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Carbon-encapsulated iron nanoparticles as ferromagnetic matrix for oxygen reduction in absence and presence of immobilized laccase

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ABSTRACT

Carbon nanocapsules with iron core appeared to be a useful modifier of glassy carbon surface. It has been found that the presence of nanocapsules on the electrode surface resulted in a shift of the reduction voltammetric signal of oxygen by circa 250 mV toward less negative potentials. A considerable increase of the signal was observed when the modified electrode was exposed to an external magnetic field.

The nanocapsules appeared to be a good substrate for immobilization of laccase. The presence of laccase on the electrode surface caused a further significant shift of the position of the oxygen reduction signal toward positive potentials. The application of external magnetic field again strongly magnified the current. The described phenomena were characterized in function of the magnetic field intensity and the angle between the electrode surface and the magnetic field direction. For explanation of the significant enhancement of O_2 reduction current the magnetic field profile in the vicinity of the electrode surface and the force of interactions of magnetic nanoparticles with paramagnetic oxygen molecules were calculated.

1. Introduction

Modification of the electrode surfaces by inorganic or organic substances often plays a key role in the mechanism of many electrode processes and lead to catalytic acceleration of those reactions. The investigation of new electrocatalytic and bioelectrocatalytic compounds/materials that are active in the process of oxygen reduction gained high importance [1,2]. The oxygen reduction reaction (ORR) is a vital cathode reaction occurring in fuel cells and metal–air batteries [3–6]. In aqueous solutions this reaction occurs mainly through two pathways: (a) the direct 4-electron reduction of O_2 to H_2O, and (b) 2-electron reduction of O_2 to H_2O_2 [7]. In non-aqueous solvents and/or alkaline solutions the one electron reduction pathway, from O_2 to O_2^-, can also occur [8]. Particularly useful are the systems that support the four-electron electroreduction of oxygen. Formation of H_2O_2 is typically unwanted, since it is known to be harmful for enzymes and other biocatalysts.

So far, for the electrocatalytic reduction of oxygen in an acidic medium, platinum is the most effective catalyst [9]. However, platinum is too expensive for making commercially viable fuel cells and still has a considerable reduction-overpotential for oxygen. Extensive research over the past several decades has been focused on the improvement of ORR catalysis by developing alternative catalysts including non-nobel metal catalysts such as Fe-, Co-, Ni- and Pt-alloys [10–14]. Different carbon materials have been also studied as an alternative (to metal based catalysts) catalytic material for reducing the undesired overpotentials observed in the ORR [15–18]. 3D electrode materials appeared to be particularly useful for improving the electrocatalysis of O_2 reduction due to the increase of the electrode surface area. Regardless of this advancement in the catalysis the oxygen reduction overpotential still requires some attention.

We have turned to a new material: paramagnetic carbon nanocapsules containing iron (Fe@C Nps) that was additionally supported by an external magnetic field. Both: magnetic field and paramagnetic materials might be very useful in electrochemistry [19,20]. Carbon-coated magnetic nanoparticles used in this study are a new class of composite hybrid nanomaterials. Their core-shell structure is composed of a core nanoparticle that is tightly coated with a carbon shell [21]. The carbon coating plays a crucial role, because it separates the magnetic nanoparticle from the environment and protects it against oxidation and dissolution. These properties stand behind the known applications of carbon-coated magnetic nanoparticles [22–24]. Iron containing carbon nanocapsules can be used as nanomagnets due to the ferromagnetic

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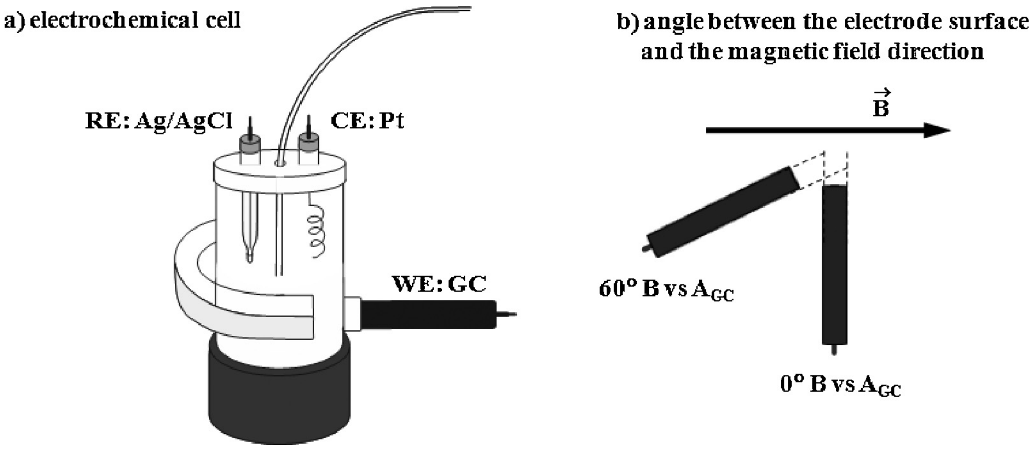

Scheme 1. Scheme of electrochemical cell with magnetic field.

character of their metal core. Their presence on the electrode surface should enhance the oxygen flux to the electrode surface, since the paramagnetic oxygen molecule will experience magnetic attraction to the electrode. In consequence an increase in the current density is expected.

