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Instytut Chemii Fizycznej PAN

PhD Thesis

Oxygen reduction and hydrogen evolution at liquid|liquid interface studied in systems with reduced volume of organic phase

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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 trihexyltetradecylphosphonium 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.

Streszczenie

Nadtlenek wodoru i wodór to ważne związki chemiczne i nośniki energii. Mogą zostać wytworzone odpowiednio w reakcji redukcji tlenu (ORR - *ang. oxygen reduction reaction*) oraz reakcji wydzielania wodoru (HER – *ang. hydrogen evolution reaction*). Obie reakcje mogą zachodzić na granicy faz ciecz-ciecz w łagodnych warunkach, czyli w temperaturze pokojowej oraz przy ciśnieniu atmosferycznym. Reakcje w układach dwufazowych są zazwyczaj badane w układach o znacznej i podobnej objętości fazy organicznej i wodnej, co skutkuje dużym zużyciem rozpuszczalników organicznych. Aby zmniejszyć ich wpływ na środowisko, objętość fazy organicznej musi zostać zmniejszona. Elektryony biorące udział w obu reakcjach dwufazowych ORR i HER pochodzą od donora elektronów, który ulega zużyciu. Gdy faza organiczna o zmniejszonej objętości jest w kontakcie z elektrodą, pozwala to na elektrochemiczną regenerację donora elektronów, która zwiększa wydajność reakcji dwufazowej. Celem badań opisanych w niniejszej rozprawie doktorskiej było zbadanie reakcji redukcji tlenu oraz wydzielania wodoru na granicy faz ciecz-ciecz w układach o zmniejszonej objętości fazy organicznej.

Ze względu na to, że przeniesienie protonu jest ważnym etapem obu badanych reakcji, jako fazę wodną zastosowano roztwór wodny HClO_4 . Natomiast jako fazę organiczną użyto roztworu dekametyloferrocenu (DMFc) lub dekametylorutenocenu (DMRc) w hydrofobowym rozpuszczalniku: eterze 2-nitrofenylooktylowym (NPOE), hydrofobowej cieczy jonowej bis(trifluorometylosulfonylo)imidku 1-butylo-3-metyloimidazoliowym ($\text{C}_4\text{mimN}(\text{Tf})_2$), w olejach spożywczych lub w mieszaninie bis(trifluorometylosulfonylo)imidku triheksyloctetradecylofosfoniowym ($\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$) i toluenu. Właściwości elektrochemiczne tych układów dwufazowych zostały zbadane za pomocą woltamperometrii cyklicznej, woltamperometrii fali kwadratowej oraz chronoamperometrii. Wydzielanie nadtlenku wodoru zostało potwierdzone za pomocą woltamperometrii cyklicznej, skaningowej mikroskopii elektrochemicznej (SECM), kolorymetrii oraz spektroskopii UV-Vis. Wodór został wykryty za pomocą woltamperometrii cyklicznej.

Aby zrealizować cel badań, zostały zaproponowane oraz zbadane trzy różne układy. Pierwszy z nich to kropla fazy organicznej – roztworu DMFc i elektrolitu w molekularnym, lepkim rozpuszczalniku (NPOE) lub roztworu DMFc w hydrofobowej cieczy jonowej $\text{C}_4\text{mimN}(\text{Tf})_2$, osadzona na powierzchni elektrody z tlenku indy domieszkowanego cyną (ITO *ang. indium tin oxide*) lub powierzchni elektrody ITO pokrytej dodatkową warstwą nanocząstek ITO. Zastosowanie takiego układu umożliwiło zmniejszenie stosunku objętości fazy organicznej do wodnej do 1:120. W tym przypadku, zaobserwowano wydzielanie H_2O_2 w warunkach tlenowych. Elektrochemiczna regeneracja donora elektronów oraz rozwiniecie powierzchni elektrody zwiększyły wydajność tego procesu. Zastosowanie podobnego układu w warunkach beztlenowych z DMRc jako donorem elektronów, pozwoliło na zaobserwowanie wydzielania wodoru w obecności światła UV.

Jako drugi układ zastosowano węglowe elektrody pastowe, przygotowane przy użyciu roztworu DMFc w oleju roślinnym (rzepakowym, słonecznikowym lub lnianym), użytym jako lepiszcze, umieszczone w wodnym roztworze HClO_4 . Wydzielanie H_2O_2 zostało zaobserwowane na granicy faz olej|woda utworzonej na powierzchni CPE, gdy donor elektronów był regenerowany elektrochemicznie.

Trzecim układem była emulsja typu olej w wodzie, składająca się z kropelek roztworu DMFc lub DMRc w mieszaninie $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ i toluenu, rozproszonego w roztworze wodnym

HClO₄. Zaobserwowano tworzenie się warstwy cieczy na powierzchni elektrody z węgla szklanego umieszczonej w emulsji. Ponadto, zostało potwierdzone wydzielanie H₂O₂ i elektrootlenianie toluenu. Również zauważono oznaki wydzielania wodoru w obecności światła UV i DMRC jako donora elektronów.

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Introduction and the aim of the PhD thesis

Hydrogen peroxide and hydrogen are crucial chemicals due to their wide applications. H_2O_2 is used in medicine, cosmetic, textile electronics industries and in metallurgy. Furthermore, it is applied for wastewater treatment, paper bleaching and in chemical synthesis. H_2O_2 can be also employed in energy conversion devices like fuel cells. Also, H_2 found its application in energy conversion and storage. Moreover, it is used in synthesis and metallurgy. Conventionally, H_2O_2 and H_2 are produced by anthraquinone method and steam reforming, respectively. Both methods require higher temperature and pressure than at ambient conditions, what results in huge energy consumption. However, oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) at the liquid|liquid interface occur at mild conditions and separation of products for ORR is easier due to good solubility of H_2O_2 in water. The majority of ORR and HER studies at Interface between Two Immiscible Electrolyte Solutions (ITIES) were performed with biphasic system consisting of both phases with similar volume. The decrease of the volume of organic phase not only decrease influence on the environment, but also allows to construct the system, where electron donor supplying electrons can be electrochemically recycled.

The aim of my thesis was to investigate ORR and HER at liquid|liquid interface, when organic solvent volume is much smaller than the aqueous one. For that, three systems: (i) based on organic liquid film deposited on the electrode surface; (ii) based on carbon paste electrode (CPE), where small volume of organic liquid is employed as a binder of carbon microparticles and (iii) emulsion oil in water consisting of small organic droplets suspended in organic phase and colliding with bare electrode, were selected. In particular ITO electrode was covered by decamethylferrocene (DMFc) or decamethylruthenocene (DMRc) solution in 2-nitrophenyloctyl ether (NPOE) or 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($\text{C}_4\text{mimN}(\text{Tf})_2$). As aqueous phase, HClO_4 aq. was used to provide H^+ needed for formation of H_2O_2 and H_2 . Application of DMFc solution in vegetables oil as CPE binder also allowed to generate H_2O_2 in acidic aqueous solution. Also, oil in water emulsion consisting of small fraction of organic solution (DMFc or DMRc solution in trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$) and toluene) were applied for ORR and HER.

This thesis is divided into three main parts. At the beginning, updated knowledge about ORR and HER at ITIES is presented. Next, employed experimental methods, chemicals and apparatus are outlined. Finally, obtained results are presented and discussed in chapters focused on a given biphasic system. At the end conclusions of the thesis are described.

List of abbreviations

ITIES	Interface Between Two Immiscible Electrolyte Solutions
HER	Hydrogen evolution reaction
ORR	Oxygen reduction reaction
CV	Cyclic voltammetry
SWV	Square wave voltammetry
CA	Chronoamperometry
SECM	Scanning electrochemical microscopy
OCP	Open circuit potential
UV-Vis	Ultraviolet-visible
RE	Reference electrode
WE	Working electrode
CE	Counter electrode
RDE	Rotating disc electrode
UME	Ultramicroelectrode
GC	Glassy carbon
ITO	Indium tin oxide
ITONPs	ITO nanoparticles
ITO ITONPs	ITO electrode covered by ITO nanoparticulate film
CPE	Carbon paste electrode
DMFc	Decamethylferrocene
DMRc	Decamethylruthenocene
C₄mimN(Tf)₂	1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
P_(6,6,6,14)N(Tf)₂	Trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide
N_(1,8,8,8)N(Tf)₂	Methyltrioctylammonium bis(trifluoromethylsulfonyl)imide
TFT	α,α,α -trifluorotoluen

TN	toluene
NPOE	2-nitrophenyloctyl ether
FcOH	Ferrocenomethanol
BATB	Bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate
LiTB	Lithium tetrakis(pentafluorophenyl)borate
THAP	Tetrahexylammonium perchlorate

1 Liquid|liquid interface

1.1 Introduction to liquid|liquid interface and its history

There are different kinds of liquid|liquid interfaces. One of them is the interface between two immiscible electrolyte solutions (ITIES), which is formed after contact of electrolyte solutions in solvents of low mutual solubility. Typically, strongly hydrophilic salt solution in water is used as aqueous phase, whereas lipophilic salt solution in hydrophobic organic polar solvents is employed as organic phase. Nitrobenzene (NB) 1,2-dichloroethane (DCE) or recently α,α,α -trifluorotoluene (TFT) are most frequently employed organic solvents in these studies [1].

First experiments at liquid|liquid interface were carried out by Negbauer, who focused on equilibrium between CdI_2 aqueous and amyl alcohol solutions to measure the potential difference [2]. First confirmation of ion transfer across ITIES was reported by Gavach in 1968 [3]. However, in the beginning of 20th century, Nernst and Riesenfeld published their works regarding ion transfer between two immiscible liquids – phenol and aqueous salt solutions [4], [5].

First report on electron transfer across the ITIES was published in 1975 and described metal deposition at water|DCE interface [6] [7]. Two years later, Samec published results on biphasic system consisting of aqueous and nitrobenzene salt solution [8]. As reactants $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ in aqueous phase and ferrocene (Fc) in organic phase were used and the voltammetric signal was observed, when both redox species have been present in the system. Authors concluded that hydrophobic Fc was oxidised and hydrophilic $\text{Fe}(\text{CN})_6^{3-}$ reduced due to the electron transfer across ITIES [8].

1.2 Structure of electrode|electrolyte interface

The electrode|electrolyte interface was first time described by Helmholtz. He analysed the charge distribution on the interface and treated the ions as charge points. He stated the existence of counter-charge on the electrode. At both sides of electrode|solution interface there is ‘layer’ of opposite charges, which is called double layer. The rigid layer of ions next to the electrode surface and ions of opposite charge separated from them form double layer [9].

Next, Gouy and Chapman developed other model by introducing the diffuse layer next to the double layer, where the concentration of charge carriers is the highest and it decreases at the further distance from the electrode surface [10]. This model can be applied only for diluted electrolyte solutions [11].

In his modification of double layer theory, Stern did not treated ions as point charges [9]. This was justified by the lack of possibility for ions to get closer to the electrode than at a distance of ion radius. The first layer of ions next to the electrode surface is called compact, Helmholtz or Stern layer. It consists of solvent molecules and/or specifically adsorbed molecules or ions. Inner Helmholtz plane (IHP) is formed by adsorbed ions, whereas solvated ions stay at outer Helmholtz plane (OHP) (Figure 1-1). In OHP ions are non-specifically adsorbed and interact with electrode by long-range electrostatic forces. From that distance diffusion layer is build up towards bulk solution [9].

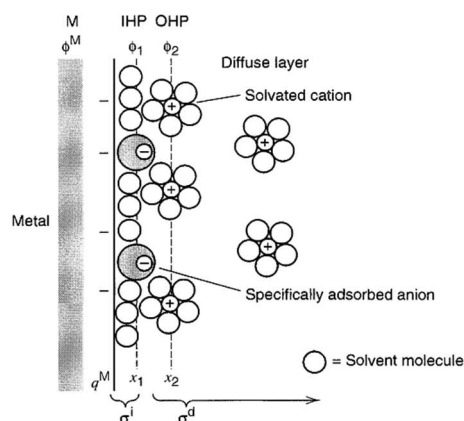


Figure 1-1. Structure of double layer at metal|electrolyte interface [9].

The above models describe the electrode|liquid interface, which is different than liquid|liquid interface. In the first case interface is formed between electronic and ionic conductor, whereas in the second one, it is created between ionic conductors. When this interface is formed by two electrolyte solutions, both ions and electrons can be transferred across liquid|liquid interface, whereas only electron can be transferred across metal|electrolyte interface. The only exception is liquid metallic electrode (i.e. mercury) where insertion of metal ions before electrochemical amalgam formation was suggested, Moreover, the nanometric layer between two liquids is considered to be mixed solvent layer [12]. Therefore, other models are used to characterise it and they are described below.

1.3 Structure of liquid|liquid interface

The first model of liquid|liquid interface was presented by Verwey and Niessen (VN model) in 1939 [13]. Their calculations were based on the Gouy-Chapman model and were not supported by experimental results. VN model assumes that two diffusion layers of immiscible liquids are in contact [13]. The potential in each phase depends on the product of concentration and relative permittivity. Although the potential drop in every phase can be different, it is possible that the thickness of both diffuse layers is similar [11].

Due to the limitation of the above-mentioned approach, the modified Verwey Niessen (MVN) model was proposed and assumes a presence of the ion-free inner layer between liquids. MVN model was built on the basis of the situation observed at water|NB interface, mostly with tetraalkylammonium or tetraphenylborate salts as supporting electrolytes in the organic phase. The water|NB system is limited by the narrow potential range comparing to other organic solvents interface with water. Therefore, MVN model cannot be applied for systems with wider potential windows [14], [15].

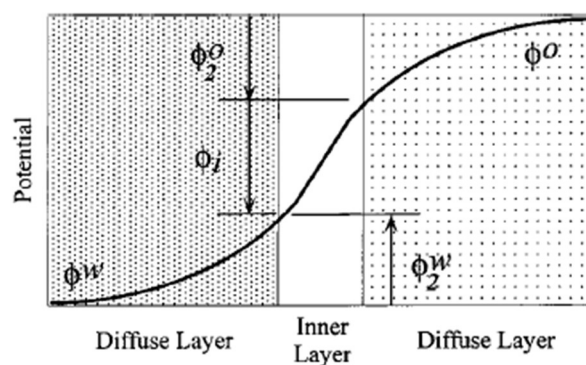


Figure 1-2. Scheme of modified Verwey-Niessen model of ITIES [16].

Later, Girault and Schiffrin presented mixed solvent layer model [17], which assumes that the interface between two liquids is not molecularly sharp and it is the mixture of both solvents. The properties of this region depend on the distance from the interface [11].

Poisson-Boltzman potential in mean force model [18] describes electron density at the interface between two immiscible liquids (measured by X-ray reflectivity). In contrast to MVN model, here ITIES is described as interface between two bulk solutions with constant dielectric permittivity and sharp ion density decrease (Figure 1-3). Interestingly, this model assumes that dielectric permittivity at ITIES depends on the orientation of solvent molecules. However, it does not consider the effect of ion distribution on the potential drop and does not work at zero or negative polarisation of ITIES [7].

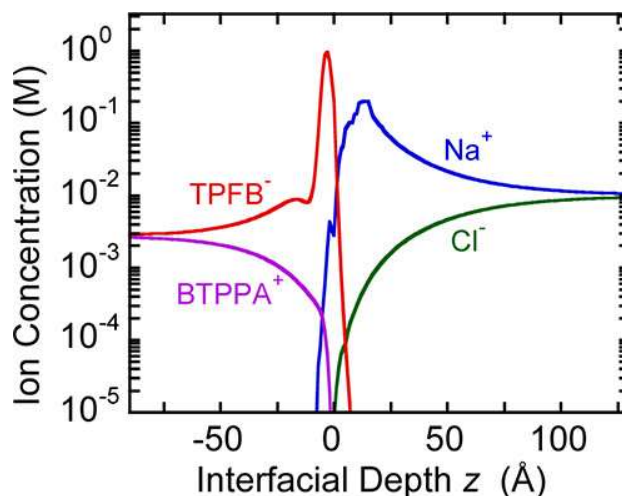


Figure 1-3. Ion concentration profiles across the DCE (5 mM bis(triphenylphosphoranylidene) ammonium tetrakis(pentafluorophenyl)borate (BTPPA⁺TPFB⁻))/water (10 mM NaCl) interface at $\Delta\phi^{w-o} = 0.346$ V: Na⁺ (blue), Cl⁻ (green), BTPPA⁺ (violet), and TPFB⁻ (red) [19].

Other idea was presented by Samec [20], [21]. The existence of double layer consisting of inner and outer Helmholtz plane at ITIES was proposed. It was confirmed by experiments with NB|water interface with tetraalkylammonium (ethyl, propyl, butyl and pentyl) bromide, when Guy-Chapman model was used to calculate the differential capacity of diffuse layer. It was concluded that the differential capacity of liquid|liquid interface is bigger than that of electrode|liquid interface, because of different thickness of inner layer [20], [21].

Nowadays simulations play a big role in investigation of the structure of ITIES. Molecular dynamic simulations (MD) are employed to understand motion of molecules in time,

considering their interactions. Two types of such simulations were applied for liquid|liquid interface, either solvent between walls or two immiscible solvents. Monte Carlo simulations have also been used for liquid|liquid interface with focus on configurations of molecules at equilibrium [11]. In turn, simulations with gas lattice model confirmed that the liquids interpenetrate at liquid|liquid interface [22], [23].

Recently, Gschwend described the challenges on the understanding of processes at liquid|liquid interface [7]. Liquid|liquid interface sharpness depends on time and this effect is reproducible [24]. The interface was considered to be sharp with the roughness below 1 nm [7] with ‘fingers’ of organic solvent penetrating the aqueous phase [25].

1.4 Potential drop at liquid|liquid interface

For better understanding of processes at ITIES, the thermodynamic description is crucial. After mixing two immiscible liquids and phase separation, the interfacial potential difference appears. There are two components of the potential: one resulting from the dipoles’ orientation near interface and second one from the excess of free charges at the interface.

The inner potential ϕ is defined as a sum of surface potential χ and outer potential ψ .

$$\phi = \chi + \psi \quad 1-1$$

At constant temperature and pressure, electrochemical potentials of given molecule or ion in organic phase - $\bar{\mu}_i^O$ and in aqueous phase - $\bar{\mu}_i^W$ being in contact are equal:

$$\bar{\mu}_i^O = \bar{\mu}_i^W \quad 1-2$$

For a given ion in the phase α (organic or aqueous), the electrochemical potential $\bar{\mu}_i^\alpha$ is a sum of its chemical (μ_i^α) and electric ($\mu_i^{\alpha,el}$) components.

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + \mu_i^{\alpha,el} \quad 1-3$$

The electric component of electrochemical potential ($z_i F \phi$) is defined as a work necessary to transfer the charged particle (in vacuum) from the infinity to inside the phase α . z_i is the charge of the particle and F is Faraday constant equal 96485 C mol^{-1} .

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi \quad 1-4$$

Combining equations 1-2 and 1-4, one can calculate the potential difference between two phases, which is called Galvani potential:

$$\Delta_O^W \phi = \phi_W - \phi_O = \frac{1}{z_i F} (\mu_i^O + \mu_i^W) \quad 1-5$$

Then, standard Galvani potential) $\Delta_O^W \phi_i^\circ$ (potential of the transfer of ion from aqueous phase to organic phase) depends on the standard Gibbs energy of the ion transfer from organic to aqueous phase ($\Delta G_i^{O \rightarrow W, \circ}$):

$$\Delta_O^W \phi_i^\circ = -\frac{1}{z_i F} \Delta G_i^{O \rightarrow W, \circ} \quad 1-6$$

The equation (1-5) can be transformed considering that chemical potential depends on the concentration:

$$\Delta_O^W \varphi = \frac{1}{z_i F} (\mu_i^{O,\circ} + \mu_i^{W,\circ}) + \frac{RT}{z_i F} \ln \frac{\gamma_i^O c_i^O}{\gamma_i^W c_i^W} \quad 1-7$$

where γ_i^O is activity coefficient and c_i^O is a concentration of ion in organic phase.

Considering that $\Delta G_i^{O \rightarrow W,\circ}$ is the difference between standard solvation energies of ion in organic and aqueous phase):

$$\Delta G_i^{O \rightarrow W,\circ} = (\mu_i^{O,\circ} + \mu_i^{W,\circ}) \quad 1-8$$

one can get Nernst type equation used already to describe potential difference at the liquid|liquid and solid|liquid interfaces:

$$\Delta_O^W \varphi = \Delta_O^W \varphi^\circ + \frac{RT}{z_i F} \ln \frac{\gamma_i^O c_i^O}{\gamma_i^W c_i^W} \quad 1-9$$

Clearly, the similarity of the equation 1-9 to the conventional Nernst equation is caused by the same redox process at ITIES as in the solution [11].

1.5 Polarisation

Polarisation is defined as a departure of the electrode potential from its equilibrium value during faradaic current flow. The parameter called overpotential (η) is used as a measure of the extent of polarisation [9]:

$$\eta = E - E_{eq} \quad 1-10$$

Polarisation curve is the E vs. I dependence measured at the steady state conditions, typically at very slow scan rate. The ideally polarisable electrode exhibits wide potential range when the big change of the potential results in small change of the current (Figure 1-4, left). Non-ideally polarisable shows opposite behaviour, even a small change of potential produces huge current (Figure 1-4, right) [9].

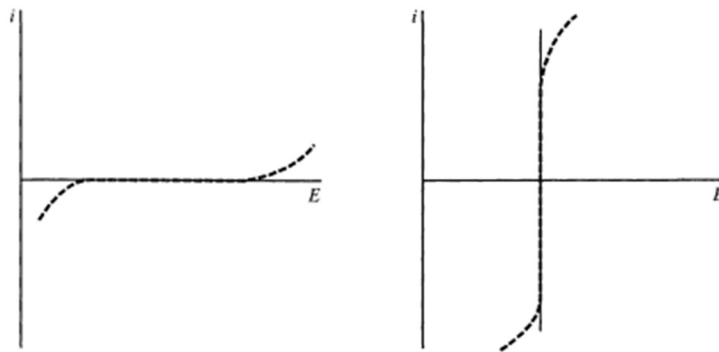


Figure 1-4. Current vs. potential plots for ideally polarisable (left), non-ideally polarisable (right) electrodes [9].

The polarisation of ITIES can be fixed either by i) applying from the external source a given potential difference across the interface ii) adding the same salt to both phases or iii) adding the salts with common ion to both phases [11].

1.5.1 Polarisable liquid|liquid interface

Applied potential difference to polarisable liquid|liquid interface below some limit does not produce significant current increase because ions are not transferred between phases. For polarised interface, the control of $\Delta_0^W \phi$ is only by external potential difference source like potentiostat [11].

1.5.2 Ideally non-polarisable liquid|liquid interface

When only one ion, for example tertbutylammonium cation (TBA^+), is common in both phases, $\Delta_0^W \phi$ can be described by the equation (1-9). When the concentration of counterions e.g. Cl^- in aqueous phase is high, their partitioning influence the interfacial potential. Such behaviour can be observed in half-cell:



Here, the potential difference at the liquid|liquid interface can be described by the following equation:

$$\Delta_0^W \phi_{\text{eq}} = \Delta_0^W \phi_{\text{TBA}^+}^\circ + \frac{RT}{F} \ln \frac{c_{\text{TBA}^+}^o}{c_{\text{TBA}^+}^w} \quad 1-11$$

Then, this interface is reversible towards TBA^+ and it can be used as reference liquid|liquid interface. Therefore, it may play a role of reference electrode together with reference electrode in aqueous phase. In practise, this type of half-cell is mostly used in nonequilibrium conditions, therefore the diffusion should be investigated to know what happens at ITIES [11].

1.6 Potential window and system of electrochemical measurements of liquid|liquid interface

The ITIES is defect-free and reproducible interface. In this respect, it is similar to reproducible surface of mercury droplets immersed in electrolyte solution. Conventional electrochemical measurements with ITIES are performed in 4-electrode system (Figure 1-5), using 2 reference electrodes (one in each phase) for ITIES's polarisation control and 2 counter electrodes (one in each phase). The potential difference between counter electrodes is controlled by bipotentiostat and as a result of interfacial ion transfer, the current flows between them [26]. If the interfacial area is reduced to micrometre size, the measured currents are so small, that 2-electrode setup can be employed. The volume of organic phase is then too low to enable positioning electrodes inside [27].

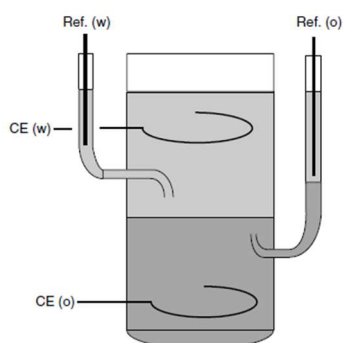


Figure 1-5. Scheme of 4-electrode setup for electrochemical measurements at liquid|liquid interface [27].

Potential window can be defined as the potential range, where only capacitive current flows (Figure 1-6). At liquid|liquid interface it is limited by ion transfer of electrolyte component. For example, the increase of current at potential difference higher than 0.2 V is caused by tetraphenylborate anion (TPB^-) transfer from organic to aqueous phase as can be judged from the value of its transfer potential ($\Delta_{\text{O}}^{\text{W}}\phi_{\text{TPB}^-}=340 \text{ mV}$). When TPB^- is replaced by more hydrophobic tetrakis(4-chlorophenyl)borate anion (TPBCl^-), increase of the current is shifted towards higher potentials. It results from Li^+ cation transfer from aqueous to organic phase because of higher transfer potential of TPBCl^- from aqueous to organic solution [27].

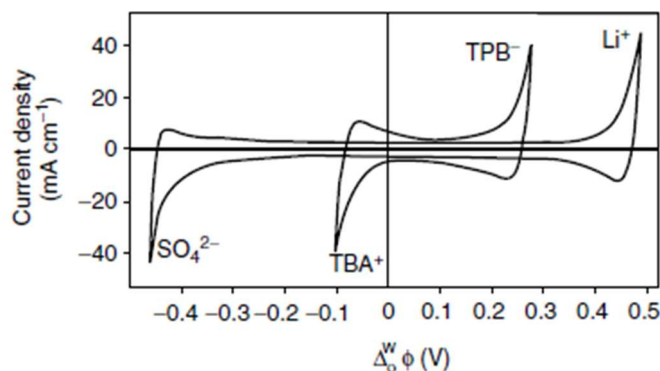


Figure 1-6. Potential window for biphasic systems consisting of: 1,2-DCE with 5mM tetrabutylammonium tetraphenylborate (TBATPB) and 5mM Li_2SO_4 in water (thinner potential range); 1,2-DCE with 5mM bis(triphenylphosphoranylidene)ammonium tetrakis(4-chlorophenyl borate) (BATPBCl) and 5mM Li_2SO_4 in water (wider potential range) [27].

1.7 Charge transfer at ITIES

As ITIES does not have any defects, it can be considered as good model system to study different types of charge transfer processes [26]. They include simple ion transfer, assisted ion transfer, electron transfer [24] or proton coupled electron transfer [26].

1.7.1 Simple ion transfer

Ion transfer (IT) is possible when the Galvani potential (*1-12*) compensates the Gibbs energy, which is necessary for ion transfer, by polarisation of interface [24].

$$\Delta_{\text{O}}^{\text{W}}\phi = \phi^{\text{W}} - \phi^{\text{O}} \quad 1-12$$

In quiescent conditions ion diffuses from the bulk of the one phase to the interface. Then, it passes the interface and diffuses from the interface to the bulk of the second phase [24]. Mass transfer is described by first Fick's law when ion appears close to the interface [24]. Mass transport is the limiting step of IT, whereas electrochemically ion transfer is reversible [27].

When hydrated ions are transferred to organic phase, they move with some water molecules around. Moreover, the aqueous 'tail' is formed and when it is broken, then the ion loses its solvation's shell and water molecules return to the aqueous phase. In turn, when ions are transferred from organic solution, they attract water molecules. They form a string, which catches and suck the ions, which are close to the liquid|liquid interface [28].

Simulations were also used to investigate the ion transfer at ITIES. However, they do not consider the other ions present in the solutions. Recently, it was concluded that for more

hydrophilic ions, their aqueous clusters move from aqueous to the organic phase instead of bare ions [7].

The voltammogram of the simple ion transfer on the example of β -phenylethylammonium cation transfer from water to nitrobenzene is shown below (Figure 1-7 A). The peak potential separation around 60 mV indicates reversible and diffusion-controlled process [29].

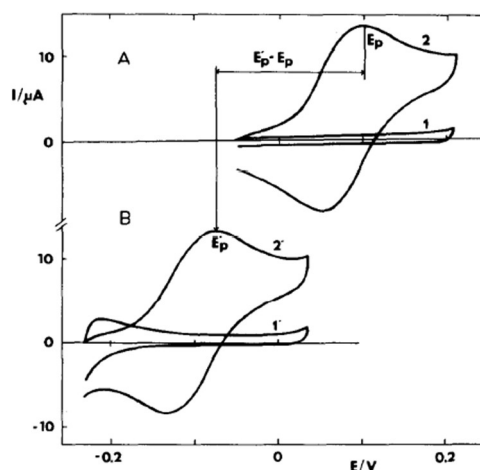


Figure 1-7. Cyclic voltammogram of A) simple ion transfer and B) assisted ion transfer (in the presence of dibenzo-18-crown-6), on the example of β -phenylethylammonium cation (2,2') transfer from water to nitrobenzene. The voltammogram was obtained with the interface formed by 0.01 M HCl in water and 0.01 M TPAsDCC (tetraphenylarsonium,3'-oxo-bis(undecahydro-1,2-dicarba-3-cobalta-closo-dodecaborate) in nitrobenzene, scan rate 20 mV s⁻¹ [29].

Photoinduced ion transfer is the specific class of ion transfer process, because it occurs under exposure of ITIES to the visible or UV light. The observed current results from the transfer of excited ion or from the transfer of the photoreaction ionic product [30]. For the first time this phenomenon was observed in 1985 by Zaitsev [31].

1.7.2 Assisted ion transfer

Assisted ion transfer (AIT) involves transfer of ions together with coordinated ligands across the interface [24]. This process is also fast and mostly reversible [27]. Its mechanism is more complex than that of simple one (Figure 1-8). The name AIT comes from the fact that complexation of solvated ion decreases energy barrier of the transfer across the liquid|liquid interface. In other words, the ligands facilitate ion transfer and this is why this process is also called facilitated ion transfer. There are four different AIT types: transfer by interfacial complexation (TIC), interfacial dissociation (TID), aqueous complexation followed by the transfer of the complex (ACT) and transfer followed by organic phase complexation (TOC) [24].

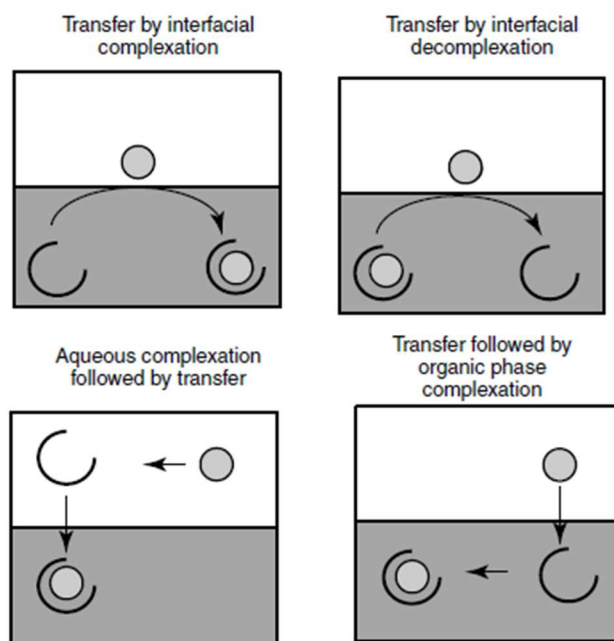


Figure 1-8. Scheme of different mechanisms of assisted ion transfer [27].

The transfer potential of assisted cation transfer is lower as compared to non-assisted one (Figure 1-8 B) and this difference depends on the equilibrium constant of the complex [29] [30].

1.7.3 Electron transfer

Electron transfer (ET) at ITIES processes can be investigated by slow cyclic voltammetry and scanning electrochemical microscopy (SECM) [30]. To allow electron transfer across liquid|liquid interface, the system must cross the level of Gibbs activation energy. According to Marcus theory, it depends of reorganisation energy (λ), formal Gibbs energy for electron transfer ($\Delta G^{\circ'}$), work to allow the product to diffuse from ITIES (w_p) and work to move the substrate to the ITIES (w_r) [24]:

$$\Delta G_{\text{act}} = \frac{(\lambda + \Delta G^{\circ'} + w_p - w_r)^2}{4\lambda} \quad 1-13$$

According to the simplest ET mechanism, oxidised form O_1 from the phase 1 and reduced form R_2 from the phase 2 move to the interfacial area to be reduced and oxidised (1-14), respectively. Then, they diffuse back to the bulk solution (Figure 1-9) [24].



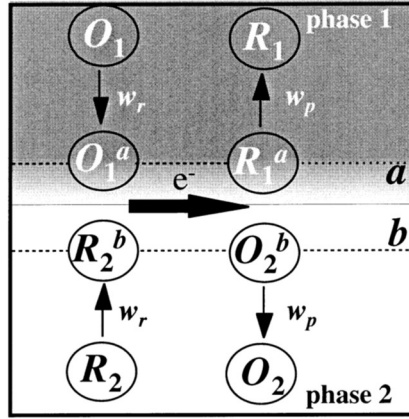


Figure 1-9. Mechanism of electron transfer at liquid|liquid interfaces scheme [24].

When system is at equilibrium, following equation:

$$\bar{\mu}_{R_1}^W + \bar{\mu}_{O_2}^O = \bar{\mu}_{O_1}^W + \bar{\mu}_{R_2}^O \quad 1-15$$

can be used to write the Nernst equation for electron transfer at liquid-liquid interface:

$$\Delta_O^W \varphi = \Delta_O^W \varphi_{ET}^\circ + \frac{RT}{F} \ln \frac{a_{R_1}^W a_{O_2}^O}{a_{O_1}^W a_{R_2}^O} \quad 1-16$$

where $\Delta_O^W \varphi_{ET}^\circ$ is a standard electron transfer potential across interface, defined by the difference of the standard potential of oxidation of R_2 and reduction of O_1 in a given solvent [26]:

$$\Delta_O^W \varphi_{ET}^\circ = \left[E_{O_2/R_2}^\circ \right]_{SHE}^O - \left[E_{O_1/R_1}^\circ \right]_{SHE}^W \quad 1-17$$

The examples of voltammograms related to quasi-reversible ET at ITIES is shown below (Figure 1-10) [32].

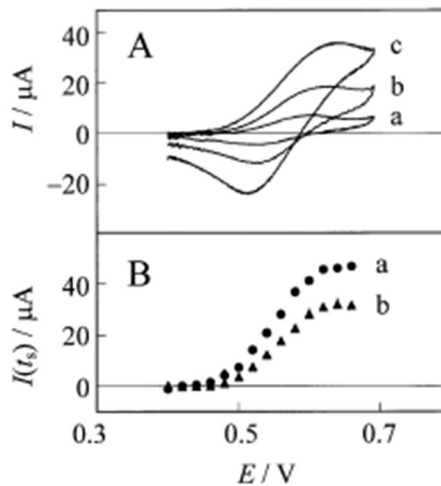


Figure 1-10. A) Cyclic voltammograms, scan rates 0.01 (a), 0.05 b) and 0.2 $V s^{-1}$ (c), B) normal pulse voltammogram (sample time: 0.02 (a) and 0.1(b) of the biphasic system consisting of 1.5 mM decamethylferrocene (DMFc) in nitrobenzene and 0.075 mM $[Fe(CN)_6]^{3-}$ and 0.015 mM $[Fe(CN)_6]^{4-}$ in water [32].

Similarly, as the ion transfer, electron transfer can be also photoinduced [30]. Already in 1988 Thomson presented the example of increase of the current related to ET at ITIES in the presence of light (Figure 1-11) [33].

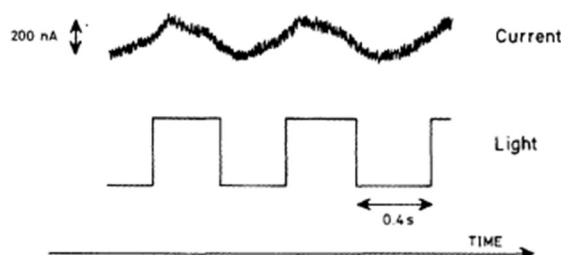


Figure 1-11. Current dependence vs. time in the presence and absence of light using hydrophobic Pt gauze, in aqueous phase was 4×10^{-4} M tris(2,2'-bipyridine)ruthenium(II)chloride $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$, organic phase contained 4×10^{-3} M $\text{C}_7\text{V}(\text{TPB})_2$ (1,1'-diheptyl-4,4'-bipyridinium tetraphenylborate) and 10^{-3} M TBATPB in 1,2-DCE Both phases were deoxygenated with nitrogen [33].

1.7.4 Proton coupled electron transfer

The electron transfer across liquid|liquid interface can be coupled with other processes. Proton coupled electron transfer (PCET) is perhaps the simplest example. In fact, both ORR paths (2- and 4-electron) and HER belong to PCET class of reactions [34]. Reduction of protons from aqueous phase by decamethylferrocene (DMFc) dissolved in organic phase and oxygen reduction involving protons from aqueous phase by ferrocene (Fc) dissolved in organic phase, occurring at molecular catalyst floating at liquid-liquid interface are the examples of these reactions (Figure 1-12).

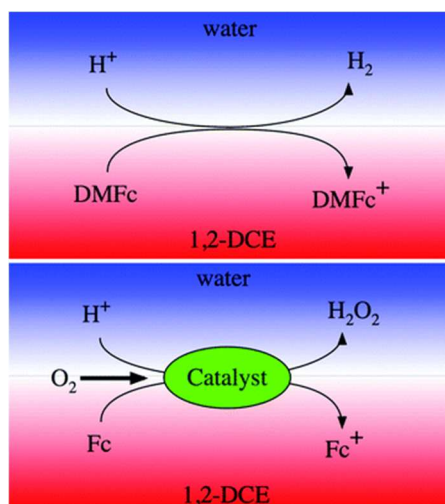


Figure 1-12. Scheme of hydrogen evolution at ITIES using DMFc as electron donor (top), proton coupled electron transfer reaction for oxygen reduction reaction with Fc as electron donor, at the interface water|DCE in the presence of catalyst (bottom) [26].

The cyclic voltammetry (CV) of the cell (Figure 1-13 b), with cobalt porphine (as catalyst) adsorbed at the liquid|liquid interface, shows the increase of current at potential higher than 0.3 V due to the proton coupled electron transfer. The set of peaks around 0.05 V comes from dimethylferrocene (DFc) cation transfer from organic to aqueous phase [26]. This demonstrates that CV is a well-suited tool to study PCET.

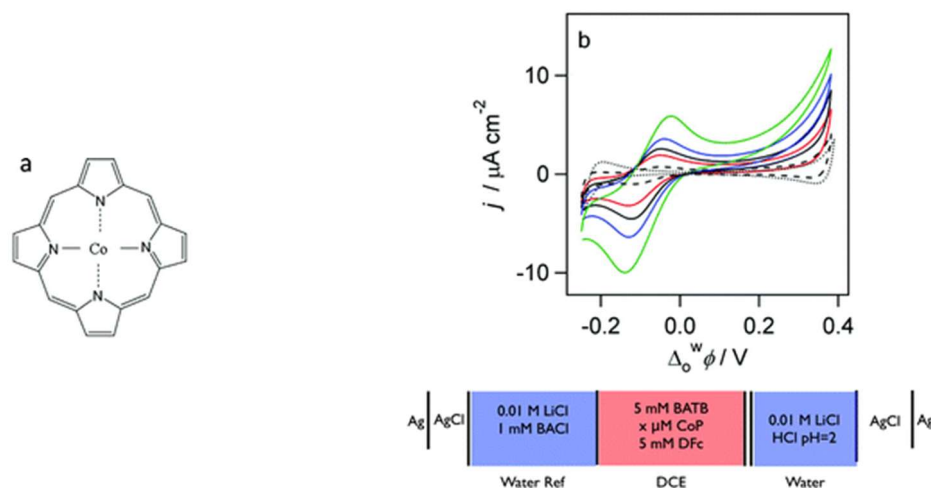


Figure 1-13. a) Structure of cobalt porphine, b) CV of proton coupled electron transfer for the example of cobalt porphine for different concentration in 1,2-DCE (10, 25, 50 and 75 mM – from red to green) in presence of DFC, only bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BATB) (dotted line), in the presence of DFC (dashed line), scan rate 50 mVs^{-1} . The scheme of the cell is shown at the bottom [26].

1.8 Potential applications of ITIES

ITIES has already many applications (predominantly in the laboratory) in extraction processes, HER, ORR, oxygen evolution reaction [25], electrocatalysis, metal deposition or drug's development [35] [36]. Unfortunately, there are limitations of usage of ITIES, like specific complexity of the setup (which can be difficult to apply in real-life) or usage of harmful organic solvents [36]. Therefore, research on reactions at ITIES is also focused on decreasing the volume of organic solvents [37] and finding environmentally friendly solvents, like true oils [38].

2 Liquid modified electrodes

2.1 Three-phase and multi-phase electrodes

Apart of the experimental system with bulk aqueous and organic phase reactions at liquid|liquid interface can be carried out, when the organic phase forms a droplet(s) on the electrode surface. In this specific arrangement also solid|liquid interface is involved, in some arrangements solid|liquid|liquid three-phase junction plays important role. Obviously, this approach allows to decrease the volume of organic solvent to reduce its influence on the environment.

In such experiments, electrode covered with the droplet of redox probe solution in organic solvent is immersed in the aqueous solution and the interface - solid electrode|organic solution|aqueous solution, is formed or not [39]. When the electrode is fully covered with the non-conductive layer of organic solution without electrolyte, it behaves like resistor due to the huge ohmic drop, what is demonstrated by characteristic shape of voltammogram (Figure 2-1 a, c). In turn, when the oil droplet does not cover the whole active area of electrode, the oxidation and reduction reactions can occur, what is visible on peak shaped CV (Figure 2-1 b, d) [40].

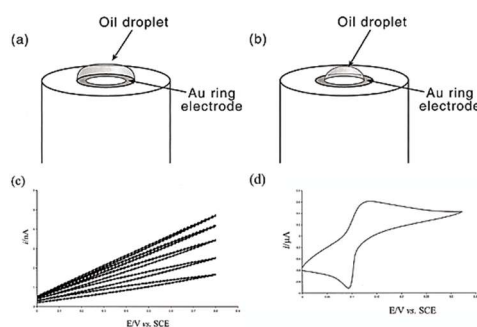


Figure 2-1. Scheme of the a) electrode fully covered by oil droplet and c) obtained CV b) electrode partially covered by oil droplet and d) obtained CV [40].

To achieve reasonable biphasic reactions efficiency, the three-phase junction should be as long as possible. For that, modification of the surface with the number of microdroplets was proposed and this kind of electrodes is called 'multi-phase electrode' which has more extended three-phase junction than single droplet modified electrode [41]. The triphasic contact length of microdroplets array of the same volume is 3 times bigger for the droplets of diameter 10 μm than for diameter 100 μm , assuming their hemispherical geometry. Clearly, larger number of smaller droplets results in longer three-phase junction [42]. Also, the advantage of multi-phase electrodes is their smaller ohmic drop as compared to the electrodes modified with single droplet [37], [43].

The research on electrodes modified by liquids was pioneered by Marken [37], [43]. He demonstrated the electrode made of basal plane pyrolytic graphite electrode or siliconized ITO electrode covered by microdroplets of redox active and oily N,N,N',N'-tetrahexylphenylene diamine (Figure 2-2). This compound was deposited by evaporation of its acetonitrile solution. Usage of this microdroplets covered electrode allowed to hold the biphasic electrochemical reaction, even when only aqueous phase contained electrolyte [37], [43].

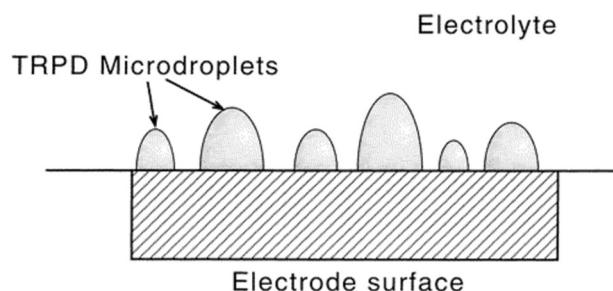


Figure 2-2. Scheme of electrode modified by microdroplets of N,N,N',N' -tetraalkyl-para-phenylenediamine oils (TRPD, $R = n$ -butyl, n -hexyl, n -heptyl, and n -nonyl) [40].

