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The Recycling of Lithium from $LiFePO_4$ Batteries into Li_2CO_3 and Its Use as a CO_2 Absorber in Hydrogen Purification

Zoltán Köntös [1,*] and Ádám Gyöngyössy [2]

[1] IOI Investment Zrt., Fehérvári út 108-112, 1116 Budapest, Hungary
[2] Department of Organic Chemistry and Technology, Budapest University of Technology and Economics, Budafoki út 8. F. II., mfsz., 1111 Budapest, Hungary; gyongyossyadam@gmail.com
* Correspondence: zkontos@ioi-investment.com

Abstract: The growing adoption of lithium iron phosphate ($LiFePO_4$) batteries in electric vehicles (EVs) and renewable energy systems has intensified the need for sustainable management at the end of their life cycle. This study introduces an innovative method for recycling lithium from spent $LiFePO_4$ batteries and repurposing the recovered lithium carbonate (Li_2CO_3) as a carbon dioxide (CO_2) absorber. The recycling process involves dismantling battery packs, separating active materials, and chemically treating the cathode to extract lithium ions, which produces Li_2CO_3. The efficiency of lithium recovery is influenced by factors such as leaching temperature, acid concentration, and reaction time. Once recovered, Li_2CO_3 can be utilized for CO_2 capture in hydrogen purification processes, reacting with CO_2 to form lithium bicarbonate ($LiHCO_3$). This reaction, which is highly effective in aqueous solutions, can be applied in industrial settings to mitigate greenhouse gas emissions. The $LiHCO_3$ can then be thermally decomposed to regenerate Li_2CO_3, creating a cyclic and sustainable use of the material. This dual-purpose process not only addresses the environmental impact of $LiFePO_4$ battery disposal but also contributes to CO_2 reduction, aligning with global climate goals. Utilizing recycled Li_2CO_3 decreases the demand for virgin lithium extraction, supporting a circular economy. Furthermore, integrating Li_2CO_3-based CO_2 capture systems into existing industrial infrastructure provides a scalable and cost-effective solution for lowering carbon footprints while securing a continuous supply of lithium for future battery production. Future research should focus on optimizing lithium recovery methods, improving the efficiency of CO_2 capture, and exploring synergies with other waste management and carbon capture technologies. This comprehensive strategy underscores the potential of lithium recycling to address both resource conservation and environmental protection challenges.

Keywords: recycling economy; lithium; $LiFePO_4$ battery; lithium carbonate; CO_2 capture; sustainable energy; gas separation

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Citation: Köntös, Z.; Gyöngyössy, Á. The Recycling of Lithium from $LiFePO_4$ Batteries into Li_2CO_3 and Its Use as a CO_2 Absorber in Hydrogen Purification. *Clean Technol.* **2024**, *6*, 1504–1518. https://doi.org/10.3390/cleantechnol6040072

Academic Editor: Leonid Tartakovsky

Received: 21 August 2024
Revised: 15 October 2024
Accepted: 29 October 2024
Published: 4 November 2024

1. Introduction

As global demand for lithium-ion batteries continues to surge, driven by the rapid expansion of electric vehicles (EVs), renewable energy storage, and consumer electronics, establishing a robust lithium recycling economy becomes increasingly crucial [1,2]. Lithium, a key component of these batteries, is a finite resource with significant environmental and economic implications. Recycling lithium not only conserves this valuable resource but also reduces the environmental impact of extraction and production [3,4]. This paper explores the importance of a lithium recycling economy, focusing on its benefits, challenges, and the steps needed to enhance recycling practices.

The primary sources of lithium today are spodumene ores and lithium-rich brines, primarily located in regions such as Australia, Chile, and Argentina [5]. As global demand rises, these sources are being depleted at an accelerating rate, heightening the need for alternatives like recycling. Recovering lithium from used batteries offers a sustainable way to relieve pressure on natural reserves while ensuring a long-term supply for future technological advancements [6]. Moreover, it supports the principles of a circular economy, where materials are reused rather than discarded after a single use [7].

Traditional lithium-ion battery recycling processes primarily rely on pyrometallurgical and hydrometallurgical technologies [8]. Pyrometallurgy involves high-temperature smelting to recover metals, but it is energy-intensive and less efficient for lithium recovery. Hydrometallurgical processes, on the other hand, use chemical leaching to extract lithium and other metals [9]. While these methods are effective in recovering valuable materials, lithium is often overlooked due to its relatively low economic value compared to metals like cobalt and nickel [10]. Research and development in these recycling technologies aim to improve the efficiency of lithium recovery, making the recycling process more economically viable and environmentally sustainable [11,12].

The environmental impact of lithium mining is substantial, particularly in regions like South America's lithium triangle [13]. Extracting lithium from brines requires massive amounts of water, leading to conflicts over water rights and environmental degradation [14]. Recycling lithium offers an opportunity to reduce reliance on environmentally disruptive mining operations, thereby mitigating the associated negative impacts [15]. The energy required to recycle lithium from batteries is significantly less than the energy needed for mining and processing lithium from primary sources, lowering the carbon footprint of battery production [16,17]. Recycling lithium also addresses the growing issue of electronic waste, preventing used batteries from ending up in landfills, where they can cause soil and water contamination [18]. Proper recycling ensures that hazardous materials are safely processed, contributing to overall environmental protection [19].

In addition to its environmental benefits, developing a robust lithium recycling infrastructure offers substantial economic advantages [20]. This initiative creates new business opportunities and jobs across various sectors, including battery collection, processing, and the development of advanced recycling technologies [21]. As the demand for recycled lithium increases, it can help stabilize lithium prices by providing a secondary supply, thereby mitigating price volatility caused by fluctuations in supply and demand [22]. Additionally, this stabilization enhances global energy security by reducing dependence on foreign lithium sources, which are often vulnerable to geopolitical risks and trade restrictions [23,24]. However, challenges persist. Current recycling methods, while promising, tend to be complex, energy-intensive, and costly [25]. Enhancing the cost-efficiency and scalability of these technologies is crucial for broader adoption. Furthermore, effective collection systems, consumer participation, and regulatory support are vital for the success of lithium recycling initiatives. By advancing lithium recycling technologies and addressing these challenges, the world can significantly lessen the environmental and economic impacts of lithium-ion battery production. A robust lithium recycling industry is essential not only for resource conservation but also for fostering the transition to a more sustainable and circular economy.

