



Electrodeposited gold nanoparticles on glassy carbon: Correlation between nanoparticles characteristics and oxygen reduction kinetics in neutral media



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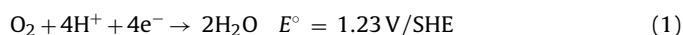
ABSTRACT

Gold nanoparticles (AuNPs) were deposited onto glassy carbon (GC) by constant potential electrolysis (CPE) using various sets of potential and duration from -0.3 to 0.7 V/SHE and 10 to 1800 s, respectively. The physico-chemical characteristics of the as-obtained deposits were investigated by cyclic voltammetry (CV) in H_2SO_4 , field emission gun scanning electron microscopy (FEG-SEM), and Pb underpotential deposition (UPD). Their performances toward the oxygen reduction reaction (ORR) in a NaCl-NaHCO_3 (0.15 M/ 0.028 M, pH 7.4) neutral solution were examined and correlated to AuNPs size and density. The best results were obtained using the deposits which exhibited a high density ($555 \pm 49 \mu\text{m}^{-2}$) of relatively small AuNPs (25 ± 12 nm). The Koutecky–Levich treatment was systematically applied to all the deposits in order to determine the number of electrons n exchanged for the ORR in the potential range from 0.1 to -1.0 V/SHE. The values of the cathodic transfer coefficients βn were also extracted and compared to the values reported for unmodified GC and bulk Au. A map of the βn values as a function of AuNPs electrodeposition potential and duration was also provided.

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1. Introduction

The oxygen (O_2) reduction reaction (ORR) is probably one of the most studied redox processes in the literature, both from the mechanistic [1–3] and kinetic [4–8] points of view. Amongst the numerous works dealing with this electrochemical system, the Damjanovic model is of particular interest which describes the ORR as a multi-electron reaction [9]. Thus, O_2 reduction may be achieved by a four-electron “direct” pathway (Eq. (1)) or via two successive bielectronic steps involving hydrogen peroxide (H_2O_2) as an intermediate species (Eqs. (2) and (3)) [10–12]:

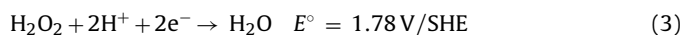
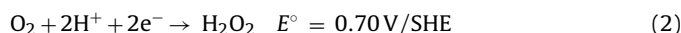


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Gnanamuthu and Petrocelli have also analyzed a series of more complex reduction paths for O_2 reduction on noble metals (Pt, Pd, Au) and alloys (Pd–Au and Pt–Au) [13].

This standing interest in ORR is mainly due to the wide range of application domains it is involved in, from chemical or biochemical analysis [14,15] to industrial fields such as pharmaceuticals [16], corrosion [17] or energy storage and conversion [18,19]. For instance, O_2 may be used directly as oxidation agent in food process [20]. It may be also reduced into H_2O_2 which can be further used as a sterilizing agent [16]. More recently the development of fuel cells drove a particular emphasis on ORR kinetic study in acidic or basic media on various catalysts including carbon-based materials, enzymes, macrocycles or coordination complexes of transition metals [21]. Amongst the numerous materials used, nanoparticles (NPs), and especially gold nanoparticles (AuNPs) have been extensively studied [22,23]. In acidic media, kinetic data have been obtained by electrochemical impedance spectroscopy [24], rotating ring disk electrode [25] and scanning electrochemical microscopy [26]. In many studies the AuNPs electrocatalytic activity toward ORR has been found to be size [25–27] and crystal structure-dependent

[26]. Indeed, the best results have been observed on small (around 20 nm diameter) [28] and very small (less than 10–15 nm) AuNPs [26,27], and for high Au(1 1 0)/Au(1 1 1) ratio, Au(1 0 0) faces being not present in small NPs [24]. Wain has postulated that small NPs possess high fractions of high index steps, edges and kink sites which may favor electrocatalysis [26]. In alkaline solution ORR is known to be faster than in acidic media [3]. A similar trend has been reported with respect to AuNPs structure, the activity toward O₂ reduction decreasing in the order Au(1 0 0) ≫ Au(1 1 0) > Au(1 1 1) [29]. However, the size effect is not as clear as in the case of acidic media: Tang et al. have noticed ORR kinetics to be 2.5 times higher on 3 nm diameter AuNPs supported on carbon than on 7 nm ones [30], whereas Lee et al. have observed better results on 8 nm NPs compared to 3 and 6 nm ones [31]. El-Deab et al. have also reported an interesting study in which relatively big AuNPs (ca. 50–300 nm) were selectively enriched in the most active crystallographic faces, namely Au(1 0 0) and Au(1 1 0), and exhibited better kinetic activity toward the ORR than smaller (ca. 10–40 nm) NPs [32]. AuNPs shape has also been reported to have an influence on their electrocatalytic response [33,34]. For instance, Kuai et al. have shown that icosahedral AuNPs exhibited enhanced electrocatalytic performances toward ORR and have proposed their multiple-twinned structure to be more chemically active because of their high surface-defect density [34].

