ELECTROCHEMICAL ACTIVITY OF SUBSTITUTED PERYLENE-DERIVATIVES FOR USE AS MEDIATOR IN ELECTROLYTES FOR ZINC-AIR FLOW BATTERIES

BY

ERIC VAN CITTEREN
STUDENT NUMBER: 4282426

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE MASTER OF SCIENCE IN
SUSTAINABLE ENERGY TECHNOLOGY

TU Delft

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To my family, friends and everyone who helped me along the way.

Eric van Citteren

Abstract

The global transition towards renewable energy sources necessitates advancements in energy storage technology to address the intermittency of renewable sources like solar and wind. Redox flow batteries, such as the zinc-air redox flow battery, offer promising solutions with flexible storage capacity and long cycle life. However, identifying a suitable redox mediator for the air side remains a significant challenge. perylene-derivatives, known for their electrochemical activity, recyclability, and redox stability, are potential candidates for this role. This research evaluates various perylene-derivatives for their electrochemical activity as mediators in zinc-air redox flow batteries, focusing on redox potential, solubility, and stability. While the study demonstrated that modifying substitution groups on the perylene core could achieve the desired reduction potential, achieving high solubility remains challenging. Therefor optimization of substitution groups is required to develop perylene-derivatives that meet the necessary criteria. Overall, although more research is required to find effective redox mediators, perylene-derivatives show significant potential for zinc-air redox flow batteries.

Contents

1 Introduction

Energy is undeniably a pivotal element in our lives. Countries worldwide are progressively transitioning towards renewable energy sources. This shift is supported by various global agreements, notably the Paris Agreement, which establishes targets for 2050 to mitigate the rising temperatures of our planet. Moreover, with the projected growth of the global population by 2050, the demand for energy will inevitably surge. Addressing this escalating demand necessitates substantial growth in the output of energy generation sources, accompanied by significant advancements in energy storage technology. [1]

Furthermore the fluctuation of energy demand and renewable energy sources, such as solar and wind, creates the need for specified energy storage technology. To fill the gap between short-term storage (e.g. li-ion batteries) and long-term (e.g. H_2 storage), redox flow batteries are a potential chemical energy storage solution. Redox flow batteries have advantages such as flexible energy storage capacity and long cycle life with minimal capacity degradation over time. [2]

Redox flow batteries have been studied for several decades, but they have only recently become commercially relevant as a storage solution. Due to the decrease in costs and innovation of the technology. With the largest redox flow battery been built in China in 2022, which is a 100 MW/400 MWh vanadium flow battery system. [3] However many other flow batteries are being studied to develop a more cost-effective and safer solution. A promising battery with growing research interest is the zinc-air redox flow battery. This battery is in its early stages of development, and has various challenges to overcome before becoming commercially viable. One such challenges is to find a redox active, and stable material for the use as mediator in the electrolyte on the air side. [4,5]

This thesis focuses on the electrochemical activity of perylene-derivatives for use as mediator in solution for zinc-air flow batteries. Perylene-derivatives show some advantages in organic batteries and other electrochemical applications such as: recyclability; abundance of materials and redox stability. [6]

First the necessity of storage technology is discussed in chapter 2, which gives an overview of different technologies, and a more in-dept overview of redox flow batteries. Chapter 3 gives the current use and research done on perylene and perylene-derivatives, including their theoretical potential and use as mediators in solutions. Furthermore, the methods and materials for the experiments are detailed in chapter 4. This chapter provides an overview of the research goals, the various perylene derivatives used, the procedures for conducting electrochemical measurements, and the compositions of the battery cells. Chapter 5 presents the results and discusses the outcomes of the experiments. Finally a conclusion is given in chapter 6.

2 Energy Storage Technologies

The necessity for energy storage technologies arises from several key factors and challenges in modern energy systems. This chapter outlines the necessity for energy storage in section 2.1, then gives an overview of some available storage technologies in section 2.2. Thirdly, different batteries are outlined in section 2.3. Going further into detail on redox flow batteries and Zinc-air redox flow batteries in section 2.4.

2.1 Necessity for Energy Storage

Renewable energy sources such as solar and wind power are inherently intermittent, meaning their generation fluctuates based on weather conditions. Figure 1 shows typical generation patterns for wind and solar energy generation in the United States. The load can not always be satisfied from generation from renewable sources depending on time and season. Furthermore excess energy can be generated at times where the load is low.

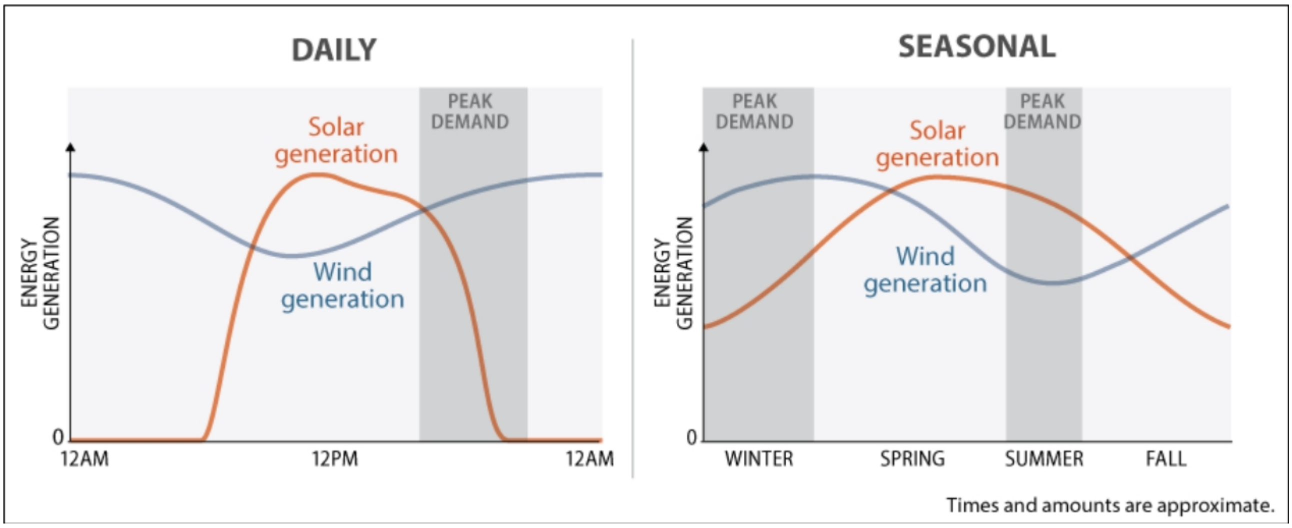


Figure 1: Typical daily and seasonal generation patterns for solar and wind energy sources in the US. [7]

There are five main drivers which lead to the necessity for energy storage. First, energy storage technologies play a crucial role in mitigating this variability by capturing excess energy when it is available and storing it for later use. By integrating energy storage with renewables, a more reliable and stable energy supply can be achieved, enabling a higher entry of clean energy into the grid.

Secondly, energy storage technologies allows for load shifting, where excess energy produced during off-peak hours can be stored and used during periods of high demand. This helps to balance the electricity grid and lowers the need for expensive power plants, which are often fossil fuel-based. Energy storage technologies can also provide additional power during peak demand periods, alleviating strain on the grid and preventing blackouts. [8,9]

Third, energy storage technologies can enhance grid stability and resilience by providing rapid response capabilities. They can regulate frequency and voltage, provide backup power during grid outages, and support grid services such as frequency regulation and grid balancing. These capabilities improve the overall reliability of the electricity grid and enhance its ability to withstand disruptions.

Fourth, Energy storage technologies are vital for establishing micro-grids or powering off-grid systems in remote areas or during emergencies. They can store energy generated from renewable sources or conventional generators, providing a reliable and independent power supply to communities, critical facilities, and disaster-stricken areas. [10,11]

Finally energy storage technologies can participate in energy markets by providing additional services, such as frequency regulation and capacity reserves. By utilizing energy storage, grid operators can optimize their energy supply and demand dynamics, resulting in cost savings, improved grid efficiency, and reduced reliance on fossil fuel-based generation. [8,12]

Overall, energy storage technologies are necessary to address the challenges posed by intermittent renewable energy sources and managing peak demand. Additionally, they enhance grid stability and resilience, enable off-grid power solutions, and optimize energy market operations. By effectively deploying energy storage systems, a more sustainable, reliable, and efficient energy infrastructure can be achieved.

2.2 Storage Technologies

In order to understand where redox flow batteries fit in, it is important to understand other energy storage technologies. There are various storage technologies that play a crucial role in energy management and grid stability. These technologies offer unique characteristics and are used in different applications. A study by Asri et al. compares energy storage systems and give an overview of important storage technologies. An overview of of these storage technologies is given in table 1 [13].

Storage Technology	Max Power Rating (MW)	Discharge time	energy density (Wh/L)	Efficiency
Pumped hydro	3,000	4h - 16h	0.2 - 2	70 - 85%
Compressed air	1,000	2h - 30h	2 - 6	40 - 70%
Molten salt	150	hours	70 - 210	80 - 90%
Li-ion battery	100	1min - 8h	200 - 400	85 - 95%
Lead-acid	100	1min - 8h	50 - 80	80 - 90%
Flow battery	100	hours	20 - 70	60 - 85%
Hydrogen	100	min-week	600 (at bar)	25 - 45%
Flywheel	20	secs-mins	20 - 80	70 - 95%

Table 1: Energy storage technologies with their technical data in chronological order. [13]

Each of these storage technologies has its own advantages and limitations, making them suitable for different applications and deployment scenarios. As the demand for energy storage continues to grow, a combination of these technologies, along with batteries, can contribute to a more reliable, efficient, and sustainable energy infrastructure. Some of these technologies are described in more detail in the following sections.

2.2.1 Pumped Hydro Storage

Pumped hydro storage is one of the most mature and widely deployed energy storage technologies. It utilizes the potential energy of water by pumping it to an elevated reservoir when excess electricity is available. During times of high demand or when additional power is needed, the stored water is released, passing through turbines to generate electricity. Pumped hydro storage systems offer large storage capacities, long-duration discharge capabilities, relatively high roundtrip efficiency, and the ability to respond quickly to grid demands. Pumped hydro storage, while beneficial for energy storage, has drawbacks like high initial costs and limited suitable sites. [13, 14]

2.2.2 Compressed Air Energy Storage

Compressed Air Energy Storage (CAES) systems store energy by compressing air and storing it in underground caverns or tanks. During discharge, the compressed air is heated and expanded, driving turbines to generate electricity. CAES offers long-duration energy storage, high efficiency, and the potential for large-scale deployment. However, it requires suitable geological formations for air storage and may have some energy loss due to heat dissipation during compression. [13, 14]

2.2.3 Flywheel Energy Storage

Flywheel energy storage systems store energy in the form of a rotating mass. Excess electricity is used to accelerate a flywheel to high speeds, storing the energy as rotational kinetic energy. During discharge, the flywheel's rotational energy is converted back into electricity. Flywheel systems provide rapid response times, high power output, long cycle life, and high efficiency. They are particularly suitable for applications that require frequent and fast charge/discharge cycles. [13, 14]

2.2.4 Thermal Energy Storage

Thermal Energy Storage (TES) technologies store energy in the form of heat or cold. These type of technologies can utilize various methods, including sensible heat storage, latent heat storage, and thermochemical storage. TES systems are commonly used in conjunction with solar power plants to store excess heat generated during the day for later use during the night or cloudy periods. TES offers long-duration storage, high energy density, and the potential for cost-effective integration with renewable energy sources. [13, 14]

2.2.5 Hydrogen Storage

Hydrogen storage technologies involve converting excess electricity into hydrogen through electrolysis. The produced hydrogen can be stored and later converted back into electricity using fuel cells or combustion engines. Hydrogen storage provides long-duration and high-capacity energy storage, as well as the potential for zero-emission energy conversion. However, challenges include hydrogen production, storage, and distribution infrastructure. [13, 14]

2.2.6 Supercapacitors

Supercapacitors store energy through electrostatic double-layer capacitance or pseudocapacitance. They offer high power density, fast charge/discharge rates, and long cycle life. Supercapacitors are commonly used for short-duration energy storage, high-power applications, and as complementary devices to batteries in hybrid energy storage systems. [13, 15]

2.3 Batteries

Batteries are a diverse group of energy storage devices that play a critical role in a wide range of applications, from portable electronics to electric vehicles and grid-scale energy storage. Some of the different types of batteries commonly used today are described in the next sections.

2.3.1 Lead-Acid Batteries

Lead-acid batteries are one of the oldest and most widely used rechargeable batteries. They consist of lead plates immersed in a sulfuric acid electrolyte. Lead-acid batteries are relatively low-cost, have good single cell voltage, and can provide high current outputs. However, they have a limited cycle life, low energy-to-weight ratio, and contain hazardous materials. [16]

2.3.2 Lithium-Ion Batteries

Lithium-ion (Li-ion) batteries have become the dominant battery technology in portable electronics, electric vehicles, and many other applications. Li-ion batteries offer high energy density, longer cycle life, and lower self-discharge compared to other battery types. They utilize lithium compounds as the electrode materials, allowing for a lightweight and high-performance energy storage solution. Li-ion batteries do have limitations, including safety concerns related to thermal runaway and the need for proper recycling due to the use of certain materials. [17, 18]

2.3.3 Nickel-Metal Hydride Batteries

Nickel-metal hydride (NiMH) batteries are rechargeable batteries that use a hydrogen-absorbing alloy as the negative electrode and a nickel oxyhydroxide compound as the positive electrode. They offer a higher energy density than lead-acid batteries and are more environmentally friendly than some other battery chemistries. However, NiMH batteries have lower energy density and shorter cycle life compared to lithium-ion batteries. [19, 20]

2.3.4 Sodium-Ion Batteries

Sodium-ion batteries are a new technology that aims to use sodium ions instead of lithium ions for energy storage. The lower cost and greater abundance of sodium compared to lithium make these batteries attractive for energy storage applications. Recently, the first sodium-ion batteries have been introduced to the market for commercial use. However, active research is still being conducted to compare the cell chemistry, heating behavior, and specific energy of these sodium-ion batteries. [21, 22]

2.4 Redox Flow Batteries

Redox flow batteries (RFBs) are a type of rechargeable battery that store and release electrical energy through a redox reaction. Unlike conventional batteries where the energy storage occurs within the battery cell itself, RFBs store energy in electrolyte solutions contained in separate tanks or reservoirs.

