Investigation of the effect of basicity and Concentration of proton accepting bases on the potential of Quinones for high potential quinone based cathode materials.

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Masterprogrammet I fysik

Master programme in physics
Abstract

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The participation of quinone in electron transfer processes is an important aspect in many areas e.g. medicine, biochemistry and battery charge carrier mechanism. Of much interest is quinone application on sustainable and renewable charge storage components. Here the option of reaching high quinone potentials in aprotic solvents by varying the \( pK_a \) values and concentration of different proton accepting bases of different basicity has been investigated. The approach has been to have a quinone monolayer attached to a platinum surface via an alkane thiol attachment. In this way complete control of the amount of material converted and also of the concentration of the protonated base is achieved. To do this electrochemical methodology (cyclic voltammetry) is employed. Cyclic voltammetry (CV) showed a single step 2H\(^+\) 2e\(^-\) process oxidation of hydroquinone to quinone showing a charge compensation in the redox process. The base is a reactant in this process and its concentration is observed to affect the redox potential of the quinone conversion. With decreased \( pK_a \) value of the pyridine bases the quinone potential was observed to shift linearly to higher potential. This high potential shift is a direct implication that the storage battery setup is of high energy. The results show that changes in \( pK_a \) upon Quinone influence the pathways for proton-couple electron redox couples which should have an impact for power generation and energy storage in battery cells.

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## Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
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<tbody>
<tr>
<td>ACV</td>
<td>Alternating current voltammetry</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>Au</td>
<td>Gold</td>
</tr>
<tr>
<td>CA</td>
<td>Chronoamperometry</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>CPCET</td>
<td>Concerted proton-coupled electron transfer</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic voltamogram</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>ET</td>
<td>Electron transfer</td>
</tr>
<tr>
<td>LIB</td>
<td>Lithium Ion Battery</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>OC</td>
<td>Open circuit</td>
</tr>
<tr>
<td>Pt</td>
<td>Platinum</td>
</tr>
<tr>
<td>PT</td>
<td>Proton transfer</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>SCE</td>
<td>Saturated calomel electrode</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
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1. Introduction

1.1. Background

The increased pressure to provide for electrical energy from renewable energy sources in the modern world, which has increased the need for rechargeable batteries. Currently famous Lithium ion batteries (LIB) use inorganic Lithium insertion compounds like LiCoO$_2$ as cathode components. However these materials are limited, expensive and pose a threat to the environment. This has triggered interest to replace these inorganic compounds with organic compounds like disulfides, nitroxides, carboxylates, and carbonyl compounds. Quinones are organic carbonyl compounds responsible for electron transport in biological mechanisms like photosynthesis and respiration. In photosynthesis quinones are used to transport electrons between Photosystem II to Photosystem I while in the respiratory electron transfer chain they serve to transport electrons from enzyme complex I to enzyme complex II. These natural occurrences of quinones in biological energy conversion systems and their relatively stable redox chemistry have made quinones attractive targets for electrical energy storage purposes.

Quinone based electrode materials can be produced at low temperatures, can be made from renewable resources, and can offer a close to carbon neutral alternative to current day inorganic electrode materials. The quinone is cheap and can be extracted from readily available biomass. Quinones could make rechargeable batteries technologically competitive with current storage methods.

Redox potential is one of the most important parameters of research for electrode materials, and this together with the capacity of the electrode determines the specific energy (energy per volume) of the material. Other properties of electrode materials that are of interest include $pK_a$ values, stability in different solvents and the prosperity towards polymerization.

This project work examines the oxidation of hydroquinone to quinone in aprotic solvents (acetonitrile) by varying the $pK_a$ values and concentration of different proton accepting bases of different basicity. The target here is to reach high quinone potentials and give a hint on the suitability of acetonitrile as a solvent and pyridine base with its derivatives as an electrolyte.

1.2. Aim of the thesis

The goals of this work are:

- To establish the effect of acidity of the added acid on the redox potential of quinones in aprotic solvents (Aprotic solvent = Acetonitrile)
- To seek correlation between quinone redox potential and $pK_a$
- To identify the base which gives high potential of quinone for quinone based cathode materials.
2. Theory
2.1. Fundamental electrochemistry
2.1.1. Terminology

Electrochemistry is concerned with how electrons are transferred due to redox reactions in presence of a metal conductor and an electrolyte, in essence energy from chemical reaction is converted into electrical energy. Two identified classes of electrochemical systems are galvanic and electrolytic cells. A galvanic or voltaic cell is a cell which creates electric current from spontaneous redox reactions and are commonly utilized as power sources. More crucial are batteries and fuel cells which is key in the advancement of vehicle energy and renewable energy sources.

The second class of this electrochemical cells are the electrolytic cells. This is where redox reaction is achieved by applying an external electrical energy. Industrially this electrolytic process has let to refining of metals and alloys from ores. An important application in this context is battery charging.

2.1.2. Equilibrium electrochemistry

In electrochemistry phenomena with no current flow in the setup being investigated naturally, at equilibrium, may be connected both to the bulk of the electrolyte solution and to the electrochemical interface between the ionically conducting electrolyte solution and the electrode Equilibrium electrochemistry is related to both the bulk of the ionic solution and to the interface at the electrode and the electrolyte. Here unlike flow of current in wires, flow of ions in the ionic solution is coupled to metals, both systems and interactions are linked at the electrochemical junction.

An electrochemical cell is a compartment with two electrodes dipped in an electrolyte, where the electrodes can be in a common compartment. The two electrodes have unique redox reactions (half reactions) of a given chemical. The two half reactions are at equilibrium at a particular applied potential. A shift from this potential will result to either electron gain (reduction) or electron loss (oxidation) in one material and a corresponding oxidation or reduction of the other electrode material as illustrated below.

\[ O + ne^- \rightarrow R \] (1)

where \( O \) and \( R \) are called redox couple. At equilibrium the potential of this couple is the electrode potential, \( E \), which is related with their respective concentrations by the Nernstian equation written as;

\[ E = E^0 + \frac{RT}{nF} \ln \frac{C_{ox}}{C_{red}} \] (2)

Where \( C_{ox} \) and \( C_{red} \) are the concentrations of the oxidized and reduced respectively, \( R \) is the gas constant, \( T \) temperature, \( E^0 \) the standard potential measured at standard pressure and temperature and \( n \) is the number of electrons involved in eqt.1 above.
2.1.3. Dynamic electrochemistry

To allow the studies of the electrochemical properties of quinone monolayer which is the focus in this master thesis, dynamic electrochemistry is used. This is achieved by applying a potential \( E \), different from the equilibrium value while controlling the current passed. This potential can be assigned \( E_{\text{cell}} \).

Commonly used dynamic technique is Voltammetry and is used for decerning rates and mechanisms. Here an electrode is selected such that reactions occurring at this electrode are monitored by observing the current as the potential is applied to force the reaction, that is between the working electrode(WE) and the counter electrode (CE) (fig.1). A working electrode WE, is the electrode at which the reaction of interest occur, in this case we have hydroquinone monolayer attached to a platinum disc. The current resulted at the electrode is recorded as a function of potential on the electrode. The scan rate \( v \) is varied steadily. Reference electrode (RE) is the other electrode which enables the potential difference \( E \) at the WE to be known, that is a reading \( E \) between the WE and the RE is taken. The commonly used RE is the standard calomel electrode (SCE).

![Figure 1. Three electrode electrochemical cell](image)

Equilibrium or no current electrochemical investigations involves recording voltage between the WE and the RE. This potential is then recorded as a function of what occurs at the solution where concentration of the electroactive reactants present are varied are altered according to Nernstian equation (eq.2). During voltammetry, charge is passed between the electrolyte and the WE which invokes the reactions. Allowing the current to go through the RE or slight passage of current would alter the composition of the electrode and hence the potential would be the wrong potential value. Due to this facts no current is allowed to pass through the RE. Therefore, another electrode called the counter electrode , CE, is used to complete the circuit and this will allow no current to pass through the RE. The main purpose of this CE is to enable current to flow at the WE, therefore the reaction,composition and alterations at the CE are of no effect to the results obtained in the electrochemical cell. Potential is not measured at the CE but reactions must take place for current to flow. This means that reduction occurs at the CE when oxidation occurs at the WE, and vice versa.
A potentiostat is a device used in conjunction with an electrochemical cell to regulate the potential across the WE and the CE. The voltage is altered in a pre-programmed manner by means of a function generator where it injects current through the WE to display the required voltage. Current improved instrumentation achieves microsecond rise times, and voltage can be tuned within 1mV. RE current is regulated to a picoamp.

