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Study of Selected Issues of Solid-State Electrochemical Energy Storage

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UNIVERSITY OF MIAMI

STUDY OF SELECTED ISSUES OF SOLID-STATE ELECTROCHEMICAL ENERGY STORAGE

By
Yuchen Wang

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Doctor of Philosophy

STUDY OF SELECTED ISSUES OF SOLID-STATE ELECTROCHEMICAL
ENERGY STORAGE

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The present dissertation focuses on three different topics of supercapacitor (SC) technology: 1) combination of galvanic cell components into SCs to mitigate the problem of self-discharge, 2) development of an all-solid-state SC/battery based on a superionic ceramic electrolyte and 3) mechanical-electrochemical study of a composite structural SC.

A new hybrid supercapacitor SC with the galvanic cell materials is proposed to mitigate the self-discharge problem and to increase the storage-life. The galvanic cell components in the hybrid SC can provide a micro-current to compensate the self-discharge current. The hybrid SC was fabricated with active carbon electrodes, a polyvinylidene fluoride (PVDF)/lithium trifluoromethanesulfonate (LiTFS) membrane with 1.5 M zinc sulfate (ZnSO₄) aqueous electrolyte. Copper and zinc foils were used as the current collectors and as the galvanic cell cathode and anode. The hybrid SC exhibited a greater maximum specific capacitance and specific energy than a baseline SC with gold foil collectors and a symmetrical design. The capacitance retention of the hybrid SC was 80% after 2000 cycles. In a month, the open circuit voltage of the charged hybrid SC declined slightly from initial 0.90 V to 0.85 V. The steady-state leakage current density was as low as 1.57 μA cm⁻² at 0.90 V. The equations derived from the equivalent circuit models fit well to the self-discharge experimental data.
In the second part of the dissertation, a high power all-solid-state SC with RbAg\textsubscript{4}I\textsubscript{5} is proposed and fabricated without sealing. RbAg\textsubscript{4}I\textsubscript{5} powders can conduct silver ions between electrodes and provide the energy storage simultaneously. The ionic conductivity of RbAg\textsubscript{4}I\textsubscript{5} powders was 0.21 S cm\textsuperscript{-1} greater than or comparable to that of a typical liquid electrolyte. The all-solid-state SC can work in oxygen and moisture environment at room temperature and show the hybrid behavior including SC and battery. The maximum specific energy can reach more than 60 Wh kg\textsuperscript{-1}. The charge capacity of the all-solid-state SC dropped to 16% of the maximum capacity after 200 cycles and the capacity can be recovered by an annealing process at 150°C for 12 hours. This SC can achieve both high specific power and energy simultaneously by reducing the thicknesses of the electrodes and the electrolyte.

The last part is on mechanical-electrochemical study of a composite structural SC based on an epoxy based adhesive polymer electrolyte. The epoxy based adhesive polymer electrolyte was prepared using PVDF, LiTFS and epoxy. The maximum conductivity of the epoxy based adhesive polymer electrolyte can achieve 10\textsuperscript{-2} S cm\textsuperscript{-1}. Structural SCs were fabricated using a vacuum bagging method. The specific energy can reach 2.64 Wh kg\textsuperscript{-1} and the ultimate tensile strength (UTS) can reach 80 MPa. The response of electrochemical performance of the structural SCs to in-plane tensile stress was studied. Before fracture, both the specific power and the specific energy increases slightly.
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CHAPTER 1 INTRODUCTION

1.1 Outline

The present dissertation reflects a 5-year research effort on three important issues of electrochemical capacitor (EC) or supercapacitor (SC) technology. The first is combination of galvanic cell components into SCs to mitigate the problem of self-discharge. The second is development of an all-solid-state supercapacitor/battery based on a superionic ceramic electrolyte. The third is mechanical-electrochemical study of a composite structural supercapacitor.

1.2 Study and mitigation of self-discharge

1.2.1 Background

With the commercialization and market expansion of electric vehicles, there is a growing demand for high performance energy storage devices. Typical SCs or electric double layer capacitors (EDLCs) are energy storage devices with fast charge and discharge capabilities suitable for applications including vehicle acceleration and regenerative braking [1]. Because SCs store the energy by the adsorption of electrolyte ions on the electrode surfaces, their charge/discharge rate is not limited by redox reaction kinetics like those of rechargeable batteries and permits a high specific power. However, one of the biggest challenges for widespread application of SCs is their intrinsic fast self-discharge rate and short “storage-life” problem [2]. Self-discharge of a SC is a phenomenon of gradual voltage decline and energy loss when the SC is not connected to an electric load or under an open circuit condition [3]. As such, SCs are considered as being not suitable for stand-alone electrical energy storages [3, 4].
Many researchers have studied the self-discharge mechanisms of SCs. Conway et al. [5] first described three self-discharge mechanisms: 1) decomposition of the SC electrolyte, 2) side reactions of the impurities, and 3) internal ohmic leakage pathways. Conway et al. [6, 7] also proposed a charge redistribution mechanism to interpret the so-called memory effect of SCs. Andreas et al. [8] found that the process of charge redistribution took place for a period up to tens of hours. Recently, Kowal et al. [9] have shown that the self-discharge rate depends on the initial voltage, temperature, charge process/duration, and short-term history.

Modeling of the self-discharge behavior seems to be a challenging task because the mechanisms of self-discharge are multiple, coupled, and not fully understood. An ultimate solution may be to adopt a multi-scale model that fully describes the physic-chemical processes in the micro-pore structures. There are two categories of modeling: 1) continuum models consisting of partial differential equations and boundary conditions and 2) equivalent circuit models [5, 7-15]. For the equivalent circuit models, the ones that describe the system using transmission line circuits are probably closer to the reality but more complicated and difficult to extract useful information. So far, most of the modeling efforts have been based on simplified equivalent circuits. Probably the earliest effort was done by Conway and his group [5, 7, 11]. They proposed an equivalent circuit consisting of a series resistor, a capacitor, and a parallel self-discharge resistor. Later studies found that the self-discharge resistance was a function of cell voltage, time, and charge history [9]. More recently, a so-called three branch equivalent circuits were proposed by other researchers [12-15]. The first branch consists of an EDLC and a capacitance proportional to voltage emulating differential capacitance. The second and third is mainly for describing the charge
redistribution. In fact, the method proposed by Kowal [9] earlier is equivalent to the three branch models by directly introducing three time constants.

In recent years, a few efforts have been made to effectively mitigate the self-discharge problem. One was to modify the electronic states of graphene surface [16] and the other one was to electrodeposit a poly(p-phenylene oxide) (PPO) thin film on the electrode surface as a blocking layer [17, 18]. However, the first method only provided a relative reduction of the self-discharge rate which was 50% reduction of the cell voltage in 3.4 hours. The blocking layer method could slow down the voltage reduction rate from 28% in one hour to 25% in one hour. These improvements by no means match the requirement for the stand-alone electrical energy storage devices and the storage-life of existing Li-ion batteries.

1.2.2 Objective

In this work, we combined galvanic cell materials into a SC to mitigate the self-discharge problem and increase the storage-life of a SC. In general, a galvanic cell is an electrochemical cell that outputs electrical current via electrochemical reactions at dissimilar electrodes [19]. If galvanic cell materials are combined in a SC, they may generate a micro-current to compensate the self-discharge current of the SC and thereby extend the storage-life of the SC. The hybrid SC is shown as Figure 1.1. The self-discharge behaviors were studied using electrochemical methods and an equivalent circuit modeling approach.
1.3 All-solid-state supercapacitor with rubidium silver iodide superionic ceramic electrolyte

1.3.1 Background

SCs store charges by adsorption of electrolyte ions at the electrode/electrolyte interface. Compared to batteries, SCs can achieve a much greater specific power because unlike in batteries the charge/discharge mechanisms in most SCs are not diffusion-controlled [20]. The maximum specific power $P_{\text{max}}$ of a SC inversely depends on the internal resistance or the equivalent series resistance (ESR) according to the following equation [21]:

$$P_{\text{max}} = \frac{V_{\text{max}}}{4mR_{ESR}}$$  \hspace{1cm} (1.1)

where $V_{\text{max}}$ is the maximum of applied voltage, $m$ is the mass of the SC, $R_{ESR}$ is the ESR of the SC including the resistance of the electrolyte.
Figure 1.2 Comparisons of cyclic voltammetry curves of EDLCs with different electrolyte ionic conductivity values: $1 \times 10^{-2}$ S cm$^{-1}$ (left) [22], and $8 \times 10^{-3}$ S cm$^{-1}$ (right) [23].

The cyclic voltammetry (CV) curves of EDLCs with different electrolyte ionic conductivity values are compared as Figure 1.2. With a greater conductivity electrolyte, the shape of the CV curve was closer to an ideal EDLC CV curve. Jow et al. [24] proposed that the conductivity of an ideal electrolyte for a SC should be greater than 0.02 S cm$^{-1}$ in order to obtain an ideal charge/discharge behavior: a rectangular CV, linear voltage vs. time relationship in a constant current charge/discharge test, and a high charge/discharge efficiency.
Figure 1.3 Conductivity of polymer electrolytes versus the year published and the approximate magnitude of traditional liquid electrolytes [25].

Solid-state SCs have been attracted extensive interests because an all-solid-state design is an ultimate solution for the safety concerns including leakage of toxic substances, evaporation or expansion of liquid electrolytes at elevated temperatures, and firing of the devices [26]. So far, all-solid-state SCs have been based on polymer electrolytes [27]. As shown in Figure 1.3, the reported conductivity values of polymer electrolytes are below $10^{-4}$ S cm$^{-1}$ at room temperature [25], which is much less than the required value of 0.01 S cm$^{-1}$.

A group of materials called superionic conductors (SICs) can be ideal electrolytes for all-solid-state SCs. SICs are solid-state ionic conductors with extremely high ionic
conductivity ($\sigma_i > 0.001 \text{ S cm}^{-1}$) [28]. The dependence of ionic conductivity on temperature for common SICs is displayed as Figure 1.4 [29].

Rubidium silver iodide (RbAg$_4$I$_5$) is a silver ion superionic conductor which has very high ionic conductivity at room temperature. The highest ionic conductivity at room temperature was reported as being 0.26 S cm$^{-1}$ by Owens and Argue [30]. RbAg$_4$I$_5$ is a promising material for high power all-solid-state SCs. So far there has been a few studies on making primary batteries. However, the idea of using RbAg$_4$I$_5$ to fabricate SCs and rechargeable batteries has not been studied.
1.3.2 Objective

In this work, we used RbAg₄I₅ as the electrolyte to develop a high power all-solid-state SC as schematically shown in Figure 1.5. Graphite plates can work as current collectors. Silver conductive adhesive paste with high surface area carbon powder which is a mixture of fine silver particles, carbon particles, and adhesive can decrease the contact resistance between RbAg₄I₅ and graphite plates, and provide electrical double layer capacitance. The all-solid-state SC was studied using electrochemical methods. For this SC, there are four possible behaviors:

1) EDLC behavior
The interfaces between silver powder and solid-state electrolyte provides electrical double layer capacitance.

2) Pseudocapacitor behavior

Cathode: \[ \frac{7}{2}I_2 + 7/2e^- \leftrightarrow 7I^- \]  \hspace{1cm} (1.2)

Anode: \[ \text{RbAg}_4\text{I}_5 + 7/2e^- \leftrightarrow 1/2\text{Rb}_2\text{AgI}_3 + 7/2\text{Ag}^+ + 7I^- \] \hspace{1cm} (1.3)
I$_2$/I$^-$ and Ag$^+$/Ag redox pairs on the electrode/electrolyte interface can provide pseudocapacitance [31].

3) Battery behavior

The possible half reactions and total reaction is:

Cathode: \[ \frac{7}{2}I_2 + \frac{7}{2}e^- \leftrightarrow 7I^- \] (1.4)

The standard electrode potential vs standard hydrogen electrode (SHE) is +0.54 V.

Anode: \[ \text{RbAg}_4\text{I}_5 + \frac{7}{2}e^- \leftrightarrow \frac{1}{2}\text{Rb}_2\text{AgI}_3 + \frac{7}{2}\text{Ag}^+ + \frac{7}{2}I^- \] (1.5)

The standard electrode potential vs SHE is -0.15 V.

If both I$^-$ and Ag$^+$ can enter into bulk electrode materials, the device will show battery behavior.

\[ \text{RbAg}_4\text{I}_5 \leftrightarrow \frac{1}{2}\text{Rb}_2\text{AgI}_3 + \frac{7}{2}\text{Ag}^+ + \frac{7}{2}I_2 \] (1.6)

The theoretical voltage is 0.69 V.

4) Hybrid behavior

The behavior of the all-solid-state SC can be the combination of SC and battery.

1.4 Structural supercapacitor with epoxy based adhesive polymer electrolyte

1.4.1 Background

While major efforts are paid to increase the specific energy and power of energy storage devices to meet the demand of transport systems, an alternative approach is to turn the structural components of the systems into energy storage devices including structural SC [32]. A structural SC is made of two multifunctional structural electrodes and a structural electrolyte [33]. There are many applications for the structural SCs, such as electric vehicles, CubeSats[34], and un-maned aero-vehicles (UAVs) [35]. Because of the
high specific power but relatively lower specific energy, the use of SCs as auxiliary power sources for acceleration/deceleration and takeoff is considered beneficial for expanding the performance range and extending the life time of the energy storage unit. Replacing some of the structural components with structural SCs will save the total mass of the carry-on energy storage unit providing an attractive option.

The multifunctional electrolyte is perhaps the most key component in a structural SC, since it must provide both mechanical strength and ion conduction \[36\]. Unfortunately, the ionic conductivity was usually inversely proportional to mechanical property \[37, 38\]. The most common structural electrolyte is the combination of epoxy and ionic liquid \[39-41\]. In epoxy/ionic liquid structural electrolyte, epoxy is an component that provide a mechanical strength, chemical and thermal stability \[42\] while ionic liquid provides a good ionic conductivity and thermal stability \[43\]. Room temperature conductivity of ionic liquid is in the range of $0.1-18 \times 10^{-3}$ S cm$^{-1}$ \[44\]. The conductivity of the mixture of epoxy and ionic liquid structural electrolyte is most likely less than $10^{-3}$ S cm$^{-1}$ \[39-41\]. For this reason, the electrolyte with an ionic conductivity below $10^{-3}$ S cm$^{-1}$ yields non-ideal behaviors including slow charge/discharge, deviation of the CV curves from the ideal rectangular shape, asymmetry of the galvanostatic charge discharge (GCD) curves, high self-discharge rate, and low energy efficiency (< 60%). Improving and advancing the structural SC technology must solve the problem of the conductivity of structural electrolytes.

Another problem of the structural SCs is that very few researchers have performed systematic study on the relationship between the electrochemical performance and the
mechanical behaviors. For my understanding, the electrochemical behaviors of structural SCs have not been evaluated under mechanical loading.

1.4.2 Objective

In this work, a new epoxy based adhesive polymer electrolyte was prepared. The conductivity of the polymer electrolyte with different compositions was measured. The structural SCs were fabricated with the combination of carbon-based electrodes and the polymer electrolyte. Tension test were conducted on the structural SC samples with different compositions. Also, in-situ electrochemical tests were carried on the structural SC samples with high conductivity (\( > 10^{-2} \text{ S cm}^{-1} \)) polymer electrolyte under loading.
CHAPTER 2 LITERATURE REVIEW

2.1 History of supercapacitors

In the middle of eighteenth century, the first capacitor “Leyden jar” was invented and the principle of charge storage in a charged capacitor was understood [45]. The historic investigations were of major significance for electrochemical engineering. Development of the supercapacitor (SC) technology was started in 1900s by Helmholtz. He first described the double layer and recognized the charge storage at the double layer between an electrode and electrolyte [46, 47]. The practical utilization of the double layer capacitors was proposed in the patent granted to Becker from General Electric Company in 1957 [48]. The patent described an electrolytic capacitor using porous carbon electrodes (Figure 2.1). Later, in 1966, the Standard Oil Company of Ohio (SOHIO) published a different electrolytic capacitor with porous carbon electrodes as “electrical energy storage apparatus” (Figure 2.2) [49]. In this patent it was specifically pointed out that the charges are stored in the electrical double layers. Following this, SOHIO publicized the concept of a disc-shaped double layer capacitor with activated carbon paste electrodes and a nonaqueous electrolyte (Figure 2.3) [50]. The disc-shaped double layer capacitor could reach 2.5 V by replacing aqueous electrolyte with a tetraalkylammonium salt electrolyte in a non-aqueous solvent [51]. The term “supercapacitor” was a brand name for the first commercial double layer capacitor by NEC. Later, supercapacitor is referred to electrochemical devices which behave like a capacitor including EDLCs and pseudocapacitors.
Figure 2.1 The electrolytic capacitor patented by General Electric Company in 1957 [48]. A container 10 is made of suitable insulating materials. Porous carbon electrodes 12 are soaked in the electrolyte 11.

Figure 2.2 The electrolytic capacitor patented by SOHIO in 1966 [49].
Figure 2.3 The electrolytic capacitor patented by SOHIO in 1970 [50]. Gaskets 14 are cemented to electric conducting members 12 to confine activated carbon electrodes 13. Separator 15 is used to prevent the contact between carbon electrodes.

Probably Conway and his colleagues were the first conducting a systematic research on ruthenium dioxide electrochemical capacitors [52]. Conway proposed the name “pseudocapacitance” which had a capacitance 10-100 times of the EDLCs [53].

Since 1980, a number of companies have started producing the EDLCs. These include: Panasonic’s “Gold Capacitor” [54], ELNA’s “Dynacap” [55]. These supercapacitors were low power devices with high internal series resistance (ESR). The first high power “PRI Ultracapacitor” was produced by Pinnacle Research Institute, Inc. (PRI) in 1982. The “PRI Ultracapacitor” incorporated metal-oxide electrodes for military applications [56]. Department of Energy (DOE) lunched a first research/development program on ultracapacitor/supercapacitor in 1989 [57].

Recently, Amatucci et al. [58] fabricated a new type SC called lithium-ion capacitor. A lithium-ion capacitor combines the anode of a double layer capacitor and the cathode of a lithium ion battery. The specific energy of a packaged lithium-ion capacitor
is approximately 20 Wh kg\(^{-1}\) [59], which is at least 4–5 times higher than conventional double layer capacitors.

Today commercial supercapacitors are available from several companies, such as AVX, Cap-XX, Cooper, ELNA, Evans, Ioxus, Maxwell Technologies, NEC and Panasonic. Researchers are paying attention to the development of high energy supercapacitors for electric vehicles.

### 2.2 Principle of supercapacitor

SCs can be classified into electrical double layer capacitors (EDLCs), pseudocapacitors and hybrid capacitors depending on the charge storage mechanisms and active materials [60]. There are two charge storage mechanisms: double layer capacitance and pseudocapacitance [61]. It is well known that two mechanisms are existed in one SC [62]. Generally one mechanism is dominant, the other mechanism is relatively weak. EDLCs exhibit 1-5% of the total capacitance as pseudocapacitance and pseudocapacitors exhibit 5-10% of the total capacitance as double layer capacitance [63]. The comparisons between double layer capacitance and pseudocapacitance are listed as Table 2.1 [61].
Table 2.1 Comparisons between double layer capacitance and pseudocapacitance [61].

