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VG09-244

Improved Cathode Material Safety via a Metal Phosphate Coating

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Prepared for
NASA Aerospace Battery Workshop 2009
Huntsville, AL

November 18, 2009

Outline

- **Overview**
- Coating of $LiCoO_2$ Material
- Coating of Mixed Metal Oxide Cathode Materials
- Summary/Acknowledgments

Physical Sciences Inc. - Who we are

Physical Sciences Inc.

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- **A technologically diverse 35 year-old company, primarily performing contract R&D, with FY ’08 revenues of $40M**
- **Headquartered in Andover, MA, with a staff of 190 talented scientists, engineers and administrative personnel, including an Energy Technologies Group with a staff of 5**
- **Three wholly-owned subsidiaries, Q-Peak, Research Support Instruments and Faraday Technologies, with complementary capabilities**
- **Employee-owned through an Employee Stock Ownership Trust**

Motivation

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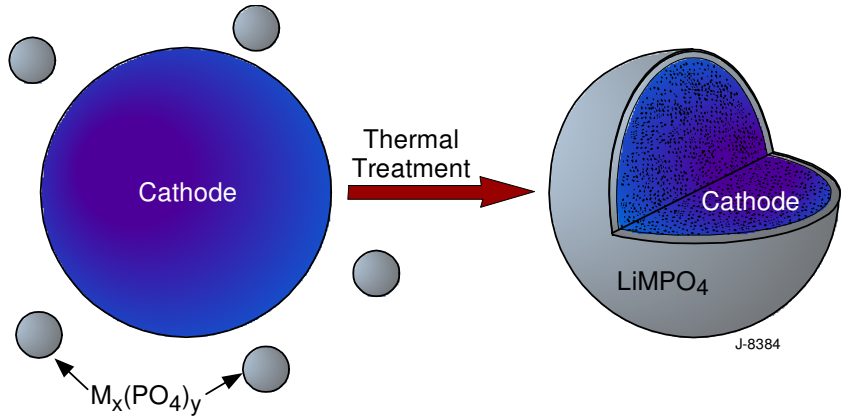
Problem:

- Under abuse conditions, exothermic reactions between high voltage cathode materials and the battery electrolyte can lead to catastrophic failure.

Remediation Approach:

- PSI formed lithium metal phosphate coatings on metal oxide cathodes by thermal treatment of a mixture of metal phosphate and the cathode.[1]



[1] H. Lee, M. Kim, J. Cho, *Electrochemistry Communications,* 9 (2007) 149–154.

Benefits of the Lithium Metal Phosphate Coating

- Coating is a lithium conductor.
- Metal phosphates offer greater stability than their metal oxide counterparts.
- Coating technique can be applied to protect any high energy density cathode material.
- Common processing steps allowing for low cost manufacturing.

Key Benefit: Cathode Surface Oxidation State

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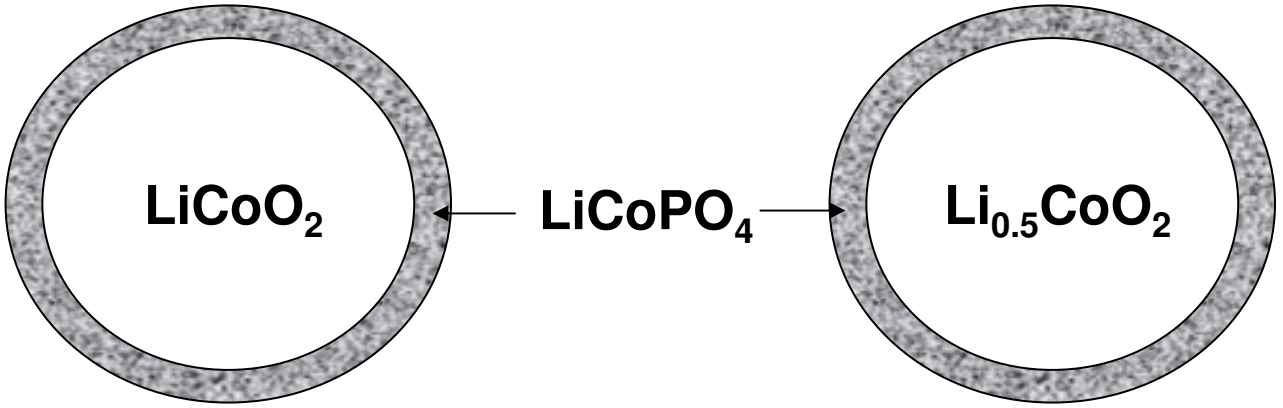
- For high voltage cathode materials:

V_{Mox} (Oxidized Metal Potential) > $V_{El\text{-}limit}$ (Stability limit of the Electrolyte)

- Results in spontaneous oxidation of the electrolyte.

- For coated material, the lithium metal phosphate layer remains in the reduced form upon full charge.



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Electrochemical Testing

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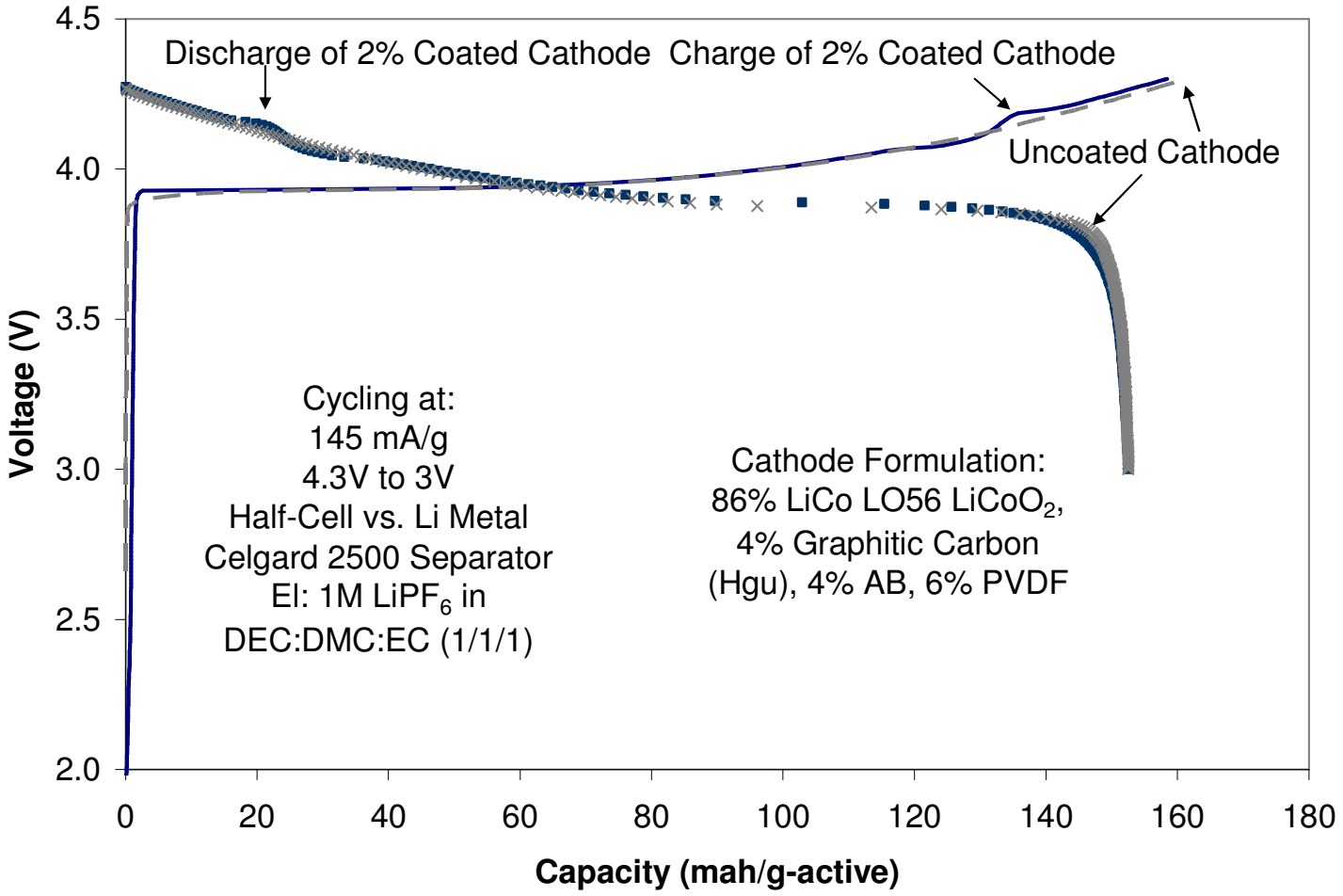
- No loss in discharge capacity on ~1.5% $LiCoPO_4$ coating.
- Discharge capacity: Uncoated - 149mAh/g; Coated - 151mAh/g



