Séminaire ASPROM

21 novembre 2017

Les Batteries du Futur : le silicium ?

nanomakers

Materials booster

Develop, produce & sell
Silicon-based nanopowders that **disruptively improve** the properties of industrial **materials**

Continuous Innovation

Continuous Innovation

- A spin off of cea (2010)
- The technology is protected by several CEA patents, granted with exclusive rights to nanomakers
- which pursued innovating and filed several own patents :

Patent Title	Grant dates	Filing dates
"Method for producing multilayer submicron particles by laser pyrolysis" : coated particles (SiΩC)	juin 2015 (France)	Juillet 2012 (France) Juillet 2013 (PCT)
"Submicron particles containing aluminium" : SiCΩAl		Nov. 2013 (France) Nov. 2014 (PCT)
"Method for producing a polymer based material"		Sep. 2015 (France)
"Valve and sealed container for submicron particles, and method for using same" : Safe Containers and NanoAirlock valves	sept. 2016 (Japan)	Nov. 2011 (PCT) Nov. 2012 (France)
"Suspension system for sub micron particles in a liquid, and method for using same" : Safe Containers external pump system		Février 2013 (France)

NM Si 99 Ω C

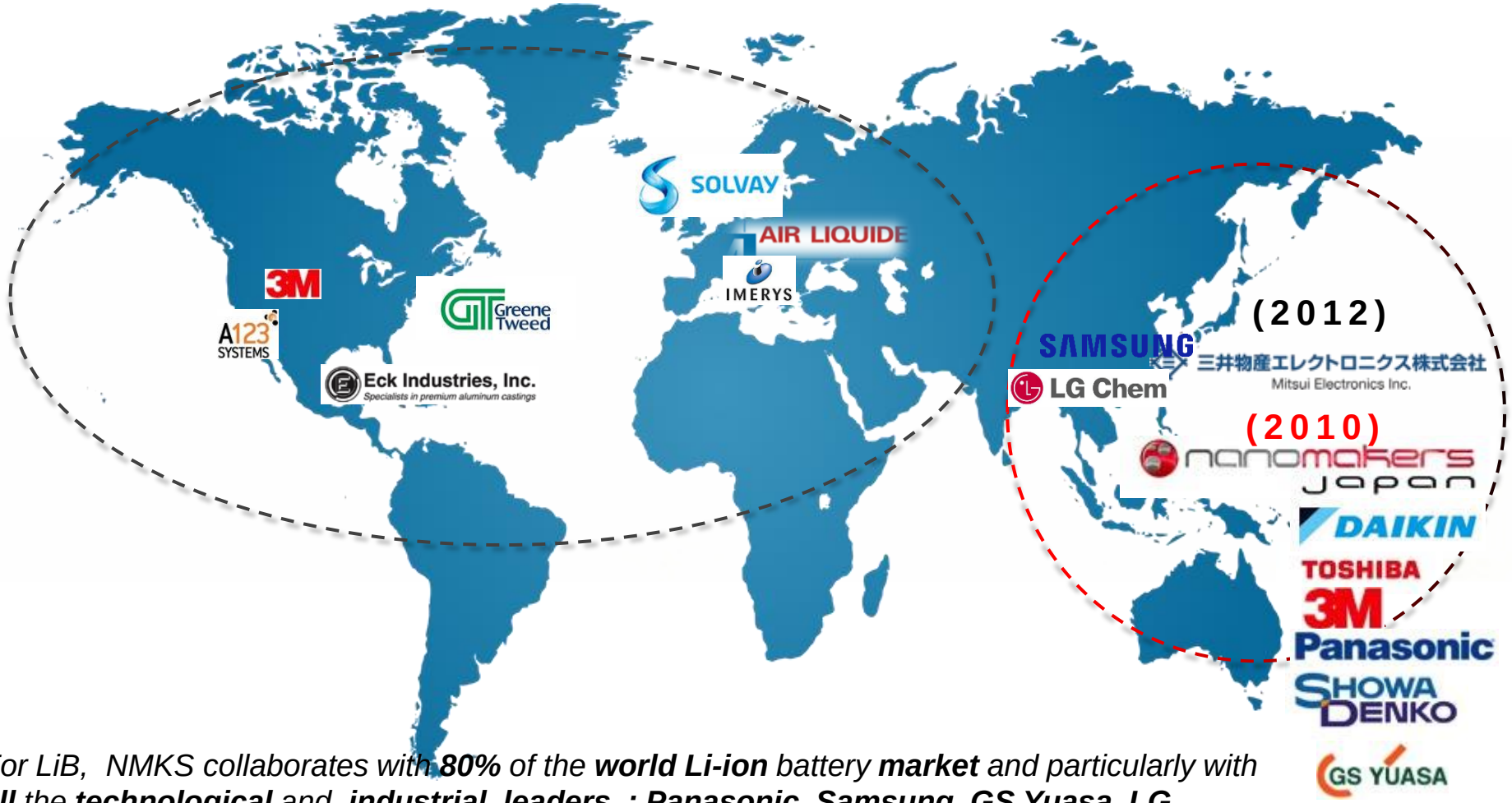
INNOVATION 2030
CONCOURS MONDIAL D'INNOVATION
Construisons l'avenir en France.