Formic acid (HCOOH) is a liquid compound particularly suited for storing and transporting hydrogen, as it can safely and efficiently bind hydrogen within its chemical structure. The RK-X process, developed by IOI Investment Zrt., leverages this property, providing a solution to decompose formic acid into hydrogen (H_2) and carbon dioxide (CO_2) gas mixtures at room temperature. This process presents significant advantages since the transportation and storage of hydrogen have traditionally been challenging, especially under high pressure or low temperatures. As a liquid hydrogen carrier, formic acid eliminates these difficulties. The resulting H_2 and CO_2 gas mixture can undergo further processing: it is passed through a Li_2CO_3 bed, where the two gasses are effectively separated. The reversible properties of Li_2CO_3 facilitate the capture of CO_2, while pure hydrogen proceeds into a fuel cell, where it can be converted into electricity. This energy conversion process offers an efficient and environmentally friendly solution for hydrogen-based power generation. The RK-X process represents an innovative approach that does not rely on traditional inorganic energy storage methods, such as lithium-ion batteries, but instead utilizes an organic-based system that stores energy in chemical bonds. The use of formic acid allows energy to be stored in liquid form, which can be easily distributed and refueled through conventional fueling networks. This solution is particularly advantageous for developing a hydrogen economy, as hydrogen does not need to be transported under high pressure or in specialized containers, resulting in significant cost savings. Another major advantage of the RK-X process developed by IOI Investment Zrt. is its potential for large-scale industrial reuse of carbon dioxide. Instead of releasing CO_2 produced during industrial processes into the atmosphere, it is converted into formic acid through a photochemical method in an aqueous environment. This process can help mitigate global warming by transforming harmful CO_2 emissions into valuable chemical compounds, which can subsequently be utilized in the energy and transportation sectors.

Formic acid can also power electric vehicles, including cars, buses, airplanes, and ships. The electricity generated from hydrogen provides a clean, carbon-neutral energy source that could significantly contribute to the widespread adoption of electric transportation and reduce dependency on fossil fuels over the long term. As the hydrogen-based energy industry advances, transportation and logistics could become more cost-effective, benefiting various sectors of the economy. The use of electric-powered buses, tractors, trucks, and ships not only offers an environmentally friendly solution but also provides economic benefits, particularly through local manufacturing and development. Furthermore, the RK-X process enables the reversible capture of CO_2 using Li_2CO_3 beds, allowing for the storage of carbon dioxide in exchangeable cartridges. For example, 100 kg of this material can capture up to 60 kg of CO_2, indicating that CO_2 emissions can be significantly reduced during the process. This system creates a completely green energy solution, contributing to the establishment of a carbon-neutral economy.

2. Materials and Methods

All chemicals used were of analytical grade and purchased from Sigma Aldrich, Darmstadt, Germany, and were used without further purification. Solutions were all prepared using doubly distilled water. A lithium iron phosphate battery ($LiFePO_4$), specifically the IFR 14500 model, was investigated for the purpose of lithium recycling. The IFR 14500 battery's (IFR 14500 type, XTAR INR 18650 H 2600 mAh 30 A, mass of the battery: 16.6228 g.) basic structure is shown in Figure 1:

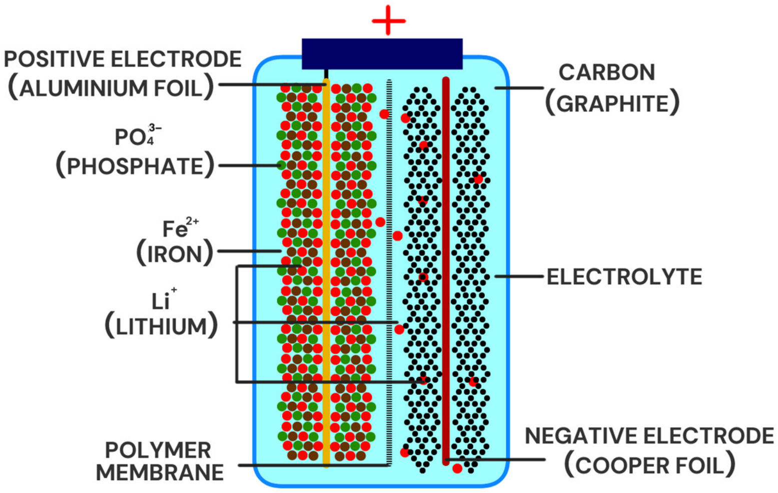

Figure 1. Composition of a $LiFePO_4$ battery.

Main components of the IFR 14500 $LiFePO_4$ battery

[1] Lithium (Li): Lithium is the active material in the battery. The $LiFePO_4$ (lithium iron phosphate) cathode material contains lithium.
[2] Iron (Fe): Found in the active material of the $LiFePO_4$ cathode and battery coat.

[3] Copper (Cu): Used as the anode current collector foil. Copper foil is commonly used with the graphite anode. It is essential for conducting current in the graphite anode of lithium-ion batteries.

[4] Aluminum (Al): Used as the cathode current collector foil. Aluminum is present in the $LiFePO_4$ cathode foil, ensuring efficient current transfer in lithium-ion batteries.

[5] Electrolyte components, such as lithium hexafluorophosphate ($LiPF_6$), supply lithium ions (Li^+) necessary for the battery's operation. $LiPF_6$ contains lithium, phosphorus, and fluorine. Ethylene carbonate (EC) is a common solvent used in the electrolytes of lithium-ion batteries. Its high dielectric constant and low viscosity make it a preferred choice for forming stable electrolytes. Ethylene carbonate is a crucial component in lithium-ion battery electrolytes.

The classical Fresenius method was employed to separate the various metals from the IFR 14500 battery. The Fresenius method of cation separation involves systematically dividing cations into five distinct classes based on their chemical properties and reactions with specific reagents. Class I utilizes hydrochloric acid (HCl) to precipitate cations such as lead (Pb^{2+}), silver (Ag^+), and mercury (Hg^{2+}), forming insoluble chlorides that can be filtered out. In Class II, hydrogen sulfide (H_2S) is employed to precipitate cations like copper (Cu^{2+}), cadmium (Cd^{2+}), and bismuth (Bi^{3+}) as metal sulfides. Class III introduces ammonium sulfide ($(NH_4)_2S$) to separate nickel (Ni^{2+}), cobalt (Co^{2+}), and manganese (Mn^{2+}) through the formation of insoluble sulfides. Class IV uses ammonium carbonate ($(NH_4)_2CO_3$) to precipitate alkaline earth metals such as calcium (Ca^{2+}), strontium (Sr^{2+}), and barium (Ba^{2+}) as carbonates. Finally, Class V typically analyzes magnesium (Mg^{2+}) and sodium (Na^+) and lithium (Li^+) directly in solution, identifying these cations after the previous classes have been separated. This systematic approach enables effective isolation and identification of the lithium cation, making the Fresenius method a valuable tool..

