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Improving Thermal Degradation Characteristics of $Li/(CF_x)_n$ Cells using Anion Binding Agent in the Electrolyte

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Outline

- Highest theoretical capacity/energy for Li/ $(CF_x)_n$ cells
- Electrolyte and electrode properties determine delivered capacity
- At high temperatures electrolytes degrade which reduces cell performance
- Develop new electrolyte to improving thermal stability
  - Add Anion-binding-agent (ABA) to the electrolyte to dissolve LiF
- Assemble coin cells
  - With $(CF_x)_n$ electrodes
    - Prepared and Coated at Sandia
  - Evaluate performance in
    - SNL ABA #3 electrolyte
    - SNL with $LiBF_4$ salt
    - HCE (Highly Conductive Electrolyte)
- Summary

$(CF_x)_n$ is an Attractive Candidate for Capacity Improvement

Chemistry	Voltage (V)	Specific Energy (Wh/kg) Theoretical	Practical
$Li/(CF_x)_n$	**3.2**	**2,260**	**220**
$LiMnO_2$	3.0	1,005	200-270
$LiSOCl_2$	3.6	1,470	320-480
$LiSO_2$	3.0	1,170	240

The low practical specific energy for the $Li/(CF_x)_n$ cells was observed at moderate discharge rates (> C/100). However, at a very low rate (C/1000) higher practical energy values (~35% of the theoretical) were observed.

Description of the Cathode

- This chemistry has solid cathode
- The equivalent weight for the $(CF_x)_n$ = 31 g
  - $(CF_x)_n$ has one of the lowest equivalent weights in primary battery chemistry.
- Capacity (mAhr/g) = 865

1 equivalent = 26.8056 Ahr.

Description of Discharge Reaction

A simplified scheme for the Li-$(CF_x)_n$ discharge reaction is given below:

$xLi \rightarrow xLi^+ + xe^-$ (anode reaction)

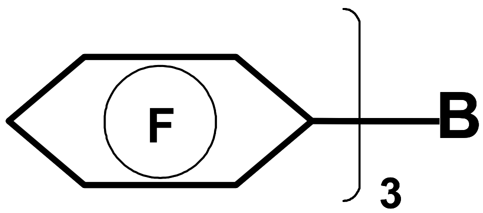
$xLi^+ + xe^- + CF_x \rightarrow C + xLiF$ (cathode reaction)

$xLi + CF_x \rightarrow xLiF + C$ (overall reaction)

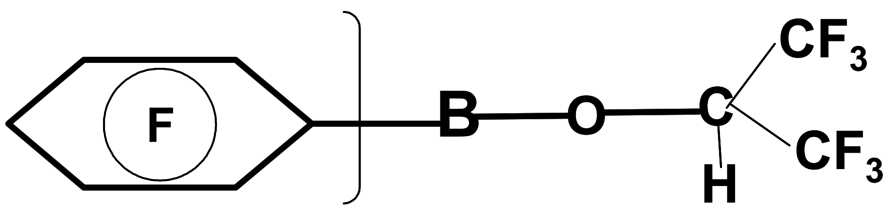
LiF is both an ionic and electronic insulator. However, it is both thermally and electrically stable. ABA allows the use of LiF itself as the salt.

Anion-Binding-Agent (ABA)

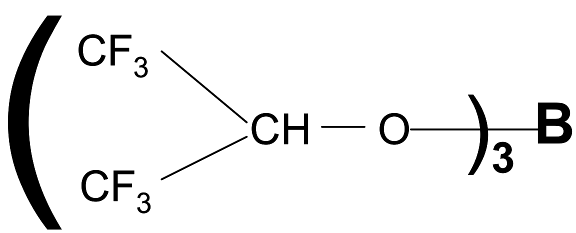
Dissolution of LiF with ABA may improve delivered capacity/energy.



ABA#1. Tris(Pentafluorophenyl) borane



ABA#2. 1,1,1,3,3,3-Hexafluoro isopropyl Bis(pentafluorophenyl)boronate)