In this paper we report on the application of carbon nanocapsules containing iron as the modifiers of the glassy carbon surface for the oxygen reduction in the absence and the presence of laccase immobilized at the modified electrode surface. The immobilization of laccase on the Fe@C nanocapsules caused a significant positive shift of the oxygen peak potential. Application of an external magnetic field additionally strongly magnified the current. The described phenomena were examined in function of magnetic field intensity and angle between the electrode surface and the external magnetic field direction. The experimental study was supported by modeling of the magnetic field existing in the vicinity of the electrode surface modified with the Fe@C nanocapsules.

2. Experimental

2.1. Materials

All chemicals were of the highest quality available. KCl (p.a., POCH, Poland), NaCl (p.a., POCH, Poland), NaH_2PO_4 (p.a., POCH, Poland), Na_2HPO_4 (p.a., POCH, Poland), HCl (p.a., POCH, Poland) were used as received. Laccase from *Trametes versicolor* was purchased from Sigma–Aldrich ($C = 15\,mg/cm^3$ in 0.02 M phosphate buffer solution, pH 3.8). Carbon-coated iron nanoparticles (Fe@C; glassy carbon modifier) were synthesized using the carbon arc route and then purified in order to remove the non-coated Fe particles; the detailed procedure and the evidence for complete encapsulation of iron are described in references [25,26]. The diameter of carbon-coated iron nanoparticles was between 10 and 130 nm; however, the major fraction of the nanoparticles (ca. 70%) was 30–70 nm in diameter. The thickness of carbon coating equaled several nm (typically 2–5 nm). X-ray powder diffraction and Mossbauer spectroscopy studies showed that Fe nanoparticles existed as three crystalline phases: bcc Fe, fcc Fe and Fe3C. The saturation magnetization measured at room temperature was 70 emu g^{-1} (70 A m^2 kg^{-1}).

2.2. Voltammetric experiments

Cyclic voltammetry (CV) and chronoamperometry (CA) were performed using an Autolab, model PGSTAT 12 potentiostat (Eco Chemie B.V., Utrecht, Netherlands). The three-electrode system was used in all measurements. A 3-mm diameter glassy carbon (GC) disk electrode (BAS, UK) was used as the working electrode. Potentials were referenced against a Ag/AgCl/3 M KCl electrode and a platinum wire was used as the auxiliary electrode. The experimental electrochemical setup is shown in Scheme 1. Before each use the disk of the working electrode was polished briefly: first with 0.3 and later with 0.05 μm Al_2O_3 powders on a wet pad. After polishing the electrode was rinsed with a direct stream of ultrapure water in order to remove alumina completely from the surface. The electrode surface was inspected optically with an Olympus inverted metallurgical microscope, model PME 3. After the cleaning procedure the electrode was modified by placing a droplet (7 μl, 0.125 mg ml^{-1}) of the Fe@C Nps water suspension on the electrode surface. The electrode was left to dry at room temperature. More details on the surface modification and characteristics of the Fe@C Nps modifier are given in [27]. All experiments were carried out in 0.02 M PBS buffer of pH 4.5 saturated with oxygen. The chosen pH is optimal for the laccase catalytic function.

For immobilization of laccase on glassy carbon electrodes covered by a Fe@C nanoparticles 10-μl drop of laccase aqueous solutions was placed on the electrode surface. The top of the electrode was covered with a lid to avoid drying and the electrode was kept overnight at 8 °C (in a fridge). The concentration of laccase used for the deposition varied from 1 to 15 mg ml^{-1}. The optimal concentration was found to be 4 mg ml^{-1}. Under such conditions the bioelectrocatalytic response of laccase was saturated and no further enhance was noticed when a higher concentrations of laccase were used.

Magnetic fields of intensity circa 20 and 140 mT (200 and 1400 Gs) were generated using the $Fe_{14}Nd_2B$ magnets. The magnets were appropriately shaped and sized to reach homogeneous intensity of the field inside the cell.

3. Results and discussion

3.1. Voltammetric studies of modified graphite electrodes (GC/Fe@C) without laccase

Oxygen reduction was studied in 0.02 M PBS buffer saturated with O_2 (99.95%). Typical cyclic voltammograms of oxygen reduction at a bare- and a Fe@C Nps modified glassy carbon electrode, obtained in the presence and absence of an external magnetic field, are presented in Fig. 1 A and 1B. The presence of the nanocapsules with iron core on the glassy carbon surface caused an increase in the current by circa 15% and shifted the voltammetric peak potential by circa 250 mV toward more positive potentials. Our earlier studies indicated that the remnant magnetization was 14 emu g^{-1} (i.e. 20% of the saturation magnetization) [27]. Oxygen is a paramagnetic