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Lignin-Derived Materials for Sustainable Development of Ionic Thermoelectric Supercapacitors †

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Abstract: Lignin, a paper and pulp industry waste product, has attracted significant attention in recent years as a promising sustainable material for high-end energy applications. Herein, we examine lignin as a potential material for ionic thermoelectric hydrogels and carbon-based materials. Optimized lignin-derived hydrogels demonstrate a remarkable Seebeck coefficient of 3.63 mV/K when subjected to an axial temperature gradient. Furthermore, synthesized lignin-based porous carbon materials exhibit exceptional performance as supercapacitor electrodes, with a superior specific capacitance of 56.3 F/g at 0.5 A/g. Lignin-based hydrogels and porous carbon electrodes offer a promising path towards the development of lignin-derived ionic thermoelectric supercapacitors.

Keywords: lignin; sustainable materials; ionic thermoelectric hydrogels; porous carbon; supercapacitors; low-grade thermal energy harvesting; ionic thermoelectric supercapacitors

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1. Introduction

Global concerns over energy issues stem from rising energy demands, finite fossil fuels resources, and their environmental impacts [1,2]. A significant challenge lies in efficiently utilizing the vast low-grade waste heat produced during industrial processes. Traditional methods for low-grade waste heat recovery fall short due to the low temperatures and high volumes of waste heat. New, efficient technologies are needed to harness this energy source sustainably [3–5].

Ionic thermoelectric supercapacitors offer a solution by combining thermoelectric conversion and supercapacitor technologies. They employ ionic thermoelectric materials, like optimized hydrogels or polymer matrices, to transport ions under temperature gradients. Waste heat induces ion movement across the hydrogel, creating a potential difference known as the Seebeck effect. This difference charges supercapacitor electrodes made of porous carbon, enabling swift energy storage [6,7].

Ionic thermoelectric technology encompasses waste heat conversion and energy storage through ionic thermoelectric materials and supercapacitor electrodes. Success relies on sustainable material selection. Lignin, an abundant byproduct of the paper industry, shows promise [8]. It is used to create ionic thermoelectric hydrogels, efficiently transporting ions under temperature gradients to convert waste heat into electricity via the Seebeck effect. Lignin-based porous carbon materials are also promising materials for supercapacitors and are vital for rapid energy storage [9]. This leads to lignin-derived ionic thermoelectric supercapacitors, innovatively addressing waste heat and storage. This marks a substantial step towards sustainable energy, spotlighting lignin's role in a greener, energy efficient landscape.

Herein, this study focuses on exploring the potential of lignin-derived materials for the development of ionic thermoelectric supercapacitors. We have synthesized lignin-based hydrogels with optimized properties to efficiently transport ions under an axial temperature gradient, thereby enabling waste heat conversion through the Seebeck effect. Our findings demonstrate a remarkable ionic Seebeck coefficient of 3.63 mV/K for these hydrogels, highlighting their suitability for waste heat utilization. Additionally, we have successfully synthesized lignin-based porous carbon materials with exceptional performance as supercapacitor electrodes, exhibiting a superior specific capacitance of 56.34 F/g at 0.5 A/g current density in a three-electrode setup. This study paves the way for the concept of lignin-derived ionic thermoelectric supercapacitors, which hold the promise of transforming waste heat into electricity while efficiently storing the generated energy. Our work signifies a pioneering step towards the realization of sustainable and environmentally friendly energy conversion and storage technologies, driving the transition towards a greener and more sustainable energy future.

2. Materials and Methods

2.1. Lignin-Based Ionic Thermoelectric Hydrogel

A mixture of 1.5 g kraft lignin and 10 mL 1M KOH solution was stirred for 4 h, dissolving the lignin. Epichlorohydrin (ECH) was added at a 1:3 ECH-to-lignin ratio, mixed for 1 h, then cast into molds and incubated at 70 °C for 4 h to form the hydrogel for ionic thermoelectric Seebeck testing.

