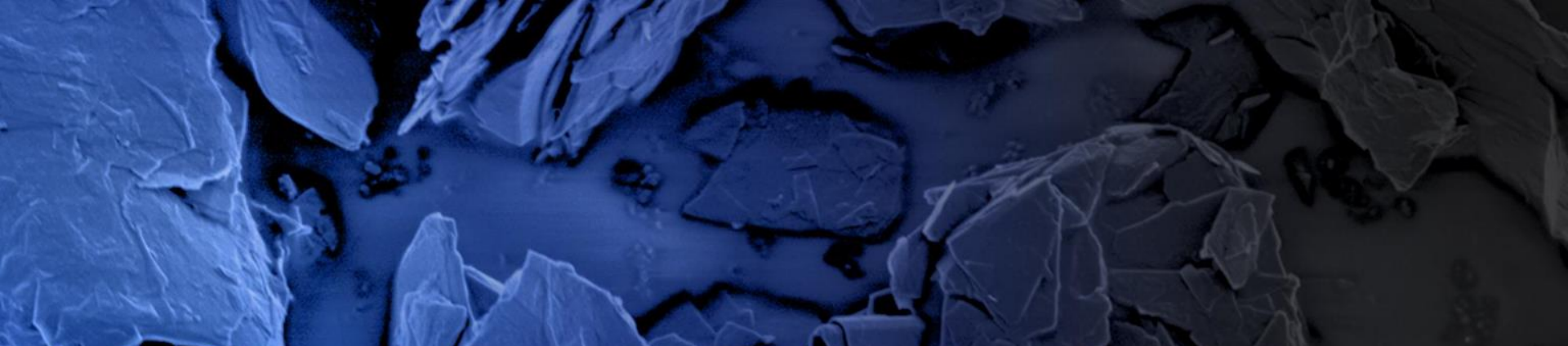


Imerys Graphite & Carbon

New Carbon Additives for Advanced Lead Batteries (ALAB)

P. García Pérez, G. Fieni, M. Duchi, D. Cericola

Presentation Date 19-09-2024

IMERYS

Contents

Section 1

- Carbon Addition to Negative Active Mass (NAM)

