

Reduction of oxygen from electrolyte emulsions with high oxygen contents

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Abstract

The kinetics of oxygen reduction from electrolyte emulsions containing oxygen carriers was studied with respect to fuel cell applications. Electrochemical experiments including stationary and nonstationary measurements under defined hydrodynamic conditions at a rotating platinum disk electrode revealed that diffusion-controlled limiting currents can be increased significantly at high oxygen concentrations. Additionally, the limiting currents show a strong correlation with the composition and the structure of the emulsions. In particular, the average droplet size of the organic phase and its distribution depends on the nature of the emulsifying agents used for stabilisation. The complex hydrodynamic behaviour of two-phase electrolyte emulsions and the influence of different surfactants seem to outweigh the effect of the total oxygen concentration on the transport kinetics of oxygen. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

The solubility of oxygen in perfluorocarbons (PFCs) like perfluorodecalin, perfluoromethyldecalin, perfluoro-*n*-heptane, perfluorotributylamine is higher by a factor of 20 in comparison to pure aqueous solutions [1]. Oxygen carriers consisting of two-phase aqueous–organic systems have been developed for the substitution of blood products for medical applications [2]. The high capability of different perfluorinated organic compounds for the dissolution of oxygen could be useful for electrochemical systems by improving the reduction kinetics of oxygen. Although the electrocatalysis of the charge transfer reaction is still crucial for the performance of oxygen-consuming cathodes, higher concentrations of oxygen could influence the behaviour of oxygen electrodes under special operating con-

ditions, e.g., if the transport by diffusion is rate-determining.

2. Experimental details

2.1. Preparation of the electrolyte emulsions

Perfluorinated organic compounds with a high oxygen solubility were selected for the preparation of aqueous emulsions. Single compounds and binary mixtures of the following basic compounds were used in various concentrations:

- perfluoromethyldecalin
- perfluorodecalin
- perfluorotributylamine

The PFCs were mixed vigorously with an aqueous solution of a surfactant using a colloid mill and an ultrasonic transmitter.

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Table 1
Composition of electrolyte emulsions; aqueous phase: 0.1 n NaOH

Short name	Perfluorocarbon	w/ v%	Surfactant	w/ v%
25Dec/tri4F68	perfluorodecalin	17.5	Synperonic F68	4
	perfluorotributylamine	7.5		
25Medec4F68	perfluoromethyldecalin	25	Synperonic F68	4
25Tri1.5FT	perfluorotributylamine	25	FT 719	1.5
10Dec/Tri1.5FT	perfluorodecalin	7	FT 719	1.5
	perfluorotributylamine	3		
25Dec/Tri1.5FT	perfluorodecalin	17.5	FT 719	1.5
	perfluorotributylamine	7.5		
25Medec1FT	perfluoromethyldecalin	25	FT 719	1
40Medec2FT	perfluoromethyldecalin	40	FT 719	2

Different surfactants were tested as emulsifying agents. Stable emulsions were achieved with the following compounds:

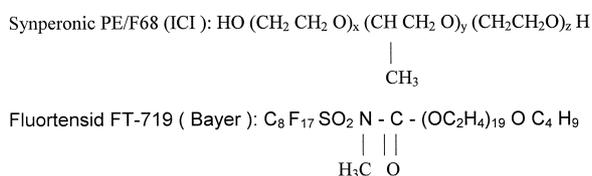


Table 1 shows the composition of the prepared emulsions.

Additionally, a commercial product (FC-43 emulsion, Green Cross) in 0.1 NaOH was investigated. FC-43 is a standard emulsion for pharmaceutical research and consists of 25% w/vol perfluorotributylamine and a nonfluorinated surfactant (Pluronic F-68; 3.2% w/vol) in water.

2.2. Characterisation

Electrochemical experiments including cyclic voltammetry, galvanostatic and equilibrium potential measurements were carried out in a 150 ml thermostatted glass cell designed for rotating disc measurements. An electrode rotator and a bi-potentiostat with a platinum disc electrode were used. A saturated mercury sulphate electrode (SMSE) served as a reference electrode. Oxygen concentrations were determined by an amperometric sensor electrode and by titration [3]. The kinematic viscosity of the electrolyte emulsions was measured in an Ubbelohde capillary vis-

cometer, and the droplet size distribution by laser light scattering.

