

ELECTROCATALYSIS IN THE PROCESSES OF ENERGY STORAGE

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The possibility of using electrochemical systems for large-scale energy storage has been extensively discussed in the literature in recent years (Kahlhammer *et al.*, 1977). Among these, the main interest is related to systems with oxygen electrodes. Such systems eliminate the need to store one of the components of the electrochemical reaction, namely oxygen; electric energy could be effectively generated by utilizing the air oxygen.

Mostly, the target parameters of such systems are determined by kinetic relations of the reactions of evolution and ionization of molecular oxygen taking place on the electrodes. Unfortunately, the oxygen electrode is an example of a poor reversible, electrode with consequent low energy efficiency. The problem of developing efficient and reversible oxygen electrodes becomes important in the field of electrocatalysis, essential for solving the problem of electrochemical storage of energy. In spite of numerous research efforts, this problem is not yet resolved. This is caused, to a great extent, by the complexity of the mechanism of electrochemical reactions involving oxygen (Bagotsky *et al.*, 1965, and Hoare, 1968).

Keywords : Electrocatalysis; Energy Storage; Oxygen Electrodes; Oxygen Ionization

OXYGEN IONIZATION REACTION

The oxygen ionization reaction is often described by the diagram of Fig. 1. A number of authors (Bagotsky *et al.*, 1969) have investigated in detail various intermediate stages of this reaction. Most of the intermediate stages shown in Fig. 1 are absent in the reverse process of anodic evolution of oxygen. This is a characteristic feature of the process. In particular, the anodic process does not include an intermediate stage of hydrogen peroxide liberation. Many of the stages shown in the figure (and first of all stages 3 and 4) are thus micro-irreversible. On the other hand, stage 2 is known to be quite reversible on many metals. It appears possible that reversibility of stage 2 is retained in some cases when the reaction proceeds in parallel through stage 1.

It is interesting to note that in principle, branching of the general process is possible for the hydrogen ionization reaction, that is the electron transition is possible both before and after dissociation of the hydrogen molecule into atoms. This

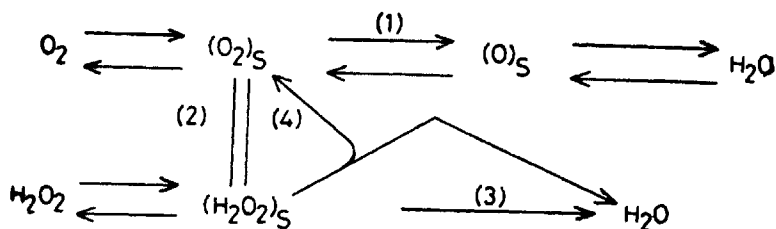


FIG. 1.

scheme was established, for instance, by analyzing the reaction rate on platinum electrode as a function of the solution pH (Osetrova & Bagotsky, 1973).

Irreversibility

To a great extent, the oxygen reaction is irreversible owing to specific features of behaviour of different forms of adsorbed oxygen on the electrode surface, and to their influence on the electrochemical reaction. It's typical behaviour is strongly dependent on the range of potential. The stage in question is reversible on platinum-group metals at positive potentials not higher than 0.9V with respect to the hydrogen electrode in the same solution (r.h.e.). Well-pronounced irreversibility appears in the more positive range of potentials, so that oxygen is removed from the surface only at potentials much more negative than the adsorption potential. The reasons for this irreversibility are different on different metals. The shift in potential of anodic and cathodic processes on iridium is purely kinetic and is related to a low rate constant of the corresponding reaction (Kurnikov *et al.*, 1973). The system approaches equilibrium as the reaction rate (current) diminishes. In contrast to this situation, platinum is characterized by a sharp hysteresis which does not disappear even at very low currents. This hysteresis points to a different nature of the oxygen adsorption and desorption processes on platinum. On the other hand, investigation of the oxygen ionization kinetics on Pt has shown that in some cases, the process of adsorption of molecular hydrogen on Pt can be rate-limiting; the reaction rate at this stage is strongly dependent on the amount and nature of oxygen adsorbed on the surface (Lukyanicheva *et al.*, 1977). Comparison of these data makes it possible to explain main kinetic features of the reaction of oxygen ionization on platinum electrodes.

The oxygen ionization reaction has been studied in recent years on different types of catalysts, and among them on a number of complex organic compounds (phthalocyanines, porphyrins, etc.) (Jasinsky, 1964). The obtained experimental data in some cases reveal the factors enhancing catalytic effects.

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Discussion

HIRA LAL (*Indian Institute of Technology, Bombay*): Adsorbed perphoryns are reported to promote the direct reduction of oxygen at platinum without the formation of H_2O_2 as intermediate. Could you comment on how this is possibly brought about ?

V. S. BAGOTSKY: Reactions without H_2O_2 formation depend on the possibility of splitting of the $-O-O$ level previously or during the transfer of the first electron. This depends on conditions of adsorption of O_2 molecules. It is interesting to note that sometimes on pure carbon surfaces conditions can be realised similar to those at a surface covered with pthalocyanine.

V. K. VENKATESAN (*Central Electrochemical Research Institute, Karaikudi*): The oxygen reduction rate on silver supported on carbon seems to be lower than that on pure silver. Would you please give the reason for this observed effect ?

V. S. BAGOTSKY: For silver, the difference of activity for smooth surface and dispersed particles is less than for platinum.

V. K. VENKATESAN: Can you please give some information on the fuel cell activity and Nickel-hydrogen systems in USSR ?

V. S. BAGOTSKY: I will give some information on this topic in the panel discussion.

P. B. MATHUR (*Central Electromicheckal Research Institute, Karaikudi*): Whether formation of hydrogen peroxide would occur on all catalysts or on a few catalysts only ?

V. S. BAGOTSKY: The intermediate formation of hydrogen peroxide is generally observed, but there seem to be some metals, where reduction of oxygen proceeds without H_2O_2 formation.