Ni-Cd Battery Separator Improvement

Based upon Mr. Paul Scardaville's research and Crane testing

DSCR and NAVAIR Sponsored program to develop a Ni-Cd battery separator system that will increase battery safety and life to highest levels

Ni-Cd Battery Separator Improvement

2009 Joint Service Power Expo

New Orleans, LA

6 May 2009

OUTLINE

- **Background: Problems that prompted program**
- **Tests:**
  - **Gurley airflow (time to pass air volume)**
  - **Rewet-ability in KOH (soak15%, rewet 30%)**
  - **Temperature-Rise & Float Charge (TR&F)**
- **Comparisons: Results of TR&F**
  - **Wetting agents**
  - **Absorbers**
  - **Gas barriers**

Background

- **Production Battery Performance began to decrement**
  - **Celgard increased average porosity of gas barrier by tightening tolerance toward high porosity limit**
  - **Kimberly-Clark (KC) dropped melt-blown polypropylene (mbPP) absorbers.***
  - **As manufacturers reached end of their KC supply, battery performance decrement accelerated.**

(Reason: "Wayfos A" no longer available)

High/Low Gurley Testing (2004)
Type M81757/16, KC mbPP Absorber

- **Celgard gas barriers with Celgard standard wetting agent**
  - **One with 37 Gurley-second (G-s) porosity**
  - **One with Celgard 3400 (24 G-s)**
- **Both performed essentially same in TRF & Life Cycling.**
- **No difference in post life capacities**

Sulfur Contamination

Sulfur in electrolyte was believed to cause a permanent decrement in capacity.

Source of the sulfur was determined to be from water-soluble dispersants that were used to apply the wetting agent to the mbPP absorber.

Surfactants Suspected

- **Dissections exhibited separator dryout and poor rewet ability in production batteries made after the 1980's**
- **Investigated why wetting agent appeared to leaving gas barrier**
- **Determined Celgard Inc was applying a wetting agent that was fugitive**

Surfactant Comparisons

- Performed a wetting agent rewet-ability using membrane with Celgard's & 2 candidate W.A.s* from Mr. Paul Scardaville's search
- Test: Samples soaked in 15% KOH solution, air dried and returned to 30% solution for rewet.
- Results of soak durations to 12 months
  - A) Celgard 3400: Lost rewet ability in 1 day
  - B) Surfonic L24-4 (alcohol/ether): Rewet
  - C) Deforest HP-739* (anionic ester): Rewet

*HP-739 is a clone of 1970- 2000 Wayfos A & has same CAS #

Baseline Testing

Type M81757/16 batteries with Celgard 37 G-s porosity gas barrier

Separators:

- #1: Manufacturer's absorber & gas barrier with fugitive wetting agent (N3400G1-P)
- #2: Grafted H&V MBPP and N3400G1-P
- #3: Grafted H&V MBPP and nonsoluble wetting agent on gas barrier, DePHOS HP 739 (CAS # 12645-31-7)

Baseline Conclusions

- **Porosity in 20-40 G-s range has large impact on charge stability***
- **Wetting agents**
  - **Nonionic (Huntsman) was unusable**
  - **Fugitive afforded no safety***
  - **Dispersant residues were generally harmful**
- **Coated & grafted absorbers have same performance**

***Influenced by wetting agent transfer**

TR&F Cycling Test

Type M81757 35Ah Batteries

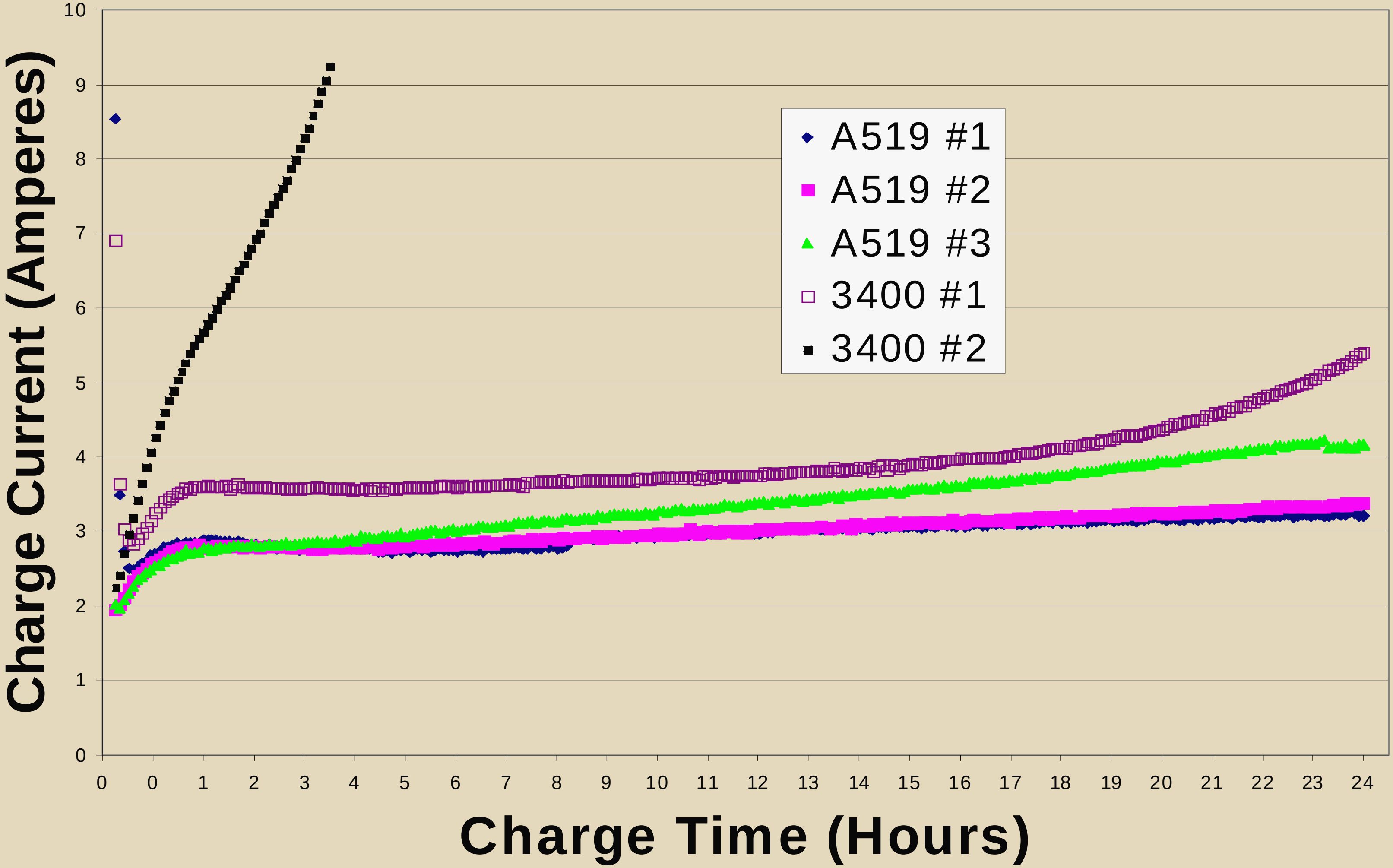
- **Initial charge: 2-Step CC with water addition**
- **TRF cycles:**
  - **Stabilize battery in Chamber @ 120ºF**
  - **315A discharge to 14.4V or 5 minutes**
  - **24-hour CP @ 28.5V**
  - **Repeat -315A and CP charges (M–F)**
  - **Sat AM: Rest open circuit and return to amb.**
  - **Sun PM: Repeat sequence above**
  - **Water additions: As needed**

