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Lithium Plating in Anode-Free Solid-State Batteries: A Model System with Artificial Grain Boundaries

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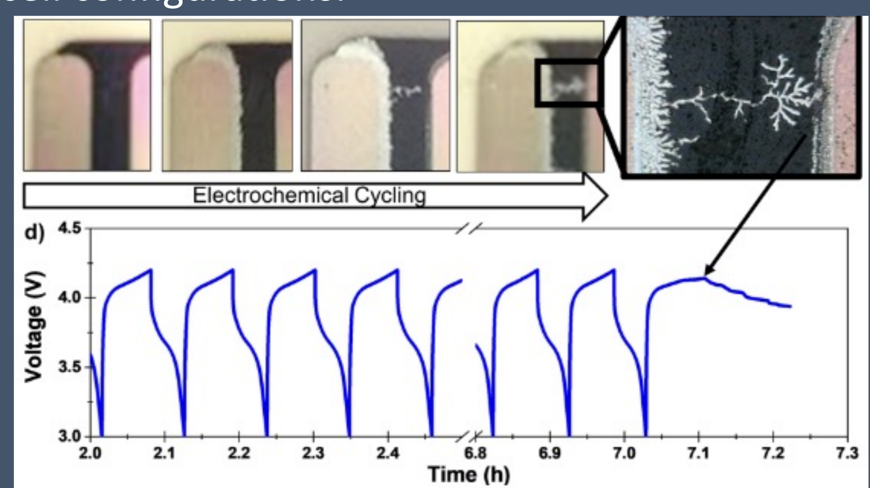
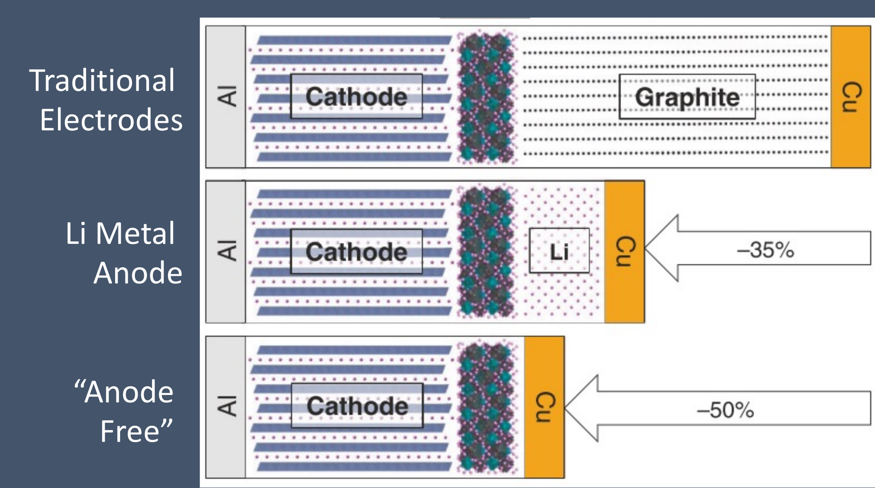
Motivation

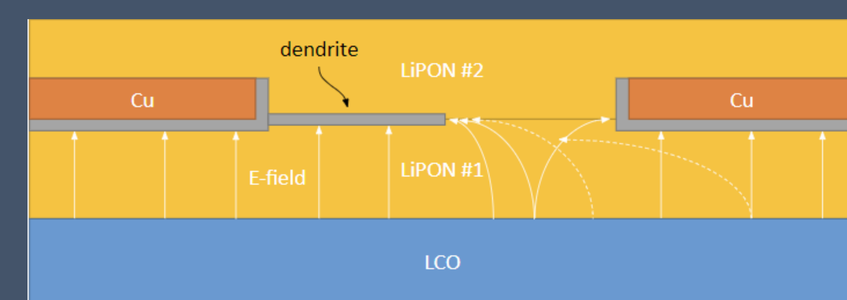
The development of rechargeable batteries with high energy density is a necessity for a green world, portable electronics, and electric vehicles. Anode-free Li-ion batteries provide the highest volumetric energy density, >1500 Wh L^{-1}, among all possible cell configurations.



The major catastrophic problem with such Li-ion batteries is lithium dendrite growth, which was assumed to not occur with solid electrolytes. Recent studies[1] have shared that lithium dendrites are able to grow through grain boundaries.