Later, the name of three-phase electrodes was introduced by Scholz [44]. The corresponding experiment was performed with the paraffin impregnated graphite electrode modified with droplet of redox probe solution in nitrobenzene immersed in aqueous electrolyte. This allows to form electrode|NB|water interface. Impregnation of the electrode with paraffin prevents the penetration of NB into the electrode material. The contact area between organic, aqueous solutions and electrode is small as shown on the scheme (Figure 2-3) [44]. Advantageously, three-phase electrodes allow usage of water-immiscible organic solvents as n -octanol [45], which have not been used for electrochemical biphasic processes studies in conventional 4-electrode system. Here, the organic solvent is in contact with both, the electrode and the aqueous solution. Electron transfer between the redox probe dissolved in organic solvent and the electrode occurs close to the three-phase junction and is followed by ion transfer between organic and aqueous phase to preserve electroneutrality of organic phase [39]. Mainly NB [46] and DCE [46], but also n -octanol [45], [47], 2-octanol [48], D-menthol [46], nitrophenyl-octyl ether [47], 4-(3-phenylpropyl)pyridine [49], and room-temperature ionic liquids [50] have been applied in three-phase electrodes.

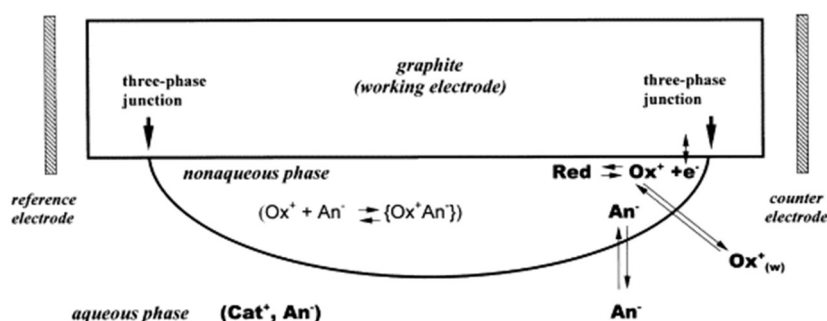


Figure 2-3. Scheme of three-phase electrode [44].

Other approaches to immobilize liquid on the electrode surface have been also proposed. For example, hydrophobic materials based on graphite [51] or carbon nanofibers [52] were used as support to make liquid deposit more stable. Moreover, carbon nanoparticles [53] and metal oxide (like TiO_2 [54] or indium tin oxide (ITO) nanoparticles (NPs) [41] were used for premodification to stabilise liquid film and increase the total length of solid|liquid|liquid three-phase junction. For example, ITO NPs were deposited by dip coating on the ITO electrode surface (Figure 2-4). Electrode modified by different number of immersion and withdrawal steps was tested and the capacitive current increased with the increasing number of deposited nanoparticles layers. Similar effect was seen for voltammetric peak current, when the redox liquid – t -butylferrocene ($t\text{BuFc}$) was used as liquid deposit [41]. In other study, the electrodes were additionally modified by hydrophobic sol-gel silica film, which did not influence the electrochemical properties in the noticeable scale. However, the mechanical stability and

durability of porous electrodes were increased [55]. The ITO electrode modified by ITONPs was also used during the research for this thesis.

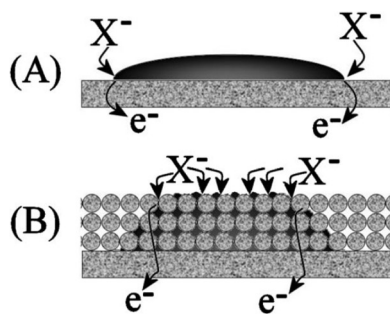
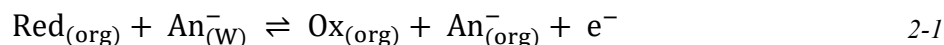


Figure 2-4. The scheme of the A) bare ITO electrode B) ITO covered with ITO NPs with the droplet of *t*-butylferrocene [41].

Furthermore, in-situ emulsion formation in hydrodynamic systems was seen close to the three-phase boundary [56]. The photo-electrochemical reactions of phenylenediamine [57] and later with rhodamine [58] have been also examined on the three-phase electrodes. The photo-electrochemical studies on the three-phase junction were summarised by Marken [42].

When the neutral molecule is dissolved in the organic phase, then after its oxidation, the positive charge appears in organic phase. To keep its electroneutrality, the oxidation is followed by interfacial ion transfer: anion transfer to the organic phase or cation transfer from the organic phase (Figure 2-3). The direction of the transfer can be concluded from the dependence of redox potential (here from square wave voltammetry (SWV) vs. anion concentration of aqueous phase (for hydrophobic and hydrophilic anions) [59]. Obviously, the direction of interfacial ion transfer depends on the hydrophobic/hydrophilic properties of ions. When cations in the organic phase are hydrophobic enough, they stay in the organic phase and anions from aqueous phase are inserted to the organic solution [39].

When the reduced form of redox probe is dissolved in the organic phase, the electrode reaction can be written as follows [60]:



Formal potential (E_f) of this redox couple could be described by the following equation [60]:

$$E_f = E_{\text{Ox}_{(\text{org})}/\text{Red}_{(\text{org})}}^\circ + \Delta_W^{\text{O}} \phi_{\text{An}^-} - \frac{RT}{F} \ln c_{\text{An}_{(\text{w})}^-} + \frac{RT}{F} \ln \frac{c_{\text{Red}_{(\text{org})}}^*}{2} \quad 2-2$$

where: $E_{\text{Ox}_{(\text{org})}/\text{Red}_{(\text{org})}}^\circ$ - the standard redox potential of the redox couple Ox/Red in the organic solvent, $\Delta_W^{\text{O}} \phi_{\text{An}^-}$ - the standard potential of anion transfer from the aqueous phase to the organic phase and $c_{\text{Red}_{(\text{org})}}^*$ - the initial concentration of the reduced form in the organic phase [60]. As $\Delta_W^{\text{O}} \phi_{\text{An}^-}$ value is more negative for more hydrophobic anions, the formal potential is shifted towards lower values. For ten-fold anion activity increase, the formal potential is decreased by 59 mV. In the first approximation, the activities can be replaced by concentrations and then by initial concentrations [60].

It was found that the formal potential of DMFc/DMFc⁺ redox couple in NB droplet deposited at the electrode immersed in aqueous solutions is linearly dependent on the hydrophobicity of

organic phase and of anions present in aqueous phase. The slope of this plot is equal 0.95, close to the expected unity value (Figure 2-5) [44].

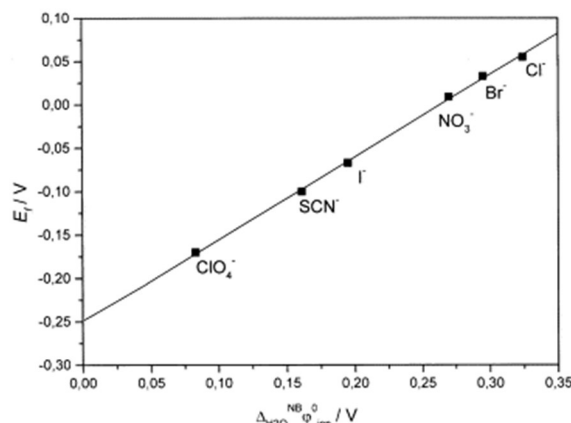
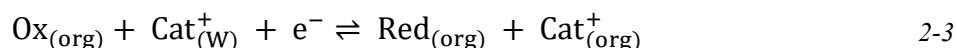


Figure 2-5. Formal potential of DMFc/DMFc⁺ determined at the three-phase junction of nitrobenzene and aqueous solution and graphite electrode vs. the standard potential difference for different anions at nitrobenzene|water interface [44].

Contrary to the above case, if the oxidised form is initially dissolved in the organic phase, then the reaction runs in the opposite direction [60]:



Then the formal potential can be calculated using the formula [60]:

$$E_c' = E_{Ox_{(org)}/Red_{(org)}}^0 + \Delta_W^O \phi_{Cat^+} + \frac{RT}{F} \ln c_{Cat_{(w)}^+} + \frac{RT}{F} \ln \frac{2}{c_{Ox_{(org)}}^*} \quad 2-4$$

In this case, $\Delta_W^O \phi_{Cat^+}$ is higher for more hydrophobic (lipophilic) cations [60].

Summarising this part, three-phase electrodes can find different applications, for example they can be used to distinguish chiral ions [61]. They can be used as a powerful and simple tool for ion-transfer [62] and catalysis [63] studies. They can be applied in pharmacy and drug design area to determine the lipophilicity of drugs, examine the kinetics of transfer across ITIES and adsorption of ionic drugs during the transfer [45]. Furthermore, they can be used for the synthesis of nanoparticles [63] and recognition of ionophores [62].

2.2 Thin liquid film electrodes

Another kind of liquid modified electrodes are these modified with thin liquid film. Contrary to three-phase electrodes, their whole surface is covered by organic solution. Therefore, the presence of the electrolyte in the organic polar solvent immiscible with water is crucial to enable electron transfer. Moreover, the conductivity of organic solution may increase in time due to the transfer of ions across liquid|liquid interface following redox reaction [39]. Thanks to the small thickness of liquid film, the iR drop is smaller than in conventional 4-electrode cell. In typical experiment, the electrode covered with thin liquid organic film of the thickness of tens micrometres is immersed in the aqueous electrolyte together with reference and counter electrodes and then voltammetry is performed (Figure 2-6). In almost all cases, the redox species are dissolved in the organic phase [64]. Interestingly, also electrode modified with thin aqueous film, operating in organic electrolyte was reported [65].

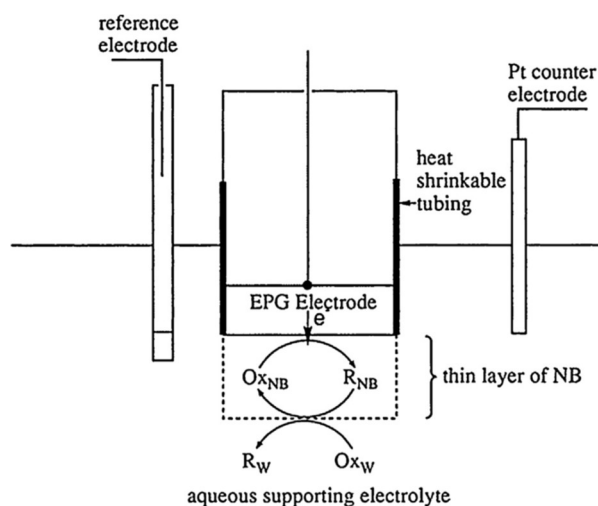


Figure 2-6. Scheme of thin liquid film electrode on edge plane graphite (EPG) immersed in the aqueous solution [64].

First time, thin liquid film electrodes were reported by Shi and Anson [66], [67]. They used edge plane graphite electrodes covered by small volume of organic solvent with dissolved redox mediator and salt. For less volatile solvents like NB or 4-methylbenzonitrile the layer's thickness was 30 μm , whereas for more volatile benzene or chloroform, larger volume was used to decrease the influence of fast evaporation [68]. Also, benzonitrile (BN) have been used for electrode modification [69] [64]. After organic phase deposition, the electrode was turned upside down and immersed in the aqueous solution. The possibility to study electron transfer by voltammetry of the thin film of organic solution was demonstrated [68].

Moreover, hydrophobic ionic liquids (ILs) were used for electrodes modification. They are less flammable and more viscous than typical polar molecular organic solvents immiscible with water. Their melting point is below room temperature and they are partially dissociated and ionically conductive. They have wide potential range and if they consist of hydrophobic ions, they exhibit low solubility in water, but water easily dissolves in them. Additionally, more complex systems with ionic liquids as a component have been implemented. They were examined in ion selective electrodes, reference electrodes, together with metal nanostructures, polymers, proteins. It seems that IL component can improve the mechanical stability and electrochemical activity of number of modified electrodes [70].

The electric charge in the liquid film produced during electrochemical redox reaction must be compensated. For example, after oxidation of DMFc dissolved in hydrophobic ionic liquid, the cation of IL is transferred to the aqueous phase (reaction 2, Figure 2-7). After the reduction of redox mediator in the film, the anion of IL is transferred to the aqueous phase (reaction 4, Figure 2-7). The hydrophobic properties of ionic liquid and aqueous solution, clearly, influence the reaction's mechanism [70].

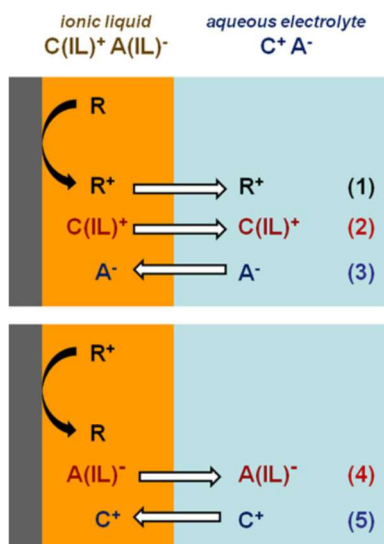


Figure 2-7. The scheme of the ion transfer following electron transfer for the electrode modified by ionic liquid immersed in the aqueous solution [70].

ORR was studied at thin liquid film electrodes. For that, the graphite electrode was covered by the layer of cobalt 5,10,15,20-tetraphenylporphyrin (CoTPP) solution in BN. This setup allowed for 4-electron reaction path, whereas CoTPP adsorbed on the electrode from CH_2Cl_2 catalyses 2-electron ORR. The voltammetric signal depends on the thickness of the layer and concentration of catalyst. Decreasing the concentration of CoTPP resulted in drop in the reaction rate. Increasing its concentration cause the peak potential transfer towards more positive values due to the plateau response for lowest concentration. This is caused by the fact that the formation of O_2 adduct with CoTPP is the limiting step of the process:



For thicker liquid film, the reduction peak current increased due to higher solubility of oxygen in benzonitrile than in water [71]. Importantly, this was the first example of biphasic ORR with electrochemical regeneration of electron donor/catalyst.

Summing up, thin liquid film electrodes do not require advanced equipment and they are feasible [64]. Their applications include studies of redox properties of hydrophobic compounds [67], determination of electron transfer rate across the ITIES [68], ion transfer [69] including ion transfer across bio membranes [72] and nanoparticles synthesis [73], [74], [75]. Additionally, they were used for construction of sensors for recognition of enzymatic products of glucoses oxidation. The measured signal is the current of transfer of gluconate ions across the water|NB interface [76]. Finally, thin liquid film electrodes were applied for investigation of ORR at ITIES [71].

2.3 Carbon paste electrodes

Carbon paste electrode (CPE) was first demonstrated by Adams in 1958 [77]. Carbon paste was prepared from carbon particles mixed with bromoform and placed in the cavity of Teflon[®] rod. Platinum wire was inserted into paste to keep the electric contact and the outer surface was polished on paper. CPEs big advantage is quick preparation and surface reproducibility [77]. Still in most of the studies similar design of CPEs is used with glass or plastic tube as the body of electrode with hydrophobic oil as a binder. CPEs can be modified with the redox probes added to the binder and they are most often employed for electrochemical sensing [78].

Typically, CPEs are made of 5-20 μm size [78] graphite powder mixed with organic viscous solvent, mostly long chain aliphatic hydrocarbons like hexa- or octadecane or silicone oil [21]. Other forms of carbon, like charcoal [79], carbon black with addition of fullerenes [80] and powdered glassy carbon [81] were used in CPEs. The choice of binder affects electrode's properties. It should be inert, electrochemically non-active, highly viscous, with low volatility, low solubility in water and immiscible with organic solvents. Paraffin, silicone oils and viscous hydrocarbon derivatives are used for CPE [78]. Also, molecular viscous polar solvents, like NPOE were applied in CPE [82]. Hydrophobic ILs were proposed as binders due to their high viscosity and ionic conductivity [83], [84]. In general, carbon paste exhibits high conductivity and electrodes surface can be quickly and easily renewed by removing the outside layer of electrode by polishing on paper. Importantly, in the CPEs there is oxygen accumulates in carbon paste due to the earlier adsorption at the porous surface of carbon particles or during homogenisation of paste and also due to its solubility in the binder [78].

The microscopical structure of CPEs is called 'solid dispersion' (Figure 2-8) [78].

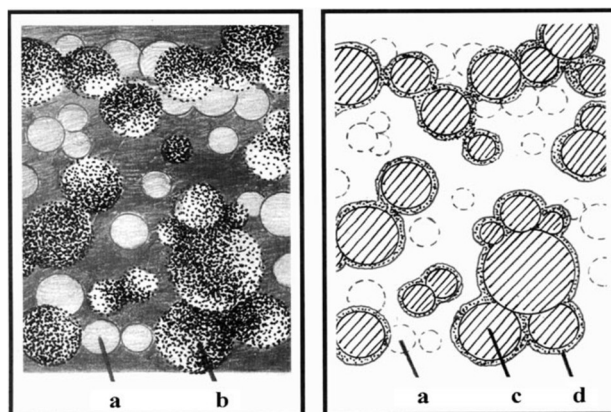


Figure 2-8. Microstructure of carbon paste from glassy carbon: a) graphite particles covered with binder, b) the outer layer. c) only graphite particles, d) thin layer of binder [78], [81].

The charge transfer rate depends on the viscosity of binder, on the proportions in the mixture and kind of groups on their surfaces [78]. The conductivity depends on the ratio of graphite powder and binder (paraffin oil or silicone oil) volume[85]. To investigate this dependence, the electric resistance of CPEs (R_{CPE}) was measured. The used compositions were: graphite powder and paraffin oil, graphite powder and silicone oil, glassy carbon powder and paraffin oil, glassy carbon powder and silicone oil. For the mixtures with extremally low percentage of binder [85], the resistance was equal few $\Omega\text{ m}$ [86] [78], what was surprising considering its value for graphite around $10 - 50\ \mu\Omega\text{ m}$ [87] and for oils around $5 \times 10^{13}\ \Omega\text{ m}$ [88]. Carbon paste resistance can be decreased, when smaller particles of graphite are used [89]. However, later it was observed that the relationship between the paste content and its conductivity is more complex [85]. When volumetric content of binder reaches 30 – 45%, there is a break point: steep rise of resistance is seen (Figure 2-9). This effect could be explained by usage of 'close-packing of spherical particles' concept. For the close cubic packing (space group $\text{Fm}\bar{3}\text{m}$) and the close hexagonal packing (space group $\text{P6}_3/\text{mmc}$), 74% of the space is filled by spheres. For the space-centred cubic packing (space group $\text{Im}\bar{3}\text{m}$) - 68% and for simple cubic packing (spheres are in the corners, space group $\text{Pm}\bar{3}\text{m}$) – 52,4%. In this model, the graphite particles are represented by the spheres. Then, for 65% volume of graphite, the maximum conductivity is achieved due to the permanent, multiple contact between the particles. For lower content of the particles, the binder blocks the contact between particles. Their contact is not stable, because

the graphite particles are on the move in the oil phase. Therefore, for large content of the binder, the probability of contact between the graphite particles is small, so the conductivity is small. This model is similar to percolation theory for solid matter. Furthermore, for the electrodes with more than 40% mass content of binder, the resistance decreases in time. This can be understood on the basis of the model of ‘packed spheres’. For the binder mass content in the range of 25-35%, the graphite particles are not much tightly packed, but the high viscosity of binder does not allow the sedimentation (due to the long time between preparation and usage) influence the uniformity. Therefore, they are stable for long time experiments. However, for the binder mass content higher than 40%, the graphite particles are more mobile and the sedimentation cause the separation of carbon phase and binder [85].

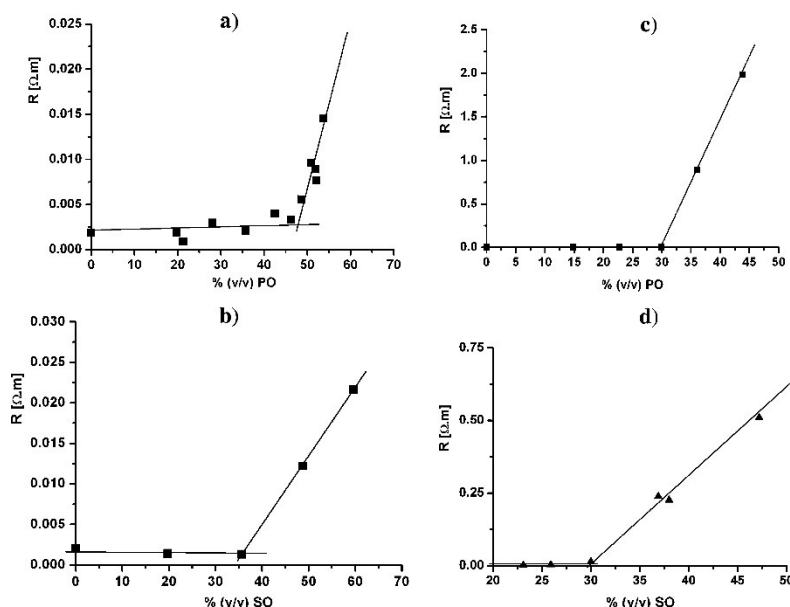


Figure 2-9. Resistivity vs. volumetric content of binder in CPE for different pastes compositions (the content of binder was in the range 0 – 60%): a) graphite powder and paraffin oil (PO), b) graphite powder and silicone oil (SO), c) glassy carbon powder and paraffin oil, d) glassy carbon powder and silicone oil [85].

Somehow similar electrodes to CPEs - ceramic carbon electrodes (CCE) consist of graphite particles immobilised in silica matrix [90]. They are prepared by the sol-gel process and contrary to CPEs their body is rigid and the motion of carbon particles is not possible. Hydrophobic CCE filled with redox liquid - *tert*-butylferrocene were applied for investigation of biphasic reaction [91].

More importantly, CPEs with NPOE [82] and ionic liquids [84] as binder have been already used in research of biphasic ORR. In the research for this PhD thesis this range of solvents was extended to vegetable oils. Such CPEs were employed to study ORR at vegetable oil|water interface.

3 Emulsions

According to the IUPAC definition, colloidal system is: ‘a state of subdivision, implying that the molecules or polymolecular particles dispersed in a medium have at least in one direction a dimension roughly between 1 nm and 1 μ m, or that in a system discontinuities are found at distances of that order’ [92].

Emulsions are thermodynamically unstable systems formed by two immiscible liquids [93]. According to IUPAC definition emulsion is: ‘a fluid colloidal system in which liquid droplets and/or liquid crystals are dispersed in a liquid. The droplets often exceed the usual limits for colloids in size.’ [94]. When the organic phase is dispersed in aqueous phase, it is named as ‘oil in water’ (O/W), whereas opposite system is called ‘water in oil’ (W/O). More complex emulsion, for example ‘oil in water in oil’ may also exist, when oil is dispersed inside aqueous droplet dispersed in the organic phase [94]. Their classification depends on the ratio of volumes of oil and aqueous phase [93]. Emulsion are mainly applied in organic synthesis [95], [96], [97] and also in electrochemical systems [98], [99], [100].

Micelles’ and microemulsions’- (Figure 3-1) thermodynamic stability can be increased by the addition of the surfactant. Both are characterised by isotropy and optical clarity (‘clarity is determined by the part of the incident light scattered at low angles.’ [101]). Micelle and microemulsion structures depend on the kind of surfactant [93].

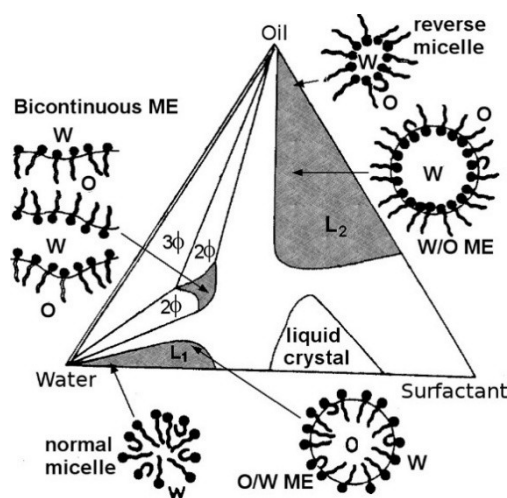


Figure 3-1. Structure of a) direct micelle, b) reverse micelle, c) microemulsion oil in water, d) microemulsion water in oil [102].

Micelles are defined by IUPAC in the following way: ‘surfactants in solution are often association colloids, that is, they tend to form aggregates of colloidal dimensions, which exist in equilibrium with the molecules or ions from which they are formed. Such aggregates are termed micelles’ [103].

The term ‘microemulsion’ was first used by Hoar in 1943 and was defined as ‘optically isotropic, transparent oil and water dispersions of droplets whose diameters were somewhat greater than swollen micelles’ [104]. According to the IUPAC, the microemulsion was defined in 2011: ‘dispersion made of water, oil, and surfactant(s) that is an isotropic and thermodynamically stable system with dispersed domain diameter varying approximately from 1 to 100 nm, usually 10 to 50 nm’ with four additional notes [105]. However, now in the online version of IUPAC GoldBook, it is not possible to find the definition of microemulsion. Considering this fact, I have chosen to accept one of the definitions from the paper, which is

based on Hoar definition [104] but updated and underlines the aspects raised by other sources. Importantly, contrary to the emulsions, microemulsions are thermodynamically stable. Moreover, importance of amphiphiles was considered in the definition, as well as the fact that the aqueous phase can be replaced by other polar solvents, like room temperature ionic liquids [102]. Stability of emulsion is defined differently. One of the presented definitions underlines the stability of the structure in time without the effect of the preparation method [106]. Most of the research in this area was focused on the kinetic stability of emulsion, when thermodynamic stability is also important and more studies related to this issue should be developed [107].

The application of emulsions and micelles as medium for electrochemical processes, was demonstrated for the first time 45 years ago by Franklin [108]. They were used to increase efficiency of the electrosynthesis and they had to be stabilised by cationic, neutral or anionic surfactants [108]. Lastly, application of the emulsion allowed for the electrosynthesis of a number of compounds in the aqueous phase in the absence of the electrolyte [109]. In general, emulsions are used for electrochemical processes to extend the contact area between phases to increase the efficiency of biphasic reaction [93]. Usage of emulsions made possible to examine the redox processes of substances insoluble in water [110]. Recently application of emulsions in redox flow batteries (RFB) was proposed, because the limitations of aqueous phase can be compensated by the organic one and opposite. The number of redox mediators soluble in water is limited. On the other hand, their larger number is soluble in organic solvent and are insoluble in water. However, in organic solvents, redox mediators have mostly low concentration. In turn conductivity of aqueous electrolytes is much higher than the conductivity of organic electrolytes. Additionally, the potential window of solid electrodes in organic electrolyte is wider as compared to the same electrode in aqueous electrolyte. Therefore, the usage of oil in water emulsion in redox flow batteries is beneficial. When emulsion is used, the redox mediator is dissolved in organic electrolyte, but the conductivity contribution comes from aqueous solution [111]. Moreover, emulsions can be also used in membrane-free RFB as a middle phase between aqueous and organic phases (Figure 3-2) [112]. Potential application of emulsion in redox flow batteries generates a lot of research focused on the optimisation of their composition. For example, it was proven that ratio between water and surfactant volume can affect the current and energy density [113]. Furthermore, emulsions can be used in the proton-exchange fuel cells, with additional catalyst (e.g. carbon supported PtCo NPs) and for ORR [114].

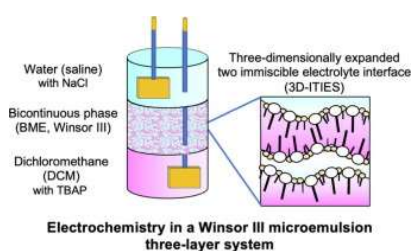


Figure 3-2. The scheme of the setup used to test the concept of membrane-free redox flow battery [112].

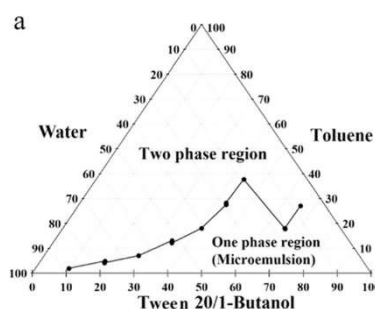


Figure 3-3. Phase diagram of different composition of emulsion prepared from Tween[®]20, 1-butanol, $\text{KNO}_{3(aq)}$ (0.5 mol/kg) at 20°C [115].

The stable emulsion prepared from toluene (TN) and water need additional component - stabiliser. Phase diagram (Figure 3-3) of four components system: consisting of water, TN, Tween[®]20 (polyethylene glycol (20) sorbitan monolaurate), and 1-butanol shows the microemulsion region at certain ratio of the components at certain temperature [115]. It was

shown that electrochemical behaviour of Fc is different in this emulsion than in single phase [115]. In general, the electrochemical behaviour of the redox probe depends on the ionic conductivity (which depends on the concentration of the electrolyte), adsorption at the electrode and coalescence of the hydrophobic domains [116].

The addition of salt to the emulsion influences its phase diagram. The effect of the addition of LiTB and BATB salts consisting of hydrophilic (Li^+) and hydrophobic ions (TB^- , BA^+) to the emulsion was investigated [117]. Importantly, the presence of salt can influence interfacial polarisation [11]. From the phase diagram (Figure 3-4) of the emulsion consisting of Tergitol NP10, LiOH and TFT obtained after addition of LiTB, one may conclude that the hydrophobic anions - TB^- move to the oil phase, whereas hydrophilic counterions - Li^+ stay in water. This means that LiTB dissociates at the liquid|liquid interface and the transfer of ions affects the structure of the stabiliser layer and stabilise the emulsion. To stabilise emulsion with LiTB, smaller amount of surfactant is needed as compared to the absence of this salt. The stabilisation results from the lowering free energy of ion transfer across oil|water interface. In fact, already adsorption of LiTB at this interface stabilise the emulsion. Salts present in emulsion can dissociate between surfactants layers, what results in generation of oppositely charged domains of oil and water. Their presence causes formation of the back-to-back double layers, what increases the distance between the surfactant layers. It affects the compressibility and bending elasticity of the monolayer and stabilises formed lamella. The additional factor contributing to the stability is the solvation of hydrophobic ions in oil and hydrophilic ions in water. Furthermore, the addition of salt with hydrophilic cations and hydrophobic anions results in decreasing the phase inversion temperature. For hydrophobic cations and hydrophilic anions, this effect is opposite [117].

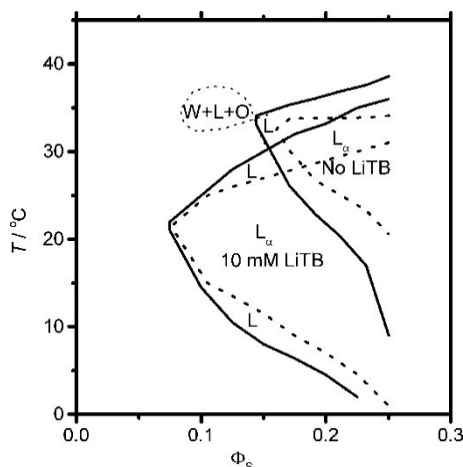


Figure 3-4. Kahlweit fish diagram of the system consisting of Tergitol NP10, LiOH and TFT in the absence (dashed lines) and in the presence of LiTB (solid lines), phase diagram depending on the temperature and surfactant volume fraction (Φ_s) [117].

The presence of other salts in emulsion affects the electrochemical behaviour of the redox probe. This was demonstrated on the example of addition of KNO_3 to the aqueous phase and Bu_4NBF_4 to the oil phase of emulsion consisting of ferrocene in Tween[®]20, 1-butanol, water and TN solution [118]. The addition of hydrophobic salt results in the increase of both anodic and cathodic peak current densities of voltammogram related to Fc oxidation and reduction. This effect was not seen for hydrophilic redox probe. In general, the electrochemical behaviour of redox probe in emulsion did not follow its behaviour in aqueous or non-aqueous solution. For example, the oxidation peak current is not linearly dependent on its concentration as it is

seen in single phase. This was explained by the presence of limited coordination group (ethylene oxide) in the surfactant than influence the current density and diffusion coefficient [118].

Also, ionic liquids were employed as components of emulsion. For example, the hydrophobic ionic liquid - trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)amide ($P_{(6,6,6,14)}NTf_2$) was implemented as stabiliser and to provide ionic conductivity. The electrochemical behaviour of Fc in emulsion based on water and $P_{(6,6,6,14)}NTf_2$ solution in TN (Figure 3-5 B) was studied by chronoamperometry at the gold ultramicroelectrode (UME) [119]. When the organic droplet collides with the electrode and then desorbs, spike at current vs. time dependence resulting from oxidation of A_{red} is expected (Figure 3-5 B). The corresponding charge allowed to calculate the concentration of redox species in the droplet. On the other hand, when redox mediator B is dissolved in the aqueous phase and the organic droplets adsorbs at the electrode, they block B oxidation process and staircase current vs. time dependence is expected (Figure 3-5 C). For this system (Figure 3-6 A), after application of potential in the chronoamperometric experiment slow current decrease is seen (Figure 3-6 B). After emulsion injection, current spikes resulting from Fc oxidation appear on steady state current vs. time dependence (Figure 3-6 A, C, D) indicating collisions of organic droplets with the electrode. The noise of current in 100 s comes from the opening of the Faraday cage, injection of emulsion and bubbling with argon. Two types of the current's spike are seen: either sharp increase and decrease (Figure 3-6 C) or sharp increase and gradual decrease (Figure 3-6 D). It may depend on the contact area (which can be different for each collision), droplet volume and the nature of collision process. In this work the diffusion coefficient of a spherical droplet and the collision frequency were calculated. Importantly, the droplet diameter estimated from the charge of the oxidation current resulting in the diameters values in the range: 400–600 nm are comparable to DLS data (634 nm) (Figure 3-6 E) [119].

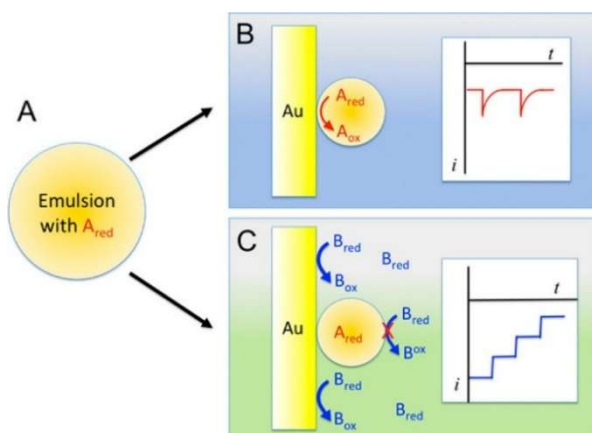


Figure 3-5. The scheme of two emulsions collision methods. A) The redox active species (A_{red}) is dissolved in the emulsion droplet, B) oxidation of A_{red} occurs in the droplet on the surface of electrode, C) oxidation of B_{red} occurs in the aqueous solution, but emulsion is blocking the electrode surface [119].

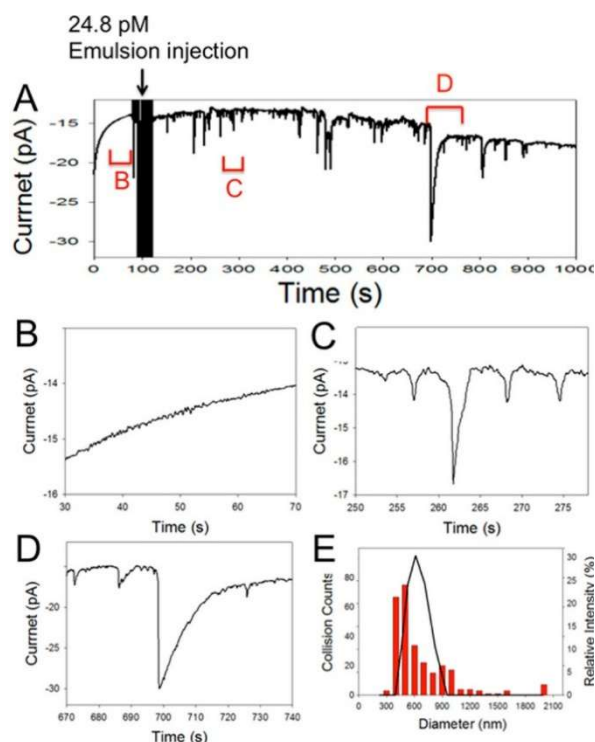


Figure 3-6. A) The current dependence on time for single droplet at Au UME, the emulsion (toluene, ionic liquid and water) was added after 100 s, B) the current dependence on time before the injection of the emulsion, C, D) the current dependence on time showing clear current spikes, E) calculated data (red) and DLS data (black solid line). The UME potential was +0.5 V vs. Ag/Ag^+ applied at zero time [119].

Similar experiments were also conducted with benzene and cyclohexane droplets suspended in aqueous electrolyte [120]. Emulsion consisting of rubrene, $P_{(6,6,6,14)}NTf_2$ and TN was applied for voltammetric studies. Then, the thermodynamics of ion transfer was estimated using single-emulsion droplet collision electrochemistry. Moreover, the distribution and shape of droplets was estimated more precisely than by other electrochemical methods [121]. Similar emulsion with trihexyl(tetradecyl)phosphonium trifluorotris(penta-fluoroethyl)phosphate was studied by the fluorescence microscopy. This allowed to monitor the electrochemical flux using the fluorescence of the droplet to conclude that the kinetics of redox processes is asymmetric at the single droplet level [122]. The usage of vegetable (castor) oil as component of emulsion stabilised by ionic liquid (1-butyl-3-methyl-imidazolium tetrafluoroborate) with the addition of salt (1-octyl-3-methylimidazolium chloride) was also reported. The addition of salt allowed to increase the number of compositions allowing to achieve one-phase area on the phase diagram of emulsion [123].

In this thesis the electrochemical behaviour of redox probe (DMFc or decamethylruthenocene (DMRc)) in emulsion consisting of $HClO_4$, toluene and $P_{(6,6,6,14)}N(Tf)_2$ was studied and features of biphasic ORR and HER were looked for.

4 Oxygen reduction reaction at liquid|liquid interface

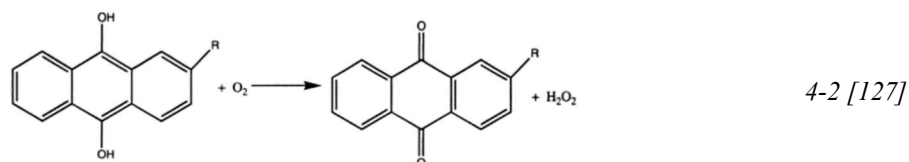
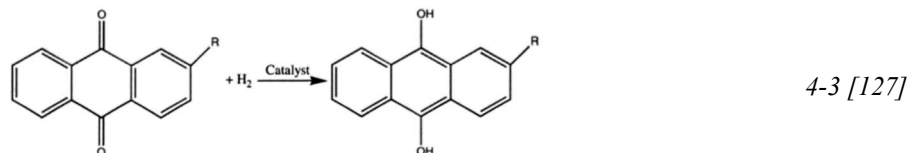
4.1 Applications of hydrogen peroxide and manufacturing methods

Hydrogen peroxide is a product of 2-electron oxygen reduction reaction. Nowadays H_2O_2 is a crucial chemical with the widespread applications in medicine, cosmetics fabrication and energy conversion [124]. It is also employed in number of industries like textile, electronics, metallurgy, paper, for bleaching, in wastewater treatment, in detergent production and chemical synthesis [125]. H_2O_2 is also used in fuel cells as both: oxidiser and fuel [126]. Importantly, H_2O_2 is a reactive oxidant, therefore it has to be handled with precaution. Its decomposition results in heat, water and oxygen generation:



so it is classified as green chemical [125]. Hydrogen peroxide is miscible with water and its 65% solution in water can be prepared. It is soluble in some organic solvents, for example in carboxylic esters. The H_2O_2 solution in water is not stable, the support of stabilisers is needed [127]. The presence of impurities decreases the stability of the solution [125].

Hydrogen peroxide is known for more than 200 years. It was first time isolated in 1818 by Thenard in reaction of barium peroxide with nitric or hydrochloric acid. The second product - BaCl_2 was removed by precipitation with sulfuric acid. This method was commercialised to produce 3% H_2O_2 aqueous solution. However, this solution was not stable due to the impurities. Therefore, in 1850's the electrochemical method to fabricate H_2O_2 was employed, firstly with acidic solutions. At the beginning of 20th century, H_2O_2 generation at the anode together with ammonium sulphate (Rediel-Lowenstein process) or potassium peroxodisulfate (Pietzsch-Adolph process) on cathodes. Alternatively, Manchot discovered that hydroquinones and hydrobenzenes in alkaline environment allow the formation of peroxides due to their auto-oxidation [127]. Importantly, Riedl and Pfeleiderer developed the technology of anthraquinone auto-oxidation process (AO), which was advanced enough to start commercial production by Farbenindustrie AG [124]. This process begins with catalytic hydrogenation of 2-alkylantraquinone, to 2-alkylantrahydroquinone (4-2) in the mixture of suitable solvents. After separation of the catalyst, the compressed air (containing oxygen) is passed through the solution to allow the formation of 2-alkylantraquinone and hydrogen peroxide. Anthraquinone can be rereduced to antrahydroquinone (4-3) and reused. Subsequently, the H_2O_2 is extracted with demineralised water and concentrated. Still there are impurities in the final product. Moreover, the side reactions, what leads to the need of the regeneration of the solutions and catalysts during this process. On the other hand, with this technology H_2O_2 can be produced continuously [125]. Unfortunately, AO process is not sustainable due to the usage of large volumes of solvents and large energy consumption due to high temperature and pressure [124].



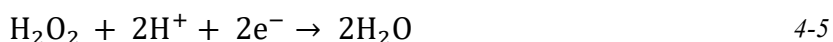
Another H_2O_2 production method is the oxidation of primary or secondary alcohols by oxygen. Then, the purification process (extraction) is more complicated due the solubility of alcohol in water. The same way of oxidation can be realised with α -methylbenzyl alcohol, but without catalysts efficiency of reaction is low. In general, those oxidation processes produce H_2O_2 of lower quality as compared to AO process [127].

Furthermore, hydrogen peroxide can be produced directly from H_2 and O_2 , what requires to follow special safety rules. However, yield of this reaction is below of AO process [125]. On the other hand, when plasma is used for activation, the ratio of H_2 to O_2 in the mixture can be far from the explosive region [128]. Moreover, the direct synthesis can be continuously performed in fuel cells, without external energy source. In these devices, membranes are employed to separate the gases to decrease the risk of explosion. Furthermore, H_2O_2 can be synthesised from the mixture of H_2 , O_2 and CO . However, the catalysts are needed and CO_2 is the second product, which does not allow to qualify this method as green. Also, photocatalytic oxygen reduction at semiconductors oxides catalysts was proposed as a method to generate hydrogen peroxide [125].

Recently electrochemical ORR in alkaline or acidic solution is extensively studied with wide range of catalysts as metals, metal oxides or different types of carbonaceous materials. The latter catalysts seem to be most promising for 2-electron oxygen reduction. However, they are still far from industrial applications [125].

4.2 Mechanism of electrochemical reduction of oxygen

Oxygen reduction reaction in the presence of protons follow two mechanisms: 2- (4-4) and 4- (4-6) electron, which occur competitively or sequentially (4-4 and then 4-5) [129].



For energy applications 4-electron pathway is favourable, whereas for selective electrosynthesis of H_2O_2 only partial reduction is needed. In both mechanisms first step is the formation of superoxide (O_2^-). The next steps for 4-electron version: electron transfer, proton transfer and proton-coupled electron transfer are less favourable than direct reduction to H_2O [129].

The ORR in aprotic solvents was investigated mostly, because of its application as cathodic reaction in non-aqueous air-metal batteries like Li/O_2 [130]. In these conditions oxygen molecule is reduced to O_2^- (4-7), which is stable in tetraalkylammonium salt solutions in the

aprotic polar solvents as dimethyl sulphoxide, N,N'-dimethylformamide, acetonitrile, acetone, pyridine and methylene chloride [131]. However, in the presence of Li^+ salts, LiO_2 is formed (4-8). Then, it can be reduced to Li_2O_2 (4-9) or disproportionate to Li_2O_2 and O_2 (4-10) [130]:

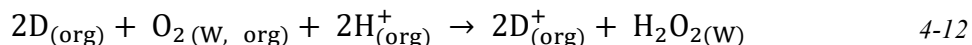
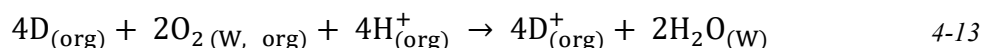


The stability of O_2^- is influenced by the presence of water in aprotic solvent [130]:



4.3 ORR at liquid|liquid interface

Similarly, as at electrode|electrolyte interface, ORR at liquid|liquid interface may follow two mechanisms: 2- (4-12) or 4- (4-13) electron path:



where D is a sacrificial electron donor. Typically, biphasic ORR results in generation of H_2O_2 what indicates significant contribution of 2-electron path [25]. Oxygen reduction to peroxide anion in the organic medium (shown on the example of DCE) occurs at more negative potential than in the aqueous solutions (Figure 4-1) [26]. As ORR overpotential in organic solvent is lower than that in aqueous solution, this reaction is thermodynamically more favourable in organic medium. Moreover, for the reaction at liquid|liquid interface, the product separation is easy (due to the solubility of H_2O_2 in water) and this method does not require high temperature and pressure [25].

