

Binder Interactions in the Electrodes of the Lithium-ion Batteries



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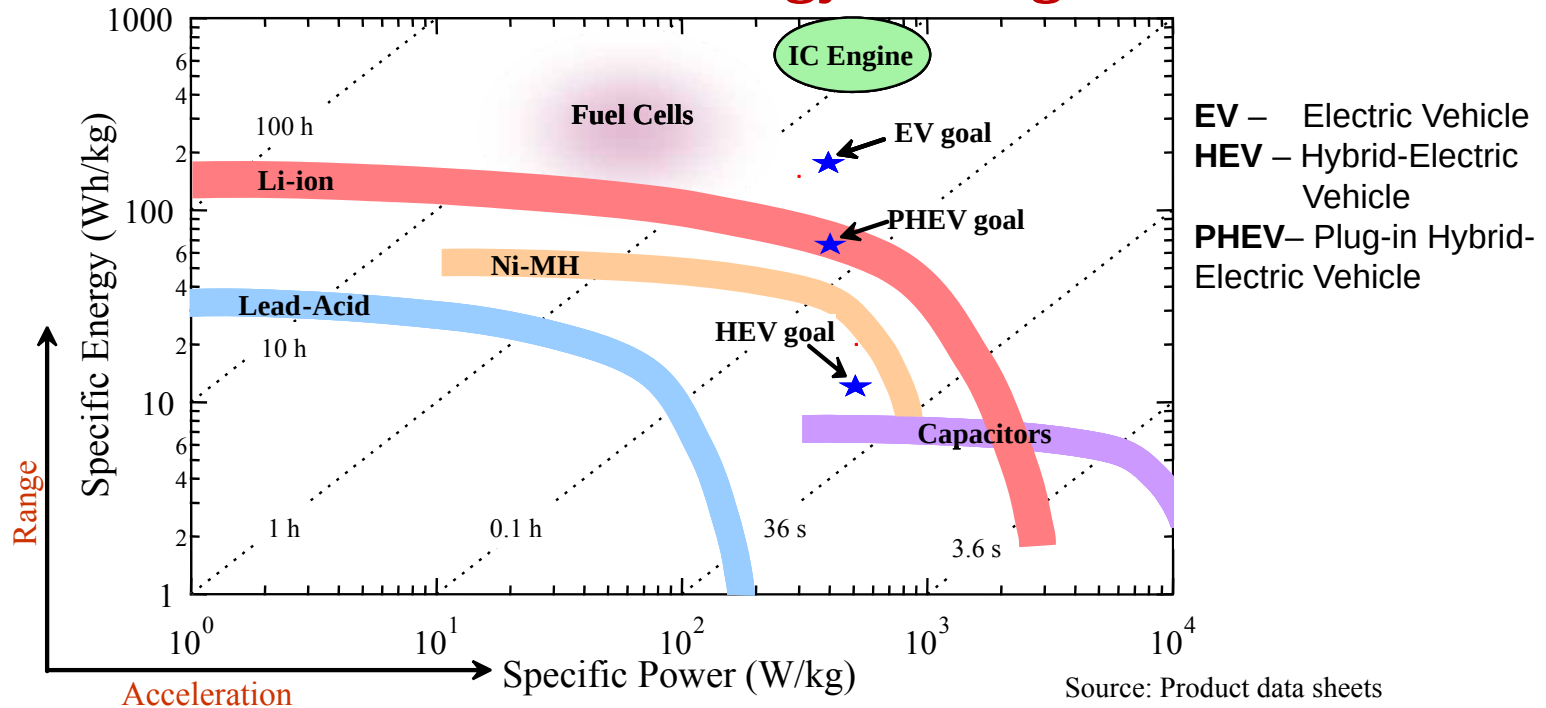
February 17th, 2009

Ascend v. Duesenfeld
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Ex. 2002-001

Outline

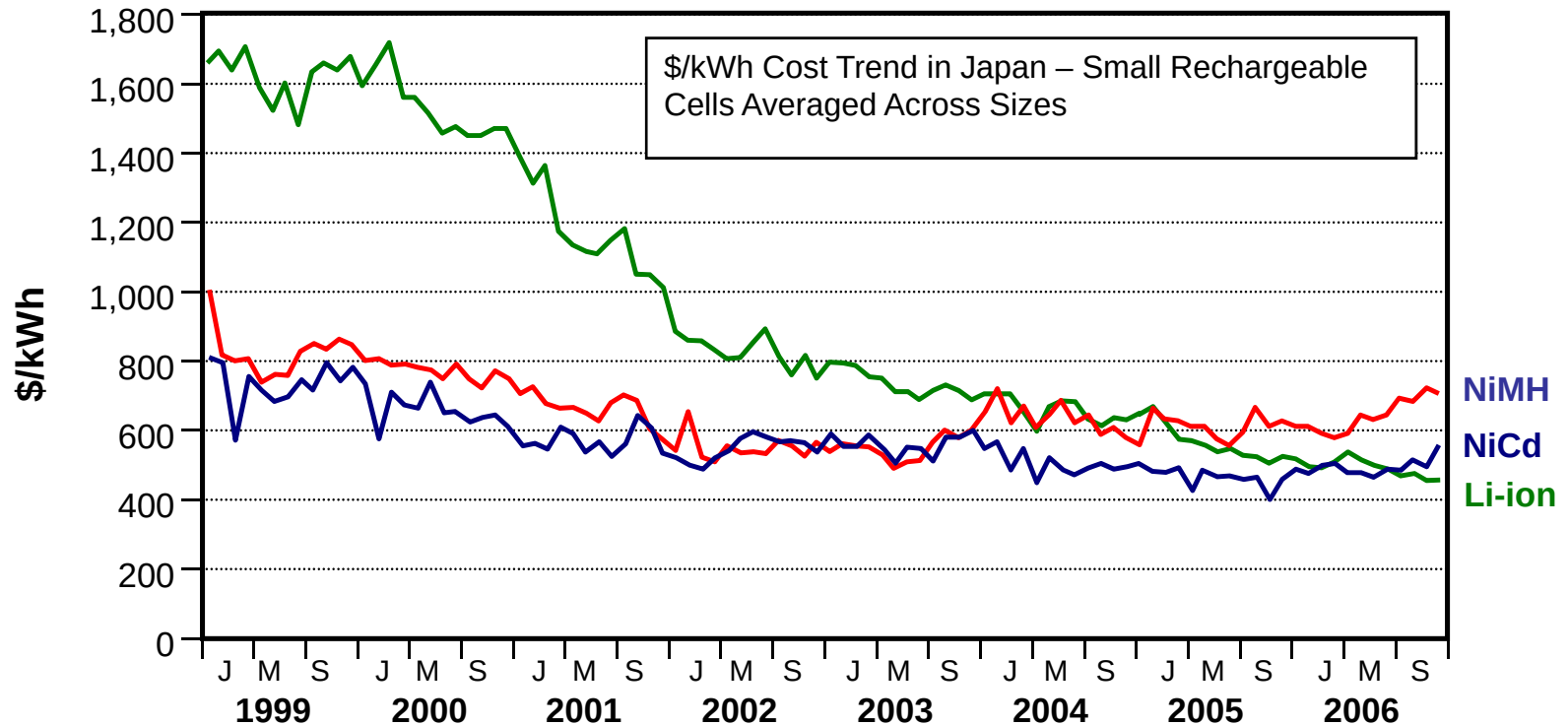
- A introduction to Lithium-ion battery.
 - Energy vs. Power.
 - Cost.
 - Structure.
 - Cathode and anode performance.
 - Cell performance improvement.
- Cathode electrode optimization.
 - Three components cathode – a polymer composite.
 - Acetylene black and polymer binder as conductive glue.
 - The mathematic modeling of the electrode electronic conductivity – the nano-scale interaction between PVDF and particles.
 - The cell performance governed by the interaction.

Relative Performance of Various Electrochemical Energy-Storage Devices



- Goals developed in cooperation with DOE and United States Advanced Battery Consortium (USABC) under the FreedomCAR partnership
 - USABC is a cooperative of major automotive manufactures
- Li-ion batteries have higher performance compared to Nickel-metal hydrides batteries. However, research is needed to simultaneously address the life, cost, and abuse tolerance issues

