Destructive Physical Analysis of Components of Cycled and Abused Li-ion Cells

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Introduction

- The destructive Physical Analysis of cycled and abused cells can provide data on changes occurring in the cells under extensive cycling and abuse conditions.

Cells Tested

DATE RCV'D	JSC HISTORY	CELL ID	CTS DISPOSITION	IMPEDANCE (mW)	RATED CAPACITY (Ah)	WEIGHT (g)
Aug-05	high ch rates	#001	capacity & DPA	150	1.5	47.715
Aug-05	not tested	#031	capacity	200	1.5	47.657
Aug-05	overcharged	#053	not tested	open	1.5	47.651
Aug-05	overdischarged	#068	not tested	220	1.5	47.667
Aug-05	overcharged	#070	not tested	200	1.5	47.764
Aug-05	fresh	M1427	capacity & DPA	125	1.5	41.968
Aug-05	external short	BP54C1	not tested	1250	1.5	39.639
Aug-05	overdischarged	BP54C2	not tested	125	1.5	41.014
Aug-05	not tested	BP54C3	capacity	930	1.5	41.136
Aug-05	overcharged	BP26C4	not tested	open	1.5	43.87
Sep-04	overcharged	#013	DPA	93	1.5	45.107
Sep-04	overdischarge	#015	not tested	95	1.5	44.808
Sep-04	external short	#047	not tested	open	1.5	43.088
Sep-04	external short	#048	capacity & DPA	25	1.5	43.834
Sep-04	overcharged	#009	DPA	open	1.5	42.005
Sep-04	overcharged	#009	DPA	open	1.5	42.005
Sep-04	overdischarged	#019	capacity & DPA	25	1.5	43.141
Sep-04	overdischarged	#020	DPA	25	1.5	41.793
Sep-04	external short	#009	DPA	open	2	42.636
Sep-04	external short	#010	not tested	open	2	43.366
Sep-04	overdischarge	#016	DPA	open	2	42.346

Cells Tested

- Moli 019 ($LiCoO_2$) 1.5 Ah- Overdischarge
- Moli 001 ($LiCoO_2$) 1.5 Ah High charge rates
- PDA 016 ($LiCoO_2$) 1.5 Ah- Overdischarge (dead)
- Moli 009 (spinel) 1.5Ah –overcharge (CID activated)
- Moli 020 (spinel) 1.5 Ah overdischarge (dead)
- Sanyo 013 ($LiCoO_2$) 1.5 Ah- Overcharge (CID activated)
- Sanyo 048 ($LiCoO_2$) 1.5 Ah High rate discharge
- Moli Spinel 1.5 Ah untested (fresh)

Visual Observations

	Sanyo High rate disch #48	Moli Over-disch #19	PDA Ext. short #9	PDA Over-disch #16	Moli Spinel Overch #9	Sanyo Overch #13	Moli Spinel Over-disch #20	Moli High rate charge #1	Moli Spinel Fresh M1427
Terminals	Good	Good	Good	Good	Good	Good	Good	Good	Good
Corrosion on tab bundle	None	Non	Non	none	none	None	None		none
Soft shorts	None	None	None	None	Hot spots	Hot spots	None		None
Disintegrated material	Severe	Severe	Slight	Slight	Severe	Severe	Severe	Slight	Slight

