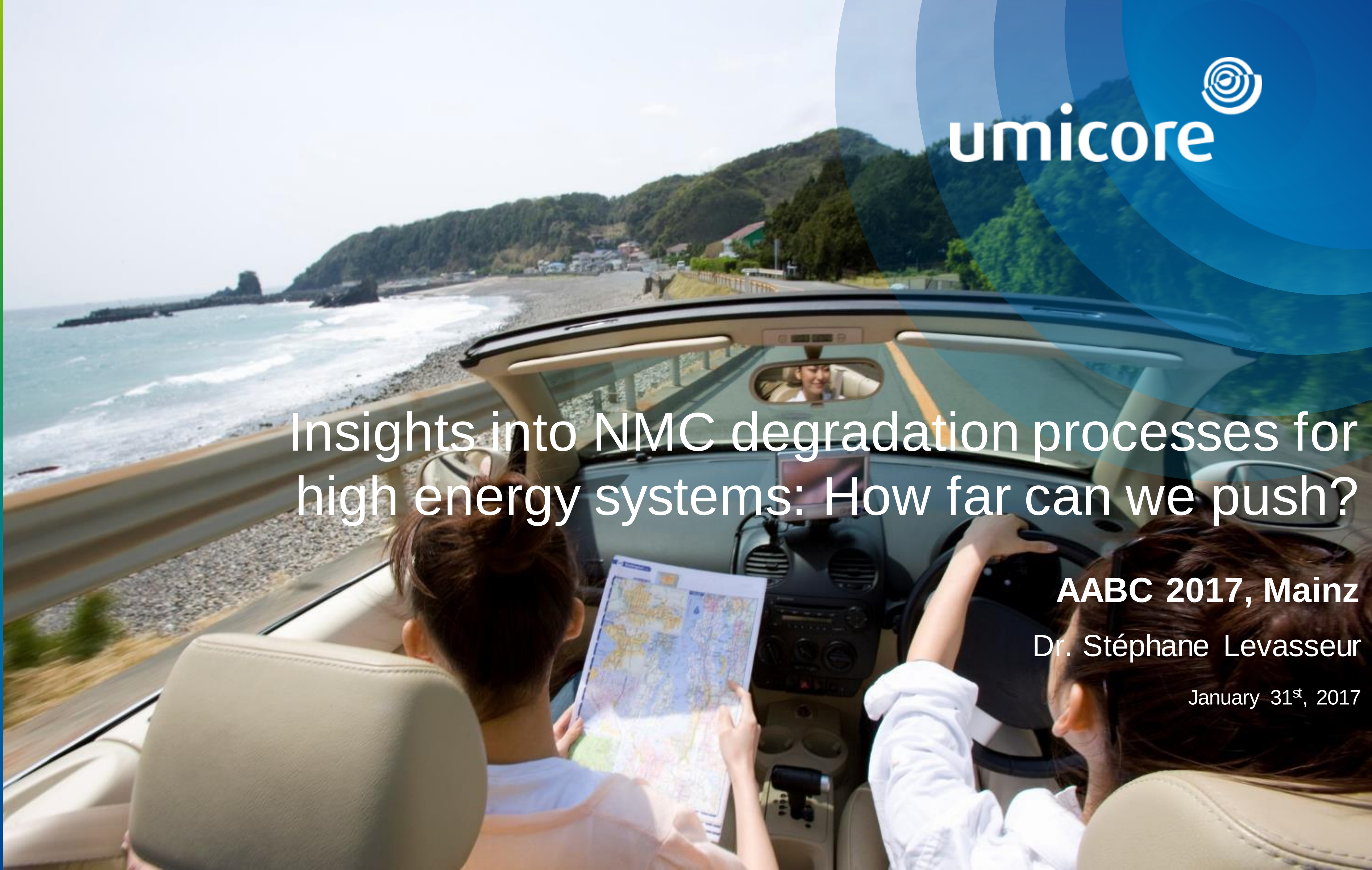


umicore

Insights into NMC degradation processes for high energy systems: How far can we push?

AABC 2017, Mainz

Dr. Stéphane Levasseur

January 31st, 2017

umicore

Agenda

Umicore : a global leader in cathode materials

NMC cathode materials: What's under the hood?

Towards an affordable higher driving range

Who we are

A global materials technology and recycling group

One of three global leaders in emission control catalysts for light-duty and heavy-duty vehicles and for all fuel types

A leading supplier of key materials for rechargeable batteries used in portable electronics and hybrid & electric cars

The world's leading recycler of complex waste streams containing precious and other valuable metals

A leading player in the industry

Market characteristics

- Li-ion battery technology is established reference for portables and automotive applications
- Cathode material is important to performance and cost of a Li-ion battery

Umicore offering

A **broad spectrum of metal-based materials** used in Li-ion batteries

Umicore is a leading cathode material supplier with a large industrial footprint. We have produced enough cathode materials to:

- Provide a smartphone **to every person on the planet**
- Power more than **1 million EVs**

Technology leadership and a proven **quality track** record combined with a **strong application know-how** are key for business success

RBM worldwide presence

RBM BU Headquarter based in Seoul, Korea

Customer teams

- Sales & marketing / Applied technology close to the customers and OEMs (EU, US, KR, JP, CN, TW)

Operations

- In the heart of the Li-ion industry
- No single point of failure

- Cathode material (KR, CN)
- Precursor (BE, CN, KR)

R&D & Industrialization

- Combining the global strength of a multi-national engineering team
- Corporate R&D (BE)
- BU RBM Product/Process R&D (BE, KR, JP)

Agenda

Umicore : a global leader in cathode materials

NMC cathode materials: What's under the hood?