The basic components of a redox flow battery include two electrochemical cells, each with an electrode and an electrolyte, as can be seen in figure 2. An ion-exchanging membrane separates the two cells. The electrolyte solutions can be circulated through the system to charge or discharge the battery.

When the redox flow battery is discharged, the electrolyte solutions from the two tanks are pumped into their respective cells. At the electrodes, the redox reactions occur, causing the electrolyte solutions to release electrons, thus generating an electrical current. During the charging process, the reverse reactions occur, with the electrolyte solutions being charged and storing electrical energy. [23]

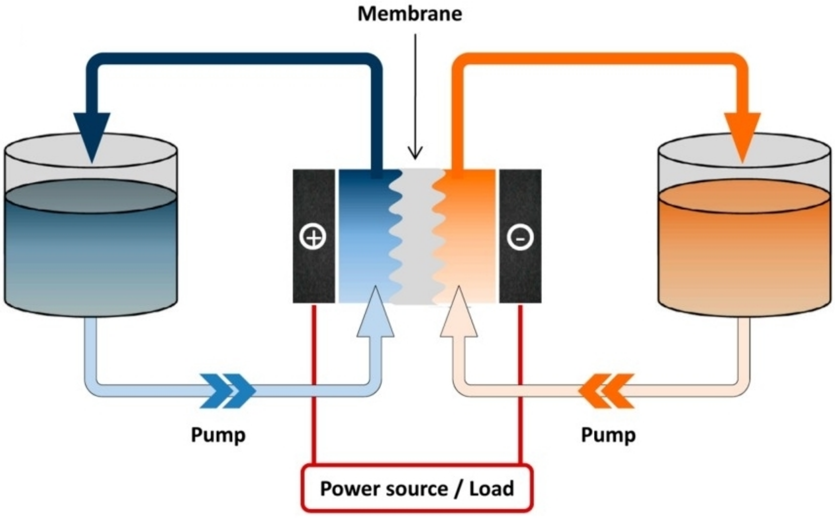


Figure 2: Schematic representation of redox flow battery. [23]

Redox flow batteries fit into the broader landscape of energy storage systems by providing specific advantages and capabilities. Their modular design and ability to decouple power and energy allow for flexible and scalable energy storage. Redox flow batteries can complement other battery technologies, such as lithium-ion batteries, by providing long-duration storage and balancing intermittent renewable energy sources. They can be integrated with solar or wind farms to store excess energy during periods of low demand and discharge it during peak demand.

One of the key advantages of redox flow batteries is their ability to decouple energy storage capacity from power output. By increasing the size of the electrolyte storage tanks, the energy capacity of the battery can be expanded without affecting the power rating. This makes redox flow batteries particularly suitable for applications where long-duration energy storage is required, such as grid-scale energy storage or renewable energy integration. [13, 24]

However, redox flow batteries also have some disadvantages. They have lower energy density compared to some other battery technologies; larger physical footprint due to the separate tanks for electrolyte storage; and higher upfront costs and complexity in system design and maintenance.

Overall, redox flow batteries represent a promising energy storage technology, offering scalability, long cycle life, and flexibility for a wide range of applications, particularly in large-scale energy storage and renewable energy integration. Continued advancements in materials and system design are expected to further improve their performance and cost-effectiveness in the future.

2.4.1 Zinc-Air Redox Flow Batteries

Zinc-air redox flow batteries are a promising energy storage technology that offers unique advantages for various applications. These batteries consist of two separate tanks, one containing the anolyte. The other holding the catholyte. When the battery operates, zinc from the anolyte tank is oxidized at the anode during discharge, while oxygen from the air is reduced at the cathode, generating electrical energy.

As described in the previous section redox flow batteries have some advantages, such as scalability, compared to other energy storage technologies. A zinc-air system also have one of the highest relative energy densities compared to the use of other materials within batteries. Although not the most important design factor for redox flow batteries, due to its stationary nature, it contributes to the overall cost effectiveness. The energy density is mainly attributed to the abundant oxygen supply from the atmosphere for the cathodic reaction, making them ideal for long-duration energy storage applications.

Another potential benefit of zinc-air redox batteries is the abundance and cost-effectiveness of zinc as an electrode material. Zinc is a widely available and relatively inexpensive metal, which translates to lower production costs for Zinc-air redox flow batteries compared to some other redox flow battery chemistries that rely on scarcer or more expensive materials. [25] Additionally, the use of air reduces the need for expensive cathode materials, further lowering the overall system cost.

At this moment zinc-air redox flow batteries are still very early in its research and development state, by which a lot of research needs to be done to find the right materials, while also maintaining high efficiency and cyclability.

One of the challenges in the development of Zinc-air redox flow batteries lies in finding suitable redox mediators for the air side of the battery. The redox mediator is a critical component that facilitates the oxygen reduction reaction. The ideal mediator should be efficient, stable, and cost-effective. A promising group of material which could be used as mediator are perylene-derivatives.

In summary, this study focuses on using perylene derivatives as suitable redox mediators for zinc-air redox flow batteries. Research indicates that zinc-air redox flow batteries have significant potential to address the sustainable energy transition due to their scalable design, where energy capacity can be decoupled. The following chapters elaborate on the use of perylene derivatives as redox mediators for these batteries. Chapter 3 provides an outline of what perylenes are and how they can be tested for their electrochemical activity.

3 Perylene and Perylene-Derivatives

This chapter outlines the conducted research and usage of perylene in section 3.1. After which an overview is given in section 3.2 of some of the common perylene-derivatives. The potential advantages and disadvantages of perylene-derivatives, as mediator in electrolyte, are discussed in section 3.3. Finally the theoretical electrochemical potentials of perylene-derivatives is shown in section 3.4.

3.1 Research and Usage of Perylene and Perylene-Derivatives

Perylene's unique molecular structure, consisting of five benzene rings, captured the attention of scientists and led to various research endeavors since last century. Perylenes have been extensively studied for their use as photostable fluorescent dyes. In order to meet specific requirements for these dyes, the solid structure and their solubility were controlled by using different substitutions of cyclic carboxylic imides to perylene. [26]

In the realm of electrochemistry, perylene and its derivatives have found significant utility. The electrochemical properties of perylene-derivatives were extensively studied, and they emerged as promising materials for various applications. One notable application is the use of perylene-derivatives in organic electronics, where they have served as redox-active components in organic light-emitting diodes (OLEDs), organic photovoltaic cells (OPVs), and organic field-effect transistors (OFETs). The redox activity of perylene-derivatives allows for efficient charge transport and facilitates their incorporation into electronic devices. [27]

Additionally, perylene-based materials have been investigated for their potential in energy storage devices. Recyclability; abundance of materials; redox stability and the reversible redox processes exhibited by perylene-derivatives make them suitable candidates for use in storage solutions. [6]

In summary, perylene's journey from its discovery to its utilization in electrochemical applications has been a tale of scientific curiosity and innovation. Its derivatives continue the interest in its use for more sustainable and efficient technologies.

3.2 Perylene-Derivatives

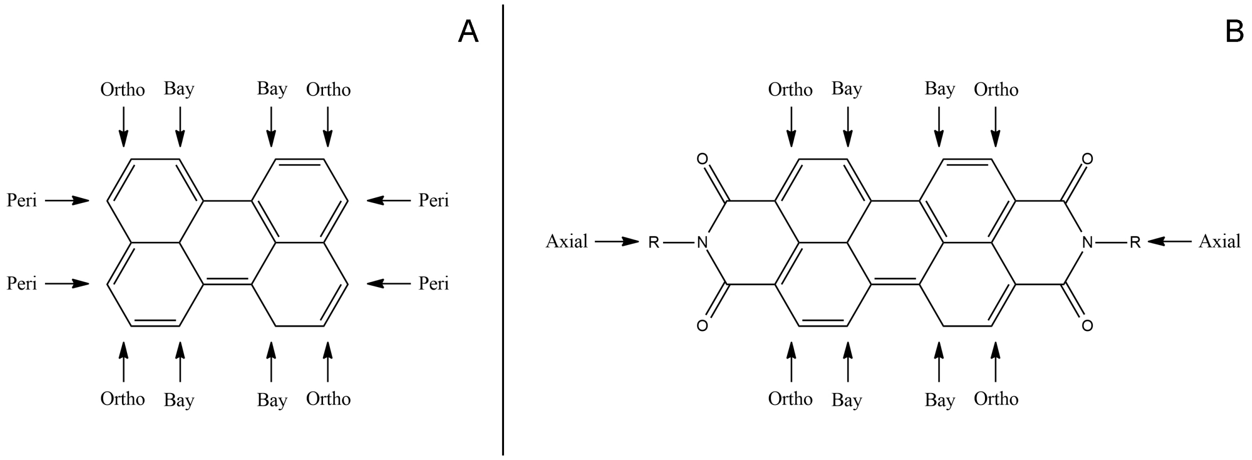


Figure 3: Substitution positions of Perylene (**A**) and Perylene imides (**B**)

Perylene-derivatives are a class of organic compounds derived from the parent molecule perylene, which consists of five fused benzene rings. These derivatives exhibit various substitution patterns, with the most common being Bay, Ortho, and Peri substitutions, as shown in figure 3A. First, Bay-substituted refers to the substitution to the carbon atoms located at the "bay" positions, which are adjacent to the central fused ring system. Second, Ortho-substituted involve functional groups attached to the carbon atoms located ortho, that will say directly adjacent to the benzene rings in the perylene structure. Third, Peri-substitutions are characterized by substituents or functional groups directly attached to the carbon atoms situated on the periphery of the aromatic core.

Different types of substitution groups can significantly influence the optical and electronic properties of the molecule, leading to changes in charge transport characteristics; molecular packing; intermolecular interactions; stability. This also led to changes in redox properties and other electrochemical behavior.

One example of perylene-derivatives is Perylene Imides, where the substitution points are shown in figure 3B. Perylene imides are obtained by incorporating imide functional groups (O=C-N-C=O) onto the perylene core.

These compounds have gained significant attention due to their excellent electron-accepting properties and high electron affinity.

The chemical and electrochemical properties of perylene-derivatives can be fine-tuned by substituting various functional groups at Bay, Ortho, or Peri positions. These substitutions impact the optical and electronic properties of the derivatives, making them versatile materials with a wide range of applications in organic electronics and related fields.

Three of the main substitution groups to perylene are given in the following sections. Describing perylene anhydrides in section 3.2.1; perylene imides in section 3.2.2; and perylene esters in section 3.2.3. In general the esters are considered the weaker electron acceptors, than anhydrides and imides are the stronger electron acceptors of the three derivative groups. [28]

3.2.1 Anhydrides

Perylene anhydrides, such as perylenetetracarboxylic dianhydride (PTCDA) shown in figure 4, are a class of perylene-derivatives characterized by the presence of two carbonyl groups (C=O) on their molecular structure. The anhydride functional group consists of two acyl groups connected by an oxygen atom, resulting in a ring-like structure. The conjugated π-system of the perylene core imparts notable electronic properties to these derivatives. Perylene anhydrides often exhibit electron-accepting capabilities, making them useful in charge-transfer processes and electron-transport applications. [28,29]

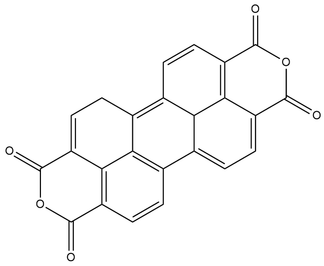


Figure 4: Structure of perylenetetracarboxylic dianhydride (PTCDA)

3.2.2 Imides

Perylene imides, shown in figure 5, are a class of derivatives where the central perylene core is functionalized with imide groups (-CONH-) on its nitrogen atoms. The introduction of imide moieties enhances the electron-withdrawing properties of the perylene core, leading to further modulation of their electronic characteristics. Perylene imides are known for their high electron affinity, making them excellent electron acceptors in organic semiconductors. In terms of electrochemical behavior, perylene imides often exhibit reversible redox processes, allowing for efficient charge transfer and transport. The tunable electronic properties of perylene imides have made them attractive candidates in the design of functional materials for optoelectronic and energy-related applications. Perylene imides are the stronger electron acceptors of the three derivative groups. [6,28,30]

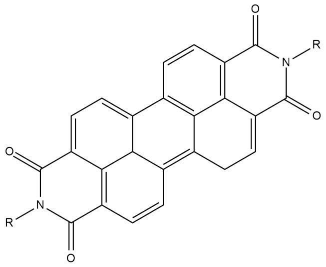


Figure 5: Structure of perylene diimides (PDI)

3.2.3 Esters

Perylene esters, such as perylene tetraester (PTE) shown in figure 6, are perylene-derivatives that feature ester functional groups (-COOR) attached to the central perylene core. The presence of ester groups introduces a degree of polarity and alters the solubility and processability of these compounds. Perylene esters possess intriguing optical properties, displaying strong absorption in the visible region, which makes them suitable candidates for dye sensitization in photovoltaic devices. The combination of the perylene core's π-conjugation and the ester group's redox activity results in versatile perylene esters with potential applications in diverse fields, including optoelectronics and energy storage. However perylene esters are the weaker electron acceptors of the three derivative groups. [28,31]

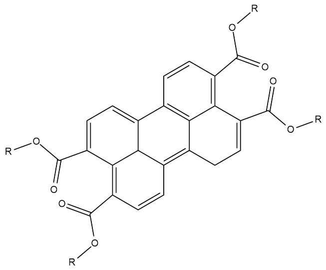


Figure 6: Structure of perylene tetraester (PTE)

3.3 Perylene-Derivatives as Mediator

Perylene-derivatives have shown promise as redox-active materials for redox flow batteries due to their stable and reversible redox behavior. Perylene-based compounds possess favorable electrochemical properties, including high stability, tunability of chemical and electrochemical properties, and a wide electrochemical window. These characteristics make them attractive for application in energy storage systems. The incorporation of perylene-derivatives as mediator into electrolytes could offer several similar potential advantages.

