ORNL/TM-2023/2909
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CRADA Final Report: CRADA Number NFE-18-07341 with Eonix LLC

Don DeRosa

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Approved for Public Release

1. Abstract

Over the past two years, my work has been focused on the development of a commercially viable electrolyte that expands the voltage window of ultracapacitors featuring standard activated carbon electrodes from 2.7V to greater than 3V. During this fellowship in collaboration with staff at Oak Ridge National Laboratory, we refined a high throughput screening process to rapidly analyze the properties and performance of electrolyte candidates in ultracapacitors and establish a quantitative structure activity relationship (QSAR) methodology for candidate selection. Over sixty electrolyte chemistries were screened using these novel techniques.

2. Statement of Objectives

The three objectives of the CRADA, and their relevant tasks:

Objective 1: Physiochemical and electrochemical properties of wide ESW solvents

Description

The first stage of this project aims to measure the physiochemical and electrochemical properties of wide ESW solvents containing industry standard salts, tetraethylammonium tetrafluoroborate (TEABF4) and 5-Azoniaspiro[4.4]nonane tetrafluoroborate (SBPBF4) to clarify the baseline performance and degradation rates of these electrolyte solutions prior to the introduction of novel salts and surfactants.

Electrolyte solutions containing either TEABF4 or SBPBF4 will be prepared with industry standard ultracapacitor solvents(such as acetonitrile and propylene carbonate), long chain nitriles(such as adiponitrile, glutaronitirle), and lactones(such as butyrolactone, valerolactone, and caprolactone). The viscosity, ionic conductivity, and solubility of each electrolyte solution will be measured at a range of temperatures. The electrochemical characteristics of each electrolyte solution will be measured in three-electrode benchtop devices containing an activated carbon quasi-reference electrode, prepared by EL-Cell, to concurrently observe full and half cell performance. The equivalent series resistance of each device will be measured using electrochemical impedance spectroscopy, while the capacitance and stability of each device will be measured through galvanostatic charge/discharge at 2.7V and 3.5V.

The ORNL research team will be consulted to provide insights into potential degradation routes causing device failure. In-situ or post-mortem electrolyte and electrode characterization will be employed to clarify the degradation routes if necessary.

Objective 2: Investigate the impact of additives

Description

The second stage of this project aims to investigate the impact of electrolyte additives on the properties and performance of the electrolyte solutions studied in the first task. The addition of aprotic, nonionic surfactants with a high thermal stability are expected to significantly enhance the wettability of the electrolyte. The increase in electrode wetting is expected to significantly reduce device resistance. Additionally, the inclusion of phosphite additives that inhibit gas evolution are expected to extend device lifetime at elevated voltages.

Fluorosurfactant, siloxane surfactant, and phosphite additives will be separately incorporated at two concentrations into the electrolyte solutions studied in the first task. The viscosity, ionic conductivity, and solubility of each additive-containing electrolyte solution will be measured at a range of temperatures and compared to the measurements from the first task. The electrochemical characteristics of each additive-containing electrolyte solution will be measured in three-electrode benchtop devices containing an activated carbon quasi-reference electrode, prepared by EL-Cell, to concurrently observe full and half cell performance. The equivalent series resistance of each device will be measured using electrochemical impedance spectroscopy (EIS), while the capacitance and stability of each device will be measured through galvanostatic charge/discharge (GCD) at 2.7V and 3.5V. Using the EIS measurements, an equivalent circuit model will be employed to de-convolute the resistive contributions of each additive-containing electrolyte solution to elucidate the role of each additive in altering device performance. Additives with non-redundant contributions to resistance reductions will be evaluated in separate electrolyte solutions.

The solvent and additive(s) employed in the highest performing device will be used to generate electrolyte solutions with EX-196 and EX-204, the two high conductivity salts previously developed by Eonix. The physiochemical and electrochemical characteristics of these solutions will then be measured. The salt concentration of EX-196 and EX-204 will be adjusted to optimize the performance of the three-electrode device.

The ORNL research team will be consulted to provide insights into potential degradation routes causing device failure. In-situ or post-mortem electrolyte and electrode characterization will be employed to clarify the degradation routes if necessary.

