Progress in high-energy-density high-safety positive electrode materials for Li-ion batteries

J.R. Dahn, Wenbin Luo, Fu Zhou, Xuemei Zhao, Zhonghua Lu, Junwei Jiang and Andrew van Bommel

Depts. of Physics and Chemistry

Dalhousie University, Canada

GM's Chevy Volt will be a plug-in hybrid using Li-ion batteries. The batteries considered were graphite/$LiFePO_4$ Li-ion batteries made by A123 Co. or graphite/$LiMn_2O_4$ batteries made by LG Chem. [2]

Hymotion 5kWh $LiFePO_4$-based Li-ion pack

About 30 km all-electric range

It’s a pretty big battery pack!

“Lithium-ion cells have high energy density”

Where has it gone?

System	Cell	V	A-hr	Volume	Mass	Wh/L
				(mL)	(g)	
A123 $LiFePO_4$	26650	3.3	2.3	35.5	70	215
Panasonic Ni-MH	18670	1.2	3.2	17.0	60	225
E-One Moli $LiMn_2O_4$	26700	3.8	2.9	37.2	101	232
Panasonic $LiCoO_2$	18650	3.7	2.55	16.5	46.5	570

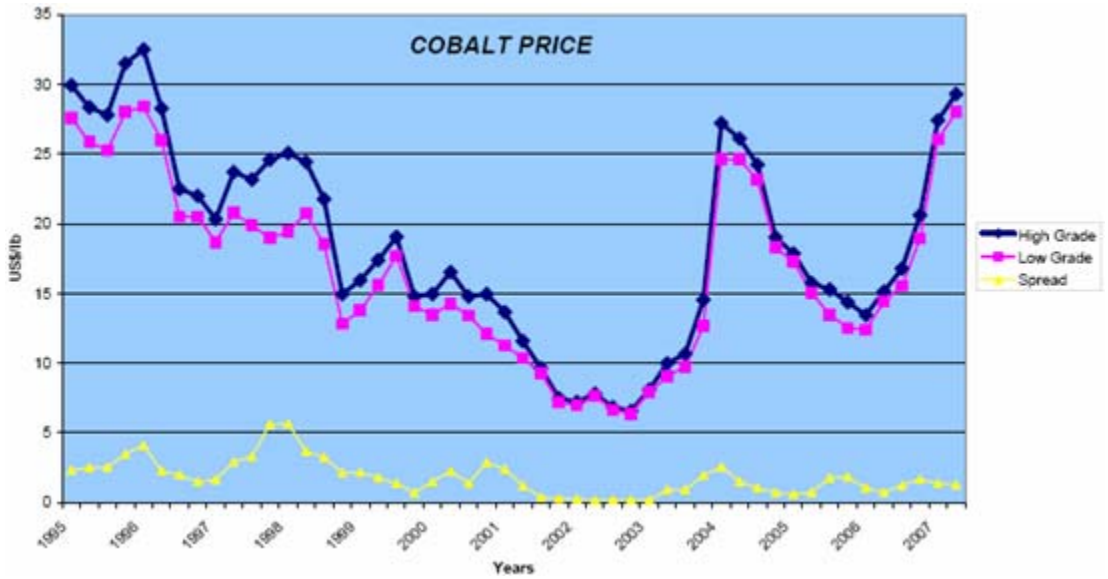
Material	Crystallographic density (g/cm^3)	Average potential (V) (vs Li)	Reversible specific capacity (Ah/g)	Volumetric energy density (Wh/cm^3)
$LiCoO_2$	5.05	3.9	0.15 (to 4.2 V)	2.95
$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ **Called NMC**	4.77	3.7	0.163 (to 4.3 V)	2.87
$Li_{1.1}Mn_{1.9}O_4$	4.18	4.1	0.120	2.06
$LiFePO_4$	3.60	3.44	0.160	1.98

$LiFePO_4$ will lead to the lowest energy density of any of the popular positive electrode choices!
$LiMn_2O_4$ is not much better.

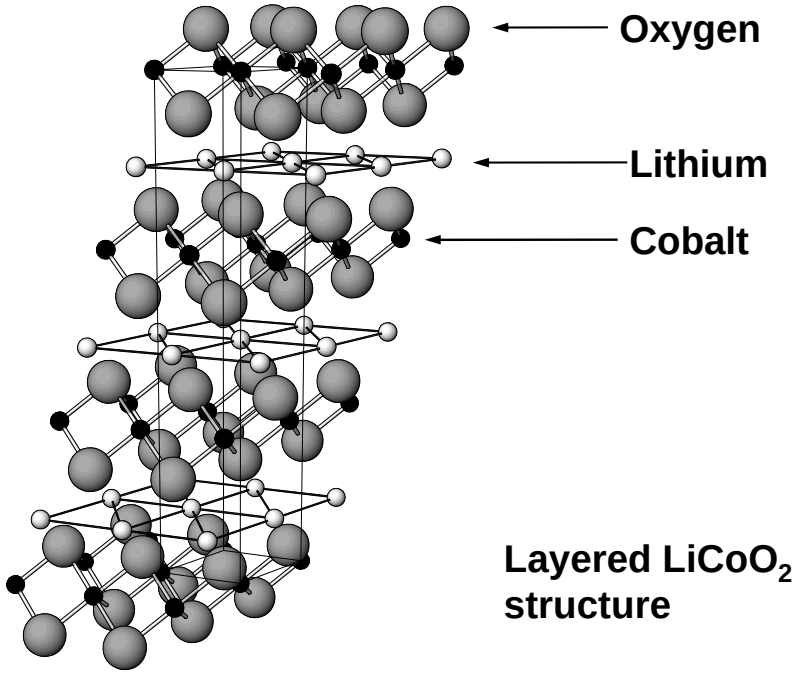
Why are they being selected?

