Carbon Materials for Li-Ion Battery: Features and Benefits

Frühjahrstagung des Arbeitskreises Kohlenstoffe
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IMERYS
TRANSFORM TO PERFORM

Carbon Materials for Li-Ion Battery: Features and Benefits

Outline

- Introduction of IMERYS
- Introduction of IMERYS Graphite & Carbon
- Electrochemical Cell – Li-Ion Battery
- Carbon black and Graphite conductive additives for the positive electrode
- Specialty Graphites for the negative electrode
- Carbon-based current collector coating

IMERYS Introduction

Imerys, the world leader in mineral specialties for industry

- Created in **1999** out of the **industrial minerals** activity of **Imetal** (French group)
- **+16,000** employees
- **250** industrial sites in **+50** countries
- **8** main R&D centres - 25 regional laboratories - **400** scientists and technicians
- 2015 sales ➔ **4,087 M€**
- **+30** minerals including bentonite, calcium carbonate, feldspar, graphite, kaolin, mica, talc and wollastonite

Imerys products, finding applications in everyday life

- Automotive, Industrial Equipments
- Energy
- Electronics
- Construction
- Decorative Materials and Fittings
- Steelmaking and Metallurgy
- Agri-Food
- Paper
- Packaging
- Health, Beauty and Care
- Horticulture, Protection of Flora

IMERYS Graphite & Carbon

IMERYS Graphite & Carbon Introduction: History

- **1908** Officine del Gottardo is founded
- **1917** Synthetic Graphite manufactured for the first time
- 1924 Acquisition of Officine del Gottardo by LONZA Ltd.
- **1982** Willebroek plant (under Erachem group) starts producing Conductive Carbon Black
- 1989 Stratmin Graphite starts mining natural graphite in Canada
- **1994** LONZA G+T is acquired by IMETAL and becomes **TIMCAL Ltd**
- 1995 TIMCAL America is founded
- 1997 Changzhou TIMCAL Graphite Corp. is established in China
- 1999 IMETAL changes name to IMERYS; TIMCAL and Stratmin are combined into TIMCAL Group
- 2000 TIMCAL Japan KK and TIMCAL Germany are set up
- 2001 TIMCAL Fuji facility opens in Japan
- 2002 Stratmin becomes TIMCAL Canada; Terrebonne plant opens
- **2003** TIMCAL acquires the Carbon Black activities at Willebroek, Belgium
- 2005 TIMCAL representative office in the UK is launched
- 2007 TIMCAL acquires 85% of Baotou Jing Yuan Graphite Co in China
- 2008 TIMCAL celebrates 100 Years of Production in its Swiss plant Bodio
- 2010 TIMCAL representative office in Singapore is launched
- **2014** TIMCAL changes its name to **Imerys Graphite & Carbon**
- 2015 Imerys Graphite & Carbon opens a R&D Center in Japan

IMERYS Graphite & Carbon Introduction: Our Markets

Main Fields of Application for TIMCAL Carbon Powder-Based Solutions

Mobile Energy

- Alkaline Batteries
- Zn-C Batteries
- Li - Batteries
- **Li-ion Batteries**
- Lead Acid
- Fuel Cells
- Supercaps
- Can Coatings

Engineering Materials

- Friction Materials
- Powder Metallurgy & Hard Metals
- Carbon Brushes
- Foils
- Ceramics
- Pencils
- Catalysts
- Synthetic Diamonds
- Powders for Lubricants

Polymers

- Conductive Plastics
- Conductive Rubbers
- Power Cable Compounds
- Filled PTFE
- Conductive Coatings & Paints

Refractories & Metallurgy

- Refractories
- Crucibles
- Hot Metal Toppings

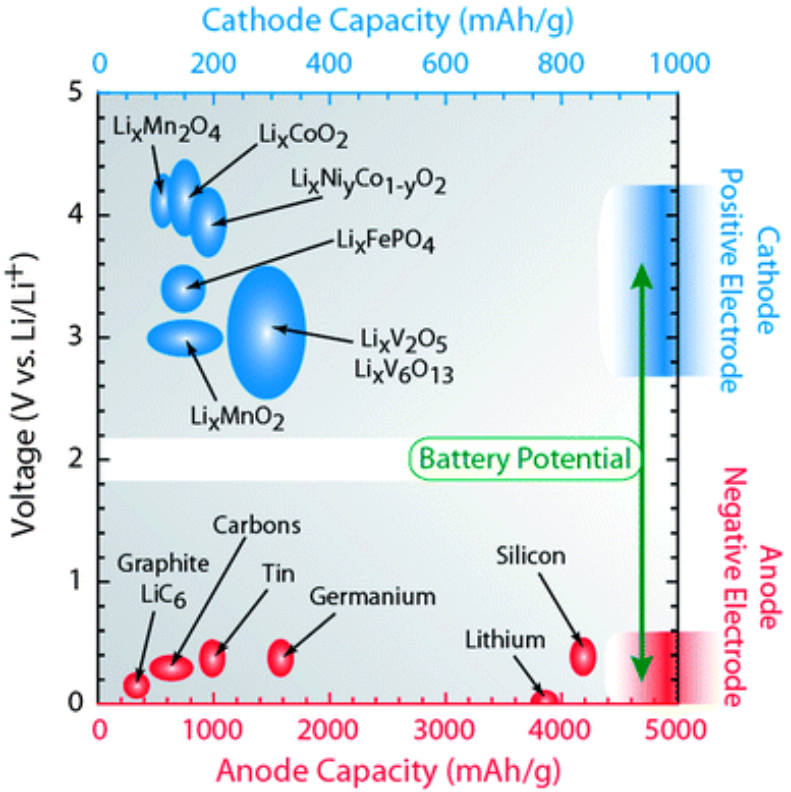
IMERYS Graphite & Carbon Introduction

- Manufacturing Plants

Electrochemical Cell – Li-Ion Battery

- Introduction: Li-Ion Battery

- Negative Electrode – Anode
  - **Graphite**
  - Hard Carbon
  - $Li_4Ti_5O_{12}$ (LTO)
  - Silicon
  - Tin
  - SiO_x
  - Metal alloys
  - …

