Future Energy Materials: Two Challenges

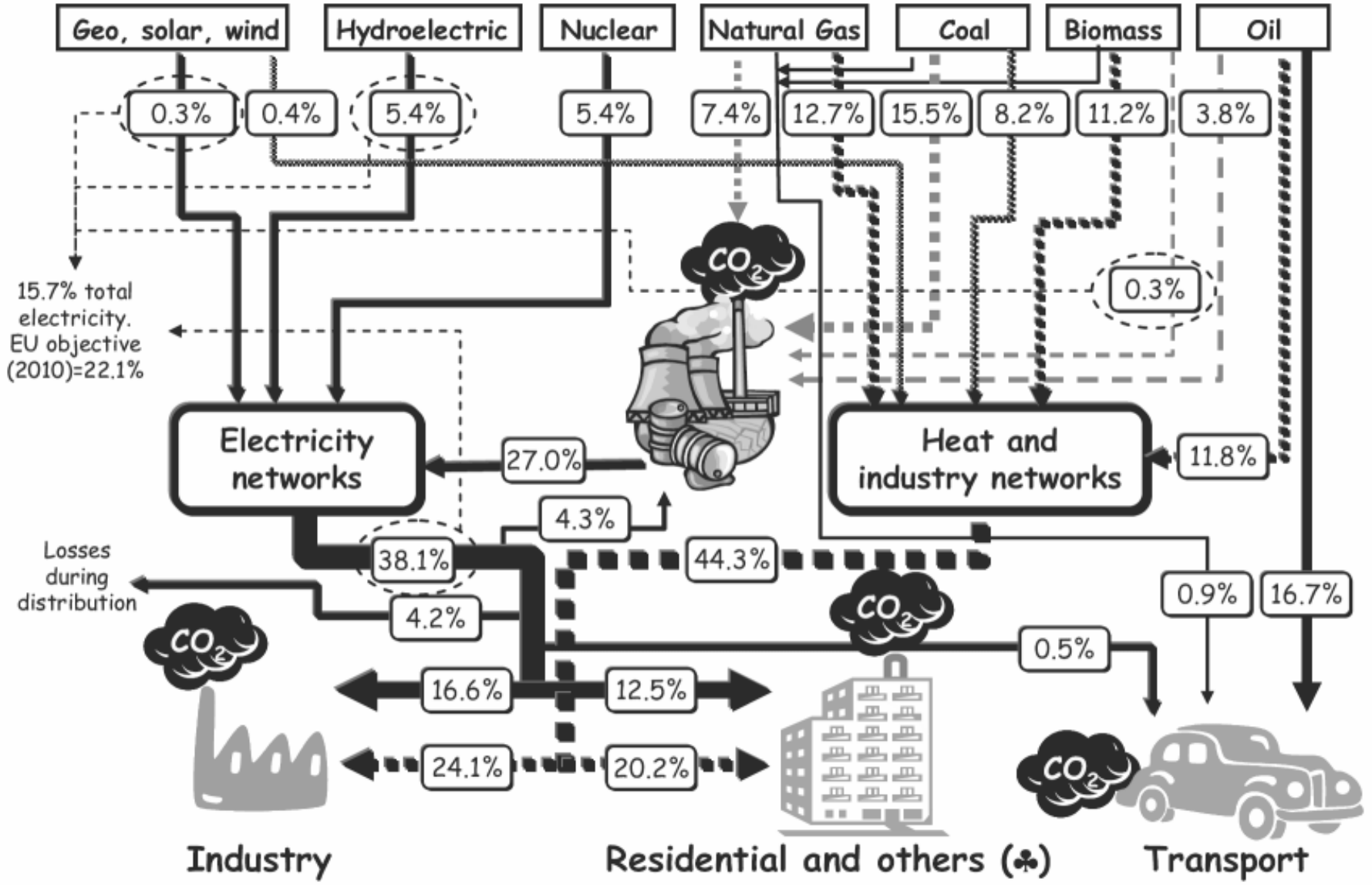
Peter P. Edwards

University of Oxford

Future Energy:
Chemical Solutions

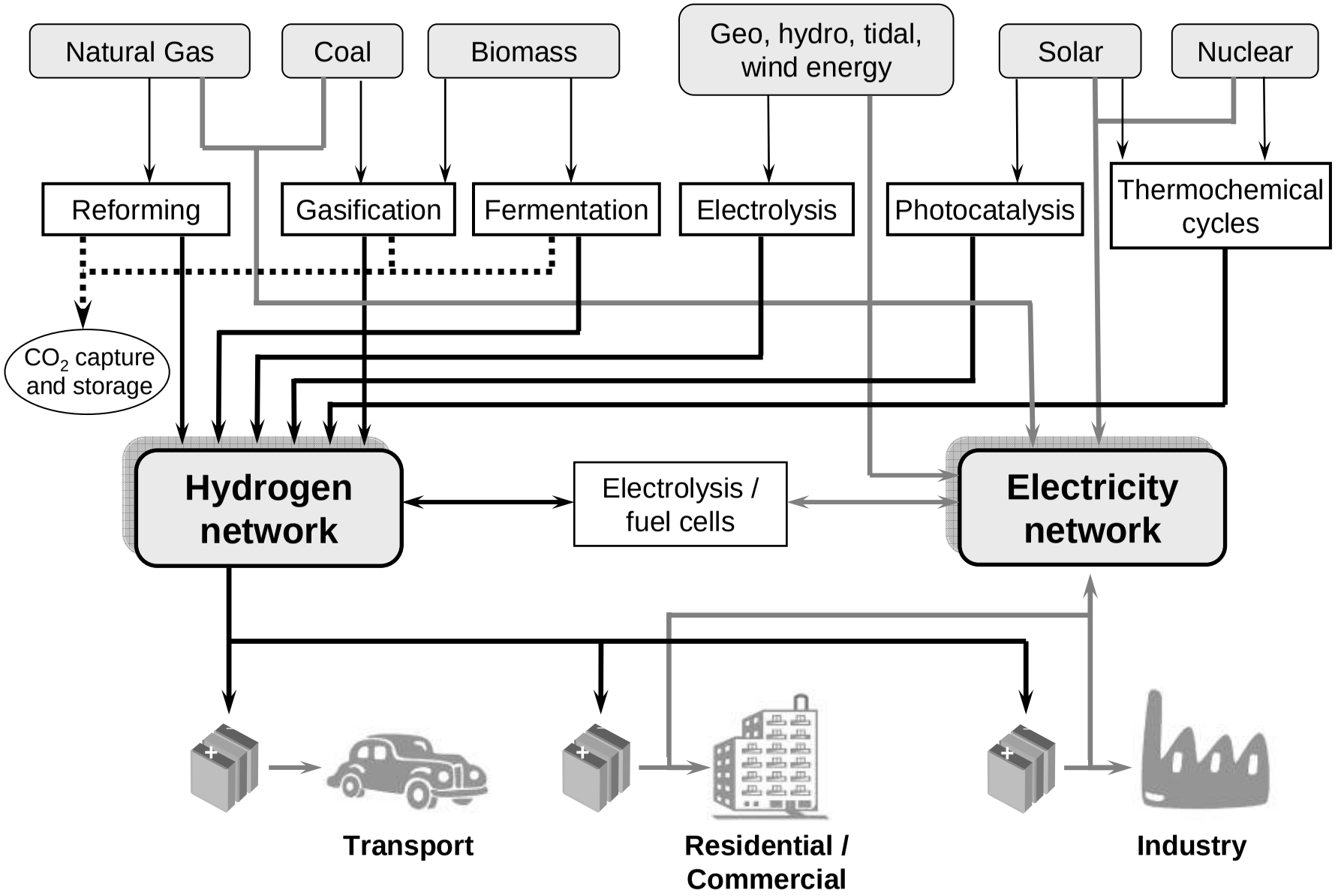
12 - 14 September 2007
University of Nottingham, UK

Current world energy scenario



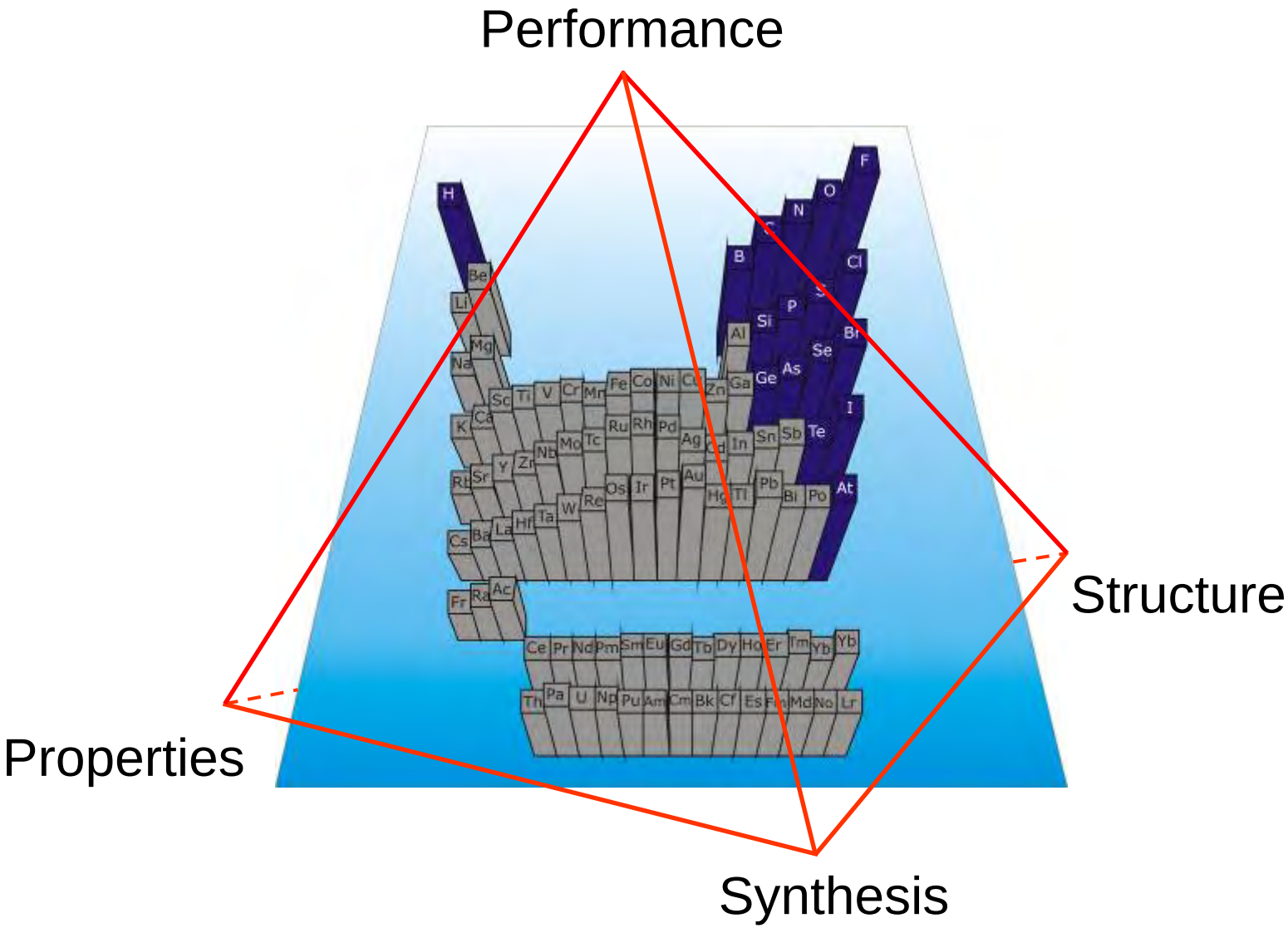
G. Marban, T. Valdes-Solis. *Int. J. Hydrogen Energy,* **32** (2007) 1625

Future energy scenario



Adapted from: G. Marban, T. Valdes-Solis. *Int. J. Hydrogen Energy,* **32** (2007) 1625

The four elements of materials science



Acknowledgements

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Matthew Lodge (University of Oxford)

Simon Johnson (University of Oxford)

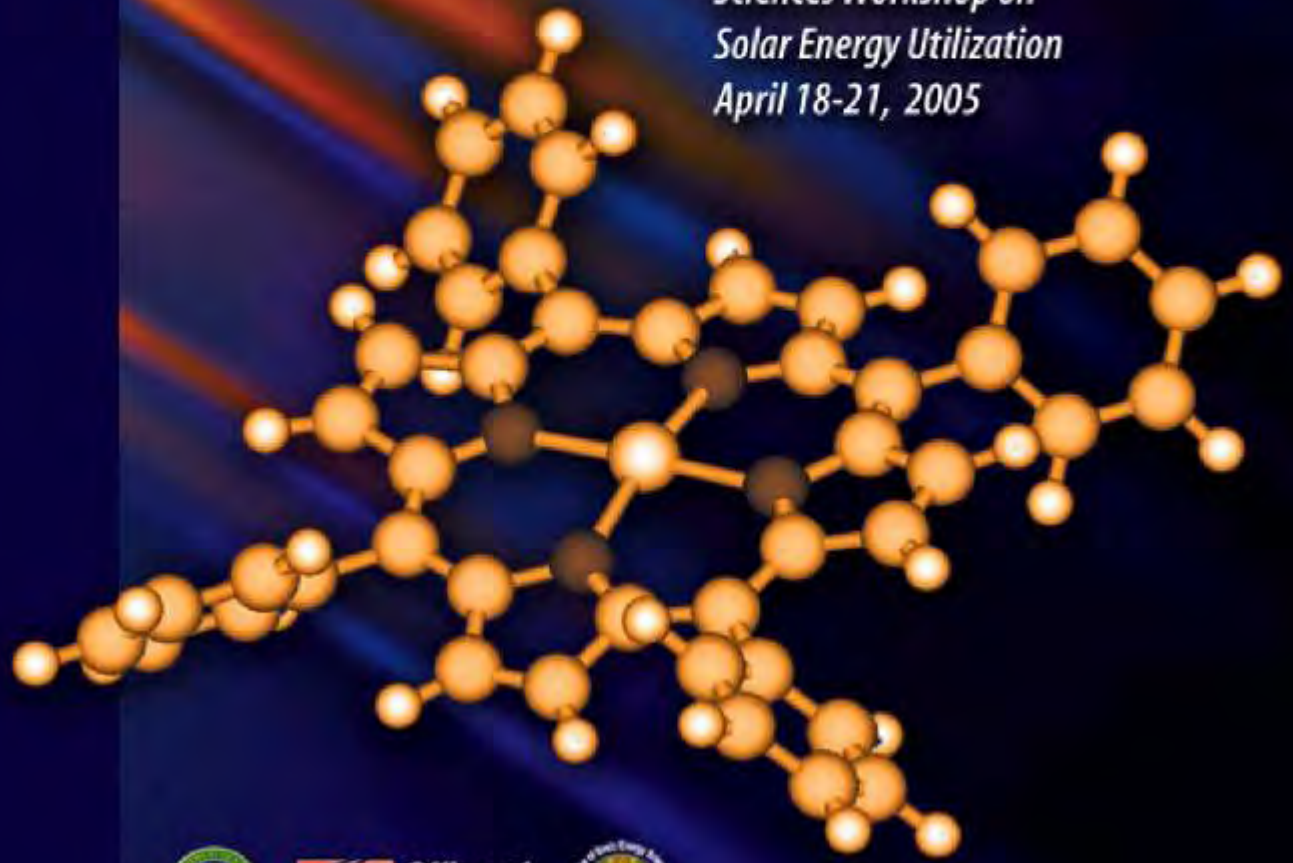
Paul Anderson (University of Birmingham)

Philip Chater (University of Birmingham)

Wojciech Grochala (University of Warsaw)

Basic Research Needs for Solar Energy Utilization

Report of the Basic Energy Sciences Workshop on Solar Energy Utilization
April 18-21, 2005



Office of Science
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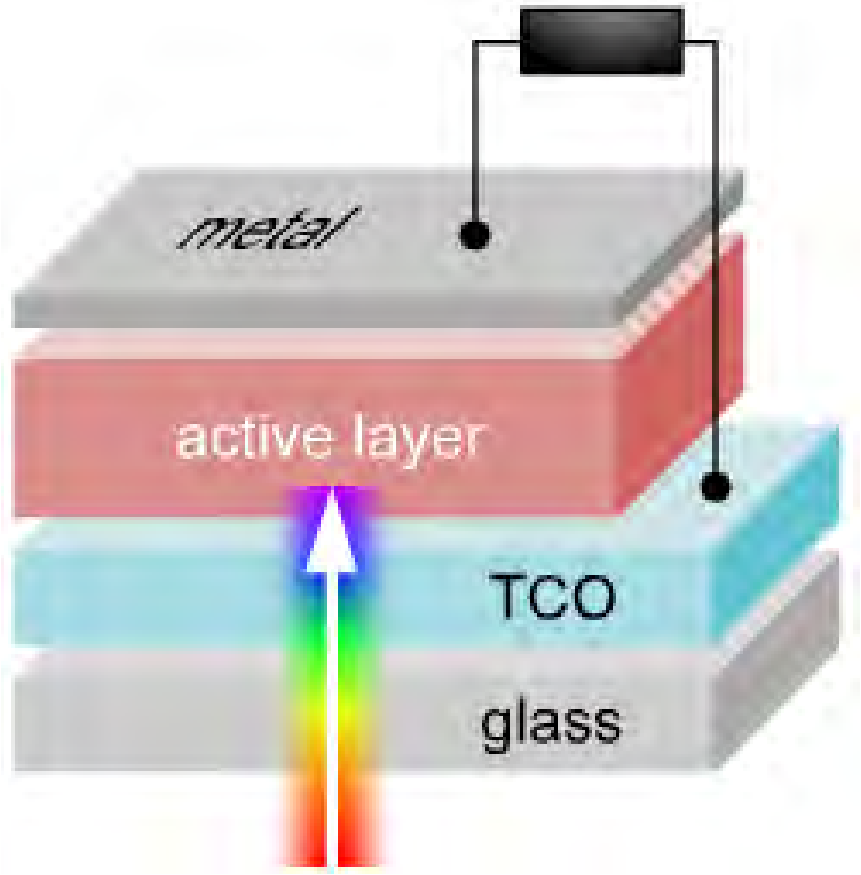
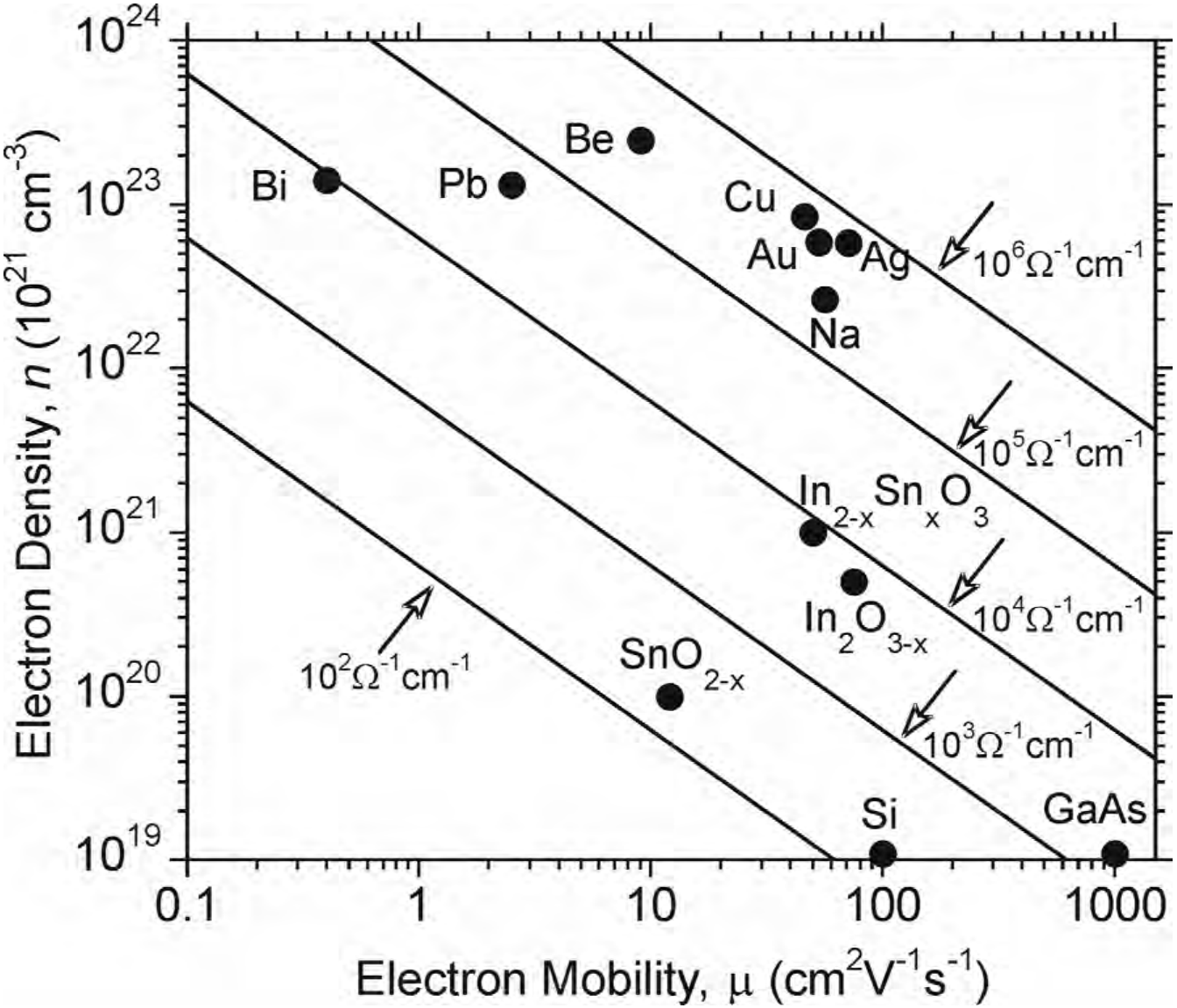
Solar cell structure

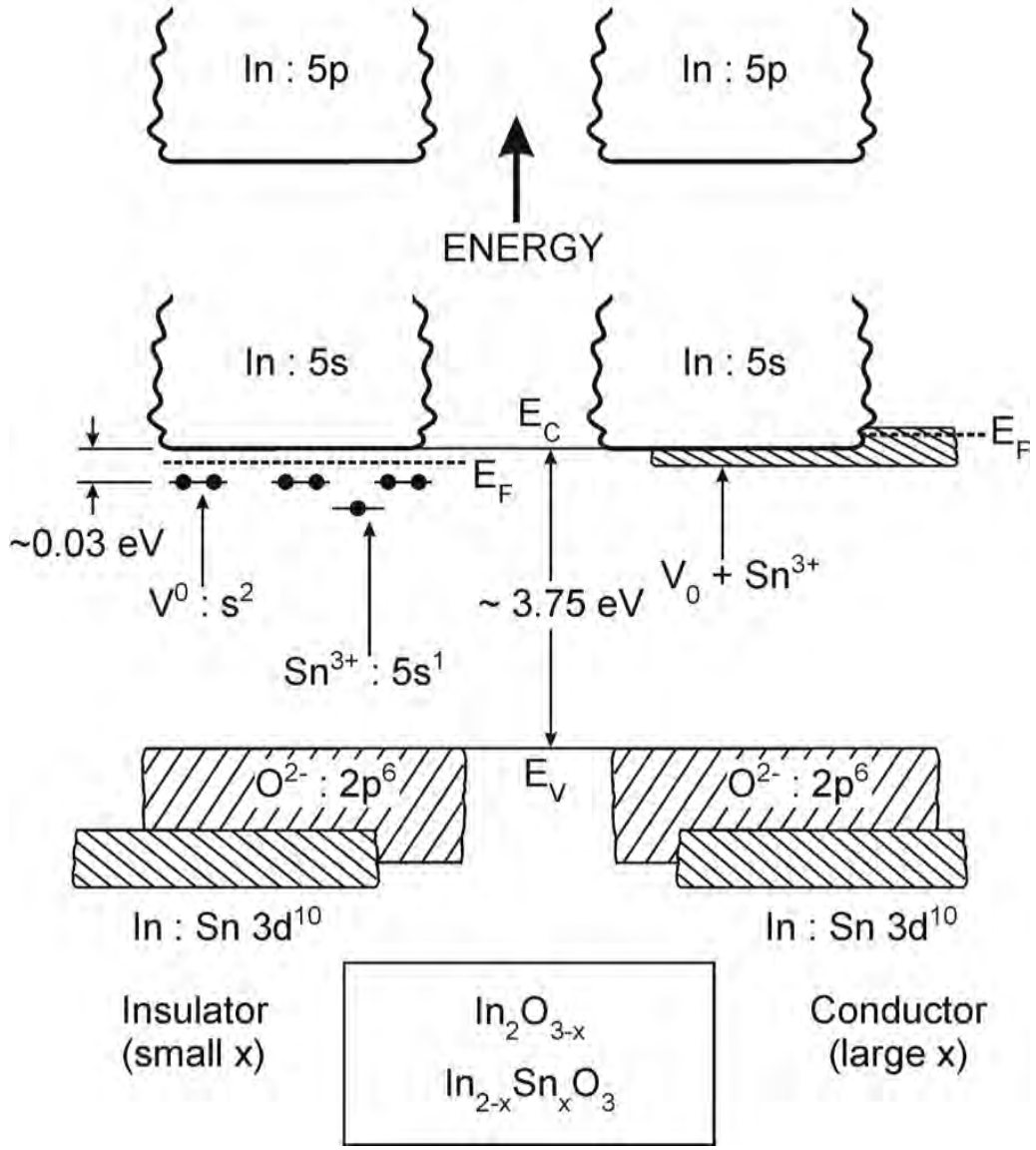


Materials sorting map



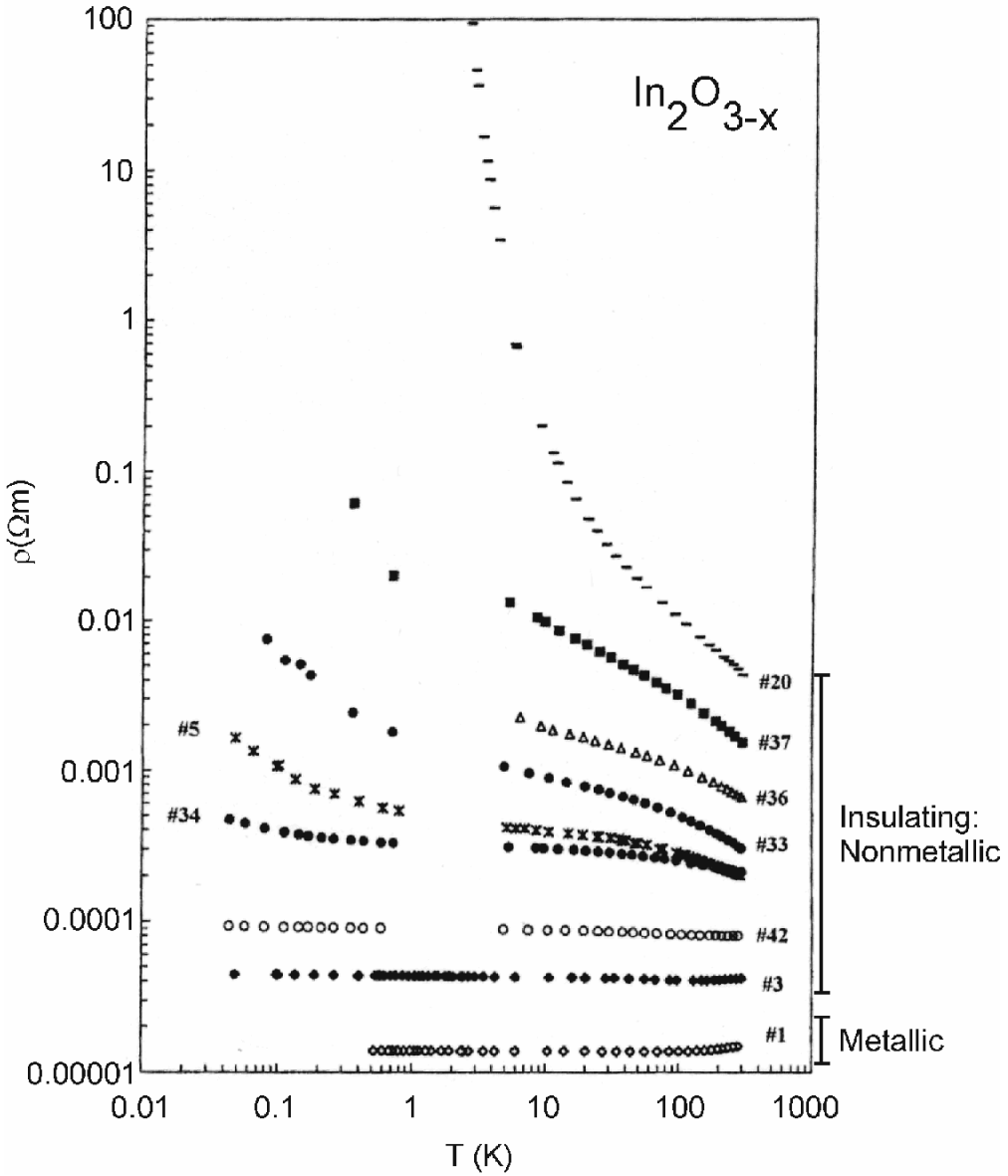
P.P. Edwards *et al* *Dalton Transactions*, **19** (2004) 2995

Band gap structure of Sn-doped In_2O_3



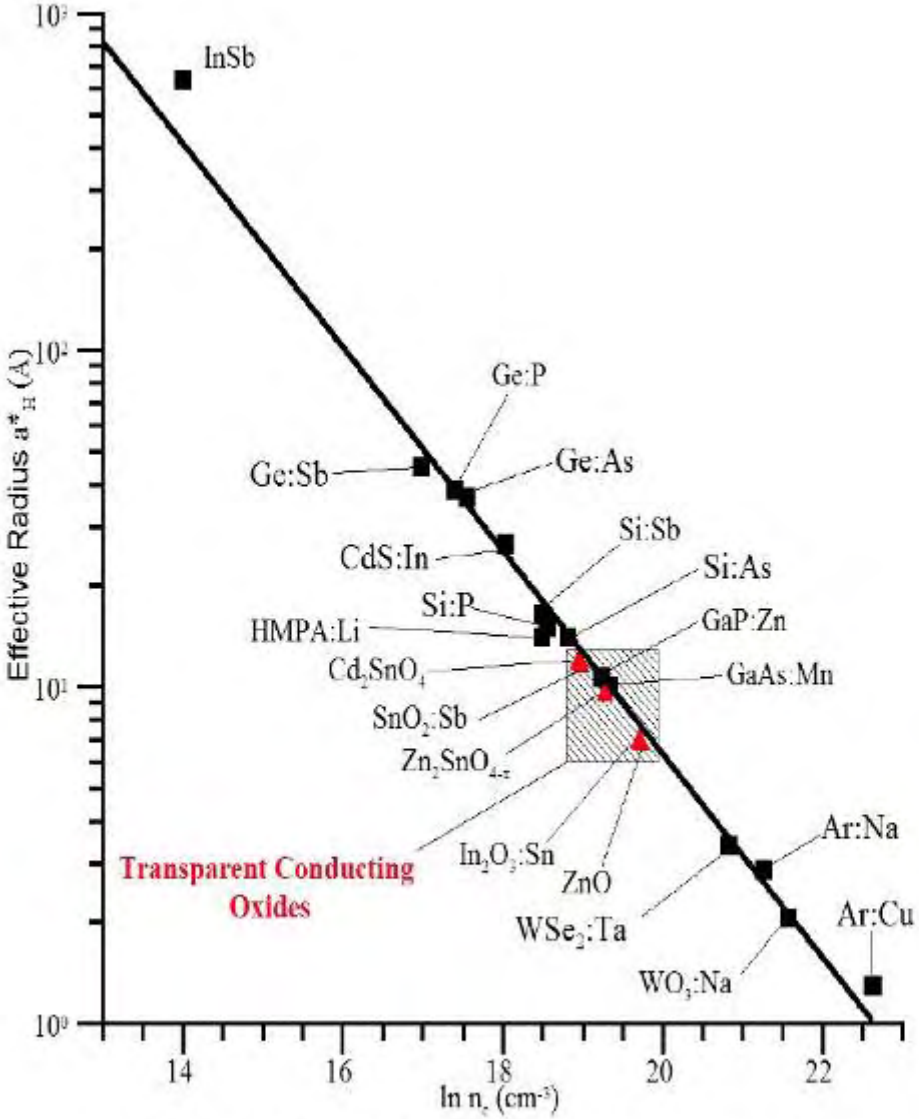
P.P. Edwards *et al* *Dalton Transactions*, **19** (2004) 2995

Temperature dependence of electrical resistivity of In_2O_3



P.P. Edwards *et al* *Dalton Transactions*, **19** (2004) 2995

Mott's criteria for metal–non-metal transition



Modified Edwards-Sienko plot highlighting metallic TCOs

The critical concentration of states for a metallic transition given by Mott criterion.

$$n_c^{1/3} a_H^* \approx 0.26 \pm 0.05$$

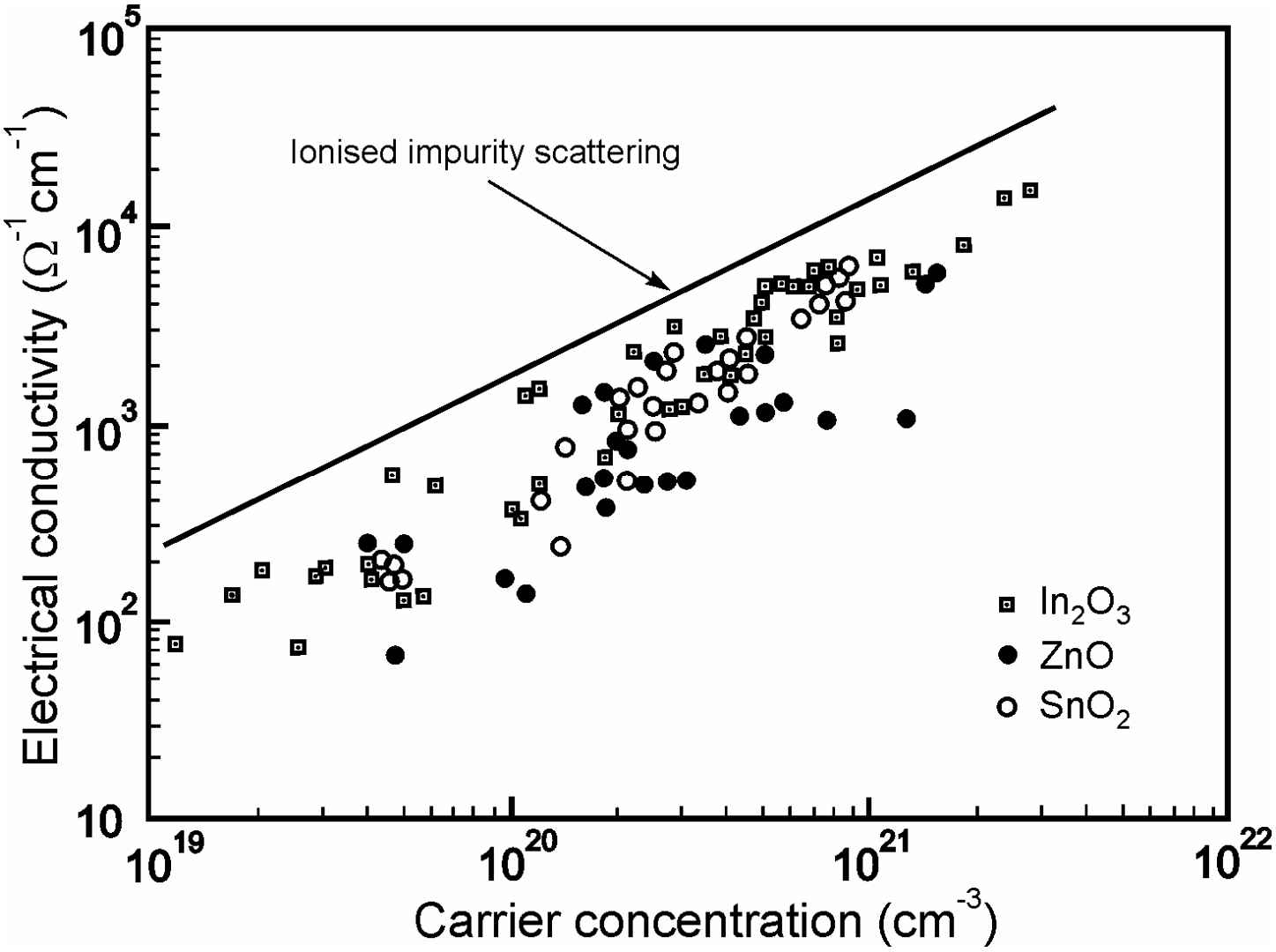
The radius of an impurity orbital a_H^* is given by

$$a_H^* = \frac{a_0 \varepsilon_r}{(m^*/m_0)}$$

…where ε_r is the relative permittivity and m^* is the effective mass.

