

# THE ACTION OF GAS EVOLUTION AT ELECTRODES ON MASS TRANSFER – AN INTRODUCTION

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## 1. Some fundamentals

In most of the important industrial electrochemical processes, gases are evolved, either at one electrode or both. Such processes comprise the decomposition of water and production of chlorine and inorganic chlorine compounds, organic compounds, and aluminium among others. In some of these processes the gases are the products, in other cases they are nothing but undesired by-products.

Gas-evolving electrodes are characterized by the formation of a gaseous phase on the electrode surface during electrolysis as an indirect consequence of the electrochemical reaction. The gaseous phase transforms the two-phase system electrode–electrolyte into a three-phase system, and this modifies the operational conditions of electrodes in many ways. The existence of a gas phase adhering to an electrode or in the electrolyte bulk significantly complicates operation of electrochemical reactors.

Gas evolution at electrodes requires several preconditions:

1. An electrochemical reaction at least at one of the electrodes produces a substance getting a stable gaseous phase under the condition of state of temperature and pressure present in the system. The complex of reaction steps at the electrode–electrolyte interface does not directly produce gas but a product initially present in dissolved form. Under common operation conditions this is for example H<sub>2</sub>, O<sub>2</sub>, Cl<sub>2</sub>, CO, CO<sub>2</sub>.
2. The supersaturation of the electrolyte liquid with dissolved gas must be sufficiently large to initiate stable growth of a tiny gas volume (bubble nucleus) available at the electrode surface.
3. The electrode surface must be in a suitable condition. It must contain nucleation sites that can be activated as the concentration of dissolved gas is large enough. Gas formation starts as heterogeneous nucleation. (Homogeneous nucleation is possible under extraordinary conditions, if at extraordinarily smooth electrode surfaces bubble

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nuclei are not available. This case is meaningless for industrial electrochemical reactors.)

A sufficient concentration of dissolved gas in the electrolyte liquid immediately at the electrode surface can further only be reached if homogeneous chemical reactions of the dissolved product do not occur or their rate is small enough. For example, in reactors for production of hypochlorite, bubbles at the electrode do not appear although the electrode product chlorine fully meets the first one of the above conditions and the other conditions may exist.

The concentration of dissolved gas at the electrode results from the balance of the reaction rate producing the substance and the mass transfer of the substance from the electrode to the liquid bulk. This is a first indication on the action of mass transfer on the operating conditions of gas evolving electrodes.

Gas evolution is not simply an accompanying process, but interferes with the electrochemical and physical events at the electrode in several aspects. The interference is not restricted to the electrode surface or an adjacent electrolyte layer, but spreads throughout the whole interelectrode gap.

Therefore, it substantially affects design and operation of the electrochemical reactors with gas-evolving electrodes and generally necessitates a design that differs significantly from that of other electrochemical systems without gas evolution. The same applies to the operating conditions.

This fact has attracted intensified research interest during the last decades and has initiated many investigations to clarify the reasons and the implications and thus to develop a tool for engineering design. Ensuring optimal operation of these electrochemical reactors requires understanding of the causes and effects of the manifold phenomena associated with gas evolution.

## **2. Physical processes in gas evolution at electrodes**

*Nucleation and Bubble Growth.* Experience shows that solid surfaces in contact with a liquid commonly carry innumerable nucleation sites, i.e., preexisting gas residues trapped in pits, scratches, and grooves on the surface. Bubble growth starts when the nucleation site becomes active. This heterogeneous nucleation requires not only a nucleation site but also a disturbance of the equilibrium which may be caused by temperature as in boiling or by concentration as in gas evolution at electrodes. Interfacial concentrations of dissolved gas may attain the 100-fold value of the saturation concentration. When the concentration exceeds a certain value, stable gas bubbles start growing at nucleation sites by supply of dissolved gas from the supersaturated electrolyte. The microprocesses of gas evolution at electrodes exhibit numerous analogies to the processes in boiling, but the analogy often referred to is limited.

The formation of bubbles can be provoked by adding artificial nucleation sites, e.g. by a