3. Results

3.1. Determination of oxygen concentrations

Test solutions of various compositions (Table 1) were saturated with pure oxygen or N₂/O₂ gas mixtures, respectively. Oxygen concentrations were determined by an oxygen sensor electrode. To enhance the reliability of the results, the oxygen contents of all electrolyte emulsions were additionally determined by chemical analysis. The dissolved oxygen was fixed by reaction with manganese(II) ions and iodometric titration of the resulting Mn(III) ions [3]. The total oxygen content of the emulsions was higher by a factor of 2–4 compared to single-phase aqueous solutions (Table 3) and depended on the type and concentration of the PFC. The type of surfactant used for stabilisation of the emulsion had only a negligible influence on the overall oxygen concentration.

3.2. Measurements of the viscosity of electrolyte emulsions

The viscosities of the electrolyte emulsions were determined using an Ubbelohde capillary viscometer. The values represented in Table 3 are mean values of 10 single measurements.

Emulsions containing a fluorsurfactant showed similar values like NaOH ($\nu \sim 1.3 \times 10^{-2} \text{ cm}^2 \text{ s}^{-1}$). The use of a nonfluorinated surfactant increased the viscosity ($\nu \sim 3.10^{-2} \text{ cm}^2 \text{ s}^{-1}$).

3.3. Determination of the droplet size

The particle (droplet) size of selected samples was determined by laser light scattering experiments. Apparently, the droplet size strongly depends on the properties of the surfactant used as an emulsifying agent. Emulsions containing the nonfluorinated surfactant, Synperonic F68, showed average diameters of the droplets of about 0.1 μm , and emulsions with the fluorinated surfactant, FT-719, about 1 μm .

An increase of the viscosity or a change of the average droplet size additionally influences the hydrodynamic behaviour of the emulsions and, as a consequence, the results of electrochemical experiments at rotating disc electrodes.

Table 2
Stationary measurements; $p\text{O}_2 = 1.0$

Electrolyte	Temperature [°C]	Equilibrium potential [V] vs. SMSE	b -value [V dec ⁻¹]	i_0^* [$\mu\text{A cm}^{-2}$]
0.1 m NaOH	25	−0.461	0.045	1.4
0.1 mNaOH	80	−0.422	0.060	0.61
10Dec/tri1.5FT /0.1 mNaOH	25	−0.480	0.050	2.44
25Dec/tri1.5FT /0.1 mNaOH	80	−0.440	0.065	1.83

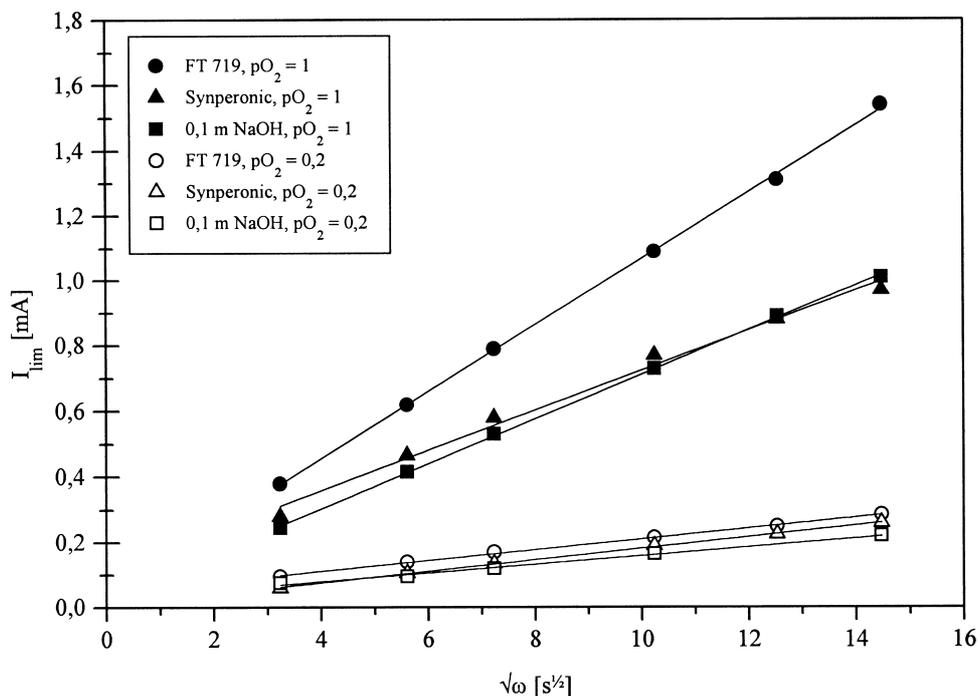


Fig. 1. PF-decalin/PF-tributylamine, 0.1 m NaOH.

