Auszug aus

Development of an Adiabatic Hydrogen Storage System Based on Lithium Reactive Hydride Composite

Von der Fakultät für Maschinenbau und Bauingenieurwesen
der Helmut-Schmidt-Universität / Universität der Bundeswehr Hamburg
zur Erlangung des akademischen Grades eines Doktor-Ingenieurs
genehmigte

DISSERTATION
vorgelegt von

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Hamburg, 2024

Abstract

In order to mitigate the emission of greenhouse gases in the atmosphere, alternatives to the current energy carriers need to be developed, with a special focus on harnessing the potential of sustainable energy production. In this context, hydrogen storage has the potential not only to provide short- and long-term energy storage solutions but also to enable the decarbonisation of sectors which are either not heavily reliant on electrical energy as its main energy source or depend on gaseous H_2 or reducing agents as reactants in their operation. Among the alternatives to store hydrogen, the storage in metal and complex hydrides allows hydrogen storage with comparatively high gravimetric and volumetric storage capacities on the material level and have a wide range of temperatures and pressures under which these materials can ab- and desorb hydrogen, depending on the material. The lithium reactive hydride composite (Li-RHC) presents advantages over other hydride materials due to its high theoretical hydrogen storage capacity of 11.5 wt.%. This material is a mixture of $LiBH_4$ and MgH_2 in the specific molar proportions of 2:1 which can reversibly react with hydrogen at temperatures of at least 350 °C under moderate pressure levels. During H_2-absorption heat is released. The opposite occurs during H_2-desorption. In most of the developed hydrogen storage systems, the released heat is dissipated as waste heat with or without the help of heat exchangers or other heat management systems. During desorption, it is usual that surplus energy has to be provided to the system. In both cases, the energy associated is eventually lost to the environment. The use of thermochemical energy storage systems (TCES) aims to allow the storage of this heat energy in the form of chemical bonds for later use. This work aims to design a system based on Li-RHC as a hydrogen storage material and $CaO/Ca(OH)_2$ as a TCES. To do that, it is first necessary to have not only descriptions of the hydride's reactions with hydrogen as a function of pressure and temperature, as well as reliable thermodynamic data. In this work, Li-RHC powders have been produced with suitable catalysts in order to acquire data for the kinetic modelling of both absorption and desorption reactions which have been investigated to help understand the material's behaviour as well as to provide the necessary equations and parameters to design the tank system using finite-element-method (FEM) simulations. This work provides thorough information on the intrinsic kinetics of the Li-RHC system, with particularly significant developments for the description of the desorption reaction. The hydrogen absorption reaction was shown to follow a Johnson-Mehl-Avrami-Erofeyev-Kholmogorov (JMAEK) with $n = 1$ reaction mechanism, with an apparent activation energy of 146 ± 3 kJ/mol H_2 after accounting for the pressure dependency. The dehydrogenation of the Li-RHC occurs in two steps, with the MgH_2 desorption reaching its completion in a couple of minutes while the $LiBH_4$ desorption takes considerably longer. The reaction mechanisms were identified to be JMAEK with $n = 1$ and Prout-Tompkins. After correcting for the pressure dependency, the apparent activation energies were calculated to be 63 ± 3 kJ/mol H_2 and 94 ± 13 kJ/mol H_2, respectively.

Using pellets instead of powder material reduces the macroscopic phase separation in Li-RHC and increases storage density. Because of this, further investigations focused on the production, determination of its kinetic properties and modelling of their behaviour under absorption and desorption conditions using FEM simulation. An empirical model to represent the change in the permeability of the H_2 gas in the pellet has been proposed, with an excellent agreement between simulated and experimental results.

The validated experimental results were used as the basis for the numerical investigation of a prototype adiabatic tank as a proof-of-concept using $CaO/Ca(OH)_2$ coupled with Li-RHC. The design optimisation was aided by 2-D and 3-D FEM simulations which took into account geometric features and was able to identify performance-limiting aspects for the hydrogen loading and unloading cases. With the chosen design, the optimised tank geometry comprises of a reactor part with 192 mm diameter, with 36 cavities drilled into a cylindric, metallic body. Half of these cavities are filled with Li-RHC and drilled from the top; the other half are drilled from the bottom and contain $CaO/Ca(OH)_2$. These cavities have different diameters (10.3 mm and 15.1 mm respectively) and the reactor is 150 mm high. In the designed prototype, up to 20 g of hydrogen can be stored.

