Alanates – Synthesis, Transformation Mechanism and Technical State of the Art

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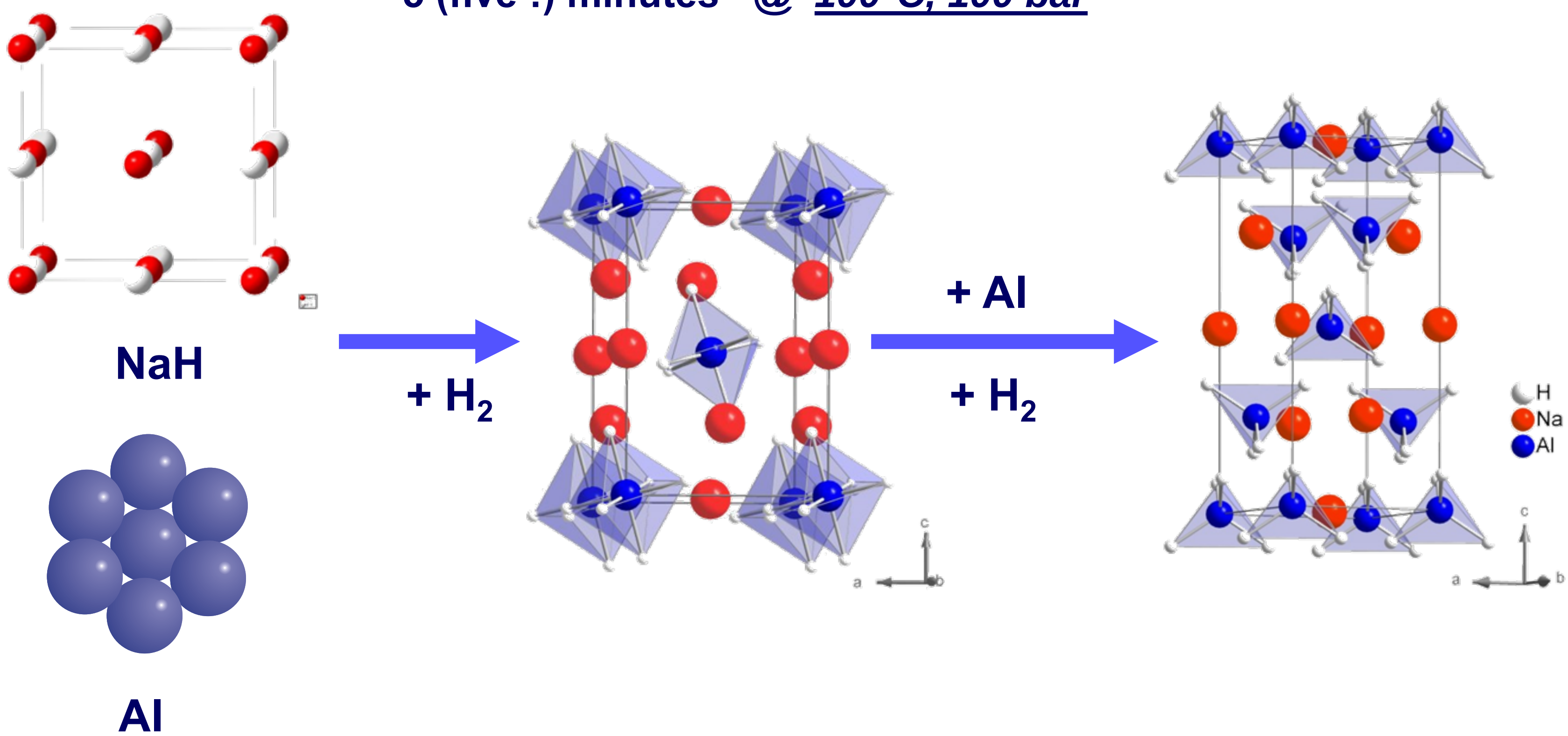
Outline

- The role of dopants
- Transformation mechanism
- Alanates on the nanoscale
- System integration

How is it possible that an alanate transforms so fast ?

$$3NaH + 3Al + 6H_2 \rightleftharpoons Na_3AlH_6 + 2Al + 3H_2 \rightleftharpoons 3\ NaAlH_4$$

5 (five !) minutes @ *100°C, 100 bar*



Facts and Questions

- Stepwise solid state reaction (2 solids + 1 gas)
- Massive mass transport in the solid
- Comparably low temperature (100 °C)

? What is the function of the catalyst

? What is the rate limiting step

? What is the diffusing species: NaH or Al or ?

? What is the reaction mechanism

Function of Ti dopant ?

Karlsruhe Institute of Technology

Early hypothesis:

Ti species can act as heterogeneous catalyst for splitting / recombination of H_2

True ! **(Schüth et al. , 2006: H_2/D_2 isotope scrambling with Ti-doped $NaAlH_4$)**

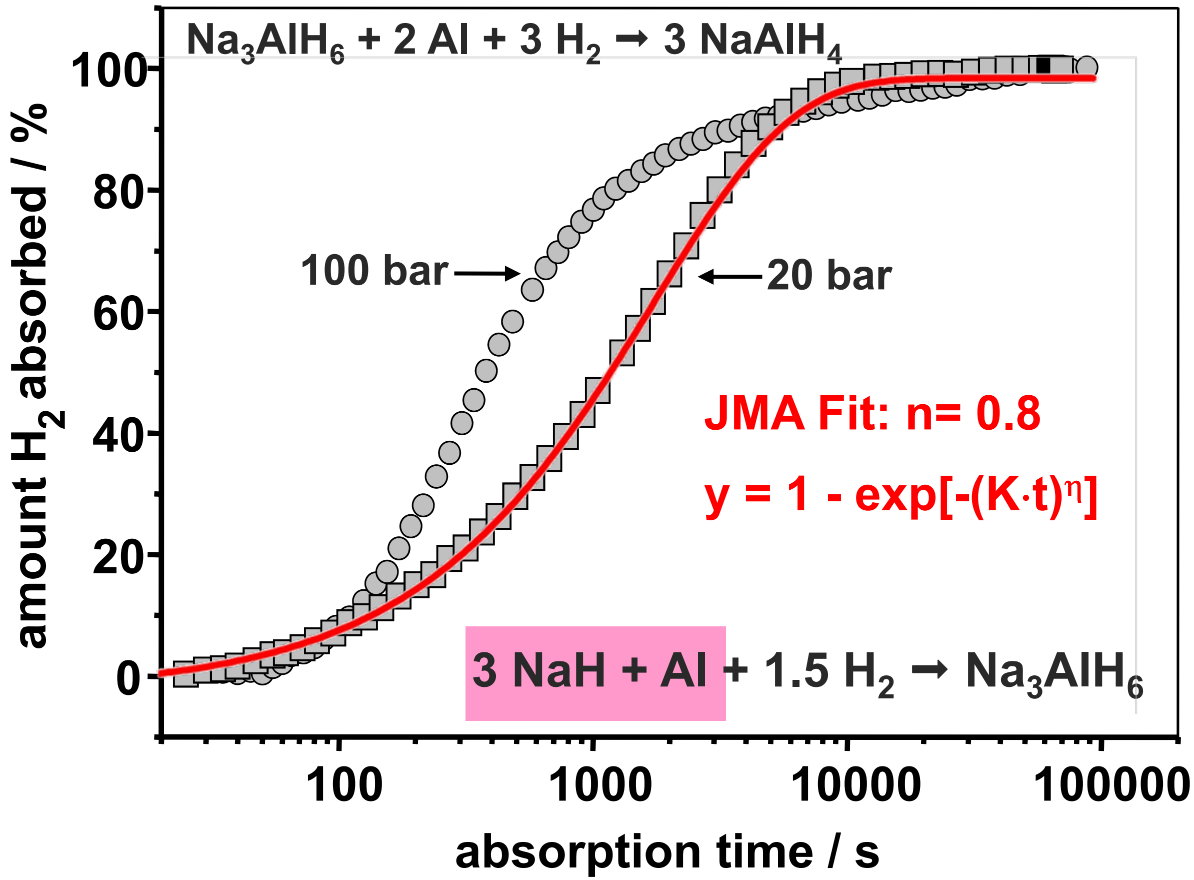
But: This is not the rate determining step ! **(*Fichtner et al, Nanotechnology, 2003*)**

