Impact of spiro ammonium electrolytes on electric double layer capacitors

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IMPACT OF SPIRO AMMONIUM ELECTROLYTES ON ELECTRIC DOUBLE
LAYER CAPACITORS

By

Donald DeRosa

A Dissertation

Submitted to the University at Albany, State University of New
York

In Partial Fulfillment of

the Requirement for the Degree of

Doctor of Philosophy

College of Nanoscale Science and Engineering

2018
Preface

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I would like to thank my parents, Donald and Donna DeRosa, for their support and enduring patience throughout the course of my doctoral research. Finally, I would like to thank my partner Sam Morris for encouraging my often lofty goals.
Abstract

Electric Double Layer Capacitors (EDLC) are high power ($10^3$ W kg$^{-1}$), durable (>500,000 cycles) energy storage devices that are promising candidates for Hybrid Energy Storage Systems (HESS), automotive and smart grid applications. EDLCs when coupled with lithium ion batteries in HESS configurations for hybrid vehicles have been shown to reduce capacity related degradation by a factor of 2 and impedance related degradation by 5.9. Despite these promising advantages, the adoption of EDLCs has been hampered due to concerns regarding the low volumetric and gravimetric energy density of these devices. Researchers have attempted to address these concerns through the development of high surface area nanomaterials for electrodes and high stability ionic liquids. These approaches, although technically successful, have failed to displace the incumbent materials, activated carbon and tetraethyl ammonium tetrafluoroborate in acetonitrile, due to the high cost of these designer materials. This research aims to increase the energy density of EDLCs through the use of modified cations that are compatible with current commercial devices and investigate the impact of the cation structure on electrochemical characteristics of the system.

The smallest spiro ammonium salt reported to date, 1M 4-Axoniaspiro[3,4]octane tetrafluoroborate (APBF$_4$), was investigated as the electrolyte with acetonitrile (AN) in an EDLC. The electrochemical characteristics of devices containing 1M APBF$_4$/AN paired with activated carbon electrodes were compared to devices containing standard EDLC electrolytes, 1M 5-Azoniaspiro[4.4]nonane tetrafluoroborate (SBPBF$_4$/AN) and 1M tetraethyl ammonium tetrafluoroborate (TEABF$_4$/AN), using cyclic voltammetry (CV), galvanostatic charge discharge (GCD), and electrochemical impedance spectroscopy (EIS). The average gravimetric capacitance of the 1M APBF$_4$ device (124.7 F g$^{-1}$) was found to be greater than the values measured for both
the 1M SBPBF$_4$ device (108.6 F g$^{-1}$) and the 1M TEABF$_4$ device (99.2 F g$^{-1}$). The equivalent series resistance (ESR) of the 1M APBF$_4$ device (383.4 mΩ cm$^2$) was found to be substantially lower than the values measured for both the 1M SBPBF$_4$ device (501.0 mΩ cm$^2$) and the 1M TEABF$_4$ device (710.8 mΩ cm$^2$). These results show that APBF$_4$, when compared to current commercial electrolytes, significantly enhances the energy storage properties of EDLC devices.

The impact of the cation as a counter-ion and co-ion on EDLC performance was clarified for the first time. The capacitance, equivalent series resistance (ESR), specific energy, and specific power of the full cell, positive, and negative electrodes were measured concurrently for devices containing four distinct acetonitrile based electrolytes with cations that vary in both molecular volume and electrostatic potential (ESP). Contrary to the notion of ion size being the primary electrolyte property that dictates capacitance, the device containing the second smallest cation (102Å) in this study demonstrated a higher capacitance than the smallest spiro-ammonium cation (98Å). This increase in capacitance was observed to occur at the positive electrode, where the cation assumes the role of the co-ion and is not expected to be a significant contributor to double layer capacitance. The increase in positive electrode capacitance was found to be directly proportional to the maximum cation ESP ($R^2 = 0.996$). Conversely, the negative electrode, where the cation is the counter-ion, capacitance was found to be inversely proportional to cation size ($R^2 = 0.999$). This study has not only established that cation structure plays a pivotal role in dictating positive electrode capacitance, but revealed that cation ESP and size are the pertinent properties at each interface.
Contents
Preface .................................................................................................................................................. ii
Acknowledgements ............................................................................................................................ iii
Abstract ................................................................................................................................................ iv

Chapter 1: Introduction .......................................................................................................................... 1

1.1 The Growing Need for High Power Energy Storage ........................................................................ 1

Impetus for Energy Storage .................................................................................................................. 1

1.2 Electrochemical Capacitors ............................................................................................................ 2

Capacitors ............................................................................................................................................. 2

1.3 Electric Double Layer Capacitors (EDLC) ....................................................................................... 4

Introduction ........................................................................................................................................... 4

Structure and Electrode Materials of the Device ..................................................................................... 5

1.4 EDLC Applications .......................................................................................................................... 6

Advantages of EDLC ............................................................................................................................ 6

Hybrid Energy Storage Systems ........................................................................................................... 6

Hybrid and Electric Buses ..................................................................................................................... 8

1.5 Research Objects ............................................................................................................................ 9

Chapter 2: Electrolytes for Ultracapacitors .......................................................................................... 11

2.1 EDLC Electrolyte Overview ........................................................................................................... 11

2.2 Properties of Organic Solvents ..................................................................................................... 14
2.3 Cations and Anions ................................................................. 16

Cations ......................................................................................... 16

Anions ....................................................................................... 18

Chapter 3: Electrochemical Methods and Materials ................................................. 20

3.1 Introduction to Electrochemical Methods ....................................................... 20

3.2 Cyclic Voltammetry (CV) ........................................................................... 21

3.3 Galvanostatic Charge/Discharge (GCD) ...................................................... 23

3.4 Electrochemical Impedance Spectroscopy (EIS) ............................................. 28

3.5 Activated Carbon Electrode ........................................................................ 32

3.6 Organic Electrolytes ................................................................................. 36

Chapter 4: EDLC Apparatus for 2 & 3 Electrode Measurements ................................. 40

4.1 Introduction .......................................................................................... 40

4.2 Coin Cell EDLC ...................................................................................... 41

Components and Fabrication ........................................................................ 41

Aluminum Coating .................................................................................... 43

Coin Cell Results and Discussion ................................................................ 44

Coin Cell Conclusions .............................................................................. 49

4.3 Two Electrode EDLC Apparatus .................................................................. 51

Benchtop Device Variability ....................................................................... 51

Two-Electrode Device Assembly .................................................................. 52
Chapter 6: Direct Measurement of the Positive and Negative Electrodes

6.1 Introduction

6.2 Computational Chemistry Cation Calculations

6.3 Full Cell Electrochemical Impedance Spectroscopy

6.4 Full Cell Galvanostatic Charge/Discharge

6.5 Negative Electrode Galvanostatic Charge/Discharge

6.6 Positive Electrode Galvanostatic Charge/Discharge

6.6 Role of Co-ion and Counter-ion

Chapter 7: Conclusions and Future Work

References
1. **Chapter 1** is an introduction to the high power energy storage, electrochemical capacitors, electric double layer capacitors, and the goals of this research.

2. **Chapter 2** reviews the different types of electrolytes presently used in EDLCs, the properties of different organic solvents previously studied, the impact of cation and anion composition on device performance, and the current understanding of the EDLC charging mechanism.

3. **Chapter 3** describes the different electrochemical techniques, electrode materials, and spiro-ammonium tetrafluoroborate salts employed in this study.

4. **Chapter 4** discusses the fabrication and measurement techniques for the two-electrode and three-electrode devices in this study.

5. **Chapter 5** reports and discusses the performance of the smallest spiro-ammonium cation in two-electrode EDLC devices with respect to the incumbent electrolytes, TEABF$_4$ and SBPBF$_4$.

6. **Chapter 6** examines the impact of cation structure on full cell EDLC device performance by directly measuring the electrochemical characteristics of the positive and negative electrodes using a novel three-electrode apparatus.

7. **Chapter 7** concludes the work with remarks on the results, discoveries and future directions towards innovations on the anions and electrode.
Chapter 1: Introduction

1.1 The Growing Need for High Power Energy Storage

*Impetus for Energy Storage*

The rising ecological and economic costs levied by the consumption of fossil fuels coupled with rapidly increasing energy demand has compelled countries and consumers alike to begin adopting renewable energy technologies, signified by the rapid deployment of solar and wind power this past decade and the initial electrification of vehicles. Despite the recent increased focus on renewables supplanting fossil fuels, the growth of global energy consumption is projected to significantly outpace the current deployment rate of renewable energy technologies resulting in increased fossil fuel consumption and CO₂ generation. The U.S. Energy Information Agency (EIA) has projected that global energy consumption will increase 48% by 2040, with the world production of oil doubling from 4.98 million barrels per day (bpd) to 10.36 million bpd[1]. This rising energy consumption will result in CO₂ emissions increasing 33% from 2012 to 2040, even though the rate of new renewable energy installations (2.6%) is projected to be the fastest growing energy segment[2]. The U.S. is a significant contributor to renewables current and projected installation rate with at least 1 GW of solar power installed for six consecutive fiscal quarters leading up to Q1 2017 and 39% of all new U.S. electric generating capacity additions in 2016 being solar powered[3]. Even with this high renewables installation rate, the U.S. is still expected to generate 59% of grid electricity from fossil fuels in 2025. Furthermore, the high installation rate of renewables is not expected to stifle the accelerating costs of oil, due to a high dependence in the transportation industry on liquid fuels, with a projected cost of $230 per barrel in 2040[1,2,4]. Accelerating the adoption of renewable energy sources and higher efficiency transportation technologies is the lone option to circumvent the
projected higher costs and CO₂ emissions of fossil fuel consumption, but this is predicated on the development of an energy storage technology that can manage the intermittent power generation of renewables and enable cost parity of electric vehicles (EV) with internal combustion engines (ICE).

1.2 Electrochemical Capacitors

*Capacitors*

![Diagram of capacitor classifications](image)

*Figure 1.1 Overview of different classifications of capacitors, the specific focus of this study involves Electrochemical Capacitors, Electric Double Layer Capacitors*

Capacitors are generally defined as devices used to store charge with two or more conducting components and an insulating separator component. Capacitors are classified as either non-electrolytic, electrolytic, or electrochemical primarily based on the materials employed to create the conducting and insulating components as well as the device architecture and charge storage mechanisms (Figure 1.1).
Despite technically storing energy, electrolytic and non-electrolytic capacitors are primarily employed to manipulate electrical signals in electronic circuits due to the low energy density of these devices. Non-electrolytic capacitors, also referred to as ceramic or film capacitors, store charge between two metal plates separated by either an insulating ceramic or film dielectric layer. The device characteristics are largely defined by the surface area of the two plates present in the device and the breakdown potential of the dielectric. Due to the superior insulating properties of the ceramic and film based dielectric layers, non-electrolytic capacitors can store charge in the range of kilovolts (kV), but the low surface area of the parallel metal plates limits these devices to microfarads and by extension a low energy density. These devices are typically employed in low pass filter, harmonic, and high voltage circuit applications.

Alternatively, electrolytic capacitors are polarized devices composed of a metal anode (aluminum or tantalum), thin non-conductive oxide layer, and solid electrolyte as the cathode. The thin dielectric layer in electrolytic capacitors results in devices with significantly higher capacitances than non-electrolytic devices, but consequently the thin dielectric layer also substantially reduces the breakdown voltage.

Unlike non-electrolytic and electrolytic capacitors, electrochemical capacitors are primarily utilized as durable, high power energy storage devices rather than electrical circuit components for signal manipulation due to their high energy density. Electrochemical capacitors are categorized as either pseudo, hybrid, or electric double layer capacitors based on the materials employed and the charge storage mechanism in the device. Pseudo capacitors are devices that store charge entirely through faradaic oxidation reduction reactions. Hybrid capacitors are asymmetric devices that rely on rapid faradic, electron transfer reactions in conjunction with electric double layers to store charge thereby resulting in electrochemical
devices with the highest energy density, lowest power density, and reduced cycle life. The most common hybrid capacitor architecture, lithium ion capacitor, is an amalgamation of lithium ion battery and capacitor energy storage technologies. The energy, density, power density, cycle life, and discharge profile of electrochemical capacitors can be significantly altered by changing the composition of the energy storage materials.

1.3 Electric Double Layer Capacitors (EDLC)

Introduction

Electric double layer capacitors (EDLC) store energy through non-faradaic interactions of anions and cations at oppositely charged electrodes in an electrostatic energy storage mechanism consistent with traditional non-electrolytic capacitors. EDLC devices utilize high specific surface area activated carbon electrodes (>1200 m²/g) to increase the volume of charge storage in the device. Researchers have explored the use of nanomaterials (graphene, nanotubes), ionic liquids, and aerogels to improve the energy density of these devices without compromising the power density (10³ W kg⁻¹) or cycle life (>500,000). Recently, there has been significant efforts to advance the fundamental understanding of EDLC device operation. New models and simulation strategies have been explored to provide more insight into the structure and formation of the electrode-electrolyte double layer that results in energy storage. These simulations have been coupled with recent in-situ measurements corroborate the notion that EDLC charging mechanisms are more complex than simply counter-ion adsorption on the surface of an electrode.
Structure and Electrode Materials of the Device

An EDLC is composed of two high surface area electrodes, an electrolyte containing cations and anions, and an electrically insulating, semi permeable membrane. The configuration of an EDLC device is analogous to a lithium ion battery, with the two electrodes divided by the separator and the electrolyte wetting the system enabling ionic conduction. An EDLC departs from the configuration of a lithium ion battery due to the symmetric chemical composition of the two electrodes in the system. Rather than contain a metal oxide cathode and graphite anode, EDLCs have two electrodes with an identical activated carbon chemical composition. The carbon slurry coated on an aluminum current collector to generate an activated carbon electrode is composed of the high surface area activated carbon material, a binder, and a conductive carbon. The activated carbon material is derived from carbonized organic precursors and is the high cost material in the device. The most popular and costly activated carbon option is carbonized coconut shells, which has superior cycle life performance relative to other activated carbon sources. The selected activated carbon is paired with either carboxymethyl cellulose (CMC), styrene butadiene rubber (SBR), or polyvinylidene fluoride (PVDF) as a binder. The CMC and SBR binders have a higher anodic stability, higher conductivity, and lower cost than the PVDF binder, but PVDF does not introduce ionic impurities, sodium and chloride, into the electrode, which reduces cycles life through parasitic side reactions. Additionally, the CMC and SBR binders have oxygen functional groups that are conduits for electrochemical nucleophilic side reactions that further diminish the cycle life of the device. To further increase the conductivity of the electrode, carbon black is added to the slurry mix prior to coating the current collector. Once coated, the two activated carbon electrodes are either rolled with a separator and
welded to the contacts inside of a “can”, cylindrical cell, or stacked to form a prismatic pouch cell.

1.4 EDLC Applications

Advantages of EDLC

The high cycle life (>500,000 cycles), high power density \(10^3 \text{ W kg}^{-1}\), and low equivalent series resistance (ESR) of EDLC devices are distinct advantages for a variety of energy storage applications. The high cycle life of EDLC devices, resulting from the non-destructive electrostatic energy storage mechanism, ensures system longevity and reduces costs associated with maintenance and replacement. This is in contrast to electrochemical energy storage systems such as lithium ion batteries with a low cycle life (5000 cycles) that require replacement, maintenance, and parasitic engineering controls for non-consumable energy storage applications. The high power density of EDLC devices is another advantage derived from the electrostatic energy storage mechanism. EDLCs rely on the movement of ions to form a capacitive double layer to store energy rather than a kinetically limited electrochemical reaction, as in a lithium ion or a lead acid battery, which enables the rapid acceptance and release of energy. Coupled with a high power density, EDLCs also feature a low ESR that enables efficient round trip efficiency (97%) during high power cycles and reduces the need for parasitic thermal management systems.

Hybrid Energy Storage Systems

Hybrid Energy Storage Systems (HESS) combine different energy storage technologies with complementing attributes in an attempt to leverage the advantages of each technology, while mitigating their individual technical deficiencies[5]. Significant research has been conducted to evaluate the merit of EDLCs paired with electrochemical energy storage
technologies such as lead acid and lithium ion batteries for a HESS configuration in electric and hybrid vehicles. The attributes of EDLCs, an electrostatic energy storage device, are in diametric opposition to the properties of electrochemical storage technologies, thus the strengths of each system are expected to remedy the deficiencies of one another[6–8].