The investigation of Li-RHC in powder and pellet forms as well as the development of the adiabatic tank prototype are valuable contributions to the development of energy-efficient hydrogen storage systems and the insights provided here are able to provide new directions for further optimisation of this system and other hydrogen storage materials.

Zusammenfassung

Um Treibhausgasenemissionen zu vermeiden, sollten Alternativen zu den heutigen Energieträgern entwickelt werden, mit dem Schwerpunkt auf der Nutzung nachhaltiger Energieerzeugung. In diesem Zusammenhang bietet die Wasserstoffspeicherung nicht nur die Möglichkeit der kurz- und langfristigen Energiespeicherung sondern ermöglicht auch die Dekarbonisierung von Sektoren, für die Strom nicht die Hauptenergiequelle ist oder die auf Wasserstoffgas als Reduktionsmittel oder als Reaktionspartner angewiesen sind. Unter den Alternativen für die Wasserstoffspeicherung ermöglicht die Speicherung in Metallhydriden und komplexen Hydriden dies mit hohen gravimetrischen und volumetrischen Kapizitäten. Die sogenannte *lithium reactive hydride composite* (Li-RHC) Legierung stellt einen Vorteil gegenüber anderen Materialen dar, da sie eine hohe theoretische Kapazität von 11.5 Gew.% aufweist. Bei dieser Legierung handelt es sich um eine Mischung aus $LiBH_4$ und MgH_2 im molaren Verhältnis 2:1, das unter Temperaturen von mindestens 350 °C und moderaten Druckbedingungen reversibel mit Wasserstoff reagiert. Bei der Wasserstoffbeladung wird Wärme abgegeben. Das Gegenteil passiert bei der Wasserstoffentladung. In den meisten der entwickelten Wasserstoffspeichersystemen wird die freigesetzte Wärme als Abwärme, mit oder ohne Benutzung von Wärmetauschern und anderen Wärmemanagementsysteme, abgeführt. Bei der Wasserstoffentladung (Desorption) ist es üblich, dass dem System überschüssige Energie zugeführt werden muss. In beiden Fällen geht häufig die Energie als Abwärme verloren. Der Einsatz von thermochemischen Energiespeichern (*thermochemical energy storage systems*, TCES) hat zum Zweck, diese Wärme in den chemischen Bindungen eines Materials zu speichern.

Ziel dieser Arbeit ist das Design eines Wasserstoffspeichersystems, das mit Li-RHC als Wasserstoffspeichermaterial und $CaO/Ca(OH)_2$ als TCES betrieben wird. Dazu ist zunächst nicht nur eine Beschreibung der kinetischen Eigenschaften unter verschiedenen Temperatur- und Druckbedigungen notwendig, sondern auch zuverlässige Daten für die thermodynamischen Eigenschaften des Systems. Li-RHC wurden in dieser Arbeit mit geeigneten Katalysatoren in Pulverform hergestellt, um die Be- und Entladung von Wasserstoff zu untersuchen. Diese Daten haben geholfen, die notwendigen Gleichungen und Parameter für ein besseres Verständnis des Systems und die Gleichungen für die Entwicklung von Finite-Elemente-Methode (FEM) Simulationen zu gewinnen. Diese Arbeit liefert somit grundlegende Daten für das Reaktionsvermögen des Li-RHC-Systems, mit wichtigen Erkenntnissen für die Beschreibung der Wasserstoff Be- und Entladungsreaktionen.

