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The effect of cooling rate after casting on electrochemical and mechanical properties of Pb-Ca-Sn alloy as positive gird alloy in lead-acid battery

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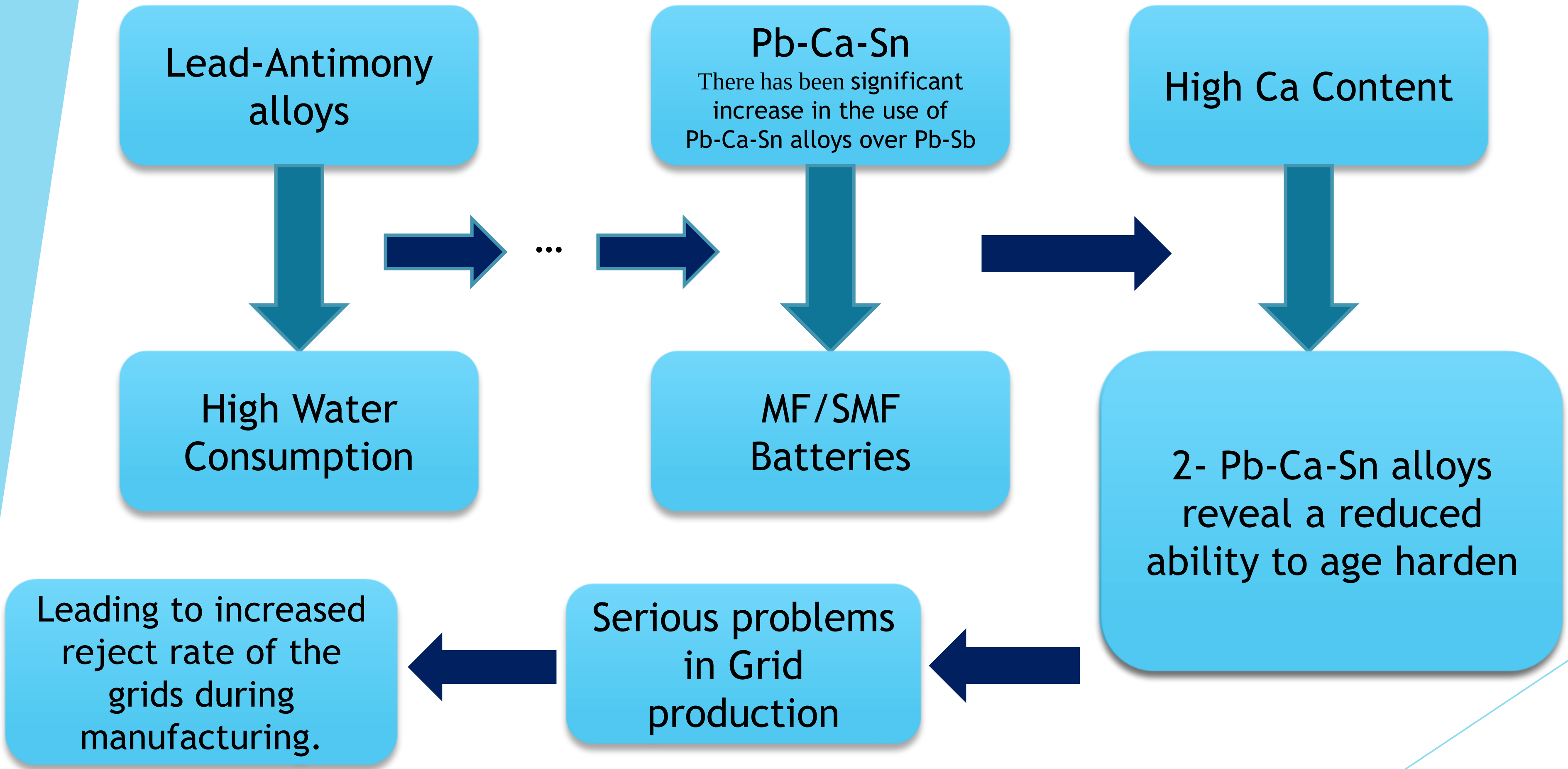
A Brief History of Grid Alloys

During the past two decades, many attempts have been made to modify grid manufacturing processes and chemical composition of the grid alloys.



Process Modification

New Applications (EFB)

- ✓ Thin Full Frame Grid.
- ✓ Improved corrosion resistance.
- ✓ Lower water consumption.

Lower Ca content

Higher Sn/Ca ratio

Dropping Grid Hardness

Grids Needs longer aging time

Grid manufacturing processes should be modified to decrease the aging time.

The process of quenching immediately after solidification has been proposed as a method to improve the aging ability of this type of alloy .

Process Modification

Quenching with water immediately after solidification

- Higher Hardness at Lower Aging Time
- Higher Corrosion Resistance
- Lower Water Consumption

Quenching process variables

- 1-Water spray nozzle diameter
- 2-Quenching temperature
- 3-Aging time

1-Water spray nozzle diameter → Considering 3 nozzles with 2,3,4mm diameters

2-Quenching temperature → Considering 3 water temperatures with 15-20-25°c

3-Aging time → Considering 3 aging times with 0-2-4 days

3 variables with 27 different conditions

The response surface method was employed to design the experiments, explore and model the aforementioned factors effect to determine the optimum operational conditions of the process or to establish a region that satisfies the operating specifications.

DOE:

The response surface method (RSM) is known as a statistical and mathematical method that is useful for modeling and analyzing engineering problems .RSM also quantifies the relationship between the controllable input parameters and the obtained response. It can be employed to evaluate the relative significance of several affecting factors even in the presence of complex interactions.

Statistical analysis:
The statistical analysis of the results was performed with Design Expert (Version 7.0) statistical software. In order to analyze the experimental data, multiple regression analyses through the least square method were used. The ANOVA combined with Fisher's statistical test (F-test) were used to evaluate the significance of the terms. The regression coefficients of all the terms including linear, quadratic and interactions involved in the model were analyzed by generating ANOVA tables. After checking the models adequacy, surface plots were constructed to evaluate the relationship between the independent variables and the response.

How to choose the Optimum condition by the surface response method ?

1- Perform multiple tests to provide reliable data about the process.

2- Find a mathematical model describing the relationship between process variables and surface response.

3- Using mathematical model to determine the Optimum levels of process variables. In other words, factors should be used at what levels to maximize (or minimize) the amount for the answers.

Samples Preparation : In order to investigate mechanical and electrochemical behavior of Quenching immediately after solidification, samples with constant Pb-Ca-Sn alloy as below table were considered.

Samples Alloy Composition (wt%)		
Ca	Sn	Pb
0.09	1.23	98.68

Melt was prepared at temperature of 510°C → Pouring the melt into a mold maintained at 200°C → The mold was immediately opened and water spraying process was performed. → Different samples were prepared with changing the water temperature and nozzle diameter. → The working electrodes were prepared by mounting the cast plates in a self-cure epoxy resin, resulting in 2 cm^2 exposed area. → Before each test, the specimens were ground down from 60 to 1200 with a silicon carbide emery papers. → The electrode was then rinsed with deionized water and put into use directly.

* The reference sample was prepared by cooling the sample taken from the mold in the air.

Electrochemical properties including PbO2 formation , oxygen evolution reaction and passive current density, were assessed using cyclic voltammetry and potentiostatic techniques. In addition, the hardness measurements were performed for various samples.

- Electrochemical tests
  - → Cyclic Voltammetry
  - → Potentiostatic tests
- Mechanical test
  - → Hardness Test

Hardness :

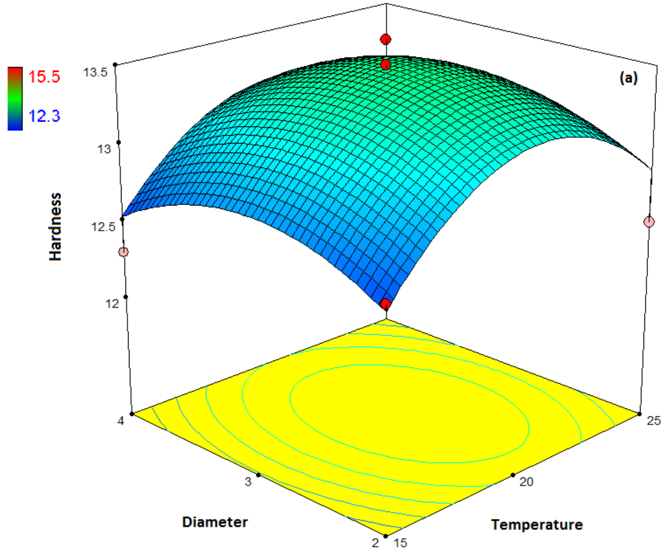
The results show that the quenching immediately after solidification totally increases the hardenability so that the hardness amount of the whole quenched samples is higher than the air-cooled one even after 4 days aging in room temperature that can help to decrease the aging time for pasting process.