We don't want to use $LiCoO_2$!

1. **Price!**



2. **Safety!**



Layered $LiCoO_2$ structure

Typically designers of new Li-ion positive electrode materials have been <u>obsessed</u> by new materials that will enable high energy density.

This is what is "needed" for portable electronics.

For vehicles and power tools, however, the goal is different. We need to design materials that have more volumetric energy than $LiFePO_4$ and $LiMn_2O_4$ AND which are similarly safe and inexpensive. It's all about cost for automotive!!

How do we study Li-ion battery safety?

1. Make and test full cells - cannot separate the anode and cathode reactions – hard to learn what is going on. However this is the “Real McCoy”.

2. Study the individual electrodes reacting with electrolyte separately - this way we can study the effect of voltage limit, electrolyte salt content, etc.

Accelerating Rate Calorimeter

Measures self heating rate of a sample under adiabatic conditions (no flow of heat into or out of the sample) –

and

Differential Scanning Calorimeter

Measures the thermal power generated by a sample as its temperature is changed at a constant rate.

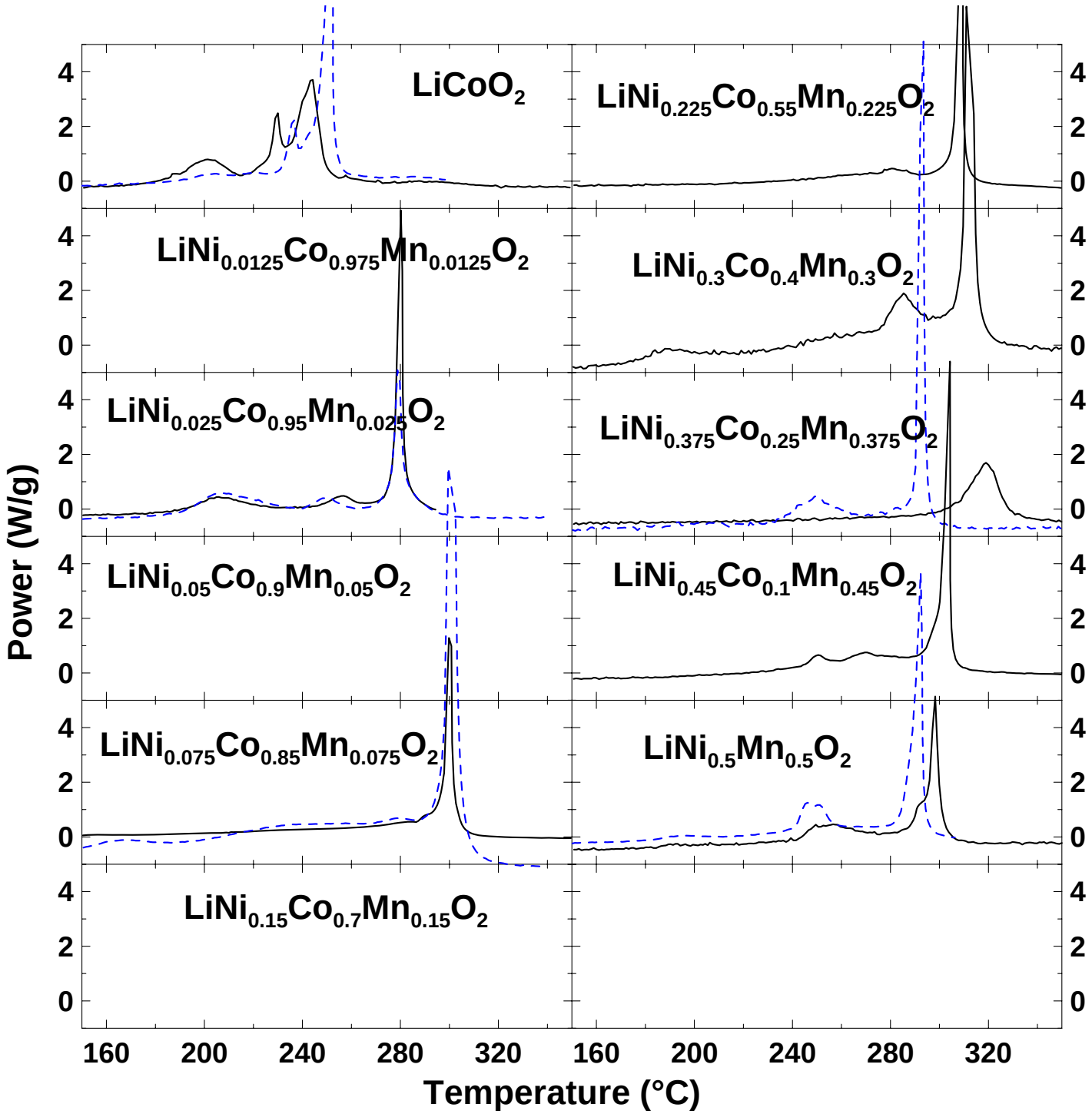
Alternative layered cathode hosts to $LiCoO_2$ by replacing Co^{3+} with equal amounts of Ni^{2+} and Mn^{4+}. This lowers cost!

