An electrochemical tool for characterizing a soft lead sample

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Agenda

1. Introduction
2. Goals
3. Action plan
4. Experimental conditions
5. Results
6. Conclusions

Introduction

Secondary reactions in a Lead-Acid Battery (LAB)

Overcharge state → Secondary reactions

PAM

Oxygen Evolution Reaction (OER)

$$H_2O \rightarrow \uparrow O_2\,(g) + 4H^+(aq) + 4e^- \quad \text{(Eq. 1)}$$

NAM

Hydrogen Evolution Reaction (HER)

$$2H^+(aq) + 2e^- \rightarrow \uparrow H_2\,(g) \quad \text{(Eq. 2)}$$

Water consumption

Metal impurities → **Catalytic effect**

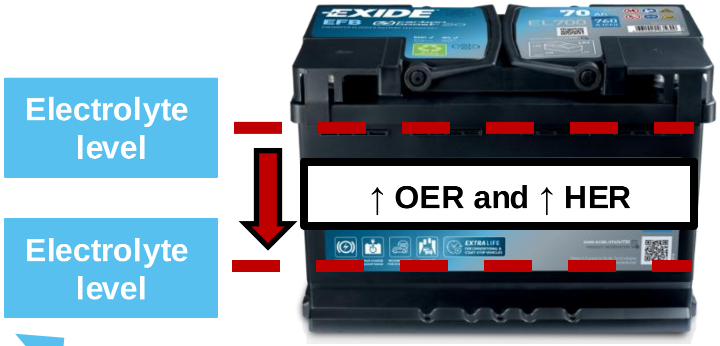


Fig. 1. Representation of gassing reactions in a LAB.

LAB issues

- ↑ Self-discharge
- ↑ Internal pressure
- ↓ Electrical properties
- ↓ Operating temperature range

Goals

1. **Predict and detect the potential water consumption of a LAB by using an electrochemical tool.**

    a) Find similar trends between the results obtained by using the new tool (study of the HER rate) and the results found in a water consumption test.

    b) Obtain traceability between the soft lead samples and their corresponding NAMs used for building negative plates.

Action plan

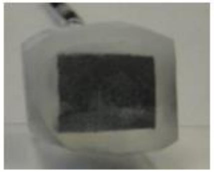
1st Stage – Electrochemical tool

2nd Stage – Electrical testing

Soft lead sample → Leady oxide → Handmade negative plate → Flooded 2 V / 22 Ah cell
(*Capacity → Discharge at 20 h rate*)

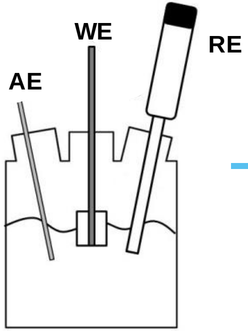
Traceability

Handmade electrode



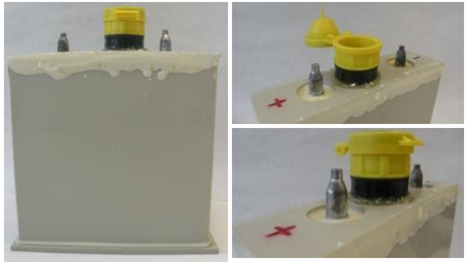
Three electrode cell

WE: Soft lead electrode
AE: High purity soft lead (+99%) electrode
RE: Hg/Hg_2SO_4



→ **Cyclic voltammetry (CV)**
(HER rate)

Assembly
3 positive plates : 2 negative plates



1. **Capacity (C_{20})**
2. **Water consumption (WC)**

Experimental conditions

1st Stage – Electrochemical tool

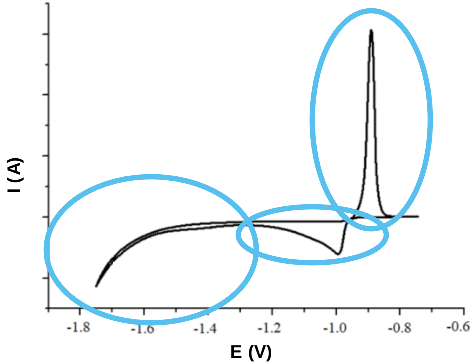


Fig. 2. Example of cyclic voltammogram.

