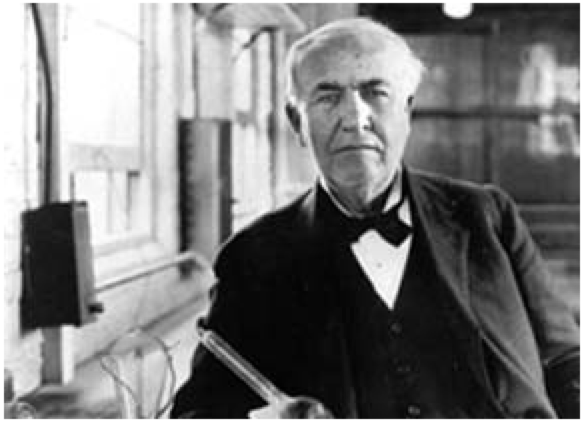
Presented at the COMSOL Conference 2009 Boston

Rechargeable Battery for Hybrid Diesel-Electric Locomotive

Michael Vallance

David Hall

GE … a heritage of innovation



Founded in 1892

$173 billion in annual revenues

Only company in Dow Jones index originally listed in 1896

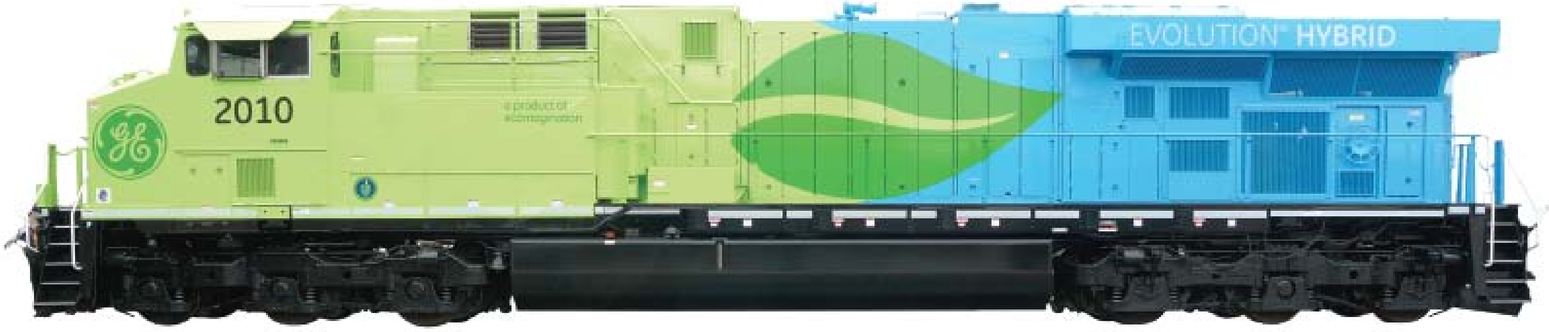
330,000 employees worldwide

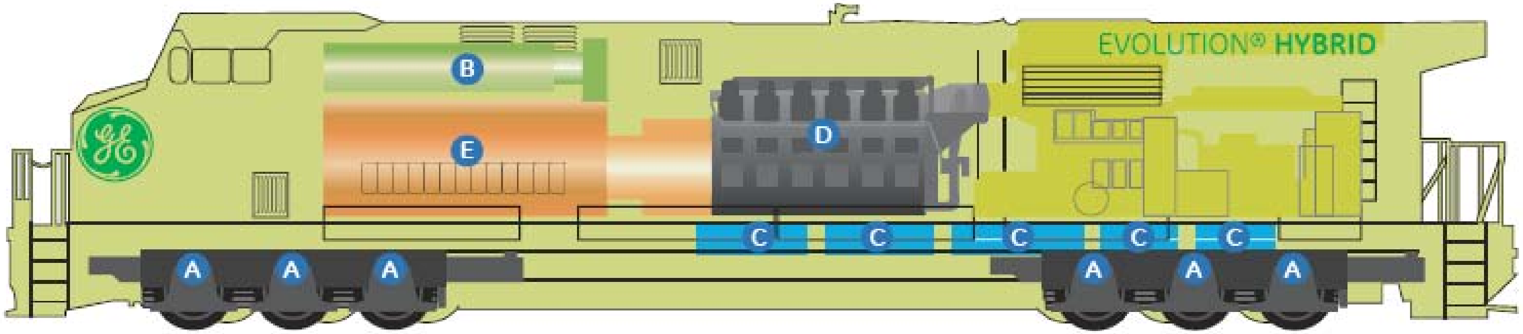
History of innovation

1909	Ductile tungsten
1913	Medical X-ray
1927	First television broadcast reception
1932	Langmuir Nobel Prize in chemistry
1938	Invisible/glareless glass
1942	First US jet engine
1953	LEXAN$^{\text{TM}}$ polycarbonate
1955	Man-made diamonds
1962	Semi-conductor laser
1973	Giaever Nobel Prize in physics
1984	Magnetic resonance imaging
1994	GE90$^{\circledR}$ composite fan blade
1999	Digital X-ray
2004	Lightspeed VCT


2010
2010
a product of ecomagination
EVOLUTION HYBRID

GE's Evolution® Hybrid Locomotive





How it works

In a conventional locomotive, energy generated by the traction motors Ⓐ during braking is dissipated entirely as heat through resistor grids Ⓑ.

In contrast, in a hybrid locomotive, some of that energy is captured in a series of lead-free, rechargeable batteries Ⓒ.

The captured energy can then be used to provide power in one of three ways:

- In combination with diesel-electric power (provided by the engine Ⓓ and the electrical system Ⓔ) to consistently deliver the required horsepower.
- As an addition to full diesel-electric power for quick acceleration from a full stop.
- As the primary power source (full battery power).

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TIMES UNION
timesunion.com
ALBANY, NEW YORK

Section: Opinion, Page: A8
Date: Wednesday, May 13, 2009

Back in January, Gov. David Paterson offered a vision in his State of the State address for New York to become a center of a green energy revolution, starting with development of a better battery.

On Tuesday we got a look at the kind of thing Mr. Paterson was talking about: General Electric plans to build a $100 million plant to produce new sodium batteries, a venture that would create 350 jobs in the Capital Region in coming years.

It's also good to see a politician's idea go from rhetoric to some measurable reality in so short a time. Too often, New York leaders talk of devoting millions upon millions of dollars to the vague, elusive goal of economic development, with no real game plan other than "if you pay for it, it will come." Here, the state is pledging $15 million; GE plans to use its own money and federal stimulus funds for the rest. The plant is projected to open in mid-2011.

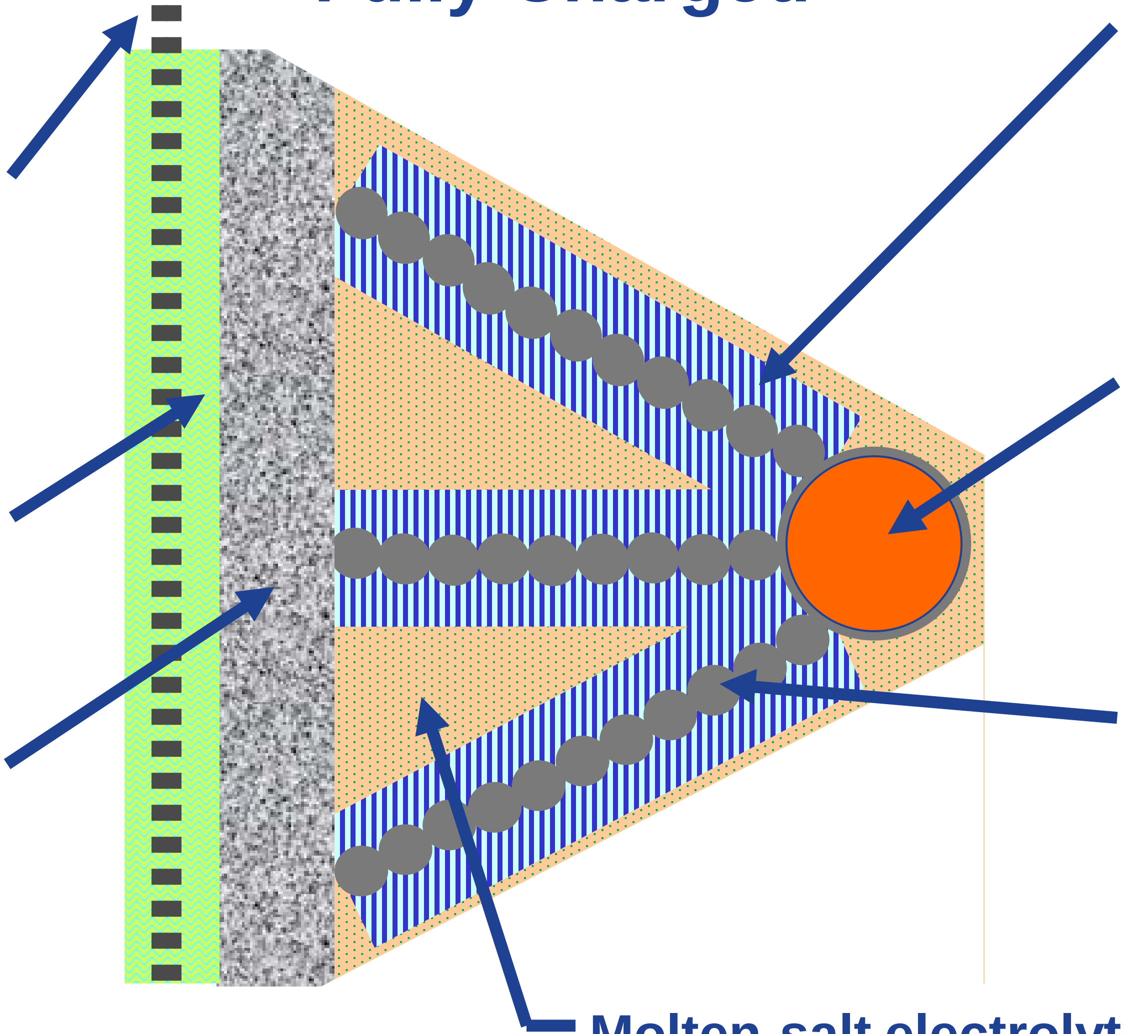
And it's gratifying to have a glimpse of what the rather broad term "green energy" can mean. These advanced sodium batteries, in which GE has already invested $150 million in research, are designed to store large amounts of energy -- measured in some applications in megawatts -- and release it slowly. While they don't have the quick jolt needed for cars, they're envisioned in things as small as locomotives and mining equipment and as large as solar or wind energy farms, which would pump excess power into them during peak production times and draw on them when the sun goes down or the wind subsides.