Performance On Extended Testing of Coating Material

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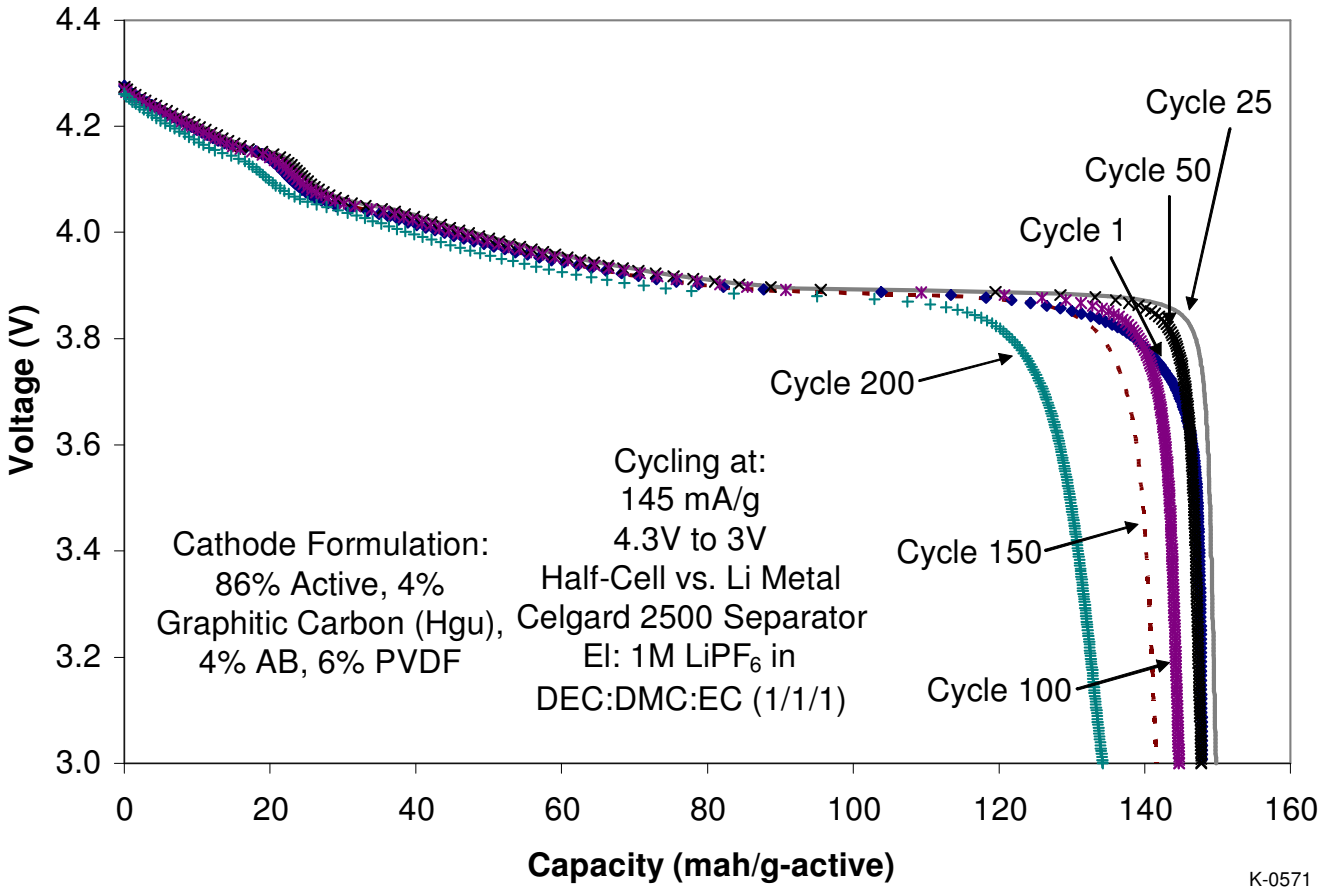
- Presence of characteristic features on cycle 200 indicates robust adhesion throughout cycling.
- 200 cycles completed with >89% discharge capacity on final cycle.



1st and 2nd Discharge Cycle for Uncoated and 1% Coated $LiCoO_2$ Cathode at 0°C

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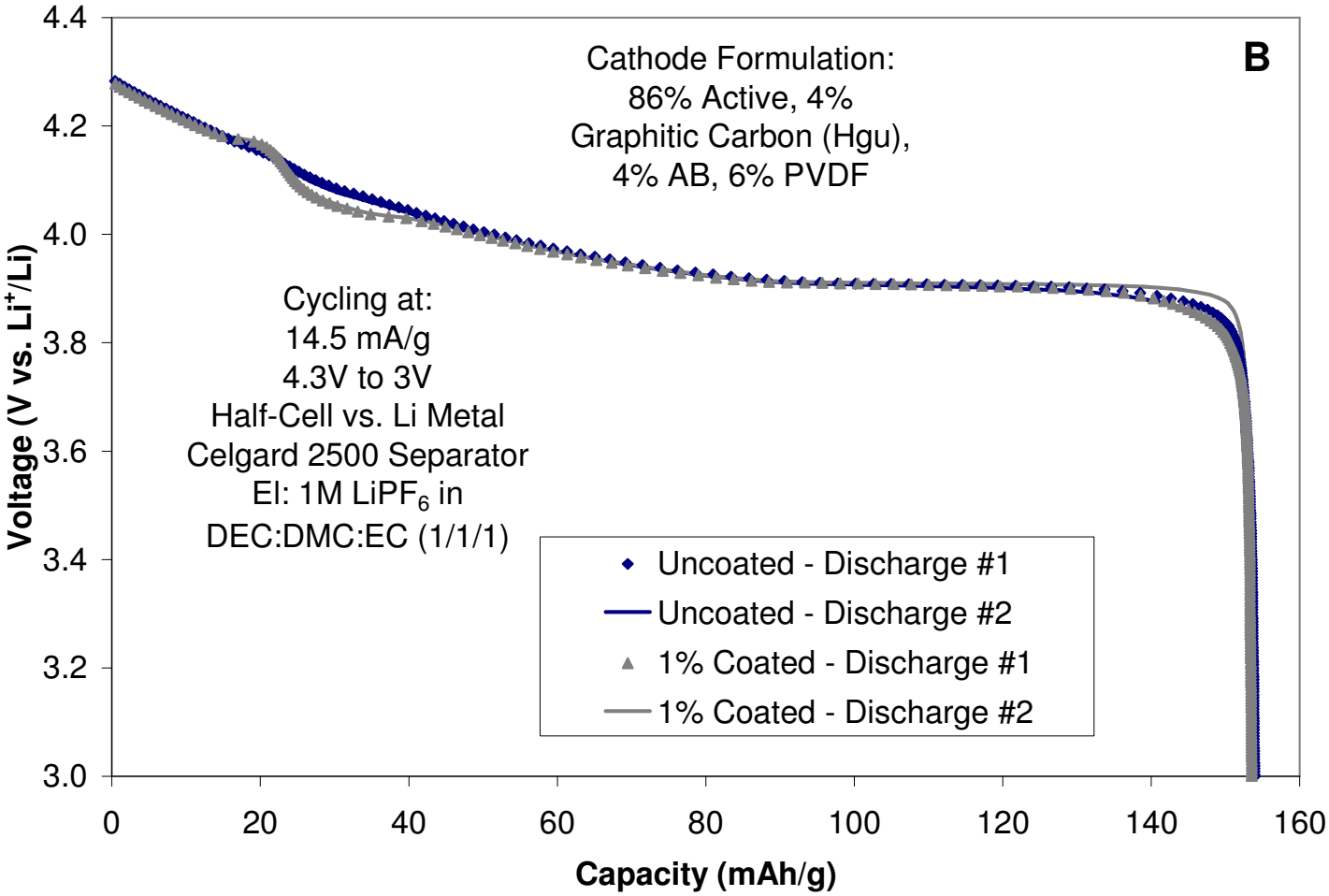
- C/10 rate cycling versus Lithium shows similar voltage vs. capacity traces before and after coating.
- Characteristic features at 4.05 and 4.2V are present.



