COMSOL CONFERENCE 2015 BOSTON

Cycling-Induced Degradation of Batteries

Michael Vallance & Andrey Meshkov, GE Global Research

Ralph White, Meng Guo, Sean Rayman, & Long Cai, R.E. White and Associates

Comsol Conference *2015* Boston

nyserda Energy. Innovation. Solutions.

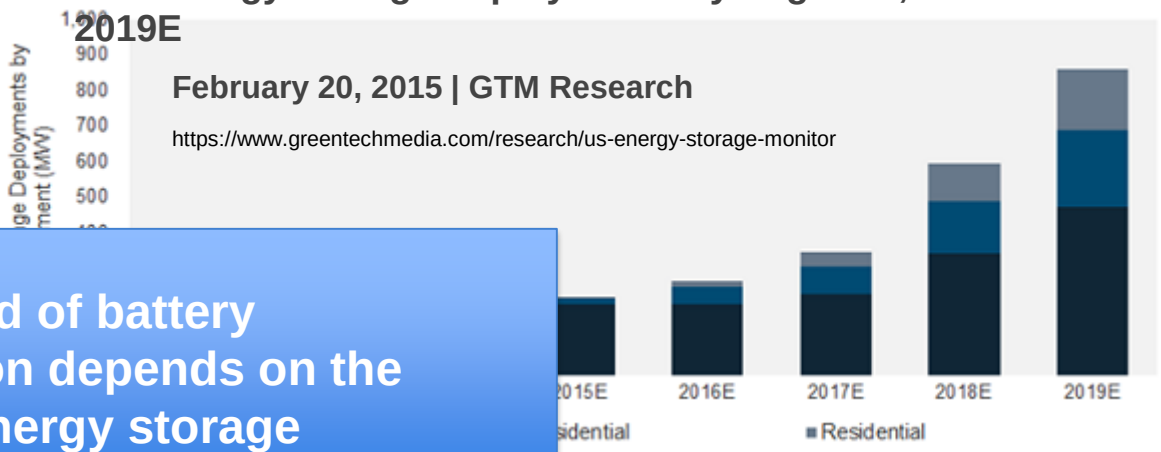
Imagination at work.

We acknowledge the financial support from the New York State Energy Research and Development Authority (NYSERDA) via the New York Battery and Energy Storage Technology Consortium (NY-BEST). NYSERDA has not reviewed the information contained herein, and the opinions expressed in this report do not necessarily reflect those of NYSERDA or the State of New York.

U.S. Energy Storage Deployments by Segment, 2012-2019E

February 20, 2015 | GTM Research

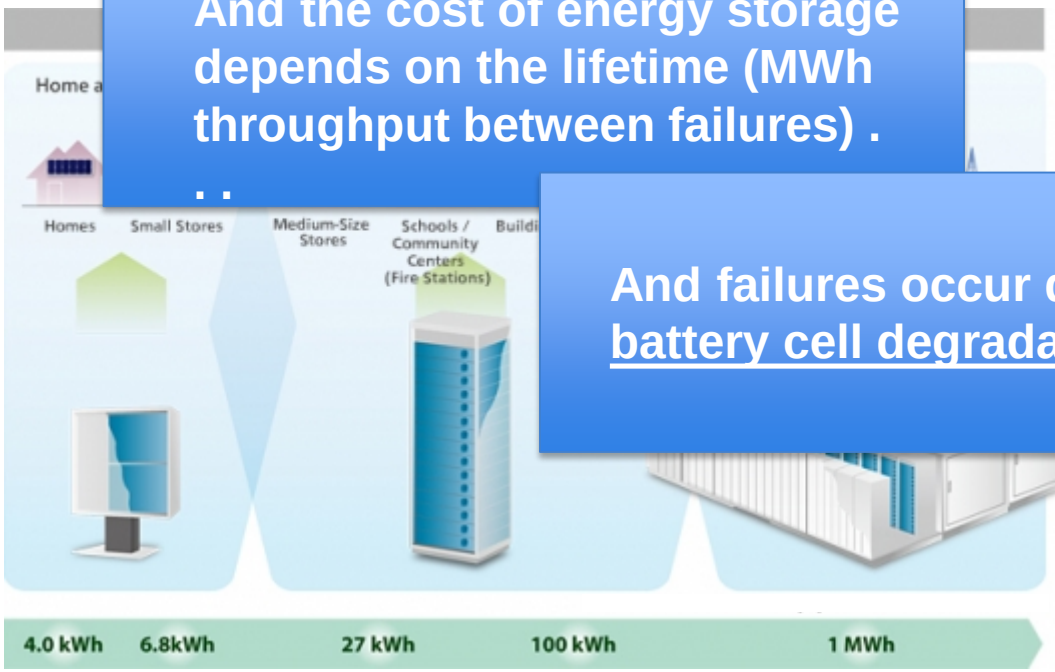
https://www.greentechmedia.com/research/us-energy-storage-monitor



The speed of battery integration depends on the cost of energy storage (MWh/$) . . .