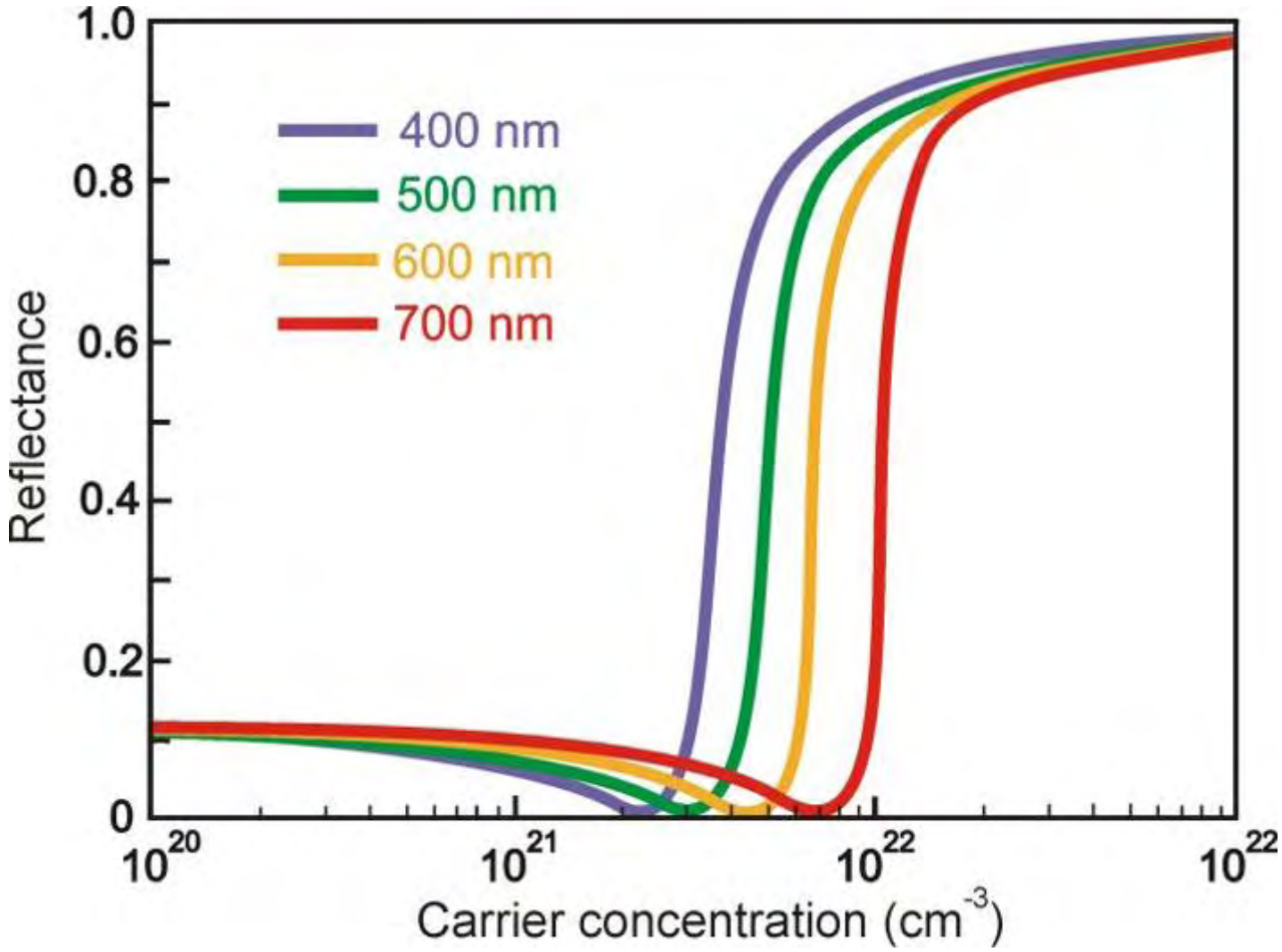
P.P. Edwards *et al* *Dalton Transactions*, **19** (2004) 2995

Impurity scattering in In_2O_3, ZnO and SnO_2



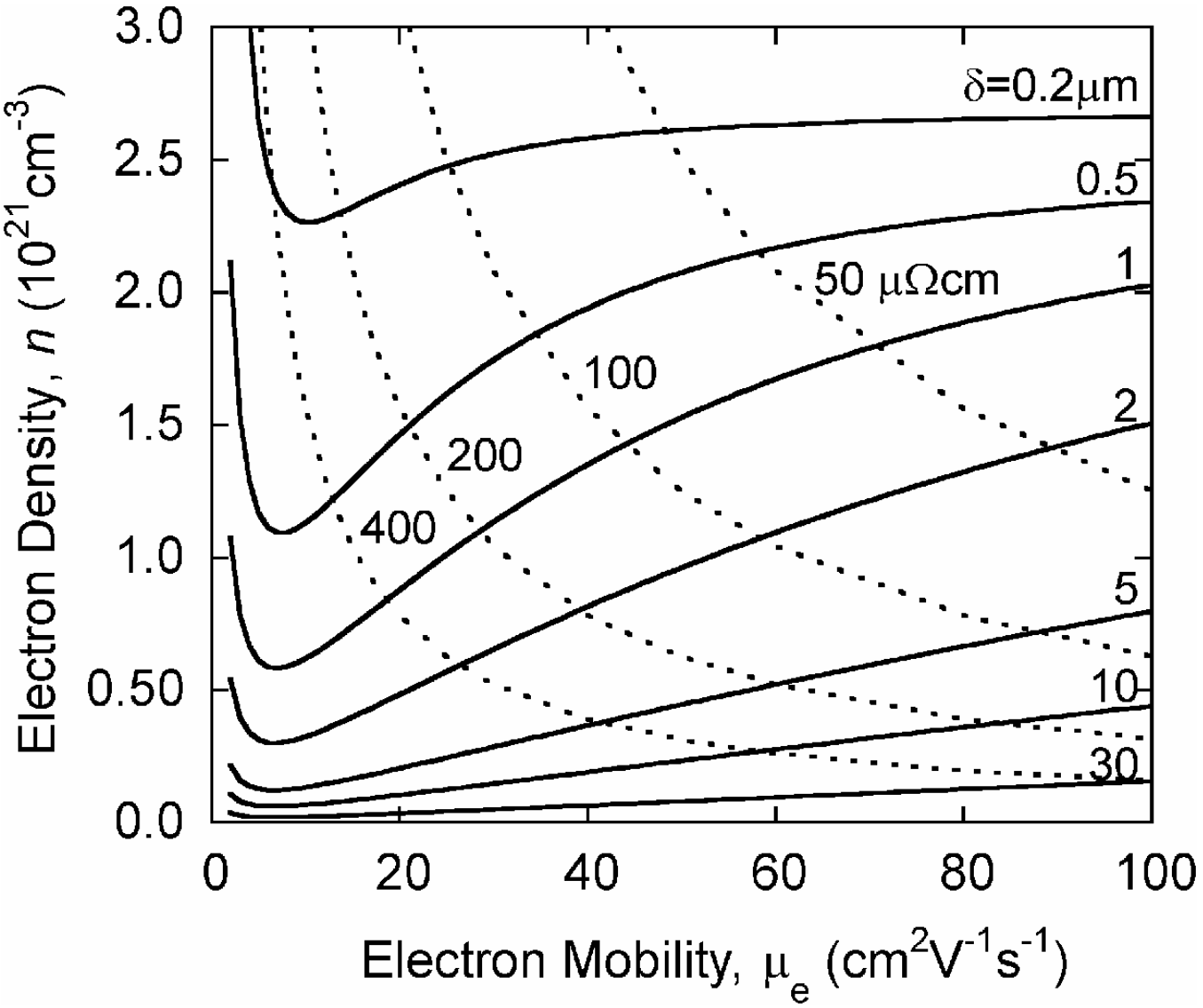
Adapted from: J.R. Bellingham *et al J. Mater. Sci. Lett.*, **11**, (1992) 263

The power reflection coefficient at the interface between a thick In_2O_3 layer and free space



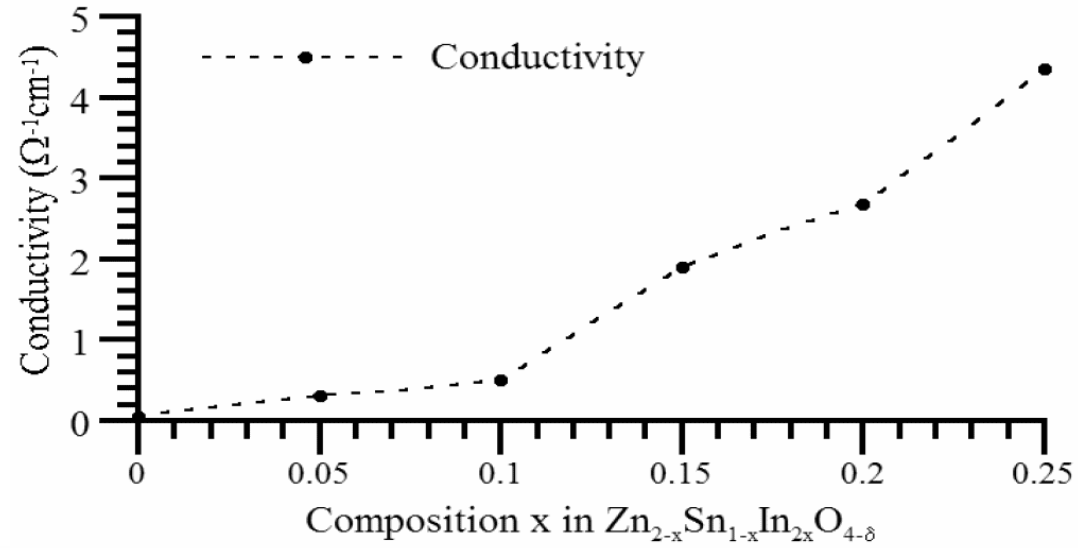
P.P. Edwards *et al* *Dalton Transactions*, **19** (2004) 2995

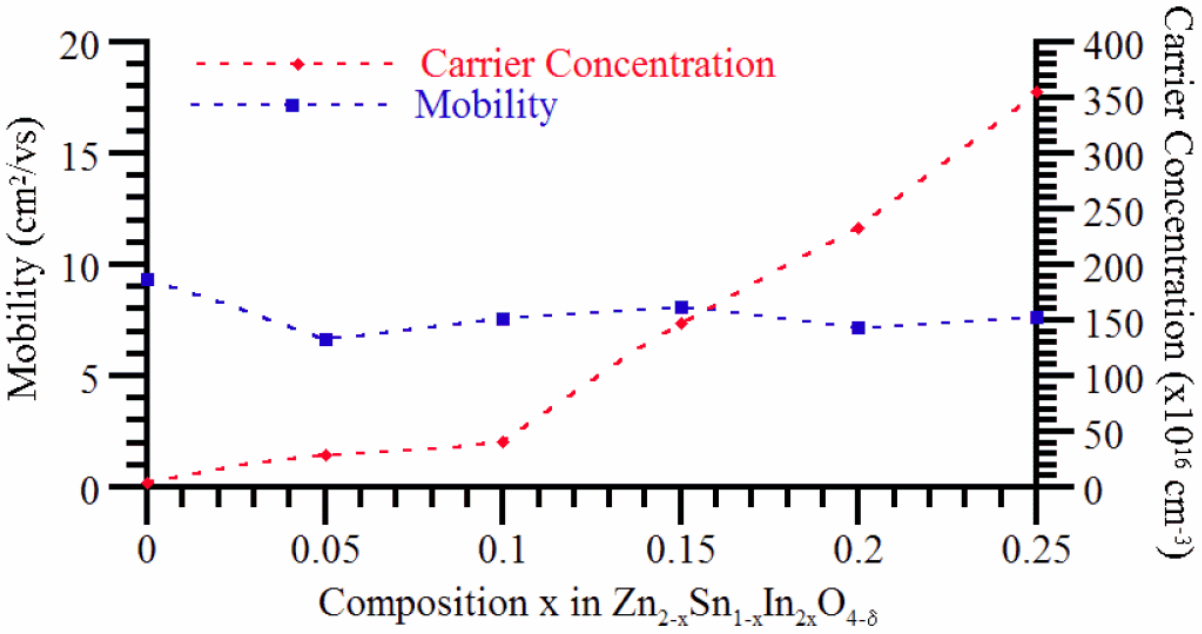
The skin depth δ (in units of μm) as a function of electron density n and mobility μ_e



P.P. Edwards *et al* *Dalton Transactions*, **19** (2004) 2995

Electrical conductivity, carrier concentration and carrier mobility in $Zn_{2-x}Sn_{1-x}In_{2x}O_{4-\delta}$

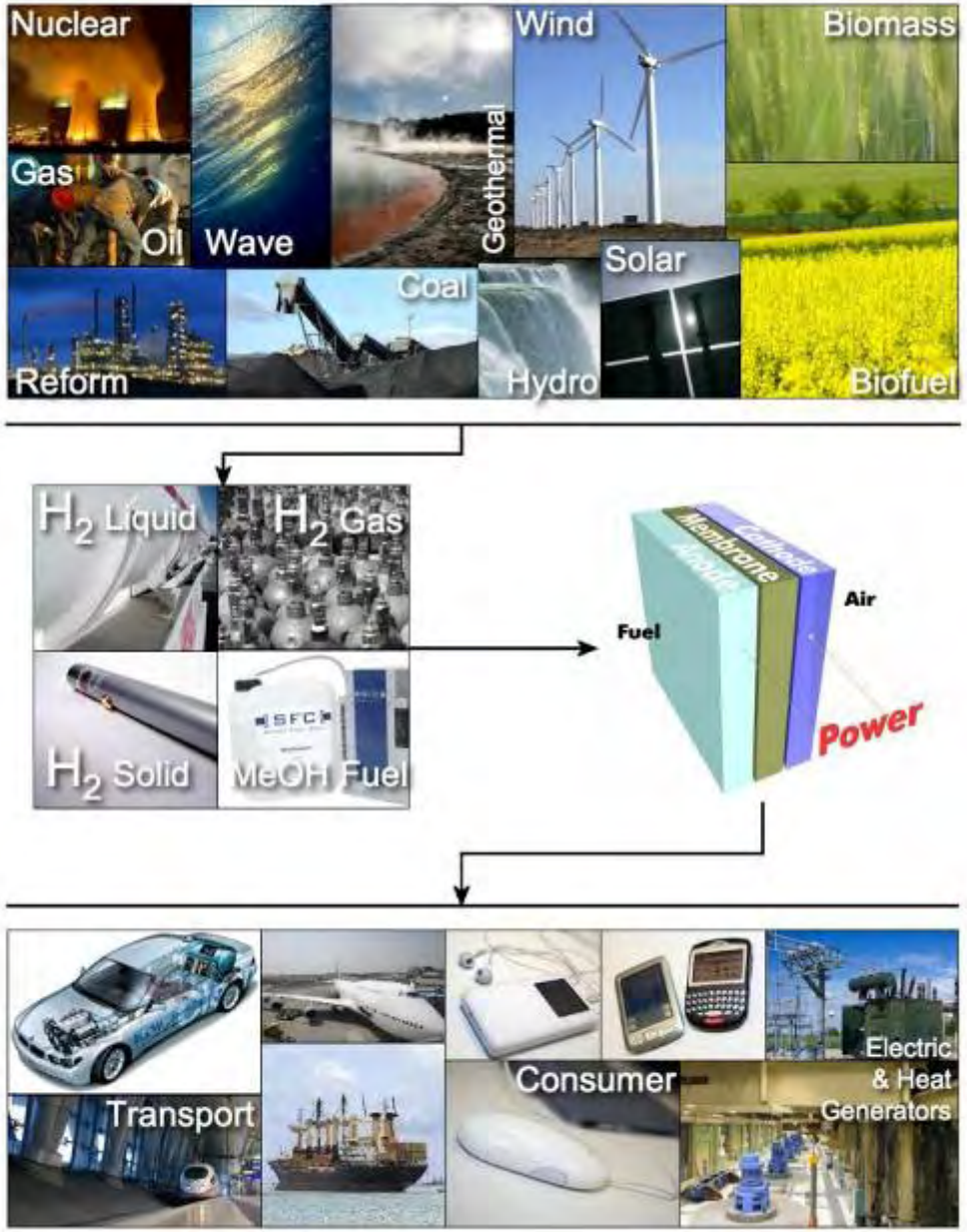




Main requirements for Transparent Conducting Oxides

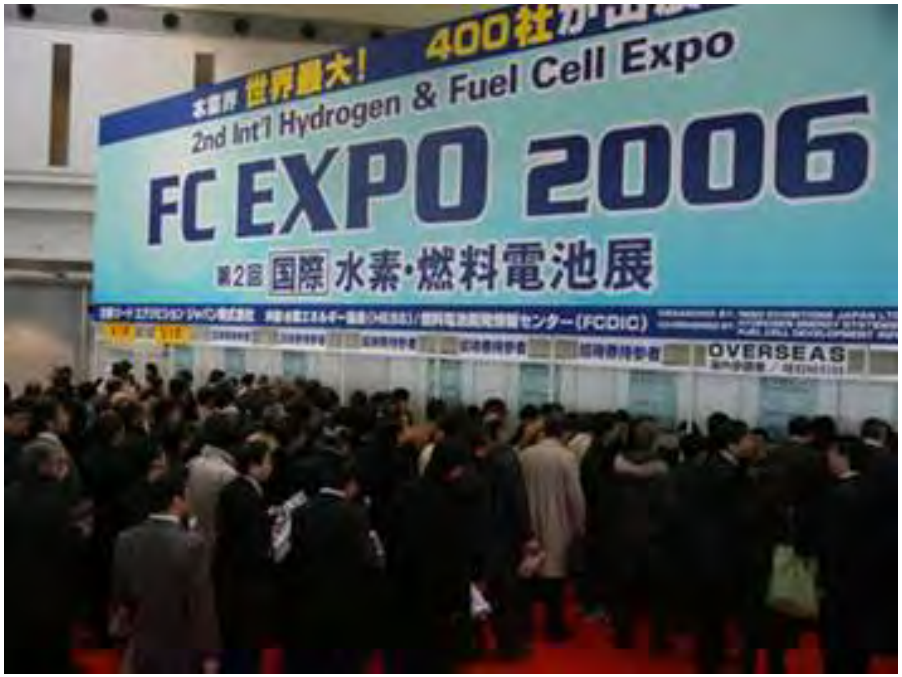
• **Optical Transparency**	$E_g > 3$ eV	Oxide composition
• **Carrier concentration**	$10^{20} – 10^{21}$ cm^{-3}	Doping
• **Carrier Mobility**	>100 cm^{2}V^{-1}s^{-1}	Scattering, relaxation time and effective mass

Hydrogen as an energy carrier



Hydrogen and Fuel Cell Expo 2006

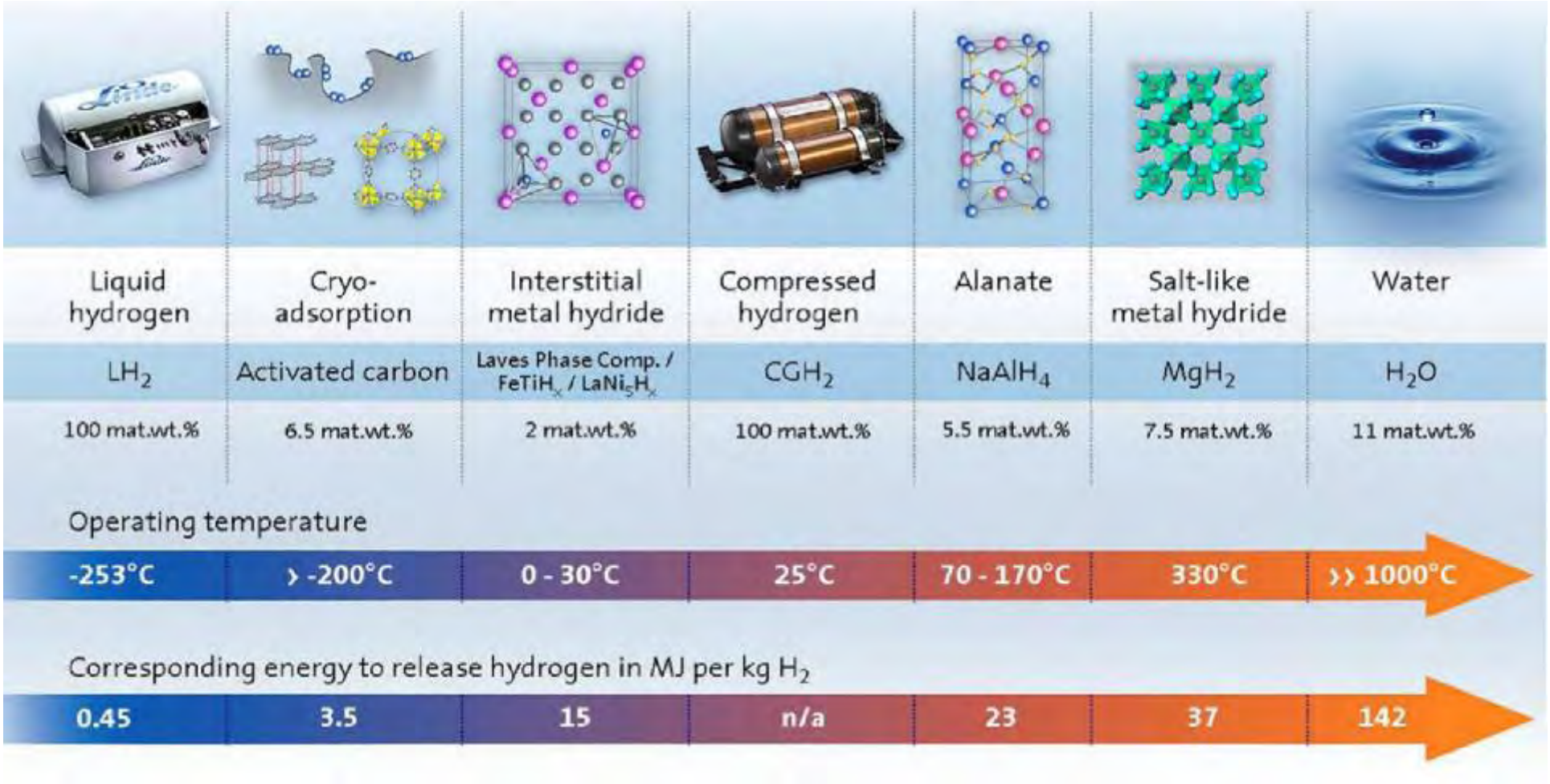
400 Exhibitors, 23,039 Professional Visitors



"There exists the necessity for an epoch-making advance in new materials for hydrogen storage…. This is the hardest challenge"

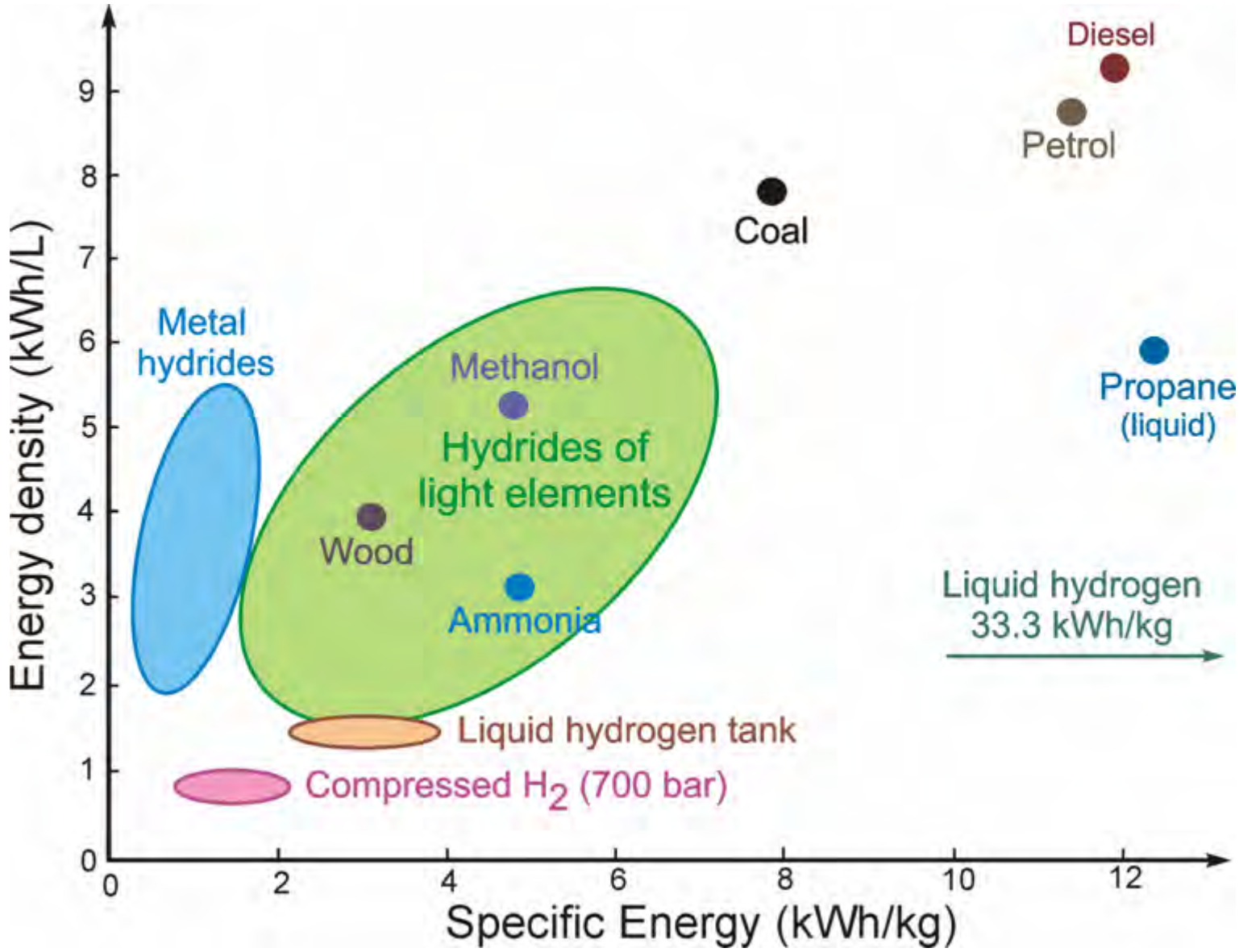
Masatami Takimoto
Executive Vice President, Toyota Motor Corporation

