Carbon Nanomaterial Compounds as Negative Active Material Enhancers for LABs

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EXIDE TECHNOLOGIES / ENERGIZING A NEW WORLD

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Carbon Nanomaterials Introduction

Carbon Nanomaterials

- Due to their inherent characteristics derived from its size and structure, nanomaterials are known to show special behavior respect to the bulk material.
- A remarkable characteristic is the **great surface/area** ratio that they can show as well as the different interaction with the materials surrounding due to its size and shape.
- Nanomaterials are already being used in nowadays technology and are expected to be more and more common as they are able to improve the characteristics of the material where they are added.
- Among the different existing nanomaterials, **Carbon Nanomaterials** are of special interest in energy accumulators including **Lead-acid Batteries (LABs)**.
- Carbon nanomaterials (CNMs) including carbon nanotubes, graphene, fullerenes, etc... have been investigated as additives into lead acid batteries due to their potential benefits.
- Similarly, special carbons with very **high specific surface area** (≈1000 m^2/g) are of great interest due to the potential increase in the material reactivity by increasing Negative Active Mass (NAM) surface area of LABs.

2
Objective

Objective

In this work **two different special carbons** have been used for the improvement of the **negative active material (NAM)** of LABs: a carbon nanomaterial and a carbon with a very high specific surface

The benefits expected are related to the increment of the mass **conductivity** and also due to the nanomaterial effect ant its interaction on the material structure

Due to the addition of this additives we can expect the following benefits:

- Sulfating reduction due to additional nucleation sites
- Increased capacity
- Improved Cycle life
- Increment of pore volume (acid and ions mobility)
- Increased charge acceptance
- Higher surface area (measured by BET calculation)

3

Setup Description

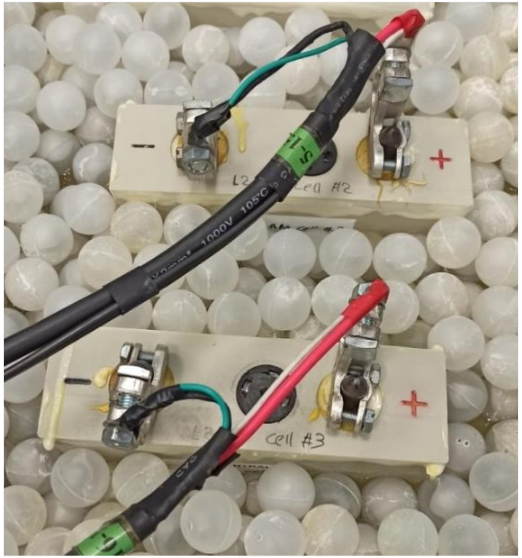
Setup Description

The experimental work was made on **2 V / 22 Ah** (at C_{20} rate) cells with a configuration of **3 positive plates and 2 negatives plates** with the carbon additives included into the NAM (limiting “reactant”):

- We used for this study “automotive” plates with standard size
- The positive plates were selected from standard production
- The negative plates were hand pasted in our R&D lab with the carbon materials added in a lab mixer
- Plate assembly was carried out using a standard COS process into our plant
- Curing and formation processes were made following standard profiles

Setup Description

Herein below some details about the 2 V cell design we used for this study, including assembly, sealing and connections for electrical testing.



4.a
Experimental Results
Carbon Nanomaterial Cells

Experimental Results

Physico-Chemical analysis of NAM with CNMs

Physico-Chemical Analysis of Unformed NAM

	Free lead (%)	Sulfate (%)	Porosity (%)	Apparent density (g/cm^3)	Median pore ⌀ (µm)	BET (m^2/g)
Control*	3,4	12,0	46,4	4,11	0,19	2,46
50 ppm CNM	3,7	9,2	50,5	4,28	0,22	2,07
100 ppm CNM	4,4	8,7	45,2	4,41	0,20	2,33

Physico-Chemical Analysis of Formed NAM

	Lead sulfate (%)		BET (m^2/g)
	Top	Bottom	
Control*	4,2	3,2	1,21
50 ppm CNM	3,0	3,3	0,62
100 ppm CNM	4,0	3,3	0,59