<table>
<thead>
<tr>
<th>Double layer Capacitance</th>
<th>Pseudocapacitance</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-Faradaic</td>
<td>Involves Faradaic process(es)</td>
</tr>
<tr>
<td>20-50 μF cm⁻²</td>
<td>2000 μF cm⁻² for single-state process;</td>
</tr>
<tr>
<td></td>
<td>200-500 μF cm⁻² for multi-state, overlapping processes</td>
</tr>
<tr>
<td>C fairly constant with potential, except through the potential of zero charge</td>
<td>C fairly constant with potential for RuO₂; for single-state process, exhibits marked maximum; for multi-state, overlapping processes, can exhibit several maxima, as for H at Pt</td>
</tr>
<tr>
<td>Highly reversible charge/discharge</td>
<td>Quite reversible but has intrinsic electrode-kinetic rate limitation determined by $R_f$</td>
</tr>
<tr>
<td>Has restricted voltage range (contrast non-electrochemical electrostatic capacitor)</td>
<td>Has restricted voltage range</td>
</tr>
<tr>
<td>Exhibits mirror-image voltammograms</td>
<td>Exhibits mirror-image voltammograms</td>
</tr>
</tbody>
</table>

2.2.1 Electrical double layer capacitor (EDLC)

EDLCs store charges by electrochemical adsorption/desorption of ions at the electrode/electrolyte interface using high surface carbon materials. Figure 2.4 is the schematic of an EDLC at the charged (left) and discharged (right) states. As shown in Figure 2.4, an EDLC is composed of two high surface carbon electrodes and a semi-permeable membrane immersed in the electrolyte [64]. The separator prevents electrical short circuit between the electrodes and allows the transport of ions in the electrolyte for
the charging/discharging processes. During charging, the electrons from the negative electrode flow to the positive electrode through an external load. In order to maintain electroneutrality, cations in the electrolyte are attracted to the negative electrode and accumulated at the negative electrode/electrolyte interface to form an electrical double layer (EDL), while anions are attracted to the positive electrode and accumulated at the positive electrode/electrolyte interface to form another EDL. During discharging, cations and anions move back to the electrolyte. The charging and discharging processes can also be expressed as following equations [65, 66]:

On the positive electrode:

\[ E_{\text{pos}} + A^- \leftrightarrow E^+_{\text{pos}} // A^+ + e^- \]  \hspace{1cm} (2.1)

On the negative electrode:

\[ E_{\text{neg}} + C^+ + e^- \leftrightarrow E^+_{\text{neg}} // C^+ \]  \hspace{1cm} (2.2)

The overall reaction:

\[ E_{\text{pos}} + E_{\text{neg}} + C^+ + A^- \leftrightarrow E^+_{\text{pos}} // A^+ + E^+_{\text{neg}} // C^+ \]  \hspace{1cm} (2.3)

where \( E_{\text{pos}}, E_{\text{neg}}, A^-, C^+ \) and \( // \) represent the positive electrode surface, the negative electrode surface, anions, cations and EDL, respectively. Because there is no charge transfer in the charging and discharging processes, charge storage of EDLCs has high reversibility and excellent cycling stability.
Figure 2.4 Schematic of an EDLC at the charged (left) and discharged (right) states [64].

Several theories have been proposed to elucidate the energy storage mechanisms at EDLs over the years. One of the classical models are shown schematically in Figure 2.5 [67]. Helmholtz introduced the concept of double layer by studying the interface between two dissimilar metals in 1853 [68]. Later, in 1879, he described a model about double layer [69]. The Helmholtz model is analogous to the conventional capacitor with two planar electrodes. Two layers of opposite charges are separated at the interface between the electrode and the electrolyte. The thickness of the Helmholtz double layer is approximately equal to the radius of solvated ions [70]. The double layer capacitance $C_{dl}$ is given by the following equation:

$$C_{dl} = \frac{\varepsilon_r \varepsilon_0 A}{d}$$

(2.4)

where $\varepsilon_r$ is the electrolyte dielectric constant, $\varepsilon_0$ is the dielectric constant of the vacuum, $d$ is the charge separation distance and $A$ is the surface area of the electrode. However, thermal motion is not considered in the Helmholtz model [71]. A more complicated model is needed to explain the double layer. In the early 1900s, Gouy [72] and Chapman [73]
developed a diffuse double layer model independently. The double layer capacitance is not constant considering the applied potential and the ion concentration. In the Gouy-Chapman model, the double layer is not compact as Helmholtz's description. The thickness of the diffuse double layer is variable. Mathematical formulation of this model uses the Poisson-Boltzmann (PB) equation to describe the electrochemical potential of ions in the diffuse layer. Ions in the diffuse layer are considered as points charges. In 1924, Stern combined the Helmholtz model and the Gouy-Chapman model [74]. Stern proposed that the compact layer of ions adhere to the electrode is followed by the diffuse layer. Grahame modified Stern in 1947 [75]. Grahame developed a model with three regions: the inner Helmholtz plane (IHP), the outer Helmholtz plane (OHP) and the diffuse layer. The IHP is formed by the centers of specifically absorbed ions. Specifically absorbed ions are ions absorbed without a solvation shell as the ions approach to the electrode. The OHP is formed by the centers of the solvated ions. The double layer capacitance \( C_{dl} \) including Helmholtz double layer capacitance \( C_H \) and diffuse double layer capacitance \( C_{diff} \) is given by the following equation:

\[
\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}} \quad (2.5)
\]

In 1963, Bockris, Devanthan and Muller (BDM) proposed a model with the effect of the solvent near the interface [76]. In the BDM model, the attached molecules of the solvent such as water molecules are present at the surface of the electrode. In the first layer, the dipoles of the attached molecules in the first layer are aligned in a fixed direction due to the charges in the electrode. Some attached molecules may be displaced by specifically adsorbed ions. In the second layer or other layers, the dipoles of the attached molecules are not fixed in one direction. Now the BDM model is most widely used.
EDLCs store more energy than a conventional capacitor with a few angstrom separation distance and high surface area electrode material. Carbon materials are most common electrode materials for EDLCs with the properties including low cost, variety of forms, ease of processability, relatively inert electrochemistry, controllable porosity and electrocatalytic active sites for redox reactions [77]. In this section, several carbon materials for EDLC electrodes are introduced.

Figure 2.5 Models of the electrical double-layer at a negatively charged surface:
(a) Helmholtz model, (b) Gouy-Chapman model, (c) Stern model, and (d) Bockris, Devanathan, and Muller (BDM) model [67].

2.2.1.1 Activated carbons

Activated carbons (ACs) are the commercial active materials in EDLCs due to high surface area and moderate cost. ACs are obtained from physical activation or chemical activation of carbonaceous source materials, such as wood, coal and petroleum pitch. The
porous structure of ACs produced by activation processes consists of micropores (< 2 nm), mesopores (2-50 nm) and macropores (> 50 nm) for having a high specific surface area. The practical specific surface area (SSA) of ACs is in the range of 1000-2000 m² g⁻¹ [78]. Most of the commercial SCs are constructed with activated carbon electrodes and organic electrolyte. The operating voltage is 2.7 V and the specific capacitance is 100-120 F g⁻¹ [79, 80]. However, the capacitance does not match the high surface area of ACs due to existence of small pores which are not accessible by ions [81-83]. Largeot et al. [84] concluded that the double layer capacitance reaches the maximum when the pore size is very close to the ion size. Hence the optimization of the pore size distribution in AC electrode during activation is one of the major research areas.

2.2.1.2 Carbon nanotubes

Carbon nanotubes (CNTs) are produced by the catalytic decomposition of certain hydrocarbon on metal particles [85]. CNTs are categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs). CNTs are considered as the choice of high-power electrode materials due to high electrical conductivity and fully accessible surface area [86]. Moreover, CNTs are excellent supports for active materials because of good mechanical property and open tubular network. However, the fundamental CNT properties are difficult to retain on a macroscopic level [87]. The specific capacitance of purified CNTs (without residual catalyst or other carbon forms) is from 15 to 80 F g⁻¹ with the surface area from 150 to 400 m² g⁻¹ [88].

The specific capacitance can be increased to around 130 F g⁻¹ using subsequent oxidative treatment. The treatment can modify the surface texture of the CNTs and introduce addition surface functionality, which contributes to pseudocapacitance [89].
et al. [90] developed a MWNT-based EDLC, which had an estimated power density of > 8 kW kg\textsuperscript{-1}. The MWNTs were treated with nitric acid and the specific capacitance of the MWNTs was 102 F g\textsuperscript{-1}. Another method to increase the specific capacitance is chemical activation of CNTs with KOH. Frackowial et al. [91] increased the surface area of MWNTs from 430 to 1035 m\textsuperscript{2} g\textsuperscript{-1} by activation with KOH. The specific capacitance increased from 15 (non-activated) to 90 F g\textsuperscript{-1} (after activation). Recently, Bordjiba et al. [92] synthesized a CNT-aerogel composite material with high surface area of 1058 m\textsuperscript{2} g\textsuperscript{-1} and high specific capacitance of 524 F g\textsuperscript{-1}. However, the preparation method was complicated and expensive.

Although EDLCs based on CNTs may offer high power capabilities, the specific energy of the EDLCs are lower than the levels achieved from conventional high surface area carbons.

**2.2.1.3 Graphene**

Graphene is a flat monolayer of tightly packed carbon atoms in a 2D honeycomb lattice [93]. The advantages of graphene are large surface area, high electrical conductivity and very high mechanical strength [94]. Graphene is an excellent candidate electrode material for EDLC. The intrinsic capacitance of the EDL in graphene is 21 µF cm\textsuperscript{-1} [95]. The electrical conductivity of graphene is much higher than other carbon materials and theoretical surface area of a mono-layer is around 2600 m\textsuperscript{2} g\textsuperscript{-1}. Also, both major faces of a graphene sheet are readily accessible by ions in the electrolyte. The specific capacitances of graphene based EDLCs were 75 F g\textsuperscript{-1} in ionic liquid electrolyte [96], 99 F g\textsuperscript{-1} with organic electrolyte and 135 F g\textsuperscript{-1} in aqueous electrolyte [97]. The specific capacitance of reduced graphene with low agglomeration can reach 205 F g\textsuperscript{-1} in aqueous electrolyte [98]. The disadvantage of this material is re-stacking due to the van der Walls interaction
between adjacent sheets [99]. Restacking of graphene sheets can reduce the surface area and lower the energy density of graphene based devices. The composites made of graphene and metal oxides is a solution to avoid the re-stacking of graphene sheets because of the synergistic effect [99]. The specific capacitance of RuO$_2$-graphene hybrid material was reported as 479 F g$^{-1}$ [100]. Most graphene/metal oxide materials are synthesized by mixing or dispersing graphene with inorganic components with graphene simply. The interfacial interaction of graphene/metal oxide materials is poor. Increasing interest should be directed achieve a well-defined uniform structure on graphene.

### 2.2.2 Pseudocapacitor

Pseudocapacitors store charges by electrosorption processes and redox reactions at electrode surfaces [61]. Pseudocapacitors are based on pseudocapacitive electrode materials including conducting metal oxides and conducting polymers [61]. Compared with EDLCs, pseudocapacitors usually provide higher energy density, but have shorter cycle lives and lower charge/discharge rates [101].

There are three types of pseudocapacitance: underpotential deposition, surface redox reaction and quasi-2D intercalation [61, 102], which are shown as Figure 2.6 [103]. Underpotential deposition refers to the electrodeposition of a metal on a foreign metal surface at a potential positive than the Nernst thermodynamic prediction [104]. The classic examples of underpotential deposition are H at Pt [105] and Pb at Au [106]. Surface redox reactions refer to the adsorption of ions onto the surface or near surface of the electrode material accompanied by a faradaic charge-transfer [107]. The examples of the materials with redox pseudocapitance are RuO$_2$, MnO$_2$, NiO and Co$_3$O$_4$. Quasi-2D intercalation is the insertion of ions into the tunnels or layers of a redox-active material accompanied by a
faradaic charge-transfer with no crystallographic phase change. This intercalation process is not limited by the diffusion of ions within the crystalline framework of redox-active materials [108]. Metal oxides are common materials for providing the intercalation pseudocapacitance, such as TiO$_2$, T-Nb$_2$O$_5$.

![Figure 2.6 Three types of pseudocapacitance: a) underpotential deposition, b) surface redox reaction, and c) quasi-2D intercalation [103].](image)

There is always a confusion about the redox reactions in rechargeable batteries and pseudocapacitors. The difference is that the redox reactions in rechargeable batteries is diffusion-controlled and the redox reactions in pseudocapacitors is not diffusion-controlled (capactive) [103, 108]. Cyclic voltammetry (CV) method can judge whether a redox reaction is diffusion-controlled or capactive. In theory, the current $i$ at a fixed potential $V$ related to the sweep rate $v$ obeys the power law [109]:

$$i = a v^b$$  \hspace{1cm} (2.6)
where \( a \) and \( b \) are adjustable parameters. When \( b = 0.5 \), the current is controlled by semi-infinite linear diffusion; when \( b = 1 \), the current is controlled by surface-controlled. On the other hand, some electrode materials exhibit a hybrid charge storage mechanism. Thus the current response \( i \) at a fixed potential \( V \) related to the sweep rate \( v \) can be described as the following equation [110]:

\[
i = k_1 v + k_2 v^{1/2}
\]

By solving for the values of \( k_1 \) and \( k_2 \), it is possible to distinguish the fraction of current arising from diffusion-controlled and that from capacitive effects.

In this section, common pseudocapacitive electrode materials are introduced.

### 2.2.2.1 Metal oxides

Metal oxides as pseudocapacitor electrodes are classified into two groups depending on different pseudocapacitance mechanisms. The first group depends on redox pseudocapacitance and the second group depends on intercalation pseudocapacitance.

**Metal oxides with redox pseudocapacitance**

Ruthenium oxide (RuO\(_2\)) is one of the most explored electrode materials with the advantages: a wide potential window of highly reversible redox reactions, remarkably high specific capacitance, long cycle life and metallic type conductivity and high rate capability [111, 112]. In 1971, the unique electrochemical features of pseudocapacitive processes was first discovered [113]. This study also demonstrated the requirement for a porous and hydrous oxide because the single-crystal materials did not exhibit a rectangular CV (Figure 2.7) [113]. The redox pseudocapacitance of hydrated RuO\(_2\) arise from three oxide states (Ru\(^{2+}\), Ru\(^{3+}\), and Ru\(^{4+}\)) within 1.4 V [52]. The charge storage mechanism of hydrated RuO\(_2\) can be expressed as [114]:
\[ \text{RuO}_x(\text{OH})_y + \delta \text{H}^+ + \delta e^- \leftrightarrow \text{RuO}_{x-\delta}(\text{OH})_{y+\delta} \]  

Specific capacitances of amorphous hydrated RuO\textsubscript{2} (RuO\textsubscript{2}·xH\textsubscript{2}O where x=0.5) was reported as 720 F g\textsuperscript{-1} [115]. Hu et al. [116] achieved the maximal utilization of RuO\textsubscript{2}·xH\textsubscript{2}O with the specific capacitance of 1340 F g\textsuperscript{-1} at 25 mV s\textsuperscript{-1} by a combined improvement in proton exchange and electronic conductivity of electrode materials during the charge storage/delivery processes. Despite the remarkable performance of this material, the high cost of ruthenium prevents Ru-based SCs for practical use.

![Cyclic voltammetry at 40 mV s\textsuperscript{-1} of a RuO\textsubscript{2} thin film (top) and single crystal (bottom) in 1 M HClO\textsubscript{4} [113].](image)

Figure 2.7 Cyclic voltammetry at 40 mV s\textsuperscript{-1} of a RuO\textsubscript{2} thin film (top) and single crystal (bottom) in 1 M HClO\textsubscript{4} [113].
Manganese oxide (MnO$_2$) is an alternative electrode material to RuO$_2$ due to low cost, environmental safety and high theoretical capacitance 1370 F g$^{-1}$ [117]. In 1999, Lee and Goodenough [118] first studied the pseudocapacitive behaviour of MnO$_2$ in a KCl aqueous electrolyte. The specific capacitance was around 200 F g$^{-1}$. Manganese has seven oxidation states including Mn(0), Mn(II), Mn(III), Mn(IV), Mn(V), Mn(VI), and Mn(VII) [119], but only Mn(III)/Mn(II), Mn (IV)/Mn(III), and Mn(VI)/Mn(IV) can provide redox pseudocapacitance [120, 121]. These redox reactions can be expressed as [120, 121]:

$$\text{MnO}_a\text{(OH)}_b + \delta \text{H}^+ + \delta \text{e}^- \leftrightarrow \text{MnO}_{a-\delta}\text{(OH)}_{b+\delta} \quad (2.9)$$

where MnO$_a$(OH)$_b$ and MnO$_{a-\delta}$(OH)$_{b+\delta}$ indicate interfacial MnO$_2$·nH$_2$O under the higher and lower oxidation states, respectively.

In recent years, nickel oxide (NiO) and cobalt oxide (Co$_3$O$_4$) have attracted great interest as pseudocapacitive electrode materials [122]. The theoretical specific capacitance of NiO is 2584 F g$^{-1}$ [123]. The redox reaction of NiO can be written as [124]:

$$\text{NiO} + \text{OH}^- \leftrightarrow \text{NiOOH} + \text{e}^- \quad (2.10)$$

The theoretical specific capacitance of Co$_3$O$_4$ is 3560 F g$^{-1}$ [125]. There are two redox reactions for different cobalt oxidation states [126, 127]:

$$\text{Co}_3\text{O}_4 + \text{OH}^- + \text{H}_2\text{O} \leftrightarrow 3\text{CoOOH} + \text{e}^- \quad (2.11)$$

$$\text{CoOOH} + \text{OH}^- \leftrightarrow \text{CoO}_2 + \text{H}_2\text{O} + \text{e}^- \quad (2.12)$$

However, Thierry et al. [128] presented that Ni or Co-based electrode materials cannot be considered as pseudocapacitive electrode materials. Ni or Co-based electrode materials exhibit a potential dependent charge storage. The specific capacitances of above materials are calculated as an average value over a limited potential window. These materials should be considered as battery electrodes.
Metal oxides with intercalation pseudocapacitance

In 2005, Kavan et al. [129] reported Li\(^+\) intercalation/deintercalation in TiO\(_2\)(B) as pseudocapacitive process. In the CV investigation, the peak current varied linearly with the scan rates \((b = 1)\). The pseudocapacitive intercalation could be due to fast Li\(^+\) transport in the open channels perpendicular to (010) face of TiO\(_2\)(B). Li et al. [130] found the pseudocapacitive Li\(^+\) intercalation in hydrogen titanate nanotubes. The pseudocapacitive intercalation could be ascribed to the open-end and layered scrolling cross-section with a much larger inter-layer spacing than normal lithium intercalation materials. Except for titanium oxides, T-Nb\(_2\)O\(_5\) also displays intercalation pseudocapacitive behaviour with 2D transport pathways and little structural change [131, 132].

Until now, most of the electrode materials with intercalation pseudocapacitance are related to Li\(^+\) intercalation. Unlike surface pseudocapacitance, charge storage in intercalation pseudocapacitance occur in the bulk of electrode materials [108].

2.2.2.2 Conducting polymers

Conducting polymers (CPs) are another major type of electrode materials for pseudocapacitors, including polyacetylene (PA), polypyrrole (PPy), polyaniline (PANI), and poly(3,4-ethylenedioxythiophene) (PEDOT). CPs are considered promising pseudocapacitive electrode materials with the advantages: fast charge–discharge kinetics, low cost, suitable morphology, and fast doping-undoping process [133]. The conductivity of CPs can reach 500 S cm\(^{-1}\) due to the conjugated bonds along the polymer backbone [134]. The pesudocapacitance of CPs arises from the fast and reversible redox processes as following reactions [135]:
where $\text{Cp}$ is conducting polymer, $A^-$ is anion, and $C^+$ is cation. The redox processes in a CP is illustrated as Figure 2.8 [136]. CPs can achieve high specific capacitance because the redox processes occur not only on the surface, but also throughout the entire bulk [137]. For example, a self-crosslinked PANI hydrogel electrode exhibited a specific capacitance of 750 F g$^{-1}$ at 1 A g$^{-1}$ [138]. However, CPs suffer from the large volumetric swelling, shrinkage, and cracking of CPs during charge/discharge (doping/de-doping) processes, which often results in mechanical deterioration of the polymer structure, degradation of electrochemical performance, and rapid decay of capacitance [139]. Compositing with other species [140] and ultrasonic irradiation during production [141] are strategies to achieve long-term cycle stability.