Operating regimes for various hydrogen storage technologies

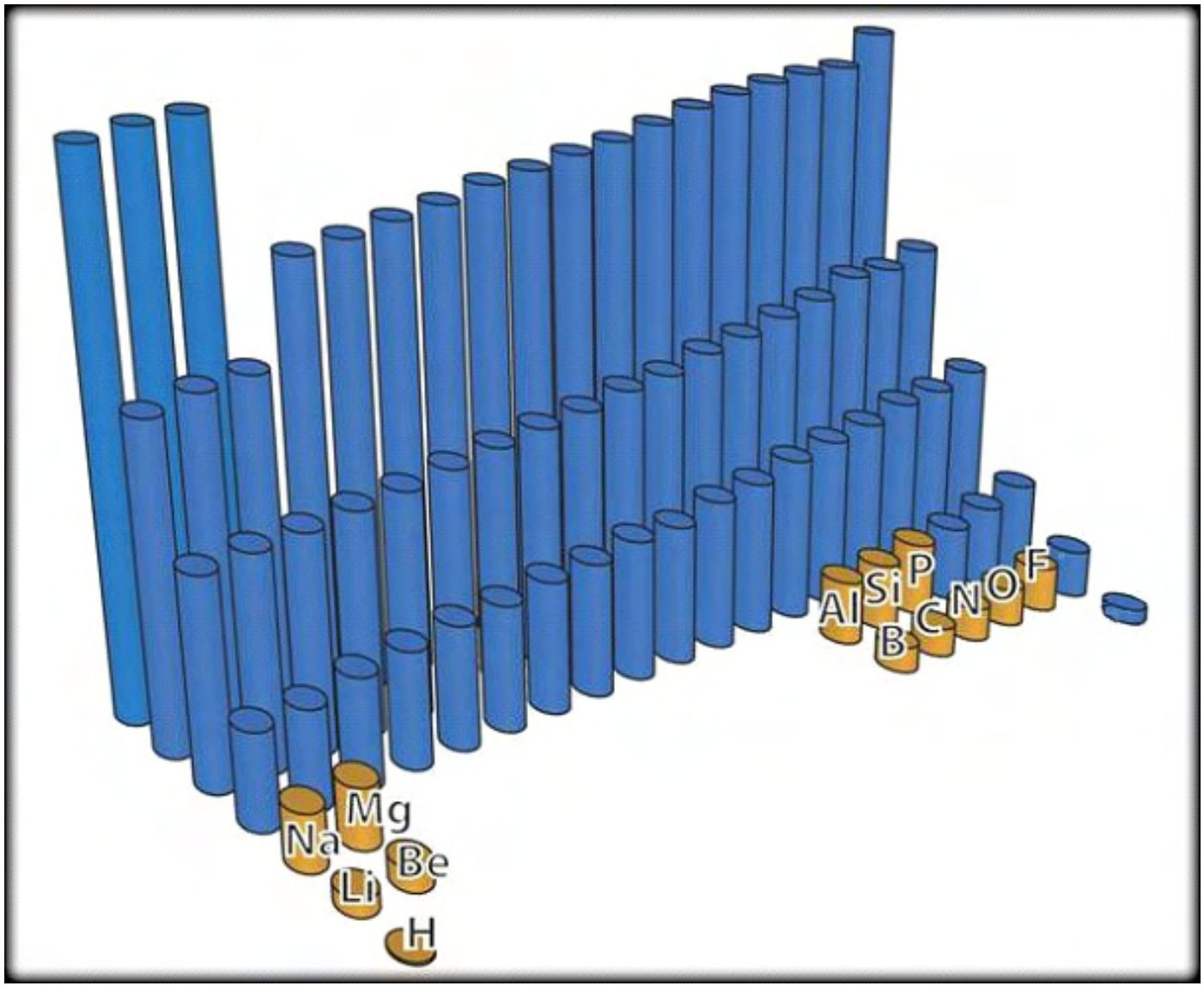


R.Helmolt, U.Eberle (General Motors), *J. Power Sources*, 2007, 165, p.833

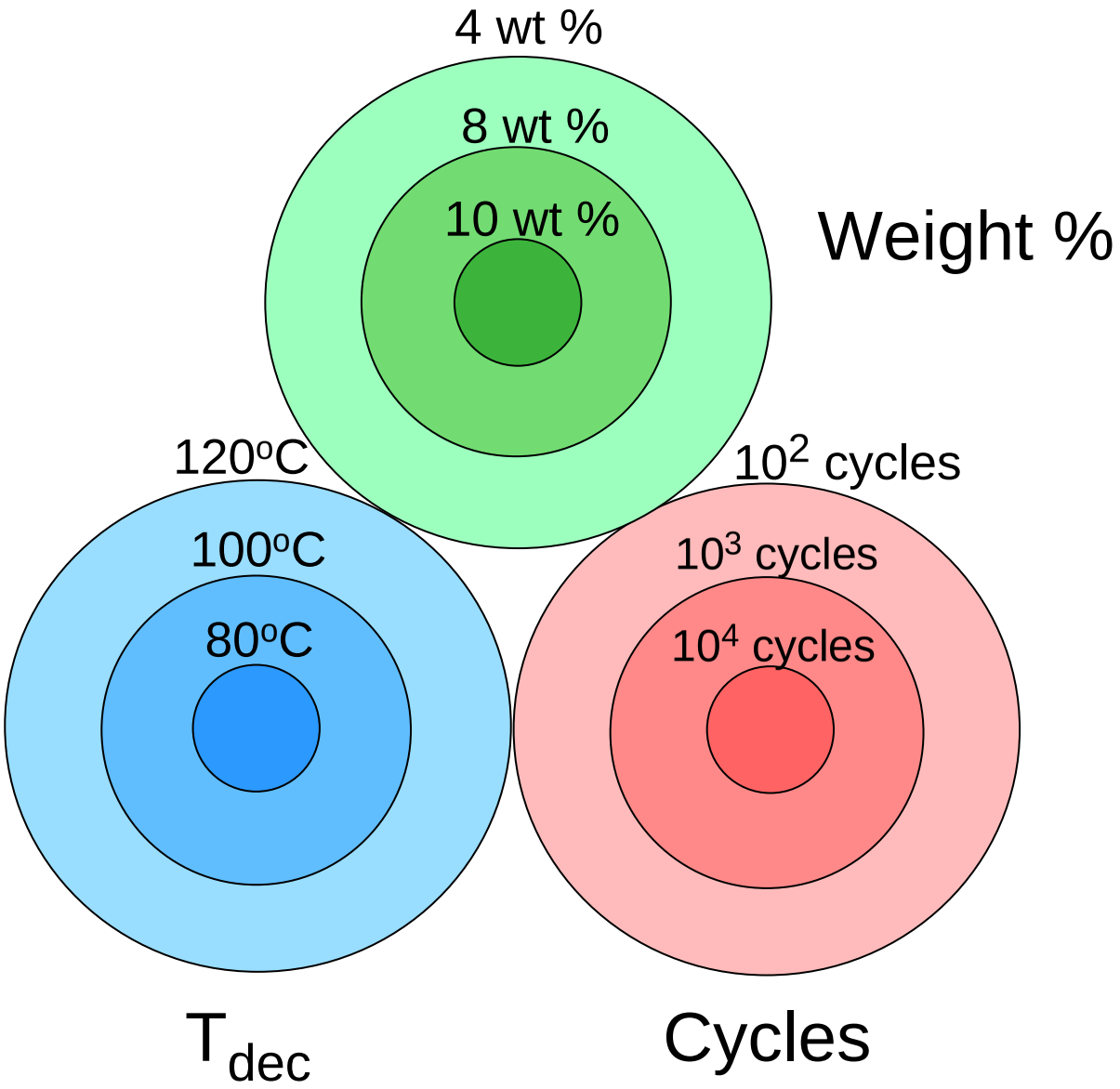
Gravimetric and volumetric densities of various energy storage options



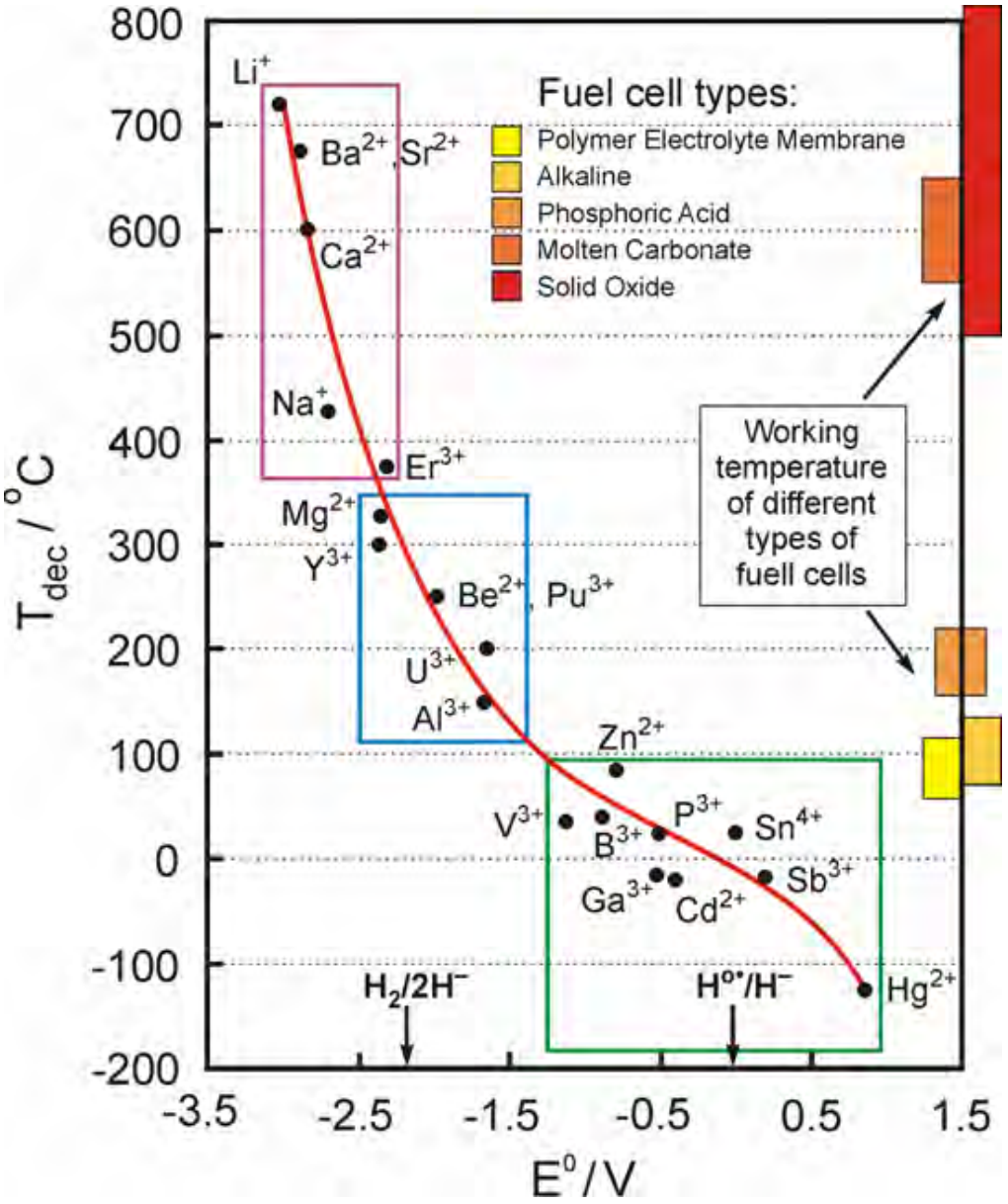
Hydrogen Energy Storage:
The Challenge of the Light Periodic Table



Performance limitations for hydrogen storage materials

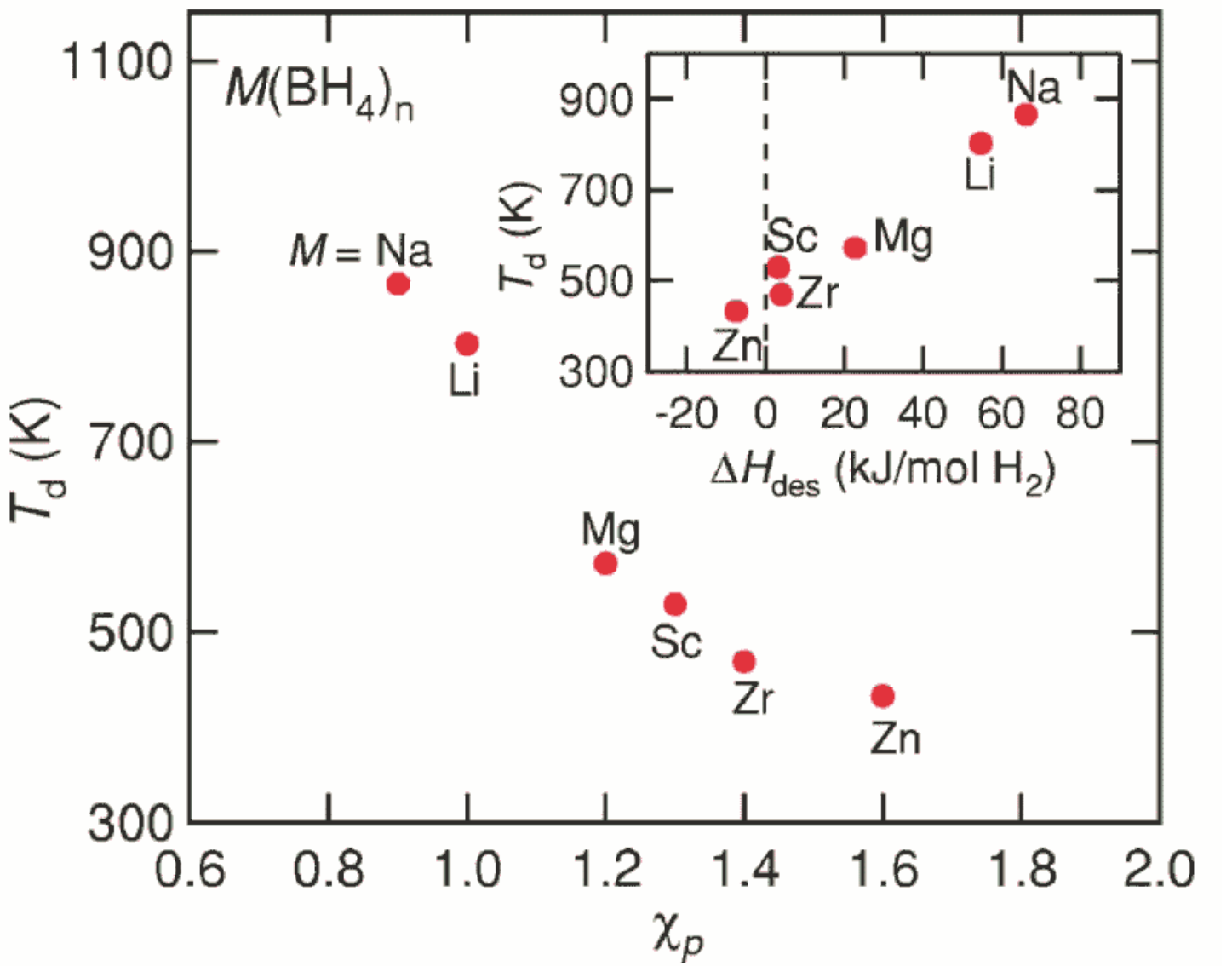


Binary hydrides: beginnings of a sorting map



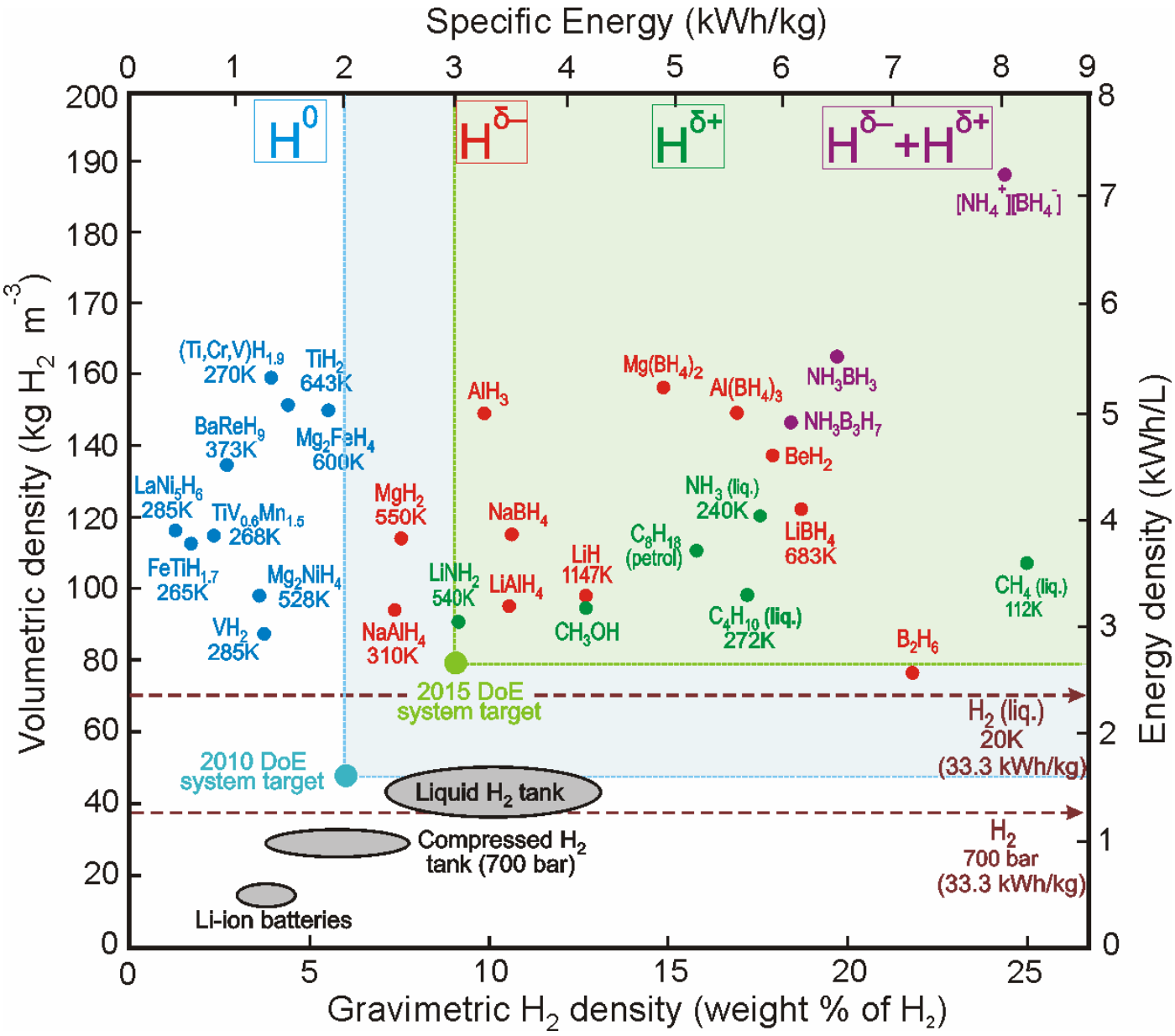
W. Grochala and P.P. Edwards, *Chem. Rev.*, 2004, **104**, 1283

The desorption temperature T_d as a function of the Pauling electronegativity χ_p

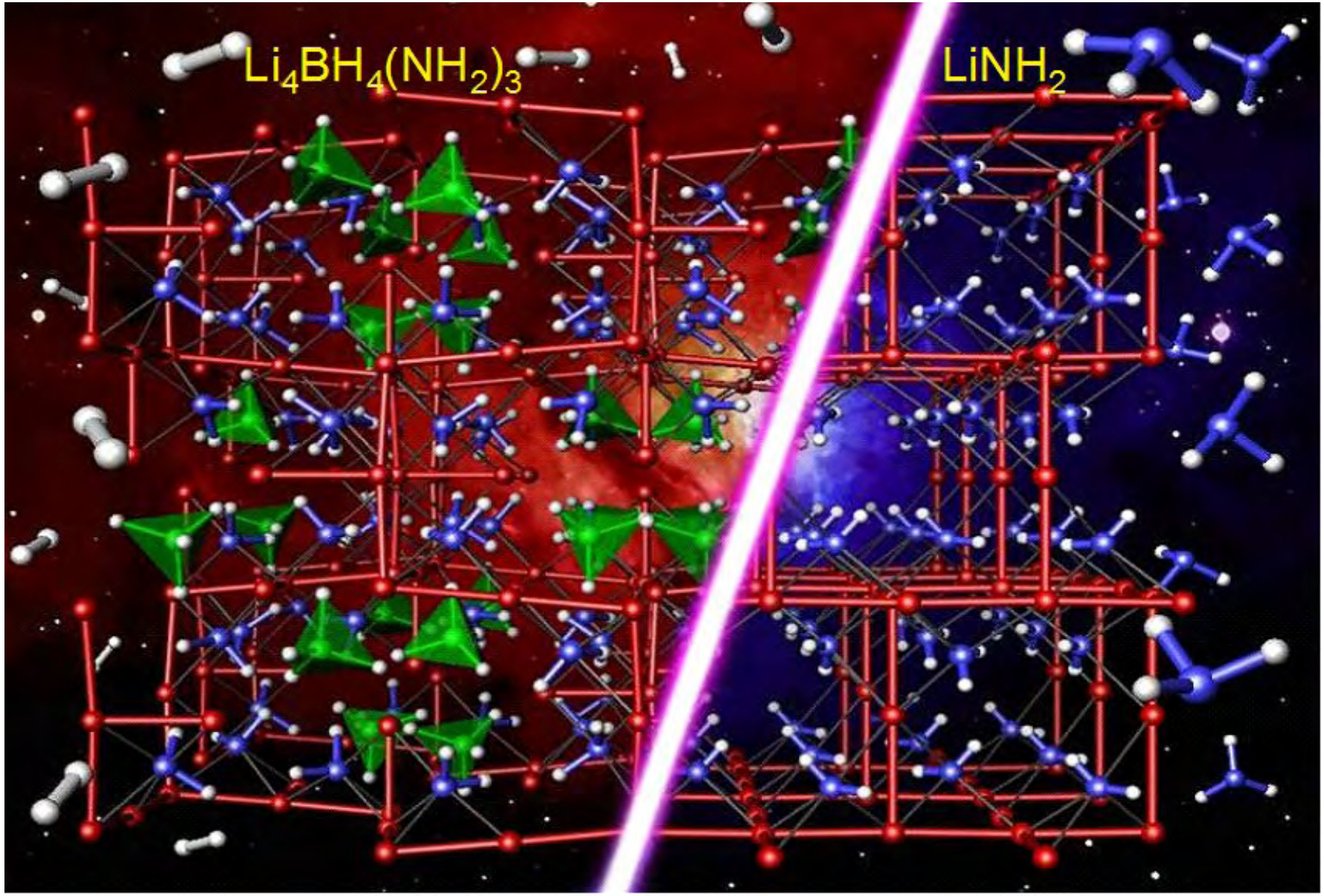


Y. Nakamori *et al*, *Phys. Rev. B*, **74** (2004) 045126

Gravimetric and volumetric densities of various hydrogen storage options

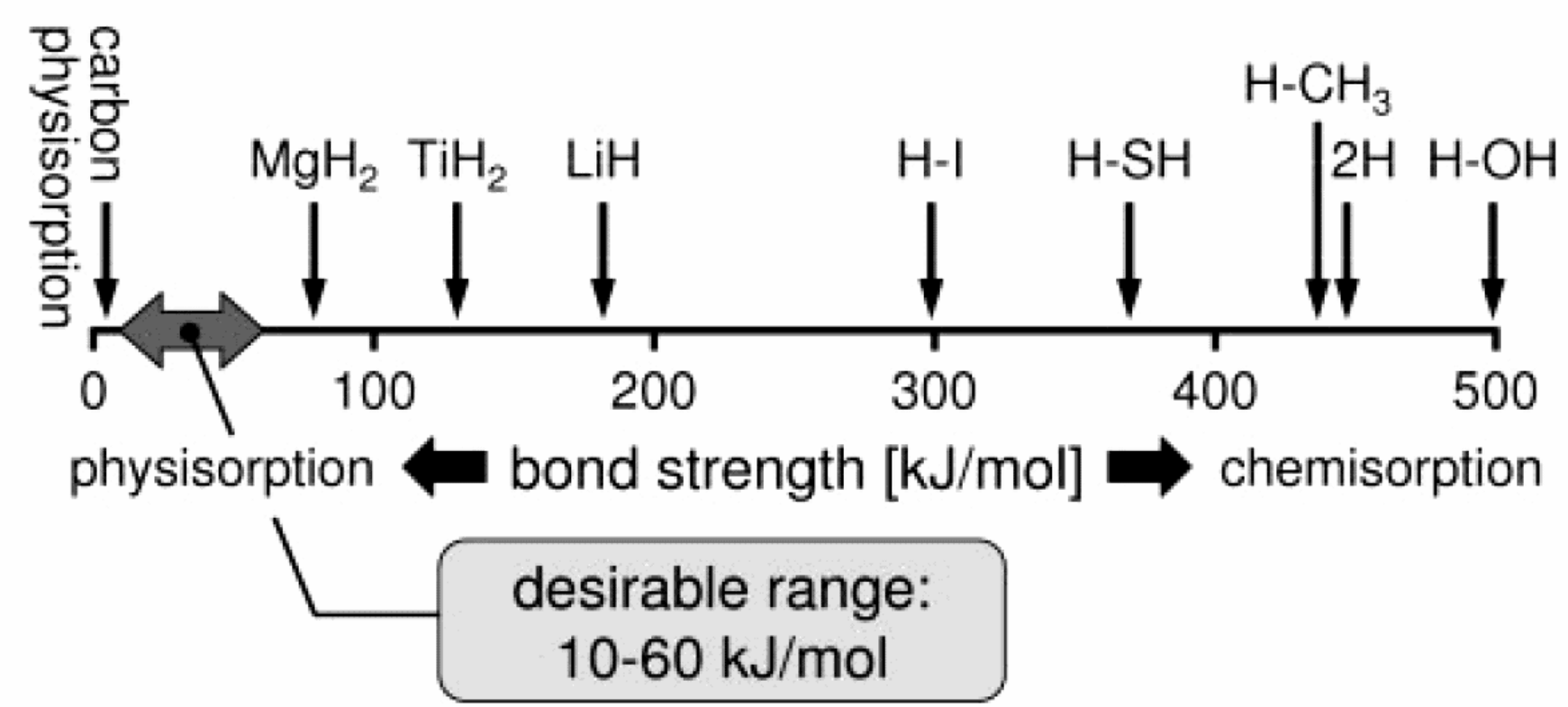


The new advance: mixed anions. $Li_4BH_4(NH_2)_3$: 11wt%



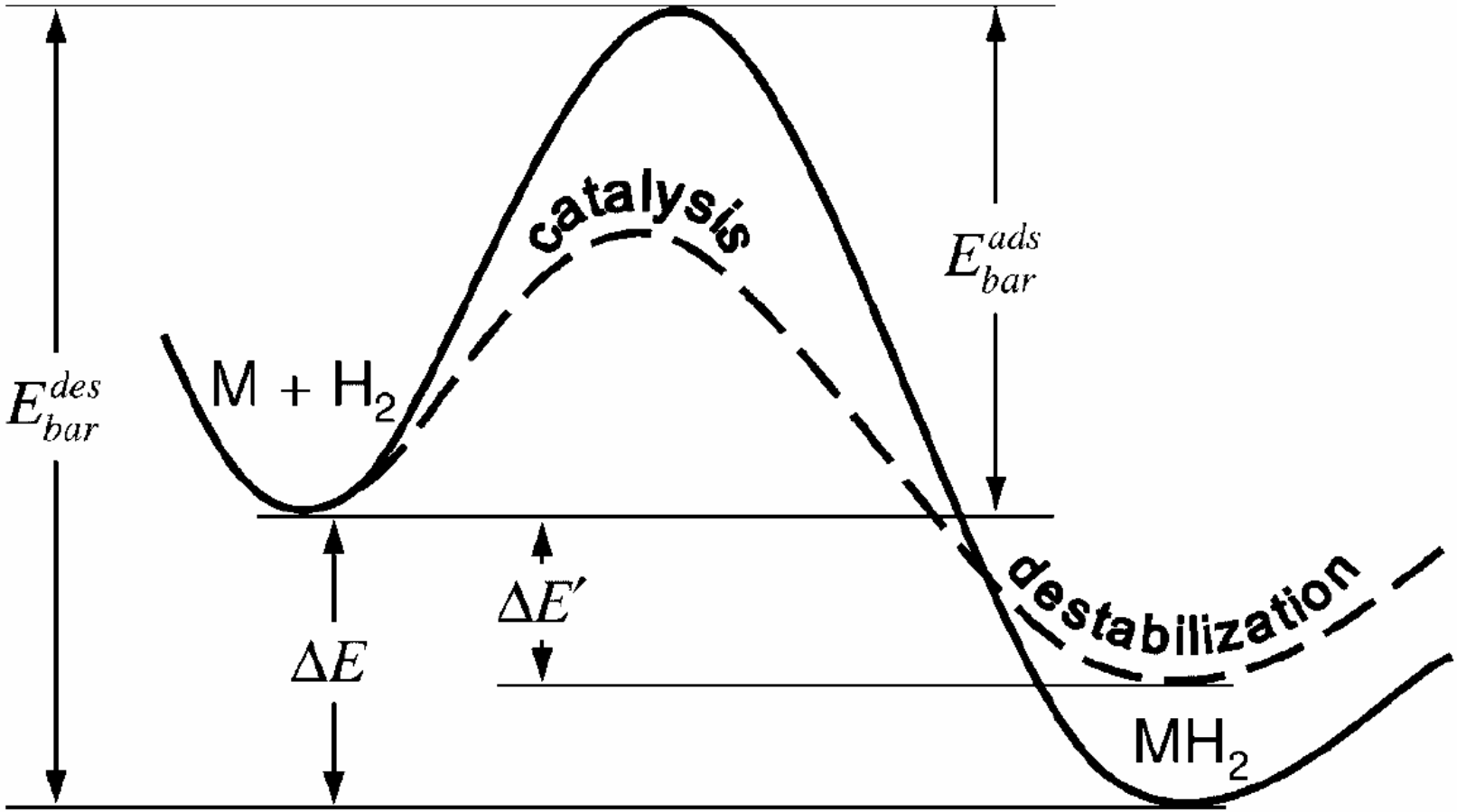
P. Chater *et al*, *Chem. Commun.* (2006) 2439

Targeted range of bond strengths for hydrogen release



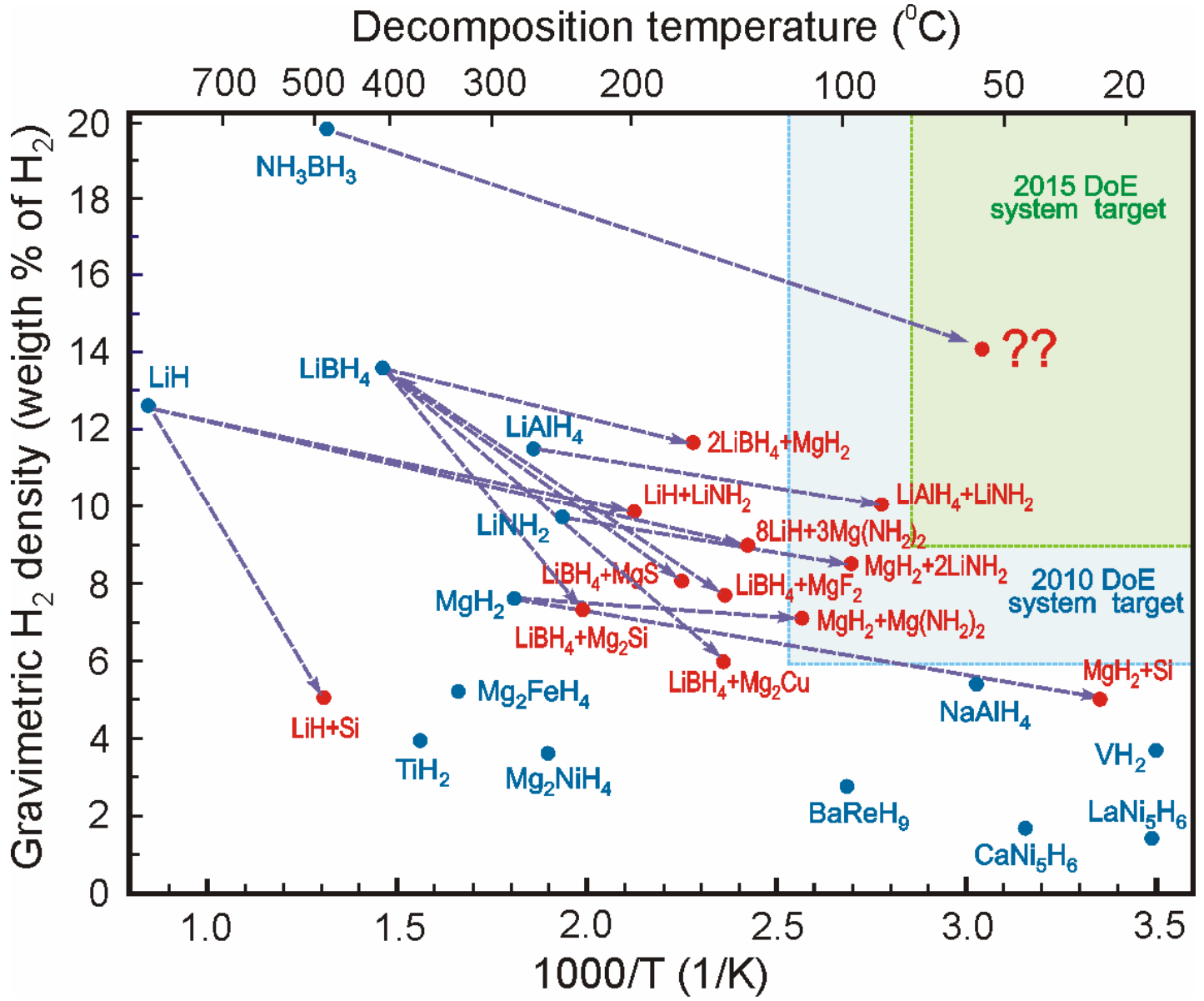
V. Berube *et al*, *Int. J. Energy Res.*, **31** (2006) 637

Energy barrier for hydrogen adsorption and desorption



V. Berube *et al*, *Int. J. Energy Res.*, **31** (2006) 637

Effect of destabilisation on gravimetric hydrogen density and hydrogen decomposition temperature



