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Magnesium
as
an energy carrier

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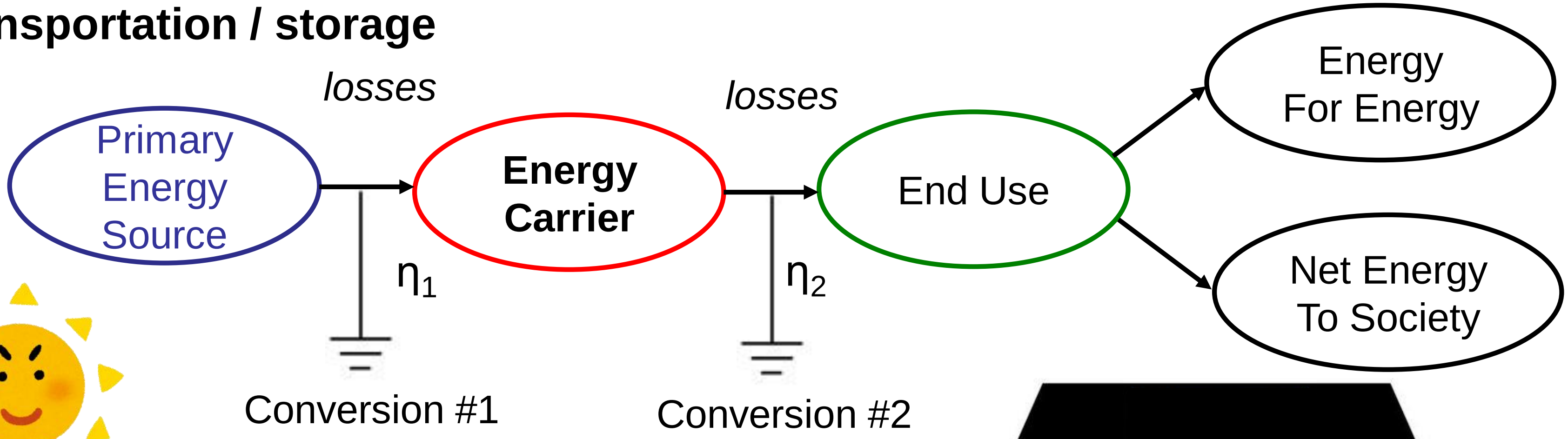
- Magnesium as thermal energy carrier
- Magnesium as hydrogen carrier
- Magnesium as thermal energy + hydrogen carrier
- Magnesium as electrical energy carrier
- Recycling of used magnesium
- Concluding remarks

What is "energy carrier"?

Definition: <u>Chemical substance</u> which serves as a carrier of energy transportation / storage



- **Sunlight**
- **Earth activity**

Renewable electric power

- Solar
- Hydro
- Geothermal
- Tidal power

<u>Fossil fuels</u>

- Coal
- Oil
- Natural gas

<u>For renewable energy</u>

- Hydrogen
- Ammonium
- Methanol
- **Magnesium**
- Aluminum

Energy carrier that contributes to <u>reduce environmental impact and secure energy</u>

https://commons.wikimedia.org/w/index.php?curid=16124211

Requirement for energy carrier[1)]

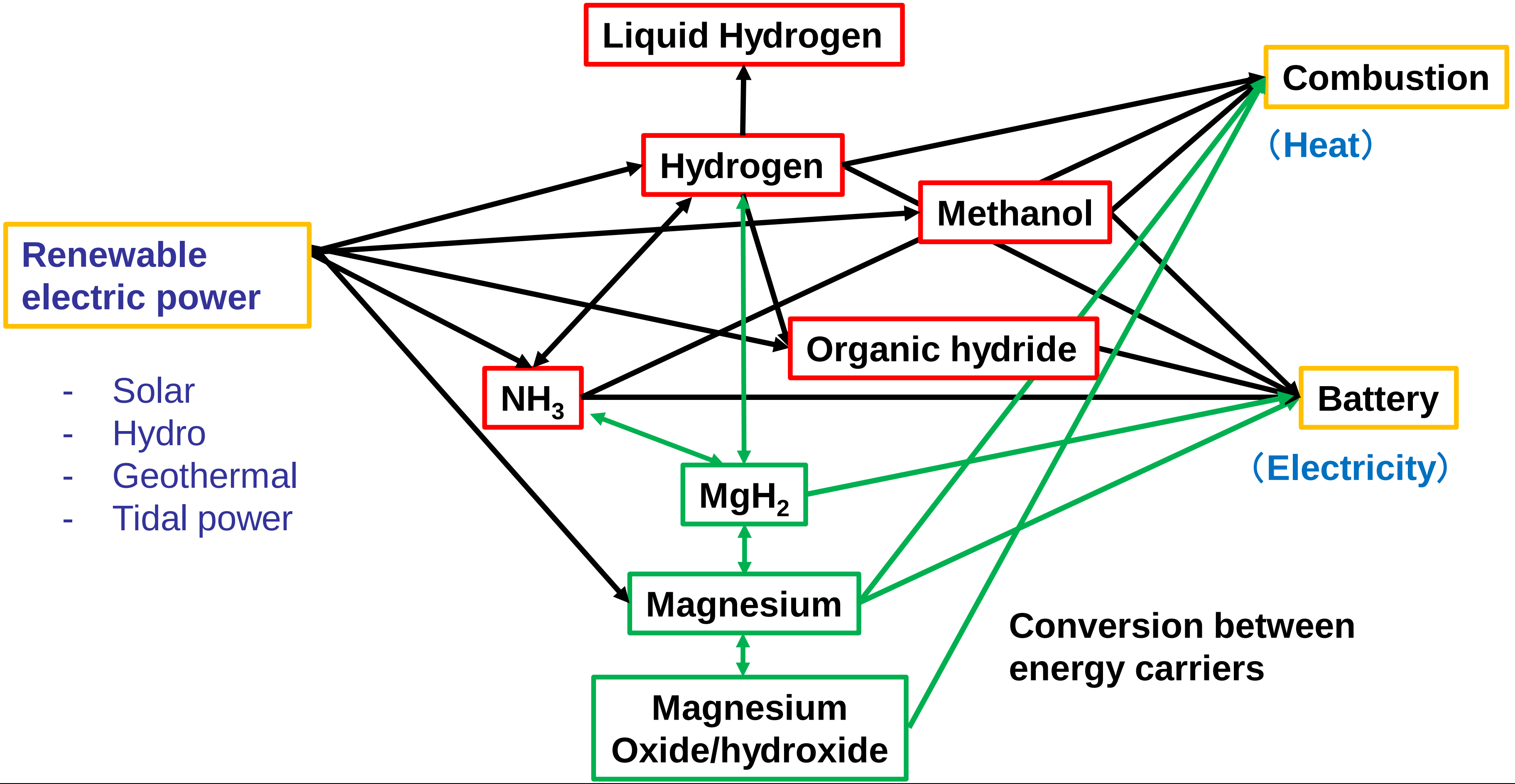
- Abundant (low cost)
- Convert to various kinds of energy
- High energy conversion efficiency
- User friendly
- Available when and where needed
- Stockpile in large/small volume
- Transport easily in short/long distance
- Release no harmful substances after use

There are no energy carrier which can satisfy all the requirements. 'Hydrogen' is considered as the most promising candidate.