* Standard NAM recipe

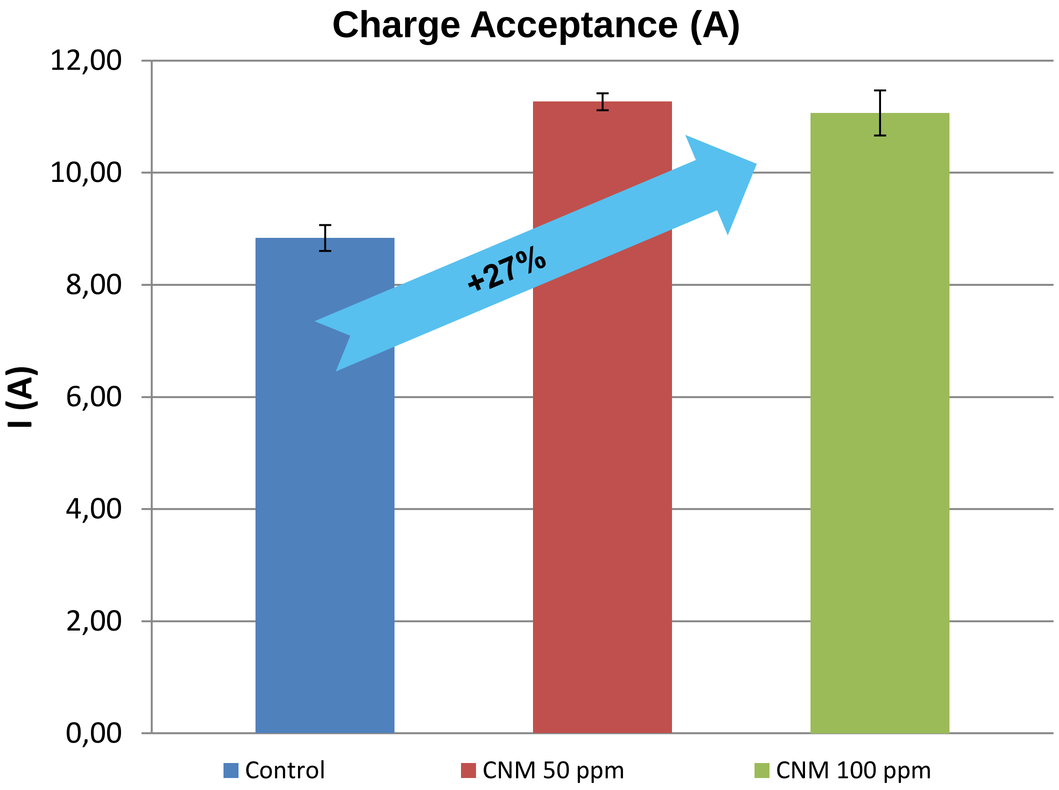
Experimental Results

Charge Acceptance

Charge Acceptance	Current at 5s at 2,42 V (A)	SD (A)	Vs. Control (%)
Control	8,8	0,23	100
50 ppm CNM	11,3	0,15	128
100 ppm CNM	11,1	0,40	125

Charge Acceptance	ECC* previous recharge (A)	ECC* of last recharge (A)
Control	0,409	0,357
50 ppm CNM	0,275	0,223
100 ppm CNM	0,302	0,248

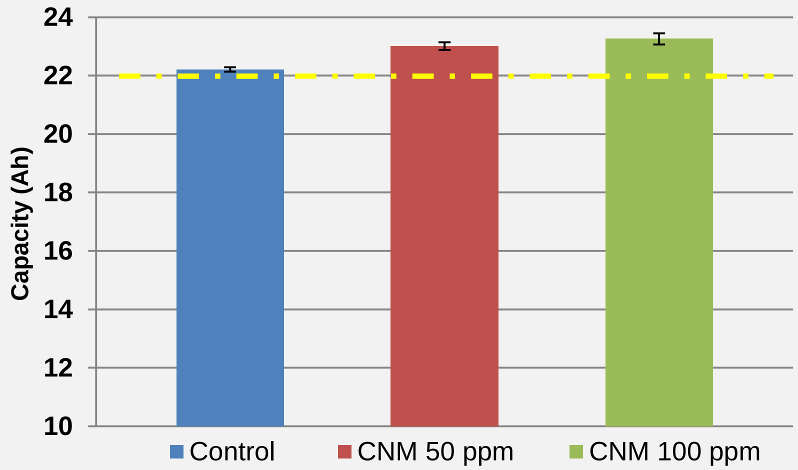
* End of Charge Current (ECC) is a good indicator for potential water consumption