ABA#3. Tris(1,1,1,3,3,3-hexafluoroisopropyl)borate

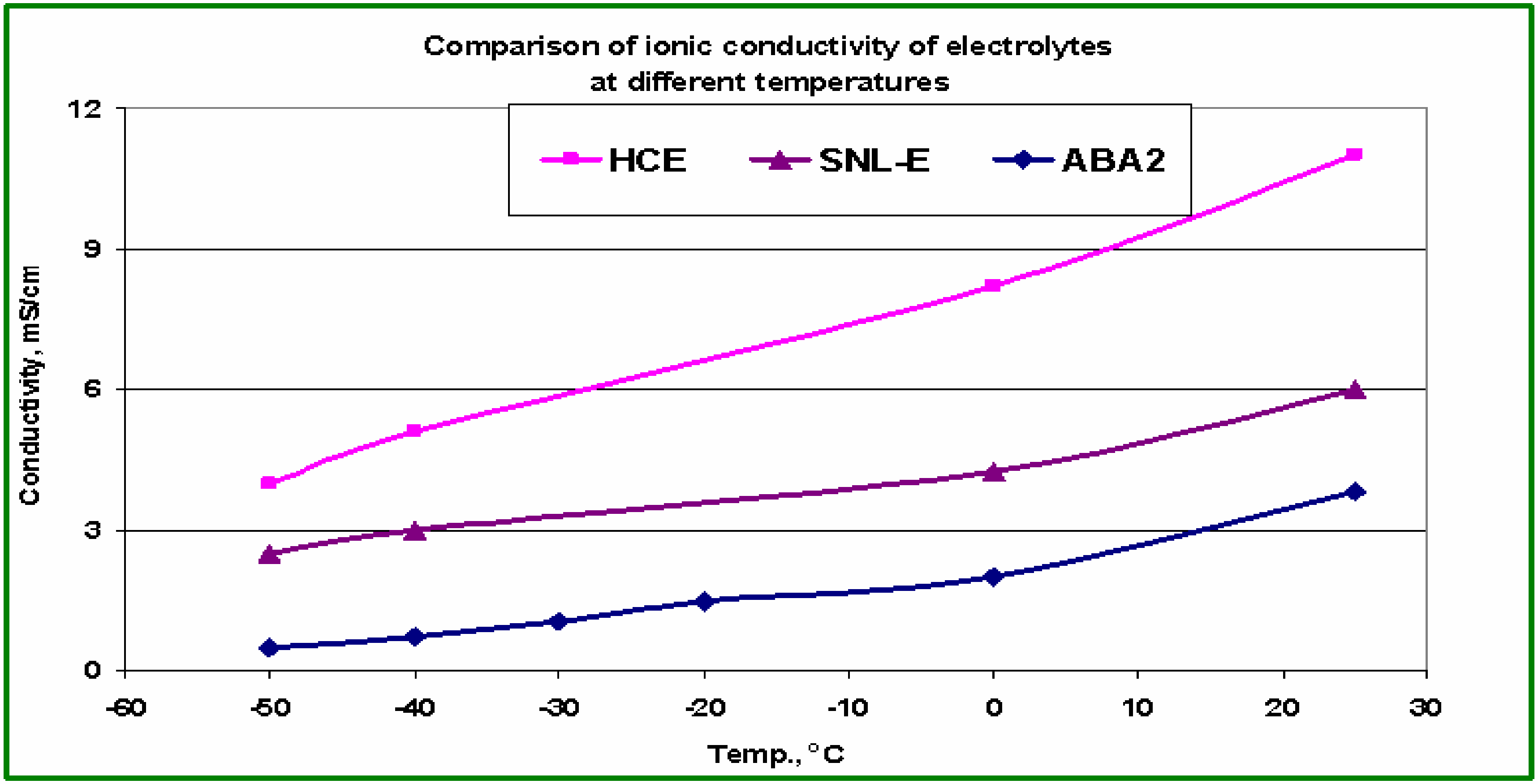
These were proposed by Mcbreen of BNL as candidates for dissolving LiF .
We took the cue from this work and are studying the benefits in Li/(CF_x)$_n$ cells.
Our initial testing of all the three ABAs #3 showed highest conductivity and cell performance. We continued to investigate ABA#3 only in our later studies.

Different Electrolytes were studied in cells and compared performance

- **The electrolytes consist of:**
  - **EC,PC and EMC(1:1:3 w%) 0.8 M LiF and 1.2 M ABA#3 (ABA2)**
  - **EC,PC and EMC(1:1:3 w%) 1 M $LiBF_4$ (SNL-E)**
  - **High Conductivity Electrolyte (HCE) consists of EC: EMC (3:7 w%) /1.2 M LiPF6.**

- **EC= Ethylene Carbonate; PC = Propylene Carbonate; EMC = Ethyl Methyl Carbonate**

Conductivity of electrolytes at different temperatures



The conductivity of our electrolyte is high but lower than the more advanced electrolytes used in Li-ion cells.