Lithium ion batteries are energy dense electrochemical devices that have been implemented successfully in electric and hybrid vehicles. Despite this initial success, there are concerns regarding the safety and longevity of these systems. The lithium ion battery packs require significant parasitic engineering controls to prevent thermal runaway and maintain a safe vehicle for operation in a myriad of climates. Furthermore the low cycle life and power density of these devices requires heavily staggered charging times to extend the longevity of the battery back. These concerns, in part, have been addressed by incorporating an EDLC module in parallel with a lithium ion battery pack to increase the power density of the system, increase system efficiency during regen/charging, and significantly extend the pack lifetime. With a considerably higher efficiency at elevated c-rates, EDLCs were shown to increase system efficiency during charging and regenerative braking from 8-25% when paired with lithium ion battery pack[9]. Investigations involving plug in hybrid duty cycles, a HESS system composed of an EDLC module and lithium ion battery pack in parallel was found to reduce lithium ion battery capacity related degradation by a factor of 2 and impedance based degradation by a factor of 5.9 relative to the baseline lone lithium ion battery pack[10,11]. The culmination of the HESS advantages results in an energy storage system that extends the lifetime, raises the safety, and increases the efficiency of lithium ion batteries for electric and hybrid vehicle applications.
Hybrid and Electric Buses

As devices with a high power density, low ESR, and high cycle life, EDLCs are ideally suited to manage the rigors of regenerative braking systems for micro, mild, and electric hybrid transportation systems. Despite these technical advantages, the adoption of these devices in consumer automotive applications has been hampered by high initial system costs that results in a long payback period. Due to the technical advantages of EDLCs in regenerative braking applications and the capital intensive financial barrier, EDLCs have been primary incorporated in hybrid buses, the largest EDLC device market segment.

The technical advantages of EDLCs in electric and hybrid buses have been demonstrated predominantly in China, the global leader in EDLC device consumption. In fully electric systems, buses travel along a fixed route with charging stations integrated into the designated stops, enabling the high power energy storage system to fully charge in 20 seconds. The high cycle life of EDLCs has ensured that these systems can be repeatedly charged and discharged at every stop without inducing rapid capacity related degradation. Hybrid systems featuring EDLCs have shown to increase energy recovery during regeneration by 18% with respect to lithium ion battery systems. Furthermore, EDLC hybrid systems were found to have lower maintenance costs than lithium ion battery systems stemming from the ability to fully discharge which allowed maintenance workers to shed the cumbersome high voltage safety personal protective equipment that extends repair times. Finally, EDLC hybrid systems were found to have greater longevity than lithium ion battery systems, thereby increasing the lifetime return on investment (ROI) of the system.

The technical advantages of EDLC devices have been shown to significantly improve the performance and cost metrics of hybrid and electric buses. The longevity and high power
efficiency of EDLCs increase the efficiency and ROI of hybrid and electric buses. These advantages have been empirically observed in the Chinese hybrid bus market, currently the largest EDLC device market.

1.5 Research Objects

The goals of this study are to improve the energy density of EDLC devices by replacing the incumbent cation, TEA, with a smaller ion that can increase capacitance through higher surface area ion population and to identify the cation structure attributes that dictate the electrochemical characteristics, specifically the capacitance and stability window, of the device. Cultivating a more comprehensive understanding of the influence of cation properties on device performance will aid in the design of next generation electrolytes for EDLCs. These goals were accomplished in two separate research phases with the first phase focused on increasing the energy density of EDLCs through cation innovations and the second phase focused on measuring the change in electrochemical characteristics of EDLC devices containing different cations.

The first phase focused on two-electrode measurements of cells containing the smallest spiro-ammonium cation synthesized to date, APBF4, and two common commercial electrolytes, SBPBF4 and TEABF4. The electrochemical characteristics of these cells were measured with Cyclic Voltammetry (CV), Galvanostatic Charge/Discharge GCD), and Electrochemical Impedance Spectroscopy (EIS). These techniques were employed to measure the electrochemical stability window (ESW), gravimetric capacitance, equivalent series resistance, and solution resistance of the devices containing APBF4, SBPBF4, and TEABF4. With a significantly smaller cation size, devices containing the AP cation (98Å) were expected to have a greater capacitance than devices containing the larger SBP(114Å) and TEA (123Å) cations.
The second phase focused on computation chemistry calculations and novel three-electrode measurements of cells containing electrolytes with different cations that varied in size and structure (AP, OP, SBP, TEA). The Schrodinger Materials suite software was employed to calculate the molecular volume, electrostatic potential energy (ESP), and orbital energies of each cation studied. The reduction potential was then calculated from the orbital energies and the electrostatic potential energy was mapped onto the electron density of each cation. A novel three-electrode apparatus with a pseudo-reference activated carbon electrode was employed to measure the full cell, negative electrode, and positive electrode electrochemical characteristics of cells containing APBF₄, OPBF₄, SBPBF₄, and TEABF₄. These measurements were used in conjunction with the computational chemistry calculations to identify the cation attributes that impacted EDLC performance.
Chapter 2: Electrolytes for Ultracapacitors

2.1 EDLC Electrolyte Overview

<table>
<thead>
<tr>
<th></th>
<th>Aqueous</th>
<th>Organic</th>
<th>Ionic Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage Stability (V)</td>
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<td>2.7</td>
<td>4.0</td>
</tr>
<tr>
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<td>59</td>
<td>8</td>
</tr>
<tr>
<td>Capacitance (F g(^{-1}))</td>
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</tr>
<tr>
<td>Energy Density (Wh kg(^{-1}))</td>
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</tr>
<tr>
<td>Power Density (W kg(^{-1}))</td>
<td>150</td>
<td>70</td>
<td>56.8</td>
</tr>
<tr>
<td>ESR (Ω)</td>
<td>0.202</td>
<td>0.9</td>
<td>54.3</td>
</tr>
</tbody>
</table>

*Figure 2.1 The properties of Aqueous, Organic, and Ionic Liquid electrolytes are compared*

**EDLC Electrolytes**

Currently, there are three different EDLC electrolyte systems, aqueous, organic, and ionic liquid. EDLC devices containing aqueous electrolytes are ecologically friendly and display the highest power density resulting from the high conductivity and mobility of protons in H\(_2\)O. Despite the advantages of high power density, aqueous systems are hampered by a low voltage stability (1V) resulting in exceptionally low energy densities. Conversely, Ionic liquid electrolytes have a high voltage limit (4V) and energy density, but the low ionic conductivity of ionic liquid based electrolytes limits the power density significantly. Organic electrolytes fail to outperform the best attributes of both aqueous and ionic liquid electrolyte systems, but offer the right combination of energy densities and power densities for high power energy storage applications[12].
The organic electrolyte plays a critical role in defining the capacitance, ESR, and electrochemical stability of an EDLC device. When selecting or designing a novel organic electrolyte for EDLCs there are four properties to consider, proton-donating availability, solvent polarity, ionic conductivity, and oxidation/reduction potentials.

To avoid the proliferation of parasitic side reactions during cycling, each compound selected for the electrolyte, particularly the solvent and additives, are be aprotic. Protic compounds contain a dissociable proton that participate in side reactions, specifically with the electron deficient and rich cations and anions, and generate by-products. These by-products reduce cell capacity and increase cell resistance through the consumption of ions and obstruction of pores, thus electrolyte compounds should be aprotic (Figure 2.2).

Figure 2.2 Overview of the organic electrolyte properties that impact EDLC device performance

The organic electrolyte plays a critical role in defining the capacitance, ESR, and electrochemical stability of an EDLC device. When selecting or designing a novel organic electrolyte for EDLCs there are four properties to consider, proton-donating availability, solvent polarity, ionic conductivity, and oxidation/reduction potentials.

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The polarity of the solvent selected for the electrolyte dictates the capacitive contributions of the solvent in the double. The dielectric constant of the solvent is directly proportional to the solvent related capacitance. Furthermore, the polarity of the electrolyte solvent determines the solubility of the organic salt. The solvents ability to disassociate and solvate the ions requires a high polarity. Unfortunately, as the polarity of the selected solvent increases, the electrochemical stability of the solvent typically diminishes with the exception of nitrile based solvents. The polarity of the solvent also has been shown to dictate conductivity.

The ionic conductivity and the electrochemical stability window of the electrolyte dictates the device ESR and operating voltage. The ionic conductivity is a significant contributor to device resistance in an EDLC. Solvent, cation, and anion selection all play a significant role in dictating the ionic conductivity within a device. The molecular volume of each chemical and the solvent ion interactions dictate ion mobility in the electrolyte, which in turn determines ionic conductivity and device ESR. The oxidation and reduction potentials of the solvent, cation, and anion in the electrolyte determine the maximum half cell potentials and total operating voltage of the device. Since EDLCs rely on the absence of faradaic reactions, the oxidation and reduction potentials determine the upper and lower potential limits of the device[13].
2.2 Properties of Organic Solvents

Figure 2.3 A comparison of the conductivity, molecular weight, and viscosity of popular organic solvents for EDLC devices

As mentioned in the previous section, the properties of the electrolyte play a significant role in determining the performance of an EDLC device. The properties of the organic solvent in particular has a large impact on the performance of the device, specifically the conductivity and electrochemical stability window. Significant work has been done to measure the change in electrolyte conductivity and electrochemical stability as different organic solvents are employed.

The ionic conductivity of the electrolyte impacts the ESR of EDLC devices, thus there have been significant research efforts to investigate the impact of solvent selection on ionic conductivity. As the molecular weight of the selected solvent increases the ionic conductivity of the electrolyte decreases. This inversely proportional relationship is also observed between the viscosity of the solvent and ionic conductivity. Both the increased viscosity and molecular
weight are considered to kinetically impede the movement of ions through the solution to the
double layer, therefore solvents with a low viscosity and molecular weight result in an electrolyte
with the highest conductivity (Figure 2.3)[14,15].

The electrochemical stability window determines the operational voltage of EDLC
devices, thus the role of solvent selection in determining electrolyte stability has been
investigated significantly. As the molecular weight and viscosity of the selected solvent
increases, the measured electrochemical stability of the electrolyte increases. The larger solvent
molecules are more stable and polarizable in the double layer electric field, therefore the stability
of the electrochemical stability solvent is higher. The selection of high stability solvents typically
results in a low conductivity electrolyte, with the exception of acetonitrile (Figure 2.4). Due to
the uniquely high conductivity and stability of acetonitrile, this solvent is in most commercial
EDLC systems[16].

Conductivity, Electrochemical Stability Window, and Viscosity of Varying Organic Solvents
with 0.65M TEABF$_4$
2.3 Cations and Anions

Cations

EDLC Cation Structures

<table>
<thead>
<tr>
<th>Cation Structure</th>
<th>Molecular Structure</th>
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</thead>
<tbody>
<tr>
<td>Ammonium (A)</td>
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</tr>
<tr>
<td>Pyrrolidinium (PYR)</td>
<td><img src="image" alt="Pyrrolidinium Structure" /></td>
</tr>
<tr>
<td>Imidazolium (EMI)</td>
<td><img src="image" alt="Imidazolium Structure" /></td>
</tr>
<tr>
<td>Tetraethyl ammonium (TEA)</td>
<td><img src="image" alt="Tetraethyl Ammonium Structure" /></td>
</tr>
<tr>
<td>Triethyl-methyl ammonium (TEMA)</td>
<td><img src="image" alt="Triethyl-methyl Ammonium Structure" /></td>
</tr>
<tr>
<td>5-Azoniaspiro[4.4]nonane (SBP)</td>
<td><img src="image" alt="5-Azoniaspiro Structure" /></td>
</tr>
<tr>
<td>1-Ethyl-3-methylimidazolium (EMIM)</td>
<td><img src="image" alt="1-Ethyl-3-methylimidazolium Structure" /></td>
</tr>
<tr>
<td>Oxazolidine-3-spiro-1'-pyrrolidinium (OP)</td>
<td><img src="image" alt="Oxazolidine-3-spiro-1'-pyrrolidinium Structure" /></td>
</tr>
</tbody>
</table>

Figure 2.5 Overview of the three most popular ammonium based cation structures, ammonium, pyrrolidinium, and imidazolium.

There are currently three classes of ammonium based cation structures that are employed in organic electrolytes for EDLCs, ammonium, pyrrolidinium, and imidazolium cations(Figure 2.5). In contrast to aqueous based cations, these cations have a filled valance shell with a formal charge of +1, rather than a donated valance electron. As a result these cations have a higher electrochemical stability and are less likely to engage as an electrophile. Each class of cation has...
different advantages in an organic electrolyte for an EDLC, with the structures being tuned to vary device properties and performance.

Ammonium cations, specifically TEA, are currently the most popular commercial options, with most manufactures utilizing TEA in their devices. The TEA cation has a simple, high yield synthesis route that results in a low cost electrolyte. Additionally, the TEA cation has been shown to be stable at 2.7V in devices with activated carbon electrodes. The versatility of the ammonium structure has enabled the development of smaller cations as well, to increase electrode surface area utilization and reduce device resistance. Triethyl methyl ammonium (TEMA) achieved a reduction in cation size through an exchange of an ethyl group for a methyl group, thereby reducing the molecular volume of the cation. The primary fault of ammonium cations is their propensity to participate in a Hoffman elimination reaction that results in ethylene gas generation. The ethyl groups on the ammonium cations are susceptible to deprotonation which leads to the formation of ethylene. The accumulation of ethylene increases the internal pressure of EDLC devices eventually leading to cell failure. The degradation routes of ammonium cations has spurred the research to develop novel cations with higher stability.

Pyrrolidinium cations, specifically SBP, have started to supplant ammonium cations due to the increased capacitance, reduced ESR, and increased stability observed in devices that feature salts with this cation structure. By replacing the tetraethyl additions with two five-membered rings, a pyrrolidinium cation with the same number of carbons has four less carbon-hydrogen bonds thereby resulting in a reduction in volume. Furthermore, the five-membered rings on pyrrolidinium cations are not free to rotate and engage in intermolecular interactions like the ammonium ethyl groups. The absence of methyl groups as proton donating structures enhances the stability of pyrrolidinium cations relative to ammonium cations.
Imidazolium cations, specifically EMIM, have been shown to be high stability cations that can enable device operation above 3V. Due to the high cost of imidazolium cations resulting from a multi-step synthesis process with expensive precursors, these cations are typically paired with the bis(TFMS)imide anion to form an solvent-free ionic liquid that expands the voltage window of EDLC devices to 3.5V for applications that do not have cost concerns. The expanded potential window devices containing imidazolium cations is attributed to resonance stabilization of the five-membered with pi-bonds.

**Anions**

**EDLC Anion Structures**

![Chemical structures of the four most common EDLC anions](image)

Figure 2.6 The chemical structures of the four most common EDLC anions.

There are currently four anions that are primarily employed in EDLC devices, tetrafluoroborate (BF₄⁻), hexafluorophosphate (PF₆⁻), bis(Fluorosulfonyl)imide (FSI), and bis(TFMS)imide (TFSI). Similar to the cation structures, these anions have a filled valance shell with a formal charge of -1. In contrast to aqueous anions, these anions do not readily participate in electron or proton exchanges, therefore these species have a higher voltage stability.

The BF₄⁻ anion is most commonly employed in EDLC devices due the small molecular volume of this structure relative to the other available anions. The small ion size results in a high positive electrode capacitance due to increased surface area utilization for capacitive energy
storage at the electrode surface. The small ion size also translates to reduced device resistance through increased ionic conductivity in the bulk solution and pore mobility.

The PF₆, FSI, and TFSI anions are commonly employed as counter-ions for solvent-free ionic liquids. These anions when paired with EMI cations with extended alky chains have a low melting point resulting in room temperature ionic liquids. These anions have a ESW than the smaller BF₄ anion, thereby enabling a higher device voltage. Although these anions enable higher voltage operation, the increased viscosity of the ionic liquid solution results in an increased device ESR that compromises the power density of the device. Significant efforts have been made by researchers to capture the stability benefits of these anions, while mitigating the detrimental impact of reduced ionic conductivity[17].

