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Safety Aspect of Large-Sized Lithium Ion Batteries

T.Horiba, T. Ishizu, T. Kojima

*D. H. Doughty,

Hitachi Vehicle Energy, Ltd.

*Sandia National Laboratories

New Company “Hitachi Vehicle Energy, Ltd.”

Shin-Kobe Electric Machinery Co.,Ltd.

43.7%

Hitachi,Ltd.,

36.7%

Hitachi Maxell Ltd.

19.6%

Joint Venture Company

(July 1, 2004)

Hitachi Vehicle Energy, Ltd.

Outline

- Introduction
  : Hitachi Vehicle Energy

1. High Energy Density Batteries

2. High Power Density Cell (1)
   -For FCHEV Application

3. High Power Density Cell (2)
   -For HEV Application

4. Summary

1. Abuse Test of High Energy Batteries

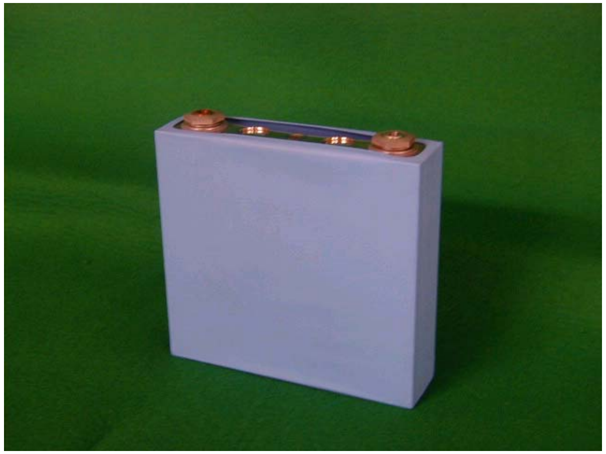
Features of Hitachi/Shin-Kobe's battery structure

Japanese National project:

Dispersed –Type Battery Energy Storage (1992-2001)

prismatic single cell

stacking structure



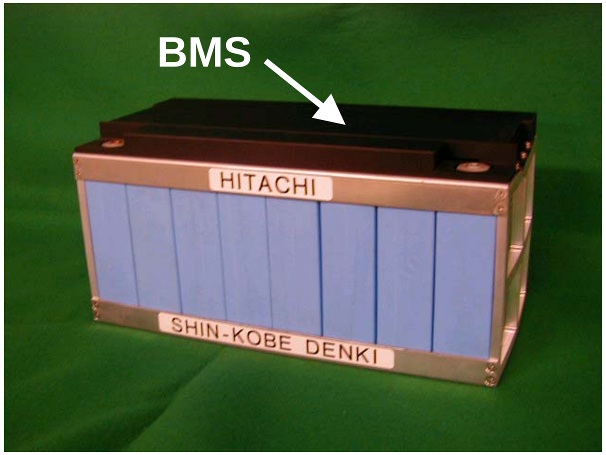
dimensions：L159 X W40 X H155

79 Ah - 3.9 V, 2.4 kg
131 Wh/kg, 295 Wh/dm^3

8 cells

2 kWh class module battery

band-binding structure



dimensions ：L349 X W164 X H171

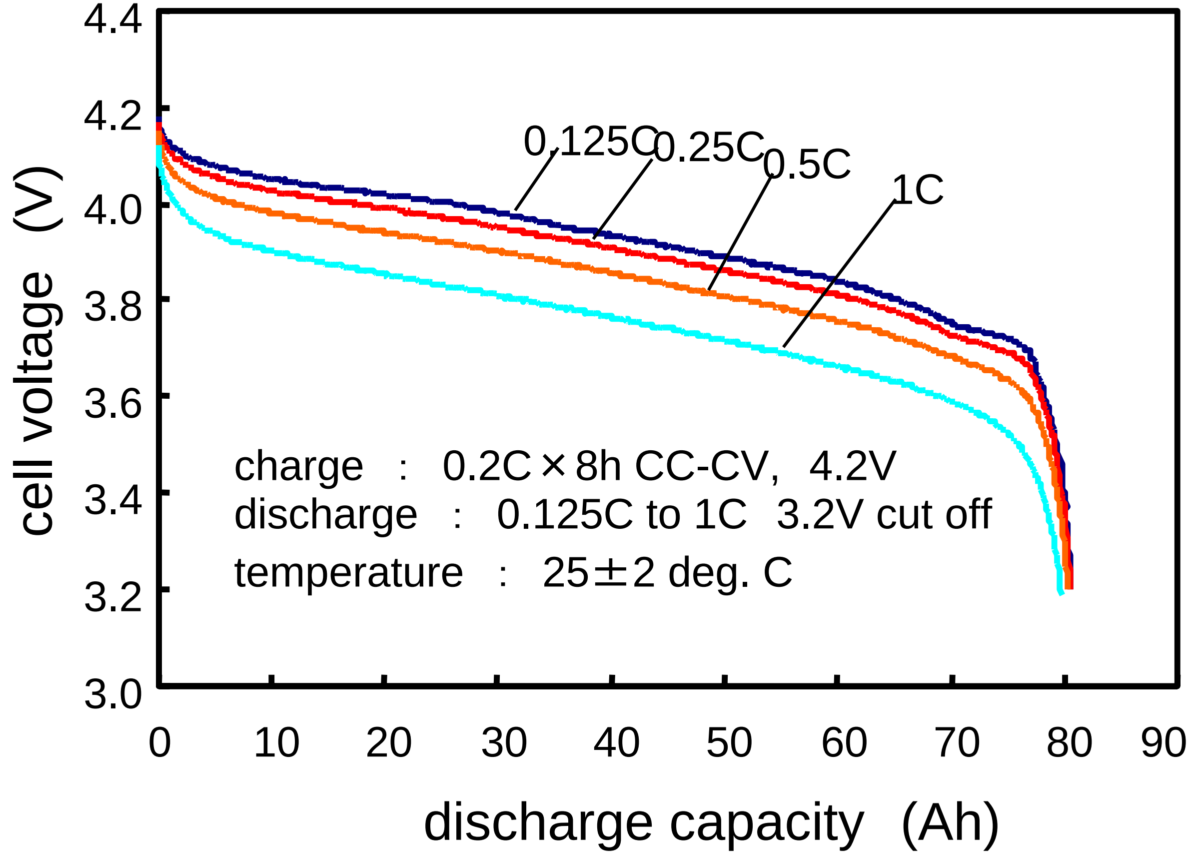
79 Ah - 31.2 V, 20.4 kg
122 Wh/kg, 255 Wh/dm^3

BMS：Battery Management System

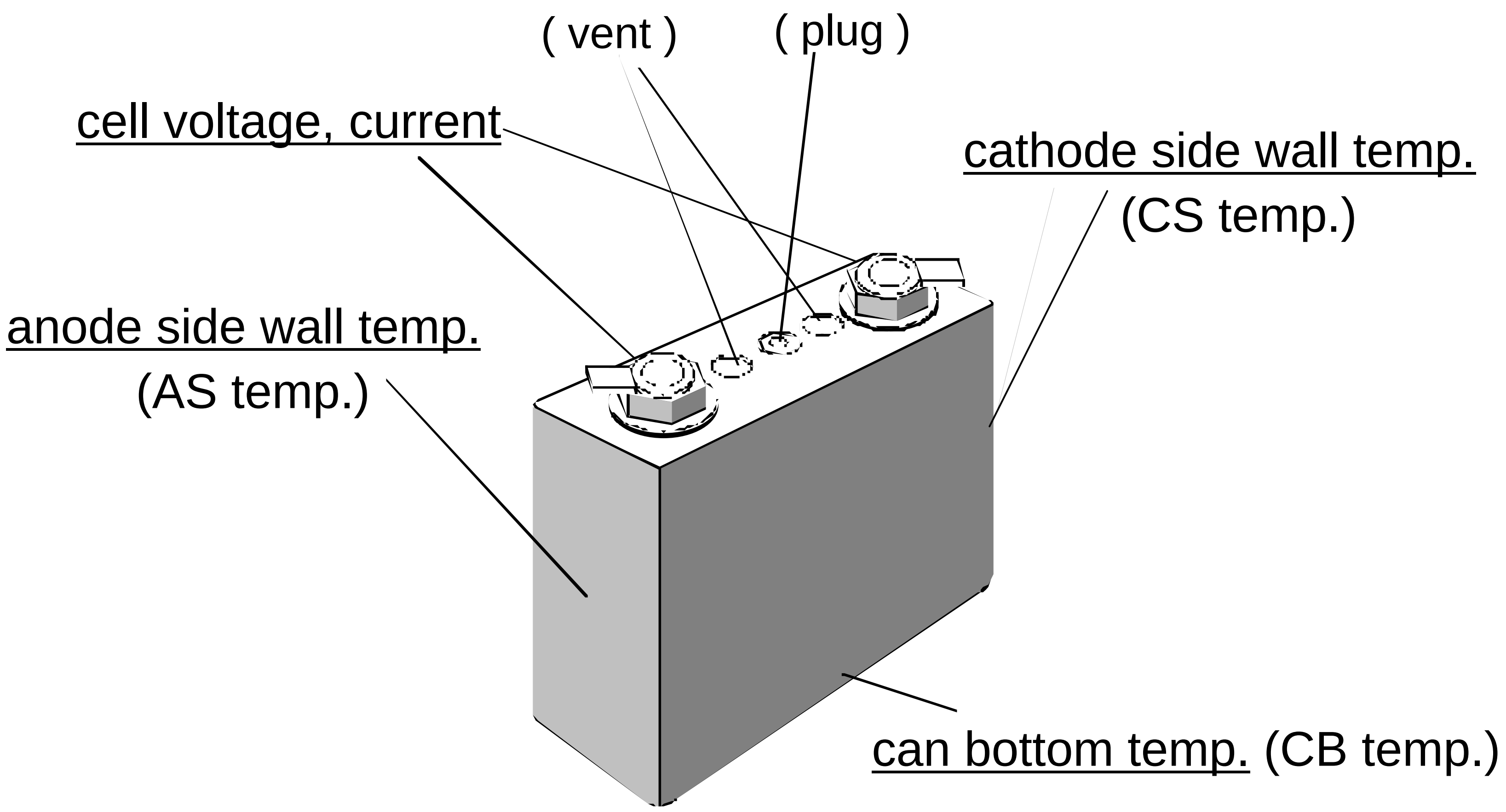
Stationary Use → High Energy Density

250 Wh class prismatic single cell

parts	material
cathode	Mn-based
anode	Ag/Graphite
separator	micro porous polyethylene
electrolyte solution	$LiPF_6$ / EC-based Mixture
cell case	Ni-plated steel