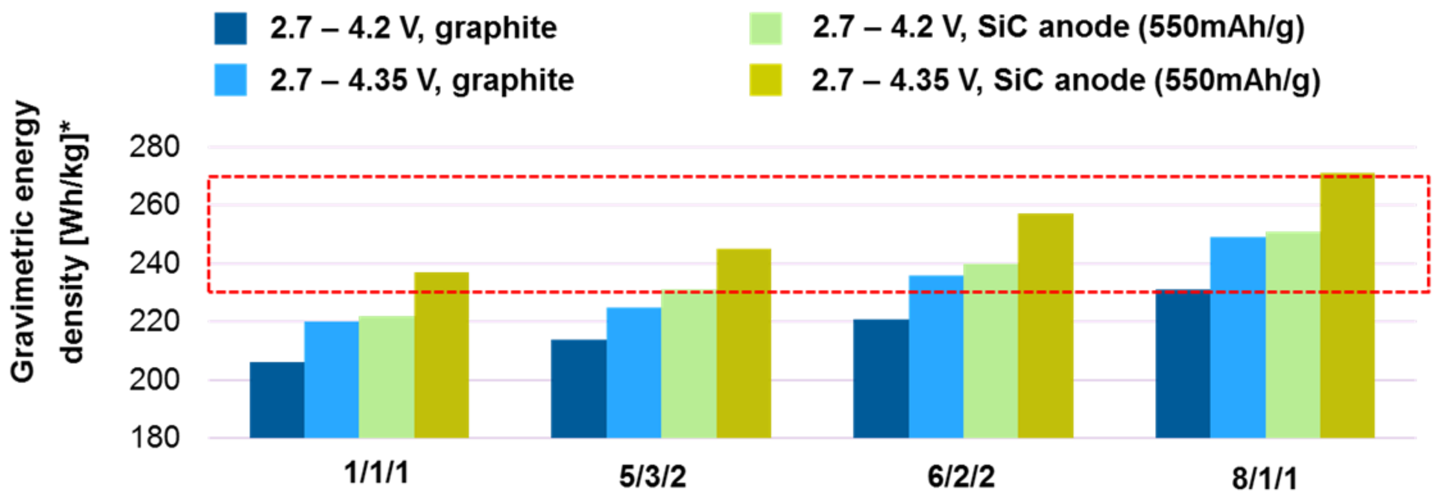
Towards an affordable higher driving range

xEV Roadmap

- 100 miles is a no go! Extended range is a prerequisite for EV success
- Higher mileage is now around the corner
- 100USD/kWh? The cost equation still needs to be solved
- No technology disruption eminent : Li-S or metal-air won't play a role
- Incremental improvement and convergence on materials strategies:
  - standard NMCs
  - Wider voltage window
  - Increased anode capacity
- Long term security of supply of sustainable feed is a must

Path towards higher energy density?

Materials and voltage will contribute



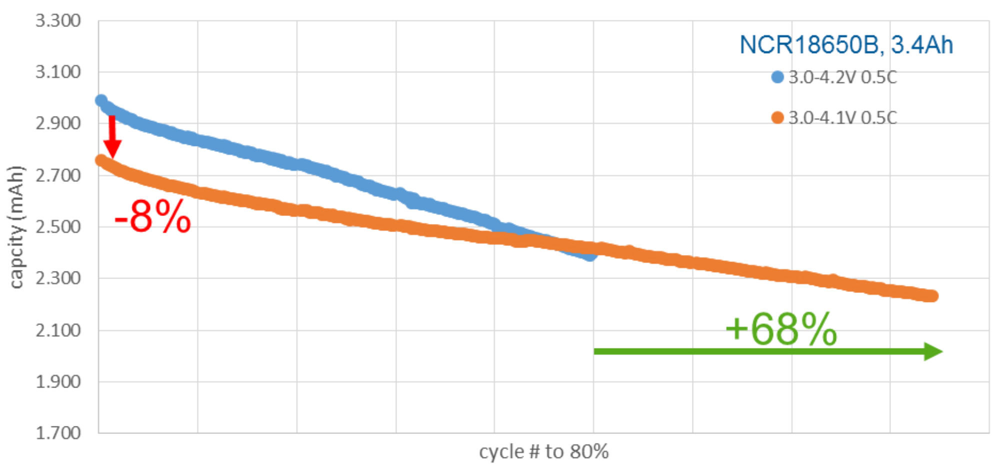
- NMC with higher Ni content allow to make it on paper
- NMC is only part of the global equation: a smart use of higher voltage and/or advanced anode is required

*Simulated full cell energy densities (20Ah pouch, nominal capacity)

High Ni chemistry

Where is the real benefit?