Some perylene-derivatives have been shown to have high Coulombic efficiency, which refers to the ability of an electrochemical system to retain and recover a high percentage of charge during the charging and discharging processes. This efficiency is crucial for maintaining the overall performance and longevity of the battery system. [32,33]

Perylene-derivatives also have good chemical and thermal stability, which helps to enhance the durability and long-term operation of batteries. Stable redox behavior ensures that the battery can undergo repeated charge and discharge cycles without significant degradation. [34,35]

Zhang et. al. describes the mediator reaction of the redox mediator (RM) and the active material (AM) for aqeous batteries as follows [36]:

Diffusion process

$$RM_{solution} \rightarrow RM_{electrodesurface} \tag{1}$$

Electrochemical process

$$RM_{electrodesurface} \pm e^{-} \rightarrow RM^{\pm}_{electrodesurface} \tag{2}$$

Diffusion process

$$RM^{\pm}_{electrodesurface} \rightarrow RM^{\pm}_{solution} \tag{3}$$

Spontaneous chemical process

$$RM^{\pm}_{solution} + AM \rightarrow RM_{solution} + AM^{\pm} \tag{4}$$

It is worth noting that the specific characteristics and performance of perylene-based electrolyte solutions can vary depending on the particular derivative, formulation, and system configuration. Further research and development are ongoing to explore the full potential of perylene-derivatives in batteries and optimize their performance in terms of energy density and stability.

3.3.1 Requirements Redox Mediator

Selecting appropriate redox mediators involves careful consideration of several requirements. Zhang et. al. have given an overview of essential criteria for selection of redox mediators [36]:

1. **Proper redox potential**: The redox potential of redox mediators is crucial in determining their suitability. It should align with the redox potential of the as-designed redox mediator couples, allowing for tunable charge or discharge potentials. For optimal performance, the redox potential of redox mediators is typically slightly lower than the oxidation potential of the active material or higher than its reduction potential, ensuring higher energy efficiency and coulombic efficiency.

2. **Spontaneous chemical reaction**: redox mediators should engage in spontaneous chemical reactions with targeted charge or discharge products of active materials. This criterion ensures that chemical steps proceed with downhill free energy ($\Delta G<0$), forming the foundation of the RM strategy.

3. **Fast electrochemical kinetics**: The electrochemical kinetics of redox mediators should be rapid, with low reaction barriers, facilitating efficient material transportation for subsequent chemical processes.

4. **Full solubility**: redox mediators must exhibit excellent solubility in electrolytes, maintaining strong wettability with electrode active materials and current collectors.

5. **Stability without side reactions**: redox mediators should remain stable and fully regenerate after each charge or discharge cycle. High stability is vital to prevent side reactions beyond the intended chemical and electrochemical processes.

3.4 Electrochemical Potential

Several studies demonstrate the tunable electrochemical potential of perylene-derivatives. Making perylene-derivatives highly versatile in a range of electrochemical applications. Their ability to undergo reversible redox processes enables efficient charge transfer and storage. As effective electron acceptors, they have found utility in organic electronics and photovoltaic devices. Additionally, their redox behavior makes them well-suited for use in redox-based sensors and energy storage systems.

The theoretical specific capacity of a molecule can be determined via equation 5. Here Q is the specific capacity (mAh/g); n is the number of electrons; F is the Faraday constant (96485 C/mol); and Mw is the molar weight (g/mol).

$$Q = \frac{nF}{3.6Mw} \tag{5}$$

As an example the reduction of Li/Li+ with perylenetetracarboxylic di-anhydride (PTCDA) is taken. The molar weight of PTCDA is 392.3 g/mol. If PTCDA would undergo a redox reaction with lithium it would exchange four electrons, as shown in figure 7A. Resulting in a theoretical specific capacity of 273.3 mAh/g.

However, it is essential to address parasitic and irreversible reactions that can occur during redox cycling, as they may impact the overall efficiency and long-term stability of these derivatives in electrochemical devices. This is also shown in figure 7B with the PTCDA example that the second step is irreversible. [6,37] Therefore only two electrons can be exchanged resulting in a specific capacity of 136.9 mAh/g.

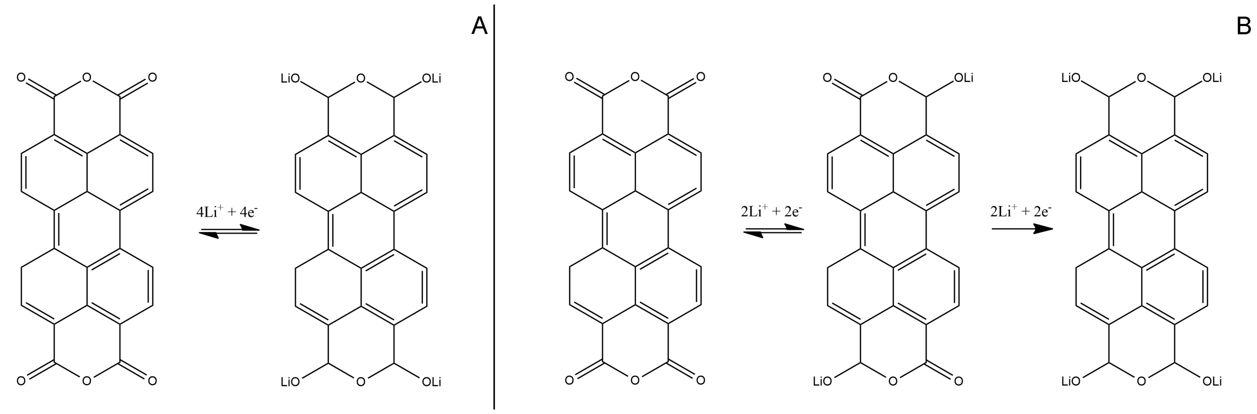


Figure 7: A) Electron and Li-ion exchange on PDI. B) Electron and Li-ion exchange on PDI with limited second step

For theoretical ends it's assumed that only two electrons will be used in the redox chemistry. However more electrons could be theoretically available as long as the step is reversible, which can be shown through experimentation.

3.4.1 Theoretical Redox Potential

Redox potential is a property related to the electrochemical behavior of a molecule, specifically its ability to undergo reduction or oxidation in an electrochemical reaction. It is a measure of the tendency of a species to be reduced or oxidized and is typically quantified in volts.

To determine the reduction potential of a molecule, you would need to employ quantum mechanical calculations, such as Density Functional Theory or other advanced computational methods, which consider the electronic structure and energetics of the chemical reactions involved in the redox process. However these calculation are complex, and get even more complicated with larger molecules. [38,39]

From literature the range of some perylene-derivatives is shown; ranging from -2.09V vs SHE for perylene tetraester to 0.51V vs SHE for perylene monoimide diesters. [6,28] To obtain the reduction potential of perylene and perylene-derivatives accurately, typically techniques such as cyclic voltammetry (see section 4.4) or other electrochemical methods are used.

4 Method and Materials

This chapter outlines the method for testing different perylene-derivatives. Giving an overview of the research goals in section 4.1. The different perylene-derivatives used are presented in section 4.2. The synthesis and characterization of some of the required perylene-derivatives are described in section 4.3; and the electrochemical measurements in section 4.4. The experiment is described in section 4.5 giving further insight into the construction of the working electrode and the battery cell setup.

4.1 Research Goal

The aim for this research is to test the electrochemically activity of perylene-derivatives for use as mediator in solution for zinc-air redox flow batteries. In order to achieve the goal, it important to look at the requirements of redox mediators in section 3.3.1. Which in summary are:

1. Proper redox potential
2. Spontaneous chemical reaction
3. Fast electrochemical kinetics
4. Full solubility
5. Stability without side reactions

To satisfy to this requirements and to choose a fitting perylene-derivative; first some ground work has to be done to find the electrochemical properties of the perylene-derivatives. The experimental method, using cyclic voltammetry, is describes in section 4.5 for testing perylene-derivatives for their electrochemical properties. Thereby attaining to the proper redox potential and the spontaneous chemical reaction.

4.2 Perylene-derivatives

The various perylene-derivatives used in the experiments are listed in Table 2. These molecules are selected to include a range of substitution groups, incorporating both electron-poor and electron-rich groups. This selection was intended to illustrate the effects of different substituents on the reduction potential. Molecule 000 PTCDA was obtained from Sigma-Aldrich and used without further purification. Molecules 008 PDI-EN and 009 PDI-PA were synthesized and analyzed as will be described in Section 4.3. Molecules 001 to 007 were synthesized, purified, and analyzed before this project and such being provided for experimentation.

Table 2: Molecule Library (Perylene-derivatives)

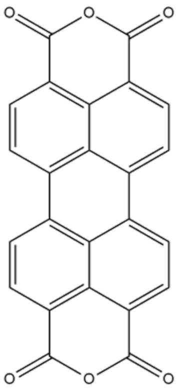
#	Name (Abbreviation)	Formula	MW (g/mol)	Structure
000	Perylene-3,4,9,10-tetracarboxylic dianhydride **(PTCDA)**	$C_{24}H_8O_6$	392.32	

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Table 2: Molecule Library (Perylene-derivatives) (Continued)

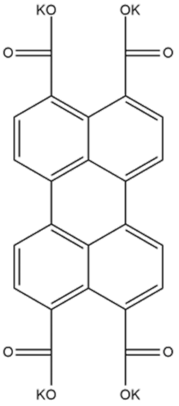
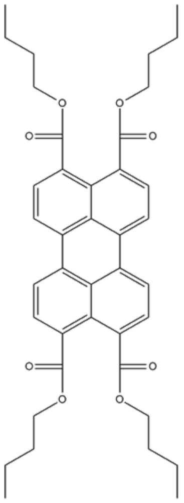
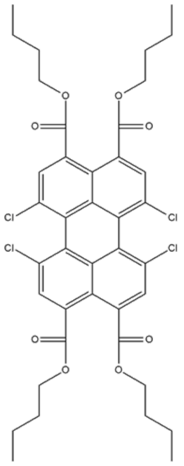
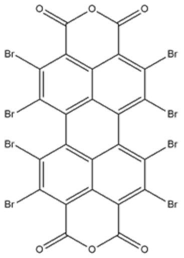
001	Perylene-3,4,9,10-tetracarboxylic-acid tetrapotassium salt **(PTAS)**	$C_{24}H_8K_4O_8$	580.71	
002	tetrabutyl-perylene-3,4,9,10-tetracarboxylate **(PTE)**	$C_{40}H_{44}O_8$	652.77	
003	tetrabutyl-1,6,7,12-tetrachloroperylene-3,4,9,10-tetracarboxylate **(PTE-Cl$_4$)**	$C_{40}H_{40}Cl_4O_8$	790.55	
004	Octabromoperylene-3,4,9,10-tetracarboxylic dianhydride **(PBA-Br$_8$)**	$C_{24}H_2Br_8O_6$	1025.50	

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Table 2: Molecule Library (Perylene-derivatives) (Continued)

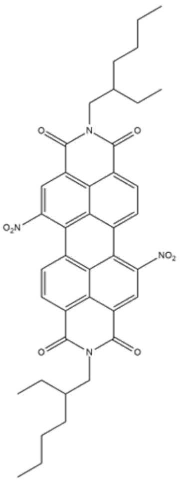
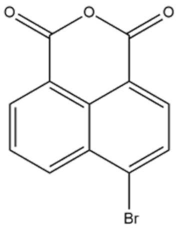
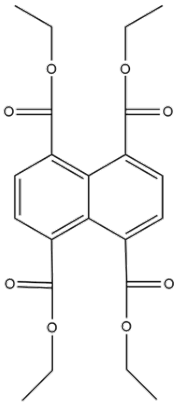
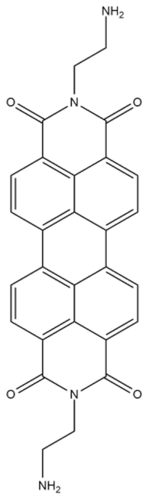
005	2,9-bis(2-ethylhexyl)-5,12-dinitroanthra[2,1,9-def:6,5,10-d′e′f′]diisoquinoline-1,3,8,10(2H,9H) tetraone **(2-et-hex PDI-(NO2))**	$C_{40}H_{40}N_4O_8$	704.77	
006	6-bromobenzo[de]isochromene-1,3-dione **(NMA-Br)**	$C_{12}H_5BrO_3$	277.07	
007	tetraethyl-naphthalene-1,4,5,8-tetracarboxylate **(et-NTE)**	$C_{22}H_{24}O_8$	416.15	
008	2,9-bis(2-aminoethyl)anthra[2,1,9-def:6,5,10-d′e′f′]diisoquinoline-1,3,8,10(2H,9H)-tetraone **(PDI-EN)**	$C_{28}H_{20}N_4O_4$	476.48	

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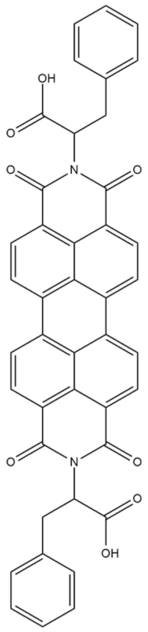
Table 2: Molecule Library (Perylene-derivatives) (Continued)

009	2,2′-(1,3,8,10-tetraoxoanthra[2,1,9-def:6,5,10-d′e′f′]diisoquinoline-2,9(1H,3H,8H,10H)-diyl)bis(3 phenylpropanoic acid) **(PDI-PA)**	$C_{42}H_{26}N_2O_8$	686.66	

4.3 Synthesis and Characterization

As described in section 4.2, molecules 008 PDI-EN and 009 PDI-PA are synthesized for this project using the same synthesis route. Figure 8 illustrates the synthesis route for PDI-PA. The reactants Perylenetetracarboxylic dianhydride (PTCDA), Phenylalanine (PA), and 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) are used in a molar ratio of 1:4:4 and dissolved in DMF in a round-bottom flask. The mixture is stirred at 80 °C for 24 hours, then allowed to cool to room temperature. Subsequently, it is poured into water to create a suspension. The pH is adjusted to approximately 1 by adding hydrochloric acid. After settling, the suspension is filtered and dried for at least 24 hours.

