Environmentally friendly conversion treatments of magnesium alloys -- taking examples of corrosion protection and scrap recycling

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Chemical conversion coating treatment/ energy-saving

- Chromate [1]/ Cr^{6+} / Waste [2]
- Cerium [3]/ phosphate [4]/ Vanadate [5]/ stannate [6], etc/ Waste [2]

- corrosion resistance
- Environmental friendly treatment / low pollution
  →carbonic acid solution

[5] J. E. Skar, E. K. Sivertsen and J. M. Ostel, in ICEFPAM – *International Conference on Environmental friendly pre-treatment for Aluminum and other Metals*, Oslo, Norway, 2004, pp. pp. 1-4.

[6] M. A. Gonzalez-Nunez, C. A. Nunez-Lopez, P. Skeldon, G. E. Thompson, H. Karimzadeh, P. Lyon and T. E. Wilks, *Corrosion Science*, 1995, 37, 1763-1772.

Carbonic acid aqueous for conversion (hard) coating on Mg alloy / corrosion protection

J.K. Lin, K.L. Jeng and J.Y. Uan*, ***Corrosion Science***, 53 (2011), pp. 3832-3839.

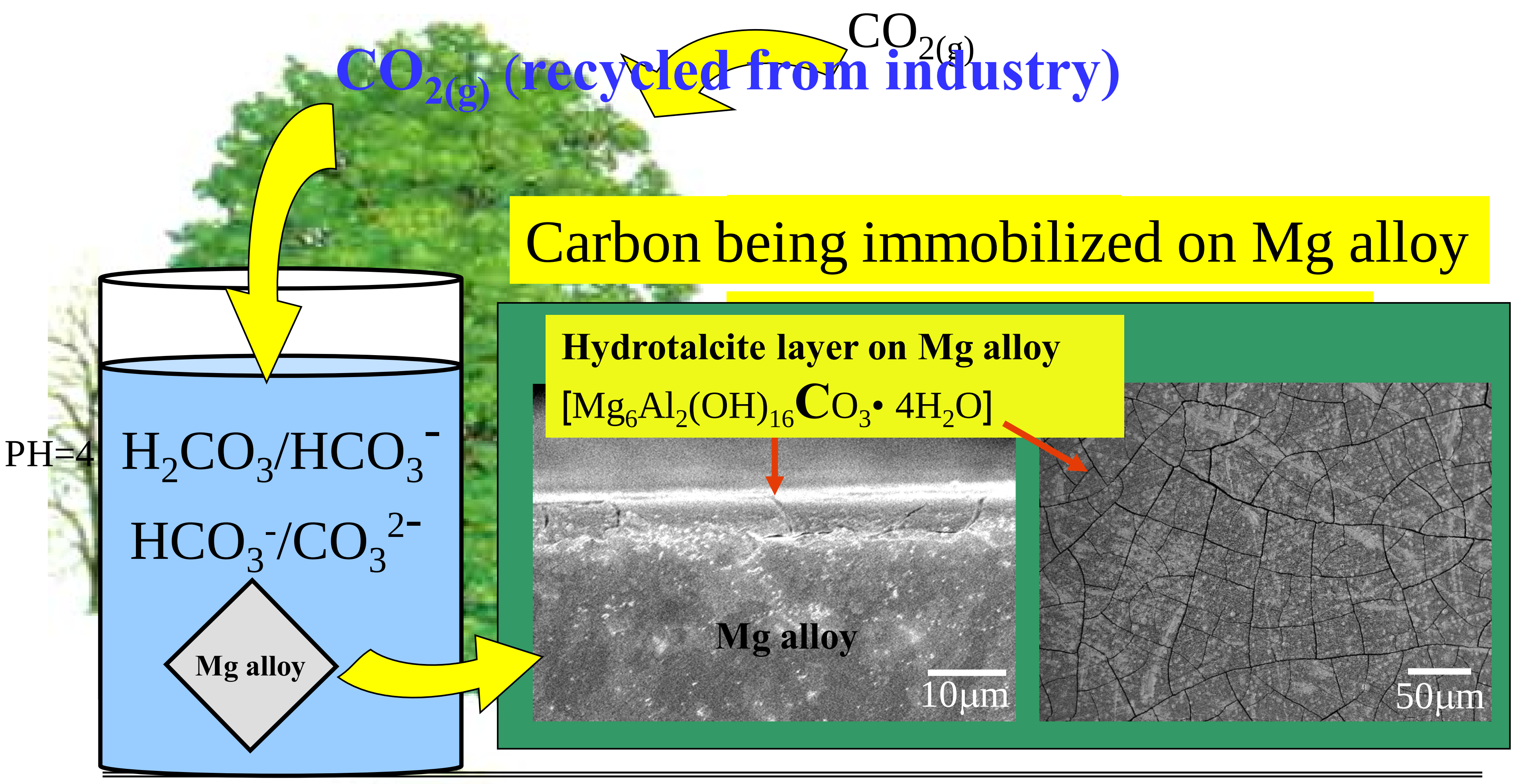
J.Y. Uan*, J.K. Lin and Y.S. Tung, ***Journal of Materials Chemistry***, 20 (2010), pp.761-766.

B.L. Yu, X.L. Pan and J.Y. Uan*, ***Corrosion Science***, 52 (2010), pp. 1874-1878.

J.K. Lin and J.Y. Uan*, ***Corrosion Science***, 51 (2009), pp. 1181-1188.

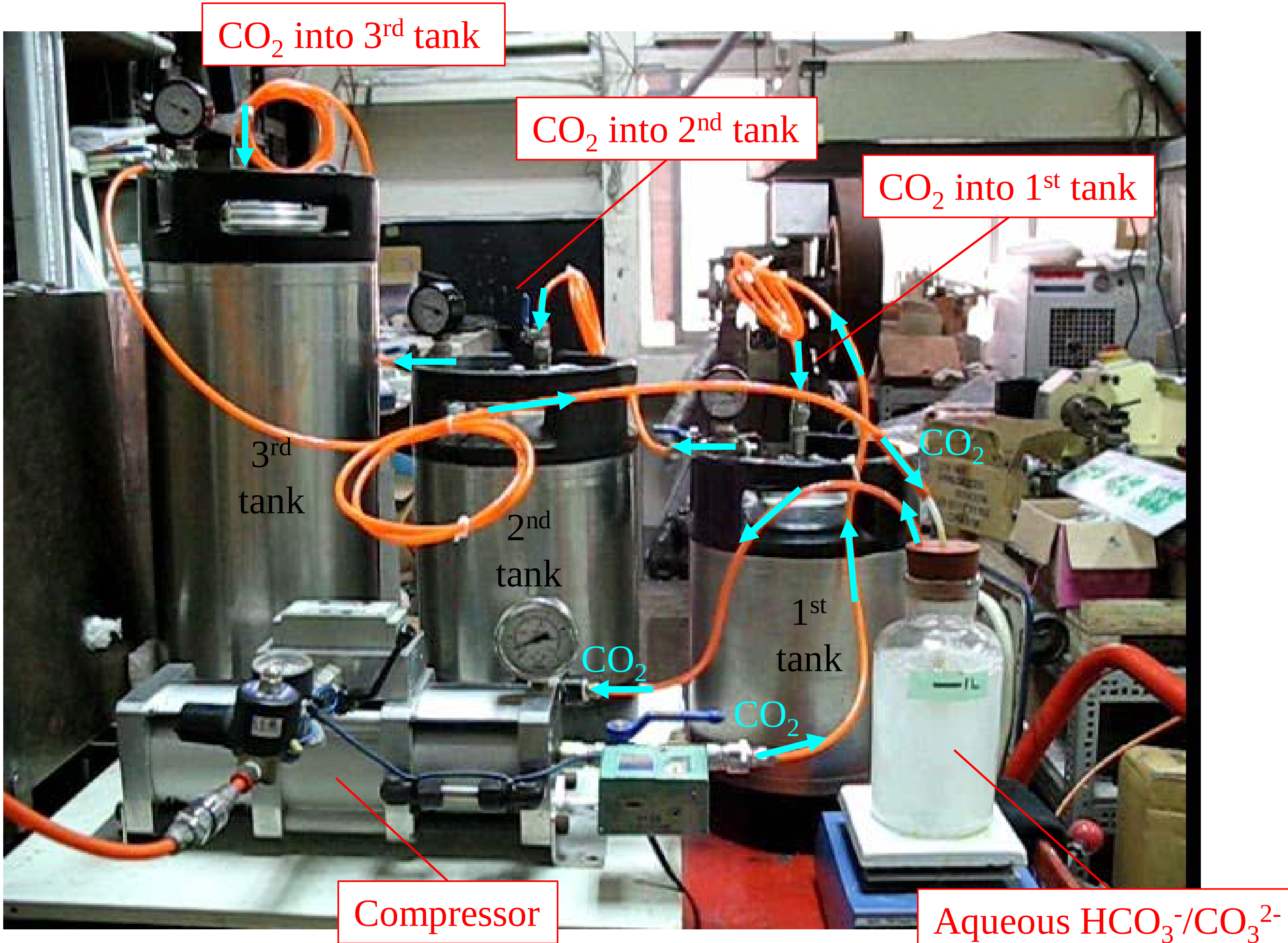
J.Y. Uan*, B.L. Yu and X.L. Pan, ***Metallurgical and Materials Transactions A***, 39A (2008), pp. 3233-3245.

J.K. Lin, C.L. Hsia and J.Y. Uan*, ***Scripta Materialia***, 56 (2007), pp. 923-925.



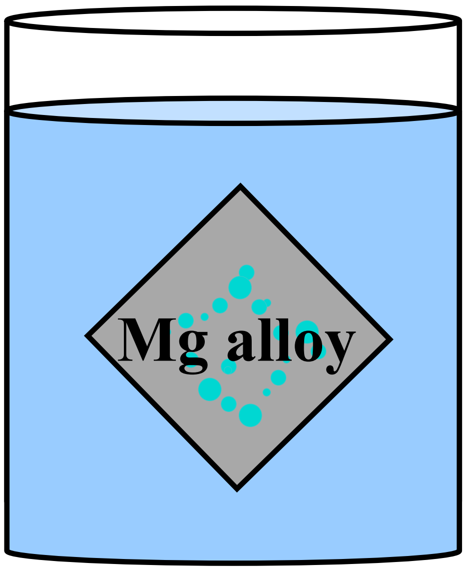
Photosynthesis is a process used by plant to convert light energy into chemical energy (sugars) which are synthesized from carbon dioxide and water.

Preparing aqueous carbonic acid (HCO_3^-/ CO_3^{2-})



Carbonic acid aqueous (pH ~4) at 50 °C

$$\mathbf{CO_2 + H_2O \leftrightarrow H_2CO_3 \leftrightarrow H^+ + HCO_3^-}$$

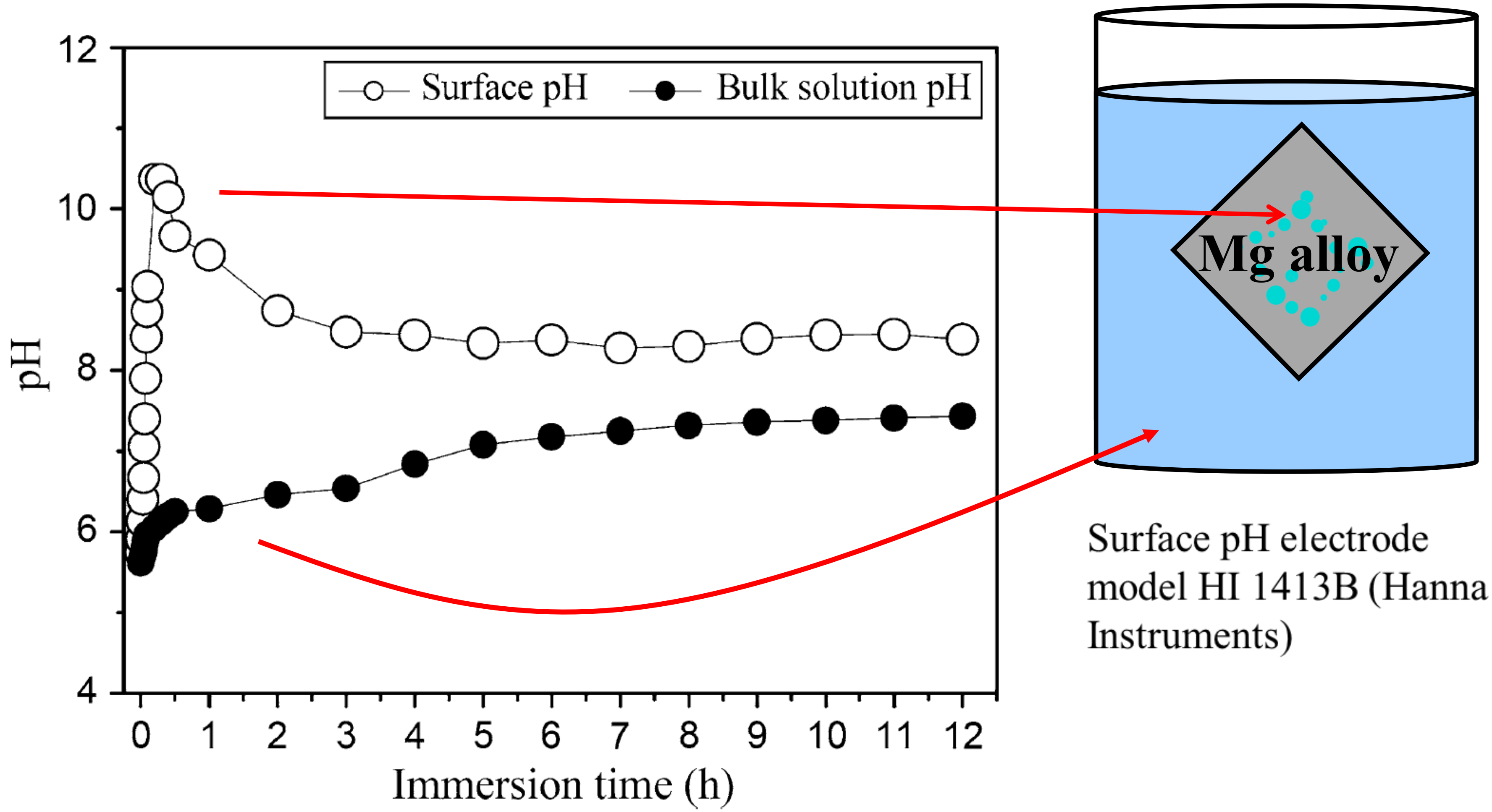


Away from sample

$HCO_3^- + H^+$ (pH ~4)