Die Absorptionsreaktion konnte im Rahmen dieser Arbeit mit einem Johnson-Mehl-Avrami-Erofeyev-Kholmogorov (JMAEK) Reaktionsmodel mit $n = 1$ beschrieben werden. Die Aktivierungsenergie wurde unter Berücksichtigung der Druckabhängigkeit mit 146 ± 3 kJ/mol H_2 ermittelt. Die Desorptionsreaktion erfolgt in zwei Schritten, wobei die Desorption von MgH_2 in wenigen Minuten abläuft, während die Desorption von $LiBH_4$ wesentlicher länger dauert. Die Reaktionsmechanismen konnten mit JMAEK mit $n = 1$ und einem Model nach Prout-Tompkins am besten beschrieben werden. Die Aktivierungsenergien wurden für die Desorption unter Berücksichtigung der Druckabhängigkeit mit 63 ± 3 kJ/mol H_2 bzw. 94 ± 13 kJ/mol H_2 bestimmt.

Die Verwendung von kompaktiertem Material (Pellets) statt Pulvermateriallen sorgte dafür, dass eine ausgedehnte makroskopische Phasentrennung unterbunden werden konnte. Ein weiterer Vorteil war die Erhöhung der volumetrischen Speicherdichte. Darüber hinaus wurden weitere Untersuchungen mit dem Schwerpunkt auf der Herstellung, der Ermittlung kinetischer Eigenschaften und deren Modellierung mittels FEM Simulationen durchgeführt.

Die Änderung der Permeabilität des H_2-Gases durch das Li-RHC-Pellet wurde Anhand einer empirische Modellierung beschrieben, wobei eine sehr gute Übereinstimmung zwischen simulierten und experimentellen Ergebnissen erreicht wurde. Die validierten experimentellen Ergebnisse wurden zur Entwicklung eines Prototypen auf der Basis von Li-RHC und $CaO/Ca(OH)_2$ verwendet.

Durch 2-D und 3-D FEM Simulationen konnte eine Designoptimierung der geometrische Merkmale vorgenommen sowie auch die limitierenden Faktoren für die Be- und Entladung mit Wasserstoff ermittelt werden. Bei dem ausgewählten Design besteht die optimierte Geometrie aus einen Reaktor mit 192 mm Durchmesser, 36 Bohrungen in einem metallischen Zylinder. Die Hälfte dieser Hohlräume ist nach oben geöffnet und mit Li-RHC gefüllt. Der übrigen Hohlräume sind nach unten geöffnet und enthalten das TCES $CaO/Ca(OH)_2$. Diese Bohrungen haben einen Durchmesser von 10.3 bzw. 15.1 mm und der Reaktor ist 150 mm hoch. In diesem Design können ca. 20 g H_2 gespeichert werden.

Die Untersuchung des Li-RHC in Pulver- und Pelletform sowie die Entwicklung des adiabatischen Tankprototyps liefert wertvolle Beiträge zur Entwicklung neuer, effezienter Wasserstoffspeichersysteme. Die hier gewonnenen Erkenntnisse können neue Wege und Perspektiven zur weiteren Optimierung dieses Systems und anderer Wasserstoffspeichermaterialien ermöglichen.

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7. Conclusions

In this work, investigations toward the development of the Li-RHC as a hydrogen storage material were carried out. Moreover, both numerical and experimental investigations of this system in powder and pellet form were performed. An excellent agreement between experimental results and numerical simulations was achieved and the design of a Li-RHC-based prototype hydrogen storage system coupled with CaO/Ca(OH)$_2$ as a thermochemical energy storage material (TCESM) was analysed numerically.

Regarding Li-RHC's thermodynamic behaviour, the enthalpy and entropy of the system were investigated for the absorption reaction with pressure-composition-isotherms (PCI) curves. The results obtained for the range between 350 °C and 400 °C for the enthalpy and entropy of reaction were -34 ± 2 kJ/mol H$_2$ and -70 ± 3 J/(K·mol H$_2$) respectively. While in this work no new PCI data for the desorption reactions were collected, the available kinetic data at different temperature and pressure conditions could be used to probe the regions which meet the conditions for LiBH$_4$ desorption, providing further insight into the equilibrium conditions of the system. The collected data showed that the thermodynamic parameters from Puszkiel *et al.* [68] could represent well the thermodynamic properties of the Li-RHC system under desorption conditions.