Visual Observations

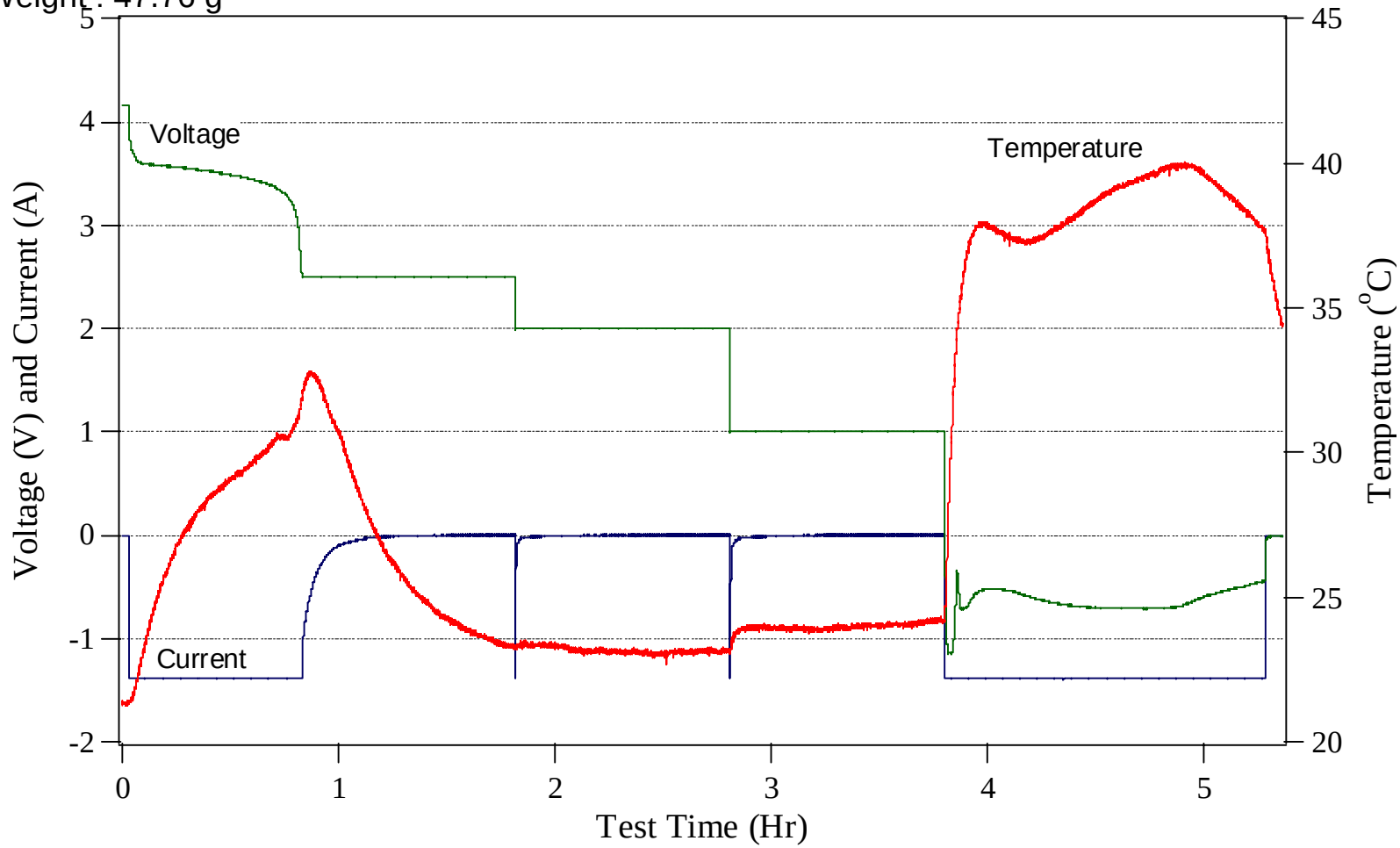
	Sanyo High rate disch #48	Moli Over-disch #19	PDA Ext. short #9	PDA Over-disch #16	Moli Spinel Overch #9	Sanyo Overch #13	Moli Spinel Over-disch #20	Moli High rate charge #1	Moli Spinel Fresh M1427
Shiny foil	Yes	Yes	Dark	Dark	Yes	Yes	Yes	Yes	Yes
Negative plate showing whiteness	None	None	None	Very slight	Yes	None	None		Slight
Plates yellowing	None	None	None	None	None	None	None		None
Separator	Gold	Gold	Gold	Very sl.gold	Very sl.gold	Very sl. gold/ brown	Gold edge/ Brown		No color
Positive plate						Brown	brown		

Post-cycling of Cells

	Charge: 500 mA to 4.1 V	Disch: 150 mA to 2.7V	Eff.	Ch: 500 mA to 4.1 V	Disch: 750 mA to 2.5 V	Eff.	Ch: 500 mA to 4.1 V	Disch: 750 mA to 2.7 V	Eff.
Moli #19 overdis	1.908 Ah	1.906 Ah	99.9	1.947 Ah	1.921 Ah	98.7	1.938 Ah	1.893 Ah	97.7
Sanyo #48 High-rate disch	1.908 Ah	1.906 Ah	99.9	1.947 Ah	1.847 Ah	94.9	1.938 Ah	1.89 Ah	97.5