To avoid interaction of the products at the CE, a separate compartment with solution is used, where ion transport is achieved via a sinter or frit.

2.1.4. Electrochemical methodology

Apart from Cyclic voltamogram other electrochemical techniques are; Chronoamperometry (CA), alternating current voltammetry (ACV) and electrochemical impedance spectroscopy (EIS). Cyclic voltammetry is key to determining half reaction formal potentials, diffusion mechanisms, stability of reactions and reaction route, encompassing electrochemical reactions at semiconductor/electrolyte interfaces. However, this involves the charge transfer processes which are complex and mainly relies on the distribution of the charge carriers at the interface of the solid and the solution as briefly looked at below.

The solid electrode (conductor)

The phenomenon of electron movement from the electrode into the solution (reduction) is as a result of change in potential at the interface of electrode and solution which is due to the varied energy levels. For solids (electrode) their electronic structure can be discussed in terms of energy bands (Fig. 2.1).

The behavior of electrons across the energy levels is described by the Fermi-Dirac distribution function given by

\[
 f(E) = \frac{1}{1 + \exp \left( \frac{E - E_F}{kT} \right)}
\]

2.1

where \( f(E) \) is the probability that a particular quantum state describing a given quantum state at an energy level \( E \) occupied by an electron, \( E_F \) is called the Fermi energy and energy level too, where it may or may not represent the energy level but it can provide a reference of comparison with other energies.

The band structure of a conductor is composed of a single energy band (conduction band) with more energy levels exceeding free electrons. At absolute zero temperature, electrons occupy the lower energy level up to a certain energy level \( E_F \) while the upper levels immediately above this highest filled level remain vacant. Therefore the Fermi level \( E_F \) can be defined as the uppermost occupied energy level in a conductor at 0 Kelvin temperature and corresponding to that Fermi energy is the maximum energy that an electron can possess in a conductor at this temperature.
At temperatures higher than absolute zero, electrons close to the Fermi level are excited to vacant levels above this Fermi level where \( E_F > kT \). However, for majority of the electrons lying deep down in the conduction band, \( kT \) does not provide sufficient energy to excite them to an unoccupied level. They remain unexcited and stay at their original level. Therefore a few energy levels within the range of \( kT \) above \( E_F \) are partially occupied and a few levels become partially depleted. However the majority of the deeper levels are left at

![Figure 2.1: Band structure of a conductor](image)

their original level as before at 0 Kelvin. Due to thermal excitation, finding electrons at energy levels \( E > E_F \) has a probability greater than zero while the probability is less than one to find electrons at a few lower levels (\( E \) less than \( E_F \)) to \( E_F \).

**Electrolyte solutions**

The fact than electrolytes have ions makes them ionic not electronic conductors as in solids. A theory relying on ‘chemical potential’ is used to explain the motion of charges in electrolytes. However, when describing the electrolyte solutions in contact with solids, it is crucial to explain the how ions behave the same way as in solids (semiconductors, metals, etc.), to mean in terms of energy levels not ‘chemical potentials’. In solution, the electronic levels of ion tells the tendency of that species to give out (occupied level) or accept (free level) electrons when the ion nears to the electrode or ion. This means that the electrolyte species can donate or accept an electron.
Energy levels of a substance dictates the chemical behavior of any substance which is the exchange of electrons near the transition from filled state to empty state. These are called the LUMO and HOMO states (fig. 2.2) but we call conduction and valence band in solids, where the Fermi level in a solid is same as the HOMO in a molecule.

**Metal-Electrolyte interface**

When a metal electrode is inserted to an electrolyte solution there is an exchange of ions in the solution and electrons in the electrode. In surface science and under this research investigation the interest is what takes place between the working electrode and an electrolyte Fig 2.3. However to make a scan through (pass current) the system two electrodes are needed (working and counter electrode) as elaborated in section 2.1.3. Further the third reference electrode whose potential is made fixed is needed to determine the potential of the working electrode. In a nut shell we take readings or observe the potential of the working electrode with respect to the reference electrode. This is the same as exiting electrons to higher energy levels of the metal electrode \(^{32, 33}\) During reduction the working electrode is connected to the negative side of a battery or power supply, this shifts the *Fermi level* upwards (energy of electrons are raised)
Figure 2.3. Electrochemical cell with a three electrode-configuration

They are now at Fermi level ($E_{F,High}$) higher enough to be transferred into vacant electronic states (LUMO) solution species. Therefore transfer of electrons from electrode to electrolyte occurs (reduction current) fig.2.4. Similarly during oxidation the electrode is charged to a more positive potential value we shift the position of the Fermi level downward up to a level ($E_{F,Low}$) where the electrons on the occupied molecular orbital (HOMO) of the solution will find a lower favorable energy state on the electrode and will shift and settle there. This flow of electrons from the electrolyte to the electrode give the oxidation current. Fermi level ($E_{F,eq}$) which corresponds to the equilibrium potential is equal to the energy of the electron at the standard potential, $E^o$ (dotted line) Fig 2.4., which is an identity for a specific chemical substances under investigation.

The core concept here is that electron transfer can occur from any given occupied energy state with the corresponding energy, $E$, with an occupied receiving state. In the case of reduction, the occupied state sits on the electrode while the receiving state on the electroreactant, O. If the process is oxidation, the occupied state sits on the R species in electrolyte, while the receiving state on the electrode.
Figure 2.4. Representation of reduction and oxidation process at an interface between a metal electrode and a solution containing species O and R at equal concentrations.

**Fermi level and electrochemical potential**

As seen in solids, the Fermi energy is a parameter of importance for solids and electrolyte solutions, i.e., the Fermi level indicates how the electrons occupy the energy levels.

The thermodynamic requirement is that for two phases to be in equilibrium their electrochemical potential should be equal. For a redox couple in solution the electrochemical potential is determined by $E_{\text{redox}}$, while in a solid the electrochemical potential of electrons is determined by the Fermi level $E_F$. Incase $E_{\text{redox}}$ and $E_F$ are different, a charge redistribution between the solution and the solid electrode is necessary in order to bring the two phases in equilibrium. This equilibrium can also be destabilized by applying an external electrode potential (scanning) which lowers the Fermi level in the electrode by an amount referred to as the overpotential (additional potential above the thermodynamic requirement). Therefore overpotential applied results to a difference in the Fermi levels of the electrode and the electrolyte solution.

However as the equilibrium is altered, the reaction proceeds in a given direction; current flows and concentrations of the species at the metal-electrolyte interface will change. For example when an electron is transferred between two phases, movement will be from the phase with a higher electrochemical potential to that of lower electrochemical potential (Fermi level) and vice versa. If the Fermi levels are the same, no electron transfer occurs. 33

Cyclic voltammogram is achieved by scanning positively to cause oxidation or negatively to cause reduction and also to a potential window where electron transfer can occur. This is done repeatedly according to the number of cycles needed while recording the flowing current. One cycle of a scan is called a ‘wave form’ and any number of waves required can be run. The data plot of the current as the y-axis and voltage as the x-axis give us a voltammogram. Variation of the voltammogram can be achieved by varying the scan rate say from a few millivolts to several hundred volts per second.

The system records the potential (x-axis) versus the cathodic ($i_{pc}$) and anodic currents ($i_{pa}$) called the “faradic current” to obtain a voltammogram (Fig.3). The corresponding potentials where oxidation ($E_{pc}$) and reduction ($E_{pa}$) occurs are also displayed in the figure.

The average of the potential, $E_{1/2} = \frac{1}{2} (E_{pc} + E_{pa})$, $E_{1/2}$ also has an alternative equation;

$$E_{1/2} = E^o + (\frac{RT}{nF})ln(\frac{D_r}{D_o})^{1/2}$$
Fig. 3. A typical cyclic voltammogram showing the important peak parameters.

Where $E^o$ is the formal potential, $D_r$ and $D_o$ are the diffusion coefficients of the reduced and the oxidized species respectively. Occasionally the diffusion coefficients are close to one another and hence $E_{1/2} \sim E^o$.

