Xanthan Gum-Based Quasi-Solid-State Electrolyte for Freeze-Resistant Zn Batteries

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Abstract

Xanthan gum-based quasi-solid-state electrolytes are investigated for freeze-resistant Zn batteries. EIS and cyclic voltammetry are performed to compare two types of electrolytes, including $ZnCl_2$ and $ZnSO_4$, from 10°C to -10°C. The $ZnCl_2$ formulation maintains stable performance, while $ZnSO_4$ fails at low temperatures (Rct >500 kΩ at 0 °C), establishing $ZnCl_2$-based QSSE as superior for cold-operating zinc batteries.

Introduction

Zinc-metal batteries are a safe and low-cost alternative to commercial lithium-ion batteries, but face three obstacles: dendrite growth, water decomposition, and freezing. Our QSSE attempts to solve all three by immobilizing concentrated salt in a biopolymer matrix to mechanically block dendrites, restrict free water and enable sub-zero operation. Cyclic Voltammetry and EIS are used to compare two formulations ($ZnCl_2$ and $ZnSO_4$) across temperature, identifying the optimal candidate for low-temperature applications.

Methods

- The two QSSE's compared consist of 10 M $ZnCl_2$ and $ZnSO_4$ saturated in a xanthan gum hydrogel.
- EIS: Applied frequency of 1MHz-0.1 Hz and 10 mV amplitude.
- CV: Electrochemical stability and Zn2+ transport were probed using cyclic voltammetry (CV) in a symmetric Zn||Zn coin cell at a scan rate of 20 mV/s.
- Tests were conducted at room temperature(20 °C), 0 °C, and -10 °C.
- A control sample of blank xanthan gum (no salt) confirmed the polymer host itself is electrochemically inert.

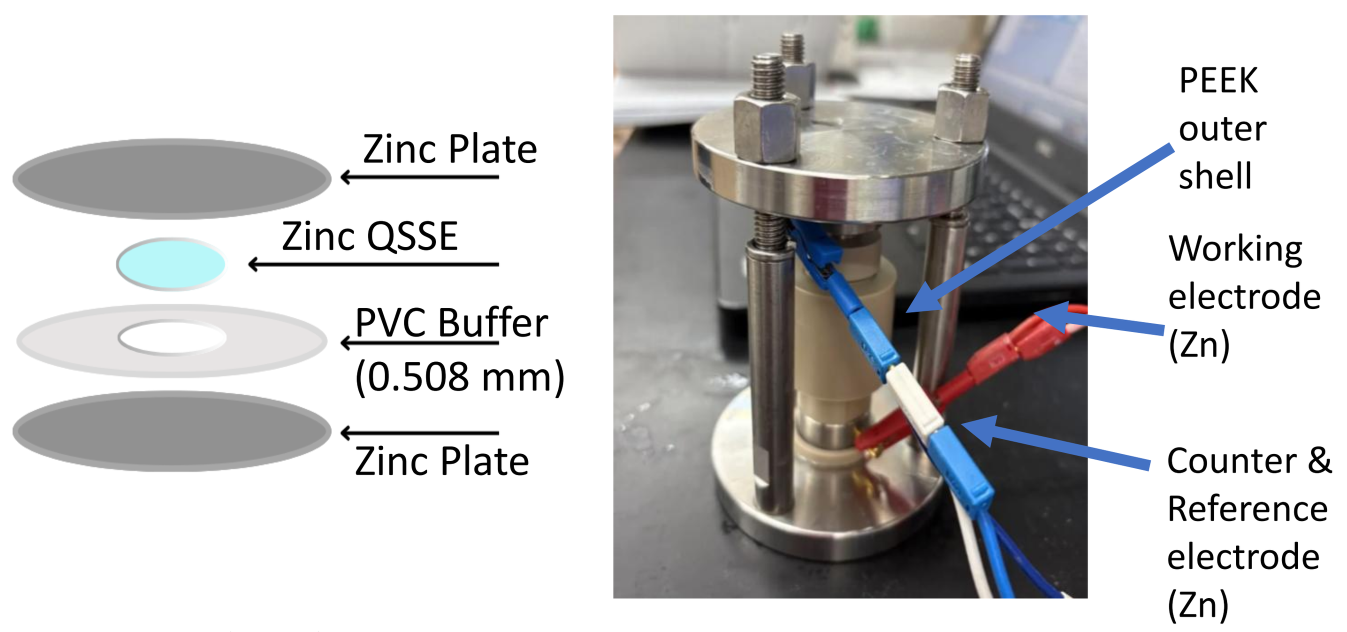

Figure 1. (Left) Schematic illustrating interior of coin cell. (Right) Photograph of exterior of coin cell.