Cyclic Voltammetry Scans for 1% Coated and Uncoated Cathodes

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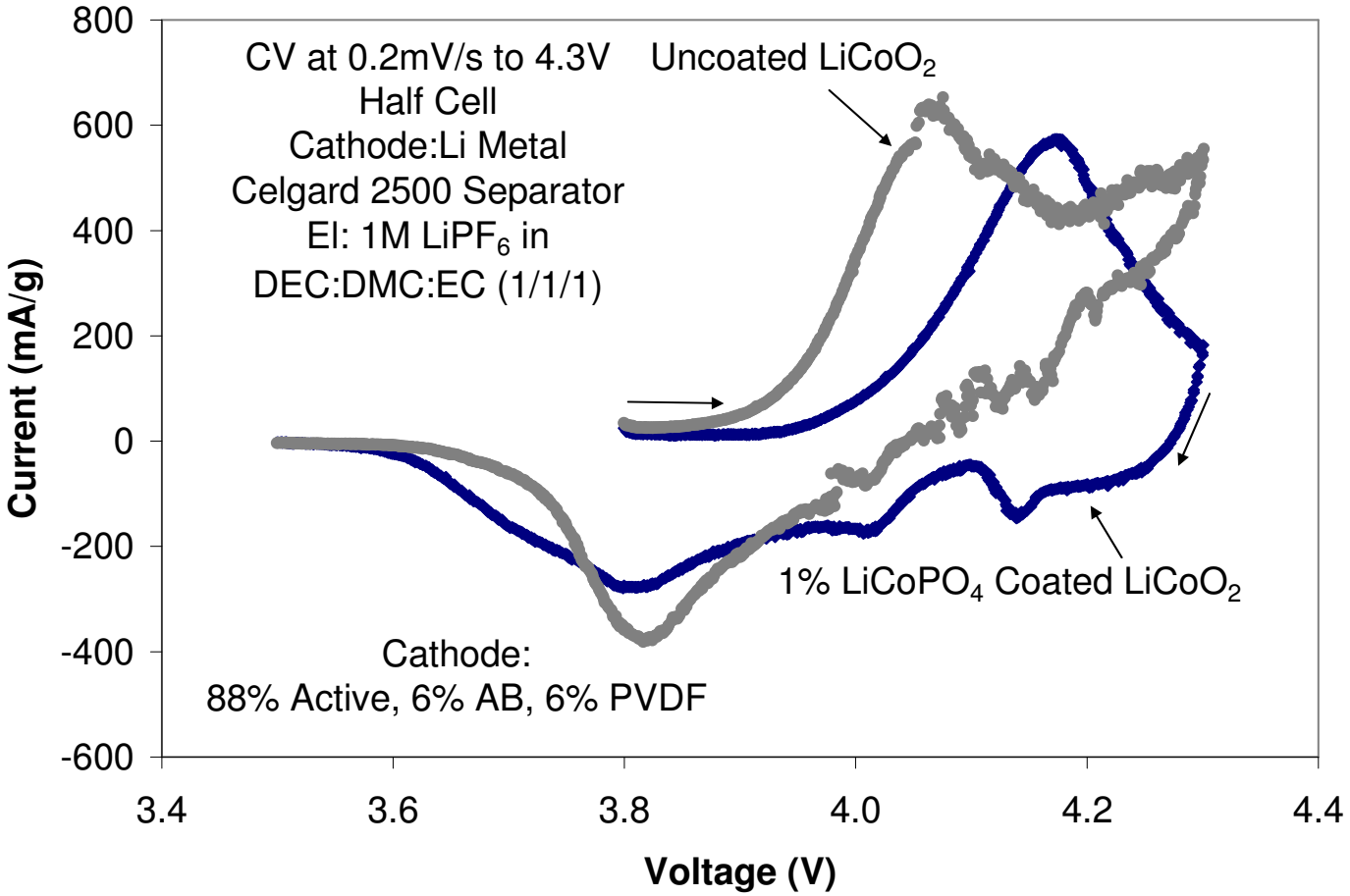
- CV scan for uncoated material shows one reversible oxidation/reduction.
- For the 1% coated material the primary oxidation peak is shifted ~100mV.
- On scan reversal three distinct reduction peaks are clearly observed.



Cyclic Voltammetry Scans for 0.5% Coated and Uncoated Cathodes

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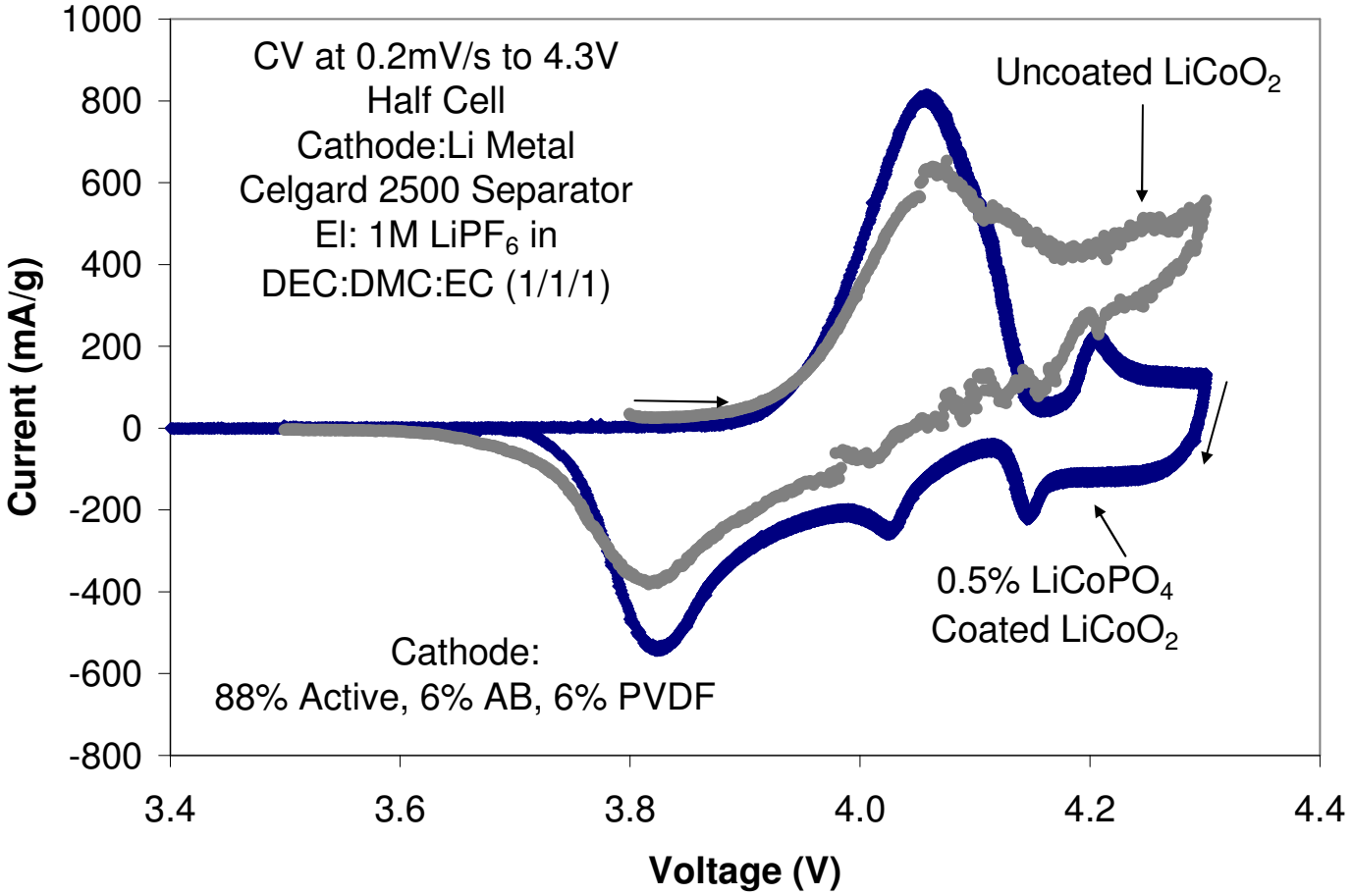
- 0.5wt% coating does not change the primary oxidation peak location.
- Two distinct oxidations are observed on the forward scan, 3 on the reversal.



