



## Removal of arsenite by coupled electrocatalytic oxidation at polymer–ruthenium oxide nanocomposite and polymer-assisted liquid phase retention

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### ABSTRACT

Nanocomposite materials synthesized by incorporation of ruthenium oxide nanoparticles into a poly(pyrrole-alkylammonium) matrix have been characterized by transmission electron microscopy and by electrochemistry. Ruthenium oxide-based nanocomposites films coated onto carbon appeared efficient electrocatalysts for the oxidation of arsenic(III) into arsenic(V) species at a remarkable low potential, *i.e.* in the 0.3–0.5 V vs. Ag/AgCl range. Bulk electrocatalytic oxidation of arsenite solutions could be performed in the presence of a water-soluble poly(quatarnary ammonium) salts acting as the supporting electrolyte and also as an As(V) complexing agent, which allowed to combine electrocatalytic oxidation of As(III) with the liquid phase polymer-assisted retention (LPR) technique to efficiently remove arsenic from polluted solutions.

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### 1. Introduction

Arsenic removal is one of the most important areas in water treatment [1]. Arsenic is a highly toxic element creating serious environmental concerns worldwide [2]. The World Health Organization (WHO) provisional guideline value for total arsenic in drinkable water is only 10 ppb and the U.S. Environmental Protection Agency is considering a new standard in the 2–20 ppb range [3,4]. Arsenic is found in both natural surface waters and groundwater, due to the release of arsenic compounds from minerals. In natural waters it occurs in a variety of forms, including soluble, particulate, and organic bound species, but it exists mostly as inorganic pentavalent arsenate (oxidation state +V) and trivalent arsenite (oxidation state +III) species [5]. The latter are more soluble in water and approximately 50 times more toxic than the arsenate ions due to their reaction with enzymes in the human respiratory system [6]. The forms, concentrations and relative proportions of As(V) and As(III) in water vary significantly with changes

in the pH and/or the redox properties of natural environments. At high redox potential, arsenic is stabilized as a series of pentavalent (arsenate) oxy-arsenic species:  $\text{H}_3\text{AsO}_4$ ,  $\text{H}_2\text{AsO}_4^-$ ,  $\text{HASO}_4^{2-}$ , and  $\text{AsO}_4^{3-}$ , whereas at lower redox potentials, and under most acidic and mildly alkaline conditions, the trivalent arsenic species (arsenite:  $\text{H}_3\text{AsO}_3$ ,  $\text{H}_2\text{AsO}_3^-$ ,  $\text{HASO}_3^{2-}$ , and  $\text{AsO}_3^{3-}$ ) become stable [7]. The high toxicity and widespread occurrence of arsenic in groundwater have produced a pressing need for new strategies for arsenic removal. Commonly used processes for removing arsenic from water include precipitation–coagulation, lime treatment, adsorption onto metal oxyhydroxydes, ion–exchange, and membrane processes [8–10].

As(III) is more soluble and more mobile than As(V) species. Therefore pre-oxidation of As(III) to As(V) is required to improve the efficiency of the available removal processes. Oxidation of As(III) can be accomplished by using different oxidants and processes, including hydrogen peroxide [11], oxygen and ozone [12], chlorine [13], manganese oxide [14], electrochemical peroxidation [15], iron(III) [16] and titanium dioxide [17] photocatalytic oxidation. In contrast, it is noteworthy that electrochemical oxidation of arsenite into arsenate prior to arsenic removal is limited to a few examples [18–24]. These include mainly electro-coagulation processes in which partial or full electrochemical oxidation of arsenite into arsenate is combined with removal of arsenic by coagulation [19–22].

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We have recently demonstrated [23–25] that electrochemical oxidation of arsenite combined with membrane ultrafiltration procedures is a promising approach to remove arsenic from contaminated aqueous solutions. Liquid phase polymer-assisted retention (LPR) is well recognized as an efficient technique for the separation of metal ions by ultrafiltration on membranes [26,27], and especially for removing As(V) species from aqueous media [28]. LPR treatment of contaminated aqueous solutions previously submitted to electrocatalytic oxidation of As(III) to As(V) carried out at a bulk platinum electrode [23], and at a platinum–polymer nanocomposite film [24] or iridium oxide-film [25] modified carbon electrodes, has been shown to allow an efficient extraction of hazardous arsenic. The efficiency of this coupled process results from the oxidation of arsenic(III) derivatives into more efficiently extractable arsenic(V) species. Treatment is achieved without adding any chemical oxidants or supporting electrolyte, the cationic water-soluble polymers involved in these processes acting both as As(V) extracting agents and as supporting electrolyte.

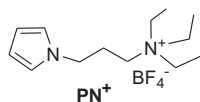
Voltammetry is also a straightforward analytic technique allowing the determination of arsenic(III) in solution [29–31]. Electrochemical methodologies thus offer the unique opportunity to simultaneously perform the exhaustive transformation of arsenite to arsenate and to monitor the associated concentration changes.

We now wish to report that the electrocatalytic oxidation of arsenic(III) to arsenic(V) can be efficiently achieved at electrodes modified with a ruthenium oxide-based nanocomposite film. Noble metals and metal oxide nanoparticles dispersed in functionalized and conducting polymer films are promising electrode materials for numerous catalytic and electrocatalytic applications [32–36]. The main reason for employing such composite materials is their excellent electrocatalytic activities which can exceed those of massive materials at relatively low catalyst loads, thus ensuring a more effective use of expensive noble metals or metal oxides. In the present article, we describe the structural and electrochemical characterization of electrosynthesized poly(pyrrole-alkylammonium)–ruthenium oxide nanocomposite films, along with their electrocatalytic properties toward the oxidation of arsenite to arsenate. We also demonstrate the ability of these electrode materials to carry out exhaustive oxidations of arsenite solutions at a remarkable low potential, thereby allowing the combination of electrocatalytic oxidation of As(III) with the LPR technique to efficiently remove arsenic from polluted solutions.

