

Xian Wen Ng

Concise Guide to Electrochemical Methods and Voltammetry

A Problem-Based Test Prep for Students



Springer

Concise Guide to Electrochemical Methods and Voltammetry

Xian Wen Ng

Concise Guide to Electrochemical Methods and Voltammetry

A Problem-Based Test Prep for Students

 Springer

Xian Wen Ng
Singapore, Singapore

ISBN 978-3-030-83413-5 ISBN 978-3-030-83414-2 (eBook)
<https://doi.org/10.1007/978-3-030-83414-2>

© The Editor(s) (if applicable) and The Author(s), under exclusive license to Springer Nature Switzerland AG 2022

This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors, and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG
The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

Preface

Electrochemical methods center around the conversion of chemical energy into electrical energy and vice versa. These quantitative techniques apply fundamental concepts in electrochemistry to engineering objectives, thereby offering tremendous insight in analytical processes that are commonplace in most industries and sectors.

The practical applications of electrochemical engineering are wide-ranging, especially with the gradual onset of a paradigm shift from traditional oil and gas powered energy sources to electricity powered ones. Emerging areas that apply electrochemical methods include the field of microfluidics upon which novel sensor technologies and “lab-on-a-chip” systems are based, fuel cells and “designer” batteries, metallization processes for computer and hardware industries, as well as membrane technologies in desalination and waste treatment processes.

For students seeking to master electrochemical methods as part of a broader engineering course, it is essential to be adept with the fine mechanics behind electrochemical reactions, starting from the molecular level which relates to charge transfer, particle movement and behavior, to broader design outcomes. This guide will help students gain a thorough understanding of electrochemical methods such as voltammetry, and train their ability through problem-based practice, to formulate mathematical models that would help interpret experimental data so as to facilitate the design and optimization of electrochemical systems and solutions.

This book serves as a supplementary learning resource as it guides students in deconstructing some of the most challenging problems commonly encountered in tests and examinations. With comprehensive worked solutions and detailed explanations provided for each problem, students will be able to follow the thought process of problem-solving from start to finish, thereby hone their skills in applying abstract theoretical concepts to solving practical problems, a critical step to acing examinations.

The combination of both numerical and open-ended problems in this book will also help students gain a well-rounded understanding of electrochemical design

principles. Students will become proficient, not only in tackling tests and examinations, but also in relating the significance of desktop problems to a larger real-world context.

Singapore, Singapore

Xian Wen Ng

Acknowledgments

My heartfelt gratitude goes to the team at Springer for their unrelenting support and professionalism throughout the publication process. Special thanks to Michael Luby and Brian Halm for your constant effort and attention towards making this publication possible. I am also deeply appreciative of the reviewers for my manuscript who had provided excellent feedback and numerous enlightening suggestions to help improve the book's contents.

Finally, I wish to thank my loved ones who have, as always, offered only patience and understanding throughout the process of making this book a reality.

Contents

Fundamentals of Electrode Processes	1
Standard Reduction Potential	1
Standard Oxidation Potential	2
Measuring Standard Reduction Potential	2
Voltage Measurement	4
Salt Bridge	4
Half-Cell Equations for the Zn-Cu Cell	6
Direction of Electron Flow	6
Voltmeter	7
Salt Bridge	9
How the Salt Bridge Works	10
Method 1: Chemical Energy to Heat Energy	14
Method 2: Chemical Energy to Electrical Energy	15
Helmholtz Model	19
Gouy-Chapman Model	21
Basic Voltammetry for Micro and Macroelectrodes	33
Growth of Boundary Layer	37
Early Part of Current Decay	37
Later Part of Current Decay	38
Modelling the Current Decay	39
Current Response to Applied Voltage	43
Why Is There a Current?	43
Why Does Current Increase?	44
Why Does Current Decline After Reaching a Peak?	45
Effect of Varying Scan Rate	46
Reversible Electron Kinetics	46
Quasi-Reversible and Irreversible Electron Kinetics	46
Key Features of Current Response	47

Current Response for Reversible Electron Transfer	48
Forward Sweep	48
Reverse Sweep	49
Reversible Electron Kinetics	50
Effects of Varying Scan Rate	50
Peak Currents Increase with Increasing Scan Rate	53
Non-Reversible Electron Kinetics (Quasi-Reversible/Irreversible)	54
Quasi-Reversible Electron Kinetics	54
Irreversible Electron Kinetics	55
Special Note About Half-Wave Potentials	58
Forward Sweep	59
Reverse Sweep	60
Forward Sweep	65
Reverse Sweep	66
Advanced Voltammetry With Coupled Chemical Reactions	71
First Forward Sweep	72
First Reverse Sweep	73
First Reduction Peak	73
Second Reduction Peak	74
Second Forward Sweep	75
First Oxidation Peak	75
Second Oxidation Peak	75
Forward Sweep	81
Reverse Sweep	81
Relationships Between Forward and Reverse Sweeps	82
First Forward Scan	88
First Reverse Scan	89
Second Forward Scan	89
First Scan	91
Second Scan	91
Effect of Varying Scan Rate	95
Reduced Current	95
Increased Peak Separation	96
Effect of Varying Scan Rate	97
Macroelectrode Profile with Current Peaks	97
Increase in Current	97
Hydrodynamic or Forced Convection Voltammetry	99
Other Factors Affecting Current	103
Reasons for Deviation from Linearity	108
Electrochemical Cell Types and Applications	109
Mechanism	110
Regeneration of Dye from Dye^+	111
Regeneration of I^- in Electrolyte	111

Key Features of the Gratzel Cell	112
Factors Affecting the Efficiency of a Solar Cell	112
Key Features	115
Platinum Electrodes	115
Reactant Gases (or “Fuel”)	116
Electrolyte	116
Concentration Polarization	117
Activation Polarization	117
Ohmic Effects	118
Basic Design Constraints	118
Reason for Not Over-Discharging	120
Index	121

About the Author

Xian Wen Ng X.W. Ng graduated with First-Class Honors from the University of Cambridge, UK, with a Master's Degree in Chemical Engineering and Bachelor of Arts in 2011 and was subsequently conferred a Master of Arts in 2014. She was ranked second in her graduating class and was the recipient of a series of college scholarships including the Samuel Taylor Marshall Memorial Scholarship, Thomas Ireland Scholarship, and British Petroleum Prize in Chemical Engineering, for top performance in consecutive years of academic examinations. She was also one of the two students from Cambridge University selected for the Cambridge-Massachusetts Institute of Technology (MIT) exchange program in Chemical Engineering, which she completed with Honors with a cumulative GPA of 4.8 (5.0). During her time at MIT, she was also a part-time tutor for junior classes in engineering and pursued other disciplines including economics, real estate development, and finance at MIT and the John F. Kennedy School of Government, Harvard University. Upon graduation, she was elected by her college fellowship to the title of scholar, as a mark of her academic distinction.

Since graduation, she has been keenly involved in teaching across various academic levels. Her area of specialization includes Mathematics, Science, and Engineering topics. Some of her recent works include "Engineering Problems for Undergraduate Students" and "Pocket Guide to Rheology" both of which were written in a similar problem-based format, specifically aimed at students taking engineering and related STEM courses at higher education and university levels. These books aim to sharpen students' problem-solving skills and put them in good stead for tests and examinations.

Fundamentals of Electrode Processes



Abstract This first chapter, Fundamentals of Electrode Processes, provides a strong foundation for understanding the basic electrochemical system set up; the principle processes involved, such as electrode kinetics and charge transfer mechanisms at the electrode surface; as well as key factors affecting the performance of an electrochemical system.

Keyword Gouy-Chapman model · Salt bridge · Outer Helmholtz plane · pH electrode · Nernst equation · Electrochemical cell · Electrolytic cell · Electrode kinetics · Quasi reversible · Fick's law · Electric double layer · Cell emf · Cell potential · Cell reaction · Helmholtz model

Problem 1

Explain what a standard reduction potential is and how it relates to a standard oxidation potential.

Using a suitable diagram, describe how the standard reduction potential of a Mg/Mg^{2+} half-cell can be obtained experimentally, and highlight any key features of the setup.

Solution 1

We should first understand what the word “standard” means in this context. Standard conditions refer to a temperature of 298 K (i.e. room temperature), pressure of 1 atm (atmospheric pressure), and all solutions having a concentration of 1 M (or 1 mole per dm^3).

Standard Reduction Potential

Standard reduction potential denoted E_{red}^0 measures how easily a particular chemical species is reduced at standard conditions. It represents how likely reduction reaction will occur, whereby the more positive the value of E_{red}^0 is, the more likely reduction will occur. Using the example of silver, we have a standard reduction potential of +0.80 V. The reduction reaction below is also known as the reduction half-cell equation.



Standard Oxidation Potential

A standard oxidation potential is simply the reverse of the standard reduction potential. Recall that a redox reaction can typically occur in the forward and reverse directions, hence the term “redox couple”, whereby if one direction was reduction, then the opposite direction would be oxidation.

The standard oxidation potential measures how likely a chemical species can be oxidized under standard conditions. Using the same example of silver, we notice that the standard oxidation potential is equivalent in magnitude to the standard reduction potential but has an opposite sign. Since $E_{oxi}^0 < 0$, oxidation of Ag is not preferred compared to reduction.

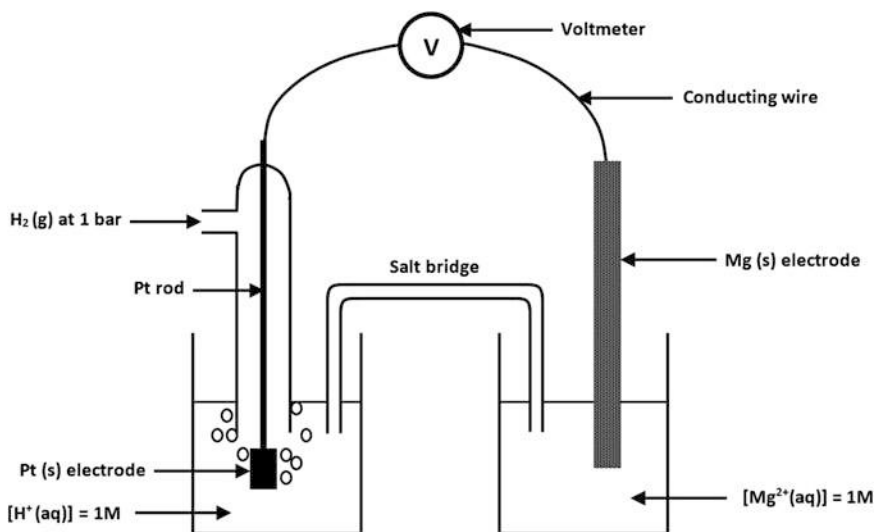


The oxidation reaction above is also known as the oxidation half-cell reaction.

Measuring Standard Reduction Potential

The standard reduction potential of a Mg^{2+}/Mg half-cell can be experimentally measured using a galvanic (or electrochemical) cell that consists of a Standard Hydrogen Electrode (SHE) on one end and a Mg^{2+}/Mg half-cell on the other end.

The SHE is also known as the reference electrode as it serves as a common baseline to which different species’ potentials can be measured against and hence be precisely defined. The potential of hydrogen in the SHE is universally defined as zero. Hence, any unknown electrode that is connected to the SHE will give a voltmeter reading that directly represents the half-cell potential of the unknown electrode alone. In this case, if we connect the Mg^{2+}/Mg half-cell to the SHE, we will be able to single out and measure the standard reduction potential of Mg^{2+}/Mg . An illustration of the experimental setup is shown below.

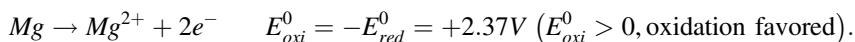
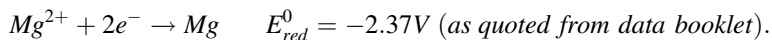


At each electrode, redox equilibrium is reached quickly as predicted by the Nernst equation, and this equilibrium is what gives each electrode its own associated half-cell potential. The value of this half-cell potential reflects how likely reduction or oxidation occurs at the particular half-cell.

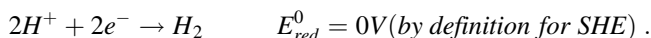
The potential difference between the two electrodes (the SHE and the Mg^{2+}/Mg half-cell) can be measured using a high-resistance voltmeter, and this value is equivalent to the standard reduction potential of Mg/Mg^{2+} . There is a non-zero potential difference when each half-cell has different redox characteristics and hence achieves different equilibrium potential values, i.e. they undergo oxidation and reduction to different extents under standard conditions.

The reduction half-cell is where reduction is favored over oxidation, as compared to the other half-cell. Conversely, the oxidation half-cell is where oxidation occurs more readily than reduction as compared to the other half-cell.

In our system, we notice that the **oxidation half-cell is the magnesium electrode** since that is where oxidation is thermodynamically favored over reduction, as seen from $E_{\text{oxi}}^0 > 0$ shown below. [Note that by convention, data booklets refer to standard potentials as standard reduction potentials. Hence we need to convert to oxidation potentials as required.]



Since magnesium prefers to undergo oxidation, the other **hydrogen electrode is the reduction half-cell**. Its potential is zero by definition.



Voltage Measurement

The voltmeter is of high resistance to minimize flow of current through the circuit. If this was not the case, electrons would flow rapidly from one electrode to the other, and this will cause the voltage reading across the two electrodes to drop until zero is reached, since current acts to even out potential difference as it brings charges from high to low potential, in the process reducing potential difference until potential difference is zero (and current flow stops). To accurately measure cell potential, which is the maximum possible potential difference between two electrodes, this electron flow (or current) is minimized.

The cell potential measured under standard conditions is denoted E_{cell}^0 . We know as well that measured voltage $E_{cell}^0 = E_{red,cathode}^0 + E_{oxi,anode}^0$. In electrochemical cells, we call the electrode where reduction occurs as the cathode and the other electrode where oxidation occurs is the anode. Therefore, our cathode is H^+/H_2 and our anode is Mg^{2+}/Mg . We found earlier that the oxidation potential of the Mg^{2+}/Mg anode is +2.37 V, and by definition the SHE electrode, i.e. the H^+/H_2 half-cell, has zero potential.

$$\begin{aligned} E_{cell}^0 &= E_{red,cathode}^0 + E_{oxi,anode}^0 = 0 + 2.37V \\ &= \text{standard oxidation potential of } Mg^{2+}/Mg \text{ anode} . \end{aligned}$$

From the above, we can see how any voltmeter reading taken between two electrodes whereby one electrode is the SHE simply gives us the potential of the other half-cell alone, in this case the standard oxidation potential of Mg^{2+}/Mg .

Finally, we can convert this to the standard reduction potential by changing the sign from positive to negative.

Standard reduction potential of Mg^{2+}/Mg half-cell is $-2.37V$.

Salt Bridge

The salt bridge acts to close the loop in the electrical circuit without affecting the potential readings. It typically consist of a glass (or an inert material) tube filled with an electrolyte (e.g. potassium nitrate solution) that does not react with the contents in either of the half-cell beakers. The ends of the glass tube may contain small balls of cotton wool to minimize excessive mixing between the electrolyte solutions in the salt bridge and in the two beakers.

Problem 2

An electrochemical cell consists of zinc and copper electrodes, each dipped in separate beakers of electrolyte solutions zinc sulphate and copper(II) sulphate respectively. A voltmeter is placed between the two electrodes and connected to them via conducting wires, and a NaCl(aq) salt bridge straddles across the two half-cell beakers. Given that the standard reduction potentials for the Zn^{2+}/Zn and Cu^{2+}/Cu redox couples are -0.76 V and $+0.34\text{ V}$ respectively,

- Show that the overall cell potential measured by the voltmeter is 1.1 V .
- Using an appropriate diagram, illustrate the electrochemical cell described above and indicate the direction of electron flow. Explain the roles of the voltmeter and salt bridge in this cell.

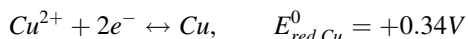
Solution 2

(a) In an electrochemical cell consisting of a zinc half-cell and a copper half-cell, we can predict which would be the reduction half-cell and which would be the oxidation half-cell, by observing the relative tendencies of each metal to be reduced (or oxidized).

At the zinc electrode, a reversible redox couple is set up as shown below. By convention, we express the reversible redox couple in terms of a reduction reaction (when read from left to right) and assign a standard potential which is the standard reduction potential.



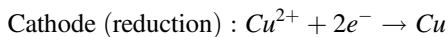
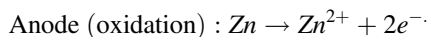
Similarly for copper, we may obtain its standard potential in data booklets, expressed in the same convention (reduction potential).



From our knowledge of metals and their relative reactivities, we know that zinc is more reactive than copper and expect that it would oxidize from zinc metal to zinc ions more easily than copper. In other words, the oxidation direction of the redox couple is favored at the zinc electrode, and the zinc electrode is also known as the anode where oxidation occurs. Conversely, at the copper electrode, the reduction reaction of the redox couple is favored, hence the copper electrode is also referred to as the cathode, where reduction occurs.

We can also predict this by comparing the half-cell potentials. Since $E_{\text{red,Zn}}^0 < E_{\text{red,Cu}}^0$, the copper electrode would undergo reduction more easily compared to the zinc electrode. This makes the copper electrode the cathode (reduction), and the zinc electrode the anode (oxidation). Having $E_{\text{red,Zn}}^0 < E_{\text{red,Cu}}^0$ is equivalent to saying $E_{\text{oxi,Zn}}^0 > E_{\text{oxi,Cu}}^0$ since $E_{\text{red}}^0 = -E_{\text{oxi}}^0$, which means the zinc electrode undergoes oxidation more easily than the copper electrode.

Half-Cell Equations for the Zn-Cu Cell



In an electrochemical cell where both half-cells are connected to a voltmeter, the voltmeter registers a reading that represents the potential difference between them. We can define a standard cell potential as follows

$$E_{\text{cell}}^0 = E_{\text{red,cathode}}^0 + E_{\text{oxi,anode}}^0 = E_{\text{red,Cu}}^0 + E_{\text{oxi,Zn}}^0$$

Since $E_{\text{oxi,Zn}}^0 = -E_{\text{red,Zn}}^0$ and $E_{\text{red,Zn}}^0 = -0.76\text{V}$ can be found from published data, we can compute the overall cell potential to be 1.1 V.

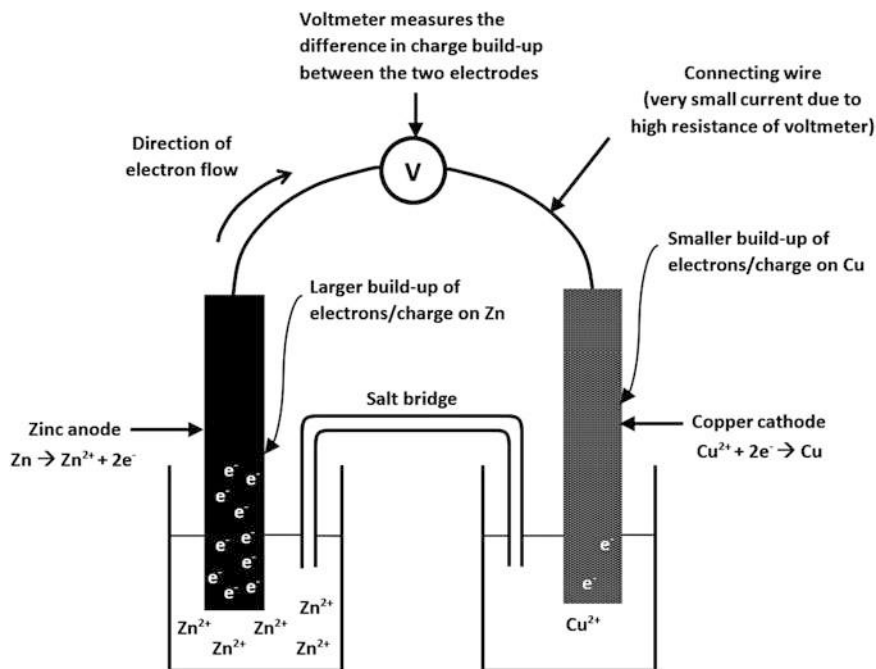
$$E_{\text{cell}}^0 = E_{\text{red,Cu}}^0 - E_{\text{red,Zn}}^0 = +0.34 - (-0.76) = 1.1\text{V}$$

(b)

Direction of Electron Flow

When the two electrodes are connected via a conducting wire, the wire provides a pathway linking the physically separated half-cells. This allows electrons released from the zinc anode to flow to the copper cathode. This flow of electrons contributes to a current in the wire.

Current flow is also a flow of charge and hence it acts to equalize potential difference. Charges flow from high to low potential from a region of excess to a region of deficit. For the zinc-copper cell, we expect more electrons to build up at the zinc electrode due to the greater tendency of zinc to oxidize than copper. At the copper electrode, electrons received are consumed in the reduction reaction. This is shown in the diagram below.



Voltmeter

The voltmeter measures the potential difference between the two electrodes, and this value is also known as the cell potential.

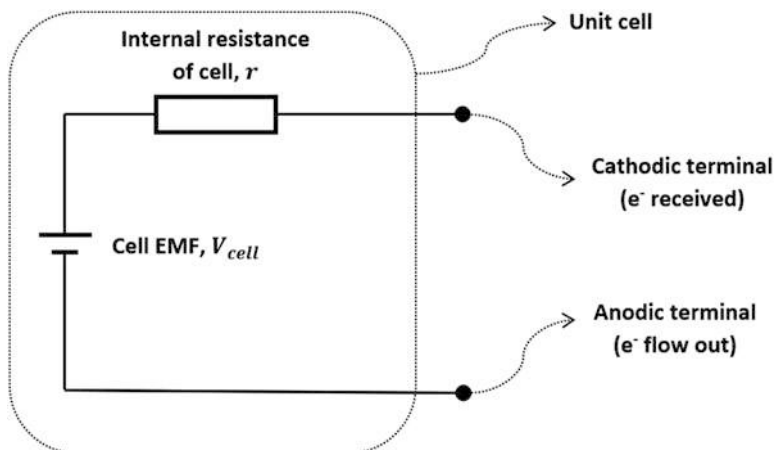
The cell potential is also referred to as cell EMF (electromotive force) or open circuit voltage. Strictly speaking, the EMF of a cell is defined as the potential difference across its terminals (or electrodes in this case) when no current flows through, hence it is also referred to as the open circuit voltage or maximum voltage of the cell.

However in real life, we often use a voltmeter to approximate cell EMF. This is an approximation because cell EMF requires no current flow, but a voltmeter is a current-controlled device that requires some current (not zero) to flow through it in order to work. Nonetheless this approximation is valid since the amount of current flow is minimized sufficiently due to the large resistance of the voltmeter.

Having a small current reduces the effect of the cell's internal resistance in affecting the accuracy of the cell potential measurement. If the voltmeter did not have a large resistance, it would show a significantly smaller cell potential than the actual EMF of the cell.

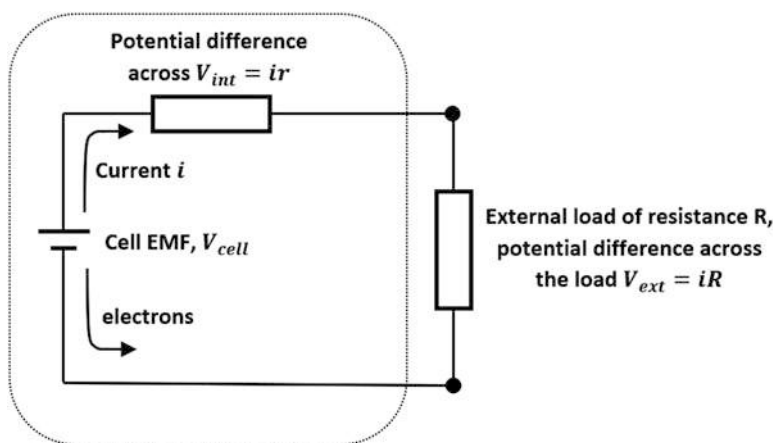
This is explained further as shown below.

When No Load Connected to Cell: Open Circuit



Each cell has an associated internal resistance, r that is inseparable with the unit cell. The end points that allow connection to external loads occur outside the unit cell (marked by the box above). When the cell is not connected to a load such as a voltmeter, there is an open circuit which means no current flows. In the above diagram, the cell terminals correspond to the cathodic and anodic half-cells of the electrochemical cell setup and V_{cell} is the cell EMF that we ultimately want to measure with as much accuracy as possible using a voltmeter.

When a Load Is Connected to the Cell



Now that when there is an external load connected to the open terminal ends of the cell, there is a closed circuit and current flows. [Note that current is conventionally defined as the rate of flow of positive charge, hence electron flow direction is the reverse of the direction of current flow.] The external load can be any current-drawing electrical device that uses electrical energy to do work, e.g. a light bulb. In our example in the diagram above, the external load is the voltmeter.

Now let us assume the current flowing in the circuit is i , and the resistance of the external load, i.e. the voltmeter is R . Then the closed circuit equation will be as follows, where the cell EMF is the sum of two voltage drops, V_{int} due to the internal resistance and V_{ext} due to the external load.

$$V_{cell} = V_{int} + V_{ext} = ir + iR = i(r + R)$$

Now we know that the voltmeter has a very large resistance, so R is large. Since V_{cell} and r are fixed for a particular cell, the above equation shows that a large R makes current i very small. Note that the voltage measured by the voltmeter is V_{ext} . Therefore if R is large, then $R \gg r$ and $(r + R) \cong R$. The equation then simplifies such that we may approximate the cell EMF (V_{cell}) as almost equivalent to the voltmeter reading V_{ext} .

$$V_{cell} = V_{int} + V_{ext} = ir + iR = i(r + R) \cong iR$$

$$V_{cell} \cong iR \rightarrow V_{cell} \cong V_{ext}$$

Salt Bridge

The salt bridge contains another electrolyte solution that is intentionally selected such that it does not react with the half-cell electrolyte solutions, i.e. the zinc sulphate and copper(II) sulphate solutions. In this case, we have NaCl(aq) which is a suitably unreactive electrolyte solution for the salt bridge. Electrolytes used in the salt bridge should ideally be one that does not itself undergo oxidation or reduction or form a complex or precipitate. Common ions in salt bridge solutions include Na^+ , K^+ , NO_3^- or SO_4^{2-} . The ions in the salt bridge also do not have to be identical with those in the half-cell solutions.

The electrolyte in the salt bridge has two main functions:

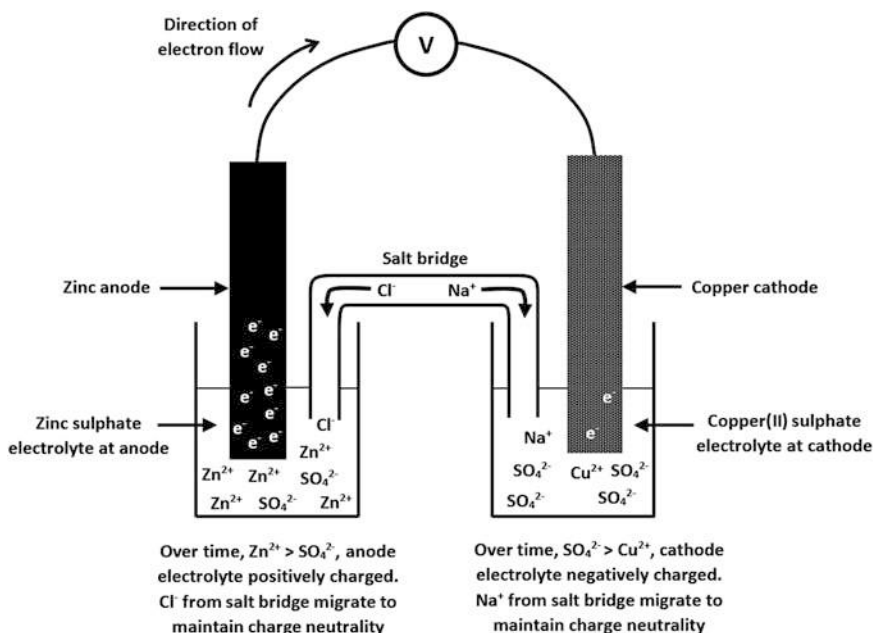
1. It closes the circuit by carrying charge in the form of ions.
 - It is important to note here that there is a difference between **ions and electrons**. Ions refer to the Zn^{2+} , Cu^{2+} ions in the half-cell electrolyte solutions, as well as Na^+ , Cl^- ions in the salt bridge electrolyte solution, and they travel in the electrolyte solutions.

- Electrons travel between the metal electrodes and the connecting wire but never enter the solution.
 - Current flow in a closed circuit is completed by a combination of electron flow through the wires and ions moving through solution.
2. It maintains electrical neutrality in both half-cell beakers by allowing ions to move between them while the beakers remain physically separated. Note that the function of the salt bridge is not to move electrons but to move ions.
- Electrochemical cells cannot maintain their electron flow without a salt bridge because the cathode and anode beakers become increasingly charged over time.
 - Without the salt bridge, the electrolyte solution in the zinc half-cell would become increasingly positively charged as zinc continues to oxidize, producing more Zn^{2+} in solution, making the ratio of Zn^{2+} to SO_4^{2-} ions higher over time. Conversely, the electrolyte solution in the copper half-cell becomes increasingly negatively charged as Cu^{2+} continues to be reduced to Cu, losing Cu^{2+} in solution and making the ratio of SO_4^{2-} to Cu^{2+} ions higher over time.
 - The flow of electrons from the zinc anode to copper cathode becomes inhibited with the positively charged zinc half-cell attracting electrons back, while the negatively charged copper half-cell becomes increasingly unable to draw electrons to itself as it repels the negatively charged electrons. Hence current eventually stops flowing without a salt bridge.

How the Salt Bridge Works

The negatively charged ions in the salt bridge electrolyte are drawn to the positively charged anodic half-cell, hence restoring charge neutrality in the anode electrolyte. Conversely, the positively charged ions in the salt bridge electrolyte move to the cathodic half-cell to neutralize its negative charge. Due to this mixing of ions, it is important to choose a salt bridge electrolyte with ions that do not react with those in the half-cell electrolytes. The presence of a salt bridge helps maintain the flow of electrons (hence current) from one half-cell to the other.

In some cases, a salt bridge may not be necessary. For example, if there is a sufficiently large amount of electrolyte solution in the half-cells to slow down the build-up of charge imbalance, or if the experimental timeframe was sufficiently short.



Problem 3

Compare an electrochemical cell with an electrolytic cell, highlighting key similarities and differences.

Solution 3

Similarities

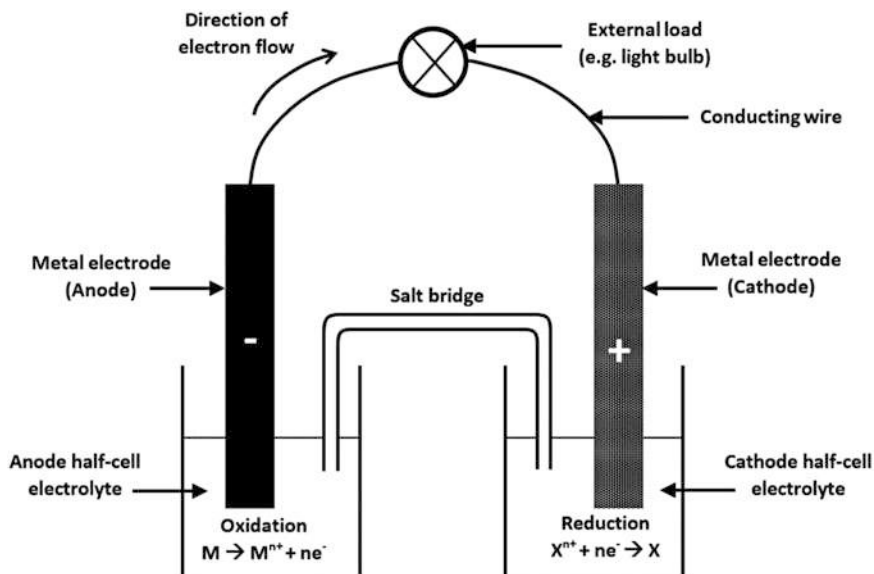
For both the electrochemical and electrolytic cells, there are two metal electrodes, each dipped in an electrolyte solution. The anode is where oxidation occurs while the cathode is where reduction occurs. Therefore, electrons flow from the anode to the cathode in both cells.

Differences

Electrochemical cell

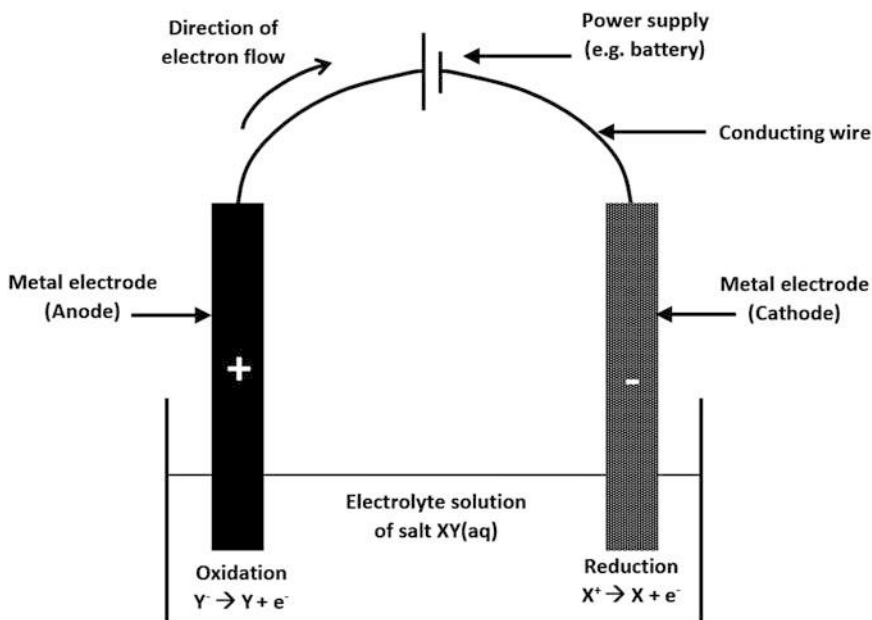
- An **electrochemical cell** is also known as a galvanic cell, and functions like a battery. It **produces electrical energy** for our electrical needs. Therefore, a key feature of an electrochemical cell is that it converts chemical energy to electrical energy (output).
- An electrochemical cell is connected to an external load (e.g. a device such as a light bulb).
- In an electrochemical cell, the chemical reaction is **spontaneous** due to the specific pairing of chemical species with differing redox characteristics, thereby enabling the cell to perform its function in generating electricity.