Section 2

- From Micro-hybrid to Auxiliary Batteries

Section 3

- Conclusions and Next Steps

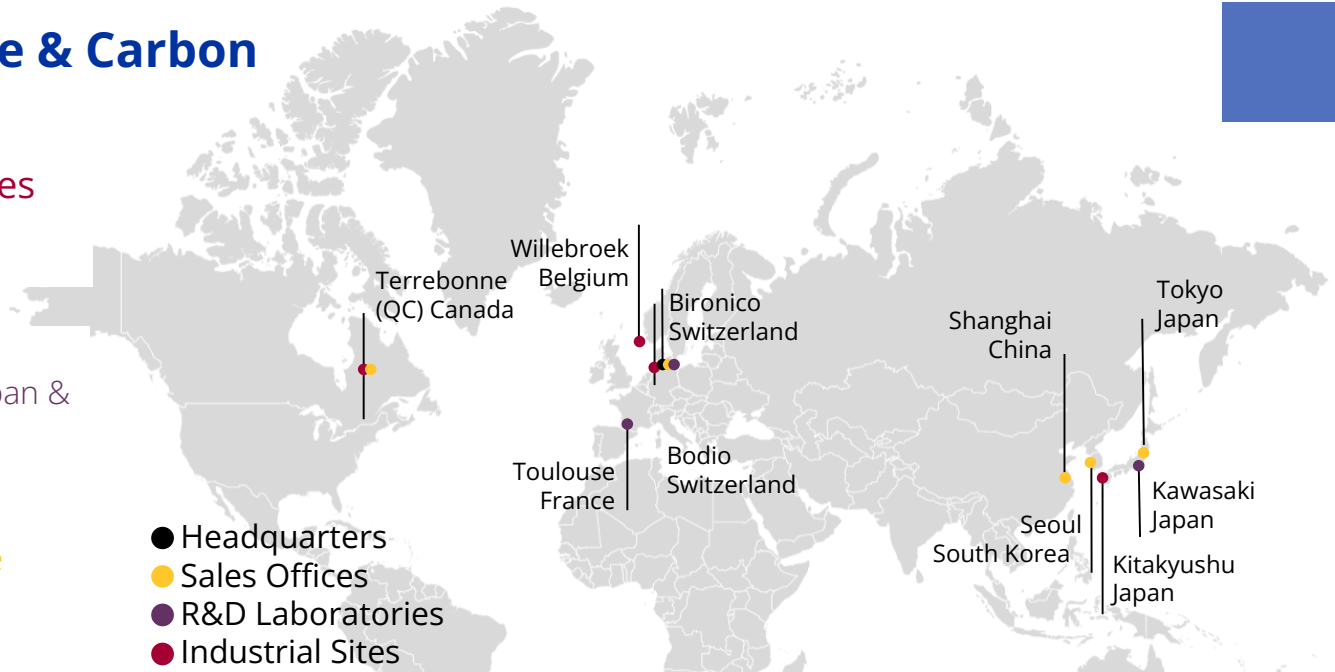
IMERYS Graphite & Carbon

Global Presence

4 Industrial Sites
For different materials

3 R&D Labs
Switzerland, Japan & France

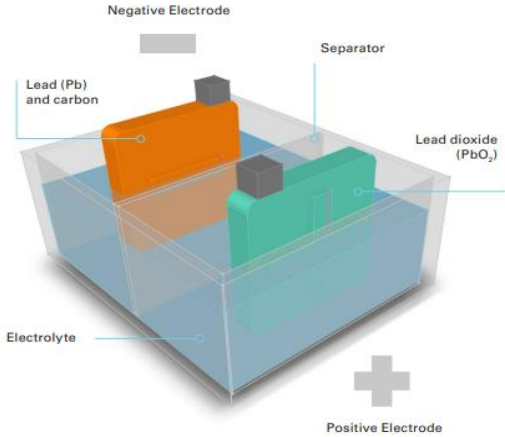
5 Sales Offices
Throughout the world



World leader in high-tech, high performance solutions based **on specialty graphites and carbons**
Unique supplier of three carbon materials: **synthetic graphite, expanded graphite and conductive carbon black**
Main end markets: automotive, energy and consumer electronics **(LIB, ALAB, fuel cells and alkaline batteries)**
Strong focus on ALAB application supported by our applicative tools and product portfolio

Carbon Addition to Negative Active Mass (NAM)

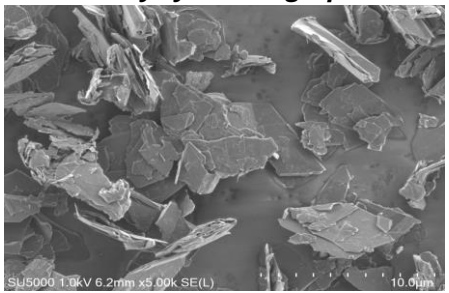
Carbon - Functionality and Requirements



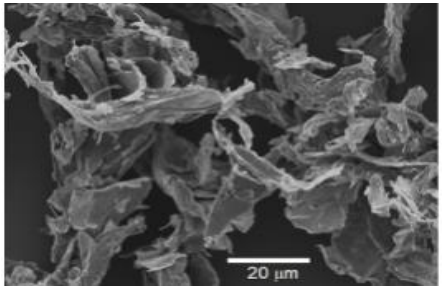
- Increase affinity to lead (nucleation points) for an efficient performance on NAM
- Increase electrical conductivity, reducing interparticle resistivity at the end of discharge
- NAM microstructure modification (specific surface / pore size) reducing sulfation
- Dynamic charge acceptance improvement - capacitor at short time recharge
- Cycle life - high rate partial state of charge and micro-cycling improvement
- High purity required to reduce water loss and self-discharge