Schematic of different solid-state battery configurations.[2]
Anode free batteries have the greatest energy density.





LiPON, lithium phosphorus oxynitride, is a solid electrolyte which normally lacks grain boundaries, but an artificial grain boundary can be made to study dendrite growth.

Science Objectives

- Create a model of solid-state batteries to study Li plating and dendrite growth.
- Investigate LiPON acting as a "dendrite blocking material" and the impact of grain boundaries.
- Understand how to create grain boundaries with different properties.

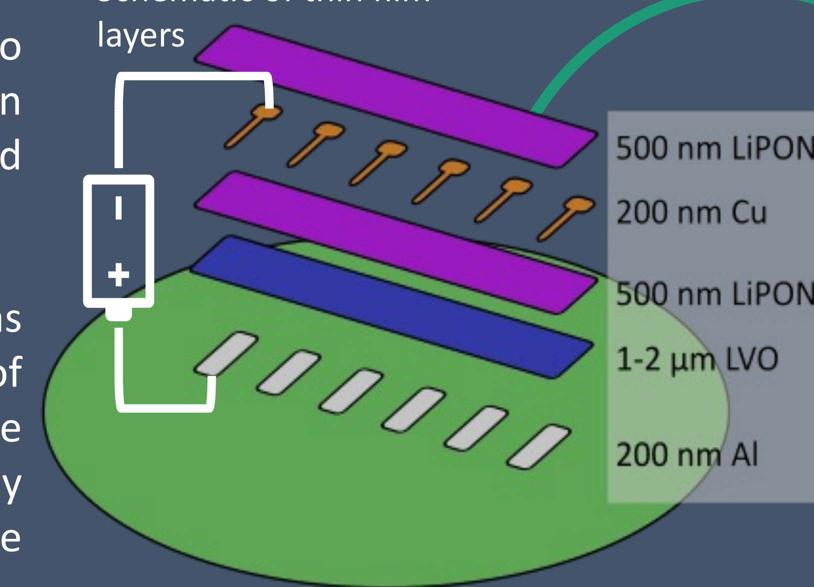
A grain boundary is where two pieces of material touch. It often has a different chemistry and different material properties.

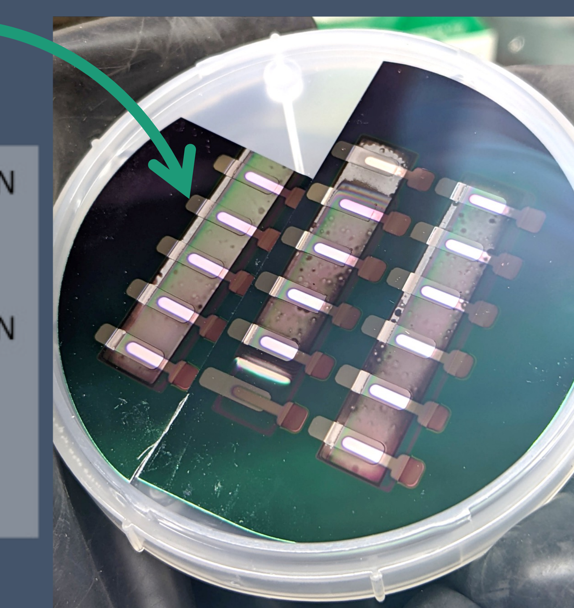
An artificial grain boundary was created between two layers of LiPON. The chemistry of the grain boundary was modified by exposing one layer to air before the second one was placed.

Summer REU Goals

- Understand the operation of anode-free solid-state batteries.
- Develop electrochemical testing procedure for artificial grain boundaries.
- Investigate physical phenomena related to Li plating.