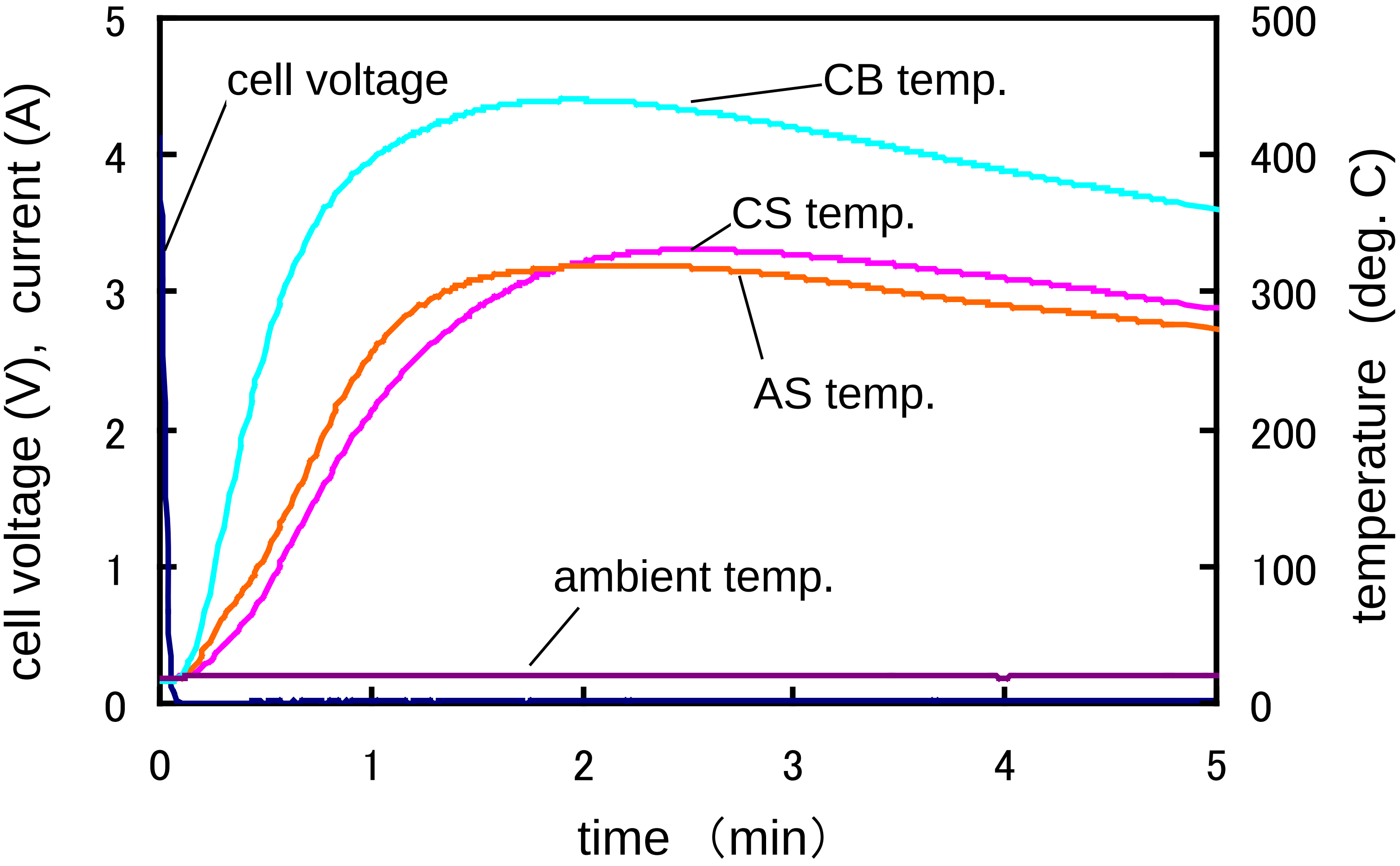
Sensing points and parameters in abuse tests



250 Wh class cell

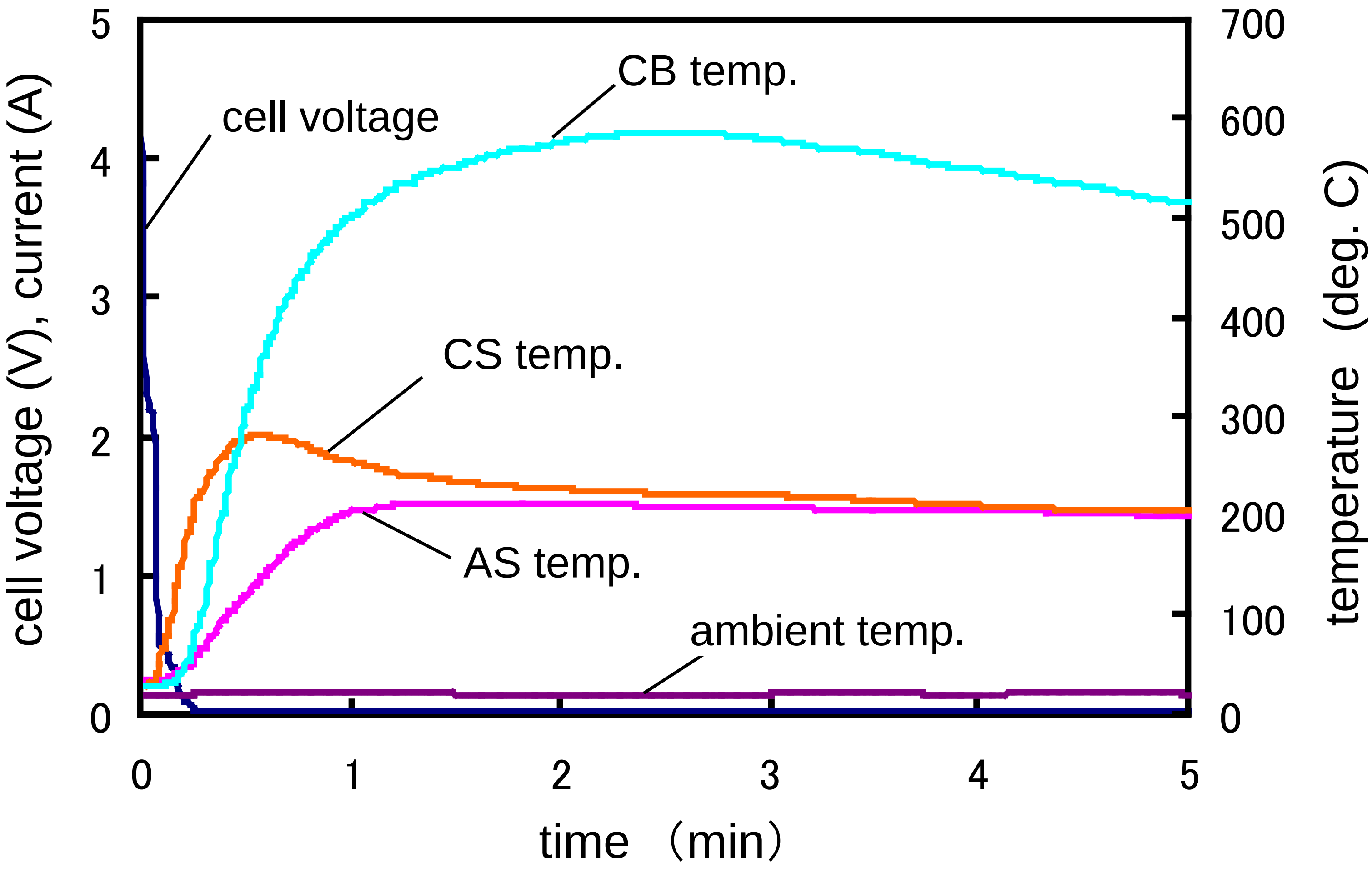
Nail penetration test for the 250 Wh class cell