IMERYS offers different carbon materials that cover these requirements

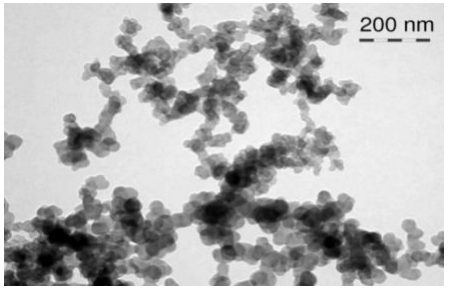
Primary synthetic graphite



Expanded graphite



Conductive carbon black



Carbon Addition to Negative Active Mass (NAM)

Carbon Properties

Carbon type	Graphite		Carbon Black
Properties	**Expanded graphite**	**Primary synthetic graphite**	**High structure conductive carbon black**
Purity (trace elements, ash)	Medium / high purity	High purity	High purity
	Elements impacting performance (water hydrolysis) - Fe, Cu, Co, Ni, Au, Pt, Re		
Structure (crystallinity, density)	High crystallinity	High crystallinity	Amorphous material (crystallinity level - primary particles)
Surface area (BET, oil absorption)	Low BET	Low / High BET	High BET
Size (PSD, density)	Microns	Microns	Primary particles - nanometers Aggregates - microns
Surface (surface chemistry, pH, BET, surface reactivity)	Acidic	Acidic	Usually Basic
	Surface chemistry, surface functional groups and pH properties can be modified		

Carbon Addition to Negative Active Mass (NAM)

Evolution of Requirements & Carbon Properties

Technology	Flooded Traditional solution (standard LAB batteries)	EFB / AGM Improved recharge (improved performance)	**EFB / AGM recharge, cycle life (higher performance)**	**Auxiliary batteries (EVs - 12V)**
Requirements	Depolarisation, electrical conductivity	First type start-stop batteries. DCA / water loss	Higher DCA, water loss and durability requirements	Charge acceptance / charge recovery
Market solution	Low structure carbon black	Expanded graphite / low structure carbon black	**High structure carbon black High BET SG**	**High structure carbon black High BET SG**
IMERYS grades	(CB) SUPER P® *	(EG) TIMREX® BNB 90 ; New SGs	(SG) TIMREX® CyPbrid™ 1; (CB) ENSACO® 350G; New CBs	ENSACO® 350G; New CBs

* SUPER P® : low BET ; high structure

Carbon Addition to Negative Active Mass (NAM)

Carbon Blacks Evaluated in this Study

Product	Reference (SLI)	Reference (EFB)	SUPER P®	RE - 488	ENSACO® 350G
BET (m^2/g)	30	175	65	135	780
Total pore volume (cm^3/g)	0.052	0.45	0.18	0.27	1.51
Ash (%)	0.02	0.03	<0.1	<0.025	<0.025
pH	6	8	7	10	9
Purity	++	++	+	+++	++

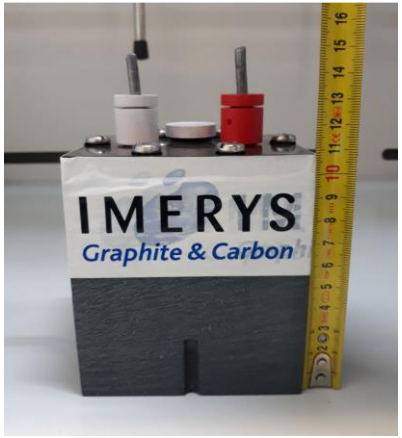
Reference 1 (low structure carbon black), Reference 2 and IMERYS grades - high structure carbon blacks

Carbon Addition to Negative Active Mass (NAM)

Performance Results - Type of Cells and Trials Performed

- **Flooded 2V batteries with H2SO4 excess**
- **PNP Configuration**
- **Trials performed with different carbons**
  - C20 normalised - EN-50342-1 2015
  - **DCA normalised - EN-50342-6 2015,** ISBAS 101
  - Cold cranking normalised - EN-50342-1 2015
  - **CA (EN-50342-1), CR-night, CR-weekend**
  - Peukert test
  - Tafel test