Sample's surface

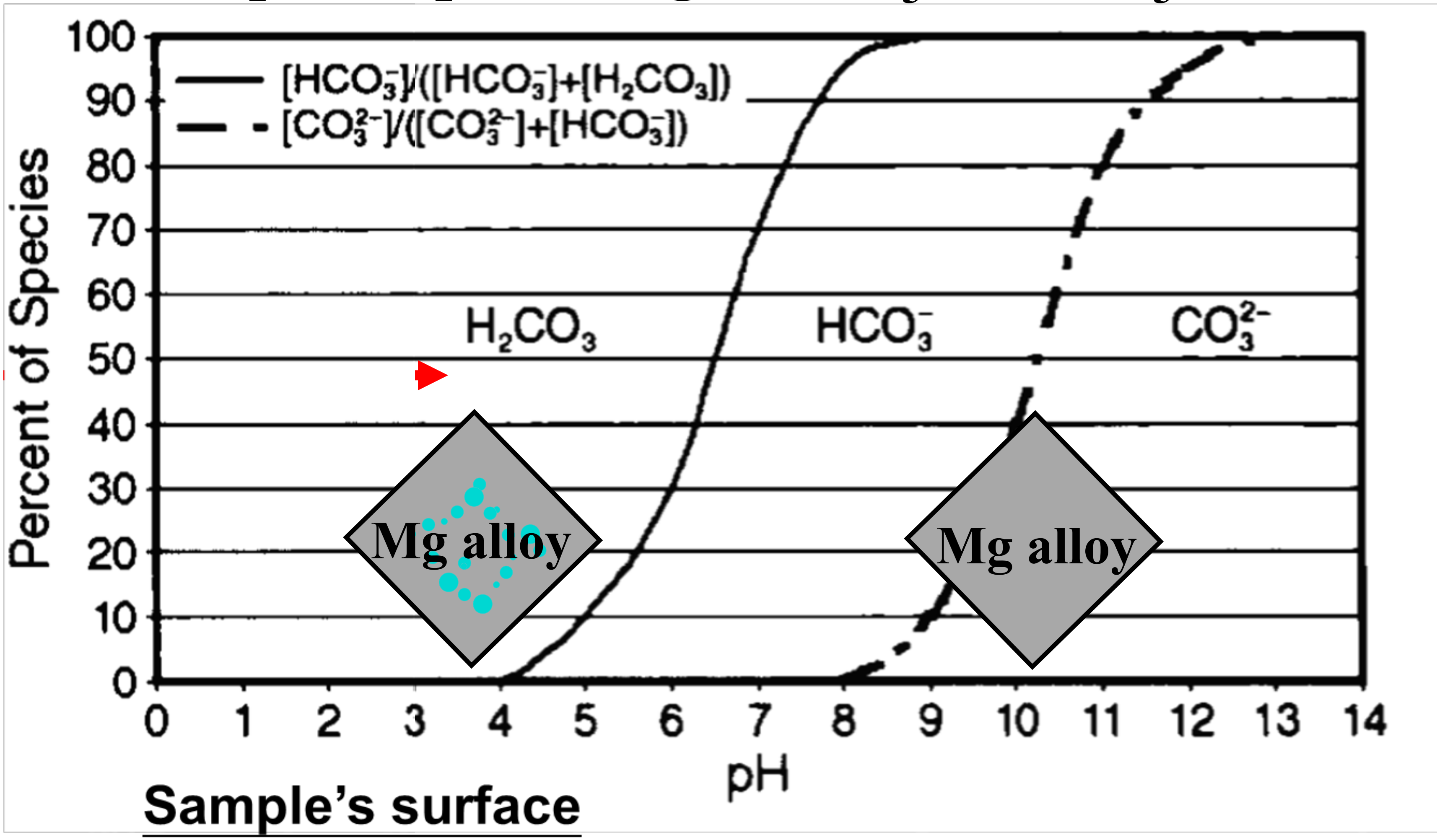
$Mg(Al) + 2H_2O \rightarrow Mg^{2+} (Al^{3+}) + 2OH^- + H_2$



Surface pH electrode model HI 1413B (Hanna Instruments)

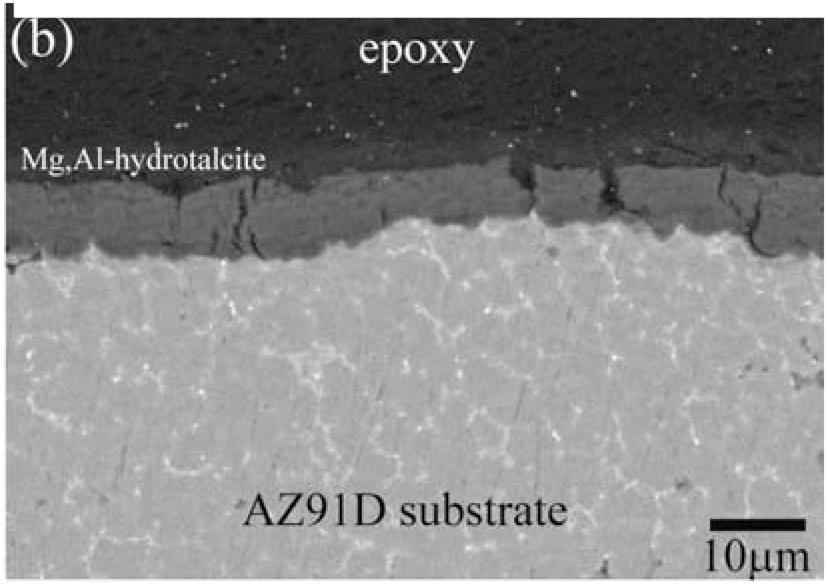
J.Y. Uan*, B.L. Yu and X.L. Pan, Metallurgical and Materials Transactions A, 39A (2008), pp. 3233-3245.

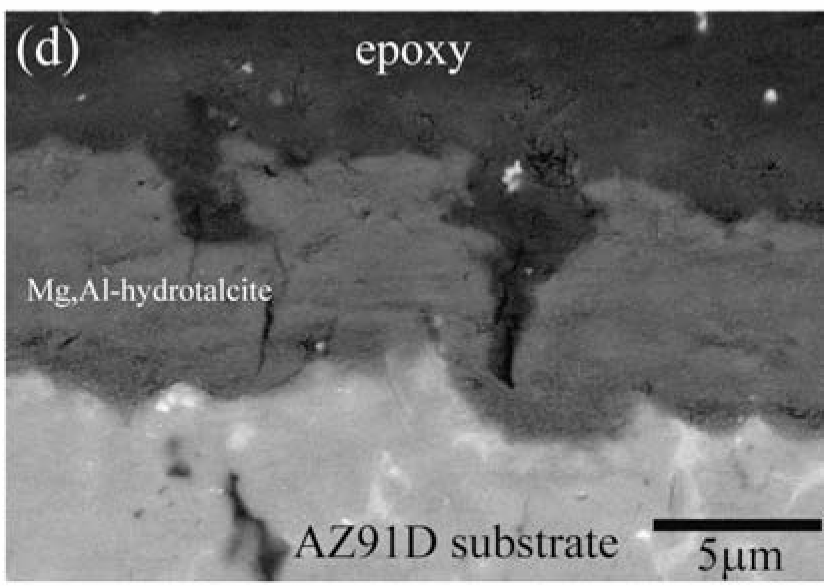
pH vs. percentage of CO_3^{2-} / HCO_3^-

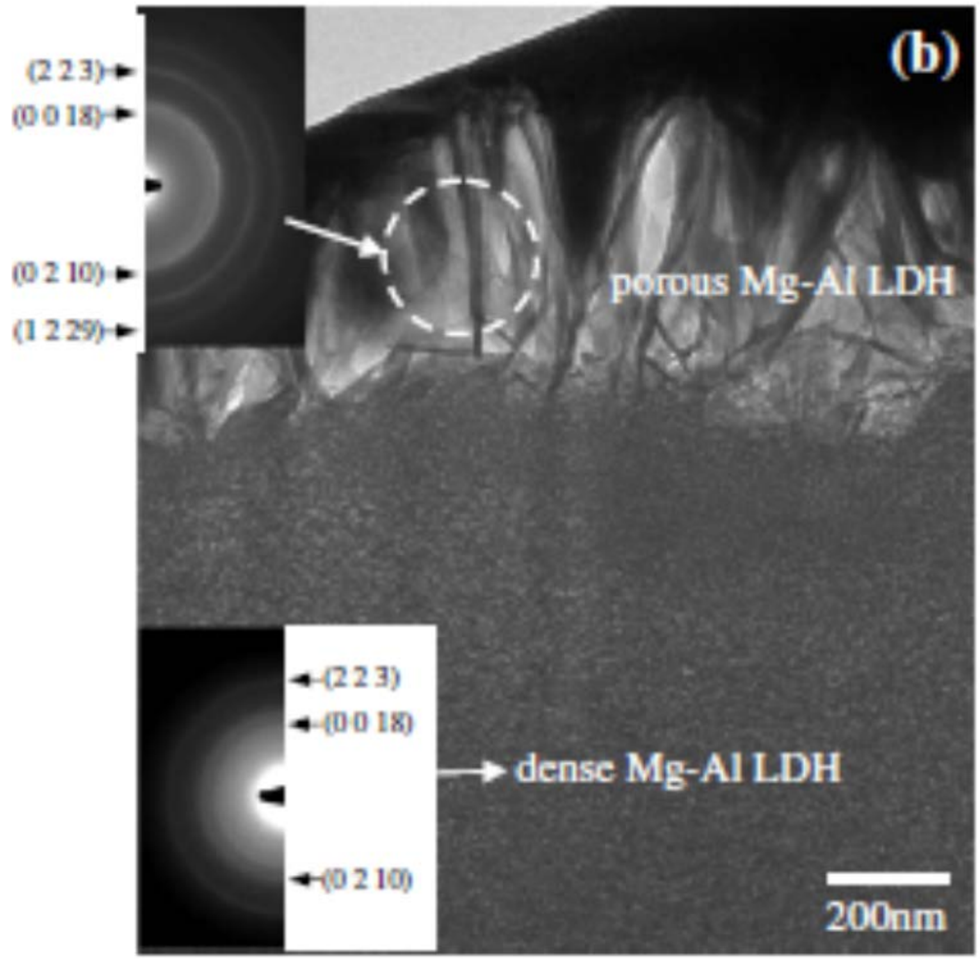


$Mg(Al) + 2H_2O \rightarrow Mg^{2+}(Al^{3+}) + 2OH^- + H_2$

$Mg_{4.38}Zn_{0.22}Al_2(OH)_{13.19}CO_3 \cdot mH_2O$



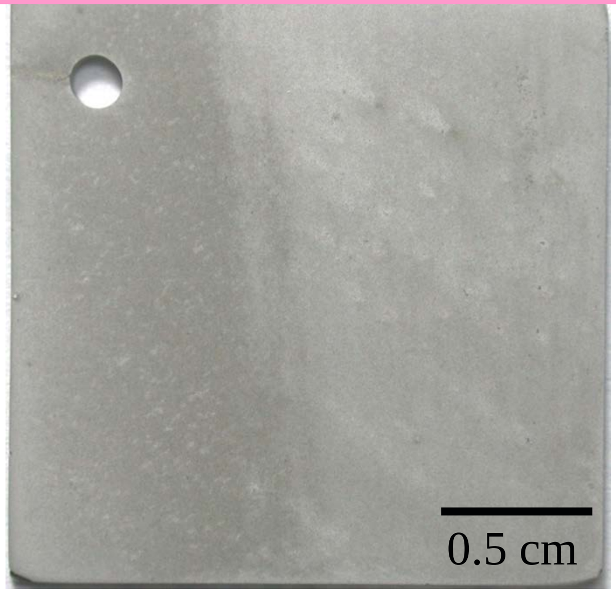




J.K. Lin, et al., ***Corrosion Science***, 53 (2011), p. 3832.