![Diagram showing properties that impact capacitance, stability and resistance.](image)

*Figure 2.7 Summarization of the properties that impact capacitance, stability and resistance.*
Chapter 3: Electrochemical Methods and Materials

3.1 Introduction to Electrochemical Methods

The critical electrochemical parameters of EDLC devices, capacitance, equivalent series resistance (ESR), impedance, current leakage, specific energy, specific power, and electrochemical stability window (ESW), are generally measured with three different electrochemical methods, cyclic voltammetry (CV), galvanostatic charge/discharge (GCD), and electrochemical impedance spectroscopy (EIS). Although each of these electrochemical techniques can be deployed to measure multiple critical electrochemical EDLC parameters, there are preferred methods for certain parameters[18]. The CV method is pseudo-quantitative technique typically employed to measure the ESW and identify the potential limits of faradic reactions in two and three electrode devices by measuring the current response resulting from a voltage scan. The GCD method is utilized to measure the capacitance, ESR, current leakage, specific energy, and specific power EDLC devices by observing the change in device potential with shifts in applied current. This method, GCD, is most commonly used to measure the attributes of commercial devices due to the similarities of the technique to the electrical stresses these devices most often encounter in applications. The EIS method is a stationary electrochemical technique that measures the phase shift of a small current or potential excitation signal at a range of frequencies in a steady state system. In contrast to the CV and GCD methods, the EIS method is rarely utilized as standard for commercial device impedance measurements, but instead is utilized to develop an equivalent circuit model for the electric double layer of a given materials system[19].
3.2 Cyclic Voltammetry (CV)

Cyclic Voltammetry (CV) is a transient electrochemical technique most commonly employed to investigate oxidative and reductive chemical reactions. From studying proton-coupled electron transfers in hydrogen generating catalysts to elucidating the synthesis mechanisms of organometallic complexes, this technique has a broad range of applications in electrochemical research[20,21]. With respect to EDLC research, the CV technique can be used to determine the capacitance, resistance, and electrochemical stability window (ESW) of a EDLC material system in either a two or three electrode configuration. Although this technique can be employed to measure the capacitance and resistance, it is most often utilized to determine the ESW for novel EDLC electrode or electrolyte materials. The ESW of the electrode/electrolyte system is the critical parameter that dictates the operating voltage of the final device, which in turn significantly impacts both the power and energy densities of the EDLC.

The CV technique can be utilized in either a three electrode or two electrode configuration. In the three electrode configuration, the potential of the working electrode is a ramped linearly at a set voltage scan rate to a designated potential measured against the reference and counter electrodes. The first sweep is referred to as the cathodic trace on the resulting cyclic voltammogram, the graph of the resulting electrochemical data. The potential of the working electrode is then linearly ramped in the opposing direction to the initial potential. This second and final sweep is referred to as the anodic trace on the cyclic voltammogram. The current response of the system is measured during these experiments and plotted on the y-axis against the change in potential to generate a cyclic voltammogram. In a two electrode configuration, the potential difference of the system is measured across the positive and negative electrodes in the absence of a reference electrode during both the cathodic and anodic traces. The two electrode
configuration does not explicitly identify reaction potentials at either the positive or negative electrodes due to the absence of a reference electrode, but instead determines the breakdown potential of the EDLC device.

The cyclic voltammogram of a sample material, measured in either a three electrode or two electrode apparatus, provides insights into the electrochemical interactions that occur. In the instance of an ideal EDLC, the cyclic voltammogram should exhibit a flat current response throughout the cathodic and anodic traces thus indicating the absence of a redox reaction. Conversely, an EDLC device undergoing an unfavorable redox reaction will display a current peak at either the cathodic or anodic trace. If a peak occurs in both the cathodic and anodic traces, then the electrochemical reaction is reversible. The Nernst equation describes the redox equilibrium for these electrochemical reactions as noted in Eq (3.1):

\[ E = E^\circ + \frac{RT}{nF} \ln \left( \frac{\text{Oxidation}}{\text{Reduction}} \right) \]

(where E is the potential of the electrochemical cell, \( E^\circ \) is the standard potential, R is the universal gas constant, T is the temperature, n is the number of electrons, F is Faraday’s constant, oxidation is the concentration of the oxidation species, and reduction is the concentration of the reduction species). The Nernst equation can be applied to reversible redox systems, where there is a lower barrier for electron transfer between the electrolyte and electrode, to model the impact of shifting concentrations or cell potentials. The peak current observed in the cyclic voltammogram is related to the scan rate, the rate at which the voltage is increased, in the experiment. The peak current observed in diffusion controlled systems is related to the scan rate through the Randles–Sevcik equation as described in Eq (3.2):
where \( n \) is the number of electrons, \( F \) is Faraday’s constant, \( A \) is the surface area, \( C \) is the capacitance, \( D \) is the diffusion constant, \( v \) is the scan rate, \( R \) is the universal gas constant, and \( T \) is the temperature. Thus according to the Randles–Sevcik equation, the peak current resulting from capacitive energy storage is directly proportional to the square root of the scan rate. Current values exceeding the peak current in a cyclic voltammogram can then be attributed to faradiac reduction oxidation reaction rather than capacitive energy storage. In instances not limited by diffusion, the peak current can be described by Eq (3.3):

\[
I = CAv
\]

(where \( I \) is the peak current, \( C \) is the capacitance, \( A \) is the surface area, and \( v \) is the scan rate)[22]. This is typically not the case for EDLC devices that employ porous activated carbon electrodes that are diffusion limited.

### 3.3 Galvanostatic Charge/Discharge (GCD)

The Galvanostatic Charge/Discharge (GCD) method is a transient electrochemical technique to measure the capacitance, ESR, current leakage, specific energy, and specific power EDLC devices by observing the change in device potential with shifts in applied current. In addition to EDLC research, the GCD method is the primary technique utilized by lithium ion battery researchers to investigate the capacity and degradation of lithium ion devices. This technique is regarded as the best practice for calculating capacitance and ESR of both commercial and benchtop EDLC devices[23,24].

The GCD method can be employed in either a two electrode or three electrode configuration, but is most often utilized to measure the capacitance, ESR, specific energy, and
specific power of two electrode devices. In a standard charge/discharge protocol with a two electrode configuration, a current density (A/g) is applied to the device and the change in potential between the positive and negative electrodes is measured. The inverse current density is then applied to the device and the discharging potential between the positive and negative electrodes is measured. The ESR of the two electrode device can be calculated from the potential drop observed between the maximum charging and discharging potentials. The capacitance of the device is calculated from the applied current and rate of change in potential vs time. This experiment can be repeated with a range of different current densities to generate a Ragone plot and investigate the impact of charge/discharge time on the energy and power densities of the EDLC device.
The capacitance and ESR can be accurately calculated for an EDLC device from the resulting potential measurements of the GCD method. The capacitance for a general capacitor is described by Eq(3.4):

$$C = \frac{Q}{V} = \frac{\Delta Q}{\Delta V}$$

(where $C$ is the capacitance, $Q$ is the charge present on the surface of the electrodes, and $V$ is the potential difference between the electrodes). The capacitance cannot be instantaneously measured at given static potential using the GCD method, but is instead calculated by measuring the observed rate of potential change with respect to the induced rate of change electrode charge, applied current. The known current applied to the EDLC device in the GCD method is described by Eq(3.5):

$$i = \frac{\Delta Q}{\Delta t}$$

(where $i$ is the applied current, $Q$ is the change in charge applied to the cell, and $t$ is change in time). By applying a known current, the change in the charge ($Q$) present on the surface of the electrodes can then be calculated. Using known value of the applied current ($i$) and the slope of the GCD figure displaying voltage with respect to time, the capacitance then can be calculated with equations 3.4 and 3.5 in Eq(3.6):

$$C = \frac{\Delta Q}{\Delta V} = i \frac{\Delta t}{\Delta V} = \frac{i}{\frac{dV}{dt}}$$
(where \( C \) is the capacitance, \( i \) is the applied current, and \( \frac{dV}{dt} \) is the change in potential vs time)[25]. This method to calculate capacitance assumes that the voltage discharge is linear and there is no energy stored or released by the device through a faradaic reduction oxidation reaction. The presence of a faradaic reaction would result in a non-linear discharge curve and a non-constant value for the charge/discharge slope (\( \frac{dV}{dt} \)). Similar to capacitance, the ESR of an EDLC device cannot be measured at a stationary potential using the GCD method, a transient technique. As an EDLC device transitions from charging to discharging during the GCD method, a sudden drop in potential is observed. The potential drop observed at the onset of this transition is utilized to calculate the ESR of the EDLC device, which represents the resistive contributions of the electrolyte, separator, interfacial contact of the active material/current collector, and the leads of the potentiostat. The equivalent resistance of a general resistor-capacitor series circuit is described by Eq(3.7):

\[
R_{\text{series}} = \frac{\Delta V}{\Delta i}
\]

(where \( R_{\text{series}} \) is the equivalent series resistance of the resistor-capacitor circuit, \( \Delta V \) is change in potential as a discharge current is applied, and \( \Delta i \) is the change in applied current). The ESR of an EDLC device is calculated from the measured change in the maximum charging potential and maximum discharging potential and known change in current during GCD testing using Eq(3.8):

\[
ESR = \frac{(V_{\text{max-charge}} - V_{\text{max-discharge}})}{(i_{\text{charge}} - i_{\text{discharge}})}
\]
(where ESR is the equivalent series resistance of EDLC device, \( V_{\text{max-charge}} \) is the maximum potential measured during charging, \( V_{\text{max-discharge}} \) is the maximum potential measured during discharge, \( i_{\text{charge}} \) is the current during charging, and \( i_{\text{discharge}} \) is the current during discharging).

The specific energy and specific power of an EDLC device can be calculated from the potential curves generated using the GCD method. The total energy stored by a device is calculated from the product of the current and the area under the discharge curve on a GCD diagram. The area under the discharge curve is represented by Eq(3.9):

\[
E = \int_{0}^{V_{\text{max}}} iV dt
\]

(where E is the total energy of the device from V=0 to V=\( V_{\text{max}} \), \( V_{\text{max}} \) is the maximum potential measured during discharge, V is the potential, dt is the change in time, and i is the current during discharge). The energy equation(3.9) can be modified by substituting the current with the equivalent capacitance relation (equation 3.6) to form Eq(3.10):

\[
E = \int_{0}^{V_{\text{max}}} C \frac{dV}{dt} dt = \int_{0}^{V_{\text{max}}} CVdV
\]

(where E is the total energy of the device, \( V_{\text{max}} \) is the maximum potential measured during discharge, V is the potential, dV is the change in potential, and C is the capacitance). This equation (3.10) can then be integrated to generate Eq(3.11):

\[
E = \frac{1}{2} CV_{\text{max}}^2
\]

(where E is the total energy of the device, \( V_{\text{max}} \) is the maximum potential measured during discharge, and C is the capacitance). Thus once the capacitance of an EDLC is calculated, the
maximum potential measured during the GCD method can be used to calculate the total energy of the device (equation 3.11). The power of an EDLC device is determined using the calculated energy and the known discharge time from the GCD curves in Eq(3.12):

\[ P = \frac{E}{t} \]

(where \( P \) is the power of the device, \( E \) is the total energy of the device, and \( t \) is the discharge time)[26]. To generate a Ragone plot depicting the change in device energy with respect to power, the energy and power values of the an EDLC device are calculated from GCD measurements conducted at a range of current densities.

### 3.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is stationary electrochemical technique commonly employed to measure the impedance of energy storage devices and develop equivalent circuit models for electrochemical reactions/interactions occurring between an electrode and electrolyte[27,28]. Due to the variability associated with pulse-power GCD ESR measurements, EIS is the preferred technique for lithium ion battery impedance measurements and enables researchers to differentiate the resistive contributions of charge-transfer resistance and solution resistance. By measuring the charge-transfer resistance and solution resistance separately, researchers can identify the different failure mechanisms in the lithium ion battery that result in capacity loss[29]. An increase in solution resistance is attributed to electrolyte degradation while an increase in charge-transfer resistance is the result of solid electrolyte interface interactions. In general electrochemical systems, EIS is employed by researchers to investigate ionic diffusion, solid state electrolyte conductivity, corrosion reaction kinetics, and semiconductor-electrolyte junction capacitance. With respect to EDLC devices, EIS enables the
measurement of solution resistance, charge-transfer resistance, complex electric double layer capacitance, diffusion impedance, and electrode polarization[30].

Figure 3.2 Annotated Nyquist plot depicting the solution resistance, charge transfer resistance, diffusion (a), and the ideal capacitance (b). The Randles circuit to model this impedance spectra is displayed (c).

EIS can be measure the electrochemical characteristics of either a two or three electrode apparatus. In a two electrode chemically symmetric system, an EIS measurement will produce an impedance spectra representative of electrochemical interactions occurring at both interfaces. The impedance spectra is generated by first applying an excitation signal, a sinusoidal potential or current, to the sample according to Eq. (3.13):
$E = E_0 e^{j\omega t}$

(where $E$ is the potential, $E_0$ is the potential amplitude, $\omega$ is the frequency in radians, and $t$ is the time). This potential excitation signal induces current flow in the system with an equivalent frequency, but the current flow peak is shifted due to the system's resistance to the change in electron flow, impedance, at this frequency. The phase shift of this system is represented by Eq. (3.14):

$I = I_0 e^{(j\omega t + \phi)}$

(where $I$ is the current, $I_0$ is the current amplitude, $\omega$ is the frequency in radians, $\phi$ is the phase shift and $t$ is the time). The impedance of the system can then be calculated using Ohm’s law and Euler’s formula in Eq. (3.15):

$Z = \frac{E}{I} = \frac{E}{I_0} e^{j\omega t} = Z_0 (\cos(\phi) + j\sin(\phi))$

(where $Z$ is the impedance, $E$ is the potential, $I$ is the current, $\omega$ is the frequency in radians, $\phi$ is the phase shift and $t$ is the time)[31]. With respect to EDLC device measurements, the impedance spectra for EIS is collected across a range of frequencies, 10 mHz to 1 MHz. The real and imaginary components of the impedance (equation 3.15) are then calculated and plotted to generate a Nyquist plot, $Z'$ vs $Z''$. The solution resistance ($R_s$) of the EDLC device, which is strongly correlated to the electrolyte conductivity, is the first intersection of the impedance spectra with the real axis on the Nyquist plot. The charge-transfer resistance ($R_{ct}$) of the EDLC device, representative of faradaic reactions at the electrode surface or current collector/electrode interactions, is the second point to intersect the real axis on the Nyquist plot. The semi-circle present between the solution resistance and charge transfer resistance is attributed to the complex
capacitance at the electric double layer. Although the semi-circle is indicative of double layer capacitance, the quantitative relevance of this measurement is currently debated[32,33]. The presence of a 45° angle following the second intersection with the real axis is the result of restricted diffusion limitations. At the lower frequencies, the upper right most section of the Nyquist plot, the presence of a vertical line is indicative of ideal capacitor behavior.

The Randle’s equivalent circuit is most commonly employed to model the impedance spectra of EDLC devices. The double layer capacitance is accounted for using either a capacitor or a constant phase element (CPE) that closely resembles attributes of a traditional capacitor. This capacitor is in parallel with a resistor represented the charge transfer resistance and a Warburg diffusion element that models the diffusion in the system. The solution resistance is accounted for in the Randle’s circuit with a resistor in series with these elements. Using the Randle’s equivalent circuit model, the values of these elements can be fit to the impedance spectra[34].
3.5 Activated Carbon Electrode

Figure 3.3 Above is an annotated image of the activated carbon electrode sheet used in this study. The 150 micron activated carbon coating is noted in the black region, while the metallic region is the uncoated aluminum section.

The available surface area for capacitive energy storage is the critical metric to consider for EDLC electrode selection. As the available surface area for counter ions to adsorb onto the surface of the electrode increases, the capacitance of the EDLC device increases. This directly proportional relationship between electrode surface area and EDLC device capacitance has been well established. Due to the ubiquity of this relationship, significant research has been conducted to increase the available surface area by either modifying the morphology of the activated carbon
electrodes or replacing the activated carbon electrodes with high surface area nanomaterials. The use of vertically aligned graphene sheets and carbon nanotubes have been shown to substantially increase the capacitance of EDLC devices through an increase in accessible surface area. Both of these nanomaterials, graphene and carbon nanotubes, do not require conductive additives or binder materials, thereby further increasing the specific capacitance of the device by reducing the parasitic mass of these additional materials. Although increasing the surface area generally increases the capacitances, researches that have developed onion-like carbon electrodes, with precisely defined pore sizes, have found that the pore size must be tuned to enable ion adsorption. High surface area materials with pore sizes smaller than the ions present in the electrolyte results in a reduction in device capacitance despite the measured increase in surface area. This deviation in the surface area capacitance trend has been highlighted by discrepancies observed between measured surface area and changes in capacitance, thus the pore structure in addition to the surface area of the material is of paramount concern for EDLC device performance. The surface area and the pore structure of EDLC device electrodes are measured using the Brunaur-Emmett Teller (BET) technique and Barret-Joyner-Halenda technique. Commercial activated carbon electrodes have a surface area between 1000 m$^2$/g to 1500 m$^2$/g, which is an order of magnitude greater than lithium ion battery graphite anodes. Commercial activated carbon electrodes have three pore structures, macroporous, mesoporous, and microporous. Pores greater than 50 nm are considered macroporous, while pores between 2nm and 50 nm are considered mesoporous structures. Pores smaller than 2 nm are considered microporous. Onion-like activated carbon electrodes with micropores were used to determine that de-solvation occurs when the solvated ion size exceeds the pore size.
Figure 3.4 Displays a scanning electron microscopy image of the commercial electrode evaluated in this study and the percent concentration of Carbon, Oxygen, Chlorine, and Sodium as determined by energy-dispersive X-ray spectroscopy.

