Chapter 6

Design and Optimisation of Metal–Air Batteries:

A Critical Review of Mechanisms and Performance

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ABSTRACT

Metal-air batteries (Li-air, Zn-air, Na-air, and Al-air) represent a promising alternative for energy storage due to their high energy density and potential for sustainable applications. However, their performance is severely limited by challenges associated with metallic anodes, including corrosion, passivation, and uncontrolled hydrogen evolution, which reduce cycle life and faradaic efficiency. This critical review examines the electrochemical mechanisms associated with metallic anodes in metal-air batteries, comparing the performance of Li-air systems (3500 Wh/kg), Zn-air (300 cycle), Na-air (1000 Wh/kg), and Al-air (2790 Wh/kg). Recent solutions, such as the use of alloyed anodes, surface modifications, and the incorporation of inhibitor additives in alkaline electrolytes, have significantly improved the performance and durability of metal-air batteries. The findings from this analysis highlight recent advancements and persistent challenges in the optimisation of metallic anodes, paving the way for more efficient and durable metal-air batteries for large-scale applications.

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INTRODUCTION

The global energy transition, driven by the urgent need to reduce greenhouse gas emissions and limit dependence on fossil fuels, is largely based on the development and massive integration of renewable energies such as wind and solar power. However, the intermittent nature of these energy sources poses a major challenge achieving efficient and sustainable energy storage (Gaele et al., 2022; Ostergaard et al., 2020; Shittu et al., 2022). In this context, energy storage is technologies have become essential pillars for ensuring grid stability, mitigating production fluctuations, and flexibly meeting growing energy demand (Branco et al., 2018; Areola et al., 2025; Di Somma et al., 2022).

Among these challenges, electrochemical energy storage systems particularly batteries occupy a central role. Their high efficiency, modularity, and scalability make them suitable for diverse applications, ranging from portable electronics to large-scale stationary storage (Shabeer et al., 2025). Since Alessandro Volta's pioneering work in the 19th century, battery technologies have undergone significant evolution, giving rise to several families such as lithium-ion, lead-acid, and redox flow batteries (Olabi et al., 2021). Despite their diversity, all these systems rely on the same fundamental mechanism: the reversible transfer of ions between an anode and a cathode through an electrolyte, enabling energy storage and release.

Within this technological landscape, metal–air batteries (MABs) have recently attracted increasing attention due to their exceptionally high theoretical energy densities and potential contribution to carbon-neutral energy systems. For example, lithium-air batteries can reach up to 3500 Wh/kg (Ye et al., 2024; Bruce et al., 2012; Imanishi et al., 2019), around ten times more than conventional lithium-ion batteries, whose density varies between 100 and 300 Wh/kg (Shabeer et al., 2025). This remarkable energy capacity makes MABs promising candidates for both large-scale stationary storage and long-range electric vehicles (EVs). Furthermore, the recyclability and natural abundance of metals such as zinc and aluminum reinforce their strategic importance in sustainable energy transitions. Unlike traditional systems, MABs utilize atmospheric oxygen as the cathodic reactant, reducing overall weight and enhancing energy density (Khan et al., 2025).

Recent advances in materials science and electrochemistry have significantly improved the performance and cycling stability of MABs. Innovations in metallic anode engineering (Li, Zn, Na, Al) and electrolyte optimization have proven particularly effective (Shinde et al., 2023; Ji et al., 2022; Chen et al., 2025; Che et al., 2025). Consequently, understanding the electrochemical mechanisms and degradation pathways of these anodes remains a key step toward developing efficient and durable systems.

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