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Advancing Li/CFX Battery Chemistry: A Study On Partially Reduced CFx As A Primary Li/CFx Cell Cathode Material

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ADVANCING Li/CFx BATTERY CHEMISTRY: A STUDY ON PARTIALLY
REDUCED CFx AS A PRIMARY Li/CFx CELL CATHODE MATERIAL

By

Martin Mathews

A Thesis
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Chemistry
in Chemistry
in the Department of Chemistry

Mississippi State, Mississippi

December 2011
Conventional primary Li/CFx batteries employ graphite and polyvinylidene fluoride additives in the cathodes. These additives usher in some un-desired side-effects, such as lower battery capacities (mAh/g) and smaller current densities (mA/g).

An innovative pretreatment was developed in this research in which CFx was subject to a “solvated electron” reduction to obtain a thin layer graphitic carbon coating on the CFx particle surfaces. Resistivity tests revealed that these partially reduced CFx particles have a higher conductivity at comparable graphitic carbon contents. Electrochemical discharge reactions demonstrated that batteries made from the reduced CFx were superior to the conventional batteries with higher current densities and higher capacities achieved. Impedance spectroscopy (EIS) studies found out that the reduced CFx particles have smaller cell reaction resistances, smaller double layer/intercalation capacitances and smaller mass transport resistances.
It appears that use of reduced CFx has the potential to replace the conventional CFx plus additives as a cathode material in Li/CFx batteries.

Keywords: Primary lithium/CFx battery, cathode material, electrochemical impedance spectroscopy, core-shell morphology, solvated electron reduction.
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<td>PVDF</td>
<td>Polyvinylidene fluoride</td>
</tr>
<tr>
<td>RCF</td>
<td>Reduced CFx</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>NMP</td>
<td>N-Methylpyrrolidine</td>
</tr>
<tr>
<td>PSI</td>
<td>Pound per square inch</td>
</tr>
<tr>
<td>FITC</td>
<td>Fluorescein isothiocyanate</td>
</tr>
<tr>
<td>DMF</td>
<td>N,N-Dimethyl formamide</td>
</tr>
<tr>
<td>DIPEA</td>
<td>N,N-Diisopropylethylamine</td>
</tr>
<tr>
<td>HOBt</td>
<td>1-Hydroxybenzotriazole hydrate</td>
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<tr>
<td>RAMRCF</td>
<td>Rhodamine B-mixed reduced CFx</td>
</tr>
<tr>
<td>FARCF</td>
<td>FITC-grafted reduced CFx</td>
</tr>
<tr>
<td>FMRCF</td>
<td>FITC-mixed reduced CFx</td>
</tr>
<tr>
<td>OCV</td>
<td>Open circuit voltage</td>
</tr>
<tr>
<td>UVW</td>
<td>Upper voltage window</td>
</tr>
<tr>
<td>DOD</td>
<td>Depth of discharge</td>
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<tr>
<td>GIC</td>
<td>Graphite intercalation compound</td>
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AC  Alternating current
CPE  Constant phase element
XPS  X-ray photoelectron spectroscopy
CHAPTER I

INTRODUCTION

1.1 Introduction to batteries

An electric battery by definition is an electrochemical device that can convert stored chemical energy into electrical energy through a discharge reaction.

The history of early batteries can be traced back to Biblical times when Baghdad batteries (a copper foil and an iron rod inside a clay pot) were possibly used for electrical plating [1], or to an even earlier time when an Egyptian relief depicted a light-bulb like device in an ancient Pharaoh’s tomb [2]. Modern batteries came into existence from the Italian scientist Alessandro Volta who in 1800 invented a device which was made of a pile of alternating pairs of two different type metal discs with brine-soaked cloth sandwiched in between [3]. This was the very first electrochemical battery created after many years of systematic study and accumulation of knowledge on electricity that could provide a reliable source of current. This opened a new field of science for exploration and venture which added to the benefit of human beings. Eventually the whole world was ‘lit up’ and connected.
1.2 Battery composition and principles

An electrical battery in principle is composed of two electrodes (an anode and a cathode), a separator, and an electrolyte solution, as depicted in Figure 1.1.

![Battery Diagram](image)

Figure 1.1 A schematic representation of a battery.

Electrodes are two electrochemically different materials with different electromotive forces (potentials) that can drive an electric current across the circuitry; they are separated by a separator to prevent them from contacting each other, but they are electrically connected by an ion-carrying electrolyte solution that enables ions to flow freely in between. In a redox reaction powered battery, an oxidative reaction takes place at the anode (negative) electrode. An anode atom can lose an electron and becomes a positively charged ion (cation). At the cathode (positive) electrode, a reductive reaction takes place. A cathode atom can gain an electron and becomes a negatively charged ion (anion). A wire physically connects the two electrodes through a load outside of the battery allowing electrons to flow from anode to cathode; in the electrolyte both cations and anions migrate towards the oppositely charged electrode to finish the circuitry.
Therefore, the energy stored in the form of chemical bonds is converted to the electrical energy via a redox reaction inside a battery and delivered to the workload outside.

1.3 Types of batteries

Basically there are two broad types of batteries: primary (non-rechargeable) and secondary (rechargeable). Primary batteries are often used for low current demands, in an intermittent application, or as an emergency backup resource. Secondary batteries are often used for high current demands, and in frequent daily applications.

A primary battery can only be used once and is discarded after discharge; the redox reaction that involves two species is irreversible. When the initial supply of electrode materials are spent, the battery reaches its end and it is not designed to be reused.

A secondary battery can be recharged after discharge and then reused. Often, there is only one species is involved in the redox reaction. When recharging, an external electric force is connected to drive the battery in the direction opposite to discharge. Neutral atoms in the anode electrode become cations by losing electrons and these cations migrate into the electrolyte solution. At the cathode, these cations capture electrons from the external source and become electrically neutral, intercalating the metal into the cathode (in the case of Li/carbon system). Thus, the power of the original battery is restored; the battery is then recharged.
1.4 Li/CFx primary batteries

1.4.1 Introduction

There are many types of primary batteries in terms of electrode material choice, electrolytic composition, heat-dissipation design, power output (voltage times current), energy density, shelf life (determined by self discharging rate), safety regulation, etc. [4] Lithium/graphite monofluoride (Li/CFx) batteries with an optimum redox system stand out currently as the most powerful, most compact electric current supplier over other designs like Li/MnO2 or Li/SOCl2 [5]. These contain lithium - the lightest metal - anodes and also low density CFx cathodes.

A Li/CFx battery uses lithium metal as the anode, graphite monofluoride CFx (x ≈ 1) as the cathode, and an electrolyte made of lithium salt (LiBF4) dissolved in organic solvents (like propylene carbonate/1,2-dimethoxyethane). It can deliver a voltage of ~ 3.1 volts, about twice that which traditional alkaline batteries can supply. It is a safe, reliable source of electric current. Since its invention in 1970s by Matsushita (Panasonic) Corp. [6], it has found a wide variety of applications in many fields ranging from celestial, marine, military to medical devices. It is often used in small consumer products of low power demand such as portable electronic devices. Its chemical reactions can be described as:

At the anode: \( \text{Li} \rightarrow \text{Li}^+ + e^- \) \hspace{1cm} (1.1)

At the cathode: \( \text{CF}_x + e^- \rightarrow \text{CF}_{x-1} + F^- \) \hspace{1cm} (1.2)

Total reaction: \( \text{CF}_x + x \text{Li} \rightarrow \text{C} + x \text{Li}^+ + x F^- \) \hspace{1cm} (1.3)
1.4.2 Advantages/disadvantage and solutions

Li/CFx primary batteries have many advantages which include high specific energy (about 2.2 kWh/kg) [5], a high theoretical voltage of 4.57 volts [7], a wide operational temperature range, and a long shelf life of up to seven years.

Li/CFx primary batteries also have many disadvantages including a low operational voltage of ~ 2.5 V which is much lower than its open circuit voltage (~ 3.2 V vs. Li⁺/Li), a significant voltage delay, heat generation, poor low temperature performance, etc.

One of the disadvantages is its initial voltage delay in the beginning of discharge. This is especially important at high discharge rates. This is largely due to the fact that the active cathode material, CFx, is non-conductive. This insulating property originates from the saturated, $sp^3$-hybridized structure of CFx and the Li-F insulating salt layer formed around reaction sites on cathode material as a product of the discharge reaction [8, 9]. A conventional method to deal with this problem is to add a conductive additive, like carbon black, into the cathode to enhance the cathode’s conductivity, and to employ a small discharge current. When a discharge reaction begins, carbon forms as an electrically conductive graphene shell on the CFx particles. This conductive shell enhances the overall conductivity of the cathode assembly. Thus, the internal resistance of the battery decreases quickly and the voltage delay soon ends.

For convenience in manufacturing, a binder like polyvinylidene fluoride (PVDF) is also added.
However, these additives also create undesired side effects. They reduce the overall battery’s energy density and PVDF reduces conductivity. This non-conductive binder polymer tends to agglomerate which makes its distribution in the cathode assembly an additional issue.

There are various approaches to address this problem. One [10] is to replace carbon black with carbon nanotubes which provide a better conductive network among CFx particles, enabling a decrease in additive usage. Another approach [11] is to add a material other than carbon black that itself discharges before CFx to avoid a voltage delay. These approaches have each achieved some success.

1.5 Low volume fraction scheme to increase cathode conductivity

We propose an initial partial reduction of CFx to generate a thin outer layer of conducting carbon on CFx particles. This will be done as a solvated electron reduction with Na/NH$_3$. The product of this partial reduction, namely reduced CFx (RCF), is expected to have a thin outer layer core-shell morphology: the reduced top layer carbon atoms will form a conductive graphitic shell while the CFx core remains intact inside each particle. The conductive shell serves the function to make the cathode conductive, just like the addition of graphitic carbon black does. In addition, the strong $\pi-\pi$ bond interaction between graphitic shells of RCF particles may serve to help bind these RCF particles, perhaps reducing the need for as much insulating PVDF binder. Combining these two effects together, reduced CFx is anticipated to exhibit superior quality as a cathode material in Li/CFx batteries without the assistance of any additive or with smaller additive amounts. This should lead to more CFx per unit volume of cathode
material. The net effect would be to enhance battery capacity per unit weight (and unit volume) and reduce the initial voltage delay problem.

1.6 Goals of this thesis

The goals of this thesis are: 1) to reduce CFx surface regions stoichiometrically; 2) to determine the amount of reduction in RCF by selective F-ion electrode measurements in the aqueous rinse liquid of the washed RCF product; 3) to evaluate the reduced CFx’s electrochemical properties (capacity, current density); 4) to compare the reduced CFx with the conventional carbon-added CFx as a cathode material; 5) to characterize the reduced CFx.

1.7 A brief introduction to experimental procedures

The amount of CFx reduction was controlled by the stoichiometric amount of reducing agent (Na) which was dissolved in the liquid NH₃, in which CFx particles were slurried. The amount of actual reduction which occurred was determined by measurement of the F⁻ concentration in water used to wash RCF after reduction. This was done with an ion-selective fluoride electrode. Resistivity of the product was also measured to serve as a reference point.

Galvanostatic discharge evaluations were carried out in a lab test cell to investigate RCF’s current density and capacity.

Characterization of RCF was carried out via optical microscopy, fluorescence microscopy, and Raman spectroscopy.
Finally, electrochemical impedance spectroscopy (EIS) was employed to investigate the electrochemical features of RCF before and after discharge.

To compare RCF with conventional cathodes made from CFx with added conductive carbon powder, control reactions were also established in a parallel fashion throughout entire characterization procedure and discharge evaluation.
CHAPTER II
PARTIAL REDUCTION OF CFx BY Na/NH₃

2.1 Introduction

To reduce CFx which is in powder form, a solvated electron reduction system was selected. As known in Birch reductions, metallic sodium (Na) dissolves in liquid ammonia with the loss of an electron. The electrons are termed “solvated electrons” because their wave functions are distributed over a shell of several NH₃ molecules [12]. These solutions are powerful reducing media. They have the capability to reduce aromatic hydrocarbon compounds with a high yield, in a homogeneous phase [13]. However, the solid CFx powder will not dissolve in liquid ammonia. It can only be slurried and dispersed through stirring; therefore, the reduction proceeds under heterogeneous conditions. The net stoichiometric reaction is shown as below:

\[
\begin{align*}
\text{Na}^+ + x \text{NH}_3 & \rightarrow \text{Na}^+ + e^-_{s(NH_3)x} \\
\text{(CF}_x)_n + e^-_s & \xrightarrow{\text{dissociative electron transfer}} \text{(CF}_{x-1})_n + F^- \\
\text{(CF}_{x-1})(\text{CF}_x)_n + e^-_s & \xrightarrow{\text{reaction}} \text{(CF}_{x-1})(\text{CF}_x)_n \rightarrow \text{(CF}_{x-2})(\text{CF}_x)_n + F^- 
\end{align*}
\]
Sodium dissolves in liquid ammonia, releasing relatively kinetically stable solvated electrons into the ammonia solution (2.1). Solvated electrons can react rapidly with dissolved oxygen, especially in the presence of traces of dissolved Fe$^{+3}$ or other transition metals ions [14]. Dissolved water can also react with solvated electrons [14]. However, solvated electrons react extremely rapidly with halogenated organic compounds, far faster than reactions with water. These solvated electrons enter the antibonding orbitals of C-F bonds, as suggested in Figure 2.1, causing the strong C-F bonds to break. Thus, F$^{-}$ ions are ejected into solution and (CF$_{x-1}$)$_{n}$ radicals are generated (2.2). This is a single energy barrier reaction; it occurs very fast.

These (CF$_{x-1}$)$_{n}$ radicals are electron deficient and very active. They each quickly capture one more solvated electron from the solution to form carbanions (negative charge formally residing on carbon). These carbanions then eliminate fluorides from neighboring carbon atoms, generating a carbon-carbon double bond. Neutral carbon structures are generated consequentially (2.3). As this process proceeds, a $sp^{2}$-hybridized (graphitic) carbon coating is generated on the outer surfaces of the reduced CF$_{x}$x particles.

This graphitic carbon coating becomes increasingly electrically conductive as fluoride elimination proceeds towards completion, ultimately forming essentially a pure graphitic carbon coating.
The goals of this chapter are: 1) to stoichiometrically reduce CFx via a solvated electron pathway and 2) to detect CFx reduction percentage by fluoride-electrode and resistivity measurements. The achievements of this chapter are: 1) stoichiometrically reduced CFx via a solvated electron pathway; 2) detected CFx reduction percentage by fluoride-electrode and resistivity measurements; 3) discovered that the reduced CFx appears darker than the un-reduced CFx and 4) discovered that the reduced CFx samples have smaller resistivity.

2.2 Experimental

2.2.1 Reagents and equipment

Fluorinated carbon \((\text{CF}x)_n\) was purchased from FluorStar (Russia), grade PC-10, \(x \approx 1.07\), median particle size 6 µm. Ammonia (anhydrous, premium grade) was purchased from LaRoche Industries Inc., Atlanta, GA. Sodium (99 %) was purchased from Aldrich Chemical Company, Inc. A standard fluoride solution (fluoride standard, 1 ml = 1 mg F) was purchased from Spectro Pure, St. Louis, Missouri. Carbon (TIMREX graphite, SFG6, median size 6 µm, dried before usage) was from TIMCAL Ltd.,
Switzerland. N-Methylpyrrolidine (NMP, 97 %) was purchased from Aldrich Chemical Company. A fluoride selective electrode was purchased from Fisher Scientific. A pH meter (pH/ion analyzer 350) is from Corning Inc., Corning, NY. An electrometer, Keithley model 6512 programmable, is from Cleveland, Ohio.

2.2.2 Methods

Ammonia (120 ml) was condensed into a N₂ filled, cooled flask (-55 °C, with an electric chiller) and then a weighed amount of CFₓ powder was added while the liquid NH₃ was being stirred under N₂. When most of the CFₓ sank towards the bottom a weighed amount of Na metal was added. The liquid briefly showed the dark blue color of the solvated electron but this was quickly consumed and the liquid color became gray and then dark. The flask was then left in a fume hood over night to evaporate all the NH₃. The solid residue (RCF, NaF) was then removed to a beaker where water was added; the suspension was stirred for about 1 h to extract Na⁺ and F⁻ ions from the reduced CFₓ solid. The solid (RCF) was then filtered and rinsed with copious amounts of water. The solid was dried at 105 °C for 2 h to afford dark gray reduced CFₓ (RCF) powder. All water fractions were combined and put into a 200 ml volumetric flask. More water was added to the mark. Then the concentration of fluoride was determined by F⁻ electrode measurements. The total amount of fluoride in the wash water solution was then calculated. This data was converted into the percentage of the carbon in CFₓ that had been reduced.

The cell body used in the resistivity tests is made of hard polytetrafluoroethylene (PTFE) plastic having a cavity diameter of 4.8 mm (from which the cross section area, A,
of a pellet is derived). The upper and lower dies are made of stainless steel. A pressure sensor is placed on top of a die when a sample is put between these two dies. Pressure is gradually applied between the bottom die and the sensor via a vertical vise. The vise is operated by twisting a hand dial. The resistance (R) between two dies is recorded when the pressure reaches a pre-selected value (equivalent to 3000 psi). The distance between the pressed dies is measured with a micrometer. This distance is then converted to the thickness of the sample pellet (l).

2.3 Results and discussion

2.3.1 Fluoride-electrode measurements

A series of diluted solutions with different fluoride concentrations was made from a standard solution and the responses of the fluoride electrode to these standards were determined to afford a calibration profile. This is shown in Figure 2.2.
The fluoride ion concentrations in a series of the aqueous wash solutions from RCF reactions were measured with the fluoride electrode. The F⁻ concentration values were calculated according to the calibration curve, and converted to molar concentrations. Since the total volumes of these wash solutions were known, the number of moles of F⁻ (total amount of F⁻ generated) of each individual Na/NH₃ reduction was also known. The number of moles of carbon formed was equal to the number of moles of F⁻ generated and therefore present in the wash solutions. The weight of carbon in the reduced CFₓ against the total reduced CFₓ weight was consequently calculated as the equivalent carbon weight percentage. These values are tabulated in Table 2.1. Note, Table 2.1 also contains the electrical resistivity of these RCF samples and these will be discussed next.
Table 2.1  Resistivity test results of reduced CFx samples.

