DISCIPLINE-SPECIFIC ELECTIVE COURSE - 24 (DSE-24)

Interfacial Electrochemistry

CREDIT DISTRIBUTION, ELIGIBILITY AND PRE-REQUISITES OF THE COURSE

Coursetitle & Code	Credits	Credit distribution of the course			Eligibility criteria	Pre-requisite of the course (if any)
		Lecture	Tutorial	Practical/ Practice		
Interfacial Electrochemistry (DSE-24)	4	2	--	2	--	--

Learning Objectives:

- To introduce the structure and thermodynamics of electrochemical interfaces including models of the electric double layer.
- To explain electrode kinetics with emphasis on Butler-Volmer kinetics, Tafel plots, and cyclic voltammetry.
- To introduce Marcus theory and concepts of electrocatalysis and corrosion with real-world relevance.
- To explain transport in electrolyte solutions using laws of diffusion laws, Debye-Hückel theory, and transport numbers.
- To explore adsorption thermodynamics and applications of electrochemical principles in energy storage and conversion devices.

Learning Outcomes:

By the end of the course, students will be able to:

- Explain and compare models of electric double layer and relate them to interfacial properties.
- Apply the Butler-Volmer equation and cyclic voltammetry to interpret reaction mechanisms.
- Describe Marcus theory and the role of parameters in HER, OER and corrosion control.
- Interpret adsorption isotherms and thermodynamic data related to interface processes.
- Evaluate electrochemical energy devices like fuel cells, batteries and supercapacitor

SYLLABUS OF DSE 24

Unit 1: Structure and Thermodynamics of Electrochemical Interface (Hours: 5)

Overview of interfaces and electrochemical systems.Electric Double Layer: Models: Helmholtz Model, Gouy-Chapman Model (derivation), Stern Model, Graham-Devanathan-Mott-Watts model, Tobin, Bockris-Devanathan model, Thermodynamics of the EDL

Electrocapillary phenomena

Unit 2: Electrode Kinetics and Cyclic Voltammetry (6 Hours)

Standard, formal and equilibrium potentials, Overpotentials and their types, Butler-Volmer equation: Derivation and its physical implications, Exchange current density and transfer coefficient, Tafel equation and graphical interpretation, Cyclic voltammetry: Theory and experimental design. Distinguishing reversible, quasi-reversible, irreversible, and capacitive processes.

Unit 3: Electron Transfer and Electrocatalysis and Transport in Electrolytes (Hours: 9)

Marcus theory (qualitative description only): activationless region, reorganization energy

Introduction to electrocatalysis, Parameters influencing HER, OER, and oxygen reduction reaction (ORR), Role of electrode material. Ionic mobility and transport number, Fick's laws of diffusion, Einstein equation for diffusion. Debye–Hückel–Onsager limiting law, Electrophoretic and relaxation effects, time of relaxation. Dependence of transport number on concentration

Unit 4: Adsorption, Surface Thermodynamics and Corrosion & its control (10 hours)

Adsorption of ions and molecules at interfaces, Thermodynamic treatment of adsorption

Adsorption isotherms:Langmuir, Frumkin, Temkin, Determination of surface excess and charge

Types of corrosion: uniform, galvanic, pitting, crevice, etc., Thermodynamics and kinetic aspects.

Monitoring methods: electrochemical noise, impedance, Inhibition and protective coatings.

Electrochemical Energy Conversion and Storage**:** Fuel cells: PEMFC, Alkaline, Methanol, Batteries: Lithium-ion, Redox flow, Supercapacitors: EDLC and pseudocapacitors. Comparative performance and limitations

Practical Component

1. Conductometric Titration of a Charge Transfer System, the formation of charge transfer complex between an electron donor and acceptor is studied and the stoichiometry of the complex is determined by following the variation of conductance of the solution with concentration of the donor and acceptor.