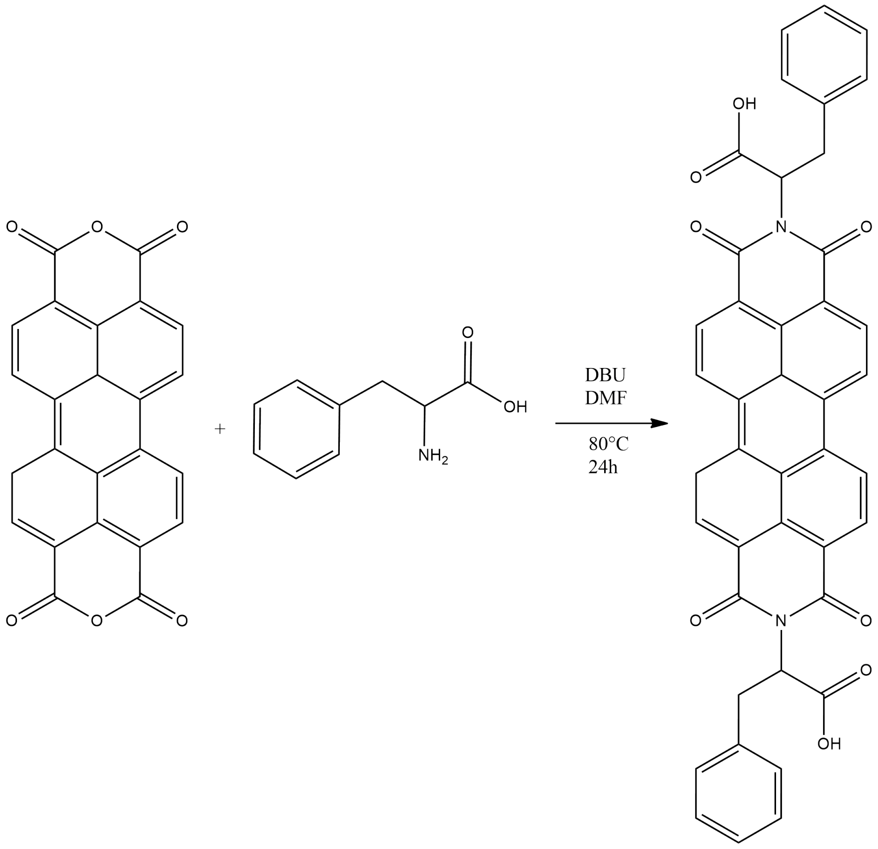


Figure 8: Synthesis route of PDI-PA

To confirm the identity and purity of the synthesized perylene-derivative, characterization is performed by using nuclear magnetic resonance (NMR) spectroscopy. NMR spectroscopy, with its ability to provide detailed molecular information and dynamic insights, is a valuable tool for characterizing and understanding materials. It aids in optimizing material synthesis, electrode formulation, electrolyte design, and overall battery performance. By providing valuable information about the chemical structure, composition, dynamics, and interactions of various components within battery systems. NMR spectroscopy can elucidate the molecular structure and bonding within battery materials. It can identify different functional groups, determine chemical shifts, and reveal details about the connectivity and arrangement of atoms within molecules. Furthermore NMR spectroscopy can be used for quantitative analysis to determine the concentrations of specific species within battery materials. By comparing the integrated signal intensities of known reference compounds, NMR can provide information about the abundance or concentration of particular components, such as active materials, solvents, or additives. [40]

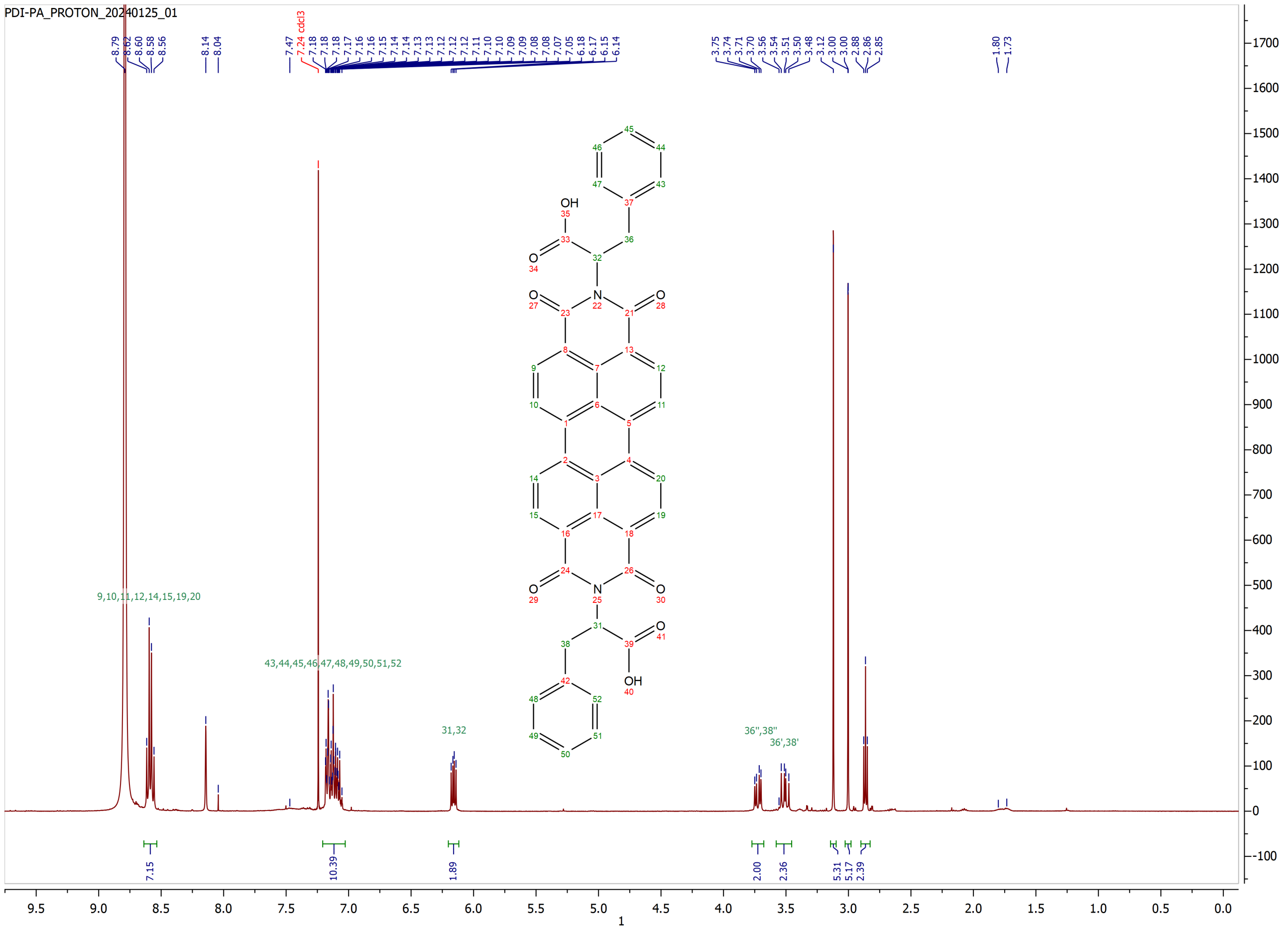


Figure 9: NMR of PDI-PA

The results of the NMR spectroscopy of PDI-PA are displayed in Figure 9. The PDI-PA peaks align with the expected peaks, confirming the successful synthesis of PDI-PA. However, the two large peaks on the right side suggest the presence of residual DMF, which explains the high yield of 91.8%.

4.4 Electrochemical Measurements

Voltammetry is a commonly used electrochemical technique for battery testing that provides valuable information about the electrochemical behavior and performance of battery materials and electrolytes. Specifically, it allows for the characterization of redox reactions, determination of redox potentials, and evaluation of kinetic parameters. In battery testing, there are several types of voltammetry techniques that can be employed, including: differential pulse voltammetry; square wave voltammetry; linear sweep voltammetry; and cyclic voltammetry.

For this research the focus is on cyclic voltammetry (CV), due to its use of investigating the electrochemical performance of the perylene-derivatives. Cyclic voltammetry involves sweeping the potential applied to the working electrode linearly over a specific range while measuring the resulting current.

Figure 10 shows an exemplary representation of a cyclic voltammetry. The technique provides information about the redox reactions occurring in the battery system, the redox potential of the active species, and the reversibility of the reactions. cyclic voltammetry is particularly useful for studying the electrochemical behavior of electrode materials and investigating the stability and performance of electrolytes. [41]

In order to evaluate the performance and suitability of perylene-derivatives use in electrolyte for required battery, one cycle (or few) will suffice to show the electrochemical activity of the material. When a suitable mediator compound has been found, multiple cycles using cyclic voltammetry could be used to determine: energy efficiency, cycling stability, and rate capability. As well to assess the stability and reversibility of the redox reactions. An overview of some important equations related to redox reaction and cyclic voltammetry is given in appendix A.

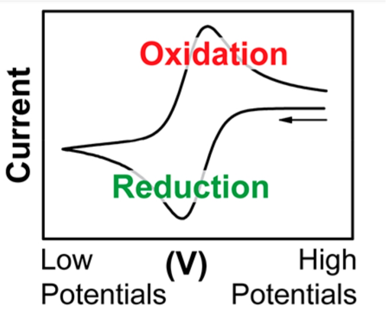


Figure 10: Exemplary representation of a cyclic voltammetry curve [41]

4.5 Experiment: Electrochemical Properties of Perylene-derivatives and CV setup

The purpose of this experiment is to test different perylene-derivatives for their electrochemical properties; such that an overview of different perylene-derivatives can be created to attain to requirements 1 and 2 from section 3.3.1. This will not only give insight if perylene-derivatives are fitted as appropriate redox mediator for Zinc-air redox flow batteries. But also creates an overview for potential other (electro-) chemical uses and other applications. An overview of battery cell compositions and materials for battery testing can be found in appendix B.

Pearce et. al. have done a study to electrochemical study of different perylene-derivatives. A method is provided using cyclic voltammetry on a three-electrode cell, of which an schematic overview is given in figure 11. The three-electrode cell was assembled with the following components [28]:

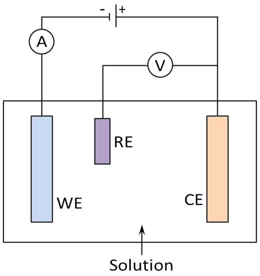


Figure 11: Schematic of a 3-electrode cell [42]

- **Working Electrode (WE)**: Glassy Carbon.
- **Reference Electrode (RE)**: Calomel.
- **Counter Electrode (CE)**: Platinum (Pt).
- **Perylene Solvent:** 2,6-(bis)diphenylmethyl-4-methylphenyl tecton.
- **Electrolyte:** An analyte concentration of 1 mM with [nBu4N][BF4] (400 mM) as a supporting electrolyte.

In the method of Pearce et. al. the perylene-derivatives are dissolved in the electrolyte, and the experiment is performed under a argon atmosphere. Although this method can be replicated; using an aqueous solvent instead of 2,6-(bis)diphenylmethyl-4-methylphenyl tecton. A similar method is proposed using a different composition of the three-electrode cell:

- **Working Electrode (WE)**: Examined Material.
- **Reference Electrode (RE)**: Ag/AgCl.
- **Counter Electrode (CE)**: Platinum (Pt).
- **Electrolyte**: aqueous (0.5M H_2SO_4)

The Ag/AgCl reference electrode is used due to its well-established stability as a reference electrode [43]. Platinum is selected as the counter electrode because of its high chemical stability and resistance to corrosion [44]. The working electrode is composed of the material being examined, which, in this case, are the perylene-derivatives.

4.5.1 Working Electrode and Cell Construction

Each working electrode for the different perylene-derivatives was made in the folowing way. A glass plate is cleaned and a sheet of aluminium foil was taped on the glass plate. A mixture of mass equivalent parts (1:1:1) of Polyvinylidene Fluoride (PVF), Super C45 (Carbon black) and perylene-derivative is mixed into a slurry with NMP as solvent. The slurry is than spread out using a doctor blade at 150 micrometer and dried for at least 24 hours to air. The electrode sheet was than cut in small strips so they can be used in the 3-electrode setup.

The working electrode, along with the Ag/AgCl reference electrode and platinum counter electrode, was then connected to the potentiostat and lowered into the container holding the appropriate electrolyte. The complete setup, ready for performing cyclic voltammetry, is shown in Figure 12.

Figure 12: 3-electrode cell setup. Green is connected to the working electrode of the perylene-derivative and C45 aluminium strip. Red is connected to the platinum wire counter electrode; and white is connected to the Ag/AgCl reference electrode.

5 Results and discussion

5.1 Cyclic Voltammetry

Cyclic voltammetry was performed on various perylene-derivatives. Appendix C presents all cyclic voltammograms of these derivatives. For the molecules PTAS (001) and et-NTE (007) listed in Table 2, clear cyclic voltammetry scans could not be obtained due to the active material dissolving in the alkaline electrolyte. However, reduction peaks for the other molecules were successfully identified, with the most stable being PDI-PA, as illustrated in Figure 13. This figure shows the cyclic voltammogram of PDI-PA using a H_2SO_4 (0.5M) electrolyte at a scan rate of 0.5 V/s.