Complete Exotherm Suppression with Coating

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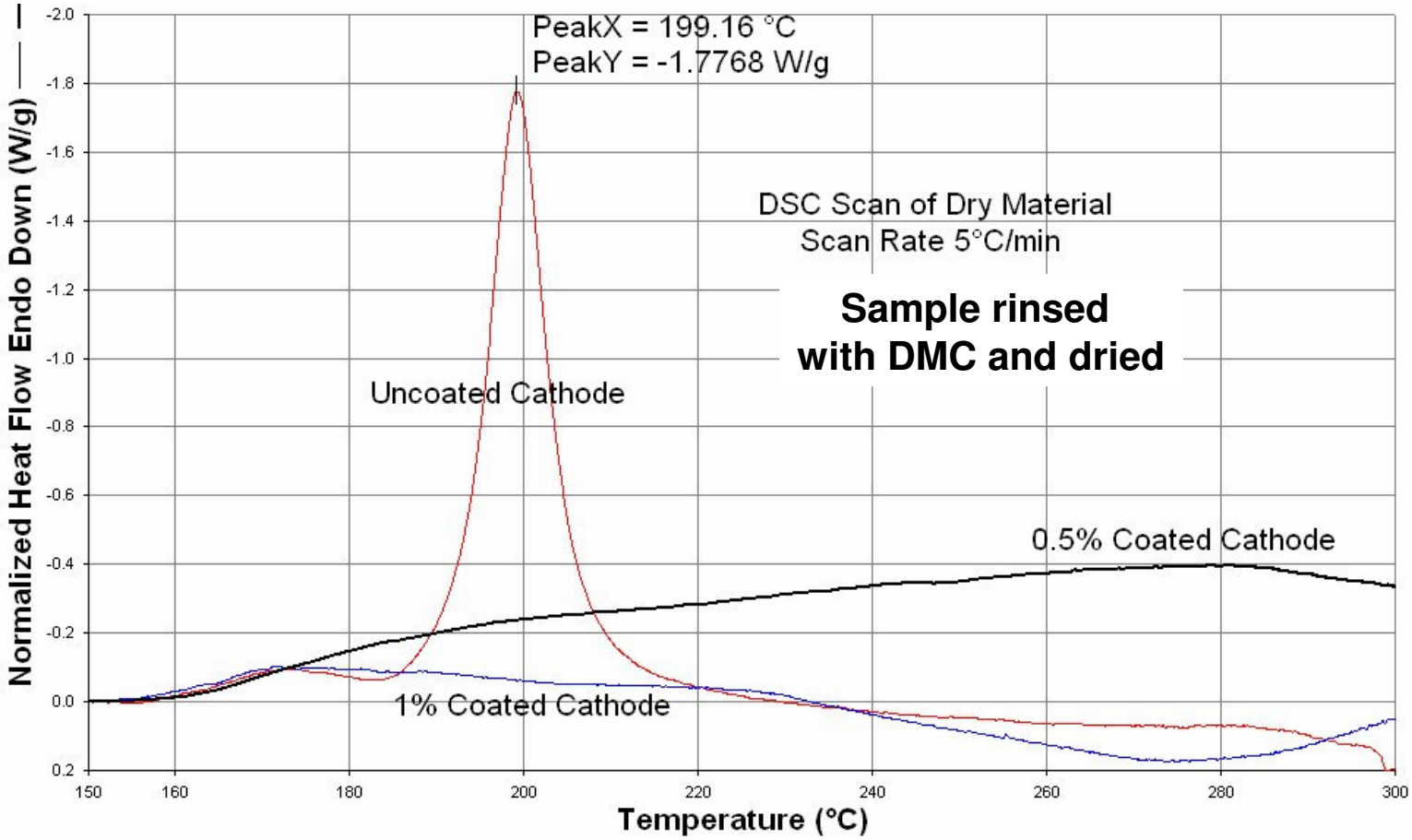
- Dry uncoated sample has -1.8W/g exotherm at 199.2℃.
- No corresponding exotherm is observed for the 1% coated sample.
- A broad exotherm is observed for the 0.5wt% coated cathode.



1C Discharge of Pouch Cell with Uncoated Cathode

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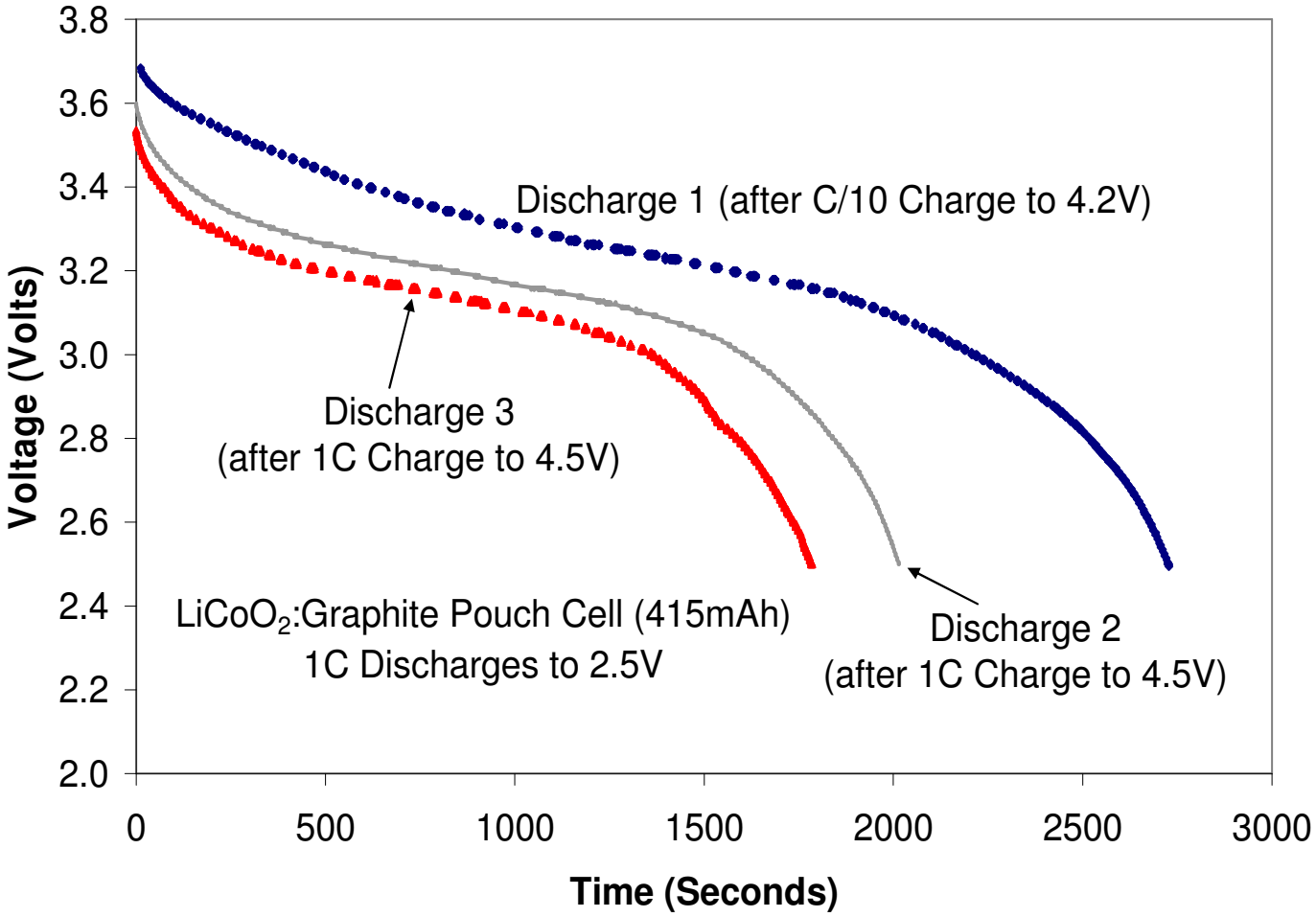
- Initial discharge performed after C/10 charging has significantly higher discharge capacity.
- Discharge capacity decreases on successive 1C charging to 4.5V.