- The **anode is the negative terminal** where electrons exit the cell while the **cathode is the positive terminal** that takes electrons back into the cell from the external circuit.
- The **electrolyte solutions for the anode and cathode are physically separated** with a salt bridge connecting the two half-cell solutions.
- A diagram of an electrochemical cell setup is shown below.



Electrolytic cell

- An **electrolytic cell** drives a chemical reaction and requires an input of electrical energy. While the electrochemical cell produces electrical energy, an electrolytic cell **consumes electrical energy**.
- An electrolytic cell is connected to a power supply.
- In an electrolytic cell, the chemical reaction is a redox reaction that is **non-spontaneous** and has to be “forced” to take place via the input of electrical energy.
- The **cathode is the negative terminal** as it is connected to the negative terminal of the power supply, while the **anode is the positive terminal** connected to the positive terminal of the power supply.
- There is a single electrolyte solution in which both the anode and cathode are dipped into.
- A diagram of an electrolytic cell setup is shown below.



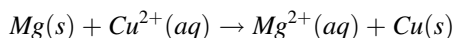
Problem 4

Using a suitable example, explain how an electrochemical cell is able to convert chemical energy of a redox reaction into useful work.

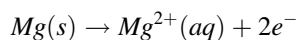
Solution 4

One way to show how a galvanic cell effectively taps on chemical energy to do useful work is to compare it with another system whereby the same chemical energy would have been “wasted” as heat energy instead. In a galvanic cell, chemical energy is converted to electrical energy which helps to power our electrical devices (hence useful work).

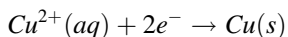
For both systems, consider the redox reaction as follows. This reaction is spontaneous since Mg is more reactive than Cu in the reactivity series for metals, it displaces the ions of the less reactive Cu (from solution).



Oxidation half-reaction (produces electrons):



Reduction half-reaction (takes in electrons):



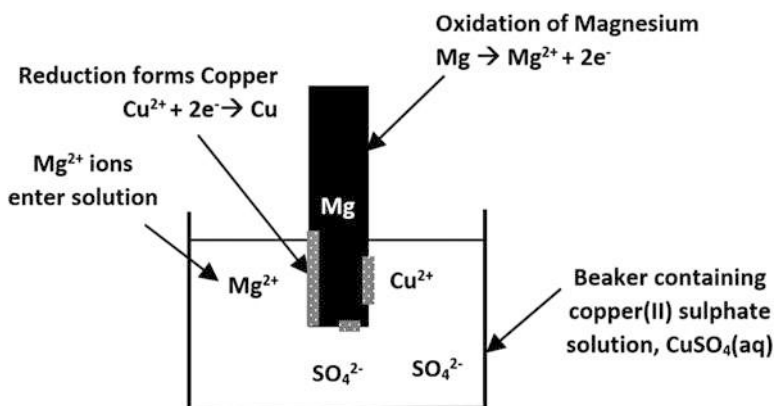
If we provided a pathway for the electrons produced by oxidation to reach the reduction site where they are absorbed for reduction, then the redox reaction would take place spontaneously. This can occur in two ways:

1. Add magnesium metal into a solution containing copper(II) ions.
2. Use an electrochemical cell with copper and magnesium electrodes each dipped in electrolytes of their respective ions.

Let us explore the two methods in detail below, specifically noting the conversion of energy.

Method 1: Chemical Energy to Heat Energy

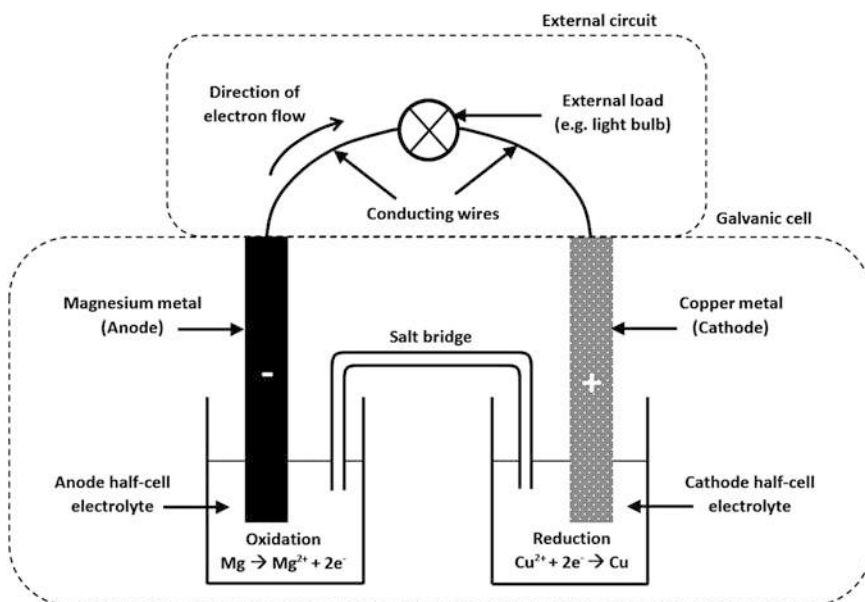
In this method, we dip a piece of magnesium metal into a solution containing copper (II) ions, e.g. copper(II) sulphate solution. The more reactive magnesium metal will displace the less reactive copper from its compound, CuSO_4 . This gives rise to a spontaneous redox reaction whereby copper metal is formed from the reduction of Cu^{2+} ions, and Mg in turn gets oxidized to Mg^{2+} ions (in other words, Mg dissolves). The electrons travel from Mg to Cu^{2+} ions in this process. As the reaction proceeds, energy is released in the form of heat which is easily lost to the surroundings.



Method 2: Chemical Energy to Electrical Energy

This method essentially describes the mechanism of a galvanic cell. A galvanic cell is useful since it provides electrical energy which can perform useful work, especially in operating our electrical devices. In order to harness the chemical energy from redox as useful electrical energy, we need to create a pathway that allows electrons flowing from Mg to Cu^{2+} ions to pass through an external circuit. If electrons were able to pass through this external circuit, then they would be able to provide current to an external load or device (e.g. light bulb) hence allowing it to work (e.g. light bulb becomes lit).

The key to the design of a galvanic cell is in the physical separation of the electrolyte solutions for the oxidation and reduction portions of the redox reaction. Both portions are then connected to each other via a conducting wire that passes through the external load. The conducting wire in the external circuit provides a path of very little resistance for the electrons to preferentially flow through, from Mg where they are produced, to the Cu/ Cu^{2+} half-cell where the electrons are used in reduction reactions. In this way, the cell is able to harness redox reactions to generate a current that can power an external electrical load.



In a galvanic cell, a salt bridge containing an inert electrolyte solution may sometimes be used to link the two electrolyte solutions of the anode and cathode. Note that electrons do not preferentially travel from one half-cell solution to the other through the salt bridge, as this path through solution poses far greater resistance than

the conducting wire. The salt bridge's main role is to complete the electrical circuit with mobile electrolyte ions (not electrons) carrying charge between the separated half-cell solutions to complete the circuit.

Problem 5

Discuss the main factors affecting the overall rate of electrolytic reactions.

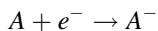
Solution 5

The overall rate of electrolytic reactions is influenced by two main factors as shown below. Their joint effects determine the final response. This could be in terms of an overall current response and/or overall cell potential difference that is measured in a voltammetric experiment:

- Electrode kinetics
 - Can be reversible (i.e. rapid), quasi-reversible or irreversible
 - Pertains to electron transfer due to oxidation and reduction reactions at the electrode surface
 - Relevant to electroactive species (background electrolyte is typically electrochemically inactive and does not take part in electrode kinetics)
- Mass transport
 - Can be diffusion, convection, or migratory transport, with each governed by their respective kinetics and modelling equations.
 - Pertains to the movement of electroactive species to and from bulk solution to the electrode surface where redox reactions occur.
 - Mass transport rate affects how fast or slow fresh reactant can be supplied to the electrode surface to sustain redox reactions that produce current.

In a voltage sweep, if mass transport effects were absent or negligible, then we would see a clear relationship between voltage change and increased redox reactions at the surface, and hence increased current. This correlation can also be seen in the equations below considering a simple example of a reduction reaction for reactant A:

Reduction reaction at the electrode surface:



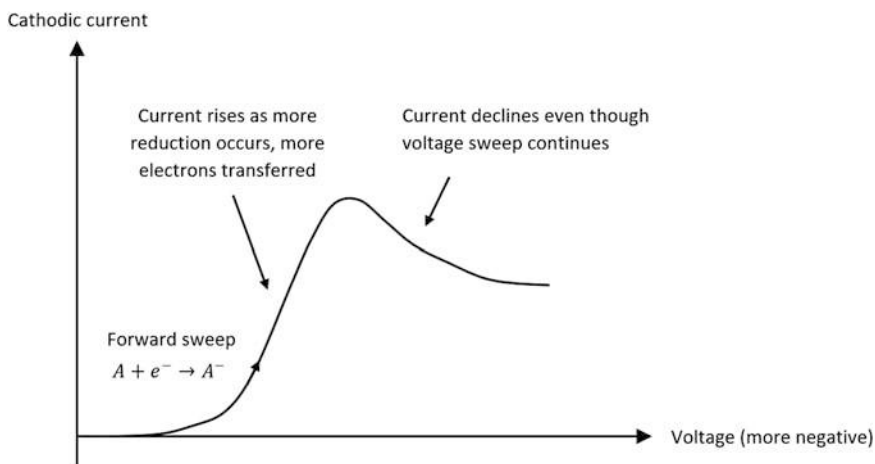
Current measured at the cathode due to reduction reactions is given by:

$$i_{\text{cathodic}} = nFAr_{\text{red}} = nFA(k_{\text{red}}[A])$$

The rate of the reduction reaction, r_{red} can be expressed as a product of the rate constant, k_{red} and the concentration of reactant available at the surface for reaction, $[A]$. From the above expression, we note that current i is expected to increase if there is a voltage sweep. With a continued voltage sweep, more moles of electrons are transferred at the electrode (whereby n represents the number of moles of electrons

transferred), therefore the value of n in the above expression increases, causing i to increase as well.

However, we note that this is often not the case in reality. One example is in the subsequent decline in current that is often observed as shown below.



This happens because at some point in time towards the later part of the voltage sweep, the continued reduction reaction at the electrode surface will not be able to sustain at the same rate, as fresh reactant is not brought to the surface fast enough from bulk solution due to mass transfer limitations.

The concentration of reactant at the surface is lower than that in the bulk solution as it is being actively consumed at the surface by the reaction. This concentration gradient drives the diffusional mass transport of more reactant to the surface for reaction. Over time, this diffusion slows down, bringing less reactant to the surface for reaction and current declines.

There are in fact three main types of mass transport. Besides diffusion, there is also bulk convection and migratory transport. The key characteristics of each are summarized in the comparison table below.

Factors	Diffusion	Convection	Migratory transport
Occurrence	Occurs in all solutions	Does not occur in all solutions. Occurs where there are density differences (natural convection) or when pumps/stirrers (forced) are used	Occurs in most solutions of electrolytic systems
Driving force	Driven by concentration gradient between bulk	External force drives bulk movement of fluid	Electrostatic effect caused by an electric field set up between

(continued)

Factors	Diffusion	Convection	Migratory transport
	solution and electrode surface		charged electrode and charged species in solution
Speed of process	Slow process	Generally faster than diffusion. Exact speed depends on the type of external force exerted (e.g. rotational speed of stirrer)	Generally faster than diffusion and varies according to the strength of electric field
Analytical models	Fick's first law: $J = -D \frac{dC}{dx}$ [rate of diffusion per area J is proportional to concentration gradient $\frac{dC}{dx}$] Fick's second law: $\frac{dC}{dt} = D \left(\frac{d^2 C}{dx^2} \right)$ [rate of change of concentration at surface $\frac{dC}{dt}$ is proportional to the rate of change of concentration gradient $\frac{d^2 C}{dx^2}$]	Assuming laminar, one dimensional flow, $\frac{dC}{dt} = -v \left(\frac{dC}{dx} \right)$ [rate of change of concentration at surface $\frac{dC}{dt}$ is proportional to the speed of solution flow velocity v and the concentration gradient $\frac{dC}{dx}$]	Generally more complex to quantify. This effect is often made negligible with the use of a background electrolytes at high concentration (relative to concentration of electroactive species)

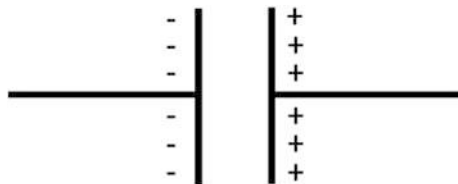
In most cases, experimental design would aim to remove as much of such mass transport complexities as possible from electrochemical experiments. This can be done through careful design and control of experimental parameters (e.g. by using an inert background electrolyte at high concentration to remove effects of migratory transport, or by using a stagnant solution at constant temperature and pressure to minimize convective effects). In this way, we would be able to more accurately probe the true kinetics of electron transfer reactions at the electrode surface.

Problem 6

The “electrical double layer” has been described by various scientists including Helmholtz in the 1800s and Gouy & Chapman in the 1900s. Compare the Helmholtz model and Gouy-Chapman model in describing the electrical double layer.

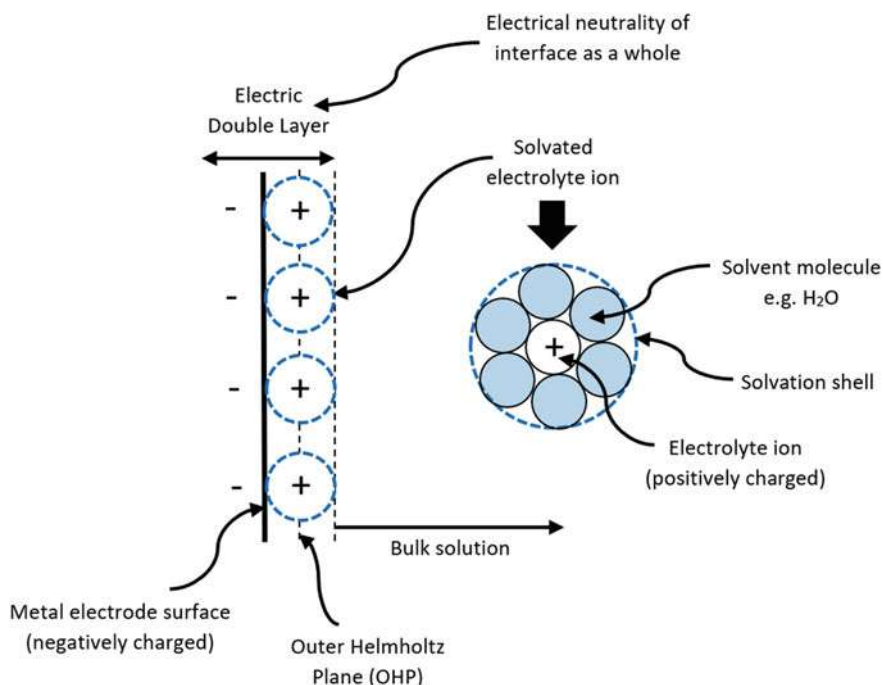
Solution 6

An electrical double layer is analogous to an electrical capacitor where there is a separation of charges at the electrode/solution interface.



Helmholtz Model

This is a geometrical model that assumes no electron transfer reactions occur at the electrode, and the solution contains only electrolyte at high concentration.



In this model, the metal electrode carries a charge density, q_M that is balanced by an equal and opposite charge density, q_s in solution, to maintain electrical neutrality for the electrode-solution interface as a whole.

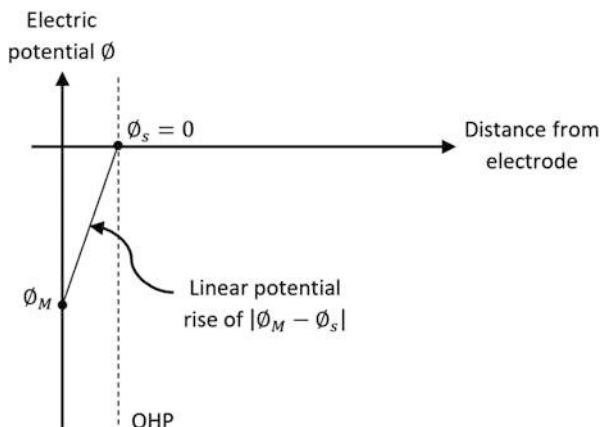
$$q_M = -q_s \text{ whereby } q_M = q \text{ and } q_s = -q$$

The forces between these two layers of opposite charges are purely electrostatic, and occur between the ions in solution and the electrode surface. The electrode surface holds charge density q_m due to an excess or deficiency of electrons. If electrons are in excess, $q_M < 0$; and if electrons are deficient, $q_M > 0$. The charge density of the solution q_s arises as a result of the redistribution of electrolyte ions at the interface, which is driven by electrostatics. The two parallel planes of opposite charges forms the “electric double layer” or EDL as shown in the diagram above (assuming $q_M < 0$). The EDL has a small length-scale of atomic dimensions (i.e. $\sim 10^{-20}$ Angstroms), hence the assumption that no electron transfer reactions occur within this short section of EDL holds.

Helmholtz assumed that the attracted electrolyte ion approaches the electrode surface at a distance of closest approach that is limited by the solvation shell surrounding the electrolyte ion. The solvation shell is assumed to comprise of a single layer of solvent molecules, and this is also referred to as a single sphere of solvation around each electrolyte ion.

This distance of closest approach depends on the size of the electrolyte ion as well as that of the solvent molecule and is measured from the electrode surface to a plane known as the Outer Helmholtz Plane (OHP). As seen from the diagram, there is a 1:1 matching of oppositely charged ions on each side of the interface.

The corresponding potential profile can be plotted for the EDL. There is a linear potential rise confined in the region between the electrode surface and OHP, and this is bounded by the potentials defined at the electrode surface, ϕ_M and in the bulk solution ϕ_s .



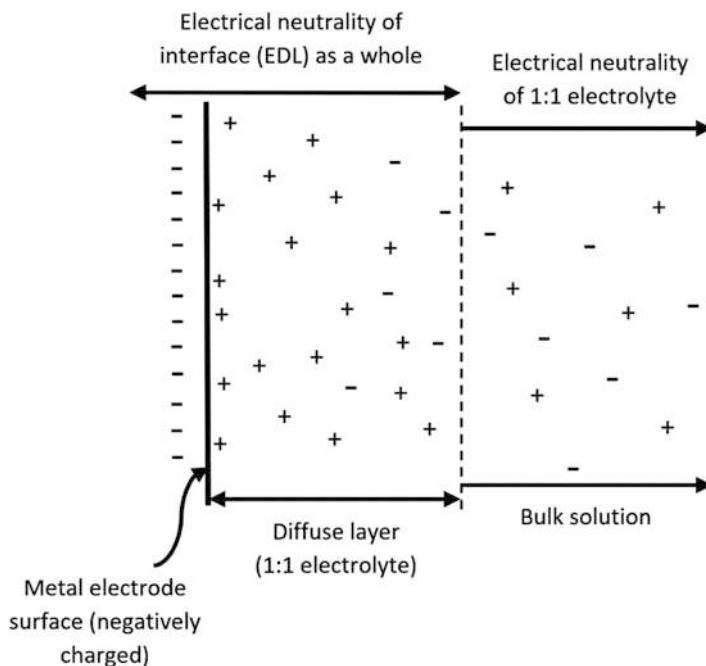
There are however some inadequacies of the Helmholtz model one should note:

- It does not account for diffusion or mixing in solution, e.g. due to Brownian motion of ions in solution. This motion becomes significant especially when temperature is close to 0 K.

- It does not account for possible adsorption effects of ions onto the electrode surface.
- It does not consider interactions between solvent dipole moments and the electrode. The only interactions considered in the Helmholtz model are those between the solvent and electrolyte ions.

Gouy-Chapman Model

The Gouy-Chapman (GC) model is a statistical model that combines the concept of electrostatics with Brownian motion and Boltzmann statistics. Electrostatic attraction of ions in solution to the electrode surface is counteracted by Brownian motion, and the net result is a region close to the electrode surface which contains excess ions (i.e. non-zero potential), beyond which the bulk solution potential of zero is reached and maintained. The region of excess charge is known as the diffuse layer and the concentration of ions in this region follows the Boltzmann distribution (Poisson-Boltzmann equation).

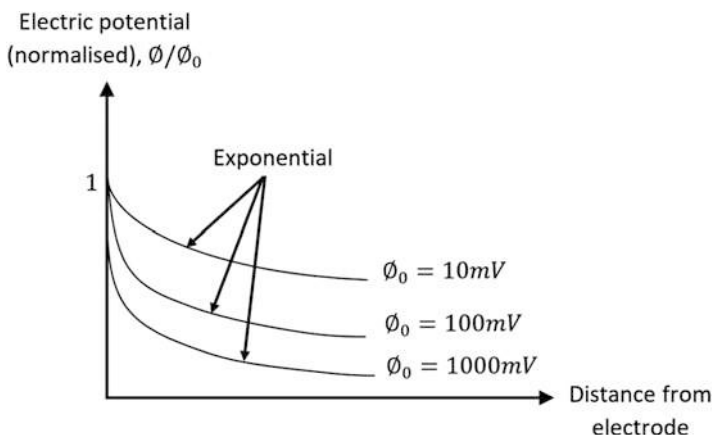


The GC model represents ions as point charges in a dielectric continuum and describes the distribution of ions in solution for planar geometry. It can be solved exactly for 1:1 (cation to anion) electrolyte solutions such as NaCl solution. This

model predicts an exponential (non-linear) variation of electric potential as the distance away from the electrode surface increases. The general form of this correlation is as shown below where ϕ_0 represents applied potential at the electrode surface, z represents charge on the ion, and C_{bulk} represents the bulk electrolyte concentration.

$$\phi = \phi_0 e^{-Kx}, K = 3.20 \times 10^7 z \sqrt{C_{bulk}}$$

Assuming a 1:1 electrolyte of concentration $C_{bulk} = 10^{-2} M$, then the potential profiles for three example cases $\phi_0 = 10$ mV, 100 mV and 1000 mV can be predicted as shown below.



One may observe that similar to the Helmholtz model, the interface as a whole (or electric double layer) maintains electrical neutrality for the GC model as the charge on the electrode q_M must be matched in solution by an equal but opposite charge q_s . However, unlike the Helmholtz model, the charges in solution are not confined within the OHP region in the GC model, instead excess charges represented as point charges are spread out over the diffuse layer.

Problem 7

The Nernst equation is often used to predict how a system will respond when the concentrations of redox species in solution change or when the electrode potential is changed. Given the Nernst equation in the following form,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_r}{a_o}$$

Explain what the symbols mean and how the equation relates to the concentrations of redox species.

Solution 7

In the Nernst equation as follows,

$$E = E^0 - \frac{RT}{nF} \ln \frac{a_r}{a_o}$$

- E refers to the cell potential under a particular set of conditions (which need not be at standard state).
- E^0 is the cell potential at standard state conditions.
- R is the universal gas constant
- T is temperature in Kelvins
- n is the number of electrons transferred in a single redox reaction equation
- F is Faraday's constant
- Assuming a single-electron transfer reaction $o + e^- \rightarrow r$, then o and r are the oxidized and reduced forms of a chemical species. Considering the reduction reaction of the redox couple, the product of reaction will be r and the reactant is therefore o . In the Nernst equation, a_r and a_o represent the activities of species r and o at equilibrium.

In a single-electron transfer reaction where $n = 1$, we are able to express activities in terms of concentrations which are easily measurable. Therefore, the Nernst equation can be simplified to the following form, in terms of the concentrations of r and o at a particular point in time, denoted $[r]$ and $[o]$ respectively.

$$E = E^0 - \frac{RT}{F} \ln \frac{[r]}{[o]}$$

In most cases, the electrochemical process is conducted at a constant room temperature and pressure, hence the value of T is typically considered a constant at 298 K. Since $R = 8.314 \text{ J/mol} \cdot \text{K}$ and $F = 96485 \text{ C/mol}$ are also constants, the equation may be simplified further to the following form.

$$E = E^0 - 0.02568 \ln \frac{[r]}{[o]}$$

Note that even though the electrochemical process is conducted at room temperature and pressure, it is not at standard state if the concentrations of the species r and o are not at 1 M or 1 mol/dm^3 . And this would mean that cell potential is not the same value as the standard state cell potential, $E \neq E^0$.

Problem 8

An electrochemical cell was used to generate 4000 kg of chlorine in 48 hours from the electrolysis of concentrated sodium chloride solution. Calculate the power input required to operate the cell at 200 V assuming that the cell is 98% efficient.

Solution 8

The electrolysis of concentrated sodium chloride solution (or brine) causes the oxidation of chloride ions to form chlorine gas. The ionic half equation can be written as follows:



Since we have 4000 kg of chlorine, we can first find the number of moles of chlorine, and relate it to the number of moles of electrons from the above reaction stoichiometry.

$$n_{chlorine} = \frac{4000 \times 10^3}{35.5 \times 2}$$

$$n_{electrons} = \frac{4000 \times 10^3}{35.5 \times 2} \times 2$$

Assuming 100% efficiency, the total charge Q generated from the oxidation reaction can be found as follows, where $F = 96480 \text{ C/mol}$ is Faraday's constant which is equivalent to the amount of charge per mole of electrons.

$$Q = n_{electrons}F = \left(\frac{4000 \times 10^3}{35.5 \times 2} \times 2 \right) \times 96480 = 1.087 \times 10^{10} \text{ C}$$

The amount of current i required, which is the rate of flow of charge, can then be calculated as follows.

$$i = \frac{Q}{t} = \frac{1.087 \times 10^{10}}{48 \times 60 \times 60} \cong 63000 \text{ A}$$

The amount of power required at an operating voltage of 200 V is therefore,

$$P = VI = 200 \times 63000 \cong 12.6 \times 10^6 \text{ W or } 12.6 \text{ MW}$$

Now we know the actual efficiency is 98% instead of 100%, therefore the actual power requirement would be more than the above, and can be determined as follows.

$$P_{98\%} = \frac{P_{100\%}}{0.98} = \frac{12.6}{0.98} = 12.8 \text{ MW}$$

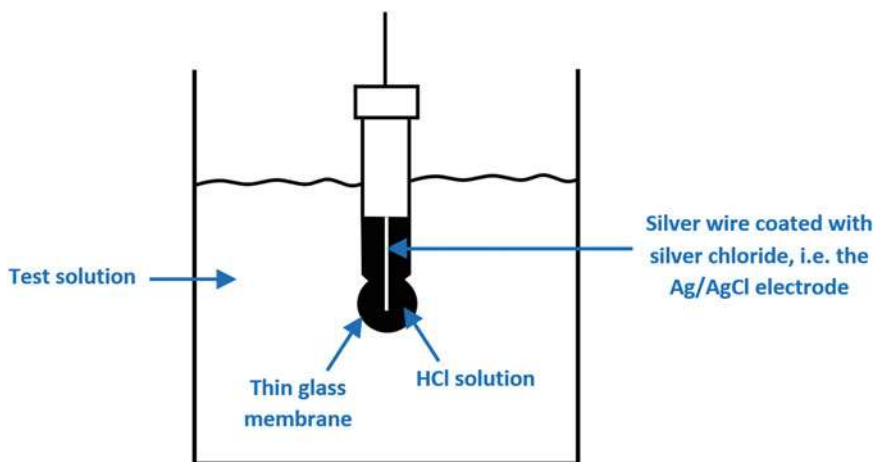
Problem 9

One of the analytical applications of the Nernst equation is in measuring pH using a glass pH electrode. Sketch a diagram showing key components of this

electrode and briefly outline how it can be used to provide quantitative information about the pH of a test solution.

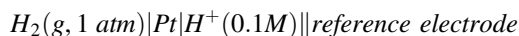
Solution 9

A pH electrode can be used as a sensor that responds to the concentration of hydrogen ions (H^+) in a solution. A diagram of the pH electrode is shown below.



In this electrode, a thin glass membrane encloses a solution of hydrochloric acid (HCl) and a potential is produced at the membrane which changes with H^+ concentration. One key feature of the glass membrane is that it contains Na^+ ions that are 'exchangeable', i.e. they can be 'pushed out' and replaced by other ions. The pH electrode also contains an in-built reference electrode that is in contact with HCl solution contained within the membrane. This reference electrode is typically a silver/silver chloride (Ag/AgCl) electrode.

The cell reaction in general, can be written as follows.



The left hand side represents the H_2/H^+ half-cell, while the right hand side represents the reference electrode which could be, for example, the Ag/AgCl reference electrode. In the cell reaction above, H^+ concentration is indicated at an arbitrary value of $0.1M$ or 0.1 mol dm^{-3} .

The H^+ ions present in the test solution diffuse through the glass membrane, and 'push out' (or exchange with) the Na^+ ions present in the glass lattice of the thin glass membrane. The ejected Na^+ ions then diffuse to other parts of the glass membrane with a lower H^+ ion concentration. These Na^+ ions, though displaced to other parts of the glass, continue to remain confined to the surface of the glass. Hence we can detect a net increase in positive charges present in the glass membrane, giving rise to a pH-dependent potential being measured.

In general, for a pH electrode, the potential produced at the membrane, E_{membrane} can be expressed in the form of the Nernst equation as shown below.

$$E_{\text{membrane}} = \text{constant} + \frac{RT}{nF} \ln [a_{H^+} + \text{constant}]$$

In the above expression, R represents the Gas Constant, T represents temperature, F represents Faraday's constant, n represents the number of moles of electrons transferred in the redox reaction, and a represents the activity of the species (a thermodynamic quantity).

Special Note:

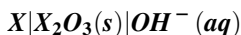
In thermodynamics, activity or a is a measure of the “effective concentration” of a species in a mixture. It can be expressed in terms of an activity coefficient, γ and the concentration of the species in the mixture, C . For example, in the case of species i , we have the following expression for its activity:

$$a_i = \gamma_i C_i$$

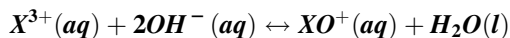
The activity coefficient γ_i is a measure of how much a solution deviates from an ideal solution, its value would be equivalent to 1 if the solution were ideal. We often assume ideal solution in problems in order to simplify the analysis, as this allows us to convert activity into concentration which is a more convenient to handle.

Problem 10

A sensor was used to detect the amount of hydroxide ions in a sample solution. Given that the relevant half-cell reaction is as shown below, where X is a metalloid element that can exist in a solid state X or as X (III) oxide (partially soluble in water),



- Express the potential measured by the sensor, in terms of the pOH of the solution.
- Assuming that another chemical equilibrium as shown below has been found to occur, derive a new expression that correlates the variation of pOH with measured potential, and explain how this new chemical equilibrium would affect the sensor's response in part a.

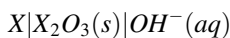


Solution 10

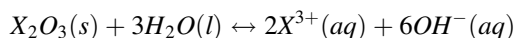
(a) Before we proceed with this problem, it is good to recap key points on the conventions used in writing voltaic cell reactions. Let us use the example of a zinc-copper voltaic cell for this purpose.

- For a complete cell reaction consisting of both the oxidation and reduction half-cells, we may write the overall cell reaction as: $Zn(s)|Zn^{2+}(aq)||Cu^{2+}|Cu(s)$.
- The double lines in the middle means that the two half-cells are physically separated, and only linked by a salt bridge.
- On the left side of the double line is the oxidation half-cell or anode, while the right side of the double line refers to the reduction half-cell or cathode.
 - For the oxidation half-cell, the direction from the left to right should be oxidation, i.e. Zn is written before Zn^{2+} or in other words, reactants are written before products.
 - For the reduction half-cell, the direction from left to right should be reduction, i.e. Cu^{2+} is written before Cu , and again, reactants are written before products.
- The single line between species indicate a phase boundary between components of a half-cell, for example between Zn metal, which is a solid, and Zn^{2+} ions which exist in a solution, there is a solid-liquid phase boundary.
- The left-most and right-most ends refer to the electrode materials used in the oxidation half-cell and the reduction half-cell respectively. So in this example, the anode electrode is $Zn(s)$ while the cathode electrode is $Cu(s)$.
- Concentrations of dissolved substances in solutions may be further indicated in brackets e.g. $Cu^{2+}(aq, 0.2M)$. If this is not indicated, then concentrations may be assumed to be at $1M$.

Going back to the problem, we can tell from the given half-cell equation that this is an oxidation half-cell with electrode X .



Also, since this electrode is used to detect OH^- ions in solution, this must mean that the solid oxide is able to dissociate in water to form the OH^- ions.



