

ABSTRACT:

Surface Modification of Lithium-Ion Sieve for Selective Direct Lithium Extraction: Role of Zirconium Coating on Adsorption Performance and Structural Stability

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The worldwide demand for lithium (Li) has surged significantly at a 15.4% annual growth rate due to its vital role in the rapid global expansion of electric vehicles and batteries [1]. The quality of conventional lithium resources like lithium ore has declined because of excessive mining, leading to the urge for sustainable lithium extraction from a variety of resources, such as salt lake brines, seawater, geothermal water, and geological formation waters [2]. To recover lithium from these brines, direct lithium extraction (DLE) has emerged as a particularly promising route, with adsorption technology at the forefront. One such lithium adsorbent material is hydrogen titanium oxide (HTO), a lithium-ion sieve (LIS) that exhibits a high adsorption capacity, lithium selectivity, and durability [3]. However, HTO is known to exhibit partial titanium (Ti) dissolution under strong acidic desorption conditions, which can lead to degradation of its crystal structure and diminish long-term performance [4]. Zirconium oxide (ZrO₂) coating was investigated as a surface modification strategy to improve the structural stability, long-term performance, and resistance to Ti dissolution of HTO-based LIS during lithium extraction from aqueous solutions [5]. Incorporation of ZrO₂ coating is expected to act as a chemically stable protective layer that reduces Ti leaching and enhances cycle stability while maintaining access to active Li⁺ adsorption sites due to its high chemical stability, corrosion resistance, and compatibility with oxide surfaces [6].

The ZrO₂-LIS was synthesized by the wet chemical coating method and then optimized by varying the zirconium coatings from 2 to 14 wt%, relative to the HTO mass. Uncoated HTO exhibited the highest Li⁺ uptake of approximately 28.5 mg/g but showed the greatest Ti loss of nearly 6%. Increasing ZrO₂ loading progressively reduced Ti leaching, while excessive coating decreased Li⁺ uptake due to partial blockage of active sites and pore pathways. Among the tested materials, 10 wt% ZrO₂-coated HTO provided the optimum balance, maintaining a high adsorption capacity of approximately 25 mg/g while reducing Ti loss to approximately 40%. FTIR and BET analyses further supported successful surface modification without major loss of the HTO framework; however, the primary goal was not to increase the surface area of the adsorbent, but to enhance regeneration stability for long-term performance.

The adsorption behavior was strongly pH-dependent, with Li⁺ uptake increasing from 13.12 mg/g at pH 6 to 27.61 mg/g at pH 12, consistent with enhanced surface deprotonation and improved Li⁺/H⁺ ion exchange under alkaline conditions. Isotherm analysis confirmed favorable Li⁺ adsorption, with maximum capacities in the range of approximately 28–31 mg/g, while kinetic experiments showed rapid initial Li⁺ uptake followed by a slower

approach to equilibrium. This behavior indicates that adsorption proceeds through fast surface ion exchange followed by diffusion-controlled transport within the particles. Competing-ion experiments further confirmed lithium selectivity, with Li^+ adsorption remaining substantially higher in both adsorbents than Ca^{2+} , Mg^{2+} , Na^+ , and K^+ uptake. The distribution coefficient for Li^+ was approximately 220 mL/g for HTO and 198 mL/g for ZrO_2 -coated HTO, confirming that the protective coating preserved lithium-selective ion-sieve behavior while reducing Ti dissolution. Overall, incorporation of ZrO_2 coating caused only a moderate reduction in Li^+ adsorption performance, approximately 10–12% relative to uncoated HTO, while decreasing Ti dissolution by nearly 40%. This tradeoff indicates that the slight compromise in adsorption capacity is acceptable, as the protective coating substantially enhances acid-regeneration stability and improves the practical reusability of the adsorbent in the long-term.

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