Pseudocapacitors for Energy Storage

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Pseudocapacitors for Energy Storage

by

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Abstract

Fluctuation in the demand for electrical power and the intermittent nature of the supply of energy from renewable sources like solar and wind have made the need for energy storage a dire necessity. Current storage technologies like batteries and supercapacitors fall short either in terms of power output or in their ability to store sufficient energy. Pseudocapacitors combine features of both and offer an alternative to stabilize the power supply. They possess high rates of charge and discharge and are capable of storing much more energy in comparison to a supercapacitor. In the quest for solutions that are economical and feasible, we have investigated Prussian Blue in aqueous electrolytes for its use as a pseudocapacitor. Two different active materials based on Prussian Blue were prepared; one that has just Prussian Blue and the other that contains a mixture of Prussian Blue and carbon nanotubes (CNTs). Four electrolytes differing in the valence of the cation were employed for the study. Cyclic voltammetry and galvanostatic charge-discharge were used to characterize the electrodes. Our experiments have shown specific capacitances of Prussian Blue electrodes in the range of 140-720 F/g and that of Prussian Blue-CNT electrodes in the range of ~52 F/g. The remarkable capacity of charge storage in Prussian Blue electrodes is attributed to its electrochemical activity ensuring surface redox and its tunnel-like structure allowing ease of entry and exit for ions like Potassium. Simple methods of synthesis have yielded specific capacitances of the order of hundreds
of Farads per gram showing that Prussian Blue has promise as an electrode material for applications needing high rates of charge-discharge.


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Chapter 1

1.1. Energy Storage

Access to electricity is a basic need in today’s lifestyle. It is in this regard that energy storage plays a significant role. Electrical power is generated in power plants and transmitted to households and industries through electrical grids.

The amount of power generated and consumed varies with time, hence storage elements have to bridge the gap. Since consumption is not at a constant level through the day or even through a year due to seasonal changes, production has to follow the load to keep the demand-supply gap at a minimum. Power plants differ in their source of energy, output capacity, response time to demand, rates of efficiency, duration of operation, infrastructure and costs of installation and operation. There are four main categories of power plants [1]:-

1. Base load power plants
2. Peaking power plants
3. Load following power plants
4. Intermittent power plants

Base load power plants are large both in terms of size and output capacity. Their energy source is usually a fossil fuel or nuclear fission. They are in general more efficient and easy to manage when made to produce a constant power. [2] Peaking power plants on the other hand are more expensive to operate but can vary output at a short notice. Gas turbines and generators fall in this category. These are not
operational year round though. A third category is the load following power plants whose response to changes in demand is intermediate between the base load and peaking power plants. They supply additional power during peak times because of their ability to cut short their output during the low demand period. Examples are hydroelectric power plants. Intermittent power plants are run on wind and solar and the output is decided based on the availability of the source, strong winds and sunlight. Base load plants that comprise a big majority in power generation require the presence of good storage to assist in reserving excess energy which can be recalled for future use. The case for intermittent power is similar in the sense that there may not necessarily be sufficient load to dissipate power at the time of distribution. Presence of wind and solar power is imperative in the long term and it can be made feasible only when there is reliable storage. Preferred features of storage in power plants include ability to manage high power, retain the energy for a considerable period of time, and give back most of the stored energy. Energy storage has applications outside the grid too. [3] These are –

- Provide backup in the case of power failures.
- Handle power surges or voltage spikes which might damage sensitive equipment at the consumer end.
- Provide reliable power for consumers who are off-grid.

While multiple technologies exist in the storage elements, our work mainly explores electrochemical energy storage, pseudocapacitor storage in particular, for its fast response and considerably large storage capability.
1.2. Types of Capacitor Energy Storage

Capacitive energy storage has the advantage of delivering high power in comparison to batteries which store relatively more energy. Simultaneous use of both types of storage elements help maintain a balance between the amount of energy stored and delivered per unit time. Capacitors differ in their structure, mode of operation, capacitance and life cycle. They are classified as Electrostatic, Electrolytic, Electrical Double Layer and Pseudocapacitor.

1.2.1. Electrostatic Capacitor

An Electrostatic capacitor is formed by two metal plates separated by a dielectric of permittivity $\varepsilon$, as shown in Figure 1.2.1.
It stores energy in the form of electrostatic field between the plates. On connecting a capacitor to an external voltage source, current flows and charges accumulate on the plates increasing the potential difference across the plates. There is no current flowing between the plates. The voltage $V$ across the capacitor is related to the charge accumulated as follows [4,5]:

$$Q = CV,$$  \hspace{1cm} (1.1)

The current-voltage relationship in a capacitor is,

$$I = C \frac{dV}{dt},$$  \hspace{1cm} (1.2)

The proportionality factor $C$ is called as capacitance and is measured in Farads when $I$ is in Amperes and $dV/dt$ is in Volts per second. It is a function of the geometric dimensions of the capacitor and the permittivity of the medium separating the plates. Capacitance reflects the capacity of the device to hold charge. It is given by [5],

$$C = \frac{\varepsilon A}{d},$$  \hspace{1cm} (1.3)

Here, $A$ is the area of the plate, $d$ is the separation between the plates and $\varepsilon$ is the permittivity of the dielectric medium.

From equation 1.2 we see that when the voltage is changed at a steady rate, $dV/dt$ is a constant. Since the capacitance is a fixed quantity for a capacitor, a constant current flows in this situation. However, in a real capacitor the dielectric may have
a finite resistance resulting in a small amount of current flow between the plates. There may also be resistance in the leads and plates.

Figure 1.2.2 Equivalent electrical circuit of a real capacitor

Figure 1.2.2 shows the equivalent electrical circuit of a real capacitor. $R_{\text{parallel}}$ corresponds to the resistance in the dielectric and is usually very large. $R_{\text{series}}$ is small and corresponds to the resistance in the leads, plates and is introduced due to operating conditions. In general, we treat the non-ideal capacitor as a capacitor in series with a resistance known as the equivalent series resistance and the reduction of the equivalent circuit given in Figure 1.2.3.
A DC capacitor in the charged state becomes an open circuit because dV/dt is 0.

1.2.1.1. Charging and Discharging a Capacitor

When a capacitor is connected to a DC power supply, current flows through the circuit and charges are transported from one plate to another and they assume opposite polarities. Figure 1.2.1 illustrates the charging mechanism. Overall, the two plates together are electrically neutral. With the increase in the accumulation of charges the potential difference between the plates increases. This is the charging phase. The current that flows through the circuit starts from a maximum and falls to 0 once the capacitor is fully charged. The voltage begins at 0 and rises to a potential difference of V depending on the medium between the plates and their geometry.

The energy stored in the capacitor is given by [5],

\[ E = \frac{1}{2} CV^2, \]  (1.4)
It is the potential energy due to the separation of opposite charges.

In the discharging phase, the capacitor is connected across a load. Current flows through the circuit leading to a decrease in the potential difference between the plates as the stored charges are dispersed and the plates individually attain electrical neutrality. Variation of the current and voltage with time for the charge and discharge phases are present in Figure 1.2.4.

