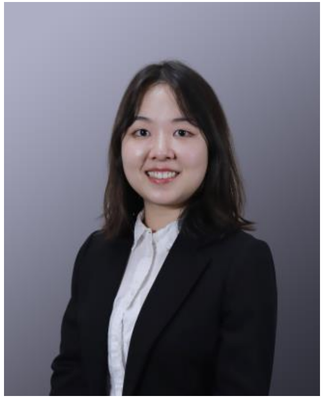
Calendar-life vs. Cycle-life Aging for Silicon Anode



Mei Luo
Prof. Leon L. Shaw
Department of Mechanical, Materials & Aerospace Engineering,
Illinois Institute of Technology
Contact: mluo12@hawk.iit.edu

Renewable Energy

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Introduction

- For silicon anode, both the physical effects of volume changes due to lithiation/delithiation and the chemical effects of prolonged exposure of the lithiated surfaces to the electrolyte will cause degradation during cycling.

- A testing protocol in which the cell is held potentiostatically (at constant voltage) is referred to as calendar-life aging. The destabilization of SEI and capacity fade would be lessen during calendar-life aging for silicon based anode because it does not involve significant volume change in the LixSi particles. [Ref.1]

- Calendar-life aging conditions are common in practical applications, for example when an automotive battery is left in a fully charged state for an extended period of time and not in use.

- In this study, both calendar-life aging and cycling-life aging performance would be examined and compared to get deeper understanding of the role of volume change of silicon anode.

Objective

- Assess the stability of Si SEI
- Evaluate the effect of Si volume change
- Assess particle break-up and electrolyte effects
- Other electrochemical phenomena

Methods

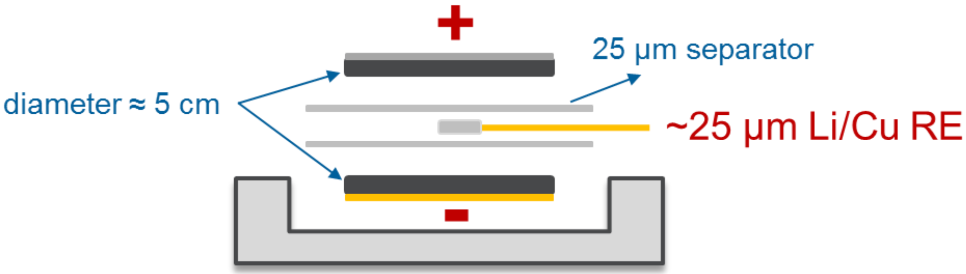

Fig. 1 Schematic image of 3-electrode cell [Ref.2]

- Anode: Si: C45: LiPAA = 80:10:10
- Cathode: NMC532:C45:PVDF = 90:5:5
  LFP:C45:PVDF = 90:5:5
- Electrolyte: Gen2 (1.2 M $LiPF_6$ in 3:7 EC:EMC by weight) + 10% FEC

- The typical cycle-life aging protocol:
  3 x C/20 (formation cycles),
  (HPPC) [Ref.3]
  92 x C/3,
  (HPPC)
  3 x C/20 (diagnostic cycles).

- The typical calendar-life aging protocol:
  3 x C/20 (formation cycles),
  (HPPC)
  hold at constant voltage
  (HPPC)
  3 x C/20 (diagnostic cycles).