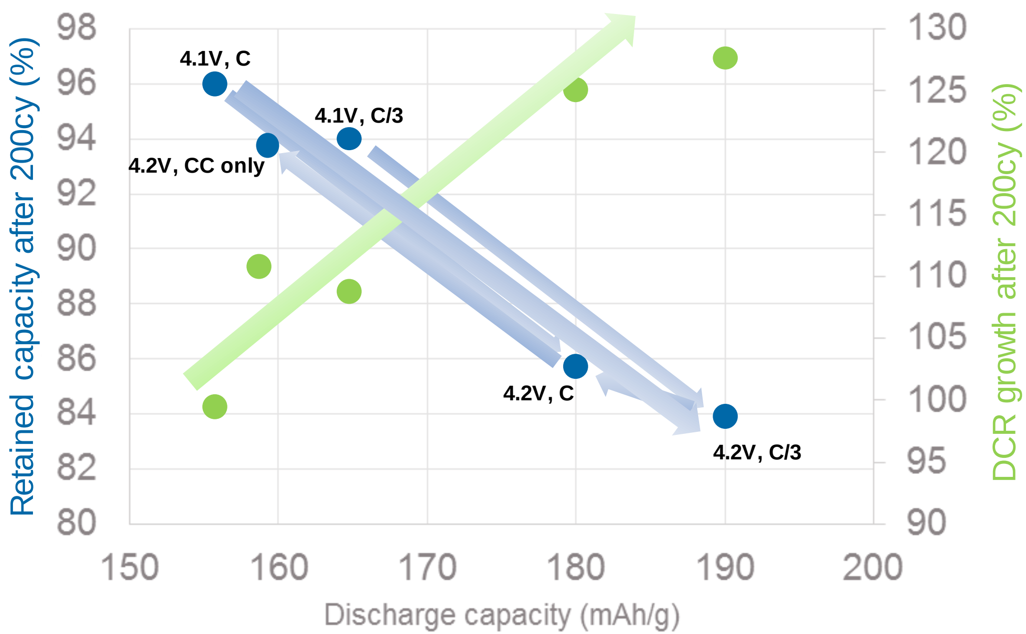
- Rated capacity for High Ni is usually given for 2.5-4.2V* operation window
- Benefits can be obtained by reducing the voltage window
- Reducing the charge cut off voltage by 100mV enhances considerably cycle life (as already demonstrated by Tesla communication)
- Step charging also improving life…but at the expense of fast charging (!)



*See datasheets NCR1850A (3100mAh) /B (3400mAh) from Panasonic

Comparing cycling behaviour

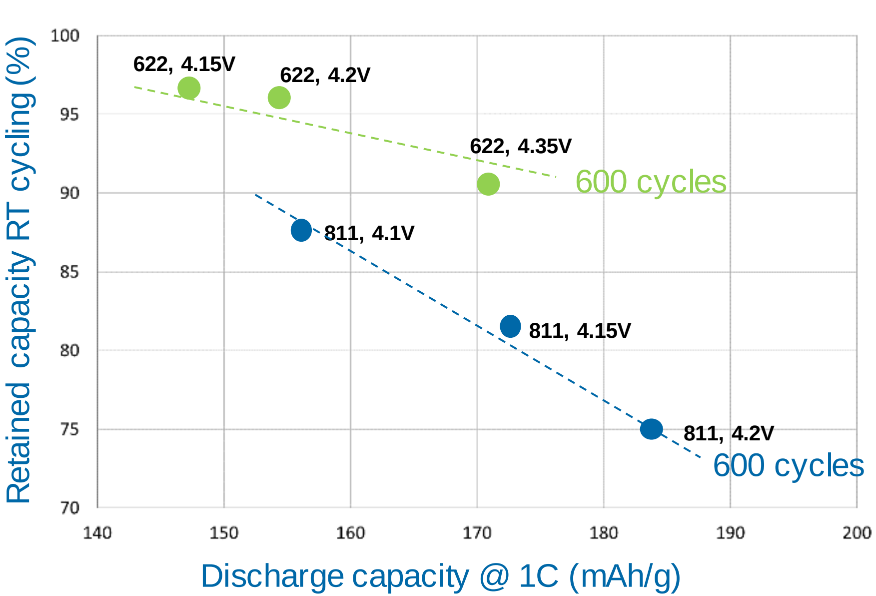
811 retention capacity dependency

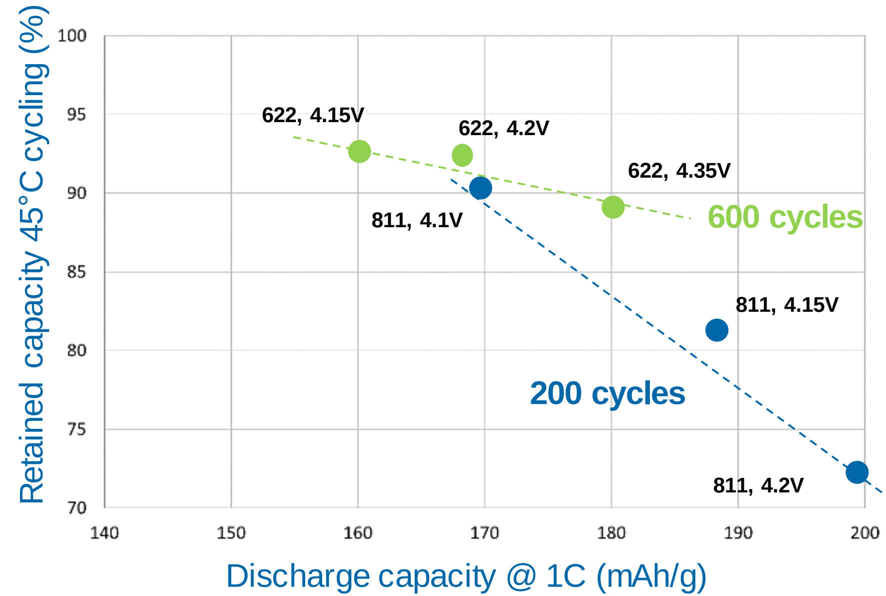


- 811 full cells cycled at different rates and cut-off voltage
- 811 retained capacity very dependent of cut-off voltage
- 811 retained capacity also very dependent of time spent at higher voltage
- Retained capacity fully correlated to DCR growth

