ECOSTORE: Novel Complex Metal Hydrides for Efficient and Compact Storage of Renewable Energy as Hydrogen and Electricity

Summary of 1st Reporting Period

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Coordinator: Dr. Klaus Taube

Helmholtz-Zentrum Geesthacht
Center for Materials and Coastal Research
Institute of Materials Research
Max-Planck-Strasse 1
D-21502 Geesthacht
Germany

http://www.ecostore-itn.eu

List of partners

Beneficiary name	Beneficiary contact	Beneficiary short name	Country
Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung GmbH	Dr. Klaus Taube, Dr. Martin Dornheim, Prof. Thomas Klassen, Dr. Claudio Pistidda, Dr. José Bellosta von Colbe	HZG	D
Institutt for Energieteknikk	Prof. Bjørn Hauback, Dr. Magnus H. Sørby, Dr. Jiri Muller	IFE	NO
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Institut de Chimie et des Matériaux Paris-Est (CNRS - ICMPE, UMR 7182)	Prof. Michel Latroche, Dr. Fermin Cuevas	ICMPE	F
The University of Birmingham	Prof. David Book, Dr. Daniel Reed	UOB	UK
University of Geneva	Prof. Radovan Cerny	UNIGE	CH
University of Stuttgart	Prof. Guido Schmitz	USTUTT	D
National Centre for Scientific Research "Demokritos"	Dr. Georgia Charalambopoulou, Dr. Theodore Steriotis	NCSRD	GR
Zoz GmbH	Prof. Henning Zoz, Mr. Deniz Yigit	ZOZ	D
SAFT Batteries SAS	Dr. Christian Jordy	SAFT	F
Rockwood Lithium GmbH	Dr. Ulrich Wietelmann	ROLI	D
Tohoku University	Prof. Shin-ichi Orimo	TU	J
Kyushu University	Prof. Etsuo Akiba	KU	J
University of Southern Denmark	Dr. Dorthe Bomholdt Ravnsbæk	SDU	DK

OBJECTIVES

Borohydride- and nitride-based materials exhibit very high hydrogen storage capacities up to 18 wt%, and they also show excellent properties as novel solid room temperature ion conductors or negative electrode materials with improved capacity, thus allowing for very high energy storage densities. For commercial use a prerequisite is the cost efficient large scale production from abundant and relatively cheap raw materials combined with scalability, and to demonstrate the techno-economical readiness on the prototype scale. The objectives of ECOSTORE are therefore to obtain a **fundamental understanding** of metal hydride based energy storage materials, and to develop them towards **industrial implementation,** achieving **high technical performance** as well as **cost effectiveness**. Detailed fundamental studies in close collaboration with those for hydrogen and those for electrochemical energy storage, including use of more cost efficient raw materials, will enable ECOSTORE to go beyond the state-of-the-art and reach its targets on energy storage materials:

- Development of (i) **novel bi- and tri-metal borohydrides**, complex **nitrogen based hydrides**, their combinations and **Reactive Hydride Composites** with high hydrogen densities, low decomposition temperatures, high ion conductivities at low temperatures, and high electrochemical capacities, respectively, (ii) techniques for stabilisation of high temperature phases towards room temperature, exhibiting **enhanced diffusion speeds for ions and other mobile active species**, (iii) **improved kinetics and thermodynamics** of release and uptake of hydrogen or ions, respectively, and **cycling stability** using suitable additives and/or nanoconfinement for reduced phase separation and crystal growth during hydrogenation, (iv) **improved safety** of materials by nanoconfinement, (vi) **facilitated hydrogenation by** functionalised scaffolds containing catalytic nanoparticles.
- **Theoretical modelling** supported by **advanced *in situ* and nanoscale characterisation,** to obtain a full understanding of the materials structural, physical and chemical properties.
- Cost reduction by **utilisation of less pure raw materials**, available on a larger industrial scale, while still preserving storage performance of the materials.
- Evaluation of the techno-economical potentials, by studying the cycling and degradation behaviour of most promising materials in a prototype **hydrogen storage tank**, and in prototype **battery cells**, respectively.
- **Hydrogen storage materials targets** (c.f. targets of 2011 FCH JU Calls for Proposals)**:**
  - gravimetric capacity >8 wt.% / >1.65 kWh/kg; volumetric capacity >80 kg H_2/m^3 / >250 kWh/l
  - reaction enthalpy as low as possible to minimise heat uptake and release, preferably $\Delta H < 40$ kJ/mol H_2
  - temperature for hydrogen release as low as possible, at least <200°C
  - loadable at < 50 bar
  - cost potential: materials <25 €/kg / ≤400 €/kg of stored H_2 / <15 €/kWh; tank ≤500 €/kg of stored H_2
- **Electrochemical energy storage materials targets** (c.f. targets of US Advanced Battery Consortium[1])**:**
  - gravimetric capacity 0.2 kWh/ kg / 400 Ah /kg; power 1 kW/kg,
  - ionic conductivity of solid electrolyte at room temperature 10 mS/cm,
  - loading time 120 min (30 min high charge rate 40-80%)
  - battery system cost ≤40 €/kg / ≤340 €/kWh

