Wettability-Controlled Tri-continuous Carbon-based Electrocatalysts for Zn-Air Batteries

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Abstract. Zn-air batteries (ZABs) are promising energy storage systems, but their performance is often limited by sluggish oxygen reduction reaction (ORR) kinetics and electrolyte flooding at the air cathode. Here, we introduce a tri-continuous carbon-based electrocatalyst (TRICE) derived from bijels-templated carbonization to address these challenges. The resulting nanoporous framework provides interconnected channels for air and electrolyte, enhancing three-phase boundary formation and mass transport. To investigate the role of wettability, two TRICE samples, specifically unmodified and hydrophobic TRICE were evaluated. The hydrophobic TRICE electrodes exhibited strong resistance to electrolyte flooding and maintained stable electrochemical operation during repeated cycling. Despite being fully metal-free, their power densities remained competitive with those of noble-metal and metal-oxide air cathodes. These results demonstrate that wettability tuning in TRICE structures effectively improves flooding tolerance and air cathode stability, offering a promising pathway for durable ZABs.

1 Introduction

The development of efficient energy storage systems (ESS) is crucial for the deployment of renewable energy technologies. Among various electrochemical storage platforms, Zn-air batteries (ZABs) are particularly appealing due to the low cost, abundance, and chemical stability of zinc in alkaline media. These advantages make ZABs promising candidates for sustainable energy storage. [1]

However, the application of rechargeable ZABs is significantly limited by the sluggish kinetics of the oxygen reduction reaction (ORR) and electrolyte flooding at the air cathode. These challenges necessitate the development of advanced electrode structures and non-noble-metal catalysts. [2, 3]

Bicontinuous interfacially jammed emulsion gels (bijels) provide a promising platform for addressing these limitations. Bijels are stabilized by nanoparticles that jam at liquid–liquid interfaces, resulting in a bicontinuous structure with two interpenetrating channels. This

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morphology enables efficient mass transport of both gas and electrolyte and provides a high interfacial area that is beneficial for electrochemical reactions. Such structural features make bijels ideal templates for improving air-cathode performance in ZABs, where the formation of stable three-phase boundaries is essential. [4]

Recent progress in bijels processing has enabled scalable fabrication of these bicontinuous structures. Methods such as solvent-transfer-induced phase separation (STRIPS) and vaporization-induced phase separation (VIPS) allow controlled formation of bijels architectures under practical conditions. These techniques overcome the limitations of early small-scale batch processes and enable the use of bijels-templated materials in electrochemical energy systems. [5, 6]

In this study, we used an advanced bijels-templating approach to synthesize a tri-continuous carbon-based electrocatalyst, referred to as TRICE. The TRICE structure incorporates three interconnected and continuous pathways that separately facilitate gas transport, electrolyte infiltration, and electron conduction through the solid carbon framework. By adjusting the surface wettability of the TRICE structure through unmodified and hydrophobic configurations, we successfully designed air cathodes that exhibit improved resistance to electrolyte flooding.

By effectively limiting electrolyte infiltration while maintaining oxygen accessibility, the wettability-controlled TRICE structures achieved stable and durable air-cathode performance. These results demonstrate the potential of bijels-derived TRICE as a robust, metal-free air-cathode structure and offer a promising pathway toward long-term performance in rechargeable ZABs.

2 Experimental

2.1 TRICE fabrication

TRICE (Tri-continuous Carbon-based Electrocatalysts) samples are synthesized following a previously reported procedure. [7]

Briefly, precursor liquids are prepared by mixing 1,6-hexanediol diacrylate (HDA), pH 3 water, ethanol with three additional components: a 50 wt.% silica nanoparticle suspension (Ludox TMA, 22 nm, pH 3), a 200 mM cetyltrimethylammonium bromide (CTAB) solution in ethanol, and 2-hydroxy-2-methylpropiophenone (HMP) as a photo-initiator. And the mixture is vortexed until a transparent precursor solution is obtained.

2.1.1 VIPS (Vaporization Induced Phase Separation)-STRIPS (Solvent Transfer Induced Phase Separation) TRICE formation:

280 μm carbon papers are dipped into the precursor mixture. A controlled airflow was applied using an adjustable air line. After 15-30 s, the samples are transferred to a water bath of pH 3 for 2 mins. Samples are then irradiated with UV light underwater to polymerize the HDA phase.

2.1.2 Pyrolysis:

Samples are pyrolyzed using a vertical tube furnace at 900ºC for 1 h under methane. During pyrolysis, methane serves as a carbon source, and the polymer framework is converted into a carbon walled channel.