![Image of Figure 1.2.4 Variation of Voltage and Current with time during charging and discharging of a capacitor [6]](image)

**1.2.2. Electrolytic Capacitor**

In this form of a capacitor, an electrolyte forms one electrode and a metal plate forms the other in analogy to the electrostatic capacitor. Two conducting media are required because presence of free carriers, electrons in the case of a metal, enable charging of the plates. For an electrolyte the free carriers are the ions. The electrolyte is either solid or liquid. An oxide layer on the metal plate acts as the
insulating layer between the plates. Oxide layers are formed by applying a voltage to the metal plate and the resulting thickness is determined by the voltage applied. Thus the plate separation can be controlled and higher capacitances relative to electrostatic capacitors can be obtained. The metal plate is also made to have a rough surface in order to increase the net surface area. Electrolytic capacitors are polarized in the sense that the leads always have to be connected the same way; the potential difference cannot change sign. Figure 1.2.5 shows an electrolytic capacitor.

1.2.3. Electrical Double Layer Capacitor (EDLC)

A single cell has two electrodes separated by an electrolyte.
Charge is stored at the interface of the electrode and electrolyte by electrostatic means. Opposite charges reside on 2 different layers which explains the origin of the name. One set resides on the electrode and the other on the electrolyte as depicted in Figure 1.2.6. There is not a dielectric medium of the sort present in the electrostatic and electrolytic capacitors. But the operating voltage is limited by the stability of the electrolyte. A potential difference develops across the double layer. The charge separation is of the order of a few Angstroms. High surface area materials are used for making the electrodes and from equation 1.3 we can see that these capacitors possess high specific capacitances in comparison to the previous capacitors of similar dimensions. Surface area $A$ on the numerator is
large and the electrode separation \( d \) on the denominator is very small rendering the net ratio a large value.

Charging of an uncharged EDLC, its completely charged state and its discharging are illustrated in Figure 1.2.7. On applying a voltage between the electrodes, ions of the electrolyte are absorbed on to the surface of the electrode of opposite polarity, thus generating a double layer at both the electrodes. On replacing the voltage source with a load, ions diffuse back into the electrolyte. Aqueous or organic electrolytes are employed. Figure 1.2.8 shows the voltage distribution across a cell of a charged EDLC and the equivalent electrical circuit. Since there is a capacitance associated with charge separation, both electrodes will then contribute resulting in \( C_1 \) and \( C_2 \) shown in Figure 1.2.8. And they are connected in series. Here as well there is a series resistance because of the resistance offered at the current collectors \( R_1 \) and \( R_2 \) and the internal resistance \( R_i \) which corresponds to ion movement within the electrolyte.
Figure 1.2.8 Voltage distribution across a charged EDLC and the equivalent electrical circuit [10]

Figure 1.2.9 Model illustrating the double layer capacitance [10]
To explain the double layer capacitance, the most commonly used model was put forth by Bockris, Devanathan and Muller [11] illustrated in Figure 1.2.9. The model considers three planes –

- Inner Helmholtz plane (IHP)
- Outer Helmholtz plane (OHP)
- Diffuse Layer

This model takes into account the polar nature of the solvents; water or organic liquids like methanol and acetonitrile. Dipoles in the solvent molecules interact with the charged electrode surface and orient themselves with the oppositely charged end nearer the electrode surface. There is a presence of specifically adsorbed ions of the electrolyte along this layer and they are partially solvated. It means that the ions are surrounded only in part by the solvent molecules as they have the electrode surface covering the other part. There is competition between the solvent molecules and the charged ions of the electrolyte for occupying the layer immediately adjacent to the electrode surface. The IHP comprises of a monolayer of the solvent molecules of the electrolyte forming the dielectric medium between the opposite charges. So it has a thickness of a single molecule. The OHP extends to the center of the charged ion from the electrolyte forming one layer of the double layer. There is a linear variation of the potential with distance along the Helmholtz plane. Outside this, the variation becomes exponential. The diffuse layer is in the bulk solution. Figure 1.2.10 depicts the variation of the potential across the double layer and in the diffuse layer. The double layer also termed as the Stern layer extends till the OHP.
The double layer capacitance is hence made up of capacitance of the Helmholtz plane/Stern layer and capacitance of the diffuse layer as a series connection also illustrated in Figure 1.2.10.

\[
\frac{1}{C} = \frac{1}{C_s} + \frac{1}{C_D},
\]

(1.5)

\(C_s\) is the capacitance of the Stern layer and \(C_D\) the capacitance of the diffuse layer.

As explained earlier, a single cell of the EDLC has two capacitors connected in series because of the formation of two parallel plate capacitor configuration at the electrodes. Figure 1.2.8 illustrates the series connection. Hence the net capacitance is the series sum of the capacitance at both the electrodes. Figure 1.2.11 shows another form of the equivalent circuit of an EDLC cell. \(R_p\) is the resistance of the insulating layer assumed to be large enough. Because there is a
capacitance and a resistance across the double layer and both are maintained at the same voltage, the circuit shows a parallel combination of $C_{dl}$ and $R_p$. Next, there is a resistance from the adjoining areas – electrolyte, electrode and current collectors and this is depicted as $R_s$. [13]

![Equivalent electrical circuit of an EDLC cell](image)

Figure 1.2.11 Equivalent electrical circuit of an EDLC cell [14]
1.2.4. Pseudocapacitor

A pseudocapacitor is a hybrid between a battery and an electric double layer capacitor. It also consists of two electrodes separated by an electrolyte. Charge storage occurs by chemical and electrostatic means.

Chemical process involves charge transfer by means of reduction-oxidation (redox) reactions. While the charge transfer is similar to that in a battery, transfer rates are higher because of use of thinner redox material on the electrode or lower penetration of the ions from the electrolyte into the structure. Because of multiple processes acting to store charge, the capacitance values are higher in pseudocapacitors. Figure 1.2.12 shows a cell of a Pseudocapacitor.

Figure 1.2.12 Pseudocapacitor exhibiting electric double layer and Faradaic reactions [15]
In the equivalent electrical circuit depicted in Figure 1.2.13, $C_\varphi$ is the pseudocapacitance that is dependent on the potential, $R_F$ is the electrode-electrolyte resistance and $R_D$ is the Faradaic resistance that may act during discharge when the ions desorb. At certain potentials, $C_\varphi$ may well exceed the double layer capacitance $C_{dl}$. The parallel combination of the capacitors help greatly build up the capacitance of pseudocapacitors because of the additive law of capacitance. [16]

1.3. Types of Electrochemical Energy Storage

Electrochemical energy storage devices employ the conversion between electrical and chemical energy. During charging electrical energy is stored in the device as chemical energy which is released to generate electrical energy upon discharging. Any electrochemical cell has two electrodes separated by an electrolyte. Electrochemical energy storage covers batteries and electrochemical capacitors which are further split into electrical double layer capacitor and pseudocapacitor. [17]
1.3.1. Battery

Perhaps the most commonly known form of a storage device, a battery stores charge by reduction and oxidation and/or intercalation of ions from the electrolyte into the electrode lattice. A cell comprises of 2 electrodes with an electrolyte separating the two. Rechargeable or secondary batteries can be charged and discharged multiple times unlike a primary battery. In a primary battery the reactions are not reversible and hence cannot be charged.

The reversible nature of reactions occurring in a secondary battery allows the storage of charge by supplying electrical energy from outside and can thus be used for multiple times. Electrodes in a secondary battery reverse roles during charging and discharging.

The electrolyte serves as a medium to transport ions of the electrolyte and/or the ions present in a host material of an electrode between the two electrodes in a cell. Two components get released on charge/discharge of a cell – an ion and an electron. The ion is directed to the other electrode by means of the electrolyte and the electron is sent to the external circuit.