There must be other functions of Ti ; e.g. Ti improves mass transport

(Kircher and Fichtner, J. Appl. Phys. 95, 2004)

Rate Limiting Steps (Isothermal absorption)

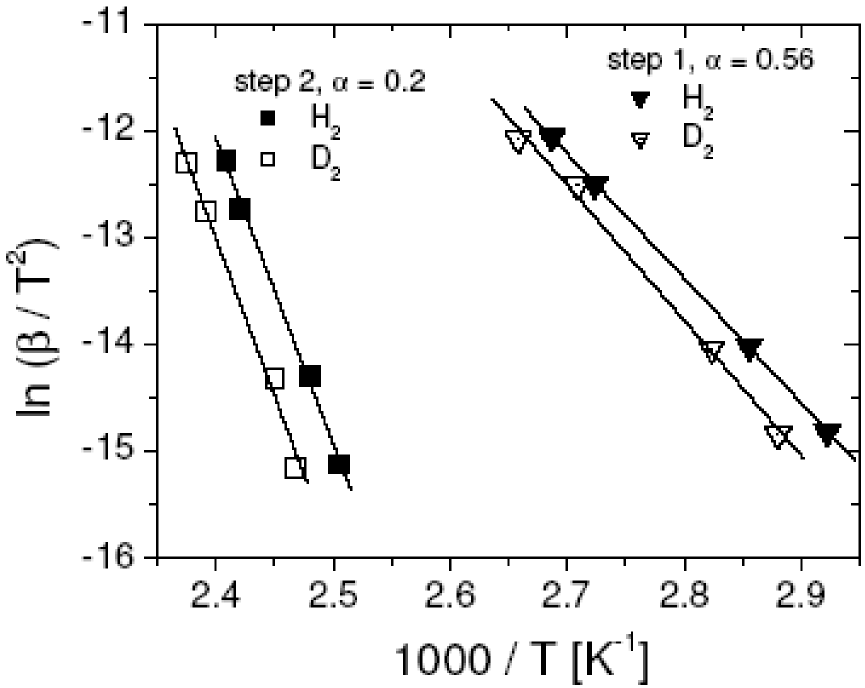
Nucleation theory: JMA equation



Diffusional growth: $n = 0.5, 1$ for 1- or 2- dimensional growth

M. Fichtner et al. (2003)

Kinetic Isotope Study with H and D



Kinetic isotope effects studied by isothermal and non-isothermal methods

$$\ln \frac{\beta}{T^2} \sim -\frac{E_a}{RT}$$ **KAS**

Activation Energy

step 1	H_2 [kJ/mol]	D_2 [kJ/mol]
KAS (average)	**95.1**	**102.6**
max rate	**92.1**	**101.6**

$$E_a \sim aE_n + bE_g$$

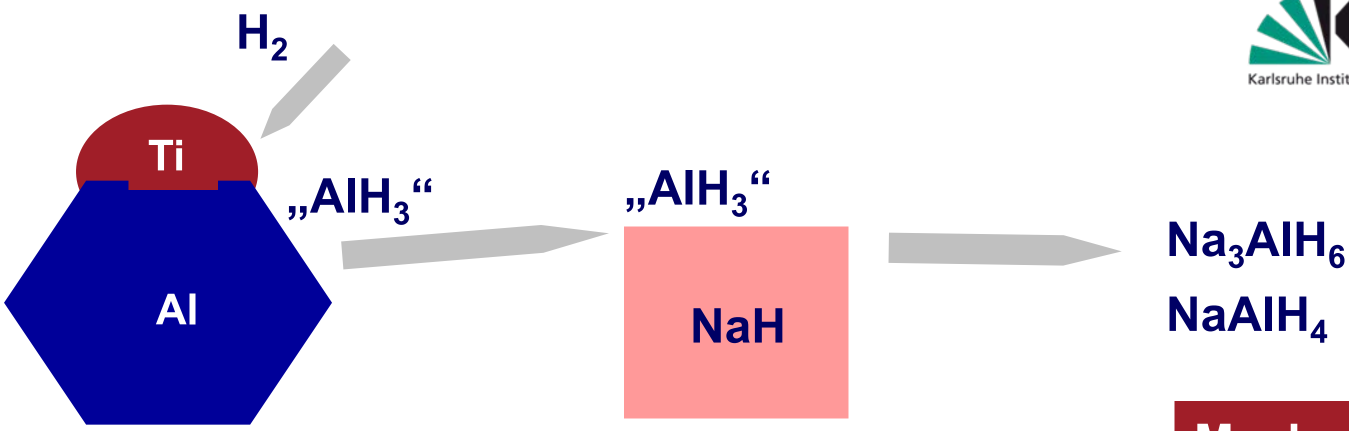
H

$$\frac{\sqrt{1}}{\sqrt{2}} \approx 0.70$$

AlH_3

$$\frac{\sqrt{30}}{\sqrt{33}} \approx 0.95$$

W. Lohstroh, M. Fichtner, Phys. Rev. B 75 (2007)



Mechanism

- ✓ Ti-Catalyst helps the formation of intermediate AlH_x species → Theoreticians
- ✓ What we see in a kinetic <u>experiment</u> is the transport limitation of the diffusing AlH_x species !
- ✓ This would explain and reunite the seemingly contradictory findings made by theoreticians and experimentalists.

M. Fichtner, MRS Fall Meeting 2006

Still open questions (stability of AlH_3 species at 100°C? etc.)