Commercial activated carbon electrodes with a ~150 µm carbon layer and a ~30 µm aluminum current collector were employed in this study to fabricate EDLC devices. Commercial electrodes were selected due to the higher consistency of the roll-to-roll process to coat the electrodes. Additionally, the use of commercial electrodes ensured that the EDLC devices in this study more accurately emulated commercial devices. The specific surface area of these
commercial activated carbon electrodes was measured with the BET method using a Quantachrome Nova 4200e. The distribution of pore sizes for these commercial activated carbon electrodes were also measured using a Quantachrome Nova 4200e with the BHJ method. The activated carbon electrodes were dried for 48 hours at 120°C under vacuum using the heating mantles in the Quantachrome Nova 4200e. The samples were then transferred to the coolant region and placed under vacuum. The Quantachrome dewar was filled with liquid nitrogen and the adsorption isotherm and desorption isotherms were collected using nitrogen gas. The specific surface area measured using the BET method was 1188.4 m²/g. The pore size distribution for these commercial activated carbon electrodes varied between 17Å and 123Å using the BHJ method.

The structure and chemical composition of the commercial activated carbon electrodes employed in this study was measured using scanning electron microscopy (SEM) and energy dispersive x-ray spectroscopy (EDX). The SEM images collected for these electrodes are consistent with the structure of other reported electrodes. The presence of sodium, chlorine, and oxygen in the EDX measurements suggests that this electrode employs a carboxymethyl cellulose (CMC) binder or styrene butadiene rubber (SBR) binder. This conclusion regarding the use of the CMC and SBR binders is compounded by the absence of fluorine from the EDX measurements. CMC and SBR are two of the most popular binders for both EDLC and lithium ion battery electrodes, while polyvinylidene fluoride (PVDF) is also employed in electrodes. If PVDF, another prevalent binder for EDLC and lithium ion battery electrodes, was present in the electrodes then the EDX measurements would have shown the presence of fluorine, thus CMC and SBR are the most probable binders present in these commercial electrodes.
3.6 Organic Electrolytes

APBF$_4$

**APBF$_4$ Synthesis**

Figure 3.5 Overview of the two step synthesis procedure for 4-Axoniaspiro[3,4]octane (AP cation) as reported by Higashiya.

The APBF$_4$ salt was synthesized through a two-step procedure. Pyrrolidine (2.0 mol) is first added to trimethylene chlorobromide (1.0 mol) in dry ether (250 ml) while the solution is stirred in an ice bath for 12 hours. The solution is diluted with ether (250ml) and extracted three times with ice cold 10% hydrochloric acid (250ml). The pH of the hydrochloric acid extracts is increased to slightly alkaline with the addition of 40% potassium hydroxide which resulted in the separation of the product from solution. The separated oil is extracted four times with ether
(200ml) and the ether extracts are dried over anhydrous potassium carbonate. The dried ether extracts are filtered, concentrated, and distilled to yield 3-(1-Pyrrolidy1)-propyl Chloride.

3-(1-Pyrrolidy1)-propyl Chloride (0.80 mol) was added dropwise to boiling H2O (400 ml) over 15 minutes and refluxed for an additional 15 minutes after dropwise addition concluded. The resulting solution was washed with dichloromethane and evaporated to yield a crude chloride salt which was converted to a BF4 salt through the addition of 50% HBF4 (0.80 mol) and ethanol (150ml). The product is evaporated and vacuum dried to yield APBF4 salt. The procedure, characterization data, and material properties have been reported by Higashiya[35].

\[ \text{SBPBF}_4 \]

**SBPBF4 Synthesis**

![Figure 3.6 Overview of the one step synthesis procedure for 5-Axoniaspiro[4,4]nonane (SBP cation) as reported by S. Higashiya.](image)

The SBP BF4 salt was synthesized through a one step procedure. Similar to the synthesis of the APBF4 salt, the SBPBF4 utilizes pyrrolidine as a precursor to generate the spiro-ammonium cation structure. Pyrrolidine (1.0 mol), 1,4 dichlorobutane (1.0 mol), and potassium
carbonate were added to acetonitrile (1.0 L) and refluxed for 18 hours. The presence of potassium carbonate significantly increased the yield of the reaction. The filtrate was vacuum dried to yield a chloride salt. An ion exchange was performed to convert the chloride salt to a BF₄ salt with the addition 50% HBF₄ (0.80 mol) and ethanol. The subsequent salt was evaporated and vacuum dried to yield SBP BF₄. This procedure has been outlined by Chimera[36].

\[ OPBF₄ \]

**OPBF₄ Synthesis**

\[
\begin{align*}
\text{Pyrrolidine} & \quad + \quad \text{2-Chloroethanol} & \quad \rightarrow \quad \text{Oxazolidine-3-spiro-1'-pyrrolidinium} \\
\text{Paraformaldehyde} & \\
\end{align*}
\]

*Figure 3.7 Overview of the one step synthesis procedure for 5-Axoniaspiro[4,4]nonane (SBP cation) as reported by S. Higashiya.*

The OP cation was produced through a one step synthesis procedure as outlined by S. Higashiya. Pyrrolidine (1.0 mol) was added to a solution containing ethanol (375 ml),
paraformaldehyde (1.0 mol), and 2-chloroethanol (1.0 mol), and refluxed for 12 hours. An ion exchange was performed with the addition of 50% HBF$_4$ (0.80 mol) and ethanol. This ion exchange resulted in the OPBF$_4$ salt[37].

$TEABF_4$

Tetraethylammonium tetrafluoroborate (TEABF$_4$) is the industry standard salt for organic electrolyte based EDLC capacitor devices. Due to the ubiquity of TEABF$_4$ in EDLC research studies, this salt was included in this study as a baseline material to provide context for the electrochemical results from the devices containing SBPBF$_4$, OPBF$_4$, and APBF$_4$. Since this salt is a popular commercial electrolyte, TEABF$_4$ was purchased from Sigma Aldrich (EC-271004).

Electrolyte Solution Preparation

One molar (1M) electrolyte solutions for this study were prepared in an Argon filled glove box that contained less than 100 ppm of H$_2$O using anhydrous acetonitrile (EC-271004) purchased from Sigma Aldrich as the solvent. Prior to transfer into the Argon filled glove box, each salt that was synthesized on-site (SBPBF$_4$, APBF$_4$, and OPBF$_4$) was dried for 48 hours in a vacuum furnace. After preparation, the conductivities of 1M TEABF$_4$ (52.1 mScm$^{-1}$), 1M SBPBF$_4$ (54 mScm$^{-1}$), 1M OPBF$_4$ (47.6 mScm$^{-1}$), and 1M APBF$_4$ (55.4 mScm$^{-1}$) were measured at 25°C in a fume hood.
Chapter 4: EDLC Apparatus for 2 & 3 Electrode Measurements

4.1 Introduction

There are variety of two and three electrode electrochemical apparatuses to investigate the properties of novel materials for EDLC applications. The most common two electrode devices to evaluate new materials are pouch cells and coin cells (2032), while the most common three electrode apparatus is a beaker cell. The infrastructure required to fabricate pouch cells and coin cells for lithium ion battery research is identical to the framework necessary to assembly EDLC devices, thus laboratories that specialize in lithium ion battery research utilize coin cells and pouch cells to evaluate materials for EDLC applications. Furthermore, pouch cells and coin cells are popular two electrode form factors for EDLC material evaluations since these benchtop devices closely resemble the architecture of commercial systems and therefore are expected to emulate the performance of commercial devices.

Despite the ubiquity of pouch cells and coin cells in EDLC research, these devices have significant technical faults that prevent the collection of accurate and reproducible data when evaluating materials for EDLC devices. Pouch cells feature a low ESR similar to commercial EDLC devices, but often suffer reproducibility issues and a low cycle life. The inconsistency in bench top pouch cell arises from electrodes shifting as the cell is being sealed. The low cycle life of pouch cells is attributed to poor seals on the exterior package that results in electrolyte leakage, thereby substantially reducing the lifetime of these devices. Electrolyte leakage also contributes to inconsistent measurements across different samples which obfuscates the conclusions of an experiment featuring pouch cells. In contrast to pouch cells, coin cells are reliably crimped with gasket to prevent electrolyte leakage during long term cycling experiments. Similar to pouch cells, high variability in electrochemical results can be observed
for studies employing coin cells, but this can be resolved by implementing procedures to standardize the crimping pressure which has a significant impact on cell ESR. Although coin cells address some of the technical deficiencies of pouch cells, the high ESR of coin cells obscures EIS spectra and reduces the specific power of devices[38]. Due to the high ESR, coin cells limit measuring materials in high power experiments. This study attempted to address the high ESR of coin cells by coating the stainless steel components with aluminum to provide a high conductivity pathway through the device.

Though the aluminum coated coin cell devices demonstrated lower ESR, this study predominantly employed standard PAT cells, developed by EL-Cell, to more accurately emulate the performance of commercial EDLC systems on the benchtop scale. The PAT cells have a low ESR, are hermetically sealed to prevent electrolyte leakage, and maintain constant pressure on the electrode separator core with a gold coated spring. The PAT cells also enable the measurement of half-cell potentials with comparable two electrode full cell performance. Prior to this study, PAT cells have been utilized to evaluate materials for lithium ion batteries.

4.2 Coin Cell EDLC

*Components and Fabrication*

Stainless steel 2032 coin cell components for benchtop EDLC devices were purchased from Pred materials. Each coin cell contained a stainless steel bottom cap, three stainless steel spacers, a stainless steel wave spring, two activated carbon electrodes, a separator, a gasket, and a stainless steel top cap (Figure 4.1). These devices were assembled in an argon filled glove box with less than 100 ppm of oxygen present. Prior to assembly, two circular activated electrodes with a diameter of 15.7 mm were cut from an electrode sheet and dried in an oven at 115°C for
24 hours. These electrodes, once dried, were transferred into the argon filled glove box with the separator material. The 2032 coin cell EDLC devices were assembled in the top cap first. The negative electrode was placed in the top cap with the exposed aluminum current collect in contact with the top cap. The separator was placed over the electrode and the gasket was then positioned around the edge of the top can to prevent the separator from being displaced during assembly. Following the placement of the gasket, a micropipette was used to inject 150 µL of the electrolyte of interest on to the separator. The micropipette was previously calibrated as recommended by the manufacturer to accurately measure solutions with acetonitrile as a solvent. The electrolyte employed during the coin cell study was 1M TEABF₄ in acetonitrile. After injecting the electrolyte of interest onto the separator, the second activated carbon electrode was placed in the top cap, with the exposed aluminum current collect positioned up. The three stainless steel spaces were placed in the top cap on the current collect of the second electrode. The wave spring and the bottom cap were then placed onto the top cap, with the bottom cap clicking into the gasket. This device was then placed in a 2032 Hohsen manual coin cell crimper to be sealed.
Figure 4.1 Overview of the internal components of a 2032 coin cell. The bottom cap, stainless steel spacers, wave spring, gasket, activated carbon electrodes, and top cap are displayed and labeled above.

Aluminum Coating

Due to the known high ESR of coin cell components, a 1µm aluminum layer was thermally evaporated onto the wave spring and spacers of a 2032 coin cell to create a bench top device that more accurately emulated the consistency, longevity, and resistance of enclosed commercial EDLC devices. A Kurt J. Lesker thermal evaporation chamber was employed with tungsten deep cut boats to thermally evaporate aluminum onto the stainless steel wave springs and spacers. Prior to evaporation, the wave springs and spacers were loaded on to the deposition plate and aluminum pellets were placed inside of the tungsten boat (Figure 4.2). The chamber
was then sealed and pumped down to a pressure of $2.20 \times 10^{-7}$ Torr. Once the desired pressure was reached, 143 A of current at 4.29V was applied to the tungsten boat. The aluminum deposited at a rate of 8 nm/s under these conditions. This process was repeated for the other side of the wave springs and spacers.

Figure 4.2 Depicts the stainless steel wave springs and spacers on the deposition plate in the Kurt J. Lesker chamber after 1 $\mu$m of aluminum was evaporated.

After the wave springs and spacers were coated with 1 $\mu$m of aluminum, these components were transferred into the argon filled glove box for device assembly. The 2032 coin cells were assembled with the aluminum coated components using the same procedure employed for devices containing stainless steel wave springs and spacers.

Coin Cell Results and Discussion

An Arbin BT2543 was employed to measure the electrochemical characteristics of EDLC coin cell devices containing stainless steel and aluminum coated components. After
fabrication, the EDLC devices were placed in the Arbin 2032 coin cell test units to ensure consistent and reliable contact throughout the experiment (Figure 4.3). The Galvanostatic Charge/Discharge (GCD) method was employed to measure the capacitance and ESR of each coin cell. These devices were charged and discharged from 0 to 2.7V at a current density of 2 A g\(^{-1}\) (15 mA) for 900 cycles. The full cell gravimetric capacitance of these devices was calculated every 25\(^{th}\) cycle using Eq. (1):

\[
C_{\text{full}} = \frac{(j\Delta t/\Delta V m)}{m}
\]  

(1)

(where \( j \) is the current, \( \Delta V \) is the potential from \( V_{\text{max}} \) to \( \frac{1}{2} V_{\text{max}} \), \( \Delta t \) is time, and \( m \) is the total activate materials mass of both electrodes). The full cell ESR of these devices was calculated from the potential drop measured during the transition from charging to discharging at the maximum potential (2.7V) according Eq. (2):

\[
\text{ESR}_{\text{full}} = \frac{(V_1 - V_2)\text{drop}}{(\Delta j A)}
\]  

(2)

(where \( V_1 \) is the maximum voltage before discharge, \( V_2 \) is the maximum voltage after discharge, \( \Delta j \) is the change in current from charge to discharge, and \( A \) is the area of the electrode).
The charge/discharge curves for both the aluminum coated and standard stainless steel coin cell devices containing 1M TEABF₄/AN with commercial activated carbon electrodes were linear with no signs of pseudo-capacitive reactions(Figure 4.4). These curves are consistent with expectations for EDLC devices. The aluminum coated devices exhibited very consistent performance, with the charge/discharge curves nearly superimposed. Although the stainless steel coin cell sample demonstrated a standard charge/discharge curve akin to the aluminum coated device curves, the potential drop observed for the stainless steel sample was significantly greater than the potential drop measured for both aluminum coated samples. The increased potential
drop observed for the stainless steel sample was attributed to the increased resistive pathway of the stainless steel components with respect to the aluminum coated components.

\[ 	ext{Figure 4.4 The galvanostatic charge/discharge curves for coin cell devices containing aluminum coated (Blue, Red) and stainless steel (Green) wave springs and spacers with 1M TEABF}_4/\text{AN electrolyte.} \]

The increased potential drop of the stainless steel coin cells observed in the GCD curves translated to a significant increase in device ESR relative to the aluminum coated coin cells (Figure 4.5). The reduction in ESR for devices with the aluminum coated components was expected due to the lower resistivity of aluminum (46.6 nΩ m) relative to stainless steel (720 nΩ m). The aluminum coated components provided a high conductivity conduit for electrons to enter and exit the device as it was charged and discharged, thereby reducing the measured potential
drop and ESR. Furthermore, the mean ESR of devices containing aluminum coated components was more consistent sample to sample (416.7 mΩ cm², 333.31 mΩ cm²) than the devices containing the standard stainless steel components (1042.32 mΩ cm², 1992.82 mΩ cm²).

![Figure 4.5 The ESR calculated for 2032 coin cell devices containing aluminum coated components (blue-circle, red-square) and stainless steel components (yellow-cross, green-triangle).](image)

The gravimetric capacitance calculated for coin cell devices containing aluminum coated components (122.24 F g⁻¹, 120.56 F g⁻¹) was slightly higher than the stainless steel devices (115.94 F g⁻¹, 115.86 F g⁻¹). This slight increase in capacitance is attributed to the reduction in ESR observed for the aluminum coated devices, which slightly increased the total discharge time. Despite the increased concentration of aluminum in the aluminum coated devices, there
were no indications that the electrolyte, specifically the BF$_4$ anion, reacted with the aluminum to accelerate the degradation of the cell. The aluminum coated devices maintained a consistent capacitance across the 900 cycles equivalent to the samples containing stainless steel components.

Figure 4.6 The gravimetric capacitance calculated for 2032 coin cell devices containing aluminum coated components (blue-circle, red-square) and stainless steel components (yellow-cross, green-triangle).