Two types of chemical reactions occur at the electrodes –

- Insertion reactions
- Displacement reactions

Insertion reactions involve host materials on the electrode with a layered structure that allow the cation to be inserted or extracted reversibly. Insertion of the ion is referred to by the term intercalation. In a displacement reaction, a more active ion
replaces a less active one in a material. In Lithium ion batteries, insertion reactions occur at both the electrodes. Figure 1.2.14 shows the charging and discharging processes in a Lithium ion battery. The charging process takes out the Lithium from the cathode host material and inserts into the anode. Lithium ions travel through the electrolyte while the electrons take the path through the external load circuit to the anode. Discharging process reverses the role of the electrodes in the sense the electrode that allowed insertion will kick off the Lithium ions and the other electrodes will accept back the Lithium ions.

![Figure 1.2.14 Charging and Discharging of an intercalation driven battery](image)

Lithium based compounds capable of releasing and inserting Lithium in its lattice are usually used as cathode active materials. Anode materials are chosen for their large interlayer distances that allow ease of intercalation while displaying minimal
strain. Materials making up the electrodes should also be willing to accept the compensating electrons during intercalation that maintain the neutrality of the electrode. In the case of Lithium ion batteries, the electrolyte is a Lithium salt that does not contain water.

Most of the electrode participates in the process of storing charge and hence high energy densities can be achieved. Because of the same reason, charge-discharge rates are lower compared to capacitive storage. Intercalation also involves expansion of host lattice to let in multiple layers of the ion and this leads to eventual material degradation.

**1.3.2. Electrical Double Layer Capacitor**

An electrochemical cell of an EDLC stores energy by means of the electrostatic charge separation. Highly porous electrodes are employed to increase the surface area exposed to the electrolyte and hence increase the capacitance of the cell.

The speed of charge and discharge is limited to the speed with which the ions move within the electrolyte. Electrolytes of high ionic conductivity show faster charge-discharge abilities. The absence of chemical reactions or of any physical insertion of an ion into the structure of the electrode enables long cycle life. However, the same can prove to be a limitation in its ability to store large amounts of energy. EDLCs thus have high power densities, lower energy densities and longer cycle lives compared to batteries of similar dimensions.
Capacitive storage can help boost the power needs in distribution and storage of power while working in tandem with batteries. While there are many types of capacitors which differ in their modes of operation, electrochemical capacitors, pseudocapacitors in particular, lead the set in terms of capacitance per unit weight of the material. Next chapter will explain the third type of electrochemical storage, the pseudocapacitor, different phenomena contributing to pseudocapacitance and the current state of the art in pseudocapacitors technology. In chapter 3 we will explore the motivation for testing our chosen material, mechanisms in surface and bulk storage and techniques used in the characterization of electrodes. Chapter 4 will detail on the process followed for the experimental work, methods used for synthesizing the active material of the electrode, setup used for executing the experiments and the metrics and variables. Next, in chapter 5 we will go over the results obtained and explain them and challenges encountered in the process of designing experiments. Finally, we conclude in chapter 6 and project future work that can be done to further the current research.
Chapter 2

2.1 Pseudocapacitor

Formation of the electric double layer and insertion/adsorption of ions from the electrolyte into/onto the electrode accompanied by reduction-oxidation reactions make up the charge storage mechanism of a pseudocapacitor. The mechanism is of quasi two-dimensional nature and hence charge-discharge rates are comparable to the EDLCs. The occurrence of chemical reactions in addition helps to improve the capacitance values. Both cycle life and storage capacity fall intermediate between those of a battery and a supercapacitor.

2.2 Current State of the Art

Pseudocapacitance was discovered by Conway, Birss, Wojtowicz and Kozlowska in collaboration with Craig of Continental Group Inc. in 1975. [16,19] Being a relatively new invention, research is still ongoing towards identifying materials and electrochemical characteristics that can render high energy density at faster charge-discharge rates. To date, transition metal oxides have displayed pseudocapacitive behavior with high specific capacitance. Transition metals possess multiple oxidation states and it is this property that gains them favor for capacitive application. [20,21]

Ruthenium IV Oxide was the first material to exhibit this property and it has specific capacitance of 720 to 1340 F/g in water. It has three oxidation states within a potential of 1.2V. Limited occurrence and high costs inhibit further exploration of
the material. [20] Nickel cobaltite has displayed very high specific capacitances in the range of 330 F/g to 2680 F/g. Existence of multiple oxidation states for Nickel and Cobalt and high electrical conductivity boosts the capacitance. Moreover the ease of availability of both Nickel and Cobalt makes the substance all the more accessible. Nanowire arrays of Nickel Cobaltite prepared by a hydrothermal process exhibits the highest reported capacitance obtained at a current density of 2Ag^{-1} in PVA-KOH polymer gel as the electrolyte. The arrays were grown on Ni foam and had a mass loading of 3 mg cm^{-2}. [22] Nickel Cobaltite aerogels prepared through an epoxide-driven sol-gel procedure have a specific capacitance of 1400 F/g at a scan rate of 25 mV/sec in a potential window of 0.5V in 1M NaOH solution. The mass loading was at 0.4 mg cm^{-2}. Electrodeposition is also utilized in the synthesis of Nickel Cobaltite. [20,21] Cobalt Hydroxide synthesized by means of electrodeposition as an ordered mesoporous film on foamed Nickel mesh has a specific capacitance of 2646 Fg^{-1}. The film studied under electron microscopes exhibits a surface with interlaced nanosheet-like appearance, pores of nanometer dimension and a regular nanostructure with extended periodicity. [20,23] Amorphous Nickel Hydroxide nanospheres deposited on a graphite rod in 1M potassium hydroxide and cycled at current densities of 20-70 Ag^{-1} show specific capacitances between 1868 to 1330 Fg^{-1}. Irregular surfaces and amorphous character render such high capacitance. [20,24]

In the non-aqueous electrolyte category, Vanadium oxide aerogels immobilized on a sticky carbon electrode in 1M Lithium perchlorate in propylene carbonate gave
specific capacitance of 2150 F/g\(^{-1}\). The aerogels were prepared by ambient drying method. The drying was done with a low surface tension solvent at ambient pressure resulting in larger pores of 10-30nm size range. Large pores combined with significant pore volume improved the probability of electrolyte penetration. Electron, ion and solvent transport are enhanced by the choice of the current collector and the aerogel morphology ensuring shorter diffusion lengths. It has ion incorporation like a battery and response of a capacitor. [20,25]

Next, we review previous work on hexacyanometallates as electrodes. Copper ferrocyanide coated on silver disc and characterized in a 0.1M KOH electrolyte with cyclic voltammetry using a two-electrode setup was measured to have a cell capacitance of 5.8F. [26] Cobalt Hexacyanoferrate (CoHCF) synthesized as nanoparticles display a specific capacitance of 250 F/g when tested in 0.5M of Sodium Sulphate from cyclic voltammetry at a scan rate of 0.5mV/sec and galvanostatic charge-discharge at 1 A/g. The working electrode was composed of the active material blended with Super P carbon black and Polytetrafluoroethylene and loaded onto a Nickel foam substrate. The electrode can retain 93.5% of its capacitance after 5000 cycles of charge-discharge. Moreover when the CoHCF electrode is combined with a carbon black modified graphene as a negative electrode, the cell showed a working voltage of 2.4V in Sodium Sulphate. [27] Prussian Blue/reduced graphene oxide nanocomposites synthesized by reaction of a single-source precursor Potassium Ferricyanide with Polyvinylpyrrolidone in the presence of graphene oxide and adjusted to a pH of 2 was reported to have a
specific capacitance of 252 F/g when cyclic voltammetry was performed in 1M KNO3 between -0.2V and 0.8V at 10mV/sec. The mass ratio of potassium ferricyanide to graphene oxide is 1:2. The mass of the active material was adjusted to be 0.2mg. Porosity of graphene as a conductive matrix enabled faster electron transport and Prussian Blue nanocrystals interlocking in its sheets cut down the diffusion path for the electrolyte. [28] Nano-sized insoluble iron, nickel and cobalt hexacyanoferrates prepared by a co-precipitation method were reported to have a specific capacitance of 425 F/g, 574.7 F/g and 261.56 F/g respectively when tested at a current density of 0.2 A/g. [29]

2.3 Types of Pseudocapacitance

Pseudocapacitance is characterized by two-dimensional or near two-dimensional processes in storing charge. Three different mechanisms contribute towards pseudocapacitance - Underpotential Deposition, Redox, and Intercalation.

