DIPARTIMENTO DI INGEGNERIA INDUSTRIALE

FIAMM
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UNIVERSITÀ DEGLI STUDI DI PADOVA

Università degli Studi di Padova – Dipartimento di Ingegneria Industriale

Corso di Laurea in Ingegneria Chimica e dei Materiali

Relazione per la prova finale
«Thin Pure Plate Lead: Technology and Patent Analysis»

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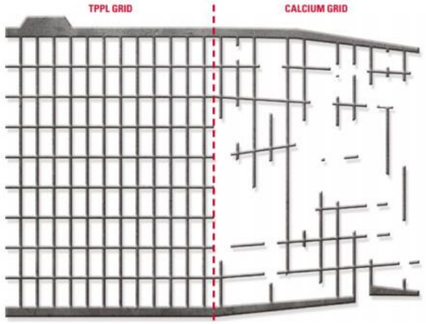
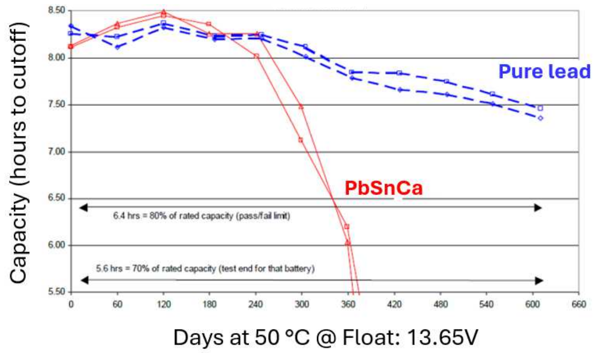
INTRODUCTION: TPPL BATTERIES

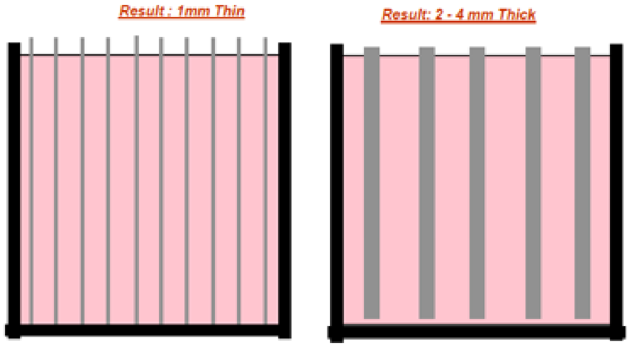
TPPL = Thin Pure Plate Lead

Lead purity affects:
- Corrosion: reduced → thin plates + prolonged battery lifetime
- Recharge capability: larger reactive surface (more plates) → faster recharge
- Gas generation: inhibited electrolysis → no dry-out and water topping up

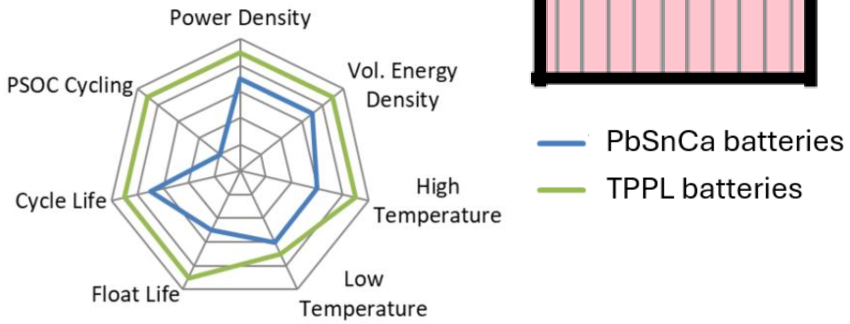




Advantadges
- Reduced corrosion
  - Higher lifetime
  - High temperature resistance
  - High energy density
  - High power
- Lower self-discharge
  - Higher shelf life
  - Reduced dry-out
  - High saefty → no gassing