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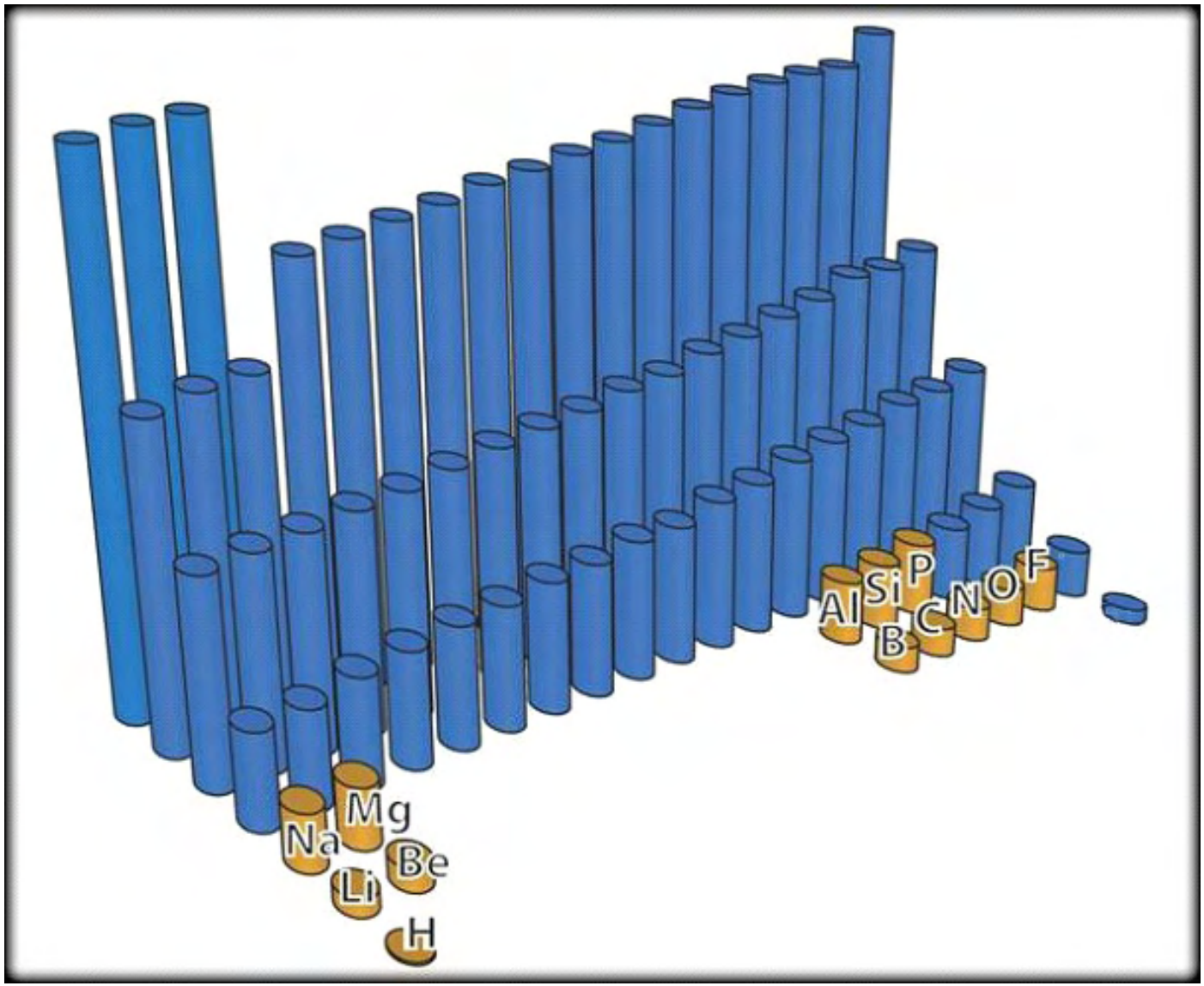
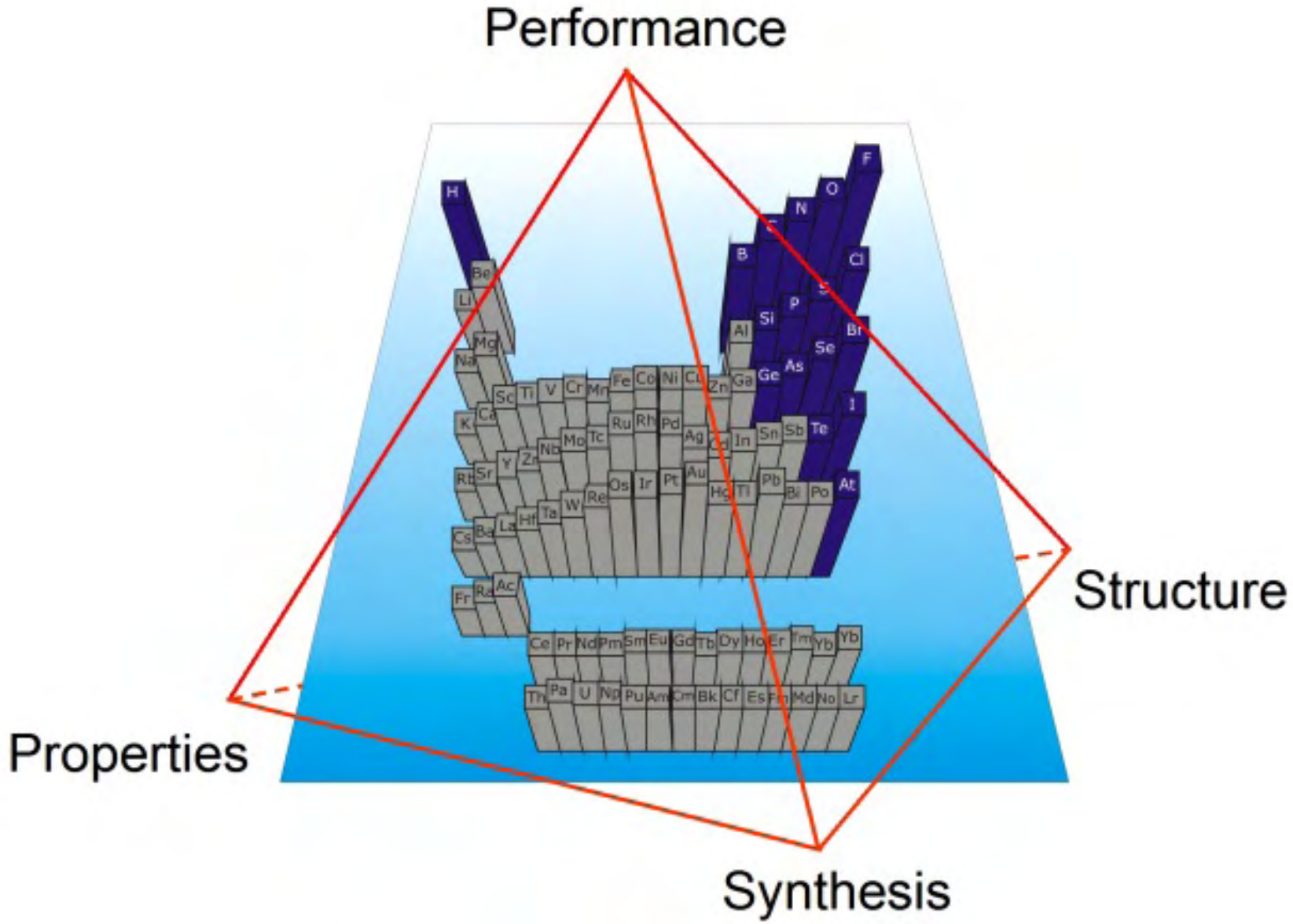
The Challenge of the Light Periodic Table



Four elements of materials chemistry



The Perfect Store for Hydrogen
Not Yet Discovered

Only a few elements can make suitable lightweight storage materials

Li	B	C	N	Na	Mg	Al	P	Si

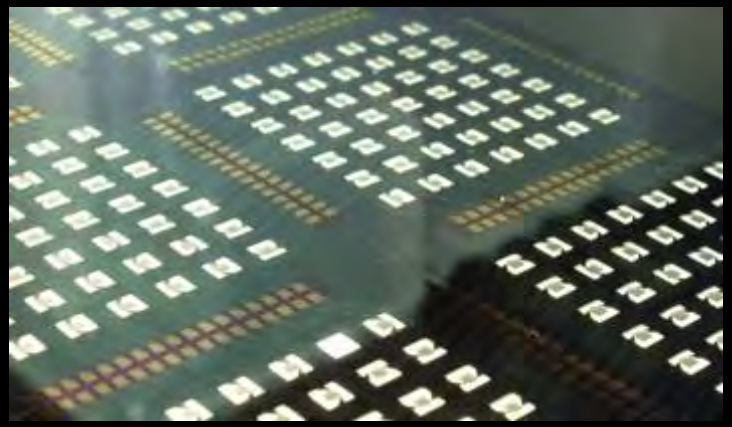
Make tens of thousands of new materials from combinations of these elements

Rapidly identify and test these new materials

Robotic Synthesis Industrial Partners

Together will aim to discover new materials with > 6wt% hydrogen storage

Primary screen



Ilika combinatorial PVD plate

diamond

How: Physical Vapour Deposition
Where: Ilika / RAL
Throughput: 10^4 material pixels / day
Quantity/sample: ~10^{-12} g
Absorption characterisation: imaging
Structural fingerprinting: ESRF/diamond

Secondary screen

X-ray robot

Volumetric analysis

How: Robotic synthesis
Where: Oxford/RAL
Throughput: 10^2 samples / day
Quantity/sample: ~10^{-3} g
Absorption characterisation: Volumetric
Structure refinement: ESRF/diamond

Tertiary screen

ISIS

IGA apparatus

How: Chemical synthesis
Where: Oxford
Throughput: 1 sample / day
Quantity/sample: ~1g
Absorption characterisation: IGA
Full structural characterisation: ISIS

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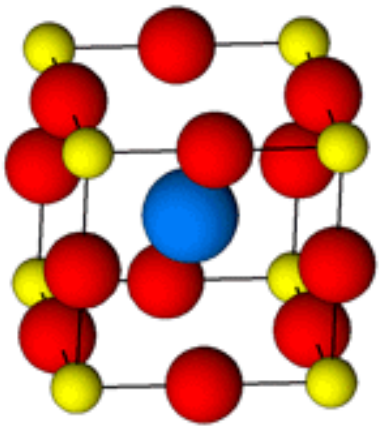
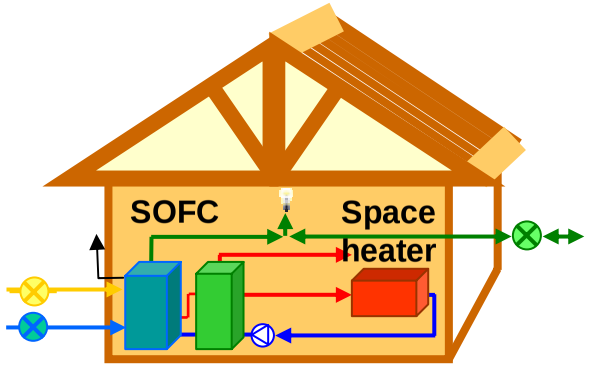


Outline

- Background & Methods
- Solid Oxide Fuel Cell (SOFC) Materials
  - Perovskite & Apatite structures
- Li Battery Cathode Materials
  - Olivine structures

Background&Methods

Fuel Cells



Local heat & power?

Lithium Batteries

Toyota Prius hybrid gas-electric car

Hybrid electric cars?

Fuel Cells

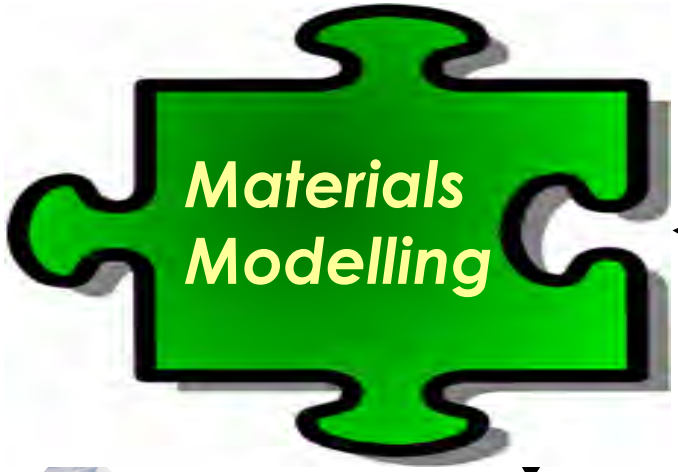
Lithium Batteries

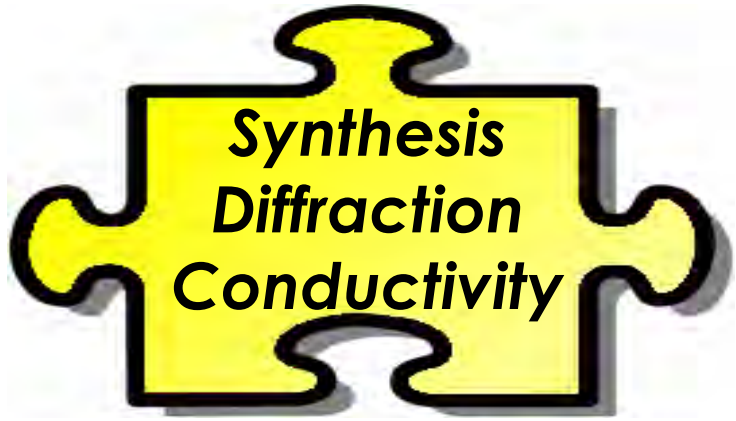
"Materials Challenge"

New or improved materials are key to major advances

Developing New Functional Materials

Combined Approach

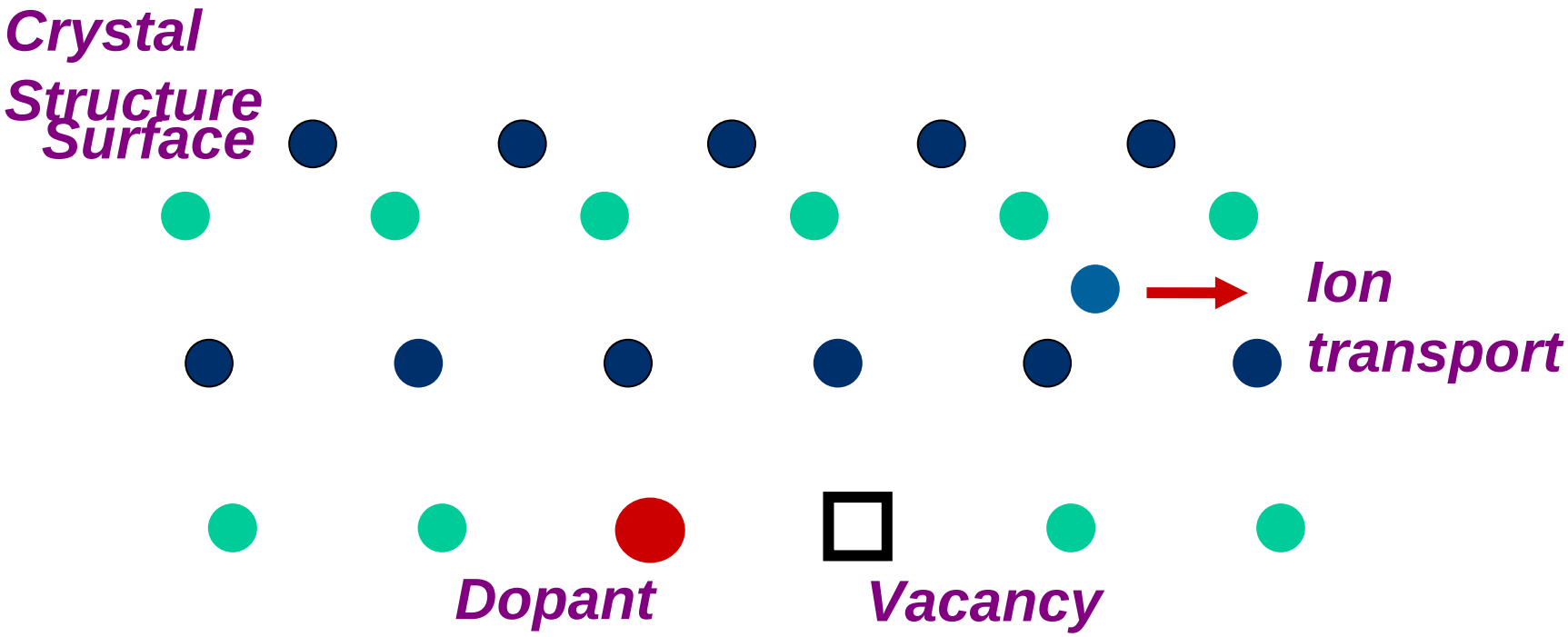




Atomistic & DFT Methods
Complement expt
Atomic-scale probe
Predictive value

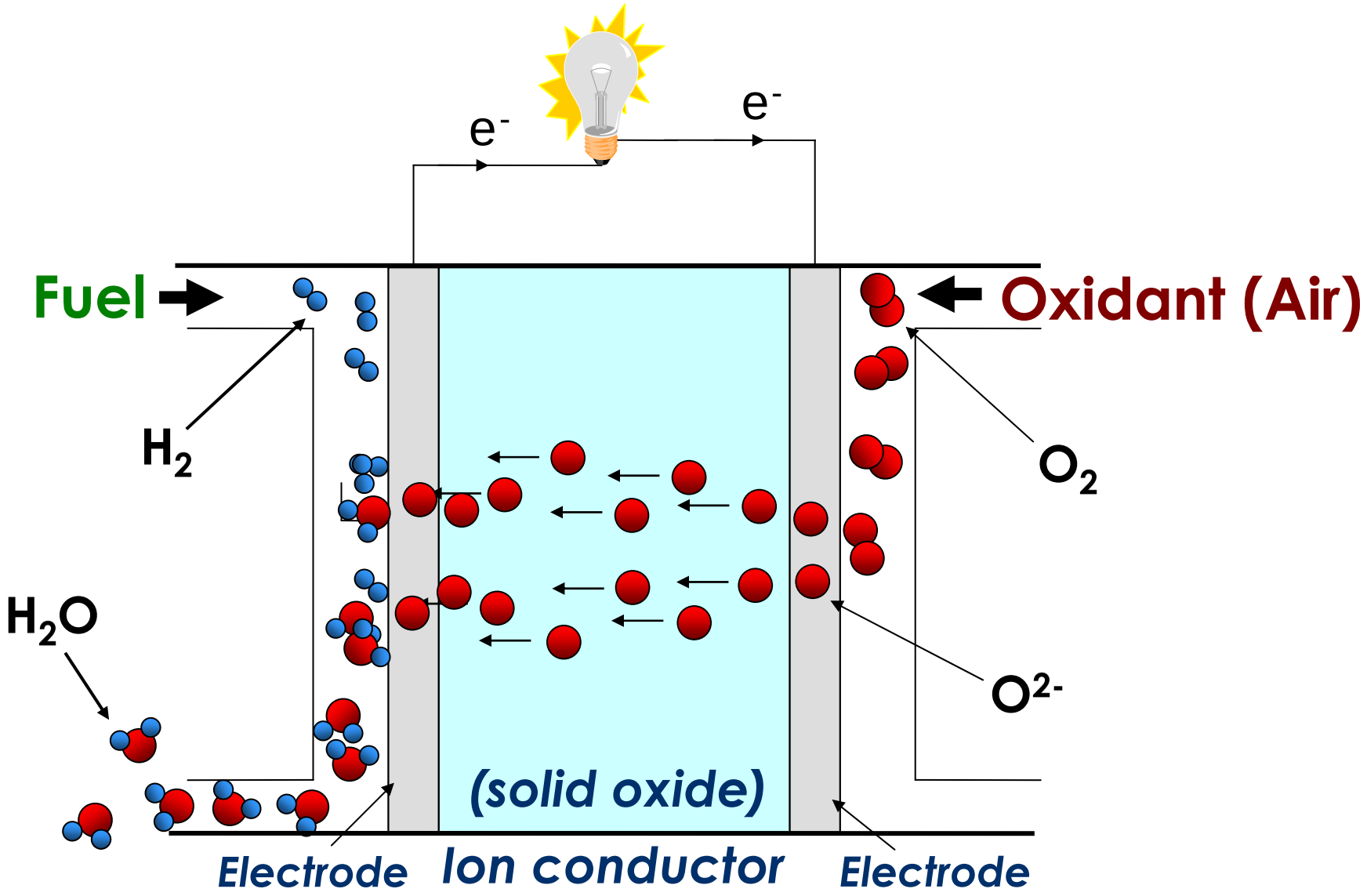
Materials Chemistry Issues

- Structure-property→ electrochemistry
- Basic science: underpins applied work



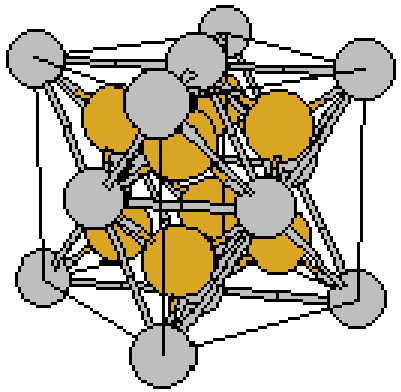
Fuel Cell Materials

Electrochemical Sandwich

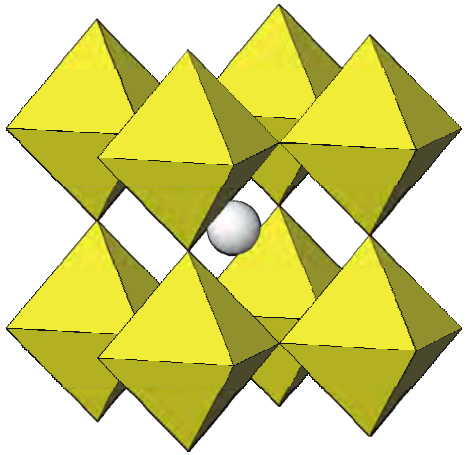


Ionic & Mixed Conductors:
Solid Oxide Fuel Cells

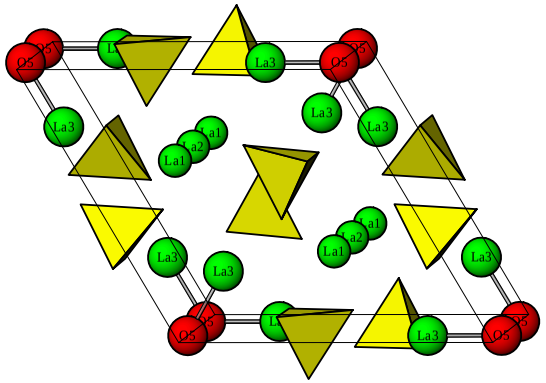
Fluorite Type — Perovskite Type — New Structures



e.g. Y/ZrO2 (vacancy)



e.g. $LaGaO_3$ (vacancy)



e.g. La-Si-O apatite

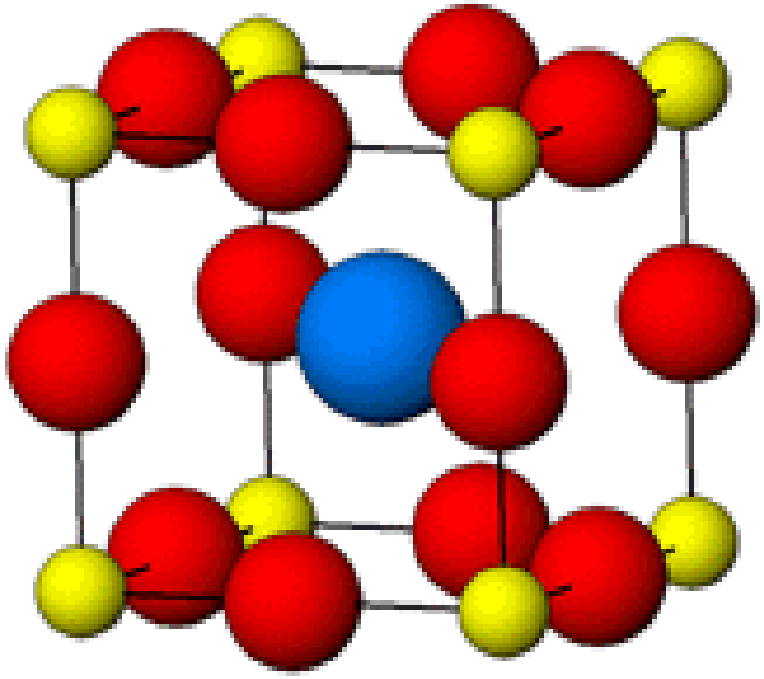
Perovskite Oxides: AMO_3

- Sr/Mg doped $LaGaO_3$

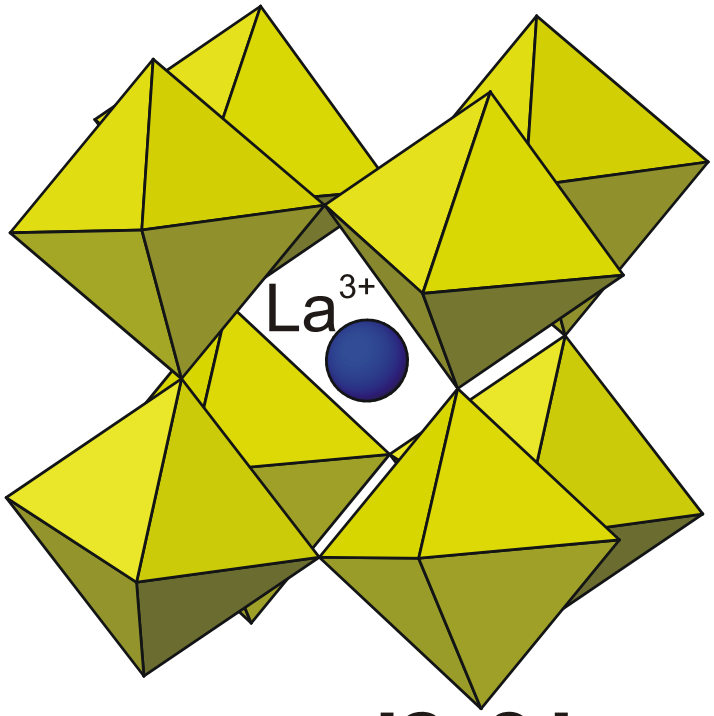
  → O^{2-} conductivity

  → Intermediate temp SOFC

- *Ishihara, Goodenough*



Structural Modelling: $LaGaO_3$

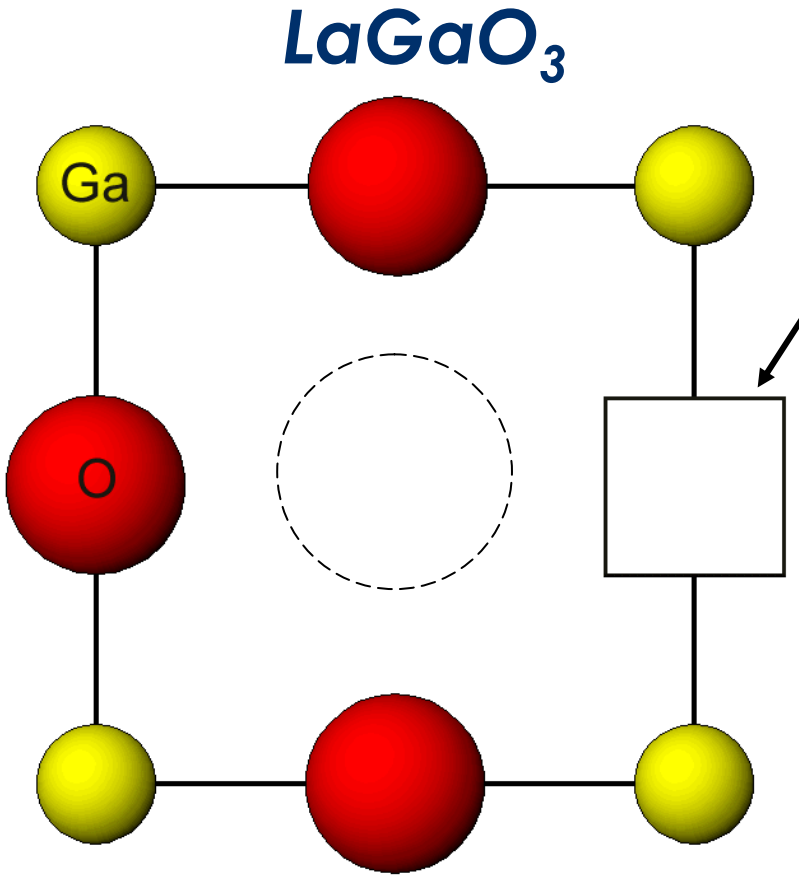


Unit cell parameters

	Calc. (Å)	Expt. (Å)	Δ (Å)
a	**5.485**	**5.527**	**0.042**
b	**7.752**	**7.781**	**0.029**
c	**5.481**	**5.496**	**0.015**

- Δ Bond Distances < 0.1 Å
- Structure reproduced

Oxide Ion Conduction

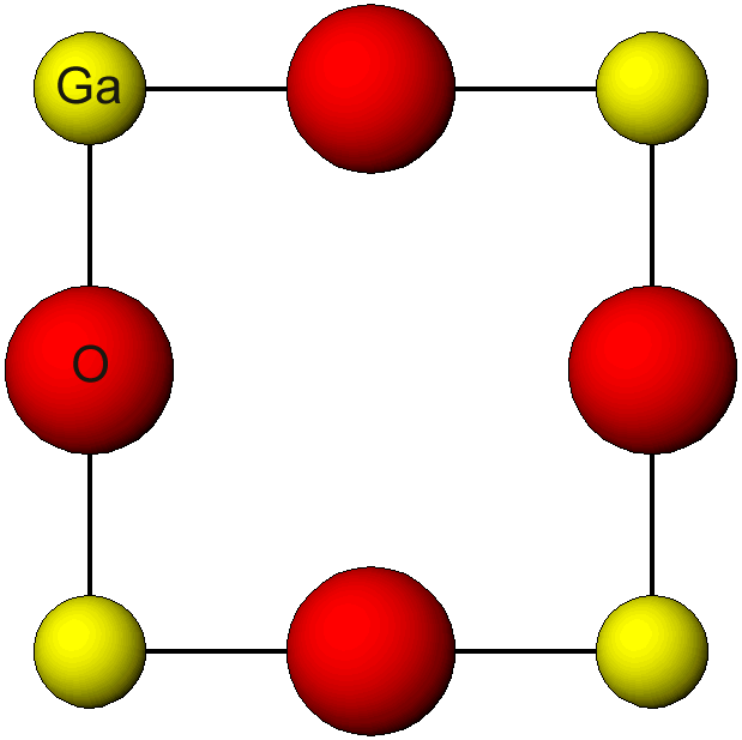


Oxide ion vacancy

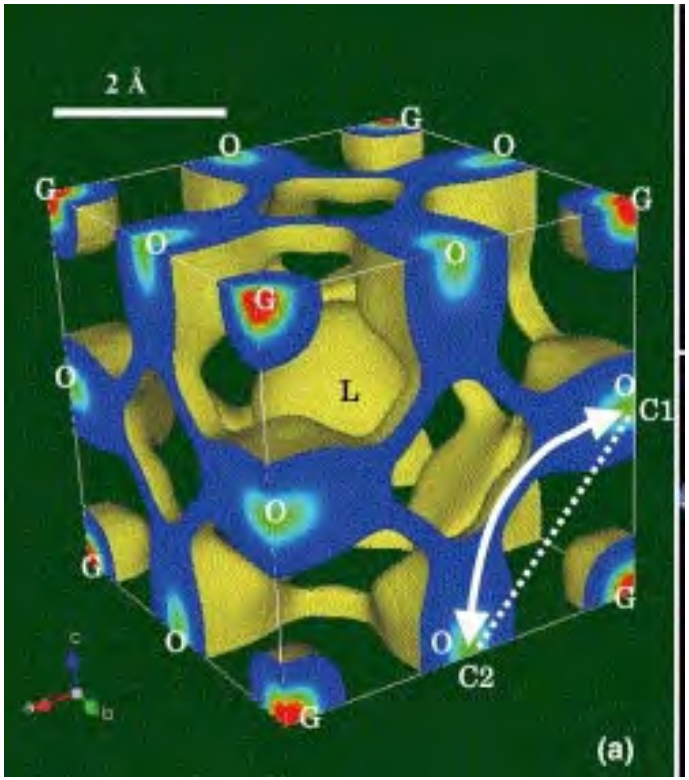
- *What is the path?*

$LaGaO_3$: Migration Pathway?

