New additives to perform the performance of a lead-acid battery

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Agenda

1. Introduction / State of the art
2. Objectives
3. Experimental methodology
4. Research plan
5. Results

Introduction / State of the art

The most common technology in the current automotive batteries

EFB
(Enhanced Flooded Battery)

AGM
(Absorbed Glass Mat)

Improvements:

- Free-maintenance
- Longer cycle life performance
- Internal oxygen cycle
- Reduction of the stratification

Outlook for future researches:

- Reduce water consumption
- Reduce the corrosion in the positive grid:
  - Improve the Cycle Life at Partial State of Charge
- Reduce the sulfation in the negative plate:
  - Improve the Cycle Life at Partial State of Charge
  - Improve the Dynamic Charge Acceptance

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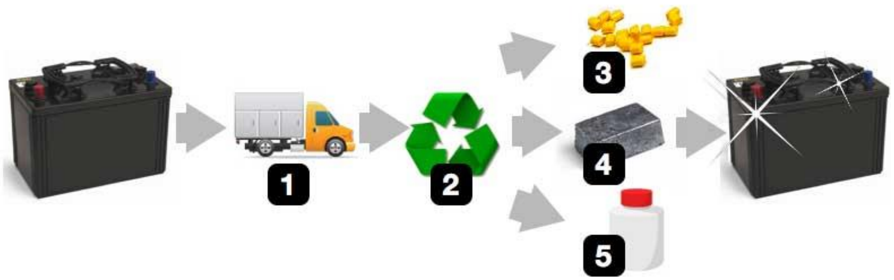
Introduction / State of the art

Water consumption



Main reactions in LABs:

$$Pb(s) + SO_4^{2-}(aq) \rightleftarrows PbSO_4(s) + 2e^-$$

$$PbO_2(s) + 4H^+ + SO_4^{2-}(aq) + 2e^- \rightleftarrows PbSO_4(s) + 2H_2O$$

Secondary reactions:

HER

(Hydrogen Evolution Reaction)

$$2H^+ (aq) + 2e^- \rightarrow H_2 (g)$$

OER

(Oxygen Evolution Reaction)

$$2H_2O (aq) \rightarrow O_2 (g) + 4H^+ (aq) + 4e^-$$

ORR / Internal Oxygen Cycle

(Oxygen Reduction Reaction)

$$O_2 (g) + 4H^+ (aq) + 4e^- \rightarrow 2H_2O (aq)$$

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Introduction / State of the art

Additives for Negative Active Material (NAM)

Expanders (Lignosulfonate):

- Increase the porosity of the $PbSO_4$ layer after the recharge process → Reduce the passivated layer of $PbSO_4$

$BaSO_4$:

- Nucleation agent for $PbSO_4$ → Reduce the size of the $PbSO_4$ crystals with a uniform distribution of these crystals through the pore surface of NAM

Carbon (nanotubes, nanofibers, graphene oxide or carbon black):

- Increase the active surface of the NAM → Reduce the size of PbSO4 and increase the electrical conductivity of the active material

Objectives

Study of the impurity effect on water consumption

- Develop a simple electrochemical procedure where the impurity effect on HER and OER can be measured at low concentrations through the a quick-low-cost system: Cyclic Voltammetry (CV) measurements in a three electrode cell.
- Find similar trends in the study of HER catalysis between the two experimental setups: Three electrode cell and 2 V/ 1 Ah cell.
- Set a HER and OER rates according to the experimental results.

Study of new type of lignosulfonate from biomass of sugar cane

- Find a new substitute that improves the performance of a commercial lignosulfonate.
- Take a second life to a waste as the biomass of plantations.

