ELECTROCHEMICAL MEASUREMENTS UNDER THIN ELECTROLYTE LAYERS USING A KELVIN PROBE

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Motivation

Phenomenon of interest

Localized corrosion of corrosion resistant alloys such as stainless steel under thin concentrated layers of electrolyte

Problem

How to get the reference electrode into thin layer

Solution

Kelvin Probe – non contact measure of corrosion potential

[1]

Background – Kelvin Probe Basics

The capacitance between electrically connected probe tip and sample [2-4]:

$$C = \varepsilon\varepsilon_0 \frac{A}{d} = \varepsilon\varepsilon_0 \frac{A}{d_0 + \Delta d \sin(\omega_1 t)}$$

The time varying capacitance will lead to a charging and discharging (AC) current if there is a difference in the contact potential, or Volta potential of the two materials:
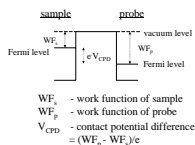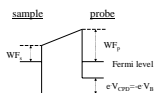
$$i_{AC} = V_{CPD} \frac{\partial C}{\partial t}$$

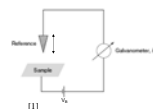$$i_{AC} = C_0 \cdot V_{CPD} \cdot \frac{\Delta d}{d_0} \cdot \omega_1 \sin(\omega_1 \cdot t)$$

If a backing potential V_B is added to the circuit and a high impedance I/V converter is used to measure current:

$$V_{KP} = RC_0 \cdot (V_B + V_{CPD}) \cdot \frac{\Delta d}{d_0} \cdot \omega_1 \sin(\omega_1 \cdot t)$$
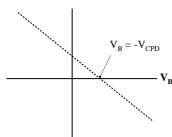
The backing potential can be varied until the V_{KP} signal (at ω_1) goes to zero, at which point $V_{CPD} = -V_B$.

WF$_s$ - work function of sample
WF$_p$ - work function of probe
V$_{CPD}$ - contact potential difference = (WF$_p$ - WF$_s$)/e

[1]

V$_{KP}$ (peak to peak)

V$_B$ = -V$_{CPD}$

V$_B$

sample   probe

WF$_p$

WF$_s$ Fermi level

e·V$_{CPD}$=-e·V$_B$

Kelvin Probe Basics

Stratmann has shown:

$$E_{Corr} = \left\{ \frac{W_{Ref}}{F} - \chi_{El} - \varepsilon_{1/2}^{standard} \right\} + \Delta\Psi_{Ref}^{El}$$
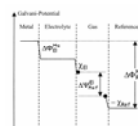
constant   measured

W_{ref} = work function of reference probe

χ_{El} = surface potential of electrolyte, a small value and not changing much

$\varepsilon_{1/2}^{standard}$ = half cell potential of ref. standard, i.e. SCE

$\Delta\Psi_{Ref}^{El}$ = Volta potential difference between ref and sample = V$_{CPD}$

Potential distribution for system metal/electrolyte/gas/ref probe [1]:

- KP signal is directly proportional to E$_{corr}$
- Provides non-contact measurement of E$_{corr}$

New Kelvin Probe System

- Tip driven at fixed frequency (ω_1 = 1 kHz) by permanent magnet and double coil
- Off-null measurement using AC backing potential (ω_2 = 10 Hz)
- Allows for height control and topographic mapping
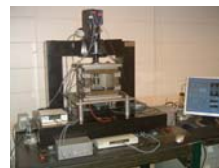
Using AC backing potential (ω_2 = 10 Hz), V$_{KP}$ is a modulation of the two frequencies:

$$V_{KP} = RC_0 \cdot (V_B \cdot \sin(\omega_2 \cdot t) + V_{CPD}) \cdot \frac{\Delta d}{d_0} \cdot \omega_1 \sin(\omega_1 \cdot t)$$
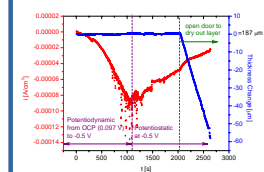
V$_{KP}$ is analyzed to determine a scaling factor that is related to the distance between the sample and the electrolyte surface. The changes of the electrolyte thickness, for example during a dry-out experiment, can therefore be observed through the equipment control.

Experimental

Electrochemical Kelvin Probe Sample
Similar to ring disk electrode

SS KP tip

1 mm

Thin electrolyte layer

Epoxy

WE (SS304)

CE (Inconel 600)
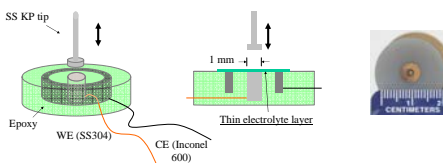
Results

Potentiostatic measurement with dry-out

- Potentiostatic measurement with SS304 ~0.87 M NaCl solution
- Potentiostatic measurement at limiting current density – current decreased
- After ~2000s, chamber door was opened; electrolyte thickness decreased
- Current also decreased in NaCl + boric/borate buffered (pH 6.5) solution

OCP measurement during dry-out
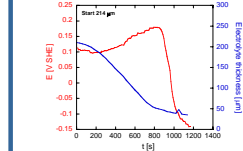
- SS304 in 0.5 M MgCl$_2$ at RT
- OCP curve during dry-out in 33% RH
- Potential dropped when pitting took place, similar to measurements made with coplanar RE
- Kelvin Probe tracks changes in electrolyte layer thickness.

Conclusion

- The Kelvin Probe is powerful tool for studying corrosion under thin electrolyte layers and polymer films.
- It provides a non-contact measure of corrosion potential.
- A KP can be used to control potential, acting as a potentiostat.
- A new KP potentiostat design is used to control potential, measure current, and track height.
- Anodic and cathodic polarization curves on 304SS under thin layers of NaCl solution were measured
- Potential associated with pit initiation during electrolyte drying was measured.

Acknowledgment

References

1. M. Rohwerder P. Leblanc, G.S. Frankel, and M. Stratmann, "Application of Scanning Kelvin Probe in Corrosion Science," in *Methods for Corrosion Science and Engineering*, Philippe Marcus and Florian Mansfeld, editors, Marcel Dekker, Inc., 2003.
2. M. Stratmann and H. Streckel, *Corr. Sci.*, 30, 681 (1990).
3. M. Stratmann and H. Streckel, *Corr. Sci.*, 30, 697 (1990).
4. M. Stratmann, H. Streckel, K.T. Kim, and S. Crockett, *Corr. Sci.*, 30, 715 (1990).