Impact of Electrolyte Salt on Cell Performance

- **High ionic conductivity improves rate capability especially at low temperatures. However, cannot improve safety or support long-life especially at high temperatures without good thermal stability characteristics.**
- **A comparative thermal stability of the conventional electrolyte salts* ranks in the following order:**
  - **$LiAsF_6 > LiBF_4 > LiPF_6$**
- **We have** also shown that after storing the electrolyte containing $LiPF_6$ at elevated temperatures the salt undergoes discoloration.**
- **These poor thermal properties will affect cell performance**
- **Development of a thermally stable salt is essential for a long-life power source.**

**J.T Dudley, et al J. Power Sources 35, 59-82 (1991)*

*** Sandia data*

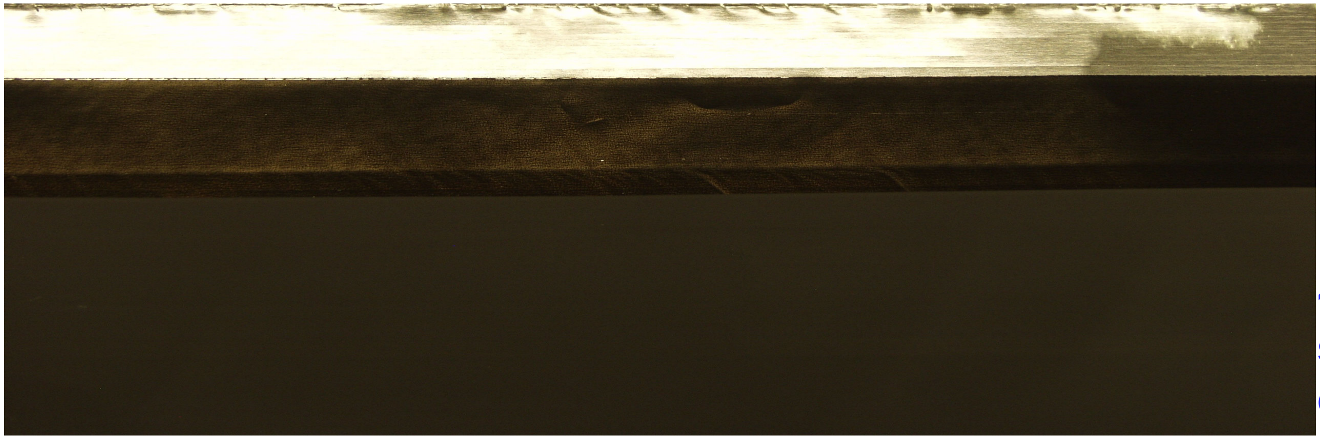
$(CF_x)_n$ electrodes with PVDF binder

We used PVDF as binder in our electrodes. In a typical run we coat ~10 cm wide and 12 meters long single sided or 6 meters long double sided electrode.

Aluminum

Carbon on Al

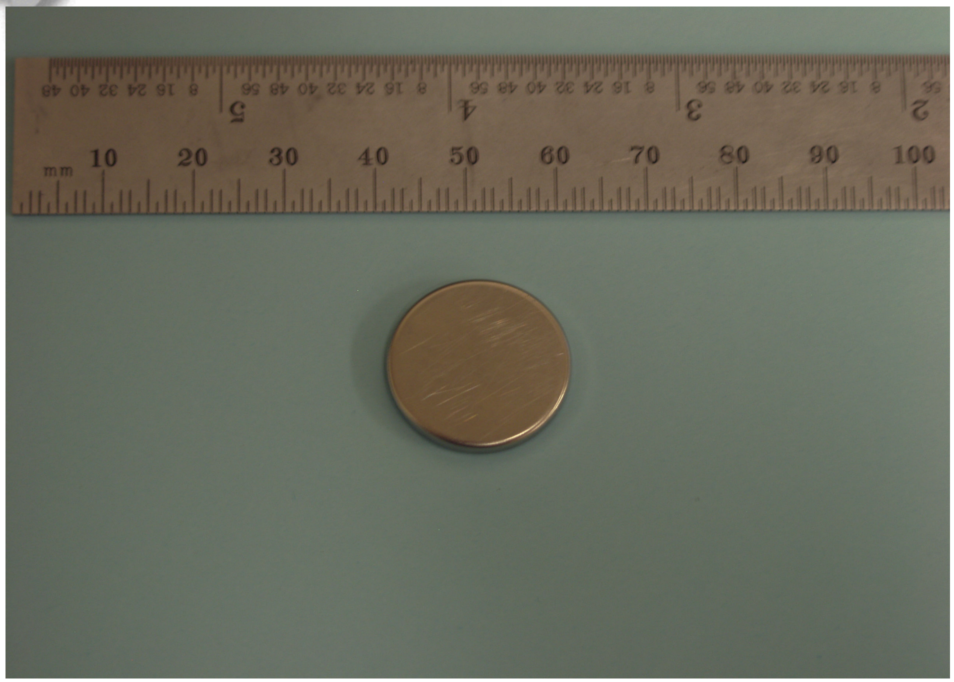
$(CF_x)_n$ coating With PVDF as binder



~2 mil thick single sided electrode

The $(CF_x)_n$ electrodes were coated at Sandia using our in-house facility.
The electrodes used in this study are made with Ozark $(CF_x)_n$ powder with x=1.0