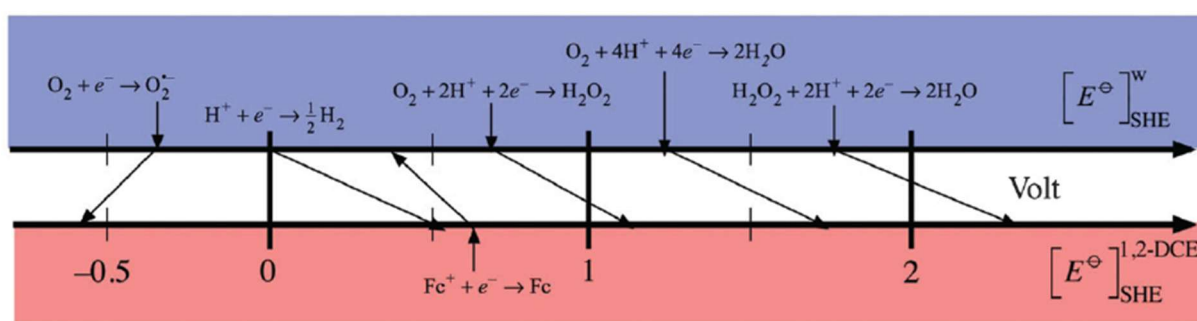


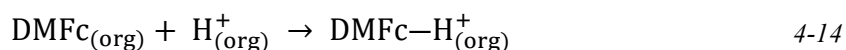
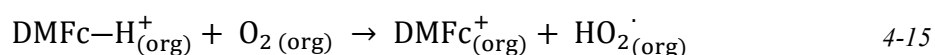
Figure 4-1. Potential of redox reactions in water (blue) and in 1,2-DCE (red) vs. standard hydrogen electrode (SHE) [26]

For biphasic ORR, the electron donor and hydrophobic salt, typically BATB [25] or tetrahexylammonium perchlorate (THAP) [132] has to be present in organic phase and H^+ in aqueous phase. If the electrolytes with common anion are present in both phases, they enable the control of Galvani potential difference at liquid|liquid interface [25]. The interfacial potential can be also control externally [133].

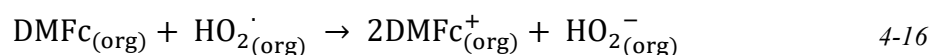
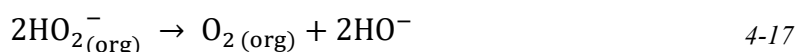
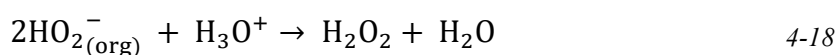
In most of the studies of biphasic ORR, DCE|water interface polarised by addition of salts with common anion to both phases with DMFc as electron donor was employed. [134], [135], [136].

In some cases, DCE was replaced by dichlorobenzene [133] or TFT [137], [138]. Also, more viscous solvents, like NPOE [82] or ionic liquids [83], [84] have been applied as solvents in an arrangement where they were employed as binder for carbon paste electrode.

Biphasic ORR with external electron donor i.e. DMFc is a multistep process. It starts from proton transfer from aqueous to organic phase [136] and hydride $\text{DMFc-H}_{(\text{org})}^+$ is formed (4-14). Then, it reacts with oxygen and DMFc^+ cation is formed (4-15).



Next, the following fast and irreversible reactions occur [136]:



Fc has lower reducing power than DMFc, because of its higher redox potential. When Fc is employed as electron donor, biphasic ORR does not occur in the absence of molecular catalyst as demonstrated on the example of DCE|water system [34]. Fc solution is more stable than DMFc solution in organic solvent, even in the oxygen atmosphere and in the absence of protons due to Fc higher redox potential as compared to that of oxygen. However, when protons are present, Fc can be oxidised because of the higher redox potential than that of the O_2 reduction in these conditions [139].

Metal porphyrins immobilised on the electrode surface were employed as catalysts for ORR [26]. Cobalt macrocyclic complexes have been chosen due to their similarity to cytochrome c oxidase – the enzyme used as a catalyst for 4-electron ORR in nature. The iron porphyrin/copper heterodinuclear centre plays a role of active centre. Then, three histidine molecules are coordinated to copper ion, which is present above the iron centre of the enzyme [133].

The first study of biphasic ORR was focused on comparison of electrocatalytic activity of CoTPP adsorbed at the graphite electrode and dissolved in the thin film of benzonitrile deposited on the electrode surface. Clearly the latter system was more effective due to more efficient regeneration of molecular catalyst (Figure 4-4) [71]. Other macrocyclic cobalt complexes: cobalt(II) 2,3,7,8,12,13,17,18-octaethylporphyrin (CoOEP), cobalt(II) porphine (CoP), amphiphilic cobalt(II) 2,8,13,17-tetraethyl-3,7,12,18-tetramethyl-5-p-aminophenylporphyrin (CoAP) dissolved in the organic phase were employed as molecular catalyst for biphasic ORR at DCE|water interface. These complexes are characterised by different redox potentials and degree of adsorption at ITIES. Interestingly, cofacial cobalt porphyrins were used as molecular catalysts for ORR in the biphasic system and its catalytic activity was higher than that of CoTPP [133]. The mechanism of ORR with cobalt porphyrins adsorbed at the ITIES (Figure 4-2) is similar for all complexes (Figure 4-3) [26]. Even Fc with too low reducing power (too high redox potential) to reduce O_2 directly, is able to reduce the cobalt(III) porphyrin. Then, oxygen reacts with the Co(II) complex and forms cofacial adduct, which is protonated at the

interface [25]. Importantly, majority of porphyrin-oxygen complexes adsorb on the liquid-liquid interface in the protonated form [26].

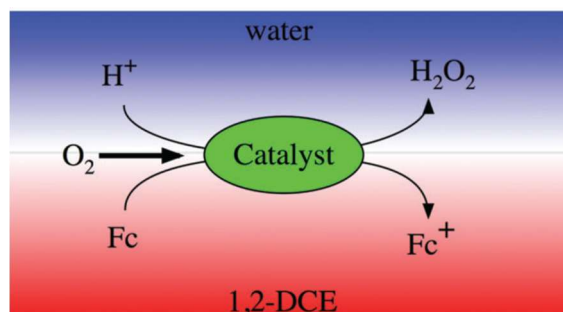


Figure 4-2. Scheme of ORR with molecular catalyst adsorbed at ITIES [26].

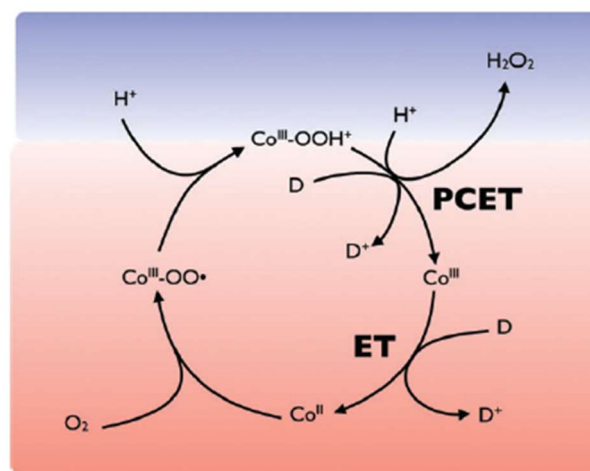


Figure 4-3. Catalytic circle for cobalt porphyrin for biphasic oxygen reduction reaction [26].

The catalytic effect of cobalt porphyrin was confirmed by cyclic voltammetry by detection of proton transfer across liquid|liquid interface being an important step of biphasic ORR. Clearly, the anodic current around 0.3 V, resulting from H^+ transfer across liquid|liquid interface, is the highest in the presence of both Fc and CoP (Figure 4-5 a). Moreover, biphasic ORR is confirmed by the fact that the magnitude of anodic current is proportional to the concentration of oxygen (Figure 4-5 b) [34].

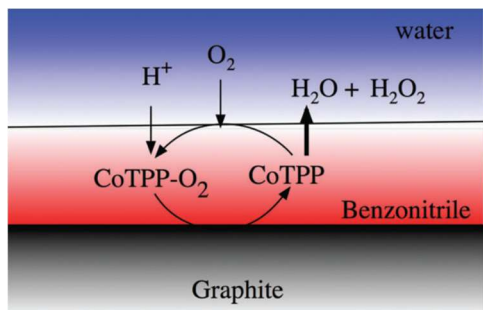


Figure 4-4. Mechanism of ORR at graphite electrode modified by benzonitrile film [26], [71].

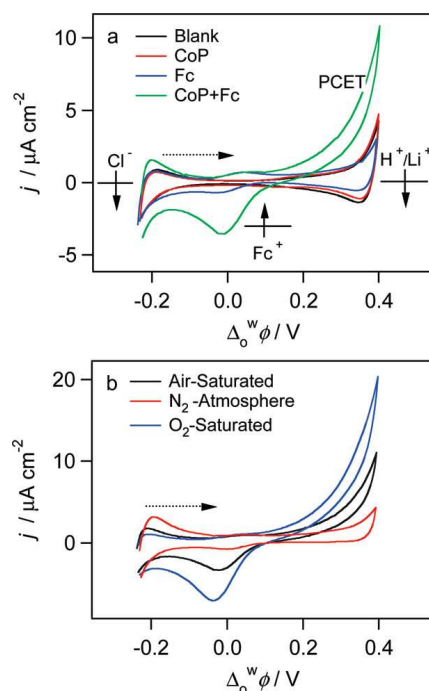
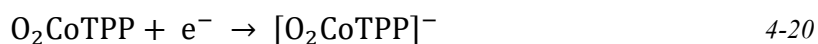


Figure 4-5. Cyclic voltammetry of the biphasic system consisting of water and DCE a) in presence and absence of cobalt(II) porphyrin (CoP) and/or Fc, b) in different atmosphere (air, N₂, O₂ – saturated) [34].

For both types of Co^{II}TPP immobilization: directly adsorbed on the electrode and dissolved in liquid thin film, the first part of mechanism is similar. Firstly, due to the weak reducing power of Co^{II}TPP, to reduce O₂ to O₂^{•-}, the porphyrin is electrochemically oxidised to O₂CoTPP (4-19). This product (CoTPP with axially coordinated oxygen) is easier to reduce (4-20, 4-21) than free complex. Then, partially reduced O₂ dissociate from the cobalt complex and H₂O₂ is formed (4-22). When O₂ stays coordinated, it is reduced to H₂O (4-23). The final products ratio depends on the relative rates of these two reactions (4-22, 4-23). For the porphyrin dissolved in the liquid film, ORR follows rather 4-electron path, whereas for adsorbed catalyst, 2-electron reaction is seen. Local protons concentration next to adsorbed CoTPP is higher due to the direct exposure to the aqueous solution as compared to molecular catalyst dissolved in liquid thin film. Also, some oxygen coordinated with cobalt centre could stay long enough to accept additional electrons [71].



Also, other molecular catalyst, like phthalocyanines found their application for ORR [140].

Moreover, the micro and nanoobjects assembled at liquid|liquid interface exhibit catalytic effect for biphasic ORR [25]. Nanoparticles, including noble metal NPs (Pt [140] [229] or Au [141] [142]), can be deposited on the interface to increase efficiency of electron transfer between phases (Figure 4-6). In some cases, nanoparticles may act also as catalysts. Nanoparticulate

metallic film play a role of electron pool, which is equilibrated with Fermi level of electron donor [141], [143]. It is charged with electron donor to provide additional driving force to allow the formation of superoxide anion, which reacts later with H^+ to form H_2O_2 [144] Then, film is discharged by electrocatalytic ORR [25].

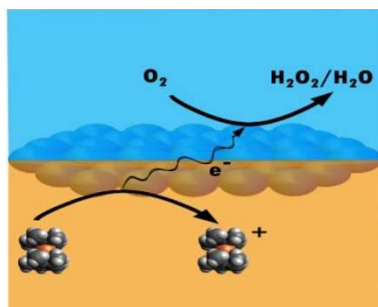


Figure 4-6. The scheme of the biphasic ORR at conductive nanoparticulate film at ITIES [25].

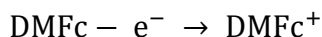
MoS_2 microparticles have been used for catalysis of biphasic ORR when they were mixed with carbon particles to prepare carbon paste electrode [82]. Among non-metallic nanomaterials, carbon ones as in situ reduced graphene oxide or interfacially assembled graphene also exhibit catalytic properties [25]. Most recently, battery waste powder, consisting mainly carbon, assembled on liquid|liquid interface was applied to increase the efficiency of biphasic ORR [145]. Interestingly, the light can be used as an energy source for hydrogen peroxide generation [146]. In this instance, benzyl alcohol|water system was used to test photocatalysts [147]. For that, metal-organic frameworks (MOFs) [148], covalent-organic frameworks (COFs) [149], [150] or metallic compound like TiO_2 [151], [152] quantum dots [153], coordination polymers with Ag [154] or heterocatalysts [155] have been investigated. Also, toluene|water [156], [157] and octanol|water [158] systems were employed for photogeneration of H_2O_2 [146].

To increase the biphasic ORR efficiency, electron donor can electrochemically regenerated. For this, the suitable potential was applied to the working electrode present in organic phase with counter and reference electrodes immersed in aqueous phase. Then, electron donor is no longer sacrificial and reaction may occur continuously [132], [82], [83], [84].

4.4 Detection of hydrogen peroxide generated at the liquid|liquid interface

When ORR follows 2 electron path, H_2O_2 is produced. This product can be detected and the efficiency of its generation can be estimated. On the other hand, overall efficiency of biphasic ORR can be estimated on the basis of the amount of oxidised electron donor. Flask experiments with equal volumes of both aqueous and organic phase are easy way to estimate the progress of reactions in the biphasic system, providing that oxidised and reduced form absorb light of different wavelength. When DMFc is employed as electron donor, yellow organic phase after some time turns green due to the generation of the oxidised form - $DMFc^+$ (Figure 4-7 a). The oxidation of sacrificial electron donor can be also traced more quantitatively by UV-Vis spectroscopy. In this case, the increase of absorption band characteristic for $DMFc^+$ at 779 nm (black line in Figure 4-7 b) and decrease of DMFc absorption band at 425 nm (black dotted line) can be observed during ORR process [135].

Another method of following the progress of biphasic ORR is steady state voltammetry with platinum ultramicroelectrode immersed in the organic phase. The entirely anodic current is visible at voltammogram (Figure 4-7 c, solid curve) recorded before the reaction starts and anodic wave corresponds to the oxidation of DMFc:



4-24

This confirms that only its reduced form is present in organic phase. When sacrificial electron donor is consumed during biphasic ORR, the cathodic wave corresponding to reduction of DMFc^+ appears and at the same time, anodic current decreases. The second CV wave was recorded after 4 hours of biphasic reaction (Figure 4-7 c, dotted curve). From the ratio of cathodic to anodic steady state currents, the ratio of DMEc and DMFc^+ concentrations can be calculated and the progress of ORR estimated. When the sum of absolute values of cathodic and anodic steady-state currents does not change as reaction proceeds, one may conclude that both forms are stable in the solution and DMFc^+ is not transferred to the aqueous phase [135].

Generation of H_2O_2 can be confirmed by the starch-iodine test of aqueous phase after its separation from biphasic system. Addition of NaI to the aqueous phase results in I^- oxidation to I_3 by H_2O_2 in two steps [135]. Firstly, iodine molecules are produced by the reaction of I^- with hydrogen peroxide in the acidic environment (4-25) [159], what is confirmed by appearance of yellow colour in the flask 2 (Figure 4-7 d) [135] and finally I_3 is formed (4-26) [160]. In order to make colour change more visible, the starch is added to the solution. Then, the solution colour turns into violet [135] (Figure 4-7 d, flask 3) due to the formation of amylose-iodine complex [161]. Furthermore, the presence of I_3 can be also confirmed by UV Vis spectroscopy by tracing absorption band at 352 nm (red solid line on Figure 4-7 b) [135].

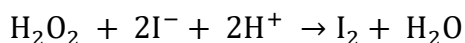
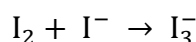
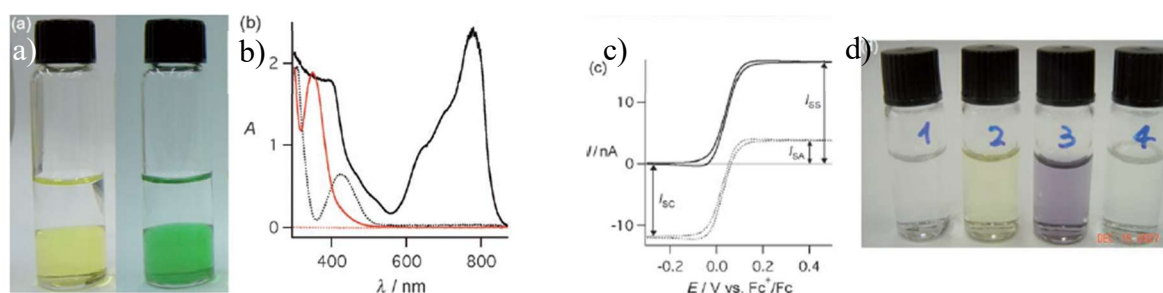
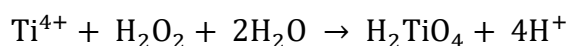


Figure 4-7. a) Flask experiment with DCE with DMEc and H_2SO_4 and TPFB $^-$ in both phases immediately (left) and after 4 h of biphasic reaction (right) b) UV Vis spectra of organic phase (solid black line), of aqueous phase immediately (dotted red line) and after 4 h of biphasic reaction (solid red line) c) voltammogram on UME of organic phase: fresh (dotted black line), and after 4 h of biphasic reaction (dotted line) d) NaI - starch experiment's result in flasks, flask 1: aqueous phase after 4 h of biphasic reaction, flask 2: flask 1 + 0.1 M NaI, flask 3: flask 2 + starch, flask 4: 5 mM LiTPFB+5 mM H_2SO_4 +0.1 M NaI+starch [135].

Although, the method described above is widely used, it is not selective. Other organic peroxides and oxidising agents may give similar result [162]. Another, more selective colorimetric method of H_2O_2 detection can be employed. For that, H_2SO_4 and potassium bis(oxalato)-oxotitanate(IV) dihydrate ($\text{K}_2\text{TiO}(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$) needs to be added to the aqueous phase [162]. Then, they react with H_2O_2 and yellow complex is produced (4-27) [163], with characteristic absorption band at 400 nm [164].



4-27

To detect H_2O_2 in situ, next to the interface, SECM can be applied, as proposed for ORR in aqueous system on PdCo alloy modified GC electrode, (Figure 4-8) [165]. For that oxidation of H_2O_2 at Pt UME as amperometric probe was employed:



When tip potential was set to 1.1 V vs. $\text{Ag}|\text{AgCl}|3\text{M KCl}$, the linear dependence of the current vs. concentration of H_2O_2 was linear within 0.05 mM - 0.6 mM range (Figure 4-9) [165].

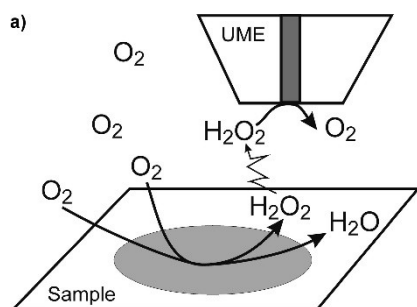
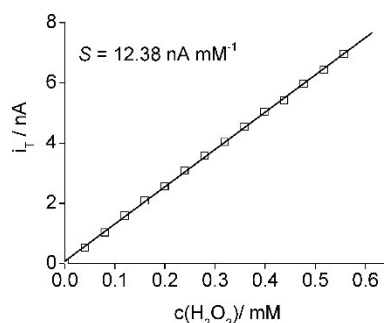


Figure 4-8. Schematic illustration of the SECM operation in the pulsed SG/TC mode for H_2O_2 detection [165]. Figure 4-9 Calibration curve of H_2O_2 oxidation current (i_t) in 0.1 M H_2SO_4 [165].

For the first time, SECM (substrate generation/tip collection mode) was employed to biphasic ORR at externally (from potentiostat) polarised DCE|water interface [166]. In this experiment, droplet of DMFc solution in DCE with BATB as electrolyte, was placed on $\text{Ag}|\text{AgCl}$ electrode. Platinum UME (25 μm) was used as SECM tip and was positioned in acidic aqueous solution, at the certain distance from liquid|liquid interface (Figure 4-10). H_2O_2 generation was detected amperometrically by applying the hydrogen peroxide oxidation potential to the SECM tip. Tip current increased when it was moved towards the interface and sharply increased when tip penetrated the interface due to the DMFc oxidation. This was assumed as point 0 (liquid|liquid interface) at x axis for approach curve (Figure 4-11). [166].

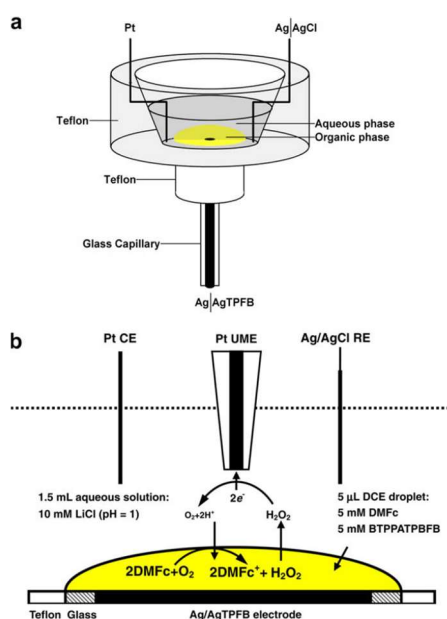
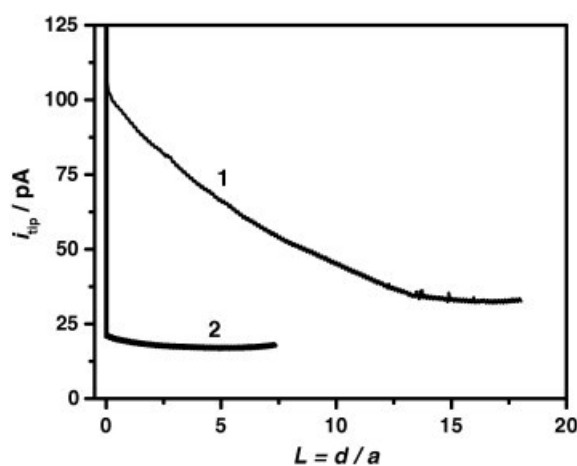


Figure 4-10. Scheme of detection of hydrogen peroxide in biphasic ORR by SECM [166].

Figure 4-11. Approach curve 1) with, 2) without applying 0.45 V to the water/DCE interface, tip potential was 0.6 V [166].

H₂O₂ was detected by SECM in biphasic systems formed by other solvents, like TFT [138], hydrophobic ionic liquids [83], [84] or NPOE [82]. SECM was also used to demonstrate that biphasic ORR results in H₂O₂ generation at DCE|water interface in unfavourable conditions with positive Galvani potential difference at liquid|liquid interface [132] or when electron donor was electrochemically regenerated to increase the efficiency of ORR [132], [82], [83], [84]. The general scheme of SECM H₂O₂ detection in the latter case, with and without nanoparticles assembled on ITIES, is shown below (Figure 4-12). [25].

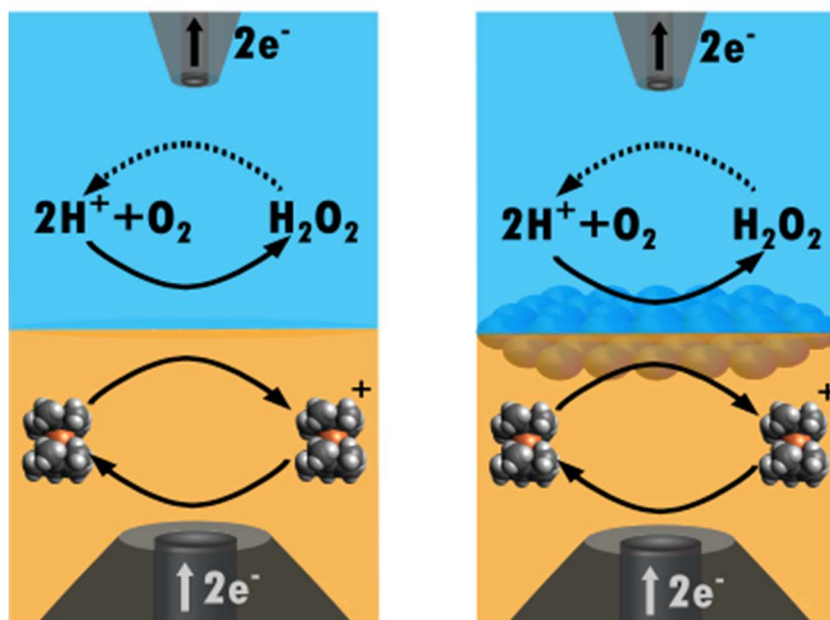


Figure 4-12. Scheme of oxygen reduction reaction at liquid|liquid interface (right one – with nanoparticles deposited on the interface) with regeneration of electron donor and microelectrode for detection of hydrogen peroxide [25].

Fluorescence was also used for detection of H₂O₂ generated at liquid|liquid interface. This was done with help of organic dye (Amplex UltraRed), which is oxidised by H₂O₂ and this reaction is catalysed by horseradish peroxidase (HRP) [167], [83]. This test has been done in the capillary filled with DMFc solution in TFT, immersed in the HClO₄ aqueous solution containing dye and HRP. After few seconds, fluorescence appeared in the organic phase because the reaction occurs only with deprotonated form of dye, which is not present in the aqueous phase (Figure 4-13) [167]. The red fluorescence observed by fluorescence microscope increased in time. Most of the emitted light was seen close to the end of the tip due to the fact that fluorophore was partially extracted to the organic phase. Besides, the oxidised Amplex UltraRed was partially protonated in the aqueous phase, what decreases fluorescence intensity. Interestingly, the size of the emitting zone depends on the ionic liquid viscosity [83].

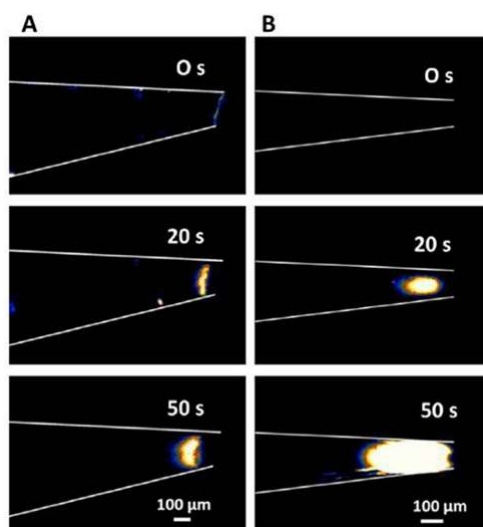


Figure 4-13. Scheme of detection of H_2O_2 using fluorescence and fluorescence intensity's changes in time A) micropipette was filled with 5 mM DMFc in TFT immersed in 0.1 M $HClO_4$ and AmplexUltraRed fluorescent dye, B) H_2O_2 was added to the aqueous phase [167].

5 Hydrogen evolution reaction

5.1 Hydrogen application and productions methods

Hydrogen is the most widespread element in the universe. It is an odourless, colourless and flammable gas in the normal conditions. It is characterised by high reactivity and can explode in the certain conditions [168]. Hydrogen has numerous applications, (Figure 5-1) including a fuel of internal combustion engines, turbines or electric power generators (for example fuel cells) [169]. Furthermore, it is used in ammonia synthesis, in metallurgy (as reducing agent and to form oxy-hydrogen flames), in petrochemistry (to remove the impurities of other elements), in production of hydrocarbons in both Fischer-Tropsch and syngas fermentation and also for energy storage (power-to-gas). Nowadays, when renewable energy sources replace the conventional ones, energy storage is crucial due to the lower stability of renewable power supplies. Although hydrogen has higher heating value than other fuels, approximately 3 times higher than gasoline, its volumetric energy density is 4 times lower [168].

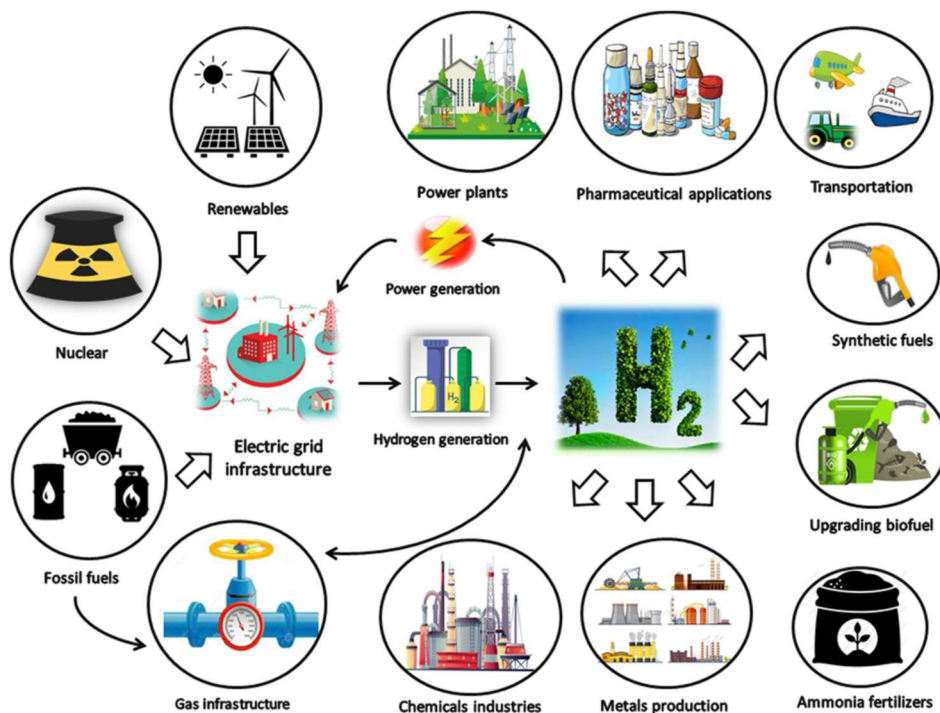


Figure 5-1. Hydrogen production routes and applications [168].

International Energy Agency in the Global Hydrogen Report 2024 summarised that nowadays most of the hydrogen is produced from fossil fuels with carbon capture, utilisation and storage (CCSU) (Figure 5-2, Figure 5-3). Then, the generated CO₂ is used for other processes, for example for food or drinks productions. Although the most of hydrogen is still produced from fossil fuels, the percentage of H₂ generated from renewable sources increases each year. For example, from 2021 to 2024, it increased twice [170].

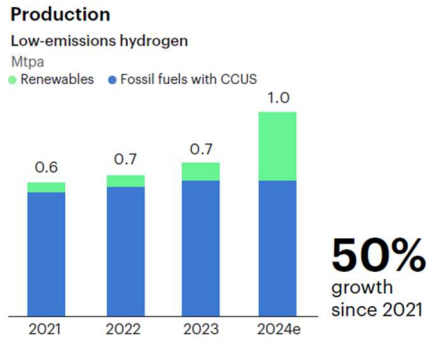


Figure 5-2. Bar graph of hydrogen production from 2021 to 2024 [170].

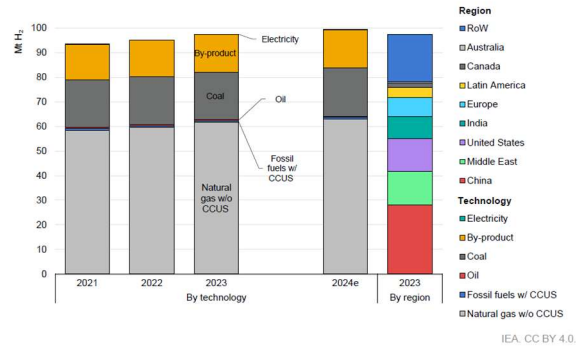


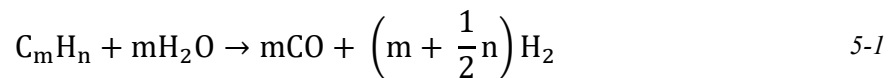
Figure 5-3. Bar graph of hydrogen production by different technology and by region [170].

There are numbers of methods to produce hydrogen from different resources (fossil fuels, biomass, water) using conventional or renewable energy sources [171]. They are described by different colours considering their influence on the environment:

- green – produced in electrolysis using wind or solar power, does not emit CO₂ during the process, the best for environment;
- blue – produced in steam reforming, mostly from natural gas, CO₂ is also a product, but carbon capture and storage (CCS) is applied;
- grey – produced in steam reforming, mostly from natural gas without any later treatment of greenhouse gases;
- black and brown – produced in gasification of hard coal or lignite, most harmful for the environment;
- pink (eventually: purple, red) – produced in electrolysis fuelled by nuclear energy,
- turquoise – produced in methane pyrolysis (results in hydrogen and carbon), but not used in the large scale yet. It could be considered as a low-emission hydrogen in future, if it will be powered by renewable energy and carbon will be used for other purposes;
- yellow – produced in electrolysis with solar power;
- white – hydrogen found underground, but now it is not used due to lack of ideas how to extract it;

The new colours may appear and the contribution of the present ones can change depending on the changes in productions strategies all over the world. However, the idea of such diversification is to underline that the energy source and generation of other products may influence the environment. This concept allows to understand that hydrogen is not always a green fuel [172].

Still the most popular method of production of H₂ is steam reforming, which requires high (over 500°C) temperatures [168]. The carbohydrates react with water steam and synthesis gas (mixture of CO and H₂) is produced [173] (5-1). In industry, mostly methane is used as a substrate and then the efficiency reaches 85%. To achieve that, the metallic catalysts, like nickel, are needed. The next step is oxidation of CO to CO₂ (water-gas shift reaction) [173] (5-2). CO₂ is absorbed by amine solvent and then H₂ is further purified [168].



At present, methane steam reforming combined with carbon capture and storage is the most economic efficient technology[174].

Alternatively, methane pyrolysis at high temperature and in the non-oxygen environment, results in formation of hydrogen molecule and carbon (5-3). However, profitability of this process depends on the natural gas prices, which are unstable and hard to predict [168].

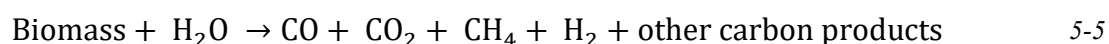


Coal gasification is another method of hydrogen production. At high temperatures (800 - 1400°C), hydrogen and CO are formed from coal in the oxygen or air atmosphere [168].



Then, part of CO reacts with water, producing CO₂ and more H₂ (water-gas shift reaction). Coal gasification is less efficient than steam reforming [168].

Another more environment-friendly method to produce hydrogen is a biomass gasification [168]. Due to the fact that biomass absorbs CO₂ from the atmosphere, it has lower carbon footprint than the conversion of fossil fuels. Unfortunately, the hydrogen content in biomass is low (~5,9%). It results in the lower efficiency and logistics problems with costs of transport and storage of biomass. Moreover, high temperatures, up to 1400°C make this process more expensive than steam reforming. Overall reaction can be simplified by [168]:



The best way to produce environmental-friendly hydrogen is electrolysis powered by renewable energy source [171]. For that, two electrodes are immersed in the electrolyte solution and separated. Different devices (because of membrane, electrolyte or electrode material) as: proton exchange membrane electrolyser (PEM), alkaline water electrolyser (AWE), alkaline anion exchange membrane (AEM) or solid oxide electrolyser (SOE) are used. The electrochemical reactions depend on the type of electrolyser (Table 5-1) [175]. In PEM - protons and in AWE and AEM - hydroxide ions are charge carriers and these technologies are commercialised. In SOE - O²⁻ is the charge carrier and this device requires much higher temperature than other technologies. At the moment, SOE is on the early stage of commercialisation. Electrolysis combined with wind power is the most promising technology for future due to its low carbon footprint [171].

Table 5-1. Electrode reactions in different electrolysers

Type of electrolyser	Anode	Cathode
PEM	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$	$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
AWE and AEM	$4\text{OH}^- \rightarrow 2\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^-$	$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
SOE	$2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$	$\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + \text{O}^{2-}$

5.2 HER at liquid|liquid interface

Hydrogen evolution reaction may occur also at the liquid|liquid interface (Figure 5-4). The reaction's requirements are the same as ORR except oxygen has to be removed. Similarly, as biphasic ORR, it necessitates strong electron donor (for example DMFc) in organic phase,

aqueous solution of acid (HCl, HClO₄, H₂SO₄) and enough positive Galvani potential to enable the proton transfer through the interface. For that, hydrophobic salts are used, typically BATB in organic phase. Biphasic HER may occur in the presence or absence of light (Figure 5-4) [25] depending on the employed electron donor (D_(org)) [25].

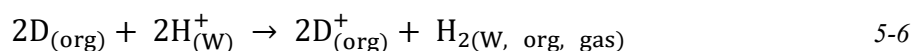
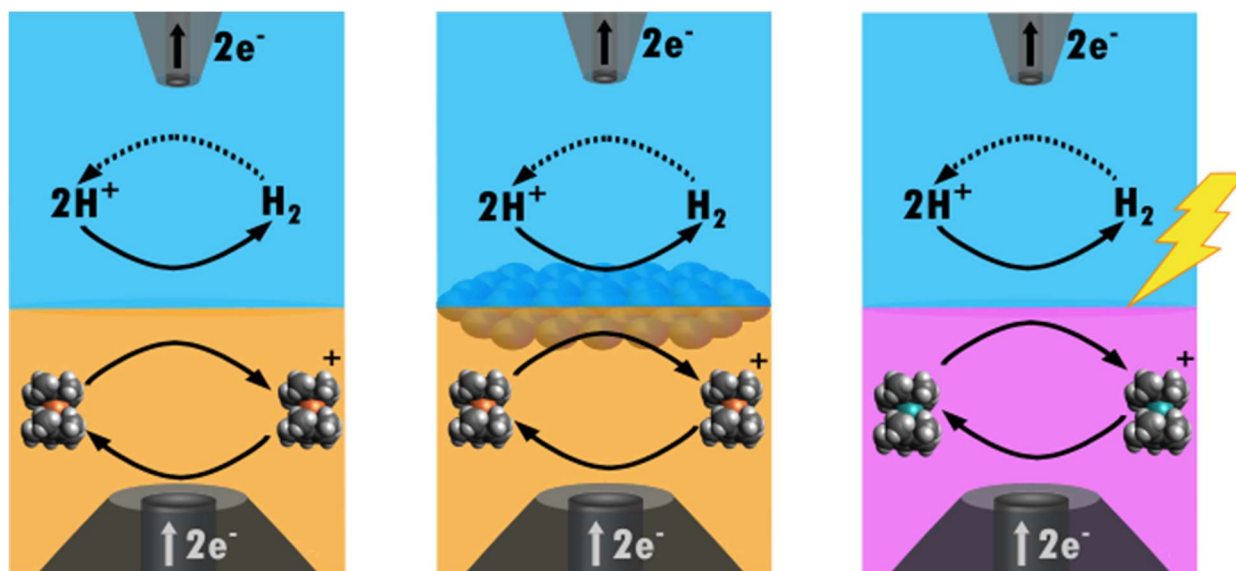


Figure 5-4. Scheme of HER at liquid|liquid interface: in the absence (on the left) and the presence (in the middle) of conductive nanoparticles at the interface and photochemical HER (on the right); all cases are shown with regeneration of electron donor and microelectrode for detection of hydrogen [25].

First reported experiments on HER at liquid|liquid interface was published by Girault group [176]. The reaction was performed in conventional 4-electrode cell and DCE|H₂O interface was externally polarized. The potential window was limited by H⁺ and Cl⁻ transfer from aqueous to organic phase at the potential higher than 0.25 V and lower than -0.15 V, respectively (Figure 5-5). After addition of DMFc, anodic current resulting from proton transfer increased and it became irreversible, because of the consumption of H⁺ cations in HER [176].

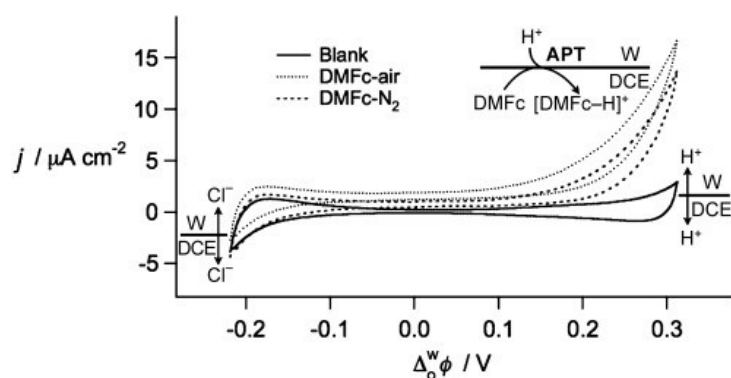
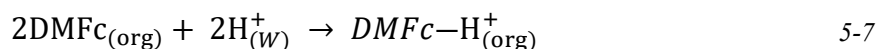
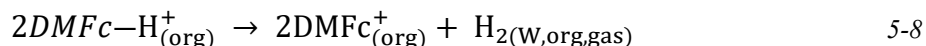


Figure 5-5. Voltammogram of liquid|liquid system, 5 mM DMFc 5 mM BATB in DCE, 10 mM LiCl in 0.1 M HCl (as reference 10 mM LiCl in 1 mM BaCl); solid line – without DMFc, dotted line - aerobic, with DMFc and dashed lines – anaerobic, with DMFc, scan rate 0.05 V s⁻¹ [176].

The first step of biphasic HER is the assisted proton transfer in the presence of electron donor (e.g. DMFc). Subsequently, there is the chemical conversion of $\text{DMFc}-\text{H}_{(\text{org})}^+$ into electron donor cation [176].



Most of the studies have been done with DCE as organic solvent [176], [25], however, TFT as a non-cancerogenic alternative was also employed [138].

DMFc is a the most efficient electron donor for HER at liquid|liquid interface [25]. Such metallocenes as DMRC, decamethyloosmocene [177] and osmocene [178] are characterised by higher redox potential. However, when they are excited by UV light, they can reduce H^+ in organic phase [25]. Therefore, proton transfer from aqueous acidic solution to organic phase is crucial to enable biphasic HER. As in the case of biphasic ORR, the interface must be polarised chemically by adding salts with the same hydrophobic anion, for example TB^- , to both phases. Consequently, the Galvani potential decreases and protons can be transferred from aqueous solution to DCE. H^+ is transferred in the form of HTB through the interface, what indicates catalytic role of TB^- [179]. The efficiency of reaction can be increased by electrochemical recycling of electron donor [180] as it was proposed for ORR (see page 45). It results in the constant flux of DMRC, which leads to the higher amount of generated H_2 [180].

To enhance biphasic HER efficiency, nanoparticulate catalysts were used. For this purpose, noble metals NPs (Pt, Pd) were deposited at liquid|liquid interface [181]. This can be done by reduction of PtCl_4^{2-} or PdCl_4^{2-} by DMFc in biphasic conditions [182]. Co [183] and Ni sulphides [184] and oxides [185] were also employed. Also, deposited Cu NPs increase the reactions efficiency [186]. Interestingly, molybdenum [187] and tungsten disulphides [188], borides and carbides [189] are better catalysts than noble metals. Moreover, the hybrid material made out of transition metal compounds (for example MoS_2) deposited on carbon nanoparticles [190] were proposed as catalysts. Except of obvious catalytic effect, conductive nanomaterials provide numerous electron transfer paths across the interface. It results in enhancing efficiency of biphasic HER [25].

5.3 Detection of hydrogen generated at the liquid|liquid interface

Similarly, like in the case of biphasic ORR, biphasic HER progress can be evaluated by colorimetry. Organic phase colour changes from yellow (DMFc) to green (DMFc^+) indicating oxidation of sacrificial electron donor and formation of bubble, presumably hydrogen, can be seen (Figure 5-6 a). Oxidation of DMFc can be also confirmed by UV-Vis spectroscopy tracing changes of characteristic absorption band of DMFc (425 nm) and its oxidised form (779 nm) (Figure 5-6 b). Moreover, the gas chromatography was applied for samples collected from above the biphasic system and signal from hydrogen was observed (Figure 5-6 c). Furthermore, cyclic voltammetry at Pt UME immersed in the organic phase qualitatively confirms consumption of electron donor and hydrogen formation (Figure 5-6 d). After 4 hours of biphasic reaction, cathodic current increased and the double anodic wave appeared on the CV at UME kept in the organic phase. Cathodic current corresponds to reduction of electron donor, whereas anodic current results from the oxidation of DMFc and oxidation of hydrogen. The pH increases during reaction, what confirms the consumption of H^+ [176]. The CV at Pt UME can also be used for H_2 detection, as shown on the example of biphasic hydrogen photogeneration with

DMRc as electron donor (Figure 5-7). Oxidation current of H₂ at -0.1 V increases after 60 minutes of biphasic reaction with the exposure to UV light in the presence of DMRc and BATB in the organic and LiTB in aqueous (0.1 M HClO₄) phase [179].