1) A. Ishihara and K. Ohta, Introduction to renewable energy, Nikkankogyo (2012),141.

Magnesium working with hydrogen carrier

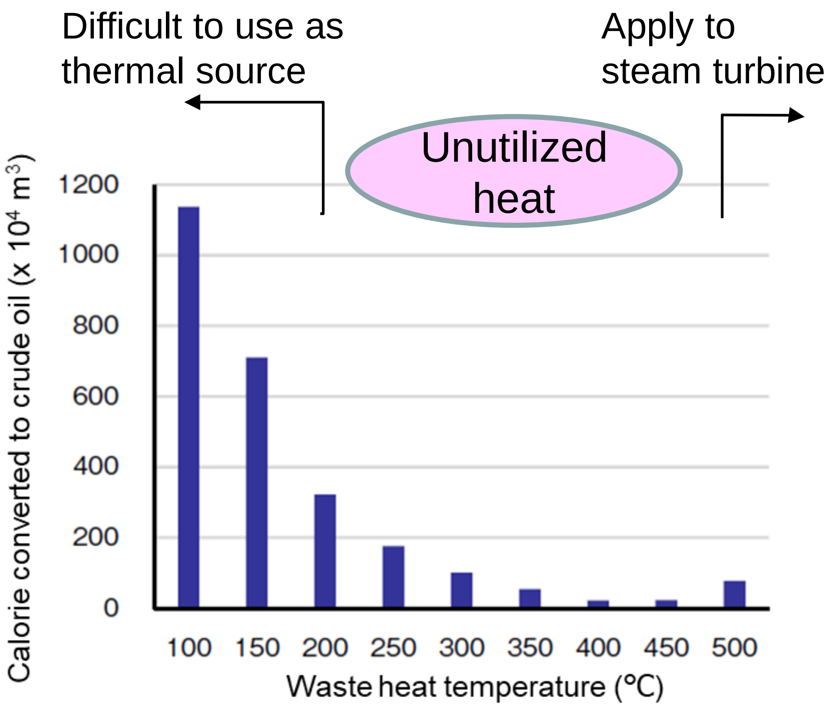
Magnesium it is expected to work alongside with H_2 energy carrier.



- Solar
- Hydro
- Geothermal
- Tidal power

Conversion between energy carriers

Magnesium as thermal energy carrier



Temperature profile of domestic waste heat[1)]

Property of heat storage material[2)]

Heat storage	Material (reaction)	Operating temp.	Storage density
Latent heat storage	Ice (ice ⇔ water)	0 °C	0.34 GJ/m^3
	Erythritol	121°C	0.48 GJ/m^3
Chemical heat storage	$MgO+H_2O$ ⇔ $Mg(OH)_2$	350°C	1.0~1.5 GJ/m^3
	$CaO+H_2O$ ⇔ $Ca(OH)_2$	500°C	

<u>Heat storage material</u> to utilize waste heat effectively

Snow collection site ($120{,}000\ m^3$)

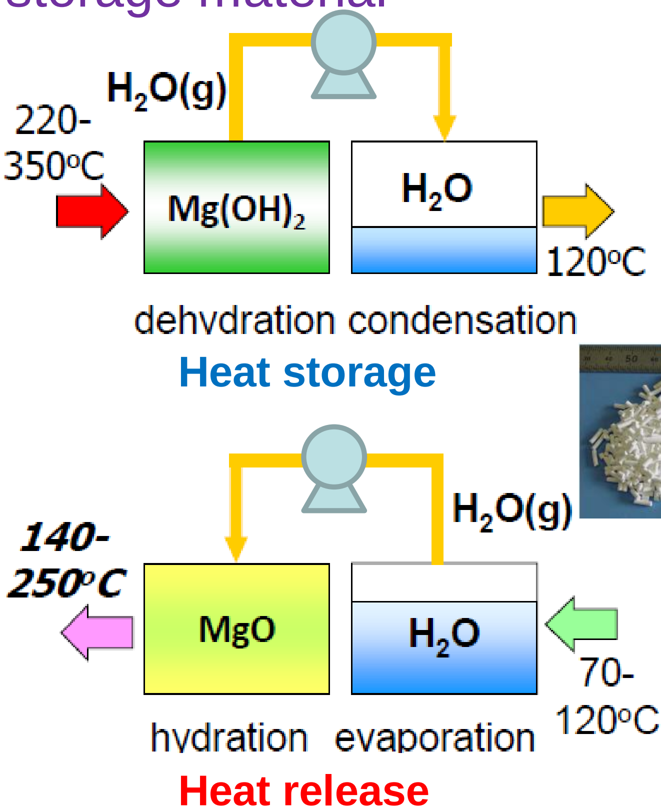
Sapporo Chitose Airport utilizes collected snow for cooling in summer.

1) S. Kobayashi, Panasonic Technical Journal, 62 (2016)121-125.
2) Y. Kato, High Density Thermal Energy Storage Workshop (2011).

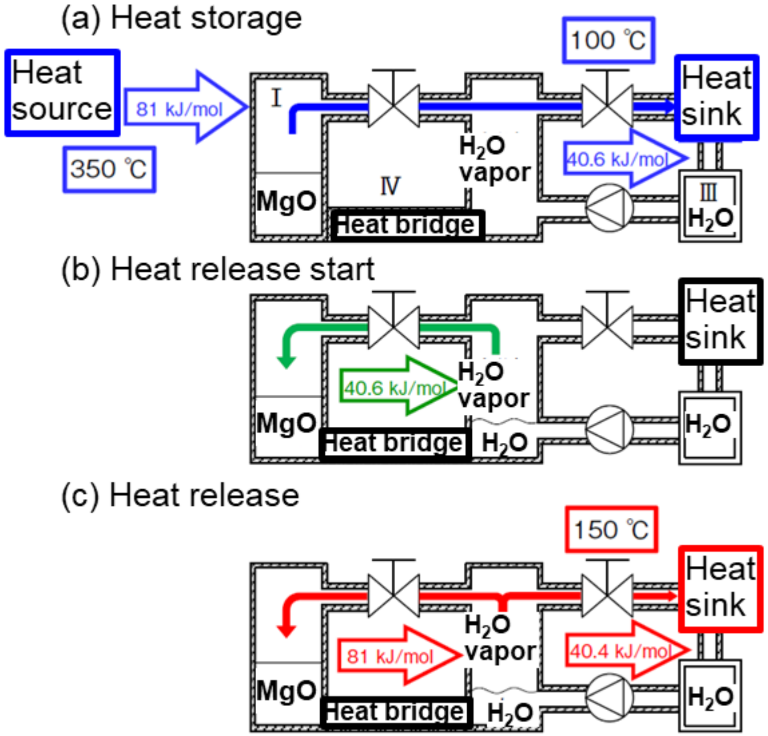
Magnesium as thermal energy carrier

$MgO + H_2O = Mg(OH)_2$ $-\Delta H = 81$ kJ/mol

Heat pump: A device that transfers heat energy from cold area to hot area using heat storage material



Chemical heat pump based on $MgO/Mg(OH)_2$ [1),2)]



Conversion rate	Water content	3.76 kg
	Water collection	2.96 kg
	Utilization rate	78 %
Regeneration efficiency	Theoretical heat collection	13616 kJ
	Released heat collection	8400 kJ
	Regeneration efficiency	62 %

1) Y. Kato, High Density Thermal Energy Storage Workshop (2011).
2) S. Kobayashi, Panasonic Technical Journal, 62 (2016)121-125.

