

Analysis of workfunction dependence of the standard exchange current density  
S.Harinipriya ,M.V. Sangaranarayanan\*

Department of chemistry  
Indian Institute of Technology – Madras  
600 036 India

### 1. Introduction

The theoretical analysis of charge transfer reactions at electrode / electrolyte interfaces has been a topic of numerous investigations during the past few decades and the mechanistic aspects of these reactions is essentially centered around the question of adiabaticity vs non- adiabaticity, inner sphere vs outer sphere, nature of solvent polarisation modes and the role of electronic density of states [1],[2]. Here, we report an explicit expression for the exchange current density in terms of work function of the metal surface, surface potentials of the species involved and Gibbs free energy changes associated with adsorption of solvent dipoles. The proposed methodology is applied to ferric / ferrous reaction whose  $i_0$  values have been reported for a variety of electrodes using experimental data and theoretical calculations.

### 2. Free energy of activation and standard exchange current density

The electron transfer rate constant  $k_{et}$  is related to standard exchange current density  $i_0$  as

$$i_0 = (nF C_R k_{et} / A) \exp\{-\beta n F E_e / RT\} \quad (1)$$

Further, one may express  $k_{et}$  in terms of free energy of activation ( $\Delta G^\ddagger$ ) as

$$k_{et} = (k_b T / h) \exp\{-\Delta G^\ddagger / RT\} \quad (2)$$

Equations (1) and (2) enable the calculation of  $k_{et}$  and  $i_0$ , using  $\Delta G^\ddagger$  estimates. Further,

$$\Delta G_{et} = -nF\xi\Phi_M \quad (3)$$

where  $\xi$  is a simple function involving the surface potential and chemical potential of electrons in solvent. After

incorporating solvation characteristics and adsorption behaviour of solvent dipoles,  $\log i_0$  is obtained as

$$\log i_0 = A + B\Phi_M \quad (4)$$

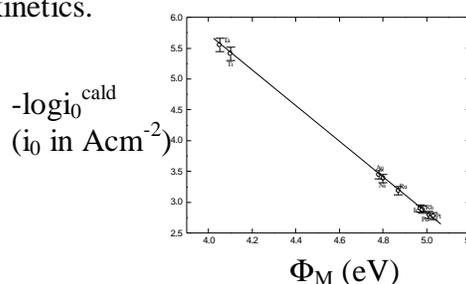
where A and B involve the bulk free energy of solvation, solvation numbers, surface potentials etc. The applicability of the above equation to  $Fe^{3+}/Fe^{2+}$  at different metal electrodes is depicted in Fig 1.

### 3. Discussion

The free energy of activation can also be obtained as

$$\Delta G^\ddagger = \alpha_1 + \alpha_2 \Phi_M \quad (5)$$

where  $\alpha_1$  and  $\alpha_2$  are parameters containing ionic and solvent characteristics. The availability of an explicit expression for the exchange current density and the free energy of activation in terms of work function of the metal, nature of the reactant species and solvent characteristics enables investigating a variety of issues arising in heterogeneous electron transfer reactions. The dependence of exchange current density on the electronic structure of metals has been a central focus of investigation in density functional theory pertaining to electrode kinetics.



### References

1. See for example, Schmickler, W, *Ann. Rep. Prog. Chem. Sect. C*, The Chemical Society London, **1999**, 95, 117 and references therein.
2. Straus, J. B; Calhoun, A; Voth, G. A; *J. Chem. Phys.*, **1995**, 102, 529.