Sample No.	Temperature(˚c)	Nozzle Diameter (mm)	Aging Time (Day)	Hardness			
				Repeat (1)	Repeat (1)	Repeat (1)	Average
1	15	2	0	12.6	13.8	13.5	13.3
2	25	2	0	11.5	12.2	12.5	12.1
3	15	4	0	12.2	13.5	11.9	12.5
4	25	4	0	12.9	13.5	13.25	13.2
5	15	2	4	13.2	13.4	13.6	13.4
6	25	2	4	15.4	15.2	15	15.2
7	15	4	4	14	14.2	14.4	14.2
8	25	4	4	14.8	15	14.6	14.8
9	15	3	2	13.5	12.8	13.4	13.2
10	25	3	2	13.9	13.4	14.3	13.9
11	20	2	2	16.1	15.8	15.5	15.8
12	20	4	2	13.5	13.8	14.3	13.9
13	20	3	0	13.8	12.3	14.9	13.7
14	20	3	4	15.5	15.7	15.9	15.7
15:Center Point	20	3	2	14.8	14.2	15.2	14.7
Reference	Air Cool		4	11.2	12.1	10.7	11.3

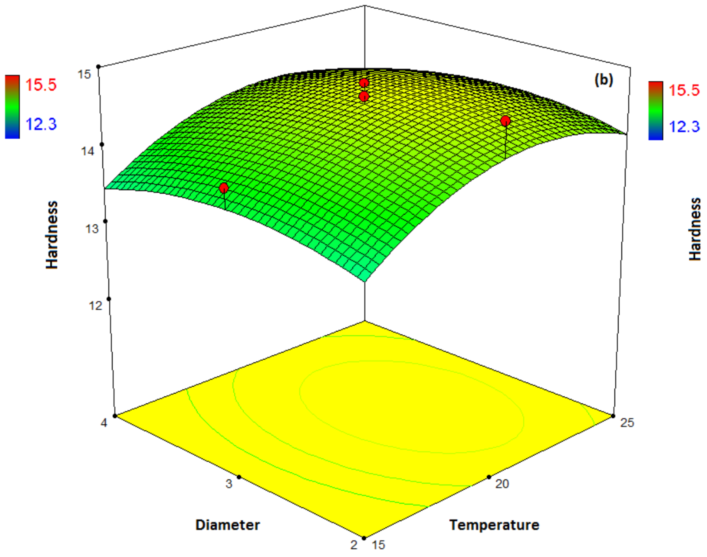
Hardness :

Hardness diagram with quenching temperature and nozzle diameter at different aging time :

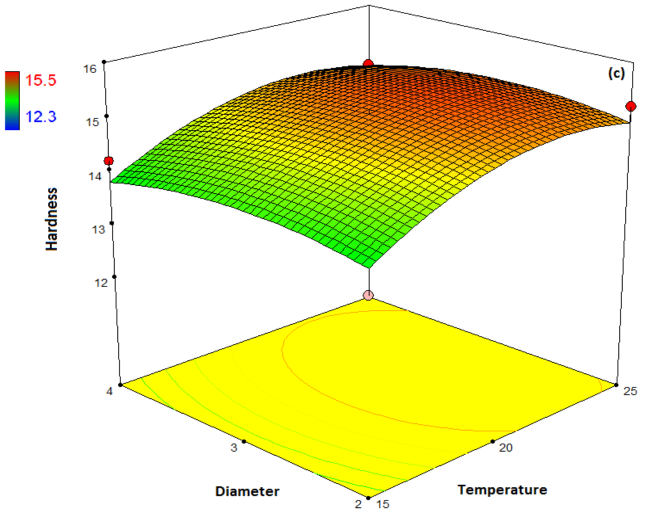
(A) 0 days



(B) 2 days

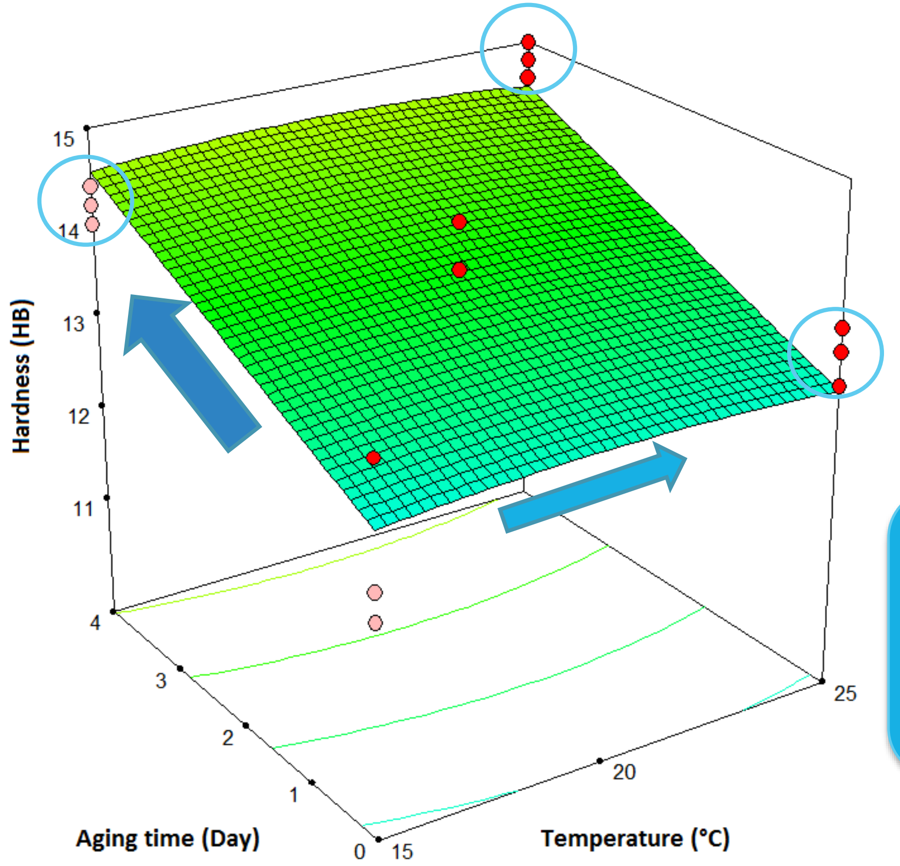


(C) 4 days



Hardness :

After statistically analyzing the data in Design Expert software, the regression model which predicts hardness as a function of different variables can be obtained. The surface plots can be construct to reveal the importance of all factors and their interactions.



The nozzle diameter had no significant effect on hardness.

The hardness increases with increasing aging time

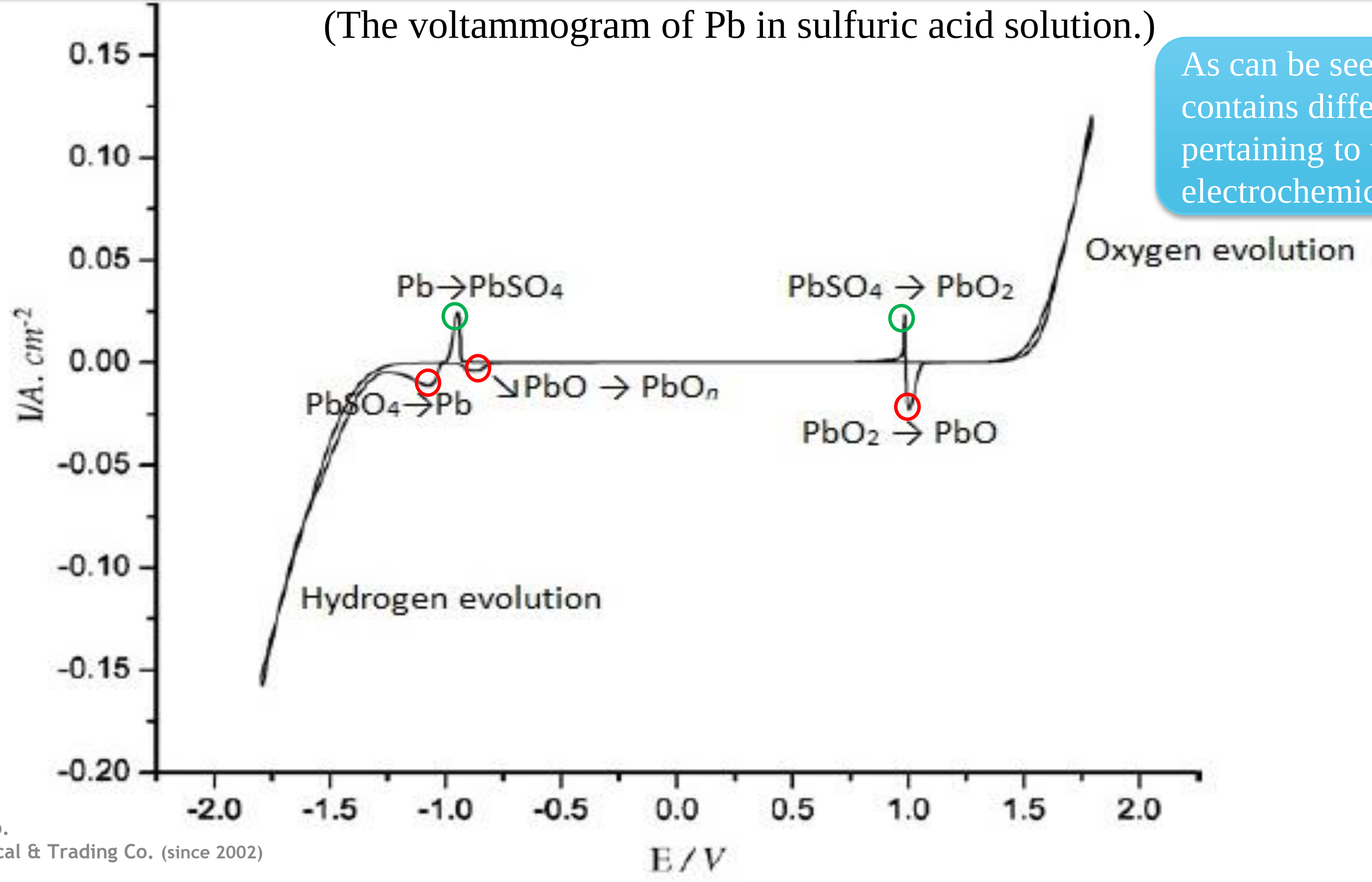
Increasing water temperature will increase the hardness but it dos not have a significant effect