Experimental methodology

Study of the impurity effect on water consumption

Impurities

Ni (Nickel (II) sulfate hexahydrate, 99+ %) **Zn** (Zinc oxide, 99+ %) **Bi** (Bismuth (III) oxide, 99+ %) **Ag** (Silver sulfate, 99+ %) **Se** (Selenium dioxide, 99+ %)

Three electrode cell – CV study

WE: Lead rotating disk
(99% purity, 1200 rpm rotation, 0.07 cm^2 area)

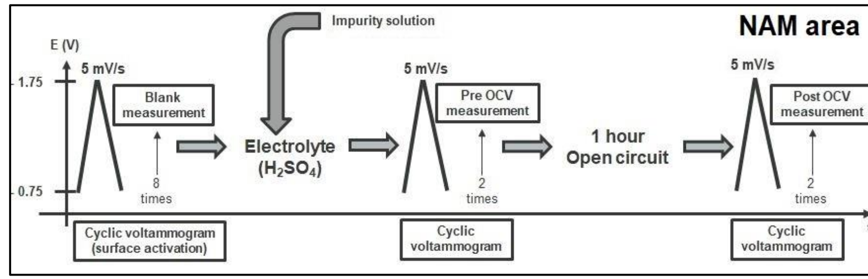
AE: Lead wire (99% purity)

RE: Hg/ Hg_2SO_4

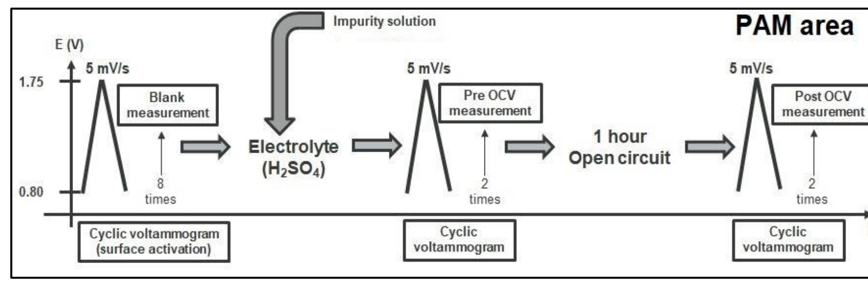
Electrolyte: 200 mL H_2SO_4 (4.88 M)

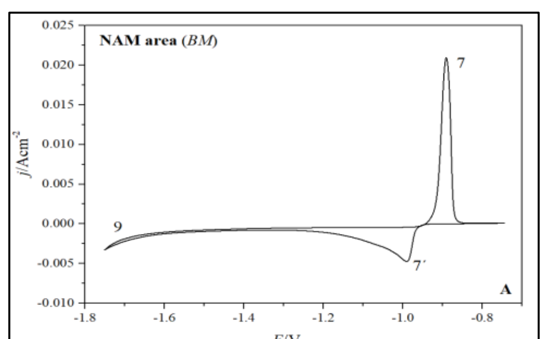
Lead rotating disk electrode used as WE

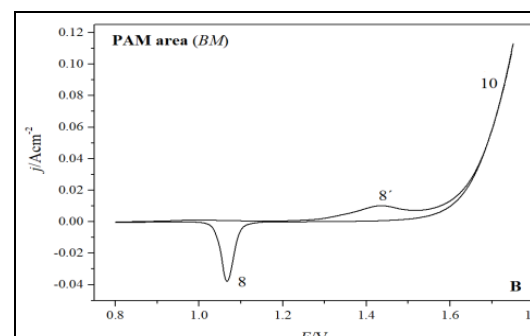
HER study → NAM area: - 1.75 V ; - 0.75 V (vs Hg/ Hg_2SO_4)



OER study → PAM area: 0.80 V ; 1.75 V (vs Hg/ Hg_2SO_4)