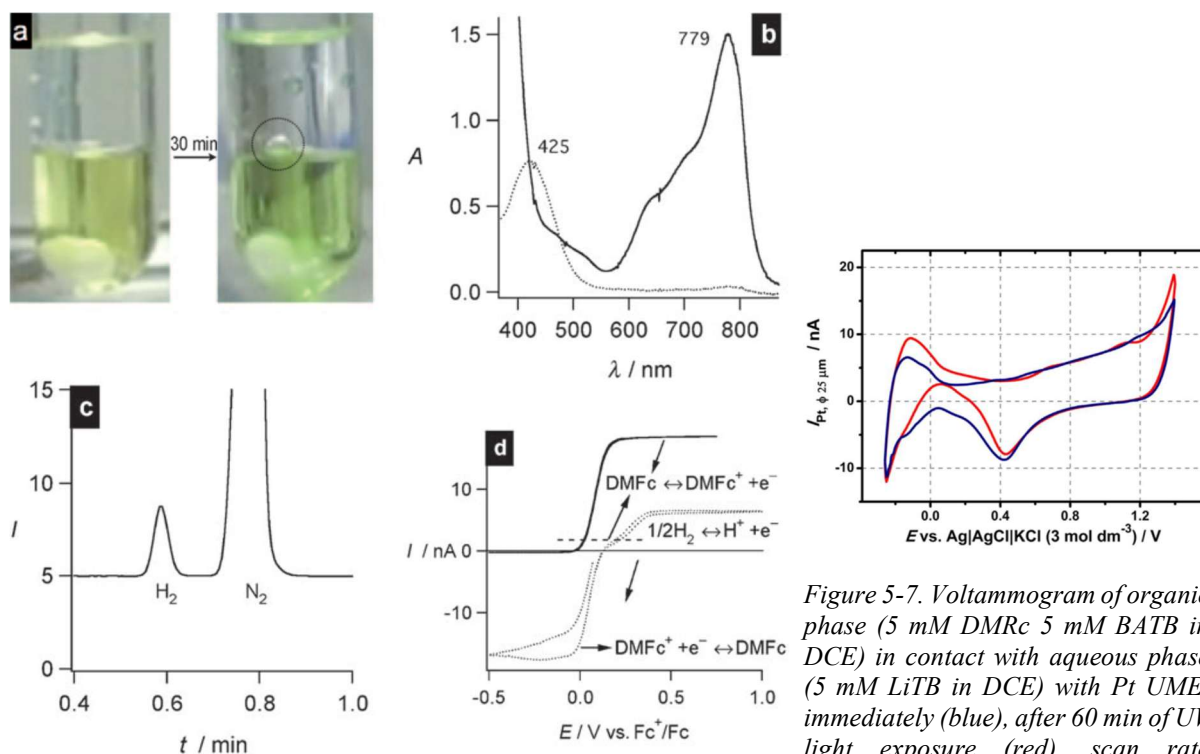


Figure 5-6. a) two-phase reaction in anaerobic conditions at the beginning (left) and after 30 min (right), b) UV Vis spectra of organic phase before the reaction (dotted line) and after 4 h of biphasic reaction in anaerobic conditions (solid line), c) GC chromatograms of the gas above the biphasic system 4 h after of biphasic reaction, d) cyclic voltammogram on UME of the organic phase after 4 hours of biphasic reaction (dotted line), CV on UME of freshly prepared solution of 5 mM DMFc in DCE in anaerobic conditions [176].

Figure 5-7. Voltammogram of organic phase (5 mM DMRc 5 mM BATB in DCE) in contact with aqueous phase (5 mM LiTB in DCE) with Pt UME, immediately (blue), after 60 min of UV light exposure (red), scan rate 500 mV s⁻¹ [179].

Importantly, SECM is a viable method to determine the H₂ flux generated at ITIES in both potentiometric [191] and amperometric mode [179].

In SECM potentiometric detection, H₂ is not consumed and H⁺ is not generated as in the amperometric mode. Both, Pt UME (100 μm) and reference electrode are immersed in the aqueous phase. Open circuit potential (E_{OCP}) is measured at Pt UME (Figure 5-8) as a function of the distance from liquid|liquid interface and the H₂ concentration is calculated from [179]:

$$[\text{H}_2] = \frac{\exp\left(-\frac{2FE_{\text{OCP}}}{RT}\right)}{k_{\text{H}}} \quad 5-9$$

where $k_{\text{H}} = 1282 \text{ dm}^3 \text{ mol}^{-1} \text{ at}$ [192] is a Henry's coefficient. Using the values of H₂ concentration, approach curve can be constructed. Clearly hydrogen concentration is decreasing as the distance from liquid|liquid interface increases next to the interface (Figure 5-9), what confirms that the reaction occurs at ITIES. The observed sharp drop of E_{OCP} (insert on Figure 5-9) is caused by the SECM tip penetration into the organic phase [191].

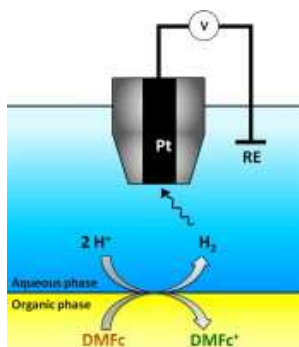


Figure 5-8. Scheme of potentiometric detection of H_2 generated at organic/aqueous interface [191].

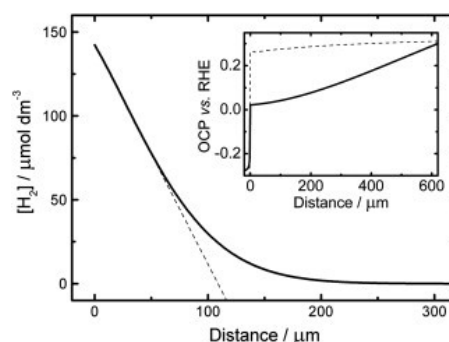


Figure 5-9. Hydrogen concentration vs. distance from the interface for biphasic system consisting of 50 mM DMFc and 5 mM BATB in DCE and 5 mM LiTB in 0.1 M $HClO_4$; potentiometric approach (insert) [191].

SECM in amperometric mode was employed for photogenerated hydrogen detection. The tip - Pt UME (25 μm) was immersed in the aqueous phase, whereas second working electrode Pt (100 μm) was placed in the organic phase, next to the interface. The potential was applied to the latter electrode, to allow the regeneration of electron donor. To construct the approach curve and for imaging of interface, the current on Pt tip was collected at 0.2 V. The increase of tip current was observed only above the bottom electrode kept at potential allowing for regeneration of electron donor - DMFc, in the presence of UV light (Figure 5-10), indicating H_2 photogeneration [179].

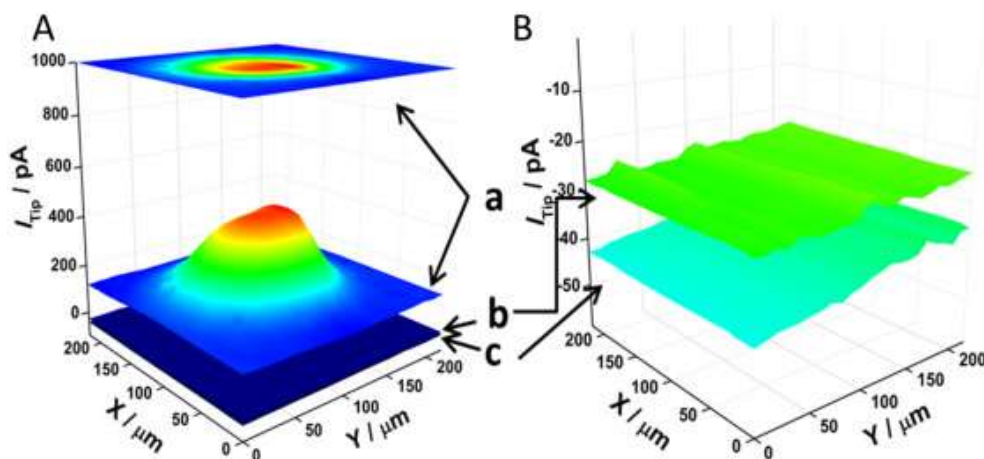


Figure 5-10. A) Current on the tip measured in the aqueous phase 5 mM LiTB in 0.1 M $HClO_4$ in contact with 5 mM DMFc 5 mM BATB in DCE, in anaerobic conditions; a) with UV light, b) in darkness, c) in darkness without applying potential; B) Images b and c from figure A with enlarged current scale [179].

6 Experimental part

6.1 Experimental techniques

6.1.1 Chronoamperometry

Chronoamperometry (CA) is an electrochemical technique, where the constant potential is applied to the working electrode (Figure 6-1 a) and the current is measured as a function of time (Figure 6-1 b). Typically, it is realised in two ways: with single or double potential step. In the latter case, after selected time potential returns to its initial value.

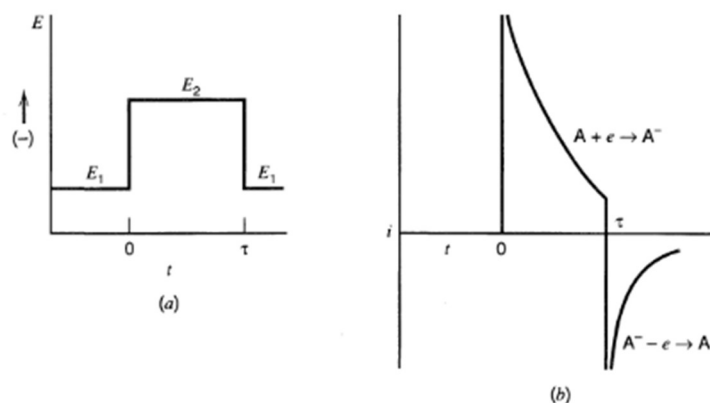


Figure 6-1. Potential and current change in time for double-step chronoamperometry [9].

When the potential applied to the flat electrode is changed to the value, when redox reaction occurs, the thickness of diffusion layer increases. For the electrode with conductive spots separated by insulating surface, like microelectrode array, at the beginning the diffusion layer grows around each spot. Later, when thickness of the diffusion layers is large enough, it overlaps with diffusion layers around neighbouring conductive spots [193].

Relationship between current and time in potential step experiment for diffusion-controlled process is described by Cottrell equation [193]:

$$i = \frac{nFAcD^{\frac{1}{2}}}{\pi^{\frac{1}{2}} t^{\frac{1}{2}}} \quad 6-1$$

Where: n – number of electrons, A – electrode's area, c – concentration of redox species, D – diffusion coefficient and t – time. It was derived assuming that the transport of the redox probe to the electrode surface follows the second Fick's law of diffusion. Cottrell equation applies quiescent conditions and the distance from the electrode to the wall of the electrochemical cell must allow unrestricted reactant diffusion in the time scale of experiment. The overpotential of reaction should be large enough to enable fast depletion of redox probe at the electrode surface, that the process will be controlled by diffusion to the electrode surface [194].

After the potential step, the current decreases according to the Cottrell equation. This equation can be used to estimate the diffusion coefficient for redox probe. Practically, it can be calculated from the slope of the Cottrell plot (I vs. $t^{-1/2}$, Figure 6-2). For example, the assumption that substrate molecules or ions are transported via planar semi-infinite diffusion is guaranteed for disc electrodes with 1 mm diameter or larger and hundred seconds potential step. For

calculations, only the linear part of the plot should be used due to the edge effects seen at long times and double layer charging at short times, which causes non-linearities [194].

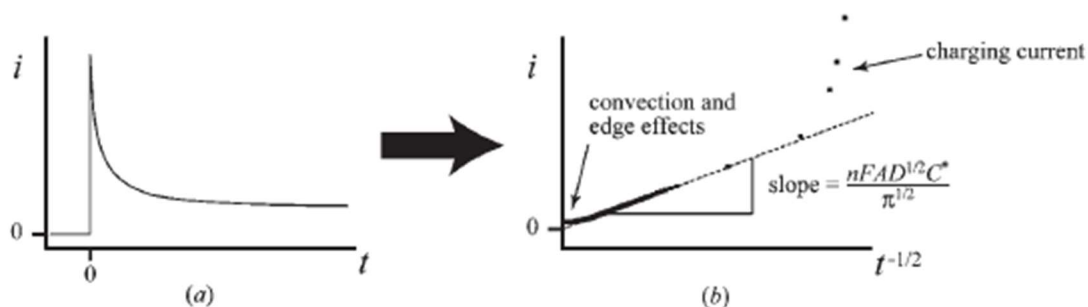


Figure 6-2. a) Raw data for chronoamperometry at a macroelectrode, b) current dependence vs. $t^{1/2}$, deviations come from charging current, convection and edge effects [194].

6.1.2 Cyclic voltammetry

Cyclic voltammetry is a powerful technique, which allows to understand electrode reactions mechanism [195]. It is commonly used for investigation of electrochemical processes including these occurring in fuel cells, capacitors, batteries and sensors [196]. During CV measurements, the potential applied to the electrode is changed linearly with constant rate between two values to complete one cycle (Figure 6-3 I). For simple electrode reaction:



when potential is changed, the ratio of concentrations of oxidised form (Ox) and reduced form (Red) also changes. If the electrode reaction rate is controlled by diffusion, its potential is described by the Nernst equation:

$$E = E^0 + \frac{RT}{nF} \ln \frac{a_O}{a_R} \quad 6-3$$

Activity of a given redox species (a_i) in the solution is defined by the ratio of concentration (c_i) to standard concentration ($c^\circ = 1 \text{ M}$) multiplied by unitless activity coefficient (γ_i) [9]:

$$a_i = \gamma_i \left(\frac{c_i}{c^\circ} \right) \quad 6-4$$

The shape of voltammogram corresponding to reaction 6-2, can be explained by analysing the concentration profile of oxidised and reduced form of redox species. In the scheme below (Figure 6-3 A-G), ferrocenium cation (Fc^+) reduction is used as an example. At the starting potential (point A), the concentration of Fc^+ does not depend on the distance from electrode and the concentration of Fc is equal to zero. When, the potential is changed towards its standard value, the cations next to the electrode surface react. Gradient of the concentration of both redox forms is formed as they diffuse to/from the electrode surface. At the redox potential their concentrations are the same (point B), as expected from the Nernst equation (6-3) [44]. The concentration gradient reaches maximum at peak potential (point C). At potential far below the peak potential (point D), Fc^+ concentration is equal to its maximal value, whereas Fc concentration decreases to zero. After potential reversal, the distance dependence of concentration of both species is more complex but peak is formed at potential (point E) higher than standard potential (point E).

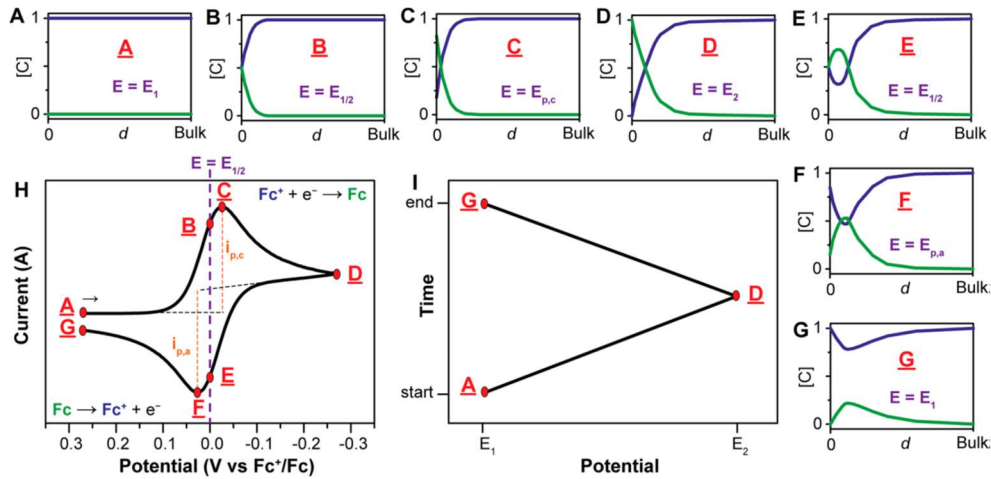


Figure 6-3. A-G) Changes in concentration profile during single scan in cyclic voltammetry, H) cyclic voltammogram (current vs. potential), I) potential change in time during cyclic voltammetry [197].

Cyclic voltammetry can be performed with different scan rates. When faster scan rate is implemented, then higher current is observed. One reason of that is the thinner diffusion layer on the electrode because of the limited time to form it [197]. Moreover, the concentration gradient increases, therefore the reactant flux $J(x,t)$ and current increases according to the first Fick's law [9]:

$$J(x, t) = D \frac{\delta c(x, t)}{\delta x} \quad 6-5$$

When electrode reactions rate is controlled by mass transport, the process is called reversible. For irreversible process, it is controlled by electron transfer. In the case of quasi-reversible one, the rates of electron transfer and mass transport are comparable. Increasing scan rate results in the concentration gradient and therefore reactant transport rate increases. As electron transfer rate is independent of scan rate, reaction changes from reversible through quasi-reversible to irreversible. Therefore, to study electrode kinetics, voltammetric scan rates has to be high enough to achieve at least quasi-reversible conditions [9].

For the electrode reversible reaction, kinetics is limited by diffusion of the redox species to the electrode and Randles–Ševčík equation can be applied. First versions of this equation were presented in 1947 [198] and 1948 [199] [200] and later it was further developed [201]. This equation shows that the peak current depends linearly on the square root of the scan rate. The version of Randles–Ševčík equation shown below works for 25°C (6-6) [9].

$$i_p = 2.69 \cdot 10^{-5} \times n^{\frac{3}{2}} A D^{\frac{1}{2}} v^{\frac{1}{2}} c \quad 6-6$$

where i_p – peak current [A], v – scan rate [$V s^{-1}$], c [$mol cm^{-3}$], D [$cm^2 s^{-1}$], A [cm^2]. Therefore, the linear dependence of peak current vs. square root of scan rate is expected (Figure 6-4, red line). For quasi-reversible process deviation from this dependence is seen. When scan rate is high enough to reach irreversible conditions also linear dependence of peak current vs. square root of scan rate is observed, but with smaller slope than for reversible process (Figure 6-4, blue line) [196].

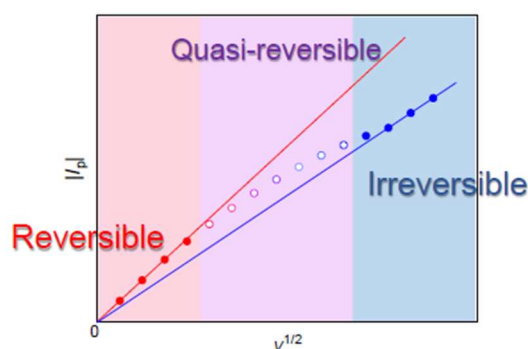


Figure 6-4. Peak current dependence vs. square root of scan rate for reversible and irreversible processes [196].

For electrochemically and chemically reversible (the reaction rate in both directions is the same [202]) 1-electron process at 25°C controlled by diffusion, for the anodic and cathodic peak potentials separation is 59 mV [197]:

$$\Delta E_p = E_a - E_c = \frac{59 \text{ mV}}{n} \quad 6-7$$

When the redox species adsorbs on the electrode surface in the oxidised or reduced form [9]. Then, ideally there is no cathodic and anodic peak potential separation as shown on the example of 1-electron process (Figure 6-5) [203]. For the high scan rate, the diffusion of adsorbed form cannot happen [9].

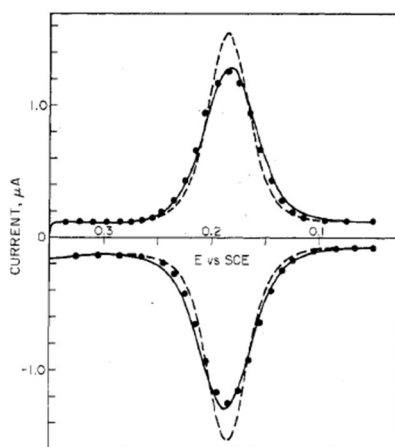


Figure 6-5. Experimental and theoretical cyclic voltammograms for $1.9 \times 10^{-10} \text{ mol cm}^{-2}$ of 9,10-phenanthrenequinone irreversibly adsorbed on a basal-plane pyrolytic graphite electrode in supporting electrolyte 1 M HClO_4 . Scan rate: 50 mV s^{-1} , experimental voltammogram (solid line), theoretical voltammogram (dashed line) and points calculated [204].

In the ideal conditions, when there are all redox centres are equal and redox process only comes from the adsorbed redox species, there are no interactions between adsorbed redox species [205] (Nernstian reactions under Langmuir isotherm conditions), the oxidation and reduction potential are the same. Then, in 25°C the half-width potential difference is equal 90.6 mV for 1-electron process [9]:

$$\Delta E_{p, \frac{1}{2}} = 3.53 \frac{RT}{nF} = \frac{90.6}{n} \text{ mV} \quad 6-8$$

And peak current is described by following formula [9]:

$$i_p = \frac{n^2 F^2}{4RT} v A \Gamma \quad 6-9$$

Determination of the amount of adsorbate is crucial for many devices, e.g. for batteries, fuel cells or sensors. For that, the surface concentration of adsorbate on the surface (Γ , mol cm⁻²) can be calculated from the oxidations or reductions peak area [203]:

$$\Gamma = \frac{1}{nFAv} \int_{E_{\text{neg}}}^{E_{\text{pos}}} |I| dE \quad 6-10$$

In practise, the integral divided by scan rate is the charge passed during the oxidation process (Q) [203].

$$\Gamma = \frac{Q}{nFA} \quad 6-11$$

For the thin film of redox species solution on the electrode surface, there is no significant influence of convection; the diffusion of species within the film is limiting factor of transport to the electrode surface (Figure 6-6) [9]. Generally, when the thickness of diffusion layer is comparable to the thickness of confined solution, then the layer can be considered as thin layer [206].

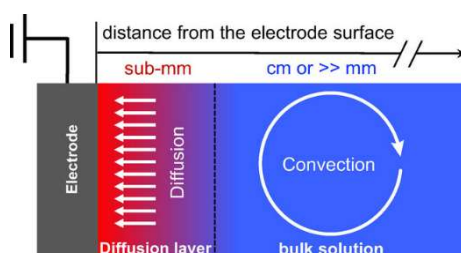


Figure 6-6. Scheme of diffusion and convection on the electrode with thin film [207].

The cyclic voltammogram of thin film of confined redox species solution is to some extent similar to that of adsorbed redox active species. It is symmetric, bell shaped and at the end of the single cycle current almost returns to the baseline. This is caused by completed oxidation of reductor, here Fe²⁺ and complete reduction of Fe³⁺ (Figure 6-7) [208]. Here, the charge transfer is a limiting factor, therefore to demonstrate this effect the scan rate must be low, typically below 10 mV s⁻¹. For higher values of scan rate, the voltammogram has the shape typical for diffusion-controlled process [207].

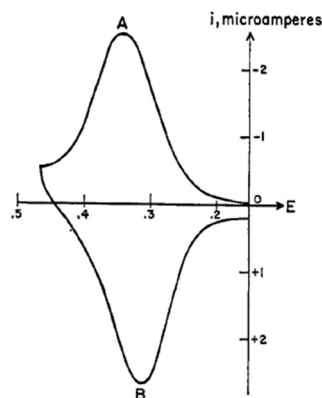


Figure 6-7. Cyclic voltammogram of oxidation of 10^{-3} M Fe^{2+} in 1 M HCl and reduction of Fe^{3+} , volume of the thin layer $1.4 \mu\text{l}$, scan rates 4 mV s^{-1} [208].

The peak current for the thin-layer voltammogram can be calculated similarly as for adsorption voltammetry, except that the surface concentration is replaced by bulk concentration c_O^* [208]:

$$i_p = \frac{n^2 F^2}{4RT} v A c_O^* \quad 6-12$$

where c_O^* is a sum of time dependent concentration of oxidised ($c_O(t)$) and reduced ($c_R(t)$) forms:

$$c_O^* = c_O(t) + c_R(t) \quad 6-13$$

Typically, cyclic voltammetry or chronoamperometry are performed with three-electrodes connected to the potentiostat (Figure 6-8). Current flows between working and counter electrodes, when reference electrode helps to control potential of the working electrode [197].

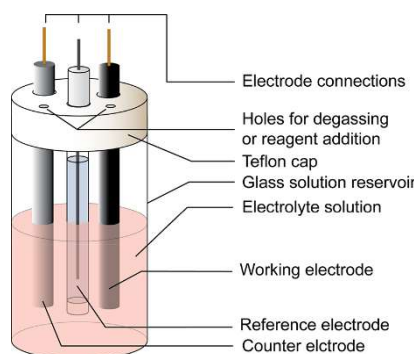


Figure 6-8. Scheme of three-electrode electrochemical cell [197].

The electrode's size and shape influence the shape of CV and the current value. According to IUPAC definition, ultramicroelectrode is the 'electrode with smallest dimension of less than 25 micrometre' [209]. Considering the same scan rate, the diffusion layer thickness of UME is bigger than the electrode diameter [210]. Then, for electrodes with larger surface area, the diffusion to its surface is predominantly linear, whereas for smaller electrodes hemispherical diffusion dominates (Figure 6-9) [9]. For a given electrode the contribution of linear and spherical diffusion depends on scan rate. At slow scan rate like 10 mV s^{-1} , contribution of spherical diffusion to UME immersed in the aqueous electrolyte is dominant. The steady state is reached and limiting current plateau is seen on the voltammogram. When the scan rate increases 100 times, contribution of spherical diffusion is almost negligible. This is because the

time of the scan is so short that the concentration gradients of the substrate and the product develop predominantly in front of the UME. Therefore, peak shaped voltammogram is obtained. (Figure 6-10) [203]. At low and high scan rate, limiting or peak current is linearly dependent on the concentration of redox active species in the solution [211].

During the voltammetric experiment, both faradaic and capacitive currents flow (resulting from double layer charging) generated by working electrode potential change. Applied potential difference is decreased by iR value (i – current, R - resistance), called ohmic drop [194]. The electrolyte solution resistance for disk-shaped electrode increases when the electrodes radius decreases according to the equation [212]:

$$R = \frac{1}{4\kappa r_0} \quad 6-14$$

where κ [S] is the conductivity of the solution and r_0 is electrodes radius. However, both faradaic and charging currents decrease for smaller electrodes radius, but faster than ohmic drop increases. Therefore, for ultramicroelectrodes the ohmic drop is smaller than for millimetre radius electrode and the shape of CV curve is less affected [194]. Thanks to that, UMEs are especially useful for specific conditions [213], like low-conductive or diluted electrolyte solutions [203] or organic solutions [194]. Moreover, fast reactions can be investigated with UMEs by fast scan voltammetry due to their ability to achieve high mass transport rate thank to faster hemispherical diffusion than planar one [211].

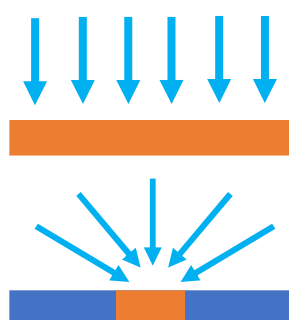


Figure 6-9. Planar diffusion to the electrode (top) and hemi-spherical diffusion to the ultramicroelectrode (bottom).

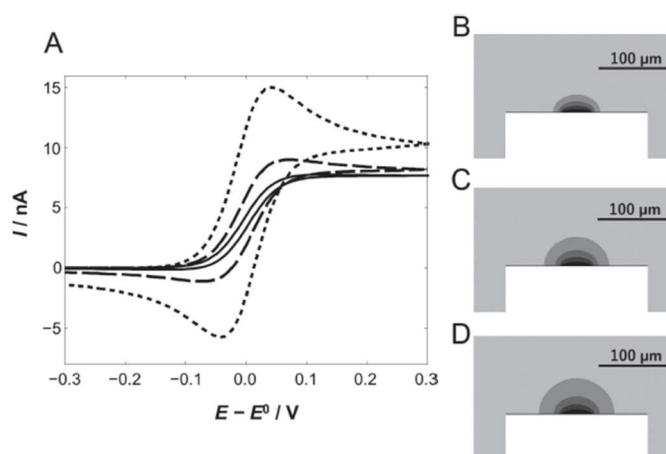


Figure 6-10. A) Voltammogram in ferrocenodimethanol (1 mM) at the microelectrode ($r=40 \mu\text{m}$), scan rates: 0.01 V s^{-1} (solid), 0.1 V s^{-1} (broken) and 1 V s^{-1} (dotted line), calculated. B, C, D). Concentration profiles of $\text{Fc}(\text{CH}_3\text{OH})_2^+$ at different scan rates: 1 V s^{-1} (B), 0.1 V s^{-1} (C), 0.01 V s^{-1} (D); concentration changes from 0.2 mM to 0.8 mM (lighter to darker grey colour) [203].

When voltammetric or chronoamperometric experiment is performed, the sum of both: faradaic and non-faradaic currents is measured. Faradaic current (I_F) comes from the electrode process with electron exchange, whereas capacitive or charging current (I_C) from charging the double layer at the electrode|electrolyte interface (Figure 6-11) [214]. The capacitive current can be decreased by usage of smaller electrode, so ultramicroelectrodes can be used for that [194]. UMEs can be applied for biological studies, especially for in vivo monitoring in cells because of their small size and not significant damage effect on cells [211]. Ultramicroelectrodes can

be used in sensors due to their stability, reproducibility of measured current and proportions of measured capacitive and faradaic current [203].

Importantly, when CV scan rate decreases, the capacitive current decreases faster than the faradaic current, so its influence can be decreased by using other measuring method (see below 6.1.3). In potential step experiment, capacitive current decreases faster than faradaic one, so there is time, when I_C is close to zero and I_F is not much below initial value. From the charging current, one can estimate the capacity of the double layer. Capacitive current can be higher than faradaic one, when the concentration of redox species is low [214].

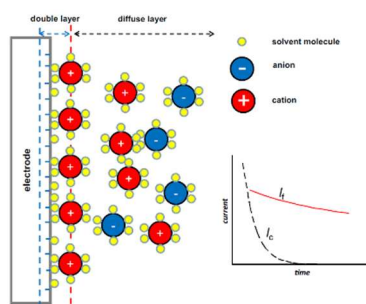


Figure 6-11. The simplified structure of electric double layer and the plots of the change of faradaic and non-faradaic current in time [214].

6.1.3 Square wave voltammetry

To decrease the contribution of capacitive current to the recorded amperometric signal, square wave voltammetry can be used. For that, two opposite potential steps of the same magnitude are applied to the working electrode (Figure 6-12 c) and the current is measured close to the end of each step (Figure 6-12 c). Therefore, SWV allows to achieve higher I_F/I_C ratio than non-pulse techniques like cyclic voltammetry. It results in the higher sensitivity than CV. In SWV experiment, two current values for the same potential are measured at forward and reverse pulse. The net current is the difference between current for forward (I_{for}) and reverse (I_{rev}) pulse which is typically shown as result of SWV experiment (Figure 6-12 e, red line – net current) [214].

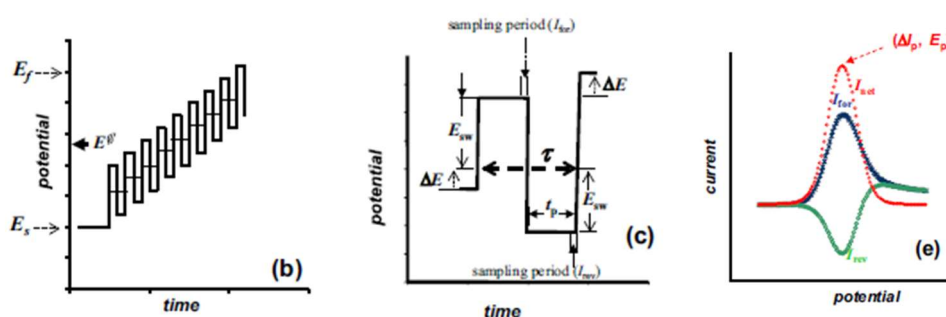


Figure 6-12. b, c) Potential vs. time dependence for SWV, e) SWV voltammogram [214].

SWV is more useful than differential pulse voltammetry (DPV), where the current is measured before and after the application of the pulse and their difference is calculated. Both methods are characterised by similar effectiveness of the background suppression. SWV has slightly better sensitivity than DPV and application of faster scan rate in more systems is possible [9].

6.1.4 Rotating disc electrode voltammetry

‘The rotating disc electrode (RDE) is the hydrodynamic electroanalytical technique used to limit the diffusion layer thickness’ [194]. In general, mass transport to the electrode can be realised by migration, diffusion and convection. Starting from certain rotation rate, mass transport to RDE is realised by convection [215]. Here, forced convection is advantageous due to fast established steady-state of mass transport [194]. Typically, RDE tip consists of conductive disc surrounded by insulating material (Figure 6-13 A). Typically, such materials as Pt, Ni, Cu, Au, Fe, Si, CdS, GaAs, glassy carbon or graphite [194] are embedded in glass, Teflon, epoxy resin or other polymer [9]. RDE is placed vertically in electrochemical cell and rotates around its vertical axis. Rotation rates between 400 and 10000 rpm are typically used [194]. The movement of the electrode results in the specific flow pattern near electrode surface (Figure 6-13 B) [215].

According to Nernst diffusion model, electrolyte next to the RDE surface can be divided into 2 regions (Figure 6-14). First stagnant layer has the thickness δ_o (typically lower than 0.002 cm) where mass transport is realised by diffusion. Second zone extends further from the electrode, where convection plays a role and concentration of redox species does not depend on the distance from the electrode surface [215]. The thickness of the diffusion layer (δ_o [cm]) is (Figure 6-14) defined as:

$$\delta_o = 1.61 D_O^{1/3} \nu^{1/6} \omega^{-1/2} \quad 6-15$$

where 1.61 [rad^{1/2}], ω - rotation rate in [rad s⁻¹] and ν - kinematic viscosity of the solvent [cm² s⁻¹]. Then, concentration profile can be used to calculate limiting current (i_l) using Levich equation [9]:

$$i_l = 0.62 n F A D_O^{2/3} \nu^{-1/6} c_O^* \omega^{1/2} \quad 6-16$$

Where 0.62 [rad^{-1/2}], c_O^* is the concentration of redox active substance in the bulk solution [mol cm⁻³], ω [rad s⁻¹] and A [cm²].

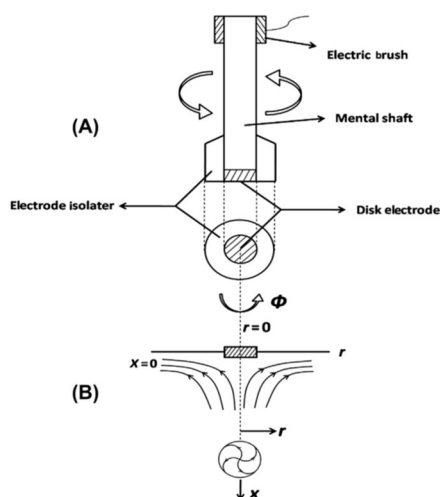


Figure 6-13. A) Scheme of the rotating disk electrode, B) solution flow pattern near the disk electrode surface (x is the coordinate direction perpendicular to the disk electrode surface, r is the coordinate direction parallel to the disk surface, and ϕ is the coordinate direction of the electrode rotation, respectively) [216].

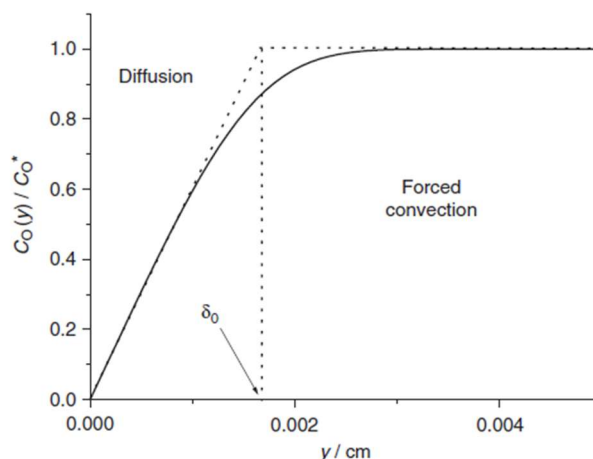


Figure 6-14. Steady-state concentration profile at the RDE, showing the well-stirred bulk solution, where convection dominates and the thin stagnant layer at the electrode surface, where diffusion dominates. $D_0 = 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$, $\omega = 100 \text{ Hz}$ [194].

According to Levich equation (6-16), the limiting current depends on the rotation rate (Figure 6-15, Figure 6-16). Importantly, for simple redox reaction the half-wave potential is independent of rotation rate. The difference in slopes (Figure 6-16) for reduction and oxidation is caused by the twice higher concentration of $\text{K}_4\text{Fe}(\text{CN})_6$ than $\text{K}_3\text{Fe}(\text{CN})_6$. From the j_L vs. $\omega^{1/2}$ plots' slopes (Figure 6-16), the diffusion coefficient of both redox forms can be calculated using Levich equation (6-16) [215].

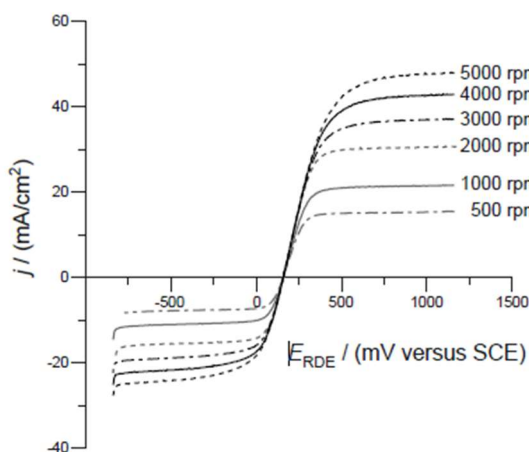


Figure 6-15. Current density vs. potential curves as a function of rotation rate for a solution of $\text{K}_3\text{Fe}(\text{CN})_6$ (10 mM) + $\text{K}_4\text{Fe}(\text{CN})_6$ (20 mM) in Na_2SO_4 (0.1 M) at a vitreous carbon RDE. Sweep rate: 5 mV s^{-1} [215].

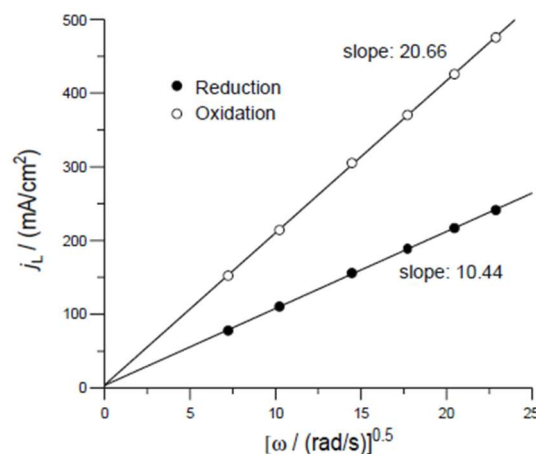


Figure 6-16. Plots of j_L vs. $\omega^{0.5}$ from the curves in Figure 6-15. Working solution: $\text{K}_3\text{Fe}(\text{CN})_6$ (10 mM) + $\text{K}_4\text{Fe}(\text{CN})_6$ (20 mM) in Na_2SO_4 (0.1 M) at a vitreous carbon RDE [215].

Voltammetry at RDE can be used to verify, whether the kinetics of the electrode reaction is controlled by charge-transfer, mass transport or both processes. For the control by charge transfer, the equilibrium potential does not depend on the rotations rate. At higher overpotentials, current starts to depend on rotation rate. For the highest overpotential, current

is independent on RDE potential and then process is controlled by mass transport [215]. Electrocatalysis is the most important area where RDE is employed. It also found application in electrodeposition and generation of nanoparticles [217].

6.1.5 Scanning electrochemical microscopy

Scanning electrochemical microscopy is a very useful technique to study surface reactivity in solution. It was invented almost 40 years ago [218], [219], [220]. For SECM experiment four components are needed (Figure 6-17):

- Bipotentiostat for application of potential program to the SECM tip and if necessary to the studied sample. Typically, the current is measured at the SECM tip and analysed. When non-conductive sample is studied, only potentiostat can be used.
- High-resolution 3D controller for tip positioning in front of the sample,
- Computer with dedicated software to drive the position controller, enable measurements and for data acquisition,
- SECM tip (typically disc UME of diameter from ten micrometres down to nanometres range) [221].

Amperometric probes are characterised by longer life-time, shorter response time and easier positioning comparing to the potentiometric ones [221]. However, the latter exhibit higher selectivity. Most frequently used amperometric probes - disc UMEs are typically made of the conductive wire sealed in the insulating material, like glass. The important probe parameter is geometric coefficient RG. For disk embedded in insulating material is defined as the ratio of the radius of insulating material (r_i) to the radius of the embedded wire (r_w) (Figure 6-18) [221]:

$$RG = \frac{r_i}{r_w} \quad 6-17$$

Typically, RG value is c.a. 10. This means that insulating sheath is much larger than disc, what helps to establish steady state current.

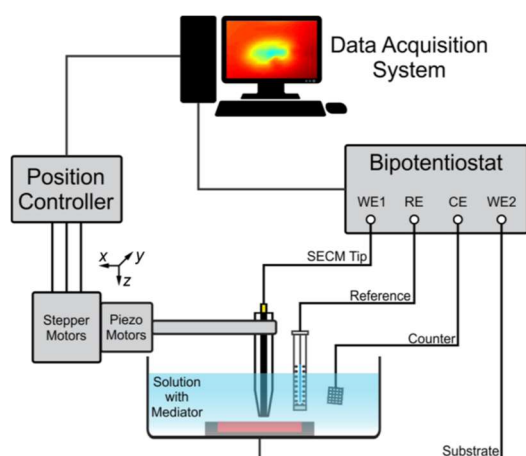


Figure 6-17. Scheme of SECM setup [221].

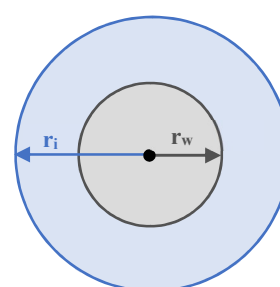


Figure 6-18. The scheme of the ultramicroelectrode, where grey part is wire and blue part is insulating material.

Among the number of operation modes of SECM, the most popular is feedback mode (Figure 6-19 A, B, C). The SECM tip can be moved in all directions in front of the studied surface. Its potential allows for redox reaction (here oxidation) of the redox probe dissolved in electrolyte solution. When SECM tip is far from the sample, diffusion of substrate is not spatially limited (Figure 6-19 A). As it moves closer, it limits the diffusion space and the tip

current decreases. For inert substrate material, the probe current is smaller than in the case of semi-infinite diffusion and this is called negative feedback mode (Figure 6-19 B). When the solid substrate is conductive, this is called positive feedback mode (Figure 6-19 C). After oxidation of redox species on the probe surface, the product can be re-reduced on the substrate, which results in the increase of tip current (Figure 6-19 C) [221].

The other modes of SECM operation are generation/collection (GC) (Figure 6-19 D, E): substrate generation/tip collection (SG/TC) and tip generation/substrate collection (TG/SC) modes. In the case of SG/TC mode (Figure 6-19 D), the redox species generated (here oxidised) on the substrate, diffuse to the tip and there they are reduced. On the other hand, in TG/SC mode, the redox species generated on the tip (here oxidised) diffuse to the substrate and there they are reduced (Figure 6-19 E). For SG/TC mode, the diffusion layer next to the substrate is larger than the one on the tip. For larger substrates, it is not possible to achieve the steady state and collection efficiency is low and there are interferences between reactions at SECM tip and substrate [221]. However, SG/TC mode is used for investigation of the concentration profile and calculation of the product flux, what is useful for corrosion [222] and catalytic reactions [223], [224] studies. On the other hand, the TG/SC mode is used for kinetic studies. When experiment starts, current on the substrate is zero, because of the lack of reduced form. Later it increases with progress of the oxidation at the tip. The reduced form diffuses from the tip to the substrate, when they are close to each other. Both currents at the substrate and the probe are measured [221].

In the case of redox competition mode (Figure 6-19, F), both tip and substrate compete for the same redox probe. The potential is applied to both electrodes, but only the tip current is measured. In this case, contribution of the background current is decreased, which results in the higher sensitivity than of TG/SC. When reducing potential is applied to the tip, the same potential is applied to the substrate to avoid complete depletion of redox species. For inert substrate, the tip current is constant. For conductive one, the current decreases due to the fact that the reduction occurs on both the substrate and the tip [221].

The direct mode (Figure 6-19, G) differs from the others because the UME and substrate play the role of counter and working electrode, respectively. Small distance between electrodes allows to achieve high patterning resolution [221]. The direct mode found the application in modifications of surface by electrodeposition [225], etching of semiconductor, micropatterning [226] and deposition of enzymes [227].

In potentiometric mode (Figure 6-19, H), the potential between the working and the reference electrode is measured [221]. Ion-selective electrodes (ISE) or Pt ultramicroelectrode were applied as SECM tip. This mode operates when E_{OCP} is linearly dependent on the activity of the specific ions or molecules. The advantage of potentiometric mode is its high selectivity. Importantly the probe used in SECM may not undergo faradaic reaction and it is not necessary to use redox species with redox potential within the electrolyte solution potential window [221].