<table>
<thead>
<tr>
<th>Equivalent C Content (wt % of total)</th>
<th>0.42</th>
<th>0.62</th>
<th>0.76</th>
<th>0.96</th>
<th>1.36</th>
<th>1.45</th>
<th>2.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Resistivity (Ωm) (3000 psi)</td>
<td>10.4x10^3</td>
<td>7.9 x 10^3</td>
<td>5.5 x 10^3</td>
<td>1.5 x 10^3</td>
<td>137 x 10^3</td>
<td>460</td>
<td>50</td>
</tr>
<tr>
<td>Reaction Number</td>
<td>RCF18</td>
<td>RCF19</td>
<td>RCF14</td>
<td>RCF16</td>
<td>RCF14</td>
<td>RCF7</td>
<td>RCF10</td>
</tr>
</tbody>
</table>

*Obtained after soaking in NMP for 2 weeks

2.3.2 Resistivity measurements

To measure the resistivity of a powdered RCF sample, it is necessary to compress the powder into a pellet under a uniform pressure per area unit (like psi). Then each sample’s resistance ($R$) was measured with an electrometer. The length ($l$) and the cross-section area of the pellet ($A$) were measured with a micrometer. The resistivity ($\rho$) can be calculated as $\rho = RA/l$. A standard pressure of 3000 psi was used. The resistivity values of RCF samples are also tabulated in Table 2.1.

The un-reduced CFx cathode materials, which contained added carbon powder to achieve conductivity, were made as follows. A known amount of carbon (graphite, SFG6) was hand-blended into a known amount (~ 100 mg) of CFx; the mixture was hand-stirred with a spatula quickly for 20 min after 0.5 ml of NMP (N-methylpyrrolidinone) was added. Then this slurry was dried under vacuum for 2 h at 105 °C to evaporate the solvent. The dried samples did not give off the smell of NMP.

The resistivity values of these un-reduced CFx/C samples were measured using the same procedure as that used for the reduced CFx samples. The results are tabulated in Table 2.2.
Table 2.2 Resistivity test results of un-reduced CFx samples.

<table>
<thead>
<tr>
<th>Added C Content (wt % of total)</th>
<th>Mean Resistivity (Ωm) (3000 psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>N/A</td>
</tr>
<tr>
<td>3.0</td>
<td>N/A</td>
</tr>
<tr>
<td>3.5</td>
<td>N/A</td>
</tr>
<tr>
<td>4.0</td>
<td>N/A</td>
</tr>
<tr>
<td>4.5</td>
<td>2.1 x 10^9</td>
</tr>
<tr>
<td>5.5</td>
<td>2.3 x 10^3</td>
</tr>
<tr>
<td>6.5</td>
<td>613.0</td>
</tr>
<tr>
<td>7.5</td>
<td>41.5</td>
</tr>
<tr>
<td>8.5</td>
<td>10.0</td>
</tr>
<tr>
<td>10.0</td>
<td>9.3</td>
</tr>
</tbody>
</table>

It is obvious from Table 2.1 and Table 2.2 that the reduced samples (RCF) are much more conductive than the un-reduced CFx/C samples at equivalent levels of added carbon content. This is probably due to the fact that the stoichiometrically controlled partial reduction took place only on the outer surfaces of CFx particles, forming a conductive graphite shell which accounts for its conductivity. In carbon-added CFx/C case, the graphite particles must form a percolative pathway throughout the cathode to allow electrons flow. In the reduced CFx case, the outer graphitic shells of the RCF particles must form the percolative pathway. With conductive carbon residing at the outer layers, the RCF particles can establish the effective percolative pathway with less weight of carbon than it is possible to achieve by adding graphite powder to unreduced CFx.
CHAPTER III

CHARACTERIZATION OF REDUCED CFx

To investigate the core-shell morphology of reduced CFx (RCF) and the reduction mechanism, optical microscopy, Raman spectroscopy and two types of fluorescence microscopy were used in this research.

3.1 Reagents and equipment

Allylamine of 98 % purity, FITC (fluorescein isothiocyanate isomer I) of 98 % purity, DMF (N,N-dimethyl formamide) of purity $\geq 99.9 \%$, DIPEA (N,N-diisopropylethylamine) of purity $\geq 99 \%$, HOBt (1-hydroxybenzotriazole hydrate), MeOH of purity $\geq 99.9 \%$, and diethyl ether (anhydrous) of purity $\geq 99 \%$ were purchased from Sigma-Aldrich. Acetonitrile was purchased from Fisher Scientific. Rhodamine B was purchased from Alfa Aesar. HATU ($O$-(7-azabenzotriazol-1-yl)-N,N,N′,N′-tetramethyluronium hexafluorophosphate), 98 % purity, was purchased from OChem Incorporation. A FTIR-diamond ATR instrument, model Nicolet 6700, was from Thermo Scientific. The confocal Raman microscope with a 633 nm excitation laser was a LabRam HR800 (Horiba Jobin-Yvon) system. Fluorescence microscopy was performed with a confocal laser scanning microscope LSM 510 of Carl Zeiss Inc.
3.2 Optical microscopy

To understand where the solvated electron reduction took place and what the reduced CFx’s morphology was, optical microscopy was used.

CFx (flakes with median size of 6 µm, shown in Figure 3.1, magnification x 100) is commercially prepared by reacting graphite with fluorine gas at a high temperature. The original global graphitic morphology largely remains unchanged. However, individual planar graphitic sheets are converted to single layers of chair cyclohexane rings within each sheet (see Figure 3.3). During the controlled partial reduction, fluorine atoms were ejected as fluoride ions from the surface-puckered sheets of CFx particles via dissociative electron transfer, generating graphene-like sheets. The original graphitic morphology was regenerated.

As a hypothetical surface graphene sheet is being generated on a CFx particle, the particle’s surface becomes electrically conductive and solvated electrons occupy extended conjugated π* orbitals. Electrons can then be transmitted to underlying puckered CFx layers where further dissociative electron transfer takes place ejecting more fluoride. Dissociative electron transfer is extremely fast [15]. Thus, the outer layers become mostly reduced before much depth penetration of reduction occurs. Succeeding layers tend to reduce at somewhat slower, though still fast, rates. This leads to a fairly distinct outer graphitic shell generation without reduction further inside the CFx particles. After reduction, the graphene layers in these reduced shell regions attract each other via strong non-bonded π-π bond interactions. This causes the reduced CFx particles to agglomerate into layer aggregates which appeared dark, as shown in Figure 3.2.
3.3 Raman spectroscopy

Raman spectroscopy is an appropriate technique to investigate the morphology of the reduced CFx which is alleged to have a Raman active surface graphitic shell, with a
CFx core underneath. The CFx core is Raman inactive in the 1st order region (800 – 2000 cm⁻¹), but the graphitic carbon on surface shell of the reduced CFx particles are Raman active. Graphite Raman spectroscopy is well studied and understood [16].

Depending on its origin and morphology, graphite in the 1st order region (800 – 2000 cm⁻¹) has two Raman absorbance bands. One occurs at 1355 cm⁻¹ (D band) which was assigned to non-graphitic (sp³-hybridized) carbons or defect sites. The other occurs at 1582 cm⁻¹ (G band) which was assigned to graphitic carbons [17]. The intensity ratio of these two bands reflects the ratio of these two forms of carbon in quantity; it can be used as a qualitative guideline.

Four samples were investigated with Raman spectroscopy: as-received CFx, as-received graphite (SFG6), and two reduced CFx samples of different degrees of reduction (RCF11 of equivalent 0.65 wt % carbon, and RCF13 of equivalent 3.90 wt % carbon). Their spectra are shown in Figure 3.4.
In the overlaid spectra, CFx is Raman inactive and its spectrum appears without any Raman bands. Graphite (SFG6) has one sharp band at 1555 cm\(^{-1}\) (G band, caused by graphitic carbon) and one flat band at 1317 cm\(^{-1}\) (D band, caused by non-graphitic carbon). Both reduced CFx samples have higher D band intensities than their G bands. Also, their G bands are shifted to higher frequency (anti-Stokes shift) \(~1592\) cm\(^{-1}\).

In general, graphite, like SFG6 seen in Figure 3.4, has more graphitic than non-graphitic atoms such as those with broken bonds on basal planes and those on edge planes; its G band is higher in intensity than its D band.

The D bands of reduced CFx come from the carbon shell when top-lying fluorine atoms were striped away in the partial reduction, and they are bigger than G bands, as seen in Figure 3.4. This suggests that basal planes of CFx have a lot of defect sites which were double fluorinated during its manufacture. Figure 3.5 highlights such double
fluorinated broken bonds on a puckered CFx plane; the rest of the fluorine atoms are omitted for clarity. This excess fluorine content of CFx (above $x = 1$) is also reflected in the supplier’s quality certificate where $x \approx 1.07$ (fluorine wt. content is 62.9 %). For a CFx with $x = 1$, the fluorine content is 61.27 wt %. So, these two facts reveal that the basal planes of reduced CFx (and the unreduced CFx) are full of structural defect sites.

![Figure 3.5 Double fluorination at broken bonds on a puckered CFx plane](image)

**Figure 3.5** Double fluorination at broken bonds on a puckered CFx plane (Note, all other fluorines have been omitted for the simplicity in viewing the double fluorination sites).

The $G$ bands’ anti-Stokes shift may come from the correlation between the Raman active outer graphene shell and its underlying CFx layers which are not Raman active. The graphene shell has π electron density above and below its plane; while the CFx layer below has electron rich fluorine atoms pointed at the graphene sheet above, interfering with or modifying some vibrations in the overlying graphene sheet. Thus, a higher energy is needed to vibrate the graphene shell of reduced CFx with an un-reduced CFx layer underneath than that for pure graphite without the interfering underlying CFx layer. The $G$ band of the reduced CFx is then shifted up-field as a consequence of this interference, creating an anti-Stokes shift.
3.4 Fluorescence microscopy

3.4.1 Introduction

Another way to investigate reduced CFx morphology is to visualize the graphene shell via a selectively grafted fluorophore using fluorescence microscopy. The $sp^2$-hybridized graphene is chemically more reactive than the un-reduced, $sp^3$-hybridized CFx region. To achieve fluorophore grafting, the correct choice of a linker to connect the fluorophore to the graphene is essential. A desired linker should have a proper spacer in the middle which provides more space and conformational flexibility (wiggle room) for a presumably large fluorophore molecule. The linker must contain two distinctive terminal moieties at either end; one moiety reacts exclusively with graphene in the first step, and the other reacts selectively to anchor a fluorophore in the second step. The attached fluorophore should remain photoactive after the final step and readily emit fluorescent light of an expected wavelength under excitation by the light source of a fluorescence microscope. The non-grafted CFx region of the same particle remains dark (no fluorescent light emitted). If surface-exposed CFx regions are large enough, fluorescence would give particle with light and dark regions observed.

An intensive reagent search led to allylamine (CH$_2$CHCH$_2$NH$_2$) as a desired linker.

Two reports of reactions that might be employed to anchor a fluorophore were found. Landis and Hamers [18] grafted a molecule with a terminal olefin function group onto lateral plane edges of carbon nanofibers with a simple lab UV-lamp irradiation step.
This photochemical reaction was simple and efficient, and isolation/purification was easy. FTIR was used to identify the product. H. Liu et al [19] photochemically grafted benzene rings onto the basal planes of graphene via a benzoyl peroxide radical decomposition pathway:

\[
\text{C}_{12}H_{10} \xrightarrow{515 \text{ nm}} 2 \text{C}_6H_5 + \text{CO}_2
\]

This is one of the few successful functionalizations accomplished on basal planes of graphene instead of on the more active edge (lateral) planes (which are \(10^5\) times more active than basal planes [17]). Similarly we have mostly basal planes to work on, because the reduced CFx has far more graphitic carbon atoms on basal planes than on edge planes.

Thus, grafting of allylamine onto (mainly) basal planes of the reduced CFx was undertaken via a photochemical route.

3.4.2 Linker grafting

A reduced CFx sample (RCF21) with a high reduction amount (equivalent 4.2 wt \% C) was chosen to increase the potential amount of grafting possible. RCF21 (101 mg)
was put into a quartz reaction vessel; allylamine (1.5 ml) was injected and the vessel was capped air-tight. A 530 mW/cm² lab UV-lamp (254 nm) was used to irradiate the vessel from above for 42 h. The vessel was shaken occasionally during this period. The product was filtered, rinsed with acetonitrile, and dried in an oven at 110 °C for 40 min to afford 82 mg of a black powder as amine-grafted reduced CFx (ARCF):

\[
\text{NH}_2 \quad + \quad \text{RCF} \quad \xrightarrow{254 \text{ nm}} \quad \xrightarrow{42 \text{ h}} \quad \text{ARCF} \tag{3.3}
\]

The FTIR-ATR spectra of overlaid RCF and ARCF in Figure 3.6 revealed the reaction did generate surface grafting. In the spectra, the ARCF product has a small band at 2919 cm⁻¹, which was assigned to the \( sp^3 \)-C-H stretches, and two sharp bands at 987 cm⁻¹ and 921 cm⁻¹. These three bands are exclusive to ARCF. Both spectra have a common big band at 1196 cm⁻¹ which was assigned to intact C-F bonds of the un-reduced CFx portions of the reduced CFx sample. It should be noticed that no N-H stretching could be observed in the 3500 – 3100 cm⁻¹ region.
Assuming the linker was successfully grafted, the reduced CFx was used in the final step of fluorophore-grafting with the primary amine moiety on the far end of the linker. Two common fluorophores, rhodamine B and FITC (fluorescein isothiocyanate), were chosen to be grafted in a similar fashion to give a comparison at different emission regions. A control reaction was conducted to each of the fluorophores in a parallel pattern to verify whether a fluorophore was chemically bonded or physically adsorbed to the starting material.

3.4.3 Rhodamine B route

Fluorophore rhodamine B (structure on the next page) is a large molecule with three aromatic rings fused together plus a benzoic acid moiety to which a surface-attached primary amine could be bonded (equation 3.4) via a well known sophisticated
amide forming peptide synthesis pathway [20]. The excitation and emission wavelengths of rhodamine B are 540 nm and 625 nm, respectively.

3.4.3.1 Grafting of rhodamine B to RCF

Amine-grafted reduced CFx (ARCF, 89 mg, ~ 0.15 mmol of equivalent amine based on an assumption of stoichiometric amine grafting) was added to 3.0 ml of N,N-dimethylformamide (DMF, 38.7 mmol) containing 1-hydroxybenzotriazole hydrate (HOBt, 296.2 mg, 1.93 mmol), and O-(7-azabenzotriazol-1-yl)-N,N,N′,N′-tetramethyluronium hexafluorophosphate (HATU, 750.4 mg, 1.97 mmol). Then rhodamine B (926.4 mg, 1.93 mmol) was added and the mixture was stirred until all reagents dissolved except ARCF. Finally, N,N-diisopropylethylamine (DIPEA, 0.67 ml, 3.93 mmol) was injected as a catalyst and stirring was continued at room temperature for 18 h. The product was filtered and rinsed with copious amounts of MeOH, CH₃CN until the rinse liquid was clear. Then the product was washed with CH₂Cl₂. The product was dried in an oven at 110 °C for 15 min to afford 55.4 mg rhodamine B-grafted reduced CFx (RARCF) as a dark brown powder.

\[
\text{Rhodamine B} \quad \text{+ H}_2\text{NARCF} \xrightarrow{\text{HOBt, HATU, DMF, DIPEA, -H}_2\text{O, rt}} \text{RARCF}
\]

A control reaction was conducted on RCF which had no allylamine grafted to it.
In the control reaction, reduced CFx (90 mg of RCF of equivalent 4.2 wt % carbon) was added into 4.0 ml of DMF (51.7 mmol) containing rhodamine B (926.0 mg, 1.93 mmol), and DIPEA (0.67 ml, 3.93 mmol) was then injected. The solution was stirred for 18 h at room temperature before the product was filtered and washed with MeOH until the wash liquid was clear. The product was then rinsed with copious amounts of CH₃CN and CH₂Cl₂, and dried in an oven at 110 °C for 15 min to afford 39.9 mg rhodamine B- mixed reduced CFx (RAMRCF) as a brown black powder.

3.4.3.2 Fluorescence images

Fluorescence microscopic images of both rhodamine B-grafted reduced CFx (RARCF) and rhodamine B, RCF, rhodamine B mixed reduced CFx (RAMRCF) were taken via a confocal laser scanning microscope LSM 510 of Carl Zeiss Inc., at excitation/emission wavelengths of 543 nm/LP650 nm, respectively. Rhodamine B-grafted reduced CFx (RARCF) is shown in Figure 3.7, solid rhodamine B is shown in Figure 3.8, rhodamine B-mixed reduced CFx (RAMRCH) is shown in Figure 3.9, amine-grafted reduced CFx (ARCF) is shown in Figure 3.10, reduced CFx (RCF) is shown in Figure 3.11 and RARCF’s optical image (magnification x 50) is shown in Figure 3.12.
Figure 3.7 RARCF’s fluorescence image.

Figure 3.8 Rhodamine B’s fluorescence image.
Figure 3.9 RAMRCF’s fluorescence image.

Figure 3.10 ARCF’s fluorescence image.
3.4.3.3 Discussion

The starting material, amine-grafted reduced CFx (ARCF), was not fluorescent, as shown in Figure 3.10; but the fluorophore, rhodamine B, exhibited strong fluorescence, as shown in Figure 3.8. The fluorophore grafted to amine-grafted reduced CFx (RARCF) exhibited weak fluorescence, as shown in Figure 3.10.
The reduced CFx (RCF21) used in the linker grafting reaction has a 4.2 wt % of equivalent carbon content from the Na/NH₃ reduction. The surface amine concentration of the amine-grafted reduced CFx (ARCF) would have a maximum grafted of 2.1 wt % using the assumption that 50 % of the surface carbons contained an amine graft. The actual concentration may be far less and it is unknown. On the other hand, the fluorophore, rhodamine B is a large molecule (~ 19 x 13 Å), the steric hindrance it faces while reacting with the surface grafted amine moiety may be substantial. So, the fluorophore concentration on the final product of RARCF could be tiny. At most it could only equal to 1 wt % provided the grafting reaction proceeded well. Consequentially, the fluorescence intensity is expected to be weak. This assumes that surface graphite does not quench rhodamine B fluorescence. Figure 3.12 shows RARCF’s optical image; some of the particles appear pinkish.

