Safe Charge Rates for Lithium-Ion Cells

Effects of Lithium Plating

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Safe Charge Rates

Objective:

Establish a procedure to determine conditions that result in safe charging of Li-ion batteries under extreme conditions of charge rate and temperature.

Approach:

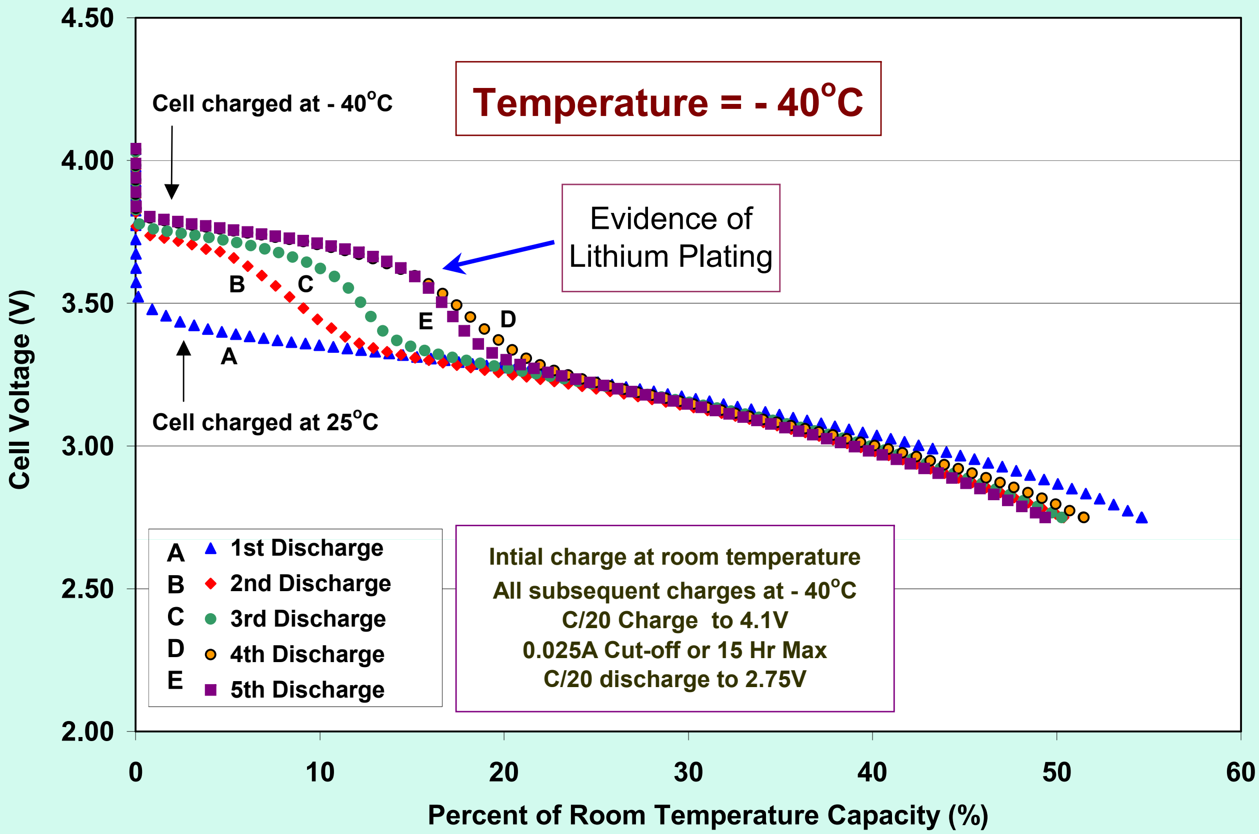
Various chemistries will be evaluated for their ability to support such charge rates without plating at different temperatures.

Background

- Li intercalation in graphite occurs ~100 mV, while Li deposition takes place at < 0 v, vs. Li.
- Conditions where Li intercalation kinetics are hindered, the anode potential goes below Li plating potentials
  - High rate charge
  - Low temperature
  - Poor interfacial conditions unfavorable for Li intercalation.
- Factors influencing Li plating
  - Nature of electrolyte
  - Nature anode composite electrode
  - Cathode to anode ratio
    - Cell designs are generally cathode limited. However, if anode is sufficiently in excess, it may polarize anode heavily.
    - Cathode/anode ratio may change upon cycling/storage, due more degradation at the anode,
- Effects of Li plating
  - May be reintercalated given time-no serious impact.
  - Will impact the stability relative to electrolytes.
  - Cycle life and reliability may be severely compromised.

Large Capacity Prototype Li-ion Cell Testing

Impact of Charging at Low Temperature (-40°C)

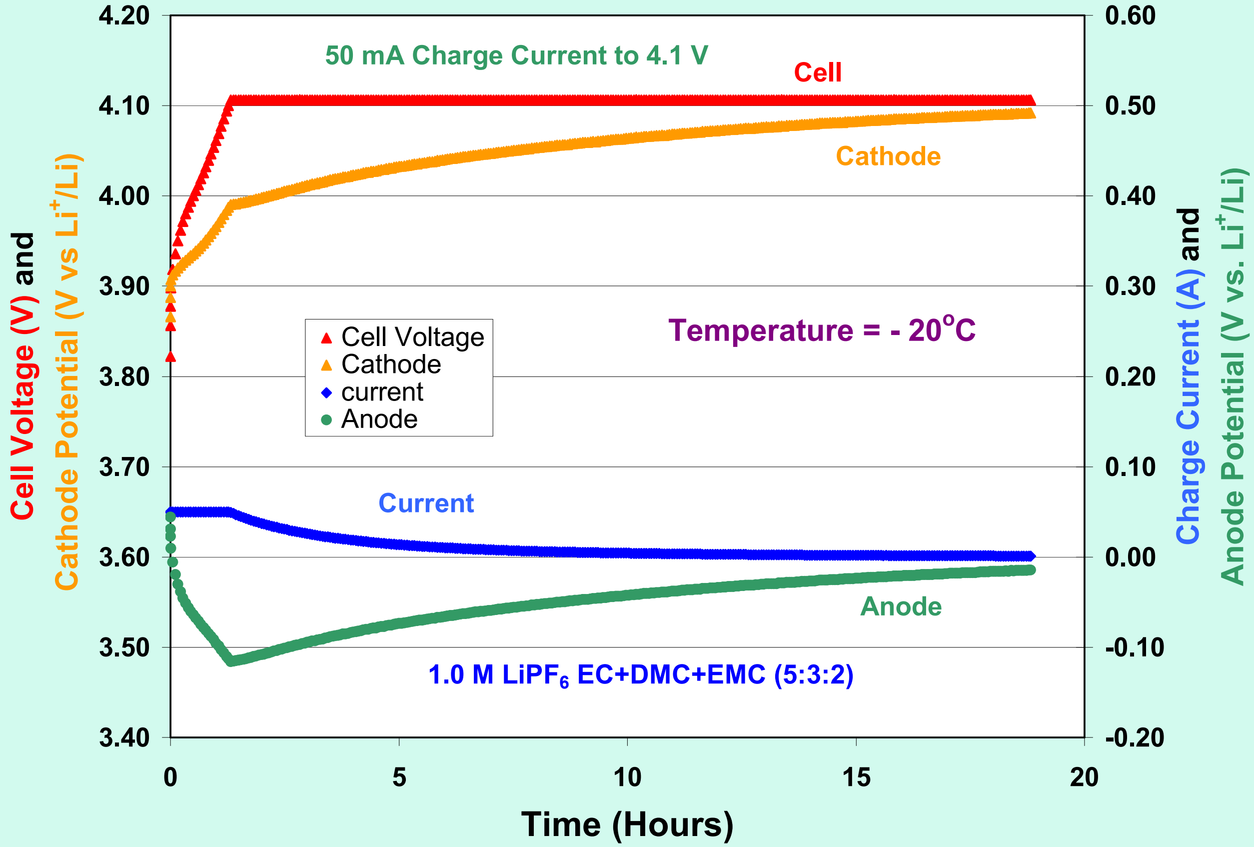


Reported in IECEC 1999

- Evidence of lithium plating observed on discharge following charge at low temperature.
- The higher discharge voltage plateau observed is most likely due to presence of a lithium stripping reaction which occurs at a higher potential compared to the lithium de-intercalation process at the anode

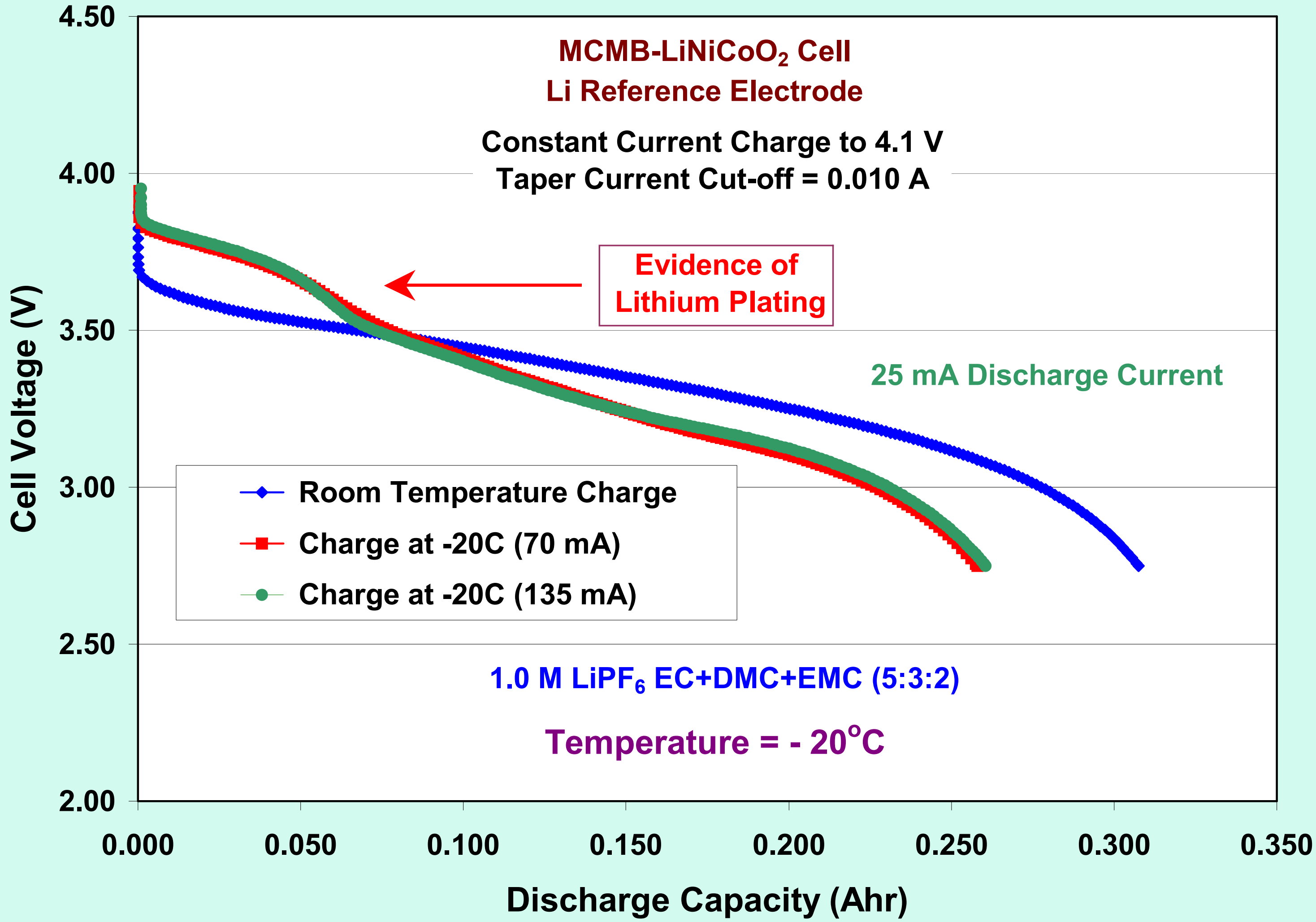
Charge Characteristics of Experimental Lithium Ion Cells