Work performed since the beginning of the project

The first period of the ECOSTORE project was dedicated to

- adjusting the scientific targets in the various tasks, based on progress in the state of the art since proposal submission,
- recruiting ESR and – later – ER fellows,
- training them to start their work and the collaboration inside the ECOSTORE network and
- organising and pursuing the local and network wide training program as well as secondments of the fellows to ECOSTORE beneficiaries, in order to let them be optimally able to follow their scientific work, and
- starting and pursuing the PhD projects of the 12 ESR fellows of ECOSTORE.

Main results achieved so far

In the following a short summary of the most important results is given:

- Establishment of strategies and protocols for materials synthesis (milestone M3 of ECOSTORE)

[1] US Advanced Battery Consortium, http://www.uscar.org/guest/teams/12/U-S-Advanced-Battery-Consortium

- Hydrogen and electrochemical energy storage: new routes for synthesis of solvent and halide free $RE(BH_4)_3$ (RE:Rare Earth) precursors for synthesizing bimetallic compounds were developed, as well as for synthesis of unstable molecular borohydrides (Task 5.1., SeyedHosein Payandeh GharibDoust). The same applies for novel strategies for amides synthesis (Task 5.2., Antonio Santoru). Suitable carbonaceous materials with different pore sizes for amides/hydrides nanoconfinement have been identified and successfully synthesized in new promising, cost and time efficient scaffold synthesis methods. (Task 5.3., Filippo Peru). Strategies and protocols for synthesis of ion conducting materials, based on borohydride garnets, were established. (Task 6.1., Matteo Brighi) as well as for both, electrode and scaffold materials (Task 6.3., Priscilla Huen)

- Identification of suitable materials for nanoconfinement in hydrogen and/or electrochemical energy storage systems (milestone M4 of ECOSTORE)
  - Hydrogen storage: The 1:1 $Mg(NH_2)_2$/ $LiNH_2$ mixture is a practically unknown system and information on synthesis is scarce. Cycling measurements of Pressure, Composition and Temperature (PCT) revealed an initial hydrogen capacity of around 8 wt.% and adequate reversibility. This mixture was for the first time successfully infiltrated in all the porous carbons mentioned above. (Task 5.3., Filippo Peru)
  - Electrochemical energy storage: two hydride materials for infiltration have been selected based on prior studies and investigations within this project: MgH_2 and $NaAlH_4$. (Task 6.3., Priscilla Huen)
- Identification of suitable materials for hydrogen storage with a focus on novel and cost effective materials
  - The $KH+Mg(NH_2)_2$ system has a reversible hydrogen capacity of roughly 2 wt.% and a starting desorption temperature of 150 °C. The reaction pathway of K-Mg-N-H systems was elucidated. The formation of crystalline $K_2Mg(NH_2)_2(NH)$, $K_2Mg(NH)_2$ and KMgN, that was hypothesized in the literature as reaction intermediates, was rejected. A new reaction mechanism for the interaction of KH with $Mg(NH_2)_2$ was proposed, involving an exchange of hydride and amide anions between the two phases. (Task 5.2., Antonio Santoru)