2.3.1 Underpotential Deposition

As the name suggests there is a deposition that occurs at potentials positive with respect to the Nernst potential. The deposition of a metal on to the electrode surface of another metal is at a reduction potential higher than that when it is deposited onto itself. The thickness of the deposit does not normally exceed a monolayer. The fractional surface coverage occurs over a continuous range of potentials. An example of Underpotential Deposition is the electrosorption of
hydrogen on platinum or lead on gold. The chemical reaction involving the deposition of lead on gold can be represented as [20]:

\[
2e + xPb^{2+} + Au \leftrightarrow Au \cdot xPb
\]

The reaction rates and the resulting surface structures depend on the nature and concentration of anions. Depending on the level of lattice match between the adsorbate and substrate, the structures of the substrate and the grown layers are in proportion. [30,19]

### 2.3.2 Redox Pseudocapacitance

The charge transfer between electrode and electrolyte occurs by means of redox reactions in the case of redox pseudocapacitance and hence Faradaic in nature. Redox reactions mean reduction-oxidation reactions. Both result in the change of oxidation state of the species involved. Reduction occurs when electrons are accepted and the oxidation state gets lowered. Oxidation indicates release of electrons and an increase in the oxidation state. For the case of ruthenium oxide (hydrated) which was first discovered to exhibit pseudocapacitance, redox occurred by accepting protons from the electrolyte and releasing them back to the electrolyte. While accepting protons it also takes in electrons and changes its oxidation state from +4 to +3. [31] Figure 2.3.1 illustrates the chemical process and the accompanying reaction. In the case of Prussian Blue, the redox in an electrolyte of Calcium salt can be represented as, [20,32]

\[
Fe^{III}_4[Fe^{II}(CN)_6]_3 + \delta Ca^{2+} + 2\delta e^- \rightarrow Ca^{2+}_\delta Fe^{III}_{4-2\delta}Fe^{II}_{2\delta}[Fe^{II}(CN)_6]_3
\]
The $\delta$ here represents the unknown amount of Ca$^{2+}$ ions getting adsorbed on the surface of the material. Because each calcium ion requires two electrons, $2\delta$ electrons hence have to come from the external circuit in this case. Depending on the $\delta$ quantity, the reduction of Fe$^{3+}$ to Fe$^{2+}$ proceeds.

$$\text{RuO}_x(\text{OH})_y + \delta \text{H}^+ + \delta \text{e}^- \leftrightarrow \text{RuO}_{x-\delta}(\text{OH})_{y+\delta}$$

The reactions are restricted to the surface of the electrode. Ions are adsorbed on to the surface of the electrode accompanied by the change in the oxidation state.

### 2.3.3 Intercalation Pseudocapacitance

Insertion of cations into the bulk lattice of a solid electrode is termed intercalation. There should be an appropriate number of electrons transferred to the host during insertion to maintain the electrical neutrality of the electrode. Conditions for intercalation to occur include: [33]
The host must contain a suitable reducing agent in order to aid in the intercalation of the incoming cation from the electrolyte and electron from the external circuit.

- Presence of Van der Waals gaps (unpopulated spaces) in the host material for the metal to enter
- Presence of low lying bands above the Fermi level in the host. If the energy gap is small enough at operating temperatures then electrons can jump to the conduction band with ease.
- Orientation of the elements in the lattice array must be preserved in the process of insertion/removal.

Insertion is limited by the ability of the ion to diffuse through the electrode material. Current flow in this case at a given voltage varies with the square root of the sweep rate. On the other hand surface redox processes are not diffusion controlled and the current flow should vary linearly with the sweep rate. Diffusion path lengths in a material of nanoscale dimensions are much shorter. Shorter path lengths translate to better electronic and ionic transport permitting operation in materials of lower conductivity too.

We have seen that pseudocapacitance results from different mechanisms such as adsorption, redox reactions and intercalation. Experiments with certain materials have shown incredible specific capacitance of the order of thousands of Farads per gram. In the next chapter we will discuss the material Prussian Blue, reasons for choosing it, mechanisms leading to surface and bulk storage and characterization techniques adopted for judging the electrodes.
Chapter 3

3.1 Motivation for investigating Prussian Blue pseudocapacitors

Prussian Blue is an inorganic pigment with a chemical formula of Fe\(^{III}\)\(_4\)[Fe\(^{II}\)(CN)\(_6\)]\(_3\)\(_x\)H\(_2\)O (x ≈ 14). Its chemical name is iron (III) hexacyanoferrate (II) and it belongs to the class of transition metal hexacyanometallates. Prussian blue possesses a zeolitic structure in the sense that it is porous enough to host or trap ions or molecules in the cavities of its lattice. There are two metal ion centers in its basic structure and both the metal ions are iron in different oxidation states. Hence Prussian Blue also falls in the category of mixed valence compounds.

![Figure 3.1.1 Simple cubic structure of Prussian Blue. Fe(II) yellow, Fe(III) red, C gray and N blue](image)

The lattice structure is a simple cubic consisting of alternating Fe\(^{2+}\) and Fe\(^{3+}\) ions connected by cyanide bridges as shown in Figure 3.1.1. Fe\(^{3+}\) ions are octahedrally surrounded by the nitrogen terminal of the cyanide group and Fe\(^{2+}\) ions are surrounded by the carbon atoms.
The presence of the cyanide group opens up the cubic structure to give plenty of room within. There is enough space in the center of the cubic cell to accept ions or molecules up to a radius of 182 pm. The spatial spread of the octahedral ferrocyanide is shown in Figure 3.1.2 and the basic octahedron shape is shown in Figure 3.1.3.

Two forms of Prussian Blue exist: Soluble and Insoluble. Soluble form has the formula $M^I\text{Fe}^{III}[\text{Fe}^{II}(\text{CN})_6].x\text{H}_2\text{O}$ where $x = 1-5$ where $M$ is a monovalent cation like Potassium or Ammonium. The chemical formula of the insoluble form is
Fe_{III}^{4}[Fe_{II}^{II}(CN)_{6}]_{3}.yH_{2}O where y = 14-16. Figure 3.1.4 depicts the soluble form and figure 3.1.5 depicts the insoluble form of Prussian Blue.

Figure 3.1.4 Potassium ions shown in purple occupy the body centers in half of the sub-cubes [34]

Figure 3.1.5 In Fe_{4}[Fe(CN)_{6}]_{3}.xH_{2}O there are fewer Fe(II) ions compared to Fe(III) ions leaving some sites vacant which are occupied by water molecules [34]

In the insoluble form of Prussian Blue, one quarter of the ferrocyanide units are missing with water molecules taking up the vacancies. Arrangement of these vacancies is completely disordered.

