

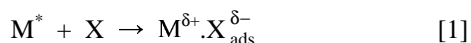
Active States of Metal Surfaces: The Nanoparticle or Quantum Dot Factor in Electrocatalysis

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It has long been accepted that active sites and disorder (or roughness (1)) play a vital role in catalysis at surfaces. The difficulty with such a view, from both a practical and theoretical viewpoint, is that the nature of active sites remains largely unidentified (2). Surface disorder is not merely a matter of increased surface area; of greater significance is the fact that roughness entails high energy, non-equilibrium, metastable states of the metal. The relationship between disorder and energy storage is well known in metallurgy (3) but this factor has been virtually ignored in surface electrochemistry. Recent evidence suggests that the chemistry taking place at high energy surface sites is significantly different from that occurring at low energy sites at the same surface.

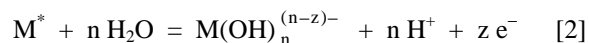
The conventional, activated chemisorption, approach to surface catalysis cannot account for the unexpectedly high catalytic (4) and electrocatalytic (5) activity of gold (the latter metal, in conventional form, has extremely poor chemisorbing properties). However, if a gold surface is highly activated, some of the surface metal atoms apparently exist virtually outside (or on) the lattice (the atoms in such a state are assumed to be transient, mobile species). Lack of lattice stabilization energy (or quantum confinement effects) means that such atoms or clusters are extremely reactive, strong electron donor, species which (i) are highly susceptible to premonolayer oxidation, (ii) yield, on oxidation in aqueous media, an unusual (hydrous) oxide product, and (iii) provide a novel, localized mode of chemisorption, viz.



that is quite different from the conventional d-band vacancy mechanism for the same type of reaction.

According to this active surface state approach, which was outlined recently in a generalized form (5,6), the active atoms or clusters (which are known to be unusually electropositive (7)) provide the mediators for electrocatalytic reactions; these active entities may be regarded as surface quantum dots. Recent data for silver in base, as shown in Fig. 1, will be described (silver, like gold, is a weak chemisorber but quite a good catalyst). It will be demonstrated that active surface state behaviour is quite complex and that electrochemical techniques provide useful (though obviously limited) data as to such behaviour.

The electrocatalytic behaviour of platinum (of interest with regard to fuel cell development) is apparently complex. This metal may exhibit two modes of behaviour: (i) activated chemisorption, e.g. of methanol (to form CO_{ads}) at sites of low thermodynamic activity, and (ii) formation of oxyspecies (to remove CO_{ads}) at sites of high activity, viz.



Controlling (or optimizing) surface site (or quantum dot) activity, which is evidently difficult, may well be a key factor in fuel cell electrocatalysis, e.g. extreme activation,

resulting in surface overoxidation, may be detrimental from a catalytic viewpoint.

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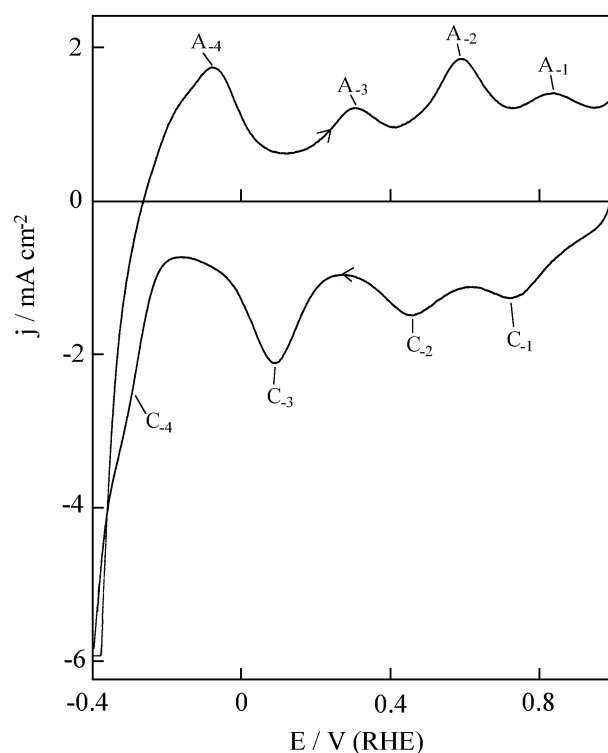


Fig. 1 Cyclic voltammogram ($-0.4 \rightarrow 1.0$ V at 100 mV s^{-1}) for a silver wire electrode in 0.5 mol dm^{-3} NaOH at 25°C following cathodic polarization at -0.7 V for 3 hr in the same solution; monolayer oxide formation for this system commences at ca. 1.15 V, i.e. the activated state responses shown here relate to the double layer region.