We can express the half-cell reduction reaction in ionic form which then helps us express it in the form of a Nernst equation as shown below:

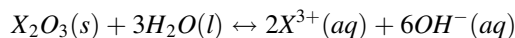
$$X^{3+} + 3e^- \leftrightarrow X$$

$$E = E_{X^{3+}/X}^0 - \frac{RT}{3F} \ln \left(\frac{a_X}{a_{X^{3+}}} \right)$$

For a solid, activity is equivalent to 1, therefore $a_X = 1$. Hence we have

$$E = E_{X^{3+}/X}^0 - \frac{RT}{3F} \ln \left(\frac{1}{a_{X^{3+}}} \right) = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln a_{X^{3+}}$$

We can express the dissociation equation in the form of a solubility product constant K_{sp} , since the dissociation of the oxide in water is the same as dissolving it in water. K_{sp} is useful as it is a constant (an equilibrium constant) as long as experimental conditions remain constant e.g. temperature, pressure and chemical species used.



$$K_{sp} = (a_{X^{3+}})^2 (a_{OH^-})^6$$

$$a_{X^{3+}} = \frac{K_{sp}^{\frac{1}{2}}}{a_{OH^-}^3}$$

The expression above can then be used to simplify our earlier Nernst equation as follows:

$$E = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln a_{X^{3+}} = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln \left(\frac{K_{sp}^{\frac{1}{2}}}{a_{OH^-}^3} \right)$$

$$E = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln K_{sp}^{\frac{1}{2}} - \frac{RT}{3F} \ln a_{OH^-}^3$$

Assuming that we have an ideal solution, then the activity of dissolved substances will be equivalent to concentration, $a_{OH^-} = C_{OH^-}$

$$E = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln K_{sp}^{\frac{1}{2}} - \frac{RT}{3F} \ln C_{OH^-}^3$$

We know that by definition,

$$pOH = -\log_{10} C_{OH^-}$$

$$C_{OH^-} = 10^{-pOH}$$

$$C_{OH^-}^3 = 10^{-3pOH}$$

Therefore, we can substitute the above expression into our Nernst equation, and derive an expression for the measured potential in terms of pOH and other known constants.

$$E = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln K_{sp}^{\frac{1}{2}} - \frac{RT}{3F} \ln (10^{-3pOH})$$

$$E = E_{X^{3+}/X}^0 + \frac{RT}{6F} \ln K_{sp} + pOH \left(\frac{RT}{F} \right) \ln 10$$

The equation above helps us easily correlate the pOH (or concentration of hydroxide ions in solution) directly to the measured potential E , since the other terms are known constants at a defined temperature and other experimental conditions. Assuming room temperature and pressure, we have:

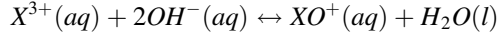
$$E = E_{X^{3+}/X}^0 + \frac{(8.314)(298)}{6(96500)} \ln K_{sp} + pOH \left(\frac{(8.314)(298)}{96500} \right) \ln 10$$

$$E = E_{X^{3+}/X}^0 + 0.0043 \ln K_{sp} + 0.059 pOH$$

If we know the identity of element X , we can look up the values of standard potential, $E_{X^{3+}/X}^0$ as well as the solubility product constant, K_{sp} from published data. This leaves us with a direct correlation between two variables only, (1) pOH , which is a quantitative measure of hydroxide ion concentration in the test solution and (2) The corresponding potential E , as measured by the sensor.

(b)

In this case, we note that the species X^{3+} formed from the dissociation of solid oxide X_2O_3 in water is no longer chemically stable, but instead undergoes a chemical reaction with the equilibrium equation as shown below.



We can again express this reversible chemical reaction in terms of an equilibrium constant K

$$K = \frac{a_{XO^{+}}}{(a_{X^{3+}})(a_{OH^{-}}^2)}$$

$$a_{X^{3+}} = \frac{a_{XO^{+}}}{K a_{OH^{-}}^2}$$

Recall that in part a earlier, the dissociation of solid oxide X_2O_3 in water gave us the Nernst equation as shown below:

$$X_2O_3(s) + 3H_2O(l) \leftrightarrow 2X^{3+}(aq) + 6OH^{-}(aq)$$

$$E = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln a_{X^{3+}}$$

Substituting our new expression for $a_{X^{3+}}$ in terms of K into our earlier Nernst equation, we have

$$\begin{aligned}
 E &= E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln \left(\frac{a_{XO^+}}{K a_{OH^-}^2} \right) \\
 E &= E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln a_{XO^+} - \frac{RT}{3F} \ln (K a_{OH^-}^2) \\
 E &= E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln a_{XO^+} - \frac{RT}{3F} \ln K - \frac{RT}{3F} \ln (a_{OH^-}^2)
 \end{aligned}$$

Again, assuming ideal solution, we may replace a_{OH^-} with concentration, C_{OH^-} ,

$$E = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln a_{XO^+} - \frac{RT}{3F} \ln K - \frac{RT}{3F} \ln (C_{OH^-}^2)$$

In the expression above, the only term that is C_{OH^-} (or pOH) dependent is the last term, i.e. $-\frac{RT}{3F} \ln (C_{OH^-}^2)$. To simplify the expression further, we can combine all constant terms into a single constant A . These terms must not vary with C_{OH^-} and remain constant at constant experimental conditions such as temperature and pressure.

$$E = A - \frac{RT}{3F} \ln (C_{OH^-}^2), \text{ where } A = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln a_{XO^+} - \frac{RT}{3F} \ln K$$

To simplify our analysis even further, we may assume that the value of the A is small as compared to the second C_{OH^-} dependent term. This is a reasonable assumption for a well-designed experiment whereby the sensor is sensitive enough to produce a sizeable output E , based on changes in C_{OH^-} . This means that the dominant term in the expression should be the C_{OH^-} dependent term instead of the constant A . Hence A may be considered negligible in our approximation as shown below.

$$E_{part\ b} = A - \frac{RT}{3F} \ln (C_{OH^-}^2) \cong -\frac{RT}{3F} \ln (C_{OH^-}^2) \text{ for small value of } A$$

In part a, we had earlier obtained the expression for measured potential $E_{part\ a}$. We can similarly combine all its constant terms into a single constant B (not dependent on C_{OH^-}), and assume that B is small enough to be considered negligible for approximation:

$$\begin{aligned}
 E_{part\ a} &= E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln K_{sp}^{\frac{1}{2}} - \frac{RT}{3F} \ln C_{OH^-}^3 \\
 E_{part\ a} &= B - \frac{RT}{3F} \ln C_{OH^-}^3, \text{ where } B = E_{X^{3+}/X}^0 + \frac{RT}{3F} \ln K_{sp}^{\frac{1}{2}}
 \end{aligned}$$

$$E_{part\ a} \cong -\frac{RT}{3F} \ln C_{OH^-}{}^3 \text{ for small value of } B$$

We can now compare the measured potentials in part a and b.

$$E_{part\ b} \cong -\frac{RT}{3F} \ln (C_{OH^-}{}^2) = -\frac{2}{3} \left(\frac{RT}{F} \right) \ln C_{OH^-}$$

$$E_{part\ b} \cong -\frac{2}{3} \left(\frac{(8.314)(298)}{96500} \right) \frac{\log_{10} C_{OH^-}}{\log_{10} e}$$

$$E_{part\ b} \cong -\frac{2}{3} (0.059) \log_{10} C_{OH^-}$$

As for part a, we have

$$E_{part\ a} \cong -\frac{RT}{3F} \ln C_{OH^-}{}^3 = -\left(\frac{RT}{F} \right) \ln C_{OH^-}$$

$$E_{part\ a} \cong -\left(\frac{(8.314)(298)}{96500} \right) \frac{\log_{10} C_{OH^-}}{\log_{10} e}$$

$$E_{part\ a} \cong -0.059 \log_{10} C_{OH^-}$$

We can deduce that the magnitude of the measured potential in part b will be reduced to approximately two thirds of that in part a.

$$E_{part\ b} \cong \frac{2}{3} E_{part\ a}$$

Basic Voltammetry for Micro and Macroelectrodes



Abstract This chapter builds on prior concepts covered in Chap. 1, and enhances in-depth understanding into electrochemical methods and voltammetric techniques. In this chapter, students are trained to apply previously-learnt concepts to solving exam-style problems. The development of detailed worked solutions will help guide students in linking theory to practical application, thereby reinforcing their ability to interpret and make logical deductions from experimental results and trends. The problems in this chapter provide ample practice in quantitative analysis of systems with known parameters, as well as exposure to common design problems covering a variety of electrochemical systems from micro to macro-scale electrodes.

Keywords Potential step · Ohmic effects · Cyclic voltammetry · Cottrell's equation · Linear sweep · Boundary layer · Diffusion layer · Glucose sensor · Capacitative charging · Charging spike · Charging effects · Limiting current · Steady state current · Microelectrode · Nernst equation

Problem 11

- Explain what voltammetry is and describe key features of this experimental technique.**
- Using the example of an applied step potential, explain why a current is produced at the cathode and describe the changes in current response with time.**

Solution 11

(a) Voltammetry is a popular technique used to study electrolytic processes whereby **voltage is applied** to the electrode, **causing redox reactions to occur at the electrode surface, hence producing a current response**. Positive current is measured at the cathodic electrode when reduction occurs, and this current is also referred to as the cathodic current i_c . Conversely, a positive current is measured at the anodic electrode when oxidation occurs, and this current is known as the anodic current i_a .

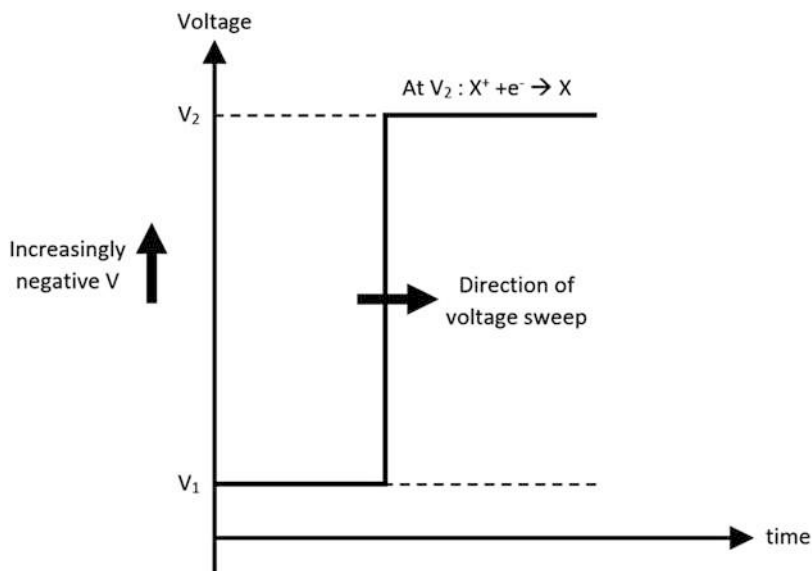
There are various types of voltammetry depending on the type of applied voltage. For example, the applied voltage could be a step change in potential step voltammetry, linearly increasing with time in a linear sweep voltammetry, or increasing and decreasing linearly in a repeated manner in cyclic voltammetry.

The key features of a voltammetric setup are as follows:

- Stagnant solution
 - This allows the assumption that the main mode of mass transport within the solution is diffusion.
- Large planar working electrode (or macroelectrode)
 - Usually made of an inert and conducting material such as Platinum.
 - Due to this geometry, only variations in one dimension are significant (i.e. the direction perpendicular to the electrode surface). This simplifies our analysis to a 1D system.
 - The working electrode is differentiated from the standard (or reference) electrode in that it is not at standard state and conditions.
 - The working electrode is connected to an external electrical circuit which is then connected to a counter-electrode that closes the circuit loop and allows current to flow. However, it is the working electrode that is of interest as it is where current is measured and analyzed.
- Background electrolyte solution
 - Comprises of a salt dissolved in a solvent. The salt is typically electrochemically inactive e.g. NaCl and is dissolved at high concentration in the solvent, e.g. 10^{-1} M. The solvent is typically polar with a high dielectric constant (e.g. water) and is therefore good at dissolving the salt.
 - The working electrode is in contact with the electrolyte solution.
 - Ions in the electrolyte solution are mobile and can diffuse within the solution.
- Electroactive species or the reactants for the redox reactions at the working electrode surface in low concentration e.g. 10^{-3} M relative to the concentration of the background electrolyte salt (typically around 10^{-1} M).

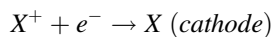
(b) Applied step potential

The applied potential jumps from V_1 to V_2 instantaneously, and current produced at the working electrode (e.g. cathode) is measured over time.

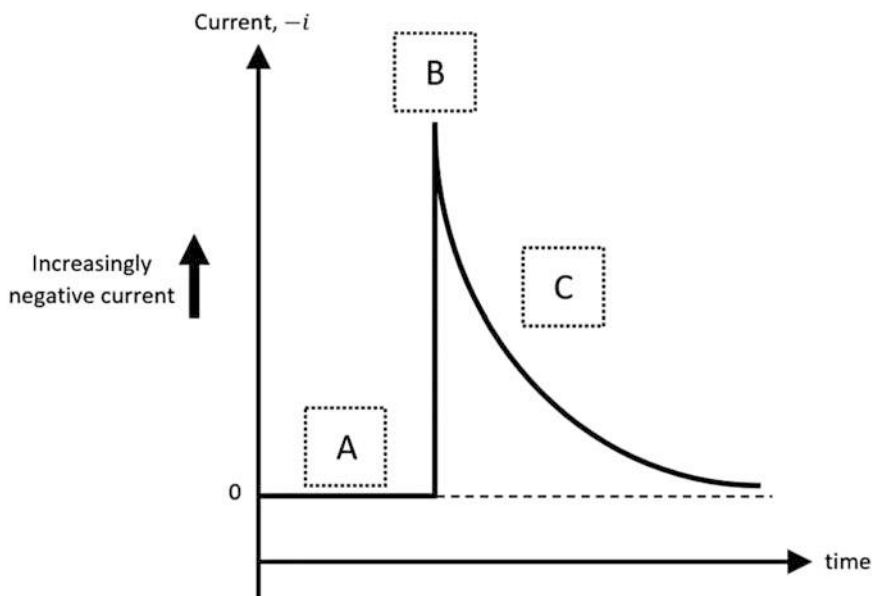


Assuming the working electrode is a cathode where reduction reactions occur, the voltage goes from less negative V_1 to more negative V_2 such that the step change in potential favors more reduction to occur at the cathode and a current response is produced. The voltage axis is correspondingly plotted as increasingly negative going upwards as shown in the plot above.

Assuming a reactant species X^+ becomes reduced to X at the cathode, the following reaction occurs when applied voltage reaches a sufficiently negative potential, V_2 .



With this potential step, the current produced rises instantaneously and then begins to drop over time. We can analyze the current response in three main stages, A, B and C as shown below.



Stage A

At V_1 , the applied potential is not sufficiently negative to cause the reduction of X^+ , in other words the reduction reaction is still thermodynamically unfavorable. Hence no current is observed.

Stage B

At V_2 , reduction of X^+ becomes thermodynamically favorable. Any reactant species X^+ close to the electrode surface will be converted to product X , and a current is produced.

We notice that the amount of current produced is at its highest instantaneously at B (“charging spike”). This is because:

- The moment right before the potential step, the electrode surface is completely surrounded by reactant X^+ . For a stagnant solution of uniform composition, the concentration of X^+ at the surface is also approximately equivalent to bulk concentration, whereby the bulk concentration is also the highest concentration that X^+ can have.
- Once the voltage step occurs, this large amount of reactant X^+ is reduced rapidly at the surface and a large current is produced.
- In cases whereby the electron transfer kinetics is fast, such as in reversible reactions where there is a high rate constant k_{red} for reduction, the current observed would be larger.
- We can express the measured current in terms of the reduction reaction rate as shown.

$$i_c = -nFAk_{red}[X^+]_{surface}$$

To sustain this large current seen at point B for long, we will need to sustain reduction reactions at the same rapid rate at the electrode surface, which means more reactant X^+ needs to be replenished quickly at the surface since it is actively consumed by the reduction reaction.

The replenishment of reactant X^+ can be done only by the diffusional flux of X^+ down a concentration gradient from bulk solution where it is at higher concentration, to the surface where it is rapidly depleted via the reduction reactions. We can already predict that the relatively slow process of diffusion would not be able to keep up with rapid redox reaction rates at the electrode surface, hence the current decline in stage C is expected, and we would notice that the maximum current occurs only instantaneously at B.

Stage C

Current declines as mass transfer rate (or diffusional flux) of X^+ now limits the extent of reduction reactions at the electrode surface. We can express the measured current in terms of diffusional flux using the Faraday's constant F .

$$i_c = -FAj_D.$$

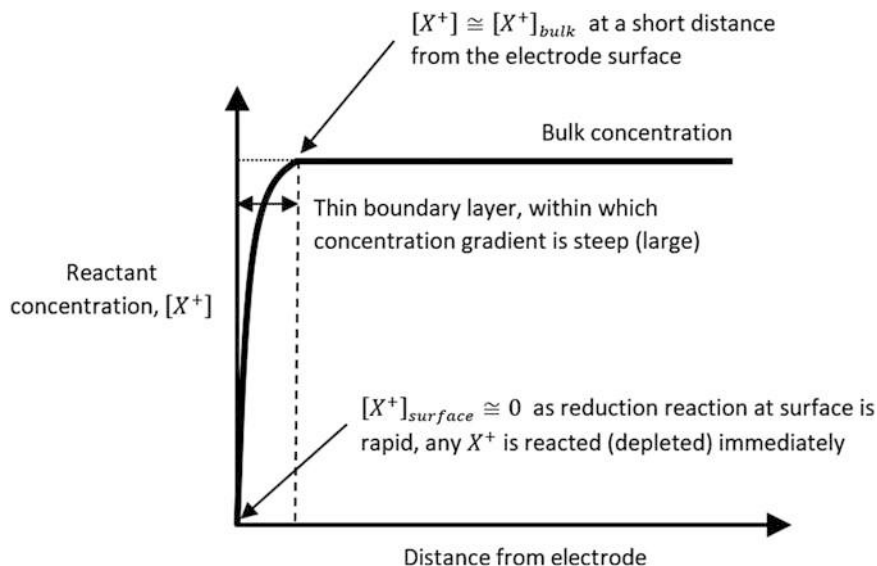
This current decline with time occurs at a rate that can be approximated as $i \sim t^{-1/2}$. As time goes on, there will be less and less reactant X^+ available at the surface because the diffusional flux of X^+ from bulk to surface decreases with time. The reason for reduced diffusional flux with time is due to the growth of a **diffusion boundary layer** from the electrode surface.

Growth of Boundary Layer

Recall from the topic of mass transfer that the rate of diffusion is affected by concentration gradient. In stage C, we require more reactant X^+ to diffuse and reach the surface in order for current to flow. The current output is therefore a direct reflection of the diffusional flux of X^+ with time.

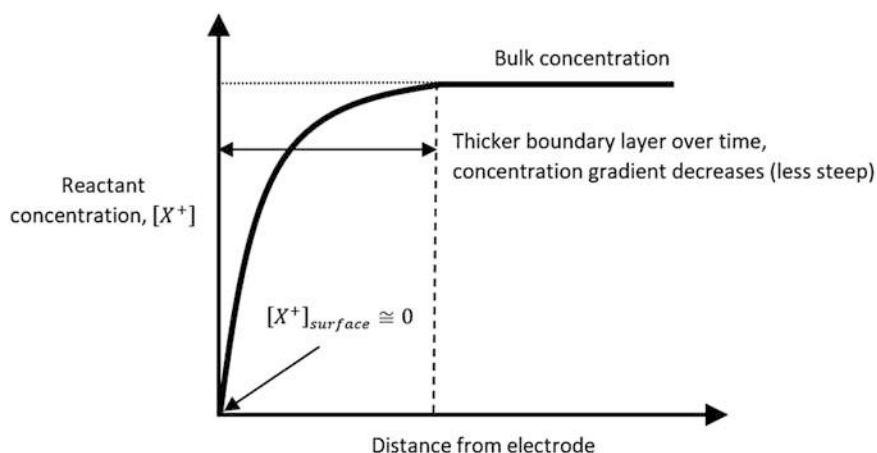
Early Part of Current Decay

At the beginning of stage C, diffusional flux is relatively high, as the concentration gradient that drives diffusion is steep (or large) across a thin boundary layer at the surface. This boundary layer is thin at early stages as it would not have had much time to grow.



Later Part of Current Decay

As time goes on, diffusional flux slows down, and becomes increasingly unable to catch up with the fast rate of consumption of reactant X^+ at the surface. This gives rise to an enlarging region near the electrode surface where X^+ is depleted. In other words, the diffusion boundary layer thickness grows with time.



Hence, we can see how the boundary layer grows with time, and the concentration gradient that drives diffusional flux of X^+ to the surface also decreases over a thicker layer. As less X^+ is available at the surface to be reduced, current output decreases with time.

Modelling the Current Decay

We can express the current decay in stage C as a function of time by solving the mass transport equation and relating it to current.

For a one-dimensional system where distance x is measured from the surface of a large planar electrode and \mathcal{D} refers to the diffusivity of reactant species X^+ , the starting equation that describes diffusion of X^+ for our system is as follows.

$$\frac{\partial[X^+]}{\partial t} = \mathcal{D} \frac{\partial^2[X^+]}{\partial x^2}$$

By relating the solution of the mass transport equation to current, it has been shown by Cottrell that current varies with time according to the following.

$$i_c = - \frac{nFA[X^+]_{bulk} \mathcal{D}^{1/2}}{\pi^{1/2} t^{1/2}}$$

The key takeaway from this correlation is the time dependence of current decay, $|i| \sim t^{-1/2}$. The plot of $|i|$ against $t^{-1/2}$ should be a straight line with a constant gradient if diffusion (mass transfer effect) was limiting electron transfer reactions at the electrode surface. This plot is useful in examining various diffusion characteristics, such as species with different diffusivities etc.

Problem 12

The Cottrell Equation as shown below may be used to determine the pH of a test solution using voltammetric methods. In the equation below, C_B represents bulk concentration of protons.

$$i = \frac{nFAC_B\sqrt{D}}{\sqrt{\pi}\sqrt{t}}$$

The following data were obtained from a potential step experiment at room temperature, using a circular disc electrode measuring 2.5 cm in diameter. The electrolyte solution contains an unknown proton concentration in a stagnant background electrolyte of 0.1 M NaCl.

Current [A]	-5.4×10^{-4}	-4.3×10^{-4}	-3.2×10^{-4}	-2.1×10^{-4}	-1.4×10^{-4}
Time [s]	0.22	0.34	0.72	1.72	3.72

Given that the diffusion coefficient of protons is $9.2 \times 10^{-5} \text{ cm}^2/\text{s}$, and that the protons participate in single electron transfer reactions at the electrode, find the pH of the test solution, stating any other key assumptions you have made in your calculations.

Solution 12

The Cottrell equation is useful in analyzing the current decay typically observed in a potential step experiment.

$$i = \frac{nFAC_B\sqrt{D}}{\sqrt{\pi}\sqrt{t}}$$

Note that the values of current are negative in the data provided as they represent cathodic current, which arises when the protons in the solution are reduced at the electrode.

To find pH, we need to determine the proton concentration, C_B in Cottrell's equation. To do so, we can use the given data values to plot a graph of i against $t^{-1/2}$. This gives us a straight line passing through the origin, with a constant gradient equivalent to $nFAC_B D^{1/2} \pi^{-1/2}$.

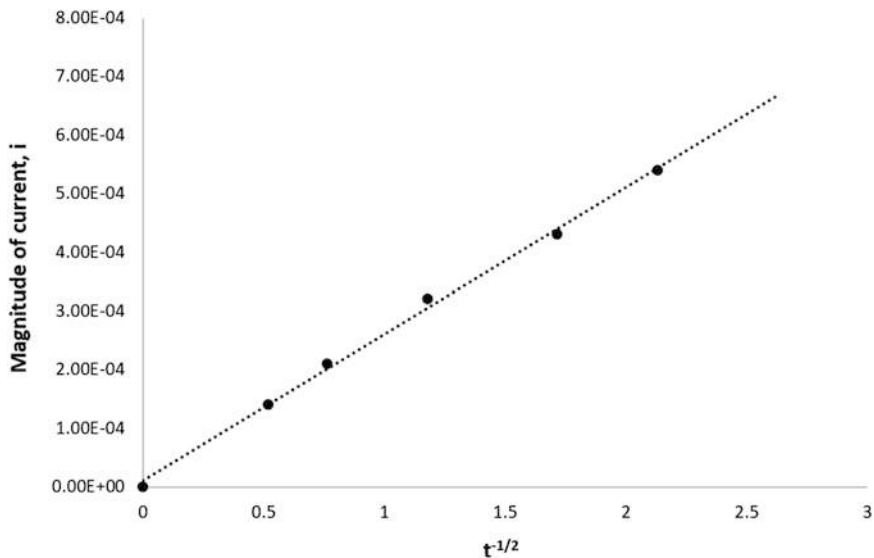
$$i = \frac{nFAC_B\sqrt{D}}{\sqrt{\pi}\sqrt{t}} = \left(nFAC_B D^{1/2} \pi^{-1/2}\right) t^{-1/2}$$

From our plot, we can find gradient and hence determine C_B , since the other parameters (i.e. n , F , A and D) are constants of known values.

The table below shows the calculated values of $t^{-1/2}$ from the data given. Units of the quantities are indicated in square brackets.

$ i $ [A]	5.4×10^{-4}	4.3×10^{-4}	3.2×10^{-4}	2.1×10^{-4}	1.4×10^{-4}
t [s]	0.22	0.34	0.72	1.72	3.72
$t^{-1/2}$ [$\text{s}^{-1/2}$]	2.13	1.71	1.18	0.762	0.518

We can now use the values of $|i|$ and $t^{-1/2}$ to plot the straight line graph below.



From the line of best fit passing through the origin, we find the gradient to be approximately equal to 0.00025. Therefore, we have

$$nFAC_B D^{1/2} \pi^{-1/2} = 0.00025$$

We can determine the values of the other parameters using information given in the problem and some simple calculations.

$$n = 1 \text{ (single electron transfer reaction)}$$

$$F = 96500 \text{ C mol}^{-1}$$

$$A = \frac{\pi D^2}{4} = \frac{\pi (2.5)^2}{4} = 4.9 \text{ cm}^2$$

$$D = 9.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$$

Substituting the above values into our gradient expression, the proton concentration can be found as follows.

$$(1)(96500)(4.9)C_B(9.2 \times 10^{-5})^{1/2} \pi^{-1/2} = 0.00025$$

$$C_B = 9.8 \times 10^{-8} \text{ mol cm}^{-3}$$

$$C_B = 9.8 \times 10^{-5} \text{ mol dm}^{-3}$$

pH can finally be determined using the relationship between proton concentration and pH as shown below.

$$\text{pH} = -\log_{10}(C_{H^+}) = -\log_{10}(9.8 \times 10^{-5}) = 4$$

The key assumption made in this calculation is that the current produced was only contributed by the reduction of protons in solution. This means that the initial state is assumed to have no current flow, while the final state is when proton electrolysis is complete.

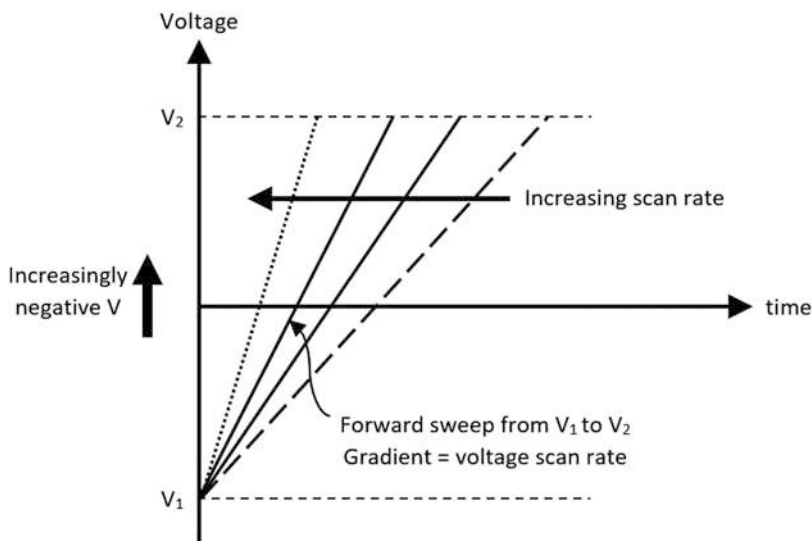
Problem 13

Describe how linear sweep voltammetry is conducted and the expected current response at the cathode.

Show on suitable plots how voltage scan rate affects current response, and how this response changes from reversible to quasi-reversible to irreversible electron transfer rates at the cathode.

Solution 13

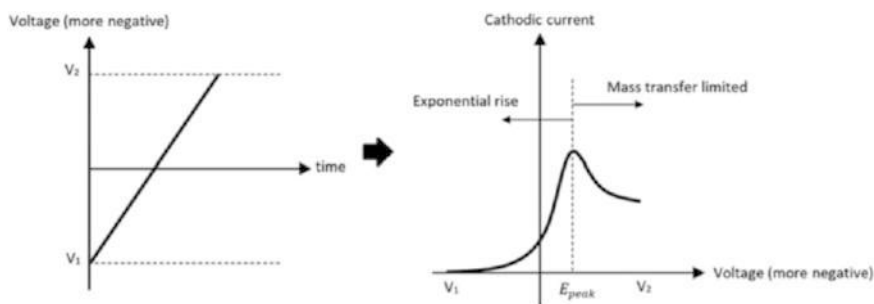
In linear sweep voltammetry (LSV), the applied voltage at the electrode varies at a constant rate from an initial value to a final value as shown by the sloped lines in the diagram below. The final potential thermodynamically favors the particular redox reaction at the electrode such that current is produced as voltage is swept along from its initial to final value.



Assuming reduction reaction occurs at the electrode with the voltage sweep, we will record a cathodic current. The linear sweep causes reactant species to be reduced at the cathodic electrode, resulting in charge transfer and hence a current output.

The lower limit V_1 of the sweep will be a less reducing potential and hence be a less negative value while the higher limit V_2 will be a more reducing potential and hence be a more negative value. The linear variation of voltage gives rise to straight line plots in a voltage against time graph, where the gradient of the lines is known as the voltage scan rate, v . As v increases, the sloped lines in the diagram above become steeper due to a larger gradient.

In voltammetry, we analyze current response to an applied voltage. For LSV, the current produced is shown below.

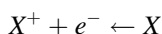


Current Response to Applied Voltage

Let us use an arbitrary example consisting of the reduction reaction of species X^+ to X . The starting electrolyte solution may be assumed to contain only X^+ , the reactant for reduction at the cathode which produces current.

Why Is There a Current?

The linear sweep or “scan” starts from the left at V_1 where there is no current. This means that no reduction occurs at the electrode as the potential V_1 is not sufficiently negative (or not reductive enough) to drive the reduction reaction (shown below) to the right. There is no conversion of reactant to product.



Current starts to flow when the applied potential is swept to the right, i.e. potential at the cathode becomes more negative (or more reductive) than V_1 . This causes X^+ to

become thermodynamically favored to be reduced to X as the applied negative potential provides electrons to X^+ , converting it to X , the product of the reduction reaction. It is this reduction reaction that gives rise to current at the cathode.

Why Does Current Increase?

Kinetics

As applied potential is swept to more negative potentials, a greater electric field is created which draws positively charged X^+ ions more rapidly to the electrode surface. Since current is related to rate of flow of charge (or electrons), with a greater supply of X^+ to the surface, $[X^+]$ increases, and the rate of reduction reaction r_{red} also increases as shown by the rate law equation below.

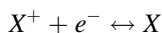
$$X^+ + e^- \xrightarrow{k_{red}} X$$

$$r_{red} = -\frac{d[X^+]}{dt} = k_{red}[X^+]$$

The higher rate of reduction causes a larger flow of electrons at the cathode, hence contributing to the rising current.

Thermodynamics

The potential sweep affects the redox reaction equilibrium at the cathode surface. Note that the reduction reaction at the cathode is reversible.



Assuming that electron transfer rate is much faster than voltage scan rate, then equilibrium will be established quickly at the surface at each potential value across the sweep. The equilibrium concentrations of reactant X^+ and product X correlate to the applied potential value E according to the Nernst equation as shown below. [E^0 refers to the standard potential]

$$E = E^0 - \frac{RT}{nF} \ln \frac{[X]}{[X^+]}$$

When the applied potential is swept from V_1 to V_2 , the value of E becomes more negative. From the equation, we see that this is possible as reduction becomes more thermodynamically favored, and $[X]$ increases while $[X^+]$ decreases. In other words, the equilibrium position of the reversible reaction proceeds more to the right to favor

reduction as applied potential is swept to more negative (or reductive) values. When the reduction reaction is favored, current increases as it reflects the greater extent of electron transfer at the electrode surface.

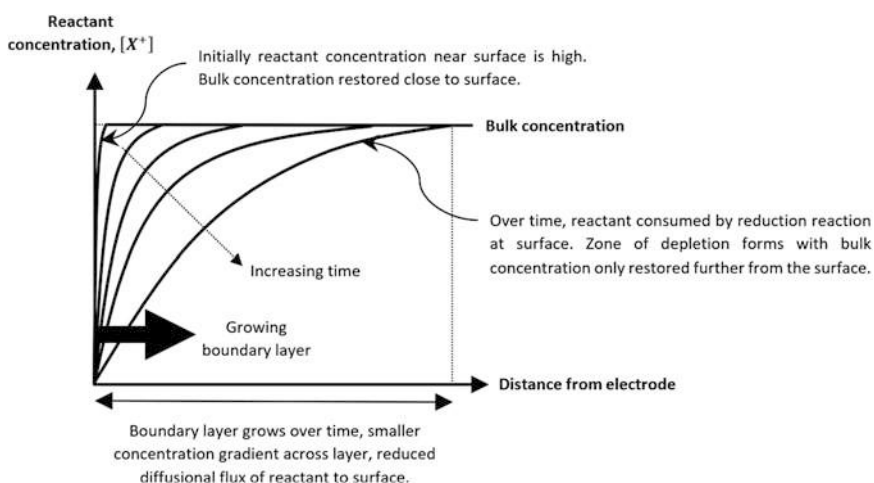
Why Does Current Decline After Reaching a Peak?

Current would keep increasing as we sweep to more negative potentials if we had an unlimited supply of reactant X^+ at the surface. However, this is rarely the case in reality since X^+ at the surface gets depleted by the reduction reactions faster than it can be replenished via diffusion from bulk solution to the surface.