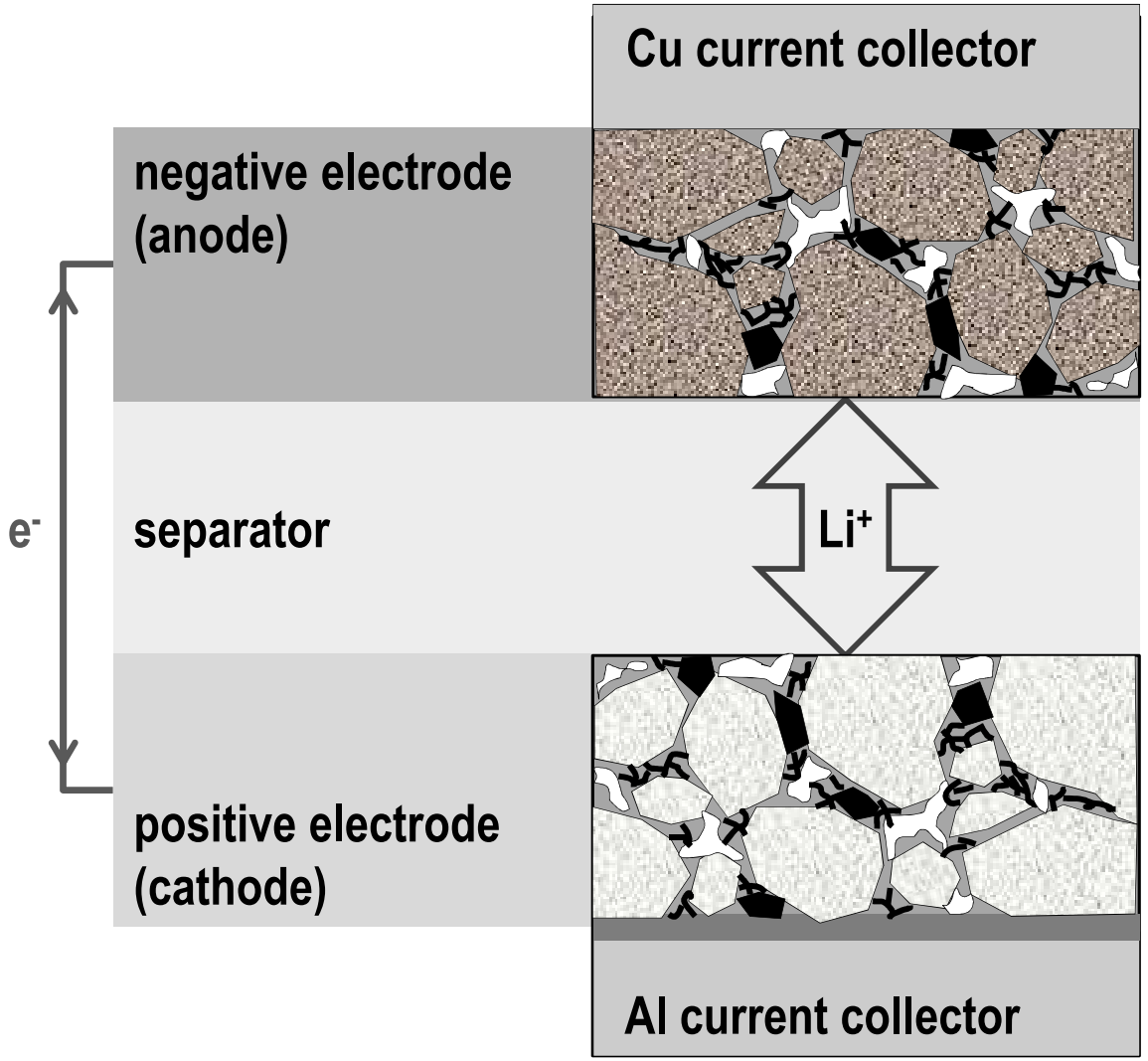


Energy Environ. Sci., 2009,**2**, 638-654

- Positive Electrode – Cathode
  - $LiCoO_2$ (LCO, layer)
  - $LiNi_xMn_yCo_zO_2$ (NMC, spinel)
  - $LiMn_2O_4$ (LMO, spinel)
  - $LiFePO_4$ (LFP, olivine)
  - …

Electrochemical Cell – Li-Ion Battery

- Li-Ion Battery or Li-Carbon Battery?



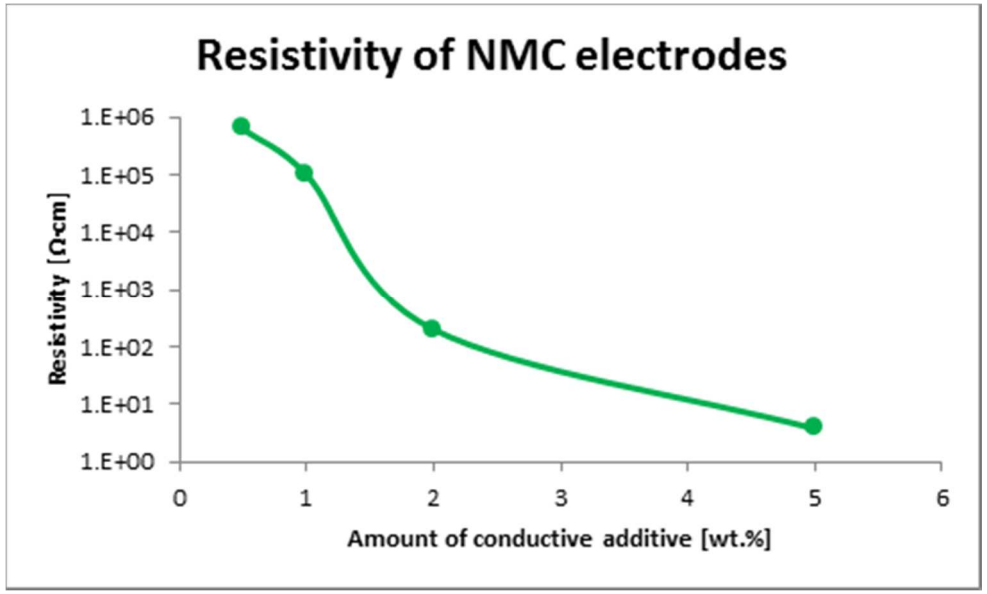
Electrolyte (in pores)
Active material
Graphite
Carbon Black
Binder

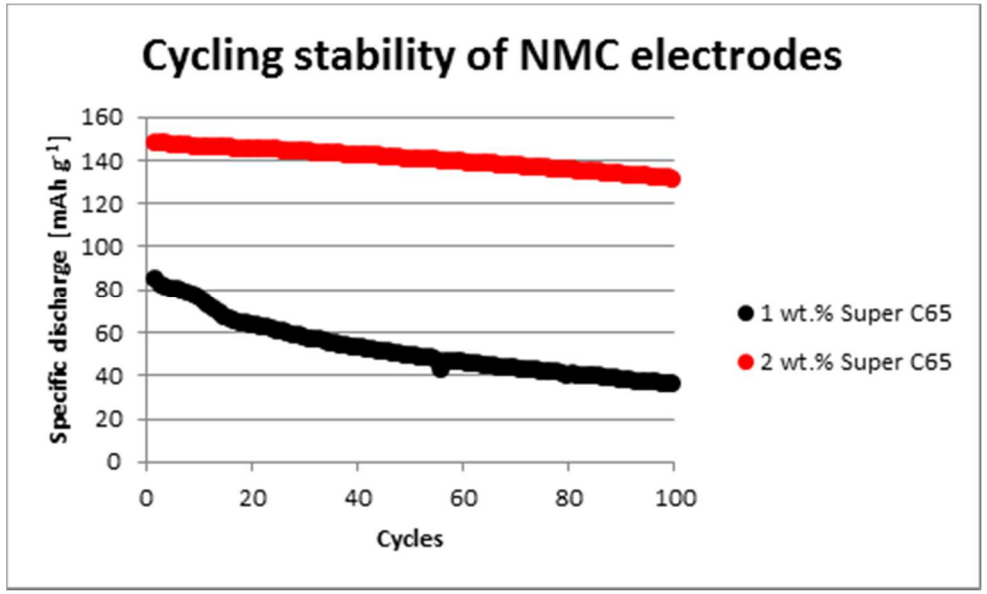
IMERYS Graphite & Carbon products are inside the positive and the negative electrode