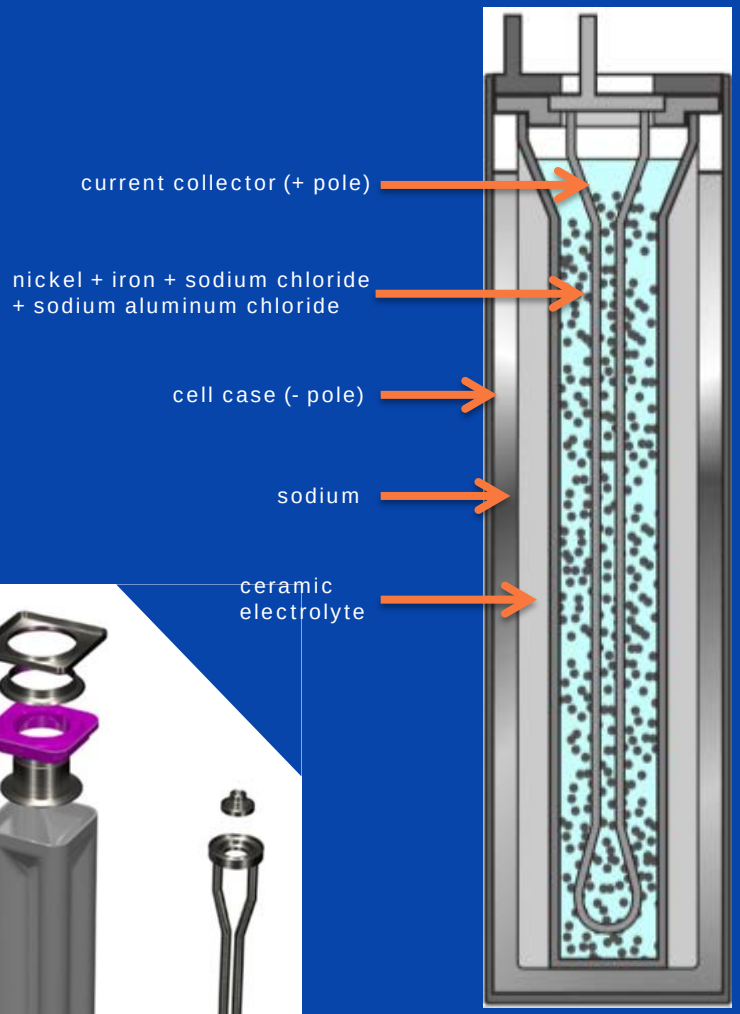
And the cost of energy storage depends on the lifetime (MWh throughput between failures) . . .

And failures occur due to battery cell degradation



http://www.greentechmedia.com/articles/read/liedo-panasonics-distributed-grid-ready-battery-network

