

Author: mgr Justyna Jędraszko

Supervisor: prof. dr hab. Marcin Wojciech Opałło

Auxiliary supervisor: dr inż. Wojciech Adamiak

Hydrogen peroxide and hydrogen generation at liquid|liquid interfaces with electron donors - metallocenes

The purpose of this work was to better understand the reaction mechanisms and to find new systems for generation H_2 and H_2O_2 at the interface between two immiscible electrolyte solutions with metallocenes as electron donors. An organic phase was a solution of decamethylferrocene or decamethylruthenocene. An aqueous phase was a solution of perchloric acid. For H_2 production, the aqueous phase additionally contained lithium tetrakis(pentafluorophenyl)borate. This salt allows the transfer of protons from the aqueous phase to the organic phase.

The H_2 generation was carried out in 1,2-dichloroethane|water and α,α,α -trifluorotoluene|water biphasic systems. H_2 generation occurs under anaerobic conditions after the transfer of protons from the aqueous phase to the organic phase. Then, in the organic phase, the protons were reduced to H_2 by decamethylferrocene or decamethylruthenocene. In the latter case, the process occurs under the white light illumination.

H_2O_2 generation was performed in: 1,2-dichloroethane|water, α,α,α -trifluorotoluene|water, 2-nitrophenyloctyl ether|water and ionic liquid|water biphasic systems. Analogically to H_2 evolution, the generation of H_2O_2 occur homogeneously in the organic phase, after proton transfer from the aqueous to the organic electrolyte or heterogeneously at liquid|liquid interface. The process was carried out using decamethylferrocene as an electron donor under aerobic conditions.

To determine the mechanisms of H_2 and H_2O_2 generation in liquid|liquid biphasic systems, ion transfer processes have been also studied. During reduction of protons and oxygen, metallocenes are oxidized to their cations, and thus a positive charge is generated in the organic phase, which must be neutralized by transfer of ions across the liquid|liquid interface. In systems with molecular solvents the anions were transferred from the aqueous to the organic phase. In the case of ionic liquids, the transfer of their cations into the water phase has been observed. Metallocene cations remained in the organic phase. In order to improve the efficiency and ensure the continuity of H_2 and H_2O_2 generation, electrochemical regeneration of electron donors was investigated in selected systems.

H_2 and H_2O_2 generation were studied by: voltammetric and potentiometric techniques, scanning electrochemical and fluorescence microscopy, UV-Vis spectroscopy. The results of the experiments expand the knowledge of H_2 and H_2O_2 generation in biphasic liquid systems remaining within the basic research. In the future these results may be helpful in applied research.

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