Effect of Charging at Low Temperature (- 20°C) - Effect of Electrolyte



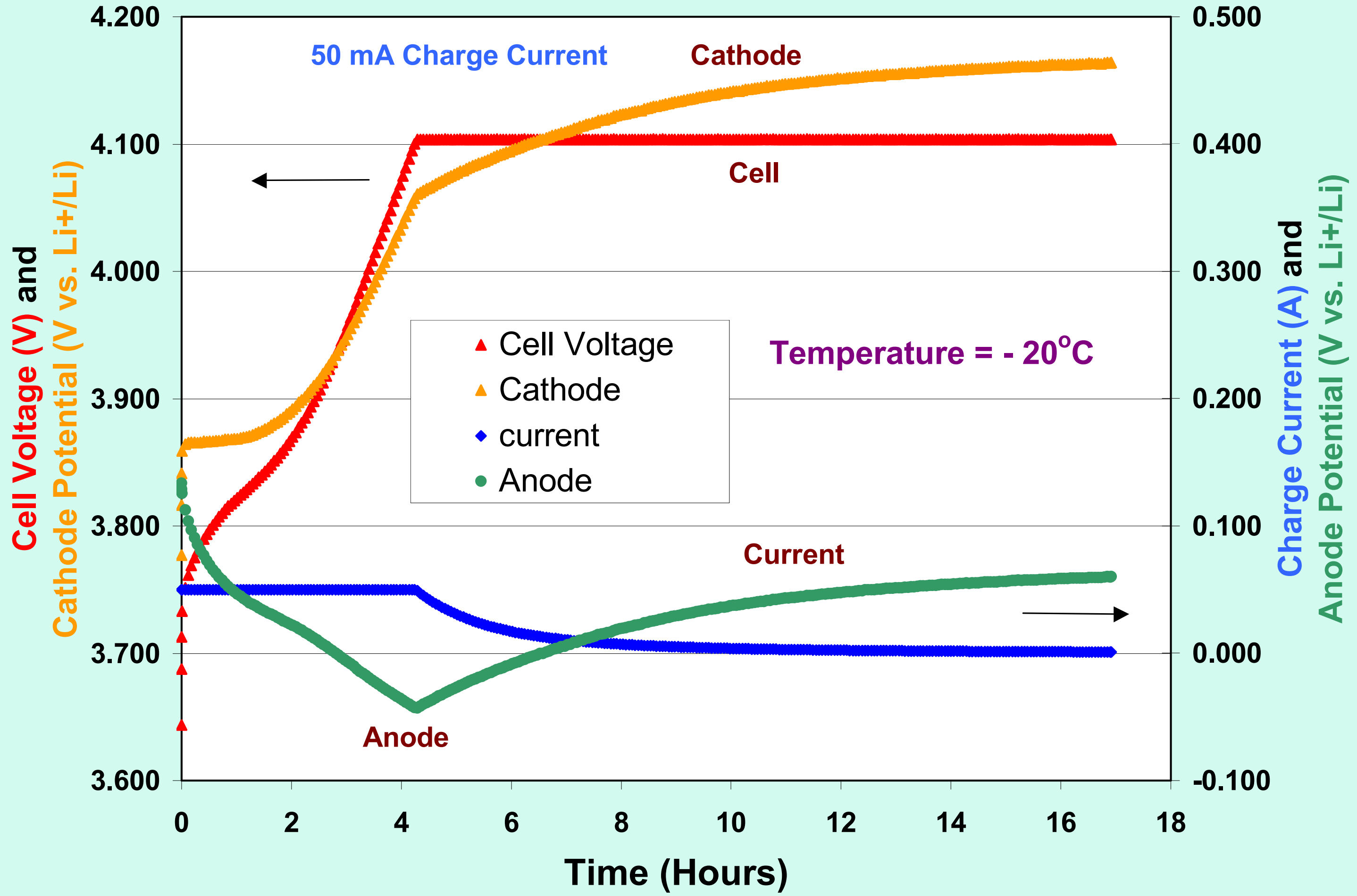
- The anode can be excessively polarized in contrast to the cathode resulting in the possibility of lithium plating occurring.
- In this example, the anode potential never becomes positive during entire charge.

Charge Characteristics of Experimental Lithium Ion Cells
Effect of Charging at Low Temperature (- 20^{o}C) -Effect of Electrolyte



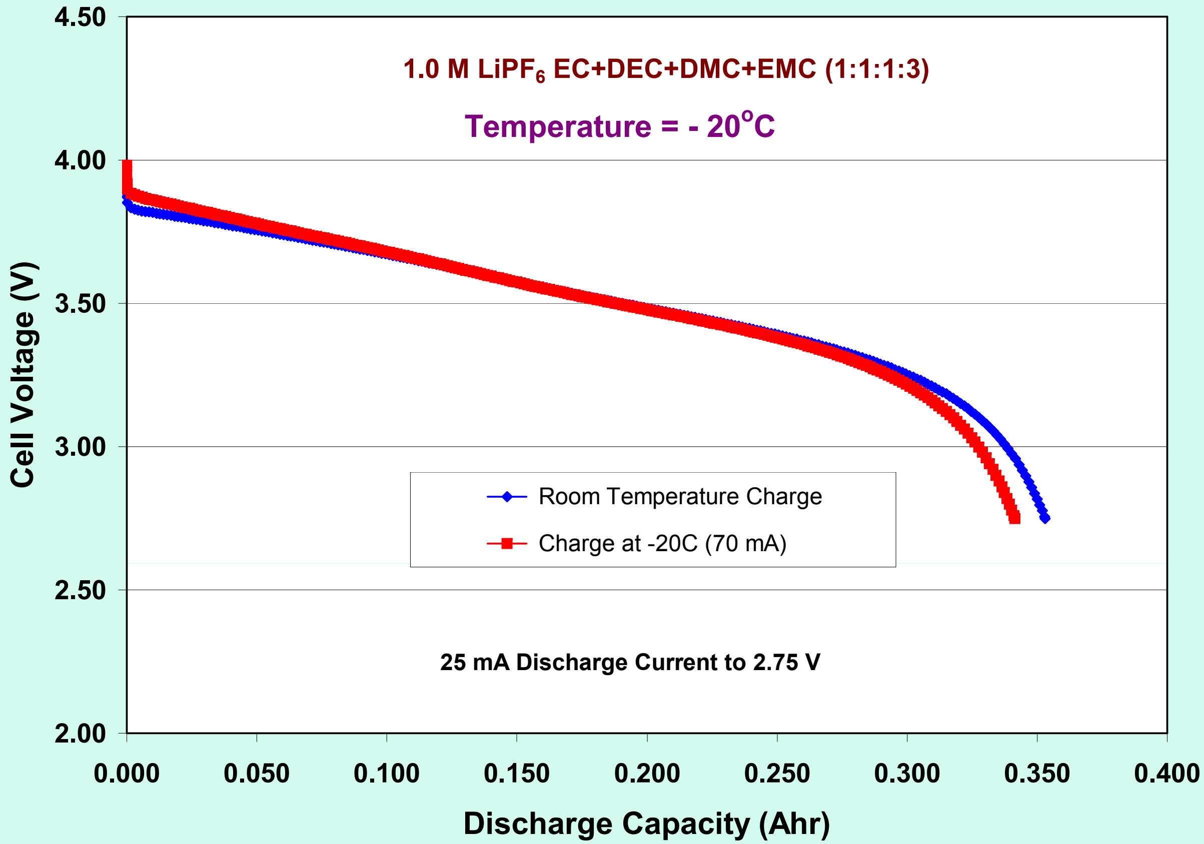
Charge Characteristics of Experimental Lithium Ion Cells at- 20°C

JPL Quaternary Carbonate Low Temperature Electrolyte (1:1:1:3)



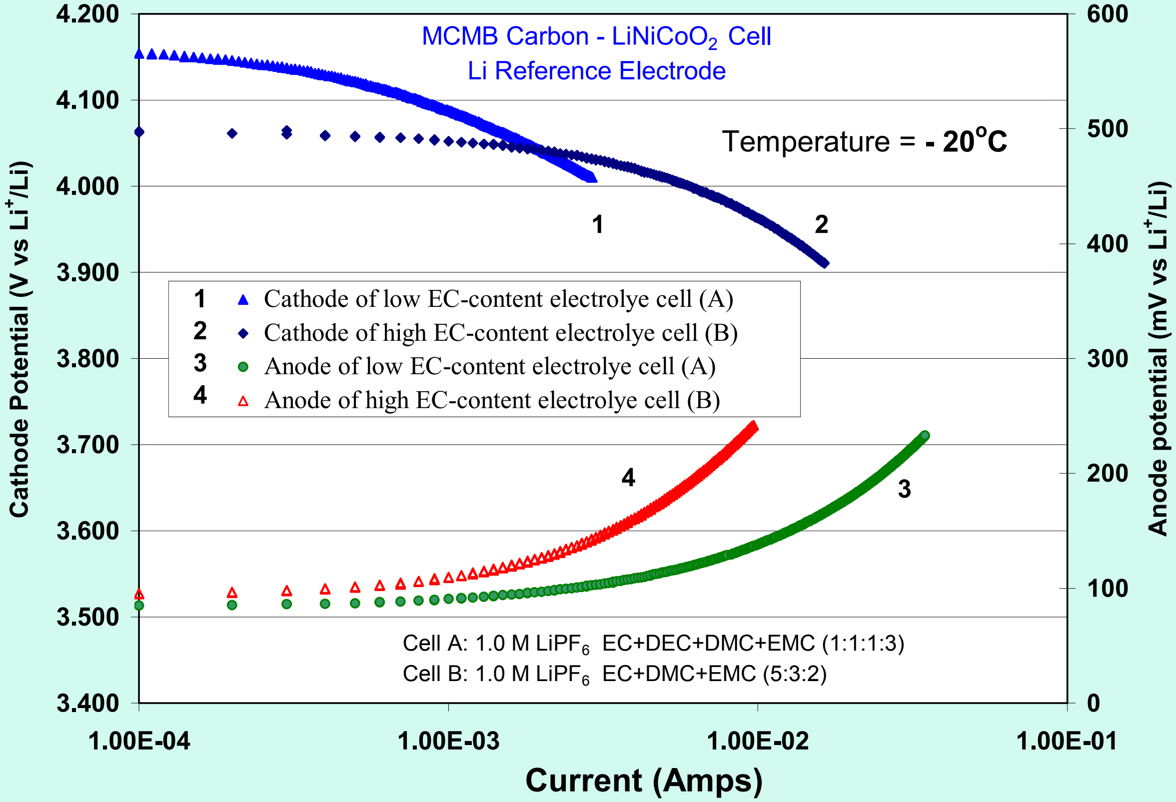
- As shown, the point at which the anode potential becomes the most negative (~ -70mV vs. Li^+/Li) is when the charge voltage and current are highest.

Charge Characteristics of Experimental Lithium Ion Cells
Effect of Charging at Low Temperature (- 20°C)



- Although the anode potential became negative, no lithium plating was observed with this cell in the subsequent discharge profiles.
- This might be due to the fact that the potentials were not sufficiently negative and/or any lithium plated on the electrode surface had time to intercalate during the taper mode.