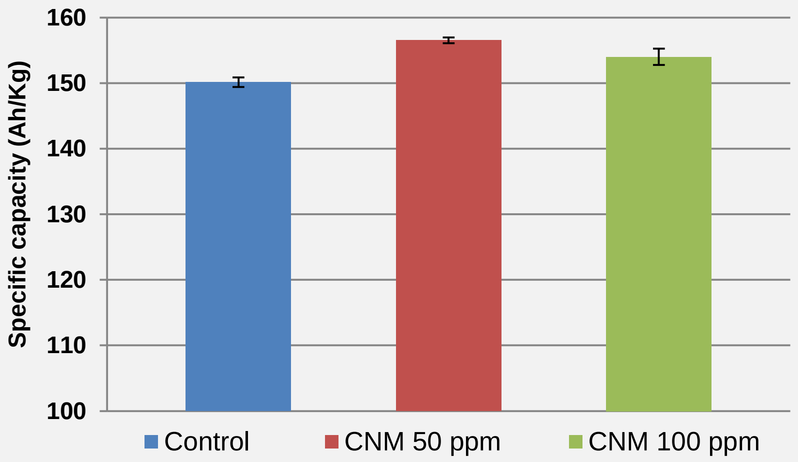
Experimental Results

Capacity at low rate (C20)

	Capacity (Ah)	S (Ah)	C20 vs. Control (%)
Control	22,2	0,07	100,0
50 ppm CNM	23,0	0,13	103,6
100 ppm CNM	23,3	0,19	104,7



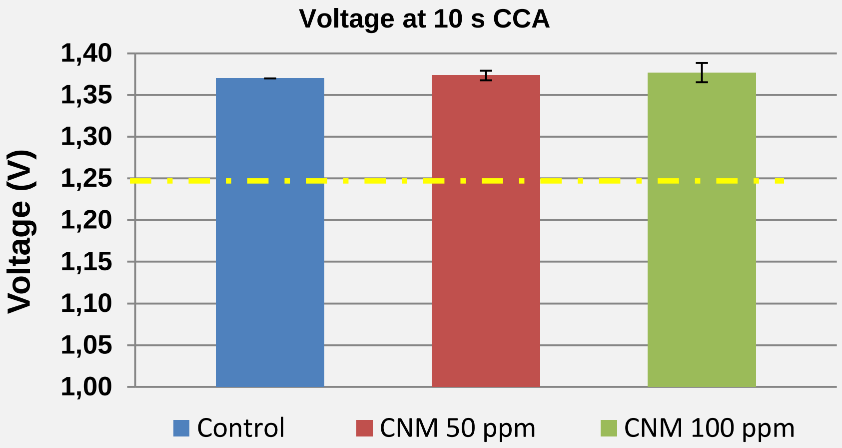
	Specific capacity (Ah/Kg)	S (Ah/Kg)	C20 vs. Control (%)
Control	150,1	0,73	100,0
50 ppm CNM	156,5	0,45	104,3
100 ppm CNM	154,0	1,25	102,6

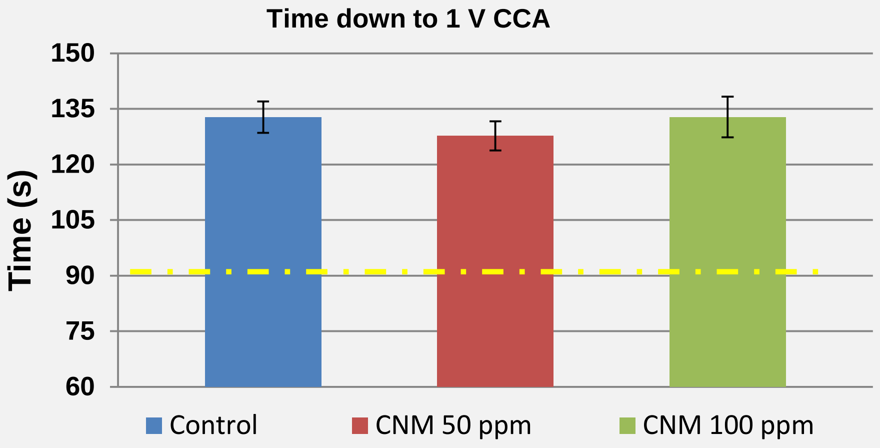


Experimental Results

Cold Cranking (EN Spec)