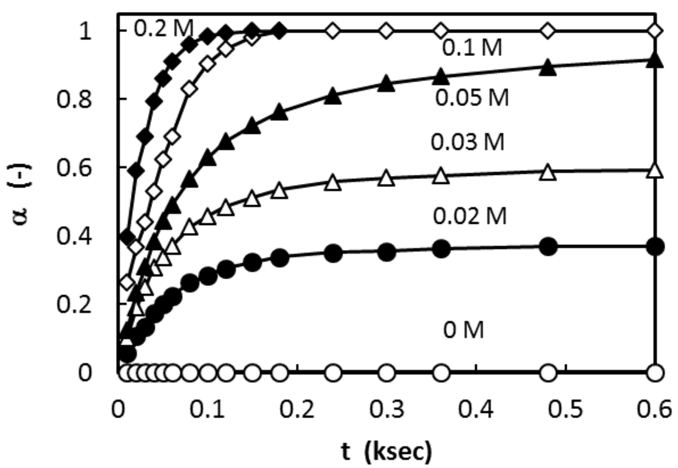
Magnesium as hydrogen carrier

Magnesium can absorb H_2 up to 7.6 wt%. High desorption temperature (~350 ℃) and sluggish reaction kinetics are concerned.

A process of H_2 production at room temperature via hydrolysis of MgH_2 is developed.

$$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + \mathbf{2}H_2,\ \Delta H = -268\ kJ/mol$$

$$\Leftrightarrow MgH_2 = Mg + H_2 \quad \Delta H = 75\ kJ/mol$$



Evolution of H_2 gas via hydrolysis of MgH_2 with different concentration of citric acid at room temperature[1].

(a) 0.3~0.5 L/min.

(b) 10 L/min.

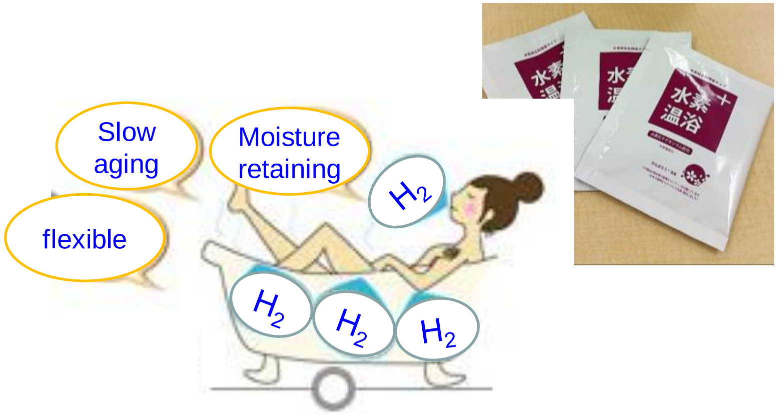
MgH_2 reactors[2].

1) I. Nakatsugawa, unpublished results
2) http://www.biocokelab.com

Magnesium as hydrogen carrier

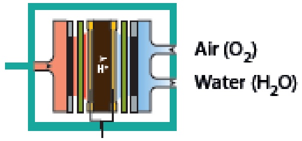
MgH_2 powder and briquette form[1)]

40W MgH_2 FC portable power generator[1)]



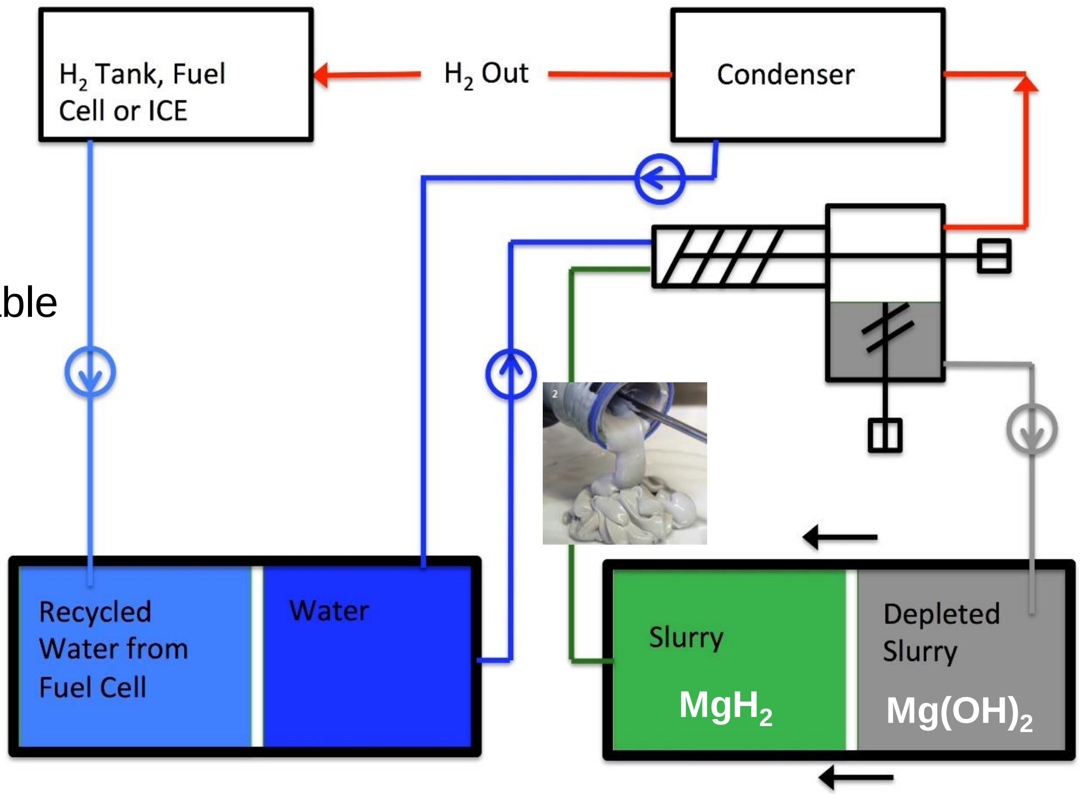
Additives for health care, cosmetics[1)]

1) http://www.biocokelab.com



Fuel cell

Hydrogen Gas Turbine



H_2 production system based on the hydrolysis of MgH_2 [2)]