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Results

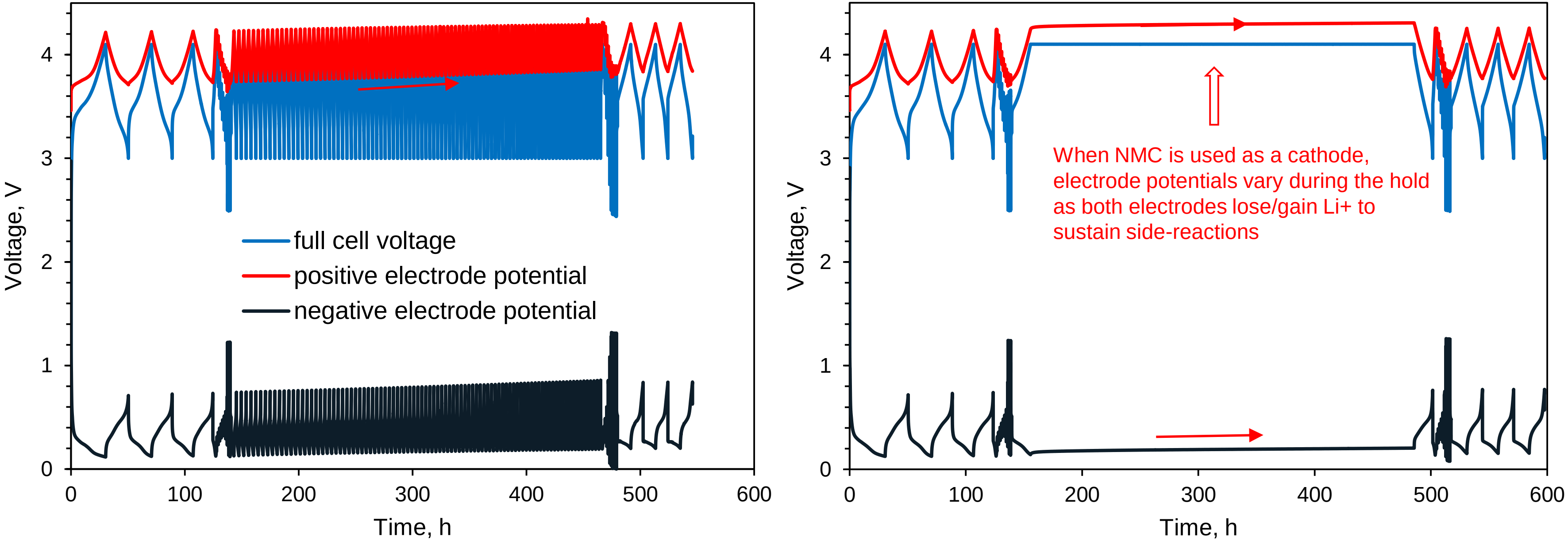

Fig.2 Changes in full cell voltage, positive electrode and negative electrode potentials during cycle-life (left) and calendar-life (right) aging of a NMC532/Si cell

Potential shift and capacity fade result from following:

- Reductive side reactions. Eg: continuous growth of SEI
- Degradation of electrode

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Results

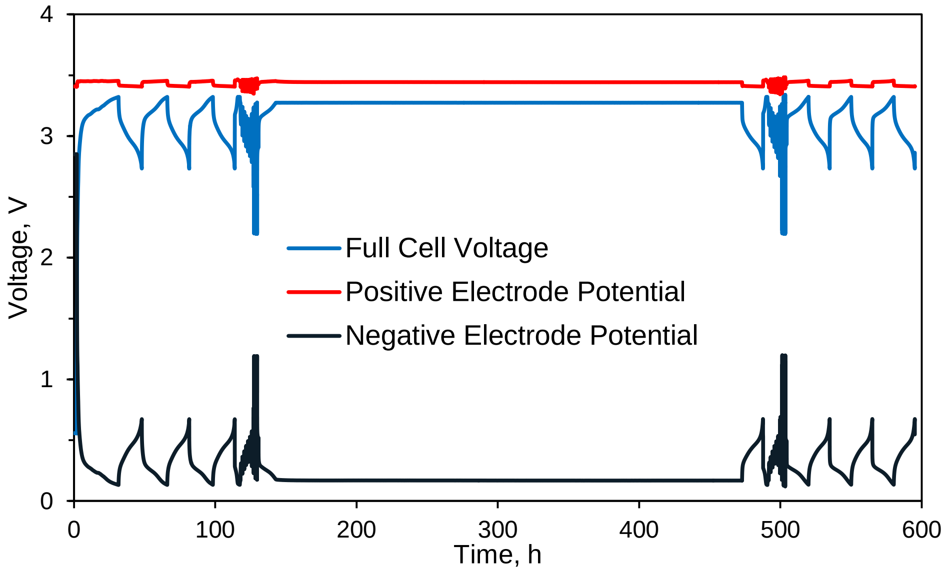

Fig.3 Changes in full cell voltage, positive electrode and negative electrode potentials calendar-life aging of a LFP/Si cell