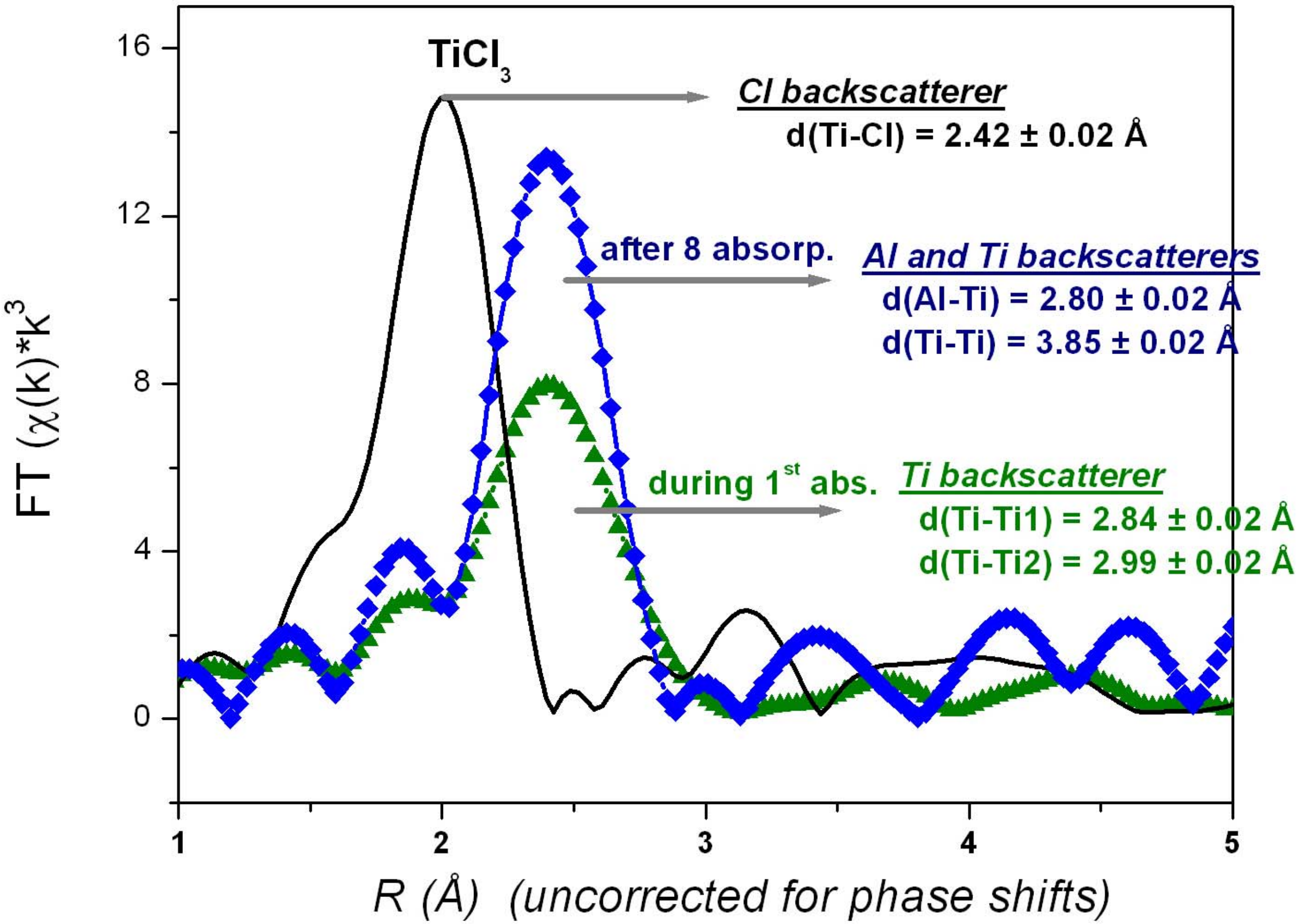
Investigation of dopants

- How does the local structure of dopant evolve during doping and cycling?

- What are the consequences?

Ti K edge / EXAFS region / $NaAlH_4 + TiCl_3$

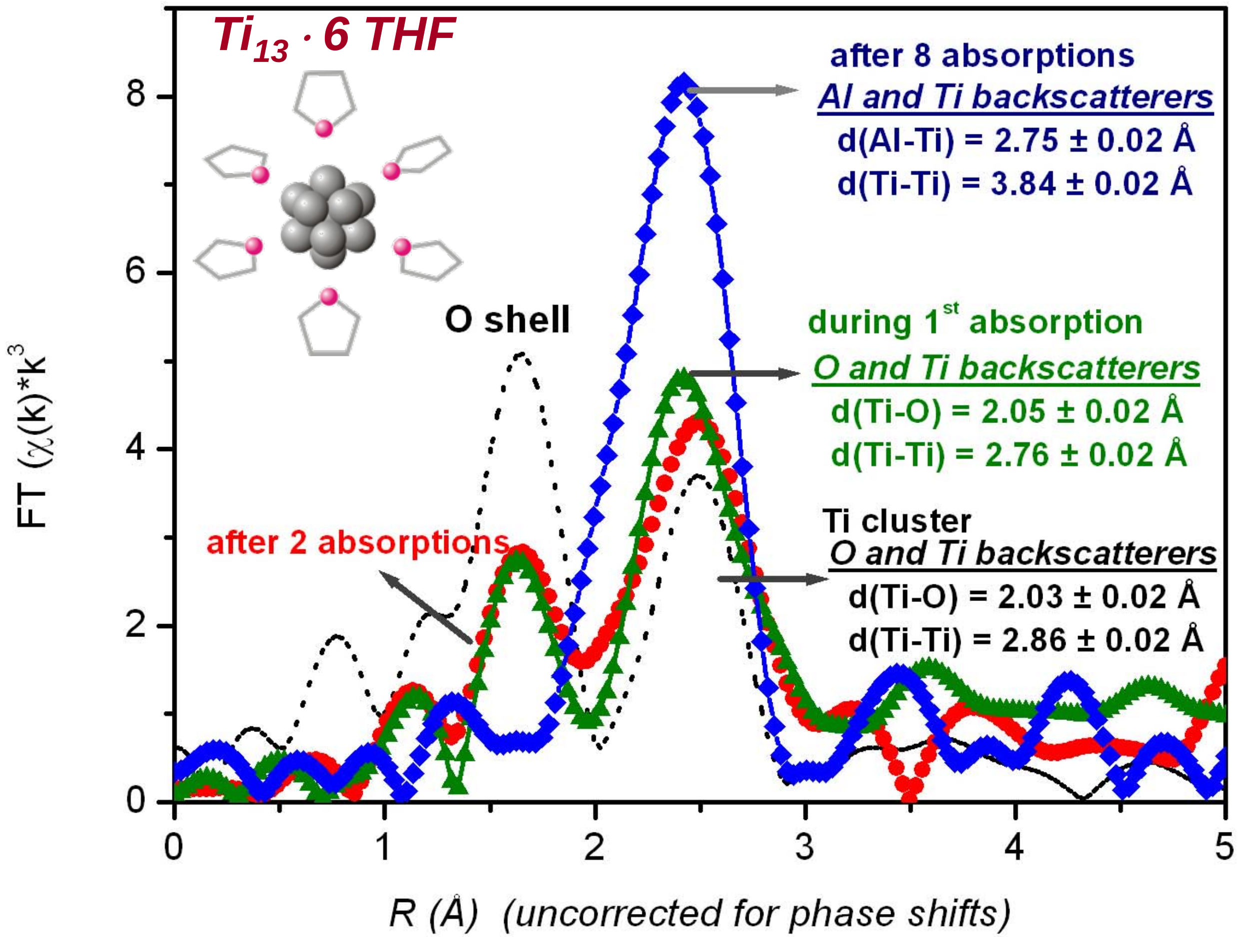
Fourier transform of the k3-weighted χ(k) function of SAH + 5 mol.% $TiCl_3$ at different cycles.



A. Leon, O. Kircher, M. Fichtner, J. Rothe, D. Schild, J. Phys. Chem B 110 (2006) 1192

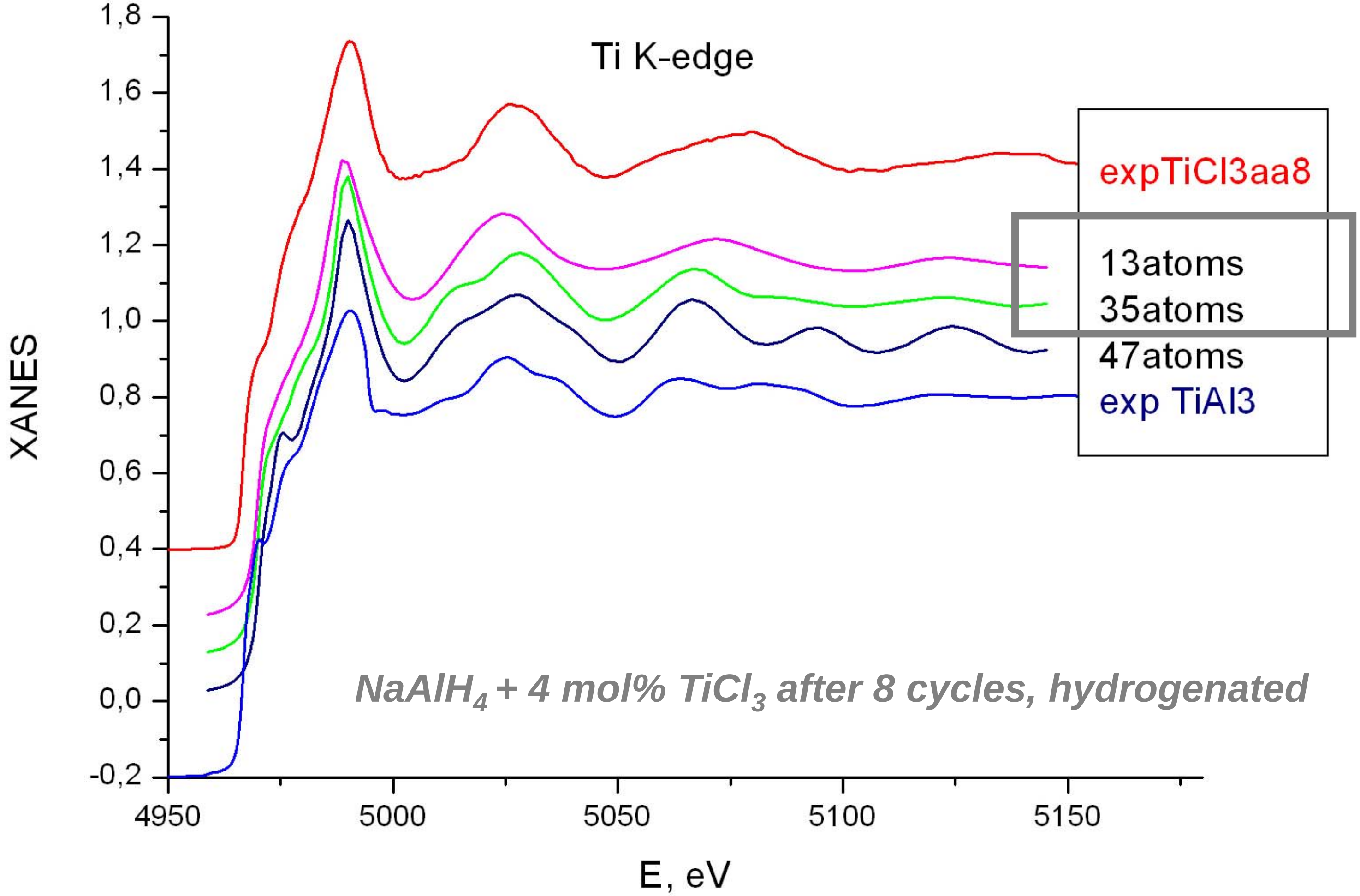
Ti K edge / EXAFS region / $NaAlH_4$ + Ti clusters

