Accelerated Cell Aging

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Introduction

Batteries for hybrid electric vehicles are being developed by many companies. The US Department of Energy established the Advanced Technology Program to help the industrial developers overcome key barriers to commercialization. Among these are life, safety and cost.

Challenges

Lithium-ion batteries have found uses in many consumer electronics. The batteries generally consist of a lithium metal oxide cathode, a liquid organic solvent containing a dissolved ionic salt, and a lithiated, carbon-based anode. The U.S. Department of Energy's FreedomCAR Partnership (formerly Partnership for a New Generation of Vehicles, or PNGV) and others are also evaluating this class of batteries for use in hybrid-electric vehicles. For this use, the batteries must exhibit 23% power fade or less over 15 years. However, during their lives, our cells show impedance increase and, hence, power fade. Thus, achieving the 15-year-life goal remains a challenge.

Argonne's Approach

Use accelerated calendar- and cycle-life testing to study batteries having two different cell chemistries

- Expedited, cost-effective results
- Data used to model changes

Cell Chemistries

Group A

Positive Electrode:	Negative Electrode:
8 wt% PVDF binder 4 wt% SFG-6 graphite 4 wt% carbon black 84 wt% $LiNi_{0.8}Co_{0.15}Al_{0.05}O_2$	8 wt% PVDF binder 92 wt% MAG-10 graphite
Electrolyte: 1.2 M $LiPF_6$ in EC/EMC (3:7 by wt)	Separator: 25 µm thick PE Celgard separator

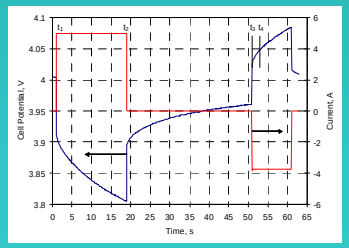
Group B: same as Group A except the cathode consists of $LiNi_{0.8}Co_{0.10}Al_{0.10}O_2$

Test Conditions and Types of Tests Conducted

Temperature, °C	25, 45, 55
State of Charge, %	60
Measurement Frequency	4 weeks
Calendar Life Tests	Pulse per day
Cycle Life Tests[1]	Scaled 25-Wh PNGV profile

Sealed 18650-size cells were used to evaluate the cell chemistries

Impedance Measured Using HPPC Test



Discharge current = 5C $R_d = \Delta V / \Delta I = (V_{11}-V_{10})/(I_{11}-I_{10})$

$P_d = 3.075(OCV-3.075)/R_d$

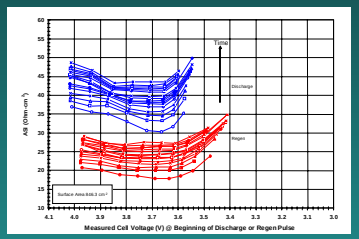
End of life; cell can't perform 6th HPPC pulse

[1]Cycle life data from Jon Christophersen and Kevin Gering, Idaho National Laboratory

Results

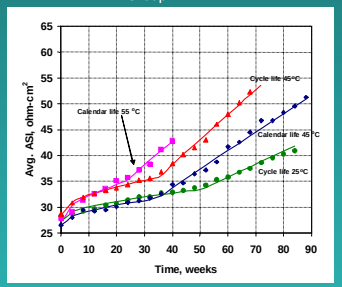
- Elevated temperatures shortened cell life
- Cycling tended to shorten cell life
- Two impedance-increase mechanisms were observed in both cell groups
- High Al content tended to increase initial cell area-specific impedance (ASI) and to increase initial rate of ASI increase; later on, the high-Al-content cells exhibited a slower rate of ASI increase

Typical HPPC Results

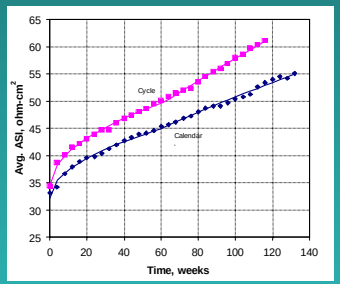


ASI at 60% SOC

Group A



Group B



Modeling of Results

- All data were fit to the nonlinear equation, $ASI = ASI_0 + at^{1/2} + c(t-t_0)$, where ASI_0 is the ASI at t=0; a, c and t_0 are constants; and c=0 when $t < t_0$
- The regression coefficients (r^2) were greater or equal to 0.99
- Effect of cathode composition, test type and temperature are clearly seen

	Values			
	a	c	ASI_0	t_0
Group A cycle life 25°C	0.85	0.14	27.34	44.30
Group A cycle life 45°C	1.23	0.40	28.46	35.15
Group A calendar life 45°C	0.89	0.30	26.44	34.48
Group A calendar life 55°C	1.63	0.31	27.04	22.78
Group B calendar life 45°C	1.64	0.05	32.16	59.70
Group B cycle life 45°C	1.96	0.10	34.44	62.60

Conclusions

- Impedance rise was sensitive to temperature and test type
- Impedance rise was sensitive to the Al concentration. The 10% Al-doped cells displayed higher impedance rise at 45°C than the 5% Al-doped cells early in life and slower impedance rise later in life
- The time-dependence of the impedance rise displayed two distinct kinetic regimes; the initial portion depended on $t^{1/2}$ and the latter portion on t
- In cells with 5% Al in the cathode, the change in mechanism from $t^{1/2}$ to t occurred at about 35 weeks. Increasing the aluminum concentration to 10% delayed the change for about an additional 30 weeks. The factors affecting the rate of increase during the parabolic and linear portions of the curve depend on cathode composition.

Future Work

ANL has identified more stable advanced materials and is building cells to assess their impact on extending calendar life

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