Use LFP as cathode, as it has a plateau

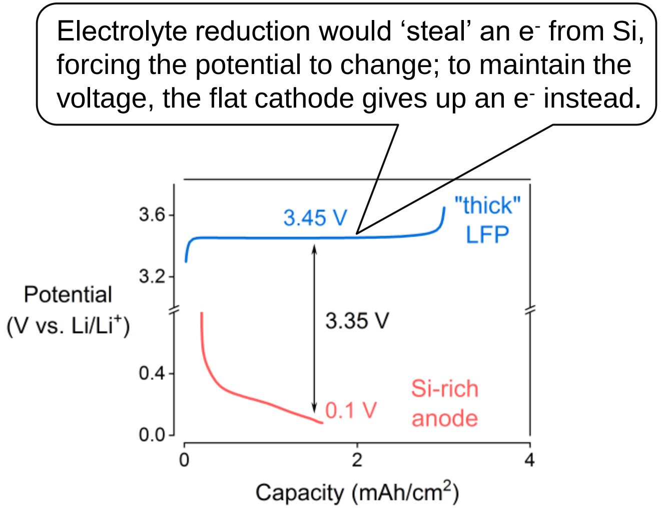

Fig. 4 Schematic plot for designing LFP/Si full cell

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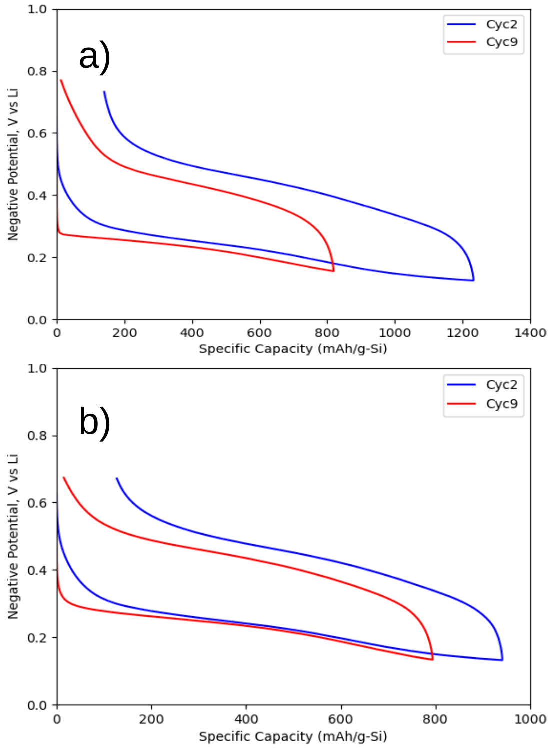
Results



- Calendar-life aging without much volume changes in silicon particle have surprisingly significant capacity fade. And previous study indicates the reason for that is likely to be high concentration HF accumulated in the electrolyte during potentiostatic hold resulting in corrosion and dissolution of silicon particle and cause worse damage to the electrode. [Ref.1]

- Capacity fade during calendar-life aging is smaller in LFP/Si cell than in NMC532/Si cell. The main reason for that is because of the potential shifts in NMC532/Si cell. This SOC shift towards to higher voltage due to reductive side reaction in NMC532/Si cell lead to less active material utilization.

Fig. 4 Specific capacity of negative electrode in (a) NMC532/Si and (b) LFP/Si cells.

