

Improvement of Low Temperature Performance of Supercapacitors using Ionic Liquid Based Electrolytes

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Abstract

Supercapacitors (SCs) are energy storage devices that are utilized for fuze setting and pre-flight data hold in weapon systems due to their high-power density. Unfortunately, at low temperatures SCs have shown poor performance due to their electrolyte reaching their freezing point within the operating/storage temperature requirements of the U.S. Army. U.S. Army Combat Capability Development Command Armaments Center (DEVCOM-AC) engineers have identified and characterized the performance of many top-of-the-line commercial off the shelf (COTS) SCs in order to elucidate the lower temperature bounds in which these devices begin to fail. Prototype SCs were fabricated in a coin cell configuration utilizing low freezing point ionic liquid-based electrolytes mixed with solvents to improve low temperature performance. The coin cells were electrochemically tested to decipher the internal series resistance, maximum working voltage, and max current draw these new electrolytes would allow at extreme low temperatures.

Keywords

Ionic Liquid; Low Temperature; Supercapacitor; Ultracapacitor

Introduction

The advancement of electrochemical storage devices is vital to meet the ever-growing energy demands[1]. Electric double-layer capacitors or supercapacitors (SCs) have been highlighted as ideal energy storage devices for high power applications. SCs offer high power density, a long cyclic life, and a faster charge/discharge time when compared to batteries, all while having an extremely long shelf life [1-2]. Despite their high power density and short charge times, SCs show poor and unreliable performance at temperatures below -30°C (-22°F). To improve upon the low temperature performance of SCs, the electrolyte that is utilized must change.

The electrolyte utilized within a SCs is prone to freezing at extreme low temperatures based on the physical properties of the electrolyte itself. Typical commercial electrolyte includes acetonitrile (AN) and polypropylene carbonate (PC) which begin to freeze at -40°C (-40°F). An ideal candidate to these regularly used solvent are ionic liquid-

based electrolytes. Ionic liquids are comprised of large asymmetric organic cations mixed with organic/nonorganic anions, while utilizing solvents with lower freezing points. Since both the cations and anions contribute to the overall conductivity, ionic liquids have a higher operational voltage range of up to 6V. The superior thermal stability of ionic liquids have also led to reliable operation at temperatures as low as -70°C (-94°F) [4-6], making them the most attractive option.

There are drawbacks to the utilization of ionic liquids. As temperature begins to fall the viscosity of the liquid increases. This increase in viscosity has been directly correlated to the decrease in overall conductivity. This would result in poor charge times as temperature decreases. Guo et al. [3] and Wong et al. [5] have studied this phenomenon and showed that an optimized molar ratio of AN to 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) can alleviate these issues at room temperatures.

In order to understand the benefits that a drop-in replacement electrolyte would have on commercial off the shelf (COTS) SCs, these cells will be charged and discharged over a wide temperature range to understand the current state-of-the-art in the commercial market. A solution of EMIMBF₄ in AN will then be formulated and utilized with porous carbon-based electrodes in a coin cell configuration to understand the low temperature performance increase these thermally stable electrolytes have compared to standard industry electrolytes.

Experimental

Commercial Off the Shelf Supercapacitors

Supercapacitors (SCs) were purchased from Digikey Electronics. The devices varied in overall capacitance in an effort to characterize SC of various sizes.

Formulation of Electrolyte

Acetonitrile (AN) and 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF₄) were purchased from Sigma-Aldrich. A solution of EMIMBF₄ in AN was measured by volume and mixed at room temperature for 1 hour prior to use. All electrolyte formulation occurred within a dry room.

Preparation of Coin Cells

CR2032 hardware, high surface active carbon, and conductive additive were purchased from MTI Corp. Poly(vinylidene fluoride) and 1-methyl-2-pyrrolidione were purchased from Sigma-Aldrich and were utilized as an electrode binder. A slurry of 80% active carbon to 10% binder and 10% conductive attritive was mixed in a dry room for 24 hours prior to being drop cast onto pre-cut aluminum current collectors. Whatman GF/C glass microfiber filter paper were purchased from Scientific Filers and utilized as the separator. All coin cells were assembled and crimped in a dry room. The coin cell preparation process is depicted in Fig. 1 in which each step of the process is highlighted.