Figure 2.8 A schematic representation of the charging and discharging processes at conducting polymer electrodes associated with (a) p-doping and (b) n-doping [136].
2.2.3 Hybrid capacitor

Hybrid capacitors can achieve high specific power and high specific energy by combining faradaic components and non-faradaic components [142]. There are three types of hybrid capacitors distinguished by their electrode configuration: composite, asymmetric and battery-type hybrid capacitors [143].

Composite hybrid capacitors are typically composed of two identical composite electrodes, including carbon-based materials and pseudocapacitive materials [144]. Asymmetric hybrid capacitors are composed of two different electrodes, one electrode with carbon-based materials and one electrode with pseudocapacitive materials. AC//MnO₂ hybrid capacitor is one type of promising asymmetric hybrid capacitor. An asymmetric AC//MnO₂ hybrid capacitor with K₂SO₄ aqueous electrolyte can reach a specific energy 10 Wh kg⁻¹ reproducibly at a specific power of 3.6 kW kg⁻¹ [145]. Another asymmetric AC//K₂SO₄/MnO₂ hybrid capacitor with MnO₂ nanorods can achieve 17 Wh kg⁻¹ at 2 kW kg⁻¹ [146].

Figure 2.9 Simplified schematic of electrode reactions of a Li-ion capacitor [58].
Battery-type hybrid capacitors are composed of a SC-type electrode and a battery-type electrode. Li-ion hybrid capacitor (Li-ion capacitor) is very promising due to its high specific energy compared with EDLCs and its high specific power compared with batteries [147]. The mechanism of a Li-ion capacitor is shown as Figure 2.9 [58]. In 1999, Amatucci et al. [60] introduced the first Li-ion capacitor with a nanostructured lithium titanate anode and an AC cathode. The first Li-ion capacitor achieved more than 10 Wh kg⁻¹ with good power capability [148]. Following his work, many studies have been conducted on Li-ion capacitors. Fuji Co. [149] proposed a Li-ion capacitor with a pre-lithiated high SSA carbon anode and an activated carbon cathode. Konon et al. [150] utilized a glass-like compound as the anode. Schroeder et al. [151] demonstrated that soft carbon anode can maintain a high capacity of 80 mAh g⁻¹ for more than 10,000 cycles. Krause et al. [152] presented the carbon black as the cathode electrode. Cao et al. [153] reported a Li-ion capacitor with hard carbon/stabilized lithium metal powder (SLMP) anode and carbon cathode (Figure 2.10). The specific energy was 82 Wh kg⁻¹ based on the weight of electrode materials and 25 Wh kg⁻¹ based on the total weight of combined electrodes, separator, electrolyte, and current collectors. Jain et al. [154] fabricated a Li-ion capacitor using pre-lithiated graphite anode and teak wood sawdust derived mesoporous AC cathode with 111 Wh kg⁻¹.
Figure 2.10 A schematic diagram of an activated carbon/SLMP surface applied hard carbon Li-ion capacitor configuration [153].

2.3 Self-discharge

One of the biggest challenges for widespread application of SCs is their intrinsic fast self-discharge rate and short “storage-life” problem [2]. Self-discharge of a SC is a phenomenon of gradual voltage decline and energy loss when the SC is not connected to an electric load or under an open circuit condition [3]. SCs always require frequent charging or a small constant current to keep SCs fully charged. As such, SCs are considered as being not suitable for stand-alone electrical energy storages [3, 4].
2.3.1 Mechanisms

Many researchers have studied the self-discharge mechanisms of SCs. Conway et al. [5] first described three self-discharge mechanisms: 1) decomposition of the SC electrolyte, 2) side reactions of the impurities, and 3) internal ohmic leakage pathways. Three mechanisms refer to activation-controlled Faradiac process, diffusion-controlled Faradiac process and ohmic leakage process.

Activation-controlled mechanism is related to non-diffusion controlled charge leakage process. The voltage $V_t$ at time $t$ is given by [5, 155]:

$$V_t = -\frac{RT}{a_F} \ln \alpha \frac{I_{0}}{C_F} - \frac{RT}{a} \ln \left[ t + \frac{C \tau}{I_{0}} \right]$$  \hspace{1cm} (2.15)

where $R$ is the gas constant, $T$ is temperature, $\alpha$ is the transfer coefficient, $F$ is Faraday’s constant, $I_0$ is the exchange current, and $C$ is the interfacial capacitance. $\tau$ is the integration constant [5, 155]:

$$\tau = \left[ \frac{RT}{aF} \right] \frac{I_0}{I_t}$$  \hspace{1cm} (2.16)

where $I_t$ is the initial polarized current.

Diffusion-controlled mechanism is due to the shuffle effect of some redox impurities, such as Fe$^{2+}$/Fe$^{3+}$ [156]. The voltage $V_t$ at time $t$ is given by [5, 155]:

$$V_t = V_i - \frac{2zFAD^{1/2}n^{1/2}c_0}{c} t^{1/2}$$  \hspace{1cm} (2.17)

where $V_i$ is the initial charging voltage, $z$, $D$ and $c_0$ are the charge, diffusion coefficient and initial concentration of the reacting species, and $A$ is the electrode area.

Ohmic leakage mechanism is most straightforward mechanism. In a SC, there is the possibility of a short circuit between the electrodes. The self-discharge related to this short circuit was modeled by representing a SC with double layer capacitance $C$ in parallel
with a constant equivalent series resistance $R$ [5]. The voltage $V_t$ at time $t$ is given by [5, 155]:

$$\ln \left( \frac{V_t}{V_i} \right) = -\frac{t}{RC} \quad (2.18)$$

Ohmic leakage mechanism is not particularly useful for the SC design exhibiting less self-discharge.

Conway et al. [6, 7] also proposed a charge redistribution mechanism to interpret the potential recovery of RuO$_2$ (Figure 2.11). The potential recovery phenomenon arises from the redistribution of oxidation state of Ru by proton and electron hopping at the near-surface region of RuO$_2$. The processes can be suggested as indicated below [6]:

$$\text{Ru}^{34} \text{(bulk)} + \text{Ru}^{II} \text{(surface)} \rightarrow \text{Ru}^{34} \text{(bulk)} + \text{Ru}^{34} \text{(surface)} \quad (2.19)$$

$$\text{Ru}^{34V} \text{(bulk)} + \text{Ru}^{III} \text{(surface)} \rightarrow \text{Ru}^{34I} \text{(bulk)} + \text{Ru}^{IV} \text{(surface)} \quad (2.20)$$
Figure 2.11 Open-circuit potential-recovery for thermally prepared RuO$_2$ in 0.5 mol dm$^{-3}$ H$_2$SO$_4$ showing (a) successive discharge/potential-recovery cycles for a thick electrode; (b) successive discharge/potential-recovery cycles for a thin electrode [6].

The charge redistribution mechanism is the voltage recovery to a fraction of the initial voltage spontaneously under open circuit condition [157]. Black et al. [8] studied the process of charge redistribution by introducing a hold step during charging of the porous carbon electrodes. As seen from Figure 2.12a, for a carbon electrode charged to 1.0 V, a reduction of self-discharge was observed with the increasing length of the hold step due to a decreasing charge redistribution effect. The charge redistribution effect is related to the porosity of the carbon electrodes. With a hold time of more than 1 h, the reduction of self-discharge became noticeable. In other words, charge redistribution became not obvious. Nevertheless, charge redistribution was still taking place for holding up to tens of hours, even after a very long hold time (> 50 h). To remove charge redistribution, much longer hold times were required. However, for an electrode discharged to 0.0 V, self-discharge related to charge redistribution was not affected by the length of the hold step.
(Figure 2.12b). Two possible reasons are used to explain why the charge redistribution effect takes place in the electrode charged to 1.0 V while the charge redistribution effect does not take place in the electrode discharged to 0.0 V. Generally, the open-circuit potential (OCV) of the carbon electrode is around 0.5 V. The electrode is considered positively charged when the electrode was charged to 1.0 V, the electrode is considered negatively charged when the electrode was discharged to 0.0 V. For positively charged electrode, the charge should be balanced with the anions in the solution. The anions usually are large and less mobile, so the balancing process is suffered from migration limitation. For negatively charged electrode, the charge should be balanced with the cations in the solution which has small size and high mobility. The balancing process is not limited to migration. It is also possible that more charges are present on the carbon electrode surface at 1.0 V compared to 0.0 V. At 0.0 V, there would be almost zero charge on the electrode surface. Therefore, charge redistribution would be minimized.
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Figure 2.12 Self-discharge profile of Spectracarb 2225 in 1.0 M H₂SO₄ with various hold times for an electrode charged to (a) 1.0 V and (b) 0.0 V [8].

Except for the main mechanisms, the initial voltage, temperature, charge process/duration, and short-term history also have an impact on self-discharge rate [9].

2.3.2 Modeling

Modeling of the self-discharge behavior is a challenging task. The mechanisms of self-discharge are multiple, coupled, and not fully understood. At present, there are two categories of modeling: 1) continuum models consisting of partial differential equations and boundary conditions, 2) equivalent circuit models [5, 7-15]. For continuum models, Hao et al. [10] proposed a mathematical model to simulate the self-discharge behavior of EDLCs considering charge movements, side reactions and the instability of electrical double layer. Most modeling regarding to self-discharge have been based on equivalent circuit models. The modeling based on equivalent circuit models originated from a transmission line circuit [158] to describe the porous carbon electrode. Conway and his
group [5, 7, 11] first proposed an equivalent circuit which is consist of a series resistor, a capacitor, and a parallel self-discharge resistor. The self-discharge resistance is a function of cell voltage, time, and charge history [9]. Recently, a three-branch equivalent circuits were proposed by other researchers [12-15]. The three branch model is illustrated as Figure 2.13 [12]. The first branch consists of an EDLC and an immediate capacitance to describe the immediate charging/discharging processes. The second branch and the third branch are mainly for describing the charge redistribution. The three-branch equivalent circuits are equivalent to the method proposed by Kowal et al. [9]. Three time constants were introduced in Kowal’s model. The equation for long-term measurement is given by:

\[
U(t) = a_4 \exp\left(-\frac{t}{\tau_1}\right) + a_2 \exp\left(-\frac{t}{\tau_2}\right) + a_3 \exp\left(-\frac{t}{\tau_3}\right) + a_4 - a_5 t \tag{2.21}
\]

where \(\tau_1, \tau_2\) and \(\tau_3\) are three time constants, \(a_4 - a_5 t\) is linear term. The linear term is only visible in the long-term measurement.

Figure 2.13 Three-branch model for self-discharge process [12].
2.4 Solid-state electrolyte

Energy storage devices such as lithium ion batteries and SCs are powered by liquid electrolytes [60, 159]. The high volatility and flammability of liquid electrolytes can cause serious safety issues in elevated voltage and temperature environment [160]. Solid-state electrolytes can improve the safety of energy storage devices significantly due to wide range of temperatures [161]. Solid state electrolyte are categorized as polymer electrode and superionic conductor [162].

2.4.1 Polymer electrolyte

In 1973, The polymer electrolyte (PE) was first studied by Fenton et al. [163], who discovered the complexion between polyethylene oxide (PEO) and alkali metal salts. A few years later, Armand et al. [164] demonstrated the significant ionic conductivity of the complexes and also proposed its possible application as battery electrolytes. After recognizing the importance of this technology, researchers have paid extensive interest on the development of new PEs for solid-state energy storage devices.

PE has several interesting properties including thin-film forming ability, flexibility, transparency, high ionic conductivity and wide electrochemical window [165, 166]. In a solid-state SC, a PE membrane can act as both electrolyte and separator [108, 167]. The use of PEs can prevent some problems, such as electrolyte leakage, internal shorting, utilization of corrosive solvent, production of harmful gases and the presence of noncombustible reaction products on the electrode surface [168]. In general, PEs are classified into three types based on their physical state and composition: solid polymer electrolyte (SPE), gel polymer electrolyte (GPE), and composite polymer electrolyte (CPE) [169]. The properties and disadvantages for different types of PEs are displayed in Table
The preparation of PEs requires at least one polymer matrix. Common polymers are listed as Table 2.3 [170].

Table 2.2 Comparison between SPE, GPE and CPE [168].

<table>
<thead>
<tr>
<th>Types of PEs</th>
<th>SPE</th>
<th>GPE</th>
<th>CPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Common features</td>
<td>Light-in weight; solvent free; low volatility; low reactivity; good operational safety; high-energy density; good flexibility and easy to process or configure; wide electrochemical window; good chemical, mechanical, photochemical, electrochemical, structural and volumetric stabilities.</td>
<td>High ionic conductivity</td>
<td>High thermal stability; good interfacial contact; high ionic conductivity</td>
</tr>
<tr>
<td>Other properties</td>
<td>High automation process; good mechanical strength</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Disadvantages</td>
<td>Low ionic conductivity at ambient temperature; high interfacial resistance</td>
<td>Poor mechanical strength</td>
<td></td>
</tr>
</tbody>
</table>
Table 2.3 Common polymers with corresponding chemical formulae, glass transition temperatures (T_g) and melting points (T_m) [170].

<table>
<thead>
<tr>
<th>Host polymer</th>
<th>Abbreviation</th>
<th>Repeat unit</th>
<th>T_g(°C)</th>
<th>T_m(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(ethylene oxide)</td>
<td>PEO</td>
<td>−(CH₂CH₂O)n−</td>
<td>-64</td>
<td>65</td>
</tr>
<tr>
<td>Poly(propylene oxide)</td>
<td>PPO</td>
<td>−(CH(CH₃)CH₂O)n−</td>
<td>-60</td>
<td>—a</td>
</tr>
<tr>
<td>Poly(vinylidene fluoride)</td>
<td>PVDF</td>
<td>−(CH₂CF₂)n−</td>
<td>-40</td>
<td>171</td>
</tr>
<tr>
<td>Poly(methyl methacrylate)</td>
<td>PMMA</td>
<td>−(CH₂C(−CH₃)(−COOCH₃))n−</td>
<td>105</td>
<td>—a</td>
</tr>
<tr>
<td>Poly(vinyl chloride)</td>
<td>PVC</td>
<td>−(CH₂CHCl)n−</td>
<td>82</td>
<td>—a</td>
</tr>
<tr>
<td>Poly(acrylonitrile)</td>
<td>PAN</td>
<td>−(CH₂CH(−CN))n−</td>
<td>125</td>
<td>317</td>
</tr>
<tr>
<td>Poly(dimethylsiloxane)</td>
<td>PDMS</td>
<td>−[SiO(−CH₃)₂]n−</td>
<td>-127</td>
<td>-40</td>
</tr>
<tr>
<td>Poly[bis(methoxy ethoxyethoxide)-phosphazene]</td>
<td>PMEP</td>
<td>−[N=P(−O(CH₂CH₂O)₂CH₃)₂]n−</td>
<td>-83</td>
<td>—a</td>
</tr>
</tbody>
</table>

*aAmorphous polymer

2.4.1.1 Solid polymer electrolyte

In SPE, salts are dissolved in the polymer matrix to provide ionic conductivity. Lithium salts are most widely used salts, such as LiClO₄, LiBF₄, LiPF₆, LiAsF₆, LiCF₃SO₃, LiN(CF₃SO₂)₂. The lithium ion mobility in lithium salts and the dissociation constants of lithium salts are shown as followings [171]: LiBF₄ > LiClO₄ > LiPF₆ > LiAsF₆ > LiCF₃SO₃ > LiN(CF₃SO₂)₂ (mobility); LiN(CF₃SO₂)₂ > LiAsF₆ > LiPF₆ > LiClO₄ > LiBF₄ > LiCF₃SO₃ (dissociation constants).
A SPE is an ion-coupled system. The ion transport in SPEs is assisted by the segmental motion of polymer chains in amorphous regions above their glass transition temperature ($T_g$) [172, 173]. Ion transfer in SPEs is dependent on two factors: the proportion of the amorphous phase in the polymer matrix and the $T_g$ [174]. The most commonly method to increase the ionic conductivity in SPEs is the modification of the polymers. The modification of polymers can increase the mobility of the polymer chains by preventing crystallization and reducing the $T_g$ [175, 176]. However, the low ionic conductivity and electrochemical stability [177] exclude SPEs from practical applications.

### 2.4.1.2 Gel polymer electrolyte

Gel polymer electrolytes (GPEs) are prepared by combining a liquid plasticizer and/or solvent into a polymer-salt system. Feuillade et al. [178] first proposed the concept of GPE in 1975 by investigating the process of plasticizing a polymer matrix with an aprotic solution containing an alkali metal salt. The plasticizers can increase the ionic conductivity of PE by dissolving enough charge carriers and providing a mobile medium for the ion transport [179]. Plasticizers including low-molar-mass organics, organic solvents or ionic liquids (ILs) are commonly used [174].

PVDF is a common polymer in GPE. With strong electron-withdrawing functional group (−C−F), PVDF-based GPE can be highly anodic stable. Besides, high dielectric constant ($\varepsilon = 8.4$) of PVDF can help in greater dissociation of lithium salts to provide a high concentration of charge carriers [162]. The first commercial GPE cell was Bellcore/Telecordia technology based on PVDF-hexafluoropropylene (HFP) copolymer electrolyte [180]. Zhang et al. [181] developed a honeycomb-like porous PVDF-HFP GPE membrane. This honeycomb-like porous GPE membrane has several advantages: 1) high
porosity leading to the electrolyte uptake of 86.2 wt%, 2) very high ionic conductivity at room temperature, 1.03 mS cm⁻¹, 3) high thermally stability up to 350 °C, 4) electrochemical stability up to 5 V, and 5) non-combustible in fire. The lithium ion battery with the PVDF-HFP GPE membrane showed high electrochemical performance because of the multi-sizes porous structure of the PVDF-HFP GPE membrane.

ILs, so-called “room temperature molten salts”, have attracted great interest as a plasticizer with several advantages: high chemical and thermal stability, negligible volatility, non-flammability, and high electrochemical stability and hydrophobicity in some cases [182-184]. Passerini et al. [185] first combined room-temperature ILs with PEs to overcome the inherent ionic conductivity limitations of SPEs. The commonly used ILs are N-alkyl-N-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (PYR1ATFSI, A = CₙH₂n+1, with n ranging from 1 to 10) ILs including PYR13TFSI and PYR14TFSI. The ionic conductivity of a PEO/lithium bis(trifluoromethane) sulfonimide (LiTFSI)/PYR13TFSI GPE achieved 10⁻⁴ S cm⁻¹ at ambient temperature, while the ionic conductivity of the IL-free PEO/LiTFSI electrolyte was only 2 × 10⁻⁶ S cm⁻¹ [185]. Hofmann et al. [186] developed a PVDF-HFP based GPE by adding PYR13TFSI IL, organic carbonates, and LiTFSI salt. The ionic conductivity of this GPE was in the magnitude of 10⁻³ S cm⁻¹ at room temperature.

In recent years, novel polymeric lithium salt/IL GPEs have become a new research focus. Cha et al. [187] obtained the novel GPEs comprising polymeric lithium salts including lithium poly(2-acrylamido-2-methylpropanesulfonate) (PAMPSLi) homopolymer and PAMPSLi-polyvinyl fluoride (PVF) copolymer, and ILs including 1-ethyl-3-methylimidazolium tricyanomethanide (EMImTCM) and N,N-dimethyl-N-propyl-
N-butylammonium tricyanomethanide (N1134TCM). The ionic conductivity of the PAMPSLi–PVF/EMImTCM copolymer system was $5.43 \times 10^{-3}$ S cm$^{-1}$ at 25°C while the ionic conductivity of the PAMPSLi/EMImTCM homopolymer system was $1.28 \times 10^{-3}$ S cm$^{-1}$ at 25°C. The ionic conductivity of the PAMPSLi-PVF/EMImTCM GPE ($5.43 \times 10^{-3}$ S cm$^{-1}$) was higher than the ionic conductivity of the PAMPSLi-PVF/N1134TCM GPE ($2.48 \times 10^{-3}$ S cm$^{-1}$).