Overdischarged Moli (#20) 18650 Li-ion Cell

Impedance: 200 mohms
Weight : 47.76 g



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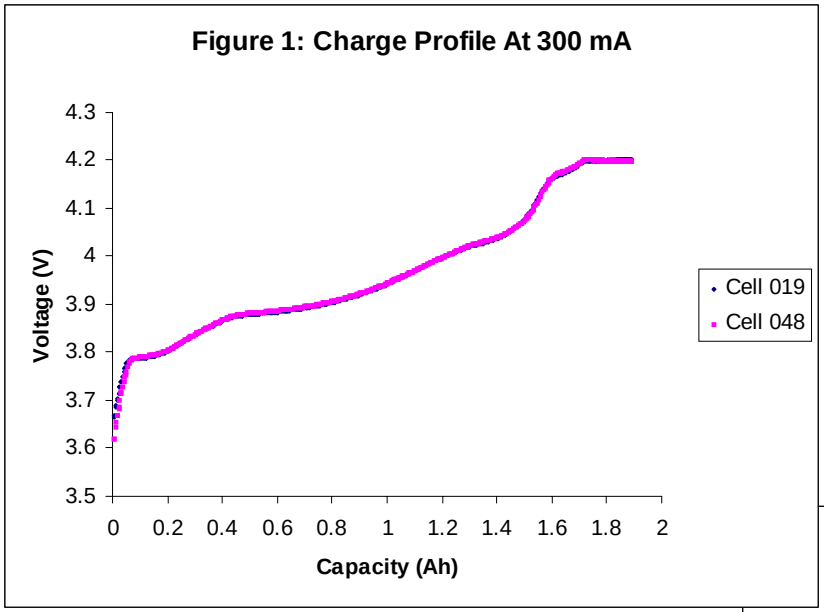
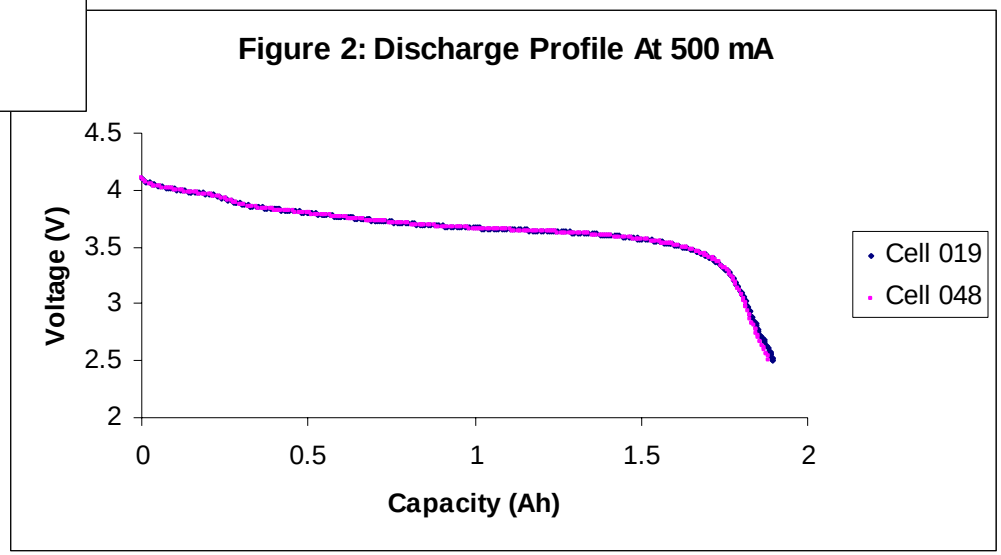
Post-test Discharge on cells





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Moli 020-Overdischarged Positive plate showing delamination and brown coloring at the separator/positive interface

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Moli 020 Overdischarged –Separator at the positive interface