Cost of Consumer Electronics Batteries



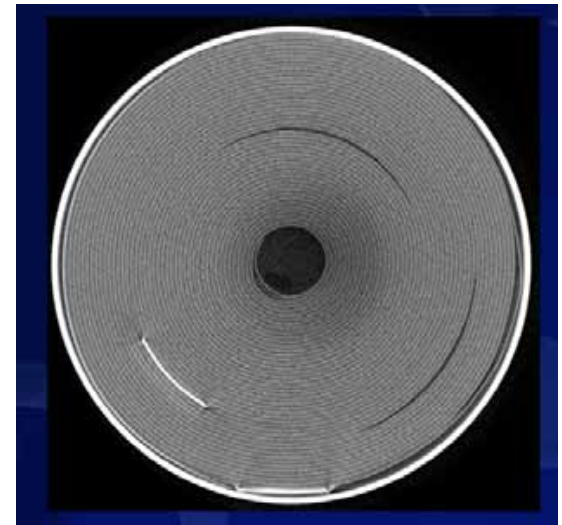
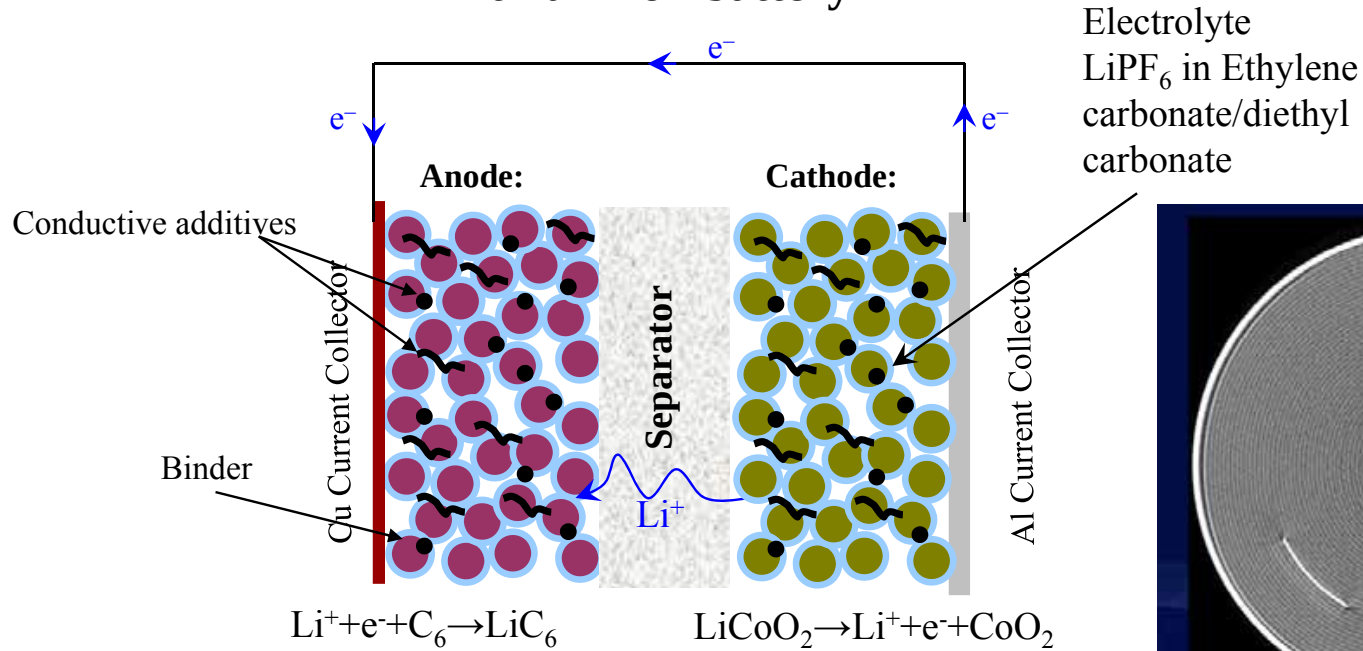
Source: U.S. DOE

Source: TIAX, based on METI data

Performance and cost drivers for Li-ion cells
However, numerous problems remain before use in vehicles

Modern Li-ion Battery

Lithium-ion battery



Innovation can occur via
new material development,
or by better engineering



A commercial Lithium-ion Rechargeable 26650 Cell



Open from the anode side



Anode crimped closed

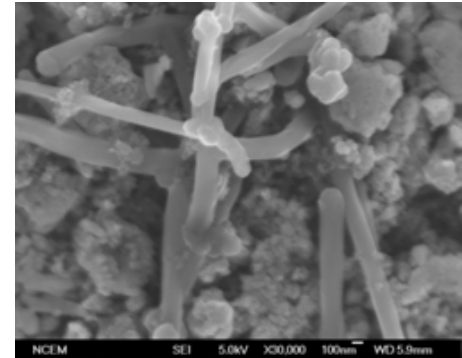
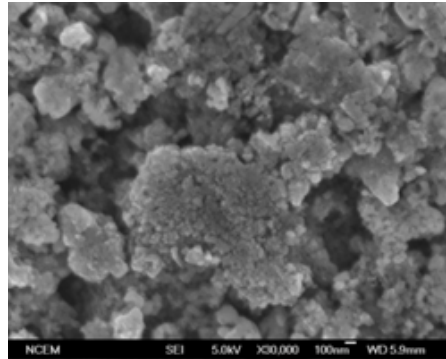
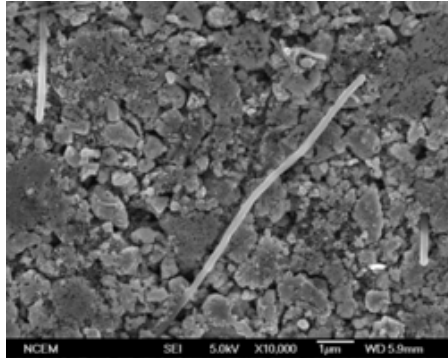


Cathode side of the jelly roll

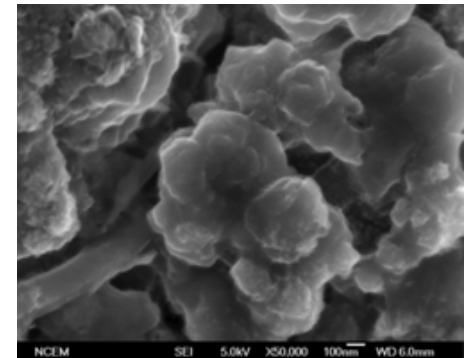
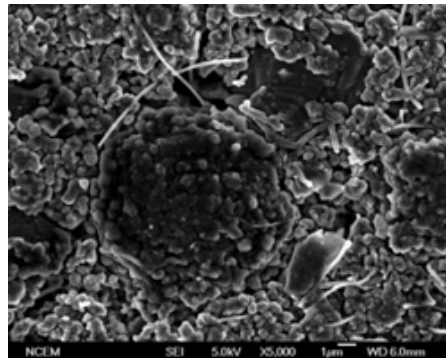
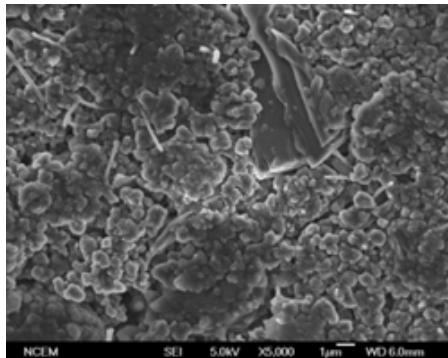