2) http://www.safehydrogen.com/technology.html

Magnesium as thermal energy + hydrogen carrier

Metal-water reaction

Corrosion of Magnesium

$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$

$\Delta H = -924$ kJ/mol

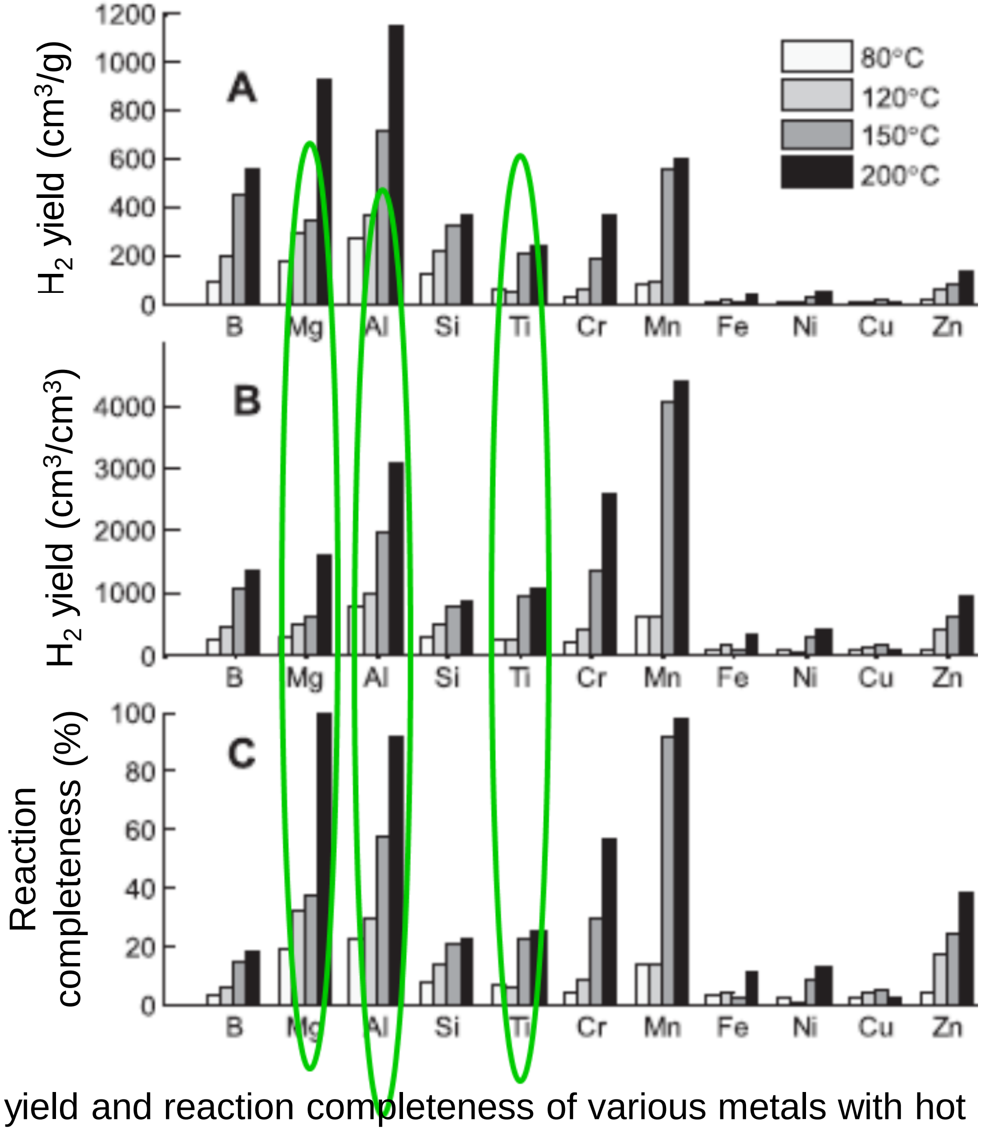
$Mg + H_2O \rightarrow MgO + H_2$

$\Delta H = -602$ kJ/mol

Combustion of H_2

$H_2 + ½O_2 \rightarrow H_2O$

$\Delta H = -285$ kJ/mol

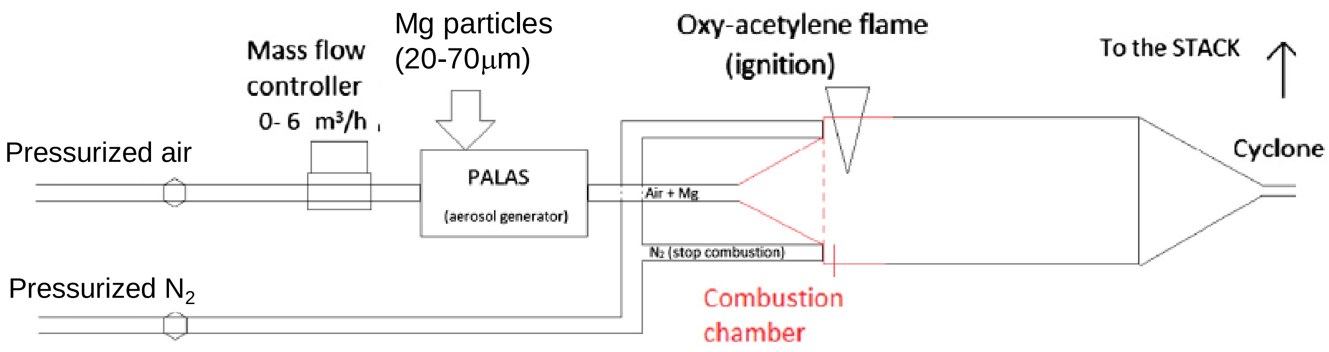


Hydrogen yield and reaction completeness of various metals with hot water[1)].

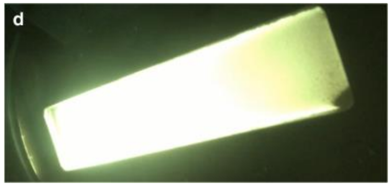
1) Y. Yavor et al, Int J Hydrogen Energy 40 (2015) 1026-1036.

Magnesium as thermal energy + hydrogen carrier

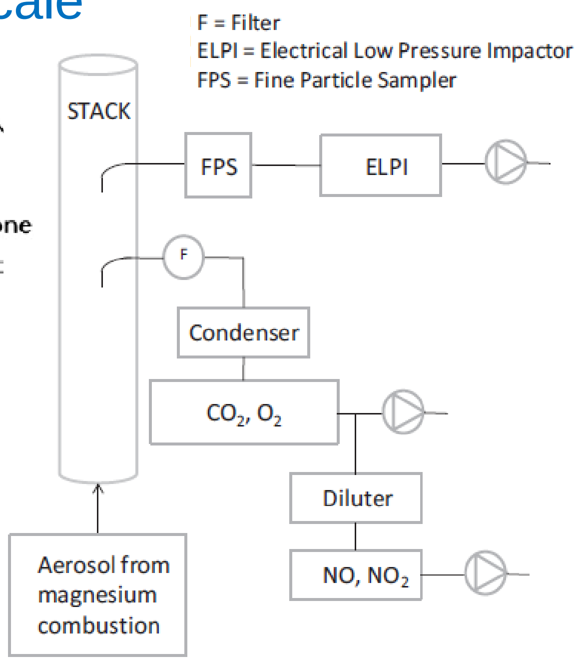
Feasibility study of Mg combustion with 3-5 kW pilot scale



Scheme of Mg/air ignition and combustion process



Self sustained Mg flame



Calibration of aerosol and exhaust gas

Results

- Combustion completion ratio : 91-100%
- Mg/O_2 molar ratio : 1.8-2.3

Task

- Emission of NOx and fine particles

1) Y. Yavor et al, Int J Hydrogen Energy 40 (2015) 1026-1036.