Make $Li[Ni_xMn_xCo_{1-2x}]O_2$

For x = 1/3, get $Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$ = NMC

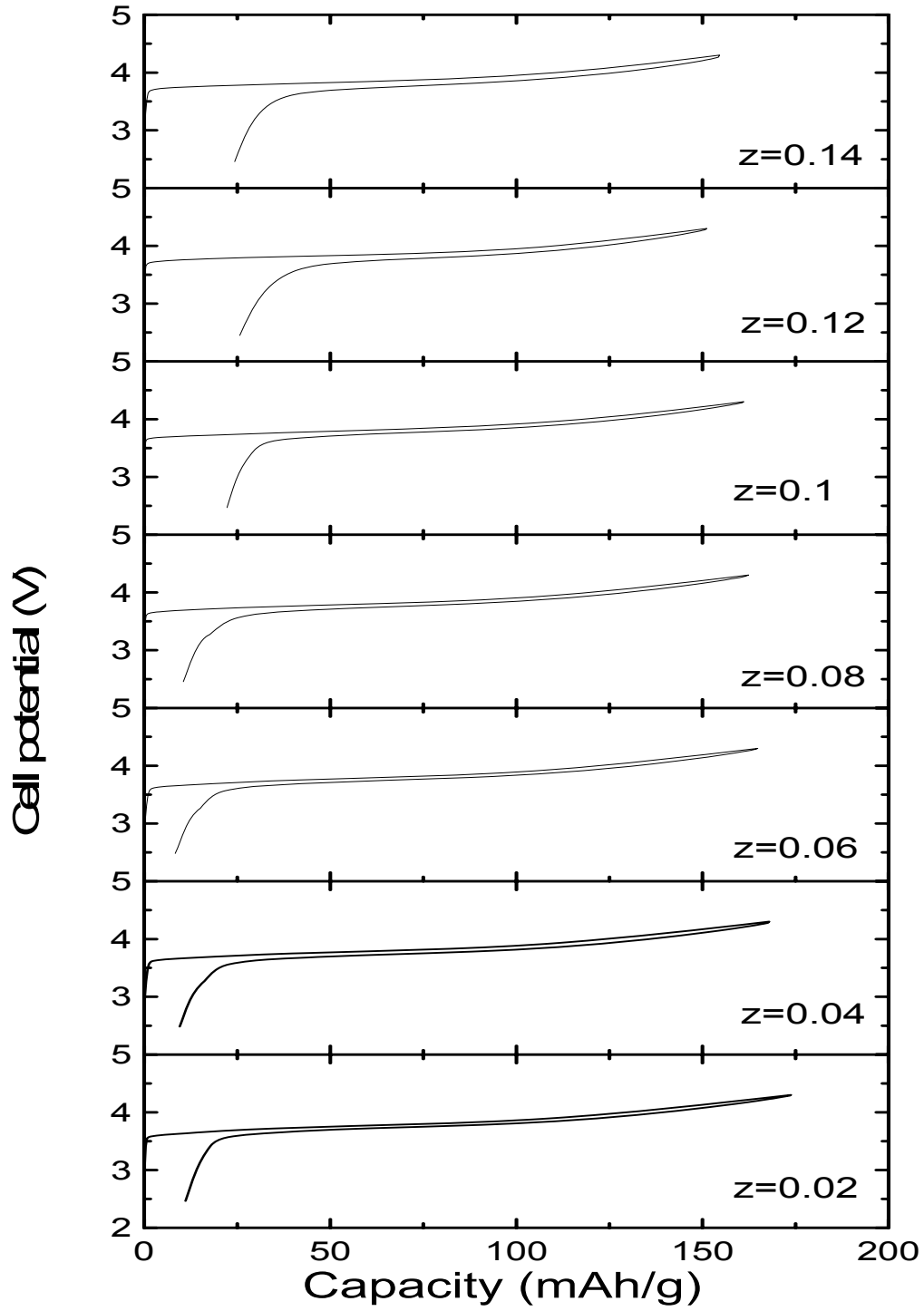
Z. Lu, D.D. MacNeil and J.R. Dahn, Electrochemical and Solid State Letters **4**, A200 (2001).