Open up the jelly roll

SEM Images of Cathode and Anode Surfaces

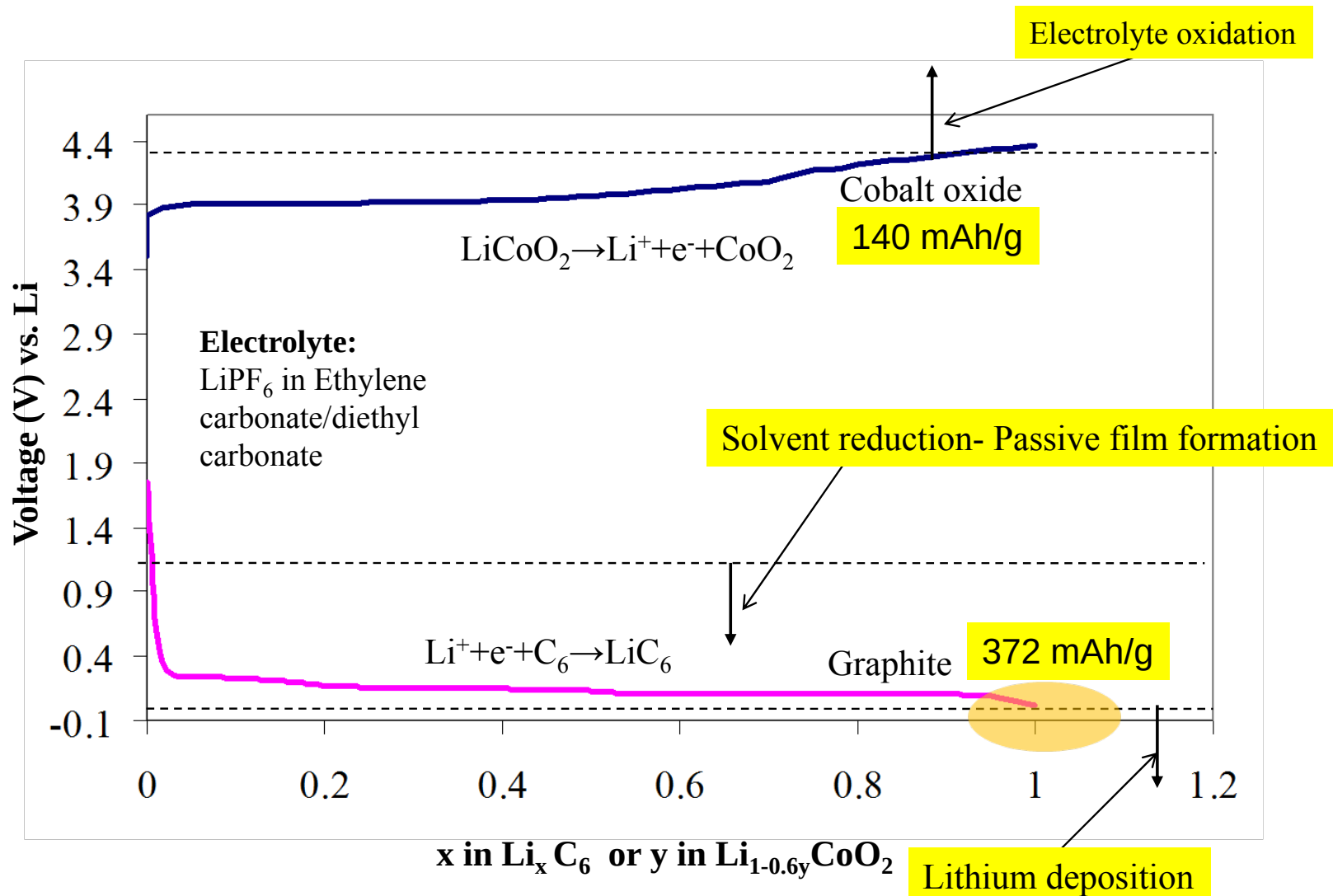


Cathode

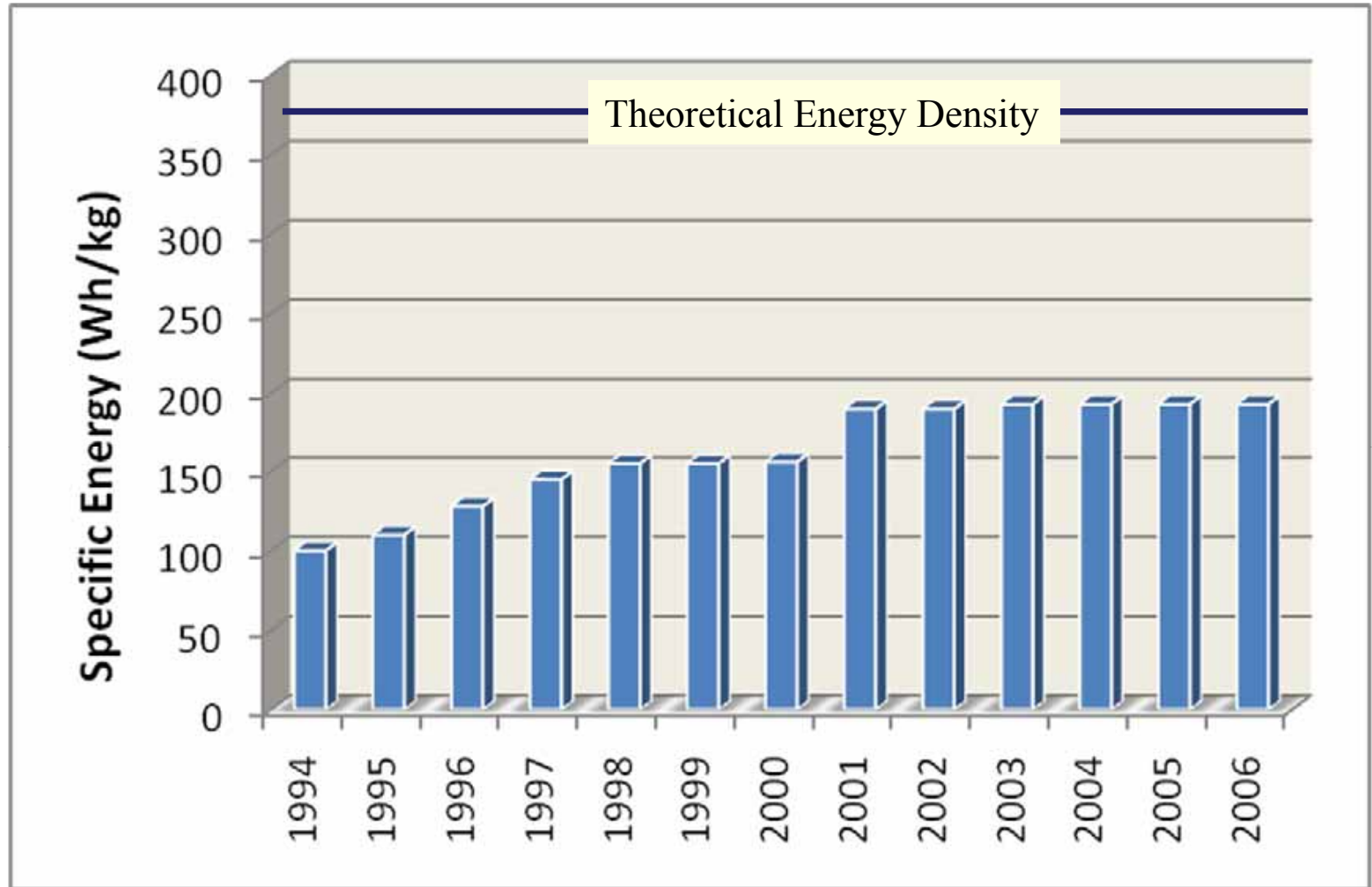


Anode

Cycling of a Graphite-LiCoO₂ Cell



Energy Density Increase of Consumer Electronic Li-ion Batteries

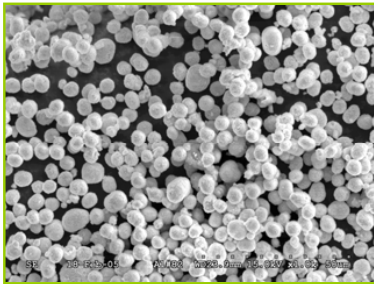
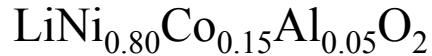


Source: TIAX, LLC

Duesenfeld Ex. 2002-009

Complete Cathode Electrodes

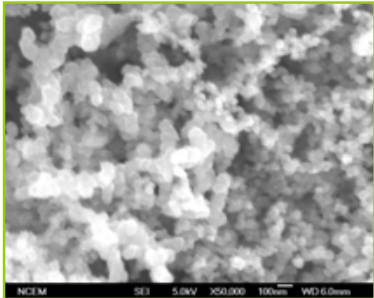
Materials



Ave. diam.: 10 μm
Surface area: 0.78 m²/g

Scale bar: 10 μm ■

Acetylene black (AB)