Salt spray test (ASTM B117)

with layered double hydroxide coating



AZ91D Mg alloy substrate

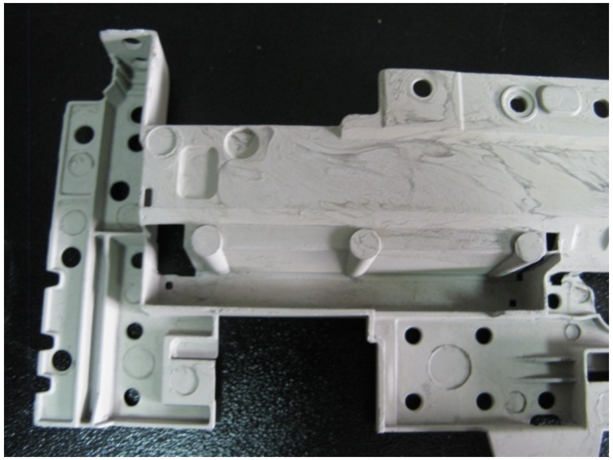
2 hr conversion treatment / salt spary 36 hr / corro. spot <5 %

0.5 hr conversion treatment / salt spary 12 hr / corro. spot <5 %

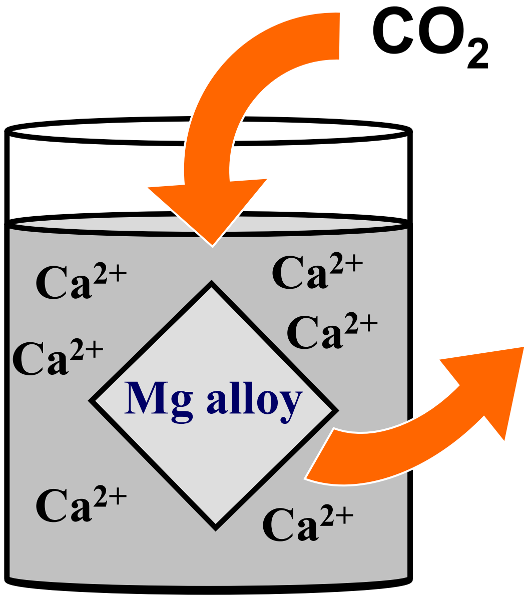
J.K. Lin, *et al*, ***Scripta Materialia***, 56, 2007, p.923.

.J.K. Lin *et al*., ***Corrosion Science***, 51, 2009, p. 1181.

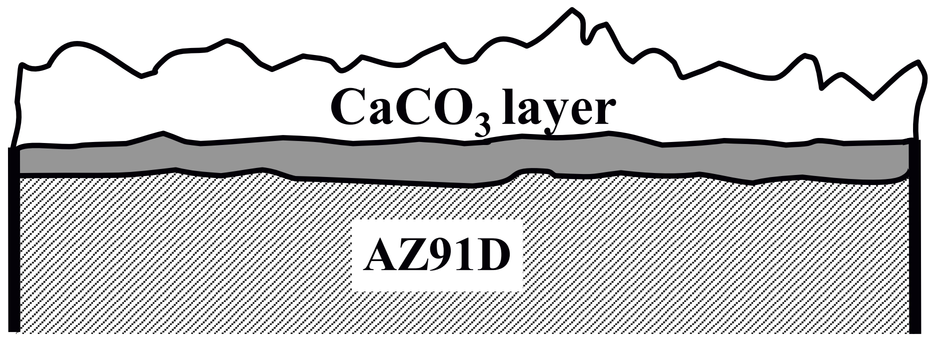
Carbonic acid conversion treatment / application examples



Chemical conversion hard coating ($CaCO_3$)



- **Mg, Al,** Pb, Sr, Ba promote aragonite formation



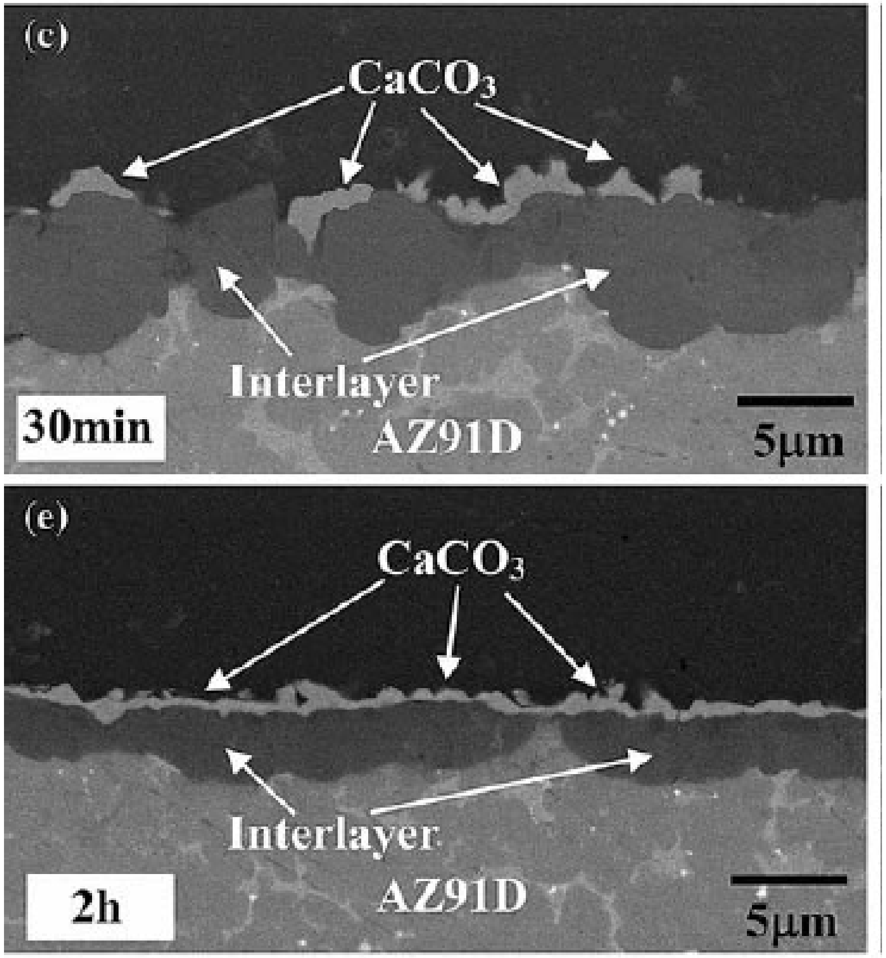
$$CaCO_3(s) + H_2O(l) + CO_2(g) = [Ca^{2+} + 2HCO_3^-]\ (aq)$$

$$Mg + H_2O = Mg^{2+} + 2OH^- + H_2$$

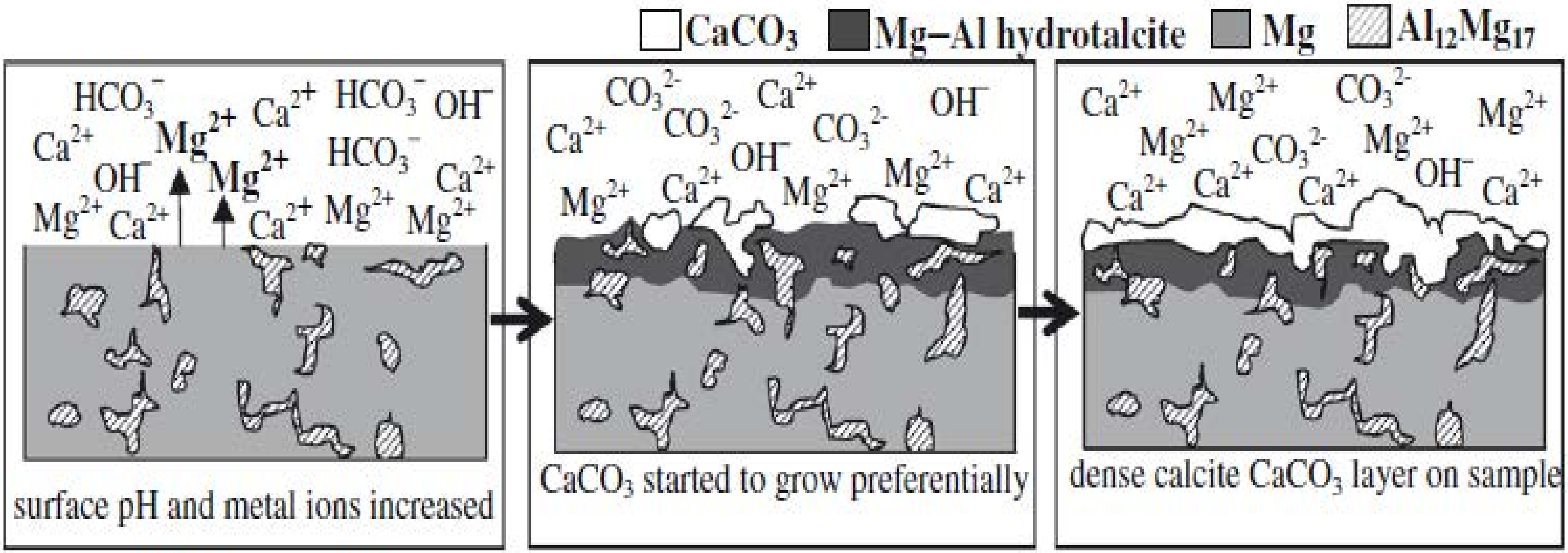
J.Y. Uan*, B.L. Yu and X.L. Pan, Metallurgical and Materials Transactions A, 39A (2008), pp. 3233-3245.

Yu, Pan, and Uan*, Corrosion Science,52 (2010), pp. 1874-1878.

<u>**Calcium ions**</u> in the carbonic acid solution



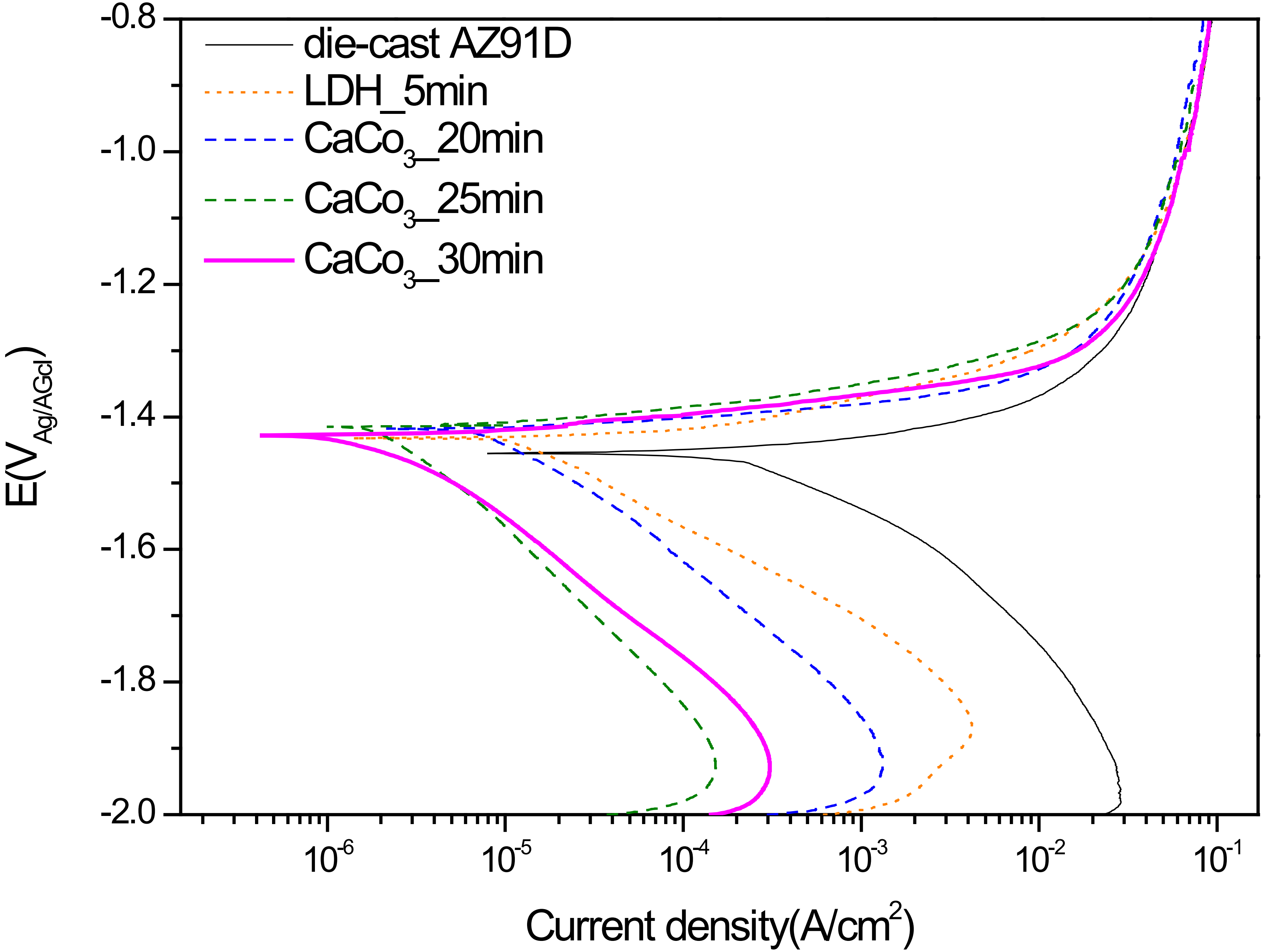
J.Y. Uan*, B.L. Yu and X.L. Pan, Metallurgical and Materials Transactions A, 39A (2008), pp. 3233-3245.



1. *Surface pH from acid to alkaline due to surf. corro. in carbonic acid*

2. *Mg^{2+} promotes the coating of $CaCO_3$*

Yu, Pan, and Uan*, Corrosion Science,52 (2010), pp. 1874-1878.



die-cast AZ91D
LDH_5min
CaCo3_20min
CaCo3_25min
CaCo3_30min
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
E(VAg/AGcl)
10-6
10-5
10-4
10-3
10-2
10-1
Current density(A/cm2)

Environmentally treatments of Mg alloy scraps: recycling and reuse

Song-Lin Li, Hung-Mao Lin and J.Y. Uan*, *International Journal of Hydrogen Energy*, 38 (2013), pp.13520-13528.