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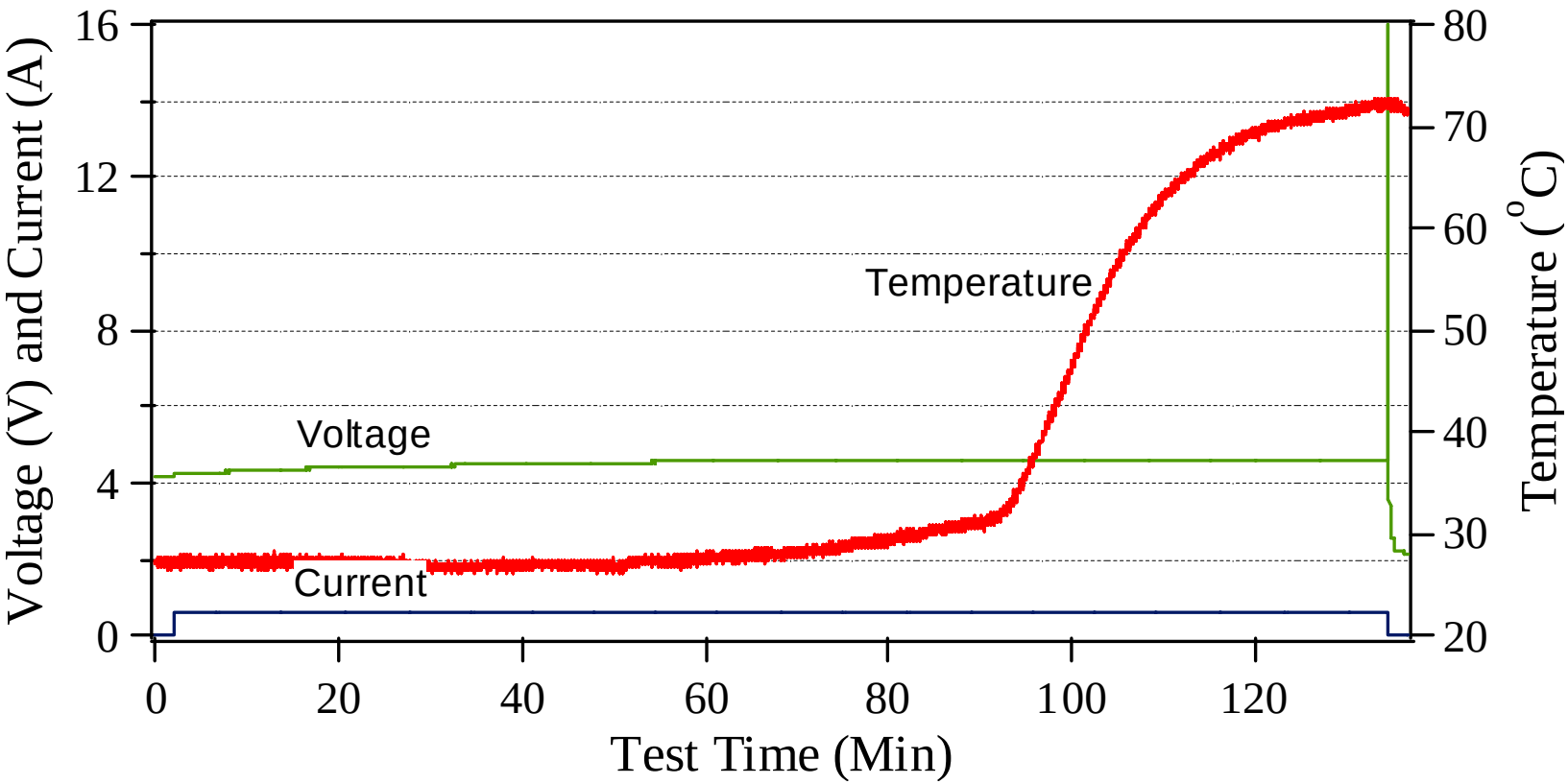
Condition of electrode stack
Overdischarged cells

- Separator- gold color
- Slight sticking of the separator to positive
- No hot spots
- Negative plate delaminates

Overcharge on Sanyo Cell to 12 V for 3 hours (0. 75 A current)



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Condition of the electrode stack- Overcharged cells

- Separator – gold color
- Pos and Neg plates – delaminated
- Severe sticking –to-complete bonding of the separator to positive
- Hot spots

Sanyo 013 Overcharged - Separator showing sticking positive material and brown discoloration of both separator and cathode