**Coin Cell Conclusions**

EDLC devices with commercial activated carbon electrodes and 1M TEABF$_4$ / AN were fabricated using both standard stainless steel 2032 coin cell components and 2032 coin cell components coated with 1 µm of aluminum. Although EDLC devices with either stainless steel
or aluminum coated components exhibited charge/discharge curves that were comparable to commercial EDLC devices, the devices that contained aluminum coated components were more consistent sample to sample and exhibited a significantly lower ESR that was more representative of low resistance commercial EDLC devices. The reduction in resistance was attributed to the lower resistivity of aluminum (46.6 nΩ m) relative to stainless steel (720 nΩ m). The capacitance and ESR of the aluminum coated devices were consistent across 900 cycles, therefore the increased concentration of aluminum in the device did not result in an increase in deleterious electrolyte corrosion reactions.

Although the use of aluminum coated components addressed the primary technical fault of coin cells for EDLC device research by significantly reducing ESR, coin cells are still not the ideal apparatus for EDLC benchtop experiments. The consistency of these devices sample to sample, even with aluminum coated components, is strongly dependent on the crimping pressure applied by the researcher, which can be highly variable. Additionally, the reduction in resistance achieved through the incorporation of aluminum coated components was asymmetric in the cell, occurring at the positive electrode. This asymmetric reduction in cell resistance may impact the degradation rate of the electrodes and the half-cell potentials. Finally, coin cells are strictly two electrode devices, with no feasible option to incorporate a reference electrode for half-cell measurements to clarify the independent impact of aluminum coated components on each electrode.
4.3 Two Electrode EDLC Apparatus

Benchtop Device Variability

Similar to EDLC researchers, lithium ion battery scientists have struggled to fabricate benchtop lithium ion devices with novel materials that have a long cycle life, yield consistent data sample to sample, and accurately emulate commercial systems. Recently, the most promising approach for lithium ion scientists to generate highly consistent benchtop devices was developed by Dr. Dahn’s research group. To fabricate lithium ion battery cells with both novel and conventional electrolytes that yielded accurate and reproducible data, Dr. Dahn’s research group purchased “dry” commercially manufactured cells from Li-Fun Technologies and then injected these cells with electrolytes of interest[39–41]. Due to the success of this method in addressing the inconsistency issues of benchtop devices, this approach has been adopted by numerous lithium ion battery research laboratories[42–44]. The fault of this approach is that it only enables the investigation of a single electrode chemistry, the Li-Fun Technologies anode and cathode.

EL-Cell, an electrochemical research equipment manufacturer, attempted to address the inconsistency of standard benchtop devices and the lack of versatility with the Dr. Dahn research group approach through the development of the PAT test cell. The PAT test cell accomplishes this through a reduction in components, a consistent internal pressure between electrodes, and a novel sealing process. The culmination of these advantages has resulted in a benchtop device that yields highly consistent data, has a long cycle life, and emulates commercial systems while testing both novel electrode and electrolyte chemistries. Due to these advantages, the PAT test cell was selected to study the impact of spiro-ammonium electrolytes on EDLC devices.
Two-Electrode Device Assembly

In this study, two-electrode EDLC devices were fabricated using a standard PAT test cell from EL-Cell. Two commercial activated carbon electrodes, a celgard 3501 separator, and 150 µL of the electrolyte of interest were used in the PAT test cell. The PAT test cell is comprised of the consumable cell core and reusable case. The cell core contains two circular disk activated carbon electrodes with a diameter of 18mm, an insulation sleeve custom fabricated by EL-Cell with a celgard 3501 separator, the electrolyte, and two stainless steel contact stubs (Figure 4.7).
The activated carbon electrodes were dried at 115°C in an oven for 24 hours and then transferred, with the insulation sleeve and polyethylene sealing ring, into an argon filled glove box with less than 100 ppm of moisture for PAT cell assembly. The lower half of the cell core was assembled by placing an electrode into the insulation sleeve followed by the lower stainless steel stub. The insulation sleeve was then placed in the PAT cell base (Figure 4.8c). Using a micropipette calibrated for use with electrolytes containing acetonitrile as the solvent, 150 µL of the electrolyte of interest was injected onto the insulation sleeve separator. The second electrode was placed in the cell core followed by the upper stainless steel stub. The sealing ring was then placed on top half of the exterior PAT cell case (Figure 4.8b). The top half of the exterior PAT cell case with a gold coated spring was then connected to the PAT base and sealed (Figure 4.8a). The fully assembled device was removed from the glovebox for measurements (Figure 4.8d).
Figure 4.8 The images above depict the different sections of a PAT test cell. The top half (a) with a gold coated spring that exerts 40N of force onto the cell core (b) and the base that houses the cell core (c). These two sections are assembled to form a full cell (d).
Two-Electrode Measurements

The electrochemical characteristics of these two-electrode devices were measured using an Arbin BT2543 potentiostat. The two-electrode PAT test cells were inserted into the PAT test cell stand with the negative lead (black) at slot 2, the base sense lead (green) at slot 2s, the positive lead (red) at slot 1, and the potential sense lead (white) at point 1s (Figure 4.9).

Figure 4.9 The above image depicts an assembled PAT test cell stand connected to the BT2543 Arbin potentiostat.

4.4 Three Electrode EDLC Apparatus

Three-Electrode Variability

A beaker cell is the standard apparatus to measure the electrochemical characteristics of an electrode/electrolyte system in a three-electrode configuration[45]. With respect to EDLC research, this beaker cell configuration can be used to measure the electrochemical stability
window (ESW), capacitance, and ESR of different electrode/electrolyte systems[46]. These measurements are conducted with a beaker cell by submerging a working electrode (the electrode of interest), counter electrode (electrode to complete the circuit), and reference electrode (establishes the potential against the working electrode) millimeters apart in electrolyte solution. Although this system is the accepted standard for ESW measurements, beaker cells fail accurately measure the capacitance, ESR, and cycle life of EDLC materials. The capacitance of EDLC materials measured in a three-electrode apparatus were found to be nearly double the values measured in a standard two-electrode device using the GCD method. This higher capacitance is attributed to the surplus of electrolyte in the beaker cell contributing ions to the double layer capacitance, thereby significantly inflating the measured value. Furthermore, the ESR of EDLC materials measured in a three-electrode apparatus were found to be an order of magnitude greater than the two-electrode devices. Electrolyte conductivity plays a significant role in dictating device ESR and as a result electrode spacing is correlated to the resistance of an EDLC system. The millimeter spacing between the working and counter electrodes in a beaker cell significantly increases the measured ESR of EDLC materials[26]. The abundance of electrolyte solution in the beaker cell also greatly extends the measured cycle life of EDLC materials in this three-electrode configuration relative to two-electrode devices. Due to the inaccuracies that arise from using a beaker cell, researchers have begun to incorporate pseudo reference electrodes in two electrode devices in attempt to measure capacitance and ESR accurately, in addition to half-cell potentials. These half-cell potentials provide insights into the capacitive and resistive contributions of the negative and positive electrodes separately. Additionally, these half-cell potentials enable the degradation rates of each electrode to be observed, thereby providing more clarity on the mechanisms of cell failure.
**Pseudo-Reference Electrodes**

Pseudo-reference electrodes, unlike standard reference electrodes, do not have a specific known potential while immersed in the sample electrolyte, but still provide a stable potential to measure against the working and counter electrodes\[47\]. These pseudo-reference electrodes can then be implanted in two electrode devices, without adhering to the cumbersome requirements of standard reference electrodes, to measure the relative half-cell potentials of the positive and negative electrodes in EDLC devices as the capacitance, ESR, and cycle life are accurately measured. The most popular pseudo-reference electrode in electrochemistry is a silver wire. Researchers have fabricated EDLC devices with an implanted silver wire as a pseudo-reference electrode to study the degradation characteristics of organic electrolytes on the positive and negative electrodes at elevated voltages and temperatures\[48\]. Although the silver wire pseudo reference electrode measured the half-cell potentials in this system, the presence of a silver wire in the EDLC device can introduce ionic impurities, \(\text{Ag}^+\), into the electrolyte that impacts the accuracy of these measurements during long term cycle experiments\[49\]. To leverage the advantages of pseudo reference electrode without potentially introducing ionic impurities into the EDLC device, activated carbon pseudo reference electrodes were evaluated as candidates to replace silver wire. These activated carbon pseudo reference electrodes were chemically analogous to the positive and negative electrodes in the device. The activated carbon pseudo reference electrodes were found to have a stable potential in EDLC systems with ionic liquid electrodes\[50,51\]. This approach was employed to study the degradation mechanisms of different EDLC solvents (acetonitrile, propylene carbonate), the impact of water concentration on each electrode, and aging rates at different potentials\[52–55\].
This study utilized a section of the activated carbon electrodes employed at the positive and negative electrodes as a pseudo-reference electrode. The activated carbon pseudo reference electrode was cut and inserted into the PAT test cell insulation sleeve by EL-Cell in place of a Li/Li\(^+\) reference.

*Three-Electrode Device Assembly*

In this study, three-electrode EDLC devices were fabricated using a standard PAT test cell from EL-Cell with two commercial activated carbon electrodes, a 260 µm glass separator, activated carbon pseudo reference electrode, and 150 µL of the electrolyte of interest. The PAT test cell was assembled following the same procedure as with the two-electrode device. The only difference between the two and three electrode samples is the presence of an activated carbon pseudo reference electrode in the insulation sleeve and the substitution of a glass fiber separator.
Three-Electrode Measurements

Figure 4.10 Depicted above is the circuit diagram for the three electrode measurements with the Arbin BT2543 potentiostat.

With incorporation of an activated carbon pseudo reference electrode into the PAT test cell, this approach enables researchers to collect data in two-electrode and three-electrode configurations in tandem for each sample. The electrochemical characteristics of the positive and negative electrodes can be measured independently, as the full cell two-electrode characteristics are measured. This approach pairs the advantages of a two-electrode configuration and three-electrode configuration, thereby providing researchers with significantly more insight into the modes of operation and degradation for different EDLC materials.
An Arbin BT2543 potentiostat was employed to measure the full cell and half-cell electrochemical characteristics of these three-electrode devices with three separate potentiostat channels concurrently. One primary channel was connected to apply a current through the devices and measure the full cell potential between the positive and negative electrodes. The data collected from the primary potentiostat channel is used to calculate the capacitance, ESR, specific energy, and specific power of the full cell in a conventional two electrode configuration. The two secondary channels measured the half-cell potentials between the negative electrode/activated carbon pseudo-reference electrode and positive electrode/activated carbon pseudo-reference electrode. The capacitance, ESR, specific energy, and specific power of the positive and negative electrodes was calculated from the half-cell potentials measured using the secondary potentiostat channels.

The Arbin BT2543, like most potentiostat channels, does not have two auxiliary voltage probes to measure multiple half-cell potentials simultaneously as a test cell is cycled. Due to the absence of auxiliary channels, three separate, identical potentiostat channels were connected to each PAT test cell to measure the full cell, positive electrode, and negative electrode potentials. The potentiostat channel responsible for applying current to the full cell was designated as the primary channel and connected to the PAT test cell stand in the same configuration as the two-electrode cells. The primary potentiostat channel was connected to the PAT test cell stand with the negative lead (black) at slot 2, the base sense lead (green) at slot 2s, the positive lead (red) at slot 1, and the potential sense lead (white) at point 1s (Figure 4.9). The potentiostat channel responsible for measuring the positive half-cell potential was designated the positive channel, while the potentiostat channel responsible for measuring the negative half-cell potential was referred to as the negative channel. The current carrying leads of both the negative and positive
channels were connected to two separate 3kΩ resistors as a safety precaution. The positive channel potential sense lead (white) was connected to point 1s on the PAT test cell base. The base sense lead (green) of the positive channel was connected to the R point on the PAT test cell base. The negative channel sense lead (white) was connected to point 2s on the PAT test cell base, while the negative channel base sense lead (green) was connected to the R point (Figure 4.10). Due to need for multiple leads from different channels to be connected to the same point on the PAT test cell base, adapters that expand the available ports are necessary (Figure 4.11).

3-Electrode Connections

Figure 4.11 Depicted above is an image of the three-electrode connections to the PAT test cell base for the primary, positive, and negative channels.
A critical component of properly evaluating the three-electrode PAT test cells in this configuration while connected to three separate potentiostat channels is correctly structuring the schedule files for each channel. It is also important to note that this apparatus can only be used to conduct GCD and sinusoidal current EIS measurements since only the half-cell potentials of the positive and negative electrodes can be measured through the sense leads. The schedule file of the primary channel, responsible for applying the current and measuring the full cell electrochemical characteristics, can be structured using any variation of a standard GCD cycle protocol. This can included methods as complex as the Maxwell 6 step procedure or IEC protocols[23]. The data collection method on the primary channel should be set to register points with a change in voltage and not time. The schedule file of the negative and positive channels, responsible for collecting the half-cell potentials, can be identical. This schedule file should only include one continuous rest step with no function included to end the test. The data collection method on the negative and positive channels schedule file should be set to register points with a change in voltage that is set to a finer grain than the primary channel schedule file. The deviations in potential measured by the positive and negative channels will inherently be lower than those observed by the primary, therefore a finer grain for data point collection is necessary for these channels.

Once the properly prepared schedule files are assigned to the correct channels, the experiment is initiated by starting the positive and negative channels first followed by the primary channel.
4.5 Processing Three Electrode Measurements

Need for Data Processing

As described in the previous sections, the three-electrode apparatus utilized in this study employs three separate potentiostat channels to measure the electrochemical characteristics of the full cell, positive electrode, and negative electrode. These measurements are recorded separately across the different potentiostat channels resulting in three data files for each sample. The full cell measurements are collected through the primary potentiostat channel as a standard two-electrode experiment which generates a comprehensive data file that includes the applied current, measured potential, energy, power, cycle index, step index, test time, and date time. Using either custom python scripts or the Arbin excel macro, this data can be easily processed to calculate the capacitance, ESR, specific energy, and specific power for each cycle. Conversely, the half-cell measurements are collected through the positive and negative potentiostat channel voltage leads, which results in a data file that only contains the measured potential, test time, and date time. Additionally since these experiments are initiated in sequence and not simultaneously, the test times of each channel data file are not synchronized. Furthermore, the absence of a cycle index to differentiate the cycles and step index to distinguish charging/discharge/rests increases the difficulty of calculating the capacitance, ESR, specific energy, and specific power for each cycle. To accurately calculate the cycle by cycle electrochemical characteristics of the positive and negative electrodes, a series of python scripts were developed to process the half-cell data collected using this apparatus.

The half-cell potential data was processed through a four step procedure. The half-cell data was converted to a csv file and the test time was synchronized with the primary channel data set. The primary channel data file cycle index was then copied to the half-cell potential files.
Finally, to aid in the ESR calculation without the presence of a step index, the potential drop for each cycle was identified and recorded for the half-cell files.

**Reading the Data**

```python
import pandas as pd
import numpy as np
import sympy

location1 = r"/Volumes/Transcend/Dropbox/Dropbox/Arbin Data/NYAS/NYAS Raw Data/APBF primary"
lifetime2 = r"/Volumes/Transcend/Dropbox/Dropbox/Arbin Data/NYAS/NYAS Raw Data/APBF4 positive"
lifetime3 = r"/Volumes/Transcend/Dropbox/Dropbox/Arbin Data/NYAS/NYAS Raw Data/APBF4 negative"
data1 = pd.read_csv(location1 + '.csv')
data2 = pd.read_csv(location2 + '.csv')
data3 = pd.read_csv(location3 + '.csv')

# sort the files from the csv conversion
data1 = data1.sort_values(by=['Data_Point'], ascending=True)
data1 = data1.rename(columns={'dV_dt': 'dV/dt'})
data2 = data2.sort_values(by=['Data_Point'], ascending=True)
data2 = data2.rename(columns={'dV_dt': 'dV/dt'})
data3 = data3.sort_values(by=['Data_Point'], ascending=True)
data3 = data3.rename(columns={'dV_dt': 'dV/dt'})
```

*Figure 4.12 Above is a screen shot of the python script used to read the three separate files with the pandas data tool.*

Prior to reading the data, the pandas, numpy, and sympy libraries were imported. These libraries are needed to read the files and calculate the electrochemical characteristics of the samples with python[56]. Every experiment for one samples involved three separate data files, the primary, positive, and negative potentiostat channel files. These files were converted into csv files and read using the pandas library. During the conversion process from an Arbin database file to a csv file, the data points are arranged out of sequence. To remedy this, each data file is sorted by using the Data_Point column (Figure 4.12). Once the each file has been read and sorted correctly, the data can be synchronized across channels.
Test Time Synchronization

Figure 4.13 Above is a screen shot of the python script used to read the three separate files with the pandas data tool.