T. Ohzuku and Y. Makimura, Chemistry Letters **7**, 642 (2001).



Charged to 4.4 V

Note big improvement in Safety



Make

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3-z}Al_z]O_2$

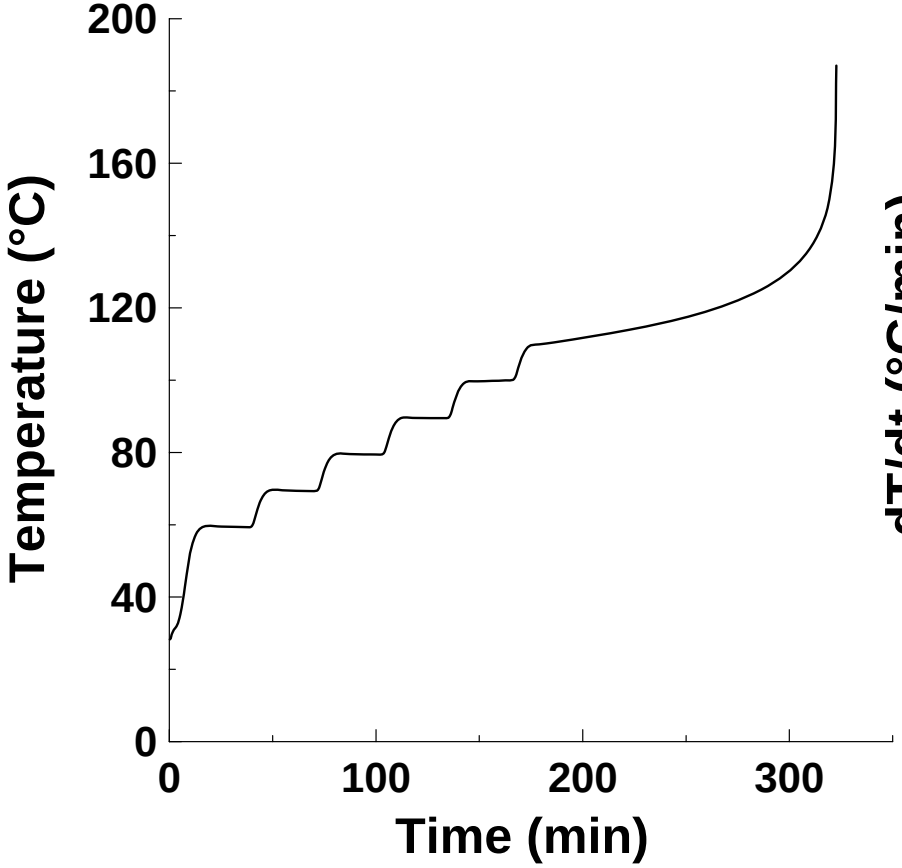
Capacity vs. Cell potential

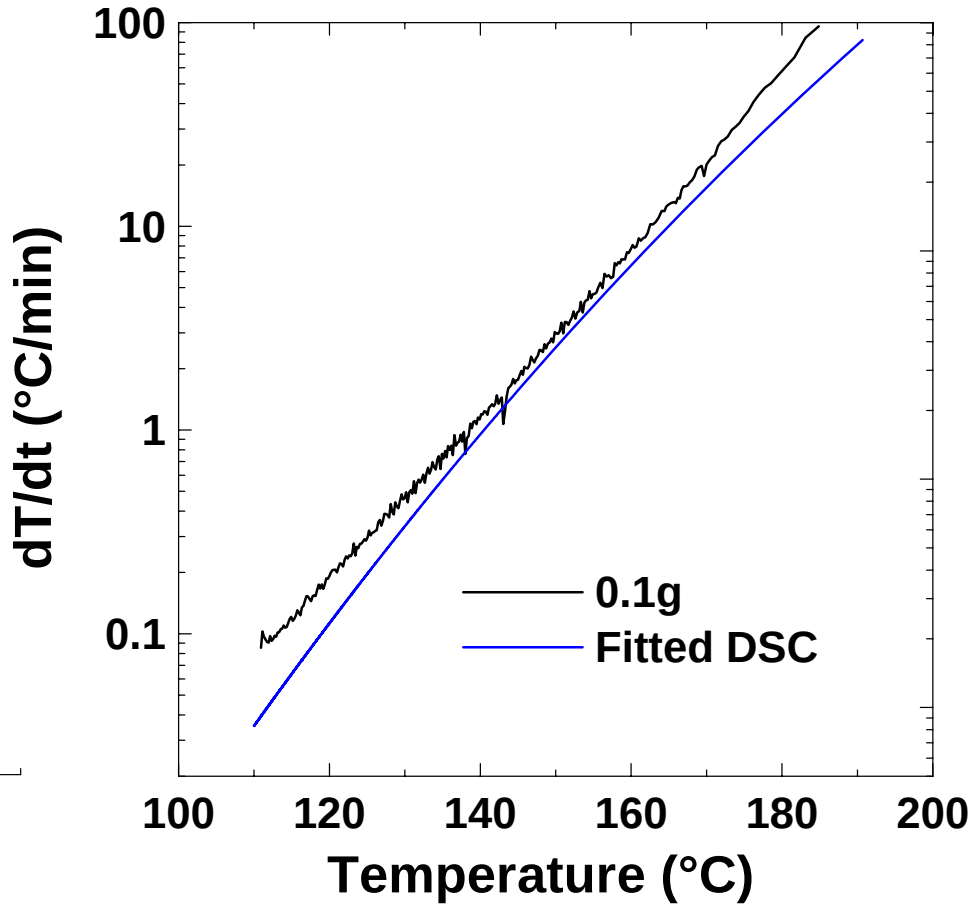
Voltage range:

2.5 to 4.3 V

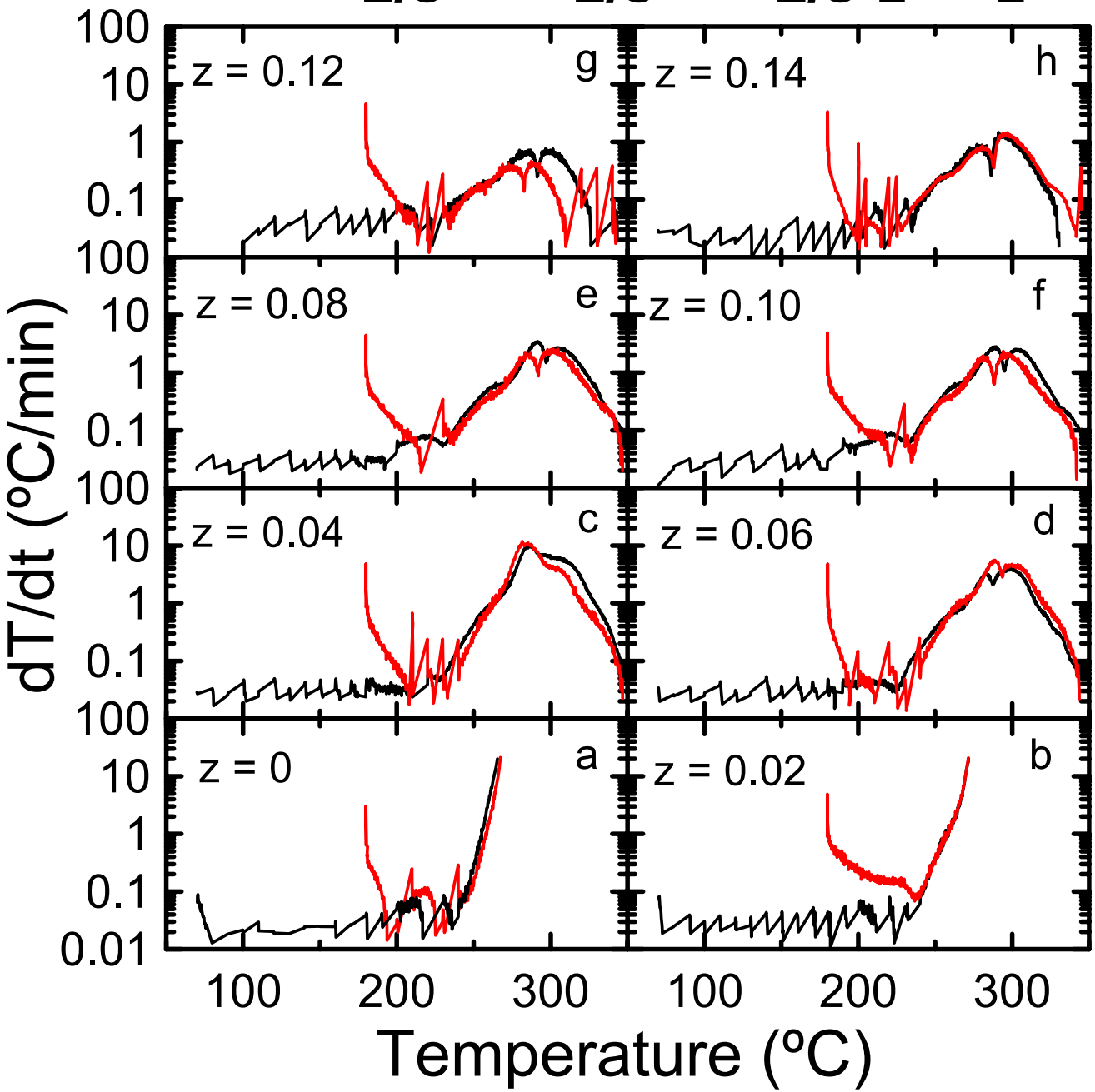
There is a small loss in capacity with Al content!