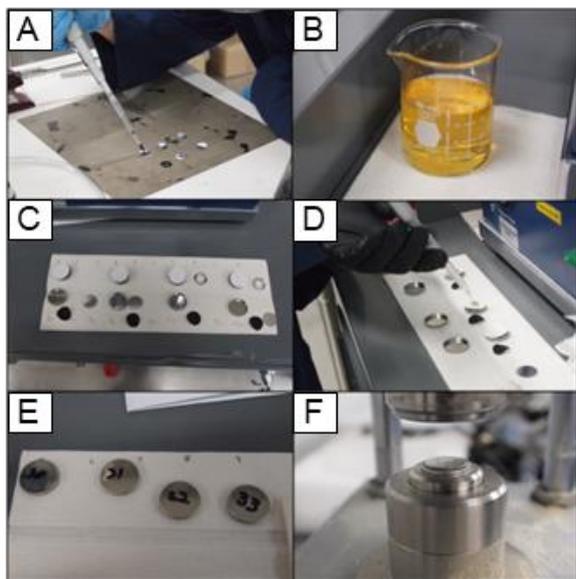


Figure 1. Coin cell preparation: (A) Drop casting of electrode material on aluminum current collector (B) Ionic Liquid Electrolyte (C) All coin cell hardware (D) Addition of electrolyte to coin cells (E) Finalized coin cells (F) Example of coin cell in crimper.

Electrochemical Testing

All electrochemical testing was conducted with a PARSTAT MC multichannel potentiostat loaded with PC100 potentiostats. All electrochemical testing was conducted within an environmental chamber to ensure a constant temperature environment during testing. The test set up can be seen in Fig. 2.

Cyclic voltammograms (CVs) were first conducted on all coin cells and COTS SCs. The voltage limit for the COTS SCs was based on the working voltage outlined in their data sheets and varied from 2.5V to 3V. The voltage limits of the coin cells were 0V to 3.5V. Scan rates varied from 0.1V/s to 1V/s.

Constant current charge and discharge cycling was then conducted on all COTS SCs and coin cells. The applied loads varied from 0.25 A/g to 5 A/g. The mass of the

packaged COTS SC was used to determine the load applied, while the mass of the electrode material was used for the load applied to the coin cells.

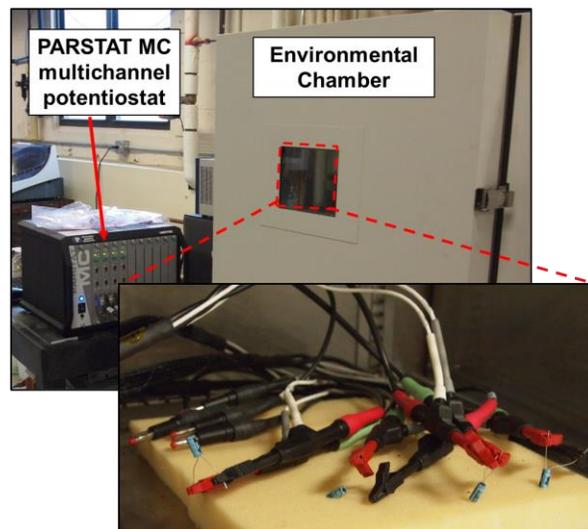


Figure 2. PARSTAT MC potentiostat running into an environmental chamber. An enlarged view of the COTS SCs is shown to display how the SCs were cycled within the chamber.

Testing was conducted from +20°C to -40°C (+68°F to -40°F). Increments of 10°C were taken in which a 30-minute dwell time occurred at each temperature to ensure proper soaking.

Discussion

Initial testing of the fabricated coin cells showed a working voltage of 3V with a total capacity of 500 μ F. To best compare the performance of COTS SCs to the fabricated coin cells, all comparisons in this work were made to the smallest capacity SCs ordered. These COTS SCs have a total capacity of 500mF with a working voltage of 2.5V. From this immediate comparison it is apparent that the utilization of an ionic liquid-based electrolyte allows for a greater operational voltage window which in turn can result in much higher cell capacity due to the direct relation between capacity and working voltage of SCs.