For a reaction incurring a proton and electron transfer it can be related with the pH where peak potentials occurs. It can be represented as below for $m$-protons and $n$-electrons;

$$A \pm mH^+ + ne \leftrightarrow B$$

In a chemically reversible reaction, the above couple behave in accordance to the Nernst equation;

$$E = E^o_{(A/B)} - \frac{RT}{nF} \ln \frac{[B]}{[A][H^+]^m}$$

$$E = E^o_{(A/B)} - \{ \frac{RT}{nF} \ln \frac{[B]}{[A]} - \frac{RT}{nF} \ln [H^+]^m \}$$

$$E = E^o_{(A/B)} + \frac{RT}{nF} \ln [H^+]^m - \frac{RT}{nF} \ln \frac{[B]}{[A]}$$

$$E = E^o_{(A/B)} + 2.303 \frac{RT}{nF} \log [H^+]^m - \frac{RT}{nF} \ln \frac{[B]}{[A]}$$

$$E = E^o_{(A/B)} + 2.303 \frac{mRT}{nF} \log [H^+] - \frac{RT}{nF} \ln \frac{[B]}{[A]}$$

$$E = E^o_{(A/B)} + \left( -2.303 \frac{mRT}{nF} * \log [H^+] \right) - \frac{RT}{nF} \ln \frac{[B]}{[A]}$$

$$E = E^o_{(A/B)} + (-2.303 \frac{mRT}{nF} * pH - \frac{RT}{nF} \ln \frac{[B]}{[A]}$$
\[ E = E^0_{A/B} - 2.303 \frac{mRT}{nF} * pH - \frac{RT}{nF} \ln \frac{[B]}{[A]} \]

At an instance where the concentrations of \([A] = [B]\) the pH dependent Nernst equation becomes;

\[ E = E^0_{A/B} - 2.303 \frac{mRT}{nF} * pH \]

\[ E = E^0_{A/B} - \frac{0.059}{n} * pH \]

This represents to a 59mV shift per pH unit at 25°C for a one electron-proton ratio in the redox reaction. In the oxidation of Hydroquinone in a proton accepting base where \([H^+] \geq [Q]\), there is an abundance of protons and the assumption is \(m = 2\) and \(n = 2\) as shown below;

\[
\text{OH} \quad \text{+ 2B} \quad \leftrightarrow \quad \text{O} \\
\begin{array}{c}
\text{OH}
\end{array} \quad \text{+ 2e}^- \quad \text{+ 2HB}^+
\]

The Henderson-Hassenbalch relation is of help in determining the pH of a buffer solution (an aqueous solution composed of a mixture of a weak acid and its corresponding conjugate base and vise versa), It is written as \(PH = pKa + \log([\text{conjugate base}]/[\text{acid}])\). As seen in the equation, the \(pKa\) of the acid will be equal to the pH of a buffer when the concentration of the conjugate base is equal to that of the conjugate acid. This would give;

\[ E = E^0_{A/B} - \frac{0.059}{n} * pKa \]

The coupled redox reaction where there is the consumption of protons would make the \(pKa\) at the electrode surface vary from the solution.

**2.2. Surface electrochemistry and monolayers**

Surface electrochemistry provides a link to kinetic data where the motion of charge exchange taking place at the metal-solution interface can readily be obtained as the electric current per unit area. Therefore mastery of the surface and the reactions at the surface are both the existing focus on experimentation. Growing focus in the past has been to achieve full control of the structure of the electrode/solution interaction interface in order to fully manage the charge transfer reactivity involving required reactants. Therefore modified electrode surface has been a broad area that facilitates research on electrochemistry, nanotechnology, material science, sensors for biology and environmental science.
2.2.1. Self-Assembled monolayers (SAM)

Spontaneously adsorbed monolayers achieved through immersion of an electrode into the desired analyte solution with surface active molecules have been explored in recent years. This research investigation deals with hydroquinone which is surface attached on the surface of a platinum disc. Commonly known redox active centers useful for the study of electron transfer kinetics are the alkane thiol monolayers. This is due to their ability to well adsorb in ordered and close packed manner onto metal surfaces.

Organic monolayers can be made by attachment on the metal surfaces using a technique called Langmuir Blodgett. This happens by transfer from air-water interface to the surface or by chemisorption from the solution,\(^{17,18}\) where the later technique has been applied in this research work. Buildup of SAMs is a thermodynamic process with basically molecular self-assembly building units where these self-assembly in nature is a process governed by inter- and intra-molecular forces which makes the molecules to be driven into a stable, low energy state. These involved forces are electrostatic interactions, van der Waals forces, hydrogen bonding and hydrophobic interactions.

As with the self-assembly in nature there exist a number of driving forces for the alkanethiols assembly onto the surfaces of noble metals. First is the affinity of sulfur component for the surface. Research has shown that the sulphur-gold interaction is approximated at 45kcal/mol, forming a semi-covalent stable bond.\(^{35}\) This is remarkable as compared to the C-C bond strength which is approximately 83kcal/mol.

The next driving force for the alkanethiol assembly is the hydrophobic, van der Waals interactions which is between the methylene carbons on the alkane chains. This interaction of alkanethiol monolayers causes the thiol chains to tilt so that it can maximize the interaction between the chains and the surface energy. A properly ordered monolayer is formed from an alkane chain of up to 10 carbons. With this length of carbon chains, hydrophobic interactions can overcome the molecules’ rotational degrees of freedom.

This spontaneous assembly of molecules results to a film called self-assembled monolayer (SAM). At times monolayer molecules don’t interact well with the substrate while in others molecules has functional group with a high affinity to the substrate and attaches the molecule to it (fig.3).\(^{19}\)

Widely used head groups are thiols, silanes and phosphates. Formation of SAM is by chemisorptions of the head group to the metal substrate from the liquid solution or vapour \(^{20,21}\) after which there is slow ordering of “tail groups”.\(^{22}\) Initially a small molecular density on the adsorbed molecules form disorganized assembly of molecules from an organized two dimensional “lying down phase” \(^{20}\) and later to a larger molecular coverage after some hours they begin to achieve a three dimensional crystal or semi-crystalline structure.\(^{23}\) The head groups order together on the surface and areas of close packed part nucleate and grow where a complete coverage in a single monolayer is achieved.
2.2.2. Types of SAM

Appropriate head group type has to be selected and this relies on the application of the SAM.\(^\text{19}\) To alter the wetting and the interfacial nature of the SAM, the terminal end is functionalized by connecting the head group to a molecular chain by adding groups such as \(-\text{OH}, -\text{NH}_2, -\text{COOH},\) or \(-\text{SH}.\)\(^\text{24, 25}\) The choice of substrate to react with the head group is also crucial where there are planar surfaces like silicon and metals (platinum, gold) or curved particles such as nanoparticles. Mostly used SAM molecules are alkane thiols, these are molecules with an alkyl (C-C)\(^\text{n}\) representing the backbone, a tail group, and a S-H head group. Other good molecules are aromatic thiols in molecular electronics where the alkane chain is substituted partly by aromatic rings. Frequently used are thiols on noble metals due to their high affinity for sulphur for these metals, e.g., Au, Ag, Pt, Cu and Hg. Among these metals the platinum is preferred due to its low cost, with fingerprints of polycrystalline bulk electrode\(^\text{26}\) and electrode and more importantly they are electrochemically stable.

2.2.3. SAM preparation on electrode surface

SAMs need to resist strong acid or base states\(^\text{27}\) and in other interactions physiological environments. Due to this thiols and disulfides have become the most preferred choices as attaching mechanisms. The self-assembled monolayers are achieved by immersing a well cleaned and polished metal surface onto a target solution of typical concentration of \(10^{-3}\) of an alkane thiol or alkyl disulfide dissolved in a well chosen organic solvent (ethanol, THF, toline, acetonitrile). On immersing the adsorption of the monolayer takes place spontaneously and irreversibly onto a metal surface (substrate) by self-assembly process. The metal substrate reacts accordingly on sulphur groups leaving the chain end group exposed at the self-assembled monolayer and air interface or self-assembled solvent interface.\(^\text{29}\)

2.3. Energetics of proton-coupled electron transfer reactions

This research work deals with the study of reactions that involve electron transfers accompanied by proton (H\(^+\)) transfer(s), which describes an investigation of the voltammetry of hydroquinone in non-aqueous media in presence of proton accepting bases. A number of
reactions exist where we have transfer of electrons are as well accompanied by the exchange of protons. An example is the $2e^-, 2H^+$ oxidation of hydroquinone to benzoquinone and vice versa (equation 3). It is not in all the reactions that exchange of electron(s) and proton(s) are intimately occurring in redox reactions where both are involved; in some reactions the proton transfer is done followed by the electron transfer or vice versa, while in some cases both proton-electron transfer happens in a one step process with no formation of a stable intermediate.

$$
\begin{align*}
\text{1,4-hydroquinone} + 2B & \rightleftharpoons \text{benzoquinone} + 2e^- + 2H^+ \\
\end{align*}
$$

(3)

The two cases where proton-electron transfer takes place differently in the same redox reaction are called stepwise pathways ETPT or PTET to mean electron transfer (ET) takes place before proton transfer (PT) or vice versa. A third case in which proton and electron exchange takes place in a single step is known as a concerted proton–coupled electron transfer and the acronym given to it is CPCET. In other version of writing CPCET is replaced by CEP, which also means ‘concerted proton-electron transfer’. ‘Concerted’ is a term employed here to mean that the transfer of proton and electron takes place with no intermediate species noted.