https://en.wikipedia.org/wiki/Molten_salt_battery



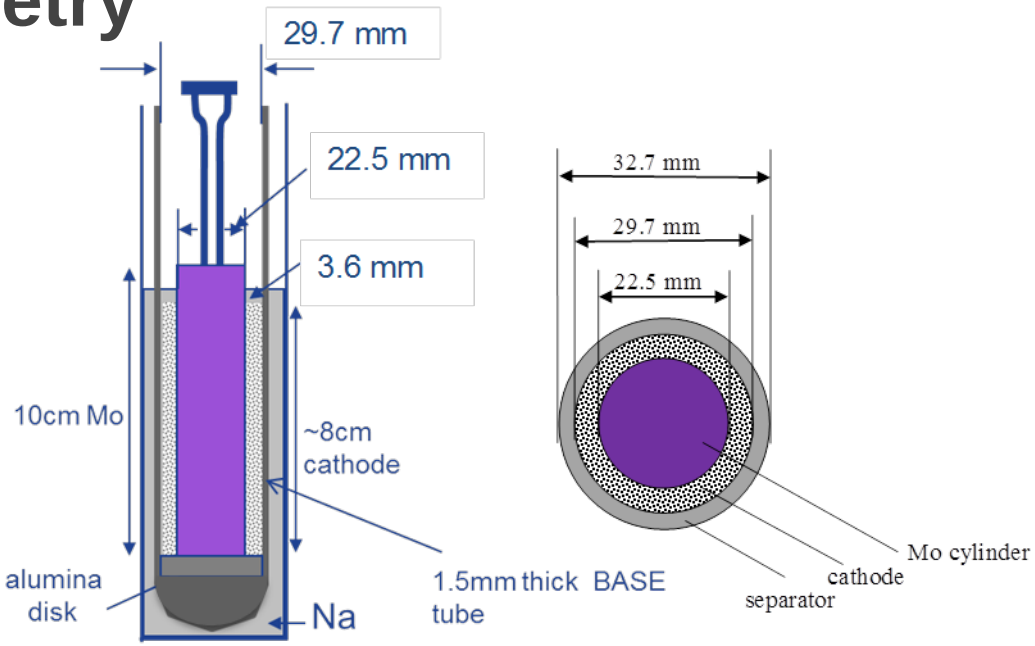
Sodium Metal Chloride Rechargeable Cell

- 260-340°C operation
- β″ alumina electrolyte
- NaCl-buffered sodium aluminum chlorate cathode electrolyte
- Compound cathode: nickel & iron & NaCl
- Net electrochemical reactions:

$$NiCl_2 + 2\,Na \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Ni + 2\,NaCl,\ U_0 = 2.58\ V$$

$$FeCl_2 + 2\,Na \underset{\text{charge}}{\overset{\text{discharge}}{\rightleftharpoons}} Fe + 2\,NaCl,\ U_0 = 2.33\ V$$

Test Geometry



CT slice of as-built cell

Cycling Protocol

-5.68 W to 2.00 V
+0.00 W to 600 s
+5.68 W to V_M
V_M to 0.142 A
+0.00 W to 600 s
Repeat

Design of Experiment

		V_M (V)	
		2.67	2.87
T (°C)	240	X	X
	300	X	X
	340	X	X

2 × 3 full factorial with partial replication

Electrochemical Reactions (Bulter-Volmer)

$$\mathrm{Ni}\,(s) + 2\,\mathrm{Cl}^{+} = \mathrm{NiCl_2}\,(s) + 2\,\mathrm{e}^{-}$$

$$\mathrm{Fe}\,(s) + 6\,\mathrm{NaCl}\,(s) + 2\,\mathrm{Cl}^{-} = \mathrm{Na_6FeCl_8}\,(s) + 2\,\mathrm{e}^{-}$$

$$\mathrm{Fe}\,(s) + \frac{1}{3}\,\mathrm{Na_6FeCl_8}\,(s) + 2\,\mathrm{Cl}^{-} = \frac{4}{3}\,\mathrm{FeCl_2}\,(s) + 2\,\mathrm{NaCl}\,(s) + 2\,\mathrm{e}^{-}$$

Cathode

$$2\,\mathrm{Na}^{+} + 2\,\mathrm{e}^{-} = 2\,\mathrm{Na}\,(\ell)$$

Anode

Non-electrochemical Reactions (First order or $\propto \Delta G$)

$$\mathrm{Na}^{+} + \mathrm{Cl}^{-} = \mathrm{NaCl}\,(s)$$

$$\mathrm{FeCl_2}\,(s) + 6\,\mathrm{Na}^{+} + 6\,\mathrm{Cl}^{-} = \mathrm{Na_6FeCl_8}\,(s)$$

Precipitation & dissolution

$$2\,\mathrm{AlCl_3}\,(\ell) = \mathrm{Al_2Cl_6}\,(\ell)$$

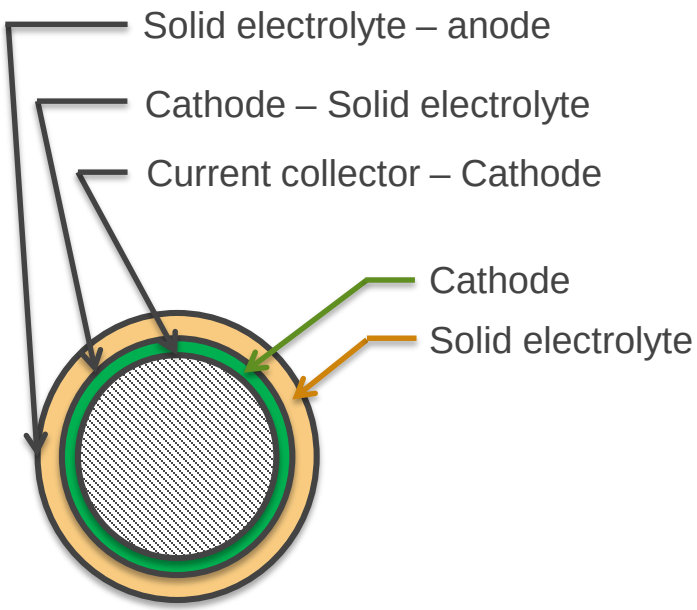
$$\mathrm{AlCl_4^-} + \mathrm{AlCl_3}\,(\ell) = \mathrm{Al_2Cl_7^-}$$

$$2\,\mathrm{AlCl_4^-} = \mathrm{Al_2Cl_7^-} + \mathrm{Cl}^{-}$$

Cathode electrolyte rearrangement

$$\mathrm{Na_6FeCl_8}\,(s) + \mathrm{Ni_AFe_{B\text{-}1}Cl_{2(A+B-1)}}\,(s) = \mathrm{Ni_AFe_BCl_{2(A+B)}}\,(s) + 6\,\mathrm{NaCl}\,(s)$$