Electrolyte (in pores)
Active material
Graphite
Current Collector coating
Carbon Black
Binder

Carbon Conductive additives for the positive electrode

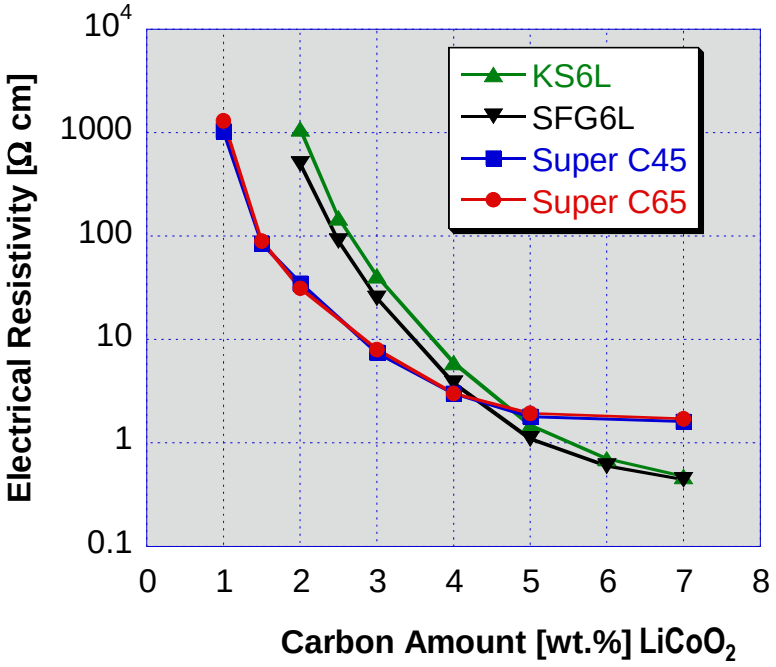
- Influence of conductive Carbon Black on the cycling stability of the positive electrode
  - Conductive Carbon Blacks improve cycling stability and efficient positive material utilisation thanks to setting up a conductive network already at low carbon additive concentration

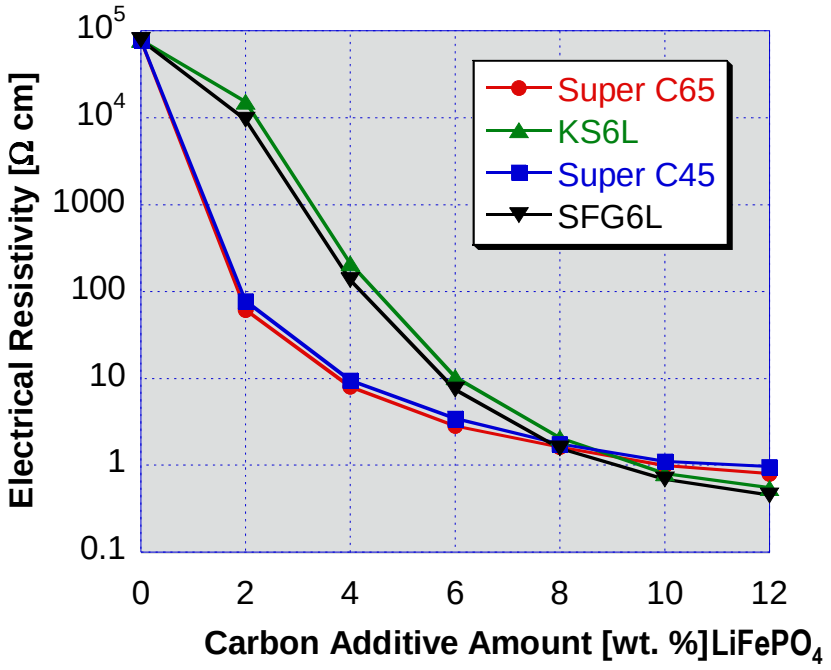




Carbon Conductive additives for the positive electrode

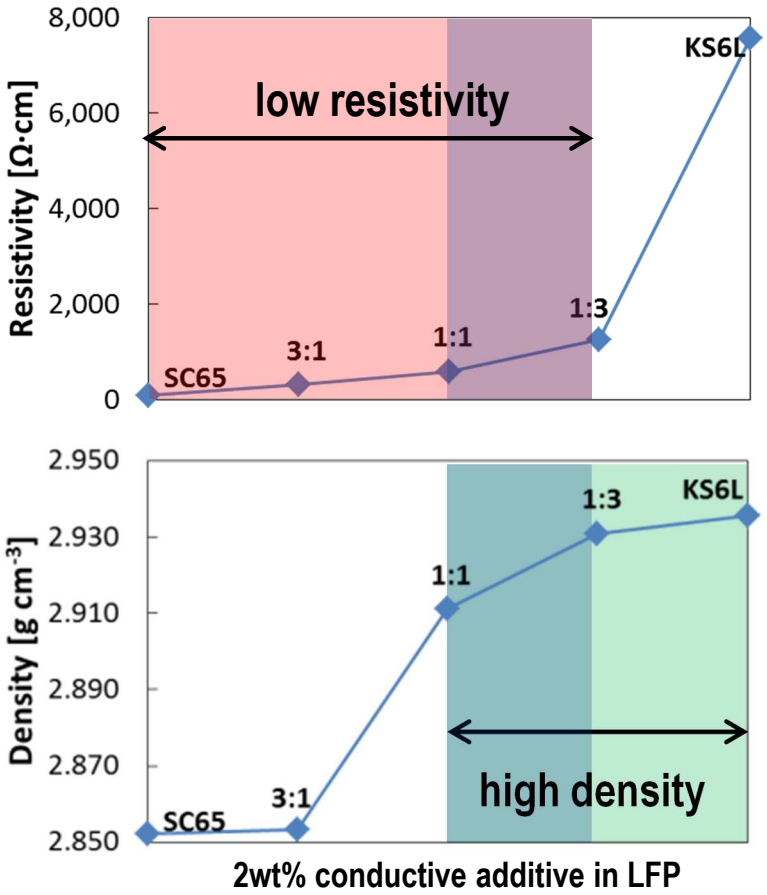
- Evaluating conductive additives for positive Li-ion battery electrode
  - Carbon Black Super C65: percolation threshold at low additive amount
  - Graphite KS 6 L: compressibility and low ultimate resistivity (at high additive amounts)