Scheme 1 below illustrates both stepwise and concerted paths i.e. proton-coupled electron transfer reactions in which the diagonal pathway is the concerted reaction (CPET) and the stepwise routes are represented by vertical to horizontal (ET-PT) and the horizontal to vertical (PT-ET).

Square schemes for proton-coupled electron transfer (PCET) (scheme 1) and 3 x 3 square scheme depicting possible electron pathways for quinone/hydroquinone redox couple (scheme 2)
The benzoquinone and hydroquinone purely exhibits electron pathways that is top and bottom route of scheme 2. However proton-electron transfer is as at scheme 4 in case of the presence and absence of proton donor and acceptor.

Scheme 3. Square scheme for net H⁺ transfer and square scheme 4. Mechanistic pathways for; Hydroquinone and quinone redox couple

The understanding of the thermodynamics of each step is crucial to draw a conclusion that a redox reaction follows concerted or a stepwise pathway. Electron and proton transfer redox reactions are characterized by potentials (E) and $pK_a$ respectively. Both are a measure of free energy ($\Delta G^o$) and can be resembled in same units as in equations 4 and 5.

$$\Delta G_{PT}^o = -RT\ln(K_a) = 2.303RT(pK_a)$$  \hspace{1cm} (4)

$$\Delta G_{ET}^o = -FE^o$$  \hspace{1cm} (5)

Redox potentials are obtained electrochemically in this work. Using the square scheme for one reagent (scheme 3), the energy of the diagonal would simply be the sum of the energies of the two steps through the vertical and horizontal to arrive at the same end. These two-step paths are two and energies of both must be equal to: $2.3RT pK_a(HX) + nFE(X/X) = nFE(HX+/HX) + 2.3RT pK_a(XH^+)$. Bond strengths i.e the enthalpy of the diagonal varies a bit with the solvent or phase. If there is no change in the bond strength for a group $XH$, then any small change in E which is as a result of solvent change must give exactly compensating shift in the $pK_a$. For example if a positive charge is introduced near $XH$, then the removal of an electron will be made difficult but simpler to dissociate a proton. On the same note it’s difficult to deprotonate $HX$ in a less polar environment but easier to oxidize the $X^-$ formed to $X$. A shift of E of 59mV must be compensated by a unit change in $pK_a$ to maintain the bond strength. This balancing of E versus $pK_a$ may not stand if the proton being picked is not close to the redox center and also if the proton exist in an extended hydrogen bond network. The indication of this is from the strange dependence of E on $pK_a$. Slopes of $n \times 59$mV/pH unit are obtained in E against pH plots.
(Pourbaix diagrams) in case of small molecule redox couples of aqueous solutions, in which \( n \) is given as the ratio of protons to those of electrons transferred in a redox couple. \(^7\) The change in potential \( (\Delta E) \) or \( \Delta pK_a \) is the thermodynamic coupling between both the proton and the electron. This describes the kind of sensitivity the proton properties to the presence or absence of the electron and vice versa. It is an important parameter to consider in a given PCET process.

2.4. Contemporary battery research

There is fast and steady increase in the world’s need for electrical energy storage, which calls for research and development of raw materials with a focus on sustainability, accessibility and environmental impact of existing electrical storage technologies.\(^8\) Lithium ion batteries currently lead in the portable electronics market, and this is mainly attributed to their cyclic stability, lifetime and high performance in reference to specific energy and power.\(^9\)

Lithium ion batteries which are mainly in use includes graphite anodes and cathodes from the following list: LiCoO\(_2\) (main), LiFePO\(_4\) (main) Li NiCoAl\(_2\)O\(_2\) (minor), Li[MnNiCo]O\(_2\) (minor) and LiMn\(_2\)O\(_4\) (minor). More important to note is that there are commercial Lithium ion batteries where disordered carbon or a combination of C, Co, Sn, (Sn being the active material that alloys with lithium), \(^10\) are utilized as the anode component to enhance stability (graphite being fragile in structure). There are other innovation attempts to fabricate novel separators that gives improved wetting from the electrolyte solutions. \(^11\) There are other innovations of Lithium ion batteries where polymeric, gel or glassy matrices serve as the electrolyte system. There are also the development of batteries in which lithium insertion used is more than one.

There are Innovative attempts to come up with improved electrolyte solutions. An important class of new important solvents under development with reference with lithium ion batteries is ionic liquids that offer wide electrochemical windows with better safety features.\(^13\) There are upcoming attempts to come up with new salts such as LiN(SO\(_2\)F)\(_2\) (LiFSI) and boron compounds. Underway also are vigorous efforts to come up with and test a large variety of additives. New attempts and developments to compete with the above given standard lithium ion battery systems include new anode and cathode materials of three families; layered, spinel and olivine compounds, and Li-sulfur systems.

Despite this developmental efforts on LIBs in comparison with Lead-acid, Ni-Cd and Ni-MH battery, there are a number of serious challenges which has recently been encountered. First and foremost is that the inorganic cathode materials e.g., LiCoO\(_2\) and LiFePO\(_4\) incorporated in lithium ion batteries are limited by their theoretical capacity, structure and stability. This makes the improvement of their energy density difficult. Secondly is that the large quantity production and incorporation of transition metals (e.g., Mn, Fe, Co, Ni) as cathode materials has caused a serious concern for resources and a threat to the environment. For these reasons, while efforts of research is still focused on coming up with high capacity cathodes {e.g., xLi\(_2\)MnO\(_3\), (1-x)LiMO\(_2\)} \(^4\) and anodes (e.g., Si) \(^5\) for conventional LIBs, research direction is now shifted to other alternative battery combinations, like Li-S, Li-O\(_2\) and Li-organic batteries. \(^14\)
As an option to inorganic electrode materials which includes intercalation reactions (e.g., LiCoO$_2$, LiFePO$_4$, graphite, Li$_4$Ti$_5$O$_{12}$) or conversion reactions (e.g., transition metal oxides and sulphides), there are other promising substitutes as electrode materials for new design of “green lithium batteries”. These are the electroactive organics or polymers involving redox reactions. They are seen as an alternative due to their environmental friendliness, potential low cost, higher theoretical capacity, safety and sustainability. Therefore for this purpose more of this organic compounds have been identified recently, for example organosulfur compounds with disulfide bonds, nitroxide and phenoxide radical based materials, conducting polymers, conjugated carbonyls including carboxylates and quinone based materials. However challenges such as low electronic conductivity, low mass density, and unwanted dissolution of electroactive materials of these organic electrode materials are some of the demerits facing commercialization and research. To overcome this challenges, there are some attempts, one of which is to synthesis and design organic polymers with a stable skeleton and highly electroactive moety e.g., quinone due to their resistance to dissolution in common electrolytes for batteries. Presented in this master thesis is part of this venture to check on the use of pyridine derivative bases in aprotic solvents to tune the potential of quinone based electrode materials.

Quinone is a typically common carbonyl compound which have been found to have a good electroactivity. The redox involvement can be taken as an enolization mechanism and a reverse reaction of this carbonyl group where it can be promoted by a conjugated structure. Apart from quinone, there are other conjugated carbonyl compounds that can go through the same electrochemical redox reaction. Due to their fast reaction kinetics with structural stability and also their high theoretical capacity it is expected so far that they are the type of organic electrode materials to take the battery system to the next level.