The applications of GPEs are limited to the poor mechanical strength [188]. The common methods to improve the mechanical properties of GPEs are chemical or physical crosslinking (light radiation [183], thermal radiation [184]) of the system and physically supported by polyolefin membranes such as polyethylene [189] or polypropylene [190]. The most efficient way to improve the mechanical properties of GPEs is the addition of inorganic fillers, which will be discussed in next section.

2.4.1.3 Composite polymer electrolyte

Weston and Steele [191] first proposed the concept of CPEs by incorporating inorganic fillers into PEs. The inorganic fillers such as SiO$_2$, Al$_2$O$_3$, Fe$_3$O$_4$, TiO$_2$ and MgO, leads to an increase in conductivity, mechanical and electrochemical properties [192]. Osińska et al. [193] postulated that a sufficiently ion transport environment can be ensured by thin layers of electrolyte adsorbed on the inorganic filler grain surfaces. Kumar et al. [194] proposed that the ionic conductivity of CPEs are dependent on the blocking and space charge effect, which can cause uncertainty in the ionic conductivity measurement.

Zhu et al. [195] developed a poly(methacrylate) (PMA)/poly(ethylene glycol) (PEG)-LiClO$_4$-3 wt% SiO$_2$ CPE with an optimum ionic conductivity of 0.26 mS cm$^{-1}$ at room temperature. Liu et al. [196] prepared Li$_{0.33}$La$_{0.557}$TiO$_3$ nanowires by electrospinning
and then synthesized a polyacrylonitrile-LiClO$_4$ CPE with 15 wt% Li$_{0.33}$La$_{0.557}$TiO$_3$ nanowire CPE. The ionic conductivity of this novel CPE was $2.4 \times 10^{-4}$ S cm$^{-1}$ at room temperature.

CPEs are suffered from particle agglomeration and phase separation due to the high surface energy of inorganic fillers [197]. Surface modification of inorganic fillers can improve their dispersibility and affinity with organic compounds. Walkowiak et al. [198] reported several surface-modified SiO$_2$ fillers with vinylene, glycidyloxy, mercapto, chloropropyl, octyl, methacryl and amino functional groups. The ionic conductivity of the CPEs with these modified SiO$_2$ fillers magnitude (close to $10^{-2}$ S cm$^{-1}$ at 20°C) was at least two orders of magnitude higher than that of the CPEs with unmodified SiO$_2$. For a CPE with bifunctional (hydrophilic/hydrophobic) SiO$_2$ filler, both the conductivity and the interfacial stability between lithium electrode and the CPE were significantly improved [199]. Li et al. [200] investigated the effects of fluorinated SiO$_2$ fillers on a composite PP nonwoven/PVDF-HFP separator. The separator with fluorinated SiO$_2$ exhibited an improved pore distribution, a high electrolyte uptake of 280 wt%, and a high ionic conductivity of $1.9 \times 10^{-3}$ S cm$^{-1}$.

2.4.2 Superionic conductors

Superionic conductors (SICs) are solid-state ionic conductors with a high level of unipolar ionic conductivity ($\sigma_i > 0.001$ S cm$^{-1}$) [28]. SICs are categorized into three types: the silver halides and chalcogenides with the cation disordered phases, the beta-alumina compounds and the defect-stabilized ceramic oxides [29]. Examples of three types of SICs are shown in Table 2.4 [29].
Table 2.4 Examples of three types of superionic conductors [29].

<table>
<thead>
<tr>
<th>Type of superionic conductors</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silver halides and chalcogenides with the cation disordered phases</td>
<td>$\alpha$-AgI, $\alpha$-CuI, Na2S, $\alpha$-Ag2S, $\alpha$-Cu2Se, Ag3SBr, $\alpha$-Ag2Te, $\alpha$-Ag3S1, Ag4HgSe2I2, $\alpha$-Ag2Se, $\alpha$-Ag3HgI4, RbAg4I5 (Rb → K, Cs, NH4).</td>
</tr>
<tr>
<td>Beta-alumina compounds</td>
<td>A2O·nM2O3</td>
</tr>
<tr>
<td></td>
<td>A = Na, Rb, Ag, K, Li, Tl; M = Al, Ga, Fe3⁺; n = 5-11.</td>
</tr>
<tr>
<td>Defect-stabilized ceramic oxides</td>
<td>CaO·A2O (A = Zr, Hf, Th, Ce); M2O3·ZrO2 (M = La, Sm, Y, Yb, Sc).</td>
</tr>
</tbody>
</table>

2.4.2.1 Rubidium silver iodide

Rubidium silver iodide (RbAg4I5) is a silver ion superionic conductor of the first group which has very high ionic conductivity at room temperature. Bradley and Greene first discovered RbAg4I5 in 1966 by studying the rubidium iodide (RbI) and silver iodide (AgI) phase diagram [201]. The phase diagram is shown as Figure 2.14 [202]. From the phase diagram, two compounds with incongruent melting points were found, RbAg4I5 (228°C) and Rb2AgI3 (298°C). An exceptionally high ionic conductivity at room temperature was found in RbAg4I5. When temperature is lower than 27°C, RbAg4I5 is unstable and decomposes according to the reaction [203]:

$$RbAg4I5 \rightarrow \frac{1}{2} Rb_2AgI_3 + \frac{7}{2} AgI$$  \hspace{1cm} (2.22)
With this reaction, the color of the electrolyte changes from white to yellow. The decomposition rate of RbAg₄I is slow in the absence of moisture. Therefore, a dry atmosphere is required to store RbAg₄I at room temperature.

Figure 2.14 Phase diagram of the Rbl-Agl system [202].
Figure 2.15 Perspective drawing of crystal structure of RbAg$_4$I$_5$ [204].

Owens and Argue reported the highest ionic conductivity of RbAg$_4$I$_5$ at room temperature, 0.26 S cm$^{-1}$ [30]. The structure of RbAg$_4$I$_5$ (Figure 2.15 [204]) accounts for the high ionic conductivity. The crystal structure of RbAg$_4$I$_5$ was studied by Geller [204] and Bradley & Greene [205] in 1967. Geller [204] determined the crystal structure of RbAg$_4$I$_5$ based on single-crystal X-ray diffraction data. The structure is cubic with $a = 11.24$ Å and each unit cell contains four formula units. In a unit cell, four Rb$^+$ ions are surrounded by distorted octahedra of I$^-$ ions. This arrangement provides 56 available sites for sixteen Ag$^+$ ions to diffuse. However, the Ag$^+$ ions are not randomly distributed. On the average, $0.88 \pm 0.30$ Ag$^+$ ions are in one set of 8-fold sites, $9.38 \pm 0.87$ and $5.50 \pm 0.83$ Ag$^+$ ions are in two sets of 24-fold sites. If the Ag$^+$ ions are randomly distributed, the number of the Ag$^+$ ions should be 2.29, 6.86, and 6.86 in the respective sites. The work of Bradley & Greene [205] showed that the structure of RbAg$_4$I$_5$ is also cubic with $a = 11.15$-
There are four Rb\(^+\) ions, sixteen Ag\(^+\) ions and twenty I\(^-\) ions per unit cell. The Rb\(^+\) ions are surrounded by either a distorted trigonal prism of I\(^-\) ions or a distorted octahedron of I\(^-\) ions. There are 72 available sites for sixteen Ag\(^+\) ions to diffuse in the model proposed by Bradley & Greene. The random distribution of the Ag\(^+\) ions give rise to the high conductivity. Argue et al. [206] stated that the conductivity of RbAg\(_4\)I\(_5\) is less than 10\(^{-8}\) S cm\(^{-1}\). This value makes RbAg\(_4\)I\(_5\) as an ideal electrolyte for solid-state batteries. However, the decomposition potential of RbAg\(_4\)I\(_5\) at 25\(^\circ\)C is 0.67 ± 0.01 V [207]. This value limits the utilization of RbAg\(_4\)I\(_5\) as electrolyte of the solid-state batteries.

RbAg\(_4\)I\(_5\) is prepared by melting the mixture of AgI and RbI, and then quenching it. This intermediate product is ground, made into pellets, and annealed at 165\(^\circ\)C for 16 hours [208]. Scrosati et al. [203] prepared the electrolyte using the procedure similar to the above method. The only difference is that the melting and the quenching were processed under vacuum to eliminate the impurities, especially moisture. However, the composition of the final product was not changed and the ionic conductivity of RbAg\(_4\)I\(_5\) was not improved with the vacuum procedure [207]. Scrosati [209] also found that RbAg\(_4\)I\(_5\) can be simply obtained by dissolving the mixture of AgI and RbI in dry acetone.

RbAg\(_4\)I\(_5\) is mostly used as the electrolyte in silver solid-state batteries. Several solid-state batteries utilizing RbAg\(_4\)I\(_5\) as solid electrolyte are introduced in detail as followings.

Argue et al. [206] developed the cell (1): Ag, C, RbAg\(_4\)I\(_5\)/RbAg\(_4\)I\(_5\)/RbI\(_3\), C, RbAg\(_4\)I\(_5\). The addition of carbon and RbAg\(_4\)I\(_5\) to the electrode mixtures is to reduce the contact polarization effect at the electrode-electrolyte interface. The composite electrodes
and the electrolyte were pressed into a one-inch diameter pellet. Three possible cell reactions were proposed [203]:

\[
14 \text{Ag} + 7 \text{RbI}_3 \rightarrow 3 \text{RbAg}_4\text{I}_5 + 2 \text{Rb}_2\text{AgI}_3 (> 27^\circ C) \tag{2.23}
\]

\[
4 \text{Ag} + 2 \text{RbI}_3 \rightarrow 3 \text{AgI} + \text{Rb}_2\text{AgI}_3 (< 27^\circ C) \tag{2.24}
\]

\[
2 \text{Ag} + \text{RbI}_3 \rightarrow 2 \text{AgI} + \text{RbI} \tag{2.25}
\]

Scrosati et al. [207] described the cell (2): \(\text{Ag(Hg)/RbAg}_4\text{I}_5/\text{I}_2\), tetrabutylammonium iodide (TBAI), C. An amalgamated silver anode was used to reduce the contact polarization effect. TBAI in the cathode mixture can retain molecular iodine to prevent tarnishing reactions on the electrolyte when the cell was not operative. In the fabrication process, cathode mixtures including iodine, TBAI and carbon were melted together and spread on the electrolyte uniformly to reduce the contact resistance. The cell structure is shown as Figure 2.16. The cell process is the reaction of silver iodide:

\[
2 \text{Ag} + \text{I}_2 \rightarrow 2 \text{AgI} \tag{2.26}
\]

The OCV of this cell was 0.56 V at 25°C. This cell was considered as a reversible battery. Figure 2.17 showed the first charge/discharge cycle of cell (2) with a constant charge/discharge current of 0.2 mA at 25°C.
Figure 2.16 Cell structure, where a is a PVC container, b is the external contact, c is the amalgamated silver anode, d is the RbAg₄I₅ pellet, and e is the cathodic mixture [207].

Figure 2.17 Charge/discharge first cycle of cell (2) at 0.2 mA constant current and at 25°C [207].

The charging/discharging processes of the cell were studied at 50°C. The cell was charged at 0.6 V and then discharged through 150 ohms load (cycle 1), 1000 ohms load (cycle 2, 3 and 4). At the fifth cycle, the cell was charged at 0.65 V and the following discharging process was unsatisfied. After disconnecting the cell, a dendritic silver
deposition was found in the negative electrode. The failure of the cell was perhaps explained by the decomposition of RbAg₄I₅ at 0.65 V.

In 1970, Takashi and Yamamoto [210] developed the cell (3): Ag/RbAg₄I₅/Te or Ag/RbAg₄I₅/Se. The OCVs of these solid-state cells at 20°C were 0.217 V and 0.265 V, respectively. These cells could work in the temperature range from -75°C to 150°C. Although the OCVs of the solid electrolyte cells with tellurium/selenium cathode are lower than that of the solid-state cells with halogen cathode, the cell of this type can discharge at a high current density of several milliamperes per square centimeter at room temperature.

In 1973, Owens et al. [211] fabricated another solid-state primary cell. The cell (4) was Ag/RbAg₄I₅/tetramethylammonium iodide (Me₄I and Me₄NI₉). In March of 1983, these solid-state batteries were tested after 10 years of storage at temperatures of -15°C and 23°C [212]. The resistances of solid-state batteries with storage at -15°C increased about two orders of magnitude due to the disproportionation reaction of the solid electrolyte. This resistive degradation of the solid-state batteries could be reversed by heating above 27°C. After 20 years of storage, these batteries were tested and still delivered 90% of their initial capacity. The average self-discharge rate was about 0.5% per year because of diffusion of iodine [213].

Base on previous cells, a silver cell (5) realized rechargeability used a typical iodine charge transfer complex cathode: Ag/RbAg₄I₅/I₂-phenothiazine (Ph) [214]. The complete discharge state was assumed to be: Ag/RbAg₄I₅/AgI-Ph. The cycling behavior of cell is shown as Figure 2.18. The cell can be charged and subsequently discharged with a 90% cycling efficiency as Figure 2.18B. However, when the cell was charged and discharged deeply after the initial charge, a deterioration ascribed to the negative electrode of the cell
readily occurs (Figure 2.18C). The deterioration originated from silver dendritic deposition at the electrode/electrolyte interface [215]. Silver could be reversed when the depth of the active silver layer is less than 0.2 µm. When the depth exceeds 0.2 µm, the number of cycles decreases. As a result, the cell could be considered as a secondary battery with shallow cycles (Figure 2.18A).

![Figure 2.18 Cycling behavior of the Ag/RbAg₄I₅/I₂-Ph cell at 25°C [214].](image)

RbAg₄I₅ is also used in solid-state SCs. There are two types of solid-state SCs with RbAg₄I₅, polar and non-polar (Figure 2.19) [216]. A polar solid-state SC was fabricated with a layer of solid electrolyte material composed of RbAg₄I₅, a layer of anode material composed of silver, activated carbon and RbAg₄I₅, and a layer of cathode material composed of activated carbon and RbAg₄I₅. A polar solid-state SC was fabricated with
identical electrodes composed of activated carbon and RbAg₄I₅ and a layer of solid electrolyte material composed of RbAg₄I₅. Non-polar solid-state SCs can prevent or reduce growth of silver dendrites which cause SCs failure by short circuiting the anode and the cathode together. The charge storage of the solid-state SC with RbAg₄I₅ is in the form of both double layer capacitance and pseudocapacitance. When the voltage is between 0.50 V and 0.66 V, a monolayer of iodine is formed by oxidization of RbAg₄I₅ at the carbon/electrolyte interface. The absorbed I₂/I⁻ couple gives rise to the pseudocapacitance. Figure 2.20 is the charging and discharging mechanisms of the pseudocapacitance in a solid-state SC with RbAg₄I₅.

Figure 2.19 The schematic of the solid electrolyte capacitor [216].
Figure 2.20 The charging and discharging mechanisms of the pseudocapacitance in a solid-state SC with RbAg₄I₅ [216].

**2.4.2.2 Rb₄Cu₁₆I₇Cl₁₃**

The discovery of the compound Rb₄Cu₁₆I₇Cl₁₃ was first carried out by Takahashi et al. [217]. Rb₄Cu₁₆I₇Cl₁₃ has the highest ionic conductivity of any solid electrolyte at room temperature. The highest ionic conductivity at room temperature was reported as 0.44 S cm⁻¹ [218]. Compare with RbAg₄I₅, Rb₄Cu₁₆I₇Cl₁₃ is more practical because copper has lower cost and greater availability than silver. However, the decomposition potential of Rb₄Cu₁₆I₇Cl₁₃ is very low. The measured value was 0.67 ± 0.01 V at 22°C [217].

Takahashi et al. [217] prepared Rb₄Cu₁₆I₇Cl₁₃ with following steps. CuCl and CuI were dried under vacuum after recrystallizing in hydrochloric acid and hydroiodic acid, respectively. RbCl was also dried under vacuum at 100°C for several hours. The appropriate quantities of CuCl, CuI, and RbCl were ground, melted, and cooled to room
temperature slowly. Then the intermediate product was ground and made into pellets. The pellets were annealed at 130°C for 17 hours in nitrogen atmosphere. The grinding and annealing processes were repeated until x-ray diffraction results was unchanged. Geller et al. [218] prepared Cu⁺ ion conductor with a different chemical formula RbCu₄Cl₃I₂. A stoichiometric mixture of RbCl, CuCl and CuI to prepare RbCu₄Cl₃I₂ was weighted into a Pyrex test tube. The mixture was melted in vacuum and then quenched to room temperature. the intermediate product was ground and made into pellets. The pellets were annealed at 200°C for 4 hours in nitrogen atmosphere. The pellets were placed in a furnace and annealed at 200°C for 4 hours. After annealing, the pellets were reground in the dry box and were annealed for additional 4 hours.

Geller et al. [218] also studied the structure of RbCu₄Cl₃I₂. The crystal structure of the solid electrolyte RbCu₄Cl₃I₂ is similar to the structure of RbAg₄I₅. The crystal structure of RbCu₄Cl₃I₂ belongs to space group P4₃32 (O6) with lattice constant 10.032 ± 0.003 Å. In RbAg₄I₅, three sets of tetrahedral sites provide a total of 56 sites for the charge carriers. In RbCu₄Cl₃I₂, the distribution of charge carriers is different from that in RbAg₄I₅. The occupancies are almost equal in two sets of 24-fold sites and the occupancies are very low in one set of 8-fold sites. As a result, the overall distribution is nonuniform.

Kanno et al. [219] developed a new rechargeable solid-state battery: CuₓMo₆S₈₋₂y/Rb₄Cu₁₆I₇Cl₁₃/CuₓMo₆S₈₋₂y. The OCV of this solid-state battery was 0.55 V and the discharging current of this solid-state battery could reach several hundreds of microamperes at room temperature. The solid-state battery could be charged and discharged at a current density of 375 µA cm⁻² for more than a thousand cycles without appreciable deterioration.
2.5 Structural Supercapacitor

Current engineering design requires more efficient material utilization and one promising approach is to fabricate multifunctional composite materials. Multifunctional composite materials exhibit at least one additional function such as chemical, mechanical, electrical, thermal, optical, and electromagnetic properties.

Over the years, multifunctional composite materials have been designed for various applications. For example, structural batteries are used in small electric unmanned vehicles (UAVs) to replace conventional structural components [220]. Figure 2.21 is the basic design of a structural battery which is consist of a carbon fiber fabric anode, a fiberglass separator, a metal mesh coated with cathode materials, and a structural solid polymer electrolyte binding the components together [221]. Each component is dual functional. The metal mesh and carbon fibers can act as current collectors and carry mechanical load. The separator provides additional mechanical strength. The polymer electrolyte conducts lithium ions between electrodes and transfers load to other structural components simultaneously.

![Figure 2.21 Concept for a structural battery [221].](image-url)
Another application of multifunctional composite materials is a structural SC which has large power density, high charge/discharge efficiency and long cycle life. Structural SCs can maintain structural integrity easily because electrode materials are not physically destroyed in the charge/discharge process [222]. The concept of structural SCs was first proposed by Luo and Chung [223]. In their work, a structural SC was fabricated with electrodes of carbon fiber and different types of paper, all bonded with epoxy. The maximum capacitance per unit area was reported as 1.23 μF m⁻².