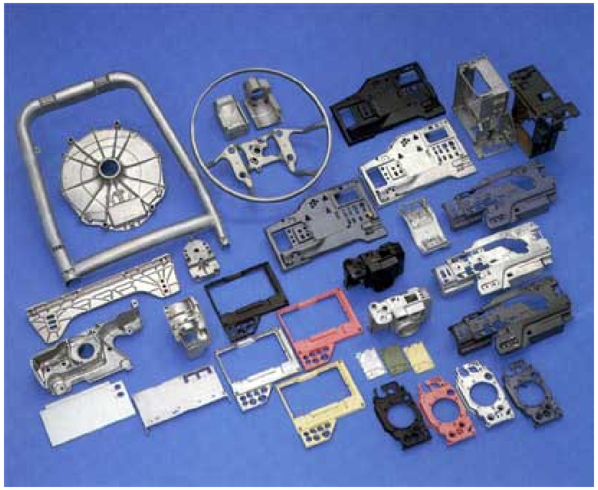
S.H. Yu, J.Y. Uan* and T.L. Hsu, *International Journal of Hydrogen Energy*, 37 (2012), pp. 3033-3040

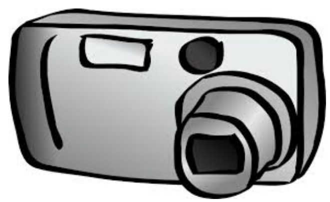
J.Y. Uan*, S.H. Yu, M.C. Lin, L.F. Chen and H.I. Lin, *International Journal of Hydrogen Energy*, 34 (2009), pp. 6137-6142.

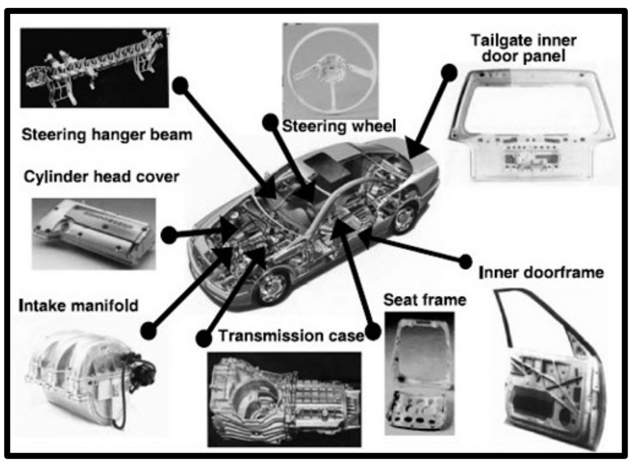
J.Y. Uan*, M.C. Lin, C.Y. Cho, K.T. Liu and H.I Lin, *International Journal of Hydrogen Energy*, 34 (2009), pp. 1677-1687.

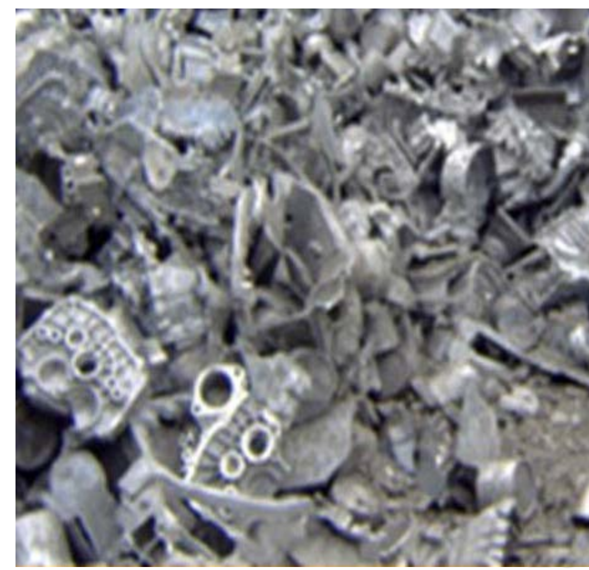
J.Y. Uan*, C.Y. Cho and K.T. Liu, *International Journal of Hydrogen Energy*, 32 (2007), pp. 2337-2343.

Y. F. Lung, Y.F. Syu, M.C. Lin and J.Y. Uan*,
Converting waste magnesium scrap into anion-sorptionable nanomaterials,
RSC Advances (2014), accepted.









Post-consumer Mg scraps

Post-consumer Mg scrap

H_2 generator

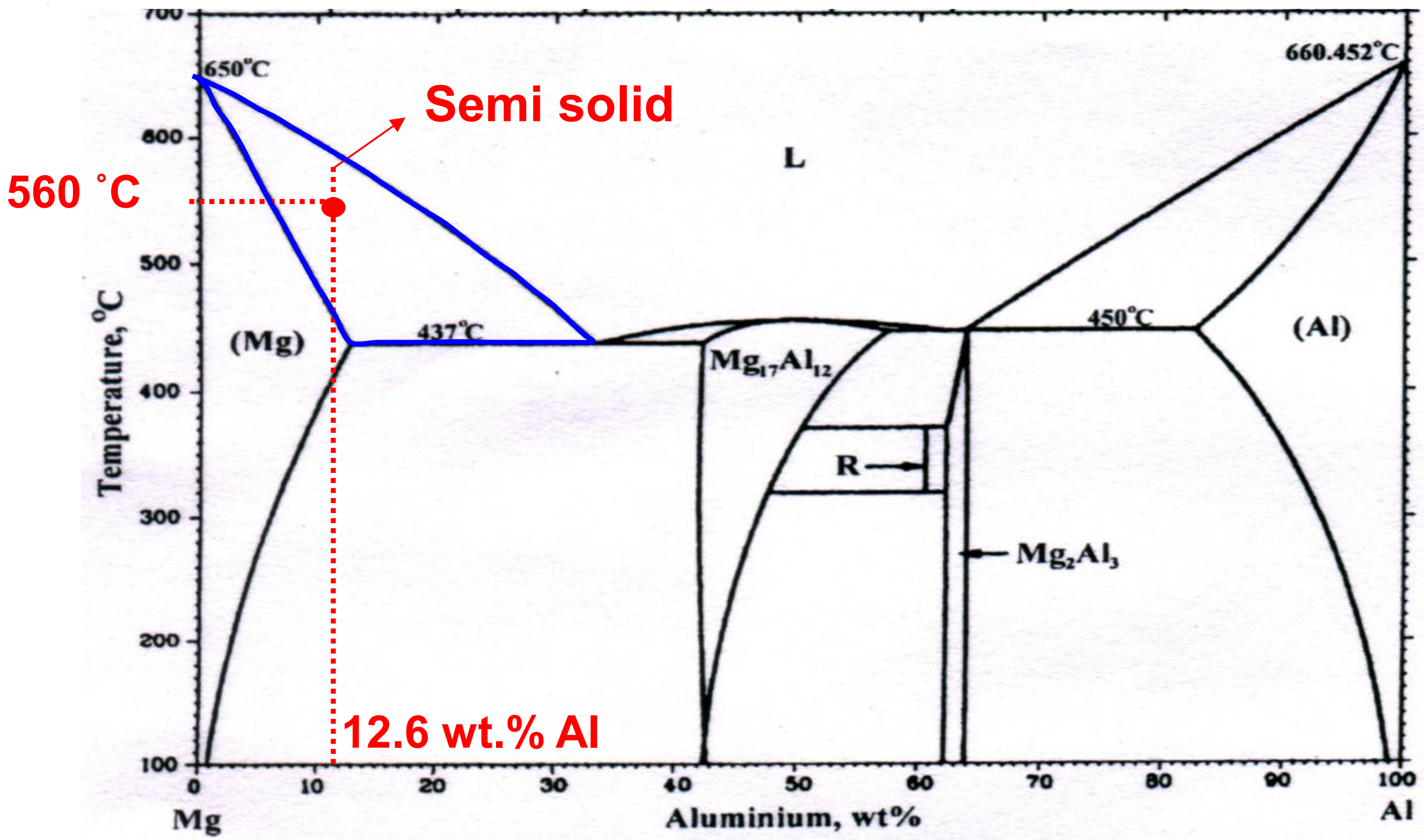
Low grade Mg scrap

Anion-sorptional mater. or catalyst

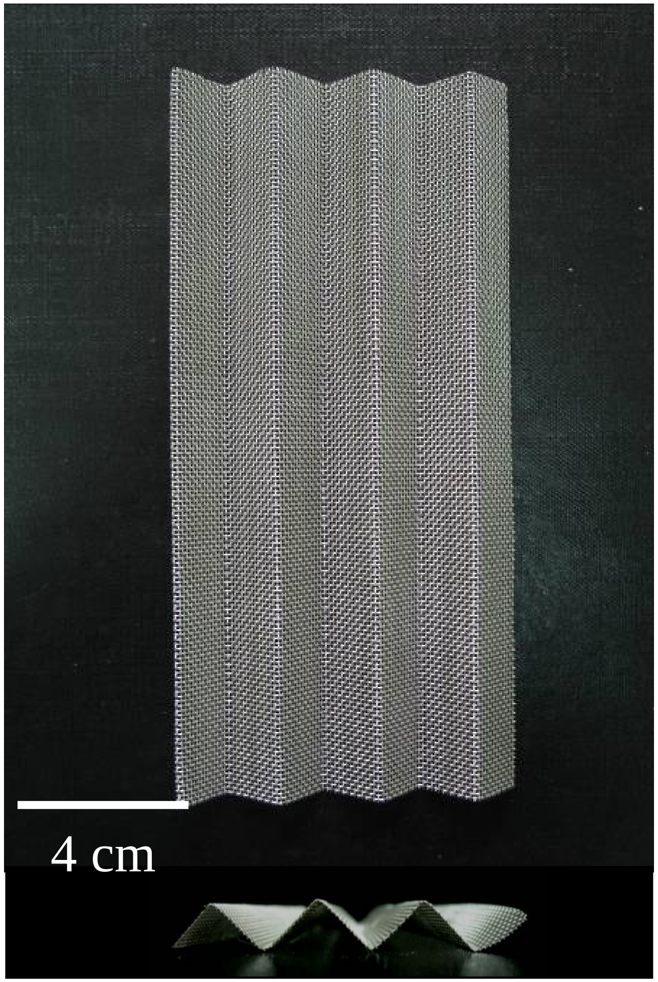
Currently, low-grade magnesium scraps and post-consumer Mg alloys (e.g., coated (Cu, Ni) magnesium) are not recycled.[9]

As an additive in aluminum alloys
As an desulfate agent in steel metallurgy

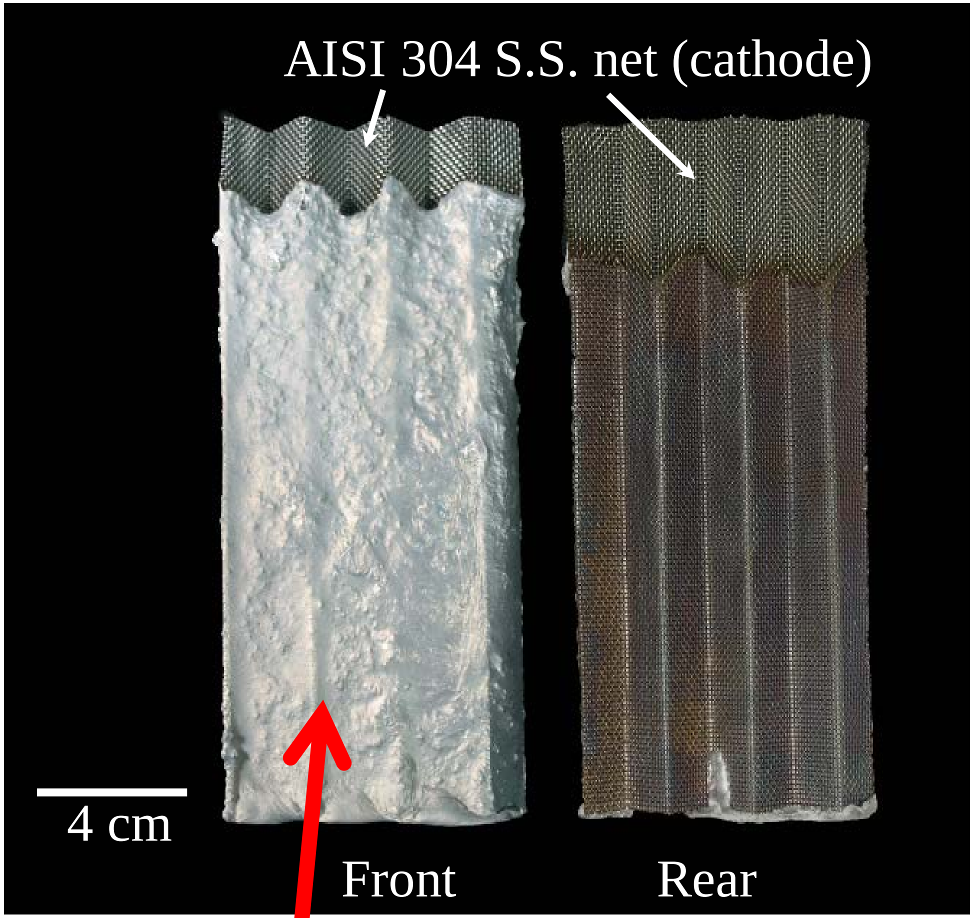
composition	Al	Si	Fe	Ni	Cu	Zn	Mn	Mg
wt.%	12.6	0.6	0.13	0.015	0.1	0.77	0.19	Bal.
AZ 91D alloy (ASTM B93)	8.5 ~ 9.5	0.08 max	0.05 max	0.001 max	0.025 max	0.45 ~ 0.9	0.17 ~ 0.4	Bal.