Since the primary, positive, and negative potentiostat channels are initiated in sequence and not simultaneously, the test times of each data file are not synchronized and the resulting GCD curves are plotted incorrectly. To resolve this discrepancy, the time recorded by the positive and negative channels prior to the initiation of the primary channel must be subtracted from the positive and negative channel test_time columns. This time was originally calculated by calculating the dv/dt for each file and identifying the first point in the positive and negative channel data files that deviated significantly from 0 (Figure 4.13). This approach was not consistently successful in identifying the correct starting test_time point. Alternatively, the correct test_time start point for the positive and negative channel data files was identified by finding the DateTime value recorded in the primary channel data file as charging began, at step 2 in this example. This DateTime value was then used to find the starting test_time in the half-cell
potential files. This value was then subtracted from the entire test_time column to synchronize the files (Figure 4.14).

```python
#### Function to syncronize files based on dv_dt or DateTime

def voltage_sync(list):
    for x in list:
        dvdt_calc(x)

    df1 = list[0]
    df2 = list[1]
    df3 = list[2]

    datetime = min(df1.DateTime[df1.Step_Index == 2])

    for x in list:
        time = min(x.Test_Time[x.DateTime == datetime])
        x.Test_Time = x.Test_Time - time

    return list
```

**Figure 4.14** Above is a screen shot of the python script used to read the three separate files with the pandas data tool.

Add Cycle Index

With the test_time columns of the three data files synchronized, the cycle index from the primary file was then added to the positive and negative files. The pandas groupby function was employed to identify the minimum and maximum test times for each cycle. These values were then used to loop through the half-cell potential files and amend the cycle_index column with the correct value between each test time range (Figure 4.15). As a result, the positive and negative channel files then had the same cycle index as the primary channel file, despite collecting a different number of data points per cycle.
Figure 4.15 Above is a screen shot of the python script used to read the three separate files with the pandas data tool.

Identify the Potential Drop

The ESR of the EDLC device is calculated, in part, from the potential drop measured in the device as it transitions from charging to discharging or a rest period. In the primary channel data file, the potential drop can be identified through condition statements on either the current or step_index columns. The half-cell potential channels are not able to record data for either the current in the device or the step_index of the primary channel, therefore another approach is
needed. First, the voltage column was differentiated using the dvdt_calc function and numpy library (Figure 4.13). The groupby function was employed again to find the maximum voltage at each cycle. The maximum voltage and cycle number were then used to locate the dv value for that point, which corresponded to the potential drop. The resistance was then calculated using this value (Figure 4.16). The efficacy of this method was corroborated by calculating the ESR in the primary file using both the standard procedure and this approach. The two methods were found to be in agreement.

```python
### New resistance strategy we calculate dv, then find dv at v = max
cycle_group = df.groupby(['Cycle_Index'])
max_voltage_group = cycle_group.Voltage.aggregate(max)
dv_values = max_voltage_group

dv_values = dv_values.rename(columns={'Voltage': 'dv'})

for x in range(0, len(max_voltage_group)):
    y = x + 1
    z = min(max_voltage_group[x:y])
    dv_interest = df['dv'].loc(((df.Voltage == z) & (df.Cycle_Index == y))]
    dv_values[x:y] = min(dv_interest)

rest_step_current = abs(current)
resistance_table = (abs(dv_values)) / (2 * rest_step_current)
resistance_table = (resistance_table / surface_area) * 1000
dftotal['resistance'] = resistance_table
```

Figure 4.16 Above is a screen shot of the python script used to read the three separate files with the pandas data tool.
Chapter 5: The Smallest Spiro-Ammonium Cation (APBF₄)

5.1 Introduction

Researchers have strived to increase the energy density of organic electrolyte EDLCs, without compromising the cycle life or power density, predominately through innovations at the activated carbon electrode and the implementation of costly pure ionic liquids, while neglecting the incumbent electrolyte salt, tetraethyl ammonium tetrafluoroborate dissolved in acetonitrile (TEABF₄/AN) [57–59]. Lately, 5-Azoniaspiro[4,4]nonane tetrafluoroborate (SBPBF₄), a spiro quaternary ammonium salt, has garnered commercial interest as a possible candidate to replace TEABF₄. The use of SBPBF₄ in EDLCs at varying concentrations has been shown to increase the capacitance, decrease the equivalent series resistance (ESR), expand the potential window, and improve low temperature performance compared to devices containing TEABF₄ [36,60–64]. Oxygen substituted SBP cation derivatives have shown similar performance increases as well [65]. The increase in capacitance for SBPBF₄ salts has been attributed to the compact SBP cation, which enables higher surface area utilization by accessing smaller pores than the larger TEA cation [61,66–68]. The increase in pore accessibility allows more cations to populate the double layer of the activated carbon electrode resulting in higher capacitance [69–71]. Additionally, the reduction in ionic resistance and by extension EDLC ESR in devices containing SBPBF₄ salts has been attributed to the higher ionic conductivity of SBPBF₄ compared to TEABF₄. Investigations examining the performance of cations with varying structures suggest that ion size is a critical property that contributes to increasing ionic conductivity and pore diffusion [72,73].

In this study, 4-Axoniaspiro[3,4]octane tetrafluoroborate (APBF₄) was synthesized to explore if a reduction in cation size with respect to SBP would result in further increases in
EDLC capacitance and reductions in EDLC ESR. Furthermore, this study aimed to investigate if the smaller cation, with respect to SBP, still maintained the electrochemical stability window (ESW) necessary to operate at the typical EDLC voltage of 2.7V despite the increased ring strain on the AP cation. CV was employed to evaluate the ESW of 1M APBF$_4$/AN in contrast to 1M SBPBF$_4$/AN. GCD cycling to 2.7V for 700 cycles was used to calculate the capacitance and ESR of devices containing 1M AP BF$_4$, 1M SBPBF$_4$, and 1M TEABF$_4$. EIS spectra were collected to confirm the ESR trend observed during GCD cycling and measure the electrolyte solution resistance in the devices.

### 5.2 Ion Size Calculation

![Space filled models showing the cations](image)

<table>
<thead>
<tr>
<th>Cation</th>
<th>TEA</th>
<th>SBP</th>
<th>AP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume ($\text{Å}^3$)</td>
<td>123</td>
<td>114</td>
<td>98</td>
</tr>
</tbody>
</table>

*Figure 5.1 Space filled models, chemical structures, and volumes generated by Schrodinger Jaguar DFT software using a hybrid B3LYP method and 6-311G**++ basis set for TEA, SBP, and AP cations. The atoms are denoted as follows: hydrogen–white, carbon–grey, and nitrogen–blue.*
The ion size of the geometrically optimized cations, TEA, SBP, and AP, is a critical parameter in interpreting the electrochemical characteristics of the cation in an EDLC. The degree of ion size reduction is expected to contribute to the capacitance differences observed between different electrolyte systems. A reduction in ion size is expected to be accompanied by higher surface area utilization on the electrode surface as the device is charged. The higher surface area utilization enables an increase in surface charge concentration, which in turn is predicted to increase the capacitive energy stored.

The ion size of the TEA, SBP, and AP cations was calculated using the Schrodinger Materials Suite software. The Jaguar Density Functional Theory (DFT) engine geometrically optimized each cation using a hybrid B3YLP method with the 6-311G**++ basis set. The volume of the geometrically optimized cations was calculated using the PyVol function in the Schrodinger Materials Suite software from the terminal[74].

The AP cation (98Å) was calculated to be smaller than both the SBP (114Å) and TEA (123Å) cations, as expected. The asymmetric removal of an sp3 carbon in one ring resulted in a significant reduction in ion volume for the AP cation.
5.3 Electrochemical Stability of APBF$_4$ with Cyclic Voltammetry

![Chemical Structure of AP cation with bond angle (88.8) and four member ring strain identified.](image)

*Figure 5.2 Chemical Structure of AP cation with the bond angle (88.8) and four member ring strain identified.*

The electrochemical stability of EDLC devices that contained 1M APBF$_4$ /AN was measured using the CV method. To provide context for the cyclic voltammograms of the devices containing the AP cation, the electrochemical stability of devices that contained a thoroughly studied electrolyte, 1M SBPBF$_4$ /AN, was also measured. The AP cation was expected to have lower electrochemical stability relative to the SBP cation due to the increased ring strain of the four-membered ring[75,76]. With a bond angle of 88.8°, the AP cation has a highly unfavorable cyclic configuration, deviating significantly from the ideal bond angle of 109° (Figure 5.2). Conversely, the SBP cation five membered ring is considerably more stable with a bond angle of 105.1°. This more favorable bond angle reduces the likelihood of an electrochemically induced ring opening reaction[77].
Figure 5.3 Cyclic voltammetry of APBF$_4$ (blue) and SBPBF$_4$ (red) comparing performance from 0 to 3V at 10 mV/s.

The CV method at a scan rate of 10 mV/s was employed to compare the electrochemical stability of devices containing 1M AP BF$_4$ and 1M SBP BF$_4$. The voltammograms of these devices (Figure 5.3) are both symmetrical with respect to the zero current line and have a nearly rectangular shape, indicative of ideal EDLC behavior, from 0V to 2.9V. The current responses for both devices begin to slightly deviate from linear behavior and increase exponentially at cell voltages $U \geq 3.0$ V, thereby potentially demonstrating EDLC breakdown. The faradaic ratio ($R$) was calculated on the third cycle at each voltage measured using Eq(1):

$$R = \left( \frac{Q_{\text{charge}}}{Q_{\text{discharge}}} \right) - 1$$

in order to quantify EDLC breakdown (where $Q_{\text{charge}}$ is the charge accumulation during positive voltage sweeps and $Q_{\text{discharge}}$ is the charge released during negative voltage sweeps). Ideally the faradaic ratio is 0 which indicates that no electrons were consumed or released during charging.
and discharging. A faradaic ratio of 0 therefore suggests the absence of redox reactions in the EDLC device. When \( R > 0.1 \) a significant irreversible redox reaction has transpired within the EDLC, demonstrating the breakdown potential. The value of \( R \) never exceeded 0.1 for either APBF\(_4\) or SBPB\(_4\) for the voltammograms collected from 0V to 1V, 2V, 2.5V, 2.6V, 2.7V, 2.8V, 2.9V, and 3.0V. The non-zero faradaic ratio for the voltammogram collected from 0V to 3V was attributed to electrolyte interactions with surface functional groups on the activated carbon electrode and the presence of residual H\(_2\)O generating low volume redox reactions. These low volume redox reactions are responsible for the small increase in the measured current response at cell voltages \( U = 3.0\)V that resulted in a non-zero faradaic ratio, thus the electrolyte breakdown voltage for both AP BF\(_4\) and SBP BF\(_4\) is greater than 3.0V (Figure 5.3).
Figure 5.4 Cyclic voltammogram of an EDLC device containing 1M SBPBF$_4$/AN cycled from 0 to 3.8V in 100mV increments above 2.7V at 1 mV/s.

![Cyclic voltammogram of an EDLC device containing 1M SBPBF$_4$/AN cycled from 0 to 3.8V in 100mV increments above 2.7V at 1 mV/s.]

Figure 5.5 Cyclic voltammogram of an EDLC device containing 1M APBF$_4$/AN cycled from 0 to 3.8V in 100mV increments above 2.7V at 1 mV/s.

The CV method was then employed from 0V to 4V at a scan rate of 1 mV s$^{-1}$ in 100 mV increments to identify and compare the breakdown voltage of devices containing 1M APBF$_4$ and 1M SBPBF$_4$. The scan rate was reduced to increase the magnitude of faradaic current responses. The voltammograms of these devices (Figure 5.4, Figure 5.5) have a nearly rectangular shape at 1V, 2V, and 3V, which is indicative of ideal EDLC behavior and consistent with the previous

75
measurements at a scan rate of 10 mV s\(^{-1}\). The current responses for both devices begin to increase exponentially at cell voltages \(U \geq 3.0\) V. This observed increase is in agreement with the previous measurement and is potentially demonstrating EDLC breakdown. The faradaic ratio was calculated on the third cycle at each voltage measured to quantify EDLC breakdown with breakdown defined as \(R > 0.1\). The breakdown potential observed for the SBP BF\(_4\) device (3.8V) was slightly higher than the APBF\(_4\) device (3.4V). The lower breakdown potential and reduced ESW of APBF\(_4\) relative to SBP BF\(_4\) was attributed to the ring strain induced by the unfavorable bond angle (88.8°) in the four membered ring of the AP cation. Both APBF\(_4\) and SBPBF\(_4\) devices were observed to have breakdown potentials greater than the typical EDLC operational voltage of 2.7V. The breakdown potential of the SBPBF\(_4\) device (3.8V) is sufficiently high to be considered a future electrolyte candidate for high voltage EDLC devices with a greater potential window (>2.7V)[60].
5.4 Influence of Current Density on APBF₄ cells

Figure 5.6 Cyclic voltammetry of APBF₄ and SBPBF₄ comparing performance from 0 to 3V at 10, 20, 40, 60, and 100 mV/s.

CV was further utilized to observe the change in charge capacity and internal resistance of devices containing 1M SBP BF₄ and 1M AP BF₄ at varying scan rates (Fig. 2b, Fig. 2c). The gravimetric capacitance (Cₘ) for each voltammogram was calculated according to Eq(2):
\[ C_m = \frac{4j}{vm} \]

(2)

(Where \( j \) is the current response in amps, \( v \) is the scan rate in mV/s, and \( m \) is the total active mass of both electrodes). The gravimetric capacitances at scan rates of 10 mV/s, 20 mV/s, 40 mV/s, 60 mV/s, and 100 mV/s were plotted against the cell voltages for both devices and were found to generate approximate current density responses of 1 A/g, 2 A/g, 4 A/g, 6 A/g, and 10 A/g. These current densities correspond well with the expected operational current densities of commercial EDLCs. The curves for devices containing both 1M SBPBF\(_4\) and 1M APBF\(_4\) are symmetrical with respect to the zero current line and maintained a near rectangular shape at each scan rate. As the scan rate was increased from 10 mV/s to 40 mV/s, the area of the voltammograms for both devices was reduced slightly as expected. This area reduction, which corresponded to reduced cell capacity, occurs predominately at the inversion of the scan rate thereby indicating that the series resistance of the device was increased[13]. The increased series resistance was attributed to both electrode polarization effects and decreased electrolyte mobility in small pore regions. Despite the increased series resistance and reduction in capacitance with an increasing scan rate, devices containing AP BF\(_4\) and SBP BF\(_4\) better maintain ideal EDLC behavior at high scan rates than most EDLC electrolytes reported. This improved performance is likely due to the high conductivity of the spiro quaternary ammonium salts and the increased pore accessibility of the smaller cations enabling rapid charge discharge at high current densities.
5.5 Galvanostatic Charge/Discharge

Figure 5.7 GCD of APBF$_4$ (blue), TEABF$_4$ (green), and SBPBF$_4$ (red) comparing performance from 0 to 2.7V at 2 A/g.

The GCD method was used to determine the gravimetric capacitance and direct current equivalent series resistance (DC ESR) of devices containing 1M TEA BF$_4$, 1M SBP BF$_4$, and 1M AP BF$_4$ in a process consistent with commercial EDLC measurement. These devices were charged/discharged at a current density of 2 A/g to a cell potential of 2.7V for 700 cycles. These GCD parameters were selected to expose the devices to the power density and cell potential encountered by commercial EDLCs in common applications. The gravimetric capacitance of these devices was calculated every 25th cycle at a current density of 500 mA/g according to Eq. (3):
\[ C_m = 4(j\Delta t/\Delta Vm) \]  
(3)

(where \( j \) is the current, \( \Delta V \) is the change in potential from 0.9V to 0.7V, \( \Delta t \) is the duration of 0.9V to 0.7V, and \( m \) is the total mass of active materials for both electrodes). The DC ESR of these devices was calculated from the potential drop measured during a 5 second rest after discharge to half the cell potential (1.35V) using Eq. (4):

\[ R_{\text{discharge}} = (V_1 - V_2)/\Delta j \]

(where \( V_1 \) is the initial voltage before the rest period, \( V_2 \) is the final voltage after the rest period, and \( \Delta j \) is the change in current from discharge to rest)[14,15]. The gravimetric capacitance and DC ESR values calculated from charge discharge cycles at a lower current density of 500 mA/g were found to be more consistent than the values calculated from bulk cycles at a charge discharge current density of 2 A/g. The lower current density enabled the ions in the electrolyte more time to travel to the deeper pores inside the electrode which contributed to high capacitance values in this study.
The average gravimetric capacitance of the 1M AP BF₄ device (125.9 F/g) was found to be considerably higher than the values calculated for both the 1M SBP BF₄ device (109.7 F/g) and the 1M TEA BF₄ device (99.8 F/g). The disparity in observed capacitance values for each device inversely corresponded with the differences in cation volume for each electrolyte. The capacitance values decreased (AP > SBP > TEA) as the cation size increased (AP < SBP < TEA). This capacitance cation size relationship was attributed to the increased pore accessibility of smaller cations. The increased pore accessibility of smaller cations enabled deeper pore penetration and an increased available surface area that directly translated to increased capacitance.
The average calculated DC ESR of the 1M AP BF$_4$ device (207.4 mΩ/cm$^2$) was found to be lower than the values calculated for both the 1M SBP BF$_4$ device (271.0 mΩ/cm$^2$) and the 1M TEA BF$_4$ device (384.5 mΩ/cm$^2$). The differences in calculated DC ESR also directly corresponded with the differences in cation volume of the electrolyte. The highest calculated DC ESR was observed in the device containing 1M TEA BF$_4$, the electrolyte with largest cation in this study. Conversely, the lowest calculated DC ESR was observed in the device containing 1M AP BF$_4$, the electrolyte with the smallest cation in this study. The reduction in device DC ESR with the reduction in cation volume was attributed to the higher mobility and ionic conductivity of smaller cations. The smaller cations have higher solution mobility and can more effectively
traverse the porous structure of the electrode during charging and discharging without being stericly encumbered resulting in lower device resistance.