Comparing cycling behaviour

811 versus 622 upon cycling

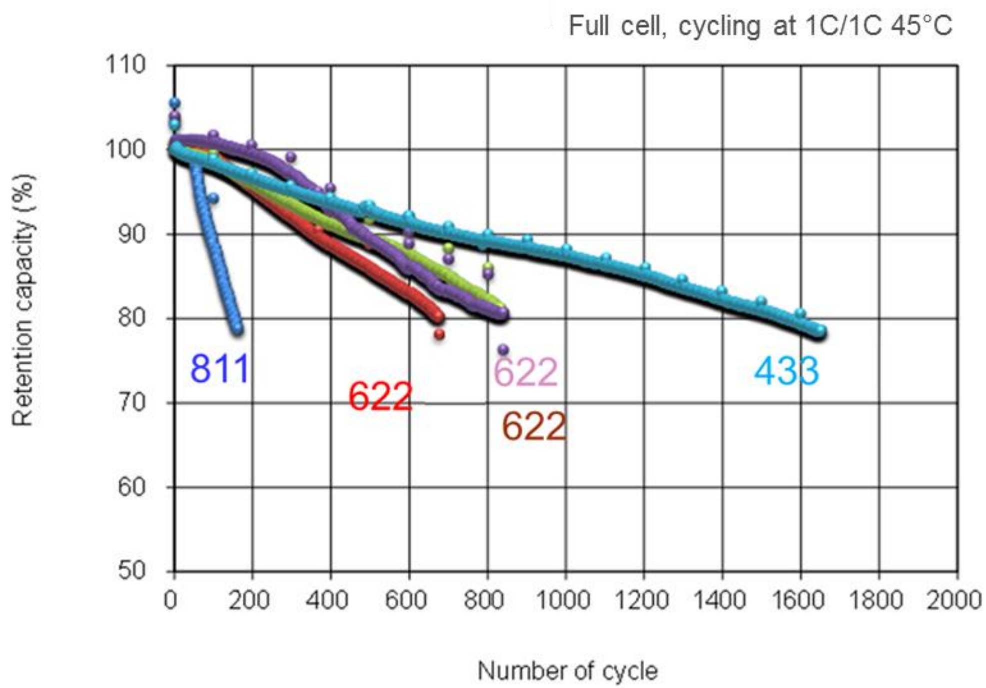




- 811 fading shows much stronger dependency to cut-off voltage than 622
- 811 fading shows much stronger dependency to temperature

Understanding NMC cycling behaviour

Post mortem of various NMC compositions

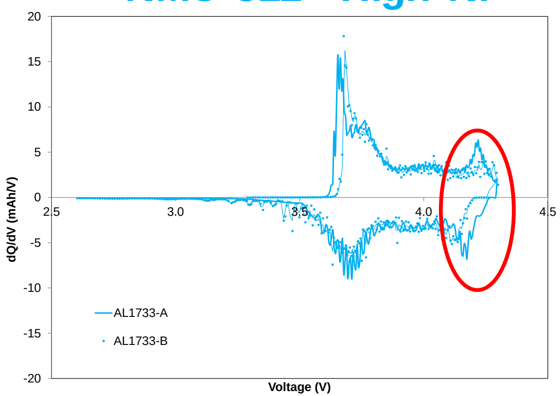


- Various compositions cycled (2.7V-4.2V) at HT up to 80% retention capacity
- Various analysis performed on the materials after cell dismantling

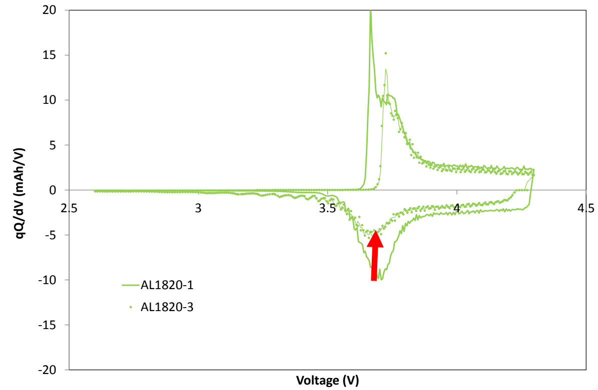
Understanding NMC cycling behaviour

Cathode material evolution

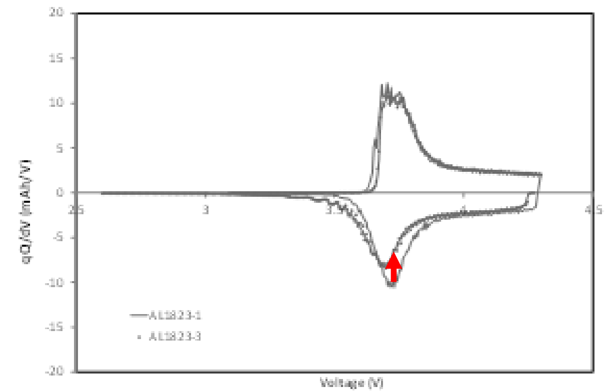
NMC 811 - High Ni



NMC 622 - Medium Ni



NMC 433 - Low Ni



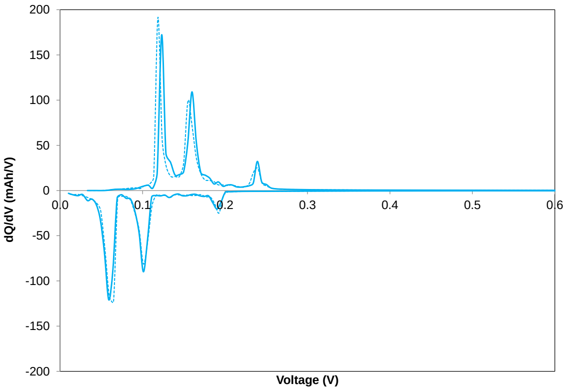
- Positive electrode recovered after cycling in full cell and tested in coin cell