Since the magnification of the microscope is small (x 20 – 100), it is impossible to tell basal planes from edge planes from its visual images.

The control reaction, where rhodamine B was reacted with reduced CFx that had not been exposed to allylamine (RAMRCF), demonstrated that some physical adsorption has taken place as shown in Figure 3.9. The starting material, reduced CFx (RCF) is not fluorescent, as shown in Figure 3.11. Surface adsorption could occur due to the polar, ionic fluorophore’s attraction to polar C-F bonds on unreduced sections of the surface or due to the fluorophore’s aromatic rings strong non-bonded π-π attractions to graphitic surface regions. A combination of these two attractions could also exist to promote physical adsorption onto the amine-grafted reduced CFx (ARCF) while the chemical reaction takes place. Therefore, all the fluorescence observed in Figure 3.7 may have
resulted from physical adsorption of the fluorophore. Thus, it is challenging to
differentiate the chemically bonded from the physically adsorbed fluorophore with a
fluorescence microscope. Ultimately this approach did not provide useful information to
characterize the surface morphology of reduced CFx. This line of investigation was
terminated.

3.4.4 Fluorescein isothiocyanate (FITC) route

Fluorophore FITC (fluorescein isothiocyanate) has excitation and emission
wavelengths at 495 nm and 525 nm, respectively. Like rhodamine B, FITC is a large
molecule with three aromatic rings fused together, but it’s not a salt; its isothiocyanate
moiety is very susceptible towards nucleophilic attack by an electron-rich group, like an
amine, or by the two phenol groups in its own structure. Therefore, a grafting reaction
with amine-grafted reduced CFx was tried based on a literature report [21]. This
reference reported that reactions of the isothiocyanate function group with nucleophiles
could go smoothly when there is enough Lewis base to suppress the acidic components
like phenol group in the system; no further explanation for this behavior was given.

3.4.4.1 Reactions

Dried N,N-dimethylformamide (DMF, 2.10 ml, 27.1 mmol) was stirred at 60 ºC
and N,N-diisopropylethylamine (DIPEA, 22 µ, 0.129 mmol) was added. Then
fluorescein isothiocyanate isomer I (FITC, 12.2 mg, 0.0313 mmol) was added. After 30
min, amine-grafted reduced CFx (ARCF, 18.2 mg, ~ 0.0319 mmol of equivalent amine)
was added. Stirring was continued at 60 ºC for 20 h before the solid residue was filtered
and washed with DMF until wash liquid was clear. Then the solid was washed with copious amounts of ice-cooled diethyl ether and dried in an oven at 60 °C for 3 h to afford 6.3 mg FITC-grafted reduced CFx (FARCF) as a black powder.

\[
\begin{array}{c}
\text{FITC} + \text{ARCF} \xrightarrow{\text{DMF, DIPEA, stir, 60°C, 20h}} \text{FARCF}
\end{array}
\]  

A control reaction was conducted on the reduced CFx (RCF) which had no allylamine grafted to it.

\[
\text{FITC} + \text{RCF} \xrightarrow{\text{DMF, DIPEA, stir, 60°C, 20h}} \text{FMRCF}
\]  

In the control reaction, dried N,N-dimethylformamide (DMF, 2.10 ml, 27.1 mmol) was stirred at 60 °C and N,N-diisopropylethylamine (DIPEA, 22 µl, 0.129 mmol) was added. Then fluorescein isothiocyanate isomer I (FITC, 12.4 mg, 0.0318 mmol) was added. Stirring was continued at 60 °C for 30 min and then reduced CFx (18.2 mg, 0.0637 mmol, 4.2 wt % of equivalent carbon) was added. Stirring was continued 60 °C for 20 h. The solid residue was filtered and washed with DMF until wash liquid was clear. Then the solid was washed with copious amounts of ice-cooled diethyl ether and
dried in an oven at 60 ºC for 3 h to afford 9.3 mg FITC-mixed reduced CFx (FMRCF) as a black powder.

The FTIR-ATR spectra of overlaid FARCF and ARCF in Figure 3.13 revealed the reaction did generate surface grafting. FARCF has three major absorbance bands distinguishing from its starting material ARCF: one broad band at 3296 cm⁻¹ which was assigned to the phenolic O-H stretches; one sharp band at 1658 cm⁻¹ and one band at 1050 cm⁻¹ which could be aliphatic C-O stretching. Both spectra have a common intense band at 1196 cm⁻¹ which was assigned to intact C-F bonds of the un-reduced CFx portions of the reduced CFx sample.

Figure 3.13 FTIR-ATR Spectra of FARCF and ARCF.
3.4.4.2 Fluorescence images

Fluorescence microscopic images (magnification x 20) of FITC-grafted reduced CFx (FARCF), amine-grafted reduced CFx (ARCF), FITC, reduced CFx (RCF) and FITC-mixed reduced CFx (FMRCF) were taken with a Confocal Laser Scanning Microscope LSM 510 of Carl Zeiss Inc. at excitation/emission wavelengths of 488/LP530 nm, respectively. FITC-grafted reduced CFx (FARCF) is shown in Figure 3.14, FITC is shown in Figure 3.15, amine-grafted reduced CFx (ARCF) is shown in Figure 3.16, FITC-mixed reduced CFx (FMRCF) is shown in Figure 3.17 and reduced CFx (RCF) is shown in Figure 3.18. Finally, FARCF’s optical image (magnification x 50) is shown in Figure 3.19.

Figure 3.14  FARCF’s fluorescence image.
Figure 3.15  FITC’s fluorescence image.

Figure 3.16  ARCF’s fluorescence image.
Figure 3.17  FMRCF’s fluorescence image.

Figure 3.18  RCF’s fluorescence image.
3.4.4.3 Discussion

The starting material for the fluorophore grafting reaction, amine-grafted reduced CFx (ARCF), is not fluorescent as shown in Figure 3.16. Its weak fluorescence (at 530 nm) may come from the cross-over of the excitation source (488 nm) which is only 42 nm up-field. Pure fluorophore FITC (Figure 3.15) has the strongest fluorescence intensity. When grafted to FITC via a linker, the reduced CFx (FARCF) gives off strong fluorescence signals as shown in Figure 3.14. The chemical reaction took place between the primary amine of the amine-grafted reduced CFx and the electrophilic isothiocyanate moiety of the fluorophore, generating a stable thioamide bond (within a thiourea group) that links the fluorophore firmly with the reduced CFx. This seems account for the strong fluorescence signals.

Serving as a comparison, the product of the control reaction, the mixture of fluorophore and reduced CFx (RCF), FMRCF, also gives off a strong fluorescence signal. The starting material (RCF) exhibits its own intrinsic fluorescent nature. Physical
adsorption may have taken place either between the graphene shell of the reduced CFx and the three benzene rings of the fluorophore via strong π-π interactions, or between the dominant polar C-F bonds of the un-reduced region of the reduced CFx and two hydroxyl moieties of the fluorophore via strong hydrogen bonds.

Since the FTIR spectrum suggested the grafting reaction might have taken place, and the control reaction proved that physical adsorption had also taken place as interference, it is reasonable to believe that these two phenomena may have taken place simultaneously to give a combined fluorescence appearance of the grafted product (FARCF). Unfortunately, it is difficult to distinguish one from the other under a microscope. The intrinsic fluorescence of the RCF could also contribute to the intensity.

As a fluorophore FITC has two advantages over rhodamine B: possessing a more active isothiocyanate moiety, and being not a salt. It was expected to have a better yield and low adsorption to facilitate a favored fluorescence signal on the basal planes of the reduced CFx. However, an intrinsic fluorescence from the starting material interfered with the control reaction (in addition to its own possible adsorption), dampening these advantages and rendering FITC no better than rhodamine B.

### 3.5 Summary

From the studies completed on characterization of the reduced CFx throughout this chapter, the following conclusions can be made about its properties.
3.5.1 Dark color of reduced CFx

Partially reduced CFx appears darker than unreduced CFx which has a light gray color. The greater the amount of reduction, the darker it appears. The dark color comes from the product of the reduction: a graphitic carbon coating on outer surfaces (mainly basal planes) of the reduced CFx particles. A single graphene shell absorbs 2.3 % of white light impinged on it [22]; a flat graphite particle made of more than 44 shells of graphene absorbs 100 % of white light and appears black. These graphitic carbons from the solvate electron reduction at the outer surfaces form a graphene coating on the reduced CFx particles. These graphene coated particles agglomerate during reduction and in the processing that followed. These two effects combine together make the reduced CFx look darker than the unreduced CFx.

Optical images (magnification x 50) of CFx and reduced CFx (RCF) are shown in Figure 3.20 and Figure 3.21, respectively. The majority of CFx particles are transparent under the optical microscope; even they look gray to naked eyes. The dark smudgy spots come from the piling-up of particles causing some of top ones to be out of the focus plane. The RCF in Figure 3.21 has 4.2 wt % of reduced graphitic carbon; the reduced particles look darker than un-reduced ones, even most of those that stay on the focus plane of the microscope.
3.5.2 Hypothesis for graphite layer formation by CFx reduction

It is proposed from the fact that reduced CFx is much more conductive than both insulating CFx and CFx mixed with an equivalent content of graphite particles. Conductive percolation pathways are more efficiently reached with reduced CFx. The bulk underlying portions of the added graphite particles do not conduct electric current as
efficiently as the surface regions and do little to assist in percolation other than provide the physical framework for the surface regions.

The Na/NH$_3$ reductions took place mainly at basal planes of CFx particles with the reaction ending when the solvated electrons had been consumed. This process takes place from the outer surface and progressively moves below the surface. Fluoride ions were produced at the surface CFx layer and moved easily from their reaction sites at surface planes into liquid ammonia with the assistance of ammonia solvation. However, as the reaction proceeds to the underlying CFx layers, fluoride ions produced should not be able to migrate from these underlying reaction sites as rapidly as the fluoride produced at the surface layer. Fluoride cannot penetrate the newly formed top-lying graphene sheets. Instead, they must follow longer, de-intercalation pathways between graphene sheets and the underlying CFx layer that is producing new fluoride ions. The diameter of a fluoride ion is 2.66 Å and the distance between a graphene sheet and a puckered CFx sheet is bigger than 3.35 Å. The fluoride ions must move past axial fluorines still attached to the reducing CFx sheet. Thus, repulsions will be encountered. To de-intercalate a CFx particle of median size of 6 µm, an F$^-$ ion with a diameter of 2.66 Å might have a maximum distance of 3 µm to migrate from the center to the edge. That is, such an F$^-$ ion would move a distance of over 10,000 times of its diameter. This long range de-intercalation from under-layer reductions of CFx likely contributed to slower reduction rates than rates at the surface layers.

Another factor could be operating. The diffusive intercalation of several ammonia molecules with a solvated electron into the region between a graphene and a CFx sheet will be slow. Thus, the hypothesis is advanced that direct electron transfer occurs from
the outer graphene sheet to the inner CFx layer causing dissociative electron transfer to
coccur. The outer graphene or partially graphene sheet is becoming increasingly
conductive. A solvated electron can be transferred from solution into a conjugated
extended π* orbital. This, in turn, might be passed to the sheet below generating a
fluoride ion. As several outer layers become reduced to graphite, this mode of electron
transfer into the CFx particle could continue, leading to the production of an increasingly
thick graphitic outer layer. The amount of reduction is ultimately controlled by the
amount of sodium added to the liquid ammonia.

Since the partial reduction did proceed swiftly, it is proposed that most reduction
reactions took place on the surface (mainly basal) planes of CFx particles. Therefore, the
reduced CFx should have thin graphene layer coating. This is core-shell morphology.
When agglomerated, connections among these conductive shells were formed to afford a
continuous percolation pathway for electrons to flow through, achieving an efficient
conductance with much smaller carbon content than that in carbon-added case of
currently produced commercial Li/CFx batteries.

3.5.3 Defect sites on basal planes and the role of edge planes

The Raman spectra of reduced CFx samples, when compared with that of
graphite, revealed that the basal planes of the reduced CFx (and the unreduced CFx, plus
its graphite precursor) possessed a large number of defect sites. These defect sites contain
carbon atoms in non-graphitic (sp^3-hybridized) states.

When graphite with large number of defect sites undergoes fluorination, it tends
to achieve over-fluorination (C_1 F_{>1}) when these sites become doubly fluorinated. The
ratio of these sites versus the total number of carbons determines the final F content of the CFx. The higher the ratio, the higher the x value will be. However, the edge planes where carbon atoms are not in their graphitic state can also achieve double fluorination together with the defect sites on the basal planes. For a puckered CFx flake (from a median size of 6 µm particle) with an aspect ratio near 1:1, its edge planes consists of only ~ 0.006 % of its total planes. The edge planes’ contribution to over-fluorination is negligible in case of CF1.07. Similarly, when a chemical reaction on the reduced CFx is to take place, like amine grafting, carbon atoms on the edge planes can be neglected; basal planes dominate stoichiometrically.

3.5.4 Challenges of a fluorophore route

The photochemical amine-grafting reaction was used to attach an –NH₂ function group onto the graphitic shell of the reduced CFx. FTIR spectroscopy suggested some evidence to confirm the presence of a product in this amine grafting step. However, in the second step, similar FTIR evidence did not materialize to confirm if rhodamine B grafting occurred via the amide bond formation synthetic pathway.

The structure of rhodamine B indicates that it exhibits a strong tendency towards physical adsorption onto the reduced CFx. As a consequence, the possibility of physical adsorption could not be ruled out versus chemical reaction.

There was clear FTIR evidence that grafting reaction took place between the amine-grafted reduced CFx (ARCF) and the FITC fluorophore, as shown in Figure 3.13. The starting material (ARCF) did not exhibit intrinsic fluorescence interference. It could then be suggested that fluorescence of the fluorophore grafted reduced CFx (FARCF)
came from the fluorophore that had been grafted onto the graphene shell of the reduced CFx via the linker. However, the control reaction revealed that physical adsorptions had also taken place on the control’s graphite-like surface. This may result from a strong $\pi-\pi$ interaction, in addition to F/H hydrogen bonds on un-reduced CFx region from the two phenol moieties of FITC fluorophore.

It remains challenging to differentiate the reduced surfaces from the un-reduced ones on the reduced CFx particles with the assistance of a fluorophore and a fluorescence microscope. Site exclusivity of fluorophore grafting is a key precondition for this task. Other requirements like a microscope with large magnification power and highly oriented crystals also may play a big part in this situation. As for the fluorophore, to favor a chemical grafting reaction over a possible physical adsorption, the ideal choice should be a small easily grafted molecule to afford a better yield and a non-aromatic, non-graphitic interactive structure to restrict any attraction to graphene regions on the reduced CFx that don’t contain the linker with amine. Also, no acidic protons should be present to avoid hydrogen bonding with the prevalent fluorine atoms of the un-reduced regions.
CHAPTER IV
GALVANOSTATIC DISCHARGE EVALUATION OF REDUCED CFx

4.1 Introduction

Galvanostatic discharge is the study of the electrochemical properties of a cathode material under a constant current flow. It is used in this research to investigate the capacity of reduced CFx (a simplified version of specific energy, Wh/kg) and current density (another simplified version of specific power, W/kg). These two properties are thermodynamic and kinetic properties, respectively.

A typical primary battery discharge testing procedure involves cathode preparation (active material casting, drying, pressing and weighing), test cell assembly, filling and equilibrating with electrolyte, parameter programming, discharge execution, plus data analysis and performance evaluation.

There are two performance goals for this research on reduced CFx: (1) a specific energy of 600 Wh/kg, and (2) a specific power of 50 W/kg. These goals stem from the Ultralife Inc./US Army contract goals. Any material, including conventional CFx/C should attempt to achieve these two goals. True values of a discharge reaction come from the integration two factors: voltage and time, when current is held constant and weight is known. Since voltage in a discharge reaction is constantly changing, it is necessary to simplify the process by setting an upper and lower cutoff voltage as a standard; any
values above this standard will be considered as equal to the standard itself, leaving only one factor (time). The cutoff voltage in this research is set at 2.0 volts.

A practical concern is the safety margin for a cathode material. An actual battery consists of various devices other than anode and cathode; these devices will eventually dilute the capacity of a cathode material. To compensate for this loss of capacity, the cathode material has to perform better than the set performance goals; a safety margin of 40 - 50 % is often adopted as a guide line. A 50 % margin has been adopted in this research.

Taking these two adjustments (cutoff voltage of 2.0 volts and a 50 % margin) into consideration, the performance goals were reset to obtain a capacity of 450 mAh/g (thermodynamics) and a current density of 38 mA/g (kinetics).

To compare the synthesized reduced CFx with the conventional CFx/C material, a series of control reactions in which the CFx/C was used as the cathode material were also conducted under similar conditions.

4.2 Experimental

4.2.1 Reagents and equipment

Carbon (Timrex graphite, SFG6) was obtained from Timcal Ltd. Switzerland. N-methylpyrrolidine (NMP, 97 %), ethylene carbonate (99.99 % anhydrous), 1,2-dimethoxyethane (99.5 % anhydrous) and lithium tetrafluoroborate (LiBF₄, 99.998 % anhydrous) were purchased from Sigma-Aldrich. Copper foil, Furakawa 15 µm thick, was from Mitsuya Boeki Ltd., Japan. Argon (UHP compressed) was purchased from
Airgas Inc. Separator glass fiber G6 filter circles were purchased from Fisher Scientific. Lithium foil, 0.03 inch thick, 99.9 % purity, was purchased from Alfa Aesar. The employed potentiostat was a Solartron 1470 E from Hampshire, England.