This zone of depletion also enlarges with time as more and reactant gets depleted faster than can be replenished. This zone is also known as the diffusion boundary layer, across which a concentration gradient drives the diffusional flux of reactant from bulk solution to the surface.

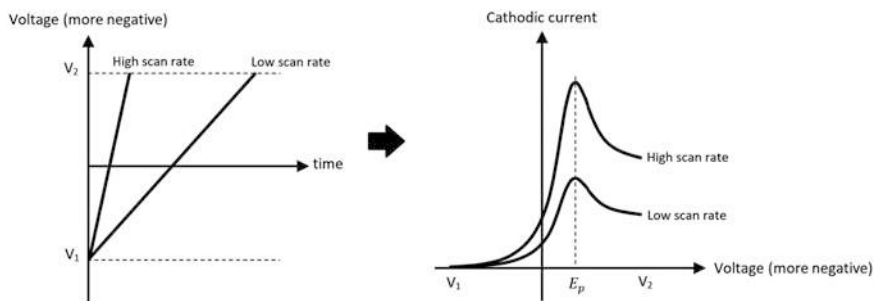
With the *growing thickness of the diffusion boundary layer*, the concentration gradient across it decreases since the same concentration difference ($= [X^+]_{bulk} - [X^+]_{surface}$) now spans over a greater thickness between $[X^+]_{surface} = 0$ at the surface and a high value of $[X^+]_{bulk}$ in the bulk solution.

With a decreasing concentration gradient, the diffusional flux of reactant to the surface also decreases, and this contributes to the reduced rate of reactions at the surface and hence reduced current over time.



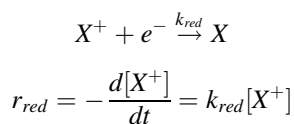
Effect of Varying Scan Rate

The voltage scan rate affects how long it takes to record the scan. At a **lower scan rate**, we will take longer to record the scan and indirectly allow **more time for the diffusion boundary layer to grow**. A thicker boundary layer gives rise to a **reduced concentration gradient** of reactant from bulk to surface, and a reduced diffusive flux of reactant to the surface. This then means a **reduced rate of reduction reactions** at the surface and ultimately leads to **reduced current**.



Reversible Electron Kinetics

Recall the reduction reaction and its associated rate constant k_{red} .



Rapid electron transfer reactions whereby k_{red} is large are also referred to as **reversible** electron transfer reactions. Assuming electron transfer reactions are rapid as compared to the range of scan rates used, then for each scan rate, the potentials E_p at which peak currents occur are fixed.

Quasi-Reversible and Irreversible Electron Kinetics

Reversibility requires that electron transfer reactions are fast enough to maintain the surface concentrations of redox species (e.g. X^+/X) at their equilibrium values as defined by the Nernst equation. Hence, reversibility depends on the electron transfer rate constant (k_{red}).

If k_{red} is small such that Nernstian equilibrium concentrations cannot be maintained, then the system is **quasi-reversible**. As the value of k_{red} decreases further, electron transfer rates become so slow that the reaction may then be referred to as **irreversible**.

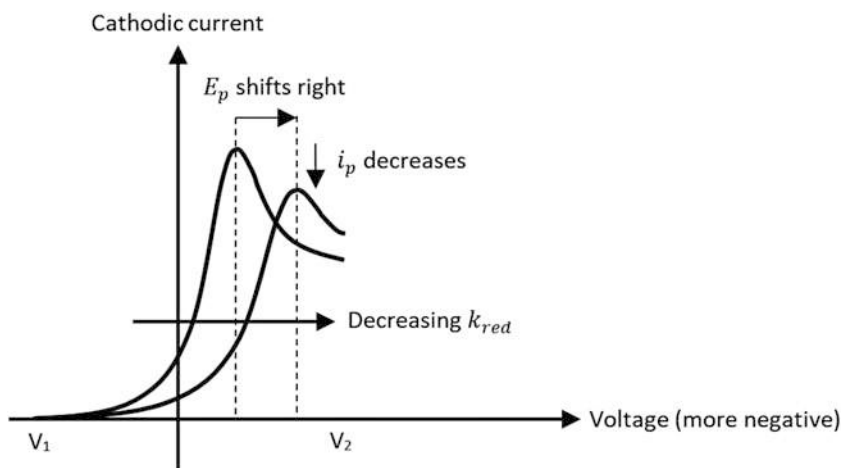
Key Features of Current Response

- Peak current occurs later in the sweep. Graphically, the peak position shifts to the right since more negative potentials are required to raise current to its peak.

Slower electron kinetics means equilibrium is not established fast enough at the electrode and the current response is slowed down. This means peak current appears later in the scan (than in the reversible case), which means peak current is shifted to the right.

- Peak current decreases (relative to reversible) as the extent of reversibility reduces.

The value of peak current is reduced with slower electron kinetics since a smaller amount of electrons is transferred per unit time at the electrode surface.



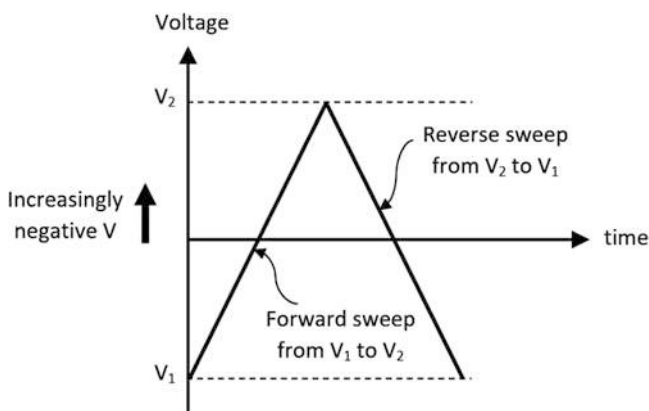
Problem 14

Describe how cyclic voltammetry is conducted and the expected current response at the cathode.

Show on suitable plots how voltage scan rate affects the current response, and how this response changes from reversible to quasi-reversible/irreversible electron transfer rates at the cathode.

Solution 14

Cyclic voltammetry is an extension from linear sweep voltammetry, whereby we combine two linear sweeps such that the second linear sweep is the reverse of the first as shown below. The current response is a combination of the responses from the two linear sweeps in succession. As shown in the diagram below, the final value of current V_2 after the first sweep becomes the starting value of current for the second or reverse sweep.

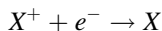
**Current Response for Reversible Electron Transfer**

The overall current response can be analyzed in two parts, the forward sweep and reverse sweep respectively.

Forward Sweep

- Initial current rise

During the forward sweep, **current initially rises** due to the increasingly reductive potential that drives reduction reactions at the cathode. Assuming a species X^+ that becomes reduced to X , we have the following reaction increasingly favored at the cathode as the potential sweeps to more negative values away from V_1 .



Since electron transfer rate is fast for reversible reactions, current responds rapidly (almost instantaneously) to the voltage sweep and reflects an increasing value as potential becomes more reductive.

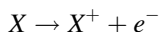
- Subsequent current drop

Cathodic current does not rise indefinitely. Instead, it reaches a peak at $i_{p, \text{cathode}}$ and declines after. This occurs when reactant X^+ becomes sufficiently depleted at the electrode surface such that it cannot satisfy the consumption rate by the rapid electron transfer reaction at equilibrium. Reactant X^+ is also not replenished fast enough due to the slow diffusional flux of X^+ to the surface from bulk solution.

A peak represents a transition point between two phases with opposing effects. Therefore, peak current occurs just after an earlier phase when rapid electron transfer reactions have a dominating effect on current response and enhances its value, and just before a later phase when the relatively slower mass transfer rate becomes dominant and limits its value.

Reverse Sweep

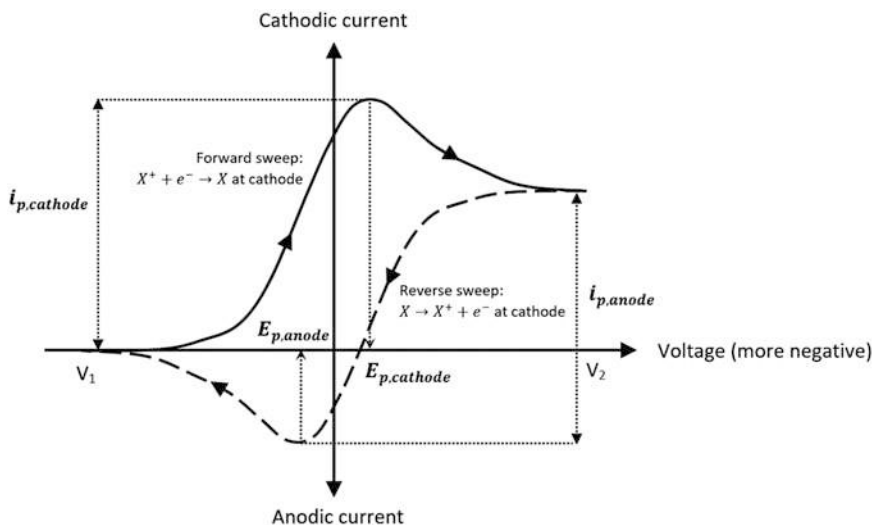
When the voltage sweep is subsequently reversed from V_2 , note that the starting value of current is non-zero (unlike in the forward sweep). The reverse sweep has an opposite effect as the forward sweep in the way it favors oxidation instead of reduction. At the cathode surface, X that was formed from the earlier forward sweep is now re-oxidized back to X^+ in the reverse sweep.



Since electrons are now produced instead of consumed at the same electrode surface, the direction of current will be reversed relative to the forward sweep, and graphically, we see this as a vertical flip of the current profile. We refer to the peak current in the reverse sweep as anodic, or $i_{p, \text{anode}}$ (which occurs at the anodic peak potential $E_{p, \text{anode}}$). Unlike the cathode where electrons are consumed for reduction, electrons are produced by oxidation reactions at the anode.

The same initial rise and subsequent drop in current now project in the opposite direction downwards on the same axes. The reasons for the variation in current (rise, peak then drop) in the reverse sweep is the same as that in the forward sweep, as the same factors of electron transfer rate and mass transfer rate are at play in the reverse sweep.

The overall current response for the forward and backward sweeps are shown in the diagram below, where the direction of the sweep is indicated by arrows.



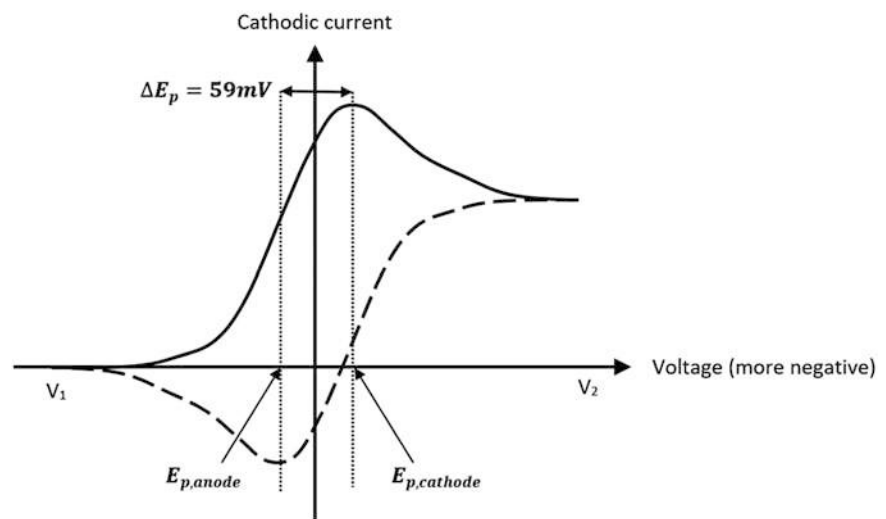
Reversible Electron Kinetics

Effects of Varying Scan Rate

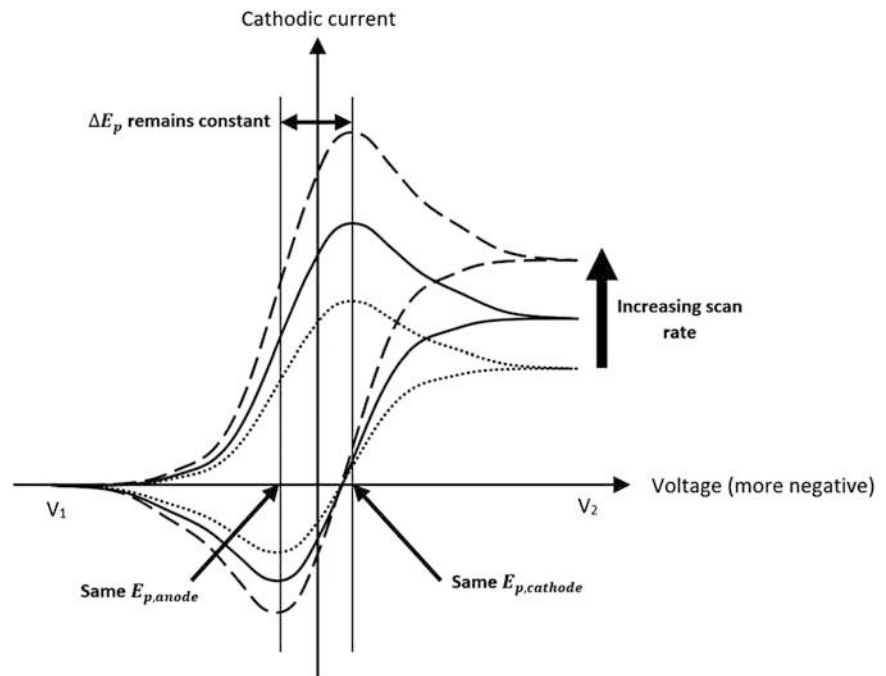
- **Constant ΔE_p regardless of scan rates**

The values of $E_{p, cathode}$ and $E_{p, anode}$ remain the same regardless of scan rate, therefore voltage separation $\Delta E_p = |E_{p, cathode} - E_{p, anode}|$ between current peaks also remains constant regardless of scan rates. This is true as long as electron transfer is reversible or fast. Assuming room temperature and standard conditions, then $\Delta E_p [mV] = 59/n$, where by n represents the number of moles of electrons transferred per redox reaction. For the example of X^+/X , $n = 1$.

Voltage separation is measured between peak current positions as shown in the diagram below.



As seen from the diagram below, voltage separation remains the same for different scan rates.



Special Note

In some cases, we may see that peak separation increases beyond 59 mV even for reversible electron kinetics. This is possible at sufficiently high scan rates. At high scan rates, (i) the diffusion boundary layer is thin as it does not have much time to grow. This makes mass transfer effects negligible and in turn makes the process dominated by electron transfer rate only. (ii) The fast rate at which applied potential is swept “forces” the redox reaction to happen in one specific direction (in the direction favored by the sweep direction) very rapidly, hence a “greater degree of irreversibility” which explains the increase in peak separation, as the redox reaction moves away from reversibility (constant peak separation at 59 mV) and tends towards more irreversibility (peak separation >59 mV). In cyclic voltammetry, the electrochemical process reflects the competition between the electrode reaction and diffusion/mass transfer effects. Scan rate is a way for us to control this interaction.

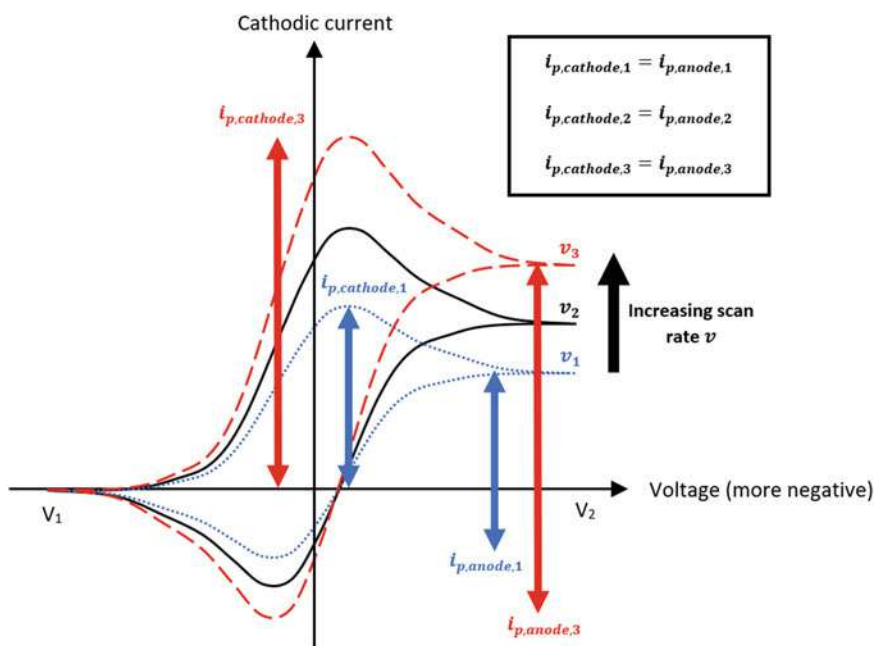
• $i_{p,forward} = i_{p,reverse}$, regardless of scan rate

The relative ratio of peak current magnitudes is equivalent to 1, regardless of scan rate. In other words, the magnitudes of peak cathodic and anodic currents are always equivalent at a particular scan rate.

$$|i_{p,cathode}| = |i_{p,anode}|$$

$$\frac{|i_{p,cathode}|}{|i_{p,anode}|} = 1$$

This can be shown in the current response curve as follows.



Peak Currents Increase with Increasing Scan Rate

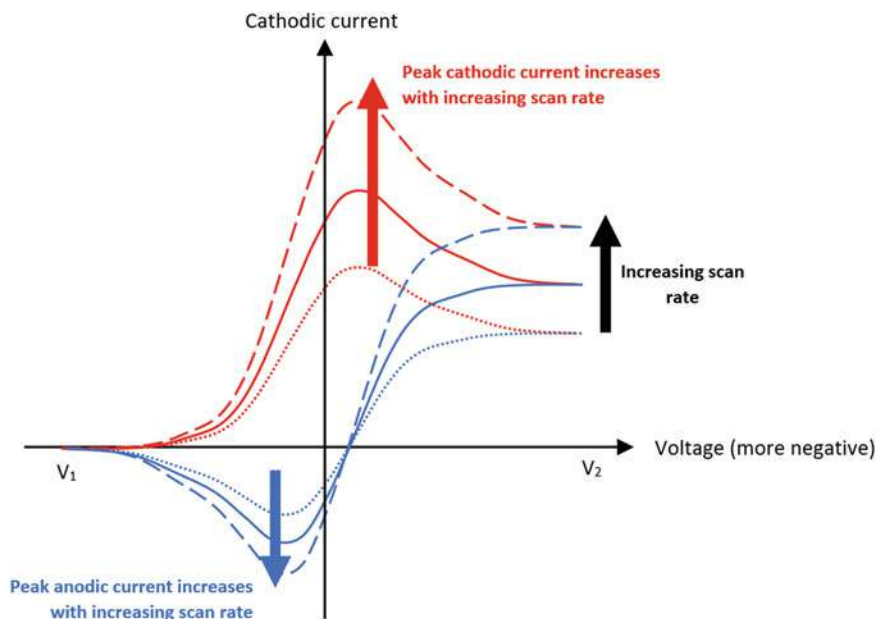
Unlike the earlier two features, current varies with scan rate. In general, the current values generally increase with increasing scan rate v , and only for reversible (and irreversible, but not quasi-reversible) electron transfer kinetics, the peak current and scan rate vary according to $i_p \sqrt{v}$.

Fast Scan Rate

If scan rate was fast, the time taken to record current response will consequently be shorter. With a shorter timeframe, there is less time for mass transfer effects to set in since there is less time for the diffusion boundary layer to grow sufficiently to reduce current.

Slow Scan Rate

At low scan rates, the time taken for the scan will be long. The diffusion boundary layer has sufficient time within this longer timeframe to grow to a significant thickness at the electrode surface. This reduces the diffusive flux of reactant to the surface, which hinders redox reactions and reduces current. Peak current fails to reach a higher value when mass transfer effects are given time to set in. As the boundary layer thickens with time, diffusive flux is even more hindered with time, and current continues to decline with time.



Non-Reversible Electron Kinetics (Quasi-Reversible/Irreversible)

We can move from a reversible process to quasi-reversible and then to irreversible by decreasing the rate constant for electron transfer reactions at the electrode.

The quasi-reversible process is intermediate between reversible and irreversible processes. Like in the reversible case, the current response for quasi-reversible systems is still controlled by both electron transfer rate (but slower than in the reversible case) and mass transfer rate.

However, for irreversible systems, the **reverse redox reaction driven by the reverse sweep does not occur** as the reaction can be thought of as one-way only. The current response for irreversible processes is controlled only by electron transfer rate, and the Nernst equation which relates to very rapid electron transfer reactions is not applicable for irreversible processes.

Let us examine some of the key changes to the cyclic voltammogram when electron transfer becomes quasi-reversible/irreversible.

Quasi-Reversible Electron Kinetics

- Peak separation, $\Delta E_p > 59/n$

This process has characteristics of both reversible and irreversible processes. Compared to the reversible case, we note that the cathodic peak current in forward scan is shifted right, while the anodic current peak in the reverse scan shifts left. This gives rise to a voltage separation between the two peaks, $\Delta E_p [mV] > 59/n$. This voltage separation will increase further if we reduce the ratio k_{red}/v .

Since it is more thermodynamically difficult for quasi-reversible reactions to reach equilibrium as compared to reversible reactions, the peaks take longer to appear and hence occur later in the scan for each direction of sweep. Hence the forward peak is shifted right while the reverse peak is shifted left. This eventually leads to the increased voltage separation between the peaks.

- Reduced peak values (compared to reversible)

The value of peak currents are reduced as compared to the reversible process since electron transfer rates are slower hence current response is lagged. A “lagged” rise in current allows mass transfer effects to kick in and act to reduce current earlier and before its value is able to rise to the original higher peak value as seen in the reversible case.

- Different magnitudes of peak currents

The forward sweep registers a higher current peak (cathodic current in this example) than that of the reverse peak (anodic peak), i.e. $i_{p, cathode}$ and $i_{p, anode}$ and are no longer equivalent like in the reversible case. In fact, $i_{p, cathode}$ in the forward scan $> i_{p, anode}$ in the reverse scan. The smaller reverse peak can be explained by looking at the species that is being reacted in the reverse scan. In the reverse scan

for a quasi-irreversible/irreversible process, the backward reaction of the redox couple does not occur as readily as the forward reaction in the forward scan. Therefore, current output and hence peak value drops to reflect this.

Irreversible Electron Kinetics

- No reverse peak current (voltage separation, ΔE_p not applicable)

Since none of the species X produced from the forward scan can be re-oxidized back to X^+ in an irreversible process (unidirectional in the forward direction), the reverse sweep does not reflect anodic current which represents the oxidation process. This also means no anodic peak current is observed.

In the reverse sweep, the cathodic current reduces in value as potential is swept in the reverse direction towards less reductive values (less negative values) which does not favor reduction, and current eventually drops to a final value of zero when no further reactions occur.

- Forward peak is shifted right (relative to quasi-reversible)

For quasi-reversible cases, we note that voltage separation increases in magnitude as we reduce k_{red} since the forward peak shifts right and the reverse peak shifts left. Irreversible reactions have only one peak in the forward scan, and this peak is expected to be further shifted right relative to the quasi-reversible case since irreversible processes are just an extreme case of quasi-reversible processes with a very much smaller value of k_{red} .

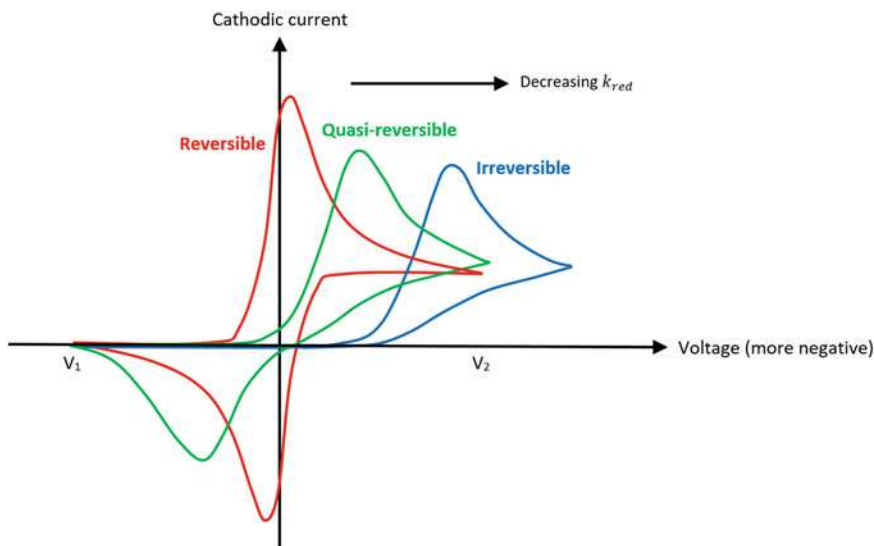
In some cases, the forward peak may be so much shifted to the right that it may not be captured within the sweep (e.g. if V_2 is not large enough) and the voltammogram appears “cut-off” when compared on the same diagram as the reversible or quasi-reversible cases.

- Reduced forward peak value (relative to quasi-reversible)

The further reduced peak for irreversible reactions as compared to quasi-reversible reactions is due to the same reason that explains the smaller peak in quasi-reversible reactions when compared to reversible reactions.

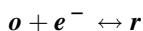
The severely lagged current response due to very slow electron transfer rates in the irreversible process means that mass transfer limitations take effect earlier and reduce current before its value is able to rise to the higher peaks seen in quasi-reversible and reversible processes.

The effect of electron transfer kinetics (quasi-reversible/irreversible) are summarized in the voltammogram as shown below.



Problem 15

Cyclic voltammetry was conducted for a reversible redox reaction as shown below where species o is reduced to form r .



The Nernst equation which describes electron transfer reactions the electrode surface is given as shown.

$$E = E^0 - \frac{RT}{nF} \ln \frac{[r]}{[o]}$$

Explain how an approximate value of E^0 can be obtained experimentally.

Solution 15

In the cyclic voltammogram for a reversible redox couple $o + e^- \leftrightarrow r$ whereby the forward scan goes towards more negative potentials favoring reduction and a cathodic current response is measured.

For a single-electron ($n = 1$) reversible reaction, we expect the distance between the cathodic peak in the forward scan and the anodic peak in the backward scan to be constant at 59 mV.

In order to approximate the standard state potential E^0 , we can find the point where the concentrations of r and o are equal, which simplifies the Nernst equation

as shown below since $\ln(1) = 0$. Assuming room temperature and conditions, we have

$$E = E^0 - \frac{8.314(298)}{1(96500)} \ln \frac{[r]}{[o]}$$

$$E = E^0 - 0.02568 \ln \frac{[r]}{[o]}$$

$$E|_{[r]=[o]} \cong E^0$$

Special Note

Note that the experimentally determined value of E when $[r] = [o]$ is not exactly identical to the theoretical standard state potential E^0 , but nonetheless offers a good approximation of it. To differentiate between the two, we refer to $E|_{[r]=[o]}$ as “formal potential” which may depend on experimental conditions.

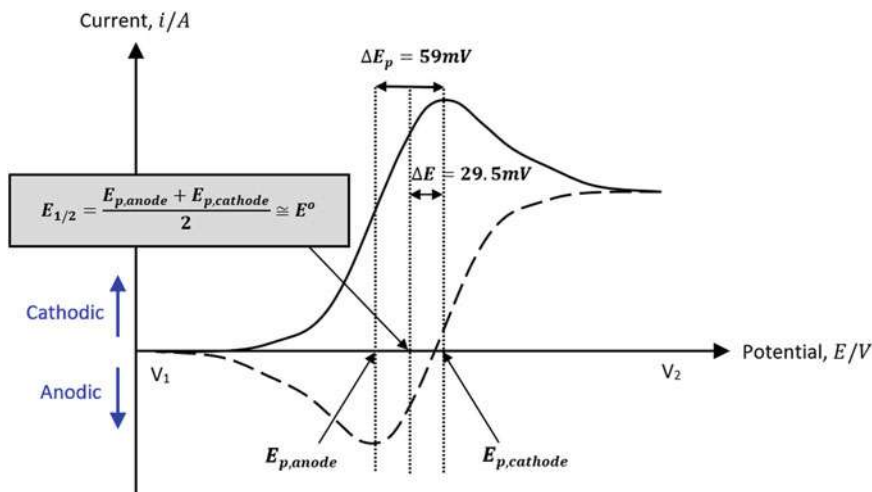
We are able to easily determine the value of $E|_{[r]=[o]}$ from a cyclic voltammogram as it occurs at the point when oxidized and reduced species are in approximately equal concentrations, and this corresponds to the potential value about halfway between the two current peaks (also called the half-wave potential $E_{1/2}$).

$E_{1/2}$ is a convenient estimate of formal potential (and hence standard state potential E^0) for reversible electron kinetics. Therefore, we have,

$$E^0 \cong E|_{[r]=[o]} = E_{1/2} = \frac{E_{p,anode} + E_{p,cathode}}{2}$$

At $E_{1/2}$ or the approximate standard state potential, the magnitudes of the anodic and cathodic currents are very close, and its value is close to one half of its limiting value.

Note that the term “half-wave potential or $E_{1/2}$ ” is general and can be used for both reversible and irreversible kinetics. It simply refers to the potential in the middle of the two current peaks. The difference between reversible and irreversible kinetics however is that for reversible kinetics, the distance between the current peaks is constant at 59 mV (for single electron transfer, $n = 1$), and so $E_{1/2}$ always occurs a distance of about 29.5 mV from each of the two peaks. For irreversible kinetics, the distance of $E_{1/2}$ from the current peaks vary according to the extent of irreversibility. The more irreversible, the greater the distance between the two current peaks and hence the distance of $E_{1/2}$ from each peak.



Special Note About Half-Wave Potentials

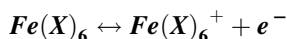
The approximation of standard state potential E^0 using the half-wave potential $E_{1/2}$ for reversible kinetics is a reasonable one as long as the **diffusion coefficients D** of both the reduced and oxidized species (i.e. o and r) are similar and they move at similar speeds in solution. This is because $E_{1/2}$ also relates to the diffusion coefficients of the species as follows

$$E_{1/2} = E^0 - \frac{RT}{F} \ln \left[\left(\frac{D_o}{D_r} \right)^{1/2} \right]$$

The half-wave potential is therefore independent of the concentration of the species. It reflects the characteristic of a particular species in a particular electrolyte solution. By measuring the half-wave potential, we are able to probe the identity of the species responsible for a particular voltammetric response.

Problem 16

An iron-based complex $Fe(X)_6$ undergoes a reversible single electron-transfer reaction as shown below.



The complex is chemically bound to the surface of a large planar working electrode immersed in a stagnant solution of conducting electrolyte with no free $Fe(X)_6$ present in solution.

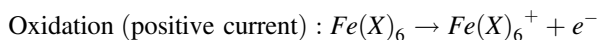
- (a) **Sketch the current response expected for a cyclic voltammetric measurement for this system and explain how voltage scan rate would affect this current response.**
- (b) **Discuss how other factors may cause the current response in part a to vary.**

Solution 16

(a) In this problem, we note that the electrochemically active species, $Fe(X)_6$ is not present in free solution and is only present at the electrode surface.

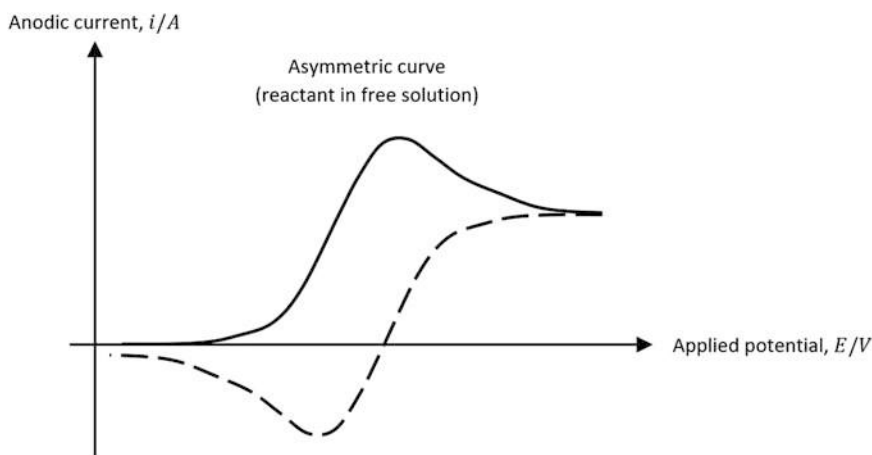
Forward Sweep

When voltage is swept to increasingly positive potential values, oxidation is favored and all the $Fe(X)_6$ attached to the electrode surface will be rapidly oxidized to $Fe(X)_6^+$, giving rise to an observed anodic current.



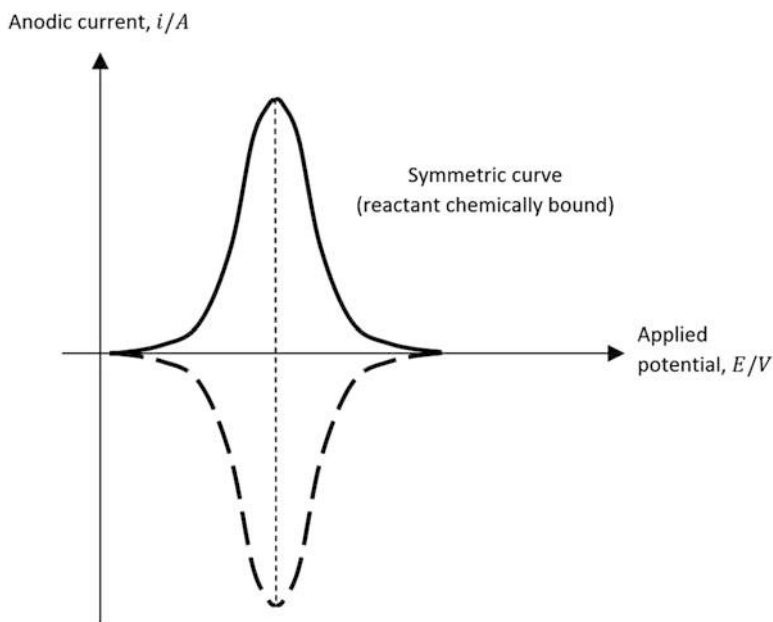
Current value peaks at a maximum value, then subsequently drops to zero when all the $Fe(X)_6$ has been completely oxidized.