- Comparing shape of derivative curves (dQ/dV) for fresh and cycled electrodes:
  - 811 shows the strongest change with strong polarization increase at end of charge
  - 622 shows a decrease of the magnitude of the peaks in charge and discharge
  - 433 barely shows no decrease of the peaks magnitude, in agreement with the excellent cycling behaviour

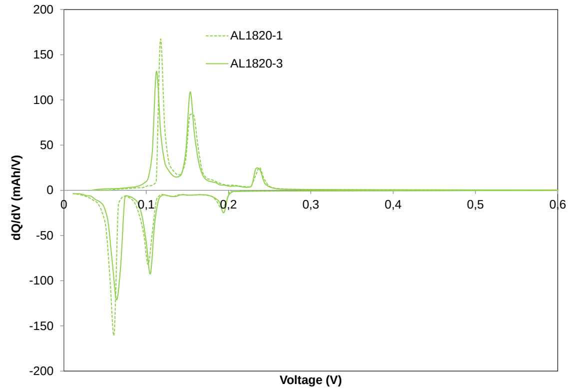
Understanding NMC cycling behaviour

Anode material evolution

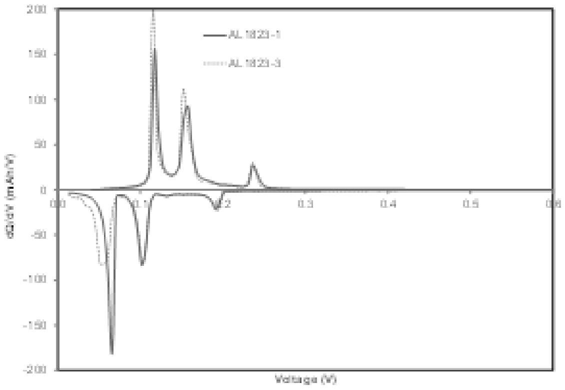
NMC 811 - High Ni



NMC 622 - Medium Ni



NMC 433 - Low Ni

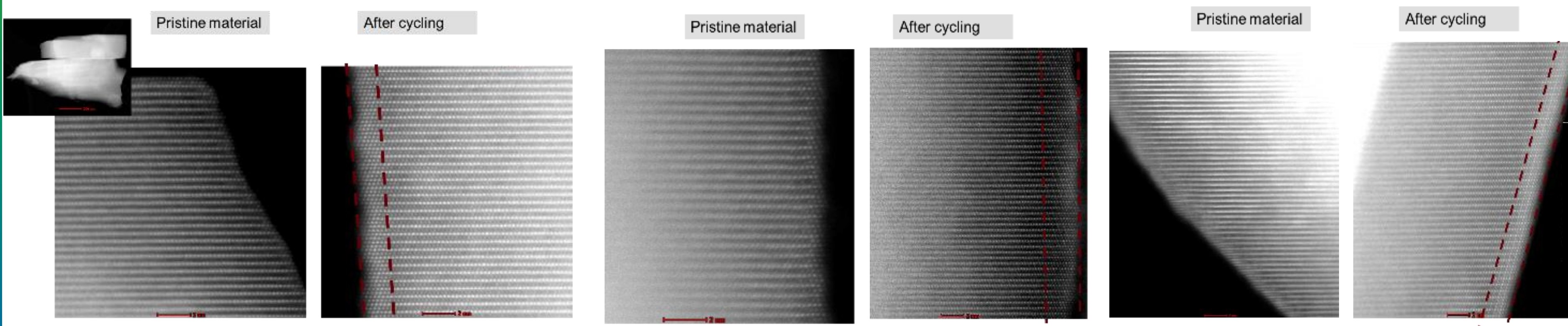


- Negative electrode recovered after cycling in full cell and tested in coin cell
- Shape of derivative curves not strongly changed considering the fresh and cycled electrodes:
  - no significant shift for the peaks in charge and discharge
  - no major decrease of peaks magnitude
- Confirms main polarization build-up in NMC with higher Ni comes from the positive side

Understanding NMC cycling behaviour

Digging into cathode material structure

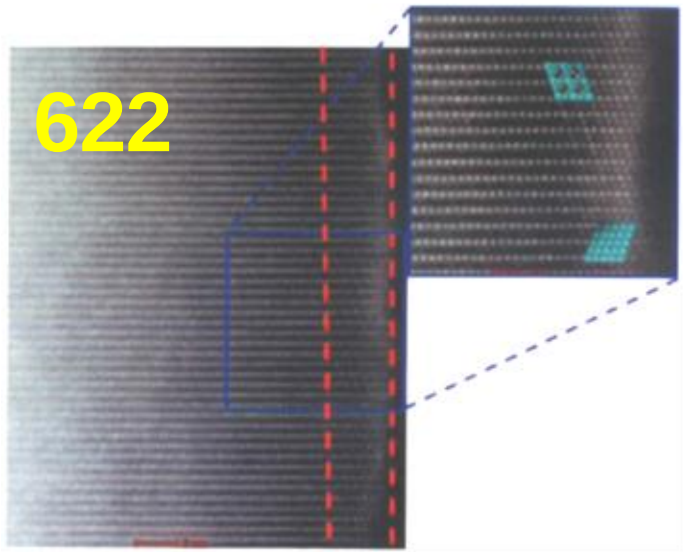
NMC 811 - High Ni | **NMC 622 - Medium Ni** | **NMC 433 - Low Ni**

