KINETICS OF REACTIONS ON SILVER AND NICKEL OXYGEN ELECTRODES IN ALKALINE SOLUTIONS

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ABSTRACT

Although the oxygen electrode has been the object of numerous studies, it remains as yet a limiting factor in the operation of hydrogen-oxygen fuel cells. In fact, whereas the hydrogen electrode operates under reversible conditions, for real oxygen electrodes it has not been possible to obtain a low enough polarization during the oxygen ionization reaction. Therefore, for an oxygen reaction it is extremely important not only to choose a proper catalyst, but also to find the optimum conditions of the occurrence of the oxygen ionization reaction. In view of a complicated stepwise nature of this reaction, the presence of competing parallel reactions, the formation of hydrogen peroxide as an intermediate product in particular, in order to create effective and stable oxygen electrodes it is necessary to study the mechanism of this reaction, the kinetics of its separate steps and to find the optimum conditions of its occurrence.

In the present paper we have studied the operation of oxygen electrodes in alkaline solutions by means of the disk-ring electrode, using silver and nickel as electrode

materials. The oxygen ionization reaction on silver and nickel in alkaline solutions occurs simultaneously by two mechanisms; by direct reduction to hydroxyl ions and with the formation of hydrogen peroxide as an intermediate product, which can be further electrochemically reduced to water and decompose catalytically to form molecular oxygen and water. We have measured partial currents and the rate constants of the individual steps of oxygen reduction reactions, allowing for the possibility of a catalytic hydrogen decomposition, and found the dependences of these partial currents on the electrode potential and its oxidation state. Particular attention has been given to the process of further reduction of hydrogen peroxide.

The analysis of the data on the kinetics of the individual steps of oxygen ionization reaction can serve as an important subsidiary means for the assessment of the suitability of a metal for use as a material for oxygen electrodes of fuel cells, in which hydrogen peroxide formation is undesirable.