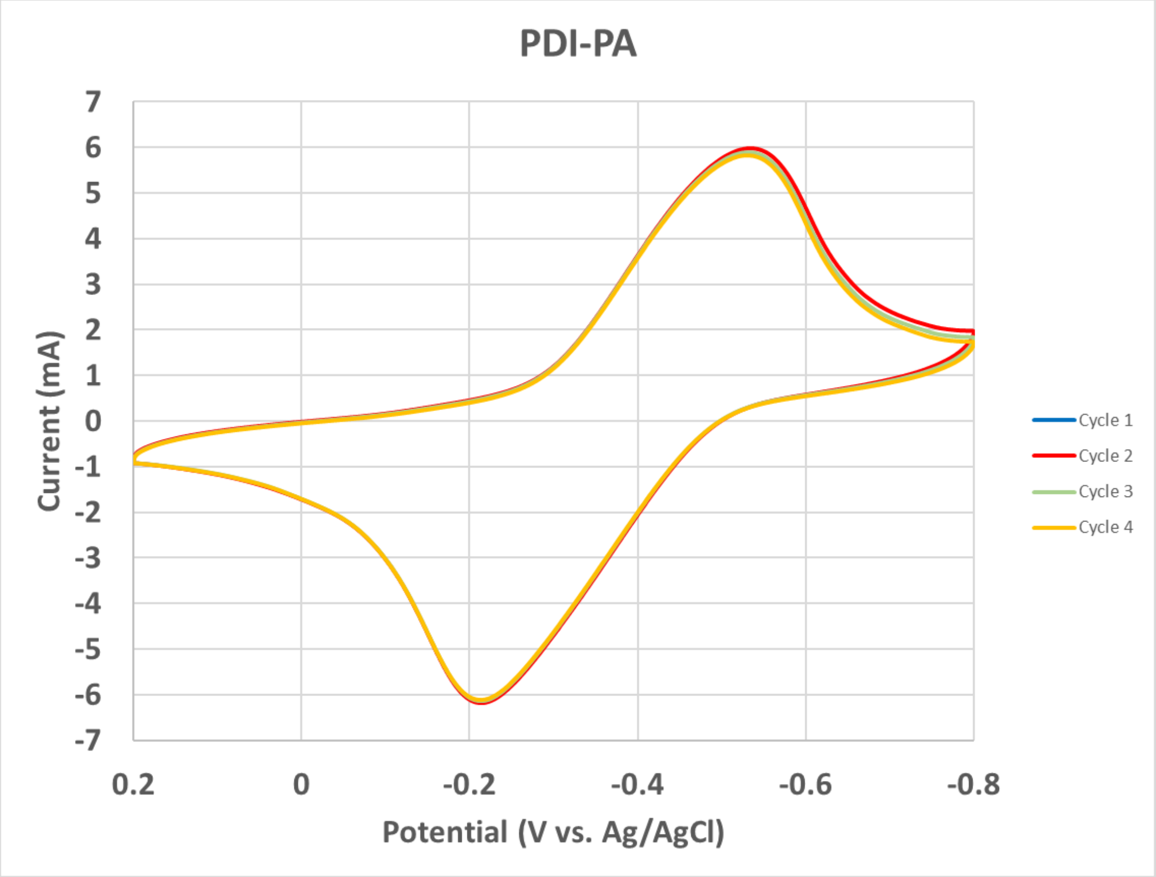


Figure 13: Cyclic voltammetry of PDI-PA using a H_2SO_4 (0.5M) electrolyte at a scan rate of 0.05 V/s

Cyclic voltammetry allows us to determine the half-potential at which specific electrochemical reactions occur at the electrodes. For instance, the peaks in Figure 13 are observed at -0.524 V vs. AgCl (-0.721 V vs. SHE) and -0.233 V vs. AgCl (-0.43 V vs. SHE). These values define the reduction potential window within which the molecule can function as a redox mediator. Additionally, from these peaks, the formal reduction potential can be deduced to be -0.379 V vs. AgCl (-0.576 V vs. SHE).

Figure 14 provides an overview of the reduction potential window and the formal reduction potentials of the various tested perylene-derivatives shown in section 4.2. The compound 2-et-hex PDI-(NO2) did not exhibit any peaks within the tested window and is therefore omitted from Figure 14. Additionally, et-NTE was highly unstable, dissolving into the electrolyte under both acidic and alkaline conditions, which made data collection impossible; thus, it is also excluded from figure 14.

From the voltammograms (Appendix C), it is evident that PTE, PTE-CL4, and NMA-Br are (partially) irreversible. NMA-Br, in particular, demonstrated instability by dissolving into the electrolyte under the acidic conditions in which it was tested. Furthermore, PBA-Br8 exhibited two redox peaks, potentially indicating irreversibility. On the other hand, PTCDA, PDI-PA, and PDI-EN displayed reversible peaks, with PTCDA and PDI-PA showing the greatest stability. These compounds would therefore be most suitable for the required potential window for oxygen reduction, depending on the acidity of the final required electrolyte medium. Showing possibilities for perylene-derivatives to attain to requirement 1 and 2 of section 3.3.1: proper redox potential and spontaneous chemical reaction.

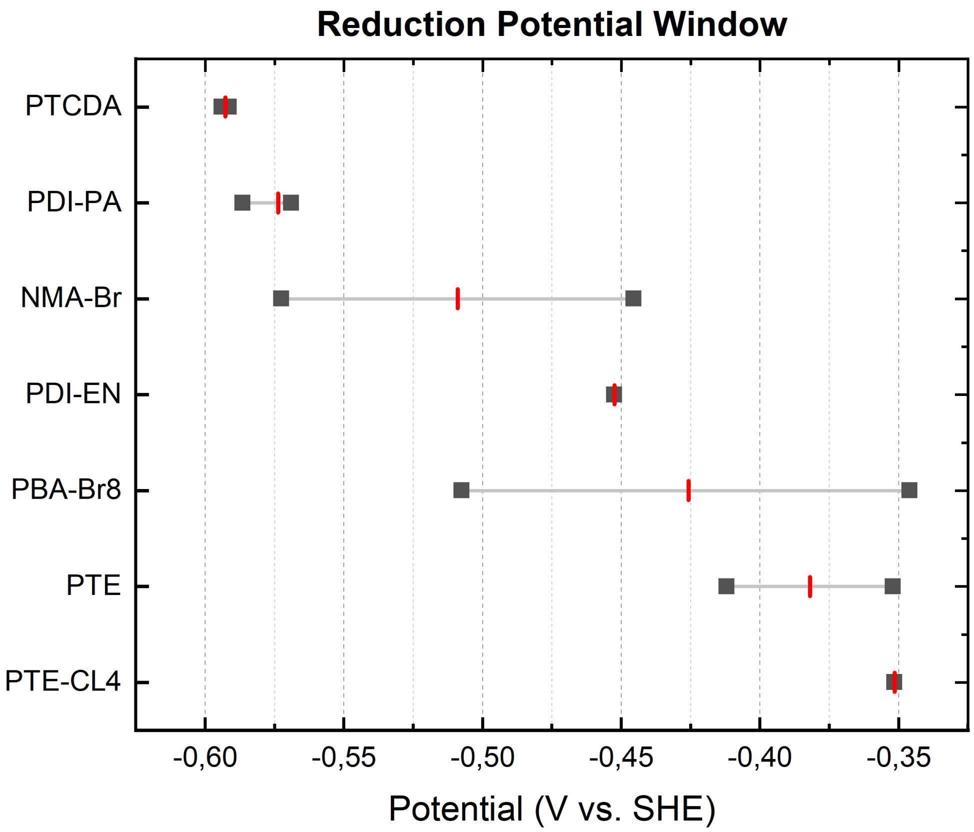


Figure 14: Reduction potential window and formal reduction potentials of the tested perylene-derivatives

5.2 Solubility of PDI-PA

As described in section 3.3.1 in requirement 4, another important aspect of using perylene-derivatives as redox mediators in solution is their solubility. An experiment has been set up to calculate the solubility of PDI-PA, chosen for its promising potential window and stability. Furthermore as of time of writing the electrolyte of the zinc-air redox flow battery is to be alkaline. Where PDI-PA is expected to be soluble under alkaline conditions and would therefor be fitting as redox mediator.

The experiment involves using a known diluted solution, in this case of 0.04 mM PDI-PA, in KOH (1M) and an unknown saturated solution of PDI-PA in KOH. These solutions are analyzed in 1 cm cuvettes using UV-Vis spectroscopy, which measures the absorbance of ultraviolet and visible light by the sample. The absorbance spectrum obtained provides information about the concentration of the solutions using the Lambert-Beer law:

$$A = \epsilon * b * c \tag{6}$$

Where A is the absorbance; ϵ is the absorptivity (L/(mol*cm)); b is the optical path length (cm); and c is the concentration (mol/L).

Figure 15 shows the UV-Vis spectra of the diluted and saturated solutions. To calculate the concentration of the saturated solution, the peak absorbance around 465 nm is used, which is 0.39 for the 0.04 mM solution and 0.475 for the saturated solution. Using the known concentration of the diluted solution and the Lambert-Beer formula (eq. 6), the absorptivity is determined to be 9933.7 L/(mol*cm). With the absorptivity and the absorbance of the saturated solution at the same peak now known, the formula is used again to calculate the solubility concentration, which is 1.48 mM or 1.02 g/L (at pH 14).

This solubility concentration is too low for practical use as a mediator in redox flow batteries. Especially as the expected electrolyte will be alkaline for the zinc-air redox flow battery. However The previously described experiment can also be repeated for some other perylene-derivatives and therefore, it is necessary to explore different perylene-derivatives that maintain the correct redox potential and stability of PDI-PA but offer higher solubility.

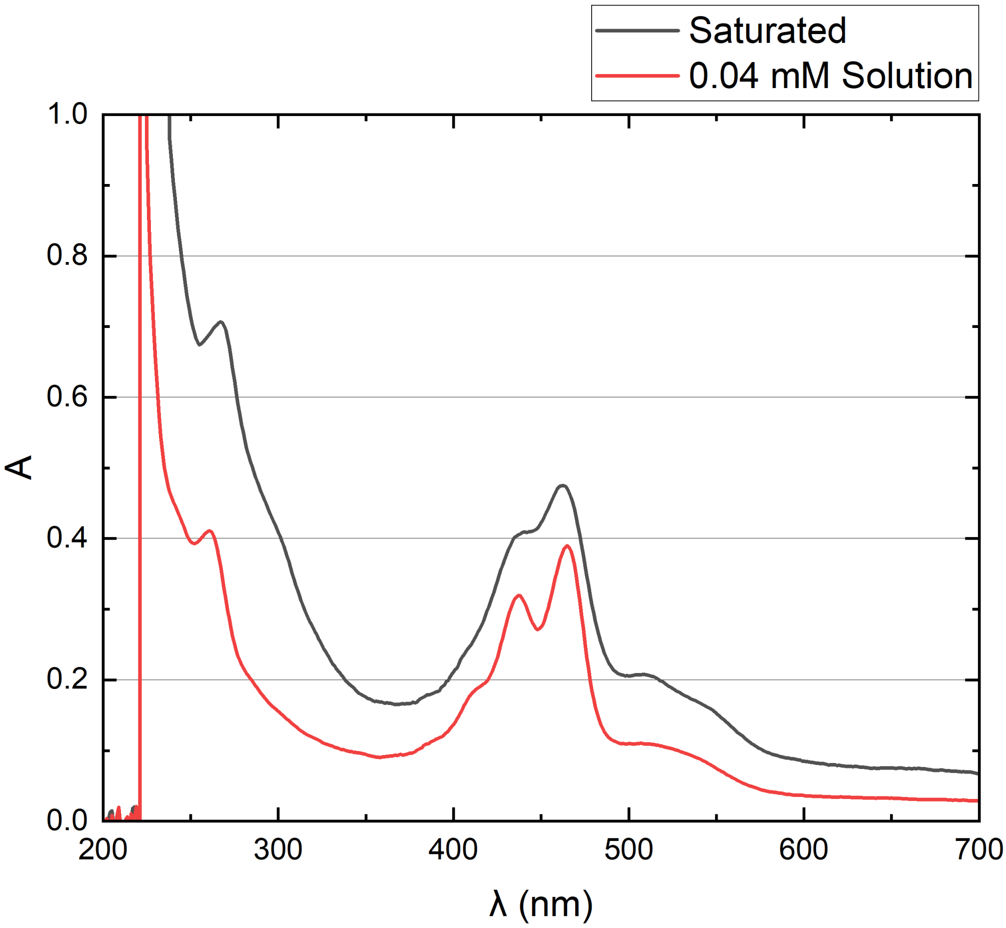


Figure 15: UV-VIS of PDI-PA in a saturated KOH (1M) solution and diluted 0.04 mM Solution in KOH

5.3 Discussion and Suggestions

As demonstrated in the literature and experimentation, perylene-derivatives are electrochemically active and suitable for electrochemical applications. However, using perylene-derivatives as redox mediators requires further research. Section 5.1 indicates that the reduction potential can be adjusted to the desired level by modifying the substitution groups on the perylene core. Nonetheless, high solubility is also essential for redox mediators, and as shown in Section 5.2, this is not the case for PDI-PA. Future research should focus on adjusting and optimizing the substitution groups on the perylene core to develop a perylene-derivative that meets the required redox potential, stability, and high solubility.

Once perylene-derivatives have been proven electrochemically active within the desired range, stable, and highly soluble, further experimentation is recommended to test additional requirements for redox mediators as described in Section 3.3.1. This could involve testing the perylene-derivative as a mediator in conventional batteries, such as coin cells or Swagelok cells, or directly in a redox flow battery setup. These cells can be evaluated using cyclic voltammetry with multiple cycles to gain further insights into the mediator's effectiveness, stability, and energy efficiency.

Another approach is to investigate a large group of perylene-derivatives using computational methods. This allows examination of a wide range of molecules to identify those with the required reduction potentials. One effective method is density functional theory (DFT), which can analyze the electronic structure of molecules and determine various theoretical properties. [28]

Overall, it is clear that more research is needed to find a suitable redox mediator for the oxygen side of zinc-air redox flow batteries. If a perylene-derivative exhibits the desired electrochemical properties, further testing should focus on its stability, electrochemical efficiency, and reactions within the complete redox flow battery. While this study has only laid the groundwork to explore the potential of perylene-derivatives as redox mediators, they show promise as organic redox mediators in redox flow batteries.

