SUPPORT MATERIAL

Balanced work function as a driver for facile hydrogen evolution reaction - comprehension and experimental assessment of interfacial catalytic descriptor

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The energy to transfer the electron from the Fermi level of the metal to the inner Helmholtz plane of the double layer (Φ^*), through the metal/solvent interface can be brought into relation with the absolute electrode potential (E_{abs}) of a metal covered by a liquid layer. In analogy to the definition of the work function, E_{abs} is defined as the minimum work to extract an electron from the Fermi level, through the solid/liquid interface (with the potential drop), through the liquid and through the surface layer of the liquid to a position just outside the liquid. It can be perceived as a modified or an "electrochemical" work function and can be expressed as following:¹

$$eE_{abs} = \Phi^* = -\mu_e^{chem} + e(\Delta_S^M \phi + \chi_S)$$
 Equation S1

where μ^{chem}_{e} is the chemical potential of electron in the metal, while $\Delta_{S}^{M}\phi$ is the Galvani (inner) potential difference between the bulk of the metal and the bulk of the electrolyte and χ_{S} is the surface potential of the electrolyte in contact with the vacuum. The electron at rest in vacuum is taken as the reference point.² By the formal definition the Galvani potential (ϕ) for one phase (metal or electrolyte) in contact with vacuum is the sum of the surface potential (χ) and the Volta (outer) potential (ψ) so the Galvani potential difference should be:

$$\Delta_S^M \phi = \phi_M - \phi_S = \Delta_S^M \chi + \Delta_S^M \psi$$
 Equation S2

However when an interface is created between two phases, surface potentials (the electrostatic work to transport the charged electron through the dipole layer of the surface) are modified for the phase interactions.³ Namely, the surface potential of the metal is changed due to the interaction with the liquid phase:

$$g_{(S)}^{M}(dip) = \chi_{M} + \delta \chi_{(S)}^{M}$$
Equation S3

At the same time the surface potential of the electrolyte is altered due to interaction with the solid phase:

$$g_{(M)}^{S}(dip) = \chi_{S} + \delta \chi_{(M)}^{S}$$
Equation S4

Consequently the potential drop at the interface induced by the altered surface potentials of two phases will be:

$$g_{S}^{M}(dip) = g_{(S)}^{M}(dip) - g_{(M)}^{S}(dip)$$
Equation S5

Besides the altered surface potentials, another contributor to the electric potential drop between the two phases is the charge separation in the double layer. That is in fact the contribution of the ions in the double layer $(\mathcal{G}_{S}^{M}(ion))$ to the overall Galvani potential difference between the two phases. Consequently, the Galvani potential difference between the bulk of the solid and the bulk of the liquid will be the sum of ionic and dipole contributions:

$$\Delta_S^M \phi = g_S^M(ion) + g_S^M(dip)$$
Equation S6

When we combine Eq.1 with Eqs.S1-S6 we get:

 ΔG^*

$$= \Delta G_{desorp} + W_{H+} + \Delta G_{desolv} - \mu_{e}^{chem} + Fg_{S}^{M}(ion) + F\chi_{M} + F\delta\chi_{(S)}^{M} - F\chi_{S} - \chi_{(M)}^{S} + F\chi_{S}$$

Equation S7

Eq.S7 lists all important contributions to the activation energy for the reduction of a proton. Worthy to stress is that the complexity of Eq.S7 is a good illustration why an individual bulk or surface property of the material is insufficient as a catalytic descriptor. As shown with Eq.S3 and Eq.S4 the presence of a neighbouring phase changes the surface region of the observed phase in an unpredictable manner.

A few reasonable assumptions can be made to reduce the complexity of Eq.S7:

1) the difference between the surface potential of the metal and the chemical potential of the electron in the metal is equal to the work function of the metal in contact with vacuum $(F\chi_M - \mu_e^{chem} = \Phi^M)$. This relation indicates that adsorbate which creates dipole at solid/liquid interface, induces change in work function through change in surface potential, because chemical potential of the metal does not change significantly with adsorption. In other words, despite we cannot access value of surface potential, we can access its change via change in work function. Change in work function is proportional to magnitude of surface dipole or to metal-adsorbate bond strength.

2) from Eq.S2-S6 it seems that
$$\Delta_S^M \psi = g_S^M(ion) + F \delta \chi_{(S)}^M - F \delta \chi_{(M)}^S$$

3) at the potential of zero charge (E_{pzc}) there is no charge separation in the double layer $(g_S^M(ion) = 0)$. However, the Volta potential (equivalent to the potential drop from the infinity point in the vacuum to a position just outside the surface of the phase) difference remains and equals to $F\delta\chi_{(S)}^M - F\delta\chi_{(M)}^S$.

Consequently, Eq.S7 can be transformed into the following expression containing the work function of the metal in vacuum (Φ^M) and the contact potential difference $\Delta_S^M \psi$ (both quantities are measurable using SKP):

$$\Delta G^* = \Delta G_{desorp} + W_{H+} + \Delta G_{desolv} + (\Phi^M + \Delta_S^M \psi)$$
Equation
S8

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