Carbon Conductive additives for the positive electrode

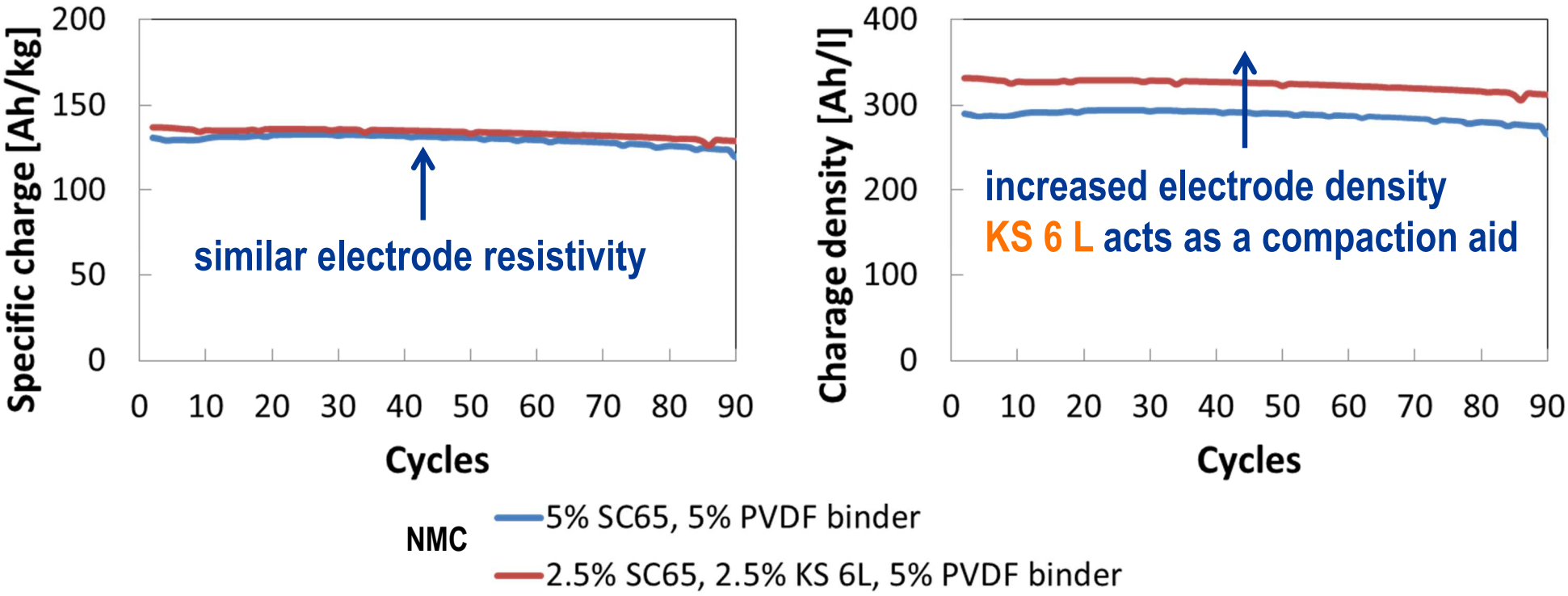
- Graphite and Carbon Black complementary properties in the positive electrode
  - Combine the low percolation threshold of conducting Carbon Black with the good compressibility of Graphite



Super C65 : KS6L ratios between 1:1 and 1:3 leads to **low resistivity & high density**

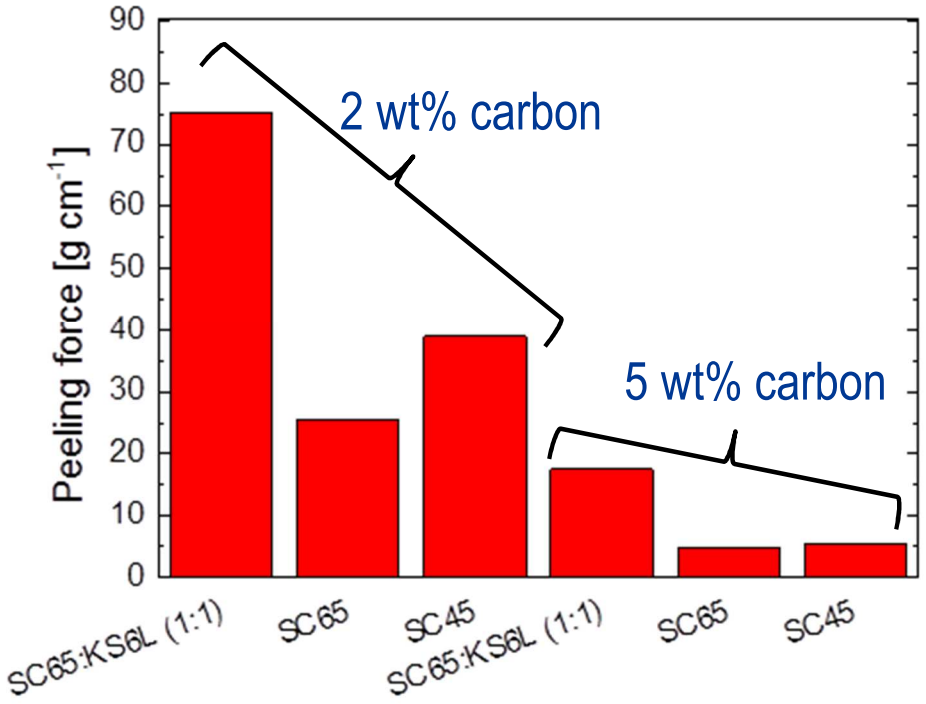
Carbon Conductive additives for the positive electrode

- Graphite and Carbon Black complementary properties in the positive electrode
  - SuperC65 : KS 6 L blend vs SuperC65 alone: same specific charge because of the similar electrical resistivity of the electrodes, but **improved charge density** when using graphite because of its greater compressibility compared to carbon black



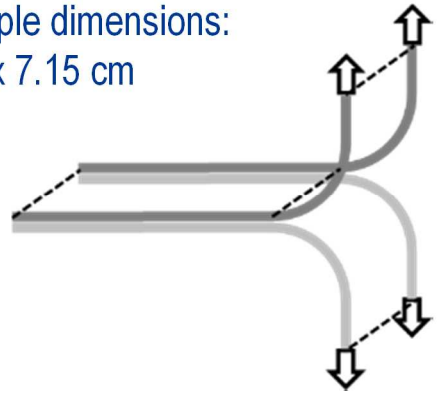
Carbon Conductive additives for the positive electrode