1C Discharge of Pouch Cell with 1% Coated Cathode

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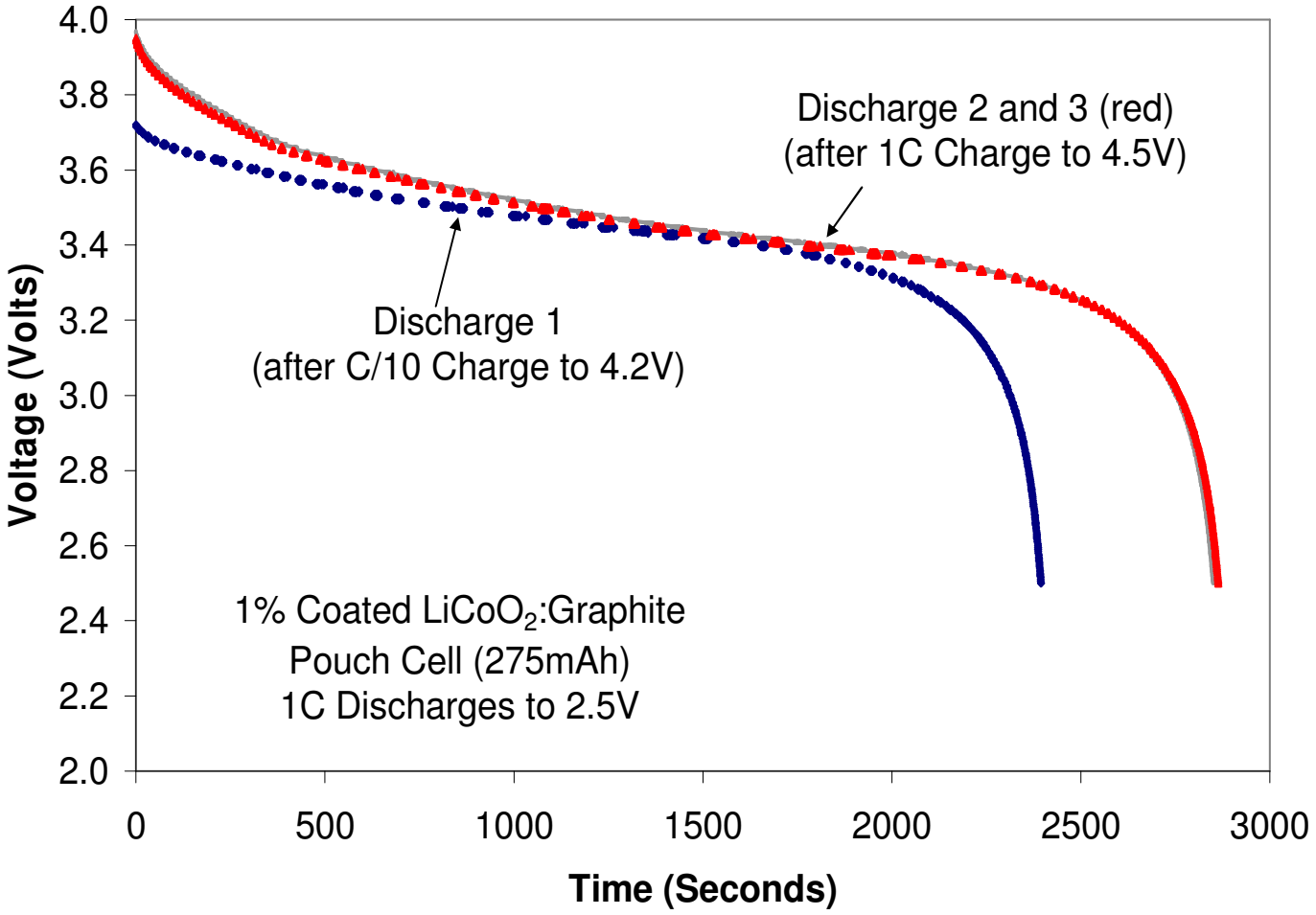
- On the initial discharge ~67% of the capacity was recovered potentially in part due to increased polarization of the cathode material.
- Discharge capacity improves on charging to 4.5V and does not fade for cycles 2 and 3.



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Performance of Coated and Uncoated $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ Cathode Material