Ave. diam.: 50 nm
Surface area: 60.4 m²/g

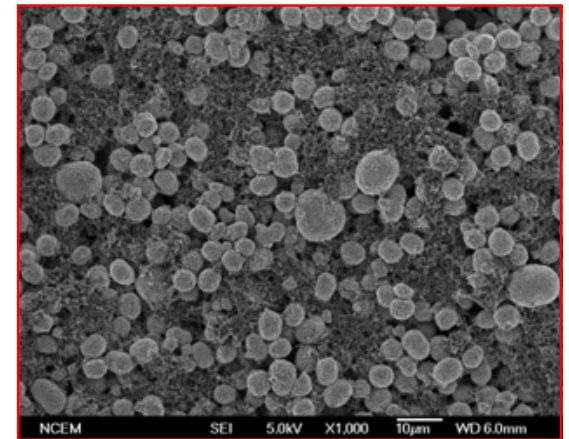
Scale bar: 100 nm ■

PVDF

Polymer Binder

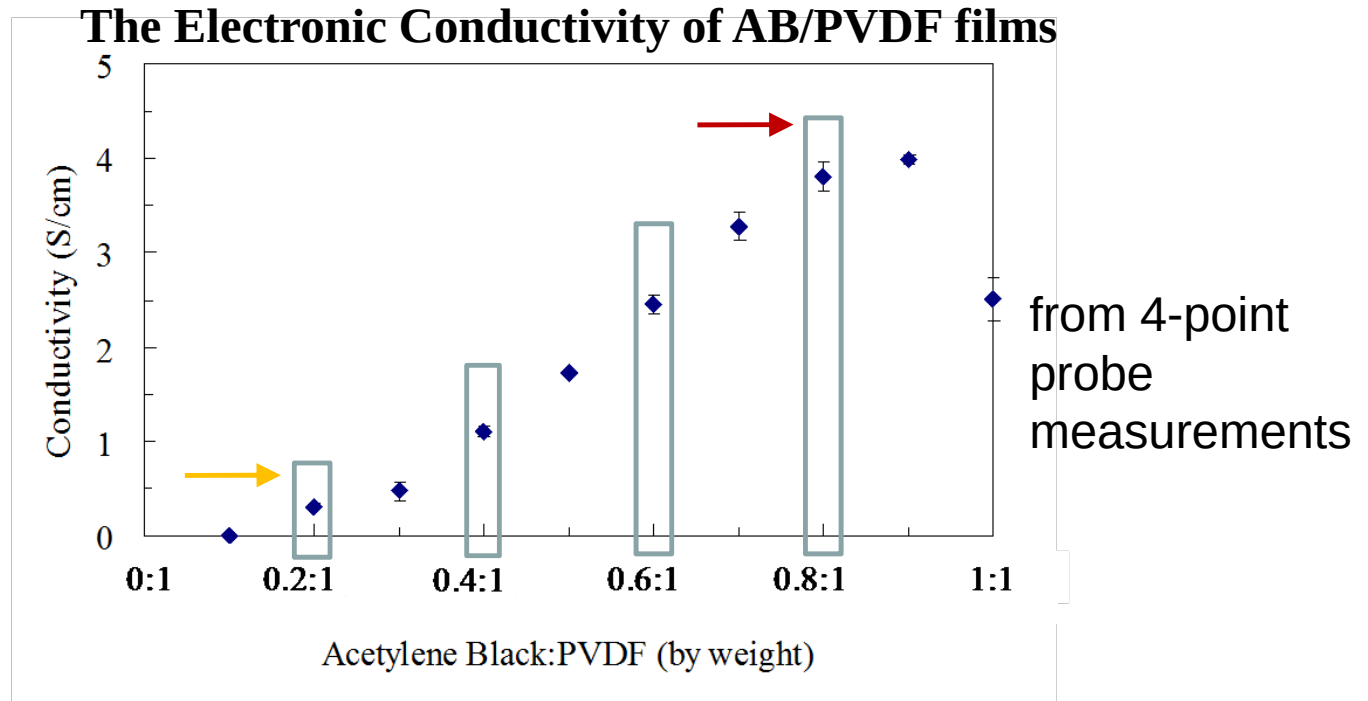
Molecular weight: 760,000

Electrode



Scale bar: 10 μm ■

Laminates without Active Material

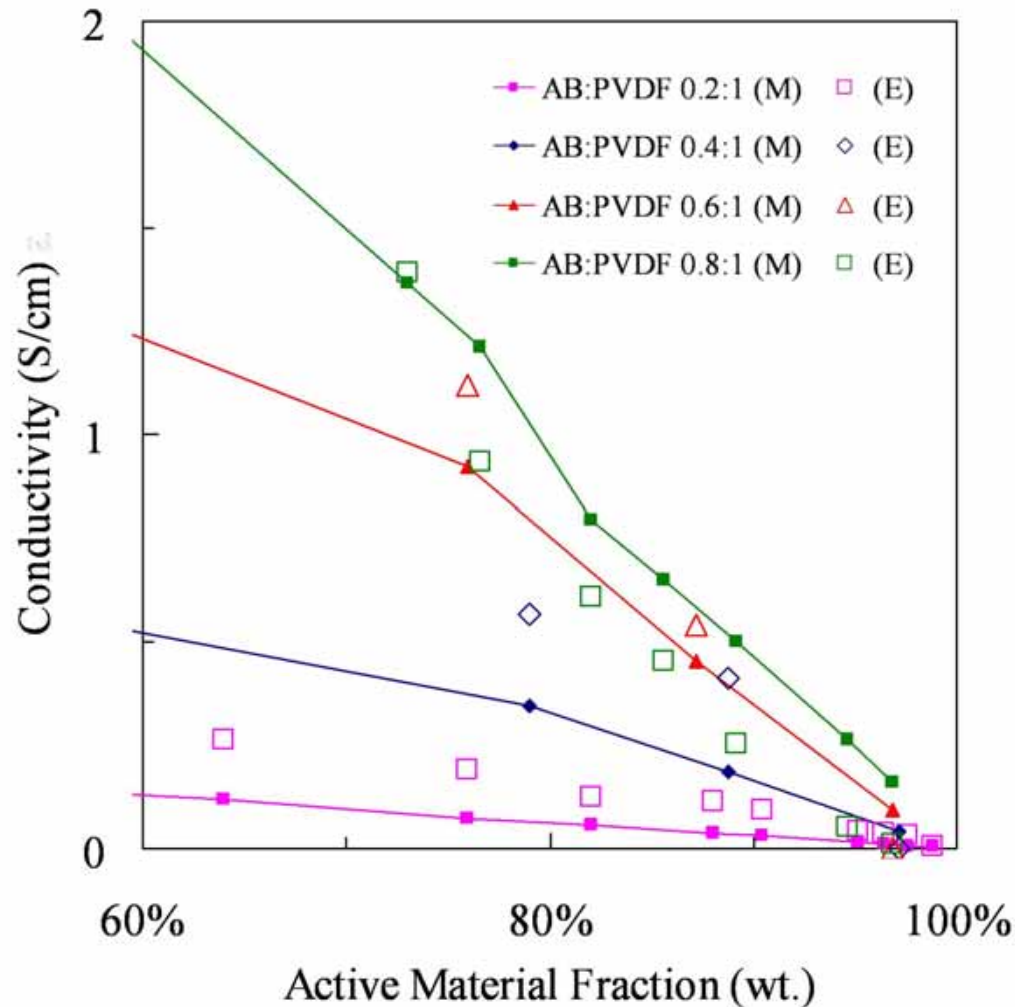


$\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$ /Graphite Cells

AB:PVDF	(AB+PVDF)% in the cathode electrode
Most conductive → 0.8:1	3.6%; 9%; 18%; 27%
Least conductive → 0.2:1	1.2%; 2.4%; 4.8%; 9.6%; 24%
0.4:1	2.8%; 11.2%; 21%
0.6:1	3.2%; 12.8%; 24%

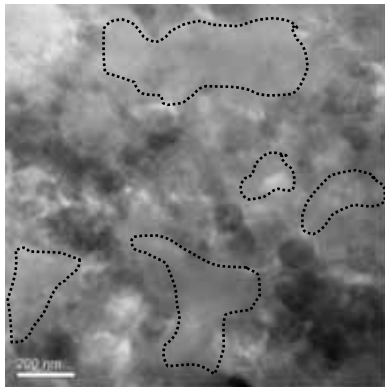
The Modeling Results of Active material/AB/PVDF

$$k_{eff} = \varepsilon^p * k_0(AB/PVDF)$$



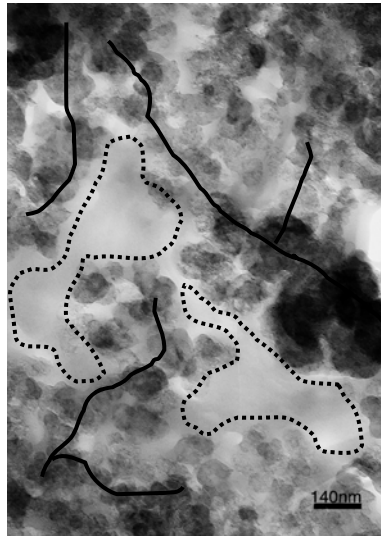
TEM Images of the Morphology of AB/PVDF Conductive Matrix

AB:PVDF = 0.2:1 (w/w)