2.5. Conducting polymer based batteries

Since the discovery of conducting polymers in the year 1977 the scientists have proofed that these organic materials can not only compete in electronic conductivity with semiconductors and metals, but also the redox reactivity of electrode materials. From this breakthrough lots of research on conducting polymers has emerged, mainly as electrode materials for rechargeable batteries. Typical conducting polymers studied in the past decades are; polypyrrole (PPy), polyacetylene (PAc), polyparaphenylene (PPP), polyaniline (PAn), and Polythiophene (PTh). The initial discovery of conducting polymers brought up proper knowledge that electroneutral polymers are completely insulators while doping makes polymers to improve in electronic conductivity. All conducting polymers with the exception of PAc pristinely exist in p-doped state, and the synthesis is by chemical or electrochemical oxidation polymerization. The doping level or the doping degree which means the ratio of doped units to all structural units is expressed as $x \ln(P^{x+}.xA^{-})_n (0 \leq x \leq 1)$. The structural unit contained by the conducting polymer is represented by P, which is taken by CH in PAc.

In approximating the theoretical capacity of the conducting polymer which is an important factor for a rechargeable battery, the $x_{\text{max}}$ is a crucial factor. What interests researchers most in conducting polymers is their high electronic conductivity. Therefore they are well
placed for energy storage application as conductive additive in composite cathode materials or as cathode for supercapacitors. The electrochemical performance of the conducting polymer is crucial in this case of application and this is achieved by working to improve on the surface area, ion conductivity and electronic conductivity. Therefore in recent efforts lots of research work is now focused on coming up with nanostructured conducting polymers, together with nanocomposites of conducting polymers with CNT or graphene.

Furthermore innovation attempts has been to synthesis and try out other polymer electrode materials composed of quinone and dianhydride. So far excellent and well defined electrochemical performance has been demonstrated unlike previous results, like high cycling stability, high capacity close to the theoretical value, high rate capability as well as high coulombic efficiency. For example a few conducting polymers with quinone pending groups have previously been reported in the literature, mostly containing large substituents such as anthraquinone and often attached to polypyrrole (PPy) on the nitrogen.\textsuperscript{15,16} Polymers with hydroquinone pending groups attached to PPy backbone via aliphatic – (CH$_2$)$_n$ – linkers have previously been made, however the hydroquinone moieties were diluted with inactive monomeric units. In this master thesis the strategy is to expound this findings.

3. Experimental and methodology

The aim is to set up an electrochemical experiment in cells which entails two parts; the preparation self-assembled monolayer (SAM) in a platinum electrode disc which will be the working electrode and the second part involves the preparation of the electrolyte from pyridine derivatives in acetonitrile solvent.

3.1. Preparation of quinone monolayer

3.1.1 Electrode cleaning of platinum disc electrodes

The platinum disc electrodes surfaces were first polished on a polishing paper of 0.1µm alumina powder then sonicated in water solution for a minute and finally electro-polishing was done using cyclic voltamograms in 0.5mol l$^{-1}$ sulphuric acid purged with N$_2$ and potential scanning initially between -0.20 and 1.55 vs Ag/AgCl sat’d electrode and then between -0.15V and 1.45 until a typical voltamogram for platinum was obtained. The stable CV is shown in fig.3 below. This was done between each set of experiments to assure no impurities or residues were adhered to the electrode surface.
3.1.2 Attachment of quinone terminated thiols to platinum disc electrodes

50mL mM solution of 10mM quinone thiol in ethanol and 10mM diluting alcoholthiol solution was prepared. The quinone SAMs preparation was simply afforded by immersing clean electrode in a solution of hydroquinone-terminated alkane thiol of mole ratio 9:1 with a background one of alkane thiol solution (fig.3.2) for overnight. Eq.6 was then used to calculate surface coverage ($\Gamma$, mol/cm$^2$) of the Q/H$_2$Q redox couple in the mixed monolayer.
3.2 Synthesis of pyridinium salts from pyridine bases

10mL of pyridine derivative (collidine, picoline, lutidine) were dissolved in approximately 20mL tetrahydrofurane (THF) while 3-chloropyridine and 4-chloropyridine were dissolved in methanol. The same molar amount of (n) of perchloric acid was dissolved in another portion of THF or methanol. The above two solutions of bases and acid were slowly and carefully mixed. Only collidine precipitated right away but the rest of the salts were recovered by evaporation in a Buchi Rotavapor R-11 Rotary evaporator and then pentane added to precipitate. The product was then filtered off and rinsed with pentane and finally dried for overnight.

3.3. Electrochemical characterization of quinone monolayers

3.3.1. In water

To get acquainted with electrochemical experiments as well as with the quinone system the PH dependence of the reduction potential for the hydroquinone to quinone redox conversion in water was determined. Electrochemical experiments were performed in aqueous electrolyte using an autolab potentiostat with 1M NaCl, 0.1M H$_3$BO$_3$, 0.1M CH$_3$COOH electrolyte purged with N$_2$ and pH adjusted with HCL during measurements. SAM quinone monolayer was used as working electrode and a platinum wire as counter electrode and Ag/AgCl reference electrode.

3.3.2. In aprotic solvents

To investigate if there are effects of added base on hydroquinone oxidation, the reduction potential for hydroquinone in MeCN (Acetonitrile = aprotic solvent) with base and corresponding acid added to the solution was determined. Electrochemical measurements was performed in the bases depicted in Table 3.1 as electrolyte using an autolab potentiostat.

This was achieved by having the protonated base at 0.5M, 0.1M or 1M and also varying the concentration of its base at 0.5M, 0.1M, 0.01M and so on. SAM of quinone was used as working electrode and platinum wire as counter electrode and Ag/Ag$^+$ reference electrode in each electrolyte in a different compartment, calibrated every time against ferrocene.

All solutions were purged with N$_2$ gas for 10 minutes to remove dissolved O$_2$. This is necessary for several reasons. The reduction of oxygen occurs in a two-step process as shown below.

\[
O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \\
H_2O_2 + 2H^+ 2e^- \rightarrow 2H_2O
\]

The large background current from the reduction or oxidation of dissolved O$_2$ can interfere with the amplitude of the current being measured as well as chemically interfering with the analyte.

The quinone reduction potential was determined by CV, DPV and SWV using the bases depicted in table 3.2. and correlation was sought between quinone redox potential and pKa.
<table>
<thead>
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<th>Base</th>
<th>Structure</th>
<th>pKa (corresponding acid)</th>
</tr>
</thead>
<tbody>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>4-Chloropyridine</td>
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<td>3.83</td>
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<td>5.23</td>
</tr>
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<td>5.95</td>
</tr>
<tr>
<td>2,6-Lutidine</td>
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<td><img src="image" alt="2,4,6-Collidine Structure" /></td>
<td>7.43</td>
</tr>
</tbody>
</table>

*Table 1. Base used in making the electrolyte in the electrochemical experiment.*

4. Results, analysis & discussion
   
4.1. Monolayer typical absorbance coverage
   
To eliminate any doubts about the possibility of the physical adsorption of quinone via alkane thiol on to the electrode surface, a control experiment was performed using consecutive cyclic voltammograms on a platinum electrode with only the alkane thiol which was later subtracted as background. No peak appeared in the voltammogram of the alkane thiol Pt electrode in the bases on acetonitrile. The control experiment showed that the voltammogram was related to the generation of quinone SAM/Pt.

As shown in fig. 5 with quinone a well-defined peak was observed which was due to the redox conversion of the quinone monolayer.
Fig. 5. Comparison of the cyclic voltamograms of the platinum electrode without (bare/Pt), with quinone SAM (unsubtracted) modification via alkane thiol and subtracted in the presence of 2,4,6-Trimethylpyridine in acetonitrile at scan rate of 5mV/s and base acid ratio of 0.02.

