IR Theory in Localized Corrosion: Its Development and A Test of Its Validity Using Oxygen

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The developments that led to the IR mechanism of localized corrosion started with Carl Wagner,[1] nearly a half century ago, with a calculation that showed (i) the dependency of the current distribution on the opening dimension, (ii) that a portion of the polarization curve existed on the wall of the crevice and (iii) the relation between the IR voltage within the crevice electrolyte and the local electrode potential, $E(x)$, on the crevice wall: $E(x) = E_{x = 0} - IR$, where the ionic current, I, is positive when it flows from inside the crevice in the $-x$ direction ($x = 0$ is at the opening of the crevice). The intervening developments, including $E(x)$ profile measurements[2,3] and discovery of gas occupancy in the local cell cavity,[3] and the status of the IR mechanism[4] are a focus of this paper.

The IR mechanism of localized corrosion includes the concept of a critical solution composition from the earlier proposed "acidification" mechanism, but it assigns a more specific role to the changes in solution composition that occur in the cavity electrolyte. The change in solution composition in the IR mechanism causes an active peak to form and grow in spontaneously passive, metal/electrolyte systems. Crevice corrosion occurs only when the active peak reaches a critical size for the prevailing IR voltage.[4] A formalization of this concept has been developed in stages over the years and is recently summarized in a review paper.[5] This criterion of growth of the active peak to a critical size also applies for polarization curves for which the size of the active peak is smaller than needed for the prevailing conditions. For all other spontaneously active systems, changes in solution composition within the crevice are not needed, in which case crevice corrosion can begin immediately. In the IR mechanism crevice corrosion is stabilized in the same way in all metal/electrolyte systems: when the IR voltage in the crevice electrolyte causes the electrode potential at the bottom of the crevice to be sufficiently negative so as to be in the active peak region of the polarization curve that exists on the crevice wall.[4] Pitting could be similarly stabilized from the metastable state.[3,6] It has been shown and confirmed in several experiments by different groups that the IR mechanism is responsible for crevice corrosion in spontaneously active systems,[5,7] but proof-of-concept experiments have as yet not been performed to test for its occurrence in spontaneously passive systems.

Separation of the anodic and cathodic reactions produces the IR voltage. As oxygen is depleted in the crevice electrolyte, an increasing fraction of the anodic (metal dissolution) reaction on the crevice wall is satisfied by cathodic reaction that occurs outside the crevice, either on the crevice's outer surface during open circuit corrosion or at the counter electrode for externally polarized samples. As more and more of the cathodic reaction moves outside of the crevice, an increasing fraction of the metal dissolution current is converted to ionic current, I, that flows from the inside to the outside of the crevice. Two situations exist: the outer surface potential is either in the passive region or in the active region of the polarization curve.

With $E_{x = 0}$ in the passive region (set by a power supply or oxidant), the increasing I means an increasing IR voltage and the possibility that the magnitude of the IR is sufficient for the electrode potential at the bottom of the crevice, $E_{x = L}$, to be in the active peak region of the crevice electrolyte's polarization curve. The moment this condition is reached, crevice corrosion starts.[4] This key role of the oxidant in the crevice electrolyte is summarized elsewhere.[5,8,9] In the case of external polarization, crevice corrosion may start immediately, i.e., prior to oxygen depletion inside the crevice electrolyte, since $E_{x = L}$ can represent higher current densities within the active peak than are permitted for open circuit conditions with its limited cathodic rate of reaction.

With $E_{x = 0}$, on the other hand, in the active region, the metal dissolution current inside the crevice decreases instead of increasing when the cathodic reaction shifts from inside to outside the crevice. The increasing I and IR cause a shift $E(x)$ to more negative potentials which yields lower metal dissolution currents while the outer surface remains at the higher metal dissolution rate characteristic of the $E_{x = 0}$ value. These situations are reviewed elsewhere.[10]

If, instead of a decreasing amount of oxidant inside the crevice it increases with time, the ionic current, I, and the IR voltage decrease with time. If this decrease in IR voltage occurs during an on-going IR-stabilized crevice corrosion process, it follows from IR theory[1,4,7,10] that at the moment when the decreasing IR voltage places the electrode potential at the bottom of the crevice in the passive, rather than active, region of the polarization curve, crevice corrosion would abruptly stop, i.e., the portion of the crevice wall that had been active would undergo immediate passivation. This concept has been demonstrated in experiments where oxygen was added to the crevice electrolyte during an ongoing crevice corrosion process with the result that crevice corrosion abruptly terminated.[5,8,9] Typical data will be presented.

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