2032 Coin Cell Built at SNL



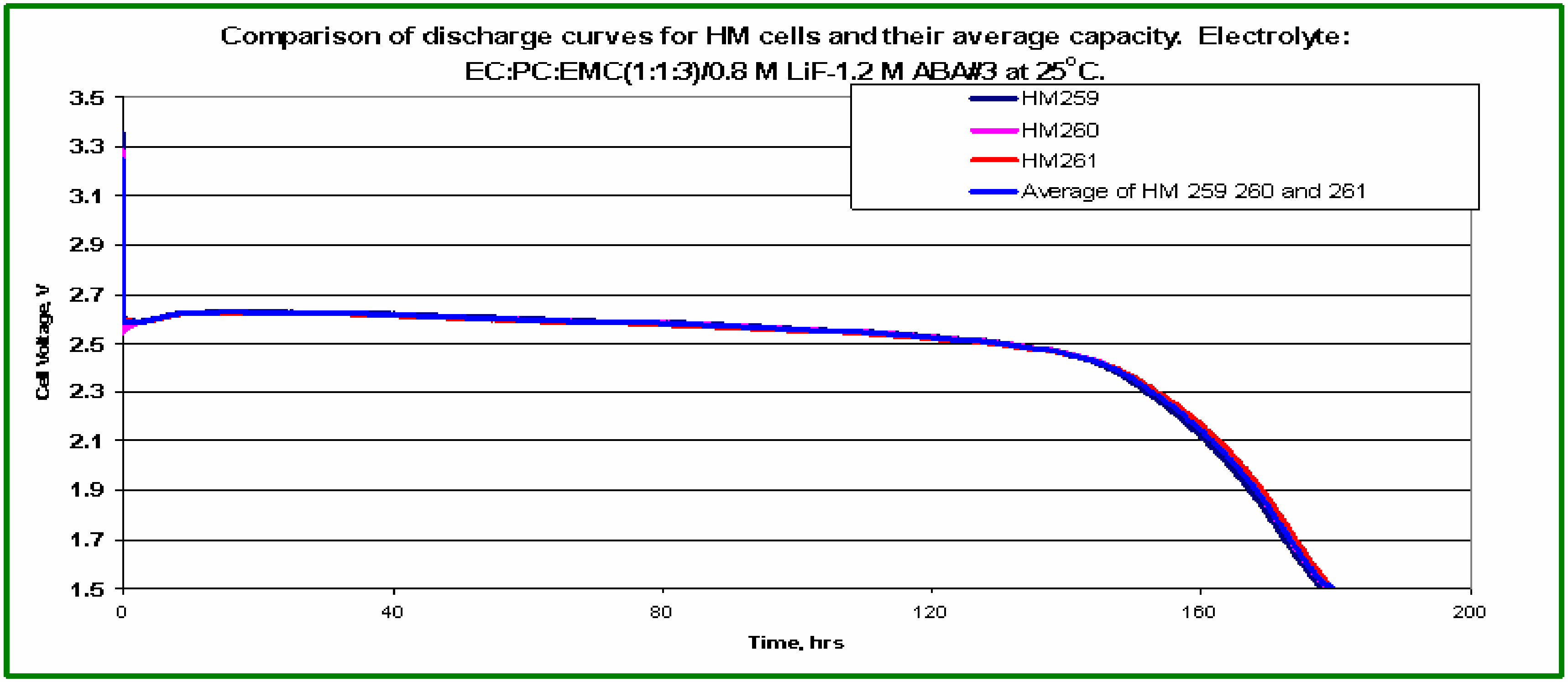
- Constant current discharge to 1.5 V at temperature
- The cell contains: Li anode; $(CF_x)_n$ cathode and electrolyte.

Test Conditions: Tested as assembled at a C/200 rate at 25C
Soaked at 80C for two weeks and tested at a C/200 rate at 25C

Performance of Electrodes with PVDF as Binder

Remember the single sided electrode thickness is ~2 mil.

Performance of electrodes in ABA electrolyte.



The plots above show performance for three cells and their average. The cells were discharged at a C/200 rate.