Electrochemical properties including PbO2 formation and oxygen evolution reaction, were assessed using cyclic voltammetry technique.

- Electrochemical tests
  - → Cyclic Voltammetry
    - (One cycle)
    - (50 cycles)
  - → Potentiostatic tests
- Mechanical test
  - → Hardness Test

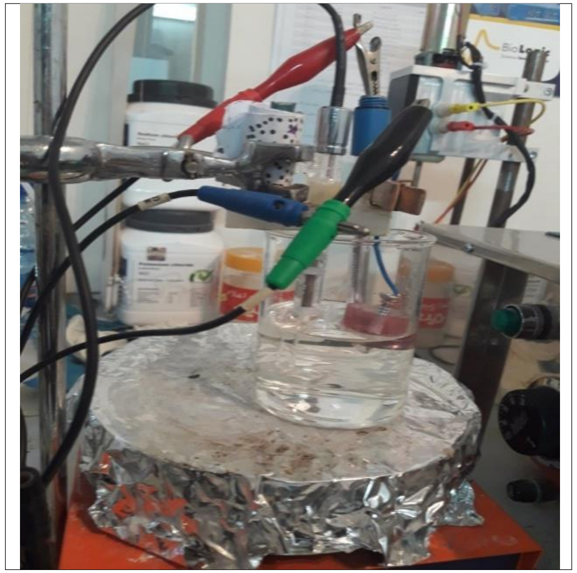
Cyclic Voltammetry (One Cycles) :Cyclic polarization is an appropriate technique to obtain valuable information about electrochemical properties of Pb alloys.

(The voltammogram of Pb in sulfuric acid solution.)



As can be seen, the curve contains different peaks pertaining to various electrochemical reactions .

Samples Preparation : To run the electrochemical experiments, the conventional three-electrode cell was used in which the saturated calomel electrode (SCE) was as reference electrode and platinum foil served as a counter electrode. The electrochemical cell was a 250 ml beaker. All the electrochemical measurements were implemented using Gill AC potentiostat (ACM instruments). All the electrochemical experiments were carried out at 25 ± 1 °C in 4.8 M H_2SO_4 solution and after each test the solution was renewed.



In order to design the experiments for electrochemical evaluations, two factors including nozzle diameter and quenching temperature were considered.

→ The intervals were the same as those regarded for hardness.

→ The electrochemical tests were carried out after different aging time at room temperature.

Cyclic Voltammetry (One Cycles)

→ The cyclic voltammetry test for one cycle were carried out at potential range of -1500 mV/SCE to +2500 mV/SCE with potential scan rate of 1500 mV/min .

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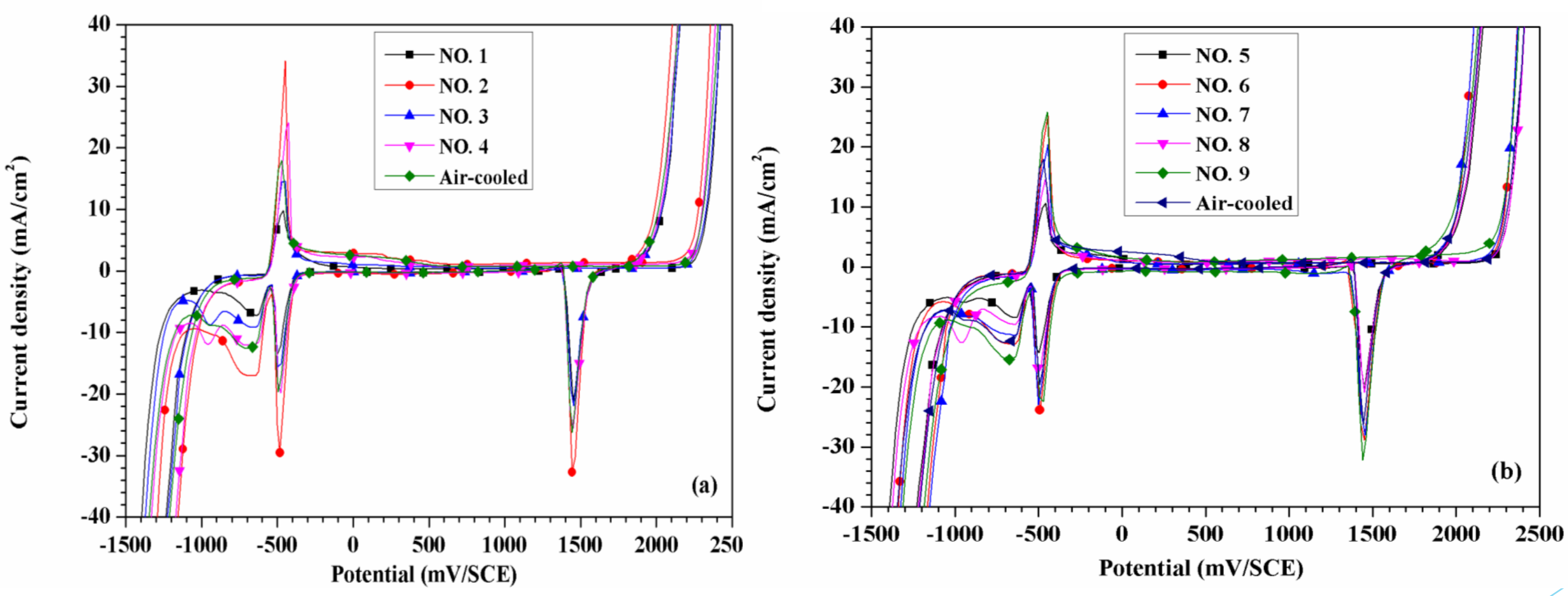
Cyclic Voltammetry (One Cycles)

First: The electrochemical tests were carried out after 4 days. Below Table presents the design points and the corresponding electrochemical parameters.

Sample No.	Temperature (°C)	Nozzle Diameter (mm)	E_{PbO2} (mV/SCE)
1	15	2	1395
2	25	2	1378
3	15	4	1356
4	25	4	1385
5	15	3	1385
6	25	3	1324
7	20	2	1352
8	20	4	1372
9: Center point	20	3	1349, 1369, 1349
Reference	Air-cooled		1378

Quenching immediately after solidification and after same aging time has no negative effect on PbO2 formation in compare with air cooling . nozzle diameter and also water temperature did not have a significant effect on PbO2 formation.

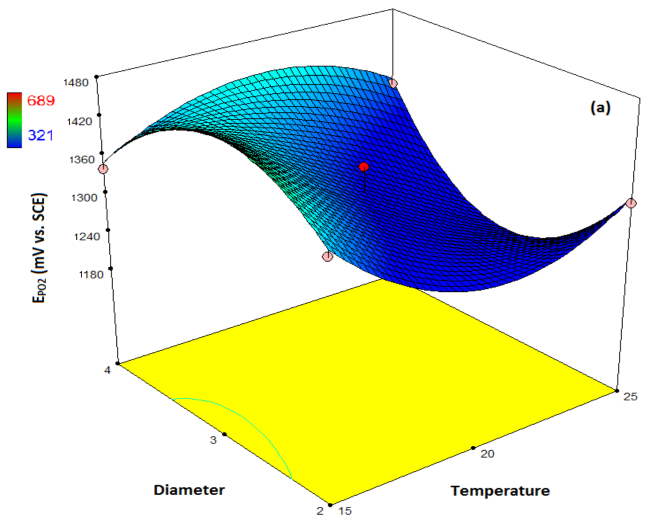
Cyclic Voltammetry (One Cycles): The cyclic voltammetry diagrams of Pb-Ca-Sn alloy for the specimens that was cooled in the air and water-sprayed with different temperatures and nozzles diameters are as below.



