Cost-effective Processing of Hydrogen Storage Alloys from their Oxides

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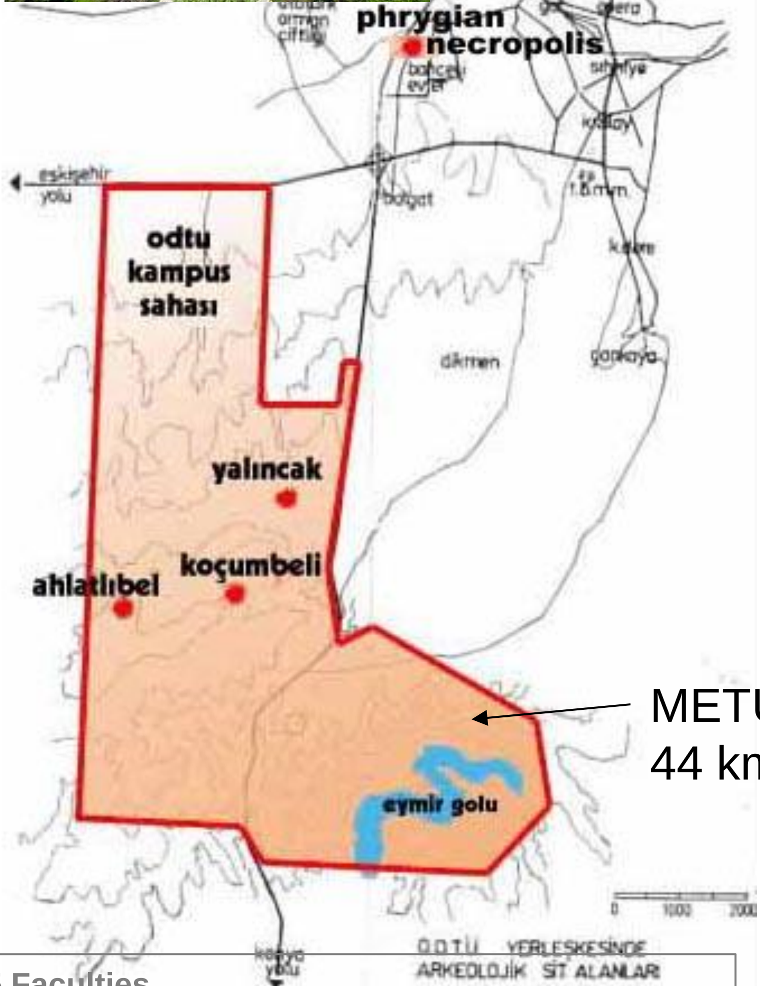
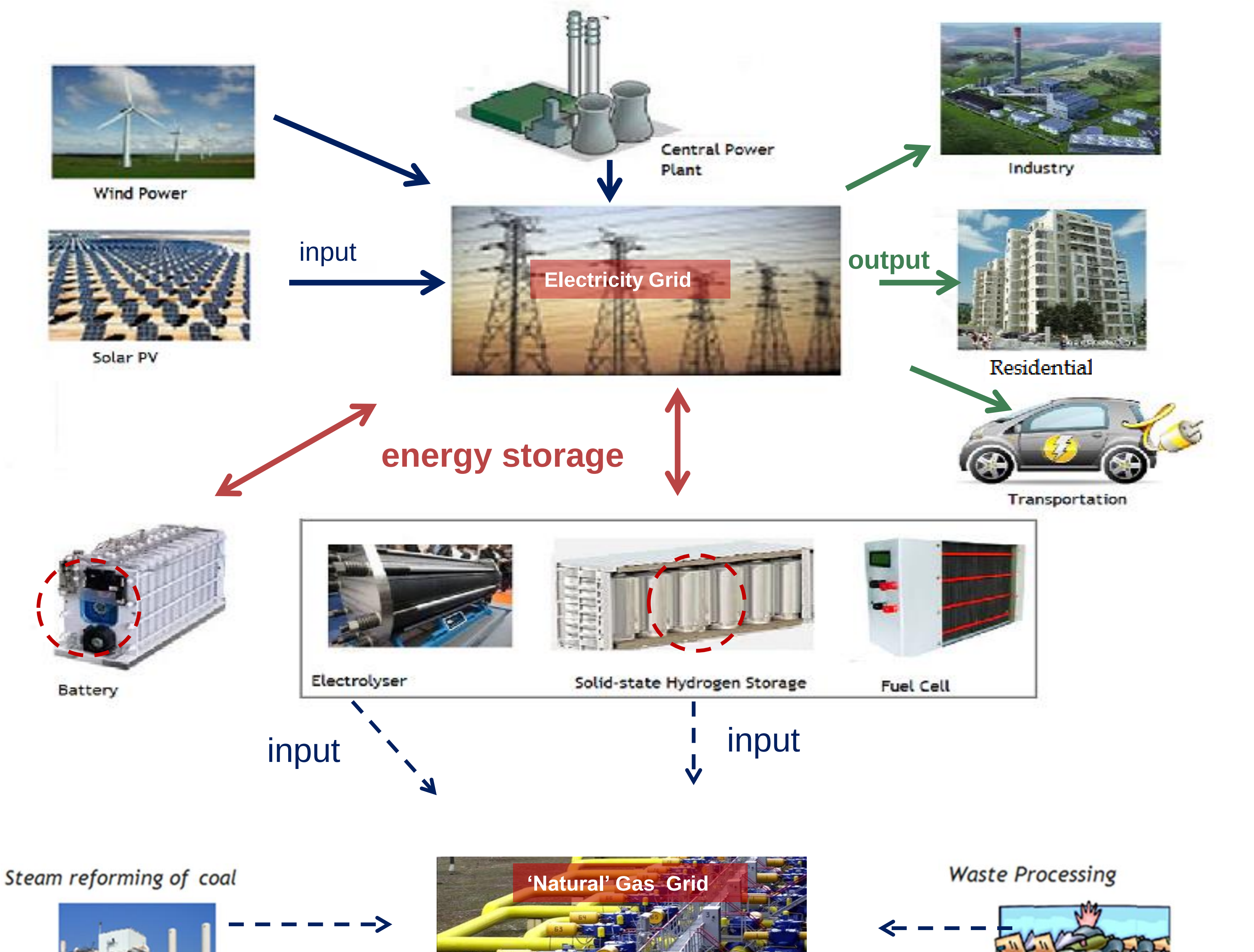
MP1103 Nanostructured materials for solid-state hydrogen storage



METU
44 km^2

5 Faculties
14 Departments in Engineering
10 Departments in Art & Sciences
85 master programs ; 65 doctorate programs

15, 000 Undergraduates
5,000 MS
3000PhD
1,500 Foreign Students


Wind Power
Central Power Plant
Industry
Solar PV
input
Electricity Grid
output
Residential
energy storage
Transportation
Battery
Electrolyser
Solid-state Hydrogen Storage
Fuel Cell
input
input
Steam reforming of coal
'Natural' Gas Grid
Waste Processing