2.1.3 Surface modification:

Functionalization of TRICE samples with 4-tert-butylaniline is performed following a literature procedure. [8]

2.1.4 Hydrophobic surface modification

Pyrolyzed TRICE samples are immersed in 1 M NaOH solution to remove the embedded silica nanoparticles. Following, the samples are rendered hydrophobic through a surface modification, the pyrolyzed TRICE samples, sodium nitrite, and 4-tert-butylaniline are dispersed in methanol. Hydrochloric acid is added, and the vial is sealed with parafilm and placed on a shaker to react overnight.

2.2 Electrowetting experiments

To investigate electrolyte flooding during electrochemical testing, an electrowetting experiment was conducted. A 100-200 µl droplet of 6 M KOH electrolyte was deposited onto the surfaces of the unmodified TRICE and Hydrophobic modified TRICE samples at room temperature. The TRICE samples served as the working electrode (WE), and a 3 cm Zn-foil was used as the counter electrode (CE). Prior to each experiment, the electrolyte droplet was gently contacted with the Zn-foil CE to establish the electrical connection. Linear Sweep Voltammetry (LSV) measurements were subsequently performed for 5 cycles on each sample, sweeping the potential from 1.4 V to 0.2 V at a scan rate of 8 mV s^{-1}.

2.3 Electrode fabrication and assembly of rechargeable Zn-air battery (ZAB)

The TRICE samples were cut into 0.5 cm × 3 cm pieces to serve as the cathode air electrode of the Zn-air battery (ZAB). The cut TRICE pieces were cleaned using an air blower. A copper wire was affixed to the top of the TRICE piece using silver paste (DuPont CP4922N-100), followed by overnight drying. Subsequently, epoxy (Devcon 14250) was applied over the silver paste, which was also allowed to dry overnight. Zn-foil (Lot.Z05K008, Thermo Fisher Scientific) was cut into 3 cm × 3 cm pieces for the anode electrode. The cut Zn-foil pieces were cleaned with deionized (DI) water prior to use. For the ZAB assembly, the Zn-foil was first placed on the bottom, and a silicone tube as the reservoir was positioned on top of the Zn-foil. Then, 6 M KOH electrolyte was added to fill the silicone tube. Finally, the prepared air cathode was placed on top of the tube, completing the cell assembly.

2.4 ZAB testing

The Zn-air battery (ZAB) testing was conducted using an Autolab electrochemical workstation at room temperature. Polarization curves were obtained via Linear Sweep Voltammetry (LSV), sweeping the potential from 1.4 V to 0.2 V at a scan rate of 8 mV s^{-1}. The reported current density and power density values were normalized to the electrode area (0.283 cm^2).

3 Results and discussion

The structural characteristics of the TRICE samples were first examined using cross-sectional and top-view scanning electron microscopy (SEM). In the cross-sectional scanning electron microscope (SEM) images (Fig. 1a-b), the morphology illustrates the carbon fibers of the

carbon paper and the overlaid TRICE structure. The formation of a spinodal structure is confirmed both on the surface and partially within the carbon paper. This configuration, where the TRICE layer is supported by the carbon paper, provides crucial mechanical stability to the air cathode. Furthermore, the top-view SEM image (Fig. 1c) confirms the successful formation of a distinctive tri-continuous pore structure. This internal spinodal structure results in a substantially increased electrode surface area and is critical for electrode functionality. The structured pores are designed to facilitate the efficient supply of air and the infiltration of the electrolyte, leading to the formation of an extensive three-phase boundary. The resulting structure, by optimizing the three-phase boundary and transport pathways, effectively mitigates limitations in cathode efficiency, such as poor transport of air and ions and limited three-phase boundaries.

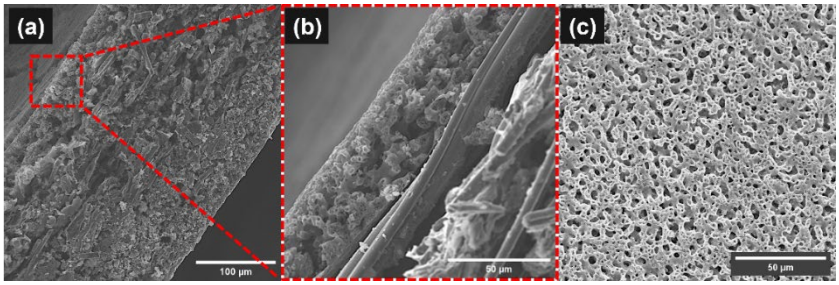

Fig. 1. (a) Low magnification scanning electron microscope (SEM) image of the cross-section of the TRICE layer, and (b) High magnification SEM image of the cross-section revealing ~ 30 µm thickness of the TRICE layer. (c) Top-view SEM image illustrating the tri-continuous pore structure of the material.