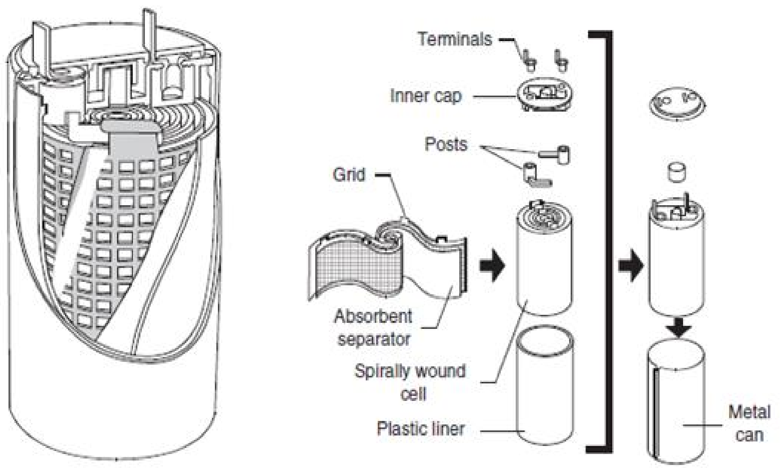
Drawbacks
- Low mechanical stability → → grid growth and deformation
- Shedding
- Creep
- Intergranular corrosion



OBJECTIVES OF THE WORK

- How can we enhance TPPL grid resistance to corrosion?
  - Tin content
  - Grains size

→ Technology study → Corrosive attack mechanism → Affected by cristallography and alloy composition → (Tin content, Grains size)



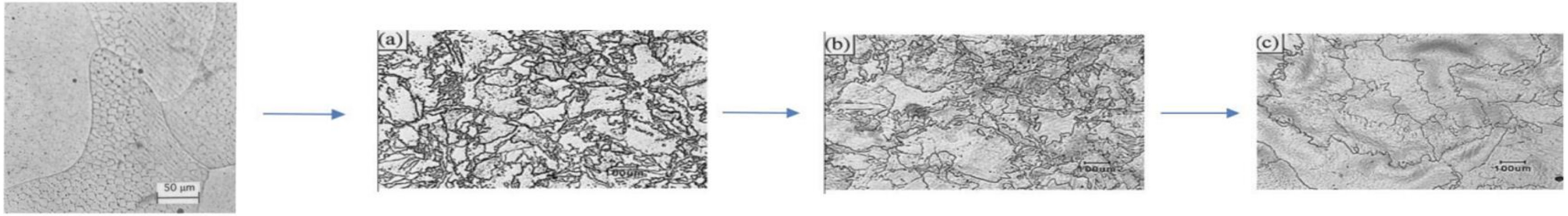
- How can we solve problems related to TPPL technology itself? → Patent analysis
  - Grid pattern
  - Post treatments
  - Optimized casting parameters

For this purpose → Fiamm grid based on TPPL technology was compared with 2 other grids, with the same technology, from competitors.

TIN CONTENT VS. GRID 'PROPERTIES AND CORROSION'

- Intergranular matrix → eutectic mixture with lamellar morphology → Volta's effect → grain boundaries subjected to corrosion
- Higher tin content → larger grains

Element	FIAMM grid	Competitor 1	Competitor 2
Sn (%)	< 1	≈ 0	≈ 0
Other elements in traces			