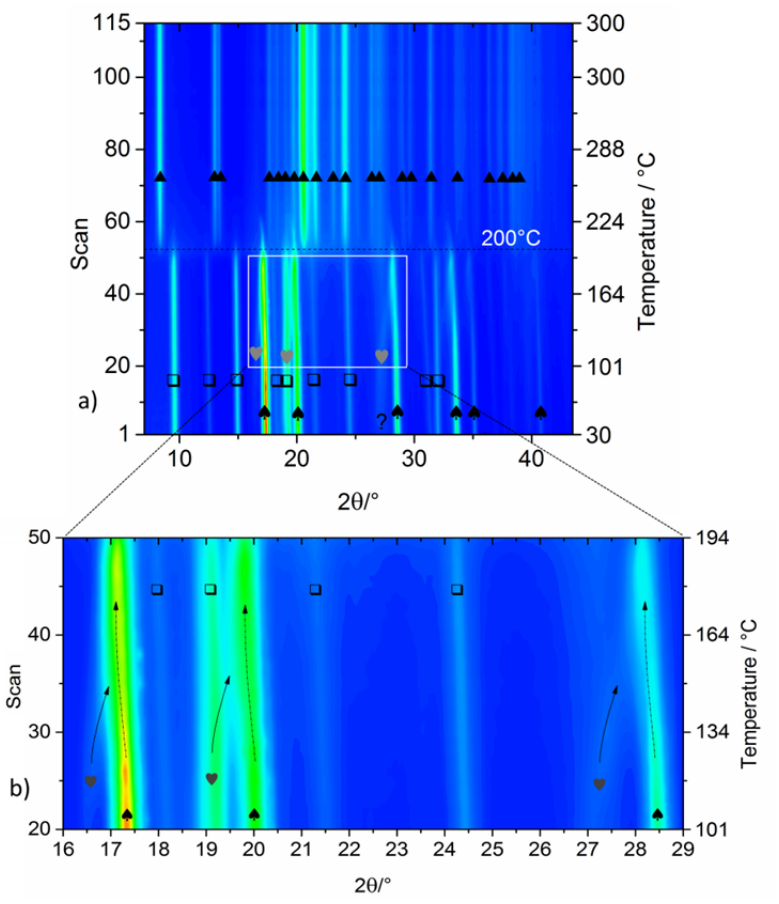

Figure 1 *In situ SR-PXD experiment on the $KH+Mg(NH_2)_2$ system (Sample C) and details showing the structural modifications taking place above 100°C. ♠=KH, ❑=$Mg(NH_2)_2$, ♥=$K(NH_2)_xH_{(1-x)}$, ◢=$KMgNH_2NH$, ?=MgO/MgNH.*

  - The effects on hydrogen sorption properties of the additives $TiCl_3$ and ($3TiCl_3.AlCl_3$) (4 times cheaper than $TiCl_3$) were studied. In the systems $2LiBH_4+MgH_2$ and $2LiH+MgB_2$, the best results in terms of

absorption/desorption rates and reversible hydrogen capacities was achieved for the system $2LiH+MgB_2+0.00625*3TiCl_3.AlCl_3$. (Task 8.1, Thi Thu Le)

- The Reactive Hydride Composite NaF-NaH-MgB_2 showed a capacity of 7.5 wt.% H in the first cycle. (Task 7.3., Michael Heere)

- Identification of suitable materials for electrochemical energy storage with a focus on novel and cost effective materials
  - In complex hydrides, ionic conductivity at room temperature is still too low (~ 10^{-6} S/cm, but is seven orders of magnitude higher at RT than in the analogue undoped oxide garnets. The ionic conductivity of borohydride garnets was still increased by one order by doping with bivalent cations such as Sr and Eu. A general strategy for tailoring ionic conductivity in complex hydrides (such as $[BH_4]^-$) has been established. (Task 6.1., Matteo Brighi)

