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Exchange current density and Tafel plot

Butler volmer equation

$$i = i_c - i_a = i_0\left[\exp\left(\frac{\alpha z F \eta_i}{RT}\right) - \exp\left(\frac{-(1-\alpha) z F \eta_i}{RT}\right)\right] \quad \text{(A)}$$

If the current density i is plotted against the overpotential in accordane with equ (A) Two cases are shown.

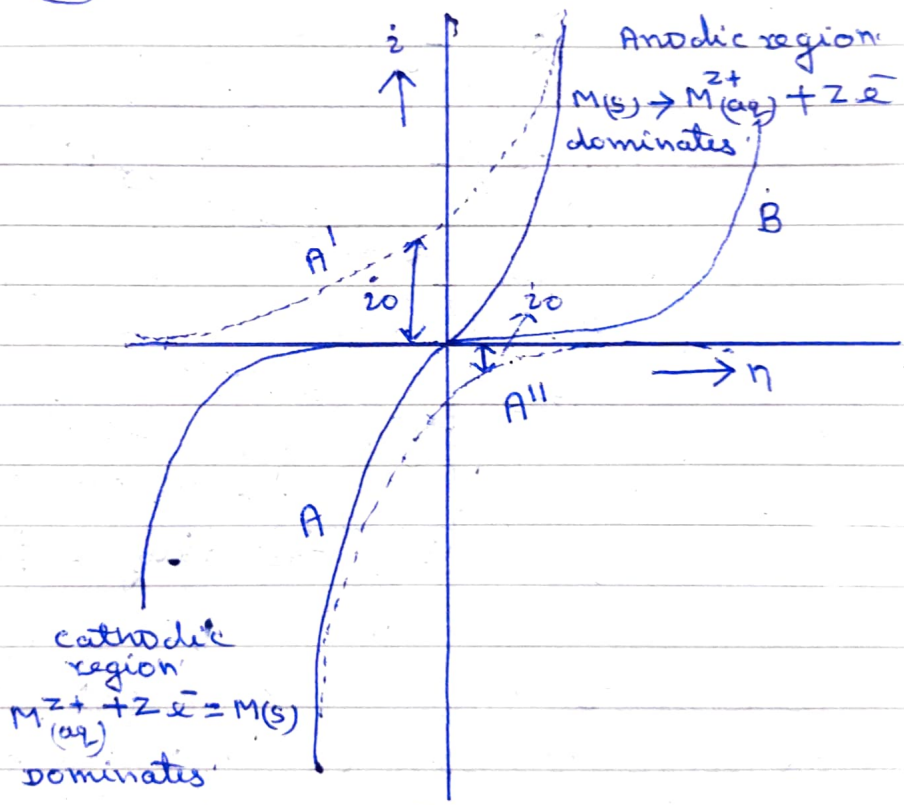

Fig (1)

one labelled 'A' is a case in which there is rather high exchange current i_0 at both electrodes. The other case labelled 'B' corresponds to a very low exchange current i_0. In this case, a large overpotential is required to cause appreciable current

flow the cell.

We see that, factor that determines the activation overpotential, in accord with Butler-Volmer equation, is the exchange current density i_0. The transfer factor α influences the shape of the current density i vs overpotential η curve as fig II

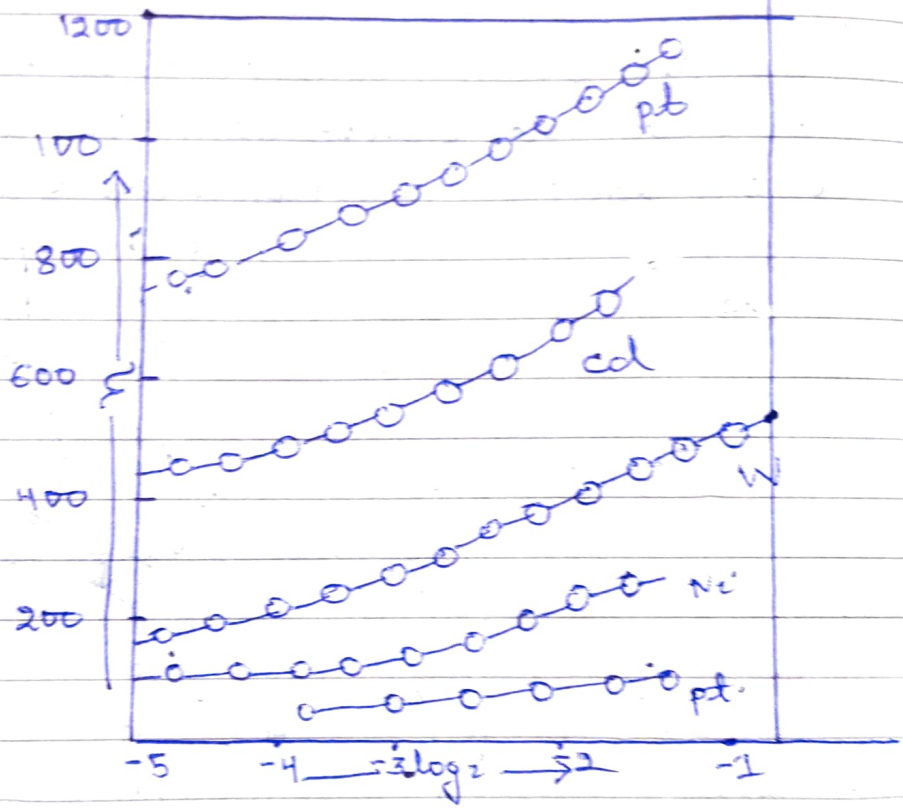

fig. II

One way to measure α to fit the experimental curve to the Butler-Volmer equ.

<u>Tafel plot or Equations</u> :-

If the overpotential has large +ve or (-ve) values $\eta \gg RT/nF$, one of the partial currents becomes much greater than the other, which is negligible in this case

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either.

$$\ln i_a = \ln i_0 - [(1-\alpha) zF/RT]\eta \quad \text{——— (B)}$$

or

$$\ln i_c = \ln i_0 + (\alpha zF/RT)\eta \quad \text{——— (C)}$$

This type of logarithmic dependence of i on η was found ~~empir~~ empirically in 1905 by Tafel.

The slop of linear $\ln i$ vs η plots gives the transfer coefficient α and the intercept gives the exchange current density i_0 by fig. II.

Over potential can be caused by slow reaction in the solution adjacent to an electrode. and in the process of deposition of a solid product on an electrode. In many cases, a diffusion overpotential occurs together with an activation over potential and methods are available for seprating these factor. Thus, a great varity of interesting chemical kinetics can be studied by electronic techniques. practical application of this branch are found in such fields as fuel cells, storage batteries for vachicle, electro-chemical synthesis. etc.