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CRADA Final Report: CRADA Number NFE-21-08827 with DayLyte, Inc.

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1. Abstract

DayLyte Batteries is developing an aqueous Sodium-Air battery made with abundant materials while being half to a third the weight of Li-ion to power electric aircraft, electric vehicles and provide renewable energy on demand. To make this battery practical, DayLyte is developing a thin film ceramic Nasicon solid electrolyte amenable to rapid scaleup as well as a protective coating that will protect the solid electrolyte from 50wt% NaOH during the battery's end-of-discharge while still allowing Na-ions to pass back and forth. If the thin film solid electrolyte and stable coating can be developed it will open the world to step change in battery performance all while not sacrificing the environment on the way. The project was designed to first focus on making and characterizing the Nasicon membrane followed by measuring its electrochemical performance, then assembling a full cell, optimizing its NaOH stability and then optimize the overall prototype design. Over the past two years, we have significantly improved the Nasicon film uniformity, demonstrated protective ligands that are stable in 50wt% NaOH by measuring no mass change with a quartz crystal microbalance, tested different heating methods like tube furnace and rapid heating and developed glassy carbon coatings on the current collector to prevent Nasicon-current collector alloying. We have found that getting film uniformity as measured by electrochemical impedance spectroscopy (EIS) is difficult because of different factors like surface roughness, deposition uniformity and heat treatment time and uniformity. The glassy carbon coating should significantly reduce the surface roughness and by tuning the coating conditions the film deposition uniformity improves and using an automated heating method should lead to much improved film uniformity.

2. Statement of Objectives

This project will:

- Develop a thin (<100µm), flexible, Nasicon solid electrolyte membrane
- Assemble a full cell prototype and demonstrate a working device under realistic operating conditions
- Characterize and improve the Nasicon stability in 50 wt% NaOH aqueous solution at 25°C to extend calendar life beyond 2 years
- Measure and if needed improve the Nasicon stability to Na metal
- Optimize Na-ion conductivity

Task 1: Synthesize 100 g Nasicon Solid Electrolyte Powder
Two compositions will be made:

1. $Na_3Zr_2PSi_2O_{12}$
2. $Na_{3.12}Zr_{1.88}Y_{0.12}PSi_2O_{12}$

Synthesizing 100 g of Nasicon (at least 50 g of each) will give Participant enough material for the remaining tasks. An example synthesis condition could include calcination at 1250°C in air for 12 hours, with the sample covered in a graphite, SiC, BN, etc. crucible.

Task 2: Fabricate the Nasicon Membranes
Two approaches will be performed:

2. Top-Down (monolayer of Nasicon particles mixed with polymer): Make a Nasicon-polymer composite membrane (< 100 µm).

1. Bottom Up (Dip Coating vs. Spray Coating): Build up tens or hundreds of nanometers thick Nasicon layers, layer by layer on the current collector until pinholes are filled and Nasicon is thin (<5 µm).
2. Top-Down (monolayer of Nasicon particles mixed with polymer): Make a Nasicon-polymer composite membrane (< 100 µm).

Task 3: Characterize Structure, Morphology and Stability in Air, Moisture, CO2, NaOH, Na Metal
Participant will vary the Nasicon synthesis parameters (time, temperature, etc.) and correlate relation between the synthesis conditions and Nasicon properties including structure, morphology, and stability. Various advanced characterization tools will be utilized.

Task 4: Characterize Electrochemical Performance in Na Symmetric cell
Participant will assemble a Na|Na symmetric cell and run electrochemical tests to determine:

1. Membrane dendrite stability
2. Critical current density
3. Charge deposited before dendrite penetration

Task 5: Assemble and Test a Prototype Battery Cell
Participant has already identified likely hurdles including increasing the Nasicon stability towards concentrated NaOH and Na metal but assembling and testing a prototype battery cell will allow us to quickly identify unknown trouble areas and not waste time addressing other potential hurdles that do not arise.