6 Conclusion

The global transition towards renewable energy sources is driven by the increasing demand for energy and the urgent need to mitigate climate change. Due to significant growth in energy generation demand, advancements in energy storage technology is required. Addressing the intermittency of renewable energy sources like solar and wind requires specialized energy storage solutions. Energy storage technologies also play a crucial role in stabilizing the grid, enabling load shifting, enhancing grid resilience, providing backup power, and participating in energy markets. By effectively deploying energy storage systems, a more sustainable and reliable energy infrastructure can be achieved, facilitating the integration of clean energy sources and reducing reliance on fossil fuels.

Flow batteries, such as the zinc-air redox flow battery, offer promising advantages with flexible energy storage capacity and long cycle life. However zinc-air redox flow batteries are still early on its research and development stage. One challenge is to find a suitable redox mediator for the air side. The use of utilizing perylene-derivatives as mediators in zinc-air flow batteries is promising due to their electrochemical activity, recyclability, and redox stability.

Perylene and its derivatives have garnered significant attention in scientific research due to their unique molecular structure and electrochemical properties. Perylene-derivatives, such as perylene imides, have been studied for their use as photostable fluorescent dyes and redox-active components in organic electronics. Moreover, perylene-based materials show promise for energy storage applications.

This research aimed to evaluate the electrochemical activity of perylene-derivatives as mediators in zinc-air redox flow batteries, focusing on key requirements such as proper redox potential, solubility, and stability. Various perylene-derivatives were synthesized and characterized using NMR spectroscopy. Cyclic voltammetry was used to investigate their electrochemical properties and performance and the solubility was determined by using UV-VIS spectroscopy.

From the cyclic voltammetry of the various perylene-derivatives it resulted that PTAS and et-NTE dissolved in the alkaline electrolyte, rendering clear scans unobtainable. Reduction peaks for the other molecules were successfully identified. The reduction potential window and formal reduction potentials for these derivatives were documented, with PTCDA, PDI-PA, and PDI-EN displaying reversible peaks and high stability; making them suitable for applications depending on the electrolyte's acidity.

However the solubility concentration of 1.48 mM of PDI-PA, which was determined using UV-Vis spectroscopy, indicated too low for practical use in redox flow batteries. Consequently, further exploration of other perylene-derivatives that offer the correct redox potential, stability, and higher solubility is necessary for developing effective redox mediators.

In conclusion, while perylene-derivatives have been shown to be electrochemically active and suitable for various applications, their use as redox mediators requires further research. Modifying the substitution groups on the perylene core can adjust the reduction potential to the desired level, but achieving high solubility remains a challenge, as demonstrated by PDI-PA. Future research should focus on optimizing these substitution groups to develop perylene-derivatives that meet the required redox potential, stability, and solubility. Once these properties are achieved, further experimentation in conventional batteries and redox flow battery setups is recommended to assess the mediator's effectiveness, stability, and energy efficiency through cyclic voltammetry and other methods. Additionally, computational methods such as density functional theory (DFT) can be employed to investigate a wide range of perylene-derivatives, identifying those with the required reduction potentials. Overall, more research is needed to find a suitable redox mediator for the oxygen side of zinc-air redox flow batteries. If a perylene-derivative meets the desired electrochemical properties, subsequent testing should focus on its stability, electrochemical efficiency, and reactions within the complete redox flow battery. While other other organic molecules should not be excluded, perylene-derivatives have shown their potential as organic redox mediators in redox flow batteries.

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Appendix

A Formula Sheet

Standard Reduction Potentials

$$E^0_{red} = -E^0_{ox} \tag{7}$$

E^0_{red}: Standard reduction potential (V)
E^0_{ox}: Standard oxidation potential (V)

$$E^0 = E^0_{red,cat} + E^0_{ox,an} = E^0_{red,cat} - E^0_{red,an} \tag{8}$$

E^0: Standard reduction cell potential (V)
$E^0_{red,cat}$: Standard reduction potential at cathode (V)
$E^0_{ox,an}$: Standard oxidation potential at anode (V)
$E^0_{red,an}$: Standard reduction potential at anode (V)

Gibbs Free Energy Change

$$\Delta G = -nFE \tag{9}$$

ΔG: Gibbs free energy change (kj/mol)
n: Number of electrons transferred
F: Faraday constant (96,500 C/mol)
E: Potential (V)

Nernst Equation

$$E = E^0 + \frac{RT}{nF} ln \frac{a_{ox}}{a_{red}} \approx E^0 + \frac{RT}{nF} ln \frac{C_{ox}}{C_{red}} \tag{10}$$

E: Potential (V)
E^0: Standard potential (V)
R: The universal gas constant (8.31446 JK^1mol^1)
T: Temperature (K)
n: Number of electrons transferred
F: Faraday constant (96,500 C/mol)
a: Chemical activity for the relevant species
C: Concentration for the relevant species (g/m^3)

Halfway-, Formal Reduction Potential

$$E_{1/2} = \frac{E_{pc} + E_{pa}}{2} \approx E^{\circ'} \tag{11}$$

$E_{1/2}$: Halfway reduction potential (V)
E_{pa}: Anodic peak potential (V)
E_{pc}: Cathodic peak potential (V)
$E^{\circ'}$: Formal reduction potential (V)

Fick's Second Law

$$\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} \tag{12}$$

C_A: Reactant concentration (g/m^3)
D_A: Diffusion coefficient (m^2)

x: Distance from the electrode (m)
t: Time (s)

Peak Current & Scan Rate

$$i_p = (2.69x10^5)n^{3/2}AD_A^{1/2}v^{1/2}C_A^* \tag{13}$$

i_p: Peak current (A)
x: Distance from the electrode (m)
n: Number of electrons transferred
A: Surface area of the working electrode (m^2)
D_A: Diffusion coefficient (m^2)
v: Sweeping rate (V/s)
C_A^*: Bulk concentration of reactant A (g/m^3)

$$i_p = 0.446nFAC^0(\frac{nFvD_0}{RT})^{1/2} \tag{14}$$

i_p: Peak current (A)
F: Faraday constant (96,500 C/mol)
A: Surface area of the working electrode (m^2)
C^0: Bulk concentration of the analyte (g/m^3)
n: Number of electrons transferred
v: sweeping rate (V/s)
D_0: Diffusion coefficient (m^2)
R: The universal gas constant (8.31446 JK^1mol^1)
T: Temperature (K)

B Battery Cell Compositions and Materials

This appendix gives an overview of battery cell compositions and materials for battery testing, in order to get a better understanding of what cells and material can be used for the testing of the electrochemical activity of perylene-derivatives. An overview of different cell types are given in section B.1. Section B.2 gives an overview of some common electrode materials. Finally section B.3 looks at different solvents and electrolyte formulation.

B.1 Cell Types

When testing for battery properties, various cell types can be used. Some most common cells for battery testing are the coin cells and swagelok cells. Also there is taken a look at three-electrode cells, half cells and full cells setup.

Coin Cells and Swagelok Cells

Coin cells, also known as button cells, are small, compact cells typically used for preliminary testing or screening electrolytes. They consist of two electrodes separated by a separator, with the electrolyte impregnated within the separator. Coin cells are relatively simple and inexpensive, making them suitable for initial characterization and basic electrochemical analysis. Swagelok cells, which can be a type of coin cell, are often used for testing liquid or gel electrolytes. They consist of a cylindrical cell holder with two electrodes, sealed with a Swagelok fitting to ensure a leak-proof enclosure. Swagelok cells are versatile and allow for easy replacement of electrolytes, making them suitable for battery optimization and performance evaluation. [45]

Three-electrode Cells

Three-electrode cells are commonly used for more advanced electrochemical analysis, such as cyclic voltammetry and impedance spectroscopy. These cells consist of a working electrode, a counter electrode, and a reference electrode. The working electrode is usually a material of interest, while the counter electrode (often platinum or graphite) and reference electrode (e.g., Ag/AgCl or saturated calomel electrode) serve as reference points for measuring the electrochemical behavior of the electrolyte. Different setups are possible for three-electrode cell testing. So can a coin cell for example be used with a wire as reference electrode. [46]

Half cells and Full cells

Half cells are used to evaluate the electrochemical properties of specific electrode materials or to study electrode-electrolyte interactions. They typically consist of a single electrode (either the positive or negative electrode) immersed in the electrolyte solution, with a reference electrode used for potential measurement. Half cells are useful for investigating the stability, reversibility, and electrochemical performance of electrode materials in different electrolytes. Full cells are complete battery configurations where both the positive and negative electrodes are present, along with the electrolyte. Full cells allow for comprehensive testing of the overall battery performance, including capacity, cycling stability, rate capability, and energy efficiency. These cells are crucial for evaluating the compatibility and effectiveness of the electrolyte in a practical battery system. [46]

B.2 Electrode Materials

Stable electrode materials are crucial for reliable and accurate testing in battery cells.

Carbon-Based Materials

Carbon-based materials, such as graphite or carbon black, are widely used as stable electrode materials in electrolyte testing. They exhibit excellent stability, good electrical conductivity, and chemical inertness, making them suitable for a variety of electrolytes and electrochemical measurements. [47]

Noble Metals

Noble metals, including platinum (Pt) and gold (Au), are often employed as stable electrode materials in certain electrochemical studies. These metals offer high chemical stability and are resistant to corrosion, making them suitable for testing a wide range of electrolytes and facilitating accurate measurement of electrochemical parameters. [44]

Metal Oxides

Various metal oxides, such as titanium dioxide (TiO2), lithium iron phosphate (LiFePO4), and manganese dioxide (MnO2), are commonly used as stable electrode materials. Metal oxides are stable, electrochemically active, and can provide insight into the performance of electrolytes in specific battery chemistries. [47]

Metal Alloys

Some stable metal alloys, like nickel-metal hydride (NiMH) and nickel-cadmium (NiCd), are utilized as electrode materials in electrolyte testing. These alloys offer good stability and specific electrochemical properties suitable for certain electrolyte systems. [47]

B.3 Electrolytes and Solvents

The choice of solvents for the electrolyte solution is crucial to ensure the solubility of salts, acids, and bases. While considering the stability and performance of the system. The choice of solvent or solvent system depends on several factors, including the solubility of the ionic compound, the redox properties of the mediator, and the compatibility with other battery components. Electrolytes for effective batteries should have a wide electrochemical window, high ionic conductivity, low electrical conductivity, low viscosity, thermal stability, good wettability, low cost, environmental friendliness, and non-corrosive properties. [47]

Organic Solvents

Organic electrolytes are widely used in batteries for electronic devices like cellphones, laptops, and vehicles. These electrolytes contain metal salts with weakly coordinating anions dissolved in organic solvents. Organic solvents are preferred due to their wider electrochemical window compared to water, making them suitable for various battery applications. One significant drawback of organic electrolytes is their flammability, which raises safety concerns. For commercial battery technologies, finding non-hazardous electrolyte alternatives is crucial. Some solvents with high flashpoints, like Gamma-butyrolactone and sulfolane, have been considered as safer alternatives to carbonates. Acetonitrile is a commonly used solvent in electrochemical studies due to its good solubility and wide electrochemical stability window. Dimethylformamide (DMF) is another organic solvent known for its high solvating power and compatibility with a wide range of electroactive species. Propylene Carbonate (PC) is a cyclic carbonate solvent that exhibits good solvating ability and is often used in combination with other organic solvents. [47]

Aqueous Electrolytes

Aqueous electrolytes offer cost advantages compared to organic ones, but there's a trade-off as they have a limited voltage range due to water splitting into hydrogen and oxygen gases above 1.23 V. This window can be extended with suitable electrode materials that slow down water electrolysis. There is ongoing research on aqueous batteries. The main challenge is finding electrode materials compatible with water and whose redox reactions occur within the limited electrochemical window, as some materials like graphite are unsuitable for aqueous lithium-ion batteries due to their thermodynamic potential. Water is the most common solvent for aqueous electrolytes.Mixtures of organic solvents and water can be employed to create mixed solvent electrolyte systems. These systems can provide a balance between the solubility and stability of perylene compounds. [47]

C Cyclic Voltammograms

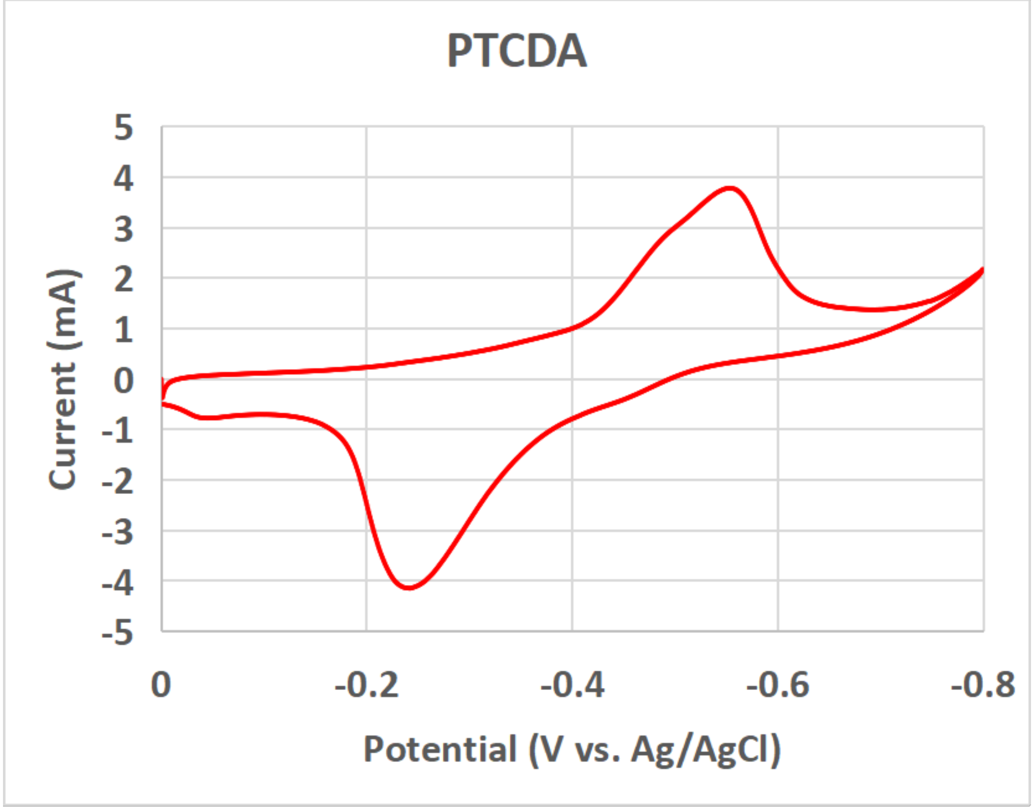

Figure 16: CV of PTCDA using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