Fourier transform of the k3-weighted χ(k) function of SAH + 5 mol.% Ti cluster at different cycles.



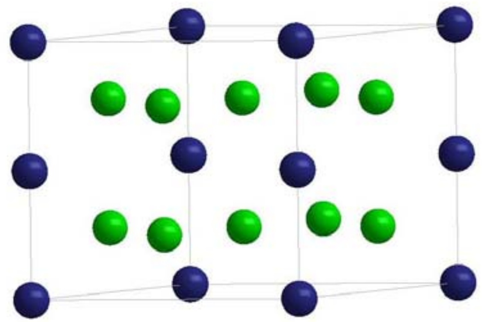
A. Leon, O. Kircher, M. Fichtner, J. Rothe, D. Schild, J. Phys. Chem B 110 (2006) 1192

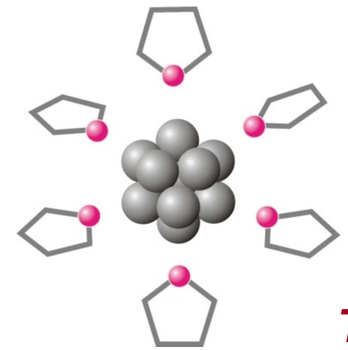
Modelling of XANES region / Estimated Size of Ti-Al Entities



A. Léon, G. Yalovega, A. Soldatov, M. Fichtner, J. Phys. Chem. C 112 (2008) 12545-12549.

$TiCl_3$





$Ti_{13} \cdot 6\ THF$

NaAlH$_4$ doping
Ball Milling

Small Ti metal particles
Distorted hcp structure

Ti cluster
Ti-Ti and Ti-O neighbours

First Cyle(s)

Small Ti metal particles
Distorted hcp structure

Ti metal particle
Stripping of O

After 8 Cyles

Small Ti – Al entities
uniform Ti-Al distance
like distorted $TiAl_3$
Ti : Al = 1 : 6

A. Leon, O. Kircher, M. Fichtner, J. Rothe, D. Schild, J. Phys. Chem. B 110 (2006) 1192

What have we learnt / what can we do ?

Experimental observations:
The transformation of Ti into Ti-Al entities in the steady state is correlated with a certain

- **Slow down of the kinetics**
- **Decrease of storage capacity**

Avoid their formation to obtain better performance of the material.

- ✓ **Change dopant**

Accept their formation and synthesize steady state directly with cheap materials.

- ✓ **Cost-effective production method**

Cost effective production

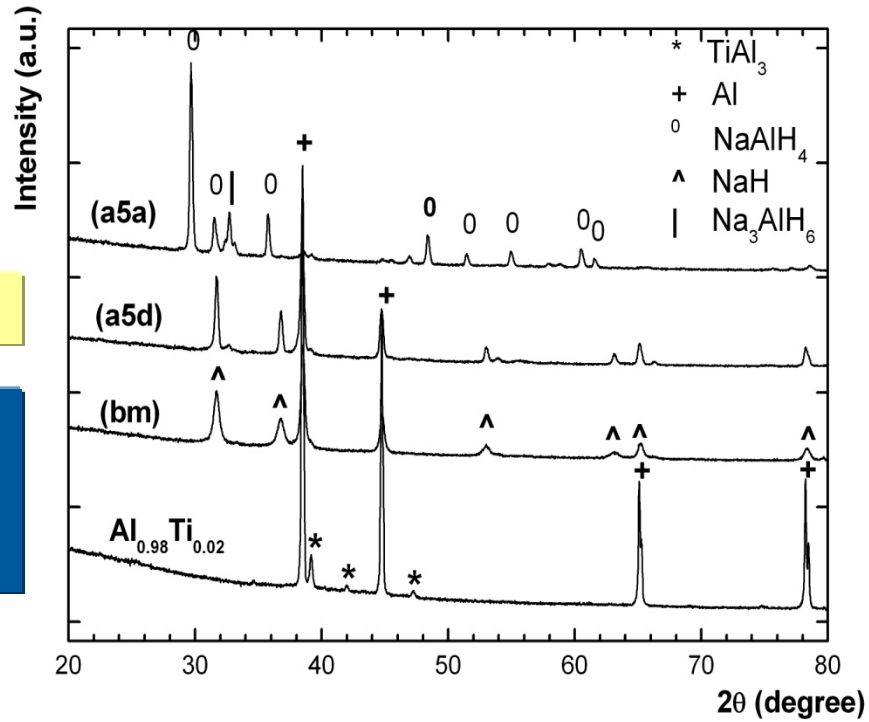
Prepare a nanocomposite which can be loaded with H_2

1) **Catalytic pretreatment of Al powder**
2) **Subsequent annealing (e.g. 500 °C, 90min)**
3) **Ball milling with NaH and cycling**

$(AlTi_{0.02} + NaH) + 3/2\ H_2 \rightleftharpoons \dots \rightleftharpoons NaAlTi_{0.02}H_4$

Cheap, fast and stable storage material is obtained.

Catalyst cost decreased by a factor of 500-1000 compared to $TiCl_3$.