Task 6: Optimize Nasicon NaOH Stability
Scientists have studied $Na_3Zr_2Si_2PO_{12}$ resistance to concentrated NaOH and found the Zr and Si atoms to be attacked by OH-. Some patents have found that adding concentrated NaCl, NaBr and NaI increases the Nasicon chemical resistance, but without explanation and without confidence at higher temperatures (>60°C). Several strategies Participant intends to employ involves coating the Nasicon with cation exchange ligands or polymers as well as adding dopant ions to the catholyte to discourage Nasicon alkaline attack.

Task 7: Optimize Nasicon Na Metal Stability
$Na_3Zr_2Si_2PO_{12}$ is unstable to Na metal at elevated temperatures (T > 150°C) but appears to be kinetically stable at ambient and realistic operating temperatures (T < 80°C). Participant will measure the degradation rate versus temperature for this task if Na metal degradation is found to be a problem.

3. Benefits to the Funding DOE Office's Mission

The EERE's mission is to "to accelerate the research, development, demonstration, and deployment of technologies and solutions to equitably transition America to net-zero greenhouse gas emissions economy-wide by no later than 2050, and ensure the clean energy economy benefits all Americans, creating good paying jobs for the American people—especially workers and communities impacted by the energy transition and those historically underserved by the energy system and overburdened by pollution" which is exactly what DayLyte is trying to accomplish by developing and scaling up an aqueous Na-Air battery that is made with abundant materials in order to power the green energy revolution.

4. Technical Discussion of Work Performed by All Parties

For Task 1, our colleague, Youngsik Kim at UNIST in South Korea provided 100g of Nasicon powder for us. The real challenge begins with Task 2.

For the top-down approach of embedded Nasicon powder in a polymer membrane with the Nasicon powder bridging to both sides we found that getting a uniform particle size distribution would be very difficult and impractical with the equipment and resources at our disposal (likely needing a fluidized bed opposed jet mill) and that if there was ever a temperature change then thermal expansion mismatch between the polymer and the Nasicon would lead to water leaks at the Nasicon-polymer interface so this method was abandoned. This left the bottom-up method of building up as the next best method. The strategy of building up the Nasicon solid electrolyte layer by layer via depositing precursors ~50-100nm thick, heat treating them and repeating until all pinholes are filled was promising to make a thin and flexible solid electrolyte with low resistance. At first, we made 5 layers of Nasicon which had a heat treatment with a propane blow torch after each layer deposition and we found in Figure 1 that the electrodes had high reproducibility and low Na-ion impedance.

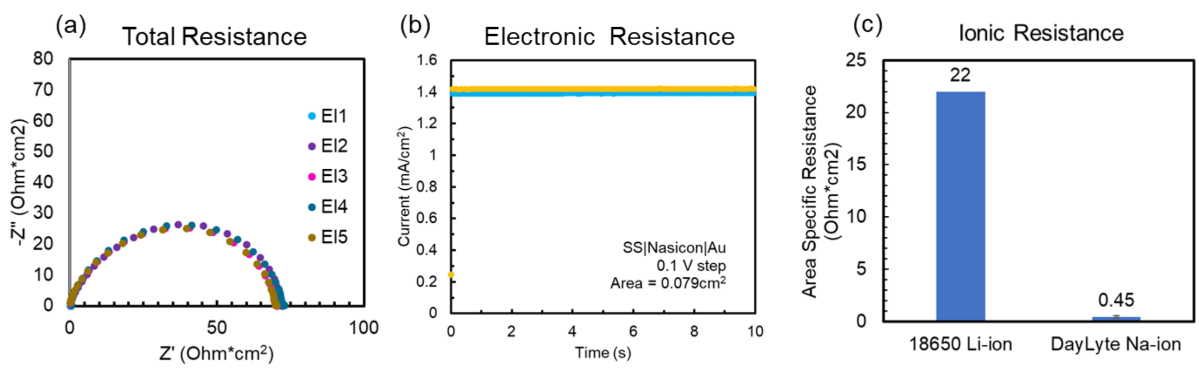

Figure 1. (a) EIS of a ss|Nasicon|Au electrode taken from 1MHz to 0.1Hz to measure the total electrode impedance, (b) chronoamperometry measurement of the same electrodes with a 0.1V step to measure the electronic impedance. By subtracting the electronic impedance in b from the total impedance in (a) we get (c) the Na-ion impedance of the Nasicon which is much lower than the area specific resistance in commercial 18650 cells.