Typical ARC experiment methodology



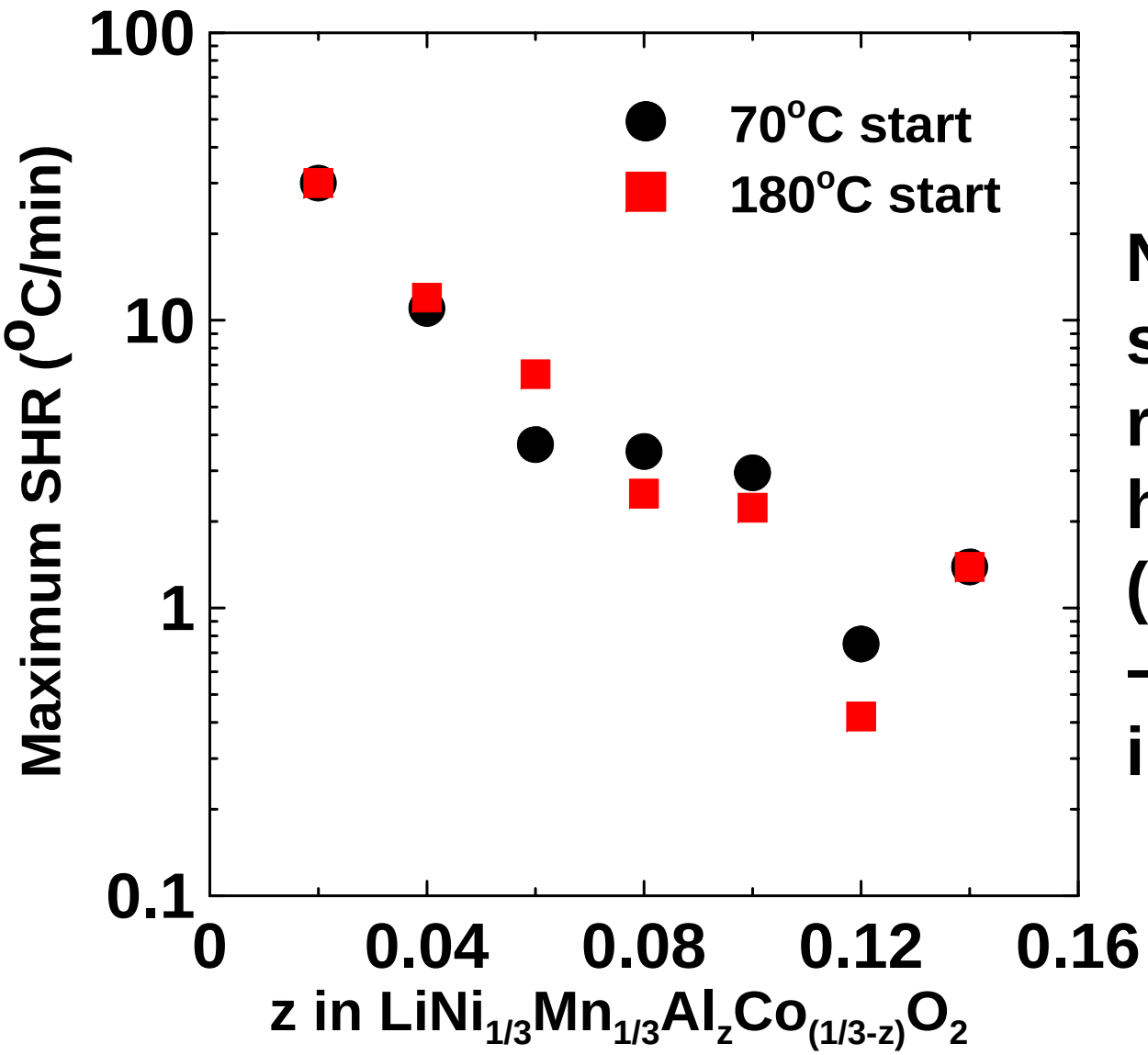


$Li[Ni_{1/3}Mn_{1/3}Co_{1/3-z}Al_z]O_2$



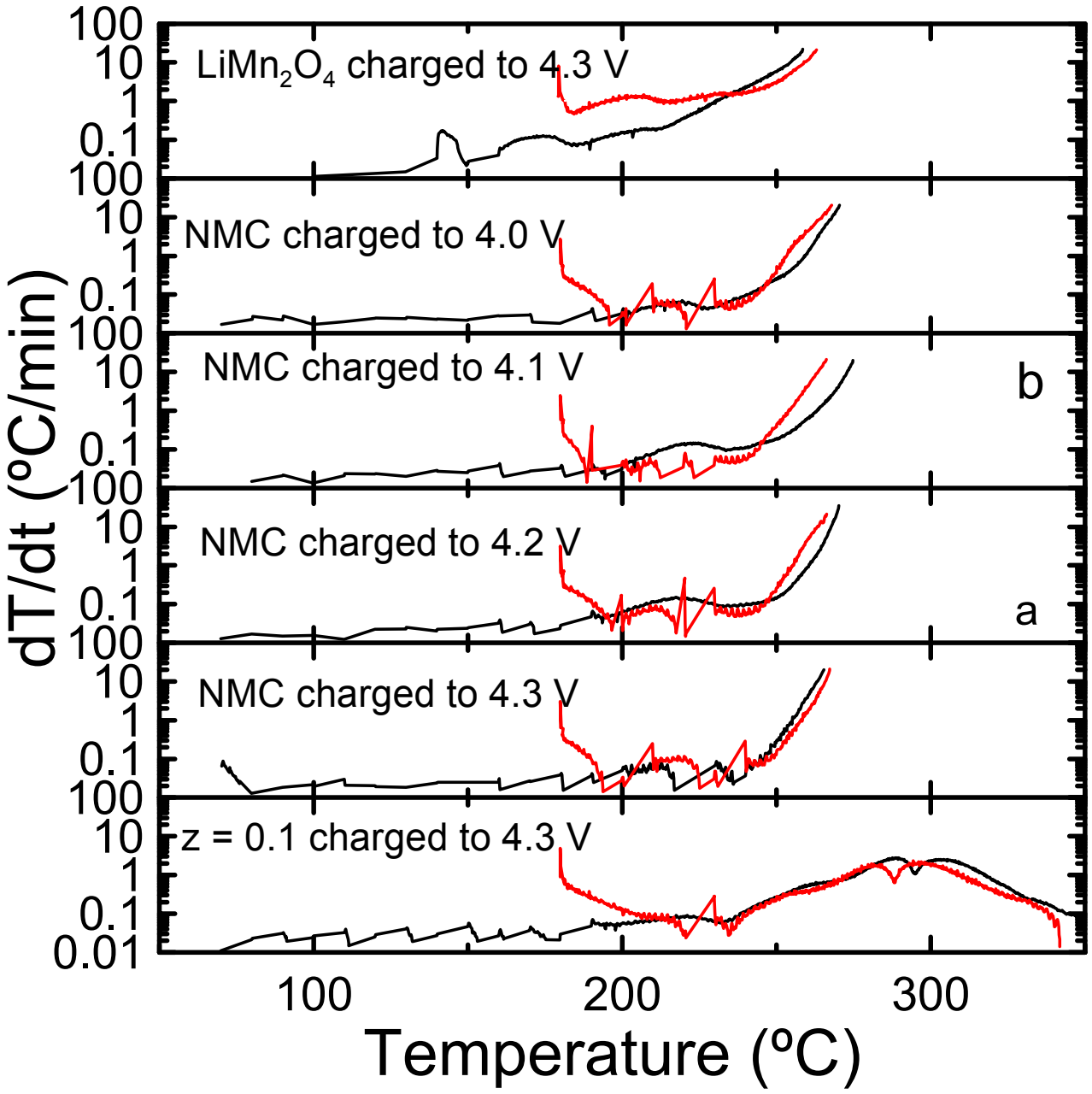
Accelerating rate calorimetry studies of the charged samples (4.3 V) in electrolyte as a function of Al content, z. Note that max self-heating-rate decreases with z.

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3-z}Al_z]O_2$



Notice the strong reduction in self heating rate (slower kinetics – good) as z increases.

