

Author of the doctoral dissertation: **mgr inż. Katarzyna Dusilo**

Supervisor: **prof. dr hab. Marcin Opallo**

Auxiliary supervisor: **dr inż. Magdalena Warczak**

Title of the doctoral dissertation: Oxygen reduction and hydrogen evolution at liquid|liquid interface studied in systems with reduced volume of organic phase

Abstract

Hydrogen peroxide and hydrogen - important chemicals and energy carriers, can be generated by oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER), respectively. Both reactions may occur at liquid|liquid interface in mild conditions: room temperature and atmospheric pressure. Conventionally, biphasic reactions are studied at the interface created by bulk organic and aqueous phases of similar volume, what results in huge consumption of organic solvents. To decrease their influence on the environment, organic phase volume has to be reduced. Typically, electrons for both biphasic ORR or HER are supplied by sacrificial electron donor. When a small volume of organic solvent is in contact with the electrode, such design allows for electrochemical recycling of electron donor, increasing efficiency of biphasic reaction. The aim of the research described in this PhD thesis was to investigate ORR and HER at liquid|liquid interface in systems with reduced volume of organic phase.

As proton transfer is an important step of studied reactions, HClO_4 aq. was chosen as proton source in aqueous phase. As organic phase, solution of electron donor - decamethylferrocene (DMFc) or decamethylruthenocene (DMRc) in hydrophobic electrolyte solution in 2-nitrophenyloctyl ether (NPOE) or hydrophobic ionic liquid - 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($\text{C}_4\text{mimN}(\text{Tf})_2$), vegetable oil or trihexyltetradecyl-phosphonium bis(trifluoromethylsulfonyl)imide ($\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$) and toluene mixture was used. Electrochemical properties of these biphasic systems were studied with cyclic voltammetry (CV), square wave voltammetry and chronoamperometry. Hydrogen peroxide, was detected by CV, scanning electrochemical microscopy (SECM), colorimetry and UV-Vis spectroscopy. Hydrogen was detected by CV.

To realise the goal of research, three different setups were proposed and studied. First one was based on droplet of organic phase (electron donor - DMFc and electrolyte solution in molecular viscous solvent (NPOE) or DMFc in hydrophobic ionic liquid $\text{C}_4\text{mimN}(\text{Tf})_2$) deposited on bare or nanoparticulate indium tin-oxide (ITO) electrode. This allowed to decrease the volume ratio of organic to aqueous phase to 1:120. Here, H_2O_2 generation in aerobic conditions was observed. Electrochemical regeneration of the electron donor and the electrode surface development enhanced efficiency of this process. Application of similar setup in anaerobic conditions, using DMRc as electron donor and in the presence of UV light enabled to observe some features indicating H_2 generation.

The second setup was based on carbon paste electrode (CPE) with DMFc solution in vegetable (rapeseed, sunflower or linen) oil as a binder, immersed in HClO_4 aqueous solution. H_2O_2 was detected next to oil|water interface formed at CPE surface with electrochemical recycling of electron donor.

Third setup was oil in water emulsion consisting of droplets of DMFc or DMRc solution in $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ and toluene mixture suspended in HClO_4 aqueous solution. It was observed that liquid film is formed on the surface of glassy carbon electrode immersed in this emulsion. Moreover, H_2O_2 generation and toluene electrooxidation in this emulsion were detected. Some features of biphasic HER in the presence of UV light and DMRc were also seen.