Schematic of thin film layers



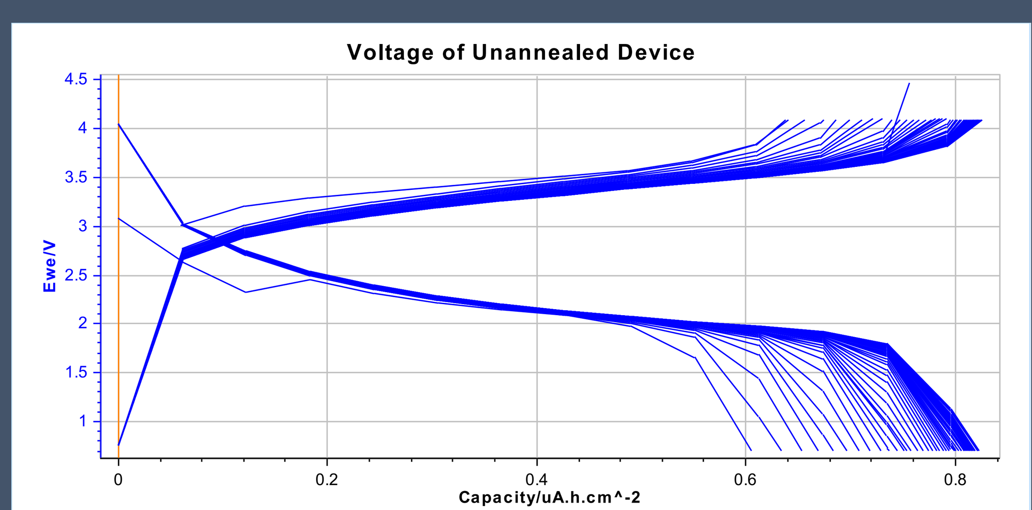


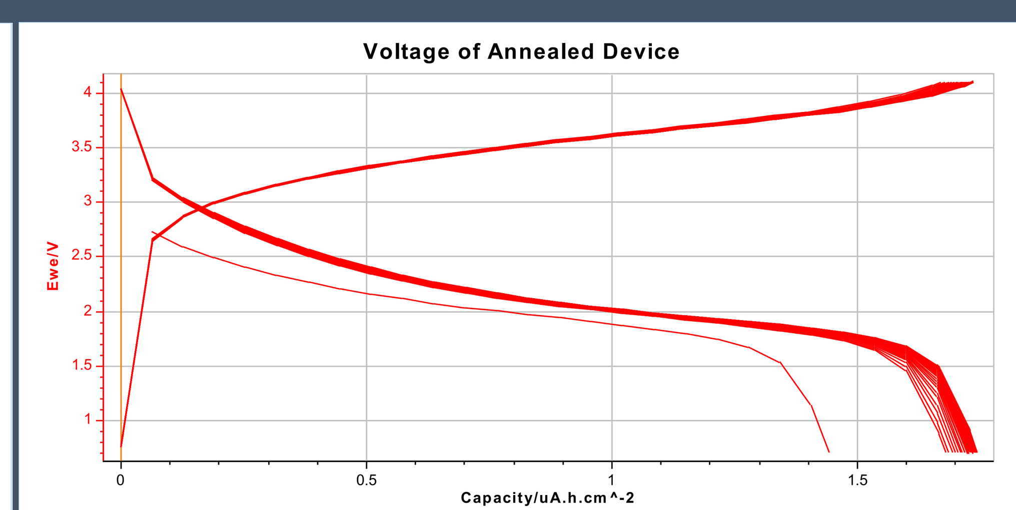
Wafer of 18 devices with an artificial grain boundary.

Each pair of Al and Cu fingers creates a different battery device and is tested independently.