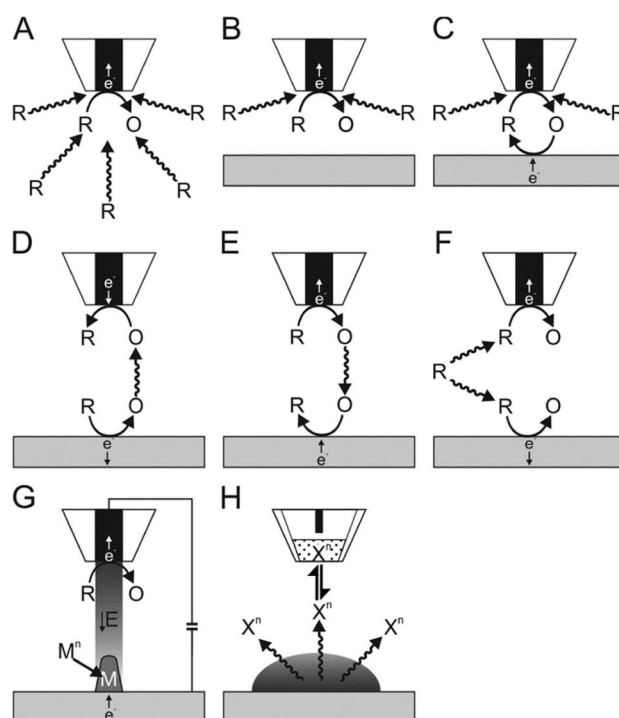


Figure 6-19. Scheme of different SECM measurement's modes A) feedback for bulk solution B) negative feedback C) positive feedback D) substrate generation/tip collection E) tip generation/substrate collection F) redox competition G) direct H) potentiometric [221].

SECM is suitable for local pH measurements, which can be performed using potentiometric or amperometric mode. For potentiometric one, tip and substrate at OCP must exhibit 59 mV/pH (Nernstian) or >59 mV/pH (super-Nernstian) potential dependence. For this, SECM tips are prepared from metal oxides or they consist of polymeric films deposited on metal surface [228]. Others are made of the metal wire sealed in the insulating material, like glass [221]. Although these are easy to miniaturize [228], they exhibit long response time (at least few seconds) due to the long equilibrium time of OCP measurement [229]. Unfortunately, the potential drop at the studied interface can affect the OCP measurement at the tip [228]. Potentiometric mode cannot be employed, when the redox species are present in the solutions and then amperometric mode has to be applied [229]. For amperometric sensing, SECM tip has to be modified with the compound undergoing redox process involving protons. Then, the change in pH causes the shift of the redox potential and the response is faster than that of potentiometric one [228]. This approach was applied for local pH monitoring [229].

SECM was used to monitor reactions *in situ* at liquid|liquid, solid|liquid and liquid|gas interfaces. It was applied to mechanistic study electrocatalytic reactions like HER, ORR and CO₂ reduction [230]. Recently, SECM found the application for the research related to solar cells [231], fuel cells (for developing catalysts) [232], rechargeable batteries [233] and supercapacitors [234], [235]. This technique allows, to determine local activity sites, and selectivity of reaction [236]. SECM can be combined with other scanning probe techniques. Its combination with scanning ion-conductance microscopy (SICM) [237] increase of the resolution of imaging [238], whereas the combination with AFM [239] results in higher resolution of topographical and electrochemical imaging [238].

In the research for this thesis, SECM positive feedback mode was used to determine H₂O₂ concentration gradient resulting from biphasic ORR.

6.1.6 UV-Vis Spectroscopy

UV-Vis Spectroscopy is a simple, cheap and non-destructive analytical technique. UV-Vis spectrophotometer detects show, how much of the incident ultraviolet or visible light is absorbed by the sample. This is described by the Lambert-Beer law [240]:

$$\frac{I}{I_0} = e^{-\sigma(N_1-N_2)l} \quad 6-18$$

where: I_0 – initial light intensity, I – light intensity after transmitting out of the sample, σ - absorption cross section, N_1 – population of initial energy states, N_2 – population of final energy states and l – light's path's length. It can be simplified to the Beer's Law [240]:

$$A = \varepsilon cl = -\log\left(\frac{I}{I_0}\right) \quad 6-19$$

where A – absorbance, c – concentration of chromophore and ε – molar absorptivity coefficient,

As a result of UV-Vis measurement, one gets a spectrum (absorbance vs. light wavelength), which is characteristic for a given solution. As non-invasive and quick technic, UV-Vis spectroscopy can be used for qualitative and quantitative analysis [241]. After creating the calibration curve, it is possible to determine the concentration of the analyte in the sample. Moreover, multicomponent analysis is also possible [240].

6.2 Chemicals

- HClO_4 (70%) from ACS reagent
- Toluene (Supelco, for analysis) from Sigma Aldrich
- $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ (>98%) from Iolitec
- $\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2$ (>99%) from Iolitec
- $\text{P}_{(6,6,6,14)}\text{NTf}_2$ ($\geq 95,0\%$) from Sigma Aldrich
- DMFc (97 %) from Aldrich Chemistry, DMFc (99%) from ABCR
- DMRc (99%, 99,9%-Ru) from Strem Chemicals
- NaClO_4 ($\geq 98\%$) from Fluka Analytical
- NaSCN ($\geq 98,0\%$) from Fluka Chemika
- KNO_3 (pure for analysis) from Chempur.
- KPF_6 (99 %) from Aldrich Chemistry
- NaClO_4 ($\geq 98\%$) from Fluka Analytical
- KCl (pure for analysis) from Chempur
- KBr (pure for analysis) and NaF (pure for analysis) from Polskie Odczynniki Chemiczne S.A.
- NPOE (99 %) from Sigma Aldrich
- THAP from ABCR and recrystallised from the mixture of water and ethanol
- Lithium tetrakis(pentafluorophenyl)borate ethyl etherate from Aldrich
- Lithium tetrakis(pentafluorophenyl)borate diethylether complex (97 %) from ABCR
- Bis(triphenyl- phosphoranylidene)ammonium chloride (97 %) from Sigma Aldrich
- BATB was prepared in methathesis lithium tetrakis(pentafluorophenyl)borate ethyl etherate (or lithium tetrakis(pentafluorophenyl)borate diethylether complex) and bis(triphenylphosphoranylidene)ammonium chloride [242] and recrystallised twice from acetone

- ITONPs powder (99,99%), 20-30 nm diameter, 90% In₂O₃, 10% SnO₂ from Getnanometaterials
- ITO NPs dispersion (diameter<100 nm, 30% wt. in isopropanol) from Aldrich
- ITO plates with resistivity 8-12 Ω/sq ft supplied by Delta Technologies (Part No. CG-511N-11115)
- Rapeseed oil from Vita'D
- Linen Oil from Rustica
- Sunflower Oil from Rustica
- Alumina 1, 0.3 (Buehler Micropolish II) and 0.05 μm (MicroPolish Alumina, Buehler) for polishing + polishing pads (MicroCloth Polishing Cloth, Item: 40-7212
- Acetone from Linegal Chemicals
- Ethanol (96%) from Linegal Chemicals
- Propanol-2 (99,8%) from Linegal Chemicals
- Graphite microparticles (<20 μm) from Aldrich Chemistry
- C₄mimN(Tf)₂ (99%) from Iolitec
- Potassium iodide (pure p.a.) from POL-AURA Odczynniki Chemiczne
- Starch soluble (pure p.a.) from Chempur
- Deionized water with a resistivity of 18.2 MΩ cm (Arium® Comfort Lab Water System, Sartorius)
- Argon gas (99,999 %)from Multax S.C.

6.3 Materials

- Sand paper, grit 600, 1200, 2000
- Glass capillary (0.86 × 1.5 mm) from Science Product GmbH
- Glass capillary (1.16 mm inner diameter)
- Pt wire (99,95 %), 25 μm diameter, from Alfa Aesar
- Glassy carbon (GC) (1 mm or 3 mm diameter) from ALS and Mineral, respectively
- Reference electrode Ag|AgCl|3M NaCl from ALS RE-1S
- Quasi-reference electrode – Ag wire (99,99 %), 0.95 mm diameter, from Mennica Polska.
- Counter electrode – Pt wire (99,9 %), 1 mm diameter, from Mennica Metale Sp. z o.o.

6.4 Apparatus

- Scale Mettler Toledo XA Dual Range (accuracy 0,01 mg)
- Faraday cage from Autolab Eco Chemie BV or from IPC workshop
- Automatic pipettes from Eppendorf
- Vortex VELP Scientifica F202A0175
- Ultrasonic bath EMAG Emmi-30HC
- Dip coater KSV NIMA Dipcoater Multivessels
- DLS Zetasizer Malvern ZEN3600
- Potentiostat Autolab PGSTAT30
- THORLABS Brushed Motor Controller Kinesis
- FEI Nova NanoSEM 450 equipped with an EDS detector
- Atomic force microscopy (AFM) (Multimode 8 microscope under control of Nanoscope V controller from Bruker)

- Bipotentiostat Palmsens 4 SQGBT900
- UV Vis spectrometer Thermo Electron Corporation Evolution 300 UV - Visible Spectrophotometer
- Rotating disk electrode, RRDE Rotator RRDE80541, Metrohm Autolab
- UV lamp Thorlabs M365L3 - 365 nm, 880 mW (Min) Mounted LED, 1000 mA with LEDD1B - T-Cube LED Driver and KPS201 - 15 V, 2.66 A Power Supply Unit
- Glove box Labconco 5220120 with gloves Honeywell worth 8B1532/8H

6.5 Preparation of electrodes

6.5.1 Platinum ultramicroelectrodes

Platinum UMEs were prepared by heating the glass capillary (0.86×1.5 mm) using the gas burner, then Pt wire (25 μm) was inserted inside and the capillary was heated again. Next, the electrode was polished using sand paper, alumina 1 μm and 0.3 μm , rinsed by water, sonicated in the mixture of water and ethanol and dried by argon, respectively. Pt UME was cycled in the 0.5 M H_2SO_4 in the potential range from -0.2 to 1.3 V in order to reduce surface oxides. Most of the prepared electrodes exhibited RG c.a. 40.

6.5.2 ITO electrodes modification with nanoparticulate film

ITO plates were cut into rectangles (1×3 cm). They were first consecutively washed using acetone, ethanol and water in sonication bath, for 10 minutes with each solvent. Next, ITO electrode was 3 times subsequently immersed and withdrawn to/from 10 times diluted commercial ITO NPs dispersion in isopropanol (3% after dilution) with the velocity of 85 mm min^{-1} to get ITONPs modified electrodes [41].

6.5.3 Carbon paste electrodes

To prepare CPE with vegetables oils (rapeseed, sunflower and linen) as binders, 110 μl of organic solution (5 mM DMFc in oil) was mixed with 0.17 mg of graphite using a mortar. Ready paste was inserted into the glass capillary (1.16 mm inner diameter) and copper wire was placed for the electric contact. The surface of CPE was smoothed using printing paper. This kind of electrodes allows the usage of non-polar solvents without additional electrolyte due to the presence of graphite particles which are providing electric contact with copper wire.

6.6 Setup and experimental procedures for electrochemical measurements

For electrochemical measurements three-electrode setup was used. $\text{Ag}|\text{AgCl}|3\text{M NaCl}$ or Ag wire (mostly for SECM to prevent the influence of chloride anions) and Pt wire were used as reference and counter electrode, respectively. For measurements with rotating disc electrode, $\text{Ag}|\text{AgCl}|3\text{M KCl}$ was used. Glassy carbon, CPE, platinum UME, ITO or ITO|ITONPs electrodes were used as working electrodes. GC electrodes were polished with alumina 1 μm and 0.3 μm and 0.05 μm before each measurement. For electrochemical measurements potentiostat Autolab PGSTAT30 was used. For the experiment with DMFc in the organic phase, the UV lamp was used to allow its excitation and Bipotentiostat Palmsens 4 SQGBT900 was used. All experiments in air were done in Faraday cage. The experiments in anaerobic conditions were done in glove box filled with argon or in the solution bubbled with argon before.

6.7 Setup and experimental procedures for scanning electrochemical microscopy

SECM was employed to obtain H_2O_2 concentration as a function of the distance from liquid|liquid interface by recording approach curves. Pt UME (as SECM tip) was moved continuously ($2\ \mu\text{m/s}$) towards the interface and at the same time cyclic voltammetry in the potential range from -0.3 to $1.3\ \text{V}$ was performed at this electrode. Every time, after recording CV, scanning was stopped for $5\ \text{s}$ and the potential was kept on $-0.3\ \text{V}$. In order to increase the efficiency of biphasic ORR, for most of the measurements, potential of the substrate electrode was set at potential lower than the redox potential of electron donor to allow for its electrochemical regeneration. Both electrodes potential was controlled by bipotentiostat module of Autolab PGSTAT 30. The motion of SECM tip was controlled by THORLABS Brushed Motor Controller Kinesis.

6.8 Emulsion preparation and experimental procedure of electrochemical measurements in emulsion

Emulsion was prepared by mixing $100\ \mu\text{l}$ of organic phase consisting of $5\ \text{mM DMFc}$ $400\ \text{mM P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ in toluene and $5\ \text{ml}$ of $0.1\ \text{M HClO}_4$. Ready composition was mixed using vortex for $20\ \text{s}$ and sonicated in the pulse mode, $3\ \text{s}$ on and $7\ \text{s}$ off, repeated 20 times [119]. Most of the electrochemical studies has been done in the stirring conditions to enable better convection towards the electrode. Some measurements have been done with the rotating disk electrode. For some experiments with DMFc in the organic phase, the UV lamp was employed.

7 Oxygen reduction reaction and hydrogen evolution reaction at NPOE|H₂O and C₄mimN(Tf)₂|H₂O interfaces with electrochemical recycling of electron donor

7.1 Optimisation of the preparation of ITO|ITONPs electrodes and setup for electrochemical measurements

Conventionally, electrochemical processes at liquid|liquid interface are demonstrated and studied in a setup consisting of both bulk phases. Here, to decrease the volume of the organic phase, its thin film was deposited on the surface of indium tin oxide (ITO) bare electrode or ITO electrode covered by ITO nanoparticulate (ITONPs) film (ITO|ITONPs electrode). Preparation of this system started with the optimisation of the shape of the cell, the position of working electrode and the deposition process of nanoparticles.

First, the dip coating process employed for ITONPs deposition was optimised. It was planned to follow the protocol used earlier in our team [41], but commercial ITO nanoparticles dispersion in methanol used at that time was not available anymore. Unfortunately, it was also not possible to find out, how NPs surface was modified by supplier. Therefore, commercial ITONPs dispersion in water was used, what required additional steps of evaporating water and preparing dispersion in a volatile solvent (here - methanol). Such dispersion was not stable, what resulted in the lack of stability and reproducibility demonstrated in results of electrochemical experiments. Also, the same nanoparticles purchased in the dried form were used after dispersing in methanol. Again, it did not result in the reproducible electrochemical response, as demonstrated by CV of three different ITO|ITONPs electrode prepared in the same way and modified by redox probe solution in viscous solvent (Figure 7-1).

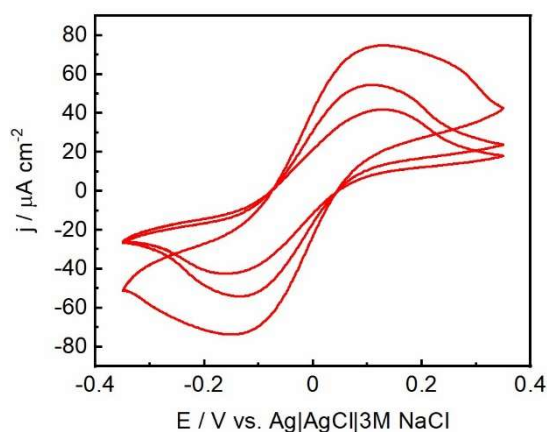


Figure 7-1. Cyclic voltammetry of three different ITO|ITONPs electrodes, prepared from ITONPs dispersion prepared from commercial powder, covered by 5 μl 10 mM DMFc in NPOE and 0.1 M HClO₄ aq., scan rate: 10 mV s⁻¹.

Therefore, commercial dispersion of ITONPs in isopropanol was finally employed in the further research. The stability of the dispersion was confirmed by the value of Zeta potential (ζ) equal 43.7 mV (Figure 7-2) and the size of nanoparticles 72 ± 29 nm was estimated by DLS (Figure 7-3).

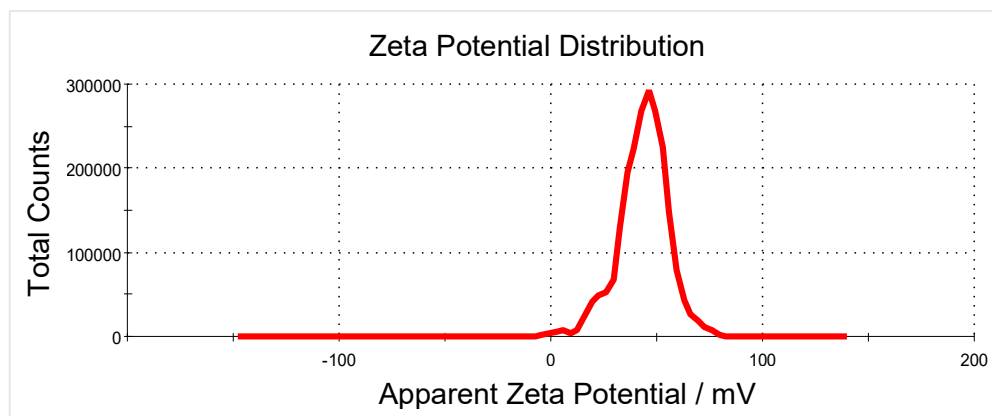


Figure 7-2. Zeta potential distribution in the ITONPs dispersion in isopropanol.

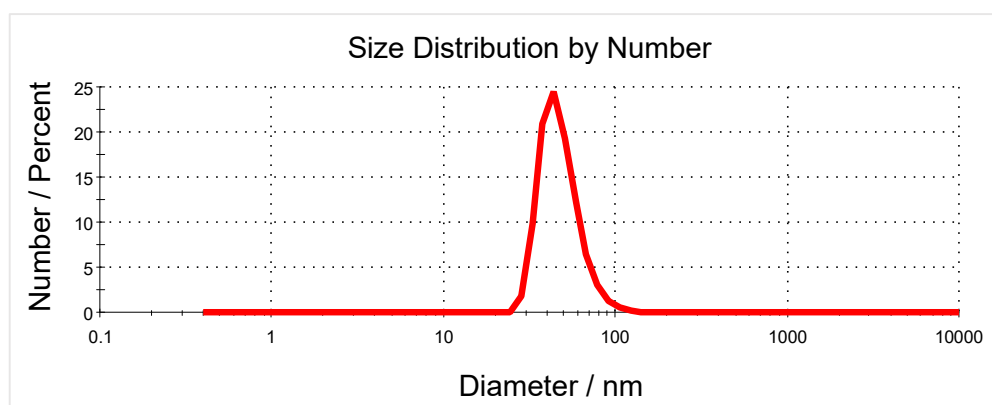


Figure 7-3. Size distribution of the ITONPs in dispersion in isopropanol.

The next step was the optimisation of the cell. When ITO electrode was fixed in vertical position, NPOE droplet was flowing down. When small amount of this viscous solvent was diluted with THF, deposited and evaporated, still liquid film was not stable enough to enable usage of vertical ITO electrode. Therefore, the electrode was fixed in horizontal position at the bottom of the SECM cell with three connected openings for other electrodes (Figure 7-4). Three other holes were for screws to assemble the cell and the seventh one was plugged. However, still the liquid film formed after evaporation of THF, did not allow to achieve reproducible electrochemical results (Figure 7-5), even though the conditions (evaporation time and usage of the same organic solution) were the same.



Figure 7-4. Photo of the electrochemical cell.

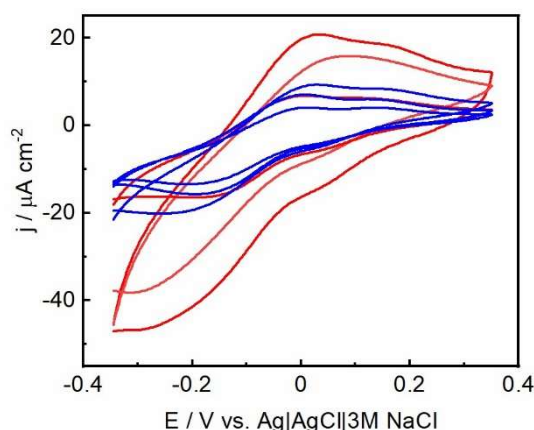


Figure 7-5. Cyclic voltammetry at three different ITO (blue) and three different ITO|ITONPs electrodes (red) with the layer of 10 mM DMFc in NPOE diluted in THF (after 1 h of evaporation) and 0.1 M HClO₄ aq., 10 mV s⁻¹.

Then, non-diluted organic droplet was deposited. The droplet of DMFc in NPOE solution (with THAP and later BATB) was placed on the ITO electrode fixed horizontally in the cell. For that micropipette tip was placed in the centre opening of the cell. Although NPOE and water has almost the same density (Table 7-1), liquid film was stable visually in the contact with aqueous solution and gave stable and reproducible electrochemical results (Figure 7-14). As aqueous phase, 0.1 M HClO₄ aq. was used to provide protons for ORR. Also hydrophobic ionic liquid C₄mimN(Tf)₂ was used as organic phase. The physicochemical properties of solvents used for biphasic system are summarised in the Table 7-1.

Table 7-1. Selected physicochemical properties of the solvents employed for biphasic reactions.

Solvent	Viscosity [mPa s]	Density [g cm ⁻³]	Static dielectric permittivity
Water	0.8903 (25 °C) [243]	0.99713 (25 °C) [244]	78.304 (25 °C) [245]
NPOE	16.9 (25 °C) [246]	1.04 (25 °C)	21 [247]
C ₄ mimN(Tf) ₂	27 [248] 59.8 (dried) 32 (water-saturated) [249]	1.43430 (25 °C) [250]	14.0±0.5 [251] 11.6 [252]

7.2 Characterisation of the electrodes

At first, ITO|ITONPs electrode and for comparison ITO electrode were characterised by SEM (Figure 7-6, Figure 7-7) and AFM (Figure 7-10). The ITO nanoparticles uniformly cover ITO electrode. From AFM images, the average diameter of nanoparticles and thickness of the nanoparticulate film were estimated as ~62 nm (Figure 7-11) and ~175 nm (Figure 7-8,

Figure 7-9), respectively. The thickness of the film is smaller than triple diameter of nanoparticles, perhaps due to the fact that during second and third immersion steps, the newly deposited nanoparticles fill the gaps between already immobilized nanoparticles. This also results in the decrease of roughness of the film to 11.6 nm.

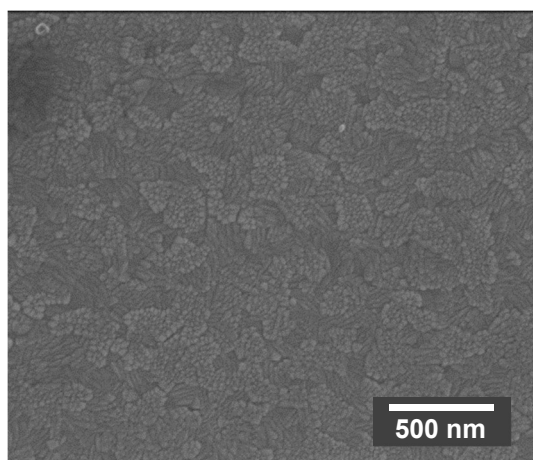


Figure 7-6. SEM image of ITO plate.

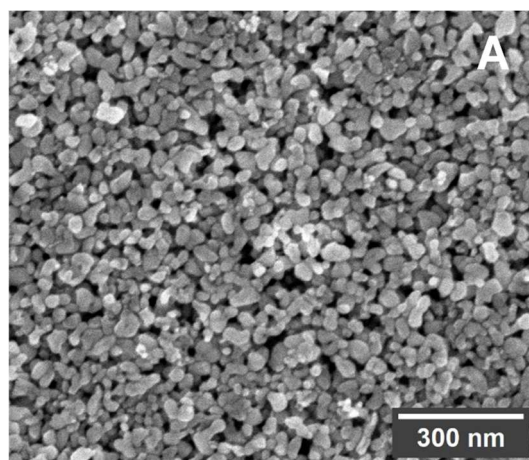


Figure 7-7. SEM image of ITO plate covered with ITO nanoparticles [59].

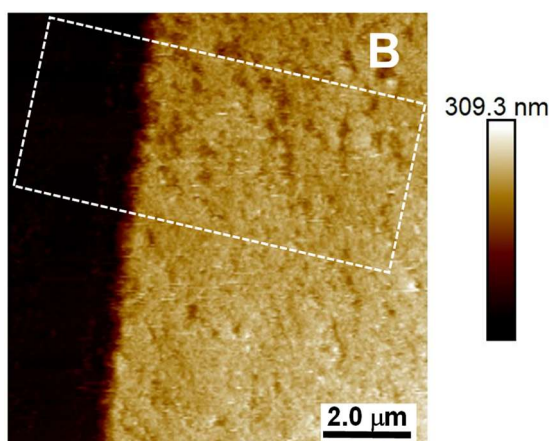


Figure 7-8. AFM image of the area of ITO plate covered with ITO nanoparticles, including the part where nanoparticles were scratched from the surface [59].

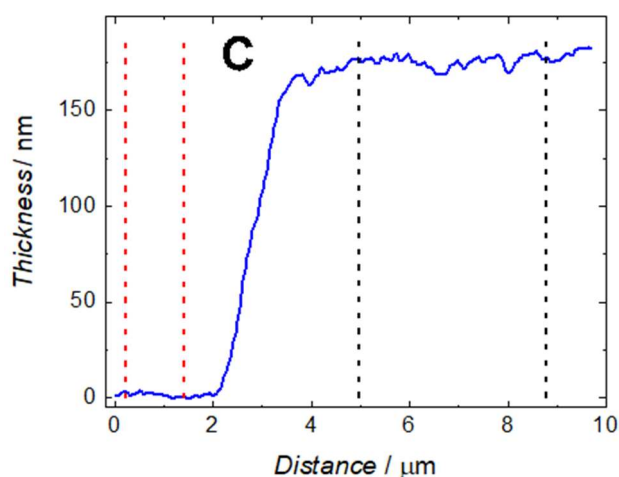


Figure 7-9. Average height profile measured for the area marked on Figure 7-8 as a white dashed line rectangle, dashed lines mark the area of the nanoparticulate film thickness measurements [59].

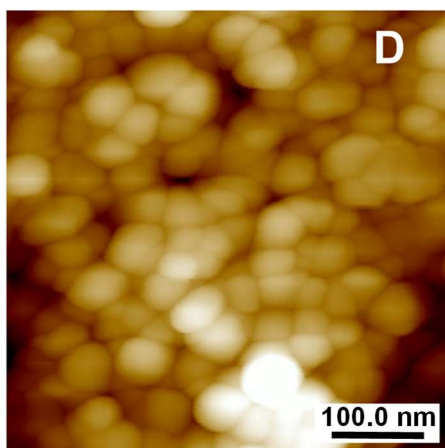


Figure 7-10. AFM image showing the topography of the nanoparticulate film [59].

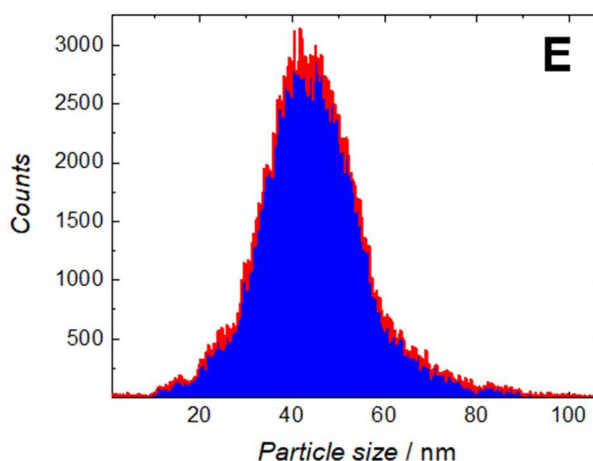


Figure 7-11. ITO nanoparticles size distribution obtained from AFM [59].

7.3 Electrochemical characterisation of ITO and ITO|ITONPs electrodes and electrochemical studies of the biphasic system

The next step was the examination of basic electrochemical properties of electrodes. For that, CV was performed with bare ITO and ITO|ITONPs electrodes in 0.1 M HClO_4 aq. (Figure 7-12 A). Then, only capacitive current was observed and its value is linearly dependent on the scan rate. For ITO|ITONPs electrode it was 5 times higher than for ITO due to the bigger electrode surface in contact with aqueous electrolyte. Next, the cyclic voltammetry in 1 mM ferrocenemethanol (FcOH) solution in 0.1 M HClO_4 aq. was performed (Figure 7-12 B). Modification with ITONPs resulted in slight increase of the peak current for faster scan rates comparing to the bare ITO as earlier observed [41]. Perhaps, heterogeneous electron transfer reaction occurs predominantly at the front of the nanoparticulate film, because the neighbouring nanoparticles share the same diffusion zone. This effect is different than capacitive current, which does not depend on the position of nanoparticle in the film.

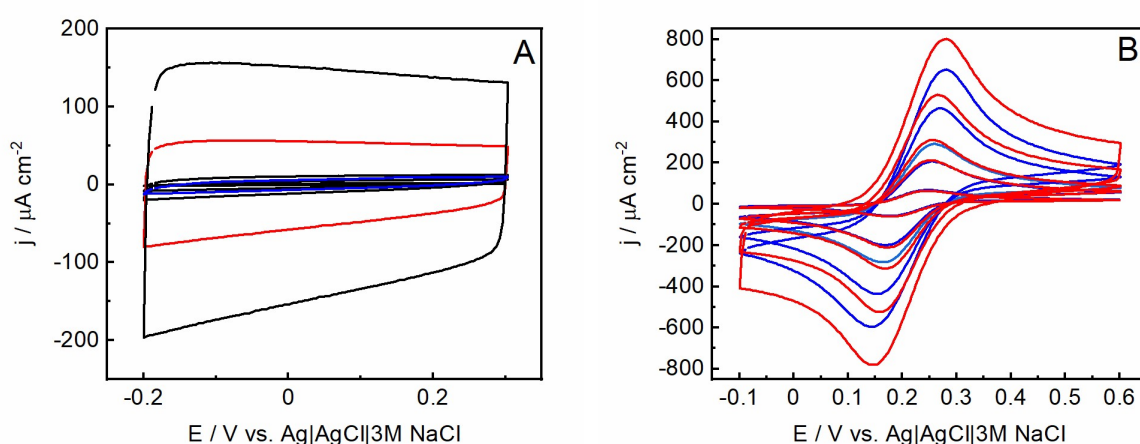


Figure 7-12. Cyclic voltammetry obtained in A) 0.1 M HClO_4 aq., for ITO|ITONPs electrode with scan rate (black): 10, 100, 200, 500 (red), 1000 mV s^{-1} and for ITO electrode at scan rate 500 mV s^{-1} (blue), B) 1 mM FcOH solution in aqueous 0.1 M HClO_4 aq. on ITO (blue) and ITO|ITONPs electrode (red), scan rates 10, 100, 200, 500 and 1000 mV s^{-1} [59].

The next step was the investigation of biphasic electrochemical process. ITO or ITO|ITONPs electrode were covered by 5 μl of organic solution (10 mM DMFc, 0.1 M THAP or 0.01 M BATB in NPOE or 5 mM DMFc in $\text{C}_4\text{mimN}(\text{Tf})_2$). Finally, 600 μl of 0.1 M HClO_4 aq. was added to the cell as a proton source to enable biphasic ORR. THAP and BATB were used to compare the effect of unfavourable and favourable interfacial potential for proton transfer across the liquid|liquid interface. The measurement's scheme is shown below (Figure 7-13). For cyclic voltammetry only WE1 was used as the working electrode.

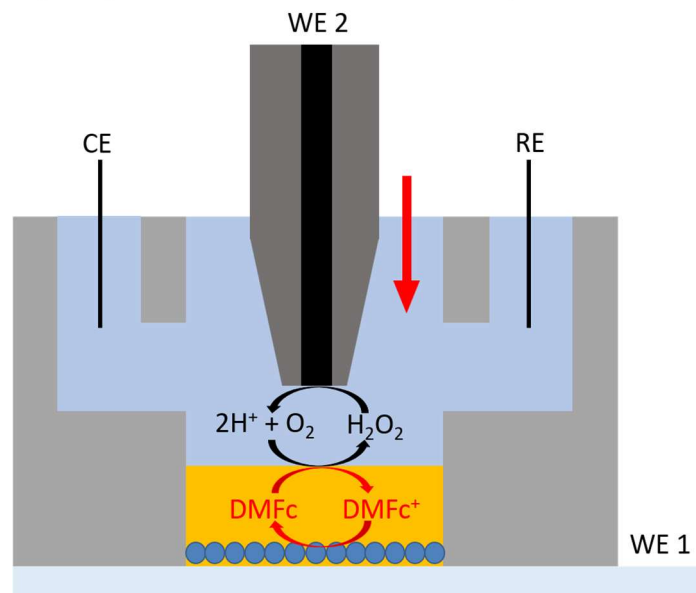


Figure 7-13. Scheme of the experimental setup (see text for explanation). WE1 - ITO or ITO|ITONPs electrode, WE2 – Pt UME, CE – Pt wire, RE – Ag|AgCl|3M NaCl or Ag wire. Red arrow shows direction of WE2 motion during SECM approach curve recording [59].

The electrochemical reproducibility of this system was much better than that of the other systems reported above (Figure 7-1, Figure 7-5). The CV curves obtained with these electrodes showed better similarity of the shape and peak current density value, especially with ITO|ITONPs electrodes (Figure 7-14).

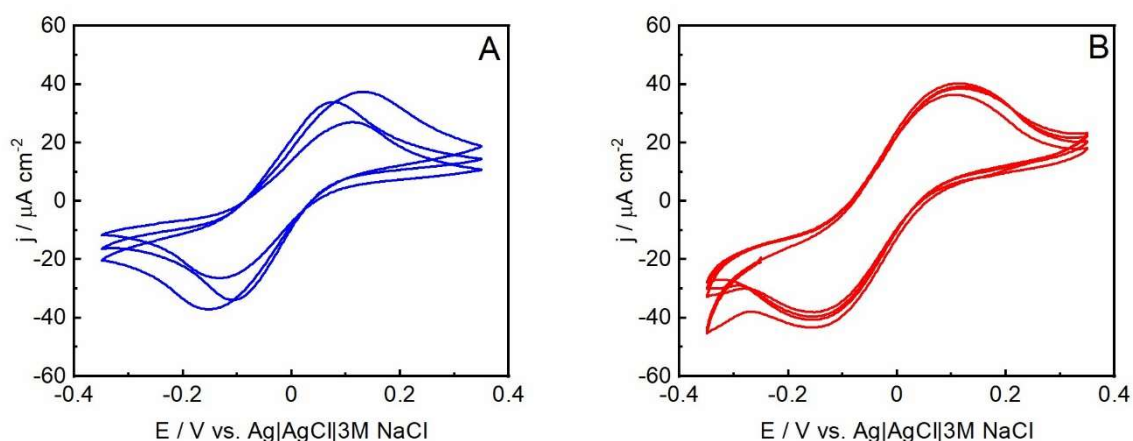
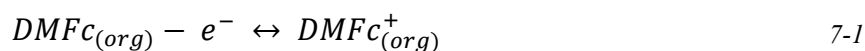


Figure 7-14. Cyclic voltammetry obtained for A) ITO and B) ITO|ITONPs electrode covered by 5 μl of 10 mM DMFc 0.1 M THAP in NPOE with 600 μl of 0.1 M HClO_4 aq. Scan rates: 10 mV s^{-1} . Results for three different electrodes.

Similar magnitude of anodic and cathodic peak currents results from the following reaction:



And such reversibility may be beneficial for biphasic ORR with electrochemical recycling [83], [82], [84]. Anodic peak current vs. the square root of scan rate dependences are linear (Figure 7-16, Figure 7-18, Figure 7-20) ($R^2 = 0.95$ for ITO|ITONPs electrode and $R^2 = 0.99$ for ITO electrode). This points that the distance between electrode|organic electrolyte interface and liquid|liquid interface is big enough to not confine diffusional space within the time scale of CV experiments. However, some differences in the shape of voltammograms and the magnitude of peak current are seen.

When ITO|ITONPs electrode was modified with DMFc and THAP solution in NPOE, the twofold increase of peak current comparing to the ITO electrode was noticed (Figure 7-15). When THAP was replaced by more hydrophobic BATB (Figure 7-17) or NPOE was replaced by $C_4mimN(Tf)_2$ as a solvent (Figure 7-19), this effect was not observed. This may be explained by better wetting of ITONPs by THAP electrolyte due to the hydrophilic nature of ITO nanoparticles. Furthermore, for BATB solution in NPOE, the CV peak currents were higher than for THAP solution. Importantly, the peak currents value in $C_4mimN(Tf)_2$ has twice lower value than for BATB solution due to the difference in redox probe concentration and larger viscosity of $C_4mimN(Tf)_2$ as compared to NPOE (Table 7-1). The redox potential of DMFc/DMFc⁺ couple in $C_4mimN(Tf)_2$ is lower by 0.25 V as compared to NPOE electrolytes, what is similar to earlier finding with CPE with the same organic phase as a binder [82] [84].

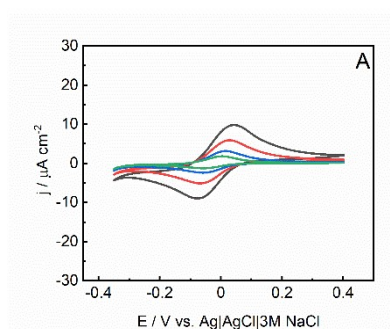
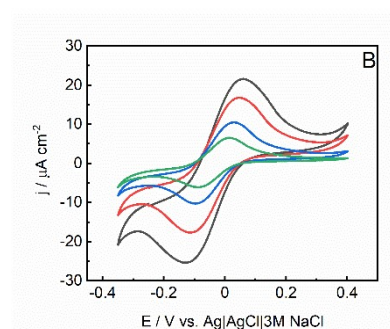


Figure 7-15. Cyclic voltammetry for ITO (A) and ITO|ITONPs electrodes (B) covered by 5 μ l of 10 mM DMFc 0.1 M THAP in NPOE with 600 μ l of 0.1 M $HClO_4$ aq. Scan rates: 1, 2, 5 and 10 $mV s^{-1}$ [59].

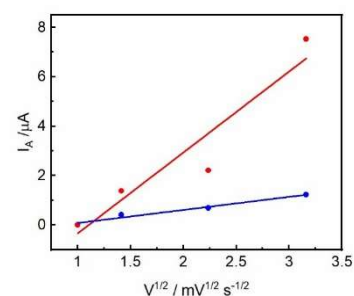


Figure 7-16. The anodic peak current dependence on the square root of scan rate for ITO|ITONPs electrode (red) and ITO electrode (blue) covered by 5 μ l of 10 mM DMFc 0.1 M THAP in NPOE with 600 μ l of 0.1 M $HClO_4$ aq. [59].

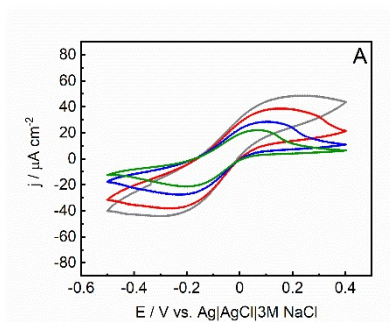
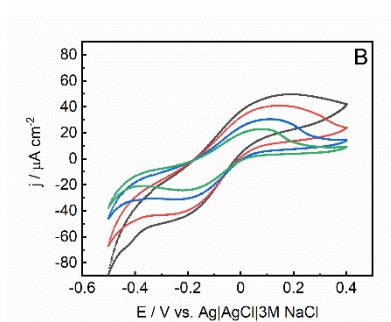


Figure 7-17. Cyclic voltammetry for ITO (A) and ITO|ITONPs electrodes (B) covered by 5 μl of 10 mM DMFc and 0.01 M BATB in NPOE with 600 μl of 0.1 M HClO_4 aq. Scan rates: 1, 2, 5 and 10 mV s^{-1} [59].

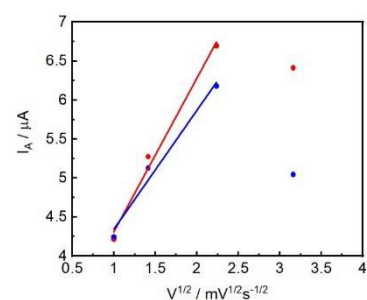


Figure 7-18. The anodic peak current dependence on the square root of scan rate for ITO|ITONPs electrode (red) and ITO electrode (blue) covered by 5 μl of 10 mM DMFc 0.01 M BATB in NPOE with 600 μl of 0.1 M HClO_4 aq.

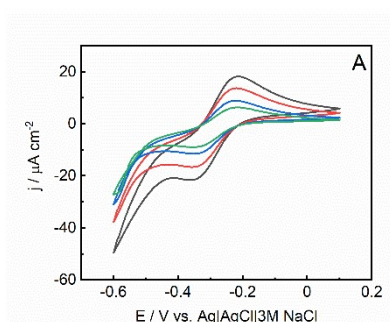
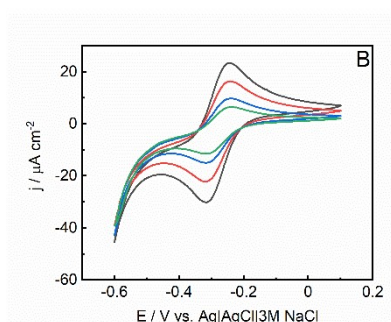


Figure 7-19. Cyclic voltammetry for ITO (A) and ITO|ITONPs electrode (B) covered by 5 μl of 5 mM DMFc in $\text{C}_4\text{mimN}(\text{Tf})_2$ and with 600 μl of 0.1 M HClO_4 aq. Scan rates: 1, 2, 5 and 10 mV s^{-1} [59].

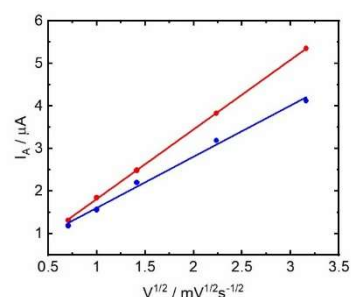


Figure 7-20. The anodic peak current dependence on the square root of scan rate for ITO|ITONPs electrode (red) and ITO electrode (blue) covered by 5 μl of 5 mM DMFc in $\text{C}_4\text{mimN}(\text{Tf})_2$ with 600 μl of 0.1 M HClO_4 aq.

It was also noticed that cathodic current (at potentials below reduction peak of DMFc^+) increased with the increase of HClO_4 aq. concentration from 0.01 M to 0.19 M (Figure 7-21 A B, Figure 7-22 A, B). This is related to proton transfer across the liquid|liquid interface. Such effect was not seen for neutral solution as aqueous phase (Figure 7-23), what confirms that it is connected to the presence of protons. Importantly, the shape of CV curves is also different than for acidic solution. Similar anodic current increase can be seen in earlier reports on the biphasic ORR with CPE modified with DMFc solution in NPOE or hydrophobic ionic liquid [82], [83], [84].

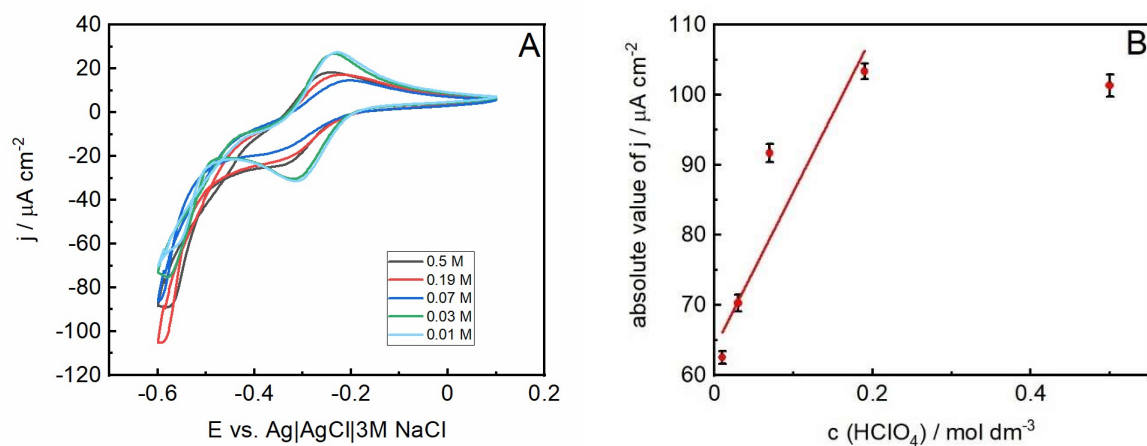


Figure 7-21. The effect of acid concentration on: A) cyclic voltammograms obtained for ITO|ITONPs electrode covered by 5 μl of 5 mM DMFc in $C_4\text{mimN}(\text{Tf})_2$ and 600 μl of 0.1 M HClO_4 aq. with scan rate 10 mV s^{-1} , B) absolute value of cathodic current density (at -0.6 V) vs. proton concentration [59].