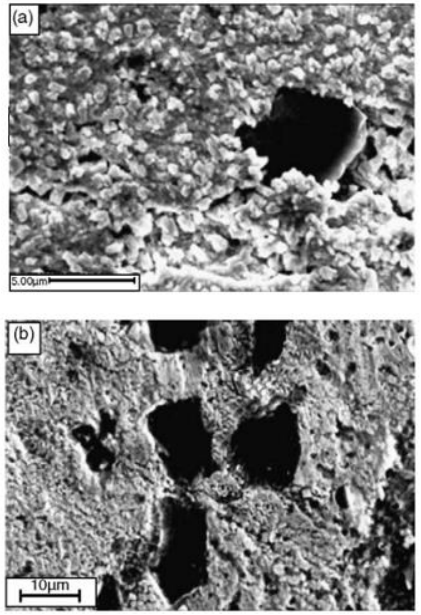


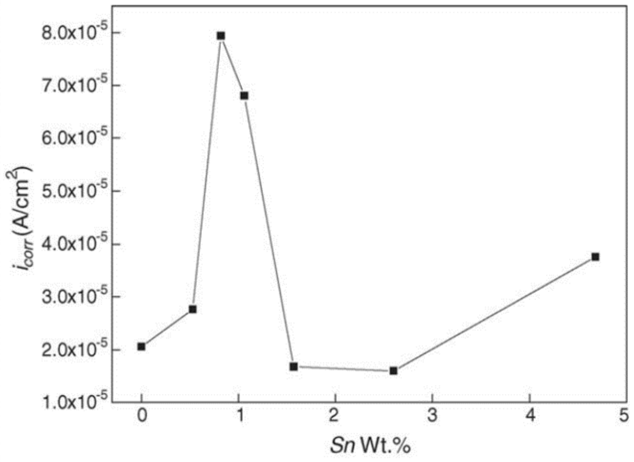
From left to right: Pure lead, 0.3% Sn, 0.6% Sn, 1.0% Sn

- Tin content affects ion and electron transportation through passivation layer → determine corrosion rate

PASSIVATION LAYER (P.L.):

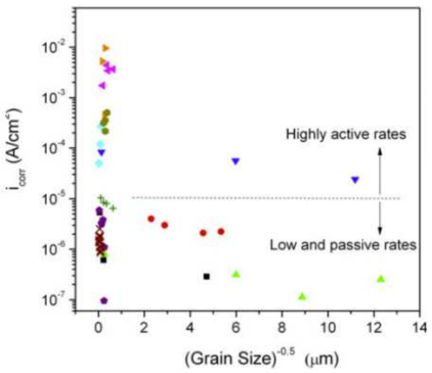
- Formation between grid and PAM, made of Pb and Sn oxides
- Sn < 0.8% wt.: pitting (mesoporous Sn(II)) + conductive $PbO_{x\,(1 < x < 2)}$
- 0.8% < Sn < 2.6% wt.: stable SnO_2 + conductive $PbO_{x\,(1 < x < 2)}$
- Sn > 2.6% wt.: excessive Sn segregated → severe intergranular corrosion





METALLOGRAPHIC ANALYSIS

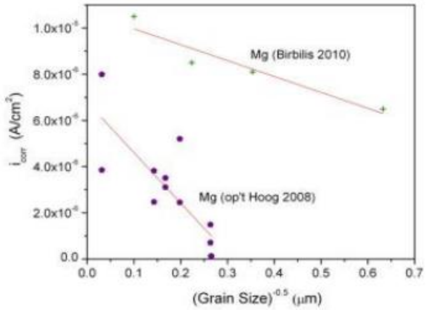
Effect of grains size → varies wether the metal passivate or not: if a P.L. is formed or not → depends on electrode-electrolyte couple

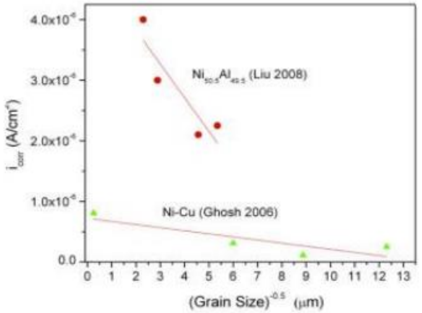


	FIAMM grid	Competitor 1	Competitor 2
Average diam.	26.92	20.50	36.99
Average perim.	84.57*	64.40*	116.2*

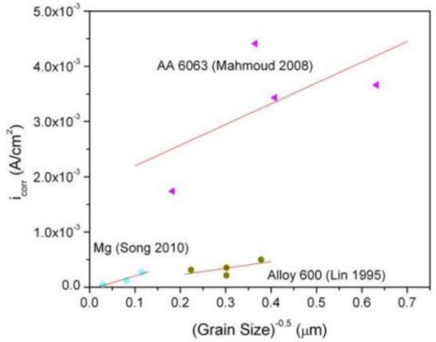
*Calculated considering a circular section

