THIRD YEAR CHEMISTRY

DYNAMIC ELECTROCHEMISTRY

Pre-Workshop questions

1. Employ the *mobility* values in table PW1 to:

(a) Calculate the *drift speed* of Li^+, Na^+ and K^+ in water at 298 K when a potential difference of 10 V is applied across a 1.0 cm conductivity cell.

(b) Estimate how long will take these ions to drift from one electrode to the other.

(c) Taking the *mobility* of SO_4^{2-} as 8.29×10^{-8} $m^2\ s^{-1}\ V^{-1}$, calculate the *limiting molar conductivity* of Li_2SO_4.

Table PW1. Ionic mobility at 298 K

	Li^+	Na^+	K^+
u / (10^{-8} $m^2\ s^{-1}\ V^{-1}$)	4.01	5.19	7.62

2. For a reaction at 298K in which $n = 1$, $\alpha = 0.5$, $j_0 = 2.0\times10^{-6}$ A cm^{-2} and ignoring mass transfer effects, calculate the current flowing at overpotentials of 30 mV and 150 mV using (a) the Butler-Volmer equation and (b) the Tafel equation. With reference to your answers, comment on the validity of the Tafel equation.

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Workshop questions

1. The data tabulated was obtained for the couple Ce^{4+}/Ce^{3+} at a 0.5 cm^2 Pt electrode at 298K. Assuming the process is controlled by the electron transfer kinetics, estimate:

(i) the exchange current density (j_0)

(ii) the transfer coefficient (α).

η / mV	150	175	200	225	250	275
i / μA	78.2	112.5	150.3	178.8	212.7	288.9

2. The current-potential curve in figure W1 corresponds to the two electron reduction of O_2 to hydrogen peroxide at a rotating disc electrode in a O_2 saturated solution ($c_{O2} = 10^{-3}$ mol dm^{-3}).

(i) Explain the origin of the current plateau at potentials lower than 0.6 V.

(ii) The current measured at 0.6 V vs SHE as a function of the rotation frequency (f) is summarised in table W1. Use these data to estimate the diffusion coefficient (D_O) of O_2 assuming that the process is fully controlled by mass transport (reversible process). Take the temperature of the solution as 298 K, the kinematic viscosity (ν) as 0.01 cm^2 s^{-1} and the surface area of the electrode (A) is 0.196 cm^2. *Hint*: Employ the Levich equation and transform the rotation frequency (f) into the angular rotation rate ($\omega = 2\pi f$)

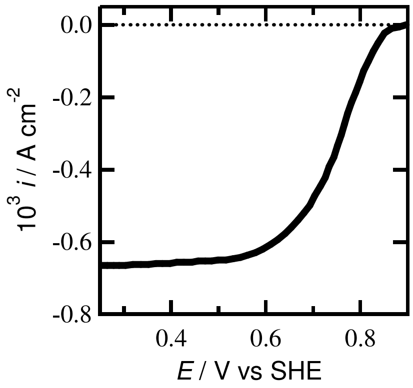

Figure W1. Current-potential curve associated with the reduction of oxygen at a rotating disc electrode at 2500 rpm.

Table W1. Current at 0.6 V vs SHE as a function the frequency of rotation.

I / A	f / rpm
0.0007194	3600
0.0006261	2500
0.0005012	1600
0.0003790	900
0.0003146	625

3. Figures W2 and W3 display cyclic voltammograms of 1 electron processes at conventional sized electrodes (e.g. 0.1 cm^2). From the shape of the voltammograms at various scan rates, identify the type of electrochemical

reaction taking place and comment on their *reversibility* (i.e. fast or slow electron transfer kinetics). Use the appropriate equations for estimating the concentration of the reduced species. When needed, take a diffusion coefficient of 1×10^{-5} cm^2 s^{-1}.

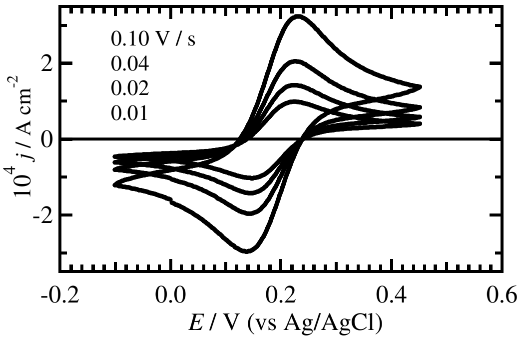

Figure W2. Cyclic voltammograms measured from 0.01 to 0.10 V s^{-1}.