**Synthesis of Prussian Blue:** - Prussian Blue is readily prepared by mixing ferric ions to an aqueous solution of ferrocyanide. In this reaction, each nitrogen
terminus in the ferrocyanide complex displaces a water molecule in the coordination sphere of Fe$^{3+}$ to build a linear Fe$^{2+}$ - CN – Fe$^{3+}$ link. [34]

$$4[\text{Fe(H}_2\text{O)}_6]^{3+} + 3[\text{Fe(CN)}_6]^{4-} \rightarrow \text{Fe}_4[\text{Fe(CN)}_6]_3 \cdot x\text{H}_2\text{O}$$

Prussian Blue is capable of being oxidized to Fe$^{III}[\text{Fe}^{III}(\text{CN})_6]$ also called Prussian Green or reduced to Prussian White Fe$^{II}[\text{Fe}^{II}(\text{CN})_6]$. This requires the flow of cations in and out of its lattice to balance the net electric charge. Hence Prussian Blue is electrochemically active suggesting its suitability for electrode material. The flow of cations is supported by the spacious character of the lattice. Prussian Blue is a light weight material with a density of 1.8 g cm$^{-3}$. A considerable portion of Prussian Blue can thus be added in the electrode material while keeping the net weight under control and also maximizing the quantity of the active material. [34]

### 3.2 Electrochemical Storage Mechanisms, surface versus bulk storage

Storage of charge in electrochemical cells differs in the amount of participation of the electrode; formation of double layers are restricted to the surface and in intercalation the involvement becomes three-dimensional. In this context we will then look at the three different mechanisms - electrical double layer, redox and intercalation. All these mechanisms occur in a pseudocapacitor and contribute to pseudocapacitance.

#### 3.2.1 Double-layer formation

It involves electrostatic surface charging and movement of ions is limited by the ionic conductivity of the electrolyte. Electrolytes of high ionic conductivity enable
quick energy uptake and delivery boosting power performance. Absence of redox reactions prevent any changes to the electrode material leading to a good cycle life. Storage of charge at the surface restricts the capacity and hence results in lower energy density. Detailed discussions were already presented in section 1.2.3.

3.2.2 Redox Mechanism

Some materials allow redox reactions based on the availability of different oxidation states within the operating range of the electrolyte. These redox reactions can be just confined to the surface leading to faster charge transfer and hence generating a charge-discharge lifetime close to that of the EDLC. In this case the electron transfer across the electrode-electrolyte interface allows for a greater capacity. Electron transfer is accompanied by the adsorption of cations on to the surface to maintain electrical neutrality. [37]

The two electrochemical mechanisms – double layer and redox – occur at the surface and hence form the capacitive behavior of a pseudocapacitor. The confinement of these mechanisms to the surface ensures faster charge-discharge rates.

3.2.3 Intercalation

In the intercalative form of pseudocapacitance entry of the cations is deeper into the material and is controlled by the ability of the ion to diffuse in the electrode. Hence the participation of the electrode goes into a three dimensional mode.
Deeper diffusion of the cations allow more of them to diffuse resulting in larger amount of charge stored and slower storage and release of energy. Electrode arrangement determines the diffusion lengths permitted. Nanostructures reduce diffusion lengths and hence speed up the charge intake. [20]

The increase in the contribution of the electrode to allow intercalation/deintercalation indicates battery behavior. This mechanism is relatively slow in occurrence because of the lengths to which the ions have to diffuse and also the higher resistance encountered in an electrode structure. Consequently, the charge-discharge rates get lower.

3.3 Characterization Techniques

In order to judge the behavior of the combination of electrode-electrolyte, we employed certain electrochemical techniques and subject the cell to these experiments. Techniques that we have used for our material are Cyclic Voltammetry and Cyclic charge-discharge.

3.3.1 Cyclic Voltammetry

In this technique, voltage is varied in steps and current is measured as a function of voltage. The resulting plot has current on the y axis and voltage on the x axis. Initial and final potentials are fed into the system and the working electrode is taken to and fro between these two potentials at a rate known as the scan/sweep rate. Current that flows through the working electrode is measured and plotted against the potential.
The plot of a cyclic voltammetric measurement is called a voltammogram. An example is shown in figure 3.3.1. The shape of the graph is indicative of the processes taking place in an electrode. The upper half represents oxidation and the lower half, reduction. Distinctive peaks indicate currents flowing due to Faradaic reactions. Flat portions form the capacitive aspect of the electrochemical process. $i_{pa}$ and $i_{pc}$ refer to the anodic and cathodic peak currents.
Figure 3.3.2 Cyclic voltammogram of a pseudocapacitive material. It is either rectangular or contains broad peaks. [20]

Figure 3.3.2 shows the general shape of a cyclic voltammogram (CV) of a Pseudocapacitor. Peaks, if present, appear broad. Otherwise, the cyclic voltammogram may take a rectangular shape. Cyclic voltammetry of Prussian Blue in electrolytes containing Al\(^{3+}\) and Sn\(^{4+}\) ions show broad peaks and some plateau-like regions as depicted in figure 3.3.3. Both were taken at a scan rate of 25mV/sec.

Figure 3.3.3 Cyclic voltammogram of Prussian Blue in electrolytes of Aluminum and Tin salts at a scan rate of 25mV/sec
3.3.2 Cyclic charge-discharge

There are two types of cyclic charge-discharges – potentiostatic and galvanostatic.

We adopted the galvanostatic method. This technique involves controlling the current that flows through the working electrode and recording its voltage. The electrode is charged and discharged in a cyclic manner. Voltage plotted against time is recorded from this measurement. Specific capacitance is calculated from the output of this method. In the potentiostatic technique, voltage of the working electrode is kept a constant and current flowing through the electrode is measured.

![Diagram of galvanostatic cycling](image)

Figure 3.3.4 Output from galvanostatic cycling [39]

An example of the plot is shown in figure 3.3.4. Voltage is plotted on the y axis and time on the x axis. For the case of potentiostatic method, current is plotted on the y axis. A purely capacitive behavior is indicated by an incline. An incline shows a gradual decrease in the voltage with respect to time and this indicates dissipation of energy. Figure 3.3.5 illustrates the sloping nature of the galvanostatic curve for...
Prussian Blue in 1.0M Calcium Nitrate and current density at 0.5A/g. The behavior is pseudocapacitive and the prominent slopes indicate confinement of redox to the surface of the material.

![Figure 3.3.5 Galvanostatic charge-discharge of Prussian Blue in Calcium Nitrate at 0.5A/g](image)

In a rechargeable battery, the redox occurs at a single potential and hence the potential spans over time until there is a complete transformation to a new phase. We have seen how Prussian Blue possessing an open framework and electrochemically active sites can suit the position as an electrode. We have gone over the difference in charge-discharge characteristics between a two dimensional and three dimensional participation of the electrode. Characterization techniques like cyclic voltammetry reveal the underlying process in storing charge and galvanostatic charge-discharge ensures an accurate method for calculating the main metric of a Pseudocapacitor. In chapter 4 we will explain the different steps followed for running an experiment, techniques used for synthesizing the two different active materials, setup used for the experiment and metrics and variables set for judging the performance of our material.
4.1 Materials and Methods

