

A study on electronic and ionic conductor for a PKL electrochemical cell

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Abstract

In this research work, it has been studied about the electronic and ionic conductor for a PKL cell. There are a lot of parameters for electronic and ionic conductor for PKL electrochemical cell. In this research work it has been studied on several parameters like the Anode & Cathode, Working electrode, Counter electrode, Reference electrode, Electrode potential, Relationship between the quantity of current(charge) and the quantity of (electro) chemical change, Modes of charge transport, the amount of chemical change and the amount of current passed, Significance of charging currents, Ion transport, Transport numbers, Conductance of an electrolyte, Modes of mass transport, Conductivity of an electrolyte, Terminal velocity of ion, mobility, opposing force, Resistance of the device, oxidation and reduction reactions and Minimizing R, IR Compensation.

Keywords: Electronic conductor, Ionic Conductor, Ion transport, mobility, Conductivity of an electrolyte, working electrode.

I. INTRODUCTION

Electrochemistry is defined as the branch of chemistry that examines the phenomena resulting from combined chemical and electrical effects [1-10]. This field covers: Electrolytic processes: Reactions in which chemical changes occur on the passage of an electrical current -Galvanic or Voltaic processes: Chemical reactions that result in the production of electrical energy. An electrochemical cell typically consists of: Two electronic conductors (also called electrodes) and An ionic conductor (called an electrolyte) [11-20].

II. Methodology

II A. Modes of charge transport

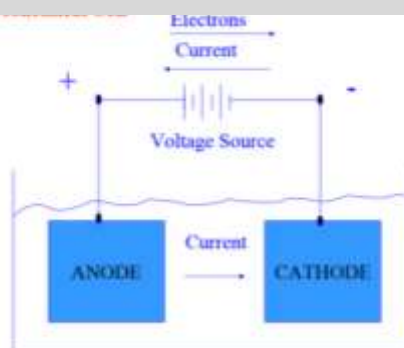


Fig.1 A normal electrochemical cell

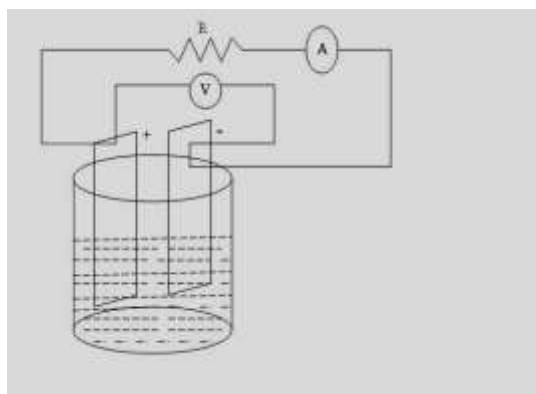


Fig.2 A PKL electrochemical cell

Charge transport in the electrodes occurs via the motion of electrons (or holes), Charge transport in the electrolyte occurs via the motion of ions (positive and negative)[21-29]. The half cell and overall reactions are: At each electrode, an electrochemical reaction occurs. This reaction is called a half cell reaction (since there are two electrodes in a typical cell at which reactions occur)[30-40]. The overall chemical reaction of the cell is given by combining the two individual half cell reactions. There are two fundamental types of half cell reactions: Oxidation reactions and Reduction reactions A reaction is classified as oxidation or reduction depending on the direction of electron transfer[41-50]. The Oxidation includes: Involves the loss of an electron and Involves the transfer of electrons from the species to the electrode [51-60]: $R = O + ne \dots\dots\dots (1)$ Oxidation is an energetic process, and occurs when the energy of the electrode dips below the highest occupied molecular orbital of the compound.

The Reduction includes: Involves the gain of an electron and Involves the transfer of electrons from the electrode to the species [61-70]: $O + ne = R\dots\dots\dots (2)$ Reduction is also an energetic process, and occurs when the energy of the electrode increases above the lowest vacant molecular orbital of the compound.