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Experimental methodology

Study of the impurity effect on water consumption

Impurities

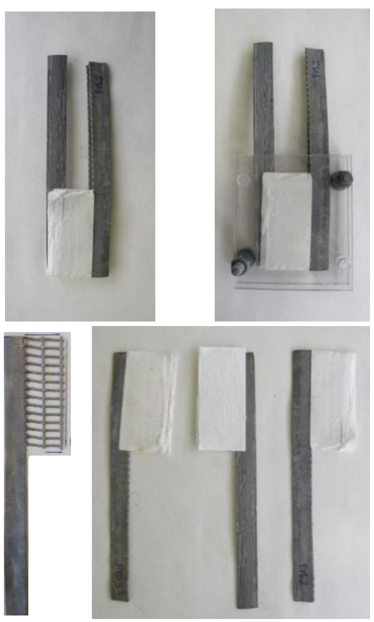
Ni (Nickel (II) sulfate hexahydrate, 99+ %) **Zn** (Zinc oxide, 99+ %) **Bi** (Bismuth (III) oxide, 99+ %) **Ag** (Silver sulfate, 99+ %) **Se** (Selenium dioxide, 99+ %)

2 V/ 1 Ah cell – C_{20} capacity, charge acceptance and Tafel tests

Plates: 8.0 g mass / 20 cm^2 geometric surface

Grid: Pb-Sn alloy

Cell system: 1.0 Ah / 2 positive plates : 1 negative plate



2 V/ 1 Ah cell assembly

Formation

↓

C_{20} Capacity test
(Discharge at I_{20} (0.05 A))

↓ **Charge** (0.25 A / 2.67 V CCCV)

Charge acceptance test
(Discharge (0.05 A) until 90% SoC → 72 h sulfation → Charge at 2.42 V for 60 s / Record current at 5 s)

↓ **Charge** (0.25 A / 2.67 V CCCV)

Tafel test
(Set of constant current densities: 10^{-2}, …, $5 \cdot 10^{-5}$ Acm^{-2})

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Experimental methodology

Study of new type of lignosulfonate from biomass of sugar cane

2 V/ 0.23 Ah cell – C_{20} capacity, charge acceptance and Tafel tests

% New lignosulfonate (LigB) (vs PbO): 0.30%

Plates: 1.8 g mass / 5 cm^2 geometric surface

Grid: Pb-Sn alloy

Cell system: 0.23 Ah / 2 positive plates : 1 negative plate

2 V/ 0.23 Ah cell assembly

Formation

↓

C_{20} Capacity test (x 2)
(Discharge at I_{20} (0.0115 A))

↓ **Charge** (0.25 A / 2.67 V CCCV)

Charge acceptance test
(Discharge (0.0115 A) until 90% SoC → 72 h sulfation → Charge at 2.42 V for 60 s / Record current at 5 s)

↓ **Charge** (0.25 A / 2.67 V CCCV)

Tafel test
(Set of constant current densities: $9 \cdot 10^{-3}$, …, $4.6 \cdot 10^{-5}$ Acm^{-2})

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Research plan

- From 2019 October to 2020 April
  - Study of the impurity effect on HER and OER in a three electrode cell
- From 2020 April to 2021 April
  - Study of the impurity effect on HER in a 2 V/ 1 Ah cell
- From 2020 March to 2020 December
  - Study of the new lignosulfonate from biomass of sugar cane in a 2 V/ 0.23 Ah cell
- From 2021 January to 2021 December
  - Study of H_3BO_3 as new additive in the electrolyte to reduce the positive grid corrosion in a 2 V/ 1 Ah and 2 V/ 22 Ah cell

Results

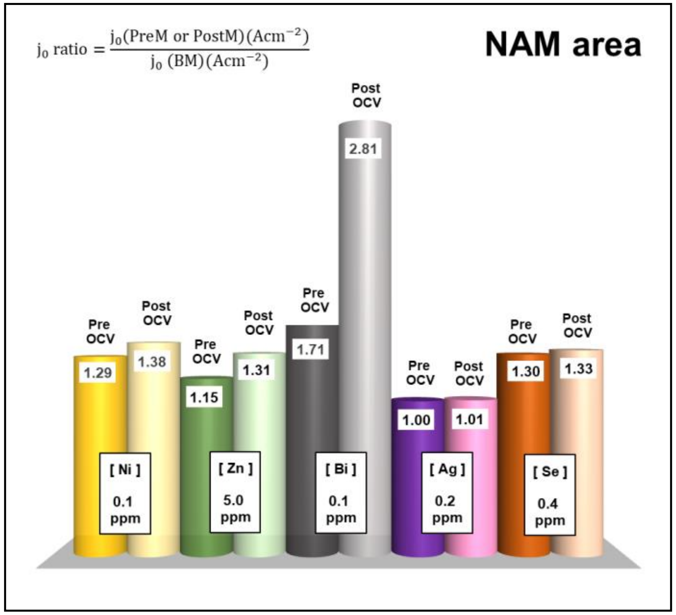
Study of the impurity effect on water consumption