Effects of Gas Barrier Porosity and Applied W.A. on Safety

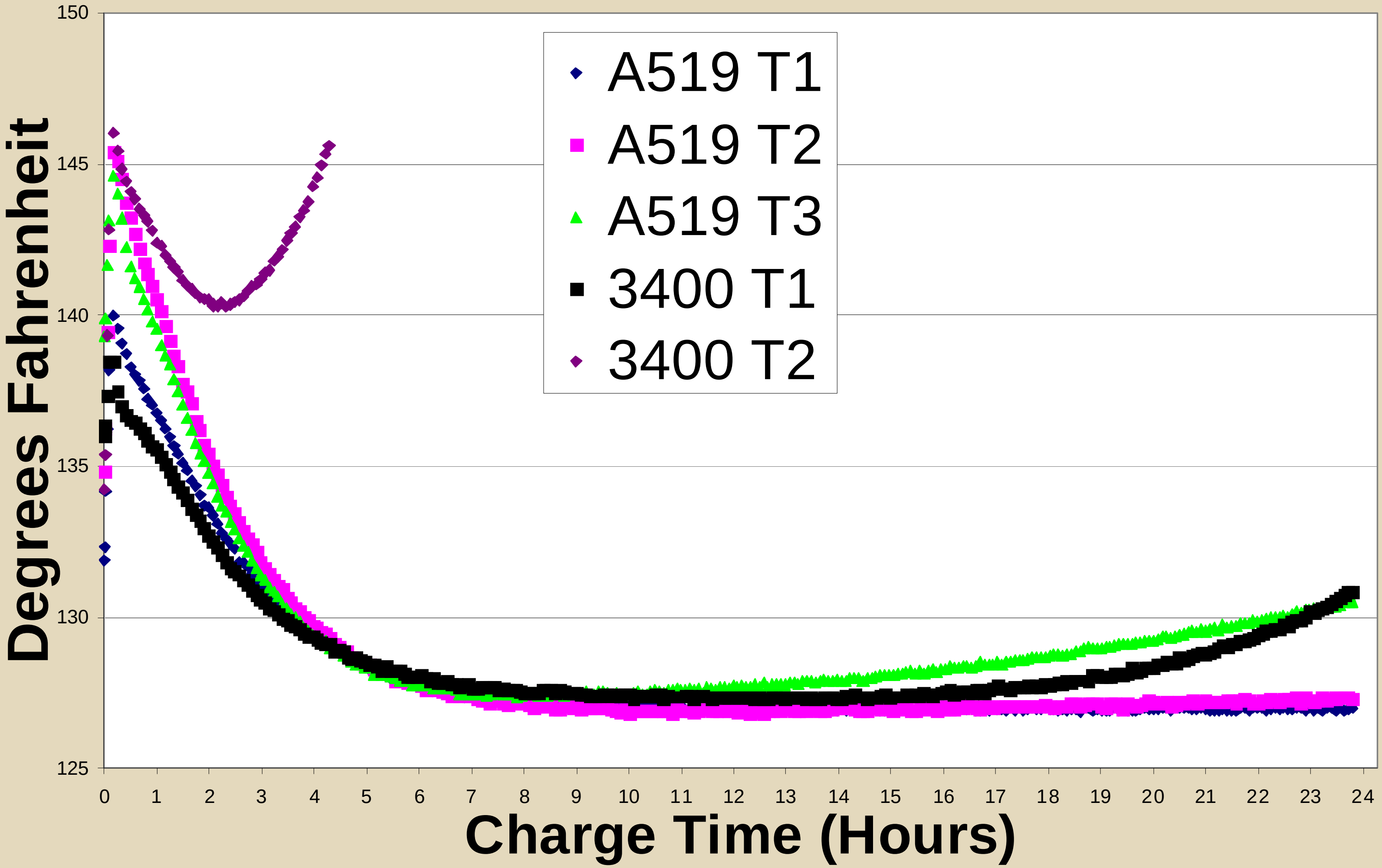
- **35Ah Batteries using Woven Nylon absorber and different gas barriers**
  - **3400: 24G-s porosity and fugitive wetting agent**
  - **A519: 37G-s porosity & insoluble wetting agent DePHOS HP 739**