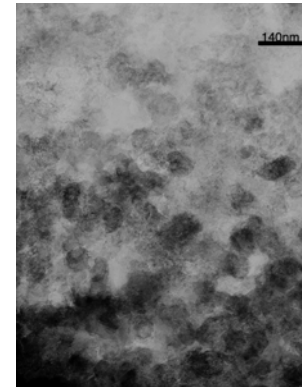
200 nm

0.5:1



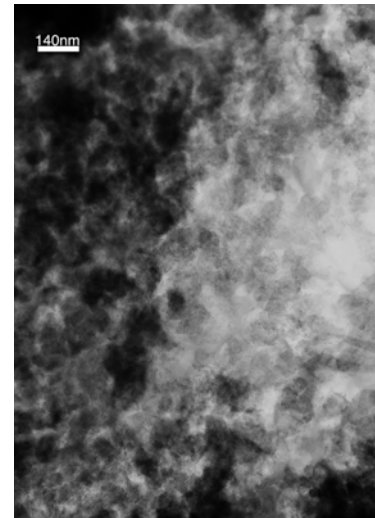
140 nm

0.8:1



140 nm

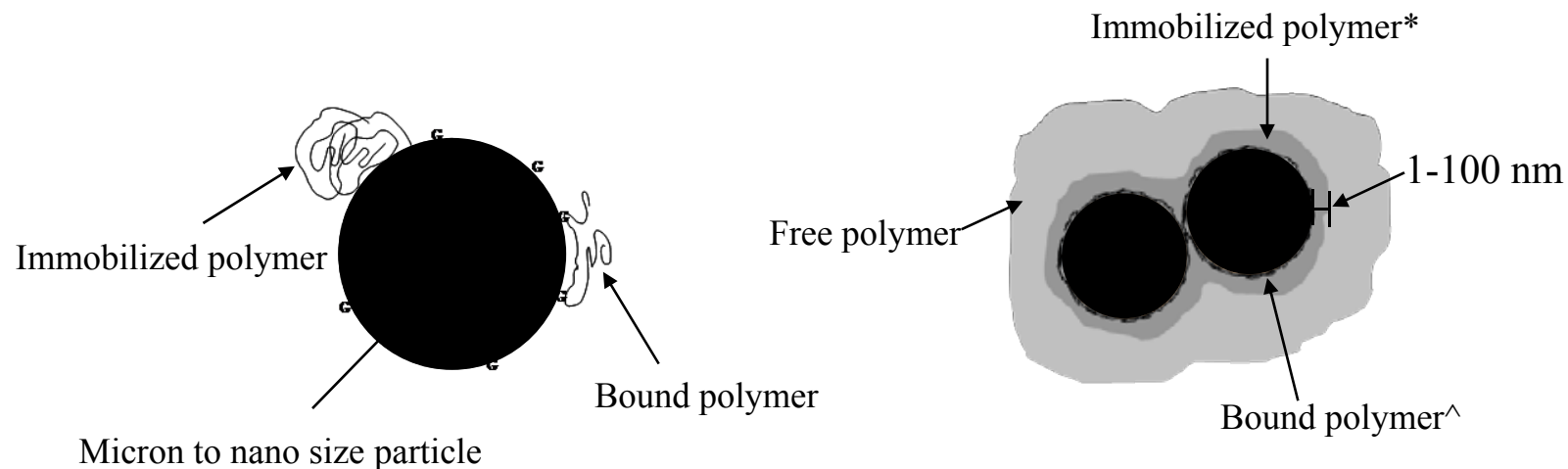
1:1



200 nm

Scale bar

Three Different States of Polymer When in Contact with Particles

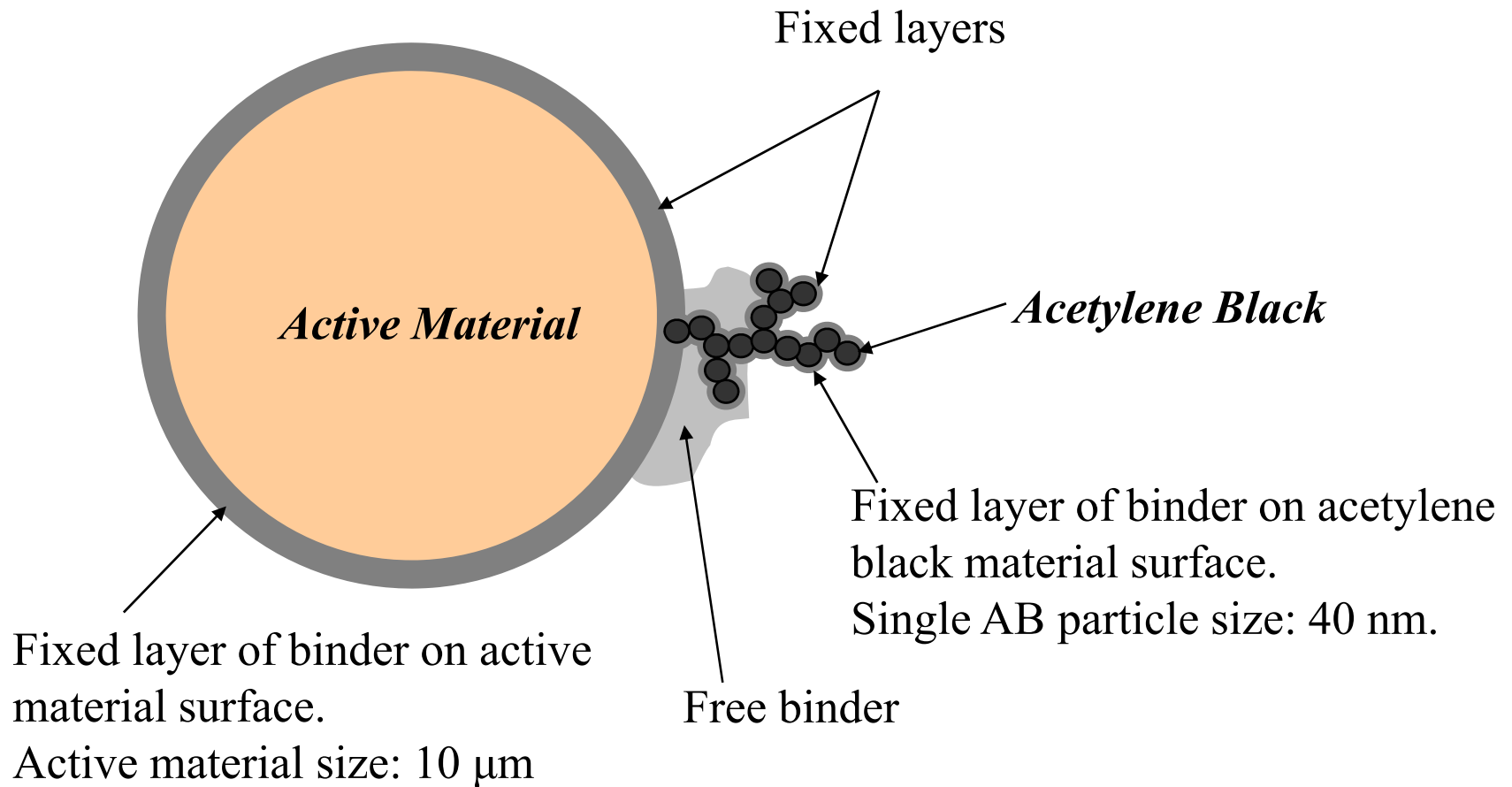


Bound polymer layer and immobilized polymer layer form Fixed Layer on the surface of particles.

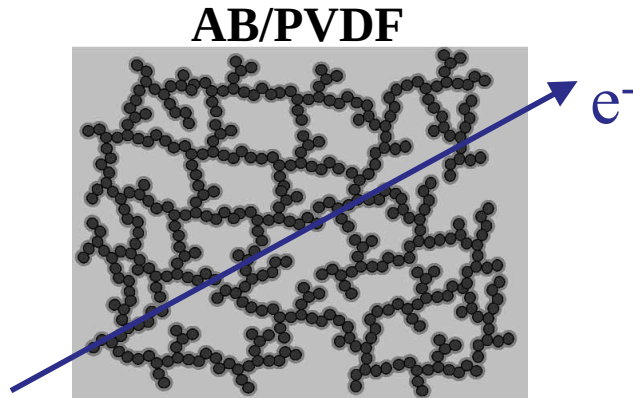
* Dannenberg, E. M., Polymer, 14, 309 (1973)

^Westlinning, H and Butecnuth, G., Makromol. Chem., 47, 215 (1961)

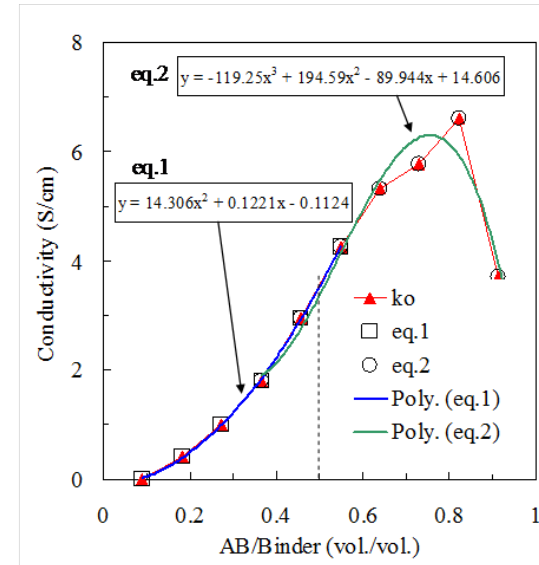
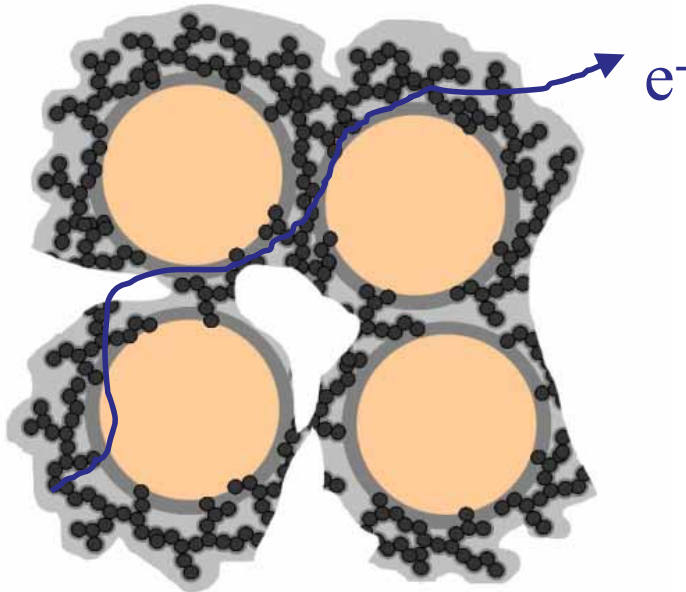
Cathode Material vs. Acetylene Black Particles



Matrix Conductivity of the Electrode Reflects the Competition for Binder between AB and Active Materials