IMERYS lab cell size - 2V



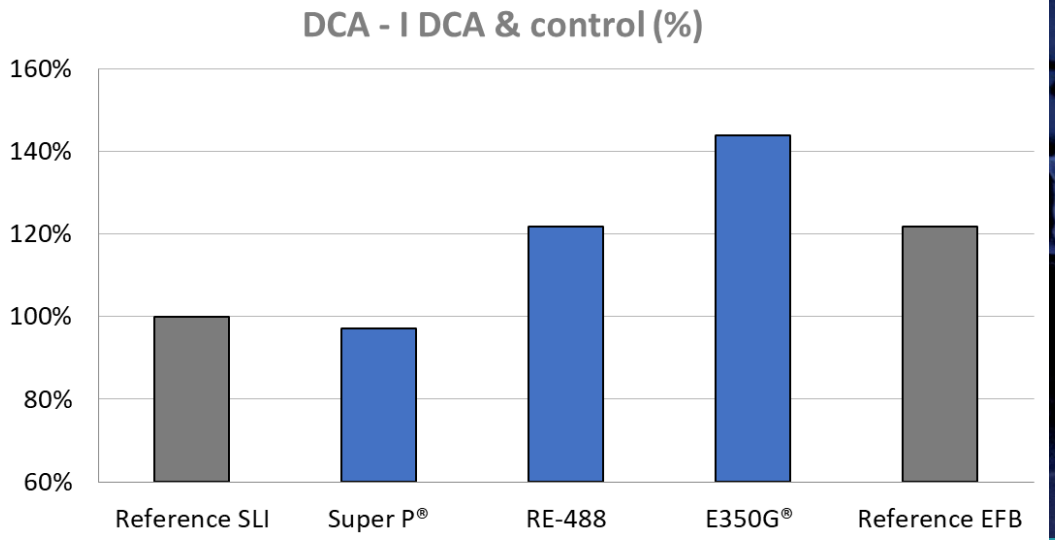
- **NAM additives & PbO:** Total (1.5%) - Lignosulfonate (0.34%); $BaSO_4$ (0.66%); Carbon (0.5%)

From Micro-Hybrid to Auxiliary Batteries

Dynamic Charge Acceptance - EN-50342-6 2015

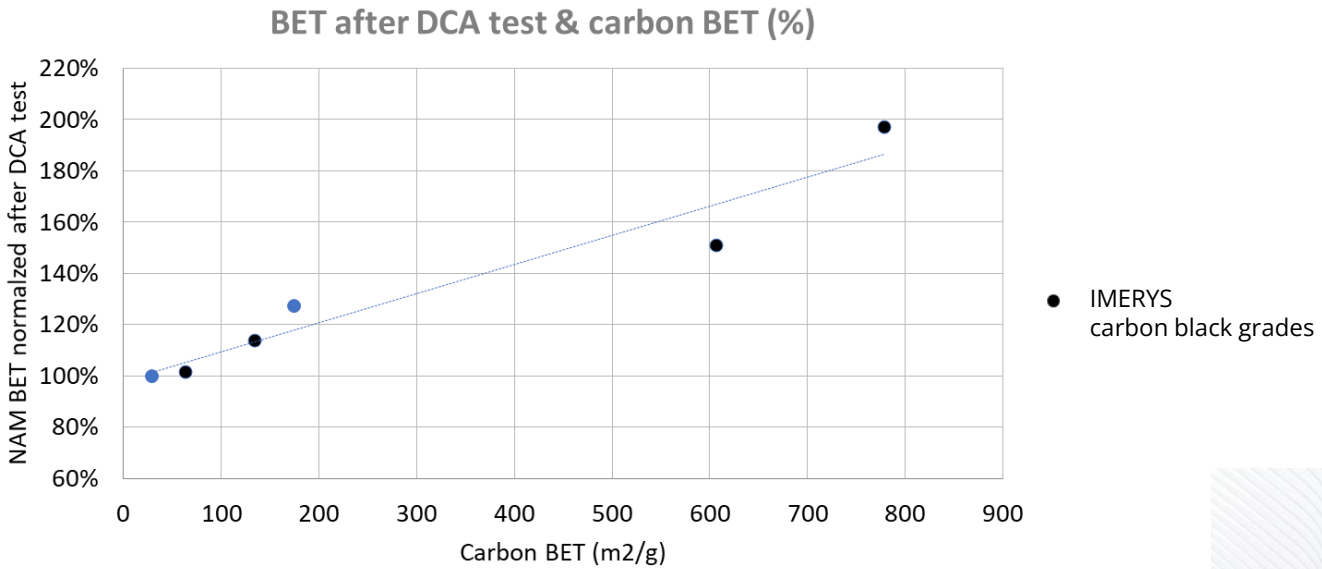
Dynamic charge acceptance (DCA) improves in function of the carbon black used.

