# Effect of Spontaneous Embrittlement on the Reactivity of Hydrogen-Evolving Metal Cathodes

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The well known conventional cyclic voltammetry responses of noble metal electrodes in aqueous media relate to low energy metal surfaces where the vast majority of surface atoms are in reasonably well embedded, low energy, states in the outer layers of the metal lattices. The monolayer oxidation responses of such atoms is in reasonable agreement with Pourbaix's thermodynamic data. Quite different responses are observed, for the same metal, when the outer layer (or layers) of metal atoms are in low coordination, or active (metastable), states. In most cases surface activation is incomplete or partial (such states are in any event intrinsically unstable but tend to remain frozen-in) and the observed cyclic voltammogram displays a combination of conventional plus active state behavior. The background to surface active state electrochemistry was discussed in some detail recently[1], as was the implications of such behavior with regard to electrocatalysis[2].

Active surface states of metals, which have an important effect on the kinetics of faradaic reactions, need not be produced prior to investigation, i.e. in the electrode pretreatment stage. As demonstrated in earlier work with gold[3], such activation may occur gradually, in an inadvertent manner, during the course of hydrogen gas evolution. Evidently some of the energy from the power supply becomes trapped during the course of electrolysis at the cathode, thereby modifying the microstructure and reactivity of the latter. Mechanistically it appears that some of the high energy intermediates such as $H_{ads}$, generated at the interface in the course of the $H_2$-evolution reaction, enter the outer layers of the cathode material and disrupt the latter, e.g. due to expulsion of metal atoms, rupturing crystals, etc. The net result is that in the course of prolonged cathodization the general character and reactivity of the cathode surface may gradually alter with time due to superactivation of the surface as a consequence of hydrogen embrittlement. Various aspects of the type of phenomena described here will be outlined for a range of metals.

## References

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