It's appropriate that General Electric, which led an energy revolution in this country, is his first major partner in this effort.

This, in so many ways, is the kind of energy New York needs right now.

Sodium / Nickel Chloride Rechargeable Battery

Fully Charged



Anode (-) current collector

Molten sodium (Na)

Na-conducting ceramic membrane β” alumina

Nickel Chloride ($NiCl_2$) **conversion layer**

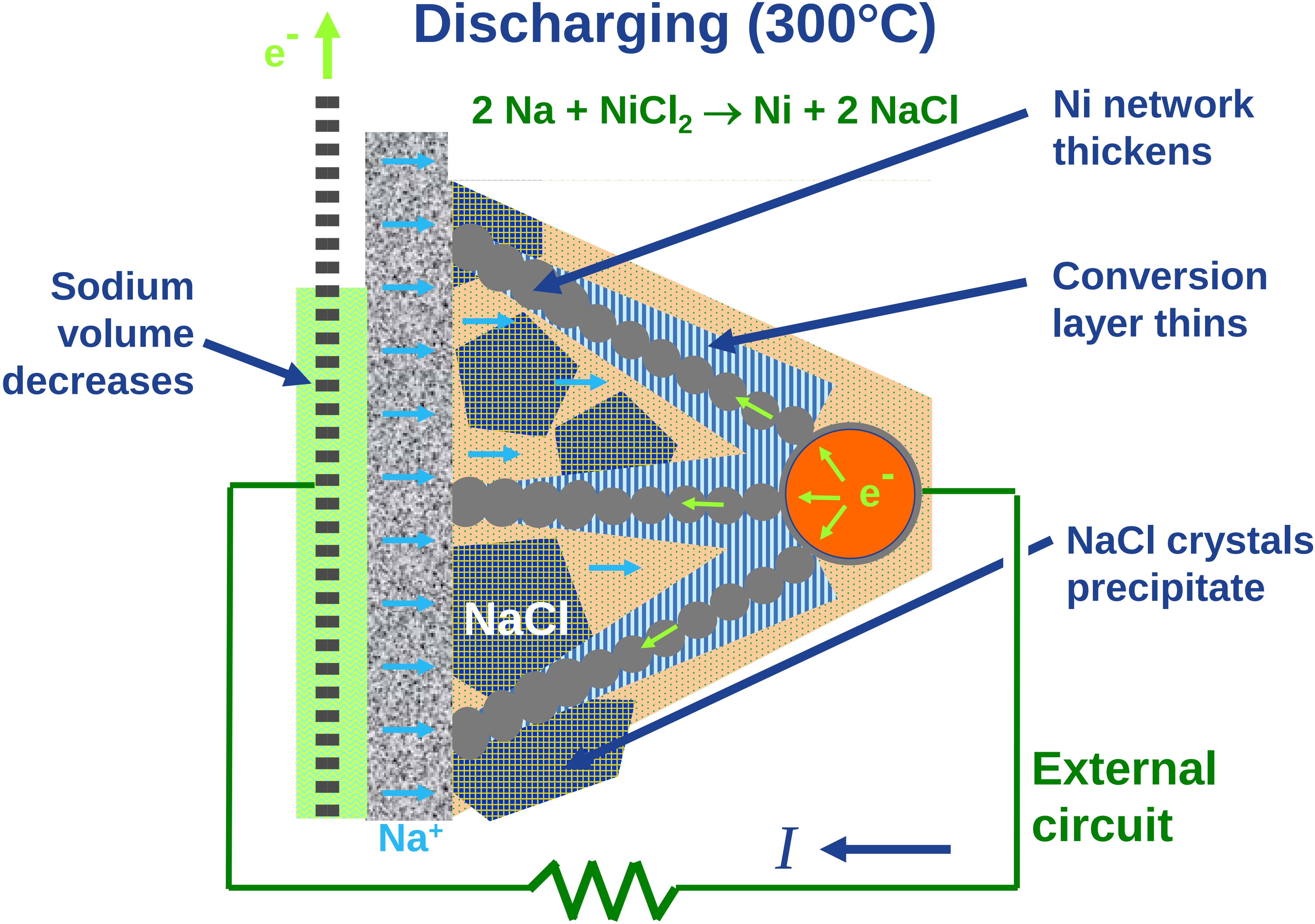
Cathode (+) current collector

Micro-dispersed nickel (Ni) **network**

Molten-salt electrolyte
NaCl-saturated sodium tetrachloroaluminate ($Na^+AlCl_4^-$)

imagination at work

Discharging (300°C)



Surface Chemistry

$$NiCl_2 + 2e^- \leftrightarrow Ni + 2Cl^- \qquad \text{(Positive Electrode)}$$

$$Na^+ + Cl^- \leftrightarrow NaCl$$

$$Na \leftrightarrow Na^+ + e^- \qquad \text{(Negative Electrode)}$$

$$NiCl_2 + 2Na \leftrightarrow Ni + 2NaCl \qquad \text{(Net Cell)}$$

Molten Electrolyte Chemistry⊗ -- 6 species: $AlCl_4^-$, Cl^-, $Al_2Cl_7^-$, $AlCl_3$, Al_2Cl_6, Na

$$2AlCl_3 \leftrightarrow Al_2Cl_6$$

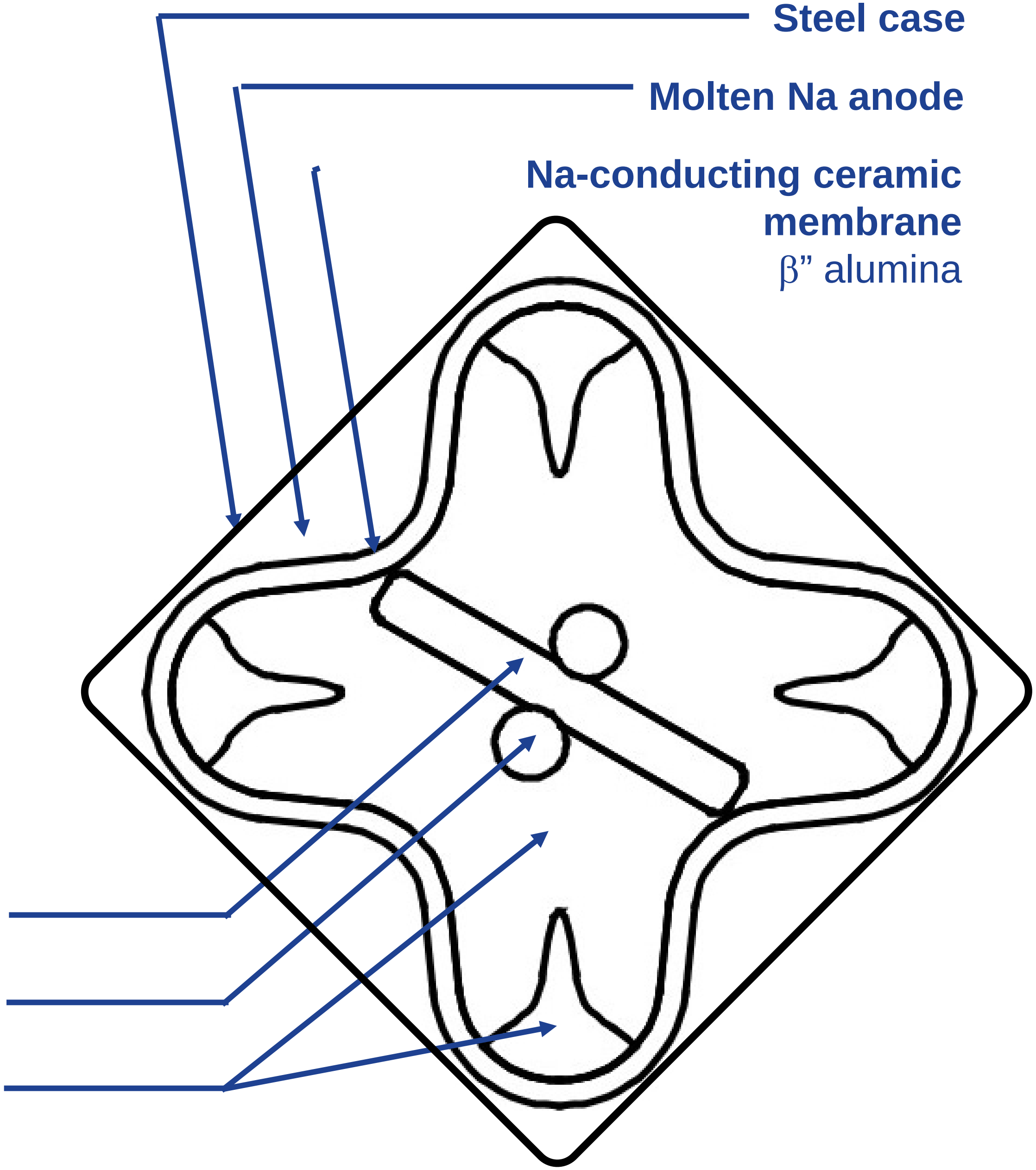
$$AlCl_4^- + AlCl_3 \leftrightarrow Al_2Cl_7^-$$