nail diameter：8 mm, nail material：carbon steel
penetration speed：20 mm/s



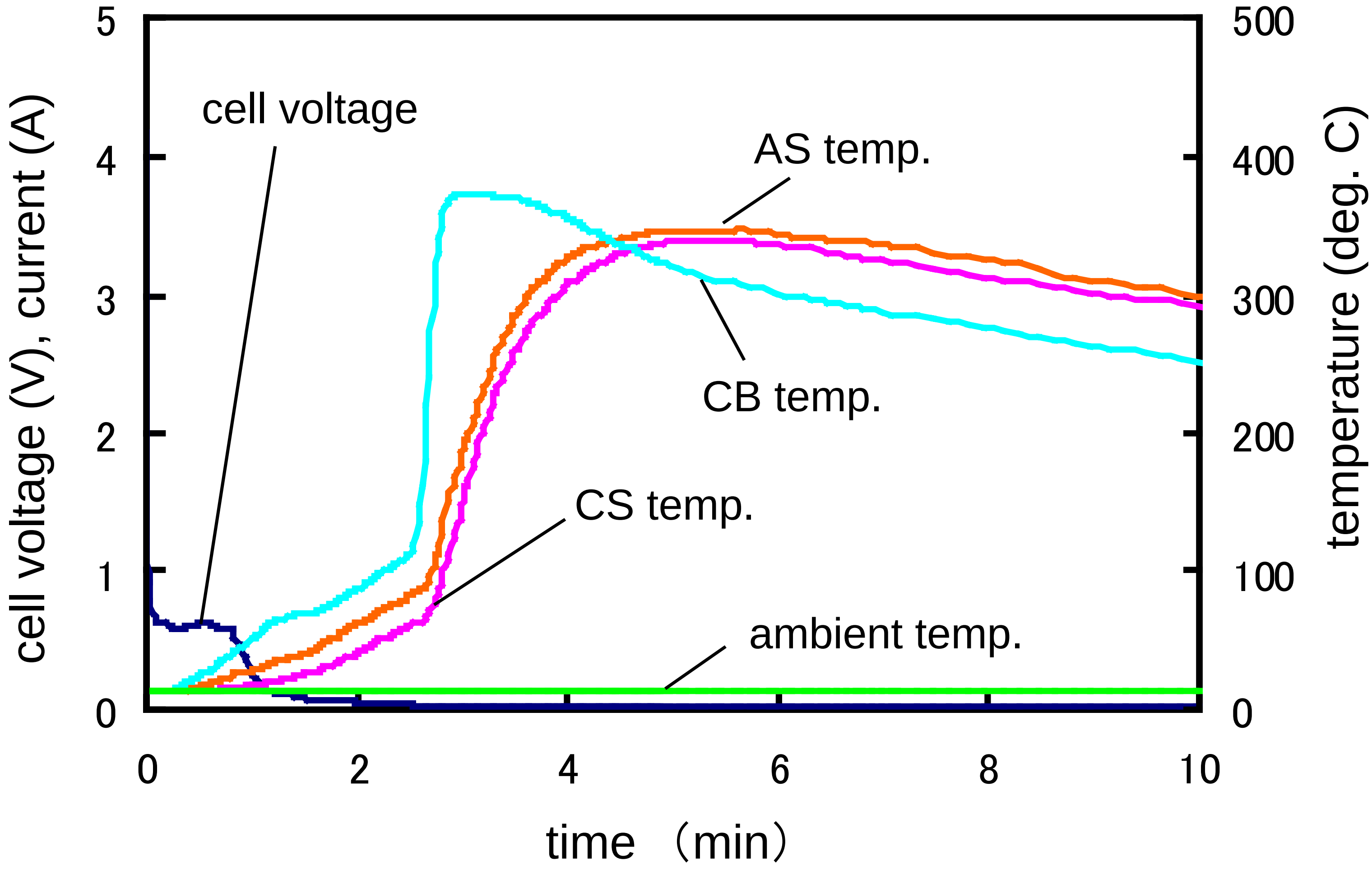
Crush test for the 250 Wh class cell

rod diameter：10 mm, crush speed：10 mm/s,
crush limit：50% of initial dimension



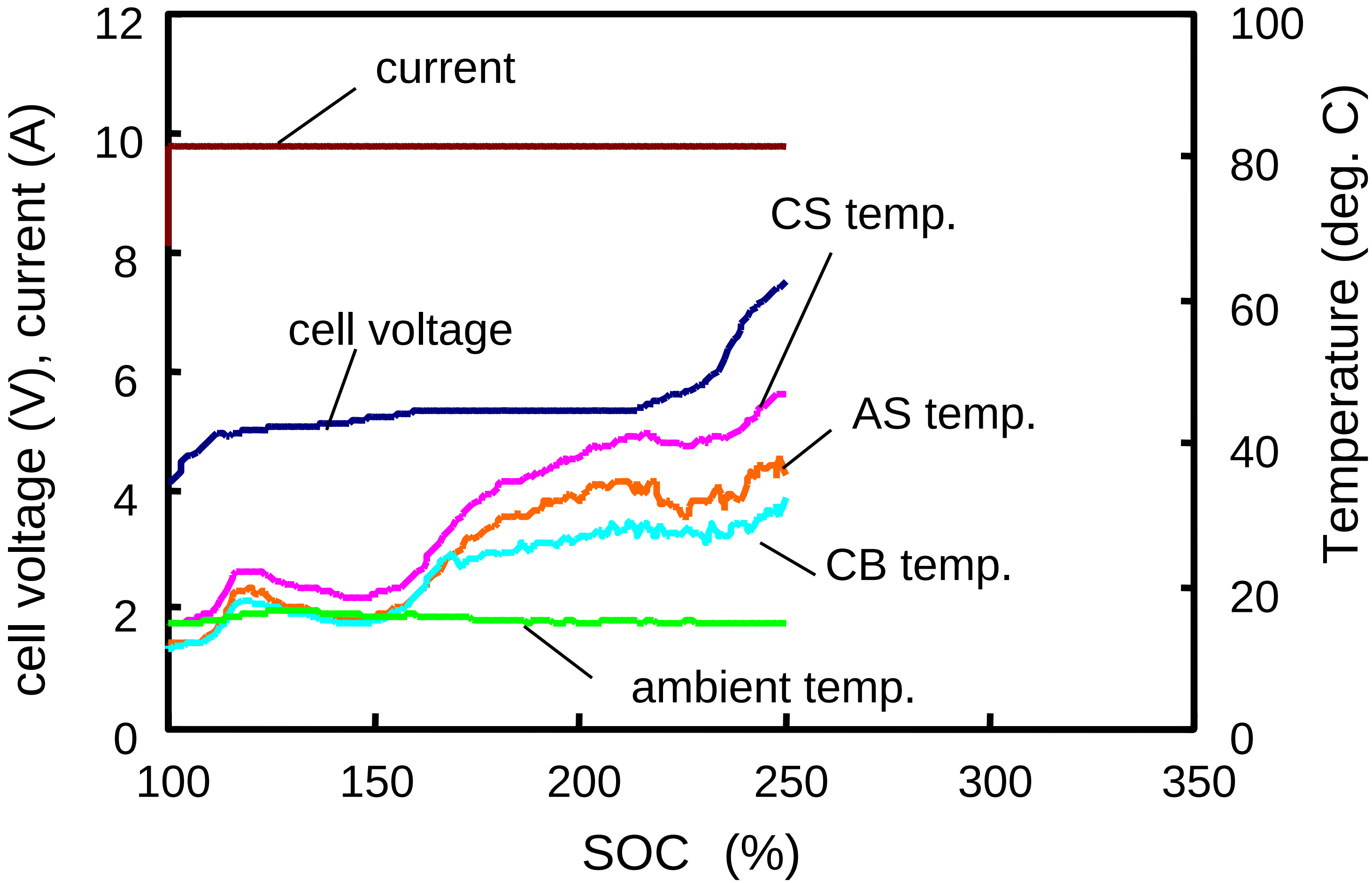
External short circuit test for the 250 Wh class cell

short circuit resistance : 0.5 m Ohm



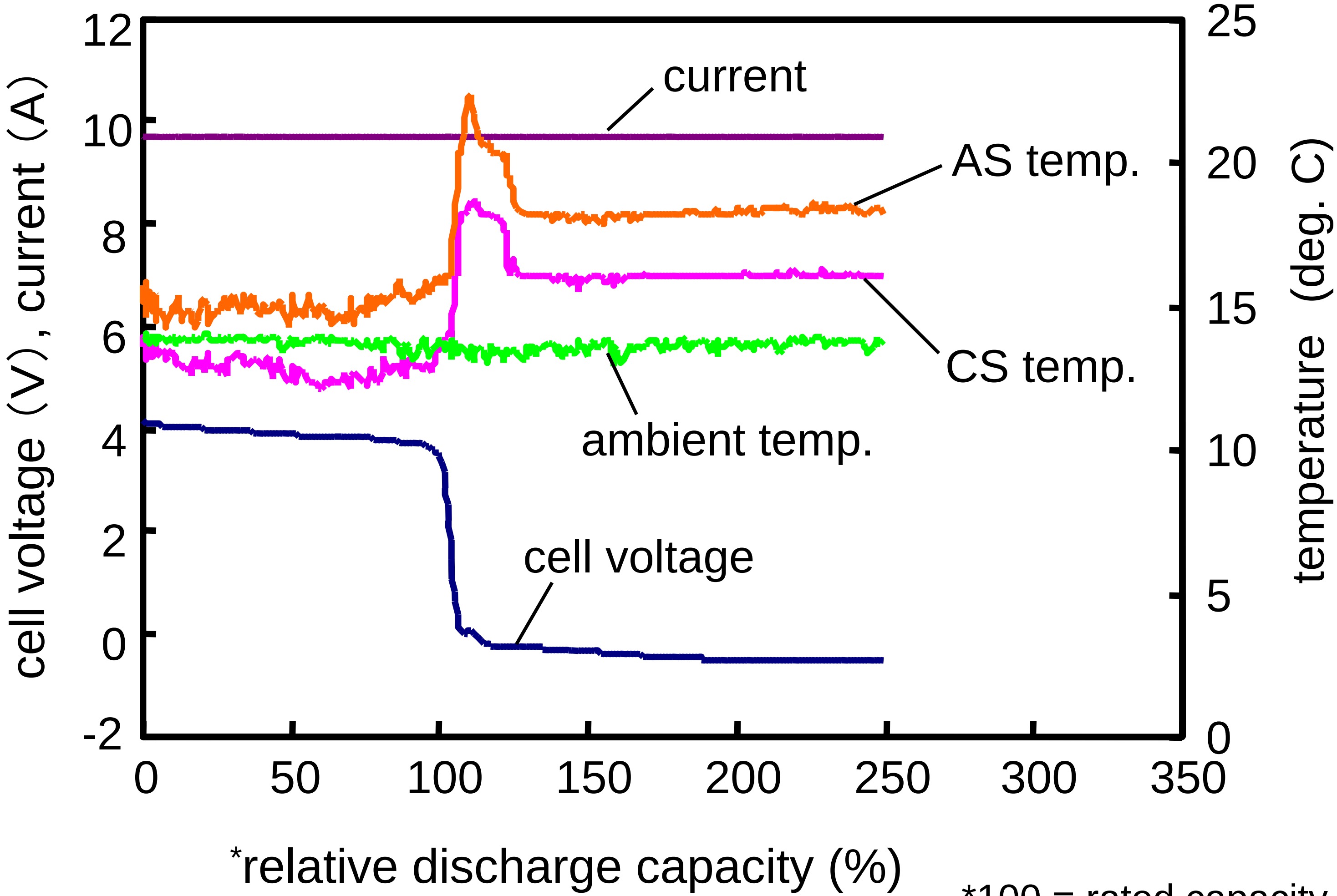
Overcharge test for the 250 Wh class cell