Magnesium as electrical energy carrier

Magnesium as electrical energy carrier

Basic feature

		Fuel cell		Primary /secondary battery			
Anode		**H_2**	**CH_3OH**	**Li**	**Mg**	**Al**	**Zn**
Standard potential (V_{NHE})		0	-	-3.01	-2.38	-1.66	-0.76
Electro-chemical equivalent	Ah/g	26.59	5.02	3.86	2.20	2.98	0.82
	Ah/cm^3	-	4.58	2.06	3.8	8.1	5.8

As electric energy carrier

Anode	**H_2**	**CH_3OH**	**Li**	**Mg**	**Al**	**Zn**
Cell performance	○	△	◎	△	△	◎
Scalability	△	△	△	△	△	△
Compatibility	◎	◎	△	○	○	×
Safety	×	×	△	○	○	○
Reserves	○	○	×	○	○	△
Price	△	○	×	△	△	△

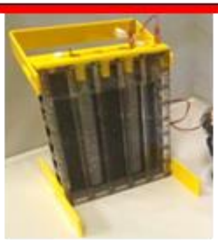
Magnesium as electrical energy carrier

- Mg battery
  - Primary battery
    - Mg-MnO_2 battery
    - Mg water-activated battery
    - Mg- air battery
      - Mg fuel cell (supply anode/electrolyte)
  - Secondary battery
    - Mg-MgX battery
    - Mg-air battery
    - Mg- molten salt battery
    - Ni-MgH_2 battery
  - Fuel cell (H_2 supply source)
    - MgH_2 desorption
    - MgH_2 hydrolysis
    - Mg-hot water oxidation

Mg-based batteries

* blue is under R&D stage

Commercialized Mg primary batteries

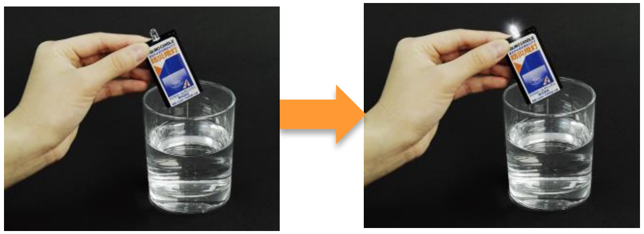
	MnO_2 dry-battery	Water-activated battery		Air battery
Example				
Cathode	MnO_2	Ag/AgCl	MnO_2	O_2
Electrolyte	$NaClO_4$	Sea water	NaCl	NaCl
OCP (V)	~1.8	~1.6	~1.6	~1.5
Potential at 5mA/cm^2 (V)	1.6~1.7	1.4~1.5	<1.2	1.2~1.3
Energy density (Wh/kg)	~120	~120	~70	~70
Comment	Dis-continued	Special use		

Water activated Mg battery

Principle

Anode : $Mg \rightarrow Mg^{2+} + 2e$

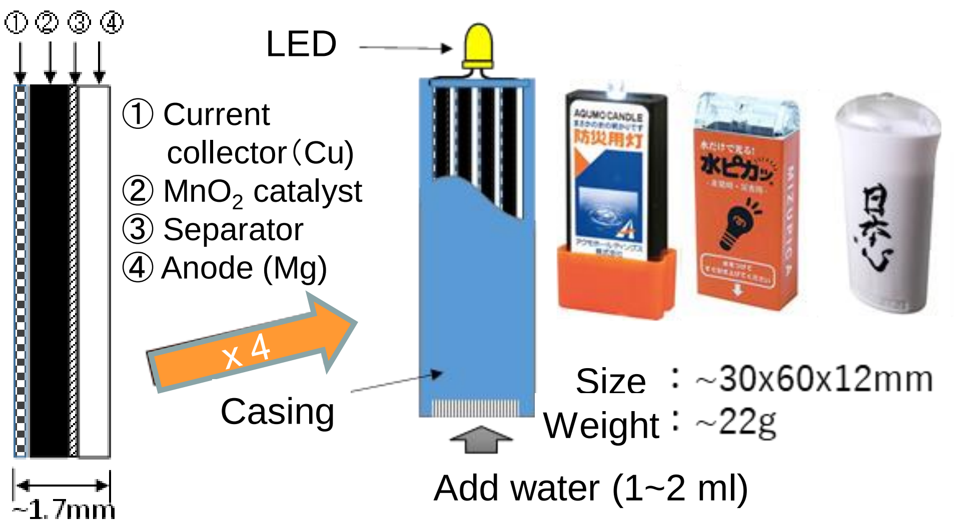
Cathode : $2MnO_2 + H_2O + 2e \rightarrow Mn_2O_3 + 2OH^-$



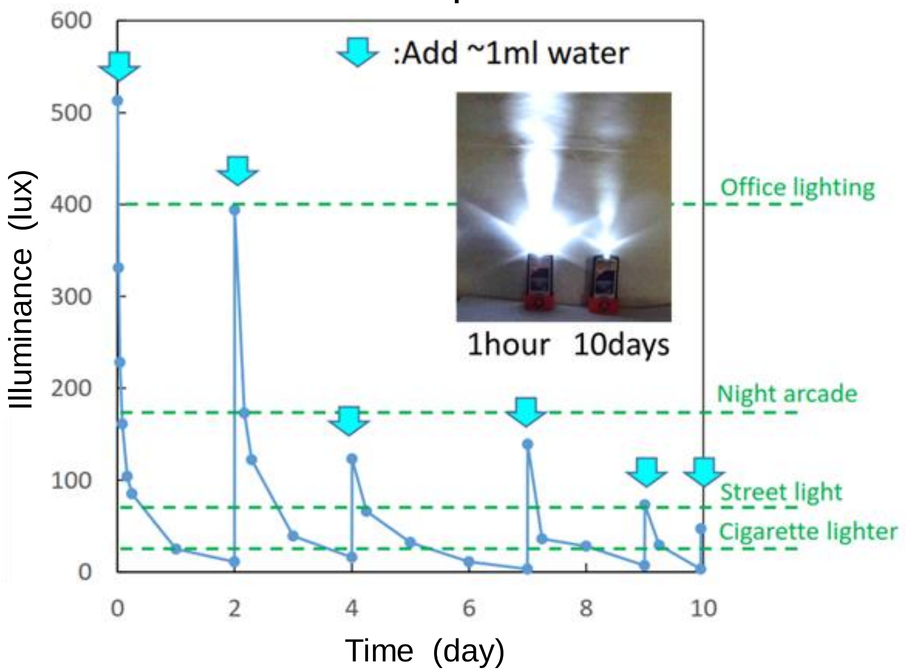
Operation

Feature

- Start discharging by adding water
- Stack 3-4 cells to supply voltage ~6.4V
- Illumination for a week by adding water