Surprisingly, there are very few reports dealing with ORR on AuNPs in neutral media, although such studies would be of great interest for biological or medical topics [35,36]. Raj et al. have highlighted the electrocatalytic effect of AuNPs anchored by different organic layers on bare Au electrodes toward the ORR in phosphate buffer solution (pH 7.2) [37]. In the case of AuNPs stabilized by cystamine, the 2-electron reduction of O₂ into H₂O₂ has been found to occur at a potential 130 mV higher than on polycrystalline Au electrode. Although the resulting peak current was enhanced 1.2 times compared to an unmodified electrode, no kinetic feature has been provided in this study. Shim et al. have reported the comparison of the ORR kinetics on bulk Au and AuNPs in phosphate buffer (pH 7.4) and have shown the influence of the electrode pretreatment, i.e. 200 successive potential scans in 1 M H₂SO₄ [38]. A Koutecky–Levich mathematical treatment of the steady-state voltammetric curves has been performed but its exploitation has been limited to the determination of the number of electrons n exchanged. Only El-Deab et al. have conducted a more detailed kinetic study upon ORR in neutral phosphate buffer solution by combining Koutecky–Levich analysis with rotating Pt ring GC disk electrode measurements [39]. The values of n have been obtained at various potentials and an interesting estimation of the energy savings during H₂O₂ production has been proposed. However this latter work did not go as far as the determination of kinetic parameters such as cathodic transfer coefficients βn so that there is a lack for kinetic data upon ORR in neutral media. Very recently, we have reported a complete kinetic study of ORR in several neutral solutions on glassy carbon (GC) and bulk Au [40]. In the present work, we describe the performances of AuNPs deposited on GC by constant potential electrolysis (CPE) using various deposition durations and potentials with respect to ORR in a NaCl–NaHCO₃ (0.15 M/0.028 M, pH 7.4) neutral medium. The different deposits were characterized by cyclic voltammetry (CV) in H₂SO₄ and field emission gun scanning electron microscopy (FEG–SEM). Furthermore, Pb underpotential deposition (UPD) experiments were conducted in order to gain information on the structure of the AuNPs. The data obtained upon structure, size and density of the deposits were correlated to the cathodic transfer coefficients βn determined using the Koutecky–Levich method. Finally, these βn values were compared to those previously obtained in the same neutral media on bulk materials.

2. Experimental

2.1. Chemicals and apparatus

All the solutions were prepared using ultra pure water (Milli-Q Millipore, 18.2 MΩ cm). HAuCl₄·3H₂O (pro analysis grade) was purchased from Acros Organics. NaNO₃ (suprapur grade) and Pb(NO₃)₂ (analytical grade) were obtained from Merck. 95% H₂SO₄ (normapur grade) and 37% HCl were supplied by VWR Prolabo. 70% HClO₄ was purchased from Aldrich. NaCl and NaHCO₃ (analytical grade) were from Fisher Scientific.

Except the electrode activation which was performed at room temperature, all the experiments were performed at controlled temperature using a Fisher Scientific Isotemp thermoregulator.

All the electrochemical experiments were carried out in a standard three-electrode water-jacketed cell using a μ–Autolab II potentiostat (Metrohm) interfaced to a personal computer controlled with NOVA 1.9 software package (Metrohm). A Metrohm Ag/AgCl/KCl 3 M electrode, separated from the electrochemical cell by a Teflon PTFE capillary containing the support electrolyte solution and terminated by a ceramic diaphragm (D type), and a Metrohm glassy carbon (GC) wire were used as reference and counter electrodes, respectively. All the potentials given in the text and the figures are referred to SHE ($E_{\text{Ag/AgCl/KCl 3 M}} = 0.199 \text{ V vs. SHE}$). Working electrodes were GC ($d = 3 \text{ mm}$, $A = 7.069 \text{ mm}^2$) and Au ($d = 2 \text{ mm}$, $A = 3.142 \text{ mm}^2$) rotating disk electrodes from Radiometer. Gold nanoparticles modified GC (AuNPs–GC) electrodes were prepared using GC plates from OrigaLys ElectroChem SAS ($d = 5.5 \text{ mm}$, $A = 23.758 \text{ mm}^2$). The corresponding value of geometrical surface area A was used to calculate current densities from currents. When necessary, working electrodes were rotated using a rotating system Model EDI 101 interfaced with a CTV 101 speed control unit from Radiometer.

When indicated, the solutions were deaerated using a N₂ stream for 15 min. A N₂ atmosphere was also maintained over the solution during the corresponding experiments.

2.2. Electrode preparation and modification

All the working electrodes were carefully polished prior to use. All electrodes were first polished by silicon carbide grinding paper (grit 1200) for 10 s. GC surfaces were polished successively by a 9 μm, 3 μm, 1 μm and 0.25 μm diamond suspension (Presi) on a cloth polishing pad during 2 min for each size. Au electrodes were polished by 5 μm, 1 μm and 0.3 μm alumina slurry (Presi) on a cloth polishing pad during 2 min for each size. Between each polishing step, the surfaces were cleaned with MilliQ water. Finally, all electrodes were rinsed in an ultrasonic 96% ethanol bath (three times for 10 min) and cleaned with MilliQ water. After drying, the quality of the polishing step was verified by checking the surface state using a Nikon Eclipse LV150 optical microscope.

AuNPs were electrodeposited at 10 °C onto GC plates using constant potential electrolysis (CPE) at a given potential (from –0.3 V to 0.7 V) for various times (between 10 s and 1800 s) from a deaerated 0.1 M NaNO₃ solution containing 0.25 mM HAuCl₄ (pH = 3). The resulting AuNPs–GC electrodes were then carefully rinsed using MilliQ water and activated in a deaerated 0.5 M H₂SO₄ solution by running 30 scans between 0.2 V and 1.6 V at a scan rate of 100 mV s^{–1}.

2.3. AuNPs characterization

The AuNPs–GC surface was characterized by field emission gun scanning electron microscopy (FEG–SEM) using Quanta 250 FEG FEI equipment with an accelerating voltage of 5 kV and a working distance between 3 and 8 mm depending on the sample. Image

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