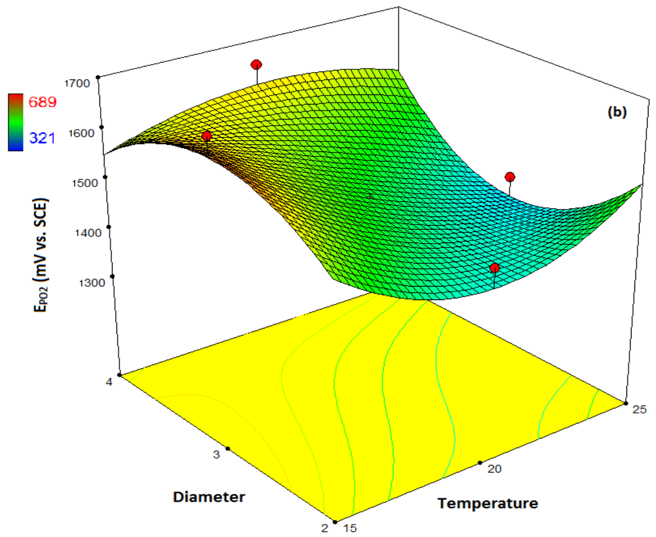
The results shows that quenching immediately after solidification has no significant effect on Pbo2 formation rate in compare with the air cooling.

Second :The electrochemical tests were carried out at different aging time. Below diagrams presents the E_{PbO2} **diagram with quenching temperature and nozzle diameter at different aging time.**

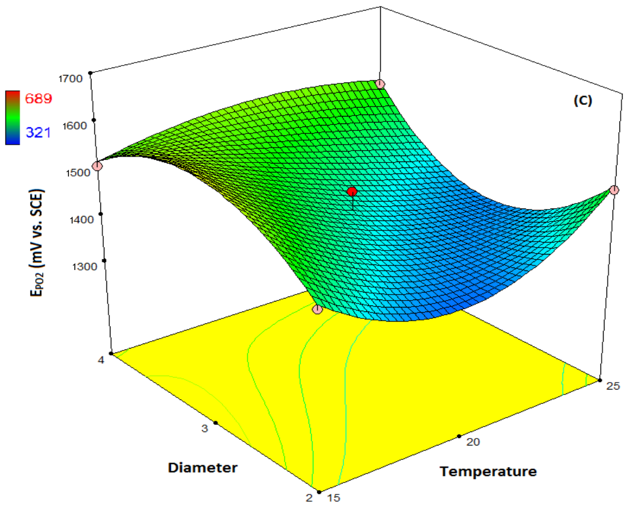
(A) 0 days



(B) 2 days

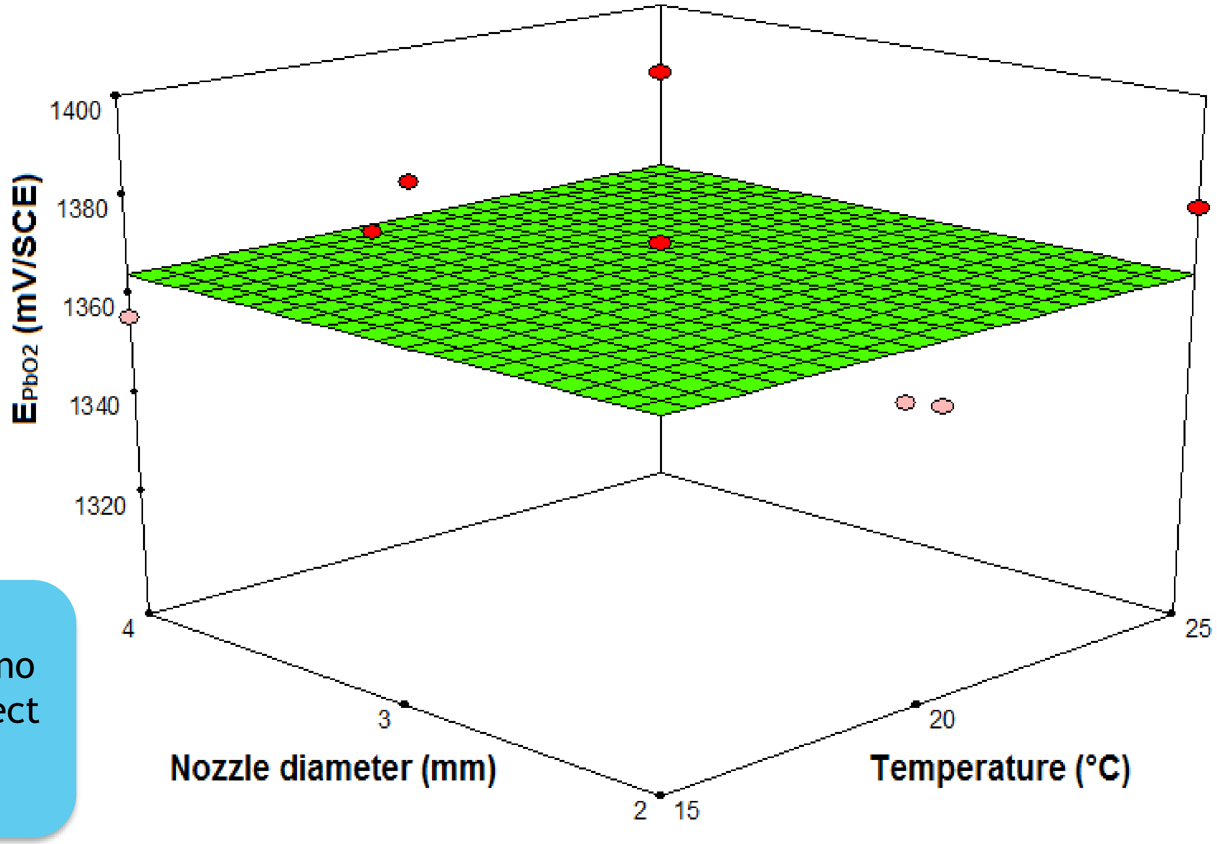


(C) 4 days



It can be said that the most effective parameter on PbO2 formation is aging time however after two days of aging time the PbO2 formation rate did not change significantly.

After statistically analyzing the data in Design Expert software, the regression model which predicts E_{PbO2} as a function of different variables can be obtained. The surface plots can be construct to reveal the importance of all factors and their interactions.



The most effective parameter on PbO2 formation is aging time.

The nozzle diameter had no significant effect on PbO2 formation.

Quenching water temperature had no significant effect on PbO2 formation.

Electrochemical properties including PbO2 formation and oxygen evolution reaction, were assessed using cyclic voltammetry technique.

- Electrochemical tests
  - → Cyclic Voltammetry
    - (One cycle)
    - (50 cycles)
  - → Potentiostatic tests
- Mechanical test
  - → Hardness Test

Samples Preparation : To run the electrochemical experiments, the conventional three-electrode cell was used in which the saturated calomel electrode (SCE) was as reference electrode and platinum foil served as a counter electrode. The electrochemical cell was a 250 ml beaker. All the electrochemical measurements were implemented using Gill AC potentiostat (ACM instruments). All the electrochemical experiments were carried out at 25 ± 1 °C in 4.8 M H2SO4 solution and after each test the solution was renewed.

In order to design the experiments for electrochemical evaluations, two factors including nozzle diameter and quenching temperature were considered → The intervals were the same as those regarded for hardness. → The electrochemical tests were carried out after different aging time at room temperature.

Cyclic Voltammetry (50 Cycles)

→ The cyclic voltammetry experiments for 50 cycles were implemented at potential range from +800 mV/SCE to +2500 mV/SCE with potential scan rate of 1500 mV/min in 4.8 M H2SO4 and then E_{O2} were extracted from 50th cycle test results.

Cyclic Voltammetry (50th Cycles)

First : The electrochemical tests were carried out after 4 days of aging time. Below Table presents the design points and the corresponding electrochemical parameters.

No.	Temperature (˚C)	Nozzle Diameter (mm)	E_{O2} (mV/SCE)
1	15	2	1994
2	25	2	2016
3	15	4	2036
4	25	4	2052
5	15	3	1934
6	25	3	2056
7	20	2	2019
8	20	4	2020
9: Center point	20	3	1980, 2000, 1989
Reference	Air-cooled		1962

Quenching immediately after solidification has no negative effect on oxygen evolution potential in compare with air cooling and oxygen evolution potential do not significantly vary with changing water temperature and nozzle diameter.