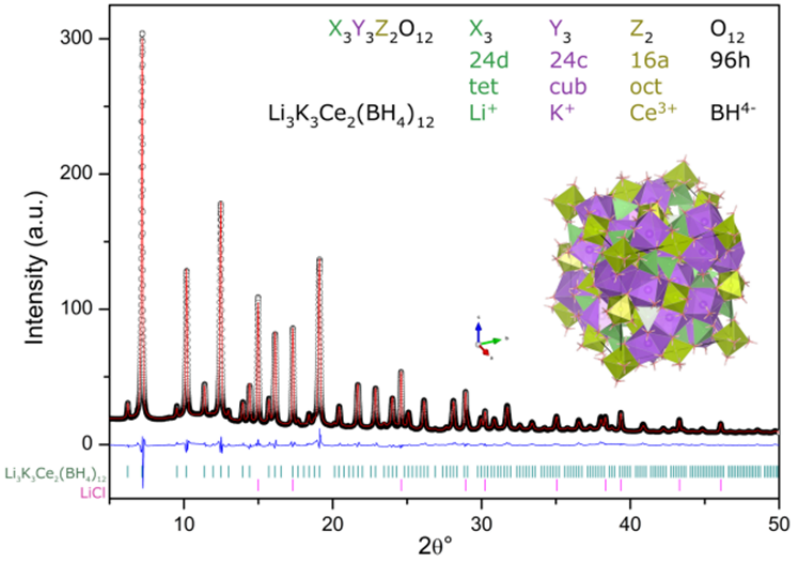

Figure 2: SR-XPD data and the structure of $Li_3K_3Ce_2(BH_4)_{12}$ garnet.

  - MgH_2-TiH_2 nano composites have shown good performance and reproducible data during several charge-discharge cycles (e.g. $0.5MgH_2$-$0.5TiH_2$ 2150 mAh/g during the first lithiation, and a reversible capacity of 875 mAh/g in the second cycle). (Task 6.2, Nicola Berti)

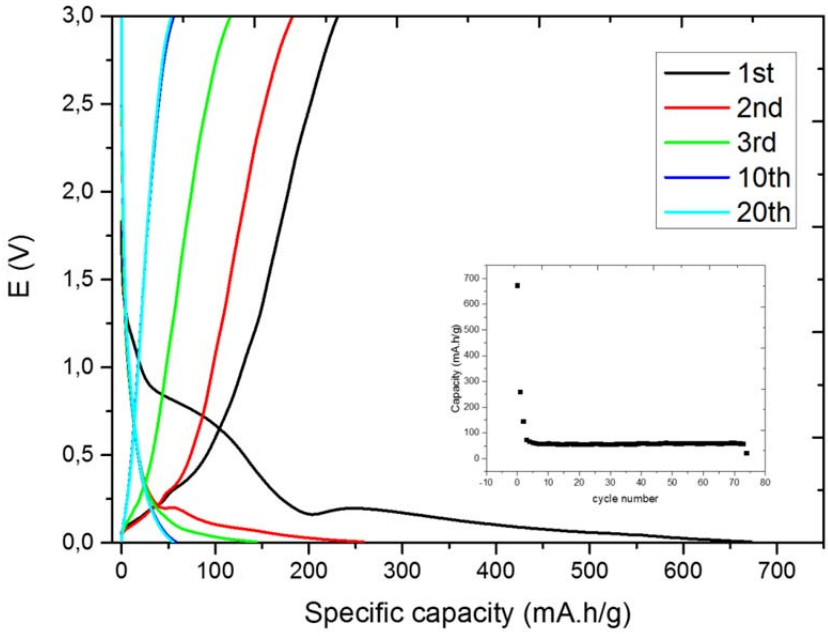

Figure 3: Discharge capacity of $7MgH_2$-$3TiH_2$ anode by adding 20% of carbon

- By using a mixture of MgH_2 and TiH_2, performance of the active materials was improved, compared to pure MgH_2. $7MgH_2$-$3TiH_2$ with 20% of active carbon and binder gave 41% of the theoretical capacity; cyclic performance was also improved, 37% for the second discharge, 21% for the third, compared to nearly 30% and 12%, respectively, with MgH_2, containing 40% of active carbon and binder. (Task 8.3, Anh Ha Dao)

