Determining the Nernst Potential in the Presence of a Mixed Potential

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When there are at least two faradaic processes contributing to the total electrode current, I_{total}, observed in the external circuit at any potential is the sum of all partial cathodic, $\sum i_c$, and all partial anodic currents, $\sum_a$

$$I_{total} = \sum i_c + \sum i_a \quad (1)$$

In the case of two redox couples, Eq. (1) becomes

$$I_{total} = i_{c,1} + i_{c,2} + i_{a,1} + i_{a,2} \quad (2)$$

At the thermodynamic (Nernst) potential, separately for each of the two components

$$I_1 = i_{c,1} + i_{a,1} = 0 \text{ and } I_2 = i_{c,2} + i_{a,2} = 0 \quad (3)$$

respectively. Comparing Eqs (3) and (2) shows that when both of these couples are reversible, the external electrode current in a solution containing both couples is also zero at the Nernst potential.

However, if the two redox couples are not in equilibrium, there is no unique potential at which both of the relationships given in Eq (3) are true. Consequently, the potential at which I_{total} is zero, is not the Nernst potential, and is the mixed potential.

Here we show how to obtain the Nernst potential in a two component system in which one of the redox couples involves one or more solid phases attached to the electrode.

Consider the case when redox couples 1 and 2 have the half reactions,

A(solid) + other species + electrons ⇄ B(solid)

Ox + ne ⇄ Red (both species soluble)

We use the EQCM to determine electrode mass changes. At open circuit, the electrode mass changes in a direction determined by the respective half cell potentials of these two couples. Applying a potential either increases or decreases the electrode mass. At some potential, there will be no mass change with time, i.e., there is no net accumulation of *A* or *B* on the electrode. This potential corresponds to equal and opposite cathodic and anodic partial currents for A/B couple, and is the Nernst potential. A current passes and corresponds to the sum of the cathodic and anodic partial currents for the Ox/Red couple at this potential

We present EQCM data, obtained with a model system Ni/Ni^{2+} {redox couple 1) in the presence of various concentrations of hydrogen peroxide (redox couple 2). Here nickel metal dissolves at open circuit. Figure1 shows the zero mass potential is constant and is not a function of hydrogen peroxide concentration, in accordance with the above theory

Fig.1