In a system where $Fe(X)_6$ is **present in free solution** (which is not the case in this problem), a fresh supply of reactant $Fe(X)_6$ will need to be transported to the electrode surface via diffusion from the bulk solution, in order to sustain oxidative electron transfer reactions at the electrode, and produce current. In this scenario, we expect to see the typical asymmetric current curve as shown below, where such mass transfer effects are present.



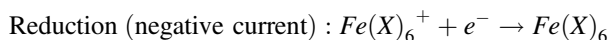
However, in this problem, since all the reactant $Fe(X)_6$ is **chemically bound** to the electrode surface, they are all **already available** at the surface for reaction. This effectively removes any influence of mass transfer on current response, giving rise to a symmetric current curve instead. Current rises and drops similarly quickly as $Fe(X)_6^+$ becomes oxidized to $Fe(X)_6$ until no more $Fe(X)_6^+$ is present in the forward direction, and $Fe(X)_6$ is reduced back to $Fe(X)_6^+$ until no more $Fe(X)_6$ is present in the reverse direction.

Since the current output simply reflects the rapid and reversible electron transfer kinetics, with no limitations by mass transfer effects, peak current reached is high and occurs early in the sweep. This is as shown below.



Reverse Sweep

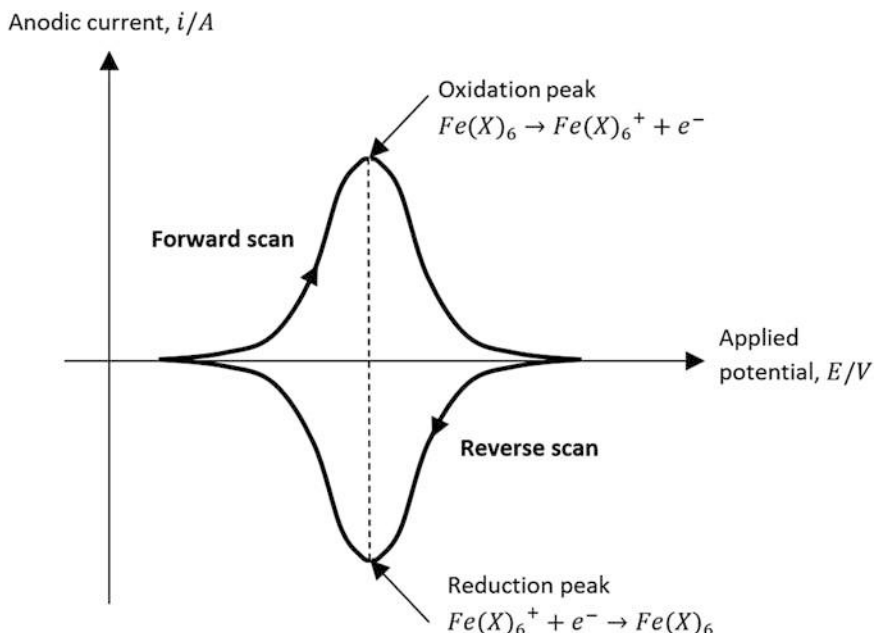
During the reverse sweep, the oxidized product $Fe(X)_6^+$ formed from the earlier forward sweep will now be reduced back to $Fe(X)_6$.



As mentioned earlier, the reverse sweep current response is symmetric and completely mirrors that of the forward sweep about the horizontal axis. The reverse

peak has the same height and position (i.e. $E_{p, \text{oxi}} = E_{p, \text{red}}$ or $\Delta E_p = 0$) as the oxidation peak for a reversible single electron transfer reaction.

The overall current response for both the forward and reverse sweeps is shown below.



(b)

There are other factors that may influence the shape of the current response in part a.

- If the species does not remain adsorbed (or chemically bound) or begins to gradually desorb from the electrode surface, the height of the current peaks will decrease since the availability of reactant for the electron transfer reactions at the electrode start to become limited by diffusion effects (mass transfer rate of reactant from bulk solution to electrode surface).
 - It is possible to study the rate of desorption by varying voltage scan rate and observing how the current response changes.
 - A high rate of desorption would give rise to a much reduced peak current, which will be more apparent especially at medium to low scan rates. Conversely if desorption rate was slow, then the reduction in peak current peak would be less, and probably only becomes more apparent at very low scan rates.
- If the electrode surface had multiple adsorption sites for different electrochemically active species with different oxidation potentials, then multiple current peaks would be observed.

- The area under the current curve is representative of the amount of charge arising from the electron transfer reactions and is therefore also indicative of the amount of electrochemical active species adsorbed on the electrode surface.

Problem 17

Microelectrodes are often used for electrolysis measurements in biosensors such as glucose sensors.

- Explain the advantages of using microelectrodes compared to a macroelectrode sensors for such devices.**
- The following data shows the measured current (mass transfer limited) obtained from a glucose sensor using a microelectrode with an area of 0.004 cm^2 in an electrolyte solution containing $4.5 \times 10^{-7} \text{ mol/dm}^3$ enzyme. C refers to the bulk concentration of the electron acceptor in the redox reaction at the electrode surface.**

$C/\text{mol/dm}^3$	1	2	3	4	5
i/nA	0.23	0.46	0.69	0.92	1.13

nA refers to nano-Ampere

The diffusion coefficient D of the electron acceptor is $2 \times 10^{-6} \text{ cm}^2/\text{s}$ and the enzymatic catalysis is known to be second order with a rate constant k . State any assumptions made in your calculations and calculate the rate constant k , stating its units.

Solution 17

- The advantages of microscale electrodes are as follows:
 - Easy to use as they are inexpensive and often disposable.
 - Small sample volume required.
 - Low cost due to small size of electrode.
 - Able to reach steady-state voltammetry easily, which ensures stable and consistent readings.
 - Faster response time.
 - Clear readings obtained due to the small size, hence higher current density and higher signal-to-noise ratio.
 - Small currents associated with microelectrodes reduces complications from ohmic resistance and capacitive charging effects which may distort readings at high currents.
 - Simplifies electronic control requirements since smaller currents are involved.
- Assumptions

The enzyme glucose oxidase which catalyzes the oxidation of glucose is assumed to be at **maximum turnover rate**, i.e. the oxidation of glucose occurs at the maximum rate and the enzymes are saturated with the glucose substrate. This means that the enzymes are working at their maximum capacity constantly, and we therefore assume enzyme concentration to be constant at $4.5 \times 10^{-7} \text{ mol/dm}^3$. This allows us to correlate measured current directly to the concentration of

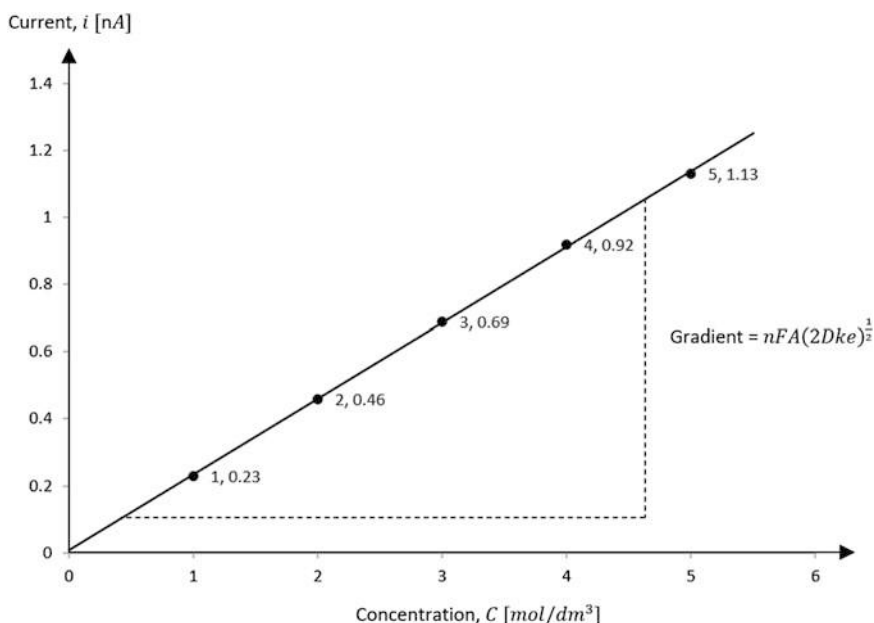
redox species at the electrode surface, and this concentration of redox species in turn relates to glucose concentration in the sample (since the oxidation of glucose drives the production of redox species, more glucose \rightarrow more redox reactions \rightarrow higher current).

Also assuming **second order Michaelis-Menten kinetics** for the enzymatic reaction, we can use the following expression which relates the limiting current i to the concentration of the electron acceptor C (the redox species participating in electron transfer reactions at the electrode)

$$i = nFAC(2Dke)^{\frac{1}{2}}$$

Using the data values provided for i and C , we can plot a graph of i against C which gives a line of best fit that passes through the origin.

$C/\text{mol/dm}^3$	1	2	3	4	5
i/nA	0.23	0.46	0.69	0.92	1.13



The resulting linear plot will have a gradient represented by the expression below, and from the plot, it can be found to be approximately equal to 0.226.

$$\text{Gradient} \left[n A / \text{mol dm}^{-3} \right] = \frac{\Delta i}{\Delta C} = nFA(2Dke)^{\frac{1}{2}} = 0.226$$

Changing the units of nano-Ampere into Ampere, and dm^3 into m^3 , we have

$$\text{Gradient} \left[A / \text{mol m}^{-3} \right] = \frac{0.226}{(10^{-9})(10^{-3})} = 0.226 \times 10^{-12}$$

In order to solve this problem, n in the expression for gradient which refers to the number of moles of reactant in solution needs to be defined, so we further assume that $n = 1$ for a **single electron transfer reaction**.

$$nFA(2Dke)^{\frac{1}{2}} = FA(2Dke)^{\frac{1}{2}} = 0.226 \times 10^{-12}$$

Given that $A = 0.004 \text{ cm}^2 = 0.004 \times 10^{-4} \text{ m}^2$, $e = 4.5 \times 10^{-7} \text{ mol/dm}^3 = 4.5 \times 10^{-10} \text{ mol/m}^3$ and $D = 2 \times 10^{-6} \text{ cm}^2/\text{s} = 2 \times 10^{-10} \text{ m}^2/\text{s}$, we can simplify the above expression to

$$(96500)(0.004 \times 10^{-4})(2 \times 2 \times 10^{-10} \times k \times 4.5 \times 10^{-10})^{\frac{1}{2}} = 0.226 \times 10^{-12}$$

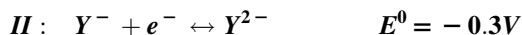
$$k = 1.9 \times 10^{-4} \text{ mol/m}^3/\text{s}$$

$$k = 1.9 \times 10^{-7} \text{ mol/dm}^3/\text{s}$$

Therefore the second order rate constant is found to be $1.9 \times 10^{-7} \text{ mol/dm}^3/\text{s}$.

Problem 18

An electrochemically active species Y is chemically tethered to an electrode surface, with no free Y present in electrolyte solution. It is known to undergo two different electron transfer reactions as shown below with the respective standard potentials indicated.

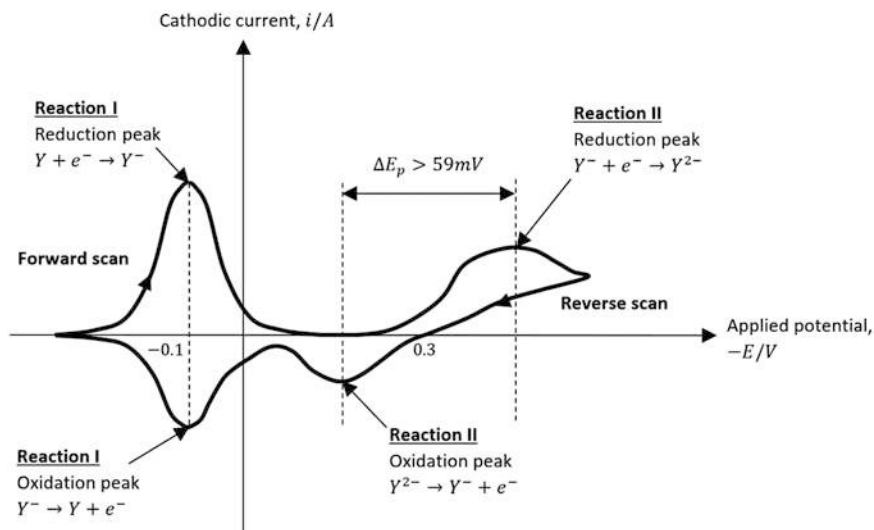


Reaction I follows reversible (Nernstian) electron transfer kinetics, while reaction II is irreversible.

Sketch the expected current output at the cathode for one cycle of a cyclic voltammetry conducted on the adsorbed species Y , assuming that the first forward sweep goes towards more reductive (or more negative) potentials. Explain any key features of the current response observed.

Solution 18

The expected current response is illustrated below.



For an adsorbed species that is not present in free solution, all the reactant is present and bound to the electrode surface, hence there is no limitation on the availability of reactant for redox reactions at the surface caused by slow diffusion from bulk solution.

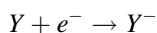
This gives rise to a cathodic current peak that occurs swiftly as voltage is swept to more reductive potentials, with the peak value at the standard reduction potential of the reaction.

After peak position, the current value declines symmetrically to zero, as the reactant species gets used up in the redox reaction and finally becomes completely depleted.

Forward Sweep

Reaction I

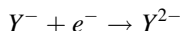
The reduction reaction of Reaction I occurs first since it has a less negative E^0 value, i.e. reduction occurs more easily. This gives rise to an increase in current until a peak value of $-E = -E^0 = -0.1V$ is reached.



As the forward sweep continues to more negative potentials, current then drops to zero from its peak. The current profile is noted to be symmetrical about $-0.1V$, which is characteristic of adsorbed species.

Reaction II

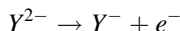
As the forward sweep continues further to more negative potentials away from $-E = -0.1V$, another current peak is observed near to $-E = -E^0 = +0.3V$ which corresponds to the reduction reaction for Reaction II.



However since this electron transfer reaction is irreversible and hence slower in comparison to Reaction I, the peak value is shifted slightly to the right (towards more negative potentials) from the standard potential value of $+0.3V$.

Reverse Sweep**Reaction II**

In the early part of the reverse sweep, the oxidation reaction of Reaction II would occur first, since it has a more oxidative potential (or less negative reduction potential) compared to Reaction I.



The species Y^{2-} formed from the earlier forward sweep is re-oxidized back to Y^- and a current peak is observed corresponding to this oxidation reaction. This peak occurs slightly to the left (less negative direction) of the standard potential value of $+0.3V$ for a similar reason as in the forward sweep due to the irreversibility of the reaction.

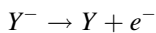
The magnitude of this peak would be lower compared to the forward peak from Reaction II since Reaction II is irreversible, therefore the oxidation reaction which is the backward direction of the redox couple occurs much less readily than the forward reduction reaction.

*This reverse peak would also not return to zero but would drop to a small non-zero value instead. This is due to the irreversible nature of Reaction II, which makes the reaction too slow to completely re-oxidize all of the Y^{2-} within the sweep.

Due to the irreversible nature of Reaction II, the peak separation between its forward and backward peaks will also be observed to be greater than (and not equal to) 59 mV .

Reaction I

As the reverse sweep proceeds further to even more oxidative potentials to the left, the oxidation reaction for Reaction I would occur, and current will rise to a peak when the applied potential reaches $-E = -0.1V$.



Like before in the forward sweep, due to the nature of the electroactive species being chemically adsorbed, the current profile would be largely symmetrical about the peak position (except for the right-hand end where it connects with the reverse peak for Reaction *II* at a small non-zero value – refer to * above). Furthermore, since Reaction *I* is reversible, the reverse peak would occur at the same position as the forward peak at the standard potential value, i.e. where $-E = -0.1V$.

The reverse peak height for Reaction *I* will be smaller than its forward peak as less reactant Y^- is now available for the oxidation reaction due to the irreversibility (i.e. slow rate of electron transfer) of Reaction *II*, which hinders the generation and supply of reactant Y^- for re-oxidation to Y .

Problem 19

Discuss the usefulness of microelectrodes as opposed to macroelectrodes in electrochemical applications.

Using suitable diagrams, highlight key differences in the current response expected for a microelectrode and macroelectrode respectively.

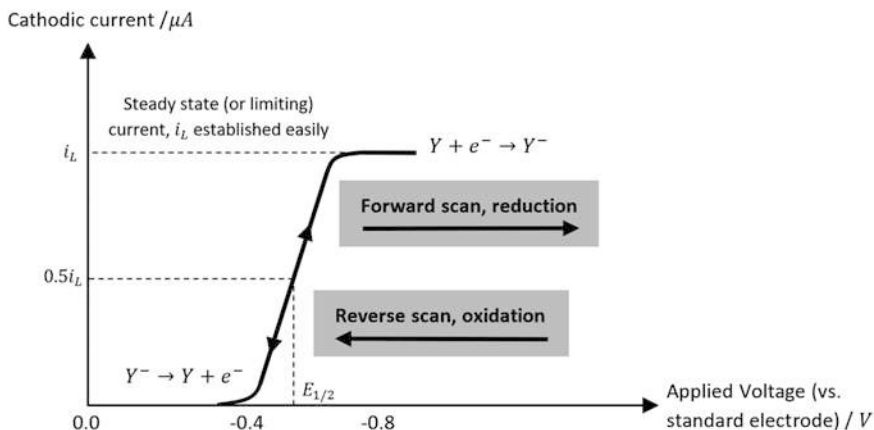
Solution 19

When the size of an electrode is reduced to a few millimeters or microns, the electrode is also known as a microelectrode or ultramicroelectrode. In general, a microelectrode has at least one dimension measuring no more than 50 microns.

The small size of microelectrodes enables specific applications such as in clinical research where in-vivo analysis can be conducted on small organs such as the brain. These electrodes can be used to stimulate or monitor the response of individual neurons, thus enabling greater insight into the workings of the central nervous system and related nervous pathways.

The key characteristics of the current response from a microelectrode are as follows:

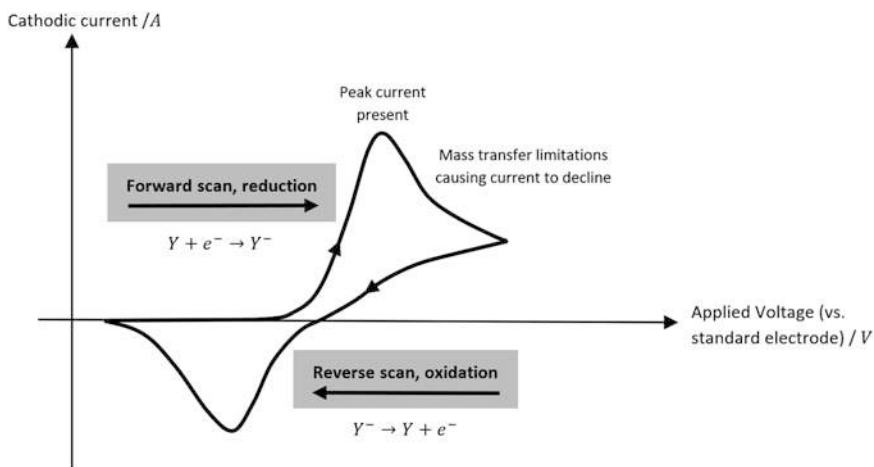
- A **steady state current** is obtained, unlike in a macroelectrode. As voltage is swept, a constant current is reached (**with no observed peak**) as shown in the voltammogram diagram below. The small size of microelectrodes allows steady state to be reached quickly, with minimal (or negligible) mass transfer effects limiting the current response. Hence a constant current can be maintained without the subsequent decline usually observed for macroelectrodes when current peaks are present.



- The midpoint between the limiting current and the starting position (zero current in this case) is marked as $E_{1/2}$, the half-wave potential that can often be approximated to the standard potential E^0 .
- The forward and reverse voltage sweeps (or scans) trace the same line as shown above in arrows.
- **Very rapid chemical kinetics** (i.e. rapid reactions/high rate constants) can be studied using microelectrodes due to their inherently fast response time. This also allows **higher scan rates (relative to macroelectrode)** to be used for microelectrodes without distorting the desired measurement to be made.
 - However, note that at **very high scan rates**, when mass transfer effects start to become significant even for a microelectrode, then current response will start to take the shape of that for a macroelectrode, with current peaks being observed.
- The **small currents** involved in microelectrodes (due to their small size) also **minimizes charging effects** that may affect the accuracy of readings.
- Microelectrodes **can operate at lower electrolyte concentrations**. Lower electrolyte concentrations make the electrolyte solution less conducting, and this poses greater resistance (greater “ohmic drop”) to current flow which is undesirable. However due to the very small currents involved in microelectrodes, the ohmic drop caused by lower electrolyte concentrations will likewise be small. This means current response would not be affected significantly and the steady-state current profile remains intact.
 - **Note that at lower electrolyte concentrations, current may be reduced** due to migratory transport effects. **Migratory transport** is an electrostatic effect that arises from the applied voltages on the electrodes.
 - A charged electrode can attract or repel charged species in the electrolyte solution, causing their migratory transport.

- These charged species could either be the reacting species that are intended to participate in redox reactions at the electrodes, or charged ions from the background electrolyte (e.g. Na^+ and Cl^- from NaCl solution).
- It is undesirable for reactants to be affected by migratory transport as this may hamper the intended redox reactions. Hence, background electrolytes also serve the purpose of shielding reactants from this effect by introducing a comparatively large quantity of their own ions into solution, which would instead undergo most of the migratory transport, thereby diminishing its effect on the reactants.
- However one key criterion is that the electrolyte ions must not be electroactive/undergo electrolysis themselves.

The current response of a macroelectrode is unlike that for a microelectrode. The voltammogram for a macroelectrode (assuming reversible electron transfer reactions) is shown below.



The key characteristics of the current response from a macroelectrode are as follows:

- We observe a peak current that subsequently declines as the voltage sweep proceeds. This arises due to mass transfer limitations as the supply of fresh reactant to the electrode surface for continued redox reactions (which produce current) becomes increasingly hindered by slowing diffusion of the redox reactant from bulk solution to the surface. This slowing diffusion arises as there is a growing boundary layer at the electrode surface which decreases diffusional flux of reactants to the surface.
- The currents measured using a macroelectrode are also of larger magnitudes.
- Macroelectrodes require high electrolyte concentrations.

- Any reduction in electrolyte concentration would mean an increase in electrolyte resistance. Coupled with the large currents seen in macroelectrodes, the resultant ohmic drop (ohmic drop $=iR$, hence increases with current and resistance) would be large, causing significant distortions to the current response. One such consequence is an increased voltage separation between the forward and reverse peaks, due to the hampering of efficient electrolysis at the electrodes.
- In addition, with a lower electrolyte concentration, migratory transport effects will be significant, causing reduced current values.

Advanced Voltammetry With Coupled Chemical Reactions



Abstract This chapter is a further build-up from the previous chapter (Chap. 2), as it delves deeper into the analysis of electrochemical processes by introducing more complex problems, specifically systems coupled with one or more other chemical reactions. This chapter will train the student's ability to approach more challenging problems systematically through the combined consideration of multiple related concepts in solving a single problem, and at the same time, provide sufficient practice in the mathematical skills required to derive final numerical solutions.

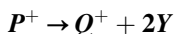
Keywords Rotating disk electrode · Rotational speed · Fick's law · Ligand exchange · Limiting current · Steady state current · Biosensor · Glucose sensor · Gratzel cell · Linear sweep · Reverse sweep

Problem 20

A particular substance P is used as the photosensitive dye in a Gratzel-type solar cell. This substance undergoes a reversible electron transfer reaction as shown below, with a standard oxidation potential $E^0 = +0.5V$.



The oxidized product, P^+ is able to undergo a further chemical reaction to form Q^+ as shown below. Y is known to be electrochemically inactive.

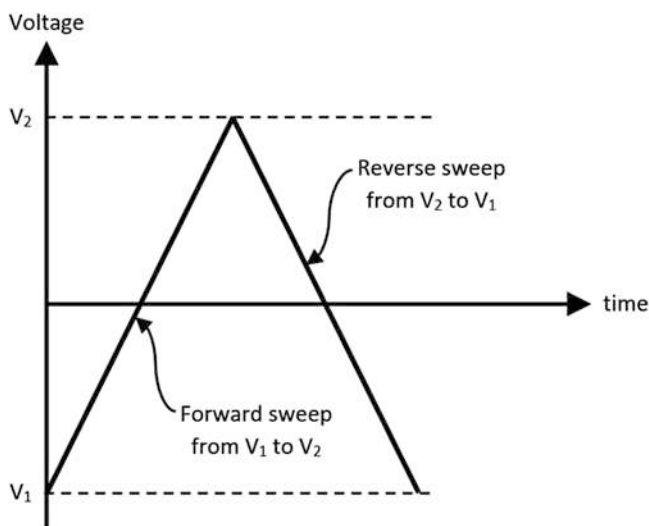


- Given that the standard oxidation potential of substance Q is $+0.3V$, and that the electrolyte contains 1 mmol of P in free solution, sketch and explain the current response expected for a cyclic voltammetric measurement for this system containing substance P .
- Explain how voltage scan rate would affect the current response in part a.

Solution 20

(a) Assuming that current is measured at the oxidation electrode, we have defined positive values of current as the anodic current in this solution.

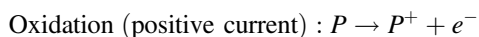
In cyclic voltammetry, voltage is first swept in a forward direction, then in the reverse direction. Graphically, we can see that voltage is swept between two values at a fixed rate as shown below.



As a result, we observe positive values of current and an oxidation peak arising from the forward sweep, and negative values of current (or “cathodic current”) and a reduction peak in the reverse sweep.

First Forward Sweep

From the problem statement, we know that the oxidation potential of P is $+0.5\text{ V}$ for the reversible oxidation reaction where P^+ is the oxidized product of P .



This is the only oxidation reaction occurring in the first forward sweep, therefore we observe results expected from a typical reversible single electron transfer reaction. For single ($n = 1$) electron transfer reactions, there is a constant voltage separation between current peaks of 59 mV under standard conditions, i.e.

$$\Delta E_p = E_{p,oxi} - E_{p,red}$$

$$\Delta E_p = \frac{59}{n} mV = \frac{59}{1} mV = 59 mV$$

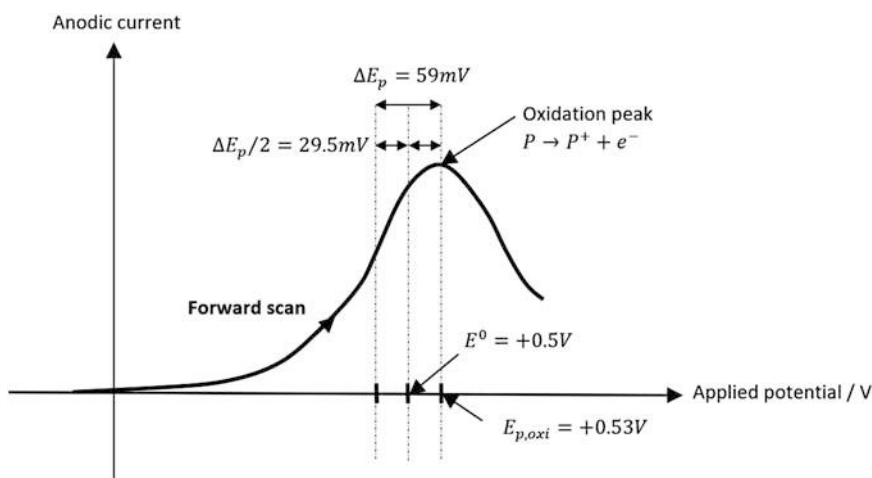
This means the peak current value occurs at the voltage value $E_{p, oxi}$ as shown below.

$$E_{p, oxi} = E^0 + \frac{59}{2} mV$$

$$E_{p, oxi} = +0.5V + 29.5 mV \cong +0.53V$$

Note that a key characteristic of reversible single electron transfer reactions is that the peak oxidation and reduction currents occur at potential values that are equidistance ($\pm 29.5 mV$) from the standard potential value which is $E^0 = +0.5V$ in this case. This means that if $E_{p, oxi} = E^0 + 29.5 mV$, then $E_{p, red} = E^0 - 29.5 mV$.

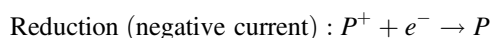
With the findings above, we can sketch the current response for the first forward sweep as shown below.



First Reverse Sweep

First Reduction Peak

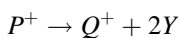
During the first reverse sweep, the oxidized product P^+ from the earlier forward sweep will now be reduced back to P .



In a simple system where P^+ does not undergo further chemical reactions (which is not the case in this problem), we would expect to see a reverse reduction peak

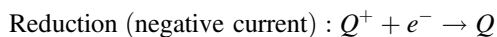
occurring at $E_{p, red} = E^0 - 29.5mV = +0.5V - 29.5mV \cong +0.47V$, and with the same peak height as the oxidation peak, for a reversible single electron transfer reaction.

However, since some of the oxidized product P^+ undergoes a further chemical reaction that is irreversible, P^+ is converted to Q^+ and less of it is available for reduction back to P . As such, we observe a smaller reverse reduction peak at the potential value $E_{p, red} = +0.47V$.

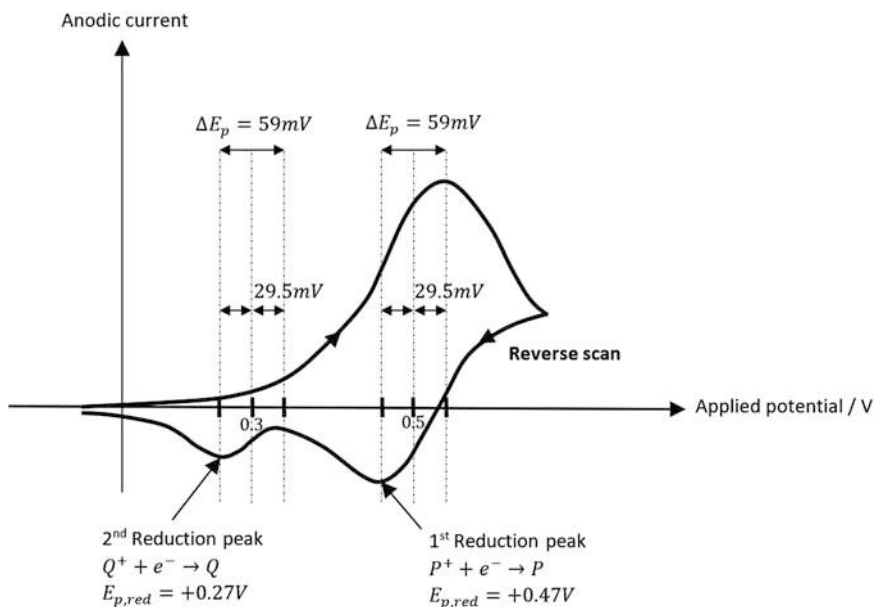


Second Reduction Peak

As we proceed with the reverse sweep and voltage values become more negative, the product Q^+ from the earlier chemical reaction $P^+ \rightarrow Q^+ + 2Y$ is now reduced since it is also electrochemically active with a standard oxidation potential of +0.3 V. As Q^+ is reduced to Q towards the later part of the reverse sweep, we see a second reduction peak occurring at $E_{p, red} = E^0 - 29.5mV = +0.3V - 29.5mV \cong +0.27V$. (Assuming reversible single electron transfer reactions for the Q/Q^+ system)



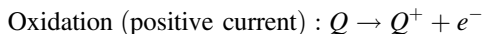
The above findings for the first reverse sweep are added to the current response plot as shown below.



Second Forward Sweep

First Oxidation Peak

When voltage is swept a second time in the forward direction, the amount of Q that was produced from the second reduction of the first reverse sweep would be re-oxidized to Q^+ , producing an oxidation current response with a positive peak current.

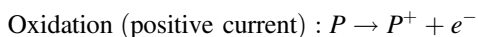


Since this electron transfer reaction remains reversible in nature, the potential value at which the oxidation peak occurs can be found to be approximately +0.33V.

$$E_{p,oxi} = E^0 + 29.5mV = +0.3V + 29.5mV \cong +0.33V$$

Second Oxidation Peak

Towards the later part of the second forward sweep at higher potential values, the amount of P that was produced from the first reduction of the first reverse sweep would also be re-oxidized to P^+ , producing a similar current response as the first forward sweep, with positive oxidation current and a positive peak current recorded.



However, unlike the first forward sweep, the magnitude of the peak current for the second forward sweep would be smaller. This is because the amount of P present at the electrode surface in the second sweep is less than that in the first sweep, as a diffusion boundary layer starts to grow from the electrode surface with time. The supply of P to the electrode surface for electron transfer reactions becomes limited by mass transfer effects.