charge to 250% SOC at 0.125 C



Overdischarge test for the 250 Wh class cell

discharge to 250% of the rated capacity at 0.125 C



*100 = rated capacity

Abuse tests for the 250 Wh class single cell

test item	result				
	venting	smoking	fire*	rupture	max temp. (deg. C)
nail penetration	yes	yes	no	no	440
crush	yes	yes	no	no	585
ext. short circuit	yes	yes	no	no	375
overcharge	no	no	no	no	47
overdischarge	no	no	no	no	22

- Crush test reached the highest temp. among the test items
- Overcharge test result seems to depend on the charge rate.

2. Abuse Test of High Power Cells (1)

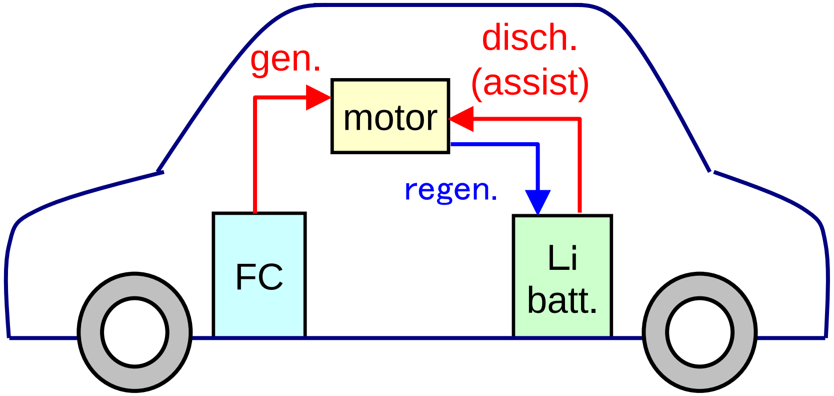
Development of Li Battery Technology for FCV and Others

Present NEDO Project ('02 –'06)

-battery developer : **Hitachi-HVE**, GS-Yuasa, Panasonic
-new material developer : MELCO, GS-Yuasa, CRIEPI, AIST, Saga Univ., Mie Univ., etc.

Target

Capacity	3 kWh
Power density	1800 W/kg
Energy density	70 Wh/kg
Life	15 years
Battery cost	50,000 ¥/kWh
Safety	- durable to abuse conditions and the environment of vehicle use



High energy efficiency FCHEV
- Power assist for FC by batt.
- Regenerative charge of batt.

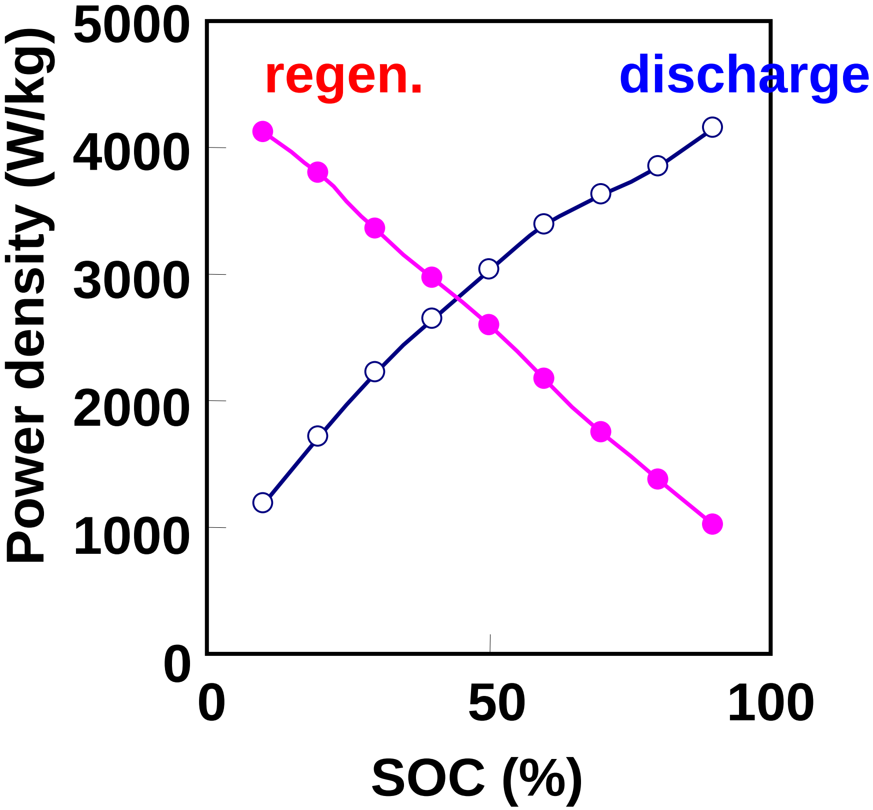
Performance of Hitachi's Single Cell

— specifications —

cathode	Mn-based
anode	amorphous carbon
dimensions	108 x 34 x 117H(mm)
capacity	15 Ah
voltage	3.6 V