There are two main strategies to fabricate structural energy storage devices. One approach is to embed energy storage devices into conventional fiber-reinforced composites [224]. The other approach is to develop truly multifunctional devices with multifunctional materials [225]. For fabricating a structural SC, two multifunctional components are required: a structural electrode, and a structural electrolyte.

Structural electrodes must have high surface area, good ionically accessibility, high conductivity, thermal stability and chemical stability. Carbon materials are incorporated into the electrodes as electronic conductive additives, supports for active materials, and agents for the control of porosity, surface area and capacitance [226]. For these reasons, carbon materials are well suited as electrode materials for structural SCs. In Luo’s work [223], electrochemical characterization of the thin structure SC was demonstrated while mechanical characterization was not performed. Shirshova et al [227] made another structural SC design (Figure 2.22). The structural SC was fabricated with two structural carbon fiber woven electrodes separated by a woven glass fiber separator, and infused with a multifunctional polymer electrolyte. The structural SC was tested with different polymer electrolytes. The maximum compressive modulus was measured as 40 GPa and the
maximum specific capacitance was measured as 55 mF g\(^{-1}\). The specific capacitance was very low because of low surface area of the electrodes. Therefore, there is a need to increase the surface area of structural carbon fibers without affecting the outstanding mechanical properties. Probstle et al. [228] designed a new multifunctional electrode by embedding in structural carbon fiber fabrics in carbon aerogel (CAG). The volumetric capacitance of the CAG-modified electrodes was above 65 F cm\(^{-3}\) in aqueous electrolyte. The carbon aerogel modification method was compatible with different carbon fiber fabrics. Qian et al. [229] achieved the specific capacitance of 62 F g\(^{-1}\) with the CAG-modified electrodes in 3 M KCl aqueous electrolyte.

Figure 2.22 Configuration for the structural SC designed by Shirshova et al [227].

The structural electrolyte in a structural SC must combine high ionic conductivity and mechanical strength. However, the ionic conductivity and mechanical strength of a structural electrolyte are inversely related [37, 38]. The most effective structural electrolyte is the combination of epoxy and IL [39-41]. Mastumoto et al. prepared various epoxy-based polymers with trimethylammonium bis(trifluoromethanesulfonyl)imide groups. The
highest ionic conductivity was achieved as $1.5 \times 10^{-3}$ S cm$^{-1}$. Shirshova et al. [41] developed a MVR444/MTM57/VTM266 epoxy resin and 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM-TFSI)/LiTFSI structural electrolyte. The optimized ionic conductivity and Young’s modulus was $8 \times 10^{-3}$ S cm$^{-1}$ and 0.18 GPa, respectively.

2.6 Experimental methods

2.6.1 Electrochemical measurements

The three most common methods to characterize SCs are electrochemical impedance spectroscopy (EIS) measurement, CV measurement and galvanostatic charge/discharge (GCD) measurement. Also, self-discharge measurements are essential to evaluate the performance of SCs including OCV measurement and leakage current measurement.

2.6.1.1 Electrochemical impedance spectroscopy

EIS is a tool for characterizing the transient processes in SCs. EIS data is usually measured by applying a small (5-10 mV) alternating voltage and measuring the alternating current [230]. There are two plots to display EIS data; Bode plot and Nyquist plot [231]. In Bode plots, the magnitude and the phase of the impedance are plotted as a function of frequency. The frequency axis is plotted logarithmically because the frequency can range from 0.001 Hz to 100,000 Hz. The magnitude axis is also plotted on a log scale since the magnitude can change by a factor of millions in a simple experiment. In Nyquist plots, the imaginary impedance component is plotted against the real impedance component.
The interpretation of EIS data depends on the equivalent circuit models [63]. According to the equivalent circuit models, the equivalent series resistance (ESR), the charge transfer resistance and the capacitance are calculated from EIS results [232-234]. The ESR is the sum of the resistance of the electrode and the electrolyte [235]. The charge transfer resistance is the resistance against the process of electron transfer from the electrode to the electrolyte at the electrode/electrolyte interface [236]. The ESR and charge transfer resistance are important to evaluate the performance of SCs such as charge/discharge rate and reversibility. However, the calculated capacitances using EIS results are not accurate. Lufrano et al. [237] observed that the difference in measured capacitances by EIS measurements and GCD measurements was around 20%. It is recommended that the capacitances of SCs are calculated through CV measurements and GCD measurements directly.

2.6.1.2 Cyclic Voltammetry

CV is a common technique for electrochemical studies. In a CV test, a constant linear sweeping potential is applied on the working electrode (WE) against the reference electrode (RE) in both forward and reverse directions. The resulting current is measured between the WE and the counter electrode (CE) as a function of time.

CV measurements can be done in two-electrode setup or three-electrode setup [238]. Two-electrode setup is used for investigating the behavior of the whole cell. In two-electrode setup, the WE is connected to the positive side of a SC and the CE and the RE are connected together to the negative side of a SC. For an ideal EDLC, the shape of CV curve is rectangular since the current is independent of the potential. For a pseudocapacitor or a hybrid SC, the shape of CV curve is a distorted rectangular due to the redox reactions.
Three-electrode setup is used for evaluating the electrochemical properties of the electrode materials. In three-electrode setup, the WE is contacted with the electrode material and the CE balances the reaction current occurring at the WE. The RE with a known reduction potential acts as a reference in measuring or controlling the WE’s potential.

2.6.1.3 Galvanostatic charge/discharge

GCD is to charge or discharge a SC within a potential range at constant currents. The voltage is recorded with respect to time. According to GCD results, several important parameters are calculated, including specific capacitance, specific power, specific energy and charge efficiency. The cycle life of the SC is tested using cyclic GCD.

2.6.1.4 Self-discharge

Self-discharge is evaluated using two experimental methods: open-circuit voltage (OCV) measurement and float current (sometimes called the “leakage current”) measurement [11]. OCV measurement evaluates decline of voltage and loss of stored energy of a charged SC when the charged SC electrodes are disconnected from the charging power source. The first step of an OCV measurement is to charge a SC to a desired voltage. The second step is to record the voltage as a function of time when the SC is placed in an open-circuit configuration. In a leakage current measurement, a SC is also charged to a specific potential. A small current from a charging power source to maintain the SC at the specific potential is recorded as a function of time. At the beginning of the leakage current measurement, the leakage current is relatively high. Then the leakage current decreases with time until the leakage current reaches to a steady state. The time for the leakage current transiting from the initial to steady state is the time for charging the SC and charge redistribution. At the steady state, the leakage current is equal to the self-discharge current.
of the SC [239]. There is often a confusion between the leakage current and self-discharge current. In this dissertation, the leakage current refers to the time-dependent current drawn from the external power source to sustain a specific voltage of the SC and the self-discharge current refers to the time-dependent current passing through the self-discharge resistance.

2.6.2 Instrumental characterization methods

Scanning electron microscope (SEM) and X-ray diffraction (XRD) have been applied to characterize the SC materials.

2.6.2.1 Scanning electron microscope

SEM is a powerful technique for the examination and analysis of the microstructure morphology and chemical composition characterizations. SEM produces images of a sample by scanning the surface of the sample with a focused beam of high-energy electrons. The interactions between the electrons and the atoms in the sample produces various signals that contain information including external morphology and chemical composition. The resolution of SEM can achieve better than 1 nm. Samples for SEM are generally mounted to a specimen holder using a conductive adhesive rigidly. For conventional SEM test, samples, at least at the surface, must be electrically conductive and electrically grounded. Nonconductive samples are coated with an ultrathin electrically conducting coating such as gold, platinum and graphite.

2.6.2.2 X-ray diffraction

XRD is a non-destructive analytical technique used for characterizing crystalline materials. XRD provides information on crystal structure, phase, preferred crystal orientation and other structural parameters, such as average grain size, strain and crystal
defects [240]. Also XRD can be used to confirm the existence of residual side reactions in the preparing process [241].
CHAPTER 3 SELF-DISCHARGE OF HYBRID SUPERCAPACITOR WITH GALVANIC CELL MATERIALS

3.1 Theoretical consideration – the equivalent circuits

We used the equivalent circuit modeling approach to analyze the experimental results for evaluating the effects of galvanic cell materials on self-discharge. This was based on Conway’s equivalent circuit [11] and Kowal’s modifications [9]. Self-discharge is often quantitatively evaluated using two experimental methods: 1) the open-circuit voltage (OCV) measurement and 2) the float current (sometimes called the “leakage current”) measurement [11]. The OCV measurement evaluates decline of voltage and loss of stored energy of a charged supercapacitor (SC) when the charged SC electrodes are disconnected from the charging power source. Thus, the first step of an OCV measurement is to charge a SC to a specific voltage $V_{\text{max}}$. The second step is to monitor the OCV decline as a function of time when the SC is disconnected to the power source. In a leakage current measurement, the external current from a charging power source is recorded while maintaining a constant cell voltage $V_{\text{max}}$ [242]. At the beginning of the leakage current measurement, the leakage current is relatively high. Then the leakage current decreases with time until the leakage current reaches to a steady state. The time for the leakage current transiting from the initial to steady state is the time for charging the SC and charge redistribution. At the steady state, the leakage current is equal to the self-discharge current of the SC [239]. There is often a confusion between the leakage current and self-discharge current. In this work, the leakage current refers to the time-dependent current drawn from the external power source to sustain a specific voltage of the SC and the self-discharge current refers to the time-dependent current passing through the self-discharge resistance.
Also, for the hybrid SC designed in this work, there is a requirement that the hybrid SC is operated at a voltage less than the electromotive force (emf) of the galvanic cell components to permit effective mitigation of the self-discharge and short storage-time problem.

3.1.1 Open-circuit voltage measurement

Figure 3.1a is the equivalent circuit of a baseline symmetrical SC without galvanic cell components under the OCV measurement [63]. For a SC, the capacitance is a combination of electrical double layer capacitance and pseudocapacitance. Even for high surface area carbon based SCs, 1-5% of the total capacitance is pseudocapacitance [63]. The self-discharge current of the SC $i_{sd}(t)$ results in the time-dependent discharging currents from the electrical double layer capacitor $i_{dl}(t)$ and from the pseudocapacitor $i_{p}(t)$ leading to reduction of the cell voltage. The OCV of the SC with respect to time is derived as:

$$V_{OCV}(t) = V_{OCV}(0)e^{-\frac{t}{R_{sd}(C_{dl}+C_{p})}}$$  \hspace{1cm} (3.1)

where $V_{OCV}(0)$ is the OCV of the SC at $t = 0$, $R_{sd}$ is the self-discharge resistance, $C_{dl}$ is electrical double layer capacitance, and $C_{p}$ is pseudocapacitance. For simplicity of derivation, $R_{sd}$ was considered as constant in a range of potential or voltage but in fact it is a function of voltage or potential [11]. When $t \to \infty$, the OCV value is

$$V_{OCV}(\infty) = 0$$  \hspace{1cm} (3.2)
Figure 3.1 The equivalent circuits of (a) a SC, (b) a hybrid SC with galvanic cell materials in the OCV measurements and the equivalent circuits of (c) a SC, (d) a hybrid SC with galvanic cell materials in the leakage current measurements.

Figure 3.1b is the equivalent circuit of a hybrid SC with galvanic cell materials in an OCV measurement. The galvanic cell anode, cathode, and electrolyte construct a galvanic cell with emf $\varepsilon_{gc}$. The galvanic cell components continuously generate a time-dependent galvanic cell current $i_{gc}(t)$ through an equivalent resistance $R_{gc}$ of the galvanic
cell and another equivalent series resistance \( R_s \) of the SC to compensate the self-discharge current and the currents passing through \( C_{dl} \) and \( C_p \). The OCV of the hybrid SC with respect to time is given by:

\[
V_{OCV}(t) = \left( V_{OCV}(0) - \frac{R_s + R_{sd}}{R_{gc} + R_s + R_{sd}} \varepsilon_{gc} \right) e^{-\frac{1}{(R_{dl} + R_p)(R_{gc} + R_s + R_{sd})}t} + \frac{R_s + R_{sd}}{R_{gc} + R_s + R_{sd}} \varepsilon_{gc} \tag{3.3}
\]

where \( V_{OCV}(0) \) is the OCV of the hybrid SC at \( t = 0 \). When \( t \to \infty \), the OCV value is

\[
V_{OCV}(\infty) = \frac{R_s + R_{sd}}{R_{gc} + R_s + R_{sd}} \varepsilon_{gc} \tag{3.4}
\]

Equations (3.1) and (3.3) show that the OCV values for the baseline SC and the hybrid SC decrease with time. When \( t \to \infty \), \( V_{OCV} \) approaches to zero for the baseline SC and \( V_{OCV} \) approaches to a constant for the hybrid SC. The OCV of the hybrid SC can stay around a specific value because of the effect of the current generated by the galvanic cell.

### 3.1.2 Leakage current measurement

Figure 3.1c is the equivalent circuit for the baseline SC in a leakage current measurement. A current \( i_{leak}(t) \) or the leakage current from an external direct current (DC) source is applied to compensate the self-discharge current. The constant output voltage of the external DC source is \( V_0 \). The leakage current, \( i_{leak}(t) \) is divided into three components. Two of the components are \( i_{dl}(t) \) and \( i_p(t) \), which are the charging currents passing through \( C_{dl} \) and \( C_p \), respectively. The third component is the self-discharge current \( i_{sd}(t) \). The expression of the leakage current \( i_{leak}(t) \) is derived as:

\[
i_{leak}(t) = \left( i_{leak}(0) - \frac{V_0}{R_s + R_{sd}} \right) e^{-\frac{1}{(R_{dl} + R_p)(R_s + R_{sd})}t} + \frac{V_0}{R_s + R_{sd}} \tag{3.5}
\]

where \( i_{leak}(0) \) is the leakage current of the SC at \( t = 0 \). When \( t \to \infty \), the leakage current is
\begin{equation}
    i_{\text{leak}}(\infty) = \frac{V_0}{R_s + R_{sd}}
\end{equation}

Figure 3.1d is the equivalent circuit of a hybrid SC with galvanic cell materials for the leakage current measurement. \(i_{\text{pc}}(t)\) and \(i_{\text{leak}}(t)\) together compensate the self-discharge current. The leakage current of the hybrid SC with respect to time is given by:

\begin{equation}
    i_{\text{leak}}(t) = \left[ i_{\text{leak}}(0) - \left( \frac{V_0}{R_s + R_{sd}} - \frac{\varepsilon_{gc} - V_0}{R_{ge}} \right) e^{-\frac{1}{(C_{dt} + C_p)(R_s + R_{sd})}t} \right] + \left( \frac{V_0}{R_s + R_{sd}} - \frac{\varepsilon_{gc} - V_0}{R_{ge}} \right)
\end{equation}

where \(i_{\text{leak}}(0)\) is the leakage current of the hybrid SC at \(t = 0\). When \(t \to \infty\), the leakage current is

\begin{equation}
    i_{\text{leak}}(\infty) = \frac{V_0}{R_s + R_{sd}} - \frac{\varepsilon_{gc} - V_0}{R_{ge}}
\end{equation}

From equations (3.5) and (3.7), the values of the leakage current in two equations decrease with time. For the baseline SC, the leakage current \(i_{\text{leak}}(t)\) approaches \(\frac{V_0}{R_s + R_{sd}}\) when \(t \to \infty\). For the hybrid SC, the leakage current \(i_{\text{leak}}(t)\) approaches \(\frac{V_0}{R_s + R_{sd}} - \frac{\varepsilon_{gc} - V_0}{R_{ge}}\) when \(t \to \infty\). Apparently, the leakage current of the hybrid SC is less than the leakage current of the baseline SC at steady state if \(V_0 < \varepsilon_{gc}\). However, the self-discharge currents of the baseline SC and the hybrid SC at the steady state are the same, \(\frac{V_0}{R_s + R_{sd}}\). Therefore, the leakage current fully compensates the self-discharge current for the baseline SC. For the hybrid SC, the leakage current compensates a portion of the self-discharge current. The other portion of the self-discharge current is compensated by the galvanic cell components that generate a current when \(V_0 < \varepsilon_{gc}\).
3.2 Experimental approach

3.2.1 Cell preparation

In the hybrid SC (Figure 3.2b), a copper foil and a zinc foil were used as the current collectors. A polyvinylidene fluoride (PVDF)/lithium trifluoromethanesulfonate (LiTFS) membrane was prepared as the separator of the hybrid SC. According to previous study, a high conductivity and chemical stability [243]. The porous electrodes on top of the current collectors were composed of PVDF, LiTFS, activated carbon and conductive carbon. The electrolyte was 1.5 M zinc sulfate (ZnSO₄) aqueous solution.

3.2.1.1 Preparation of PVDF/LiTFS membrane

PVDF (99.5%, MTI Corporation) powders were added into a glass beaker containing acetone (99.9%, Sigma-Aldrich) and stirred using a Teflon coated magnet stirrer at 60°C until PVDF powder was completely dissolved in acetone. Then LiTFS (99.995%, Sigma-Aldrich) powders were added into the PVDF solution. The mass ratio of LiTFS to PVDF in acetone is 1:1. After stirring for 2 hours, the PVDF/LiTFS in acetone became a translucent gel. The gel was slowly poured on a glass sheet, trimmed using an adjustable film applicator (doctor blade), and dried overnight. The thickness of the PVDF/LiTFS membrane was 40 μm after drying.

3.2.1.2 Preparation of electrodes

PVDF powder was fully dissolved in acetone. Then LiTFS powder, high surface activated carbon (AB-520, MTI Corporation), conductive carbon black (TIMCAL Super C45, MTI Corporation) were successively added into the PVDF solution. The concentrations of PVDF, LiTFS, high surface activated carbon and conductive carbon black are 5%, 10%, 75% and 10%, respectively. After mixing/stirring for 6 hours, the slurry
was applied on carbon papers (Spectracarb 2050A-1050, Fuel Cell Store) using the adjustable film applicator. The coated carbon paper was dried in air for 12 hours. Then the coated carbon paper was cut into 2 cm × 2 cm pieces which were used as electrodes later. The loading mass of each 2 cm × 2 cm electrode after drying was 0.025 g.

### 3.2.1.3 Assembly of the hybrid SC

The PVDF/LiTFS membrane was used as the separator. The separator was immersed in 1.5 M ZnSO₄ (99.0%, Sigma-Aldrich) aqueous electrolyte for 2 minutes. Then the separator was sandwiched between the electrodes. A copper and zinc foil were used as the current collectors. The electrode with a copper foil (99.9%, MTI Corporation) collector was the positive electrode and the electrode with a zinc foil (99%, McMASTER-CARR) collector was the negative electrode. To assemble hybrid SCs, the electrodes and the PVDF/LiTFS membrane containing 1.5 M ZnSO₄ aqueous electrolyte were vacuum sealed in a blue bag. All these assembling steps were carried out in nitrogen atmosphere. A baseline SC (Figure 3.2a) was fabricated with the same steps for fabricating the hybrid SC. Two gold foils (99.9975%, Alfa Aesar) were used to replace copper and zinc foils as the collectors. For sake of convenience, the hybrid SC with copper foil and zinc foil as the collectors is called “CuZn-SC” and the baseline SC with gold foils as the current collectors is called “Au-SC”. Also, a copper-zinc galvanic cell was prepared to evaluate the OCV of the galvanic cell in the ambient environment. A PVDF/LiTFS membrane containing 1.5 M ZnSO₄ aqueous electrolyte was directly sandwiched between a copper foil and zinc foil to construct the copper-zinc galvanic cell.
Figure 3.2 The schematic of (a) a baseline SC assembly using gold foils with the PVDF/LiTFS membrane containing 1.5 M ZnSO₄ aqueous electrolyte; (b) a hybrid SC assembly using copper foil (+) and zinc foil (-) with the PVDF/LiTFS membrane containing 1.5 M ZnSO₄ aqueous electrolyte.

