Post-Test Analysis of Lithium-Ion Battery Materials at Argonne National Laboratory

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Project ID: ES166

Post-test Analysis of Lithium-Ion Battery Materials at Argonne National Laboratory

Overview

Timeline

- Facility Planning: 2010
- Facility Commissioned: 2011
- End: Open – this is an ongoing activity to provide information which is complementary to that obtained during battery testing

Budget

- FY15: $ 700k
- FY14: $ 700k
- FY13: $ 300k
- FY12: $ 350k
- Status: Ongoing

Objectives

- To provide DOE and its contractors with an independent assessment of state-of-the-art battery technology
- To help elucidate causes of battery performance decline
- To develop analysis procedures, which could be used as part of a standard or accepted practices

Collaborations

- CAMP, MERF (ANL)
- JCI
- Maxwell
- ARL
- JPL
- Maxwell Technologies
- ORNL
- ABR
- U. Hawaii
- Illinois Inst. Tech.
- CIC Energigune (Spain)
- Miltec

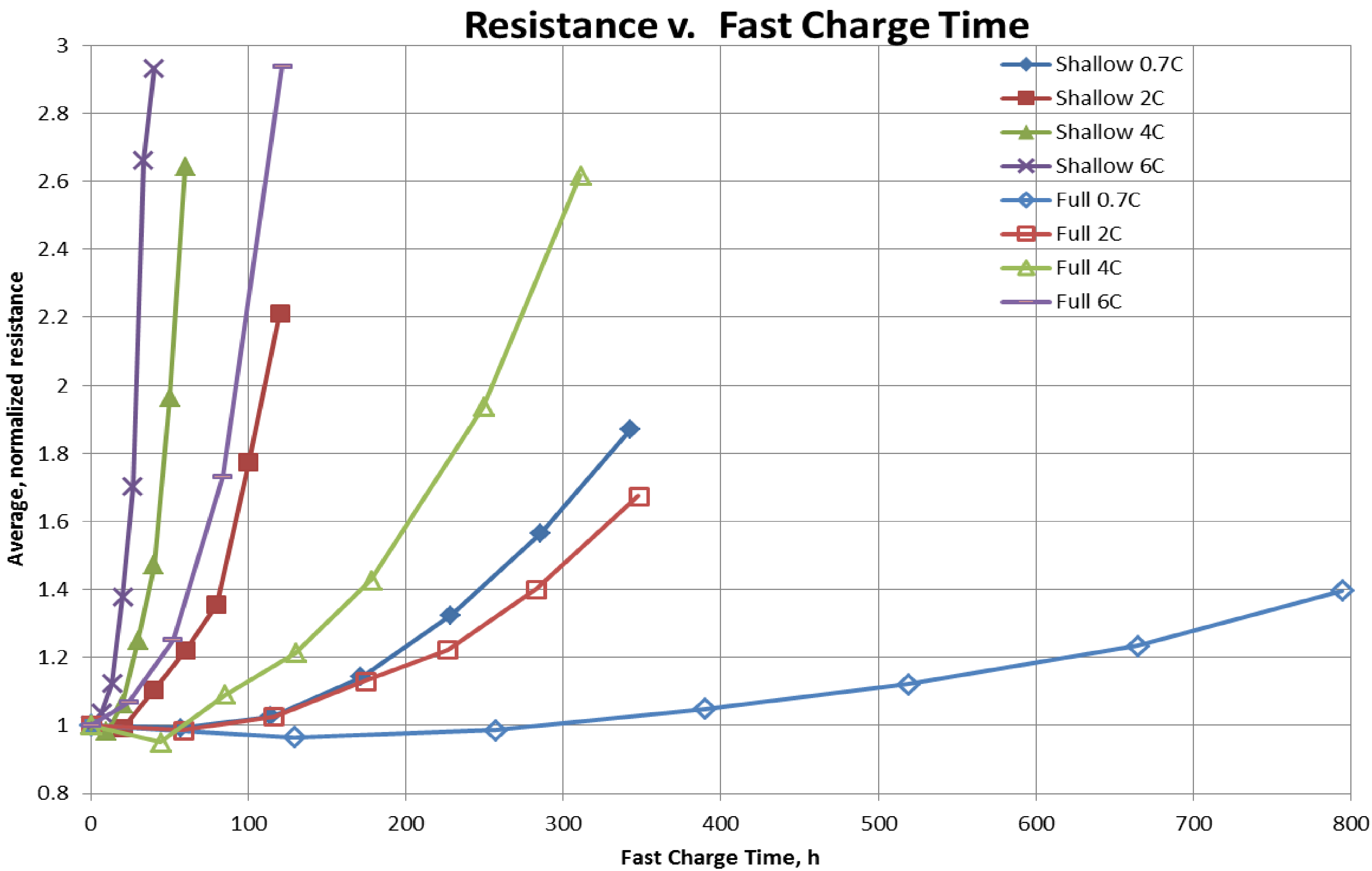
Post-Test Facility at Argonne -- Relevance

- Battery performance and life testing is an on-going program at Argonne. Here, batteries from USABC and DOE projects are objectively evaluated according to a given set of protocols
- Testing provides a lot of information about how battery performance changes with time under a given set of conditions
- Post-test diagnostics of aged batteries can provide additional information regarding the cause of performance degradation, which, previously, could be only inferred
- Here, the results from physical, spectroscopic, metallographic, electrochemical tests will be used to aid in the further improvement of a given technology
- The experience and techniques developed in DOE's applied battery R&D program will be used in a standardized fashion, similar to the performance test protocols. This will make comparisons of failure modes within a given technology and, perhaps, across technologies easier
- Facility is available to help DOE's ABR, BATT and USABC Programs and to help industrial battery developers better understand life-limiting mechanisms specific to their technology