To test for lithium, the Thorin test was conducted as follows: 1 mL of the sample was mixed with a saturated suspension of calcium carbonate ($CaCO_3$) for 5 min and then filtered. Subsequently, 3 drops of a 20% potassium hydroxide (KOH) solution, 3 drops of acetone, and 0.1% Thorin solution were added. The presence of lithium ions resulted in the solution turning yellow. Aluminum was detected using the Morin test. Specifically, 3 drops of Morin reagent were added to 1 mL of the sample, and the presence of aluminum ions was confirmed by the solution's fluorescence under UV light.

3. Results

The research presented explores the recycling of lithium from $LiFePO_4$ batteries and its conversion into lithium carbonate (Li_2CO_3) using the Fresenius method. While the Fresenius method is a known process for lithium carbonate preparation, its application in this specific context, the recycling of lithium from $LiFePO_4$ batteries and subsequent use as a CO_2 absorber, provides a novel approach that addresses several modern environmental and industrial challenges. The growing demand for electric vehicles (EVs) and renewable energy storage, combined with the increasing volume of spent batteries, creates an urgent need for efficient recycling methods that recover valuable materials like lithium.

The pure lithium carbonate (Li_2CO_3) salt was prepared using the method of Fresenius. When handling the electrolyte of the IFR 14500 $LiFePO_4$ battery, it is essential to consider the presence of $LiPF_6$ (lithium hexafluorophosphate), a crucial component of the IFR 14500 $LiFePO_4$ battery. $LiPF_6$ decomposes upon reacting with water or sodium hydroxide (NaOH) solution. In a basic medium such as a NaOH solution, $LiPF_6$ undergoes hydrolysis in several steps, resulting in the generation of lithium (Li^+) ions. Initially, the plastic casing of the battery was removed, weighing 0.3561 g. Subsequently, the coating was stripped off, with a mass of 4.0550 g, and the copper strip was extracted, weighing 1.0525 g. The graphite layer was separated from the white plastic strip, with a mass of 0.6137 g and then washed with distilled water before drying, resulting in a mass of 2.3254 g. The electrolyte was then partially dissolved in 300 mL of a 20% NaOH solution. Testing of the solution yielded positive results for lithium using the Thorin test and for aluminum using the Morin test, indicating the presence of both metals.

Ammonium carbonate ($(NH_4)_2CO_3$) was added to the solution to precipitate calcium, strontium, and barium ions, although these cations were determined to be irrelevant to our investigation. The filtrate tested positive for lithium (Thorin test) and was subsequently treated with aqueous sodium carbonate ($(NH_4)_2CO_3$) to form a Li_2CO_3 solution. The $LiFePO_4$ electrode was dissolved in a 15% nitric acid (HNO_3) solution, resulting in a dark yellow solution. This filtrate was then neutralized with a 20% NaOH solution to separate lithium ions from iron, leading to the formation of $Fe(OH)_3$ precipitates. The $Fe(OH)_3$ precipitates dissolved only upon boiling in concentrated hydrochloric acid, suggesting they were likely iron hydroxide. The mass of the $Fe(OH)_3$ precipitates was recorded as 1.6643 g. The pH of the filtrate was adjusted to pH 3 using 15% nitric acid (HNO_3) before further investigation. Although ammonium carbonate ($(NH_4)_2CO_3$) was again added to the solution, these cations were found to be irrelevant. The filtrate confirmed the presence of lithium (Thorin test) and was treated with aqueous sodium carbonate (Na_2CO_3) to produce a Li_2CO_3 solution. The two light-colored Li_2CO_3 solutions from the aforementioned processes were combined, and the water was evaporated. Crude Li_2CO_3 was redissolved three times in saturated carbonated water. The purified Li_2CO_3 was then dried at 100–120 °C until completely dry, yielding a final mass of 1.0449 g. The XRD spectra of the purified Li_2CO_3 are displayed in Figure 2.

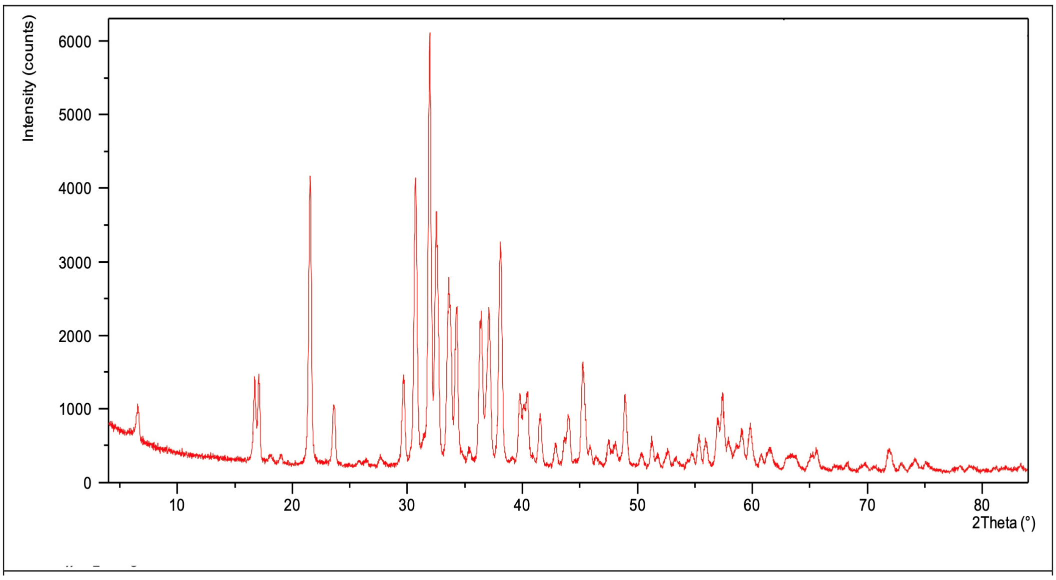

Figure 2. The XRD spectra of the purified Li_2CO_3.