- Understanding of Dynamics of Reactions in Energy Storage Materials
  - Creation of Mg thin film layers by ion beam sputtering (DC source) and Ar-plasma and further hydrogenation at 10bar H_2 pressure and at 300°C, followed by creation of MgH_2 has been achieved. Faster hydrogenation with a Pd 50nm thin film on top of the Mg layers has been investigated. Creation of Ti thin film layers from ion beam sputtering (DC source) and Ar-plasma, followed by hydrogenation has also been achieved. (Task 7.1, Efi Hadjixenophontos)
  - A measurement technique was established, allowing the measurement Raman spectra under 1 bar Ar as function of temperature (from -196 °C to 600 °C). A Differential Scanning Calorimetry (DSC) Raman cell allowed concurrent Raman and DSC in situ measurements, under the same conditions. The Influence of surface roughness was identified: rougher surfaces lead to a higher measured $[B_{12}H_{12}]^{2-}$ to B ratio which indicates that decomposition pathway forming $Li_2B_{12}H_{12}$ could be promoted by surface roughness. The addition of 5 mol% SiO_2 to $LiBH_4$ increased the amount of H_2 released by seven times. (Task 7.2, Yinzhe Liu)
  - The reaction pathway of $3LiBH_4–Er(BH_4)_3–3LiH$ was clarified. Addition of 2 mol% of the NbF_5 and Ni_3B enhanced the hydrogen sorption properties of alpha-$Mg(BH_4)_2$ and gamma-$Mg(BH_4)_2$, respectively. (Task 7.3, Michael Heere)
  - In the $LiBH_4$-$LiNH_2$ system, pure 1:1 and 1:3 compounds could be obtained from quenching after a thermal treatment. A phase diagram for the $LiBH_4$-$LiNH_2$ system was constructed, comparing experimental and calculated values. (Task 7.4, Anna Wolczyk)

CONCLUSIONS AND PERSPECTIVES

With relation to chemical energy storage by hydrogen, we expect ECOSTORE to demonstrate novel routes for cost effective synthesis of high capacity hydrogen storage materials (capacity > 8wt.%, >80 kg H_2/m^3) and being loadable at hydrogen pressures below 100 bar. Together with hydrogen release temperatures below 200°C, this will open up perspectives for cost effective low pressure, high capacity hydrogen storage for stationary and maybe also mobile hydrogen storage. This could lead to a boost in application of hydrogen technologies in various markets, where current high pressure or liquid hydrogen storage technologies prevent the introduction due to the high technical and cost efforts, necessary for applications of these technologies. Foreseen applications are e.g. in the field of weekly to monthly energy storage (larger residential or commercial buildings, off-grid energy storage for farms or islands, off-grid telecommunication) and combination with high temperature Polymer Electrolyte Membran (PEM) fuel cells, or Solid Oxide Fuel Cells (SOFC) and Solid Oxide Electrolyser Cells (SOEC).

With respect to electrochemical energy storage in rechargeable batteries, we expect ECOSTORE to demonstrate novel highly conductive solid state ion conductors as well as high capacity electrode materials. The introduction of cost effective solid state ion conductors, together with novel electrode materials to Li-ion battery technology would allow for a drastic increase of capacity and safety of rechargeable batteries. Furthermore, a cost decrease by introducing a homogeneous manufacturing technology, based on solid state materials only, is expected. The combination of “better” materials with cheaper manufacturing is expected to lead to a much broader application of electricity based solution e.g. in transport and many other applications, where current battery technology is at the limits of its usability due to limited electrical capacity and high cost. Potential applications can be found as well as in mobility and consumer products as well as in daily to weekly energy storage applications, short time grid balancing and the like.