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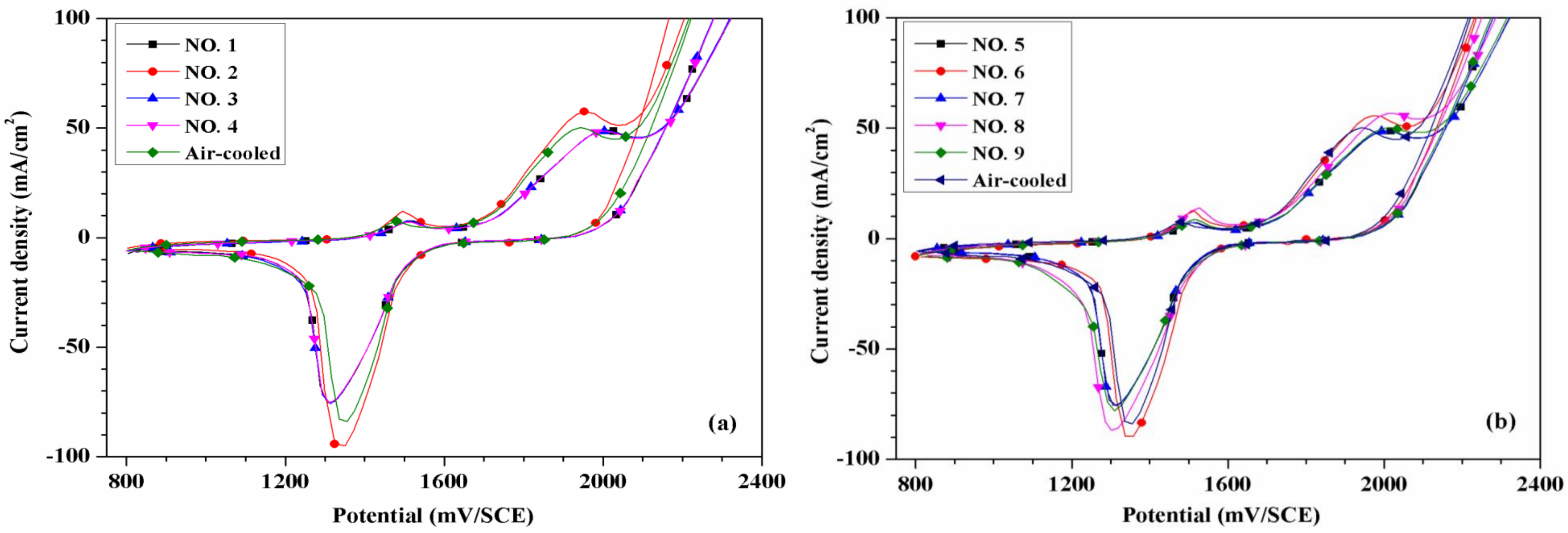
Cyclic Voltammetry (50th Cycle):

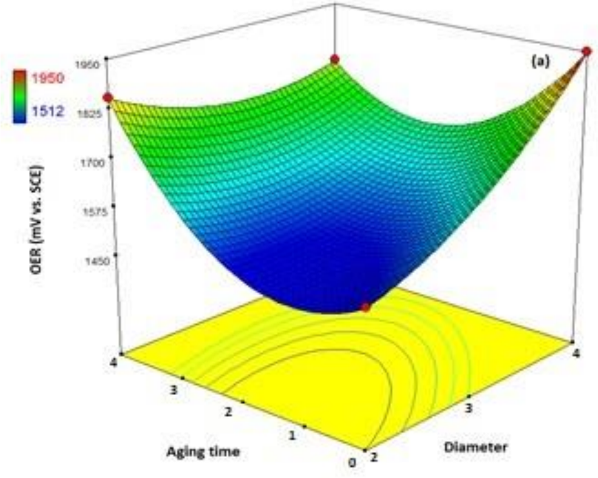
The cyclic voltammetry diagrams of Pb-Ca-Sn alloy for the specimens that was cooled in the air and water-sprayed with different temperatures and nozzles diameters are as below.



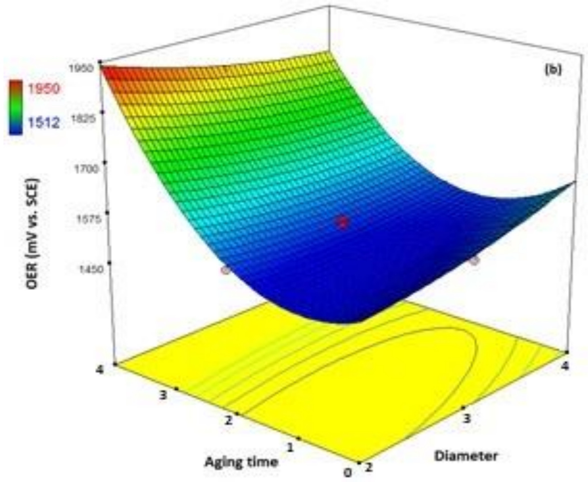
The results shows that quenching immediately after solidification has no significant effect on oxygen evolution potential in compare with the air cooling.

Second: The electrochemical tests were carried out at different aging time. Below diagrams presents the **OER** diagrams with quenching temperature and nozzle diameter at different aging time.

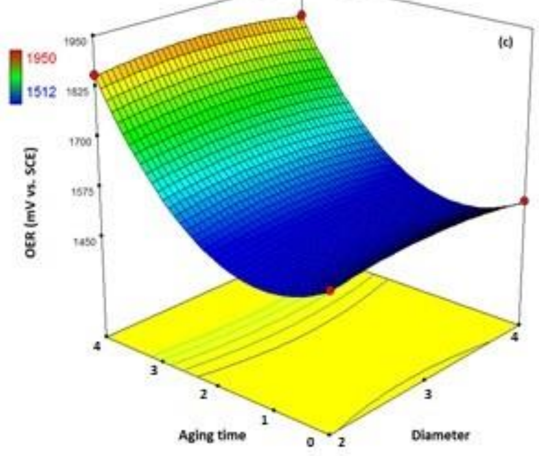
(A) 15°C



(B) 20°C

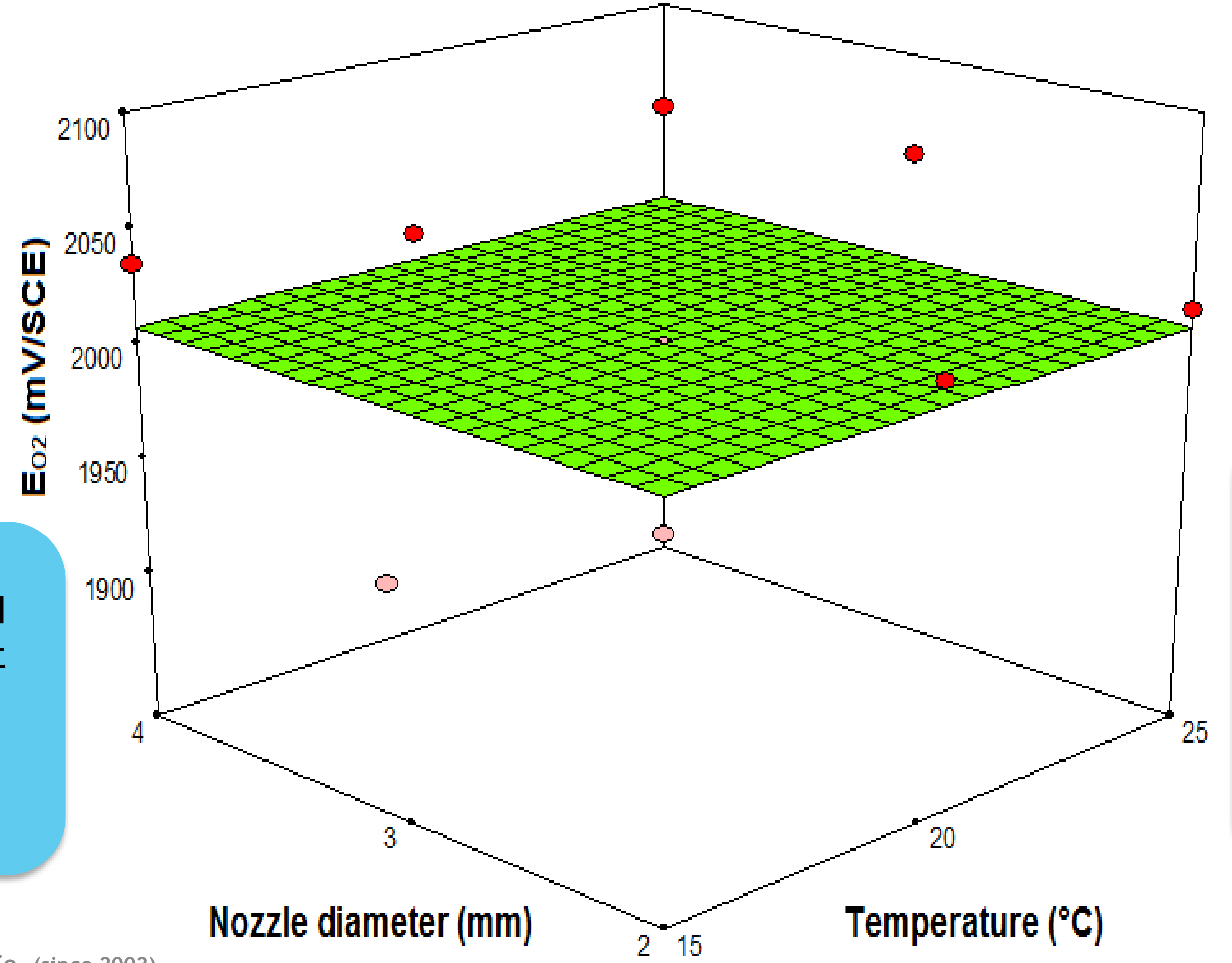


(C) 25°C



The results shows that the most effective parameter on oxygen evolution potential is aging time.