Case study: Effect of Fast Charge on NMC/graphite Lithium-Ion Cells

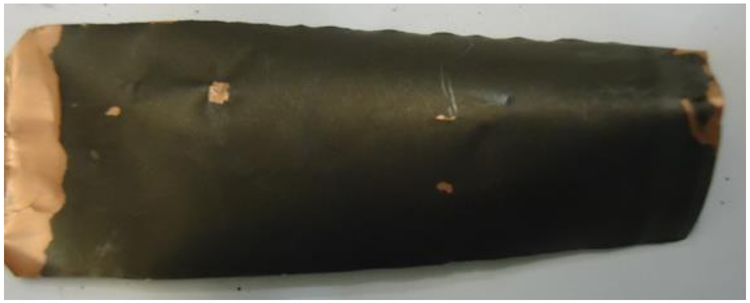
- Effects of fast charge rates on life of cylindrical 18650 NMC/graphite lithium-ion cells were investigated using EV cycle protocols
- Four test conditions, three cells per condition:
  - Charge at 0.7C (manufacturer's suggested rate) to 4.2V
  - Charge at 2C rate to 4.2V
  - Charge at 4C rate to 4.2V
  - Charge at 6C rate to 4.2V
- Method
  - Two SOC-returned fast-charge windows:
    - 40% (shallow)
    - 100% (full)
  - Fully discharged at C/3 or C/1 rates, respectively
  - RPT every 100 cycles (~300-400 h)
    - One C/3 capacity test
    - One peak power test
- **Performance test results: see poster ES201**

Faster Degradation at Higher Rates and Shallow Cycles

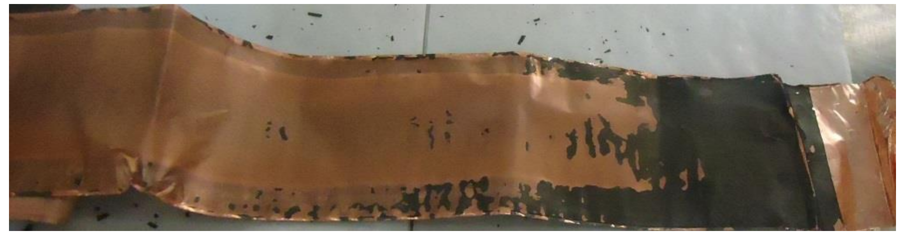


Fast Charging Causes Physical Damage on Cell Anodes

Full Charge



Shallow Charge



0.7 C

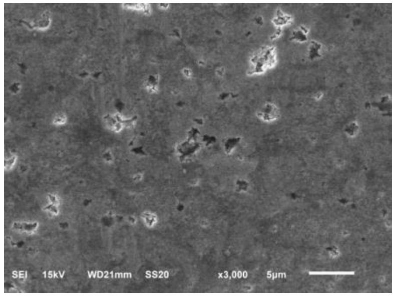
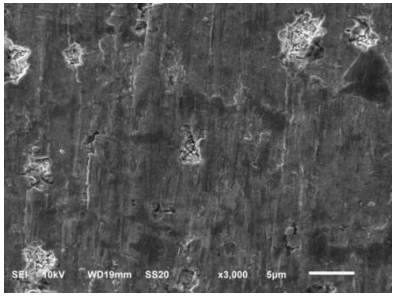
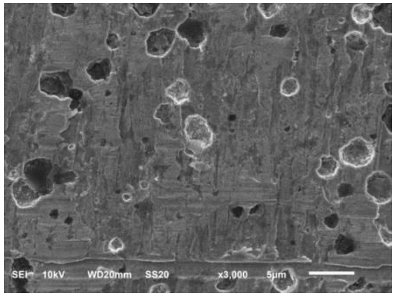
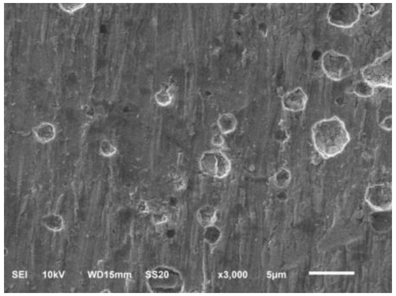
2 C

4 C

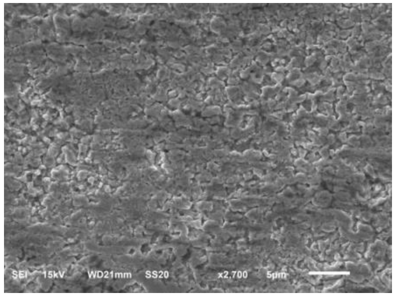
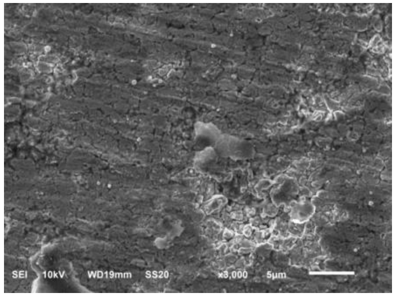
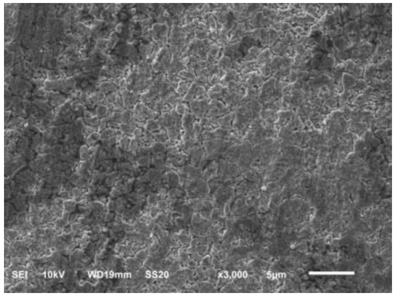
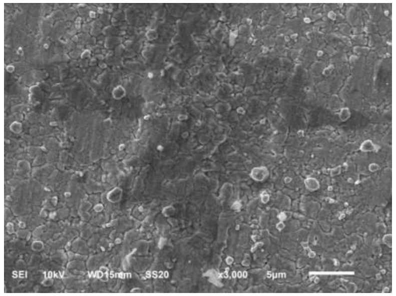
6 C