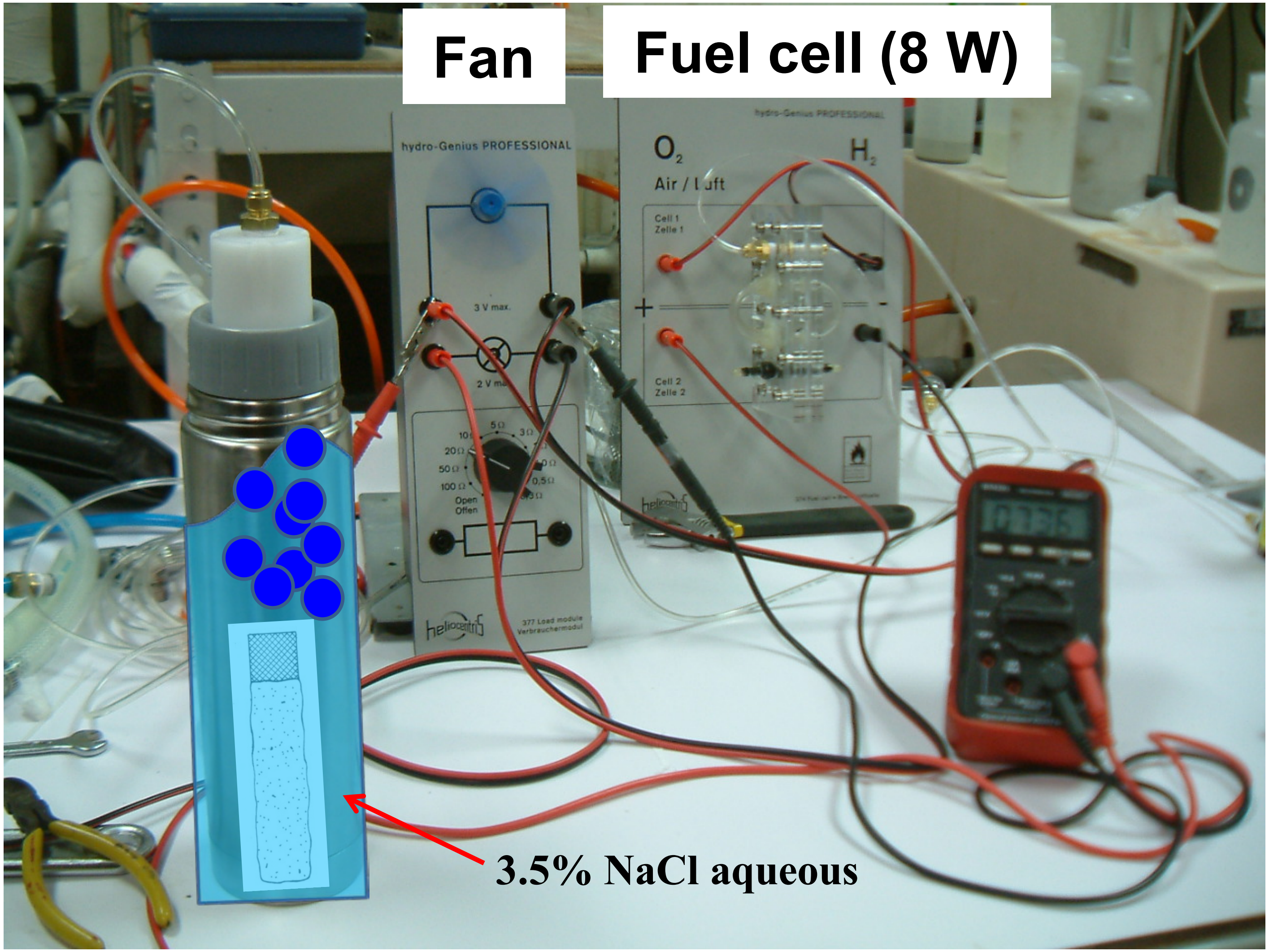
Stainless steel net

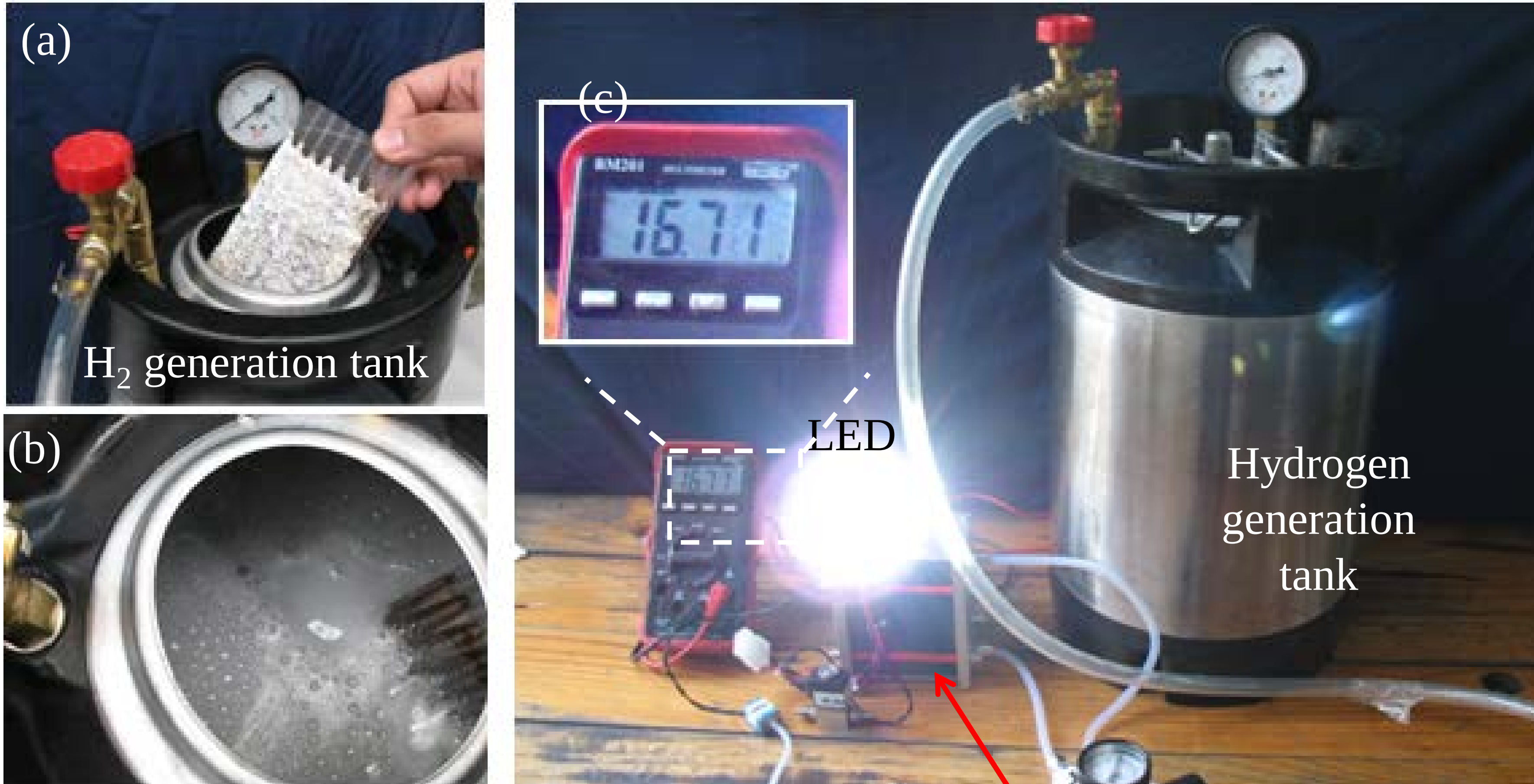


Mg/steel couple for H_2 generation



Hydrogen-on-demand





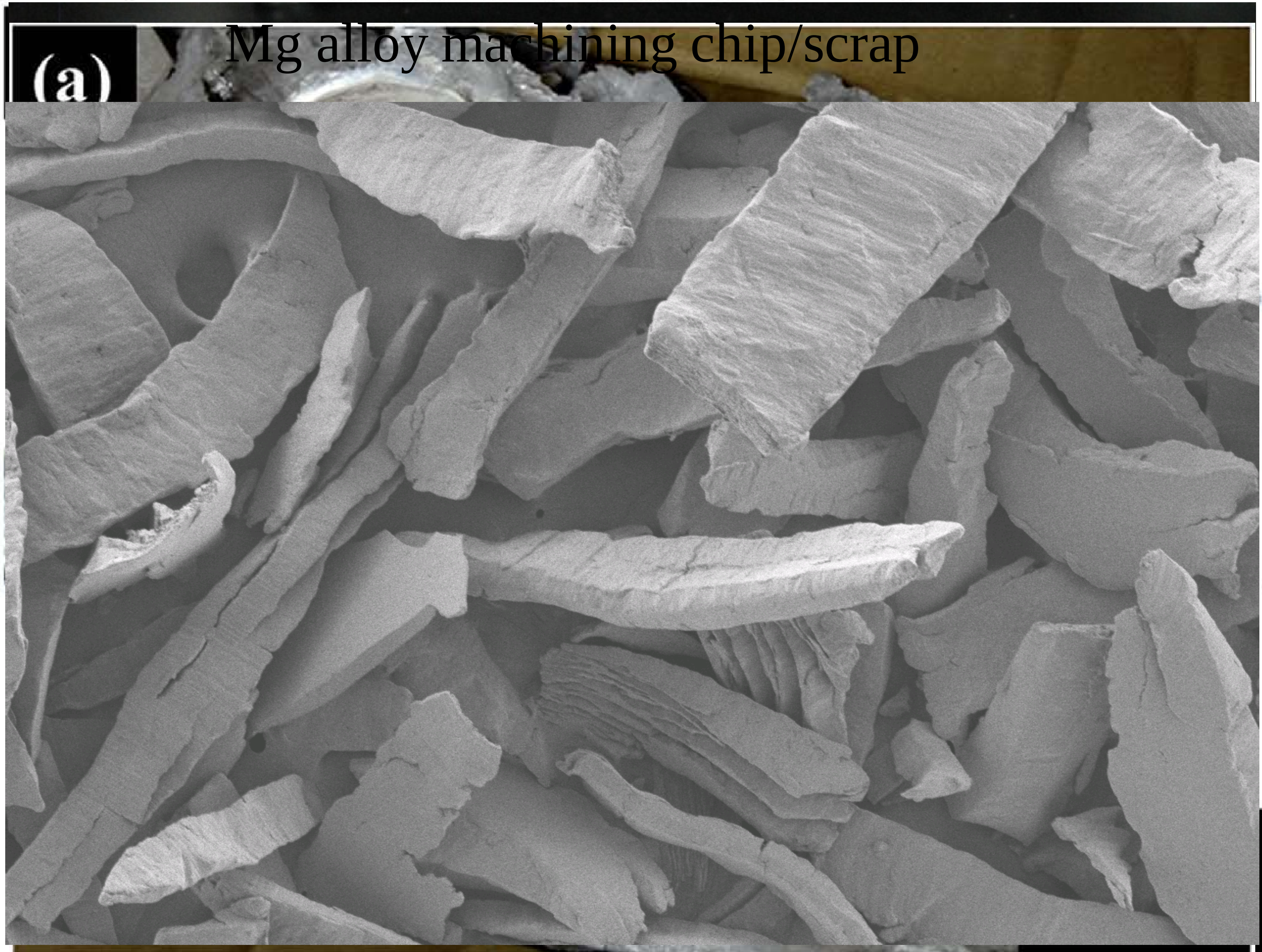
100 W PEMFC Stack


台塩高級精鹽
HIGH QUALITY SALT

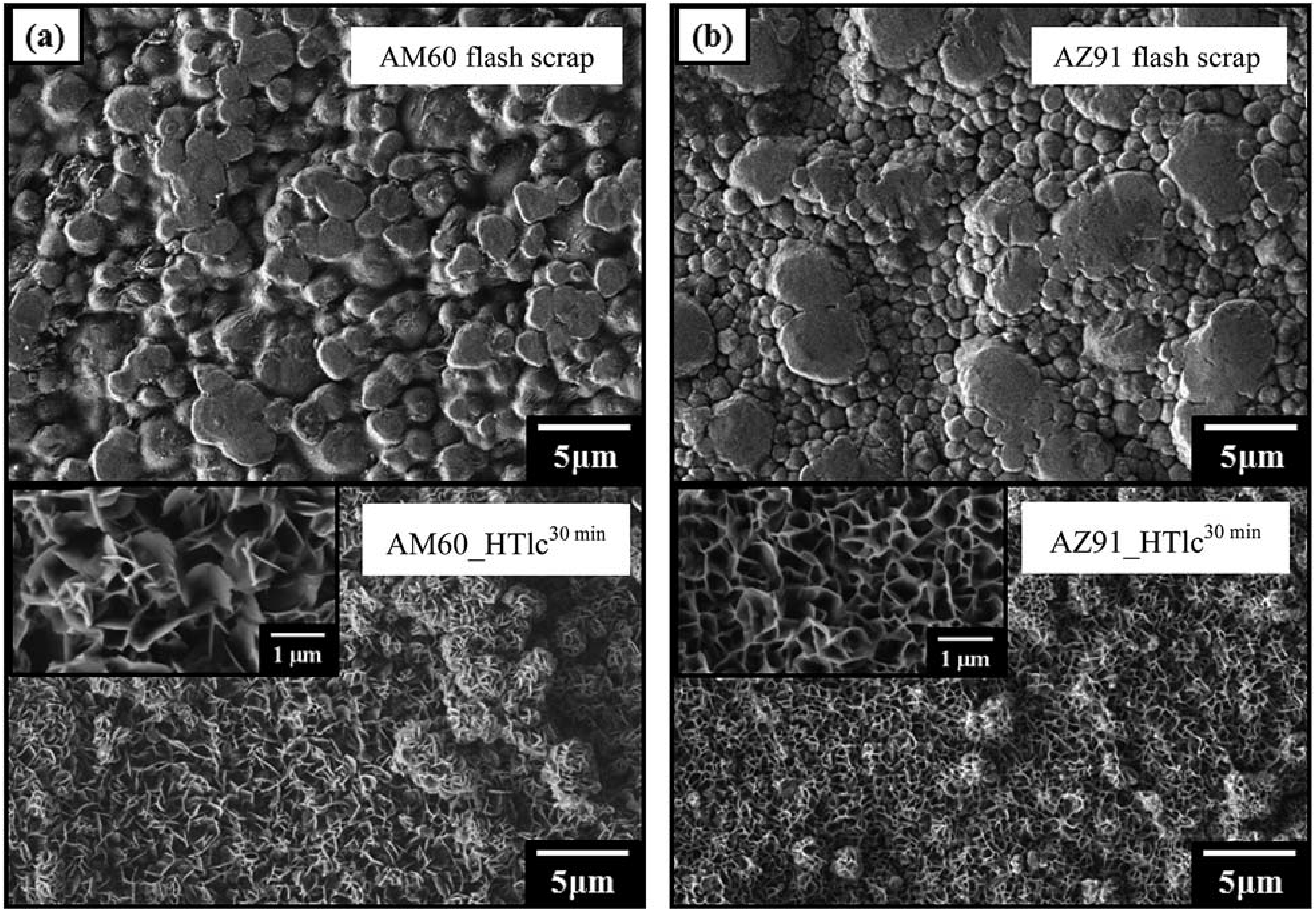
Mg alloy machining chip/scrap

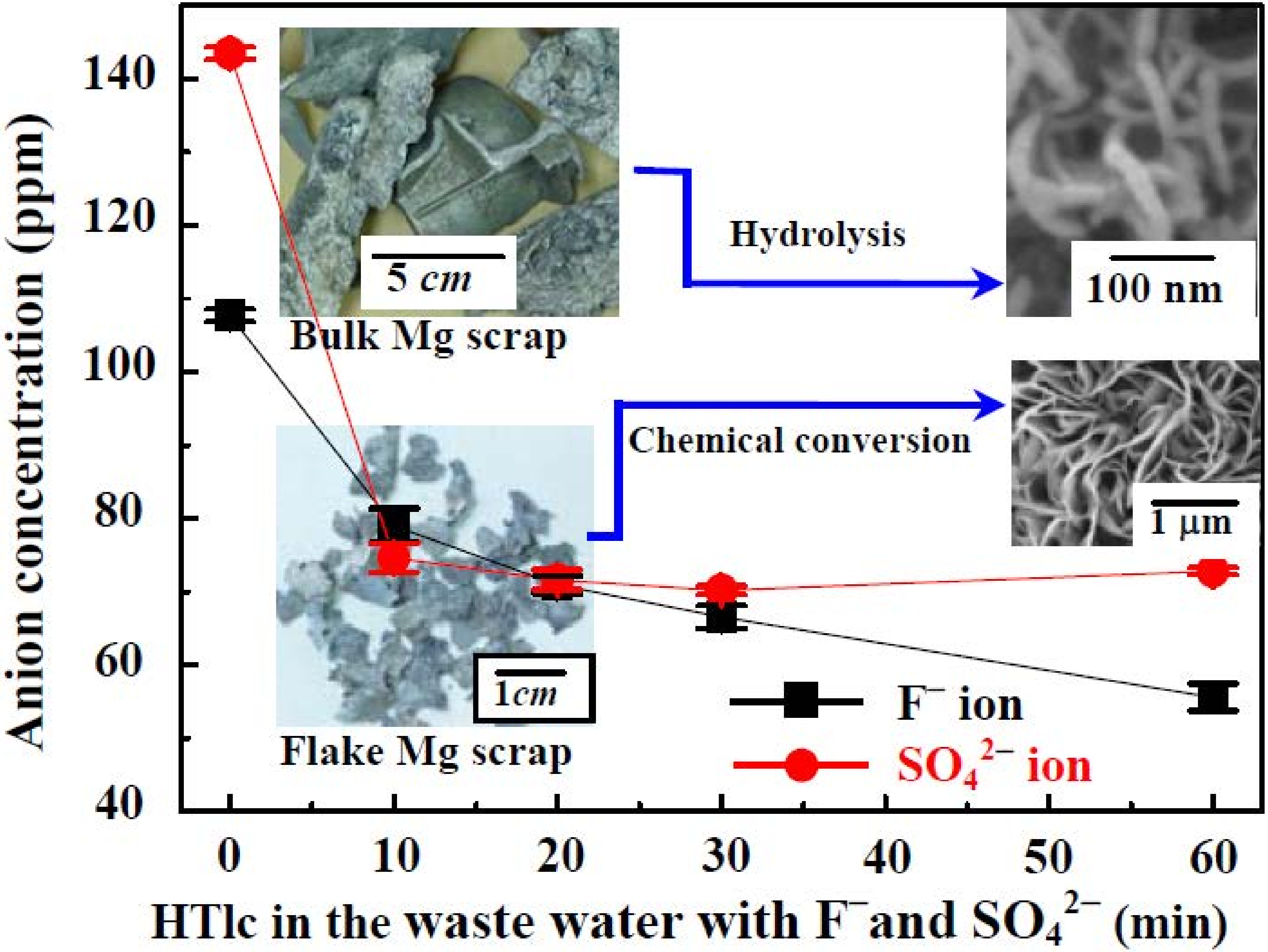
(

a



Chemical conversion in pH 1.5 NaCl aqueous at 25 °C




Anion concentration (ppm)
140
120
100
80
60
40
0
10
20
30
40
50
60
HTlc in the waste water with F⁻ and SO₄²⁻ (min)
5 cm
Bulk Mg scrap
Hydrolysis
100 nm
Chemical conversion
1 μm
1cm
Flake Mg scrap
F⁻ ion
SO₄²⁻ ion

Summary

For AZ Mg alloys, **carbonic acid** is good for chemical conversion coating treatment.

Ca^{2+}/carbonic acid is good for **conversion hard coating** with $CaCO_3$ film on AZ Mg alloys.

Post-consumer Mg scraps/ Hydrogen generator

Recycling fine flake-type Mg waste/anion-sorptionable thin **film can directly form on the surface of the flake**, the Mg waste being able to function to take up fluoride and sulfate anions from waste water.

Thanks for Your Attentions

Metal	Corrosion potential (volts) vs. SCE
Mg	-1.73
Mg alloys	**-1.67**
Zn	-1.05
Mild steel, Cd-plated	-0.86
Al (99.99 %)	-0.85
Mild steel	-0.78
Cast iron	-0.73
Pb	-0.55
Sn	-0.50
Stainless steel 316	-0.43
Stainless steel 304	-0.38
Cu	-0.22
Ni	-0.14
Au	+0.18
Pt	**+0.88**

$\Delta E = 1.29$ V

$\Delta E = 2.55$ V

R. S. Busk, "Magnesium products design", Marcel Dekker Inc., New York (1987), p. 519.