AB/PVDF/Active material



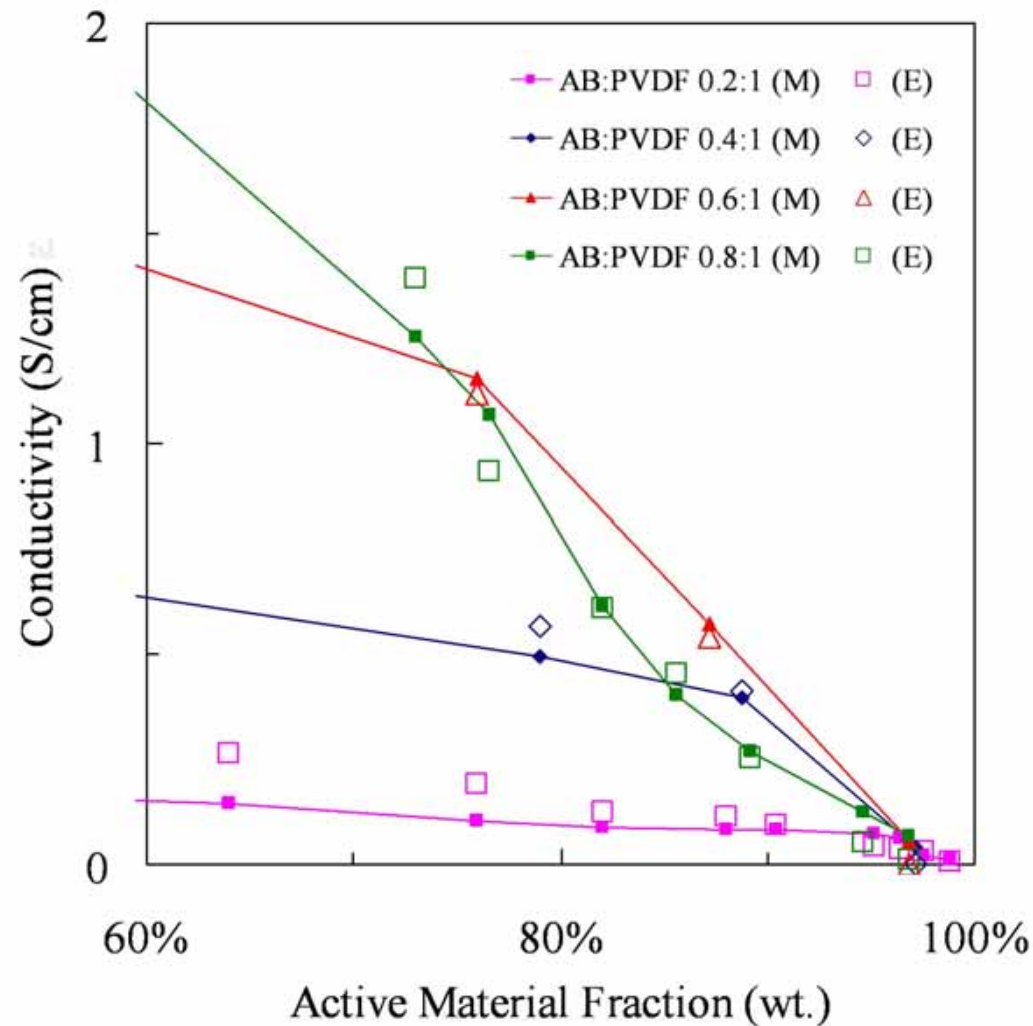
from
AB/PVDF
films

$$k_0 = f(AB/PVDF)$$

$$k_{eff} = \epsilon^p * k_0(AB/PVDF')$$

*PVDF' = PVDF - cathode particle
immobilized PVDF*

A Model and Experimental Comparison of the Conductivities Active Material/AB/PVDF

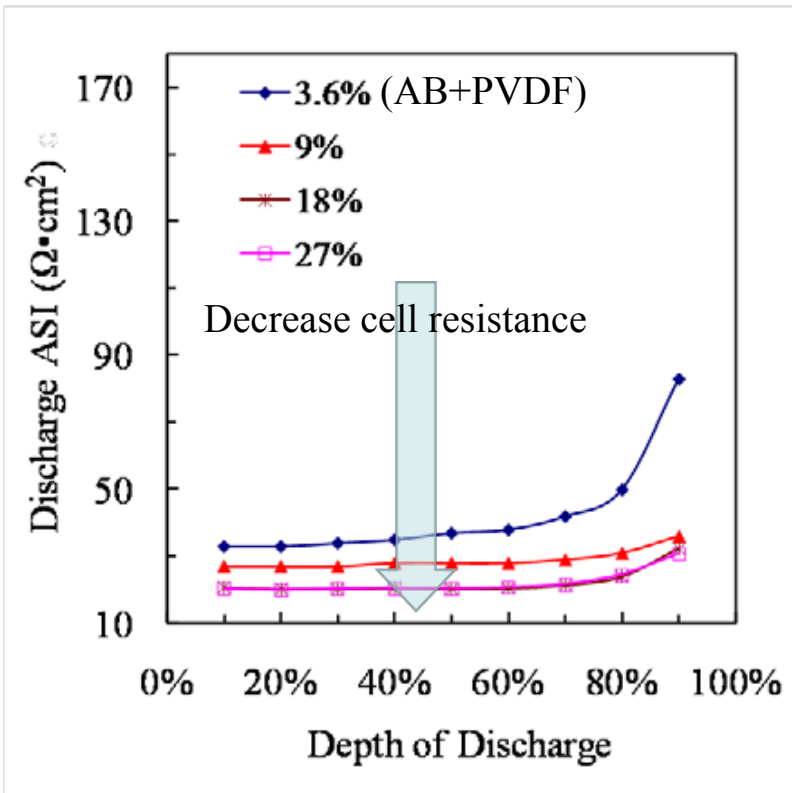


Complete Cells

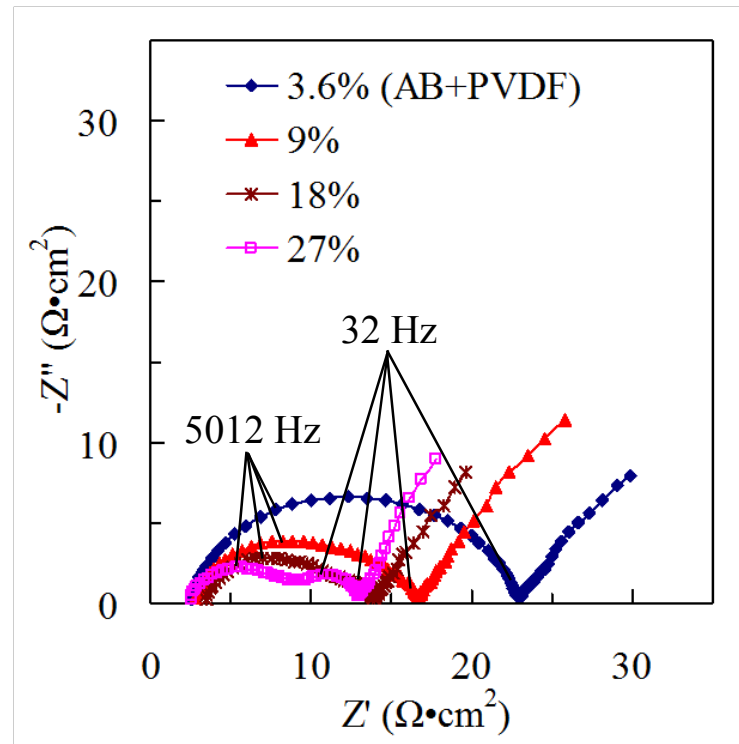
$\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2/\text{Graphite Cells}$

AB:PVDF = 0.8:1 (Most Conductive)