After statistically analyzing the data in Design Expert software, the regression model which predicts E_{O_2} as a function of different variables can be obtained. The surface plots can be construct to reveal the importance of all factors and their interactions.



The most effective parameter on oxygen evolution potential is aging time.

Quenching water temperature had no significant effect on oxygen evolution potential .

The nozzle diameter had no significant effect on oxygen evolution potential .

Electrochemical properties including passive current density, were assessed using potentiostatic technique.

Electrochemical tests → Cyclic Voltammetry

Electrochemical tests → Potentiostatic tests

Mechanical test → Hardness Test

Samples Preparation : To run the electrochemical experiments, the conventional three-electrode cell was used in which the saturated calomel electrode (SCE) was as reference electrode and platinum foil served as a counter electrode. The electrochemical cell was a 250 ml beaker open to the. All the electrochemical measurements were implemented using Gill AC potentiostat (ACM instruments). All the electrochemical experiments were carried out at 25 ± 1 °C in 4.8 M H2SO4 solution and after each test the solution was renewed.

In order to design the experiments for electrochemical evaluations, two factors including nozzle diameter and quenching temperature were considered → The intervals were the same as those regarded for hardness. → The electrochemical tests were carried out after different aging at room temperature.

Potentiostatic tests → The potentiostatic polarization tests were carried out at 900 mV/SCE for 3600 s at 25 ± 1 °C in 4.8 M H2SO4 solution.

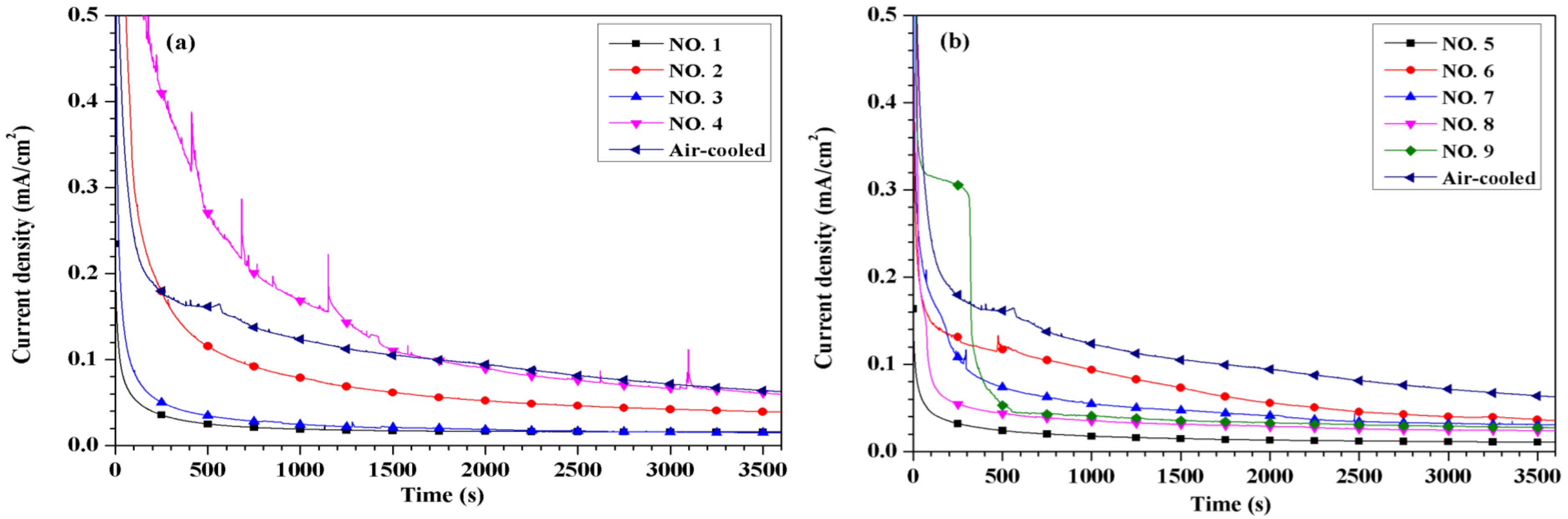
Potentiostatic tests : In order to access the water spraying effect on corrosion resistance ,the potentiostatic tests were run for different specimens.

First: The electrochemical tests were carried out after 4 days aging time. Below Table presents the design points and the corresponding electrochemical parameters.

No.	Temperature (˚C)	Nozzle Diameter (mm)	I_{pass} (mA/cm^2)
1	15	2	0.0156
2	25	2	0.0412
3	15	4	0.0104
4	25	4	0.0632
5	15	3	0.0108
6	25	3	0.0349
7	20	2	0.0314
8	20	4	0.0228
9: Center point	20	3	0.0242, 0.0266, 0.0295
Reference	Air-cooled		0.0615

A robust passive layer is formed while holding the surface at this potential. In this way, comparison of the measured passivity current densities (Ipass) for the whole samples shows that quenching can significantly reduce the passive current density and the elevated quenching temperature increases the corrosion rate while nozzle diameter has no significant effect.

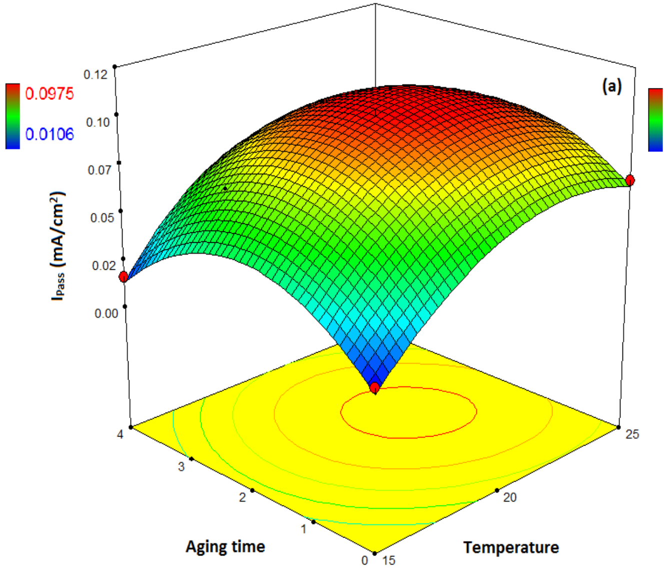
Potentiostatic tests: The Potentiostatic diagrams of Pb-Ca-Sn alloy for the specimens that was cooled in the air and water-sprayed with different temperatures and nozzles diameters are as below.



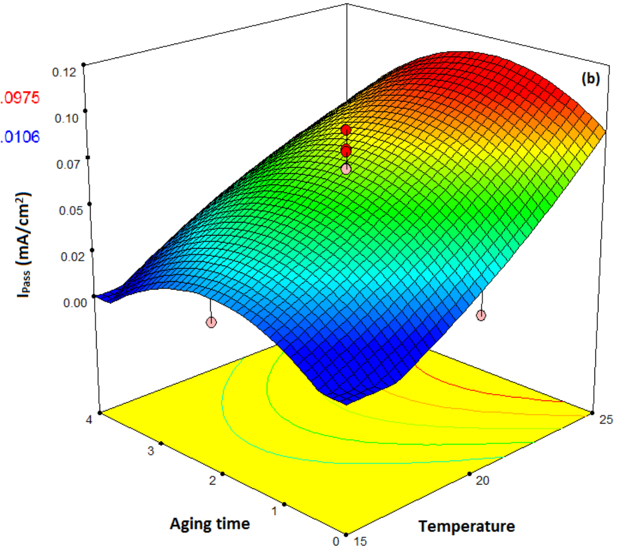
The results shows that the quenching can significantly reduce the passive current density .

Second: The electrochemical tests were carried out at different aging time. Below diagrams presents the I_{Pass} diagrams with quenching temperature and nozzle diameter at different aging time.

