

Surface Energy as a Variable in Electrochemistry

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The electrochemical behaviour of metal electrodes in aqueous media is often summarized in the form of cyclic voltammograms which are widely regarded as being invariant (deviations usually being dismissed in terms of impurity responses). This assumption of fixed responses is regarded here as valid for low energy surfaces but marked variations can arise with highly active, non-equilibrated, surfaces. Bulk metals (and their surfaces) can store energy, the latter being inserted into the system during fabrication, pretreatment or use; indeed there is a considerable market¹ for metals in energy-rich states. Energy storage is based on the presence of amorphous, poorly crystalline, metastable phase and/or highly defective states of metals; atoms in such states are unusually active ($\mu_M > \mu_M^\circ$) due to their low lattice stabilization energies. Similar conditions often prevail at real metal surfaces where the presence of "energy-rich atoms" is widely accepted.²

Useful ideas as to the behaviour of superactive metal surfaces are provided by Henglein's work³ on discrete metal clusters. The latter exhibit non-linear behaviour; as the number (n) of metal atoms per particle (M_n) becomes extremely small ($< \text{ca. } 100$) the electropositive character of the particle increases dramatically with decreasing value of n ; hence the cluster becomes susceptible to oxidation or dissolution at unusually low potentials. Superactivated metal surfaces may be regarded as surfaces coated with attached, partially embedded, microclusters of atoms of the same metal (n may range from 1, i.e. an adatom, to quite large values).

Superactive surface states are intrinsically unstable and the atoms involved have a degree of mobility; these atoms possess a range of energy states based on different surface configurations, e.g. terrace adatoms, step adsorbed, kink and step embedded atoms, clusters of different sizes, etc. Thermally induced motion between different sites means that even high energy sites have a significant occupancy (the fact that metastable metals are marketable¹ clearly demonstrates that the states involved have surprisingly long life spans).

As technology becomes more complex and the techniques involved in metal fabrication more exotic the effect of superactivation becomes more obvious. Examples of the relevance or involvement of superactive state behaviour in areas such as microelectronic and microelectrode fabrication, hydrogen gas evolution and oxide reduction will be outlined. Some of the controversies of the past, e.g. the existence of dermasorbed oxygen in platinum, unusual redox transitions in the double layer region and even anomalous heat generation (or "cold fusion") may be manifestations of the linkage between energy storage and disorder at surfaces. For example, subjecting a metal cathode in aqueous media to quite prolonged severe cathodization superactivates the outer layers of the electrode material to quite a significant degree (via hydrogen or deuterium embrittlement⁴). The spontaneous collapse of the active state in the case of palladium is likely to release energy in the form of a heat burst. Continued cathodization is likely to lead to a periodic sequence of heat emissions.

In summary, it appears that energy storage in the outer layers of a metal lattice is an important topic in corrosion science and electrochemistry; it is responsible, largely via enhanced corrosion behaviour, for a range of anomalous effects, some of which have significant technological implications.

References

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