Interplay of diffusion and dissociation mechanisms during hydrogen absorption

- Ronald Griessen
- Robin Gremaud
- Flavio Pendolino
- C. Rongeaut
- S. Kato
- M. Bielmann
- Andreas Züttel

Andreas Borgschulte
Laboratory Hydrogen & Energy @ EMPA
HYDROGEN & ENERGY

Materials Science & Technology

Director: Prof. Louis Schlapbach

Head of Laboratory 138 “Hydrogen & Energy:
Prof. Andreas Züttel

Dept. Mobility, Energy and Environment
Lab. 138 “Hydrogen & Energy”

Überlandstrasse 129
CH-8600 Dübendorf, Switzerland
Tel.: (+41) (44) 823 4038,
e-mail: andreas.borgschulte@empa.ch
URL: http://www.empa.ch/h2e
Activities

EDUCATION

R&D PROJECTS

RESEARCH

DEMONSTRATIONS

Sun

Dissociation of water

Transport Storage

Combustion

Electrolysis

Photovoltaics & Hydropower

Energy

H₂O

H₂

O₂

H₂

O₂

H₂O

Brennstoffzellen

Forschungszentrum Karlsruhe

in der Helmholtz-Gemeinschaft

Materials Science & Technology

Barrett Poehlschuh

Empa

Materials Science & Technology
OUTLINE

- How to measure hydrogen content in metal hydrides: static/dynamic experiments

- Thin film experiments

- Connecting surface and bulk: The Two Layers model – derivation and thin film experiments

- outlook
Gravimetric hydrogen sorption measurements

Measurement principle to correct for buoyancy contribution to the sample mass.

“Sieverts” Pressure automation

<table>
<thead>
<tr>
<th>valve 1, 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>p</td>
</tr>
<tr>
<td>time</td>
</tr>
</tbody>
</table>
Gravimetric pcT measurements on LaNi$_5$
Non-equilibrium pcT-measurements

**normality: up to months!**
Extrapolation to equilibrium?

Extrapolated $P_{eq}$

Physics? Mechanisms?
Mechanisms of Kinetics of Hydride formation

splitting the H$_2$ molecule
$\Delta E_{\text{diss}} \sim 0\ldots1$ eV

diffusion into bulk
$\Delta E_{\text{diss}} > \Delta E_{\text{diff}} \sim 0\ldots1$ eV

nucleation and growth
**Hydrogen Diffusion**

\[ x = \sqrt{6Dt} \]

- Water in pasta: 1 mm in 5 min
- \( H \) in NiMH batteries: \( \sim 10 \, \mu\text{m} \) in min
- \( \text{Li} \) in Li-ion batteries: \( \sim \mu\text{m} \) in min
- \( H \) in complex hydrides: \( \sim \mu\text{m} \) in days

\[
\begin{align*}
\text{Li in Li} & \text{BH}_4 \\
\text{H in Ni} & \text{MH batteries} \\
\text{Li in Li} & \text{ion batteries}
\end{align*}
\]
Surface mechanisms

Depicting reality: Thin metal hydride films

- Switch. Mirrors: Pd-clusters, Y-oxide, YH_x
- LaNi_5: Ni-clusters, La-oxide, LaNi_5H_x
- MgH_2: Surface (additive), MgH_2, MgH_0

A. Borgschulte et al., PRB 78, 094106 (2008)
Hydrogen in materials changes optical properties

- Measurements of hydrogen content in thin films
- Determination of thermodynamics and kinetics
- Thin film setup for testing models

Temperature dependence of H-uptake in yttrium catalyzed by noble metal coatings.

The higher the activation energy, the higher the rate?

What cluster material is the best?
The catalytic effect of noble metals on yttrium

**Depicting reality: The two layers model**

- **Constant plateau pressure:**
  \[ p(x_{ae} \ldots x_{ba}) = p_{pl} \sim \text{const.}, \ p_{pl} \neq f(t) \]
- **One dissociation step**
- **One diffusion step**

A. Borgschulte et al., PRB 78, 094106 (2008)
The chemical potential at the surface is equal to that under the surface:

\[
\frac{\theta_H}{1 - \theta_H} e^{-\Delta G_{\text{surf}} / kT} = \frac{c_H}{1 - c_H} e^{-\Delta G_{\text{bulk}} / kT}
\]
Diffusion through material

Model potential
In the diffusion layer

Model potential
In the hydride layer
Chemical potential in NON-EQUILIBRIUM

Chemical potential of hydrogen gas ... Chemical potential in metal hydride

Rate is defined by

\[ j = -L \frac{d\mu}{dx} \]
Analytical solution and approximation

$$R \propto \frac{D}{L} \left[ -\frac{D}{L} + \sqrt{\left(\frac{D}{L}\right)^2 + 4B \left(\frac{\alpha D}{L} \sqrt{p_{pl}} + Ap\right)} \right] - \alpha \sqrt{p_{pl}}$$