Main reaction in NAM

$$Pb\ (s) + H_2SO_4 \leftrightarrow PbSO_4(s) + 2H^+(aq) + 2e^- \quad \text{(Eq. 3)}$$

Recharge process: $PbSO_4(s) \rightarrow Pb(s)$

Discharge process: $Pb(s) \rightarrow PbSO_4\ (s)$

Secondary reaction in NAM

Overcharge state (HER): $\mathbf{2H^+(aq) + 2e^- \rightarrow\uparrow H_2(g)}$ (Eq. 2)

Three electrode cell

WE: Soft lead electrode
AE: High purity soft lead (+99%) electrode
RE: Hg/Hg_2SO_4
Electrolyte: 1.28 gmL^{-1} H_2SO_4

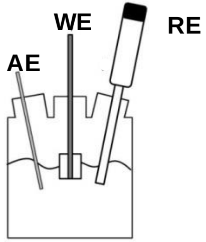


Fig. 3. Three electrode cell assembly.

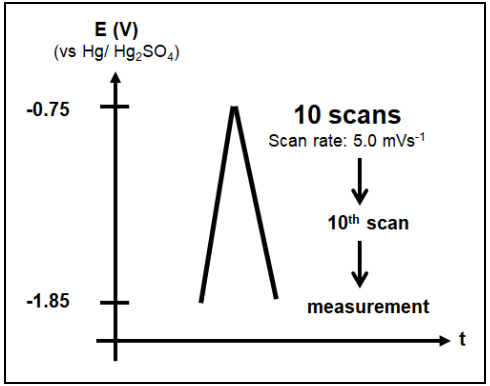


Fig. 4. Experimental conditions during the CV sutdy of the HER rate.

From the 10th scan → HER study

Two parameters:

E_0 (HER) (V)

j_0 (HER) (Acm^{-2})

Tafel equation

$$E = -\frac{2.30RT}{\alpha nF}\log(j) + \frac{2.30RT}{\alpha nF}\log(-j_0) + E_{eq} \quad \text{(Eq. 4)}$$

Experimental conditions

2^{nd} Stage – Electrical testing

Table 1. NAM recipe for negative plates.

NAM recipe	
Raw material	Percentage vs PbO (%)
Expander	< 0.35
Carbon Black	< 0.20

Table 2. Experimental conditions for electical testing.

C_{20} (25 ^{O}C)	
Discharge	I_{20} (A) *Limit: Voltage < 1.75 V*
Water consumption (60 ^{O}C) **/ Unit**	
Charge	2.40 V *Limit: 21 days*
Completed units	2 (*42 days*)

Flooded 2 V/ 22 Ah cell

Assembly: 3 positive plates : 2 negative plates
Cell sealing: Epoxy resin
Cap: Vapor condenser

Fig. 5. Example of a flooded 2 V/ 22 Ah cell.

Experimental conditions

Variables

Table 3. Comparison among the chemical analyses of soft lead samples and their corresponding PbOs and Dry Unformed (DUF) NAMs.

REFERENCE			Purity %		IMPURITIES (ppm)											
			Ag	Bi	Sb	As	Cr	Cu	Ni	Cd	Co	Mn	Zn	Fe	Se	Te
A	Lower purity	Pb	18.7	74.6	<0.5	<0.5	0.6	0.8	<0.5	<0.5	<0.5	0.5	<0.5	0.8	<0.5	0.5
		PbO	15.5	63.8	2.2	<0.5	0.6	0.5	<0.5	<0.5	<0.5	0.5	<0.5	<0.5	<0.5	0.5
		DUF NAM	13.6	57.1	2.7	<0.5	0.6	0.6	<0.5	<0.5	<0.5	0.5	<0.5	<0.5	<0.5	0.5
B	Lower purity	Pb	17.2	78.4	<0.5	<0.5	<0.5	0.7	0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
		PbO	16.5	69.0	<0.5	<0.5	<0.5	0.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
		DUF NAM	14.7	63.0	<0.5	<0.5	<0.5	3.0	0.5	<0.5	<0.5	<0.5	<0.5	1.1	<0.5	<0.5
C	Higher purity	Pb	3.1	24.3	<0.5	<0.5	0.6	<0.5	<0.5	<0.5	<0.5	0.5	<0.5	1.8	<0.5	0.5
		PbO	2.9	15.7	<0.5	<0.5	0.5	<0.5	<0.5	0.5	<0.5	0.5	<0.5	<0.5	<0.5	0.6
		DUF NAM	3.4	13.0	0.6	<0.5	0.6	<0.5	<0.5	0.5	<0.5	0.5	<0.5	<0.5	<0.5	0.5
D	Higher purity	Pb	10.4	45.2	<0.5	<0.5	<0.5	<0.5	0.8	<0.5	<0.5	<0.5	<0.5	0.7	<0.5	<0.5
		PbO	9.5	40.4	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
		DUF NAM	8.5	37.0	<0.5	<0.5	<0.5	0.6	0.8	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5