4.2.2 Method

4.2.2.1 Cathode preparation

A weighed quantity (~ 150 mg) of active material, either reduced CFx with a known wt % of equivalent carbon or pristine CFx with a known wt % of added carbon (graphite, SFG6), was put into a vial, N-methyl pyrrolidine (NMP) was blended in to make a slurry. Then these slurries were hand cast onto Cu foils (1/2 inch in diameter and 5 µm in thickness). These copper foils were polished, pressed for smoothness, rinsed with diluted base solution (NaOH, 0.05M) to remove any remaining surface grease, dried and weighed before casting.

The cathodes were dried at 105 °C for 2 h, then dried in a vacuum oven at 105 °C for 2 h, cooled to room temperature, pressed to a designated pressure (0, 70, 110 or 170 psi) and weighed. Then the cathodes were moved inside a dry box for test cell assembly.

4.2.2.2 Cell assembly and equilibration

Test cells [23] were assembled inside a dry box filled with argon using the following sequence: (1) a cathode was placed next to the positive electrode, (2) a separator of 1/2 inch in diameter was placed next to the cathode, (3) a lithium metal disc (1/2 inch in diameter) was placed next to the separator and (4) the negative electrode was
then attached. The entire assembly was screwed tight to the cell to achieve a uniform connectivity among these assembled components. A photograph of the test cell is shown in Figure 4.1, and a schematic of the cell assembly is shown in Figure 4.2.

![Figure 4.1 A photo of the test cell [23].](image)

![Figure 4.2 A schematic of the test cell assembly.](image)

The electrolyte was composed of three ingredients: LiBF$_4$ (1.0 M) dissolved into ethylene carbonate and 1,2-dimethoxy ethane in 1:1 molar ratio. The electrolyte solution was dripped from the fill port (Figure 4.1) into the assembled test cell until the port was
full. The filled cell’s voltage was monitored between its electrodes with a voltage meter until its open circuit voltage stabilized. This equilibration process took about 2 – 9 hours to complete.

4.2.2.3 Galvanostatic discharges

An equilibrated test cell was connected to the potentiostat (Solartron 1470E) at its electrodes. A discharge reaction parameter was programmed into the potentiostat with a cutoff point set at 2.0 volts and a pre-selected current. A high current setting represents a fast discharge rate while a low current setting corresponds to a slow discharge rate. Reaction time and voltage were recorded automatically by the potentiostat once reaction began after an initial 60 s programmed rest step was over. If the current was too high for the cell to sustain, the reaction will be terminated by the potentiostat when cell voltage fell below 2.0 volts. Then a smaller current was re-selected and programmed in, the whole process started again until voltage remained above 2.0 volts and the reaction proceeded continuously. The discharge reaction was programmed to stop when cell voltage fell below 2.0 volts after active material on the cathode was exhausted.

The following cell discharge data were collected when a discharge reaction was complete: cathode material weight (g), current in milliampere (mA), time in hour (h) and a voltage of 2.0 (V) for all cases. The capacity was calculated as mAh/g and the current density was calculated as mA/g.
4.2.2.4 Voltage delay

One of the main disadvantages of Li/CFx primary batteries is their voltage delay. When a workload is connected, a Li/CFx battery does not produce the desired voltage immediately like other type batteries. The voltage will drop sharply to a certain value (upper voltage window) and then it rises back slowly to its desired working voltage zone after a short time. The total length of the delay and the how low the lower voltage point will be depends on the value of the current density and the properties of the cathode. The smaller the current density, the shorter the delay will be and the higher the upper voltage window will be.

A typical discharge profile (A) of a conventional Li/CFx battery with carbon and binder additives (assembled in this lab) is presented in Figure 4.3 together with its discharge data (B). The voltage delay is shown in the first 5 s where voltage of the battery dropped quickly from 3.0 V (open circuit voltage) to 2.25 V (upper voltage window). It then rose to about 2.53 V in about 30 s and was stabilized at a desired working zone (voltage plateau).
Figure 4.3 Discharge profile (A) and data (B) of a conventional Li/CFx battery.

The voltage delay is inherent to this cathode material of a conventional Li/CFx battery design. It comes from the fact that active cathode material of CFx is a non-conductive polymer; each carbon atom is saturated with four covalent bonds ($sp^3$-
hybridized), there is no conducting band to support electron flow. Thus, internal current flow cannot occur.

To solve this non-conductivity problem, the conventional method is to mix a conductive additive (graphite particles) into the CFx particles which does not participate in discharge reaction. Once the reaction begins, a graphite product is created on the CFx which then becomes conductive. This contributes progressively to the conductivity; the voltage delay will soon be over. As shown in this research, the use of a new reduction pre-treatment of the cathode’s CFx creates a conductive coating on CFx before discharge is started. This provides conductivity from the start of the discharge.

The results in this chapter revealed how well this scheme works versus the conventional method.

4.3 Results and discussion

4.3.1 Capacities

Thermodynamic discharge tests focused on the highest capacity a cell can deliver; a higher capacity is desired. Thermodynamic discharge data of un-reduced CFx cells (with various amount of added carbon) is shown in Table 4.1. The key box indicates the definitions and units of each data set. These five items, in the order listed in the key box, are also given in the same order (vertically) for each added carbon content and each pressure for which data was obtained. This can be seen in the upper left of Table 4.1 and this same format/order applies at every pressure. The pressure (psi) column in Table 4.1 indicates the pressure applied to cathodes. Both of these comments also apply to Table
4.1, where thermodynamic discharge data from reduced CFx cells (with equivalent carbon content) is shown.

Table 4.1  Thermodynamic discharge data for cells made from un-reduced CFx with carbon added (conventional cells).

<table>
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<th>Pressure (psi)</th>
<th>Added Carbon Content (wt %)</th>
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<th>2</th>
<th>3.5</th>
<th>4</th>
<th>4.8</th>
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<td>7.2</td>
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<td>73.0</td>
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<td></td>
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<td>73.0</td>
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<td>2.01</td>
<td>62</td>
<td>73.0</td>
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<tr>
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Key:
- Capacity (mAh/g)
- Upper voltage window (V)
- Load density (mg/in²)
- Current density (mA/g)
- Reaction # replicate

\[4.6 \text{ wt } \% \text{ PVDF (polyvinylidene fluoride) binder was added.}\]

\[\text{Discharges were not conducted on samples with carbon contents of 6.5 wt } \% \text{ and 8.5 wt } \%.\]

Table 4.2  Thermodynamic discharge data for cells made from reduced CFx.

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Key:
- Capacity (mAh/g)
- Upper voltage window (V)
- Load density (mg/in²)
- Current density (mA/g)
- Reaction # replicate

\[\text{Higher pressure cathode discharges were not conducted.}\]
In each data set (as shown in the key box), the values are put in this specific sequence: capacity (mAh/g) of a test cell is put at the top of the set, followed by the upper voltage window (V) which indicates the lowest voltage reached immediately after discharge began. The third item is the load density (mg/in\(^2\)), which indicates total quantity of material on the Cu foil (1/2 inch in diameter) in the cathode. The fourth item is the current density (mA/g) stating the current/cathode weight used in the test. Finally, the reaction or mixture number replicate is placed at the bottom of the set representing the individual cathode made from the same reduction product (RCF) or from the same CFx plus C mixture.

In every discharge reaction, lithium was present in excess, so the capacity of each test cell was solely determined by the capacity of its cathode. Thus, cathode capacities can be directly studied as a function of their composition.

All cathodes made of either reduced or un-reduced CFx passed the capacity goal of 450 mAh/g. Pressure exerted on the cathodes during preparation seemed did not affect their capacities. In contrast, capacities decreased with an increase in carbon content in both cases.

The carbon content in Na/NH\(_3\) reduced CFx samples is the product of partial reduction. Capacity was sacrificed in these samples to achieve percolative conductivity. As the carbon content increases, capacity logically decreases as a consequence. But in case of un-reduced CFx, there was no reduction performed. The capacities of these samples, based on the CFx weight charged, remained unchanged when more carbon was added to achieve conductivity. However, this added carbon increases the cathodes’ weight and volume. Thus, on a cathode wt. basis (CFx + C) or a volume basis, the
capacity decreases. Added carbon dilutes the capacity of the active material (CFx) which is an undesired side effect. The net effect is that CFx/Li batteries can be constructed with higher capacities per unit weight and unit volume using reduced CFx.

4.3.2 Current densities

Kinetic discharge tests focused on the highest current density that a cell could sustain; a higher current density is desired. Kinetic discharge data of un-reduced CFx cells (with various amounts of added carbon) is shown in Table 4.3. The key boxes within each table indicate the definitions and units of the specific values of each data set and the order (as discussed earlier for Tables 4.1 and 4.2) they appear for each pressure and added carbon content. Pressure (psi) values designate the pressure applied to cathodes. All these same comments also apply to Table 4.4, where kinetic discharge data from reduced CFx cells (with equivalent carbon content) is shown.
Table 4.3  Kinetic discharge data for cells made from un-reduced CFx with carbon added (conventional cells).

<table>
<thead>
<tr>
<th>Pressure (pa)</th>
<th>Added Carbon Content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.5</td>
</tr>
<tr>
<td>170</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>16.5</td>
</tr>
<tr>
<td>110</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>16.5</td>
</tr>
<tr>
<td>70</td>
<td>2.66</td>
</tr>
<tr>
<td></td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>16.5</td>
</tr>
</tbody>
</table>

Table 4.4  Kinetic discharge data for cells made from reduced CFx.

<table>
<thead>
<tr>
<th>Pressure (pa)</th>
<th>Equivalent Carbon Content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.42</td>
</tr>
<tr>
<td>170</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>2.06</td>
</tr>
<tr>
<td></td>
<td>116</td>
</tr>
<tr>
<td></td>
<td>19.4</td>
</tr>
<tr>
<td>110</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>19.7</td>
</tr>
<tr>
<td>70</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>2.03</td>
</tr>
<tr>
<td></td>
<td>107</td>
</tr>
<tr>
<td></td>
<td>18.7</td>
</tr>
<tr>
<td>0</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>2.04</td>
</tr>
<tr>
<td></td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>18.7</td>
</tr>
</tbody>
</table>

Key:
- Current density (mA/g)
- Upper voltage window (V)
- Load density (mg/in²)
- Reaction # replicate

Rxn #: RCF18  RCF19  RCF17  RCF16  RCF14  RCF7  RCF10

58
In each data set (as shown in the key box), the values appear in this sequence: (1) the current density (mA/g) of a test cell is put at the top of the set, followed by (2) upper voltage window (V) which indicates the lowest voltage reached immediately after discharge began. (3) Then the load density (mg/in²) is given which indicates total the quantity of material on the Cu foil (1/2 inch in diameter) in the cathode. Finally, (4) the reaction or mixture number replicate is placed at the bottom of the set representing the individual cathode made from the same reduction product (RCF) or from the same CFx plus C mixture.

It is obvious that not only the carbon content, but also the pressure applied on the cathodes and the load density affected these cathode’s kinetic performances. So, it is necessary to rearrange the data to address these factors.

### 4.4 Analysis of kinetics

The analysis of reduced CFx test cell kinetic performances is presented in Table 4.5. That of un-reduced CFx plus C test cell is presented in Table 4.6. An interpretation of kinetic discharge test data is given by the letters P, C and F. The letter C indicates the kinetic (current density) goal of 38 mA/g has been reached; the letter P shows the goal has been exceeded (≥39 mA/g) and the letter F states that this goal was not achieved (≤37 mA/g). Each letter elucidates the performance of each individual cathode in its respective discharge reaction.
Table 4.5  Kinetic performances of test cells made from reduced CFx.

<table>
<thead>
<tr>
<th>Load Density (mg/in(^2))</th>
<th>Pressure (psi)</th>
<th>Equivalent Carbon Content (wt %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.42</td>
<td>0.62</td>
</tr>
<tr>
<td><strong>≤ 80</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>PP</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td><strong>81 – 90</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td>PP</td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td><strong>91 – 100</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td><strong>101 -- 110</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>P</td>
</tr>
<tr>
<td><strong>111 -- 120</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>P</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70</td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>C</td>
</tr>
<tr>
<td><strong>≥ 121</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>170</td>
<td>C</td>
<td></td>
</tr>
<tr>
<td>110</td>
<td></td>
<td>F</td>
</tr>
<tr>
<td>70</td>
<td>F</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td></td>
<td>CF</td>
</tr>
</tbody>
</table>

Note: Current densities are described in terms of the goal of 38 mA/g. \(\text{P}\): Pass \(≥39\) mA/g; \(\text{C}\): 38 mA/g; \(\text{F}\): Fail \(≤37\) mA/g.
Table 4.6  Kinetic performances of test cells made from un-reduced CFx/C.

<table>
<thead>
<tr>
<th>Load Density (mg/in²)</th>
<th>Pressure (psi)</th>
<th>Added Carbon Content (wt %)</th>
<th>2.5</th>
<th>3.0</th>
<th>3.5</th>
<th>4.0</th>
<th>4.5</th>
<th>4.9</th>
<th>5.5</th>
<th>6.5</th>
<th>7.5</th>
<th>8.5</th>
<th>10.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 40</td>
<td>170 110 70 0</td>
<td>P C C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>41 - 50</td>
<td>170 110 70 0</td>
<td>C P P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51 - 60</td>
<td>170 110 70 0</td>
<td>P P P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>61 – 70</td>
<td>170 110 70 0</td>
<td>F F P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>71 – 80</td>
<td>170 110 70 0</td>
<td>P P P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>81 – 90</td>
<td>170 110 70 0</td>
<td>F C P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>91 – 100</td>
<td>170 110 70 0</td>
<td>F C C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>101 – 110</td>
<td>170 110 70 0</td>
<td>F C C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>111 – 120</td>
<td>170 110 70 0</td>
<td>F P P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>≥ 121</td>
<td>170 110 70 0</td>
<td>F F P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: Current densities are described in terms of the goal of 38 mA/g. P: Pass ≥39 mA/g; C: 38 mA/g; F: Fail ≤37 mA/g.

In both Tables, as the carbon content increases and the load density decreases, the kinetic performances are acceptable and the cells tend to exceed the 38 mA/g. That is, higher cathode carbon content leads to higher conductivity and smaller resistance; smaller load densities indicate thinner cathodes, shorter electron flow pathways and smaller resistances. Thus, these cells can support higher currents.
Higher pressures applied on the cathodes create better connectivity among particles of the cathodes, enabling more electrons to flow through and supporting higher currents. High pressures assist cells to pass the current density goal.

In both of the Tables, at the top right corner there is a pass zone where most of the cells have passed the kinetic goal ($\geq 38 \text{ mA/g}$) for this research. At the lower left corner there is a fail zone where most of the cells have failed the kinetic goal for this research. In the middle there is an intermediate zone where some cells have passed the goal while the others have failed.

A direct comparison between these two types of cells (reduced CFx and un-reduced CFx plus C) can be made when these two sets of performances were combined into one figure. This is represented in Figure 4.4 where the pressure (psi) factor was combined, and test results are illustrated with colored patches. The green patches confirm that the test cell has passed the current density goal while the red patches indicate that the test cell has failed to reach 38 mA/g. Yellow patches (inter) show that the cell has reached the current density goal and the blue triangle patches (acceptable) represent the zones where the current density goal has been exceeded. The grey regions show where no discharge reactions were conducted.
The kinetic discharge test results from both types of cathode material are clearly visualized in this rather complex figure made possible by the use of color patches. When the equivalent carbon content approaches 2.15 wt %, the reduced CFx becomes substantially conductive and can sustain larger currents even at higher load density areas; while the conventional carbon-added CFx can sustain no currents even at lower load density areas. The kinetic superiority of the reduced CFx as a cathode material in Li/CFx batteries to the conventional CFx + C material is fundamentally illustrated in Figure 4.4 with color codes.
4.5 Investigation of other issues

4.5.1 Pressure effect

A Li/CFx cell’s kinetic performance is expressed as the open circuit voltage (OCV), the upper voltage window (UVW), the voltage delay and the value of the voltage plateau. These values result from the combined effect of such factors as carbon content, current density, depth of discharge (DOD), homogeneity of cathode mixture, load density, cathode smoothness, pressure applied on cathode, nature of the electrolyte, equilibration of electrolyte filling, etc. No single factor rules over the others. Therefore, the challenge is try to connect specific factors exclusively with kinetic performance.

The pressure applied to cathode was found to significantly affect a test cell’s kinetic discharge profile. This is demonstrated clearly in Figure 4.5 where two identical cells performed differently during the initial discharge stage. Specific data sets for these two cells are shown in Table 4.7.
Figure 4.5 Kinetic discharge profiles of test cell reactions RCF14-4 and RCF14-5 where Na/NH$_3$ reduced CFx was used in the cathode.

Table 4.7 Kinetic discharge data from RCF14-4 and RCF14-5.

<table>
<thead>
<tr>
<th>Reaction Number</th>
<th>Equivalent Carbon Content (wt %)</th>
<th>Open Circuit Voltage (V)</th>
<th>Upper Voltage Window (V)</th>
<th>Current Density (mA/g)</th>
<th>Load Density (mg/in$^2$)</th>
<th>Depth of Discharge (DOD)</th>
<th>Pressure Applied $^a$ (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCF14-4</td>
<td>1.36</td>
<td>2.76</td>
<td>2.29</td>
<td>40</td>
<td>70</td>
<td>0</td>
<td>70</td>
</tr>
<tr>
<td>RCF14-5</td>
<td>1.36</td>
<td>2.87</td>
<td>2.04</td>
<td>40</td>
<td>70</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$This is the pressure applied to the cathode before it was assembled into the test cell.

These two cathodes were identical in every aspect except one of them (RCF14-4) was pressed at 70 psi before assembly and the other (RCF14-5) was not. When discharged at the same current density, the pressed cathode (RCF14-4) exhibited a lower open circuit voltage (OCV) and a higher upper voltage window (UVW).
The pressure applied on the cathode created more contact points among reduced CFx particles, creating more conductive pathways throughout the entire length of the cathode. This decreased the internal (charge transfer) resistance. When discharged at the same current density, the smaller internal resistance (hence voltage drop) led to a bigger external voltage shown as a higher upper voltage window (UVW).