Metal chloride reorganization

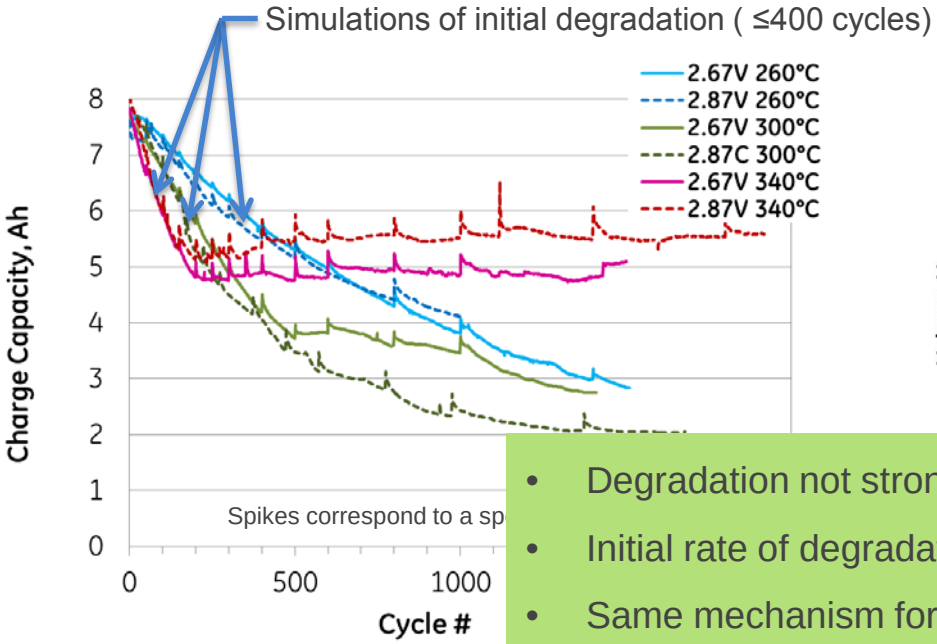


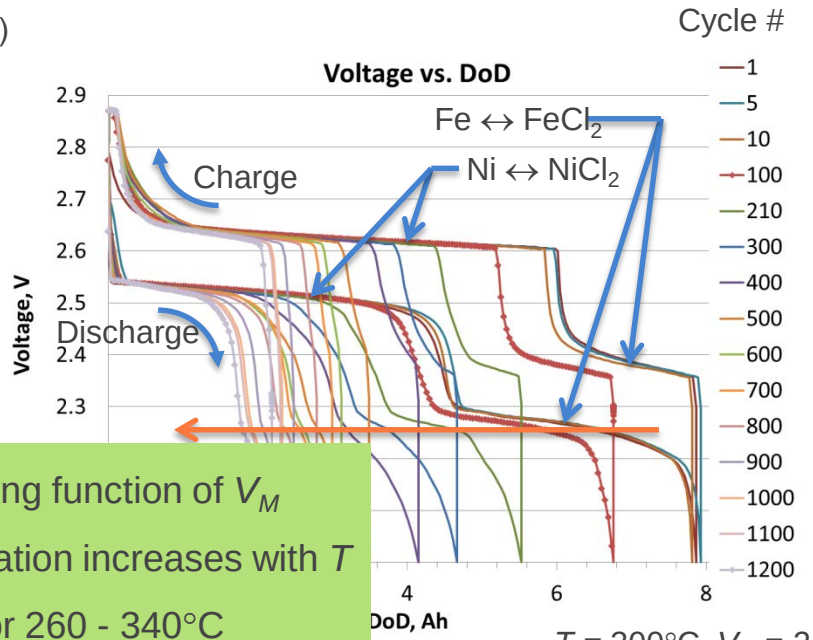
Dependent variable	Flux constitutive law
Ionic charge	Nernst-Planck
Electronic charge	Ohm's law
$AlCl_4^-$ concentration	Nernst-Planck
Cl^- concentration	Nernst-Planck
$Al_2Cl_7^-$ concentration	Nernst-Planck
$AlCl_3$ concentration	Nernst-Planck
Al_2Cl_6 concentration	Nernst-Planck
Fe concentration	Not applicable
NaCl concentration	Not applicable
Na_6FeCl_8 concentration	Not applicable
$FeCl_2$ concentration	Not applicable
$NiCl_2$ concentration	Not applicable