Experimental cycle	1	2	3	4	5	Average
H_2 generated in 50 min (liter)	19.3	18.8	14.8	8.8	8.4	16.1 ± 7.8
LGMS consumed in 50 min (g)	18.1	15.7	14.5	7.7	8.6	14.8 ± 7.0
H_2 generated/ LGMS consumed (L/g)	1.1	1.2	1.0	1.1	0.9	1.1 ± 0.1

生命週期評估-盤查資料(Inventory analysis)

Mg scraps		Energy requirement (MJ (kg of Mg)$^{-1}$)		Green warming potential (kg of CO_2 equival. (kg of Mg)$^{-1}$)	Acidification potential (g (kg of Mg)$^{-1}$)	Smog, dross and sludge (g (kg of Mg)$^{-1}$)	Dioxins (μg (kg of Mg)$^{-1}$)	Energy production (MJ (kg of Mg)$^{-1}$)
Recycling Process	Albright et al.[43]	151	X 5%	19	25	515	0.24	0
	Kiefer et al.[44-45]	164	X 5%	42	34	Unavailable	Unavailable	0
Present study (H_2 and energy production)	Pt-coated Ti net	2.8[a]		10	Unavailable	27	Unavailable	136.1[b]
	AISI 304 S.S. net							114.7[c]

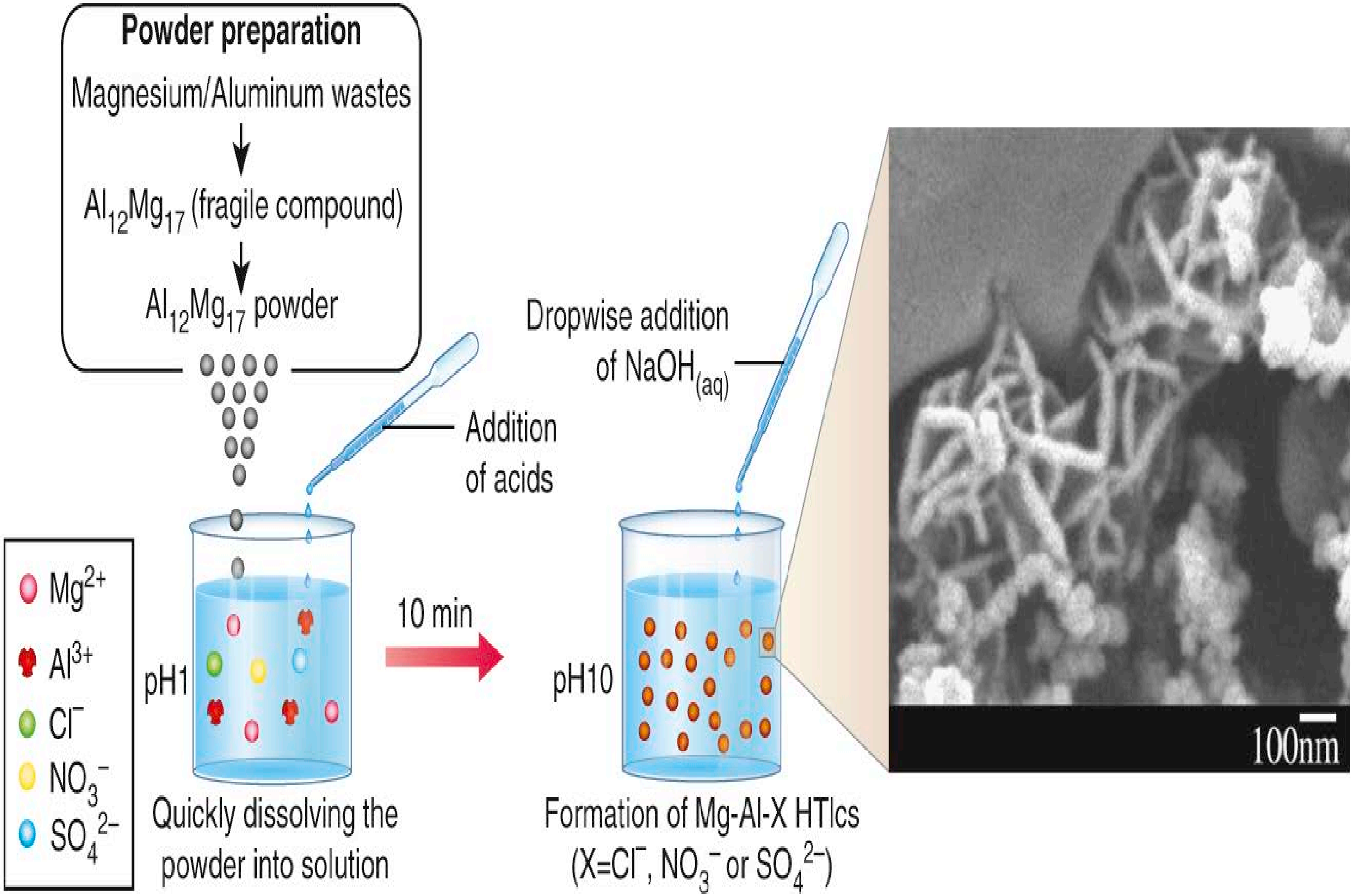
~8=

Melging 800 W (2.2 Kg scraps), 2.2 hr, 6.34 MJ (1760 Wh) needed

$$\frac{6.34\ (\text{MJ})}{2.2\ (\text{Kg Mg scraps})} = \frac{A\ (\text{MJ})}{1\ (\text{Kg Mg scraps})}$$

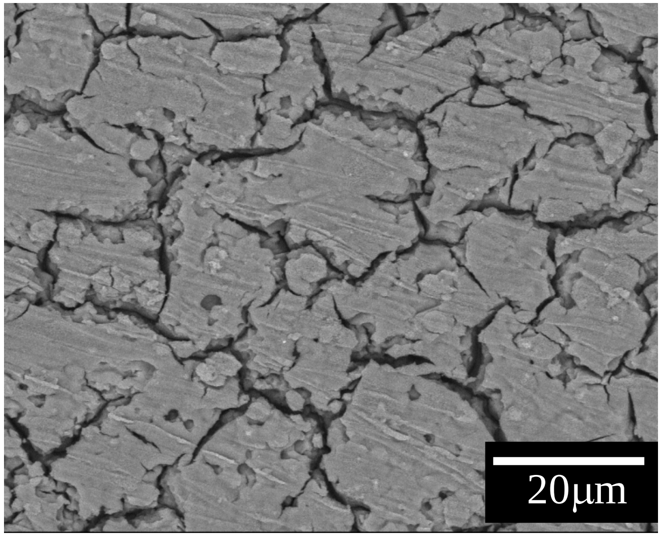
H_2 produce electric power

44 D.L. Albright and J.O. Haagensen, *IMA Annual World Conference*, International Magnesium Association, Toronto, Canada (1997).
45 B. Kiefer, G. Deinzer, J.O. Haagensen and K. Saur, SAE paper no. 982225, (1997).
46 G. Deinzer, B. Kiefer, J.O. Haagensen and H. Westengen, in "*Magnesium alloys and their applications*", edited by B.L. Mordike and K.U. Kainer, Werkstoff-Informationsgesellschaft mbH, Germany (1998), pp. 119-124.