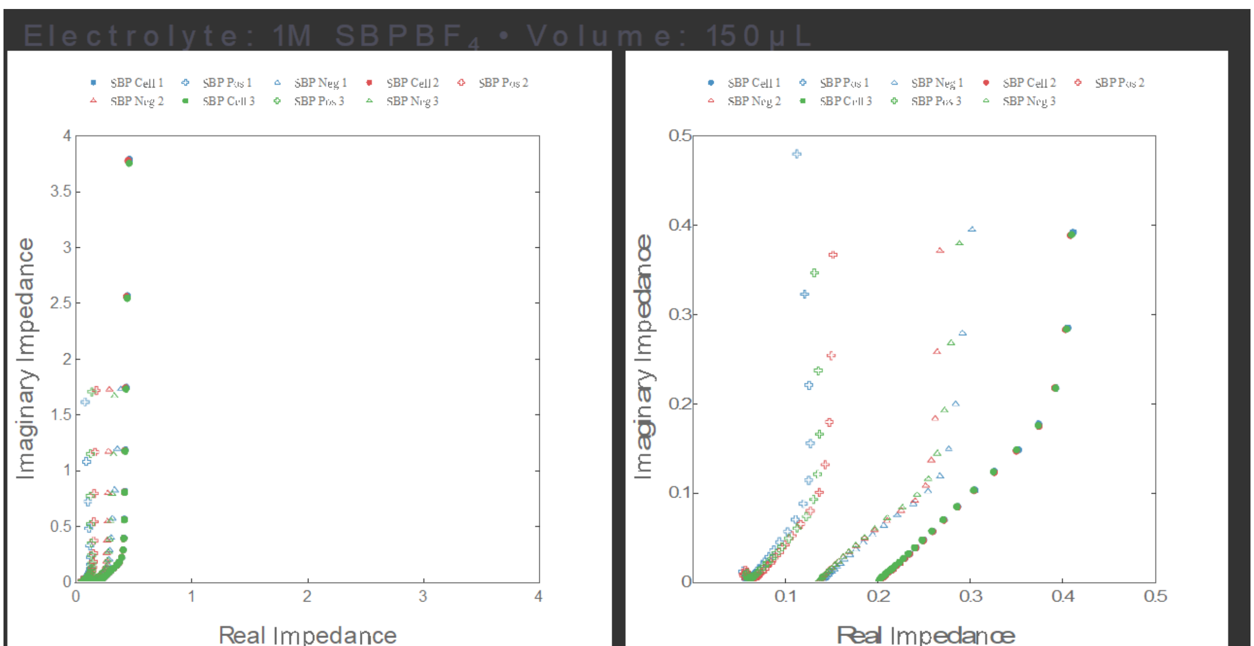
3. Benefits to the Funding DOE Office's Mission

Oak Ridge National Laboratory researchers are uniquely qualified to aid in the design and development of next generation ultracapacitor electrolytes having previously leveraged beyond lithium ion technology to develop novel sodium based electrolytes that achieved a remarkable 4V operational window. This prior research experience has equipped these ORNL researchers with a comprehensive understanding of the material challenges and degradation mechanisms associated with an operating ultracapacitors devices beyond 2.7V. Furthermore, ORNL is outfitted with a plethora of in-situ electrochemical analysis tools that can aid in clarifying not only which electrolyte components are degrading, but also the degradation by-products that may be contributing to precipitous cell failure. The presence of research staff acclimated with the technical challenges of this project paired with the broad spectrum of characterization equipment makes ORNL the ideal facility to develop this technology.

4. Technical Discussion of Work Performed by All Parties

During this fellowship at Oak Ridge National Laboratory (ORNL), a high throughput electrolyte screening process was refined to study the structure activity relationships of electrolytes in electric double layer capacitors, also referred to as ultracapacitors. This process leverages a previously developed pseudo reference electrode to independently measure the cathode and anode of a standard cell while observing full cell behavior. In collaboration with ORNL staff scientists, we expanded two electrochemical techniques to explicitly measure the reaction kinetics, capacity fade, and electrolyte electrode interface growth of the cathode, anode, and full cell. These techniques were then used to screen over sixty chemistries to develop a high voltage electrolyte for ultracapacitors. A byproduct of the development of this technique is a publication, in preparation, with ORNL on the measurement of single point charge in a double layer capacitor.

The primary technique developed in collaboration with ORNL scientists was a high resolution electrochemical impedance spectroscopy (HREIS) procedure that enabled the cathode, anode, and full cell to be measured concurrently with a high level of accuracy (Figure 1). The summed impedances of the cathode and anode were found to nearly match the measured impedance of the full cell thereby demonstrating the high conductivity and minimal impedance contribution of the pseudo reference electrode. Furthermore, the apparatus was configured to optimize reproducibility, with samples containing the same materials set exhibiting impedance measurements within 3%. This reproducibility and half-cell accuracy are considered remarkably high for electrochemical impedance spectroscopy leading our collaborates to refer to this as a “high resolution” technique.



Cell Section	Cell 1	Cell 2	Cell 3
Full Cell (Pos. vs. Neg.)	0.412 Ω	0.409 Ω	0.411 Ω
Positive (Pos. vs Ref.)	0.127 Ω	0.137 Ω	0.146 Ω
Negative (Neg. vs Ref.)	0.284 Ω	0.262 Ω	0.272 Ω

Figure 1. The figure above displays HREIS measurements on three different cells with the same materials.