A detailed modelling for absorption and desorption reactions was provided concerning the kinetic behaviour of the ball-milled Li-RHC with the addition of 0.05 mol TiCl$_3$. The absorption reaction was modelled with a JMAEK with n = 1, with a pressure dependency function $F(P) = (P - P_{eq}) / P_{eq}$ and an apparent activation energy of 146 ± 2 kJ/mol H$_2$ and a pre-exponential factor of $(1.8 \pm 1.0) \cdot 10^8$ s^{-1} after applying the pressure function $F(P)$.

For the desorption reactions, a combination of two models has been used. The MgH$_2$ desorption has been represented with the JMAEK with n = 1 and the LiBH$_4$ with the Prout-Tompkins (PT) model. For each of the reactions, different pressure functionalities were proposed. For the first reaction, the pressure dependency was described with $F(P) = (P_{eq}/P)$ and the second reaction with $F(P) = ((P_{eq} - P)/P_{eq})^2$. After considering appropriate pressure functionalities $F(P)$ for each reaction, the apparent activation energy yielded values of, 63 ± 3 kJ/mol H$_2$ and 94 ± 3 kJ/mol H$_2$ respectively.

Alongside implementing these pressure functionalities and developing a comprehensive modelling for the Li-RHC desorption reactions, a novel method for modelling the t_0-parameter has been proposed. These developments are valuable contributions for the description of systems with multi-step reactions. Furthermore, they also expand the usability of the PT model by providing a suitable mathematical treatment of the equations and an empirical framework to obtain predictive models for the t_0-parameter as a function of pressure and temperature conditions. Additionally, the desorption model has been validated with the help of finite-element-method (FEM) simulations to showcase its usefulness and to prove its validity in representing the kinetic properties of the Li-RHC under desorption conditions. The resulting curves had an excellent coefficient of determination across reactions with different time scales and both reactions were adequately represented with the proposed model.

In relation to the scaling up of the system, the production of over 350 g of Li-RHC with 0.00625 mol 3TiCl$_3$·AlCl$_3$ was investigated, as well as the preparation of pellets for use in a tank prototype. The kinetic parameters for the new catalyst were recalculated based on the newly performed experiments and the available data from the literature. These recalculated values were used to develop a FEM model to investigate the agreement between the recalculated results with the new catalyst and to help explain the kinetic behaviour observed in pellet samples. With the development of an empirical modelling for the H_2-gas permeability in the Li-RHC it was possible to obtain an excellent agreement between the FEM data and the experimental kinetic curves. These validated results, alongside the empirical permeability model, were then used to design a proof-of-concept hydrogen storage vessel that implements the adiabatic tank concept.

Based on the validated results obtained in Chapters 3, 4 and 5 concerning powder and pellet Li-RHC samples, a numerical analysis of a prototype tank applying the adiabatic tank concept coupling Li-RHC as a hydrogen storage material with $CaO/Ca(OH)_2$ as a thermochemical energy storage material (TCESM) was performed to evaluate the behaviour of the system as a function of its geometrical configurations, as well its performance-limiting factors.

The designed tanks' configuration was developed to investigate the adiabatic tank concept, allowing fast heat exchange between the different cavities which contained the hydride material and the TCESM separately. The H_2 and H_2O pressures in the designed tank can be independently controlled and with the configuration of alternate cavities with different reacting species arranged in alternated arrays for each line, the amount of mass (by varying the cavity's radius) can be easily adjusted in order to reach the condition in which the total enthalpy of reaction for both compartments was the same. That means that neglecting thermal losses, the system should reach the same temperature as the one initially set after reaching near completion of the reaction in both materials.

In the case of the Li-RHC pellet, the permeability of the gas phase through the pellet has shown to be one of the most important factors, particularly for the H_2-loading case. The reaction front for the hydride material proceeds in a ring-shaped manner, mainly because the pellet material should retain its shape during absorption and desorption cycles, allowing for the hydrogen gas to flow between the reactor walls and the pellets freely, providing a good distribution of H_2 gas across the height of the tank.