Theoretical storage capacity of some hydrogen storage alloys

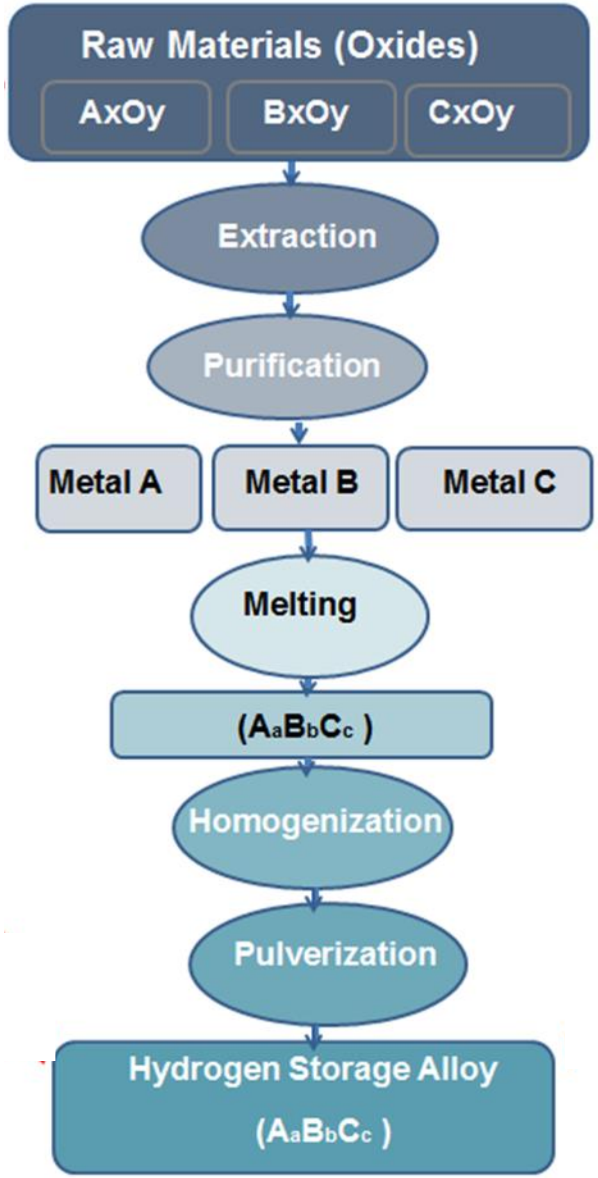
Alloy	**Capacity (wt %Hydrogen)**	**Capacity (mAh/g)**
TiNi	0.9	250
RE based AB_5 Alloy*	1.4	372
Ti based AB_2 Alloy*	1.5	400
Ti_2Ni	1.6	432
TiFe	1.9	515
ZrV_2	2.8	750
Mg_2Ni	3.7	1002
$Mg_{95}Cu_5$**	5.5	1490

Commercial Alloys

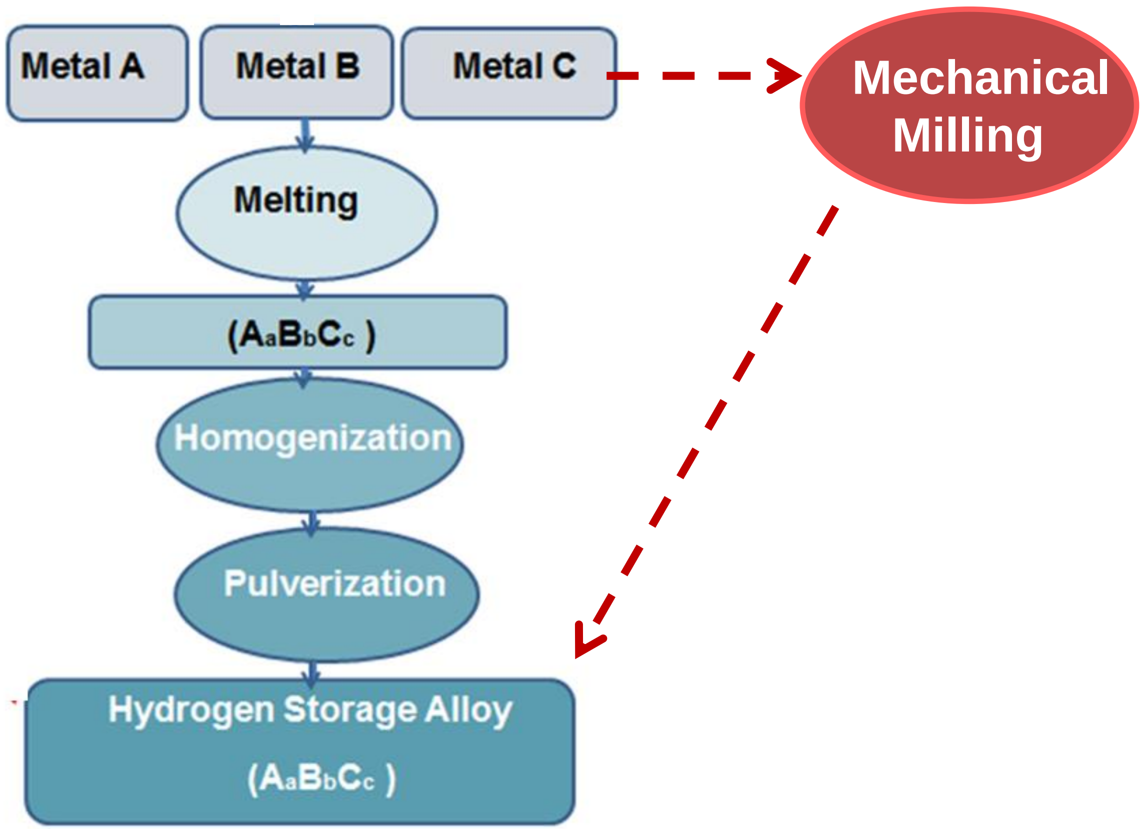
Current Work

* Liu et al. J. Mater. Chem., 2011, 21, 4743

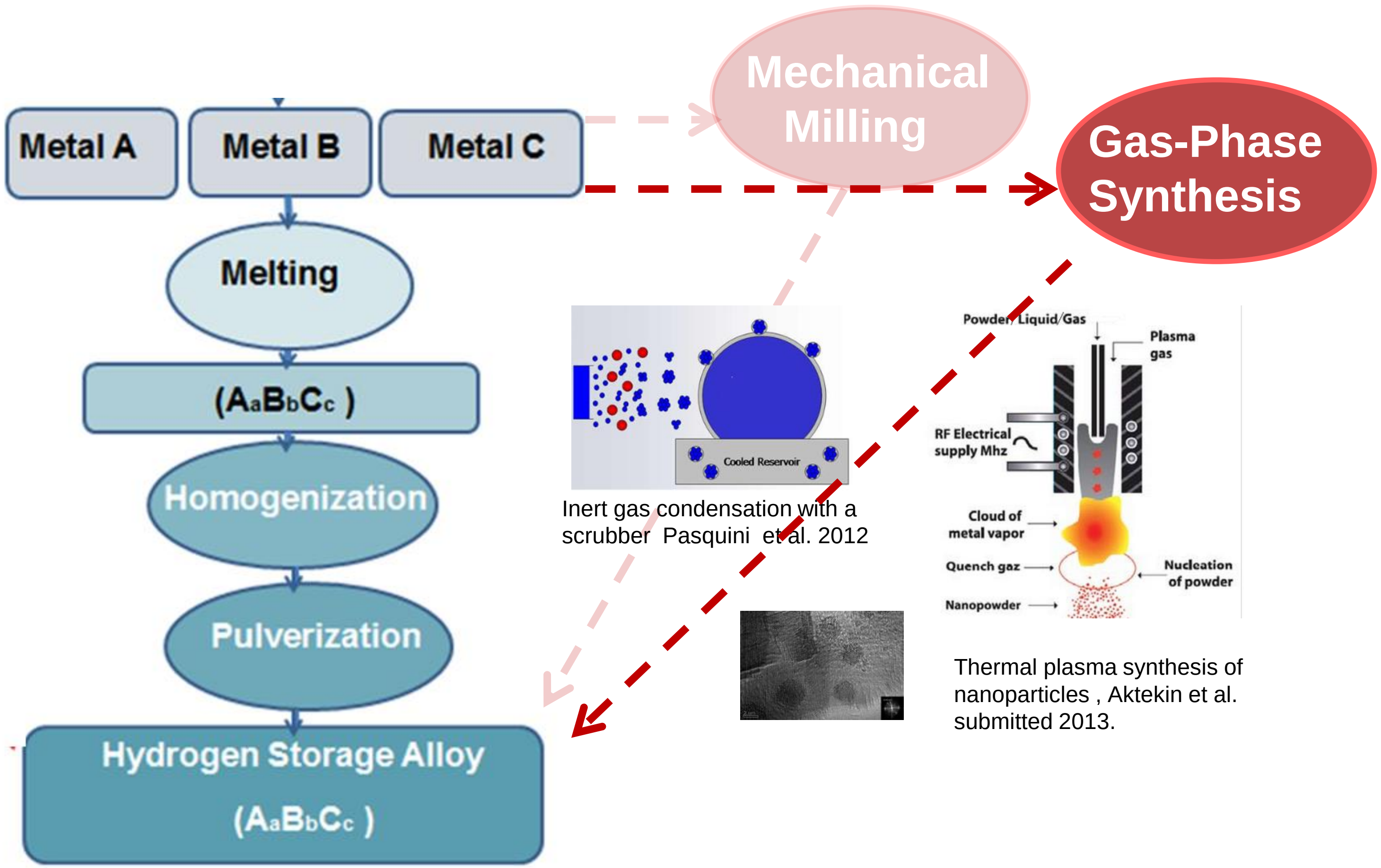
** Akyıldız & Ozturk Journal of Alloys and Compounds 492 (2010) 745–750