- E_{mig} : Curved = 0.75 eV (Expt = 0.7- 0.8eV)



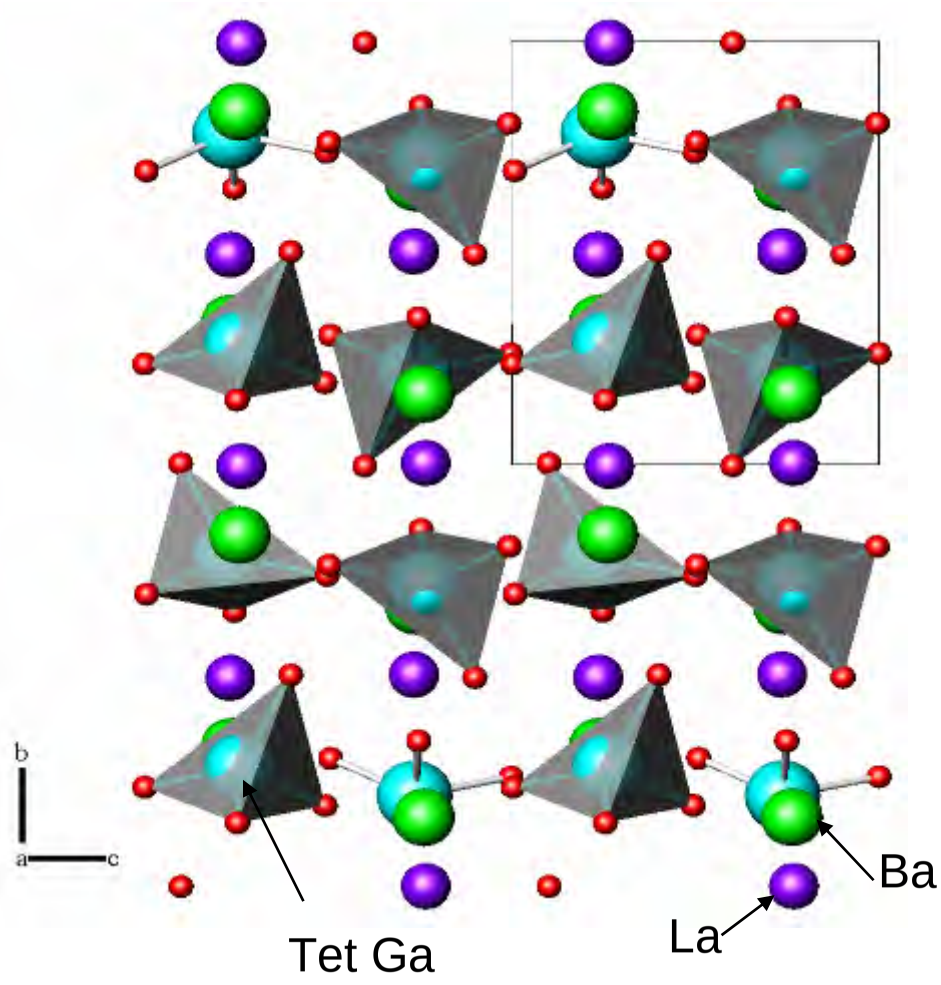
Range of perovskites since 1995



Neutron diff: Yashima et al (2003)

Recent: Oxides with Tetrahedral Ga

- Good H^+ (and O^{2-}) conductor
- $La_{0.8}Ba_{1.2}GaO_{3.9}$
  - Oxygen vacancy
  - Ga2O7 unit
  - Unusual migration



Nature Materials (2007)

Apatite for Fuel Cells

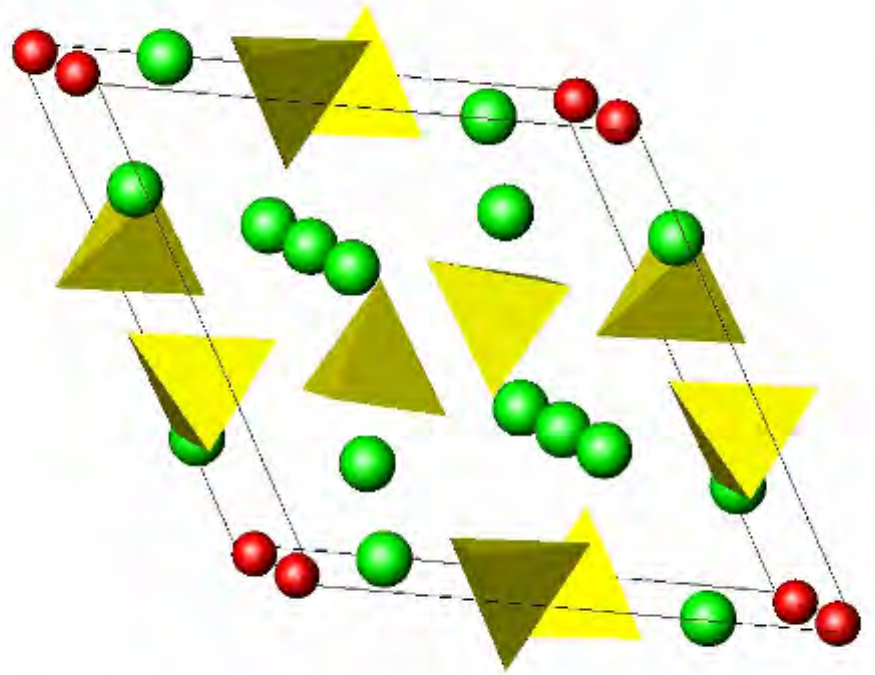
Apatites: From Nature to Applications?

- **Hydroxyapatite - bones & teeth**

- **Silicates: $La_{10-y}(SiO_4)_6O_{2\pm z}$**

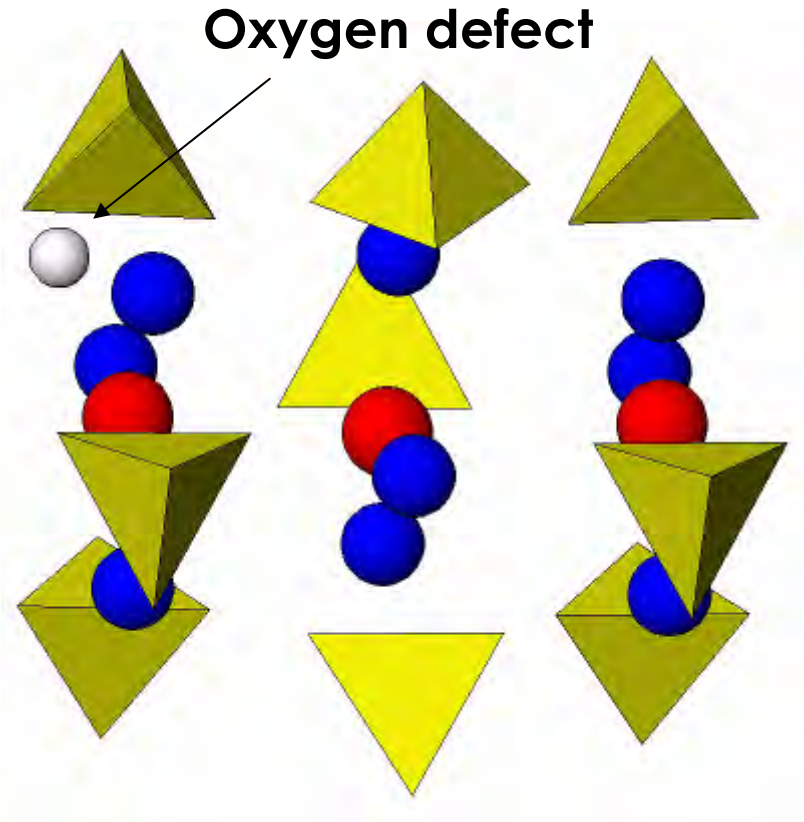
→ **New class of *fast-ion* conductor**

- **Defect site & conduction mechanism?**



SiO_4 tetrahedra

An Apatite for Ion Conduction



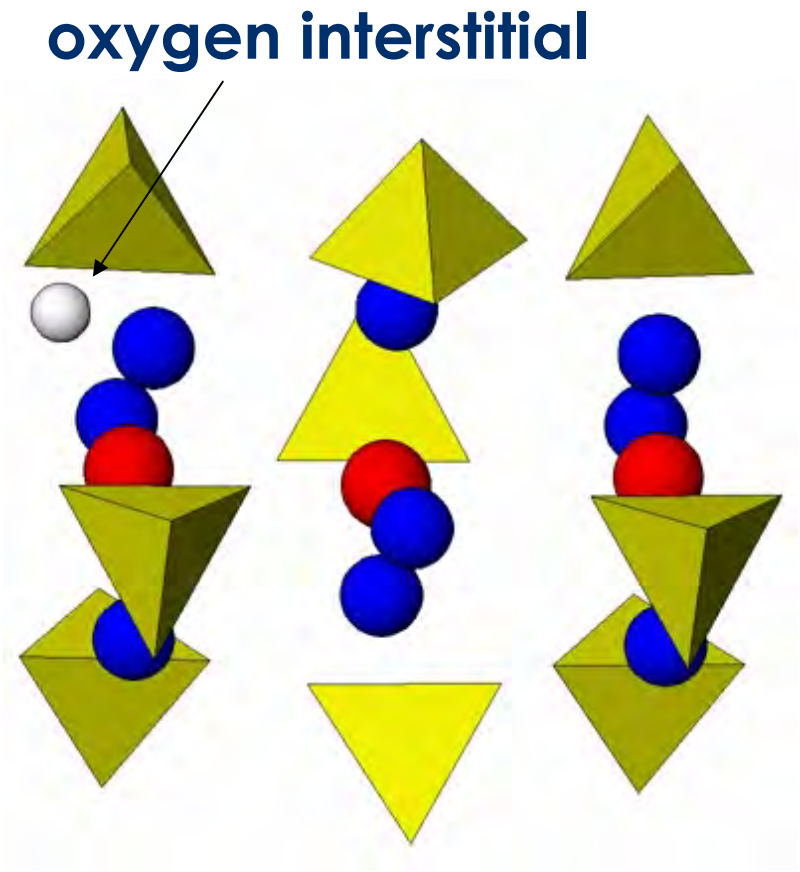
- Apatites: $La_{10-y}(SiO_4)_6O_{2\pm z}$
- "Energy landscape"

→ oxygen defect site

- Neutron diffraction, Fe Mossbauer & Si NMR

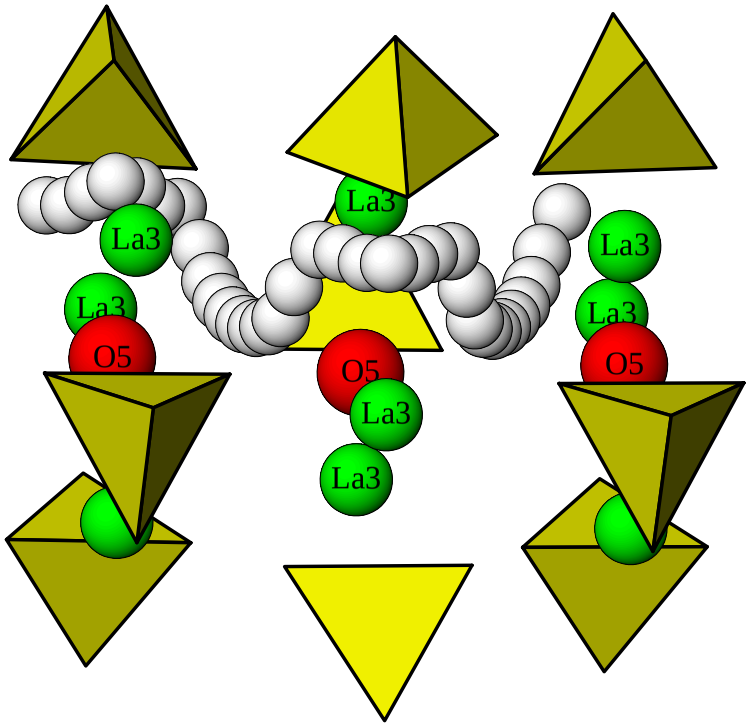
Chem.Comm., 2003

Ion Conduction Path?



- Silicates: $La_{10-y}(SiO_4)_6O_{2\pm z}$
- Unusual "snake-like"path
- SiO_4 relaxation
- *Current: cation doping & Ge-apatites*

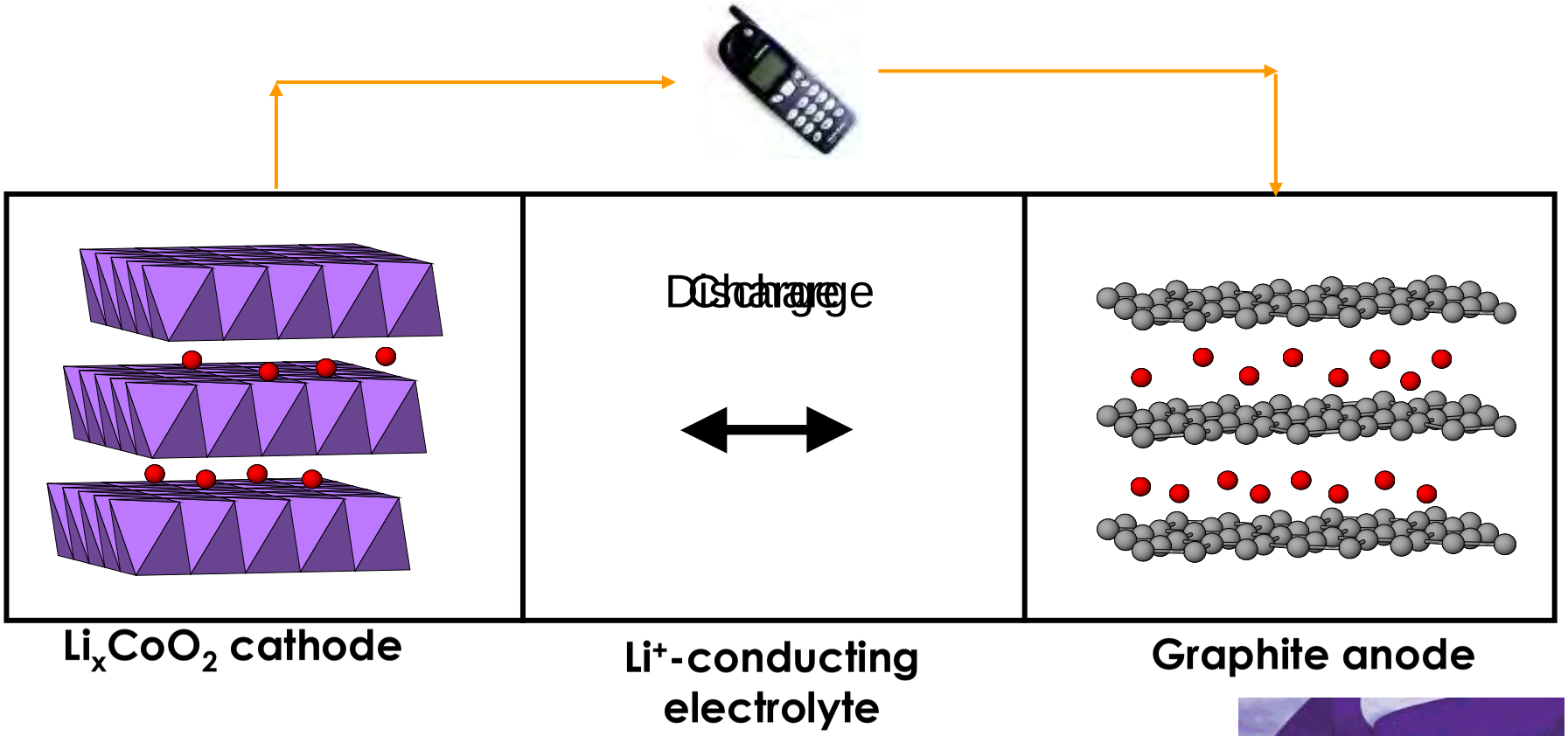
Apatite: Ion Conduction Pathway?



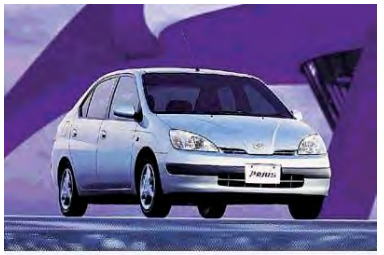
- Silicates: $La_{10-y}(SiO_4)_6O_{2\pm z}$
- Unusual "snake-like"path
- SiO_4 relaxation
- Tolerant to range of dopants (e.g. Ga, Mg)

Lithium Battery Materials

Lithium Battery Revolution



- Major success: portable devices
- New materials needed: hybrid electric cars

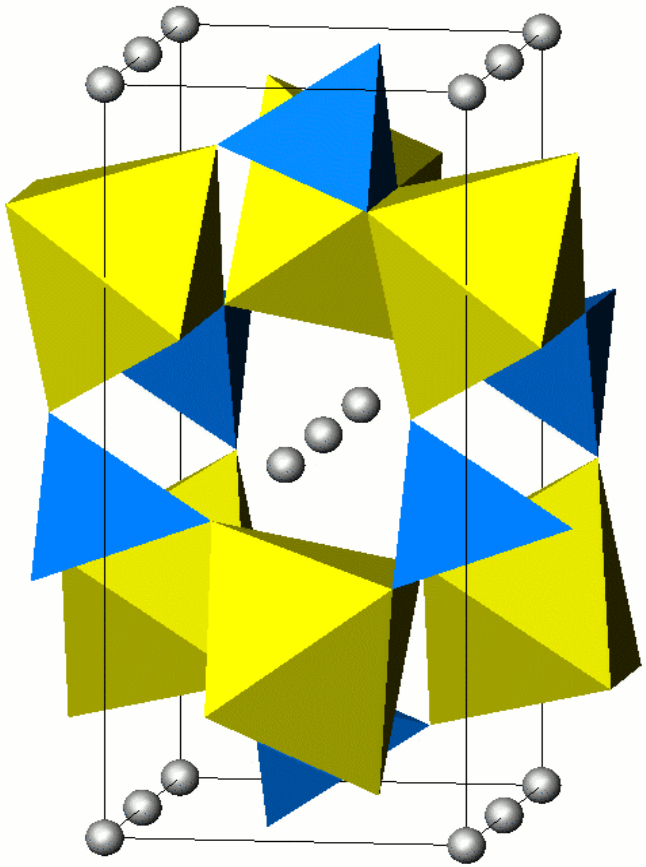


Toyota Prius hybrid gas-electric car

New Battery Material

Lithium iron phosphate: $LiFePO_4$

- Non-toxic
- Cheaper
- Scale-up



2006

$LiFePO_4$: Doping Controversy!

- Poor electronic conductivity

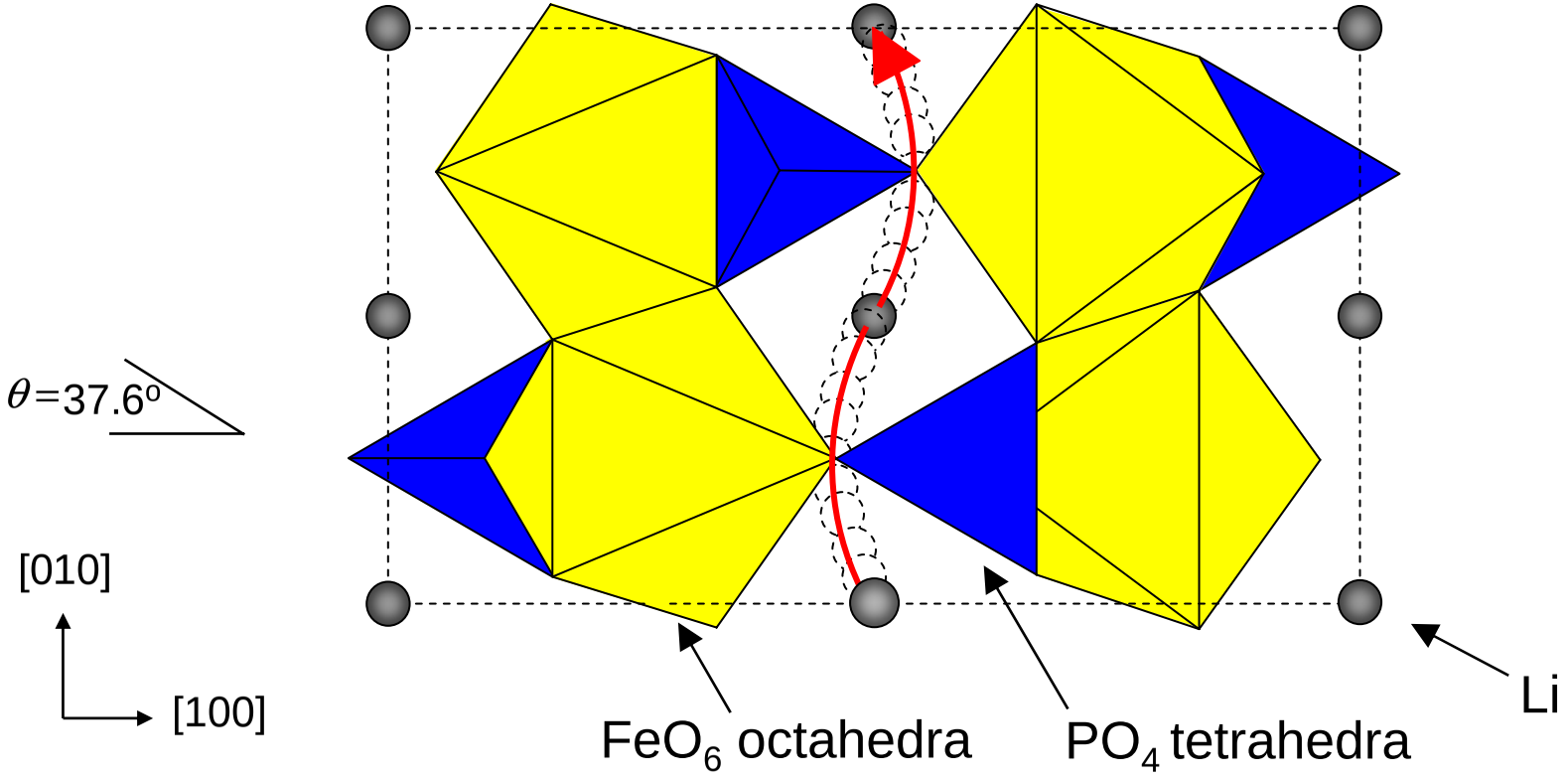
- "Supervalent" doping (e.g. Zr, Nb) increases conductivity [Chung, *Nature Mater*. 2002]

- Carbon contamination [*Nature Mater*. 2003, 2005]

- *Atomic-Scale Modelling - shed some light?*

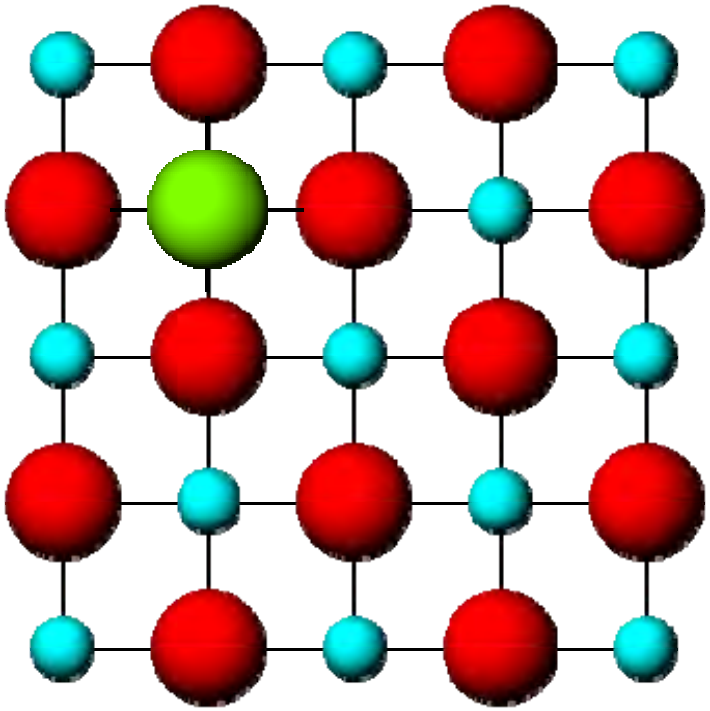
$LiFePO_4$: Li Migration Path?

- Non-linear, curved path (with lattice relaxation)



$LiFePO_4$: High Valent Doping?

- Calculate dopant incorporation energies

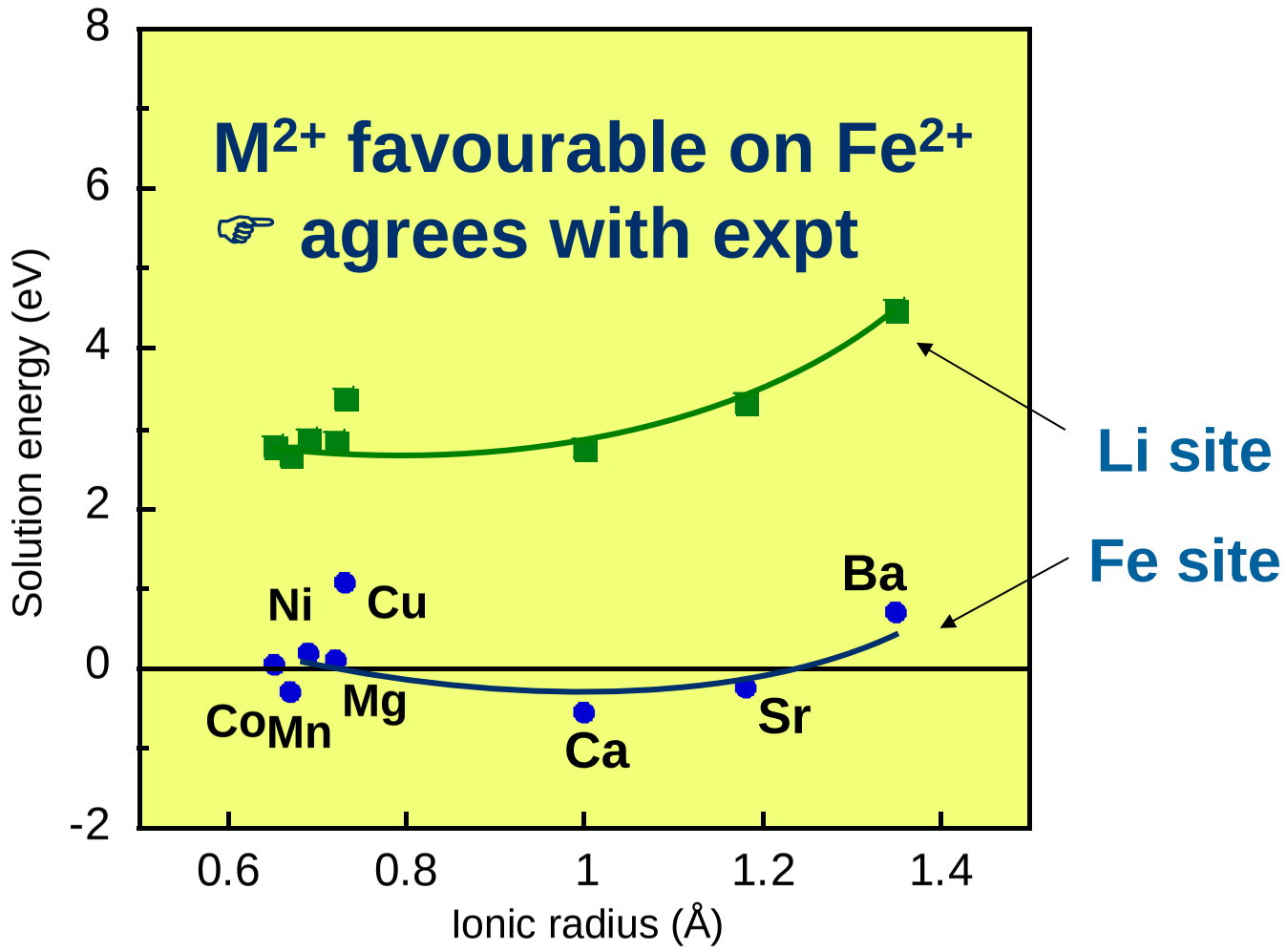


- Charge-compensation

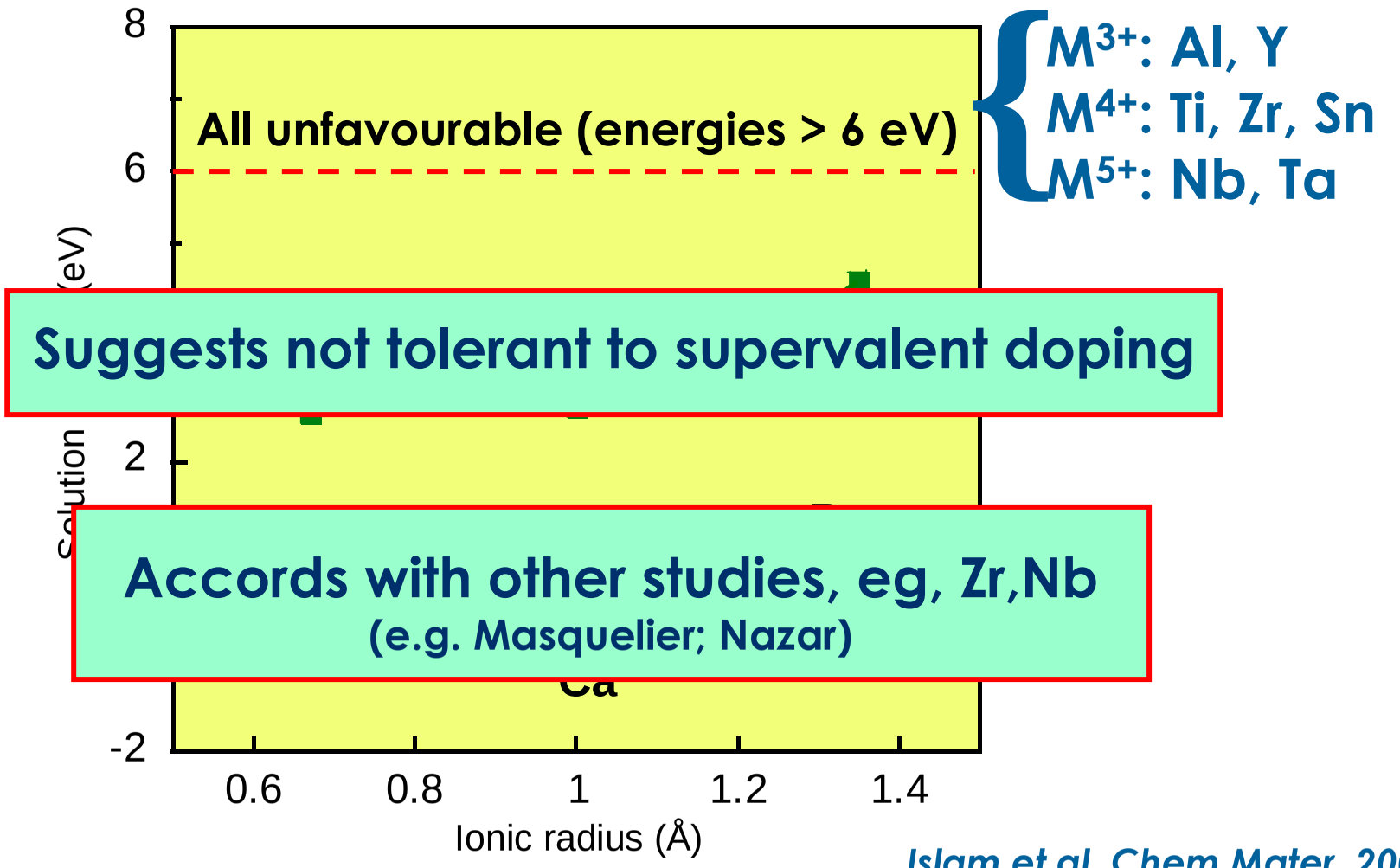
- Trends in energetics

→ lowest most favourable

Divalent Dopants in $LiFePO_4$



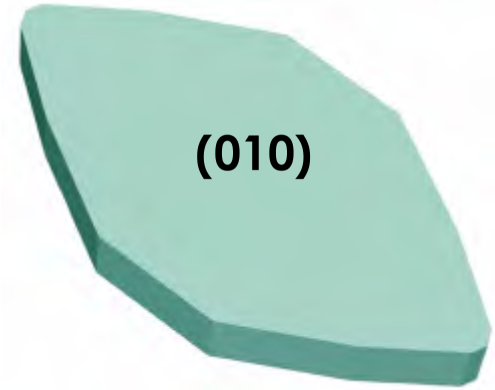
Di- and Higher Valent Dopants



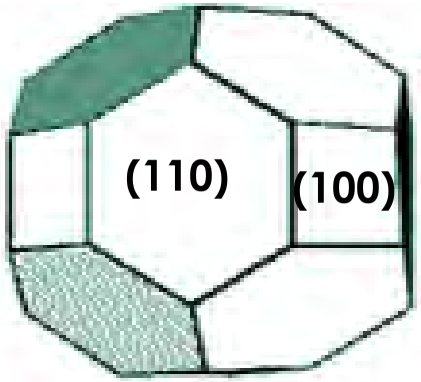
Islam et al, Chem Mater, 2005

Surfaces & Crystal Morphology

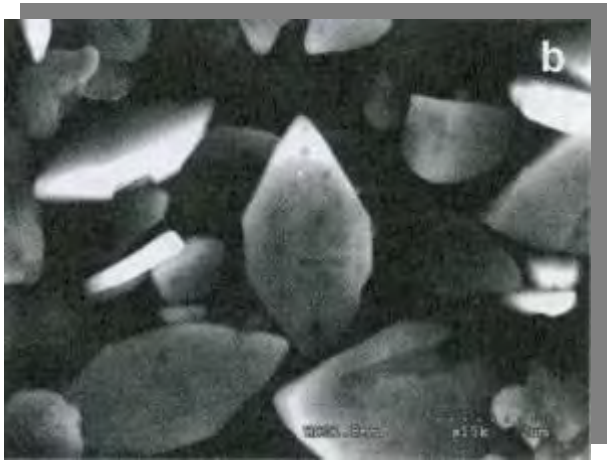
Li battery: $LiFePO_4$



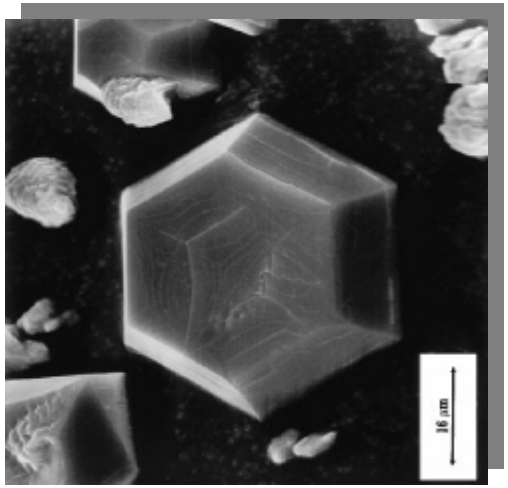
Fuel cell: $LaCoO_3$



Modelling



Microscopy



Concluding Remarks

Summary

- Probed structure-property relationships of functional materials on atomic-scale

- Perovskite & apatite ionic conductors
  - *Ion transport mechanisms*
  - *Defect association*

- Li intercalation oxides
  - *dopant effects*
  - *surfaces & morphology*

Acknowledgements

- *Postdocs:* C. Fisher; A. Jones; E. Kendrick
- *PhD students:* J. Percival; S. Stokes

  P. Slater (Surrey)

- ££: EPSRC & SUPERGEN

www.bath.ac.uk/Chemistry

The **End**

Hydrogen Storage in New Complex Hydrides

Paul Anderson

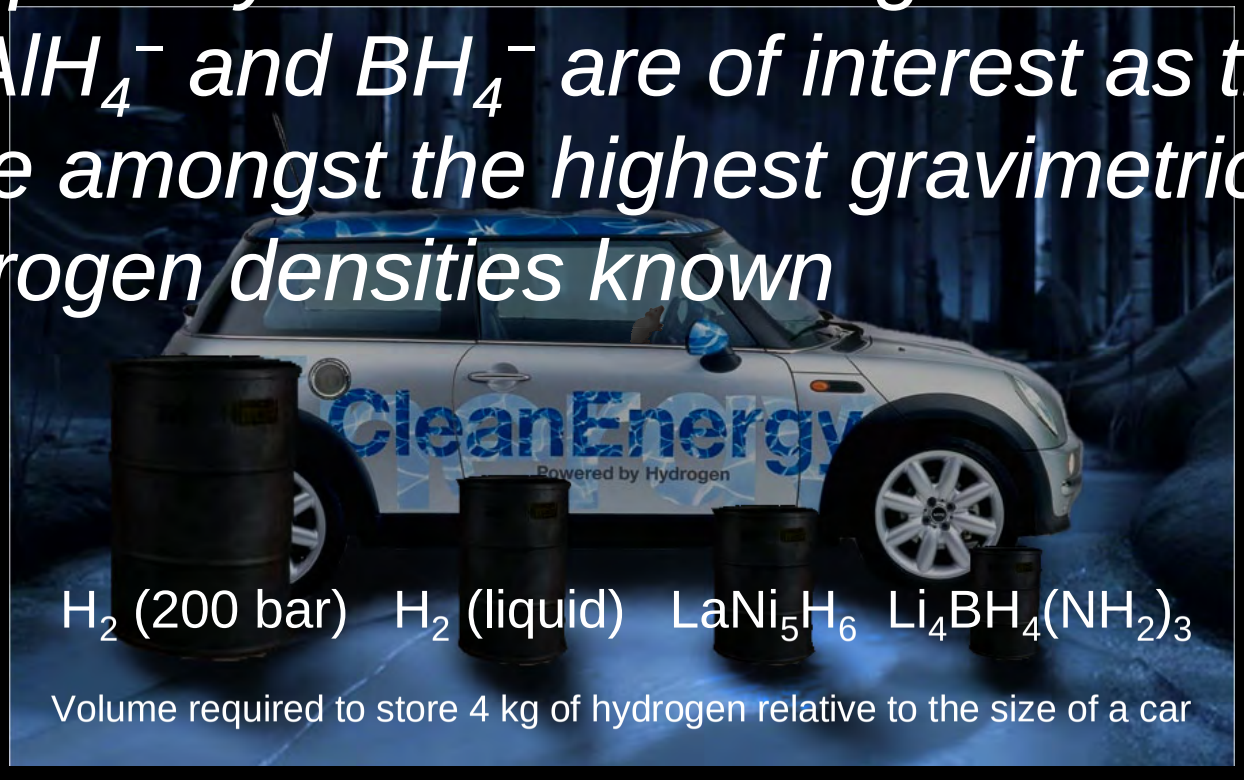
UNIVERSITY OF BIRMINGHAM

Hydrogen as a Mobile Fuel

- Cleanest burning fuel
- Molar heating value three times that of petroleum
- No natural source of H_2
- Low gravimetric energy content
  - *Storage is a major technical obstacle to the implementation of a hydrogen based economy*

Storage of Hydrogen

- *The problem of hydrogen storage is essentially one of volumetric compression*
- *complex hydrides containing anions such as AlH_4^- and BH_4^- are of interest as they have amongst the highest gravimetric hydrogen densities known*



H_2 (200 bar) H_2 (liquid) $LaNi_5H_6$ $Li_4BH_4(NH_2)_3$

Volume required to store 4 kg of hydrogen relative to the size of a car

Hydrogen Producing Reactions

- $LiNH_2 + 2\ LiH \rightarrow Li_2NH + LiH + H_2 \rightarrow Li_3N + 2\ H_2$
  - overall 10.2 wt%[†]
  - step 1: ΔH_{des} = 45 kJmol^{-1} reversible
  - step 2: ΔH_{des} = 148 kJmol^{-1}

- thermodynamic fine tuning of storage systems
- chemical control of decomposition pathways
  - $3\ LiNH_2 \rightarrow NH_3 + 3\ LiH + N_2$

  - Ammonia mediated reaction
  - Interaction between $H^{\delta-}$ and $H^{\delta+}$?