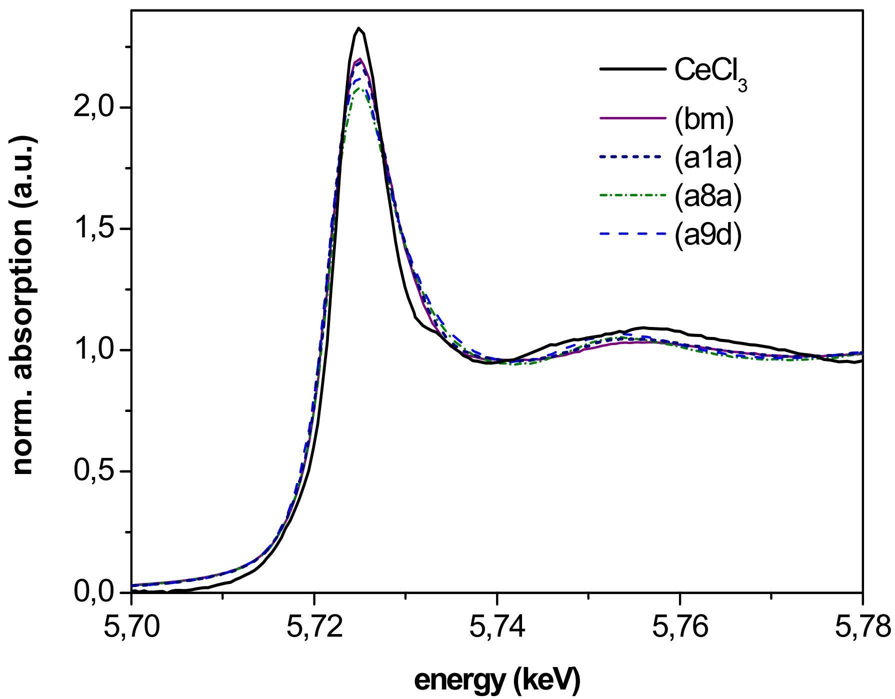


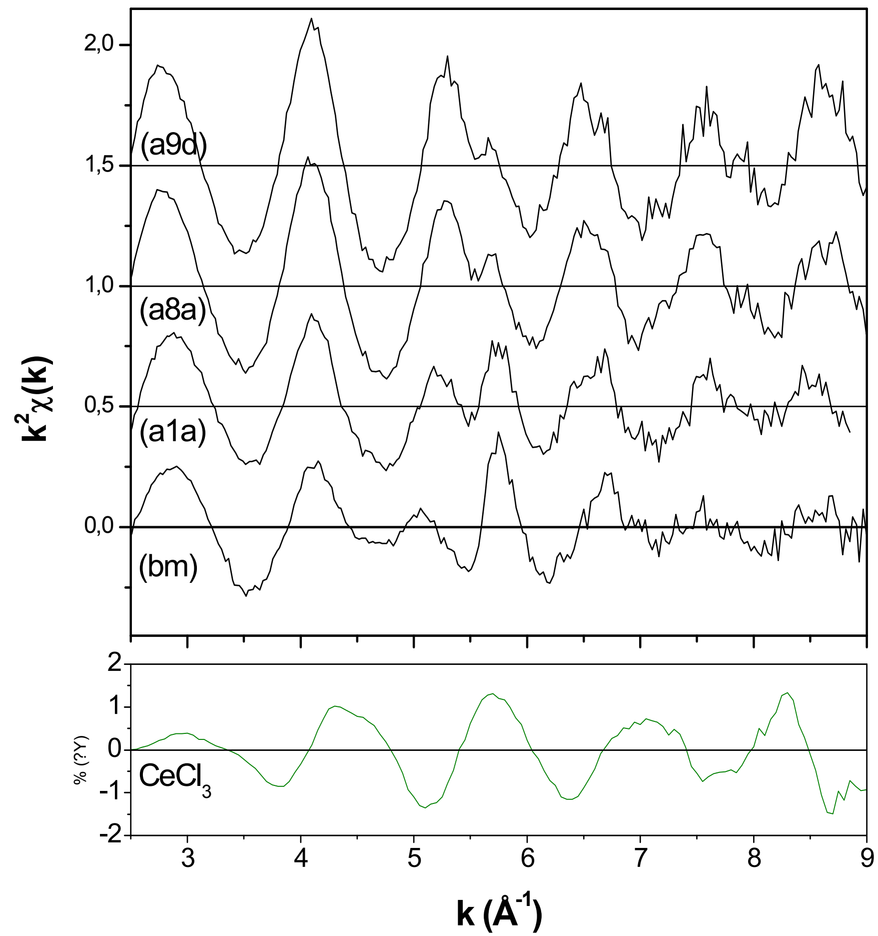
M. Fichtner, Ch. Frommen, Patent DE-PS 10 2005 037 772 (2006), WO-OS 2007/17129 (2007) , EP-OS 1 912 891 (2008)

Other Catalysts: Ce

Karlsruhe Institute of Technology

Ce L-edge; XAS





Oxidation state does not change !

A. Léon *et al.*, Phys. Chem. Chem. Phys. 11 (2009) 8829 – 8834.

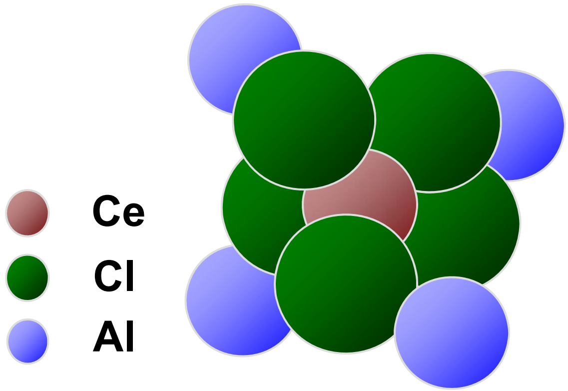
Coordination around Ce

(a) Ce in the alanate samples is surrounded by a strongly distorted Cl coordination polyhedron, A stable Ce(III) valence state is observed during ball milling and hydrogen cycling.

(b) Ce as next neighbour can be ruled out (would lead to fitting failure) → Atomic dispersion of Ce

(c) The ball-milled sample shows an intimate mixture between $CeCl_x$ entities and the alanate host matrix (Al as overnext neighbour).

(d) A steady state seems to have been reached after 8 absorption cycles, no significant changes of the local Ce coordination environment occur after the 9th desorption.



2 shells after 8 cycles:

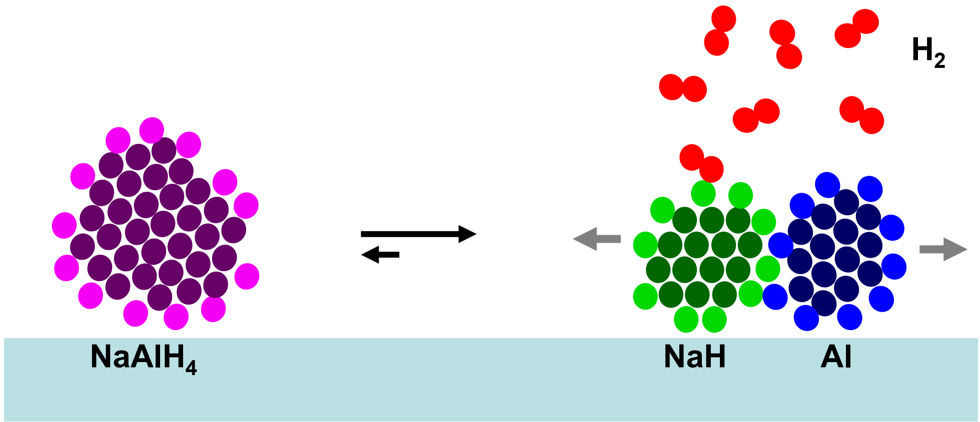
Ce – 5 Cl ~ 3.0 Å

Ce – 4 Al ~ 4.1 Å

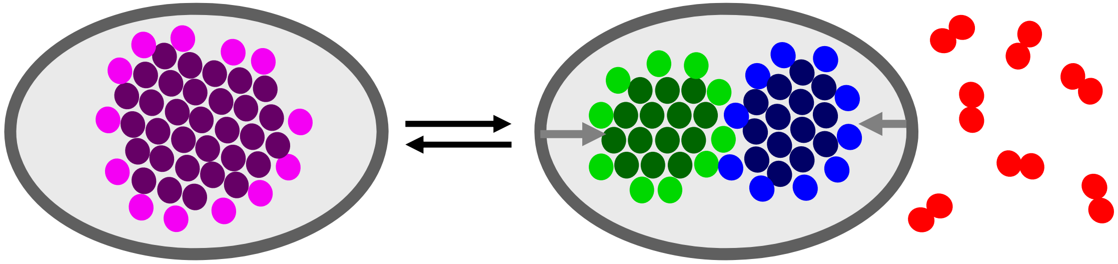
A. Léon *et al.*, Phys. Chem. Chem. Phys. 11 (2009) 8829 – 8834.