NM SiC 99 Ω Al

inpi INSTITUT NATIONAL DE LA PROPRIÉTÉ INDUSTRIELLE

Continuous Innovation

nanomakers with & for **global partners**



*For LiB, NMKS collaborates with **80%** of the **world Li-ion** battery **market** and particularly with **all** the **technological** and **industrial leaders : Panasonic, Samsung, GS Yuasa, LG Chem…** and their suppliers*

Highest quality process & products

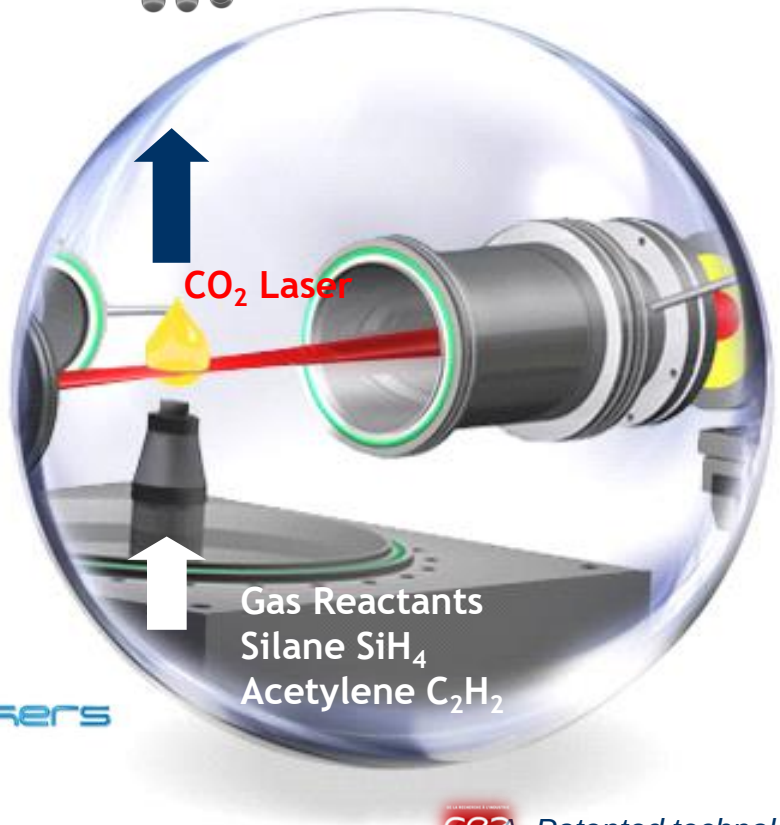
Highest quality process & products

Precise, reliable and secure technology … guarantee of results

Laser pyrolysis process:

1. The laser beam breaks the molecules of gaseous or vapor–phase precursors
2. Nanoparticles start building up abruptly
3. Particle size is controlled by a fast quenching which stops the particle growth

SiC, SiΩC / Si nanopowders



Experience and expertise:

- 33 years of CEA know how
- 7 years at pilot scale
- 5 years at industrial scale

Patented technology

Highest quality process & products

Various value propositions … under different forms

SiΩC | NM Si 99 Ω C

Very High Purity
(20 - 100 nm)
internally patented

SiC

NM SiC 99

Very High Purity
(15 - 100 nm)
Mass production

NM SiC 97

High Purity « Mass Market »
(30 - 100 nm)
under devt

Valu

Flowing powder

Granulated powder

Suspension

Highest quality process & products

Laser pyrolysis nanomakers … 4 advantages

Homogeneous :
Low particle size deviation.