On the other hand, pressure caused densification of the cathode material; it became more difficult for Li\(^+\) ions to intercalate into the reduced CFx particles. The open circuit voltage (OCV) dropped as the result of this high intercalation resistance.

### 4.5.2 Depth of discharge (DOD) effect on un-reduced CFx

Among the disadvantages of Li/CFx batteries, voltage delay is the most prominent. It has attracted much attention from the day the batteries were invented [6]. At the initial discharge stage, its voltage falls straight below its working area to a certain point (UVW) and then recovers gradually. The depth of this voltage drop and the speed of its recovery are determined by a host of factors including the content of the conductive ingredient, current density, depth of discharge, cathode thickness, pressure, electrolytic composition, storage time, etc.

The cause of voltage delay originates at both electrodes immediately after electrolyte filling. At the anode, highly reactive lithium reacts with the non-aqueous organic electrolyte, along with impurities in the vicinity, forming a protective interfacial film (a passivation layer). This film preserves the battery for the length of its shelf-life. This passivation process also creates a minor resistance when compared with the impedance at cathode side. Further consideration of this process is beyond the scope of
this research. At the cathode, any voltage delay comes from two main sources: the non-conductivity of the main cathode material CFx and the large activation energy of the discharge reaction due to the strong covalent C-F bond.

A good method to investigate voltage delay is to study one possible contributing factor at a time while holding other factors constant. An example of this method uses the depth of discharge (DOD) as a factor in an un-reduced CFx cell. This is represented by the experimental voltage versus time profiles during a series of intermittent (a controlled discharge/rest pattern) discharges (see CFx22-8-1 through CFx22-8-6 in Figure 4.6) conducted on a single cell (CFx22-8). These discharge profiles are summarized in Figure 4.6. Data from these experiments are shown in Tables 4.8 and 4.9.
Figure 4.6 Voltage versus time discharge reaction profiles for intermittent discharges from CFx22-8-1 to CFx22-8-6.

Table 4.8 CFx22-8 discharge/rest time schedule and data.

<table>
<thead>
<tr>
<th>Rest Time</th>
<th>Discharge Reaction Number</th>
<th>Discharge Time</th>
<th>Current Density (mA/g)</th>
<th>Upper Voltage Window (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq. 7 h</td>
<td>CFx22-8-1</td>
<td>&lt; 1 s</td>
<td>70</td>
<td>1.8689</td>
</tr>
<tr>
<td>10 min</td>
<td>CFx22-8-2</td>
<td>10 min</td>
<td>40</td>
<td>2.0451</td>
</tr>
<tr>
<td>195 min</td>
<td>CFx22-8-3</td>
<td>10 min</td>
<td>40</td>
<td>2.3343</td>
</tr>
<tr>
<td>10 min</td>
<td>CFx22-8-4</td>
<td>10 min</td>
<td>40</td>
<td>2.3895</td>
</tr>
<tr>
<td>10 min</td>
<td>CFx22-8-5</td>
<td>10 min</td>
<td>40</td>
<td>2.4184</td>
</tr>
<tr>
<td>10 min</td>
<td>CFx22-8-6</td>
<td>13.8 h</td>
<td>40</td>
<td>2.4350</td>
</tr>
</tbody>
</table>
Table 4.9  CFx22-8 specific data.

<table>
<thead>
<tr>
<th>Added Carbon (wt %)</th>
<th>6.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode Weight (mg)</td>
<td>13.3</td>
</tr>
<tr>
<td>Pressure (psi)</td>
<td>0</td>
</tr>
<tr>
<td>Specific Power (W/kg)</td>
<td>&gt; 80</td>
</tr>
<tr>
<td>Capacity (mAh/g)</td>
<td>579</td>
</tr>
<tr>
<td>Specific Energy (Wh/kg)</td>
<td>&gt; 1,158</td>
</tr>
</tbody>
</table>

A test cell made from the un-reduced CFx (CFx22-8) was discharged six times intermittently (designated as CFx22-8-1 to CFx22-8-6) after an initial 7 h equilibration was finished. The first five discharges were shallow and the last discharge was carried to exhaustion. Each discharge was flanked by two EIS sweeps where a 10-mV alternating voltage was applied to the test cell with the alternating frequency ranging from $10^5$ Hz to $10^{-2}$ Hz. The studies of these EIS sweeps will be given in the next chapter.

As the discharge reactions proceeded, conductive graphitic carbon was produced on the cathode, causing the cathode’s conductivity to increase as the reaction progressed. As a consequence, the voltage delay was alleviated steadily. This is exhibited as a gradual elevation of upper voltage windows in the initial stages of the following reactions. This gradual elevation effect is well visualized in Figure 4.7 where these discharge profiles are placed on the same Y-axis.
As shown in Figure 4.7, the initial stages of these discharge reaction profiles are stacked together with the exception of CFx22-8-1. CFx22-8-1 was discontinued within a second by the Potentiostat when its voltage fell below 2.0 V. The lowest points (upper voltage windows) of these profiles continued to rise as reactions proceeded from 1.8689 V of CFx22-8-1 to 2.4350 V of CFx22-8-6, as shown in Table 4.8.

Open circuit voltage (OCV) recovery is a function of time and the depth of discharge (DOD). When a discharge reaction is over, the open circuit potential of a cell will rise slowly towards its pre-discharge value. The longer the rest time and the smaller the DOD allows the OCV to recover to a higher value. This phenomenon was demonstrated at the beginning of the 3\textsuperscript{rd} reaction (CFx22-8-3) after the cell rested for 195
minutes. In this case the OCV recovered from 2.9409 V at the end of CFx22-8-2 to 2.9771 V at the beginning of CFx22-8-3. This 36.2 mV of OCV recovery resulted directly from a relatively long rest period (195 min). In contrast, a short rest period (10 min) resulted only in minor recoveries (2 ~ 6 mV) as demonstrated between other discharge reactions of CFx22-8.

4.5.3 Depth of discharge (DOD) effect on reduced CFx

Another study to investigate voltage delay using the depth of discharge (DOD) method was conducted on a test cell made from reduced CFx (RCF10-6). This cell was intermittently discharged four times (see RCF10-6-1 to RCF10-6-4 in Figure 4.8) after an initial 4 h equilibration was finished. The first discharge was deep; the middle two were shallow and the last one was conducted to exhaustion. Each discharge was flanked by two EIS sweeps in which a 10 mV alternating voltage was applied the test cell with frequencies ranging from $10^5$ Hz to $10^2$ Hz. Discussions of these EIS sweeps are given in the next chapter. These discharge profiles are placed in Figure 4.8 and the data from these discharges are shown in Tables 4.10 and 4.11.
Figure 4.8 Intermittent discharge reaction profiles from RCF10-6-1 to RCF10-6-4 of a test cell made from reduced CFx with 2.15 wt % equivalent graphitic carbon.

Table 4.10 RCF10-6 discharge/rest time schedule and data.

<table>
<thead>
<tr>
<th>Rest Time</th>
<th>Discharge Reaction Number</th>
<th>Discharge Time</th>
<th>Upper Voltage Window (V)</th>
<th>Open Circuit Voltage (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eq. 4 h</td>
<td>RCF10-6-1</td>
<td>3.6 h</td>
<td>2.3085</td>
<td>3.1576</td>
</tr>
<tr>
<td>10 min</td>
<td>RCF10-6-2</td>
<td>10 min</td>
<td>2.4368</td>
<td>2.8789</td>
</tr>
<tr>
<td>2 h</td>
<td>RCF10-6-3</td>
<td>10 min</td>
<td>2.4135</td>
<td>2.9759</td>
</tr>
<tr>
<td>11 h</td>
<td>RCF10-6-4</td>
<td>6.3 h</td>
<td>2.3613</td>
<td>3.0342</td>
</tr>
</tbody>
</table>

Table 4.11 RCF10-6 specific data.

<table>
<thead>
<tr>
<th>Equivalent Carbon (wt %)</th>
<th>2.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathode Weight (mg)</td>
<td>12.9</td>
</tr>
<tr>
<td>Pressure (psi)</td>
<td>0</td>
</tr>
<tr>
<td>Current Density (mA/g)</td>
<td>70</td>
</tr>
<tr>
<td>Specific Power (W/kg)</td>
<td>&gt; 140</td>
</tr>
<tr>
<td>Capacity (mAh/g)</td>
<td>736</td>
</tr>
<tr>
<td>Specific Energy (Wh/kg)</td>
<td>&gt; 1,472</td>
</tr>
</tbody>
</table>
In contrast to the un-reduced CFx case (CFx22-8), this cell (RCF10-6) was first discharged to 1/3 of its capacity (DOD ~ 35 %) after an initial 4 h equilibration. Then two shallow discharges were followed at longer intermissions (10 min and 2 h, respectively). The last discharge was carried to exhaustion after an 11 h rest.

This cell (RCF10-6) has a much lower (equivalent) graphitic carbon content of 2.15 wt % when compared with 6.5 wt % added carbon in CFx22-8, but it sustained a higher current (70 mA/g). It succeeded in its first trial giving a high UVW bench mark of 2.3085 V. In contrast, the un-reduced CFx cell, CFx22-8 with higher carbon content, failed at the same current density on the first try. This success of kinetic discharge once again supported the superiority of the reduced CFx in electric conductivity compared to the conventional un-reduced CFx plus C.

Even the discharge at a later stage of a cell’s life (DOD ~ 38 %) will still exhibit an apparent voltage delay, as shown in RCF10-6-4. At this late discharge stage, the cathode had already acquired enough conductive substance from previous discharge reaction(s) to sustain higher currents; the lack of electronic conductivity was no longer an issue. Thus, the voltage delay might come from other reason(s) than a lack of conductivity.

Finally, unlike the un-reduced CFx + C case, this series of discharge reactions was carried out with a progressively elongated rest period, giving ample time for other factor(s), like ion diffusion, to take effect. Therefore, this series of discharge reactions uncovered a different result which is better shown in Figure 4.9. Here the initial stages of these intermittent discharge reaction profiles were stacked on the same Y-axis.
Recovery of open circuit voltage (OCV) relates to the ion diffusion process [24]. Li$^+$ cations and F$^-$ anions produced through the discharge reactions accumulated around CFx particles, forming an insulating LiF salt layer. This salt layer gradually diffused away into the bulk of electrolyte, allowing fresh Li$^+$ cations to diffuse into the CFx layers. The values of the OCV reflected the extent of the Li$^+$ diffusion. Given enough time, the OCV would reach back towards its original value (3.1576 V). As shown in Figure 4.9, the OCV values displayed a full recovery trend (from 2.8789 V towards 3.1576V) through these four discharges.

Figure 4.9 Initial stages of discharge reaction profiles from RCF10-6-1 to RCF10-6-4.
The continuous decline of the upper voltage window (UVW) values from RCF10-6-2 (2.4368 V) to RCF10-6-4 (2.3613 V) originated from the fact that this test cell had passed the highest voltage point it can deliver in its first discharge of RCF10-6-1. The power the cell could deliver would only decrease from that point onwards. The large current of 70 mA/g used in this cell’s reactions, when compared with the small current of 40 mA/g in CFx22-8’s reactions, consumed the active cathode material (CFx) at a fast rate, making this cell pass its prime performance zone in its early 1/3 DOD stage.

4.5.4 Mechanism of Li/CFx discharge reaction

It was once believed that Li/CFx discharge reaction proceeded by a simple mechanism:

\[
\text{Li} + \text{CF}_{1.0} \rightarrow \text{C} + \text{LiF} \quad (4.1)
\]

In 1975 Whittingham [25] proposed a new mechanism in which the reaction went through via an intermediate state. The commonly accepted modern version of this mechanism [26] is that Li\(^+\) ions, which are coordinated to (one or more) solvent molecule(s), intercalate into CFx layers during equilibration process. When a discharge reaction begins, the fluoride ions produced join this intercalated complex, forming an intermediate compound (a quaternary phase) which is commonly referred as the graphite intercalation compound (GIC). This intermediate exists for some time before it finally decomposes into the final discharge products of graphite and LiF salt.

This CFx discharge reaction mechanism can be described as:
At the anode:

\[ x \text{Li}^+ + x \text{S} \longrightarrow x \text{Li}^+ \cdot \text{S} + x e^- \quad (4.2) \]

At the cathode:

\[ \text{CF}_x + x \text{Li}^+ \cdot \text{S} + x e^- \longrightarrow (\text{Li}^+ \cdot \text{S} - \text{F}^-)_x \longrightarrow \text{C} + x \text{LiF} + x \text{S} \quad (4.3) \]

Overall reaction:

\[ \text{CF}_x + x \text{Li} + x \text{S} \longrightarrow (\text{Li}^+ \cdot \text{S} - \text{F}^-)_x \quad (4.4) \]

Decomposition of the intermediate:

\[ (\text{Li}^+ \cdot \text{S} - \text{F}^-)_x \longrightarrow \text{C} + x \text{LiF} + x \text{S} \quad (4.5) \]

Here S represents one or more solvent molecules coordinated with each Li$^+$ ion; \((\text{Li}^+ \cdot \text{S} - \text{F}^-)_x\) represents the quaternary intermediate compound.

When solvated Li$^+$ ions intercalate into CF\(x\) layers during the equilibration process, they lower the cell’s open circuit voltage from its theoretical value of 4.57 V (Li vs. Li$^+$) [7] to about 2.8 – 3.2 V. The CF\(x\)’s lack of electric conductivity also drops the voltage in the beginning of discharge (voltage delay), which is quickly relieved by the formation of graphite which is one of the products of discharge. However, the other product, LiF creates a progressively increasing insulating salt layer which increases the internal resistance of the cell. The combination of these two opposing trends further lowers the voltage that the cell can deliver to its working zone at ~ 2.5 V.

Diffusion is a slow process at ambient temperature. A long resting time between discharges may return the open circuit voltage close to its original value when salt layer eventually diffuses into the bulk of the electrolyte.
4.6 Summary

Partially reduced CFx has a higher conductivity than the conventional carbon-added CFx with same carbon content. It can support higher currents and gives superior kinetic performances. Even though partially reduced CFx’s thermodynamic performance (at equivalent CFx amounts) did not exceed that of carbon-added CFx, it did greatly exceed the specific energy goal of this research. Furthermore, the reduced CFx allows more CFx to be packed into a unit cathode volume since less total weight of carbon is needed to achieve equal conductivities. Therefore, the thermodynamic (capacity) properties of reduced CFx can exceed those of the conventional CFx + carbon. This is true on both a volume and weight basis. These intensive tests have proved that reduced CFx has the capability to replace the conventional cathode material in Li/CFx batteries to give a better product.

These discharge tests were executed without using of a binder which is usually a non-reactive, non-conductive polymer inclined to agglomerate the particles. Therefore, one more factor interfering with current flow was eliminated. This is another important consideration favoring the use of reduced CFx. Experiments that re-introduce a binder into the cathode can be done in the future studies should circumstances dictate this is needed.

The kinetic superiority of reduced CFx may come from its proposed thin layer core-shell morphology obtained through the reductive pre-treatment. A larger fraction of the carbon exists as surface conductive graphitic atoms than where added graphite particles are employed. This surface carbon took part in electronic conductivity during
discharge and provides the percolative pathway. The combination of graphitic carbon basal planes and its core-shell morphology yielded outstanding kinetic performances, which were fully demonstrated in this research.

The origin of the voltage delay comes largely from the fact that the main cathode material CFx is non-conductive. It is an intrinsic property of this material; it can not be eliminated. However, lack of conductivity can be alleviated by introducing a conductive ingredient into its cathode mixture, either from a pre-treatment (a de facto discharge reaction) of its cathode material leaving a conductive coating, or from an alien species like pre-added carbon black particles. After discharge begins the conductive carbon product from CFx aids conductivity by allowing electron transfer to be more efficient between CFx and added carbon phases. This improves the conductivity of the overall cathode material, enabling a quick voltage recovery from the initial voltage delay. There is a fundamental distinction between these two types of ingredients in terms of morphology and distribution; this widely separates their electrochemical performances apart from the conventional carbon-added scheme. Thus, the current CFx plus added carbon method seems obsolete. The key question is whether or not CFx producers or battery producers will take advantage of solvated electron reduction reactions. This chemical reaction is not part of a battery company’s culture or skill set.
CHAPTER V
ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS) STUDIES

5.1 Introduction

Electrochemical impedance spectroscopy (EIS) measures the dielectric properties of a medium as a function of frequency. It is also an experimental method to characterize electrochemical systems by measuring the impedance response (both real and imaginary) of a system over a range of frequencies to determine various microstructure properties like Ohmic resistance, charge transfer resistance, double layer capacitance and Faradaic (chemical bond breaking) resistance, etc. It is based on the interaction of an external field (often an alternating current) with the electric dipole moment of the sample. EIS reveals information about the reaction mechanism of an electrochemical process by telling if different reaction steps dominate at certain frequencies.

EIS is now being widely employed in a variety of scientific fields such as fuel cell testing, biomolecular interaction and microstructural characterization [27].

EIS uses an Impedance analyzer to sweep the frequency (from high to low) and the software, Zview, for simulation to find the equivalent circuit and fitting data. EIS spectra consist of three diagrams: one Nyquist plot where the real (Ohmic) and imaginary (capacitive) impedances are plotted perpendicularly versus each other and two Bode plots.
where the absolute impedance and angle $\theta$ (angular difference between real and imaginary impedance) are plotted against frequency.

Generally, impedance is the opposition to the flow of alternating current (AC) in a complex system. A passive complex electrical system contains both energy dissipation (resistor) and energy storage (capacitor) elements. They have different responses to the same stimulation. A resistor has a resistive (Ohmic) impedance which is not a function of frequency; a capacitor has capacitive (also called reactive, or imaginary) impedance, which is a function of frequency. In a capacitor the current lags behind the voltage by 90 degrees (expressed as $\theta = -90^\circ$), in ideal conditions. When a resistor and a capacitor are connected in parallel, a complex system is created. There are three variables that can represent the properties of this complex system: a resistance in ohms ($\Omega$), a capacitance in farads (F) and a unit-less exponential term that reflects its character. When this exponent approaches 1, the system resembles a capacitor and when the exponent approaches 0, the system resembles a resistor. As the exponent value shifts, the character of the complex system changes from one element to the other.