Alanates on the nanoscale

Complex hydrides on the nanoscale



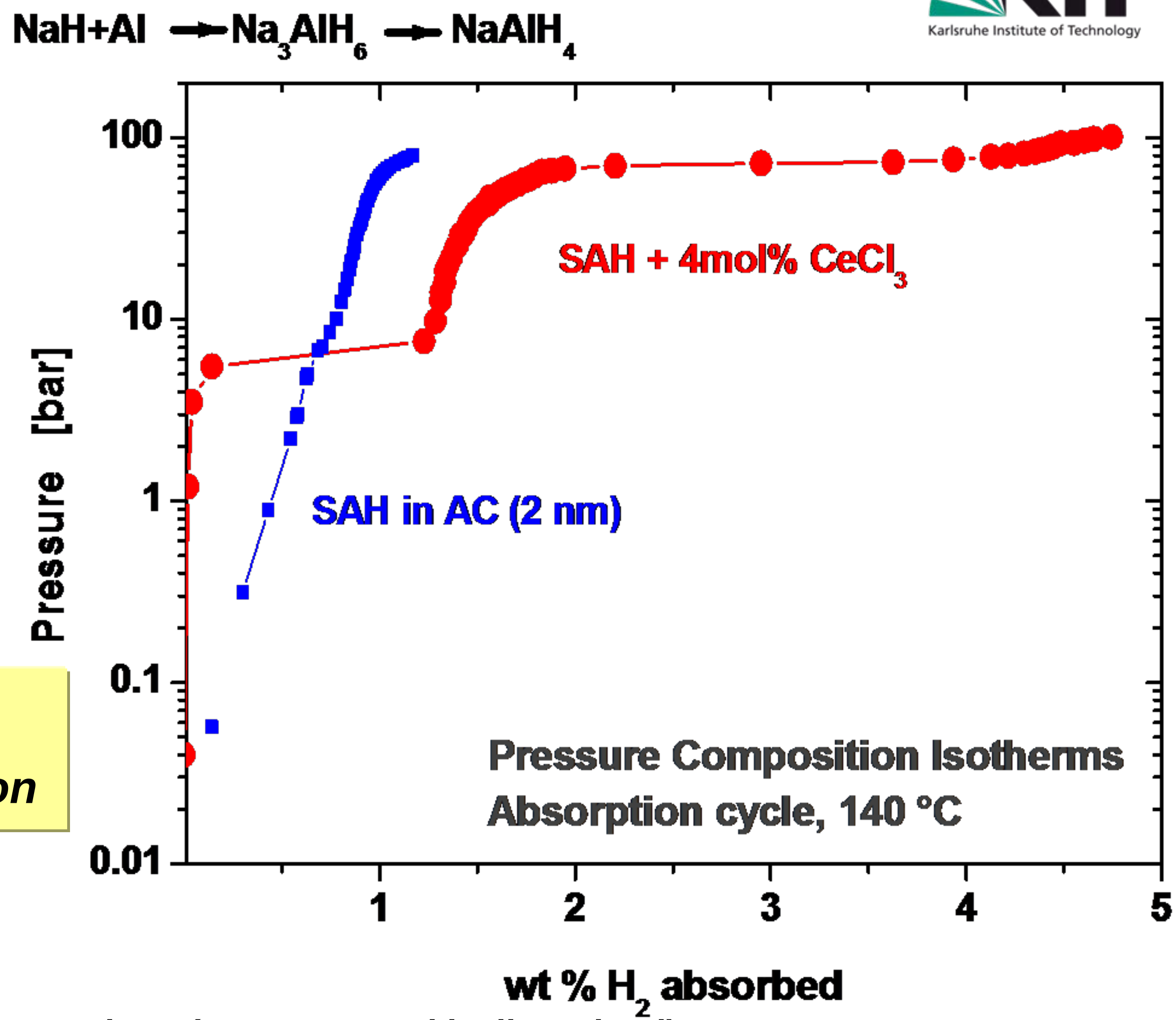
a) Free-standing on a surface
→ kinetics (+)
→ reversibility (-)
→ thermodynamics (?)



b) Nanoconfined in matrix
→ *kinetics (+)*
→ *reversibility (+)*
→ *thermodynamics (?)*

M. Fichtner, Nanotechnology 20 (2009) 204009

Nanoconfined $NaAlH_4$



First indication for altered thermodynamics of a nanoconfined complex hydride

- ***Enhanced H solubility***
- ***Narrowed 2-phase region***

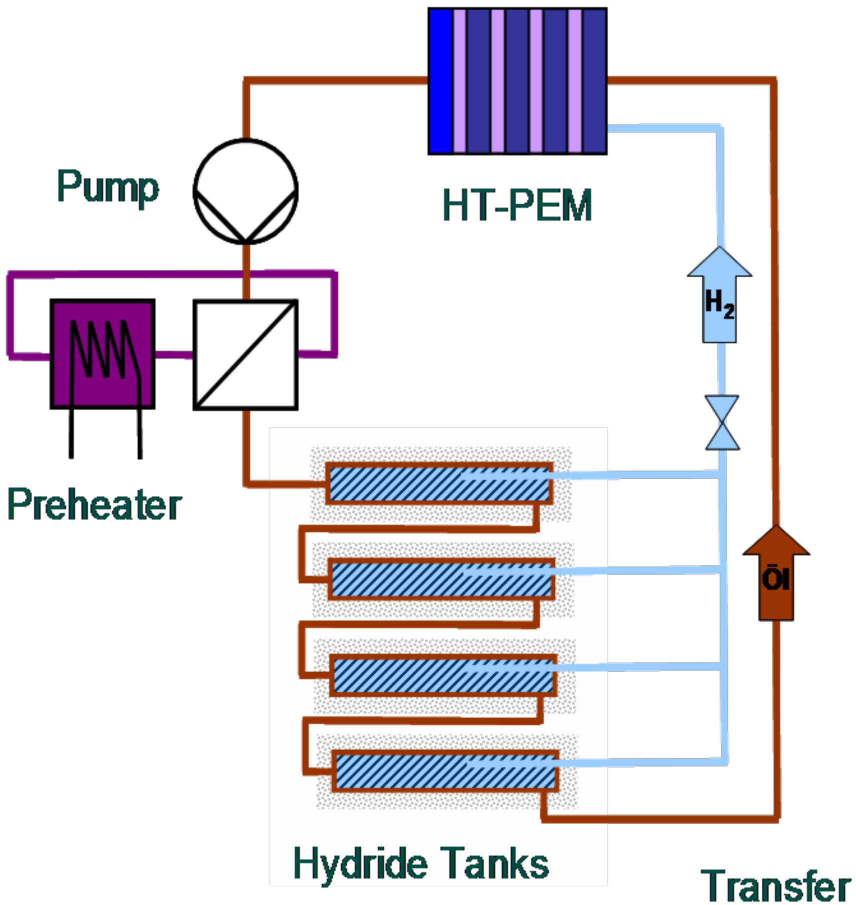
M. Fichtner, W. Lohstroh, A. Roth, O. Zabara (MH 2008, Reykjavik, Iceland),

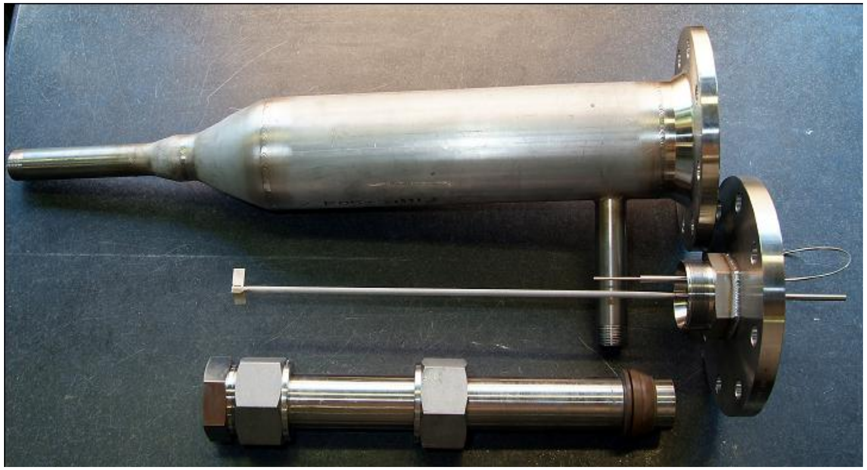
W. Lohstroh, A. Roth, H. Hahn, M. Fichtner, Chem.Phys.Chem. (2010)