Three electrode cell – CV study

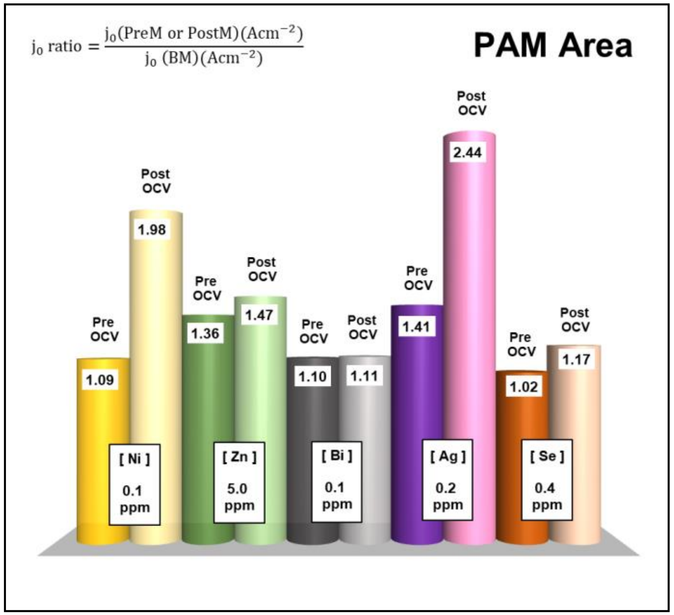
Experimental impurity concentrations in the electrolyte (Red color → Limit concentration):

Ni (**0.10** ; 0.25 ; 0.50 ; 2.00 ppm)
Zn (0.20 ; **2.00** ; 5.00 ppm)
Bi (**0.10** ; 0.30 ; 1.00 ppm)
Ag (**0.20** ; 0.40 ; 1.00 ppm)
Se (**0.40** ; 0.80 ; 1.50 ppm)

HER study



OER study



Results

Study of the impurity effect on water consumption

Three electrode cell – CV study

Experimental impurity concentrations in the electrolyte (Red color → Limit concentration):

Ni (**0.10** ; 0.25 ; 0.50 ; 2.00 ppm)

Zn (0.20 ; 2.00 ; **5.00** ppm)

Bi (**0.10** ; 0.30 ; 1.00 ppm)

Ag (**0.20** ; 0.40 ; 1.00 ppm)

Se (**0.40** ; 0.80 ; 1.50 ppm)

HER rate

Bi >> Se ≈ Ni >> Ag >> Zn

OER rate

Ag >> Ni > Se ≈ Bi >> Zn

Results

Study of the impurity effect on water consumption

2 V/ 1 Ah cell – C_{20} capacity test

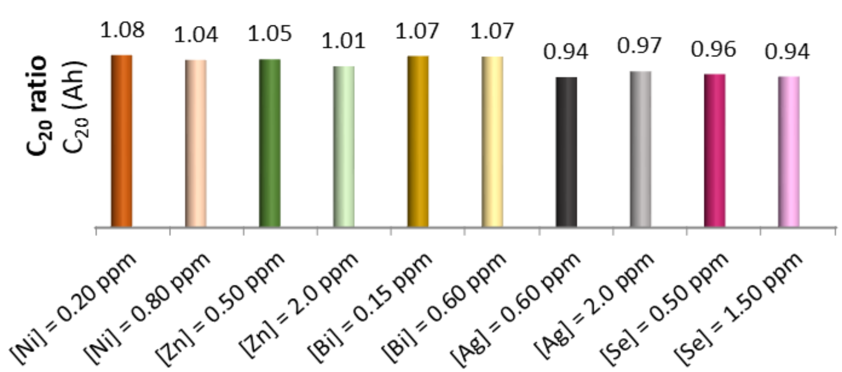
Experimental impurity concentrations in the electrolyte:

Ni (0.20 ; 0.80 ppm) Zn (0.50 ; 2.00 ppm) Bi (0.15 ; 0.60 ppm)
Ag (0.60 ; 2.00 ppm) Se (0.50 ; 1.50 ppm)

Experimental impurity concentrations in the NAM:

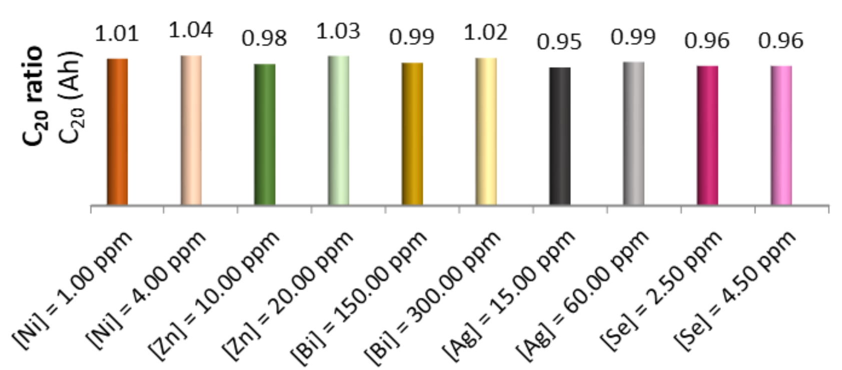
Ni (1.00 ; 4.00 ppm) Zn (10.00 ; 20.00 ppm) Bi (150.00 ; 300.00 ppm)
Ag (15.00 ; 60.00 ppm) Se (2.50 ; 4.50 ppm)

C_{20} capacity test – Electrolyte



$$C_{20}\,\text{ratio} = \frac{C_{20}\ (\text{Ah})(\text{Impurity})}{C_{20}\ (\text{Ah})(\text{NAM Control})}$$

C_{20} capacity test – NAM



$$C_{20}\,\text{ratio} = \frac{C_{20}\ (\text{Ah})(\text{Impurity})}{C_{20}\ (\text{Ah})(\text{NAM Control})}$$

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Results

Study of the impurity effect on water consumption

2 V/ 1 Ah cell – C_{20} capacity test

Experimental impurity concentrations in the electrolyte:

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C_{20} capacity test – Electrolyte or NAM

No impurity effect

Results

Study of the impurity effect on water consumption

2 V/ 1 Ah cell – Charge acceptance test

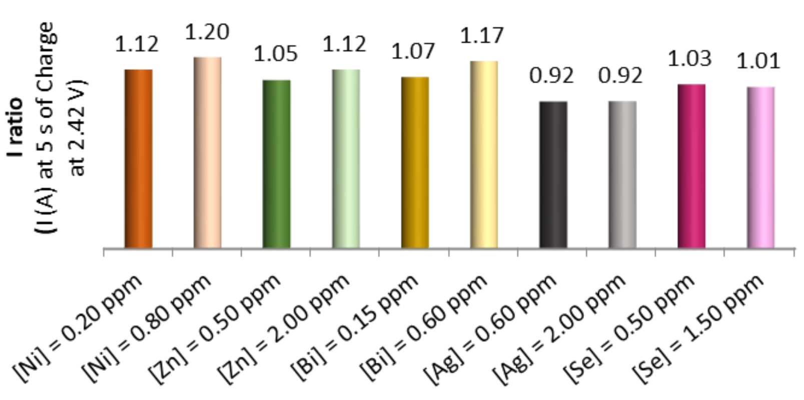
Experimental impurity concentrations in the electrolyte:

Ni (0.20 ; 0.80 ppm)   Zn (0.50 ; 2.00 ppm)   Bi (0.15 ; 0.60 ppm)
Ag (0.60 ; 2.00 ppm)   Se (0.50 ; 1.50 ppm)

Experimental impurity concentrations in the NAM:

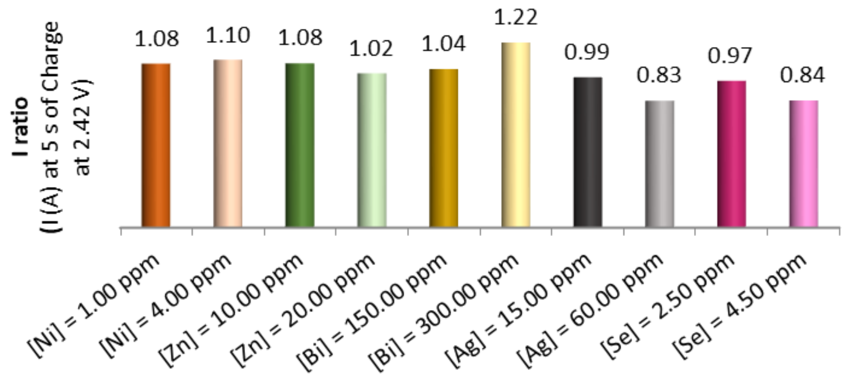
Ni (1.00 ; 4.00 ppm)   Zn (10.00 ; 20.00 ppm)   Bi (150.00 ; 300.00 ppm)
Ag (15.00 ; 60.00 ppm)   Se (2.50 ; 4.50 ppm)

Charge acceptance test – Electrolyte



$$\text{I ratio} = \frac{\text{I (A)(Impurity)}}{\text{I (A)(NAM Control)}}$$

Charge acceptance test – NAM



$$\text{I ratio} = \frac{\text{I (A)(Impurity)}}{\text{I (A)(NAM Control)}}$$

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Results

Study of the impurity effect on water consumption

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Charge acceptance test – Electrolyte or NAM