### 3.2.2 Characterization

Electrochemical impedance spectroscopy (EIS) measurements and cyclic voltammetry (CV) measurements of the Au-SC and the CuZn-SC were performed using a Gamry Reference 3000. The frequency range of EIS measurements was from 1 Hz to 100 kHz. In CV measurements, the potential range was from 0.00 V to 1.00 V and the scan rate
was from 2.5 mV s\(^{-1}\) to 100 mV s\(^{-1}\). For three-electrode measurement, a small capillary filled with saturated potassium chloride (KCl) solution and caped with a porous ceramic pin was inserted into the blue bag and located in vicinity of the electrode assembly. The capillary served as a salt bridge between the cell and a silver/silver chloride reference electrode purchased from Gamry Instruments. Galvanostatic charge/discharge (GCD) measurements and cycle life measurements of both SCs were conducted using a Neware CT-4008 system. The charge/discharge specific current was from 0.24 A g\(^{-1}\) to 6.40 A g\(^{-1}\) in GCD measurements and the charge/discharge specific current was 0.24 A g\(^{-1}\) for 2000 cycles in cycle life measurements. The voltage range of GCD measurements and cycle life measurements was between 0.40 V and 1.00 V. The OCV and leakage current measurements of the SCs were carried out using the Gamry Reference 3000. In the OCV measurements, the SCs were pre-charged to 0.90 V with a charging specific current of 0.10 A g\(^{-1}\). The OCVs of the SCs were monitored for 810 hours (~33 days). After 810 hours, the discharging of both SCs was carried out immediately with a discharging specific current of 0.10 A g\(^{-1}\) to evaluate the retention of charge and energy. In the leakage current measurements, the currents for maintaining a voltage of 0.90 V were monitored for 16 hours. All the measurements were carried out at room temperature.

3.3 Results

3.3.1 Electrochemical impedance spectroscopy

Nyquist plots for the Au-SC and the CuZn-SC are shown in Figure 3.3. The data indicate that both SCs show the elements of electric double layer capacitance and pseudocapacitance [63]. Combining the copper-zinc galvanic cell components into a SC
results in an increase in the equivalent series resistance which are the sum of the electrode resistance, the electrolyte resistance, and the contact resistance [235]. Also, the larger semi-circle of the CuZn-SC shows that the charge transfer resistance of the CuZn-SC is greater than that of the Au-SC. The tails of two EIS curves at low frequency represents the semi-finite diffusion of ions in porous electrode materials [63].

![Nyquist plots for the Au-SC (baseline SC) and the CuZn-SC (hybrid SC) from 1 Hz to 100 kHz.](image)

3.3.2 Cyclic voltammetry

The results for three-electrode measurements are given in Figure 3.4a. A two-electrode CV curve obtained under the same condition is given in Figure 3.4b. It was recognized that when the cell is polarized from 0.000 V to 1.000 V, the electrode with Cu
foil was polarized from -0.925 V to about 0.050 V (SSC) and the potential for the electrode with Zn foil varied in a narrow range from -0.975 V to -0.925 V (SSC) or -0.778 to -0.728 V (SHE) close to the standard electrochemical potential for Zn ↔ Zn$^{2+}\text{+2e}^-$. Dissolution of Cu occurred at potential more positive than 0.050 V (SSC) or 0.247 V (SHE). Because the concentration of Cu$^{2+}$ is low, the equilibrium potential of Cu ↔ Cu$^{2+}\text{+2e}^-$ is more negative than the standard electrochemical potential of 0.337 V (SHE). Overall, the two-electrode CV is similar to that for the electrode with Cu foil within current range of -0.004 and 0.004 ampere. Both curves show good charge reversibility.
Figure 3.4 (a) Three-electrode cyclic voltammetry curves for the electrode with Cu foil (red) and the electrode with the Zn foil (grey). (b) The two-electrode cyclic voltammetry curve for the same electrodes under the same condition. The scan rate is 10 mV s\(^{-1}\).

Figure 3.5 illustrates CV curves of the Au-SC and the CuZn-SC with different scanning rates from 2.5 mV s\(^{-1}\) to 100 mV s\(^{-1}\). The specific current increases with the increasing scanning rate. It is well known that an ideal EDLC has rectangular-shaped CV curves. For the Au-SC, the shape of CV curves is close to, but not exactly a perfect rectangular shape. A sign of pseudocapacitance may originate from the electrochemical adsorption and desorption of zinc ions on the surface of activated carbon or Au foils [244]. For the CuZn-SC, the average specific current of the CuZn-SC was greater than that of the Au-SC. At the scanning rate of 2.5 mV s\(^{-1}\), the average specific current of the CuZn-SC and the Au-SC was 0.16 A g\(^{-1}\) and 0.06 A g\(^{-1}\), respectively. Except for the absorption/desorption of zinc ions from the electrolyte and the electrical double layer capacitance, more charges must be stored through the electrochemical reactions of the galvanic cell components in the CuZn-SC. The main electrochemical redox reactions are
1) $Zn^{2+} + 2e^- \leftrightarrow Zn^0$ at the Zn foil and 2) $Cu^{2+} + 2e^- \leftrightarrow Cu^0$ and $2H^+ + 2e^- \leftrightarrow H_2$ at the Cu foil. The asymmetric profile of CV curves is also related to the reversibility of the electrochemical reactions.

According to the CV results, the specific capacitances of the Au-SC and the CuZn-SC with different scanning rates were calculated using the equation [245]:

$$C_{CV} = \frac{\text{Min}(q_a,q_c)}{m\Delta V}$$

(3.9)

where $C_{CV}$ is the specific capacitance calculated from the CV tests, $q_a$ and $q_c$ are the charges of the anodic half cycle and cathodic half cycle, respectively, $m$ is the total mass of the electrodes, $\Delta V$ is the potential range. The calculated specific capacitance values of both SCs are shown as Figure 3.6. The specific capacitance values of the Au-SC are almost constant with respect to the scanning rate, $23.33 \text{ F g}^{-1}$. The specific capacitance of the CuZn-SC was $55.24 \text{ F g}^{-1}$ at $2.5 \text{ mV s}^{-1}$ and the specific capacitance decreased with increasing scanning rate. The specific capacitances of the CuZn-SC were 1-2 times greater than those of the Au-SC because of the redox reactions of the copper-zinc galvanic cell components.
Figure 3.5 Cyclic voltammetry curves of (a) the Au-SC and (b) the CuZn-SC with different scanning rates of 2.5 mV s\(^{-1}\), 5 mV s\(^{-1}\), 10 mV s\(^{-1}\), 25 mV s\(^{-1}\), 50 mV s\(^{-1}\) and 100 mV s\(^{-1}\) between 0.00 V and 1.00 V.

Figure 3.6 Specific capacitance values of the Au-SC and the CuZn-SC with different scanning rates of 2.5 mV s\(^{-1}\), 5 mV s\(^{-1}\), 10 mV s\(^{-1}\), 25 mV s\(^{-1}\), 50 mV s\(^{-1}\) and 100 mV s\(^{-1}\).
3.3.3 Galvanostatic charge/discharge

Figure 3.7 illustrates the GCD curves of the Au-SC and the CuZn-SC with different charge/discharge current densities. The GCD curves of the Au-SC were linear and the GCD curves of the CuZn-SC were also linear except for a sharp drop at the starting moment of the discharging period. The IR drop of the CuZn-SC was considered as a reflection of a greater series resistance and polarization resistance for the CuZn-SC. Specific energy (SE, Wh kg\(^{-1}\)) and specific power (SP, kW kg\(^{-1}\)) were also calculated using the GCD results according to the following equations [246]:

\[
SE = \int VdQ = \frac{I \int_{t=0}^{t+\Delta t} V(t) dt}{m \cdot 3600}
\]

\[
SP = \frac{SE}{\Delta t}
\]

where \(I\) is the discharge current, \(V(t)\) is the voltage as a function of time in the discharge step, \(\Delta t\) is the discharge time and \(m\) is the total mass of the electrodes.

Figure 3.8 is the Ragone plot based on the calculated specific energy values and specific power values from the GCD curves. The maximum specific energy of the CuZn-SC is 4.51 Wh kg\(^{-1}\), which is twice as much as that of the Au-SC. The difference can be contributed to the pseudocapacitance originated from the redox reactions at the Zn and Cu foils. When the specific power is 4.50 kW kg\(^{-1}\), the specific energy of the CuZn-SC is 20% of that of the Au-SC due to 1) mismatching between the slow reaction rates at copper-zinc galvanic cell electrodes and the high current density (6.40 A g\(^{-1}\)) resulting diminished pseudocapacitance and 2) greater IR drop at the high current density resulting diminished discharge energy.
Figure 3.7 Galvanostatic charge/discharge curves of (a) the Au-SC and (b) the CuZn-SC with different specific currents of 0.24 A g$^{-1}$, 0.40 A g$^{-1}$, 0.80 A g$^{-1}$, 1.60 A g$^{-1}$, 3.20 A g$^{-1}$ and 6.40 A g$^{-1}$ between 0.40 V and 1.00 V.
3.3.4 Cycle life

The cycle stability and durability of both SCs were studied using the GCD measurements at a constant specific current, 0.24 A g\(^{-1}\). The specific capacitance values are calculated according to the equation [247]:

\[
C_{GCD} = \frac{I\Delta t}{m\Delta V}
\]  

(3.12)

where \(I\) is the discharge current, \(\Delta t\) is the discharge time, \(m\) is the total mass of the electrodes and \(\Delta V\) is the potential range. Figure 3.9 demonstrates the cycling performance of both SCs. The specific capacitance of the Au-SC remained at 27.84 F g\(^{-1}\) (~96%) after 2000 GCD cycles. This indicates that the Au-SC has a good stability and excellent cyclability. For the CuZn-SC, the specific capacitance value dropped rapidly in first 250 cycles. After 250 cycles, the decrease of the specific capacitance value was slow. At 2000th
cycle, the specific capacitance value was 54.90 F g⁻¹, which was 80% of the initial specific capacitance value but was still 2-fold of that for the Au-SC.

![Graph showing specific capacitance and capacitance retention with cycle numbers for Au-SC and CuZn-SC.](image)

Figure 3.9 (a) Specific capacitance with respect to cycle numbers for the Au-SC and the CuZn-SC with the constant charging/discharging specific current of 0.24 A g⁻¹ between 0.40 V and 1.00 V. (b) Capacitance retention with respect to cycle numbers for the Au-SC and the CuZn-SC.
3.3.5 Self-discharge

3.3.5.1 OCV measurement

Figure 3.10 exhibits the OCV experimental results of the Au-SC and the CuZn-SC. The OCVs of both SCs declined with time. For the Au-SC, the OCV declined rapidly in the first few hours probably because of charge redistribution [7]. Then decay of the OCV became slower. The OCV of the Au-SC was at 0.50 V after 810 hours or 55.6% of the initial voltage was retained. On the other hand, for the CuZn-SC, the OCV declined slightly in the entire voltage monitoring period of 810 hours. The OCV of the CuZn-SC stabilized at around 0.85 V after several days or 94.4% of the initial voltage was retained after one month. The self-discharge rate for the CuZn-SC is much slower than that of the Au-SC due to the continuous compensating current provided by the copper-zinc galvanic components. Figure 3.11 displays the galvanostatic discharge curves of both SCs with the specific current of 0.10 A g⁻¹ right after the OCV measurements (after one month). The CuZn-SC can still work in a good condition without obvious increase of IR drop after one month. The advantage of extremely small loss of energy for this hybrid SC is very desirable for the practical applications that require a long storage-life. The emf of the Cu-Zn galvanic cell was evaluated using the galvanic cell consisting of a Cu foil electrode, Zn foil electrode, and PVDF/LiTFS membrane containing 1.5 M zinc ZnSO₄ aqueous solution. The obtained value was 0.92 V. If the potential of the Zn electrode is controlled by the redox reactions of Zn, which is about -0.76 V vs SHE and the equilibrium potential for the redox reactions of hydrogen is more negative than zero volt (SHE), the potential of the Cu electrode is not controlled only by the redox reaction of hydrogen but by the redox reactions of hydrogen and Cu with a mixed potential.
Figure 3.10 The comparison between the experimental OCV curve and the theoretical OCV curve of (a) the Au-SC and (b) the CuZn-SC for one-month testing.
Figure 3.11 Galvanostatic discharge curves of the Au-SC and the CuZn-SC with the specific current of 0.10 A g⁻¹ after the one-month OCV measurement.

From the experimental OCV results of the Au-SC, the OCV range was 0.50-0.90 V. According to the theoretical model in Section 3.1.1, the derived equations with a single self-discharge resistance are not possible to fit the measured curve with large change of the OCV values during the OCV measurement. Kowal et al. [9] proposed that two or more exponential functions with different time constants had to be used to fit the experimental results of the OCV measurements because the self-discharge resistance were found to be potential-dependent. Considering the length of 810 hours, instead of Eq. (3.1), three exponential functions with three different time constants are used to fit the experimental results as following equations:
\[ V_{OCV}(t) = \alpha V_{OCV}(0)e^{-\frac{t}{R_{sd1}(C_{dl}+C_p)}} + \beta V_{OCV}(0)e^{-\frac{t}{R_{sd2}(C_{dl}+C_p)}} + (1 - \alpha - \beta)V_{OCV}(0)e^{-\frac{t}{R_{sd3}(C_{dl}+C_p)}} \]  

(3.13)

where \( \alpha \) and \( \beta \) are the ratios of contributions of the first and second exponential functions respectively, and \( R_{sd1}, R_{sd2} \) and \( R_{sd3} \) are corresponding self-discharge resistances.

For the Au-SC, the theoretical OCV curve is plotted in Figure 3.10a to fit to the experimental OCV data. The values of parameters in Eq. (3.13) are derived by the curve fitting: \( \alpha = 0.1, \beta = 0.2, R_{sd1} = 3.0 \times 10^4 \Omega, R_{sd2} = 3.5 \times 10^5 \Omega \) and \( R_{sd3} = 9.0 \times 10^6 \Omega \), and \( C_{dl} + C_p \) is a constant 1.256 F, which was defined in the CV tests and \( R_s = 0.26 \Omega \), which was defined by the EIS measurements. It was found that the smaller and medium self-discharge resistances dominated respectively the short and medium time self-discharge behaviors and the larger constant dominated the long-term behavior. Kowal studied long-term self-discharge behaviors of large SCs (600 F) using the modified equivalent circuit model [9]. The self-discharge resistances were found to be 149 \( \Omega \), 990 \( \Omega \), and 10380 \( \Omega \) [9]. If we assume that the electrode area of the SCs is proportional to capacitance and self-discharge resistance is inversely proportional to the electrode area, extrapolation of the self-discharge resistance values for the same area of the Au-SC should give \( R_{sd1} = 7.1 \times 10^4 \Omega, R_{sd2} = 4.7 \times 10^5 \Omega, R_{sd3} = 5.0 \times 10^6 \Omega \). In this sense, the results in Kowal’s work [9] are in consistence with the results of our analysis for the Au-SC in orders of magnitude. For the CuZn-SC, the change of the OCV values during the OCV measurement was small because of the continuous charging by the galvanic cell components in the hybrid SC. Figure 3.10b shows a comparison between the experimental OCV data and the OCV curve fitting (Eq. (3.3)). The curve fitting results give, \( R_{sd1} = \)}
3.0 \times 10^4 \, \Omega, \quad R_{sd2} = 3.5 \times 10^4 \, \Omega, \quad R_{sd3} = 4.0 \times 10^4 \, \Omega, \quad \text{and} \quad \varepsilon_{gc} = 0.92 \, \text{V}, \quad R_s = 0.44 \, \Omega, \quad R_{gc} = 2.5 \times 10^3 \, \Omega, \quad C_{dl} + C_p = 3.15 \, \text{F}. \quad \text{The self-discharge resistances for the SC are similar because of a narrow voltage range (0.05 V) in the long test duration. In fact, an exponential function with one time constant with } R_{sd} = 3.5 \times 10^4 \, \Omega \text{ can fit well to the self-discharge data.}

### 3.3.5.2 Leakage current measurement

Figure 3.12 shows the leakage current experimental results of the Au-SC and the CuZn-SC. The current for both SCs dropped exponentially and then became stable. The stable leakage current density of the Au-SC and the CuZn-SC were 7.34 μA cm\(^{-2}\) and 1.57 μA cm\(^{-2}\), respectively. The CuZn-SC exhibited a better performance in terms of leakage current than the Au-SC. This is in line with the experimental results of the OCV measurements. The difference of the two leakage current density, 5.77 μA cm\(^{-2}\) should approximate the compensating current density from the galvanic cell components.

According to Section 3.1.2, the derived equations with a single self-discharge resistance should fit well to the experimental data because the voltage of the SCs is constant during the leakage current measurements. The theoretical fitting curves according to Eq. (3.5) and Eq. (3.7) and the corresponding experimental data are plotted in Figure 3.12a and Figure 3.12b, respectively. The self-discharge resistances for the Au-SC and the CuZn-SC are 3.5 \times 10^4 \, \Omega \text{ and } 4.5 \times 10^4 \, \Omega, \text{ respectively. The derived self-resistances from the OCV measurements and the leakage measurements are slightly different. The differences between the results for the OCV and leakage current measurements may be due to the different ways of charging/discharging and different voltage range during the OCV and leakage current measurements [9].}
Figure 3.12 The comparison between the experimental leakage current curve and the theoretical leakage current curve of (a) the Au-SC and (b) the CuZn-SC with constant voltage 0.90 V for 16 hours.

3.4 Discussion

From EIS results, the equivalent series resistance of the CuZn-SC was 0.18 Ω greater than that of the Au-SC. This may be due to formation of the oxide layers on the
current collectors (Zn and Cu). The electronic conductivity of the oxide layers are in the magnitude of \(10^{-3} \text{ S cm}^{-1}\) [248, 249], whereas the conductivities of pure Zn and Cu are in the level of \(10^7 \text{ S cm}^{-1}\).

According to the CV results (Figure 3.5 and Figure 3.6), the specific capacitance of the CuZn-SC was 2.5 times greater than that of the Au-SC at 2.5 mV s\(^{-1}\). This indicates that the redox reactions at copper and zinc galvanic cell components in the hybrid SC provide a pseudocapacitance which is 60% of the total capacitance. At 100 mV s\(^{-1}\), the specific capacitance of the CuZn-SC was 1.2 times as much as that of the Au-SC indicating that only 17% of the total capacitance was provided by the redox reactions. The decreasing pseudocapacitance with the increasing scanning rates is due to mismatching between the limited redox reaction rates and the scan rate. The hybrid SC behaves like an EDLC at fast scanning rates and like a hybrid SC at slow scanning rates. This is also confirmed by the GCD results (Figure 3.7) and Ragone plots (Figure 3.8). At a specific charge/discharge current of 0.24 A g\(^{-1}\), the specific energy of the hybrid SC is 50% greater than that of the Au-SC. At specific current greater than 1.60 A g\(^{-1}\) or the specific power is greater than 1.00 kW kg\(^{-1}\) the specific energy of the hybrid SC is almost the same as that of the Au-SC. Above 1.60 A g\(^{-1}\), the specific energy of the hybrid SC is less than that of the Au-SC apparently due to the large IR drop.

The reversibility of the hybrid SC is also assessed with the charge efficiencies (Table 3.1). Generally for a SC, the charge efficiency is greater when the charge/discharge current is smaller. However, for the hybrid SC the charge efficiency is smaller when the charge/discharge current is greater. From the GCD results, it is clear that a significant portion of the charge capacity is provided by the redox reactions at the Zn and Cu foils at
smaller charge/discharge currents. However, this introduces some irreversibility and thereby charge/discharge imbalance. When the charge/discharge current is greater, the redox reactions cannot proceed significantly during the short period and most of charges are stored in the form of EDLC which gives a perfect charge/discharge balance. The critical charge/discharge current is apparently 1.60 A g\(^{-1}\).