Results

Cyclic Voltammetry Comparison

For $ZnCl_2$ there is a clear decrease in peak current from 1.4 mA (20 °C) to 0.04 mA (-10 °C) confirming a moderate temperature dependence, but maintaining functional electrochemistry. Compared to the $ZnSO_4$ system, it exhibits higher current response and enhanced electrochemical activity.

$$T(chiller) = T(inside) - \frac{QL}{kA} \quad (1)$$

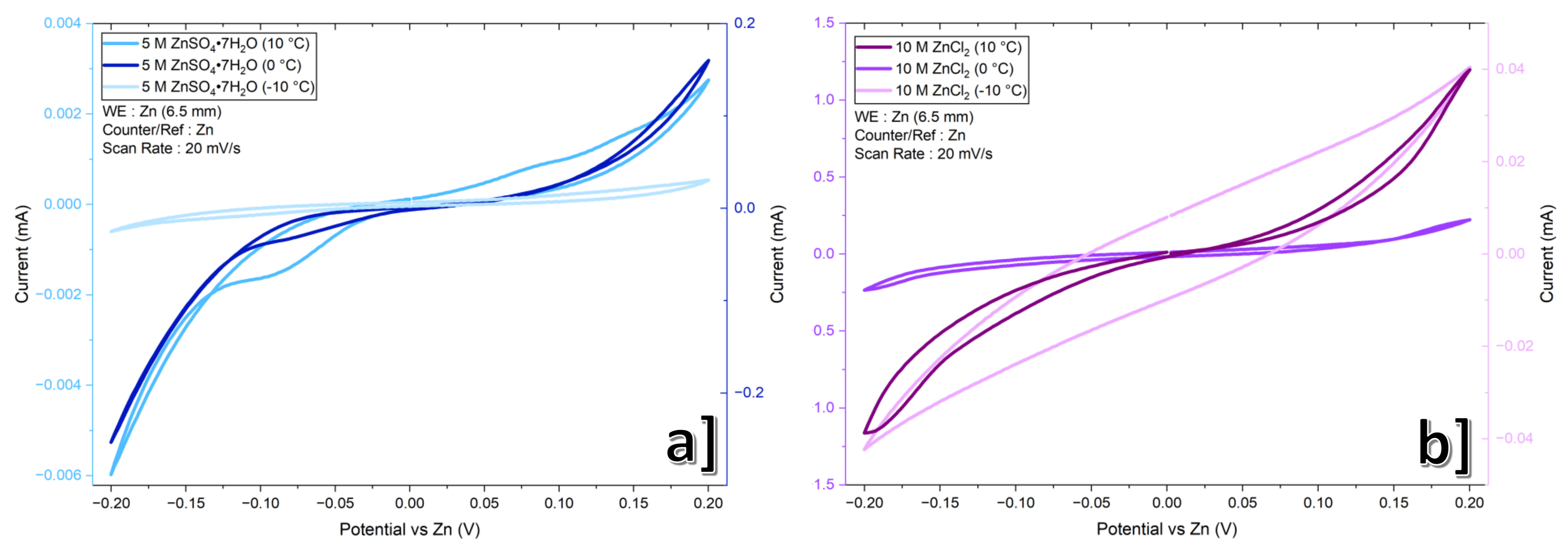

Figure 2. Cyclic voltammograms of a] $ZnSO_4$ and b] $ZnCl_2$ at 20 °C, 0 °C, and -10 °C. $ZnCl_2$ shows clear, reversible Zn plating/stripping peaks at all temperatures. $ZnSO_4 \cdot 7H2O$ exhibits minimal current response (0.01 mA).