- Graphite and Carbon Black complementary properties in the positive electrode
  - The adhesion decreases with increasing amount of conductive additive due to the contribution of the conductive additive to binder consumption
  - Thanks to its lower surface area compared to carbon black, graphite helps maintaining sufficient adhesion



Al current collector
PVDF binder: 5 wt.%

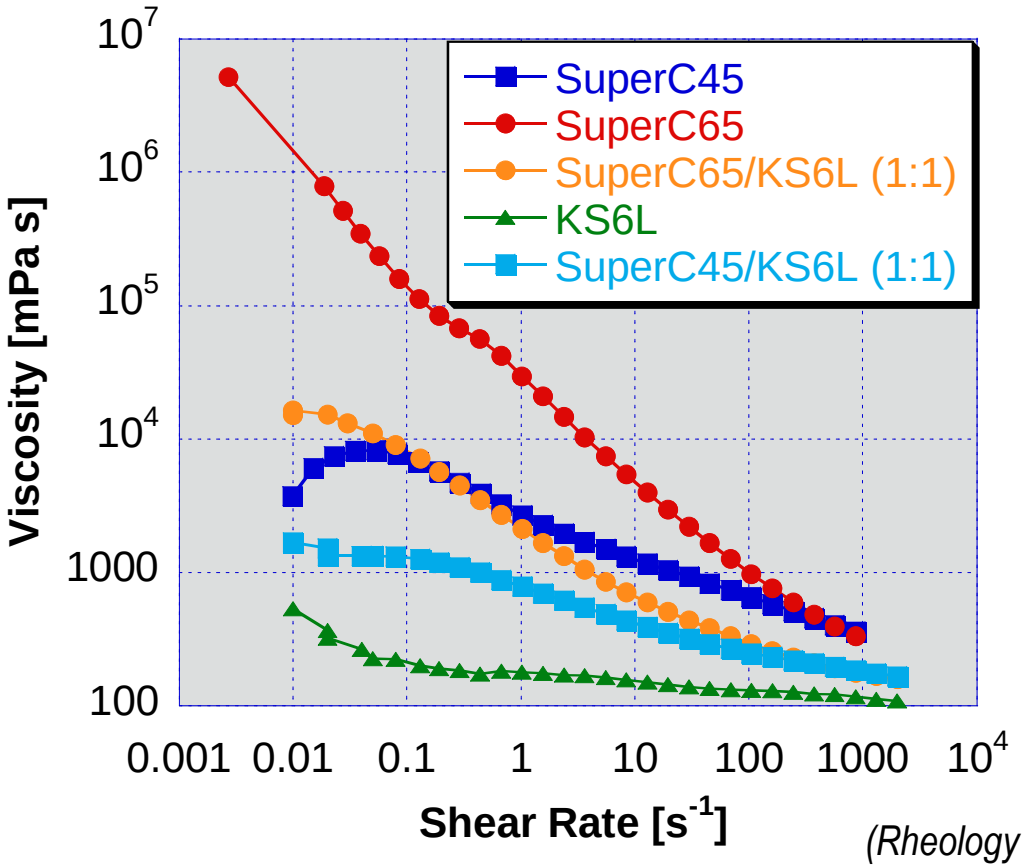
T-peel test (180°C)
sample dimensions:
3.5 x 7.15 cm



C-NERGY	BET SSA [m²/g]
Super C45	45
Super C65	65
KS 6 L	20

Carbon Conductive additives for the positive electrode

- Graphite and Carbon Black complementary properties in the positive electrode
  - Thanks to its lower surface area compared to carbon black, graphite helps favorable rheology for electrode processing



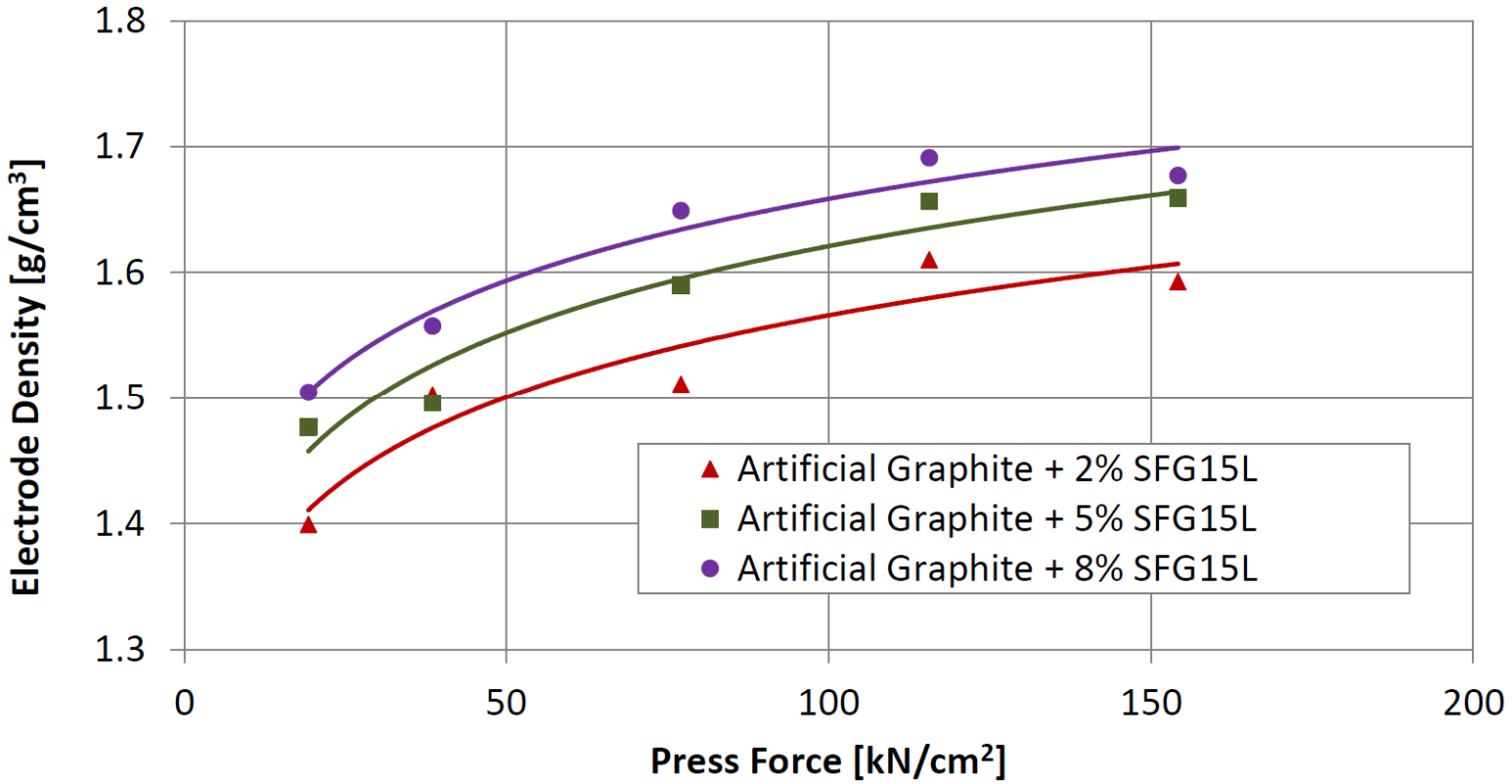
C-NERGY	BET SSA [m²/g]
Super C45	45
Super C65	65
KS 6 L	20