$$2AlCl_4^- \leftrightarrow Al_2Cl_7^- + Cl^-$$

Chemical Kinetics –

- **3 surface reactions**
- **3 bulk reactions**
- **Conversion-layer passivation kinetics**

⊗ L.G. Boxall, H.L. Jones and R.A. Osteryoung, *J. Electrochem. Soc.: Electrochemical Science and Technology*, **120**(2) 223-231, 1973.



Steel case

Molten Na anode

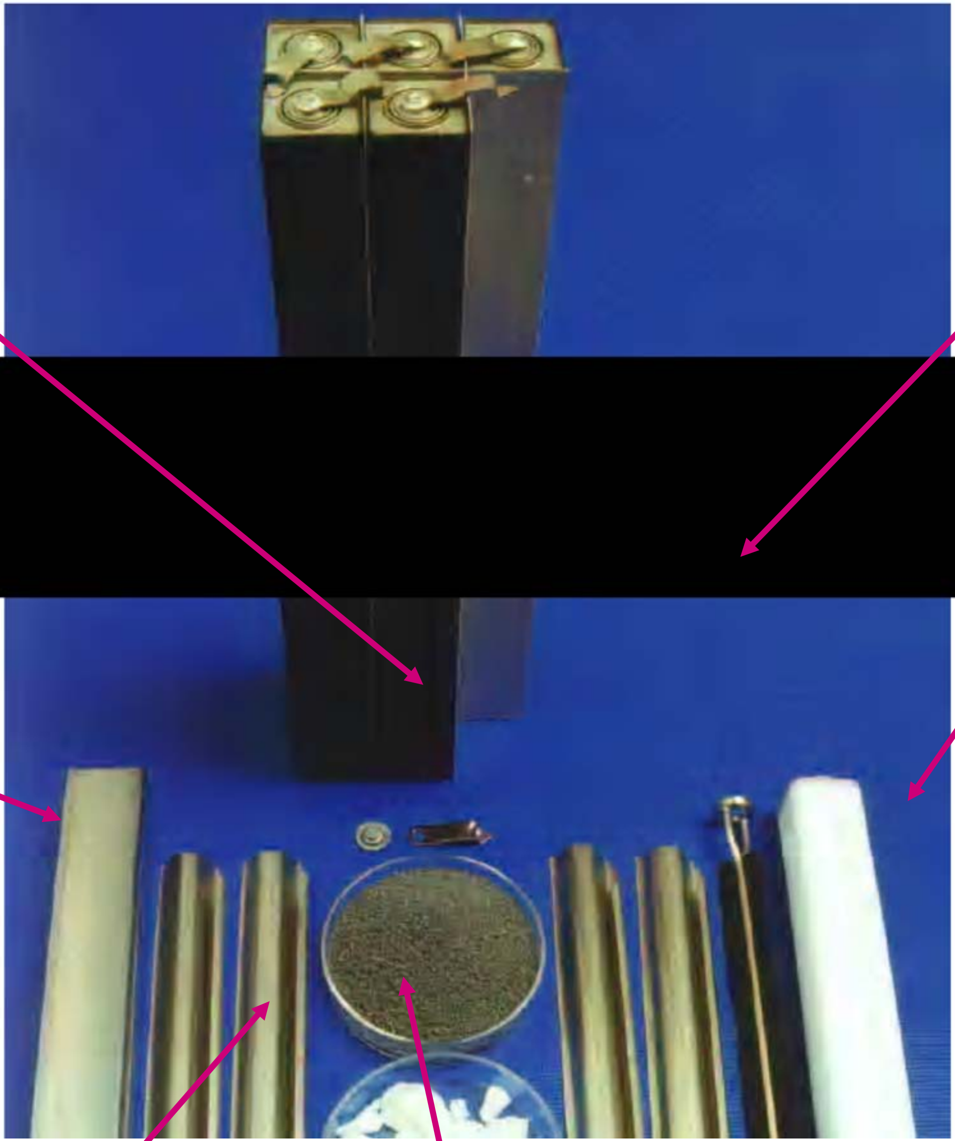
Na-conducting ceramic membrane
β” alumina

Carbon wick

Ni current collector

Cathode
Ni | $NiCl_2$ | NaCl | $NaAlCl_4$

imagination at work



[redacted]

Granulated
Ni + NaCl

Nickel cathode
current collector
and carbon wick

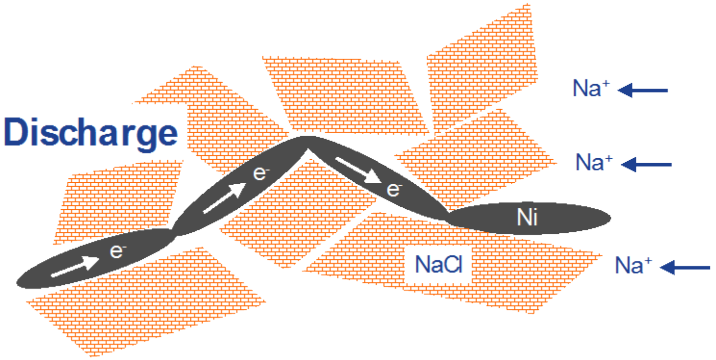
β” alumina
ceramic membrane

Steel case

Steel anode
current collectors (4)

$NaAlCl_4$
electrolyte (mp 185°C)

Cathode Kinetics



Discharge

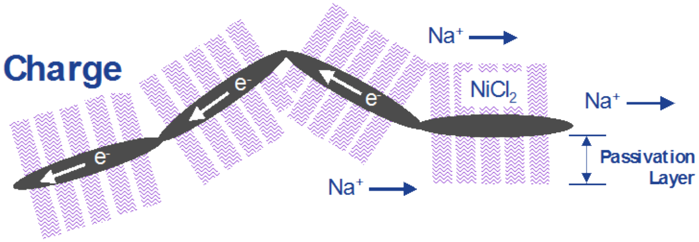
$$j = k_0 a_0 (1 - A)^m \frac{nF}{RT}\eta, \quad \eta < 0$$

⊕

⊖

Charge

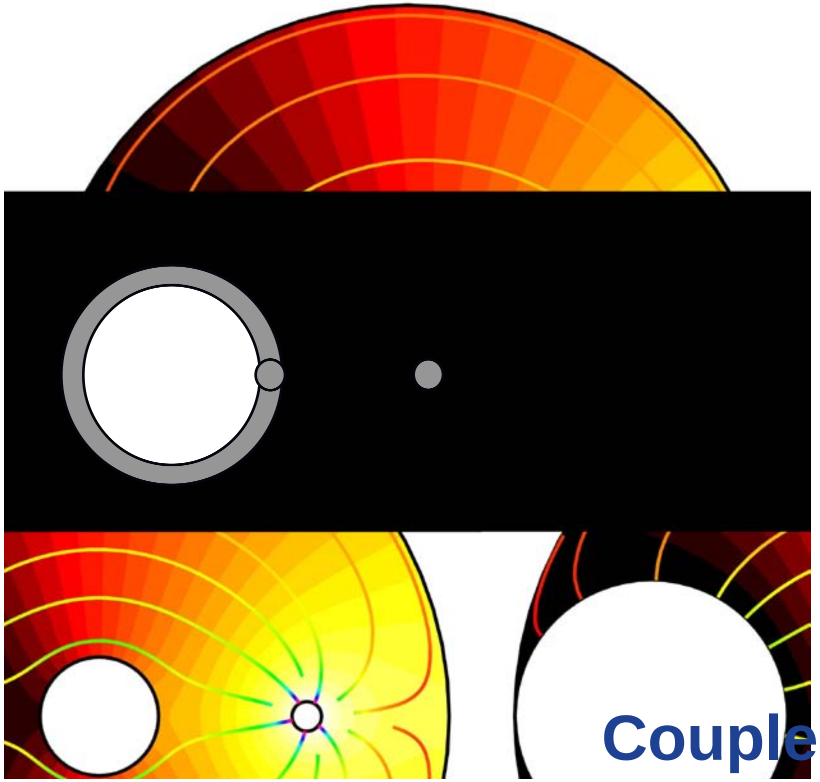
$$j = i_0 \left(\frac{c_2}{c_{20}}\right)^2 a_0 A^m \frac{nF}{RT}\eta, \quad \eta > 0$$