3.4. Stationary galvanostatic current density/potential measurements

Stationary measurements were carried out on a rotating platinum disc electrode at 500 rpm. Equilibrium potentials, the slope of the linear Tafel regions (b -values) and exchange current densities, i_0^* , were determined in pure 0.1 m NaOH and different electrolyte emulsions based on 0.1

NaOH as an aqueous phase (Table 2). The exchange current densities, i_0^* , determined in emulsions indicate that the presence of the organic phase had an influence on the reaction rate of the charge transfer.

3.5. Determination of the reaction order

Reaction orders were calculated from the dependence of the current densities on the oxygen concentration at a fixed

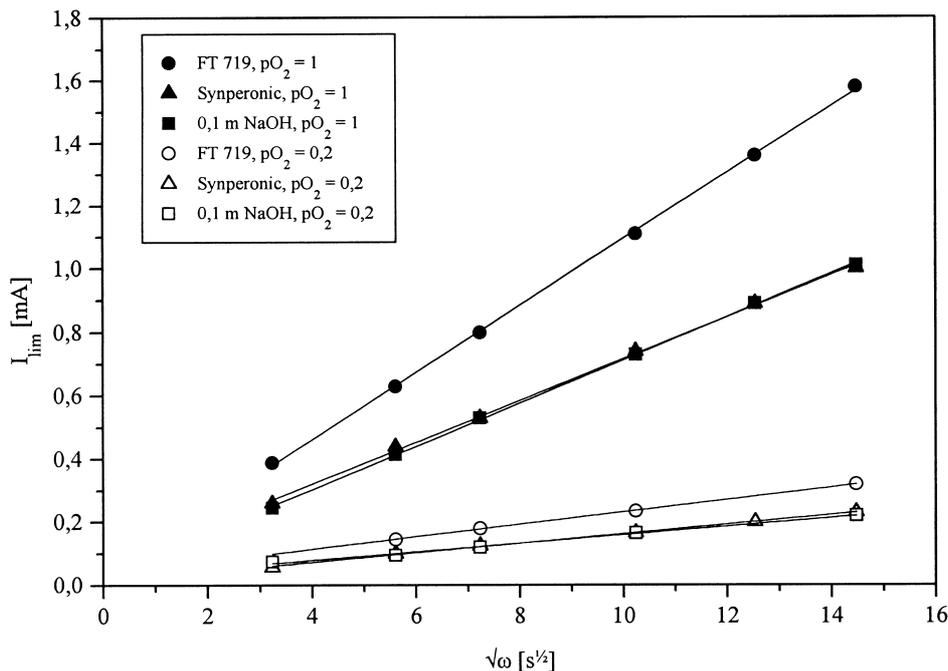


Fig. 2. PF-methyldecalin, 0.1 m NaOH.

potential. The electrolytes were saturated with N_2/O_2 gas mixtures at different oxygen partial pressures. Log i vs. log pO_2 plots revealed a reaction order of +1 in all cases, indicating a fast decay of the intermediate peroxide species on the platinum electrode.

Clearly, the presence of organic phases saturated with oxygen had no influence on the mechanism of the charge transfer reaction.

3.6. Determination of the limiting currents

Limiting currents were determined by stationary galvanostatic and cyclic voltammetric measurements at a low scan rate (0.010 V s^{-1}).

All measurements revealed that the limiting currents significantly depended on the total oxygen content of the electrolyte. In pure aqueous alkaline solutions, a variation of the rotational speed showed a linear dependence of the limiting currents on $\omega^{1/2}$ according to the Levich equation (Eq. (1)):

$$I_{\text{lim}} = 0.62 nFAD^{2/3}\nu^{-1/6}\omega^{1/2}c_0, \quad (1)$$

where I_{lim} = limiting disc current [mA]; c_0 = bulk concentration of oxygen [M]; A = area of disk electrode [cm^2]; D = diffusion coefficient [$\text{cm}^2 \text{ s}^{-1}$]; ν = kinematic viscosity [$\text{m}^2 \text{ s}^{-1}$]; ω = angular velocity of electrode rotation [rad s^{-1}].