The reaction in both $CaO/Ca(OH)_2$ hydration and dehydration followed a parabolic profile that evolved from the H_2O in-/outlet to the top of the reactor. This is explained by the expected low permeability of H_2O in the TCESM material and the fact that the powder material will likely occupy the cross-section of the cavity, making it likely, that the water vapour would have to go through the porous medium in order to allow the reaction to proceed.

The distance between the cavities containing each of the reactive materials and the tank's height were investigated using parametric analysis. While the distances between the cavities have shown to have negligible influence on the tank's performance, the tank's height plays an important role, but solely for the times for completion of the $CaO/Ca(OH)_2$ reactions for the reasons stated above. The reaction times for the Li-RHC were barely influenced by the change in this factor.

By investigating the influence of the geometric parameters on the tank's behaviour, it was possible to find a suitable set of design configurations that can take into account scalability, manufacturability, storage capacity and performance. The optimised design that was chosen to allow for fast heat exchange (without allowing mass exchange) between the hydride material and the TCESM is comprised of a metallic, cylindric body with 192 mm diameter, with 36 cavities, 18 of which, are machined from the top part and contain the Li-RHC, while the other 18 are drilled from the bottom and contain the TCESM. The cavities for the materials have 10.3 and 15.1 mm, respectively. The optimum tank height was identified to be around 150 mm and, with this geometry, the prototype is able to store approximately 20 g of hydrogen.

8. Outlook

Related to the more fundamental properties of the Li-RHC, the most pressing matter is likely related to the differences in the values for the enthalpy and entropy of reaction obtained for absorption and desorption reactions, which, even after compensating for stoichiometry and other small experimental uncertainties, still present a considerable mismatch. This mismatch should be addressed properly in future works, potentially with the use of other experimental methods to quantify experimentally the amount of heat involved in each of the absorption and desorption reactions.

Excellent agreement between experimental and simulated results for the small-scale experiments with powder and pellets could be obtained. However, for further improving of the reliability of these models and FEM simulations, future studies should gather more data about several aspects of the Li-RHC system. An important aspect is the lack of information about some material properties at operational conditions, like the effective heat conductivity and the H_2-gas permeability in the powder and the pellet samples. Moreover, there is also no information about how these properties change during absorption and desorption reactions. It is expected that the insight gained by investigating such a complex system will also result in interesting and useful analytic frameworks with which other metal and complex hydride systems could be analysed.

While the investigation of the milling process for the production of powder in the hundreds-of-grams scale has been successful in replicating the kinetic properties obtained for milling processes with a very small degree of filling, with a good compromise between cost, time and energy for its production, the process was nonetheless very labour-intensive. In order to produce Li-RHC powder in the kilogram scale with similar properties, after considering the limitations imposed by the degree of filling, ball-milling devices with higher capacity and higher power should be considered. However, further investigations to verify the specific properties of the powder would then be necessary to achieve desirable hydrogen storage properties. Another challenge for the scaling up of the production of Li-RHC powder is the necessity of processing and handling it in an inert atmosphere. Similar challenges and labour intensiveness are also present in handling and preparing Li-RHC pellets. One of the investigated alternatives is the use of polymers to either coat individual particles, create scaffolds or protect the produced pellets with polymeric layers. Also here, more studies are necessary to understand the impact of using such strategies on the kinetic and thermophysical properties of these samples. Moreover, for scaled-up applications, it is also necessary to consider how scalable and cost-intensive such strategies would be to improve the air resistance and ease the handling of these powder or pellet samples.

The chosen adiabatic tank prototype design allows for rapid heat exchange and independent operation of the reactor compartments and the optimisation of the geometric features performed with FEM simulation have shown that the tank performance has a strong dependency on the tank’s height. One possible alternative is to use sintered filters and changes in the geometry to improve and speed up the distribution of water vapour in the tank reactor. This challenge has to be overcome in this kind of adiabatic tank system for the development of new, more scalable designs that can be employed for future investigations or pilot-plant projects.

With the simulated results for the tank design, which are based on validated models for Li-RHC and $CaO/Ca(OH)_2$ systems, various configurations can be investigated to develop scaled-up systems for efficient hydrogen storage. The hours-long reaction kinetics, the high operating temperatures and the need to reduce environmental energy losses suggest that the use of such systems in large-scale applications might be compatible with the operating conditions present in concentrated solar power (CSP) plants.

