

Some reflections on Electrochemical Active Surface (EAS)

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Electrochemical Active Area (EAS) is a parameter conventionally employed to denote or account for the decreased electrochemical activity as compared to the quantity that is expected on the basis of the amount of the active component loaded on an electrode. This has been often employed to denote the activity of Pt loaded on carbon substrates in Fuel cells. For example if x mg of Pt is loaded only a fraction of the amount x loaded will be active and hence account for the current that is experimentally realized. In essence various postulates have been proposed to explain this short coming in the electrical response of a metal loaded system and this is usually taken to mean that the total loaded system does not give rise to a very fine dispersion and hence there are always lesser number of exposed metal species as compared to the total metal species loaded. This can arise due to various reasons like agglomeration or the dispersion itself is not atomic or molecular as the case may be. Even when the dispersion is good enough the exposed metal species may not orient in the required crystallographic planes and hence the active species may be less than the loaded amount. The conventional concept of active centres in catalysis can also be extended to such situations and in this sense anchoring species may be able to increase the electrochemical active surface. However, all these concepts will give rise to an arithmetic sum for the activity, while the observed activity is far beyond simple arithmetic can provide. In this connection, it is our intention to bring in this short note some conceptual frame work wherein the EAS can be interpreted in a slightly different manner.

In electrochemical sense, especially in power sources like Fuel cells, one needs both electrical and ionic conductivity for the efficient electrochemical reaction. In metal loaded on carbon substrates one ensures electrical conductivity but ionic conductivity (in this case protonic conductivity) is provided by the Nafion which is employed. In some cases the Platinum particles may not have this three phase boundary and hence cannot be active in electrochemical reactions.

Secondly if the metallic particles because of this three phase boundary exist in an electronic configuration different from that of the metallic state (slightly negatively or positively charged) these charged state species may be active and when the metals cluster together this charge density may not be appropriate for the activity to be exhibited by the system. This can be established in a number of ways like the determination of point of zero charge or by XPS measurements.

In a subsequent write up we shall discuss this issue in great detail and also outline the procedure normally adopted for determining the electrochemical active surface of supported metal electrodes.