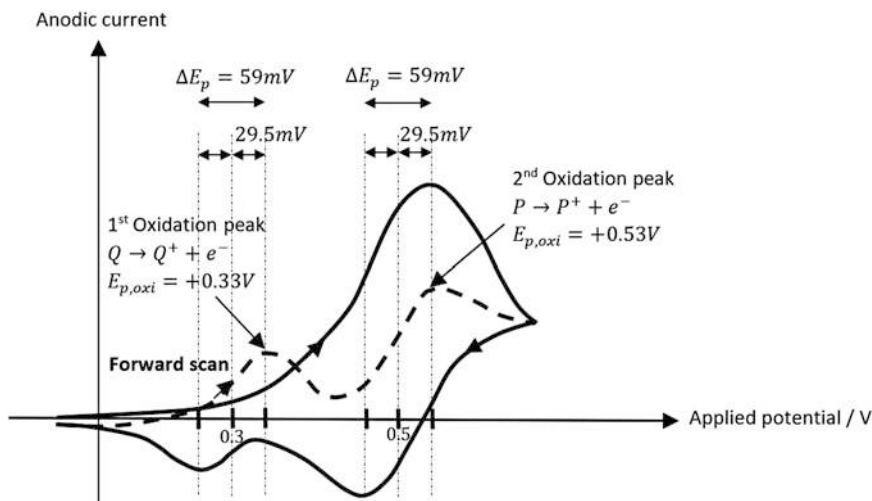
The amount of P^+ also becomes increasingly diminished with more sweeps, as P^+ is irreversibly consumed by a second chemical reaction. This will consequently also reduce the amount of P available for oxidation in further forward sweeps, since it is reformed from the reduction of P^+ .

Like before, the peak current still occurs at approximately +0.53V, as electron transfer reactions are still reversible.

$$E_{p,oxi} = E^0 + 29.5mV$$

$$E_{p,oxi} = +0.5V + 29.5mV \cong +0.53V$$

The current response as described above is shown in the plot below.



(b) The following changes occur to the current response when voltage scan rate ν increases for reversible electron transfer reactions.

- As voltage scan rate ν increases, the magnitude of the peak oxidation current at $+0.53V$ also increases. This is due to a thinner diffusion boundary layer, which means a greater diffusional flux that drives more rapid electron transfer reactions, hence larger currents. For reversible electron transfers, peak current i_p scales proportionally with scan rate ν according to $i_p \sim \nu^{1/2}$.
- The ratio of the forward peak current to the reverse peak current will increase until a limiting value of 1 (reversible reactions) where both peak currents are equivalent in magnitude. This occurs because at higher scan rates, electron transfer rates are rapid and dominate over chemical reaction ($P^+ \rightarrow Q^+ + 2Y$) and mass transfer effects which both serve to limit (reduce) the reverse peak current.

$$\frac{i_{p,forward}}{i_{p,reverse}} = 1$$

- The peak current at $0.33V$ will be reduced in magnitude with increasing scan rate, since the rate of the chemical reaction ($P^+ \rightarrow Q^+ + 2Y$) now becomes slower relative to the rapid (reversible) electron transfer rate.
- ΔE_p remains at $59mV$ for single-electron reversible systems, therefore the difference between the potential at which peak current occurs is still $\Delta E/2$ relative to the standard potential value.

Problem 21

Electrochemical techniques are often applied to biosensors, which are widely used in medical diagnostics. Using an appropriate example, explain how an enzyme-driven biosensor can be used to achieve diagnostic outcomes.

You may assume that for a general second order enzymatic reaction with Michaelis-Menten kinetics, the limiting current i at maximum turnover can be expressed as follows,

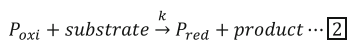
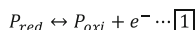
$$i = nFAC(2Dke)^{\frac{1}{2}}$$

where C refers to the bulk concentration of the electron acceptor for the redox reaction at the electrode surface, D refers to the diffusion coefficient of the electron acceptor, k refers to the rate constant for the enzymatic reaction and e refers to the total amount of enzymes in solution.

Solution 21

A common example of a biosensor is the glucose sensor used by diabetic patients to monitor their blood glucose concentrations.

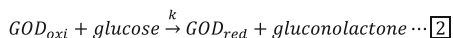
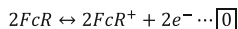
The underlying mechanism which produces a current from a glucose sensor device is summarized as follows, where the first step is an electron transfer or redox reaction, while the second step is a chemical reaction that converts an intended substrate (e.g. glucose) into a product. The chemical reaction is catalyzed by an enzyme (e.g. a glucose oxidase, denoted *GOD*) and occurs at a rate constant k . The purpose of the second chemical reaction (see reaction 2 below) is also to regenerate reactant P_{red} for the oxidation reaction 1.



In glucose sensors, an additional redox mediator molecule may be used due to the following advantages.

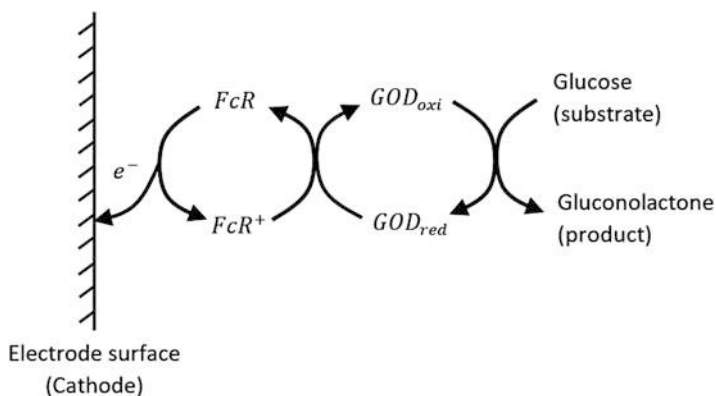
- Ensures high interface rates of reaction with reversible electron transfer kinetics
- Stable over long periods of time in both reduced and oxidized states
- Requires only a small potential value to drive its redox reaction

Such mediators are typically ferrocene (*FcR*) derivatives which are able to take part in redox reactions which are coupled to the redox reactions of the glucose oxidase enzyme (*GOD*).



The redox reaction of the mediator FcR is written as step 0 above, which precedes step 1 in the mechanism. In the above specific example for a glucose sensor, reactant P is specified as GOD , the substrate is specified as glucose and the oxidized product is specified as gluconolactone.

We can illustrate how these coupled reactions work to correlate the glucose oxidation reaction (which correlates to the presence of glucose in a test sample) with the electrochemical reaction at the electrode surface (producing a measurable current).



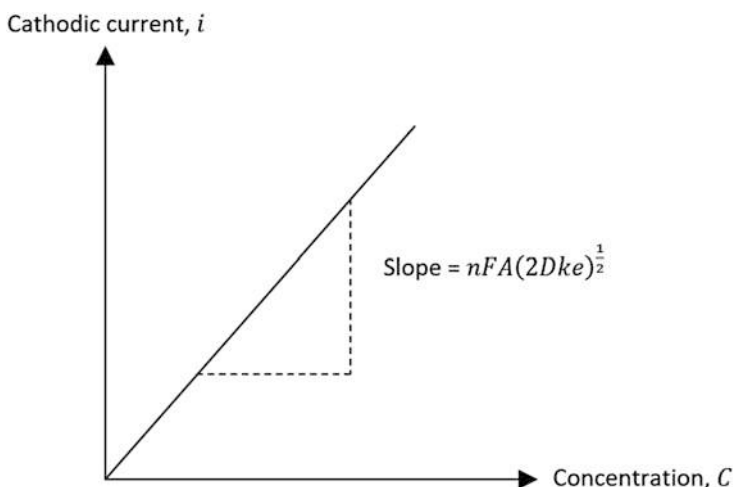
When glucose substrate is present, the coupled reactions shown above will eventually lead to the regeneration of mediator FcR at the electrode surface, which drives the reduction reaction at the electrode surface and produces a measurable current in the sensor device. The enzyme glucose oxidase or GOD is typically at maximum turnover rate, i.e. the enzyme is catalyzing the oxidation of glucose at the maximum rate and is therefore not a limiting factor in the current reading. This is possible when the enzymes are saturated with the substrate. This also means that the glucose concentration in the sample can be accurately correlated with the measured current, assuming enzyme concentration is a constant at its maximum working capacity at all times (e is constant).

Assuming Michaelis-Menten kinetics for the enzymatic reaction, the current at maximum turnover rate can be expressed as follows, where C refers to the concentration of the electron acceptor (i.e. FcR^+) and D refers to the diffusion coefficient of FcR^+ .

$$i = nFAC(2Dke)^{\frac{1}{2}}$$

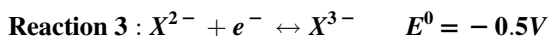
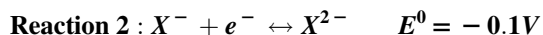
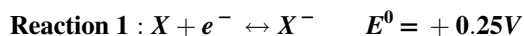
The only two experimental variables in this equation are simplified to just i and C . Hence this equation allows us to relate the magnitude of measured current i (our dependent variable) with C , the concentration of FcR^+ (and hence glucose) in the solution (our independent variable).

A plot of i against C would give us a straight line passing through the origin with a constant slope equivalent to $nFA(2Dke)^{\frac{1}{2}}$. By computing the value of gradient from the plot, we can also gain insight into the magnitude of other parameters, such as diffusivity D , rate constant k , and enzyme concentration e .

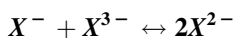


Problem 22

An electrochemically active species X is known to undergo three electron transfer reactions as shown below:



- (a) **Reactions 1 and 2 are reversible, while reaction 3 is irreversible. Using your knowledge about reversible and irreversible electron transfer reactions, explain how they can be differentiated from each other using voltammetry.**
- (b) **Sketch the expected current response for a cyclic voltammetry conducted on X , assuming that X is dissolved in an electrolyte solution.**
- (c) **If a further chemical reaction as shown below was found to also occur in solution, explain how the current response in part b would change.**



Solution 22

(a) We need to first understand the differences between electrochemically reversible and irreversible reactions.

Reversible electron transfer or redox reactions are also known as Nernstian, and some of their key characteristics are as follows:

- The position of peak voltage, E_p does not vary with sweep rate or scan rate. In other words, at different scan rates, the peak current will still be found at the same potential value.
- In cyclic voltammetry comprising of a forward sweep followed by a reverse sweep, the distance (or voltage separation ΔE_p) between the forward current peak and the reverse current peak is fixed and independent of scan rate.
 - At room temperature and standard conditions, $\Delta E_p = E_p^{anode} - E_p^{cathode} = \frac{59}{n} mV$
 - n refers to the number of electrons transferred per reaction, hence for single electron transfer reactions, $\Delta E_p = 59 mV$
- The ratio of peak currents is equal to 1, regardless of scan rate.

$$\frac{i_p^{anode}}{i_p^{cathode}} = 1$$

- For repeated cycling, a diffusion boundary layer grows near the electrode surface. As a result, $i_p^{cathode}$ decreases while i_p^{anode} increases until a steady state is reached.
- The peak currents are proportional to the square root of scan rate $v^{1/2}$

$$i_p v^{1/2}$$

On the other end of the spectrum irreversible electron transfer reactions can be characterized as follows:

- Unlike reversible reactions, E_p varies with scan rate.
 - E_p is shifted to the right and becomes more negative (or is shifted further away from standard potential) as scan rate increases.
- Similar to the reversible case, the peak current is proportional to the square root of scan rate $v^{1/2}$

$$i_p \propto v^{1/2}$$

- Note that this is not the case for quasi-reversible kinetics.
- The magnitude of peak current for irreversible reactions is smaller than that for reversible reactions

$$i_{p,rev} > i_{p,irrev}$$

- Unlike in reversible cases, there is no reverse peak observed on the reverse sweep for irreversible reactions. Hence ΔE_p is irrelevant.

(b) *Key Features of the CV current response*

Forward Sweep

- The forward sweep starts from zero current since there is no reactant for reduction reaction at the beginning of the sweep.
- Three reduction reactions occur in the forward sweep (assuming sweep direction towards more negative potentials), hence **three current peaks** will be seen in the forward sweep.
- The **second peak (from reaction 2) would be higher than the first peak (from reaction 1)** since the reduction reactions are consecutive (or sequential), hence current values add cumulatively in producing the overall current response.
- The third reaction is irreversible, hence the **third redox step is slow** compared to the rapid and reversible electron transfers in reactions 1 and 2. This gives rise to a smaller third peak than would have been expected if it was a reversible reaction.

Reverse Sweep

- Three oxidation reactions occur in the reverse sweep, hence **three current peaks** will be seen in the reverse sweep.
- Since reaction 3 is irreversible and hence **slow** compared to the rapid and reversible reactions 1 and 2, less starting material is available for

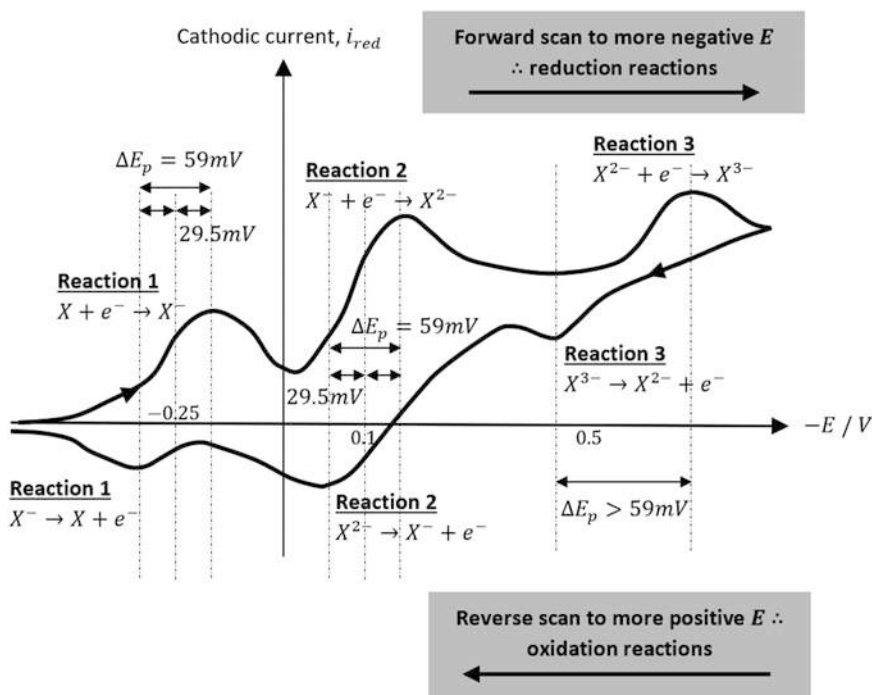
reactions 1 and 2 in the reverse sweep and this results in the **reverse peaks for reactions 1 and 2 having smaller magnitudes** compared to the forward peaks for reactions 1 and 2.

- At the end of the reverse sweep, current does not return to zero but tapers off to a small non-zero value. This is because there would remain a non-zero reactant concentration (the equilibrium concentration) at the end of the reverse oxidative sweep.

Relationships Between Forward and Reverse Sweeps

- The voltage separation ΔE_p between the pairs of current peaks at $E = +0.25\text{V}$ and -0.1V would be equivalent to 59 mV since these peaks correspond to reactions 1 and 2 (in the forward direction) which are reversible electron transfer reactions.
- Conversely, ΔE_p for the pair of current peaks at $E = -0.5\text{V}$ would be greater than 59 mV , since reaction 3 is irreversible. The third peak in the forward sweep will be shifted more to the right, than the case if the reaction was reversible.

The above points are shown in the voltammetric plot shown below.



- In the plot above, current is plotted against $-E$ axis, i.e. the direction to the right represents more negative and hence more reductive potentials. The **forward sweep to the right therefore corresponds to the reduction reactions**, and the **reverse sweep to the left corresponds to oxidation reactions**.

- Reaction 1: $E^0 = +0.25V$, or $-E^0 = -0.25V$
- Reaction 2: $E^0 = -0.1V$, or $-E^0 = +0.1V$
- Reaction 3: $E^0 = -0.5V$, or $-E^0 = +0.5V$

- The current values for the reduction reactions are plotted as positive values, hence the vertical axis represents cathodic current.
- Note that the above two assumptions can also be reversed, i.e. to define anodic current against more oxidative potentials. This does not change the final result.

(c) The reduced species X^- and X^{3-} will only be formed after the first forward sweep. Therefore, any effects of the chemical reaction $X^- + X^{3-} \leftrightarrow 2X^{2-}$ will only be apparent starting from the first reverse sweep. The key changes that will be observed are as follows:

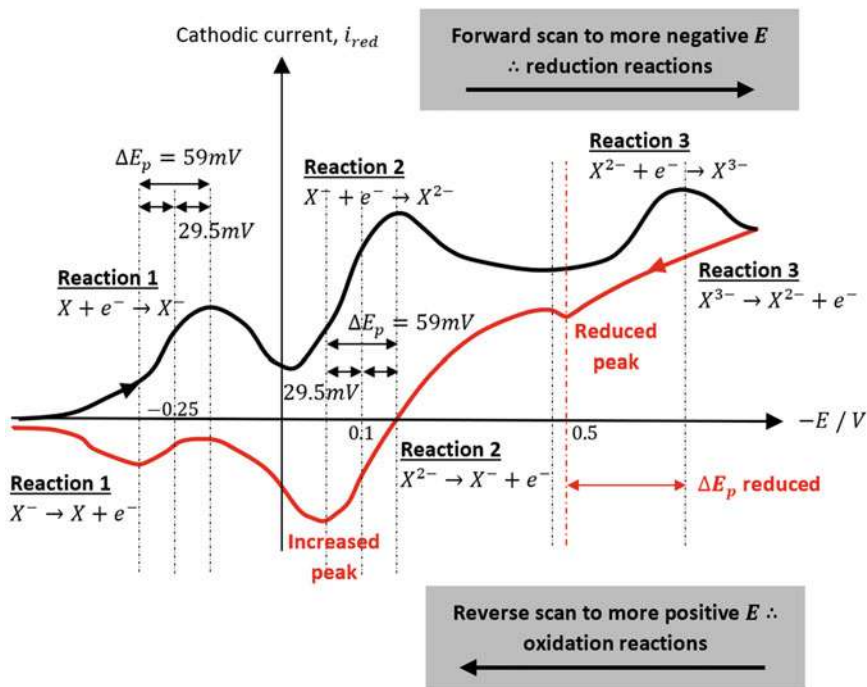
- As more X^{2-} is produced from the chemical reaction, we will have a larger amount of reactant for the oxidation of Reaction 2, causing oxidation in Reaction 2 to go faster and contributing to a **larger second peak**.
- The **magnitude of the oxidation peak for Reaction 3 will be reduced**, since reactant X^{3-} is consumed by the chemical reaction, less is available for oxidation in the reverse scan.
- ΔE_p for the pair of current peaks near $E = -0.5V$ was originally greater than 59 mV in part b. With the chemical reaction, X^{3-} is consumed more and this enhances the reverse oxidation direction of Reaction 3. Hence, the “degree of irreversibility” of Reaction 3 becomes less, and the **peak separation ΔE_p also reduces**. Note however that ΔE_p is still greater than 59 mV as long as Reaction 3 is not fully reversible.

	Forward direction (reduction)	Reverse direction (oxidation)	
Reaction 3	$X^{2-} + e^- \rightarrow X^{3-}$	$X^{3-} \rightarrow X^{2-} + e^-$	ΔE_p
Part b	Dominant over oxidation reaction	Minimal oxidation, due to irreversibility	$\Delta E_p \gg 59mV$
Part c	Still occurs	Oxidation enhanced by chemical reaction, “less irreversible reduction direction”	$\Delta E_p > 59mV$

- As for the oxidation peak of Reaction 1, it will not change significantly. Even though X^- is also consumed by the chemical reaction and is therefore less available for oxidation in the reverse direction of Reaction 1 (causing a lower peak height for Reaction 1), at the same time, more X^- is also produced from the enhanced oxidation of Reaction 2, supplying more reactant X^- for oxidation in Reaction 1 (causing an increased peak height for Reaction 1). Since these two

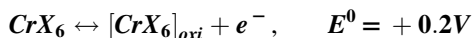
factors work against each other, a less apparent difference in the oxidation peak for Reaction 1 will be observed.

The changes described above for the first reverse scan are shown below in red.

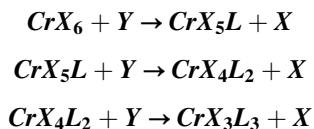


Problem 23

A microelectrode was used to study the single electron oxidation of a Chromium-containing complex CrX_6 with a standard oxidation potential $E^0 = +0.2V$. The electron transfer reaction is known to be quasi-reversible and is shown as follows.



In the presence of a ligand Y , further chemical reactions are known to occur as shown below. The Chromium-containing products of these reactions, i.e. CrX_5L , CrX_4L_2 and CrX_3L_3 are able to undergo reversible one electron oxidation reactions, with standard oxidation potentials of $E^0 = +0.3V$, $+0.35V$ and $+0.37V$ respectively.



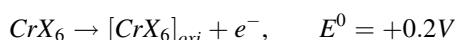
Sketch and explain the voltammetry expected in the oxidation of the CrX_6 system if

- (a) **Ligand Y was absent**
- (b) **Ligand Y was present**

Solution 23

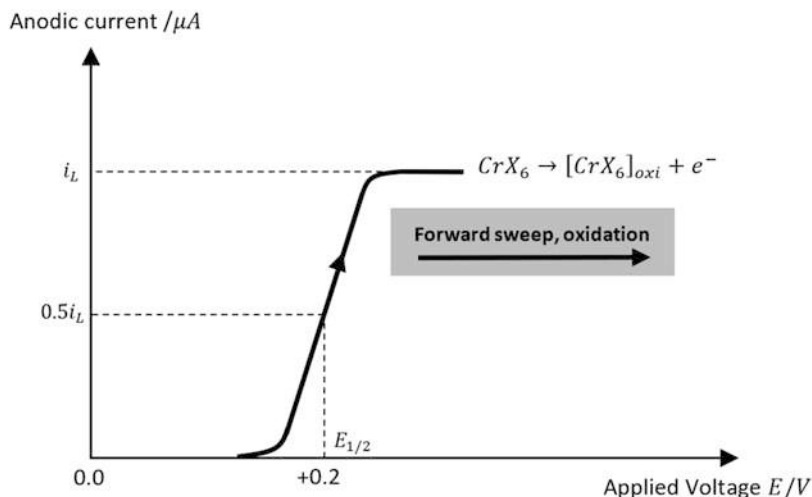
(a) The current response expected for a microelectrode is one that shows a steady-state current being reached as voltage is swept. In an oxidation reaction, voltage is swept to less reductive/negative potentials or more oxidative/positive potentials, and an anodic current is observed. [Conversely, a cathodic current is observed when voltage is swept to more negative potentials, favoring reduction]

When ligand Y is absent, the only oxidation reaction that occurs in the voltage sweep is the one as shown below.

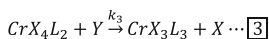
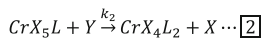
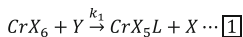


For a microelectrode, current rises as voltage is swept until it reaches a constant limiting value at the later part of the sweep. Furthermore, current rises to half of its limiting value at the standard potential value of +0.2 V, as shown in the sketch below.

It is worth noting that since this is a quasi-reversible electron transfer reaction, the slope of the curve would be gentler (i.e. slower rate of increase of current) than that expected for a fully reversible reaction as electron transfer rate is slower for a quasi-reversible reaction compared to a reversible reaction.



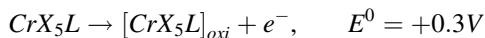
(b) If ligand Y was present, then the three chemical reactions would occur as follows, with their respective rate constants indicated as k_1 , k_2 and k_3 .



At the beginning of the voltammetric experiment, CrX_6 is present. It can undergo both chemical reaction [1], *as well as* its own oxidation reaction (like in part a) as voltage is swept to more oxidative potentials. The outcomes of these two reactions happening at the same time are as shown below.

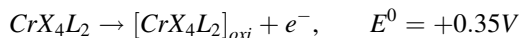
- Chemical reaction [1] causes the formation of CrX_5L .
- Oxidation reaction causes current to rise and reach a steady state value near to and slightly after $E = +0.2V$ (like in part a).

Since CrX_5L is formed from reaction [1], it is able to undergo its own oxidation reaction as voltage continues to be swept to more oxidative potentials.



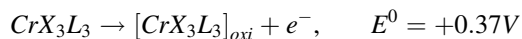
Given that the standard oxidation potential of CrX_5L is $E^0 = +0.3V$, we will observe that current rises from the earlier steady state value, to a new and higher steady state value close to (and just exceeding) $E^0 = +0.3V$.

Separately, the formation of CrX_5L also causes chemical reaction [2] to proceed, producing CrX_4L_2 . In the same way, the CrX_4L_2 that is formed is then able to undergo its own oxidation reaction as voltage continues to be swept to more oxidative potentials.



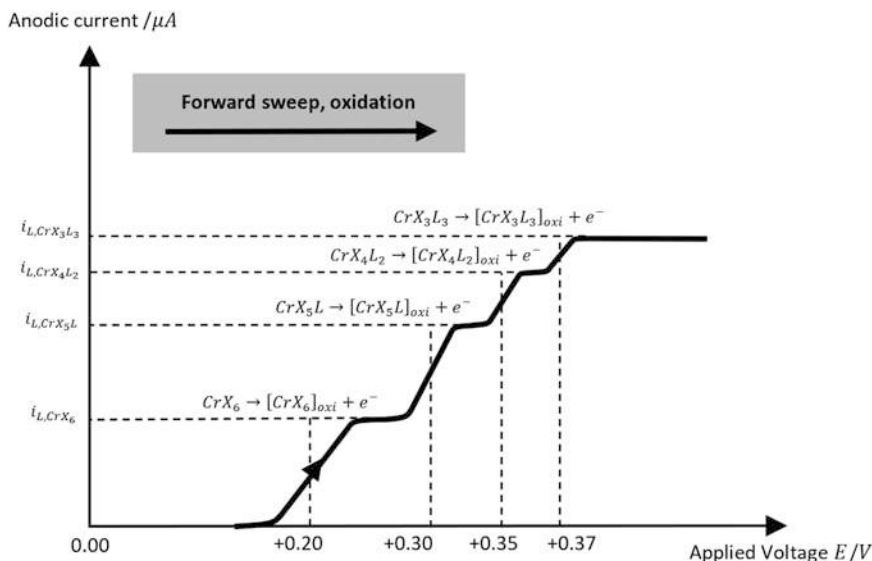
Given that the standard oxidation potential of CrX_4L_2 is $E^0 = +0.35V$, we will observe that current rises from the previous steady state value, to a new (third) steady state value close to (and just exceeding) $E^0 = +0.35V$.

Like before, the formation of the formation of CrX_4L_2 simultaneously causes chemical reaction [3] to proceed, producing CrX_3L_3 . In the same way as before, the CrX_3L_3 that is formed is then able to undergo its own oxidation reaction as voltage continues to be swept to even more oxidative potentials.



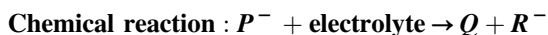
Given that the standard oxidation potential of CrX_3L_3 is $E^0 = +0.37\text{V}$, we will observe that current rises from the previous steady state value, to a final (fourth) steady state value close to (and just exceeding) $E^0 = +0.37\text{V}$.

The overall current response can therefore be shown in the sketch below.



Problem 24

A particular species P is known to undergo a rapid one-electron reduction reaction. The product of this reduction then takes part in a homogenous chemical reaction with the background electrolyte, forming a neutral compound Q and an anion R^- as shown below.

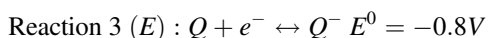
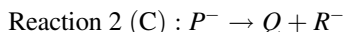
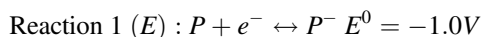


- Given that the standard potentials of Q and P are -0.8V and -1.0V respectively, sketch the current response for this system assuming a cyclic voltammetry was conducted using a macroelectrode.
- Explain how the current response would change if a microelectrode was used.
- Explain briefly how it is possible to use voltammetric methods to analyze the kinetics of the chemical reaction.

Solution 24

(a) It is first important to identify all possible reactions in this system. Possible reactions could be redox reactions (reversible reactions with an associated standard potential), as well as chemical reactions (irreversible).

This is in fact an ECE mechanism, where “E” denotes electron transfer/redox reactions and “C” denotes chemical reactions.

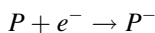


Reaction 1 is a reduction reaction, which is rapid and hence may be assumed reversible. Reaction 2 is a chemical reaction. Reaction 3 is often overlooked. It involves the reduction of electroactive species Q .

We should also note that since the standard potential of reaction 3 is less negative than reaction 1, it means that species Q is more easily reduced than P , therefore reaction 3 will also be a rapid and reversible reaction (since we know that reaction 1 is rapid and reversible, reaction 3 has to be rapid and reversible too since it takes place more easily).

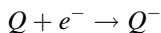
First Forward Scan

Initially, only species P is present. Assuming that the forward scan goes towards more reductive/negative potentials, the reduction reaction in Reaction 1 would occur, causing a rise in current that peaks slightly to the right of the potential value $E = -1.0V$.



Since this reaction follows reversible electron transfer kinetics, there would be a relatively high peak current (as opposed to quasi or irreversible reactions). After the peak, current subsequently declines due to mass transfer effects.

Subsequent to Reaction 1, the chemical reaction in Reaction 2 consumes species P^- ($P^- \rightarrow Q + R^-$), forming another electroactive species Q . At an applied potential value in the region of $E = -1.0V$, species Q will be able to undergo the reduction reaction in Reaction 3 readily, since it has a standard potential of $E = -0.8V$ which is less negative than the applied potential near to $-1.0V$. Therefore, we would expect the reduction reaction in Reaction 3 to contribute (add to) to the peak current value in the first forward scan.



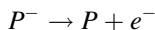
A higher rate constant for Reaction 2 would mean a faster rate at which Q is formed. Therefore, the contributory effect of Reaction 3 to the peak current value will also be enhanced by a higher rate constant for Reaction 2.

Also, if scan rate were sufficiently slow, Reaction 2 would have “enough time” to completely convert all of P^- to Q , and the Q formed will then be able to reduce to Q^- . This means that at low scan rates, we can expect a peak current value that is around twice (since two electroactive species are undergoing reduction simultaneously, and each a single electron-transfer reaction) that expected for a single electroactive species undergoing a single electron transfer reaction.

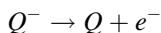
First Reverse Scan

Two current peaks will be observed going from more negative to less negative potentials in the reverse sweep direction.

The first peak is caused by the re-oxidation of P^- to P , occurring slightly to the left of the potential value $E = -1.0V$. [Recall that for reversible reactions, the cathodic and anodic current peaks occur on each side of the standard potential value, and are also equidistant from it.] The presence of this first reverse peak also assumes that there is still some P^- present, i.e. not all of it is reacted away/consumed away by Reaction 2 before the reverse scan takes place.



The second reverse peak will be observed around the potential value of $E = -0.8V$ and this is caused by the re-oxidation of Q^- to Q . The presence of a second reverse peak assumes that there is some Q^- produced from the earlier forward scan (for e.g. if rate constant of Reaction 2 is sufficiently high)

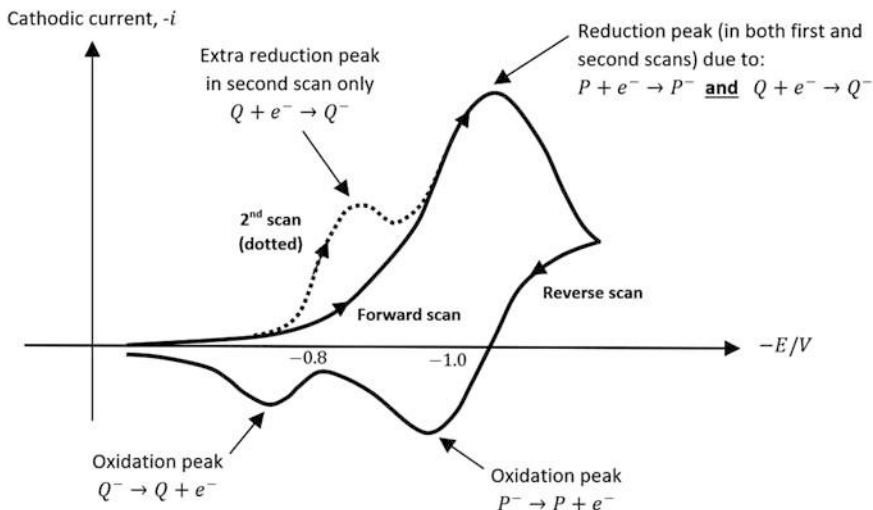


Second Forward Scan

In the second forward scan, we would observe two peaks instead of one, since both species P and Q would be present. The first peak would occur slightly to the right of the potential value $E = -0.8V$ corresponding to the reduction of Q , while the

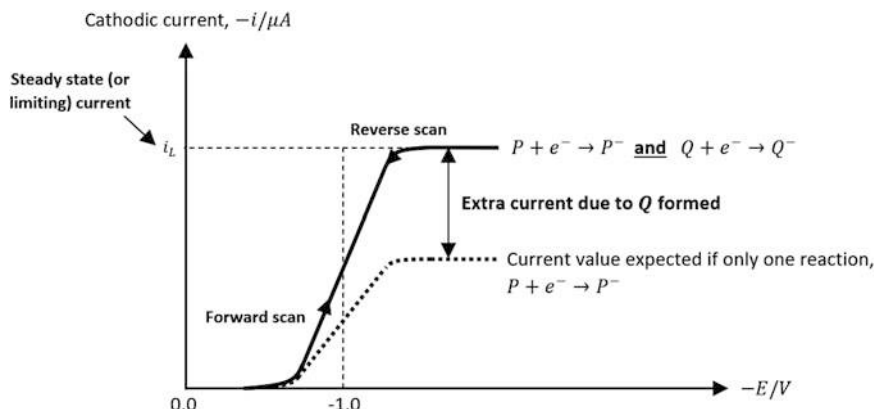
second peak would occur slightly to the right of $E = -1.0\text{V}$ corresponding to the reduction of P .