Pure :
High purity batches, low O2 & metallic content

Reproducible :
Similar particle size distribution, chemical composition from one lot to another.

Customizable:
Size, Surface, Coating

*Our **customers** say* (**Eck Industries (USA),** April 2014) **:**

« First of all the **quality** of the powder received from Nanomakers was **very good**. The particle **distribution** was **very tight** and there was **no** apparent chemical **contamination**. From a practical aspect that means better incorporation into the melt and shorter processing times to get an acceptable particle distribution. I do not hesitate to say the **Nanomakers SiC** is the **best on the market**. »

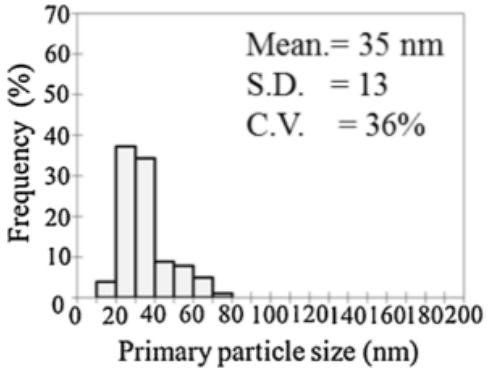
Highest quality process & products

Superior quality recognized … by **experts** :

Kazuya Shimoda and Takaaki Koyanagi
NIMS - National Institute for Materials Science, Ibaraki and **Kyoto** University, Kyoto

nanomakers **n°1**

- IEST - Institute of Energy Science & Technology Co. Ltd., **Japon**
- Marketech International Inc., **USA**



regarding :

- **Particles size distribution**,
- **C/Si ratio**,
- **Impurities** content and **O2**,
- **Industrial** production **capability**

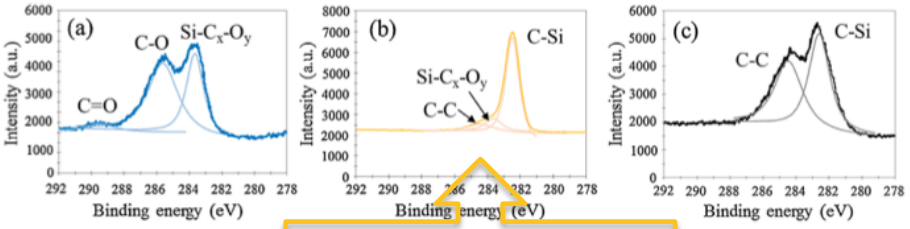


Fig. 7. XPS spectra of C 1s peak for (a) SiCN-1, (b) SiCN-2, and (c) SiCN-3.

In :
« Surface properties and dispersion behaviors of **SiC nano**powders »,
in Colloids and Surfaces A: Physicochem. Eng. Aspects 463 (**Sept. 2014)** 93

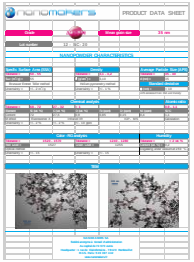
An Industrial Company

An industrial company

Industrial production facility in Rambouillet … since 2012

- **10-20 t/year**
- Storage & distribution AIR LIQUIDE **for 200+ t/year**

- **Quality control**
- Procedures, Certificate of Analysis
- Own control lab
- ISO 9001