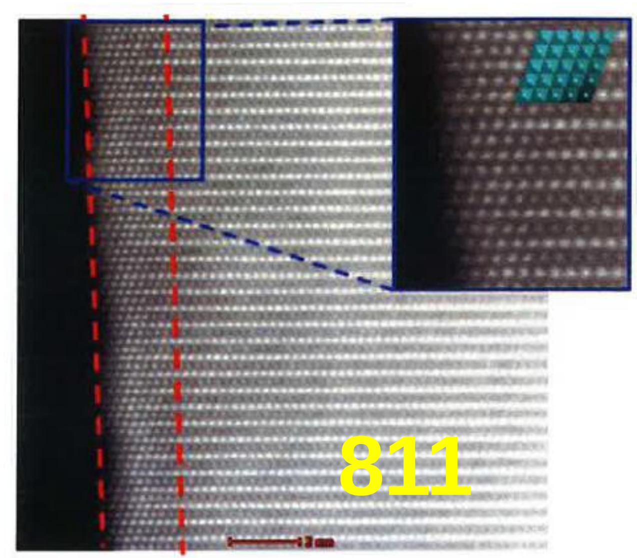


- HR-STEM images of NMC 433, 622 and 811 after 4.2V-45°C full cell cycling at 80% retention capacity
  - All materials show some quite degree of disorder on the surface (~2nm deep)
  - The materials with higher Ni also show some disorder in the bulk

Understanding NMC cycling behaviour

Digging into cathode material structure



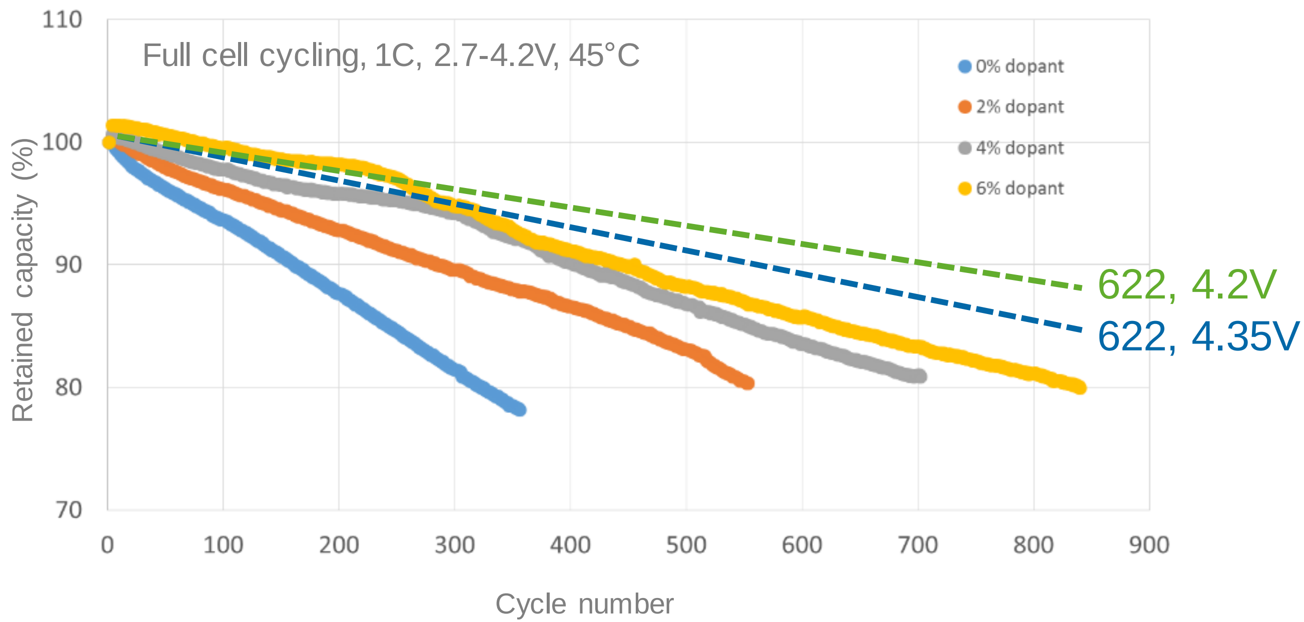


- NMC433/622: surface collapses to “D-spinel”, core shows minor disorder
- NMC811: surface collapses to “rock-salt”, core shows more disorder
- “D-spinel” surface believed to be conducting, while rocksalt is insulating, resulting in DCR growth
- Fully confirms results from literature on commercial NCA materials*

*Hwang et al., Chem Mat. 26 (2014) 1084; **Abraham et al., J. Electrochem. Soc. 150 (2003) A1450