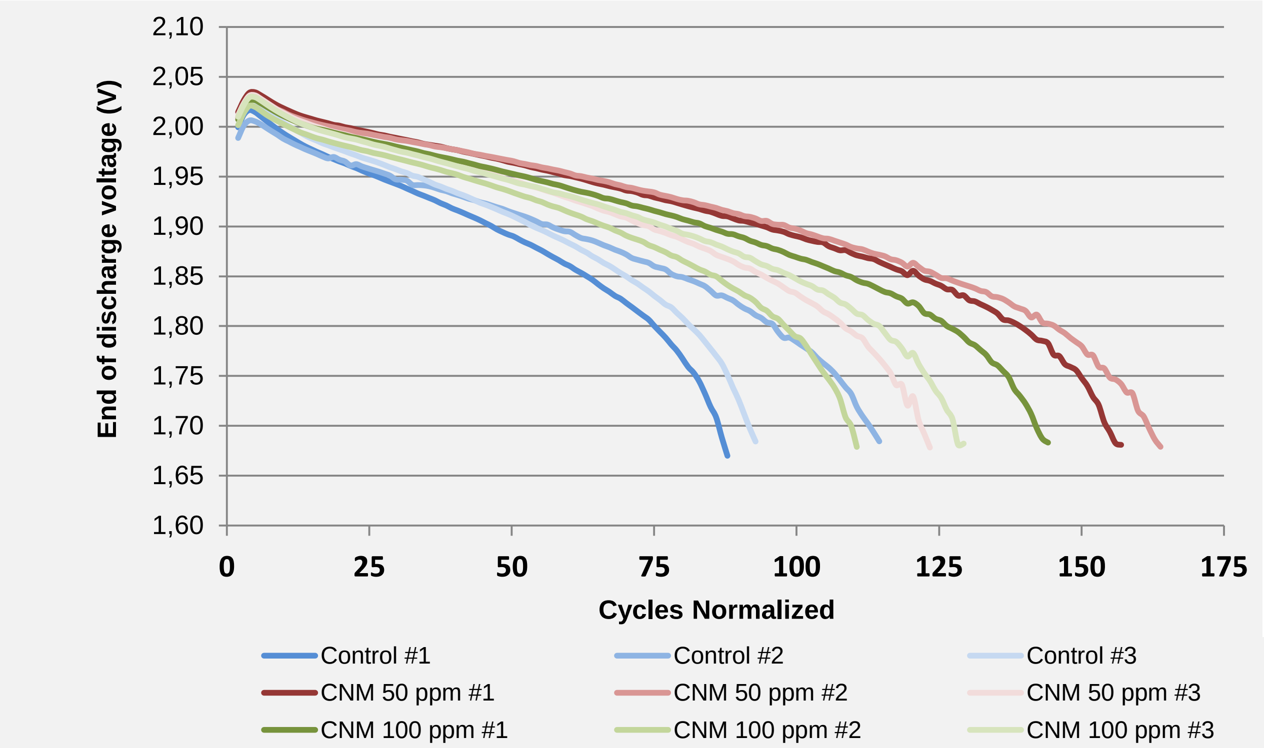
CCA at -18ºC	Time down to 1 V Mean (s)	SD (s)	Time down to 1V vs. Control (%)	V (10s)
Control	133	4	100	1
50 ppm CNM	128	4	96	1
100 ppm CNM	133	5	100	1