The cathode material in Li/CFx batteries is an electrochemical microstructure which represents a complex system and it is made of distributed elements (particles). Each particle has its own resistive feature, with its own double layer formed instead of the lumped elements in an ideal circuit. This complex system responds differently at different frequencies when AC stimulations are applied. At high frequencies, the basic resistance of a cell dominates the spectra indicating the internal resistance without the cathode’s participation. When frequency decreases the charge-transfer resistance begins to develop in the spectra, reflecting the resistance of electron transport inside cathode,
together with double layer capacitances created by each individual particle. The combination of resistance and capacitance creates a semi-circle in the Nyquist plot. Eventually, Faradaic resistance will appear when the frequency continues to decrease. This indicates the chemical reaction (activation) resistance of a cell (C-F bond breaking resistance in Li/CFx batteries), together with capacitance and resistance from ion diffusion process (solvated Li\(^+\) intercalation and product de-intercalation in Li/CFx batteries).

An EIS frequency sweep, followed by a simulation will reveal all these electrochemical information in a Li/CFx cell. A comparison among different cells made of different cathode materials will elucidate their differences numerically. An analysis of spectra from the same cell, before and after exhaust discharge, will disclose details about what has changed and in what way during the course of discharge. The reason for these changes may be interpreted in some cases.

5.2 Experimental

Cathode preparation and test cell assembly procedures were as same as those described in Chapter IV. Two-electrode Li/CFx electrochemical cells were employed for EIS studies and discharge tests. A Solartron SI 1250 frequency response analyzer and a Solartron SI 1287 electrochemical interface were used to measure the discharge variables in the current-control mode and cell impedance in the potential-control mode, respectively. In the potential-control mode, test cells were applied to an alternating potential of 10 mV amplitude with a frequency ranging from \(10^5\) Hz to \(10^{-2}\) Hz. The subsequent data were collected and analyzed using the ZPlot and the ZView software
(Scribner Associates Inc, Southern Pines, NC). All tests were carried out at ~ 22 °C in an argon-filled dry-box.

5.3 Basic principles

5.3.1 Li/CFx test cell components

Figure 5.1 A schematic illustration of a Li/CFx test cell components.

A Li/CFx test cell is illustrated in Figure 5.1. The cathode material is represented at top the reduced CFx, with its core-shell morphology; the un-reduced CFx is displayed
at the bottom in white circles. Solid black represents the conductive carbon ingredient, either derived through a partial reduction pre-treatment (outer black shells in the top section) or blended as separate particles of graphite (black spheres at the bottom). Other components are labeled in the Figure.

5.3.2 Discharge reaction process and parameters

![Figure 5.2 A schematic illustration of a discharge reaction process.](image)

A discharge reaction encounters various internal resistances and capacitances that are denoted and listed below. The block green arrows in Figure 5.2 represent the pathways of the current flow inside a cell (excluding a cathode) where various resistances will be encountered. These resistances are created when electrons (released by lithium atoms) (1) move inside the lithium metal, (2) cross double layers surrounding the Li
metal and the negative electric lead and (3) move inside the electric leads at both ends of
the cell. The block purple arrows in Figure 5.2 represent the pathways of the Li$^+$ cations
migration inside a cell (excluding the cathode) where these resistances will be
encountered. These resistances are created when Li$^+$ cations (4) move through double
layers at various interfaces and (5) diffuse through the electrolyte solution towards the
cathode material. All these resistances in pathways shown by the green and purple arrows
are combined together to form the (Ohmic) basic resistance of a cell. This is denoted as
$R_b$. $R_b$ is determined by the properties of all the components of the cell except those of
the cathode. $R_b$ is constant.

The curved blue arrows in Figure 5.2 represent the pathways of the current flow
to and within a cathode where various resistances will be encountered. These resistances
are created when (1) electrons (delivered at the positive electric lead) move from the
substrate to conductive carbon atoms, (2) move through the carbon material (added
particles or outer shell coating) to the CFx reaction sites and (3) move through double
layers at various interfaces. All the resistances are combined together to form the charge-
transfer resistance that is denoted as $R_{ct}$. $R_{ct}$ is determined by the properties of the
cathode. $R_{ct}$ is not constant because the cathode changes during the discharge reaction.

At the CFx reaction sites, covalent C-F bonds are being broken by dissociative
electron transfer after overcoming an activation energy barrier. This resistance is denoted
as Faradaic reaction resistance, $R_F$. $R_F$ is determined by the C-F bond dissociation
energy. $R_F$ is constant.

According to the Whittingham intermediate theory [25], Li$^+$ ions in the electrolyte
intercalate into CFx layers during the equilibration process and discharge reaction. This
diffusion creates a resistance that is denoted as Warburg resistance, \( R_w \). When a discharge reaction proceeds, its final product, LiF, begins to extrude from the CFx particles containing the developing graphitic layers. Net LiF accumulation will occur around CFx particles at the reaction sites when reaction rate is faster than that of LiF diffusion. The accumulation of this insulating LiF salt layer is schematically represented as the brown circles in Figure 5.2. This salt buildup creates an additional resistance to both electron transfer and \( \text{Li}^+ \) intercalation. This resistance is also included in the Warburg resistance, \( R_w \). The value of \( R_w \) is a function of current, depth of discharge (DOD) and time.

All these internal resistances cause heat generation according to Ohm’s law. These Li/CFx test cell resistances are summarized in Table 5.1 with their causes and either constant or variable character.

Table 5.1  The internal resistances of a Li/CFx cell.

<table>
<thead>
<tr>
<th>Resistance</th>
<th>Definition</th>
<th>Causes and Locations</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_b )</td>
<td>basic Ohmic resistance</td>
<td>electric leads, anode disc, separator, electrolyte, double layers.</td>
<td>constant</td>
</tr>
<tr>
<td>( R_{ct} )</td>
<td>charge transfer resistance</td>
<td>electron transfer pathways</td>
<td>variable</td>
</tr>
<tr>
<td>( R_F )</td>
<td>Faradaic reaction resistance</td>
<td>chemical reaction of C-F bond breaking</td>
<td>constant</td>
</tr>
<tr>
<td>( R_w )</td>
<td>Warburg resistance</td>
<td>ion diffusion, salt layer buildup</td>
<td>function of ( I ), depth of discharge and time</td>
</tr>
</tbody>
</table>

Double layer capacitances at both electrodes and at cathode particle surfaces are denoted as \( C_{dl} \). These capacitances are determined by the properties of the cathode...
particles and the properties of the electrolyte. The value of $C_{dl}$ is constant for a given cathode. The capacitance created by $Li^+$ ion intercalation into $CFx$ particles is denoted as $C_{ic}$ and $C_{ic}$ is determined by the properties of the solvent solvating the $Li^+$ ions and by the $CFx$ particles. The value of $C_{ic}$ is a function of current and depth of discharge (DOD). These capacitances are summarized in Table 5.2.

Table 5.2 The capacitances of a Li/CFx cell.

<table>
<thead>
<tr>
<th>Capacitance</th>
<th>Definition</th>
<th>Location and Cause</th>
<th>Character</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{dl}$</td>
<td>double layer capacitance</td>
<td>double layers at interfaces</td>
<td>constant</td>
</tr>
<tr>
<td>$C_{ic}$</td>
<td>intercalation capacitance</td>
<td>$Li^+$ intercalation into CFx</td>
<td>function of I and DOD</td>
</tr>
</tbody>
</table>
5.3.3 EIS spectra of a Li/CFx cell

Figure 5.3 EIS spectra consist of a modified Nyquist plot (A) and two Bode plots (B and C).
Figure 5.3 (continued)

Figure 5.3 represents a typical EIS spectra that consists of one (modified) Nyquist plot and two Bode plots. The Nyquist plot graphs $Z'$ vs. $Z''$ as a function of frequency. $Z'$ represents the “real” impedance created by the Ohmic elements of a cell; $Z''$ represents the “imaginary” impedance created by the capacitive elements of a cell which is a function of the AC stimulation frequency. The real and imaginary components are always $90^\circ$ apart on the complex plain. A negative (-) sign placed in front of the $Z''$ values on the Nyquist plot’s Y-axis represents that current lags behind voltage at a capacitive element by $90^\circ$ in an ideal case.

In the Bode plots, $|Z|$ represents the absolute impedance value, where $|Z|^2 = Z'^2 + Z''^2$. Theta ($\theta$) represents the angle between $Z''$ and $Z'$, and $\theta = \arctan (Z'' / Z')$. The X-axis
is the frequency which has been swept through the range marked on the log scale from \(10^5\) to \(10^{-2}\) Hz. The actual frequency range executed in this work was from 65,535 Hz to \(10^{-2}\) Hz.

The Nyquist and the Bode plots are two equivalent but alternate methods of plotting the data collected in the EIS. The Nyquist plot gives a more visual result, which is easier for humans to interpret.

In the Nyquist plot, point (a) indicates the basic Ohmic resistance of the cell, \(R_b\), and the semicircle between points (a) and (b) reflects the charge transfer resistance, \(R_{ct}\), on the \(Z'\) axis and the double layer capacitance, \(C_{dl}\), on the \(Z''\) axis. The semicircle between point (b) and (c) reflects the Faradaic resistance, \(R_F\), on the \(Z'\) axis and the intercalation capacitance, \(C_{ic}\), on the \(Z''\) axis. Point (c) reflects the Warburg resistance and capacitance associated with (solvated) Li\(^+\) ion intercalation, product de-intercalation and the LiF salt layer accumulation around CFx particles.

### 5.4 EIS studies and simulations

EIS sweeps with a 10 mV magnitude from 65,535 Hz to 0.01 Hz were carried out on four cells at a DOD = 0 % state and on three cells at DOD = 90 % state using the Solartron frequency response analyzer. The results were simulated with the ZView software. Equivalent circuit models, fitting data with individual error percentages and fitting indicators were collected. These data were later combined and analyzed.

There are four elements used in the simulation process, their definitions, symbols, parameters and equations are given in Table 5.3. Each individual element was simulated
separately using the same program. Example simulation profiles are given in Figure 5.4 with some randomly assigned parameters used in the demonstration process.

In order to simulate a real cell discharge process, these elements were selected and combined into an equivalent circuit; then the parameters would then be selected to correlate the real battery variables. Such simulations of experimental EIS sweeps are given later in the chapter. The simulation program in the ZView software was used to determine the fitting result with a set of indicators and error rates.

For brevity, only one EIS spectra from each cathode type and their simulation data were exhibited and analyzed herein. All other EIS spectra and simulations were summarized in Tables 5.4, 5.5 and 5.6.

Table 5.3 The elements used in the simulation process. 

<table>
<thead>
<tr>
<th>Element</th>
<th>Definition</th>
<th>Symbol</th>
<th>Equation</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>Resistor</td>
<td>~</td>
<td>Z=R</td>
<td>Z'=R,Z''=0</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant phase element</td>
<td>→→→</td>
<td>Z=1/[T(i×ω)^p] (^b)</td>
<td>CPE-T, CPE-P</td>
</tr>
<tr>
<td>Wo</td>
<td>Warburg resistance, open circuit terminus</td>
<td>Wo</td>
<td>Z=R×ctnh([(iTω)^p]/(iTω)^p)</td>
<td>Wo-R, Wo-T, Wo-P</td>
</tr>
</tbody>
</table>

\(^a\) These elements and their symbols appear in the high resistance circuit model in Figure 5.6 and in the low resistance circuit model in Figure 5.8.

\(^b\) \(ω = 2\pi f\). f = frequency.
Figure 5.4 Simulation profiles of individual elements: (A) resistor; (B) CPE; (C) Ws and (D) Wo.
5.4.1 Cells at DOD = 0 % state

5.4.1.1 High resistance model

Figure 5.5 EIS spectra of CFx23-5-1 and their fitting profiles.
The EIS spectra and the simulation profiles of the first discharge (CFx23-5-1) of the test cell CFx23-5 were displayed as different color curves in the three plots in Figure 5.5. This cell was made from un-reduced CFx plus 8.5 wt % added carbon particles. The suffix -1, which is attached to the cell number CFx23-5 in Figure 5.5 represents the first discharge reaction of this cell (at DOD = 0 % state). This experimental data was fitted using the equivalent high resistance circuit model. In the Nyquist plot (A), point (a) (c. f. Figure 5.3) appears at $Z' = 19.3 \, \Omega / Z'' = 4.9 \, \Omega$; point (c) is at $Z' = 9929.0 \, \Omega / Z'' = 4738.5 \, \Omega$ but point (b) is not clear. In the upper Bode plot (B), the values of $|Z|$ are 11002.0 $\Omega$ at $10^{-2} \, \text{Hz}$ and 19.9 $\Omega$ at 65,535 Hz. In the lower Bode plot (C), the values of $\theta$ are $-25.5^\circ$ at $10^{-2} \, \text{Hz}$, $-39.3^\circ$ at 207.2 Hz and $-14.3^\circ$ at 65,535 Hz.
The equivalent circuit model at the top of Figure 5.6 was chosen by the computer software where $R_b$ reflects the basic Ohmic resistance of the cell, $R_1$ reflects the Faradaic (C-F bond breaking) resistance $R_F$, $R_{ct}$ reflects the charge transfer resistance and $W$ reflects the Warburg resistance $R_w$. The term CPE is defined as the “constant phase element” reflecting distributed (deformed) capacitors. CPE1 reflects the intercalation capacitance, $C_{ic}$, and CPE2 reflects the double layer capacitance, $C_{dl}$.

The CPEs have two terms: CPE-T and CPE-P. CPE-T represents the capacitance in farads (F) and CPE-P is a unit-less exponential term representing the character of this element. That is, when CPE-P approaches 1, the element will behave close to that of an ideal capacitor. However, when CPE-P approaches 0, the element will act close to that of an ideal resistor.

Figure 5.6 The equivalent high resistance circuit model and fitting data of CFx23-5-1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Freedom</th>
<th>Value</th>
<th>Error</th>
<th>Error %</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_b$</td>
<td>Free(t)</td>
<td>15.82</td>
<td>0.30686</td>
<td>1.9387</td>
</tr>
<tr>
<td>$R_1$</td>
<td>Free(t)</td>
<td>54.48</td>
<td>6.6995</td>
<td>12.297</td>
</tr>
<tr>
<td>$R_{ct}$</td>
<td>Free(t)</td>
<td>5808</td>
<td>187.54</td>
<td>3.2301</td>
</tr>
<tr>
<td>CPE2-T</td>
<td>Free(t)</td>
<td>0.00013426</td>
<td>2.7481E-06</td>
<td>2.0468</td>
</tr>
<tr>
<td>CPE2-P</td>
<td>Free(t)</td>
<td>0.58071</td>
<td>0.005944</td>
<td>1.0236</td>
</tr>
<tr>
<td>CPE1-T</td>
<td>Free(t)</td>
<td>5.0124E-08</td>
<td>1.1581E-08</td>
<td>23.105</td>
</tr>
<tr>
<td>CPE1-P</td>
<td>Free(t)</td>
<td>0.88734</td>
<td>0.028502</td>
<td>3.2861</td>
</tr>
<tr>
<td>W-R</td>
<td>Free(t)</td>
<td>13308</td>
<td>608.02</td>
<td>4.5688</td>
</tr>
<tr>
<td>W-T</td>
<td>Free(t)</td>
<td>90.43</td>
<td>6.9333</td>
<td>7.667</td>
</tr>
<tr>
<td>W-P</td>
<td>Free(t)</td>
<td>0.48292</td>
<td>0.0081342</td>
<td>1.7537</td>
</tr>
</tbody>
</table>

Chi-Squared: 6.7948E-05
Weighted Sum of Squares: 0.008833
The W has three terms, W-R, W-T and W-P. The W-R represents the Ohmic resistance part of this element (in units of Ω) and W-T represents either the capacitance (in units of F) or the time constant (in units of s that equals RC) of the capacitance part of this element. Finally, W-P is a unit-less exponent term representing a character that is between an ideal capacitor (1) and an ideal resistor (0).

The Chi-Squared ($\chi^2$) and the Weighted Sum of Squares are two indicators representing how close the model fits in the experimental spectra. In an ideal fitting situation, the sweep curves and the fitting curves, profiled in the Nyquist and the Bode plots, will superimpose. In this case, the Chi-Squared and the Weighted Sum of Squares approach infinitesimally small values. In this research Chi-Squared is used as the measure of fitting in the text and both values are given in the figures.
5.4.1.2 Low resistance model

Figure 5.7 The EIS spectra of RCF10-6-1 and their simulation profiles.
The EIS spectra of the first discharge reaction (RCF10-6-1) of the cell RCF10-6 and their simulation profiles were displayed as different color curves in Figure 5.7. This cell was made from reduced CFx (with equivalent 2.15 wt % carbon). In the Nyquist plot (A), point (a) (c.f. Figure 5.3) is at $Z' = 19.1 \Omega$, $Z'' = -3.4 \Omega$; point (b) is at $Z' = 1038.3 \Omega$, $Z'' = -280.1 \Omega$ and point (c) is at $Z' = 2983.9 \Omega$, $Z'' = -4285.1 \Omega$. In the upper Bode plot (B), the values of $|Z|$ are 5221.7 Ω at $10^2$ Hz and 19.4 Ω at 65,535 Hz. In the lower Bode plot (C), the values of $\theta$ are $-55.2^\circ$ at $10^2$ Hz, $-45.3^\circ$ at 260.9 Hz, $-39.9^\circ$ at 207.2 Hz and $-10.2^\circ$ at 65,535 Hz.

In Figure 5.8, the equivalent low resistance circuit model was chosen by the computer software where every element remains similar to that of the high resistance model with two exceptions: (1) $R_{cr}$ represents the cell reaction resistance that is a
combination of the charge transfer resistance ($R_{ct}$) and the Faradaic resistance ($R_F$). (2)
CPE1 represents all the capacitances in the cell.

### 5.4.1.3 Tabulated data and analyses

![Equivalent circuits](image)

Figure 5.9 The equivalent circuits for the high (A) and the low (B) resistance model.