- **« no contact » Strategy**
- for small and larger quantities

Creating value for our customers

Creating value for our customers

Examples of applications: mech & chem **reinforcement / batteries density**

PRODUCT	MATERIAL improved	APPLICATIONS	MARKETS	LOAD nano SiC	VALUE PROPOSITIONS nanomakers
SiC 99 NM SiC 99	Perfluorolastomers marketed	Very high performances seals	Semi-Conductors (Production equipment)	10-20%	Purity (ppm) Chemical resistance Seal lifetime Eqpt. reliability & availability
SiC97 NM SiC 97	Fluoroelastomers	High performances seals	Aerospace, Automotive	5-20%	Mechanical performances Seal lifetime
SiC99, SiC97 NM SiC 99 NM SiC 97	Aluminum	Structure Envelope	Aerospace, Defence, Automotive	2-5%	Lighter vehicle (-30% aluminum mass) Carbon footprint
SiC99, SiC97	Metallic, plastic or composite powders	Additive manufacturing	Aerospace, Automotive		Mechanical performances
SiΩC99 NM SiΩC 99	Anodes INNOVATION 2030 CONCOURS MONDIAL D'INNOVATION	Li-ion batteries	Electric vehicles Mobile communication	15-30%	**Energy density (x 2)** Patent n°13 63098

Creating value for our customers

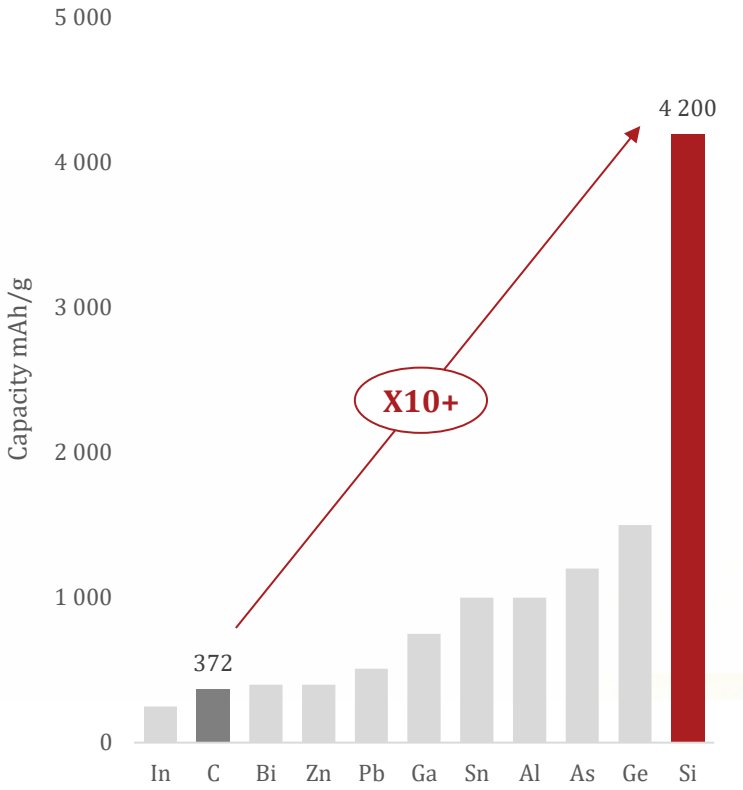
Application for Lithium-ion Battery

The industry consensus around silicon-based anode material

- Strong demand for innovation with major R&D efforts aiming at:
  i. **improving density** (autonomy)
  ii. improving lifetime
- Technical improvements have mainly taken place on the cathode material so far
- Industry research efforts currently cast on **improving anode capacity** using **silicon** instead of graphite, multiplying energy storage but generating **two major challenges**:

