Metastability and Surface Active Site Behaviour - L.D. Burke (University College Cork)

A basic assumption in this work is that current descriptions of the electrochemical behaviour of noble metals in aqueous media are oversimplified and overemphasized Such descriptions concentrate largely on double layer charging and monolayer (α) oxide behaviour in the case of gold, plus one additional process, chemisorption of hydrogen, in the case of platinum. This conventional view is considered as being restricted rather than invalid; it is assumed to apply to low energy states of metal surfaces but it ignores surface metal atomic activity (or chemical potential, μ) as an important variable; such a view is especially detrimental from an active site and electrocatalysis viewpoint.

Some of the important aspects of surface electrochemistry that are ignored in conventional accounts of noble metal behaviour are as follows, viz.

(i) Metastable, non-equilibrium, high energy states of metals and their surfaces: Such states, and in particular the control of metastability, are the essence of metallurgy[1] but are widely ignored in electrochemistry. Metals, and their surfaces, can store energy via defect generation, as for instance in the case of rapidly thermally quenched metals. The difficulty here is that metastable metals have variable properties; however, this is an advantage as surfaces may be treated to produce a metastable state of optimum activity with regard to a particular electrocatalytic reaction. The vast potential in this area has been demonstrated by the (verified[2]) work of Haruta and coworkers[3] on the amazing catalytic activity of supported gold nanoparticles.

(ii) Hydrous (β) oxides[4]: These are quite different from the α oxides, this dissimilarity being highlighted by the marked charge storage and electrochromic behaviour of β (but not α) iridium oxide films. Hydrous oxides are now know for most of the noble metals; they possess quite unusual properties; like metastable metals they tend to be structurally ill-defined, but they are obviously a part of noble metal electrochemistry and should be incorporated into accounts of same.

(iii) Surface active sites: The vital role of the latter in surface catalysis is widely acknowledged but their existence is often ignored in surface electrochemistry. A formal definition of such sites[5] is worth noting; they involve "atoms which by their position on a surface, such as the apex of a peak, at a step on the surface or a kink in a step, or on the edge or corner of a crystal, share with neighbouring atoms an abnormally small portion of their electrostatic field [or bonding energy] and, therefore, have a large residual field available for catalytic activity and for adsorption". Clearly atoms at both active sites and in metastable metals have in common a state of low lattice stabilization energy and thus an unusually high chemical potential, or low oxidation potential.

Atoms at metal/solution interfaces can undergo quite a variety of chemical reaction, e.g. hydration, anion adsorption, redox transitions (the latter may be accompanied by hydroxylation). Since the extent of atom protrusion from the surface, and hence the chemical potential, is variable (especially at active sites) the surface chemistry (or redox behaviour) is also variable. This is assumed to be the basis of different types of active sites and electrocatalytic properties at the same metal surface, as demonstrated recently for silver in base[6]. Current work on uniform single crystal surfaces may be intrinsically interesting but the notion of well defined, monatomically flat surfaces seems to be the antithesis of the active site, rough surface approach which is well established in heterogeneous catalysis[7]. For any metal, surface metal atom activity (and indeed surface electrochemistry) is a variable that needs to be optimised, e.g. in terms of microstructure, for a particular electrocatalytic application. Surface metastablility will be discussed with particular reference to gold; with the later metal in base active state oxidation may commence at E<0.0V (RHE).

References

1. R.W. Cahn, in: Rapidly Solidified Alloys (H.H. Liebermann, Ed.) Dekker, New York (1993) p.1.
2. G.C. Bond and D.T. Thompson, Cat. Revs, 41 (1999) 319.
3. M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, J. Cat., 115 (1989) 301.
4. L.D. Burke and M.E.G. Lyons, Modern Aspects of Electrochem., 18 (1986) 169.
5. D.M. Cosidine, Van Nostrand's Scientific Encyclopaedia (8th Ed.), Van Nostrand Reinhold, New York (1995) p.36.
6. A.J. Ahern, L.C. Nagle and L.D. Burke, J. Solid State Electrochem., 6 (2002) 451.
7. G.A. Somorjai, Chem. Revs, 96 (1996) 1223.