    (CAS # 12645-31-7)

Charge Current TR&F Cycling
W.N. & A519 VS. W.N. & 3400



Battery Temperature TR&F Cycling
W. N. & A519 VS. W. N. & 3400



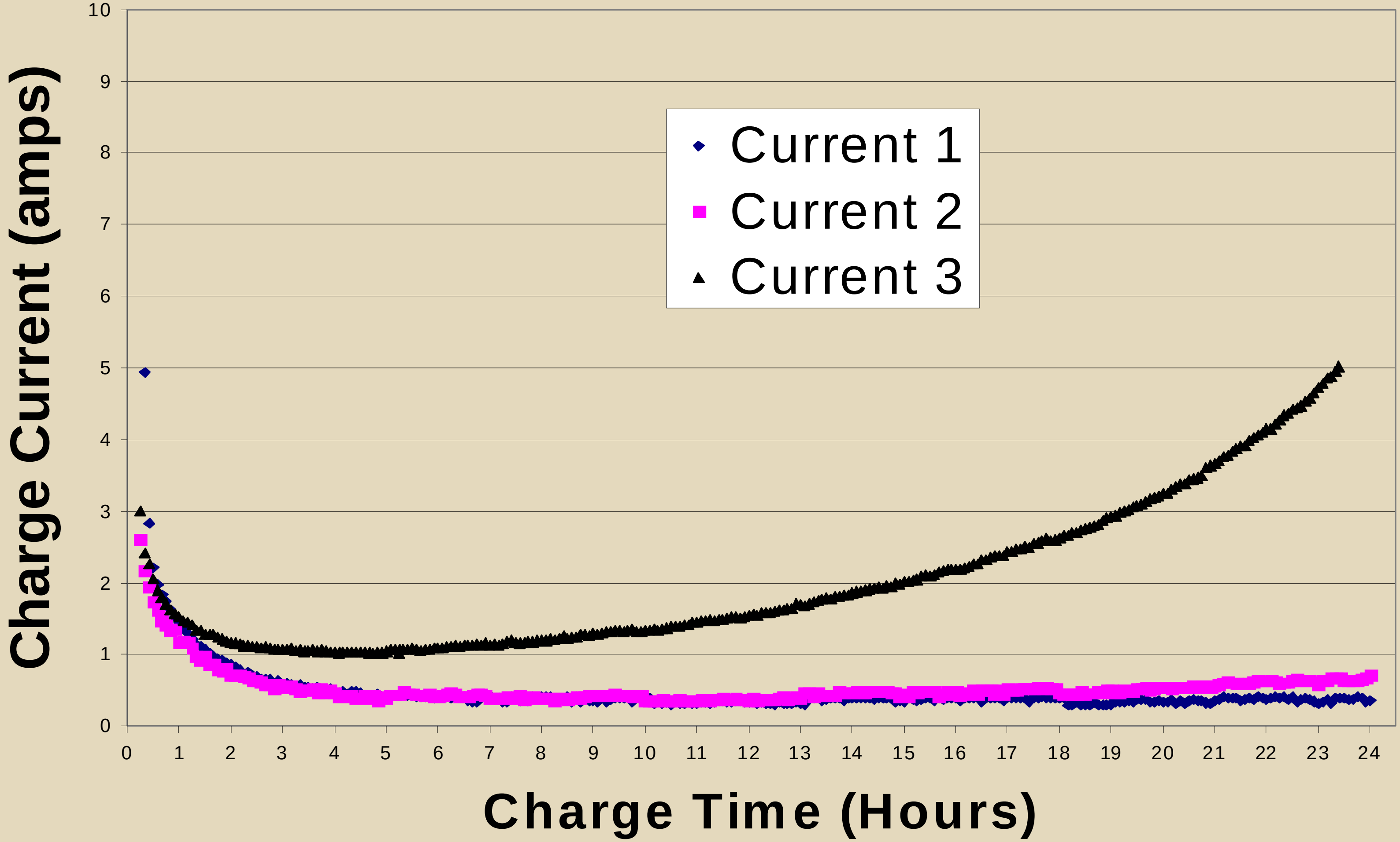
Wetting Agent Mobility
Effect on gas barrier performance

- **Gas barrier (N3400G1-P)**
  - **Porosity: 37G-s**
  - **Wetting agent: Fugitive - Celgard proprietary**

- **Absorbers**
  - **Grafted mbPP**
  - **Coated mbPP (CAS # 12645-31-7)**

TR&F Charge Current (PL)