Cracking ***Oxidation***

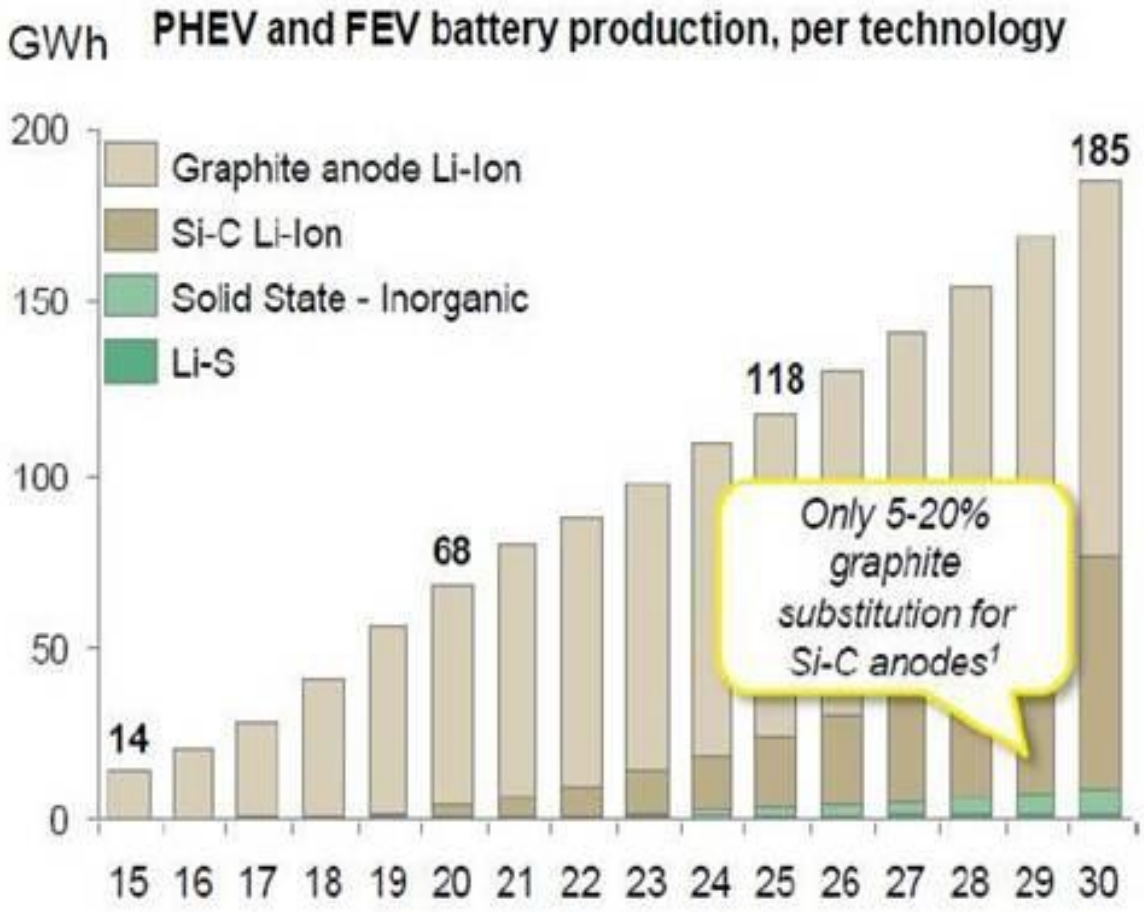
Silicon performances vs. carbon



*Solving the cracking and oxidation issues are **key enablers** for the **commercialization** of **new generation** Li-ion **batteries : NM SiΩC***