HPPC Test



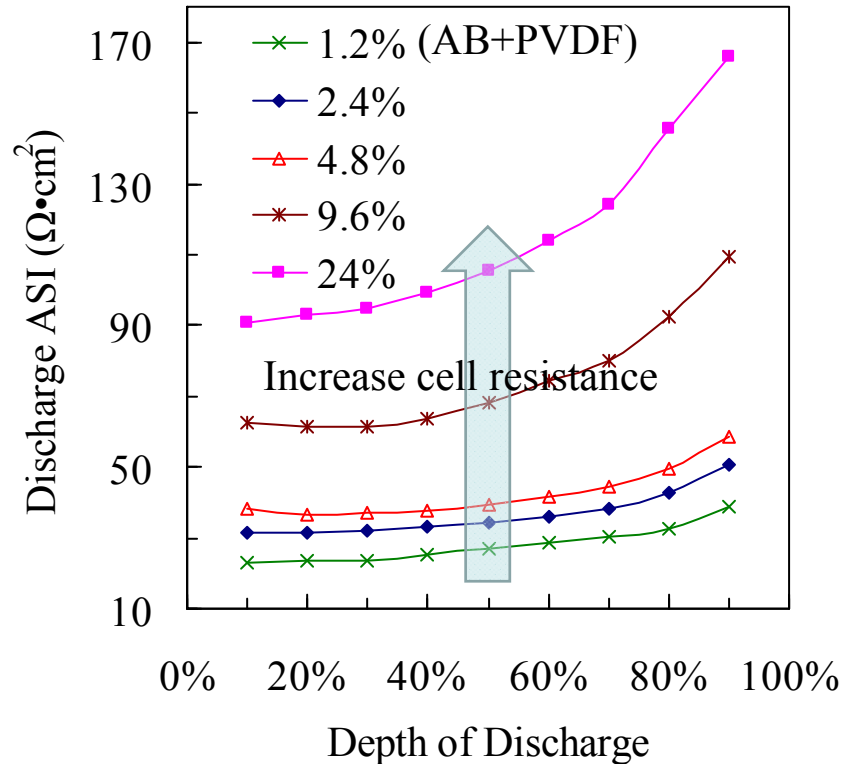
EIS at 40% DOD



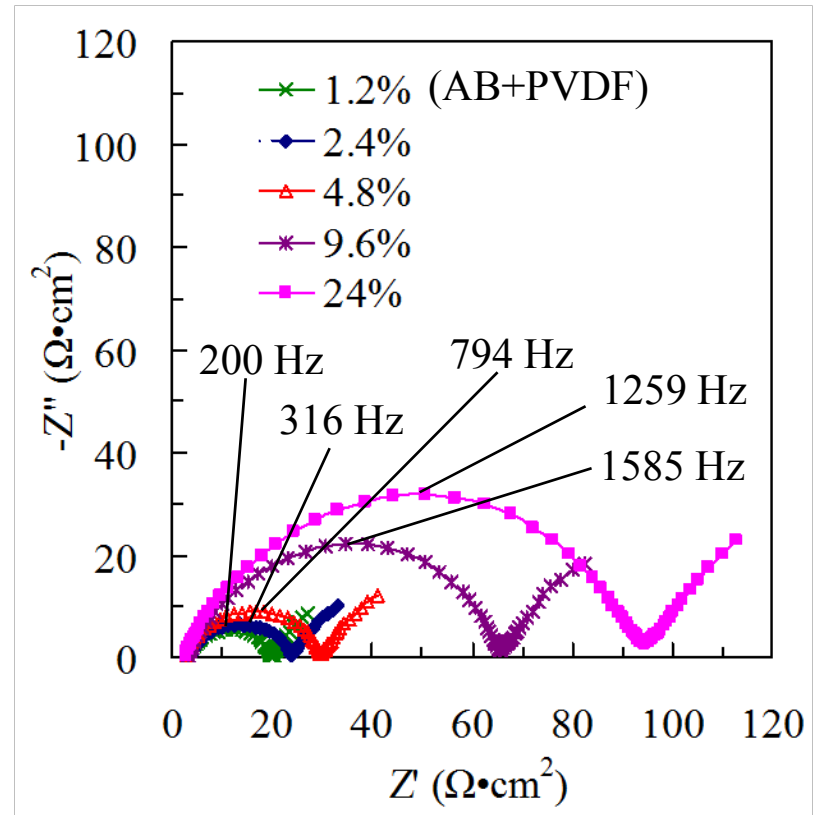
$\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2/\text{Graphite Cells}$

AB:PVDF = 0.2:1 (Least Conductive)

HPPC Test



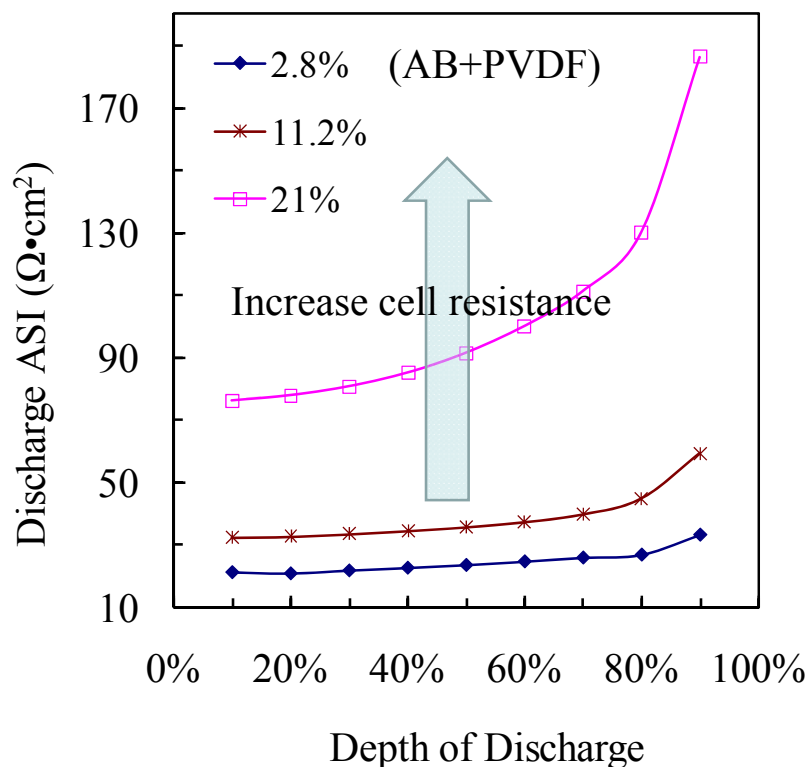
EIS at 40% DOD



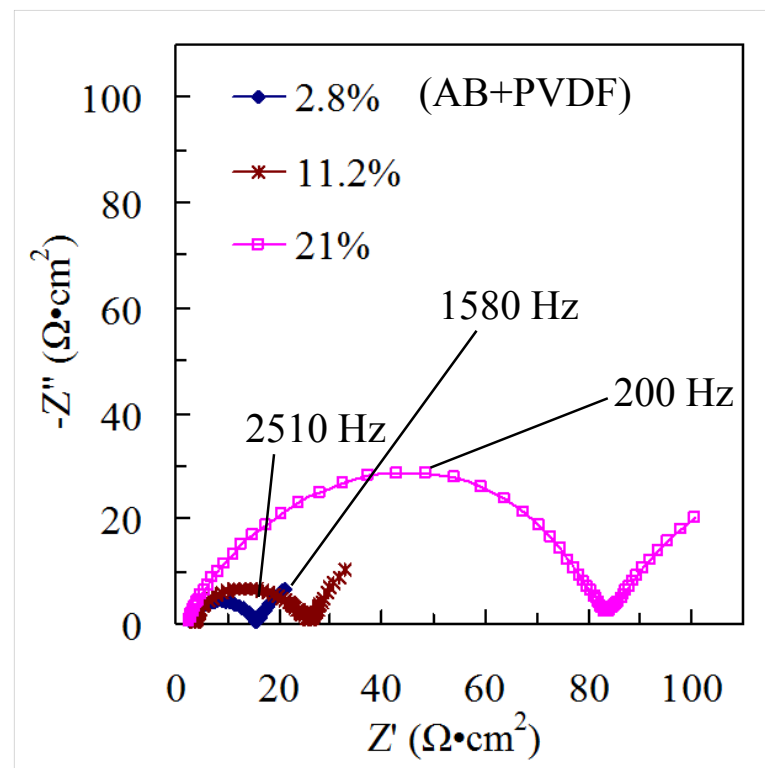
$\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2/\text{Graphite Cells}$

AB:PVDF = 0.4:1

HPPC Test



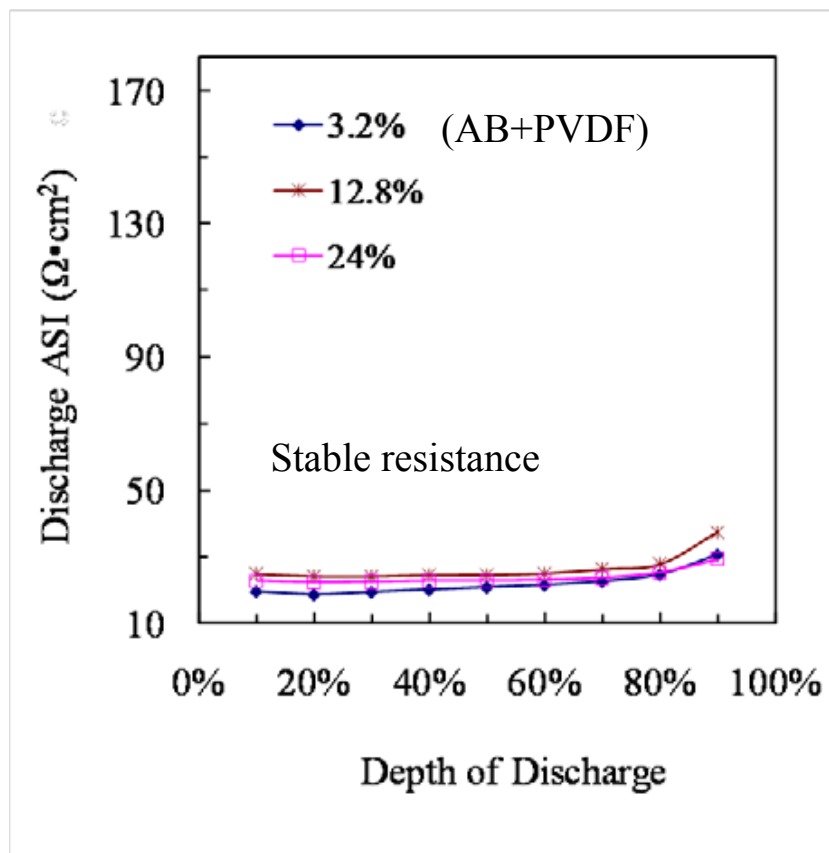
EIS at 40% DOD



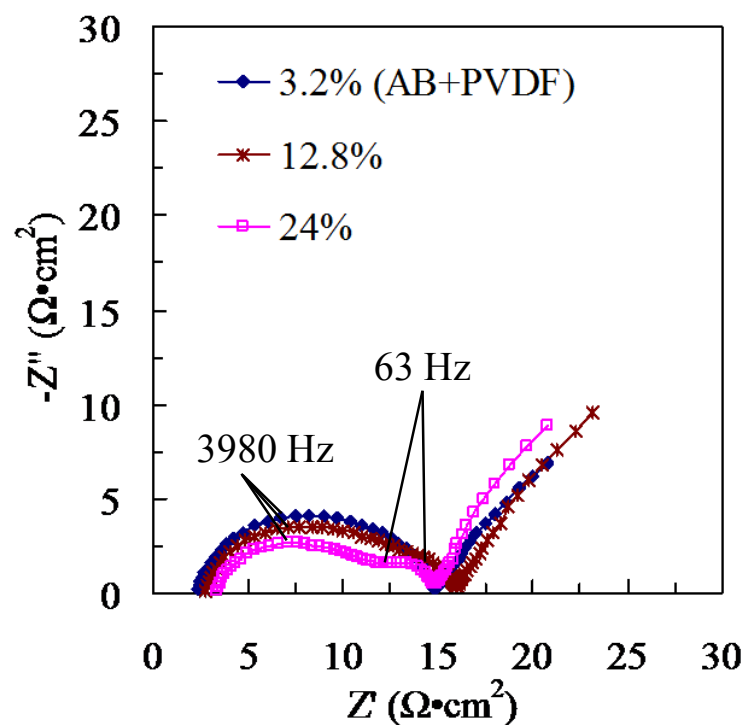
$\text{LiNi}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2/\text{Graphite Cells}$