2.2. Lignin-Derived Porous Carbon Synthesis

Lignin of 35 wt.% was mixed with 10 mL 3.3 M NaOH and stirred for 3 h at 45 °C for lignin dissolution. Poly (propylene glycol) diglycidyl ether (PEGDGE) crosslinker (0.55 g/g_{lignin}) was added, stirred for 30 min, and poured into molds. After incubating at 40 °C overnight, lignin-derived hydrogels were obtained. Stabilization at 250 °C for 3 h and carbonization at 950 °C for 30 min of these hydrogels yielded porous carbon.

2.3. Material Characterization and Testing

Morphology analysis was conducted using scanning electron microscopy (SEM, Hitachi), while Seebeck measurements involved subjecting the hydrogel to an axial temperature difference and recording the open circuit voltage (V_{oc}) in response to the temperature change (ΔT), utilizing the formula $S = V_{oc}/\Delta T$. IVIUM Electrochemical workstation was employed for porous carbon testing. Specific capacitance (C) was determined from GCD graphs using the formula $C = I_m \times \Delta t/\Delta V$, where C (F/g) denotes specific capacitance, I_m (A/g) signifies current density, Δt (s) represents discharge time, and ΔV (V) indicates potential window.

3. Results and Discussion

The morphological analysis performed on the lignin-derived hydrogel utilizing SEM unveiled a distinctive and intricate three-dimensional interconnected porous framework (Figure 1A), which plays a pivotal role in facilitating the efficient movement of ions within the material when subjected to a thermal gradient. This connected porous architecture demonstrates great potential for enhancing the ionic thermoelectric performance of the hydrogel, enabling the enhanced transport of charge carriers across the hydrogel.

When the hydrogel was exposed to an axial temperature difference, a significant response was observed in terms of the V_{oc}. In particular, a peak V_{oc} of 58 mV was achieved with a 20 °C temperature difference (Figure 1B). Analyzing the temperature difference versus the voltage curve through linear fitting yielded a Seebeck coefficient of 3.63 mV/K (Figure 1C). This emphasizes the favorable thermoelectric properties of the lignin-based hydrogel, indicating its potential for efficient thermal energy conversion and related applications. The Seebeck coefficient measures the hydrogel's ability to convert temperature

differences into electrical energy, making it a promising candidate for thermoelectric device development and sustainable energy-harvesting systems.

