Electroreduction of oxygen on nitrogen-doped graphene oxide supported silver nanoparticles

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A B S T R A C T

Nitrogen-doped graphene oxide supported silver nanoparticles (Ag/NGO) have been synthesised using three different methods. The prepared catalysts were studied by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and electrochemically tested for oxygen reduction reaction (ORR) in alkaline solution. The Ag/NGO catalysts prepared by borohydride reduction showed the least degree of nanoparticle agglomeration and the material which was prepared using ascorbic acid yielded the biggest Ag particles. XPS revealed that the nitrogen to carbon atomic ratio was about 0.07 and EDS mapping showed that nitrogen was uniformly distributed over the graphene. The ORR on all the Ag/NGO catalysts proceeded via 4-electron pathway yielding water while on the support material, N-doped graphene oxide, the number of electrons transferred per O_2 molecule was lower than four. The mass activity of all Ag/NGO catalysts was determined to be at least twice higher than that of NGO.

1. Introduction

Silver-based catalysts have shown high electrocatalytic activity towards the oxygen reduction reaction (ORR) in alkaline solution [1,2]. For platinum and silver it has been demonstrated that the ORR process is similar for both metals in alkaline media and four electrons are transferred to O_2 molecule [3]. Even though the Pt catalysts have higher ORR activity than silver, it has been shown that the cost difference of these metals favours Ag-based catalysts [4].

The ORR mechanism on silver catalysts has been elucidated in several studies. It has been demonstrated that on carbon-supported Ag nanoparticles (AgNPs) both two-electron and four-electron pathways occur simultaneously [5]. It was found that on smaller Ag particles (4.1 nm) a two-electron pathway is favoured for the ORR, while on larger particles (174 nm) a four-electron pathway is preferred. On Ag (hkl) single crystal electrodes it has been proposed that the ORR proceeds via a series $2e^- + 2e^-$ electron pathway [6]. Based on the results obtained on Ag nanodecahedra and nanocubes, it has been concluded that on Ag(111) single crystal facet the ORR follows a direct 4-electron pathway, while on Ag(100) it proceeds via $2e^- + 2e^-$ pathway [7]. In accordance to this, Lee and Syu have found that four electrons are being transferred to O_2 molecule on electrochemically deposited Ag nanosheets with prevailing (111) facets [8]. In contrast, Lee et al. studied triangular Ag nanoplatelets with predominant (111) facets and found that 3.16–3.27 electrons were transferred per O_2 molecule, thus showing incomplete reduction of O_2 [9]. Alia et al. have studied the ORR on differently terminated Ag nanowires and explained the changes in the ORR activity with differences in crystallography [10].

The ORR mechanism and electrocatalytic activity of the catalysts also depends on the Ag catalyst loading. It has been well established that on carbon-based catalyst support materials the ORR follows predominantly a $2e^-$ pathway [11,12]. Guo et al. prepared and tested Ag/C catalysts with metal loadings from 10 to 60 wt% [13]. They reported that carbon-supported silver catalyses predominantly the four-electron pathway of ORR, only for 10 wt% Ag/C it was suggested that the ORR proceeding on carbon support may lower the electron transfer number (n). The ORR onset potential shifted by 62 mV to more positive values with increasing the Ag content [13]. Garcia et al. reported $n = 2.7$ for Ag/C with the particle size of ~10 nm, their interpretation was that the metal loading in 10 wt% Ag/C catalyst is not sufficient for the $4e^-$ pathway and therefore the O_2 reduction

reaction follows partly the $2e^-$ pathway [14]. Similarly, Novikova et al. related the decrease of the *n* value with decreasing Ag loading to increasing contribution of the two-electron pathway of ORR catalysed by the carbon support. In addition, they noted that a 4-electron pathway is dominant on Ag terraces and 2-electron pathway on edge sites [15]. Obviously, the ORR activity of Ag catalysts depends on the size of Ag nanoparticles. It has been reported that the activity of 99 nm triangular nanoplatelets surpasses that of 136 nm Ag nanoplatelets [9] and the 3–5 nm AgNPs exhibit higher activity than 6–8 nm and 12–15 nm AgNPs [16]. Similarly, Ag nanoclusters with the size of 0.7 nm displayed higher electrocatalytic activity than that of 3.3 nm particles, whereas the ORR was found to follow a two-electron pathway that was explained by the blocking effect of capping agents used in the synthesis [17]. Ohyama et al. commented that the ORR specific activity is not influenced by the particle size for AgNPs larger than 10 nm, but the particles smaller than 3 nm might show unique electrocatalytic behaviour as a result of large number of unsaturated Ag atoms and quantum dot effect [18].

