The Importance of Catalysis in the Electrochemical Oxygen Transfer Reactions (EOTR)

by

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Abstract

Oxidative electrochemical processes promising versatility, environmental compatibility and cost effectiveness have a continuously growing importance both in selective organic synthesis and in the electrochemical incineration (ECI) of organic pollutants in aqueous media. In case of organic electrosynthesis selectivity is to be enhanced and in the ECI process the aim is the mineralization of the toxic and non-biocompatible pollutants with high current efficiency. Anodic oxidation of organics may proceed by several mechanisms including direct and indirect oxidation.

In this work the electrochemical oxidation of organics at DSA® type electrodes based on synthetic boron-doped diamond (BDD) and metal oxide anodes in acid medium are presented. Both the direct and indirect electron transfer reaction are discussed.

In case of facile outer-sphere electrode reactions, both BDD and oxide electrodes behave similarly to that of noble metal electrodes.

In oxidation reactions of more complex mechanism, these anodes show no activity below the potential of oxygen evolution and electrochemical oxygen transfer reactions (EO-transfer) can take place only in the potential region of water discharge.

A simplified mechanism of EO-transfer reactions catalyzed by intermediates of oxygen evolution has been proposed distinguishing between two limiting electrode behaviors:

(i) At ‘non-active’ anodes (typically BDD and fully oxidized metal oxides) EO-transfer occurs at a high anode potential through physisorbed hydroxyl radicals.
(ii) At ‘active’ electrodes (IrO₂, RuO₂) the reaction takes place at lower potentials characteristic of the metal oxide and results in an EO-transfer reactions through the higher oxidized metal oxide surface sites.

Finally a kinetic model of organics oxidation at ‘non-active’ and ‘active’ type anodes is proposed and confirmed by preparative electrolysis.

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