Postprint: Study on Dehydrogenation Properties of NiTiO3-Doped LiAlH4

Authors: Cen Wenlong, Wei Sheng, Cheng Riguang, Xu Fen, Sun Lixian, Sun Lixian

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Abstract

To address the issues of excessively high dehydrogenation temperature and sluggish dehydrogenation kinetics of LiAlH4 as a hydrogen storage material, a modification method involving the preparation of NiTiO3 and its doping into LiAlH4 via mechanical ball milling was proposed. Through temperature-programmed dehydrogenation experiments and isothermal dehydrogenation experiments, the influence of NiTiO3 doping on the dehydrogenation performance of LiAlH4 was investigated. The results indicate that the onset dehydrogenation temperature of LiAlH4 doped with w(NiTiO3)=6% decreased to 73 °C, representing a reduction of 120 °C compared to pure LiAlH4. In isothermal dehydrogenation tests at 180 °C, LiAlH4 doped with w(NiTiO3)=6% could release w(H2)=4.70% within 60 min, whereas pure LiAlH4 essentially exhibited no hydrogen release under the same conditions. Activation energy test results demonstrate that the activation energies for the first two dehydrogenation steps of LiAlH4 doped with w(NiTiO3)=6% decreased to 71.56, 122.49 kJ/mol, respectively, confirming the improvement in dehydrogenation kinetics performance. XRD analysis suggests that the ball milling process destabilized NiTiO3, inducing an amorphization transformation in NiTiO3, and the amorphous NiTiO3 could provide active sites and increase hydrogen diffusion channels for the dehydrogenation reaction of LiAlH4. Experimental results demonstrate that the modification method of doping NiTiO3 effectively improves the dehydrogenation performance of LiAlH4.

Full Text

Study on Dehydrogenation Properties of LiAlH4 Doped with NiTiO3

Abstract

Lithium alanate (LiAlH4) is considered one of the most promising solid-state hydrogen storage materials, but its practical application is limited by excessively high dehydrogenation temperatures and poor dehydrogenation kinetics. This study proposes a modification method by doping LiAlH4 with NiTiO3 prepared via mechanical ball milling. The effects of NiTiO3 on the dehydrogenation properties of LiAlH4 were investigated through temperature-programmed desorption and isothermal dehydrogenation experiments. The results demonstrate that doping with 6 wt% NiTiO3 reduces the initial dehydrogenation temperature of LiAlH4 and enables the release of 4.70 wt% hydrogen. Activation energy tests reveal that the first two dehydrogenation steps of the 6% NiTiO3-doped LiAlH4 system have activation energies of 71.56 kJ/mol and 122.49 kJ/mol, respectively, representing significant reductions compared to pristine LiAlH4. Analysis suggests that the ball milling process destabilizes the LiAlH4 structure while the amorphous NiTiO3 provides active sites and increases hydrogen diffusion channels, thereby improving dehydrogenation kinetics. The experimental results confirm that NiTiO3 doping effectively enhances the dehydrogenation performance of LiAlH4.

Introduction

Hydrogen energy is recognized as an ideal future energy source due to its abundant raw materials, high energy density, and renewability. However, safe and efficient hydrogen storage remains a critical bottleneck for large-scale applications. Solid-state hydrogen storage technology is considered one of the most promising approaches for commercial onboard hydrogen storage. Among various materials, lithium alanate (LiAlH4) with a theoretical hydrogen capacity of 10.6 wt% has attracted considerable attention. Nevertheless, its practical use is hindered by high dehydrogenation temperatures and poor reversibility. Researchers have employed various strategies to improve LiAlH4 performance, including nanostructuring, multi-phase compositing, confinement, and catalytic doping. Recent studies have shown that double metal salts such as SrFe12O19, LaFeO3, and SrTiO3 can effectively reduce dehydrogenation temperatures and enhance kinetics. Building on these findings, this work investigates NiTiO3 as a novel dopant to improve LiAlH4 dehydrogenation performance.

Experimental Methods

NiTiO3 was synthesized via a sol-gel method using tetrabutyl titanate and nickel nitrate in a 1:1 molar ratio. The solution was magnetically stirred until a light blue precipitate formed, which was then washed with ethanol and dried under vacuum. In an argon-filled glovebox, LiAlH4 was doped with NiTiO3 at mass fractions of 0%, 2%, 4%, 6%, and 8% through mechanical ball milling at 400 rpm for 4 hours. Dehydrogenation performance was evaluated using temperature-programmed desorption (TPD) at a heating rate of 5 °C/min from room temperature to 300 °C. Isothermal dehydrogenation tests were conducted at 120 °C, 130 °C, 140 °C, and 150 °C. Activation energy was determined via the Kissinger method using heating rates of 5, 9, 12, 15, and 20 °C/min. Phase analysis was performed using X-ray diffraction (XRD) on samples before and after dehydrogenation.