Couple with
- Low corrosion rates / P.L. formed → corrosion rates decrease with grains size reduction →





- High rate of corrosion / P.L. not formed → corrosion rates increase with grains size reduction →



P.L. is formed for the couple: Pb + H_2SO_4 → fine grain array is preferable → more corrosion resistant

To obtain a fine grain array → suggested fast cooling rate of 0.8-1.5 °C/s

WEIGHT LOSS TEST

	FIAMM grid	Competitor 1	Competitor 2
Weight loss	3	1	2
Corrosion rate	3	1	2
Sn (%)	< 1	≈ 0	≈ 0
Average perim. (µm)	84,57	64,4	116,19

Legend: best performance = 1; worst performance = 3

Best configuration in terms of corrosion resistance: Competitor 1

- very low tin content → no pitting and low conductivity
- fine grain array → inhibited corrosion thanks to P.L. presence

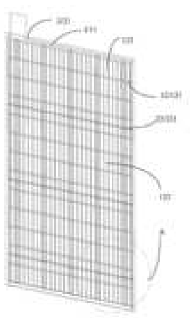
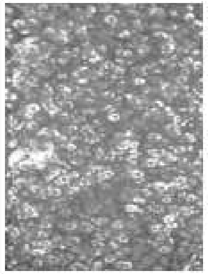
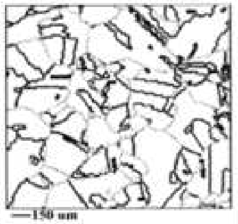
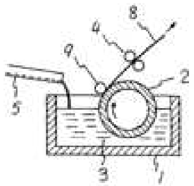
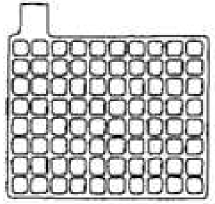
Grid's tin content vs. corrosion resistance:

- Fiamm grid: highest Sn concentration → → worst corrosion resistance → highest weight loss and corrosion rate
- Competitor grids: similar Sn content → → other parameters affect grid corrosion

Grid's grain size vs. corrosion resistance:

- Competitor grid 1: fine grain array → → best corrosion resistance → lowest weight loss and corrosion rate
- Competitor grid 2: coarse grain array → → weight loss and corrosion rate slightly higher than Competitor grid 1

PATENT ANALYSIS

PROBLEM	SOLUTION	DRAWINGS	PATENT	APPLICANT
Corrosion Shedding Deformation	<u>Grid pattern:</u> The cross-section of the hole is a triangular structure Reinforcing polymeric frame and ribs	 	CN215955327U CN211957792U	HOPPECKE CAMEL
Shedding Corrosion	<u>Post treatment:</u> Recrystallization is obtained by deformation and annealing Sandblasting improves active mass adhesion	  GBE™	CA2468022A1 CN109065890A	INTEGRAN TECHNOLOGIES JIANGSU HUAFU STORAGE NEW TECH
Quality casting (no reference to alloy composition)	Casting wheel with a concave groove on the peripheral surface. The molten lead is continuously solidified in the concave groove. Casting speed is about 300 mm/s, diameter of the rotating wheel is 250 mm and thickness of the lead lattice is 3 mm.	 	JPH0665035B2 JPS6012668A	HITACHI

CONCLUSIONS

- **DESIGN FEATURES:**

  - Sn as close as possible to 0% wt.
  - The ribs mesh is triangular
  - Reinforcing polymeric frame and ribs

  } to prevent grid deformation and shedding

- **CASTING PARAMETERS:**

  - Fast cooling rate to obtain fine grain arrays: 0.8-1.5 °C/s
  - Casting speed: 300 mm/s (ϕ_{wheel} = 250 mm; $thickness_{grid}$ = 3 mm)

- **POST TREATMENT:**

  - Mechanical deformation among 40-95°C
  - Annealing between 150 and 330°C (T_m)

  } to ensure recrystallization

  - Sandblasting to improve active mass adhesion and prevent shedding

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