Flowchart for synthesis of hydrogen storage compounds
(**Conventional Route**)

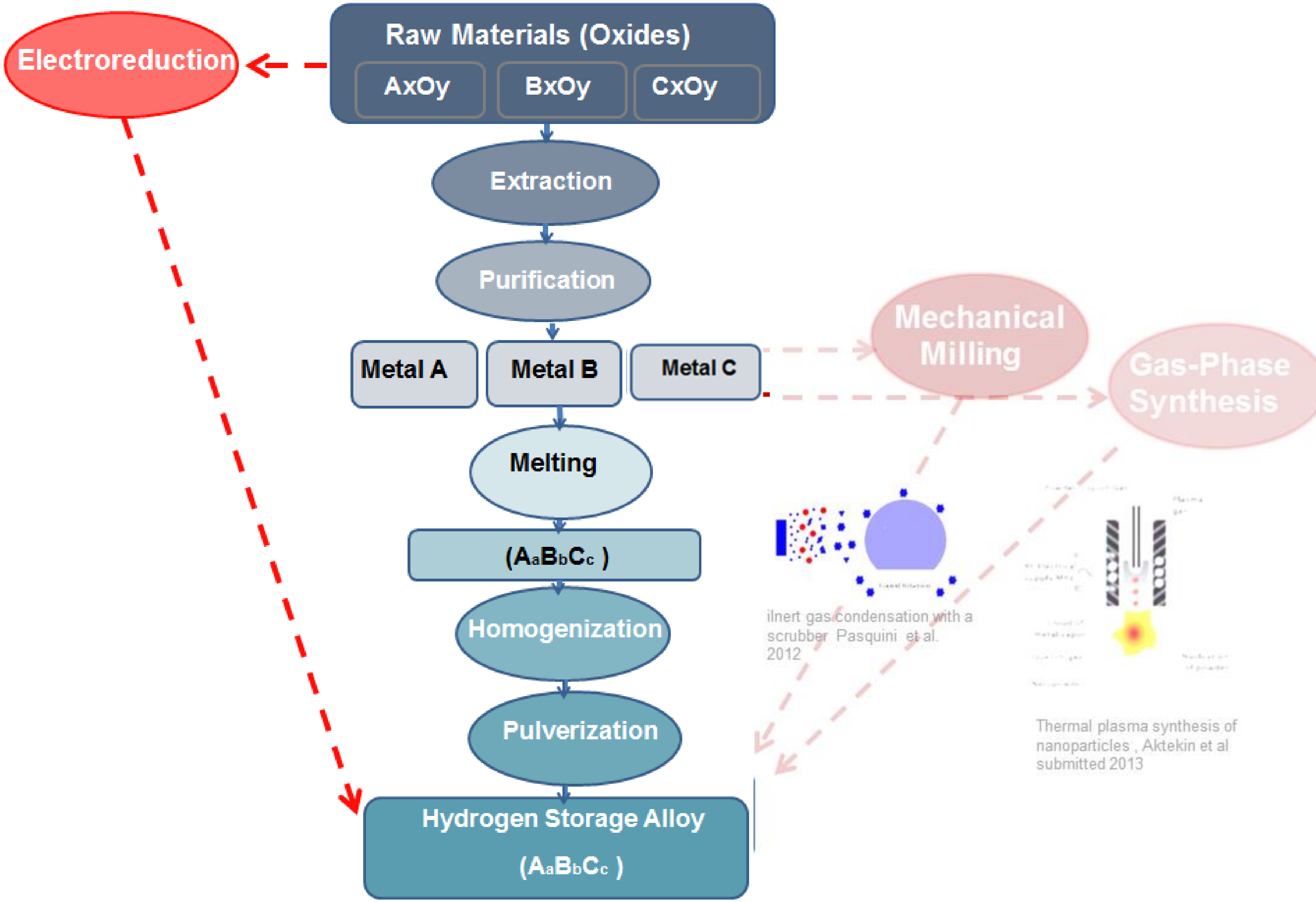


Flowchart for synthesis of hydrogen storage compounds
(Nanostructured HSA via Mechanical Milling)



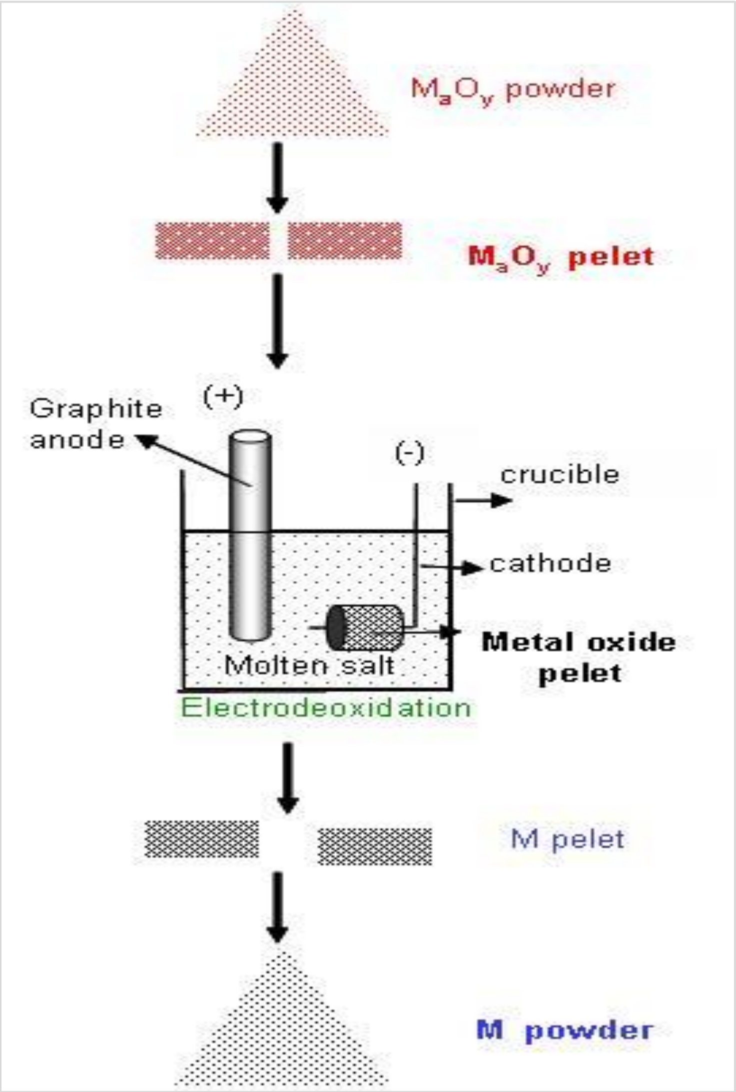
Flowchart for synthesis of hydrogen storage compounds

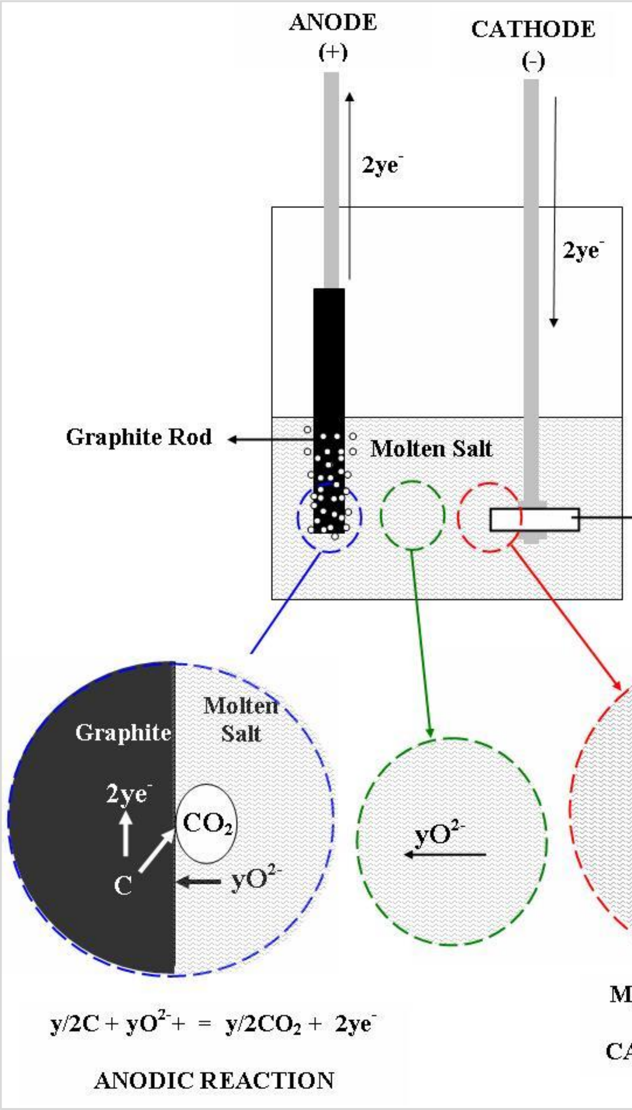
(Nanostructured HSA via Gas-Phase Synthesis)