Tafel Polarization Measurements of MCMB and $LiNiCoO_2$ Electrodes Effect of Electrolyte upon Polarization at Different Temperatures

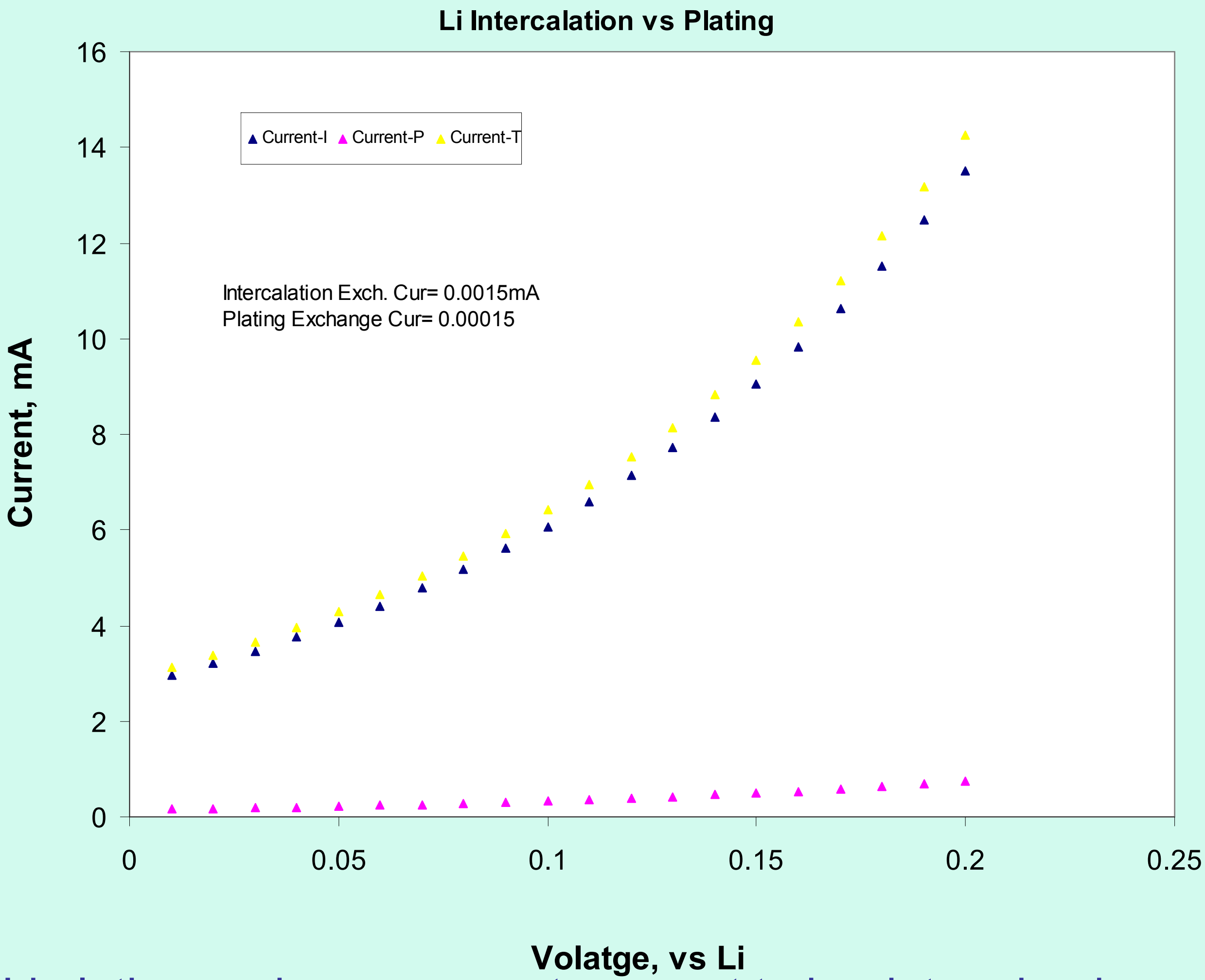


- In the case where no lithium plating was observed (good low temp electrolyte), the cathode was observed to have poorer kinetics at low temperature.
- Whereas, in the case where lithium plating was observed (poor low temp electrolyte), the anode displayed poorer kinetics and increased polarization.

Relative kinetics of Li Plating and Li Intercalation

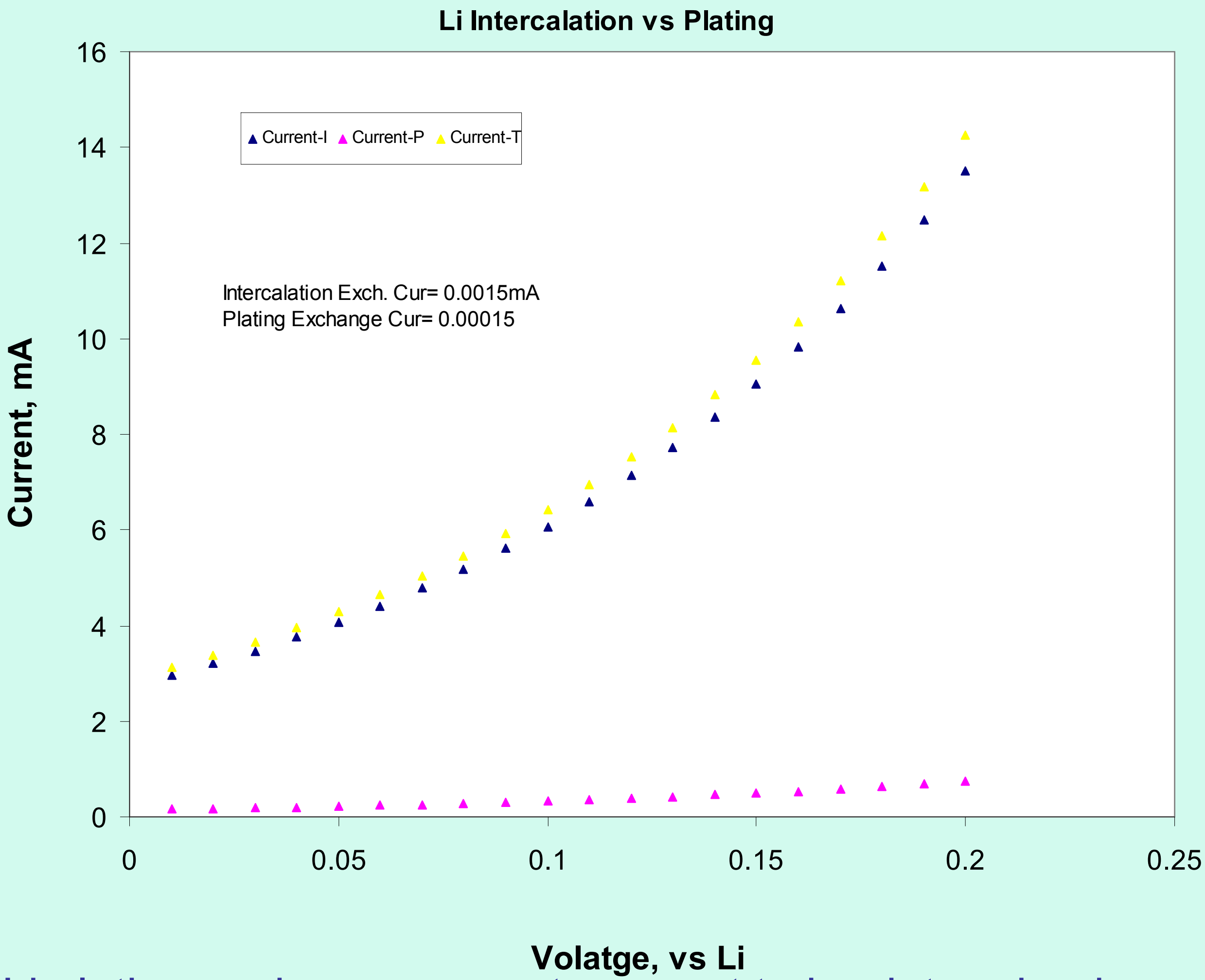
- Currents towards Li plating and Li intercalation at a given potential have been estimated with the assumption that both Li processes are in the Tafel mode.
- Reversible potential for Li intercalation: 85 mV vs L, Li plating: 0 V vs. Li.
- Reintercalation not taken into consideration
- The objective is only to show the effect of reduced kinetics for intercalation at low temperatures

Relative kinetics of Li Plating and Li Intercalation



- Li plating exchange currents are yet to be determined experimentally.

Relative kinetics of Li Plating and Li Intercalation



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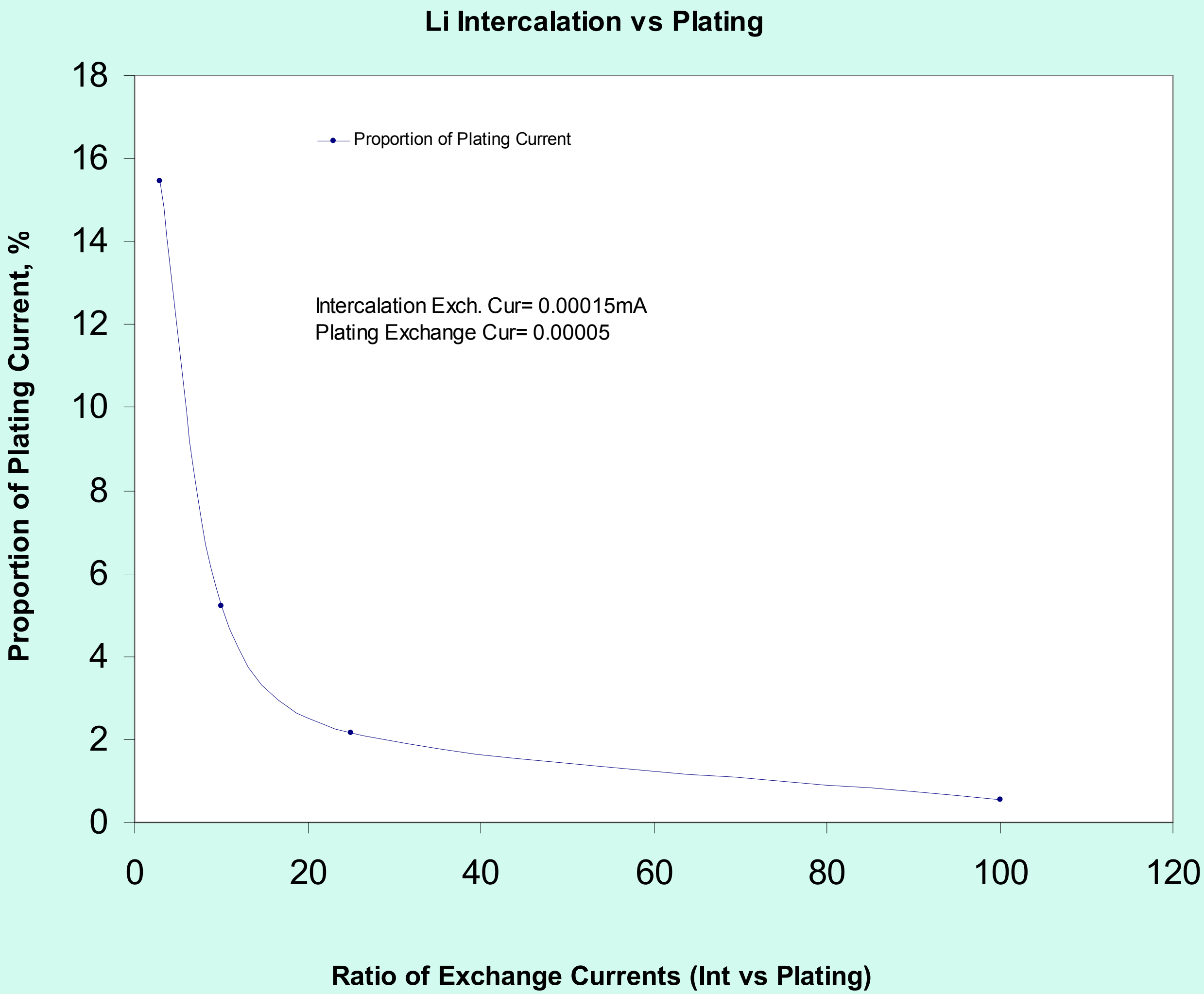


- Li plating exchange currents are yet to be determined experimentally.