CC-foil Corrosion Depends on Rate & SOC Window

Full Charge

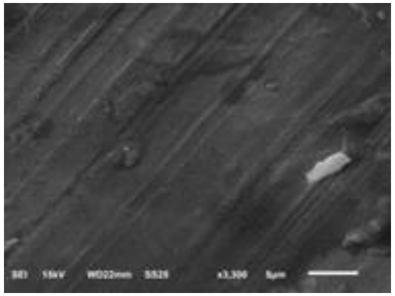





Shallow Charge

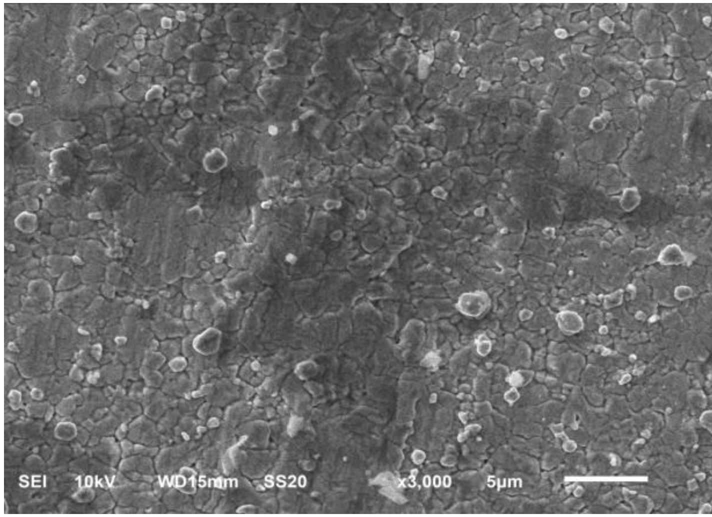
0.7 C | 2 C | 4 C | 6 C

- Grain boundary corrosion and surface pitting observed
- More damage to copper surface at higher rates and shallow charge
- All scale bars are 5 μm

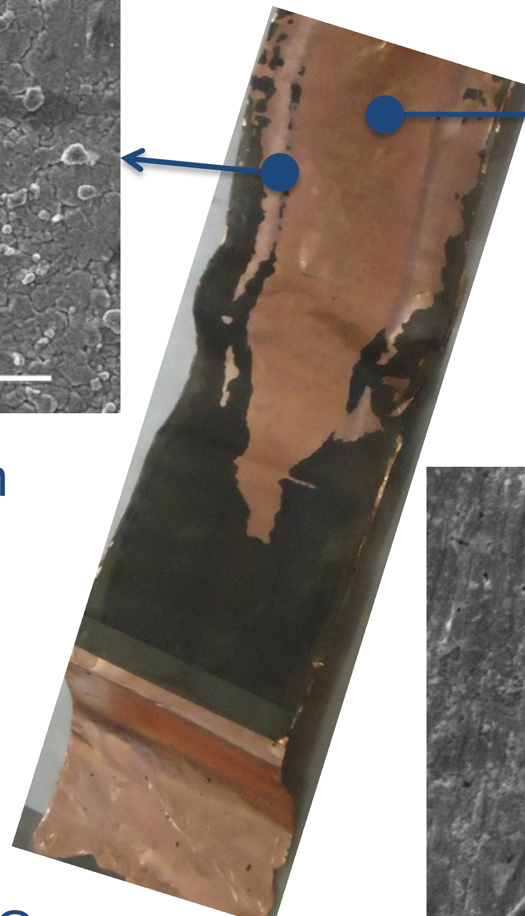


Pristine Cu foil (comparison)

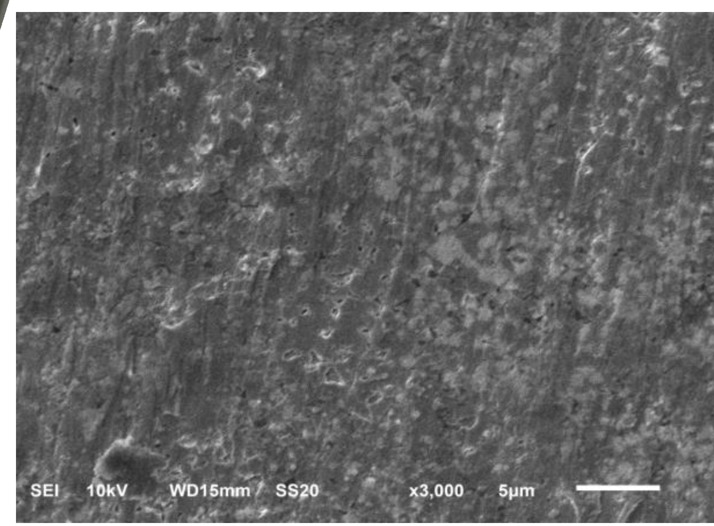
Damage to Current Collector Also Depends on Location