5.5 Electrochemical Impedance Spectroscopy (EIS)

![EIS Diagram](image)

Figure 5.10 Electrochemical Impedance Spectroscopy of TEABF<sub>4</sub>, SBPBF<sub>4</sub>, and APBF<sub>4</sub> with a Randel’s equivalent circuit model.

EIS was employed to verify the resistance trend observed using GCD and measure the varying electrolyte solution resistances (R<sub>s</sub>) of devices containing 1M TEABF<sub>4</sub>, 1M SBPBF<sub>4</sub>, and 1M APBF<sub>4</sub> at room temperature. The EIS spectra for each device was collected prior to
cycling at 57 frequencies between 1 MHz and 10 mHz. The Nyquist plot at low frequencies demonstrates ideal capacitance behavior represented by a straight line for each device (Fig 4a.). At high frequencies, a semi-circle was observed, representative of the contact resistance between the stainless steel stubs, aluminum current collector, and activated carbon material present in the devices. The 45° Warburg diffusion slope characterizing electrolyte ion mass transport was also identified for each device in the intermediate frequency range[78–81].

The electrolyte solution resistance, the first intersection to the real axis of in the high frequency range, of the 1M APBF₄ device (548 mΩ) was found to be lower than devices containing 1M SBPBF₄ (657 mΩ) and 1M TEABF₄ (767 mΩ). The magnitude of the electrolyte solution resistance was found to increase (AP < SBP < TEA) with cation ion size. The electrolyte solution resistance was found to correspond to the same trend as the measured conductivity of the electrolytes and GCD measured ESR of the assembled devices.
5.6 Impact of APBF\textsubscript{4} on EDLC Performance

![Graph showing electrochemical impedance spectroscopy of TEABF\textsubscript{4}, SBPBF\textsubscript{4}, and APBF\textsubscript{4} with a Randel’s equivalent circuit model.]

The breakdown potential, capacitance, and direct current ESR for EDLC devices using APBF\textsubscript{4}, the smallest known spiro ammonium salt, as the electrolyte with commercial activated carbon electrodes were compared to devices containing 1M SBPBF\textsubscript{4} and 1M TEABF\textsubscript{4} using CV and GCD. Devices containing APBF\textsubscript{4} and SBPBF\textsubscript{4} displayed near ideal EDLC behavior at high scan rates while cycled at potentials from 0V to 3V. The breakdown potential observed for APBF\textsubscript{4} (3.4V) devices was lower than SBPBF\textsubscript{4} (3.8V), but was still sufficiently greater than the typical EDLC operation potential of 2.7V. The average gravimetric capacitance of devices containing 1M APBF\textsubscript{4} (124.7 F g\textsuperscript{-1}), the electrolyte with the smallest cation in this study, was found to be significantly higher than devices containing 1M SBPBF\textsubscript{4} (108.6 F g\textsuperscript{-1}) and 1M TEABF\textsubscript{4} (99.2 F g\textsuperscript{-1}). The capacitance values observed increased (TEA < SBP < AP) as the size...
of the cation employed in the EDLC devices decreased (TEA > SBP > AP). Alternatively, the average ESR calculated decreased as the size of the cation employed in the EDLCs decreased.

The ESR of EDLC devices containing 1M APBF$_4$ (383.4 mΩ cm$^{-2}$) was considerably lower than devices containing 1M SBPBF$_4$ (501.0 mΩ cm$^{-2}$) and 1m TEABF$_4$ (710.8 mΩ cm$^{-2}$). As a result, devices containing APBF$_4$ possessed the highest capacitance and lowest ESR compared to devices containing the industry incumbent electrolytes SBPBF$_4$ and TEABF$_4$. 
Chapter 6: Direct Measurement of the Positive and Negative Electrodes

6.1 Introduction

Research to address the low energy density of EDLCs has predominantly focused on increasing the effective surface area utilized for capacitive energy storage by modifying the active material on the electrodes, reducing the size of the ions present in the electrolyte, or removing the solvent entirely from the electrolyte[57,59,70,71,82,83]. These innovations assume that the available area for oppositely charged ions, counter-ions, to adsorb onto the surface of the porous electrode is directly proportional to the capacitance of an EDLC device[12,84–86]. In most instances this has been the case, with a reduction in ion size corresponding to an increase in device capacitance[67,69,72,86–90]. The most prominent commercial example of this being 5-Axoniaspiro[4,4]nonane tetrafluoroborate (SBPBF$_4$), a spiro quaternary ammonium salt that has gained interest as a replacement for the industry standard electrolyte salt tetraethylammonium tetrafluoroborate (TEABF$_4$) due to the increased device performance observed resulting from a reduction in cation volume[36,60–64]. Despite these instances that demonstrate improved performance with a reduction in cation size, investigations that featured electrolytes with larger ions were observed to have greater device capacitance, particularly those that involved oxygen-substituted ammonium salts[66]. Furthermore, recent in-situ measurements on the charging mechanisms of EDLC devices have suggested that the co-ion, the like-charged ion, de-adsorbing and exiting the electrode pores has a role in dictating EDLC performance[91–95]. Clarifying the charging mechanisms and pertinent electrolyte properties will aid in the design of novel materials that more effectively address the low energy density of EDLC devices[96,97].
The electrochemical characteristics of the positive and negative electrodes were independently measured against an activated carbon pseudo-reference electrode in novel devices that contained four distinct electrolytes to elucidate the impact of cation structure as a counter-ion and co-ion on EDLC performance. Galvanostatic Charge/Discharge (GCD) cycling to 2.7V was employed to measure the capacitance, ESR, specific energy, and specific power between the positive/negative, negative/reference, and positive/reference electrodes of devices containing tetraethylammonium tetrafluoroborate (TEABF₄), 5-Axoniaspiro[4,4]nonane tetrafluoroborate (SBPBF₄), Oxazolidine-3-spiro-1’-pyrrolidinium tetrafluoroborate (OPBF₄), and 4-Axoniaspiro[3,4]octane tetrafluoroborate (APBF₄). The SBP, OP, and AP cations were selected due to the similar spiro-quaternary ammonium structure, but deviations in molecular volume and electrostatic potential (ESP), while the TEA cation was included for baseline comparisons [65,98].

6.2 Computational Chemistry Cation Calculations

The ion size, ESP, and orbital energies were calculated for the geometrically optimized TEA, SBP, OP, and AP cations in this study to provide a theoretical framework to predict and understand device capacitances, ESR, and stabilities. The molecular volume of the cation is expected to be directly proportional to device capacitance. The increase in device capacitance with a reduction in cation size is attributed to an increase in surface area utilization by the smaller ion, which corresponds to an increase in capacitive energy storage. This capacitance ion size relationship was observed in two electrode experiments conducted in Chapter 5 (AP>SBP>TEA). Furthermore, the ESR of EDLC devices and ionic conductivity of electrolytes has been observed to be strongly dependent on ion size, with smaller ions exhibiting lower resistances due to increased pore diffusion and mobility. This ESR trend was also corroborated
by the results in Chapter 5 (AP<SBP<TEA). Unlike ion size, the impact of cation ESP on EDLC device performance has not been investigated. The ESP provides insights into the site specific intermolecular interactions of a molecule which can impact the solution mobility or electrode adsorption of an ion. The change in electron distribution of ionic liquids that feature ammonium cations has been analyzed by mapping the ESP on a molecular surface[99]. The mean, maximum, and minimum ESP was calculated to quantify these effects for each cation. In contrast to ESP calculations, the impact of orbital energies on EDLC device performance has been thoroughly studied[100]. The computed values for the Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) of a molecule have been shown to accurately predict the electrochemical stability window[101,102]. The calculated HOMO-LUMO orbital energies have been employed to successfully identify solvents with wide ESWs for high voltage EDLC devices[13,103,104]. Moreover, the LUMO orbital energies calculated for ammonium cations was found to have a linear impact on the cathodic limit than steric hindrance from alkyl branching or chain length[105]. Alternatively, the HOMO orbital energies calculated for popular anions were misleading, with the empirically least stable anion (BF$_4$) having the highest calculated oxidation potential. After accounting for ion-dipole effects resulting from solvent anion interactions, the correct HOMO orbital energies and oxidation potentials were calculated for these anions[17].

_Cation Molecular Volume_

The molecular volume of the TEA, SBP, OP, and AP cations was calculated with Schrodinger Materials Suite using the Jaguar DFT module. The structures were geometrically optimized using the hybrid B3LYP method with the 6-311G**++ basis set. The volume of the structures was then calculated using the PyVol function.
The AP cation (98Å) was the smallest cation calculated followed by the OP (102Å), SBP (114Å), and TEA (123Å) cations. The OP and AP cations deviate significantly in structure, but have similar ion sizes which is expected to correspond to similar device capacitance and ESR, with devices containing the AP cation to exhibit slightly higher capacitances and lower ESRs.

**Electrostatic Potential (ESP)**

![Image of Electrostatic Potential (ESP)]

<table>
<thead>
<tr>
<th>Properties</th>
<th>TEA</th>
<th>SBP</th>
<th>OP</th>
<th>AP</th>
</tr>
</thead>
<tbody>
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<td>Volume (Å³)</td>
<td>123</td>
<td>114</td>
<td>102</td>
<td>98</td>
</tr>
<tr>
<td>ESP Average (kcal mol⁻¹)</td>
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<td>94.41</td>
<td>97.69</td>
<td>96.38</td>
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<tr>
<td>ESP Max (kcal mol⁻¹)</td>
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<td>119.34</td>
<td>128.82</td>
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</tbody>
</table>

*Figure 6.1 Mapped Electrostatic Potential (MEP) surfaces, ball and stick models, cation volumes, average Electrostatic Potentials (ESP), and maximum ESP generated by Schrodinger Jaguar Density Function Theory (DFT) software using a hybrid B3YLP method and 6-311G**++ basis set for TEA, SBP, OP, and AP cations. The atoms are denoted as follows: hydrogen–white, carbon–grey, oxygen-red and nitrogen–blue.*

The electrostatic potential of the geometrically optimized TEA, SBP, OP, and AP cations was calculated with the Schrodinger Jaguar DFT single point energy module using the hybrid
B3YLP method with the 6-311G**++ basis set. The resulting electrostatic potential surfaces then were mapped on the space filled structures to create MEP structures. The maximum electrostatic potential was found to increase as the ion size was reduced due to the removal of electron donating groups, with the exception of the OP cation. The oxygen present in the OP cation has a significant impact on the ESP by acting as an electron withdrawing group with two lone pairs. The increased elenegativity of the oxygen increases the maximum ESP throughout the OP cation, while the two lone pairs depresses minimum ESP of the oxygen. As a result of the electron withdrawing effects of the oxygen, the maximum ESP of the OP cation is greater than the other three cations. Due to the lone pairs on the oxygen, the minimum ESP of the OP cation is lower than the other three cations. Despite the significant disparity in minimum and maximum ESP, the mean ESP of the OP cation is only slightly greater than the AP cation. The significantly different ESP of the OP cation may impact EDLC device performance due to different ion-dipole interactions with the solvent and electrode adsorption effects.
Orbital Energies (ESP)

Figure 6.2 Highest Occupied Molecular Orbital (HOMO) – Lowest Unoccupied Molecular Orbital (LUMO) orbital energy values calculated using Schrodinger Jaguar Density Function Theory (DFT) software using a hybrid B3LYP method and 6-311G**++ basis set for TEA, SBP, OP, and AP cations. The atoms are denoted as follows: hydrogen–white, carbon–grey, oxygen–red and nitrogen–blue.
The HOMO-LUMO orbital energies of the geometrically optimized TEA, SBP, OP, and AP cations were calculated with the Schrodinger Jaguar DFT single point energy module using the hybrid B3YLP method with the 6-311G**++ basis set with and without a Poisson-Boltzmann solvent model. Previous investigations have shown that there is a significant difference in calculated orbital energies when the solvent system is included[106–108]. The ion dipole interactions between the cation and acetonitrile molecules are expected to have a significant impact on the calculated orbital energies due to the high polarity of the electrolyte solvent. The acetonitrile molecules (Dielectric Constant: 37.5, Probe Radius: 2.19) are expected to displace the electrons in the cations resulting in an orbital energy shift. This orbital energy shift was observed with the calculations performed by the Jaguar module. The cations in the absence of the Poisson-Boltzmann solvent field had significantly different HOMO-LUMO energy values. These non-solvent values are in agreement with the calculations of other investigations for spiro-ammonium cations[109]. As expected, the orbital energies calculated while accounting for the solvent, with the Poisson=Boltzmann solvent field, were elevated significantly due to the highly polar acetonitrile molecules inducing shifts in electron density.

The reduction potential of the cations is related to the HOMO-LUMO orbital energies through the gibbs free energy of the reduced species. The reduction gibbs free energy of the cations is related to the HOMO-LUMO energy through Eq():

$$\Delta G_{\text{reduction}} = EA = -(E_{HOMO} + E_{LUMO}) - IP$$

(where $G_{\text{reduction}}$ is the gibbs free energy of the reduced species, $EA$ is the electron affinity, $E_{HOMO}$ is the energy of the HOMO orbitals, $E_{LUMO}$ is the energy of the LUMO orbitals, and $IP$ is the ionization potential). This relation assumes that the change in gibbs free energy is approximately equivalent to the electron affinity. The reduction voltage can then be calculated through Eq():
\[ V_{\text{reduction}} = -\frac{\Delta G_{\text{reduction}}}{nF} \]

(where \( V_{\text{reduction}} \) is the reduction potential, \( \Delta G_{\text{reduction}} \) is the gibbs free energy of the reduced species, \( n \) is the moles of the species, and \( F \) is faradays constant). Despite the difficulty in calculating electron affinities, this relationship has been shown to accurately predict reduction potential[110].

<table>
<thead>
<tr>
<th>Properties</th>
<th>TEA</th>
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<th>OP</th>
<th>AP</th>
</tr>
</thead>
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<tr>
<td></td>
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</tr>
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<td>-2.05</td>
<td>-2.24</td>
<td>-1.67</td>
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<td></td>
<td>Poisson-Boltzmann Solvent Model (Acetonitrile)</td>
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<tr>
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<td>12.70</td>
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<tr>
<td>IP min (eV)</td>
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<td>10.71</td>
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<tr>
<td>( V_{\text{red}} )</td>
<td>1.62</td>
<td>1.52</td>
<td>2.15</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Figure 6.3 The mean/minimum Ionization potentials and reduction potentials for the TEA, SBP, OP, and AP cations calculated with and without the Poisson-Boltzmann Solvent Model with Schrodinger Jaguar Density Function Theory (DFT) software using a hybrid B3YLP method and 6-311G**++ basis set. A \( E_{\text{SHE}} \) value was not incorporated in the calculations.

