



# Liquid–liquid electro-organo-synthetic processes in a carbon nanofibre membrane microreactor: Triple phase boundary effects in the absence of intentionally added electrolyte

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## ABSTRACT

An amphiphilic carbon nanofibre membrane electrode (ca. 50 nm fibre diameter, 50–100 μm membrane thickness) is employed as an active working electrode and separator between an aqueous electrolyte phase (with reference and counter electrode) and an immiscible organic acetonitrile phase (containing only the redox active material). Potential control is achieved with a reference and counter electrode located in the aqueous electrolyte phase, but the electrolysis is conducted in the organic acetonitrile phase in the absence of intentionally added supporting electrolyte. For the one-electron oxidation of *n*-butylferrocene coupled to perchlorate anion transfer from aqueous to organic phase effective electrolysis is demonstrated with an apparent mass transfer coefficient of  $m = 4 \times 10^{-5} \text{ m s}^{-1}$  and electrolysis of typically 1 mg *n*-butylferrocene in a 100 μL volume. For the two-electron reduction of tetraethyl-ethylenetetra-carboxylate the apparent mass transfer coefficient  $m = 4 \times 10^{-6} \text{ m s}^{-1}$  is lower due to a less extended triple phase boundary reaction zone in the carbon nanofibre membrane. Nevertheless, effective electrolysis of up to 6 mg tetraethyl-ethylenetetra-carboxylate in a 100 μL volume is demonstrated. Deuterated products are formed in the presence of D<sub>2</sub>O electrolyte media. The triple phase boundary dominated mechanism and future microreactor design improvements are discussed.

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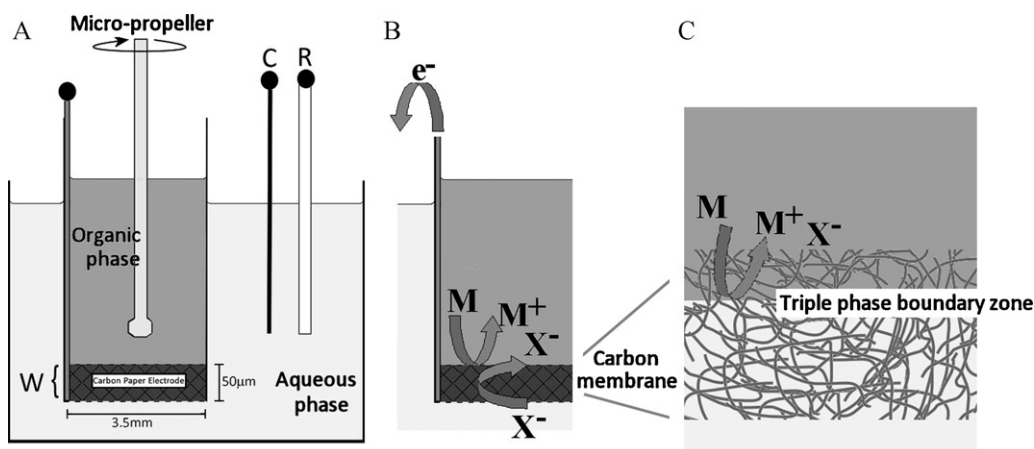
## 1. Introduction

Electro-organo-synthetic reactions offer versatile and clean laboratory protocols for example in hydrogenation/deuteration [1], decarboxylation [2], halogenation [3], and carboxylation [4] processes. New microreactor systems have been proposed for continuous flow-electrolysis processes [5,6]. In order to avoid the use of undesirable supporting electrolyte in organic media, novel particulate electrolyte systems [7], self-supported micro-gap reactions [8], and biphasic processes [9] have been proposed. Although dry reaction conditions are sometimes desirable, there are many processes which occur readily in the presence of moisture or in the presence of a separate aqueous phase [10]. Therefore, flow [11], ultrasound-assisted [12], and ultra-turrax-assisted [13] processes for “biphasic” aqueous-organic electrolysis systems have been developed. These systems have in common that electron transfer is localised in an aqueous electrolyte|organic|electrode triple phase boundary reac-

tion zone [14]. The use of the liquid|liquid interface as a reaction environment opens up a wide range of new chemistries where (i) ionic species (reactive or passive) are supplied from the aqueous phase into the organic phase, (ii) “external” pH control can be achieved by buffering the aqueous phase, and (iii) precipitation reactions can be avoided. The use of a novel “biphasic” microreactor with a carbon nanofibre membrane electrode separating the aqueous and the organic liquid phases is described here.

Fig. 1A shows a schematic drawing explaining the experimental design. The liquid|liquid interface, here typically 2 mol dm<sup>-3</sup> NaCl aqueous electrolyte and an immiscible acetonitrile phase, are in contact at a carbon nanofibre membrane of ca. 50–100 μm thickness. The carbon membrane acts as the working electrode allowing anion and cation transport into the organic phase. Fig. 1B shows a schematic reaction involving oxidation of molecule “M” in the organic phase coupled to the transfer of the anion “X<sup>-</sup>” from the aqueous into the organic phase. A closer consideration of the carbon membrane (see the schematic drawing in Fig. 1C) suggests the presence of a complex interface with an extended triple phase boundary reaction zone. In this report it is shown that after optimisation of all

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**Fig. 1.** (A) Schematic cartoon drawing of an electrochemical cell with working, counter, and reference electrode (W, C, R) in the aqueous phase and an immiscible organic phase separated by a carbon nanofibre membrane. (B) Schematic drawing of an oxidation process at the carbon membrane working electrode, which is accompanied by the transfer of an anion from the aqueous into the organic phase. (C) Expanded view of the triple phase boundary reaction zone within the carbon membrane. This cartoon drawing is not realistic and the true distribution of organic and aqueous phase within the membrane is currently not well understood.

other parts of the system, the process at the triple phase boundary is limiting the rate of electrolysis.