Close to edge of can

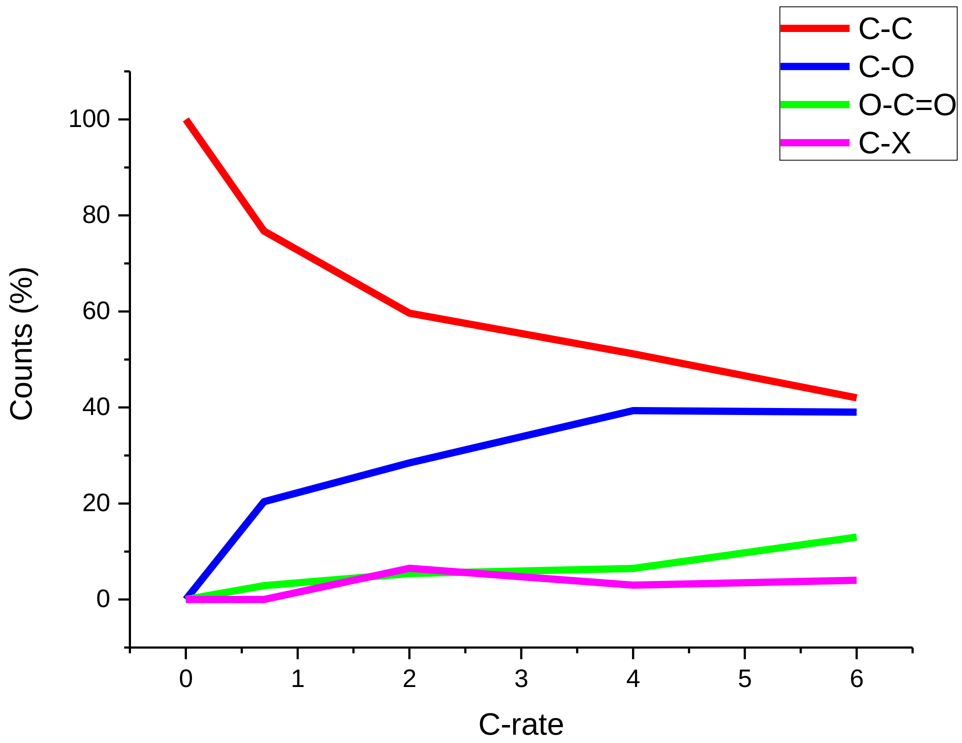


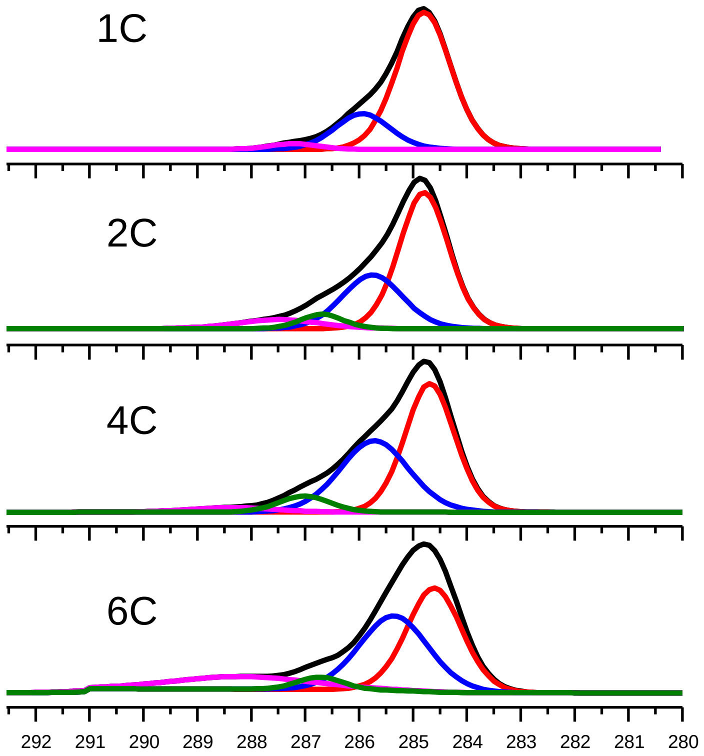
Close to center of can



Shallow charge, 6 C

XPS Indicates Changes in Surface Chemistry





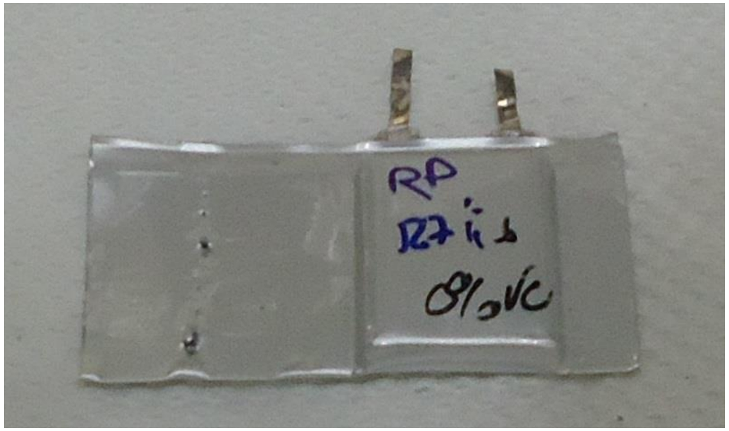
- C1s XPS data , after Ar^+ sputtering
- Higher C-rates associated with more oxidized C species