Experimental Details

- **Prototype Cell Testing**
  - Cylindrical and Prismatic Designs
  - Cell sizes ranging from 18650 to 42 AHr
- **Experimental Cell Design/Chemistry**
  - MCMB anodes and $LiNiCoO_2$ cathodes
  - Cells equipped with Li metal reference electrodes
  - Number of different electrolyte studied (esp. low temp)
  - 300-400 mAhr size cells
  - Jelly roll design (cylindrical)
- **Charge acceptance at various rates and temperatures**
  - Effect of charge voltage
  - Effect of charge current and taper current cut-off
  - Effect of electrolyte (and corresponding SEI layers formed) upon charge characteristics
  - Identification of conditions which lead to lithium plating

Planned Tests for Charge Rate Effects-Test Articles

Manufacturer	Type	Chemistry	Tests		
			Characterization	LT Charge Rates	High rate charge at 40°C
Quallion	18650SA	$C\text{-}LiCoO_2$	3	2	1
ABSL	18650	$HC\text{-}LiCoO_2$	3	2	1
A123	262650	$LiFePO_4$	3	2	1
SKC	Pouch	$C\text{-}LiCoO_2$	3	2	1
Yardney	Prismatic	$C\text{-}Li(NiCo)O_2$	3	2	1
SAFT	Cylindrical	$C\text{-}Li(NiCo)O_2$	3	2	1

Quallion 4 Ah Lithium-Ion Pouch Cells

- Quallion 4 Ah Prismatic 7 Ah Li-ion Cells
  - 20 Cells Received Total (12 cells under D-RATS Program)
  - Five different electrolyte types
    - Quallion Low Temperature Electrolyte (“ED-1”) ***4 Cells***
    - Quallion Low Temperature Electrolyte (“ED-2”) ***4 Cells***
    - Quallion Baseline Electrolyte (“ED-1”) ***2 Cells***
    - JPL Low Temperature Electrolyte (JPL-2)
    - JPL Low Temperature Electrolyte (JPL-5)
- Completed the following initial characterization tests:
  - **5 Cycles at 20°, 0°, and -20°C**
  - **C/5 Charge current (1.40 A) to 4.1V, 0.070 A Taper current cut-off (C/100)**
  - **C/5 Discharge current (1.40 A) to 2.75 V**
  - **Current-interrupt pulse measurements performed vs. SOC**
- Initiated the following initial characterization tests:
  - Charge Characterization vs. Temperature
  - Low Temperature Discharge Characterization

Quallion 4 Ah Lithium-Ion Pouch Cells

Initial Characterization/Conditioning at 20^{o}C

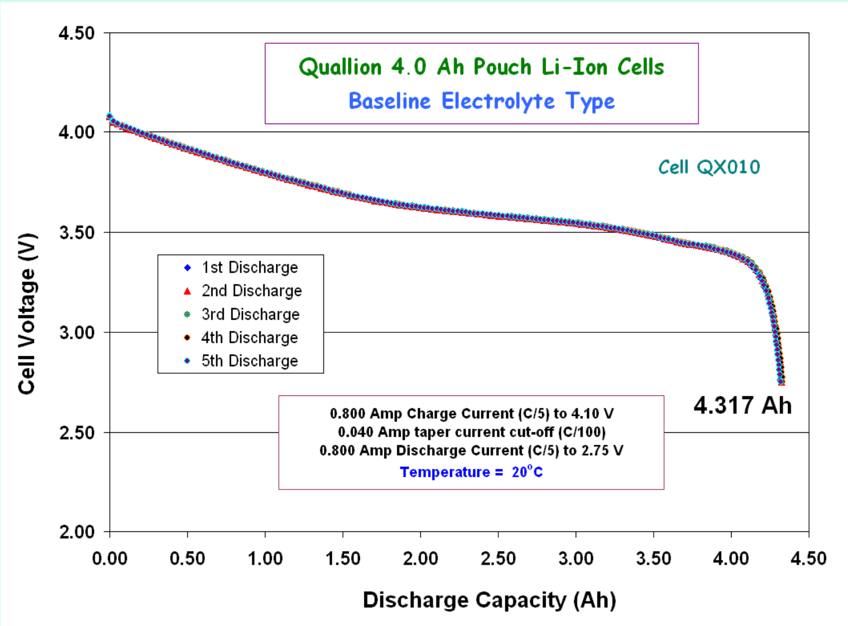
Summary of Conditioning Results

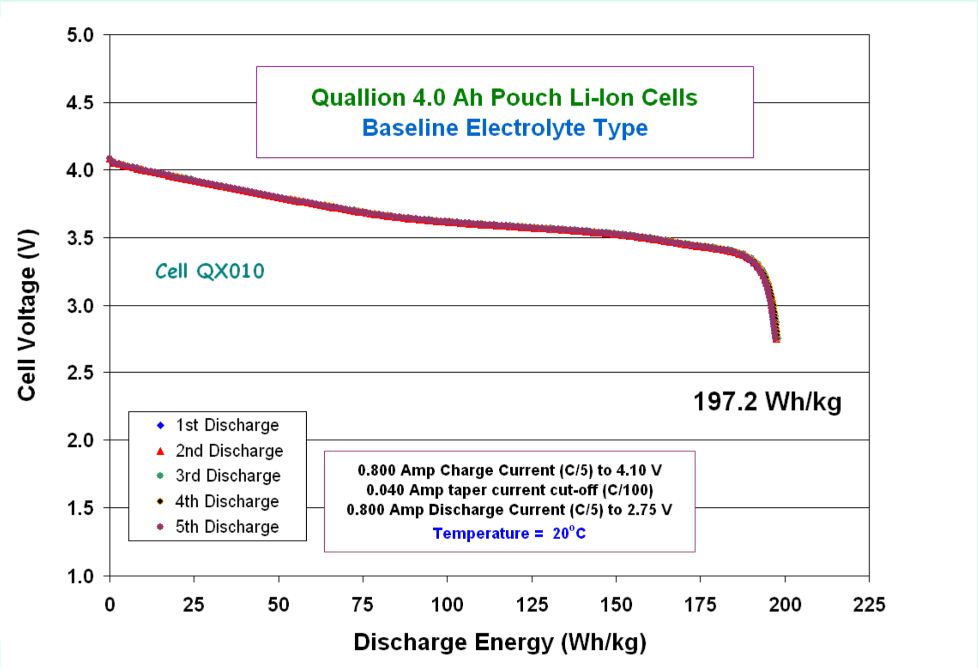
Cell ID	Cell Weight (Grams)	Cell Weight (kg)	Initial Voltage	Initial Capacity (Ah)	Initial Watt-Hours	Initial Wh/kg	Calculated Impedance (mOhms) (100% SOC)	Calculated Impedance (mOhms) (80% SOC)	Calculated Impedance (mOhms) (60% SOC)	Electrolyte Type
QA05	79.18	0.0792	3.426	4.3847	16.009	202.19	29.98	39.52	30.44	ED-1
QA06	78.39	0.0784	3.446	4.3864	16.019	204.34	29.83	39.22	29.68	ED-1
QA07	79.11	0.0791	3.451	4.3714	15.951	201.63	30.98	40.74	33.88	ED-1
QA08	79.92	0.0799	3.703	4.3750	15.963	199.73	32.88	42.50	34.10	ED-1
QB04	78.47	0.0785	3.477	4.2974	15.626	199.14	35.86	45.93	37.16	ED-2
QB05	78.69	0.0787	3.461	3.5360	12.640	160.63	65.23	77.21	68.67	ED-2
QB06	79.28	0.0793	3.480	4.2537	15.477	195.22	35.48	47.46	37.92	ED-2
QB07	79.07	0.0791	3.483	4.2530	15.492	195.93	31.43	42.65	32.20	ED-2
QX010	80.31	0.0803	3.431	4.3436	15.818	196.96	33.88	44.10	34.49	Baseline Electrolyte
QX018	79.66	0.0797	3.4176	4.3172	15.712	197.24	34.56	45.93	35.78	Baseline Electrolyte
Average	79.21	0.08	3.48	4.25	15.47	195.30	36.01	46.53	37.43	

Quallion 4 Ah Lithium-Ion Pouch Cells

Initial Characterization/Conditioning at 20°C

Discharge Capacity (Ah)

