

MGX Minerals Announces Development of Highly Stable Zinc Metal Anodes Enabled by Atomic Layer Deposited Al₂O₃ Coating for Aqueous Zinc-Ion Batteries

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VANCOUVER, Feb 3, 2021 - [MGX Minerals Inc.](#) ("MGX" or the "Company") (CSE: XMG / FKT: 1MG / OTCQK: MGXMF) is pleased to report that, in its collaborative research partnership with the University of British Columbia ("UBC"), has developed a new dendrite free Zinc-Ion battery under US Provisional Patent #62/993,177. As published in the Royal Journal of Chemistry: Journal of Material Chemistry A:

"Rechargeable aqueous zinc-ion batteries (ZIBs) have attracted increasing attention as an energy storage technology for large-scale applications, due to their high capacity (820 mA h g⁻¹ and 5854 A h L⁻¹), inherently high safety, and their low cost. However, the overall performance of ZIBs has been seriously hindered by the poor rechargeability of Zn anodes, because of the dendrite growth, passivation, and hydrogen evolution problems associated with Zn anodes. Herein, Al₂O₃ coating by an atomic layer deposition (ALD) technique was developed to address the aforementioned problems and improve the rechargeability of Zn anodes for ZIBs. By coating the Zn plate with an ultrathin Al₂O₃ layer, the wettability of Zn was improved and corrosion was inhibited. As a result, the formation of Zn dendrites was effectively suppressed, with a significantly improved lifetime in the Zn-Zn symmetric cells. With the optimized coating thickness of 100 cycles, 100Al₂O₃@Zn symmetric cells showed a reduced overpotential (36.5 mV) and a prolonged life span (over 500 h) at 1 mA cm².

In addition, the 100Al₂O₃@Zn has been verified in Zn-MnO₂ batteries using layered d-MnO₂ as the cathode and consequently exhibits superior electrochemical performance with a high capacity retention of 89.4% after over 1000 cycles at a current density of 1 mA cm² (3.33C for MnO₂) was demonstrated. It is expected that the novel design of Al₂O₃ modified Zn anodes may pave the way towards high performance aqueous ZIBs and shed light on the development of other metal anode-based battery systems.

Introduction

Nonaqueous lithium-ion batteries (LIBs) have dominated the global energy storage market over the past few decades, due to their high energy density, high power density, and long cycle life.

However, the increasing concerns over limited lithium resources, high cost, and safety issues limit their future applications in large-scale energy storage.

Sodium-ion batteries (SIBs) and potassium-ion batteries (KIBs) have been developed as alternatives to LIBs, because of their relatively abundant sodium (or potassium) resources in the Earth's crust. However, they still suffer from low energy density, the use of highly toxic and amiable organic electrolytes, high manufacturing cost and safety issues.

The drawbacks of these nonaqueous-based systems motivate us to explore alternative battery chemistry with lower cost, higher safety, and longer cycle life.

Recently, aqueous zinc-ion batteries (ZIBs) have gained remarkable attention as a promising energy storage technology, owing to the appealing advantages of Zn anodes, including high theoretical capacity (820 mA/h), low redox potential (0.762 V vs. SHE), high abundance, and environmental benignity. More importantly, the replacement of organic electrolytes with aqueous electrolytes is of great significance to achieve intrinsic safety, environmental protection, and cost saving. Additionally, aqueous electrolytes offer about 2 orders of magnitude higher ionic conductivity than nonaqueous ones.

However, the development of aqueous ZIBs is limited by the Zn anodes, which suffer from dendrite growth, low efficiency, and poor cycle life. The sharp and highly resistant Zn dendrites could not only lead to short circuit by penetrating the separator and the consequent sudden failure of ZIBs, but also cause rapid capacity decay by lowering efficiency and elevating internal resistance.

To circumvent these problems resulting from Zn dendrites, various strategies have been proposed to stabilize Zn anodes, including novel structure design, Zn alloying, surface modification, conductive substrates and electrolyte optimization. Among these strategies, surface modification represents a facile and effective approach to tune the interaction between Zn anodes and the electrolyte. Metal nanoparticles, organic polymers, carbon-based materials² and metallic compounds, have been investigated as protective layers on Zn-based electrodes, resulting in better electrochemical performance. For example, Zhi's group reported that quasi-isolated nano-Au particles on the Zn surface served as heterogeneous seeds for Zn deposition, and enabled stable Zn-plating/stripping processes on the Zn anodes.