Fast Charge: Lessons Learned

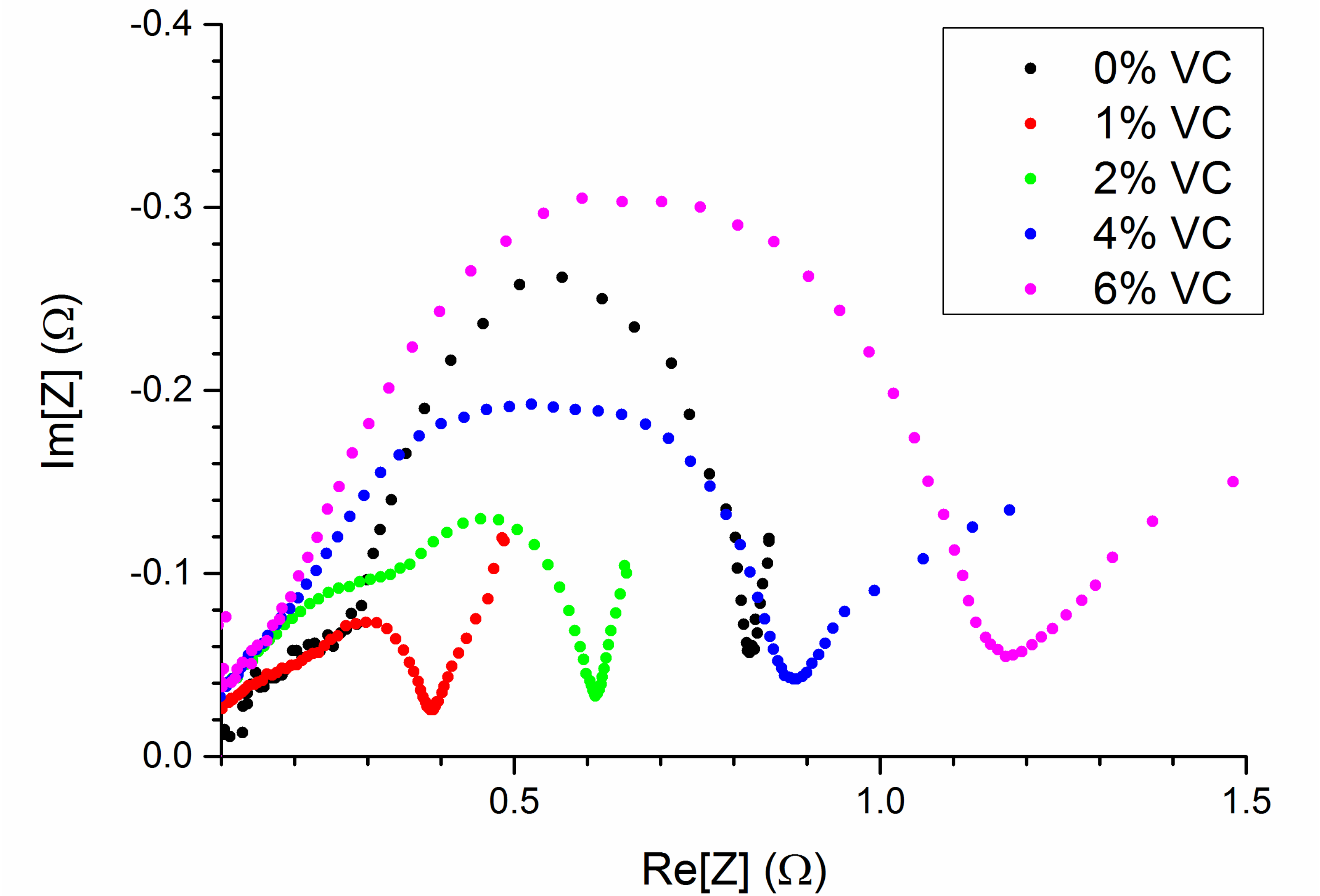
- Fast charging causes performance decline in lithium-ion batteries
- The extent of decline is proportional to charge rate and dependent on SOC window, strongly suggesting relation to i^2R heating
- Post-test examination of these cells indicates that one cause of performance decline is from the degradation of the binder in the anode, causing loss of contact between the current collector and active materials
- In the field, infrequent fast charging of electrified vehicles, while not to the extent observed here, may also accelerate degradation
- It may be possible to lessen these effects through effective thermal management of the vehicle battery pack, which we will seek to study