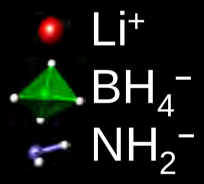
[†]*P. Chen et al., Nature, 2002, 420, 302; T. Ichikawa et al., J. Phys. Chem. B, 2004, 108, 7887*

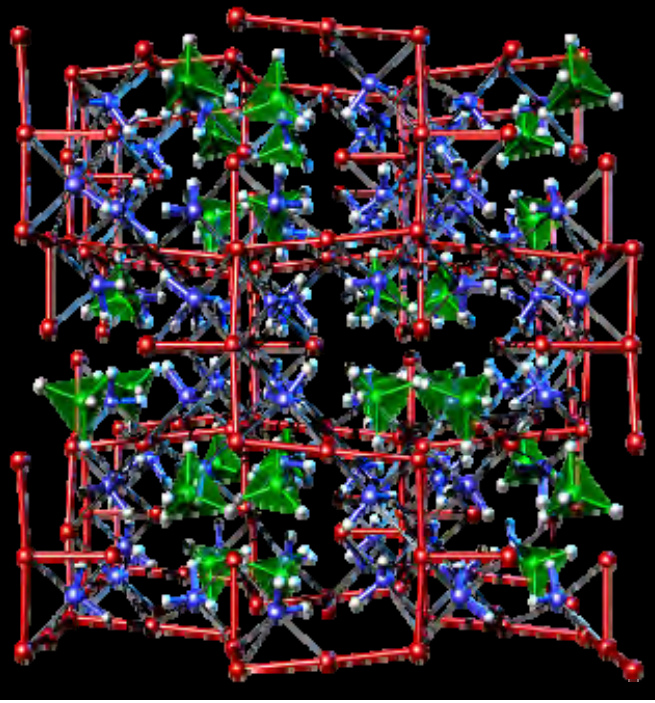
$Li_4BH_4(NH_2)_3$

- $LiBH_4$ reacts with $LiNH_2$ at around 100°C to produce the new mixed anion complex hydride of composition $Li_4BN_3H_{10}$
- FTIR spectroscopy confirmed that the BH_4^- and NH_2^- anions remain intact
  - $Li_4BH_4(NH_2)_3$
- Structure solution was performed using combined synchrotron X–ray and neutron powder diffraction data

$Li_4BH_4(NH_2)_3$ Structure

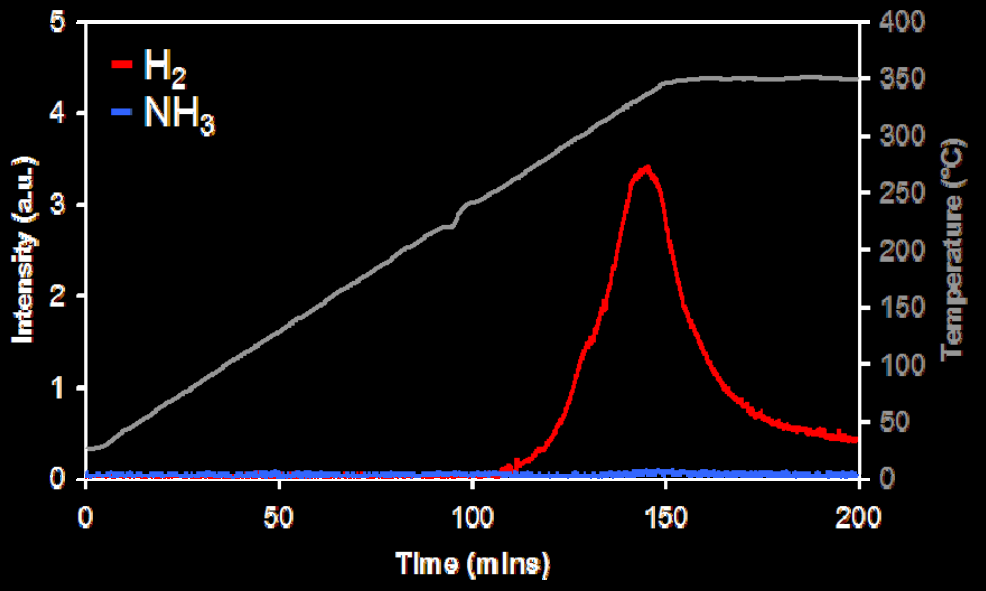
- Body centred cubic structure
  - *a* = 10.66 Å
- Close relationship to $LiNH_2$ structure





$Li_4BH_4(NH_2)_3$ Desorption

- TPD–MS analysis showed that neither $LiBH_4$ nor $LiNH_2$ released gas at temperatures up to 350°C
- The mixed amide–borohydride released hydrogen
  - Starts at 260°C
  - Peaks at 320°C
  - Shoulder
  - Melts at 210°C



$Li_4BH_4(NH_2)_3$ Desorption

- The decomposition pathways of the component $LiBH_4$ and $LiNH_2$ materials have been radically altered
  - Pure $LiBH_4$ releases hydrogen at higher temperatures
  - Pure $LiNH_2$ releases ammonia
- Analogous to the $LiNH_2$–LiH system[†]
  - Interaction between $H^{\delta+}$ and $H^{\delta-}$?
  - Ammonia mediated reaction?

[†]*P. Chen et al., Nature, 2002, 420, 302; T. Ichikawa et al., J. Phys. Chem. B, 2004, 108, 7887*

$Li_4BH_4(NH_2)_3$ Summary

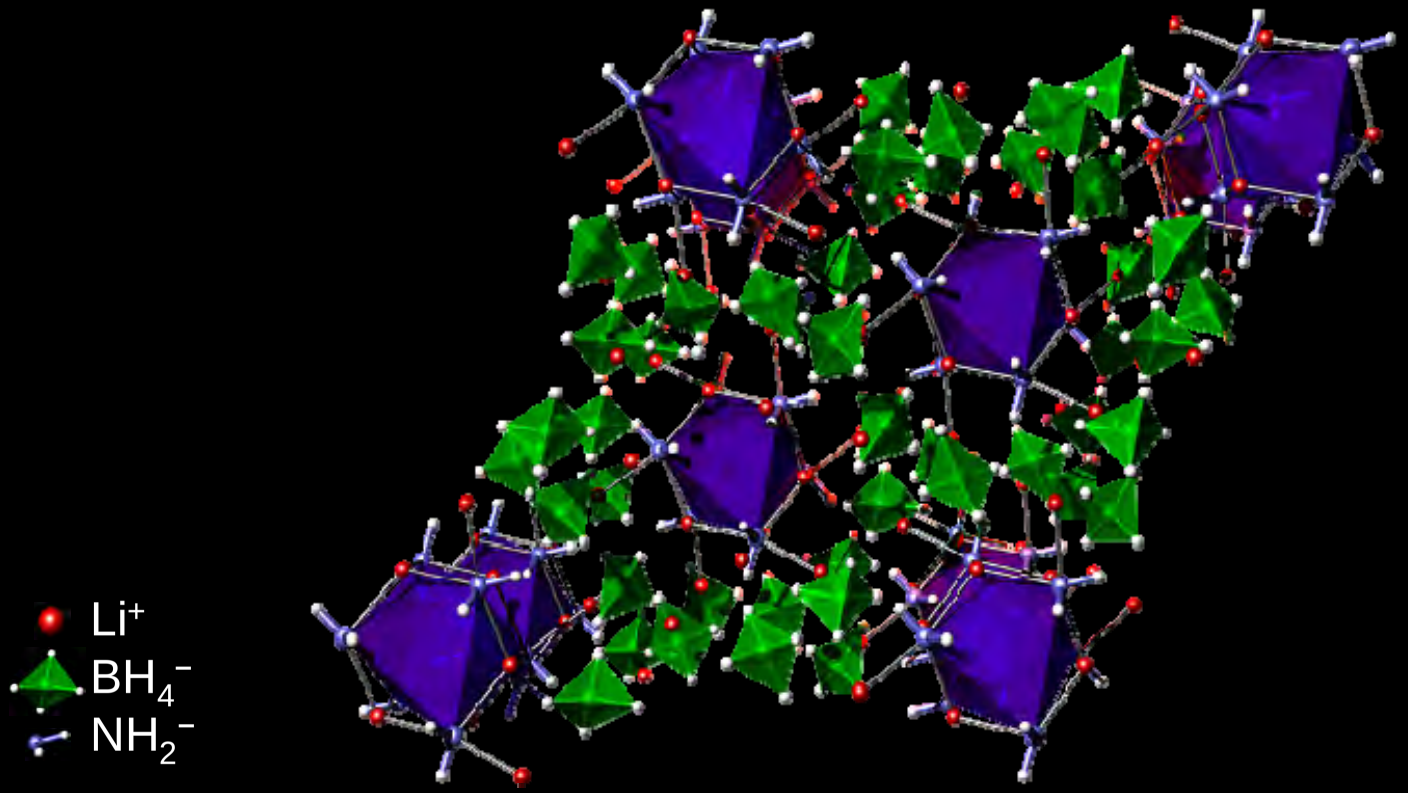
- New mixed anion complex hydride
- 11% hydrogen by mass
- Anions perfectly mixed on an atomic scale within the compound
- Hydrogen evolution starts at 260°C
  - No NH_3 observed
- System not reversible
  - Lithium boron nitrides (mainly Li_3BN_2) formed upon desorption

$Li_2BH_4NH_2$

- $LiBH_4$ + $LiNH_2$ mixtures form a eutectic with a melting point minimum of 100°C
- A second new amide–borohydride is formed from a quenched melt
- Structure solved by combined synchrotron X–ray and neutron powder diffraction
- Rhombohedral symmetry
  - *a* = 14.49 Å, *c* = 9.24 Å (hexagonal setting)

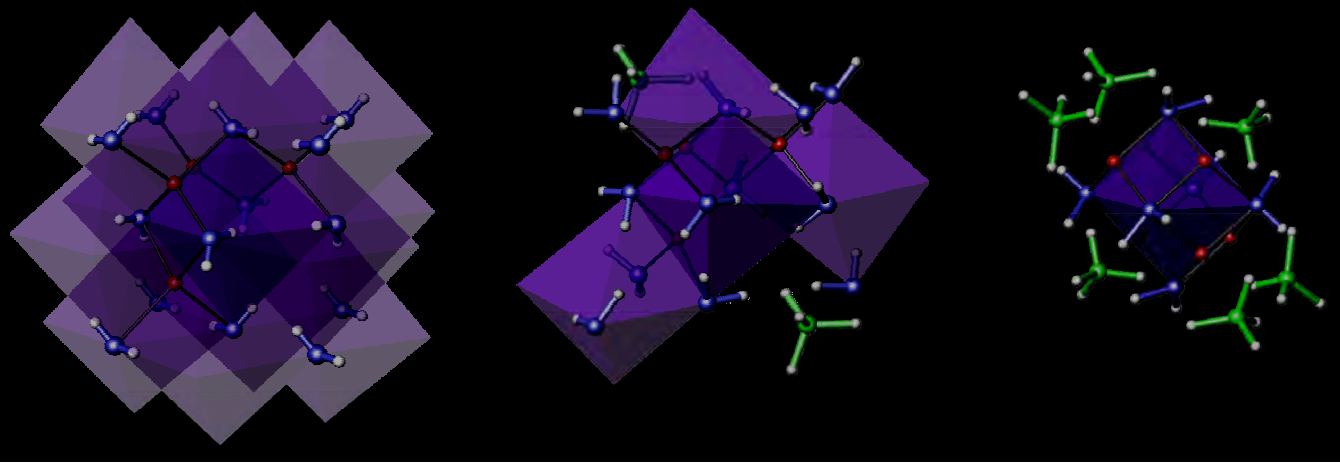
$Li_2BH_4NH_2$

- $(LiNH_2)_6$ octahedra dissolved in a borohydride lattice



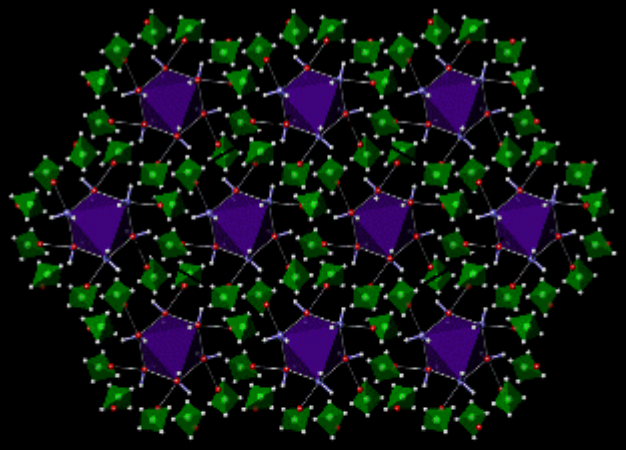
$LiNH_2$, $Li_4BH_4(NH_2)_3$ and $Li_2BH_4NH_2$

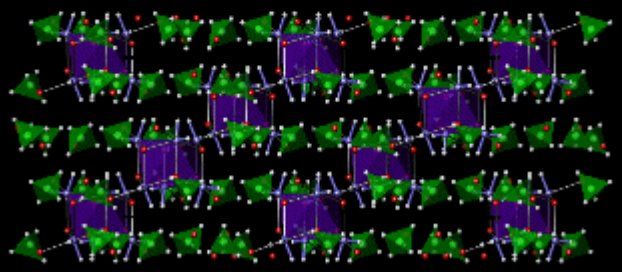
- This family of compounds can be described in terms of edge sharing nitrogen octahedra
  - $LiNH_2$: all edges shared
  - $Li_4BH_4(NH_2)_3$: quarter of edges are shared
  - $Li_2BH_4NH_2$: octahedra are isolated



$LiNH_2$, $Li_4BH_4(NH_2)_3$ and $Li_2BH_4NH_2$

- Relationships between structures





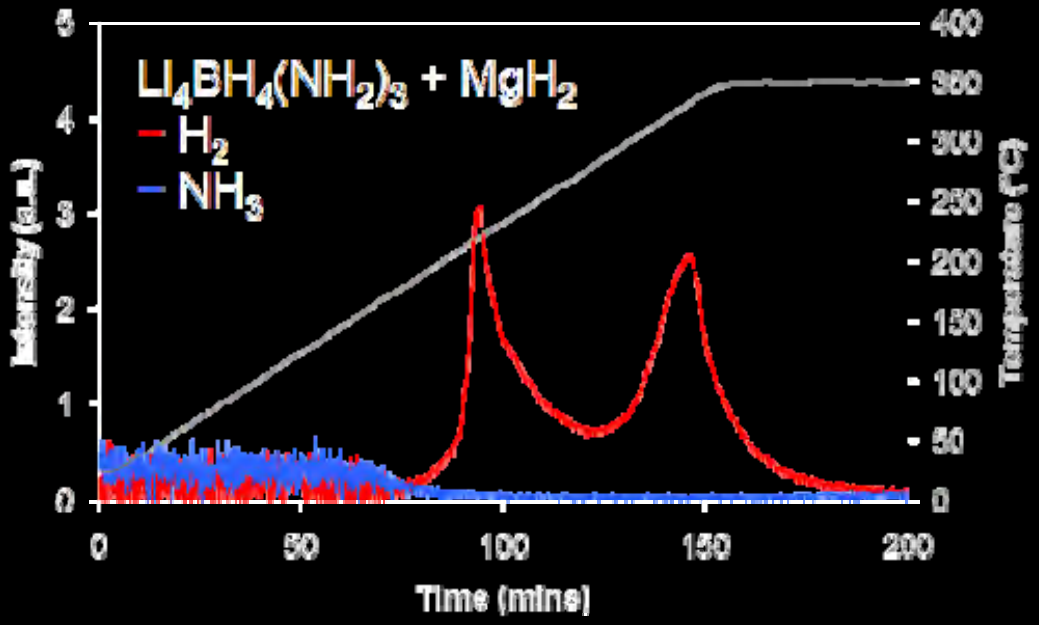
- Structures viewed down (110) plane (below) and a perpendicular plane (top)
- BH_4^- ions penetrate the regular NH_2^- lattice

$Li_2BH_4NH_2$ Summary

- Second mixed anion complex hydride
- 13.5% hydrogen by mass
- *$LiNH_2$ structure dissolved in $LiBH_4$*
- Low melting point of 100°C
- Desorption equivalent to $Li_4BH_4(NH_2)_3$ desorbing the presence of excess $LiBH_4$

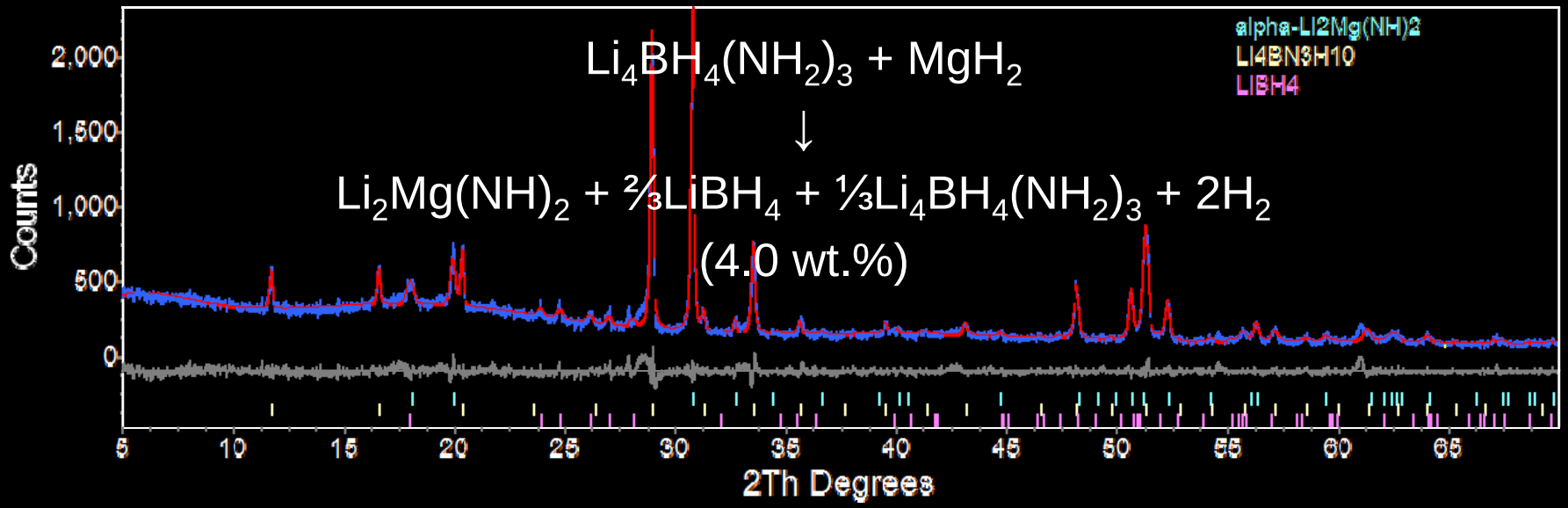
$Li_4BH_4(NH_2)_3 + MgH_2$

- Addition of MgH_2 changes the desorption profile
- Two desorptions starting at 210 and 260°C
  - The first desorption step was investigated



$Li_4BH_4(NH_2)_3 + MgH_2$

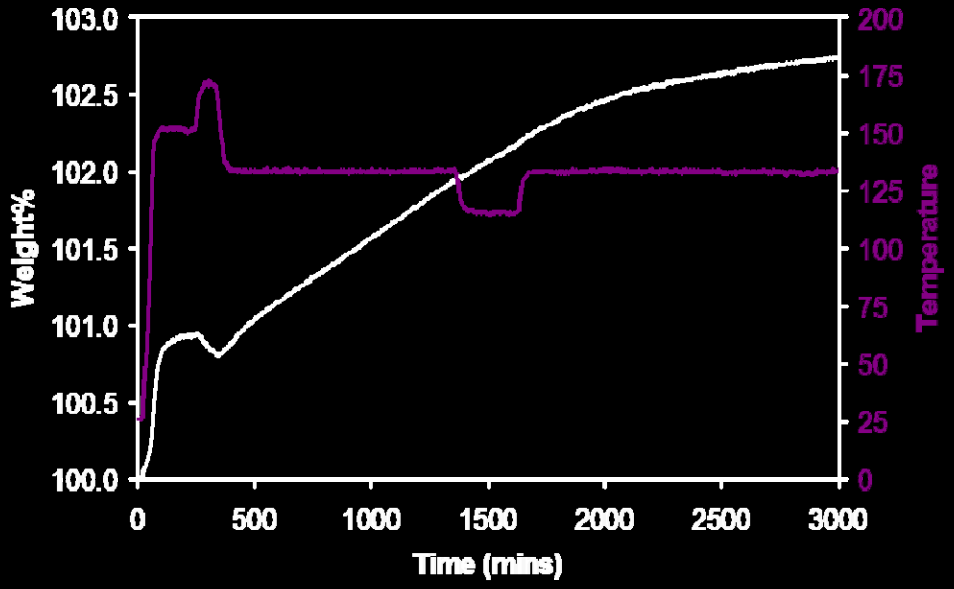
- Sample heated up to 220°C
  - XRD showed that MgH_2 had reacted completely to form $Li_2Mg(NH)_2$†
  - $Li_4BH_4(NH_2)_3$ and $LiBH_4$ were also present



†*J. Rijssenbeek et al., J. Alloys Compd., 2007, doi:10.1016/j.jallcom.2006.12.008*

$Li_4BH_4(NH_2)_3 + MgH_2$

- Reversibility investigation



- Absorption slow at 150°C
- Desorption observed at 170°C
- Main absorption observed at 135°C

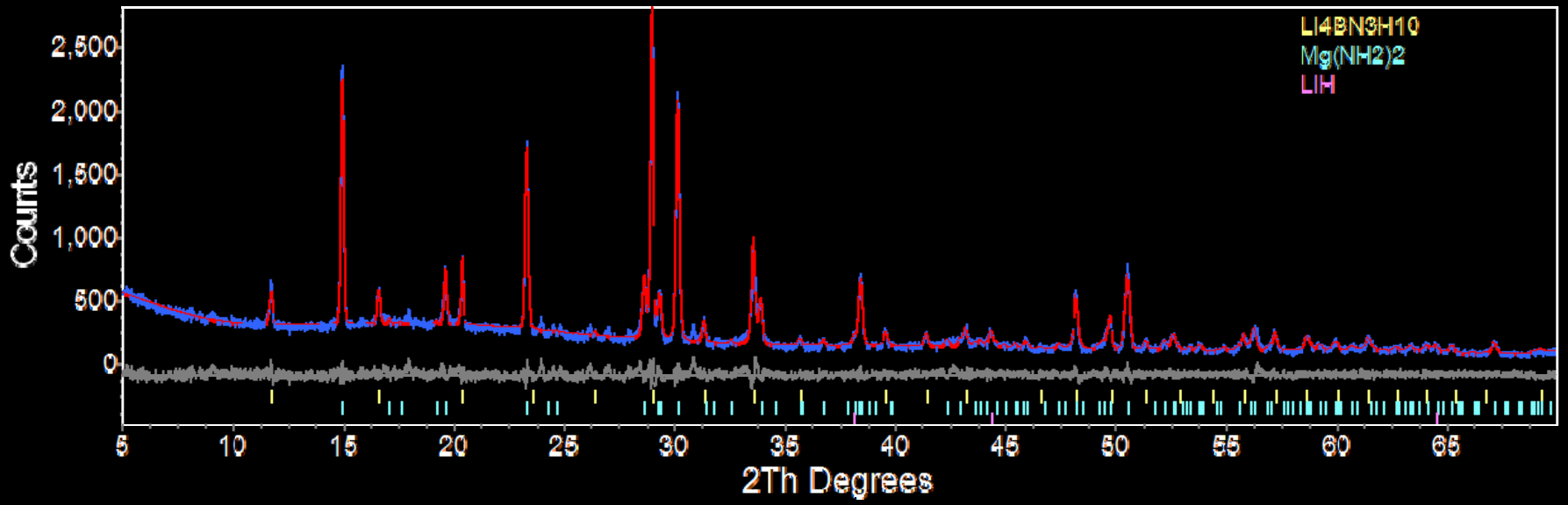
– 2.7 wt.% absorbed at 135°C, 18 bar H_2, 2 days

– Reversible reaction occurring in equilibrium at 160°C and 18 bar H_2?

$Li_4BH_4(NH_2)_3 + MgH_2$

- XRD analysis after absorption showed presence of $Mg(NH_2)_2$ and LiH
  - Reversible reaction appears to be

$$Li_2Mg(NH)_2 + H_2 \leftrightarrow Mg(NH_2)_2 + 2LiH^{\dagger}$$



†W. Luo, J. Alloys Compd., 2004, 381, 284; T. Ichikawa et al., J. Alloys Compd., 2005, 400, 245

$Li_4BH_4(NH_2)_3 + MgH_2$ Summary

- Desorption of $Li_4BH_4(NH_2)_3$ modified by presence of MgH_2
- Reaction partly reversible

$$Li_2Mg(NH)_2 + H_2 \leftrightarrow Mg(NH_2)_2 + 2LiH$$

- Large temperature reduction for production of $Li_2Mg(NH)_2$
  - Typically formed above 280°C rather than at 220°C

Acknowledgments

- Hydrogen Storage Chemistry Group
  - James Prendergast
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  - Allan Walton, David Book, Dan Reed (Met & Mat)
  - Bill David (ISIS)
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- Funding:
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UNIVERSITY OF BIRMINGHAM

EPSRC

Engineering and Physical Sciences Research Council

Hydrogen Storage in Novel Nitrides

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Department of Chemistry
University of Glasgow
Glasgow G12 8QQ, UK.