2. Study of the oscillating reaction using the Ce^{3+}/Ce^{4+} system; and the dependence of the oscillation period on the metal ion concentration.
3. Intercalation of sodium into vanadium oxide and potentiometric estimation of extent of intercalation.
4. Effect of ionic strength on reaction rate (persulfate-iodine reaction).
5. Potentiometric determination of solubility and solubility product of AgCl(s) in water.
6. Potentiometric determination of mean ionic activity coefficient of HCl at different concentrations.
7. Potentiometric titration of Phosphoric acid vs NaOH.
8. Determination of dissociation constant of acetic acid from its potentiometric titration curve.

Instruction Mode: Demonstration/ Discussion of working principle/ Hands-on with substantial literature analysis/ Laboratory exercise

9. Record cyclic voltammogram for the electrochemical capacitors (electric double layer) response with varying scan rates,

i) plot anodic and cathodic plateau currents vs scan rates.

(Use aqueous solution of 1.5 M $NaNO_3$)

10. Record cyclic voltammogram for a reversible heterogeneous electron transfer system with varying scan rates,

(i) Determine anodic and cathodic peak current ratio.

(ii) Determine anodic and cathodic peak potential difference.

(iii) Plot peak current vs square root of scan rates.

(Use aqueous solution of 10 mM $K_4Fe(CN)_6$ + $K_3Fe(CN)_6$ + 1.5 M $NaNO_3$)

11. Record cyclic voltammogram for a quasi-reversible heterogeneous electron transfer system with varying scan rates,

(i) Determine anodic and cathodic peak current ratio.

(ii) Determine anodic and cathodic peak potential difference.

(iii) Plot peak current vs square root of scan rates.

(Use aqueous solution of 10mM $Fe(NH_4)_2(SO_4)_2$ + $Fe(NH_4)(SO_4)_2$ + 1 M $HClO_4$)

12. Record the CV of aqueous solution of sulphuric acid (0.5 M) at Pt electrode as working electrode and counter electrode.

(i) Interpret and explain various peaks and region of the CV and their significance.

Determine the area and roughness factor of the electrode by Pt oxide region.

Recommended References and Text Books: (For theory)

1. Bard, A. J. Faulkner, L. R. Electrochemical Methods: Fundamentals and Applications, 2nd Ed., John Wiley & Sons: New York, 2002.
2. Oldham, K. B., Myland, J. C. and Bond, A. M. Electrochemical Science and Technology: Fundamental and Applications, John Wiley & Sons, Ltd. (2012).
3. Bagotsky, V.S., Fundamentals of electrochemistry 2nd Ed. Wiley – Interscience, (2006)

Supplementary References

1. Bockris, J. O' M. & Reddy, A. K. N. Modern Electrochemistry 1: Ionics 2nd Ed., Springer (1998).
2. Bockris, J. O' M. & Reddy, A. K. N. Modern Electrochemistry 2B: Electrodics in Chemistry, Engineering, Biology and Environmental Science 2nd Ed., Springer (2001).
3. Bockris, J. O' M., Reddy, A. K. N. & Gamboa-Aldeco, M. E. Modern Electrochemistry 2A: Fundamentals of Electrodics 2nd Ed., Springer (2001).
4. Brett, C. M. A. & Brett, A. M. O. Electrochemistry, Oxford University Press (1993).
5. Koryta, J., Dvorak, J. & Kavan, L. Principles of Electrochemistry John Wiley & Sons: NY (1993).
6. Hamann, Carl H., Hamneff, Andrew &Vielstich, Wolf., Electrochemistry, 2nd Ed. (2007)

Recommended References and Text Books: (For practicals)

1. Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. A Practical Beginner's Guide to Cyclic Voltammetry, *J. Chem. Educ.***2018**, *95*, *2*, 197–206.
2. B. D. Khosla, V. C. Garg, A. Gulati, Senior Practical Physical Chemistry, R. Chand & Co, New Delhi.
3. Field, R. J.; Schneider, F. W. Oscillating Chemical Reactions and Nonlinear Dynamics, *J. Chem. Educ.***1989**, *66*, *3*, 195–204.