Table 3.1 Charge efficiency of the Au-SC and the CuZn-SC with different specific currents, 0.24 A g\(^{-1}\), 0.40 A g\(^{-1}\), 0.80 A g\(^{-1}\), 1.60 A g\(^{-1}\), 3.20 A g\(^{-1}\) and 6.40 A g\(^{-1}\) between 0.40 V and 1.00 V.

<table>
<thead>
<tr>
<th>Charging/discharging specific current (A g(^{-1}))</th>
<th>Au-SC</th>
<th>CuZn-SC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.24</td>
<td>101.61%</td>
<td>90.35%</td>
</tr>
<tr>
<td>0.40</td>
<td>100.00%</td>
<td>93.55%</td>
</tr>
<tr>
<td>0.80</td>
<td>100.00%</td>
<td>96.00%</td>
</tr>
<tr>
<td>1.60</td>
<td>100.00%</td>
<td>100.00%</td>
</tr>
<tr>
<td>3.20</td>
<td>100.00%</td>
<td>100.00%</td>
</tr>
<tr>
<td>6.40</td>
<td>100.00%</td>
<td>100.00%</td>
</tr>
</tbody>
</table>

The self-discharge behaviors of the baseline Au-SC and hybrid CuZn-SC are very different. The OCV of the CuZn-SC can hold at a high level for a long period of time and only one time constant is required to fit the OCV data. Because the micro-current from the galvanic cell components continuously compensates the self-discharge current and hold the OCV at a high level, charge redistribution cannot be completed to the extent as in the
baseline SC. However, the self-discharge resistance and current for the hybrid SC are almost constants which are similar to those of the baseline SC at the initial self-discharge stage (35000 $\Omega$ vs. 30000 $\Omega$). This is not a surprise because the main charge storage material for both SCs is high surface area carbon and the electrolyte is the same for both SCs.

The lifetime of the hybrid SC is also very important. The life-time of the hybrid SC may be limited by corrosion or dissolution of Zn of the galvanic cell, the variation of the composition of the electrolyte, and degradation of carbon materials. Suppose that the lifetime of the hybrid SC is dominated by corrosion of zinc metal in the hybrid SC, the lifetime of the hybrid SC can be evaluated using the following equation [250]:

$$\frac{dl}{dt} = \frac{i_{corr} M_A}{n F \rho}$$

(3.14)

where $\frac{dl}{dt}$ is the corrosion rate in centimeter sec$^{-1}$, n is number of electrons in a redox reaction which is 2 for Zn$^{2+} + 2e^- \leftrightarrow$ Zn, F is Faraday’s constant, $M_A$ is the molecular weight of Zn (65.38 g mol$^{-1}$), $\rho$ is the density of Zn (7.14 g cm$^{-3}$), and $i_{corr}$ is the current density for corrosion (A cm$^{-2}$). According to the leakage current measurements, the self-discharge current density compensated by the galvanic cell is estimated as 5.77 $\mu$A cm$^{-2}$. The corrosion rate for a current of 5.77 $\mu$A cm$^{-2}$ is equivalent to $2.74 \times 10^{-10}$ cm s$^{-1}$ or $0.86 \times 10^{-2}$ cm year$^{-1}$. Since the thickness of the Zn foils is 0.05 cm, the estimated lifetime of a charged hybrid SC (0.85-0.90 V) is 5.8 years or the half lifetime is 2.9 years. If the SC is alternatingly charged and discharged, the lifetime should be longer.
3.5 Conclusion

A hybrid SC with galvanic cell materials is proposed to mitigate the self-discharge problem by providing a micro-current to compensate the self-discharge current. The theoretical equations are derived based on equivalent circuit models. A hybrid SC was fabricated by the carbon electrodes, a PVDF/LiTFS membrane, a copper foil (positive electrode collector) and a zinc foil (negative electrode collector) together. Another SC with gold collectors was also fabricated using the same method and was used as a baseline.

For the hybrid SC with copper and zinc collectors, the maximum specific capacitance was 55.24 F g\(^{-1}\), which is 2.5-fold of that for the SC with gold collectors at 2.5 mV s\(^{-1}\). The maximum specific energy was 4.51 Wh kg\(^{-1}\), which is 1.5-fold of that for the SC with gold collectors when the specific power is 0.10 kW kg\(^{-1}\). When the specific power is 1.00 kW kg\(^{-1}\), the specific energy of the hybrid SC is the same as that of the baseline SC. Redox reactions at Cu and Zn foils enable greater specific capacitance and specific energy at lower specific power. When the charge/discharge rate is greater than 1.60 A g\(^{-1}\) or the specific power is greater than 1.00 kW kg\(^{-1}\), the specific energy of the hybrid SC is less than that of the baseline SC. The hybrid SC showed an acceptable cyclability of 80% voltage retention after 2000 cycles. In the self-discharge measurements, the OCV of the hybrid SC was stable at 0.85 V or 94% of the initial voltage after a month. The leakage current density was as low as 1.57 μA cm\(^{-2}\) and compensating current from the galvanic cell components is 5.77 μA cm\(^{-2}\) at a constant voltage of 0.90 V. The computational results based on the equivalent circuits are in good agreement with the experimental results. The derived self-discharge resistances of the hybrid SCs are similar to or slightly greater than those of the baseline SCs in the early self-discharge stage. The approximate lifetime of a
fully charged hybrid SC with respect to corrosion of the galvanic cell components is 5.8 years, which is acceptable for practical applications.
CHAPTER 4 ALL-SOLID-STATE-SUPERCAPACITOR WITH SILVER SUPERIONIC ELECTROLYTE

A lot of efforts were made to design an all-solid-state supercapacitor (SC) that can work in the ambient environment. With the design in Section 1.3, the device had almost zero capacity. Figure 4.1 is the schematic of a new all-solid-state SC with rubidium silver iodide (RbAg₄I₅) in this work.

![Figure 4.1 The schematic of a new all-solid-state SC with RbAg₄I₅.](image)

4.1 Experimental approach

4.1.1 Preparation of RbAg₄I₅

Silver iodide (AgI) (99.9%, Alfa Aesar) powders and rubidium iodide (RbI) (99.8%, Alfa Aesar) powders were ground and melt together. The molar ratio of AgI to RbI was 4:1. The melt mixture was quenched to room temperature. The crystalline products were ground and annealed at 165°C for 48 hours. After the annealing process, white RbAg₄I₅ powders were obtained by grinding.
4.1.2 Cell preparation

4.1.2.1 Preparation of the electrodes

Two graphite plates (Fuel Cell Store) were cut to 2.0 cm × 1.5 cm × 0.5 cm as current collectors. The graphite plates were covered by heat-shrink tube (McMASTER-CARR) to avoid short-circuit between the electrodes. The tubes were very stable at elevated temperature. 0.25 cm² square area was cut on top surface of each graphite plate. The uncovered square areas of graphite plates were applied by silver conductive adhesive paste (0.025 ohm sq⁻¹, Alfa Aesar). Silver conductive adhesive paste can decrease the contact resistance of the battery compared with silver foil. Then the electrodes are ready for assembly.

In addition, another set of electrodes were prepared using a mixture of Ag paste and high surface activated carbon (AB-520, MTI Corporation). However, with these electrodes, zero charge storage capacity was obtained. Thus, the study was focused on the experimental work using the first set of the electrodes without the high surface activated carbon.

4.1.2.2 Assembly of the cell

Certain amount of rubidium silver iodide powders was applied between the electrodes as the electrolyte. Then the all-solid-state SC was pressed at 500 kg cm⁻² with a clamp. The all-solid-state SC prototype is shown as Figure 4.2. After assembly, the SC was heated at 150°C for overnight to cure the silver conductive adhesive paste.
4.1.3 Characterization

4.1.3.1 RbAg4I5 powders

X-ray diffraction (XRD, Bruker D5000) was used for investigation of the structure of RbAg4I5 powders. The ionic conductivity of RbAg4I5 powders were evaluated using a four-electrode method [251] by electrochemical impedance spectroscopy (EIS) measurement with the frequency range from 1 Hz to 100 kHz. EIS measurement was studied using a Gamry Reference 3000. The schematic of a four-point fixture for the conductivity measurement is illustrated as Figure 4.3. A slot of the bottom rubber was filled with RbAg4I5 powders. The powders were pressed into the slot at 1000 kg cm\(^{-2}\). Then the rubbers were pressed at 1000 kg cm\(^{-2}\) again using a clamp.
4.1.3.2 All-solid-state SC in air and moisture environment

EIS measurements, cyclic voltammetry (CV) measurements, galvanostatic charge/discharge (GCD) measurements, cycle life measurements of the all-solid-state SC were performed using the Gamry Reference 3000. The frequency range of EIS measurements was from 1 Hz to 100 kHz. In CV measurements, the potential range was from 0.0 V to 1.0 V and the scan rate was 2.5 mV s\(^{-1}\). The charge/discharge current density was from 0.4 mA cm\(^{-2}\) to 4.0 mA cm\(^{-2}\) in GCD measurements to get the Ragone plot. The charge/discharge current density was 1.0 mA cm\(^{-2}\) for 250 cycles in cycle life measurements. The voltage range of GCD measurements and cycle life measurements was between 0.0 V and 0.7 V. EIS and CV measurements of the all-solid-state SC were proceeded at cycle 0, 200 and 250, respectively. All the measurements were carried out in air and moisture environment (RH 80%) at room temperature.

Figure 4.3 Schematic of the fixture for a four-point conductivity measurement.

4.1.3.3 All-solid-state SC after 12-hour annealing

There was a very interesting phenomenon that the capacity of the all-solid-state SC got recovered after overnight annealing at 150°C. Cycle life measurements of the all-solid-
state SC were performed again using the Gamry Reference 3000 with current density of 1.0 mA cm$^{-2}$.

4.2 Results

4.2.1 RbAg$_4$I$_5$ powders

4.2.1.1 X-ray diffraction

The XRD spectrum of RbAg$_4$I$_5$ powder is illustrated in Figure 4.4. All the diffraction peaks are indexed. RbAg$_4$I$_5$ powder has a simple cubic structure with a lattice parameter of 1.124 nm at room temperature.

![XRD spectrum of RbAg$_4$I$_5$ powder.](image)

4.2.1.2 Ionic conductivity of RbAg$_4$I$_5$

Figure 4.5 is Bode plot for measuring the ionic conductivity of RbAg$_4$I$_5$. The impedance magnitude was constant, and the phase angle was at zero over the large
frequency range. This means that the system for measuring the conductivity behaves like a pure resistor. The ionic conductivity of RbAg₄I₅ was evaluated using the following equation [252]:

\[
\sigma = \frac{l}{RS}
\]  (4.1)

where \( \sigma \) is the ionic conductivity of RbAg₄I₅, \( l \) is the distance between the silver wires connected with working sense and reference electrode (6 mm), \( R \) is the resistance value at 1 kHz from Bode plot and \( S \) is the cross section of the slot in bottom rubber (0.5 mm²). The calculated value is 0.21 S cm⁻¹, which is consistent with the values in previous papers [203].

Figure 4.5 Bode plot for measuring the ionic conductivity of RbAg₄I₅ using the four-electrode method.
4.2.2 All-solid-state SC in oxygen and moisture environment

4.2.2.1 Electrochemical impedance spectroscopy

Nyquist plots for the all-solid-state SC at different cycles are shown in Figure 4.6. The equivalent series resistance (ESR) is $0.83 \, \Omega$, $4.66 \, \Omega$, and $15.48 \, \Omega$ at cycle 0, 200, and 250, respectively. With the increase of the cycle number, the ESR of the all-solid-state SC increases possibly due to the decomposition of the electrolyte [207].

![Figure 4.6 Nyquist plots for the all-solid-state SC at cycle 0, 200, and 250 from 1 Hz to 100 kHz.](image)

4.2.2.2 Cyclic voltammetry

Figure 4.7 are the CV curves of the all-solid-state SC with scanning rate of 2.5 mV s$^{-1}$ at cycle 0, 200 and 250. The CV curves are irreversible, which are typically battery-type
There are a couple of redox peaks at about 0.4 V and 0.9 V corresponding to the association and dissociation of AgI which is decomposed from RbAg₄I₅ according to Eq. (2.22) [203]. With the increase of the cycle number, the current density increases and then decreases. The maximum current density should be speculated before cycle 200.

Figure 4.7 Cyclic voltammetry curves of the all-solid-state SC with scanning rate of 2.5 mV s⁻¹ at cycle 0, 200 and 250 between 0.0 V and 1.0 V.

4.2.2.3 Galvanostatic charge/discharge

Figure 4.8 illustrates the GCD curves of the all-solid-state SC with different charge/discharge current densities. The GCD curves demonstrate that the behavior of the SC is mainly battery-type and a very small part of the behavior is SC-type. The all-solid-state SC is a hybrid SC. According to the GCD curves, the voltage of charging platform and discharging platform is approximately 0.69 V and 0.63 V. The voltage is very close to
the theoretical value, 0.69 V. The theoretical value depends on the standard electrode potential of the positive electrode (Eq. (1.4)) and the negative electrode (Eq. (1.5)), which is +0.54 V (vs SHE) and -0.15 V (vs SHE), respectively [253].

Figure 4.8 Galvanostatic charge/discharge curves of the all-solid-state SC with different current densities of 0.4 mA cm\(^{-2}\), 1.0 mA cm\(^{-2}\), 2.0 mA cm\(^{-2}\), 3.0 mA cm\(^{-2}\), and 4.0 mA cm\(^{-2}\) between 0.0 V and 0.7 V.

![Figure 4.8 Galvanostatic charge/discharge curves](image)

Figure 4.9 is Ragone plot which is calculated according to Eq. (3.10) and Eq. (3.11). For this all-solid-state SC, it is very special that the electrolyte has dual functions: providing ionic conductivity between electrodes and providing the energy storage. In this case, the mass for calculating Ragone plot is the mass of the electrolyte that participates in the redox reaction. From the Ragone plot, the specific energy can reach 45 Wh kg\(^{-1}\) with the specific power of 0.062 kW kg\(^{-1}\). The maximum specific energy can be over 60 Wh kg\(^{-1}\).
4.2.2.4 Cycle life

The cycle life was studied using the GCD measurements at a constant current density, 1.0 mA cm\(^{-2}\). Figure 4.10 demonstrates the cycling performance of the all-solid-state SCs. The results are consistent with CV results. With the increase of cycle number, the capacity increased then decreased. At cycle 40, the all-solid-state SC reached the maximum capacity, 0.07 mAh.
4.2.3 All-solid-state SC after 12-hour annealing

Figure 4.11 is the comparison of the galvanostatic discharge curves before annealing and after annealing at current density of 1.0 mA cm\(^2\). Obviously, the capacity is recovered after overnight annealing.

The all-solid-state SC was tested for 200 cycles with the current density of 1.0 mA cm\(^2\) after overnight annealing. The cycling performance is shown as Figure 4.12. The trend of the capacity change respect to cycle number is similar. The maximum capacity was even larger after overnight annealing, 0.11 mAh. This capacity recovery can be repeated several times.
Figure 4.11 The comparison of the galvanostatic discharge curves before annealing (red) and after annealing (purple) with current density of 1.0 mA cm$^{-2}$.

Figure 4.12 Cycling performance of the all-solid-state SC with the current density of 1.0 mA cm$^{-2}$ after overnight annealing.
4.3 Discussion

For the all-solid-state SC, the behavior is mainly battery-like. The electrochemical process is related to the electrolyte, RbAg₄I₅. Unlike other types of rechargeable batteries, this all-solid-state battery has a unique feature. In other rechargeable batteries, the charges are mainly stored via chemical reactions of the electrode materials while maintaining the composition of the electrolyte. However, the overall reaction of this all-solid-state battery is as follows:

\[
\text{RbAg}_4\text{I}_5 \leftrightarrow \frac{1}{2}\text{Rb}_2\text{AgI}_3 + \frac{7}{2}\text{Ag} + \frac{7}{2}\text{I}_2
\]  

Electrode materials Ag and C are not included in the reaction during charging. The electrodes materials are just electrical current collectors while in the typical Li-ion batteries the anode will be converted from C into LiC₆ and cathode from Li₁.₂Mn₀.₄Co₀.₄O₂ into Li₀.₁Mn₀.₄Co₀.₄O₁.₆. The electrolyte is not consumed. A small amount of electrolyte is required. In the case of lead-acid batteries, the following reactions proceed during charging:

Cathode reaction: \( \text{PbO}_2 (\text{electrode}) + \text{HSO}_4^- (\text{electrolyte}) + 3\text{H}^+ (\text{electrolyte}) + 2e^- \rightarrow \text{PbSO}_4 (\text{electrode}) + 2\text{H}_2\text{O (electrolyte)} \)  

Anode reaction: \( \text{Pb} (\text{electrode}) + \text{HSO}_4^- (\text{electrolyte}) \rightarrow \text{PbSO}_4 (\text{electrolyte}) + \text{H}^+ (\text{electrolyte}) + 2e^- \)  

Both electrode materials and electrolyte are consumed during charging process. Large amounts of electrode materials and electrolyte are required. Because electrode materials are not consumed, for this all-solid-state battery, only small amounts of the electrolyte materials are required. This provides a possibility of reducing the battery weight.
The electrochemical properties of the all-solid-state battery are the function of cycle number. With the increase of cycle number, the charge capacity of the all-solid-state SC first increases and then decreases. The initial increase of the charge capacity was probably due to a break-in effect as being true for many other electrochemical power sources including fuel cells, Li-ion batteries, and pseudocapacitors. In the break-in process, reaction and mass diffusion paths that were initially absent were created and established by the flux of current and electrochemical reactions. For the reduction of the charge capacity, three explanations are proposed: 1) moisture or oxygen; 2) loss of iodine via diffusion or sublimation; 3) a portion of the reduced iodine does not return back into the lattice of RbAg₄I₅ but remains in the form of AgI. Several verification tests were carried out to understand the reduction of the charge capacity.

For the first explanation, another all-solid-state SC with same configuration was tested in nitrogen atmosphere. Then the all-solid-state SC was taken out immediately and tested in oxygen and moisture environment at room temperature. Figure 4.13 and Figure 4.14 are the comparison of CV curves and GCD curves in nitrogen atmosphere and in oxygen and moisture atmosphere, respectively. The results demonstrate that the SC cannot operate well in nitrogen atmosphere and oxygen and/or moisture is actually essential for a good performance of this all-solid-state SC. Then additional tests were performed to verify the effects of oxygen or moisture or their combination to the performance of the SC. Two all-solid-state SCs with same configuration was first tested in oxygen and moisture environment, and then tested in dry oxygen atmosphere and then in humidified argon atmosphere. Figure 4.15 is the comparison of GCD curves in dry oxygen atmosphere and in humidified oxygen atmosphere. Figure 4.16 is the comparison of GCD curves in
humidified argon atmosphere and in humidified oxygen atmosphere. The SC cannot work well in dry oxygen environment while worked well in in humidified oxygen or argon atmosphere. In conclusion, moisture is very important for the excellent performance of the solid-state SC. Figure 4.17 is the cycling performance of the all-solid-state SC in humidified argon atmosphere.

Figure 4.13 The comparison of cyclic voltammetry curves in nitrogen atmosphere (blue) and in oxygen and moisture atmosphere (red) with scanning rate of 2.5 mV s\(^{-1}\) between 0.0 V and 1.0 V.
Figure 4.14 The comparison of galvanostatic charge/discharge curves in nitrogen atmosphere (blue) and in oxygen and moisture atmosphere (red) with current density of 1.0 mA cm$^{-2}$.