$Li[Ni_{1/3}Mn_{1/3}Co_{1/3-z}Al_z]O_2$



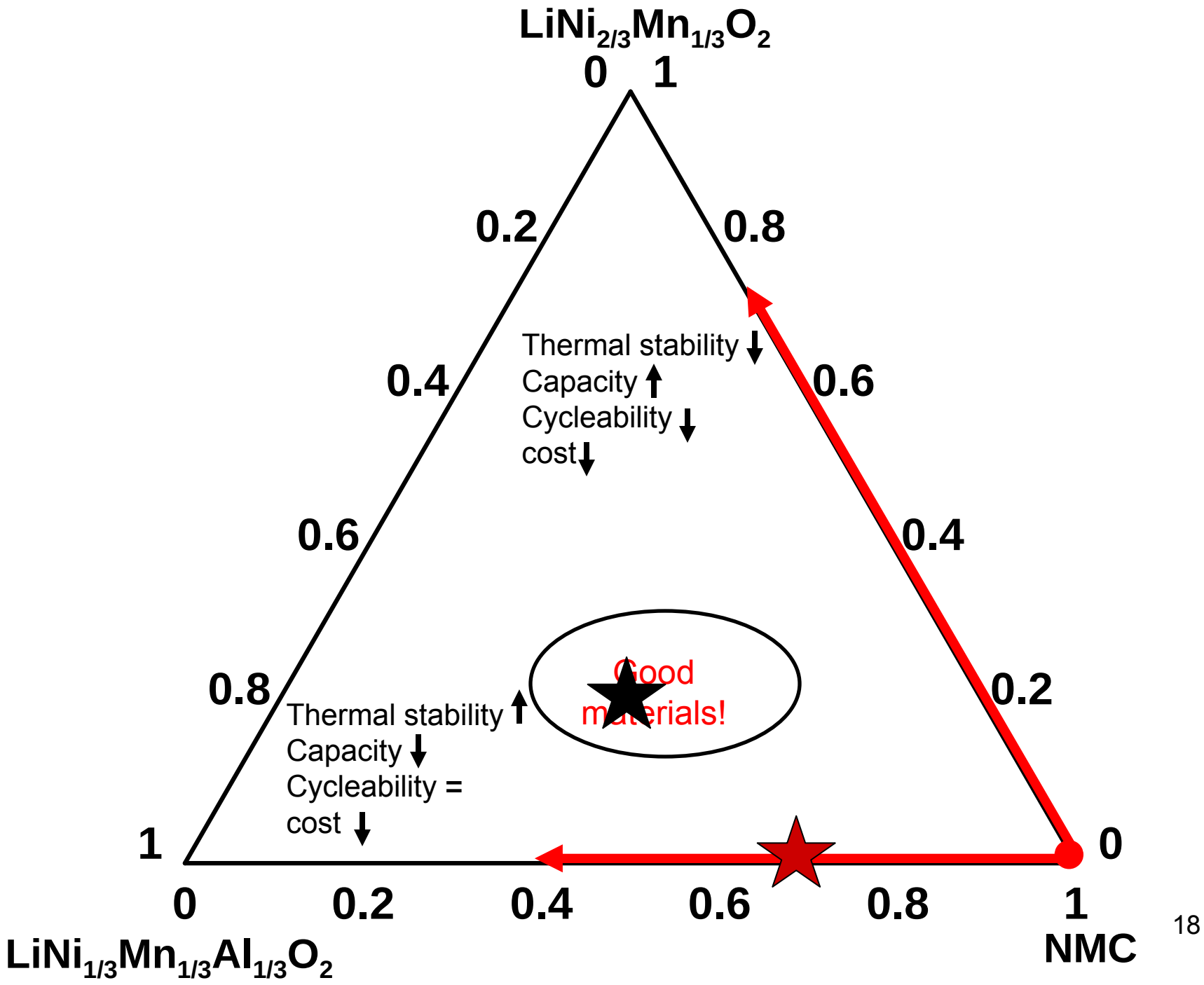
z = 0.1 is a very good compromise between capacity and safety.