Key Novel Aspects:

1. Integration of Recycling and CO_2 Capture: One of the unique contributions of this study lies in the integration of lithium recovery from $LiFePO_4$ batteries with its use in CO_2 capture. While the use of Li_2CO_3 as a CO_2 absorber is known, this research demonstrates how lithium, efficiently recovered from battery waste, can be repurposed for environmental benefits. This dual-purpose use of recycled Li_2CO_3 contributes to sustainability by addressing both the environmental impact of battery disposal and the challenge of greenhouse gas emissions. Combining these two applications highlights a novel approach to resource recovery that aligns with the principles of a circular economy, where materials are continuously reused, minimizing waste and environmental impact.
2. Optimization of the Fresenius Method for Battery Recycling: The research applies the Fresenius method specifically to the complex material composition of $LiFePO_4$ batteries, a process that requires careful separation of lithium from various other

metals like aluminum and iron. The study demonstrates how this well-established method can be adapted and optimized to target lithium recovery from batteries, which is an increasingly important area of focus given the shift toward electric vehicles. The detailed steps in handling components like the $LiPF_6$ electrolyte and the use of multiple separation processes (hydrometallurgical and chemical) for lithium extraction showcase how traditional methods can be refined for specific applications, which is an important technical advancement.

3. Efficient Separation of Metals: A novel aspect of the study is the efficient separation and purification of lithium from other metals commonly found in $LiFePO_4$ batteries, such as aluminum, iron, and trace amounts of other transition metals. The use of the Fresenius method, combined with selective chemical precipitation, allows for high-purity lithium carbonate to be obtained, as evidenced by the X-ray diffraction (XRD) analysis of the final product. While the recovery of lithium from batteries is not entirely new, this study demonstrates a methodical and efficient process for isolating lithium while avoiding the loss of material to slag or impurities, an issue that affects other recycling processes such as pyrometallurgy.
4. Recovery Efficiency and Environmental Impact: The study reports a final yield of 1.0449 g of purified Li_2CO_3, demonstrating the effectiveness of the process in recovering lithium from battery waste. This high recovery rate is an essential contribution, particularly when compared to the lower efficiencies seen in some conventional pyrometallurgical recycling methods, which often result in significant lithium loss. The process described not only achieves high lithium recovery efficiency but also mitigates hazardous waste production, as the careful handling of electrolyte components like $LiPF_6$ and the use of controlled chemical reactions minimize the risk of environmental contamination. The ability to recover lithium efficiently without creating secondary environmental issues adds further value to the process.
5. Practical Application and Scalability: The study contributes to the practical understanding of how recycled Li_2CO_3 can be applied in industrial processes, specifically in hydrogen purification. As hydrogen is increasingly viewed as a critical energy carrier in the transition to a low-carbon economy, the need for high-purity hydrogen is becoming more important. The use of recycled lithium carbonate in CO_2 capture during hydrogen purification offers a cost-effective and environmentally friendly alternative to sourcing fresh materials. The scalability of this process is particularly noteworthy, as the anticipated increase in spent $LiFePO_4$ batteries from the electric vehicle market could provide a continuous supply of recyclable lithium. This steady supply ensures that the process could be scaled up to meet industrial demand while reducing the need for new lithium extraction, which is often environmentally damaging.
6. Environmental and Economic Benefits: The dual-purpose application of lithium carbonate as both a battery material and a CO_2 absorber highlights the economic benefits of this recycling process. By recovering lithium for reuse in new batteries and repurposing it for hydrogen purification, the process creates multiple revenue streams. This reduces the overall cost of raw material procurement for battery production and enhances the cost-effectiveness of CO_2 capture. Furthermore, the ability to reduce hazardous waste through efficient recycling methods reduces the environmental burden associated with traditional lithium mining and battery disposal. The process described not only conserves natural resources but also supports global efforts to reduce carbon emissions.

While the techniques used in this study, such as the Fresenius method for lithium carbonate preparation, may be established, their application to $LiFePO_4$ battery recycling and the integration with CO_2 absorption processes present a novel and practical solution to modern challenges. By achieving a high recovery rate of lithium and demonstrating the effective reuse of Li_2CO_3 in hydrogen purification, the study offers a promising path forward for sustainable battery recycling. The process supports the broader goals of reducing the environmental impact of both battery disposal and CO_2 emissions, aligning with the principles of a circular economy. Additionally, the scalability and economic viability of this approach position it as a crucial component in the transition to a low-carbon, sustainable energy future. Ongoing research and optimization could further improve the efficiency and applicability of this method, ensuring its relevance as the demand for electric vehicles and renewable energy storage continues to grow.

The study also improves upon conventional recycling methods through enhanced separation techniques. Traditionally, pyrometallurgical processes are less efficient, with lithium recovery rates around 50–60%. By contrast, this study achieves a significantly higher recovery rate of 84.83% using hydrometallurgical methods combined with precise chemical precipitation. This improvement not only reduces material loss but also enhances the economic viability of lithium recovery, particularly for $LiFePO_4$ batteries, which are increasingly used in electric vehicles and energy storage systems. A further innovation is the introduction of an additional purification step for lithium carbonate. After initial recovery, crude lithium carbonate is redissolved multiple times in saturated carbonated water, ensuring higher purity. This step improves the quality of the Li_2CO_3, making it more suitable for use in industrial applications such as CO_2 capture and hydrogen purification. The XRD spectra of the purified Li_2CO_3 is shown in Figure 2.

The main components of the of the purified Li_2CO_3 sample is crystalline lithium carbonate (Li_2CO_3, PDF-00-022-1141), while the other crystalline component is a negligible amount of sodium carbonate monohydrate ($Na_2CO_3{\cdot}H_2O$, PDF-00-022-1141) as seen in Figure 3.

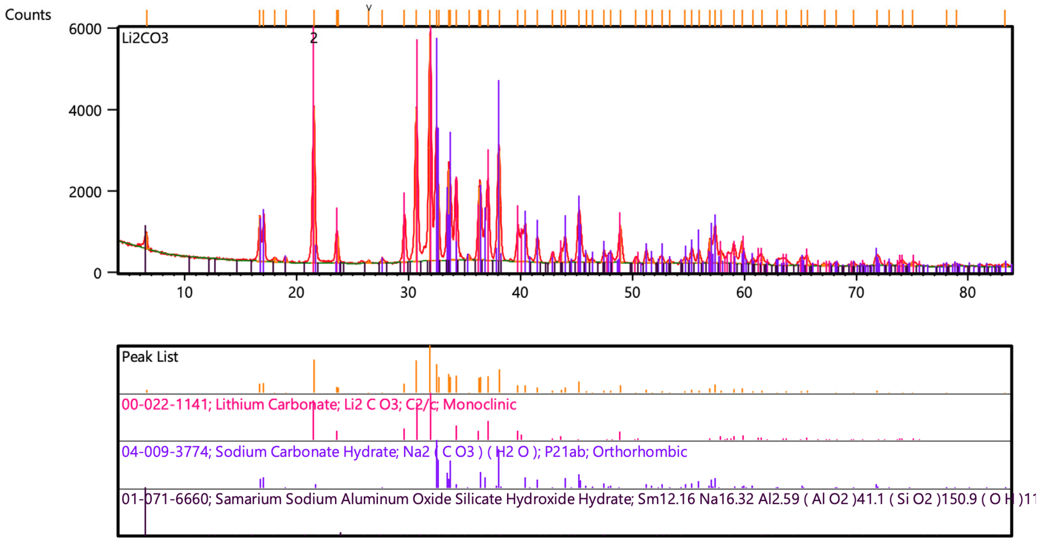

Figure 3. The peek list and the identified components of the purified Li_2CO_3.