energy density 70Wh/kg

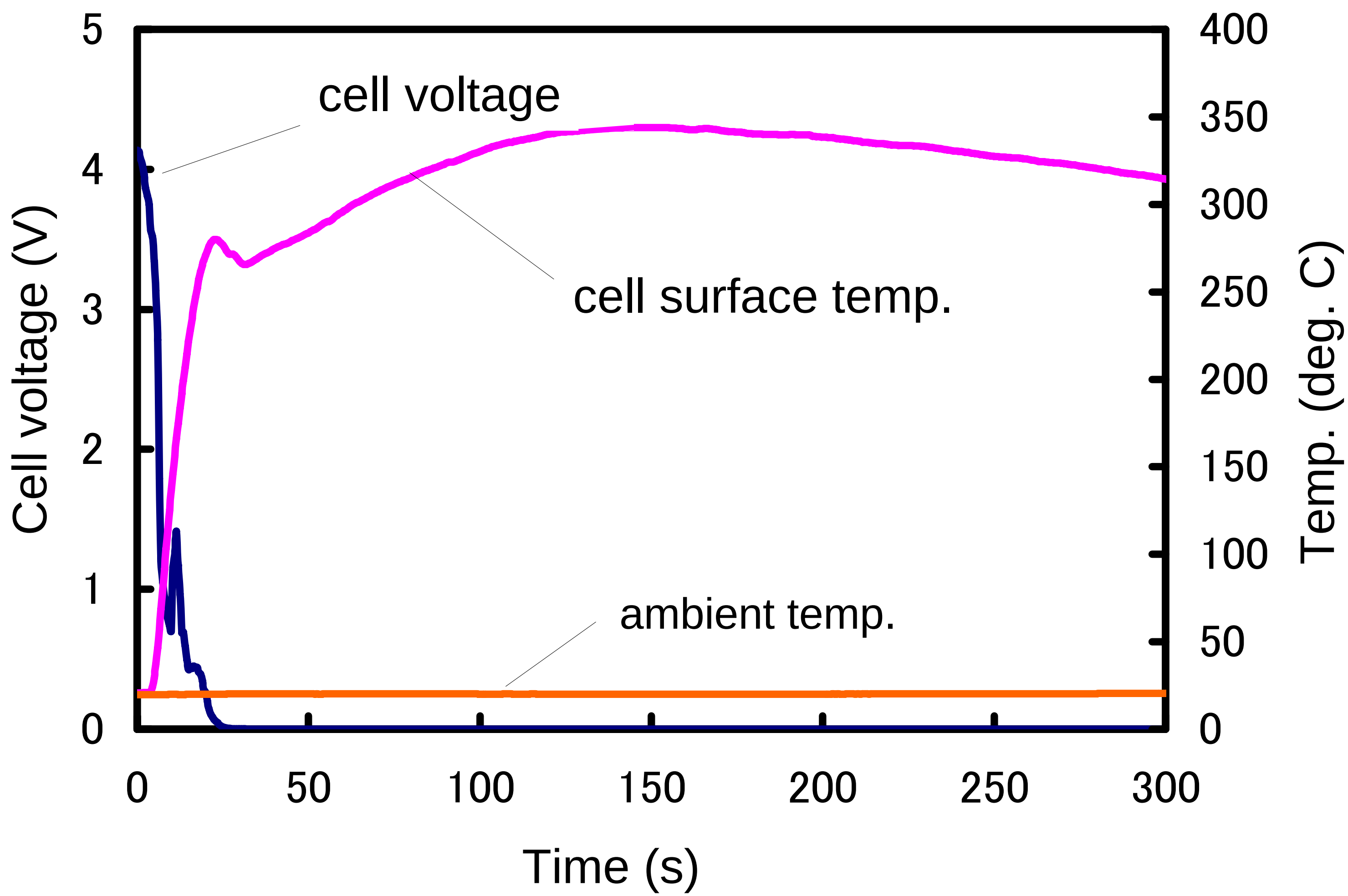
—— power ——



discharge 3000W/kg
regen. 2500W/kg

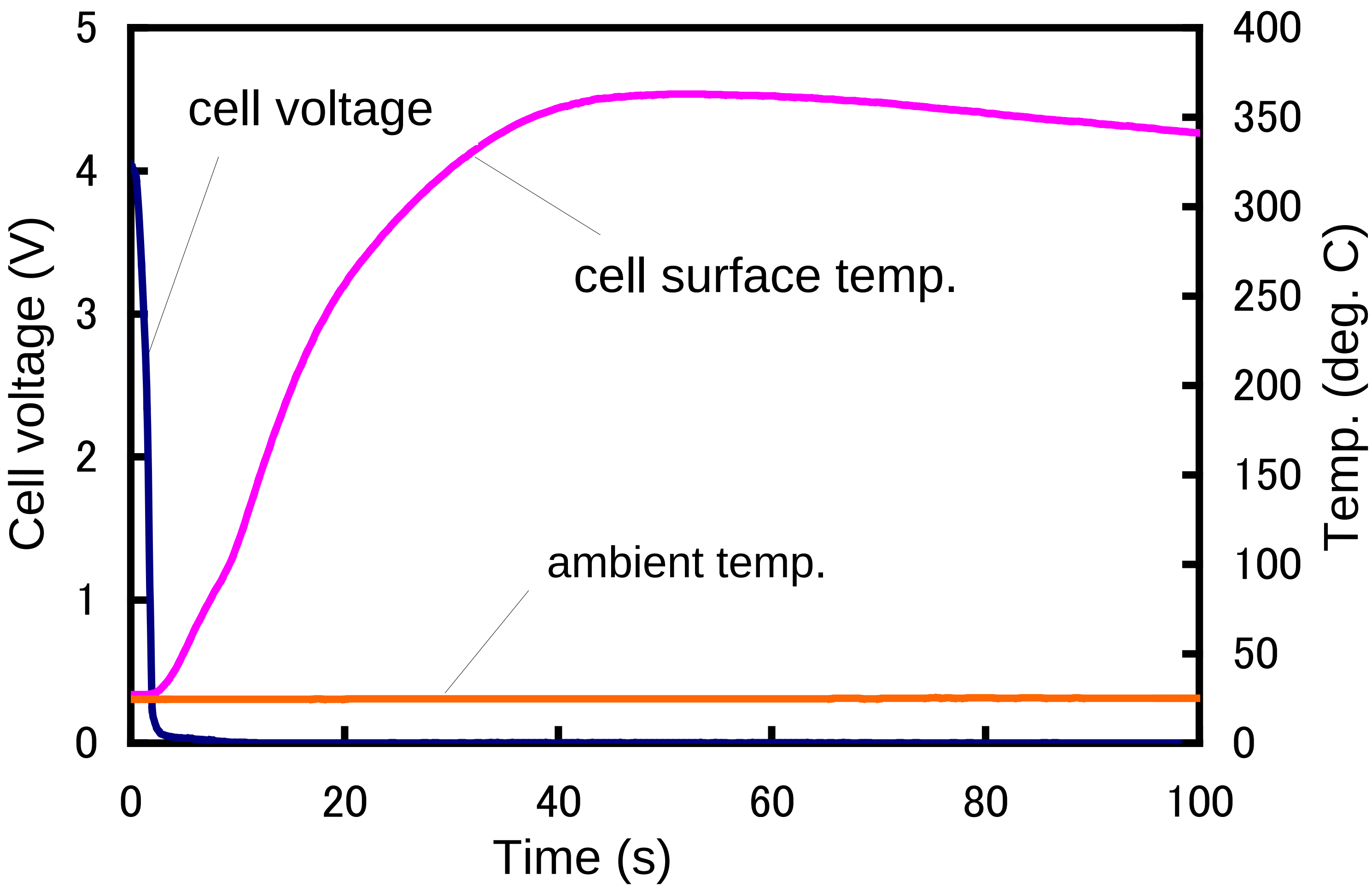
Nail penetration test for the 10 Wh class cell