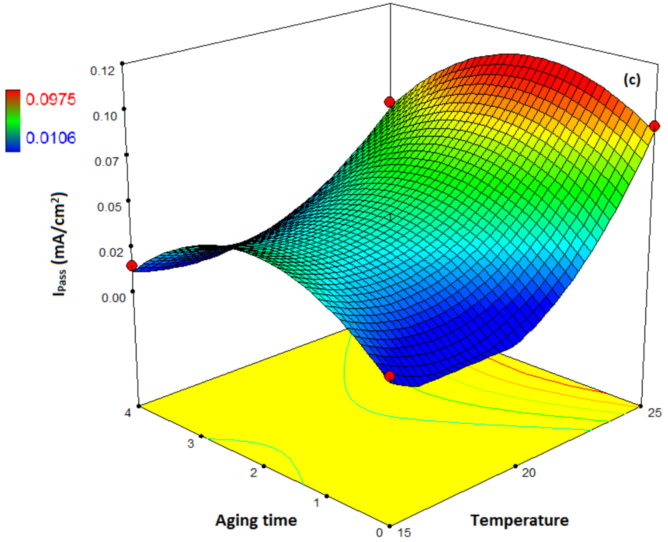
(A) 2mm nozzle diameter



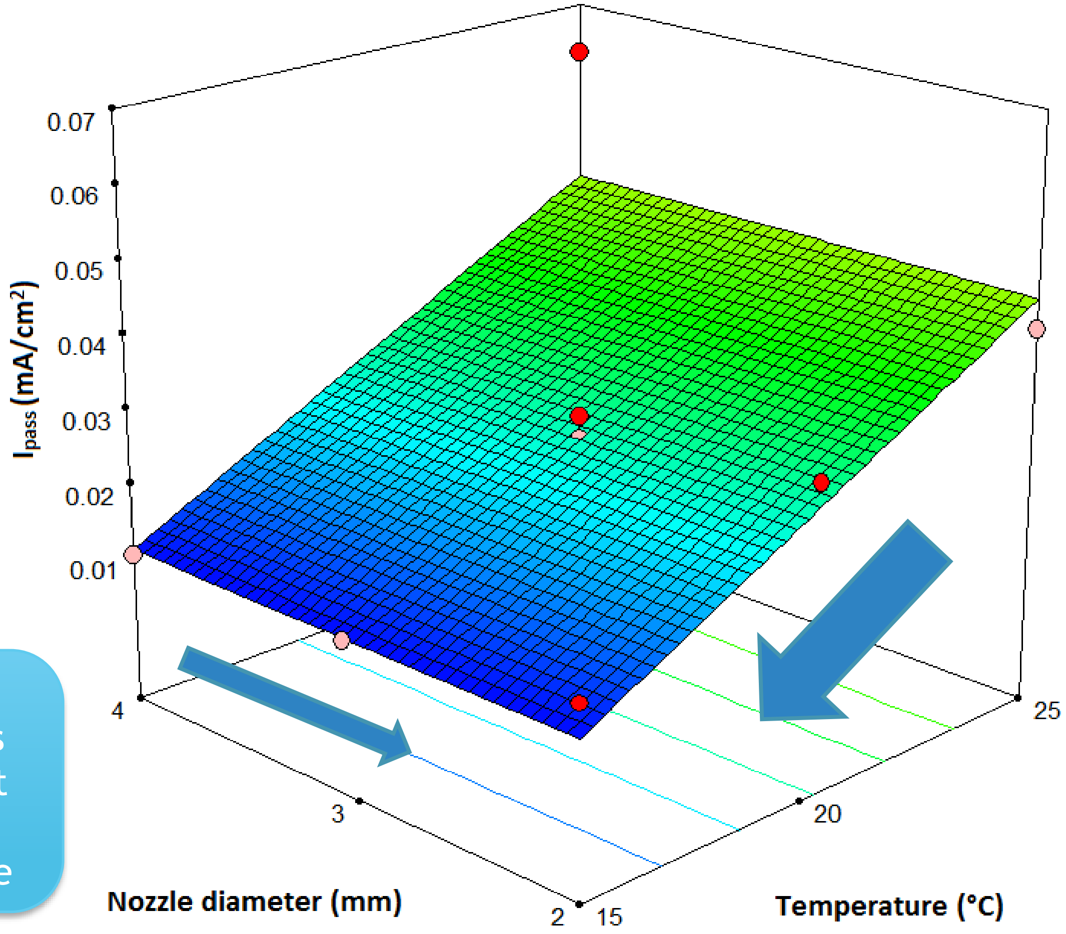
(B) 3mm nozzle diameter



(C) 4mm nozzle diameter



After statistically analyzing the data in Design Expert software, the regression model which predicts I_{Pass} as a function of different variables can be obtained. The surface plots can be construct to reveal the importance of all factors and their interactions.



Comparison of the measured passivity current densities (I_{pass}) for the air-cooled and different water-sprayed samples reveals that quenching after solidification can reduce the corrosion rate.

Decreasing quenching water temperature will decrease corrosion rate.

Nozzle diameter has no significant effect on corrosion rate

Summery of the Mechanical and Electrochemical test results :

No.	Temperature (˚C)	Nozzle Diameter (mm)	E_{PO2} (mV/SCE)	E_{O2} (mV/SCE)	I_{pass} (mA/cm^2)
1	15	2	1395	1994	0.0156
2	25	2	1378	2016	0.0412
3	15	4	1356	2036	0.0104
4	25	4	1385	2052	0.0632
5	15	3	1385	1934	0.0108
6	25	3	1324	2056	0.0349
7	20	2	1352	2019	0.0314
8	20	4	1372	2020	0.0228
9: Center point	20	3	1349, 1369, 1349	1980, 2000, 1989	0.0242, 0.0266, 0.0295
Reference	Air-cooled		1378	1962	0.0615

The results showed that water spraying promotes the aging process of Pb-Ca-Sn alloy so that the higher hardness value can be obtained at short aging time in compare with the air-cooled sample even after 4 days of aging time at room temperature that can help to achieve acceptable hardness for pasting in shorter period . Statistically analyzing the data revealed that aging time increases the hardness value while the water temperature and nozzle diameter had no significant effect.

The results shows that the quenching after solidification has no negative effect on the rate of PbO2 formation and oxygen evolution in compare with air cooling . Statistically analyzing the data revealed that the PbO2 formation and oxygen evolution potential do not significantly vary with changing water temperature and nozzle diameter and the most effective parameter on PbO2 formation and oxygen evolution potential is aging time.

The results shows that the quenching after solidification can reduce the corrosion rate and the elevated quenching temperature increases the corrosion rate while nozzle diameter has no significant effect.

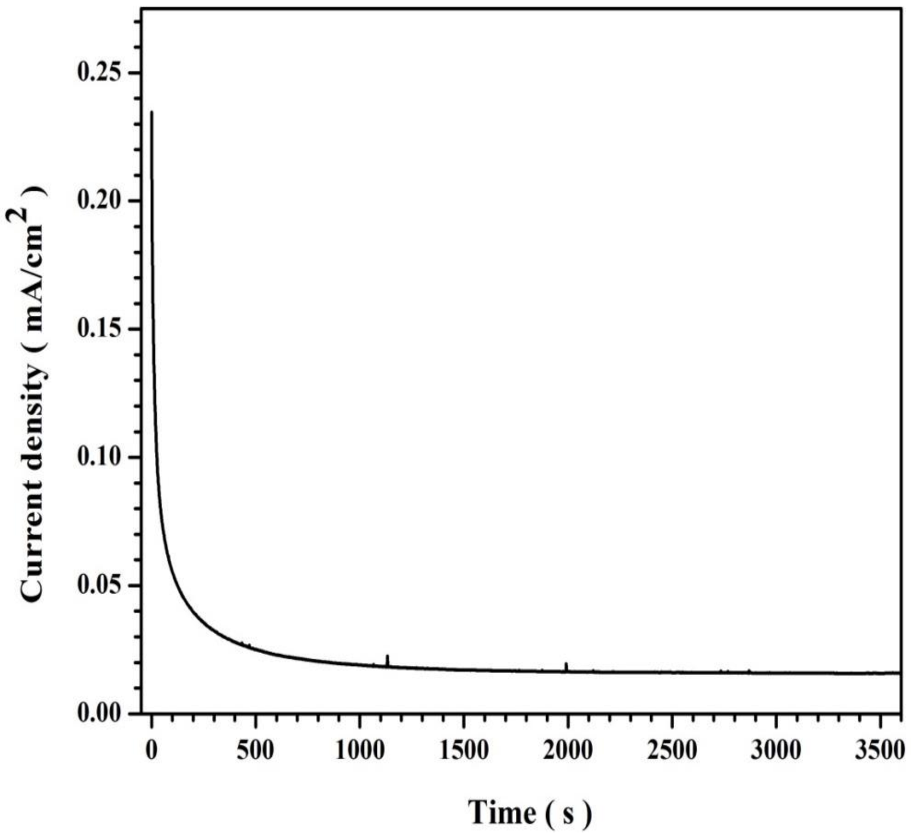
After statistically analyzing the data in Design Expert software it was anticipated that Water-quenched samples at 15°C and with 2mm nozzle diameter and after two days aging time, have the highest corrosion resistance, the highest potential for oxygen evolution and the highest PbO_2 formation rate.

To ensure about predicted results, below samples was re-prepared and the entire electrochemical tests was repeated for them.