Traceability

Results

1st Stage – Electrochemical tool / CV study

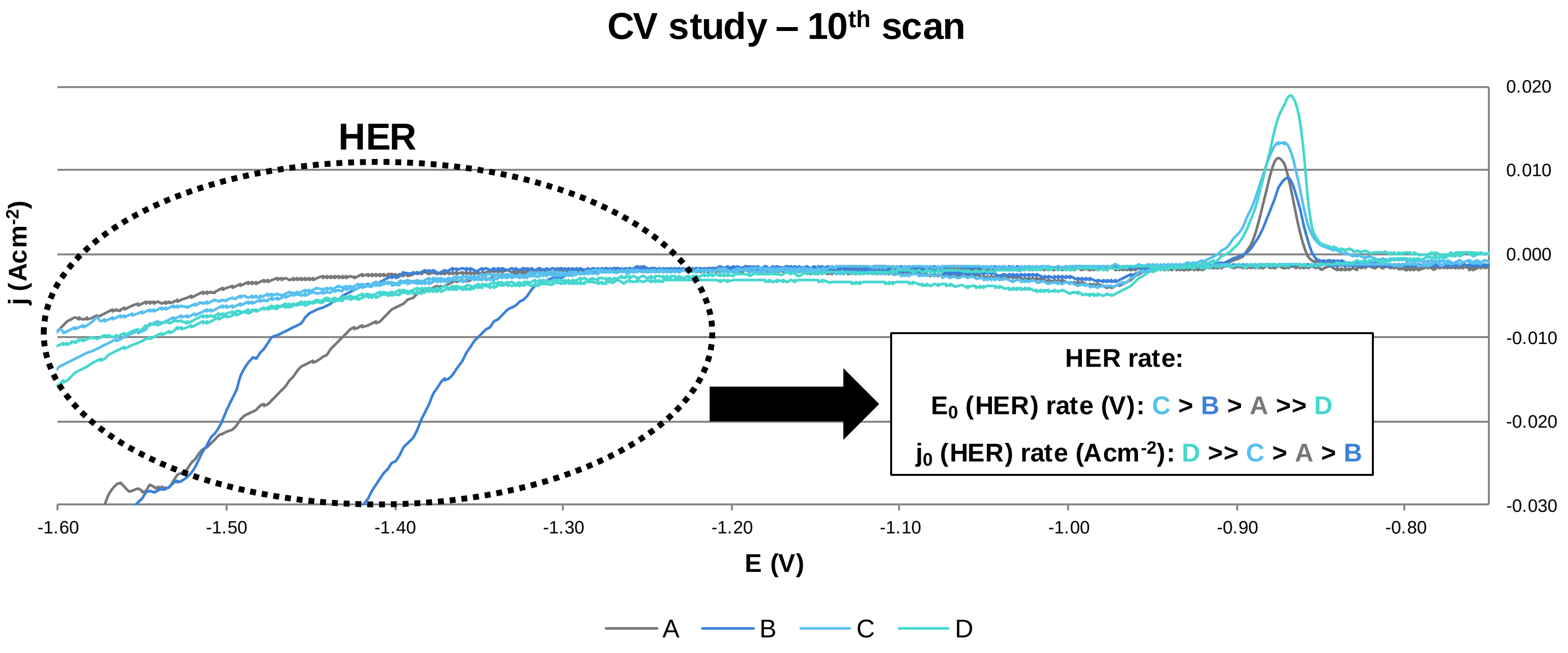


Fig. 6. 10th CVs obtained from soft lead samples.