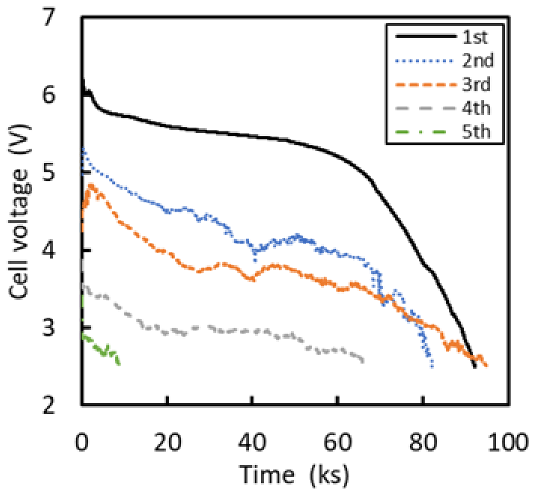
Structure of LED light



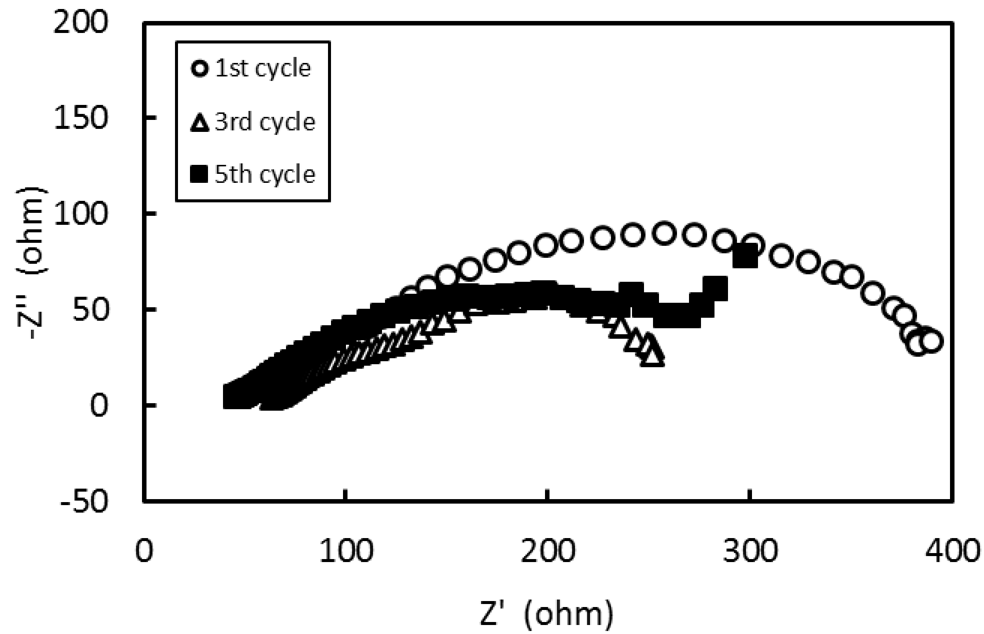
Time change of illuminance of LED light (30 cm distance from light source)[1)]

1) I. Nakatsugawa: 3rd Mg technical seminar, Japan Magnesium Association (2016).

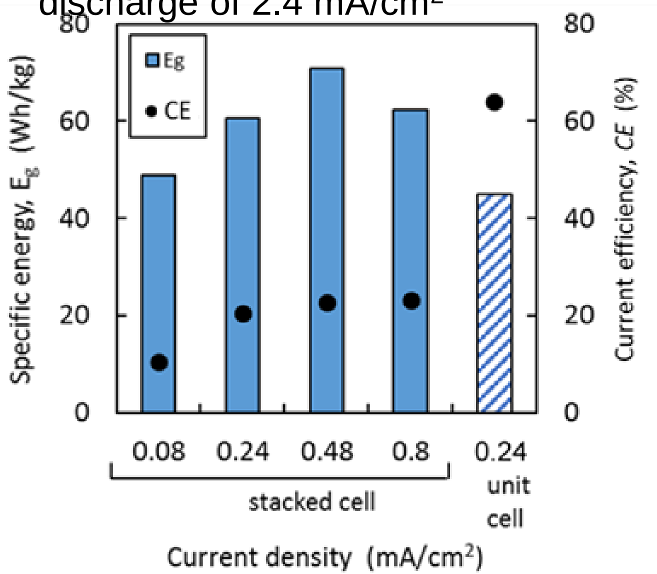
Water activated Mg battery



Change of cell voltage under constant discharge of 2.4 mA/cm^2



Nyquist diagram of water activated Mg battery at the terminal voltage.



Dependence of energy density and current efficiency on discharge current density.

- Anode and cathode impedance increase with water injection cycle.
- Warburg impedance was observed at cathode, suggesting the depression of MnO_2.
- Gravimetric energy density took the maximum at 0.48mA/cm^2.
- Current efficiency was decreased by staking cells.