The results described above are shown in the voltammogram shown below.



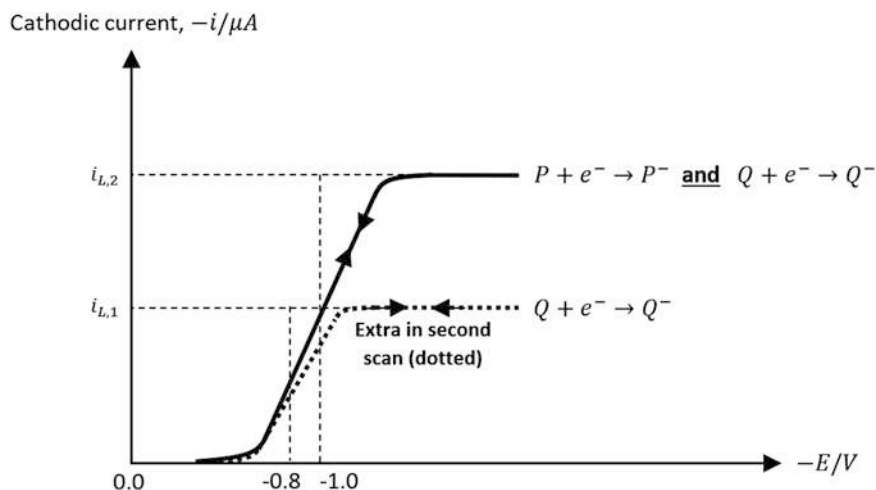
(b) If a microelectrode were used, we would expect a steady-state current profile instead of current peaks, whereby the forward and backward current values trace along the same line. Note that in the first scan, the steady state current reached would be higher (since two electroactive species P and Q can undergo electron transfer reactions) than what we would expect if only one electroactive species was present (e.g. if only P was present). This higher current value would also be almost twice if the rate of the chemical step in Reaction 2 was fast.

First Scan



In the second scan, we may observe an extra steady state current at a lower value, in addition to the earlier current value observed in the first scan. This is due to the presence of species Q from the second forward scan onwards, which gives rise to this new current value as a result of its own redox reactions.

Second Scan



(c) In order to study the kinetics of the chemical reaction (i.e. to find out the rate constant k_{ECE} of the chemical reaction step for the ECE mechanism), we can measure current i_L at varying scan rates v . We then fit the data values obtained to a kinetic model in order to extract quantitative information.

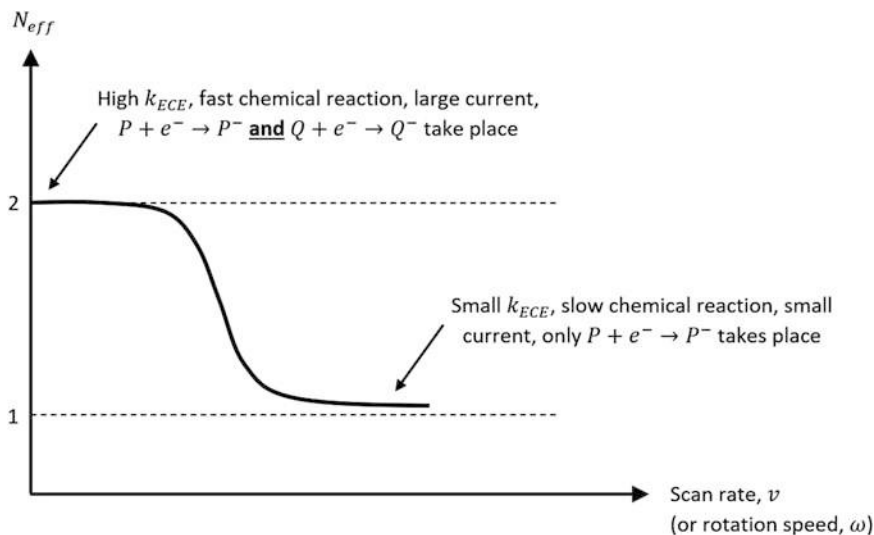
- If k_{ECE} were small, then i_L will be small, since the number of electrons transferred, n will tend to 1.
 - This is because the chemical reaction is too slow to form Q , and the second reduction reaction of Q cannot take place without reactants present.
- If k_{ECE} were large, then i_L will be large, with a maximum value corresponding to when $n = 2$.
 - This is because the chemical reaction is fast enough to fully convert the product of the first reduction, P^- into Q which is the reactant for the second reduction reaction. This second reduction reaction will be able to take place concurrent to the reduction of P , enhancing the current value to double the value you expect for the case of $n = 1$.
- Scan rates are easily adjustable experimentally and effectively relate to the experimental time frame. As scan rate increases, it will increasingly “overshadow” chemical reaction rate, i.e. a high scan rate means there is “not enough time” for the chemical reaction to take its effect. **When scan rates are high**, the system would behave as though the chemical reaction was not present, i.e. the **chemical reaction rate is slow** (relative to scan rate), and **current will tend to the lower limit (when $n = 1$)** corresponding to the case of a **low k_{ECE}** .
- As such, we can experimentally vary scan rate and obtain a range of i_L . As we increase scan rate, i_L decreases. We can identify the point at which i_L drops from its upper limit (when $n = 2$) to lower limit (when $n = 1$), as that is when chemical reaction rate becomes slow or comparable to the electron transfer rate. This allows us to have a quantitative measure of the chemical reaction rate constant.
 - This type of analysis can be simplified using a simple ratio, N_{eff} whereby

$$N_{eff} = \frac{\text{Total measured current}}{\text{Current from } P \rightarrow P^- \text{ only}}$$

- At the upper limit where total current is largest, $N_{eff} = 2$. This is because the total measured current will be a sum of current from $P \rightarrow P^-$ and $Q \rightarrow Q^-$. This is also the case when the number of moles of electrons transferred is $n = 2$.
- At the lower limit where total current is smallest, $N_{eff} = 1$. This is when the total current comes from $P \rightarrow P^-$ only, and no chemical reaction (too slow) takes place. This is also the case when the number of moles of electrons transferred is $n = 1$.
- Note that the abovementioned experimental method involves varying scan rates for a stagnant electrolyte solution. Alternatively, we can also obtain a series of i_L values without altering scan rate, but by **varying convection rate of bulk solution** such as by using a rotating disc electrode. As we **increase rotational speed** of the disc, it has a similar effect as increasing scan rate, i.e. **current will decrease to the lower limit (when $n = 1$)** corresponding to the case of a low k_{ECE} . This is because a high convection rate will cause any P^- formed from the

first reduction reaction to be quickly swept away, and hence less will be available for the chemical reaction to convert it to Q , and less Q means the second reduction reaction is hampered, thus producing a lower current.

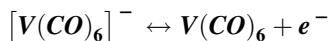
A graphical analysis is shown in the diagram below.



Problem 25

Cyclic voltammetry was conducted in a stagnant and non-aqueous solution containing 0.001 M of the electroactive species, potassium vanadium hexacarbonyl ($K^+[V(CO)_6]^-$) in an inert background electrolyte of 0.1 M of tetrabutyl ammonium perchlorate (TBAP).

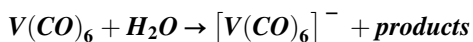
The vanadium hexacarbonyl anion undergoes a quasi-reversible single electron transfer oxidation reaction ($E^0 = +0.28V$) as shown below:



Sketch the current response expected at varying voltage scan rates for

- A macroelectrode
- A microelectrode

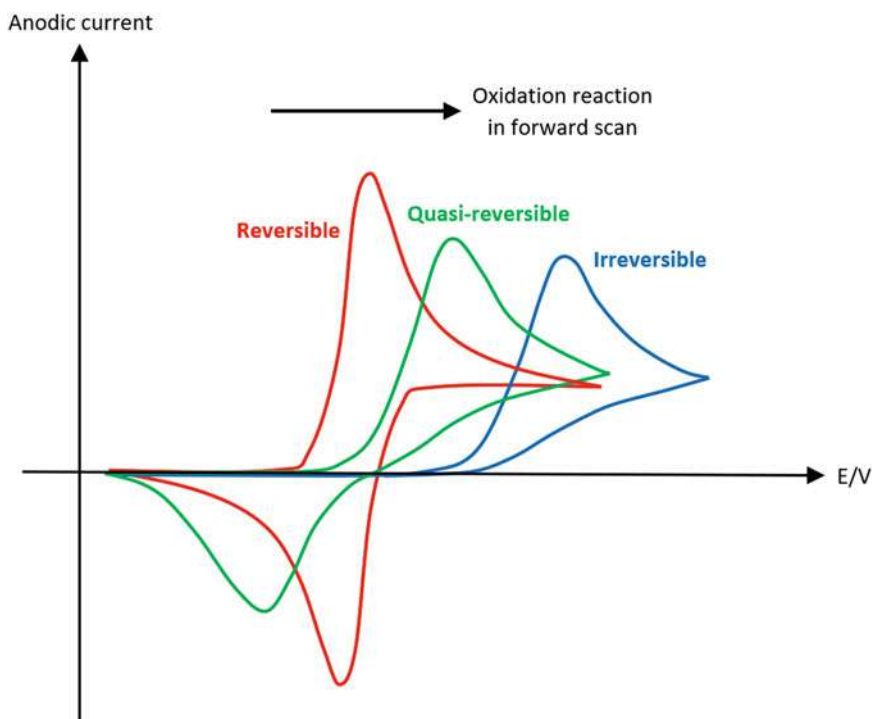
Given that water chemically reacts with $V(CO)_6$ as shown in the reaction below,



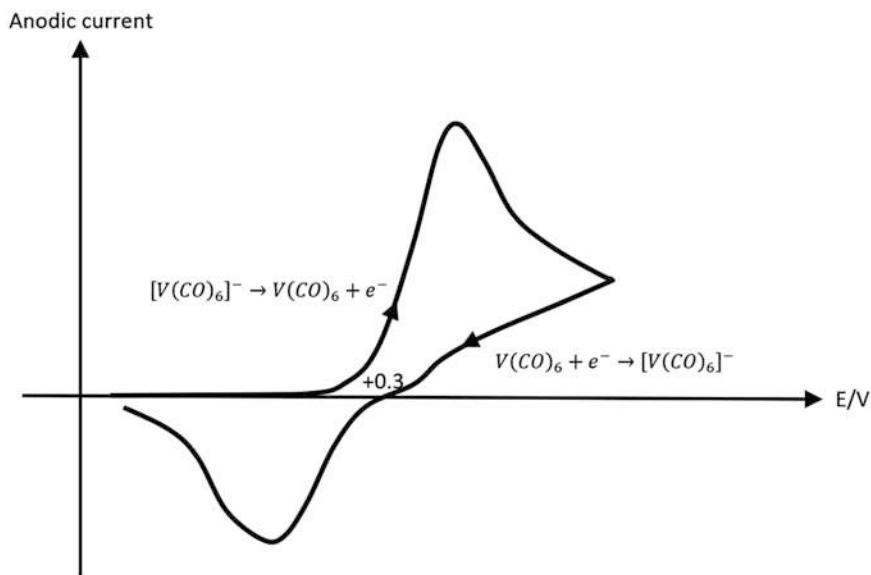
- (c) For a microelectrode, sketch the current response that would be expected if water were added.

Solution 25

(a) For a quasi-reversible oxidation reaction using a macroelectrode, the current response would take the shape that is intermediate between what we would expect for a reversible reaction and an irreversible reaction, as shown in green below. Compared to the reversible case, a quasi-reversible reaction gives a current response with a greater peak separation and smaller peak heights.



Therefore we can sketch the current response for our quasi-reversible system as follows, with the forward scan corresponding to oxidation and the backward scan corresponding to reduction:



- In a quasi-reversible reaction, the electron transfer kinetics at the electrode surface are slower than in the reversible case, so we have a reduced peak height.
- The peak separation between the forward and reverse peaks is not exactly 59 mV (like in the case for reversible kinetics for single electron transfer reactions) but will be greater than 59 mV. The exact voltage separation depends on scan rate.

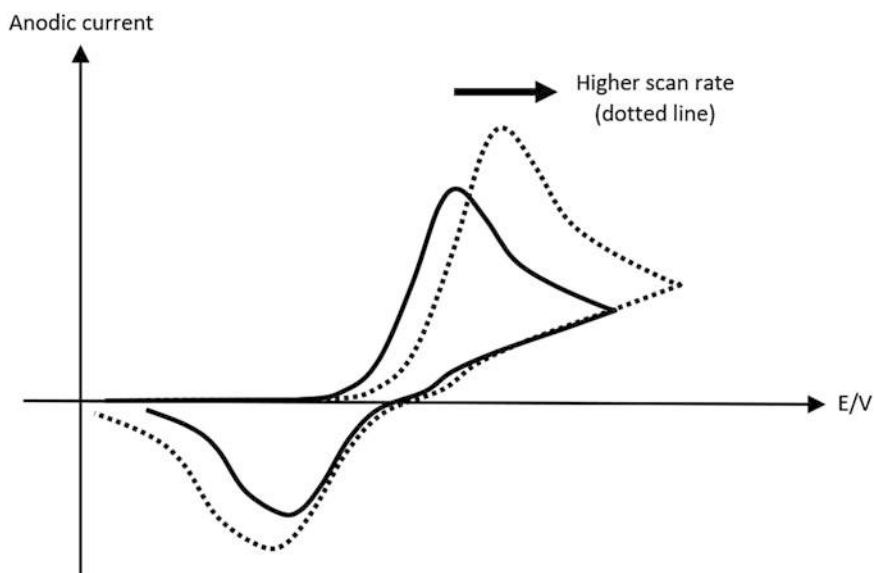
Effect of Varying Scan Rate

Reduced Current

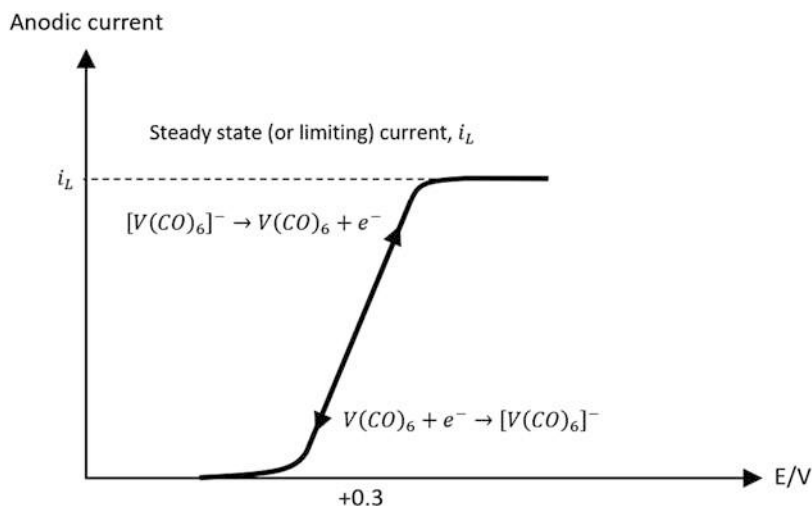
When scan rate is low, the diffusion layer will grow much further from the electrode surface, resulting in a thicker diffusion boundary layer. A thicker boundary layer means a smaller concentration gradient for the diffusion of reactant species to the electrode surface for redox reactions. A smaller flux to the electrode surface at slower scan rates, results in a lower rate of electron transfer at the surface, giving rise to a smaller current (since current relates to the amount of charge transferred per unit time). Therefore, if we increase scan rate, the diffusion boundary layer will be thinner and overall current values would increase.

Increased Peak Separation

For quasi-reversible reactions, there is a correlation between voltage separation between current peaks in the forward and backward scans. [This is unlike reversible reactions, the voltage separation between peak currents is fixed at 59 mV for single electron transfer reactions.] Therefore, as we increase scan rate, we would expect an increase in voltage separation between the peaks.



(b) For a microelectrode, the current response is expected as shown below.



The current response would not have a peak, but would instead reach a steady-state limiting current value towards the later part of the voltage sweep. The forward and backward sweeps will also trace the same line along the current response curve.

And since this is a quasi-reversible reaction, the magnitude of the limiting current reached will be lower than that expected for a reversible case due to the slower electron transfer kinetics at the electrode surface, contributing to less current being produced.

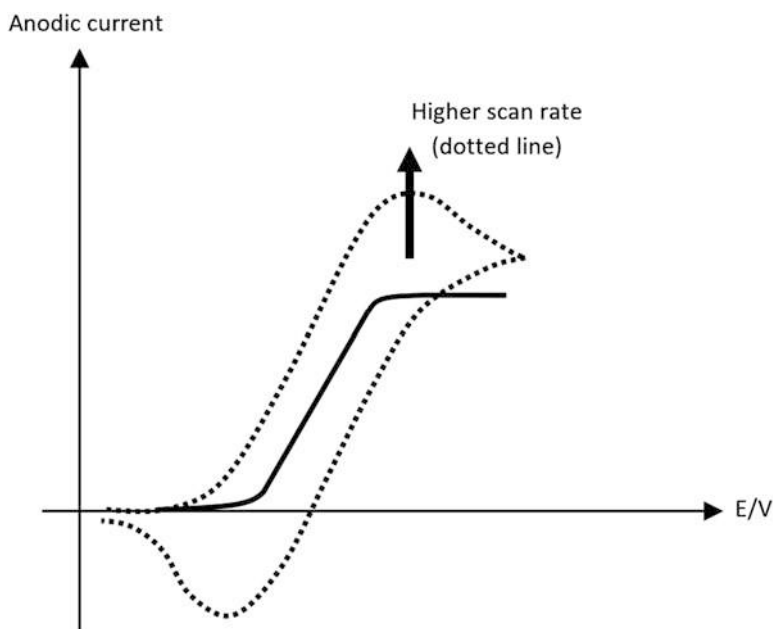
Effect of Varying Scan Rate

Macroelectrode Profile with Current Peaks

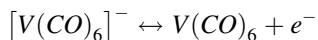
If we increase scan rate, electron transfer kinetics start to become limited by mass transfer rate. Hence, we will start to observe current peaks in the forward and reverse scans like in the response for a macroelectrode.

Increase in Current

In addition, current values increase as scan rate increases, due to a thinner diffusion layer at the electrode surface, resulting in greater diffusional flux of redox species for reactions at the electrode, producing larger current.



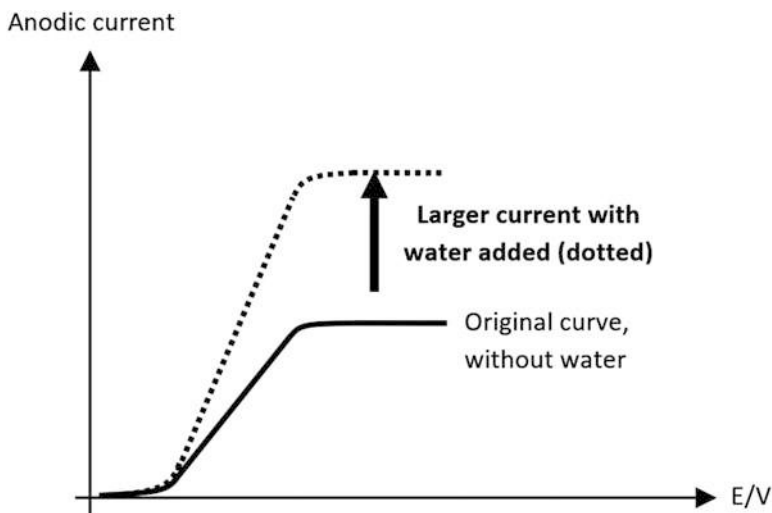
(c) Initially we had the following redox reaction occurring at the electrode:



If water were added, an additional chemical reaction as shown below would occur.



Water does two things to the system, (1) it consumes the product $V(CO)_6$ formed from the earlier oxidation step, (2) it also regenerates more reactant $[V(CO)_6]^-$ to enhance the earlier oxidation step. In other words, water acts as a catalyst for the oxidation reaction at the electrode. As such, we expect the following current response for a microelectrode if water was added.



With more reactants available for the oxidation reaction, more electrons will be produced (hence transferred) at the electrode, and a greater current will be produced.

Hydrodynamic or Forced Convection Voltammetry



Abstract Similar to the previous chapter (Chap. 3), this chapter includes more advanced electrochemical scenarios to train the student's ability to handle a wide range of problems. In this topic, the focus is on electrochemical systems that introduce external convection and hydrodynamic factors which add another dimension to electrochemical problems. This chapter would require students to borrow concepts from other related topics such as mass transport principles, in order to be able to approach the problems holistically and arrive at the final solutions.

Keywords Channel electrode · Levich equation · Mass transport limiting · Rotating disc electrode · Diffusion boundary layer · Laminar flow · Turbulent flow · Bulk convective flow · Diffusion layer · Limiting current

Problem 26

Discuss the advantages that hydrodynamic voltammetry offers compared to voltammetry done using stagnant electrolyte solutions.

Solution 26

Hydrodynamic voltammetry is done by introducing convective bulk flow to the electrolyte solution. This can be done by moving the fluid while keeping the electrode stationary (e.g. channel electrode or wall jet electrode), or by moving the electrode to drive movement of the fluid (e.g. rotating disc electrode).

[Note that similar to stagnant solution voltammetry, the background electrolyte used in hydrodynamic voltammetry should also ideally be inert, conducting and at a relatively high concentration to minimize electrostatic migratory effects.]

The starting point for such methods is to enhance mixing in the solution such that the region near to the electrode surface can maintain a relatively high reactant concentration, instead of becoming rapidly depleted of reactant as compared to bulk concentration. In this way, electron transfer reactions at the electrode can occur with negligible mass transfer effects/limitations and the current response would therefore also not be unnecessarily limited or complicated by secondary effects.

The key advantages of hydrodynamic voltammetry are as follows:

- Allows steady-state current to be achieved (no peak) as voltage is swept to high values. This means the absence of the subsequent decline in current which occurs after a peak.
- Having a steady-state (or limiting) current allows measurements to be easily taken.
- Under controlled hydrodynamics, specific flow characteristics can be created and quantified which allows the electrochemical response to be systematically analyzed. This is possible especially since mass transport processes are distinctly different from electron transfer processes in that the former is non-Faradaic while the latter is Faradaic.
 - One dimensional laminar flow conditions can be easily set up experimentally and quantified analytically.
 - Convection and mass transport rates can be individually varied, and this flexibility in control helps in the analysis of more complex systems such as in estimating electron transfer rates in coupled homogeneous or heterogeneous reactions.
- Only a small amount of forced convection is effective in minimizing mass transfer limitations, as well as other complications such as possible signal noise from natural convection that arises from density differences.
- Currents obtained are moderate to large in magnitude, hence able to produce a large response from a relatively small input (i.e. sensitive technique)
- Hydrodynamic devices can be easily incorporated with electrochemical instrumentation.

Problem 27

In a hydrodynamic voltammetry experiment, a rotating disc electrode is used to drive the flow of an electrolytic solution. The background electrolyte is an inert, conducting aqueous solution of sodium chloride at 0.1 mol/dm^3 .

The electroactive species to be studied, P is known to undergo oxidation when a high potential is applied. The results of a voltammetric experiment done on a solution containing 0.001 mol/dm^3 of P in the background electrolyte are shown below, where the steady-state (or limiting) oxidation current is measured against varying rotation rates of the disc.

$i_L/\mu\text{A}$	2.95	6.7	9.1	10.9	12.0	12.6
$\omega/\text{rad s}^{-1}$	4.4	23	42	60	79	98

- (a) Describe and explain the relationship between current i_L and rotation speed of the disc ω . Other than rotation speed, comment on other factor(s) that might affect current.
- (b) Given that a mass-transport limited current for a rotating disc electrode can be modelled according to the equation below, where F refers to Faraday's

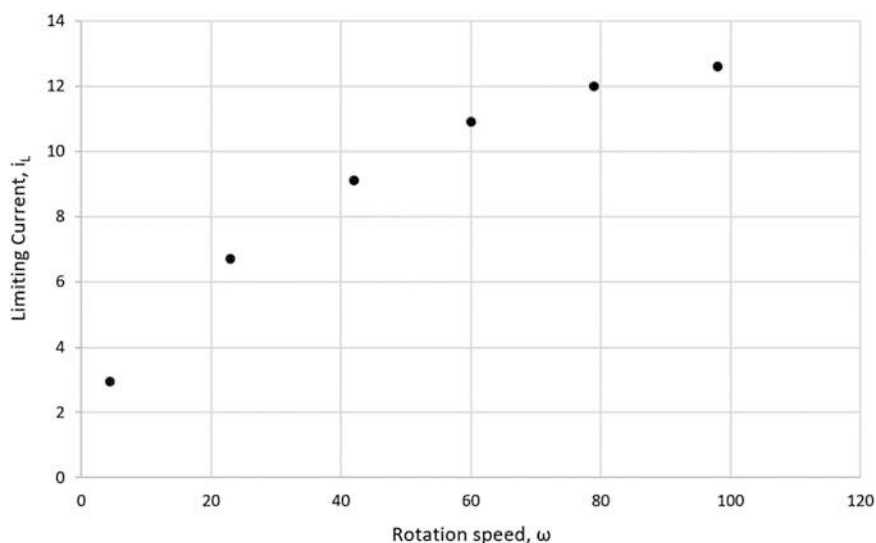
constant, A refers to the electrode surface area, n refers to the number of electrons transferred, C_{bulk} refers to bulk concentration of the electroactive species, D refers to diffusivity, and ν refers to the kinematic viscosity of the solution,

$$i_L = -0.62nFAC_{bulk}D^{2/3}\nu^{-1/6}\omega^{1/2}$$

Comment on whether the electron transfer reaction in the experiment is reversible, explaining your reasons.

Solution 27

(a) Using the data points given, the relationship between the oxidation limiting current i_L and rotation speed ω can be shown in the plot below.

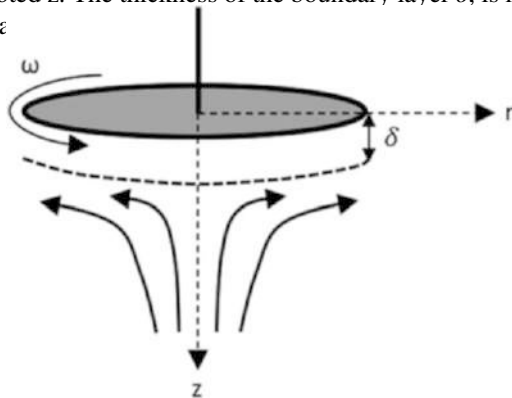


There is a clear dependence between rotation speed and current, and this dependence is more apparent at low to moderate rotation speeds. As ω increases, i_L increases. This positive correlation between rotation speed and current is due to the effect of the rate of mass transport on current. For rapid electron transfer rates, current becomes limited by mass transport (since electron transfer rate is fast enough not to be the limiting factor instead).

Although the rotating disc creates forced convection which drives reacting species from bulk solution closer to the electrode surface, there will always still be a diffusion boundary layer that will form near to the electrode surface (because the surface of the disc is defined by the no-slip condition where fluid velocity is zero). The only variability is in the thickness of this boundary layer at different rotation speeds.

The boundary layer is illustrated in the diagram below. The radial direction from the centre of the disc is denoted r , while the perpendicular direction from the surface

of the disc is denoted z . The thickness of the boundary layer δ , is measured from the surface of the rot:



The disc rotates at a speed of ω rad/second, and fluid moves towards the disc surface and subsequently fan outwards in the radial direction just as they reach the boundary layer ($z = \delta$).

To quantitatively analyse this flow scenario, we can model the flux of reactant species to the electrode surface across the boundary layer using Fick's law (left hand side of equation below). Knowing that mass transport is the limiting factor on current, we can then correlate this diffusional flux with the current produced at the electrode surface as shown below. On the right hand side of the equation, F refers to Faraday's constant, A refers to the electrode surface area, n refers to the number of electrons transferred. While on the left hand side D refers to diffusivity and $\frac{dC}{dz}$ refers to the concentration gradient established across the boundary layer.

$$D \frac{dC}{dz} = \frac{i_L}{nFA}$$

In the presence of forced convection in hydrodynamic systems such as this one, the solution would be largely well-mixed. Therefore, we may assume that reactant concentration anywhere outside of the diffusion boundary layer is uniform and equivalent to bulk concentration C_{bulk} . This means that at $z = \delta$ and beyond, $C = C_{bulk}$.

Since electron transfer rates are rapid, we may also assume that reactants are immediately consumed at the surface and hence $C = 0$ at $z = 0$.

We can now re-express the earlier equation as follows.

$$i_L = nFAD \left(\frac{C_{bulk} - 0}{\delta} \right)$$

As rotation speed ω increases, there is more rapid mass transport of species to the surface and the diffusion boundary layer becomes thinner, i.e. δ decreases.

From the equation above, we know that i_L **will increase** as a result. This explains the observed data and trend that i_L increases with ω .

Other Factors Affecting Current

From the equation above, we may also observe the dependence of i_L on diffusivity D . A higher diffusivity of the species, the more rapid mass transport will be across the boundary layer, and hence a larger current will be observed.

(b) For a reversible electron transfer reaction, the redox reaction at the electrode surface will be rapid, which means that the limiting factor on current would be mass transport rate instead. Using the given equation as shown below for a mass-transport limited system, we can find out if the reactions in the given problem is mass transport limited by using the data points to fit the following correlation (note that this is also known as the Levich equation).

$$i_L = -0.62nFAC_{bulk}D^{2/3}\nu^{-1/6}\omega^{1/2}$$

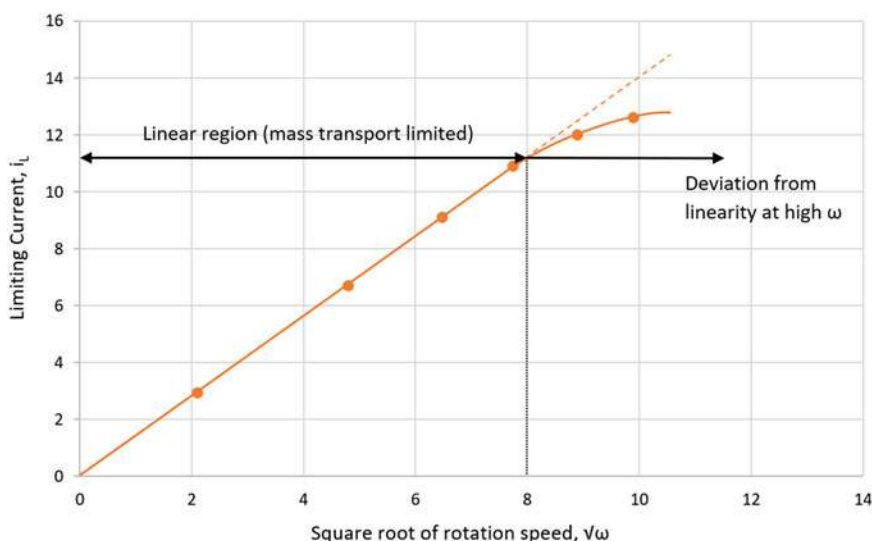
Since we have data for i_L and ω , we can plot a graph of i_L against $\omega^{1/2}$.

i_L	2.95	6.7	9.1	10.9	12.0	12.6
$\omega^{1/2}$	2.098	4.796	6.481	7.746	8.888	9.899

This plot which would give us a straight line with a constant gradient if the reactions were indeed mass transport limited.

$$\text{Gradient} = \frac{\Delta i_L}{\Delta \omega^{1/2}} = -0.62nFAC_{bulk}D^{2/3}\nu^{-1/6} = \text{constant.}$$

The graph obtained from the given data is shown below.



From the graph, we note that at smaller rotation speeds, whereby $\omega^{1/2} \leq 8$ or $\omega \leq 64 \text{ rad s}^{-1}$, the data points fit a linear line of best fit, which verifies that the reaction under the given experimental conditions in this region is mass transport limited. Electron transfer rates are relatively rapid and hence electron transfer reactions are considered reversible in this region.

However, at higher rotation speeds exceeding 64 rad s^{-1} , the linear correlation starts to break down, which means that electron transfer reactions at these speeds are no longer mass transport limited (or only mass-transport limited), and this therefore corresponds to electron transfer rates being less rapid or slower and the electron transfer reactions at these higher speeds can be deduced to be non-reversible.

Deviation from linearity occurs when the rate of electron transfer reactions at the electrode surface slow down until they begin to become comparable to the rate of mass transport (e.g. similar order of magnitude). Some possible reasons that may contribute to this deviation from linearity include:

- Transition from laminar flow into turbulent flow
- Disruptions to mass transport when applied potentials become very high
- Increased resistance effects at high currents
- Slow electron transfer rates at high currents (since the Levich equation assumes rapid electron transfer rate).

Problem 28

A hydrodynamic voltammetry experiment is set up using a channel electrode in an aqueous solution containing an electroactive species that takes part in single electron transfer reactions. The dimensions of the channel electrode, as well as the experimental conditions are shown below.

- Channel size: Height $h = 0.05\text{cm}$; width $w = 0.5\text{cm}$
- Electrode (platinum) size: Length $l_e = 0.35\text{cm}$ and width $w_e = 0.35\text{cm}$
- Background electrolyte: Aqueous solution of NaCl at 0.1 mol/dm^{-3}
- Diffusivity of electroactive species $D = 4.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$

The mass transport limited reduction current i_L was measured as a function of the volumetric flow rate V_f of the bulk fluid in the channel, with the results shown in the table below.

$i_L/\mu\text{A}$	-9.6	-23.4	-35.2	-38.9	-41.8	-43.9
$V_f/\text{cm}^3 \text{ s}^{-1}$	3.2	7.8	15.4	26.0	42.9	63.8

The Levich equation below may be used to model mass transport limited current in this channel electrode:

$$i_L = -0.9nFC_{\text{bulk}}D^{\frac{2}{3}}\left(\frac{l_e^2 w_e^3}{h^2 w}\right)^{\frac{1}{3}}V_f^{\frac{1}{3}}$$

- (a) Assuming that the applied potential is sufficient to fully reduce all the electroactive species at the electrode surface, explain why i_L varies with V_f .
- (b) Explain why current varies with distance along the channel electrode, and comment on any differences with another hydrodynamic device, the rotating disc electrode.
- (c) From the above results, determine the bulk concentration of the electroactive species and list down any assumptions made.