Results

2nd Stage – Electrical testing / C_{20}

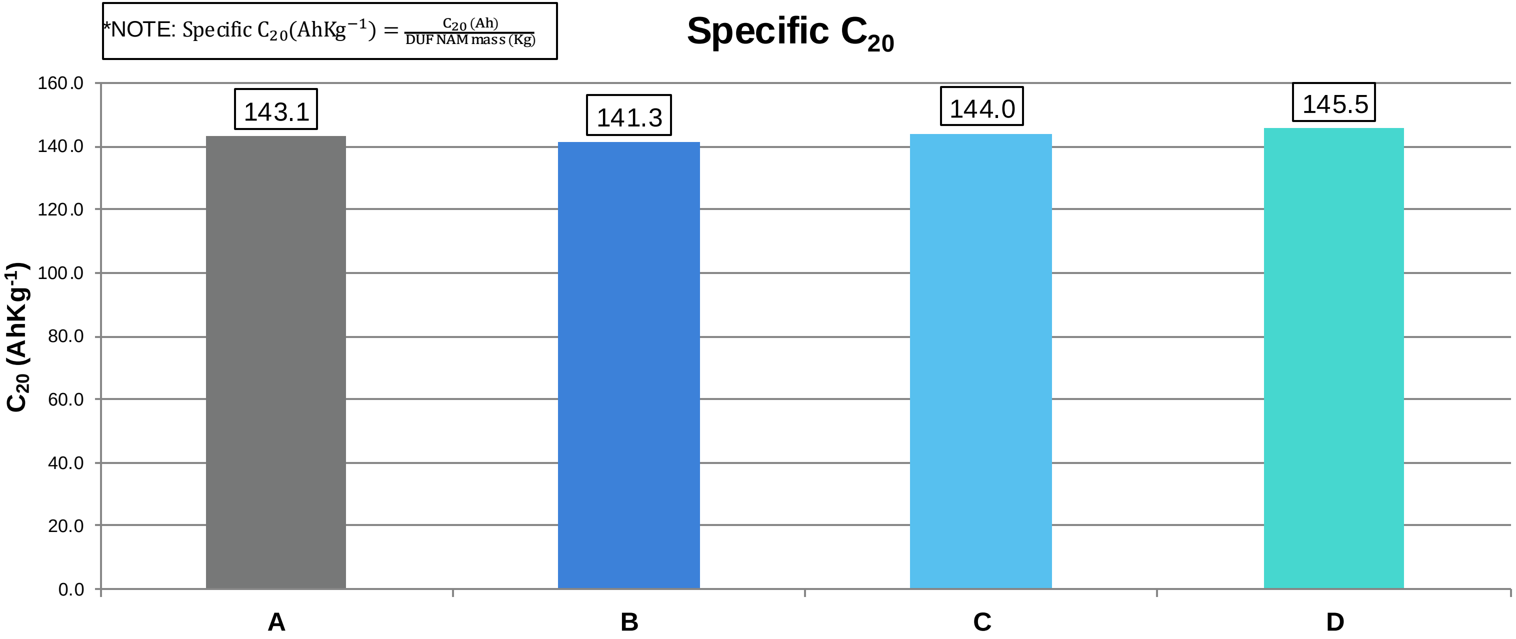


Fig. 7. Results obtained form the C_{20} test.

Results

2nd Stage – Electrical testing / Water consumption

Because of cell design issues related to leak points in the seal→ The mass loss produced after each WC unit could not be used as a parameter → It was replaced by electrical parameters:

- Specific accumulated charge (**Qacc**) ($AhkgAh^{-1}$)
- Specific end current (**EC**) ($AkgAh^{-1}$)

Calculation:

1. **Qacc ($AhkgAh^{-1}$):** Total charge (Ah) accumulated during the WC unit → Normalized by the specific C_{20} ($Ahkg^{-1}$).

2. **EC ($AkgAh^{-1}$):** End current (A) collected at the end of the WC unit → Normalized by the specific C_{20} ($Ahkg^{-1}$).