Flowchart for synthesis of hydrogen storage compounds
(**Electro-reduction of Oxides to HSA**)

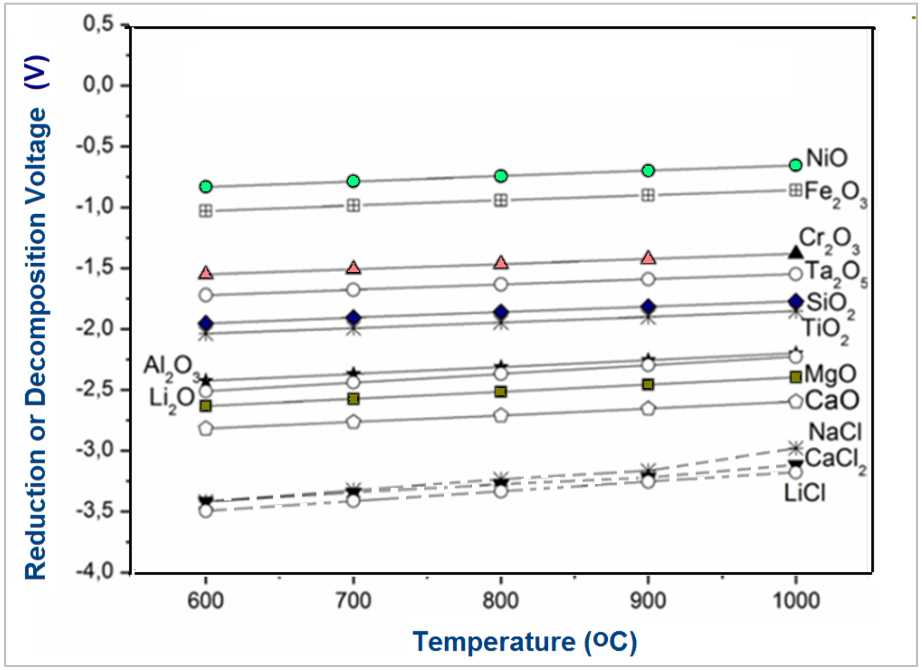
SOLID STATE ELECTROREDUCTION



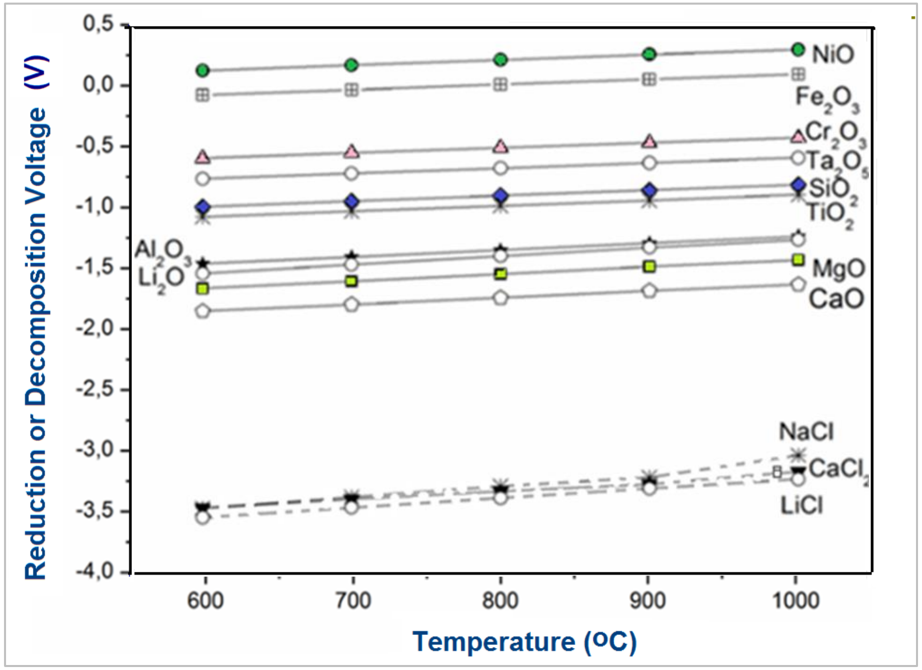


V_{dec} @ 900°C	
NiO	0.33
Nb_2O_5	-0.42
TiO_2	-0.87
MgO	-1.42
NaCl	-3.18
$CaCl_2$	-3.21

Chen et al. Nature 407 (2000) 361–364.