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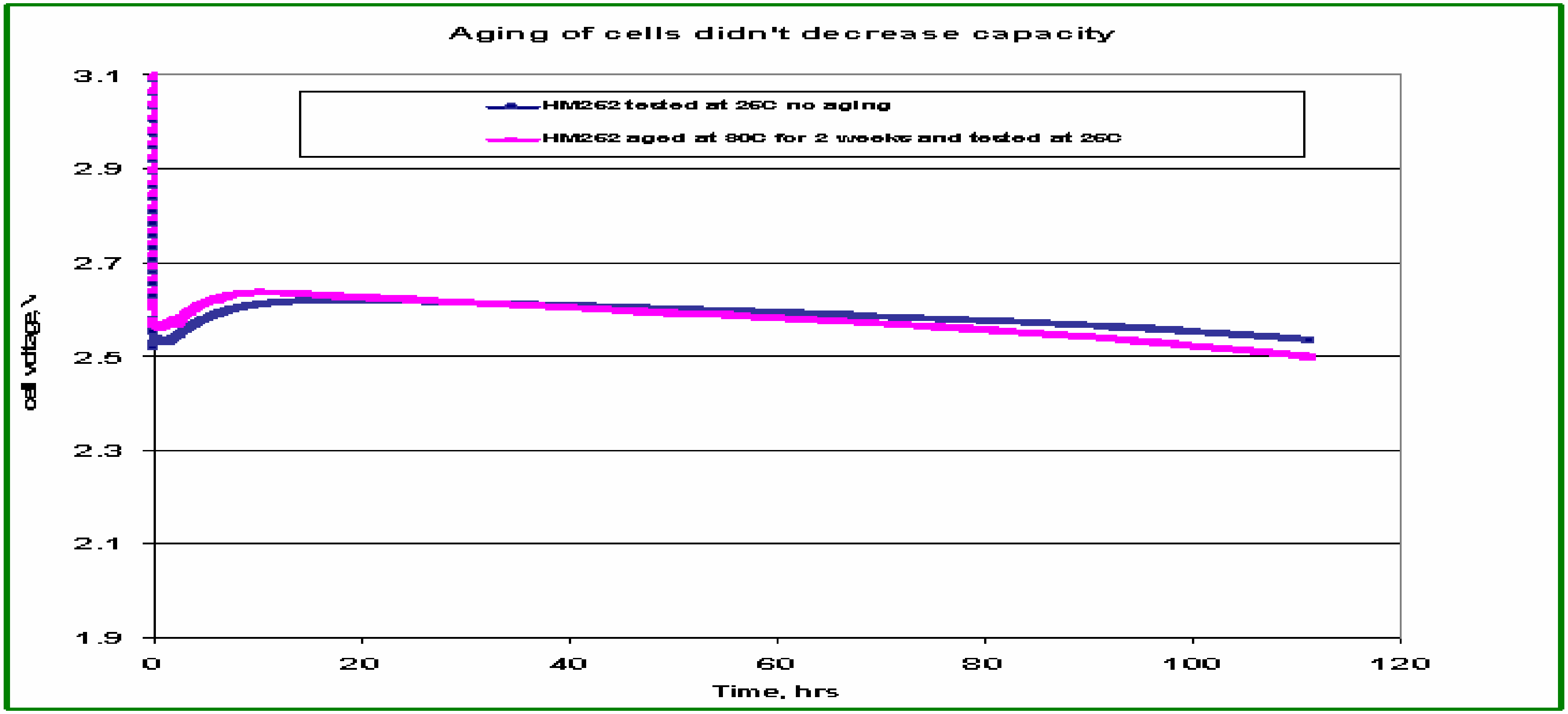
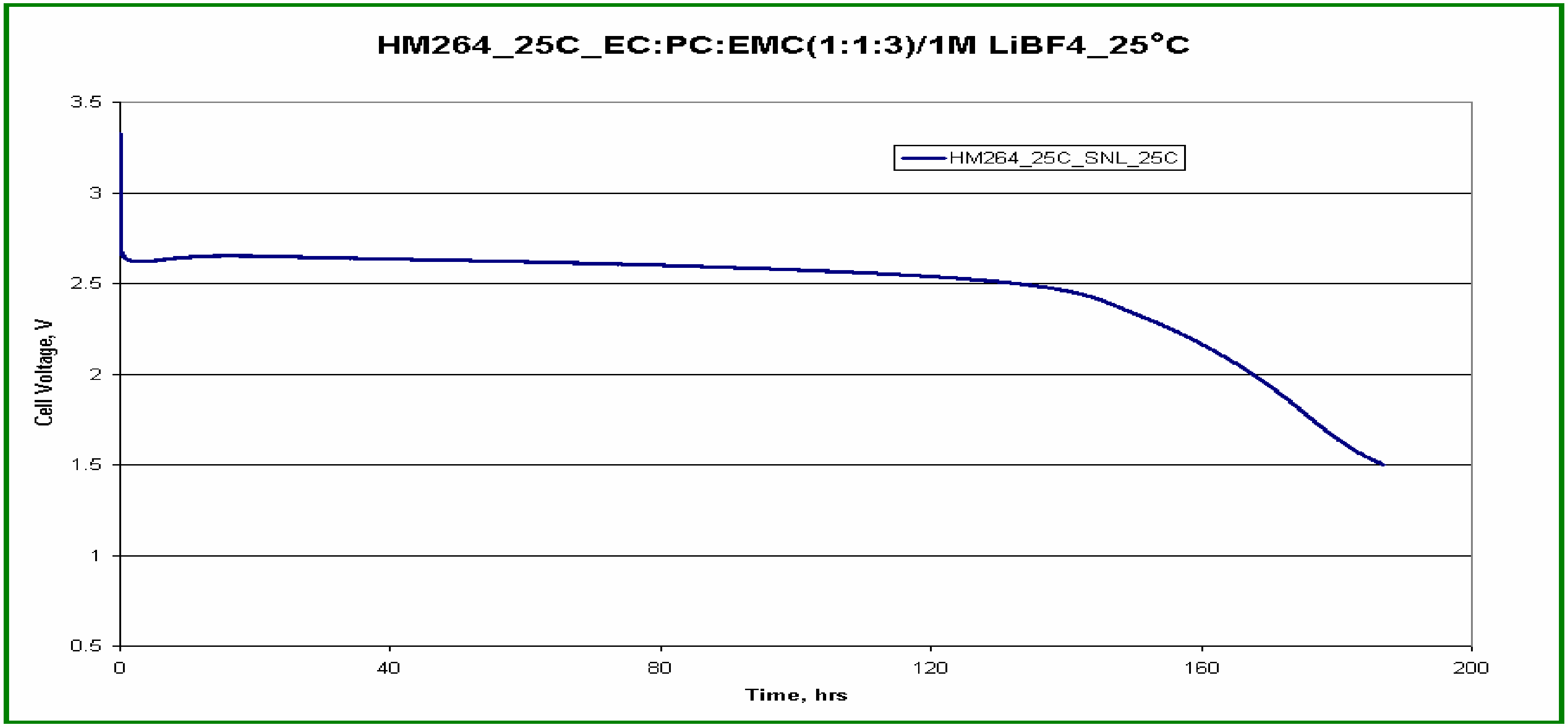
Aging at 80°C didn't degrade cell performance in ABA electrolyte