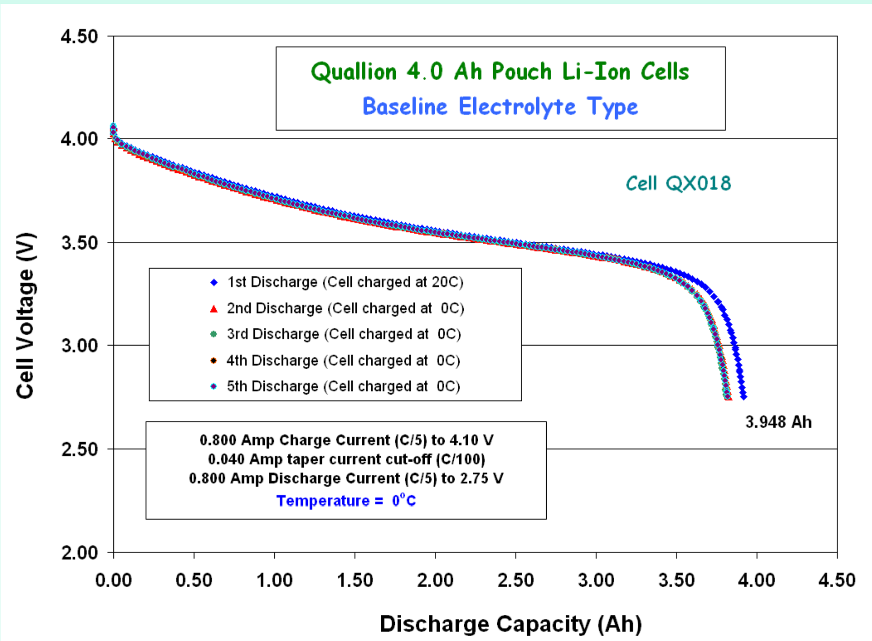


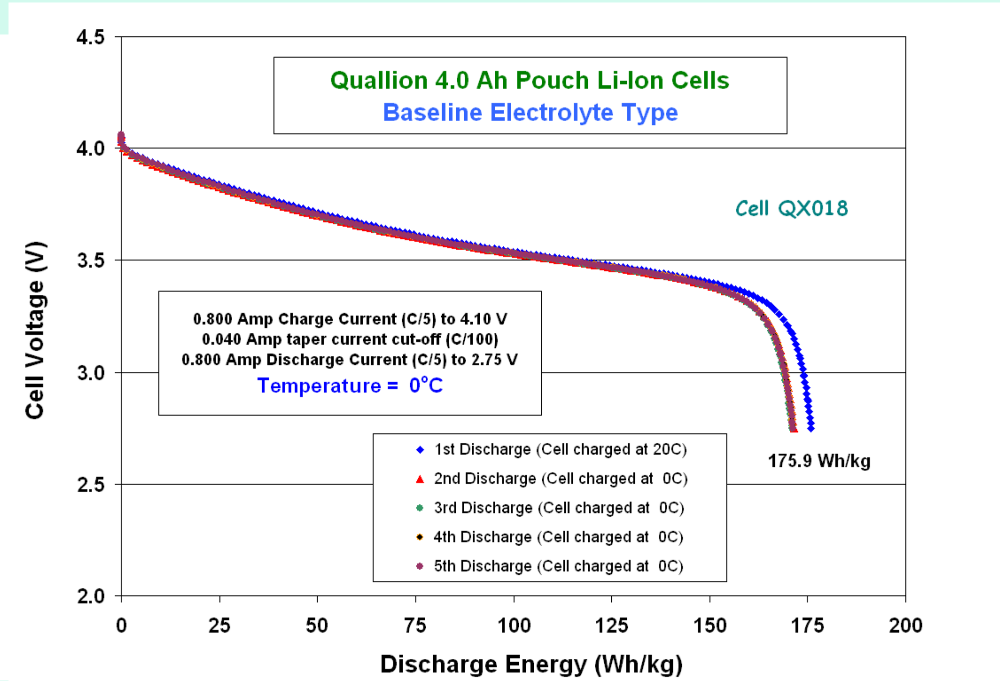


Quallion Baseline Electrolyte

Quallion 4 Ah Lithium-Ion Pouch Cells

Initial Characterization/Conditioning at 0°C

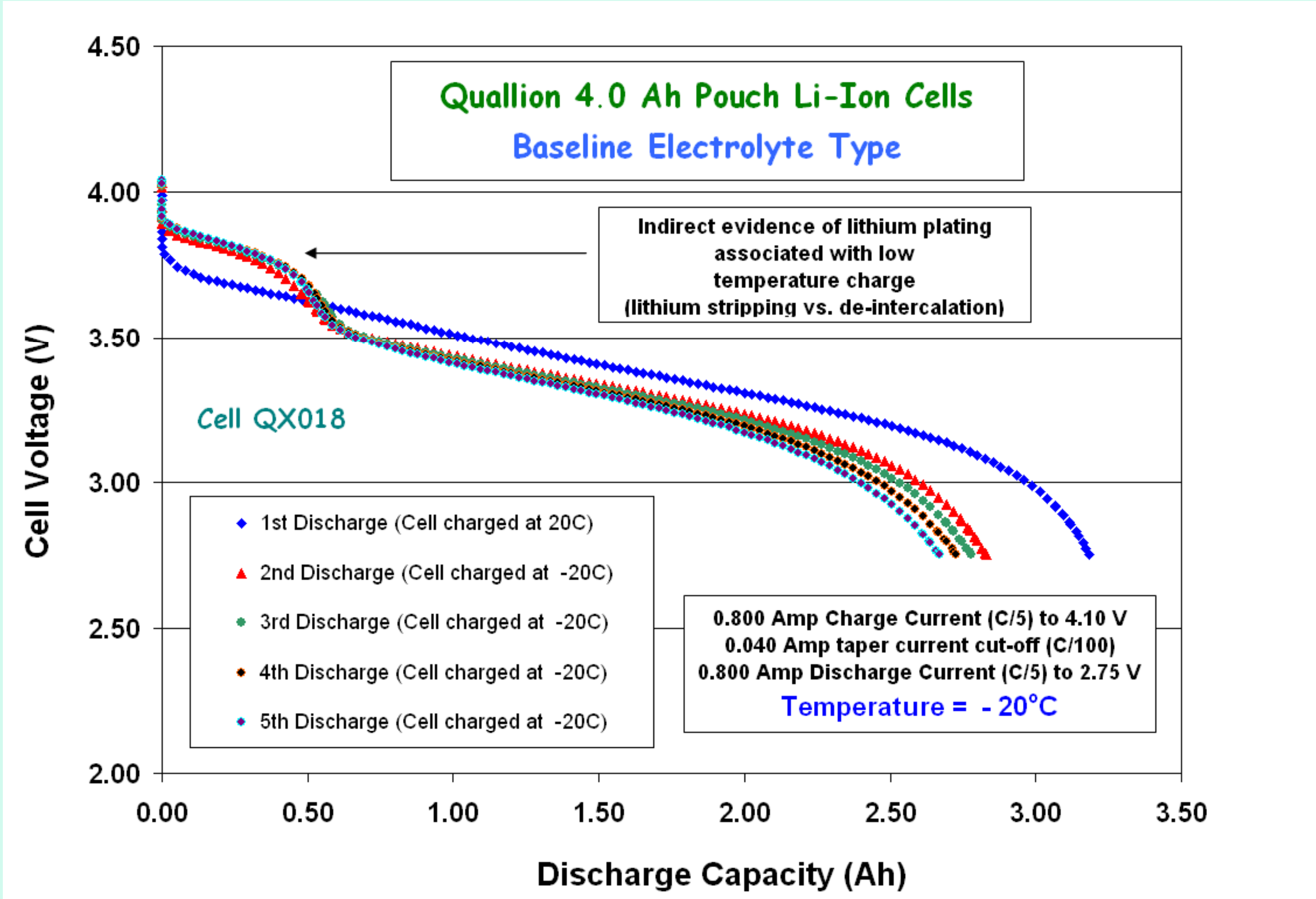




- Quallion Baseline Electrolyte

Quallion 4 Ah Lithium-Ion Pouch Cells

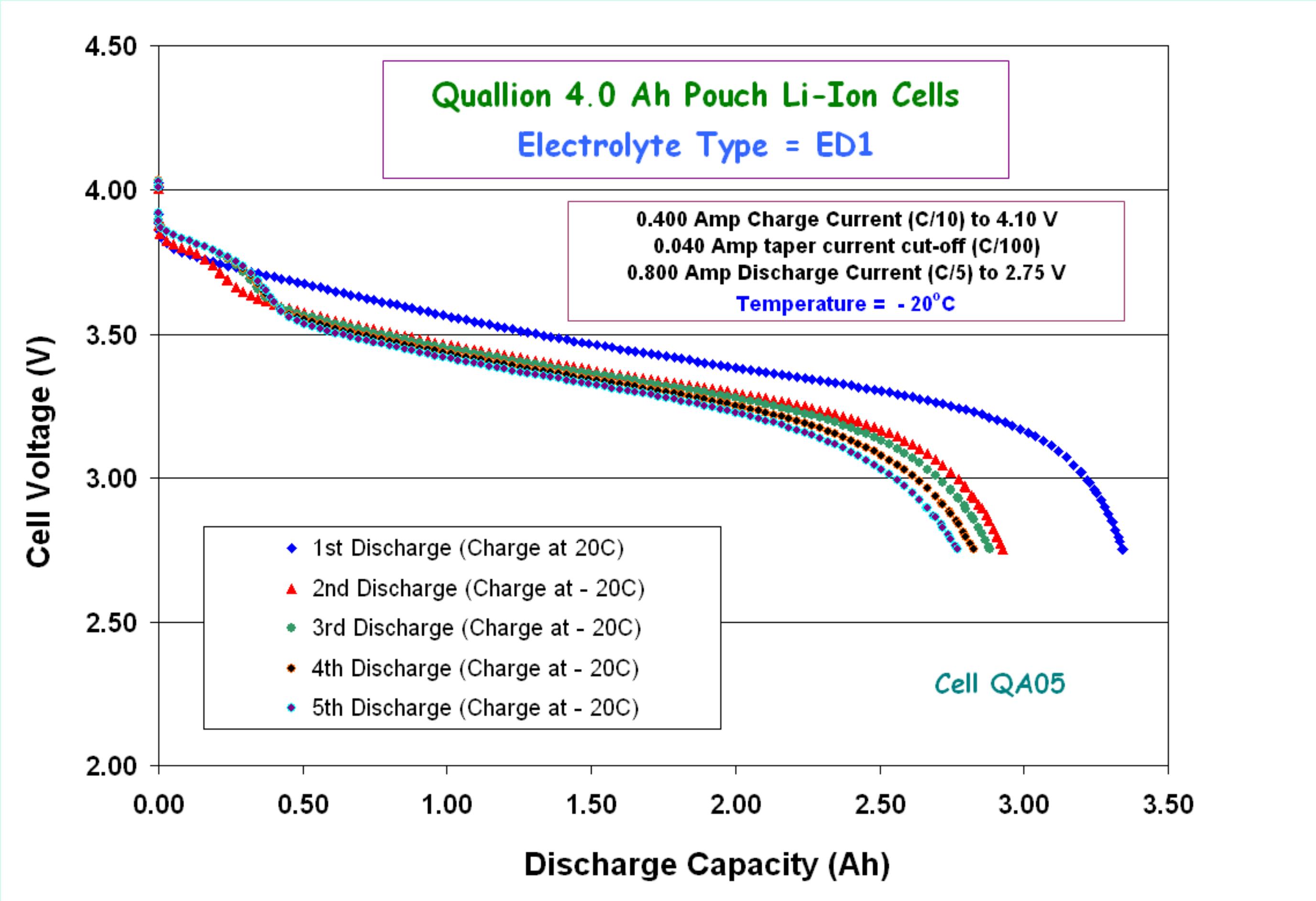
Initial Characterization/Conditioning at - 20°C



- Low temperature charging of cells observed to lead to lithium plating behavior

Quallion 4 Ah Lithium-Ion Pouch Cells

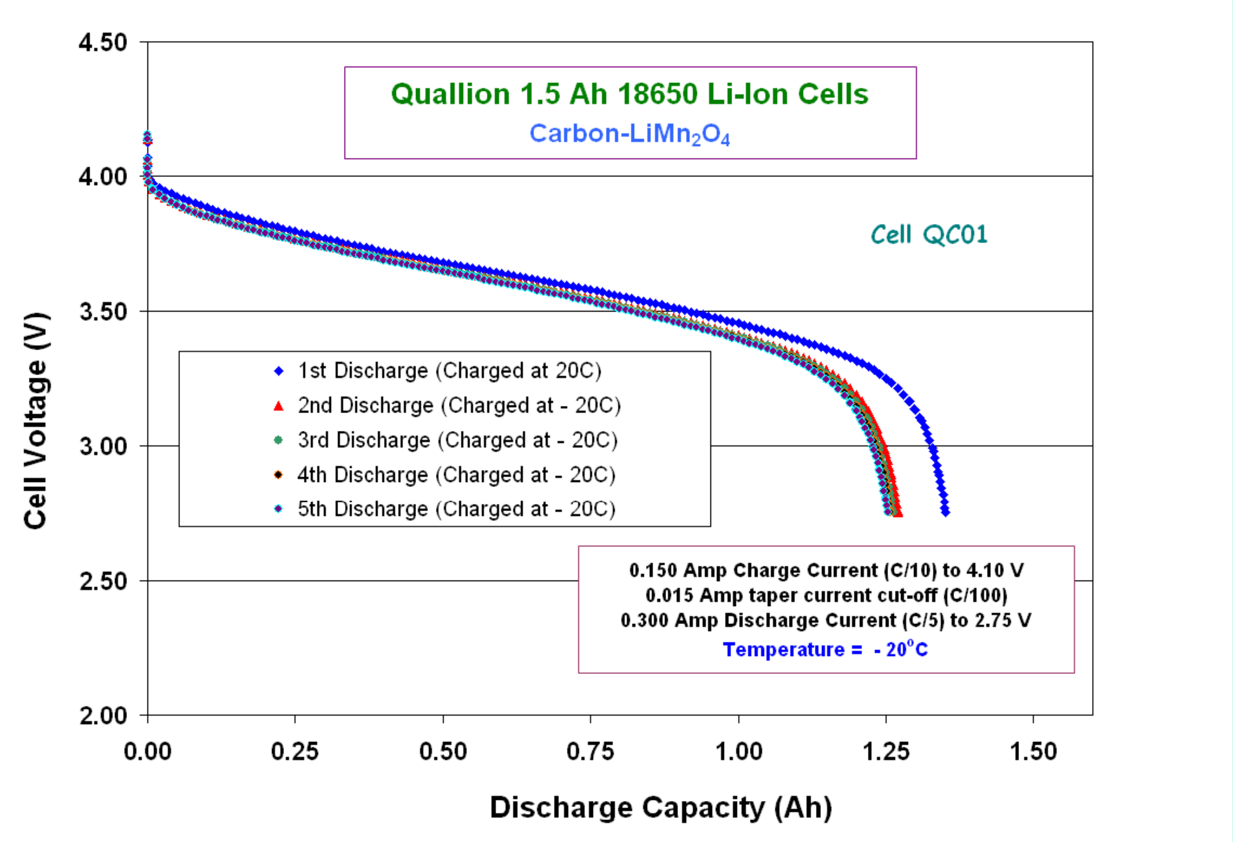
Initial Characterization/Conditioning at - 20°C



- Low temperature plating behavior also observed with different electrolyte systems suggest behavior is more strongly associated with C/A ratio in cell design

Quallion 18650 Ah High Power Lithium-Ion Cells

Initial Characterization/Conditioning at - 20°C



- Under similar cycling conditions plating behavior was not observed in high power 18650 design (different chemistry also)