This newly developed HREIS technique was used in conjunction with 6 probe galvanostatic charge discharge cycling to rapidly screen 60 electrolyte chemistries. During this screening, unique reduction oxidation interactions for different chemistries were observed suggesting that certain additives could be electrochemically activated for benefits. These interactions were further studied leading to the development of a novel site selective reactions (SSR) approach. Specific compounds were classified as "active additives" with the intention of being activated electrochemically during charging to selectively react with functional groups on the electrode surface that contribute to device failure at elevated potentials (Figure 2). These additives when initiated with a SSR were found to increase the stability of the cathode and enable high voltage operation for ultracapacitors containing activated carbon.

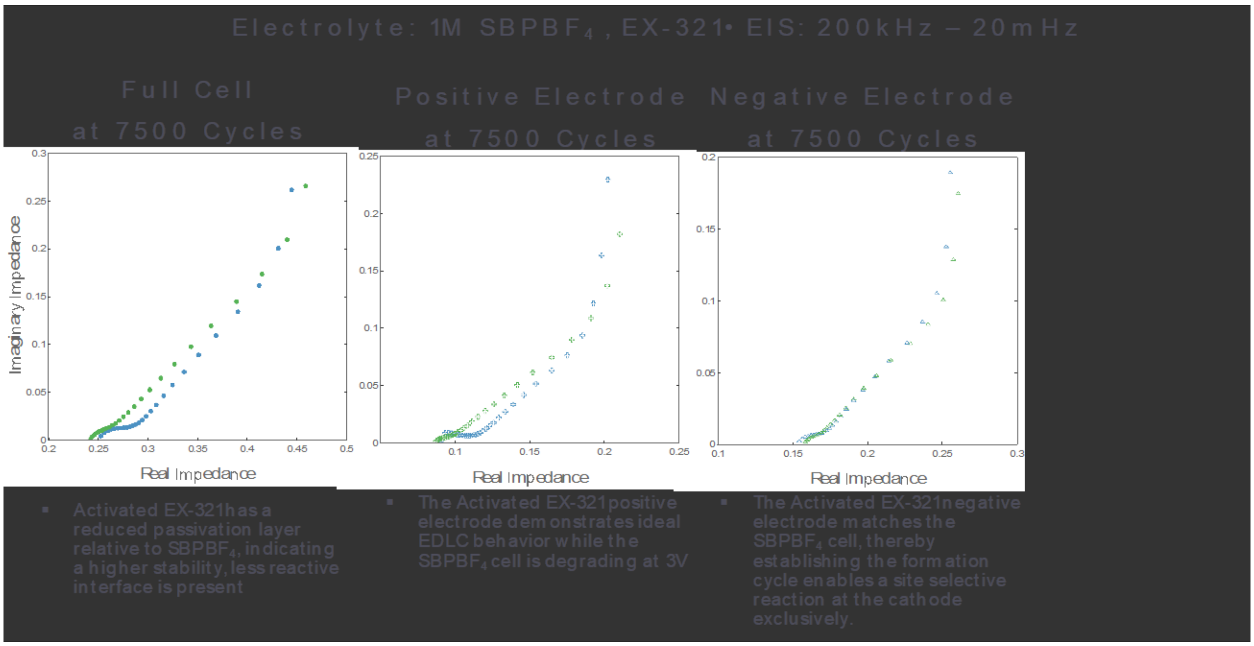


Figure 2. The figure above displays three HREIS measurements on a baseline cell (blue) and a cell with additives that were activated using an SSR.

5. Subject Inventions (As defined in the CRADA)

None

6. Commercialization Possibilities

During this fellowship, I was able to advance and forge relationships with the largest manufacturers in the ultracapacitor space. Our group received electrode samples from Maxwell Technologies (the largest ultracapacitor manufacturer by revenue), Graphenix Development Inc., and Custom Electronics Inc. Furthermore with the guidance of the advisors from ORNL, I was able to develop a comprehensive understanding of the ultracapacitor value chain, draft a go to market strategy, and map a preliminary electrolyte sales cycle.

7. <u>Plans for Future Collaboration</u>

This fellowship has yielded a bevy of significant professional development benefits that will aid my entrepreneurial pursuits. The Innovation Crossroads and advisory team provided me with the professional tools needed to perform market research in a hard tech space, commercialize a high-tech product with limited consumers, and manage a research team with a product development. These skills will be instrumental moving forward as I aim to grow our business.

8. <u>Conclusion</u>

The culmination of these efforts has resulted in an electrolyte that expands the voltage of ultracapacitors to 3.3V and has a conductivity that is consistent with nitrile-based solvents. Furthermore, relationships in the ultracapacitor industry were furthered and forged to begin commercializing this technology.