I. Nakatsugawa, H. Nakano: J. Jpn Inst. Light Metals, 67 (2017) 503-510.

Mg - air battery

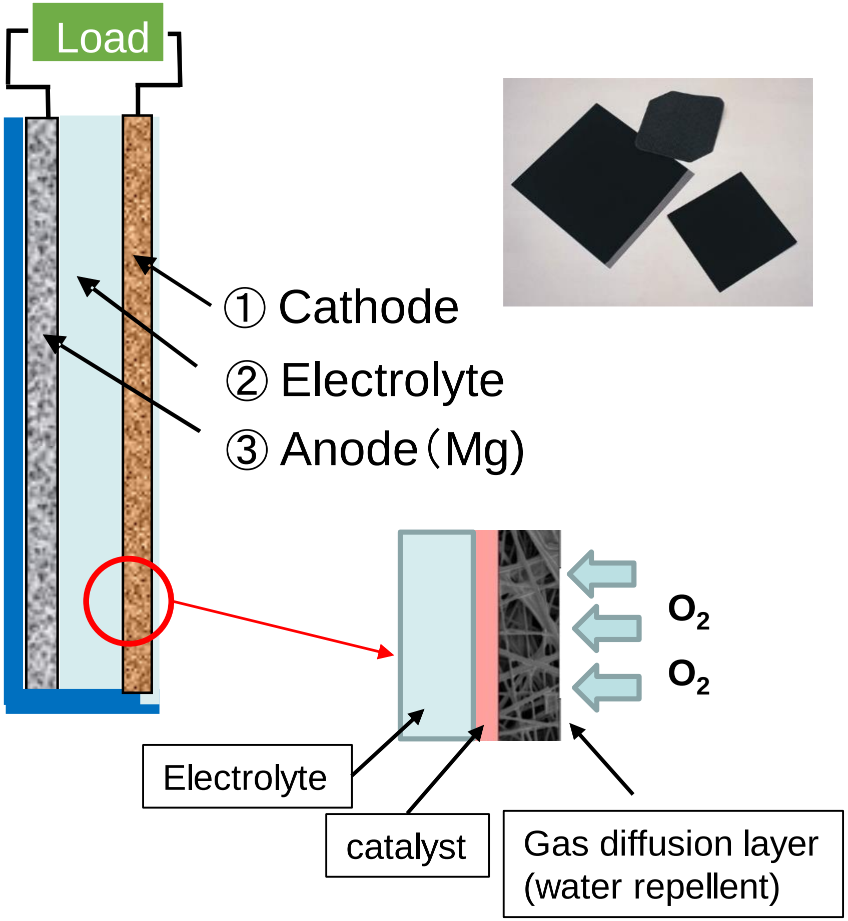
Principle

Anode : Mg → Mg^{2+} + 2e

Cathode : 1/2 O_2 + H_2O + 2e → 2OH^-

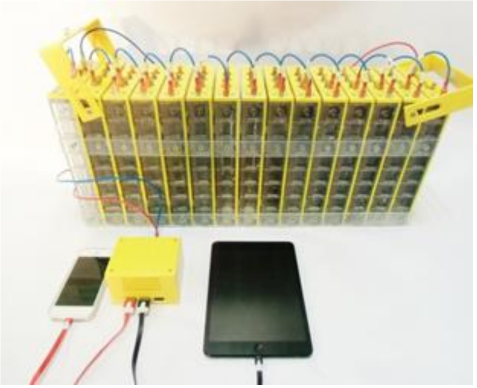
Feature

- Start discharging by adding 5~10% NaCl
- Continuous operation is possible by replacing used Mg anode and electrolyte.
- The current efficiency is ~60 %.



Structure of Mg-air battery

2.2W unit cell

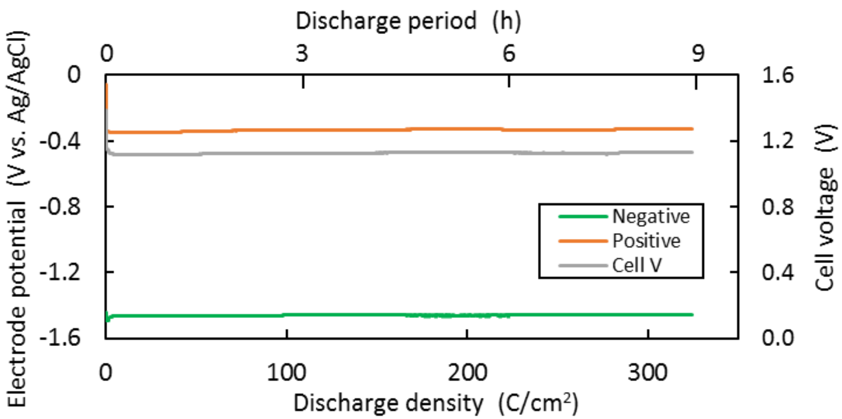


30W stacked cell

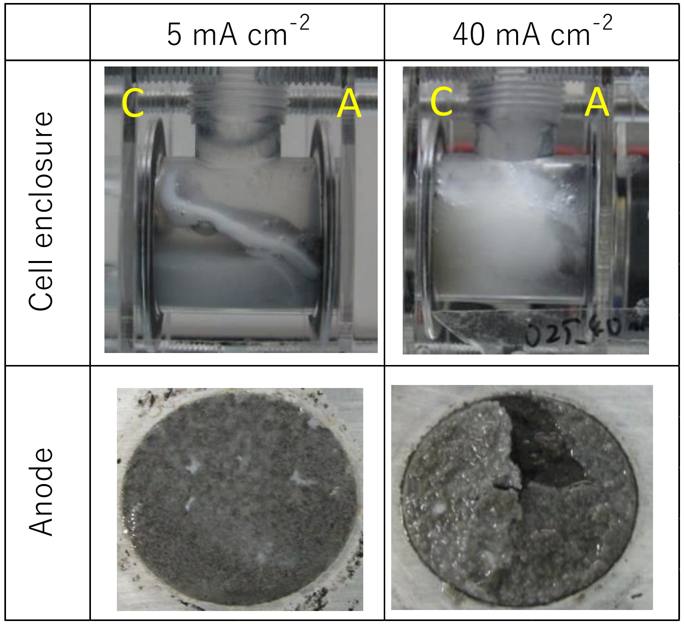
An example of Mg-air battery[1)]

1) photo: courtesy of ARV corporation, Japan.

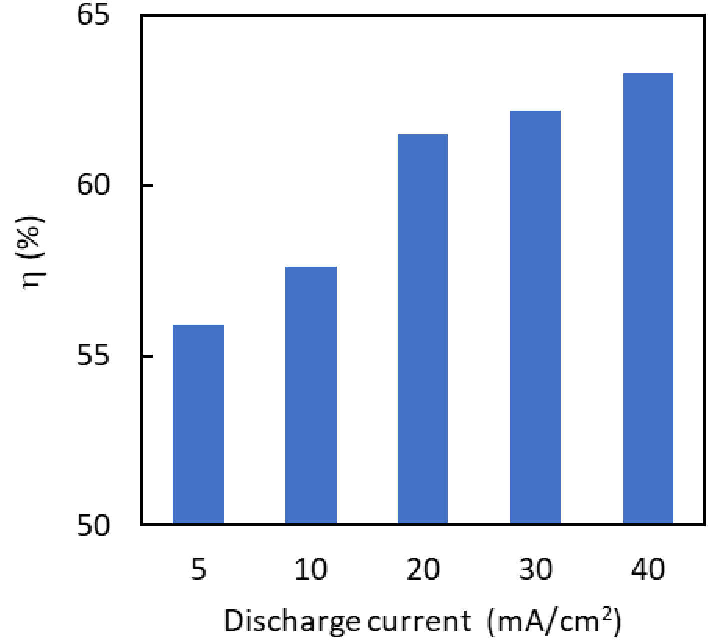
Mg - air battery



Discharge performance of Mg-air cell at 10 mA/cm^2



Appearances of Mg anode after discharging



Current efficiency of Mg-air battery.

- Stable discharge is possible up to 40 mA/cm^2.
- Adherent reaction product tends to form at higher discharge current.
- Current efficiency increases with higher discharge current.