The battery coat was dissolved in 15% nitric acid, producing a dark yellow solution. The filtrate was then neutralized with a 20% NaOH solution, which led to the formation of $Fe(OH)_3$ precipitates. The total mass of these $Fe(OH)_3$ precipitates was 2.9844 g. Notably, the $Fe(OH)_3$ precipitates dissolved only when boiled in concentrated hydrochloric acid, indicating that they were likely iron hydroxide.

4. Discussion

Formic acid (HCOOH) serves as a promising hydrogen source for electricity generation, particularly when combined with hydrogen fuel cells. As a simple organic compound, it decomposes into hydrogen (H_2) and carbon dioxide (CO_2), providing a compact and transportable medium for hydrogen storage. The subsequent separation and absorption of CO_2 using lithium carbonate (Li_2CO_3) enhance the efficiency and environmental sustainability of the process. The extracted hydrogen can be directly utilized in hydrogen fuel cells to generate electricity, playing a vital role in advancing clean energy solutions.

One primary challenge in adopting hydrogen as an energy carrier is the difficulty of storing and transporting it in its molecular form. Formic acid offers a unique solution to this issue. Through catalytic decomposition, formic acid can be broken down into a mixture of hydrogen and carbon dioxide. This reaction occurs at relatively low temperatures (around 40–50 °C) and can yield pure hydrogen when paired with effective CO_2 separation. Formic acid's high hydrogen density (53 g/L) makes it an attractive liquid carrier for hydrogen, simplifying the storage and transportation processes compared to compressed hydrogen gas. A critical step in the process is the efficient separation and capture of CO_2 to purify the hydrogen stream. Lithium carbonate (Li_2CO_3) acts as an effective material for CO_2 absorption. When exposed to the H_2/CO_2 mixture, Li_2CO_3 reacts with CO_2 to form lithium bicarbonate ($LiHCO_3$). This reaction allows for CO_2 capture, resulting in a purified stream of hydrogen that can be fed into a fuel cell. The captured CO_2 can be regenerated by reversing the reaction, enabling the cyclic use of lithium carbonate. This efficient CO_2 absorption ensures that the hydrogen produced is of high purity, which is essential for optimal fuel cell performance.

Calculation of Li_2CO_3 Formation

To determine the mass of the resulting Li_2CO_3, we first calculate the available lithium mass from the $LiFePO_4$ cathode and $LiPF_6$ electrolyte, then estimate the theoretical mass of Li_2CO_3. The measured mass of $Fe(OH)_3$ from the $LiFePO_4$ cathode is 1.6643 g, corresponding to 2.4574 g of $LiFePO_4$, which agrees with the literature. Since 1 mole of $LiFePO_4$ contains 1 mole of lithium, the number of moles of lithium in the cathode is 0.01557 mol. Given that the molar mass of $LiPF_6$ is 151.9 g/mol and the electrolyte weighs 2.7 g [26,27], the moles of lithium from the electrolyte total 0.01777 mol. The combined moles of lithium from both sources are 0.03334 mol. With the molar mass of Li_2CO_3 at 73.89 g/mol, 1.2317 g of Li_2CO_3 should theoretically form. From our recycling process, 1.0449 g of Li_2CO_3 was recovered, yielding a lithium recovery efficiency of 84.83%. Li_2CO_3 is increasingly important in CO_2 absorption from an environmental perspective. The next section outlines Li_2CO_3's role in CO_2 absorption, reactions involved in formic acid (HCOOH) decomposition, and the required quantities. As a CO_2 absorbent, Li_2CO_3 is effective in capturing carbon dioxide, reducing pollution, and mitigating climate change. The principle behind this absorption is that Li_2CO_3 reacts with CO_2, converting lithium carbonate to lithium bicarbonate.

CO_2 absorption measures (hydrogen purifying) with recycled Li_2CO_3

The H_2 and CO_2 gas mixture generator was provided by IOI Investment Zrt., as illustrated schematically in Figure 4. This system is used to generate CO_2 and H_2 from formic acid (HCOOH) under controlled conditions, such as in fuel cells or chemical processes that require hydrogen production. The choice of formic acid decomposition for generating the H_2 and CO_2 gas mixture is based on its simplicity and efficiency in delivering a controlled flow of CO_2 and H_2, making it ideal for testing CO_2 absorption and hydrogen purification processes. Formic acid (HCOOH) is a convenient CO_2 source, as it decomposes cleanly at relatively low temperatures, producing CO_2 and H_2 without any unwanted byproducts.

The decomposition of formic acid (HCOOH) can occur through different pathways, depending on conditions such as temperature and the presence of catalysts as shown in Figure 5, making it an efficient source of pure CO_2 and H_2 for experimental purposes.

In summary, a 500 cm^3 round-bottom glass flask, equipped with a stirrer and positioned in an oil bath, was fitted with a funnel containing formic acid and connected to a gas separation apparatus (CO_2 absorber) via a gas outlet (Figure 6). Upon heating the flask to 40 °C, a mixture of H_2 and CO_2 gasses was produced. The decomposition rate of formic acid at 40 °C was 1.00 g/h, yielding 0.02173 mol/h or 0.9565 g/h of CO_2. Continuous dosing of formic acid ensured a consistent CO_2 production rate. This process showcases the ability of Li_2CO_3 to absorb CO_2, which is a vital step in hydrogen purification and carbon capture. Utilizing formic acid as a CO_2 source supports the establishment of a closed-loop system where Li_2CO_3 captures CO_2 and can be regenerated, enhancing process sustainability. This method not only aids in the experimental recovery of Li_2CO_3 but also provides an environmentally friendly and efficient means of generating pure hydrogen for practical applications. The CO_2 absorber (gas separator) apparatus, shown in Figure 6, was provided by IOI Investment Zrt. The 500 cm^3 glass CO_2 absorber contains a saturated Li_2CO_3 solution to capture CO_2. During a 5 h absorption test, a CO_2 stream of 0.02173 mol/h or 0.9565 g/h was used. Initially, the saturated Li_2CO_3 solution absorbs CO_2, forming $LiHCO_3$, with the bicarbonate concentration starting at zero. Li_2CO_3 has a solubility of 15.7 g/L, while $LiHCO_3$'s solubility is 57.4 g/L.