Novel nitrides – contents

1. Introduction
   - State of the art
   - Lithium nitride and derivatives
2. Hydrogen storage in lithium nitrides
   - Materials and mechanisms
3. New forms of lithium nitrides

Introduction

•State of the art

H Storage Materials:

- 60% reduction in CO_2 emissions by 2050 - 2003 UK Energy White Paper
- H_2 – clean fuel for H powered Fuel cells
- US DoE Material storage requirement of 6.5 wt % hydrogen; low cost, low toxicity, reversible, low desorption T

No *single materials* system yet meets all DoE requirements

Introduction

•State of the art

Table 1. Comparison of the Key Properties of Main (Condensed-Phase) Hydrogen Stores

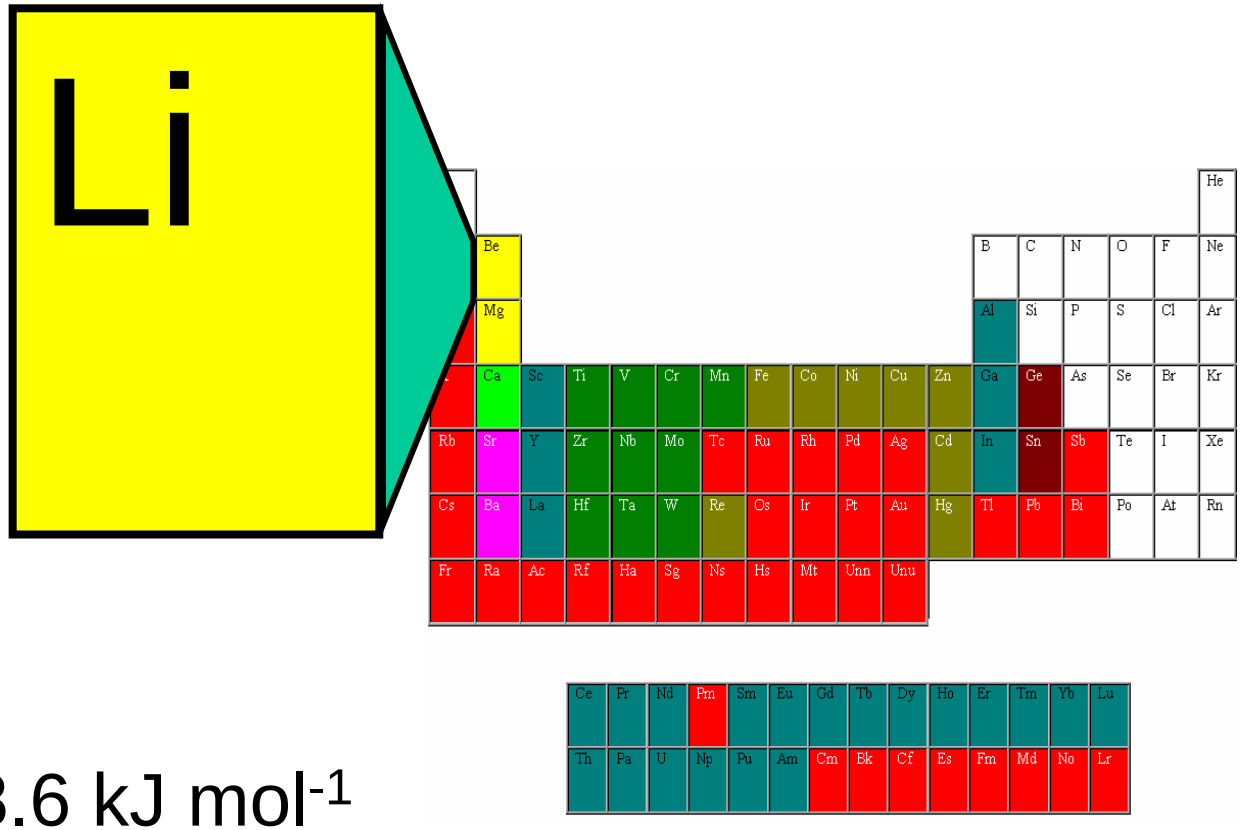
material[a]	practical wt % H	kinetic reversibility	T_{dec}/°C	notes	criteria met
$PdH_{0.6}$	0.6	excellent	ambient	$1000/oz.	(ii,iii,v)
NaH	4.2	good	425	cheap Na metal	(iii,iv,v)
BN[b]	4.2	sufficient	300	expensive	(iii,v)
Mg_2NiH_4	3.6	very good	ambient	fails to meet wt % criterion	(ii,iii,iv,v)
CaH_2	4.8	good	600	cheap Ca metal	(iii,iv)
$HF_{(l)}$	5.0	*c*	boils at +20	highly toxic and corrosive	(iv)
$NaAlH_4$:TiO_2	5.5	good	125	fails to meet wt % criterion	(ii,iii,iv,v)
	6.5			*DOE limit*	
Li_2NH	6.5–7.0	good	285		(i,iii,iv,v)
MgH_2	7.6	very poor[33]	330	cheap Mg metal	(i,iv,v)
$LiAlH_4$:TiO_2	7.9	*d*	*d*	*e*	*d*
"$Li_3Be_2H_7$"	8.7	sufficient	300	toxic and expensive	(i,iii)
$PH_{3(g)}$	8.8	irreverisble	broad range	*f*	(i)
$LiBH_4$:SiO_2	9.0[g]	so far irreversible[d]	200–400	at present $LiBH_4$ is expensive	(v)
$NaBH_4/H_2O_{(l)}$	9.2	irreversible	ambient	expensive Ru-containing catalyst	(i,ii,iv,v)
AlH_3	10.0	irreversible	150	very cheap Al metal	(i,iv,v)
$H_2O_{(l)}$	11.1	*c*	*h*	environmentally friendly MHS	(i,iii,iv,v)
NH_3AlH_3	11.6–12.8	irreversible	broad range		(i,iv,v)
$MeOH_{(l)}$	12.5	irreversible	*h*	toxic liquid	(i,iv)
$SiH_{4(g)}$	12.5	irreversible	broad range	*f*	(i,iv)
LiH	12.6	poor	720	aggressive Li vapor formed upon decomposition	(i,iv,v)
$NaBH_4$	13.0	irreversible	400	cheap	(i,iv,v)
$NH_4F/LiBH_4$	13.6	irreversible	> ambient	laboratory-scale reaction	(i,ii,v)
$NH_{3(g)}$	17.6	irreversible	*h*	toxic liquid	(i,iv)
C[i]	???[l]	*j*	*j*	very expensive and ill-defined at present	(i,ii,iii,v) ???
petroleum	17.3				
BeH_2	18.2	irreversible	250	extremely toxic and volative powder	(i)
NH_3BH_3	18.3	irreversible	melts at +104	multistage decomposition	(i,iv,v)
$LiBH_4$	19.6	irreversible	380	expensive as compared to Na compound	(i)
$Be(BH)_2$	20.6	irreversible	sublimes at +40	toxic, flammable, and expensive	(i)
$B_2H_{6(g)}$	21.7	irreversible	ambient	explosive	(i,ii,iv)
NH_4BH_4	24.4	irreversible	−40 to +100	multistage decomposition	(i,iv)
$CH_{4(g)}$	25.0	irreversible	*h*	gas difficult to liquidify	(i,iv)

i) High storage capacity >6.5 wt%
ii) T_{dec} = 60 -120 °C
iii) Readily reversible
iv) Low cost
v) Low toxicity

Grochala and Edwards, *Chem. Rev.*, 2004, **104**, 1283.

Introduction

- Lithium nitride and derivatives



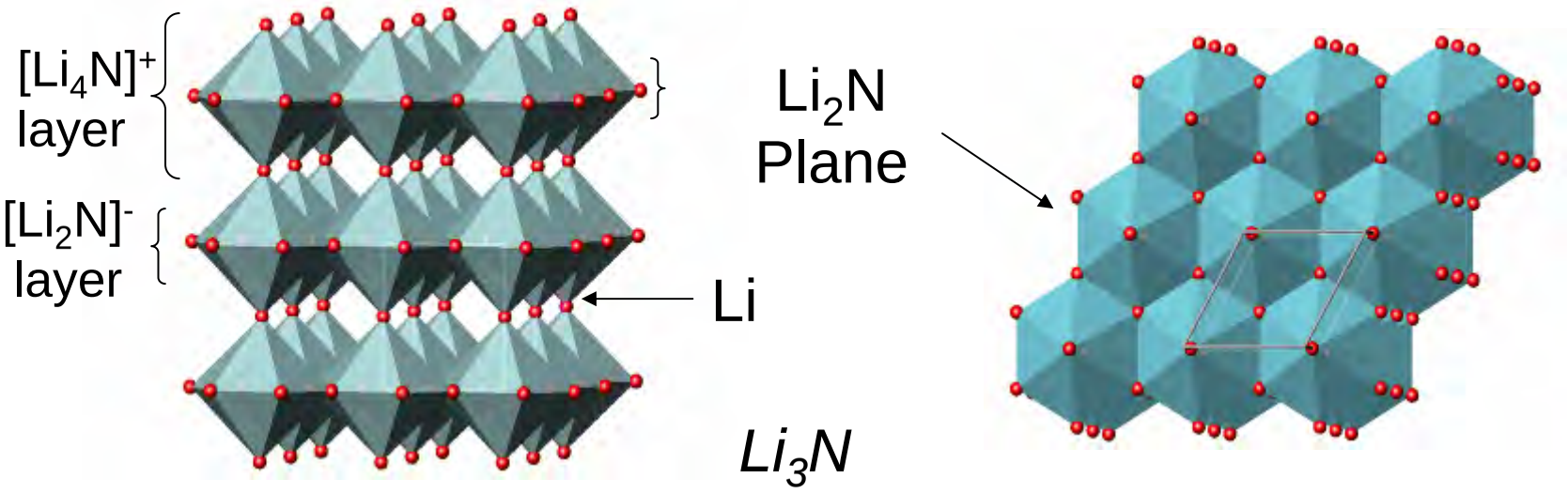
Li_3N:

- "$(Li^+)_3N^{3-}$"
- ΔG_f = -128.6 kJ mol^{-1}
- T_m = 815 ºC
- E_g = 2.1 eV

Introduction

•Lithium nitride and derivatives

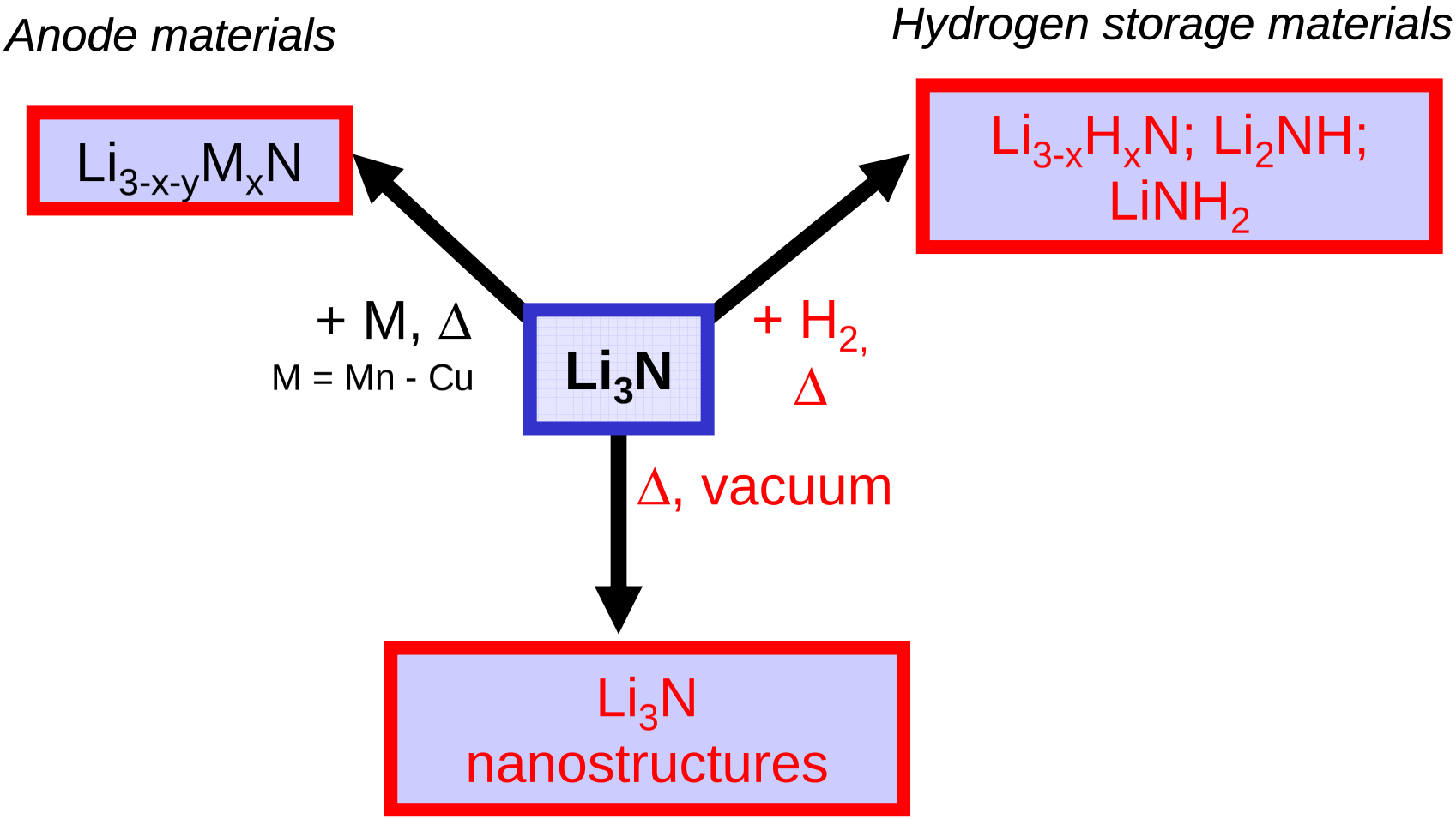
1892 – First reported by Ouvrard.
1935 – First crystal structure by Zintl and Brauer
1976 – Definitive single crystal structure by Rabenau and Schulz



- Unique structure
- Li^+ fast ion conductor; 1-2% vacancies in $[Li_2N]$ plane

Introduction

- Lithium nitride and derivatives



Novel nitrides – contents

1. Introduction

2. Hydrogen storage in lithium nitrides

3. New forms of lithium nitrides

Hydrogen storage in lithium nitrides

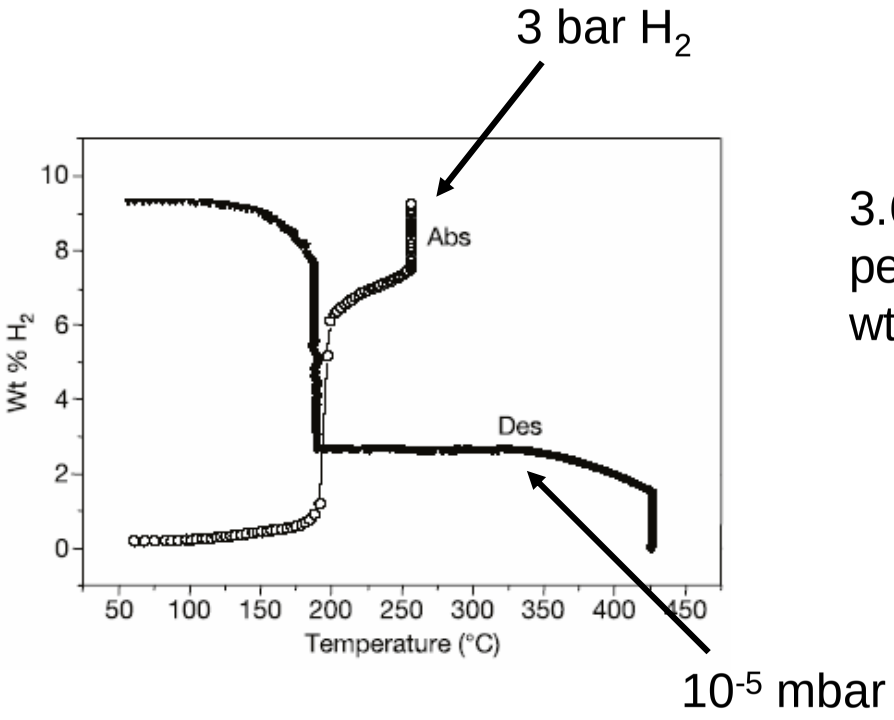
•Hydrogen uptake in the Li-N system

Ca 11.5 wt %

$$Li_3N + 2\,H_2 \Rightarrow Li_2NH + LiH + H_2 \Leftrightarrow LiNH_2 + 2\,LiH$$

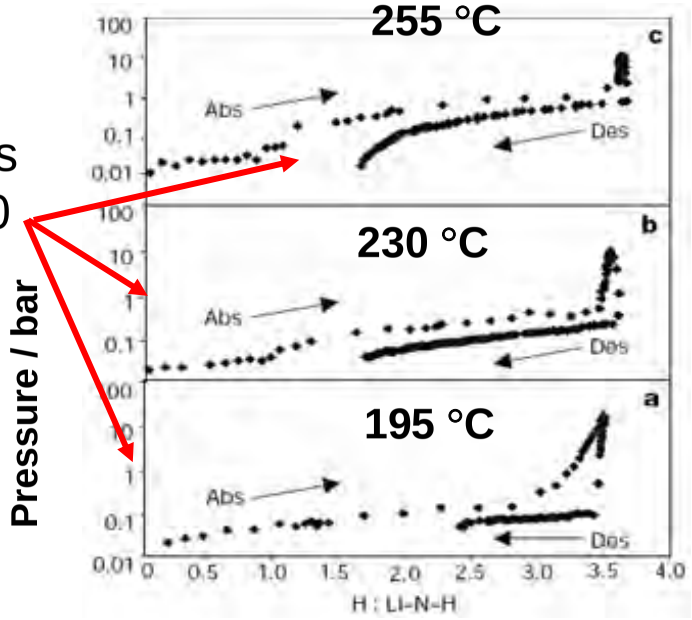
Ca 7 wt %

Chen *et al, Nature*, 2002, **420**, 302.



Wt % vs. temperature, uptake and release

3.6 H atoms per Li_3N; 10 wt %



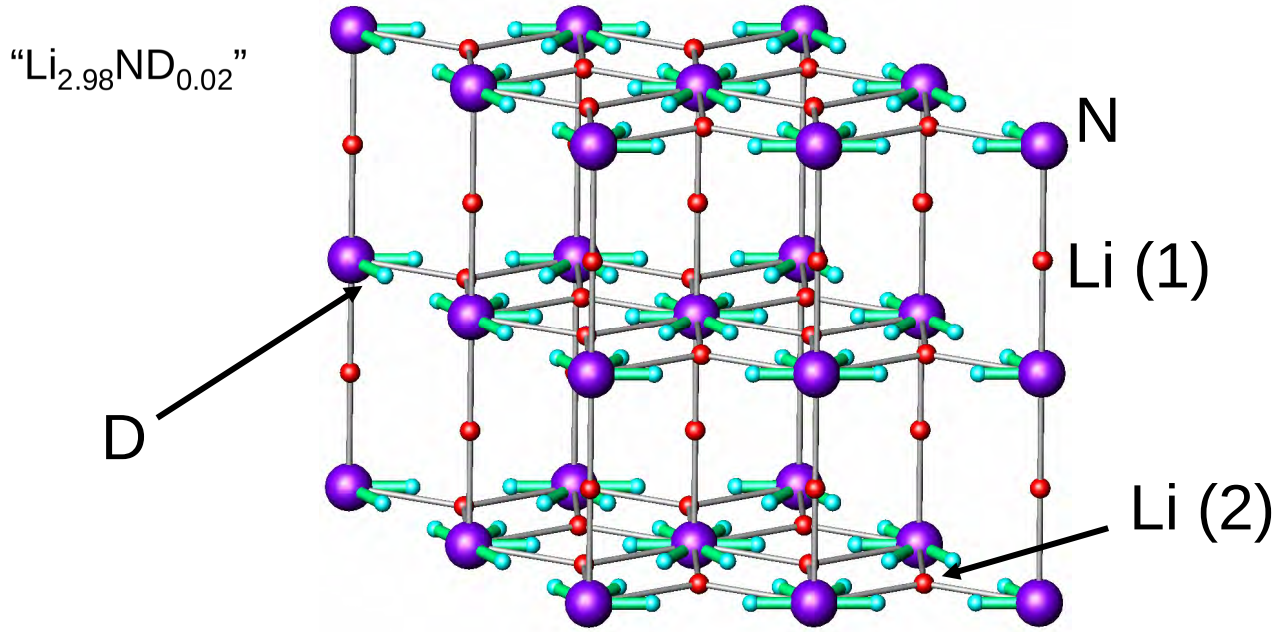
H atoms vs. pressure, uptake and release

Hydrogen storage in lithium nitrides

•Hydrogen in the Li-N system

Early Evidence for H content

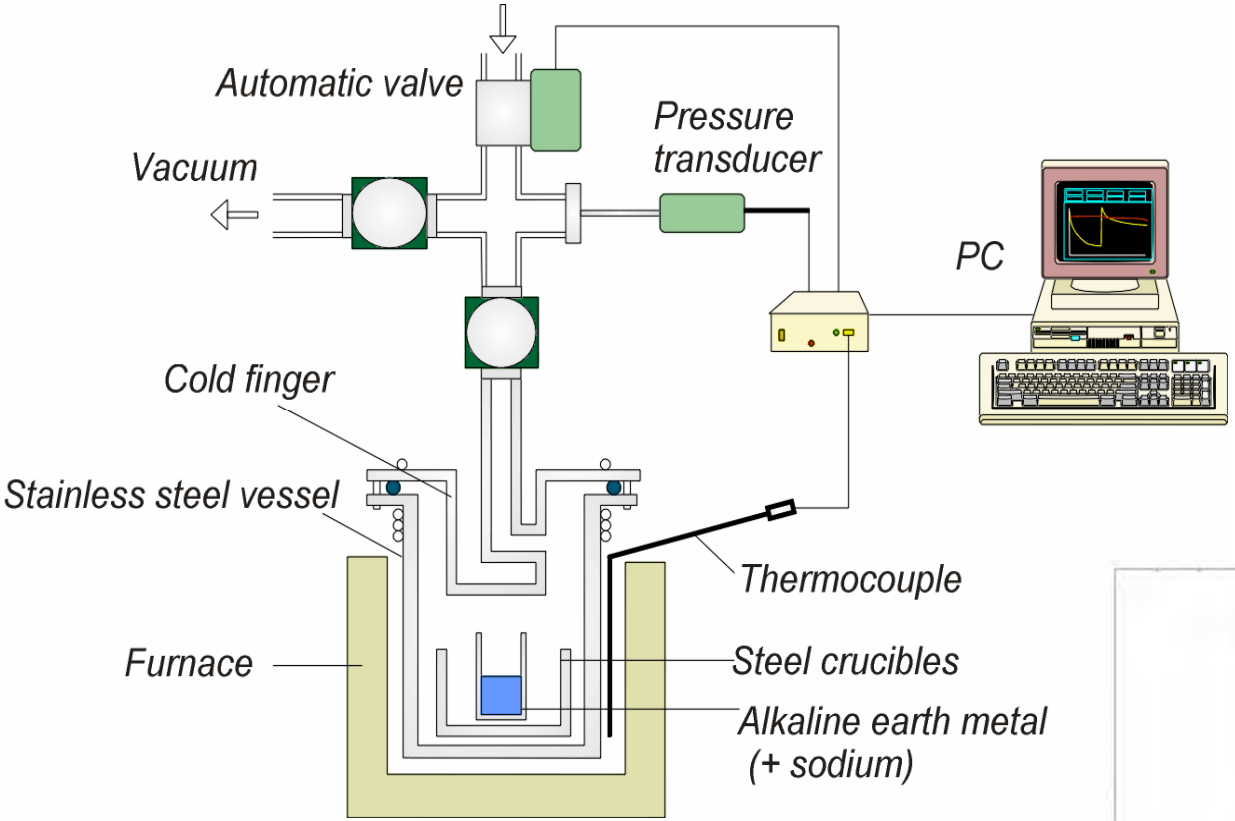
1979-8 IR spectroscopy (Whal, Hooper *et al*, Von Alpen *et al)*
1981 ^{7}Li and ^{1}H NMR (Messer *et al*)
1981 Powder neutron diffraction (PND) of deuterated Li_3N (Thomas & Tellgren)



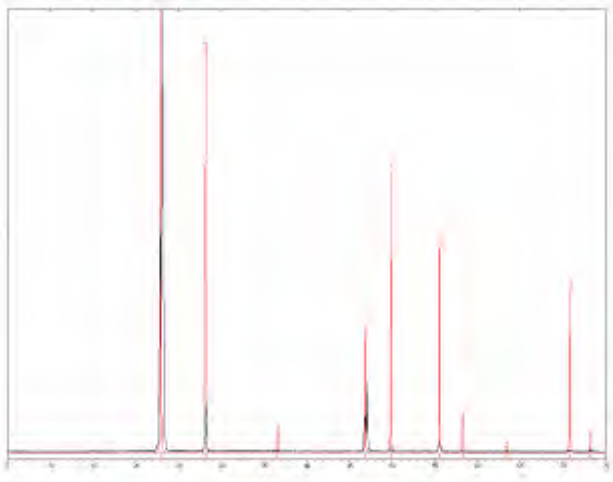
- Apparent dependence of Li^+ ion conductivity on H content
  ⟶ Implies increased vacancy concentration and $(NH)^{2-}$ creation

Hydrogen storage in lithium nitrides

- Synthesis of Li_3N



$$6\ Li + N_2 + Na_{(l)} \rightarrow 2\ Li_3N + Na \uparrow$$

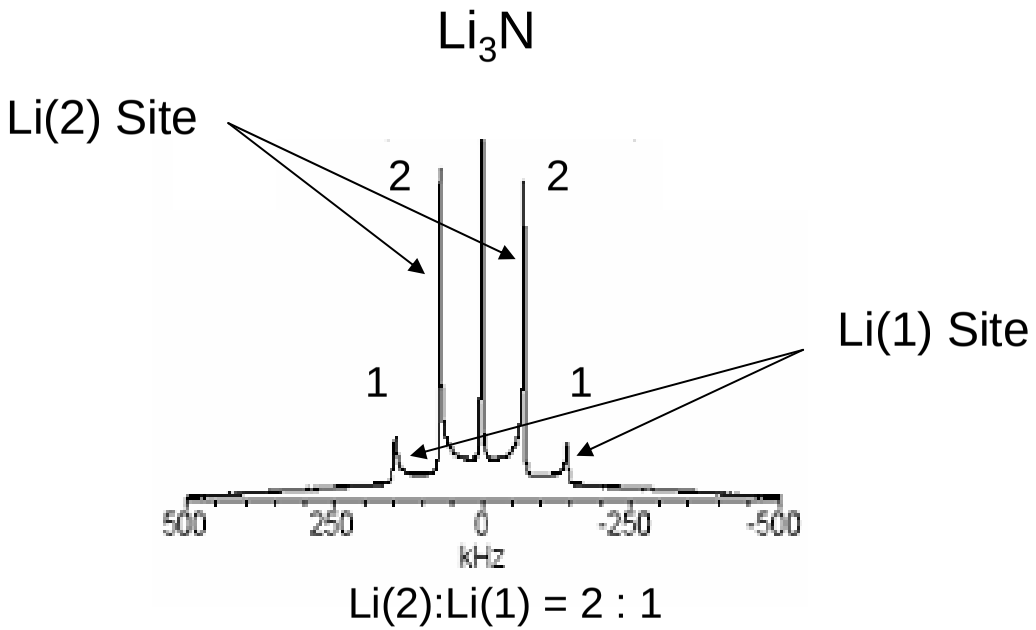


PXD: Exceptionally pure α-Li_3N

Hydrogen storage in lithium nitrides

- Structure and Li+ ion diffusion behaviour of Li_3N

^{7}Li NMR



Li(2):Li(1) = 2 : 1

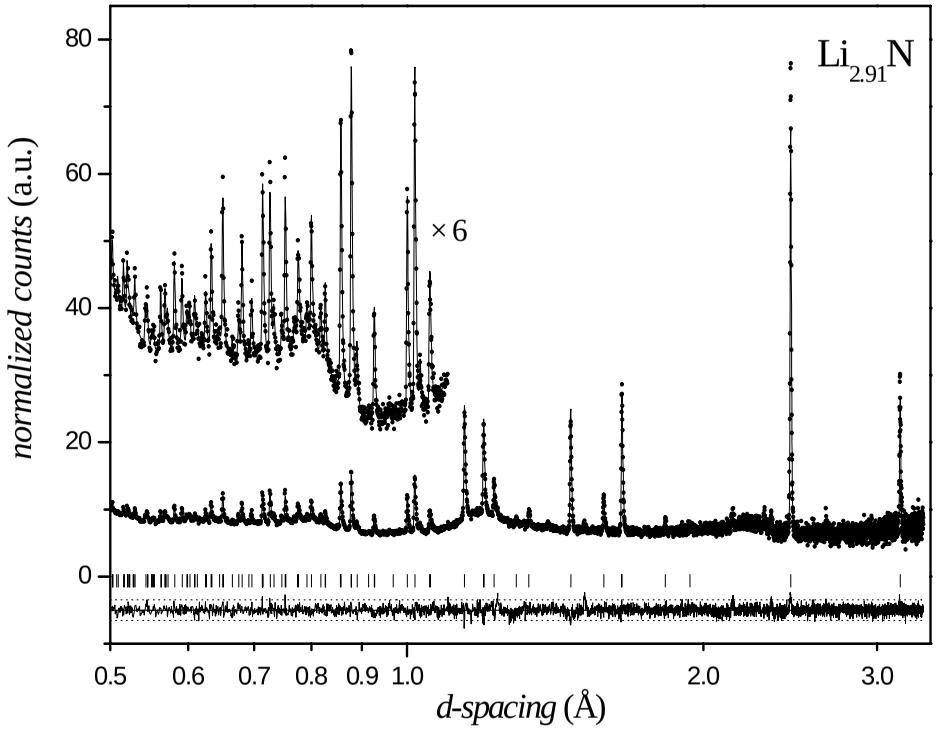
From line broadening with temperature and Spin-Lattice relaxation (T_1) measurements,

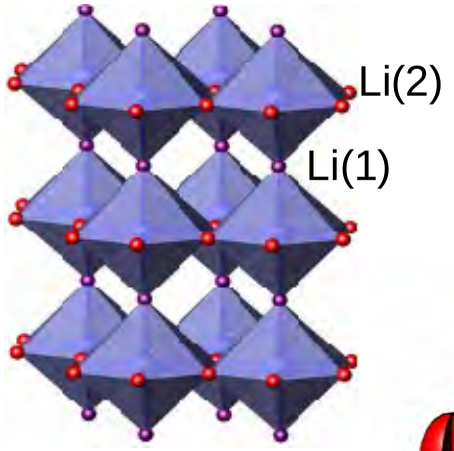
For Li^+ diffusion (hopping) E_a = 0.11 eV – mobile Li^+

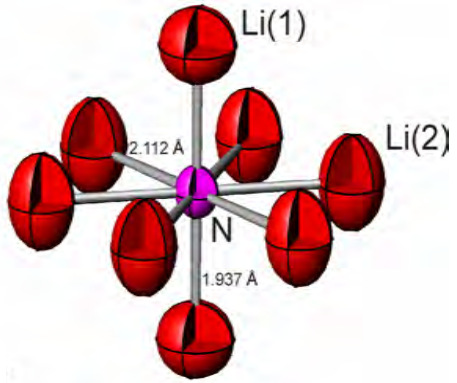
Hydrogen storage in lithium nitrides

- Crystal structure of "Li_3N"

Na-synthesised α-Li_3N - PND at IPNS, Argonne, USA







Refines to $Li_{2.91}N$ - suggests "$Li_{2.91}N_{0.91}(NH)_{0.09}$"

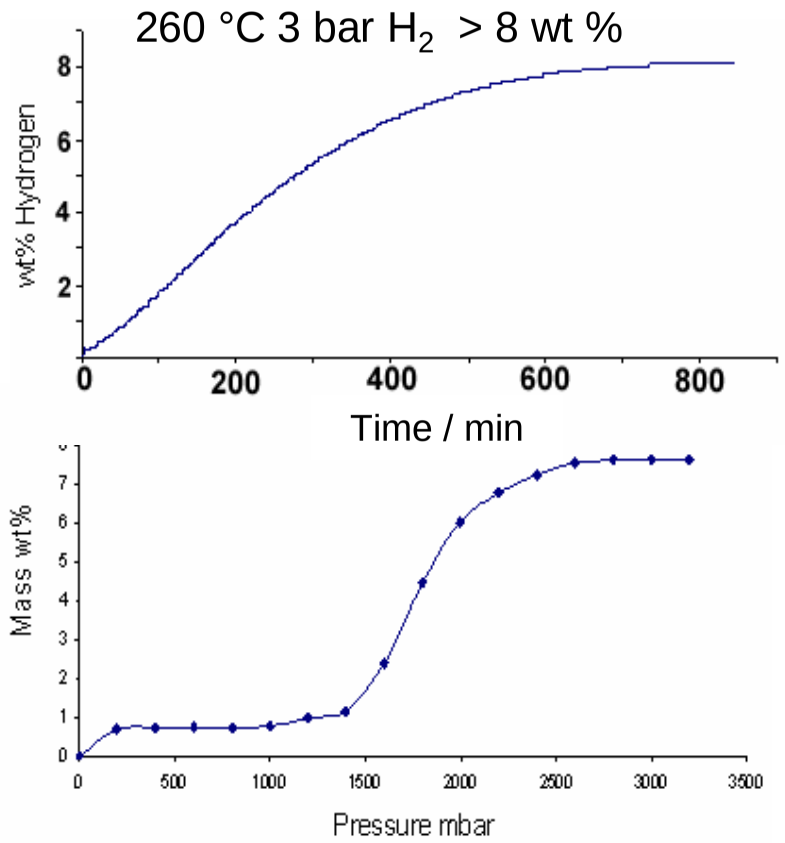
Chem. Mater. 2002, **14**, 2063.