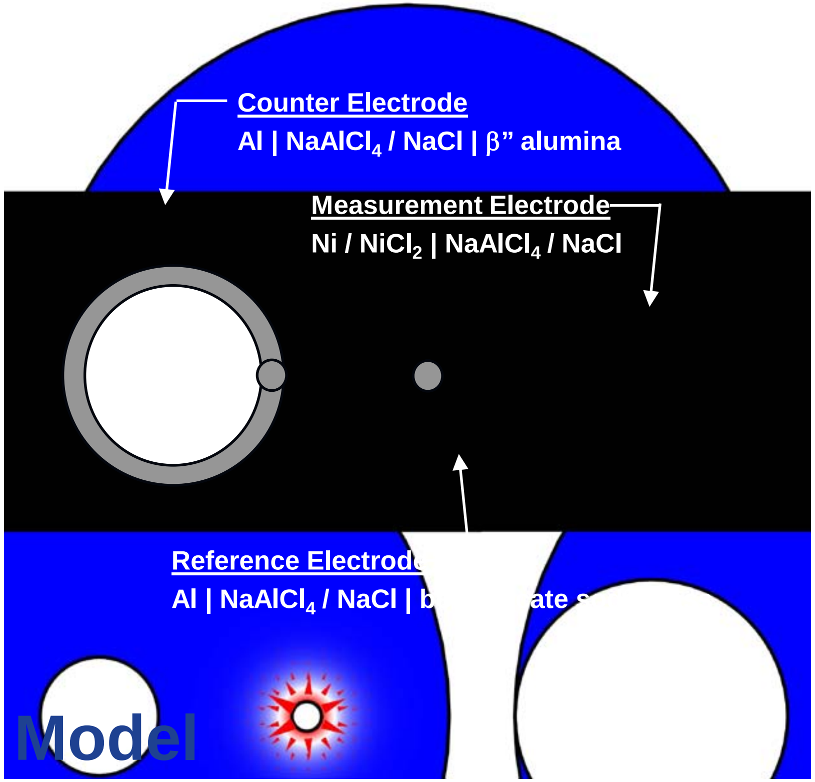
Butler-Volmer Equation$^{\otimes}$ with Mass Transfer Limitations

- c_2 – Cl$^-$ concentration [mol/cm^3]
- a_0 – as-built Ni surface area density [cm^2/cm^3]
- A – nickel surface availability (non-passivated fraction)
- j, η – transfer current density [A/cm^3], over-potential [V]
- k_0, i_0 – NiCl$_2$ mass transfer coefficient [A/cm^2], exchange current density [A/cm^2]

$^{\otimes}$ Truncated Taylor series expansion



DC Conducitivity



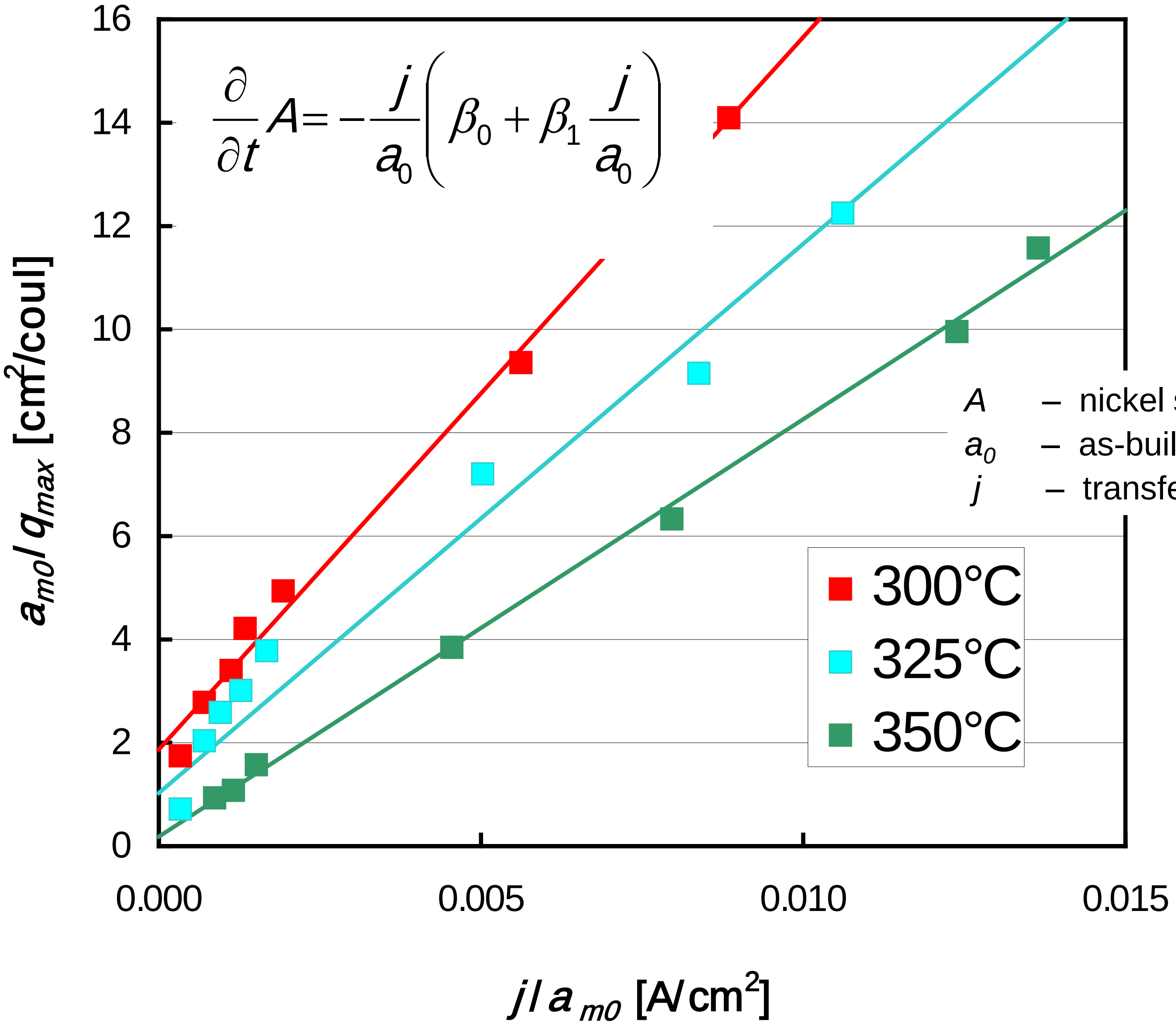
NaCl Diffusion

Coupled Model

Measurment Electrode $NiCl_2\ (solid) + 2\ e^- \leftrightarrow Ni\ (solid) + 2\ Cl^-$

Reference/ Counter Electrodes $Al\ (solid) + 4\ Cl^- \leftrightarrow AlCl_4^- + 3\ e^-$

Cylindrical Cell for Electrode Kinetics



$$\frac{\partial}{\partial t}A = -\frac{j}{a_0}\left(\beta_0 + \beta_1 \frac{j}{a_0}\right)$$

A – nickel surface availability
a_0 – as-built Ni surface area density [cm^2/cm^3]
j – transfer current density [A/cm^3]