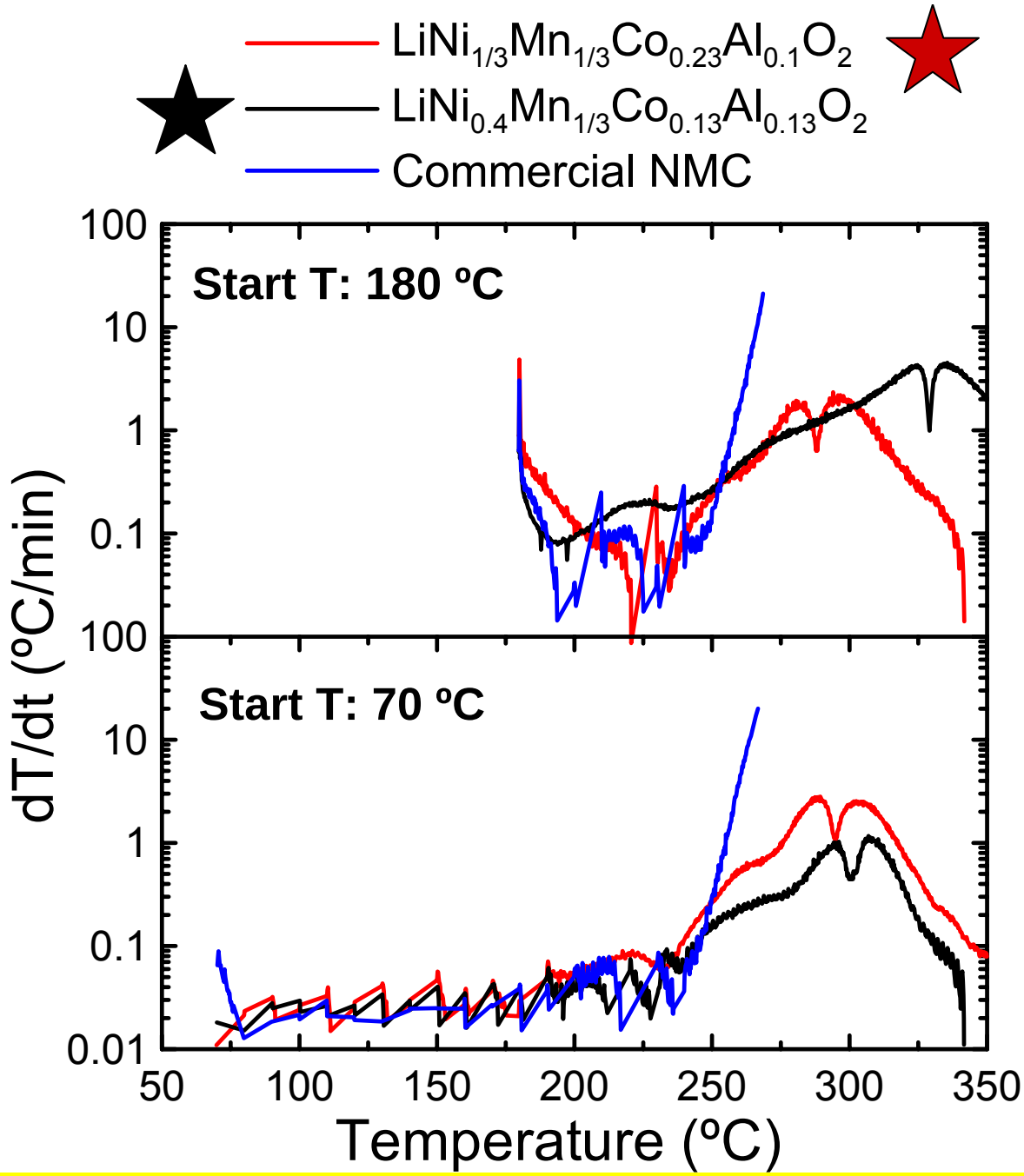
Safer than $LiMn_2O_4$!!!!!

Where do we stand now?

Material	Density (g/cm^3)	Average potential (V)	Reversible specific capacity (Ah/g)	Volumetric energy density (Wh/cm^3)
$LiCoO_2$	5.05	3.9	0.15 (to 4.2 V)	2.95
$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$	4.77	3.7	0.163 (to 4.3 V)	2.87
$Li_{1.1}Mn_{1.9}O_4$	4.18	4.1	0.120	2.06
$LiFePO_4$	3.60	3.44	0.160	1.98
$Li[Ni_{1/3}Mn_{1/3}Co_{0.233}Al_{0.1}]O_2$	4.60	3.75	0.140 (to 4.3 V)	**2.42**

This work published in:
Electrochem. Solid-State Lett. 11 (2008) A155-A157.
Electrochem. Commun. 10 (2008) 1168-1171.


LiNi2/3Mn1/3O2
0
1
0.2
0.8
0.4
0.6
0.6
0.4
0.8
0.2
1
0
0
0.2
0.4
0.6
0.8
1
LiNi1/3Mn1/3Al1/3O2
NMC
Thermal stability
Capacity
Cycleability
cost
Thermal stability
Capacity
Cycleability =
cost
Good
materials!



Thermal stability comparison (Charged to 4.3V)

Material	Crystallographic density (g/cm^3)	Average potential (V)	Reversible specific capacity (Ah/g)	Volumetric energy density (Wh/cm^3)
$LiCoO_2$	5.05	3.9	0.15 (to 4.2 V)	2.95
$Li[Ni_{1/3}Mn_{1/3}Co_{1/3}]O_2$	4.77	3.7	0.163 (to 4.3 V)	2.87
$Li_{1.1}Mn_{1.9}O_4$	4.18	4.1	0.120	2.06
$LiFePO_4$	3.60	3.44	0.160	1.98
$Li[Ni_{1/3}Mn_{1/3}Co_{0.233}Al_{0.1}]O_2$	4.60	3.75	0.140 (to 4.3 V)	2.42
$LiNi_{0.4}Mn_{0.33}Co_{0.13}Al_{0.13}O_2$	4.53	3.85	0.146(to 4.3 V)	2.56

Conclusions:

1. Al substitutions in NMC can improve safety significantly for a small tradeoff in capacity.

2. The capacity tradeoff can be mitigated by adding more Ni and Al for Co.

3. $Li[Ni_{0.4}Mn_{1/3}Co_{0.13}Al_{0.13}]O_2$ stores 25-30% more energy than either $Li_{1.1}Mn_{1.9}O_4$ or $LiFePO_4$. It appears to be safer than $Li_{1.1}Mn_{1.9}O_4$ and rivals $LiFePO_4$.

4. Many scientists are working on SAFE materials that are better than $LiFePO_4$ and $LiMn_2O_4$, with an eye to cost reduction.

Acknowledgements

Dahn group

Funding

3M

NSERC CRSNG

3M collaborators - useful discussions and assistance.