The developments in this project led to the design of a prototype tank that takes into account aspects such as manufacturability, yieldability (specially considering handling the system in inert atmosphere), the maximum allowable dimensions of the currently available test bench and the optimisation based on the FEM simulations presented in this work. This prototype tank is currently under commissioning and is expected to provide experimental data which will be invaluable to verify the predictions made by the numerical model along with further insights on the operation and on the critical factors for the performance of this kind of hydrogen storage systems.

9. Acknowledgements

I would like to start by thanking the first person I contacted from the then, so-called, Helmholtz-Zentrum Geesthacht (HZG) (now Helmholtz-Zentrum Hereon) while I was looking for new experiences and new challenges outside my home country. Dr. Klaus Taube was from the first moment very straightforward to address my request of collaborating and I am thankful that he decided to hear my proposal for him and the department at the time. This changed a lot of things in my life for the better and I enjoyed every time I had the chance to learn from your experiences in our interactions.

At that time, in my obliviousness, I was unaware that this department concentrated a lot of the literature citation authors that I respected and whose work I constantly consulted in search of answers. Klassen, Puszkiel, Capurso, Bellosta von Colbe, Dornheim, Pistidda… It was a pleasant surprise, especially in the cases in which I ended up being able to call some of those not only colleagues, but friends. My admiration for their academic integrity was proven day after day justified as I grew to know each of them less and less by their last names and more by their given names. Please, note that the order from this point on bears no explicit or implicit meaning of importance or hierarchy, so feel free to read the text in shuffle mode if you feel the urge to do so.

But since I need to start somewhere, I will start by thanking nominally my former Department Head, Dr. rer. nat. Martin Dornheim. While during the journey things changed and our interactions were rather brief, the rare discussions we had about some of the pressing matters about materials science were very interesting and I wish we will eventually cross paths again to have more discussions about these topics in the future.

I would like to thank Prof. Dr. Thomas Klassen for many things. For being such a role model for me of lightness, passion for the act of teaching and humbleness. Also, for giving it all in every single opportunity we had to discuss about science with me and our colleagues, for being kind to me and enthusiastic about all his ideas and all my ideas. His inspiring attitude about our work made a strong, lasting impression on me.

Next, would like to thank Prof. Dr. Julian Jepsen, which would, a couple of years ago, give me one of the happiest moments in my scientific career. Unknowingly to me, I was about to work with one of the most caring professionals I could ever imagine working with. I am pretty convinced that in these years I learned much from his efficient and pragmatic approach to solving problems and his diplomatic ways of dealing with communication and sometimes, conflict. Never overbearing, but always present when requested, I learned very soon that if I ever ran out of cards to play, he'd deal me a new hand, never letting me down. Deeply empathetic, he never made me feel as if was alone, whether I faced private or professional challenging moments. His diligence with his team member's needs and desires is for me a role model of leadership more professionals in his position should follow.

No less important, I'd like to thank a thousand times Dr. Julián Atílio Puszkiel. Something about the way I work seems to work well with the way he works. And that became clear even before we even knew ourselves personally. It has been always so natural to work with him. The attention to detail, the experience, the relentlessness to close all flanks, protect against all the flaws in the argumentation, the will to exhaust all the shades of doubt that one can think of is admirable. It goes without saying how much I learned from working with him, his work ethic and his unabating dedication to the scientific work while never letting his family down. I cannot count how many times I came to him asking for advice and he gave me encouragement, motivation and most importantly, fertile ideas to work with.

A lot of colleagues provided valuable support in various moments of this adventure. All of them share the same treats: I wished I could have learned more from them, but circumstances were so that we were only tangentially able to intensively exchange. Honourable mentions here are Dr. Giovanni Capurso and Dr. José Maria Bellosta von Colbe. I thank you for everything you have shown me and how you would simply stop everything you were doing to support me in any way needed. I am deeply thankful for that.