94 wt.% LiCoO2
3 wt.% carbon black
3 wt.% PVDF
in NMP

(Rheology measurement: cone-plate)

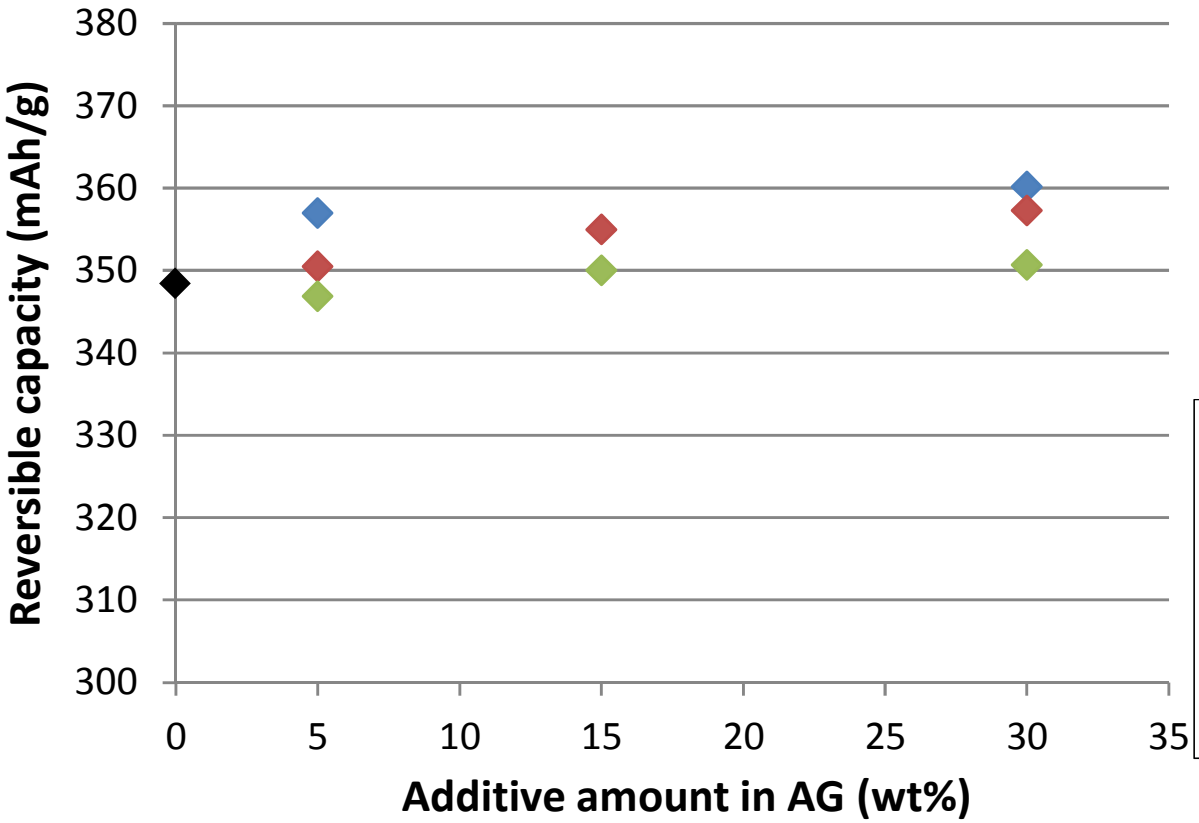
Specialty Graphites for the Negative electrode

- Increased electrode density with Specialty Graphites Additives
  - Addition of 2 – 8 % **C-NERGY™ SFG 15 L** significantly increases density of artificial graphite based negative electrodes
  - Optimal amount of SFG 15 L depends on hardness of active material and targeted electrode density



Specialty Graphites for the Negative electrode

- Specialty Graphites Additives also work as an active material in the negative electrode
  - Very high reversible capacity: close to 372 Ah/kg, theoretical limit
  - Very high electrical conductivity



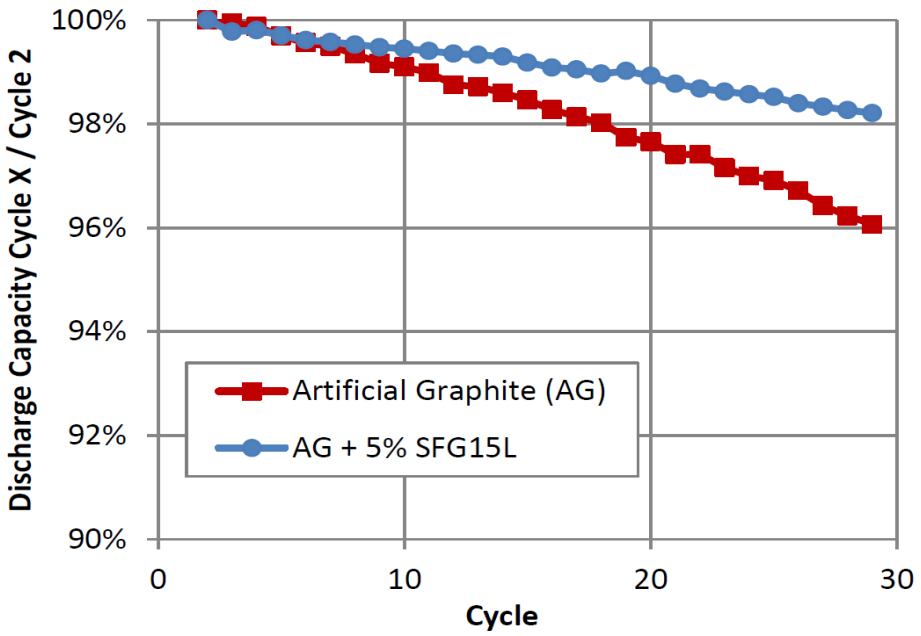
C-NERGY	BET SSA [m^2/g]
SFG 6 L	17
SFG 15 L	9
KS 15 L	12