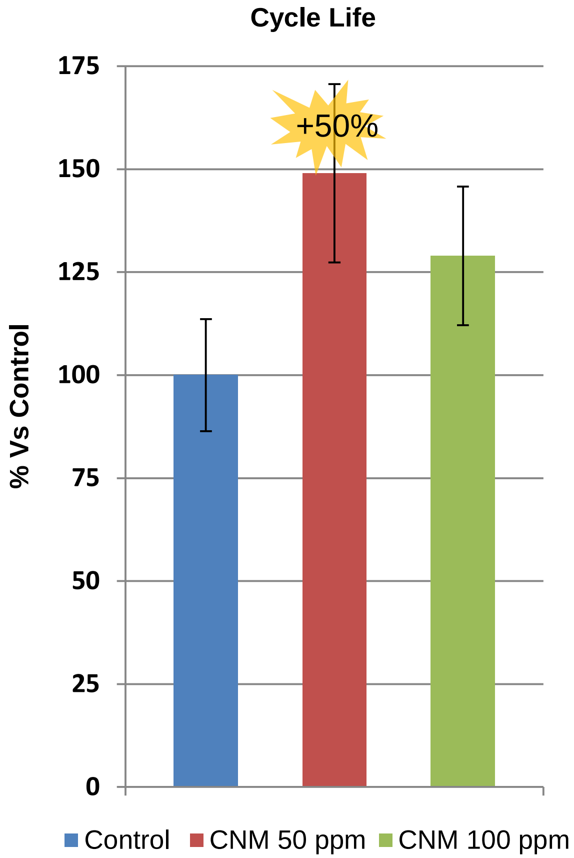




Experimental results

Cycling at PSoC





Experimental Results

Teardown Analysis after Cycling at PSoC

Chemical Analysis of Negative Mass					
	Lead sulfates (%)		Carbon (%)[1]		BET (m^2/g)
	Top	Bottom	Top	Bottom	
Control	3,3	69,4	0,9	0,7	1,04
50 ppm CNM	2,4	81,0	0,3	0,2	0,46
100 ppm CNM	3,4	73,1	0,3	0,2	0,52

Chemical Analysis of Positive Mass					
Lead sulfates (%)		PbO_2 (%)		BET (m^2/g)	Cycles (%)
Top	Bottom	Top	Bottom		
2,2	21,8	94,2	72,9	5,74	100
3,0	21,2	93,6	76,0	5,24	149
2,3	21,0	96,8	77,1	5,53	129

- Failure mode seems to be sulphation of NAM in all the cases
- Even having a higher surface (BET) at the end of life, Control cells had a shorter life than the ones containing Carbon Nanomaterials. This could be explained by the positive contribution of CNMs on NAM performance under Partial State of Charge (PSoC) duty

5a
Conclusions

Conclusions

CNMs into NAM

- The new NAM formula including Carbon Nanomaterial shows a better general electrical behavior than Control cells
- 2 V Cells with 50 ppm of CNM show remarkably better results in **Charge Acceptance (+27%)** and **Cycle Life (+50%)** vs. Controls. Capacity at low rate around 5% improvement
- Cold Cranking values between CNM and Controls are quite similar in terms of Voltage and Duration
- CNM formulas shows lower values of end of charge current

4.b

Experimental Results
High Specific Surface Area Carbon Cells

Experimental Design

High Surface Area Carbon into NAM

- In this experiment, a novel HSA Carbon material was studied vs. an optimized NAM formula intended for high charge acceptance performance
- This HSA material was tested at low, medium and high dosages
- After the mixing, “hand” pasting, 2 V cell assembly, curing and formation, negative plates containing HSA carbon were analyzed and we observed that **NAMs with the higher dosage of the new additive had a BET surface area more than double that of Control recipe**