Results

Anode Free Cells exhibit stable, reversible reactions

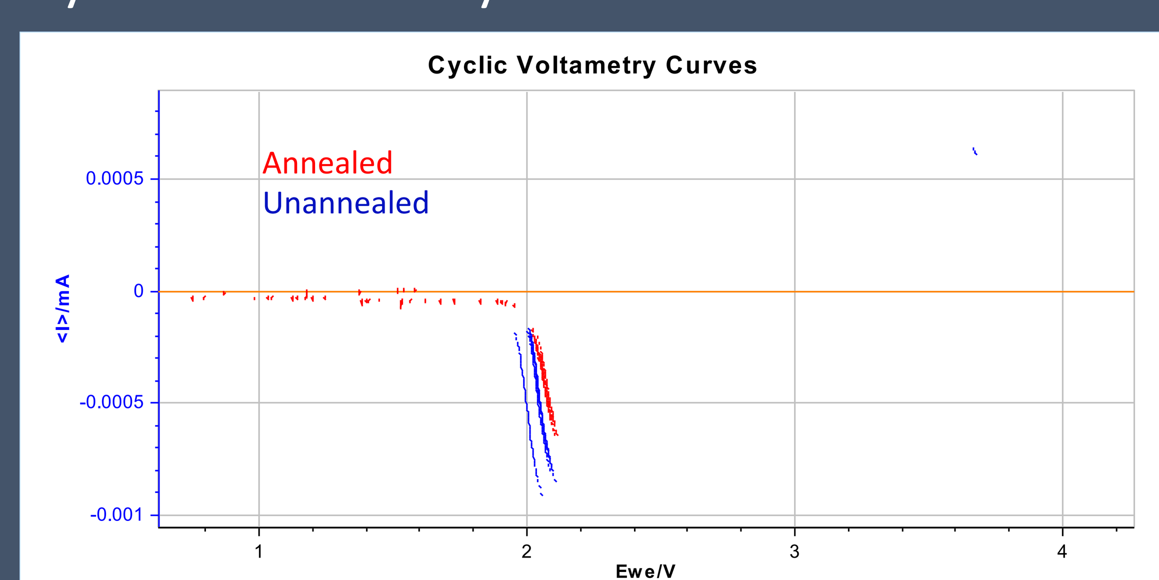




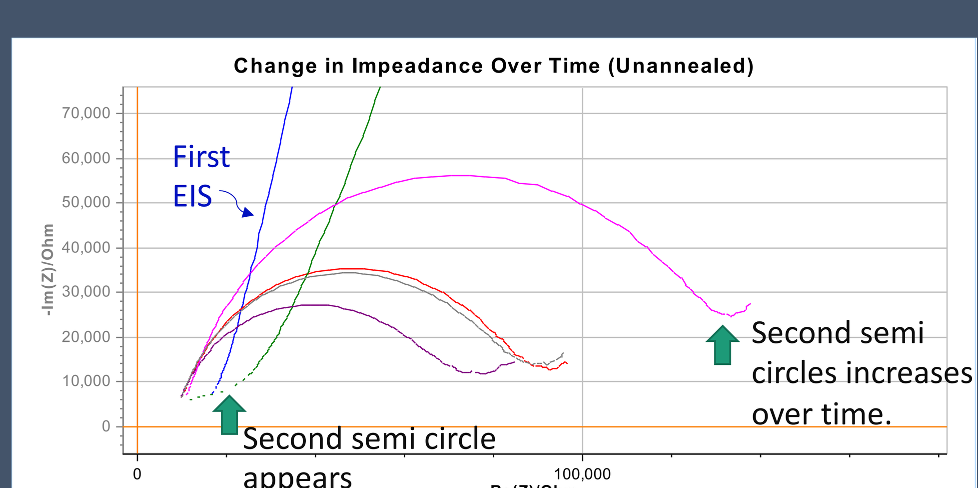
Very stable charge-discharge curves showing the ability to withstand repeated cycles with various amount of applied current.

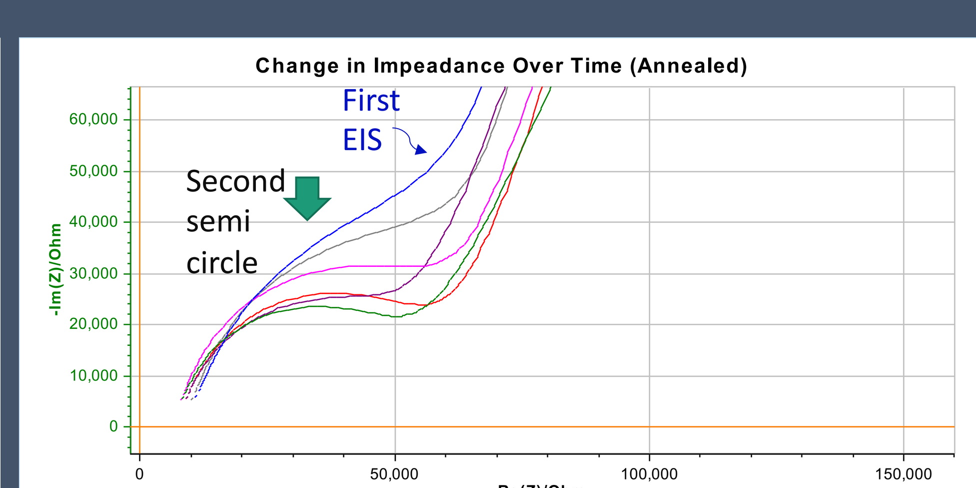
Cyclic Voltammetry

Clear redox peaks sharing that we are able to strip and transfer lithium in our devices. We also replicated our results in different cells in both annealed and unannealed devices.