Non-linear relation between passivation rate and transfer current density

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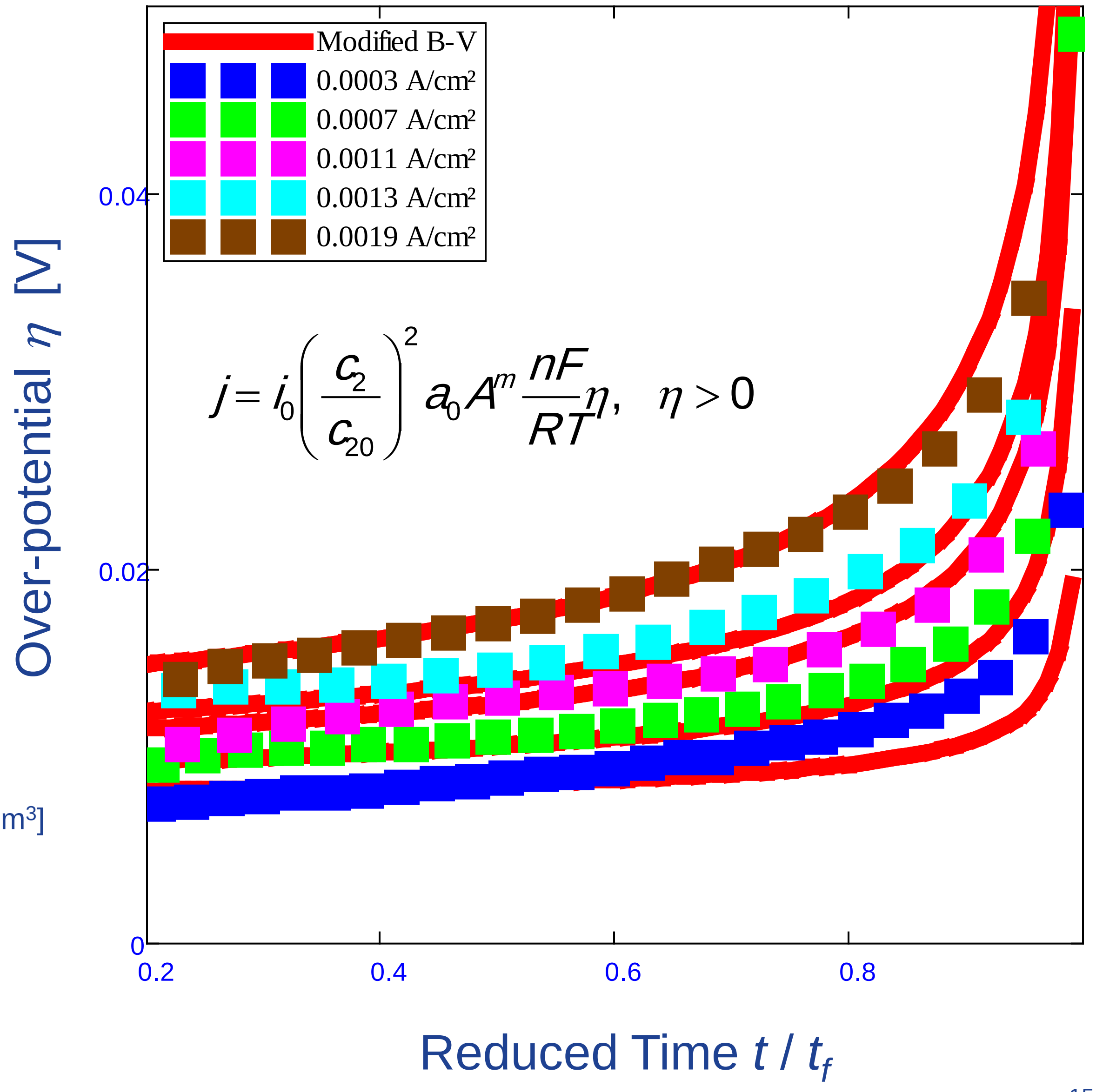
Charging kinetics described by modified Butler-Volmer equati



$$j = i_0 \left(\frac{c_2}{c_{20}} \right)^2 a_0 A^m \frac{nF}{RT} \eta, \quad \eta > 0$$

c_2 – Cl^- concentration [mol/cm^3]
a_0 – as-built Ni surface area density [cm^2/cm^3]
A – nickel surface availability
j – transfer current density [A/cm^3],
η – over-potential [V]
i_0 – exchange current density [A/cm^2]

Ni Network Conductivity

Depends on

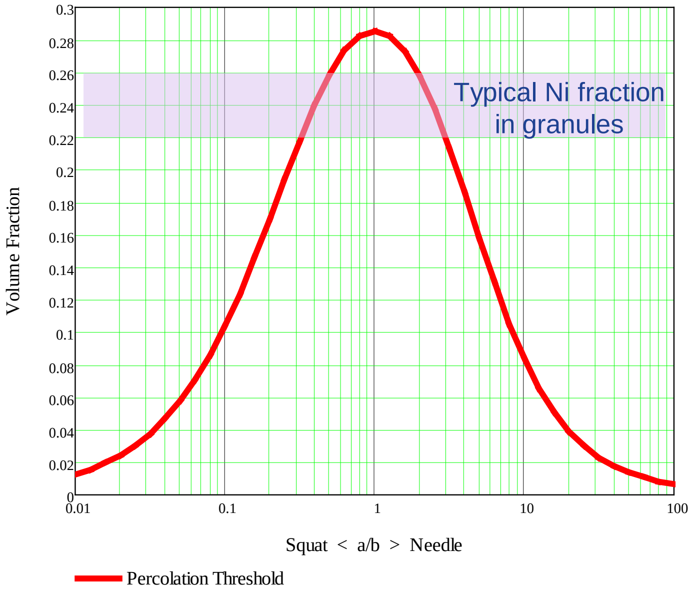
- state of charge
- cathode organization

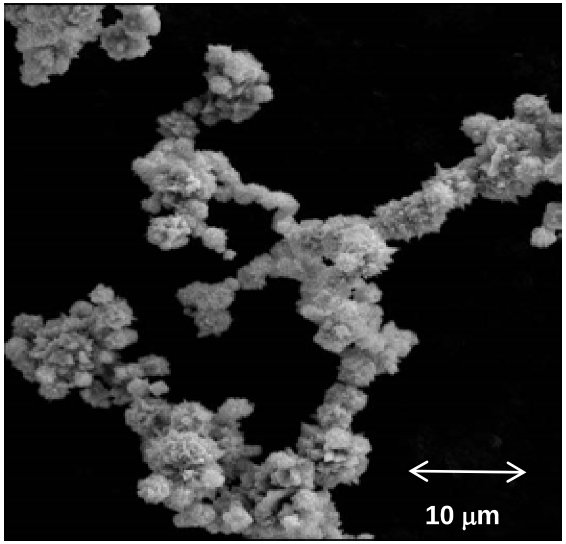
☛ ***in situ* measurement + modeling**

Hierarchical model

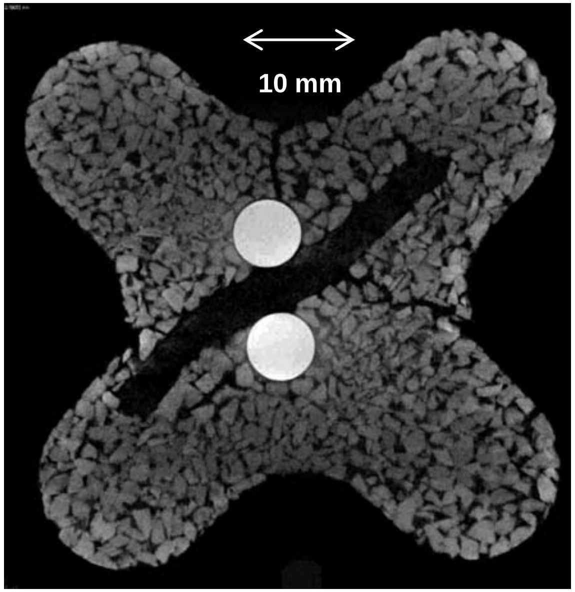
Granule: Micromechanical (μ-wire) model

athode: Bruggeman mean-field model (sphere)





SEM of Ni powder showing filamentary microstructure



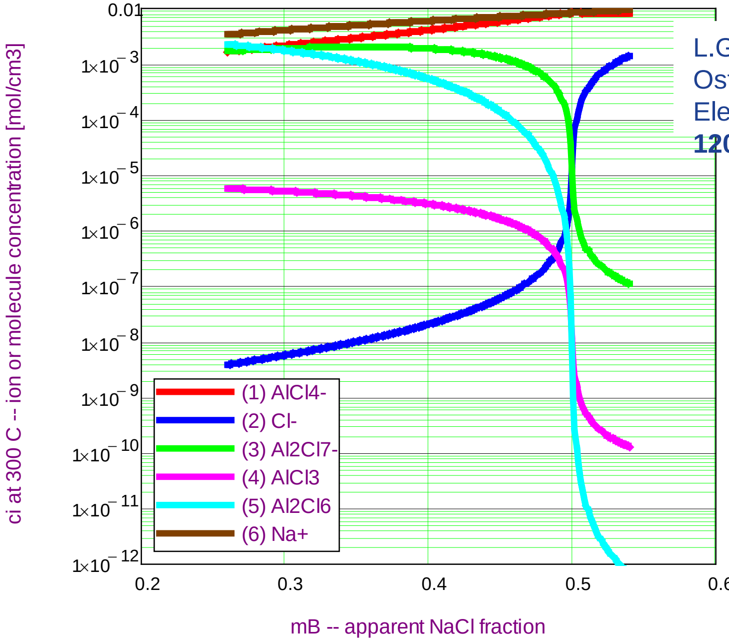
Phoenix|X-ray nanotom of cycled positive electrode showing granular structure