## 2. Experimental details

### 2.1. Chemical reagents

Sodium perchlorate monohydrate (98%, Sigma Aldrich), sodium sulphate decahydrate ( $\geq 99\%$ , ACS reagent, Sigma Aldrich), *n*-butylferrocene (98%, Alfa Aesar), phosphoric acid (Sigma Aldrich ACS reagent, 85 wt%), sodium chloride ( $\geq 95\%$ , SigmaUltra reagent, Sigma Aldrich), sodium hydroxide ( $\geq 97\%$ , ACS reagent, Sigma Aldrich), hydroquinone, and tetraethyl-ethylenetetra-carboxylate (98+%, Lancaster Synthesis) were used without further purification. Demineralised and filtered water was taken from a Millipore water purification system with not less than  $18\text{ M}\Omega\text{ cm}$  resistivity.

### 2.2. Instrumentation

Voltammetric experiments were performed with a microAuto-lab III system (Ecochemie, Netherlands) in staircase voltammetry mode. The step potential was maintained at approximately 1 mV. The counter and reference electrodes were platinum gauze and KCl-saturated calomel (SCE, Radiometer), respectively. The working electrode was a 4 mm diameter carbon nanofibre membrane disc (see Fig. 2, “Bucky paper”, Nanolabs US, with low resistivity ( $\sim 0.1\ \Omega\text{ cm}$ ) and relatively low impurity levels (Fe 0.36, Si 0.31, Al 0.23, Na 0.32, S 0.23 at%) and several recent applications e.g. in Hall measurements with Pt nanoparticles, for catalytic hydrogenation with Rh nanoparticles, and for processes in ionic liquids [15–17] mounted with Ambersil silicone (Silicoset 151) on a glass capillary of 3.5 mm inner diameter and 5 mm outer diameter. The electrical contact was made with a 1 mm stripe of pyrolytic graphite film (Goodfellow, UK) inside of the glass capillary. Solutions were de-aerated with argon (Pureshield, BOC). The pH was measured with a glass electrode (3505 pH meter, Jenway). All experiments were conducted at a temperature of  $22 \pm 2^\circ\text{C}$ .

### 2.3. Procedure for electro-organo-syntheses

Prior to all measurements aqueous solutions were thoroughly degassed using argon. After the carbon membrane electrode was fabricated, the glass capillary reactor was submerged ca. 5 mm deep into the aqueous electrolyte solution (so that the

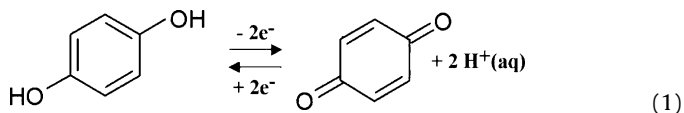
electrode could be checked for possible leaks).  $100\ \mu\text{L}$  of tetraethyl-ethylenetetra-carboxylate solution in acetonitrile was added into the interior of the glass microreactor tube and allowed to equilibrate with the aqueous electrolyte for 10 min. A micropropeller stirrer (1 mm diameter stainless steel with flattened end) was placed into the glass tube to agitate the acetonitrile solution with a rotation rate of ca. 300 Hz (Dremel tool). Constant potential electrolyses were conducted in chronoamperometry mode. After completion of the electrolysis, the organic phase was removed and the microreactor was rinsed with one aliquot of clean acetonitrile. This was followed by removal of acetonitrile in vacuo, and dissolution of product into deuterated chloroform for NMR and MS analysis. **Tetraethyl ethane-1,1,2,2-tetracarboxylate:**  $^1\text{H}$  NMR (300 MHz;  $\text{CDCl}_3$ ):  $\delta_{\text{H}} = 4.22$  (8H, q,  $J = 7.2\text{ Hz}$ ,  $\text{CH}_2\text{CH}_3$ ), 4.13 (2H, s,  $\text{CH}(\text{CO}_2\text{Et})_2$ ), 1.27 (12H, t,  $J = 7.2\text{ Hz}$ ,  $\text{CH}_2\text{CH}_3$ );  $^{13}\text{C}\{^1\text{H}\}$  NMR (75 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{C}} = 167.2, 62.2, 51.6, 14.1$ ; HRMS:  $m/z$  (ES) 341.1211,  $\text{C}_{14}\text{H}_{22}\text{NaO}_8$   $[\text{M}+\text{Na}]^+$  requires 341.1212. In the deuterated product  $^1\text{H}$  NMR lines at  $\delta_{\text{H}} = 4.13$  were absent.

## 3. Results and discussion

### 3.1. Carbon nanofibre membrane oxidation of hydroquinone dissolved in the aqueous phase

Initially, the carbon nanofibre membrane is investigated in contact with the aqueous electrolyte phase. Hydroquinone ( $2 \times 10^{-3}\text{ mol dm}^{-3}$ ) in  $0.1\text{ mol dm}^{-3}$  phosphate buffer is employed as an aqueous redox system in contact with the high surface area carbon nanofibre electrode.

The 2-electron oxidation of hydroquinone produces benzoquinone (see Eq. (1)) in a chemically reversible process, which at carbon nanofibre electrodes results in a well-defined voltammetric response (see Fig. 3A).



The carbon nanofibre membrane is amphiphilic as shown in Fig. 2D (both acetonitrile and aqueous electrolyte readily absorb into the membrane and in a biphasic mixture the membrane binds into the liquid|liquid interface; similar phenomena have been reported for example for carbon nanoparticles [18,19] and for carbon nanotubes [20]) and interacting with the aqueous phase to

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