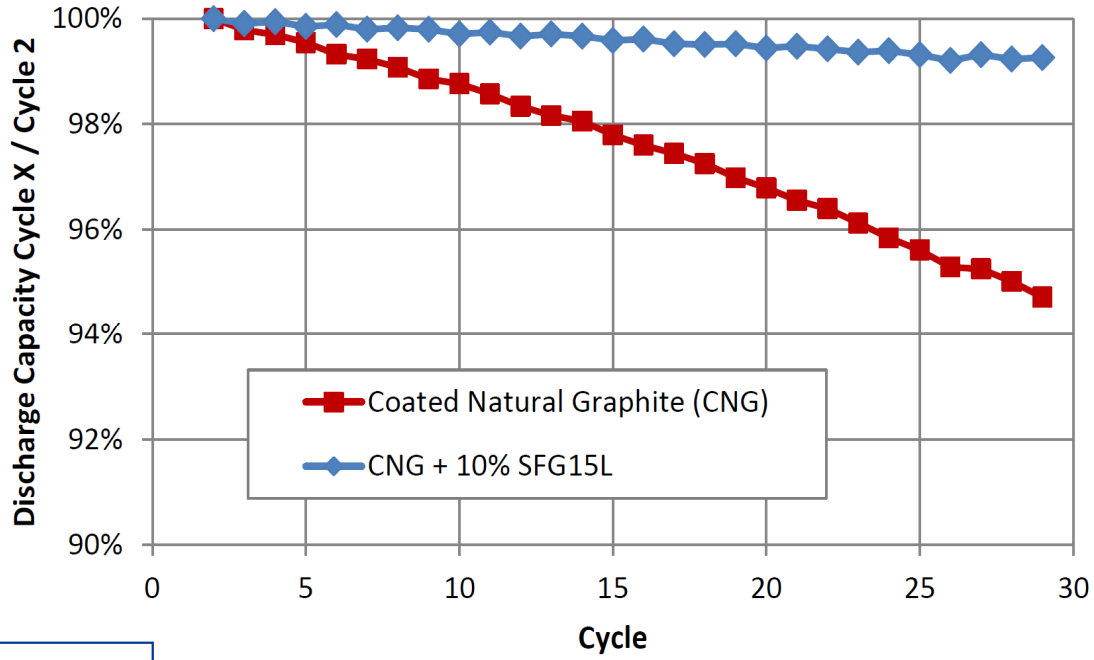
- Formulation: (AG + additives) : CMC : SBR = 98 :1 : 1
- Loading : 7.5±0.5 mg/cm^2
- Density : 1.6 ±0.05 g/cm^3
- Half coin cells vs. Li/Li^+
- Electrolyte : EC/EMC 1:3(v/v), 1M $LiPF_6$
- Test condition:
  - Charge : (CC/CV) 0.1C/5mV, 0.005C cut
  - Reversible : (CC) 0.1C/1.5V

Specialty Graphites for the Negative electrode

Specialty Graphites Additives improves Cycling Stability

- Improved cycling stability is achieved by adding 2 – 8 % C-NERGY™ SFG 15 L to active material, independent if artificial or coated natural graphite
- Improvement in cycling stability has to be balanced vs increase in BET surface area and binder absorption due to SFG 15 L addition



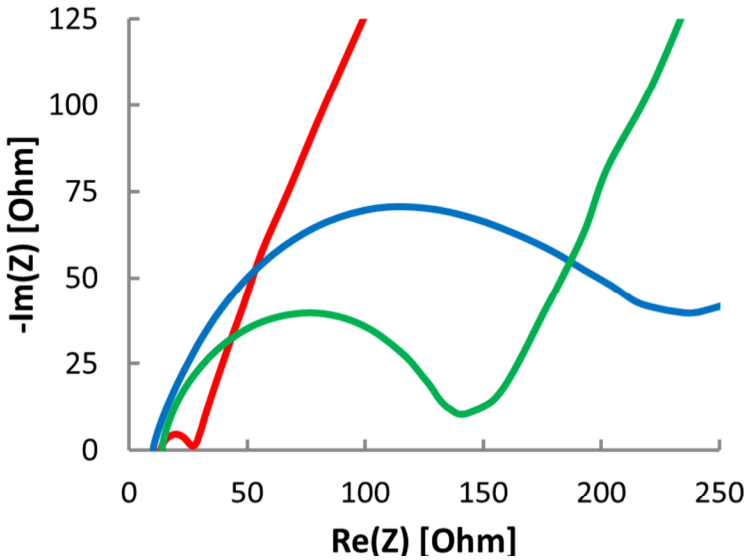


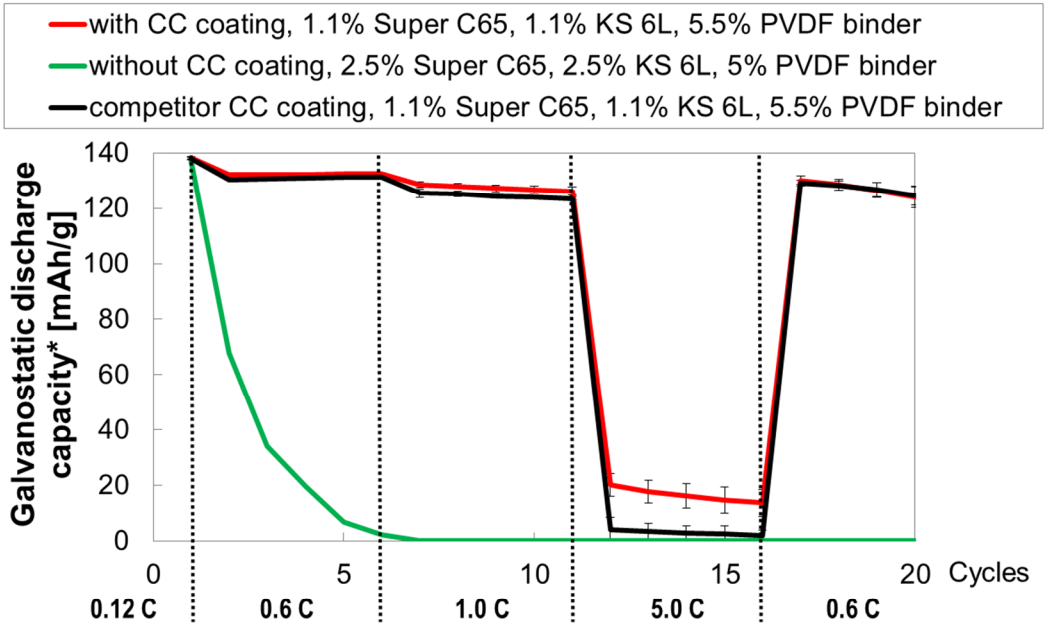
- Half cells vs. Li/Li^+
- Electrolyte: EC/EMC 1:3 (v/v), 1 M $LiPF_6$
- SBR/CMC binder
- Cycling program:
  1st cycle 20 mA/g charge/discharge, then 50 mA/g charge (CCCV),
  3 C discharge (CCCV)