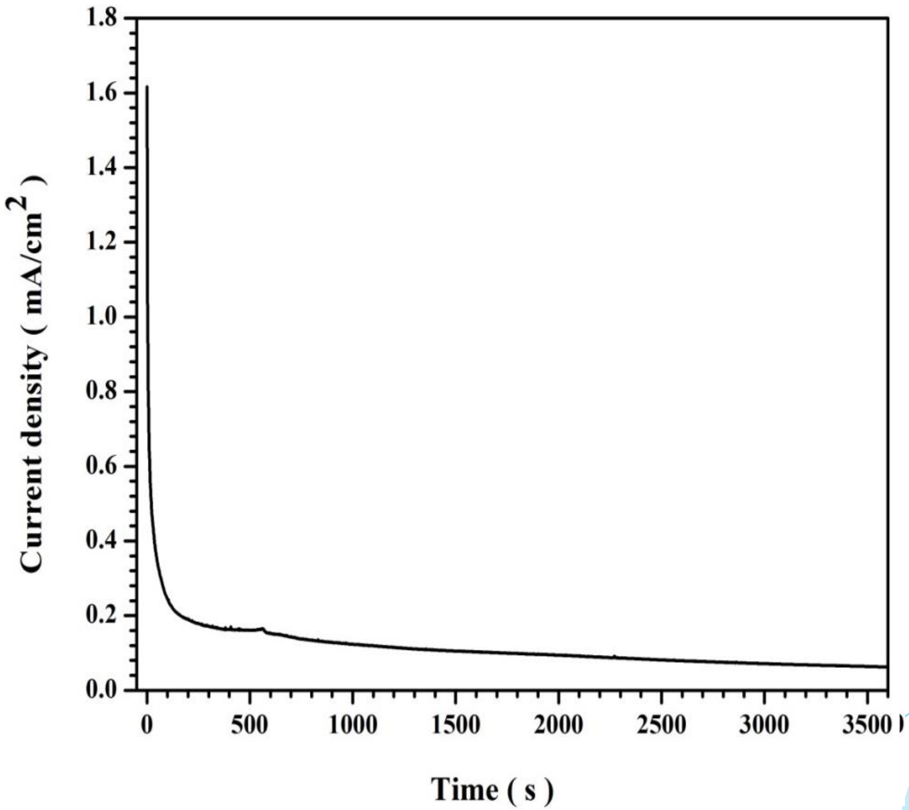
Sample (1):Water-quenched samples at 15°C and with 2mm nozzle diameter and after two days of aging time.

Sample (2):Air cooled sample at 25°C and after 4 days aging time at room temperature.

Electrochemical Tests Repeats Results:



EDLR2 diagram for sample (1) / I_{Pass} diagram for sample (1)



EDLR2 diagram for sample (2) / I_{Pass} diagram for sample (2)

Electrochemical Tests Repeats Results:

Sample No.	Temperature (˚C)	Nozzle Diameter (mm)	Aging time (Day)	Hardness (Birinel)	E_{PO2} (mV/SCE)		E_{PO2} (mA/cm2)	E_{O2} (mV/SCE)		I_{pass} (mA/cm^2)	
				Repeat	Initial	Repeat	Repeat	Initial	Repeat	Initial	Repeat
1	15	2	2	12.9	1395	1390.7	0.18	1994	1998.6	0.0156	0.0149
(2)Reference	Air-cooled		4	12.6	1378	1378.3	0.15	1962	1962.5	0.0615	0.0615
Improvment				2.38%	1.23%	0.90%	20.00%	1.63%	1.84%	74.63%	75.77%

All repeated test results approve the initial tests results.

The results shows the correctness of the proposed mathematical model.

Battery Performance Test Results According to PSA Standard

To compare the electrochemical and mechanical results with the battery performance tests and Verifying the results of the mathematical modeling ,66 Ah Batteries were considered to be tested according to PSA standard. In this case two types of batteries samples were manufactured :

- Sample(1) : Batteries grids were quenched with water spray at 15˚c and 2mm nozzle diameter and after 2 days of aging time (As a best condition according to statistical analyzing).
- Sample(2) : Batteries grids were air cooled and with 4 days aging time.
- Used paste in batteries for pasting the positives and negative plates was made with 1.4 gr/cm3 sulfuric acid and 9.2% acid/oxide ratio.

→ The grids were pasted and cured with the same condition.

Battery Performance Test Results According to PSA Standard

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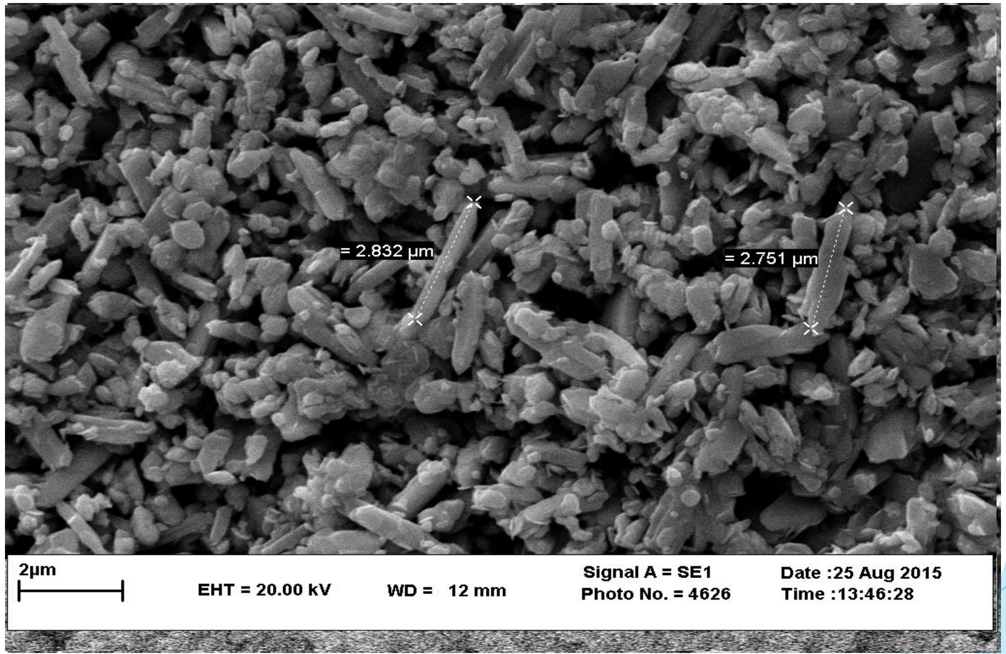

Positive and Negative plates PAM&NAM XRD analysis				
plate type	α-PbO	Pb3O4	4PbO. PbSO4	3PbO.Pb SO4.H2O
POS	45	-	9	46
NEG	44	-	-	56

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Sample(2) : Batteries grids were air cooled and with 4 days aging time.

Used paste in batteries for pasting the positives and negative plates was made with 1.4 gr/cm3 sulfuric acid and 9.2% acid/oxide ratio.

The grids were pasted and cured with the same condition.

The batteries were assembled with 6 positive and 6 negative plates .

The batteries were formed with same formation schedule.

The batteries were tested according to PSA standard.

Battery Test Results According to PSA Standard

No.	C20 (Ah)	CCA (-18 °C) 550 A	Charge Acceptance (A)	Cycle Life
Acceptable Result	66	V_{10s}=7.5 t_{6v}=90	13.2	6 Units Each unit 32 cycles (192 cycle)
Sample (1)	66.1	V_{10s}=8.02 t_{6v}=160	17.27	7 Units and 29 cycles 253 Cycles
Sample (2) (Ref)	66.4	V_{10s}=7.9 t_{6v}=136	16.32	6 Units and 12 cycles 204 Cycles

5.82% increasing in charge acceptance test

24% improving in cycle life test

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Plate photos after Cycle life test for sample (1)

Plate photos after Cycle life test for sample (2)

- ✓ Improvement in PbO_2 formation rate.
- ✓ Improvement in oxygen evolution.
- ✓ Decreasing passive current density.

Improvement in charge acceptance and cycle life and affectingly better AM/Grid adhesion even after more passed cycles in cycle life test.

Battery Test Results According to PSA Standard

Water lost: *Battery weight lose after charging with* 14.4±0.05 V for 500hr at 40°C will be measured in this test :

No..5	*Test*	*C20*	**CCA**				*Acceptable range*	*result*
			I dis	*V10*	*V30*	*t 6v*		
1	*Water lost*	*66*	*550*	*7.94*	*7.5*	*150*	*Water loss less than 1 gr/AH*	*0.7gr/AH*
2(Ref)			*550*	*7.86*	*7.32*	*132*		*0.8gr/AH*

12.5% decreasing in Water consumption.

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Comparing electrochemical tests with battery performance tests :

Electrochemical and Mechanical Test results Summary:

- ✓ 2.38% Higher Hardness with 2 days less aging time.
- ✓ 1.23% improvement in PbO2 formation .
- ✓ 1.63% % improvement in oxygen evolution.
- ✓ 74.63 increasing in corrosion resistance.

Battery performance Test results Summary:

- ✓ Equal Battery Capacities .
- ✓ 1.53% improving in cold cranking ability.
- ✓ 5.82% increasing in charge acceptance.
- ✓ 24% improving in cycle life.
- ✓ 12.5% decreasing in Water consumption.

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