Case study: Effect of Washing on Anode SEI

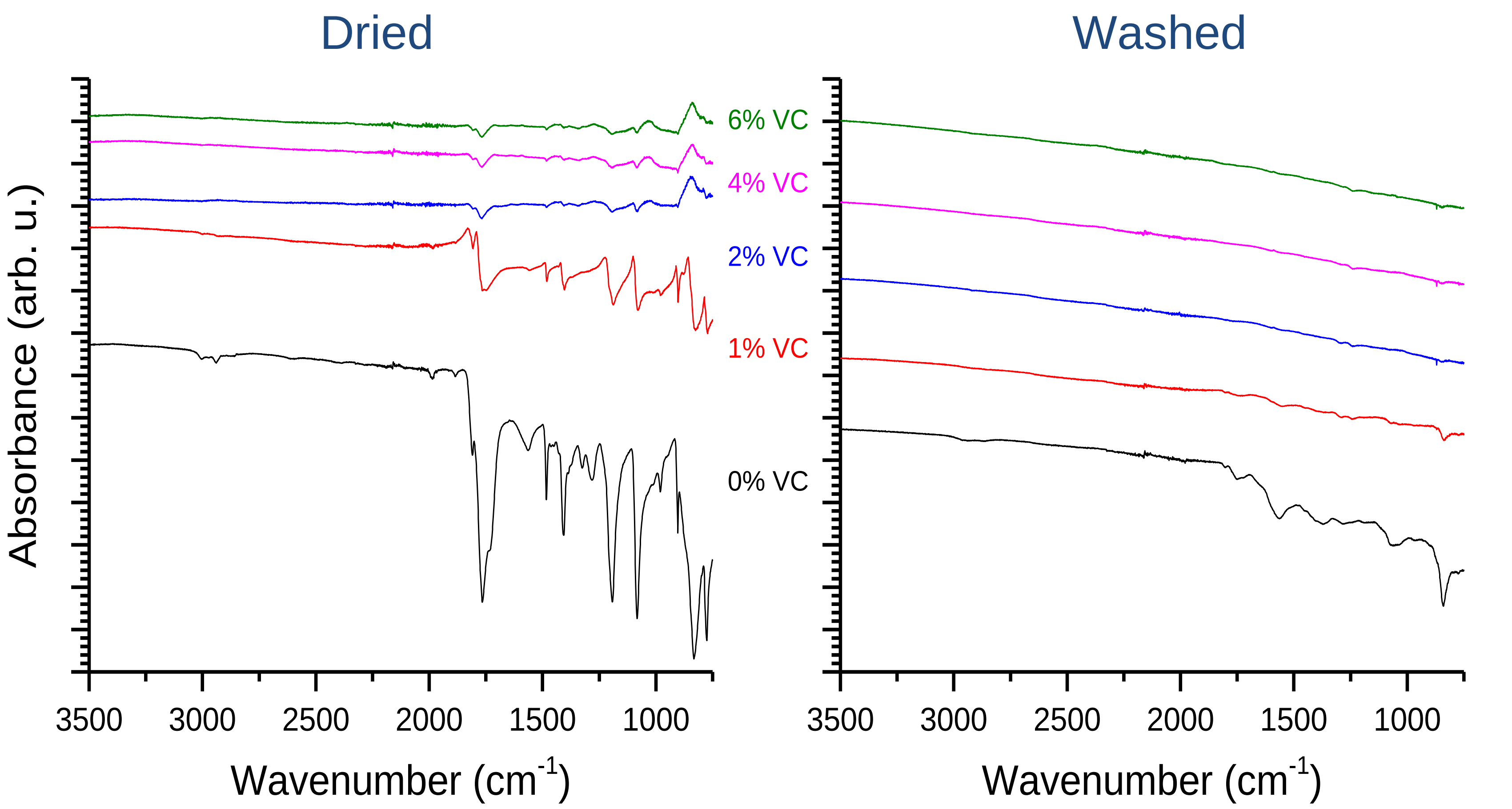
- A series of LCO/graphite cells with varying contents of VC additive were made and cycled at Dalhousie University to study the effect of VC on aging properties
- Cells were sent to PTF to characterize SEI's at end of test
- Washing anodes in DMC significantly altered the observed surface films



VC Effect on Impedance Growth is not Monotonic

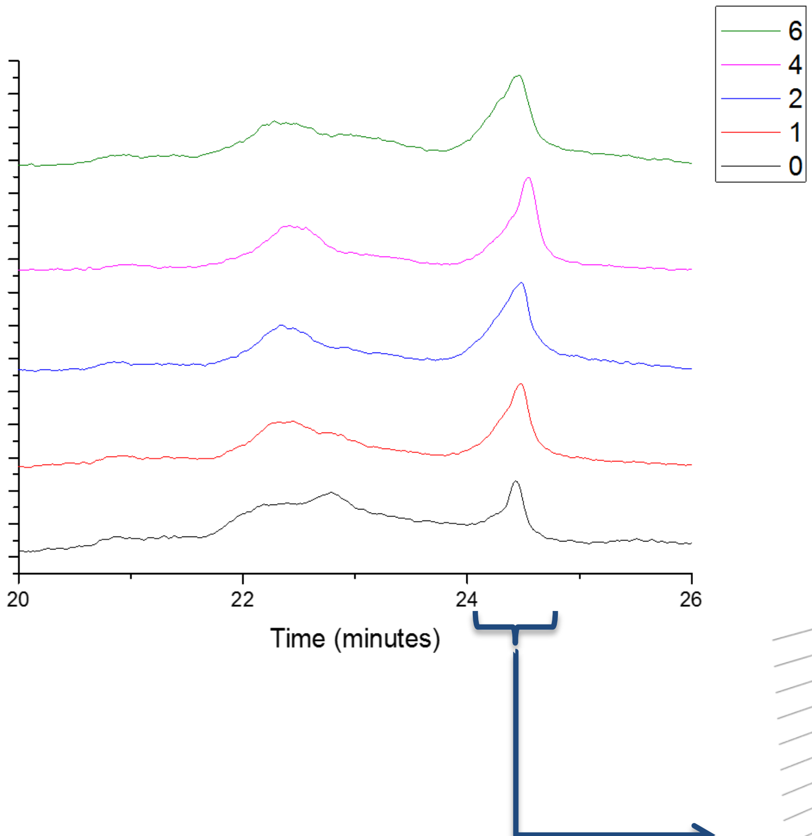


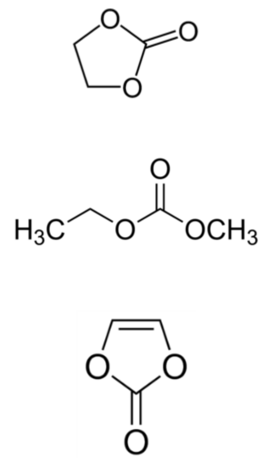
FTIR Reveals Thinner Films on Washed Anode