Figure 4.15 The comparison of galvanostatic charge/discharge curves in dry oxygen atmosphere (blue) and in humidified oxygen atmosphere (red) with current density of 0.4 mA cm$^{-2}$.
Figure 4.16 The comparison of galvanostatic charge/discharge curves in humidified argon atmosphere (blue) and in humidified oxygen atmosphere (red) with current density of 0.4 mA cm$^{-2}$.

Figure 4.17 Cycling performance of the all-solid-state SC with the current density of 0.4 mA cm$^{-2}$ in humidified argon atmosphere.
For the second explanation, an all-solid-state SC with an iodine layer as positive electrode was designed (Figure 4.18). The positive electrode was immersed in iodine melt (melting point = 113.7°C) at 130°C for two hours. It was observed that the electrode contained sufficient iodine on surface. However, as shown in Figure 4.19, the cyclability of the device was not improved.

![Figure 4.18 The schematic of an all-solid-state SC with an iodine layer as positive electrode.](image)

![Figure 4.19 Cycling performance of the all-solid-state SC with the current density of 1.0 mA cm⁻². The positive electrode was immersed in melting iodine at 130°C for two hours.](image)
For the third explanation, According the phase diagram (Figure 2.14), the most possible composition of is Rb$_2$AgI$_3$ and β-AgI at room temperature. Because of this reason, the conductivity of the electrolyte will get lower and lower with charge/discharge cycles. This is confirmed by EIS results. With the increase of cycle number, the increase of the ESR is due to conversion of RbAg$_4$I$_5$ into Rb$_2$AgI$_3$, which is less conductive than RbAg$_4$I$_5$ [201]. The decomposition of the electrolyte is responsible for the reduction of charge capacity.

In the cycling measurements, the capacity drops to 16% of the maximum capacity after 200 cycles. However, by an annealing process at 150°C for 12 hours, the charge capacity returned to the previous value. After a few more annealing processes, the charge capacity could not be fully recovered. The possible reason is that Rb$_2$AgI$_3$ and β-AgI produced by the electrochemical cycling are converted into RbAg$_4$I$_5$ in the annealing process. However, the electrolyte could not be fully recovered since some iodine was lost via diffusion or sublimation. When much of electrolyte was lost at the interface areas after several annealing recover cycles, the annealing recovery became ineffective.

For the Ragone plot, the mass used for calculation is the mass of RbAg$_4$I$_5$ powders involved in the redox reaction. The highest specific energy can reach more than 60 Wh kg$^{-1}$ while the specific power is in the same level as lithium-ion battery [254]. The specific power can be improved by decreasing the thickness of the RbAg$_4$I$_5$ layer and the thickness of the electrodes. In this way, the device with RbAg$_4$I$_5$ powders can achieve both high specific power and high specific energy.
4.4 Conclusion

A high power all-solid-state SC with RbAg₄I₅ is proposed and fabricated without sealing. RbAg₄I₅ powders can conduct silver ions between electrodes and provide the energy storage simultaneously. The ionic conductivity of RbAg₄I₅ powders was 0.21 S cm⁻¹. The all-solid-state SC can work in oxygen and moisture environment at room temperature. The all-solid-state SC shows the hybrid SC-like and battery-like behaviors. The maximum specific energy of the all-solid-state SC can reach more than 60 Wh kg⁻¹. With charge/discharge cycles, the charge capacity first increased and then decreased, and the capacity dropped to 16% of the maximum capacity after 200 cycles. The trend of the cycling performance is because of break-in effect and the decomposition of the electrolyte. Also, it was found that moisture is essential for maintaining the excellent performance of the solid-state SC. Another interesting phenomenon of the SC is that the capacity can be recovered by an annealing process at 150°C for 12 hours. The possible reason is that Rb₂AgI₃ and AgI produced in charge/discharge cycles are converted back to RbAg₄I₅ in the annealing process. In current design, the thicknesses of RbAg₄I₅ electrolyte layer and electrodes is not optimized. If the thicknesses can be reduced to a proper value, the device can achieve both high specific power and energy.
5.1 Experimental approach

5.1.1 Cell Preparation

5.1.1.1 Preparation of the epoxy based adhesive polymer electrolyte

Polyvinylidene fluoride (PVDF) (MTI Corporation) was dissolved in tetrahydrofuran (THF, Sigma-Aldrich) and was stirred in a beaker at 80°C until PVDF is fully dissolved in THF. Then lithium trifluoromethanesulfonate (LiTFS) (Sigma-Aldrich) were added to the PVDF solution. After stirring for 1 hour, epoxy resin (#2000, Fibre Glast) and epoxy hardener (#2020, Fibre Glast) was added into PVDF/LiTFS solution resulting in a translucent homogeneous gel. Typically, the mass ratio of epoxy resin and epoxy hardener was 100:23.

5.1.1.2 Preparation of the electrodes

PVDF was added to 1-Methyl-2-pyrrolidinone (NMP, 99.5%, Sigma-Aldrich) and was stirred at 130°C until the solution was transparent. LiTFS, super C45 conductive carbon black (MTI Corporation) and high surface activated carbon (MTI Corporation) were mixed and dissolved in PVDF solution. The concentration of PVDF, LiTFS, C45 and activated carbon is 5%, 10%, 10%, and 75%. The above solution was stirred for 6 hours. The electrodes were dried at 50°C in air for overnight after applying the solution on an aluminum foil (99.9%, MTI Corporation).

5.1.1.3 Assembly of the structural supercapacitor

To assemble a structural SC, two electrodes and the epoxy based adhesive polymer electrolyte were pressed about 20 lb. Then the assembly was sandwiched between carbon
fibers ($2 \times 2$ Twill Weave Carbon Fiber, Fibre Glast) using epoxy. The schematic of a structural SC was illustrated as Figure 5.1. Finally, the structural SC were cured using vacuum bagging method (Figure 5.2) for 12 hours.

Figure 5.1 The schematic of a structural SC with epoxy based adhesive polymer electrolyte.

Figure 5.2 Vacuum bagging method for fabricating a structural SC.
5.1.2 Characterization

This epoxy based polymer electrolyte has two components: epoxy as the structural component and PVDF/LiTFS as the base electrolyte component. Thus the electrochemical properties and mechanical properties of the epoxy based polymer electrolytes depend on the concentration of epoxy and PVDF/LiTFS. In this work, the concentration of epoxy was from 0% to 45% and the mass ratio of PVDF/LiTFS was from 75:25 to 25:75.

5.1.2.1 Electrochemical measurement

The conductivity of epoxy based adhesive polymer electrolytes were tested using four-electrode method [251] by electrochemical impedance spectroscopy (EIS) measurement with the frequency range from 1 Hz to 100 kHz. EIS measurement was studied using a Gamry Reference 3000. The schematic of a four-point fixture for the conductivity measurement is illustrated as Figure 5.3.

![Figure 5.3 Schematic of the four-point fixture for measuring the conductivity of epoxy based adhesive polymer electrolytes.](image)

Based on the results of conductivity measurement, epoxy based adhesive polymer electrolytes with more than $10^{-2}$ S cm$^{-1}$ were selected to make structural SCs. A structural SC is presented in Figure 5.4. EIS measurements, cyclic voltammetry (CV) measurements,
galvanostatic charge/discharge (GCD) measurements of the structural SC were performed using the Gamry Reference 3000. The frequency range of EIS measurements was from 1 Hz to 100 kHz. The potential range was from 0 V to 1 V and the scan rate was 10 mV s\(^{-1}\). The charge/discharge current was from 1 mA to 16 mA in GCD measurements. The voltage range of GCD measurements and cycle life measurements was between 0 V and 1 V.

![Figure 5.4 A structural SC fabricated using vacuum bagging method.](image)

5.1.2.2 Mechanical measurement

The samples for tensile tests are shown in Figure 5.5. A baseline sample was prepared using pure epoxy instead of epoxy based polymer electrolyte. Al foils were cut for convenience. Tension tests were performed using MTS 858 materials testing system (Figure 5.6). The force loading speed was 5000 N min\(^{-1}\).
Figure 5.5 The samples for tension tests.

Figure 5.6 A sample ready for tension test using MTS 858 materials testing system.
5.1.2.3 In-situ electrochemical measurement

CV, GCD measurements of a structural SC were tested under increasing tensile strength until failure. The in-situ measurement is illustrated as Figure 5.7 and Figure 5.8 (Clamped).

![Figure 5.7 In-situ measurement of a structural SC.](image1)

![Figure 5.8 In-situ measurement of a structural SC (Clamped).](image2)
5.2 Results

5.2.1 Conductivity

The conductivity of epoxy based adhesive polymer electrolytes was calculated using the following equation [252]:

$$\sigma = \frac{l}{RS}$$  \hspace{1cm} (5.1)

where $\sigma$ is the conductivity, $l$ is the distance between the platinum wires connected with working sense and reference electrode, $R$ is the resistance and $S$ is the cross section of epoxy based adhesive polymer electrolytes.

The conductivity values of epoxy based adhesive polymer electrolytes with different compositions are displayed in Table 5.1. The conductivity increases with decrease of the concentration of epoxy and with decrease of the mass ratio of PVDF/LiTFS. When the polymer electrolyte is only composed of epoxy and LiTFS, the conductivity is almost constant because lithium ions are hard to diffuse in epoxy.

Table 5.1 The conductivity values of epoxy based adhesive polymer electrolytes with different compositions.

<table>
<thead>
<tr>
<th>PVDF/LiTFS</th>
<th>Epoxy 0%</th>
<th>Epoxy 15%</th>
<th>Epoxy 30%</th>
<th>Epoxy 45%</th>
</tr>
</thead>
<tbody>
<tr>
<td>75:25</td>
<td>9.44\times10^{-3} S cm^{-1}</td>
<td>8.12\times10^{-4} S cm^{-1}</td>
<td>1.39\times10^{-5} S cm^{-1}</td>
<td>1.04\times10^{-7} S cm^{-1}</td>
</tr>
<tr>
<td>50:50</td>
<td>2.89\times10^{-2} S cm^{-1}</td>
<td>6.51\times10^{-3} S cm^{-1}</td>
<td>3.41\times10^{-3} S cm^{-1}</td>
<td>7.39\times10^{-6} S cm^{-1}</td>
</tr>
<tr>
<td>25:75</td>
<td>3.96\times10^{-2} S cm^{-1}</td>
<td>2.48\times10^{-2} S cm^{-1}</td>
<td>1.08\times10^{-2} S cm^{-1}</td>
<td>4.20\times10^{-4} S cm^{-1}</td>
</tr>
</tbody>
</table>
5.2.2 Electrochemical results

In Table 5.1, the conductivities of four compositions are more than $10^{-2}$ S cm$^{-1}$ and two compositions are pure polymer electrolytes. The epoxy based adhesive polymer electrolytes with $2.48 \times 10^{-2}$ S cm$^{-1}$ and $1.08 \times 10^{-2}$ S cm$^{-1}$ were selected to make structural SCs. The sample with higher conductivity electrolyte was S1 and the sample with lower conductivity electrolyte was S2. The loading mass of S1 and S2 was 0.0356 g and 0.0316 g, respectively.

5.2.2.1 Electrochemical impedance spectroscopy

Figure 5.9 shows Nyquist plots for two structural SCs from 1 Hz to 100 kHz. The equivalent series resistance (ESR) of two samples are almost same. The larger semi-circle of S2 demonstrates that the charge transfer resistance of S2 is greater than that of S1.

![Nyquist plots for two structural SCs from 1 Hz to 100 kHz.](image-url)
5.2.2.2 Cyclic voltammetry

CV curves of two samples with scanning rate of 10 mV s\(^{-1}\) are illustrated in Figure 5.10. For S1, the average specific current was greater, and the shape of CV curve was closer to a rectangular shape.

![Cyclic voltammetry curves of two structural SCs with scanning rate of 10 mV s\(^{-1}\) between 0 V and 1 V.](image)

5.2.2.3 Galvanostatic charge/discharge

Figure 5.11 illustrates the GCD curves of two structural SCs with different charge/discharge current. The GCD curves were all linear with a very small IR. The GCD curves of S1 was more symmetric and smaller IR drop due to a lower charge transfer resistance. Figure 5.12 is the Ragone plot calculated from the GCD curves. The maximum specific energy of S1 is 2.64 Wh kg\(^{-1}\), which is 30% more than that of S2.
Figure 5.11 Galvanostatic charge/discharge curves of (a) S1 and (b) S2 with different current of 1 mA, 2 mA, 4 mA, 8 mA, and 16 mA between 0 V and 1 V.
5.2.3 Tension test

As Figure 5.13, the fracture occurred in the middle of the sample. Figure 5.14 is the stress-strain curves for structural SCs with different compositions. The stress-strain curves show typical mechanical behavior of fiber-reinforced polymer composite materials [255]. The stress-strain curves are bilinear prior to the fracture of structural SCs.

Figure 5.12 Ragone plots for S1 and S2.
Figure 5.13 The failure of the structural SC.
Table 5.2 is the relationship between ultimate tension strength (UTS) and the concentration of epoxy. With the increasing concentration of epoxy, the UTS of the structural SC increase. The mechanical properties of the structural SCs are mainly
dependent on mechanical properties of the epoxy. The strength of the structural SCs can be further increased significantly using stronger epoxy. Using a statistical analysis, it was found that the average UTS was 91 MPa with a relative standard deviation of ±24%. The relative standard deviation of the UTS for composite materials fabricated using state-of-the-art processes is typically 10% due to the variations of materials and manufacture processes. In the present experiment, the variations were magnified by the manual process that was adopted in the experiment.

Table 5.2 The relationship between ultimate tension strength and the concentration of epoxy.

<table>
<thead>
<tr>
<th>Epoxy</th>
<th>0%</th>
<th>15%</th>
<th>30%</th>
<th>45%</th>
<th>100%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVDF/LiTFS</td>
<td>75:25</td>
<td>106 MPa</td>
<td>87 MPa</td>
<td>93 MPa</td>
<td>95 MPa</td>
</tr>
<tr>
<td></td>
<td>50:50</td>
<td>136 MPa</td>
<td>97 MPa</td>
<td>117 MPa</td>
<td>70 MPa</td>
</tr>
<tr>
<td></td>
<td>25:75</td>
<td>66 MPa</td>
<td>55 MPa</td>
<td>80 MPa</td>
<td>92 MPa</td>
</tr>
</tbody>
</table>

Toughness is the ability to absorb the energy before fracture. The toughness can be determined by the area of stress-strain curve before fracture. Table 5.3 is the relationship between toughness and the concentration of epoxy. Obviously, the toughness of the baseline structural SC is lower than that of the structural SCs with epoxy concentration 15%, 30%, and 45%. In other words, the structural SCs with epoxy based polymer electrolyte are strong and ductile.
Table 5.3 Toughness values of structural SCs with different epoxy based adhesive polymer electrolytes.

<table>
<thead>
<tr>
<th>Epoxy PVDF/LiTFS</th>
<th>0%</th>
<th>15%</th>
<th>30%</th>
<th>45%</th>
<th>100% No electrolyte</th>
</tr>
</thead>
<tbody>
<tr>
<td>75:25</td>
<td>10.0 MJ m⁻³</td>
<td>11.2 MJ m⁻³</td>
<td>14.2 MJ m⁻³</td>
<td>20.5 MJ m⁻³</td>
<td>6.2 MJ m⁻³</td>
</tr>
<tr>
<td>50:50</td>
<td>5.8 MJ m⁻³</td>
<td>7.6 MJ m⁻³</td>
<td>6.9 MJ m⁻³</td>
<td>12.9 MJ m⁻³</td>
<td></td>
</tr>
<tr>
<td>25:75</td>
<td>12.9 MJ m⁻³</td>
<td>21.3 MJ m⁻³</td>
<td>23.3 MJ m⁻³</td>
<td>15.3 MJ m⁻³</td>
<td></td>
</tr>
</tbody>
</table>

5.2.4 In-situ electrochemical measurement

A structural SC with the same configuration as S1 was tested. Figure 5.15 shows Nyquist plots for the structural SC from 1 Hz to 100 kHz under different tensile stress. The tensile stress was from 0 MPa to 80 MPa. At 80 MPa, the structural SC failed. The ESR and the charge transfer resistance increase with the increasing tensile stress. Figure 5.16 is CV curves of the structural SC with scanning rate of 10 mV s⁻¹ under different tensile stress. Figure 5.17 are Ragone plots of the structural SC under different tensile stress. With the increase of tensile stress, both the average specific current and capacitance in the CV tests increased slightly. GCD tests were also conducted. The results are shown with the Ragone plots (Figure 5.17). The specific energy at a given specific power increased with the applied tensile stress. These data demonstrate that the electrochemical performance of the structural remains the same or increases slightly under an in-plane tensile loading before fracture.
Figure 5.15 Nyquist plots for a structural SC from 1 Hz to 100 kHz under different tensile stress.

Figure 5.16 Cyclic voltammetry curves of a structural SC with scanning rate of 10 mV s\(^{-1}\) between 0 V and 1 V under different tensile stress.
5.3 Discussion

According to EIS, CV and GCD results, the structural SC with 15\% epoxy polymer electrolyte shows better electrochemical performance than that with 30\% epoxy polymer electrolyte. In other words, the structural SC fabricated using adhesive polymer electrolyte with a higher conductivity exhibits better electrochemical performance.

In Shirshova’s [227] review on different structural SCs, the maximum specific power and specific energy was 0.09 kW kg\(^{-1}\) and 0.01 Wh kg\(^{-1}\), respectively. For the structural SCs with epoxy based polymer electrolyte in this work, the specific power is 0.01-0.19 kW kg\(^{-1}\) and the specific energy is 0.78-2.64 Wh kg\(^{-1}\). According to Eq. (1.1), the maximum specific power can be calculated as 6.69 kW kg\(^{-1}\), 7.83 kW kg\(^{-1}\) for S1 and S2, respectively. The estimated maximum specific energy is 3.00-5.00 Wh kg\(^{-1}\). The results in this work prove that this epoxy based polymer electrolyte developed in the present work is a promising candidate adhesive polymer electrolyte for structural SCs.

Figure 5.17 Ragone plots of a structural SC under different tensile stress
For mechanical properties, the strength of the structural SCs in this work is acceptable. For example, the specific tensile strengths of carbon steel, Ti, and Cu are respectively, 46.4, 76.0, and 24.7 kN m kg\(^{-1}\). That for the structural SC taking 80 MPa and 2.0 g cm\(^{-3}\) is 40.0 kN m kg\(^{-1}\). The mechanical strength of the carbon fiber reinforced structural SCs mainly depends on the epoxies [36]. One of interesting directions for future study is to use high strength epoxies to improve the mechanical strength.

For in-situ electrochemical measurement, the electrochemical performance increases slightly. When the SC is subjected to an in-plane tensile stress, the thickness of the SC decreases. This improves the contact between current collectors, active materials layers, and electrolyte layer thereby slightly reducing the ESR according and improving the specific power according to Eq. (1.1). This explanation is confirmed by EIS results (Figure 5.15).

### 5.4 Conclusion

Epoxi based adhesive polymer electrolyte was prepared using PVDF, LiTFS and epoxy. The conductivity of the epoxy based adhesive polymer electrolyte is in the magnitude of 10\(^{-2}\) S cm\(^{-1}\) when the concentration of epoxy resin is less than 30%. Structural SCs were fabricated using the epoxy based adhesive polymer electrolyte with a vacuum bagging method. The maximum specific energy is achieved as 2.64 Wh kg\(^{-1}\). Considering the conductivity of epoxy based adhesive polymer electrolyte, the largest UTS of the structural SC can reach 80 MPa while the UTS of the baseline structural SC is 112 MPa. The strength of the structural SCs can be improved significantly using a stronger epoxy.
The response of electrochemical performance of the structural SCs to in-plane tensile stress was studied. Before fracture, the specific power and energy increases slightly.
REFERENCES