<table>
<thead>
<tr>
<th>EIS sweep # (DOD = 0 %)</th>
<th>C (wt %)</th>
<th>$\rho$ (Ωm) (3000 psi)</th>
<th>$\chi^2$</th>
<th>$R_b$ (Ω)</th>
<th>$R_1$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>$R_w$ (Ω)</th>
<th>CPE1 - T (F)</th>
<th>CPE1 - P (exp.)</th>
<th>RCF17-4-1&lt;sup&gt;a&lt;/sup&gt;</th>
<th>5.5E3</th>
<th>5.5</th>
<th>9.4</th>
<th>885.5</th>
<th>2.1E5</th>
<th>2.0E-5</th>
<th>0.83</th>
<th>6.3E-5</th>
<th>0.54</th>
<th>1.2E3</th>
<th>0.70</th>
<th>0.50</th>
<th>2.0</th>
<th>21.2</th>
<th>8.4</th>
<th>11.8</th>
<th>2.0</th>
<th>3.4</th>
<th>1.8</th>
<th>15.8</th>
<th>14.7</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFx22-8-1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>6.5</td>
<td>613.0</td>
<td>6.8</td>
<td>14.6</td>
<td>334.2</td>
<td>2.3E4</td>
<td>2.2E-5</td>
<td>1.05</td>
<td>1.2E-4</td>
<td>0.53</td>
<td>3.4E4</td>
<td>65.8</td>
<td>0.50</td>
<td>1.5</td>
<td>142.9</td>
<td>20.0</td>
<td>49.0</td>
<td>7.5</td>
<td>3.2</td>
<td>6.2</td>
<td>8.4</td>
<td>14.2</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFx23-5-1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>8.5</td>
<td>10.0</td>
<td>0.68</td>
<td>15.8</td>
<td>54.5</td>
<td>5.8E3</td>
<td>5.0E-6</td>
<td>0.87</td>
<td>1.3E-4</td>
<td>0.58</td>
<td>1.3E4</td>
<td>90.4</td>
<td>0.46</td>
<td>1.9</td>
<td>12.3</td>
<td>3.2</td>
<td>23.1</td>
<td>3.3</td>
<td>2.0</td>
<td>4.6</td>
<td>7.7</td>
<td>1.8</td>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Error %                  |         |                         |         |          |          |            |          |             |              |            |        |      |       |         |         |       |     |          |          |         |      |           | |
|--------------------------|---------|--------------------------|---------|----------|----------|-------------|-----------|-------------|----------|----------|--------|----------|-----|-------|-----|---------|-----|-------|-----|---------|-----|-------|
| RCF17-4-1<sup>a</sup>   | 2.0     | 21.2                     | 8.4     | 11.8     | 2.0       | 3.4         | 1.8       | 15.8       | 14.7     | 3.0       |        |          |     |      |     |         |     |      |     |         |     |      |     |
| CFx22-8-1<sup>b</sup>   | 1.5     | 142.9                    | 20.0    | 49.0     | 7.5       | 3.2         | 6.2       | 8.4        | 14.2     | 1.3       |        |          |     |      |     |         |     |      |     |         |     |      |     |
| CFx23-5-1<sup>b</sup>   | 1.9     | 12.3                     | 3.2     | 23.1     | 3.3       | 2.0         | 1.0       | 4.6        | 7.7      | 1.8       |        |          |     |      |     |         |     |      |     |         |     |      |     |

<sup>a</sup> Obtained after soaking in N-methylpyrrolidine (NMP) for 2 weeks.

<sup>b</sup> The suffix number (–1) attached to a cell number indicates the first intermittent discharge reaction conducted on this cell.
Table 5.5  Fitting data from RCF10-6-1 (DOD = 0 %) employing the low resistance model.

<table>
<thead>
<tr>
<th>EIS sweep # (DOD = 0 %)</th>
<th>C (wt %)</th>
<th>ρ (Ωm) 3000 psi</th>
<th>χ² (E-4)</th>
<th>R₀ (Ω)</th>
<th>R_cr (Ω)</th>
<th>CPE1-T (F)</th>
<th>CPE1-P (exp.)</th>
<th>R_W-R (Ω)</th>
<th>R_W-T (s)</th>
<th>R_W-P (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCF10-6-1 a E 2.15</td>
<td>50.0</td>
<td>5.1 E-15</td>
<td>1.2E-5</td>
<td>6.2E-5</td>
<td>0.62</td>
<td>6.2E-3</td>
<td>0.38</td>
<td>8.43E-3</td>
<td>297.5</td>
<td>0.61</td>
</tr>
<tr>
<td>Error %</td>
<td>2.0</td>
<td>1.4</td>
<td>2.9</td>
<td>1.3</td>
<td>226.0</td>
<td>1.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a The suffix number (–1) attached to a cell number indicates the first intermittent discharge reaction conducted on this cell.

The high (A) and the low (B) resistance model’s equivalent circuits are displayed in Figure 5.9. Table 5.4 lists the fitting data from three EIS sweeps conducted on three cells (RCF17-4-1, CFx22-8-1 and CFx23-5-1), Table 5.5 lists the fitting data from one EIS sweep conducted on a reduced CFx cell (RCF10-6 with equivalent carbon of 2.15 wt %). These two tables divide the simulations into two different models represented by two different equivalent circuits (high and low resistance). Nevertheless, they still can be compared with respect to their common resistances and capacitances listed in Tables 5.1 and 5.2, respectively. That is, R₀ and R_W can be compared directly; R_cr can be compared with the sum of R₁ and R_ct and CPE1 in the low resistance model can be compared with the sum of CPE1 and CPE2 in the high resistance model.

The EIS sweeps of CFx cells with added carbon (CFx22-8 with 6.5 wt % and CFx23-5 with 8.5 wt %) fitted best to the high resistance model. The EIS sweep of the reduced CFx cell (RCF17-4) with a low equivalent carbon content (E 0.76 wt %) fitted best to the same high resistance model. This suggests that cells made from either un-reduced CFx plus C or a slightly reduced CFx have a high resistance in their initial (DOD = 0 %) state. However, the reduced CFx cell with a “higher” carbon content of E 2.15 wt % (RCF10-6) fitted best to the low resistance model with a simple equivalent circuit. Its
resistances associated with the discharge reaction (\(R_w\) and \(R_{ct}\) in the place of \(R_1 + R_{ct}\)) were orders of magnitude smaller than that of the other three cells. Furthermore, its intercalation capacitance, CPE1-T, was also smaller than the sum of the CPE1-T and CPE2-T values of any cell in the high resistance group. Finally, its Warburg capacitance (C) is worth considering. The Warburg capacitance can be calculated by dividing \(R_{w-T}\) by \(R_{w-R}\), according to the equation \(R_{w-T} = R_{w-R} \times C\). The Warburg capacitance of cell RCF10-6-1 (~0.45 mF) is much smaller than that (~1.9 mF) of cell CFx22-8-1 at DOD = 0 state.

This confirms that the small amount of surface graphitic carbon on the reduced CFx particles provided a better overall cathode conductivity than large amounts of added graphitic particles in the carbon-added CFx cells. This improved conductivity, in turn, lowered the cell reaction resistance, \(R_{ct}\), to a great extent. It seems possible that the surface graphitic carbon layer may have further enhanced Li\(^+\) ion diffusion in the CFx solid state, which would lower the intercalation-induced Warburg resistance (\(R_{w-R}\)) by a large magnitude, making the cell have a higher resistor character (lower capacitor character). This was reflected by its smaller \(R_{w-P}\) value (0.38) when compared with that of the high resistance model cells (0.46 -0.50).

The \(R_b\) values of these four cells were numerically similar because their components were assembled with the same procedure and sequence. These cells were filled with same electrolyte solution and equilibrated in the same manner.
A combined Nyquist plots of two cells at DOD = 0 % state. Cell CFx23-5-1 has 8.5 wt % added graphite while cell RCF10-6-1 has 2.15 wt % of equivalent graphitic carbon from solvated electron reduction.

The Nyquist plot of the reduced CFx cell (RCF10-6) with an equivalent carbon content of 2.15 wt % is compared with the Nyquist plot of the un-reduced CFx cell (CFx23-5) with a larger added carbon content of 8.5 wt % in Figure 5.10. The differences in their resistivity are clearly visualized in this figure.

The EIS sweep itself introduced a significant discharge reaction in the more conducting reduced CFx cell (RCF10-6). This discharge reaction is reflected in the Nyquist plot as an early depression in its profile around 1300 Ω on the Z’ axis (point “b”). A final low resistance of 2984 Ω was registered on the Z’ axis (point “c”). Conversely, the EIS sweep created only a minor discharge reaction in the poorly conducting un-reduced CFx cell (CFx23-5). This minor discharge reaction was reflected in the Nyquist...
plot as a barely noticeable late depression in its profile around 7000 Ω on the Z’ axis
(point “b”) and a final high resistance of 9929 Ω was registered on the Z’ axis (point “c”).

The slope’s value in the low frequency region in a Nyquist plot can be used to
indicate the electrochemical activity level of and the extent of Li⁺ ion diffusion into CFx
layers [28, 29 and 30]. A high slope means faster discharge reaction and faster Li⁺
intercalation. The reduced CFx cell (RCF10-6) with only 2.15 wt % of reduced carbon
content had a steeper slope than the un-reduced CFx cell (CFx23-5) with 8.5 wt % added
carbon particles, as can be seen in Figure 5.10. This shows that the graphitic carbon
surface in the reduced CFx particles supported a faster kinetic discharge reaction and
more efficient Li⁺ ion diffusion into the cathode.

Again, EIS studies clearly illustrated the advantage of the thin layer core-shell
morphology of the reduced CFx obtained from the partial Na/NH₃ reduction pre-
treatment as a cathode material in Li/CFx batteries over the conventional carbon-added
scheme.

5.4.2 Cells at DOD = 90 % state

Only one equivalent circuit model fitted to experimental results after all cells
reached a 90 % depth of discharge state. In each case it was the low resistance model that
fit the EIS sweeps (as in Figure 5.9). The 90 % depth of discharge state is represented
with a suffix (– x) attached to the cell number. These cells’ EIS spectra and their
simulation profiles were omitted from this Thesis for brevity. However, all the fitting
data were listed in Table 5.6.
Table 5.6  Fitting data of the low resistance model to the experimental EIS spectra from cells at DOD = 90 % state.

<table>
<thead>
<tr>
<th>EIS sweep # (DOD= 90 %)</th>
<th>C (wt %)</th>
<th>ρ (Ωm) (3000 psi)</th>
<th>$\chi^2$</th>
<th>$R_b$ (Ω)</th>
<th>$R_{cr}$ (Ω)</th>
<th>CPE1-T (F)</th>
<th>CPE1-P (exp.)</th>
<th>Rw-Rw-P (Ω)</th>
<th>Rw-P-P (s) (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFx22-8-6 a</td>
<td>6.5</td>
<td>613.0</td>
<td>27.9</td>
<td>9.51E-4</td>
<td>15.8</td>
<td>6.4E-5</td>
<td>0.78</td>
<td>42.7</td>
<td>12.1</td>
</tr>
<tr>
<td>Error %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CFx23-5-3 a</td>
<td>8.5</td>
<td>10.0</td>
<td>15.3</td>
<td>11.8</td>
<td>15.1</td>
<td>6.9E-5</td>
<td>0.78</td>
<td>44.8</td>
<td>14.0</td>
</tr>
<tr>
<td>Error %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCF10-6-4 a</td>
<td>2.15</td>
<td>50.0</td>
<td>23.4</td>
<td>13.8</td>
<td>18.7</td>
<td>11E-5</td>
<td>0.71</td>
<td>46.2</td>
<td>13.4</td>
</tr>
<tr>
<td>Error %</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*The suffix number (–x) attached to a cell number indicates the specific intermittent discharge reaction conducted on this cell.*

When the fitting data at the DOD = 90 % state (Table 5.6) is compared to those at the DOD = 0 % state (Tables 5.4 and 5.5), the internal resistances ($R_b$) of the three thermodynamically exhausted cells in Table 5.6 decreased a small amount (from 14.6 – 15.8 Ω to 9.5 – 13.8 Ω) after numerous intermittent discharges. This suggests that the only changeable variable in these cell’s internal resistances, the electrolytic resistance, decreased a large percentage (13 % - 53 %) in their magnitude over the course of discharges. This result is contrary to what is usually anticipated. Normally, as the insulating LiF salt product of the discharge reaction is added into the electrolyte, the electrolyte becomes more resistive rather than more conductive and the electrolytic resistance should have increased. Therefore, it seems likely that there may be one or more other factors that are causing this behavior.

The P terms of the two thermodynamically exhausted cells (CFx22-8-6 and CFx23-5-3 in Table 5.6) dropped slightly when compared to the P terms from their DOD = 0 % state. This is observed in both of the Warburg $R_w$-P (from ~ 0.50 to ~ 0.40) and the combined (CPE1-P + CPE2-P) capacitance P terms (from ~ 1.05 - 0.53 to 0.78).
likely due to the conductive carbon product obtained during the 90% discharge. The decrease in P terms made the two cells have a more resistor-like character. However, the P term of the reduced CFx cell (RCF10-6-4) rose slightly (from 0.62 to 0.71) and the Warburg R_w-P remained almost unchanged. The reduced CFx cell maintained lower P terms than those of the two un-reduced CFx cells.

The capacitances (CPE1-T) of the two thermodynamically exhausted cells (CFx22-8-6 and CFx23-5-3 in Table 5.6) dropped by half of their original values (from ~14 x 10^{-5} F to ~6 x 10^{-5} F) when compared to the combined capacitances (CPE1-T + CPE2-T) at their DOD = 0% state. However, the capacitance (CPE1-T) of the reduced CFx cell (RCF10-6-4) rose to about twice of its original value (from 6.2 x 10^{-5} F to 11 x 10^{-5} F) during the exhaust discharges. All the three cells in Table 5.6 ended at the same 10^{-5} F capacitance level. This suggests that the remaining 10% CFx core possibly created this capacitance, despite the fact that the un-reduced CFx cells used to have bigger capacitances at their DOD = 0% state. A poor distribution of the added conductive graphite particles in the un-reduced CFx cells would have contributed to the higher initial capacitance.

The cell reaction resistances (R_cr) of the three thermodynamically exhausted cells decreased dramatically (~1000 fold) when compared to the combination of the Faradaic (R_F) and the charge transfer resistance (R_ct) at the DOD = 0% state. All three cells in Table 5.6 ended at the same cell reaction resistance level (15.1 – 18.7 Ω), despite the initial differences of their conductive carbon’s origin (from reduction or added-in), resistance magnitude and the distinct intermittent discharge pathways. At this late discharge state, the initial lack of electronic conductivity was almost eliminated; the
charge transfer resistance ($R_{ct}$) would be negligible. It is likely that the Faradaic resistance ($R_F$) dominates this ($15.1 – 18.7 \ \Omega$) cell reaction resistance. Distinct kinetic discharge routes led these distinct cells to the same thermodynamic (resistance) end.

The Warburg resistance ($R_{w-R}$) of these two un-reduced CFx cells in Table 5.6 dropped dramatically from $\sim 10^4 \ \Omega$ at DOD = 0 % (in Tables 5.4 and 5.5) to $\sim 40 \ \Omega$ after the exhaust discharge. On the contrary, that of the reduced CFx cell (RCF10-6) rose from 8 $\ \Omega$ to the same 40 $\ \Omega$ level. The surface conductive shell of the reduced CFx particles allowed easier Li$^+$ ion intercalation in the beginning, but the accumulation of the LiF salt layer around the reaction sites through a fast discharge slowed down the intercalation (hence the reaction rate). It takes time for the LiF salt layer to diffuse away from the cathode into the bulk of the electrolyte. Then the $R_{w-R}$ value will begin to decrease. On the other hand, Li$^+$ ions had to take a much longer pathway to intercalate into the remaining 10 % CFx core after exhaust discharge. This long distance intercalation would attribute to the resistance increase in the reduced CFx cell.

The time constant term ($R_{w-T}$) representing the Warburg capacitance is expressed in second (s) units. The Warburg capacitance ($R_{w-T}$) is equal to the Warburg resistance ($R_{w-R}$) multiplied by the Warburg capacitance ($R_{w-T} = R_{w-R} \times C$). When the Warburg capacitance is being considered, the $R_{w-R}$ term also has to be taken into consideration. Before its exhaust discharge, the reduced CFx cell (RCF10-6-1) in Table 5.5 had a smaller Warburg capacitance (0.45 mF) than that of the two un-reduced CFx cells ($\sim 2$ to 7 mF) in Table 5.4. After the exhaust discharge, the Warburg capacitance of the three cells all ended at the same level of $\sim 0.3$ F. This was a thousand-fold increase in their Warburg capacitances. During the course of the discharge, the LiF reaction product had
accumulated around the reaction sites at CFx particles, creating a wider gap between the intercalated Li⁺ cations and their BF₄⁻ counter anions. Since capacitance is governed by the total charges separated and the distance of the separation, these cells’ Warburg capacitances were increased by the insulating LiF salt layer. Additionally, the intercalated Li⁺ cations inside the residual 10 % CFx core were further separated from their BF₄⁻ counter anions by the newly formed 90 % graphitic shell, because the smaller Li⁺ cations could move faster than the larger BF₄⁻ anions in the limited spaces between puckered CFx sheets. This physical separation of these counter ions may have caused the huge Warburg capacitance increase between the different depths of discharge (DOD) states of the three cells.

### 5.5 Analyses of EIS studies on the same cells at different DOD states

The fitting data from the same cells (CFx22-8, CFx23-5 and RCF10-6) at different discharge states are tabulated through Tables 5.7 to 5.9. The 0 % depth of discharge state is represented by a suffix (– 1) attached to a cell number; the 90 % depth of discharge state is represented by a suffix (- 3, - 4 or - 6) attached to a cell number.