I would also like to thank all my other colleagues from WTS, especially those who shared the most time with me, like my first office-mate, M.Sc. Maximilian Passing, who was always welcoming and shared the best cups of coffee during my first years while we talked about nothing or about kinetic modelling. And thanks also for the help with the FEM Simulation tricks! You did helped me a lot when I was struggling a lot with that topic! And you taught me so much German I cannot even thank you properly for that!

Mainly due to the fear that I will forget someone in the list of colleagues of WTS, I will refrain from doing so. If you have been with me during this period, know that you all were important to keep me going and all the help is deeply appreciated!

The colleagues of WTN also deserve their fair share of praise here! Dr. Thi Thu Le (Kate), Dr. Gökhan Gizer and M.Sc. Yuanyuan Shang (Hannah), thanks for all the company, the support, the shared experience in the lab, the camaraderie and the understanding throughout these years. Thanks also for all the valves you opened and closed for me! I hope I can return all the favours someday! Thanks for M.Sc. Archa Santhosh for being a good friend and taking care of

Koda. A special thanks to M.Sc. Ebert Alvares for being also a great friend and for all the coffee pauses, for all the stimulating discussions, for bringing me somehow closer to home and for teaching me so much. Thanks to Dr. Paul Jerabek for being also a great friend, for teaching me a lot and for being empatetic to the bone.

Special thanks here goes to Dr. Claudio Pistidda, who since the beginning was always open to teach, to discuss, to support, to make jokes, to laugh, to scold when necessary and to be someone to look up to when one thinks about experimental prowess and knowledge. Also, someone whom I supported with great pleasure, even without prior request. Usually too much keen in seeing too much potential in me that not even I see and always showing great generosity at every chance he had to do so. It has been an honour to work beside you for these years.

No less important has been the technical support that I received from our engineers throughout the years. Namely, Oliver Metz and Helge Kutzner. I thank you for all the work you guys put into making all these complicated machines run almost 24/7. Without you, the work of inexperienced researchers like me would be incredibly hard, if not impossible!

I would like to thank also our project partners from Deutschen Zentrums frü Luft- und Raumfahrt (DLR) in Stuttgart. Thanks for Dr.-Ing. Marc Linder for receiving me so well during my visit and for Dr. Michael Lutz, that taught me a lot of what he had fought very bravely to learn with big generosity. Special thanks go to Dr. Inga Burger, who was someone who measured no efforts to support me in any way she could, accessing knowledgeable colleagues on my behalf and proving insightful feedback in several instances.

For all the colleagues at Helmut-Schmidt-Universität (HSU), I would also like to thank you for all the time we spent together. It has been always pleasant to be around you all be at the lunch breaks or when we had to marathon-correct quite a few dozen tests from the students by the end of the trimester.

This work would have been even more difficult were not the support of people that literally put their hands in my work to push it forward. Countless times I think of how it would have been more difficult without the help of (now M.Sc.) Carolin Fritsch. I hope I managed to share some of my insights with you, although that will hardly repay how great your support in sharing work in the lab was. I am happy to have you as a colleague again after your short pause to take care of more important matters… Also noteworthy have been the contributions of Thomas Rieger, who has shown outstanding performance and commitment to the work, presenting very competently its bachelor thesis, which has led to a better understanding of some of the paths to follow in this work.

Reaching this point, however, would never have been possible were not my prior achievements. While Prof. Dr. Walter José Botta and Prof. Dr. Daniel Leiva have not been involved in this work, I owe them thanks nonetheless. The bulk of the toolkit I brought here when I first arrived and the credentials that I accumulated until the end of my Masters were mainly due to our interactions before I left Brazil. The great scientific freedom I enjoyed, the great support provided, their guidance, their trust in me and the opportunities that I was given made me prepared to take bigger challenges and I could not have made it so far were not for them.

Thanks also to Prof. Dr. Maria Zanin, that taught me lessons I could never have learned otherwise and for all the life-changing experiences she has provided me with the chance to have.