- RE-488 performs much better than SLI reference material
- ENSACO® 350G presents the highest charge acceptance
- IMERYS can provide carbon blacks that cover low-end to high-end performance requirements



From Micro-Hybrid to Auxiliary Batteries

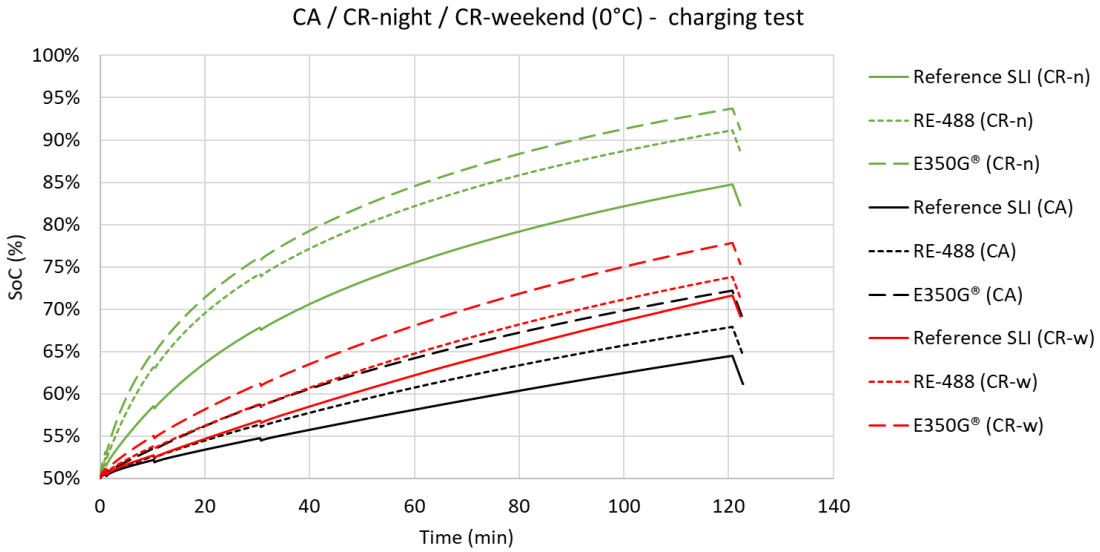
Dynamic Charge Acceptance - EN-50342-6 2015



- Carbon black BET modifies the microstructure of the negative plate.
- Increase in NAM specific surface allows for improved dynamic charge acceptance.
  - IMERYS carbon blacks are covering a large BET range providing the requested dynamic charge acceptance targets.