Results

Electrochemical tool (HER rate study) vs Electrical testing (WC test)

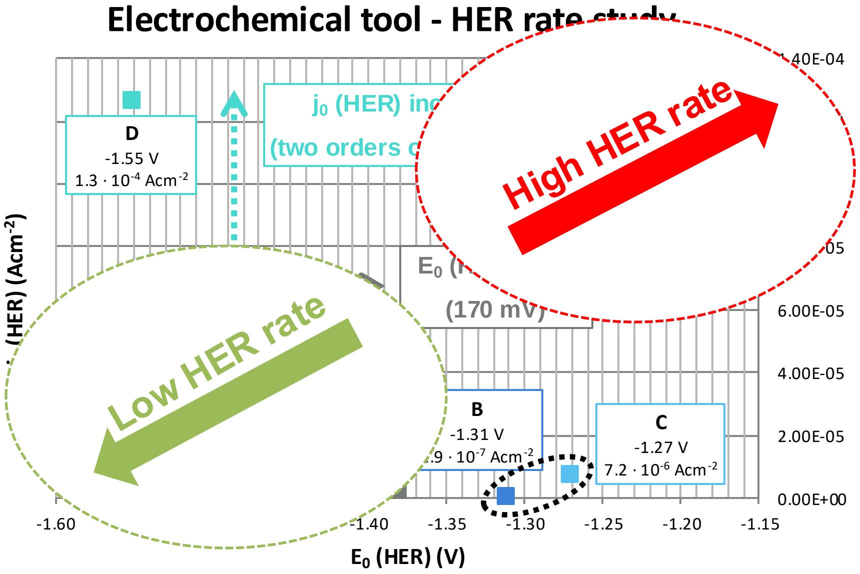


Fig. 8. Comparison of HER rates obtained from soft lead samples.

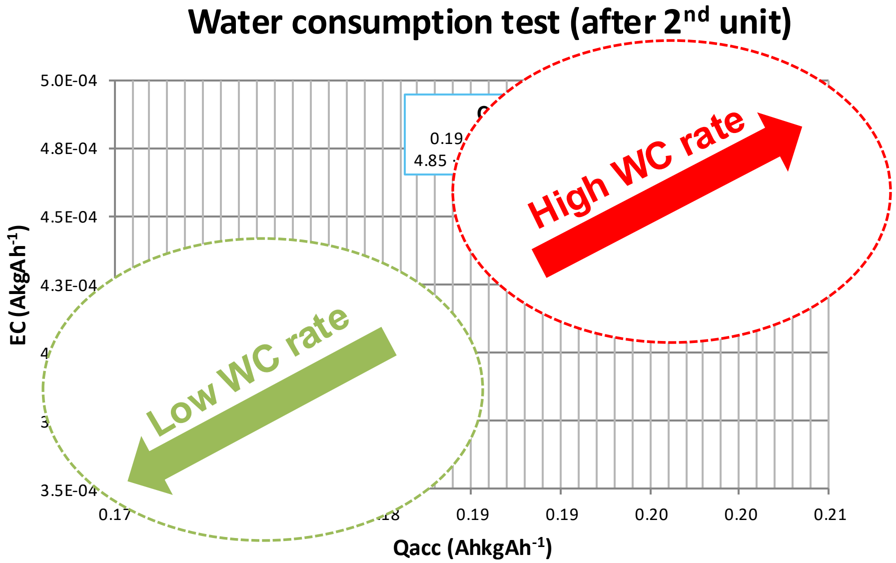


Fig. 9. Results obtained from the WC test.

Results

Electrochemical tool (HER rate study) vs Electrical testing (WC test)

HER rate

E_0 (HER) rate (V)

C > B > A >> D

j_0 (HER) rate (Acm^{-2})

D >> C > A > B

WC rate

Qacc rate ($AhkgAh^{-1}$)

B > C >> A ≈ D

EC rate ($AkgAh^{-1}$)

C > B >> A ≈ D

Conclusions

1. **According to the results of the CV study and the WC test → High accuracy of the electrochemical tool:**

    a) B and C samples showed the highest rates of HER and WC.

2. **The WC was influenced by the effect of the two electrochemical parameters j_0(HER) and E_0(HER):**

    a) A and D samples showed significant differences in the CV study, but resulted in a similar WC rate.

    b) B sample showed one of the highest WC rate because the low j_0 (HER) value was compensated by the E_0 (HER) value.

Thank you

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