4.1.1 Preparation of Electrodes

The process of fabricating the electrodes begins with synthesizing the active material which is Prussian Blue. Next, a slurry was prepared combining the active material, binder, a conductive additive and a solvent. The slurry was then coated on a number of carbon papers cut to 1cm x 2cm area. The coating was applied on both sides to an area of 1cm x 0.5cm. The carbon papers were air-dried, then subjected to low pressure and heat and left aside for a day. The weights of the carbon paper before coating and after the heat treatment were determined to arrive at the weight of the electrode material on it. Electrolyte of a salt of Potassium, Calcium, Aluminum or Tin of 1M concentration was prepared and made acidic by adding a few drops of Nitric acid or Hydrochloric acid depending on the salt chosen. The electrolyte was made acidic because it ensures that the salt is completely ionized in the solution and promote ionic conductivity. pH of 2 was achieved and tested by means of litmus paper. Nitric acid was used when the electrolyte was of a nitrate salt and hydrochloric acid used when the salt had chloride. A three-electrode cell was set up with the test electrode, a graphite rod as a working electrode and Ag/AgCl in saturated KCl as the reference electrode, all dipped in the electrolyte. The level of the electrolyte was adjusted so as to reach just the top of the coated area on the test electrode. First, 30 cycles of cyclic voltammetry were run between -0.3V and 1.1V to get an understanding of the behavior of the system.
Next, galvanostatic cycling was executed between 0V and 1V for current densities varying from 0.5Ag\(^{-1}\) to 5Ag\(^{-1}\). Fifty cycles were executed for each current density. The resulting data was used to then calculate specific capacitance.

4.1.2 Methods of Synthesis

4.1.2.1 Prussian Blue

A solution of ferric nitrate was prepared by mixing 10 milli-moles in 20ml of water. An aqueous solution of potassium ferrocyanide was prepared by mixing 5 milli-moles in 20ml of water. The ferric nitrate solution was added in a dropwise manner to the solution of potassium ferrocyanide. The resulting mixture was subject to magnetic stirring at a speed of 250 rpm and heated to a temperature of 60°C. The stirring was done for two hours and then the solution was left aside for a day. The solution was then centrifuged to get Prussian Blue and finally cleansed with ethanol. The extracted Prussian Blue was then left to air-dry for two to three days. Once dried, the electrode material was prepared by grinding Prussian Blue, activated carbon and Polyvinylidene Fluoride in the ratio 80:11:9. The ground mixture was made into a paste by adding solvent N-Methyl-2-Pyrrolidone.
The dropwise addition of ferric nitrate to a solution of potassium ferrocyanide produces Prussian Blue instantaneously as depicted in Figure 4.1.1.

### 4.1.2.2 Prussian Blue coated CNTs

Aqueous solutions of potassium ferrocyanide and ferric nitrate were prepared by dissolving 10 milli-moles of the substance in 30ml of water. 0.5g of multi-walled carbon nanotubes were taken and put in 30ml of water. Stirring of the solution was initiated and 30 ml of the ferric nitrate solution was added. Next the combination was heated to 60°C. The solution of potassium ferrocyanide was then added dropwise. The stirring was continued for an hour and the solution left aside for a day. Next day, the mixture was centrifuged and cleansed with methanol. Finally, the Prussian Blue CNT mixture was allowed to air-dry for two to three days. Electrode powder was prepared by grinding together Prussian Blue CNTs, Activated Carbon and Polyvinylidene fluoride in the ratio 80:11:9. A paste was made by mixing the solvent N-Methyl-Pyrrolidone to the powder.
4.2 Experimental Setup

A three-electrode cell was used for running the experiments and a potentiostat for making the measurements. An EG&G Princeton Applied Research Potentiostat/Galvanostat Model 273A was employed for the purpose.

![Experimental setup of three-electrode cell and potentiostat](image)

The actual experimental setup is depicted in the Figure 4.2.1. A potentiostat is an electronic instrument that can measure and control the voltage between the working and reference electrodes and measure the current between the working and counter electrodes. We used a three-electrode cell setup for the measurements. All the electrodes were dipped in a jar of conductive electrolyte.
Figure 4.2.2 shows a close up view of the three-electrode cell setup. The working electrode is the test electrode. A graphite rod served as the counter electrode. Silver/Silver Chloride in Saturated KCl was the reference electrode. The reference electrode has a constant electrochemical potential, possesses a high input impedance and hence does not allow current to flow through it. [40] Its potential is treated as the zero point on the potential axis. The potential of the test electrode is thus measured in reference to the baseline. The specific reference was chosen because of the ease and low cost of its preparation. Moreover its potential is relatively stable over a period of time. [41,42] Neither the reference nor the counter electrode takes part in the chemical reactions.
Figure 4.2.3 Three-Electrode Cell Setup used for electrochemical characterization and measurement

Figure 4.2.3 illustrates a schematic of the three-electrode cell showing the potential measurement and the current flow.

4.3 Metrics and Variables

Specific capacitance was used as the main metric in deciding the suitability for a Pseudocapacitor. Variables of the experiment include valence of electrolyte ion, electrode weight and current density. Electrode of a specific material is tested in four electrolytes containing ions of valence ranging from +1 to +4 and subjected to six different current densities – 0.5A/g, 1A/g to 5A/g in steps of 1A/g at the rate of 50 cycles in each current density.

A general electrochemical cell testing went through most of the processes outlined. We ended up preparing two different materials for testing their use as electrode in
a Pseudocapacitor. A three-electrode cell was used and measurements done using a potentiostat. We had gone over the purpose of each of the electrodes in the setup. Four variables were used – electrode material, electrolyte, electrode weight and current density – in deciding the suitability of the electrode. Chapter 5 will have the results obtained accompanied by a discussion and the challenges encountered.
Chapter 5

5.1 Results & Discussion

5.1.1 Regular Prussian Blue

Trend of Specific capacitance versus discharge cycle for electrodes of similar weight in different ions –

![Graph](image)

Figure 5.1.1 Variation of Specific Capacitance with Discharge cycle for 0.2mg electrodes in cations K+, Ca2+ and Al3+ at 0.5A/g of current density

When electrodes of similar weights were tested with different cations, the one with Potassium outperformed the others as shown in figures 5.1.1, 5.1.2 and 5.1.3 corresponding to three different current densities – 0.5A/g, 2A/g and 5A/g respectively. The variation of specific capacitance with discharge cycle in potassium shows a gradient in figure 5.1.1, while there is a considerable stability to the values of specific capacitance in the other cations and for Potassium corresponding to the other current densities. 0.5 A/g was the first current density
to be tested for Prussian Blue in potassium corresponding to the 0.2mg electrode and the specific capacitance takes some cycles to settle down to a stable value. Even though there is a drop from the initial value, specific capacitance in potassium reigns over the others.

Figure 5.1.2 Variation of Specific Capacitance with Discharge cycle for 0.2mg electrodes in cations K+, Ca2+ and Al3+ at 2A/g of current density
Figure 5.1.3 Variation of Specific Capacitance with Discharge cycle for 0.2mg electrodes in cations K+, Ca2+ and Al3+ at 5A/g of current density

Figure 5.1.4 Cyclic Voltammogram of Prussian Blue in K+ at 25mV/sec

Figure 5.1.4 illustrates the cyclic voltammogram of the electrode in potassium at a scan rate of 25mV/sec. It yielded two distinct peaks both on the oxidation and reduction cycles. The peaks speak of the three states – oxidation to Berlin green
(Prussian Green) at around 1V, reduction to Prussian Blue at 0.874V, reduction to Prussian White at 0.197V, oxidation to Prussian Blue at 0.289V and the cycle continues this way.