However, a major challenge we faced was in reliably making uniform electrode impedances which is very difficult when you are making optical films because you need to ensure the film is deposited uniformly, is heat treated uniformly, that you address the substrate surface roughness and substrate-film interactions. With a lot of work, we improved the film deposition methods, explored substrate modifications and worked to improve heat treatment uniformity which was the bulk of Task 3.

For Na symmetric cell cycling in Task 4, we assembled a coin cell in a ss|Nasicon|Na metal|ss configuration. We built a homemade sodium evaporator to evaporate sodium onto the Nasicon to make a perfect Nasicon-Na interface to minimize the chance of forming dendrites from surface imperfections.

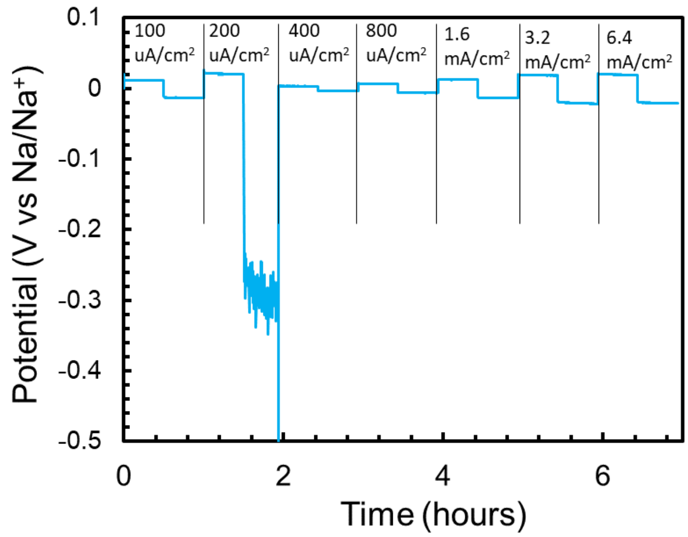

Figure 2. Critical current density measurements of Na-symmetric cell.

Figure 2 shows the critical current density measurements we made for the coin cell and it appears that a short circuit formed above 200 μA/cm^2. When we opened the coin cell, we found that sodium metal dendrites went around the solid electrolyte edge as shown in Figure 3. This is not terribly surprising because coin cells were designed for Li-ion and not our thin film solid electrolyte approach. Discussions with Andrew Westover at Oak Ridge National Lab suggested to us that the best way forward to measure the solid electrolyte performance is to skip to the full pouch cell design.

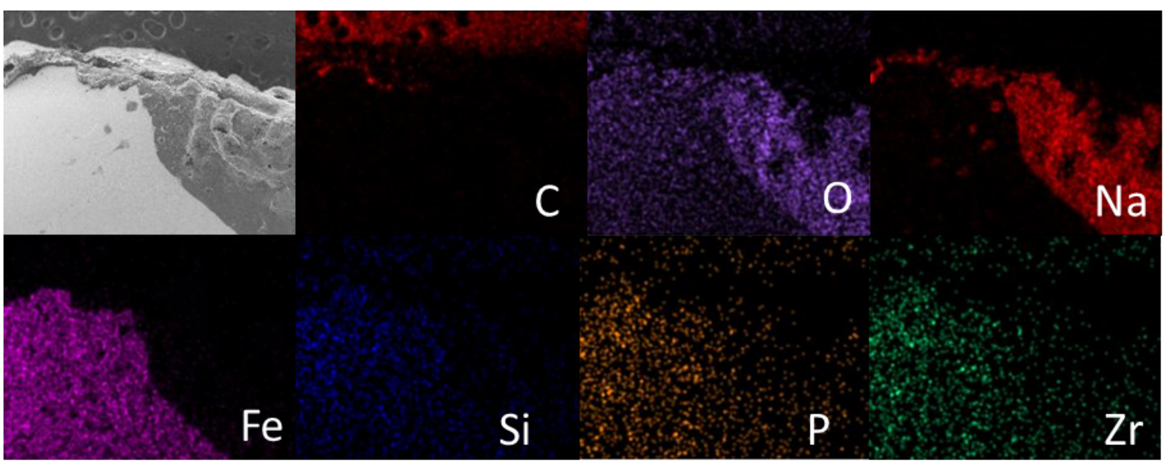

Figure 3. SEM and EDX of Na metal dendrites reaching around the solid electrolyte's edge to be the cause of the electrical short.