Figs. 1 and 2 show limiting current vs. $\omega^{1/2}$ plots from cyclic voltammetry at different oxygen partial pressures. Electrolyte emulsions based on different oxygen carriers in 0.1 m NaOH were prepared with two types of surfactants — a fluorinated (FT719) and a nonfluorinated (Synperionic F68) compound — and compared with pure NaOH solutions.

4. Discussion

The limiting currents determined in emulsions increased with the total oxygen content but not linearly as expected from Eq. (1). The deviation from linearity is apparently due to the hydrodynamic implications of the inhomogeneous two-phase systems. The oxygen equilibrium between the organic and the aqueous phase and the hydrodynamic peculiarities of emulsions influence the transport kinetics.

Due to the higher oxygen saturation of the emulsions, the limiting currents depend not only on the oxygen partial pressure, pO_2 , and the rotational velocity, ω , but also on the chemical and physical compositions of the electrolyte. The droplet size and distribution of the organic oxygen carrier phase influence the oxygen transport kinetics and depend on the type and concentration of the surfactant. Emulsions prepared with a nonfluorinated surfactant showed an average droplet size of $\sim 0.1 \mu\text{m}$ and a

generally higher viscosity than emulsions containing a fluorinated surfactant.

Emulsions prepared from identical PFCs, but different surfactants, showed different limiting currents under identical conditions (Fig. 1). The total amount of dissolved oxygen is not influenced by the surfactant used for stabilisation, both types of oxygen-enriched electrolytes showed comparable oxygen concentrations (Section 3.1, Table 2). The exchange current densities decrease with increasing temperature due to a lower solubility of oxygen at elevated temperatures both in aqueous and organic solutions. Electrolytes based on different oxygen carriers (Figs. 1 and 2) show a very similar behaviour, i.e., significant differences of the limiting currents at a given rotational velocity but only in the presence of a fluorinated surfactant (FT 719).

Emulsions stabilised by a nonfluorinated surfactant (SynperionicF68) showed similar limiting currents as for single-phase aqueous electrolytes. This result indicates that the dissolved oxygen seems to be trapped inside the organic phase and that the transport kinetics is dominated by the properties of the coherent aqueous phase.

On the contrary, emulsions containing a fluorinated surfactant (FT 719) showed a significant increase of the limiting currents. Here, the transport of oxygen from the organic phase to the electrode surface is enhanced by the use of a fluorinated surfactant which may be due to a fast transport across the liquid/liquid phase boundary. The hydrodynamic behaviour of an emulsion with low viscosity and a droplet size bigger by a factor of 10 could have some additional influence.

According to Saffarian et al. [4], a significant increase in the limiting currents, found in aqueous phosphoric acid in the presence of trifluoromethanesulfonic acid, is due to a high oxygen solubility and to a high value of the O_2 diffusion coefficient in trifluoromethanesulfonic acid. A comparison between the diffusivities of oxygen in concentrated trifluoromethanesulfonic acid and in phosphoric acid revealed a diffusivity of oxygen which is about 60 times higher in trifluoromethanesulfonic acid. A mechanism with fast diffusion in the presence of different fluorinated compounds was also suggested by other authors [5,6] but most of these experiments had been done in single-phase aqueous systems.

The hydrodynamic behaviour of emulsions with a high-density difference between the phases is characterised by a pronounced tendency to phase separation. This could have a strong influence on the transport of oxygen from the organic phase into the aqueous electrolyte phase and up to the electrode surface. Flowing emulsions, with a high-density difference between the dispersed and the coherent phase, separate in the vicinity of a solid surface. In the vicinity of the rotating electrode, a layer of pure aqueous phase should be formed. This assumption is confirmed by the results of stationary measurements (Sections 3.4 and 3.5) where no significant influence of the organic components on the mechanism and rate of the charge