![Cyclic Voltammogram of Prussian Blue in Ca2+ at 25mV/sec](image)

Figure 5.1.5 Cyclic Voltammogram of Prussian Blue in Ca2+ at 25mV/sec

In comparison, the cyclic voltammograms in Calcium and Aluminum as shown in figures 5.1.5 and 5.1.6 display broader and shorter peaks. When metal ions are in water a solvation shell forms around them composed of water molecules. The solvation shell is formed by solvent molecules and in our case water has been employed as the solvent. Metal ions with greater charge or larger radius will have a larger solvation shell. The radius of the hydration shell is determined by the charge/size ratio of the cation. [43,44] Hence cations with smaller hydration shells like potassium are capable of intercalating in the lattice structure of Prussian Blue generating higher currents on a voltammogram. Intercalation is accompanied by change in the redox state of iron giving rise to the different forms of Prussian Blue.
Differences in the charge-discharge profile of Prussian Blue in the three ions can also be seen from Figure 5.1.7 which is the output from galvanostatic cycling. The relatively flatter portions for K+ curve correspond to the maximal redox conversions.
of Prussian Blue. Presence of a large gradient in the curves corresponding to Calcium and Aluminum indicate a largely capacitive behavior because of the two-dimensional nature of the participation of the active material. With redox occurring only because of the adhesion of the cation to the surface, the charge-discharge occurs fairly quickly. When the redox extends to the volume as in the case of intercalation of potassium, the time for charging and discharging increases as evident from the broad nature of the peak in Figure 5.1.7 and also the capacitance. The triangular shape of a two dimensional process gets stretched out at various points in the three dimensional case.

On a similar trend comparison of Prussian Blue in electrolytes of cations Sodium, Calcium, Aluminum and Tin, Sodium leads the pack. Figures 5.1.8 and 5.1.9 display the results of the variation of specific capacitance with discharge cycle for 2 different current densities – 1A/g and 2A/g. But the capacitance in Sodium still is
much lower compared to that in Potassium because of the larger hydration shell around sodium as a result of the larger charge to size ratio. [43,44] This restricts the lengths to which the ion can diffuse into the structure and hence the charge that can be stored.

Another interesting trend to observe from figures 5.1.8 and 5.1.9 is the higher specific capacitance of Prussian Blue with Tin compared to that in Aluminum. Tin possesses a bigger solvation shell. But we made the electrolyte of Tin Chloride acidic by the addition of nitric acid. Presence of an additional cation $\text{H}^+$ boosted the specific capacitance by increasing the redox activity. Figure 5.1.10 shows a smaller gradient for Tin in support of this conclusion.
Figure 5.1.10 Galvanostatic charge-discharge of Prussian Blue in Al3+ and Sn4+ at 1A/g

Trend of Specific Capacitance versus discharge cycle for electrodes of varying weights in an electrolyte –

Figure 5.1.11 Variation of Specific Capacitance with Discharge cycle for 0.2mg, 0.3mg & 0.4mg electrodes in Ca2+ at 0.5A/g of current density

Electrodes of lower weight have thinner films of the material on them because the area coated is kept a constant across all electrodes. Figures 5.1.11 and 5.1.12
illustrate specific capacitance recorded for Calcium for different electrode weights and the one corresponding to 0.2mg shows the highest specific capacitance. We would expect the one with 0.3mg of material to display a better specific capacitance in comparison to the 0.4mg electrode but the figures tell it is the other way. The reason the 0.3mg electrode shows a lower specific capacitance is because it was subjected to more charge-discharge runs at lower current densities that resulted in significant material degradation.

![Graph](image-url)  
Figure 5.1.12 Variation of Specific Capacitance with Discharge cycle for 0.2mg, 0.3mg & 0.4mg electrodes in Ca2+ at 2A/g of current density
The same is seen when electrodes were subject to additional cycling runs in Aluminum. 0.2mg electrodes were subject to additional runs at lower current densities and hence their specific capacitance dropped lower in relation to 0.3mg electrodes as shown in figures 5.1.13 and 5.1.14. Low-weight electrodes still show better promise because in the cases where capacitance is the result of a surface based redox process, having most of the material only as a layer on the current collector helps improve the specific capacitance. Otherwise, the presence of material not participating only increases the amount of dead weight on the electrode.
Figure 5.1.14 Variation of Specific Capacitance with Discharge cycle for 0.2mg, 0.3mg & 0.4mg electrodes in Al\textsuperscript{3+} at 2A/g of current density

Trend of Specific Capacitance versus Discharge cycle for an electrode in Potassium electrolyte subjected to over 1000 cycles

Figure 5.1.15 1\textsuperscript{st} cycle of Galvanostatic charge-discharge of Prussian Blue in K\textsuperscript{+} at 2A/g
As a test of capacity retention, an electrode was subjected to 1000 cycles of galvanostatic charge-discharge at 2A/g in Potassium. The result is displayed in figures 5.1.15, 5.1.16, 5.1.17 and 5.1.18.

There is a change in the shape of the curve with the width becoming less as the number of charge-discharge cycles increases. The width shows the time taken to charge and discharge. The initial time is 382 seconds (figure 5.1.15) and it halves by the time it reaches the 500th cycle (figure 5.1.16) but between the 500th and 1000th cycle (figure 5.1.17) there is only an 18% fall in the total time.
There is a decrease in the intercalation because of the structural variations in the material. Most of the capacitive behavior at later cycles is from the surface redox reactions. As the electrode is subjected to cycling, there is gradual increase in the internal resistance – resistance to the movement of the ions in the electrolyte,
resistance across the electrode-electrolyte interface and resistance within the electrode structure. There could also be ions from the electrolyte permanently trapped in the electrode structure which could have brought down the specific capacitance. However, the last 400 cycles display a stable specific capacitance averaged at 145F/g with a standard deviation of only 5.71F/g as can be seen from a plateau type region in Figure 5.1.18.

SEM Analysis –

![SEM Image](image)

**Figure 5.1.19 Fresh Prussian Blue Electrode.** Grainy appearance of the particles at a high magnification. Particle size of the order of 20nm. Carbon nanotubes visible underneath the surface.

The Prussian Blue electrode was studied under the Scanning electron microscope to get an understanding of the topography of the surface. At high magnification, a grainy appearance is revealed with a particle size of ~20nm as shown in Figure
5.1.19. The fiber-like structures are carbon nanotubes which enhance the permeability of the electrode to the electrolyte. These structures are more prominent in the following figure 5.1.20.

Figure 5.1.20 Fresh Prussian Blue Electrode. Presence of Carbon nanotubes render a porous character to the bulk material thus enabling penetration of the electrolyte to active material underneath.
Figure 5.1.21 Fresh Prussian Blue Electrode. Image taken at low magnification. Manual coating results in a layered appearance.

At low magnification, the surface exhibits a layered appearance as a result of the manual coating. This is shown in Figure 5.1.21.

5.1.2 Prussian Blue coated CNT Electrodes

Electronic transport in the carbon nanotubes occurs without scattering and this enables them to carry high currents without getting heated up. Moreover a low density of 2.6 gcm$^{-3}$ will help keep the weight of the electrode material under control. There is also the advantage of a large specific surface area to the carbon nanotubes [45,46,47]. If Prussian Blue was coated on the nanotubes, it allows for good distribution of Prussian Blue in the electrode material raising the possibility of having more Prussian Blue molecules for cations to access. This reduces the length required for ions to diffuse (at least for the Prussian Blue confined to the
outermost layer of the nanotubes), and allows quick transport of electrons through the matrix to the current collector. It also enables formation of double layer on parts of the matrix that do not contain Prussian Blue.