The main electrochemical data compared in this work is the constant current charge and discharge data of both the COTS and ionic liquid-based electrolyte coin cell SC. This data set was chosen based on the low temperature performance of the COTS SC. At -40°C (-40°F) the COTS SC struggled to cycle and generated mostly noise, which can be seen in Fig. 3. It is important to note that this erratic behavior began at -30°C (-22°F). The current density of 5A/g was chosen because this rate allowing for fast, yet stable charging of both the COTS and coin cell SCs at all temperature in which the SCs cycled. The coin cells were able to charge at up to 10A/g, while the COTS SC were only able to charge up to 5A/g.

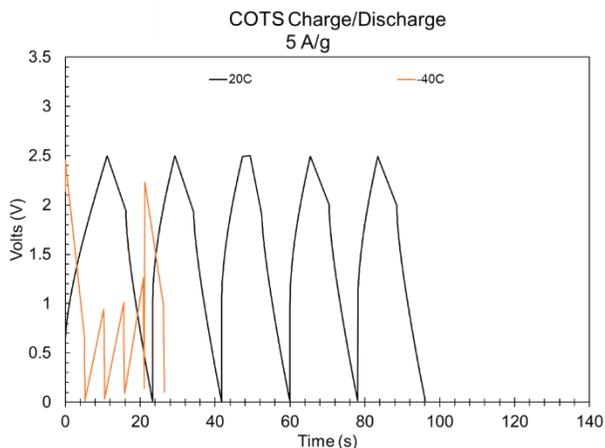


Figure 3. Charge/Discharge data of a 300mF COTS SC. The rate of charging was 5A/g. Data for charging at +20°C (+68°F) (black) and -40°C (-40°F) (orange) is shown.

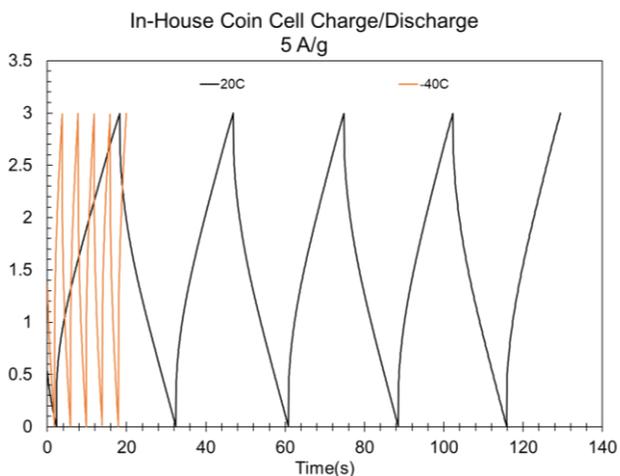


Figure 4. Charge/Discharge data of a 500µF coin cell SC with ionic liquid-based electrolyte. The rate of charging was 5A/g. Data for charging at +20°C (+68°F) (black) and -40°C (-40°F) (orange) is shown.

Fig. 4 shows the charge and discharge data of an in-house ionic liquid-based coin cell. From this data, the charge and discharge time is dramatically reduced when comparing the +20°C (+68°F) data to the -40°C (-40°F). This is due to a loss in capacity of the coin cell as the temperature drops. The capacity loss is shown in Fig. 5 in which the capacity of three cells are displayed. The capacity decreases from 500µF to 100µF between +20°C (+68°F) and -40°C (-40°F). When utilizing the room temperature capacity measurements as a baseline, the capacity loss as a percentage was calculated and shown in Fig. 5. What was observed was a loss of up to 75% the original capacity as temperature reached -40°C (-40°F).