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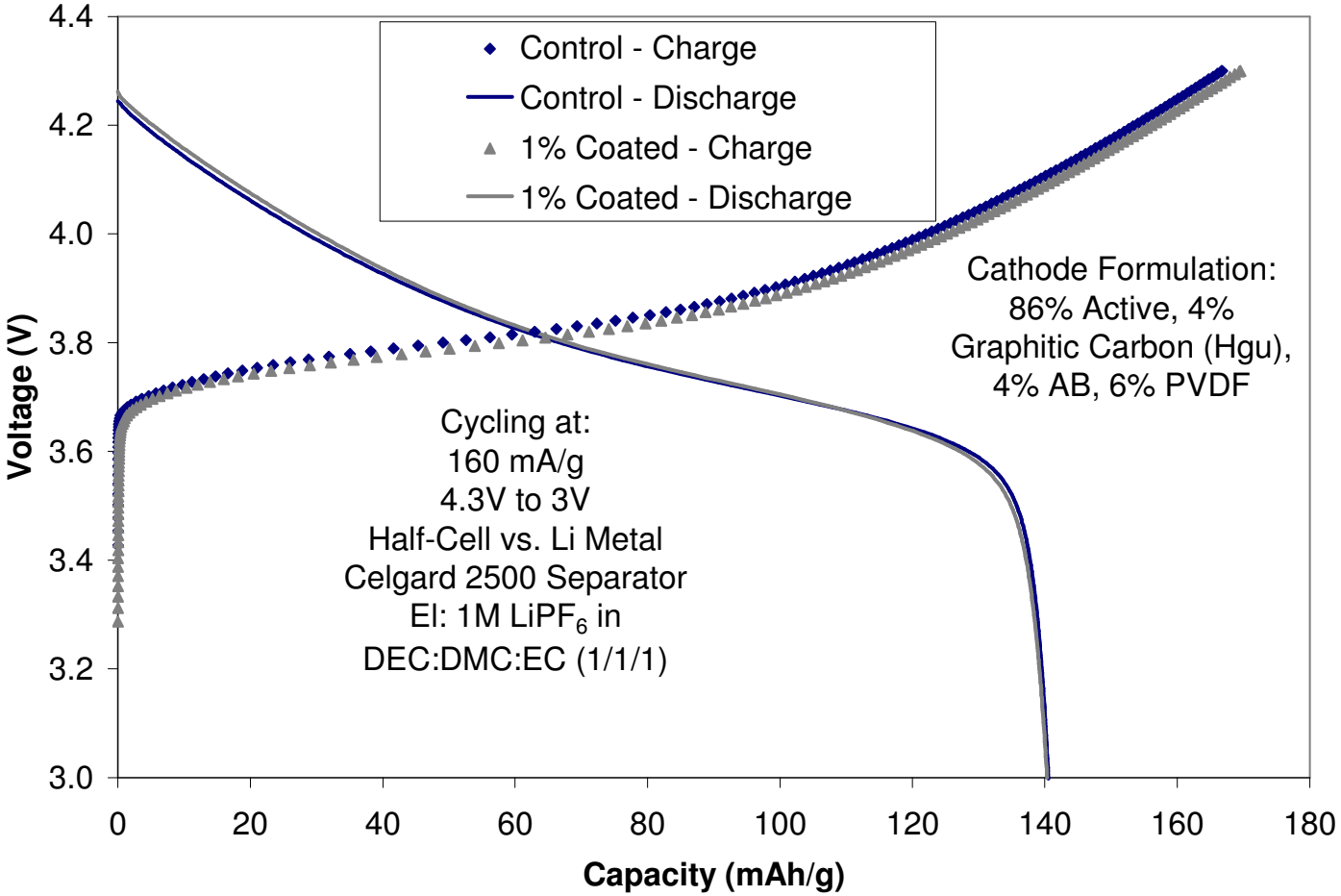
- $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$ (Seimi L-333 from Argonne National Labs) was tested between 4.3 and 3V at 160mA/g.
- Coated voltage trace shows no overpotential or change in capacity.



1st and 2nd Charge Profile for 1% Coated and Uncoated LNCM Material from JPL

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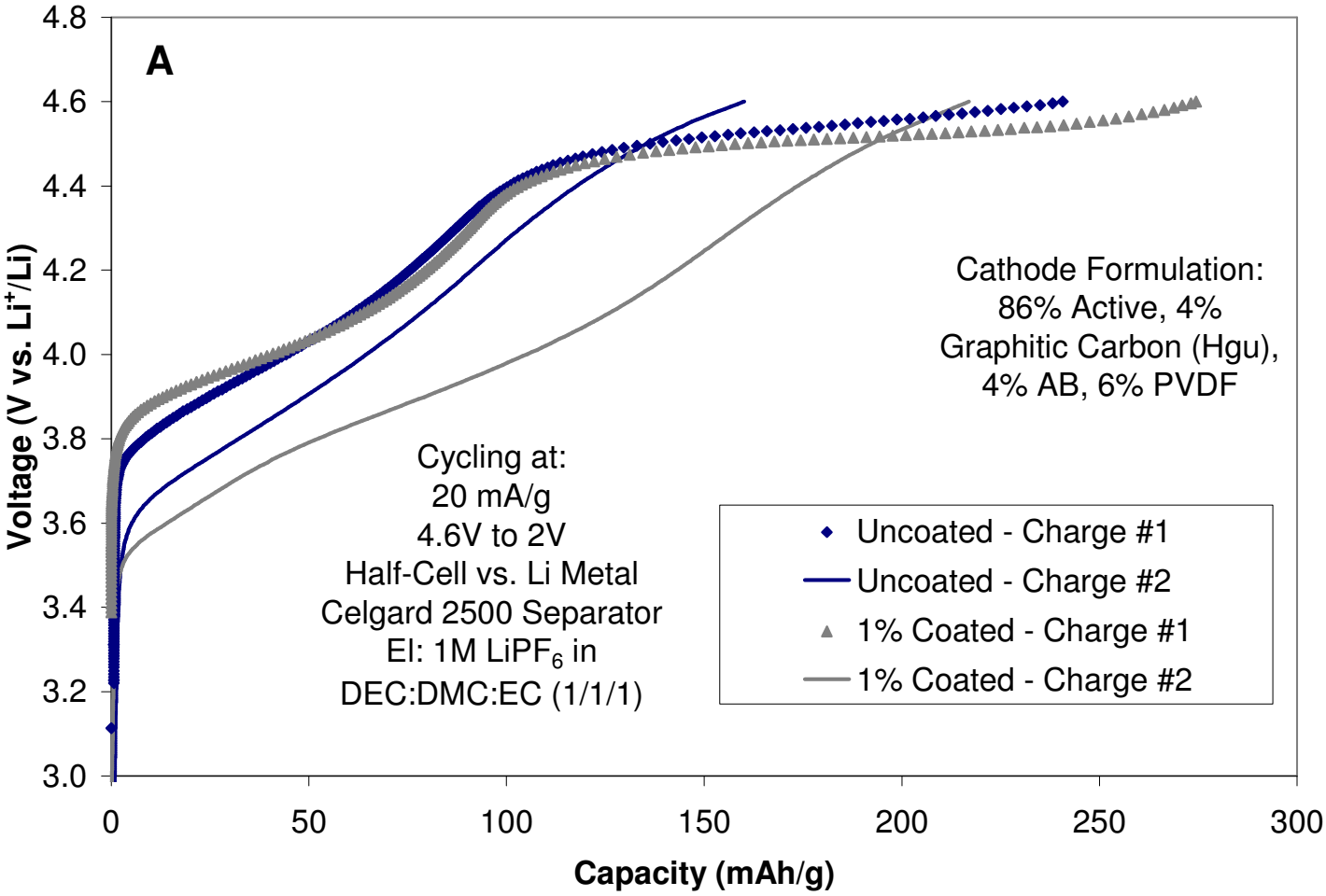
- All testing carried out with by cycling between 4.6 and 2V at C/10.
- Coated sample demonstrated considerably higher first cycle charge capacity.