nail diameter : 5 mm, nail material : carbon steel
penetration speed : 2 mm/s



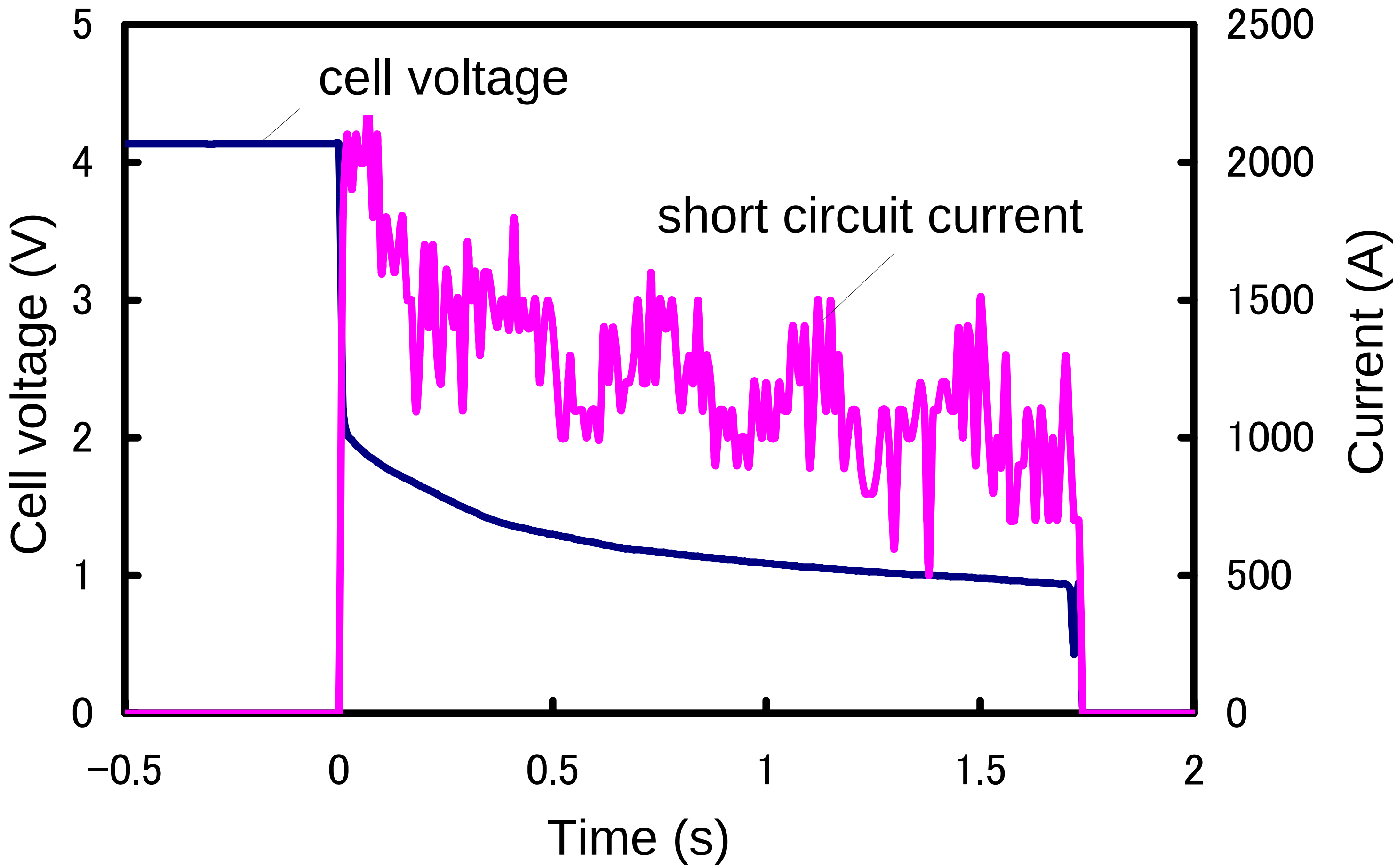
Crush test for the 10 Wh class cell

rod diameter：30 mm, crush speed：2 mm/s,
crush limit：50% of initial dimension



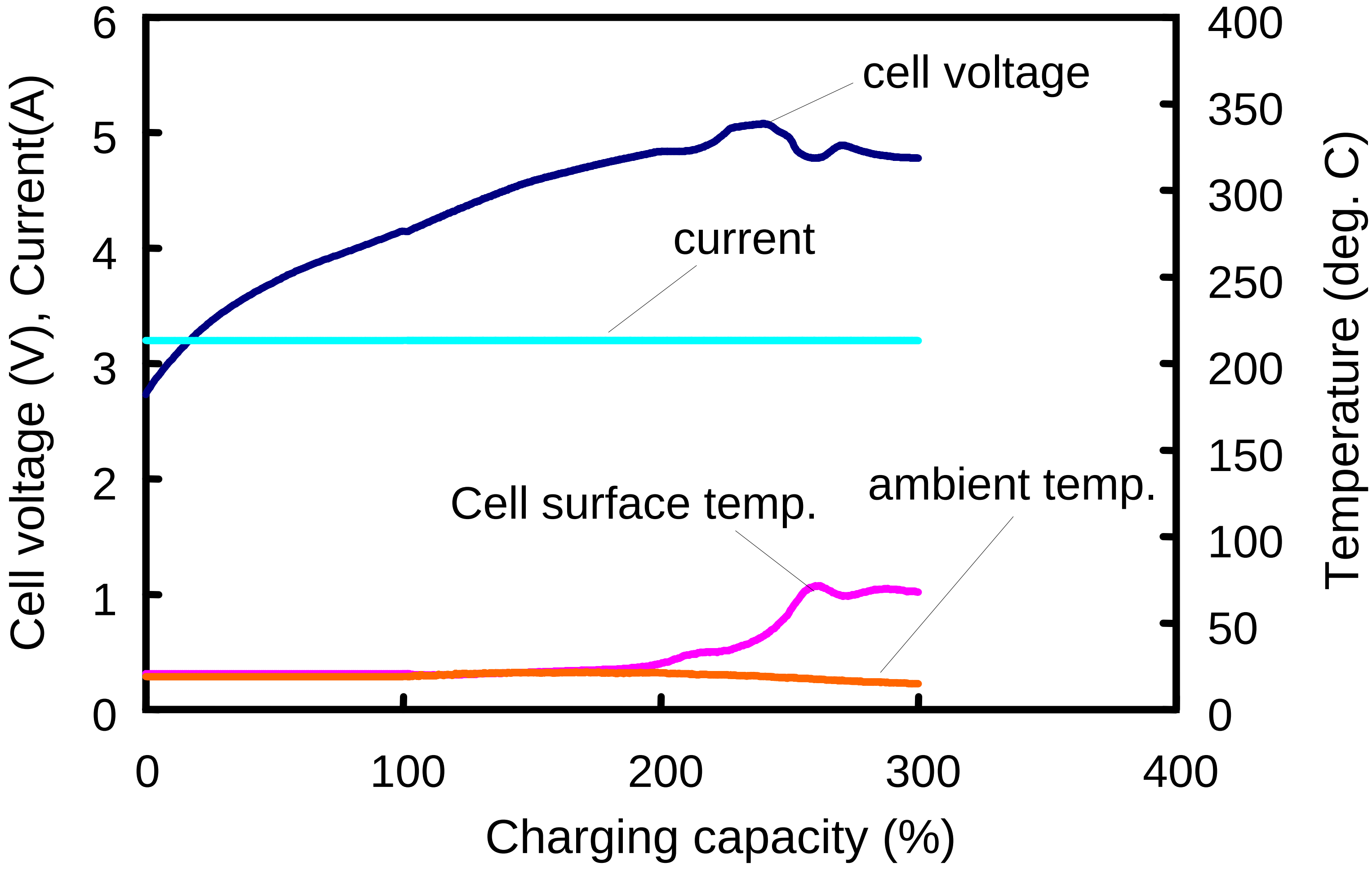
Short Circuit test for the 10 Wh class cell

short circuit resistance：2.8 m Ohm



Overcharge test for the 10 Wh class cell

charge to 250% *SOC at 0. 2 C



Abuse tests for the 210 Wh class single cell

Item		results				
		venting	smoking	fire	rupture	max. temp. (deg. C)
nail penetration	100% SOC	yes	yes	No	No	340
	50% SOC	No	yes	No	No	116
crush	100% SOC	yes	yes	No	No	363
	50% SOC	yes	yes	No	No	98
short circuit	100% SOC	No	No	No	No	*44
	50% SOC	No	No	No	No	*39
overcharge		No	No	No	No	70
overdischarge		No	No	No	No	34

***Busbar melted down**

-The lower SOC, the lower max. temp.

-Overcharge and overdischarge showed rather mild results

3. Abuse Test of High Power Cells (2)

Performed at Sandia National Laboratories

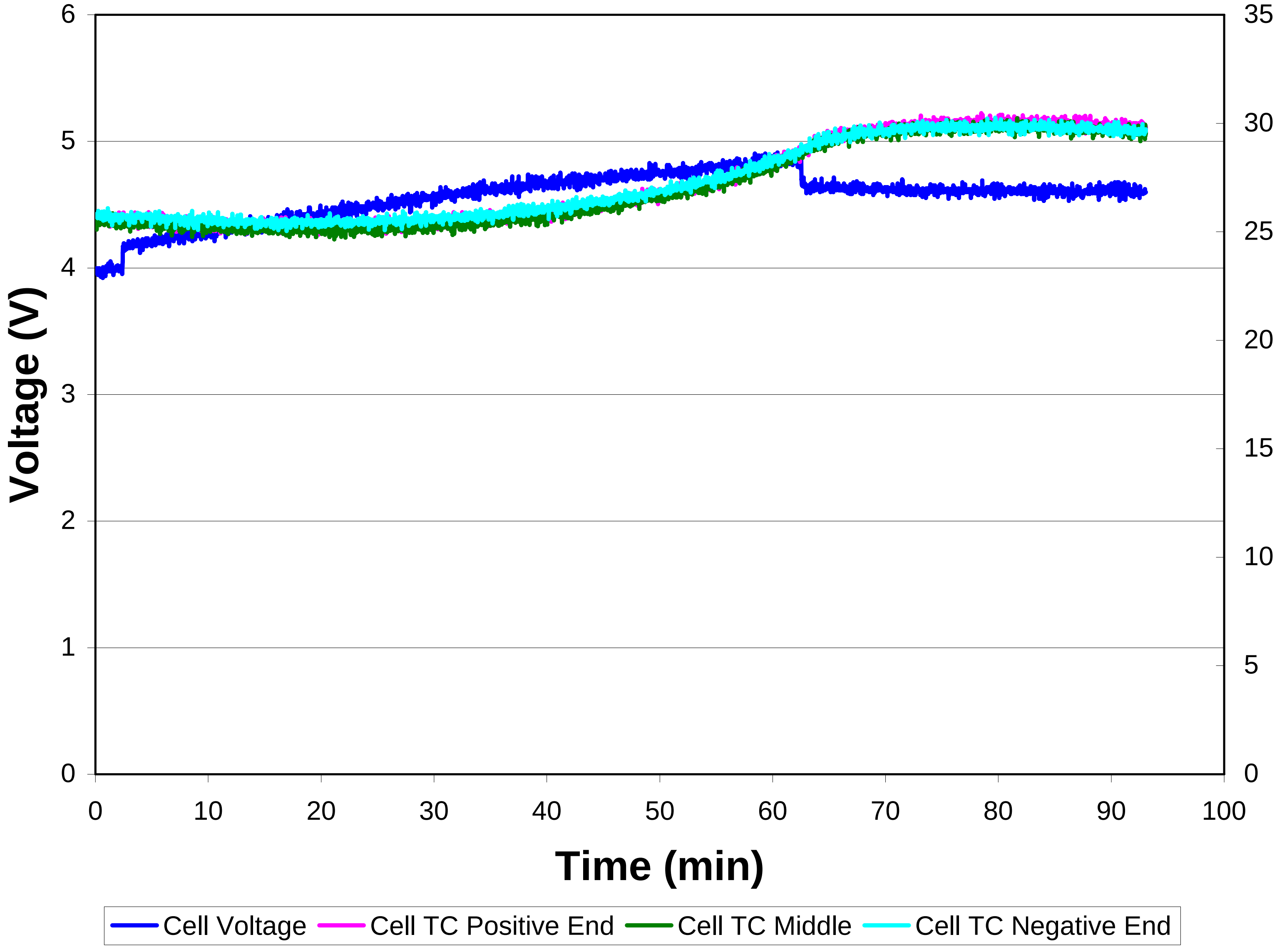
High Power Li-ion Cell (for HEV)

parts	material
cathode	Mn-based
anode	hard carbon
separator	micro porous polyethylene
electrolyte solution	$LiPF_6$ / EC-based Mixture
cell case	Ni-plated steel

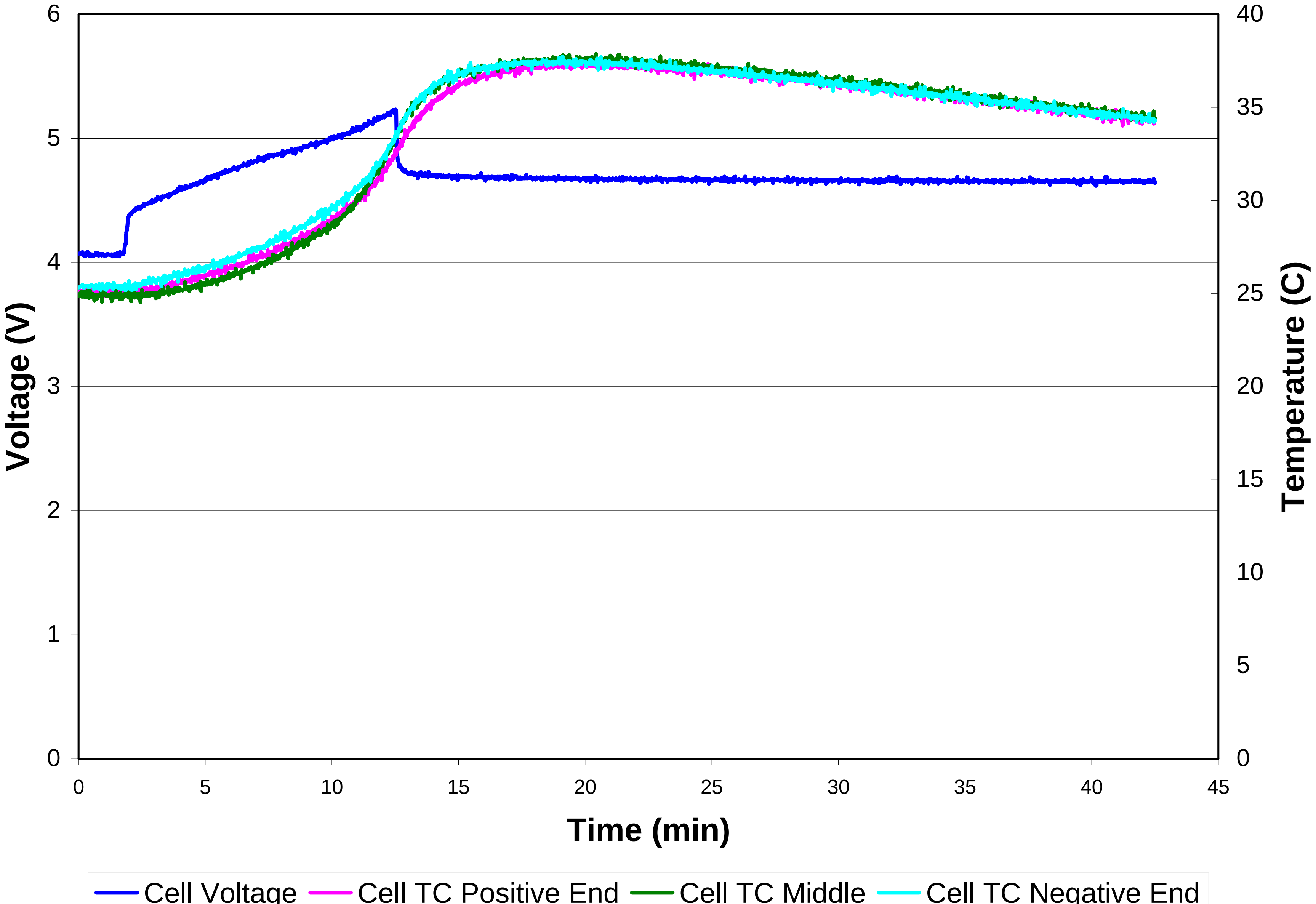
dimensions (mm)	ϕ40 x108
mass (g)	300
nominal voltage (V)	3.6
capacity (Ah)	5.5
# output power density (W/kg)	3000
# input power density (W/kg)	2200