If $Ap_{H_2} \gg \frac{D}{L}$ i.e. low diffusion, the rate is

**Diffusion-limited**

$$R \propto \frac{D}{L} \left[ \sqrt{\frac{A}{B}} \cdot \sqrt{p - \alpha \sqrt{p_{pl}}} \right]$$

If $Ap_{H_2} \ll \frac{D}{L}$ i.e. high diffusion, the rate is

**Dissociation-limited**

$$R \propto \alpha \sqrt{p - p_{pl}}$$

Pressure dependence

<table>
<thead>
<tr>
<th>rate-limiting step conditions</th>
<th>simplified kinetics</th>
<th>activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td>dissociation $p \gg p_{pl}$</td>
<td>$R = A p$</td>
<td>$E_1$</td>
</tr>
<tr>
<td>dissociation $p \approx p_{pl}$</td>
<td>$R = A(p - p_{pl})$</td>
<td>$E_1 + \frac{p_{pl}}{p - p_{pl}} 2 \Delta H_{MH}$</td>
</tr>
</tbody>
</table>
| diffusion $p \gg p_{pl}$, diffusion $p \approx p_{pl}$ | $R = -\frac{D}{L} \sqrt{\frac{A}{B} \cdot p}$  
\[ R = \frac{D}{L} \alpha \cdot \sqrt{p} \]  
\[ R = \frac{D}{L} \alpha \left[ \sqrt{p} - \sqrt{p_{pl}} \right] \] | $\Delta H_{sol} + E_{diff}$  
\[ \Delta H_{aol} + F_{diff} + \frac{\sqrt{p_{pl}}}{\sqrt{p} - \sqrt{p_{pl}}} \Delta H_{MH} \] |
| diffusion $p_{pl} \gg p \approx 0$, recombination $p_{pl} \gg p \approx 0$ | $R = -\frac{D}{L} \sqrt{\frac{A}{B} \sqrt{p_{pl}}}$  
\[ R = \frac{D}{L} \alpha \cdot \sqrt{p_{pl}} \]  
\[ R = -A p_{pl} \] | $\Delta H_{sol} + E_{diff} - \Delta H_{MH}$  
\[ E_1 - 2 \Delta H_{MH} \] |

A. Borgschulte et al., PRB 78, 094106 (2008)
Pressure dependence of Pd-capped Mg$_y$Ni$_{1-y}$ thin films

\[ R \propto \frac{D}{L} \left( \sqrt{\frac{A}{B}} \cdot \sqrt{p - \alpha \sqrt{p_{pl}}} \right) \]

A. Borgschulte et al., PRB 78, 094106 (2008)
Hydrogen absorption of Pd-capped Mg$_2$Ni thin films: pressure dependence

\[ E_{AA} = kT^2 \frac{\partial \ln R}{\partial T} \]

\( E_{AA} \) can be negative!

\[ R \propto e^{-E_1/kT} \cdot (p - p_{pl}) \]
Hydrogen absorption of Pd-capped Mg$_2$Ni thin films:
activation energy

\[ R \propto e^{-E_1/kT} \cdot (p - p_{pl}) \]

A. Borgschulte et al., PRB 78, 094106 (2008)
Hydrogen absorption of Pd-capped Mg$_2$Ni thin films: pressure dependence

$$R \propto e^{-E_1/kT} \cdot (p - p_{pl})$$

A. Borgschulte et al., PRB 78, 094106 (2008)
Hydrogen absorption of Pd-capped Mg$_2$Ni thin films: equilibrium pressure

A. Borgschulte et al., PRB 78, 094106 (2008)
Stability and Kinetics of LaNi$_5$H$_x$ 

**Literature values:**

$\Delta H = -32$ kJ/mol $H_2$: H.H. van Mal, Phips Res. Repts. Suppl. 1 (1976);


$E_A = 0.19$ ... 0.5 eV (several original Refs., see A. Andreasen et al., J. Phys. Chem. B 109, 3340 (2005))
Sorption kinetics in MgH$_2$

$$R = f(p, x_H, t)$$

nucleation @ plateau boundaries
The knowledge of the **hydrogen sorption mechanism** is mandatory
- To extrapolate equilibrium values
- To gain information on kinetics, i.e. barrier heights etc.

**Analysis of kinetic curves**
- Qualitatively: nucleation, diffusion, dissociation
- Quantitatively: Two-step model

Thank you for interest!
First Conference Announcement

Under the auspices of:
The International Association for Hydrogen Energy (IAHE)

Organized by: EnergieAgentur.NRW

In cooperation with:
Jülich, Deutscher Wasserstoff und Brennstoffzellentechnologie

Supported by:
Messe Essen, NOW, European Hydrogen Association, NWIBA, Europäische Union, EMPA

Hydrogen Energy

WHEC 2010
18th World Hydrogen Energy Conference

May 16 - 21, 2010
Essen, Germany

First Major Sponsor:
RWE
The energy to lead

www.whec2010.com