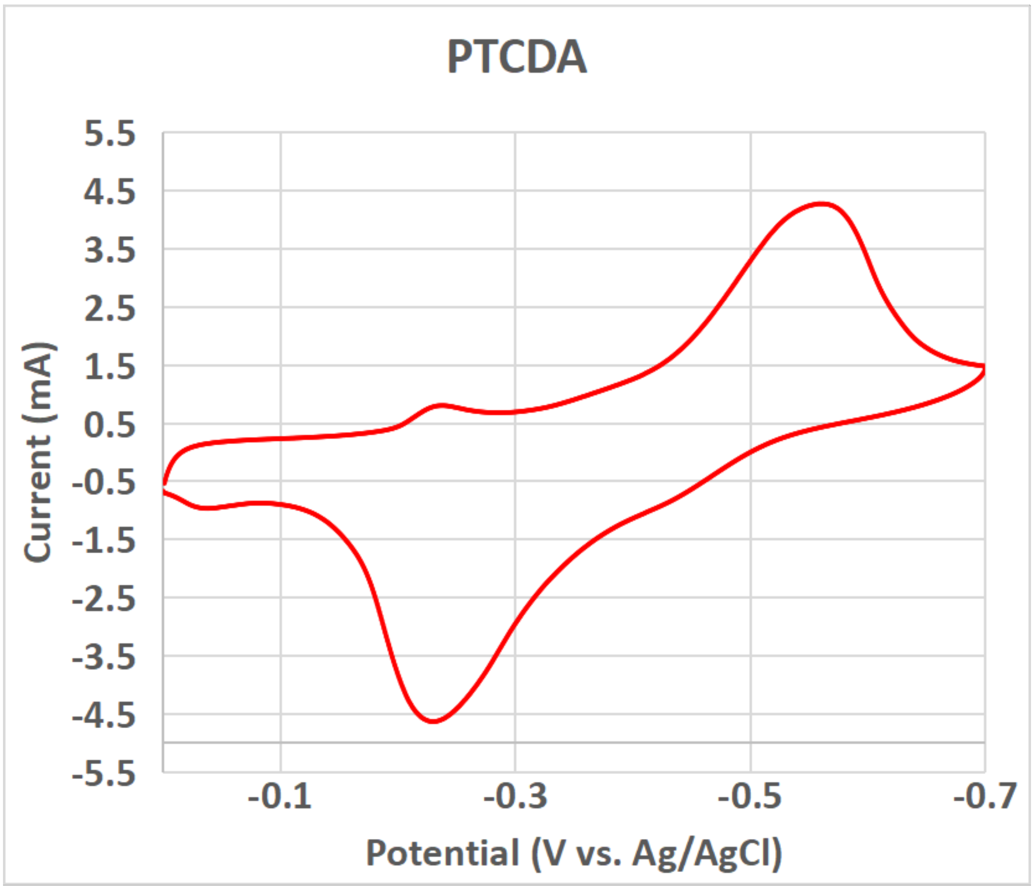

Figure 17: CV of PTCDA using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

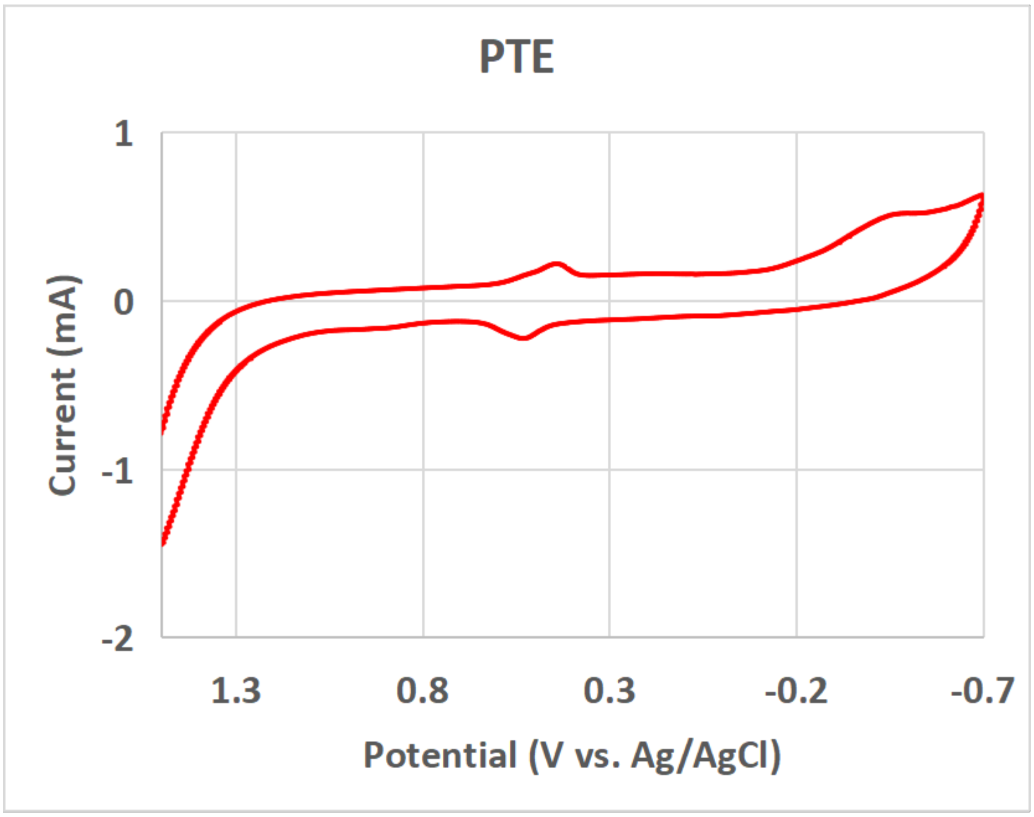

Figure 18: CV of PTE using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

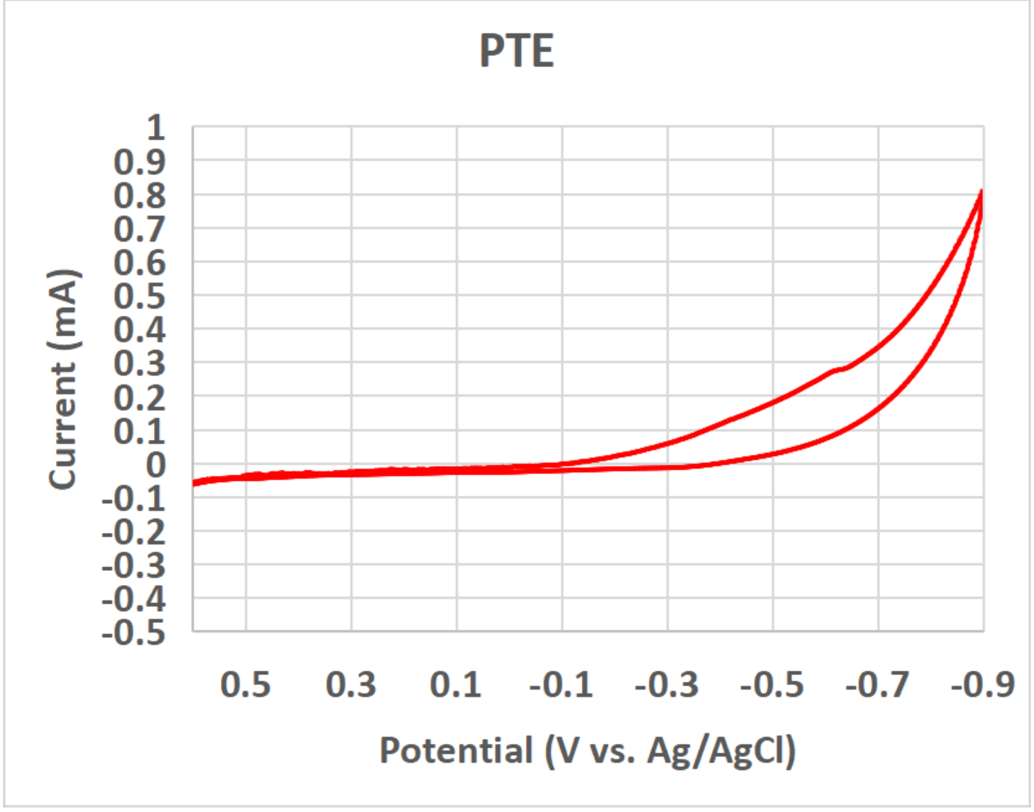

Figure 19: CV of PTE using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

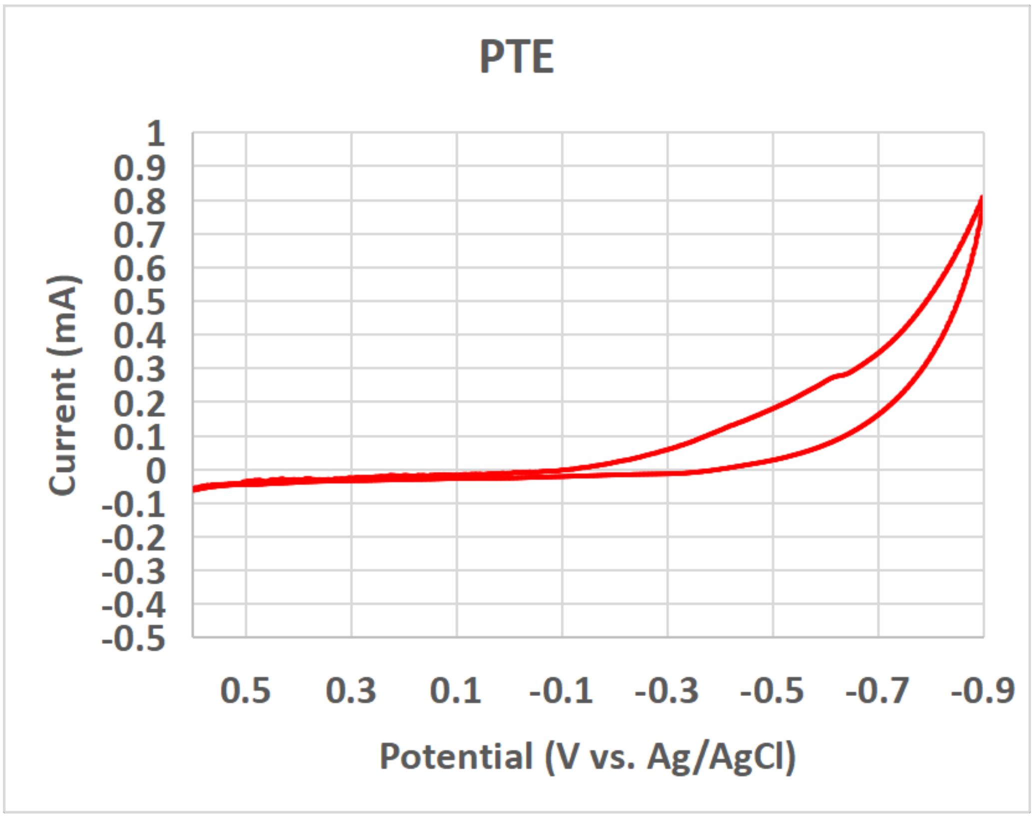

Figure 20: CV of PTE-Cl_4 using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

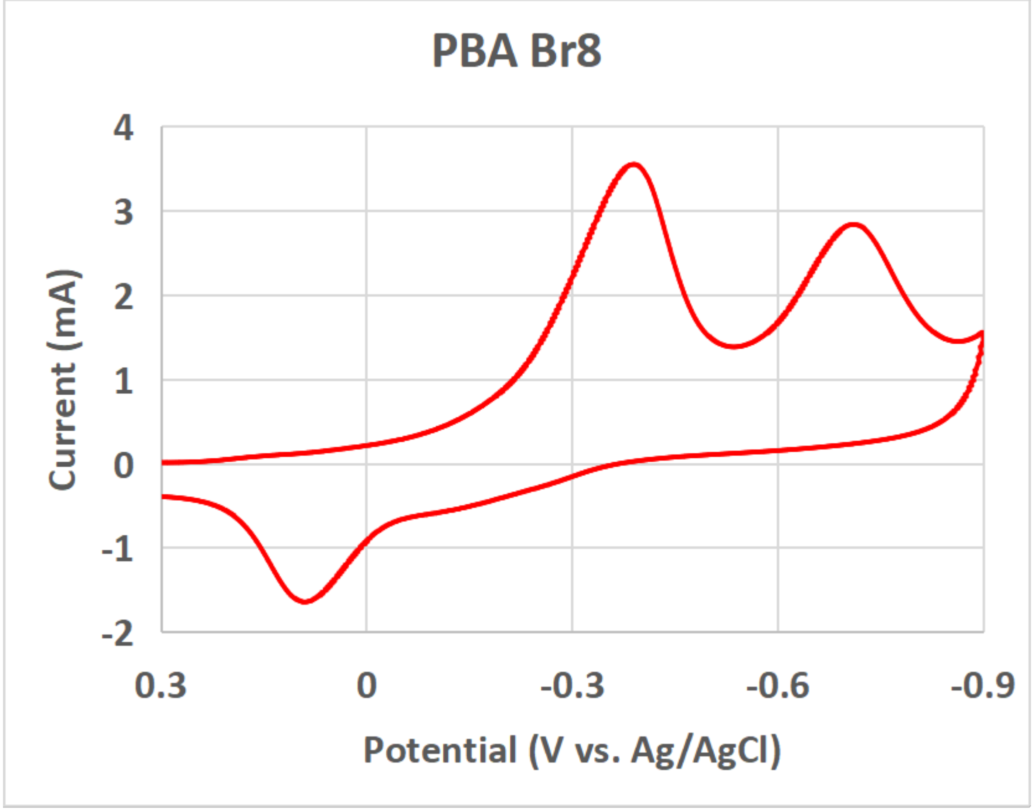

Figure 21: CV of PBA-br_4 using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