Market study for Lithium-ion Battery

nano-Si in post-Li-ion, too

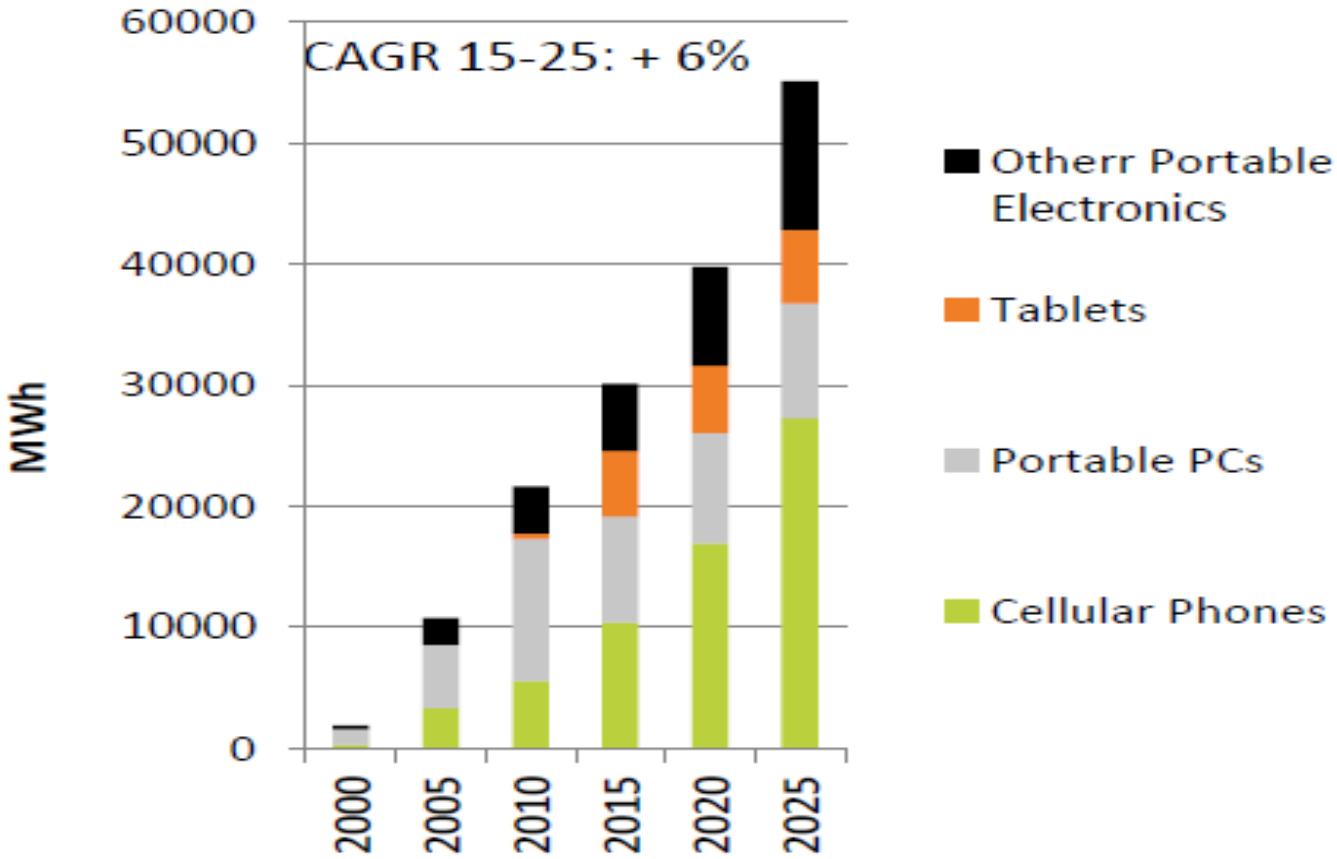


source: BCG Study

… and then far beyond 2030

Market study for Lithium-ion Battery

2000-2025 LIB market, MWh, by application (3C)



Source: Avicenne Energy

Market study for Lithium-ion Battery

Perspectives nano-Si @ 2030 (tpa)

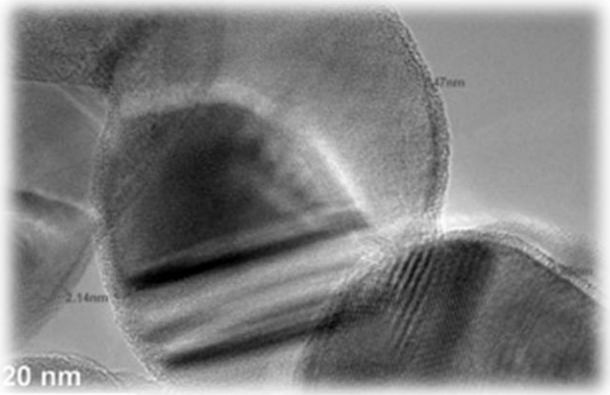
Forecast	2020			2025			2030		
Target markets	**Anode material (ton)**	**Composite Si-C (ton)**	**% Si-C in overall power**	**Anode material (ton)**	**Composite Si-C (ton)**	**% Si-C in overall power**	**Anode material (ton)**	**Composite Si-C (ton)**	**% Si-C in overall power**
EV	62 468	1 750	7%	93 701	7 000	16,6%	109 318	24 500	37,4%
3C	40 000	2 000	5%	55 000	5 500	10%	64 000	21 120	33%
Other niche markets	8 000	1200	15%	12 000	3 000	25%	14 000	8 400	60%
	110 500	4 950					187 318	54 100	

CAGR = 5,5 % (AM) / 27% (Si-C)