No impurity effect

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Results

Study of the impurity effect on water consumption

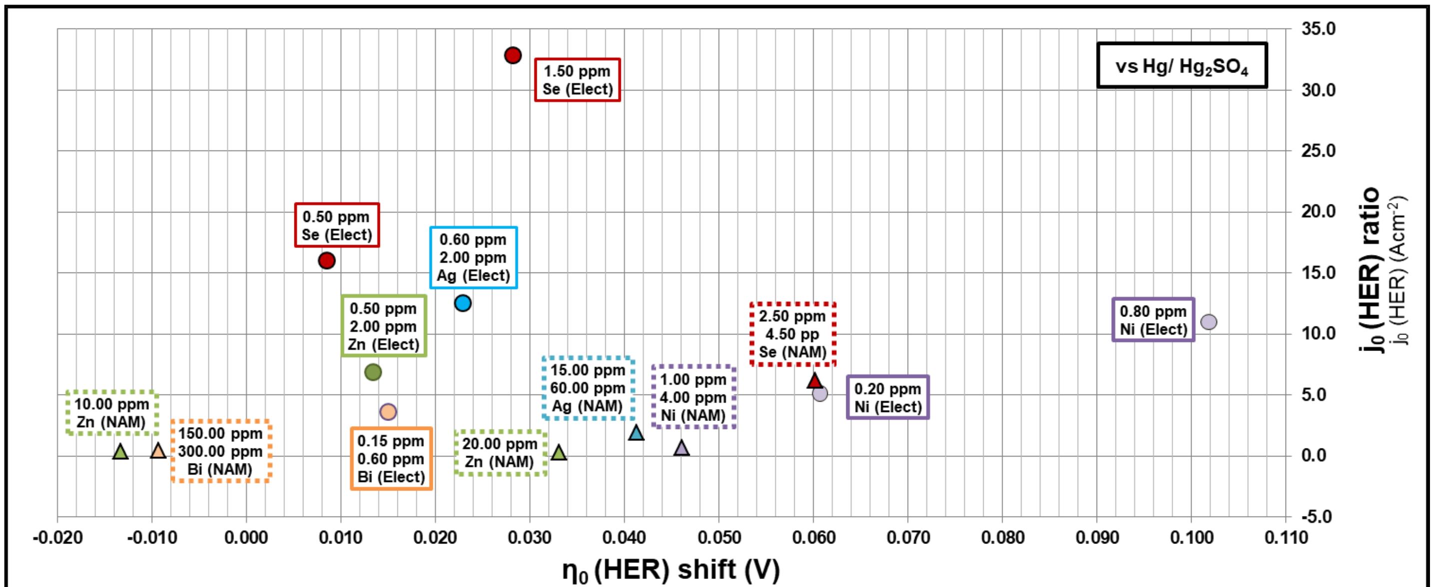
2 V/ 1 Ah cell – Tafel test

Experimental impurity concentrations in the electrolyte:

Ni (0.20 ; 0.80 ppm) Zn (0.50 ; 2.00 ppm) Bi (0.15 ; 0.60 ppm)
Ag (0.60 ; 2.00 ppm) Se (0.50 ; 1.50 ppm)

Experimental impurity concentrations in the NAM:

Ni (1.00 ; 4.00 ppm) Zn (10.00 ; 20.00 ppm) Bi (150.00 ; 300.00 ppm)
Ag (15.00 ; 60.00 ppm) Se (2.50 ; 4.50 ppm)



$$\eta_0\ (\text{HER})\text{shift}\ (\text{V}) = \eta_0\ (\text{HER})(\text{Impurity})\ (\text{V}) - \eta_0\ (\text{HER})(\text{NAM Control})\ (\text{V})$$

$$j_0\ (\text{HER})\ \text{ratio} = \frac{j_0\ (\text{HER})(\text{Impurity})(\text{Acm}^{-2})}{j_0\ (\text{HER})(\text{NAM Control})(\text{Acm}^{-2})}$$

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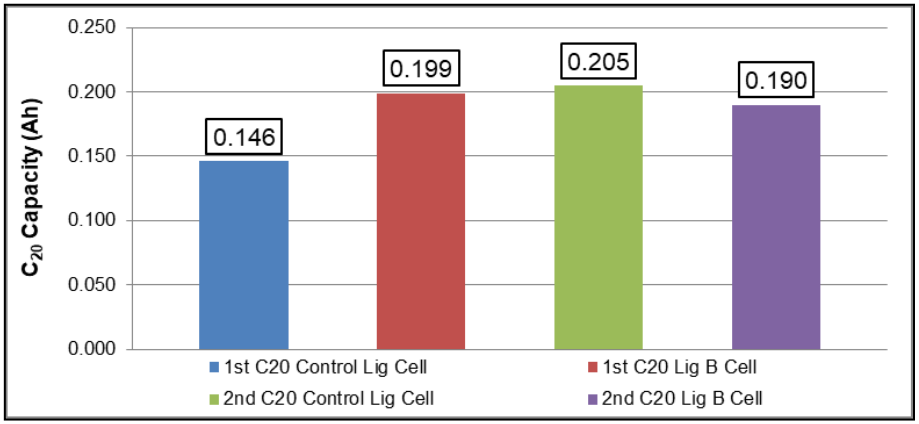
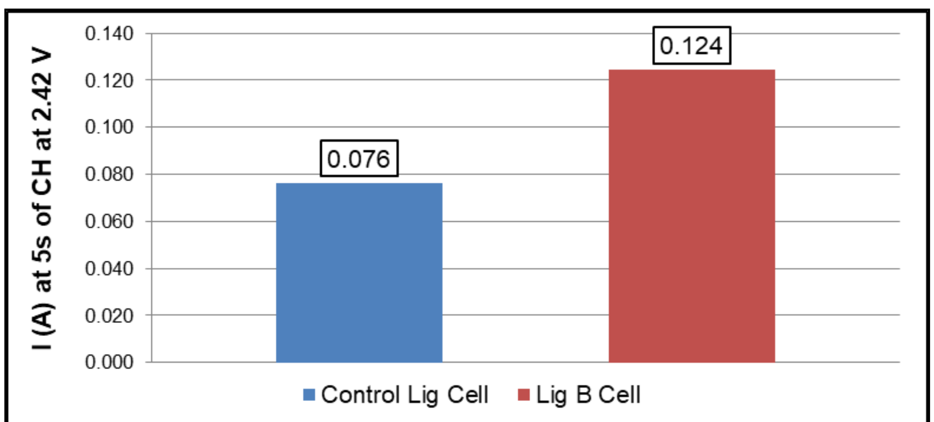
Results