I. Nakatsugawa, Y. Chino, H. Nakano, J. Power Sources, submitted.

Magnesium as electrical energy carrier

Verification test of Mg-air battery (MAB) as an emergency power supply

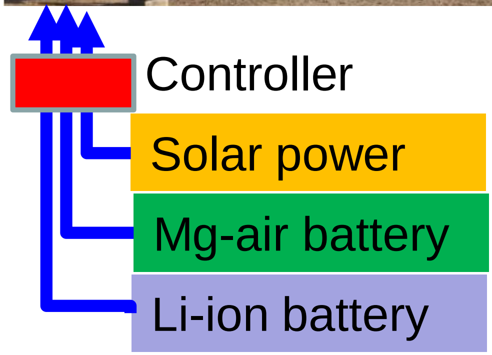
EV[1)]

275 Wh unit cell

stack of 100 unit cells

1) photo: courtesy of ARV corporation, Japan.
2) photo: courtesy of Seven corporation, Japan.

Trailer house[2)]



MAB: 300 Wh x 12-16pcs

LIB: 2.5kWh

Recycling of used magnesium

Recycling of used magnesium

Hot water oxidation, battery

$Mg + 2H_2O \rightarrow Mg(OH)_2 + \frac{1}{2} H_2$

$Mg + H_2O \rightarrow MgO + H_2$

Hydrolysis

$MgH_2 + 2H_2O \rightarrow Mg(OH)_2 + H_2$

Battery

$Mg + 2e \rightarrow Mg^{2+}$

$\frac{1}{2} O_2 + H_2O \rightarrow 2OH^-$

$Mg + 1/2O_2 + H_2O = Mg(OH)_2$

Recycle, Reuse of $MgO/Mg(OH)_2$

Recycling of used magnesium

Reuse $MgO/Mg(OH)_2$ as chemical additives

Collection → $Mg(OH)_2$ slurry → Dry ~100℃ → $Mg(OH)_2$ powder → Firing ~350℃ → MgO powder

MgO powder

- Flue gas desulfurization
- Neutralizer of acid waste

- Additives for plastic
- Ceramics
- Additives for fuel oil

- Insulator
- Refractory material
- Additives for cement
- Fertilizers

Global production of Magnesium compound : 7,000 ktpy (2014)[1)]
⇔ Magnesium metal : 900 ktpy (2014)[1)]

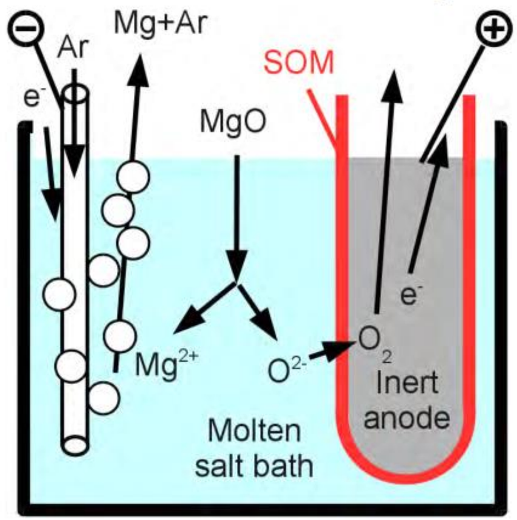
1) http://www.discoveryinvesting.com/blog/2015/8/10/a-closer-look-at-magnesium

Reduction to Mg metal

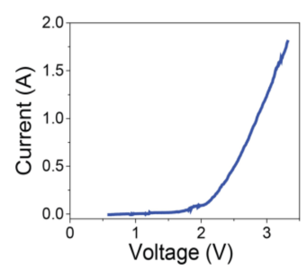
- Thermal reduction: $MgO \rightarrow Mg + \frac{1}{2}O_2$ $(MgO + C \rightarrow Mg + CO)$
- Electrolysis: $Mg^{2+} + 2e \rightarrow Mg$ $(MgCl_2 \rightarrow Mg + Cl_2)$

Electrolysis of molten MgO[1),2)]

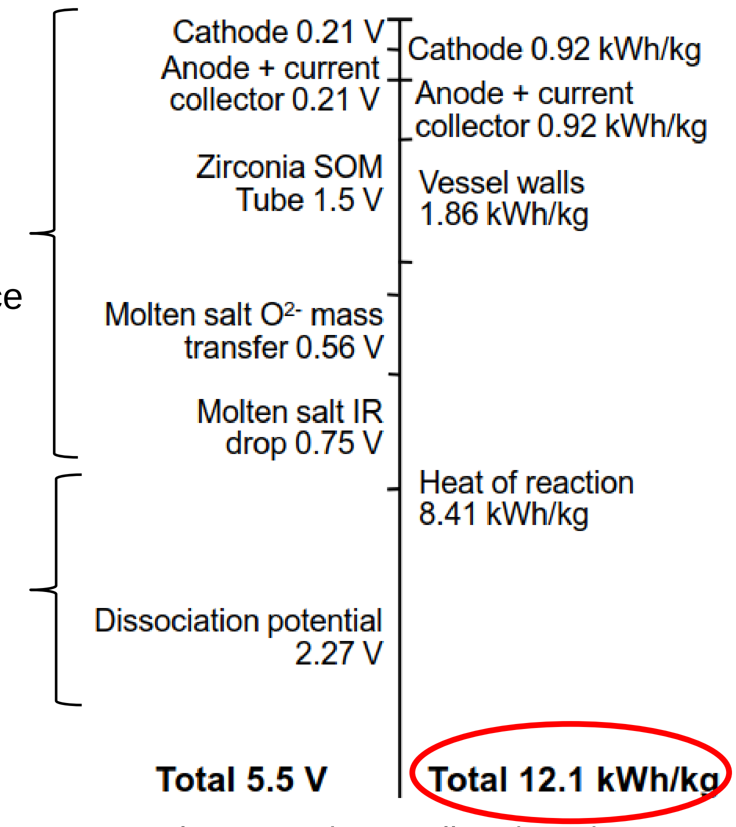
Cathode: $Mg^{2+} + 2e \rightarrow Mg$
Anode: $O^{2-} \rightarrow 1/2O_2 + 2e$
SOM: Y-stabilized ZrO_2
Operation T.: 1150~1300℃
Molten Mg efficiency: 48~63%



Principle of Mg electrolysis using SOM.



V-I curve of Mg reduction using SOM.



1) X. Guan et al., J. Sustain. Metall., 2 (2016) 152–166.
2) http://energy.gov/sites/prod/files/2014/03/f11/lm035_derezinski_2011_o.pdf

Conclusion

Evaluation of Magnesium as energy carrier

Requirement	Evaluation	Comment
Abundant (low cost)	△	Abundant Ores. Metal price is high. The cost competitive and green production is anticipated.
Easily converted from/to various kinds of energy	△	Need economical/green refining process for full-scale operation
High energy conversion efficiency	△	Need to improve current efficiency for electrical energy application.
Easy to handle by consumers	○	In the forms of plate, consolidated powder and slurry are available
Available when and where needed	○	Mg and MgH_2 are stable in the atmosphere. Attention to powder explosion.
Stockpile large / small quantity	○	
Easy to transport in short/long distance	○	
Do not release harmful substances after use	○	NO_2 is released in hot water oxidation process.

Thank you!