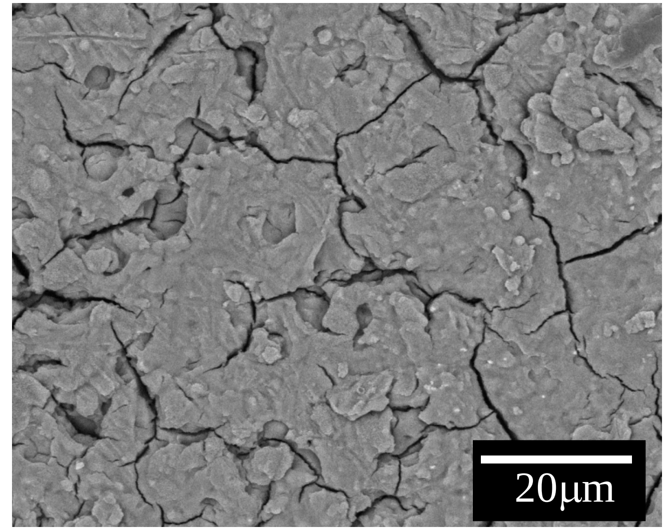

Powder preparation
Magnesium/Aluminum wastes
$Al_{12}Mg_{17}$ (fragile compound)
$Al_{12}Mg_{17}$ powder
Addition of acids
Dropwise addition of $NaOH_{(aq)}$
Mg^{2+}
Al^{3+}
Cl^-
NO_3^-
SO_4^{2-}
pH1
10 min
pH10
Quickly dissolving the powder into solution
Formation of Mg-Al-X HTlcs ($X=Cl^-$, NO_3^- or SO_4^{2-})
100nm

CO_2-2h/pH11.5-different temperature

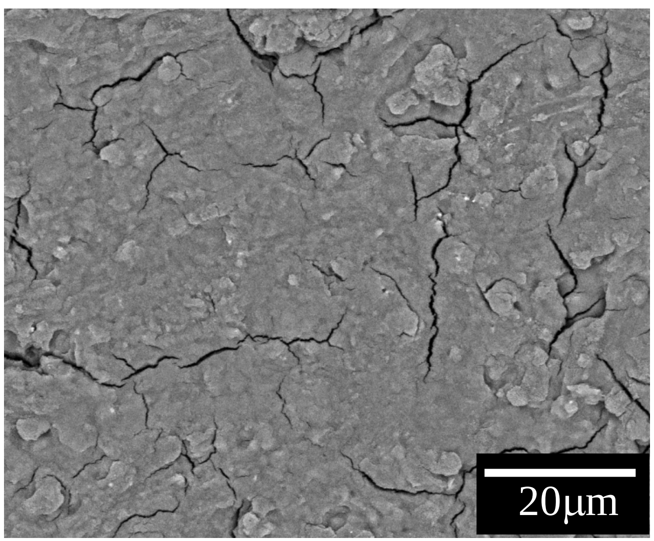
50°C



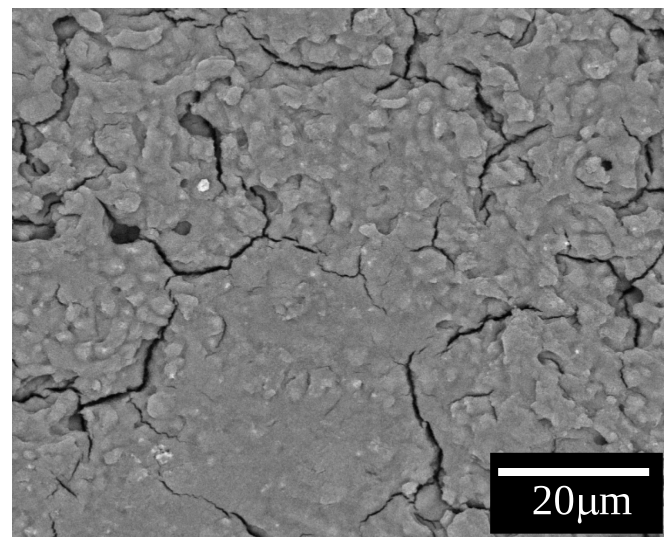
60°C



70°C



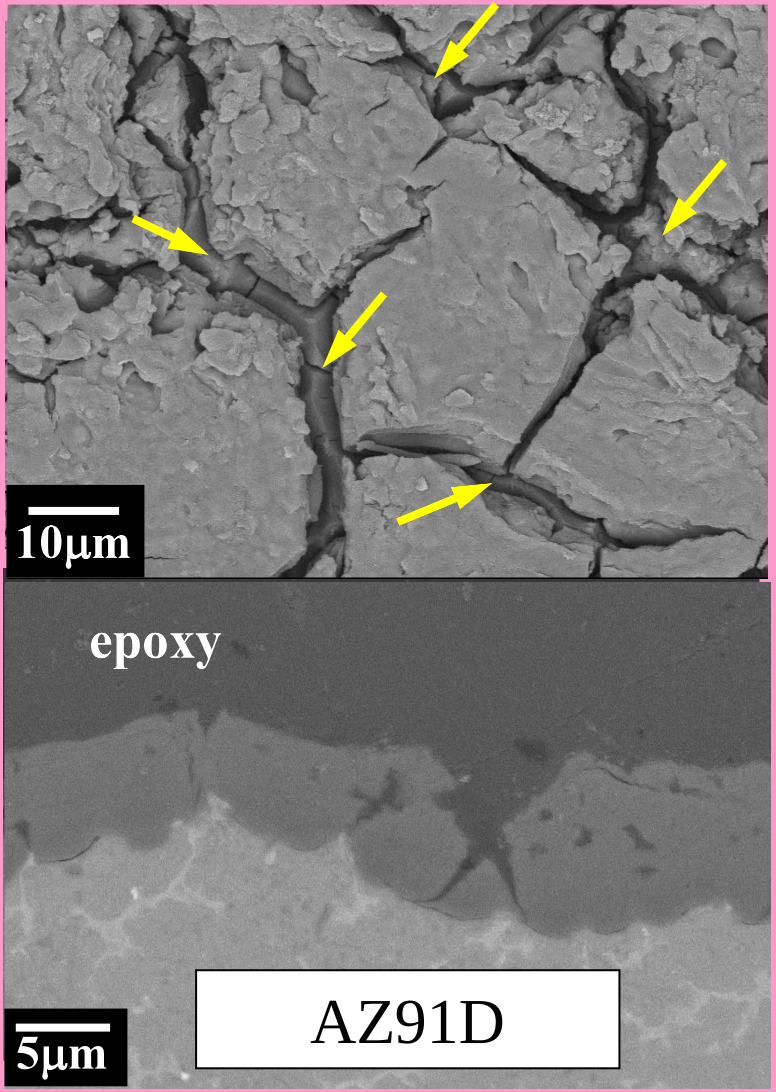
80°C

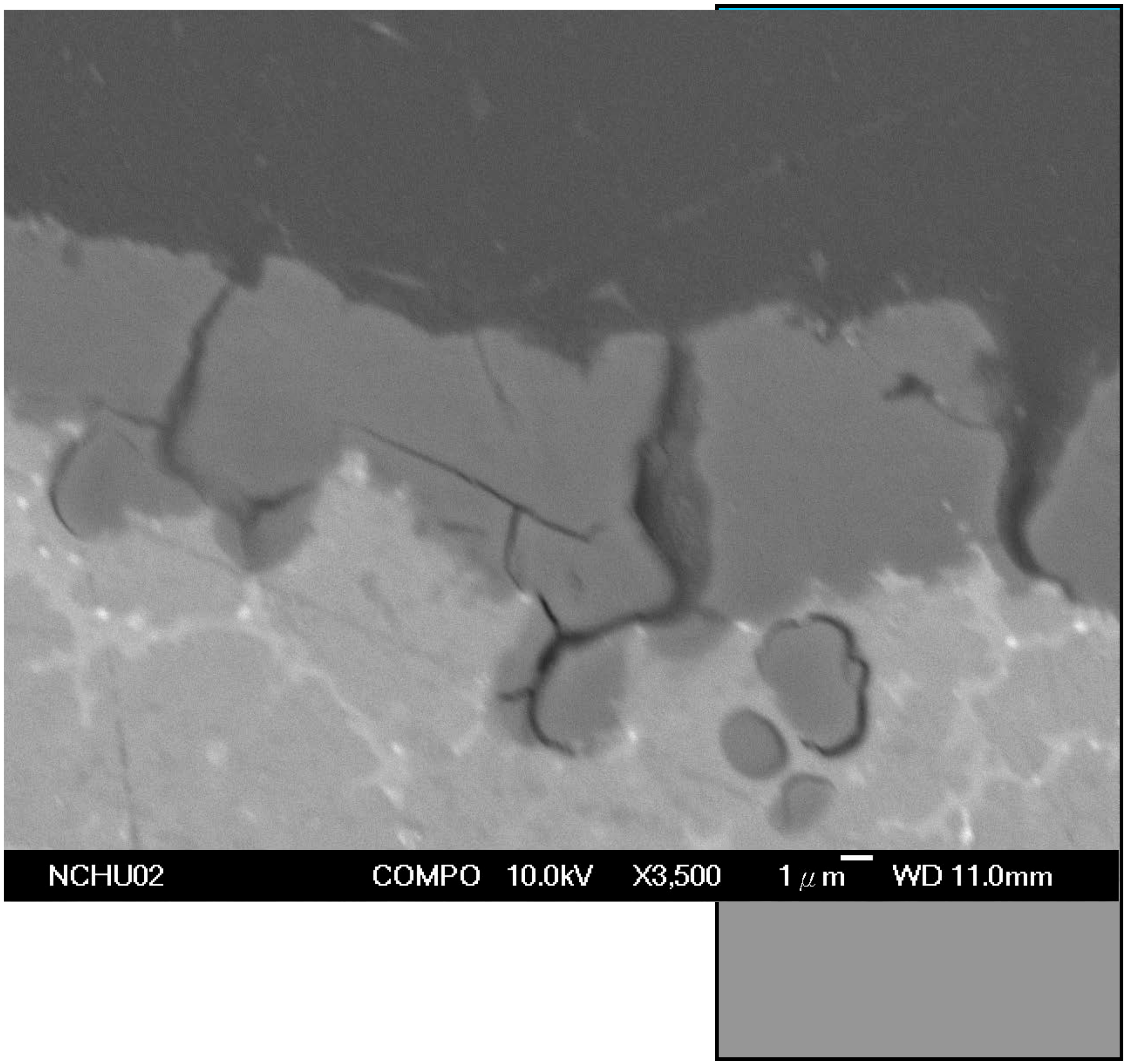


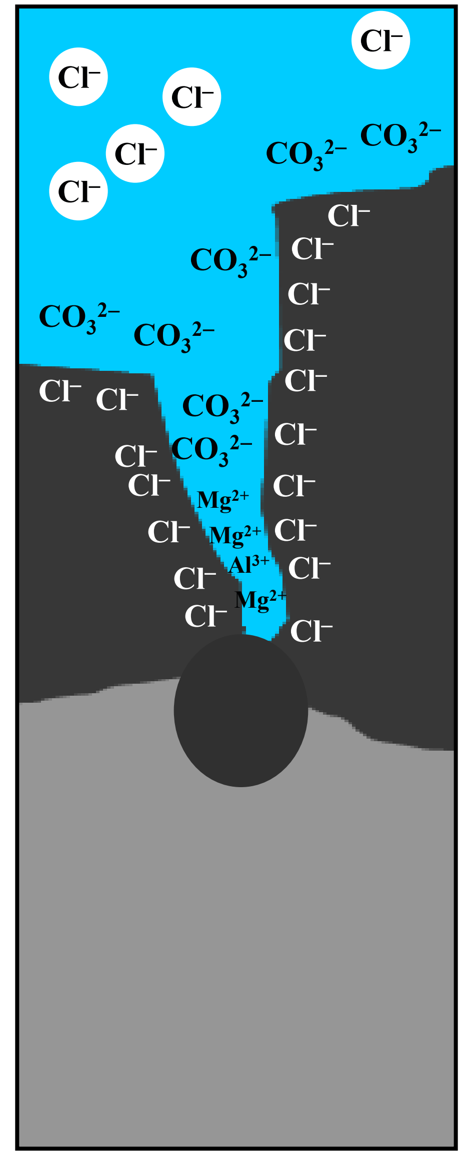
.Lin and Uan*, ***Corrosion Science***, 51, 2009, p. 1181.