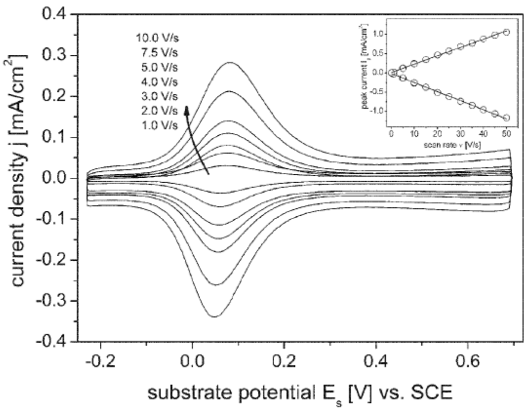

Figure W3. Cyclic voltammograms measured from 1 to 10 V s^{-1}. Taken from Albrecht et al., Faraday Disc. 2006.

Useful constants,

Viscosity of water: $\eta = 0.891\times10^{-3}$ kg m^{-1} s^{-1}

Gas constant: $R = 8.314$ J K^{-1} mol^{-1}

Faraday constant: $F = 96485$ C mol^{-1}

Boltzmann constant: $k_B = 1.38\times10^{-23}$ J K^{-1}

Dynamic Electrochemistry

List of symbols

a	Activity Hydrodynamic radius	 m
A	Electrode area Debye- Hückel constant (e.g. eqn. 1.7) Arrhenius constant (e.g. eqn. 2.5)	m^2 0.509 mol^{-1} dm$^{3/2}$ s^{-1}
c	Molar concentration	mol m^{-3}
D	Diffusion coefficient	m^2 s^{-1}
e	Elementary charge	1.602×10^{-19} C
E	Electrode potential	V
$\vec{E}$	Electric field	V m^{-1}
f	Frequency of rotation	rpm
F	Faraday constant	96485 C mol^{-1}
$\mathbb{F}$	Force	N
G	Conductance Gibbs Energy	S(siemens) J
i	Electrical current	A
j	Flux of species Current density	mol m^{-2} s^{-1} A m^{-2}
k	Rate constant	het. first order - cm s^{-1}
k_B	Boltzmann constant	1.38×10^{-23} J K^{-1}
L	Distance separating the electrodes in a conductivity cell	m
K	Kohlrausch constant	S mol$^{-3/2}$ m$^{5/2}$
n	Number of electrons transferred in a redox step	
Q	Charge transferred in a electrochemical process	C
r	Ultramicroelectrode radius	m
R	Gas constant Distance between redox species from the electrode surface (solv. reorganisation eqn. 2.18)	8.314 J mol^{-1} K^{-1} m
R_{ct}	Charge transfer resistance	Ω
s	Drift speed	m s^{-1}
t	Time	s
T	Temperature	K
u	Mobility	m^2 s^{-1} V^{-1}
v	Reaction rate	mol cm^{-2} s^{-1}
x	Distance normal to the surface	m
z	Ionic charge number	

α	Electron transfer coefficient Degree of ionisation (eq. 1.9)	
β	Tunnelling attenuation constant (eqn. 5.3)	Å^{-1}
χ	Dimensionless current (eqn. 4.18)	
δ	Diffusion layer thickness	m
ε	Permittivity of free space	8.854×10^{-12} J^{-1} C^2 m^{-1}
ε_r	Relative permittivity	
ε_o	Optical permittivity	
ϕ	Galvani potential	V
γ	Activity coefficient	
Γ	Surface excess	mol m^{-2}
η	Solution viscosity Overpotential	Kg m^{-1} s^{-1} V
κ	Conductivity	S m^{-1}
κ_{el}	Electronic transmission coefficient (eqn. 2.7)	
λ	Limiting molar conductivity of an ion Electron transfer reorganisation energy (eqn. 2.18)	S m^2 mol^{-1} J
Λ_m	Molar conductivity	S m^2 mol^{-1}
$\Lambda_m{}^\circ$	Limiting molar conductivity of a salt	S m^2 mol^{-1}
μ	Chemical potential	J mol^{-1}
$\tilde{\mu}$	Electrochemical potential	J mol^{-1}
ν	Ionic number per formula unit Kinematic viscosity Potential scan rate	 cm^2 s^{-1} V s^{-1}
ν_n	Electron transfer nuclear frequency factor (eqn. 2.7)	s^{-1}
θ	Concentration ratio of the redox species at the electrode surface	
σ	Dimensionless potential scan rate	
ω	Angular rotation rate	s^{-1}
ψ	Dimensionless rate constant	