Improvement strategies

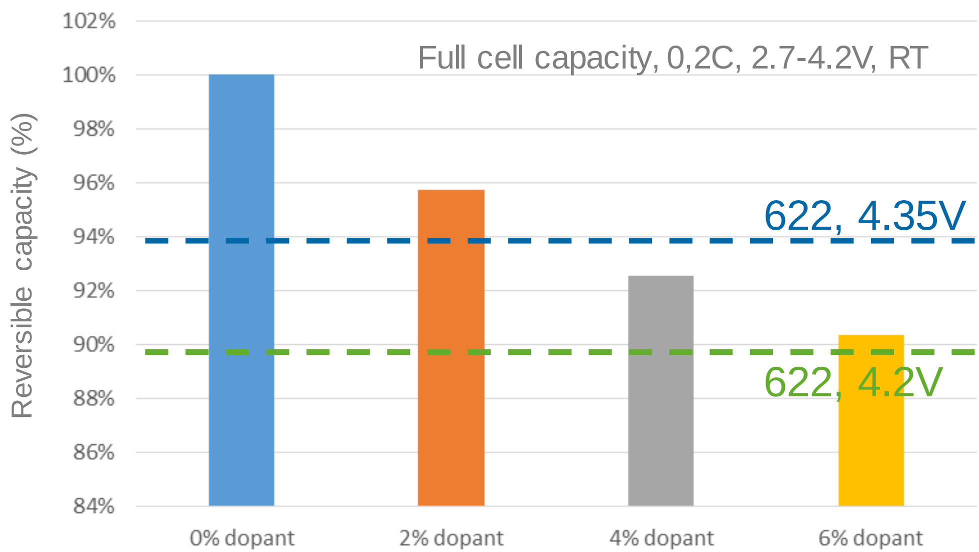
Mitigation attempts to get better life from High Ni



- Electrolyte formulations for 811 with various commercial and pre-commercial solvents, additives or external formulations tested without success
- Possibility of doubling cycle life via structure stabilization
- Still cycle life not at level of NMC 622 materials

Improvement strategies

The price to pay



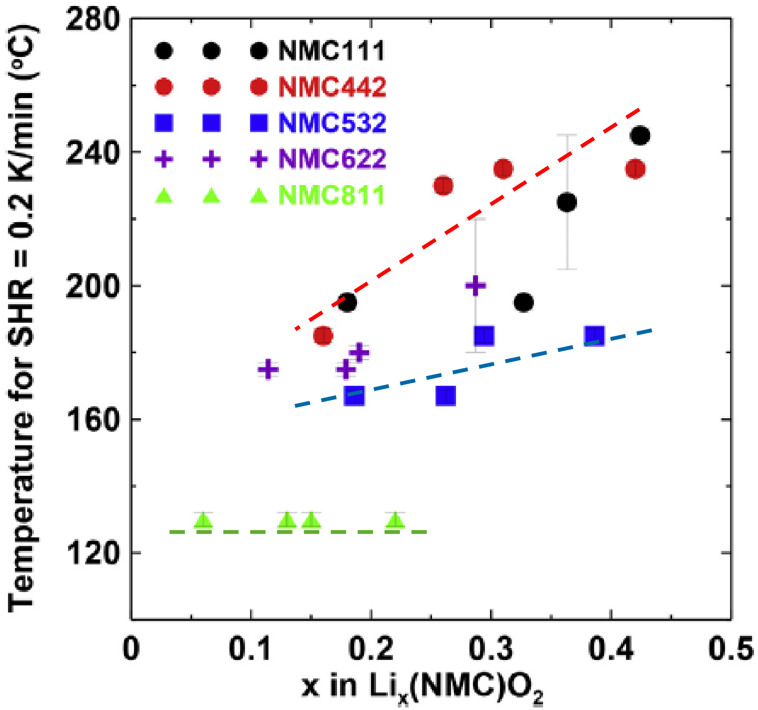
- If doping in Higher Ni content improves cycle life, it also decreases strongly the reversible capacity with more than 2% capacity loss per wt% dopant
- Reversible capacity of stabilized High Ni material overlapping with 622 playfield

And on safety…

Is stability high enough?

- Internal DSC tests on charged electrodes show that:
  - Independently of chemistry, total heat increases with charged capacity
  - At constant capacity, higher Ni release more heat than lower Ni
  - Fully in line with thermodynamics, the more Ni, the more O release expected

- ARC study from Dahn* group confirms that:
  - High Ni, low Mn compositions show dramatic evolution of thermal runaway T
  - There is a gap in reactivity between low/medium Ni (incl. 622) and High Ni



* Ma et al., JPS, 327 (2016), 145

And on safety…

Is stability high enough?

Nickel content increases →

Material type		622	811	NCA (2%Al)	NC
Nail penetration	**Charge to 170mAh/g**	**2/2P, 4.24V**	**2/2P, 4.12V**	**2/2P, 4.11V**	**1/2P, 4.08V**
	Charge to 180mAh/g	**2/2P, 4.33V**	**2/2P, 4.15V**	**0/2P, 4.18V**	**0/2P, 4.12V**
	Charge to 190mAh/g	**2/2P, 4.43V**	**0/2P, 4.23V**	**0/2P, 4.30V**	**0/2P, 4.20V**
	Charge to 200mAh/g	**2/2P, 4.52V**			
Hot box	165°C, charge to 180mAh/g	**90min**	**85min**	**80min**	**80min**

Pouch cell : 1.4Ah at 4.2V, Nail penetration : 2.5mm, 20mm/sec; "x/2P" means x cells over 2 pass the test

- Nail penetration tests performed at Umicore confirm higher stability of 622 material up to charge cut-off voltage of 4.5V (~200mAh/g)
- The higher the Ni content, the lower the stability
- Hot box tests confirm the trend

Agenda

Umicore : a global leader in cathode materials

NMC cathode materials: What's under the hood?