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Sanyo 013-Overcharged Negative plate material sticking to the separator

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Positive Plate Analysis

	Sanyo High rate disch #48	Moli Over-disch #19	PDA Ext. short #9	PDA Over-disch #16	Moli Spinel Overch #9	Sanyo Overch #13	Moli Spinel Over-disch #20	Moli High rate charge #1	Moli Spinel Fresh M1427
De-lamination of positive	Slight	Slight	None	None	Severe	slight	Severe		none
Stickiness to separator	Slight	Slight	None	None	Severe	slight	Severe		none

Positive Plate Analysis

SAMPLE	Li-Co CATHODES			Li-Mn CATHODES	
HISTORY	SANYO 48 good	SANYO 13 overcharged	MOLI 19 overdischarged	MOLI 9 overcharged	MOLI 20 overdischarged
active material weight	15.844	14.608	15.626	14.652	16.503
Li/Co molar relation	0.94	1.08	1.60		
Li/Mn molar relation				0.47	1.97
inactive material					
Ni (% of plate)	0.06	0.00	0.00	0.00	0.00
Na (% of plate)	0.03	0.03	0.00	0.02	0.03
C/PVDF(% of plate)	13.2	13.5	30.6	73.1	72.4

Negative Plate Visual Inspection

	Sanyo High rate disch #48	Moli Over-disch #19	PDA Ext. short #9	PDA Over-disch #16	Moli Spinel Overch #9	Sanyo Overch #13	Moli Spinel Over-disch #20	Moli High rate charge #1	Moli Spinel Fresh M1427
De-lamination of negative	Severe	Severe	Slight	Slight	Slight	Severe	slight		none
Stickiness to separator	Severe	Severe	Slight	Slight	Complete bonding	Severe	slight		none

Negative Plate Analysis

SAMPLE	Li-Co Cell		Li-Mn Cell	
HISTORY	SANYO 13 overcharged	MOLI 19 overdischarged	MOLI 9 overcharged	MOLI 20 overdischarged
active material weight	8.104	6.559	8.22	3.962
Co (% of plate)	1.3	3.2	NA	NA
Mn (% of plate)			1.39	1.07
total weight Na (g)	0.000146	0.0000	0.000062	0.000012

Metals from cathode found on negative plate

Electrolyte Visual Observations

	Sanyo High rate disch #48	Moli Over-disch #19	PDA Ext. short #9	PDA Over-disch #16	Moli Spinel Overch #9	Sanyo Overch #13	Moli Spinel Over-disch #20	Moli High rate charge #1	Moli Spinel Fresh M1427
pH	2-3	3-4	4	4	Very dry	3	3	2-3	2-3
Color	Okay	Okay	Yellow -tinge	Yellow -tinge	Okay	Okay	Okay		Sl. yellow