 # : @50% SOC for 5 s discharge

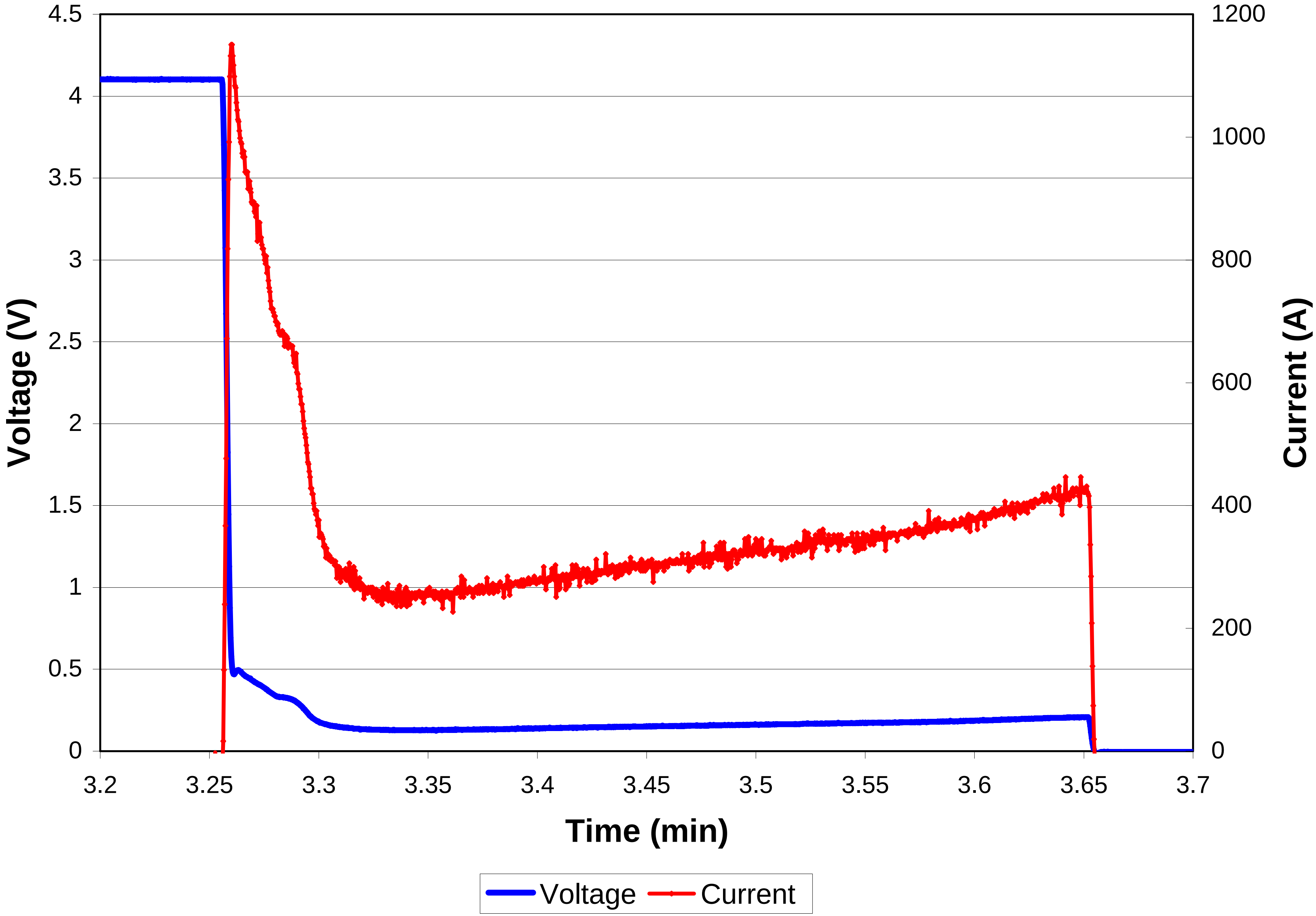
Overcharge Test at 5.5 A(1C)



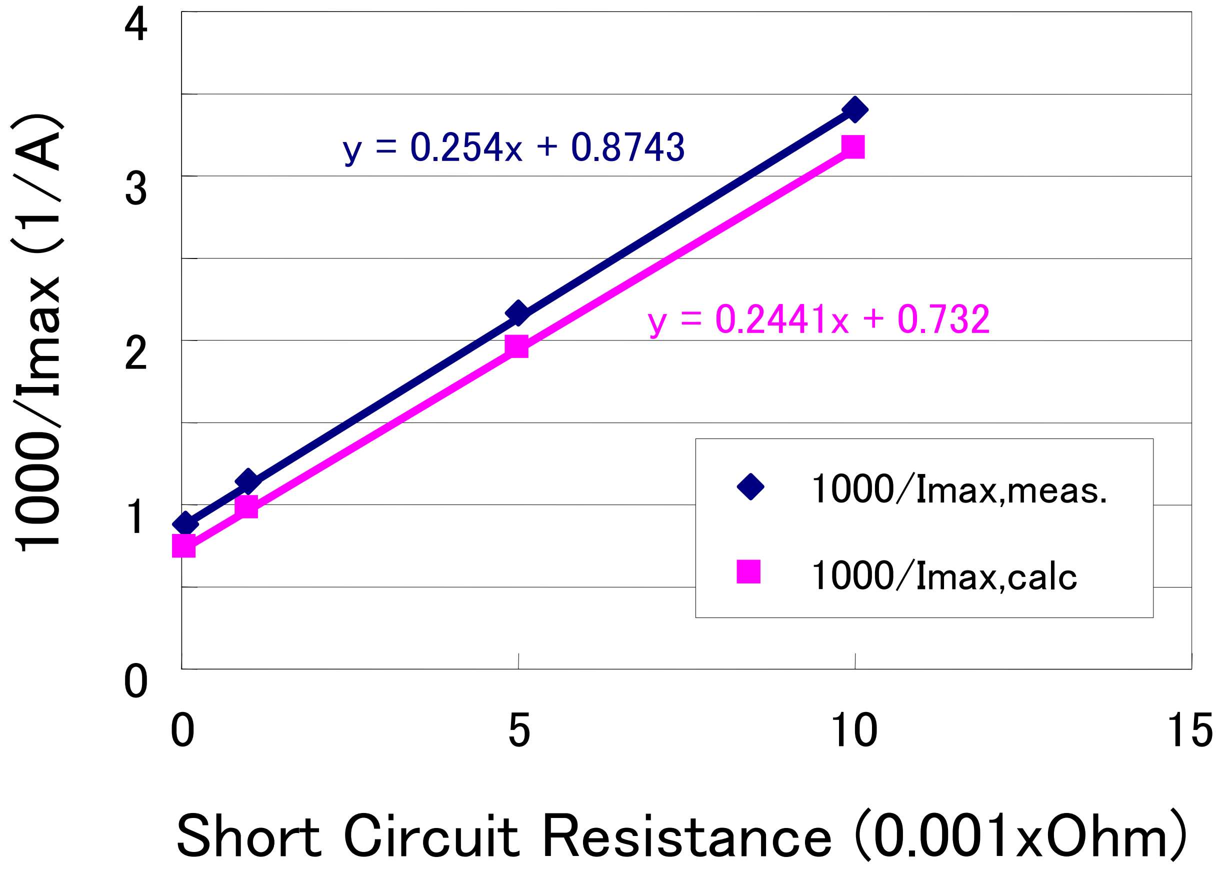
Overcharge Test at 32 A(5.8 C)



External Short Circuit (0.05 m Ohm)