- Absorption bands are more pronounced in dried cells, indicating thicker film
- Composition of film on 0% VC cell changes upon washing

HPLC of Electrode Washings Contains Species Heavier than Electrolyte Components

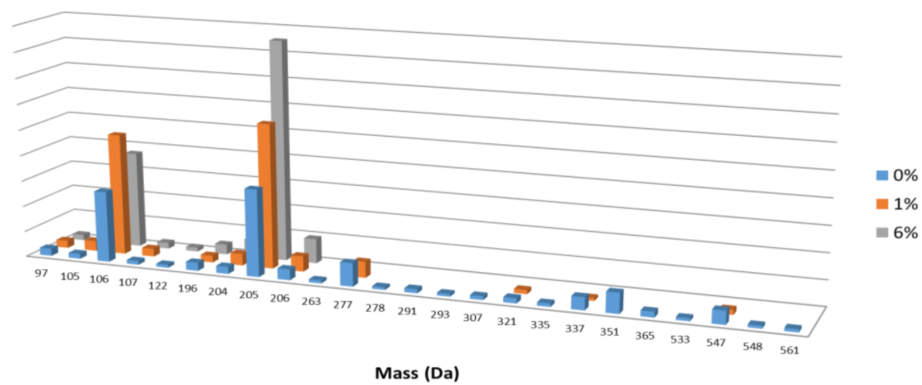




M(EC) = 88 Da

M(EC) = 104 Da

M(VC) = 86 Da



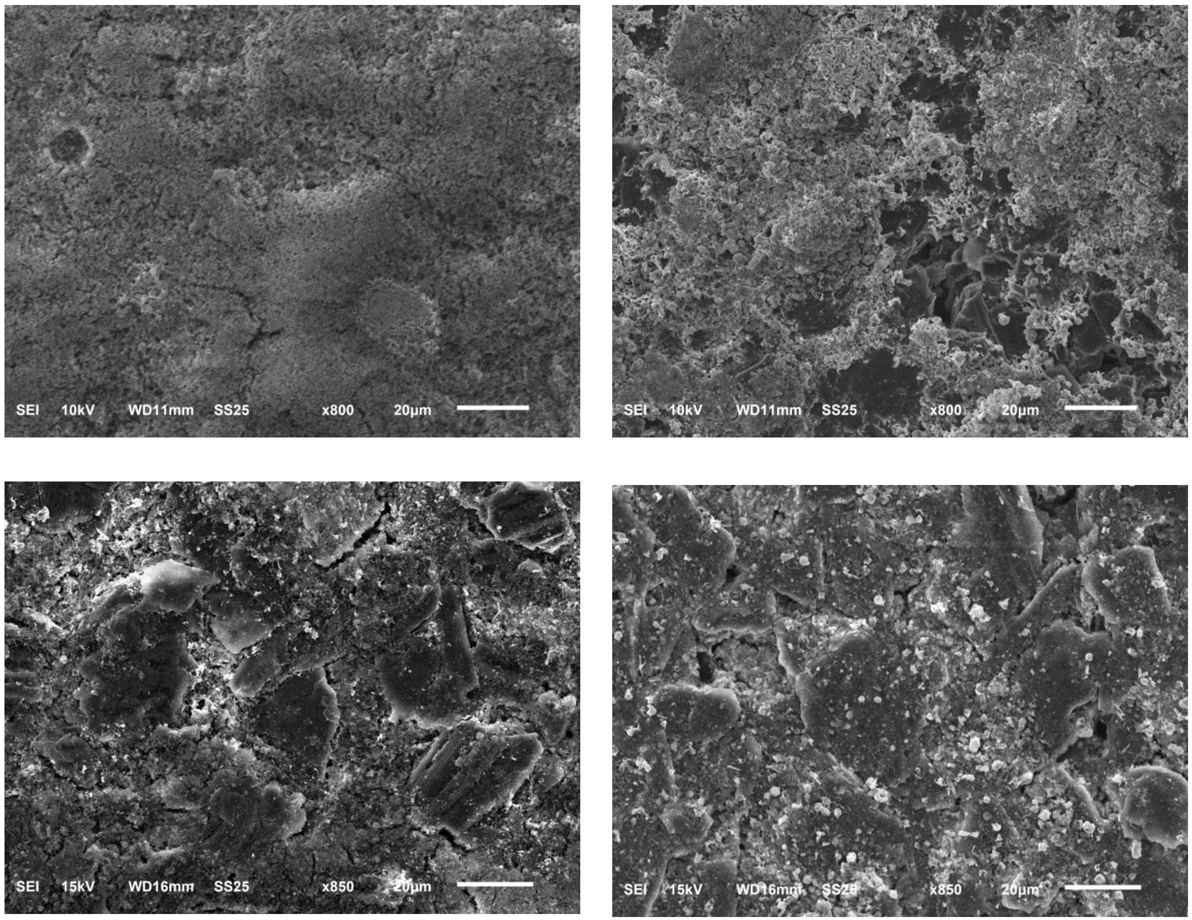
SEM: Low VC Content. Thicker Film, Partial Removal