Surface morphology / cross-section structure

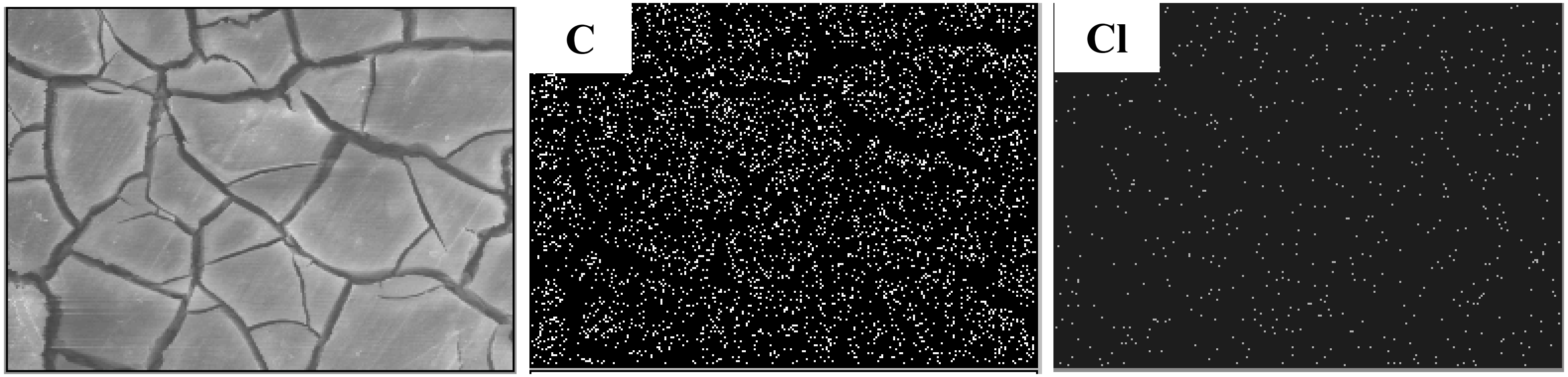
CO_2-2h/pH11.5-2h sample



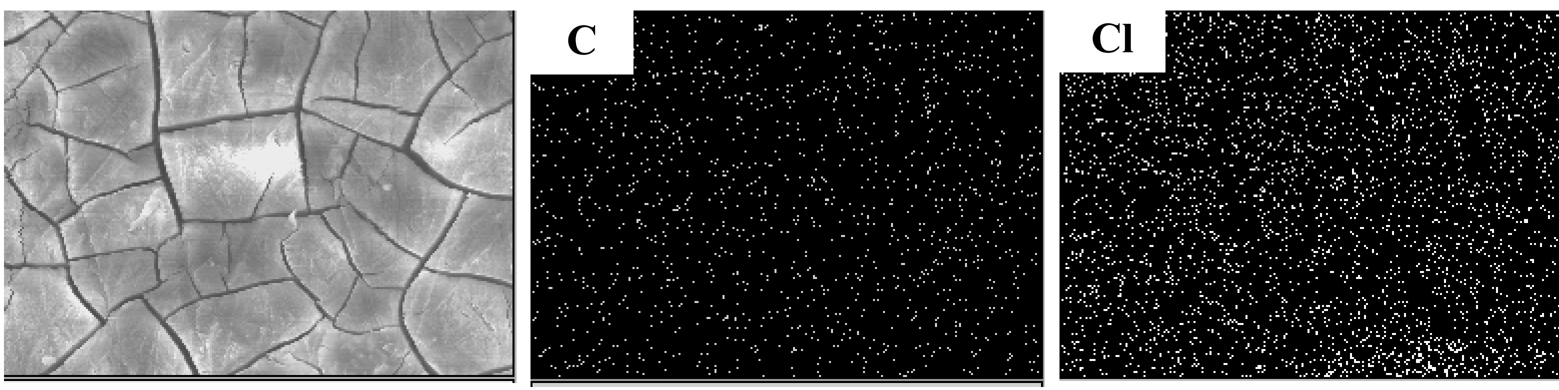

NCHU02
COMPO
10.0kV
X3,500
1 μm
WD 11.0mm


Cl^-
CO_3^{2-}
Mg^{2+}
Al^{3+}

EPMA-Mapping



hydrotalcite



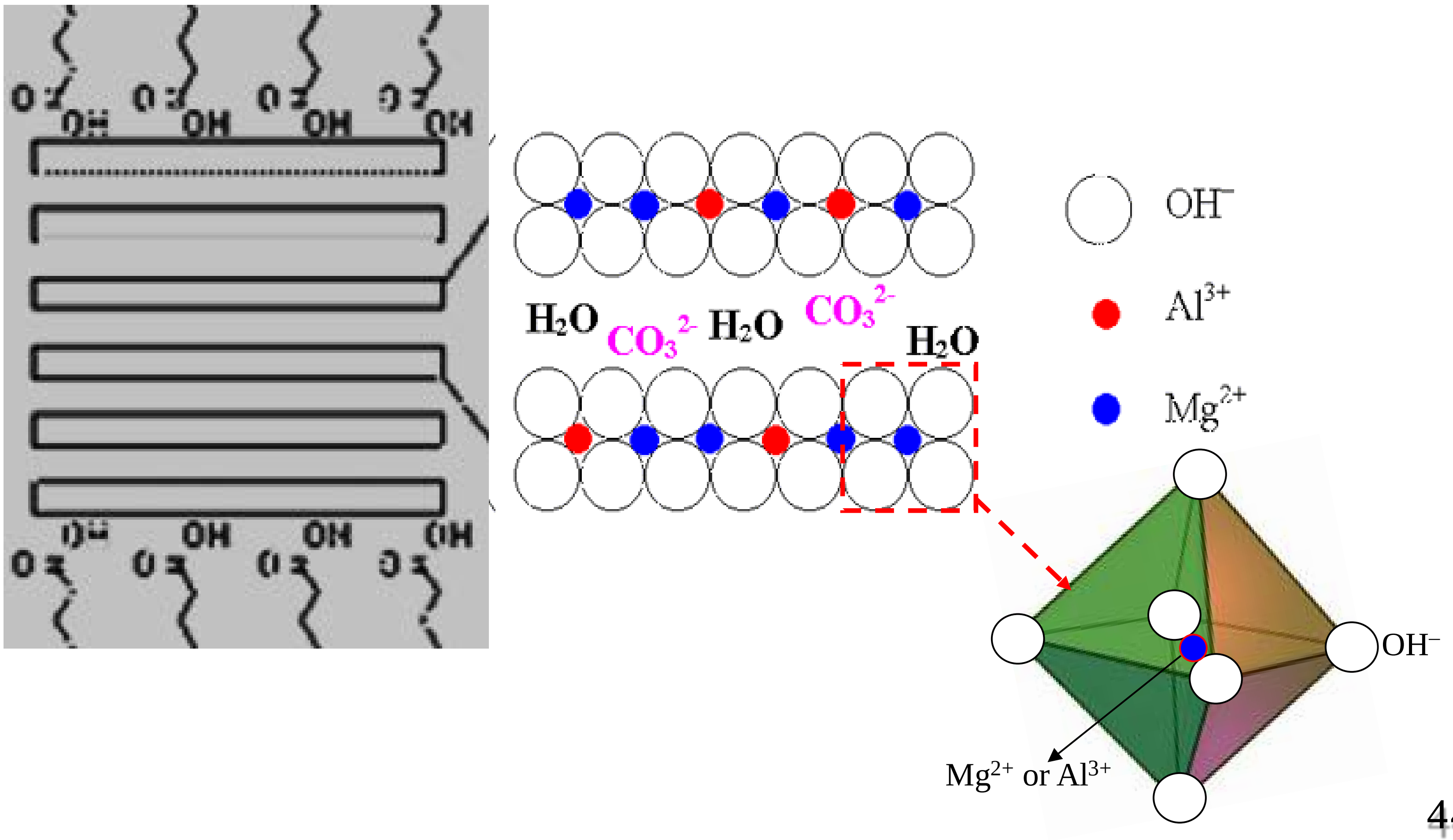
hydrotalcite in

salt water (5 hr)

43

Layered double hydroxides structure (LDH)

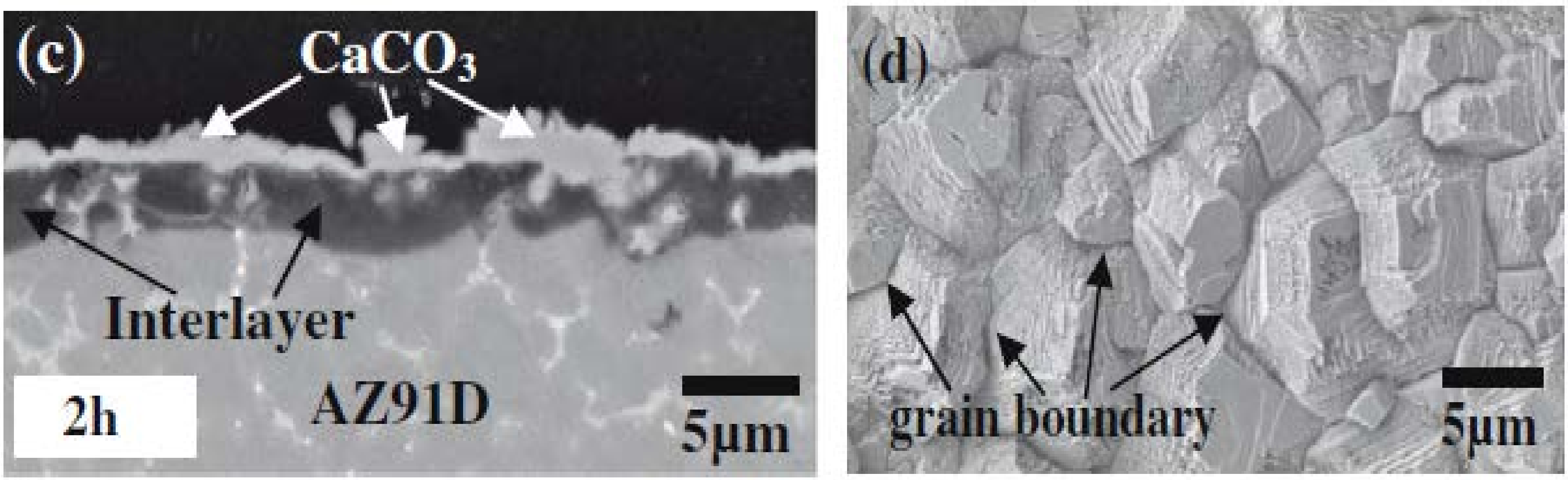
$Mg_6Al_2(OH)_{16}CO_3 \cdot 4H_2O$ on Mg alloy



Mg-Al-F^- LDH

Green Chemistry, 2001, 3, 257–260

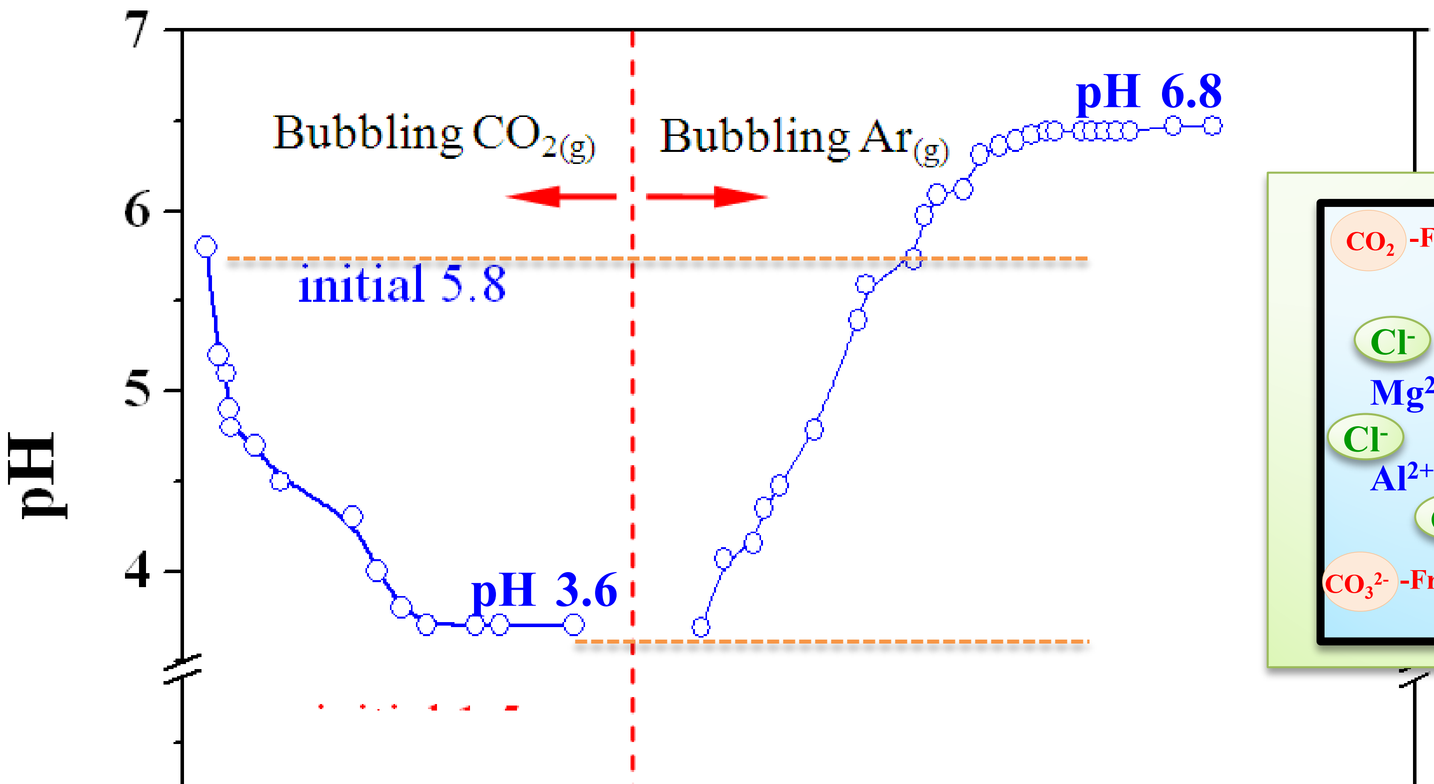
- **novel solid base catalyst for C–C bond formation**
- **unprecedented catalytic activity in both the important Knoevenagel and Michael reactions**

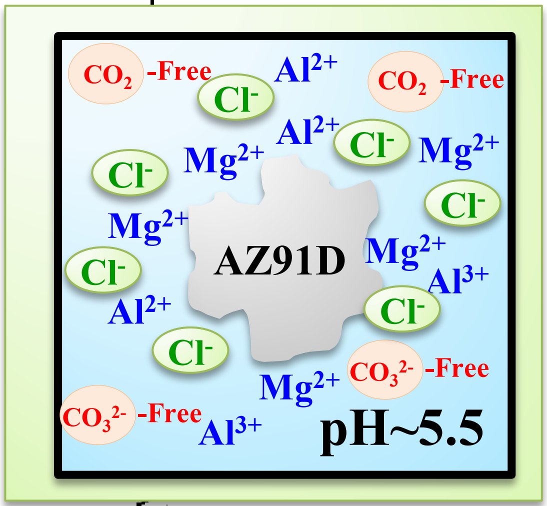


Yu, Pan, and Uan*, Corrosion Science,52 (2010), pp. 1874-1878.

Mechanism

Bubbling Ar gas to remove CO_3^{2-}





Deintercalation of Carbonate Ions:

Bubbling Ar gas → Remove CO_3^{2-}