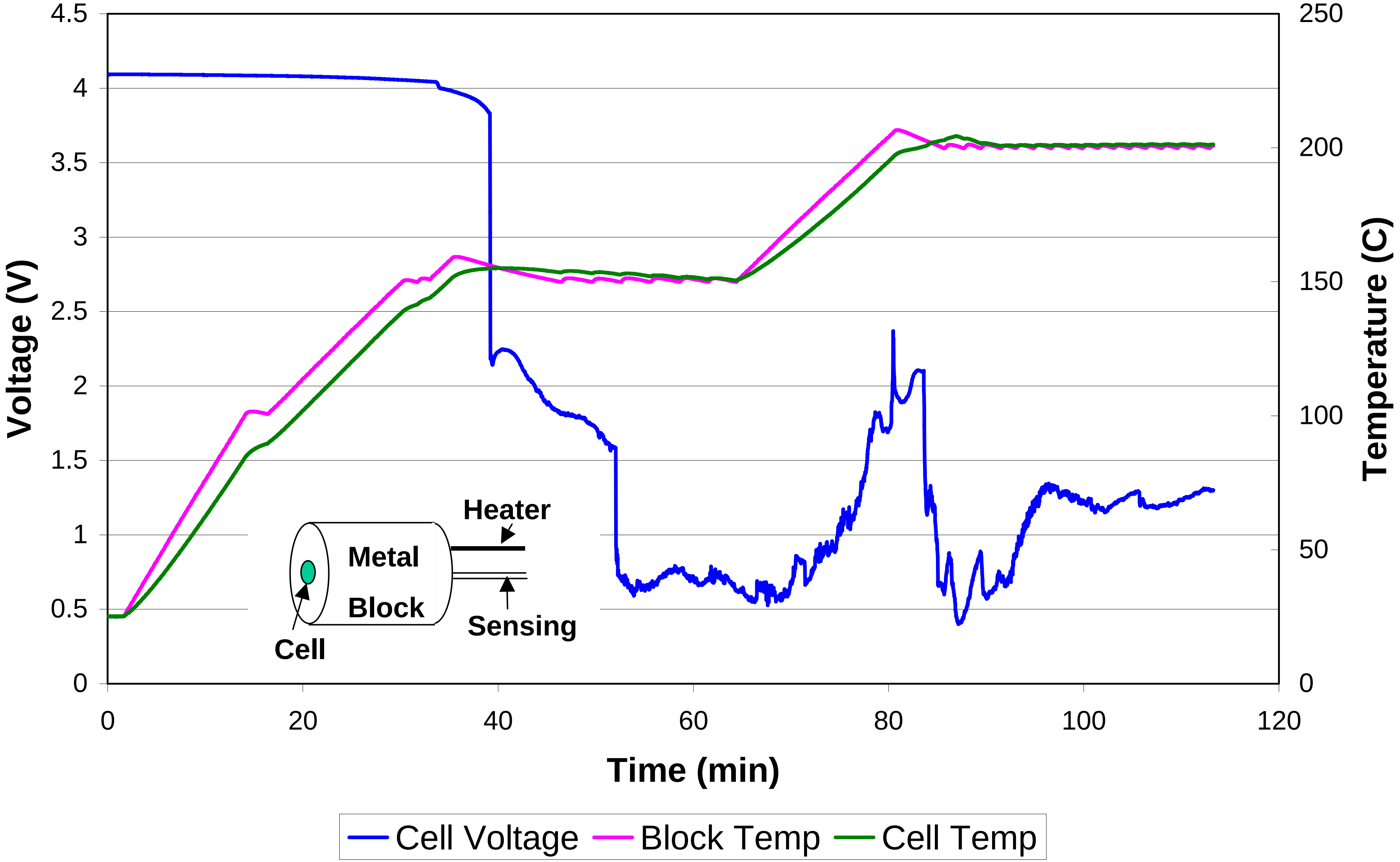
External Short Circuit : Resistance & Max Current



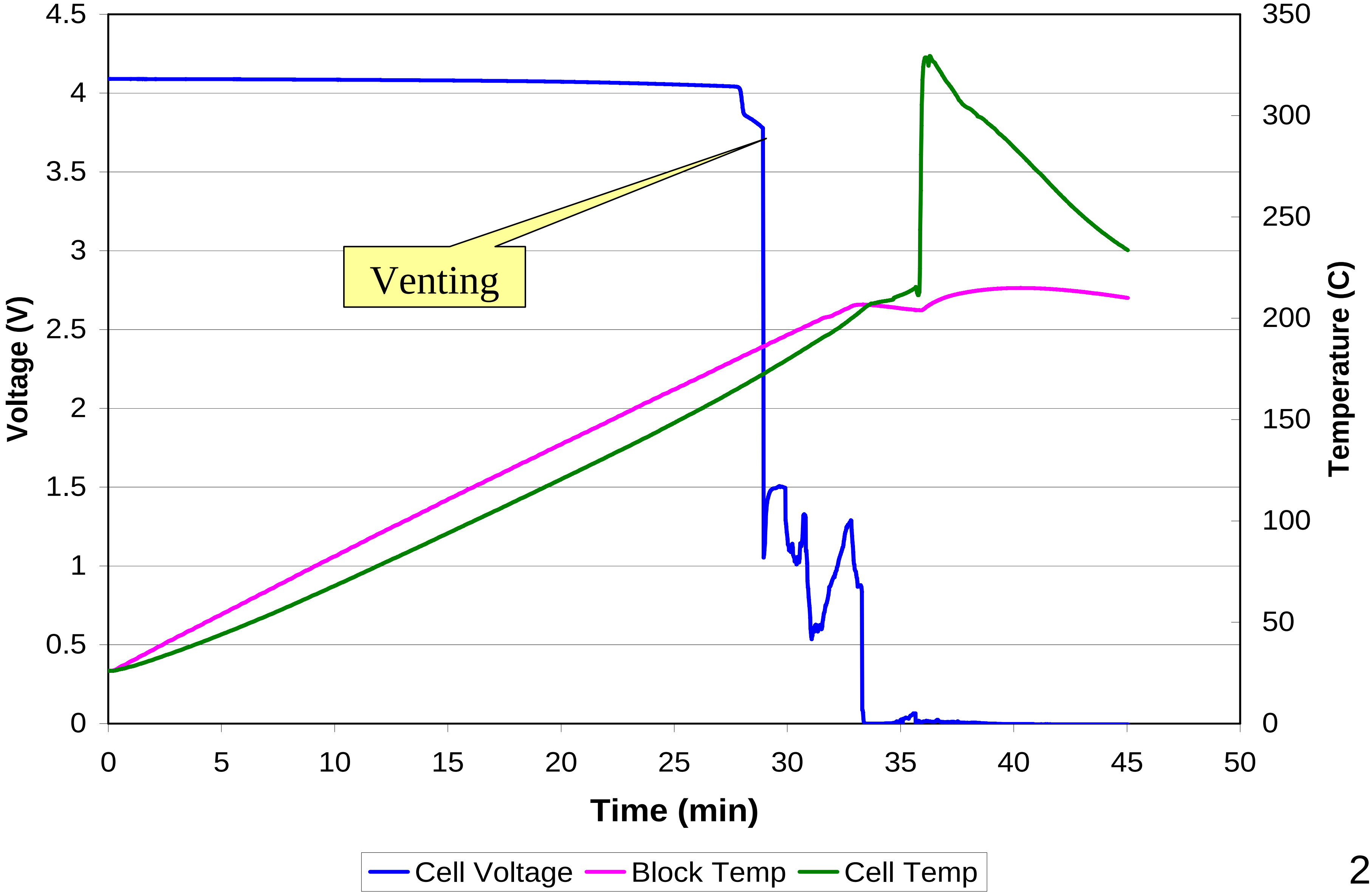
$1000/Imax = (1/V_0)R + R_0/V_0 = 1/(4.1)R + 3/(4.1) = 0.2441R + 0.732$

That is, Imax can be approximated by $I\ max = V_0/(R+R_0)$.

Overheating at 3 deg. C/min with a 30 min rest at 150 deg. C



Overheating at 5.5 deg. C/min with no Rest



Comments on the results for Li-ion cell for HEV

1. Overcharge at 32 A up to 200% SOC did not show any remarkable phenomena

2. Maximum current in short circuit test can be displayed by " $I_{max} = V_o / (R+R_o)$".

3. Overheat test results strongly depend on the heating rate and time, which implies the internal successive (thermal runaway) reactions are triggered simply by the thermal energy.

Devices to Enhance Abuse Tolerance

Cell level

1. Shut down of the separator
2. Pressure SW
3. PTC
4. Gas relief vent
5. Choice of cell chemistry
6. Modification of electrolytic solution :
   low flammable solvent, additive (electrolyte)

Module level

1. Preventive control : overcharge, overdischarge, over heat
2. Redundant control system
3. Fuse
4. Low flammable material

Internal energy content of a Li ion cell

1.suppose a model cell

HEV cell of 4Ah- 4V

2.electrochemical energy

4Ah × 4V ＝ 16 Wh = **57.6 kJ**

3.combustion energy of the solvents

- basis of calculation : ethylene carbonate ($C_3H_4O_3$)
- combustion energy of EC : ＞1000 kJ/mol
- solvent content in a cell : 50 g
- molecular weight of EC : 88
- combustion energy of EC in a cell : **568 kJ**

4.conclusion

Combustion energy is much larger than the electrochemical, even at extremely overcharged state up to 200 or 300% SOC.

5. Summary

1. The behavior of Li ion batteries in many kinds of abuse conditions are shown clearly.
2. The data convince us that the batteries are not always vital but it rather shows very mild result in some conditions, which suggests the capability to control the behavior of Li battery at various abuse conditions.
3. The key to the goal seems to be the development of the material to control the vitality of the electrolytic solution, other than the system control technology of the battery system.

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Thank you for your attention!!