Tonnage calculated based on graphite with a capacity of 300 mAh/g and Si-C composite with a capacity of 800 mAh/g

Batteries of the future

NM SiΩC99 Product features:



- Silicon nanoparticles with carbon coating
- Different sizes:
  - 40 nm
  - 75 nm
- **Uniform amorphous carbon coating of 1-2nm**
- **High purity**
- **Homogeneous** particle **size distribution**
- **Crystalline silicon core –** mainly **amorphous carbon** shell
- **Low oxygen** content (< 2 % wt)
- **No SiC**

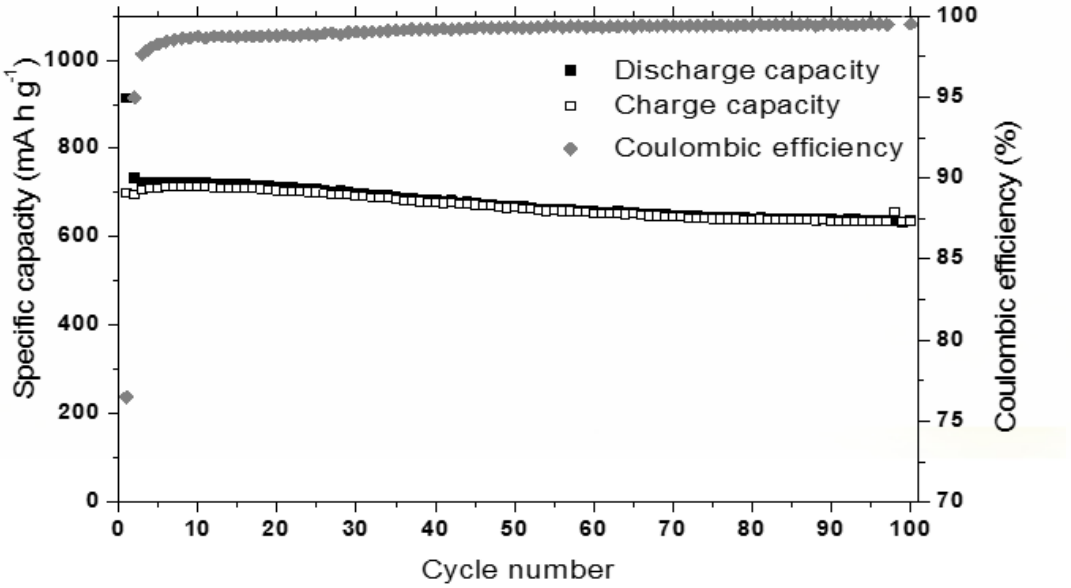
NM SiΩC99 (intrinsic) **Product Advantages:**

- **Silicon's lithium storage** capacity potential of more than **10X** that of graphite (4000 instead of 400 mAh/g) enables high energy densities.
- Our novel nanocomposite **SiΩC overcomes** the **limitations** of pure or bulk **Si** (cracking and oxydation)
- **Carbon** shell **i) protects Si** from direct **electrolyte** exposure, **ii)** favors the creation of a **stable SEI** layer, and **iii)** improves the **affinity of Si** with most **graphites** and **binders** (CMC, PVDF…).
- **Chain like** structure enables high electronic and ionic **conductivities** of SiΩC.
- Softness and compliance of low crystallized carbon allows **SiΩC** to **change shape** and size without failure.