Ni Network Conductivity

Four Point Probe Testing of Hot Cathode Sections

FEM for geometry factor

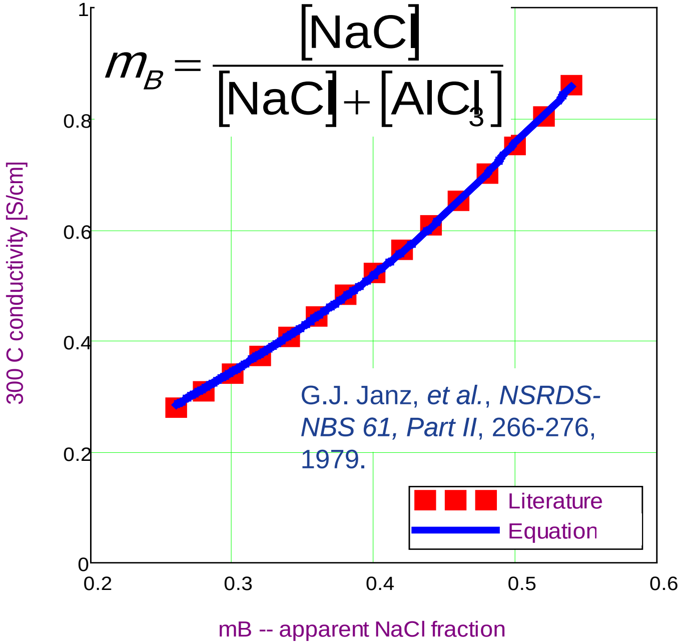
Ion Mobilities



L.G. Boxall, H.L. Jones and R.A. Osteryoung, *J. Electrochem. Soc.: Electrochemical Science and Technology*, **120**(2) 223-231, 1973.

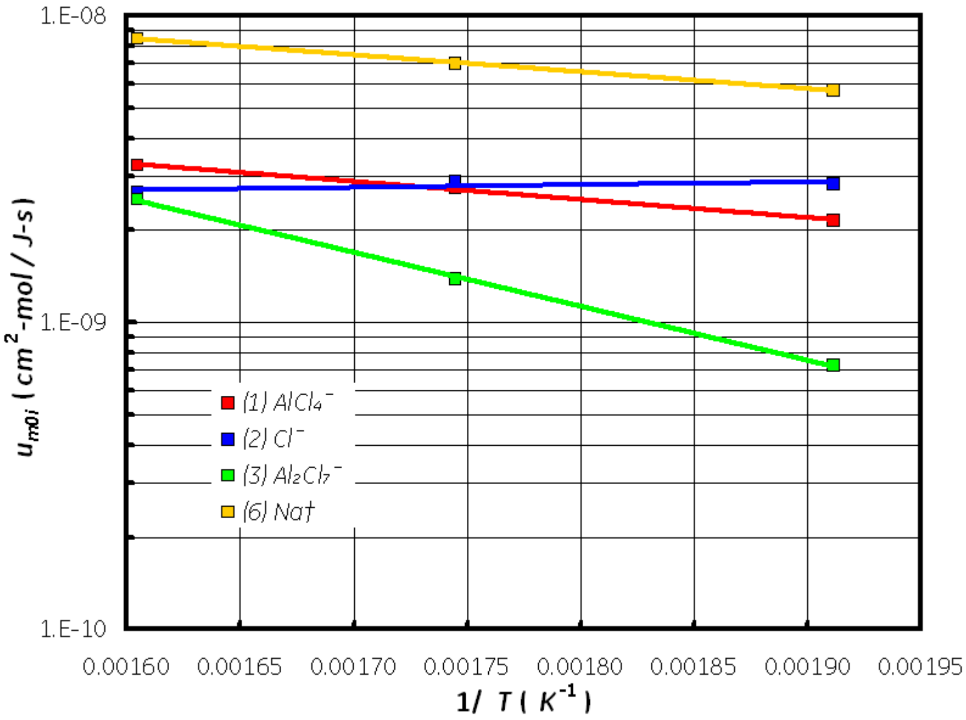
$$\kappa_e = F^2\left(\sum_i z_i^2 u_{m0i} c_i\right)$$

$$u_{m0i}(T) = A_{ui} e^{-\frac{E_{ui}}{RT}}$$



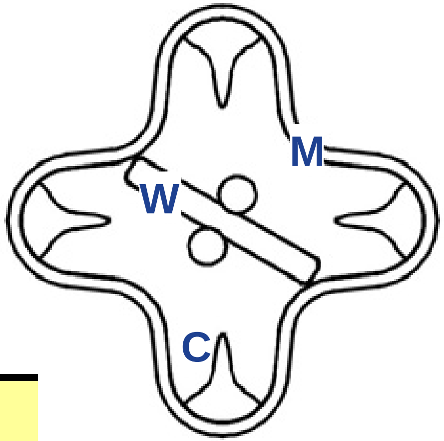
$$m_B = \frac{[\mathrm{NaCl}]}{[\mathrm{NaCl}] + [\mathrm{AlCl_3}]}$$

G.J. Janz, *et al.*, *NSRDS-NBS 61, Part II*, 266-276, 1979.



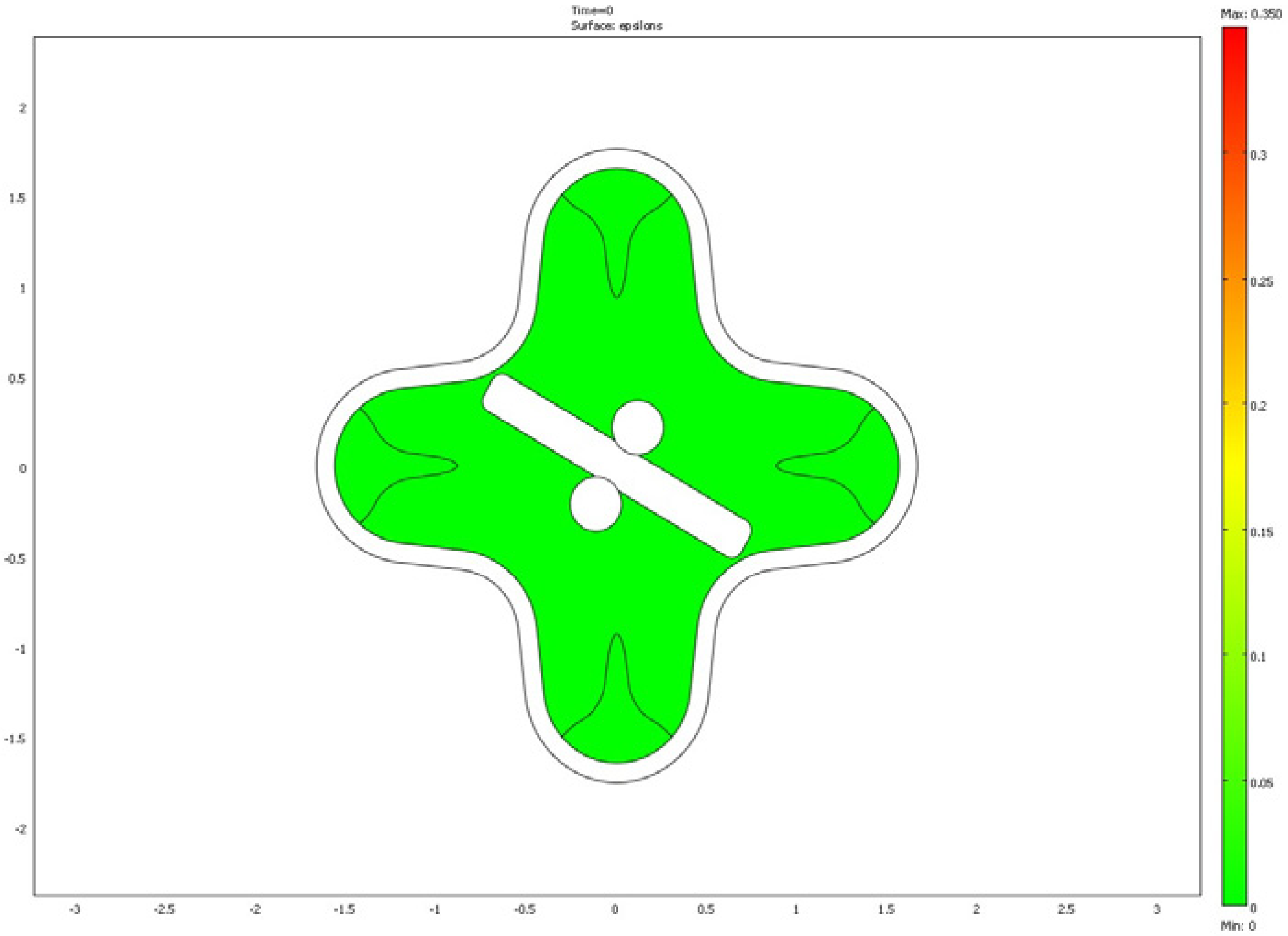
Conductivity data supports Nernst-Planck approximation