A sincere thank you to all the people that have taken care of me, Koda and Camila during these last years. I would like to mention nominally my neighbours, Anke Lidke, Ralf Lidke, Christel Meier, my friends Luiza Bisotto, Francisco Bandeira, Ana Rodrigues Cameirão and M.Sc. Carla Amavisca. Special thanks to my friends Anis Rosa Terra, M.Sc. Renata Victoratti and Letícia França who did a marvellous job even from many miles away. They were our support net for many of these years and did their best to care for one another as a family would. Without them, our life would have been even harder. It has been a great privilege to have people looking out for us during these years.

This work would not have been possible without the financial support from Karl-Vossloh-Stiftung (Project Number S047/10043/2017).

Lastly (and in this case, they are yes, more important), I'd like to thank M.Sc. (soon-to-be-Dr.) Camila Caroline de Castro and Koda Kodalino, who were companions on every single day of this rather long walk, providing support, laughter, happiness and wisdom, making everything so much more pleasant, so much more fun and exciting, as if every battle was not won nor lost alone. There was no limit to your commitment to helping me when I was in need, be that in the fastest-approaching deadlines, hours-long discussions about the trickiest technical problems or lamenting the experimental misfortunes with an empathetic optimism that screamed in my face that trying again wasn't pointless. I would never have gotten so far were not the support from you both. With you, I learned invaluable lessons and for that, I cannot thank you enough.

11. List of Publications

The list below is a complete list of all the other works produced related to this study.

Published in Peer-Reviewed Journals

A.M. Neves, J. Puszkiel, G. Capurso, J.M. Bellosta von Colbe, C. Milanese, M. Dornheim, T. Klassen, J. Jepsen, Modeling the kinetic behavior of the Li-RHC system for energy-hydrogen storage: (I) absorption, Int. J. Hydrogen Energy. (2021). https://doi.org/10.1016/j.ijhydene.2021.06.227.

A.M. Neves, J. Puszkiel, G. Capurso, J.M. Bellosta von Colbe, T. Klassen, J. Jepsen, Development of a new approach for the kinetic modeling of the lithium reactive hydride composite (Li-RHC) for hydrogen storage under desorption conditions, Chem. Eng. J. 464 (2023). https://doi.org/10.1016/j.cej.2023.142274.

Extended Abstracts

World Hydrogen Energy Conference (WHEC), from 26th June to 30th June, 2022, Istambul, Turkey: **A.M. Neves**, J. Puszkiel, J.M. Bellosta von Colbe, T. Klassen, J. Jepsen, *Modeling the kinetic behavior of the Li-RHC system for hydrogen storage under desorption conditions*

Oral Presentations in Conferences

European Materials Research Society (E-MRS), from 20th September to 23rd September 2021, online conference, oral presentation: **A.M. Neves**, J. Puszkiel, G. Capurso, J.M. Bellosta von Colbe, C. Milanese, M. Dornheim, T. Klassen, J. Jepsen, *Modeling the kinetic behavior of the Li RHC system for hydrogen storage under absorption conditions*

World Hydrogen Energy Conference (WHEC), from 26th June to 30th June, 2022, Istambul, Turkey, oral presentation: **A.M. Neves**, J. Puszkiel, J.M. Bellosta von Colbe, T. Klassen, J. Jepsen, *Modeling the kinetic behavior of the Li-RHC system for hydrogen storage under desorption conditions*

Poster Presentations in Conferences

Gordon Research Seminar – Hydrogen-Metal Multifunctional Energy Storage Materials: Towards Industrial Applications, from 24th to 25th of June, 2023, Les Diablerets, Switzerland, poster presentation: **A. Neves**, J. Puszkiel, G. Capurso, J. M. Bellosta von Colbe, T. Klassen, J. Jepsen, *Hydrogenation and dehydrogenation kinetic modelling and validation of the Li-RHC for storage applications*

Gordon Research Conference – Dynamics of Hydrogen in Materials and Molecules, from 25th to 30th of June, 2023, Les Diablerets, Switzerland, poster presentation: **A. Neves**, J. Puszkiel, I. Bürger, T. Klassen, J. Jepsen, *Numerical study of a coupled lithium reactive hydride composite (Li-RHC) hydrogen storage system with* $CaO/Ca(OH)_2$ *as a thermochemical storage material (TCESM)*