Reactions at Zinc and Copper metal: Zinc metal gets oxidized which goes into PKL solution [71-80]: $Zn = Zn^{2+} + 2e \dots\dots\dots (3)$, where, the Copper ions in solution are reduced; the copper metal deposited on the cop

per electrode: $Cu^{2+} + 2e = Cu \dots\dots\dots (4)$

Anode & Cathode: Electrode at which the oxidation reaction occurs is called the anode and the Electrode at which the reduction reaction occurs is called the cathode. Thus in the above example, the zinc electrode was the anode and the copper electrode was the cathode [81-86].

Working electrode: The electrode at which the reaction of interest occurs is called the working electrode[87-90].

Counter electrode: The electrode at which the other (coupled) reaction occurs is called the counter electrode.

Reference electrode: A third electrode, called the reference electrode may also be used. For a given set of two reversible redox reactions, Thermodynamics predicts which reaction proceeds as an oxidation and which proceeds as a reduction. It was studied PKL sap as a bio-electrolyte and selected because of some properties like low pH, high electrical conductivity, economic value, cultivation facility and availability [91-95].

II B. Electrode potential:

The electrode potential for a reaction is derived directly from the free energy change for that reaction, $\Delta G = -nFE$.

The standard oxidation potential is equal in magnitude, but opposite in sign to the standard reduction potential. There are a set of 2 competing reactions with the lower standard reduction potential gets oxidized and the other reaction proceeds as a reduction[96-100]:

$Zn = Zn^{2+} + 2e \dots\dots\dots(3)$, where, $E^{\circ}_{red} = - 0.7618 V$

$Cu^{2+} + 2e = Cu \dots \dots (4)$, where, $E_{red} = 0.341 V$

Thus, in the above example, Zn is oxidized, and Cu is reduced. $\Delta G_{cell} = -nFE_{cell}$, where,

$E_{cell} = E_{cathode} - E_{anode}$, For a feasible reaction: E_{cell} must be positive (so that ΔG_{cell} is negative and recall thermodynamic criterion for feasibility). Therefore:

$E_{cathode} - E_{anode} > 0$ or $E_{cathode} > E_{anode}$

Since oxidation occurs at the anode –the species with the lower reduction potential will get oxidized. This is to ensure that ΔG_{cell} is negative[101-110]. This is why Zn got oxidized (and Cu reduced) in the above example. In this case: $E_{cell} = 1.102$. If the reverse were to occur, E_{cell} would be -1.102 , leading to a positive ΔG_{cell} .

II C. Relationship between the quantity of current(charge) and the quantity of (electro) chemical change:

The relationship between the quantities of current (charge) passed through a system, and the quantity of (electro) chemical change that occurs due to the passage of the current is given by the following equation[111-120]: $m = M I t / n F \dots \dots (5)$, where, m = mass of substance, M = molecular weight of the substance, I = current passed (A), t = time for which the current is passed (s), n = number of electrons transferred, F = Faraday constant (96475 C /eqv).

II D. The amount of chemical change and the amount of current passed through the electrochemical cell:

All processes that obey Faraday’s law are termed faradaic processes. All these processes involve electron transfer at an electrode / electrolyte interface. These reactions are also called electron / charge transfer reactions. Electrodes at which these processes occur are called charge transfer electrodes. Sometimes changes exist in the electrode / electrolyte interface without charge transfer taking place[121-127]. These changes are due to processes such as adsorption and desorption. Such processes are called nonfaradaic processes. No electrons flow through the electrode / electrolyte interface during nonfaradaic processes. However, transient external currents can be generated by nonfaradaic processes. An electrode at which there is no charge transfer across the electrode / electrolyte interface over all potential ranges is called an ideally polarized electrode (IPE).