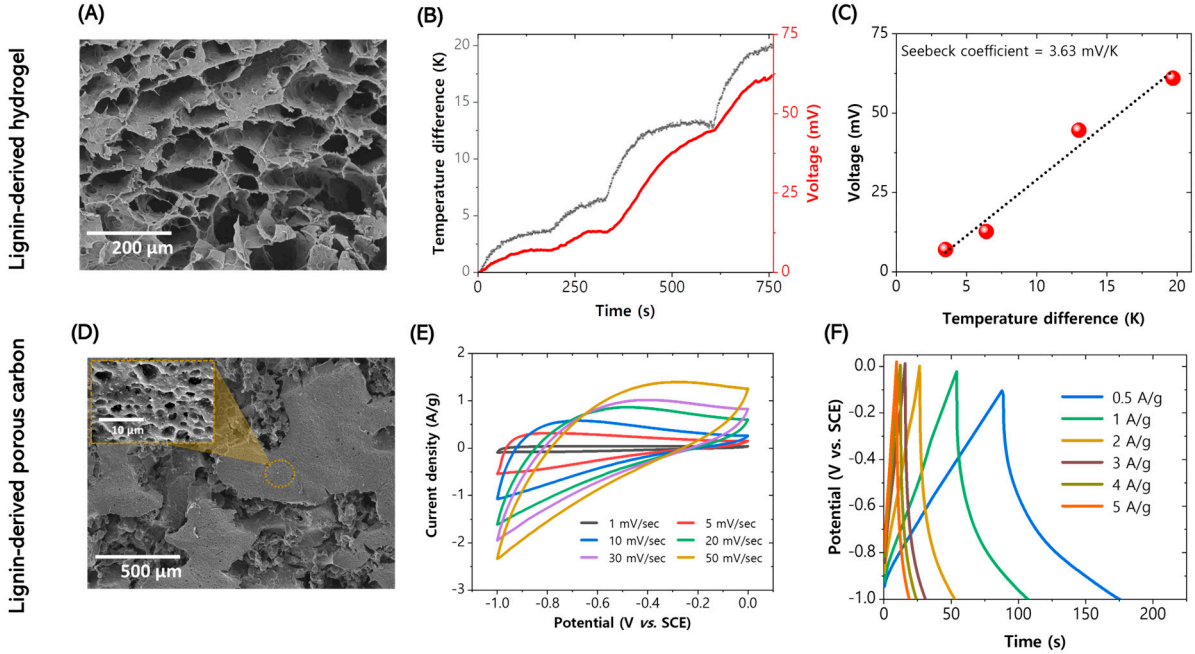

Figure 1. Lignin-derived hydrogel (**A**) morphology, (**B**) voltage response to axial temperature difference, and (**C**) Seebeck coefficient. Lignin-derived porous carbon (**D**) porous morphology, (**E**) cyclic voltammetry graphs, and (**F**) galvanostatic charge—discharge curves.

The morphology of lignin-derived porous carbon reveals a complex network of numerous small pores spanning a range from a few hundred nanometers up to 5 μm (Figure 1D). This intricate pore structure imparts a significantly expanded surface area, a pivotal factor contributing to its enhanced electrochemical performance. The abundance of tiny pores provides ample active sites for electrochemical reactions, facilitating efficient charge storage and transfer within the material.

A three-electrode configuration was employed for the electrochemical testing of lignin-based porous carbons (LPCs), with the results presented in Figure 1E,F. Cyclical voltammetry (CV) analysis encompassing scan rates of 1 mV/s, 5 mV/s, 10 mV/s, 20 mV/s, 30 mV/s, and 50 mV/s, within a potential range of −1.0 to 0 V, illuminated the material's behavior. The quasi-rectangular shape observed across all scan rates signifies LPC's suitability for energy storage applications, although with slight irregularities attributed to pseudocapacitive behavior. Consistency in quasi-rectangular shapes, even at high scan rates, suggests the presence of a dual-layer capacitor mechanism conducive to rapid charge transfer [9].

Specific capacitance determination through galvanostatic charge—discharge (GCD) testing, conducted in the −1.0 to 0 V potential window at varying current densities, reflects the same behavior as observed in CV curves, with slight bending due to pseudocapacitive behavior and faradic surface reactions. The longest GCD cycle was recorded at 0.5 A/g, demonstrating reduced discharge cycle durations at higher current densities due to the limited charge propagation time through the pores. The specific capacitance analysis yielded a maximum of 56.34 F/g at 0.5 A/g, with diminishing capacitance at elevated current densities due to sluggish electrochemical activities and internal resistance.

The lignin hydrogels and carbon samples can be coupled together to make a special kind of supercapacitor that uses heat and ions to store energy. This new system could convert heat into useful energy and store it effectively, offering a promising solution for better and more sustainable power storage.

4. Conclusions

In this study, we investigated the viability of lignin for developing ionic thermoelectric hydrogels and carbon-based materials. Our findings reveal that optimized lignin-derived hydrogels exhibit an impressive Seebeck coefficient of 3.63 mV/K under axial temperature gradients. Additionally, the synthesized lignin-based porous carbon materials exhibit exceptional performance as supercapacitor electrodes, showcasing a remarkable specific capacitance of 56.3 F/g at 0.5 A/g. The synergy between lignin-based hydrogels and porous carbon electrodes presents an encouraging avenue for the realization of lignin-derived ionic thermoelectric supercapacitors, opening up exciting prospects in sustainable energy storage and utilization.

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