The trend of Specific Capacitance with discharge cycle for varying current densities are shown below –

![Specific Capacitance in Ca2+ at varying current densities](image)

**Figure 5.1.22** Variation of specific capacitance with discharge cycle for Prussian Blue CNT in Ca2+ at different current densities

The variation of the specific capacitance over discharge cycle for different current densities – 0.5A/g, 1A/g, 2A/g, 3A/g, 4A/g and 5A/g - is illustrated in Figure 5.1.22. The Prussian Blue CNT electrode had a relatively larger mass of 2.6mg in comparison to the Prussian Blue electrodes. While the greater weight may have hindered getting high values of specific capacitance, a low concentration of Prussian Blue which is the only material capable of undergoing redox could have
also been a reason for lower charge storage ability. With a greater percentage of CNTs, there would have been formation of the double layer on the surface which does not contribute as much towards specific capacitance.

Figure 5.1.23 Fresh Prussian Blue CNT electrode. Porosity is enhanced relative to the Prussian Blue electrode by the dominant presence of CNTs.

Figure 5.1.23 shows the SEM image of the Prussian Blue CNT electrode. Even at this low level of magnification a porous surface is seen unlike the Prussian Blue electrode. The permeable look is attributed to a large chunk of Carbon nanotubes. While the double layer effect may dominate, resulting capacitance is relatively low because of minimal redox processes.
5.2 Summary of the Results on Prussian Blue electrodes

<table>
<thead>
<tr>
<th>Electrolyte Ion</th>
<th>Specific Capacitance (F/g)</th>
<th>Electrode Weight (mg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potassium</td>
<td>720</td>
<td>0.2</td>
</tr>
<tr>
<td>Calcium</td>
<td>320</td>
<td>0.2</td>
</tr>
<tr>
<td>Aluminum</td>
<td>292</td>
<td>0.3</td>
</tr>
<tr>
<td>Tin</td>
<td>145</td>
<td>0.4</td>
</tr>
</tbody>
</table>

Table 1 Summary of the Results on Prussian Blue electrodes

5.3 Challenges Encountered

Synthesis of the materials and the electrodes took time. The consistency of the electrode paste depended on the ratio of the reactants. A paste-like consistency enabled us to coat a thin layer and thus reduce the weight of the electrode. In preparing the Prussian Blue CNT material, several ratios were tried to get a fine consistency. The dominating presence of carbon nanotubes was a deterrent in ensuring an even spread of the material on the carbon paper.

Prussian Blue electrodes have far superior performance in relation to the Prussian Blue-CNT counterparts. Variation of specific capacitance with discharge cycle in different electrolytes showed promising results with Potassium, Calcium and Aluminum ions. When varying electrode weights were examined, lower weights had an upper hand because of the confinement in the activity of the electrode to the surface. Scanning electron microscope images showed a very porous topography for the PB-CNT electrodes in comparison to the PB electrodes. Addition of another cation to the electrolyte is also shown to boost the specific capacitance. In chapter 6 will give our conclusions and cite future work that can be done improving the current methods.
Chapter 6

6.1 Conclusion

Two different materials based on Prussian Blue were tested for their ability as electrodes in aqueous solutions for the purpose of building a pseudocapacitor, and their performance was compared with different ions. Electrodes with just Prussian Blue came out better in terms of specific capacitance in all four ions – Potassium, Calcium, Aluminum and Tin. Peak performance occurred in Potassium with the highest specific capacitance of 720F/g because of the added advantage of intercalation at virtually all the six current densities tested. The specific capacitance of Prussian Blue in Calcium was 320F/g, in Aluminum was 292F/g and in Tin was 144F/g. Contrary to intuition, specific capacitance in multi-valent ions were lower than that in monovalent ion. The reason behind this anomaly was seen to be the size of the hydration shell. The hydration shell formed around Potassium ion is the smallest of the shells among the four ions. [43,44] There are two aspects to the pseudocapacitive behavior – capacitive and battery. The capacitive behavior is made up of the double layer and surface redox. The battery aspect comes from the participation of the electrode beyond its surface. An ion with a smaller hydration shell can increase both the capacitive and the battery features by aligning in sufficient numbers along the surface and also penetrating deeper into the electrode structure. Entry of the ions into the structure enables redox of the iron atoms present interior of the structure. The electrode structure has Prussian Blue molecules spread across both the surface and volume. As far as ions with bigger
hydration shells are concerned, their penetration inside the electrode structure and hence access to the number of Prussian Blue molecules are limited. Also, there are fewer of the ions that can adhere themselves to the surface. This limits the charge that can be stored from the redox. In the formation of a double layer there is an increase in the width of charge separation because of the larger shell. This brings down the double layer capacitance. Thinner films on electrodes present a better specific capacitance by lowering the passive weight of the electrode. In comparison, bringing up the earlier work reported on hexacyanometallates for capacitive electrodes; Prussian Blue/reduced graphene oxide nanocomposites were determined to have a specific capacitance of 252 F/g when cyclic voltammetry was performed in 1M KNO3 between -0.2V and 0.8V at 10mv/sec [28]. Cobalt hexacyanoferrate synthesized as nanoparticles has shown a specific capacitance of 250 F/g in 0.5M Sodium Sulphate from cyclic voltammetry at 0.5 mV/sec and galvanostatic charge-discharge at 1A/g [27]. Nano-sized insoluble iron, nickel and cobalt hexacyanoferrates prepared by a co-precipitation method were reported to have specific capacitance of 425 F/g, 574.7 F/g and 261.56 F/g respectively when tested at a current density of 0.2 A/g [29]. These electrodes have their active material synthesized at the nanoscale and at this scale the diffusion lengths have been reported to be relatively smaller [20]. While the values are comparable with our work, the earlier work has been performed in electrolytes of monovalent cations. Our work reports much higher specific capacitance with a monovalent cation while it shows comparable values with multivalent cations to earlier work. It is remarkable though that the cobalt hexacyanoferrate was also
reported to retain 93.5% of its specific capacitance after 5000 cycles of charge-discharge. This is an area we hope to focus on as part of our future work. While the specific capacitance in the other ions are lower compared to that in Potassium, they are remarkably high for use intended as pseudocapacitors considering the cost and availability of materials. Moreover, thin films have proven to be the key in utilizing multi-valent ions which can store sufficient charge from surface processes and also enable faster rates of charge-discharge at higher energy density. Considering the simple methods of synthesis of the electrode material that yielded such high storage values, refining these techniques can lead to still higher performance. Choice of the material, electrolytes and processes adopted were definitely cost efficient for laboratory testing. The other material which was a mixture of Prussian Blue and multi-walled carbon nanotubes showed a relatively poor performance due to a low percentage of redox-active material and higher weight for the current collector. Prussian Blue shows promise as a material capable of redox, allowing cations entry into its lattice structure and even giving room for sufficient surface redox. The ease of preparation opens possibilities to explore highly crystalline structures, nano-sized structures and structures with a replacement of the ferric ion. Though aqueous electrolytes have a lower voltage window of stability, they are very safe and not prone to explode. Moreover, using multiple electrochemical cells in series can increase the voltage window.
6.2 Future Work

Cycle life and percentage of capacity retention are important metrics as far as an electrode is concerned and these should also receive attention. The class of hexacyanometallates with one or both of the Fe ions of Prussian Blue replaced can show similar possibilities. Alternate structures which are more crystalline or are nanoscaled can bring up the specific capacitance by reducing the diffusion lengths. Mixtures of Prussian Blue with transition metal oxides which are already known for their capabilities in the Pseudocapacitor range should also be investigated. Spherical capacitive plates can also be explored for maximizing the exposed surface area.

6.3 References


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