The Ag-based ORR electrocatalysts have been prepared using different support materials and synthesis methods. Bidault and Kucernak have proposed to use porous silver as a membrane, catalyst support and charge collector for alkaline fuel cells [19,20]. Carbon nanotube-Ag nanowire composites have been shown to be feasible catalysts for ORR in alkaline media [21]. Tammeveski et al. studied Ag-based catalyst that was prepared by magnetron sputtering onto carbon nanotubes and observed that the ORR activity of this nanostructured composite catalyst surpassed that of bulk Ag and unmodified carbon nanotubes [22]. Silver nanoparticles can be also deposited onto graphene and such catalyst material has been shown to catalyse a 4-electron reduction of oxygen [23,24]. It was found to be beneficial to increase the porosity of graphene support by adding carbon powder [25]. Recently, graphene has gained much attention in electrochemistry research [26]. Pure graphene itself is rather inactive catalyst for ORR [27], but the activity can be greatly increased by nitrogen-doping [28,29]. The benefits of nitrogen-doping of various carbon materials have been demonstrated earlier [30–33]. Thus, it would be of particular interest to study the effect of N-doped carbon nanomaterial supports on the ORR activity of AgNPs. Cao et al. used N-doped hollow carbon tubes as a support for AgNPs and found that such composites are good electrocatalysts for ORR as a result of the favourable porosity and synergistic effect of surface nitrogen species and silver [34]. The synergistic effect observed is described as following: pyridinic and graphitic nitrogen have good adsorption capacity for oxygen that is reduced on silver nanoparticles. Nitrogen doping of graphene is also suggested to improve oxygen diffusion in the catalyst material by creating channels within graphene sheets [35]. Improved ORR activity has also been attributed to bonding interactions between AgNPs and nitrogen in the graphene structure that have been observed by X-ray photoelectron spectroscopy and surface enhanced Raman spectroscopy [36]. Jin et al. listed several factors that increase the ORR electrocatalytic activity of Ag nanoclusters deposited on N-doped graphene: small size of AgNPs, good contact between surface nitrogen species and silver nanoparticles, enhanced mobility of charge carriers of nitrogen-doped graphene and the amount of pyridinic nitrogen [37]. AgNPs have also been bound to the nitrogen-doped graphene by linker molecules and a clear tendency was observed: shorter chain of the linker favours high electrocatalytic ORR performance [38]. The advantages of graphene-based composite materials as Ag catalyst supports for ORR have been highlighted by Shypunov et al. [39].

Previously we have explored the electrochemical O_2 reduction behaviour of N-doped graphene-supported Pd and Pt catalysts [40,41]. In this study three different methods have been employed to synthesise Ag nanoparticles supported on nitrogen-doped graphene oxide and the O_2 reduction activity is compared in alkaline solution using a rotating disk electrode.

2. Experimental

2.1. Preparation of Ag/NGO catalysts

Graphene oxide (GO) was prepared using modified Hummers method as described in Ref. [28]. Briefly, graphite powder was mixed with concentrated sulphuric acid, which was then sonicated for 1 h. In the next step sodium nitrate and potassium permanganate were added in small portions. Then the mixture was heated for 18 h at 35 °C, after which it was cooled down in ice bath and deionised water was added to the solution. Hydrogen peroxide was then added, after which the suspension was washed with hydrochloric acid and finally several times with water. The final product was dried at 75 °C.

As a next step the obtained graphene oxide was doped with nitrogen using dicyandiamide (DCDA, Aldrich) as described previously [28]. Briefly, GO was mixed with polyvinyl pyrrolidone (PVP) in the mixture of deionised water and ethanol and then DCDA was added. The mixture was sonicated for 2 h and subsequently dried at 75 °C. Then the mixture was pyrolysed at 800 °C for 2 h in a constant flow of nitrogen gas. After that the furnace was allowed to cool down and nitrogen-doped graphene oxide (NGO) was collected.

In the next step silver nanoparticles were synthesised using three different methods, for all methods the nominal Ag content was fixed at 40 wt%. First, citrate stabilised AgNPs were prepared by reducing $AgNO_3$ with $NaBH_4$ in an aqueous solution in the presence of NGO and sodium citrate [42]. In what follows this catalyst is designated as Ag/NGO1. For the preparation of the second catalyst (Ag/NGO2) an aqueous solution of glycerol and sodium hydroxide was added to the suspension of NGO containing $AgNO_3$ [43]. The third catalyst (Ag/NGO3) was prepared using ascorbic acid as a reducing agent [44]. In this synthesis a suspension of NGO and $AgNO_3$ was made and the latter compound was reduced by slowly adding ascorbic acid to the mixture under constant stirring. After the synthesis of Ag/NGO catalysts the suspensions were filtered and dried at 75 °C.

2.2. Characterisation of Ag/NGO catalysts

The prepared catalyst materials were characterised by scanning electron microscopy (SEM, Helios Nanolab 600, FEI) operated at 2 kV, scanning transmission electron microscopy (STEM, Titan 200, FEI), equipped with energy dispersive X-ray spectrometer (EDS) Super-X™ system, operated at 200 kV, and X-ray photoelectron spectroscopy (XPS, SCIENTA SES-100). The XPS analysis was performed using non-monochromatised Mg Kα X-ray source (incident energy 1253.6 eV), a take-off angle of 90° and a source power of 300 W. The pressure in the analysis chamber was less than 10^{-9} Torr. For collecting the survey spectra, the following parameters were used: energy range 600–0 eV, pass energy 200 eV and step size 0.5 eV. In specific regions, high-resolution scans were performed with the pass energy of 200 eV and the 0.1 eV steps.

Samples for SEM measurements were prepared by transferring the Ag/NGO ink in ethanol onto glassy carbon (GC) disk, samples for XPS analysis were transferred onto a 1 cm^2 GC plate and for TEM studies onto holey carbon-coated copper TEM grids. For EDS X-ray mapping low-background double-tilt HiVis Super-X sample holder was used.

Electrochemical measurements were carried out in 0.1 M KOH solution prepared from KOH pellets (p.a., Aldrich) and Milli-Q water (Millipore, Inc.). The solution was either saturated with O_2 (99.999%, AGA) or deaerated with Ar (99.999%, AGA). Saturated calomel electrode (SCE) separated by Luggin capillary was used as reference and all potentials are given with respect to SCE. Pt wire served as a counter electrode and was separated from the main cell by a glass frit. The catalysts were tested using glassy carbon disk (GC-20SS, Tokai Carbon) as electrode substrate, which was polished with alumina slurries (1 μm and 0.3 μm, Buehler) and treated in Milli-Q water in ultrasonic bath for 5 min.