Reduction via O_2 evolution



Reduction via CO_2 evolution

Standard reduction voltage (ΔEo) of selected oxides

Synthesis of FeTi : Sintered Pellets

Mixing

Fe2O3:TiO2=1:1

→

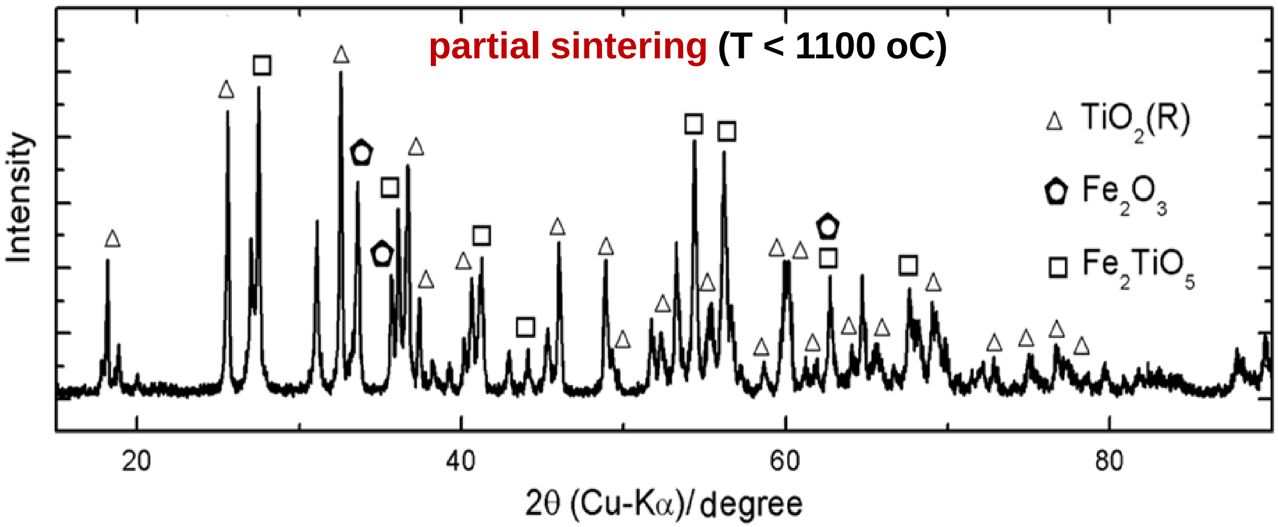
Cold Pressing

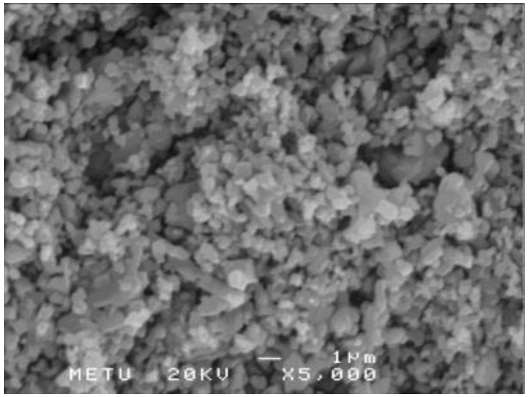
100 MPa

→

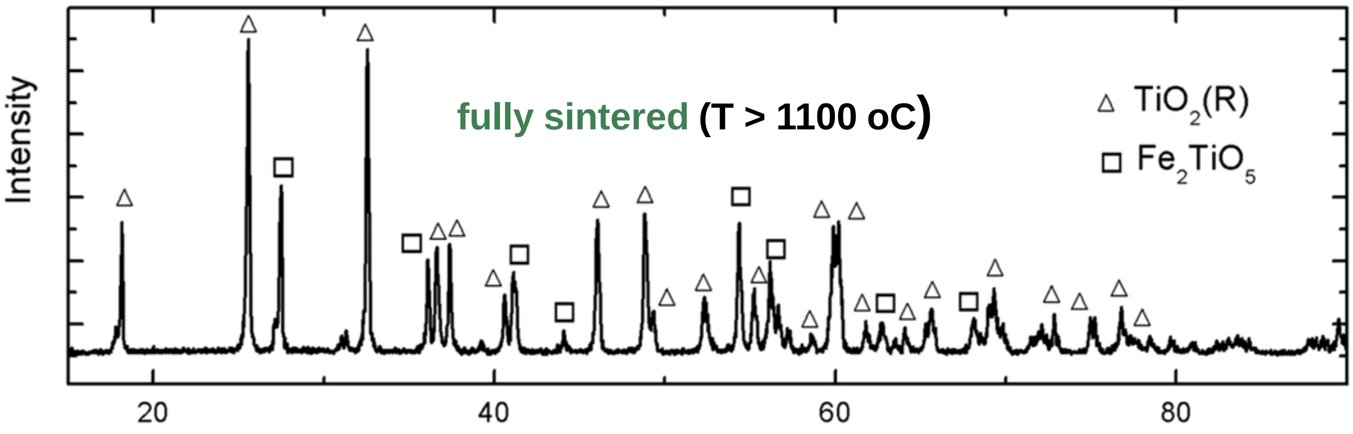
Sintering

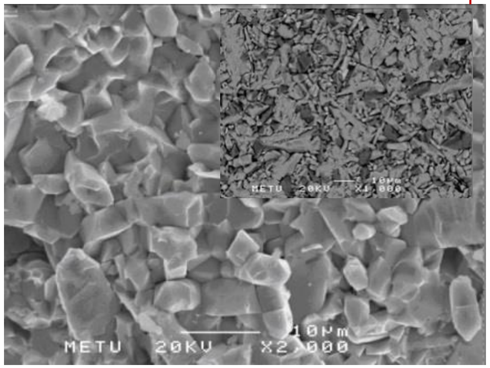
900 ◦C, 2h





1300 ◦C, 2h.



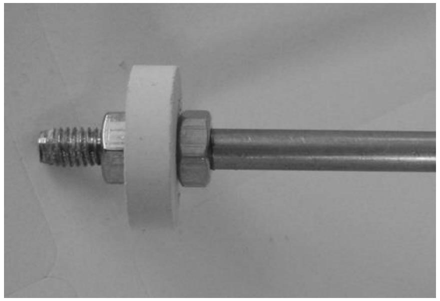


Synthesis of FeTi : Electroreduction of pellets

Pre-electrolysis
Stainless wire -graphite
3.0 V ; 6 hrs 900 oC)
Ar flow = 100-150 ml / min

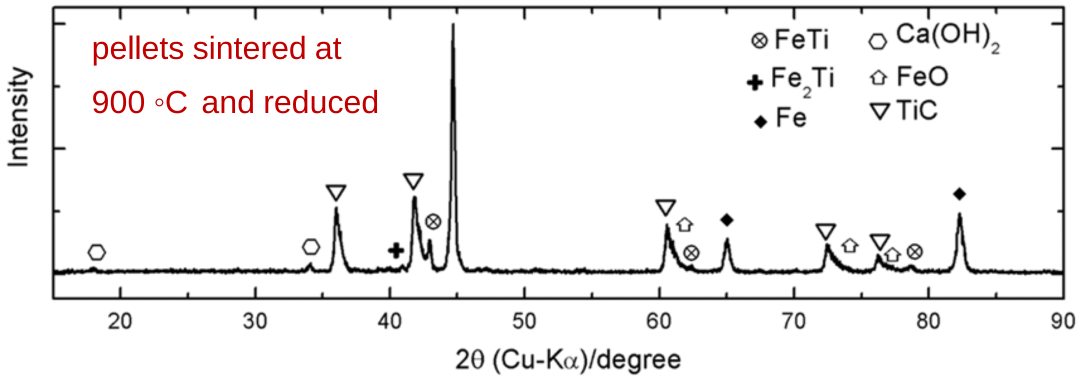
↓

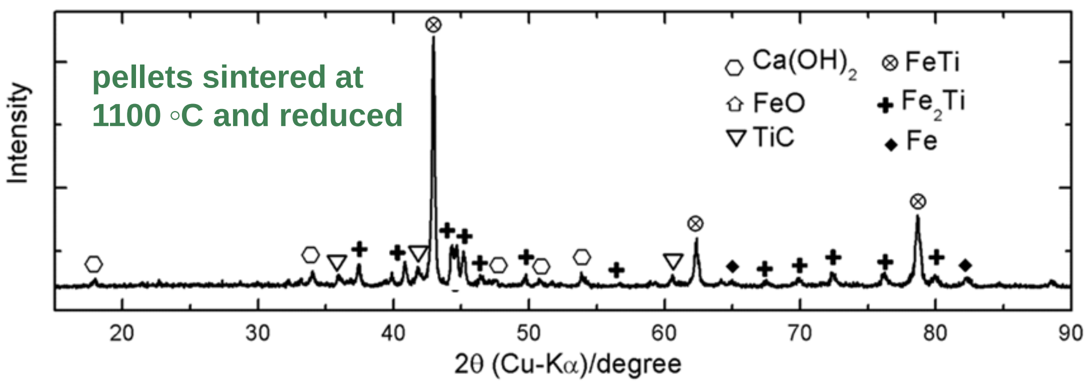
Electrodeoxidation
Sample –Graphite
(3.2 V ; 24 hrs 900)
Ar flow = 100-150 ml/min