The trend of the calculated reduction potentials using this method were not found to be in agreement with experimental observations. The incorporation of a solvation model reduced the reduction potential significantly for all the cations, thereby reducing the calculated ESW, but did not alter the calculated stability trend. The solvated reduction potentials of the AP and SBP cations are nearly equivalent despite empirical evidence demonstrating the lower stability of the AP cation relative to the SBP cation. A different computational approach is needed to accurately predict the stability of different spiro-ammonium cations.
6.3 Full Cell Electrochemical Impedance Spectroscopy

Figure 6.4 Two Electrode EIS spectra of EDLC devices containing 1M APBF$_4$ (blue-circle), 1M SBPBF$_4$ (red-square), 1M TEABF$_4$ (green-triangle), and 1M OPBF$_4$ (orange-diamond).
EIS was employed to measure the device resistance and solution resistance ($R_s$) of each three-electrode EDLC device 1M TEABF$_4$, 1M SBPBF$_4$, 1M OPBF$_4$, and 1M APBF$_4$ at room temperature. The EIS spectra was collected prior to cycling for each device at 57 frequencies between 1 MHz and 10 mHz. At low frequencies, the Nyquist plot demonstrates near ideal capacitor behavior with a vertical straight line for each device. The device containing 1M OPBF$_4$ at low frequencies deviates slightly from ideal capacitor, thus indicating that slow diffusion is occurring through the system. This is attributed to the high ESP of the OP cation interacting with the anion and solvent in bulk solution, inhibiting pore diffusion. At high frequencies, a semi-circle was observed, indicative of contact resistance between the stubs, aluminum current collector, activated carbon electrodes, and electrolyte. The 45° Warburg diffusion slope was also identified for each device in the intermediate frequency range. This diffusion slope is representative of electrolyte ion mass transport in the double layer. The mass transport for each device occurs at the same “knee” frequency, thereby indicating there is no difference in mass transport between the different cations[31].

The electrolyte solution resistance, the first intersection to the real axis of in the high frequency range, of these three-electrode devices was observed to be greater than the two-electrode devices. The increased solution resistance of the three-electrode devices is attributed to the use of a 260 µm glass separator in place of the 25 µm Celgard separators which increased electrode separator. Although the electrolyte solution resistances of the three-electrode devices exceeded the two-electrode devices, the measured solution resistances still corresponded directly with the electrolyte conductivity measurements (AP < SBP < TEA < OP).
6.4 Full Cell Galvanostatic Charge/Discharge

The GCD method was employed to measure the gravimetric capacitance, ESR, specific energy, and specific power of devices containing 1M TEABF$_4$, 1M SBPBF$_4$, 1M OPBF$_4$, and 1M APBF$_4$ in a process consistent with commercial EDLC measurement. These devices were charged and discharged from 0 to 2.7V at a current density of 2 A g$^{-1}$ for 1000 cycles. The full cell gravimetric capacitance of these devices was calculated every 10$^{th}$ cycle using Eq. (1):

$$C_{\text{full}} = \frac{j \Delta t}{\Delta V m}$$  \hspace{1cm} (1)

(where $j$ is the current, $\Delta V$ is the potential from $V_{\text{max}}$ to $\frac{1}{2} V_{\text{max}}$, $\Delta t$ is time, and $m$ is the total activate materials mass of both electrodes)[24,26,111]. The full cell ESR of these devices was calculated from the potential drop measured during the transition from charging to discharging at the maximum potential (2.7V) according Eq. (2):

$$\text{ESR}_{\text{full}} = \frac{(V_1 - V_2)_\text{drop}}{(\Delta j A)}$$  \hspace{1cm} (2)

(where $V_1$ is the maximum voltage before discharge, $V_2$ is the maximum voltage after discharge, $\Delta j$ is the change in current from charge to discharge, and $A$ is the area of the electrode)[25,112].

After cycling, the gravimetric capacitances and discharge times of each device were measured at a range of current densities from 100 mA g$^{-1}$ to 6 A g$^{-1}$ to generate a Ragone plot (Fig.2c). The specific energy of these devices was calculated from the gravimetric capacitance using Eq. (3):

$$E = \frac{1}{2} C_g V^2$$  \hspace{1cm} (3)

(where $C_g$ is the calculated gravimetric capacitance and $V$ is the maximum discharge voltage).

The power density of these devices was calculated from the energy density and discharge time according to Eq. (4):
\[ P = \frac{E}{t_{\text{discharge}}} \]  \hspace{1cm} (4)

(where \( E \) is the calculated specific energy and \( t_{\text{discharge}} \) is the discharge time)[19]. These calculated full cell specific energy and power values for each device were found to be in agreement with the values directly measured by the primary potentiostat channel.

Figure 6.5 Full cell gravimetric capacitance for devices containing 1M APBF\textsubscript{4} (blue-circle), 1M SBPBF\textsubscript{4} (red-square), 1M TEABF\textsubscript{4} (green-triangle), and 1M OPBF\textsubscript{4} (orange-diamond).

The average full cell gravimetric capacitance of the 1M OPBF\textsubscript{4} device (33.47 F g\textsuperscript{-1}) was found to exceed the values calculated for the 1M TEABF\textsubscript{4} device (27.49 F g\textsuperscript{-1}) , 1M SBPBF\textsubscript{4}
device (29.35 F g$^{-1}$), and 1M APBF$_4$ device (32.22 F g$^{-1}$). This capacitance trend (OP > AP > SBP > TEA) is not in agreement with the conclusion of previous studies that suggest cation size is inversely proportional to device capacitance (Fig. 2a). The reduced size of the AP cation (98Å) relative to the OP cation (102Å) is expected to enable increased pore accessibility for the AP cation, thereby corresponding to a greater accessible surface area for capacitive energy storage. Despite the generally accepted capacitance ion size relationship, the increased capacitance of devices containing larger oxygen substituted cations has been observed in previous studies. The increased full cell capacitance of devices containing oxygen substituted cations is attributed to ion-electrode electrostatic interactions at the positive electrode.
Figure 6.6 Full cell ESR for devices containing 1M APBF$_4$ (blue-circle), 1M SBPBF$_4$ (red-square), 1M TEABF$_4$ (green-triangle), and 1M OPBF$_4$ (orange-diamond).

The average full cell calculated ESR of the 1M APBF$_4$ device (680.26 mΩ cm$^2$) was found to be lower than the values calculated for the 1M TEABF$_4$ device (959.78 mΩ cm$^2$), 1M SBPBF$_4$ device (881.72 mΩ cm$^2$), and 1M OPBF$_4$ device (989.46 mΩ cm$^2$). The ESR values increased (AP < SBP < TEA < OP) as measured ionic conductivity of the electrolyte decreased and did not correspond with cation size (Fig. 2b). The highest calculated ESR was observed in the device containing 1M OPBF$_4$. The high ESR and low ionic conductivity of the electrolyte containing the OP cation is attributed to the strong intermolecular attraction between the OP cation and acetonitrile solvent molecules. These intermolecular forces impede ion movement through the bulk solution and result in more resistive devices.
Figure 6.7 Full cell gravimetric capacitance Ragone plot for devices containing 1M APBF₄ (blue-circle), 1M SBPBF₄ (red-square), 1M TEABF₄ (green-triangle), and 1M OPBF₄ (orange-diamond).

6.5 Negative Electrode Galvanostatic Charge/Discharge

The GCD method was employed to measure electrochemical characteristics of the negative electrode for devices containing 1M TEABF₄, 1M SBPBF₄, 1M OPBF₄, and 1M APBF₄. As these devices were charged and discharged from 0 to 2.7V at a current density of 2 A g⁻¹ for 1000 cycles using a primary potentiostat channel, a secondary potentiostat channel measured the change in half cell potential between the negative electrode and pseudo reference electrode. The gravimetric capacitance, ESR, specific energy, and specific power were calculated from the measured half cell potentials with Eq. (1-4).
Figure 6.8 Negative electrode gravimetric capacitance for devices containing 1M APBF$_4$ (blue-circle), 1M SBPBF$_4$ (red-square), 1M TEABF$_4$ (green-triangle), and 1M OPBF$_4$ (orange-diamond).

The average negative electrode capacitance of the 1M APBF$_4$ device (143.28 F g$^{-1}$) was found to be greater than the values calculated for the 1M TEABF$_4$ device (116.97 F g$^{-1}$), 1M SBPBF$_4$ device (126.12 F g$^{-1}$), and 1M OPBF$_4$ device (138.39 F g$^{-1}$). These capacitance values are inversely proportional to the size of the cation (Fig. 3a). As the size of the cation decreased (TEA < SBP < OP < AP), the capacitance values calculated for each device increased (AP > OP > SBP > TEA). At the negative electrode, the cation assumed the role of the counter-ion.
diffusing into the pores of the electrode from bulk solution and adsorbing on the pore surface. The increase in device capacitance with a reduction in cation size was attributed to the greater accessible surface area available for counter ion adsorption in the pores and capacitive energy storage. The negative electrode capacitance was found to be inversely correlated ($R^2=0.999$) to the calculated size of each cation (Fig. 3d).

Figure 6.9 Negative ESR for devices containing 1M APBF$_4$ (blue-circle), 1M SBPBF$_4$ (red-square), 1M TEABF$_4$ (green-triangle), and 1M OPBF$_4$ (orange-diamond).

The average negative electrode ESR of the 1M APBF$_4$ device (396.17 mΩ cm$^{-2}$) and 1M SBPBF$_4$ device (418.91 mΩ cm$^{-2}$) were found to be significantly lower than the values calculated
for the 1M TEABF$_4$ device (556.51 mΩ cm$^{-2}$) and 1M OPBF$_4$ device (607.96 mΩ cm$^{-2}$). The ESR values corresponded with the ionic conductivity measurements for each electrolyte and the resistance trend observed for the full cell measurements (Fig. 3b). The highest calculated ESR was observed in the 1M OPBF$_4$ device, which is attributed to the strong intermolecular interactions between the OP cation and the acetonitrile solvent molecules that impeded cation pore mobility and adsorption.

Figure 6.10 Negative electrode Ragone plot for devices containing 1M APBF$_4$ (blue-circle), 1M SBPBF$_4$ (red-square), 1M TEABF$_4$ (green-triangle), and 1M OPBF$_4$ (orange-diamond).
Figure 6.11 Negative electrode capacitance/cation size plot for devices containing 1M APBF₄ (blue-circle), 1M SBPBF₄ (red-square), 1M TEABF₄ (green-triangle), and 1M OPBF₄ (orange-diamond).

6.6 Positive Electrode Galvanostatic Charge/Discharge

The GCD method was also applied to measure the electrochemical characteristics of the positive electrode for devices containing 1M TEABF₄, 1M SBPBF₄, 1M OPBF₄, and 1M APBF₄. As these devices were charged and discharged from 0 to 2.7V at a current density of 2 A g⁻¹ for 1000 cycles using a primary potentiostat channel, a secondary potentiostat channel measured the change in half cell potential between the positive electrode and pseudo reference electrode. The
gravimetric capacitance, ESR, specific energy, and specific power were calculated from the measured half cell potentials with Eq. (1-4).

Figure 6.12 Positive electrode gravimetric capacitance for devices containing 1M APBF$_4$ (blue-circle), 1M SBPBF$_4$ (red-square), 1M TEABF$_4$ (green-triangle), and 1M OPBF$_4$ (orange-diamond).

Despite each electrolyte containing the same anion (BF$_4$), the capacitance values varied considerably at the positive electrode between the devices with different cations. The average positive electrode capacitance of the 1M OPBF$_4$ device (130.62 F g$^{-1}$) was found to be significantly greater than the values calculated for the 1M TEABF$_4$ device (101.22 F g$^{-1}$), 1M SBPBF$_4$ device (107.27 F g$^{-1}$), and 1M OPBF$_4$ device (118.26 F g$^{-1}$). The significant increase in
capacitance at the positive electrode for the device containing 1M OPBF$_4$ clarifies the full cell measurements and establishes that the positive electrode is responsible for the increased full cell performance of this device. Furthermore, the positive electrode capacitance trend (OP > AP > SBP > TEA) differs from the observed trend for the negative electrode, in that it is not correlated with cation size (Fig. 4a). At the positive electrode, the cation assumes the role of the co-ion and is expected to de-adsorb from the electrode surface and exit the pores into the bulk solution. The increase in capacitance at positive electrode was attributed to the increase in cation maximum ESP, which resulted in more prevalent ion-electrode electrostatic interactions. The maximum ESP of the cation was found to be directly proportional ($R^2=0.996$) to the positive electrode capacitance(Fig. 4d).
Figure 6.13 Positive electrode ESR for devices containing 1M APBF$_4$ (blue-circle), 1M SBPBF$_4$ (red-square), 1M TEABF$_4$ (green-triangle), and 1M OPBF$_4$ (orange-diamond).

The average positive electrode ESR of the 1M APBF$_4$ device (261.2 mΩ cm$^{-2}$) was found to be significantly lower than the values calculated for the 1M TEABF$_4$ device (370.24 mΩ cm$^{-2}$), 1M SBPBF$_4$ device (433.17 mΩ cm$^{-2}$), and 1M OPBF$_4$ device (344.5 mΩ cm$^{-2}$). The ESR values did not correspond with the ionic conductivity measurements for each electrolyte (Fig. 4b).

Figure 6.14 Positive electrode Ragone plot for devices containing 1M APBF$_4$ (blue-circle), 1M SBPBF$_4$ (red-square), 1M TEABF$_4$ (green-triangle), and 1M OPBF$_4$ (orange-diamond).
Figure 6.15 Positive electrode capacitance/max ESP plot for devices containing 1M APBF₄ (blue-circle), 1M SBPBF₄ (red-square), 1M TEABF₄ (green-triangle), and 1M OPBF₄ (orange-diamond).
6.6 Role of Co-ion and Counter-ion

Negative Electrode

\[
\text{Cation Size } \propto \frac{1}{\text{Capacitance}}
\]

Positive Electrode

\[
\text{Cation ESP } \propto \text{Capacitance}
\]

Figure 6.16 Comparison of the impact of cation properties on the positive and negative electrodes.

The capacitance, ESR, specific energy, and specific power of the full cell, positive, and negative electrodes were measured concurrently for EDLC devices containing 1M TEABF$_4$, 1M SBPBF$_4$, 1M OPBF$_4$, and 1M APBF$_4$. Contrary to the notion of ion size being the primary electrolyte property that dictates device capacitance, the device containing 1M OPBF$_4$, the second smallest cation in this study (102Å), demonstrated a higher gravimetric capacitance (33.47 F g$^{-1}$) than devices containing 1M TEABF$_4$ (27.49 F g$^{-1}$, 123Å), 1M SBPBF$_4$ (29.35 F g$^{-1}$, 114Å), and 1M APBF$_4$ (32.22 F g$^{-1}$, 98Å), the smallest spiro-ammonium cation. The increase in full cell capacitance observed for the OPBF$_4$ device was found to be the result of a significant rise in positive electrode capacitance. The increase in positive electrode capacitance was found to be directly proportional to the maximum cation ESP ($R^2 = 0.996$). Conversely, the negative electrode capacitance was found to be inversely proportional to cation size ($R^2 = 0.999$).
The electrolyte properties that dictate EDLC device performance were clarified in this study. Additionally, the improved performance of devices that contain oxygen substituted cations was determined to be the result of increased capacitance at the positive electrode.
Chapter 7: Conclusions and Future Work

Future Work

A critical necessity moving forward in developing an empirically derived model for predicating EDLC device capacitance, and by extension energy density, is to clarify the impact of anion structure and electrode composition on the electrochemical characteristics of the positive electrode, negative electrode, and full cell.

Having already thoroughly studied the impact of cation structure on EDLC performance, it is imperative that the role of anion structure on device performance is clarified to garner a complete understanding of the electrolyte – capacitance relationship. The anion is expected to perform in a similar manner to the cation as a co-ion and counter-ion at the positive and negative electrodes. At the positive electrode, the anion assumes the role of the counter-ion and migrates into the pores of the electrode to adsorb on the surface as the device is charged. The positive electrode capacitance is expected to vary inversely with the counter-ion molecular volume, as this was observed at the negative electrode for the cation. As the molecular volume of the anion is reduced, the surface of the positive electrode can be occupied by the counter-ion thereby resulting in a higher capacitance. At the negative electrode, the anion assumes the role of the co-ion and migrates out of the pores of the electrode into the bulk solution as the device was charged due to electrostatic repulsion. The negative electrode capacitance is expected to vary directly with the ESP of the anion, as this was observed at the positive electrode for the cation. If the anion co-ion mechanism is akin to the proposed cation co-ion mechanism, then the negative electrode capacitance is expected to be directly proportional to the minimum ESP of the anion. The four proposed anion candidates for this study are Bis(TFMS)imide, Bis(fluorosulfonyl)imde, Hexafluorophosphate, and the industry standard tetrafluoroborate.
Significantly research has been conducted in both two and three electrode studies to clarify the impact of the electrode composition and morphology on the electrochemical characteristics of EDLC devices, but the ion structure electrode relationship has not been thoroughly investigated. Expounding the influence of electrode composition on ion adsorption and pore mobility would aid in the design of both new electrolytes and electrodes that can optimize EDLC performance. The three-electrode apparatus employed in this study can elucidate the impact of different electrode materials as a positive and negative electrode in system that accurately emulates two electrode devices.

The proposed electrode and anion research would help address significant vacancies in our understanding of EDLC devices, thereby enabling the development of novel electrolyte and electrode design strategies to increase device performance.
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115


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