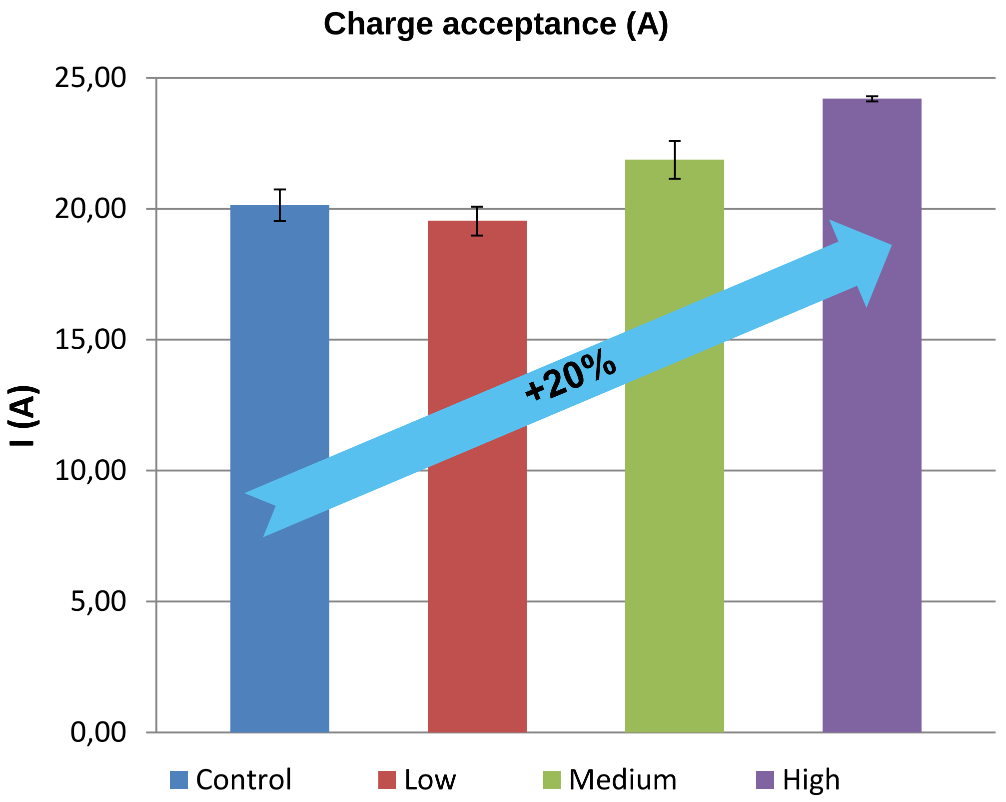
Experimental Results

Charge Acceptance

Dosage	Current at 5s at 2,42 V (A)	SD (A)	Vs. control (%)
Control	20,1	0,60	100
Low	19,5	0,55	97
Medium	21,9	0,72	109
High	24,2	0,10	120

Dosage	ECC* previous recharge (A)	ECC* of last recharge (A)
Control	0,354	0,338
Low	0,387	0,365
Medium	0,457	0,428
High	0,502	0,447

* End of Charge Current (ECC) is a good indicator for potential water consumption

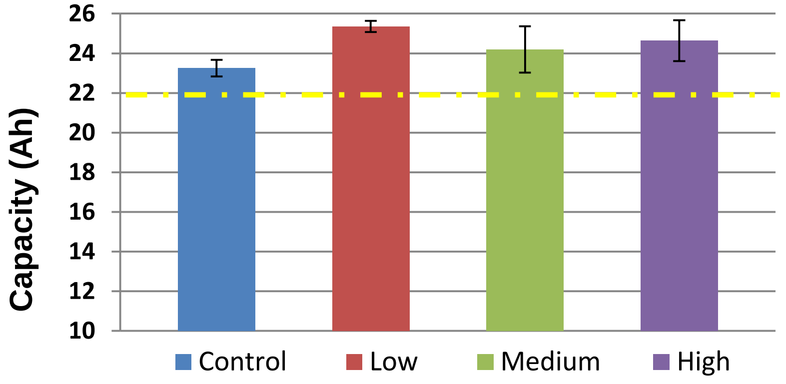


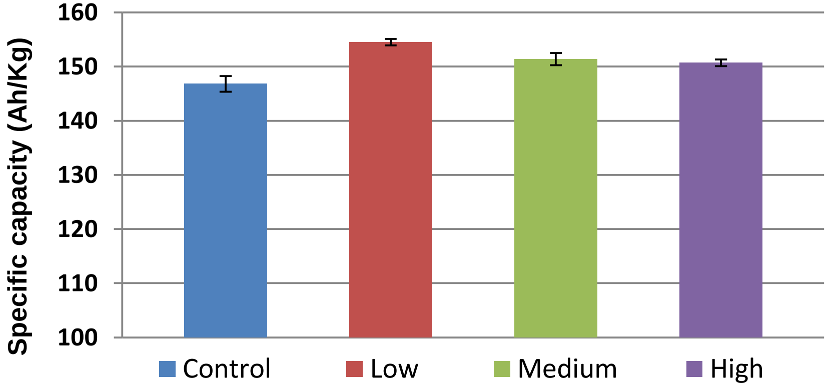
Experimental Results

Capacity at low rate (C20)