Alanates

System Integration

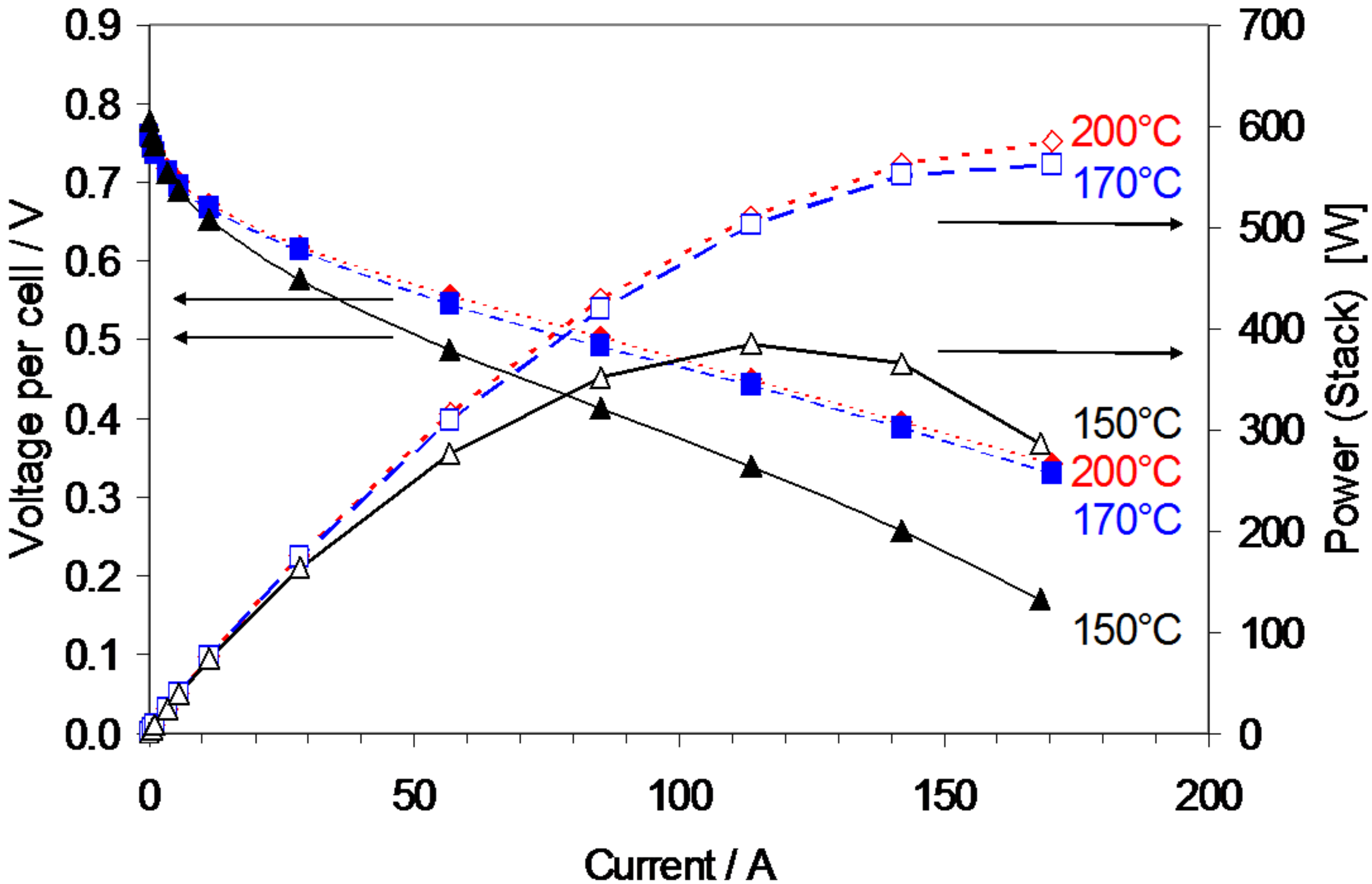
Thermal coupling of alanate tanks with a HT-PEM FC



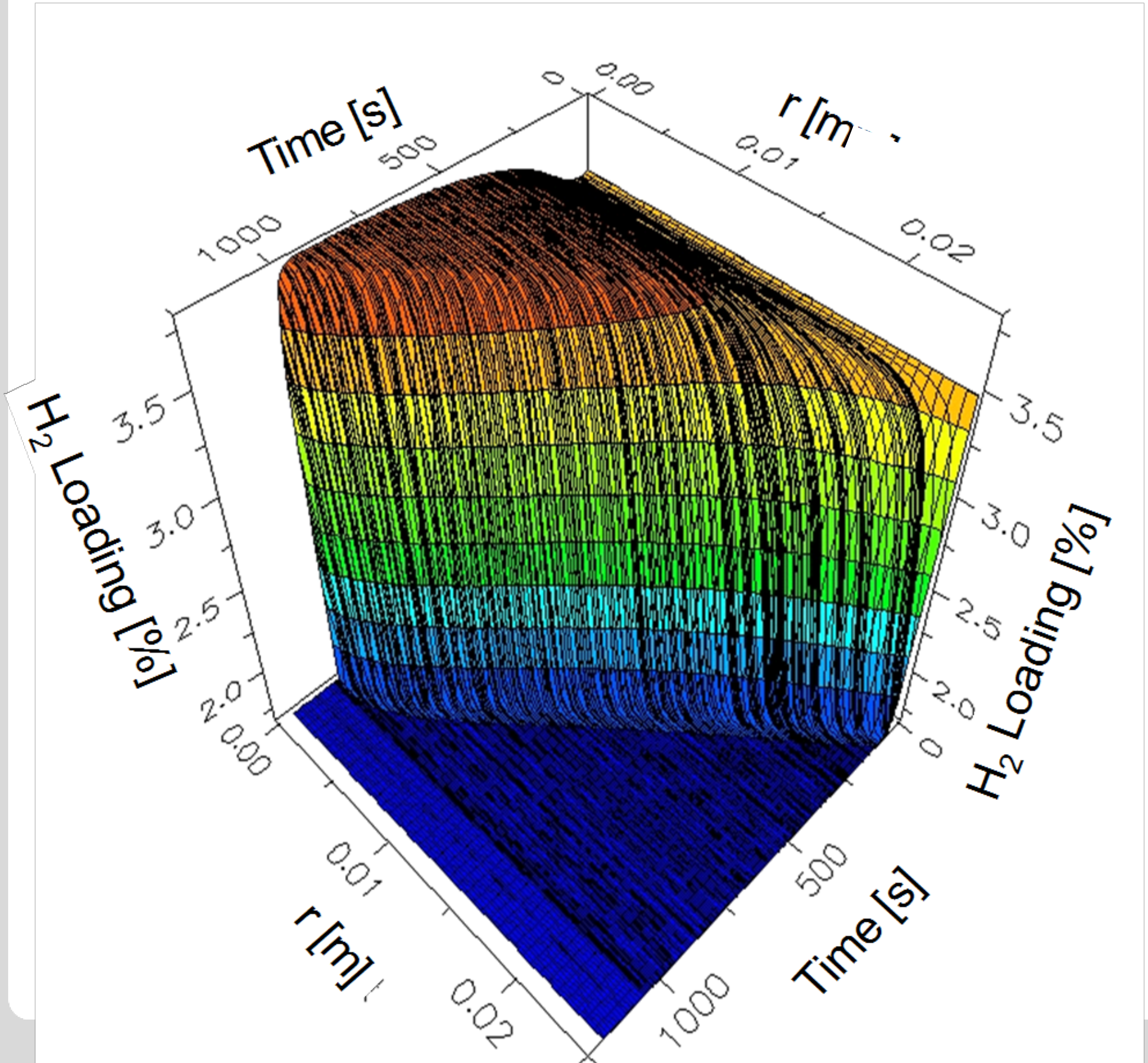


P. Pfeifer, C. Wall, J. O. Jensen, H. Hahn and M. Fichtner, Int. J. Hydr. Energy 34 (2009) 3457

Thermal coupling of alanate tanks with a HT-PEM FC
Characteristics of the HT PEM FC stack