Results

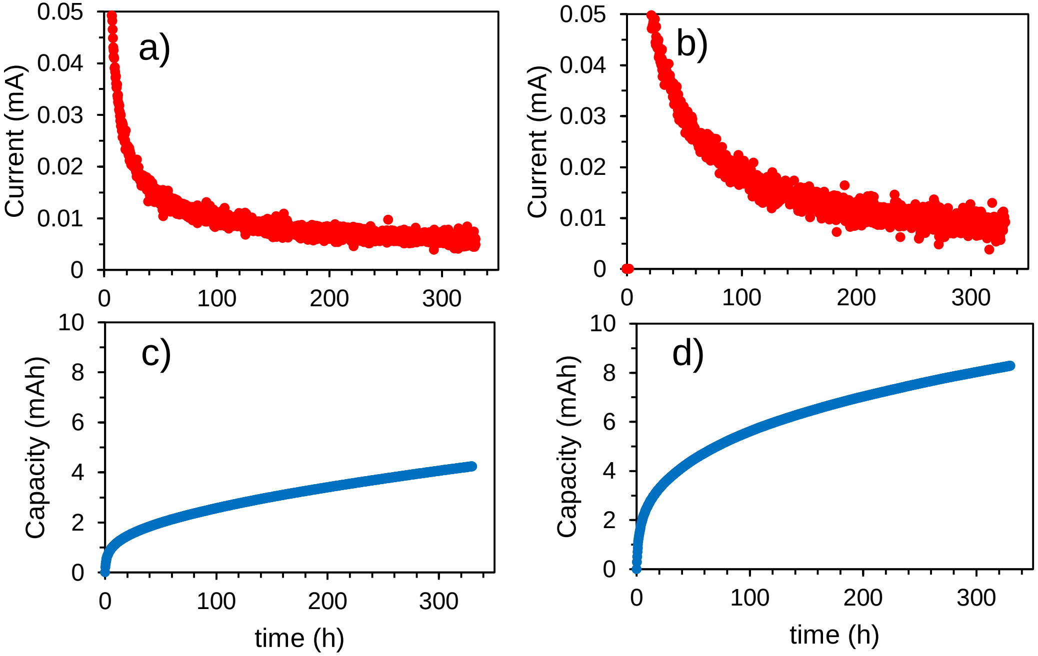


Fig. 5 Parasitic current flowing through the (a) NMC532/Si cell and (b) LFP/Si cell

- For both cells, the current shows an exponential decay over short times and a power law decay for longer times.
- The random current bursts may reflect the processes described below:

    access to newer sites (“higher impedance” sites)and SEI growth thereon;

    the charge consumed to “repair” the pre-existing SEI layer that could be damaged (by dissolution into the electrolyte) during the potentiostatic hold.

- Capacity is simply an integral of the time.

Conclusions

- Capacity fade for NMC532/Si cells is greater for cycle-life aging than for calendar-life aging, because the former involves more volume change during cycling.
- Capacity fade during calendar-life aging is smaller in LFP/Si cell than in NMC532/Si cell because SOC shift towards to higher voltage in NMC532/Si cell lead to less active material utilization.
- During potentiastatic hold, the parasitic currents are observed to be larger than zero all the time indicates an unstable SEI at silicon negative electrode.
- This study shed light on the role of silicon volume change as well as chemical effects of SEI reduction reaction in Li-ion cells with silicon anode. Moreover, this study offer other researchers who also work in the silicon-anode area a baseline as well as an instruction they can followed to examine the properties of their silicon anode.

Future work

- Specially designed silicon anode are prepared which is supposed to alleviate the volume change and minimize the side reaction. This calendar-life aging protocol will be used to identify the properties of this special material.

- Different electrolytes would be study in the future using this calendar-life aging protocol. Parasitic current would be lower with better electrolyte.

References

1. Kalaga, K., Rodrigues, M. T. F., Trask, S. E., Shkrob, I. A., & Abraham, D. P. (2018). Calendar-life versus cycle-life aging of lithium-ion cells with silicon-graphite composite electrodes. *Electrochimica Acta*, *280*, 221-228.

2. Rodrigues, M. T. F., Kalaga, K., Trask, S. E., Dees, D. W., Shkrob, I. A., & Abraham, D. P. (2019). Fast charging of li-ion cells: part I. Using li/cu reference electrodes to probe individual electrode potentials. *Journal of The Electrochemical Society*, *166*(6), A996.

3. Abraham, D. P., Dees, D. W., Christophersen, J., Ho, C., & Jansen, A. N. (2010). Performance of high-power lithium-ion cells under pulse discharge and charge conditions. *International Journal of Energy Research*, *34*(2), 190-203.

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