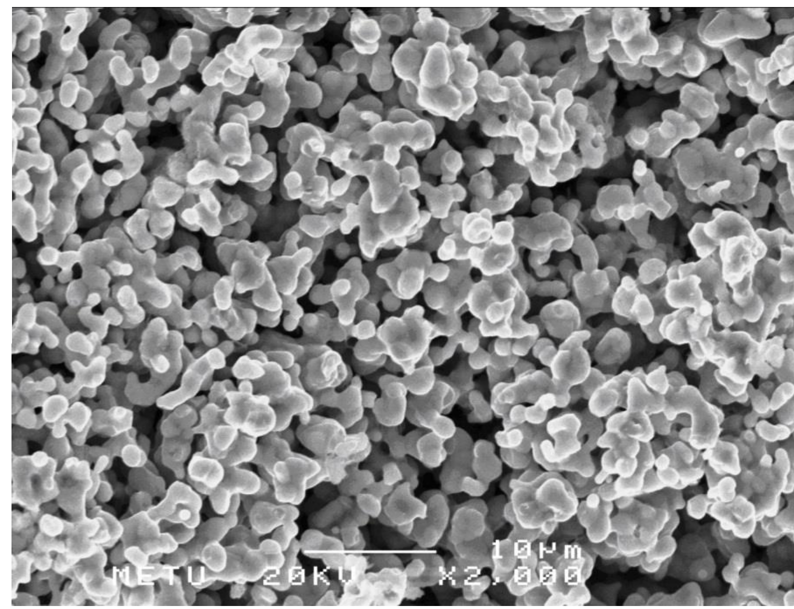


Before reduction

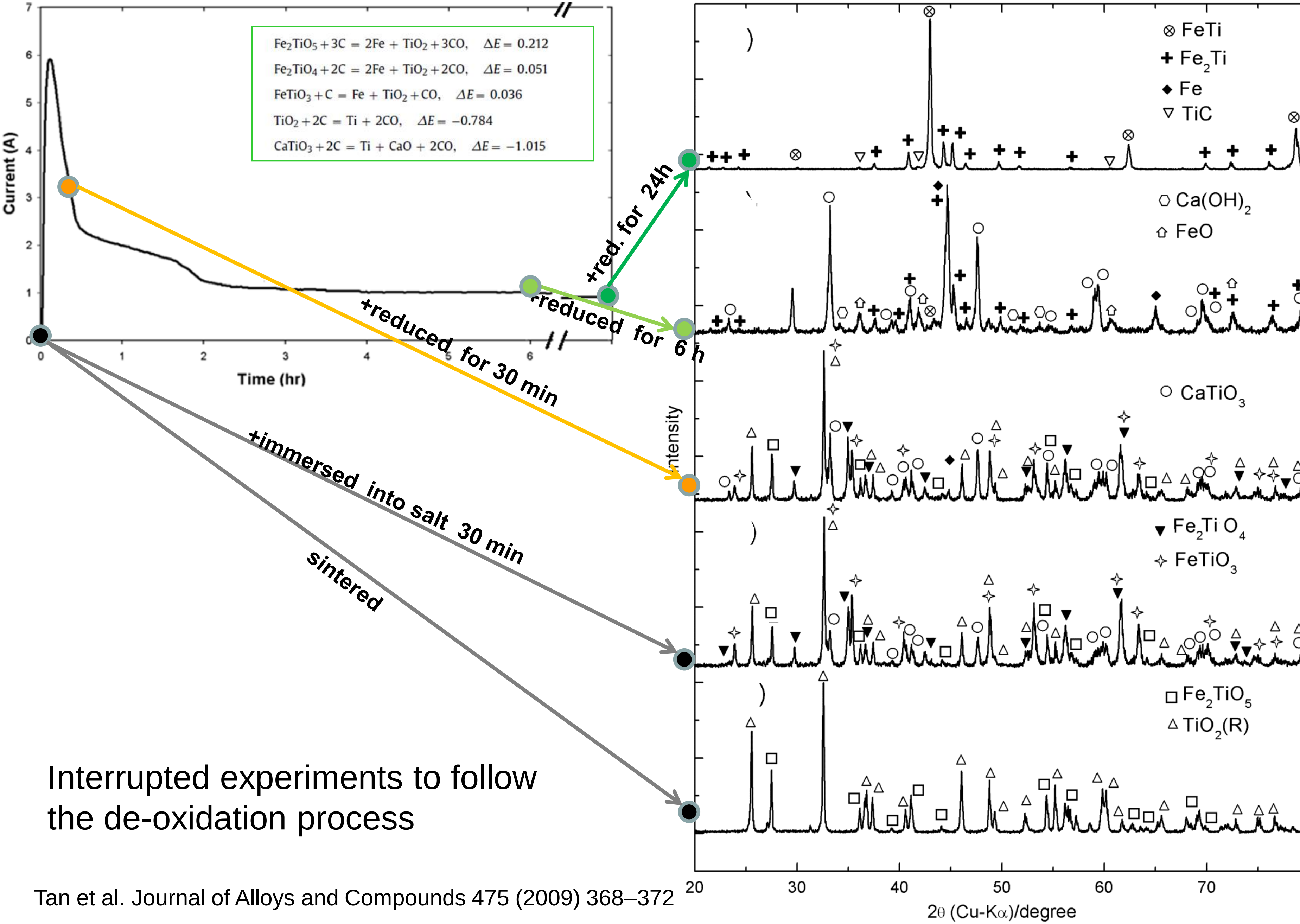
after reduction







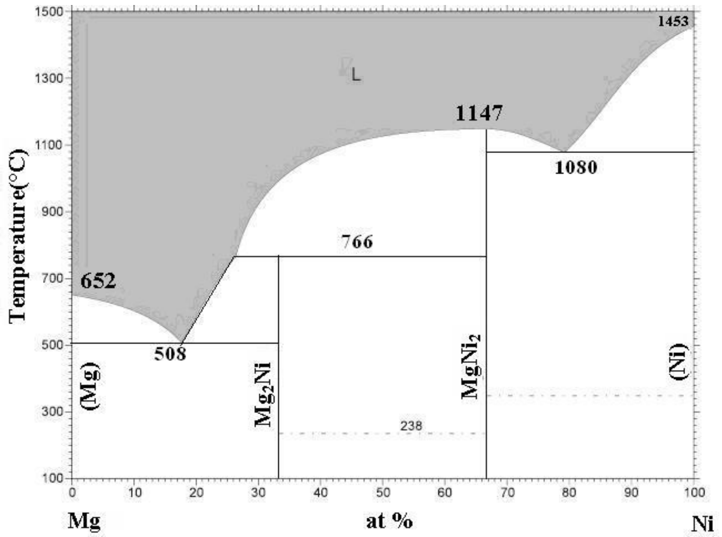
FeTi, obtained from deoxidation of mixed oxide pellet sintered at 1100◦C.



Interrupted experiments to follow the de-oxidation process

Tan et al. Journal of Alloys and Compounds 475 (2009) 368–372

Mg-Ni system

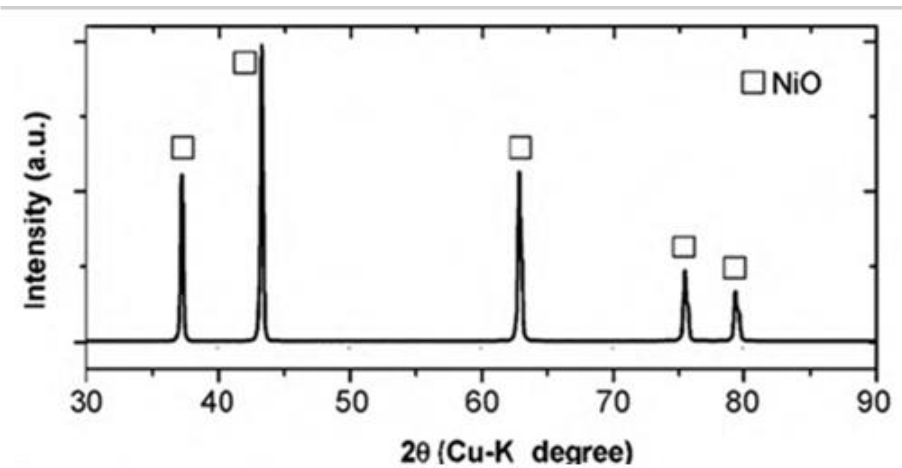


Mg-Ni Phase diagram

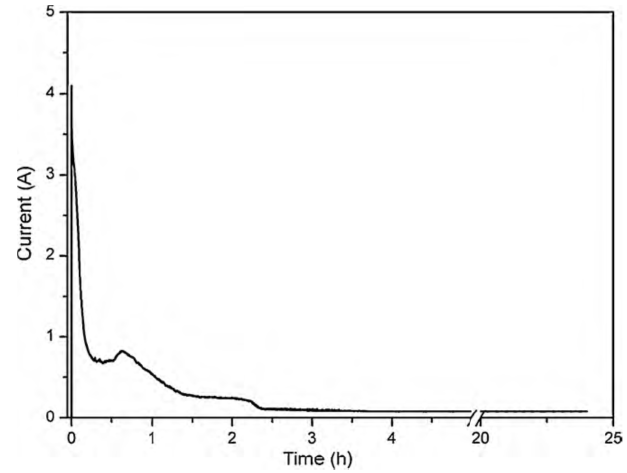
Conditions of electro-reduction

System	Target Phase	Electrolyte	V applied	T (oC)	t hr	Porosity (%)
NiO	Ni	CaCl2 +NaCl	3.2	900 725 600	24	57
MgO:NiO=1:2	MgNi2	CaCl2 +NaCl	3.2	900 600	24	42
MgO:NiO= 2:1	Mg2Ni	CaCl2 +NaCl	3.2 5.0	600	24	35
MgO	Mg	CaCl2 +NaCl	3.2 5.0	600	24	35