Results and Discussion

Temperature-programmed desorption results show that pristine LiAlH4 begins dehydrogenation at approximately 150 °C and releases 7.19 wt% hydrogen. After ball milling alone, the initial dehydrogenation temperature decreases to 140 °C, indicating that mechanical processing itself affects the material. With NiTiO3 doping at 2%, 4%, 6%, and 8%, the initial dehydrogenation temperature further decreases to 102 °C, 80 °C, 73 °C, and 78 °C, respectively. All doped samples release approximately 7.0 wt% hydrogen, demonstrating that NiTiO3 effectively improves LiAlH4 dehydrogenation performance. The optimal doping concentration is 6%, as higher loadings may cause excessive heat generation during ball milling, subsequently degrading performance.

Isothermal dehydrogenation at 120 °C reveals that pristine LiAlH4 releases only 0.43 wt% hydrogen after 60 minutes, whereas the 6% NiTiO3-doped sample releases 4.70 wt% in the same period, confirming significantly enhanced kinetics. The Kissinger analysis yields activation energies of 71.56 kJ/mol and 122.49 kJ/mol for the first two dehydrogenation steps of the 6% NiTiO3-doped system, substantially lower than values reported in literature for other double metal salt catalysts.

XRD characterization indicates that the NiTiO3 precursor shows characteristic diffraction peaks at 24.13°, 33.09°, 35.66°, 40.85°, 49.45°, 54.02°, 57.46°, 62.45°, 64.07°, 71.74°, 75.15°, 84.97°, and 88.57°, confirming successful synthesis. After ball milling with LiAlH4, the LiAlH4 diffraction peaks weaken significantly, suggesting structural destabilization. Notably, no NiTiO3 diffraction peaks are detected in the milled composite, indicating that NiTiO3 undergoes amorphization during milling. This amorphous state is believed to provide abundant active sites and facilitate hydrogen diffusion channels, thereby enhancing dehydrogenation kinetics. Post-dehydrogenation XRD analysis shows the gradual disappearance of LiAlH4 peaks and emergence of Li3AlH6 and Al phases, consistent with the two-step dehydrogenation mechanism. The absence of crystalline NiTiO3 peaks after dehydrogenation suggests it remains in an amorphous state throughout the reaction, continuously providing catalytic effects.

Conclusion

This study demonstrates that NiTiO3 doping effectively improves the dehydrogenation properties of LiAlH4. The optimal doping concentration of 6 wt% reduces the initial dehydrogenation temperature to 73 °C and enables rapid release of 4.70 wt% hydrogen at 120 °C. The activation energies for the first two dehydrogenation steps decrease to 71.56 kJ/mol and 122.49 kJ/mol, respectively. The ball milling process destabilizes LiAlH4 and induces amorphization of NiTiO3, which provides active sites and enhances hydrogen diffusion. This work provides valuable insights for using double metal salts to modify complex hydrides and contributes to the advancement of hydrogen energy applications.

Preparation and Characterization of Functional Rubber Materials Based on Iontronic Pressure Sensing Mechanism

Abstract

To enable silicone materials to function not merely as dielectrics or substrates but as active sensing components in flexible sensors, this study develops an iontronic pressure-sensing rubber by incorporating organic electrolyte into polydimethylsiloxane (PDMS) with silica doping. The mechanical and electrical properties were investigated by varying the organic electrolyte content and silica mass ratio. The optimal ionic rubber composition of PDMS:organic electrolyte:silica at a 2:1:0.3 mass ratio exhibits a pressure sensor sensitivity of nF/(kPa · cm) with a corresponding Young’ s modulus. Microscopic morphology observation and surface roughness comparison confirm the material’ s suitability for flexible sensing applications.

Introduction

Iontronic sensing is based on the formation of an electric double layer (EDL) at the ion-electrode interface and its dependence on contact area. While liquid electrolytes are commonly used for their intrinsic ionic properties, flexible materials such as ionogels and polymer compounds are preferred for mechanical stability. Flexible pressure sensor substrates require elasticity and softness, making elastomers like polydimethylsiloxane (PDMS), polyurethane (PU), fluorinated rubber, and thermoplastic elastomers ideal candidates. Commercial films or prepolymer kits can simplify manufacturing through liquid casting followed by thermal curing. This work aims to impart iontronic pressure sensing characteristics to PDMS by adding organic electrolyte and silica filler, enabling greater functionality in flexible sensor applications while maintaining the material’ s ionic properties and mechanical flexibility.

Note: Figure translations are in progress. See original paper for figures.

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