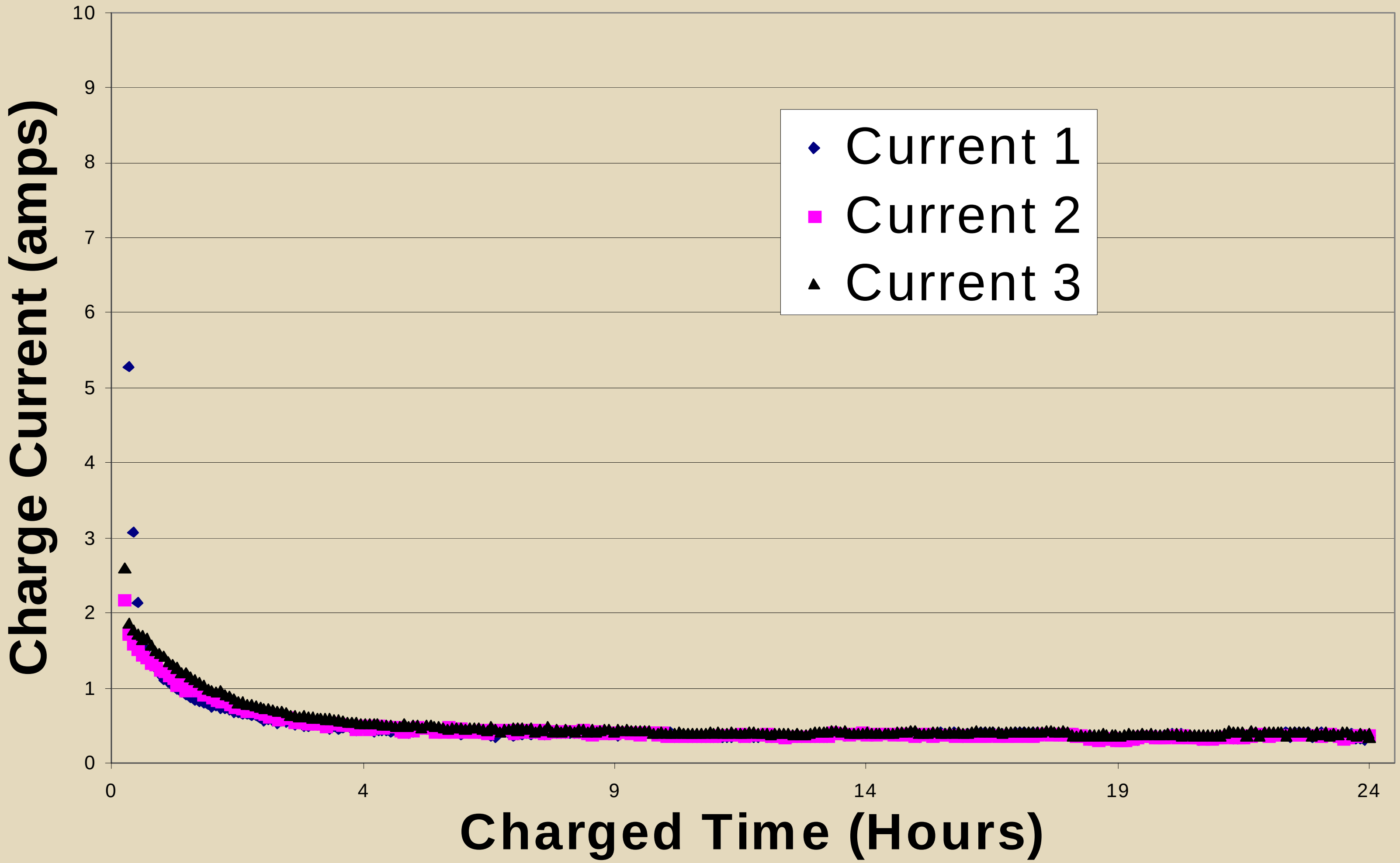
Grafted Absorber, N3400G1-P



Distribution Statement A: Approved for Public Release; Unlimited Distribution

TR&F Charge Current (PL)