NM SiΩC99 Product Advantages (in composite) **:**

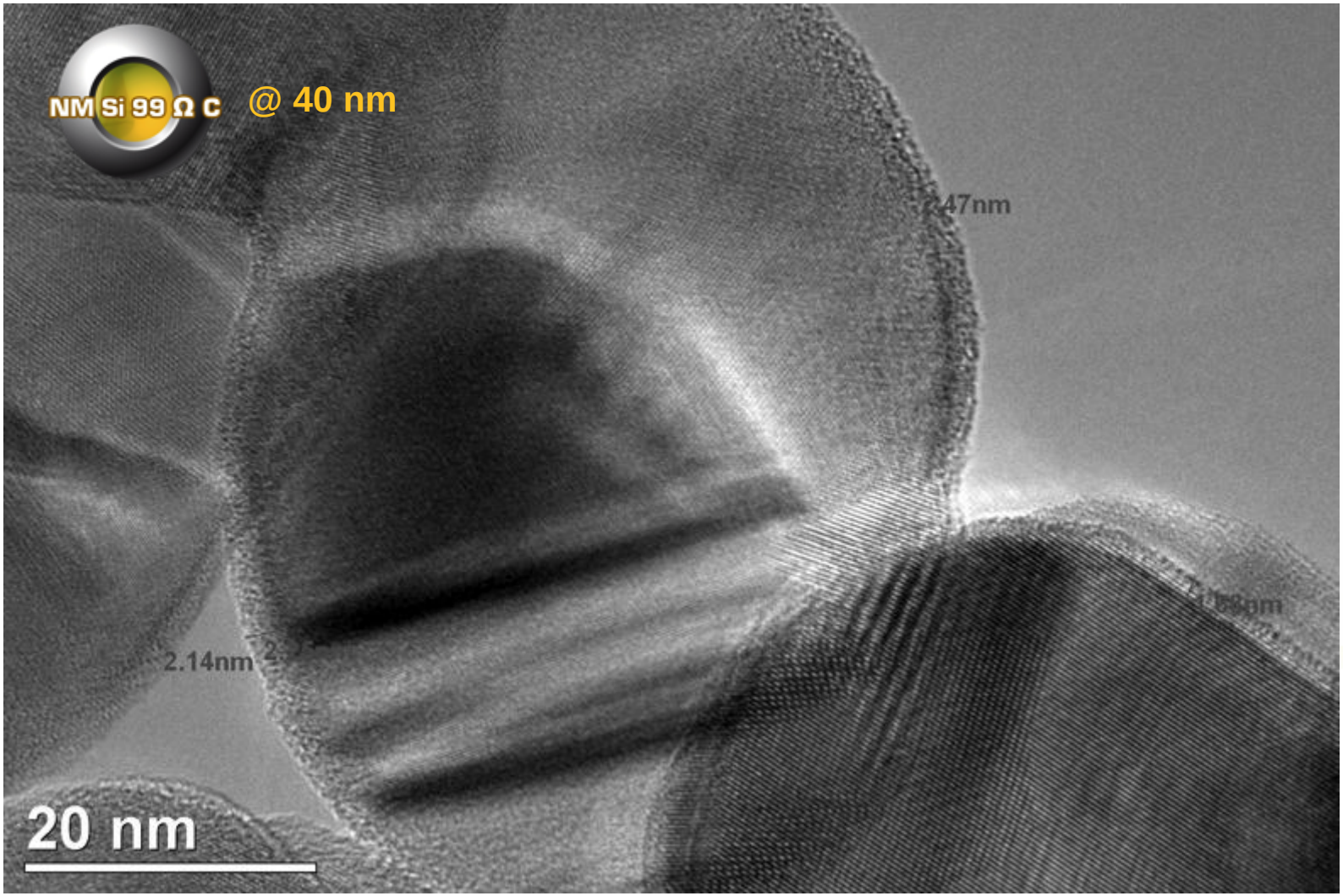
- Anode performance is improved when using a **structured Graphite/n-Si composite**, which offers significant improvements in both the **specific capacity** and the volumetric capacity over commercially used graphite.
- Such composites show **excellent cycling performance** and **first irreversible** capacity.

Half cell versus metal Li
SiΩC99 composite (80) : VGCF (2,5) : Super P (2,5) : CMC (15)
Total Si content : 16%
Grammage : 2 mg.cm-2
Electrolyte EC:PC:DMC 1:1:3 + 1wt%VC + 5wt%FEC + 1M LiPF6
Lithiation CCCV to 10 mV
Delithiation CC 1,5 V
Rate : C/5 (first cycle C/20)



- The superior electrochemical properties are attributed to the **uniform distribution** of **nano-sized Si** phase, the protecting and buffering action of graphite and an **enhanced** electronic and ionic **conduction** by carbon-coating.

Batteries of the future



MERCI

pour votre attention !

nanomakers

> When infinitely small makes a difference :

the « **Nano effect** »

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