These nano-Au particles with high curvature and large local electric field preferentially absorbed Zn²⁺ to uniformly nucleate and grow as Zn-flake-arrays, effectively suppressing the formation of big and uneven dendrites/protrusions. As a result, the Au nanoparticle decorated Zn anodes demonstrated excellent cycling stability for 2000 h in Zn|Zn symmetric cells and 2000 cycles in Zn-MnO₂ batteries. Cui and co-workers designed a polyamide coating layer on the Zn anodes to elevate the nucleation barrier and restrict 2D diffusion of Zn²⁺, which effectively regulated Zn deposition behavior in the aqueous electrolyte. This polyamide coating served as a buffer layer that isolated active Zn from bulk electrolytes and suppressed the corrosion induced by water and O₂. With this synergic effect, the polyamide-modified Zn anodes exhibited 60-fold enhancement in lifetime (over 8000 hours) compared to bare Zn, even at a high areal capacity of 10 mA h cm² (10 mA cm² for 1 h and 85% depth of discharge). Wang et al. obtained a spontaneously reduced graphene oxide coating on Zn foil (Zn/rGO) to promote uniform Zn electrodeposition and improve the cycling stability. This self-assembled, layered rGO on a Zn surface provided a large electroactive area and a so substrate for Zn electrodeposition, which significantly mitigated Zn dendritic growth by eliminating its driving force. Compared with bare Zn, the Zn/rGO anode exhibited much lower overpotential (20 mV at 1 mA cm²) and excellent long-life cyclability. Recently, Kang et al.³⁰ designed a porous nano-CaCO₃ coating as a protective layer to achieve uniform and bottom-up Zn stripping/plating.

This strategy effectively suppressed the development of Zn dendrites that may cause large polarization and internal short circuit, thus improving the coulombic efficiency (CE) and cycling stability of Zn batteries. All these results suggest that surface modification is an efficient way to construct robust Zn anodes, contributing to superior electrochemical performance during repeated Zn stripping/plating cycles.

Atomic layer deposition (ALD) is a promising thin film deposition technique that is capable of precisely controlling film thickness at the atomic level, owing to its self-limiting nature of gas-solid reactions during the deposition process.

Over the past few years, ALD has been extensively applied to deposit protection layers on anode and cathode materials to prevent direct exposure of the electrode to the electrolyte, leading to improved electrochemical performance in lithium/sodium-based batteries. Performance enhancement could be achieved using just a few nanometers of surface coatings by ALD, therefore adding negligible weight to the electrode. Moreover, the ALD coating has great potential for industrial application through a roll-to-roll or fluidized bed ALD process. However, the application of ALD in aqueous ZIBs is yet to be fully exploited. Recently, Mai's group first applied ALD TiO₂ coating as a protective layer on Zn anodes. The amorphous TiO₂ layer acted as a buffer layer between the Zn anode and electrolyte and suppressed hydrogen evolution and the formation of inactive reaction by-products, leading to enhanced electro-chemical performance of ZIBs. Nevertheless, the ALD deposition of TiO₂ employed TiCl₄ as a Ti precursor, which yielded HCl as a by-product during deposition and was not ideal for practical application. In contrast, ALD Al₂O₃ is the most widely used coating material in LIBs, due to its effectiveness among all available ALD materials and its well established industrial deposition process. However, there is no report of using ALD Al₂O₃ on Zn anodes, to the best of our knowledge. Al₂O₃ coating has been previously synthesized onto Zn particles by a sol-gel method and reported to be able to mitigate the hydrogen evolution reaction and delay the corrosion of the Zn anode in alkaline electrolytes. Despite the improved performance, the Al₂O₃ coating by the sol-gel method was uneven and rough on Zn particles, affecting its function as a protection layer. So, it is expected we conduct a systematic study on the effect of uniform Al₂O₃ coating on the Zn anodes with nanometer thickness by the ALD technique.

In this work, we demonstrated the use of an ultrathin protective Al₂O₃ coating layer by ALD on Zn anodes to

achieve dendrite-free Zn deposition and high-performance Zn-MnO₂ batteries. The effect of ALD Al₂O₃ thickness on the cycling of Zn|Zn cells was investigated in detail. It was found that Zn anodes with the Al₂O₃ coating deposited using 100 ALD cycles (100Al₂O₃@Zn) showed reduced overpotential (36.5 mV) and prolong cycling lifespan (over 500 h) at 1 mA cm² in Zn|Zn symmetrical cells. Furthermore, the Zn-MnO₂ battery built with 100Al₂O₃@Zn anode exhibited a high capacity retention of 89.4% after 1000 cycles at a current density of 1 mA cm² (3.33C for MnO₂). The improved electrochemical performance was ascribed to the robust Zn metal anode enabled by nanoscale Al₂O₃ coating, which improved the surface wettability, enhanced the corrosion resistance of Zn metal, and effectively suppressed the formation of less conductive Zn dendrites. It is expected that this work will provide new insight into interfacial engineering for metal anodes and into the fundamental understanding of interfacial phenomena for high performance metal-based batteries."

About MGX Minerals Inc.

MGX Minerals is a diversified Canadian resource and technology company with interests in global advanced material, energy and water assets.

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