Coated Absorber, N3400G1-P



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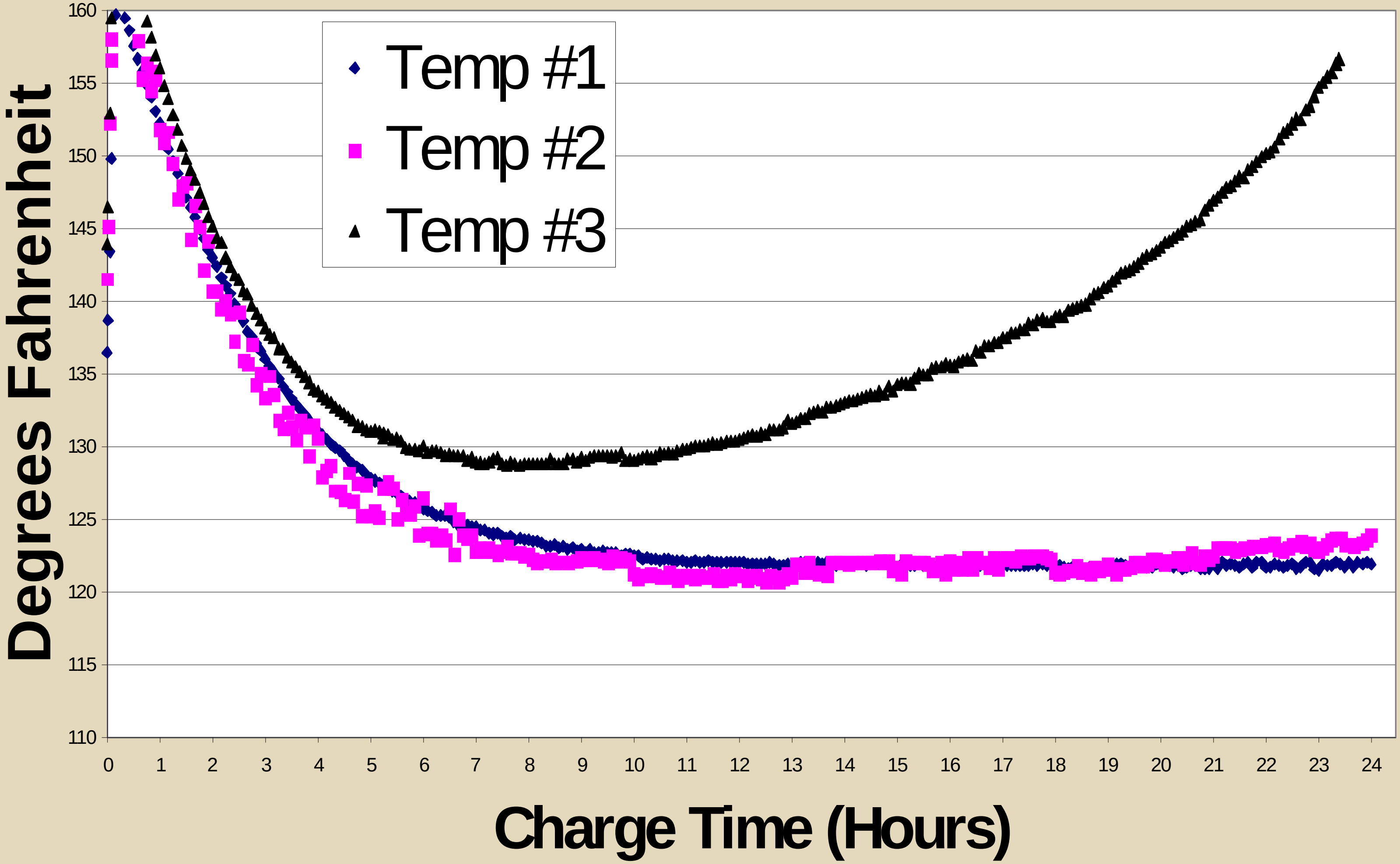
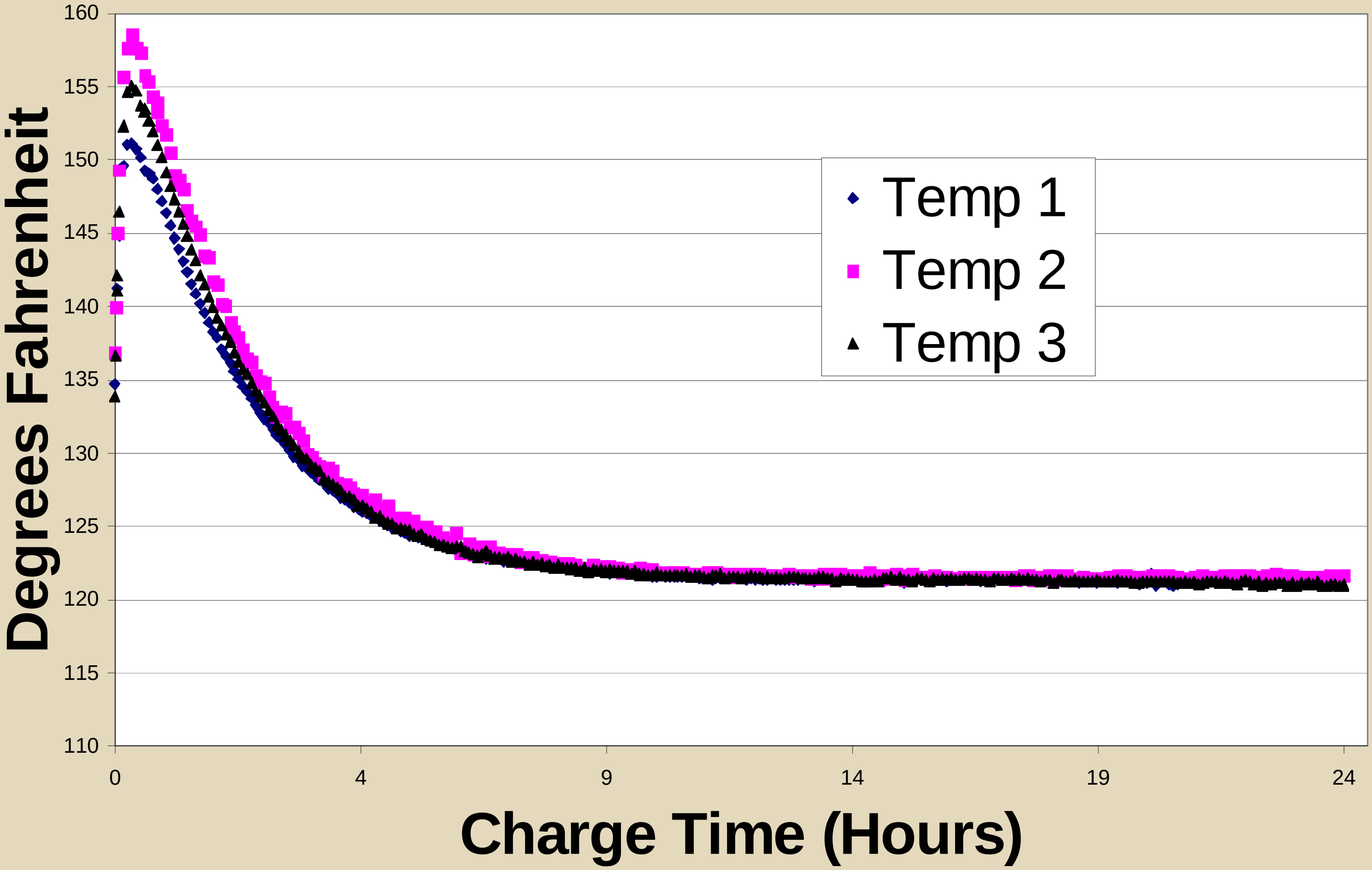
TR&F Charge Temperature (PL)