Towards an affordable higher driving range

High Ni chemistry

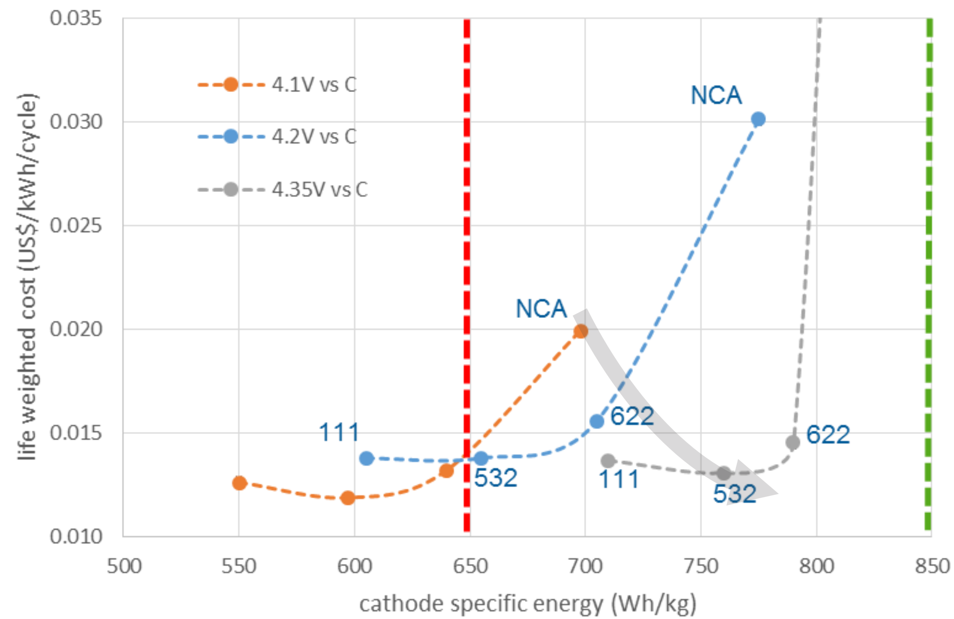
Under the hood…

- Cycle life of 811 and higher Ni strongly dependent of SOC range, rate and T.
- Electrolyte optimization not successful in improving cycle life
- Cycle life improvement strategies by material design while keeping high capacity not successful.
- 811 and higher Ni form insulating surface layer at low to medium cut-off voltages responsible for large impedance growth upon cycling
- Safety behavior of 811 and higher Ni confirmed to be “borderline” over 180mAh/g charge capacity by ARC, DSC, nail penetration and hot box tests.

Towards an affordable EV

Is life about compromise?

- Increasing voltage of Medium Ni materials over 4.2V gives appropriate energy density
- Safety demonstrated to be superior
- US$/kWh/cycle* is better for medium Ni region versus High Ni
- Technology is ready for large scale implementation
- Medium Ni is best path forward towards affordable "200miles" cars



* #cycle to achieve 80% life 1C cycling 100%SOC, RT

Conclusions

What chemistry for what car?

- While attractive for premium longer range cars and specific cell designs, High Ni is not the holy grail the EV industry is looking for

- Medium Ni materials (50-60% Ni) allow improving TCO at system level for mass market affordable EVs
- It will speed up penetration of EVs in suburban areas while improving customer perception, providing enough range at decent cost

- By creating “Peace of Mind” for our customers, Umicore offers a unique combination of strengths in the race towards an affordable electrified car

Umicore investments demonstrate its commitment to the industry

Expansion in Korea and China

Regulated information 27 April 2016

Umicore to triple capacity for rechargeable battery cathode materials by 2018

Umicore announced today an acceleration of its capacity expansion investments for NMC (nickel manganese cobalt) cathode materials. The acceleration is required to meet a surge in demand for materials used in hybrid and electric vehicles.

The expansion program entails investments of some € 160 million over a period of three years at the company's existing facilities in Cheonan (South Korea) and Jiangmen (China), as well as greenfield investments on adjacent land in both locations. Umicore will deploy its latest generation of proprietary production technologies which will enable the company to triple existing capacity by the end of 2018 across a broad range of material grades. These are in compliance with the very highest quality standards for the automotive industry. The new capacity should start coming on stream in the second part of 2017.

Vehicle electrification is being driven by the need to reduce CO_2 emissions and improve air quality. In many regions this is being supported by ambitious emission legislation. The number of electrified vehicle models being launched has been surging in recent months and the penetration of these vehicles, ranging from mild hybrid cars to full electric models, is projected to grow at an increasingly fast pace. There is also a trend towards electrification of vehicles used for public transportation such as electric buses. Umicore's NMC cathode materials are key ingredients in enabling the improvements required for battery technology to increase driving range and reduce the total cost of electrified vehicle ownership.

Marc Grynberg, CEO of Umicore, commented: "We are excited by the acceleration of demand and, thanks to the hard work of our teams in the past several years, we are well prepared to add significant capacity fast in support of our customers' growth. Umicore has a unique position in cathode materials and these investments underscore our ambition to be a global leader in materials that enable clean mobility. We are proud to be playing this role in sustainable transportation."

umicore

materials for a better life

Looking for a new challenge:
Apply at http://www.umicore.com/en/careers/