1st and 2nd Discharge Profile for 1% Coated and Uncoated LNCM Material from JPL

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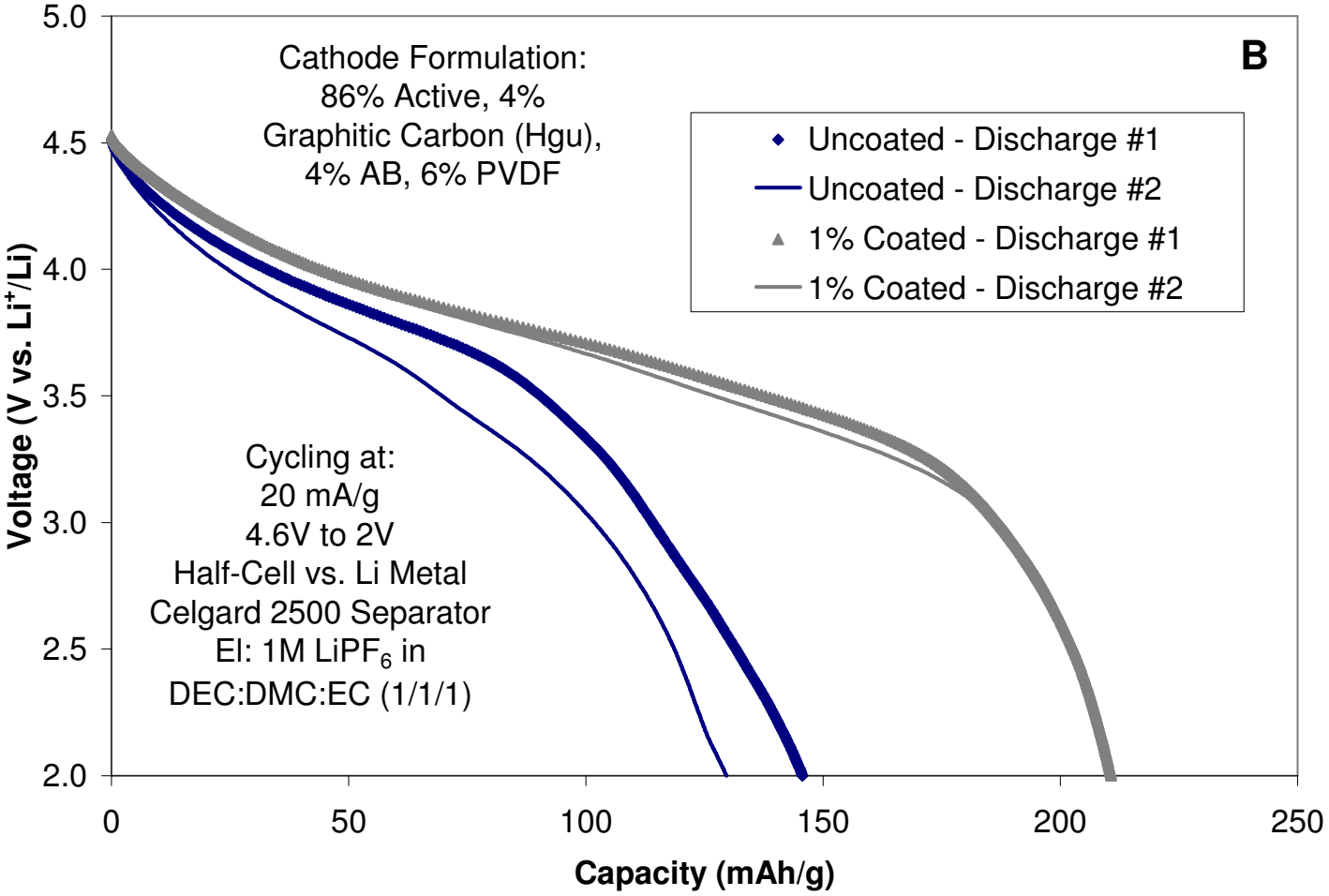
- Discharge capacity for the coated sample is ~210mAh/g.
- Uncoated sample had discharge capacity of <150mAh/g.



Coin Cell Cycling

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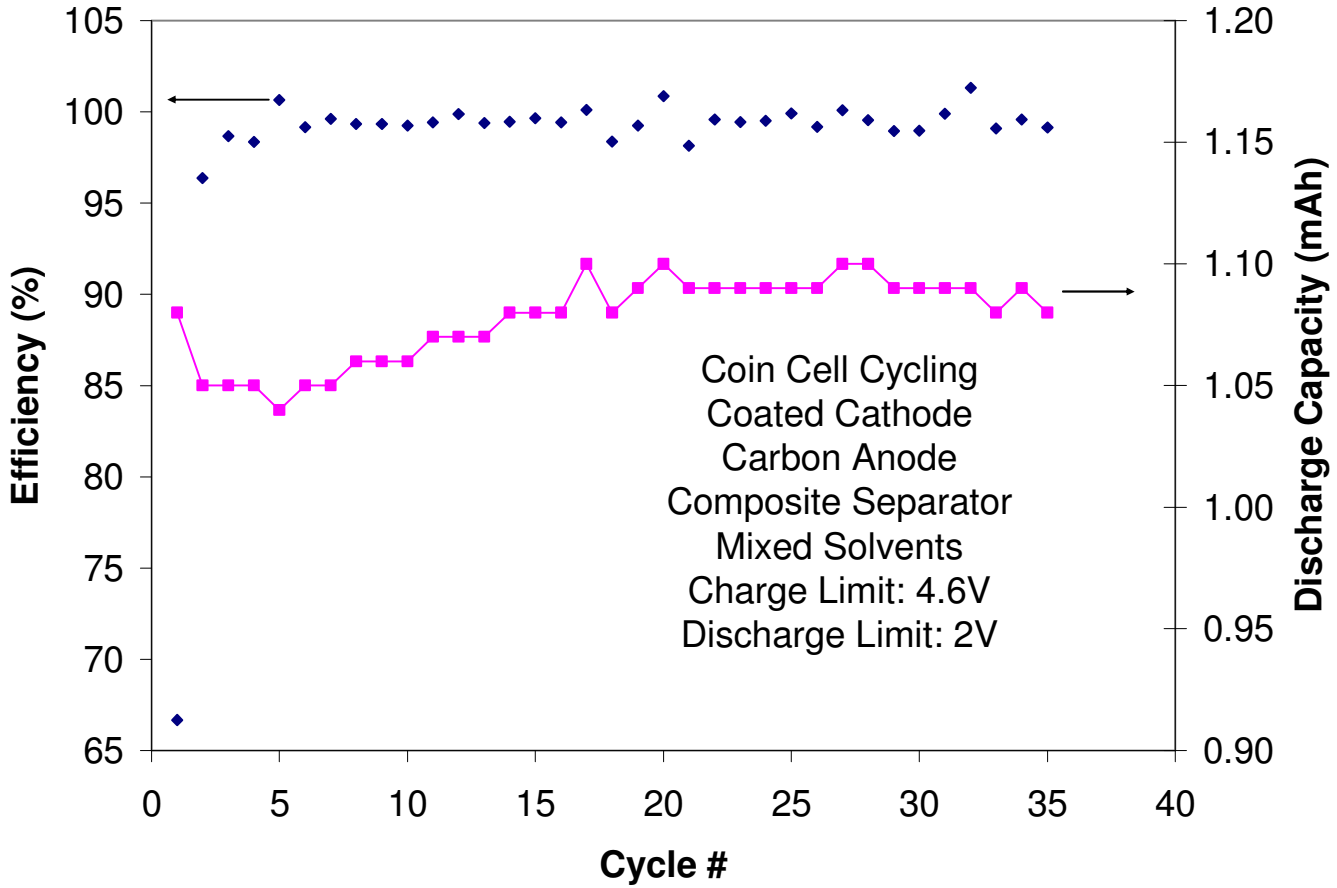
- The coated cathode was matched up with a commercial anode and cycled at a C/4 rate.
- After the initial SEI formation period, the cell cycles with ~100% efficiency.