A123 2.20 Ah High Power Lithium-Ion Cells

Charge Rate Characterization Testing

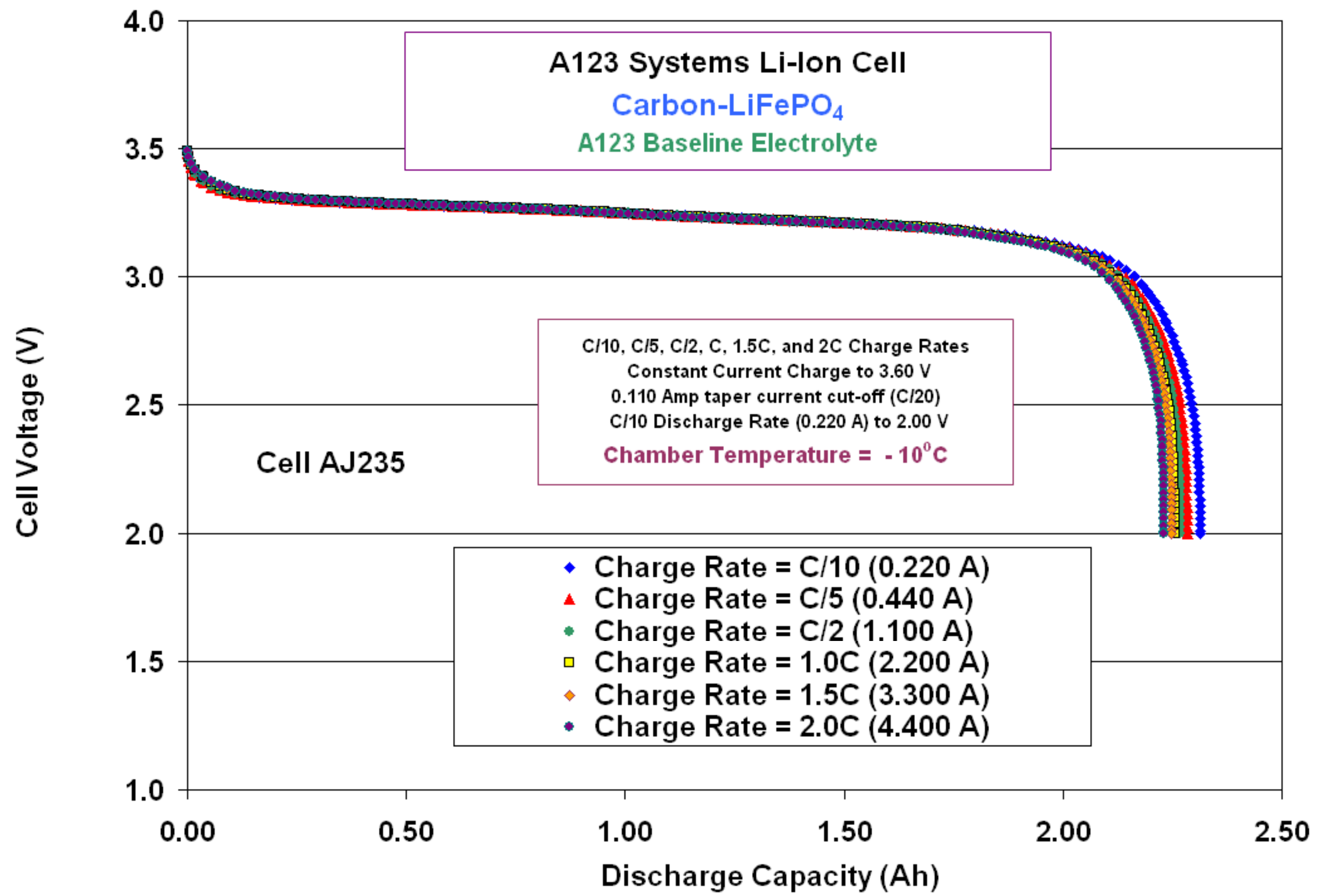
Summary of Results at - 10°C

Cell AJ 235			A123 Baseline Electrolyte						
Temperature	Discharge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-Hr (Wh)	Discharge Watt-Hr (Wh)	Watt Hour Efficiency (%)
-10°C	C/10	0.220	2.3071	10.5323	100.00	95.71	7.7373	7.4100	95.77
	C/5	0.440	2.2759	5.4073	98.65	94.42	7.7094	7.3225	94.98
	C/2	1.100	2.2609	2.5739	98.00	93.79	7.8137	7.2749	93.10
	C	2.200	2.2518	1.7134	97.60	93.42	7.9254	7.2380	91.33
	1.5C	3.300	2.2455	1.4711	97.33	93.16	7.9795	7.2131	90.40
	2C	4.400	2.2298	1.3958	96.65	92.51	7.9690	7.1615	89.87

A123 2.20 Ah High Power Lithium-Ion Cells

Charge Rate Characterization Testing at - 10°C

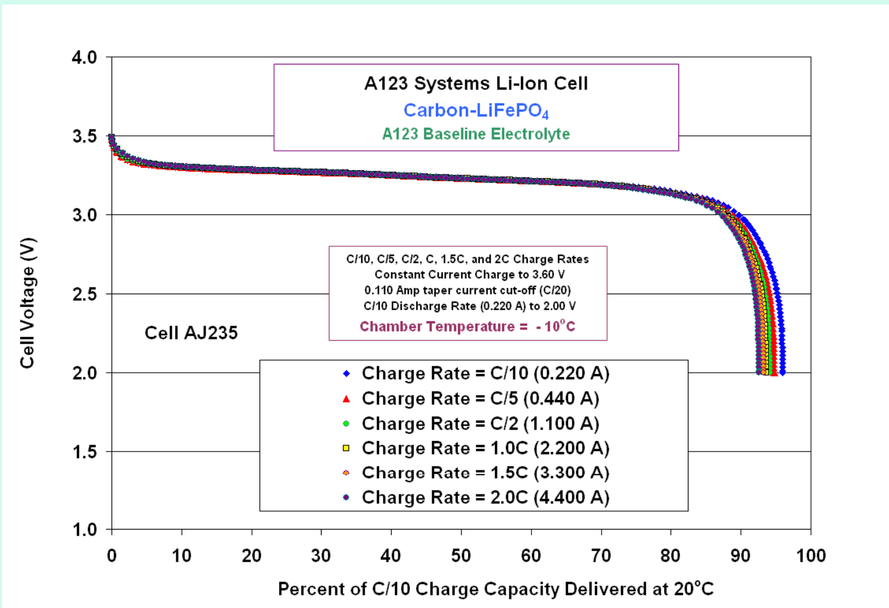
Discharge Capacity (Ah)

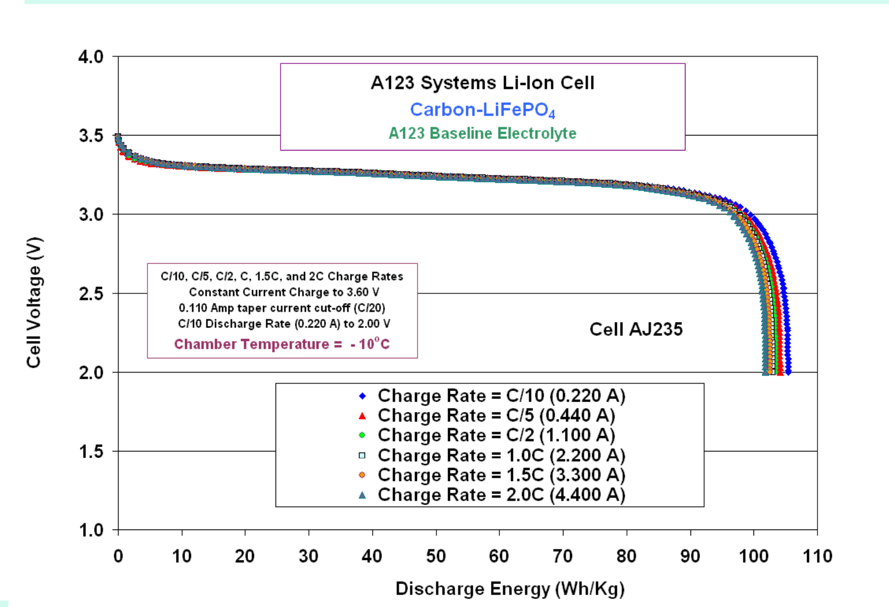


A123 2.20 Ah High Power Lithium-Ion Cells

Charge Rate Characterization Testing at - 10°C

Discharge Energy (Wh/Kg)





Yardney 7 Ah Prismatic Lithium-Ion Cells
Charge Rate Characterization Testing
Testing Overview

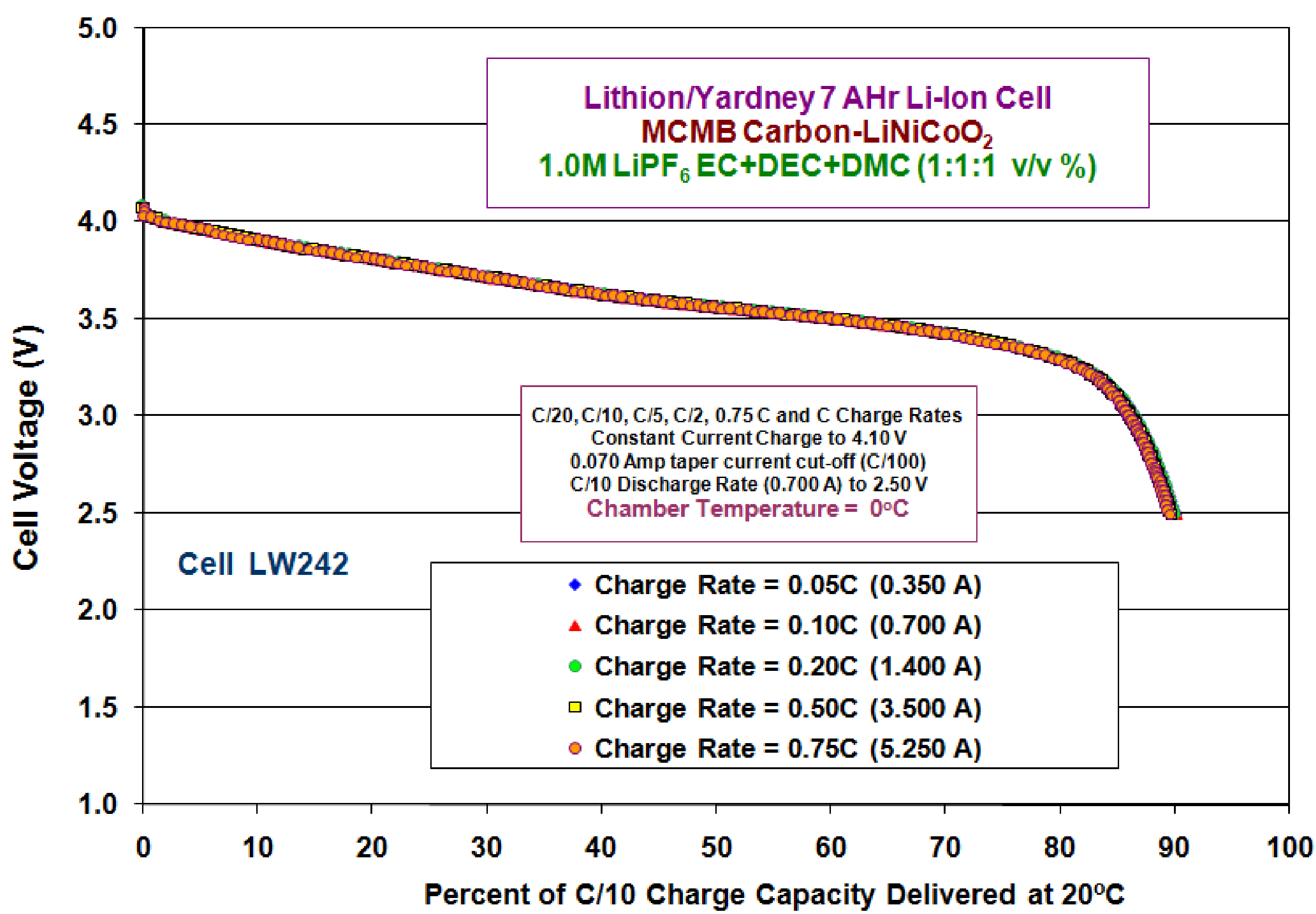
- *Charge Characterization Test Procedure (2 cells on test)*
  - Six different charge rates evaluated (C/20, C10, C/5, C/2, 0.75C and C Rates)
  - All C rates based on nameplate capacity of 7.00 Ah
  - 7 different temperatures to be evaluated (20, 0, -10, -20^o, -30^o, and -40^{o}C)
  - Charge and discharge performed at prescribed temperature
  - Two cycles performed for each rate (data plotted from second cycle)
  - Cells charged to 4.10 V (with C/100 taper current cut-off)
  - Cells discharged to 2.50V
  - Cells allowed to soak in chamber 6 hours prior to testing
  - Higher charge rates will be considered depending upon results of testing.