1-D, axisymmetric, time-dependent simulation

1 full cycle using experimental cycling protocol

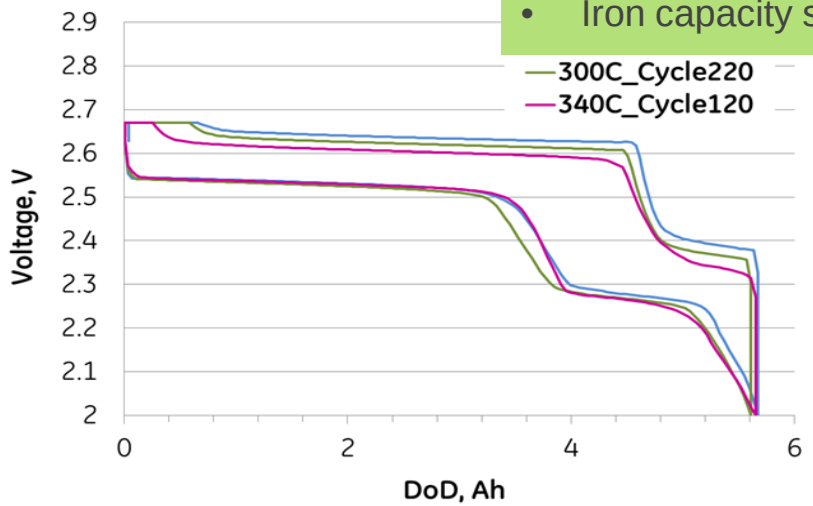
Reaction moduli used as fitting parameters

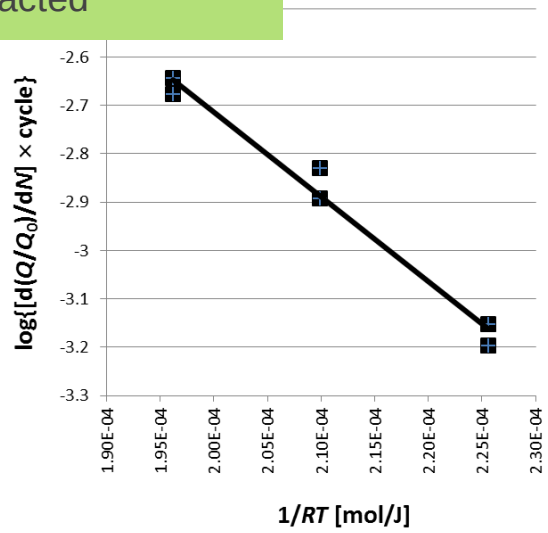


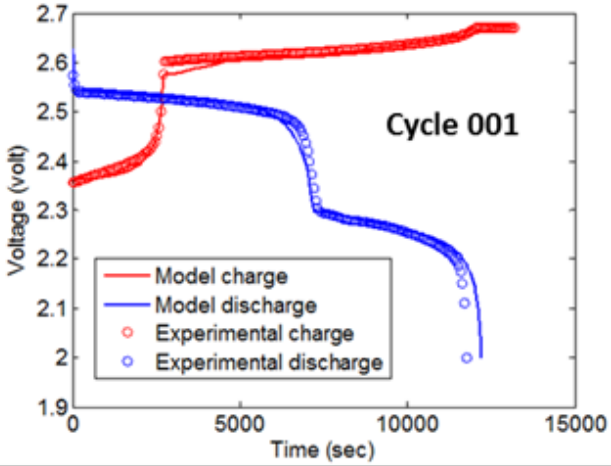


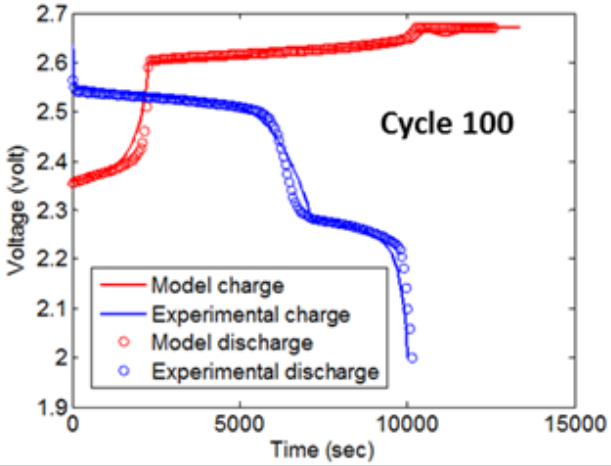
- Degradation not strong function of V_M
- Initial rate of degradation increases with T
- Same mechanism for 260 - 340°C
- Iron capacity strongly impacted