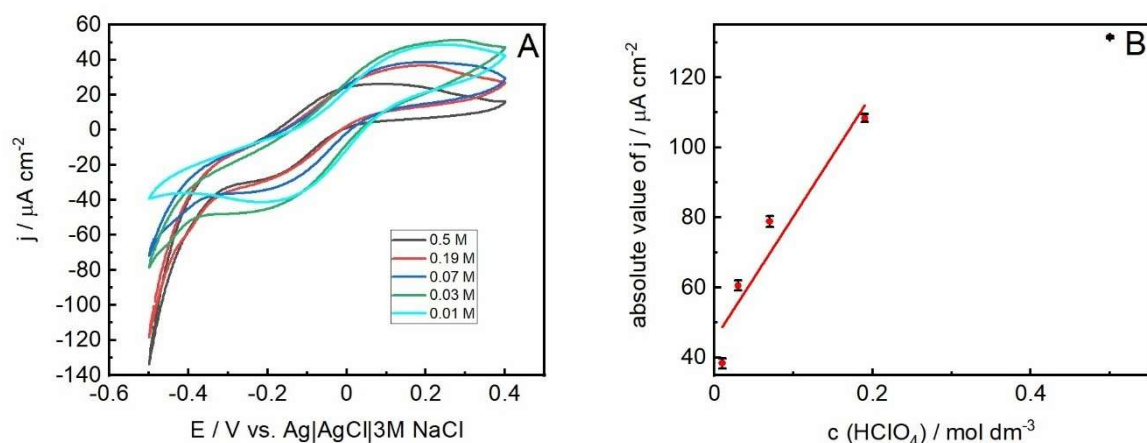


Figure 7-22. The effect of acid concentration on: A) cyclic voltammetry obtained for ITO|ITONPs electrode covered by 5 μl of 5 mM DMFc 0.01 M BATB in NPOE and 600 μl of 0.1 M HClO_4 aq. with scan rate 10 mV s^{-1} , B) anodic current density (at -0.5 V) vs. proton concentration.

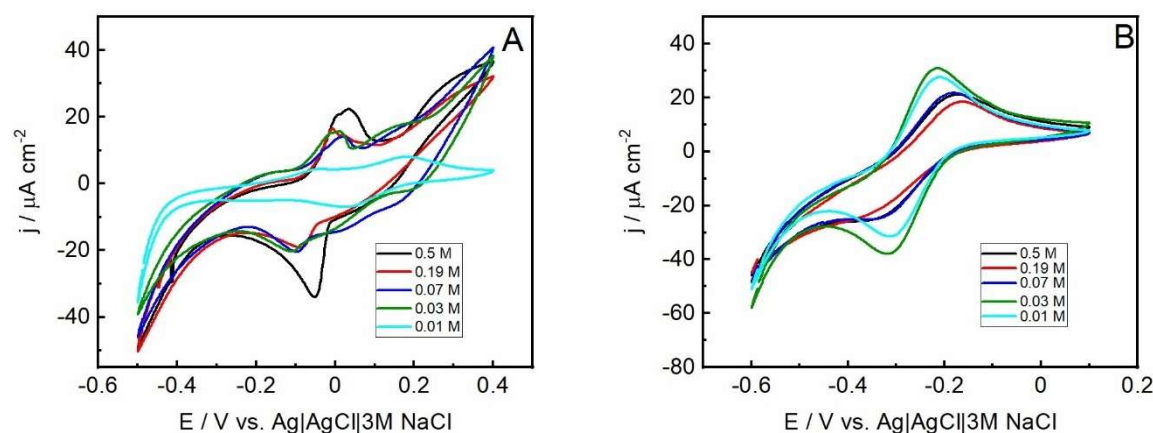


Figure 7-23. The effect of KCl concentration on cyclic voltammetry obtained for ITO|ITONPs electrode covered by A) 5 μl of 5 mM DMFc 0.01 M BATB in NPOE or B) 5 μl of 5 mM DMFc in $C_4\text{mimN}(\text{Tf})_2$ and 600 μl of 0.1 M HClO_4 aq. with scan rate 10 mV s^{-1} .

The effect of increasing cathodic current (for potentials -0.5/-0.6 V) was also visible, when only 1 μl of organic phase was deposited (Figure 7-24). The observed peak current density for DMFc oxidation/reduction was 5 times lower than for 5 times bigger volume of organic phase. This may result from partial coverage of ITO electrode by the organic solution.

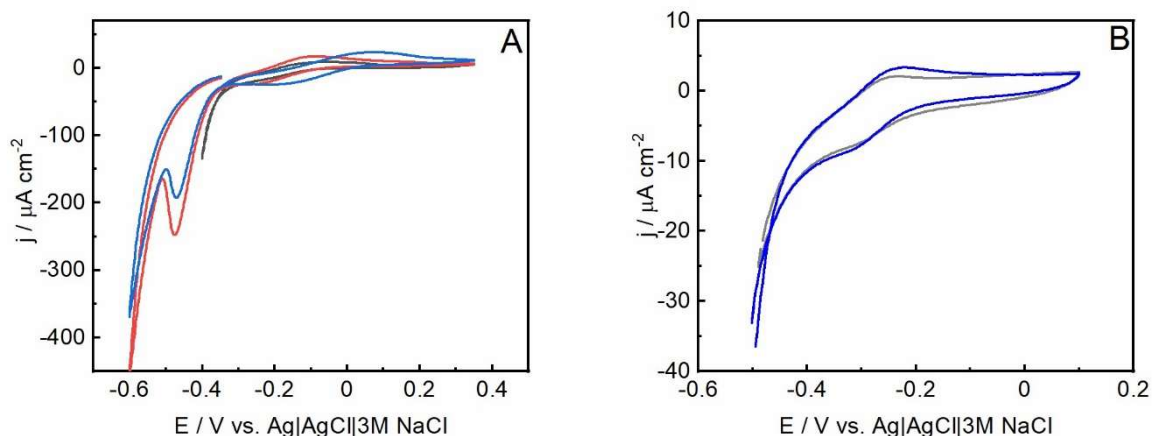


Figure 7-24. Cyclic voltammetry for ITO covered by 1 μl of A) 10 mM DMFc 0.01 M BATB in NPOE or B) 5 mM DMFc in $\text{C}_4\text{mimN}(\text{Tf})_2$ with 600 μl of 0.1 M HClO_4 aq. Scan rate: 10 mV s^{-1} , CV's of different colours were obtained at different modified electrodes.

Chronoamperometric experiments confirm the effect of limited volume of organic phase or in other words limited distance between electrode|organic phase and liquid|liquid interface. The logarithmic dependence of the current density vs. time is far from linear with a slope of -0.5 expected for semi-infinite diffusion (Figure 7-25). Its slope gradually decreases from short to long times. As heterogeneous electron transfer (7-1) is fast, because of solvent dynamics control [253], [254], the weak dependence of current on time seen below 1 s may indicate that electrode reaction rate is controlled by the kinetics of ion transfer across the liquid|liquid interface [255], [256]. After approximately 200 s slope of logarithmic j vs. t plot decreases below -0.5 due to the exhaustive electrolysis of DMFc in the liquid organic film. The diffusion coefficient of DMFc in $\text{C}_4\text{mimN}(\text{Tf})_2$ was calculated from the Stokes-Einstein equation [257], assuming DMFc radius as 0.48 nm [258], equal $1.4 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Using random walk equation, it was estimated that the redox probe concentration gradient reaches the liquid|liquid interface after c.a. 2200 s. Such discrepancy and lack of rapid current decrease may result from the meniscus formed at the liquid|liquid interface, what is seen by the naked eye from the top of the cell. Additional contribution of convective current may be the other reason that the current decreases at longer distances than expected.

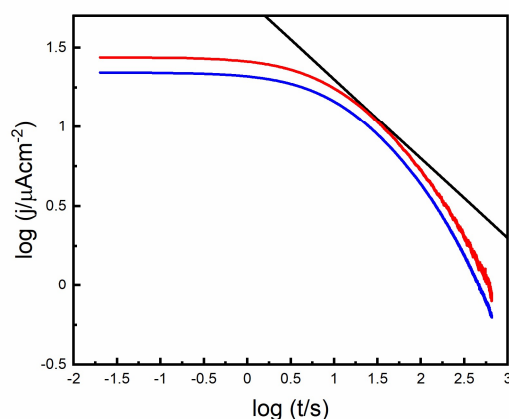


Figure 7-25. Logarithmic dependence of current vs. time obtained with ITO (blue) and ITO|ITONPs electrode (red) after the potential step from -0.6 V to 0.1 V with 5 mM DMFc in $C_{4}mimN(Tf)_2$. The slope of black line is -0.5 [59].

After the oxidation of DMFc molecules, the same number of ions must be transferred across the ITIES to compensate the charge appearing in organic phase. In order to detect the direction of ion transfer after the oxidation of DMFc (7-1) (either anion insertion into organic phase or cation ejection from organic phase), the DMFc/DMFc⁺ redox potential dependence on the aqueous electrolyte concentration was examined. For that, SWV measurements in hydrophobic ClO₄⁻ and hydrophilic Cl⁻ were performed. It was observed that SWV peak potential depends on the HClO₄ aq. concentration (Figure 7-26 A), whereas the analogous effect of KCl aq. concentration was not much seen (Figure 7-26 B).

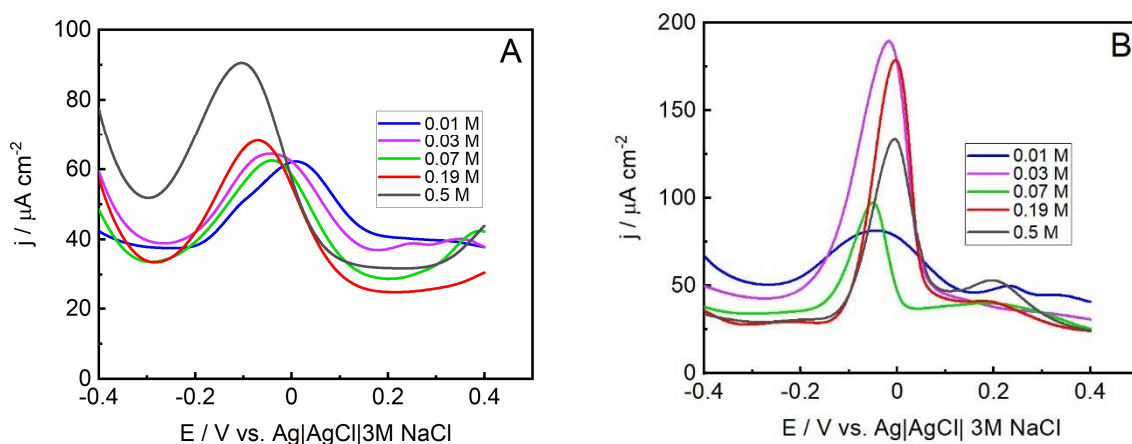
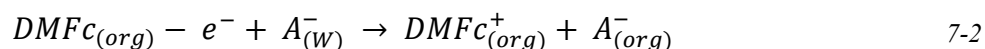


Figure 7-26. SWV curves recorded with ITO electrode covered by 5 μ l of 5 mM DMFc in 0.01 M BATB solution in NPOE and 600 μ l of HClO₄ aq. (A) and KCl (B) aqueous solution of different concentrations (marked on the figure). Step potential: 1 mV, frequency: 8 Hz, amplitude: 50 mV [59].

If anion is inserted into the organic phase, the reaction can be written as follows:



The anion concentration in the aqueous phase vs. SWV peak potential (E_p) dependence (Figure 7-27) can be interpreted in the context of the third term of the right side of the following Nernst type equation [259]:

$$E_p = E_{\text{DMFc}^{0/+}}^0 + \Delta_W^{\text{org}} \phi_{\text{An}^-}^0 - \frac{RT}{F} \ln c_{\text{An}^-}(\text{w}) + \frac{RT}{F} \ln \frac{c_{\text{DMFc}(\text{org})}^*}{2} \quad 7-3$$

where $E_{\text{DMFc}^{0/+}}^0$ - a redox potential of DMFc/DMFc⁺ couple in NPOE or C₄mimN(Tf)₂ and $c_{\text{DMFc}(\text{org})}^*$ - a bulk concentration of DMFc in organic phase and $(\Delta_W^{\text{org}} \phi_{\text{An}^-}^0)$ - the value of anion transfer potential across the liquid|liquid interface. Therefore, when reaction (7-2) occurs, E_p vs. $\ln c_{\text{An}^-}(\text{w})$ dependence should be linear with Nernstian slope.

For both 0.1 M THAP and 0.01 M BATB solutions in NPOE in contact with HClO₄ aqueous solution, the linear slope around -44 mV dec⁻¹ ($R^2 = 0.96$) (Figure 7-27 A red and orange dots) and -48 mV dec⁻¹ ($R^2 = 0.99$) (Figure 7-27 B red and orange dots) was evaluated, which is below 59 mV dec⁻¹ expected from equation (1-3). For electrode in contact with KCl aqueous solution, the lack of monotonic dependence was observed (Figure 7-27 blue dots).

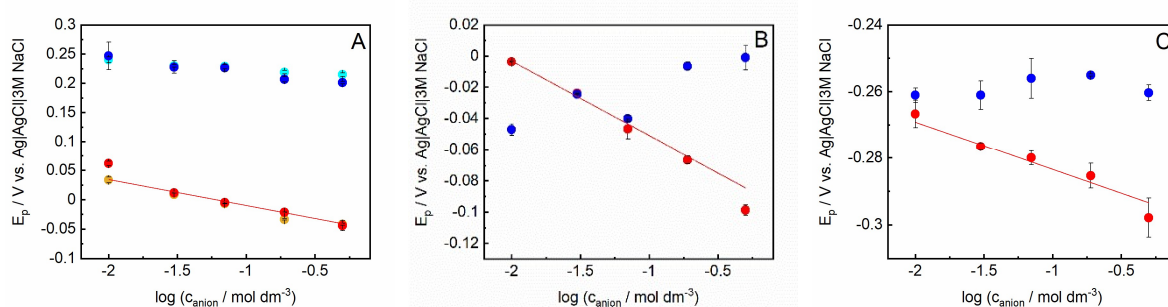
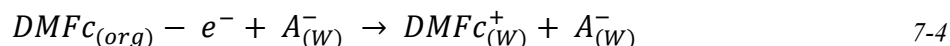
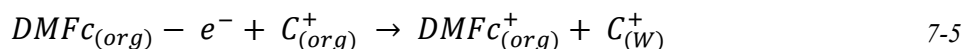


Figure 7-27. SWV peak potential dependence on logarithm of concentration of HClO₄ aq. (ITO|ITONPs - red and ITO - orange) and KCl (ITO|ITONPs - dark blue and ITO - light blue) for biphasic system containing: (A) 10 mM DMFc and 0.1 M THAP in NPOE, (B) 10 mM DMFc 0.01 M BATB in NPOE and (C) 5 mM DMFc in C₄mimN(Tf)₂ as organic phase [59].

Therefore, one may conclude that mainly ClO₄⁻ anion insertion to the organic phase follows the DMFc oxidation (7-4). On the other hand, DMFc⁺ or electrolyte cations as C₄mim⁺, THA⁺ or BA⁺ are ejected to KCl aqueous solution (7-5).



When hydrophobic organic ionic liquid was used as the organic phase, even when HClO₄ solution was employed as aqueous phase, the slope of the dependence E_p vs. c_{anion} was far from Nernstian, namely -14 mV dec⁻¹ ($R^2 = 0.93$). This means that even in the presence of as hydrophobic anion as ClO₄⁻ in the aqueous phase, the cation (C₄mim⁺ or DMFc⁺) is ejected to the aqueous phase (7-4, 7-5) after the oxidation of DMFc [84].

7.4 Hydrogen peroxide detection at NPOE|H₂O and C₄mimN(Tf)₂|H₂O interfaces in the biphasic system on ITO electrode using scanning electrochemical microscopy

In order to detect H₂O₂ generated by biphasic ORR, SECM was applied. For this purpose, cyclic voltammograms were recorded at the Pt UME at different distances from the sample

(Figure 7-28). In some experiments, potential (-0.2 V) was applied to ITO or ITO|ITONPs electrode to enable electrochemical regeneration of electron donor DMFc (see Figure 7-13).

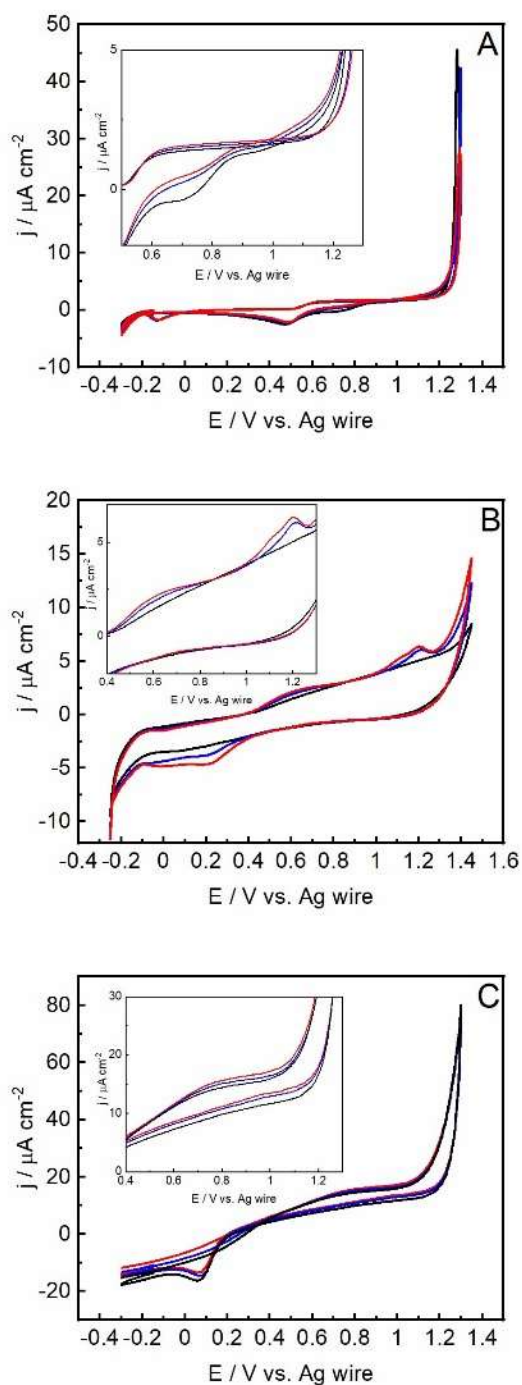


Figure 7-28. Cyclic voltammetry obtained at Pt UME)) recorded in 0.1 M HClO_4 aq. for ITO|ITONPs electrode with regeneration of electron donor at different distance from the interface: A) next to the interface (red), 269.3 μm (blue) and 763 μm (black) from the liquid|liquid interface, The composition of the organic phase: 10 mM DMFc 0.1 M THAP in NPOE, B) next to the interface (red), 290.1 μm (blue) and 780.1 μm (black) from the liquid|liquid interface, The composition of the organic phase: 10 mM DMFc 0.01 M BATB in NPOE, C) next to the interface (red), 294 μm (blue) and 798 μm (black) from the liquid|liquid interface, The composition of the organic phase: 5 mM DMFc in $C_4\text{mimN}(\text{Tf})_2$.

The anodic plateau seen at voltammograms in potential range 0.6 - 1.0 V can be attributed to the electrooxidation of H_2O_2 . For each CV, the average current at potential range 0.8 - 0.9 V

was estimated. Then it was plotted vs. distance of the tip from the electrode surface with liquid|liquid interface chosen as point zero. The latter was selected as point where the current related to electrooxidation of H_2O_2 has the largest value. Then, from the given value of the current (Figure 7-29), hydrogen peroxide concentration was calculated:

$$c_{H_2O_2} = \frac{i}{4nFD_{H_2O_2}r} \quad 7-6$$

where i - the current on the UME [A], $D_{H_2O_2}$ - H_2O_2 diffusion coefficient in H_2O (here $8.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ [260]), n - the number of electrons (here 2) and r - the radius of SECM tip [μm] [221] (here $12.5 \mu\text{m}$).

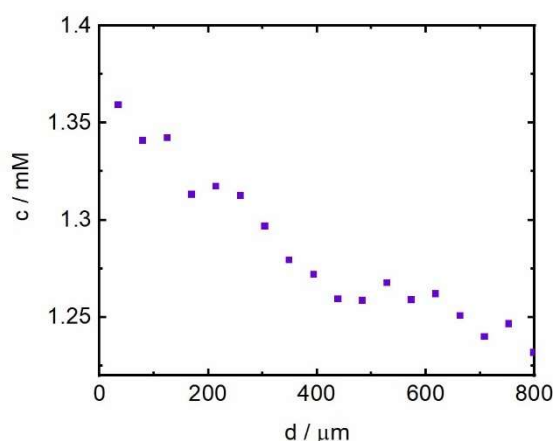


Figure 7-29. Approach curves (H_2O_2 concentration (c) vs. distance (d)) recorded in $0.1 \text{ M HClO}_4 \text{ aq.}$ (A) for ITO|ITONPs electrode with regeneration of electron donor. The composition of the organic phase: 5 mM DMFc in $C_4\text{mimN}(\text{Tf})_2$.

In order to compare obtained approach curves obtained for different systems the current was normalised to its lowest value from all experiments. At first, the lowest current value for each sample separately was set as 0 and the other values were recalculated. Then, current values for samples were compared. The highest current value was set as 1 and all the others values were recalculated to be in the range 0 - 1. Here, the highest current value was obtained for ITO|ITONPs electrode with regeneration of electron donor with 5 mM DMFc in $C_4\text{mimN}(\text{Tf})_2$.

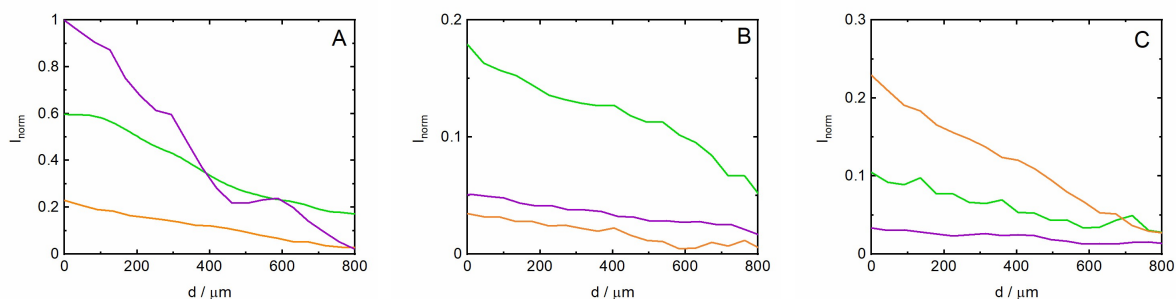


Figure 7-30. Approach curves (normalized current (I_{norm}) vs. distance (d)) recorded in $0.1 \text{ M HClO}_4 \text{ aq.}$ (A) for ITO|ITONPs electrode with regeneration of electron donor; (B) for bare ITO electrode with regeneration of electron donor and (C) for ITO|ITONPs electrode without regeneration of electron donor. The composition of the organic phase: 5 mM DMFc in $C_4\text{mimN}(\text{Tf})_2$ (purple), 10 mM DMFc and 0.01 M BATB in NPOE (green) and 10 mM DMFc 0.1 M THAP in NPOE (orange) [59].

From the linear part of the plot of concentration vs. distance, the slope was determined and the flux of H_2O_2 was estimated using Fick's first law:

$$J_{H_2O_2} = -D_{H_2O_2} \frac{\delta c_{H_2O_2}}{\delta x} \quad 7-7$$

The hydrogen peroxide flux values for different samples are shown in the Table 7-2. One can see that electrochemical recycling of electron donor allowed to increase its value, approximately by one order of magnitude for ITO|ITONPs electrode covered by DMFc and BATB solution in NPOE or DMFc solution in $C_4mimN(Tf)_2$. Such effect was observed earlier for CPE with NPOE (0.5 and 13 $\mu mol\ cm^{-2}\ s^{-1}$ without and with electrochemical regeneration [82]) or in $C_4mimN(Tf)_2$ (4.3 and 32.4 $\mu mol\ cm^{-2}\ s^{-1}$ without and with electrochemical regeneration [83]). It demonstrates that the distance between electrode|electrolyte interface and liquid|liquid interface is short enough for efficient transport of electron donor between two interfaces. The presence of nanoparticulate film also increases the reaction efficiency, although it was not visible at the voltammograms (Figure 7-17, Figure 7-19). Therefore, it can be concluded that the efficiency of electroreduction of $DMFc^+$ is controlled by electrode surface area.

Table 7-2. H_2O_2 flux values at the liquid|liquid interface for all systems studied [$\mu mol\ cm^{-2}\ s^{-1}$].

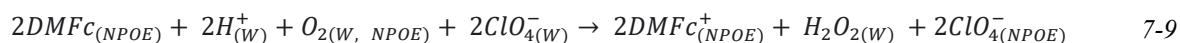
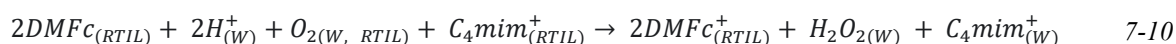
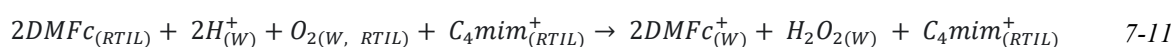
Organic phase Electrode	10 mM DMFc, 0.1 M THAP in NPOE	10 mM DMFc, 0.01 M BATB in NPOE	5 mM DMFc in $C_4mimN(Tf)_2$
ITO electrode with regeneration	0.4 ± 0.04	2.1 ± 0.4	0.9 ± 0.3
ITO ITONPs electrode with regeneration	2.7 ± 0.1	24.1 ± 2	12.9 ± 5.4
ITO ITONPs electrode without regeneration	4.0 ± 1.3	5.2 ± 3.5	1.2 ± 0.7

Moreover, the type of electrolyte influences H_2O_2 flux magnitude. For electrode modified with BATB solution in NPOE, $J_{H_2O_2}$ value was higher than for the electrode modified with THAP solution in the same solvent. On the other hand, replacement of NPOE by ionic liquid resulted in comparable fluxes, considering twice lower concentration of DMFc in $C_4mimN(Tf)_2$ solution. The influence of the type of electrolyte in NPOE on the H_2O_2 flux can be explained by the unfavourable potential drop for proton transfer across the liquid|liquid interface created by the presence of common ion in both phases [132]. When THAP is used as electrolyte in NPOE, the Galvani potential can be calculated from the following equation:

$$\Delta_W^{DCE} \varphi = \Delta_W^{NPOE} \varphi_{ClO_4^-}^\circ + \frac{RT}{F} \ln \frac{a_{ClO_4^-(NPOE)}}{a_{ClO_4^-(W)}} \quad 7-8$$

where: $\Delta\phi_{\text{W}}^{\text{NPOE}}(\text{ClO}_4^-) = 0.175 \text{ V}$ [261] [262] with assumption that activity of anions in both phases is equal their concentration. This is much higher than the value of proton transfer potential $\Delta\phi_{\text{W}}^{\text{NPOE}}(\text{H}^+) = -0.458 \text{ V}$ [261], what makes proton transfer across the NPOE|W interface unfavourable. This explains smaller flux of H_2O_2 with THAP as electrolyte in NPOE as compared to BATB supported solvent. The similar effect of the electrolyte is also visible for the situation with regeneration of electron donor.

Considering the earlier discussed mechanism of ion transfer following oxidation of electron donor (see above), the whole biphasic reaction can be described by following equations:



7.5 Hydrogen evolution reaction at NPOE|H₂O interface - flasks experiments

The next step of the research was applying similar setup for biphasic HER studies in anaerobic conditions. BATB solution in NPOE or $\text{C}_4\text{mimN}(\text{Tf})_2$ was used as organic phase. When first organic phase was employed, LiTB was added to 0.1 M HClO_4 aqueous solution to promote proton transfer across liquid|liquid interface. Experiments were done in the glove box filled by argon to avoid influence of biphasic ORR (see above). Firstly, to check whether biphasic HER occurs at NPOE|H₂O interfaces with DMFc as electron donor, the flask tests have been performed. For that, the same volume of each phase was poured into the flask and it was left in anaerobic conditions for certain time with stirring. Next, the clear organic phase colour changed from yellow to green was observed indicating DMFc^+ formation (Figure 7-31).

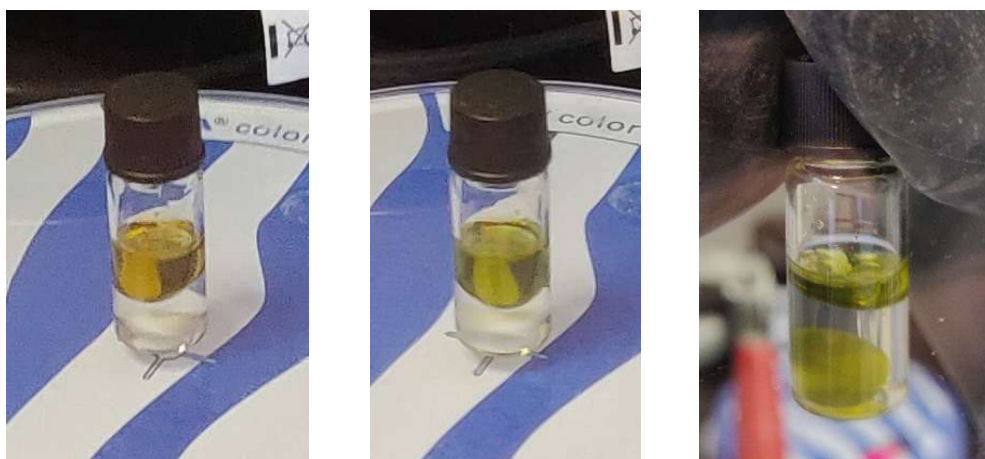
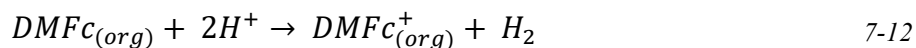


Figure 7-31. The picture of biphasic system consisting of 5 mM LiTB in 0.1 M HClO_4 aq. and 5 mM DMFc 5 mM BATB in NPOE, with stirring 500 rpm, picture immediately after connecting phases together (left), after 5 min of stirring (middle), after 10 min of stirring (right), in glove box.

DMFc solution in $\text{C}_4\text{mimN}(\text{Tf})_2$ in anaerobic condition was yellow (different than in the air atmosphere). However, after addition of 5 mM LiTB in 0.1 M HClO_4 , the colour of organic phase changed into green after two days due to oxidation of DMFc (7-1). Due to the visible

oxidation of DMFc, it can be concluded that hydrogen evolution reaction occurred in this biphasic setup regarding the reaction [176]:

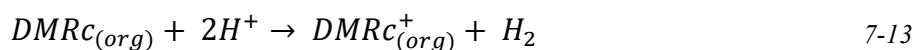


Next, DMFc was replaced by another electron donor - DMRC in NPOE. In the presence of light, the colour changed from light brown to brownish-red colour indicating formation of DMRC⁺ cations in NPOE (Figure 7-32), similarly as it was observed for DCE|H₂O system [179].



Figure 7-32. The picture of biphasic system consisting of 5 mM LiTB in 0.1 M HClO₄ aq. and 5 mM DMRC 5 mM BATB in NPOE, with stirring 500 rpm, picture was taken after the weekend of employing UV light (left flask), after the weekend without light (right flask), in glove box.

As there is no other molecule/ion present in the system, it can be concluded that HER occurs also at NPOE|H₂O interface according to the following mechanism [180]:



7.6 Attempts to detect hydrogen generated at NPOE|H₂O interface

Next, the electrochemical experiments focused on hydrogen detection were performed. For that, Teflon[®] SECM cell was placed in the glove box and UV light was applied from the bottom of the cell (Figure 7-33).

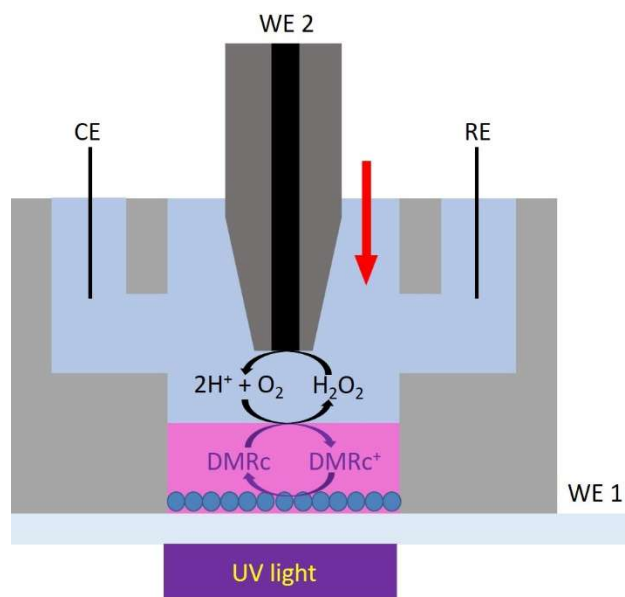


Figure 7-33. Scheme of the experimental setup with DMFc as electron donor. WE1 - ITO or ITO/ITONPs electrode, WE2 – Pt UME, CE – Pt wire, RE – Ag|AgCl|3M NaCl or Ag wire. Red arrow shows direction of WE2 motion during recording of SECM approach curve.

As a blank, BATB solution NPOE without electron donor was used as organic phase. The CV's were recorded with Pt UME positioned at different distance from the liquid|liquid interface (Figure 7-34). When Pt UME was moved closer to the interface, the increase in hydrogen oxidation current was observed. However, for the closest distance to the liquid|liquid interface, the current value slightly decreased. This experiment was done to allow comparison of further systems containing electron donor with this blank one.

Next, CV's of biphasic system with DMFc and BATB solution in NPOE were recorded. Then, higher anodic peak current at potential c.a. -0.25 V than in blank experiment described above, which confirms the HER at the interface NPOE/H₂O. Importantly, the peak current measured 30 minutes after the cell was filled, was larger than immediately after filling the cell.

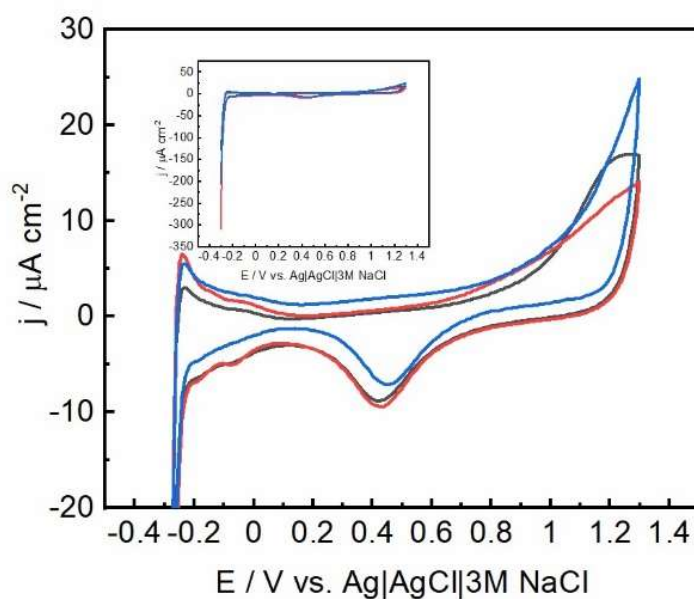


Figure 7-34. CV curves obtained at Pt UME recorded at different distance from the interface, grey (the furthest), red (closer), blue (the closest) in 5 mM LiTB in 0.1 M HClO₄ aq. for ITO electrode. The composition of the organic phase: 0.01 M BATB in NPOE.

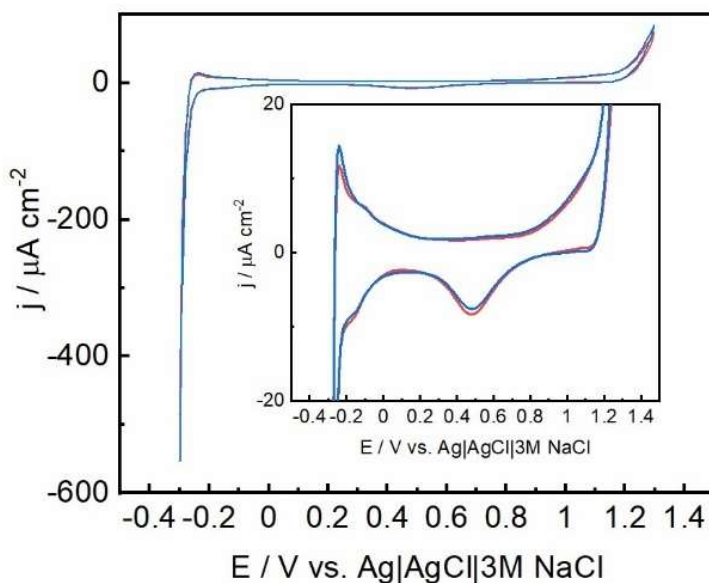
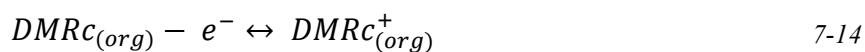


Figure 7-35. CV curves obtained at Pt UME recorded immediately (red) and after 30 min of biphasic reaction (blue) in 5 mM LiTB in 0.1 M HClO₄ aq. for ITO electrode. The composition of the organic phase: 5 mM DMFc and 0.01 M BATB in NPOE.

Next experiments were done with DMFc as electron donor under UV light to allow its excitation [263] (Chapter 5.2). The obtained voltammogram (Figure 7-36) exhibits features characteristic of DMFc oxidation/reduction:



As reaction is fast, so the significant peak potentials difference does not come from kinetics of heterogenic electron transfer [263].

Then, CV was recorded using Pt UME in front of the liquid|liquid interface with exposure to UV light (Figure 7-37). After 15 to 45 min, the increase of anodic current at potentials -0.2 - 0.0 V was observed. Moreover, the highest current was obtained when -0.2 V potential was applied to ITO electrode. These are signs of biphasic H_2 photogeneration, which is enhanced by electrochemical recycling of DMFc. Interestingly, H_2 oxidation current is much higher than that obtained with DMFc as electron donor. In these experiments long time was required to obtain oxygen free atmosphere, especially to get rid of the oxygen absorbed in Teflon[®]. Perhaps, it was difficult to get reproducible results, because of the biphasic reduction of traces of oxygen.

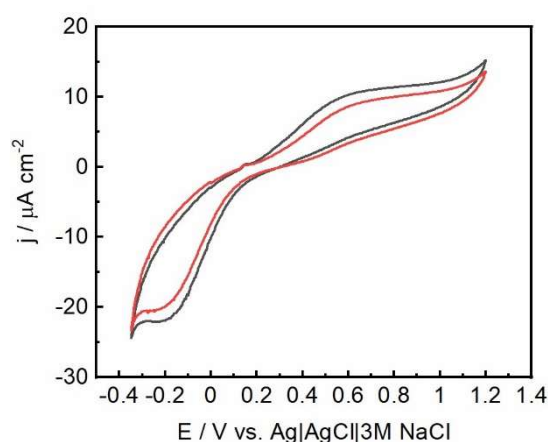


Figure 7-36. CV curves obtained in 5 mM LiTB in 0.1 M $HClO_4$ aq. for ITO electrode. The composition of the organic phase: 5 mM DMFc 0.01 M BATB in NPOE. The comparison of curve without light (red) and with UV light (black).

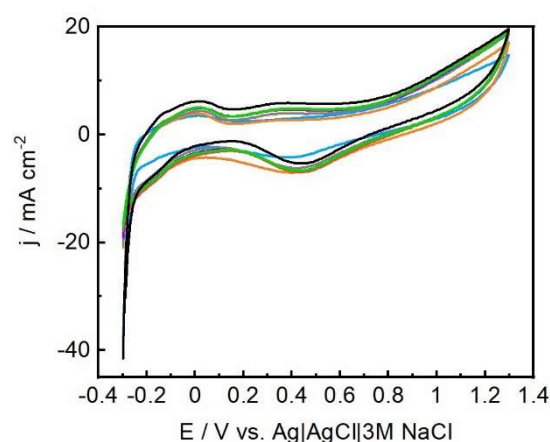


Figure 7-37. CV curves obtained at Pt UME recorded in 5 mM LiTB in 0.1 M $HClO_4$ aq. for ITO electrode. The composition of the organic phase: 5 mM DMFc 0.01 M BATB in NPOE. CV taken after 15 min (blue), after 45 min (green), after 1 h (orange), after 1 h 10 min of exposition to UV light and -0.2 V applied to ITO electrode (black).

7.7 Conclusions:

- Oxygen reduction reaction occurs at the interfaces ITO|NPOE(THAP)| H_2O , ITO|NPOE(BATB)| H_2O , ITO| $C_4mimN(Tf)_2$ | H_2O with and without the electrochemical recycling of DMFc in biphasic system with reduced volume of organic phase.
- The values of flux of H_2O_2 are comparable to the one for the CPEs with NPOE [82] and $C_4mimN(Tf)_2$ [83], [84] as binder for CPEs.
- The modification of the electrode with ITO nanoparticulate film increases hydrogen peroxide flux in the employed setup.
- Electrochemical recycling results in the increase of the flux of generated hydrogen peroxide.
- H_2O_2 flux is higher for BATB solution in NPOE and $C_4mimN(Tf)_2$ as compared to THAP solution in NPOE due to the favourable proton transfer [132].
- The effect of the direction of ion transfer generated by redox reaction in the organic phase is not seen [84], when one compares experiments performed with electrolyte solution in molecular solvent and with hydrophobic ionic liquid of similar viscosity.

- The reactions at ITO|NPOE(THAP)|H₂O, ITO|NPOE(BATB)|H₂O, ITO|C₄mimN(Tf)₂|H₂O interfaces can be called electrocatalytic [269].
- Some indications of biphasic photogeneration of H₂ at NPOE|H₂O interface with reduced volume of organic phase were spotted, but this requires further studies.

8 Oxygen reduction reaction at vegetable oil|H₂O interface with electrochemical recycling of electron donor

8.1 General characterisation of the properties of used oils and vegetable oil|H₂O interface

So far, in almost all studies of biphasic ORR polar solvents or ionic liquids were used [25]. However, the recent study demonstrating ion transfer across nonpolar liquid|H₂O interface with avocado, coconut and walnut oils as organic phase [38] motivated us to apply true oils as solvents for biphasic reactions. As vegetable oils are highly hydrophobic and their viscosity is much higher than that of water, we followed methodology earlier applied to ORR studies at NPOE|H₂O [82] or hydrophobic ionic liquid|H₂O [83] [84] interfaces. Vegetable oils have been already applied as a binders in CPE for different purpose [256]. Here, cheap and easily available vegetables oils: rapeseed (RO), sunflower (SO) and linen (LO) were used. The preparation of CPE was described in details in the experimental part (Chapter 6.5.3).

In all experiments 5 mM DMFc solution in vegetable oil was used as CPE binder. Employed oil samples consist of the triglycerides of unsaturated fatty acids, mostly cis-9-oleic, linoleic and linolenic acid [264], [265], [266], [267] as determined by gas chromatography (Table 8-1) [264]:

Table 8-1. Composition of rapeseed oil sample calculated from GC peak area after methylation [264].

Fatty acid	% content in rapeseed oil	% content in sunflower oil	% content in linen oil
palmitic	4.73	6.30	5.81
stearic	1.81	3.25	4.61
cis-9-oleic	62.13	30.27	20.68
unknown	2.89	0.69	0.67
linoleic	18.55	58.49	15.32
linolenic	7.47		52.92
arachidic	0.62		
cis-11-eicosenoic	1.3		
behenic	0.33	0.73	
lignoceric	0.16	0.27	

DMFc solution in cis-9-oleic acid was used for comparison due to its high content in each oil. After dissolving DMFc in cis-9-oleic acid, the solution turned green (Figure 8-1), which confirms at least partial oxidation of DMFc. This is not surprising, because of extremely low

redox potential of DMFc 0.568 V vs. SCE (in DCE) as compared to non-functionalised ferrocene [268]. However, this was not observed in the case of DMFc solutions in vegetable oil solutions due to the presence of antioxidants, which prevented oxidation.

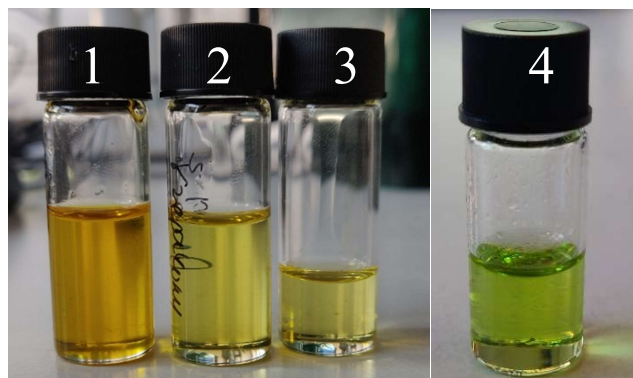


Figure 8-1. Photos of DMFc solution in 1) linen, 2) sunflower, 3) rapeseed oils and 4) oleic acid.