- Completed testing at 20, 10, 0, -10, -20, -30o and -40^{o}C

Yardney 7 Ah Prismatic Lithium-Ion Cells
Charge Rate Characterization Testing at 0°C

			Cell LW 242 1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v %)						
Temperature	Charge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-Hr (Wh)	Discharge Watt-Hr (Wh)	Watt Hour Efficiency (%)
0°C	0.05C	0.350	7.2584	21.4949	100.00	90.09	26.9728	25.9934	96.37
	0.10C	0.700	7.2665	11.5890	100.11	90.19	27.1700	26.0100	95.73
	0.20C	1.400	7.2649	6.8085	100.09	90.17	27.4519	25.9692	94.60
	0.50C	3.500	7.2390	4.2259	99.73	89.85	28.0234	25.8735	92.33
	0.75C	5.250	7.2338	3.8083	99.66	89.78	28.4049	25.8399	90.97
	1.00C	7.000	7.2195	3.6276	99.46	89.61	28.6730		

Yardney 7 Ah Prismatic Lithium-Ion Cells
Charge Rate Characterization Testing at 0°C

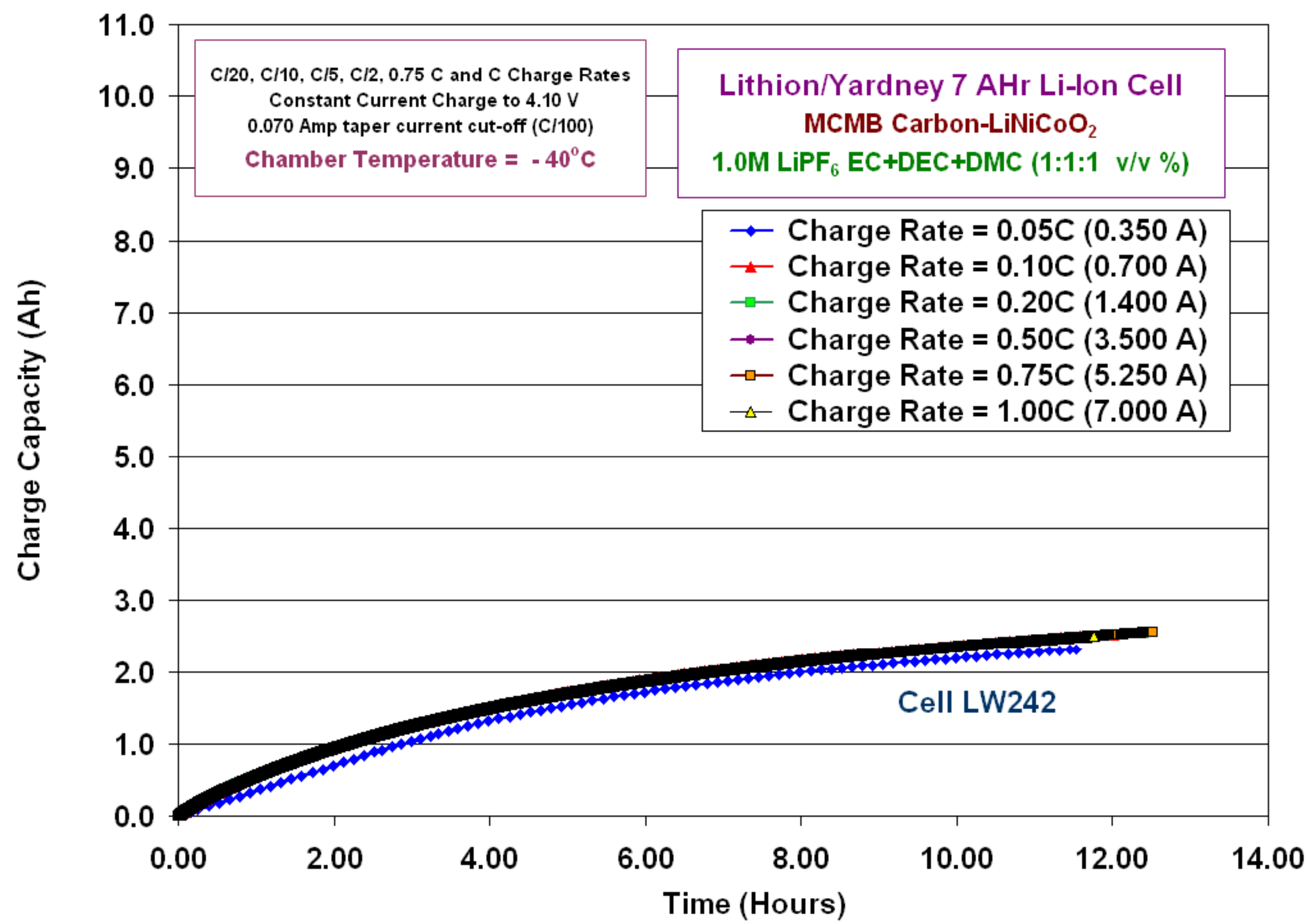


Yardney 7 Ah Prismatic Lithium-Ion Cells

Charge Rate Characterization Testing at -40°C

			Cell LW 242 1.0 M $LiPF_6$ EC+DEC+DMC (1:1:1 v/v %)						
Temperature	Charge Rate	Discharge Current (A)	Charge Capacity (Ah)	Charge Time (Hours)	Percent C/10 Capacity	Percent C/10 Capacity at 20°C	Charge Watt-Hr (Wh)	Discharge Watt-Hr (Wh)	Watt Hour Efficiency (%)
- 40°C	0.05C	0.350	2.3155	11.5376	100.00	28.74	9.4238	7.4320	78.86
	0.10C	0.700	2.5426	12.1132	109.80	31.56	10.4195	7.4810	71.80
	0.20C	1.400	2.5536	12.4072	110.28	31.70	10.4692	7.4183	70.86
	0.50C	3.500	2.5583	12.4359	110.48	31.75	10.4887	7.4318	70.86
	0.75C	5.250	2.5640	12.5156	110.73	31.82	10.5120	7.4359	70.74
	1.00C	7.000	2.5637	12.5045	110.72	31.82	10.5108	7.4364	70.75

Yardney 7 Ah Prismatic Lithium-Ion Cells
Charge Rate Characterization Testing at -40°C



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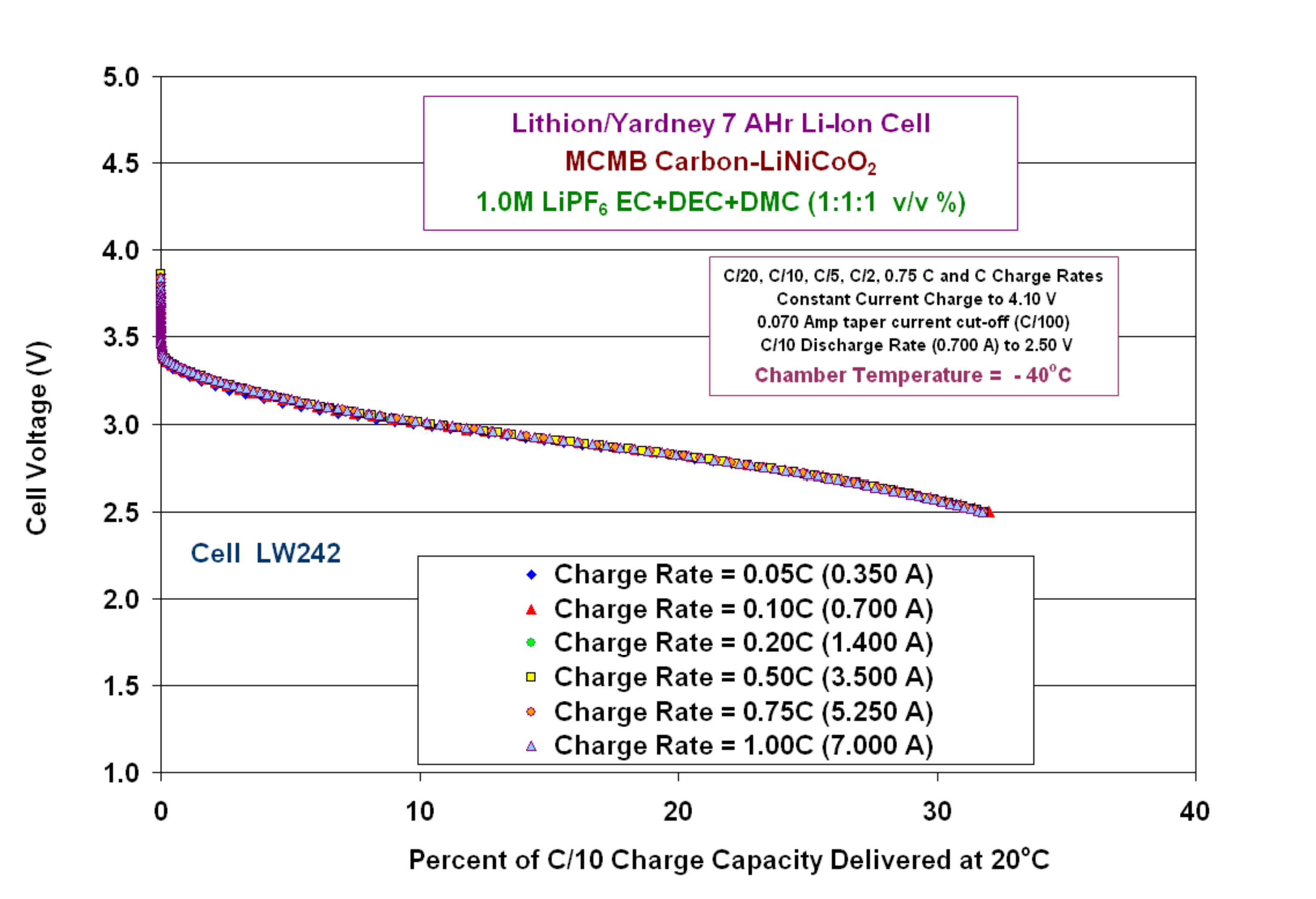
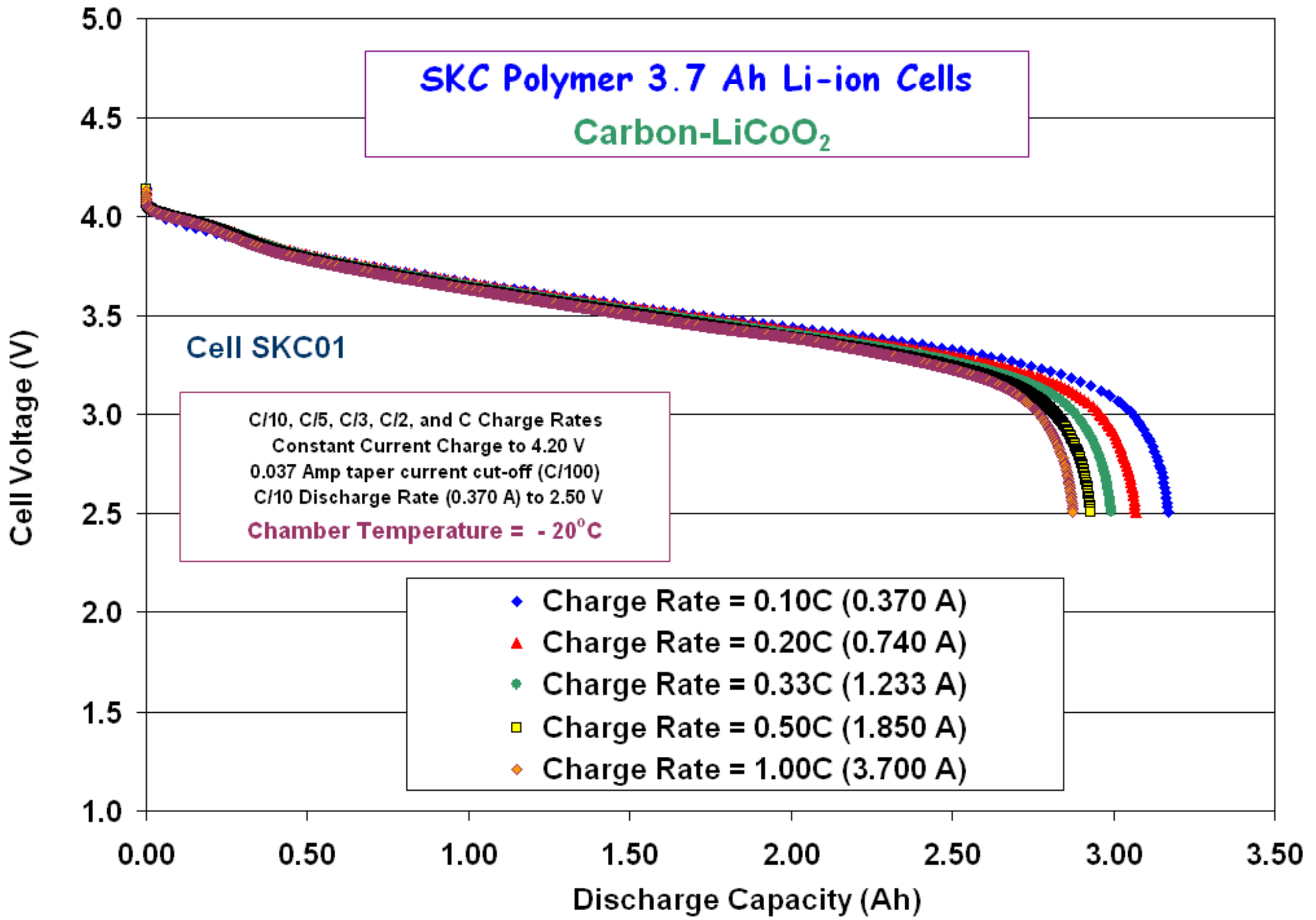