DSC Testing of Uncoated JPL Material

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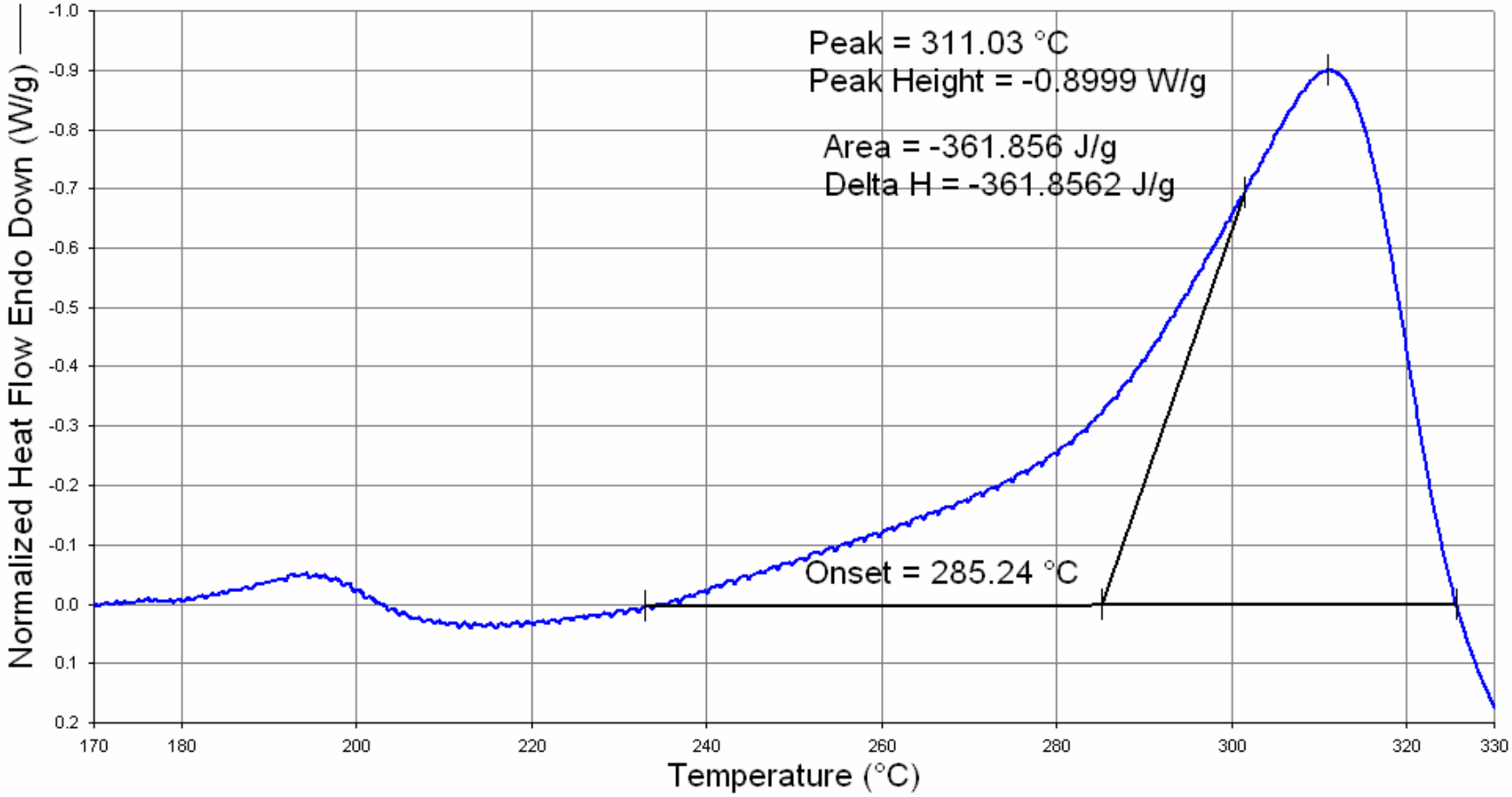
- Testing performed dry after C/10 charge to 4.6V versus lithium.
- Beginning of exotherms at ~235°C with significant onset at 285°C.
- Peak is at 311°C with total heat release of 362 J/g.



DSC Testing of 1% Coated JPL Material

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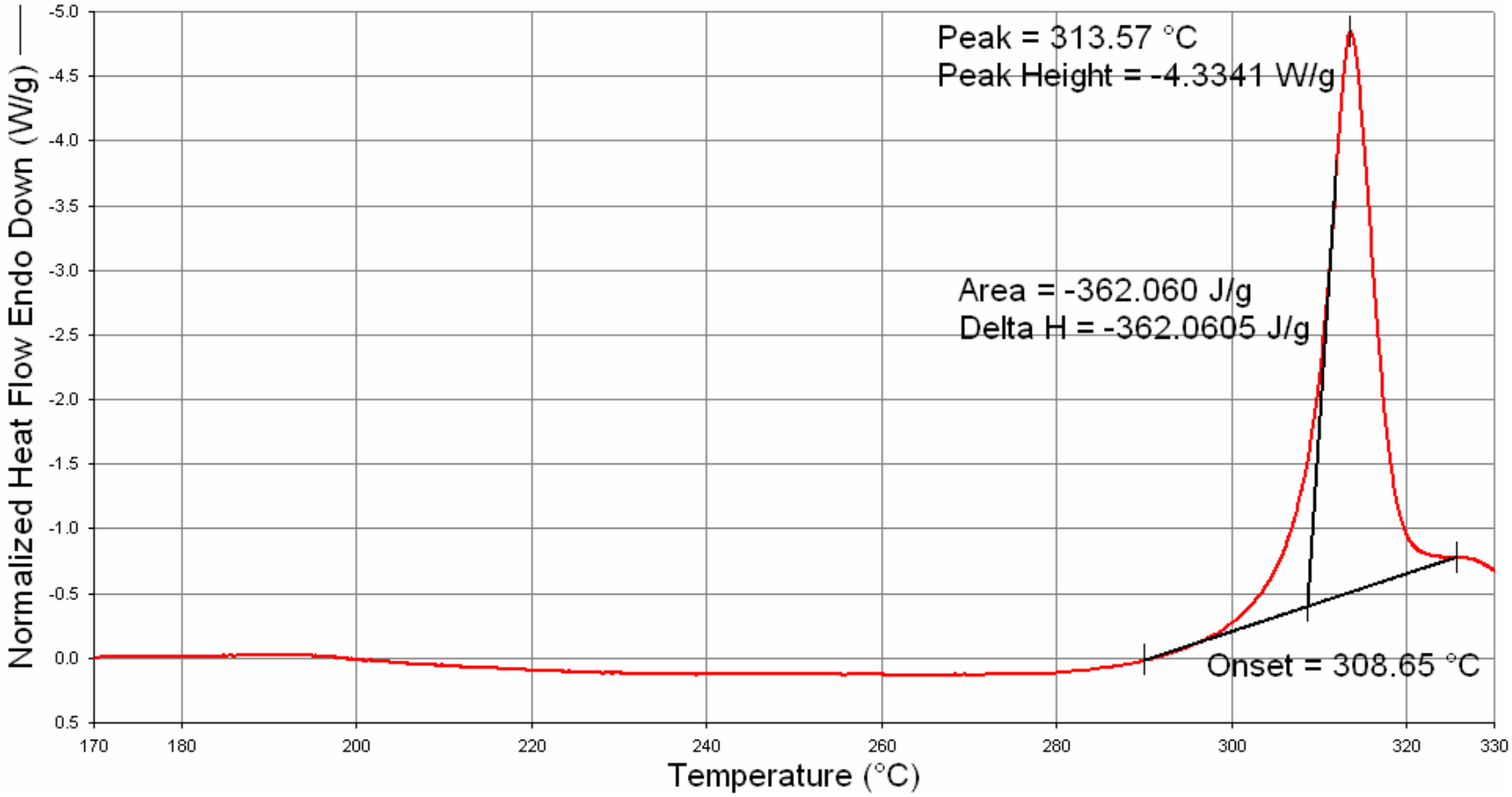
- Testing performed dry after C/10 charge to 4.6V versus lithium.
- No exotherm observed until ~290°C with significant onset at 308°C.
- Peak is at 313°C with total heat release of 362 J/g.



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Summary

- Coated samples demonstrated equivalent (~150mAh/g) electrochemical performance to uncoated $LiCoO_2$ material.
- Phosphate coating is robust allowing for 200 cycles at 1C rate with >89% capacity retention.
- The optimized process resulted in complete suppression of the exotherm using only 1% lithium metal phosphate.
- Improved discharge capacity and performance was observed on coating NASA's mixed metal oxide material.
- The coating shifts the peak exotherm, though the total generated heat is unchanged.

Acknowledgments

- This work is supported by NASA Johnson Space Center, Houston, TX 77058 and NASA Glenn Research Center, Cleveland, OH 44135

- Funding: NASA NRA – Dr. Judith Jeevarajan (COTR)
  - Dr. Thomas B. Miller
  - Dr. Jon S. Read
  - Dr. Pranav Patel

- PSI Staff:
  - Benjamin K. Leipzig
  - Alex W. Elliott

Thank you for your time.
Any Questions?