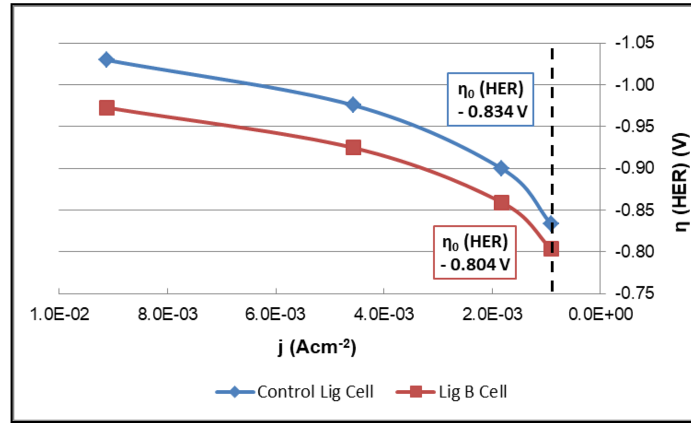
Study of new type of lignosulfonate from biomass of sugar cane

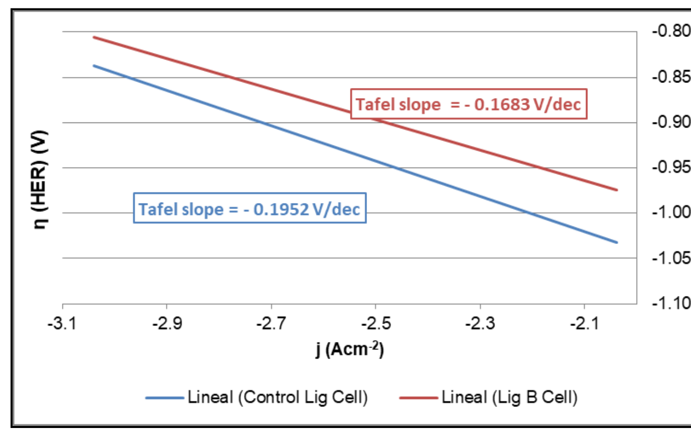
2 V/ 1 Ah cell – C_{20} capacity, charge acceptance and Tafel tests

% LigB (vs PbO): 0.30%









	Control Lig Cell	Lig B Cell
η_0 (HER) (V)	-0.834	-0.804
Tafel slope (V/dec)	-0.195	-0.168
j_0 (Acm^{-2})	$3.21 \cdot 10^{-8}$	$1.50 \cdot 10^{-8}$

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Next steps

- Study of new type of lignosulfonate from biomass of sugar cane
    - To collect more amount of LigB to repeat more measurements in cells at higher nominal capacities (1 Ah).

- Study of H3BO3 as new additive in the electrolyte to reduce the positive grid corrosion
    - To study the effects of this new additive making the addition either before the formation or after formation.
    - To run C_{20} capacity, cold cranking ampere, charge acceptance, Tafel and corrosion tests in 2 V/ 1 Ah cells.

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Thank you