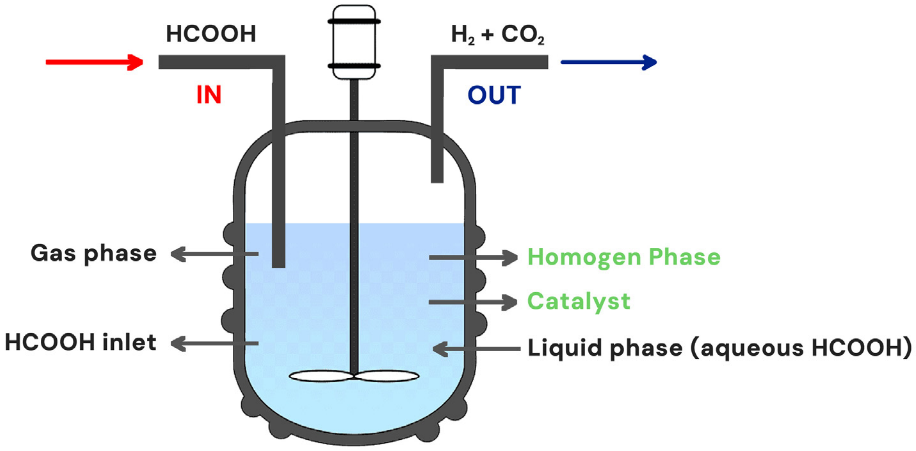

Figure 4. Model of the CO_2 generator.

$$HCOOH \rightarrow CO_2 + H_2$$

Figure 5. Decomposition of Formic Acid.

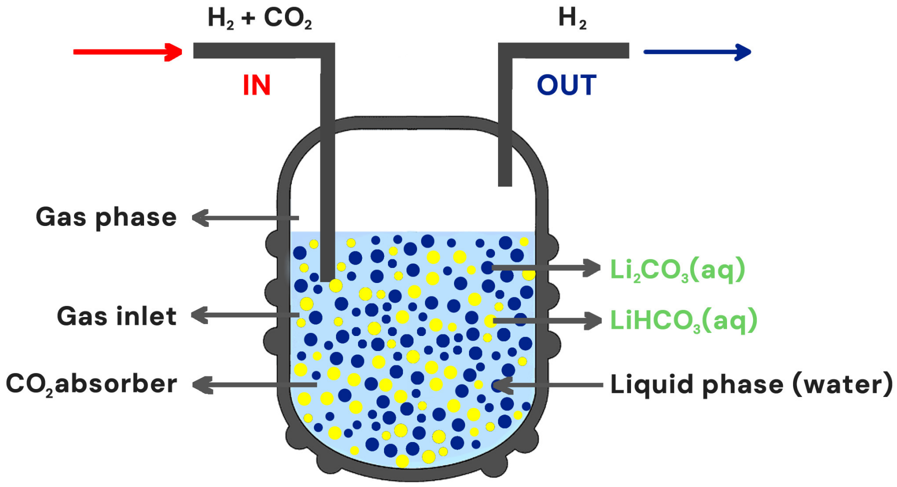

Figure 6. Model of the CO_2 absorber (gas separator).

The reaction between lithium carbonate (Li_2CO_3), carbon dioxide (CO_2), and water to form lithium bicarbonate ($LiHCO_3$) is a reversible process as seen in Figure 7. The reaction can proceed in both directions depending on conditions such as temperature, pressure, and concentrations of the reactants and products.

$$Li_2CO_3 + CO_2 + H_2O \rightleftharpoons 2LiHCO_3$$

Figure 7. Reaction equlibra between Li_2CO_3 and $LiHCO_3$.

The forward reaction occurs when lithium carbonate (Li_2CO_3) reacts with carbon dioxide and water to form lithium bicarbonate ($LiHCO_3$), while the reverse reaction involves heating lithium bicarbonate ($LiHCO_3$) to decompose it back into lithium carbonate

(Li_2CO_3), carbon dioxide, and water. During the CO_2 absorption process, the concentrations of carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-) were measured in mol/L using Warder's method at 30 min intervals. Briefly, Warder's method involves adding solid NaCl to the measured sample portion, ensuring that by the end of the titration, the solution is half-saturated with respect to NaCl (approximately 18 g NaCl per 100 mL). With one drop of phenolphthalein added, a 10 mL sample was titrated with 0.1 N HCl until a faint pink color appeared, and the volume of 0.1 N HCl used was recorded as A mL. Subsequently, methyl orange was added to the solution, and titration continued until the transition color was reached. Before determining the endpoint, CO_2 was removed from the solution by boiling, and the cooled solution was then titrated to completion, with the additional volume of 0.1 N HCl recorded as B mL. For example, the volumes of 0.1 N HCl required for titrating the carbonate and bicarbonate in a 10 mL sample "A" and "B" are shown in Table 1 for the 60 min and 120 min marks. From measurement "A", the alkali carbonate content (equivalent weight = molecular weight) was calculated, while the bicarbonate content was determined from ("B"–"A"). The addition of NaCl suppresses the hydrolysis of bicarbonate, facilitating precise titration without the need for a comparison solution.

Table 1. The required volumes of 0.1 N HCl for titrating carbonate and bicarbonate at 60- and 120 min using Warder's Method with a 10 mL sample.

Time (Minutes)	Volume of 0.1 N HCl for Carbonate (mL)	Volume of 0.1 N HCl for Bicarbonate (mL)
60	16.93	8.69
120	12.58	17.39

The amount of CO_2 absorbed over time was calculated based on bicarbonate concentration. For every mole of CO_2 absorbed, 1 mole of Li_2CO_3 is consumed, resulting in the formation of 2 moles of $LiHCO_3$. As CO_2 is absorbed, the concentration of Li_2CO_3 decreases, while the concentration of $LiHCO_3$ increases over time. Specifically, the change (decrease) in Li_2CO_3 is -0.01087 mol every 30 min, and the change (increase) in $LiHCO_3$ is 2×0.01087 mol = +0.02174 mol every 30 min. Table 2 displays the changes in carbonate and bicarbonate concentrations (in mol/L) at 30 min intervals over a total duration of 300 min. Figure 8 illustrates the time dependency of the carbonate (red) and bicarbonate (green) concentrations throughout the 300 min period.