The capacity reduction is attributed to the increase of the equivalent series resistance of the cells as temperature is decreased. The ESR increase is most likely due to the AN beginning to freeze. This conclusion can be made when analyzing Fig.5 and Fig.6. As temperature is reduced from +20°C (+68°F) to -20°C (-4°F) a linear reduction in capacity

can be seen. As temperature continues to drop, the reduction of capacity becomes more exponential. The temperature range in which this occurs is also the temperature range the AN begins to freeze. Despite its use as an electrolyte additive for increased conductivity, AN is still not an ideal additive when operating at temperatures below -30°C (-22°F).

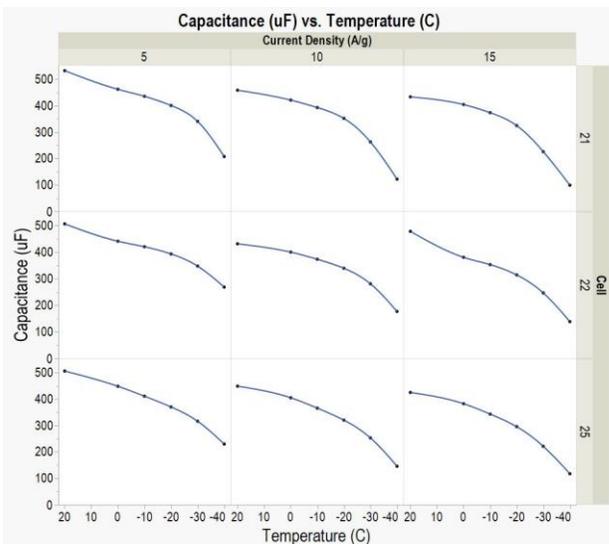


Figure 5. Charge/Discharge data of a 500µF coin cell SC with ionic liquid-based electrolyte. The rate of charging was 5A/g. Data for charging +20°C (+68°F) (black) and -40°C (-40°F) (orange) is shown.

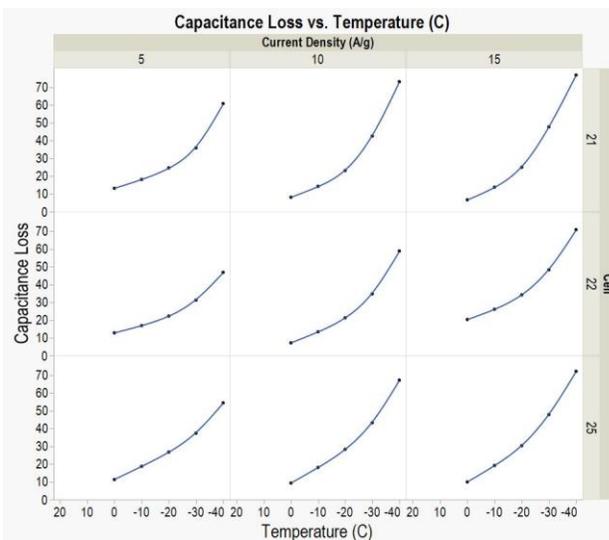


Figure 6. Charge/Discharge data of a 500µF coin cell SC with ionic liquid-based electrolyte. The rate of charging was 5A/g. Data for charging at +20°C (+68°F) (black) and -40°C (-40°F) (orange) is shown.

Conclusion

COTS SCs were cycled from +20°C to -40°C (+68°F to -40°F) to understand their performance stability at extreme low temperatures. From this testing it was observed that they begin to show poor and unreliable performance at

temperatures at and below -30°C (-22°F). A solution of EMIMBF₄ in AN electrolyte was formulated as a drop-in replacement to the standard AN electrolyte to improve performance. The electrolyte was studied in a coin cell configuration in which improved performance was observed. The working voltage of the coin cells outperformed COTS SCs, while the electrolyte was also able to handle higher current loads. Additionally, the electrolytes allowed for the charging and discharging at temperature up to -40°C (-40°F).

Although the coin cells did cycle, there was still a considerable 75% reduction of capacity at -40°C (-40°F) which can make this electrolyte unreliable when high power applications are vital. This reduction of capacity is due to the freezing of the AN additive. Further optimization of a drop-in replacement electrolyte is needed with a focus on solvents that have freezing points lower than -40°C (-40°F) if low temperature operation is desirable.

Acknowledgements

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