#### Table 5.7  Fitting data from the un-reduced CFx cell (CFx22-8) at 0 and 90 % DOD states.

<table>
<thead>
<tr>
<th>EIS sweep #</th>
<th>C (wt %)</th>
<th>ρ (Ωm) (3000 psi)</th>
<th>$\chi^2$ (E-4)</th>
<th>$R_b$ (Ω)</th>
<th>$R_1$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
<th>CPE1-T (F)</th>
<th>CPE1-P (exp.)</th>
<th>CPE2-T (F)</th>
<th>CPE2-P (exp.)</th>
<th>$R_{W-R}$ (Ω)</th>
<th>$R_{W-T}$ (s)</th>
<th>$R_{W-P}$ (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFx22-8-1</td>
<td>6.5</td>
<td>613.0</td>
<td>6.8</td>
<td>14.6</td>
<td>334.2</td>
<td>2.3E4</td>
<td>2.2E-5</td>
<td>1.05</td>
<td>0.53</td>
<td>13.7</td>
<td>0.16</td>
<td>0.42</td>
<td></td>
</tr>
<tr>
<td>CFx22-8-6</td>
<td>6.5</td>
<td>613.0</td>
<td>7.9</td>
<td>9.51</td>
<td>36.2</td>
<td>4.6E-5</td>
<td>0.70</td>
<td>13.7</td>
<td>0.16</td>
<td>0.42</td>
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</table>
Table 5.8 Fitting data from the un-reduced CFx cell (CFx23-5) at 0 and 90 % DOD states.

<table>
<thead>
<tr>
<th>EIS sweep # (DOD = 0 %)</th>
<th>C (wt %)</th>
<th>ρ (Ωm) (3000 psi)</th>
<th>χ² (E-4)</th>
<th>R_b (Ω)</th>
<th>R_1 (Ω)</th>
<th>R_cr (Ω)</th>
<th>CPE1-T (F)</th>
<th>CPE2-T (F)</th>
<th>CPE1-P (exp.)</th>
<th>CPE2-P (exp.)</th>
<th>R_W-R (Ω)</th>
<th>R_W-T (s)</th>
<th>R_W-P (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CFx23-5-1</td>
<td>8.5</td>
<td>10.0</td>
<td>0.68</td>
<td>15.8</td>
<td>54.5</td>
<td>5.8E3</td>
<td>0.87</td>
<td>0.58</td>
<td>1.3E-4</td>
<td>0.46</td>
<td>90.4</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>CFx23-5-3</td>
<td>8.5</td>
<td>10.0</td>
<td>15.3</td>
<td>11.8</td>
<td>15.1</td>
<td>6.9E-5</td>
<td>0.78</td>
<td>44.8</td>
<td>14.0</td>
<td>0.40</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.9 Fitting data from the reduced CFx cell (RCFx10-6) at 0 and 90 % DOD states.

<table>
<thead>
<tr>
<th>EIS sweep # (DOD = 0 %)</th>
<th>C (wt %)</th>
<th>ρ (Ωm) (3000 psi)</th>
<th>χ² (E-4)</th>
<th>R_b (Ω)</th>
<th>R_cr (Ω)</th>
<th>CPE1-T (F)</th>
<th>CPE1-P (exp.)</th>
<th>R_W-R (Ω)</th>
<th>R_W-T (s)</th>
<th>R_W-P (exp.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RCF10-6-1</td>
<td>2.15</td>
<td>50.0</td>
<td>5.11E15.61</td>
<td>6.2E-5</td>
<td>0.62</td>
<td>8.438E-3</td>
<td>0.38</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCF10-6-4</td>
<td>2.15</td>
<td>50.0</td>
<td>23.4</td>
<td>13.8</td>
<td>11E-5</td>
<td>0.71</td>
<td>46.2</td>
<td>13.4</td>
<td>0.39</td>
<td></td>
</tr>
</tbody>
</table>

After the 90 % discharge, the internal resistance (R_b) of all the three cells did not change much as expected, as shown in Tables 5.7 through 5.9. They appear to have varied slightly. The reaction related resistances (R_1, R_cr and R_cr) of the three cells decreased by ~ a thousand fold. Since the value of the Faradaic resistance (R_F, shown as R_1) can not change by its nature, the only variable that would be changing during the course of discharge was the charge transfer resistance (R_cr) that was dominated by an initial lack of electronic conductivity. So, the cell reaction resistance (R_cr) dropped...
substantially as a consequence of the production of the conductive graphitic carbon shell. That alleviated the lack of conductivity, as the discharge reaction proceeded.

The Warburg resistance ($R_w$-$R$) decreased by orders of magnitude in the unreduced CFx cells, but increased by ~5 fold in the reduced CFx cell during the discharges. In both cases, their $R_w$-$R$ values ended up within a fairly narrow range (14 - 46 $\Omega$). Two factors may have contributed to this phenomenon: (1) the poor initial conductivity at the beginning of the discharge and (2) the LiF salt layer-induced resistance’s domination in the end.

The Warburg capacitance ($R_w$-$T/R_w$-$R$) increased by 6 fold in CFx22-8 cell, 45 fold in CFx23-5 cell and 600 fold in RCF10-6 cell during the course of discharge. That is, the more conductive a cell was in the beginning, the more its Warburg capacitance increased in the end. It appears that better conductivity led to more efficient reactions and thicker LiF salt layer accumulation surrounding the reaction sites in the end. The combination of the insulating LiF layer and the newly formed graphitic shell creates a wider separation gap between the intercalated $Li^+$ cations and their $BF_4^-$ counter anions, boosting the Warburg capacitance dramatically by the end of the exhaust discharge.

The P-term values of the Warburg resistance ($R_w$-$P$) of the un-reduced CFx cells dropped by ~20 % in CFx22-8 cell (with 6.5 wt % added graphite) and by 15 % in CFx23-5 cell (with 8.5 wt % added graphite). However, the $R_w$-$P$ had a negligible ~3 % increase in the reduced CFx cell (RCF10-6). All of these cell’s $R_w$-$P$ ended up at the same level ~0.40. That is, the two un-reduced CFx cells acquired more resistor character and the reduced CFx cell acquired minor capacitor character through the exhaust discharge, despite their distinct differences in the beginning. It seems likely that the 10 %
CFx core residue present after discharge is responsible for the common 0.40 P-term value. The more conductive a cathode is, the lower the cell’s P-term value becomes and the more resistor-like a cell becomes.

The intercalation induced capacitance (CPE1-T) and the double layer induced capacitance (CPE2-T) were combined into one capacitance term (CPE1-T) at the end of the exhaust discharge in the two un-reduced CFx cells. The combined capacitance dropped by three fold in cell CFx22-8 and two fold in cell CFx23-5, respectively. The reduced CFx cell (RCF10-6) had only one capacitance term (CPE1-T). However, RCF10-6’s capacitance increased by ~ two fold during the exhaust discharge. Additionally, all these cell’s capacitances ended up at about the same level (5 – 11 x 10⁻⁵ F), despite of their vast differences in the beginning. This suggests that, as described in the previous section (5.4.2 Cells at DOD = 90 % state), the remaining 10 % CFx core seems responsible for the similar 5 -11 x 10⁻⁵ F capacitances, despite the fact that the un-reduced CFx cells used to have higher capacitances and the reduced CFx cell used to have lower capacitance at their 0 % DOD state.

It seems likely that the P terms of the combined capacitances (CPE1-P + CPE2-P) followed a similar decreasing trend in the un-reduced CFx cells and increasing trend in the reduced CFx cell during the course of exhaust discharge.

**5.6 Summary**

Electrochemical impedance spectroscopy (EIS) is a powerful technique to explore the electrochemical characteristics of Li/CFx battery cathode materials. It can unveil the hidden facts and the minute differences in various stages of discharge in distinct
electronic microstructures. This differentiates the use of EIS from simple resistance measurements (like resistivity tests on reduced CFx powder samples). Earlier in this Thesis it was shown that reduced CFx had much lower cathode resistances than CFx to which graphite particles were added, when the systems were measured at equal carbon contents. It has unique advantages which can not be easily replaced by other means of detection. EIS studies will allow one to probe such internal cell resistances and capacitances as $R_b$, $R_{cr}$, $R_F$, $R_{ct}$, $R_{w}-R$, CPE(s), $R_{w}-T$, depending on the model that best applies. These variables can also be probed as a function of depth of discharge (DOD).

In this chapter, EIS sweeps and simulation were used mainly to study cells from two distinct groups: two of the un-reduced CFx cells (CFx22-8 and CFx23-5) and one reduced CFx cell (RCF10-6). It was found that at their depth of discharge (DOD) = 0 % state, the reduced CFx cell (possessing an equivalent 2.15 wt % graphitic surface carbon) has only ~ 1/3 resistance that these un-reduced CFx cells have, despite the fact that these un-reduced CFx cells have a higher added graphite content (6.5 wt % in CFx22-8 and 8.5 wt % in CFx22-8).

To take a look at how a reduced CFx cathode (2.15 wt % equivalent C) compared to un-reduced CFx with 8.5 wt % of added graphite, a table was constructed showing how the values for the individual resistances and capacitances varied as these cells were taken from 0 % to 90 % depth of discharge. Thus, Table 5.10 was constructed from selected data of Tables 5.8 and 5.9 to highlight the properties before and after a 90 % discharge.
Table 5.10 Properties of selective cells at 0 % and 90 % states.

<table>
<thead>
<tr>
<th>Cells of different cathode materials</th>
<th>Variables</th>
<th>Unit</th>
<th>DOD states</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>0 %</td>
</tr>
<tr>
<td>Reduced CFx (E 2.15 wt % graphite)</td>
<td>( R_b )</td>
<td>( \Omega )</td>
<td>15.6</td>
</tr>
<tr>
<td>Un-reduced CFx (8.5 wt % added graphite)</td>
<td>( R_{cr} )</td>
<td>( \Omega )</td>
<td>1.2\times10^3</td>
</tr>
<tr>
<td>Reduced CFx (E 2.15 wt % graphite)</td>
<td>( R_{ct} )</td>
<td>( \Omega )</td>
<td>5.8\times10^3</td>
</tr>
<tr>
<td>Un-reduced CFx (8.5 wt % added graphite)</td>
<td>( R_{w-R} )</td>
<td>( \Omega )</td>
<td>8.4</td>
</tr>
<tr>
<td>Reduced CFx (E 2.15 wt % graphite)</td>
<td>CPE1-T</td>
<td>F</td>
<td>6.2\times10^{-5}</td>
</tr>
<tr>
<td>Un-reduced CFx (8.5 wt % added graphite)</td>
<td>CPE1-T + CPE2-T</td>
<td>F</td>
<td>1.3\times10^{-4}</td>
</tr>
<tr>
<td>Reduced CFx (E 2.15 wt % graphite)</td>
<td>( R_{w-P} )</td>
<td>n/a</td>
<td>0.38</td>
</tr>
<tr>
<td>Un-reduced CFx (8.5 wt % added graphite)</td>
<td></td>
<td></td>
<td>0.46</td>
</tr>
</tbody>
</table>

Table 5.10 reveals the advantages of the reduced CFx over un-reduced CFx plus graphite at DOD = 0 % state determined by EIS. These advantages are: 1) smaller cell reaction resistance (\( R_{cr} \) or \( R_1 + R_{ct} \)), 2) smaller mass transport resistance (\( R_{w-R} \)), 3) smaller double-layer/intercalation induced capacitances (CPE1-T or CPE1-T + CPE2-T) and 4) higher resistor characteristics (lower \( R_{w-P} \) value). (Other factors like the load density and the distribution of the added graphite in cathode may have also contributed to alter their properties.)

Two points of interest emerge on examining Table 5.10. The cell with the reduced CFx cathode keeps the same degree of resistive nature during the discharge (\( R_{w-P} \) goes from 0.38 to 0.39). However, the un-reduced CFx/8.5 wt % added graphite cell moves to a more resistive (less capacitor-like) nature during discharge (\( R_{w-P} \) goes from 0.46 to 0.40). The second point is quite pronounced. The \( R_{w-R} \) resistance of the reduced CFx cell is low to start with (8.4 \( \Omega \)) and increases to 46.2 \( \Omega \) during discharge. In stark contrast, the un-reduced CFx/added graphite cell has a huge initial resistance (1.3 \( \times 10^4 \) \( \Omega \)) which
sharply decreases to 44.8 Ω during discharge. The physical meaning of this is that there is a very high initial barrier to lithium ion mass transport in the un-reduced CFx cathode. Only after significant discharge does this barrier drop to that of the reduced CFx cell. This point may be related to the intimate contact between the shell-like carbon layer and the underlying CFx/C partially reduced interface to the core CFx.

Conclusions drawn from these cells’ property changes in Table 5.10 during an exhaust discharge are listed in Table 5.11.

Table 5.11 Cells’ property changes during an exhaust discharge.

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>Changes (from 0 % to 90 % DOD state)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Basic resistance (R_b)</td>
</tr>
<tr>
<td>Reduced CFx (with 2.15 wt % equivalent graphite)</td>
<td>decreased</td>
</tr>
<tr>
<td>Un-reduced CFx (with 8.5 wt % added graphite)</td>
<td>decreased</td>
</tr>
</tbody>
</table>

After the exhaust discharge, all the three cells (CFx22-8, CFx23-5 and RCF10-6) had their cell reaction resistances greatly decreased to a very similar level (15 - 36 Ω). Their double layer/intercalation capacitances also ended up at similar levels (46 - 110 μF). Moreover, their Warburg resistances ended at similar values (14 - 46 Ω) and their Warburg capacitances had significantly risen and reached similar values (~ 0.3 F). In other words, distinct kinetic discharge routes led initially distinct cells to the same thermodynamic end level.
When the three cells were compared to themselves between 0 % and 90 % depth of discharge states, it was found that the reaction resistance decreased dramatically, the double layer/intercalation capacitances did not change much, the Warburg resistance changed greatly and the Warburg capacitance rose to a significant extent with a slight character variation. All the cell’s internal resistances were similar and changed only a small amount over the course of the exhaust discharge.

It is therefore concluded that the reduced CFx with a thin layer core-shell morphology affords a superior conductivity to the conventional carbon-added CFx as a cathode material in the Li/CFx batteries at a comparable graphitic carbon content. It was demonstrated through these EIS studies that the cell made from the reduced CFx has low cell reaction resistance, low intercalation/double layer capacitances and low Warburg resistance/capacitance. All the reduced and the un-reduced CFx cells ended up in a similar state of resistance and capacitance after the 90 % exhaust discharge reaction, despite of their distinctive pre-discharge states where the amounts, the origins and the distribution of the conductive graphite were fundamentally different.
CHAPTER VI

CONCLUSIONS

Partially reduced CFx has superior electrical conductivity to un-reduced CFx with added graphite powder as the cathode material in primary Li/CFx batteries, at comparable carbon content.

Partially reduced CFx was obtained from a stoichiometrically controlled partial reduction pre-treatment of pure CFx via a Na/NH$_3$(ℓ) solvated electron reduction. A reduction extent that leaves an equivalent graphitic carbon content above 2 wt % is considered to be appropriate for a CFx cathode starting material with a median particle size of 6 µm. This reduced CFx can sustain a large current which enable a cell to achieve the goal of a specific energy of 600 Wh/kg and of specific power of 50 W/kg. By eliminating the need for adding a substantial amount of added graphite powder, the use of reduced CFx gives higher capacities per unit cathode weight and per unit volume.

Partially reduced CFx is darker than CFx even at low reduction stoichiometries. The dark color is believed to come from both the graphite formed on its surface and the agglomeration of its particles via π-π interactions between graphitic carbon-sites derived from the reductive reaction. The agglomeration takes place immediately after reduction as well as during subsequent processing. This particle-particle adhesion may introduce another major advantage to reduced CFx as a cathode material. It seems likely that the
need for an added binder is eliminated. This can contribute to a higher capacity per unit weight.

Partially reduced CFx, as a cathode material in Li/CFx batteries, exhibited a superior kinetic performance (current density) to the conventional carbon-added CFx batteries at equivalent carbon contents. Cells made with reduced CFx cathodes of same thickness and same material quantity surpassed those cells made of the conventional unreduced CFx plus carbon cathodes in Galvanostatic discharge performances with a higher voltage benchmark of the upper voltage window (UVW) at equivalent carbon contents.

Partially reduced CFx is proposed to have core-shell morphology. The carbon formed an aromatic, conductive graphene sheet at reduction sites which occurred on the outer surfaces of CFx particles, while the core composition of CFx particles remained intact. Whether the surfaces were completely or partially covered with these graphitic layers was not definitively established, but clearly percolation pathways were established throughout the cathode. These conductive graphitic sites supported large currents through the cathode in discharge tests without the need of adding any conductive additive(s).

Raman spectra demonstrated that basal planes of the reduced CFx (fluorinated carbon provided by FluorStar™) possessed large amounts of defect sites where carbon atoms were not $sp^2$-hybridized.

Despite the kinetic advantage the reduced CFx can offer, the batteries it afforded still suffered from the same voltage delay problem as the conventional carbon-added CFx does. The non-conductive nature of CFx, which provides these cells’ capacity, remains unchanged. The basic resistance of this portion of the cell remains unchanged; breaking
C-F bonds still must overcome the same energy barrier and LiF insulating layer still accumulates during the course of discharge. These are probably the root causes of the problems that Li/CFx batteries made of reduced CFx cathodes are still facing.

The proposed core-shell morphology of reduced CFx has not yet been characterized through visualization under a microscope, with the help of a fluorophore or a special liquid with a large refractive index. A suitable fluorophore should be a small molecule with a long excitation wavelength and a large gap between its excitation/emission bands. Furthermore, a high-yielding grafting reaction of the fluorophore would be advantageous. The microscope up to this demand should have a large magnification power to tell the differences between edge and basal planes of a particle with a median size as small as 6 µm. As for the particles, they should have perfect crystalline structure aligned at their outer surfaces; any defect site would blur the image at focus plane and confuse an inexperienced observer.

Future characterization work on reduced CFx should be employing XPS to probe its alleged core-shell morphology and sliced reduced CFx particles should be examined across their cross sections by TEM.
REFERENCES


[23] Ekta Goel, A lithium-ion test cell for characterization of electrode materials and solid electrolyte interphase, Mississippi State University, Mississippi State, MS 39762, **2008**.


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