Grafted Absorber, N3400G1-P



TR&F Charge Temperature (PL)
Coated Absorber, N3400G1-P



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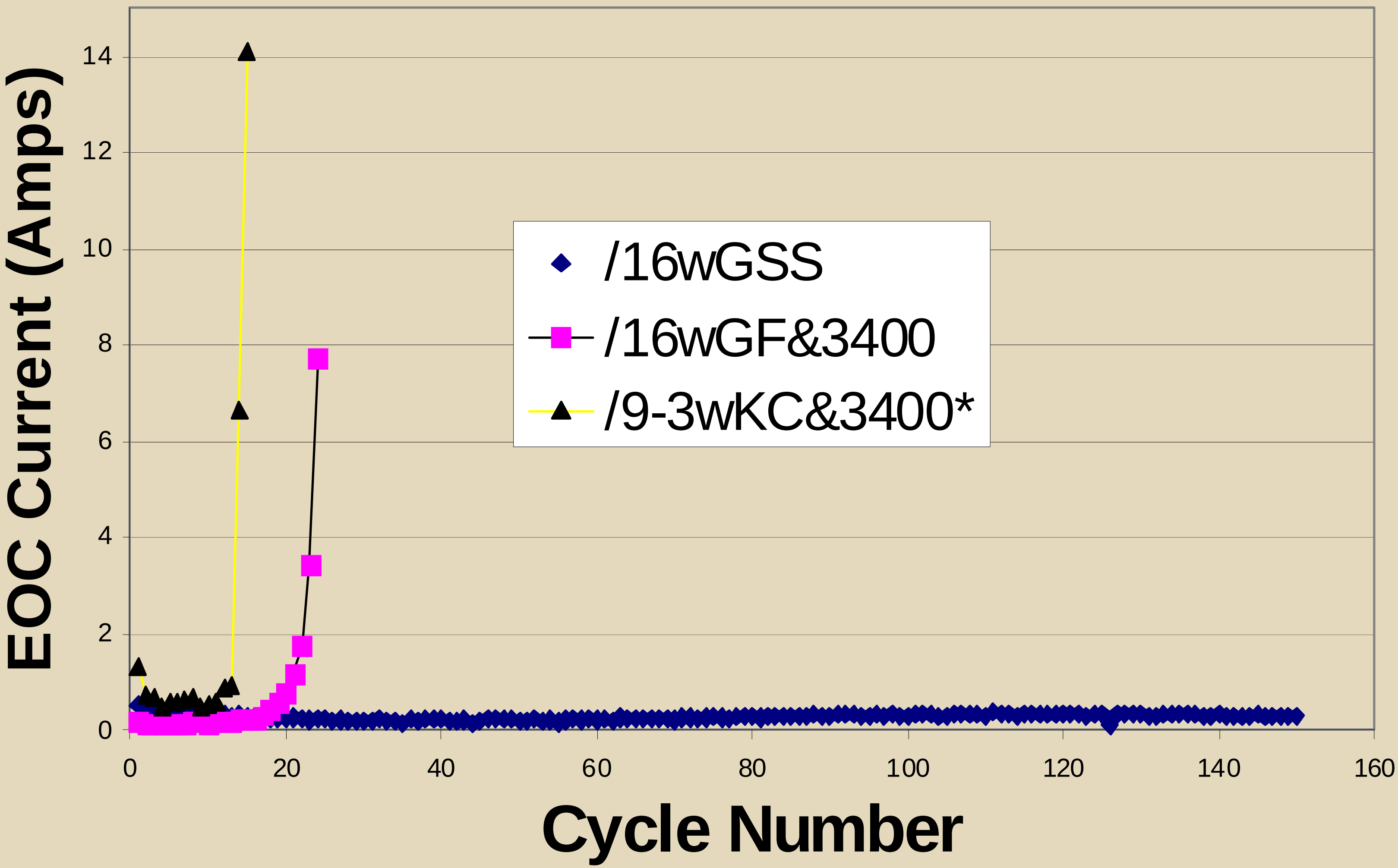
TR&F Conclusions

- **Gas barrier porosity does not control charge stability if wetting agent is absent.**
- **Anionic wetting agent (CAS 12645-31-7) on absorber “caused" charge stability. It appears W.A. can transfer from absorber to the gas barrier.**
- **The wetting agent in the pores IS the gas barrier.**

How Good is Good?