AB:PVDF = 0.6:1

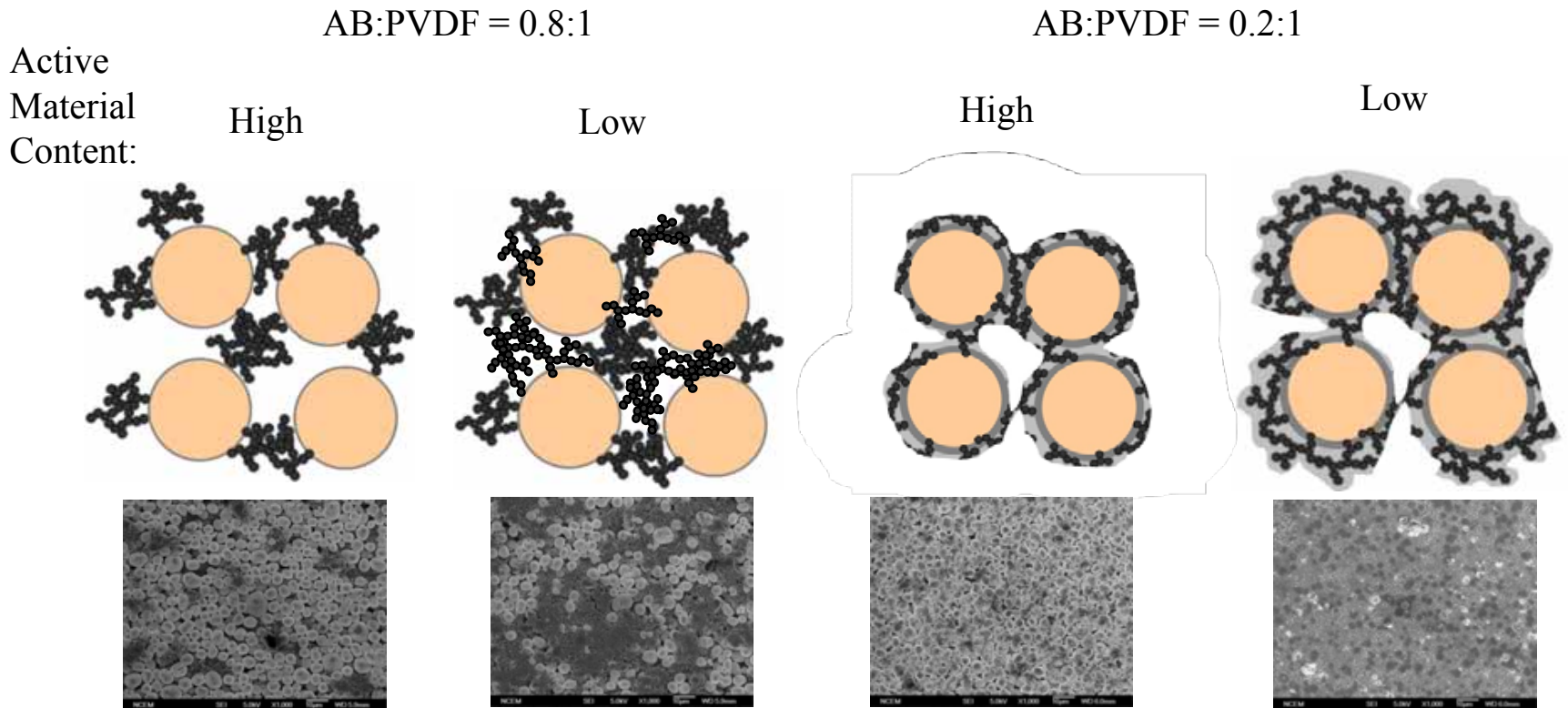
HPPC Test



EIS at 40% DOD



The Distribution of Binder, AB, and Active Material at Different Combinations



Electronic Conductivity:



Small Change



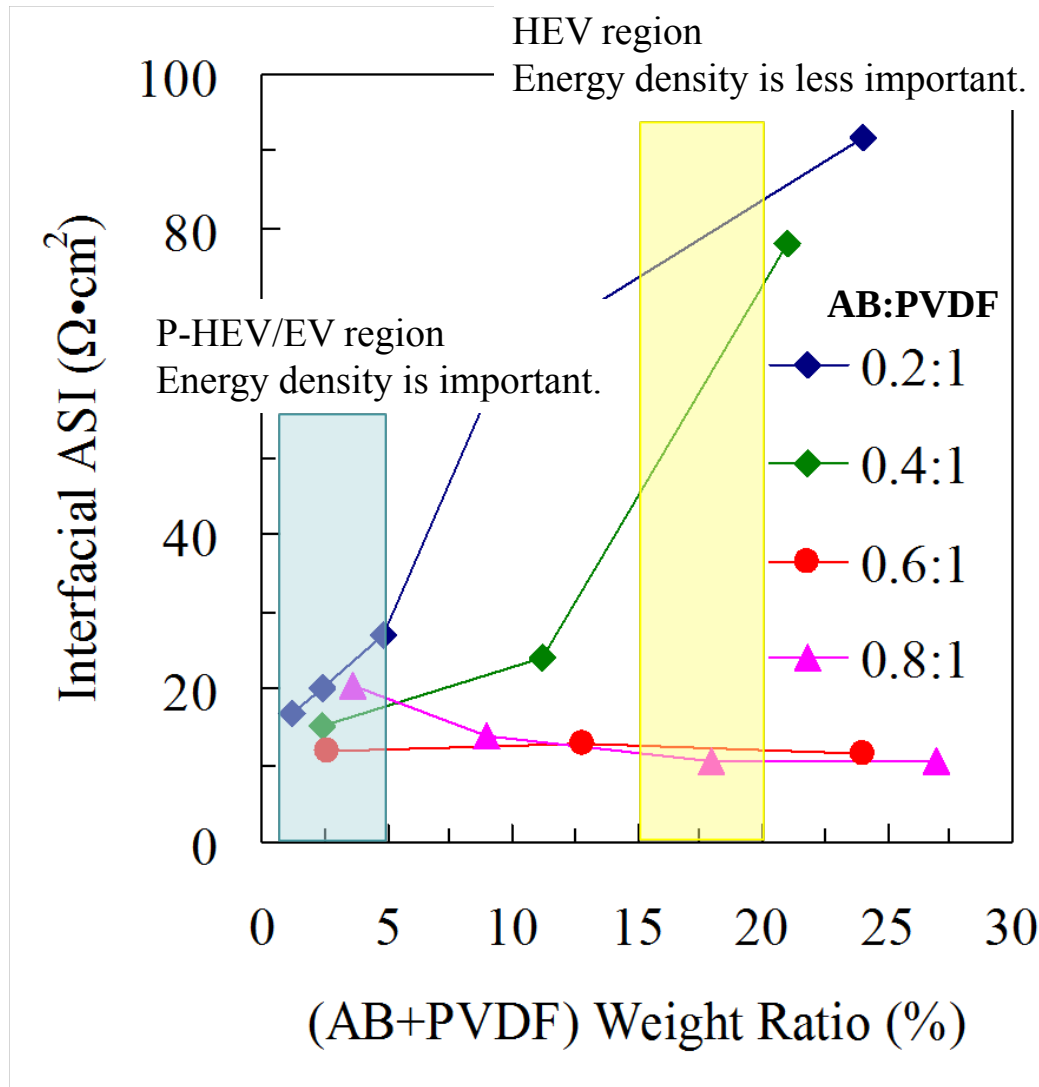
Small Change

Interfacial impedance of the electrodes:



Duesenfeld Ex. 2002-022

The Interfacial Impedances of All Compositions



Conclusions

- The amount of binder plays critical role in the composite electrode beyond providing mechanical integrity.
- The binder to conductive carbon ratio dictates the electronic conductivity of the laminate. The addition of active material alters the ratio through competition for the binder.
- The electronic conductivity of a laminate appears to be reflected in the charge transfer capability of the laminate.
- High acetylene black content, such as AB:PVDF $> 0.8:1$, tends to produce electrodes with lower electronic conductivity and higher charge transfer at high active material loadings.
- Low acetylene black content, such as AB:PVDF $< 0.4:1$, tends to produce electrodes with higher electronic conductivities at high active material loadings.

Acknowledgments

- Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies of the U.S. Department of Energy. Contract # DE-AC03-76SF00098.
- Electron microscopy performed at the National Center for Electron Microscopy, Lawrence Berkeley Lab, U.S. Department of Energy. Contract # DE-AC02-05CH11231.
- Toda American for the NCA Material.
- Denka Japan for the acetylene black conductive additive.

Thank you for your attention!

End