C20	Capacity (Ah)	S (Ah)	C20 vs. control (%)
Control	23,3	0,42	100,0
Low	25,4	0,28	109,0
Medium	24,2	1,17	104,1
High	24,6	1,03	105,9

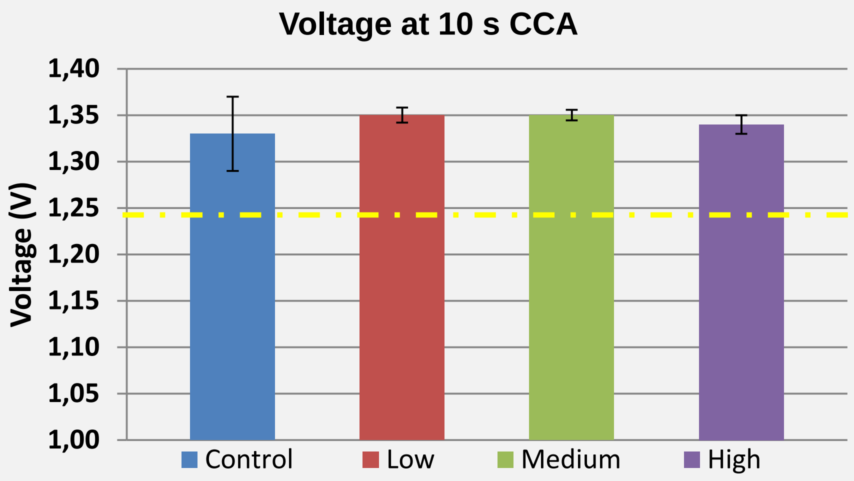
C20	Specific capacity (Ah/Kg)	S (Ah/Kg)	C20 vs. control (%)
Control	146,8	1,45	100,0
Low	154,5	0,60	105,3
Medium	151,4	1,13	103,1
High	150,7	0,63	102,7

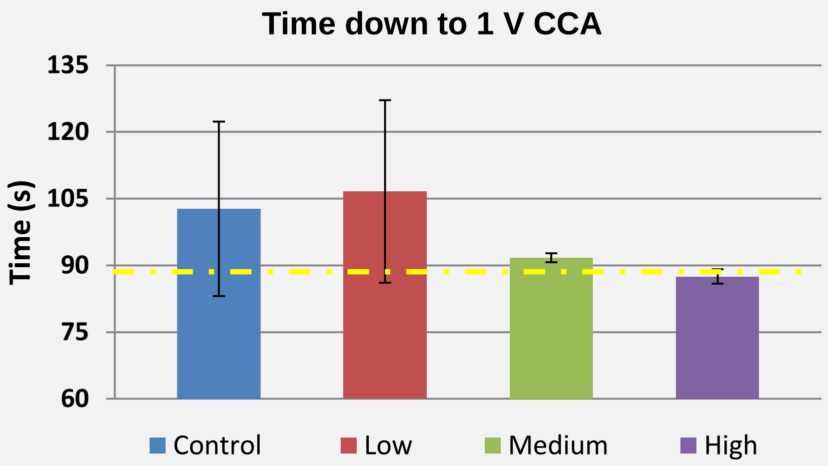




Experimental Results
Cold Cranking (EN Spec)

