ABSOLUTE ELECTRODE POTENTIAL IN SOLID AND AQUEOUS ELECTROCHEMISTRY

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A two Kelvin probe arrangement has been used to measure, simultaneously for the first time, the work function of emersed and spillover modified electrodes (working, counter and reference), in aqueous and solid electrolyte galvanic cells, respectively. The measurements have shown that the cell potential reflects the difference in the work functions of the emersed or spillover-modified electrodes:

$$eU_{WR} = \Phi_W - \Phi_R \qquad (1)$$
$$e\Delta U_{WR} = \Delta \Phi_W \qquad (2)$$

where the subscripts W and R refer to the working and reference electrode respectively.

These results suggest directly that the work function of emersed or spillover modified electrodes can be used as the absolute electrode potential, in agreement with theoretical considerations (1,2).

Some data showing the validity of Equations (1) and (2) in solid state and aqueous electrochemistry, respectively, are presented in Figures 1 and 2. In the former case the electrolyte is Yttria-stabilized-ZrO$_2$ (YSZ). In the latter case the electrolyte is 0.1 M HCl aqueous solution with Pt electrodes.

The values of 4.65 V and 5.14 eV, respectively, have been obtained for the absolute electrode potential of the standard hydrogen electrode in H$_2$O (pH=0) and for the standard oxygen electrode in contact with Yttria-stabilized-Zirconia (YSZ) in solid state electrochemistry.

References

1. S. Trasatti, "Structure of the metal/electrolyte solution interface: New data for theory", *Electrochimica Acta,* **36**, 1659 (1991).
2. D. Tsiplakides and C.G. Vayenas, "Electrode work function and absolute potential scale in solid state electrochemistry", *J. Electrochemical Soc.*, **148**(5), E189-E202 (2001).
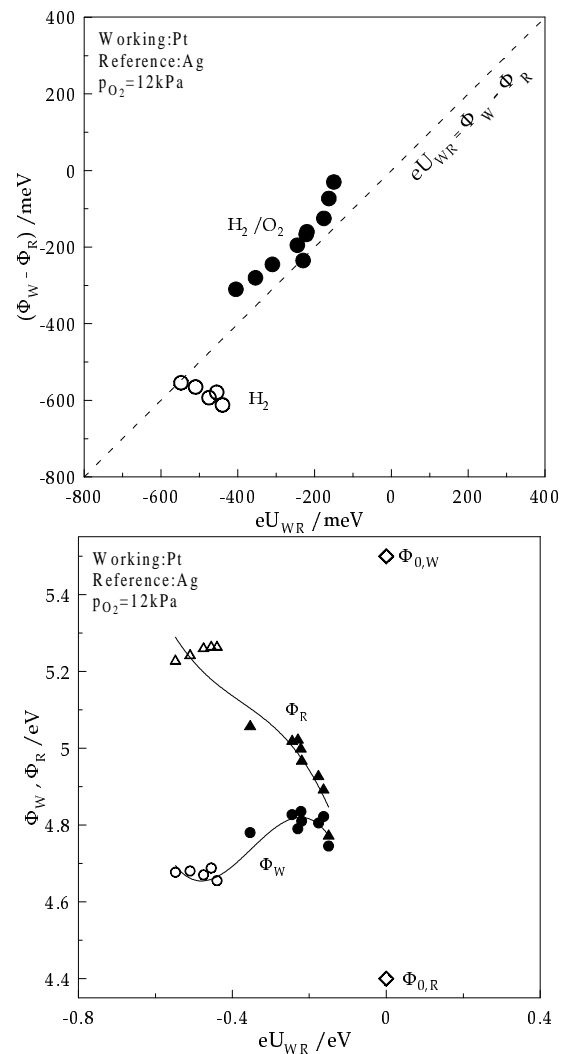
Fig. 1. (top) Dependence of $\Phi_{W(Pt)}-\Phi_{R(Ag)}$ on potential U_{WR} for the system Pt(W)-Ag(R) exposed to H$_2$-He mixtures (open-symbols, p$_{H_2}$ varying between 0.53 and 0.024 kPa) and H$_2$-O$_2$ mixtures (filled symbols, p$_{O_2}$=12kPa, p$_{H_2}$ varying between 0.28 and 7.8 Pa); open-circuit operation, T=673K, Au counter electrode. (bottom) Work function of working (W) and reference (R) electrode as a function of open-circuit potential U_{WR}. Symbols and conditions as in (top). Diamonds show the literature values of $\Phi_{0,W(Pt)}$ and $\Phi_{0,R(Ag)}$.
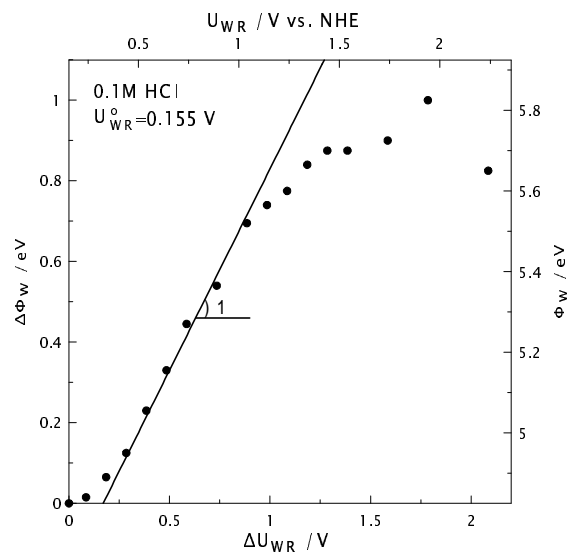

Fig. 2. Effect of potential U_{WR} and overpotential ΔU_{WR} on the work function, Φ_W, of the emersed working Pt electrode.