To evaluate the influence of surface chemistry on electrolyte interaction, the wettability behavior of the TRICE samples was examined under electrochemical conditions. The unmodified TRICE exhibited hydrophilic characteristics and showed a pronounced increase in wettability after Linear sweep voltammery (LSV) cycling, indicating that electrolyte readily infiltrated the porous structure. In contrast, the hydrophobic TRICE maintained a strongly non-wetting surface throughout the measurements, displaying only a slight reduction in hydrophobicity after cycling but still effectively resisting electrolyte penetration.
Collectively, these observations confirm that the hydrophobic modification significantly suppresses electrolyte flooding, whereas the unmodified TRICE readily absorbs electrolyte during operation. This qualitative difference in wettability directly influences the stability of the air cathode by determining the degree to which oxygen pathways remain accessible under electrochemical conditions.

Their electrochemical behavior in a Zn-air battery configuration was subsequently evaluated. A ZAB consisting of a Zn foil anode, a TRICE air cathode, and a 6 M KOH electrolyte was constructed (Fig. 2a), and a homemade ZAB was assembled using unmodified and hydrophobic TRICE samples as the air electrodes (Fig. 2b). The initial open-circuit voltages (OCVs) of the devices were measured to be 1.452 V for the unmodified TRICE and 1.354 V for the hydrophobic TRICE (Fig. 3a-b).

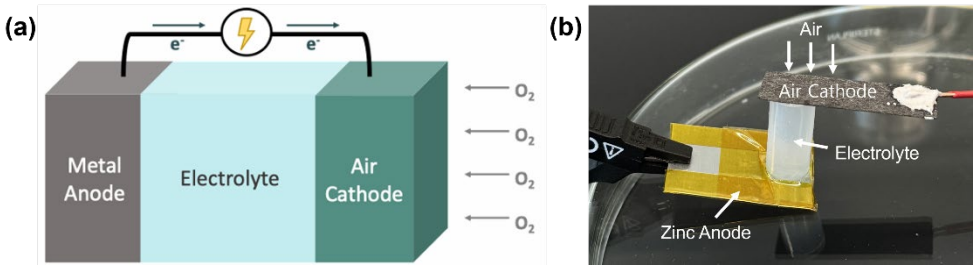

Fig. 2. (a) Diagram of Zn-air battery (ZAB), (b) Photograph of homemade Zn-air battery (ZAB) setup.

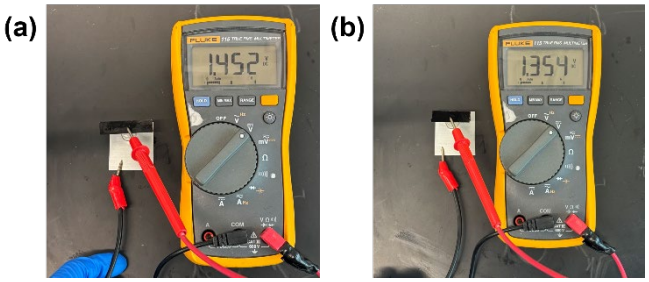

Fig. 3. (a)-(b) Open-circuit voltage (OCV) of the ZAB using (a) Unmodified TRICE and (b) Hydrophobic TRICE as the air cathodes.

The electrochemical performance of the TRICE samples as air cathodes was examined through repeated Linear Sweep Voltammetry (LSV) cycling to evaluate their resistance to electrolyte flooding. The unmodified TRICE exhibited a rapid decline in performance after the initial cycle, indicating severe electrolyte flooding and blockage of the oxygen transport pathways. This rapid degradation aligns with its hydrophilic nature, which allows electrolyte to readily infiltrate and saturate the porous structure during operation.

In contrast, the hydrophobic TRICE exhibited significantly improved stability during electrochemical cycling. Both the peak power density and peak current density showed only minor reductions throughout repeated cycles, indicating that the hydrophobic modification effectively optimizes the balance between electrolyte management and oxygen accessibility. Specifically, the introduced hydrophobicity prevents electrolyte flooding while facilitating a stable three-phase boundary, which is crucial for enhanced durability and efficient oxygen reduction/evolution reactions.

4 Conclusions

To summarize, this study demonstrates that controlling surface wettability in TRICE air cathodes is an effective strategy to mitigate electrolyte flooding induced performance loss in Zn-air batteries (ZABs). SEM analysis confirmed that TRICE possesses a highly porous, tri-continuous pore structure that is favorable for three-phase boundary formation.
The unmodified TRICE, which exhibits hydrophilic characteristics, showed substantial degradation during electrochemical cycling due to rapid electrolyte infiltration and blockage of air pathways.
In contrast, the hydrophobic TRICE exhibited the most robust and stable performance. This enhanced durability is directly attributed to its ability to limit excessive electrolyte penetration while preserving continuous oxygen diffusion channels.

Overall, the hydrophobic TRICE air cathode offers an ideal combination of stability and flooding resistance, positioning it as a highly efficient and durable structure for next-generation ZAB applications.

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