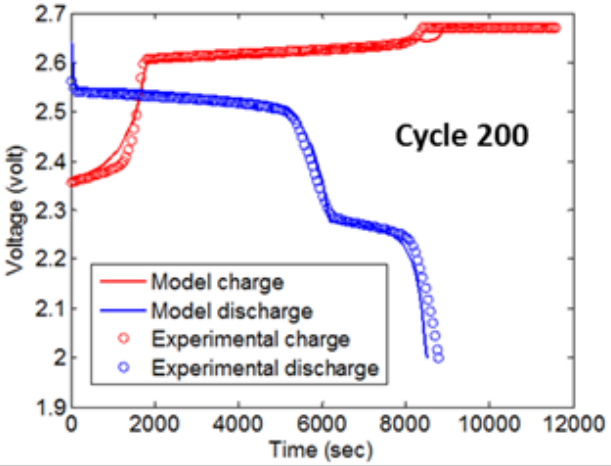
T = 300°C, V_M = 2.87 V

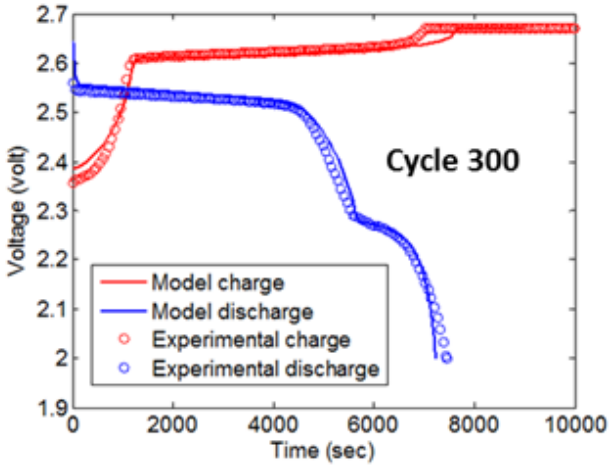


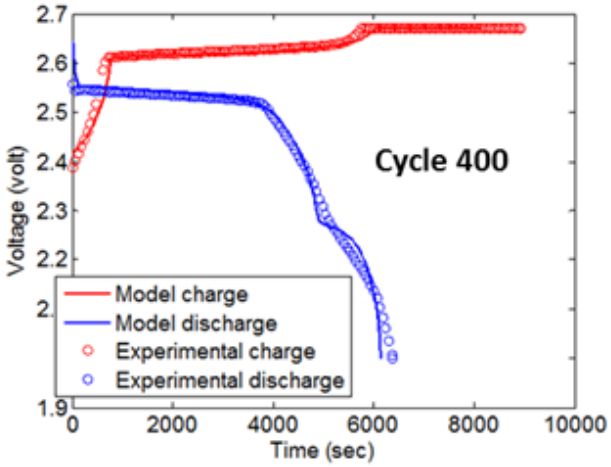








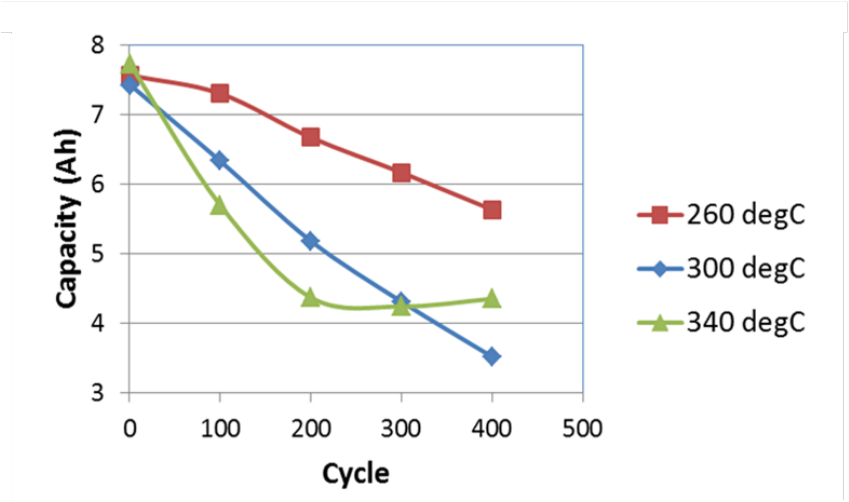


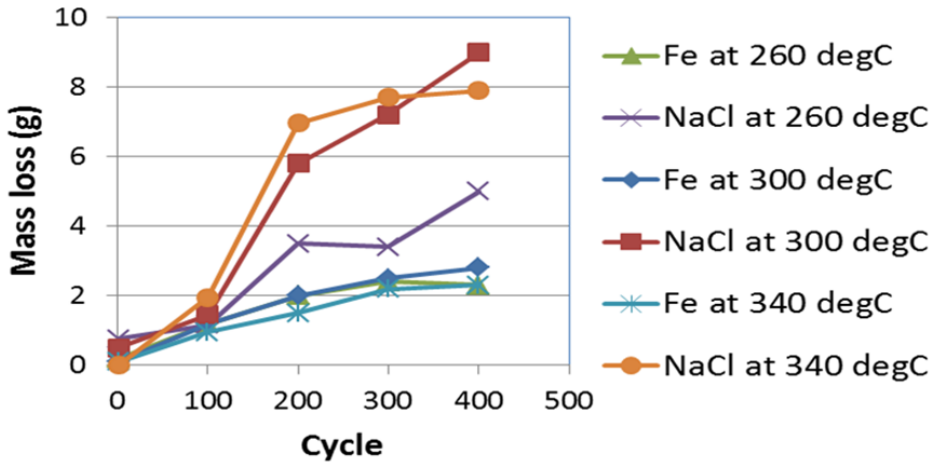


V_M = 2.67 V
T = 300°C

Measured *vs* Simulated Charge & Discharge