For monolayer the typical absorbance coverage is approximately between $10^{-10}$ to $10^{-9}$ molcm$^{-2}$. Hence exact surface area of the platinum is crucial to be known for the purpose of attachment of quinone monolayer. To get this and know the surface concentration ($\Gamma_s$) it was necessary in this master thesis to know the surface area of the platinum exposed for the attachment of the quinone monolayer. To calculate the coverage ($\Gamma$, mol/cm$^2$) of the Q/H$_2$Q redox couple in the mixed monolayers eqt. (4) was used and both cathodic and anodic peaks in the CVs to obtain Q. In eq. (4), $n=\text{the number of electrons in the redox reaction}$, $F = \text{Faradays constant}$ and $A = \text{the area of the electrode}$.\(^1\)

\[
\Gamma_s = \frac{Q}{FA}
\] (4)

From this equation the surface concentration of the ten electrodes used was found to range between $5 \times 10^{-11}$ to $3 \times 10^{-9}$.\(^1\)
4.2. Determination of formal potentials

Quinone chemistry oxidation-reduction included cyclic voltamogramms at the concentrations of 1 and those above or below this. This would give how concentrations other than 1:1 would affect the quinone potential or the peak separation. The kinetics at the surface bound analyte of Hydroquinone was also investigated by varying the scan rates between 1mV/s to 50mV/s. Comparison of anodic peak potentials \( E_{pa} \) and cathodic peak potentials \( E_{pc} \) of the bases with varying basicity lead to the determination of formal potential by employing equation 5 below. All values of potential was also calibrated against Ferrocene. This was obtained from the best conditions of scan rate and concentration.

\[
E^o = \frac{E_{pa} + E_{pc}}{2}
\]  

(5)

General formal potential for each base was finally obtained by plotting formal against ln[base]/[Acid] a relationship which obeys equation 6 below;

\[
E = E^o - \frac{RT}{F} \ln \frac{[B]}{[A]}
\]

(6)

The hydroquinone analyte in this investigation was surface attached unlike other cases where we have it in the solution. Therefore in this case of a surface bound analyte, the oxidation peak currents \( i_{p,ox} \) is given by;

\[
i_{p,ox} = \frac{Z^2F^2}{4RT} \nu A\Gamma^*_{red}
\]

(7)

where \( A \) is the electrode area and \( \Gamma^*_{red} \) is the total surface coverage of the oxidized species. This shows that oxidation peak current is proportional to scan rate \( \nu \).

4.2.1. 3-chloropyridine

Among the six bases investigated was 3-Chloropyridine with the lowest \( pK_a \) value of 2.81. Figure 6(a) shows the cyclic voltammogram of this base at equal concentrations of base and acid. The anodic peaks \( E_{pa} \) occurs at \(-0.17V\), \(-0.134V\) and \(-0.183V\) while the cathodic peaks \( E_{pc} \) occurs at 0.034V, 0.014V and \(-0.019V\) at scan rates of 10, 5 and 1mV/s respectively. To investigate the effect of concentration, other values of [base]/[acid] were used as shown in figure 6 (b). Compared to the ratio of 1 both at 0.1 and 0.01 shifted to the right but the peak separations widened more, this is due to a shift brought when equation 6 is considered where we have \( \ln(0.01) = -4.6 \), and \( \ln (0.1) = -2.3 \).
Figure 6. (a) Cyclic voltammogram (CV) of SAM of quinone on 3-chloropyridine at (Base/Acid = 1) at varying scan rates from 10mV/s to 1mV/s and CV of SAM of quinone on 3-chloropyridine at a scan rate of 1mV/s in varying [base]/[acid] ratio.

Kinetic information of 3-Chloropyridine base was explored in figure 7. Peak potentials were plotted against the log of scan rate at base-acid ratios of 0.01, 0.1 and 1 (Fig.7 a,b,c). Peak currents deviates from linearity as the scan rate increases. A confirmation that the hydroquinone analyte was bound to the platinum disc is shown in fig.7(d), where the slope is $\approx$ unity.

To obtain a comparative formal potential at this $pK_a$ value of 2.81, the formal potential value from eqt. 5 was considered at each base-acid concentration. The scan rate chosen here is 1mV/s since this gave us a small peak separation as depicted in figure 6. Having calibrated against Ferrocene the values are; 0.198V, 0.12V and 0.033V at base-acid ratio of 0.01, 0.1 and 1 respectively. This values with their corresponding base-acid ratios gives us the formal potential of 0.034 fig.8. This value will be used as a comparative value from other bases.
Figure 7. a, b, c. Peak potentials on 3-Chloropyridine base ($pK_a = 2.83$) at varying base acid ratios (d) Oxidation peak currents at various scan rates of 3-chloropyridine at 1:1 concentration

Figure 8. 3-Chloropyridine ($pK_a = 2.81$) Graph of formal potential ($E^o'$) vs ln[base]/[acid] at a scan rate of 1mV/s
4.2.2. 4-chloropyridine

Figure 9(a) below shows cyclic voltammograms of 4-Chloropyridine \((pK_a = 3.83)\) at base-acid ratio of 1 recorded at 50, 10, 5, and 1mV/s. We have \(E_{pa}\) at \(-0.117\)V, \(-0.175\)V, \(-0.194\)V and \(-0.243\)V while \(E_{pc}\) occurs at \(0.066\)V, \(0.109\)V, \(0.127\)V, \(0.181\)V for scan rate at 1, 5, 10, and 50mV/s respectively. It can clearly be seen that the peak separation increases with increase in scan rate. This gave a choice to use the lower scan rate of 1mV/s to obtain the formal potential. Other base-acid strengths were also tried out in the experiment to observe the influence of change of concentration.

Figure 9(b) shows cyclic voltammograms at acid-base ratios of 0.1 and 1. Concentration of 0.5 was also tried but it was not possible to obtain a CV at a scan rate of 1mV/s because the 4-Chloropyridine base electrolyte formed a paste. At these two concentrations \(E_{pa}\) occurred at \(0.06\)V and \(-0.117\)V at 0.1 and 1 base-acid concentrations respectively. From the CV the 0.1 base–acid concentration widens the peaks. From the nernstian equation below;

\[
E = E^o - \frac{RT}{F} \ln \frac{[B]}{[A]}
\]

Substituting base-acid concentrations will imply that;
\[
\ln(0.1) = -0.23 \quad \text{and} \quad \ln(1) = 0.
\]
Therefore shifting base acid concentration will bring a corresponding deviation of the formal potential.

To get information about the kinetics of quinone oxidatio-reduction in 4-Chloropyridine as the electrolyte base scan rate was varied extensively. Figure 10 (a) and (b) shows peak potentials against the logarithim of scan rate at the base acid ratio of 0.1 and 1. At both concentrations the anodic and cathodic peak currents scaled linearly with scan rate from 1mV/s to 50mV/s which is consistent with the surface bound centre\(^1\). At higher scan rates the peak currents deviate from linearity due to slow rate of the surface redox reaction.

**Fig 9(a).** Cyclic voltammogram (CV) of SAM of quinone on 4-Chloropyridine \((pK_a = 2.81)\) at \((\text{Base/Acid} = 1)\) at varying scan rates from 50mV/s to 1mV/s \((b)\). Cyclic voltammogram (CV) of SAM of quinone on 4-Chloropyridine at scan rate of 1mV/s at varying base acid ratios of 0.1 and 1.
For a surface bound analyte, the oxidation peak current is governed by equation 7. As compared to an analyte in the solution where the slope is \( \approx 0.5 \) oxidation peak currents for a surface bound analyte gives a slope of unity. This shows that the hydroquinone was well assembled on the surface of the platinum disc.

From figure 9(a) and 10 (a) and (b) it’s evident that the scan rate which gives the required small peak separation is 1mV/s. Therefore at this scan rate the formal potentials \( E^o' \) are 0.095V and -0.026V at base-acid ratio of 0.1 and 1 respectively. This was obtained by getting the average between the cathodic peak and the anodic peak, that is;

\[
E^o = \frac{E_{pa} + E_{pc}}{2}
\]

Having calibrated this values against Ferrocene and to get a comparative value of the formal \( E^o' \) with the other bases, the formal potentials at were plotted against the \( \ln[\text{Base}]/[\text{Acid}] \). This information is depicted in figure 11 below. The guiding nernstian equation is;

\[
E = E^o - \frac{RT}{F} \ln \left[ \frac{B}{A} \right]
\]

Our formal potential here at \( pK_a \) of 3.83 is -0.832 which represents the intercept. This is lower as compared to one for 3-Chloropyridine with a smaller \( pK_a \) value of 2.81
**Fig 10.** (a) & (b) Peak potentials on 4-chloropyridine ($pK_a = 2.83$) (c) Oxidation peak currents at scan rate of 1mV/s.

**Figure 11.** 4-Chloropyridine ($pK_a = 3.83$) Graph of formal potential ($E^\circ$) vs ln[base]/[acid] at a scan rate of 1mV/s.
4.2.3. Pyridine

Figure 12(a) shows the CV of Pyridine ($pK_a = 5.23$) of various scan rates at base acid ratio of 1:1. Anodic peaks ($E_{pa}$) occurs at $-0.181V$, $-0.147V$, $-0.134V$ and $-0.155V$, while cathodic peaks ($E_{pc}$) occurs at $-0.013V$, $-0.067V$, $-0.083V$ and $-0.112V$ at scan rate of 50, 10, 5 and 1mV/s respectively. The small peak separation at a scan rate of 1mV/s shows favorable conditions of oxidation-reduction of quinone.