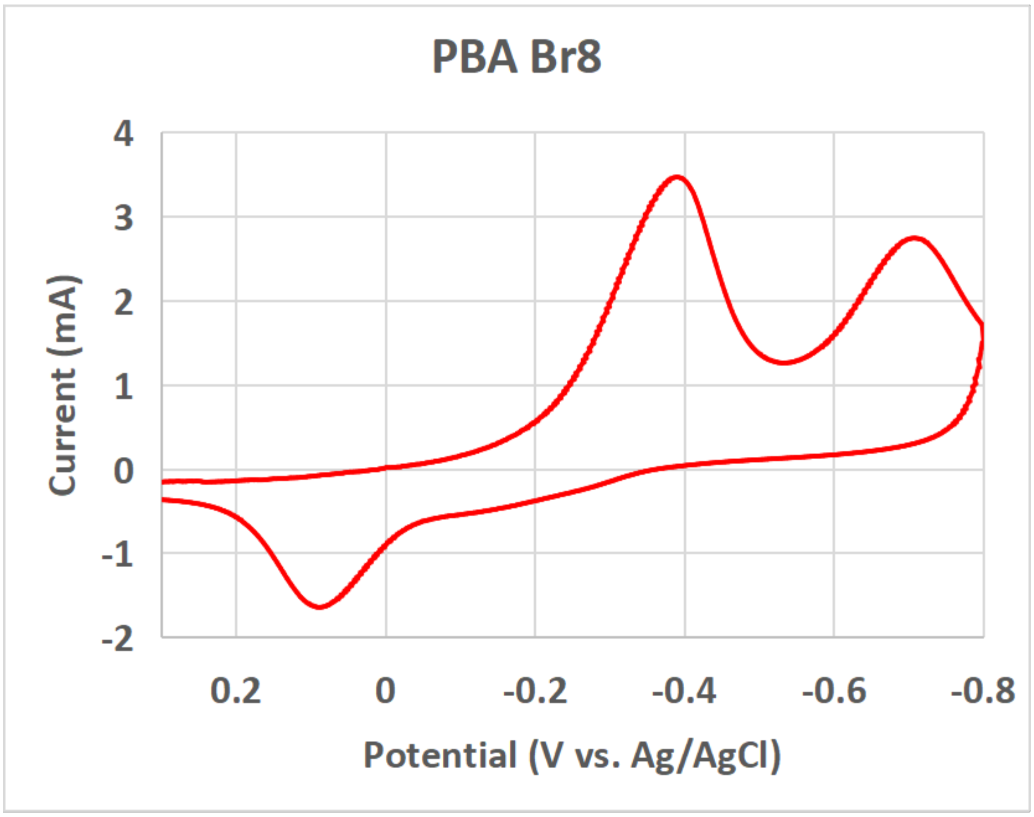

Figure 22: CV of PBA-br4 using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

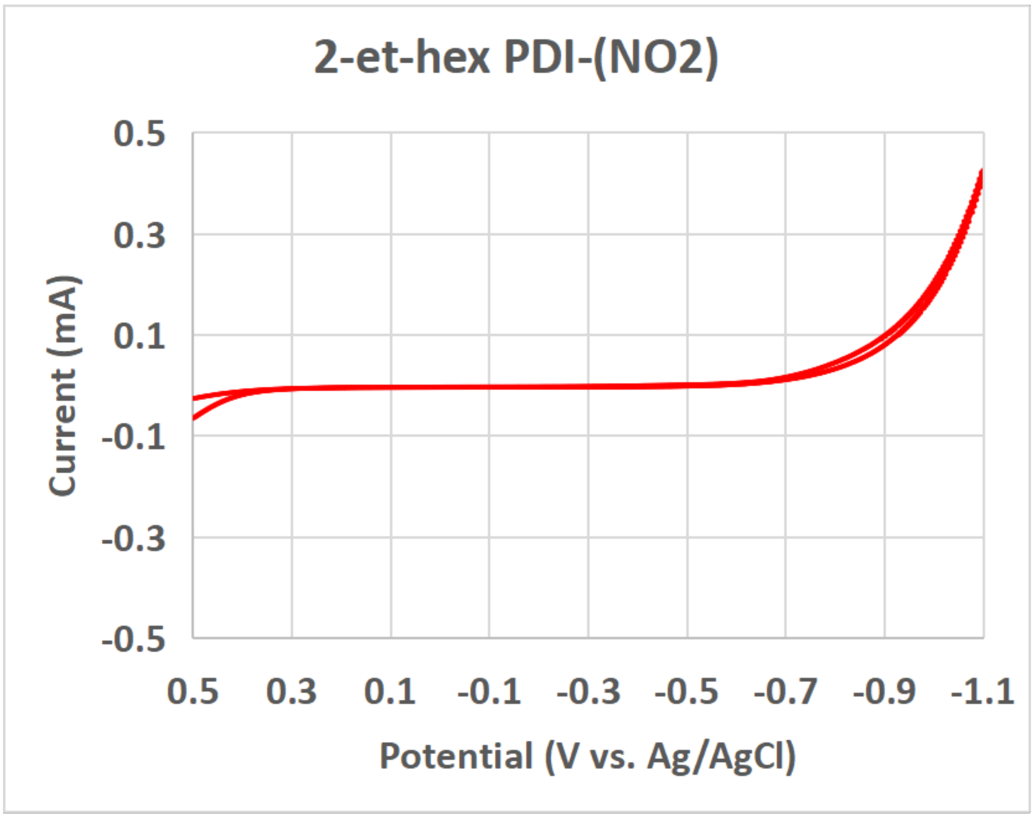

Figure 23: CV of 2-et-hex PDI-(NO2) using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

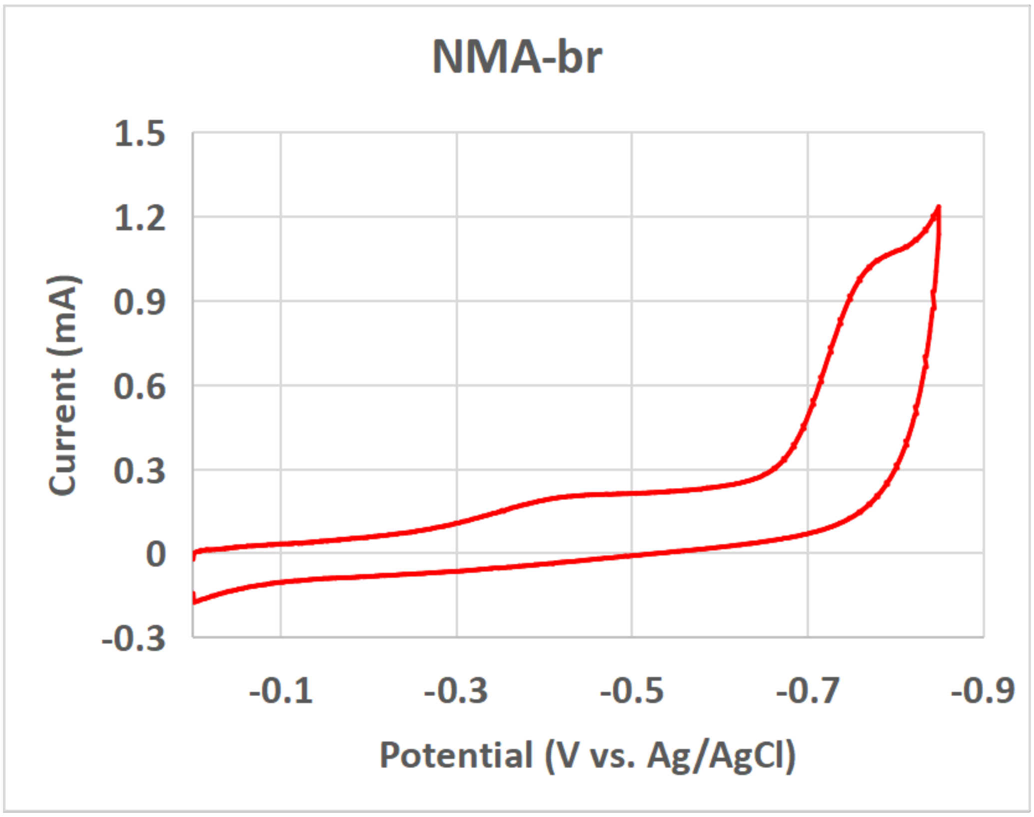

Figure 24: CV of NMA-br using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.1 V/s

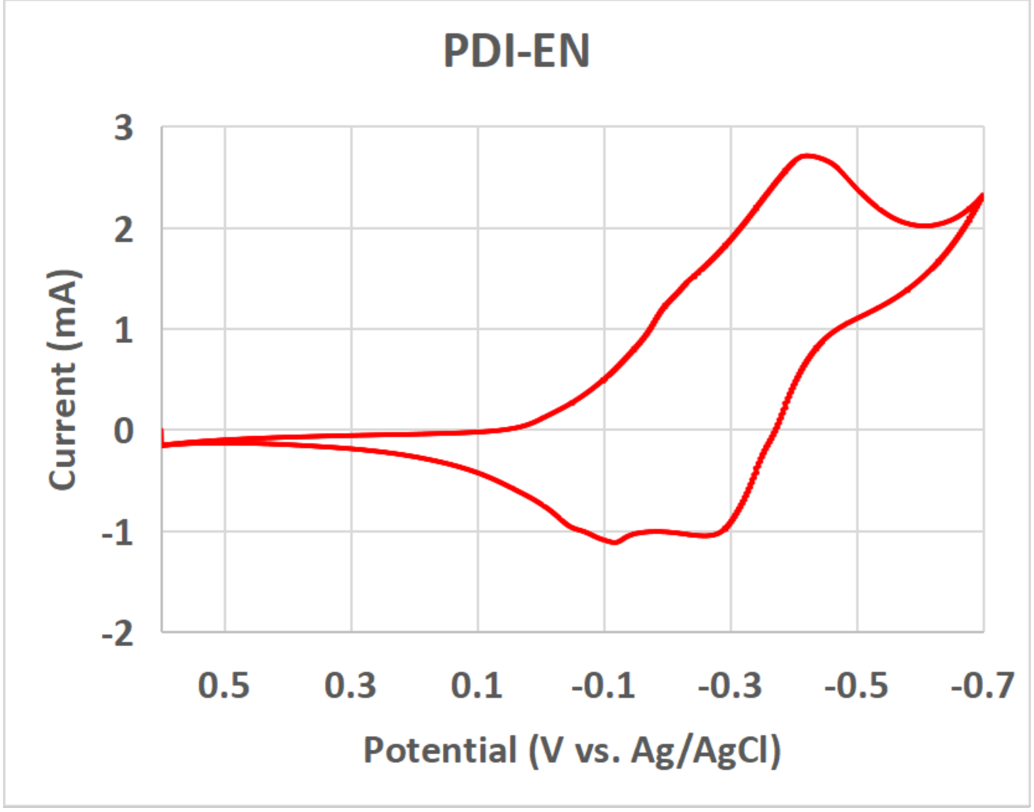

Figure 25: CV of PDI-EN using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s

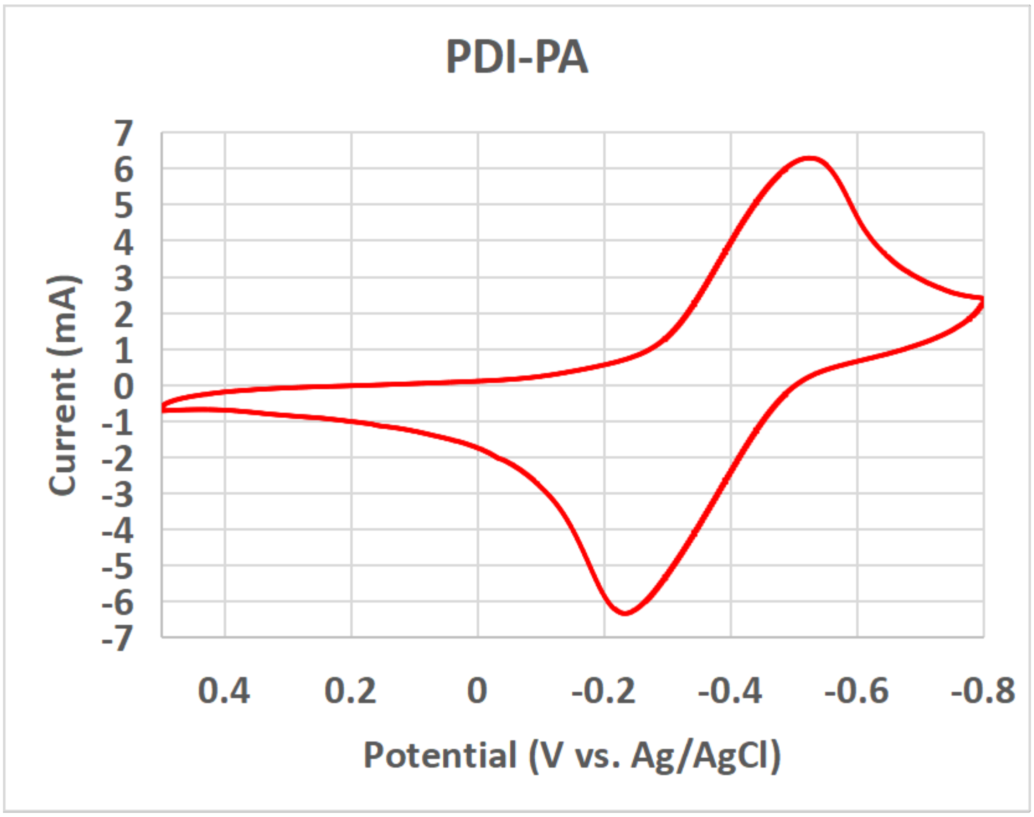

Figure 26: CV of PDI-EN using a H_2SO_4 (0.5M) electrolyte with a scan rate of 0.05 V/s