

Electrode Work Function and Absolute Potential Scale in Solid State Electrochemistry

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The concept of “absolute” electrode potentials is discussed. The so-called “absolute” electrode potential is defined as the electrode potential not referred to another electrode system but to a given reference electronic energy taken as zero (1). A thermodynamically legitimate choice of the zero energy level commonly used in aqueous electrochemistry is the *she* scale where one chooses as the reference state of electrons (and assigns the zero value to it) the state of an electron at the Fermi level of a metal electrode in equilibrium with an aqueous solution of pH=0 and $p_{H_2}=1$ atm at 25°C. But in reality one would like to choose the zero level for the electronic energy in such a way that the energy scale of electrochemical systems can be directly compared with that of solid/gas or solid/vacuum interfaces.

A two Kelvin probe arrangement was used to measure for the first time in situ the work functions, Φ , of the gas exposed surfaces of porous Pt, Au and Ag working and reference electrodes, exposed to O_2 -He, H_2 -He and O_2 - H_2 mixtures, and deposited on 8% Y_2O_3 -stabilized- ZrO_2 (YSZ) in a three-electrode solid electrolyte cell.

It was found (2, 3) that at temperatures above 600 K the potential difference, U_{WR} , between the working (W) and reference (R) electrode reflects the difference in the actual, spillover and adsorption-modified, work functions, Φ_W and Φ_R of the two electrodes (Figure 1):

$$eU_{WR} = \Phi_W - \Phi_R \quad [1]$$

This equation, typically valid over 0.8 –1V wide U_{WR} ranges, was found to hold for any combination of the Pt, Au and Ag electrodes. It is consistent with the previously reported equation (4, 5):

$$e\Delta U_{WR} = \Delta\Phi_W \quad [2]$$

also confirmed here. This is due to the creation via ion spillover of an effective electrochemical double layer on the gas exposed electrode surfaces in solid electrolyte cells, which is similar to the double layer of emersed electrodes in aqueous electrochemistry (3, 5, 6).

Equation [1] allows the definition of a natural absolute electrode potential $U_{O_2}(\text{abs})$ in solid state electrochemistry from:

$$U_{O_2}(\text{abs}) = \Phi/e \quad [3]$$

where Φ is the work function of the gas exposed electrode surface of the metal (any metal) electrode in contact with the YSZ solid electrolyte. It expresses the energy of “solvation” of an electron from vacuum to the Fermi level of the solid electrolyte. The value $U_{O_2}^0(\text{abs})=5.14(\pm 0.05)$ V was determined as the standard $U_{O_2}(\text{abs})$ value for YSZ at $p_{O_2}=1$ bar and $T=673$ K.

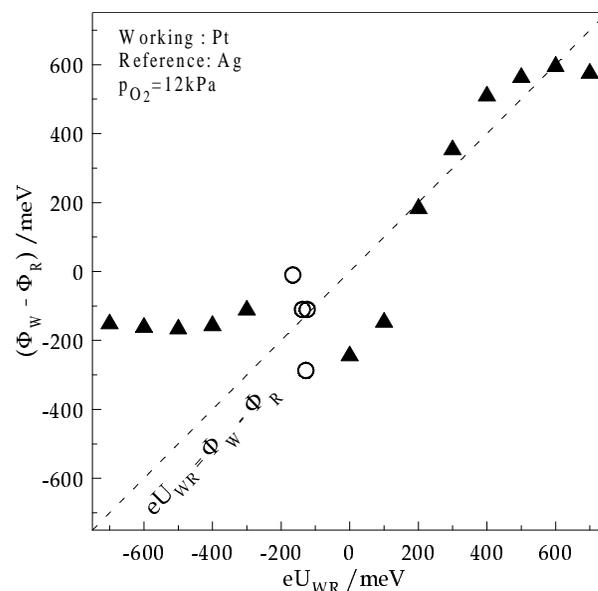


Figure 1: Dependence of $\Phi_{W(Pt)} - \Phi_{R(Ag)}$ on potential U_{WR} for the system Pt(W)-Ag(R). Open symbols: Open-circuit operation. Filled symbols: Closed circuit operation $T=673$ K.

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