SKC Polymer 3.7 Ah Lithium-Ion Cells

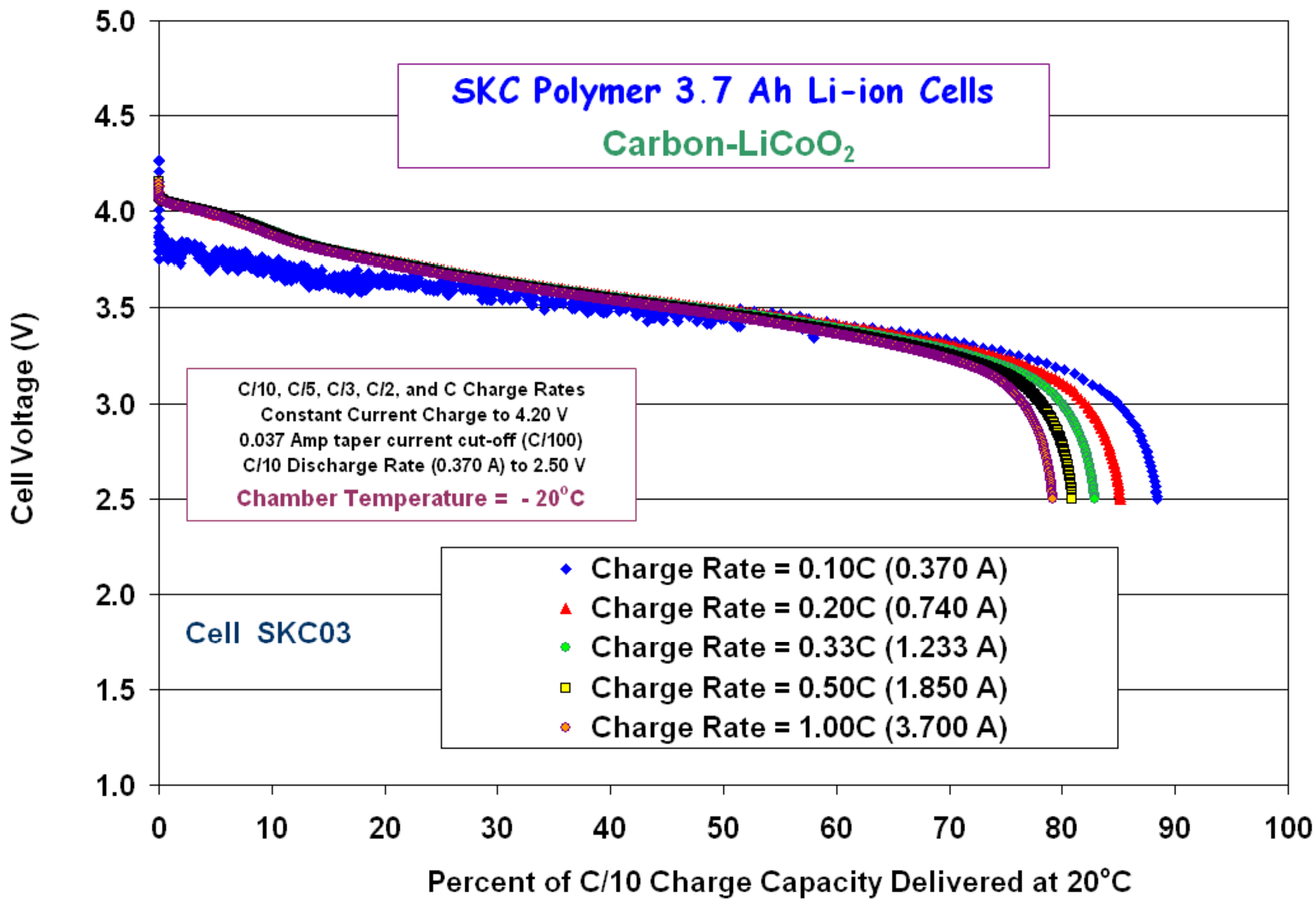
Charge Rate Characterization Testing at - 20°C



- *Some possibility that limited lithium plating is occurring on charge*

SKC Polymer 3.7 Ah Lithium-Ion Cells

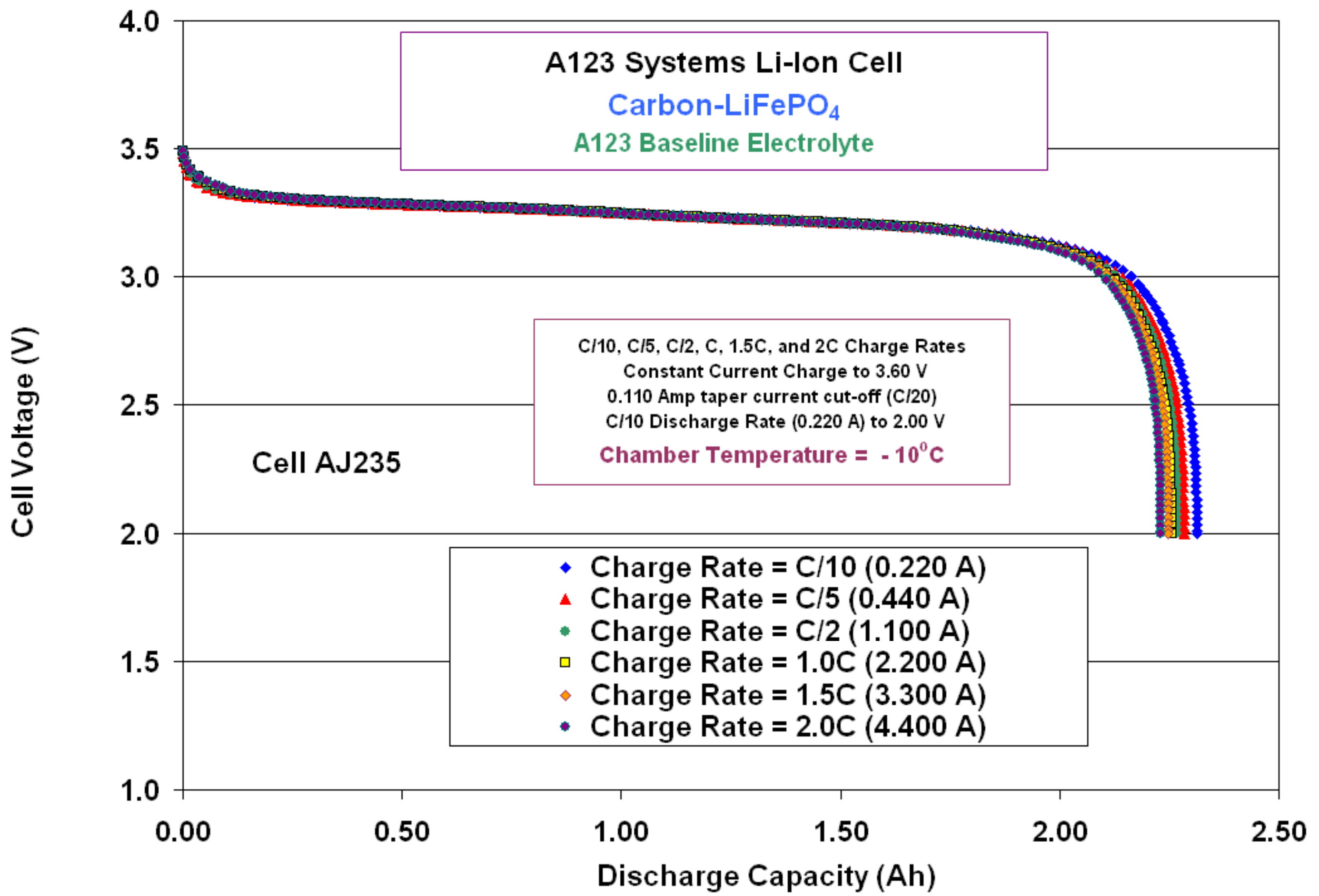
Charge Rate Characterization Testing at - 20°C



A123 2.20 Ah High Power Lithium-Ion Cells

Charge Rate Characterization Testing at - 10°C

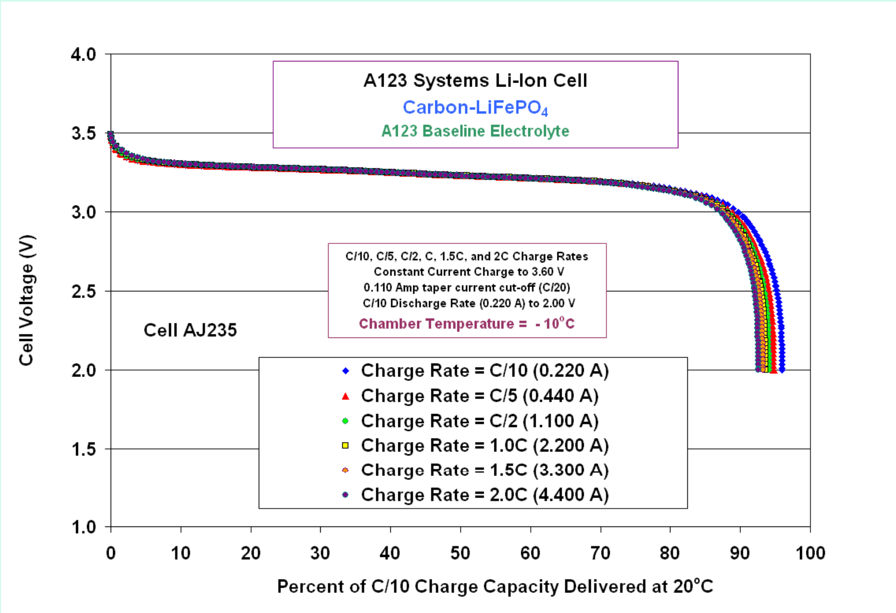
Discharge Capacity (Ah)

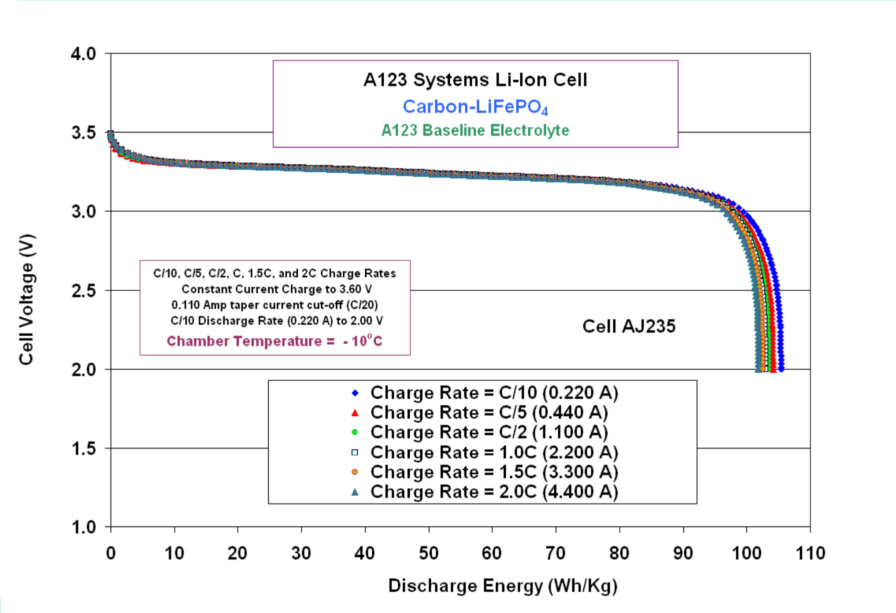


A123 2.20 Ah High Power Lithium-Ion Cells

Charge Rate Characterization Testing at - 10°C

Discharge Energy (Wh/Kg)





Summary

- We have started examining Quallion standard cells, Quallion pouch cells (with low temperature electrolytes), SKC cells, Yardney and SAFT cells, A123 COTS cells and A123 cells with low temperature electrolytes.
- Li plating has been observed in some of the cells.
- Three-electrode cells are also being fabricated and tested for more fundamental understanding of this problem.

Acknowledgments

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