## 2. Experimental

### 2.1. Chemicals and reagents

(3-Pyrrol-1-yl propyl)triethylammonium tetrafluoroborate, denoted **PN<sup>+</sup>** (Scheme 1), was prepared according to a previously reported procedure [37]. Potassium ruthenate ( $K_2RuO_4 \cdot H_2O$ , Merck), poly(diallyldimethylammonium) chloride (P(CIDDA), Aldrich), sodium(meta)arsenite ( $NaAsO_2$ , Fluka), acetonitrile (Rathburn HPLC, grade S) and tetra-*n*-butylammonium perchlorate (TBAP, Fluka puriss) were used as received. Distilled water was obtained from an Elgastat water purification system (5 M $\Omega$  cm).



**Scheme 1.** Pyrrole-containing monomer (**PN<sup>+</sup>**) used in this work.

### 2.2. Electrodes, electrochemical cells and instrumentation

All electrochemical experiments were performed using a conventional three-electrode system. Electroanalytical experiments were performed using a CHI 660B electrochemical analyzer (CH Instruments). Electrosynthesis of nanocomposites and bulk electrolyses were carried out with an EGG PAR model 273 potentiostat equipped with an  $x$ - $y$  recorder. Potentials are referred to the Ag|AgCl (3 M KCl) or to the Ag|Ag<sup>+</sup> (10 mM in CH<sub>3</sub>CN + 0.1 M TBAP) reference electrodes in aqueous and non aqueous electrolytes, respectively. Glassy carbon electrodes (3 mm diameter) were polished with 1- $\mu$ m diamond paste. All experiments were conducted at room temperature under an argon atmosphere.

### 2.3. Preparation of the nanocomposite film modified electrodes

The ruthenium oxide-based nanocomposite films were synthesized using a previously reported ion exchange-electroreduction procedure [37,38]. The polymer films (denoted poly**PN<sup>+</sup>**) were grown by potentiostatic oxidative electropolymerization carried out from unstirred solutions of the monomer **PN<sup>+</sup>** (4 mM) in CH<sub>3</sub>CN containing TBAP (0.1 M) as supporting electrolyte. The extent of polymerization was controlled through the anodic charge recorded during electrolyses. The amount of pyrrole units in the films and the apparent surface coverage in ammonium units  $\Gamma_{N^+}$  (mol cm<sup>-2</sup>) were determined, after transfer of the modified electrodes into monomer-free CH<sub>3</sub>CN electrolyte, from the integration of the polypyrrole oxidation wave recorded at low scan rate (10 mV s<sup>-1</sup>), assuming that one in three pyrrole units is oxidized [39].

For the preparation of modified microelectrodes, films of  $\Gamma_{N^+}$  ranging from  $2.0 \times 10^{-8}$  to  $6.0 \times 10^{-8}$  mol cm<sup>-2</sup> were grown onto glassy carbon disc (3 mm diameter) electrodes by bulk oxidation carried out at  $E = 0.85$  V vs. Ag|Ag<sup>+</sup> ( $10^{-2}$  M) using polymerization charges from 0.5 to 2 mC. In order to obtain clean voltammograms without the large wave for the polypyrrole redox system in the positive potentials region, its electroactivity was destroyed prior to the incorporation of ruthenate anions, by cycling the electrode potential several times between  $-0.2$  and  $1.6$  V in clean aqueous electrolyte [40]. The resulting C|poly**PN<sup>+</sup>** modified electrodes were then immersed in a 10 mM aqueous solution of  $K_2RuO_4 \cdot H_2O$  for 60 min to ensure a large incorporation of  $RuO_4^{2-}$  anions into the polymer film by ion exchange, then they were transferred to a 0.1 M aqueous LiClO<sub>4</sub> electrolyte and submitted to bulk reduction at  $E = +0.2$  V vs. Ag|AgCl to precipitate ruthenium oxide particles into the polymer matrix. The metal oxide loading in the polymer film was determined from the cathodic charge consumed throughout the reduction process.

Modification of large surface electrodes was achieved by potentiostatic oxidative electropolymerization in acetonitrile electrolyte of **PN<sup>+</sup>** at  $E = 0.9$  V vs. Ag|Ag<sup>+</sup> ( $10^{-2}$  M) onto carbon felt (RVC 2000, 65 mg cm<sup>-3</sup>, from Le Carbone Lorraine) electrodes (20 mm  $\times$  20 mm  $\times$  4 mm), using a polymerization charge of 5C. This process led to the deposition onto the carbon felt of a polymeric material containing about 10  $\mu$ mol of ammonium groups (polymerization yield around 45%). Precipitation of ruthenium oxide into the polymer was then performed under the same conditions as described above for the preparation of analytic electrodes, leading to composite films containing about 5.5  $\mu$ mol of ruthenium oxide.

### 2.4. Transmission electron microscopy experiments

TEM samples were prepared by precipitation of ruthenium oxide into the polymer deposited onto ITO-coated glass electrodes (1 cm<sup>2</sup>) by potentiostatic oxidative electropolymerization in acetonitrile electrolyte of **PN<sup>+</sup>** at 1.1 V vs. Ag|Ag<sup>+</sup> ( $10^{-2}$  M), using charges of 80 mC. The anion exchange-electroreduction process

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