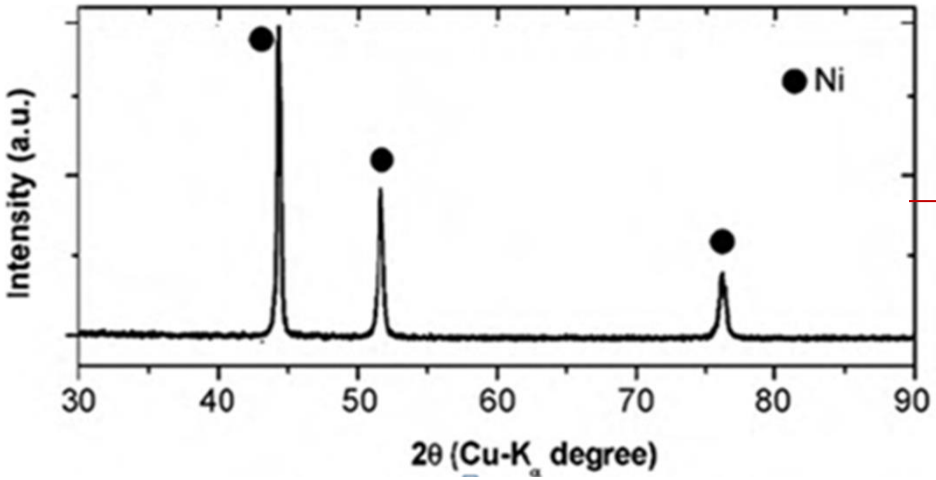
Synthesis Mg-Ni system : Ni synthesis

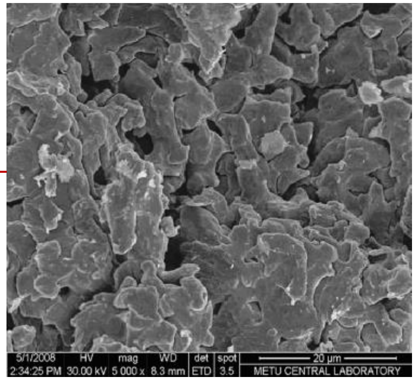


NiO pellet sintered at 1200 ◦C for 6 h



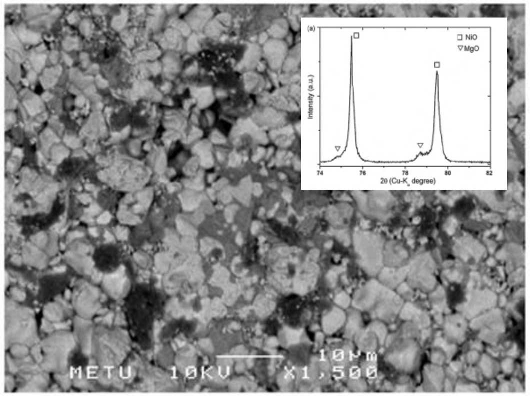
Current–time data collected during electroreduction



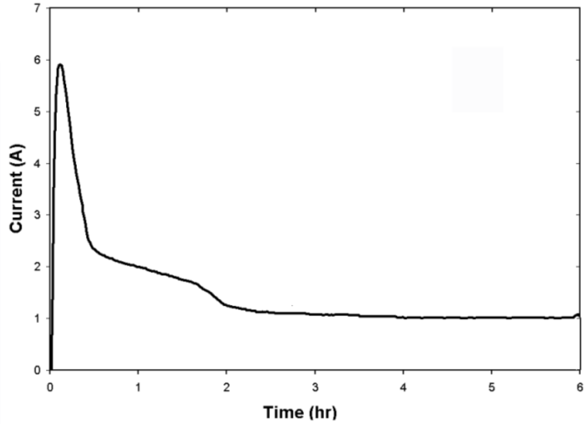


Electroreduced at 900 ◦C for 24 h (3.2 V).

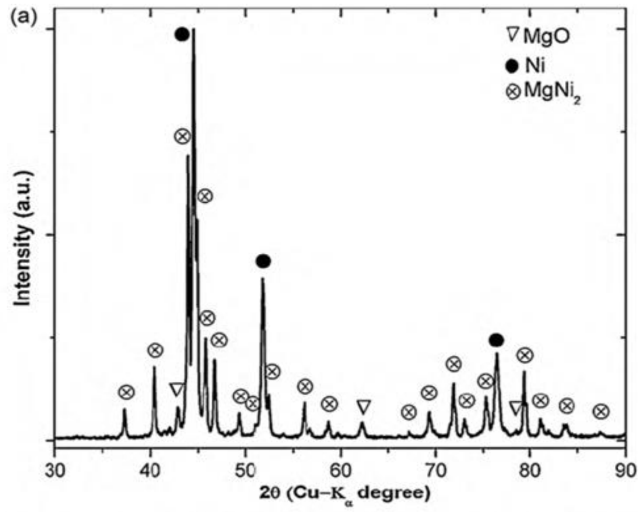
Synthesis in Mg-Ni system : $MgNi_2$

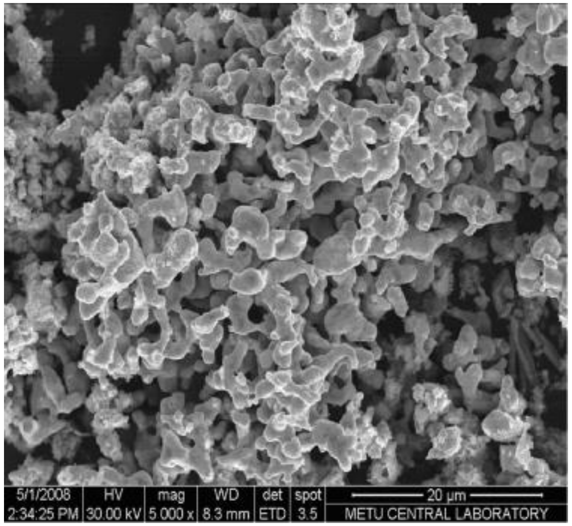


MgO:NiO = 1:2 pellet sintered at 1200◦C for 6 h



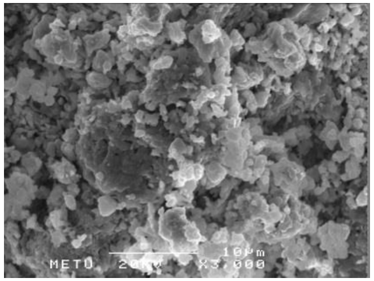
Current–time data collected during electroreduction at 900 oC 3.2 V

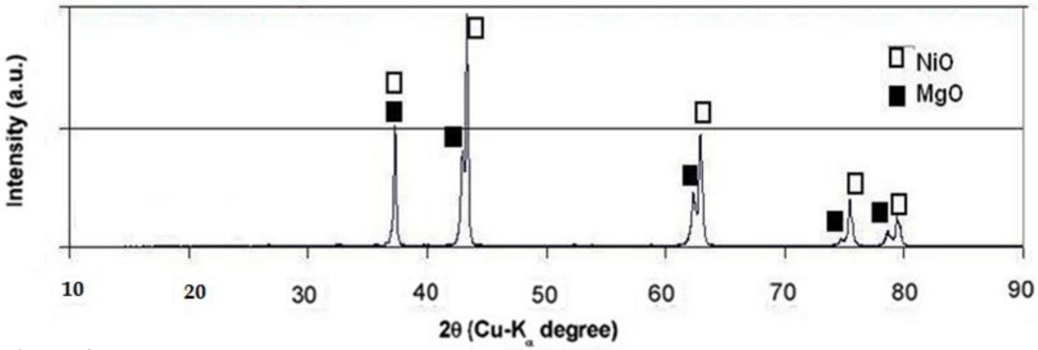




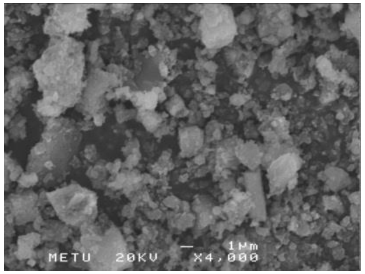
Electroreduced at 900 ◦C for 24 h (3.2 V).