II E. Mathematical treatment

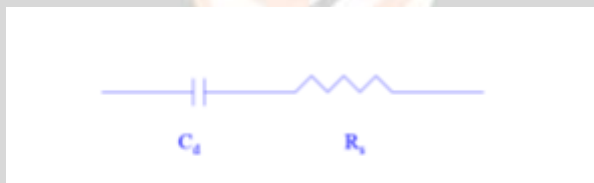


Fig.3 Resistor and capacitor are in series combination

The charge, $Q = C_d E \dots \dots (6)$, which is known as capacitor equation. Here, Q = charge stored in coulombs (C) C_d = capacitance in farads (F), E = potential across the capacitor /IPE (V), When voltage is applied across an IPE, the “electrical double layer” is charged until equation (6) is obeyed. During charging, a charging current flows through the system.

II F. Significance of charging currents

It contributes to total current measured. It cannot be ignored especially for low faradaic currents and it may exceed faradaic currents in such cases. To better understand the effect of charging, we need to examine mathematically the responses of an IPE to various electrochemical stimuli. It is shown that , the model representation

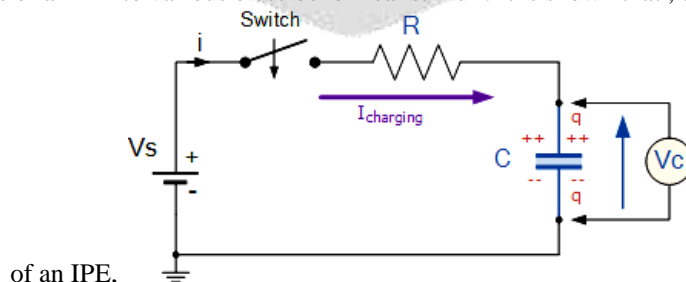


Fig.4 RC circuit for charging case.

The IPE system can be represented as a capacitance(C) in series with the electrolyte resistance@.

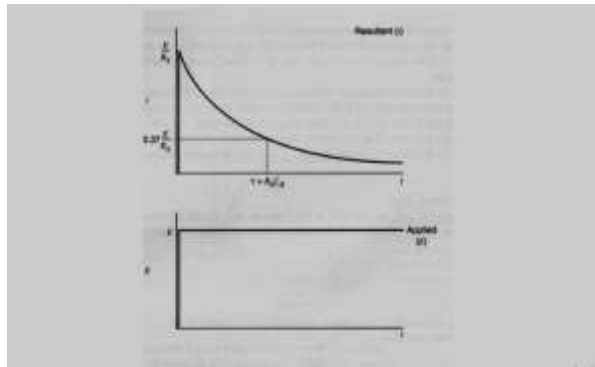


Fig.5 Exponential behavior of the electrochemical cell

II G. Types of resistance

Electronic resistance: It is due to electronic current through electrodes and external circuit and can be minimized by using electron conducting materials.

Ionic resistance: It is due to ionic current through electrolyte and needs to be considered seriously as it leads to losses.

II H. Ion transport

At the anode: excess of positive ions – build up of positive charge.

At the cathode: excess of negative ions build up of negative charge.

Buildup of ionic charge: released by the ion transport.

Positive ions move from anode to cathode and vice versa

II I. Transport numbers

The fractions of current carried by the positive and negative ions are given by their transport numbers t_+ + t_- respectively. Each mole of current passed corresponds to 1 mole of electrochemical change at each electrode. Therefore the amount of ions transported in the electrolyte also equals 1 mol. Thus: $t_+ + t_- = 1$ (7)

For multiple species More generally, $\sum t_i = 1$ (8) This equation is valid when more than one type of ion is in solution. The transport numbers of ions are determined by the conductance (L) of the electrolyte.

II J. Conductance of an electrolyte:

The conductance of an electrolyte is given by:

$L = \kappa A / l$ (8), Where, A = active area of contact, l = length (thickness) of electrolyte matrix, κ = conductivity -intrinsic property of the electrolyte. Conductance has units of Seimens (S), and conductivity of S/cm.