The performance of the aged cell was nearly equal to that of the un-aged cell

Performance of electrodes with PVDF as binder in EC:PC:EMC-1M



The plots above show performance for two cells.

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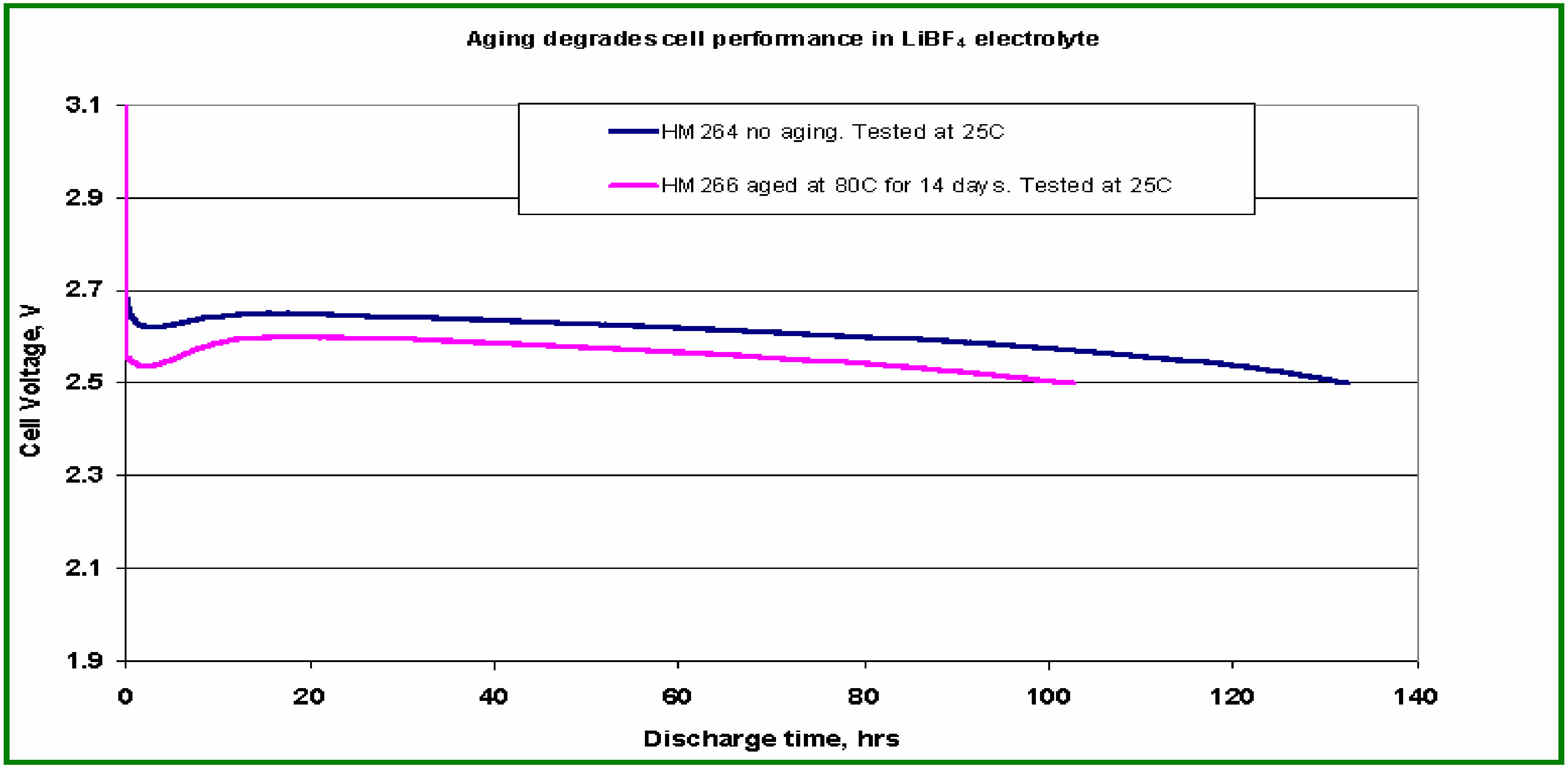
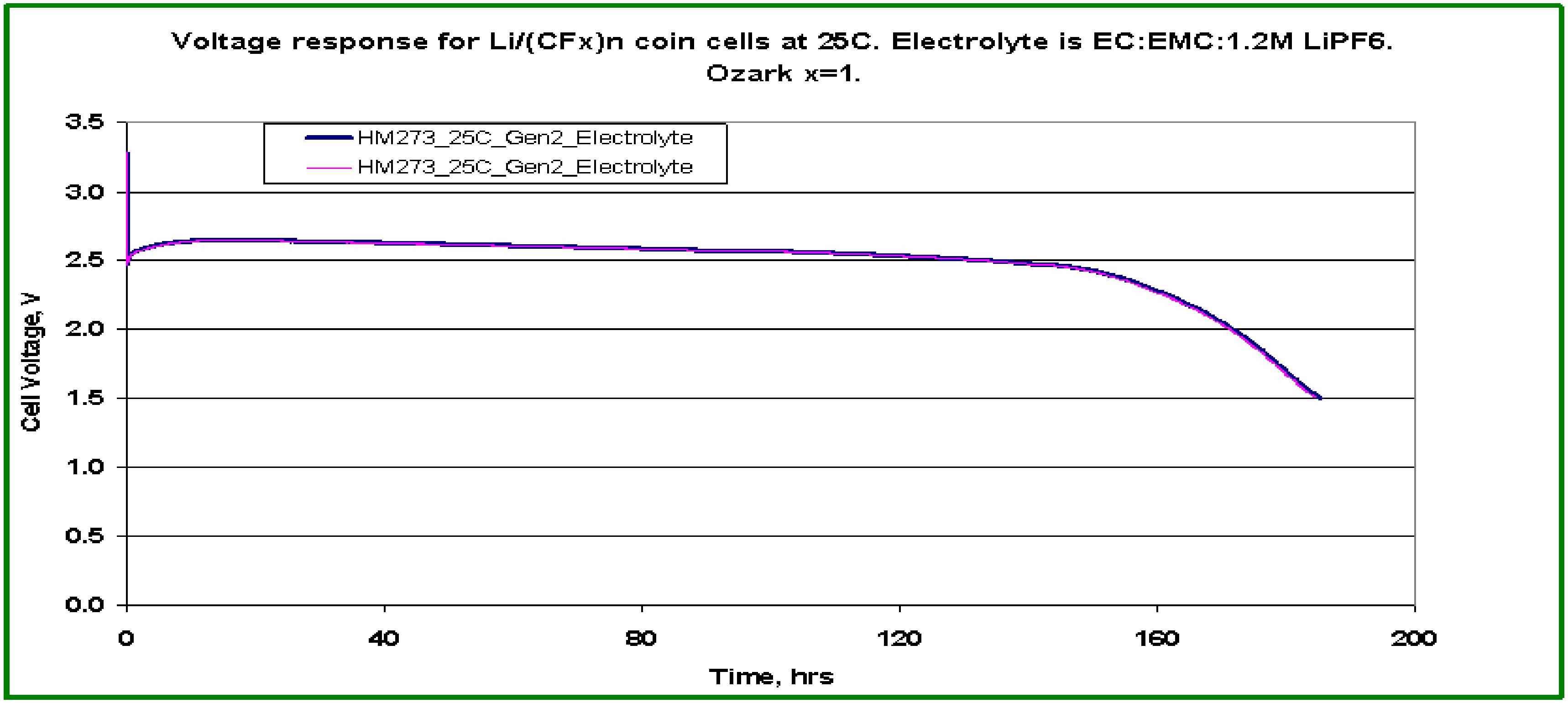
Aging at 80°C degrades cell performance in $LiBF_4$