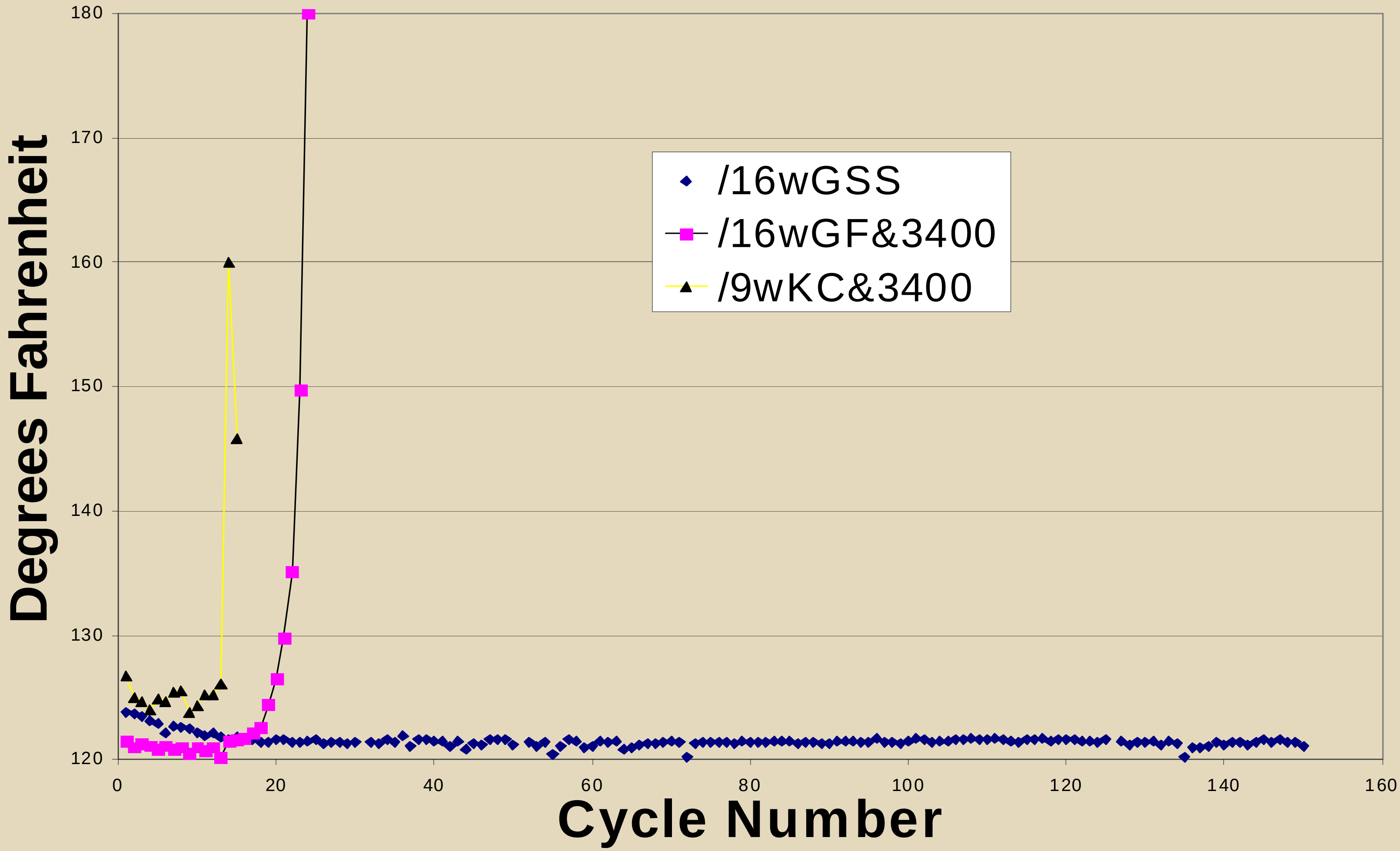
- **Type M81757/16 battery with GSS was subjected to continuous TR&F cycling**
- **Results:**
  - **Battery's charge stability remained completely stable throughout test.**
  - **Testing was terminated after 226 days on test and completing 150 TR&F cycles**

