Effect: Balancing High S and High σ\_ionic:**

Introducing **‘S-enhancing additives’** (e.g., urea, guanidinium, methanol), proven effective in liquid systems, into the polymer gel system.¹,⁸

The key challenge is to ensure that these small molecule additives, while modifying the solvation shell of the redox pair, do not severely disrupt the polymer network structure or excessively increase viscosity, thus avoiding a sharp drop in ionic conductivity.

**Incorporating Conductive Fillers:**

Adding small amounts of materials like **carbon nanotubes (CNTs)** or **graphene** into the gel. These fillers do not directly participate in the thermoelectric conversion but can build an ‘electron wire’ network within the gel. This can help **reduce the interfacial resistance** between the electrode and the electrolyte and may indirectly improve overall performance by influencing ion distribution through electrostatic interactions.

**5. Conclusion and Future Outlook**

Future breakthroughs will depend on designing advanced polymer networks that can simultaneously provide mechanical stability and low-resistance pathways for ion transport, ultimately leading to the next generation of high-performance, flexible thermoelectric devices.