Table 2. The concentration of Li_2CO_3 and $LiHCO_3$ over time as CO_2 is absorbed.

Time (Minutes)	CO_2 Absorbed (g)	Li_2CO_3 (mol/L)	Li_2CO_3 (g/L)	$LiHCO_3$ (mol/L)	$LiHCO_3$ (g/L)
0	0	0.2128	15.7	0	0
30	0.47825	0.19106	14.11	0.04348	3.20
60	0.9565	0.16922	12.52	0.08696	6.39
90	1.43475	0.14739	10.92	0.13044	9.59
120	1.913	0.12556	9.28	0.17392	12.79
150	2.39125	0.10373	7.67	0.2174	15.99
180	2.8695	0.08189	6.04	0.26088	19.19
210	3.34775	0.06006	4.43	0.30436	22.38
240	3.826	0.03823	2.82	0.34784	25.58
270	4.30425	0.0164	1.21	0.39132	28.78
300	4.7825	0	0	0.4348	31.98

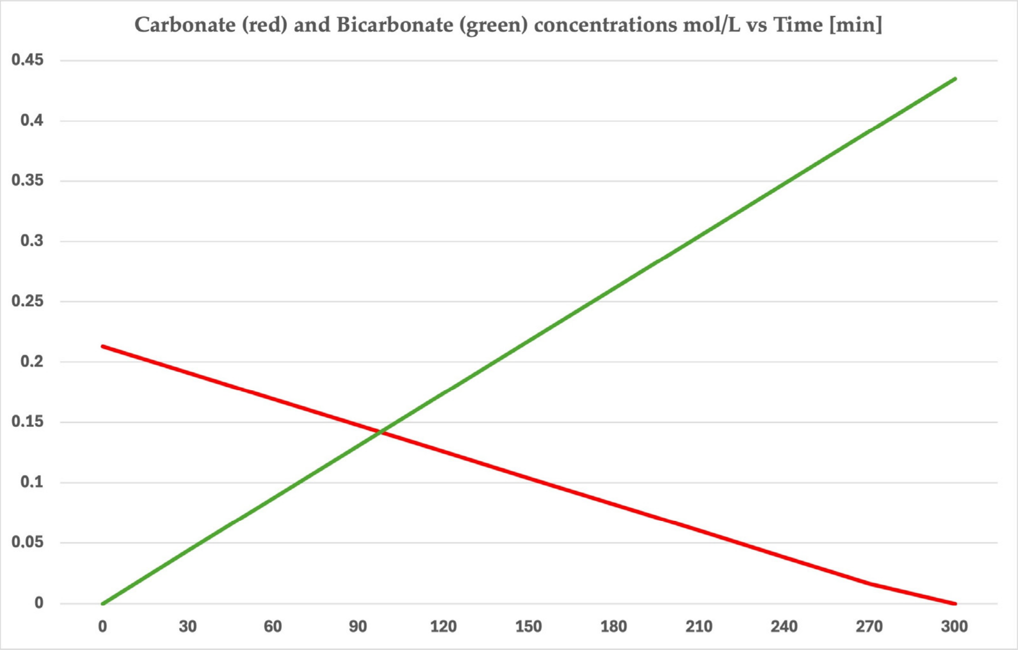

Figure 8. Carbonate (red) and bicarbonate (green) concentrations in time.

One of the primary outcomes of this experiment is the accurate identification and direct utilization of the hydrogen produced during the CO_2 absorption process. The generated hydrogen was utilized in the hydrogenation of methyl trans-cinnamate (MC) to yield methyl-3-phenyl propionate (MP), which not only confirms the existence of molecular hydrogen but also underscores its practical application. This dual functionality showcases both effective CO_2 capture and the immediate use of the hydrogen byproduct in valuable chemical reactions, thereby enhancing the overall value of the process. Molecular hydrogen was detected at the outlet of the gas absorber (Figure 6), and its identification was verified through the hydrogenation reaction of methyl trans-cinnamate (MC) to methyl-3-phenyl propionate (MP), as demonstrated in Figure 9.

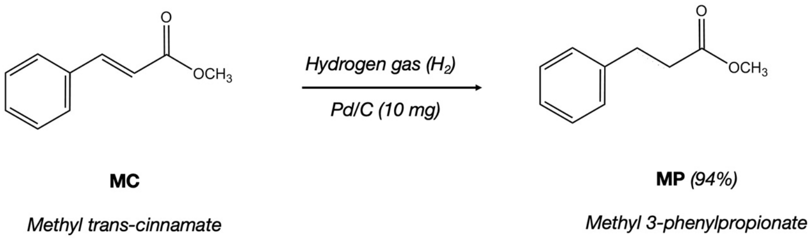

Figure 9. Identification of molecular hydrogen.

This reaction functions as a highly precise method for identifying molecular hydrogen. Hydrogen from the CO_2 absorber was directly transferred to the hydrogenation setup. In a microscale glass apparatus, a 10 mL round-bottom flask equipped with a stirrer bar, 10 mg of 5% Pd/C catalyst and 162 mg (1 mmol) of methyl trans-cinnamate (MC) were carefully introduced. The hydrogenation occurred over 60 min and was monitored by TLC using a solvent system of 20% ethyl acetate and 80% hexane, confirming the successful conversion. While this method reliably identifies hydrogen, the process carries significant implications beyond this. As the system indicates, if formic acid could be decomposed at room temperature into pure hydrogen, it would mark a major advancement. Achieving this would offer a highly efficient and low-energy method of hydrogen production for diverse applications, greatly enhancing the potential of formic acid as a hydrogen carrier in energy generation and chemical synthesis.

Formic acid presents several advantages as a hydrogen carrier. First, it is a liquid at room temperature, making it easier to store and transport than hydrogen gas, which requires compression or liquefaction. Second, the catalytic decomposition of formic acid into hydrogen and CO_2 is a well-understood and controllable process, offering a practical pathway for on-demand hydrogen production. Furthermore, by coupling formic acid decomposition with CO_2 absorption using lithium carbonate, the environmental impact of the process is minimized [28–31].