TR&F Cycling Comparisons
EOC Currents

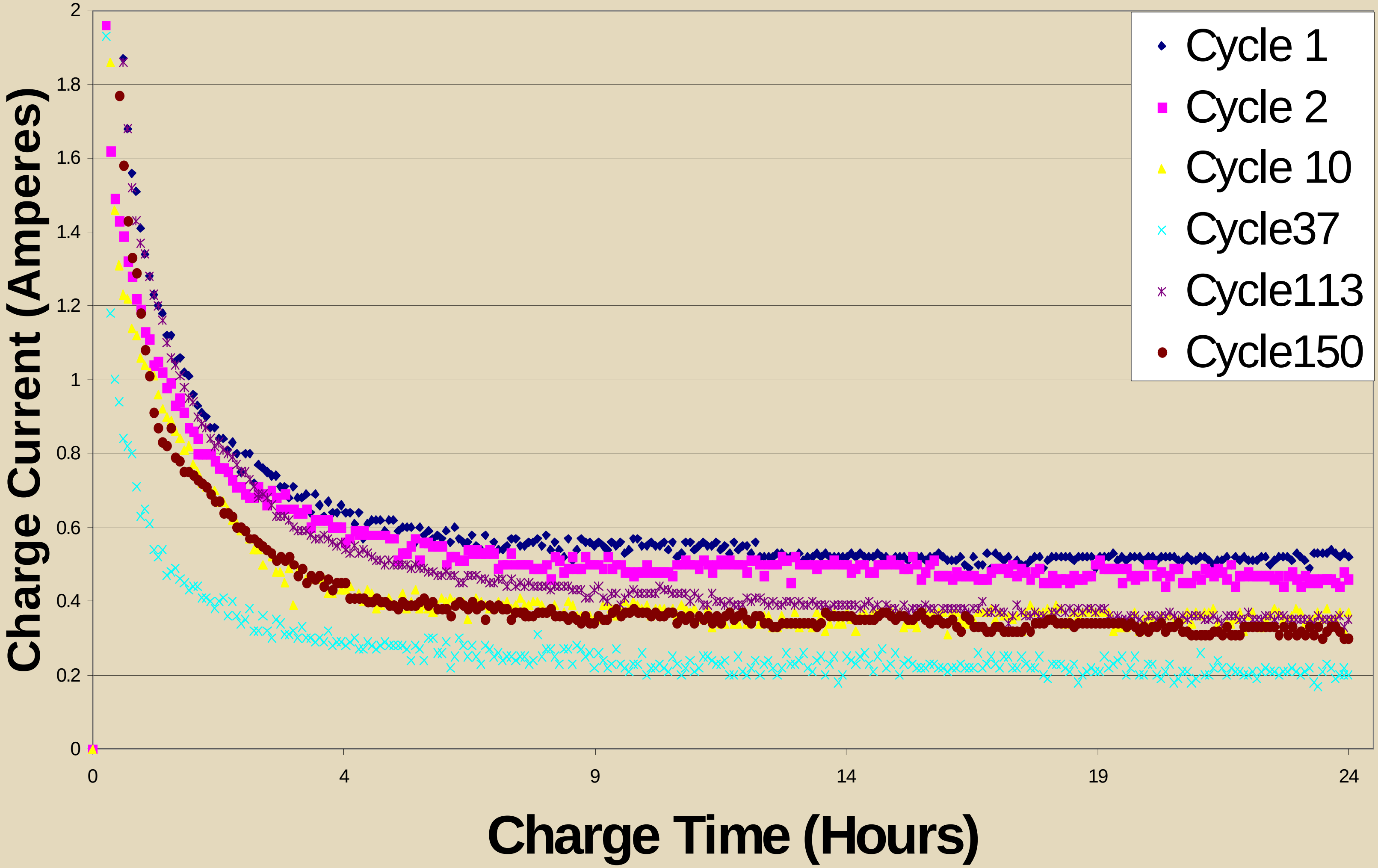


TR&F Cycling Comparisons

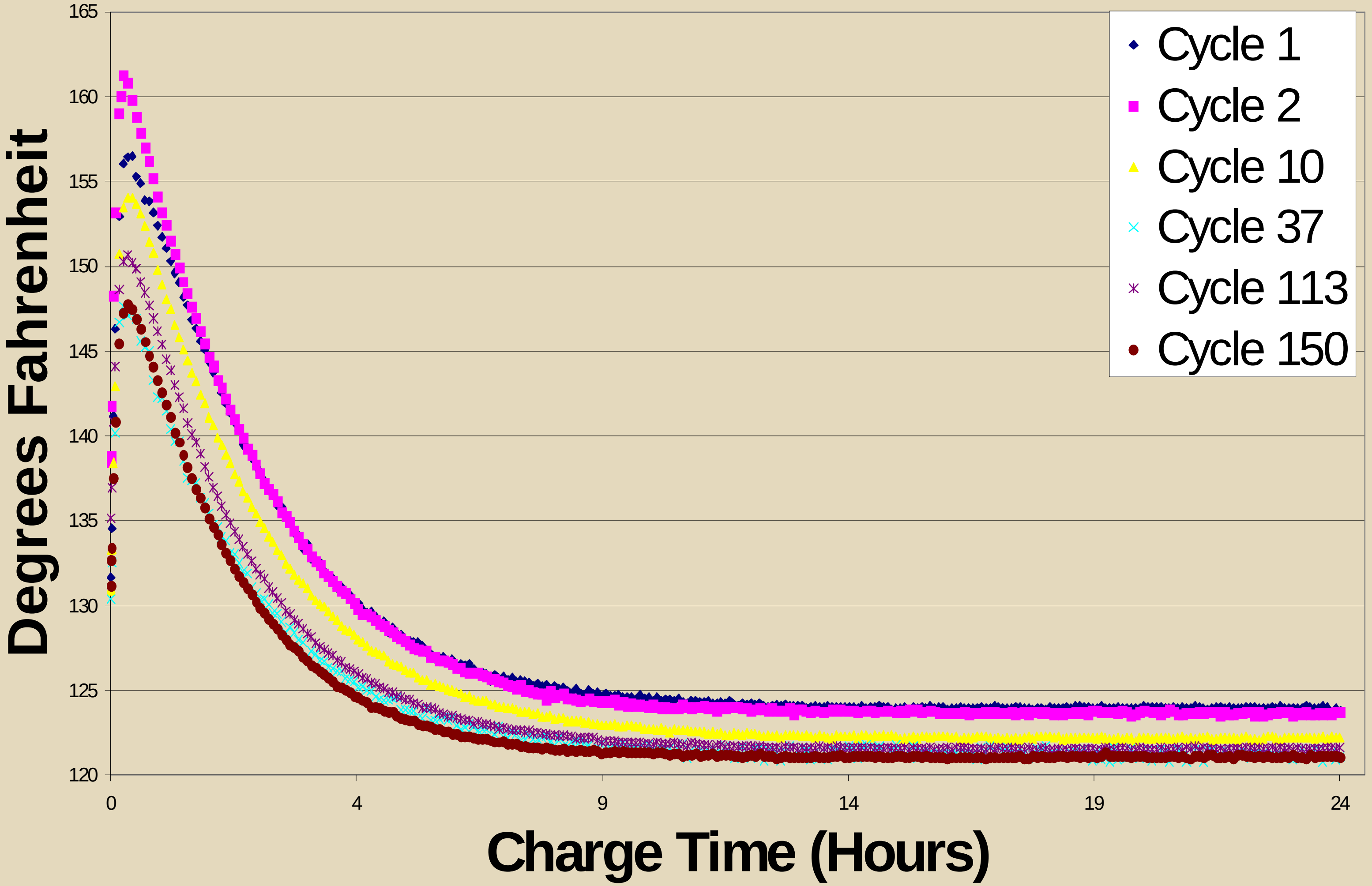
EOC Battery Temperatures



Charge Current
Individual TR&F Cycles



Battery Temperature Individual TR&F Cycles



Specifying a Separator System

- **Wetting agent**
  - **Anionic**
  - **Unaffected by charge V using special test cell**
  - **Insoluble in electrolyte**
  - **Dispersant must leave no residue that can disperse into electrolyte**

Specifying a Separator System

- **Gas Barrier**
  - **Polyolefin membrane**
  - **Thickness: 1mil ± 0.1 mil**
  - **Maximum Resistance: 18-milliohm-sq. inch**
  - **Porosity (35 to 40 G-s)**
    - **High enough for low resistance**
    - **Low enough to keep wetting agent in pores.**

Specifying a Separator System

Absorber:

- Hydrophilic (W.A. coated preferred)
- Highly absorbent
- High tortuosity for better protection (mbPP)
- Weight: Governed by performance

Any Questions?

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TR&F Cycle Data by Days
on Test GSS: A519 & TRC0950KG