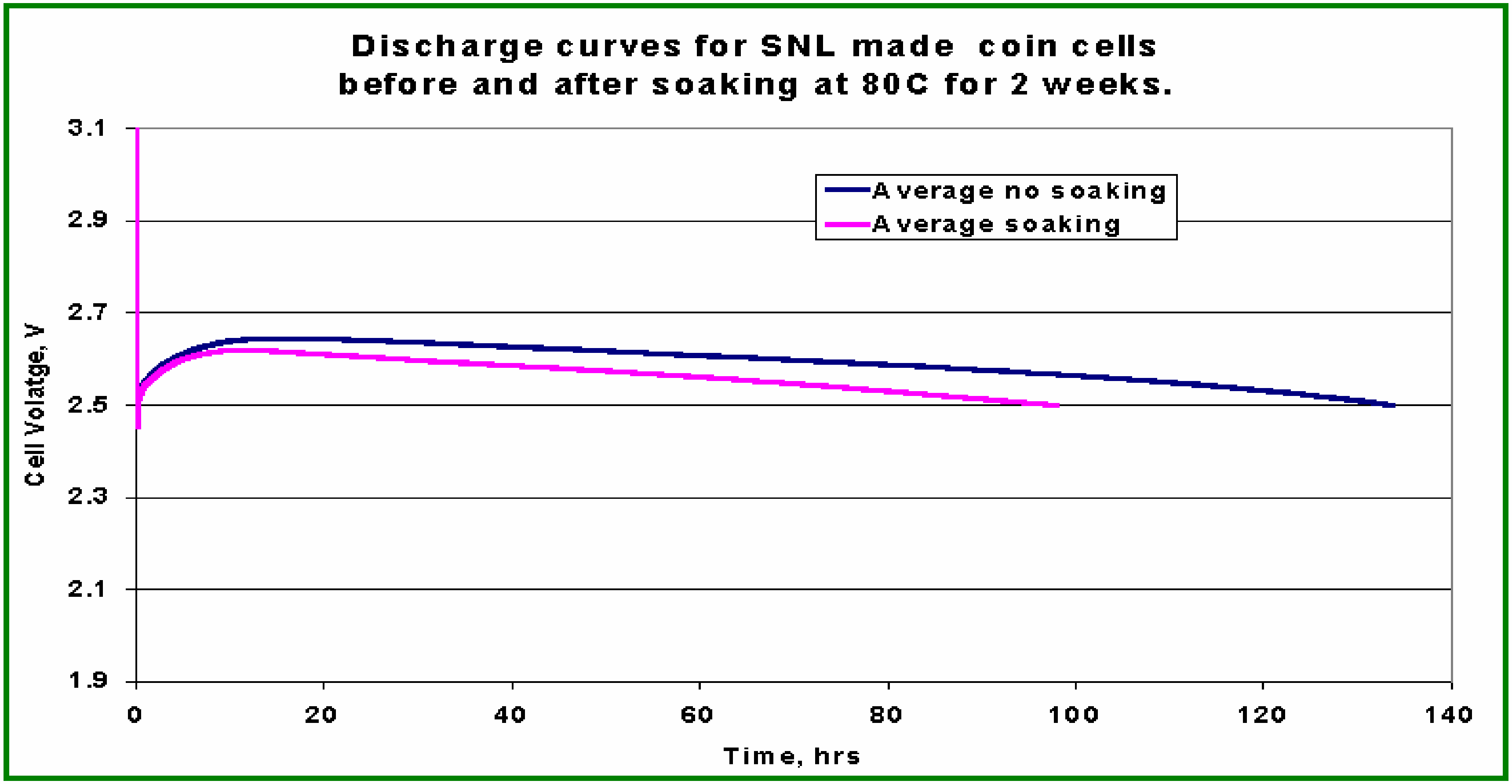


Aging at 80°C lowers cell performance as evidenced by lower operating voltage.

Performance of cells with PVDF as binder in EC:EMC-1.2M $LiPF_6$ electrolyte.



Aging at 80°C degrades cell performance in $LiPF_6$ Electrolyte



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Time to reach 2.5 V for each electrolyte before and after aging

Electrolyte	Time (hrs) to reach 2.5 V		
	Before soaking	After soaking	ΔT (hrs)
$LiPF_6$	133	98	35
$LiBF_4$	132	103	29
ABA	123	112	11

Summary

- $(CF_x)_n$ electrodes with PVDF binder were prepared at Sandia.
- We have developed a new ABA-LiF containing electrolyte
- SNL electrodes were tested in coin cells in different electrolytes, before and after aging. These include:
  - SNL-Developed ABA-LiF Electrolyte
  - EC:PC:EMC-1 M $LiBF_4$
  - EC:EMC-!.2 M $LiPF_6$ (High Conductivity Electrolyte)
  - Aged at 80^{o}C for 14 days
- ABA-LiF electrolyte show very little performance degradation with aging.
- Performance degradation increases in the following order. ABA<$LiBF_4$<$LiPF_6$