0% VC

1% VC

Dried

Washed

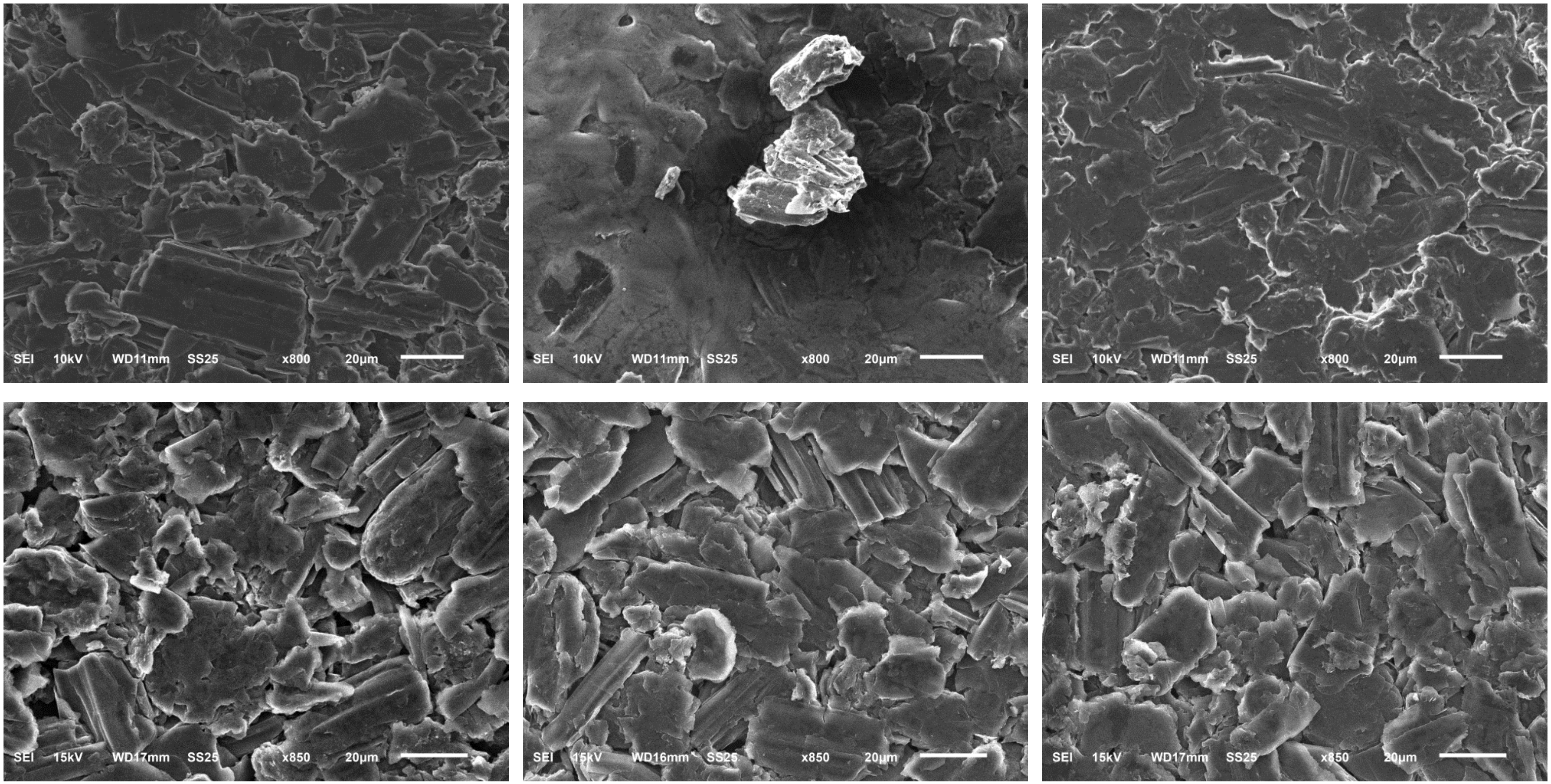


SEM: High VC Content. Thinner Film, Complete Removal

2% VC | 4% VC | 6% VC

Dried

Washed



Electrode Washing: Lessons Learned

- VC additive concentration affects the thickness and chemistry of surface film grown on anode
- DMC washing removes a significant portion of this film and appears to change its chemistry
- Electrode washing needs to be further characterized, including comparison between different solvents, and has to be considered an integral part of the analysis process

Acknowledgments

- The work at Argonne National Laboratory was performed under the auspices of the U.S Department of Energy (DOE), Office of Vehicle Technologies, under Contract No. DE-AC02-06CH11357. Program managed by Peter Faguy.

- Further details on collaborations can be found at:
  - I. Bloom, ANL: Electrochemical Performance Testing. ES201
  - David Wood, ORNL: IR Thermography as a Non-Destructive Evaluation (NDE) Tool for Lithium-Ion Battery Manufacturing. ES207
  - A. Jansen, ANL: Cell Analysis, Modeling, and Prototyping (CAMP) Facility Research Activities. ES030
  - A. Burrell, ANL: Enabling High-Energy/Voltage Lithium-Ion Cells for Transportation Applications: Part 2 Materials. ES253