From Micro-Hybrid to Auxiliary Batteries

CA, CR-night, CR-weekend at 0°C - Normalised



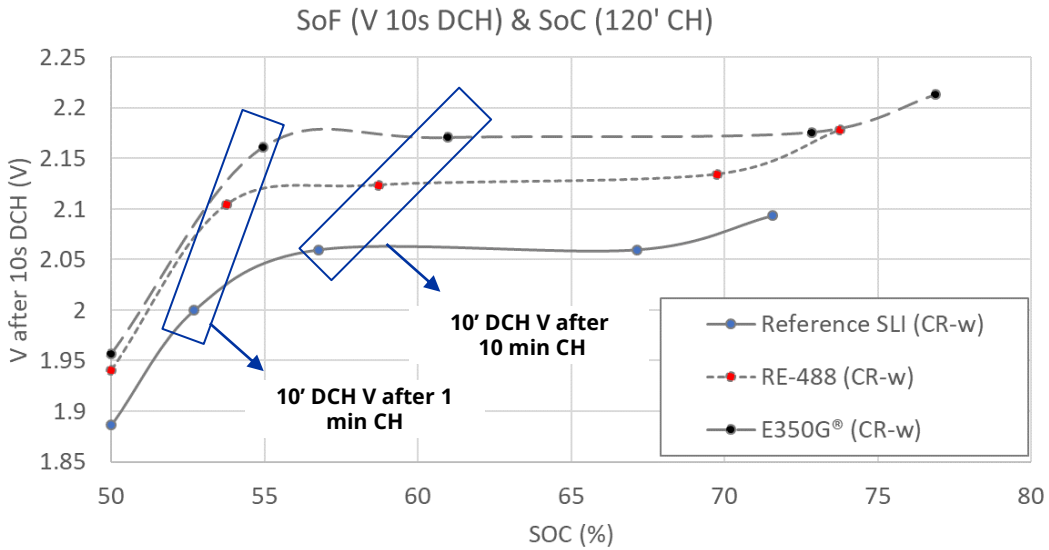
TEST VARIANT	Charge Acceptance (EN-50342-1)	Charge Recovery night	Charge Recovery weekend
CHARGE temperature	0°C	0°C	0°C
Initial condition	Fully charged at room temperature		
Discharge at room temperature	5hr by 50%	. /.	7.6hr by 38%
Discharge at CHARGE temperature	. /.	10hr by 50% (parking lights)	72hr by 12% (quiescent load)
Pause at CHARGE temperature	(only soak)	1’	1’
Charge test	2hr charging, interrupted by 10s, 1-C rate discharge tests after 1’, 10’, 30’, 120’		

- Carbon black type has an impact on final State of Charge (SoC) during 2 hours recharge step at 0°C.
- High BET carbon blacks like RE-488 and Ensaco® 350G show higher performance on SOC recovery.

IMERYS

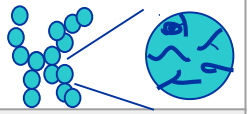
From Micro-Hybrid to Auxiliary Batteries

CA, CR-night, **CR-weekend** at 0°C - Normalised



- Carbon black type has an impact on State of Function (SoF) recovery during 2 hours recharge step at 0°C.
- Lower voltage drop (10 seconds pulse) after 1 and 10 minutes recharge is obtained with higher specific surface area carbons.

Conclusions

Carbon blacks					
	BET	Low	Low	Medium	High
	Structure	Low 	High 	High 	High 
	Grade	Reference SLI	Super P	RE-488	Ensaco® 350G
	Charge acceptance	↑	↑	↑↑	↑↑↑
	Water loss			↑	↑↑

- Charge acceptance performance is related to carbon black material properties (BET and surface chemistry).
- Charge recovery at 0°C for auxiliary batteries present different behavior in function of the carbon in the NAM.
- Imerys has developed new medium range BET carbon black grades completing our portfolio.
- RE-488 presents the best compromise between charge acceptance and water loss.

Next Steps

Experimental capabilities:

- Imerys is continuously researching, innovating and improving production efficiency to deliver beneficial product solutions to its customers.
- Development of new carbon blacks with new properties for ALAB is a focus activity for IMERYS (primary particles, aggregates size, BET, porosity distribution, surface properties).

ALAB application testing:

- Dedicate ALAB application laboratory to study
  - New carbon black developments (e.g. surface properties modifications)
  - New graphite grades developments (expanded & synthetic)
- New tools for data generation on auxiliary, energy storage.

Don't hesitate to contact us: pascual.garcia@imerys.com

IMERYS

Thank you for your time

Visit our website imerys.com
or connect via LinkedIn

Pascual García Pérez, PhD
R&D Team Leader
Application Development Alkaline and
Advanced Lead Acid Batteries

Tel : +41 (0) 91 936 1241
Mobile: +41 (0) 79 398 0779
E-mail : pascual.garcia@imerys.com

Imerys Graphite & Carbon
Via Cantonale 65 | 6804 Bironico | Switzerland