Then, cyclic voltammetry was performed to check the electrochemical behaviour of DMFc - ORR electron donor and to estimate the potential for its regeneration. The voltammograms (Figure 8-2) has to some extent similar shape with comparable anodic and cathodic peak currents. The midpeak potentials are equal: 0.070, 0.073 and 0.116 V for RO, LO and SO based CPE respectively. The peak separation (less than 0.1 V) indicates the quasi-reversible oxidation of DMFc:

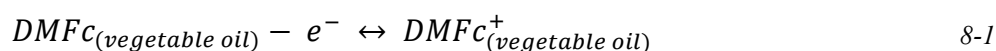
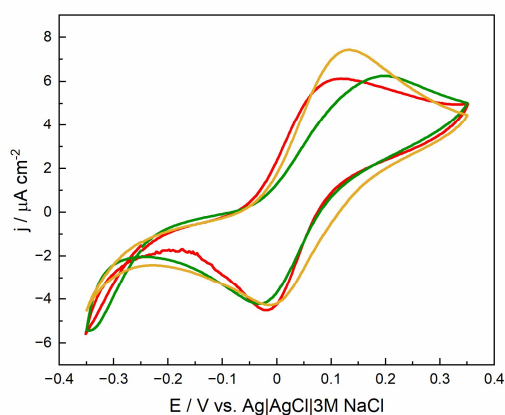


Figure 8-2. Cyclic voltammetry in 0.1 M HClO₄ aq. for CPE with vegetables oil as a binder: rapeseed (red), sunflower (green), linen (yellow) [264].

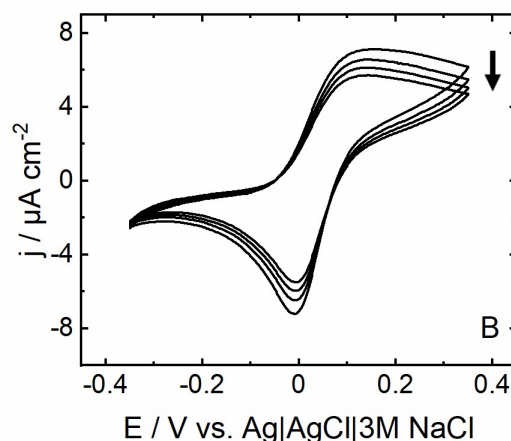
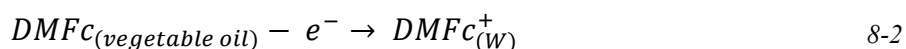


Figure 8-3. Cyclic voltammetry for CPE with rapeseed oil immersed in 0.1 M HClO₄ aq. immediately, after 25, 50 and 75 minutes (decreasing currents, scan rate: 10 mV s⁻¹) [264].

After the oxidation of DMFc, ion transfer must compensate the presence of DMFc⁺ in organic phase. Here, DMFc⁺ transfer to the aqueous phase was confirmed by the decrease of both oxidation and reduction currents with increasing number of voltammetric cycles in voltammetry [264]. This is understandable because of non-polar nature of vegetable oils. Therefore, for fraction of DMFc molecules, equation 2-1 has to be rewritten as follows:



8.2 Hydrogen peroxide detection at the vegetable oil|H₂O interface using scanning electrochemical microscopy

The next step was attempt to detect of hydrogen peroxide as a product of biphasic ORR at vegetable oil|H₂O interface by SECM employing substrate generation tip collection mode (Figure 8-4). According to earlier concept [82], [83], [84], organic phase (binder) of CPE is supported by carbon microparticles, what allows for regeneration of electron donor – DMFc by application of potential -0.05 V to this electrode. It was chosen on the basis of the CV (Figure 8-2) as the value where DMFc⁺ cations are electroreduced. Blank SECM measurements at open circuit were also performed to evaluate the effect of regeneration.

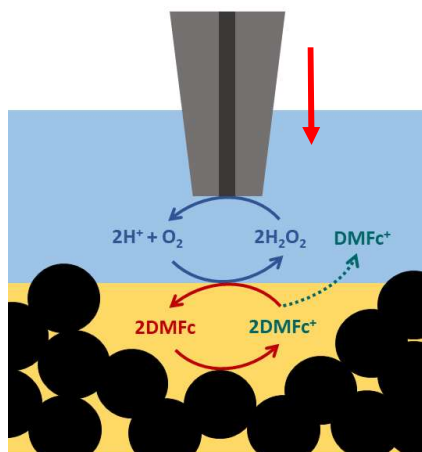


Figure 8-4. Scheme of the hydrogen peroxide detection by SECM on the CPE electrode prepared from the graphite particles mixed with 5 mM DMFc solution in vegetables oils, immersed in 0.1 M HClO₄ aq. Red arrow shows direction of SECM tip motion during SECM approach curve recording [264].

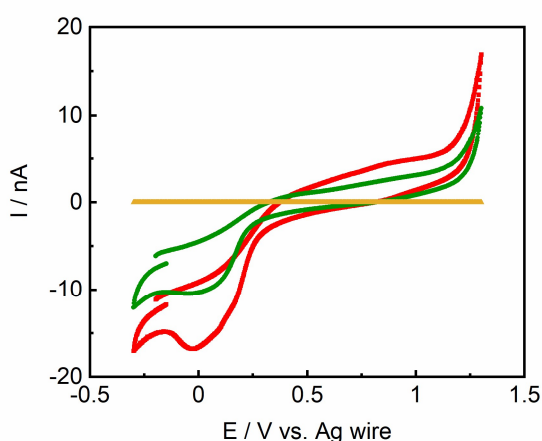


Figure 8-5. Cyclic voltammetry obtained on the UME during SECM analysis for different oils: rapeseed (red), sunflower (green), linen (yellow) at 126 μm from the interface [264].

To obtain the approach curve, the CV curves in the potential range -0.3 - 1.3 V were recorded at SECM tip at the different distances from the CPE. The plot (Figure 8-5) shows the example of CVs curves for different oils as CPE binders 126 μm from the interface, what clearly demonstrates effect of the type of oil. Next, the average anodic current recorded at the potential range 0.95–1.05 V, was calculated and used to construct approach curves (Figure 8-6). The current was normalised using the same methodology as for ITO electrodes (Chapter 7.4). Here, the highest current value was obtained for sunflower oil in the distance 0 from the interface, so its value was assumed to be equal 1 and the other values were recalculated accordingly. From the linear part of the plot of concentration vs. distance from the interface (for maximum 500 μm), the flux of hydrogen peroxide was calculated in the same way as described above (Chapter 7.4).

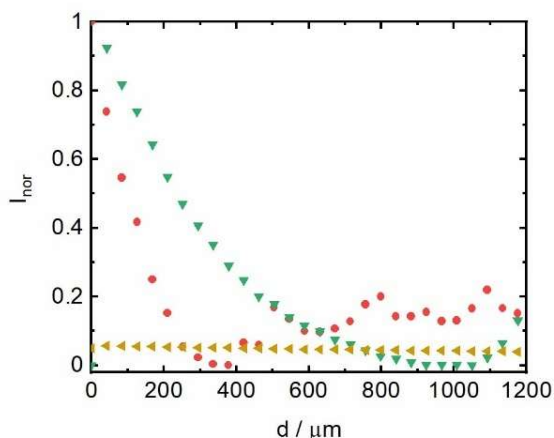


Figure 8-6. Approach curves constructed from CV curves recorded at Pt tip approaching CPE prepared with RO (red circles), SO (green triangles) and LO (blue triangles) immersed in aqueous $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$. CPE potential 0.05 V to allow the regeneration of DMFc^+ [264].

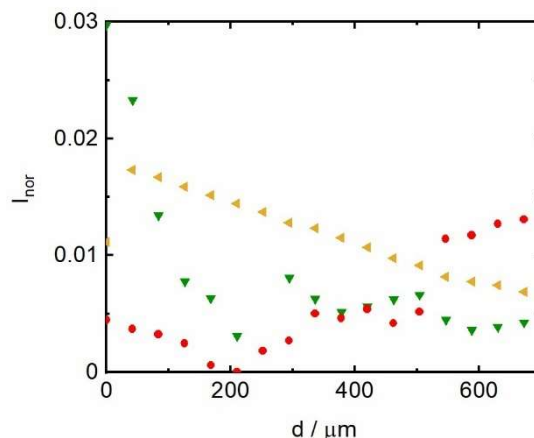
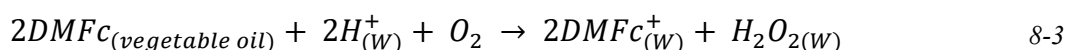


Figure 8-7. Approach curves constructed from CV curves recorded at Pt tip approaching CPE prepared with RO (red circles), SO (green triangles) and LO (blue triangles) immersed in aqueous $0.1 \text{ mol dm}^{-3} \text{ HClO}_4$. CPE without potential applied.

Interestingly, when electron donor was regenerated, $J_{\text{H}_2\text{O}_2}$ value was similar for liquid|liquid interface formed by rapeseed ($29.8 \text{ pmol cm}^{-2} \text{ s}^{-1}$) and sunflower ($27.0 \text{ pmol cm}^{-2} \text{ s}^{-1}$) oil, whereas for linseed oil ($0.6 \text{ pmol cm}^{-2} \text{ s}^{-1}$) was almost negligible. H_2O_2 fluxes for rapeseed and sunflower oils are within the range of obtained for NPOE ($13 \text{ pmol cm}^{-2} \text{ s}^{-1}$ with regeneration) [82] and hydrophobic ionic liquids ($9 - 35 \text{ pmol cm}^{-2} \text{ s}^{-1}$ with regeneration) with the same methodology [84].

The approach curves obtained without regeneration do not show monotonic distance dependence except CPE made of sunflower oil and some current fluctuations are seen (Figure 8-7). Probably the efficiency of biphasic H_2O_2 generation without the regeneration of DMFc is too small, to allow for its reliable detection by SECM.

Based on the above results, biphasic generation of H_2O_2 at graphite|vegetable oil|water interface part can be described by following reaction:



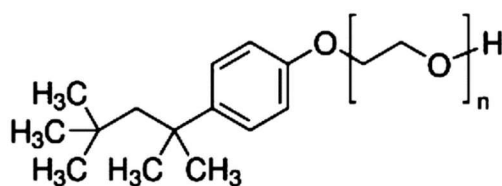
8.3 Conclusions

- Hydrogen peroxide was generated on the three-phase interface graphite|vegetable oil| H_2O interface, with regeneration of electron donor and detected using SECM.
- The biphasic reaction at graphite|vegetable oil| H_2O interface can be called electrocatalytic [269].
- These results allow to extend the range of solvent for biphasic ORR studies to non-polar true oils, which are environmentally friendly bioproducts.
- The ejection of oxidised form of electron donor to aqueous phase decreases its concentration in organic phase and is unfavourable for longer time experiment [84].

9 Electrochemical studies of selected emulsions

9.1 Optimisation of the emulsion's composition

The study of biphasic reactions in emulsion was started from optimisation of its composition. Aqueous phase was aimed to be a proton source to enable biphasic ORR and HER reaction. Therefore 0.1 M HClO₄ aq. solution was used. The presence of electron donor (DMFc or DMRc) in the organic phase was crucial to enable these reactions to occur at liquid|liquid interface. Due to the usage of TFT in previous studies at liquid|liquid interface [1], it was chosen as organic component of emulsion. The role of surfactant as emulsion stabilizer was considered. Here, Triton X-100 (TX100) (Figure 9-1) was chosen due to its previous application in emulsions containing ionic liquids [270], [271], [272]. It is non-ionic, biodegradable and non-toxic surfactant [273]. Therefore, emulsion consisting of perchloric acid, DMFc solution in TFT and TX100 surfactant was selected for first experiments.



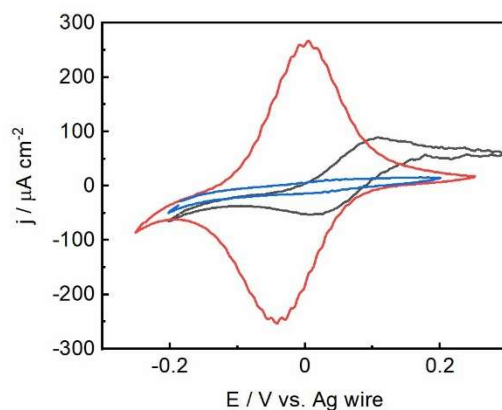


Figure 9-2. Cyclic voltammetry recorded at a GC electrode of the emulsion consisting of 150 μl of 30 mM DMFc in TFT and 1 μl of TX100 and 5 ml of 0.1 M HClO_4 aq., different colours mark voltammograms obtained with different emulsion samples, scan rate: 10 mV s^{-1} .

Therefore, instead of TX 100 surfactant, hydrophobic ionic liquid was employed as surfactant, component of organic phase and electrolyte in organic phase. The emulsion composition was similar to that used in earlier studies focused on stochastic electrochemistry (20 mM Fc and 400 mM $\text{P}_{(6,6,6,14)}\text{NTf}_2$ solution in toluene (TN) and water [119]). However, here as aqueous phase 0.1 M HClO_4 aq. was used. The organic phases consisting of DMFc solution of different concentration and 400 mM of ionic liquid in TN were prepared. Two similar hydrophobic ionic liquids with common anion: trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$) and methyltrioctylammonium bis(trifluoromethylsulfonyl)imide ($\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2$) were also employed to compare their influence on the emulsion's stability and its electrochemical properties. Interestingly, the colour of the freshly prepared DMFc solution depends on the type of ionic liquids. For $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ it was green, for $\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2$ – yellow and for $\text{P}_{(6,6,6,14)}\text{NTf}_2$ – light green. This difference can be explained by the different DMFc^+ concentration due to partial oxidation of DMFc. Importantly, DMFc oxidation in the emulsion containing $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ was not observed (solution colour was yellow), when it was dissolved in anaerobic conditions. The oxidation of DMFc in air was confirmed by CV with Pt UME in organic phases consisting of DMFc and $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ (Figure 9-3) and DMFc and $\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2$ (Figure 9-4) solutions in TN. DMFc is easier oxidised than Fc due to its lower redox potential [139]. Importantly their redox potentials are lower than the redox potential of oxygen [26], [25]. The position of voltammograms vs. current axis indicates that the presence of $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ results in oxidation of half of DMFc molecules present in the solution, whereas in $\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2$, only one third was oxidised. This is caused by more hydrophobic properties of $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$. Additionally, the UV-Vis spectra of DMFc solution in $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ and TN ($\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2/\text{TN}$) and DMFc in $\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2/\text{TN}$ (Figure 9-5) mixtures were collected. For the first mixture, characteristic absorption band for DMFc^+ at 779 nm (red) is observed. For the second one, the absorption band characteristic for DMFc at 425 nm (blue) can be seen [135]. Oxidation of DMFc can be explained by the presence of protons from water or acid impurity in the ionic liquid, contributing to the reaction [83], [84], [275]. Perhaps $\text{P}_{(6,6,6,14)}\text{N}^+$ cation also catalyse this reaction as it was earlier observed for alkali metal cations [276], [277].

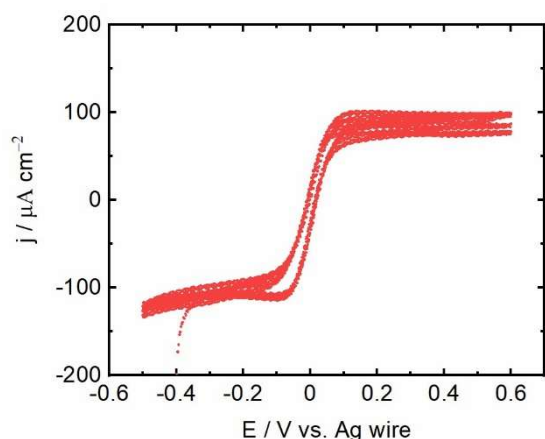


Figure 9-3. Consecutive scans of cyclic voltammetry recorded at Pt UME in 5 mM DMFc and 400 mM $P_{(6,6,6,14)}N(Tf)_2$ solution in TN, scan rate 50 mV s^{-1} [278].

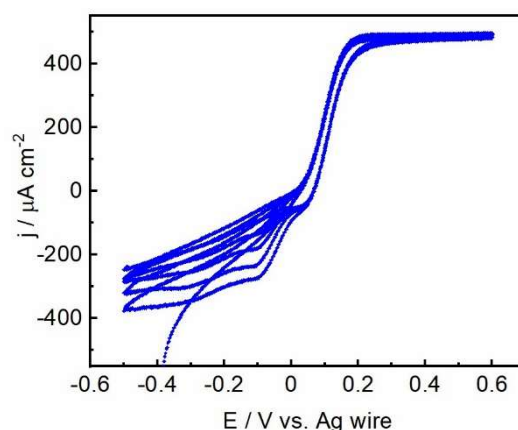


Figure 9-4. Consecutive scans of cyclic voltammetry recorded at UME in organic phase, consisting of 5 mM DMFc 400 mM $N_{(1,8,8,8)}N(Tf)_2$ in TN, scan rate 50 mV s^{-1} .

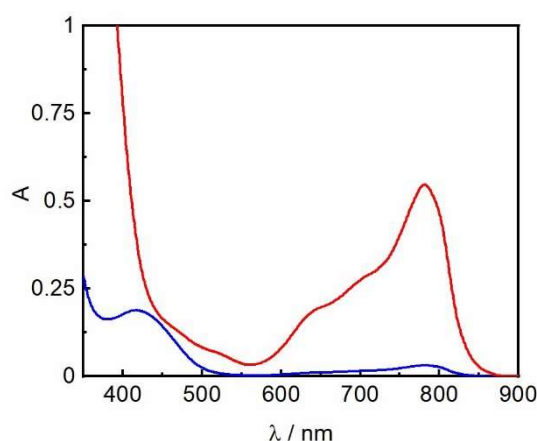


Figure 9-5. UV-Vis spectra of 4 times diluted 5 mM DMFc and 400 mM $P_{(6,6,6,14)}N(Tf)_2$ solution in TN (red) and 3 times diluted 5 mM DMFc and 400 mM $N_{(1,8,8,8)}N(Tf)_2$ solution in TN (blue).

Next, emulsions with different concentrations of DMFc were tested to choose the most appropriate one from the point of view of its stability and reproducibility of voltammetric signal. Clearly the reproducibility of cyclic voltammograms obtained in different samples of emulsion prepared from 30 mM DMFc solution in $P_{(6,6,6,14)}N(Tf)_2/TN$ (Figure 9-6 A) and $N_{(1,8,8,8)}N(Tf)_2/TN$ (Figure 9-6 B) is better than the one obtained in emulsion with TX 100 (Figure 9-2), taking into account the usage of Ag pseudo-reference electrode.

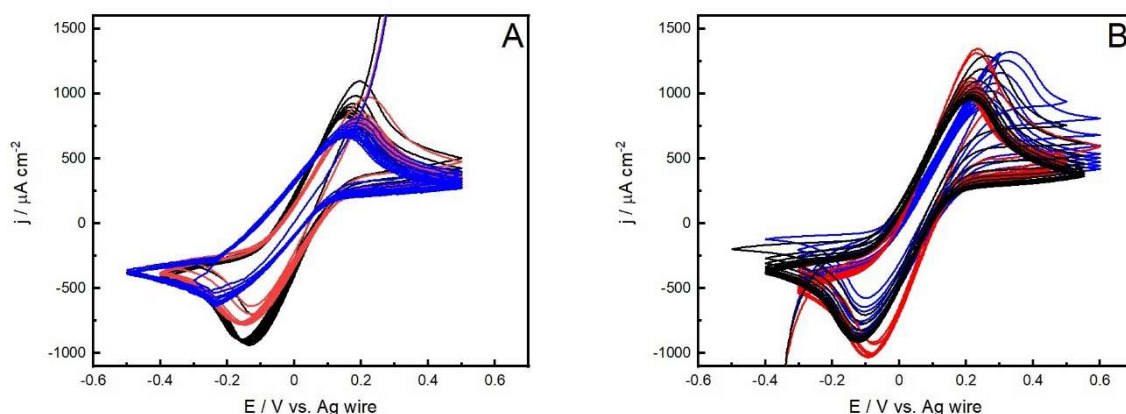


Figure 9-6. Consecutive scans of cyclic voltammetry (10 cycles) recorded at a GC electrode in a stirred emulsion (200 rpm) consisting of 100 μl of 30 mM DMFc and A) 400 mM $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$, B) $\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aq.. Different colours mark different emulsion samples, scan rate: 10 mV s^{-1} .

The next optimisation step was to decrease DMFc concentration down to 5 mM. For the emulsion with $\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2/\text{TN}$, the lack of redox potential reproducibility was observed (Figure 9-7). Therefore, the $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2/\text{TN}$ was chosen as organic phase additive to toluene for emulsion due to better influence on emulsions reproducibility (Figure 9-8 A). Moreover, the visible stability of the emulsion with 5 mM DMFc in the organic solution was better than for the emulsion containing 30 mM DMFc solution.

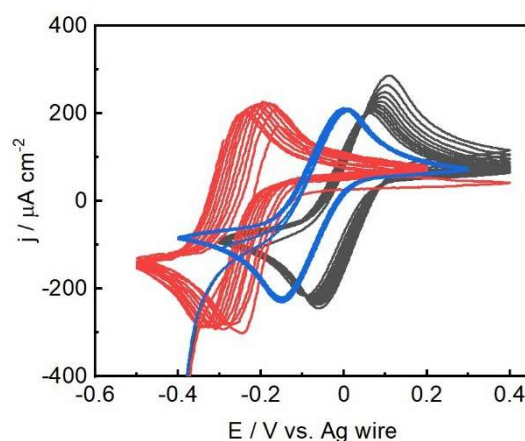


Figure 9-7. Consecutive scans of cyclic voltammetry (10 cycles) recorded at GC electrode in a stirred emulsion (200 rpm) consisting of 100 μl of 5 mM DMFc and 400 mM $\text{N}_{(1,8,8,8)}\text{N}(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aq., different colours mean different emulsion samples, scan rate: 10 mV s^{-1} .

Lastly, the comparison of the electrochemical behaviour of emulsion prepared from 0.1 M HClO_4 aq. and 0.1 M NaClO_4 aq. (Figure 9-8 B) was done. Quite similar voltammograms were obtained (Figure 9-8 A, B). However, acid was chosen to enable biphasic ORR and HER. Stability of the emulsion was achieved as it was milky for 1-2 hours (Figure 9-9). After that time, green droplets suspended in the aqueous phase appeared. Some of them were already present at the top of the emulsion just after preparation. Nevertheless, electrochemical response did not change during 2-3 hours of electrochemical experiments.

Summarising, the composition of used emulsion consisted of 0.1 M HClO₄ aqueous solution and organic solution 5 mM DMFc 400 mM P_(6,6,6,14)N(Tf)₂ in toluene was selected due to its better reproducibility of voltammograms shape and visual stability.

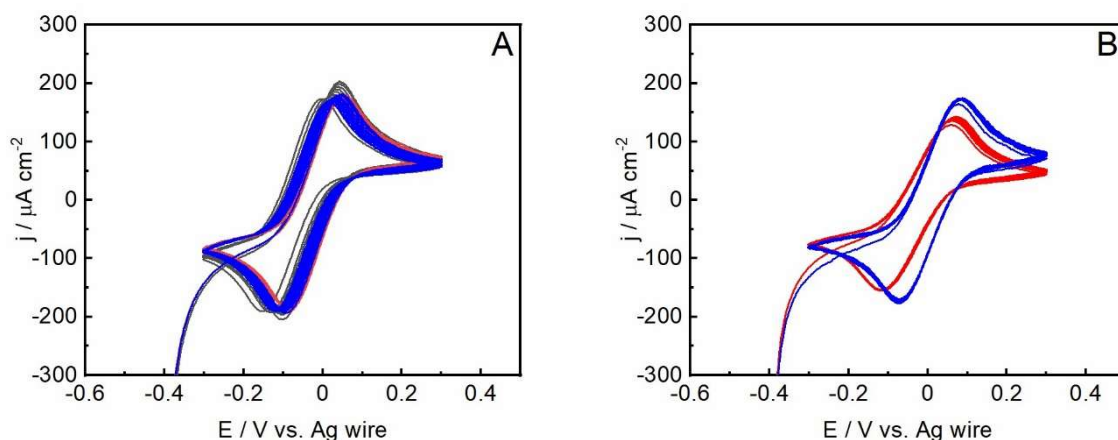


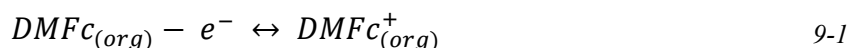
Figure 9-8. Consecutive scans of cyclic voltammetry (10 cycles) recorded at a GC electrode in a stirred emulsion (200 rpm) consisting of 100 μ l of 5 mM DMFc and 400 mM P_(6,6,6,14)N(Tf)₂ solution in toluene and 5 ml of A) 0.1 M HClO₄ aq., B) 0.1 M NaClO₄ aq., different colours mark different emulsion samples, scan rate: 10 mV s⁻¹.



Figure 9-9. Emulsion consisting of 100 μ l of 5 mM DMFc and 400 mM P_(6,6,6,14)N(Tf)₂ solution in toluene and 5 ml of 0.1 M HClO₄ aqueous solution after preparation [278].

9.2 General electrochemical studies of emulsion

Next, the electrochemical properties of the emulsion were examined. In these experiments true reference electrode was used. The reversible, stable cyclic voltammogram indicating DMFc oxidation/reduction:



in stirred redox active emulsion was obtained for 90 consecutive cycles (Figure 9-10). The dependence of anodic peak current vs. square root of scan rate is linear for both stirred and quiescent solution (Figure 9-10, insert). Therefore, one may conclude that the reaction is controlled by diffusion and it is not affected by convective transport of redox active droplets. The influence of stirring rate on the magnitude of the peak current (Figure 7-27) confirms that the electrode process is almost not affected by forced convection. The difference between peak potentials is much larger than expected for pure diffusional control, what is probably caused by uncompensated ohmic drop.

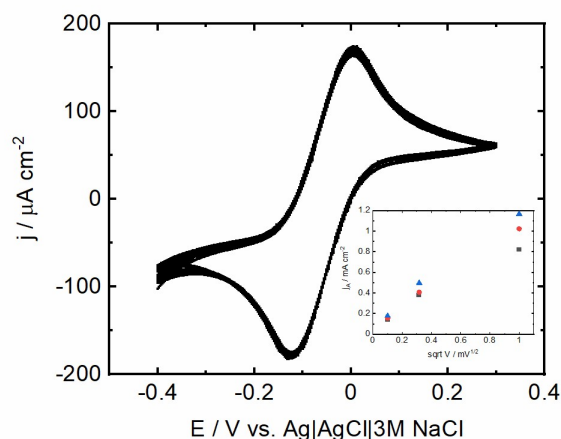


Figure 9-10. Consecutive scans of cyclic voltammetry (90 cycles) recorded at a GC electrode in a stirred emulsion (200 rpm) consisting of 100 μl of 5 mM DMFc and 400 mM $P_{(6,6,6,14)}N(Tf)_2$ solution in toluene and 5 ml of 0.1 M $HClO_4$ aqueous solution. Scan rate: 10 mV s^{-1} . The insert shows the anodic current dependence on the square root of the scan rate in the same emulsion: not stirred (black squares), stirred at 200 rpm (red circles) and stirred at 1000 rpm (blue triangles). Data from Figure 7-27 [278].

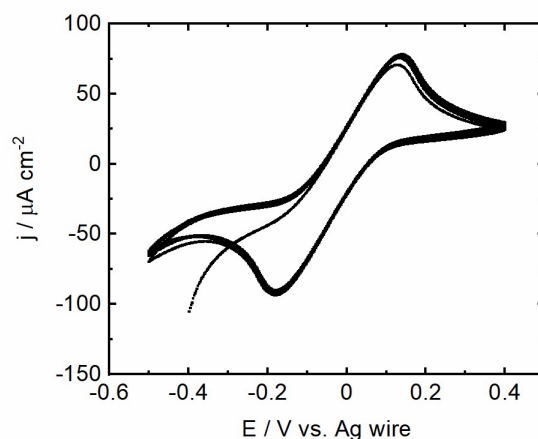


Figure 9-11. Cyclic voltammetry recorded at a GC electrode in quiescent 1 mM DMFc 400 mM $P_{(6,6,6,14)}N(Tf)_2$ solution in toluene. Scan rate 10 mV s^{-1} [278].

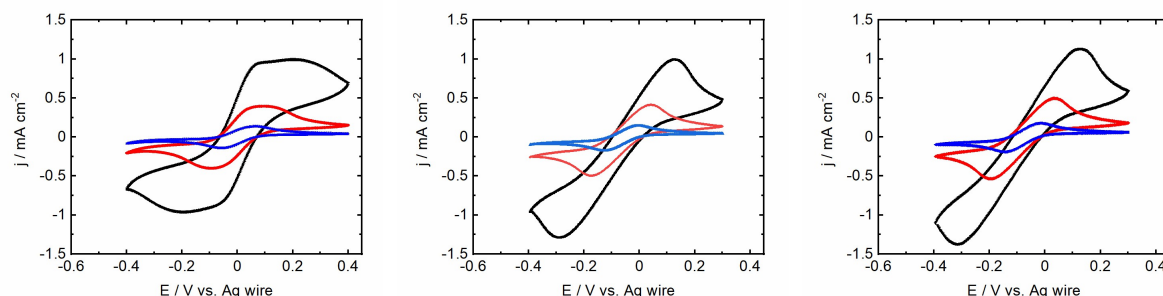


Figure 9-12. Cyclic voltammetry recorded at a GC electrode in quiescent emulsion -left, in stirred emulsion: 200 rpm - middle. 1000 rpm – right, consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(Tf)_2$ in toluene and 5 ml of 0.1 M $HClO_4$ aqueous solution. Scan rate: 10 (blue), 100 (red) and 1000 mV s^{-1} (black) [278].

CV peak current density achieved in 0.098 mM DMFc emulsion, (Figure 9-10) is twice higher than for 1 mM DMFc solution in $P_{(6,6,6,14)}N(Tf)_2/TN$ (Figure 9-11). This is rather unexpected for collective effect of direct collisions of the redox active droplets with the electrode surface, because DMFc solution in $P_{(6,6,6,14)}N(Tf)_2/TN$ is a minor component of biphasic electrolyte (0.0197 by volume). Importantly, effective DMFc concentration in emulsion is 50 times smaller than in bulk organic phase.

For further analysis, viscosity of $P_{(6,6,6,14)}N(Tf)_2/TN$ mixture was calculated to compare it with viscosity of water. This was done using the following equation already tested on a number of molecular liquids [279]:

$$\ln \eta^{ID} = \sum_i x_i \ln \eta_i \quad 9-2$$

where η^{ID} - ideal viscosity of the mixture, x_i – mole fraction and η_i - viscosity of the mixture's component. For calculations, viscosity (in 25°C) of toluene and $P_{(6,6,6,14)}N(Tf)_2$ equal 0.5542 mPa s [280] and 304 mPa s [281], respectively, was taken into account. The calculated value of viscosity of studied toluene/ $P_{(6,6,6,14)}N(Tf)_2$ mixture is 0.938 mPa s, which is close to the viscosity of water - 0.89 mPa s [282].

With this value, DMFc diffusion coefficient of DMFc (D) in toluene and $P_{(6,6,6,14)}N(Tf)_2$ mixture was calculated using Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi r} \quad 9-3$$

where k_B – Boltzmann coefficient [$1.38 \cdot 10^{-23}$ J K⁻¹], T - temperature [K], r – radius of DMFc. Assuming DMFc radius equal 0.48 nm [258], D was calculated as equal 4.76×10^{-6} cm² s⁻¹. This value may not be accurate, because of non-ideality of ionic liquid and toluene mixture. Therefore, the value of D was also calculated from cyclic voltammograms obtained with ultramicroelectrode in this mixture using the following equation:

$$i = k n F a D c \quad 9-4$$

where i – plateau current, a – electrode's radius, c – DMFc concentration. The obtained value of D - 1.04×10^{-6} cm² s⁻¹ was our times lower than obtained above.

The viscosity of the $P_{(6,6,6,14)}N(Tf)_2/TN$ is similar to that of water. Therefore, significantly smaller value of the peak current would be expected for emulsion than for organic phase. Therefore, such difference in peak current may be explained by the organic film formation on the GC electrode surface. The similarity of CV in emulsion and on GC electrode modified by a droplet of organic phase, measured in the same acidic solution (Figure 9-13), supports this conclusion. The independence of peak current on the number of consecutive scans (Figure 9-10) suggests that $P_{(6,6,6,14)}N(Tf)_2/TN$ film is formed on electrode at least within a minute after immersion of GC electrode into redox emulsion.

The hypothesis on film formation was also proven by chronoamperometric experiment in the stirred solution. For that, the electrode potential was changed from -0.4 to 0.5 V to allow oxidation of DMFc (9-1). The slope of the logarithms of current density vs. logarithms of time is close to -0.5 at shorter times, as expected for semi-infinite diffusion (Figure 9-14). At longer times than 100 s, the slope decreases, what could be caused by exhaustive electrolysis of DMFc and by gradient of organic droplets concentration beyond liquid-liquid interface [283]. The thickness of the layer (x) was estimated as 100-200 μ m from random walk equation using calculated value diffusion coefficient of DMFc in $P_{(6,6,6,14)}N(Tf)_2/TN$ (4.76×10^{-6} cm² s⁻¹) (Figure 9-15):

$$x = \sqrt{Dt} \quad 9-5$$

Interestingly, the magnitude of peak currents of voltammogram recorded at GC electrode modified with 8 μ l DMFc solution in $P_{(6,6,6,14)}N(Tf)_2/TN$ (this volume corresponding to 200 μ m liquid film on GC electrode) are close to that recorded in emulsion. Moreover, the midpeak

potential (-0.08 V, Figure 9-13) is also close to the one recorded in emulsion (-0.06 V, Figure 9-10). This observation also supports hypothesis on film formation on GC surface.

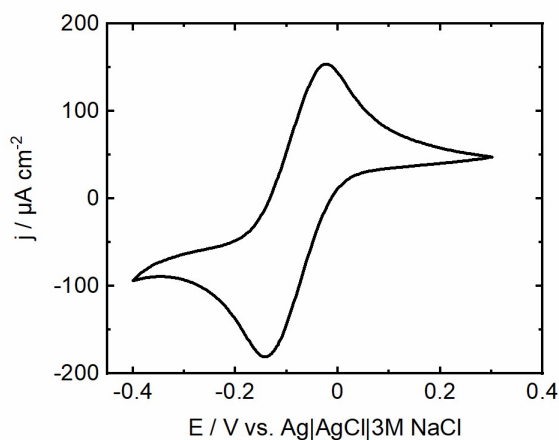


Figure 9-13. Cyclic voltammetry recorded at a GC electrode modified with 8 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ in toluene, immersed in 0.1 M HClO_4 aqueous solution. Scan rate 10 mV s^{-1} [278].

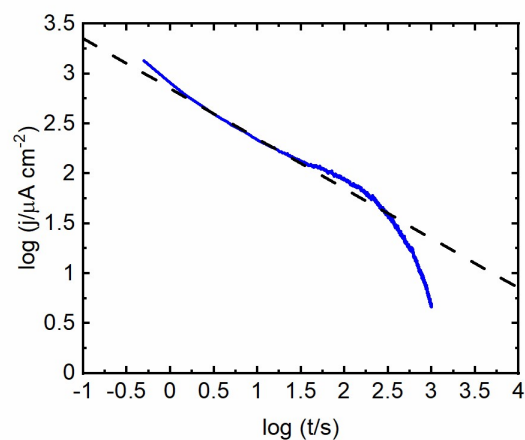


Figure 9-14. Chronoamperometry (blue) recorded at a GC electrode obtained after a potential step to 0.5 V in stirred (200 rpm) emulsion consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ in toluene and 5 ml of 0.1 M HClO_4 aqueous solution. The slope of the dashed black line is -0.5 [278].

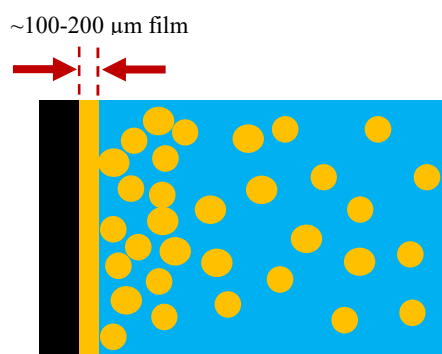


Figure 9-15. The scheme of the GC electrode immersed in the emulsion. Black rectangle marks GC electrode. Orange and blue colours mark organic and aqueous phase, respectively.

When organic phase is in contact with aqueous electrolyte, reaction (9-1) is followed by ion exchange between $P_{(6,6,6,14)}N(\text{Tf})_2/\text{TN}$ and aqueous electrolyte to keep electroneutrality condition [98], [284], [259]. In order to examine the ion transfer direction after DMFc oxidation, SWV of GC electrode modified by droplet of organic phase in salts containing various anions (PF_6^- , ClO_4^- , SCN^- and NO_3^-) was performed (Figure 9-16). The curved E_p dependence on anion transfer potential from NPOE to aqueous phase (as measure of anion hydrophobicity [259], [82]) (Figure 9-17) indicates gradual transition from anion insertion into $P_{(6,6,6,14)}N(\text{Tf})_2/\text{TN}$ to cation ejection to aqueous phase following oxidation of DMFc [98], [284], [259]. The unity slope (solid line) indicates expected dependence when only anion insertion (9-6) follows electrochemical redox reaction (9-1). The obtained results indicate that the redox reaction at solid|liquid interface is followed by the following ion transfer processes at liquid|liquid interface:

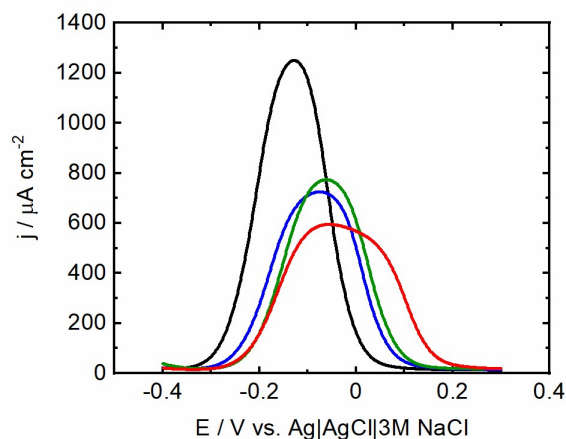


Figure 9-16. Square wave voltammetry recorded at a GC electrode modified with 8 μl of 5 mM DMFc in 400 mM $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ in toluene, immersed in 0.1 M KPF_6 (black), NaClO_4 (blue), NaSCN (green) and KNO_3 (red) aqueous solutions. Parameters of SWV: step: 0.001 V, amplitude: 0.05 V, frequency: 1 Hz [278].

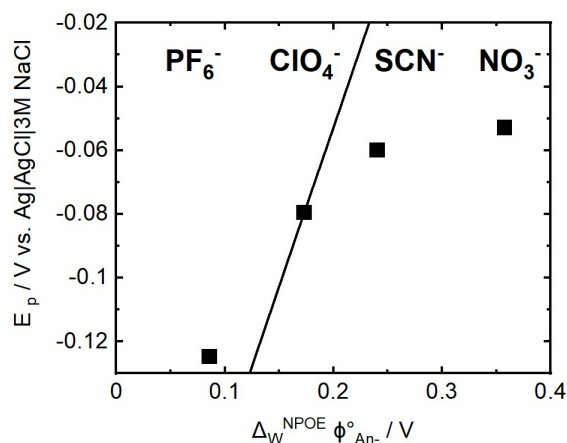


Figure 9-17. The plot of peak potential obtained from the results presented on Fig. S8 vs. anion transfer potential of anion from NPOE to water [278].

The overall electrochemical process at glassy carbon electrode immersed in redox active emulsion can be summarized as below (Figure 9-18):

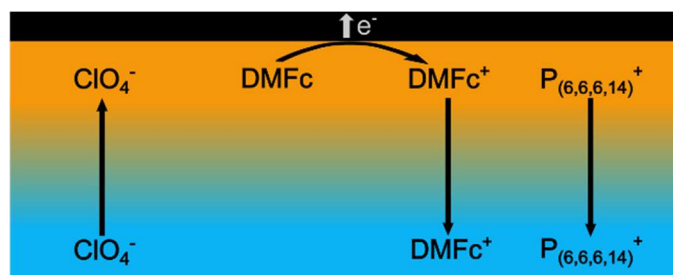
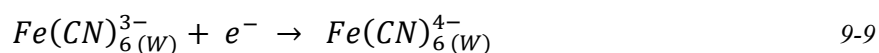


Figure 9-18. Scheme of reactions occurring at electrode immersed in $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2/\text{TN}$ emulsion [278].

Importantly, when HClO_4 solution is employed as aqueous phase of emulsion, ClO_4^- insertion (1-6) dominates.

Other way to detect the formation of the liquid film on the electrode surface was to carry out CV experiments in $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2/\text{TN}$ emulsion containing redox active $\text{Fe}(\text{CN})_6^{3-}$ anions dissolved in 0.1 M HClO_4 aq. These highly hydrophilic anions are expected not to enter organic droplets. Evidently, the CV peak current resulting from the following reaction:



in the emulsion are much smaller as compared to these seen in the aqueous solution (Figure 9-19). This confirms that large part of the electrode surface is covered by organic film, which blocks access of $\text{Fe}(\text{CN})_6^{3-}$ anions from the aqueous phase.

In order to further confirm the film formation at the electrode surface, so called ‘transfer experiment’ was carried out. The GC electrode was immersed into the emulsion for 1 or 10 minutes. After this time, it was removed, rinsed with water and placed in the 0.1 M HClO₄ aq. Then, consecutive voltammograms were recorded (Figure 9-20). Clearly, the voltammetric signal corresponding to DMFc redox reaction (9-1) was observed and the peak current density was ten times larger for 10 min immersion indicating that redox active organic liquid covers only fraction of the surface. CVs are almost stable: small decrease of the peak current is seen during first consecutive scans, although the recorded signal were not that much reproducible as for the emulsion with DMFc. The difference between peak potentials decreases from 0.16 to 0.03 V indicating redox probe restricted diffusion in liquid film [98] or the presence of solid deposit. Interestingly, the shape of voltammogram is similar to that obtained with carbon electrode modified with DMFc microcrystals immersed in the same electrolyte (Fig. 6 in ref [285]).

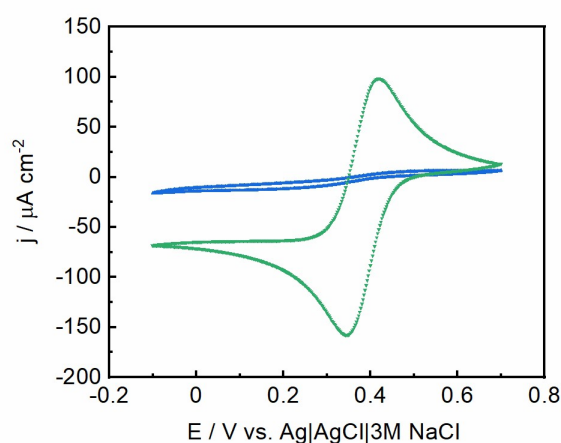


Figure 9-19. Cyclic voltammetry recorded at a GC electrode obtained using 2 mM K₃[Fe(CN)₆] solution in 0.1 M HClO₄ aq. in the absence (green) and presence (blue) of emulsion consisting of 100 μl of 400 mM P_(6,6,6,14)N(Tf)₂ in toluene. Scan rate 10 mV s⁻¹ [278].

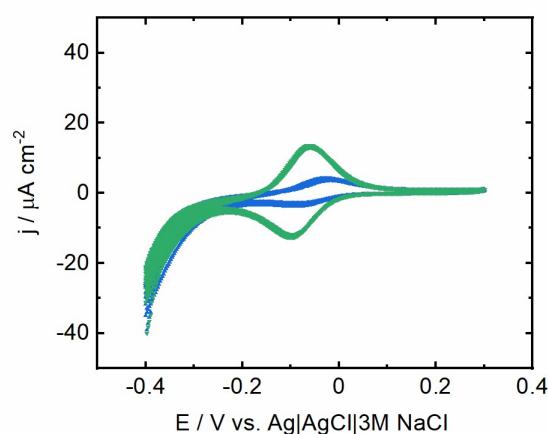


Figure 9-20. Cyclic voltammetry recorded at a GC electrode transferred after 1 min (blue) and after 10 min (green) from a stirred (200 rpm) emulsion consisting of 100 μl of 5 mM DMFc 400 mM P_(6,6,6,14)N(Tf)₂ in toluene and 5 ml of 0.1 M HClO₄ aq. to 0.1 M HClO₄ aqueous solution. No stirring, scan rate 10 mV s⁻¹, 10 consecutive scans [278].

For that reason, SEM images were made and the difference between images of pure GC and GC covered with film (pulled out from the emulsion) was observed (Figure 9-21). The microcrystals of dozens μm size with sharp edges were found at the electrode earlier immersed in the emulsion containing DMFc. They were not seen at the electrode pulled out of the emulsion without DMFc. Therefore, EDS experiment focused on spots, where microcrystals are present, was conducted. It confirmed the presence of P_(6,6,6,14)N(Tf)₂ elemental components and iron (Figure 9-22, Figure 9-23, Table 9-1). The latter element indicates that DMFc microcrystals precipitated during evaporation of volatile toluene from P_(6,6,6,14)N(Tf)₂/TN.