Table 3
Apparent diffusion coefficient, D^* , calculated from experimental data

Electrolyte	T [°C]	Partial pressure [bar]	I_{lim} [mA]	Viscosity, ν [cm ² s ⁻¹]	Oxygen concentration, c_0 [mol l ⁻¹]	Diffusion coefficient, D^* [cm ² s ⁻¹]
0.1 m NaOH	25	0.2	0.12	1.14×10^{-2}	0.25	2.27×10^{-5}
0.1 m NaOH	25	1.0	0.53	1.14×10^{-2}	1.25	1.88×10^{-5}
FC43	25	0.2	0.145	2.31×10^{-2}	0.674	0.81×10^{-5}
FC43	25	1.0	0.65	2.31×10^{-2}	3.37	0.69×10^{-5}
Tri 25% FT	25	0.2	0.18	1.47×10^{-2}	0.674	1.00×10^{-5}
Tri 25% FT	25	1.0	0.73	1.47×10^{-2}	3.37	0.73×10^{-5}
Dec/Tri 10% FT	25	0.2	0.14	1.26×10^{-2}	0.436	1.27×10^{-5}
Dec/Tri 10% FT	25	1.0	0.65	1.26×10^{-2}	2.18	1.14×10^{-5}
Dec/Tri 25% Synp	25	0.2	0.13	2.98×10^{-2}	0.706	0.69×10^{-5}
Dec/Tri 25% Synp	25	1.0	0.58	2.98×10^{-2}	3.53	0.58×10^{-5}
Dec/Tri 25% FT	25	0.2	0.17	1.37×10^{-2}	0.706	0.84×10^{-5}
Dec/Tri 25% FT	25	1.0	0.79	1.37×10^{-2}	3.53	0.76×10^{-5}
Medec 25% Synp	25	0.2	0.125	2.77×10^{-2}	0.626	0.76×10^{-5}
Medec 25% Synp	25	1.0	0.53	2.77×10^{-2}	3.13	0.60×10^{-5}
Medec 25% FT	25	0.2	0.18	1.39×10^{-2}	0.626	1.10×10^{-5}
Medec 25% FT	25	1.0	0.8	1.39×10^{-2}	3.13	0.93×10^{-5}
Medec 40% FT	25	0.2	0.21	1.61×10^{-2}	0.806	0.99×10^{-5}
Medec 40% FT	25	1.0	0.94	1.61×10^{-2}	4.03	0.84×10^{-5}

transfer reaction was detected. The thickness of this aqueous electrolyte film generally depends on the droplet size, the density difference and the viscosity [7].

Finely dispersed systems form only thin segregation films of pure aqueous solution at the phase boundary between the solid electrode surface and the emulsion. The volume fraction of the aqueous segregation film increases with the droplet size. Finely dispersed emulsions, therefore, should have a higher volume fraction of the oxygen-rich organic phase in the vicinity of the electrode. Additionally, small droplets are expected to facilitate the transport of oxygen through the phase boundary because of their higher surface area. On the other hand, the higher viscosity (\sim factor 2) of emulsions containing the nonfluorinated surfactant showed a lower droplet size and should, therefore, decelerate the transport inside the electrolyte, although the influence of the viscosity on limiting current is only marginal ($\nu^{-1/6}$) compared to the influence of the oxygen concentration according to Eq. (1).

4.1. Diffusion coefficients

A calculation of diffusion coefficients from the experimental data yields higher values according to Ref. [6] when electrolyte emulsions consisting of a PFC in combination with a fluorinated surfactant were used; however, the validity of Eq. (1) is limited primarily to single-phase electrolytes with simple hydrodynamic properties. The values calculated are shown in Table 3. The calculations did not take into account the implications of a two-phase electrolyte system and, therefore, the limited validity of the resulting apparent diffusion coefficients, D^* , has to be considered. For instance, the values for D^* depend on the oxygen concentrations, c_0 , which represent the overall

oxygen content of the organic and the aqueous phase. Because the effective oxygen concentration of the saturated aqueous phase is limited to a constant low value, the calculated values of D^* decrease with an increasing amount of oxygen stored in the organic phase.

5. Conclusions

Diffusion-controlled limiting currents can be enhanced by the use of fluororganic compounds as oxygen carriers in liquid electrolytes due to this higher oxygen concentration. The diffusion coefficients calculated by Eq. (1) from the experimental data showed higher values if the emulsions had been stabilised by a fluorsurfactant.

In spite of the implications of a two-phase electrolyte system with different steps of diffusion transport and complicated hydrodynamic conditions, the results showed that the diffusion across the liquid/liquid phase boundary is facilitated in the presence of fluorinated surfactants.

The experimental results indicate that the limiting currents and diffusion coefficients are partly influenced by the hydrodynamic properties of two-phase electrolytes but mainly by the influence of the surfactant which is used for the stabilisation of the emulsions.

A fast diffusion mechanism in the presence of fluorinated compounds is suggested by other authors [4,5] and [6] is confirmed by our experimental results.

Acknowledgements

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