FEM Model

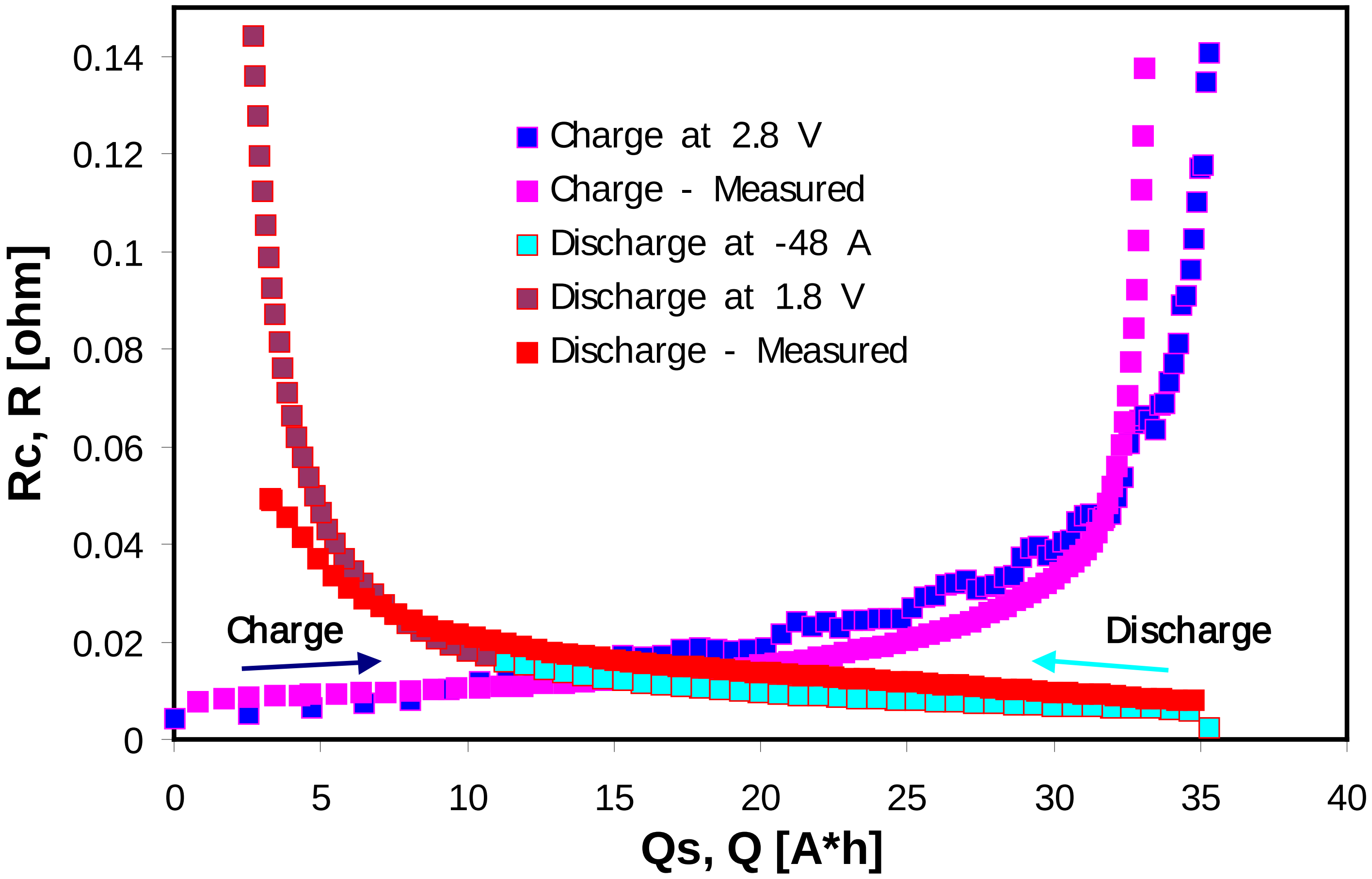


4 Application Modes
15 Dependent Variables

Dependent Variable	Description	Domains	Application Mode
ϕ_2	Electric field potential in electrolyte	C	Nernst-Planck
c_2	Cl^- concentration in electrolyte		
c_3	$Al_2Cl_7^-$ concentration in electrolyte		
c_4	$AlCl_3$ concentration in electrolyte		
c_5	Al_2Cl_6 concentration in electrolyte		
c_6	Na^+ concentration in electrolyte		
c_m	Ni volume fraction	C	Diffusion
c_p	NaCl volume fraction		
c_s	$NiCl_2$ volume fraction		
c_A	Surface availability		
ϕ_1	Electric field potential in Ni network and reservoir	C, W	Conductive media DC
ϕ_2	Electric field potential in BASE	M	
p	Pressure associated with convection	C	Darcy's law
V_{in}	Electric field potential of current collector	Global	Global equations
V_{ex}	Electric field potential across cell	Global	



Reaction Front Translates Inward from Ceramic Membrane Charging and Discharging



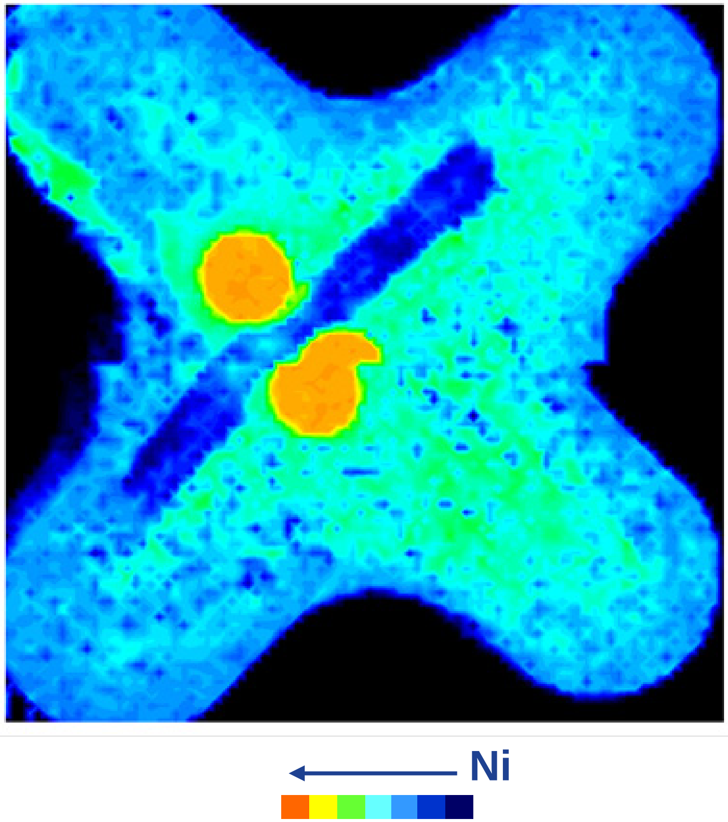
Model Predictions Agree with Measured Cell Performance

imagination at work

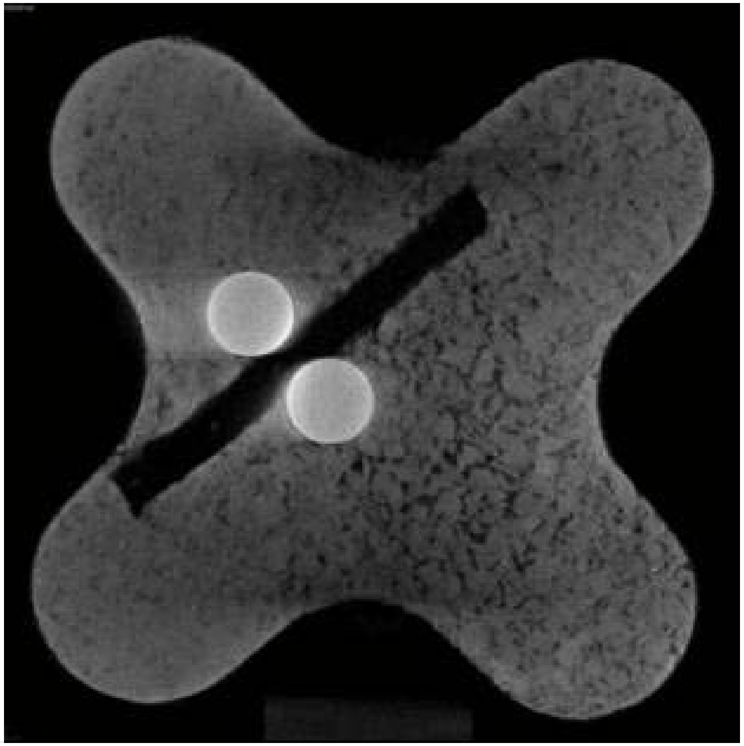
Microstructure of Discharged, Degraded Cathode