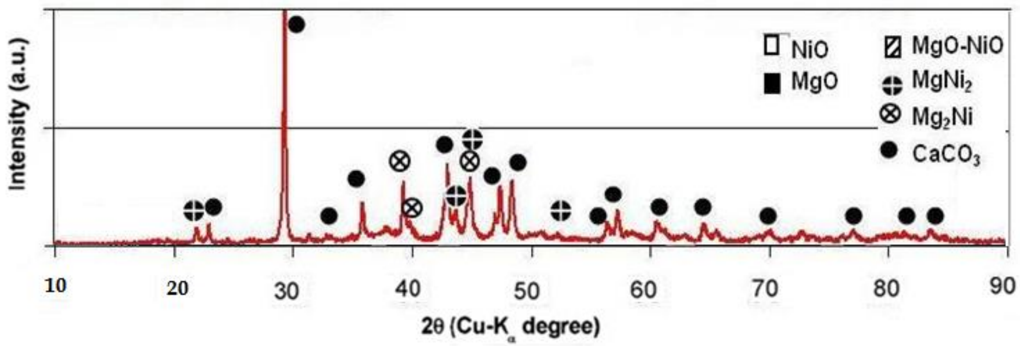
Synthesis in Mg-Ni system : Mg2Ni





MgO:NiO = 2:1 pellet sintered at 1200◦C for 6 h



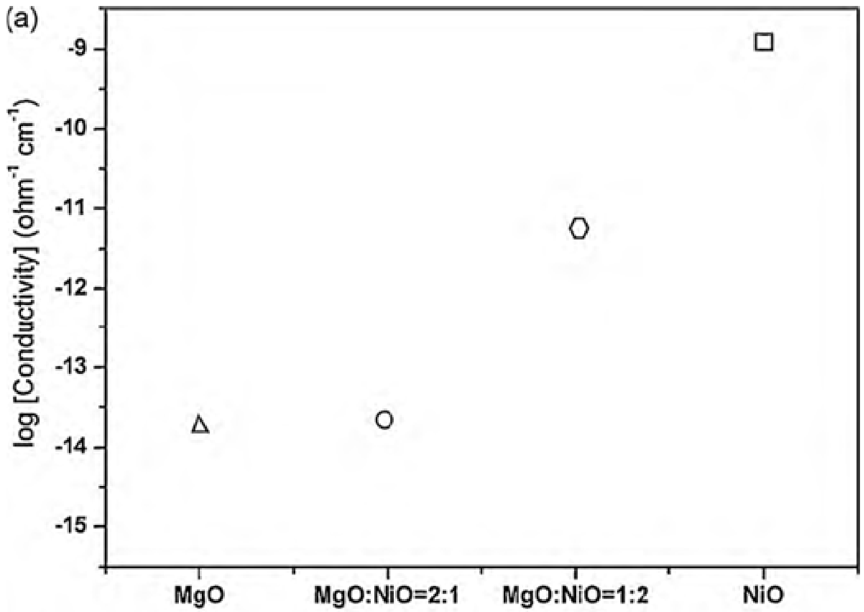


Electroreduced at 600 ◦C for 24 h (5 V).

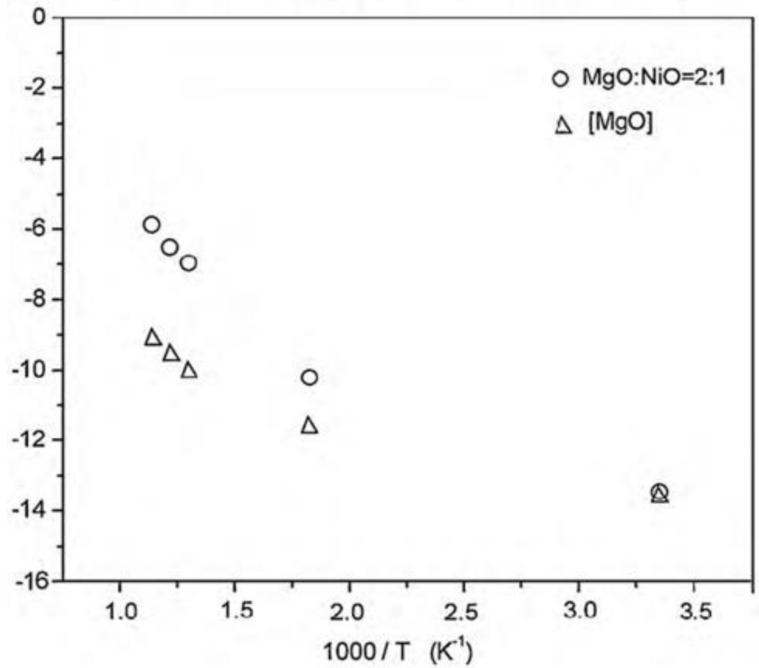
Tan et al Journal of Alloys and Compounds 504 (2010) 134–140

Standard reduction potentials at 900◦C, 725◦C and 600◦C.

Reaction	E° (V)		
	600 °C	725 °C	900 °C
$NiO_{(s)} + 0.5C_{(s)} = Ni_{(s)} + 0.5CO_{2(g)}$	+0.20	+0.25	+0.33
$MgO_{(s)} + 2NiO_{(s)} + 3C_{(s)} = MgNi_{2(s)} + 3CO_{(g)}$	-0.36	-0.24	-0.09
$2MgO_{(s)} + 4NiO_{(s)} + 3C_{(s)} = 2MgNi_{2(s)} + 3CO_{2(g)}$	-0.32	-0.26	-0.18
$2MgO_{(s)} + NiO_{(s)} + 3C_{(s)} = Mg_2Ni_{(s,l)} + 3CO_{(g)}$	-0.98	-0.86	(-0.70)
$4MgO_{(s)} + 2NiO_{(s)} + 3C_{(s)} = 2Mg_2Ni_{(s,l)} + 3CO_{2(g)}$	-0.94	-0.87	(-0.78)
$MgO_{(s)} + C_{(s)} = Mg_{(s,l)} + CO_{(g)}$	-1.64	(-1.52)	(-1.34)
$MgO_{(s)} + 0.5C_{(s)} = Mg_{(s,l)} + 0.5CO_{2(g)}$	-1.60	(-1.53)	(-1.43)
$CaO_{(s)} + C_{(s)} = Ca_{(s,l)} + CO_{(g)}$	-1.83	-1.71	(-1.52)
$CaO_{(s)} + 0.5C_{(s)} = Ca_{(s,l)} + 0.5CO_{2(g)}$	-1.79	-1.72	(-1.63)
$NaCl_{(l)} = Na_{(l)} + 0.5Cl_{2(g)}$	(-3.37)	(-3.28)	(-3.16)
$CaCl_{2(l)} = Ca_{(s,l)} + Cl_{2(g)}$	-3.40	-3.32	(-3.21)



Electrical conductivities of MgO, MgO:NiO = 2:1, MgO:NiO = 1:2 and NiO at room temperature



Conductivity values as a function of temperature up to 600 ◦C for MgO and MgO:NiO = 2:1.

Volume change upon reduction

Material	Molecular weight g/mol)	Density g/cm3	Normalized Molar volume cm3/mol	Change in volume %
MgO	40.30	3.58	11.26	+34.9
Mg	24.31	1.60	15.19	-
NiO	74.69	6.67	11.20	-36.33
Ni	58.69	8.23	7.13	
Fe2O3	159.69	5.24	15.24	-50.18
Fe	55.85	7.36	7.59	-
TiO2	79.87	4.25	18.79	-40.72
Ti	47.87	4.29	11.14	-

Conclusions

Conventional processing of hydrogen storage alloys involve an excessive number of steps which contributes to their high cost;

- Electroreduction is one–step process that converts the oxide(s) directly into the product in particulate form (1-3 μm).
- For successful conversion, It is necesssary to sinter the oxides fully while keeping an acceptable level of prorosity.
- FeTi was successfully synthesized when sintered at >1100 oC and reduced in CaCl2 at 3.2 V at 900 oC.
- The method could be used for many compounds. This is except for Mg and Mg rich compounds which have a peculiar property of volume expansion upon reduction.
- Electroreduction would give only equilibrum structures due to the high temperature involved.For non-eqilibrium structure post-processing might be necessary via mechanical milling or gas-phase synthesis,

Current

- Fatih Pişkin
- Burak Aktekin
- Ezgi Onur
- Seda Oturak
- Cavit Eyövge

Support

DPT
DPT-ÖYP
DPT-YUUP: "Hidrojen Gazı Üretimi, Depolanması ve Yakıt Hücrelerinde Elektrik Elde Edilmesi"

TÜBİTAK- MİSAG
TÜBİTAK-MAG

Collaborators

Dr. Eren Kalay
Prof. Kadri Aydınol
Prof. İshak Karakaya
Prof. Macit Özenbaş

NESSHY
Novel Efficient Solid Storage for H_2

Previous

- Elif Bayböru
- Murat Güvendiren
- Taylan Örs
- Çağla Özgit
- Rabia Ölmez

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