2014

Interdisciplinary Graduate School of Medicine and Engineering, Doctoral Course, University of Yamanashi

Entrance Examination

Course or Program	Special Doctoral Program for Green Energy Conversion Science and Technology	Subject	Electrochemistry

If necessary, use the following constants for the calculation.
R = 8.314 J K^{-1} mol^{-1}, F = 96500 C mol^{-1}

Question 1

Answer the following question.

(1) The Butler-Volmer equation for an electrochemical reaction $O + n\,e^- \leftrightarrows R$ is written as

$$\frac{i}{i_0} = \left(\frac{C_R}{C_R^{eq}}\right)\exp\left(\frac{\alpha_a nF\eta}{RT}\right) - \left(\frac{C_O}{C_O^{eq}}\right)\exp\left(-\frac{\alpha_c nF\eta}{RT}\right)$$

Derive the equations for the activation overpotential η as a function of the current density i for three cases (a) $\eta >> 0$ (positive enough), (b) $\eta << 0$ (negative enough), and (c) $\eta \approx 0$ (close to zero) with the use of an appropriate approximation. Explain the meaning of i_0, α_a, and α_c briefly.

(2) When n = 1, α_a = 0.50, and T = 298 K, calculate the value of Tafel slope and the current density i at η = 0.12 V with i_0 = 0.10 mA cm^{-2}. Neglect the ohmic loss and the concentration polarization.

(3) Name a practical storage battery with an alkaline electrolyte solution and one with an acidic electrolyte solution. Explain the materials of electrodes and electrolyte of each battery. Explain the characteristics (applications, advantages, disadvantages, etc) of each battery.

(4) Select one type of fuel cell among PEFC, MCFC, and SOFC. Explain the operation principle schematically, component materials, possible applications, and one of major problems to be solved for the large-scale commercialization (simple answer such as a cost reduction or performance improvement cannot be acceptable).

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Question 2

Answer the following questions.

(1) The ohmic resistance of 0.200 mol L^{-1} KCl aqueous solution with the conductivity of 2.50 S m^{-1} (Ω^{-1} m^{-1}) was measured to be 12.0 Ω in a conductivity cell. Calculate the cell constant (l/A) of the cell employed and the molar conductivity of the NaCl solution.

(2) The molar ionic conductivities of K^+ and SO_4^{2-} at the infinite dilution and 298 K are 0.00735 and 0.0160 S m^2 mol^{-1}, respectively. Calculate the transference number (transport number) and mobility of each ion in the K_2SO_4 solution.

(3) Explain the standard hydrogen electrode and the standard electrode potential, clarifying the meaning of "standard".

(4) A galvanic cell Pt | H_2 (1 atm) | H^+ ‖ Fe^{2+}, Fe^{3+} | Pt was assembled at 298 K. The standard electrode potential of the right-hand electrode of the cell is 0.771 V.
(a) Write the reactions of left-hand and right-hand electrodes, and the overall cell reaction.
(b) Calculate the standard Gibbs free energy and the equilibrium constant of the cell reaction.
(c) Write the Nernst equation for the electromotive force of the cell as a function of activities, $a[Fe^{3+}]$, $a[Fe^{2+}]$, and pH. Calculate the value of electromotive force with $a[Fe^{3+}]/a[Fe^{2+}] = 2$ and pH = 3.