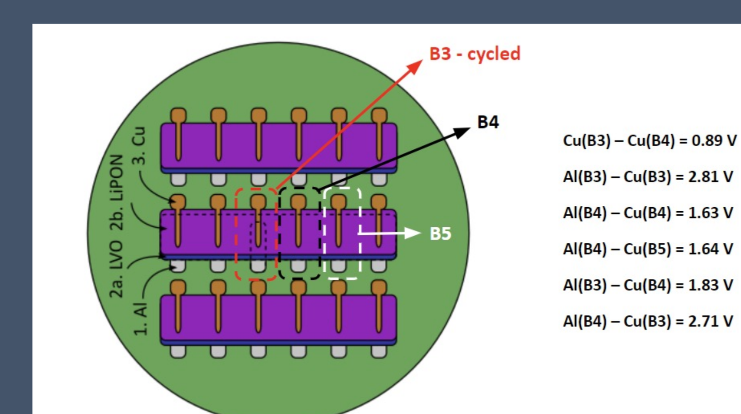
Impedance Evolution





Unannealed sample shows a significant increase in impedance over time. The second semi-circle appeared after first cycling. In opposite, two semi-circles seem to already exist on the first EIS for the annealed sample. It also shows much more stability in comparison to the unannealed.

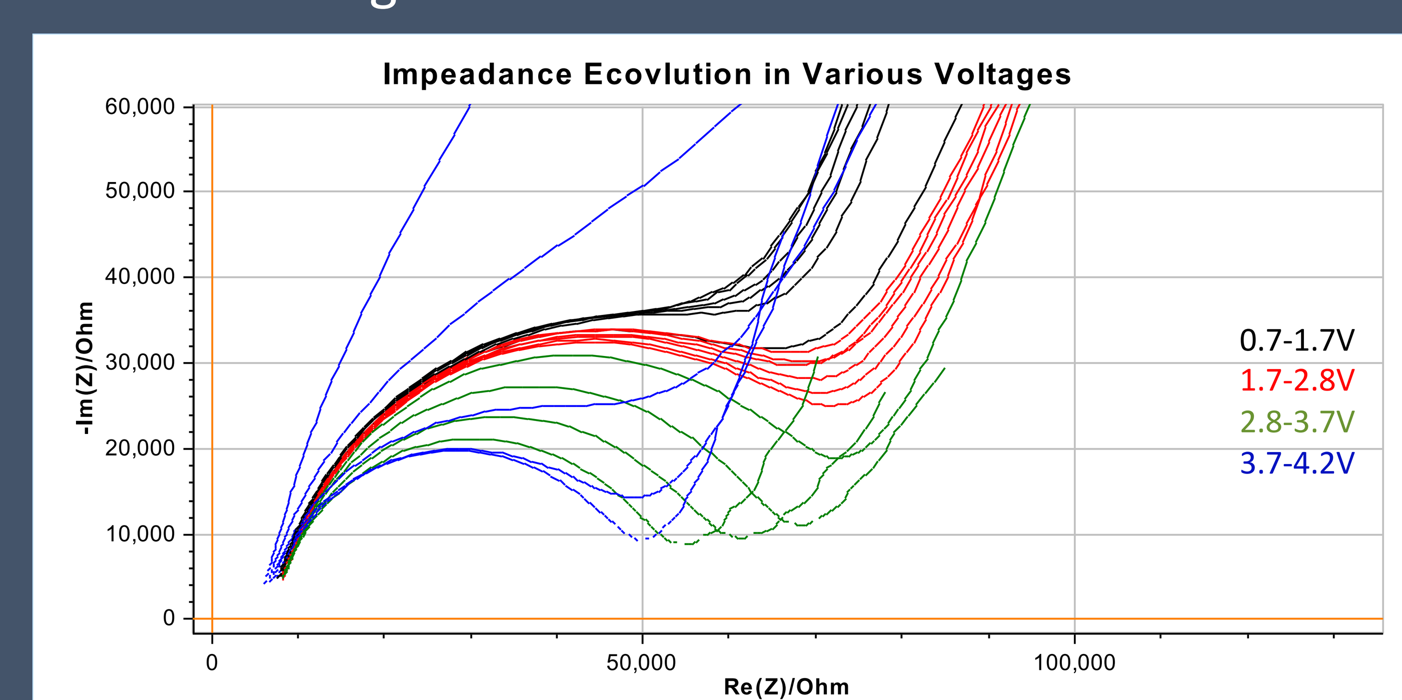
Anode Electrochemical Reactions Change After Cycling