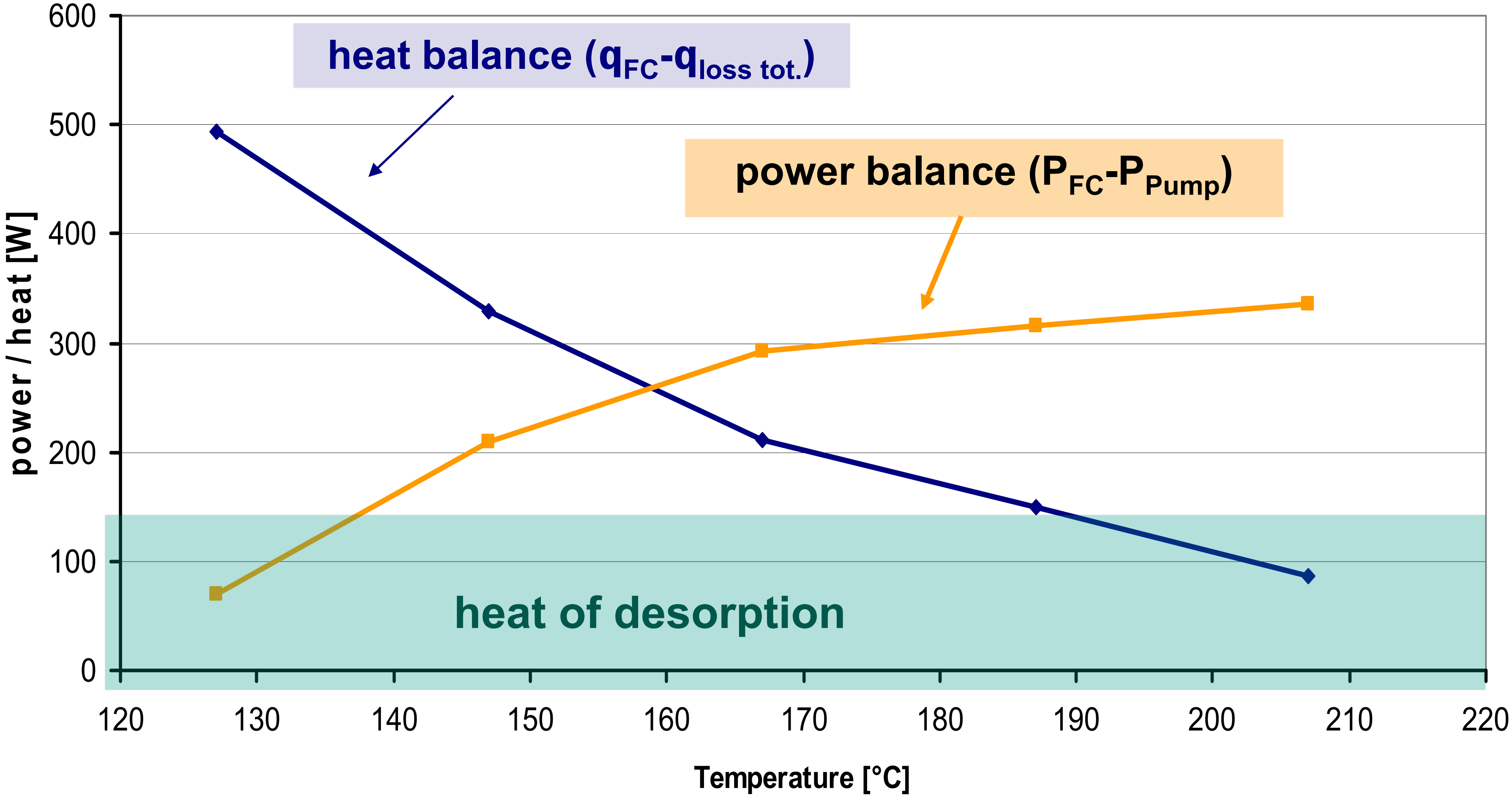


Thermal coupling of alanate tanks with a HT-PEM FC
Modelling of the tank behaviour

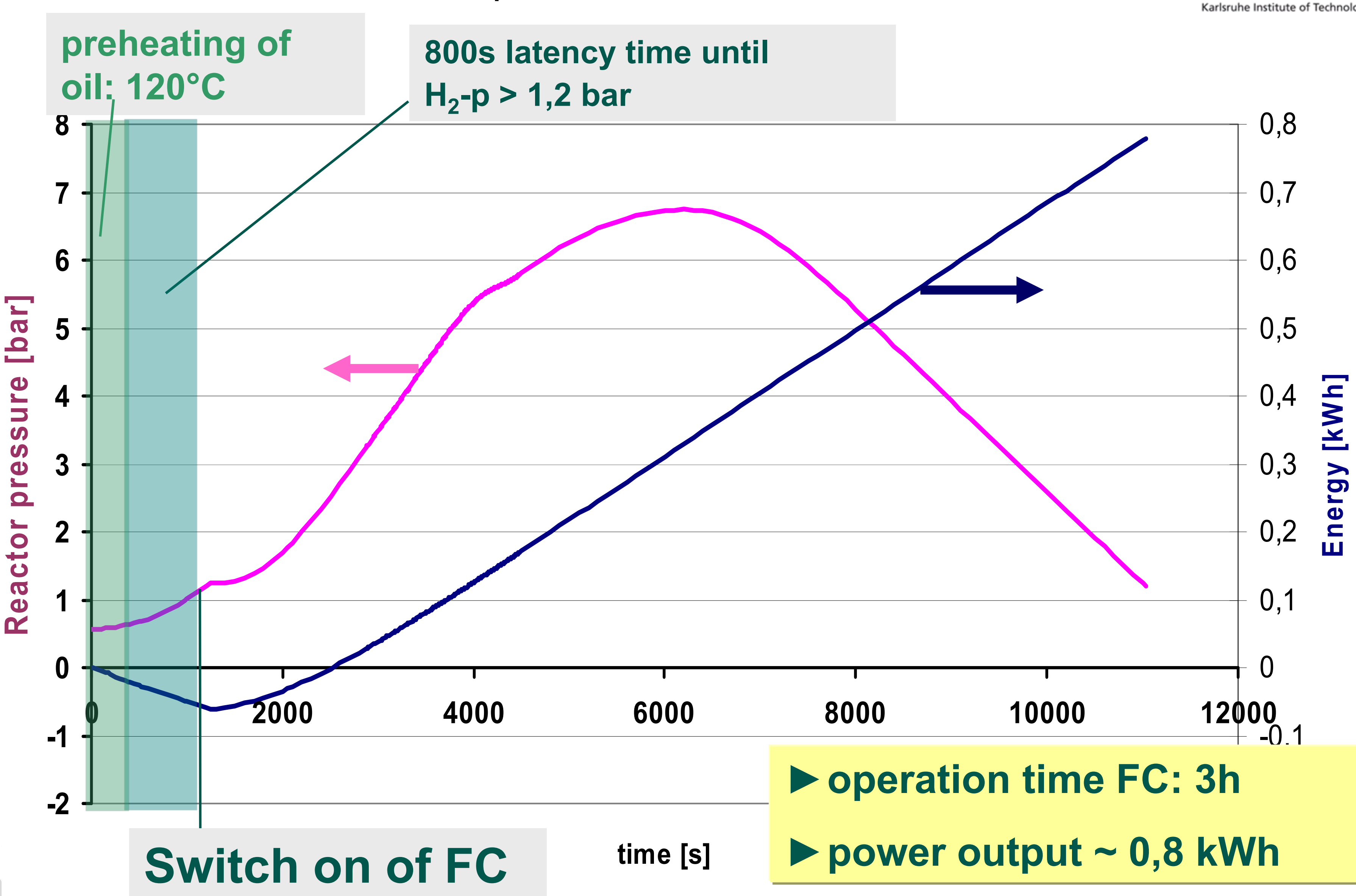


Hydrogen content in the alanate in radial direction versus time (time = 0 corresponds to start of heating up); overall heat dissipation, heat loss and heat capacity of the system considered.

Identification of stable operation regimes



Cold start / Cumulative power output for 1kW HT PEM FC system with 2 kg $NaAlH_4$ H storage



Results

- ***Highly effective nanoscale catalysts were synthesized and tested.***
- ***Rate limiting steps in the transformation of $NaAlH_4$ were identified.***
- ***Hints for nature of moving species were gained.***
- ***Understanding of the microstructure of Ti and Ce dopant during preparation and cycling.***
- ***Development of cost-effective Ti doped alanate.***
- ***Change of thermodynamics by infiltration in microporous scaffold.***
- ***First system integration of an alanate tank in the environment of a HAT-PEMFC***

Thank You !