IMERYS Graphite & Carbon

Carbon-based current collector coating

- Water-based Ready-to-use dispersion of very fine carbon powder
  - Allows for coating of a homogeneous carbon layer of ca. 1 µm on the current collector
  - Very little contribution to inactive volume and weight
  - Dramatically reduced impedance in positive electrodes, leading to improved high rate performance of the cell



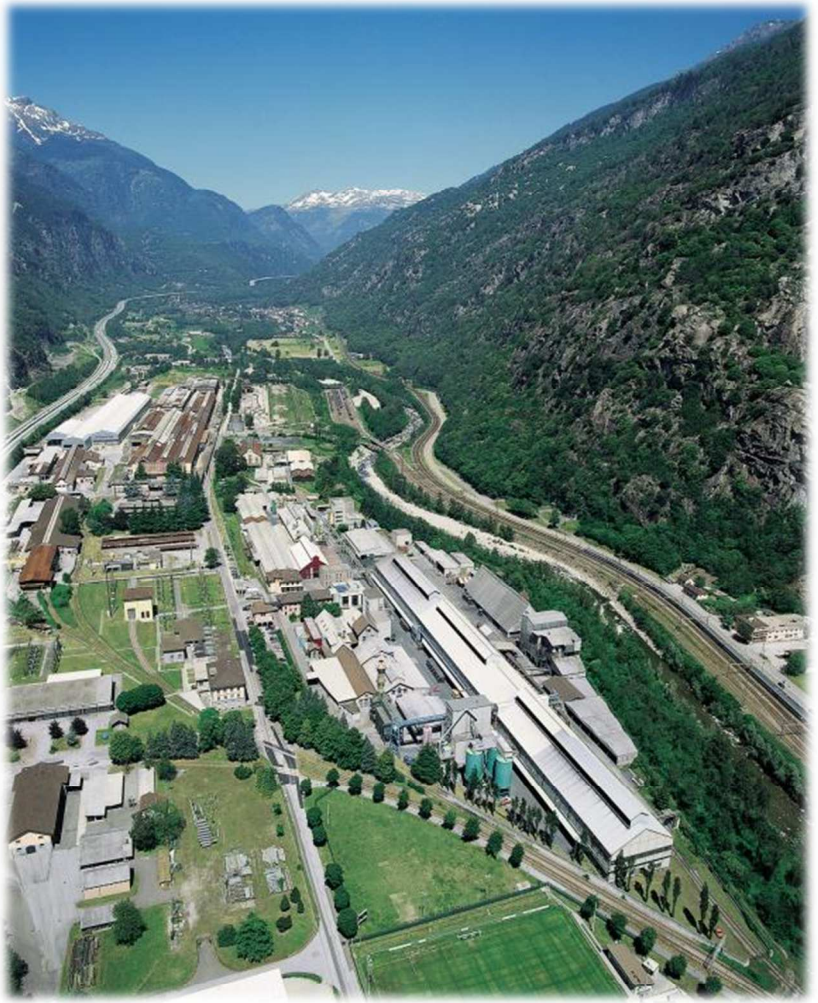


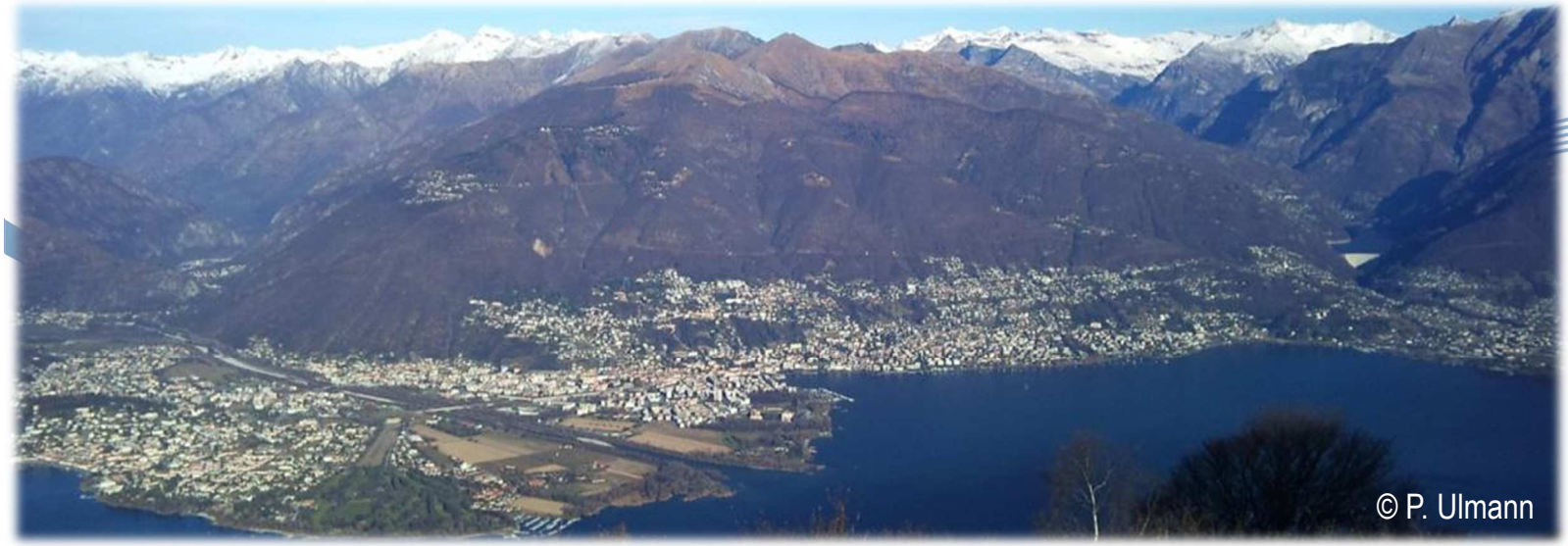
Summary

- C-NERGY™ conductive Carbon Blacks and Graphites have **complementary properties** for Li-ion battery **cathodes**
  - Conductive Carbon Blacks lead to lower percolation threshold enabling higher specific charge
  - Graphite additives help to improve the reversible charge density and the electrode adhesion
  - Graphite additives help to improve the manufacturing of electrode due to favorable rheology
- C-NERGY™ L-grades **specialty graphites** are very efficient as **active additive** for Li-ion battery **anodes** thanks to
  - improved cycling stability and battery lifetime
  - increased electrode density
  - reduced volume resistivity
- C-NERGY™ water-based ready-to-use dispersions for **current collector**
  - Dramatically reduced impedance in positive electrodes, leading to improved high rate performance of the cell

My special thanks to:

T. Hiroyuki, F. Mornaghini, P. Ulmann





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