Typical of all T and V_M





Key Learning from Simulation:

Degradation manifests as uniform loss of Fe and NaCl from the cathode, in the molar ratio ~1:3.

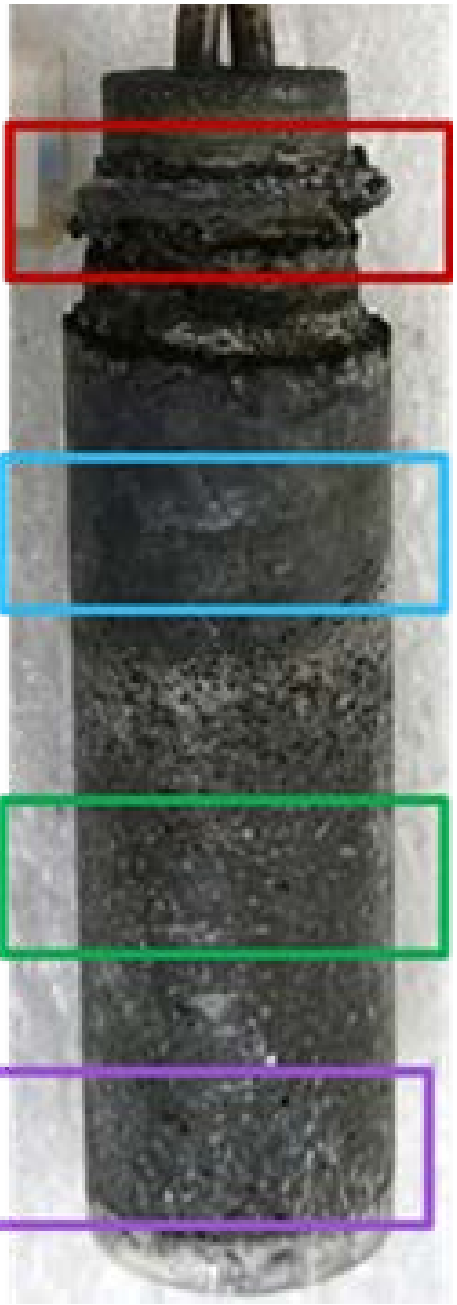
Known solid species:

$FeCl_2$ (1:2), Na_6FeCl_8 (1:8)

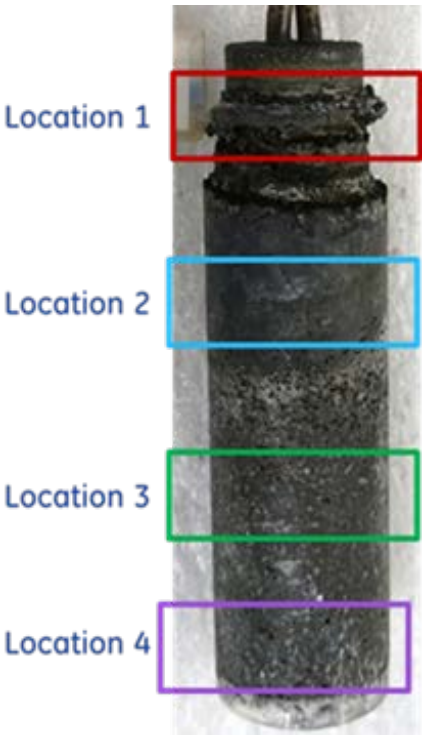
Possible mobile species:

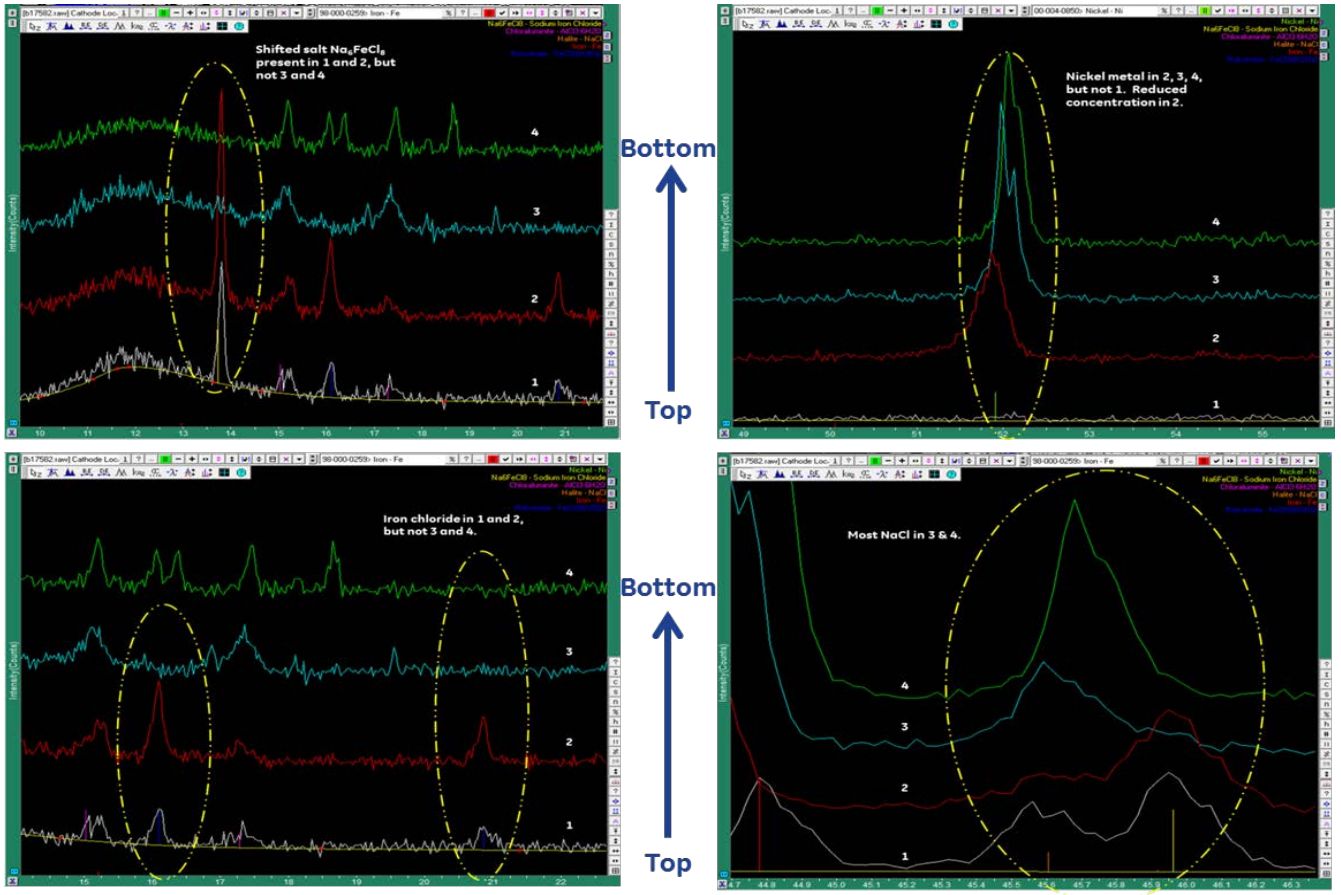
$Na_2Fe_3Cl_8$ (3:8), $Na_4Fe_3Cl_{10}$ (3:10)

How do Fe & NaCl move, and where do they go?



Cathode from disassembled cell. V_M = 2.87 V and T = 300°C. Location 1 contains slag deposit formed at the top of electrolyte pool. Location 2, top third of granules packed bed, is devoid of granules structure.





Stacked X-ray diffraction patterns, by location.
Discharged state. V_M = 2.87 V and T = 300°C.

• Na_6FeCl_8 & $FeCl_2$:	Locations 1 & 2.	*Should be absent in discharged cell.*
• $(Ni,Fe)_{fcc}$:	Locations (2)♠, 3 & 4.	*Should be uniformly distributed throughout.*
• NaCl:	Locations (1), (3) & 4.	*Should be uniformly distributed throughout.*

♠ ( ) indicates low level

Summary

- Sodium / nickel chloride / iron(II)chloride high *T* rechargeable cell
- Degradation mechanism in present geometry associated with iron species mobility
- Porous electrode, finite element model at different states of degradation
- **Model:** Iron & sodium chloride “disappear”
- ***Post-mortem* XRD:** Unreactive iron chloride species concentrate at top of cathode