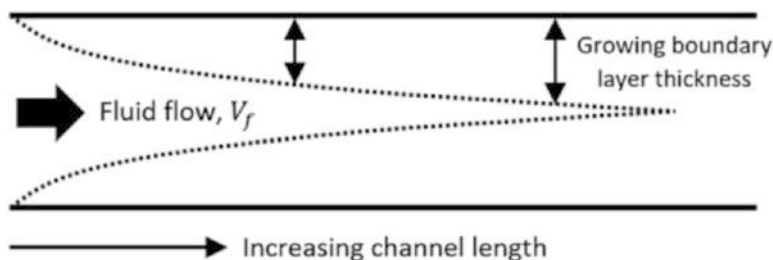
Solution 28

(a) An increase in volumetric flow rate in the channel results in a reduced thickness of the diffusion boundary layer that develops near the walls of the channel. With a thinner diffusion boundary layer, the concentration gradient across it is steeper and electroactive species get transported across this thinner layer to the electrode surface for redox reactions much faster, resulting in a higher current.

(b) Assuming one dimensional laminar flow in the channel, then current is expected to decrease as we move further along the channel from the entrance of flow. This is due to an increasing thickness of the diffusion boundary layer with increasing channel length.

Special Note

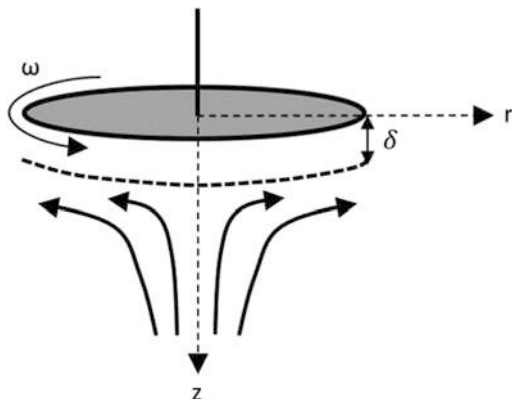
For a circular pipe, the growing boundary layers eventually meet at the midpoint of the channel, after which the flow is known as fully developed. For fully developed laminar flow in a pipe, the velocity profile is parabolic, with a maximum velocity along the centreline of the pipe.



Channel electrodes typically consist of an electrolyte solution subjected to bulk convective flow over a stationary electrode mounted on the channel surface along the channel length. Channel electrodes, unlike rotating disc electrodes are not uniformly accessible by the electroactive species due to this non-uniform thickness of boundary layer along its length. Thus, current varies with distance along the channel electrode.

On the other hand, rotating disc electrodes are different such that the boundary layer near the electrode surface is of uniform thickness across the entire disc. This is shown in the diagram below where δ denotes the uniform thickness of the diffusion boundary layer. A disc is placed in solution and rotated at a constant speed ω . As solution is spun out from the disc surface radially, fresh reactant is drawn upwards

towards the disc (along the z axis). The boundary layer grows in the direction along the z axis from the disc surface, perpendicular to the surface.



(c) Given the mass-transport limited equation for limiting current in a channel electrode as follows:

$$i_L = -0.9nFC_{bulk}D^{\frac{2}{3}}\left(\frac{l_e^2w_e^3}{h^2w}\right)^{\frac{1}{3}}V_f^{\frac{1}{3}}$$

We may substitute values for the defined parameters as follows:

- $n = 1$ for a single electron transfer reaction
- $F = 96500 \text{ C mol}^{-1}$
- $D = 4.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$.
- $l_e = 0.35 \text{ cm}$
- $w_e = 0.35 \text{ cm}$
- $h = 0.05 \text{ cm}$
- $w = 0.5 \text{ cm}$

This gives us the following simplified equation for current:

$$i_L = -0.9(1)(96500)C_{bulk}(4.8 \times 10^{-6})^{\frac{2}{3}}\left(\frac{0.35^2 0.35^3}{0.05^2 (0.5)}\right)^{\frac{1}{3}}V_f^{\frac{1}{3}}$$

$$i_L[\text{A}] \cong -40C_{bulk}V_f^{\frac{1}{3}}[\text{Cs}^{-1}]$$

Note that the units of current i_L on the left hand side of the expression above is in Amperes (indicated in square brackets). By definition, current is a rate of flow of charge and is measured in Amperes which is numerically equivalent to Coulombs

per second or Cs^{-1} . Therefore, the units of the combined expression on the right hand side must also be in Cs^{-1} .

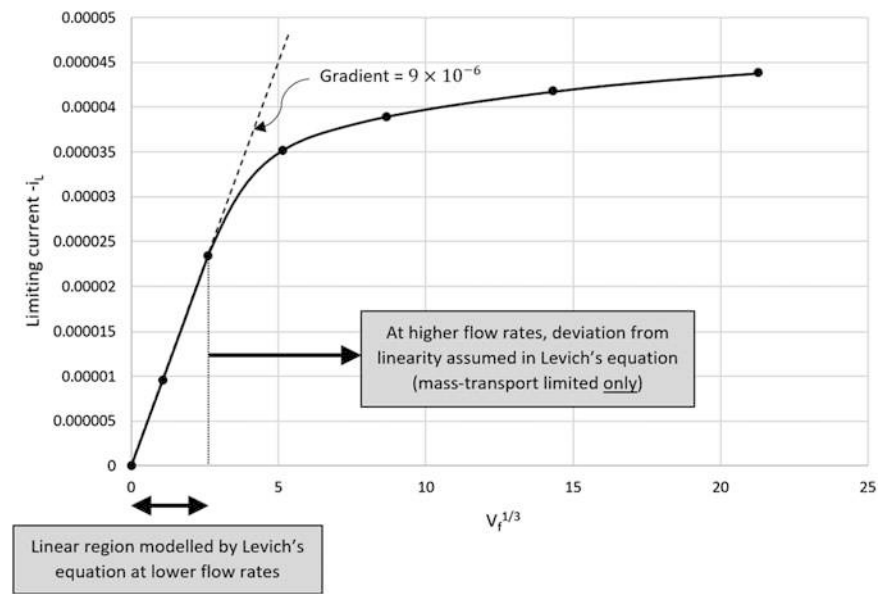
Now we can use the given data for current at different volumetric flow rates to find C_{bulk} . Note that current values in the table are negative as they refer to **reduction** current. This explains why our expression above has a negative sign on the right hand side. To simplify our analysis, we can convert the negative current values to positive and calculate data points to plot a graph of $-i_L$ against $V_f^{\frac{1}{3}}$. This is shown below.

$-i_L \text{ (positive values)} \cong 40C_{bulk}V_f^{\frac{1}{3}}$

$i_L/\mu A$	-9.6	-23.4	-35.2	-38.9	-41.8	-43.9
$-i_L/A$ (positive values)	9.6×10^{-6}	23.4×10^{-6}	35.2×10^{-6}	38.9×10^{-6}	41.8×10^{-6}	43.9×10^{-6}
$V_f/cm^3\ s^{-1}$	3.2	7.8	15.4	26.0	42.9	63.8
$V_f^{\frac{1}{3}}/cm\ s^{-\frac{1}{3}}$	1.067	2.600	5.133	8.667	14.300	21.267

Our plot should be a **straight line that passes through the origin** with a constant **positive gradient** equivalent to $40C_{bulk}$, **if it was mass-transport limited only**, according to the **underlying assumption in using Levich's equation**.

We notice from our plot however that there is a deviation from linearity at high volumetric flow rates (beyond $\sim 8\ cm^3s^{-1}$), which means that the assumption of having only mass-transport limitations breaks down in that region. Therefore, we should select only the linear region at lower flow rates in determining an accurate gradient from our plot to compute the value of C_{bulk} .



Note that the units of C_{bulk} would be **moles per cm^3** based on the units we have adopted in this solution.

$$\text{Gradient value} = 9 \times 10^{-6} = 40C_{bulk}$$

$$C_{bulk} = \frac{9 \times 10^{-6}}{40}$$

$$C_{bulk} = 2.25 \times 10^{-7} \text{ mol cm}^{-3} \text{ or } 0.225 \text{ mmol dm}^{-3}$$

Reasons for Deviation from Linearity

Deviation from linearity means that the rate of electron transfer reactions at the electrode surface slow down until they begin to become comparable to the rate of mass transport (e.g. similar order of magnitude). This may occur at high current values and/or high flow rates due to the following factors:

- Transition from laminar flow into turbulent flow
- Increased resistance effects at high currents
- Slow electron transfer rates at high currents (Levich equation assumes rapid electron transfer rate).

Electrochemical Cell Types and Applications



Abstract This chapter serves to widen the student's understanding beyond textbook examples, by including real-life scenarios that mimic modern day electrochemical systems and considerations, examples include fuel cells, renewable batteries, and solar cells. This chapter therefore aims to provide contextual and hence well-rounded understanding of electrochemical methods and how they relate to current real-world problems and constraints. The combined use of free-response and numerical problems in this chapter will help enhance this understanding.

Keywords Fuel cell · Concentration polarization · Gratzel cell · Solar cell · Dye-sensitized · Conduction band · Semiconductor · Reforming · Water gas shift reaction · Activation polarization

Problem 29

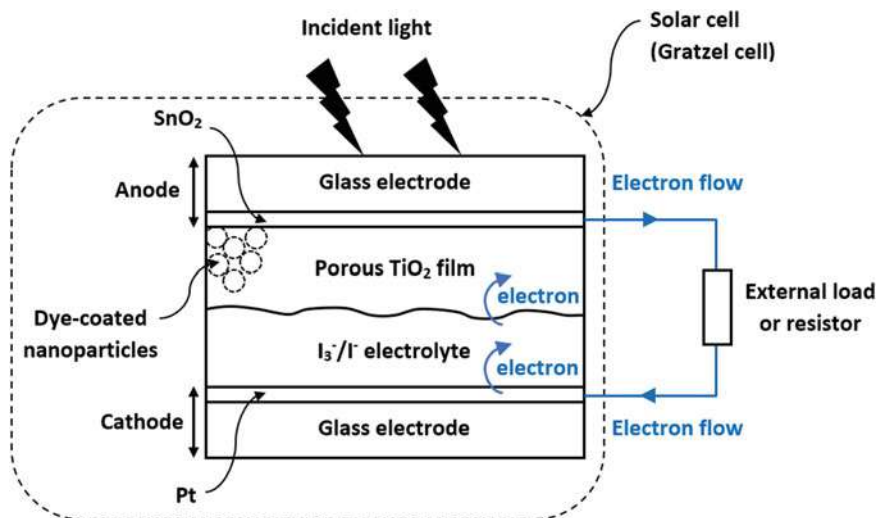
Describe the main components of a dye-sensitized solar cell (e.g. a Gratzel cell) and explain how the device can be used to generate an electric current. Discuss factors affecting the efficiency of a solar cell that operates similarly to a Gratzel cell.

Solution 29

Solar cells convert light energy to electrical energy that supplies our electrical needs. A Gratzel cell is specific type of solar cell that operates on a similar principle as photosynthesis in plants, specifically the electron transport mechanism in the light dependent reaction of photosynthesis.

A Gratzel cell is also called a dye-sensitized solar cell or DSSC. The DSSC uses a Ruthenium-based dye that is coated on nanoparticles of a semiconductor, titanium dioxide (TiO_2). This acts as an absorber of light for the cell. There are glass electrodes at each end of the cell that connects to an external circuit, and each glass electrode is coated with a conducting film; the anode is coated with tin oxide, SnO_2 while the cathode is coated with platinum.

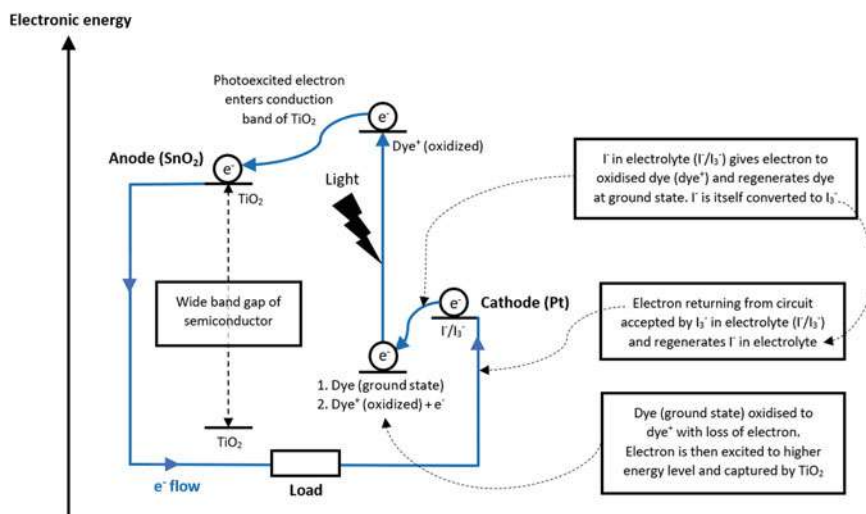
Electrons flow out of the solar cell from the anode and returns to the cell at the cathode.



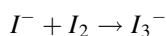
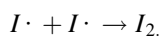
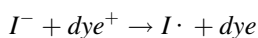
Mechanism

The electrolyte solution of the Gratzel cell is an iodine/iodide solution (I^-/I_3^-) that is able to supply and receive electrons via its redox reactions. Near the cathode end, electrons are supplied by the I^-/I_3^- electrolyte to the ground state (i.e. lowest energy state or unexcited state) of the dye. Under incident light, the electrons of the dye molecule absorb energy (photons) and become excited from ground state to an excited state or higher energy state. The excited electrons of the dye molecules are captured by the conduction band of TiO_2 since dye molecules are in close proximity to the TiO_2 particles (dye-coated). The electrons diffuse through TiO_2 to the collecting anode which is connected to an external circuit. The capture of electrons by TiO_2 also leaves the dye molecule positively charged (dye^+) as it loses electrons to TiO_2 . The positively charged (or oxidized) dye accepts electrons from the surrounding liquid electrolyte to regenerate its original un-oxidized state. As for the electrolyte, it regains its balance of electrons by receiving electrons back from the external circuit.

In summary, the dye layer on TiO_2 effectively helps ‘pump’ electrons from one electrode (the liquid electrolyte) to the other electrode (the solid TiO_2).



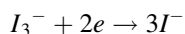
Regeneration of Dye from Dye^+



Note that I is an uncharged iodide atom.

Regeneration of I^- in Electrolyte

Since I^- was used to regenerate dye, it itself gets converted to I_3^- . The supply of I^- is then regenerated via the reduction reaction that occurs at the platinum electrode where electrons are received.

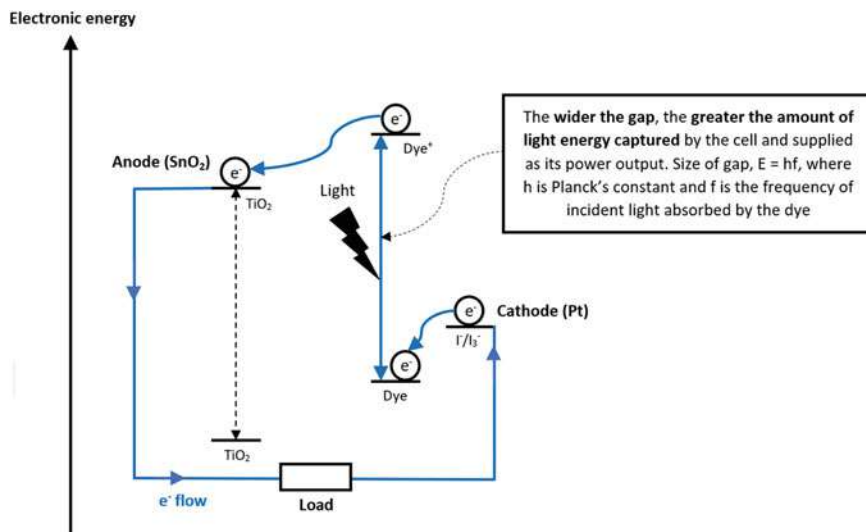


Key Features of the Gratzel Cell

- The use of nanocrystalline TiO_2 particles (~ 20 nm) coated by a photosensitive dye ensures high optical absorption which means almost all light within the spectral range of the dye can be absorbed by just a very thin coating of no more than a few angstroms.
- The TiO_2 particles form a porous colloidal layer in the cell, measuring about $10\mu\text{m}$ thick. Within this thin TiO_2 film or layer, there is a high surface area of contact with the electrolyte solution. Therefore, the efficiency of the cell is largely dependent on the characteristics of the dye-coated nanoparticle (e.g. particle size, surface energy states, particle size distribution, absorption wavelength of dye).
- TiO_2 is a low-cost material that can be easily produced in bulk quantities, and is desirable due to its chemically inert, non-toxic and biocompatible properties.
- TiO_2 allows easy adsorption of molecules to its surface, hence a suitable material for dye coating.

Factors Affecting the Efficiency of a Solar Cell

- **Back reaction:** instead of getting captured by the anode, the photoexcited electron may recombine with the surrounding electrolyte. This leads to major power losses for the cell.
- **Absorption wavelengths of the dye:** the lower the absorbed wavelength, the larger the absorbed frequency. The energy of a photon is directly related to its frequency, hence the larger absorbed frequency leads to a greater amount of light energy captured by the cell. This contributes to a higher photovoltage and larger power output of the cell.



- **Characteristics of the nanoparticle:** particle characteristics such as particle size, particle size distribution will affect the surface area that the dye coating is exposed to its contacting medium. The greater the contact area, the more efficient the cell. Other characteristics such as the adsorption ability of the particle to dye will also affect the robustness of the cell.
- **Type of semiconductor used:** different semiconductors come with different properties and the specific choice depends largely on the application of the solar cell. For example, crystalline silicon cells are used widely in the photovoltaic market due to its well-established technology, long lifetime and good production efficiency. They are more expensive as single crystals; hence multi-crystalline forms are also used for cost effectiveness. Another type of silicon cell, the amorphous silicon cell is cheaper but less efficient, and is more suitable to power consumer products. As for specialized applications such as satellites or other systems that operate under intense sunlight, high efficiency cells are made using gallium arsenide, indium phosphide or their derivatives.

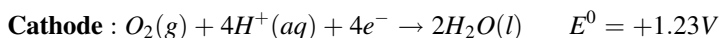
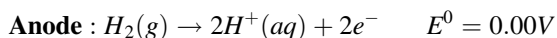
Problem 30

Fuel cells are electrochemical devices that bring together hydrogen and oxygen to generate electricity, in the process producing byproduct water. One of the notable benefits of fuel cells is in the ability to produce 'clean energy' since it produces water which is a harmless waste product, unlike conventional energy sources such as coal and fuel oils that emit pollutive substances upon combustion.

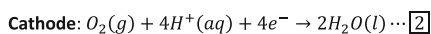
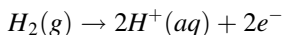
- (a) **With the aid of a suitable diagram, explain how a basic fuel cell works by describing key redox reactions that take place at the electrodes, as well as mass transfer processes occurring in the region near to the electrodes.**
- (b) **Discuss the use of alternative hydrocarbons to replace the use of hydrogen in fuel cells.**
- (c) **Comment on the potential drawbacks in the use of fuel cells, and discuss how these issues may be addressed or minimized.**

Solution 30

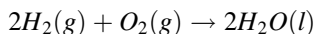
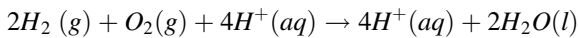
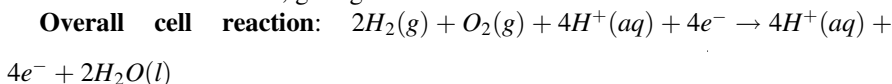
(a) The spontaneous redox reactions that occur at the two platinum electrodes of a hydrogen-oxygen fuel cell are shown below. At the anode, oxidation occurs, producing electrons. At the cathode, reduction occurs, taking in electrons.



The overall cell reaction can be written by combining the two half equations at the anode and cathode respectively, after balancing the number of electrons per half equation as shown below in red.



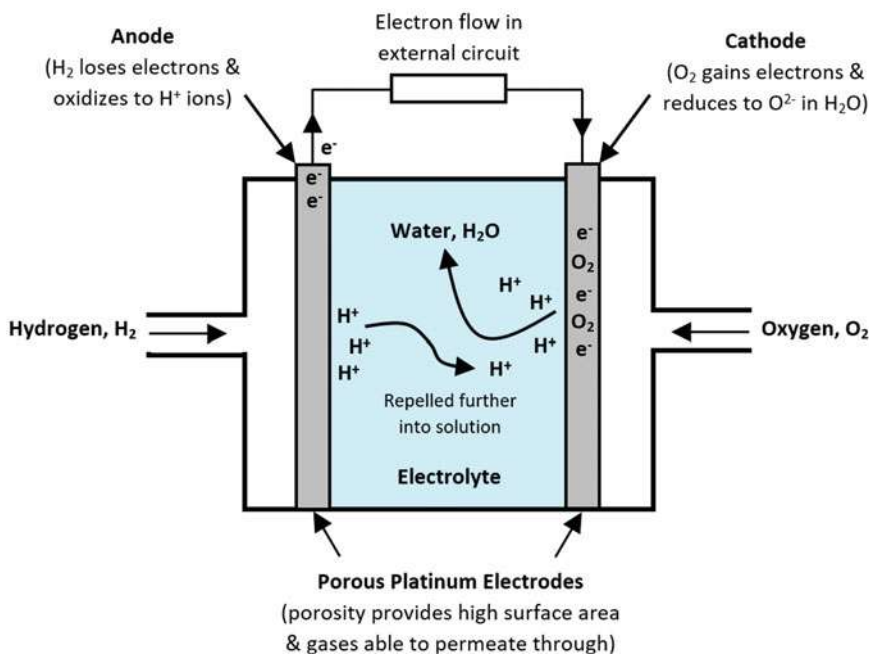
Summing up half equations [1] and [2], common terms on the left and right hand sides can be cancelled off, giving us



Therefore, the overall cell reaction shows the production of water from hydrogen and oxygen fuels, at a standard cell potential of 1.23 V. If multiple cells are connected in series, the combined cell would achieve a combined cell potential

equivalent to the sum of the individual cell potentials, for e.g. 10 cells connected in series would yield 12.3 V. This cell potential is then able to drive an external circuit.

The basic structure and components of a hydrogen-oxygen fuel cell is shown below.



Key Features

Platinum Electrodes

- Platinum is a relatively inert and stable material. Hence its use would prevent unnecessary side reactions from occurring at the electrodes that might disrupt the operations of the cell.
- The electrodes are porous to allow reactant gases to permeate easily, as well as to provide a large surface area for redox reactions to occur, hence optimizing cell efficiency.
- Liquid water that is produced needs to be removed from the reaction sites to prevent blockages that might hinder further redox reactions.
- At the anode, oxidation reactions release hydrogen ions and electrons. Electrons flow out into an external circuit, generating electrical energy. The hydrogen ions

accumulate on the anode, causing a positive potential to be created, which helps repel the positively charged hydrogen ions away from the anode.

- At the cathode, reduction reactions occur as electrons are received back from the external circuit. These electrons combine with the free hydrogen ions present in the electrolyte solution as well as oxygen gas that permeates through the electrode from the gas inlet. The product of this reduction reaction is liquid water.

Reactant Gases (or “Fuel”)

- Gaseous reactants should be as pure as possible to minimize chances of any impurities being left behind and stuck on the electrodes as gases diffuse through them, causing disruptions to the redox reactions.
- Gases diffuse down a concentration gradient from the gas inlet channels to the reaction sites at the electrodes. This concentration gradient varies with temperature and pressure of the gases, as well as the diffusion coefficient of the electrode material.

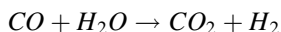
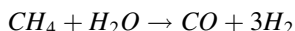
Electrolyte

- An electrolyte is a solution that contains mobile charge carriers which make it an electrical conductor. This is necessary to ensure a closed circuit for electricity to flow.
- Early fuel cells used phosphoric acid as the electrolytic solution, however, the use of liquids lead to bulky devices as there is a need to maintain a minimum separation distance between the electrodes to avoid internal shorting (i.e. electricity flows from one electrode to the other electrode directly through the electrolyte, without going through the external circuit). These issues led to advancements in the use of polymeric membranes as electrolytes instead of liquid electrolytes. These membranes are also known as Proton Exchange Membrane (PEM) or Polymer Electrolyte Membrane (PEM).

(b) Methanol or CH_3OH is sometimes used in place of hydrogen gas as the fuel for fuel cells due to several reasons:

- Safer to handle as compared to hydrogen gas which is highly flammable.
- Methanol is stored as a liquid and can hence be easily transported and stored, unlike hydrogen gas which needs to be liquefied at high pressures for storage and transport.
- Methanol is easily obtainable in its pure form from petroleum refining.
- Methanol can be easily converted into hydrogen via the methanol-steam reforming reaction $CH_3OH + H_2O \rightarrow CO_2 + 3H_2$

Methane or CH_4 (also known as natural gas) can also be used as the fuel substitute for hydrogen gas. Similar to methanol, methane undergoes a methane-steam reforming reaction, producing carbon monoxide and hydrogen gas. The hydrogen gas produced then reacts with more steam in a subsequent reaction called the water-gas shift reaction, forming more hydrogen.



Other than methanol and methane, other types of hydrocarbon fuels can also be used to generate hydrogen via the reforming reaction. Examples include ethanol, propane, or gasoline.

(c) Drawbacks of the hydrogen-oxygen fuel cell can be largely categorized into concentration polarization, activation polarization, ohmic effects and basic design constraints.

Concentration Polarization

- As liquid water is produced in the fuel cell, it may block reaction sites at the electrodes, causing obstruction to the transport of reactant gases from reaching the reaction sites.
 - Water can collect at the anode or cathode, but is more severe at the cathodic side.
- The relatively large size of the oxygen molecule at the cathode side also hinders its transport to the reaction sites at the cathode from the inlet channel.
- Concentration polarization can be minimized by:
 - Increasing the pressure or flow velocity of inlet gas to clear off any blockages.
 - Increasing the surface area of electrodes and hence the availability of reactions sites.
 - Using thinner electrodes to enhance the diffusion /permeability of gases through the electrode material.

Activation Polarization

- Activation polarization as the name suggests, is related to activation energy. It is caused by bond-forming/breaking at the cathode and anode.
- The amount of energy required to form or break bonds has to come from the reactant/fuel itself, this therefore reduces the overall energy output of the cell.
- Activation polarization can be minimized by:

- Increasing the flow rate of reactant gases at the inlet channels, especially at higher reaction rates. This increases kinetic energy of the gas molecules, thereby reducing the amount of energy required to break the bonds within the more energetic gas molecules.
- Increasing temperature of the inlet gases also increases the average kinetic energy of the molecules.
- Increasing the number of reaction sites at the electrode.
- Using a suitable catalyst to reduce activation energy.

Ohmic Effects

- Ohmic effects arise as a result of electrical energy losses in the cell due to increased resistance. Resistance to the flow of electric current can be contributed by components in the fuel cell, such as resistance of movement of reacting species through the electrode materials, resistance to ion movement within the electrolyte, contact resistance at the interfaces between the electrodes and the external circuit.
- Ohmic effects can be reduced by selecting materials with more favorable properties (i.e. with reduced resistance) to be used for contact interfaces and electrodes, as well as suitable electrolytes that are highly conducting with minimal resistance to ionic flow.

Basic Design Constraints

- Issues with the use of hydrogen gas as a fuel relate to difficulties in storage and transport. Some reasons are as follows:
 - It has a very small molecular size and is therefore prone to diffusing through substances, hence escaping from containment vessels.
 - Hydrogen is inherently an excellent reducing agent, and is therefore unstable when in contact with other materials or elements. Hydrogen reacts with most metals and materials, except a select few such as gold, silver, platinum, aluminum (a layer of aluminum oxide forms around the metal, serving as a protective barrier) and stainless steel.
 - Hydrogen is flammable and must also not be placed close to ignition sources to reduce the risk of explosions.
- There are also issues with using oxygen gas as a fuel, some reasons are as follows:
 - Oxygen makes up a relatively small fraction of atmospheric air, therefore, the flow rate of oxygen or the size of the oxygen gas inlet must be sufficiently large in order to support the demands of the cell.
 - Oxygen can easily relight ignition sources, and hence must be placed far away from them.

- Oxygen can easily oxidize other materials, causing corrosion of materials. Therefore, the cell components must be made of pre-selected materials that are less susceptible to such effects.
- Over time, the cell would heat up especially when multiple cells are stacked together. If unregulated, this would hinder the performance of the cell as well as cause safety issues.
 - This effect can be mitigated by introducing cooling fluids that remove heat continuously from the cell, or by using thinner cells (higher surface area to volume ratio) that enhance the rate of heat loss to the surroundings.
- Shorting of the cell may occur easily, especially if the electrolyte is a liquid or if the electrodes are placed too close to each other. This occurs when electric current flows directly from one electrode to the other without passing through the external circuit.
 - This issue can be mitigated by using conducting polymer membranes instead of bulk liquid solutions as the electrolyte.

Problem 31

Electrochemical systems are applied in the automotive industry, particularly in their ability to function as batteries to power vehicles.

- (a) **Explain the difference between primary, secondary, and tertiary batteries.**
- (b) **One of the automotive batteries commonly used is the lead acid battery, due to the ability of lead and its compounds to undergo various electrochemical reactions. Describe the main features of a typical lead acid battery, including the relevant redox reactions that occur, and explain why it is not advisable to over-discharge lead acid batteries.**

Solution 31

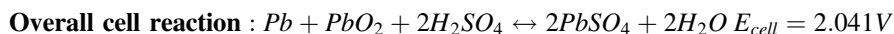
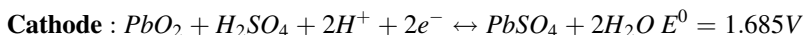
(a) A primary battery is one that is single-use and cannot be recharged. They are often discarded upon use, and some examples include the zinc-carbon dry cell and other regular alkaline batteries (contain alkaline electrolytes).

A secondary battery is one that is rechargeable, and examples include the nickel-cadmium, lead acid and lithium ion batteries. These batteries are normally found in devices such as smartphones, electronic tablets, and automobiles.

Tertiary batteries require a continuous fuel supply. One example is the fuel cell which converts chemical energy into electrical energy. Fuel cells are similar to batteries but require a continuous source of fuel, often hydrogen. They continue to produce electricity as long as there is fuel available. Hydrogen fuel cells have been used to supply power for satellites, space shuttles, automobiles and boats.

(b) The lead acid battery is a type of secondary battery commonly found in automobiles. It is generally low-cost and capable of producing high currents required for vehicle starter motors.

The redox reactions that take place in a lead acid battery are shown below, resulting in an overall supply of approximately 2 V per cell.



Typically, six cells are connected in series to produce a 12 V car battery. Although lead acid batteries are quite heavy as they contain a liquid electrolyte, they are still valued due to their high current output. Due to the significant amount of lead found in these batteries, they must always be disposed of properly.

Reason for Not Over-Discharging

- Lead(II) sulphate, $PbSO_4$ is an electrical insulator and is also an insoluble compound.
- Going back to the overall cell reaction, we note that the direction towards the right represents discharge (or usage) of the battery, while the direction towards the left represents recharge.
- During current flow, both the anode and cathode reactions are driven to the right, producing $PbSO_4$. The $PbSO_4$ that is formed is deposited on the Pb and PbO_2 electrode surfaces.
- If the battery was over-discharged, the layer of $PbSO_4$ formed becomes too thick.
- Therefore, it may not be possible to recharge the battery again for reuse, since the reverse redox process (to the left) cannot take place if the layer of $PbSO_4$ develops into a significantly thick barrier.

Index

A

Activation polarization, 117–120

B

Biosensor (glucose sensor), 62, 77, 78

Boundary layer, 37–39, 45, 46, 52, 53, 69, 75, 76, 80, 95, 101–103, 105, 106

C

Capacitive charging (charging effects), 62

Cell EMF, 7–9

Cell potentials, 4–7, 16, 23, 114, 115

Cell reactions, 25–27, 114, 120

Channel electrodes, 99, 104–106

Concentration polarization, 117

Cottrell's equation, 40

Cyclic voltammetry, 34, 47, 48, 52, 56, 64, 72, 80, 87, 93

E

Electrical neutrality, 10, 19, 22

Electric double layer (EDL), 20, 22

Electrochemical cells, 4–6, 8, 10–14, 23

Electrode kinetics (reversible, quasi-reversible, irreversible), 16

Electrolytic cells, 11, 12

F

Fick's law, 18, 102

Fuel cells, v, 113–119

G

Gouy-Chapman (GC) model, 21

Gratzel cell, 109, 110, 112

H

Half-cell, 1–6, 9, 10, 12, 15, 16, 25–27

Helmholtz model, 18–22

I

Internal resistance, 7–9

L

Lead acid batteries, 119, 120

Levich equation, 103, 104, 108

Ligand (Ligand exchange reaction), 84–86

Limiting current, 63, 68, 77, 97, 101, 106

Linear sweeps, 34, 42, 43, 48

M

Microelectrodes, 62, 67–69, 84, 85, 87, 90, 93, 94, 96, 98

N

Nernst equation, 3, 22–24, 26–29, 44, 46, 54, 56

O

Ohmic effects, 117, 118

Outer Helmholtz plane (OHP), 20, 22

P

pH electrode (pH sensor), 24–26

Polarization effects, 117

Potential step, 34–36, 39, 40

R

Reference electrode (standard hydrogen electrode/SHE), 2, 3

Rotating disc electrodes, 92, 99, 100, 105

Rotational speed, 18, 92

S

Salt bridge, 4–5, 9–16, 27

Solar cells, 71, 109, 112–114

Steady state current, 67, 68, 85, 90, 91, 100