Offset current collector causes varied degradation

Ni XRF Map



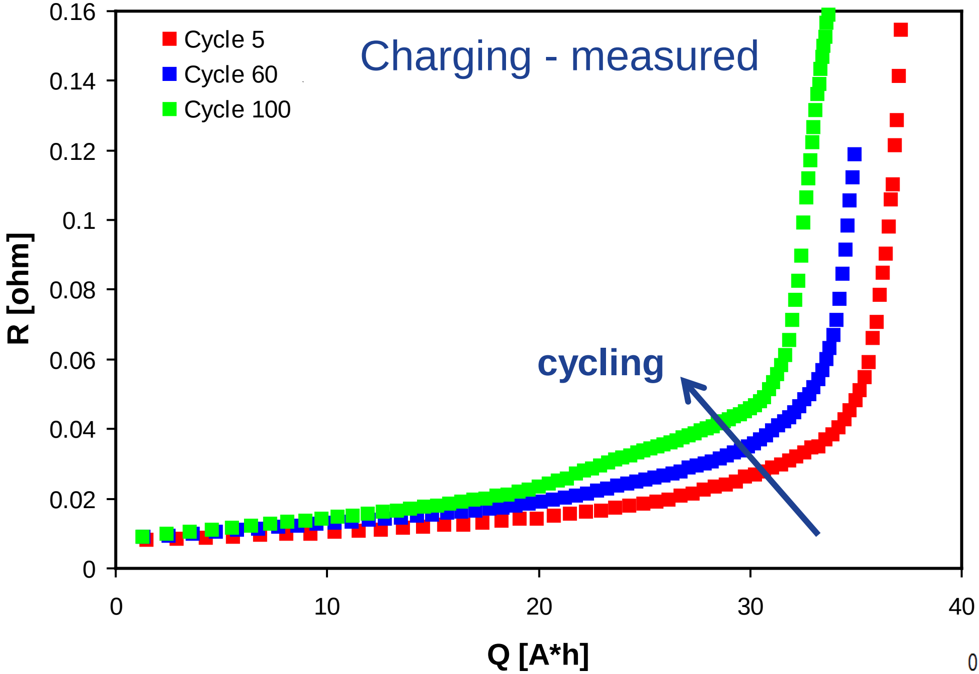
CT Slice



Courtesy of Phoenix | X-ray

Ni fluorescense decreased:
- lower Ni concentration, or
- increased matrix effects

Granule structure distorted in highly utilized volume

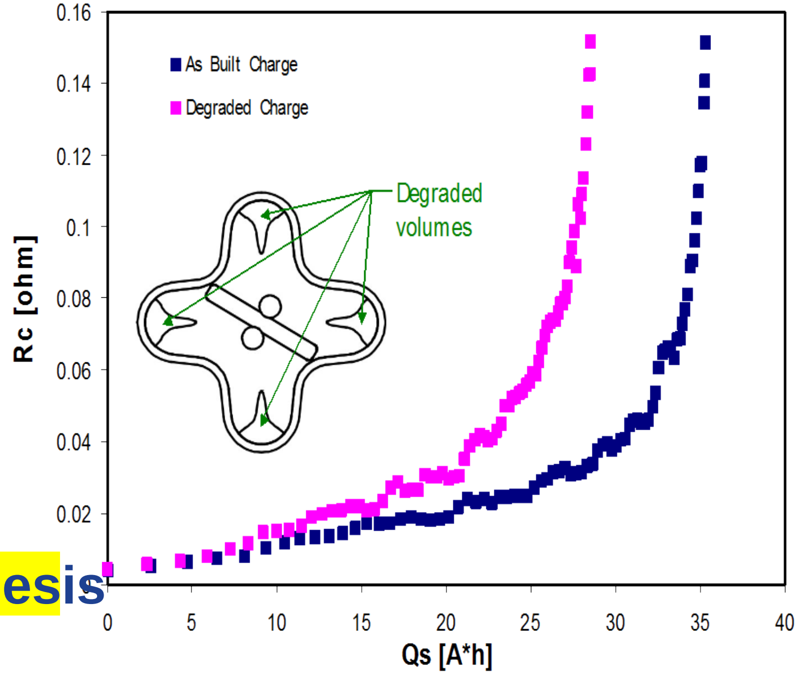


Degradation due to deep-discharge cycling

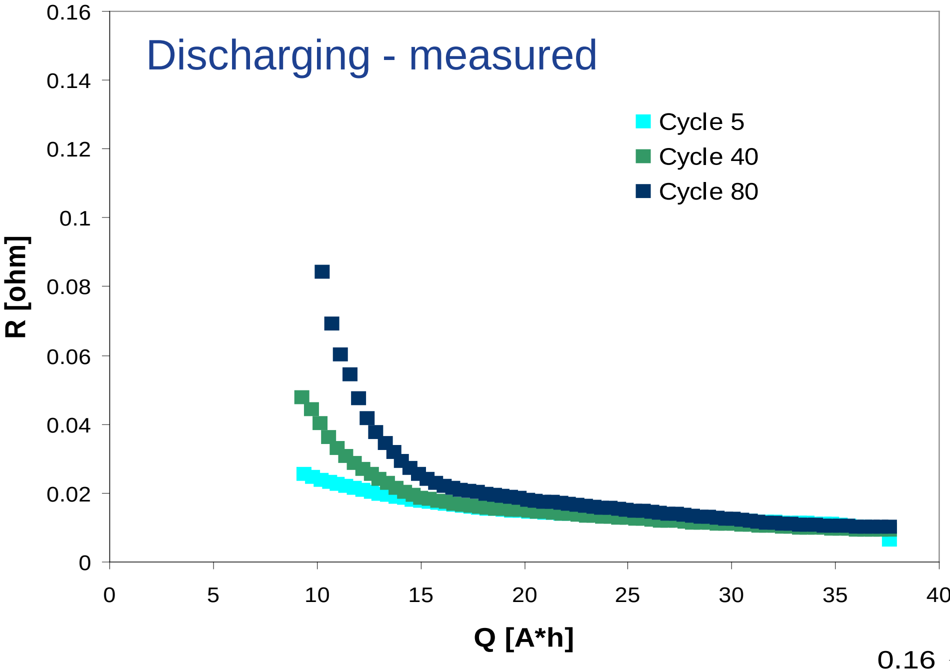
- R rises with cycling and state of charge
- Charge capacity decreases with cycling

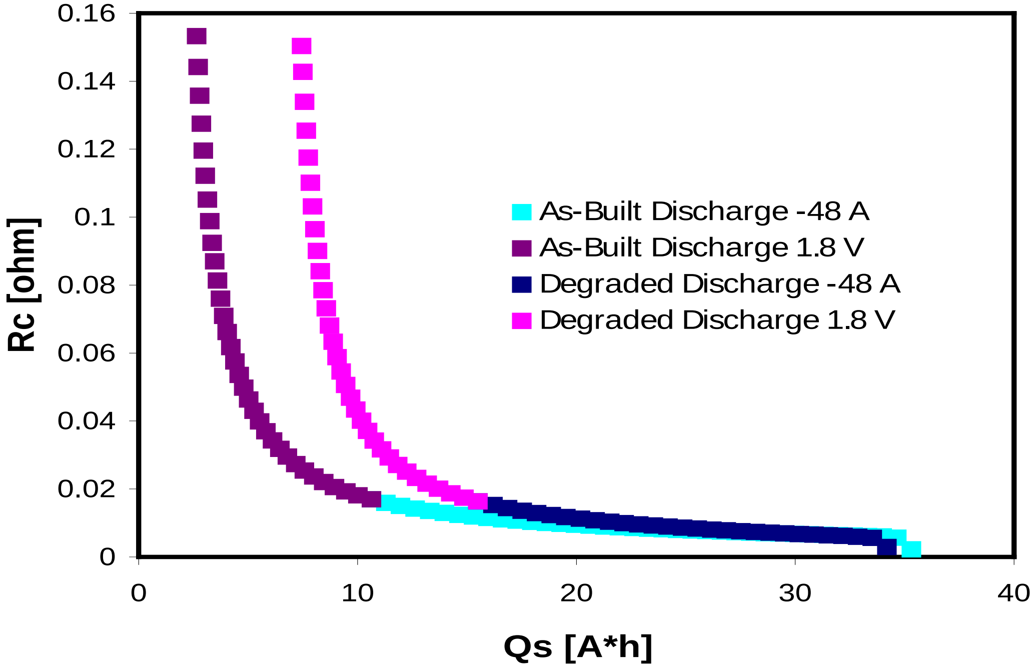
Modeling degraded cathode

- Typcial degraded volumes (CT & microfocus XRF)
- Loss of electrochemical activity in degraded volumes



Model supports degradation hypothesis


Discharging - measured
Cycle 5
Cycle 40
Cycle 80
R [ohm]
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
5
10
15
20
25
30
35
40
Q [A*h]


As-Built Discharge -48 A
As-Built Discharge 1.8 V
Degraded Discharge -48 A
Degraded Discharge 1.8 V
Rc [ohm]
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
10
20
30
40
Qs [A*h]

Chemical engineering models are no better than underlying kinetics data.

2-D modeling of the Na | $NiCl_2$ storage cell provides realistic response.

Isolation of cathode portions describes degradation during deep-discharge cycling

Acknowledgements:
David Bogdan
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