Hydrogen storage in lithium nitrides

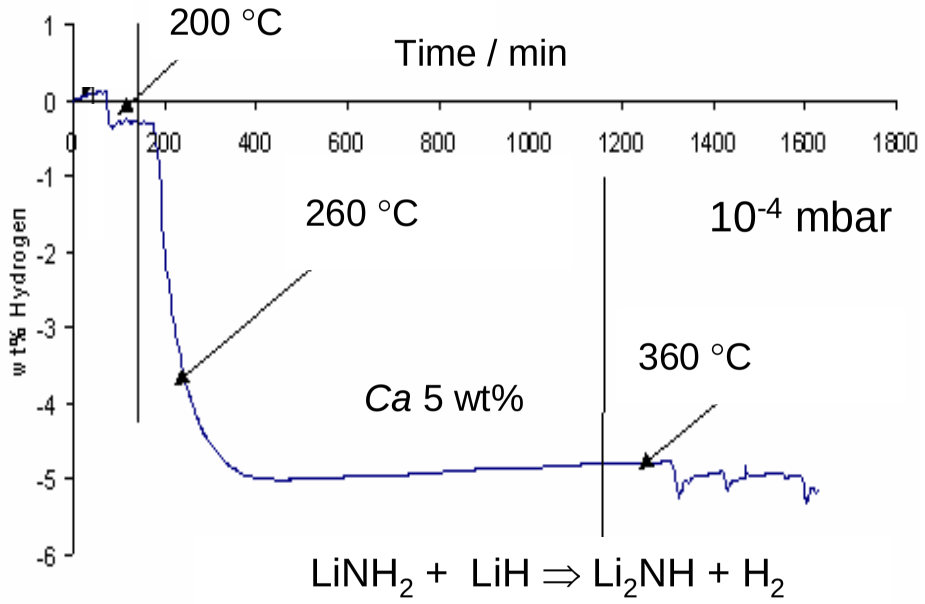
- H adsorption and desorption in the Li-N-H system

Na-synthesised α-Li_3N - gravimetric measurements (IGA)

Uptake



Release



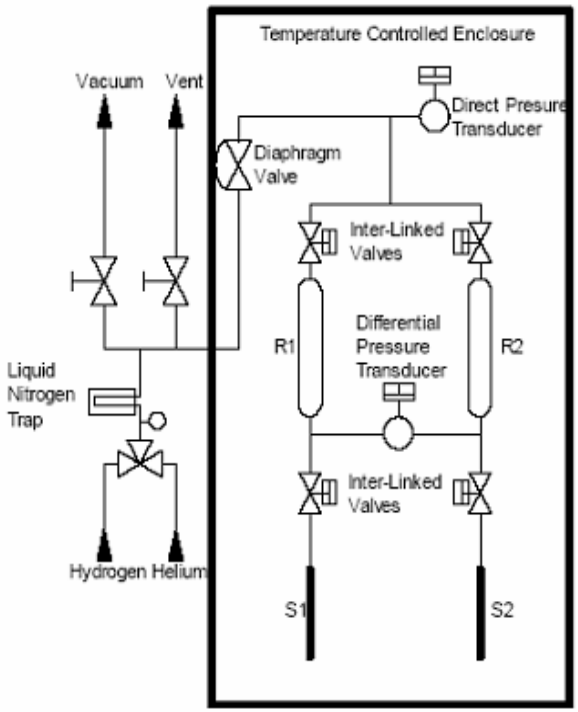
$LiNH_2 + LiH \Rightarrow Li_2NH + H_2$

$Li_3N + 2\ H_2 \Rightarrow Li_2NH + LiH + H_2 \Leftrightarrow LiNH_2 + 2\ LiH$

Hydrogen storage in lithium nitrides

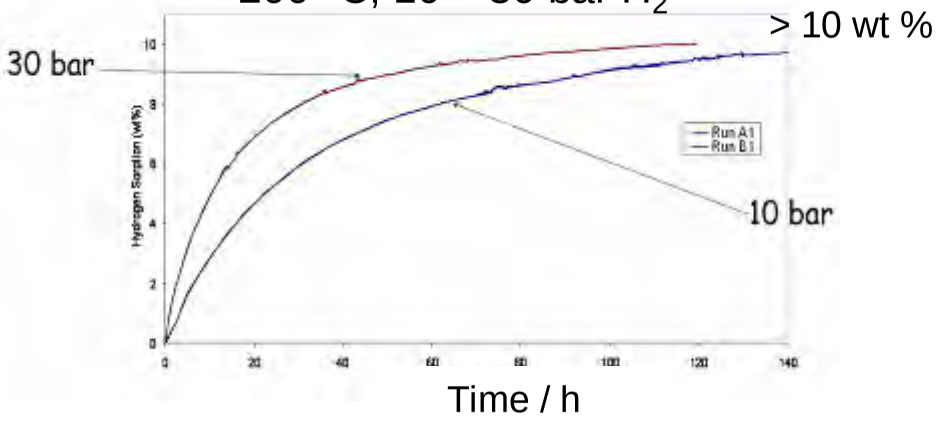
•H adsorption and desorption in the Li-N-H system

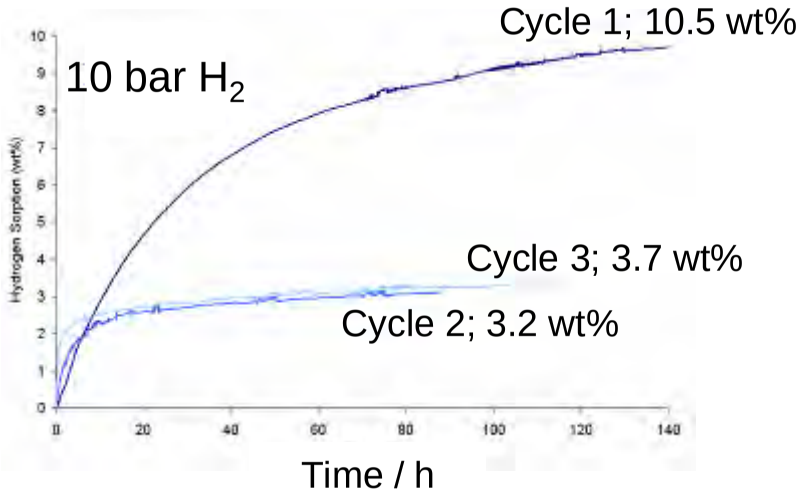
Na-synthesised α-Li_3N - differential pressure (volumetric) measurements



Uptake

200 °C, 10 – 30 bar H_2





Colin Snape, James Blackman,
School of Chemical, Mining and Environmental Engineering,
University of Nottingham

Hydrogen storage in lithium nitrides

- H adsorption and desorption in the Li-N-H system

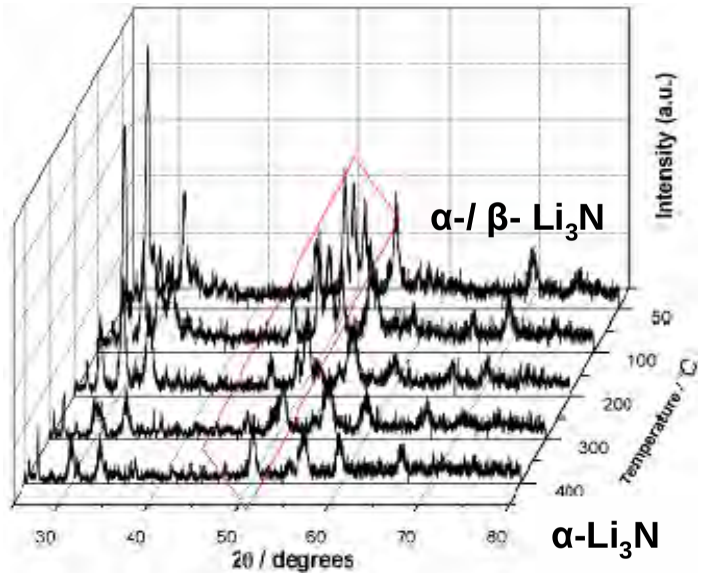
Commercial (α/β) Li_3N *vs.* α-Li_3N *vs.* β-Li_3N

Aldrich (α/β) Li_3N —**Ball mill, 2h**→ β-Li_3N

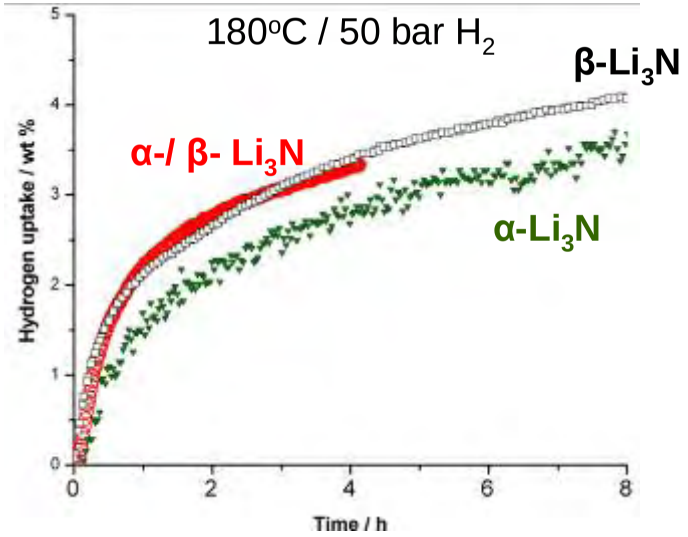
370 °C, 20 h ↓

α-Li_3N

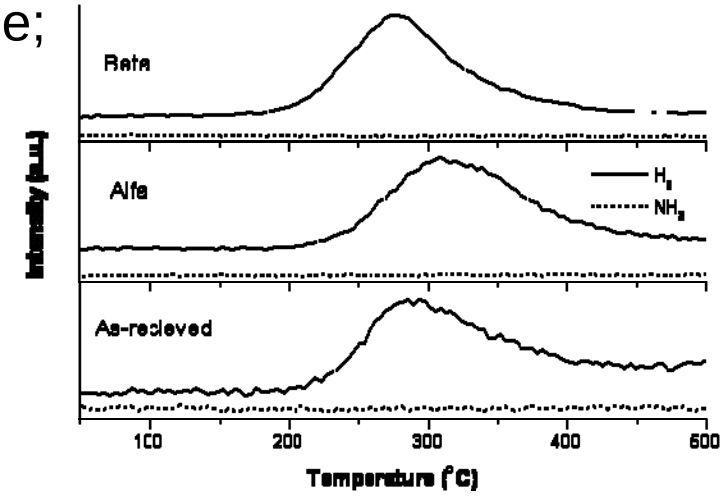
In situ-XRD



Uptake



Release; TPD



β-Li_3N: faster sorption, lower T_{des} ?

Hydrogen storage in lithium nitrides

•Optimising H sorption in the Li-N-H system

West CHEM UNIVERSITY of GLASGOW

Li_3N cycle step 2; desorption direction:

$$Li_2NH + H_2 \Leftarrow LiNH_2 + LiH$$

- Ichikawa, Fujii *et al* (2003) – $TiCl_3$ catalyst (1 mol%) → $T_d \approx 200$ °C (*cf.* 260 °C for as-grown Li_3N)
- Orimo *et al* (2004) – Mg sub^n (10 at%) → $T_d \approx 230$ °C

Li_3N cycle step 1; adsorption direction:

$$Li_3N + H_2 \Rightarrow Li_2NH + LiH$$

- Hu *et al* (2004) – "Heat pre-treatment of Li_3N" → 3 wt% H_2 in 3 min, 9.5 wt% in 303 min / 7 atm, 230 °C
- Hu *et al* (2004) – "Partly oxidised + hydrogenated/dehydrogenated Li_3N" → 5 wt% H_2 in 3 min; reversible / 7 atm, 198 °C

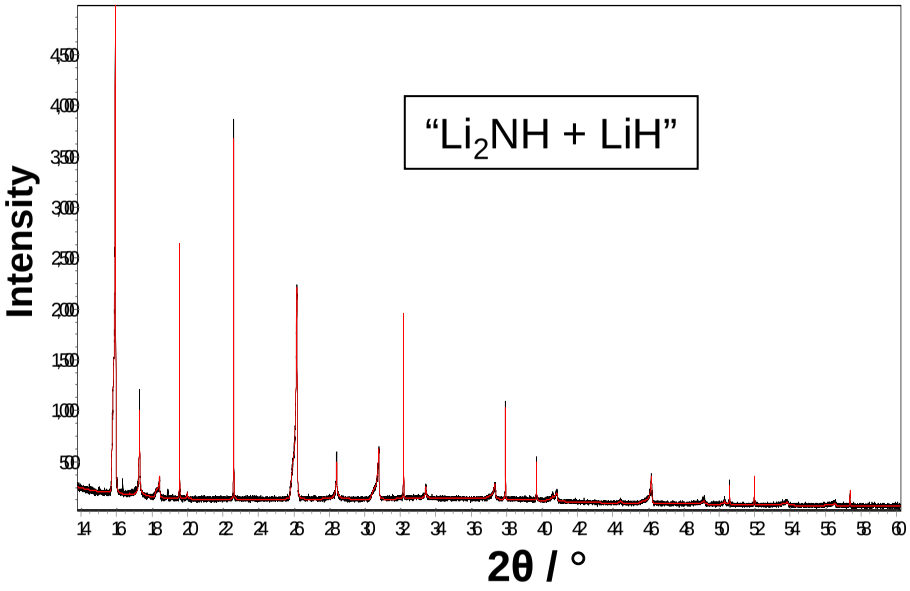
Hydrogen storage in lithium nitrides

•H storage in Li nitrides; ex-situ PXD

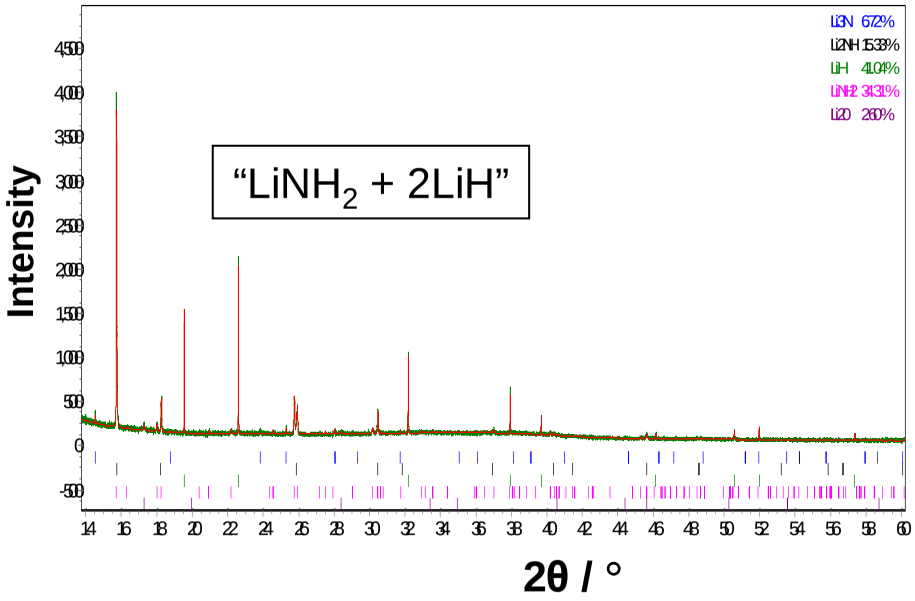
Synchrotron PXD (SPXD) of (de)hydrogenated bulk Li_2NH and $LiNH_2$

SPXD on Li_3N after hydrogenation @ 533 K, 10 bar H_2

- Sample **1** - Single desorption (outgas, 1 absorption, 1 desorption)
- Sample **2** - Cycled (outgas, 6 absorptions, 5 desorptions)



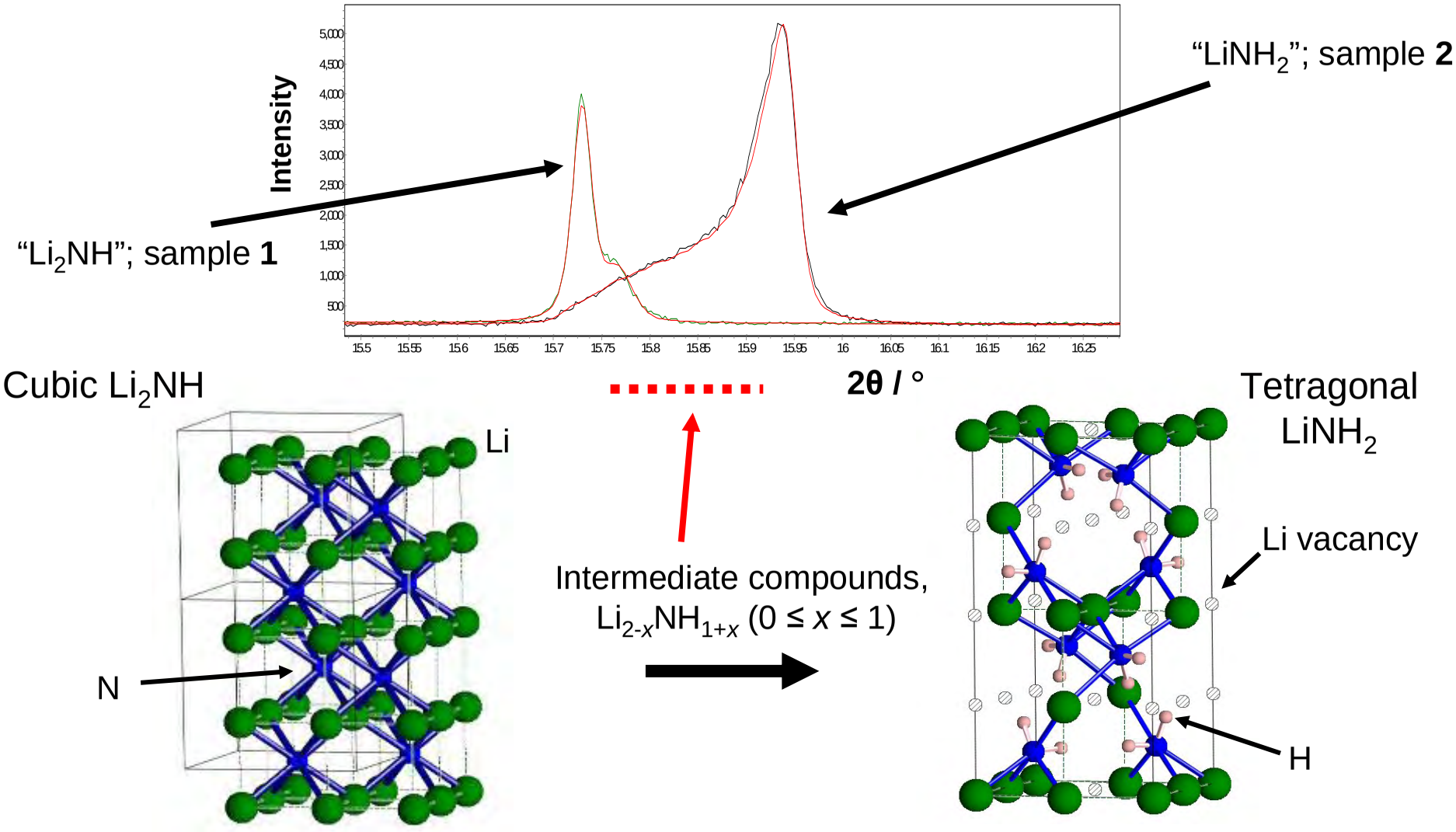
Sample **1**



Sample **2**

Hydrogen storage in lithium nitrides

- H storage in Li nitrides; ex-situ SPXD



W.I.F. David, M. O. Jones, D. H. Gregory, C. M. Jewell, S.R. Johnson, A. Walton, P. P. Edwards, *JACS,* 2007, **129**, 1594

.

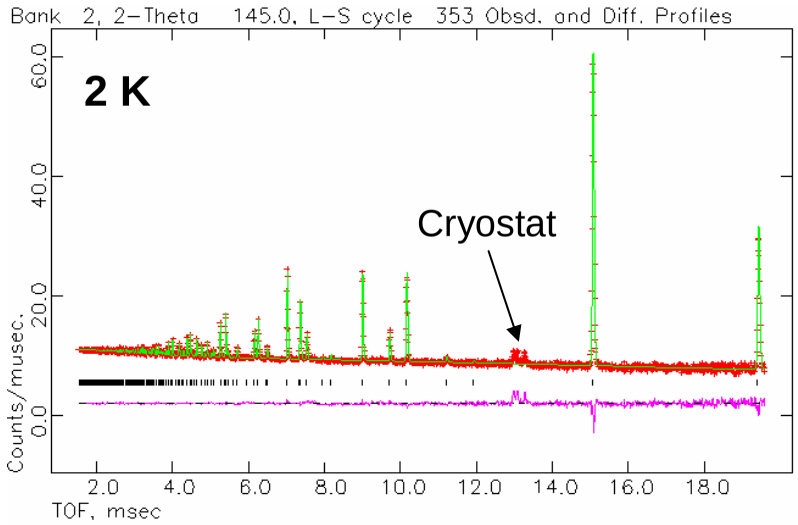
Hydrogen storage in lithium nitrides

•H storage in Li nitrides; **Low** T storage

• INS → Expansion of Li_3N lattice to admit more H_2 at low T as T **decreases**. Negative thermal expansion (NTE)?

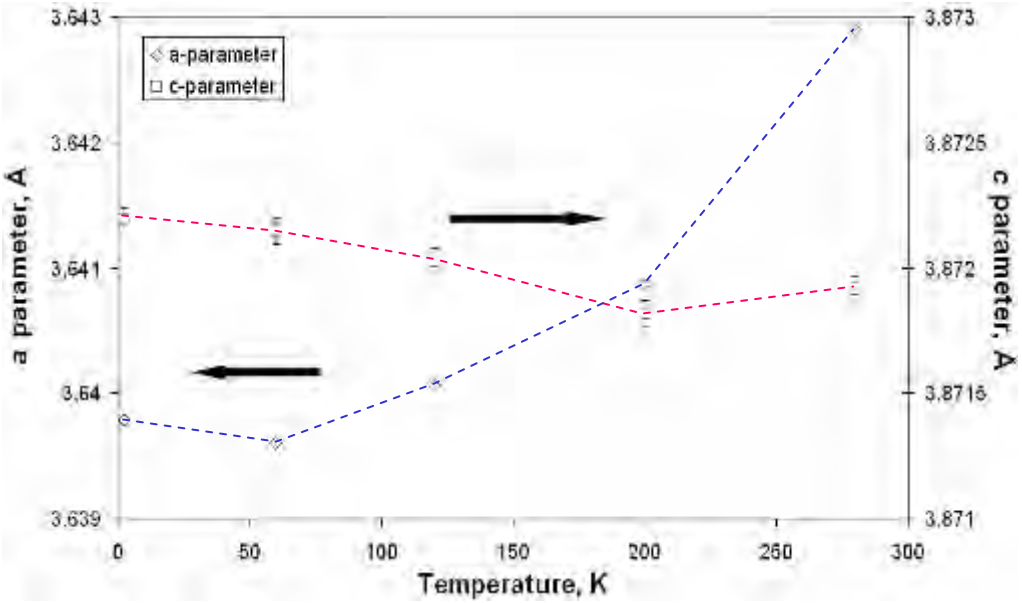
• Schulz *et al*, 1979: Single crystal XRD, 100 K ≤ T ≤ 900 K *a* increases; *c* "nearly constant".

• PND of pristine Li_3N:



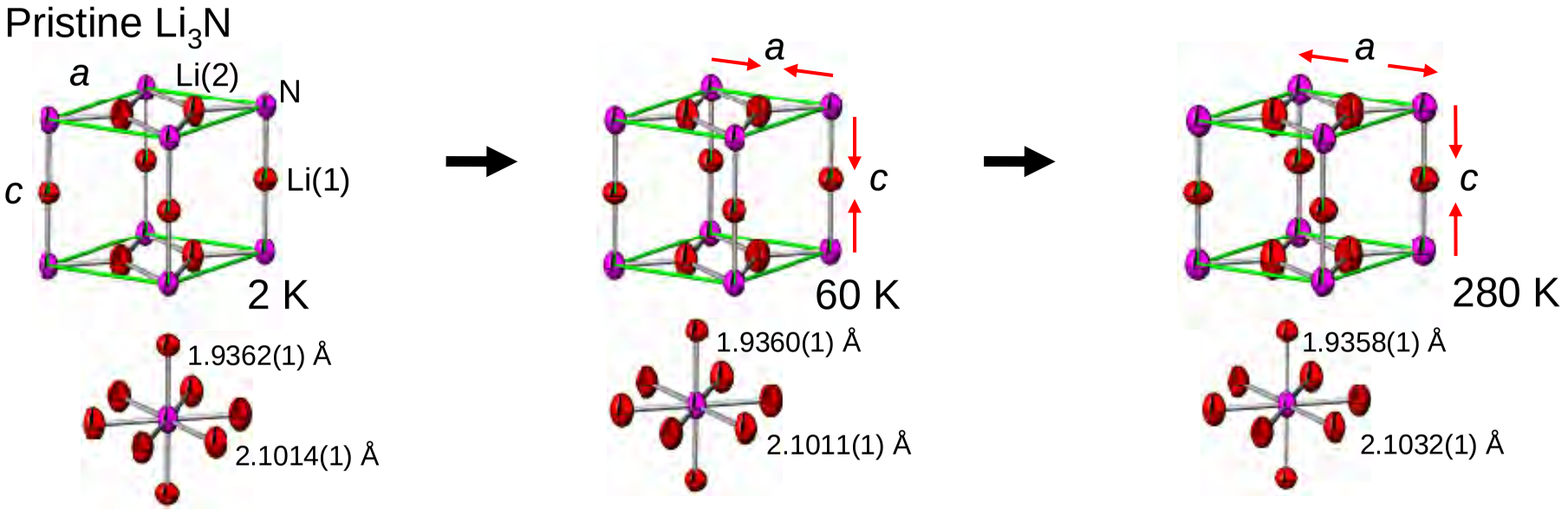
Anisotropic NTE

for *c*: 2 ≤ T ≤ 200 K for *a*: 2 ≤ T ≤ 60 K



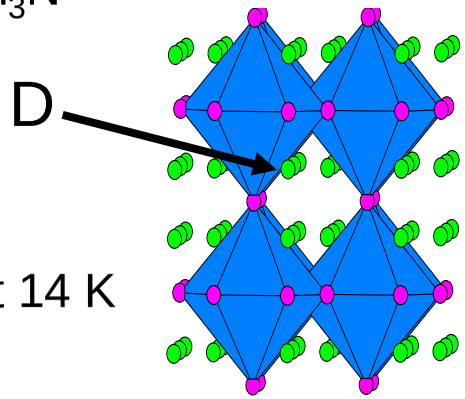
Hydrogen storage in lithium nitrides

- H storage in Li nitrides; **Low** T storage



Lattice expands with decreasing T (30 → 2 K) ⟶ enhanced H_2 diffusion into bulk.

- PND: In-situ deuteration of Li_3N



PND Model for $Li_{3-x}D_xN$ at 14 K

$Li_{2.8}ND_{0.2}$
Partially occupied new interstitial at (1/3,2/3,0.313(3))

Novel nitrides – contents

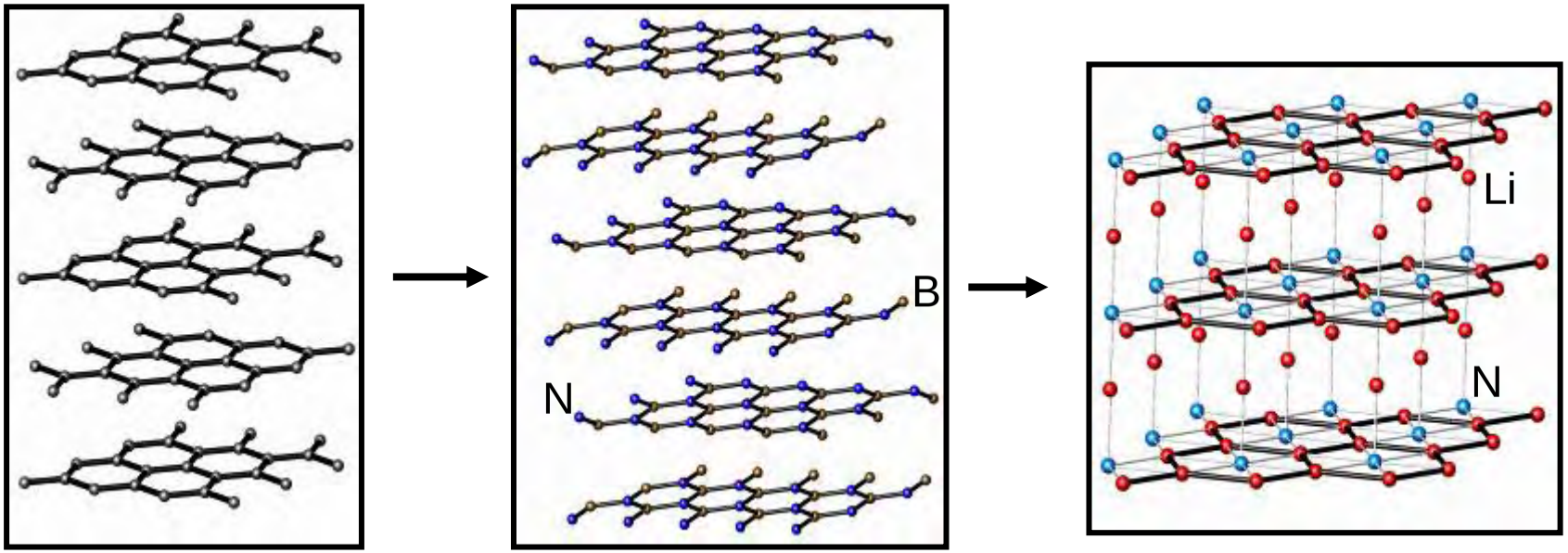
1. Introduction

2. Hydrogen storage in lithium nitrides

3. New forms of lithium nitrides

New forms of lithium nitrides

- Structural parallels



C BN Li_3N

New forms of lithium nitrides

•Property parallels

C but also BN:

- Ma *et al, J. Am. Chem. Soc.*, 2002, **124**, 7672

MWNT from $B_4N_3O_2H$ / (NH_3 + N_2) / *Ca.* 2000 K ⟶ 1.8 wt % at 10 MPa / 293 K

"Bamboo" NT from BN powder / (NH_3 + N_2) / *Ca.* 2000 K ⟶ 2.6 wt % at 10 MPa / 293 K

70 % reversible; 4 h to equilibrate; chemisorption

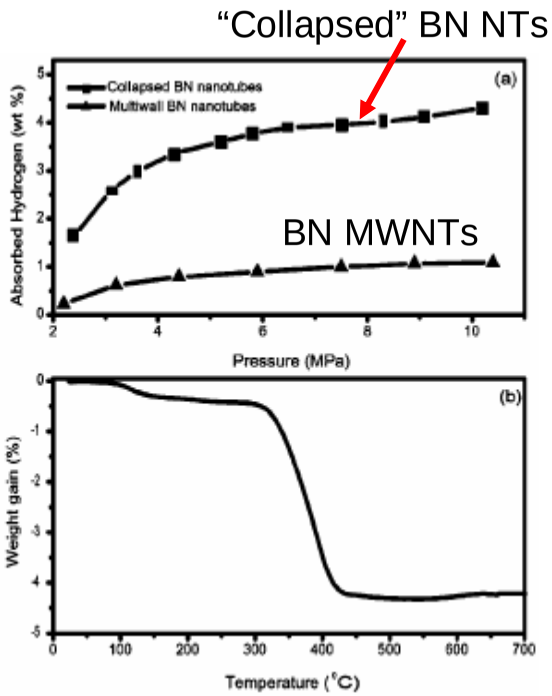
Cf. BN powder ⟶ 0.2 wt % at 10 MPa / 293 K

- Tang *et al, J. Am. Chem. Soc.*, 2002, **124**, 14551

"Collapsed" BN NTs (from B_2O_2 / Mg) ⟶ 4.2 wt %

"Collapsing" : 254 $m^2\ g^{-1}$ to 789.1 $m^2\ g^{-1}$

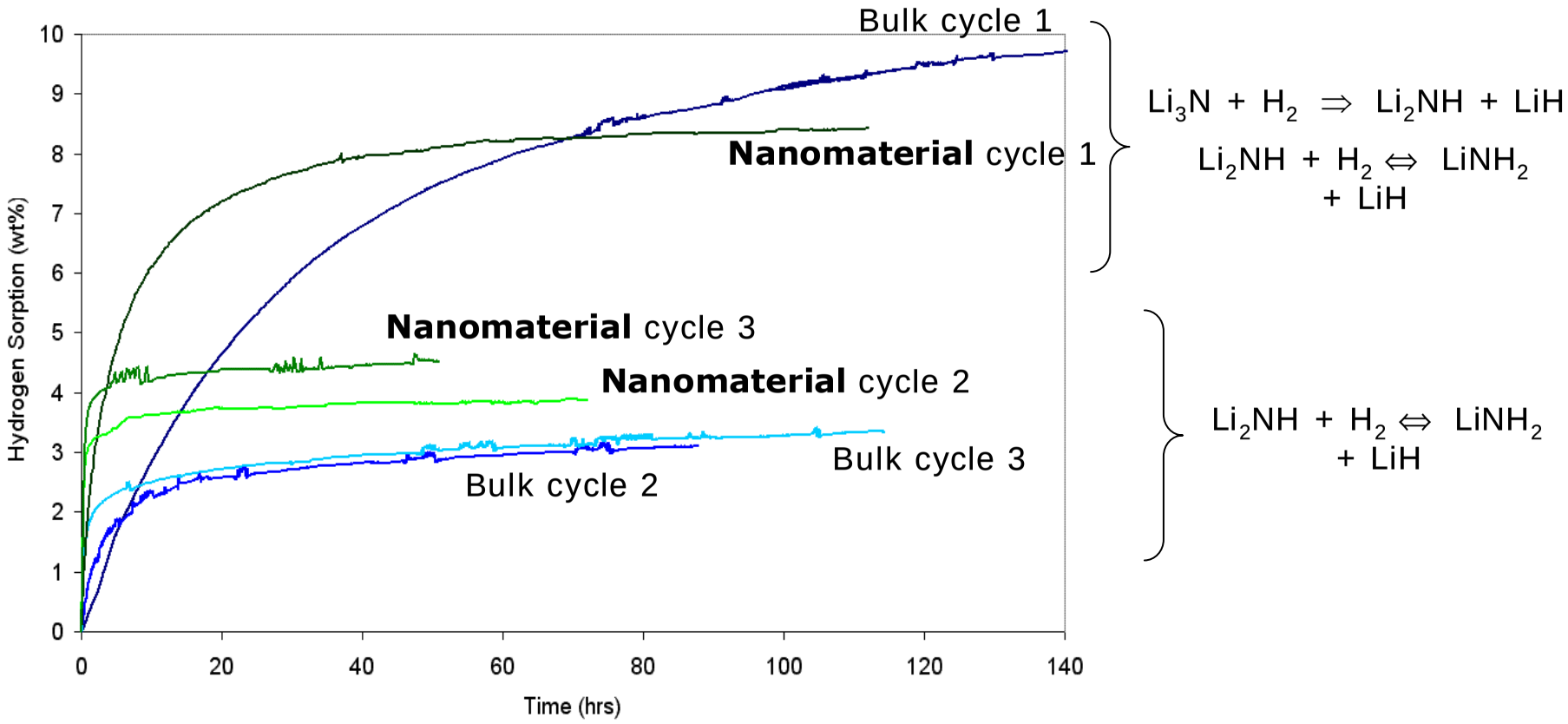
Chemisorption: internal surface available



New forms of lithium nitrides

•H sorption in nanomaterials

- H storage in the Li-N-H system at 200 ºC, 10 bar H_2



- Lower initial uptake for nanotubes vs. bulk but kinetics *ca*. ***3 x* faster**.
- Improved subsequent capacity and reversibility between imide and amide.

Acknowledgements

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Dr M Fey,

Prof. C Snape,

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