The practical application of the by-products, particularly hydrogen, is another significant area where this research contributes to the broader field of sustainable energy. While lithium recovery and CO_2 absorption are the main focus, hydrogen production as a by-product offers additional economic and environmental value. Hydrogen, produced as a by-product during the purification process, is highly valuable for clean energy systems. In this study, the use of Li_2CO_3 as a CO_2 absorber in hydrogen purification results in high-purity hydrogen, which meets the stringent standards required for applications like fuel cells. This hydrogen can be deployed in several energy systems, contributing to decarbonization efforts. Specific methods for hydrogen utilization include:

1. Fuel Cell Technologies: Pure hydrogen can be fed into proton exchange membrane (PEM) fuel cells, which power electric vehicles, stationary power systems, and portable electronics. The high purity achieved through the use of recycled Li_2CO_3 enhances the efficiency of fuel cells, reducing emissions and promoting cleaner transportation options.
2. Hydrogen as an Energy Carrier: Hydrogen is often touted as a key energy carrier in the transition to a low-carbon economy. The hydrogen produced and purified in this process can be stored and transported, providing an additional revenue stream and creating an integrated circular economy for energy production, storage, and utilization.
3. Industrial Applications: High-purity hydrogen is also critical in various industrial processes, including ammonia synthesis, petrochemical refining, and metallurgy. The ability to recover and purify hydrogen efficiently through this process opens up new opportunities for utilizing the by-products of lithium recycling in broader industrial settings. By capturing CO_2 and purifying hydrogen, this system not only reduces carbon emissions but also maximizes resource use in line with circular economy principles. The combined use of recycled lithium carbonate for both battery production and hydrogen purification underscores the practical and scientific value of this research. The ability to produce high-purity hydrogen as a by-product adds another layer of innovation, as it enhances the sustainability and economic feasibility of the overall system.

This research introduces several innovative aspects that enhance the existing methods for lithium recovery from $LiFePO_4$ batteries. By optimizing the Fresenius method and applying it to battery recycling, this study achieves high-purity lithium carbonate while minimizing waste and environmental impact. The unique application of Li_2CO_3 in CO_2 absorption and hydrogen purification offers practical benefits, contributing to cleaner energy production and supporting the transition to a low-carbon economy. Additionally, the detailed discussion of hydrogen as a by-product highlights the broader utility of this process, providing a comprehensive solution that addresses both environmental challenges and economic opportunities [32]. By combining efficient lithium recovery with sustainable hydrogen production, this research sets the stage for future advancements in battery recycling and clean energy technologies.

5. Conclusions

The recycling of lithium from lithium iron phosphate ($LiFePO_4$) batteries into lithium carbonate (Li_2CO_3) for use as a CO_2 absorber in hydrogen purification represents a significant advancement in sustainable energy. This process not only addresses environmental challenges from spent $LiFePO_4$ batteries but also introduces a method for CO_2 capture and hydrogen purification, which are essential for a low-carbon economy. Combining recycling and purification processes results in benefits beyond resource conservation, contributing to carbon reduction and clean energy production. A key achievement is the high recovery efficiency of lithium, with an 84.83% yield as Li_2CO_3. This rate is competitive compared to other recycling methods, like hydrometallurgical techniques, which recover 80–90% of lithium, and pyrometallurgical methods, which recover 50–60%. Direct recycling can exceed 90% but requires highly sorted battery feedstock. The 84.83% efficiency in this study shows strong potential for widespread adoption of lithium recovery from $LiFePO_4$ batteries. $LiFePO_4$ batteries, increasingly used in electric vehicles (EVs) and renewable energy storage, present a growing environmental challenge. Traditional recycling methods have focused on recovering cobalt and nickel, often overlooking lithium. This new process proves lithium can be recovered efficiently and converted into Li_2CO_3, which has various industrial applications, especially as a CO_2 absorber in hydrogen purification. This dual functionality highlights the technical, environmental, and economic benefits of the process, making a strong case for broader implementation. A primary application of recycled Li_2CO_3 is in hydrogen purification. Hydrogen is a clean energy carrier, used in fuel cells and industrial processes. However, hydrogen often contains impurities like CO_2, which must be removed to meet purity standards. In this study, Li_2CO_3 successfully removed CO_2 from hydrogen streams, producing pure hydrogen. This demonstrates the technical viability and effectiveness of the process in improving hydrogen quality, which is crucial for hydrogen-powered systems. The environmental benefits of this integrated recycling and purification process are substantial. Recycling lithium from spent $LiFePO_4$ batteries reduces hazardous waste and minimizes the need for lithium mining, conserving natural resources and lowering the environmental footprint of lithium extraction. Additionally, using Li_2CO_3 as a CO_2 absorber helps reduce carbon emissions, as it reacts with CO_2 to form lithium bicarbonate ($LiHCO_3$), which can be regenerated into Li_2CO_3 for reuse. This cyclical process enhances system sustainability, contributing to global efforts to combat climate change.

Economically, this process offers dual advantages. First, recovering lithium as Li_2CO_3 reduces the need for raw lithium procurement, leading to cost savings given the increasing demand for lithium in EVs and renewable energy. Second, using Li_2CO_3 as a CO_2 absorber in hydrogen purification creates a new revenue stream, as the material serves a valuable industrial purpose beyond battery production. The scalability of this process is a key advantage. As the EV market grows and more $LiFePO_4$ batteries reach the end of life, the supply of recyclable lithium will increase, ensuring a steady source of material. This scalability is vital for meeting the rising demand for lithium without resorting to harmful mining practices. Additionally, the scalability of CO_2 absorption in hydrogen purification suggests broad applicability across industries, further enhancing its economic and environmental benefits.

In conclusion, this innovative recycling process offers a multifaceted solution to environmental and industrial challenges. With high lithium recovery and proven success in hydrogen purification, it provides significant technical, economic, and ecological benefits. As research and industry collaboration continue, this process could become a cornerstone of sustainable energy practices, supporting the shift to a circular, low-carbon economy.

Author Contributions: Conceptualization, Z.K.; methodology, Z.K.; validation, Z.K. and Á.G.; formal analysis, Z.K.; investigation, Z.K.; resources, Z.K.; data curation, Á.G.; writing—original draft preparation, Z.K.; writing—review and editing, Z.K.; visualization, Á.G.; supervision, Z.K.; project administration, Z.K.; funding acquisition, Z.K. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: All data are within the document.

Conflicts of Interest: The authors declare no conflicts of interest. Z.K. is a paid employee of the IOI Investment Zrt. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

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