Figure 12(b) shows CV of Pyridine at varying concentrations at the same scan rate of 1mV/s. Reduction peaks occurs at $-0.155V$ and $-0.179V$, while oxidation peaks occurs at $-0.112V$ and $-0.148V$. The shift displayed is due to change in the amount of reactants of acid and bases (eq.6).

**Figure 12(a).** Cyclic voltammogram (CV) of SAM of quinone on Pyridine ($pK_a = 5.23$) at (Base/Acid = 1) at varying scan rates from 50mV/s to 1mV/s (b). Cyclic voltammogram (CV) of SAM of quinone on Pyridine at scan rate of 1mV/s at varying base acid ratios of 1 and 2.

A linear plot of log($i_{p,oX}$) vs log($v$) gave a check of surface confinement where the slope is $\approx$ unity (Fig.13c). Figure 13 a, b & c shows graphs of peak potentials across the scan rates. The peaks spread out and deviate from linearity where slow rate of surface reaction happens at faster scan rates. Slow scan rate peak values were used to obtain the formal potentials ($E^o$). Using eq.6, the formal potentials obtained after calibration against Ferrocene are $-0.045V$, $-0.1155V$ and $-0.13V$ at base-acid ratio of 0.02, 1 and 2 respectively. A plot of these formal potentials against ln[Base]/[Acid] ratios (Fig.14) give a general value of $-0.018V$. This is a shift to a more negative value compared to 4-Chloropyridine above.
Fig 13. (a), (b), (c) Peak potentials on Pyridine ($pK_a = 5.23$) (d) Oxidation peak currents at various scan rates

Figure 14. Pyridine graph of formal potential ($E^0$) vs $\ln([\text{Base}]/[\text{Acid}])$ at scan rate of 1mV/s
4.2.4. 2-Picoline

The next base whose $pK_a$ value is 5.95 under investigation as an electrolyte is 2-methylpyridine (2-Picoline). Figure 15 (a) shows its CV at various scan rates with equal concentrations of base and the protonated base. Reduction peak potentials ($E_{pa}$) occurs at -0.334V, -0.3V, -0.284V and -0.25V while the oxidation peak potentials ($E_{pa}$) occurs at -0.52V, -0.107V, -0.134V and -0.196V at scan rates of 50, 10, 5, and 1mV/s. These potentials displays a shift as compared to Pyridine. The favourable scan rate is the lowest i.e, 1mV/s since it gives a smaller peak separation. This shows that reactants get enough time to interact.

Apart from base-acid concentrations of 1, other values of 0.02 and 0.2 were also used to investigate the effect of concentration (Fig.15,b). Compared to the $E_{pa}$ at 1, there is a shift to -0.225V for 0.02 ratio and -0.22V for 0.2 ratio. $E_{pc}$ also shifts to -0.171V for 0.02V and -0.166V for 0.2V. This is justified by eq.6.

Kinetic information on 2-picoline was obtained by varying the scan rate (Fig.15.a). Fig.16(a,b,c) shows peak potentials against scan rate. Small peak separation is seen at slow scan rates but deviation from linearity occurs at faster scan rates. A plot of log($i_{p,ox}$) against log $v$ (Fig.16.d) gives a slope of 0.84, which is close to one, confirming the confinement of quinone on the surface of the platinum disc. The average of peak potentials at the lowest scan rate of 1mV/s calibrated against Ferrocene gives a $E^0$ of -0.204V, -0.197V and -0.233V at base-acid ratio of 0.02, 0.2 and 1 respectively (Fig.16). Figure 17 shows graph of this formal potentials against ln[Base]/[Acid]. From equation 6, its clear that the formal potential at this $pK_a$ value of 5.95 is $-0.223V$, this is a drop compared to Pyridine.

![Cyclic voltammogram (CV) of SAM of quinone on 2-Picoline ($pK_a = 5.95$) at (Base/Acid = 1) at varying scan rates from 50mV/s to 1mV/s.](image1)

**Figure 15.(a)** Cyclic voltammogram (CV) of SAM of quinone on 2-Picoline ($pK_a = 5.95$) at (Base/Acid = 1) at varying scan rates from 50mV/s to 1mV/s. **(b)** Cyclic voltammogram (CV) of SAM of quinone on 2-Picoline at scan rate of 1mV/s at varying base acid ratios of 0.02, 0.2 and 1.
Fig 16. (a), (b), (c) Peak potentials on 2-Picoline ($pK_a = 5.95$) (d) Oxidation peak currents at various scan rates.

Figure 17. 2-Picoline graph of formal potential ($E^o$) vs $\ln([\text{Base}]/[\text{Acid}])$ at scan rate of 1mV/s
4.2.5. 2,6-lutidine

Cyclic voltammogram of 2, 6-Lutidine of \( pK\alpha \) 6.6 is shown in figure 18(a), shown is with reactants at base-acid ratio of \( \approx 1 \), which was carried out at scan rates of 50, 10, 5 and 1mV/s. Anodic peaks \( (E_{pa}) \) are seen at -0.427V, -0.392V, -0.38V and -0.347V while cathodic peaks \( (E_{pc}) \) are seen at -0.073V, -0.147V, -0.208V and -0.258V at scan rates of 50, 10, 5 and 1mV/s respectively. The scan rate which gives appropriately small peak separation is 1mV/s due to the fact that the reaction is favored by the scan rate. Other values of base-acid ratio tested in 2,6-Lutidine are 0.022 and 2.16 (fig.18,b). This is seen to slightly shift the potential peak separation.

Figure 19 (a, b, c) shows peak potentials against logarithm of scan rate \( (v) \). This displays a deviation from linearity as scan rates increase, hence showing consistency with the surface bound redox centre. Slow scan rates facilitates surface redox reaction. A linear plot of log \( (i_{p,ox}) \) vs log scan rate \( (v) \) with slope of 0.8 and close to unity confirms that the quinone self assembled monolayer was surface confined.

![Figure 18(a)](image)

**Figure 18(a).** Cyclic voltammogram (CV) of SAM of quinone on 2,6-lutidine \( (pK\alpha = 6.6) \) at (Base/Acid = 1) at varying scan rates from 50, 10, 5 and 1mV/s. **(b).** Cyclic voltammogram (CV) of SAM of quinone on 2,6-Lutidine at scan rate of 1mV/s at varying base acid ratios of 0.022, 1.08 and 2.16.

Figure 19 (a,b,c) also displays formal potentials \( E_\text{Ox} \) obtained from the lowest scan rate of 1mV/s using equation 5 and calibrating the values against Ferrocene. We have \(-0.341V, -0.2915V\) and \(-0.2925V\) at base-acid ratio of 0.022, 1.08 and 2.16 respectively. This values of formal potentials were then plotted against \( \ln[\text{Base}]/[\text{Acid}] \) (Fig.20). From this graph and using equation 6, the formal potential of quinone redox reaction at this \( pK\alpha \) value of 6.6 is \(-0.28V\). This is a shift the negative potential compared to 2-Picoline.
Fig 19. (a),(b) (c) Peak potentials on 2,6-Lutidine ($pK_a = 6.6$) (d) Oxidation peak currents at various scan rate and base-acid ratios.

Figure 20. 2,6-Lutidine graph of formal potential ($E^0$) vs ln[Base]/[Acid] at scan rate of 1mV/s
4.2.6. 2,4,6-Collidine

2,4,6-Collidine is the base with the highest $pK\alpha$ value (7.43) to be used to investigate how the potential of quinone is shifted. At this region the potential window was on the lowest among the other bases. Figure 21(a) shows the CV at [Base]/[Acid] of 1:1 across varying scan rate. The reduction ($E_{pa}$) of quinone at this concentration took place at -0.401V, -0.367V, -0.347V, -0.322V while the oxidation ($E_{pc}$) of hydroquinone was seen at -0.184V, -0.252V, -0.274V and -0.29V at scan rates of 50, 10, 5, and 1mV/s. The slow scan rate of 1mV/s positions the peaks under a small separation range showing that slow scan rate favors the reaction. At this $pK\alpha$ value the peak potentials are shifted further to the negative.