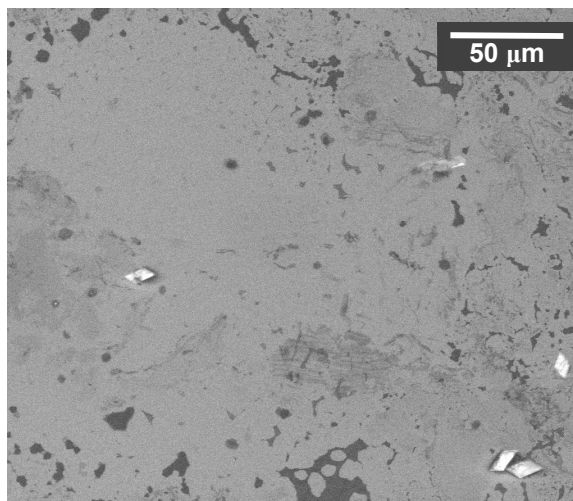


Figure 9-21. SEM image of a GC electrode removed from the emulsion consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(Tf)_2$ in toluene and 5 ml of 0.1 M $HClO_4$ after 10 min [278].

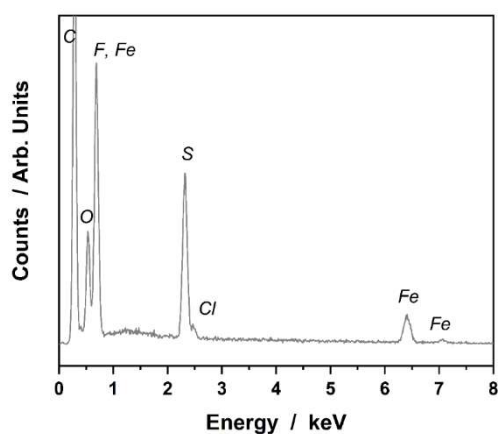


Figure 9-22. EDS spectrum of the spot with crystals seen on SEM image of GC electrode after transfer experiment [278].

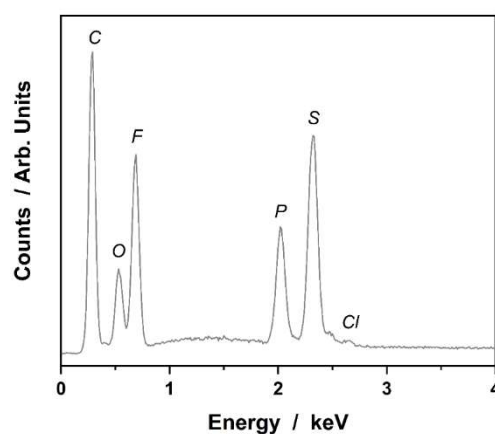


Figure 9-23. EDS spectrum of the spot without crystals seen on SEM image of GC electrode after transfer experiment [278].

Table 9-1. Atomic mass percentage estimated from EDS spectra of GC electrode after transfer experiments obtained from the spots with and without microcrystals seen at SEM image, together with calculated for $P_{(6,6,6,14)}N(Tf)_2$ and DMFc.

Atom	Spot with microcrystals	Spot without microcrystals	$P_{(6,6,6,14)}N(Tf)_2$ calculated	DMFc calculated
C	62.03	62.55	53.46	73.55
O	11.56	11.11	8.39	
F	14.05	15.88	9.43	
P		3.06	4.06	
S	6.25	7.19	8.39	
N			1.83	
H			8.91	9.19
Fe	6.00			17.16

Formation of liquid film was also seen on Au disc electrode during preliminary experiments. The 10 times smaller magnitude of current density and smaller difference of peak potentials (less than 0.05 V) as compared to GC electrode points out on the effect of the electrode material. Perhaps smaller fraction of the surface and/or thinner film is formed at electrode material being more hydrophilic than GC. Also, after Au electrode was used for ‘transfer experiment’, the clear signal in 0.1 M $HClO_4$ aq. was visible (Figure 9-24). Moreover, the peak current density increases during cycling in the emulsion, whereas it decreases after transfer to acid aqueous solution. These effects may be explained by slow liquid film formation and the rearrangement of liquid deposit in the emulsion, and transfer of formed $DMFc^+$ cation to acid solution. The redox potential shift towards lower value was also seen in experiments with GC electrode. However, this can be apparent, because of application of Ag wire as reference electrode (Chapter 9.1) [286]. When it was replaced by $Ag|AgCl|3M\ NaCl$ electrode, this effect was not seen anymore. Possibly, the liquid film is formed on the Ag wire surface, contributing to lack of its potential stability.

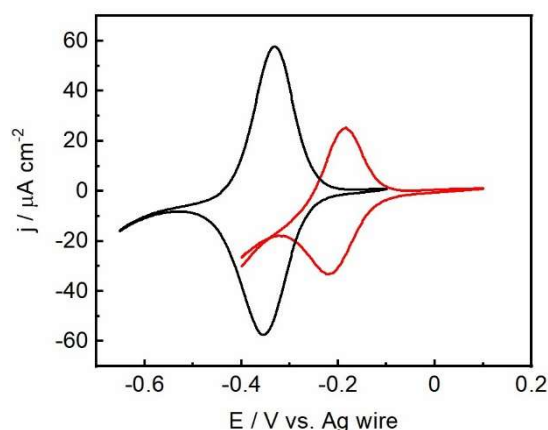


Figure 9-24. Cyclic voltammetry recorded at a Au disc electrode transferred from a stirred (200 rpm) emulsion consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ in toluene and 5 ml of 0.1 M HClO_4 after 10 CV (red) to a 0.1 M HClO_4 aq. no stirring (black), scan rate 10 mV s^{-1} , 3rd scan.

9.3 Electrochemical studies of emulsion with rotating disc electrode

Mass transfer conditions in emulsions are affected by penetration of organic droplets to the electrode and its wetting [287]. The rate of electrochemical reaction of the redox probe dissolved in organic droplets is controlled either by its kinetics or by the rate of hydrodynamic boundary layer penetration by organic droplets. The rate of the latter process depends on the size of organic droplets [286]. Here, voltammetric studies with RDE were done to explore further the film formation in emulsion in hydrodynamic conditions.

Firstly, CV was performed with RDE at different rotation rates. Experiment was started from 2000 rpm. Next, the following rotation rates: 1000, 500, 200, 100, 0, 100, 200, 500, 1000 and 2000 rpm were applied. The peak shaped voltammograms were obtained at all rotation rates, what indicates DMFc redox reaction in liquid film (9-1). For each rotation rate, 2 cycles were performed. The peak current densities increased with each cycle (Figure 9-25). It seems that in this case, rotation rate does not influence the peak current value. It can be explained by continuous film formation during electrode rotation, which began for 2000 rpm.

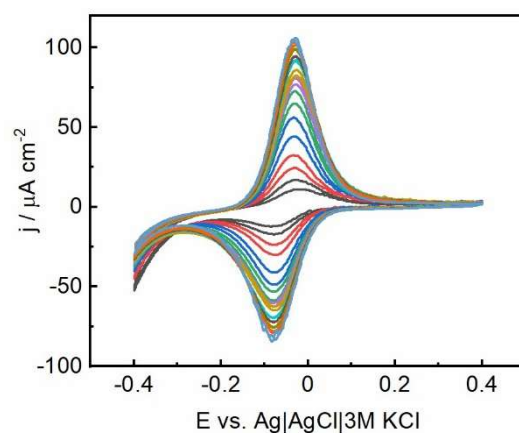


Figure 9-25. Cyclic voltammetry obtained in emulsion consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ in toluene and 5 ml of 0.1 M HClO_4 aq. using GC RDE for different rotating rates: 2000 (black), 1000 (red), 500 (blue), 200 (green), 100 (purple), without (yellow), 100 (light blue), 200 (brown), 500 (dark green), 1000 (orange), 2000 rpm (blue-grey). Peak current density increased in this order. Scan rate: 10 mV s^{-1} .

When 200 rpm was chosen as starting rotation rate, this effect was not observed. Peak current value at 200 rpm was either similar to that obtained in emulsion stirred with 200 rpm (Figure 9-10) for peak-shaped CV (Figure 9-26) or higher for more sigmoidal CV shape (Figure 9-27). When electrode was polished before experiment with different rotation rate, the sigmoidal shape of CV with small peaks was seen (Figure 9-28). In all cases, when CV was run with rotation rate 200 rpm, the current value decreases in subsequent scans, whereas for ten times higher rotation rate, it increases (Figure 9-27). It seems that smaller rotation rate does not promote liquid film formation contrary to higher rotation rates (Figure 9-25).

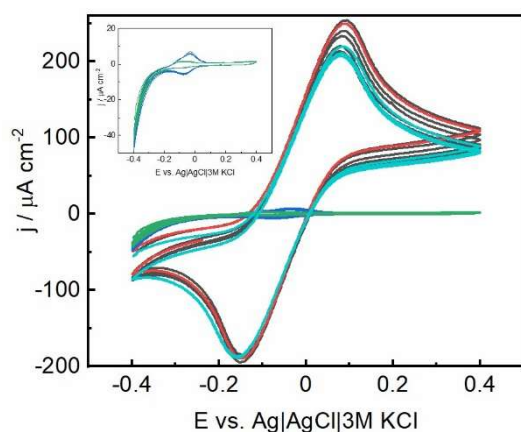


Figure 9-26. Cyclic voltammetry obtained in emulsion consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(Tf)_2$ in toluene and 5 ml of 0.1 M $HClO_4$ aq. using GC RDE for different rotation rates: 200 (black, red - after polishing), 2000 (blue), 1000 (green), 500, 200 (light blue). Insert – zoom of CV for rotation rate 2000 and 1000 rpm. Scan rate: 10 mV s^{-1} .

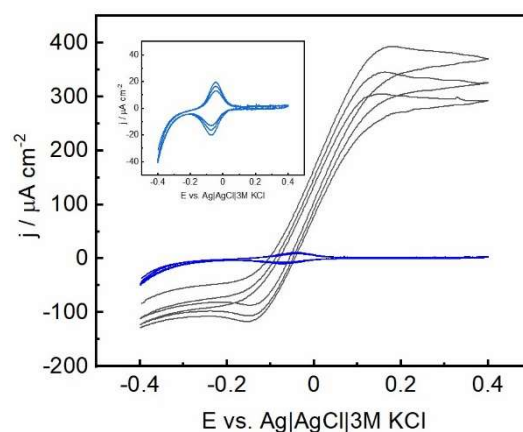


Figure 9-27. Cyclic voltammetry obtained in emulsion consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(Tf)_2$ in toluene and 5 ml of 0.1 M $HClO_4$ aq. using GC RDE for different rotation rates: 200 (black), 2000 (blue). Insert – zoom of CV for rotation rate 2000 rpm. Scan rate: 10 mV s^{-1} .

Also, CV with RDE was performed in emulsion consisting of 100 μl of 400 mM $P_{(6,6,6,14)}N(Tf)_2$ in toluene and 5 ml 2 mM $Fe(CN)_6^{3-}$ solution in 0.1 M $HClO_4$ aq. (Figure 9-29). Here, the observed effect is opposite than for emulsion with DMFc. For 2000 rpm, the observed current density is much larger than for 200 rpm. This is understandable if one considers that this redox probe reacts only at the electrode surface not covered by organic film. For smaller rotation rate, slight peaks are seen, whereas for larger one, the shape of voltammogram is sigmoidal. The opposite trend than for emulsion with DMFc is caused by different nature of reactant. Namely $Fe(CN)_6^{3-}$ is hydrophilic and is not expected to dissolve in organic film on the electrode, whereas organic redox probe is hydrophobic. The systematic decrease of the current recorded at 2000 rpm in experiments with $Fe(CN)_6^{3-}$, as the redox probe may result from gradual formation of organic film at this rotation rate and its increasing blocking effect.

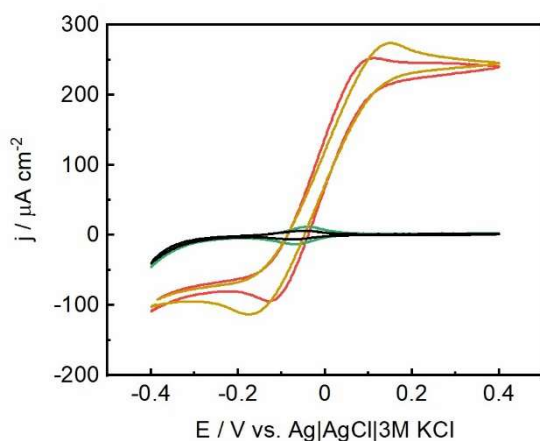


Figure 9-28. Cyclic voltammetry obtained in emulsion consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(Tf)_2$ in toluene and 5 ml of 0.1 M $HClO_4$ aq. using GC RDE for different rotation rates: 200 (red), 2000 (green), 200 (yellow), 2000 rpm (black), RDE was polished between each rotation rate, 2nd scan. Scan rate: 10 mV s^{-1} .

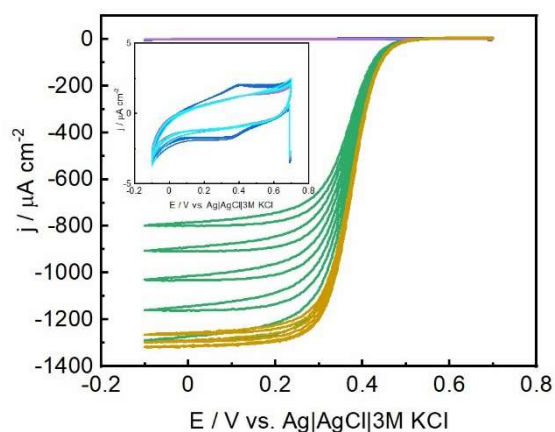


Figure 9-29. Cyclic voltammetry obtained in 2 mM $K_3[Fe(CN)_6]$ solution in 0.1 M $HClO_4$ aq. in the presence of emulsion consisting of 100 μl of 400 mM $P_{(6,6,6,14)}N(Tf)_2$ in toluene and 5 ml of 0.1 M $HClO_4$ aq. Scan rate 10 mV s^{-1} , using GC RDE for different rotation rates: 200 (blue), 2000 (green), 200 (purple), 2000 (yellow) and 200 rpm (light blue). Insert – zoom of CV for rotation rate 200 rpm. Scan rate: 10 mV s^{-1} .

9.4 Oxygen reduction reaction at $P_{(6,6,6,14)}N(Tf)_2$, toluene| H_2O interface in emulsion

In the next step, experiments were focused on possible H_2O_2 generation in emulsion. For detection of this product, 0.1 M KI aq. and 10% starch aq. were both added to the emulsion (250 μl of KI and starch to 1 ml of sample) and shaken for a while. After that, it turned purple (Figure 9-30). The UV-Vis spectrum of the emulsion shows bands characteristic for hydrogen peroxide (300, 350 and 600 nm). They were identified by the spectra of H_2O_2 , KI and starch solution in aqueous perchloric acid (Figure 9-31). Calibrations curves were tried to be prepared in these conditions to perform the quantitative analysis. Unfortunately, the colour intensity of H_2O_2 solution was time dependent and not reproducible for a given concentration. It was observed that the absorbance of pure acid with certain concentration of H_2O_2 (0.049 mM), KI aq. and starch aq. increased with time. Moreover, the rate of colour change was different for different emulsion samples of (Figure 9-30). Even some of them did not change colour after a week. It seems that organic droplets somehow inhibit the formation of colourful complex. Therefore, this method allowed only to confirm qualitatively formation of H_2O_2 as a product of biphasic ORR in emulsion.

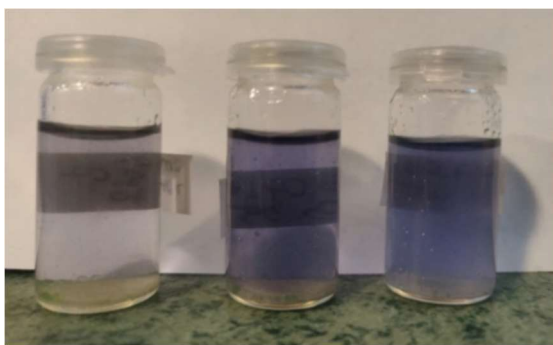


Figure 9-30. The picture of emulsions consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ in toluene and 5 ml of 0.1 M HClO_4 and addition of 250 μl 10% starch aq. and 0.1 M KI aq. after 73, 53 and 51 hours after starting experiment.

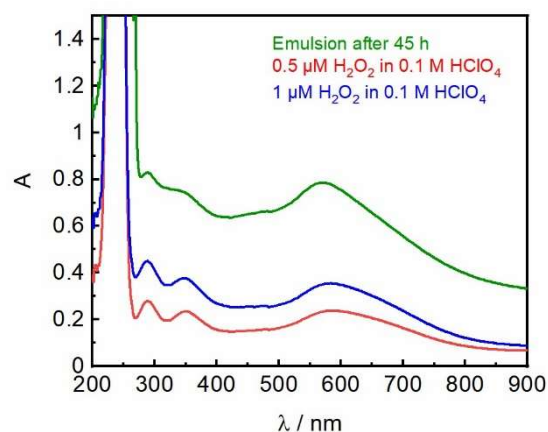


Figure 9-31. UV-Vis spectra of emulsions with DMFc and addition of 250 μl 10% starch after 45 h (green), 0.1 M HClO_4 with addition of H_2O_2 aq.: 0.5 μM (red) and 1 μM (blue)

Next, the possibility of detection of hydrogen peroxide by cyclic voltammetry was attempted. For that, CV was performed in the emulsion with and without DMFc. Firstly, the voltammetry was performed with Pt UME (Figure 9-32). Unfortunately, for some samples the voltammetric signal obtained in emulsion with DMFc and without DMFc was not much different. Also, the shape of CV of emulsion with DMFc is different than the shape of CV in acid with addition of H_2O_2 (Figure 9-33 A) or emulsion with addition of H_2O_2 (Figure 9-33 A). After all these experiments this approach was rejected.

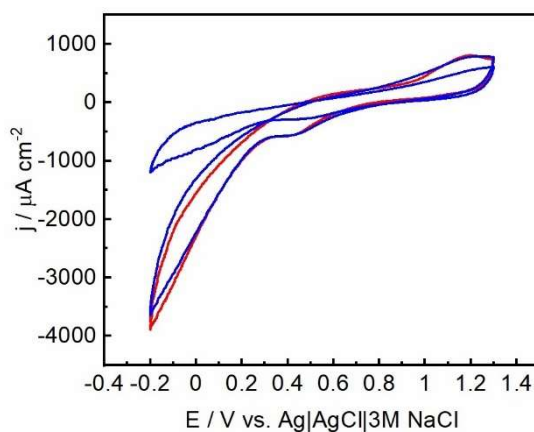


Figure 9-32. Cyclic voltammetry recorded at Pt UME in emulsion consisting of 100 μl of 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aqueous solution (red), emulsion consisting of 100 μl of 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aqueous solution (blue, two different samples), scan rate: 10 mV s^{-1} .

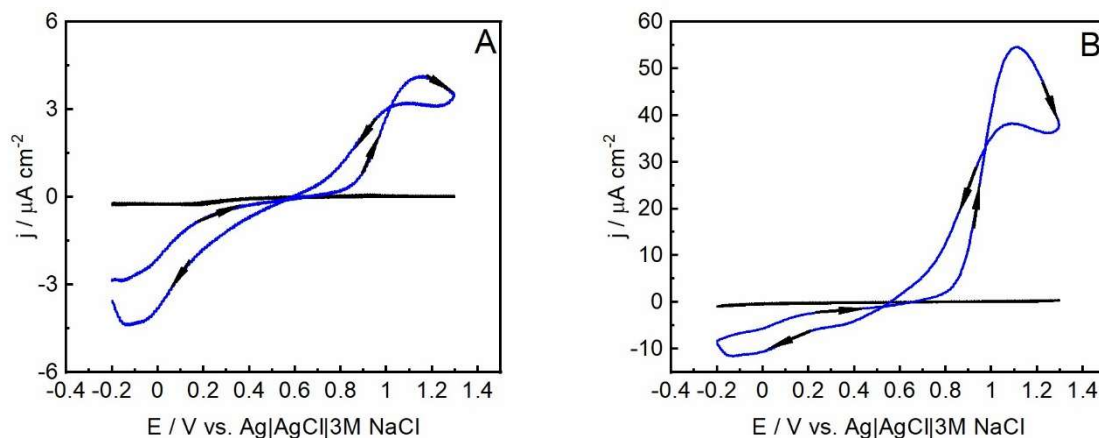


Figure 9-33. Cyclic voltammetry recorded at Pt UME in A) 0.1 M HClO_4 aqueous solution (black) with addition of 5 μl of 30% H_2O_2 (blue), B) emulsion consisting of 100 μl of 5 mM DMFc 400 mM $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aqueous solution (black) with addition of 50 μl of 30% H_2O_2 (blue), scan rate: 10 mV s^{-1} .

Next, CV experiments were carried out with GC disc electrode in the potential range corresponding to oxidation of H_2O_2 . The increase of anodic current at potentials above 1.1 V was observed only in the presence of DMFc in the emulsion (Figure 9-34). Also, CV at GC electrode modified by organic film of 400 mM $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ solution in toluene and mixed with H_2O_2 just before dropping, was compared with CV recorded at GC electrode in emulsion with DMFc (Figure 9-35). The solubility of H_2O_2 in toluene is low [288] and its solubility in $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ may be also low due to hydrophobic properties of ionic liquid. Importantly, CV obtained in emulsion without DMFc (Figure 9-34) exhibits lower current at potentials above 1 V with addition of H_2O_2 (Figure 9-35). Additionally, the shape of the increasing current is wider than for emulsion with electron donor. Therefore, it was concluded that the increase of current for potentials above 1 V results from the electrochemical oxidation of H_2O_2 . However, it was further investigated, whether another compound was oxidised.

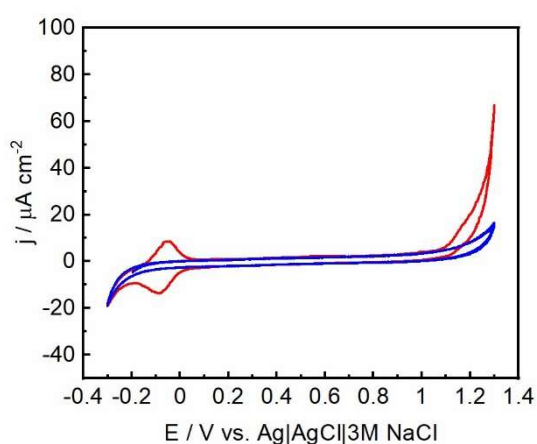


Figure 9-34. Cyclic voltammetry recorded at a GC electrode in emulsion consisting of 100 μl of 5 mM DMFc and 400 mM $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aqueous solution (red) and emulsion without DMFc (blue), scan rate: 10 mV s^{-1} .

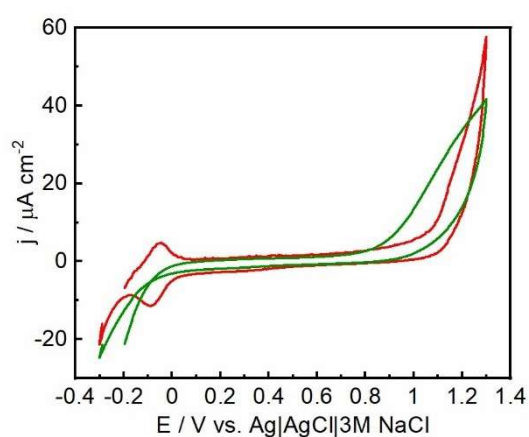


Figure 9-35. Cyclic voltammetry recorded at a GC electrode in emulsion consisting of 100 μl of 5 mM DMFc and 400 mM $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aqueous solution (red) and GC electrode covered by organic film made from 400 mM $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ solution in toluene mixed with H_2O_2 before dropping (green), scan rate: 10 mV s^{-1} .

In order to estimate the concentration of H_2O_2 generated in emulsion by electrochemical experiment, the calibration curve had to be prepared. For that, the CV of emulsion without DMFc containing different amounts of H_2O_2 was performed in the wide potential range (-0.3 - 1.3) (Figure 9-36). Clearly, the plot of current density value at 1.3 V vs. the concentration of H_2O_2 in emulsion is linear (with $R^2=0.999$) (Figure 9-37). However, intercept of this line is above zero. Moreover, H_2O_2 concentration in the emulsion with DMFc was calculated as 0.015 M, which is 3 orders of magnitude higher than the highest possible concentration of H_2O_2 (0.049 mM) produced by all DMFc molecules present in the emulsion, assuming that O_2 molecules are reduced by 2 electron path:

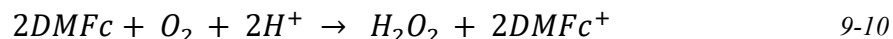
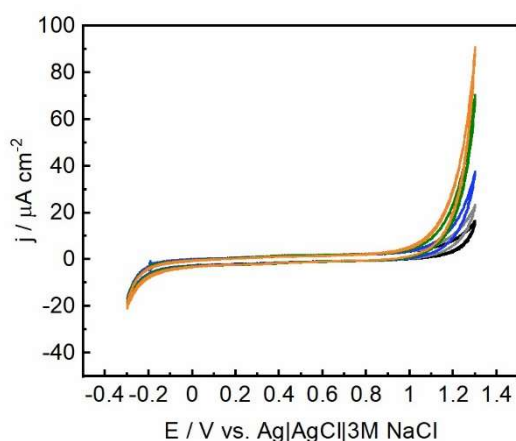


Figure 9-36. Cyclic voltammetry recorded at a GC electrode in emulsion consisting of 100 μl of 400 mM $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aqueous solution without (black) after addition of H_2O_2 to achieve 0, 2, 5.9, 15.6, 21.5 mM concentration, scan rate: 10 mV s^{-1} .

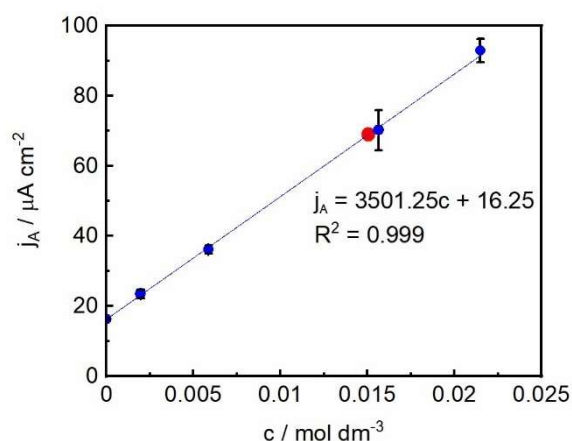


Figure 9-37. Calibration curve constructed from the current density at potential 1.3 V from the data presented on Figure 9-36.

Therefore, CV was performed in wider potential range to check, if there are some other processes occurring in the system. For these experiments, organic phase with and without DMFc and with H_2O_2 added were used. For each composition of organic phase, the current decreased during consecutive cycling. Clearly, anodic current peak at potential c.a. 2 V is visible (Figure 9-38). Its value is c.a. 5 times higher in the presence of DMFc than in its absence. This peak may result from the electrooxidation of toluene, in the presence of $\text{P}_{(6,6,6,14)}\text{N}(\text{Tf})_2$. Similar effect was observed in CoCl_2 and toluene solution in other ionic liquid N-butyl-N-methyl-pyrrolidinium bis(trifluoromethylsulfonyl)imide. Anodic peak at potential below 2 V (Figure 9-39) was ascribed to toluene oxidation in the presence of Co^{2+} cations [289]. Perhaps here, we see catalytic effect of DMFc^+ cations which are formed at potentials above 0.4 V. Also, anodic peak current obtained in the emulsion without DMFc and with H_2O_2 is higher than the peak current seen in the absence of hydrogen peroxide. The increase of anodic current for potentials above 1 V was already observed in the presence of H_2O_2 in emulsion without DMFc (Figure 9-35). The presence of H_2O_2 seems to enhance the efficiency of electrooxidation of toluene [290], [291]. Due to this fact, cyclic voltammetry did not allow for reliable estimation of H_2O_2 concentration. However, one may suspect that presence of both: DMFc^+ and H_2O_2 in the emulsion with DMFc, result in better efficiency of toluene oxidation than the emulsion

without electron donor. Also, oxidation of H₂O₂ may influence the value of anodic current slightly. Anyway, this system requires further investigations.

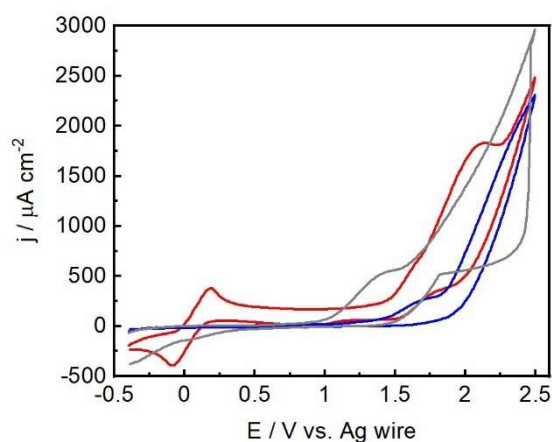


Figure 9-38. Cyclic voltammetry recorded at a GC electrode in the organic phase of emulsion consisting of 100 μ l of 400 mM $P_{(6,6,6,14)}N(Tf)_2$ solution in toluene and 5 ml of 0.1 M $HClO_4$ aqueous solution with 5 mM DMFc (red), without DMFc (blue), without DMFc with addition of H_2O_2 (grey), 1st scan, scan rate: 10 $mV s^{-1}$.

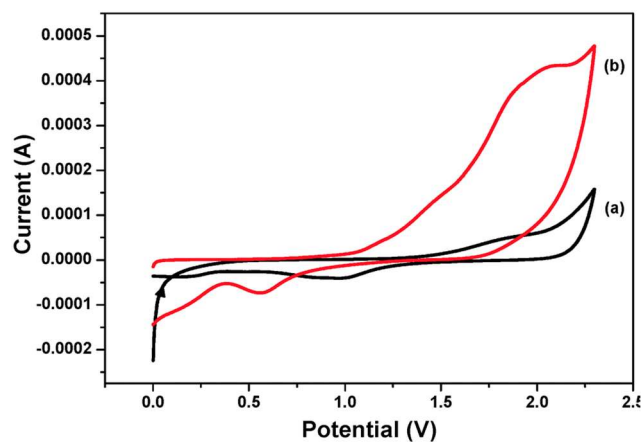


Figure 9-39. Cyclic voltammetry recorded at a Pt disc electrode in N-butyl-N-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide containing 0.015 mmol of toluene (a); 0.015 mmol toluene + 0.05 mmol $CoCl_2$, b) measured at a scan rate of 50 $mV s^{-1}$ and at 25 $^{\circ}C$ (Ag wire as a quasi-reference electrode) [289].

9.5 Hydrogen evolution reaction in the emulsion

Emulsion used in biphasic ORR study (Chapter 9.4), was employed for studies of biphasic HER in anaerobic conditions. For this purpose, DMFc as electron donor was replaced by DMRC. Obviously, UV light was needed for its excitation to allow DMRC to reduce H^+ . In ground state DMRC is a poor reductor [25]. In order to check reversibility of its redox process, CV in emulsion containing DMRC was carried out in different conditions (Figure 9-40). The reversible CV curve with peak separation below 0.1 V is obtained. This suggests that the oxidation/reduction of DMRC (7-14) is quasi-reversible in these conditions.

Then, open circuit potential (E_{OCP}) was measured after different time of exposure to UV light (Figure 9-41). Although E_{OCP} decreases in time, its value after 20 min is above 0 V, also considering the $Ag|AgCl|3M NaCl$ potential as 0.195 V vs. RHE [292]. Therefore, the concentration of H_2 generated from this emulsion can be estimated as zero, using following equation [179]:

$$[H_2] = \frac{\exp\left(-\frac{2FE_{OCP}}{RT}\right)}{k_H} \quad 9-11$$

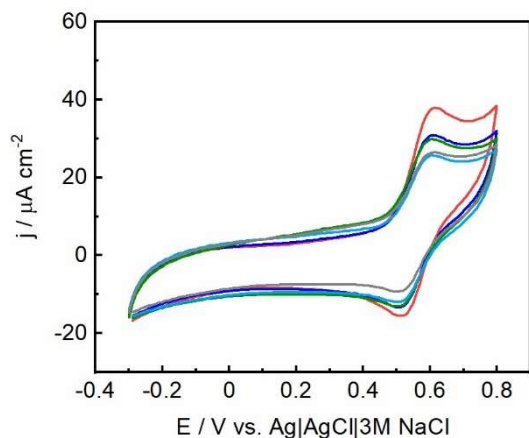


Figure 9-40. Cyclic voltammetry (consecutive scans) recorded at a GC electrode in emulsion consisting of 100 μl of 5 mM DMRC and 400 mM $P_{(6,6,6,14)}N(Tf)_2$ solution in toluene and 5 ml of 0.1 M $HClO_4$ aqueous solution, immediately without light (red), immediately with light (dark blue), after 5 min (green), 10 min (light blue) and 20 min (grey) of light exposure, in Ar atmosphere, 100 mV s^{-1} .

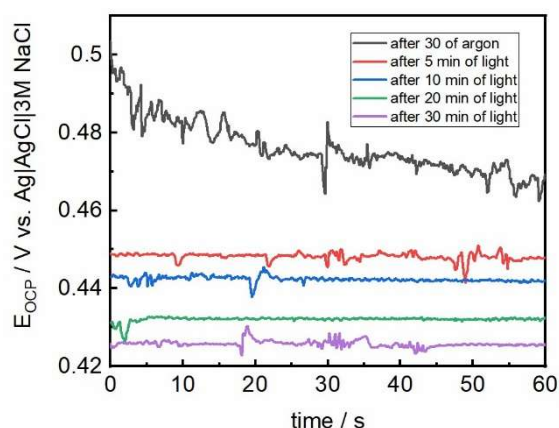


Figure 9-41. E_{OCP} changes in time of exposure to UV light to emulsion consisting of 100 μl of 5 mM DMRC and 400 mM $P_{(6,6,6,14)}N(Tf)_2$ solution in toluene and 5 ml of 0.1 M $HClO_4$ aqueous solution, immediately without light (grey), immediately with light (red), after 5 min (blue), 10 min (green) and 20 min (purple) of exposure to light, recorded at Pt 100 μm , in Ar atmosphere.

In order to check, whether biphasic HER occurs, CV with Pt UME immersed in emulsion with and without DMRC was performed [179]. Then, it was compared with the CV obtained in $HClO_4$ aq. (Figure 9-42). The anodic peak current at the potential -0.35 V can be assigned to the oxidation of hydrogen. Clearly, its current value is higher for acid solution than for emulsions, because in the latter significant part of the surface is probably covered by the liquid film as observed in earlier experiments (Chapter 9.2 [278]). Importantly, the peak current obtained in emulsion with DMRC in the presence of light is higher than in the absence of electron donor. This can be explained by some contribution resulting from oxidation of hydrogen produced by biphasic HER. However, CV experiment was started after 30 s of keeping the potential at 1.5 V to increase HER efficiency. Therefore, this is not univocal judgement and more experiments are required to prove it. Also, CV was performed with Pt UME above the surface of GC electrode fixed upside down in the bottom of the cell. The GC electrode was first immersed in the emulsion for 10 minutes and then it was washed with water and immersed in the acid solution. Then, the potential -0.2 V was applied to the GC electrode to enable the regeneration of DMRC. In the presence of UV light, CV on UME was recorded (Figure 9-43). However, reached current density was smaller than the one without GC with applied potential. It may be caused by too big distance between Pt UME and GC electrode, which did not allow to detect all the hydrogen produced in biphasic process. Also, the volume of organic phase was smaller comparing to the one used for emulsion preparation, which may result in lower current.

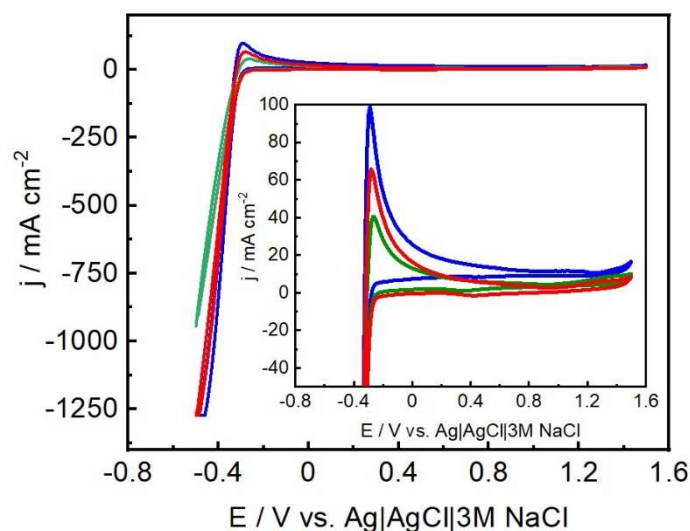


Figure 9-42. Cyclic voltammetry recorded at Pt UME emulsion consisting of 100 μl of 5 mM DMRC and 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aqueous solution after applying potential 1.5 V for 30 s before measurement (red), emulsion without DMRC (green), in 0.1 M HClO_4 aq. (blue), scan rate: 500 mVs^{-1} , in Ar atmosphere.

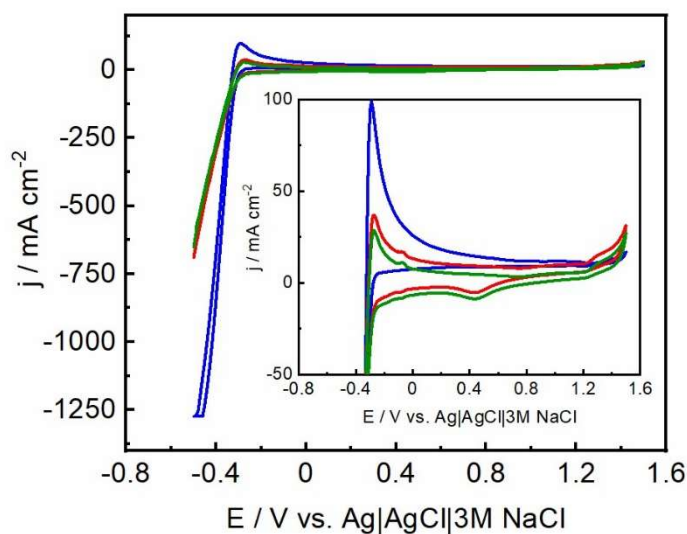


Figure 9-43. Cyclic voltammetry recorded at Pt UME in 0.1 M HClO_4 aq. with GC electrode (with applied potential -0.2 V) after 10 min in emulsion consisting of 100 μl of 5 mM DMRC and 400 mM $P_{(6,6,6,14)}N(\text{Tf})_2$ solution in toluene and 5 ml of 0.1 M HClO_4 aq. with light (green), without light (red) and UME in 0.1 M HClO_4 aq. without GC (blue), scan rate: 500 mVs^{-1} , in Ar atmosphere.

In attempt to detect hydrogen photogenerated in emulsion, experiments in photoreactor [293] combined with gas chromatography or mass spectrometer were performed. Unfortunately, no hydrogen was detected. This could be caused by small amount of hydrogen generated in emulsion, below detection limit. This is possible due to the fact that the concentration of hydrogen for 100% efficiency of reaction is 0.049 mM, which could be challenging to detect by this method.

Perhaps, addition of the salt containing the same anion as ionic liquid present in organic phase: (trihexyltetradecylphosphonium bis(trifluoromethylsulfonate)), may increase the efficiency of HER [176]. However, this will influence the phase diagram and therefore affect emulsion stability and its composition optimisation would be necessary. For now, only slight change in the CV after addition of DMFc to the emulsion provide some indication biphasic H_2 photogeneration.

9.6 Conclusions

- Organic liquid film is formed on GC electrode immersed in emulsion consisted of 0.1 M $HClO_4$ aqueous solution and organic solution 5 mM DMFc 400 mM $P_{(6,6,6,14)}N(Tf)_2$ in toluene. This appears to be as an extreme case of prediction of organic phase concentration gradient next to the electrode surface in contact with emulsion with redox active species dissolved in microdroplets [283]. Alternatively, it allows to preserve continuous supply of redox reagent dissolved in organic phase to the liquid film.
- Described method can be an alternative way for electrode surface modification with liquid, when continuous exchange of material with suspended droplets occurs.
- Film was formed not only on hydrophobic GC also, but also at less hydrophobic Au electrode. This effect could find the application in analysis of redox reactions in emulsions formed by other components.
- Only fast (2000 rpm) rotation of the electrode accelerates liquid film formation.
- Generation of H_2O_2 in emulsion was qualitatively confirmed.
- The voltammetric detection of H_2O_2 produced by biphasic reaction in studied emulsion is impossible, perhaps because of the anodic oxidation of toluene.
- There is some indication of biphasic hydrogen photogeneration in studied emulsion.

10 Summary and conclusions

During the research for this PhD thesis, oxygen reduction and hydrogen evolution reactions have been investigated at liquid|liquid interface using reduced volume of organic phase. They included liquid film modified electrodes, carbon paste electrodes and oil in water emulsion. In the latter case some fundamental studies of redox active emulsion were performed. In general, my research can be summarised as follows:

- Film of organic phase (decamethylferrocene (DMFc) in tetrahexylammonium perchlorate (THAP) or bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluorophenyl)borate (BATB) solutions in 2-nitrophenoctyl ether (NPOE) or DMFc in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($C_4mimN(Tf)_2$)) was deposited on indium-tin oxide (ITO) electrode and was covered by $HClO_4$ aqueous solution. As a result, 2-electron oxygen reduction reaction (ORR) occurred with ITO|NPOE(THAP)| H_2O , ITO|NPOE(BATB)| H_2O and ITO| $C_4mimN(Tf)_2$ | H_2O systems, as H_2O_2 was detected by SECM in front of the liquid|liquid interface. In most cases, the modification of ITO electrode by ITO nanoparticles (ITONPs) film and recycling of electron donor increased reaction efficiency. Due to the small thickness of organic, the regeneration was effective. Moreover, the efficiency of ORR was comparable to one seen at carbon paste electrodes (CPEs) with similar organic phases as a binder. One may predict that similar setup can be applied for other reactions at liquid|liquid interface.
- Films of DMFc or decamethylruthenocene (DMRc) solution in BATB solution in NPOE in contact with $HClO_4$ aqueous solution and addition of LiTB (for DMRc) in aqueous phase were used for hydrogen generation in the dark or in the presence of UV light, respectively. Some indications of biphasic hydrogen photogeneration were seen with ITO|NPOE(BATB)| H_2O (LiTB) system. Higher efficiency was achieved for the biphasic system with DMRc than for DMFc. Obviously, this system needs further investigation.
- Vegetable oils were first time employed as solvents for ORR at liquid|liquid interface using earlier proposed methodology where organic phase was a binder of carbon paste electrode. 2-electron ORRs product was detected by scanning electrochemical microscopy (SECM). This reaction occurs only when electrochemical regeneration of electron donor was enabled. The volume of used oils was much smaller than of aqueous phase. This study extended the range of solvents employed for ORR at liquid|liquid interface to environmentally friendly bioproducts, being alternative for harmful organic solvents. As solubility (if any) of electrolytes is low in these solvents and they are not completely dissociated, three-phase electrodes are the optimal tool for these organic phases.
- Film formation at GC electrode immersed in the emulsion with low content of organic phase in aqueous phase (50 times smaller than aqueous phase) consisting of small amount of DMFc solution in the mixture of trihexyltetradecylphosphonium bis(trifluoromethylsulfonyl)imide ($P_{(6,6,6,14)}N(Tf)_2$) and toluene and $HClO_4$ aqueous solution was observed and its electrochemical behaviour was investigated on electrode surface. This effect may be important when electrodes are in contact with emulsion and alternatively extends the methods of electrodes modifications with liquid.

- Some indications of biphasic 2-electron ORR in the emulsion consisting of microdroplets of DMFc and $P_{(6,6,6,14)}N(Tf)_2$ solution in toluene suspended in $HClO_4$ aqueous solution were noted with a help of voltammetry. However, electrochemical detection of the product was not straightforward and perhaps is impeded by oxidation of toluene. Clearly, this requires further investigation, but obtained results could be beneficial for development of ORR due to bigger contact area between phases.
- Some indications of biphasic HER in the presence of UV light in the emulsion consisting of microdroplets of DMRC and $P_{(6,6,6,14)}N(Tf)_2$ solution in toluene suspended in $HClO_4$ aqueous solution were noted with a help of voltammetry. These results are rather preliminary and require further investigations. Addition of salt with the same anion as ionic liquid, e.g. sodium bis(trifluoromethylsulfonyl) to the aqueous phase would result in the polarisation of liquid|liquid interface. Therefore, HER could be more efficient. However, this idea needs investigation starting from the optimisation of emulsions composition due to high influence of salt presence and its concentration on the phase diagram of the emulsion.

To summarise, both ORR and HER were demonstrated at liquid|liquid interface formed in systems with reduced volume of organic phase. However, studies HER in both systems have to be considered rather preliminary as they are based on small number of results and produce number of yet unanswered questions. Studies of ORR in emulsion were complex due to the presence of toluene. However, the generation of hydrogen peroxide was clear, as well as on ITO electrodes and CPEs. Moreover, ORR at CPEs introduced new, environmentally-friendly and cheap solvents for this reaction.

11 References

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