The chemical potential of the anode has changed after cycling, but the potential at the cathode remains relatively constant . This suggest that we have formed some sort of surface between LiPON and Cu.

	Cycled Anode	Uncycled Anode	Uncycled Anode
Cycled Cathode	2.81V	1.83V	-
Uncycled Cathode	2.71V	1.63V	1.64V

Interface changes at different voltages



At lower voltages, the EIS data is much the same to results at OCV. The second semicircle is stable and slightly increases over times, as seen in prior experiments. However, at higher voltages it compresses and fades away. This suggests that the surface layer we believe we have created is reversible and has dissociated.

Conclusions and Future Works

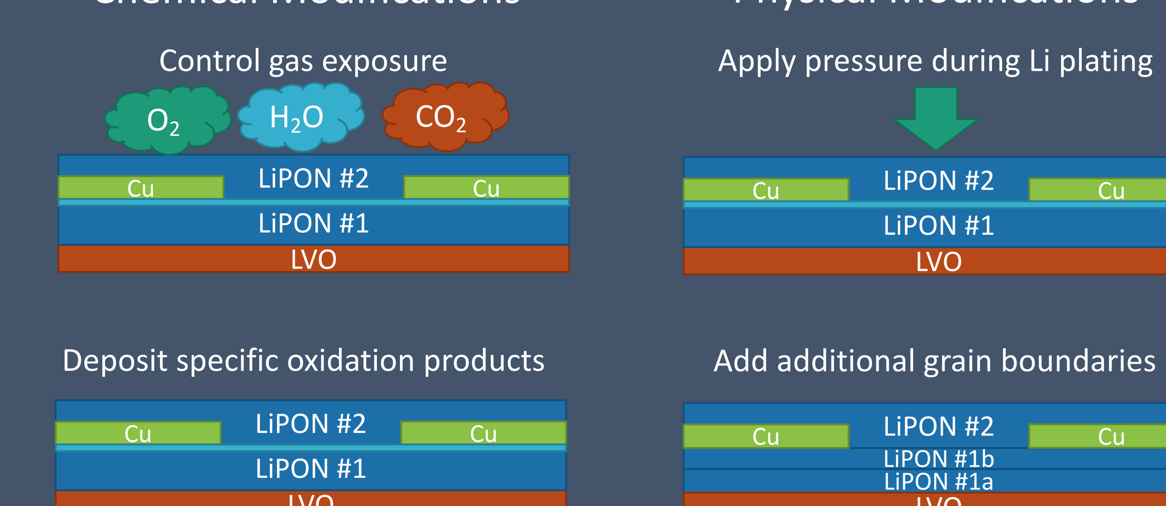
- Established device functionality and testing procedure
  - EIS measurements prove to be extremely useful at measuring small changes at interface.
- Device capacity too low to see dendrite growth
  - Possible to correct with further refinement of fabrication.
- Evidence suggesting a new interface is formed between LiPON and Cu.
  - Probable beginning of Lithium formation on Cu side
- Interface between LiPON and Cu is highly reversible
- Perform further testing on samples with no air exposure
- Complete a SEM cross section to analyze the surfaces

Extensions of the Model System

With the basic procedures established here, we can look ahead and begin designing other artificial grain boundaries to investigate.

Chemical Modifications

Physical Modifications



References

1. Westover, Andrew S., et al. "Deposition and Confinement of Li Metal along an Artificial Lipon–Lipon Interface." *ACS Energy Letters*, vol. 4, no. 3, 2019, pp. 651–55. *Crossref*, https://doi.org/10.1021/acsenergylett.8b02542.
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Acknowledgements

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