Temperature Performance

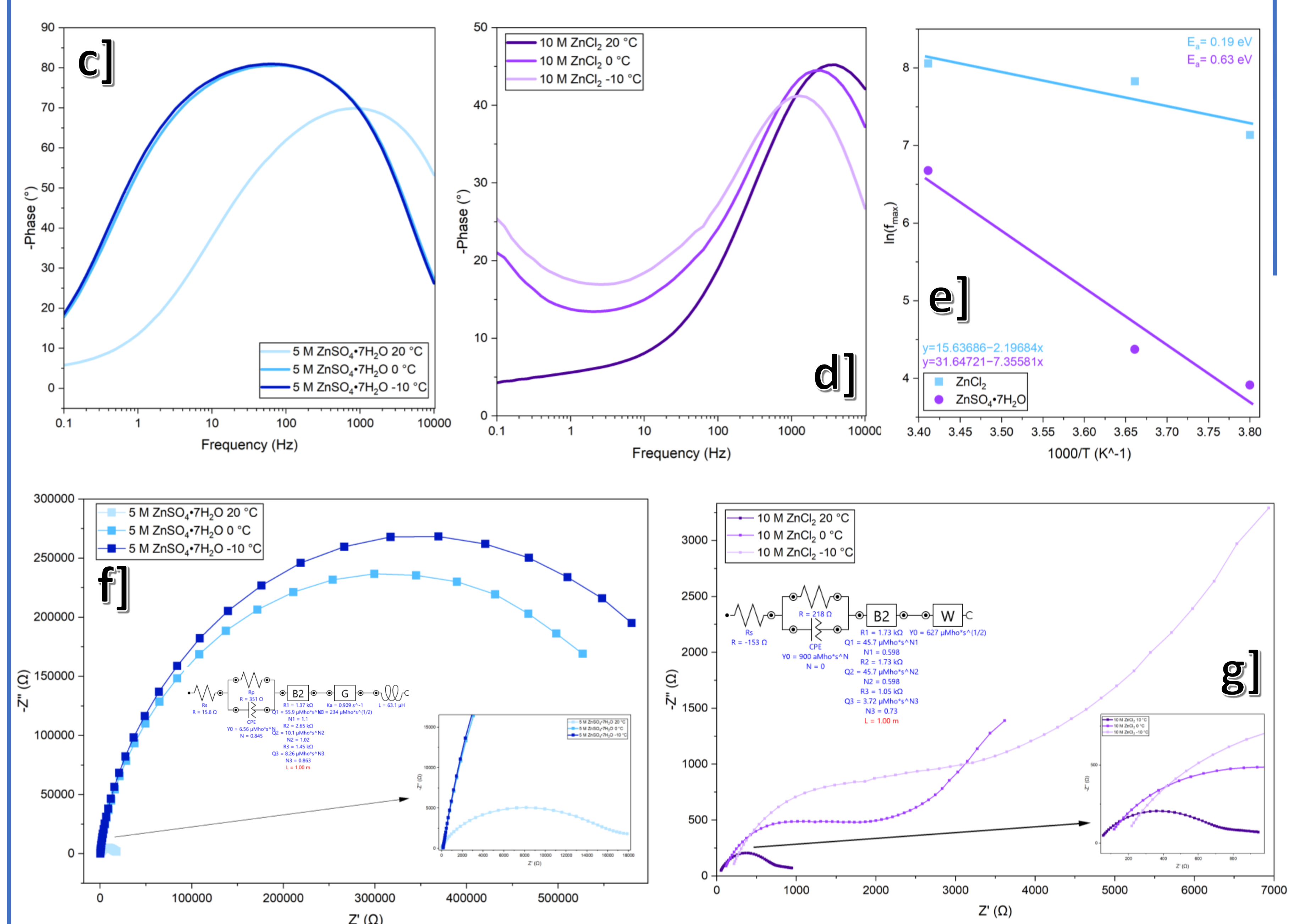

Figure 3. Nyquist and Bode plots of symmetric Zn|Zn coin cell, with c], f] for 5 M $ZnSO_4$ and d] and g] for10 M $ZnCl_2$. f], g] Nyquist plots and associated circuit model for the respective electrolyte at 20 °C. $ZnCl_2$ shows complete semicircles with moderate temperature dependence. $ZnSO_4$ exhibits dramatically increasing impedance below 0°C with unstable behavior (negative resistance artifacts at low frequencies). e] Arrhenius plot of ionic conductivity for $ZnCl_2$ QSSE.

Table 1. EIS Results Summary

ZnCl2 QSSE			
Temperature	20 °C	0 °C	-10 °C
Ru (Ω)	55.38	119.4	218.5
Rct	889.0 Ω	3.552 kΩ	>13 kΩ
Conductivity (S/cm)	0.0057	0.0027	0.0015
Conductivity Retention	100%	46.40%	25.35%
fmax (Hz)	3162	2512	1259
χ^2	0.0382	0.0012	0.0025
Activation Energy (Ea)	0.19 eV		
$ZnSO_4$ QSSE			
Temperature	20 °C	0 °C	-10 °C
fmax (Hz)	794.3	79.43	50.12
χ^2	0.0997	0.0688	0.0310
Activation Energy (Ea)	0.63 eV		

$$\sigma = \frac{L_{QSSE}}{R_u \times A_{QSSE}} \quad (2)$$

$$E_a = -Slope \times k_B \times 1000 \quad (3)$$

Conclusion

- $ZnCl_2$-based QSSE demonstrates superior low-temperature performance due to retiaing 26% of room-temperature conductivity at -10 °C and low activation energy (0.19 eV) which enables sustainable charge transfer kinetics.
- $ZnSO_4$-based QSSE fails at sub-zero temperatures as resistance values are negative, no reversible redox peaks in CV, and high activation energy (0.63 eV) confirming system instability.
- $ZnCl_2$ would be the optimal candidate of these two formulations for low-temperature batteries. This formulation maintains functional electrochemistry down to -10 °C, with acceptable fits based on retrieved χ^2 values.

Citations

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