Apart from equal concentrations of base and acid, solution with more acid ([Base]/[Acid] = 0.02) and that with more base ([Base]/[Acid] = 2) were also investigated (fig.21.b). At the lowest scan rate of 1mV/s, base-acid ratio of 0.02 shifts the anodic potential to -0.261V and cathodic peak to -0.219V, while the base acid ratio of 2 makes a shift to -0.336V and -0.288V respectively. This is due to the alteration of the amount of reactants where its effect is justified by equation 6.

![Figure 21(a)](image1.png)  
![Figure 21(b)](image2.png)

**Figure 21(a).** Cyclic voltammogram (CV) of SAM of quinone on 2,4,6-Collidine ($pK\alpha = 7.43$) at (Base/Acid = 1) at varying scan rates from 50, 10, 5 and 1mV/s. **(b)** Cyclic voltammogram (CV) of SAM of quinone on 2,4,6-Collidine at scan rate of 1mV/s at varying base acid ratios of 0.1, 2 and 5.
Fig 22. (a),(b) (c) Peak potentials on 2,4,6-Collidine ($pK_a = 6.6$) (d) Oxidation peak currents at various scan rate and base-acid ratios.

Figure 22 (a,b,c) displays graphs of peak potentials against the log of scan rate ($v$). Important kinetic information is obtained here by varying the scan rate. Peak separation at slower scan rates are closer but deviates away from linearity due to the fact that faster scan rates don’t favor the redox reaction of quinone. On the other hand figure 22(d) with slope of $\approx$ unity shows that the hydroquinone monolayer was well surface attached to the platinum electrode.

At each base acid ratio the formal potential was calculated by averaging the anodic and the cathodic peak using equation 5. The values obtained after calibrating against Ferrocene are; $-0.2415V$, $-0.3225V$ and $-0.3345V$ at base acid ratio of 0.02, 1 and 2 respectively. To get the formal potential at this $pK_a$ value of 7.43, the above formal potential values were plotted against the $\ln[\text{Base}]/[\text{Acid}]$ (fig.23), where the guiding equation is eq.6. The formal potential (intercept) obtained from figure 23 is $-0.33V$. This is the formal potential of quinone at $pK_a$ of 7.43, which is the least from all the other bases.
Figure 23. 2,4,6-Collidine graph of formal potential \( (E^0') \) vs ln[Base]/[Acid] at scan rate of 1mV/s

4.3. Quinone formal potential on pyridine basicity

Cyclic voltammograms carried out at \( pK_a \) values from 2.81 to 7.43 were displayed at section 4.3, Quinone formal potential at each base strength was obtained according to the Nernstian equation:

\[
E = E^0 + \frac{RT}{nF} \ln \frac{C_{ox}}{C_{red}}
\]

Where \( C_{ox} \) and \( C_{red} \) represents concentration of the oxidized and reduced respectively. This gives;

\[
E = E^0 - \frac{RT}{nF} \ln \left( \frac{[B]}{[H_2B]} \right),
\]

Table 2 and figure 24 shows a summary obtained from each \( pK_a \) value of the base. It is evident that with decreased \( pK_a \) value of the pyridine bases the quinone potential was observed to shift linearly to higher potential. From the hypothesis and using the nernstian equation \( E = E^0 - 59mVpK_a \) the quinone formal potential on Pyridine basicity is 0.27V. The slope of the graph obtained is 82mV, which is slightly higher than the theoretical value of 59mV which is normally observed in aqueous solvent with an acid.

<table>
<thead>
<tr>
<th>( pK_a )</th>
<th>2.81</th>
<th>3.83</th>
<th>5.23</th>
<th>5.95</th>
<th>6.6</th>
<th>7.43</th>
</tr>
</thead>
<tbody>
<tr>
<td>( E^0' )</td>
<td>0.034</td>
<td>-0.0383</td>
<td>-0.115</td>
<td>-0.223</td>
<td>-0.28</td>
<td>-0.33</td>
</tr>
</tbody>
</table>

Table 2. Table of quinone formal potentials
4.4. HOMO, LUMO and Fermi Level information

The approach used in this research work is electron transfer by tunneling through blocking films where electrons can tunnel through the film and bring up faradic reactions. In electron-transfer theory, the extend of interaction or electronic coupling between an electrode and a reactant has been shown to determine the extent to which a reaction proceeds from O to R and vice versa.

One other valuable finding to our desired quinone based electrode material from the above electrochemical method is that we can get an insight into the electronic properties of molecules, that is information on the position of the energy levels. This information is on the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) and is easily detectable from the above findings. The HOMO position of a molecule obtained by determining its anodic potential ($E_{red}$), while that of LUMO is probed from its cathodic potential ($E_{ox}$). These energy level positions were referenced against the vacuum level by using ferrocene/ferocenium (Fc/Fc⁺) redox couple. Table 3, shows a summary of how change of $pK_a$ values of pyridine bases varies the anodic and cathodic potentials. The results shows that low $pK_a$ values raises the energy levels of Hydroquinone oxidation on pyridine bases. The electrochemical ‘band gap’ (HOMO-LUMO), can also be obtained from $E_{1/2}$ which is the average of anodic and cathodic potential.
Table 3. Table of values of $E_{\text{ox}}$, $E_{\text{red}}$, and $E_{1/2}$ across the $pK\alpha$ values of pyridine bases hinting on the position of HOMO and LUMO

An analysis of the quinone formal potential on Pyridine bases shows that a higher potential can be achieved by lowering the $pK\alpha$ value. The oxidation-reduction occurring in this investigation is;

$$H_2Q + 2B \leftrightarrow Q + 2HB^2+ + 2e^-$$

Where Q and $H_2Q$ are the oxidized quinone and reduced hydroquinone in the presence of proton accepting base. As the charged species are in the quinone side, the quinone state will be destabilized hence higher potential seen as the base strength changes. As the base is a reactant that is consumed during the reaction above, the concentration of base affects the redox potential of the quinone conversion. The oxidation-reduction of hydroquinone to quinone is a single $2H^+ 2e^-$ step process in protonated bases in acetonitrile solvent.

Khan\textsuperscript{30} identified the relationship between Fermi level and redox potential as

$$\bar{u}_e = E_F = -nFV_{\text{redox}}(\text{Vacuum}) + \text{constant}.$$ 

Where $\bar{u}_e$ is the electrochemical potential, $E_F$ is the Fermi level and $V_{\text{redox}}$ is the redox potential. This implies that the scanning potential give information on what amount of energy level the charged species are transferred. Table 2 shows a summary of formal potentials of the redox reaction of quinone at different base strengths of pyridine bases. The results shows a linear relationship of increased formal potential with decreased $pK\alpha$ value. It is therefore clear that the Fermi level or the electrochemical potential at which the quinone redox reaction occurs is increased by decreasing the basicity of the base.
5. Summary & Conclusion

- The oxidation-reduction of hydroquinone to quinone is a single $2H^+ \ 2e^-$ step process in protonated bases in acetonitrile solvent. The option of using protonated base as our electrolyte worked well in aprotic solvents despite the fact that there are no protons available to charge compensate the reduction and the reduction potential. This was evident from the fact the single step $2H^+ / 2e^-$ single peak process i.e. proton and electron exchange takes place in a single step known as concerted proton-electron transfer (the transfer of proton and electron takes place with no intermediate species noted). This hints quinones in such a combination of acetonitrile and pyridine bases as useful in cathode materials.
- With decreased $pK_a$ value of the pyridine bases the quinone potential was observed to shift linearly to higher potential
- Base acid concentration at all pKa values plays a factor in electron transfer kinetics.
- The results shows that low $pK_a$ values raises the energy levels of Hydroquinone oxidation on pyridine bases, that is the HOMO and LUMO position of molecules are raised with decreased basicity.
- The Fermi level or the electrochemical potential at which the quinone redox reaction occurs is increased by decreasing the basicity of the base.
- Also given that the formal potential for a reaction reflects the Gibbs free energy ($\Delta G$) of the reaction according to; $\Delta G = -nFE^0$. Therefore changes in base pKa impacts the quinone potential and its energy storage and power generation in battery cells.

Polymers like polypyrrole derivative with pending group of hydroquinone groups have been investigated. Future work would be to use the bases above on aprotic solvents to find out if the dissolution problem of the active material is reduced and conductivity in the combination increased.

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7. References

17. Langmuir IJ. Chem. soc. 1917; (39): 1848-1906