Electrolyte in cells

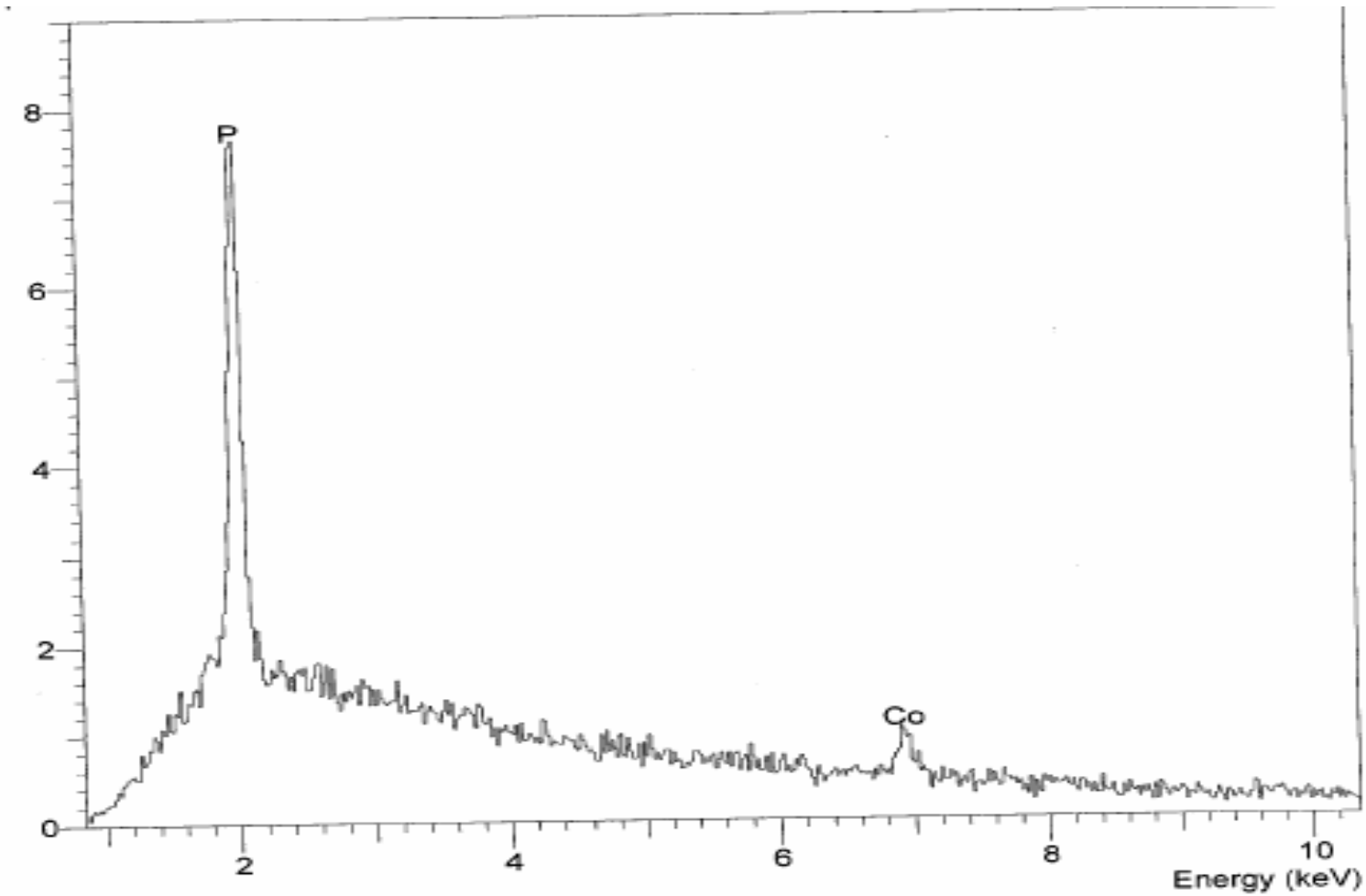
	ITEM	SANYO	PDA	Moli	Sanyo	Moli
		48 hi rate dischg	**16** overdis	**9** overcharge	**13** overchg	**20** overdis
Weight, g		2.942	4.086	2.217	3.408	2.421
Li Content						
	Weght,mg	7.6	14.5	2.2	6.9	26.9
	M Li in cell	0.44	0.60	0.17	0.34	1.88
	mg Na	3.02	0.60	0.40	1.20	36.22
	mg K			0.93	0.30	30.55
	mg Mn					0.93
	Cu,Fe,Co, Ni	none	none	none	none	none

More Li in overdisch cells

Water Content of Electrolyte

SAMPLE	run 1	run 2	run 3	average	delta blank
DMC blank	110.2	100.4	105.2	105.3	
Sanyo 48	5.8	7.7	6	6.5	less than, ergo H2O absorbed by cell
Moli 19	45.7	49.8	51.9	49.1	less than, ergo H2O absorbed by cell
PDA 9	205.7	210.1	208.5	208.1	102.8
PDA 16	276.9	277.8	279.6	278.1	172.8

Separator for Sanyo #48



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Conclusions

- Occasionally cells survive overdischarge but not overcharge
- Overcharged cells fail due to dry out and fusing of the separator
- Overdischarge cells failed due to structural breakdown of the positive
- Li in the electrolyte is less than expected and spinel overdisch cells showed an increase
- Physical degradation more at the anode
- It is not clear whether metallic Co is produced during overdischarge
- The pH of the electrolyte in abused cells shows more acidity than fresh cells showing the presence of more HF in cells after abuse.
- There is also an increase in the water content and a decrease in the $LiPF_6$ concentration.

Acknowledgment

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