II K. Conductivity of an electrolyte:

The conductivity of the electrolyte has a contribution from every ion in solution/sap/extract. Conductivity is proportional to: concentration of the ion (C) , charge of ion (z) and mobility (a property that determines its migration velocity–also called mobility)[128].

II L. Mobility

Mobility is defined as the limiting velocity of the ion in an electric field of unit strength. Now, force exerted by an electric field of strength E is given by[129]:

$F = e E z$... (9), Where e is the electronic charge.

II M. Opposing force

An opposing force exists due to frictional drag. This is represented by the Stokes equation: $F_{opp} = 6\pi\eta r v$... (10), η = viscosity of the solution, r = ionic radius and v = velocity of the ion in solution/extract/sap.

II N. Terminal velocity of ion

When the forces exactly counterbalance each other, the ion attains a steady state velocity called the terminal velocity[130]. This terminal velocity is termed the mobility (u) when the electric field strength is unity:

$u = z e / 6\pi\eta r$ (11)

II O. Back to conductivity

With the above expression for mobility (Equation-9), we write the following expression for κ ,

$$\kappa = F \sum z_i u_i C_i \dots \dots \dots (12)$$

Now it can be said that transport no. (t) is the contribution made by each individual ion to the total current carried in solution.

II P. Expression for transport number

The transport no. may be represented as the ratio of the contribution to conductivity made by a particular ion to the total conductivity of the solution [131].

$$\text{Thus: } t_i = z_i u_i C_i / \sum z_i u_i C_i \dots \dots \dots (13)$$

II Q. Resistance

Resistance is defined as: $R = l / \kappa A \dots \dots (14)$

The ionic resistance is an inherent property of the ion in motion and the electrolyte. Effect of resistance in electrochemical cells get Ohm's law:

$$V = IR \dots \dots \dots (15)$$

R will introduce a potential drop and V which will increase with current. More appropriately Ohm's law is expressed as [132]: $I = \kappa (d\Phi/dx) \dots \dots (16)$,

Where, $d\phi(x)/dx =$ potential gradient.

III A. Minimizing R, IR Compensation

R can be minimized by: minimizing distance between electrodes and increasing area of contact (not preferred—this is governed by many other factors). It is needed to realize that some portion of R will always remain. So realistically:

$$E_{\text{measured}} = E_{\text{cathode}} - E_{\text{anode}} - IR \dots \dots (17)$$

If the value of R is known, one can compensate for ohmic drop then the compensated E is a closer representation of the actual E:

$$E_{\text{compensated/actual}} = E_{\text{measured}} + IR \dots \dots \dots (18)$$

III A. Modes of mass transport

There are 3 fundamental modes of mass transport in solution. They are:

1. Migration—this is the motion of a charge body (such as an ion) under the influence of an electrical potential gradient.
2. Diffusion—this is the motion of a species under the influence of a chemical potential gradient.
3. Convection—this is hydrodynamic transport either due to density gradients (natural convection) or due to external means such as stirring (forced convection)

IV. Results and Discussion

Ohmic drops occur due to IR in the electrolyte and the electrodes. So that the IR in the electrode should not be neglected. The IR compensation in both the electrolyte and the electrode shall be considered seriously. A thin layer of electrolyte (thickness δ) in contact with the electrode surface -ion transfer controlled solely by diffusion. The Concentration of species is maintained constant outside this layer (in the bulk) by convective transfer. When the potential is 0 V then no net faradaic current When the potential exceeds 0V then the faradaic oxidation $H_2 = H^+ + e^-$. As potential moves to more positive values then overpotential/ electrochemical driving force is for oxidation increases and reaction proceeds faster until it hits the mass transport limit, since hydrogen oxidation kinetics are fast, this limit is quickly attained.

V. Conclusions:

It is shown that the reactants are consumed at the electrode.

The larger the current, the faster the rate of consumption, which follows the Faraday's law. The reactants arrive at the electrode via transport from the bulk

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