When making a pouch/beaker cell, we found that our solid electrolyte was so thin that electrons were able to conduct through it, so the Nasicon electrode was performing the hydrogen evolution reaction rather than the Na electroplating reaction. Using the Nasicon electronic conductivity of 10^{-8} S/cm and having a target of 1% self-discharge/week, we calculated the minimum Nasicon thickness needed would be 2-3microns thick. This meant we needed to build a roll-to-roll coater to reliably coat and heat treat 20-40 coatings which took until the end of the CRADA.

Without the 2-3micron thick Nasicon we haven't yet been able to complete a pouch/beaker cell prototype for Task 5. For Task 6, we sputtered SiO_2 onto quartz crystal microbalance electrodes as a proxy for Nasicon, then we coated them with three protective coatings we believed would impart protection against 19M NaOH while still allowing Na-ions to freely pass back and forth. We found in Figure 4 that all three coatings survive and provide protection against 1M NaOH, but two of the three coatings survive in 19M NaOH. This was a major accomplishment because it means that with these coatings, the Na-Air battery has the potential for a long cycle life and long calendar life.

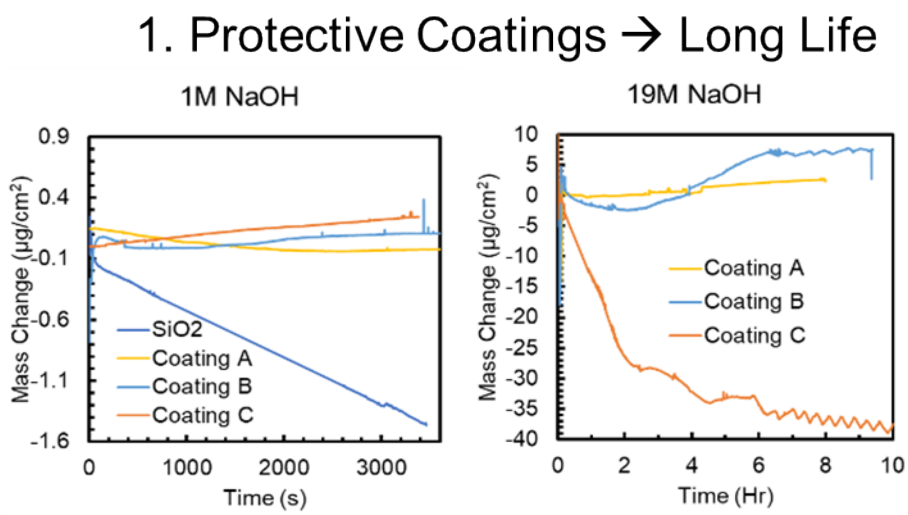

Figure 4. Quartz crystal microbalance data of different coatings in (a)1M NaOH and (b) 19M NaOH.

For Task 7, we found from discussions with Eric Spoerke at Sandia National Lab that Nasicon is stable against Na metal at the operating temperatures of interest.

5. Subject Inventions (As defined in the CRADA)

None

6. Commercialization Possibilities

With the final demonstration of the thin film Nasicon solid electrolyte, we will be able to assemble and test a full cell. We have already begun cell designs including cell packaging that could also apply for redox flow batteries as well. We have been in talks with various potential customers that are eager to get battery samples to test and implement in their solutions.

7. Plans for Future Collaboration

DayLyte has entered into a User Agreement with UT-Battelle to allow it to continue its research and development with ORNL. DayLyte has also been building partnerships with various universities, companies and institutions for roll-to-roll coating and heat treating and cell fabrication and scale up.

8. Conclusion

In conclusion, much was done, learned and accomplished with still more to go. This CRADA paved the way for DayLyte to make breakthroughs in protective coatings, design and implement optical thin film coatings and win a DOE Phase I and Phase II grant which is funding further work to make the Nasicon thin film solid electrolyte and ultimately the water-based Na-Air battery to store renewable energy and power the world with DayLyte.