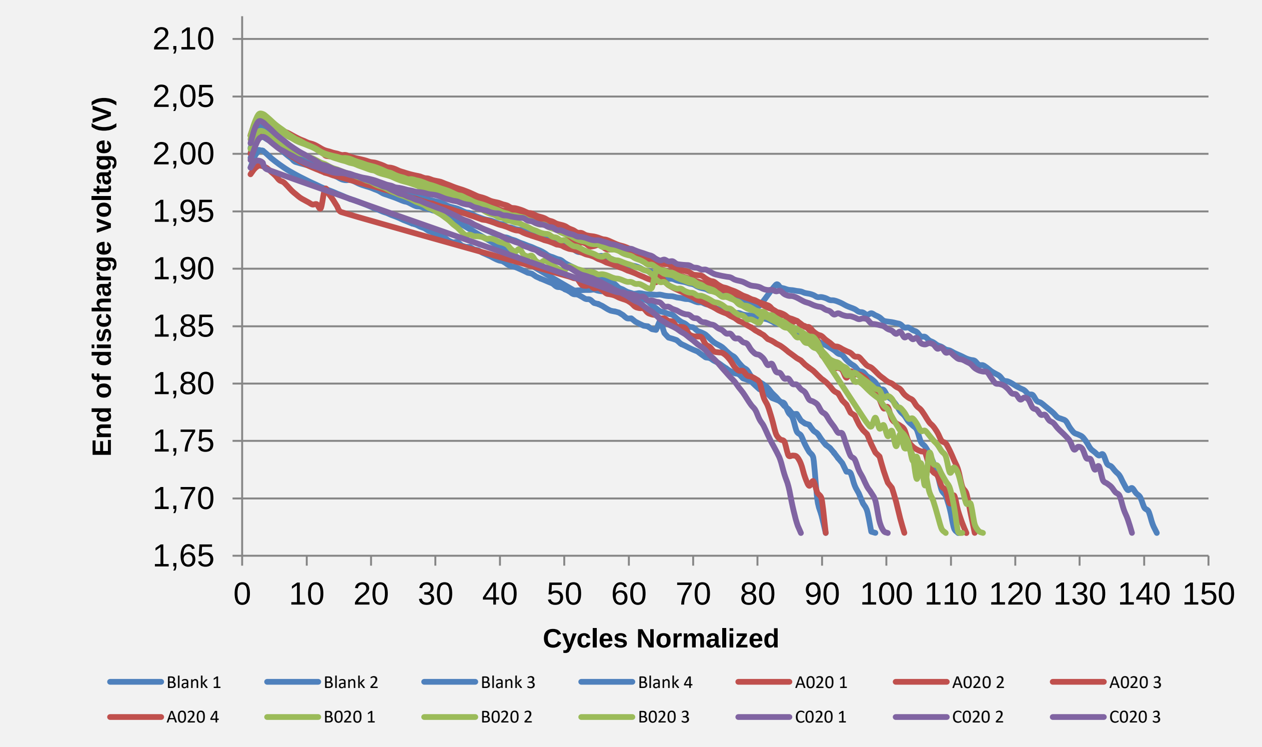
CCA	Time down to 1 V Mean (s)	SD (s)	Time down to 1V respect to control (%)	V (10s)
Control	103	20	100	1,33
Low	107	21	104	1,35
Medium	92	1	89	1,35
High	88	2	85	1,34

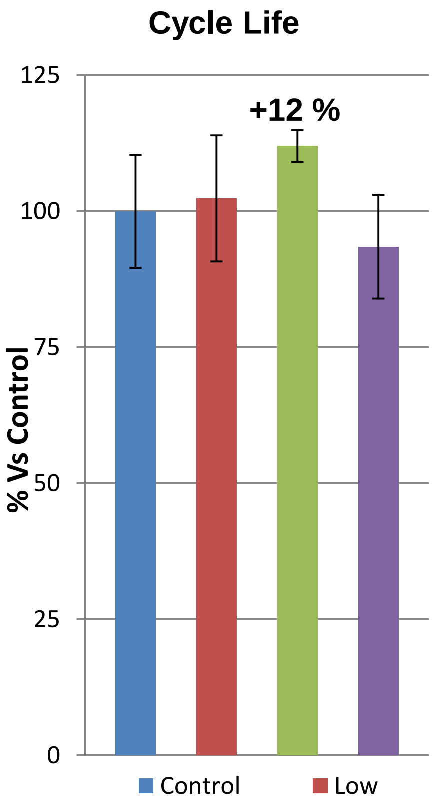




Experimental results

Cycling at PSoC





5b
Conclusions

Conclusions

High Surface Area Carbon into NAM

- The new formula including High Surface Area Carbon improves electrical performance vs. Control cells in some aspects, but also some negative impact has been observed
- **Charge Acceptance** is significantly increased **(+20%)** with the higher HSAC dosage
- Capacity at low rate (C20) is generally improved with the novel carbon (up to 9 %)
- Voltage at 10 s in CCA is similar for all the recipes, however the CCA duration is negatively impacted with the carbon addition at higher dosages
- In this particular case, since we have used as Controls negative plates with an optimized NAM recipe intended for high Charge Acceptance performance, the impact of HSA Carbon in PSoC life has been only moderate (**12 % higher** at medium carbon dosage)

Thank you!

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